

AROMATIC NITRODESILYLATION



A Thesis  
presented for the degree of  
Doctor of Philosophy in the Faculty of Science  
of the University of Leicester.

by

Keith Leyshon

The University, Leicester.

July, 1962.

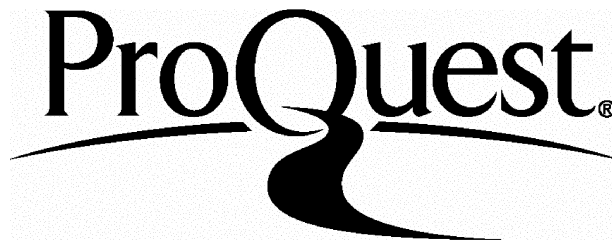
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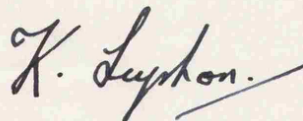
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I wish to express my sincere appreciation of the kind help and encouragement received from Professor C. Eaborn and Mr. R. W. Bott during every aspect of this work.

My thanks are also due to Professor L. Hunter and the members of the Staff of the Department of Chemistry, The University, Leicester, for their interest in this work.

The financial support of Midland Silicones Ltd., Barry, is gratefully acknowledged.

Signed,

A handwritten signature in cursive script, reading "K. Leyshon." with a horizontal line extending from the end of the name.

K. Leyshon.

July, 1962.

### STATEMENT

The work embodied in this thesis was carried out by the Candidate in the Chemistry Laboratories of the University of Leicester, under the supervision of Professor C. Eaborn and Mr. R. W. Bott. The work has not been submitted, and is not concurrently being submitted, in candidature for any other degree.

Signed,

A handwritten signature in cursive script, reading "K. Leyshon", with a horizontal line extending from the end of the name.

K. Leyshon.

July, 1962.

## SUMMARY

Reviews are given of the cleavage of the aryl-silicon bond by electrophilic reagents and of aromatic nitration by reagents other than nitric acid or nitric acid - sulphuric acid mixtures.

The mechanism of nitrodesilylation has been studied, using p-tolyltrimethylsilane as the representative compound. With nitric acid - acetic anhydride - acetic acid the ratio of nitrodesilylation to nitration is decreased by increasing the concentration of nitric acid, is increased by the addition of a small quantity of sulphuric acid (the rate of the reaction is increased), and is not altered by the addition of nitrate ion (the rate of the reaction is decreased markedly). Similar alterations of reaction rate and ratio of desilylation to nitration occur when dinitrogen pentoxide - acetic anhydride - acetic acid is used as the nitrating mixture, except that the addition of sulphuric acid does not alter the ratio. It is suggested that with these reagents the nitronium ion and to some extent the dinitrogen pentoxide molecule are the effective agents in the nitration process, and that desilylation proceeds via a multi-centre mechanism in which dinitrogen pentoxide is the attacking entity. No cleavage of the aryl-silicon bond occurs when nitronium tetrafluoroborate is used as the nitrating agent. Limits to the use of nitrodesilylation as a preparative technique are discussed.

The preparation of forty three new organic and organo-silicon compounds is described. It has been shown that the addition of  $\text{Cl}_3\text{SiH}$  to m- or p- $\text{Cl}\cdot\text{C}_6\text{H}_4\cdot(\text{CH}_2)_2\text{CH}=\text{CH}_2$  gives m- or p- $\text{Cl}\cdot\text{C}_6\text{H}_4\cdot(\text{CH}_2)_4\text{SiCl}_3$  and m- or p- $\text{Cl}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{SiCl}_3)\text{CH}_2\text{CH}_2\text{CH}_3$ . The mechanism of these addition reactions is discussed.

A study has been made of the protodesilylation of the compounds o-, m-, and p- $\text{Me}_3\text{Si}\cdot\text{C}_6\text{H}_4\cdot(\text{CH}_2)_n\text{SiMe}_3$  (where  $n = 1$  to  $4$ ). The rates of cleavage for the ortho and para compounds fall in the order ( $n =$ )  $1 \gg 2 > 4 > 3$ , whereas for the meta compounds the order is ( $n =$ )  $1 > 3 > 2 > 4$ . These results are discussed, together with those of Chernyshev et al. for the competitive nitration of the compounds  $\text{C}_6\text{H}_5\cdot(\text{CH}_2)_n\text{SiMe}_3$  (where  $n = 1$  to  $4$ ).

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**SECTION 1**  
**INTRODUCTION**

## CHAPTER 1

### Introduction

Silicon lies in Group 1V B of Mendelēef's Periodic Table between carbon and germanium. It is, therefore, to be expected that its compounds will resemble both those of carbon and of germanium. Since about 1945 both the industrial and fundamental aspects of organosilicon chemistry have received increasing attention, although relatively little work has been carried out on the mechanisms of reactions of organosilicon compounds.<sup>1</sup>

The electronic configurations of silicon is  $1s^2 2s^2 2p^6 3s^2 3p^2$  thus giving it a covalency of four which is the normal covalency of the Group 1V B elements, although tin and lead are usually divalent in their ionic compounds. The carbon atom cannot co-ordinate either as an electron donor or acceptor because it normally uses all its valency electrons and cannot expand its valency shell. Silicon, however, has d-orbitals available for chemical bonding and this fact explains many of the differences between analagous carbon and silicon compounds.<sup>2,3</sup>

The co-ordination number of silicon rises above four only when it is bonded to highly electronegative elements e.g., fluorine, chlorine, oxygen or nitrogen where the bonds between silicon and these elements have considerable ionic character. Although silicon has five d-orbitals, its covalency like that of other elements in the second

short period, does not rise above six. However, a few complexes have been reported in which silicon apparently exerts a co-ordination number greater than six (e.g.,  $\text{SiCl}_4, 4\text{Et}_3\text{N}$ ;  $\text{SiCl}_4, 4\text{Et}_2\text{NH}$ ;  $\text{SiCl}_4, 4\text{C}_5\text{H}_5\text{N}$ ;  $\text{SiI}_4, 4\text{C}_5\text{H}_5\text{N}$ ;  $\text{SiI}_4, 4\text{Quinoline}$ ;  $\text{SiI}_4, 4\text{Collidine}$ )<sup>4-9</sup> but they have not been well characterised. In fact Wannagat and Vielberg<sup>4</sup> have concluded that the compound described as  $\text{SiCl}_4, 4\text{C}_5\text{H}_5\text{N}$  is probably a mixture of silicic acid and pyridine.<sup>10</sup>

The best known example of the use of the d-orbitals of silicon is in the hexafluorosilicate ion,  $\text{SiF}_6^{2-}$ , which has been shown by X-ray crystallographic analysis to have an octahedral arrangement of fluorine atoms around silicon,<sup>11</sup> and thus involves  $sp^3d^2$  hybridisation. In pentaco-ordinated complexes (e.g.,  $\text{H}_3\text{SiCl}, \text{NMe}_3$ )<sup>12</sup> the hybridisation of the silicon orbitals is presumably  $sp^3d$ , and the configuration bipyramidal.

Pauling<sup>15</sup> gave the electronegativities of carbon, silicon and hydrogen as 2.5, 1.8, and 2.1 respectively. These values are in excellent agreement with those recently published,<sup>13,14</sup> although there is considerable controversy about the values for the other Group IV B elements, especially for lead.<sup>13,14,186</sup>

The electronegativity differences ( $\Delta_{E1}$ ) between Si-C and Si-H are 0.7 and 0.3 respectively. The Si-C bonds would, therefore, be expected to cleave in the direction of  $\text{Si}^+ \text{C}^-$ , under electrophilic attack at carbon or

nucleophilic attack at silicon, and cleavage of the bond always occurs in this way.<sup>28</sup> An interesting point is that  $\Delta_{E1}$  in the Si-H bond is 0.3 in the direction  $\text{Si}^+\text{H}^-$ , while the figure for the C-H bond is 0.4 in the direction  $\text{C}^-\text{H}^+$ . Thus, while the C-H bond usually breaks in the direction  $\text{C}^-\text{H}^+$  the Si-H bond breaks in the opposite direction e.g.



Reactions whose rates are determined primarily by processes occurring at, or close to, the Group IV B atom will be influenced by the vacant d-orbitals of that atom. In nucleophilic substitution reactions it has been shown that electronegativity effects are secondary to effects of d-orbital availability.<sup>16</sup> This situation, however, is reversed in the case of electrophilic cleavage. The rate of cleavage, in aqueous methanolic perchloric acid, of aryltrialkyl-metallic compounds was found by Eaborn and Pande to rise in the order<sup>17</sup>



This order is in accordance with the rising electronegativity difference of the metal-carbon bond.<sup>14</sup>

Because silicon is more electropositive than carbon, trisilylamine,  $(\text{H}_3\text{Si})_3\text{N}$ , should be a stronger base than the carbon analogue, trimethylamine. Experimental evidence, however, indicates that it has only weak electron donor powers.<sup>29,30</sup> It has been suggested that the lone pair of

the nitrogen is engaged in bonding with the d-orbitals of the silicon.<sup>29</sup> As a consequence of this  $\pi$ -bonding, the trisilylamine molecule is almost planar,<sup>31</sup> whereas trimethylamine is tetrahedral. There are many other examples of such  $d\pi$ - $p\pi$  bonding between silicon and nitrogen, oxygen, sulphur, and halogens.<sup>2,32</sup>

The concept of  $d\pi$ - $p\pi$  bonding between silicon and a benzene ring has been used to explain the dipole moments of substituted phenyltrimethylsilanes.<sup>33,34</sup>

The  $\text{SiMe}_3$  group, relative to the hydrogen atom, should release electrons by an inductive, (+I), effect and there is considerable evidence that it does so.<sup>3</sup> Comparison of the ionisation constants of the trimethylsilylmethylbenzoic acids with the corresponding toluic acids and benzoic acids,<sup>35</sup> shows the considerable acid-weakening influence of the  $\text{SiMe}_3$  group; this indicates the operation of a strong +I effect especially when it is realised that this effect has to be transmitted through an insulating methylene group.

The acid  $p\text{-Me}_3\text{SiC}_6\text{H}_4\text{COOH}$  would be markedly weaker than benzoic acid if the +I effect of the  $\text{SiMe}_3$  group were the only one operating when this group is attached to the benzene ring. This acid, however, is only slightly weaker than benzoic acid in water and is in fact, slightly the stronger in 60.1 wt.-%  $\text{H}_2\text{O}/\text{EtOH}$ .<sup>36-9</sup> It is, therefore, apparent that the +I effect of the  $\text{SiMe}_3$  group is opposed

by a -T effect, that is by  $d\pi-p\pi$  bonding between the  $\pi$ -electrons of the ring and the d-orbitals of silicon.

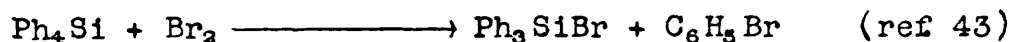
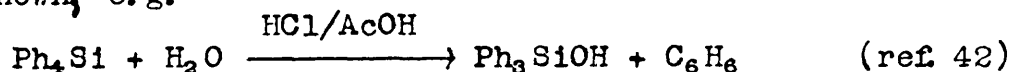
The variability of electrical effects of the  $\text{SiMe}_3$  group which results from the varying importance of the -T effect is best indicated by the value of the Hammett  $\sigma$  constant<sup>40</sup> derived from various reactions and equilibria of p-trimethylsilyl substituted compounds.

Since the +I effect of the  $\text{SiMe}_3$  group is opposed by a -T effect, the group activates the aromatic nucleus only weakly towards electrophilic reagents and is very weakly ortho-para directing (see Chapter 2).

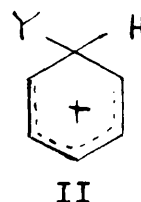
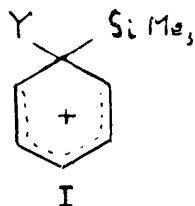
## CHAPTER 2

### Reactions of Aryl-Silicon Compounds with Electrophilic Reagents.

As would be expected from the electronegativity differences between carbon and silicon of 0.7 (see Chapter 1) the C-Si bond is readily susceptible to cleavage by electrophilic reagents. The fact that aryl groups can be cleaved from silicon by electrophilic reagents has long been known, e. g.

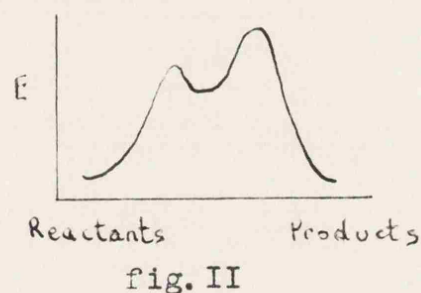
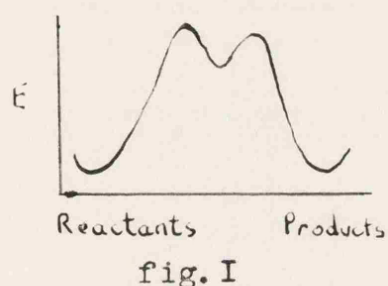


However, these cleavage reactions were only recently recognised as aromatic substitutions.<sup>18, 44-6</sup> Reactions involving cleavage of a substituted silyl group from the ring may involve intermediates of type I, analogous to those postulated for electrophilic aromatic substitution<sup>47</sup> (type II).



If intermediates such as I exist, the same problem exists with desilylation, as with aromatic electrophilic substitution, namely, whether formation or destruction of the intermediate is rate determining. It is probable that in nitration and bromination the formation of the

intermediate (II) is the rate determining process and the subsequent proton loss is fast: the energy profile being shown in fig. I. In sulphonation, however, the destruction of the intermediate is at least partially rate-determining, and in some azo-couplings the destruction is the slow step (the energy profile being shown in fig. II).<sup>47-8</sup>



In any desilylation reaction it is probable that the transition states for formation and destruction of the intermediate (I) are not far removed in energy and structure from the intermediate, and from one another. The effects of variation in structure on the rate of reaction, therefore, are not likely to be very dependent on which step is rate-determining.<sup>49</sup>

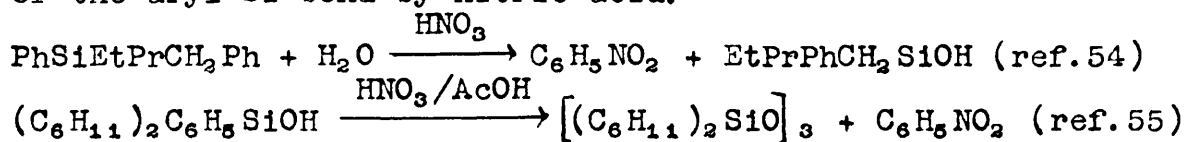
#### A. Reactions with Nitrating Agents.

When nitric acid, either alone or in the presence of sulphuric acid, is reacted with aryl-silicon compounds, nitration of the aromatic or cleavage of the aryl-Si bond can occur. When cleavage occurs it would not be clear whether this was actually nitrodesilylation (cleavage of the aryl-Si bond by the nitrating agent) or whether acid cleavage, followed by nitration of the aromatic, is

occurring. Despite the considerable reactivity of the aryl-Si bond towards electrophilic reagents, several compounds of the formula  $R_3SiC_6H_5$  have been successfully nitrated.

In the first reports of the action of nitrating agents on aryl-Si compounds ( tetraphenylsilane was the compound used), no cleavage of the aryl-Si bond was found.<sup>42,50,52-3</sup> A variety of products were reported by the various workers but it was Kipping and Blackburn who first successfully isolated tetra-(nitrophenyl)silane (93% yield) using nitric acid (d,l.5) in carbon tetrachloride.<sup>53</sup> They determined the composition of the product by bromine cleavage and concluded that in nitration the proportion of meta to para nitration was 2:1.

Kipping and co-workers<sup>54-5</sup> first reported cleavage of the aryl-Si bond by nitric acid.



Cusa and Kipping determined the percentage of isomerides formed in the nitration of phenyltriethyl-, diphenyldiethyl-, and triphenylethyl-silane with nitric acid (d,l.5) in acetic anhydride.<sup>56</sup> They concluded that the  $\text{Ph}_3\text{Si}$ -group was strongly meta-directing whereas the  $\text{SiEt}_3$  group was essentially para-directing. These results are almost certainly incorrect, since the  $\text{SiMe}_3$  group has been found to be weakly o-p directing under similar conditions<sup>51</sup> (see page 9). Phenyltriethylsilane has also been successfully

nitrated by Dolgov and Panina using nitric acid in acetic anhydride at 0° but the composition of the product was not determined.<sup>57</sup>

Phenyltrimethylsilane and benzyltrimethylsilane were successfully nitrated using copper nitrate in acetic anhydride; however, some cleavage occurred, 25% and 5% of nitrobenzene and nitrotoluene, respectively, were obtained.<sup>58</sup> From a study of the isomers obtained by the nitration of the isomeric tolyltriethylsilanes with copper nitrate in acetic anhydride it was concluded that the methyl group, and not the trimethylsilyl group, was the dominating factor in determining the orientation of the products.<sup>59</sup> In every case the incoming nitro group entered ortho or para to the methyl group even though, in some cases, this was meta to the triethylsilyl group. The nitrations were carried out at 40°, and the maximum amount of nitrotoluene formed by cleavage of the aryl-Si bond, was 26% of p-nitrotoluene from the corresponding p-tolyltriethylsilane.

Table 2.1

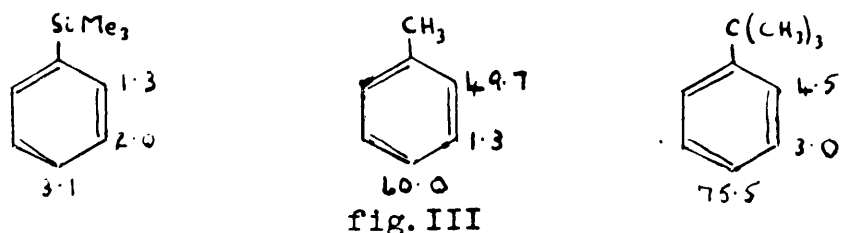
Nitration of Phenyltrimethylsilane with HNO<sub>3</sub>/Ac<sub>2</sub>O.<sup>51</sup>

Temp °C	Ratio of Nitrophenyltrimethylsilanes			Nitrobenzene (% Yield)
	<u>ortho</u>	<u>meta</u>	<u>para</u>	
0-10	26.6	41.7	31.6	6.8
25-70	32.5	34.7	32.7	13.0

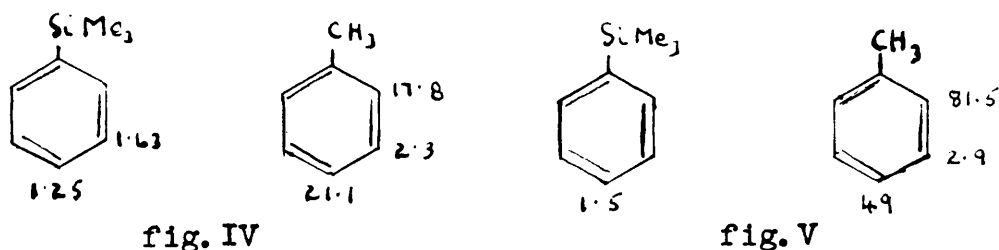
Phenyltrimethylsilane is nitrated 1.64 times as fast as benzene<sup>51</sup> in competitive nitrations using fuming

nitric acid in acetic anhydride at  $-10^{\circ}\text{C}$ . The isomer distribution was determined at  $0-10^{\circ}$ , and  $25-70^{\circ}$ , cleavage of the aryl-Si bond occurring to a small extent as indicated by the formation of nitrobenzene (see Table 2.1).

The reactivities of the o-, m-, and p-positions relative to a single position in benzene were calculated from these results,<sup>51</sup> and are shown in fig. III, together with the corresponding figures for the nitration of toluene and t-butylbenzene.<sup>60</sup> As can be seen, the  $\text{SiMe}_3$  group



activates the para position only about 0.05, the meta position about 1.5, and the ortho position only 0.04 times as effectively as the methyl group. This weak activating effect of the  $\text{SiMe}_3$  group has been demonstrated in other electrophilic substitutions, for example in the acid cleavage,<sup>18,95</sup> and bromine cleavage<sup>61</sup> of the bistrimethylsilylbenzenes. The results, together with those for the

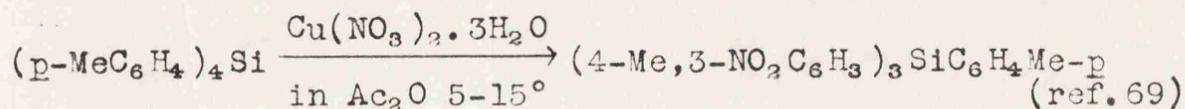
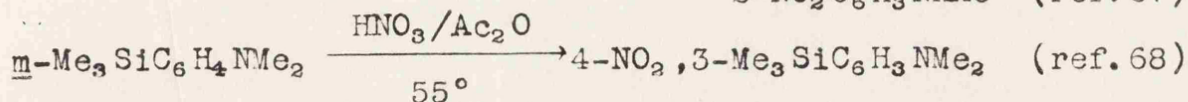
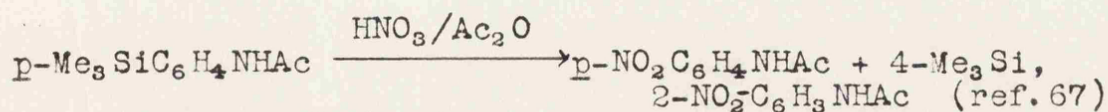
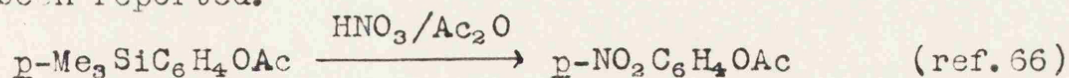


cleavage of the tolyltrimethylsilanes are shown in fig. IV (acid cleavage),<sup>18,95</sup> and fig. V (bromine cleavage).<sup>61-2</sup>

Chvalovský and Bažant have developed a method for the determination of aryl groups directly bound to silicon in mixed arylalkylsilanes and arylalkylsiloxanes by the selective removal of the aryl group with 71% nitric acid in refluxing acetic anhydride.<sup>63</sup>

The preparation of pure para-nitrophenyltrimethylsilane, free of ortho and meta isomers, from p-bistrimethylsilylbenzene by treatment with fuming nitric acid in refluxing acetic anhydride was described by Deans and Eaborn.<sup>64</sup> This use of aryl-Si bond cleavage by nitrating agents to introduce a nitro group at a selected position in an aromatic molecule is of considerable synthetic value and has been extended to aryl-germanium compounds.<sup>65</sup>

Recently the reaction of several trimethylsilyl substituted aromatic compounds with nitric acid in acetic anhydride,<sup>66-8</sup> or with copper nitrate in acetic anhydride,<sup>69</sup> have been reported.



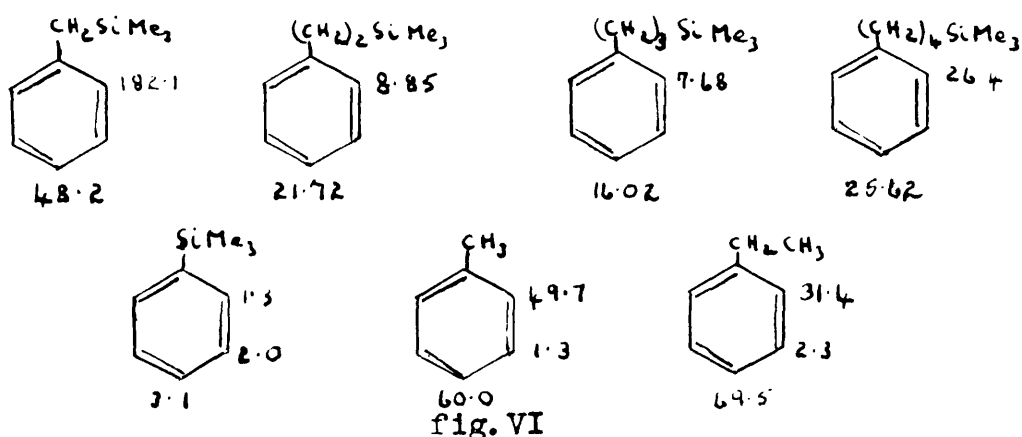
Chernyshev, Dolgaya and Petrov<sup>70</sup> nitrated the compounds  $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n\text{C}_6\text{H}_5$  (where  $n = 1$  to  $4$ ) in competition with

benzene, using 90% nitric acid in acetic anhydride at 0 to -10°. Their values of  $k_{rel}$ , ( $k_{rel} = k_{compound}/k_{benzene}$ ), together with the isomer distribution are given in Table 2.2, and their partial rate factors in fig. VI, together with published values for the nitration of phenyltrimethylsilane,<sup>51</sup>

Table 2.2

Nitration of $Me_3Si(CH_2)_n C_6H_5$				
$Me_3Si(CH_2)_n C_6H_5$	n = 1	n = 2	n = 3	n = 4
$k_{rel}$	77.2	8.87	10.62	18.96
% ortho	85.0	45.8	49.2	64.9
% para	15.0	54.2	50.8	35.1

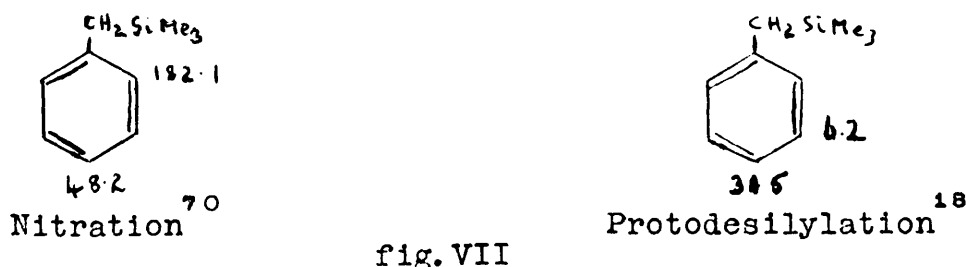
toluene,<sup>68</sup> and ethylbenzene.<sup>68</sup> These values for  $k_{rel}$  and the partial rate factors are not self-consistent - for example



the partial rate factors for benzyltrimethylsilane are equivalent to a  $k_{rel}$  value of 68.7 - and will be considered further in the discussion.

The results for the nitration of benzyltrimethylsilane are in agreement with the qualitative results obtained by

other workers.<sup>58,71</sup> The  $\text{Me}_3\text{SiCH}_2$  group in nitration obviously activates the ortho-para positions far more strongly than does the  $\text{SiMe}_3$  group. A comparison of these

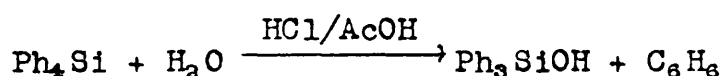


results with those for protodesilylation (fig.VII) shows that the  $\text{Me}_3\text{SiCH}_2$  group activates the para position in acid cleavage about 6.5 times greater than in nitration.

It is interesting to note that when compounds of the type  $p\text{-R}_3\text{SiC}_6\text{H}_4(\text{CH}_2)_n\text{SiMe}_3$  are treated with nitric acid in acetic anhydride, instead of giving good yields of the  $p\text{-NO}_2\text{C}_6\text{H}_4(\text{CH}_2)_n\text{SiMe}_3$  as one would expect, they are almost quantitatively oxidised and the expected nitro compounds are formed in yields of less than 3%.<sup>72</sup> This is surprising when one considers the fact that the  $\text{C}_6\text{H}_5(\text{CH}_2)_n\text{SiMe}_3$  compounds, (where  $n = 1$  to 4), may be readily nitrated in good yields.<sup>70-1</sup> This problem has been investigated and will be dealt with fully in the discussion.

#### B. Reactions with Acids.

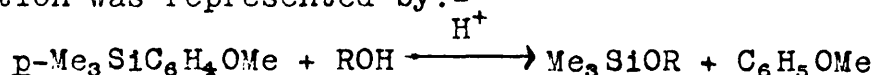
The first report of the acid cleavage of an aryl-Si bond was by Kipping and Lloyd<sup>42</sup> e.g.



Since then many workers have reported similar cleavages of aryl-Si bonds.<sup>56-7,78-8</sup> *p*-Trimethylsilylbenzaldehyde may, however, be steam distilled from an acid solution without cleavage of the aryl-Si bond.<sup>84</sup>

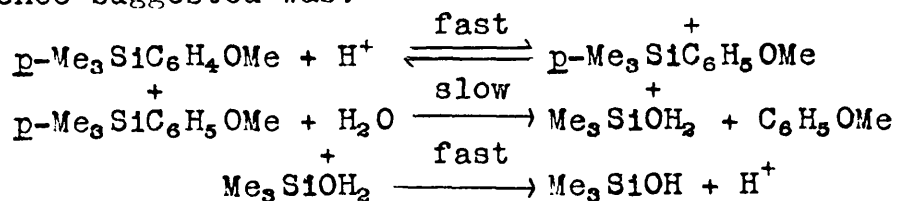
Dry hydrogen chloride in refluxing acetic acid readily cleaves the aryl-Si bond, and this reaction has been studied by several workers:<sup>46,79-83</sup> of these, Benkeser and Krysiak<sup>46</sup> have shown that there is a rough correlation between the ease of cleavage and the Hammett substituent constants.

The first quantitative study of the cleavage of the aryl-Si bond by acids was made by Eaborn,<sup>44</sup> who studied the kinetics of the acid-catalysed cleavage of *p*-methoxyphenyltrimethylsilane using hydrochloric acid or perchloric acid in aqueous methanol. The overall course of the reaction was represented by:-



The reaction was found to be first order in the silane, and for a given solvent the rate of reaction is governed by the acidity of the system, which measures the ability of the medium to donate a proton to a neutral base. The straight line relationship between log *k* and *H*<sub>0</sub> (Hammett's acidity constant) for an acid catalysed reaction is usually thought to indicate the existence of a fast, reversible, proton transfer from the solvent to the substrate before the rate-determining step.<sup>85-7</sup> The reaction

sequence suggested was:-



Since silicon is very susceptible to nucleophilic attack, and should be especially so in a positively charged complex, it seems reasonable to suppose that nucleophilic attack on silicon would be involved in the decomposition of the protonated intermediate. The precise mechanism of this cleavage reaction is still very much in doubt, however. The transition state, of this fast proton transfer, is thought to be reasonably close to the protonated phenyl-trimethylsilane (fig. VIII).<sup>18</sup>

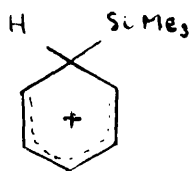
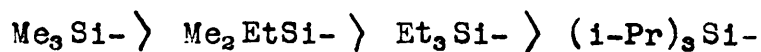


fig. VIII

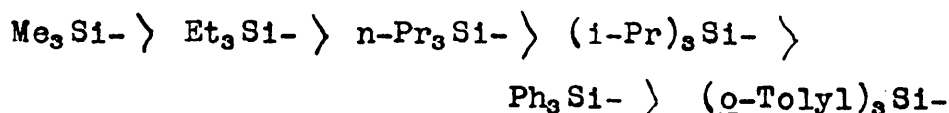
Recently, numerous kinetic studies of the cleavage of trialkylaryl silanes have been made by Eaborn and his co-workers using sulphuric acid in water-acetic acid,<sup>19,89-90</sup> and by hydrochloric or perchloric acids in aqueous methanol or dioxan.<sup>17-8,88,91,107</sup> Their results show that electron supplying substituents accelerate the reaction while electron withdrawing substituents retard it. The general pattern of substituent effects is similar to that observed for other electrophilic aromatic substitutions. There is,

in fact, an excellent correlation between the substituent effects in acid cleavage and the substituent constants,  $\sigma^+$ , recently proposed for electrophilic substitutions by Brown;<sup>24</sup> a plot of  $\log k_{rel}$  vs  $\sigma^+$  (where  $k_{rel}$  is the rate of reaction of a substituted compound relative to that of phenyltrimethylsilane) being a good straight line.<sup>19</sup> Better straight lines are obtained<sup>21</sup> when the values of  $\log k_{rel}$  for desilylation are plotted against the Yukawa parameter,<sup>25</sup>  $\sigma + r(\sigma^+ - \sigma)$  where  $r = 0.7$  for desilylation and  $\sigma$  is Hammett's original substituent constant<sup>26</sup> for R.

Benkeser et al. have studied the acid cleavage of aryl-Si bonds using hydrochloric acid in acetic acid,<sup>92-4</sup> p-toluenesulphonic acid,<sup>45,93-4</sup> and also hydrogen sulphate in acetic acid.<sup>96</sup> The effect of varying the other groups attached to silicon was studied and clear evidence was obtained for the operation of steric effects,<sup>93</sup> the rates of desilylation decreasing in the order:



Greasley<sup>95</sup> has shown that for compounds of the type p-MeC<sub>6</sub>H<sub>4</sub>SiR<sub>3</sub> the rate of cleavage in methanol-perchloric acid falls in the order:-



Steric effects are clearly operating and it is, therefore, possible that nucleophilic attack at silicon is involved in the rate-determining step of the reaction, but hinderance

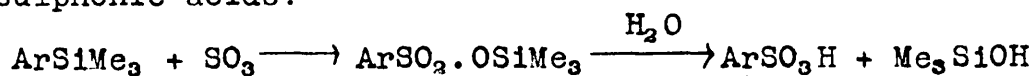
could also occur in the formation of the intermediate of the type in fig. VII (page 15).

Using the technique developed by Eaborn,<sup>44</sup> Nasielski and Planchon have recently studied the protodesilylation of a series of trimethylarylsilanes.<sup>97</sup> Burkhard and Norton developed a method, involving the heating of the organosilicon compound with concentrated sulphuric acid, for the determination of hydrocarbon substituents in organosilicon compounds and polymers. Chvalovský and Bažant, however, have recently recommended the use of 60% sulphuric acid instead of concentrated sulphuric acid.<sup>98</sup> They found that lower concentrations of sulphuric acid resulted in the formation of benzene whereas high concentrations gave sulphonic acids. Formic acid has also been found to cleave aryl-Si bonds.<sup>100</sup>

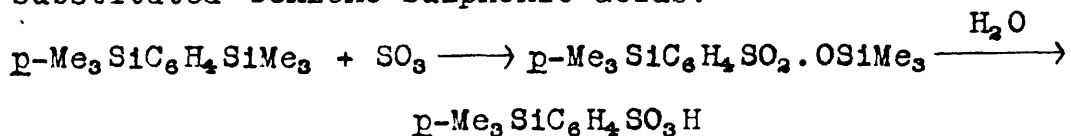
### C. Reactions with Sulphonating Agents.

Sulphonating media have frequently been found to cause cleavage of aryl-Si bonds.<sup>42-3, 54, 103, 124-6</sup> It is not clear, however, whether it is sulphodesilylation (that is, cleavage of the aryl-Si bond by the sulphonating agent) or whether it is acid cleavage, followed by sulphonation of the aromatic. The same problem arises with the recent observation of Chvalovský and Bažant that aryl-Si bond cleavage occurs with 60% sulphuric acid giving benzene, and with concentrated sulphuric acid giving benzenesulphonic acid.<sup>98</sup>

The first clear case of sulphodesilylation was recently reported by Eaborn and Hashimoto.<sup>127</sup> Aryltrimethylsilanes on reaction with sulphur trioxide in carbon tetrachloride give compounds of the type  $\text{ArSO}_2\text{OSiMe}_3$ , which can readily be hydrolysed to the corresponding sulphonic acids:-



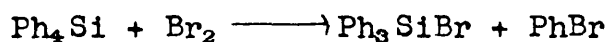
They used this reaction to prepare some organosilicon-substituted benzene sulphonic acids:-<sup>127</sup>



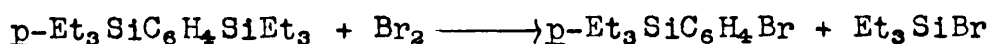
This reaction has considerable potential value in synthetic organic chemistry for the introduction of sulpho groups into an aromatic compound at a specified position (c.f., nitrodesilylation).

#### D. Reactions with Halogens.

The first cleavage of an aryl-Si bond by a halogen was reported in 1907 by Ladenburg,<sup>43</sup> who prepared triphenylsilyl bromide by the treatment of tetraphenylsilane with bromine at 100°



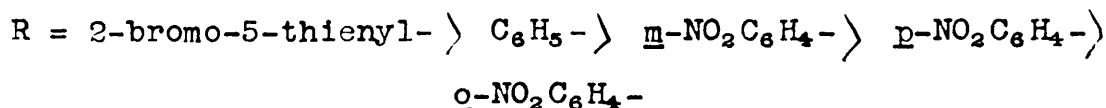
Bromine cleavage, in the presence of iron filings, was also used to prepare p-bromophenyltriethylsilane:<sup>101</sup>



and trimethylsilyl bromide was first prepared in this manner.<sup>102</sup>

The bromine cleavage of the aryl-Si bond (i. e. , bromodesilylation) has often been used to identify the point of attachment of a silicon atom to a substituted aromatic ring,<sup>53,55-6,58,103-5</sup> bromine water frequently being used.

Benkeser and Torkelson made the first kinetic study of bromodesilylation, using bromine in carbon tetrachloride.<sup>106</sup> The reactions were found to exhibit overall third order kinetics (second order in bromine) and the following sequence, representing decreasing ease of cleavage, was observed for compounds of the type RSiMe<sub>3</sub>:-



They concluded that there was a strong similarity between bromodesilylation and aromatic bromination.

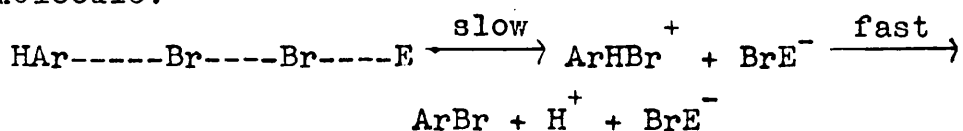
The reaction between aryltrimethylsilanes and bromine in acetic acid containing 1.5% water has been studied by Eaborn and his co-workers.<sup>61-2,90,107</sup> They also demonstrated the similarity between bromodesilylation and aromatic bromination, although the cleavage is of rather lower order in bromine (approx. first order) than is aromatic bromination (of anisole) at the same bromine concentration.<sup>61</sup> The order of reaction, like molecular bromination,<sup>108</sup> was found to increase with initial concentrations of bromine<sup>62</sup> and, in fact, can even exceed 3; at all concentrations studied, however, it is lower than

that for bromination. These observations are consistent with the view that the overall kinetic form under these conditions should be written:-

$$-d[\text{ArSiMe}_3]/dt = k_2[\text{ArSiMe}_3][\text{Br}_2] + k_3[\text{ArSiMe}_3][\text{Br}_2]^2 + \dots$$

It has been suggested that an electrophile, E, is needed to remove the bromide ion from the attacking bromine

molecule:<sup>108</sup>



It appears that the greater availability of electrons in the Ar-SiMe<sub>3</sub> bond compared with that of the Ar-H bond leads to a smaller need for the additional electrophil in bromodesilylation than in bromination, even when the Ar-SiMe<sub>3</sub> and ArH compounds are of comparable reactivity. In view of the ease of "flank" attack at silicon,<sup>109</sup> a cyclic transition state (fig. IX) must be regarded as

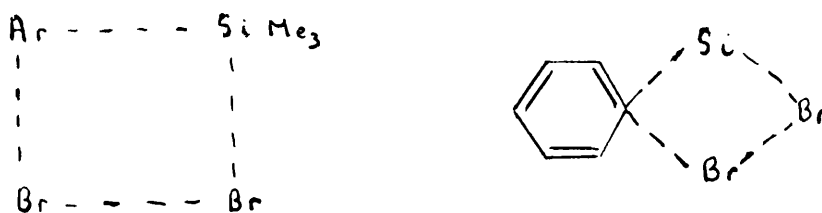


fig. IX

probable.

A qualitative correlation was observed between substituent effects on bromodesilylation and on proto-desilylation, a plot of  $\log k_{rel}$  for bromodesilylation

against  $\log k_{rel}$  for proto-desilylation being a good straight line.<sup>61</sup> It therefore follows that, as for protodesilylation, a plot of  $\log k_{rel}$  against the substituent constant  $\sigma^+$  applicable to aromatic substitution is also a good straight line.<sup>24</sup>

Surprisingly, chlorine does not appear to be an active chlorodesilylating agent and often chlorination of the aromatic nucleus occurs rather than cleavage of the aryl-Si bond.<sup>53,104,110-9</sup> The orientation in iron-catalysed chlorination of phenylsilanes containing  $SiF_3$  and  $SiMe_3$  groups has been studied:<sup>120</sup> the  $SiMe_3$  group was found to be ortho-para directing whereas the  $SiF_3$  group was meta directing. Considerable amount of aryl-Si bond cleavage occurred with both the  $C_6H_5SiMe_3$  and  $C_6H_5SiF_3$  compounds in bromination and chlorination in the presence of iron filings.<sup>120</sup>

In view of the fact that the  $SiMe_3$  group is very weakly ortho:para directing it might be expected that the  $SiCl_3$  group, with three strongly electronegative groups attached to silicon, would be meta directing. The initial product of the exhaustive chlorination of phenyltrichlorosilane in the presence of iron has been described as the para isomer,<sup>117</sup> but more recently the isomer distribution has been determined for chlorination and bromination, in the presence of iron filings (see Table 2.3 page 22, the figures being based on Raman spectral analysis of the

Table 2.3

Bromination and Chlorination of C<sub>6</sub>H<sub>5</sub>SiCl<sub>3</sub>

Chlorination			Bromination			Ref.		
Temp.	% <u>o</u> -	% <u>m</u> -	% <u>p</u> -	Temp.	% <u>o</u> -		% <u>m</u> -	% <u>p</u> -
70°	24	74	2	62-5	31	31	38	137
50-60°	21	75	4	50-55	31	(32)	37	135

mixed m- and p-isomers).<sup>137</sup> In a recent determination, under analagous conditions, the SiCl<sub>3</sub> group was found to be chiefly meta directing in chlorination but ortho: para directing in bromination.<sup>135</sup>

Chlorine in acetic acid containing 1.5% water, does cleave phenyltrimethylsilanes but only at about the same rate as does bromine,<sup>62</sup> whereas in halogenation of aromatics chlorination is faster than bromination.<sup>121</sup> The small difference between the rates of chloro- and bromo-desilylation is another consequence of the greater nucleophilic power of the silyl group in phenyltrimethylsilanes than of the hydrogen atom in simple aromatic compounds; the more reactive a nucleophil, the less it discriminates between two electrophils.

*t*-Butyl hypochlorite with ultra-violet irradiation has been found to chlorinate the methyl group of phenyltrimethylsilane, no aryl-Si bond cleavage or nuclear substitution being reported.<sup>122</sup> However, since this is a free radical chlorination, aryl-Si bond cleavage would not be expected.

Iodine also cleaves the aryl-Si bond but less readily than bromine. Trimethylsilyl iodide was first prepared in this way.<sup>102</sup>



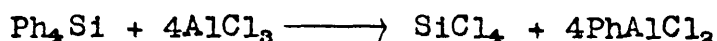
Iodine cleavage has also been used to identify the point of attachment of a silicon atom to a substituted ring.<sup>59</sup>

Eaborn has found that the aryl-Si bond is easily cleaved by iodine in the presence of aluminium iodide.<sup>123</sup>

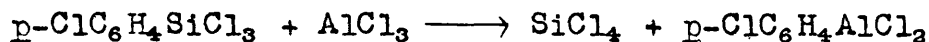
#### E. Reactions with Aluminium Chloride and Covalent

##### Halides.

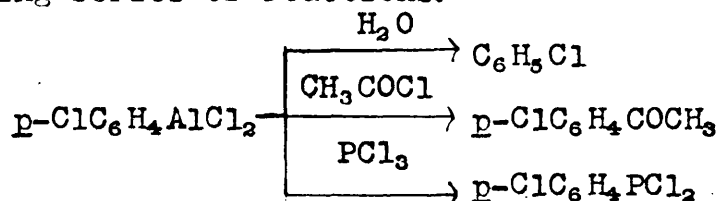
Since Kipping and Evison first reported that tetraphenylsilane gives silicon tetrachloride in more than 80% yield when treated with aluminium chloride in chloroform at 50°,<sup>128</sup> e. g.



similar cleavages have been observed with other phenyl- and halogenophenyl-silanes,<sup>76, 129-31</sup> and the reaction is claimed to be potentially of considerable value for the preparation of organo-aluminium compounds<sup>131</sup> e. g.



It should be noted however that the compound  $p\text{-ClC}_6\text{H}_4\text{AlCl}_2$  was not isolated, its presence being inferred from the following series of reactions.



This reaction with aluminium chloride has also been used to identify the halogeno-phenyl groups attached to silicon.<sup>117</sup>

In contrast to this, Benkeser and Krysiak have successfully acylated toluene with *m*- and *p*-trimethylsilylbenzoyl chlorides in the presence of aluminium chloride (or stannic chloride).<sup>132</sup>

Russell has studied the disproportionation of phenyltrimethylsilane (amongst other compounds) in the presence of metal halides by the use of vacuum techniques.<sup>133</sup> These studies were complicated by aryl-Si bond cleavage which occurred with almost all the metal halides used ( $\text{Al}_2\text{Br}_4$ ,  $\text{Al}_2\text{Cl}_6$ ,  $\text{Ga}_2\text{Br}_6$ ,  $\text{Ga}_2\text{Cl}_6$  and  $\text{ZrCl}_4$ ), the boron halides being the exception.

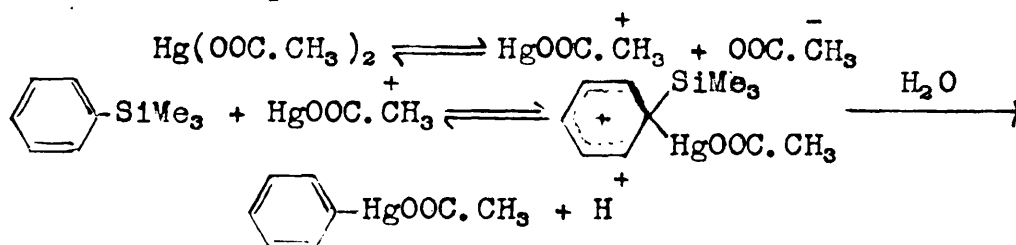
It has recently been found, however, that aluminium chloride is not such a good cleaving agent as the literature would suggest, less than 2% cleavage occurring with phenyltrichlorosilane and aluminium chloride when the reaction is carried out in a vacuum line under anhydrous conditions.<sup>134</sup> Previous workers have not taken such stringent precautions to exclude moisture from their reaction systems and, in fact, traces of water may account for these different observations.

Few other covalent halides have been examined for their ability to cleave aryl-Si bonds; antimony pentachloride does cause cleavage whereas the trichloride is ineffective.<sup>112</sup> In fact for successful chlorination of

aryl-silicon compounds both antimony trichloride and iron (ferric chloride) are effective catalysts, causing little aryl-Si bond cleavage.<sup>117-8,135</sup> Boron trifluoride, in fact, has been used as a catalyst for the acylation of phenyltrimethylsilanes using acetyl fluoride or benzoyl-fluoride, no aryl-Si bond cleavage occurring.<sup>136</sup>

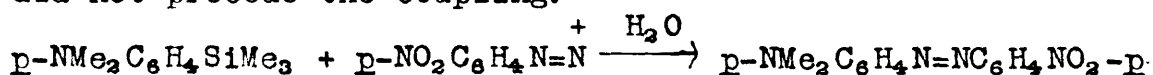
#### F. Reactions with Mercuric Salts.

Mercuric acetate in acetic acid-water readily cleaves aryl-Si bonds; this reaction has been studied kinetically by several workers.<sup>90,107,138-40</sup> Substituent effects in the compounds  $\text{RC}_6\text{H}_4\text{SiMe}_3$  show a similar pattern to that in protodesilylation. Mercuridesilylation was found to be second order,<sup>140</sup> the reaction product being an aryl-mercuric acetate. The most probable mechanism is one closely paralleling that proposed for the mercuration of aromatic compounds:-

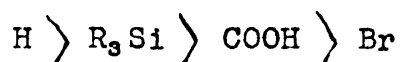


#### G. Reactions with Diazonium Ions.

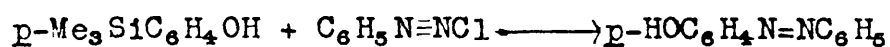
Sunthanker and Gilman found that the diazonium ion caused cleavage of aryl-Si bonds in suitably activated positions, although it was not proved that acid cleavage did not precede the coupling.<sup>83</sup>



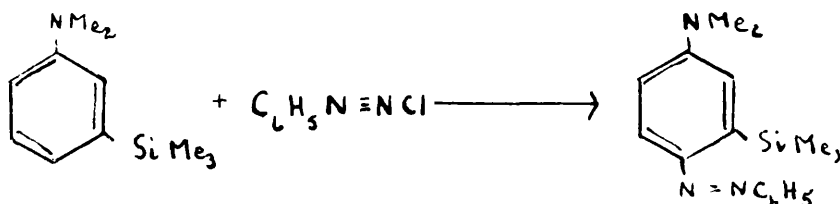
From competitive coupling reactions and replacement reactions the ease of replacement of substituents during diazo-coupling was found to decrease in the order:-



Sakata and Hashimoto have recently reported the cleavage of the aryl-Si bond in *p*-Me<sub>3</sub>SiC<sub>6</sub>H<sub>4</sub>OH with diazonium chloride<sup>68</sup> e. g.



whereas in *N,N*-dimethyl-3-trimethylsilyl aniline cleavage of the aryl-Si bond did not occur<sup>68</sup> e. g. ,



Similarly, *p*-nitrophenyldiazonium chloride gave 4-(*p*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>N=N), 3-Me<sub>3</sub>Si-C<sub>6</sub>H<sub>3</sub>NMe<sub>2</sub>.

### CHAPTER 3.

#### Mechanism of Nitration.

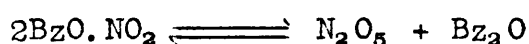
The range of nitrating agents which could be used for the study of the cleavage of aryl-Si bonds (nitro-desilylation) was somewhat limited by the need to avoid the possibility of protodesilylation. Therefore, nitric acid, either alone or with sulphuric acid, in aqueous or organic solvents, was not used in the present study, and the mechanisms of nitration under these conditions will not be reviewed. There are several excellent reviews dealing with this aspect of nitration to which reference will be made.<sup>141-3</sup>

##### A. Nitric Acid in Acetic Anhydride (Acyl Nitrates).

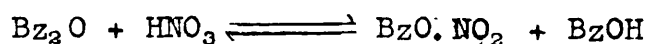
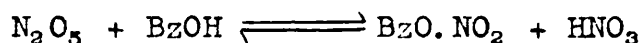
Acetyl nitrate was first prepared by Oxford who used it for the nitration of phenols and phenol ethers.<sup>144</sup> Benzoyl nitrate, prepared by the same method, was shown to be a useful nitrating agent,<sup>145</sup> and was found to give high ortho:para ratios in the nitration of anisole,<sup>146,177</sup> and of phenyl-ethyl ether.<sup>145</sup>

A kinetic study of the nitration of benzene with benzoyl nitrate in carbon tetrachloride was made by Gold, Hughes, and Ingold,<sup>147</sup> who found that with benzene in constant excess the reaction was approximately first order. Since benzoic anhydride was found to depress the rate of nitration it was suggested that benzoyl nitrate might be exerting its nitrating action through a small

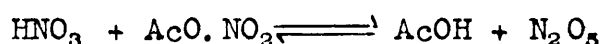
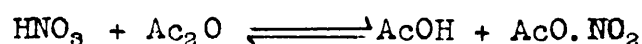
stationary concentration of dinitrogen pentoxide formed, together with benzoic anhydride, in the following rapidly established equilibrium:-



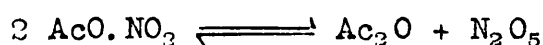
They found that the rate of nitration by benzoyl nitrate could be simulated by using dinitrogen pentoxide and benzoic anhydride. From the effects observed due to varying the relative concentrations of benzoic anhydride and benzoic acid they proposed that the following equilibria were present:<sup>147</sup>



No evidence was obtained for the nitration of aromatic compounds by benzoyl nitrate itself. On the basis of these results they suggested that nitration by acetyl nitrate, or by a solution of nitric acid in acetic anhydride, proceeded through dinitrogen pentoxide formed by the following systems of reactions:<sup>147</sup>



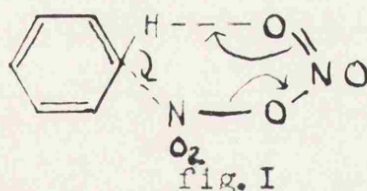
and therefore:-



Burton and Praill, however, on studying the structure of acyl nitrates found that they showed no tendency to react in the form  $\text{RCO} \cdot \text{NO}_3$ , and since they failed to isolate any anhydride from the nitration of anisole with

acetyl, benzoyl, or p-nitrobenzoyl nitrate concluded that, although this did not exclude the possibility of nitration by dinitrogen pentoxide, the acyl nitrates themselves might be the nitrating agents.<sup>148</sup>

Halvarson and Melander have investigated the kinetic isotope effect in the nitration of anisole with nitric acid in acetic anhydride, benzoyl nitrate in carbon tetrachloride, and with benzoyl chloride plus silver nitrate in acetonitrile.<sup>177</sup> They found no kinetic isotope effect ( $k_T/k_H = 1.0 \pm 0.1$  at  $0^\circ$ ) and this, therefore rules out a possible concerted mechanism suggested by Ingold and co-workers for the attack of dinitrogen pentoxide (see fig. I).<sup>178</sup> It does not, however, rule out dinitrogen



pentoxide as the attacking entity; it shows only that hydrogen replacement proceeds as in ordinary nitronium ion nitrations, that is the attachment to carbon is the slow step and the splitting off of the hydrogen is kinetically insignificant.

The use of solutions of nitric acid in acetic anhydride was first introduced by Orton for the N-nitrations of aromatic amines.<sup>149</sup> Pictet and Khotinsky isolated acetyl nitrate from solutions of dinitrogen pentoxide in acetic

anhydride,<sup>150</sup> and found that its nitrating properties were similar to those of Orton's solution and Francis's benzoyl nitrate.

Solutions of nitric acid in acetic anhydride have been found to be particularly effective for the nitration of alcohols,<sup>151-4</sup> and recently for the nitration of alkenes.<sup>155-8</sup> It has long been known that the use of this nitration medium gives high ortho:para ratios in the nitration of anisole,<sup>146,177</sup> acetanilide,<sup>159,161</sup> propionanilide,<sup>161</sup> and also phenol.<sup>160</sup> Nitric acid in acetic anhydride was also used by Ingold and co-workers<sup>162-6</sup> for competitive nitration studies of substituted aromatic compounds.

Despite the many and varied uses of nitric acid in acetic anhydride, the identity of the nitrating agent has, until recently, received little attention. This study of the nature of the nitrating agent is complicated by the fact that tetranitromethane can be prepared in almost theoretical yield by allowing concentrated nitric acid and acetic anhydride to stand together for several days.<sup>167-8</sup>



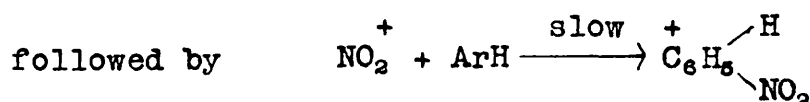
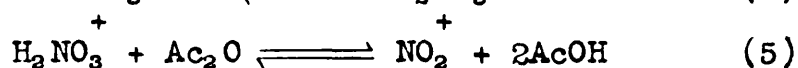
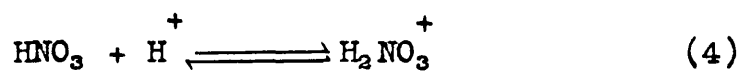
However, Cohen and Wibaut found that the rates of disappearance of nitrate from such solutions is fairly slow (about half the nitrate is consumed in 24hr. at 25°),<sup>169</sup> so that this side reaction does not need to be considered in fairly fast reactions.

Recently, physical measurements of various types have been made on solutions of nitric acid and acetic anhydride,<sup>170-2</sup> and these results are consistent with the series of reactions 1-3.



Thus, Vandoni and Viola concluded from vapour pressure measurements of acetic anhydride and absolute nitric acid at  $-10^\circ$  that at equal mole fractions of each component, only acetyl nitrate and acetic acid are present.<sup>170</sup> At higher nitric acid concentrations the vapour pressure rises rapidly due to the formation of dinitrogen pentoxide. Similarly, it was concluded from Raman spectral measurements that when an excess of acetic anhydride is present the only nitrating agent detectable is acetyl nitrate.<sup>171</sup> With a slight excess of nitric acid, dinitrogen pentoxide is observed to be present. The presence of nitronium ion could not be detected by infra-red spectral measurements,<sup>172</sup> even when the mole percentage of acetic anhydride was as low as 31. The formation of nitronium ions from absolute nitric acid was promoted, however, by low concentrations (8 mole%) of acetic anhydride. Finally, the presence of acetyl nitrate and dinitrogen pentoxide was indicated by density, viscosity, and refractive index measurements.<sup>173-4</sup>

While it remains reasonably well established that aromatic nitrations by solutions of nitric acid in aqueous media and in organic solvents proceed by a mechanism involving the nitronium ion, there remains uncertainty in the case of nitrations in acetic anhydride. In a recent study of the nitration of benzene with 90% nitric acid in excess acetic anhydride, Paul found that the reaction was approximately second order in nitric acid, that the reaction rate was retarded by nitrate ion, and was strongly accelerated by sulphuric acid. Changing the composition of the medium from 90% acetic anhydride/10% acetic acid to 50% acetic anhydride/50% acetic acid had no effect on the rate, but when the acetic anhydride concentration was reduced to 5% the rate of nitration of benzene was reduced almost to zero. Paul, therefore, concluded that the active nitrating species was the nitronium ion ( $\text{NO}_2^+$ ) formed in the following series of reactions:<sup>178</sup>



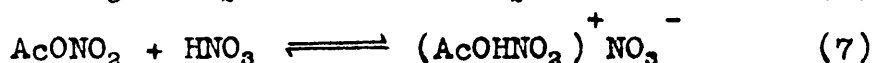
The addition of a small amount of sulphuric acid (2 mole%) in nitric acid-acetic anhydride solutions was found to increase the proportion of para-isomer in the nitration of bromo- and chloro-benzene.<sup>178</sup> Paul states

that this effect is opposite to that observed previously for anisole, where a higher proportion of ortho isomer was obtained; he attributes the change in orientation to an electrostatic interaction between ion and dipole, this effect playing a more significant part in the medium of lower dielectric constant.<sup>176</sup>

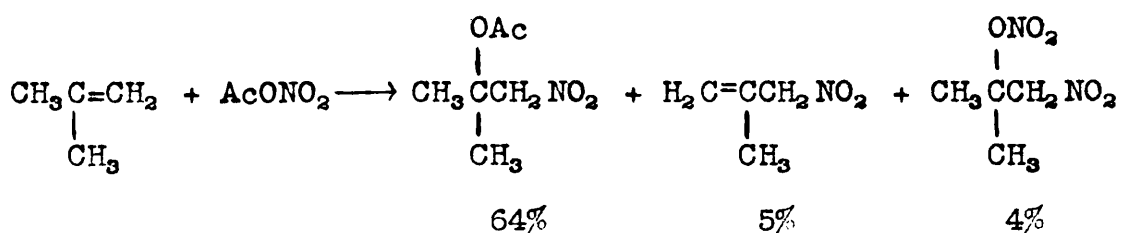
Nitration at oxygen centres by nitric acid containing between 0 - 10% acetic anhydride is second order with respect to nitric acid.<sup>179</sup> Within this range of media a maximum rate of reaction appeared at 7% acetic anhydride although at much higher acetic anhydride content the reaction was found to be immeasurably fast. Bonner has interpreted these results in terms of nitration by dinitrogen pentoxide.<sup>179</sup>

Bordwell and Garbisch have recently studied the nitration of simple alkenes with nitric acid in acetic anhydride<sup>158</sup> have and/made several very interesting observations, and suggestions. They found that when the nitric acid was added to the acetic anhydride at  $-10^{\circ}$  little or no nitration occurred on addition of the alkene, whereas when the nitric acid and acetic anhydride were mixed at  $20-25^{\circ}$ , good yields of nitration products were then obtained. They concluded that the formation of acetyl nitrate is essential to successful nitrations, inferring that it is not formed at  $-10^{\circ}$ . This conclusion was supported by the reaction of anisole under the same conditions.

The reactions were found to be catalysed by small amounts of sulphuric acid, and addition of nitrate and acetate ions retarded the reaction. They suggested that protonated acetyl nitrate,  $[\text{AcOHNO}_2]^+$ , was the reactive species, which is consistent with Paul's observations. They suggested the following series of equilibria:-



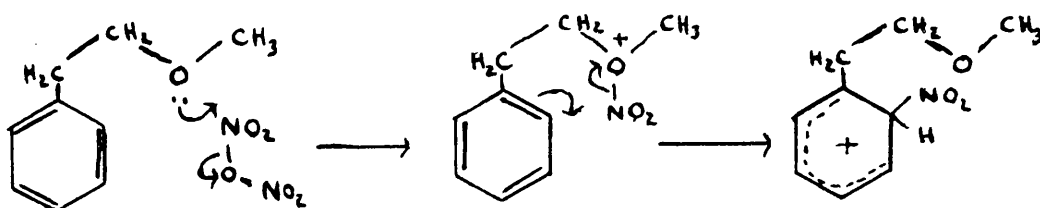
In these reactions with alkenes the principal product is generally the  $\beta$ -nitro acetate formed by the Markownikoff addition to the double bond. Smaller amounts of  $\beta$ -nitro alkenes and of  $\beta$ -nitro nitrates are also formed:-



The formation of the  $\beta$ -nitro nitrates was thought to be due to the presence of dinitrogen pentoxide.

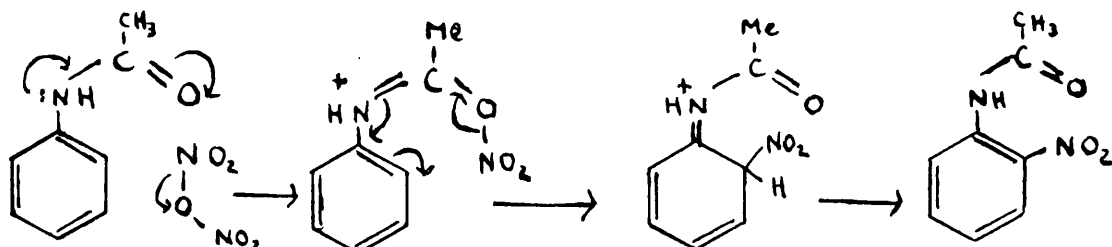
The latest ideas on the mechanism of nitration in nitric acid-acetic anhydride solutions comes from Norman and co-workers.<sup>180</sup> They have investigated the ortho:para ratio in aromatic nitrations using vapour phase chromatography for the analysis of the products.<sup>60,180-4</sup> They explained the high ortho:para ratios, on nitration with nitric acid in acetic anhydride, in terms of displacement of the nitrate ion from covalent dinitrogen pentoxide by

the oxygen of the ether, forming an intermediate which rearranges to the usual transition state for ortho-substitution,<sup>180</sup> e. g.



This provides a route for the formation of the o-nitro derivative which is available neither at the para-position of the ether, nor at the ortho-position of ethyl benzene or toluene.

In support of these conclusion they found that anisole gives the same proportions of nitro derivatives with dinitrogen pentoxide as with acetyl nitrate. The nitro derivatives of methyl 3-phenylpropyl ether are formed in essentially the same proportions when nitric acid or acetyl nitrate is the reagent. Here the operation of a mechanism as suggested above would involve the formation of a seven-membered cyclic transition state which would be less readily formed than its six-membered analogue. On the basis of these ideas they proposed the following mechanism for the increased ortho-reactivity in



the nitration of acetanilide with acetyl nitrate.<sup>180</sup>

However, Gray and Lewis<sup>185</sup> found that with *p*-terphenyl in nitric acid-acetic acid-acetic anhydride media the rate of nitration was strongly retarded by the addition of nitrate ions, and unaffected by the addition of perchlorate ions. They concluded that in all cases the attacking entity must be the nitronium ion.<sup>185</sup>

#### B. Nitronium Salts.

It has been suggested by Kuhn and Olah<sup>187</sup> that aromatic nitration involving nitryl halides, dinitrogen pentoxide and dinitrogen tetroxide (the halides and anhydrides of nitric acid) should be considered as a Friedel-Crafts type reaction. A close analogy obviously exists with the corresponding Friedel-Crafts ketone synthesis involving acyl halides and anhydrides.

##### 1. Nitrations with Dinitrogen Pentoxide.

Dinitrogen pentoxide has been known for a long time to be an effective agent for the nitration of amines,<sup>188-9</sup> alcohols,<sup>190-1</sup> and aromatic compounds.<sup>192-8</sup> The nitration of benzotrichloride in carbon tetrachloride with dinitrogen pentoxide was found to occur without hydrolytic loss of chlorine,<sup>192</sup> and benzoyl chloride<sup>195</sup> and nitroso benzene<sup>193</sup> have been successfully nitrated using dinitrogen pentoxide in the presence of phosphorous pentoxide.

Dinitrogen pentoxide has also been found to add to olefins.<sup>194,197-8</sup> Stevens and Emmons found that nitrate

ion had no effect on the rate of this addition and, in fact, the presence of nitrate ion in a mixture of benzene and 1-octene in methylene chloride reduced the rate of aromatic nitration almost to zero, and clean olefin addition occurred.<sup>197</sup>

The first kinetic studies of nitration by dinitrogen pentoxide were made by Ingold and co-workers,<sup>178</sup> who studied the nitration of a number of halogen- and carboxyl-substituted benzenes in aprotic solvents, such as carbon tetrachloride. A simple limiting kinetic form was distinguished as the uncatalysed reaction upon which was superposed other forms of reaction all catalysed by nitric acid.

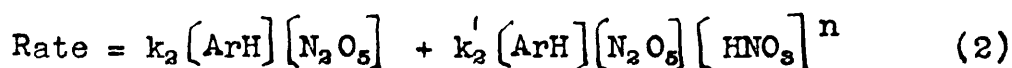
The uncatalysed reaction was isolated and found to be a second order process, obeying the rate law:-

$$\text{Rate} = k_2 [\text{ArH}] [\text{N}_2\text{O}_5] \quad (1)$$

It was found to have a normal temperature coefficient and showed a large positive salt effect, ionic nitrates also catalysing the reaction.

The catalysed reactions were found to have lower temperature coefficients than the uncatalysed reactions and to depend upon higher powers of the nitric acid concentrations. The initial increase in rate is much more marked at lower temperatures, the concentrations of nitric acid needed to cause auto-catalysis then being much lower. This can be predicted if the equation has an

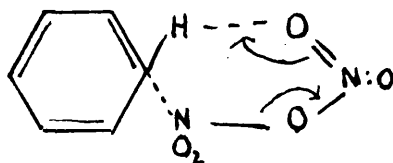
additional term, (Equation 2), and if variation of  $k_2'$  with temperature is much less than that of  $k_2$ .



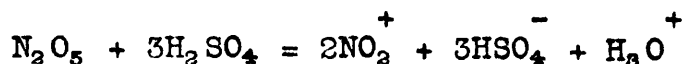
The uncatalysed reaction was interpreted as a nitration of the aromatic molecule by the covalent dinitrogen pentoxide molecule. This agrees with the kinetic form of the reaction, with the absence of retardation by ionic nitrates, and with the small solvent effect on the rate.

The catalysed reaction was thought to be attack by the  $[\text{NO}_2^+ \cdot \text{NO}_3^-]$  ion pair which was assumed to require solvation by molecules of nitric acid. As the nitric acid content increased so the catalysed reaction should be transformed into one in which the attacking species is a free nitronium ion.

As a speculation, they suggested that the transition state might have a cyclic form.



Solutions of dinitrogen pentoxide in sulphuric acid have been shown to be very effective nitrating agents having nitrating properties closely similar to those of solutions of nitric acid in sulphuric acid,<sup>199</sup> and Millen found the ionisation of dinitrogen pentoxide in sulphuric acid to be <sup>200</sup> :-



Bachman and Dever found that the stable insoluble complex formed from dinitrogen pentoxide and boron trifluoride, namely,  $\text{N}_2\text{O}_5 \cdot \text{BF}_3$ , which was first discovered by Schmeisser,<sup>202</sup> was a very effective nitrating agent.<sup>201</sup> Its physical and chemical properties indicated that the complex was ionic and its formula was thought to be<sup>201</sup>



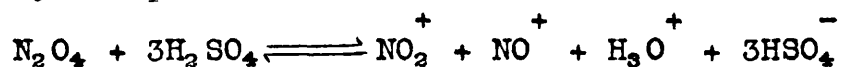
This structure has since been proved to be correct by the use of chemical analysis, X-ray powder patterns, infrared spectra, magnetic susceptibilities and electrical conductivity measurements.<sup>203</sup>

The use of dinitrogen pentoxide as an effective nitrating agent in Friedel-Crafts type nitrations in the presence of Lewis acid catalysts (such as  $\text{BF}_3$ ,  $\text{TiCl}_4$ ,  $\text{SnCl}_4$ , and  $\text{PF}_5$ ) in tetramethylene sulphone has been extended by Kuhn and Olah.<sup>187</sup> Halobenzenes (fluoro-, chloro-, bromo-, dihalo-benzenes, benzotrifluoride) were nitrated with yields of 79-89%. When the dinitrogen pentoxide nitrations are carried out in liquid anhydrous hydrogen fluoride as solvent with catalysts such as the fluorides  $\text{BF}_3$ ,  $\text{SbF}_5$ ,  $\text{PF}_5$ ,  $\text{AsF}_5$ ,  $\text{SiF}_4$ ,  $\text{NbF}_5$ ,  $\text{TaF}_5$ ,  $\text{WF}_6$  etc., a quantitative yield of the corresponding nitronium salt occurs, and since hydrogen fluoride also acts as a good ionising solvent an extremely active nitration medium is obtained.<sup>187</sup>

## 2. Nitrations with Dinitrogen Tetroxide.

The catalytic effect of aluminium chloride and ferric chloride on the nitration of aromatics with dinitrogen tetroxide was first studied by Schaarschmidt.<sup>204</sup> Pinck found that when sulphuric acid was used to catalyse this nitration only half of the dinitrogen tetroxide was used up, the remainder being present as nitrosyl sulphuric acid.<sup>205</sup> Titov et al. have used dinitrogen tetroxide in sulphuric acid as a nitrating agent.<sup>206-7</sup>

Raman spectroscopic,<sup>200,208</sup> and cryoscopic<sup>209</sup> investigations of solutions of dinitrogen tetroxide in sulphuric acid provided proof that the effective nitrating agent in these solutions is the nitronium ion, and also explained the formation of an equimolecular amount of nitrosyl sulphuric acid:-

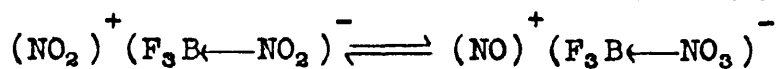


The addition of dinitrogen tetroxide to olefins has been extensively used for the preparation of dinitro-paraffins, nitro-alcohols and nitro-alkylnitrates.<sup>210-5</sup> The reaction was, at first, thought to occur by heterolytic addition,<sup>210-2</sup> but recent studies have been interpreted in terms of a homolytic process.<sup>213-4</sup>

The stable  $\text{N}_2\text{O}_4 \cdot \text{BF}_3$  complex, prepared as a crystalline insoluble salt,<sup>216</sup> has been used as a nitrating agent but was found to be only moderately reactive.<sup>216-7</sup> Bachman et al. suggested a nitronium salt structure for the complex:<sup>216</sup>



This complex, however, also shows an ability to nitrosate and diazotise, thus acting as a nitrosonium salt. Kuhn and Olah suggested that the complex is actually an equilibrium mixture of the nitronium and nitrosonium forms.<sup>187</sup>

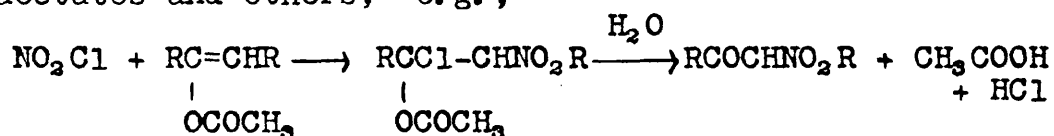


Recent work by Sprague et al.<sup>203</sup> shows this to be the case.

During the course of their investigations Olah and Kuhn found that homogeneous Friedel-Crafts type nitrations with dinitrogen tetroxide and Lewis acid catalysts (e.g.,  $\text{TiCl}_4$ ,  $\text{BF}_3$ ,  $\text{BCl}_3$ ,  $\text{PF}_5$ , and  $\text{AsF}_5$ ) could be carried out in tetramethylene sulphone solution.<sup>187</sup> When chloride and bromide catalysts were used (e.g.,  $\text{AlCl}_3$ ,  $\text{AlCBr}_3$ ) a considerable amount of ring chlorination and bromination occurred.

### 3. Nitrations with Nitryl Chloride.

Nitryl chloride itself is not usually a nitrating agent since it dissolves unchanged in benzene, and chlorinates the alkyl benzenes;<sup>218</sup> it will, however, nitrate phenol although the mechanism of the reaction is not known.<sup>219</sup> Nitryl chloride has recently been found to be a fairly successful agent for the nitration of enol-acetates and ethers,<sup>220</sup> e.g.,



A Friedel-Crafts type nitration using nitryl chloride was first reported by Price and Sears who found that aluminium chloride was the most suitable catalyst.<sup>221</sup> Deactivated aromatics, however, were nitrated only with difficulty.

Kuhn and Olah, however, have shown that aromatic compounds, including deactivated ones, can be nitrated with ease using nitryl chloride and a suitable Friedel-Crafts catalyst. Titanium tetrachloride was found to be the most effective catalyst but the halides FeCl<sub>3</sub>, ZrCl<sub>4</sub>, AlCl<sub>3</sub>, and AlBr<sub>3</sub> were also satisfactory, although the reaction was more difficult to handle.<sup>187</sup>

Anhydrous silver tetrafluoroborate, suggested as being a cation-forming agent in aromatic substitutions,<sup>221</sup> has been found to be suitable for the formation of nitronium tetrafluoroborate directly from nitryl chloride, for example:<sup>187, 221-2</sup>



Anhydrous silver tetrafluoroborate can be dissolved in the aromatic, or in a suitable solvent and added to the aromatic. The silver tetrafluoroborate forms a stable complex with the aromatic, and when the nitryl chloride is added it reacts with this complex. The silver halide is eliminated in a relatively slow reaction which possibly takes place simultaneously with the interaction of the nitro group with the aromatic. As a result, this type

of nitration gives a considerably higher selectivity in nitration than the alternative process, in which nitryl chloride and silver tetrafluoroborate are reacted together,<sup>187</sup> before being added to the aromatic compound. However, a certain amount of chlorination always occurs, probably due to the presence of some free chlorine in the nitryl chloride.

#### 4. Nitrations with Nitryl Fluoride.

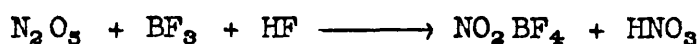
The nitration of aromatics with nitryl fluoride in the absence of catalysts has been reported;<sup>224</sup> it being suggested that in the solution nitryl fluoride dissociates into  $\text{NO}_2^+$  and  $\text{F}^-$ . Less reactive aromatics were, however, not nitrated. Using Lewis acid type fluoride catalysts, such as the fluorides  $\text{BF}_3$ ,  $\text{PF}_5$ ,  $\text{AsF}_5$ , and  $\text{SbF}_5$ , it has been shown that simple Friedel-Craft type nitrations can be carried out using nitryl fluoride.<sup>187</sup> When  $\text{BF}_3$  is used as catalyst, nitronium tetrafluoroborate is formed.<sup>222-3, 225-6</sup>

#### 5. Nitrations with Nitryl Bromide.

Nitrations with the solutions obtained by halogen exchange of nitryl chloride with potassium bromide in sulphur dioxide have been carried out at  $-20^\circ$ , using titanium tetrabromide as catalyst.<sup>187</sup> The yields of nitrations are lower than those obtained with nitryl chloride, due to the formation of more ring brominated products.

## 6. Nitrations with Stable Nitronium Salts.

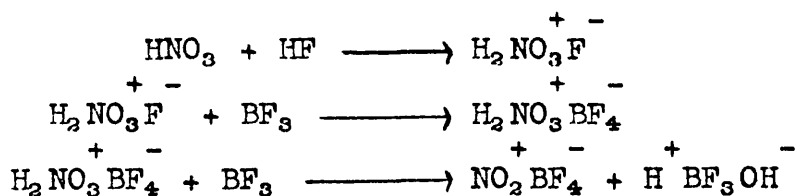
The existence of nitronium salts such as  $\text{NO}_2\text{ClO}_4$ ,  $\text{NO}_2\text{FSO}_3$ ,  $\text{NO}_2\text{BF}_4$ , and  $\text{NO}_2\text{SbF}_6$ , has been known for a number of years.<sup>227-8</sup> It was Olah, Kuhn and Mlinko who first reported nitrations by nitronium salts<sup>229</sup> such as  $\text{NO}_2\text{BF}_4$ ,  $\text{NO}_2\text{AsF}_6$ ,  $\text{NO}_2\text{PF}_6$  etc. These were prepared from nitromethane solutions of dinitrogen pentoxide, catalyst, anhydrous hydrogen fluoride systems, e. g.,



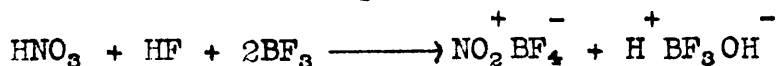
Improved yields have now been obtained by increasing the ratio of hydrogen fluoride and boron trifluoride to dinitrogen pentoxide.<sup>187</sup>



and, in fact, it was found that nitric acid itself is converted practically quantitatively into nitronium tetrafluoroborate according to the following series of equations:<sup>187</sup>



the overall reaction being:-



Infrared spectroscopic investigations of the isolated nitronium salts was in agreement with the linear  $\text{O}=\text{N}=\text{O}$  structure.<sup>230</sup> Nitronium tetrafluoroborate has been found to be a very active nitrating agent,<sup>222-3, 225-6, 229</sup> the

reactions being carried out in heterogeneous solutions since nitronium tetrafluoroborate is almost insoluble in most organic solvents. Tetramethylene sulphone has recently been found to be a satisfactory solvent for nitronium tetrafluoroborate, enabling the reactions to be carried out in homogeneous solutions.<sup>187</sup>

Continuing with this work, Olah et al.<sup>231-2</sup> have studied the nitration of the alkylbenzenes and halobenzenes in tetramethylene sulphone solution using Ingold's method of competitive nitration.<sup>162</sup> The reaction mechanism was considered to involve oriented (or localised)  $\pi$ -complex formation, between the nitronium ion and the aromatic, as the rate-determining step. This was in accordance with the fact that normal partial rate factors and empirical selectivity factors are not applicable to these systems.

#### 7. Nitrations with Metallic Nitrates.

The use of metallic nitrates in acetic anhydride or glacial acetic acid has been investigated by several workers.<sup>233-5</sup> Bacharach found that copper nitrate in acetic anhydride was the most effective,<sup>235</sup> and this reagent has been used by several workers for the nitration of aryl-Si compounds.<sup>58-9,69</sup>

Recently, the use of sodium or potassium nitrate in sulphuric acid as a nitrating agent has been reported;<sup>196,236-7</sup> the uranium nitrate-water-nitrogen tetroxide complex in acetic anhydride has also been used.<sup>238-9</sup>

SECTION 2  
EXPERIMENTAL

## Chapter 4.

### Preparation of Organosilanes.

#### A. General Experimental Techniques.

##### 1. Grignard reactions

Preparations involving the use of Grignard reagents were carried out in three-necked round-bottomed flasks, fitted with a central mechanical stirrer, a dropping funnel and a double-surface condenser. Moisture was excluded from the apparatus by means of sulphuric acid bubblers, and all apparatus was dried thoroughly before use. Magnesium turnings for Grignard reactions (Hopkin and Williams) were used without further treatment, but commercial 'anhydrous ether' (Macfarlane) was further dried over sodium wire before use.

The reactions were initiated by the addition of a few drops of dibromoethane when necessary. Unless otherwise stated, magnesium salts and unreacted Grignard reagent were hydrolysed by the addition of saturated ammonium chloride solution to the vigorously stirred reaction mixture until two clear layers separated. The ethereal layer was then separated, washed several times with water and dried over anhydrous sodium sulphate.

##### 2. Lithium reactions

Organo-lithium reagents were prepared from lithium metal (Associated Lead Manufacturers) which was beaten, under a protective coating of paraffin oil, into foil;

this in turn was washed with ether and cut, under nitrogen, into small fragments. The preparations of organo-lithium reagents were executed in an atmosphere of dried, oxygen-free nitrogen, in an apparatus similar to that used for the preparation of Grignard reagents. The ether was again dried over sodium wire.

Tetrahydrofuran was used as a solvent for some organo-lithium reactions. It was dried, first by storage over sodium wire, followed by treatment with several small portions of lithium aluminium hydride. It was finally distilled, immediately before use, from a fresh sample of lithium aluminium hydride.

The reactions were usually initiated by warming. The reaction mixtures were finally hydrolysed with saturated ammonium chloride, the ethereal layer separated, washed several times with water, and finally dried over anhydrous sodium sulphate.

### 3. Wurtz-Fittig reactions.

The reactions were carried out in apparatus similar to that described for the preparation of Grignard reagents. The sodium metal was heated in dried sulphur-free toluene, which was vigorously stirred. When the sodium had become molten (refluxing toluene temperature), approximately 5% of the volatile reactant (usually trimethylchlorosilane) was added. The combined reactants were then added dropwise to this solution, the heat of reaction usually being

sufficient to maintain the reflux. The reaction mixtures were refluxed for 1.5hr. after the addition of the reactants had been completed, cooled, and filtered through a scintered glass funnel.

#### 4. Fractionation.

Four fractionating columns were used:-

- a). A glass-helices packed column - 15 theoretical plates - diameter 2.54cm., packed length 72cm.
- b). A Dixon-gauze packed column - 45 theoretical plates diameter 1.1cm., packed length 55cm., (packing - 1/16×1/16 Dixon-gauze rings).
- c). A Vigreux column - 18 theoretical plates - diameter 0.8cm., indentated length 86cm.
- d). A Vigreux column - 12 theoretical plates - diameter 0.8cm., indentated length 55cm.

The still pot heating for the fractionations was by electrothermal heating mantle, with heat regulation by a 'Variac' controller. A silicone oil bath was used for heating the still pot for the majority of vacuum fractionations.

Vacuum fractionations were carried out using a Edwards high vacuum pump, the vacuum being controlled with a mercury manostat and the pressure measured by a differential mercury pressure gauge or a vacustat.

#### 5. General

In all preparations the solvent was first removed

at atmospheric pressure through the glass-helices packed column. The residue was then fractionated, either at atmospheric pressure through the Dixon-gauze column, or at atmospheric pressure or under reduced pressure through a precision Vigreux column. The larger Vigreux column was the column used unless otherwise stated.

Microanalyses for carbon, hydrogen or nitrogen were made by Drs. Weiler and Strauss, Oxford or by Dr. Bernhardt, Germany.

#### B. Preparation of Some Organic Intermediates.

##### p-Chlorotoluene

Commercial p-chlorotoluene was carefully fractionated through the Dixon-gauze packed column. b.p. 162.5°/766mm.,  
 $n_D^{20}$  1.5209 Lit.<sup>27</sup>, b.p. 162°,  $n_D^{20}$  1.5199

##### Chlorobenzene

Commercial chlorobenzene was carefully fractionated through the Dixon-gauze packed column. b.p. 132°/754mm.,  
 $n_D^{20}$  1.5251 Lit.<sup>27</sup>, b.p. 132°,  $n_D^{20}$  1.5248

##### m-Bromochlorobenzene

Prepared from m-chloroaniline (223.3g., 1.75mole) by means of a Sandmeyer reaction.<sup>240</sup> Fractionation, through the Vigreux column, gave m-bromochlorobenzene in 89.5% yield (369.1g.). b.p. 195°/759mm. Lit.<sup>27</sup>, b.p. 196°

##### o-Bromochlorobenzene

Prepared from o-chloroaniline (127.6g., 1.0mole) by means of a Sandmeyer reaction.<sup>240</sup> Fractionation, through

the smaller Vigreux column, gave o-bromochlorobenzene in 77.9% yield (149.5g.). b.p. 200-2°/760mm. Lit.<sup>27</sup>,

b.p. 204°

#### m-Chlorobenzylbromide

Prepared, by the method of Barnes and Gordon,<sup>241</sup> from m-chlorotoluene (530g., 4.20mole) and bromine (720g., 9.0mole), in 67.2% yield (620.8g.). b.p. 120-7°/21±2mm. Lit.<sup>27</sup>, b.p. 109°/10mm.

#### m-Chloroanisole

Prepared from m-anisidine (153.9g., 1.25mole) by means of a Sandmeyer reaction.<sup>240</sup> Fractionation, through the smaller Vigreux column, gave m-chloroanisole in 60.3% yield (107.4g.). b.p. 193-4°/769mm.,  $n_D^{25}$  1.5327 Lit.<sup>27</sup>, b.p. 193-4°

#### o-Bromonitrobenzene

Prepared, by the method of Carlin and Larson,<sup>242</sup> from o-nitroaniline (138g., 1.0mole) in 92.6% yield (188g.). m.p. 41-42.5° Lit.<sup>27</sup>, m.p. 42°

#### p-Methylbenzylbromide

A mixture of benzoyl peroxide (2g.) and N-bromo-succinimide (80g., 0.45mole) was added to a solution of p-xylene (53.1g., 0.50mole) in carbon tetrachloride (500ml.) and the reaction mixture heated slowly. After approximately 20min. a vigorous reaction occurred and the solution boiled vigorously. The reaction mixture was refluxed for a further 1hr., cooled, filtered, and the carbon tetrachloride

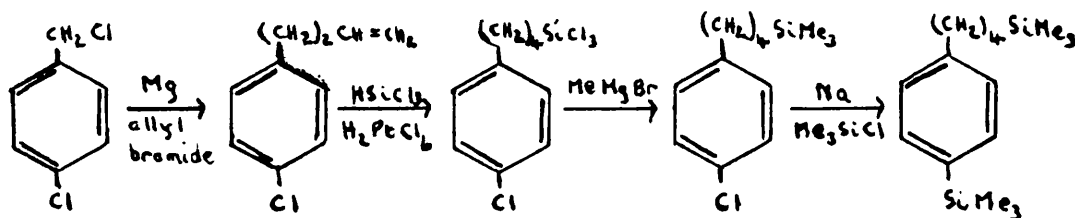
distilled off. The residue, on fractionation through the Vigreux column, gave *p*-methylbenzylbromide in 64.5% yield (53.8g.). b.p. 132-4°/55mm. Lit.<sup>27</sup>, b.p. 218-20°/740mm., m.p. 35°

C. Preparation of Organosilanes.

The preparation of *o*-, *m*-, and *p*-Me<sub>3</sub>SiC<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>n</sub>SiMe<sub>3</sub> (where n = 1 to 4).

1. *o*-, *m*-, and *p*-Me<sub>3</sub>SiC<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>4</sub>SiMe<sub>3</sub>

These compounds were prepared by the following general route:



4-(*p*-Chlorophenyl)-but-1-ene.

The Grignard reagent, prepared from *p*-chlorobenzylchloride (203.8g., 1.25mole) and magnesium turnings (36.5g., 1.50mole), was coupled with allyl bromide (181.5g., 1.50mole), the heat of reaction being sufficient to maintain reflux during the addition of the allyl bromide. The reaction mixture was then refluxed for a further 20hr., and hydrolysed. Fractionation, through the Vigreux column, gave 4-(*p*-chlorophenyl)-but-1-ene in 74.3% yield (154.7g.). b.p. 92-3°/9-10mm.,  $n_D^{25}$  1.5239 (Found: C, 71.97; H, 7.04. C<sub>10</sub>H<sub>11</sub>Cl requires C, 72.04; H, 6.65%).

4-(m-Chlorophenyl)-but-1-ene.

The Grignard reagent, prepared from m-chlorobenzyl-bromide (232.9g., 1.25mole) and magnesium turnings (36.5g., 1.50mole), after coupling with allyl bromide (181.5g., 1.50mole), gave 4-(m-chlorophenyl)-but-1-ene in 72.2% yield (150.7g.). b.p. 93-4°/10±0.5mm.,  $n_D^{25}$  1.5240 (Found: C, 72.81; H, 6.75.  $C_{10}H_{11}Cl$  requires C, 72.04; H, 6.65%).

4-(o-Chlorophenyl)-but-1-ene.

The Grignard reagent, prepared from o-chlorobenzyl-chloride (203.8g., 1.50mole) and magnesium turnings (36.5g., 1.50mole), after coupling with allyl bromide (181.5g., 1.50mole), gave 4-(o-chlorophenyl)-but-1-ene in 68.5% yield (142.5g.). b.p. 86-8°/10±0.5mm.,  $n_D^{25}$  1.5253 (Found: C, 71.60; H, 6.62.  $C_{10}H_{11}Cl$  requires C, 72.04; H, 6.65%).

4-(p-Chlorophenyl)-butyltrichlorosilane.

The catalyst, 0.1M chloroplatinic acid in 2-propanol (2ml.), was added to the trichlorosilane (135.5g., 1.0mole) and the mixture refluxed. 4-(p-Chlorophenyl)-but-1-ene (143g., 0.86mole) was then added dropwise, the temperature of the reaction mixture rising to 80°C during the addition. The reaction mixture was finally refluxed for 5hrs., the temperature remaining constant at approximately 80°C. The excess of trichlorosilane was distilled off, and the residue, on fractionation through the Vigreux column, gave

two products:

a). 4-(p-chlorophenyl)-butyltrichlorosilane in 61.0% yield (158.7g.). b.p. 140-2°/2.0±0.5mm.,  $n_D^{25}$  1.5228 (Found: hydrolysable chlorine, 35.17.  $C_{10}H_{12}Cl_3Si$  requires hydrolysable chlorine, 35.39%).

b). 1-(p-chlorophenyl)-1-trichlorosilyl-n-butane in 14.8% yield (38.6g.). b.p. 122-7°/2.5±0.5mm.,  $n_D^{25}$  1.5291 (Found: hydrolysable chlorine, 35.19.  $C_{10}H_{12}Cl_3Si$  requires hydrolysable chlorine, 35.39%).

4-(m-Chlorophenyl)-butyltrichlorosilane.

4-(m-Chlorophenyl)-but-1-ene (149.4g., 0.90mole), on addition to trichlorosilane (135.5g., 1.00mole) and 0.1M chloroplatinic acid in 2-propanol (2ml.), gave two products:

a). 4-(m-chlorophenyl)-butyltrichlorosilane in 61.6% yield (167.8g.). b.p. 129-31°/1.0±0.2mm.,  $n_D^{25}$  1.5230 (Found: hydrolysable chlorine, 35.19.  $C_{10}H_{12}Cl_3Si$  requires hydrolysable chlorine, 35.39%).

b). 1-(m-chlorophenyl)-1-trichlorosilyl-n-butane in 10.8% yield (29.2g.). b.p. 128-30°/5.0±0.5mm.,  $n_D^{25}$  1.5286 (Found: hydrolysable chlorine, 35.20.  $C_{10}H_{12}Cl_3Si$  requires hydrolysable chlorine, 35.39%).

4-(o-Chlorophenyl)-butyltrichlorosilane.

4-(o-Chlorophenyl)-but-1-ene (131.7g., 0.79mole), on addition to trichlorosilane (135.5g., 1.00mole) and 0.1M chloroplatinic acid in 2-propanol (2ml.), gave

4-(o-chlorophenyl)-butyltrichlorosilane in 76.3% yield (182.6g.). b.p. 119-21°/1.0±0.2mm.,  $n_D^{25}$  1.5236 (Found: hydrolysable chlorine, 35.17.  $C_{10}H_{12}Cl_3Si$  requires hydrolysable chlorine, 35.39%).

The problem of the addition of trichlorosilane to o-, m-, and p-chlorophenylbut-1-ene, and the products obtained, will be discussed in chapter 9.

4-(p-Chlorophenyl)-butyltrimethylsilane.

Methyl bromide (207g., 2.18mole) in ether (350ml.), cooled to -70°C, was added dropwise to magnesium turnings (54g., 2.25mole) in ether (500ml.), the temperature of the reaction being maintained below 5°C. The reaction mixture was refluxed for 30min., after the addition of the methyl bromide had been completed. 4-(p-Chlorophenyl)-butyltrichlorosilane (149.5g., 0.50mole) was then added dropwise, the heat of reaction being sufficient to maintain reflux during the addition. The reaction mixture was finally refluxed for 16hr., and hydrolysed. Fractionation, through the Vigreux column, gave 4-(p-chlorophenyl)-butyltrimethylsilane in 81.9% yield (98.0g.).

b.p. 113-5°/2.0-2.5mm.,  $n_D^{25}$  1.4957 (Found: C, 64.58; H, 8.83.  $C_{13}H_{21}ClSi$  requires C, 64.80; H, 8.79%).

4-(m-Chlorophenyl)-butyltrimethylsilane.

4-(m-Chlorophenyl)-butyltrichlorosilane (156.2g., 0.52mole), after coupling with the Grignard reagent prepared from methyl bromide (207g., 2.18mole) and

magnesium turnings (54g., 2.25mole), gave 4-(m-chlorophenyl)-butyltrimethylsilane in 82.7% yield (103.1g.).  
b. p. 128-30°/5.0±0.5mm.,  $n_D^{25}$  1.4949 (Found: C, 65.10; H, 9.02.  $C_{13}H_{21}ClSi$  requires C, 64.80; H, 8.79%).

4-(o-Chlorophenyl)-butyltrimethylsilane.

4-(o-Chlorophenyl)-butyltrichlorosilane (168.2g., 0.56mole), after coupling with the Grignard reagent prepared from methyl bromide (207g., 2.18mole) and magnesium turnings (54g., 2.25mole), gave 4-(o-chlorophenyl)-butyltrimethylsilane in 74.6% yield (100g.).  
b. p. 124-6°/5.0±0.5mm.,  $n_D^{25}$  1.4963 (Found: C, 65.01; H, 8.93.  $C_{13}H_{21}ClSi$  requires C, 64.80; H, 8.79%).

1-(p-Chlorophenyl)-1-trimethylsilyl-n-butane.

1-(p-Chlorophenyl)-1-trichlorosilyl-n-butane (33.4g., 0.11mole), after coupling with the Grignard reagent prepared from methyl bromide (34.0g., 0.36mole) and magnesium turnings (9.7g., 0.40mole), gave 1-(p-chlorophenyl)-1-trimethylsilyl-n-butane in 69.3% yield (18.4g.).  
b. p. 114-5°/5.0±0.5mm.,  $n_D^{25}$  1.5074 (Found: C, 64.55; H, 8.70.  $C_{13}H_{21}ClSi$  requires C, 64.80; H, 8.79%).

1-(m-Chlorophenyl)-1-trimethylsilyl-n-butane.

1-(m-Chlorophenyl)-1-trichlorosilyl-n-butane (26.3g., 0.087mole), after coupling with the Grignard reagent prepared from methyl bromide (34.0g., 0.36mole) and magnesium turnings (9.7g., 0.40mole), gave 1-(m-chlorophenyl)-1-trimethylsilyl-n-butane in 84.7% yield (17.8g.).

b. p. 111-2°/5.0±0.5mm.,  $n_D^{25}$  1.5070 (Found: C, 65.38; H, 8.97.  $C_{13}H_{21}ClSi$  requires C, 64.80; H, 8.79%).

4-(p-Trimethylsilylphenyl)-butyltrimethylsilane.

A mixture of 4-(p-chlorophenyl)-butyltrimethylsilane (95.0g., 0.39mole) and trimethylchlorosilane (48.6g., 0.45mole), after addition to sodium (20.7g., 0.90mole) in toluene (400ml.), on fractionation through the Vigreux column gave 4-(p-trimethylsilylphenyl)-butyltrimethylsilane in 58.3% yield (64.1g.). b. p. 144-6°/5.0±0.5mm.,  $n_D^{25}$  1.4837 (Found: C, 68.91; H, 10.16.  $C_{16}H_{30}Si_2$  requires C, 69.00; H, 10.86%).

4-(m-Trimethylsilylphenyl)-butyltrimethylsilane.

A mixture of 4-(m-chlorophenyl)-butyltrimethylsilane (99.0g., 0.41mole) and trimethylchlorosilane (47.5g., 0.44mole), after addition to sodium (20.7g., 0.90mole) in toluent (400ml.), on fractionation gave 4-(m-trimethylsilylphenyl)-butyltrimethylsilane in 59.2% yield (67.6g.). b. p. 138-9°/5.0±0.5mm.,  $n_D^{25}$  1.4823 (Found: C, 68.87; H, 10.40.  $C_{16}H_{30}Si_2$  requires C, 69.00; H, 10.86%).

4-(o-Trimethylsilylphenyl)-butyltrimethylsilane.

A mixture of 4-(o-chlorophenyl)-butyltrimethylsilane (94.0g., 0.39mole) and trimethylchlorosilane (48.6g., 0.45mole), after addition to sodium (19.6g., 0.85mole) in toluene (400ml.), on fractionation gave 4-(o-trimethylsilylphenyl)-butyltrimethylsilane in 57.6% yield (62.6g.). b. p. 140-2°/5.0±0.5mm.,  $n_D^{25}$  1.4897 (Found: C, 68.51;

H, 10.62.  $C_{16}H_{30}OSi_2$  requires C, 69.00; H, 10.86%).

1-(p-Trimethylsilylphenyl)-1-trimethylsilyl-n-butane.

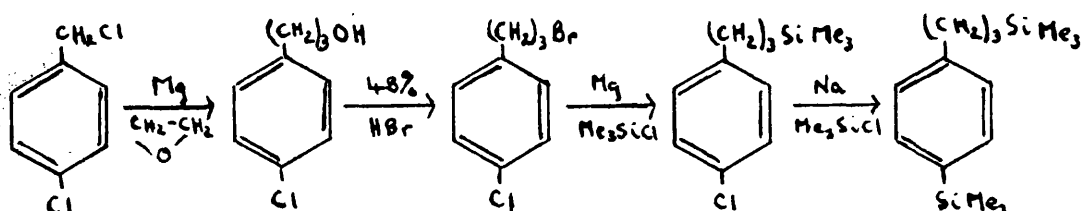
A mixture of 1-(p-chlorophenyl)-1-trimethylsilyl-n-butane (15.7g., 0.065mole) and trimethylchlorosilane (8.6g., 0.080mole), after addition to sodium (4.2g., 0.18mole) in toluene (75ml.), on fractionation gave 1-(p-trimethylsilylphenyl)-1-trimethylsilyl-n-butane in 51.8% yield (9.4g.). b.p.  $128-9^\circ/5.0 \pm 0.5\text{mm.}$ ,  $n_D^{25}$  1.4921 (Found: C, 69.14; H, 10.56.  $C_{16}H_{30}OSi_2$  requires C, 69.00; H, 10.86%).

1-(m-Trimethylsilylphenyl)-1-trimethylsilyl-n-butane.

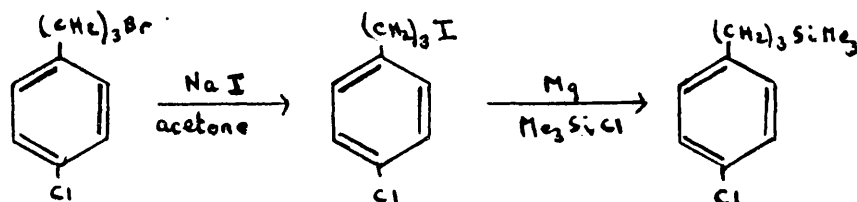
A mixture of 1-(m-chlorophenyl)-1-trimethylsilyl-n-butane (17.0g., 0.070mole) and trimethylchlorosilane (9.2g., 0.085mole), after addition to sodium (4.4g., 0.19mole) in toluene (75ml.), on fractionation gave 1-(m-trimethylsilylphenyl)-1-trimethylsilyl-n-butane in 66.6% yield (13.0g.). b.p.  $119-21^\circ/5.0 \pm 0.5\text{mm.}$ ,  $n_D^{25}$  1.4862 (Found: C, 68.55; H, 10.42.  $C_{16}H_{30}OSi_2$  requires C, 69.00; H, 10.86%).

2. o-, m-, and p-Me<sub>3</sub>SiC<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>3</sub>SiMe<sub>3</sub>

The preparation of these compounds was first attempted by the following general route:



This scheme was later modified as follows:



3-(p-Chlorophenyl)-propan-1-ol.

p-Chlorobenzylchloride (203.8g., 1.25mole) in ether (250ml.) was added dropwise to magnesium turnings (36.5g., 1.50mole) in ether (500ml.), the heat of reaction being sufficient to maintain reflux during the addition. The reaction was heated under reflux for a further 1hr., and then cooled to below 0°C with ice/salt mixture. Ethylene oxide (100g., 2.27mole) in ether (250ml.), cooled to -30°C, was then added dropwise to the Grignard solution, the temperature being maintained below 10°C. The reaction mixture was finally allowed to warm up to room temperature and hydrolysed with 10% sulphuric acid. Fractionation through the Vigreux column gave 3-(p-chlorophenyl)-propan-1-ol in 74.7% yield (159.5g.). b.p. 113-4°/1.5 ±0.2mm.,  $n_D^{25}$  1.5404 (Found: C, 63.65; H, 6.68. C<sub>9</sub>H<sub>11</sub>ClO requires C, 63.27; H, 6.50%).

3-(m-Chlorophenyl)-propan-1-ol.

The Grignard reagent, prepared from m-chlorobenzyl-bromide (232.9g., 1.25mole) and magnesium turnings (36.5g., 1.50mole), after coupling with ethylene oxide (100g., 2.27mole), gave 3-(m-chlorophenyl)-propan-1-ol in 66.5%

yield (133.5g.). b.p.  $106-7^{\circ}/1.0\pm 0.2\text{mm.}$ ,  $n_D^{25}$  1.5412  
(Found: C, 63.10; H, 6.45.  $C_9H_{11}ClO$  requires C, 63.27;  
H, 6.50%).

3-(o-Chlorophenyl)-propan-1-ol.

The Grignard reagent, prepared from o-chlorobenzyl-  
chloride (203.8g., 1.25mole) and magnesium turnings (36.5g.,  
1.50mole), after coupling with ethylene oxide (100g.,  
2.27mole), gave 3-(o-chlorophenyl)-propan-1-ol in 70.6%  
yield (150.5g.). b.p.  $104-7^{\circ}/1.5\pm 0.5\text{mm.}$ ,  $n_D^{25}$  1.5420  
Lit.<sup>243</sup> b.p.  $100-1^{\circ}/2\text{mm.}$ ,  $n_D^{25}$  1.5390

3-(p-Chlorophenyl)-1-bromopropane.

3-(p-Chlorophenyl)-propan-1-ol (155g., 0.91mole)  
and 48% hydrobromic acid (470g., 2.80mole) were heated  
under reflux for 6hr., cooled, diluted with water (1 litre),  
and extracted with ether. The ethereal extract was  
washed with sodium bicarbonate solution, then water, and  
finally dried over anhydrous sodium sulphate. Fractionation  
through the Vigreux column gave 3-(p-chlorophenyl)-1-  
bromopropane in 80.0% yield (171.9g.). b.p.  $100-3^{\circ}/1.0\text{mm.}$ ,  
 $n_D^{25}$  1.5558 (Found: C, 47.81; H, 4.59.  $C_9H_{10}BrCl$  requires  
C, 46.27; H, 4.31%).

3-(m-Chlorophenyl)-1-bromopropane.

3-(m-Chlorophenyl)-propan-1-ol (125.5g., 0.74mole),  
after refluxing with 48% hydrobromic acid (470g., 2.80mole),  
gave 3-(m-chlorophenyl)-1-bromopropane in 91.2% yield  
(156.5g.). b.p.  $96-8^{\circ}/0.7-1.0\text{mm.}$ ,  $n_D^{25}$  1.5572 (Found:

C, 43.88; H, 4.10.  $C_9H_{10}BrCl$  requires C, 46.27; H, 4.31%.

3-(*o*-Chlorophenyl)-1-bromopropane.

3-(*o*-Chlorophenyl)-propan-1-ol (145g., 0.85mole), after refluxing with 48% hydrobromic acid (470g., 2.80mole), gave 3-(*o*-chlorophenyl)-1-bromopropane in 90.3% yield

(179.3g.). b.p.  $91-3^\circ/1.0\pm 0.2\text{mm.}$ ,  $n_D^{25}$  1.5588 (Found:

C, 47.07; H, 4.72.  $C_9H_{10}BrCl$  requires C, 46.27; H, 4.31%.)

Lit.<sup>243</sup> b.p.  $95-6^\circ/2\text{mm.}$

3-(*p*-Chlorophenyl)-propyltrimethylsilane.

3-(*p*-Chlorophenyl)-1-bromopropane (70.2g., 0.30mole) in ether (100ml.) was added dropwise to magnesium turnings (8.6g., 0.35mole) in ether (250ml.), the heat of reaction being sufficient to maintain reflux during the addition. The reaction was heated under reflux for a further 1hr. Trimethylchlorosilane (43.4g., 0.40mole) was then added, the reaction refluxed for 24hr., and hydrolysed.

Fractionation through the Vigreux column gave no pure product. b. range  $115-20^\circ/5.0\pm 0.5\text{mm.}$ ,  $n_D^{25}$  1.4963-1.5031

3-(*o*-Chlorophenyl)-propyltrimethylsilane.

The Grignard reagent, prepared from 3-(*o*-chlorophenyl)-1-bromopropane (70.2g., 0.30mole) and magnesium turnings (8.6g., 0.35mole), after coupling with trimethylchlorosilane (43.4g., 0.40mole), gave no pure product.

b. range  $107-12^\circ/5.0\pm 0.5\text{mm.}$ ,  $n_D^{25}$  1.4981-1.5038

Since no pure products could be obtained by coupling the Grignard reagents, prepared from the bromides, with

trimethylchlorosilane the synthetic route was modified; the bromides were, therefore, converted to the corresponding iodides.

3-(p-Chlorophenyl)-1-iodopropane.

3-(p-Chlorophenyl)-1-bromopropane (89.4g., 0.38mole) was refluxed with anhydrous sodium iodide (97g., 0.65mole) in 'Analar' acetone (1,250ml.) for 48hr. The acetone was distilled off, and water (1 litre) added to the residue. The solution was then extracted with ether, the ethereal extract washed with 5% sodium thiosulphate (2×50ml.), and finally with water (3×50ml.), and dried over anhydrous sodium sulphate. Fractionation through the Vigreux column gave 3-(p-chlorophenyl)-1-iodopropane in 55.4% yield (59.6g.).  
b. p. 95-7°/0.2-0.4mm.,  $n_D^{25}$  1.5915 (Found: C, 38.88; H, 3.58.  $C_9H_{10}ClI$  requires C, 38.53; H, 3.59%).

3-(m-Chlorophenyl)-1-iodopropane.

3-(m-Chlorophenyl)-1-bromopropane (145g., 0.62mole), after refluxing with anhydrous sodium iodide (180g., 1.20mole) in 'Analar' acetone (2 litre), gave 3-(m-chlorophenyl)-1-iodopropane in 80.8% yield (142.8g.).  
b. p. 102-5°/0.4-0.6mm.,  $n_D^{25}$  1.5924 (Found: C, 38.39; H, 3.48.  $C_9H_{10}ClI$  requires C, 38.53; H, 3.59%).

3-(o-Chlorophenyl)-1-iodopropane.

3-(o-Chlorophenyl)-1-bromopropane (88.0g., 0.38mole), after refluxing with anhydrous sodium iodide (97g., 0.65mole) in 'Analar' acetone (1 litre), gave 3-(o-chloro-

phenyl)-1-iodopropane in 71.8% yield ( 76.0g. ).

b. p. 99-101°/0.4-0.6mm.,  $n_D^{25}$  1.5935 (Found: C, 38.35; H, 3.70.  $C_9H_{10}ClI$  requires C, 38.53; H, 3.59%).

3-(p-Chlorophenyl)-propyltrimethylsilane.

3-(p-Chlorophenyl)-1-iodopropane (56.1g., 0.20mole) in ether (50ml.) was added dropwise to a vigorously stirred solution of magnesium turnings (6.1g., 0.25mole) in ether (150ml.), the heat of reaction being sufficient to maintain reflux during the addition. The reaction mixture was heated under reflux for a further 1hr. Trimethylchlorosilane (32.4g., 0.30mole) was then added, the solution refluxed for 24hr., and hydrolysed. Fractionation through the Vigreux column gave 3-(p-chlorophenyl)-propyltrimethylsilane in 43.8% yield (20.1g.). b. p. 117-8°/5.0±0.5mm.,  $n_D^{25}$  1.4978 (Found: C, 64.08; H, 8.48.  $C_{12}H_{19}ClSi$  requires C, 63.54; H, 8.44%).

3-(m-Chlorophenyl)-propyltrimethylsilane.

The Grignard reagent, prepared from 3-(m-chlorophenyl)-1-iodopropane (135.8g., 0.48mole) and magnesium turnings (12.2g., 0.50mole), after coupling with trimethylchlorosilane (64.8g., 0.60mole) gave 3-(m-chlorophenyl)-propyltrimethylsilane in 27.9% yield (30.1g.).

b. p. 114-7°/5.0±0.5mm.,  $n_D^{25}$  1.4982 (Found: C, 63.56; H, 8.44.  $C_{12}H_{19}ClSi$  requires C, 63.54; H, 8.36%).

3-(o-Chlorophenyl)-propyltrimethylsilane.

The Grignard reagent, prepared from 3-(o-chlorophenyl)-

1-iodopropane (70.2g., 0.25mole) and magnesium turnings (7.3g., 0.30mole), after coupling with trimethylchlorosilane (43.2g., 0.40mole), gave 3-(o-chlorophenyl)-propyltrimethylsilane in 20.2% yield (11.4g.).

b.p. 111-4°/5.0±0.5mm.,  $n_D^{25}$  1.4998 (Found: C, 63.76; H, 8.12.  $C_{12}H_{19}ClSi$  requires C, 63.54; H, 8.44%).

3-(p-Trimethylsilylphenyl)-propyltrimethylsilane.

A mixture of 3-(p-chlorophenyl)-propyltrimethylsilane (18.2g., 0.08mole) and trimethylchlorosilane (10.8g., 0.10mole), after addition to sodium (4.6g., 0.20mole) in toluene (75ml.), on fractionation through the Vigreux column, gave 3-(p-trimethylsilylphenyl)-propyltrimethylsilane in 71.3% yield (15.0g.).

b.p. 133°/5.0±0.5mm.,  $n_D^{25}$  1.4852 (Found: C, 67.95; H, 10.52.  $C_{15}H_{28}Si_2$  requires C, 68.06; H, 10.66%).

3-(m-Trimethylsilylphenyl)-propyltrimethylsilane.

A mixture of 3-(m-chlorophenyl)-propyltrimethylsilane (27.2g., 0.12mole) and trimethylchlorosilane (14.1g., 0.13mole), after addition to sodium (4.0g., 0.18mole) in toluene (150ml.), gave 3-(m-trimethylsilylphenyl)-propyltrimethylsilane in 40.2% yield (12.8g.).

b.p. 127°/5.0±0.5mm.,  $n_D^{25}$  1.4832 (Found: C, 68.38; H, 10.62.  $C_{15}H_{28}Si_2$  requires C, 68.06; H, 10.66%).

3-(o-Trimethylsilylphenyl)-propyltrimethylsilane.

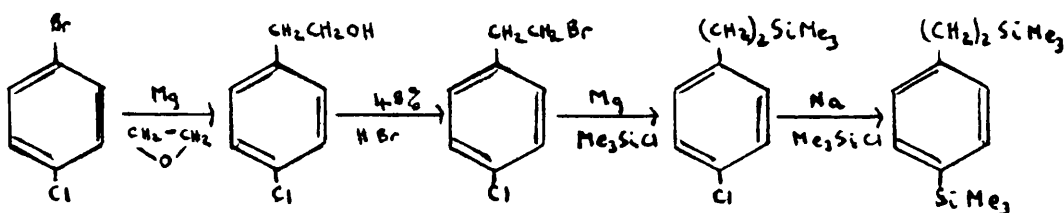
A mixture of 3-(o-chlorophenyl)-propyltrimethylsilane (11.0g., 0.049mole) and trimethylchlorosilane

(5.4g., 0.050mole), after addition to sodium (2.64g., 0.11mole) in toluene (75ml.), gave 3-(o-trimethylsilyl-phenyl)-propyltrimethylsilane in 34.2% yield (4.4g.).

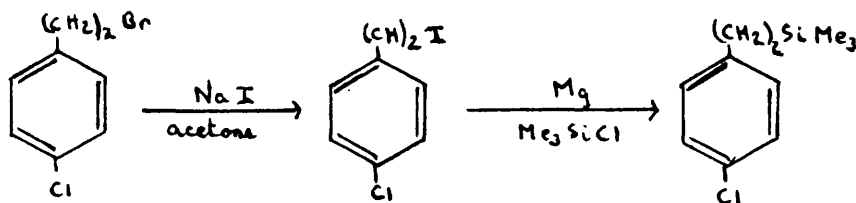
b.p. 129-30°/5.0±0.5mm.,  $n_D^{25}$  1.4912 (Found: C, 68.28; H, 10.27.  $C_{15}H_{28}Si_2$  requires C, 68.06; H, 10.66%).

3. o-, m-, and p- $Me_3SiC_6H_4(CH_2)_2SiMe_3$

The preparation of the meta- and para-compounds was attempted by the following general route:



This scheme was later modified as follows:



2-(p-Chlorophenyl)-ethan-1-ol.

The Grignard reagent, prepared from p-bromochlorobenzene (191.7g., 1.00mole) and magnesium turnings (30.4g., 1.25mole), was coupled with ethylene oxide (100ml., 2.05mole), the temperature of the reaction during coupling being maintained below 5°C. The reaction mixture was then kept below 5°C for 16hr., before being allowed to warm up to room temperature. After hydrolysis with 10% sulphuric acid, the ethereal layer was separated,

washed with water until neutral, and dried over anhydrous sodium sulphate. Fractionation through the Vigreux column gave 2-(p-chlorophenyl)-ethan-1-ol in 63.6% yield (99.6g.). b. p. 99-100°/1.0±0.2mm.,  $n_D^{25}$  1.5472 Lit.,<sup>244</sup> b. p. 77-8°/0.5mm.,  $n_D^{25}$  1.5482

2-(m-Chlorophenyl)-ethan-1-ol.

The Grignard reagent, prepared from m-bromochlorobenzene (191.7g., 1.00mole) and magnesium turnings (30.4g., 1.25mole), after coupling with ethylene oxide (100ml., 2.05mole), gave 2-(m-chlorophenyl)-ethan-1-ol in 58% yield (91.0g.). b. p. 92-5°/1.0±0.2mm.,  $n_D^{25}$  1.5489 (Found: C, 61.77; H, 5.75.  $C_8H_7ClO$  requires C, 61.37; H, 5.75%).

2-(p-Chlorophenyl)-ethyl bromide.

2-(p-Chlorophenyl)-ethan-1-ol (162.3g., 1.04mole), after refluxing with 48% hydrobromic acid (500g., 2.98mole), gave 2-(p-chlorophenyl)-ethyl bromide in 83% yield (188.8g.). b. p. 85°/1.0±0.2mm.,  $n_D^{25}$  1.5690 Lit.,<sup>244</sup> b. p. 86.5°/1.6mm.,  $n_D^{25}$  1.5697

2-(m-Chlorophenyl)-ethyl bromide.

2-(m-Chlorophenyl)-ethan-1-ol (84.0g., 0.54mole), after refluxing with 48% hydrobromic acid (296g., 1.75mole), gave 2-(m-chlorophenyl)-ethyl bromide in 85.6% yield (100.1g.). b. p. 107-9°/5.0±0.5mm.,  $n_D^{25}$  1.5680

2-(p-Chlorophenyl)-ethyltrimethylsilane.

The Grignard reagent, prepared from 2-(p-chlorophenyl)-

ethyl bromide (65.8g., 0.30mole) and magnesium turnings (8.6g., 0.35mole), after coupling with trimethylchlorosilane (43.4g., 0.40mole), gave no pure product.

b. range 103-7°/5.0±0.5mm.,  $n_D^{25}$  1.5035-1.5070

Since no pure product was obtained by coupling the Grignard reagent, prepared from the bromide, with trimethylchlorosilane the synthetic route was modified; the bromides were, therefore, converted to the corresponding iodides.

2-(p-Chlorophenyl)-ethyl iodide.

2-(p-Chlorophenyl)-ethyl bromide (116.1g., 0.53mole), after refluxing with anhydrous sodium iodide (119.9g., 0.80mole) in 'Analar' acetone (1,200ml.), gave 2-(p-chlorophenyl)-ethyl iodide in 75.8% yield (107.4g.).

b. p. 91-4°/0.6-0.7mm.,  $n_D^{25}$  1.6093 (Found: C, 36.36;

H, 3.03.  $C_8H_9ClI$  requires C, 36.06; H, 3.02%).

Lit.<sup>253</sup> b. p. 115-7°/1mm.

2-(m-Chlorophenyl)-ethyl iodide.

2-(m-Chlorophenyl)-ethyl bromide (100.1g., 0.46mole), after refluxing with anhydrous sodium iodide (86.5g., 0.58mole) in 'Analar' acetone (1 litre), gave 2-(m-chlorophenyl)-ethyl iodide in 79.4% yield (100g.).

b. p. 105-6°/1.0±0.1mm.,  $n_D^{25}$  1.6084 (Found: C, 36.24;

H, 3.01.  $C_8H_9ClI$  requires C, 36.06; H, 3.02%).

2-(p-Chlorophenyl)-ethyltrimethylsilane.

2-(p-Chlorophenyl)-ethyl iodide (93.4g, 0.35mole) in ether (50ml.) was added dropwise to a vigorously stirred

solution of magnesium turnings (9.73g., 0.40mole) in ether (150ml.), the heat of reaction being sufficient to maintain reflux during the addition. The reaction mixture was heated under reflux for a further 1hr. Trimethylchlorosilane (54.3g., 0.50mole) in ether (100ml.) was then added, and the solution refluxed for 1hr. The ether (approx. 200ml.) was then distilled off, and simultaneously replaced by dry benzene (200ml.). The reaction mixture was then refluxed for 48hr., and hydrolysed. Fractionation through the Vigreux column, gave 2-(p-chlorophenyl)-ethyltrimethylsilane in 16.6% (12.4g.). b.p. 104-5°/5.0±0.5mm.,  $n_D^{25}$  1.4998 (Found: C, 62.24; H, 7.78.  $C_{11}H_{17}ClSi$  requires C, 62.09; H, 8.06%).

2-(m-Chlorophenyl)-ethyltrimethylsilane.

The Grignard reagent, prepared from 2-(m-chlorophenyl)-ethyl iodide (96.0g., 0.36mole) and magnesium turnings (9.8g., 0.40mole), was coupled with trimethylchlorosilane (54.3g., 0.50mole). The reaction mixture was then refluxed for 48hr., and hydrolysed. Fractionation through the Vigreux column, gave 2-(m-chlorophenyl)-ethyltrimethylsilane in 14.9% yield (11.4g.). b.p. 105-6°/5.0±0.5mm.,  $n_D^{25}$  1.4998 (Found: C, 62.08; H, 7.84.  $C_{11}H_{17}ClSi$  requires C, 62.09; H, 8.06%).

2-(p-Trimethylsilylphenyl)-ethyltrimethylsilane.

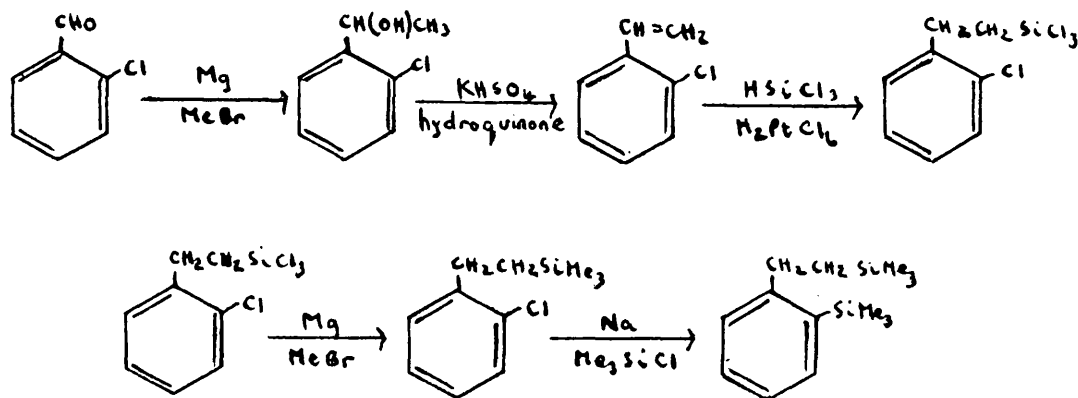
A mixture of 2-(p-chlorophenyl)-ethyltrimethylsilane (12.0g., 0.057mole) and trimethylchlorosilane (6.5g.,

0.060mole), after addition to sodium (4.0g., 0.15mole) in toluene (75ml.), on fractionation through the Vigreux column, gave 2-(p-trimethylsilylphenyl)-ethyltrimethylsilane in 67.2% yield (9.8g.). b.p. 120-2°/5.0±0.5mm.,  $n_D^{25}$  1.4850 (Found: C, 66.93; H, 10.44.  $C_{14}H_{26}Si_2$  requires C, 67.11; H, 10.47%). Lit.<sup>254</sup> b.p. 110-2°/5mm.,  $n_D^{25}$  1.4788

2-(m-Trimethylsilylphenyl)-ethyltrimethylsilane.

A mixture of 2-(m-chlorophenyl)-ethyltrimethylsilane (11.0g., 0.052mole) and trimethylchlorosilane (6.0g., 0.055mole), after addition to sodium (4.0g., 0.15mole) in toluene (75ml.), gave 2-(m-trimethylsilylphenyl)-ethyltrimethylsilane in 52.7% yield (7.0g.). b.p. 113-4°/5.0±0.5mm.,  $n_D^{25}$  1.4843 (Found: C, 67.19; H, 9.94.  $C_{14}H_{26}Si_2$  requires C, 67.11; H, 10.47%).

The preparation of o- $Me_3SiC_6H_4(CH_2)_2SiMe_3$  was attempted by the following route:



1-(o-Chlorophenyl)-ethan-1-ol.

o-Chlorobenzaldehyde (175.8g., 1.25mole) was added

dropwise to the Grignard reagent, prepared from methyl bromide (173g., 1.82mole) and magnesium turnings (45.5g., 1.82mole), the heat of reaction being sufficient to maintain reflux during the addition. The reaction mixture was then refluxed for 16hr., and hydrolysed with 10% sulphuric acid. Fractionation through the Vigreux column, gave 1-(o-chlorophenyl)-ethan-1-ol in 90.8% yield (178.3g.).

b. p. 109-11°/10±0.5mm.,  $n_D^{25}$  1.5430 Lit.<sup>245</sup> b. p. 108-9°/7mm.,  $n_D^{25}$  1.5457

#### o-Chlorostyrene.

1-(o-Chlorophenyl)-ethan-1-ol (170.0g., 1.80mole) was heated with powdered fused potassium bisulphate (2g.) and hydroquinone (2g.), by means of an oil bath, to a temperature of 200°, under a reduced pressure of 110-40mm. The products distilled over at 125-65°. The distillate was dissolved in ether, and washed successively with 5% sodium bicarbonate solution, and calcium chloride solution, and finally dried over calcium chloride. Fractionation, under reduced pressure in an atmosphere of dry, oxygen-free nitrogen, through the Vigreux column gave o-chlorostyrene in 44.8% yield (67.4g.). b. p. 52-4°/5.0±0.5mm.,  $n_D^{25}$  1.5647 Lit.<sup>245</sup> b. p. 60-1°/4mm.,  $n_D^{20}$  1.5648

#### 2-(o-Chlorophenyl)-ethyltrichlorosilane.

o-Chlorostyrene (65.0g., 0.47mole), on addition to trichlorosilane (75.0g., 0.55mole) and 0.1M chloroplatinic acid in 2-propanol (2ml.), gave 2-(o-chlorophenyl)-ethyl-

trichlorosilane in 76.2% yield (97.7g.). b.p. 87-9°/  
1.0±0.2mm.,  $n_D^{25}$  1.5281 (Found: hydrolysable chlorine,  
38.29;  $C_8H_8Cl_4Si$  requires hydrolysable chlorine, 38.81%).

2-(o-Chlorophenyl)-ethyltrimethylsilane.

2-(o-Chlorophenyl)-ethyltrichlorosilane (89.8g.,  
0.33mole), after coupling with the Grignard reagent,  
prepared from methyl bromide (178g., 1.82mole) and  
magnesium turnings (48.6g., 2.00mole), gave 2-(o-chloro-  
phenyl)-ethyltrimethylsilane in 80.5% yield (56.9g.).

b.p. 99-100°/5.0±0.5mm.,  $n_D^{25}$  1.5005 (Found: C, 62.19;  
H, 7.76.  $C_{11}H_{17}ClSi$  requires C, 62.09; H, 8.06%).

2-(o-Trimethylsilylphenyl)-ethyltrimethylsilane.

A mixture of 2-(o-chlorophenyl)-ethyltrimethylsilane  
(63.3g., 0.25mole) and trimethylchlorosilane (29.7g.,  
0.28mole), after addition to sodium (13.8g., 0.60mole) in  
toluene (350ml.), gave 2-(o-trimethylsilylphenyl)-ethyl-  
trimethylsilane in 42.8% yield (27.3g.). b.p. 117-8°/  
5.0±0.5mm.,  $n_D^{25}$  1.4912 (Found: C, 67.38; H, 10.07.  
 $C_{14}H_{26}Si_2$  requires C, 67.11; H, 10.47%).

4. The Preparation of Some Benzyltrimethylsilanes.

Benzyltrimethylsilane.

The Grignard reagent, prepared from benzyl chloride  
(126.6g., 1.00mole) and magnesium turnings (26.8g.,  
1.20mole), after coupling with trimethylchlorosilane  
(130.3g., 1.20mole) gave, on fractionation through the  
Vigreux column, benzyltrimethylsilane in 71.8% yield

(118.1g.). b.p. 189-91°/759mm.,  $n_D^{25}$  1.4906

Lit.<sup>58</sup>, b.p. 188°/743mm.,  $n_D^{20}$  1.4932

p-Chlorobenzyltrimethylsilane.

The Grignard reagent, prepared from p-chlorobenzylchloride (161g., 1.00mole) and magnesium turnings (120g., 1.10mole) gave, on fractionation through the smaller Vigreux column, p-chlorobenzyltrimethylsilane in 57.4% yield (114.2g.). b.p. 229°/755mm.,  $n_D^{20}$  1.5113

Lit.<sup>35</sup>, b.p. 231-2°,  $n_D^{12}$  1.5154

m-Chlorobenzyltrimethylsilane.

The Grignard reagent, prepared from m-chlorobenzylbromide (103g., 0.50mole) and magnesium turnings (13g., 0.55mole), after coupling with trimethylchlorosilane (59.7g., 0.55mole) gave, on fractionation through the smaller Vigreux column, m-chlorobenzyltrimethylsilane in 73.5% yield (73.0g.). b.p. 225°/748mm.,  $n_D^{20}$  1.5099

Lit.<sup>35</sup>, b.p. 228-9°,  $n_D^{20}$  1.5108

p-Trimethylsilylbenzyltrimethylsilane.

A mixture of p-chlorobenzyltrimethylsilane (99.4g., 0.50mole) and trimethylchlorosilane (54.3g., 0.50mole), after addition to sodium (27.6g., 1.20mole) in toluene (350ml.) gave, on fractionation through the smaller Vigreux column, p-trimethylsilylbenzyltrimethylsilane in 76.0% yield (89.9g.). b.p. 131-2°/21±0.5mm.,  $n_D^{25}$  1.4919

Lit.<sup>71</sup>, b.p. 151-5°/45mm.,  $n_D^{25}$  1.4915

m-Trimethylsilylbenzyltrimethylsilane.

A mixture of m-chlorobenzyltrimethylsilane (60g., 0.30mole) and trimethylchlorosilane (32.6g., 0.30mole), after addition to sodium (18.4g., 0.80mole) in toluene (250ml.) gave, on fractionation through the smaller Vigreux column, m-trimethylsilylbenzyltrimethylsilane in 85.4% yield (60.6g.). b.p.  $127^{\circ}/21\pm 0.5\text{mm.}$ ,  $n_D^{20}$  1.4895

p-Methylbenzyltrimethylsilane.

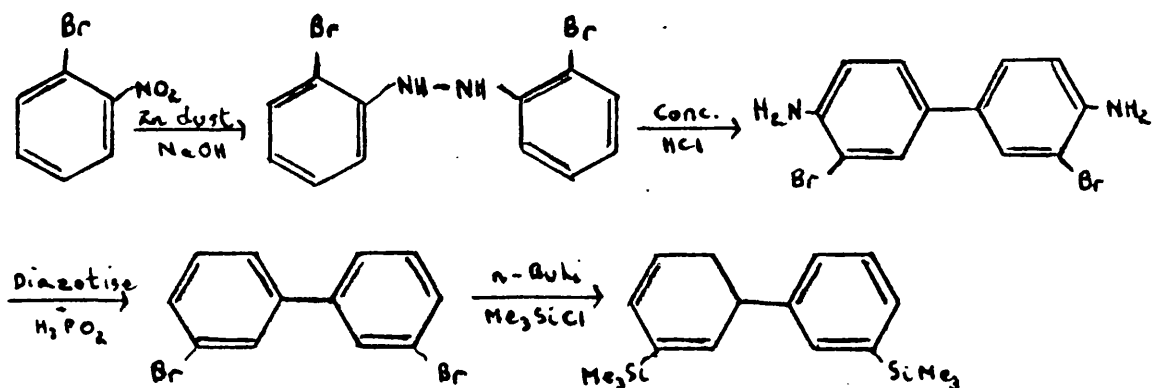
The Grignard reagent, prepared from p-methylbenzylbromide (53.8g., 0.29mole) and magnesium turnings (8.5g., 0.35mole), after coupling with trimethylchlorosilane (43.2g., 0.40mole) gave, on fractionation through the Vigreux column, p-methylbenzyltrimethylsilane in 49.4% yield (25.5g.). b.p.  $119^{\circ}/50\pm 1.0\text{mm.}$ ,  $n_D^{25}$  1.4917  
Lit.<sup>71</sup>, b.p.  $211.5^{\circ}$ ,  $n_D^{25}$  1.4917

o-Trimethylsilylbenzyltrimethylsilane.

This compound was prepared by Hashimoto in this department. b.p.  $76-7^{\circ}/1\text{mm.}$

5. The Preparation of 3,3'-Bistrimethylsilylbiphenyl.

This compound was prepared by the following route:



### 3,3'-Dibromobenzidine dihydrochloride.

Prepared, by the method of Snyder, Weaver and Marshall,<sup>20</sup> from o-bromonitrobenzene (80g., 0.40mole) and zinc dust (140g.) in 81.4% yield (66.6g.).

### 3,3'-Dibromobiphenyl.

A solution of 3,3'-dibromobenzidine dihydrochloride (63.0g.) and concentrated hydrochloric acid (75ml.) was diluted with ice (40g.) and water (40ml.). This solution was then tetrazotised with sodium nitrite (21g.) in water (75ml.), the temperature being maintained below 10°C. The reaction mixture was stirred for 1.5hr., and finally allowed to stand. The clear supernatant solution was added to 30% hypophosphorous acid (500ml.) at 10°, and the mixture allowed to stand for 40hr. at 0-10°, and finally at room temperature for 24hr. with occasional shaking. The solid material was filtered off, washed with water, and dissolved in ether. The ethereal solution was washed with 5% sodium hydroxide (3×100ml.), with water (4×100ml.), and finally dried over anhydrous sodium sulphate. The ether was removed by distillation, the residue distilled under reduced pressure (b.p. approx. 150°/1.0mm.), and the solid on recrystallisation, after charcoaling, from ethanol gave 3,3'-dibromobiphenyl in 52.0% yield (49.2g.). m.p. 52-3°C. Lit., m.p. 53°C<sup>27</sup>

### 3,3'-Bistrimethylsilylbiphenyl.

n-Butyl bromide (41.1g., 0.30mole) was added dropwise

to lithium (5.6g., 0.80mole) in ether (150ml.), the temperature being kept at  $-10^{\circ}\text{C}$ . The reaction mixture was then allowed to warm up to room temperature, and filtered through a glass wool plug under nitrogen. The solution was assumed to be approximately 0.25 molar in n-butyl-lithium.

3,3'-Dibromobiphenyl (23.4g., 0.075mole) in ether (100ml.) was added dropwise to the n-butyl-lithium solution, the temperature being maintained at  $-10^{\circ}\text{C}$ . The reaction mixture was then allowed to warm up to room temperature over a period of 3hr. Trimethylchlorosilane (54.3g., 0.50mole) was then added dropwise and the reaction mixture stirred at room temperature for 4hr., allowed to stand overnight, and finally refluxed for 7hr., and hydrolysed. Fractionation, through the Vigreux column, gave 3,3'-bistrimethylsilylbiphenyl in 82.6% yield (18.5g.).  
b.p.  $118^{\circ}/0.02\text{mm.}$ ,  $n_{\text{D}}^{20}$  1.5459 Lit.<sup>22</sup>, b.p.  $103-4^{\circ}/0.005\text{mm.}$ ,  
 $n_{\text{D}}^{20}$  1.5480

#### 6. The Preparation of Other Organosilanes.

##### Phenyltrimethylsilane.

A mixture of chlorobenzene (112.6g., 1.00mole) and trimethylchlorosilane (108.6g., 1.00mole), after addition to sodium (50.6g., 2.20mole) in toluene (500ml.), gave on fractionation through the Dixon-gauze packed column, phenyltrimethylsilane in 75.2% yield (113.0g.).

b.p.  $170.0^{\circ}/756\text{mm.}$ ,  $n_{\text{D}}^{20}$  1.4904,  $n_{\text{D}}^{25}$  1.4888.

Lit.<sup>19</sup>, b.p. 171.6°,  $n_D^{20}$  1.4904

p-Tolyltrimethylsilane.

A mixture of p-chlorotoluene (190.0g., 1.50mole) and trimethylchlorosilane (163.0g., 1.50mole), after addition to sodium (76g., 3.30mole) in toluene (1 litre) gave, on fractionation through the Dixon-gauze packed column, p-tolyltrimethylsilane in 79.1% yield (195g.).

b.p. 193°/761mm.,  $n_D^{20}$  1.4918,  $n_D^{25}$  1.4892

Lit.<sup>111</sup>, b.p. 192°/748mm.,  $n_D^{25}$  1.4892

m-Tolyltrimethylsilane.

A mixture of m-chlorotoluene (63.3g., 0.50mole) and trimethylchlorosilane (54.0g., 0.50mole), after addition to sodium (27.6g., 1.20mole) in toluene (350ml.), gave, on fractionation through the Dixon-gauze packed column, m-tolyltrimethylsilane in 54.4% yield (44.4g.).

b.p. 190°/765mm.,  $n_D^{25}$  1.4902 Lit.<sup>111</sup>, b.p. 188°/748mm.,

$n_D^{25}$  1.4902

o-Tolyltrimethylsilane.

A mixture of o-chlorotoluene (63.3g., 0.50mole) and trimethylchlorosilane (54.0g., 0.50mole), after addition to sodium (27.6g., 1.20mole) in toluene (350ml.), gave, on fractionation through the Dixon-gauze packed column, o-tolyltrimethylsilane in 40.8% yield (33.4g.).

b.p. 197.5°/744mm.,  $n_D^{25}$  1.5018 Lit.<sup>111</sup>, b.p. 196°/748mm.,

$n_D^{25}$  1.5005

### p-Methoxyphenyltrimethylsilane

p-Methoxyphenyl-lithium, prepared from p-bromoanisole (116.3g., 0.60mole) and lithium (9.0g., 1.30mole), was coupled with trimethylchlorosilane (97.7g., 0.90mole). The reaction mixture was finally hydrolysed and on fractionation, through the Vigreux column, gave p-methoxyphenyltrimethylsilane in 73.6% yield (79.9g.).

b.p. 220-1°/761mm.,  $n_D^{25}$  1.5022 Lit.<sup>44</sup>, b.p. 222.5-3.5°,  $n_D^{25}$  1.5073

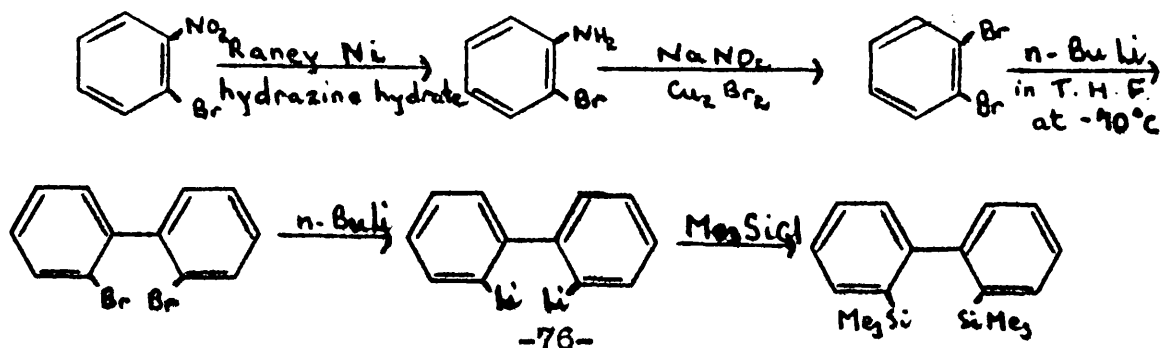
### m-Methoxyphenyltrimethylsilane

A mixture of m-chloroanisole (107.0g., 0.75mole) and trimethylchlorosilane (81.5g., 0.75mole), after addition to sodium (40.3g., 1.75mole) in toluene (450ml.), gave on fractionation through the Vigreux column, m-methoxyphenyltrimethylsilane in 82.0% yield (111.1g.).

b.p. 217°/764mm.,  $n_D^{25}$  1.4999 Lit.<sup>19</sup>, b.p. 213°,  $n_D^{20}$  1.5025

### 7. The Attempted Preparation of 2,2'-Bistrimethylsilyl-biphenyl.

The following route was used for the attempted preparation of 2,2'-bistrimethylsilylbiphenyl:-



#### Preparation of *o*-bromoaniline.

*o*-Bromonitrobenzene (101.5g., 0.50mole) was dissolved in methanol (100ml.) and added to Raney nickel<sup>255</sup> ( $\approx$ 3g.) and hydrazine hydrate (75g., 1.50mole 100%  $N_2H_4 \cdot H_2O$ ) in methanol (350ml.). The rate of addition was such that the evolution of gases from the reaction mixture did not become too vigorous; stirring was maintained throughout the reaction. When the *o*-bromonitrobenzene had been added, a further quantity of Raney nickel ( $\approx$ 3g.) was added and the solution refluxed for 1 hr. A clear colourless solution being obtained after filtration. The methanol was then removed by distillation and the residue steam distilled. The distillate was extracted with ether and the ethereal solution dried over anhydrous sodium sulphate. The ether was removed by fractionation through the glass-helices packed column, and the residue, after fractionation under reduced pressure through the Vigreux column, gave *o*-bromoaniline in 84.2% yield (72.3g.). b. p.  $92-4^\circ/7-8\text{mm.}$ , Lit.<sup>27</sup>, b. p.  $138-41^\circ/48-53\text{mm.}$

The method used for the reduction was essentially that of Leggetter and Brown.<sup>23</sup>

#### Preparation of *o*-dibromobenzene.

Prepared from *o*-bromoaniline (319g., 1.27mole) by means of a Sandmeyer reaction.<sup>240</sup> Fractionation at atmospheric pressure through the Vigreux column gave *o*-dibromobenzene in 69.8% yield (209.5g.).

b. p. 225-6°/769mm.,  $n_D^{20}$  1.6107 Lit.<sup>27</sup>, b. p. 224°

2,2'-Dibromobiphenyl.

n-Butyl-lithium (approx. 0.20mole in ether) was prepared by the addition of n-butyl bromide (34.3g., 0.25 mole) to lithium (4.2g., 0.60mole) in ether (120ml.) the temperature being kept at -10°(ice-salt). The addition was completed in 45min., and the solution was allowed to warm to room temperature over a period of 1 hr. The solution was then filtered through a glass wool plug under an atmosphere of dry oxygen-free nitrogen.

o-Dibromobenzene (94.5g., 0.40mole) in anhydrous tetrahydrofuran was cooled to -75° and the ethereal solution of n-butyl-lithium added dropwise at such a rate that the temperature did not rise above -70°. The reaction mixture was then allowed to warm up to room temperature, hydrolysed with 5% hydrochloric acid, the ethereal layer separated, washed with water, and dried over anhydrous sodium sulphate.

The ether and most of the tetrahydrofuran was removed by distillation, absolute alcohol (100ml.) added and the solution cooled. Charcoaling and recrystallisation from absolute alcohol gave 2,2'-dibromobiphenyl in 50.0% yield (31.3g.), m. p. 79-81°

The method of preparation was essentially that of Gilman and Gaj<sup>248</sup> who reported a 73.7% yield and a m. p. 80-81°.

### 2,2'-Bistrimethylsilylbiphenyl.

The 2,2'-dilithiobiphenyl (which was not isolated) was prepared by the method of Gilman and Gorsich,<sup>247</sup> who obtained an estimated yield of 70%.

n-Butyl-lithium (approx. 0.25mole) in ether (150ml.) was added dropwise to a vigorously stirred solution of 2,2'-dibromobiphenyl (31.2g., 0.10mole) in ether (250ml.) cooled in ice-salt mixture. The reaction mixture was finally stirred for 5 hr. at room temperature. Trimethylchlorosilane (43.4g., 0.40mole) was then added dropwise and the reaction mixture allowed to stand overnight and finally refluxed for 4 hrs. Fractionation, under reduced pressure, through the Vigreux column gave 18.0g. of product b.p. 99-103°/0.4mm. Recrystallisation from methanol finally gave 15.0g. of product, m.p. 59.5° (Found: C, 79.66; H, 6.76. C<sub>18</sub>H<sub>26</sub>Si<sub>2</sub> requires C, 72.45; H, 8.78%).

### 8. The Attempted Preparation of o-Chlorophenyltrimethylsilane.

o-Bromochlorobenzene (38.3g., 0.20mole) in ether (100ml.) was added dropwise to a vigorously stirred solution of n-butyl-lithium (approx. 0.20mole) in ether (250ml.), the temperature being maintained between -80° and -100° (toluene-liquid nitrogen bath). The reaction mixture was stirred for a further 1 hr. at -100°. Trimethylchlorosilane (64.8g., 0.60mole) was then added dropwise, the temperature

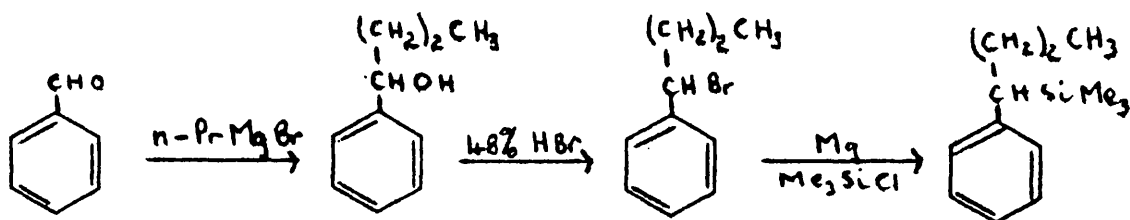
being maintained below  $-80^{\circ}$ . The reaction mixture was kept at  $\langle -80^{\circ}$  for 3 hr., and then allowed to warm up to room temperature overnight. The reaction mixture was finally hydrolysed, and after several fractionations through the Vigreux column two products were isolated.

a). 2-Chloro, 2'-trimethylsilyl-biphenyl (7.0g.)  
 b.p.  $142^{\circ}/5.0 \pm 0.5\text{mm.}$ ,  $n_D^{25}$  1.5673 (Found: C, 69.73; H, 6.57.  $C_{15}H_{17}ClSi$  requires C, 69.10; H, 6.57%).

b). A compound (10.8g.) b.p.  $157-8^{\circ}/5.0 \pm 0.5\text{mm.}$ ,  $n_D^{25}$  1.5668 (Found: C, 78.95; H, 5.41%). This compound could not be further purified by fractionation and is thought to be 2-chloro, 2'-n-butyl-biphenyl. ( $C_{18}H_{17}Cl$  requires C, 78.56; H, 6.98%).

9. The Attempted Preparation of 1-Phenyl-1-trimethylsilyl-n-butane.

The synthesis was attempted by the following route:-



1-Phenylbutan-1-ol.

Benzaldehyde (106g., 1.0mole) was added dropwise to the Grignard reagent prepared from n-propylbromide (135.3g., 1.1mole) and magnesium turnings (30.5g., 1.25mole), the heat of reaction being sufficient to maintain reflux during the addition. The reaction mixture was then refluxed for

16 hr., and hydrolysed. Fractionation, through the Vigreux column, gave 1-phenylbutan-1-ol in 58.6% yield (88.1g.).

b.p.  $110-1^{\circ}/10\pm 0.5\text{mm.}$ ,  $n_D^{25}$  1.5112 Lit.<sup>266</sup> b.p.  $117-8^{\circ}/18\text{mm.}$ ,  
 $n_D^{22}$  1.5166

1-Phenyl-1-bromobutane.

1-Phenylbutan-1-ol (45g., 0.30mole), after refluxing with 48% hydrobromic acid (168g., 1.00mole), gave two products.

a). 1-Phenylbut-1-ene in 57.8% yield (22.9g.).

b.p.  $61-3^{\circ}/5.0\pm 0.5\text{mm.}$ ,  $n_D^{25}$  1.5352 Infrared spectrum showed the presence of a  $\text{CHR}_1=\text{CHR}_2$  grouping ( $10.3\mu$ ).

Chemical tests showed the absence of bromine and the presence of an unsaturated grouping. Lit.<sup>27</sup> 1-phenylbut-1-ene has b.p.  $78^{\circ}/12\text{mm.}$ ,  $n_D^{16}$  1.5381

b). 1-Phenyl-1-bromobutane in 32.2% yield (20.6g.).

b.p.  $96-7^{\circ}/5.0\pm 0.5\text{mm.}$ ,  $n_D^{25}$  1.5402 Sodium fusion showed the presence of bromine and infrared examination indicated the absence of -OH and -CH=CH- groups. Lit.<sup>267</sup> 1-phenyl-1-bromobutane has b.p.  $110^{\circ}/10\text{mm.}$ ,  $n_D^{20}$  1.613, but 4-phenyl-1-bromobutane has<sup>27</sup> b.p.  $132^{\circ}/12\text{mm.}$ ,  $n_D^{19}$  1.5408

1-Phenyl-1-trimethylsilyl-n-butane.

The Grignard reagent, prepared from 1-phenyl-1-bromobutane (20.0g., 0.094mole) and magnesium turnings (2.7g., 0.11mole), after coupling with trimethylchlorosilane (15.5g., 0.15mole) gave  $\alpha, \alpha'$ -di-n-propyldibenzyl in 15.2% yield (3.8g.). b.p.  $173-4^{\circ}/10\pm 0.5\text{mm.}$ , m.p.  $96-7^{\circ}$ (ethanol).

Lit.<sup>271</sup> b.p. 165-75°/10mm., m.p. 97.5-8°.

## CHAPTER 5

### Spectra and Rate Studies.

#### 1. Reagents.

Perchloric Acid:- 60% and 72% 'Analar' acid, supplied by Messrs. B. D. H. Ltd., was used, and diluted with distilled water when necessary. The acid-strength was then determined in each case by titration against known weights of 'Analar' borax, using methyl red as indicator.

Methanol:- Methanol (150ml.) was allowed to react with magnesium turnings (10g.) and iodine (1g.); after the initial reaction had subsided the methanol was boiled under reflux until no magnesium remained. A further 2.5 litres of methanol was added, and the solution boiled under reflux for 3-4 hrs. The dry methanol was distilled through a fractionating column, the first 150ml. being rejected.

#### 2. Spectra.

The spectra were determined using methanolic solutions of the silanes at suitable concentrations, methanol being used as the blank. Readings were taken usually over the range 2,300-2,900Å.

The molar extinction coefficient,  $\epsilon$ , was calculated from the equation:-

$$\epsilon = \frac{aM}{bc}$$

where a = optical density; M = molecular weight; b = cell thickness (cms.); c = concentration (g./l.).

The spectra of the  $\text{Me}_3\text{Si}\dot{\text{C}}_6\text{H}_4(\text{CH}_2)_n\text{SiMe}_3$  compounds

(where  $n = 1$  to  $4$ ), and m-, and p- $\text{Me}_3\text{SiC}_6\text{H}_4\text{CH}(\text{CH}_2\text{CH}_2\text{CH}_3)\text{-SiMe}_3$ , together with those of their respective cleavage products, are given on pages 85-92.

Table 5.1

Spectra of  $\text{RC}_6\text{H}_4(\text{CH}_2)_n\text{SiMe}_3$  Compounds.

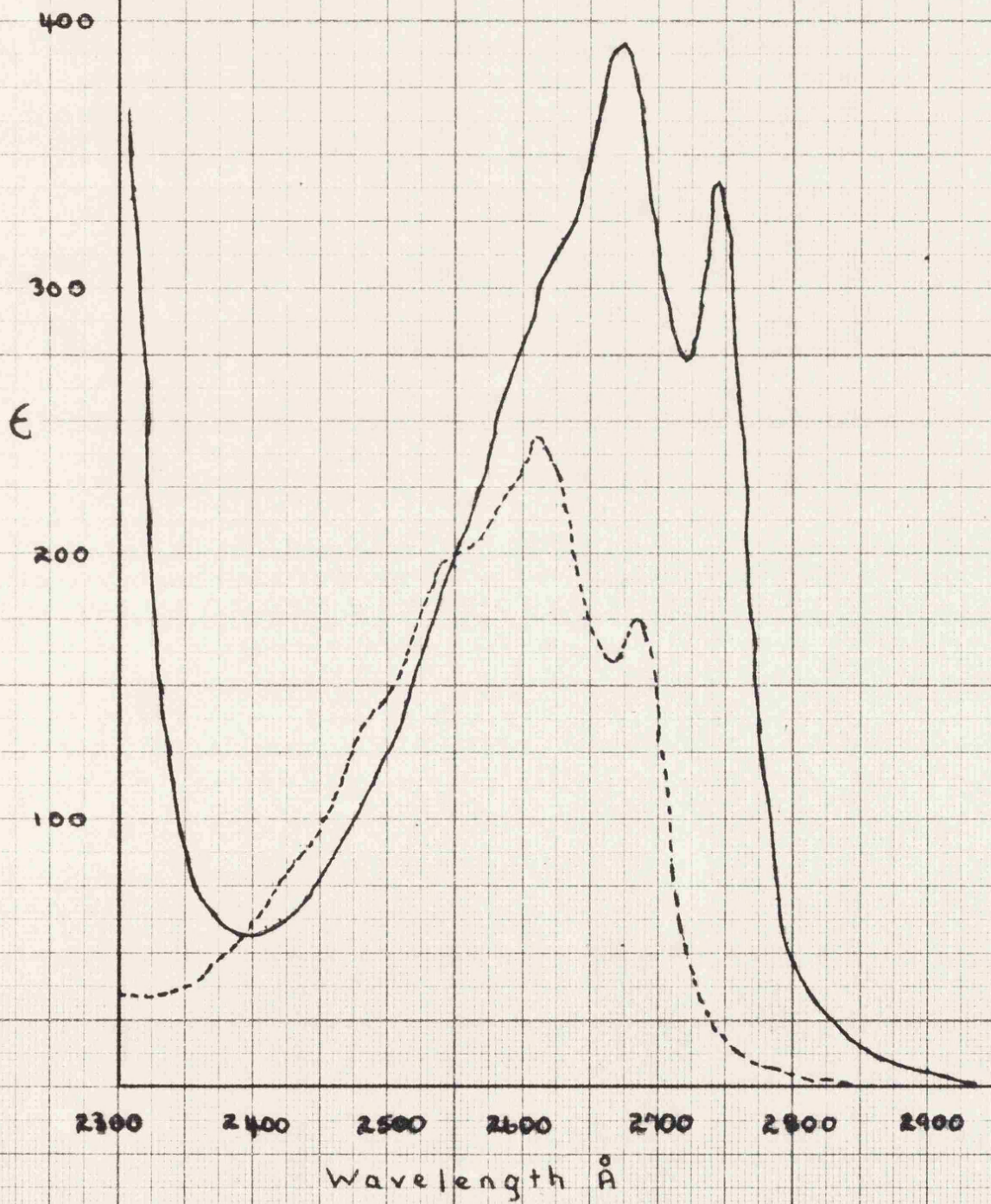
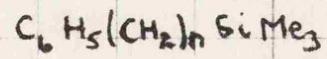
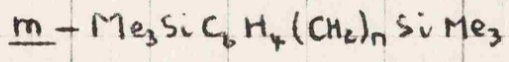
R	n = 2		n = 3		n = 4	
	$\lambda_{\text{max}}$ ( $\text{\AA}$ )	$\epsilon$	$\lambda_{\text{max}}$ ( $\text{\AA}$ )	$\epsilon$	$\lambda_{\text{max}}$ ( $\text{\AA}$ )	$\epsilon$
<u>p</u> - $\text{Me}_3\text{Si}$ -	2580	227.2	2575	217.2	2575	220.6
	2635	269.5	2630	260.0	2630	259.9
	2695	195.4	2690	193.3	2690	192.0
<u>m</u> - $\text{Me}_3\text{Si}$ -	2675	407.5	2675	389.4	2675	391.8
	2750	351.8	2745	333.2	2745	339.5
<u>o</u> - $\text{Me}_3\text{Si}$ -	2685	474.2	2680	423.7	2680	407.8
	2755	412.5	2750	372.0	2750	359.4
H	2555	209.3	2555	201.8	2555	202.8
	2615	254.0	2615	241.2	2610	243.7
	2680	190.4	2685	178.8	2685	173.9

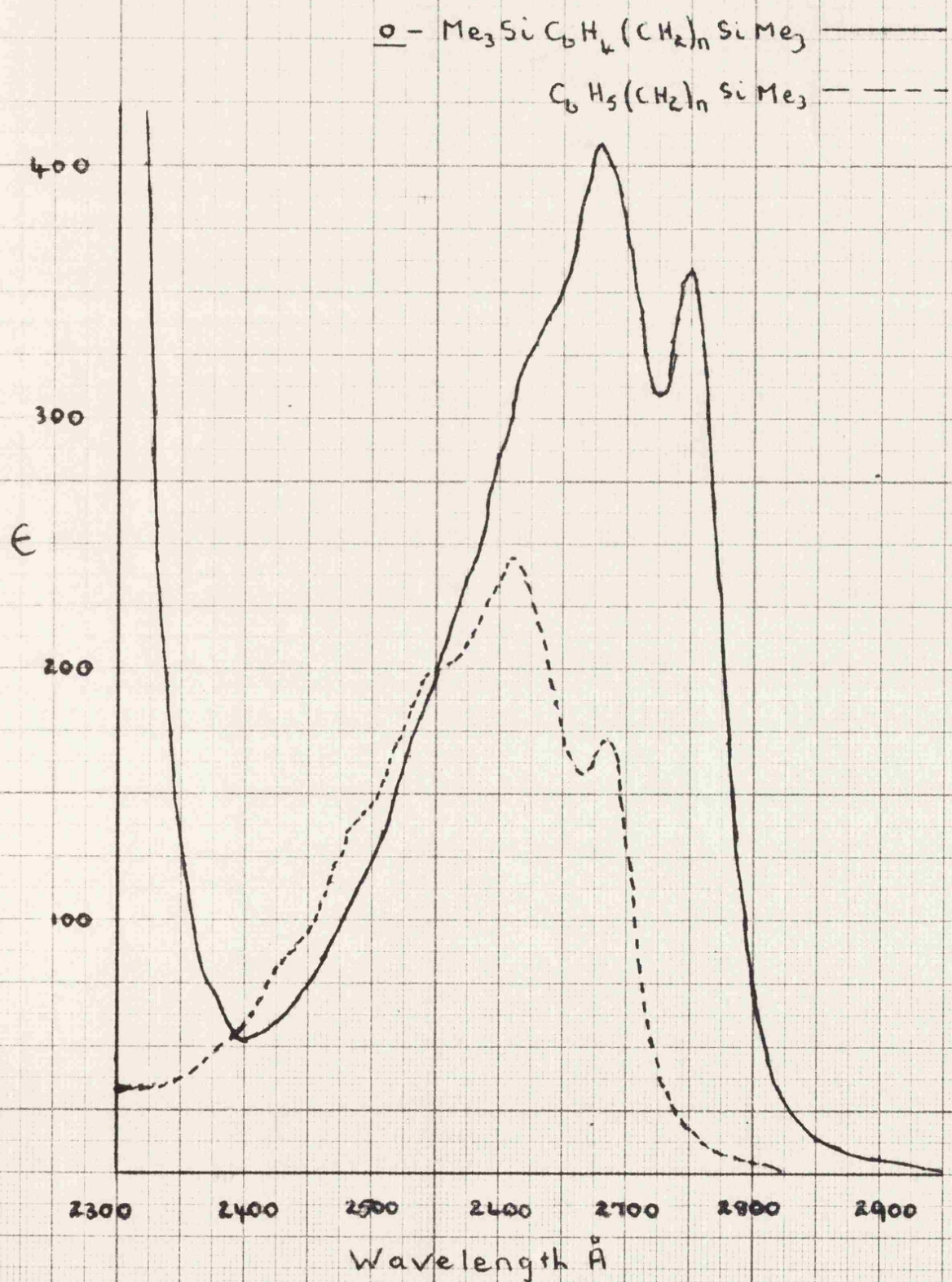
It was found that the spectra of the corresponding isomers in the series  $n = 2$  to  $4$  were similar, and only one spectrum of each isomer has been given. The experimental values of  $\lambda_{\text{max}}$  and  $\epsilon$  of these compounds are given in Table 5.1.

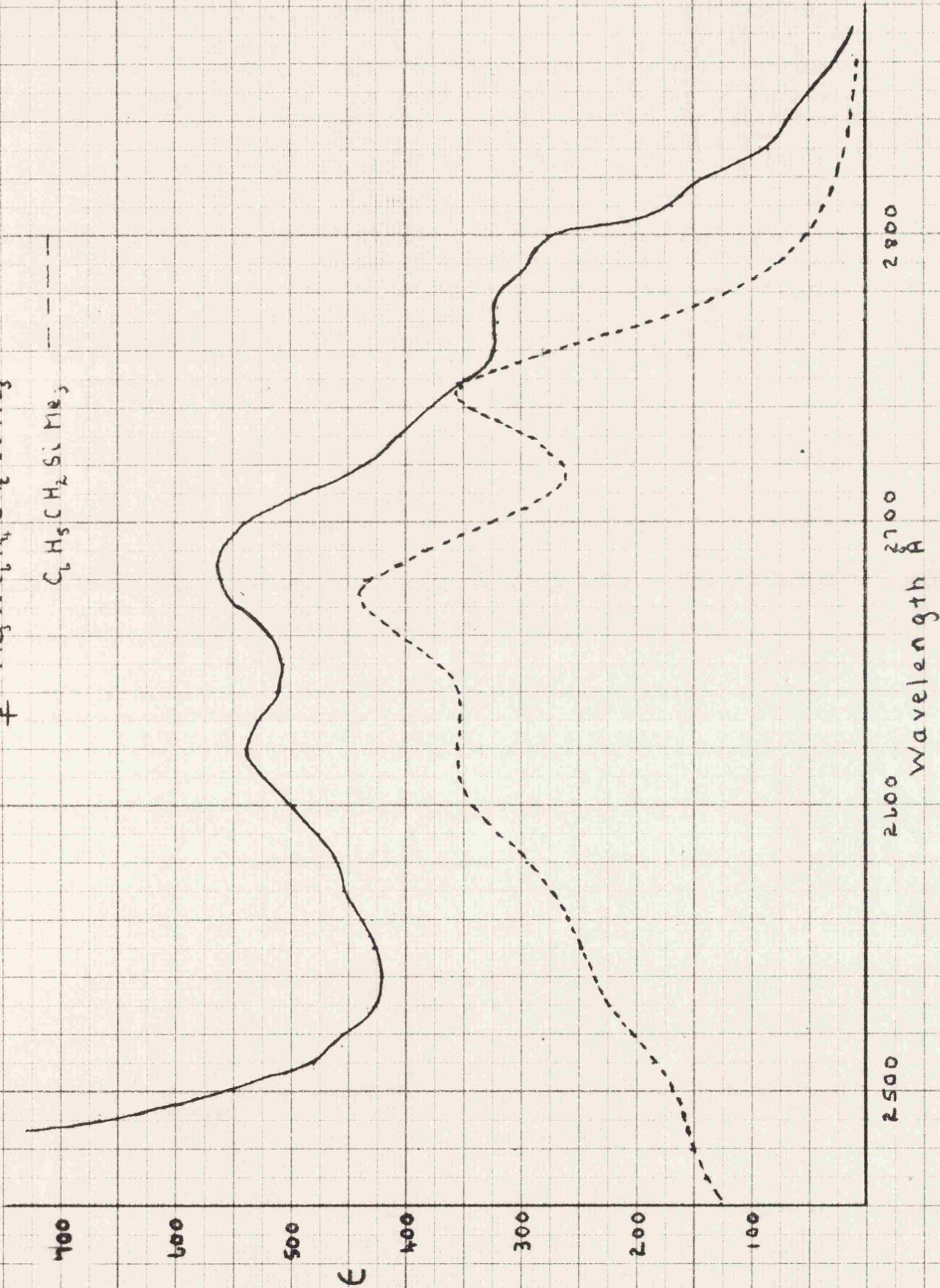
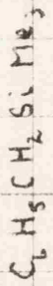
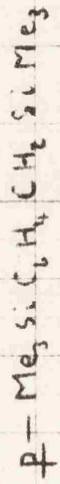
### 3. Rate Measurements.

The acid cleavage of an arylsilane in the presence of

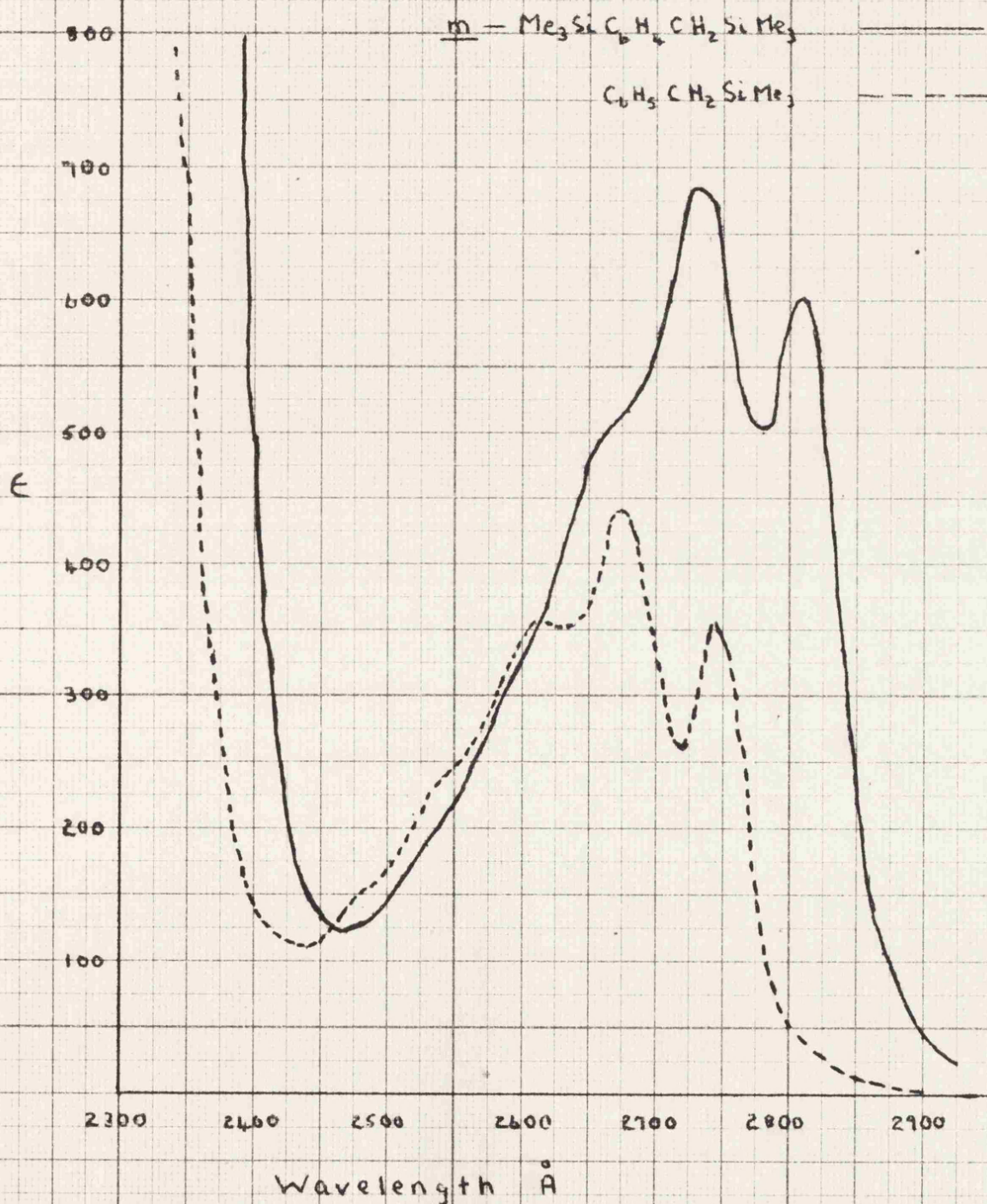


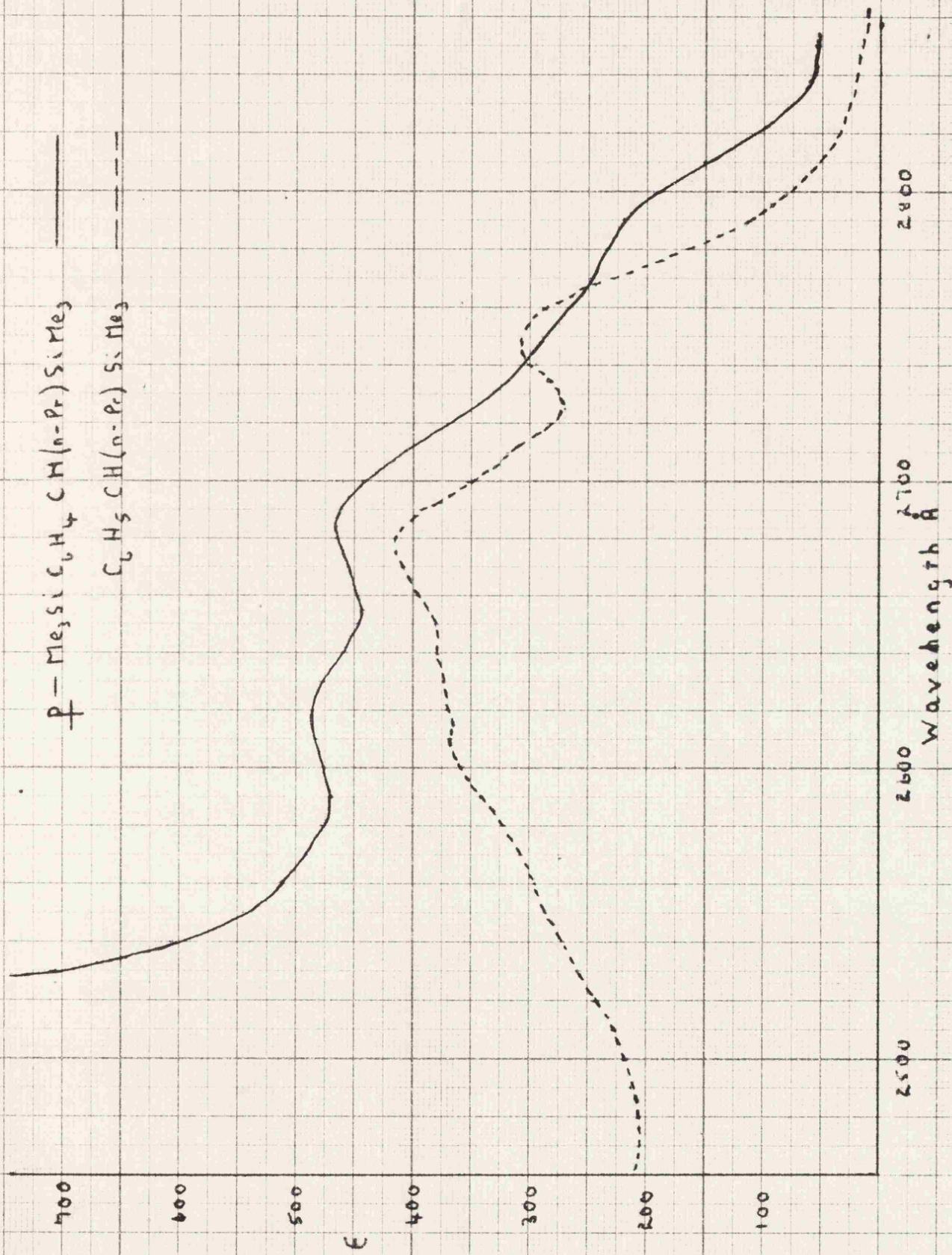


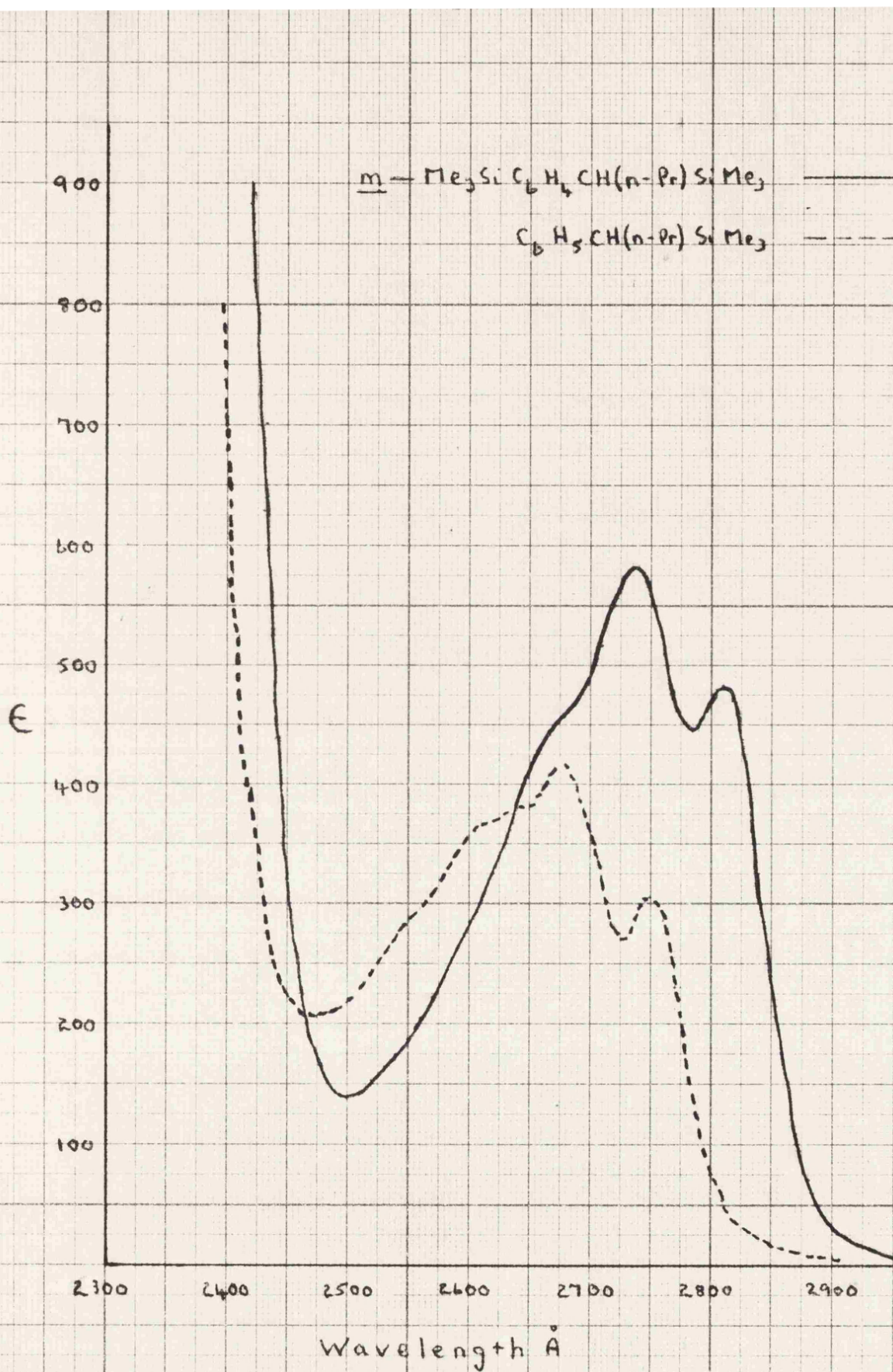












a large excess of acid is pseudo first-order. The reaction has, therefore, been studied by following the removal of the trimethylsilyl group from the aromatic ring using a Unicam S. P. 500 Spectrophotometer. To determine a suitable wavelength for the kinetic study, the ultra-violet spectra of the silane and its cleavage product were determined in each case, and a region of maximum difference between the two spectra was chosen for the kinetic determinations.

When it was convenient to do so, the optical density readings were taken at a wavelength where the rate of change of extinction coefficient of both reactant and product with wavelength was small, to minimise the effects of errors in the wavelength setting.

Whenever possible, cleavage studies were made in the 2,600-2,800Å band, as the instrument is very sensitive in this region of the ultra-violet spectrum. The initial reactant concentration was selected, solubility permitting, to give an optical density in the region of 0.8, as this enabled the major part of the reaction to be followed over the most sensitive part of the optical density scale, namely 0.8-0.3.

Cells.

A matched pair of stoppered, 1cm. quartz cells were used in the instrument, the same cell being used each time for the solvent blank. This avoids any slight discrepancies

due to differences in the cells.

#### Temperature Control.

The Unicam S. P. 500 Spectrophotometer was fitted with an Adkins thermostatted cell-holder, in which the temperature was controlled to within  $\pm 0.02^{\circ}\text{C}$  by a Mullard temperature control unit. The time taken for a cell placed in the holder to reach the temperature of the holder was about 8 minutes; hence no kinetic readings were taken for the first 8 minutes.

#### End-points.

The end-point (infinity value) was taken at 10 times the half-life of the reaction. End-points of runs with half-lives of less than 1 hr. were obtained by leaving the cells in the cell-holder for the requisite length of time; this was the preferred method. With runs of half-lives greater than 1 hr., three further samples of the kinetic solution were taken, (at the same time as the sample was transferred to the cell), and these were sealed in pyrex test-tubes and placed in a thermostat bath at  $50^{\circ}$ , for the requisite length of time; the tubes were then opened and the end-point determined, the mean of the three values being taken.

#### Kinetic Determinations.

The silane solution (5ml. or 25ml.) was pipetted into a clean, dry, stoppered container and 2ml. (or 10ml.) of perchloric acid of the appropriate strength added. The

solution was then thoroughly shaken and a sample transferred to the 1cm. stoppered quartz cell which was quickly transferred to the cell-holder. The blank solution used was made up of the solvent methanol (5ml.) and the perchloric acid (2ml.). Optical density measurements were taken after suitable time-intervals.

#### Calculation of the Rate Constants.

The cleavage reaction may be treated as a first-order reaction in silane. For first-order reactions

$$dx/dt = k_1(a-x)$$

where  $k_1$  = first-order rate constant;  $a$  = initial concentration of the reactant;  $x$  = amount reacted after time  $t$ .

Integration between the limits  $t = 0$  and  $t = t$  gives

$$\log a/(a-x) = k_1 t$$

Beers law states that the optical density of a solution is proportional to the concentration of the compound in that solution at a specified wavelength, hence

$$\log a/(a-x) = \log(D_0 - D_\infty)/(D_t - D_\infty) = k_1 t$$

and

$$t = - \frac{2.303}{k_1} \log_{10}(D_t - D_\infty) + \frac{2.303}{k_1} \log_{10}(D_0 - D_\infty)$$

where  $D_0$  = optical density after time zero;  $D_t$  = optical density after time  $t$ ;  $D_\infty$  = optical density at the end-point.

Hence the gradient of a plot of  $t$  vs  $\log_{10}(D_t - D_\infty)$  is  $-2.303/k_1$  and  $k_1 = -2.303 \times \text{gradient}$ .

All rate constants obtained during the present work were obtained using the graphical method. It can be seen that a knowledge of the optical density at the beginning of the reaction is not required.

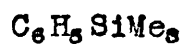
#### Tabulation of Kinetic Results.

A selection of the experimental points taken during each run is given. The rate constants for individual points have been calculated for several runs. The values of  $k_{calc}$  were within 1% of the values determined by the graphical method. All rate constants were reproducible to within  $\pm 1\%$ .

All the kinetic runs were carried out at  $50.15 \pm 0.02^\circ\text{C}$ .

The following runs were carried out using 25ml. silane and 10ml. perchloric acid, the same pipettes being used throughout. The results obtained are summarised in Table 5.2.

<u>C<sub>6</sub>H<sub>5</sub>SiMe<sub>3</sub></u>		Conc. = $1.18 \times 10^{-2}$ M						
Run 39		Wavelength 2700Å <sup>o</sup>					9.09M HClO <sub>4</sub>	
Time (mins.)	0	45	135	270	420	615	∞	
10 <sup>3</sup> D	842	792	698	579	475	369	072	
Slope = $-0.674 \times 10^{-3}$		k = $1.55 \times 10^{-3} \text{ min.}^{-1}$						
Run 40		Wavelength 2700Å <sup>o</sup>					9.09M HClO <sub>4</sub>	
Time (mins.)	0	45	180	360	480	660	∞	
10 <sup>3</sup> D	835	783	648	508	435	346	077	
Slope = $-0.681 \times 10^{-3}$		k = $1.57 \times 10^{-3} \text{ min.}^{-1}$						
		<u>Mean k = <math>1.56 \times 10^{-3} \text{ min.}^{-1}</math></u>						



Conc. =  $1.19 \times 10^{-2}$  M

Run 41                      Wavelength 2700Å<sup>o</sup>                      12.05M HClO<sub>4</sub>

Time (mins.)	0	60	100	130	150	200	∞
10 <sup>3</sup> D	837	571	448	378	338	261	087

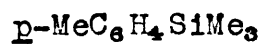
Slope =  $-3.17 \times 10^{-3}$                       k =  $7.30 \times 10^{-3} \text{ min.}^{-1}$

Run 42                      Wavelength 2700Å<sup>o</sup>                      12.05M HClO<sub>4</sub>

Time (mins.)	10	50	75	110	150	170	∞
10 <sup>3</sup> D	762	591	508	413	329	296	084

Slope =  $-3.16 \times 10^{-3}$                       k =  $7.28 \times 10^{-3} \text{ min.}^{-1}$

Mean k =  $7.29 \times 10^{-3} \text{ min.}^{-1}$



Conc. =  $9.91 \times 10^{-3}$  M

Run 53                      Wavelength 2730Å<sup>o</sup>                      9.09M HClO<sub>4</sub>

Time (mins.)	1	9	16	22	36	45	∞
10 <sup>3</sup> D	602	510	447	404	331	298	199

Slope =  $-1.38 \times 10^{-2}$                       k =  $31.8 \times 10^{-3} \text{ min.}^{-1}$

Run 54                      Wavelength 2730Å<sup>o</sup>                      9.09M HClO<sub>4</sub>

Time (mins.)	1	7	18	22	30	40	∞
10 <sup>3</sup> D	593	524	427	400	354	311	198

Slope =  $-1.39 \times 10^{-2}$                       k =  $32.0 \times 10^{-3} \text{ min.}^{-1}$

Run 56                      Wavelength 2730Å<sup>o</sup>                      9.09M HClO<sub>4</sub>

Time (mins.)	0	10	22	30	40	50	∞
10 <sup>3</sup> D	600	490	397	352	310	279	196

Slope =  $-1.37 \times 10^{-2}$                       k =  $31.6 \times 10^{-3} \text{ min.}^{-1}$

Mean k =  $31.8 \times 10^{-3} \text{ min.}^{-1}$

<u>m-MeC<sub>6</sub>H<sub>4</sub>SiMe<sub>3</sub></u>		Conc. = $3.70 \times 10^{-3}$ M					
Run 55	Wavelength 2755Å						12.05M HClO <sub>4</sub>
Time (mins.)	7	22	40	60	85	110	∞
10 <sup>3</sup> D	652	502	368	263	176	121	029
Slope = $-8.06 \times 10^{-3}$		k = $18.6 \times 10^{-3} \text{ min.}^{-1}$					
Run 63	Wavelength 2755Å						12.05M HClO <sub>4</sub>
Time (mins.)	0	10	22	50	90	110	∞
10 <sup>3</sup> D	728	612	499	310	164	122	030
Slope = $-8.00 \times 10^{-3}$		k = $18.4 \times 10^{-3} \text{ min.}^{-1}$					
		<u>Mean k = <math>18.5 \times 10^{-3} \text{ min.}^{-1}</math></u>					

<u>p-MeC<sub>6</sub>H<sub>4</sub>SiMe<sub>3</sub></u>		Conc. = $9.91 \times 10^{-3}$ M					
Run 59	Wavelength 2730Å						4.54M HClO <sub>4</sub>
Time (mins.)	0	45	165	195	210	225	240
10 <sup>3</sup> D	808	743	607	578	566	553	542
10 <sup>3</sup> k <sub>calc.</sub>		2.74	2.70	2.70	2.70	2.69	2.69
Time (mins.)	285	300	330	375	420	450	∞
10 <sup>3</sup> D	509	498	478	451	428	413	249
10 <sup>3</sup> k <sub>calc.</sub>	2.68	2.69	2.70	2.71	2.70	2.72	
Slope = $-1.17 \times 10^{-3}$		k = $2.69 \times 10^{-3} \text{ min.}^{-1}$					
		(k <sub>calc.</sub> = $2.70 \times 10^{-3} \text{ min.}^{-1}$ )					
Run 61	Wavelength 2730Å						4.55M HClO <sub>4</sub>
Time (mins.)	45	90	150	195	315	420	∞
10 <sup>3</sup> D	708	658	598	559	472	416	247
Slope = $-1.17 \times 10^{-3}$		k = $2.69 \times 10^{-3} \text{ min.}^{-1}$					
		<u>Mean k = <math>2.69 \times 10^{-3} \text{ min.}^{-1}</math></u>					

p-Me<sub>3</sub>SiC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>SiMe<sub>3</sub>      Conc. = 2.24 × 10<sup>-3</sup> M

4.54M HClO<sub>4</sub>

Run 70	Wavelength 2490Å						
Time (mins.)	0	6	8	10	12	14	18
10 <sup>3</sup> D	797	688	658	627	602	575	530
10 <sup>3</sup> k <sub>calc.</sub>		35.7	35.2	35.7	35.2	35.6	35.5
Time (mins.)	24	28	32	36	40	50	∞
10 <sup>3</sup> D	474	440	413	388	368	326	231
10 <sup>3</sup> k <sub>calc.</sub>	35.2	35.6	35.5	35.6	35.5	35.7	

Slope = -1.54 × 10<sup>-2</sup>      k = 35.5 × 10<sup>-3</sup> min.<sup>-1</sup>  
(k<sub>calc.</sub> = 35.5 × 10<sup>-3</sup> min.<sup>-1</sup>)

Run 71      Wavelength 2490Å      4.54M HClO<sub>4</sub>

Time (mins.)	7	11	16	24	36	45	∞
10 <sup>3</sup> D	677	620	558	478	394	350	232

Slope = -1.52 × 10<sup>-2</sup>      k = 35.1 × 10<sup>-3</sup> min.<sup>-1</sup>  
Mean k = 35.3 × 10<sup>-3</sup> min.<sup>-1</sup>

p-Me<sub>3</sub>SiC<sub>6</sub>H<sub>4</sub>CH(CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>)SiMe<sub>3</sub>      Conc. = 1.58 × 10<sup>-3</sup> M

4.54M HClO<sub>4</sub>

Run 47	Wavelength 2530Å						
Time (mins.)	0	12	19	32	40	55	∞
10 <sup>3</sup> D	878	688	608	501	454	394	306

Slope = -1.47 × 10<sup>-2</sup>      k = 33.9 × 10<sup>-3</sup> min.<sup>-1</sup>

Run 51	Wavelength 2530Å						
Time (mins)	0	8	17	26	34	45	∞
10 <sup>3</sup> D	872	738	623	539	483	428	307

Slope = -1.49 × 10<sup>-2</sup>      k = 34.3 × 10<sup>-3</sup> min.<sup>-1</sup>  
Mean k = 34.1 × 10<sup>-3</sup> min.<sup>-1</sup>

Table 5.2

Cleavage of p-XC<sub>6</sub>H<sub>4</sub>SiMe<sub>3</sub> with MeOH-HClO<sub>4</sub> at  
50.15°C.

Substituent X	HClO <sub>4</sub> (M)	10 <sup>3</sup> k <sub>1</sub> (min.)	Relative Rate (k <sub>rel.</sub> )
H	12.05	7.29	1
<u>n</u> -Me	12.05	18.5	2.54
H	9.09	1.56	1
p-Me	9.09	31.8	20.4
p-Me	4.54	2.69	
p-Me <sub>3</sub> SiCH <sub>2</sub>	4.54	35.3	267
p-Me <sub>3</sub> Si(n-Pr)CH	4.54	34.1	259

p-MeC<sub>6</sub>H<sub>4</sub>SiMe<sub>3</sub>

Conc. = 8.56 × 10<sup>-3</sup> M

Run 21                      Wavelength 2730 Å                      9.09M HClO<sub>4</sub>

Time (mins.)      3      8      16      26      36      50      ∞

10<sup>3</sup> D              573    518    445    378    329    282    201

Slope = -1.41 × 10<sup>-2</sup>                      k = 32.5 × 10<sup>-3</sup> min.<sup>-1</sup>

Run 34                      Wavelength 2730 Å                      9.09M HClO<sub>4</sub>

Time (mins.)      1      8      16      24      38      50      ∞

10<sup>3</sup> D              603    521    448    392    322    283    201

Slope = -1.41 × 10<sup>-2</sup>                      k = 32.5 × 10<sup>-3</sup> min.<sup>-1</sup>

Mean k = 32.5 × 10<sup>-3</sup> min.<sup>-1</sup>

p-Me<sub>3</sub>SiC<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>SiMe<sub>3</sub>                      Conc. = 5.50×10<sup>-3</sup> M

Run 10                      Wavelength 2725Å<sup>o</sup>                      9.09M HClO<sub>4</sub>

Time (mins.)	0	4	8	16	20	28	∞
10 <sup>3</sup> D	476	428	390	330	307	272	188
Slope =	-1.91×10 <sup>-2</sup>		k = 44.0×10 <sup>-3</sup> min. <sup>-1</sup>				

Run 14                      Wavelength 2725Å<sup>o</sup>                      9.09M HClO<sub>4</sub>

Time (mins.)	2	7	12	14	18	32	∞
10 <sup>3</sup> D	458	408	367	354	329	273	208
Slope =	-1.95×10 <sup>-2</sup>		k = 44.9×10 <sup>-3</sup> min. <sup>-1</sup>				
<u>Mean k = 44.4×10<sup>-3</sup> min.<sup>-1</sup></u>							

Run 57                      Wavelength 2385Å<sup>o</sup>                      9.09M HClO<sub>4</sub>

Time (mins.)	0	8	19	36	45	55	∞
10 <sup>3</sup> D	853	678	515	377	337	307	253
Slope =	-1.90×10 <sup>-2</sup>		k = 43.8×10 <sup>-3</sup> min. <sup>-1</sup>				

Run 58                      Wavelength 2385Å<sup>o</sup>                      9.09M HClO<sub>4</sub>

Time (mins.)	3	6	16	26	32	36	∞
10 <sup>3</sup> D	803	738	573	463	417	391	262
Slope =	-1.88×10 <sup>-2</sup>		k = 43.3×10 <sup>-3</sup> min. <sup>-1</sup>				
<u>Mean k = 43.5×10<sup>-3</sup> min.<sup>-1</sup></u>							

p-Me<sub>3</sub>SiC<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>3</sub>SiMe<sub>3</sub>                      Conc. = 5.12×10<sup>-3</sup> M

Run 6                      Wavelength 2725Å<sup>o</sup>                      9.09M HClO<sub>4</sub>

Time (mins.)	4	10	18	26	36	50	∞
10 <sup>3</sup> D	373	327	278	241	208	177	128
Slope =	-1.52×10 <sup>-2</sup>		k = 35.0×10 <sup>-3</sup> min. <sup>-1</sup>				

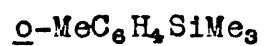
Run 7		Wavelength 2725Å <sup>o</sup>						9.09M HClO <sub>4</sub>
Time (mins.)	0	3	8	14	16	18	22	
10 <sup>3</sup> D	414	386	344	303	292	280	262	
10 <sup>3</sup> k <sub>calc.</sub>		34.4	35.1	35.1	34.8	35.1	34.5	
Time (mins.)	28	36	40	45	55	60	∞	
10 <sup>3</sup> D	236	210	200	188	171	164	128	
10 <sup>3</sup> k <sub>calc.</sub>	34.8	34.7	34.5	34.7	34.5	34.5		
		Slope = -1.50×10 <sup>-2</sup>		k = 34.5×10 <sup>-3</sup> min. <sup>-1</sup>				
		(k <sub>calc.</sub> = 34.7×10 <sup>-3</sup> min. <sup>-1</sup> )						

Run 12		Wavelength 2725Å <sup>o</sup>						9.09M HClO <sub>4</sub>
Time (mins.)	0	4	10	16	32	45	∞	
10 <sup>3</sup> D	396	361	317	280	212	179	121	
		Slope = -1.51×10 <sup>-2</sup>		k = 34.8×10 <sup>-3</sup> min. <sup>-1</sup>				
		<u>Mean k = 34.8×10<sup>-3</sup> min.<sup>-1</sup></u>						

Run 67		Wavelength 2370Å <sup>o</sup>						9.09M HClO <sub>4</sub>
Time (mins.)	7	12	16	20	30	38	∞	
10 <sup>3</sup> D	697	615	558	509	408	348	149	
		Slope = -1.43×10 <sup>-2</sup>		k = 32.9×10 <sup>-3</sup> min. <sup>-1</sup>				

Run 69		Wavelength 2370Å <sup>o</sup>						9.09M HClO <sub>4</sub>
Time (mins.)	10	14	18	30	38	45	∞	
10 <sup>3</sup> D	638	581	527	402	343	302	148	
		Slope = -1.45×10 <sup>-2</sup>		k = 33.4×10 <sup>-3</sup> min. <sup>-1</sup>				
		<u>Mean k = 33.2×10<sup>-3</sup> min.<sup>-1</sup></u>						

<u>p-Me<sub>3</sub>SiC<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>4</sub>SiMe<sub>3</sub></u>		Conc. = 4.67×10 <sup>-3</sup> M					
Run 8		Wavelength 2725Å <sup>o</sup>					9.09M HClO <sub>4</sub>
Time (mins.)	2	6	14	20	30	50	∞
10 <sup>3</sup> D	353	319	270	242	206	164	127
	Slope = -1.64×10 <sup>-2</sup>			k = 37.8×10 <sup>-3</sup> min. <sup>-1</sup>			
Run 9		Wavelength 2725Å <sup>o</sup>					9.09M HClO <sub>4</sub>
Time (mins.)	1	5	12	22	30	50	∞
10 <sup>3</sup> D	362	328	282	233	204	162	124
	Slope = -1.62×10 <sup>-2</sup>			k = 37.3×10 <sup>-3</sup> min. <sup>-1</sup>			
	<u>Mean k = 37.5×10<sup>-3</sup> min.<sup>-1</sup></u>						
Run 62		Wavelength 2370Å <sup>o</sup>					9.09M HClO <sub>4</sub>
Time (mins.)	0	5	10	20	30	36	∞
10 <sup>3</sup> D	714	622	543	426	342	305	157
	Slope = -1.61×10 <sup>-2</sup>			k = 37.1×10 <sup>-3</sup> min. <sup>-1</sup>			
Run 64		Wavelength 2370Å <sup>o</sup>					9.09M HClO <sub>4</sub>
Time (mins.)	7	10	15	20	26	32	∞
10 <sup>3</sup> D	597	554	489	432	378	333	157
	Slope = -1.60×10 <sup>-2</sup>			k = 36.8×10 <sup>-3</sup> min. <sup>-1</sup>			
Run 66		Wavelength 2370Å <sup>o</sup>					9.09M HClO <sub>4</sub>
Time (mins.)	0	6	12	30	38	46	∞
10 <sup>3</sup> D	718	608	519	339	290	253	147
	Slope = -1.59×10 <sup>-2</sup>			k = 36.6×10 <sup>-3</sup> min. <sup>-1</sup>			
	<u>Mean k = 36.8×10<sup>-3</sup> min.<sup>-1</sup></u>						



Conc. =  $3.87 \times 10^{-3}$  M

Run 43                      Wavelength 2750Å                      9.09M HClO<sub>4</sub>

Time (mins.)	1	20	36	55	65	90	∞
10 <sup>3</sup> D	777	498	348	236	196	132	064

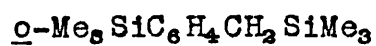
Slope =  $-1.15 \times 10^{-2}$                       k =  $26.5 \times 10^{-3} \text{ min.}^{-1}$

Run 44                      Wavelength 2750Å                      9.09M HClO<sub>4</sub>

Time (mins.)	0	9	26	40	65	90	∞
10 <sup>3</sup> D	800	639	429	316	190	125	057

Slope =  $-1.16 \times 10^{-2}$                       k =  $26.7 \times 10^{-3} \text{ min.}^{-1}$

Mean k =  $26.6 \times 10^{-3} \text{ min.}^{-1}$



Conc. =  $1.74 \times 10^{-3}$  M

Run 49                      Wavelength 2815Å                      9.09M HClO<sub>4</sub>

Time (mins.)	0	7	19	28	40	80	∞
10 <sup>3</sup> D	668	490	298	212	142	065	052

Slope =  $-2.09 \times 10^{-2}$                       k =  $48.1 \times 10^{-3} \text{ min.}^{-1}$

Run 50                      Wavelength 2815 Å                      9.09M HClO<sub>4</sub>

Time (mins.)	0	3	5	7	10	16	20
10 <sup>3</sup> D	670	587	538	492	432	338	288
10 <sup>3</sup> k <sub>calc.</sub>		48.6	48.6	49.1	49.3	48.9	49.0
Time (mins.)	24	26	32	36	45	50	∞
10 <sup>3</sup> D	248	231	187	164	127	112	058
10 <sup>3</sup> k <sub>calc.</sub>	48.8	48.6	48.7	48.8	48.4	48.5	

Slope =  $-2.11 \times 10^{-2}$                       k =  $48.6 \times 10^{-3} \text{ min.}^{-1}$   
(k =  $48.8 \times 10^{-3} \text{ min.}^{-1}$ )

Mean k =  $48.4 \times 10^{-3} \text{ min.}^{-1}$

o-Me<sub>3</sub>SiC<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>SiMe<sub>3</sub>      Conc. = 3.71 × 10<sup>-3</sup> M

Run 15      Wavelength 2750Å<sup>o</sup>      9.09M HClO<sub>4</sub>

Time (mins.)	0	3	10	13	17	21	30
10 <sup>3</sup> D	885	818	683	629	568	515	407
10 <sup>3</sup> k <sub>calc.</sub>		27.2	26.9	27.3	27.2	27.0	27.3
Time (mins.)	34	40	48	60	73	102	∞
10 <sup>3</sup> D	370	319	262	196	146	083	029
10 <sup>3</sup> k <sub>calc.</sub>	27.1	27.1	27.1	27.2	27.3	27.1	

Slope = -1.18 × 10<sup>-2</sup>      k = 27.2 × 10<sup>-3</sup> min.<sup>-1</sup>  
(k = 27.2 × 10<sup>-3</sup> min.<sup>-1</sup>)

Run 17      Wavelength 2750Å<sup>o</sup>      9.09M HClO<sub>4</sub>

Time (mins.)	1	10	21	40	55	75	∞
10 <sup>3</sup> D	862	683	516	322	226	146	034

Slope = -1.18 × 10<sup>-2</sup>      k = 27.2 × 10<sup>-3</sup> min.<sup>-1</sup>  
Mean k = 27.2 × 10<sup>-3</sup> min.<sup>-1</sup>

o-Me<sub>3</sub>SiC<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>3</sub>SiMe<sub>3</sub>      Conc. = 3.88 × 10<sup>-3</sup> M

Run 20      Wavelength 2750Å<sup>o</sup>      9.09M HClO<sub>4</sub>

Time (mins.)	2	14	32	48	65	90	∞
10 <sup>3</sup> D	896	728	538	414	318	222	058

Slope = -8.06 × 10<sup>-3</sup>      k = 18.6 × 10<sup>-3</sup> min.<sup>-1</sup>

Run 22      Wavelength 2750Å<sup>o</sup>      9.09M HClO<sub>4</sub>

Time (mins.)	5	20	30	42	55	75	∞
10 <sup>3</sup> D	835	642	541	443	358	262	050

Slope = -8.18 × 10<sup>-3</sup>      k = 18.8 × 10<sup>-3</sup> min.<sup>-1</sup>

Mean k = 18.7 × 10<sup>-3</sup> min.<sup>-1</sup>

o-Me<sub>3</sub>SiC<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>4</sub>SiMe<sub>3</sub>                      Conc. = 3.77×10<sup>-3</sup> M

Run 16                      Wavelength 2750Å                      9.09M HClO<sub>4</sub>

Time (mins.)	2	18	34	48	70	105	∞
10 <sup>3</sup> D	815	588	427	324	211	112	019

Slope = -9.09×10<sup>-3</sup>                      k = 20.9×10<sup>-3</sup> min<sup>-1</sup>

Run 18                      Wavelength 2750Å                      9.09M HClO<sub>4</sub>

Time (mins.)	4	20	30	55	70	110	∞
10 <sup>3</sup> D	838	612	508	321	248	137	053

Slope = -9.11×10<sup>-3</sup>                      k = 21.0×10<sup>-3</sup> min<sup>-1</sup>

Mean k = 21.0×10<sup>-3</sup> min<sup>-1</sup>

m-MeC<sub>6</sub>H<sub>4</sub>SiMe<sub>3</sub>                      Conc. = 3.67×10<sup>-3</sup> M

Run 48                      Wavelength 2755Å                      12.05M HClO<sub>4</sub>

Time (mins.)	3	10	28	38	60	90	∞
10 <sup>3</sup> D	703	622	450	379	262	163	037

Slope = -8.34×10<sup>-3</sup>                      k = 19.2×10<sup>-3</sup> min<sup>-1</sup>

Run 52                      Wavelength 2755Å                      12.05M HClO<sub>4</sub>

Time (mins.)	8	18	26	36	65	85	∞
10 <sup>3</sup> D	631	532	464	391	244	181	044

Slope = -8.23×10<sup>-3</sup>                      k = 19.0×10<sup>-3</sup> min<sup>-1</sup>

Mean k = 19.1×10<sup>-3</sup> min<sup>-1</sup>

m-Me<sub>3</sub>SiC<sub>6</sub>H<sub>4</sub>CH(n-Pr)SiMe<sub>3</sub>                      Conc. = 3.58×10<sup>-3</sup> M

Run 33                      Wavelength 2810Å                      12.05M HClO<sub>4</sub>

Time (mins.)	1	5	10	18	24	38	∞
10 <sup>3</sup> D	885	723	572	406	324	215	133

Slope = -2.59×10<sup>-2</sup>                      k = 59.6×10<sup>-3</sup> min<sup>-1</sup>

Run 38	Wavelength 2810Å <sup>o</sup>							12.05M HClO <sub>4</sub>
Time (mins.)	0	4	8	12	16	20	22	
10 <sup>3</sup> D	885	731	607	552	430	371	346	
10 <sup>3</sup> k <sub>calc.</sub>		58.4	58.9	58.9	59.7	59.3	59.3	
Time (mins.)	24	28	32	36	∞			
10 <sup>3</sup> D	323	286	254	232	145			
10 <sup>3</sup> k <sub>calc.</sub>	59.4	59.2	59.9	59.4				
Slope = -2.58 × 10 <sup>-2</sup>								k = 59.4 × 10 <sup>-3</sup> min. <sup>-1</sup>
								(k <sub>calc.</sub> = 59.2 × 10 <sup>-3</sup> min. <sup>-1</sup> )
								<u>Mean k = 59.5 × 10<sup>-3</sup> min.<sup>-1</sup></u>

<u>m-Me<sub>3</sub>SiC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>SiMe<sub>3</sub></u>	Wavelength 2810Å <sup>o</sup>							Conc. = 2.80 × 10 <sup>-3</sup> M	12.05M HClO <sub>4</sub>
Run 29	Wavelength 2810Å <sup>o</sup>							12.05M HClO <sub>4</sub>	
Time (mins.)	0	5	7	11	14	20	24		
10 <sup>3</sup> D	912	738	678	582	516	412	357		
10 <sup>3</sup> k <sub>calc.</sub>		47.7	47.4	47.4	47.7	47.7	47.8		
Time (mins.)	30	34	40	45	50	∞			
10 <sup>3</sup> D	293	259	219	193	173	099			
10 <sup>3</sup> k <sub>calc.</sub>	47.8	47.8	47.8	47.9	47.9				
Slope = -2.08 × 10 <sup>-2</sup>								k = 47.9 × 10 <sup>-3</sup> min. <sup>-1</sup>	
								(k <sub>calc.</sub> = 47.7 × 10 <sup>-3</sup> min. <sup>-1</sup> )	

Run 31	Wavelength 2810Å <sup>o</sup>							12.05M HClO <sub>4</sub>
Time (mins.)	0	4	10	16	26	45	∞	
10 <sup>3</sup> D	935	793	622	492	348	203	107	
Slope = -2.08 × 10 <sup>-2</sup>								k = 47.9 × 10 <sup>-3</sup> min. <sup>-1</sup>

Mean k = 47.9 × 10<sup>-3</sup> min.<sup>-1</sup>

<u>m-Me<sub>3</sub>SiC<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>SiMe<sub>3</sub></u>		Conc. = 3.79×10 <sup>-3</sup> M					
Run 28	Wavelength 2745Å <sup>o</sup>						12.05M HClO <sub>4</sub>
Time (mins.)	2	10	18	42	60	90	∞
10 <sup>3</sup> D	768	636	528	318	228	147	081
Slope = -1.16×10 <sup>-2</sup>		k = 26.7×10 <sup>-3</sup> min. <sup>-1</sup>					
Run 30	Wavelength 2745Å <sup>o</sup>						12.05M HClO <sub>4</sub>
Time (mins.)	2	13	24	40	55	80	∞
10 <sup>3</sup> D	781	603	469	333	247	162	071
Slope = -1.15×10 <sup>-2</sup>		k = 26.5×10 <sup>-3</sup> min. <sup>-1</sup>					
		<u>Mean k = 26.6×10<sup>-3</sup> min.<sup>-1</sup></u>					

<u>m-Me<sub>3</sub>SiC<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>3</sub>SiMe<sub>3</sub></u>		Conc. = 3.91×10 <sup>-3</sup> M					
Run 23	Wavelength 2745Å <sup>o</sup>						12.05M HClO <sub>4</sub>
Time (mins.)	1	10	24	36	46	80	∞
10 <sup>3</sup> D	754	598	424	319	256	134	059
Slope = -1.22×10 <sup>-2</sup>		k = 28.1×10 <sup>-3</sup> min. <sup>-1</sup>					
Run 25	Wavelength 2745Å <sup>o</sup>						12.05M HClO <sub>4</sub>
Time (mins.)	1	10	22	34	46	70	∞
10 <sup>3</sup> D	767	607	448	336	257	158	056
Slope = -1.22×10 <sup>-2</sup>		k = 28.1×10 <sup>-3</sup> min. <sup>-1</sup>					
		<u>Mean k = 28.1×10<sup>-3</sup> min.<sup>-1</sup></u>					

<u>m-Me<sub>3</sub>SiC<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>4</sub>SiMe<sub>3</sub></u>		Conc. = 3.84×10 <sup>-3</sup> M					
Run 26	Wavelength 2745Å <sup>o</sup>						12.05M HClO <sub>4</sub>
Time (mins.)	0	4	8	10	15	20	24
10 <sup>3</sup> D	804	732	667	638	570	510	468
10 <sup>3</sup> k <sub>calc.</sub>		25.9	25.9	25.7	25.7	25.7	25.6

Time (mins.)	30	38	46	55	65	105	$\infty$
$10^8 D$	411	348	297	250	210	121	072
$10^8 k_{\text{calc.}}$	25.7	25.7	25.7	25.7	25.7	26.0	
Slope = $-1.12 \times 10^{-2}$				$k = 25.8 \times 10^{-3} \text{ min.}^{-1}$			
			$(k_{\text{calc.}} = 25.7 \times 10^{-3} \text{ min.}^{-1})$				

Run 27                      Wavelength 2745Å                      12.05M HClO<sub>4</sub>

Time (mins.)	0	5	15	28	40	60	$\infty$
$10^8 D$	828	737	588	443	347	238	074
Slope = $-1.11 \times 10^{-2}$				$k = 25.6 \times 10^{-3} \text{ min.}^{-1}$			

Mean  $k = 25.7 \times 10^{-3} \text{ min.}^{-1}$

For the compounds  $p\text{-Me}_3\text{SiC}_6\text{H}_4(\text{CH}_2)_n\text{SiMe}_3$  (where  $n = 2$  to 4) the runs were carried out at two different wavelengths. The results obtained are summarised in Table 5.3

Table 5.3

Cleavage of  $p\text{-Me}_3\text{SiC}_6\text{H}_4(\text{CH}_2)_n\text{SiMe}_3$  with MeOH-HClO<sub>4</sub>

at 50.15°C.

n.	2725Å	2385Å	2370Å	Average
	$10^8 k_1 (\text{min.}^{-1})$	$10^8 k_1 (\text{min.}^{-1})$	$10^8 k_1 (\text{min.}^{-1})$	
2	44.4	43.5	-	44.0
3	34.8	-	33.2	34.0
4	37.5	-	36.8	37.2

Table 5.4

Cleavage of  $\text{XC}_6\text{H}_4\text{SiMe}_3$  with  $\text{MeOH-HClO}_4$

at 50.15°C.

Substituent X	$\text{HClO}_4$ (M)	$10^3 k_1$ (min. <sup>-1</sup> )	Relative Rate ( $k_{\text{rel.}}$ )
p-Me	9.09	32.5	20.4
p-Me <sub>3</sub> Si(CH <sub>2</sub> ) <sub>2</sub>	9.09	44.0	27.5
p-Me <sub>3</sub> Si(CH <sub>2</sub> ) <sub>3</sub>	9.09	34.0	21.4
p-Me <sub>3</sub> Si(CH <sub>2</sub> ) <sub>4</sub>	9.09	37.2	23.3
o-Me	9.09	26.6	16.7
o-Me <sub>3</sub> SiCH <sub>2</sub>	9.09	48.4	30.1
o-Me <sub>3</sub> Si(CH <sub>2</sub> ) <sub>2</sub>	9.09	27.2	17.1
o-Me <sub>3</sub> Si(CH <sub>2</sub> ) <sub>3</sub>	9.09	18.7	11.7
o-Me <sub>3</sub> Si(CH <sub>2</sub> ) <sub>4</sub>	9.09	21.0	13.2
m-Me	12.05	19.1	2.54
m-Me <sub>3</sub> Si(n-Pr)CH	12.05	59.5	7.91
m-Me <sub>3</sub> SiCH <sub>2</sub>	12.05	47.9	6.37
m-Me <sub>3</sub> Si(CH <sub>2</sub> ) <sub>2</sub>	12.05	26.6	3.54
m-Me <sub>3</sub> Si(CH <sub>2</sub> ) <sub>3</sub>	12.05	28.1	3.74
m-Me <sub>3</sub> Si(CH <sub>2</sub> ) <sub>4</sub>	12.05	25.7	3.42

N. B. The above compounds were studied by taking 5ml. of silane and 2ml. of perchloric acid, the same pipettes being used throughout.

The Attempted Alkaline Cleavage of

1-(m- and p-trimethylsilylphenyl)-1-trimethylsilyl-n-butane.

The methanolic silane solution (5ml.) was added to 2N sodium hydroxide (5ml.) in 32 vol% water-methanol. Two samples of each solution, including a blank solution prepared from methanol (5ml.) and 2N sodium hydroxide, were sealed in pyrex tubes and heated in a thermostat bath at 72° for the requisite length of time. The samples were then withdrawn, the tubes broken and the spectra of the solutions measured.

Time (hr)	p-Me <sub>3</sub> SiC <sub>6</sub> H <sub>4</sub> CH(n-Pr)SiMe <sub>3</sub>		m-Me <sub>3</sub> SiC <sub>6</sub> H <sub>4</sub> CH(n-Pr)SiMe <sub>3</sub>	
	λ <sub>max</sub> (Å)	ε <sub>max</sub>	λ <sub>max</sub> (Å)	ε <sub>max</sub>
0	2625	482	2740	583
	2690	464	2810	484
72	2625	410	2740	515
	2690	380	2810	418
220	2625	380	2740	465
	2690	321	2810	356

## CHAPTER 6.

### Nitration

#### General

The reactions were carried out in a 250ml. three-necked round-bottomed flask with ground glass joints, fitted with a 100ml. dropping funnel, a thermometer and a glass sleeved stirrer. The glacial acetic acid and acetic anhydride were supplied by May and Baker Ltd., and were used without further purification.

The method of nitration was varied and will be described for each set of experiments. The general method for isolating the products, however, was standard and is given below.

The reaction mixture was cooled, when necessary, and added to a cooled solution of sodium hydroxide (140g.) in ice-water (500ml.), and the products extracted with ether (100ml. and 6×50ml.). The ethereal extract was washed with water until neutral; the aqueous washings were then extracted with ether (2×50ml.), this ethereal extract washed with water and finally combined with the main ethereal extract, and dried over anhydrous sodium sulphate.

The ether was removed through the glass helices-packed column, and the residue fractionated under reduced pressure through the Vigreux column (ca. 18 theoretical plates). In some cases benzyl benzoate was used as chaser. The products were identified by boiling point and refractive

index measurements. The composition of the fractions were calculated from standard refractive index/composition graphs and the results tabulated.

Reaction of p-Tolyltrimethylsilane with Nitric Acid  
in Acetic Anhydride.

Several different methods of nitration were employed.

Nitration method 1.

Nitric acid, 70%w/w (18.0g., 0.20mole) was added dropwise to a well stirred solution of acetic anhydride (140g.), the temperature being maintained at 20-25°C. The nitrating solution was then cooled to -20±5° and maintained at this temperature for 30min. before commencing the nitration. p-Tolyltrimethylsilane (16.43g., 0.10mole) was then added dropwise at such a rate so as to maintain the temperature at -20±5° (the cooling bath temperature being -25 to -30°). The reaction mixture was maintained at this temperature for the requisite length of time (inclusive of the time for addition of the silane), and then worked up by the standard procedure.

Nitration medium:-

0.20mole 70% HNO<sub>3</sub>, 18.0g. ≡ 12.6g. HNO<sub>3</sub> + 5.4g. H<sub>2</sub>O

Since 
$$\begin{array}{ccc} \text{Ac}_2\text{O} & + & \text{H}_2\text{O} & \longrightarrow & 2\text{AcOH} \\ (30.6\text{g.}) & & (5.4\text{g.}) & & (36.0\text{g.}) \end{array}$$

then the medium is 
$$\text{Ac}_2\text{O} - \underset{75\%}{109.4\text{g.}} \quad + \quad \text{AcOH} - \underset{25\%}{36\text{g.}}$$

Results.

<u>Experiment 94</u>		Reaction time 10 min.		
Boiling Range °C/10±0.5mm.	Wt. (g.)	$n_D^{20}$	Composition	
72 - 74	10.14	1.4922	p-tolyltrimethylsilane	
74 - 110	0.32	1.5032	p-tolyltrimethylsilane + p-nitrotoluene	
110 - 134	1.63	1.5302	p-nitrotoluene + nitrosilane	
134 - 140	4.37	1.5248	nitrosilane	
140 - 176	0.88	1.5475	nitrosilane + benzyl benzoate	
<u>Experiment 88</u>		Reaction time 15 min.		
72	7.63	1.4922	p-tolyltrimethylsilane	
72 - 110	0.30	1.5053	p-tolyltrimethylsilane + p-nitrotoluene	
110 - 132	1.05	1.5291	p-nitrotoluene + nitrosilane	
132 - 138	5.29	1.5245	nitrosilane + benzyl benzoate	
<u>Experiment 93</u>		Reaction time 15 min.		
74	8.68	1.4922	p-tolyltrimethylsilane	
74 - 108	1.40	1.4938	p-tolyltrimethylsilane + p-nitrotoluene	
108 - 134	1.07	1.5278	p-nitrotoluene + nitrosilane	
134 - 140	4.71	1.5248	nitrosilane	
140 - 175	1.60	1.5424	nitrosilane + benzyl benzoate	

<u>Experiment 85</u>			Reaction time 30 min.	
Boiling Range	Wt. (g.)	$n_D^{20}$	Composition	
72	6.60	1.4920	p-tolyltrimethylsilane	
72 - 110	2.13	1.4983	p-tolyltrimethylsilane + p-nitrotoluene	
110 - 134	0.77	1.5360	p-nitrotoluene + nitrosilane	
134	7.20	1.5242	nitrosilane	

<u>Experiment 92</u>			Reaction time 30 min.	
72 - 74	7.17	1.4920	p-tolyltrimethylsilane	
74 - 110	1.39	1.5032	p-tolyltrimethylsilane + p-nitrotoluene	
110 - 134	1.34	1.5326	p-nitrotoluene + nitrosilane	
134 - 140	6.54	1.5247	nitrosilane	
140 - 175	0.82	1.5433	nitrosilane + benzyl benzoate	

<u>Experiment 87</u>			Reaction time 45 min.	
72	5.14	1.4918	p-tolyltrimethylsilane	
72 - 110	1.37	1.4992	p-tolyltrimethylsilane + p-nitrotoluene	
110 - 132	1.56	1.5343	p-nitrotoluene + nitrosilane	
132 - 138	8.86	1.5245	nitrosilane	

<u>Experiment 97</u>			Reaction time 45 min.	
73 - 74	6.27	1.4920	p-tolyltrimethylsilane	
74 - 110	1.23	1.4990	p-tolyltrimethylsilane + p-nitrotoluene	
110 - 134	2.22	1.5307	p-nitrotoluene + nitrosilane	

Boiling Range °C/10±0.5mm.	Wt. (g.)	$n_D^{20}$	Composition
134 - 138	6.39	1.5242	nitrosilane
138 - 174	2.31	1.5514	nitrosilane + benzyl benzoate

Experiment 72

Reaction time 540 min.

74 - 102	0.53	1.5140	p-tolyltrimethylsilane + p-nitrotoluene
102 - 129	2.89	47-51°	p-nitrotoluene
129 - 142	12.95	1.5253	nitrosilane

Experiment 95

Reaction time 540 min.

72 - 108	0.76	1.5048	p-tolyltrimethylsilane + p-nitrotoluene
108 - 135	4.99	1.5356	p-nitrotoluene + nitrosilane
135 - 140	9.85	1.5248	nitrosilane
140 - 177	1.84	1.5444	nitrosilane + benzyl benzoate

Table 6.1

Nitration of p-Tolyltrimethylsilane with HNO<sub>3</sub>/Ac<sub>2</sub>O

at -20±5°

Expt. No.	Reaction Time (min.)	Unreacted Silane %	p-Nitrotoluene %	Nitrosilane %	Yield of Reaction %
94	10	63.24	3.21	28.92	95.32
88	15	59.29	2.77	29.44	91.50
93	15	61.05	1.46	31.45	93.96
85	30	51.56	4.23	36.57	92.36
92	30	50.28	5.18	37.94	93.40
87	45	38.53	5.40	47.12	91.05
97	45	44.62	5.18	42.91	92.71
72	540	1.95	22.60	61.89	86.45
95	540	3.61	15.83	66.24	85.68

Using the same nitration technique, experiments were carried out in which small amounts of sulphuric acid, lithium nitrate or sodium nitrate had been added to the nitrating solution before the addition of the silane.

Experiment 84

Reaction time 45 min.

0.002moles NaNO<sub>3</sub>

Boiling Range °C/10±0.5mm.	Wt. (g.)	<sup>20</sup> <sub>n</sub> <sub>D</sub>	Composition
72 - 74	13.57	1.4918	p-tolyltrimethylsilane
74 - 140	2.17	1.5210	p-tolyltrimethylsilane + nitrosilane

Experiment 100

Reaction time 45 min.

0.002moles  $\text{LiNO}_3$ 

74 - 76	11.65	1.4918	p-tolytrimethylsilane
76 - 110	0.49	1.4944	p-tolytrimethylsilane + p-nitrotoluene
110 - 134	0.61	1.5280	p-nitrotoluene + nitrosilane
134 - 176	4.83	1.5383	nitrosilane + benzyl benzoate

Experiment 82

Reaction time 15 min.

0.002moles  $\text{H}_2\text{SO}_4$ 

72 - 109	2.09	1.5084	p-tolytrimethylsilane + p-nitrotoluene
109 - 116	0.44	47-49°	p-nitrotoluene
116 - 134	1.46	1.5345	p-nitrotoluene + nitrosilane
134 - 138	12.75	1.5242	nitrosilane

Experiment 102

Reaction time 300 min.

0.002moles  $\text{H}_2\text{SO}_4$ 

103 - 135	7.26	1.5330	p-nitrotoluene + nitrosilane
135 - 137	8.22	1.5242	nitrosilane
137 - 176	1.89	1.5548	nitrosilane + benzyl benzoate

Table 6.2

The Effect of Added Acid and Nitrate Ions on the  
Nitration of p-Tolyltrimethylsilane.

Expt. No.	Reaction Time (min.)	Reagent Added (moles)	Unreacted Silane %	p-Nitro-toluene %	Nitro-silane %	Yield of Reaction %
84	45	NaNO <sub>3</sub> 0.002	83.87	-	9.37	93.24
100	45	LiNO <sub>3</sub> 0.002	73.77	0.8	18.34	92.91
82	15	H <sub>2</sub> SO <sub>4</sub> 0.002	8.83	11.74	65.36	85.93
102	300	H <sub>2</sub> SO <sub>4</sub> 0.002	-	16.85	65.80	82.65

Nitration method 2.

Nitric acid, 70%w/w (18.0g., 0.20mole) was added dropwise to a well stirred solution of acetic anhydride (140g.), the temperature being maintained at  $-20 \pm 5^{\circ}\text{C}$  (cooling bath at  $-25$  to  $-30^{\circ}$ ). The nitrating solution was kept at this temperature for 30min. before commencing the nitration. p-Tolyltrimethylsilane (16.43g., 0.10mole) was then added dropwise at such a rate so as to maintain the temperature at  $-20 \pm 5^{\circ}$  (the cooling bath temperature being  $-25$  to  $-30^{\circ}$ ). The reaction mixture was maintained at this temperature for the requisite length of time (inclusive of the time for the addition of the silane), and then worked up by the standard procedure.

Medium:- Ac<sub>2</sub>O - 75% + AcOH - 25%

Results

<u>Experiment 80</u>		Reaction time 30 min.	
Boiling Range °C/10±0.5mm.	Wt. (g.)	$n_D^{20}$	Composition
72 - 74	3.13	1.4917	p-tolyltrimethylsilane
74 - 110	1.05	1.5005	p-tolyltrimethylsilane + p-nitrotoluene
110 - 132	2.16	1.5358	p-nitrotoluene + nitrosilane
132 - 138	10.95	1.5245	nitrosilane

<u>Experiment 90</u>		Reaction time 30 min.	
70 - 74	4.89	1.4931	} p-tolyltrimethylsilane + p-nitrotoluene
74 - 110	0.86	1.5188	
110 - 134	2.87	1.5310	p-nitrotoluene + nitrosilane
134 - 138	8.20	1.5242	nitrosilane

<u>Experiment 71</u>		Reaction time 9 hours	
73 - 104	0.46	1.5185	p-tolyltrimethylsilane + p-nitrosilane
104 - 130	2.77	46-50.5	p-nitrotoluene
130 - 140	13.04	1.5252	nitrosilane

Table 6.3

Nitration of p-Tolyltrimethylsilane with HNO<sub>3</sub>/Ac<sub>2</sub>O  
at -20±5°C.

Expt. No.	Reaction Time (min.)	Unreacted silane %	p-Nitrotoluene %	Nitrosilane %	Yield of Reaction %
80	30	24.41	7.88	58.30	90.59
90	30	31.78	9.12	49.45	90.35
71	540	1.46	21.81	62.30	85.57

Nitration method 3.

The acetic acid/acetic anhydride concentrations in the following experiments were varied. Nitric acid, 70%w/w (18.0g., 0.20mole) was added dropwise to acetic acid/acetic anhydride, the temperature being maintained at 20 - 25°. This nitrating solution was then added dropwise to p-tolyltrimethylsilane (0.10mole. 16.43g.) in acetic acid/acetic anhydride the temperature being maintained at 25±2.5°. The reaction mixture was maintained at this temperature for the requisite length of time and then worked up by the standard method.

Experiment 68

Reaction time 480 min.

Medium:- Ac<sub>2</sub>O - 90% (112.5g.) + AcOH - 10% (12.5g.)

Boiling Range °C/10±0.5mm.    Wt.(g.)     $n_D^{20}$  or M.Pt.    Composition

103 - 125	7.75	45-50.5°	} p-nitrotoluene
125 - 130	0.36	40 - 49°	
130 - 140	6.40	1.5254	nitrosilane



Nitration method 4.

The required amount of 89.1%w/w nitric acid was added dropwise to a solution of acetic acid/acetic anhydride the temperature being maintained at  $25 \pm 2.5^\circ$ . p-Tolyltrimethylsilane (16.43g., 0.10mole) was added dropwise to the vigorously stirred solution, the temperature being maintained at  $25 \pm 2.5^\circ$ . The reaction mixture was maintained at this temperature for 300min., and then worked up by the standard procedure.

Medium:- Ac<sub>2</sub>O - 75% + AcOH - 25%

<u>Experiment 121</u>			89.1% HNO <sub>3</sub> (10.6g., 0.15mole)
Boiling Range °C/10 $\pm$ 0.5mm.	Wt. (g.)	n <sub>D</sub> <sup>20</sup>	Composition
74 - 108	0.38	1.5072	p-tolyltrimethylsilane + p-nitrotoluene
108 - 113	6.21	50-51°	p-nitrotoluene
113 - 136	4.95	1.5300	p-nitrotoluene + nitrosilane
136 - 138	3.30	1.5267	
138 - 176	5.41	1.5656	nitrosilane + benzyl benzoate

<u>Experiment 122</u>			89.1% HNO <sub>3</sub> (21.2g., 0.30mole)
Boiling Range °C/10 $\pm$ 0.5mm.	Wt. (g.)	n <sub>D</sub> <sup>20</sup>	Composition
106 - 112	3.20	50-51.5°	p-nitrotoluene
112 - 135	1.61	1.5328	p-nitrotoluene + nitrosilane
135 - 136	10.00	1.5259	nitrosilane + benzyl benzoate
136 - 175	3.83	1.5477	

<u>Experiment 123</u>		89.1% HNO <sub>3</sub> (31.8g., 0.45mole)		
Boiling Range °C/10±0.5mm.	Wt. (g.)	$n_D^{20}$	Composition	
106 - 115	2.00	50 - 51°	p-nitrotoluene	
115 - 135	1.80	1.5347	p-nitrotoluene + nitrosilane	
135 - 137	12.58	1.5262	} nitrosilane + benzyl benzoate	
137 - 177	3.18	1.5618		

Table 6.5

Nitration of p-Tolyltrimethylsilane with HNO<sub>3</sub>/Ac<sub>2</sub>O

at 25°C.

Expt. No.	Moles HNO <sub>3</sub>	Recovered Silane %	p-Nitrotoluene %	Nitrosilane %	Yield of Reaction %
121	0.15	1.64	55.95	34.97	92.56
122	0.30	-	26.99	60.10	87.09
123	0.45	-	19.47	65.27	84.74

Reaction of p-Tolyltrimethylsilane with Dinitrogen Pentoxide in Acetic Anhydride/Acetic Acid.

The dinitrogen pentoxide was prepared according to the method given in Inorganic Syntheses,<sup>294</sup> from fuming nitric acid (100g.) and phosphorous pentoxide (200g.). The product was obtained as very pale yellow crystals.

Nitration method.

Dinitrogen pentoxide (11.9g., 0.11mole) was dissolved in acetic anhydride (109g.) and acetic acid (36g.) at -20°. The solution was transferred to the reaction vessel and

kept at  $-20 \pm 5^\circ$  for 30 min. p-Tolyltrimethylsilane (16.43g., 0.10mole) was then added dropwise to the nitrating solution at such a rate so as to maintain the temperature at  $-20 \pm 5^\circ$  (the cooling bath being at  $-25$  to  $-30^\circ$ ). The reaction mixture was maintained at this temperature for the requisite length of time (inclusive of the time of addition of the silane), and then worked up by the standard procedure.

Medium:-  $\text{Ac}_2\text{O}$  -75% +  $\text{AcOH}$  - 25%

Results.

<u>Experiment 83</u>		Reaction time 15 min.	
Boiling Range $^\circ\text{C}/10 \pm 0.5\text{mm.}$	Wt. (g.)	$n_D^{20}$	Composition
72	8.54	1.4918	p-tolyltrimethylsilane
72 - 108	0.72	1.5186	p-tolyltrimethylsilane + p-nitrotoluene
108 - 134	2.82	1.5361	p-nitrotoluene + nitrosilane
134 - 138	3.70	1.5242	nitrosilane

<u>Experiment 98</u>		Reaction time 15 min.	
Boiling Range $^\circ\text{C}/10 \pm 0.5\text{mm.}$	Wt. (g.)	$n_D^{20}$	Composition
72	9.19	1.4920	p-tolyltrimethylsilane
72 - 108	1.60	1.5043	p-tolyltrimethylsilane + p-nitrotoluene
108 - 138	4.71	1.5312	p-nitrotoluene + nitrosilane
138 - 176	1.60	1.5564	nitrosilane + benzyl benzoate

<u>Experiment 76</u>		Reaction time 540 min.	
Boiling Range °C/10±0.5mm.	Wt. (g.)	$n_D^{20}$	Composition
72 - 104	1.23	1.5056	p-tolyltrimethylsilane + p-nitrotoluene
104 - 112	5.73	50 - 52°	p-nitrotoluene
112 - 134	2.06	1.5363	p-nitrotoluene + nitrosilane
134 - 140	6.69	1.5236	nitrosilane

<u>Experiment 96</u>		Reaction time 540 min.	
92 - 106	0.31	1.5302	p-tolyltrimethylsilane + p-nitrotoluene
106 - 110	4.95	48.5-47.5	p-nitrotoluene
110 - 136	3.43	1.5342	p-nitrotoluene + nitrosilane
136 - 139	6.05	1.5242	nitrosilane
139 - 176	1.57	1.5538	nitrosilane + benzyl benzoate

Table 6.6

Nitration of p-Tolyltrimethylsilane with Dinitrogen  
Pentoxide in Ac<sub>2</sub>O/AcOH at -20±5°C.

Expt. No.	Reaction Time (mins.)	Unreacted Silane %	p-Nitrotoluene %	Nitrosilane %	Yield of Reaction %
83	15	54.24	11.09	25.57	90.90
98	15	62.58	12.26	18.83	93.97
76	540	5.60	50.55	37.56	93.71
96	540	0.61	46.54	42.01	89.16

Using the same nitration technique, experiments were carried out with small amounts of sulphuric acid, lithium nitrate, and sodium nitrate added to the nitrating solution before addition of the silane.

Experiment 86

Reaction time 15 min.

		0.002moles H <sub>2</sub> SO <sub>4</sub>		
Boiling Range °C/10±0.5mm.	Wt. (g.)	<sup>20</sup> n <sub>D</sub>		Composition
74 - 76	2.37	1.4942	}	p-tolyltrimethylsilane
76 - 105	1.01	1.5229		+ p-nitrotoluene
105 - 110	3.72	49-51°		p-nitrotoluene
110 - 132	2.13	1.5315		p-nitrotoluene + nitrosilane
132 - 136	5.95	1.5242		nitrosilane

Experiment 78

Reaction time 540 min.

		0.002moles H <sub>2</sub> SO <sub>4</sub>		
105 - 112	4.86	49-51°		p-nitrotoluene
112 - 135	2.39	1.5360		p-nitrotoluene + nitrosilane
135 - 140	7.71	1.5238		nitrosilane

Experiment 99

Reaction time 15 min.

		0.002mole LiNO <sub>3</sub>		
72 - 74	13.79	1.4918		p-tolyltrimethylsilane
74 - 110	0.55	1.5041		p-tolyltrimethylsilane + p-nitrotoluene
110 - 134	0.45	1.5320		p-nitrotoluene + nitrosilane
134 - 177	1.30	1.5524		nitrosilane + benzyl benzoate

Experiment 101

Reaction time 540 min.

0.002mole LiNO<sub>3</sub>

74	4.30	1.4918	p-tolyltrimethylsilane
74 - 108	0.79	1.5208	p-tolyltrimethylsilane + p-nitrotoluene
108 - 134	6.44	1.5363	p-nitrotoluene + nitrosilane
134 - 138	3.00	1.5248	nitrosilane
138 - 177	3.32	1.5492	nitrosilane + benzyl benzoate

Table 6.7Nitration of p-Tolyltrimethylsilane with DinitrogenPentoxide in Ac<sub>2</sub>O/AcOH at -20±5°C.

Expt. No.	Reaction Time (min.)	Reagent Added (moles)	Unreacted Silane %	p-Nitrotoluene %	Nitrosilane %	Yield of Reaction %
86	15	0.002 H <sub>2</sub> SO <sub>4</sub>	16.56	36.11	35.88	88.55
78	540	0.002 H <sub>2</sub> SO <sub>4</sub>	-	42.82	42.96	85.78
99	15	0.002 LiNO <sub>3</sub>	86.52	1.90	3.82	92.24
101	540	0.002 LiNO <sub>3</sub>	28.48	23.27	38.86	90.61

Using the same nitration technique, nitrations were carried out using different amounts of dinitrogen pentoxide, and also with added nitric acid.

Experiment 155

Reaction time 45 min.

0.15 mole  $N_2O_5$ 

Boiling Range $^{\circ}C/10^{\pm}0.5mm.$	Wt. (g.)	$n_D^{25}$ or M. Pt.	Composition
67 - 103	7.38	1.4928	p-tolyltrimethylsilane + p-nitrotoluene
103 - 125	3.65	50 - 52 $^{\circ}$	p-nitrotoluene
125 - 143	3.31	1.5243	p-nitrotoluene + nitrosilane
143 - 175	2.58	1.5578	nitrosilane + benzyl benzoate

Experiment 157

Reaction time 45 min.

 $N_2O_5$  (0.15mole) +  $HNO_3$  (1g.)

69 - 109	7.61	1.5059	p-tolyltrimethylsilane + p-nitrotoluene
109 - 133	7.60	1.5239	p-nitrotoluene + nitrosilane
133 - 175	3.82	1.5555	nitrosilane + benzyl benzoate

Experiment 158

Reaction time 300 min.

0.15 mole  $N_2O_5$ 

70 - 105	1.92	1.5184	p-tolyltrimethylsilane + p-nitrotoluene
105 - 110	3.83	51-52.5 $^{\circ}$	p-nitrotoluene
110 - 135	8.97	1.5239	p-nitrotoluene + nitrosilane
135 - 175	10.14	1.5582	nitrosilane + benzyl benzoate

Experiment 156

Reaction time 300 min.

0.24 mole  $N_2O_5$

Boiling Range $^{\circ}C/10 \pm 0.5mm.$	Wt. (g.)	$n_D^{25}$ or M. Pt.	Composition
97 - 103	0.82	49 - 51 $^{\circ}$	} p-nitrotoluene
103 - 107	2.96	50 - 51.5 $^{\circ}$	
107 - 133	3.11	1.5283	p-nitrotoluene + nitrosilane
133 - 135	7.71	1.5216	nitrosilane
135 - 175	9.06	1.5615	nitrosilane + benzyl benzoate

Table 6.8

Nitration of p-Tolyltrimethylsilane with Dinitrogen

Pentoxide in  $Ac_2O/AcOH$  at  $-20 \pm 5^{\circ}C.$

Expt. No.	Reaction Time (min.)	$N_2O_5$ (moles)	Unreacted Silane %	p-Nitrotoluene %	Nitrosilane %	Yield of Reaction %
155	45	0.15	42.0	33.2	16.0	91.2
157	45	0.15 1g. $HNO_3$	32.0	22.0	37.6	91.6
158	300	0.15	5.5	33.8	48.1	87.4
156	300	0.24	-	33.2	52.7	85.9

Reaction of p-Tolyltrimethylsilane with Acetyl Nitrate

in Acetonitrile- $Ac_2O$ - $AcOH$  at  $-20 \pm 5^{\circ}C.$

Silver nitrate (34.0g., 0.20mole) was dissolved in acetonitrile (25g.) and cooled to  $0^{\circ}$ . Acetyl chloride (15.7g., 0.20mole) was then added dropwise to the solution. The precipitated silver chloride was filtered off through

a scintered glass funnel and washed with acetonitrile (10g.). The filtrate was then transferred to the reaction vessel, cooled to  $-20^{\circ}$  and a solution of acetic anhydride (70g.) added. *p*-Tolyltrimethylsilane (16.43g., 0.10mole) was then added dropwise to the nitrating solution, at such a rate so as to maintain the temperature at  $-20^{\circ}$ . The reaction mixture was then maintained at  $-20\pm 5^{\circ}$  for 9 hr., added to a cooled solution of sodium hydroxide (96g.) in ice-water (400ml.) and filtered through a scintered glass funnel. The products were then isolated by the standard procedure. In experiment 77, 0.25 mole of acetyl nitrate was prepared and in experiment 74, sulphuric acid (0.002 mole) was added to the nitrating solution.

Experiment 73

Boiling Range $^{\circ}\text{C}/10\pm 0.5\text{mm.}$	Wt. (g.)	$n_D^{20}$	Composition
72 - 80	10.16	1.4918	<i>p</i> -tolyltrimethylsilane
80 - 140	4.68	1.5264	<i>p</i> -nitrotoluene + nitrosilane

Experiment 77

72	8.52	1.4919	<i>p</i> -tolyltrimethylsilane
72 - 110	0.67	1.4968	<i>p</i> -tolyltrimethylsilane + <i>p</i> -nitrotoluene
110 - 131	1.48	1.5337	<i>p</i> -nitrotoluene + nitrosilane
131 - 136	5.45	1.5242	nitrosilane

Experiment 74

Boiling Range °C/10±0.5mm.	Wt. (g.)	$n_D^{20}$	Composition
72 - 102	3.17	1.4922	p-tolyltrimethylsilane
102 - 126	4.07	46 - 51.5	p-nitrotoluene
126 - 136	8.61	1.5245	nitrosilane

Table 6.9

Nitration of p-Tolyltrimethylsilane with Acetyl Nitrate  
in Ac<sub>2</sub>O-AcOH-MeCN at -20±5°C.

Expt. No.	Reagent Added (moles)	Unreacted Silane %	p-Nitrotoluene %	Nitrosilane %	Yield of Reaction %
73	-	61.84	3.65	19.97	85.46
77	-	55.58	4.30	30.59	90.47
74	H <sub>2</sub> SO <sub>4</sub> 0.002	19.30	29.69	41.14	91.13

Reaction of p-Tolyltrimethylsilane with  
Nitryl Chloride

Preparation of Nitryl Chloride.

Oleum, 20% SO<sub>3</sub> (100g.) was added dropwise to a vigorously stirred solution of nitric acid, 96%w/w (98.1g., 1.50mole) at 0°. Chlorosulphonic acid (174.8g., 1.50mole) was then added dropwise over 3 hours, with vigorous stirring, the temperature being maintained at 0°. The nitryl chloride was collected in a flask hooded with ethanol/Drikold and finally redistilled through a short Vigreux column. b.p. -14°C. Yield - 81.5g.

### Nitration Method.

Nitryl chloride (36.7g., 0.45mole) was added dropwise to a vigorously stirred solution of p-tolyltrimethylsilane (32.86g., 0.20mole) in dry carbon tetrachloride (250ml.)-experiment 107, or dry nitromethane (200ml.)-experiment 108, the reaction mixture being maintained at -25° for 3 hours. The reaction mixture was then allowed to warm up to room temperature. Sodium bicarbonate was added to the reaction mixture until no further reaction occurred. It was then washed with water until neutral, and dried over anhydrous sodium sulphate. The solvent was removed through the glass helices-packed column, and the residue fractionated under vacuum through the Vigreux column.

It was noticed that when nitryl chloride was added to p-tolyltrimethylsilane in carbon tetrachloride no violent reaction occurred, whereas when nitromethane was the solvent a violent reaction took place.

The products were identified by boiling point, refractive index, melting point, and infrared spectroscopy.

### Results.

<u>Experiment 107</u>		<u>NO<sub>2</sub>Cl in CCl<sub>4</sub></u>		
Boiling Range	Wt. (g.)	$n_D^{20}$ or M. Pt.	Composition	
78- 80	50±1.0mm.	13.31	1.5202	p-chlorotoluene
80-110		1.59	1.5262	p-chlorotoluene + nitrotoluenes

cont.

Boiling Range	Wt. (g.)	$n_D^{20}$ or M. Pt.	Composition
91-103	10±0.5mm.	5.46	p-nitrotoluene
103-105		41 - 51°	
105-120		0.81	p-nitrotoluene + nitrosilane
120-175		2.52	
		2.04	nitrosilane + benzyl benzoate

#### Products.

p-Chlorotoluene	57.6%
Nitrotoluenes	29.5% (essentially p-nitrotoluene).
Nitrosilane	3.0%
Yield of Reaction	90.1%

<u>Experiment 108</u>		$\text{NO}_2\text{Cl}$ in $\text{MeNO}_2$	
45- 75	50±1.0mm.	3.25	nitromethane +
75- 92		1.4033	
92-112		8.49	p-chlorotoluene + nitrotoluenes nitrotoluenes
112-120		0.86	
		2.42	(semi-solid)
90-130	10±0.5mm.	4.26	p-nitrotoluene
130-180		5.01	p-nitrotoluene + benzyl benzoate

#### Results.

p-Chlorotoluene	36.5%
Nitrotoluenes	35.1% (essentially p-nitrotoluene)
Yield of Reaction	71.6%

## Nitration of p-Tolyltrimethylsilane with Silver

### Tetrafluoroborate and Nitryl Chloride.

#### Preparation of Silver Tetrafluoroborate.

Boron trifluoride-ether complex (60.0g., 0.43mole) was added dropwise to a well stirred suspension of dried silver oxide (51.5g., 0.22mole) in anhydrous nitromethane (150ml.). The solution was stirred for 3 hours and filtered through a scintered glass funnel, the precipitate being washed with nitromethane (50ml.). The filtration was carried out under dry nitrogen.

The silver tetrafluoroborate solution was then estimated by precipitation of the  $\text{AgBF}_4 \cdot \text{MeCN}$  complex:- 10 ml. of  $\text{AgBF}_4$  solution + 5 ml. MeCN taken and the complex was precipitated with ether (50ml.). This was filtered, dried, and weighed.

0.11mole  $\text{AgBF}_4 \cong$  87.7 ml. nitromethane soln.

#### Nitration Method.

Several methods of nitration were attempted but in all cases very little nitro product was obtained and no unreacted p-tolyltrimethylsilane was recovered.

1). Addition of  $\text{AgBF}_4$  solution to the p-tolyltrimethylsilane at  $-25^\circ$  and  $-70^\circ$ , prior to the addition of the nitryl chloride.

2). Addition of p-tolyltrimethylsilane to  $\text{AgBF}_4$  solution plus nitryl chloride at  $-25^\circ$  and  $-70^\circ$ .

Reaction of p-Tolyltrimethylsilane with  
Nitronium Tetrafluoroborate.

Preparation of Nitronium Tetrafluoroborate.

Prepared according to the method of Kuhn and Olah<sup>187</sup> from fuming nitric acid, anhydrous hydrofluoric acid and boron trifluoride.

Boron trifluoride was slowly passed into a solution of fuming nitric acid (70g., 1.0mole) and anhydrous hydrofluoric acid (20g., 1.0mole), at  $-5^{\circ}$ , over a period of 3 hours. The solution was then decanted and the precipitated nitronium tetrafluoroborate washed twice by decantation with anhydrous nitromethane (2x50ml.), filtered through a scintered glass funnel and washed with "Arcton 113" (1,1,2-trifluoro-trichloroethane). The solid nitronium tetrafluoroborate, kept moist with Arcton 113, was transferred to a round bottomed flask and dried under vacuum for 2 hr. Yield - 86.5% (115g.).

Nitration Method.

The nitration method of Olah<sup>187</sup> was first employed but it was found that p-tolyltrimethylsilane was immiscible, with tetramethylene sulphone. Acetonitrile was, therefore, used as solvent for the silane.

Nitronium tetrafluoroborate (20g., 0.15mole) in tetramethylene sulphone (300ml.) was added dropwise to p-tolyltrimethylsilane (82.2g., 0.50mole) in anhydrous acetonitrile (150ml.) at  $25 \pm 2.5^{\circ}$ . The reaction mixture

was maintained at 25° for 3hrs., added to a solution of sodium hydroxide (20g.) in water (1,500ml.) and extracted with ether (3×150ml.). The ethereal extract was washed with water (6×50ml.) and dried over anhydrous sodium sulphate. The solvent was removed through the packed column and the residue fractionated, under vacuum, through the Vigreux column.

Result.

<u>Experiment 160</u>			
Boiling Range °C/10±0.5mm.	Wt. (g.)	<sup>25</sup> n <sub>D</sub>	Composition
60 - 73	2.3	1.4901	p-tolyltrimethylsilane
73 - 85	36.4	1.4903	
85 - 100	0.6	1.5278	p-tolyltrimethylsilane + nitrotoluenes
100 - 114	1.5	1.5435	nitrotoluenes
114 - 130	2.2	1.5329	p-nitrotoluene + nitrosilane
130 - 135	17.0	1.5222	nitrosilane

Products.

p-Tolyltrimethylsilane recovered = 38.9% (0.24mole)  
 Nitrotoluenes = 13.6%  
 Nitrosilane = 58.5%  
 Yield of Reaction = 72.1% (based on  
 NO<sub>2</sub>BF<sub>4</sub> used).

From boiling point and refractive index measurements it was concluded that the nitrotoluenes recovered were chiefly a mixture of the ortho-para isomers. Since no

pure p-nitrotoluene could be isolated, the nitrotoluenes must arise from nitration of toluene formed by acid cleavage of the silane. It is evident that virtually no nitrodesilylation could have occurred otherwise p-nitrotoluene would have been isolated. A certain amount of toluene was isolated after fractionation of the material collected in the cold trap during the vacuum distillation.

Reaction of Phenyltrimethylsilane with  
Nitric Acid in Acetic Anhydride.

Nitration Method.

Nitric acid, 70%w/w (18.0g., 0.20mole) was added dropwise to a well stirred solution of acetic anhydride (140g.), the temperature being maintained at 20-25°. The nitrating solution was then heated to 50±2.5° and phenyltrimethylsilane (15.03g., 0.10mole) added dropwise at such a rate so as to maintain the temperature at 50°. The reaction mixture was maintained at this temperature for the required length of time and then worked up by the standard method. In experiments 118 and 125 sulphuric acid (0.002mole) was added to the nitrating solution prior to the addition of the silane.

Nitration medium:-



Results.

<u>Experiment 118</u>		Reaction time 180 min.		
		0.002 mole H <sub>2</sub> SO <sub>4</sub>		
Boiling Range °C/10±0.5mm.	Wt. (g.)	$n_D^{20}$	Composition	
87 - 93	7.35	1.5520	nitrobenzene	
93 - 126	1.05	1.5387	nitrobenzene + nitrosilane	
126 - 127	3.88	1.5268	nitrosilane	
127 - 129	3.52	1.5638	nitrosilane + benzyl benzoate	

<u>Experiment 120</u>		Reaction time 540 min.		
86 - 100	5.42	1.5519	nitrobenzene	
100 - 127	2.17	1.5355	nitrobenzene + nitrosilane	
127 - 137	6.45	1.5293	nitrosilane +	
137 - 176	3.16	1.5648	benzyl benzoate	

<u>Experiment 125</u>		Reaction time 10 min.		
		0.002 mole H <sub>2</sub> SO <sub>4</sub>		
55 - 60	8.90	1.4915	}	phenyltrimethylsilane
60 - 92	1.84	1.5434		+
92 - 126	0.90	1.5388		nitrobenzene
126 - 135	1.54	1.5292		+
135 - 178	3.92	1.5674		nitrosilane
				nitrosilane + benzyl benzoate

Table 6.10

Nitration of Phenyltrimethylsilane with  
HNO<sub>3</sub>/Ac<sub>2</sub>O at 50±2.5°C.

Expt. No.	Reagent Added (moles)	Reaction Time (min.)	Recovered Silane %	Nitro-benzene %	Nitro-silane %	Yield of Reaction %
125	H <sub>2</sub> SO <sub>4</sub> 0.002	10	59.00	18.52	11.01	88.53
118	H <sub>2</sub> SO <sub>4</sub> 0.002	180	-	63.53	25.20	88.73
120	-	540	-	49.64	40.25	89.89

Nitration of Anisole.

Two general methods for working up the reaction products were employed, together with several different methods of nitration.

General Method 1.

70%w/w Nitric acid (18.0g., 0.20mole) was added to acetic anhydride (140g.) and anisole (10.81g., 0.10mole) then added.

The reaction mixture was finally added to a cooled solution of sodium hydroxide (140g.) in ice-water (500ml.), and the products extracted with ether (100ml., + 6×50ml.), the ethereal extract washed with water until neutral (3×50ml.), and dried over anhydrous sodium sulphate. The aqueous washings were extracted with ether (3×50ml.), the ethereal extract washed with water (2×50ml.) and combined with the main ethereal extract. The ether was removed

through the glass-helices packed column and the residue fractionated under reduced pressure through the Vigreux column.

#### Nitration Procedures.

A. The nitric acid was added dropwise to the well stirred acetic anhydride, the temperature being maintained at  $-20$  to  $-25^{\circ}$ . The nitrating solution was then kept at  $-20 \pm 5^{\circ}$  for 30 min. before commencing the nitration. The anisole was added dropwise at such a rate so as to maintain the temperature at  $-20 \pm 5^{\circ}$  (cooling bath at  $-25$  to  $-30^{\circ}$ ). The anisole was added in 21-4 minutes and the reaction time was 25 minutes.

B. The nitric acid was added dropwise to the well stirred acetic anhydride, the temperature being maintained at  $20$ - $25^{\circ}$ . The solution was then cooled to  $-20 \pm 5^{\circ}$  and maintained at this temperature for 30 minutes before commencing the nitration. The anisole was added dropwise at such a rate so as to maintain the temperature at  $-20 \pm 5^{\circ}$  (the cooling bath at  $-25$  to  $-30^{\circ}$ ). The anisole was added in 19-24 min. and the total reaction time was 25 minutes.

C. The nitration procedure was the same as that described in method A except that the anisole was added in 2 to 3 minutes (cooling bath at  $-70^{\circ}$ ) and the total reaction time was 3-4.5mins.

D. The nitration procedure was the same as that described in method B except that the anisole was added

in 1.5 to 2.5 minutes (cooling bath temperature was  $-70^{\circ}$ ) and the total reaction time was 3 to 4.5 minutes. In expt. 146 the anisole was added in 200 secs.

Results.

<u>Experiment 130</u>	Nitration method A.
Boiling Range $136-44^{\circ}/10\text{mm.}$	14.36g. $n_D^{25}$ 1.5657

<u>Experiment 131</u>	Nitration method B.
Boiling Range $137-43^{\circ}/10\text{mm.}$	14.31g. $n_D^{25}$ 1.5655

<u>Experiment 132</u>	Nitration method A.
Boiling Range $137-9^{\circ}/10\text{mm.}$	14.58g. $n_D^{25}$ 1.5662

<u>Experiment 133</u>	Nitration method B.
Boiling Range $137-8^{\circ}/10\text{mm.}$	14.56g. $n_D^{25}$ 1.5661

<u>Experiment 134</u>	Nitration method C.
Boiling Range $137-8^{\circ}/10\text{mm.}$	14.53g. $n_D^{25}$ 1.5661

<u>Experiment 135</u>	Nitration method D.
Boiling Range $137-8^{\circ}/10\text{mm.}$	14.45g. $n_D^{25}$ 1.5652

<u>Experiment 138</u>	Nitration method G.
Boiling Range $135-6^{\circ}/10\text{mm.}$	13.97g. $n_D^{25}$ 1.5655

<u>Experiment 139</u>	Nitration method D.
Boiling Range $136-8^{\circ}/10\text{mm.}$	14.12g. $n_D^{25}$ 1.5653

Table 6.11

Nitration of Anisole with HNO<sub>3</sub>/Ac<sub>2</sub>O at -20±5°C.

Expt. No.	Nitration Method	Reaction Time (min.)	Yield of Mononitro-anisoles %
130	A	25	93.80
131	B	25	93.46
132	A	25	95.21
133	B	25	95.08
134	C	4.5	94.91
135	D	4.5	94.91
138	C	164 sec.	91.24
139	D	187 sec.	92.21

General Method 2.

70%w/w Nitric acid (36.0g., 0.40mole) was added to acetic anhydride (280g.) and anisole (21.62g., 0.20mole) was then added. The total reaction time was 5 Minutes at -20±5°.

The reaction mixture was finally added to 1 litre of ice-water, and allowed to stand with occasional stirring until the acetic anhydride had completely hydrolysed. The products were then extracted with ether (2×100ml., + 6×50ml.), the ethereal extract washed with water (2×100ml.), with 5% sodium bicarbonate solution and finally with water (3×50ml.). The aqueous washings were extracted with ether (4×50ml.) and the ethereal solution washed with water (3×50ml.). The combined ethereal solutions were dried

over anhydrous sodium sulphate. The ether was removed through the glass-helices packed column and the residue fractionated under reduced pressure through the Vigreux column.

In experiment 147, the reaction mixture was added to a well cooled solution of sodium hydroxide (280g.) in water (1 l.) and the products worked up as described above except that the washings with sodium bicarbonate solution were omitted.

#### Nitration Procedure.

E. The nitric acid was added rapidly to the vigorously stirred acetic anhydride, the temperature being maintained at 20 to 25° (cooling bath temperature -30°). The nitric acid was added in 3 minutes. The nitrating solution was then cooled to -20±5° and the anisole immediately added, the temperature being maintained at -20° (cooling bath temperature -70°). The anisole was added in 2.75 minutes and the total reaction time was 5 minutes.

F. The nitric acid was added rapidly to the vigorously stirred acetic anhydride, the temperature being maintained at -20±5° (cooling bath temperature -70°). The nitric acid was added in 2.75 minutes. The anisole was immediately added, the temperature being maintained at -20° (cooling bath temperature -70°). The anisole was added in 2 minutes and the total reaction time was 5 minutes.

Results.

Experiment 143 Nitration method E.  
Boiling Range 122-7°/5.0mm. 29.64g.  $n_D^{25}$  1.5655

Experiment 145 Nitration method C.  
Boiling Range 123-4°/5.0mm. 29.68g.  $n_D^{25}$  1.5655

Experiment 146 Nitration method D.  
Boiling Range 125°/5.0mm 29.38g.  $n_D^{25}$  1.5664

Experiment 144 Nitration method F.  
Boiling Range Wt. (g.)  $n_D^{25}$  Composition  
63 - 65 30±1.0mm. 15.51 1.5145 anisole  
40 - 41 5.0±0.5mm. 0.41 1.5103 anisole  
118 - 125 4.20 1.5624 mononitroanisoles

Experiment 147 Nitration method F.  
57 - 60 16.24 1.5148  
25±1.0mm. 60 - 65 0.24 1.5149 anisole  
123 - 125 5.0±0.5mm. 3.89 1.5643 mononitroanisoles

Table 6.12

Nitration of Anisole with HNO<sub>3</sub>/Ac<sub>2</sub>O at -20±5°C.

Expt. No.	Nitration Method	Recovered Anisole %	Mononitro-anisoles %
143	E	-	96.81
144	F	73.58	13.72
145	C	-	96.94
146	D	-	95.96
147	F	76.23	12.71

Nitration of Toluene with Nitric Acid in  
Acetic Anhydride.

Nitration Method.

Nitric acid, 70%w/w (18.0g., 0.20mole) was added dropwise to a well stirred solution of acetic anhydride (140g.), the temperature being maintained at 20 to 25°. The nitrating solution was then cooled to  $-20 \pm 5^\circ$  and maintained at this temperature for 30 min. before commencing the nitration. Toluene (9.21g., 0.10mole) was then added dropwise at such a rate so as to maintain the temperature at  $-20 \pm 5^\circ$ . The reaction mixture was maintained at this temperature for the requisite length of time (inclusive of the time of addition of the toluene), and then worked up by the standard procedure. In experiment 115 the nitric acid was added to the acetic anhydride at  $-20 \pm 5^\circ$ .

Nitration Medium:-



Results.

<u>Experiment 116</u>			Reaction time 15 min.
Boiling Range °C/10±0.5mm	Wt. (g.)	$n_D^{20}$	Composition
95 - 108	4.70	1.5452	nitrotoluenes
108 - 176	2.94	1.5667	p-nitrotoluene + benzyl benzoate
<u>Experiment 103</u>			Reaction time 45 min.
96 - 109	11.54	1.5455	nitrotoluenes
109 - 130	0.31	semi-solid	

<u>Experiment 103</u>		Reaction time 15 min.	
Boiling Range °C/10±0.5mm.	Wt. (g.)	$n_D^{20}$	Composition
95 - 107	8.94	1.5452	nitrotoluenes
107 - 177	4.43	1.5650	p-nitrotoluene + benzyl benzoate

Table 6.13

Nitration of Toluene with HNO<sub>3</sub>/Ac<sub>2</sub>O at -20±5°C.

Expt. No.	Reaction Time	% Nitrotoluenes.
116	15 min.	37.5
103	45 min.	86.4
115	15 min.	73.4

Nitration of Toluene with Nitryl Chloride in  
Carbon Tetrachloride.

Nitryl chloride (26.7g., 0.35mole) was added dropwise to a vigorously stirred solution of toluene (18.42g., 0.20mole) in dry carbon tetrachloride at -25±5°. The reaction mixture was maintained at -25° for 3 hr., and then allowed to warm up to room temperature. Sodium bicarbonate was then added until no further reaction occurred, and the solution washed with water until neutral and dried over anhydrous sodium sulphate. The solvent was removed through the glass-helices packed column and the residue fractionated under vacuum through the Vigreux column using benzyl benzoate as chaser.

Result.

Boiling Range °C/10±0.5mm.	Wt. (g.)	<u>Experiment 109</u>		Composition
		<sup>20</sup> n <sub>D</sub>		
47 - 100	0.50	1.5236	chlorotoluenes + nitrotoluenes	
100 - 180	0.74	1.5485	nitrotoluenes + benzyl benzoate	

The factions were identified by infrared analysis.

Products.

Chlorotoluenes = 2%

Nitrotoluenes = 3%

Nitration of Toluene with Silver Tetrafluoroborate  
and Nitryl Chloride at -25°C.

Silver tetrafluoroborate solution (95.8ml., 0.10mole AgBF<sub>4</sub>) was added slowly to a solution of toluene (10.13g., 0.11mole) in dry carbon tetrachloride (200ml.) at -25°. Nitryl chloride (8.15g., 0.10mole) was then added dropwise to the vigorously stirred solution, the temperature being maintained at -25°. The reaction mixture was maintained at -25° for 5 hr., and then allowed to warm up to room temperature. The reaction mixture was filtered through a scintered glass funnel and the precipitate (silver chloride) was washed with ether. Sodium bicarbonate was added to the reaction solution and when no further reaction occurred the solution was washed with water until neutral,

and finally dried over anhydrous sodium sulphate. The solvent was removed through the glass-helices packed column and the residue fractionated, under vacuum, through the Vigreux column using benzyl benzoate as chaser.

Result.

<u>Experiment 114</u>			
Boiling Range °C/20*1mm.	Wt. (g.)	$n_D^{20}$	Composition
53 - 105	2.12	1.5179	p-chlorotoluene
105 - 135	8.32	1.5445	nitrotoluenes
135 - 194	3.76	1.5638	p-nitrotoluene + benzyl benzoate

Products.

% Chlorotoluenes - 15.2  
% Nitrotoluenes - 71.1

## CHAPTER 7.

### Reaction of Benzyltrimethylsilanes with Nitrating Agents.

#### 1. Reaction with Nitric Acid in Acetic Acid/Acetic Anhydride.

##### General.

The method of nitration was varied and will be described separately for each experiment. The procedure for isolating the products was the same for all the experiments and is described below.

The reaction mixture was cooled, when necessary, added to 500ml. of ice-water and allowed to stand, with occasional stirring, until the acetic anhydride had completely hydrolysed (usually overnight). The products were then extracted with ether (500ml.). The ethereal extract was washed with water (2x50ml.), 5% sodium bicarbonate solution until no longer acid, and finally with water (4x50ml.). The aqueous washings were extracted with ether (3x50ml.), this ethereal extract washed with water (2x50ml.), and the combined ethereal solutions dried over anhydrous sodium sulphate. The ether was removed through the glass-helices packed column and the residue fractionated through the Vigreux column. The products were identified by boiling point and refractive index measurements and by their infrared spectra.

Benzyltrimethylsilane

Experiment 1

Temperature 100±5°C

70%w/w Nitric acid (18.0g., 0.20mole) was added dropwise to acetic anhydride (50g.), the temperature being maintained at 20-25°. This nitrating solution was then added dropwise to a vigorously stirred solution of benzyltrimethylsilane (16.43g., 0.10mole) in acetic anhydride (90g.), the temperature being maintained at 100°. The reaction mixture was maintained at 100° for 2 hr., and the products isolated.

Result.

Boiling Range °C/10±0.5mm.	Wt. (g.)	<sup>25</sup> n <sub>D</sub>	Composition
59 - 81	0.36	1.5037	benzyltrimethylsilane + nitrotoluenes
81 - 95	1.01	semi-solid	} nitrotoluenes
95 - 105	1.35	semi-solid	
105 - 123	1.06	1.5235	} nitro-benzyltrimethyl- silanes
123 - 126	1.06	1.5249	
126 - 150	10.26	1.5258	
150 - 165	0.47	1.5259	

Residue - 4.4g.

Nitrotoluenes 17.2%

o-, and p-Nitrobenzyltrimethylsilanes 61.3%

Experiment 2

Temperature 50±2.5°C

70%w/w Nitric acid (18.0g., 0.20mole) was added

dropwise to acetic anhydride (140g.), the temperature being maintained at 20-25°. The nitrating solution was then heated to 50°. Benzyltrimethylsilane (16.43g., 0.10mole) was then added dropwise, the temperature being maintained at 50°. The reaction mixture was heated at 50° for 3 hr., and the products isolated.

Result.

Boiling Range °C/10±0.5mm.	Wt. (g.)	$n_D^{25}$	Composition
85 - 121	2.44	1.5195	benzyltrimethylsilane + nitrobenzyltrimethyl- silanes
121 - 129	8.45	1.5262	
129 - 152	5.94	1.5330	nitrobenzyltrimethyl- silanes
152 - 158	1.77	1.5397	

Residue - 2.6g.

o-, and p-Nitrobenzyltrimethylsilanes - 87.2%

Benzyltrimethylsilane + p-Tolyltrimethylsilane

Experiment 3

Temperature 100±5°

70%w/w Nitric acid (18.0g., 0.20mole) was added dropwise to acetic anhydride (50g.), the temperature being maintained at 20-25°. The nitrating solution was then added dropwise to a vigorously stirred solution of benzyltrimethylsilane (8.22g., 0.05mole) and p-tolyltrimethylsilane (8.22g., 0.05mole) in acetic anhydride (90g.), the temperature being maintained at 100°. The reaction mixture was maintained at 100° for 2 hr., and the products isolated.

Result.

Boiling Range °C/10±0.5mm.	Wt. (g.)	<sup>25</sup> n <sub>D</sub>	Composition
55 - 85	1.42	1.4910	benzyltrimethylsilane + p-tolyltrimethylsilane
85 - 100	7.84	1.5378	p-nitrotoluene + nitrosilane
100 - 125	4.17	1.5232	nitrosilane

Residue - 3.8g.

Yield of nitro-products is approximately 75%

p-Trimethylsilylbenzyltrimethylsilane

Experiment 4

Temperature 50±2.5°

70%w/w Nitric acid (18.0g., 0.20mole) was added dropwise to acetic anhydride (140g.), the temperature being maintained at 20-25°. The nitrating solution was then heated to 50°. p-Trimethylsilylbenzyltrimethylsilane (23.65g., 0.10mole) was then added dropwise, the temperature being maintained at 50°. The reaction mixture was heated at 50° for 2.5 hr., and the products isolated. A considerable amount of tar was formed which could not be analysed.

Result.

Fraction	Boiling Range °C/10±0.5mm.	<sup>25</sup> n <sub>D</sub>	Wt. (g.)
A	81 - 101	1.5048	0.53
B	101 - 128	solid	0.71
C	128 - 136	solid	3.05
D	136 - 146	solid	0.54

Fractions B and C:- identified as p-nitrobenzaldehyde.

After charcoaling and repeated recrystallisation from acetone/petroleum spirit (60-80°) a sample was obtained with m. p. 104.5-105°. Infrared examination showed the presence of a -CHO group (5.85 $\mu$ ). A mixed melting point with pure p-nitrobenzaldehyde (m. p. 106°) was not depressed. Fraction D:- identified as p-nitrobenzoic acid.

After charcoaling and repeated recrystallisation from acetone/petroleum spirit (60-80°) a sample was obtained with m. p. 239-40°. A mixed melting point with pure p-nitrobenzoic acid (m. p. 239-40°) was not depressed.

m-Trimethylsilylbenzyltrimethylsilane

Experiment 5

Temperature 100 $\pm$ 5°

70%w/w Nitric acid (13.5g., 0.15mole) was added dropwise to acetic anhydride (50g.), the temperature being maintained at 20-25°. The nitrating solution was then added dropwise to a vigorously stirred solution of the m-trimethylsilylbenzyltrimethylsilane (17.74g., 0.075mole) in acetic anhydride (90g.), the temperature being maintained at 100°. The reaction mixture was maintained at 100° for 3 hr., and the products isolated.

Result.

Fractionation at 10 $\pm$ 0.5mm. gave 13.1g. product  
boiling range 113 - 159°  $n_D^{25}$  1.5082 - 1.5230

On refractionation no pure fraction could be obtained. The products probably consist of a mixture of m-nitro-

benzyltrimethylsilane and the nitro-isomers of m-trimethylsilylbenzyltrimethylsilane.

p-Methylbenzyltrimethylsilane

Experiment 6

Temperature 50±2.5°

70%w/w Nitric acid (18.0g., 0.20mole) was added dropwise to acetic anhydride (140g.), the temperature being maintained at 20-25°. The nitrating solution was then heated to 50°. p-Methylbenzyltrimethylsilane (17.83g., 0.10mole) was then added dropwise, the temperature being maintained at 50°. The reaction mixture was heated at 50° for 8 hr., and the products isolated.

Result.

Boiling Range °C/5.0±0.5mm.	Wt. (g.)	<sup>25</sup> n <sub>D</sub>	Composition
87 - 110	3.6	1.5176	p-methylbenzyltrimethylsilane + nitrosilane
110 - 120	4.0	1.5260	} nitrosilane
120 - 126	7.5	1.5262	
126 - 130	1.0	1.5263	

Residue - 3.9g.

Yield of nitrated p-methylbenzyltrimethylsilane - 82.5%

p-Chlorobenzyltrimethylsilane

Experiment 7

Temperature 50±2.5°

70%w/w Nitric acid (18.0g., 0.20mole) was added dropwise to acetic anhydride (140g.), the temperature being maintained at 20-25°. The nitrating solution was then

heated to 50°. p-Chlorobenzyltrimethylsilane (19.88g., 0.10mole) was then added dropwise, the temperature being maintained at 50°. The reaction mixture was heated for 3 hr., and the products isolated.

Result.

Boiling Range °C.	Wt. (g.)	$n_D^{25}$	Composition
57- 82    2.0mm	2.8	1.5298	<u>p</u> -chlorobenzyltrimethylsilane + nitrosilane
70- 95 } 95-105 }	6.7 6.1	1.5406 1.5432	} nitrosilane
Residue - 4.2g.			

Yield of nitrated p-chlorobenzyltrimethylsilane - 72.5%

Reaction of Benzyltrimethylsilane with  
Acetic acid/Acetic anhydride.

Experiment 8

Benzyltrimethylsilane (16.48g., 0.10mole) was added to a solution of acetic acid (70g.) and acetic anhydride (70g.) and refluxed for 3 hr. Isolation of the products by the standard method gave, on fractionation, benzyltrimethylsilane (89.5%).

Reaction of p-Trimethylsilylbenzyltrimethylsilane  
with Acetyl Nitrate in Acetonitrile.

Experiment 9.

Silver nitrate (42.5g., 0.25mole) was dissolved in purified acetonitrile (120ml.), and cooled to 0°. Acetyl chloride (18.8g., 0.24mole) was added dropwise to the

vigorously stirred solution, the temperature being maintained below 10°. The solution was stirred for 30 min., and then filtered through a scintered glass funnel. The silver chloride residue was washed with acetonitrile (50ml.) and the clear filtrate transferred to the reaction vessel and warmed to 25°. p-Trimethylsilylbenzyltrimethylsilane (17.74g. 0.075mole) was added dropwise to the vigorously stirred acetyl nitrate solution, the temperature being maintained at 20-25°. The reaction mixture was heated at 20-25° for 22hr., and then added to ether (400ml.). The ethereal solution was washed with 5% sodium bicarbonate solution (3x100ml.), with water (3x100ml.), and finally dried over anhydrous sodium sulphate. The ether was removed through the packed column, and the residue was then filtered through a scintered-glass funnel to give a precipitate (I), and a filtrate which was fractionated through the Vigreux column.

Result.

Fraction	Boiling Range °C/10±0.5mm.	$n_D^{25}$	Wt. (g.)
A	110 - 130	1.5054	0.44
B	130 - 139	solid	0.73
C	139 - 151	solid	1.70
D	151 - 152	solid	0.63
E	152 - 159	semi-solid	2.23
F	159 - 162	semi-solid	4.12

Residue - 3.5g.

Precipitate I:- identified as p-nitrobenzoic acid.

After charcoaling, and recrystallisation from acetone/  
petroleum spirit (60-80) a compound was obtained (2.1g.)  
with m.p. 239-41°. A mixed melting point with pure  
p-nitrobenzoic acid (m.p. 239-40) was not depressed.

Fractions B, C, and D:- identified as p-nitrobenzaldehyde.

Charcoaling and recrystallisation from acetone/  
petroleum spirit (60-80) gave a sample (1.1g.) with  
m.p. 103-5°. Infrared examination showed the presence of  
a -CHO group (5.85 $\mu$ ) and a mixed melting point with pure  
p-nitrobenzaldehyde (m.p. 106) was not depressed.

Fractions E, and F:- these fraction were not identified  
as no pure product could be isolated.

## CHAPTER 8

### Nitrodesilylation - The Preparation of Nitro-aryl

#### Silicon Compounds.

#### The Nitrodesilylation of 4,4'-Bistrimethylsilylbiphenyl.

70%w/w Nitric acid (18.0g., 0.20mole) was added dropwise to acetic anhydride (60g.), the temperature being maintained at 20-25°. This nitrating solution was then added dropwise to a solution of 4,4'-bistrimethylsilylbiphenyl (10.8g., 0.037mole) in acetic anhydride (80g.), the temperature being maintained at 100°. The reaction mixture was maintained at 100° for 1.5 hr., cooled, and added to a cooled solution of sodium hydroxide (140g.) in water (500ml.) and the products extracted by the standard procedure described on page 112. The ether was removed through the glass-helices packed column and the residue, chromatographed on an alumina column to give two products I and II.

I. Recrystallisation from petroleum spirit (60-80) gave 4-nitro-4'-trimethylsilylbiphenyl in 28.5% yield (2.8g.). m.p. 116-116.5° (Found: C, 66.60; H, 6.34; N, 5.78.  $C_{18}H_{17}NSi$  requires C, 66.40; H, 6.32; N, 5.16%).

II. Recrystallisation from ethanol gave a product (0.2g.) with m.p. 233-4°. A mixed melting point with 4,4'-dinitro-biphenyl (m.p. 237°) showed no depression.

#### Nitrodesilylation of 3,3'-Bistrimethylsilylbiphenyl.

70%w/w Nitric acid (9.0g., 0.10mole) was added dropwise to acetic anhydride (25g.) the temperature being maintained at 20-25°. This nitrating solution was then added dropwise to a solution of 3,3'-bistrimethylsilylbiphenyl (13.9g., 0.047mole) in acetic anhydride (45g.) the temperature being maintained at 100°. The reaction mixture was maintained at 100° for 2 hr., cooled, and added to a cooled solution of sodium hydroxide (70g.) in water (300ml.) and the products extracted by the standard procedure. On fractionation 28% (3.9g.) of unreacted 3,3'-bistrimethylsilylbiphenyl was recovered. The other fractions were combined and chromatographed on an alumina column, but no pure product could be isolated.

#### Preparation of 4- $[\text{}^3\text{H}_1]$ -4'-nitrobiphenyl.

70%w/w Nitric acid (6.75g., 0.075mole) was added dropwise to acetic anhydride (25g.) the temperature being maintained at 20-25°. This nitrating solution was then added dropwise to a solution of 4- $[\text{}^3\text{H}_1]$ -4'-trimethylsilylbiphenyl (7.3g., 0.032mole) in acetic anhydride (45g.) the temperature being maintained at 100°. The reaction mixture was maintained at 100° for 2 hr., cooled, and added to a cooled solution of sodium hydroxide (70g.) in water (300ml.) and the products extracted by the standard procedure. Fractionation through the Vigreux column gave

crude 4- $[\text{}^3\text{H}_1]$ -4'-nitrobiphenyl in 78.1% yield (5.0g.).  
 Recrystallisation from alcohol gave m.p. 113.5-114.5°.  
 Little activity was lost during the nitrodesilylation.  
 Lit.<sup>27</sup> 4-nitrobiphenyl m.p. 114.0-114.5°.

Nitrodesilylation of p-Methoxyphenyltrimethylsilane.

70% Nitric acid (18.0g., 0.20mole) was added dropwise to acetic anhydride (140g.), the temperature being maintained at 20-25°. The nitrating solution was warmed, or cooled, to the required temperature and p-methoxyphenyltrimethylsilane (18.04g., 0.10mole) added dropwise, the temperature being maintained at that required. The reaction mixture was then kept 15 min. at 25° (experiment 140), or 40 min. at -20° (experiment 141) before addition to a cooled solution of sodium hydroxide (140g.) in water (500ml.). The products were then extracted by the standard procedure (page 112) and fractionated.

Results.

Boiling Range °C/5.0±0.5mm.	Experiment 140		Composition
	Wt. (g.)	$n_D^{25}$ or M. Pt.	
125	0.47	48-53	p-nitroanisole
125	9.32	50-53.5	
125 - 130	2.57	49-53	
130 - 152	2.64	1.5436	p-nitroanisole + nitrosilane
Residue - 1.4g.			

<u>Experiment 141</u>				
Boiling Range °C/5.0±0.5mm.	Wt. (g.)	$n_D^{25}$	or M. Pt.	Composition
125	10.34	50 - 53.5		p-nitroanisole
125 - 156	4.62	1.5521		p-nitroanisole + nitrosilane

Residue - 2.7g.

Experiment No.	140	141
% p-Nitroanisole	85.2	82.6
% Nitrosilane	8.7	10.3
Yield of Reaction	93.9	92.9

Purification of the Combined Nitrosilane Fractions  
obtained in Experiments 140-1.

Fractionation through the Vigreux column gave a sample of nitrosilane b.p. 153°/5.0±0.5mm.,  $n_D^{25}$  1.5343 m.p. 43.5° (petroleum spirit). (Found: C, 53.40; H, 7.14; N, 6.10.  $C_{10}H_{15}NO_3Si$  requires C, 53.30; H, 7.01; N, 6.22%). The compound was assumed to be 4-methoxy-3-nitro-phenyl-trimethylsilane on consideration of the very much greater reactivity of the 3-position to the 2-position in p-methoxy-phenyltrimethylsilane.

Nitrodesilylation of m-Methoxyphenyltrimethylsilane.

70%w/w Nitric acid (18.0g., 0.20mole) was added dropwise to acetic anhydride (70g.) the temperature being maintained at 20-25°. This nitrating solution was then

added to a solution of m-methoxyphenyltrimethylsilane (18.04g., 0.10mole) in acetic anhydride (70g.) at the required temperature. The reaction mixture was then kept at 100±5° for 3 hr. (experiment 137), or at 135-40° for 1.5 hr. (experiment 142), before addition to a cooled solution of sodium hydroxide (140g.) in water (500ml.). The products were then extracted by the standard procedure (page 112) and fractionated.

Results.

<u>Experiment 137</u>			
Boiling Range °C/5.0±0.5mm.	Wt. (g.)	$n_D^{25}$	Composition
113 - 139	0.93	1.5465	<u>m</u> -nitroanisole + nitrosilane
139 - 141	1.07	1.5356	} nitrosilane
141 - 154	16.63	1.5350	
Residue - 1.9g.			

<u>Experiment 142</u>			
Boiling Range °C/5.0±0.5mm.	Wt. (g.)	$n_D^{25}$	Composition
80 - 84	3.26	1.4995	<u>m</u> -methoxyphenyl- trimethylsilane.
106 - 139	1.59	1.5429	<u>m</u> -nitroanisole + nitrosilane
139 - 154	10.18	1.5354	nitrosilane
Residue - 2.2g.			

Experiment No.	137	142
% <u>m</u> -Methoxyphenyltrimethylsilane (recovered)	-	18.1
% <u>m</u> -Nitroanisole	2.1	2.5
% Nitrosilane	81.3	50.6
Yield of Reaction	83.4	71.2

SECTION 3

A DISCUSSION OF EXPERIMENTAL RESULTS

CHAPTER 9

Synthetic Methods.

New Organic Intermediates.

Compound	Boiling Point °C	<sup>25</sup> n <sub>D</sub>
4-( <u>p</u> -Chlorophenyl)-but-1-ene	92-3°/9-10mm.	1.5239
4-( <u>m</u> -Chlorophenyl)-but-1-ene	93-4°/10±0.5mm.	1.5240
4-( <u>o</u> -Chlorophenyl)-but-1-ene	86-8°/10±0.5mm.	1.5253
3-( <u>p</u> -Chlorophenyl)-propan-1-ol	113-4°/1.5±0.2mm.	1.5404
3-( <u>m</u> -Chlorophenyl)-propan-1-ol	106-7°/1.0±0.2mm.	1.5412
3-( <u>o</u> -Chlorophenyl)-propan-1-ol*	104-7°/1.5±0.5mm.	1.5420
3-( <u>p</u> -Chlorophenyl)-1-iodopropane	95-7°/0.2-0.4mm.	1.5915
3-( <u>m</u> -Chlorophenyl)-1-iodopropane	102-5°/0.5±0.1mm.	1.5924
3-( <u>o</u> -Chlorophenyl)-1-iodopropane	99-101°/0.5±0.1mm.	1.5935
2-( <u>m</u> -Chlorophenyl)-ethan-1-ol	92-5°/1.0±0.2mm.	1.5489
2-( <u>p</u> -Chlorophenyl)-ethyl iodide	91-4°/0.6-0.7mm.	1.6093
2-( <u>m</u> -Chlorophenyl)-ethyl iodide	105-6°/1.0±0.1mm.	1.6084

Note:- compounds marked \* have been prepared before, but different physical properties were quoted.

New Organo-silicon Compounds.

Compound	Boiling Point °C	<sup>25</sup> n <sub>D</sub>
4-( <u>p</u> -Chlorophenyl)-butyl-trichlorosilane	140-2°/2.0±0.5mm.	1.5228
4-( <u>m</u> -Chlorophenyl)-butyl-trichlorosilane	129-31°/1.0±0.2mm.	1.5230
4-( <u>o</u> -Chlorophenyl)-butyl-trichlorosilane	119-21°/1.0±0.2mm.	1.5236

Compound	Boiling Point °C	<sup>25</sup> n <sub>D</sub>
1-( <u>p</u> -Chlorophenyl)-1-trichlorosilyl-n-butane	122-7°/2.5±0.5mm.	1.5291
1-( <u>m</u> -Chlorophenyl)-1-trichlorosilyl-n-butane	128-30°/5.0±0.5mm.	1.5286
4-( <u>p</u> -Chlorophenyl)-butyltrimethylsilane	113-5°/2.0-2.5mm.	1.4957
4-( <u>m</u> -Chlorophenyl)-butyltrimethylsilane	128-30°/5.0±0.5mm.	1.4949
4-( <u>o</u> -Chlorophenyl)-butyltrimethylsilane	124-6°/5.0±0.5mm.	1.4963
1-( <u>p</u> -Chlorophenyl)-1-trimethylsilyl-n-butane	114-5°/5.0±0.5mm.	1.5074
1-( <u>m</u> -Chlorophenyl)-1-trimethylsilyl-n-butane	111-2°/5.0±0.5mm.	1.5070
4-( <u>p</u> -Trimethylsilylphenyl)-butyltrimethylsilane	144-6°/5.0±0.5mm.	1.4837
4-( <u>m</u> -Trimethylsilylphenyl)-butyltrimethylsilane	138-9°/5.0±0.5mm.	1.4823
4-( <u>o</u> -Trimethylsilylphenyl)-butyltrimethylsilane	140-2°/5.0±0.5mm.	1.4897
1-( <u>p</u> -Trimethylsilylphenyl)-1-trimethylsilyl-n-butane	128-9°/5.0±0.5mm.	1.4921
1-( <u>m</u> -Trimethylsilylphenyl)-1-trimethylsilyl-n-butane	119-21°/5.0±0.5mm.	1.4862
3-( <u>p</u> -Chlorophenyl)-propyltrimethylsilane	117-8°/5.0±0.5mm.	1.4978
3-( <u>m</u> -Chlorophenyl)-propyltrimethylsilane	114-7°/5.0±0.5mm.	1.4982
3-( <u>o</u> -Chlorophenyl)-propyltrimethylsilane	111-4°/5.0±0.5mm.	1.4998
3-( <u>p</u> -Trimethylsilylphenyl)-propyltrimethylsilane	133°/5.0±0.5mm.	1.4852

Compound	Boiling Range °C	<sup>25</sup> n <sub>D</sub>
3-( <u>m</u> -Trimethylsilylphenyl)-propyltrimethylsilane	127°/5.0±0.5mm.	1.4832
3-( <u>o</u> -Trimethylsilylphenyl)-propyltrimethylsilane	129-30°/5.0±0.5mm.	1.4912
2-( <u>o</u> -Chlorophenyl)-ethyl-trichlorosilane	87-9°/1.0±0.2mm	1.5281
2-( <u>p</u> -Chlorophenyl)-ethyl-trimethylsilane	104-5°/5.0±0.5mm.	1.4998
2-( <u>m</u> -Chlorophenyl)-ethyl-trimethylsilane	105-6°/5.0±0.5mm.	1.4998
2-( <u>p</u> -Chlorophenyl)-ethyl-trimethylsilane	99-100°/5.0±0.5mm.	1.5005
2-( <u>p</u> -Trimethylsilylphenyl)-ethyltrimethylsilane*	120-2°/5.0±0.5mm.	1.4850
2-( <u>m</u> -Trimethylsilylphenyl)-ethyltrimethylsilane	113-4°/5.0±0.5mm.	1.4843
2-( <u>o</u> -Trimethylsilylphenyl)-ethyltrimethylsilane	117-8°/5.0±0.5mm.	1.4912
2-Chloro-2'-trimethylsilyl-biphenyl	142°/5.0±0.5mm.	1.5673
4-Nitro-4'-trimethylsilyl-biphenyl	m. p. 116-116.5°	
4-Methoxy-3-nitro-phenyl-trimethylsilane	153°/5.0±0.5mm.	1.5343
	m. p. 43.5°	

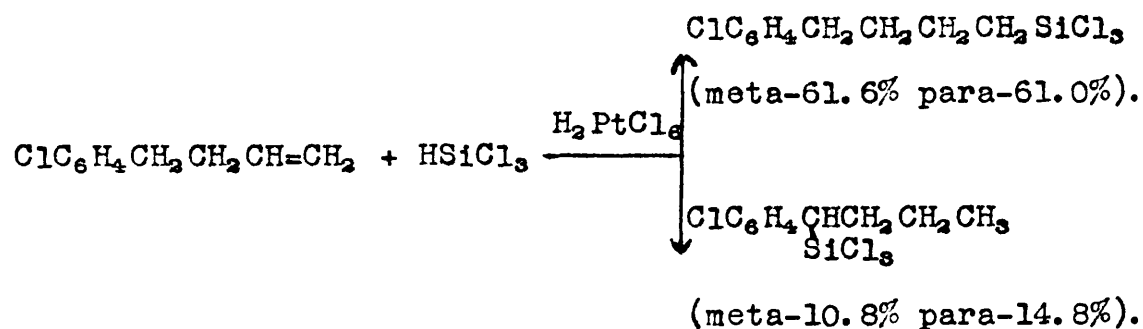
Note:- compounds marked \* have been prepared before, but different physical properties were quoted.

1. Synthesis of *o*-, *m*-, and *p*-Me<sub>3</sub>SiC<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>n</sub>SiMe<sub>3</sub>

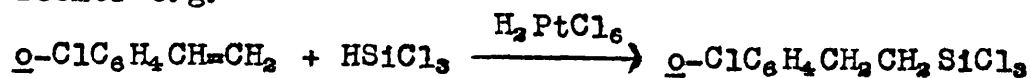
where n = 2 to 4.

A. The Addition of Trichlorosilane to Alkenylbenzenes.

Two pure products were isolated from the addition of trichlorosilane to 4-(*m*-, or *p*-chlorophenyl)-but-1-ene, using chloroplatinic acid as catalyst. These were shown to be the isomeric 4-(*m*-, or *p*-chlorophenyl)-butyltrichlorosilane and 1-(*m*-, or *p*-chlorophenyl)-1-trichlorosilyl-n-butane e.g. ,



In contrast to this, with 4-(*o*-chlorophenyl)-but-1-ene only one pure product could be isolated, namely the straight chain compound; a small amount of the branched chain isomer was probably formed (< 2%) but could not be isolated pure. In the addition of trichlorosilane to *o*-chlorostyrene only the straight chain isomer was formed, there being no indication of the formation of any branched chain isomer e.g.



The physical properties of the compounds obtained by the addition of trichlorosilane to the 4-(chlorophenyl)-but-1-ene are given in Table 9.1.

Table 9.1

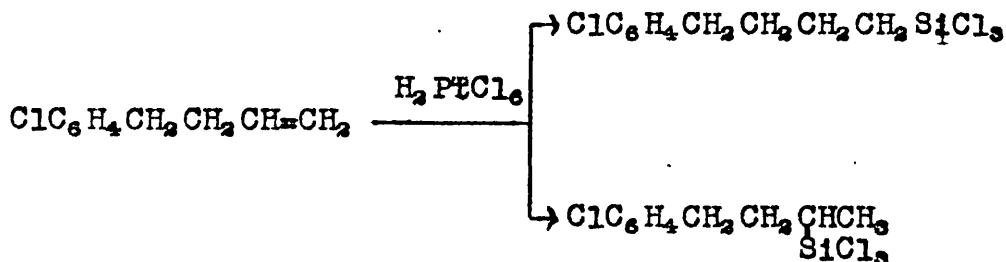
Physical Properties of the  $\text{ClC}_6\text{H}_4\text{C}_4\text{H}_8\text{SiCl}_3$

Compounds.

Isomer	$\text{ClC}_6\text{H}_4(\text{CH}_2)_4\text{SiCl}_3$		$\text{ClC}_6\text{H}_4\text{CH}(\text{SiCl}_3)\text{CH}_2\text{CH}_2\text{CH}_3$	
	<sup>25</sup> $n_D$	b. p.	<sup>25</sup> $n_D$	b. p.
ortho	1.5236	119-21°/1.0mm.	-	-
meta	1.5230	129-31°/1.0mm.	1.5286	128-30°/5.0mm.
para	1.5228	140-42°/2.0mm.	1.5291	122-27°/2.5mm.

The isomers with the lower boiling point and higher refractive index were assigned the branched chain formulae. This generalisation from organic chemistry has also been found to apply in organosilicon chemistry.<sup>256-7</sup>

The compounds were at first thought to be 4-(m-, or p-chlorophenyl)-butyltrichlorosilane and 4-(m- or p-chlorophenyl)-2-trichlorosilyl-n-butane resulting from Markovnikoff and anti-Markovnikoff addition, respectively, of the trichlorosilane e.g.



The fact that in the branched chain compounds the silyl groups had migrated to the  $\alpha$ -position, and that the straight chain structures assigned to the other isomers were correct was investigated by several different methods.

1). Alkali cleavage of the branched chain compounds.

If the branched chain compounds are benzyl type silicon compounds, then they should be cleaved by alkali. It was found, however, that although *p*-trimethylsilylbenzyl-trimethylsilane was completely cleaved by 2N sodium hydroxide solution after 72 hr. at 72°, the compounds in question were only partially cleaved, even after 220 hr. at 72°. That  $\alpha$ -substituted benzyl-silicon compounds might be less susceptible to alkali cleavage is to be expected because of the increased electron release to the silicon atom from the  $\alpha$ -substituted alkyl group.

An attempt to synthesise one such  $\alpha$ -substituted benzyl-silicon compound, by an unambiguous method, failed (this will be discussed later).

2). Comparison of Ultra-violet spectra.

An examination of the spectra of the compounds *o*-, *m*-, and *p*-Me<sub>3</sub>SiC<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>n</sub>SiMe<sub>3</sub> (where n = 1 to 4) together with those of the branched chain isomers (details are given on pages 85-92) reveal that:-

a). The values of  $\lambda_{\max}$  and  $\epsilon_{\max}$  for the para- compounds where n = 2 or 3 are very similar to those for the compound where n = 4, which had been assigned the straight chain structure. As the compounds where n = 2 or 3 were synthesised by unambiguous routes, the assignment of the straight chain structure to the compound where n = 4 would seem to be correct.

b). The spectra of the para-compound, where  $n = 4$ , which had been assigned the branched chain structure is entirely different from that of the other para isomers, other than where  $n = 1$ , to which it bears a striking similarity. This supports the suggestion that the silyl group is at the position  $\alpha$  to the ring, and not at the position  $\gamma$  as was originally supposed. The spectrum of the latter compound would be very similar to the straight chain compound where  $n = 3$ .

c). The same considerations apply for the meta-compounds.

d). The values of  $\lambda_{\max}$  and  $\epsilon_{\max}$  for the ortho-compound where  $n = 3$  are very similar to those for the compounds where  $n = 2$  or  $4$  which had been assigned the straight chain structures. As the compound where  $n = 3$  was synthesised by an unambiguous route, the assignment of the straight chain structures to the compounds where  $n = 2$  or  $4$ , would seem to be correct.

### 3). Comparison of Nuclear Magnetic Resonance Spectra.

The N.M.R. spectra were obtained at the Rice University, America by Professors' E. S. Lewis and C. Eaborn. The N.M.R. spectra of several compounds have been reproduced on pages 172-174.

The spectra of o-, and p- $\text{ClC}_6\text{H}_4\text{CH}_2\text{SiMe}_3$  are shown in figs. I and II. The large peak at 0 p.p.m. is due to the hydrogen atoms of the methyl groups attached to the silicon atom; these act as an internal standard. The peak

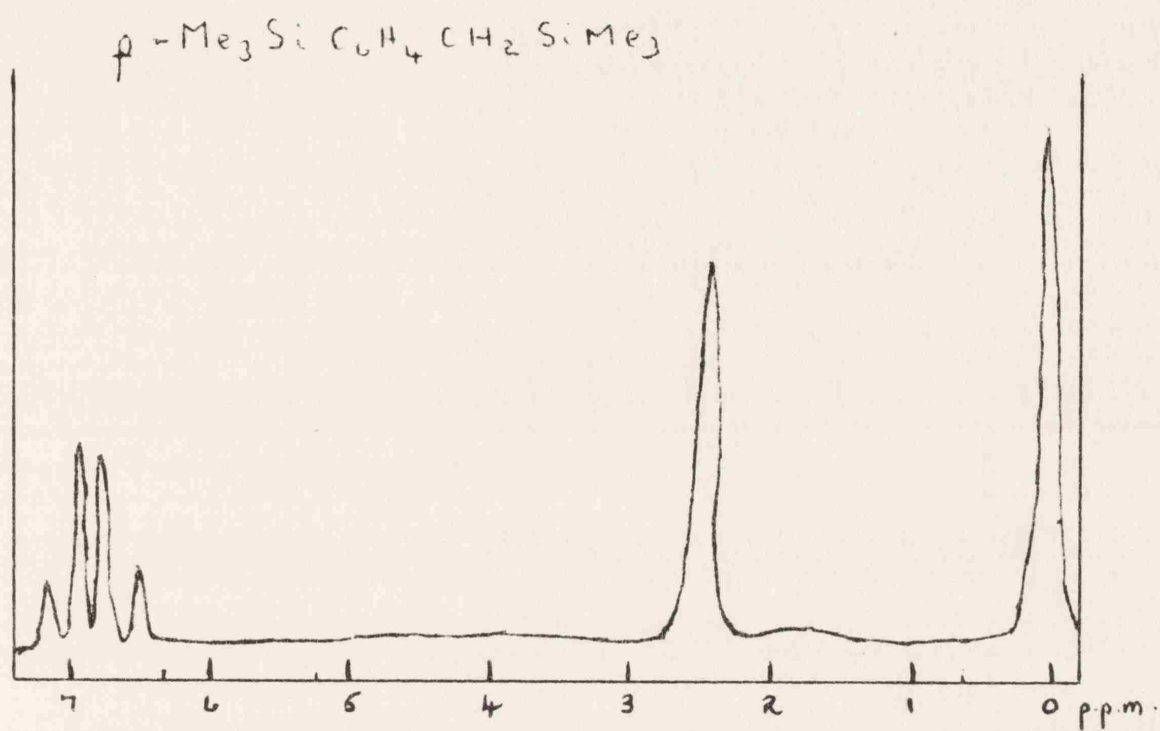


fig. I

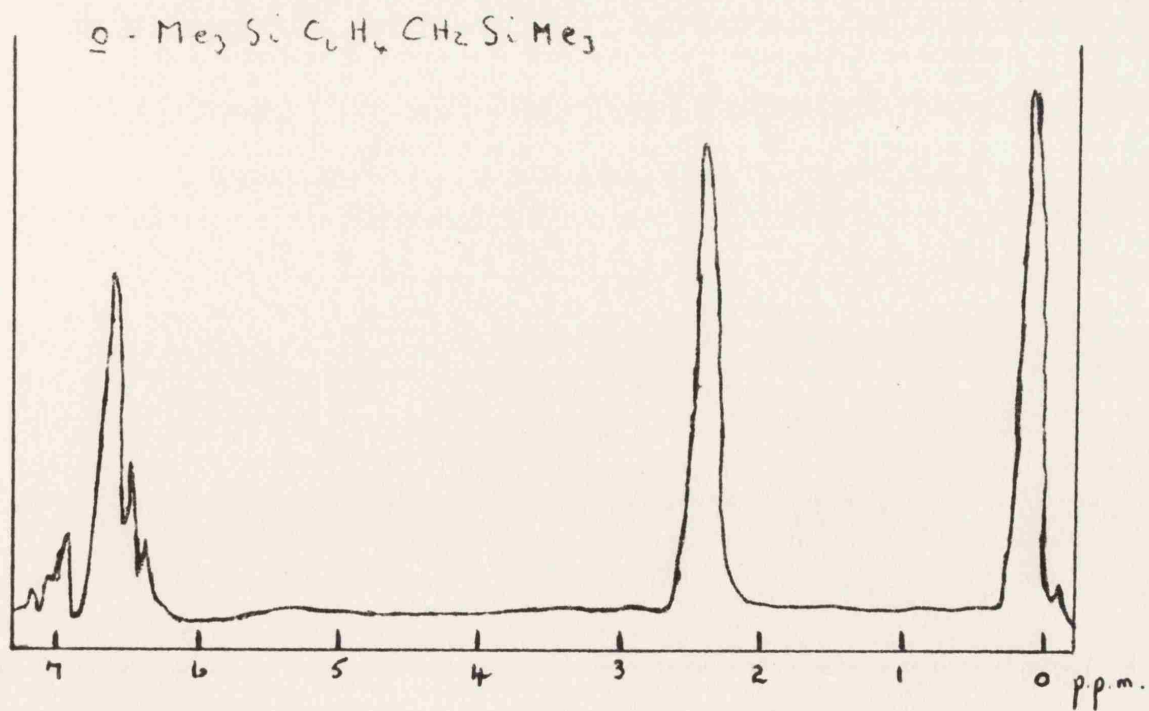


fig. II

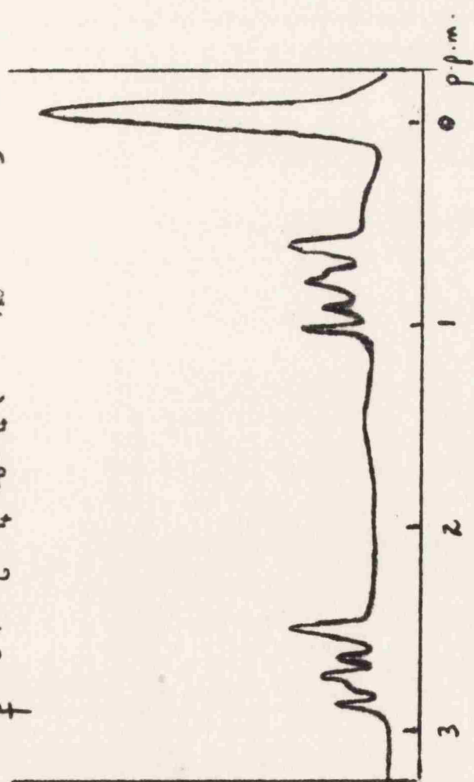


fig. III

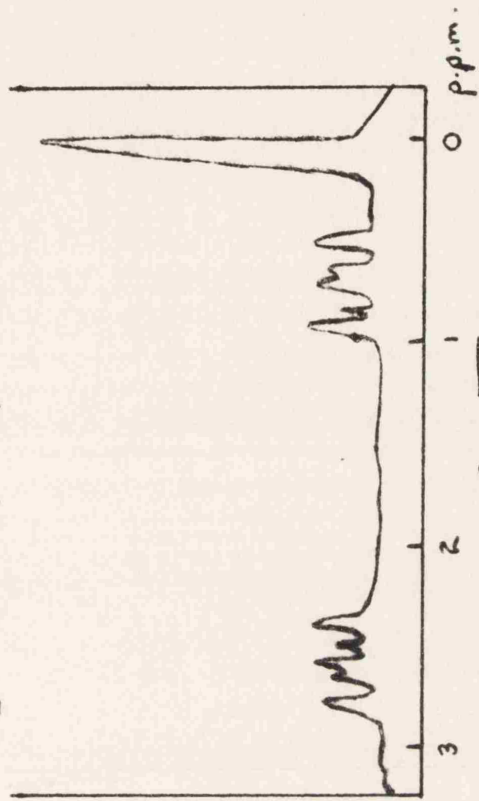
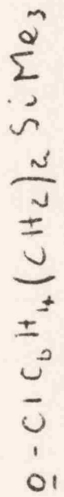


fig. IV

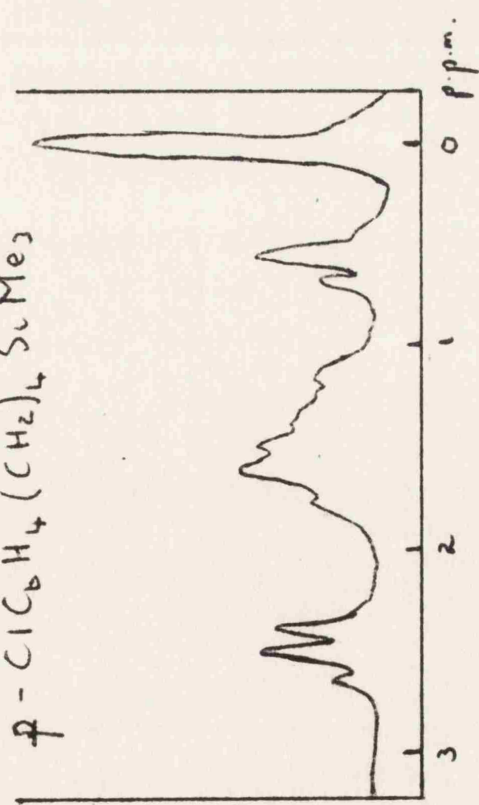


fig. V

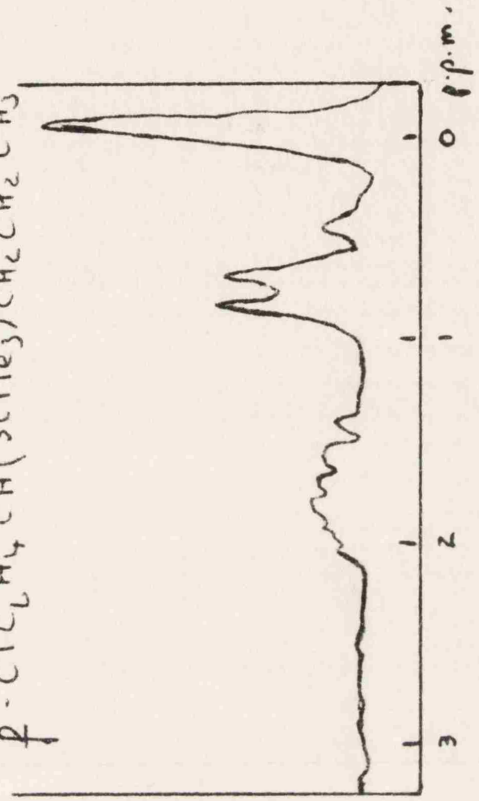
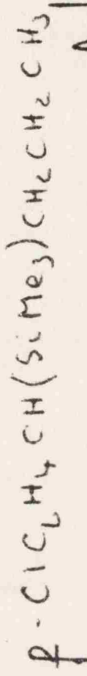
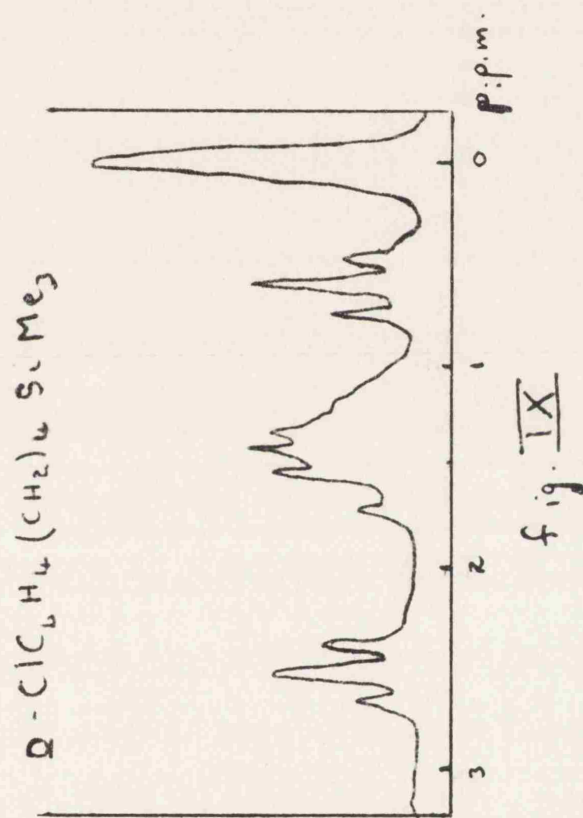
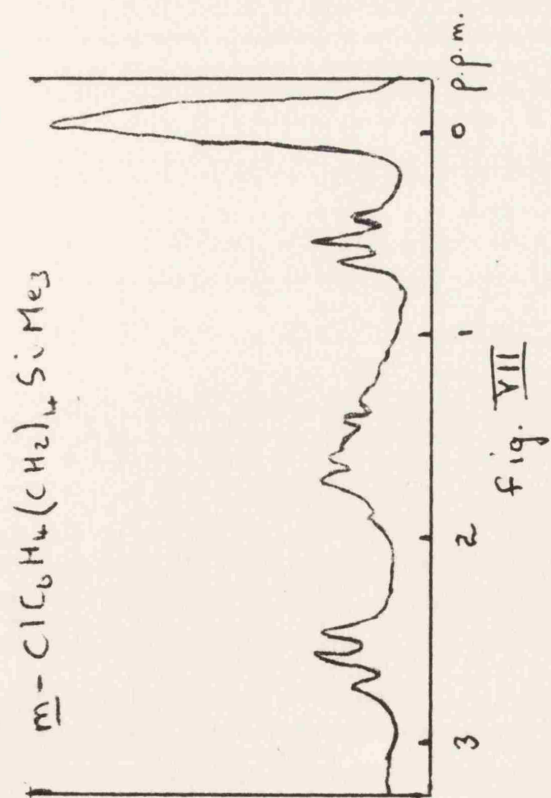
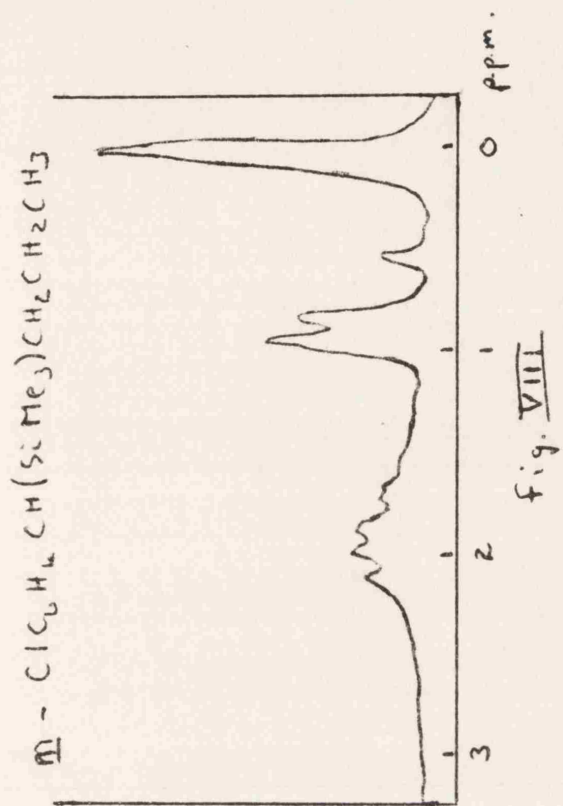


fig. VI



at 2.5 p.p.m. is due to the hydrogen atoms of the  $\text{CH}_2$  group, and the peaks at approximately 7 p.p.m. are caused by the hydrogen atoms of the aromatic ring. The pattern of peaks at 7 p.p.m. in fig. I is characteristic of a para-disubstituted benzene ring; there are two kinds of hydrogen atoms, each of which gives a doublet which are mirror images of each other.

The portion of the spectra, shown in figs. III and IV, for o-, and p- $\text{ClC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{SiMe}_3$  are identical. There are two sets of quintuplet peaks which are mirror images of each other. This is not as expected since two sets of triplets should have been obtained. Presumably the three centre peaks of the quintuplet represent a split of the single peak of the triplet. The same kind of effect was found in  $\text{PhCH}_2\text{CH}_2\text{Br}$ , and may mean that the two hydrogens on either carbon are not equivalent because of some conformational effect arising from restriction of rotation about the  $\text{CH}_2\text{-CH}_2$  bond. The phenyl group shifts the C-H vibrations to the left by almost the same amount as the trimethylsilyl group shifts it to the right.

The spectra of p- $\text{ClC}_6\text{H}_4(\text{CH}_2)_4\text{SiMe}_3$  and p- $\text{ClC}_6\text{H}_4\text{CH}(\text{SiMe}_3)\text{CH}_2\text{CH}_2\text{CH}_3$  are shown in figs. V and VI, respectively. It is evident that these two spectra are not identical. The spectrum shown in fig. V for p- $\text{ClC}_6\text{H}_4(\text{CH}_2)_4\text{SiMe}_3$  is as would be expected from this structure. The chemical shifts for the proton of the  $\text{CH}_2$

adjacent to the phenyl group and of that adjacent to the trimethylsilyl group are the same as in the previous spectra (figs. III and IV); in this case, however, the peaks arising from them are separated by those from the protons of the  $\text{CH}_2\text{-CH}_2\text{-}$  group in the centre of the chain. On examination of the spectrum shown in fig. VI, the absence of a  $\text{CH}_2$  adjacent to the phenyl ring is apparent. The peaks expected for a  $\text{CH}_2$  adjacent to the trimethylsilyl group are present. The expected triplet for the  $\text{Ar-C-(SiMe}_3\text{)H}$  group might well be hidden by the peaks arising from the central  $\text{CH}_2\text{-CH}_2$  group.

The spectra of the  $\underline{m}\text{-ClC}_6\text{H}_4(\text{CH}_2)_4\text{SiMe}_3$  and  $\underline{m}\text{-ClC}_6\text{H}_4\text{CH(SiMe}_3\text{)CH}_2\text{CH}_2\text{CH}_3$  shown in figs. VII and VIII, respectively, are similar to the spectra of the respective para compounds and similar considerations apply.

The spectra of  $\underline{o}\text{-ClC}_6\text{H}_4(\text{CH}_2)_4\text{SiMe}_3$  shown in fig. IX is similar to the spectra obtained for the corresponding meta and para compounds (figs. VII and V).

4). The  $k_{\text{rel}}$  ( $k_{\text{rel}} = k_{\text{compound}}/k_{\text{C}_6\text{H}_5\text{SiMe}_3}$ ) values for the protodesilylation of  $\underline{m}\text{-}$  and  $\underline{p}\text{-RC}_6\text{H}_4\text{SiMe}_3$  compounds in aqueous-methanolic perchloric acid are given in Table 9.2 (page 177).

If the branched chain compounds had the structure,  $\underline{m}\text{-}$  and  $\underline{p}\text{-Me}_3\text{SiC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{CH(SiMe}_3\text{)CH}_3$ , as was first thought, then their  $k_{\text{rel}}$  values would not be expected to be greatly different from the  $k_{\text{rel}}$  values of  $\underline{m}\text{-}$  and  $\underline{p}\text{-Me}_3\text{SiC}_6\text{H}_4(\text{CH}_2)_n\text{-}$

SiMe<sub>3</sub> (where n = 3 and 4). As can be seen from the results, in Table 9.2, the k<sub>rel</sub> values of these branched chain compounds more closely resemble the k<sub>rel</sub> values of *m*- and *p*-Me<sub>3</sub>SiC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>SiMe<sub>3</sub> respectively. They would, therefore, appear to be benzyl type silicon compounds.

Table 9.2

Relative Reactivities of RC<sub>6</sub>H<sub>4</sub>SiMe<sub>3</sub> Compounds in  
Protodesilylation at 50.15°

R	k <sub>rel</sub> meta	k <sub>rel</sub> para
Me <sub>3</sub> Si(CH <sub>2</sub> ) <sub>4</sub>	3.42	23.3
Me <sub>3</sub> Si(CH <sub>2</sub> ) <sub>3</sub>	3.74	21.4
Me <sub>3</sub> Si(CH <sub>2</sub> ) <sub>2</sub>	3.54	27.5
Me <sub>3</sub> SiCH <sub>2</sub>	6.37	267
Me <sub>3</sub> Si(CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> )CH	7.91	259

It can be concluded, therefore, that the structure of the branched chain compounds is as shown in fig. X.

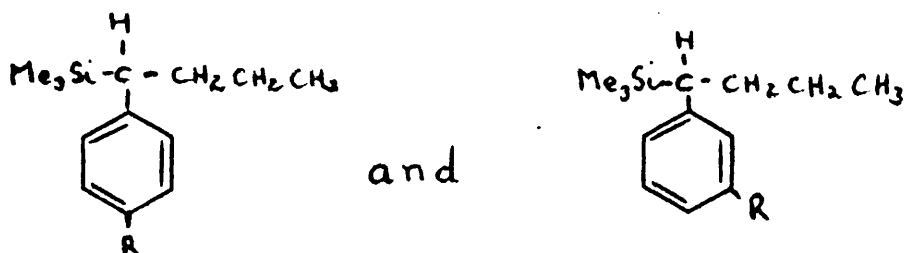
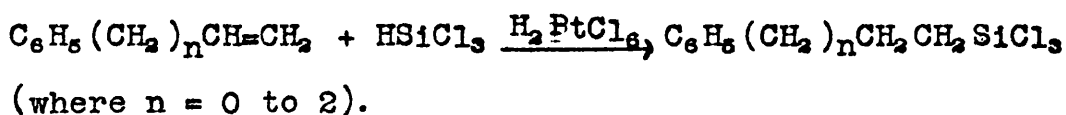


fig. X

The problem now arises, however, as to how these branched chain compounds could be formed by the addition of trichlorosilane to the 4-chlorophenyl-but-1-enes. In

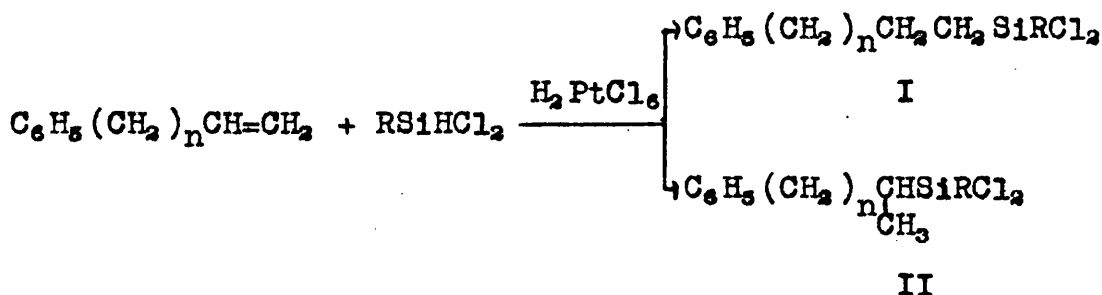
order to answer this problem, we must first consider the general problem of the mechanism of these silane addition reactions in the presence of chloroplatinic acid as catalyst.

Petrov and co-workers studied the addition of trichlorosilane, methyldichlorosilane and ethyldichlorosilane to the alkenylbenzenes  $C_6H_5(CH_2)_nCH=CH_2$  (where  $n = 0$  to 2) in the presence of chloroplatinic acid as catalyst.<sup>257</sup> Trichlorosilane was found to add easily (with yields of 25-60%) to styrene, allylbenzene and  $\gamma$ -butenylbenzene; in all three cases only one isomer was obtained—the straight chain compound e. g. ,



(Compare this with the addition of trichlorosilane to the chlorophenylbut-1-enes where we isolated two isomers).

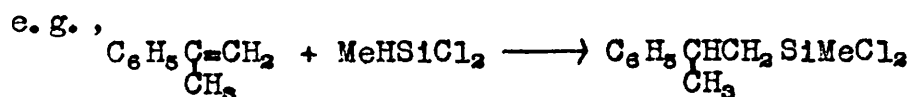
Methyl- and ethyl-dichlorosilane were found to add to the same alkenylbenzenes giving, however, two isomers e. g. ,



These compounds were assigned structures I and II on Raman spectral evidence. It is interesting to note that the structure of the branched chain isomer produced by

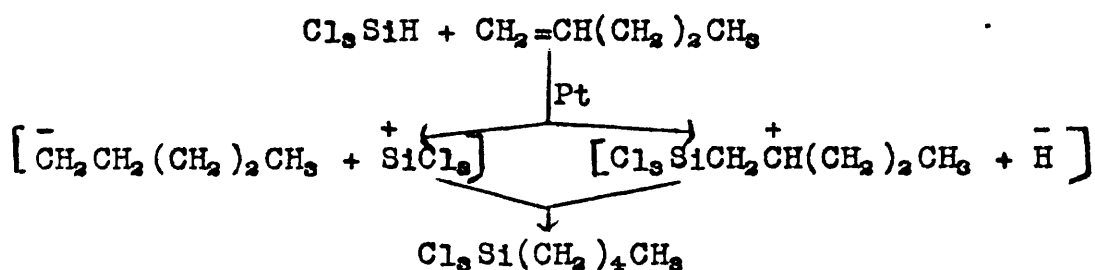
the addition of methyl- and ethyl-dichlorosilane is different to that obtained by us for the addition of trichlorosilane.

Styrene, with methyldichlorosilane, was originally reported to give only one product in the presence of platinised carbon, namely (2-phenylethyl)-methyldichlorosilane,<sup>253</sup> but later work showed the presence of two isomeric products.<sup>256</sup> It was found, however, that under the same conditions  $\alpha$ -methylstyrene formed only one product, that is (2-phenylpropyl)-methyldichlorosilane<sup>256</sup>



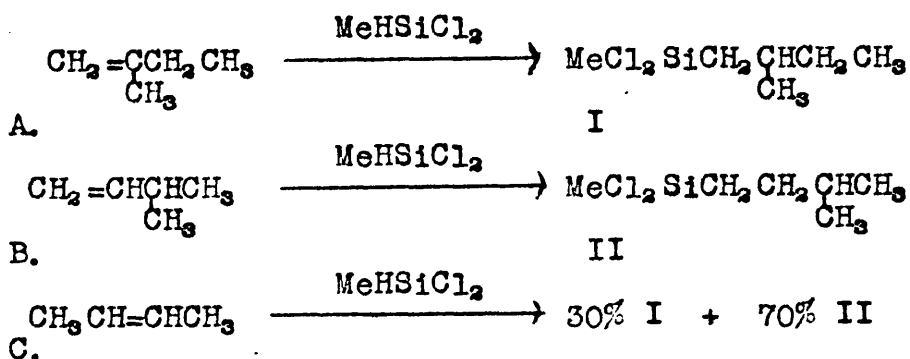
Addition reactions of silicon hydrides to alkenes and alkynes catalysed by group VIII metals and their derivatives are not retarded by polymerisation inhibitors,<sup>258-9</sup> and the reactions, therefore, are best represented by an ionic mechanism.<sup>259-60</sup> Since the Si-H bond is polarised in the direction  $\text{Si}^{\delta+} - \text{H}^{\delta-}$  (see chapter 1) the direction of the addition can be compared to that found in the ionic additions of hydrogen halides.<sup>261</sup> The direction of addition is widely referred to as proceeding contrary to Markovnikoffs' rule;<sup>262</sup> this is true only in the sense that the hydrogen atom attaches itself to the least hydrogenated ethylenic carbon. Considering the polarisation of the Si-H bond, the observed direction of addition is as would be expected.

There are two possible mechanistic paths which have been considered for the first step of this reaction, both of which assume that polarisation of the Si-H bond occurs on the surface of the catalyst, followed either by nucleophilic attack by the hydride ion or electrophilic attack by the siliconium ion<sup>263</sup> e. g. ,



The addition of trichlorosilane, methyldichlorosilane and dimethylchlorosilane to hept-3-ene in the presence of chloroplatinic acid gives n-heptyl products only. Since excess of olefin is not rearranged during the addition and 3- and 4-trichlorosilylheptane are stable under the conditions of the reaction, a mechanism involving rearrangement during addition is necessary.<sup>264</sup> These and other<sup>263</sup> rearrangements suggest that nucleophilic attack of hydride ion on the olefin may be the normal initiation step in the metal-catalysed additions.

Saam and Speier have obtained further confirmation of this suggestion by a study of the addition of methyldichlorosilane to an excess of olefin in the presence of chloroplatinic acid.<sup>265</sup> Using the methylbutenes, good yields of addition products were obtained e. g. ,



The addition products I and II were found to be quite pure, no trace of one was to be found in the other despite the fact that excess of olefins A and B were recovered as a mixture which consisted mainly of C.

The relative reactivities of A, B, C and methallyl chloride were determined by competitive addition reactions and were found to be as follows:-

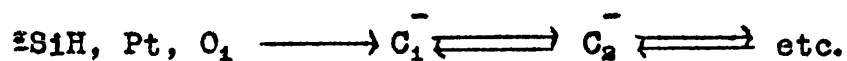
B : methallyl chloride : A : C = 1 : 0.8 : 0.07 : 0.02

Since the rates of addition of A and C differ only by a factor of 3.5, the formation of pure I from A cannot be ascribed to the inability of C to compete with A but indicates that C forms from A only after all, or almost all of the I has been formed. When methyldichlorosilane was added slowly to A under reflux over 3 hrs. a mixture of 82% I with 18% II was obtained.

2-Methylbut-1-ene was heated with chloroplatinic acid alone and with methyldichlorosilane; in neither case did isomerisation of the olefin occur. This suggests that an active catalytic species forms by a reaction of chloroplatinic acid and the silicon hydride. The catalyst

apparently exists after the addition reaction is complete, and no stoichiometric relationship can be seen among the catalyst, silane, and isomerised olefins.

Saam and Speier suggested that the available data could be explained by use of the following reaction scheme.<sup>265</sup>



The reaction was thought to commence by interaction of the silane, catalyst and the olefin, resulting in the transfer of a hydride ion by nucleophilic attack upon a molecule of olefin,  $\text{O}_1$ , to give rise to a carbanion,  $\text{C}_1^-$  which is thought to be capable of rapid tautomerisation. The most stable carbanions would predominate in a mixture of tautomers and, therefore, terminal carbanions would likely be most available for the second step of the mechanism.



This step is visualised as nucleophilic attack of the carbanion upon a silane, perhaps to form a pentacovalent intermediate  $[\equiv\text{SiRH}]^-$  which in turn attacks a molecule of olefin to generate a new carbanion and a molecule of alkylsilane.

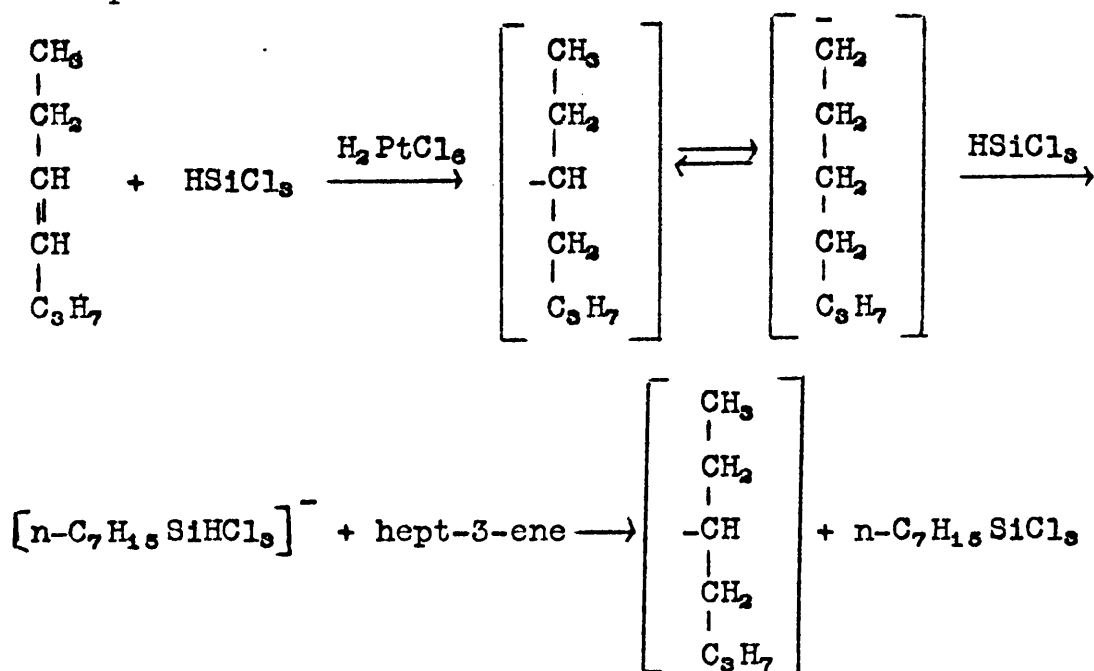
A third process may be thought of as responsible for the isomerisations of the olefin.



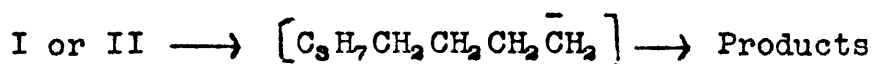
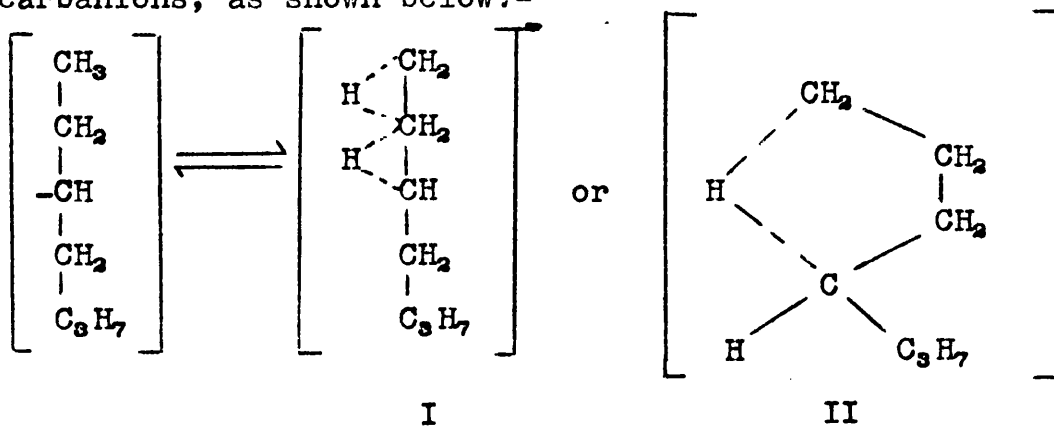
This step is thought to involve the transfer of a hydride ion from a carbanion to a molecule of olefin and a new carbanion. If  $\text{C}_1^-$  is a terminal carbanion and  $\text{O}_2$  is a

non-terminal olefin the equilibrium should be far to the right.

This reaction sequence is shown below for the reaction of hept-3-ene and trichlorosilane.

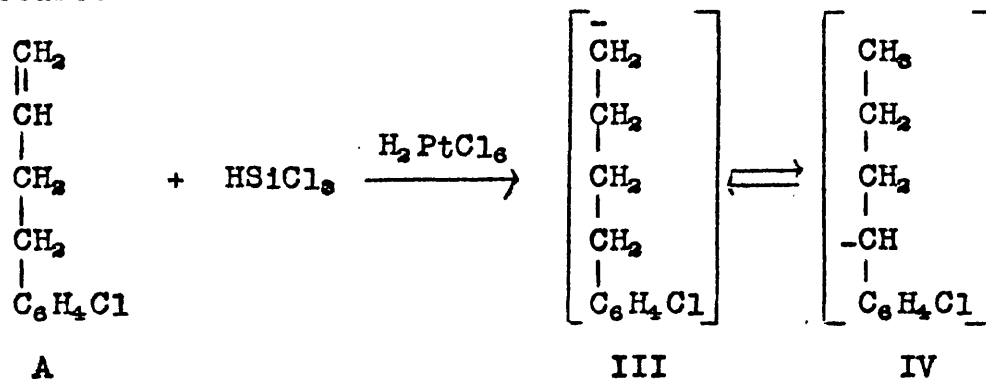


Two possible mechanistic paths have been suggested by Saam and Speier<sup>264</sup> for the tautomerisation of the carbanions, as shown below:-

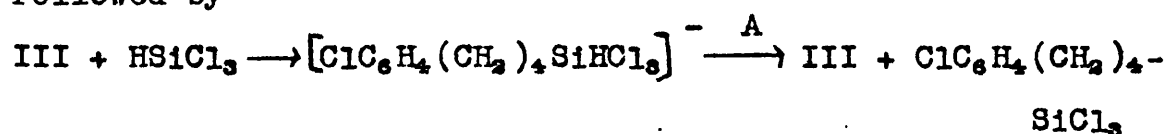


In this way a plausible explanation can be given for the apparently exclusive formation of terminal alkylsilanes from non-terminal olefins such as pent-2-ene, hept-2-ene, and 2-methylbut-2-ene. Stabilisation by resonance of carbanions such as  $\text{CH}_3\text{C}^-\text{HC}_6\text{H}_5$  explains why 1-phenylethylsilanes result from addition to styrene.

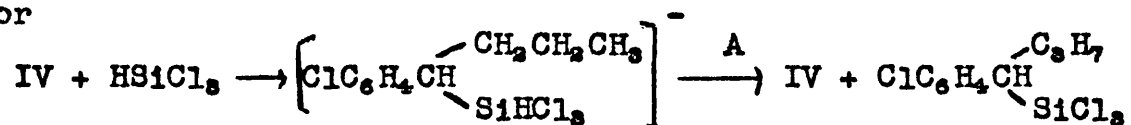
We can now put forward a mechanism for the addition of trichlorosilane to the 4-(chlorophenyl)-but-1-enes. It is suggested that the following reaction sequence occurs:-



followed by-



or



The ratio of straight chain to branched chain isomer depends on the relative stabilities of the carbanions III and IV, and on their rates of reaction with the trichlorosilyl group. Primary carbanions, e.g. III, are

normally the most stable and, therefore, the straight chain isomer would be expected to be the major product. However, in this case the secondary carbanion, IV, is stabilised by resonance, and is probably more stable than the carbanion III. The determining factor in these additions is, therefore, the relative reactivities of the carbanions III and IV. The negative charge of carbanion IV would be dissipated over the phenyl ring and, therefore, the  $\alpha$ -carbon atom would not be as negatively charged as the terminal carbon atom of carbanion III. Thus the primary carbanion III should be more reactive than the secondary carbanion IV, and the straight chain product should predominate, as is found.

There is the possibility of a total of four isomers being formed during this addition (there being three possible secondary carbanions and one primary carbanion). That only two products are obtained can clearly be reconciled to the relative stabilities of the carbanions, the two secondary carbanions  $\text{ClC}_6\text{H}_4\text{CH}_2\overset{-}{\text{C}}\text{HCH}_2\text{CH}_3$  and  $\text{ClC}_6\text{H}_4\text{CH}_2\text{CH}_2\overset{-}{\text{C}}\text{HCH}_3$  being unstable.

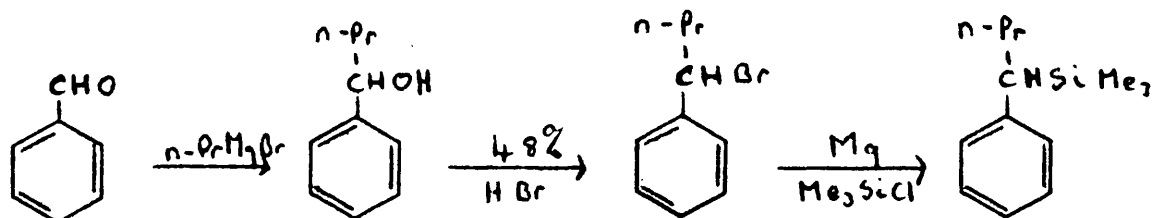
This is another reason why the branched chain isomer obtained should have the structure  $\text{ClC}_6\text{H}_4\text{CH}(\text{SiCl}_3)\text{CH}_2\text{CH}_2\text{CH}_3$  and not  $\text{ClC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{CH}(\text{SiCl}_3)\text{CH}_3$ , the carbanion  $\text{ClC}_6\text{H}_4\overset{-}{\text{C}}\text{HCH}_2\text{CH}_2\text{CH}_3$  being stabilised by resonance whereas the carbanion  $\text{ClC}_6\text{H}_4\text{CH}_2\text{CH}_2\overset{-}{\text{C}}\text{HCH}_3$  is not.

The other problem which arises from this addition of

trichlorosilane to the 4-(chlorophenyl)-but-1-enes is that with the meta and para compounds, 10.8 and 14.8% respectively, of branched chain isomer was obtained, whereas <2% of branched chain isomer was obtained in the case of the ortho compound. The operation of steric factors may account for the absence of appreciable amounts of the branched chain isomer. Molecular models indicate that this should only be very slight, there being a certain amount of restricted rotation about the aryl-carbon bond with a chlorine atom in the ortho position of the phenyl nucleus and a trichlorosilyl group on the  $\alpha$ -carbon atom. The operation of a stronger inductive effect from the ortho chlorine atom, thus increasing the stability of the secondary carbanion, and making it less reactive, might also be a contributing factor. The rate of formation of the branched chain isomer need only be reduced by a factor of 5, however, to give the observed results.

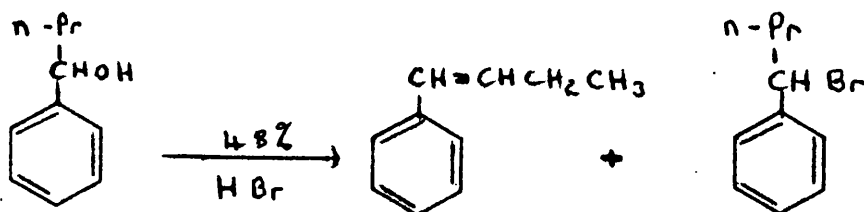
B. The Attempted Preparation of 1-Phenyl-1-trimethylsilyl-n-butane.

The synthesis was attempted by the following route:-



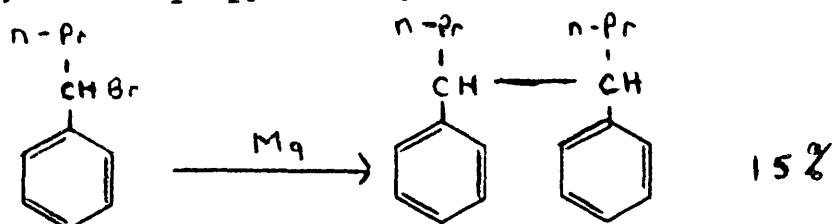
The preparation of the 1-phenylbutan-1-ol was carried

out successfully. Bromination of this compound gave two products, one of which was identified as the 1-phenylbut-1-ene and the other was assumed to be the 1-phenyl-1-bromobutane. Although the bromide had the correct boiling point (b.p.  $96-7^{\circ}/5\text{mm.}$ , Lit.<sup>267</sup>  $110^{\circ}/10\text{mm.}$ ) the refractive index was completely different from that quoted in the literature ( $n_D^{25}$  1.5402, Lit.<sup>267</sup>  $n_D^{20}$  1.613). However, infrared examination showed the absence of OH and  $-\text{CH}=\text{CH}-$  groups and sodium fusion showed the presence of bromine. Also it was noted that the refractive index of 4-phenyl-1-bromobutane was very near the value determined for the bromide isolated in the above reaction ( $n_D^{19}$  1.5408).<sup>27</sup> Since the refractive index of the branched chain isomer should only be slightly higher than that of the straight chain isomer it was assumed that the compound isolated was in fact 1-phenyl-1-bromobutane. However, the formation of 1-phenyl-2-bromobutane cannot be excluded if 1-phenylbut-1-ene is formed during the reaction. Since the structure of the bromide was no longer unambiguous the synthesis was not repeated. The reaction of the alcohol with 48% hydrobromic acid, therefore, was:-



The Grignard reagent was prepared from the 1-phenyl-

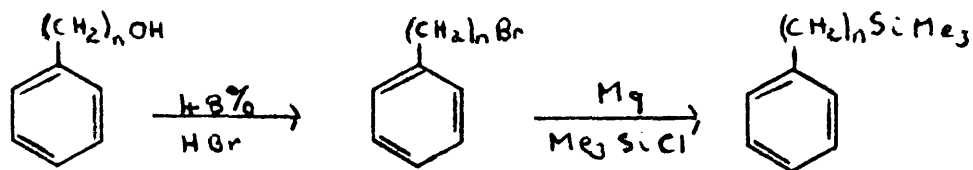
1-bromobutane, but on coupling with trimethylchlorosilane, no trimethylsilyl derivative was obtained. Instead, a 15% yield of  $\alpha, \alpha'$ -di-n-propyldibenzyl was obtained e.g.,



Since peroxides catalyse this type of coupling all starting materials and solvents should be freshly distilled before use. The formation of  $\alpha, \alpha'$ -di-n-propyldibenzyl is an indication that the correct bromide had been prepared.

### C. The Preparation of Organo-trimethylsilanes from the Corresponding Bromides.

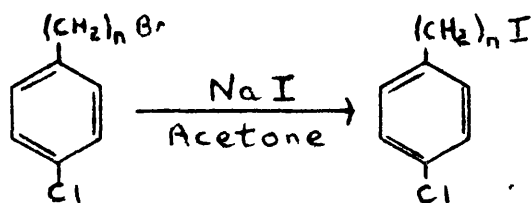
The preparation of several of the compounds was at first attempted by the following route:-



Although the conversion of alcohols to the corresponding bromides has been described on numerous occasions in the literature, it was found, with all the compounds used in the present study, that pure bromides could not be obtained. In all cases the bromides were contaminated with traces of unreacted alcohol, it being impossible to separate them by fractionation due to the similarity of

their boiling points. The preparation of the corresponding trimethylsilyl compounds via these magnesium bromides was attempted but no pure products could be obtained on fractionation.

To overcome this difficulty it was decided that the bromides should be converted to the corresponding iodides using sodium iodide in acetone e.g. ,

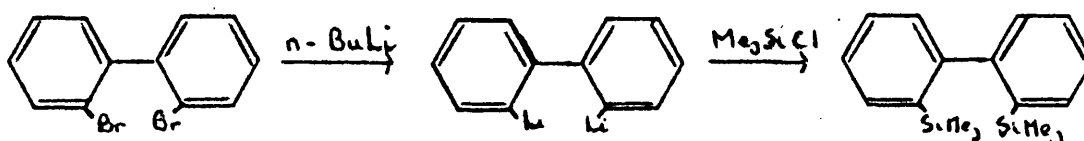


Fractionation of the products of these reactions gave pure iodides in good yields, free from traces of the corresponding alcohols and bromides.

Conversion of these iodides to the corresponding trimethylsilyl derivatives via the Grignard reagent was carried out in the usual manner. It was found, however, that although pure products could be obtained, these reactions gave very poor yields (15-44%).

## 2. The Attempted Preparation of 2, 2'-Bistrimethylsilyl-biphenyl.

The final two stages in this attempted synthesis were:-

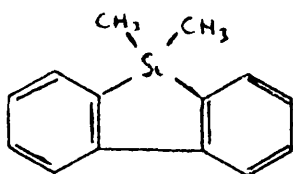


Recrystallisation of the final product from methanol gave a compound m.p. 59.5° (Found:- C, 79.66; H, 6.76.

$C_{18}H_{26}Si_2$  requires C, 72.45; H, 8.79%).

If the compound is assumed to contain only C, H, and Si then the analysis corresponds to a molecular formula of  $C_{14}H_{14}Si$ .

A compound which has the required molecular formula is the silicon analogue of 9,9-dimethylfluorene, that is



5,5-Dimethyldibenzsilole

( $C_{14}H_{14}Si$  requires C, 79.95;  
H, 7.01%).

This compound has been prepared previously by Gilman and Gorsich<sup>248</sup> (who reported a m. p. 60-1°), and also by Moore<sup>249</sup> (who reported a m. p. 59.5°). In both these cases it was prepared by the reaction of dimethyldichlorosilane with 2,2'-dilithiobiphenyl, poor yields, however, being obtained.

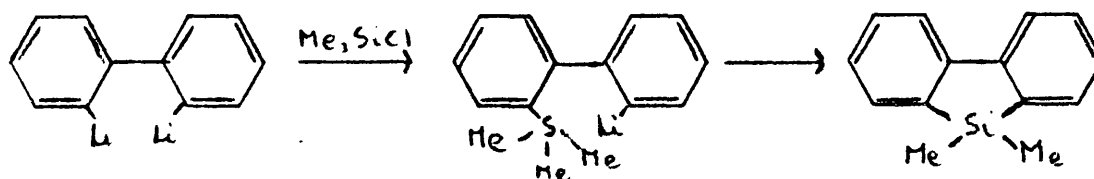
The ultraviolet absorption spectrum of the compound in methanol appears to be identical with the ultraviolet spectrum of 5,5-dimethyldibenzsilole prepared by Moore.

Table 9.3

Compound		5,5-Dimethyldibenzsilole	
(Å)	$\epsilon$	(Å)	$\epsilon$
2092	$4.66 \times 10^4$	2092	$3.64 \times 10^4$
2294	$2.55 \times 10^4$	2294	$2.17 \times 10^4$
2358	$1.85 \times 10^4$	2358	$1.54 \times 10^4$
2725	$1.49 \times 10^4$	2725	$1.29 \times 10^4$
2849	$1.26 \times 10^4$	2849	$1.09 \times 10^4$

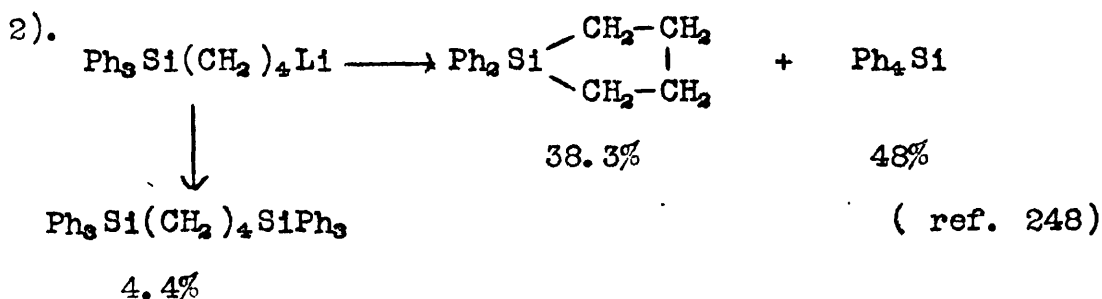
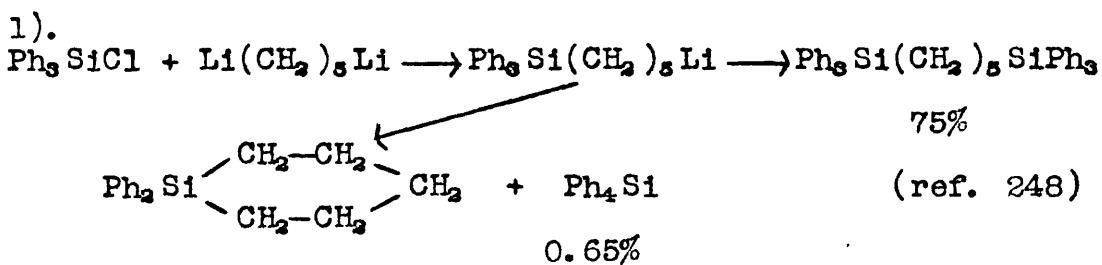
The wavelengths and molar extinction coefficients of the main peaks for both compounds are given in Table 9.3.

The compound 5,5-dimethyldibenzsilole has, therefore, been prepared by the following reaction:-



During the course of the reaction a silicon-methyl bond must have been broken with the formation of methyl-lithium.

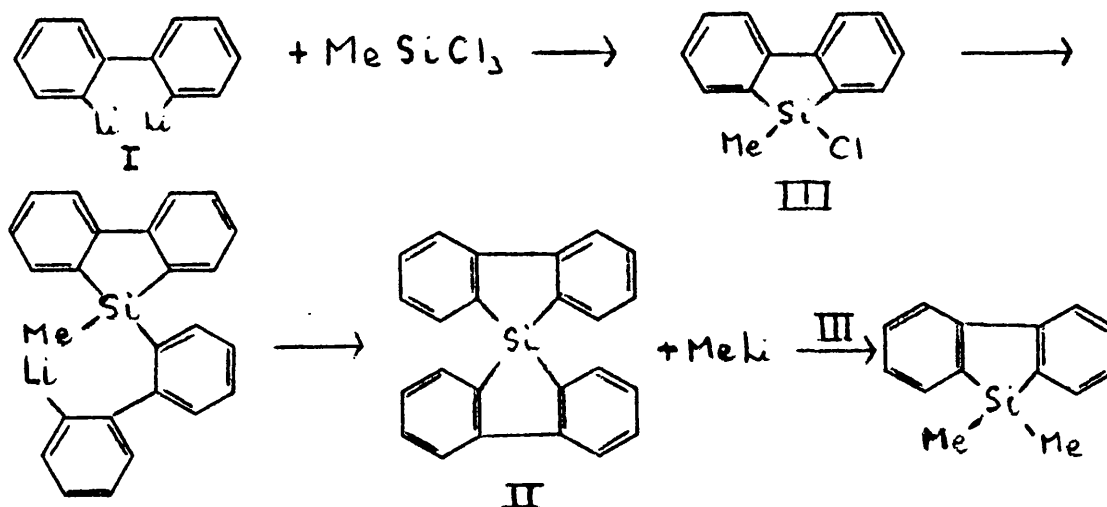
Such cleavages of carbon-silicon bonds by lithium reagents have been observed before but in more complicated systems,<sup>248, 250-1</sup>



3). Gilman and Gorsich prepared the 5,5-dimethyldibenzsilole using dimethyldichlorosilane or methyltrichlorosilane and 2,2'-dilithiobiphenyl.<sup>248, 251</sup>

They proposed the following reaction steps for the

reaction of 2,2'-dilithiobiphenyl and methyltrichlorosilane



They suggested that I first reacts with the methyltrichlorosilane forming compound III, and the next step is the reaction of I with the Si-Cl bond of III; the Me-Si bond is then cleaved simultaneously, or in a rapid stepwise fashion, by the second anion of I to yield II and MeLi which in turn can couple with unreacted III to give the dimethyl derivative.

Gilman and Gorsich also found rather unexpectedly that II was attacked by phenyl-lithium in tetrahydrofuran or in ether to give 5-(2-biphenyl)-5-phenyldibenzsilole.<sup>251</sup> This reaction is essentially the reverse of the one in which II was formed from I and III but for one striking difference. In the reaction in which II was formed, the methyl-lithium arising from scission of the  $\text{CH}_3\text{-Si}$  bond can interact with unreacted III. On the other hand, in the reaction of II with phenyl-lithium, no Si-Cl bond is available for a possible organo-lithium intermediate,

resulting from the ring opening of III, to react with. This reaction appears to be peculiar to II since 5,5-diphenyldibenzsilole was unaffected by phenyl-lithium under similar conditions. In fact it has been demonstrated that alkyl- and aryl-silicon compounds are unaffected by n-butyl-lithium in ether.<sup>252</sup> During the present study it has been shown that phenyl-lithium in ether did not attack phenyltrimethylsilane, even after refluxing for 120hr.

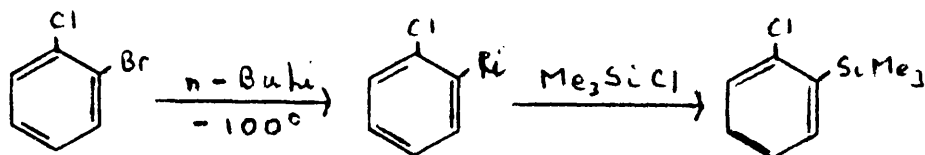
The reaction of trimethylchlorosilane with 2,2'-dilithiobiphenyl gives a high yield (71.5%) of 5,5'-dimethyldibenzsilole. During the course of the reaction a Si-CH<sub>3</sub> bond is cleaved with the formation of methyl-lithium; the methyl-lithium probably reacts with trimethylchlorosilane with the formation of silicon tetramethyl.

From molecular models of the 2,2'-biphenyl compounds involved it is apparent that there is considerable steric hinderance to the formation of the 2,2'-bistrimethylsilylbiphenyl. Therefore, even though excess trimethylchlorosilane was used the intramolecular methyl-silicon bond cleavage is the preferred reaction with the resulting formation of a high yield of the cyclic silicon compound.

### 3). The Attempted Preparation of *o*-Chlorophenyl-trimethylsilane.

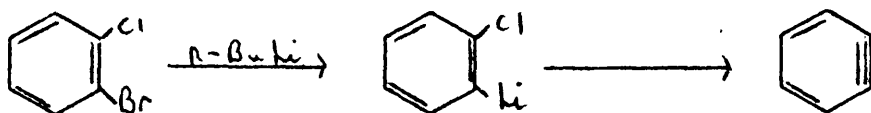
In order to prepare *o*-bistrimethylsilylbenzene the preparation of *o*-chlorophenyltrimethylsilane was necessary. This synthesis of *o*-chlorophenyltrimethylsilane was

attempted by the following route:-

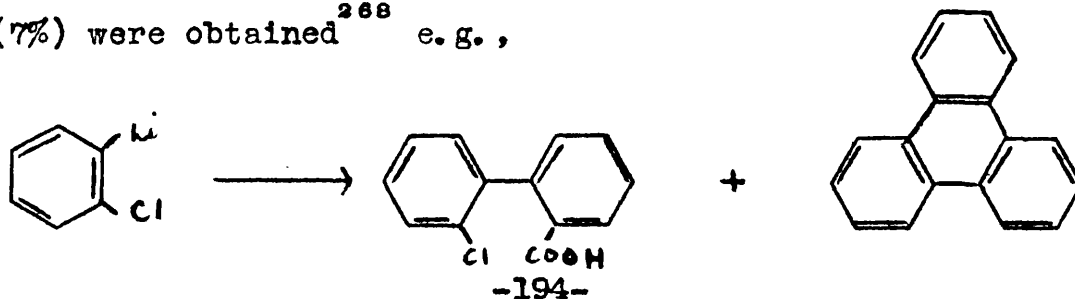


No o-chlorophenyltrimethylsilane was obtained; instead two compounds were obtained, one of which was identified as 2-chloro-2'-trimethylsilyl-biphenyl and the other was thought to be 2-chloro-2'-n-butyl-biphenyl.

o-Fluoro-, o-chloro-, and o-bromophenyl-lithium have been prepared<sup>268</sup> by treating the corresponding o-bromo-halogenobenzenes with ethereal n-butyl-lithium at temperatures below  $-50^\circ$ . All are highly reactive (o- $\text{BrC}_6\text{H}_4\text{Li}$ ) > o- $\text{ClC}_6\text{H}_4\text{Li}$  > o- $\text{FC}_6\text{H}_4\text{Li}$ ), and their coupling reactions<sup>268-9</sup> have been interpreted as involving 'benzyne' intermediates e.g.,

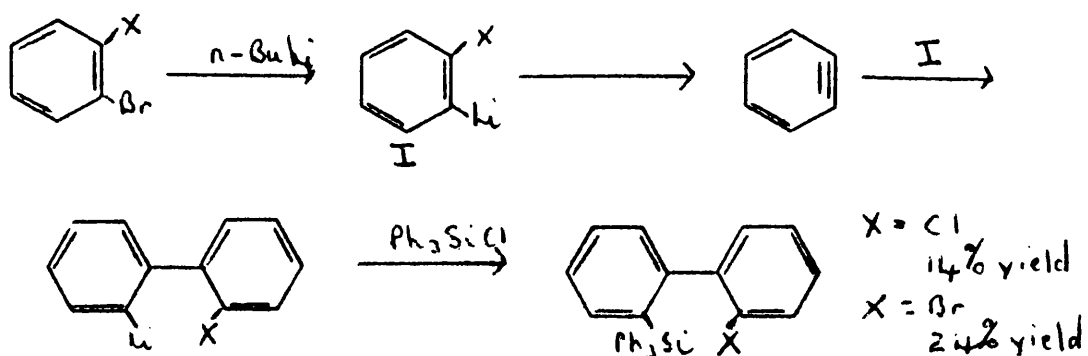


Carbonation of o-chlorophenyl-lithium (prepared at  $-90^\circ$ ), and then allowing the reaction to warm to room temperature gave o-chlorobenzoic acid in 93% yield. If the reaction was allowed to warm to room temperature before carbonation then 2-chloro-2'-carboxy-biphenyl (22%) and triphenylene (7%) were obtained<sup>268</sup> e.g.,



Recent investigations by Gilman and Gaj<sup>246</sup> show that the solvent plays an important part in the reaction of bromohalogenobenzenes with an alkyl-lithium compound. For example, two equivalents of o-dibromobenzene in tetrahydrofuran react with one equivalent of n-butyl-lithium to give good yields of 2,2'-dibromobiphenyl. Apparently o-bromophenyl-lithium couples with o-dibromobenzene rather than pass through the benzyne intermediate.

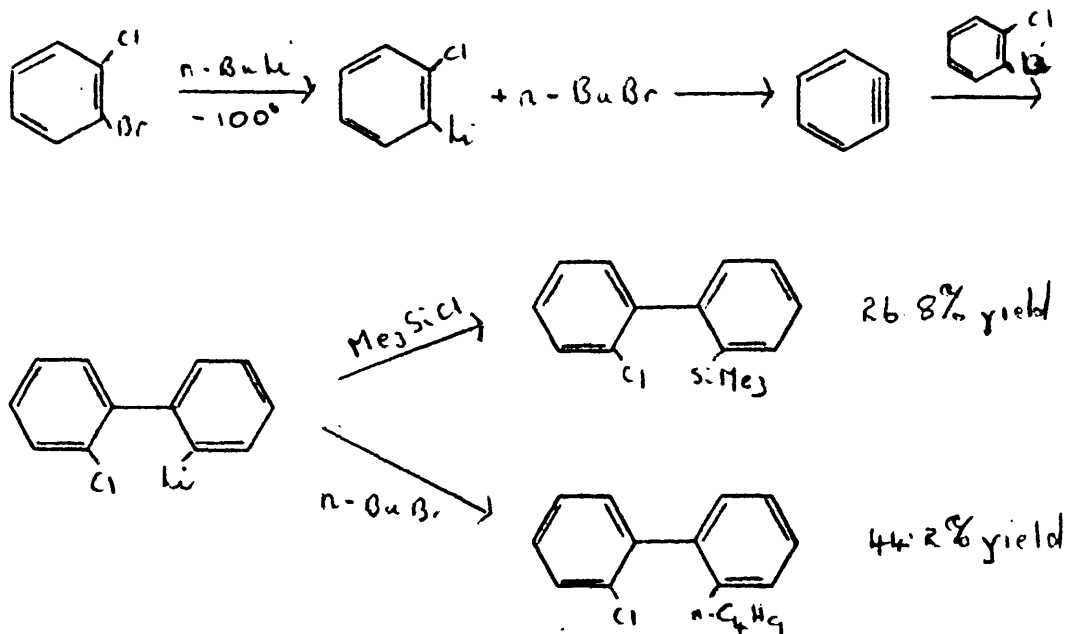
2-Chloro-, and 2-bromo-2'-triphenylsilyl-biphenyl have been prepared by allowing an ethereal solution of o-chlorophenyl-lithium to warm up to room temperature in the presence of triphenylchlorosilane<sup>270</sup> e. g. ,



This reaction is analogous to the one described in this thesis. The production of 2-chloro-2'-trimethylsilyl-biphenyl can, therefore, be readily explained. The presence of the second product which was isolated is rather more difficult to explain. It is suggested that it is probably 2-chloro-2'-n-butyl-biphenyl. This compound does not contain silicon, and the analysis result for carbon agrees with the calculated value, although the result

for hydrogen is rather low. It was, at first, thought to be simply 2-chlorobiphenyl; the boiling point, however, is too high (b.p. 157-8°/5.0mm., Lit.<sup>27</sup> b.p. 154°/12.5mm.) and the analysis figures are completely different from those required by 2-chlorobiphenyl.

The reaction of o-bromochlorobenzene with n-butyllithium at -100°, followed by warming to room temperature in the presence of trimethylchlorosilane is thought to proceed as follows:-



## CHAPTER 10

### Reactivity Studies on the Compounds $C_6H_5(CH_2)_nSiMe_3$

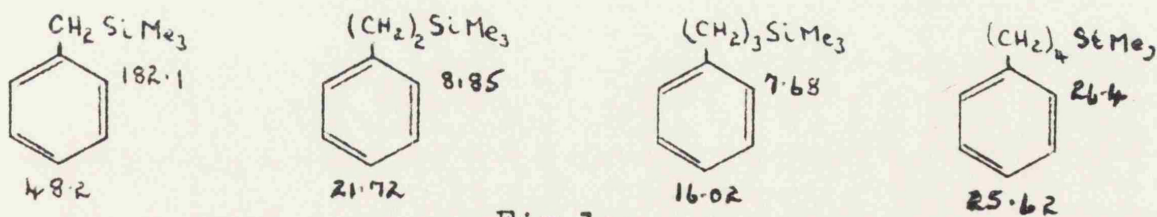
(where  $n = 1$  to  $4$ )

Chernyshev, Dolgaya and Petrov<sup>70</sup> determined the relative reactivities and partial rate factors of the compounds  $C_6H_5(CH_2)_nSiMe_3$  (where  $n = 1$  to  $4$ ) in competitive nitrations with benzene using 90% nitric acid in acetic anhydride at 0-10°. Their values of  $k_{rel}$  ( $k_{rel} = k_{compound}/k_{benzene}$ ), together with the isomer distributions are given in Table 10.1, and their partial rate factors in fig. 1.

Table 10.1

Nitration of  $Me_3Si(CH_2)_n C_6H_5$

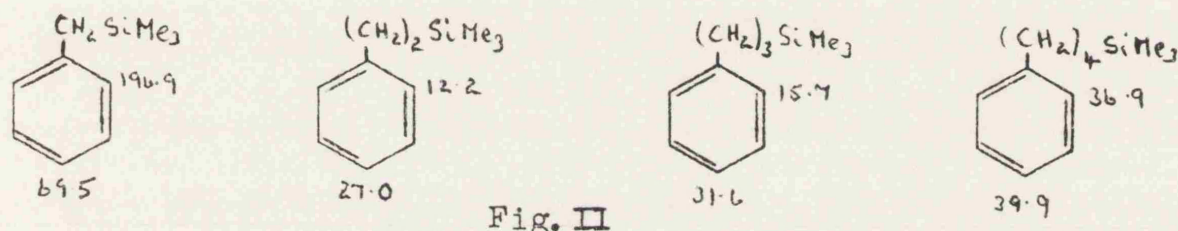
n	1	2	3	4
$k_{rel}$	77.2	8.87	10.62	18.96
% ortho	85.0	45.8	49.2	64.9
% para	15.0	54.2	50.8	35.1



On consideration of these results it is evident that there are several points of interest. It was thought, therefore, that a determination of the relative reactivities for protodesilylation might be of interest. Before

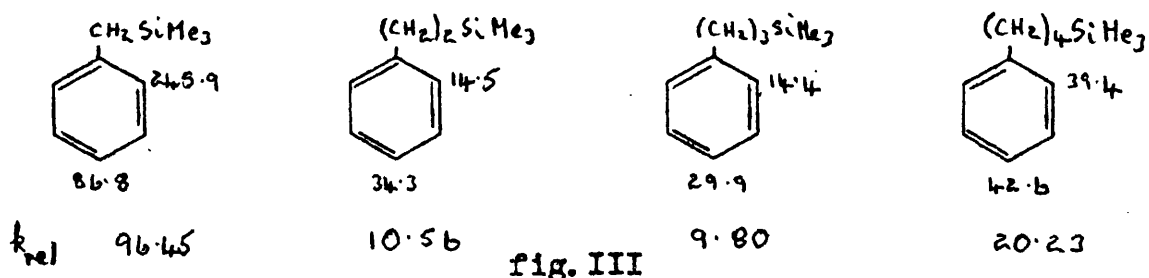
discussing these results, however, a comment must be made about the results of Chernyshev et al.<sup>70</sup>

Their values for the partial rate factors are not consistent with the isomer distributions and  $k_{rel}$  values. Calculation of the partial rate factors from the isomer distributions and  $k_{rel}$  values given in Table 10.1 gives entirely different values; these are shown in fig. II.



It was also found impossible to arrive at the  $k_{rel}$  values, given in Table 10.1, from the experimental data given, although the isomer distribution was found to be correct. It was noted that considerable residues were sometimes obtained after fractionation and that the amount of reactants used up did not agree with the amount of products isolated. The values of  $k_{rel}$  were therefore, recalculated using the following data:-final concentration of benzene = initial concentration of benzene - concentration of nitrobenzene formed, and the experimental value for the final concentration of silane. The final concentration of benzene was calculated in this way because it was thought that, due to the volatility of benzene, the amount recovered would be too low. These values for  $k_{rel}$  and the partial rate factors thus

obtained are given in fig. III.

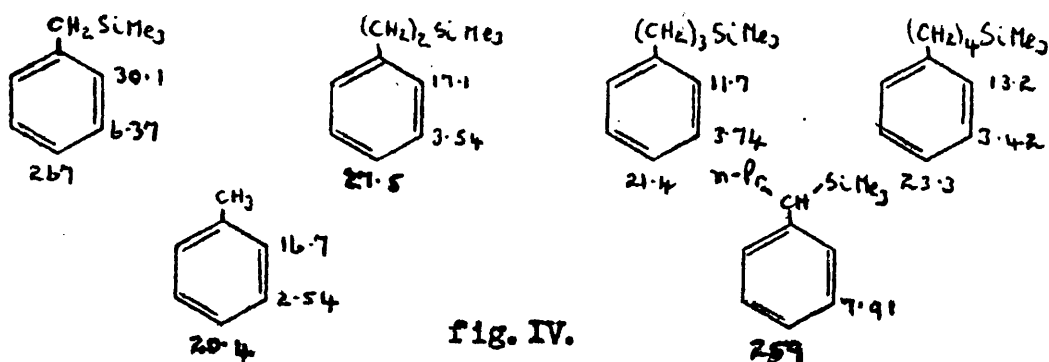


The relative rates ( $k_{rel}$ ) determined for the proto-desilylation of  $\text{XC}_6\text{H}_4\text{SiMe}_3$  compounds with aqueous-methanolic perchloric acid are given in Table 10.2 and are illustrated in fig. IV.

Table 10.2

Relative Reactivities of  $\text{X.C}_6\text{H}_4\text{SiMe}_3$  Compounds in Perchloric Acid-Methanol at  $50.15^\circ$ .

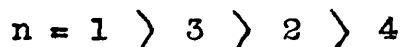
X	para $k_{rel}$	meta $k_{rel}$	ortho $k_{rel}$
Me	20.4	2.54	16.7
$\text{Me}_3\text{SiCH}_2$	267	6.37	30.1
$\text{Me}_3\text{Si}(\text{CH}_2)_2$	27.5	3.54	17.1
$\text{Me}_3\text{Si}(\text{CH}_2)_3$	21.4	3.74	11.7
$\text{Me}_3\text{Si}(\text{CH}_2)_4$	23.3	3.42	13.2
$\text{Me}_3\text{Si}(\text{CH}_2\text{Pr})\text{CH}$	259	7.91	-



The most striking feature of these results is that, in both nitration and in protodesilylation, the reactivities of the ortho and para positions of the compounds  $C_6H_5(CH_2)_nSiMe_3$  falls sharply from  $n = 1$  to  $n = 2$ ; and still further to  $n = 3$ . However, in the compound where  $n = 4$ , the reactivity of the ortho and para positions, instead of falling further, in fact shows a slight increase.

This peculiarity of the  $Me_3Si(CH_2)_4-$  group is much more marked in nitration, than in protodesilylation but is a definite effect which needs comment.

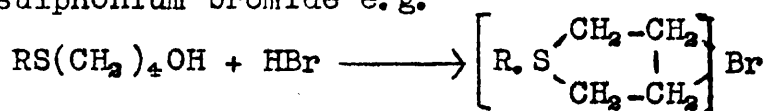
In the series of meta compounds the effect, however, is slightly different; the relative reactivities being in the order



This anomaly in the compounds containing n-propyl or n-butyl groups, has been observed in other reactions, although there is conflicting evidence in the literature as to which group is anomalous. In many cases the anomaly of the n-propyl or n-butyl group is associated to the formation, either in the product or as an intermediate, of a five or six-membered ring.

The abnormal behaviour of n-butyl groups was first noted by Bennett and Mosses,<sup>279</sup> who showed that under the conditions in which a  $\gamma$ - or  $\epsilon$ -hydroxy-sulphide,  $RS(CH_2)_nOH$  where  $n = 3$  or  $5$ , was not attacked by hydrobromic acid a

$\delta$ -hydroxy-sulphide  $RS(CH_2)_4OH$ , readily yielded the cyclic sulphonium bromide e.g.



There is no doubt that this reactivity is due to the fact that when the carbon chain is four atoms long, then the  $CH_2OH$  and S are adjacent to each other, therefore, facilitating their reaction, and also to the fact that the product has a five-membered ring.

Salomon et al.<sup>285</sup> have studied the cyclisation of compounds of the type  $H_2N(CH_2)_nBr$  where  $n = 2$  to 6, their results being shown in Table 10.3.

Table 10.3

Rates of cyclisation of  $\omega$ -Aminoalkylbromides in Water at 25°

Compound	$10^4 k_1 \text{ sec}^{-1}$
$H_2N(CH_2)_2Br$	6
$H_2N(CH_2)_3Br$	0.08
$H_2N(CH_2)_4Br$	5000
$H_2N(CH_2)_5Br$	80
$H_2N(CH_2)_6Br$	0.1

In these examples the factors of neighbouring group participation and the ring size of the product are clearly operating.

The abnormality of a n-propyl group, i. e. , a 3-carbon alkyl chain, is evident in the strengths of saturated straight chain aliphatic acids,<sup>272, 280</sup> whose strengths fall in the order

acetic > n-butyric > n-propionic > n-valeric

Table 10.4

Dissociation Constants of Saturated Aliphatic Carboxylic Acids<sup>280</sup>

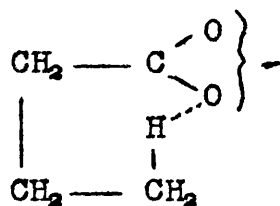
	10 <sup>5</sup> K		10 <sup>5</sup> K
Acetic Acid	1.75	n-Heptoic Acid	1.28
Propionic Acid	1.33	n-Octoic Acid	1.27
n-Butyric Acid	1.50	n-Nonoic Acid	1.11
n-Valeric Acid	1.38	iso-Valeric Acid	1.67
n-Hexoic Acid	1.32	Diethylacetic Acid	1.77

It was also noted that ~~the~~ iso-valeric acid and diethylacetic acid, which also possess a 3-carbon atom alkyl chain, have unusually high dissociation constants.<sup>280</sup> On the basis of inductive effects alone, the order of strengths should be

n-butyric > iso-valeric > diethylacetic acid,  
whereas the converse is true.

It was suggested,<sup>280</sup> that the concept of hydrogen

bond formation as applied to o-toluic acid,<sup>281</sup> might cause this spatial interaction in the case of n-butyric acid, thus high acid strength would be attributed to the reluctance of the proton to recombine with the anion in consequence to the formation of the following structure.<sup>280</sup>



Evidence of another kind also shows that the ionisation of n-butyric acid is affected by some disturbance. Harned and Sutherland<sup>282</sup> found that n-butyric acid had a maximum dissociation constant at 8°, whereas for acetic acid and propionic acid the maximum dissociation constant lies between 20° and 25°. Examination of other physical properties, however, does not reveal any unusual behaviour on the part of n-butyric acid.<sup>280</sup>

Hydrogen bond formation might also account for the order:-

diethylacetic > iso-valeric > n-butyric

Chain branching would mean that the terminal groups would be closer to the carboxyl group in these cases thus leading to an increased possibility of hydrogen bond formation.

It is interesting to note the changes brought about in basic strengths upon lengthening the alkyl chain. The

results of Hall and Sprinkle<sup>273</sup> for the N-alkyl and N,N-dialkylanilines indicate throughout that ionisation is facilitated, not in the manner anticipated from operation of the normal inductive effects, but always in the order

ethyl > n-propyl > methyl > hydrogen

meaning that either the ethyl or the n-propyl group is behaving anomalously. Similarly Davies<sup>276</sup> concluded from

Table 10.5

Dissociation Constants of Bases  $RC_6H_4NMe_2$  at 20°

R	H	Me	Et	n-Pr	n-Bu
pK	4.22	4.77	4.69	4.43	4.62

data of the reactivities (Table 10.6) and base strengths (Table 10.5) of p-alkyldimethylanilines, that the anomalous

Table 10.6

Reaction between Methyl Iodide and  $p-RC_6H_4NMe_2$

R	H	Me	Et	n-Pr	n-Bu
100k at 35° (l.g.mol. min.)	2.67	6.99	5.41	3.49	5.26

group was the n-propyl group, in each case the n-propyl derivative having a lower value than was expected.

In the nitration of alkylbenzoates the order of diminishing percentage of m-nitro derivative follows the sequence<sup>284</sup>

Me > n-Pr > Et > n-Bu

In this series the n-propyl group is displaced relative to the ethyl group. The rates of the acid catalysed,<sup>274</sup>

and base catalysed<sup>275</sup> bromination of phenylalkylketones are given in Table 10.7.

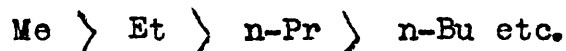
Table 10.7

Bromination of Phenylalkylketones PhCOCH<sub>2</sub>R

R	Me	Et	n-Pr	n-Bu
k <sub>25</sub> (Acid catalysed) <sup>274</sup>	0.104	0.072	0.085	0.082
k <sub>45</sub> (Base catalysed) <sup>275</sup>	0.0080	0.0062	0.0070	-

It was suggested that it was the n-propyl group which was anomalous<sup>274-5, 288</sup> but this is not strictly correct; the anomaly really arises when there is a 4-carbon atom chain attached to the ketonic carbon atom.

Numerous series of alkyl compounds have been studied in order to determine the relative effects of the alkyl groups in influencing a reaction. The theoretical sequence of the inductive polar effects of the alkyl groups, namely



is not universally followed. The possible agreement of an observed sequence with the theoretical one seems to depend, primarily on whether the alkyl group is itself participating directly in the reaction, or is merely exerting its influence in the reacting molecule. In the former case the theoretical sequence of the alkyl groups is generally observed, for example, in the hydrolysis of alkyl halides by alkali hydroxides, alkoxides and aryl-

oxides in anhydrous alcohol.<sup>286</sup> With the second main type of reaction, that in which the alkyl group exerts its influence in the reacting compound, no similar uniformity prevails. Departures from the normal sequence are frequent, leading to simple relative displacements in the sequence of groups, and in these cases the anomaly apparently begins with the propyl derivative.

Berliner and Berliner<sup>277</sup> while studying the bromination of monoalkylbenzenes found that their relative reaction rates were not in the order predicted by the inductive effects of the alkyl groups. For the series of n-alkylbenzenes:- methyl to n-hexyl-benzene it was found that n-propylbenzene was displaced relative to n-butylbenzene (see Table 10.8). These observations were then extended,<sup>278</sup>

Table 10.8

Relative Rates of Bromination of n-Alkylbenzenes.<sup>277</sup>

R	Me	Et	n-Pr	n-BU	n-Am	n-Hex
$k_{rel}$	1.00	0.70	0.55	0.59	0.52	0.48

and it was found that all alkylbenzenes with a basic straight four-carbon atom chain, were brominated faster than the corresponding compounds containing a straight three-carbon atom chain. These results are summarised in fig. V. (page 207).

These results strongly support their suggestion that a straight four-carbon chain makes a contribution

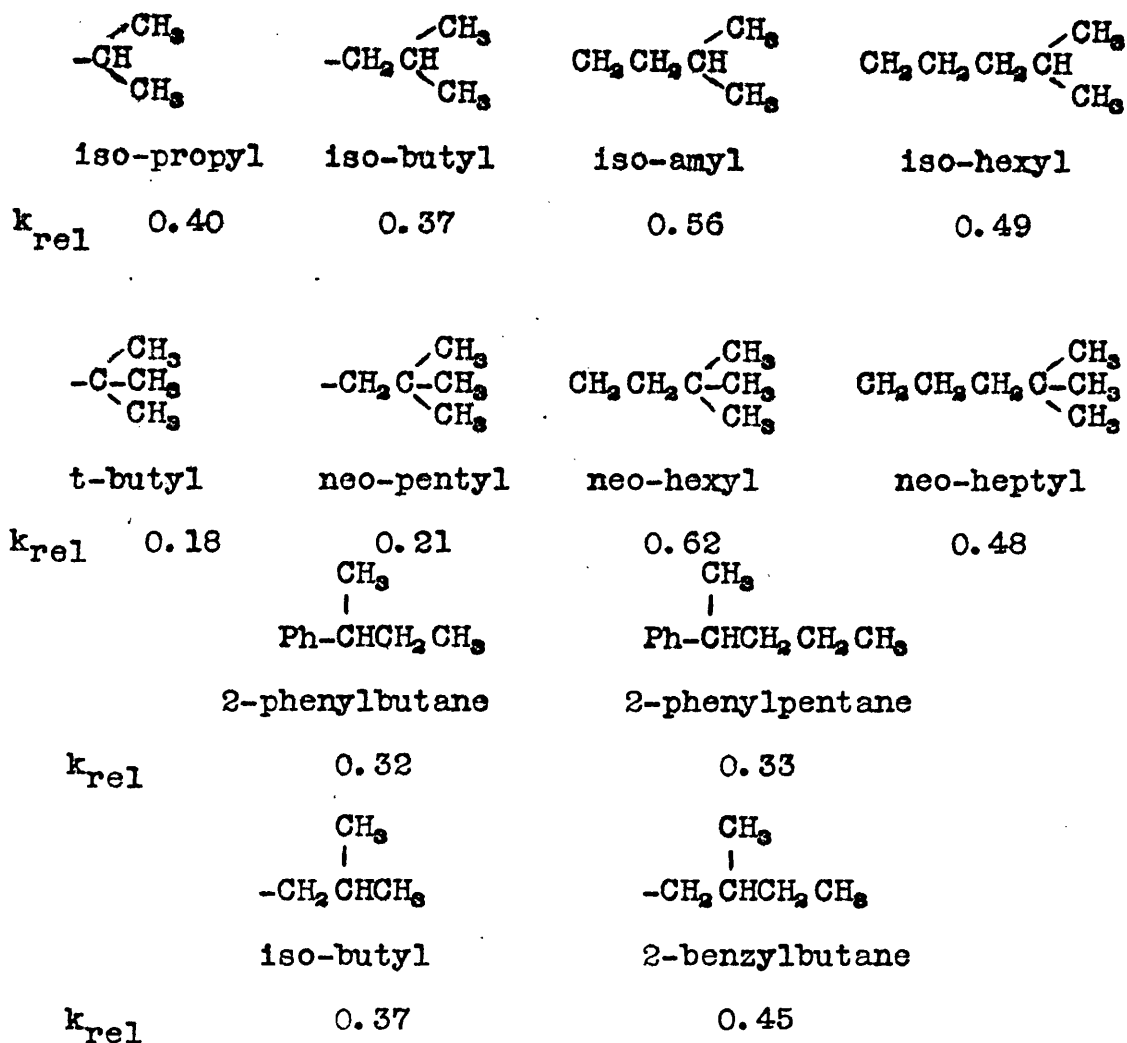
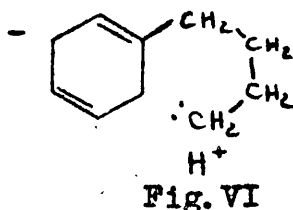


fig. V

to the reactivity of a benzene ring in excess of the contribution it would make if the electron releasing effect of the delta hydrogens could only be transmitted to the ring through the intervening carbon atom chain.

Berliner and Berliner<sup>277</sup> put forward a possible mechanism which might explain these facts. They suggested that a type of chelation might occur which was pictured in terms of the hyperconjugation structure shown in

fig. VI.



If canonical forms, such as that shown in fig. VI, contributed to the resonance hybrid, then hyperconjugation would increase the rate of bromination of the molecule, but of the meta position more than the ortho and para.

A factor which appears to influence the nuclear reactivities of the monoalkylbenzenes is the number of hydrogen atoms in the side chain, and their positions relative to the benzene ring. The reactivities depend primarily on the number of hydrogen atoms alpha to the benzene ring. However, if the number of alpha hydrogen atoms is constant, the reactivities decrease as the number of beta hydrogens decreases. The bromination data showed that the four alkyl groups:- methyl, ethyl, isopropyl, and tert-butyl continue to effect the reactivity of the aromatic ring in the Baker-Nathan order, even when they are removed from the ring by one or two methylene groups. It was, therefore, suggested<sup>277</sup> that second order carbon-hydrogen hyperconjugation involving the alpha and beta C-H bonds was the mechanism by which the effect of the beta hydrogens could be transmitted through a saturated methylene group, as shown in fig. VII.

This type of hyperconjugation must be less important than hyperconjugation involving alpha hydrogen atoms, for otherwise ethylbenzene would be brominated faster than toluene. Further types of hyperconjugation involving

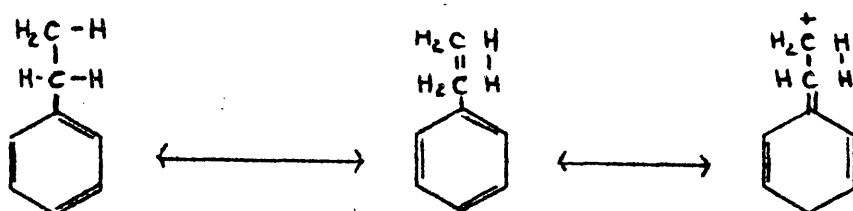


Fig. VII

gamma and delta carbon-hydrogen bonds are also thought to occur. Hyperconjugation involving delta C-H bonds is shown in fig. VIII.

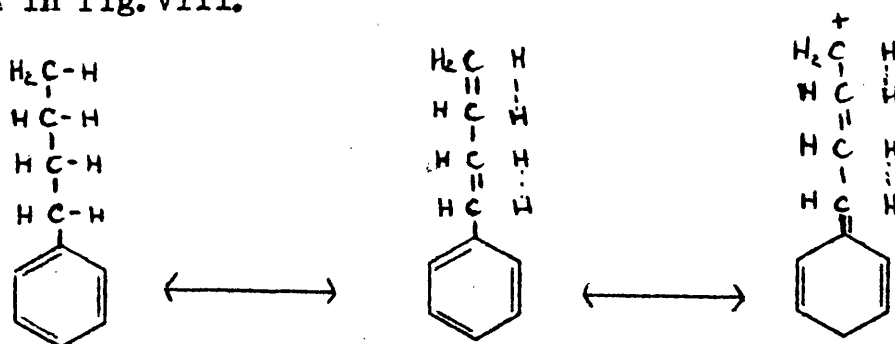


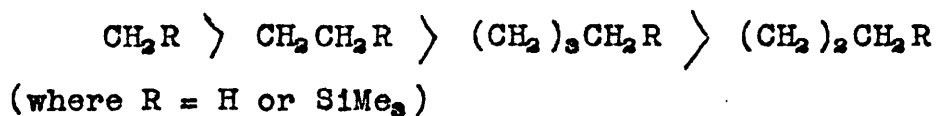
Fig. VIII

Berliner and Berliner suggested that an alkyl chain when attached to the highly polarisable benzene ring may acquire enough double bond character to permit transmission of an effect, in a similar manner to that in which such an effect can be transmitted through a system of conjugated double bonds.

It should be noted that these second order C-H hyperconjugation factors would tend to increase the

relative reactivities of the ortho and para positions relative to the meta position. However, while these effects may be operating an additional factor must apply in the cases of compounds containing a 4-carbon atom chain.

The results obtained by Chernyshev et al.<sup>70</sup> for nitration, and our results for protodesilylation are in agreement with those obtained by Berliner and Berliner<sup>277-8</sup> for the bromination of the n-alkylbenzenes; that is the overall rates of reaction vary with the alkyl groups in the order:-



From our results on protodesilylation it is apparent that a four-carbon atom alkyl chain increases somewhat abnormally the reactivity of the ortho-para positions but not the meta position, whilst a 3-carbon atom alkyl chain increases the reactivity of the meta position a little more than expected. This would indicate that structures such as shown in fig. VI(p-208), (that is, chelate hyperconjugation), do not contribute to the resonance hybrid and, therefore do not account for this anomaly.

It seems surprising that our overall result should agree with that obtained by Berliner and Berliner. It, therefore, appears that the presence of a terminal Si(CH<sub>3</sub>)<sub>3</sub> group on the alkyl chain has little effect on the relative reactivities of the compounds, the anomalous increase in

rate with the 4-carbon atom alkyl chain being unaffected. A study of the corresponding n-alkylphenyltrimethylsilanes would first have to be made before the effects of the terminal Si(CH<sub>3</sub>)<sub>3</sub> group can be assumed. The activating effect of the p-ethyl group is known, however, and the p-CH<sub>2</sub>CH<sub>2</sub>SiMe<sub>3</sub> group is somewhat more activating.

The  $f_o/f_p$  ratios for the series of compounds C<sub>6</sub>H<sub>5</sub>(CH<sub>2</sub>)<sub>n</sub>SiMe<sub>3</sub>, (where n = 1 to 4) in nitration and protodesilylation derived from the data given in figs. III and IV (page 199), respectively, are shown in Table 10.9. Several interesting points arise from these results 1). The very high  $f_o/f_p$  ratio in the nitration of benzyltrimethylsilane is of particular interest in the light of the recent series of papers by Norman and his co-workers<sup>180-1, 188-4, 287-8</sup> on ortho/para ratios in aromatic

Table 10.9

Ortho/Para Ratios for C<sub>6</sub>H<sub>5</sub>(CH<sub>2</sub>)<sub>n</sub>SiMe<sub>3</sub> Compounds

(where n = 1 to 4).

	$f_o/f_p$	
	Nitration	Protodesilylation
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> SiMe <sub>3</sub>	2.84	0.11
C <sub>6</sub> H <sub>5</sub> (CH <sub>2</sub> ) <sub>2</sub> SiMe <sub>3</sub>	0.42	0.62
C <sub>6</sub> H <sub>5</sub> (CH <sub>2</sub> ) <sub>3</sub> SiMe <sub>3</sub>	0.48	0.55
C <sub>6</sub> H <sub>5</sub> (CH <sub>2</sub> ) <sub>4</sub> SiMe <sub>3</sub>	0.93	0.57

substitution. Only a summary of their main conclusions will be given here as this problem will be discussed more

fully in Chapter 11.

The suggestion of de la Mare and Ridd<sup>289</sup> that the high ortho/para ratios obtained in nitrations with acetyl nitrate are due to an additional mode of nitration superimposed upon the normal nuclear nitration by the nitronium ion was used by Norman and Radda<sup>180-1, 184</sup> to account for their results on the nitration of methylphenyl-ether.

The first step of this is an  $S_N2$  displacement of nitrate ion from covalent dinitrogen pentoxide by the oxygen of the ether. The charged intermediate then rearranges through a six-membered cyclic transition state to yield the o-nitro isomer (fig. IX).

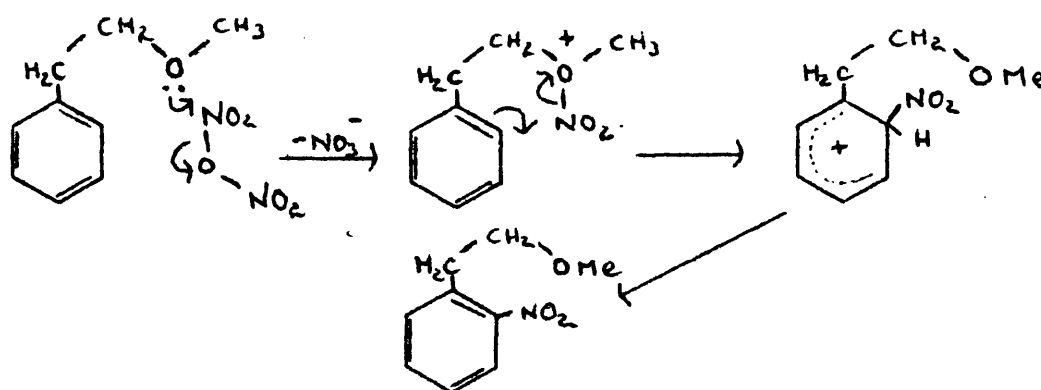


Fig. IX

They tentatively proposed that this mechanism would also explain the high ortho/para ratios observed for anisole and acetonitrile.

This specific ortho-interaction was thought to depend on two factors.<sup>184</sup> Firstly there is a stereochemical

requirement, the ease of rearrangement of the intermediate depending upon the ring-size of the cyclic transition state and secondly it depends on the presence of a nucleophilic atom in the side chain.

An additional mode of nitration must be present to explain the high ortho/para ratio which is observed in the nitration of benzyltrimethylsilane with nitric acid in acetic anhydride. This ortho/para ratio is extremely large, especially when one considers that in protodesilylation the ortho/para ratio is very much lower than would have been expected. Unfortunately, in the case of benzyltrimethylsilane, there is no information available for the isomer distribution with other methods of nitration. Copper nitrate in acetic anhydride is the only other nitrating agent which has been used, and its mode of nitration is thought to be very similar to that observed for nitric acid in acetic anhydride.

There is, however, an outstanding difference between benzyltrimethylsilane and phenylethylether with regard to "specific ortho interaction" as proposed by Norman and Radda. In benzyltrimethylsilane there is no nucleophilic atom in the side chain, in fact the silicon atom is electrophilic in nature. Therefore a different mechanism must operate in this case.

Chernyshev et al.<sup>70</sup>, suggested that the organo-silicon compound and the nitronium ion form a reaction complex

in which the silicon is attached to an oxygen of the nitronium ion as shown in fig.X. In view of our ideas as

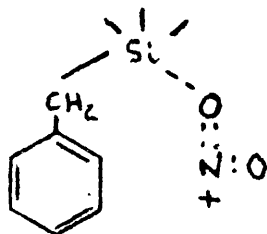
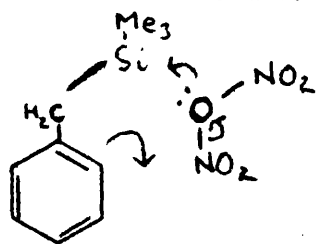


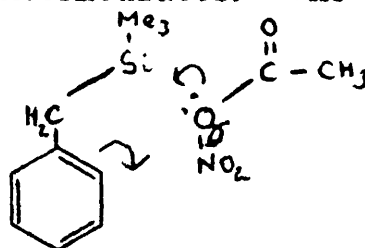
Fig.X

to the mechanism of nitrodesilylation, and the possible nitrating entities present in nitric acid/acetic anhydride solutions (discussed in Chapter 11), we do not think that this suggestion is correct. Furthermore, the silicon atom in tetra-organosilanes does not seem to form complexes even with strong electron donors such as nitrogen bases, and so is very unlikely to do so with a positively-charged species.

Two possible cyclic intermediates involving dinitrogen pentoxide (I), or acetyl nitrate (II), may be drawn, both of which involve six-membered cyclic intermediates. The



I



II

intermediate, I, although formally similar to that proposed by Norman and Radda (see fig. IX), is in fact different. In the intermediate, I, it is the oxygen atom

of the dinitrogen pentoxide molecule which acts as the electron donor. As a result of our studies on nitrodesilylation involving acetyl nitrate solutions, we think that the intermediate involving dinitrogen pentoxide is the most likely. The intermediate involving an acetyl nitrate molecule, II, however cannot be ignored.

It was found by Norman and Radda<sup>180</sup> that nitration of methyl 3-phenylpropylether with acetyl nitrate or nitric acid itself gave essentially the same isomer distribution. Specific ortho-interaction in this compound on their mechanism, would involve a seven-membered cyclic transition state, which would be less readily formed than its six-membered analogue. Similarly a seven-membered cyclic transition state would be necessary for the specific ortho nitration of 2-phenylethyltrimethylsilane; thus a high ortho/para ratio is not obtained with this compound.

2). In the nitration studies there is an increase in the  $f_o/f_p$  ratio for  $C_6H_5(CH_2)_4SiMe_3$  (see Table 10.8). Here again there appears to be an anomaly when a four-carbon atom alkyl chain is present in the molecule.

Calculation of the  $f_o/f_p$  ratios from the partial rate factors determined in nitration with fuming nitric acid in acetic anhydride at 25° (fig. XI, page 216),<sup>60</sup> gives:-

$$\overset{\text{Me}}{f_o} / \overset{\text{Me}}{f_p} = 0.83 \quad \text{and} \quad \overset{\text{Et}}{f_o} / \overset{\text{Et}}{f_p} = 0.45$$

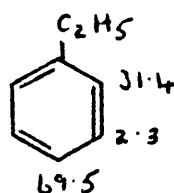
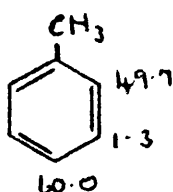


fig. XI

It appears that as we go from methyl to ethylbenzene the  $f_o/f_p$  ratio falls; whether this fall continues for the n-propyl group is not known, although preparative nitration of n-propylbenzene with nitric acid-sulphuric acid is reported to give approximately the same proportion of ortho isomer as ethylbenzene.<sup>298</sup> The  $f_o/f_p$  ratio (Table 10.8) show that in nitration of the compounds  $C_6H_5(CH_2)_2SiMe_3$  and  $C_6H_5(CH_2)_3SiMe_3$  the values 0.42 and 0.48, respectively, are close to the value determined for ethylbenzene. The increase in the  $f_o/f_p$  ratio for  $C_6H_5(CH_2)_4SiMe_3$  would, therefore, appear to be significant although no explanation can, at present, be given.

3). The  $f_o/f_p$  ratio obtained in the protodesilylation of benzyltrimethylsilane ( $f_o/f_p = 0.11$ ) is very low compared with the ~~value~~ values for the other compounds of the series (n = 2 to 4) which are comparable with  $\overset{\text{Me}}{f_o} / \overset{\text{Me}}{f_p}$  (0.82). This result ( $f_o/f_p = 0.11$ ) is completely contrary to that which would have normally been expected.

It has been shown that when the trimethylsilyl group is attached to a benzene ring there is an important -T

effect which opposes the expected +I effect (see Chapter I). When a methylene group is introduced between the Si atom and the phenyl nucleus then the +I effect must be reduced, although the -I effect is eliminated, and the strengths of the (trimethylsilylmethyl)-benzoic acids reveal the overall result.<sup>35</sup> The apparent ionisation constants of the acids in 50%-ethanol-water at 18° are shown in Table 10.10.

Table 10.10  
Apparent Ionisation Constants of RC<sub>6</sub>H<sub>4</sub>COOH in  
50% Aqueous Ethanol at 18°

R	H	<u>o</u> -Me	<u>o</u> -Me <sub>3</sub> SiCH <sub>2</sub>	<u>m</u> -Me	<u>m</u> -Me <sub>3</sub> SiCH <sub>2</sub>	<u>p</u> -Me	<u>p</u> -Me <sub>3</sub> SiCH <sub>2</sub>
10 <sup>6</sup> K <sub>A</sub>	2.00	2.00	0.457	1.70	1.00	1.32	0.832

It is evident from these results that the trimethylsilylmethyl group is strongly electron supplying. The most striking feature of the results is the decrease in acid strength caused by the group in the ortho position. This is extremely large in view of the general conclusion that all ortho substituents increase the strength of benzoic acids.<sup>290</sup> Also there is a relatively small difference between the effects caused by the Me<sub>3</sub>SiCH<sub>2</sub> group in the meta and para positions on the acid strengths. It was concluded that these results are consistent with the operation of a large +I effect from the silicon atom.<sup>35</sup> In o-(trimethylsilylmethyl)-benzoic acid the +I effect

operates so strongly as to outweigh the acid strengthening steric factors which normally predominate for ortho substitution.

Eaborn<sup>18</sup> concluded (from protodesilylation results), that the large difference observed in activating power of this group in the para and meta positions (activation ratio is 42:1 compared with 8:1 for the methyl group) arises from hyperconjugation of the type shown in fig. XII, since this could operate only to the ortho-para positions. It

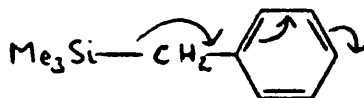


Fig. XII

was thought that the anomalously low activation by the m- $\text{Me}_3\text{SiCH}_2$  group, in view of the large inductive effect,<sup>35</sup> might possibly be due to steric hinderance to solvation since this bulky group must interfere with solvent approach to both positions ortho to itself, on which a substantial portion of the positive charge resides in the transition state.

All the data so far obtained on the effect of the  $\text{Me}_3\text{SiCH}_2$  group in aromatic systems suggests a high activation of the ortho-para positions. The result obtained for the protodesilylation of o-trimethylsilylbenzyltrimethylsilane is at present completely contrary to all expectations. It cannot be a steric effect, since

a bulky ortho group usually assists protodesilylation. As yet no reasonable hypothesis can be suggested to explain the observed facts.

An interesting feature which arises on comparison of the data given in figs. III and XI for nitration is the values of  $F_p$ . It appears that for the compounds  $C_6H_5(CH_2)_nSiMe_3$ , where  $n = 2$  to  $4$ , the para position is less reactive than the para position in toluene. This is completely contrary to what would have been predicted for these compounds. It is even more peculiar in the light of the corresponding figures for protodesilylation in which the  $f_p$  values are all greater than  $f_p^{Me}$  (fig. IV), and the possibility must be advanced that the partial rate factors for nitration are inaccurate.

## CHAPTER 11

### Acetyl Nitrate Solutions - The Mechanism of Nitrodesilylation.

In order to avoid the possibility of protodesilylation, solutions of nitric acid in acetic anhydride were used in the study of the mechanism of the cleavage of aryl-silicon bonds by nitrating agents (nitrodesilylation). Before we can discuss the mechanism of nitrodesilylation, however, the nature of nitric acid/acetic anhydride solutions and their mechanism of nitration must be discussed.

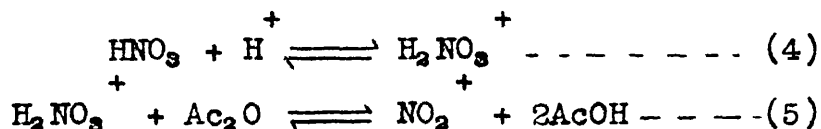
Despite the many and varied uses of nitric acid/acetic anhydride, the identity of the nitrating agent has, until recently, received little attention. Gold, Hughes and Ingold,<sup>147</sup> on the basis of their results with benzoyl nitrate, suggested that nitration by acetyl nitrate, proceeded through dinitrogen pentoxide formed in the following system of reactions:-



and therefore



Paul,<sup>178</sup> however, concluded from a study of the nitration of benzene with 90% nitric acid in excess acetic anhydride that the active nitrating species was the nitronium ion, formed in the following equilibria:-



Paul found that the reaction was approximately second order in nitric acid, that the reaction rate was retarded by nitrate ion, and was strongly accelerated by sulphuric acid.

Completely different conclusions were reached by Bordwell and Garbisch<sup>158</sup> during a study of the nitration of alkenes. They found that when the nitrating agent was prepared at  $-10^\circ$ , there was little evidence of reaction during the addition, and little or no nitration occurred on addition of the alkene at  $-15$  to  $-20^\circ$ . On the other hand, an exothermic reaction occurred when the acid was added to the anhydride at about  $20-25^\circ$  and addition of the alkene at  $-15$  to  $-20^\circ$  now gave a highly exothermic reaction.

The nitrating agent prepared at  $20-25^\circ$  gave, on nitration of anisole, a 80% yield of mononitroanisoles within five minutes at  $-10^\circ$ , whereas the nitrating agent prepared at  $-10^\circ$  gave only a 27% yield of mononitroanisoles. Addition of sulphuric acid (0.02mole) to the nitrating agent (prepared at  $20-25^\circ$ ) immediately prior to the addition of anisole produced a considerable increase in reactivity of the nitrating solution. In this case 37% of 2,4-dinitroanisole was obtained together with 41% of a mixture of mononitroanisoles.

Bordwell and Garbisch<sup>158</sup> interpreted these results

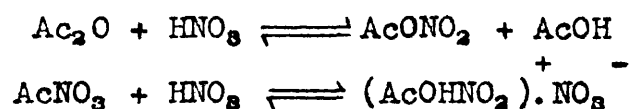
as meaning that addition of 70% nitric acid to acetic anhydride at  $-10^{\circ}$  produces little or no acetyl nitrate, and that solutions of nitric acid in water-acetic anhydride thus prepared are relatively ineffective nitrating agents. At  $20-25^{\circ}$  addition of nitric acid to acetic anhydride is accompanied by hydrolysis of the acetic anhydride, and reaction of the nitric acid with acetic anhydride to give acetyl nitrate. Acetyl nitrate or protonated acetyl nitrate ( $\text{AcOHNO}_2^+$ ) was thought to be a more effective nitrating agent than nitric acid or the nitric acidium ion ( $\text{H}_2\text{NO}_3^+$ ). Support for these conclusions was obtained by them when it was found that on addition of urea to the nitration solution prepared at  $-10^{\circ}$  the nitric acid was almost quantitatively precipitated as urea nitrate whereas the nitration solution prepared at  $20-25^{\circ}$  gave only 30-35% of the nitric acid as urea nitrate.

During our work we have repeated the experiments of Bordwell and Garbisch with anisole and have confirmed their experimental results (see Chapter 6, tables 6.11 and 6.12 for a summary of these results). It was found that when the nitric acid was added rapidly (3min.) to the acetic anhydride at  $-20 \pm 5^{\circ}$ , reaction with anisole at this temperature for 5 minutes gave only a 12-14% yield of mononitroanisoles. When the nitric acid was added dropwise, or rapidly, to the acetic anhydride at  $20-25^{\circ}$ , however, reaction with anisole for 2.5-3mins. gave mono-

nitroanisoles in yields of 91-5%. It was found, however, that when the nitric acid was added dropwise to the acetic anhydride at  $-20 \pm 5^\circ$  over a period of 30 minutes, nitration of anisole at this temperature gave 91-5% yields of mono-nitroanisoles. It appears that to prevent the formation of the nitrating entity the nitric acid must be added rapidly at temperatures below  $-10^\circ$ .

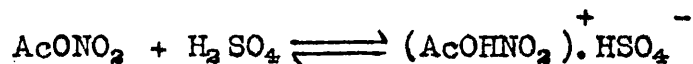
The nitration of alkenes with nitric acid/acetic anhydride<sup>158</sup> was found to give  $\beta$ -nitro acetates and  $\beta$ -nitro alkenes together with small amounts of  $\beta$ -nitro nitrates. Sulphuric acid was found to catalyse the reaction, while addition of nitrate ion, acetate ion, or urea lowered the rate of reaction, and also markedly increased the proportion of  $\beta$ -nitro nitrate formed.

The  $\beta$ -nitro acetate obtained from cis- and trans-2-butene were stereoisomeric and resulted from stereospecific cis addition to the double bond; the stereochemistry of the acid catalysed nitration was found to be identified with the non-catalysed reaction even though strong acid catalysts are known to cause interconversion of cis-trans isomers. Bordwell and Garbisch proposed that the nitrating species was protonated acetyl nitrate formed in the following reactions:-

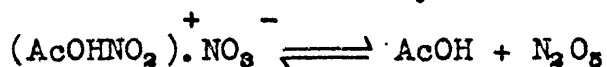


Catalysis by sulphuric acid was thought to be due to the

following reaction:-

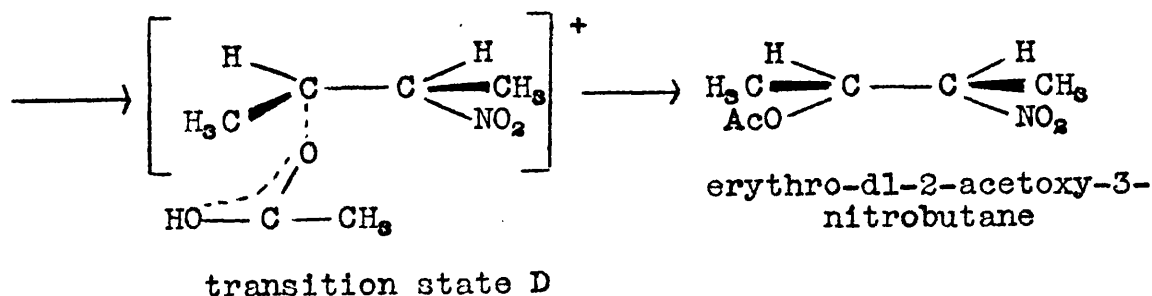
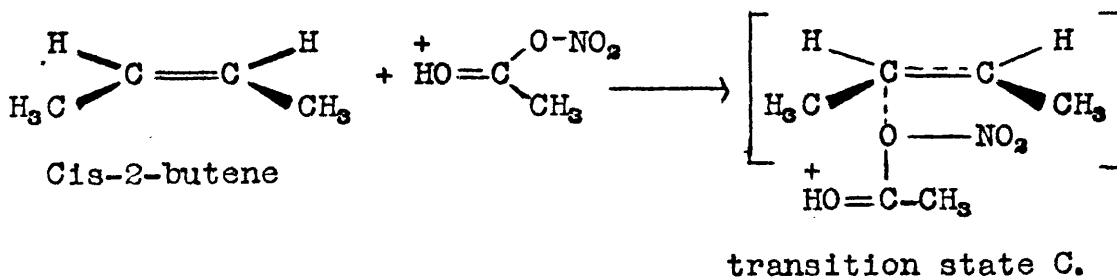


The formation of  $\beta$ -nitro nitrates was said to be due to the presence of small concentrations of dinitrogen pentoxide which could be formed by the reaction:-



The retarding effect of acetate ion and urea on the nitration was accounted for as destruction of the  $(\text{AcOHNO}_2)^+$  species by proton abstraction, and the retarding effect of nitrate ion was suggested to originate in increasing ratio of dinitrogen pentoxide to protonated acetyl nitrate.

The stereospecific cis-addition was thought to be due to a concerted addition of protonated molecular acetyl nitrate (or acetyl nitrate) to the double bond e.g.,



Although the presence of nitronium ions in acetic

anhydride-acetic acid solutions has not been detected in studies using several different methods<sup>170-4</sup> it cannot be excluded. Bordwell and Garbisch concluded that protonated acetyl nitrate and dinitrogen pentoxide were the active species since it is impossible to explain the stereochemistry of the alkene reaction to form  $\beta$ -nitro acetates<sup>158</sup> if the nitronium ion is assumed to be the nitrating species.

However, the addition to alkenes and the nitration of aromatic compounds are completely different reactions. Therefore, although the presence of acetyl nitrate (or protonated acetyl nitrate) and dinitrogen pentoxide in solutions of nitric acid/acetic anhydride have been conclusively demonstrated, that the nitronium ion is not the active nitrating species in the majority of electrophilic aromatic nitration reactions cannot be assumed. The fact that toluene gives ortho:para derivatives in the same proportions with acetyl nitrate as with nitric acid,<sup>177</sup> is evidence that there is a nitrating species common to both systems. This must be the nitronium ion, which is known to be responsible for nitration with nitric acid.

That anisole and acetanilide give rise to higher proportions of o-nitro derivatives when nitrated with nitric acid/acetic anhydride than when nitric acid or mixed acid is the reagent has long been known.<sup>146, 159, 161, 177</sup> de la Mare and Ridd suggested that some substitution might occur by an initial attack at the hetero-atom joined to

the aromatic ring, followed by intramolecular rearrangement.<sup>289</sup>

Norman and Radda extended this suggestion during an investigation of the ortho:para ratio in aromatic substitution.<sup>180, 184</sup> Investigation of the nitration of methylphenethyl ether showed that the ortho:para ratio was considerably higher in nitrations by acetyl nitrate (see Table 11.1), whereas the meta:para ratios were essentially the same for nitration with nitric acid and with acetyl nitrate.<sup>180</sup> If the change were the result of protonation of the oxygen atom in the aromatic compound by nitric acid, not only would the ortho:para ratio be lower in the acid conditions, but the meta:para ratio should be higher, for such protonation would result in greater deactivation of the para than of the meta-position; this, however, is not the case.

If the nitronium ion, alone were responsible for nitration of the ether with acetyl nitrate, the isomer ratio should be the same as that for nitration with nitric acid. There must, therefore, be another nitrating species present in acetyl nitrate which is capable of preferentially nitrating the ortho position of the ether.

Nitration of methyl phenethyl ether with benzoyl nitrate and with p-nitrobenzoyl nitrate in acetonitrile solution gives nitro derivatives in the same proportions as when acetyl nitrate is the reagent (see Table 11.0).<sup>180</sup>

Table 11.0

Nitration of Methyl Phenethyl Ether.<sup>180</sup>

Reagent	% Isomer Distribution		
	ortho	meta	para
HNO <sub>3</sub> -H <sub>2</sub> SO <sub>4</sub>	31.6	9.4	59.0
HNO <sub>3</sub>	40.2	6.6	53.2
HNO <sub>3</sub> -Nitromethane	41.2	3.0	55.8
HNO <sub>3</sub> -Ac <sub>2</sub> O	62.3	3.7	34.0
AcONO <sub>2</sub> -Acetonitrile	66.0	4.2	29.8
BzONO <sub>2</sub> -Acetonitrile	65.7	3.6	30.7
p-NO <sub>2</sub> BzONO <sub>2</sub> -Acetonitrile	64.9	4.7	30.4
N <sub>2</sub> O <sub>5</sub> -Acetonitrile	68.8	3.3	27.9

It therefore appeared, that the species which is responsible for the enhanced ortho reactivity must be common to the three acyl nitrates. The only nitrating species (other than the nitronium ion) known to be present is dinitrogen pentoxide,<sup>170-1, 173</sup> which was thought to be the nitrating entity in benzoyl nitrate.<sup>147</sup> Since dinitrogen pentoxide in acetonitrile gives the same isomer distribution as the acyl nitrates, the high ortho substitution in these nitrations must be due to dinitrogen pentoxide. Furthermore, toluene was found to give the same isomer distribution with dinitrogen pentoxide as with acetyl nitrate.

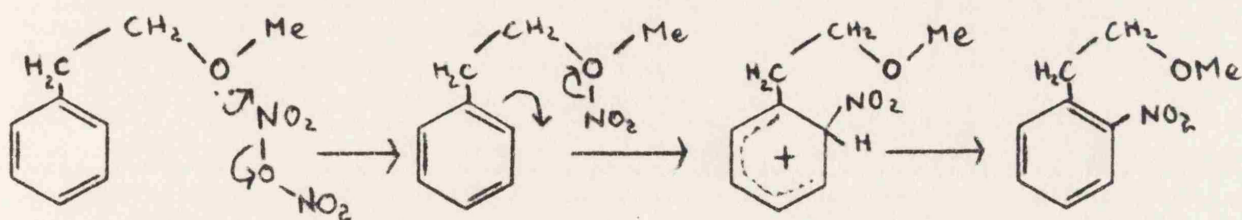
Norman and Radda<sup>180</sup> concluded that acyl nitrate, itself not reactive enough to bring about nitration of the aromatic compound, gave rise to acyl anhydride and dinitrogen pentoxide which reacts in two ways. It

undergoes slow heterolysis to the nitronium ion which reacts with the aromatic compound to give o-, m-, and p-nitro-derivatives in the same proportions as when nitric acid is the reagent; at the same time there is an additional mode of nitration at the ortho-position, dependent on the presence of the oxygen atom of the ether, and brought about by dinitrogen pentoxide itself.

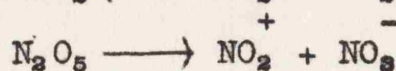
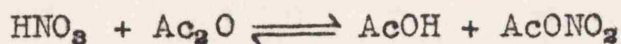
It is possible that the nitronium ion might be generated directly from the acyl nitrate by heterolysis of the O-N bond. If this were to happen, it was thought unlikely that each of the three acyl nitrates should generate nitronium ion at the same relative rate, as is required by the finding that the isomer distribution is constant for these three reagents.<sup>180</sup> This route to nitronium ion was, therefore, excluded.

The mechanism of the nitration of methyl phenethyl ether by dinitrogen pentoxide was considered as involving an S<sub>N</sub>2 displacement in which the oxygen atom displaces nitrate ion from covalent dinitrogen pentoxide, giving a charged intermediate. This rearranges through a six-membered cyclic transition state to a  $\sigma$ -bonded intermediate and finally to the o-nitro derivative. It was thought reasonable that the displacement occurs on dinitrogen pentoxide rather than on acyl nitrate since the nitrate ion has a greater stability than a carboxylate ion and should, therefore, be a better leaving group in such

displacements.



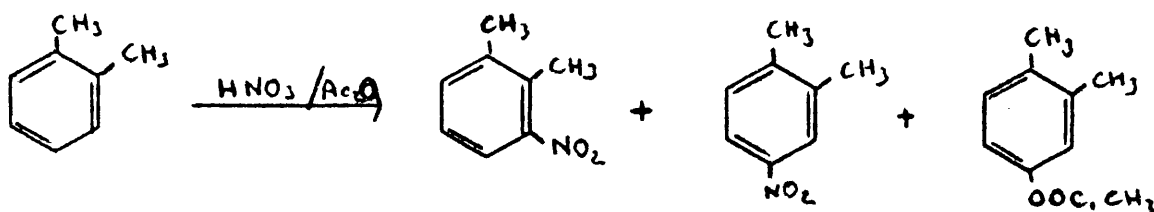
Further evidence for these suggestions was obtained when it was found that addition of catalytic amounts of sulphuric acid in the nitration of methyl phenethyl ether with acetyl nitrate decreases the proportion of *o*-nitro derivative from 62.3 to 55.1% while the meta:para ratio remained constant. It is known that both nitric acid and sulphuric acid bring about the dissociation of dinitrogen pentoxide into nitronium ions, the acid molecules aggregating around the covalent dinitrogen pentoxide causing ionic dissociation.<sup>147</sup> The normal rate of nitration is, therefore, increased relative to that which occurs by displacement on dinitrogen pentoxide. The conclusions of Norman and Radda as to the mechanism of nitration with nitric acid in acetic anhydride may be summarised in the following equations.



Gray and Lewis<sup>185</sup> found that the nitration of *p*-terphenyl by nitric acid in acetic anhydride and acetic acid was strongly retarded by nitrate ion whilst perchlorate ion had no effect. They concluded that in all cases the

attacking species was the nitronium ion.

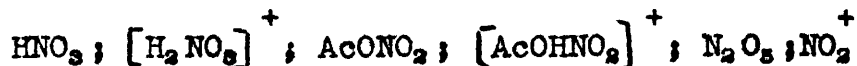
It was recently reported<sup>295</sup> that nitration of *o*-xylene at 0° with nitric acid in acetic anhydride besides giving the expected nitro derivatives, namely 3-nitroxylene (16%), and 4-nitroxylene (33%) also gave 3, 4-dimethylphenylacetate (51%), that is



With toluene, only 2% acetoxylation occurred, which is consistent with presence of an electrophilic acetoxyating species. Addition of sulphuric acid was found to increase the yield of acetoxy product. It was found that acetoxylation was accompanied by the release of an equivalent amount of nitrite ions.

On the basis of these results,<sup>295</sup> it was suggested that the acetoxyating species was protonated acetyl nitrate and that nucleophilic attack by an activated carbon takes place on the oxonium oxygen of the  $\text{AcOHNO}_2^+$  ion.

On consideration of all these results, the possible nitrating entities which may be present in nitric acid/ acetic anhydride solutions are as follows:-



It has been proved that nitric acid dissolved in excess

acetic anhydride is a relatively ineffective nitrating agent and that reaction of nitric acid with acetic anhydride is essential to successful nitrations. Therefore it is thought that both nitric acid and the nitric acidium ion can be rejected as possible nitrating species in these solutions. The conclusion of Paul,<sup>175</sup> that nitration in nitric acid/acetic anhydride solution occurs through the nitronium ion is thought to be correct, although the mechanism he proposed for its formation is not regarded as the main one.

We have shown that acetyl nitrate, prepared from acetyl chloride and silver nitrate in acetic acid/acetic anhydride/acetonitrile, is a relatively ineffective nitrating agent for p-tolyltrimethylsilane, only 29% of nitration occurring after 9 hours at -20°, whereas nitration with nitric acid in acetic anhydride occurs much more rapidly as shown in Table 11.1. Therefore, acetyl nitrate itself cannot be a very effective nitrating

Table 11.1

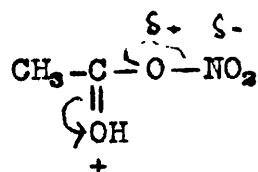
Nitration of p-Tolyltrimethylsilane at -20±5°C.

Reagent	Reaction Time	% Nitro Products
Acetyl nitrate	9hr	29.3
Acetyl nitrate (+0.002mole H <sub>2</sub> SO <sub>4</sub> )	9hr.	70.8
HNO <sub>3</sub> /Ac <sub>2</sub> O	15min.	32.5
HNO <sub>3</sub> /Ac <sub>2</sub> O	45min.	50.3

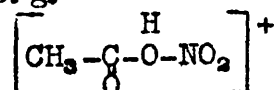
Note: Results from Tables 6.1 and 6.9

agent and cannot be the active species present in nitric acid/acetic anhydride solutions.

With solutions of nitric acid/acetic anhydride there is the possibility of acetoxylation occurring;<sup>295</sup> this is catalysed by sulphuric acid and must be an electrophilic substitution. It was concluded that protonated acetyl nitrate was the acetoxyating species. If this is the case, then protonated acetyl nitrate must be polarised in the direction shown below, which is consistent with the view that protonation of acetyl nitrate would occur at the carbonyl oxygen.



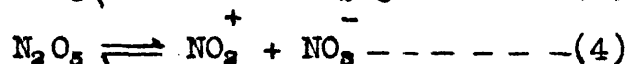
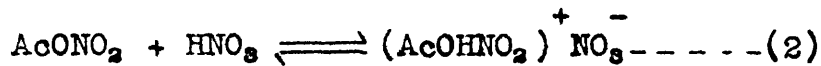
However, the possible existence in small amounts of another species e. g.



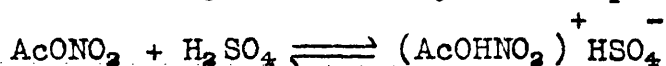
cannot be excluded. It is thought, however, that protonated acetyl nitrate is not the nitrating species in these solutions.

The only nitrating entities remaining are the nitronium ion and dinitrogen pentoxide, both of which are known to be powerful nitrating species. These nitrating entities are thought to be formed by the following series of reactions;



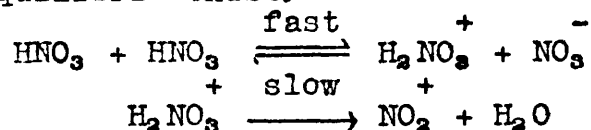


Addition of sulphuric acid increases the concentration of protonated acetyl nitrate by direct protonation

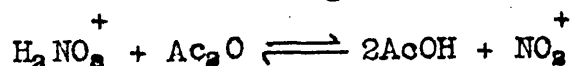


Nitrate ions would obviously reduce the concentration of protonated acetyl nitrate by shifting the equilibrium of equation 2 to the left thereby reducing the concentration of dinitrogen pentoxide and hence nitronium ion.

However it is known that in organic solvents the following equilibria exist.



Therefore Paul's suggestion that the nitric acidium ion reacts with the acetic anhydride with the formation of the nitronium ion cannot be ignored.



It is thought, however, that the nitric acid molecule would more readily protonate a C=O group than another nitric acid molecule and, therefore, the concentration of nitric acidium ion present in these solutions would be very small.

The possibility of the following reaction cannot be ignored:



This is probably the method of formation of  $N_2O_5$  in acetyl nitrate itself. If this equilibrium lies well to the left, it would account for the apparently poor reactivity of acetyl nitrate solutions.

### The Mechanism of Nitrodesilylation

It has been shown that the *p*-nitrotoluene obtained in the reaction of *p*-tolyltrimethylsilane with nitric acid in acetic anhydride solution is formed by nitrodesilylation and not by nitration of toluene formed by prior protodesilylation.<sup>296</sup> The actual mechanism of this nitrodesilylation reaction is, however, in doubt and an attempt will be made to propose a reasonable mechanism for this reaction.

Before we start considering possible mechanisms of nitrodesilylation it would be convenient to summarise the more important experimental facts which have been obtained and which any theory proposed must explain.

1). It was found that as the reaction proceeded so the amount of nitrodesilylation increased compared with the amount of nitration (see Table 11.2, page 235). This is thought to be due to the change in nitric acid concentration as the reaction proceeds. This supposition is supported by the fact that as the nitric acid concentration is increased so the ratio nitration/nitrodesilylation increases (see Table 11.3, page 235).

Table 11.2

Nitration of p-Tolyltrimethylsilane with

HNO<sub>3</sub>/Ac<sub>2</sub>O at -20°.

Reaction Time	Unreacted Silane %	Nitro-desilylation (p-nitrotoluene) %	Nitration (nitrosilane) %	Ratio of Nitration/Nitro-desilylation
10min.	63.2	3.2	28.9	9.0
15min.	60.2	2.1	30.4	14.4
30min.	50.9	4.7	37.3	7.9
45min.	41.6	5.3	45.0	8.5
9hr.	2.8	19.2	64.1	3.3

Note: These results are obtained from Table 6.1.

Table 11.3

Effect of Nitric Acid Concentration on the Nitration

of p-Tolyltrimethylsilane at 25°C.

HNO <sub>3</sub> (moles)	Nitrodesilylation %	Nitration %	Nitration/Nitrodesilylation
0.15	61.6	38.4	0.6
0.30	31.0	69.0	2.2
0.45	23.0	77.0	3.3

Note: These results are quoted as percentages of nitro products isolated. See Table 6.5.

Therefore the nitration reaction (cleavage of C-H bonds) depends on a higher power of the nitric acid concentration than does nitrodesilylation.

2). Addition of small quantities of sulphuric acid (0.002moles) not only increased the rate of reaction, but also reduced the ratio nitration/nitrodesilylation (that is, increased the proportion of nitrodesilylation) as shown in Table 11.4 for phenyltrimethylsilane.

Table 11.4

Effect of Sulphuric Acid on the Nitration of  
Phenyltrimethylsilane at 50°C.

Reaction Time	H <sub>2</sub> SO <sub>4</sub> added moles	Recovd silane %	Nitro-desilylation (nitrobenzene) %	Nitration (nitrosilane) %	Ratio of Nitration/ Nitro-desilylation
9hr.	-	-	49.6	40.3	0.8
10min.	0.002	59.0	18.5	11.0	0.6
3hr.	0.002	-	63.5	25.2	0.4

Note: These results are from Table 6.10.

This result must mean that sulphuric acid increases the concentration of a nitrating species which preferentially attacks the aryl-Si bond. Since the addition of sulphuric acid would increase the concentration of protonated species then either this protonated species preferentially attacks the aryl-Si bond or it is a necessary precursor in the formation of a nitrating species which attacks the aryl-Si bond.

3). The addition of nitrate ions was found to decrease markedly the rate of reaction (see Table 11.5, page 237),

although having no effect on the composition of the products (see Table 11.6). This means that nitrate ions affect the entities which attack the aryl-Si bond and the aryl-H bond to the same extent.

Table 11.5

Effect of Nitrate Ions on the Nitration of  
p-Tolyltrimethylsilane at  $-20 \pm 5^\circ\text{C}$ .

Reaction Time	Nitrate added (moles)	Unreacted Silane %	Nitro Products %
45min.	-	41.6	50.3
45min.	$\text{NaNO}_3$ (0.002)	83.9	9.4
45min.	$\text{LiNO}_3$ (0.002)	73.8	19.1

Note: These results are from Tables 6.1 and 6.2

Table 11.6

Effect of Nitrate Ion on the Nitration of  
p-Tolyltrimethylsilane at  $0-5^\circ\text{C}$ .

Nitrate Added (moles)	Nitrodesilylation %	Nitration %	Nitration/Nitrodesilylation
-	37.6	62.4	1.7
$\text{NaNO}_3$ 0.002	37.4	62.6	1.7
$\text{LiNO}_3$ 0.002	38.9	61.6	1.6

Note: These results are quoted from Leyshon, M.Sc. Thesis, University of Leicester, 1960.

4). Changing the composition of the medium from 90%  $\text{Ac}_2\text{O}$  - 10%  $\text{AcOH}$  to 20%  $\text{Ac}_2\text{O}$  - 80%  $\text{AcOH}$  caused a

marked increase in the nitration/nitrodesilylation ratio, but further change to 10% Ac<sub>2</sub>O - 90% AcOH caused a large decrease in the ratio (see Table 11.7).

Table 11.7

Nitration of p-Tolyltrimethylsilane at 25°C.

Nitration Medium	Nitro-desilylation %	Nitration %	Nitration/Nitro-desilylation
10% AcOH - 90% Ac <sub>2</sub> O	65.8	34.2	0.5
80% AcOH - 20% Ac <sub>2</sub> O	47.3	52.7	1.1
90% AcOH - 10% Ac <sub>2</sub> O	80.3	19.7	0.3

Note: These results are from Table 6.4.

5). Nitration of p-tolyltrimethylsilane with dinitrogen

Table 11.8

Nitration of p-Tolyltrimethylsilane with Dinitrogen

Pentoxide in Ac<sub>2</sub>O/AcOH at -20°C.

Reaction Time	Added Reagent (moles)	Recov'd Silane %	Nitro-desilylation %	Nitration %	Nitration/Nitro-desilylation
15min.	-	58.5	11.7	22.2	1.9
9hr.	-	3.1	48.6	39.8	0.8
15min.	H <sub>2</sub> SO <sub>4</sub> 0.002	18.7	36.1	35.9	1.0
9hr.	0.002	-	42.8	43.0	1.0
15min.	LiNO <sub>3</sub> 0.002	86.5	1.9	3.8	2.0
9hr.	0.002	28.5	23.3	38.9	1.7

Note: These results are obtained from Tables 6.6 and 6.7.

pentoxide in acetic acid/acetic anhydride was found to give similar results to those obtained with solutions of nitric acid/acetic anhydride. A higher percentage of nitrodesilylation (a lower nitration/nitrodesilylation ratio), however, was observed under analagous conditions (see Table 11.8). Although sulphuric acid increased the rate of reaction, it did not increase the proportion of nitrodesilylation as in nitric acid/acetic anhydride solutions; in fact, there was a slight increase<sup>in</sup> the nitration/nitrodesilylation ratio. Nitrate ions were found to decrease the rate of reaction as with nitric acid/acetic anhydride solutions, although in this case a slight increase in nitration/nitrodesilylation ratio was observed.

6). Nitric acid was found not only to increase the rate of reaction of dinitrogen pentoxide with *p*-tolyltrimethylsilane in acetic acid/acetic anhydride but also to markedly increase the rate of nitration compared with nitrodesilylation (see Table 11.9). Increasing the concentration of dinitrogen pentoxide did not produce a corresponding increase in the nitration/nitrodesilylation ratio, in contrast to the results obtained for nitric acid/acetic anhydride solutions.

7). Increasing temperature favours the nitrodesilylation reaction to such an extent that in the case of phenyltrimethylsilane, the reaction changes from one in which there is almost complete nitration at 0-5° to one in

which there is almost complete nitrodesilylation at 100°, as shown in Table 11.10.

Table 11.9

Nitration of p-Tolyltrimethylsilane with Dinitrogen Pentoxide in Ac<sub>2</sub>O-AcOH at -20°C.

Reaction Time	N <sub>2</sub> O <sub>5</sub> moles	Recovd Silane %	Nitro-desilylation %	Nitration %	Nitration/Nitro-desilylation
45min.	0.15	42.0	33.2	16.0	0.5
45min.	0.15 *	32.0	22.0	37.6	1.7
5hr.	0.15	5.5	33.8	48.1	1.4
5hr.	0.24	-	33.2	52.7	1.6

Note: \* 1g. HNO<sub>3</sub> added. These results are obtained from Table 6.8.

Table 11.10

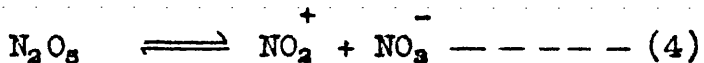
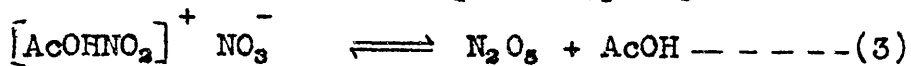
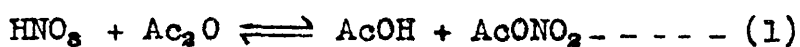
The Effect of Temperature on the Reaction of Phenyltrimethylsilane with HNO<sub>3</sub>/Ac<sub>2</sub>O.

Temperature °C.	0-5°	50±2.5°	100±5°
Nitrodesilylation %	5.3	50.6	92.3
Nitration %	94.7	49.4	7.7

Note: These results are quoted from Keyshon, M.Sc. Thesis, University of Leicester, 1960.

As was stated earlier, of the possible nitrating species which are present in nitric acid/acetic anhydride

solutions it was concluded that the two main nitrating agents were the nitronium ion and dinitrogen pentoxide formed in the following system of reactions:-

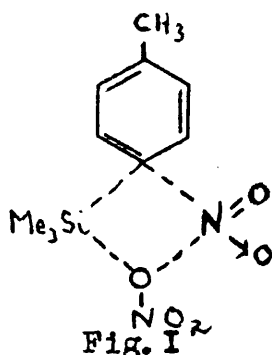


It has been shown that nitric acid itself, in acetic anhydride solutions, is not an effective nitrating agent and similarly acetyl nitrate was shown to be a relatively ineffective agent for the nitration of *p*-tolyltrimethylsilane. Also protonated acetyl nitrate was considered to be an acetoxyating agent and not a nitrating agent, and the nitric acidium ion is known to undergo heterolysis into the nitronium ion. Therefore, it is considered that the nitronium ion and dinitrogen pentoxide are the active species for the reaction with aryl-silicon compounds.

The experiments with nitronium tetrafluoroborate have shown, however, that the nitronium ion itself, does not, at least to an appreciable extent, cause cleavage of aryl-silicon bonds. This, at first, may seem surprising when one considers that the nitronium ion is a powerful electrophilic reagent, and that aryl-Si bonds readily undergo electrophilic attack. However, it is now thought likely that whenever electrophilic attack at an aryl-Si bond is much faster than at an aryl-H bond, the cleavage

proceeds via a cyclic process in which nucleophilic attack on silicon accompanies electrophilic attack on carbon and, therefore, cleavage by the nitronium ion which contains no nucleophilic entity does not occur readily.

It seems that the cleavage of aryl-silicon bonds in acetyl nitrate solutions must involve dinitrogen pentoxide, and proceed by a four-centre transition state as shown below



These conclusions as to the mechanism of the reaction of aryl-silanes with acetyl nitrate solutions, and to the manner in which the dinitrogen pentoxide and nitronium ions formed can account for the majority of the experimental facts obtained.

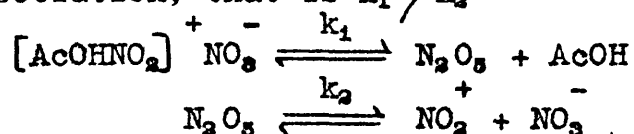
On consideration of equations 1-4 (page 241) it is obvious that both nitration and nitrodesilylation are second order in nitric acid and, therefore, their rates of reaction should have the same dependence on the nitric acid concentration. However, it is known that this is not so; the rate of nitration increasing faster than the rate of nitrodesilylation with increasing concentration

of nitric acid. The dissociation of covalent dinitrogen pentoxide into nitronium ions is known to be catalysed by nitric acid; therefore, addition of nitric acid increases the rate of dissociation of the dinitrogen pentoxide. This would result in a reduced rate of nitrodesilylation and an increased rate of nitration.

The catalysis by sulphuric acid must occur through the increased production of a positive species. This cannot be the nitronium ion because it is the rate of nitrodesilylation which is increased more than the rate of nitration. Therefore addition of sulphuric acid must increase the concentration of protonated acetyl nitrate according to the following equation:-



In order to explain the increase in nitrodesilylation as compared with nitration it is necessary to propose that the rate of formation of dinitrogen pentoxide, from protonated acetyl nitrate, is slightly faster than its rate of dissociation, that is  $k_1 > k_2$



The addition of nitrate ions, since it retards both nitration and nitrodesilylation to the same extent must act by reducing the concentration of protonated acetyl nitrate.

The variation in nitration/nitrodesilylation ratio with

the composition of the medium may have something to do with the dielectric constant favouring dissociation of the dinitrogen pentoxide into nitronium ions.

The effect of variation of temperature upon the composition of the products is possibly a combination of several factors. The series of reactions resulting in nitration may well have, overall, a low apparent log A factor (resulting from a high order of reaction), and a low activation energy. Nitrodesilylation, on the otherhand, could have a higher activation energy and a higher log A factor. Increasing the temperature would thus not only increase the rate of nitrodesilylation more than it would increase the rate of nitration, but it would also enable nitrodesilylation to become predominant. Temperature would also affect the various equilibria to differing extents which are not easily predictable. Also at higher temperatures nitrodesilylation via acetyl nitrate and the nitronium ion may become important.

The increased percentage of nitrodesilylation with solutions of dinitrogen pentoxide in acetic anhydride is to be expected if dinitrogen pentoxide is responsible for aryl-Si bond cleavage. The slight increase in the nitration/nitrodesilylation ratio on the addition of small quantities of sulphuric acid can be explained by the increased dissociation of dinitrogen pentoxide into nitronium ions caused by the sulphuric acid. Similar

equilibria would be present with solutions of dinitrogen pentoxide in acetic anhydride as with nitric acid/acetic anhydride, therefore, nitrate ions would be expected to decrease the rate of reaction. The increase in the ratio nitration/nitrodesilylation could be due to catalysis of nitration by dinitrogen pentoxide.

In conclusion it can be said that reaction of aryl-silicon compounds with nitric acid/acetic anhydride occurs by attack of dinitrogen pentoxide on the aryl-Si bond and by nitronium ion attack on the aryl-H bond, perhaps with some attack also by dinitrogen pentoxide on the aryl-H bond. The cleavage of the aryl-Si bond by dinitrogen pentoxide is thought to proceed via a four-centre mechanism which is not available for the nitronium ion.

## CHAPTER 12

### Nitrodesilylation of Benzyltrimethylsilanes.

Direct nitration of benzyltrimethylsilanes<sup>58, 70-1</sup> gives o-nitrobenzyltrimethylsilane (80%) and p-nitrobenzyltrimethylsilane (20%). Therefore, pure p-nitrobenzyltrimethylsilane can only be obtained in very poor yields, whilst the meta-isomer cannot be made by direct nitration.

It was thought that the best method for the preparation of p-nitrobenzyltriethylgermane would be the nitrodesilylation of p-trimethylsilylbenzyltriethylgermane according to the procedure described for the preparation of nitroarylgermanes.<sup>65</sup> This reaction was attempted by Swaddle,<sup>16</sup> who found that no pure product could be isolated, a complex mixture of solid products being obtained.

It was thought, therefore, that an investigation of the nitrodesilylation of m- and p-trimethylsilylbenzyltrimethylsilane would be of interest.

It was found that although m-trimethylsilylbenzyltrimethylsilane, on reaction with nitric acid in acetic anhydride at 100°, gave nitro products in approximately 75% yield, no pure m-nitrobenzyltrimethylsilane could be isolated. Instead, a mixture of m-nitrobenzyltrimethylsilane and nitrated m-trimethylsilylbenzyltrimethylsilane was obtained. This is due to the influence of the trimethylsilyl group on the other positions of the phenyl nucleus (this is discussed in Chapter 13).

When *p*-trimethylsilylbenzyltrimethylsilane, however, is treated with nitric acid in acetic anhydride at 50° no nitroarylsilicon compounds are isolated. Instead, as was found by Swaddle<sup>16</sup> for *p*-trimethylsilylbenzyltriethylgermane, a complex mixture of products was obtained from which were isolated small quantities of *p*-nitrobenzaldehyde and *p*-nitrobenzoic acid.

This result supports the findings of Chernyshev and Tolstikova<sup>72</sup> who reported that when, the compounds  $p\text{-R}_3\text{SiC}_6\text{H}_4(\text{CH}_2)_n\text{SiMe}_3$  (where  $n = 1$  to 4), are treated with nitric acid in acetic anhydride they are almost quantitatively oxidised, and the expected nitro compounds are formed in yields of less than 3%.

It was thought that nitration with acetyl nitrate, prepared from acetyl chloride and excess silver nitrate, would avoid the problem of oxidation, but even higher yields of *p*-nitrobenzaldehyde and *p*-nitrobenzoic acid were obtained.

Since benzyltrimethylsilane is nitrated readily by nitric acid in acetic anhydride, it was thought that the products obtained on cleaving a  $\text{SiMe}_3$  group from the phenyl ring might be causing the oxidation in the case of *p*-trimethylsilylbenzyltrimethylsilane. For this reason the nitration of benzyltrimethylsilane was carried out in the presence of *p*-tolyltrimethylsilane; however, good yields of nitro products were obtained and, therefore, the removal

of the  $\text{SiMe}_3$  group cannot be causing this oxidation. Nitration of p-methyl-, and p-chlorobenzyltrimethylsilane were also carried out successfully. Since m-trimethylsilylbenzyltrimethylsilane was not oxidised under these conditions, it appears that only when there is a p- $\text{Me}_3\text{Si}$  group in the benzylsilane (or germane) does this oxidation occur.

These results are very surprising since the p- $\text{Me}_3\text{Si}$  group should not influence the reactivity of these compounds appreciably. It is even more surprising with p- $\text{Me}_3\text{SiC}_6\text{H}_4(\text{CH}_2)_n\text{SiMe}_3$ , if  $n > 1$ , since it is not appreciably different from  $\text{Me}_3\text{SiC}_6\text{H}_4(\text{CH}_2)_n\text{H}$ . It would appear that p-trimethylsilylbenzyltrimethylsilane is an extremely reactive compound especially towards electrophilic reagents, No logical explanation can, however, be suggested for this phenomenon.

## CHAPTER 13

### Nitrodesilylation - A Synthetic Method.

It was Deans and Eaborn<sup>64</sup> who first utilised the cleavage of an aryl-Si bond by a nitrating agent (nitrodesilylation) to prepare a pure nitroaryl silicon compound. They treated *p*-bistrimethylsilylbenzene with fuming nitric acid in refluxing acetic anhydride and obtained an 80% yield of pure *p*-nitrophenyltrimethylsilane.

This technique has recently been successfully employed for the preparation of nitroaryl-germanium compounds.<sup>65</sup> Triethyl-*m*-, and *p*-nitrophenylgermane have been prepared by the analogous reaction, nitrodegermylation of *m*-, and *p*-bistriethylgermylbenzene with nitric acid-acetic anhydride at 100°.

Chvalovský and Bazant<sup>66</sup> have used this technique for the determination of aryl groups directly bound to silicon in mixed arylalkylsilanes and arylalkylsiloxanes by the selective removal of the aryl groups with nitric acid. Thus, this method of introducing a nitro group into a specified position in an aromatic ring could also be applied to the preparation of pure nitro isomers of aromatic compounds.

In the nitrodesilylation of 4,4'-bistrimethylsilylbiphenyl, on addition to the expected 4-nitro-4'-trimethylsilylbiphenyl, a very small amount of 4,4'-dinitrobiphenyl was obtained. In the nitrodesilylation of the bis-trimethyl-

silylbiphenyl, on addition to the expected 4-nitro-4'-trimethylsilylbiphenyl, a very small amount of 4,4'-dinitrobiphenyl was obtained. In the nitrodesilylation of the bistrimethylsilylbenzenes no dinitro product was obtained, the introduction of one nitro group into the aromatic ring being sufficiently deactivating as to prevent the cleavage of the second aryl-Si bond. In the biphenyl system, however, it would appear that the introduction of a nitro group in the 4-position does not deactivate the 4'- position sufficiently to prevent a small amount of cleavage of the second aryl-Si bond.

This result is to be expected from the work of Greasley,<sup>291</sup> who found that in protodesilylation<sup>291</sup> a 4'-nitro substituent only deactivates the 4-position in biphenyl by a factor of only 10.

In the present work the nitrodesilylation of several other aryl-Si compounds have been attempted, and several limitations of the method as a synthetic route have been found.

Almost exclusive nitrodesilylation of *p*-methoxyphenyltrimethylsilane was attempted, it was found that less than 3% of nitrodesilylation in fact occurred, even at 135-40°; the preferred reaction being nitration of the aromatic ring with the formation of a mixture of nitro-aryl silanes.

That this should be the case is understandable when

the relative reactivities of the ortho, -meta, -and para-positions of anisole, as determined by protodesilylation, is considered (see fig. 1).<sup>292</sup>

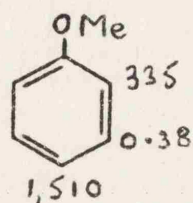


Fig. 1.

Therefore, in order that nitrodesilylation may occur, the aromatic compound must not contain a group which strongly activates other positions of the nucleus relative to the aryl-Si bond.

This is the reason why the compound m-Me<sub>3</sub>SiC<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>SiMe<sub>3</sub> did not yield m-nitrobenzyltrimethylsilane on reaction with nitric acid in acetic anhydride. The Me<sub>3</sub>SiCH<sub>2</sub> group strongly activates the ortho-para positions in nitration, and, therefore nitration of the aromatic ring occurs rather than aryl-silicon bond cleavage.

Another limitation of the use of nitrodesilylation as a synthetic route has been discussed in Chapter 12. Compounds of the type p-Me<sub>3</sub>SiC<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>n</sub>SiMe<sub>3</sub> on treatment with nitric acid in acetic anhydride or with acetyl nitrate, prepared from acetyl chloride and silver nitrate, are oxidised, no nitroaryl silicon compounds being isolated.

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