

Cleavage of Aryl-Silicon Bonds by  
Electrophilic Reagents

A Thesis

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

by

Robert Charles Moore

The University, Leicester

November, 1961

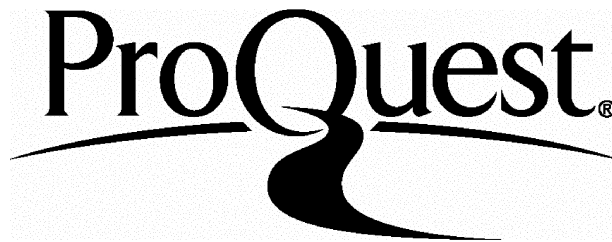
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Statement

All the experimental work described within this thesis has been carried out by the author in the laboratories of the Department of Chemistry, The University, Leicester, between October 1958 and the present date.

The work has not been presented, and is not being concurrently presented for any other degree.

*R. C. Foote.*

November 1961



### Acknowledgement

I would like to express my sincere thanks to Dr C. Eaborn who suggested the subject of this thesis and who has been a source of kindly guidance and encouragement in every aspect of this work.

My thanks are also owed to Professor L. Hunter, members of the staff and members of the research department of the Department of Chemistry, The University, Leicester, for their interest in the work.

Finally, I would like to thank the Aeronautical Research Laboratory of the U.S.A.F. who through its European Office provided a maintenance grant.

R. C. Foote.

### Summary

A survey is presented of the literature on cleavage of aryl-silicon bonds by electrophilic reagents.

The following compounds have been prepared: (i) a series of triaryl- and trialkyl-*p*-anisylsilanes (ten of them new), (ii) the compounds (*p*-anisyl)<sub>4-x</sub> Si(OEt)<sub>x</sub>, where x=1 to 3, (all new), and (iii) four cyclic compounds (one of them new), in which silicon, joined to two aromatic nuclei, is part of the ring system.

Rates of cleavage of these compounds by aqueous-methanolic perchloric acid have been measured at 50°. For triaryl-*p*-anisylsilanes, (X·C<sub>6</sub>H<sub>4</sub>)<sub>3</sub> SiC<sub>6</sub>H<sub>4</sub>·OMe-*p*, and trialkyl-*p*-anisylsilanes, R<sub>3</sub>SiC<sub>6</sub>H<sub>4</sub>·OMe-*p*, increase in electron supply from X and R increases the rate of cleavage. The logarithms of the relative rates of cleavage for the (X·C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>SiC<sub>6</sub>H<sub>4</sub>·OMe-*p* compounds correlate satisfactorily with Hammett's σ constants for the various substituents, X. When X=O-Me, the rate of cleavage is very low, presumably because of steric hindrance to cleavage. For the series Me<sub>3-x</sub>Ph<sub>x</sub>SiC<sub>6</sub>H<sub>4</sub>·OMe-*p* (x=0 to 3), stepwise replacement of methyl by phenyl causes a stepwise decrease in the rate of cleavage. The rates of cleavage of the compounds (*p*-anisyl)<sub>4-x</sub> Si(OEt)<sub>x</sub> (x=0 to 3) differ little from one another but are in the order x=0 < 1 < 2 > 3. When silicon is part of the ring system the Si-aryl bond appears to have increased stability.

Rates of cleavage of the triaryl- and trialkyl-*p*-anisylsilanes and of the cyclic organosilicon compounds by bromine in 1.5 wt.% aqueous acetic acid at 25° have been measured. The logarithms of

the relative rates for the cleavage correlate well with the logarithms of the relative rates for acid cleavage, but there are deviations, which are discussed.

Rates of cleavage of triaryl- and trialkyl-p-anisylsilanes by mercuric acetate in 20 wt.% aqueous acetic acid at 25° have been measured. The logarithms of the relative rates for the cleavage correlate well with both the logarithms of relative rates for cleavage by acid and for cleavage by bromine; again some deviations occur and these are discussed.

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SECTION I. Introduction

## CHAPTER I

### Electrophilic cleavage of aryl-silicon bonds

Kipping<sup>1a,b,c</sup> has shown that a phenyl group is easily cleaved from silicon by concentrated sulphuric acid. When substituents were present in the aromatic nucleus, the ease of cleavage paralleled the ease of electrophilic aromatic substitution, for the  $\text{Si-C}_6\text{H}_4\text{NH}_2\text{-p}$  link was readily and the  $\text{Si-C}_6\text{H}_4\text{NH}_2\text{-m}$  link much less readily cleaved by acid, but the  $\text{Si-C}_6\text{H}_4\text{NO}_2$  link, was very stable to acid<sup>2</sup> for both meta- and para- nitro groups.

Similar observations were made when nitrophenyltrimethylsilanes were treated with bromine<sup>3</sup>. The trimethylsilyl group was removed with great difficulty from o-nitrophenyltrimethylsilane by bromine but the corresponding meta- substituted compound was cleaved readily by this reagent. It was therefore concluded that this could possibly be due to steric requirements of the bulky ortho substituents or that elimination of the trimethylsilyl group from the aromatic nucleus indicated an attack by an electrophilic group on the aromatic carbon holding the silicon. Consequently o-nitrophenyltrimethylsilane would resist cleavage more than the meta isomer and there would not be any marked difference between the ortho and para isomers.

Towards hydrogen chloride in glacial acetic acid the lability of the trimethylsilyl group in para-substituted trimethylarylsilanes,  $\text{Me}_3\text{SiAr}$ , decreased in the order:  $\text{Ar=p-anisyl}$  and  $\text{p-dimethylaminophenyl}$ >

p-tolyl > phenyl > p-chlorophenyl, <sup>4</sup> i.e. the ease of cleavage by an acidic reagent thus appeared to be facilitated when the trimethylarylsilane contained substituents capable of furnishing a high electron density at the aryl C-Si bond. This observation led Benkeser to postulate the following mechanism <sup>5</sup> which involved proton attack on the carbon atom holding silicon. (Fig.I)



R = o- or p- director

In an extended series of meta- and para- substituted aryltrimethylsilanes, the rate of cleavage by hydrogen chloride in glacial acetic acid was

p-methoxyphenyl and p-dimethylaminophenyl > p-tolyl > m-methoxyphenyl > m-tolyl > phenyl > p-chlorophenyl > m-chlorophenyl > m-dimethylaminophenyl. This order was as would be

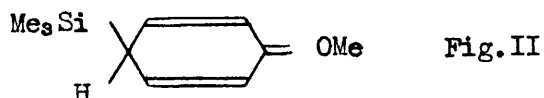
expected when considering electron supply by the substituent in the ring. <sup>5</sup>

Eaborn <sup>6</sup> also observed by consideration of the work of Gilman and Marshall <sup>4</sup> in which para-substituted trimethylarylsilanes were cleaved by hydrogen chloride in glacial acetic acid and because p-methoxyphenyltrimethylsilane was cleaved much faster than phenyltrimethylsilane that the effects of substituents on the acid cleavage of silicon-aryl bonds appeared to parallel those on aromatic substitution. It was concluded that the p-methoxy-group probably activated through its +E effect, and that the reaction was in fact an electrophilic aromatic substitution in which a proton



initially solvated was the attacking species.

An intermediate of the structure (Fig.II)



was postulated and a mechanism for the reaction was given (see Chapter III). This intermediate was later considered to be the usual  $\sigma$ -complex (Fig.III), of the type which have been postulated



for other electrophilic aromatic substitution reactions.<sup>7</sup>

The general pattern of effects of nuclear substituents R on the reactivity of  $\text{RC}_6\text{H}_4\text{SiMe}_3$  compounds towards perchloric acid in aqueous methanol<sup>7</sup> and sulphuric acid in acetic acid/water<sup>8a,b</sup> was similar to that obtained for electrophilic aromatic substitution and there was an excellent correlation between the substituent effects in acid cleavage and the substituent constants  $\sigma^+$ <sup>8a,b</sup> which have been proposed for electrophilic aromatic substitution. A plot of  $\log k_{\text{rel}}$  against  $\sigma^+$  (where  $k_{\text{rel}}$  is the rate of reaction of a substituted compound relative to that of phenyltrimethylsilane) was a good straight line.

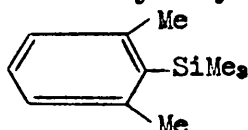
Steric effects have been observed in the cleavage of trimethylsilylxylenes by *p*-toluenesulphonic acid in acetic acid.<sup>10a,b</sup> The observed and calculated rates of cleavage are given in Table I.

TABLE I

Compound (R=Me <sub>3</sub> Si-)	Partial Relative Rate	
	Calculated	Observed
2-R- <u>p</u> -xylene	34.4	34.8
4-R- <u>m</u> -xylene	225	277
2-R- <u>m</u> -xylene	246	3380
4-R- <u>o</u> -xylene	31.3	33.6
3-R- <u>o</u> -xylene	34.4	94
R-benzene	-	1.00
<u>o</u> -R-toluene	-	15.7
<u>m</u> -R-toluene	-	2.19
<u>p</u> -R-toluene	-	14.3

The agreement, which showed that the effects were additive, was generally good except in the case of 2-trimethylsilyl-m-xylene and 3-trimethylsilyl-o-xylene. The acceleration in rate has been ascribed to a relief of steric strain when desilylation occurred.

The structure of 2-trimethylsilyl-m-xylene passes from



to the protonated intermediate Fig. IV in which the bonds at the C of the C-Si bond are tetrahedrally disposed

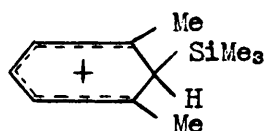


Fig. IV

and thus a relief of steric strain occurs.

With 3-trimethylsilyl-o-xylene the presence of two adjacent methyl groups was thought to cause a buttressing effect and this would favour the formation of the reaction intermediate and the subsequent cleavage.

The analogy between bromodesilylation and aromatic bromination also exists, for the relative rates of cleavage of the trimethylsilyl group by bromine in carbon tetrachloride were in the order  
 2-bromo-5-trimethylsilylthiophene > phenyltrimethylsilane >  
m-nitrophenyltrimethylsilane > p-nitrophenyltrimethylsilane >  
o-nitrophenyltrimethylsilane as would be predicted for electrophilic  
 11  
 substitution.

The reaction between a range of substituted phenyltrimethylsilanes and bromine in glacial acetic acid containing 1.5 wt % of water was very similar to aromatic bromination in the same medium.<sup>12a,b</sup>  
 Bromodesilylation of phenyltrimethylsilane was approximately second order for initial bromine concentrations < 0.01M but bromination of anisole, which had a comparable rate, was of markedly higher order. In molecular bromination the order increased with initial concentration of bromine<sup>13</sup> and this was also true of bromodesilylation. The order can even exceed three but at all concentrations studied it was lower than that of bromination. The pattern of substituent effects was very similar to that in acid cleavage and hence also very similar to that observed for electrophilic aromatic substitution. However, this pattern differed widely from molecular halogenation and resembled more closely bromination by  $\text{Br}^+$  and  $\text{BrOH}_2^+$ .

Mercuridesilylation by mercuric acetate in glacial acetic acid is also an electrophilic aromatic substitution, the attacking species being the mercuriacetate ion. The reactivities of trimethyltolyl- and trimethylxylylsilanes towards this cleavage reagent were essentially the same as those observed for the acid cleavages.<sup>14</sup> For a series of nuclear substituted aryltrimethylsilanes the general pattern of substituent effects for mercuridesilylation correlated well with those found for bromodesilylation and protodesilylation of the same series of silanes.<sup>15</sup> However, there was poor correlation between the substituent effects and  $\sigma^+$  constants as a plot of  $\log k_{rel}$  against  $\sigma^+$  did not give a good straight line, some of the points, in particular m-phenyl and p-fluoro and the unsubstituted compound being well off the line.

## CHAPTER II

### Effects of varying R in $R_3Si-Ar$

Cleavage studies have been largely limited to the removal of the trimethylsilyl group because removal of such a group can be conveniently followed.

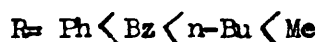
In the reaction between aryltrimethylsilanes and hydrogen chloride in glacial acetic acid,<sup>4</sup> cleavage occurred readily and the volatile cleavage product trimethylchlorosilane could be condensed in a cold trap, and the course of the reaction thus followed. With aryltriphenylsilanes ( $Ph_3SiR$ ) the rate of cleavage of silicon-phenyl bonds was of the same order as that for the breaking of the Si-R bond and therefore it was difficult to separate cleavage products.

The reactivity of substituted phenyltrimethylsilanes towards aqueous methanolic perchloric acid was followed by an ultra-violet spectrophotometric method.<sup>7</sup> Hexamethyldisiloxane, the cleavage product, since it does not absorb in the ultra-violet does not interfere with kinetic measurements.

Other advantages of trimethylarylsilanes are the easy commercial availability of trimethylchlorosilane and the relative ease of preparation of aryltrimethylsilanes. Hence considerable emphasis has been placed on the study of the rate of cleavage of the trimethylsilyl group from various aromatic nuclei and little systematic work has been carried out on the effect of varying the alkyl groups attached to silicon. However, in general, increase in the size of the group R attached to silicon raises the stability

of the Si-C aryl bond towards electrophilic reagents.

For silanes of the type  $R_3Si-Ar$ , the reactivity of the Si-Ar bond toward hydrogen chloride in glacial acetic acid was found to decrease in the following order<sup>4</sup>



The difference in stabilities of the  $Ph_3Si-C$  bond and the  $Me_3Si-C$  bond was shown by the reaction of tetraphenylsilane and trimethylphenylsilane with hydrogen chloride in refluxing glacial acetic acid. With the former slow decomposition occurred to give benzene and triphenylsilanol<sup>16</sup> but the latter gave a 70% yield of trimethylchlorosilane after 6 hours.<sup>4</sup>

Similarly, 4-triphenylsilyldibenzothiophene was unattacked by hydrogen chloride in boiling glacial acetic acid but under these conditions complete cleavage of the corresponding 4-trimethylsilyl compound occurred.<sup>17</sup> This difference in stabilities of the  $Ph_3Si-C$  and  $Me_3Si-C$  bonds was again demonstrated by the cleavage of trimethylsilyl- and triphenylsilylnaphthols.<sup>18</sup>

6-Trimethylsilyl-2-hydroxynaphthalene was cleaved by refluxing with 20% hydrochloric acid for 6 hours whereas the corresponding 6-triphenylsilyl-compound in refluxing glacial acetic acid was cleaved by dry hydrogen chloride after 24 hours.

It may be that the electron-withdrawing nature of the phenyl group makes the triphenylsilyl group more difficult to remove than trialkylsilyl groups because the triphenylsilyl group withdraws electrons from the benzene ring whereas the trimethylsilyl group normally supplies them to the ring.<sup>19</sup>

In the malonic esters  $\text{CH}_3 \cdot \text{C}_2\text{H}_5\text{PhSiCH}_2\text{CH}(\text{COOEt})_2$  and  $\text{CH}_3\text{Ph}_2\text{SiCH}_2\text{CH}(\text{COOEt})_2$  the replacement of the ethyl group attached to silicon by a phenyl group causes a considerable increase in the resistance of the silicon-phenyl bond to cleavage by hydrochloric acid.<sup>27</sup>

Possibly because of the presence of electron-withdrawing groups on the silicon atom, diphenyldichlorosilane was quite stable to hydrogen chloride in boiling glacial acetic acid<sup>20</sup> and the compound  $(\text{O}-\text{C}_6\text{H}_5\text{C}_6\text{H}_4)_3\text{SiCl}$  was less readily cleaved by boiling formic acid than the compounds  $(\text{O}-\text{C}_6\text{H}_5\text{C}_6\text{H}_4)_3\text{SiH}$  and  $\text{O}-\text{C}_6\text{H}_5\text{C}_6\text{H}_4\text{SiPh}_3$ . However, the silanol  $(\text{O}-\text{C}_6\text{H}_5\text{C}_6\text{H}_4)_3\text{SiOH}$  was the most readily cleaved and solubility differences may be involved. From the silanol, diphenyl was obtained in yield corresponding to the cleavage of 76% of all the Si-C bonds after 48 hours' boiling.<sup>21</sup>

Nitric acid has been observed to cause cleavage of silicon-aryl bonds,<sup>22a,b</sup> but the  $\text{Ph}_3\text{Si}-\text{C}$  bond was again relatively stable and nitration of the phenyl groups occurred when tetraphenylsilane was treated with nitric acid.<sup>23</sup> When trimethylphenylsilane was treated by 71% nitric acid in acetic anhydride cleavage occurred<sup>22</sup> thus showing that the  $\text{Me}_3\text{Si}-\text{C}$  bond is weaker than the  $\text{Et}_3\text{Si}-\text{C}$  bond, as triethylphenylsilane may be successfully nitrated using the same nitrating medium.<sup>24</sup>

Similarly, all three isomeric tolyltriethylsilanes can be nitrated by copper nitrate in acetic anhydride, neither cleavage of the starting material nor of the mononitrotolyltriethylsilanes

obtained having occurred.<sup>26</sup> Nitration of phenyltrimethylsilane with copper nitrate in acetic anhydride resulted in a 25% yield of nitrobenzene as cleavage product.<sup>26</sup>

More detailed study of the effect of the size of the group removed in desilylation has been made.<sup>28</sup> The rates of acid cleavage of m-substituted alkylphenyltrimethylsilanes and the corresponding triethylsilyl series were determined. A glacial acetic acid, hydrochloric acid and water mixture was used for cleavage. On cleavage an expansion in volume occurred and this was followed by means of a dilatometer.

TABLE II

Rate constants for the acid-catalysed cleavage of some m-trimethyl- and m-triethylsilylalkylbenzenes in a glacial acetic acid solution (2.35 molar in hydrogen chloride and 7.23 molar in water at 25° ).

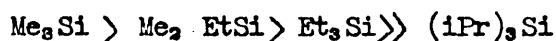
<u>m</u> -Alkyl group	Average rate constant $\times 10^3$ , min. <sup>-1</sup>	
R	Me <sub>3</sub> SiC <sub>6</sub> H <sub>4</sub> R( <u>m</u> )	Et <sub>3</sub> SiC <sub>6</sub> H <sub>4</sub> R( <u>m</u> )
H	3.84	1.64
CH <sub>3</sub>	8.31	3.87
C <sub>2</sub> H <sub>5</sub>	8.54	4.69
i-C <sub>3</sub> H <sub>7</sub>	9.08	5.14
t-C <sub>4</sub> H <sub>9</sub>	10.8	5.90

Removal of a triethylsilyl group was in general slower than that of a trimethylsilyl group (see Table II). This would be predicted as both proton attack on the carbon holding silicon and attack by water molecules on silicon is rendered slower by the bulkier ethyl groups.



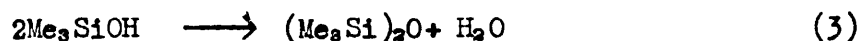
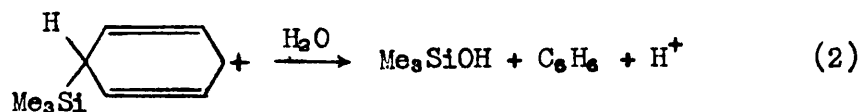
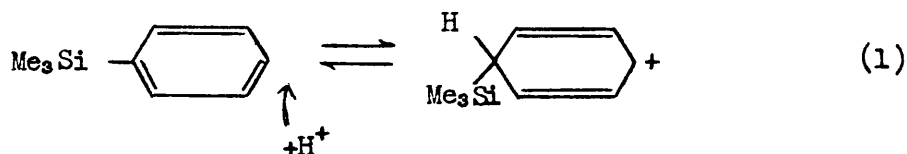
The slower cleavage was also attributed to a possible buttressing effect. A large group substituted on the benzene ring would possibly distort the C-H bonds of the ortho-hydrogens. Another large group meta to the first would increase the distortion of the C-H bond between the two large groups. Thus, the larger the m-substituents the larger would be the strain due to this buttressing effect. The relief of strain in the triethyl series would be greater than for the trimethyl series. This would therefore mean that the rate of cleavage of the triethyl series would be more rapid than that of the trimethyl series but the opposite was found and therefore this buttressing theory may be discounted.

In an extension of this work cleavage of mixed trialkylphenylsilanes by acetic acid/p-toluenesulphonic acid/water has been carried out and the rates of desilylation were found to decrease in the order



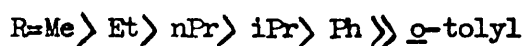
It was concluded that this indicated a steric effect.

Eaborn<sup>6</sup> has proposed the following mechanism



As with aromatic substitution, whether formation or destruction of the intermediate is rate determining is not certain. However, increase in the size of groups attached to silicon should decrease the rate of acid cleavage since proton attack in (1) and attack by water in (2) would be slowed down the bulkier the alkyl groups attached to silicon. In fact, the attacking species in (1) is probably the hydronium ion rather than the simple proton and hence a steric effect would be very likely.

Similar work has been carried out<sup>30</sup> using the spectrophotometric method as described by Eaborn.<sup>7</sup> In a perchloric acid/water/methanol system, cleavage of the *p*-anisyl-silicon bond in some *p*-anisyltrialkyl- and triarylsilanes ( $\text{pMeOC}_6\text{H}_4\text{SiR}_3$ ) was investigated. The following order of rate of cleavage was observed



The object of the work was to ascertain if bulky alkyl groups attached to silicon would cause steric hindrance to nucleophilic attack on silicon.

with destruction of the intermediate  
If Eaborn's mechanism operates, as the slow step, it would be expected that replacement of  $\text{Me}_3\text{Si}$  or  $(\text{nPr})_3\text{Si}$  by  $(\text{iPr})_3\text{Si}$  would lead to considerable reduction in rate due to increased steric hindrance to nucleophilic attack on silicon. Also triisopropyl-*p*-anisylsilane might react more slowly than triphenyl-*p*-anisylsilane.

However, it was found that a triisopropyl group caused only a relatively small decrease in rate and from this it would appear that it is unlikely that nucleophilic attack at silicon is important in the rate determining step. But it was concluded that there must be some

steric hindrance as polar effects alone would tend to make triisopropyl-p-anisylsilane more reactive than tri(n-propyl)-p-anisylsilane.

In cleavage of aryl silanes  $\text{ArSiR}_3$  (where  $\text{R}=\text{Et}$  and  $\text{C}_6\text{H}_{11}$ ) by ethanolic aqueous perchloric acid, the rate of removal of a triethylsilyl group is approximately 11 times greater than that of a tricyclohexylsilyl group. This decrease in rate has also been attributed to steric effects.

The relative rates of cleavage of m-substituted phenyltrialkylsilanes ( $\text{m-R}^1\text{C}_6\text{H}_4\text{SiR}_3$ ) by glacial acetic acid/sulphuric acid/water are in the order  $\text{R}=\text{iPr} < \text{Et} < \text{Me}$  and this would be predicted in terms of steric hindrance to attack of a hydronium ion on the ring carbon to which silicon is attached.<sup>31</sup>

For the detriisopropylsilylation reaction it was concluded that there is little steric hindrance to solvation or any buttressing between m-alkyl groups on phenyl and groups R attached to silicon.

The difference in rates of cleavage from  $\text{R}^1=\text{CH}_3$  to  $\text{t-C}_4\text{H}_9$  increased from detrimethylsilylation to detriethylsilylation to detriisopropylsilylation (Table III).

TABLE III

Relative rates of cleavage of m-alkyl substituted tri-  
alkylphenylsilanes ( $\underline{m}$ -R<sup>1</sup>C<sub>6</sub>H<sub>4</sub>SiR)

<u>m</u> -Alkyl group R <sup>1</sup>	Relative rates		
	R=Me	Et	iPr
H	1	1	1
CH <sub>3</sub>	2.1	2.4	5.4
C <sub>2</sub> H <sub>5</sub>	2.2	2.9	6.4
i-C <sub>3</sub> H <sub>7</sub>	2.4	3.1	7.9
t-C <sub>4</sub> H <sub>9</sub>	2.8	3.6	9.3

This was attributed to the nature of the transition states.

Detrimethylsilylation was the most vigorous and therefore the geometry of the transition state would most strongly resemble the structure of the starting silane i.e. breaking of the C-Si bond in the transition state had not progressed as far as in detriethylsilylation which, in turn has not progressed as far as in detriisopropylsilylation.

Hence, the positive nature of the ring in the transition state was greatest in detriisopropyl<sup>silyl</sup>silylation and least for detrimethylsilylation.

There was thus a greater electron demand on m-alkyl substituents in the removal of a triisopropylsilyl group than in the removal of a trimethylsilyl group, and hence a greater spread of rates in

proceeding from m-methyl to m-t-butyl (see Table III). Therefore,

detrimethylsilylation was the least selective and detriisopropylsilylation the most selective and the selectivity factor<sup>32</sup> depended not only on the activity of the attacking species but also on the nature of the leaving group.

The  $\text{Ph}_3\text{Si-C}$  bond of tetraphenylsilane can be broken by bromine at  $100^\circ$ <sup>33</sup> but cleavage of the  $\text{Me}_3\text{Si-C}$  bond of trimethylphenylsilane was readily accomplished by means of bromine in carbon tetrachloride<sup>11</sup> or glacial acetic acid.<sup>12</sup> It was possible to cleave a further phenyl group only by heating the monobromo derivative with bromine to  $150^\circ$ ;<sup>33</sup> this increased stability could be due to the presence of the bromine atom attached to silicon withdrawing electrons.

In cleavage of phenyltriisopropylsilane and phenyltrimethylsilane by bromine in 1.5%<sup>wt. %</sup> water/acetic acid<sup>12b</sup> the rate was about 158 and 330 times as great for the latter compound at initial reactant concentrations of 0.0118M and 0.067M respectively. It was concluded that steric hindrance had reduced the reactivity of the triisopropyl compound, the effect apparently being greater for higher order components of the reaction.

Chlorine in glacial acetic acid<sup>12b</sup> has also been used for cleavage. Cleavage of phenyltrimethylsilane occurred readily but when phenyltriethylsilane was treated with chlorine the phenyl-silicon bond was not broken and chlorination of the phenyl group occurred.<sup>34</sup>

Electron-withdrawal by the chlorine atom attached to silicon rendered the compounds phenyltrichlorosilane and diphenyldichlorosilane resistant to cleavage and they may be chlorinated and brominated in the rings with only little desilylation.<sup>35,36</sup>

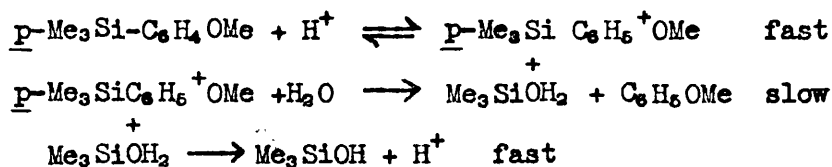
### CHAPTER III

#### Mechanism of the cleavage of aromatic C-Si bonds by electrophilic reagents

##### (a) Cleavage by acid

As acid cleavage of trimethylarylsilanes is facilitated by substituents in the aromatic nucleus capable of furnishing a high electron density at the aryl-silicon bond, a mechanism has been postulated<sup>5</sup> whereby a proton presumably initially solvated attacks the carbon atom holding silicon (see Chapter I).

The rate of cleavage of the carbon-silicon bond is governed by the Hammett acidity function<sup>37</sup> of the medium and also by the concentration of water present and hence the following mechanism has been proposed.<sup>6</sup>



The structure of the intermediate was thought to be a  $\sigma$ -complex and the reaction would have the energy profile (Fig.V).

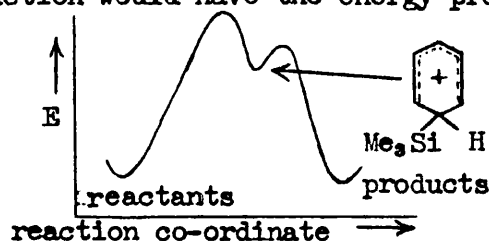
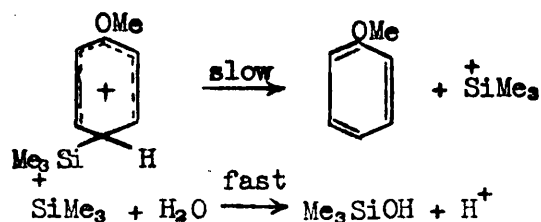


Fig.V

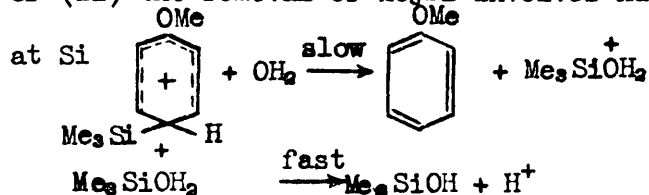
It was not clear whether formation or breakdown of the intermediate was the rate determining step.

In the mechanism given if destruction of the intermediate is rate determining, then either

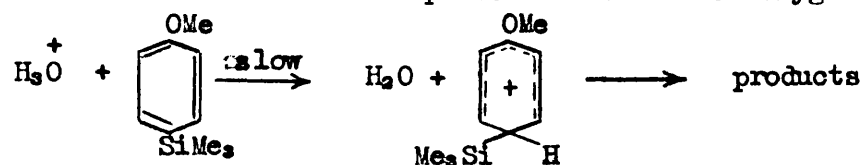
- (i) the  $\text{R}_3\text{Si}$  group could separate as a siliconium ion



or (ii) the removal of  $\text{Me}_3\text{Si}$  involves nucleophilic attack by solvent



For the formation of the intermediate to be rate determining it would involve a direct proton transfer from oxygen to carbon.



The cleavage of tri-*n*-propylsilyl and tri-isopropylsilyl groups from aryl carbon indicated that destruction of the intermediate by nucleophilic attack on silicon was not important in the rate determining step for there was relatively little difference in the rate of cleavage of triisopropyl-*p*-methoxyphenylsilane and tri-*n*-propyl-*p*-methoxyphenylsilane by aqueous methanolic perchloric acid, see Table IV.

TABLE IV

Cleavage of trialkyl-*p*-methoxyphenylsilanes  $\text{R}_3\text{SiC}_6\text{H}_4\text{-OMe-}p$  by  $\text{HClO}_4$  in 28.6% water/methanol at  $50^\circ$

R=	Relative rate of cleavage
Ph	1
iPr	3.55, 2.42
nPr	24.5
Et	28.4
Me	58.8

If the rate-determining step is formation of the intermediate, the reaction will now have the energy profile (Fig.VI).

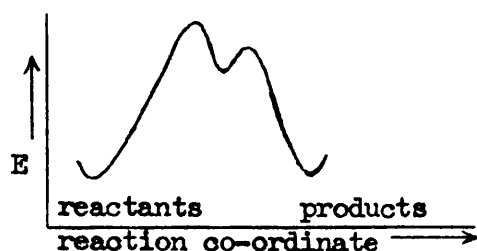
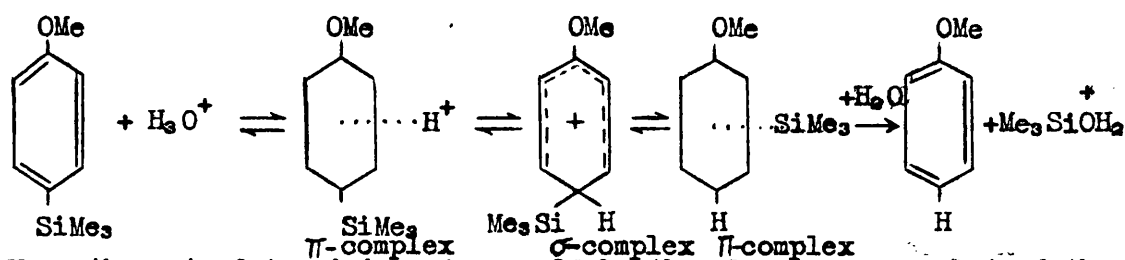


Fig.VI

The mechanism could involve both  $\sigma$ - and  $\pi$ - complexes



Here the rate determining step could be the slow rearrangement of the  $\pi$ - complex to give the  $\sigma$ - complex or vice versa.

However, it is likely that in any desilylation the transition states for formation and destruction of the intermediate are not far removed in energy from the intermediate and thus from one another; consequently the effects of variation of structure on the rate of reaction are not likely to be greatly dependent on which step is rate-determining.<sup>11</sup>

#### (b) Bromine cleavage

In carbon tetrachloride at 35° and 40° the reaction was found to be overall third order (second order with respect to bromine and first order in silicon compound).<sup>11</sup> However, no mechanism was postulated.

Much more detailed work has been carried out by following the kinetics of bromodesilylation in glacial acetic acid containing 1.5 wt % water.<sup>12,16</sup> At low initial bromine concentrations (0.01M) the reaction was approximately second order but this could exceed

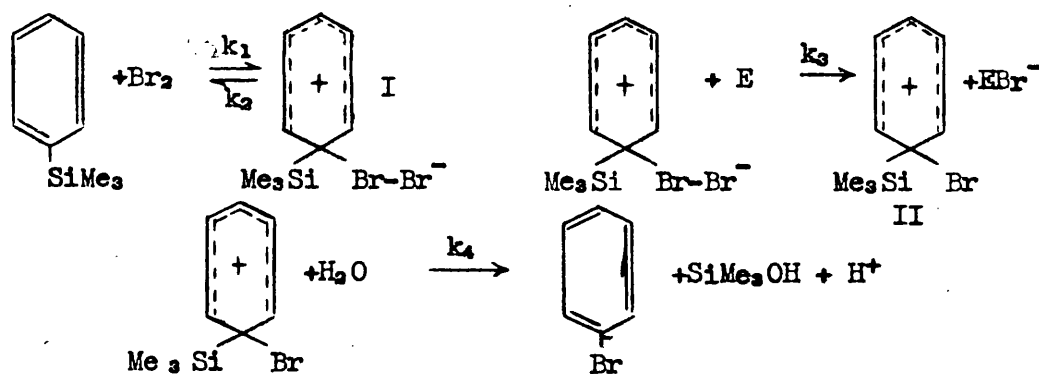


three for higher initial concentrations of bromine (see Chapter I).

By comparison with aromatic bromination it was concluded that bromodesilylation involved molecular bromine and not positively charged species such as  $\text{Br}^+$ ,  $\text{H}_2\text{O}^+\text{Br}$  and  $\text{HOAc}^+\text{Br}$ . Sodium acetate did not catalyse the reaction beyond the expected salt effect and this indicated that removal of the trimethylsilyl group was not involved in the rate-determining step of bromodesilylation which probably involves formation of the intermediate



The overall reaction was postulated as <sup>15</sup>



The energy profile would be (Fig.VII)

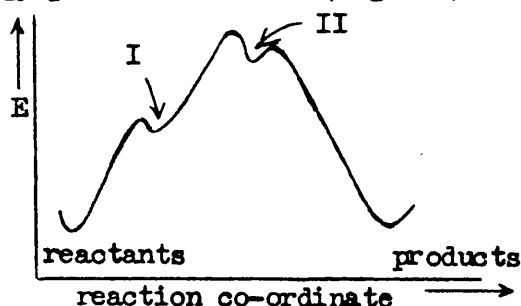


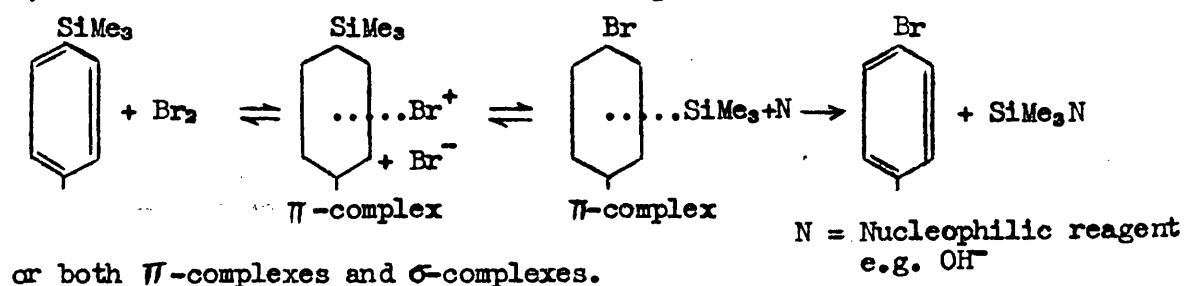
Fig.VII

An alternative mechanism for the third order process involves formation of a  $\text{Br}_4$  complex and this attacks the arylsilane

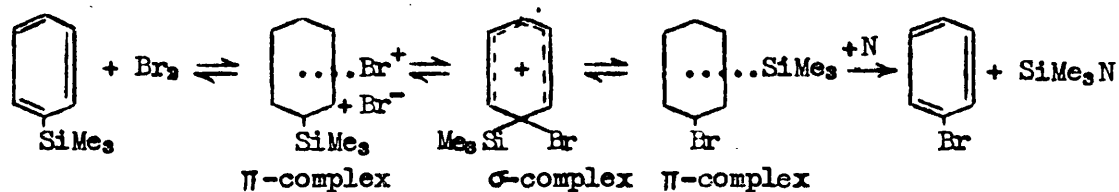


This is not favoured for aromatic bromination and there would be no reason to suppose that the mechanism of the bromodesilylation reaction is significantly different from that of aromatic bromination.

The mechanism could involve  $\pi$ -complexes

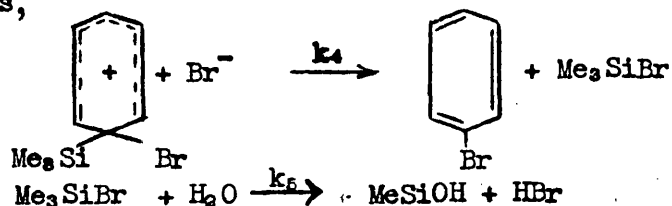


or both  $\pi$ -complexes and  $\sigma$ -complexes.

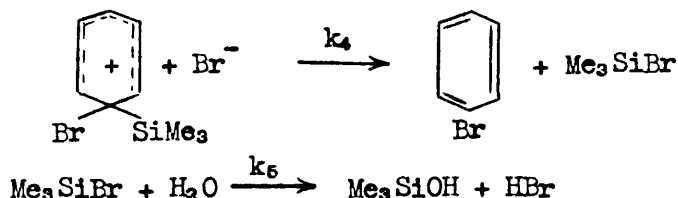


If this is the mechanism, the loss of the siliconium ion from the intermediate could be the rate determining step. Such a mechanism is analogous to that proposed by Gold and Satchell<sup>89</sup> for aromatic dedeuteration, sulphonation and desulphonation.

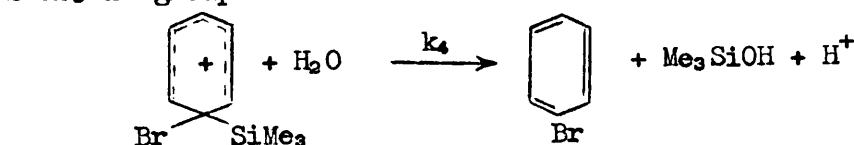
The mechanism of the final stage of the reaction can be as follows,



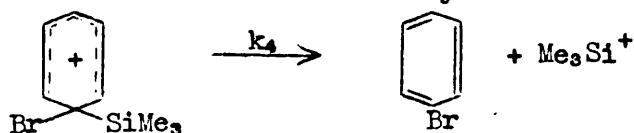
Alternatively, water rather than bromide ion, can help to pull off the  $\text{Me}_3\text{Si-}$  group.



Alternatively, water, rather than bromide ion, can help to pull off the  $\text{Me}_3\text{Si}$ - group



The formation of siliconium ions may also occur



There is a possibility of a cyclic transition state (Fig.VIII) in

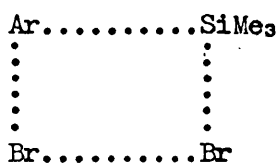


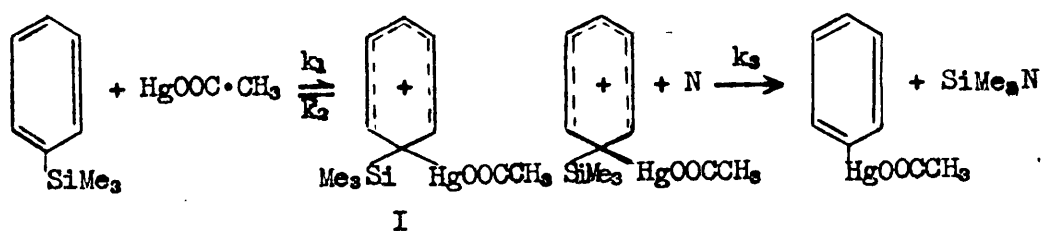
Fig. VIII

the second-order bromodesilylation<sup>12b</sup> in view of the probable ease of flank attack at silicon.<sup>40</sup>

It has been suggested<sup>13</sup> that an electrophile, E, is needed to remove the bromide ion from the attacking bromine molecule and this may be a solvent molecule or an additional bromine molecule. It seems that the greater availability of electrons in the  $\text{Ar-SiMe}_3$  bond compared with that in an  $\text{Ar-H}$  bond leads to a smaller need for the additional electrophile in bromodesilylation even when the  $\text{ArSiMe}_3$  and  $\text{ArH}$  compounds are of comparable reactivity.

### (c) Mercuric acetate cleavage

Cleavage of aryl-silicon bonds has been carried out by mercurio acetate in glacial acetic acid.<sup>14, 15</sup> The reaction is second order, the reaction product being an aryl mercury acetate. The most probable mechanism is one very similar to those postulated for other electrophilic aromatic substitutions.



N is a nucleophilic entity, either the acetate ion or more probably a water molecule. This was indicated by the experimental fact that when the water content was low the order was higher.<sup>16</sup>

The rate-determining step is probably formation of the intermediate and the energy profile will be: (Fig.IX)

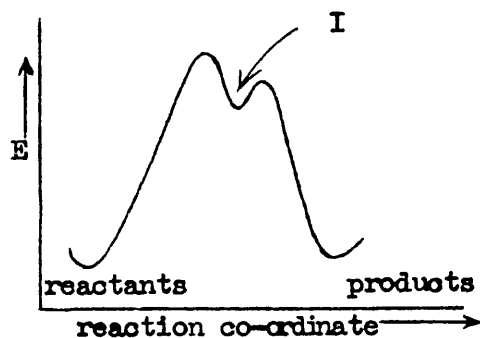


Fig.IX

## SECTION II. Discussion

#### CHAPTER IV

##### Acid cleavage of triaryl- and trialkyl-p-anisylsilanes

Desilylation has been shown by Eaborn<sup>6</sup> to be an electrophilic aromatic substitution reaction. As removal of a trimethylsilyl group from nuclear substituted aryltrimethylsilanes by electrophilic reagents<sup>7,8,12,15</sup> provides valuable information about the effect of these nuclear substituents in electrophilic aromatic substitution, emphasis has been placed on the removal of a trimethylsilyl group.

Removal of other trialkylsilyl groups has been studied and this is also electrophilic aromatic substitution, but little quantitative work has been carried out either on removal of trialkylsilyl or triarylsilyl from aromatic carbon. Two series of arylsilanes have been prepared (i)  $R_3Si-p\text{-anisyl}$  and (ii)  $Ar_3Si-p\text{-anisyl}$  and the effect of varying R and Ar was studied by cleavage of the p-anisyl group from silicon by aqueous methanolic perchloric acid.

The radical R was varied by successively replacing the methyl groups of  $Me_3Si-$  by phenyl and it was hoped to investigate the effect of replacing methyl by  $CH_2Cl$ ,  $CH_2NH_2$  and  $CH_2OH$  but cleavage occurred during preparation of the alcohol.

The fourth group of these silanes was chosen to be p-anisyl for this would (i) be cleaved at a convenient rate for measurement over the range of acid concentrations used and (ii) be cleaved at a much faster rate than other aryl groups attached to silicon and thus overcome the difficulty of having more than one aryl group removed.

This difference in cleavage rates is demonstrated by the

removal of a dimethylchloromethylsilyl group from *p*-anisyl- and *p*-tolyl dimethylchloromethylsilanes (see Table V) by perchloric acid.

TABLE V

Relative rates of cleavage of aryl dimethylchloromethylsilanes,  $\text{ArSi}(\text{CH}_3)_2\text{CH}_2\text{Cl}$  by aqueous methanolic perchloric acid at  $50.00 \pm 0.02^\circ$ .

Ar	Strength of acid, M	Rate of cleavage $\times 10^2, \text{min}^{-1}$	Average rate of cleavage $\times 10^2, \text{min}^{-1}$	Rate of cleavage relative to $\text{Ph}_3\text{SiC}_6\text{H}_4\text{-OMe-p}$	Relative rate of cleavage
<i>p</i> -anisyl	6.00	4.52, 4.52	4.52	7.34	127
<i>p</i> -tolyl	12.19	1.00, 1.00	1.00	0.0578	1

*p*-Anisyldimethylchloromethylsilane is cleaved relatively 127 times as fast as *p*-tolyl dimethylchloromethylsilane. For the former, the half life was of a convenient time (ca 15 min.) whereas it was about 70 min. for the latter where acid of the highest available concentration was used for cleavage.

The rate of cleavage was measured spectrophotometrically and the reaction was followed up to 75% completion and was found to be first order in silane as straight lines were obtained for plots of  $\log(D_t - D_\infty)$  versus time (see Chapter IX).

The rates of cleavage, concentration of acid, concentration of silane and wavelength at which a run was carried out are given in Table VI.

TABLE VI

Cleavage of p-anisyltriaryl- and p-anisyltrialkylsilanes,  $R_3SiC_6H_4-OMe-P$ , by perchloric acid in water/methanol<sup>1</sup> at  $50.00 \pm 0.02^\circ$ .

$R_3$	Concentration of acid, M.	Concentration of silane $\times 10^4$ , M.	Wavelength at which studied $m\mu$	Rate of cleavage $\times 10^2, min^{-1}$	Average rate of cleavage $\times 10^2, min^{-1}$
$Me_3$	4.26	8.17	281	13.1 12.9	13.0
$Me_2Ph$	4.26	8.14	281	4.03 4.07	4.05
Benzyl <sub>3</sub>	4.26	6.37	281	1.18 1.14	1.16
$P-[(CH_3)_3SiCH_2C_6H_4]_3$	4.26	0.753	281	0.99 0.98	0.985
$(p-anisyl)_3$	2.55	2.64	281	1.30 1.29	1.30
$Me_2Ph$	2.55	7.71	281	1.28 1.30	1.29
$(Me)_2CH_2Cl$	6.00	5.13	282	4.52 4.52	4.52
$(Me)_2CH_2NHMe^e$	6.00	6.40	282	0.709 0.710	0.710
$Ph_2Me$	6.00	6.02	281	2.24 2.33	2.29



TABLE VI (Continued)

$R_3$	Concentration of acid, M.	Concentration of silane $\times 10^4$ , M.	Wavelength at which studied $m\mu$	Rate of oleavage $\times 10^2$ , min <sup>-1</sup>	Average rate of cleavage $\times 10^2$ , min <sup>-1</sup>
(p-tolyl) <sub>3</sub>	6.00	3.30	281	1.27 1.28	1.28
Ph <sub>3</sub>	7.50	3.10	281	1.57 1.58	1.58
Me <sub>2</sub> Ph	7.50	11.2	281	29.5 29.5	29.5
Ph <sub>2</sub> Me	7.50	8.98	281	5.85 5.90	5.88
Ph <sub>3</sub>	9.20	3.16	281	3.81 3.74	3.78
(m-tolyl) <sub>3</sub>	9.20	2.33	282	4.98 4.97	4.98
Me(CH <sub>2</sub> Cl) <sub>2</sub> <sup>c</sup>	9.20	6.56	248	ca 10.0 ca 10.0	ca 10.0
(m-tolyl) <sub>3</sub>	9.48	3.32	282	5.88 5.88	5.88
(p-tolyl) <sub>3</sub> <sup>d</sup>	9.48	7.25	281	- -	-
(p-chlorophenyl) <sub>3</sub>	9.48	5.67	281	1.35 1.35	1.35
(m-chlorophenyl) <sub>3</sub> <sup>a</sup>	9.48	2.39	282.5	0.478 0.478	0.478

TABLE VI (Continued)

$R_3$	Concentration of acid, M.	Concentration of silane $\times 10^4$ , M.	Wavelength at which studied $\mu$	Rate of cleavage $\times 10^2$ , min <sup>-1</sup>	Average rate of cleavage $\times 10^2$ , min <sup>-1</sup>
$\text{Me}_2\text{CH}_2\text{NHEt}$	9.48	9.12	282	3.60 3.63	3.62
( <i>m</i> -chlorophenyl) <sub>3</sub>	12.19	2.38	282.5	1.85 1.85	1.85
( <i>o</i> -tolyl) <sub>3</sub> <sup>b</sup>	12.19	2.01	281	0.0568 0.0564	0.0566
$\text{Me}_3$ <sup>a</sup>	0.293	8.79	281	0.220 0.224	0.222
$\text{Me}_2\text{Ph}$	3.05	10.1	281	1.88 1.88	1.88
$\text{Me}_3$	3.12	8.72	281	5.90 5.95	5.93
$\text{Me}_2\text{Ph}$	3.12	8.56	281	1.80 1.79	1.80

1. 2 volumes of aqueous acid were added to 5 volumes of a solution of the organosilane in methanol.

a. End point determined by leaving sample in sealed tube at 50° for ca. 10 x half-life.

b. Run carried out in sealed tubes at 50.0 ± 0.05°.

c. This figure has been included for qualitative comparison only.

d. Slow cleavage of a *p*-tolyl group also occurred.

e. Straight line plot of  $\log (D_t - D_\infty)$  against  $t$  was not obtained for first 5% reaction.

f. It was found that on cleavage of this compound all four *p*-anisyl groups were removed, finally giving anisole. Tri-*p*-anisylethoxysilane was prepared and its optical density measured in a solution of methanol containing 10% water and 0.5% 9.20M perchloric acid. The ethoxy group would be hydrolysed and the measured optical density would in effect be that of tri-*p*-anisylsilanol, the cleavage product obtained by removal of one *p*-anisyl group. By measurement of the optical density of anisole in the same solvent a synthetic end point was calculated.

### Qualitative Discussion

#### (a) Triarylsilyl groups, $\text{Ar}_3\text{Si}$

Relative rates of cleavage are given in Table VII, together with values of the Hammett substitution constant,  $\sigma$ .

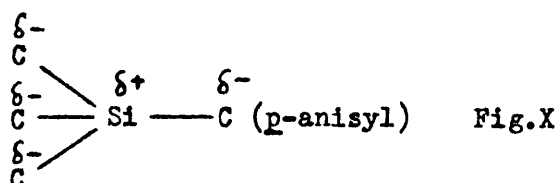
TABLE VII

Relative rates of cleavage of triaryl-*p*-anisylsilanes,  
 $\text{Ar}_3\text{SiC}_6\text{H}_4\text{-OMe-}p$ , by perchloric acid.

Ar	Relative rate of cleavage	$\sigma$ <sup>37</sup>
Ph	1	0
<i>m</i> -tolyl	1.32	- 0.069
<i>p</i> -tolyl	2.08	- 0.170
<i>m</i> -chlorophenyl	0.107	+ 0.373
<i>p</i> -chlorophenyl	0.302	+ 0.227
$p\text{-(CH}_3)_3\text{SiCH}_2\text{C}_6\text{H}_4$	4.57	- 0.260
<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub>	18.8 <sup>a</sup>	- 0.268
<i>o</i> -tolyl	0.0033	-

<sup>a</sup> As four *p*-anisyl groups can be removed from silicon, for comparison with other compounds the relative rate is  $\frac{18.8}{4}$  i.e. 4.70

An increase in rate was observed when an electron supplying group was present in the aryl group and a decrease when an electron withdrawing group was present. The polarity  $\delta^+ \delta^-$  facilitates formation of the intermediate and hence cleavage of the Si - C bond.<sup>6</sup> An electron supplying group in Ar will supply electrons to the ring carbon attached to silicon. The Si - C bond is already polarised due to the



presence of the -OMe group. Therefore when three more carbon atoms are attached to silicon, the polarity of the Si - C(p-anisyl) bond is increased and hence cleavage occurs more readily. Electron withdrawing substituents have the reverse effect

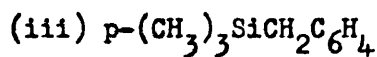
(i) para- and meta- tolyl groups

As expected by consideration of the +I effects of para- and meta- methyl groups tri-p-tolyl-p-anisylsilane was cleaved faster than tri-m-tolyl-p-anisylsilane. Tri-p-tolyl-p-anisylsilane and tri-m-tolyl-p-anisylsilane were cleaved considerably slower than trimethyl-p-anisylsilane. Since it is known that (i) trimethylsilyl is a weak electron-supplying group<sup>41</sup> and (ii) triphenylsilyl is an electron withdrawing group<sup>42</sup> and as the rates of cleavage of a tri-p-tolylsilyl (2.15) and tri-m-tolyl (1.31) are not far removed from that of triphenylsilyl (1) it is possible that tri-p-tolylsilyl and tri-m-tolylsilyl are also electron withdrawing groups. This would mean that the +I effect of the methyl groups is not large enough to overcome the electron withdrawing effect of the Ph<sub>3</sub>Si group. However, this slow rate of cleavage of tri-p-tolyl- and tri-m-tolyl-p-anisylsilanes could be attributed to steric hindrance to attack by oxonium ion at the ring carbon (p-anisyl) attached to silicon because of these large groups attached to silicon.

(ii) ortho-tolyl

By consideration of the +I effect it would be expected that tri-o-tolyl-p-anisylsilane could be cleaved at approximately the same rate as tri-p-tolyl-p-anisylsilane but a very slow rate of cleavage was observed. Tri-o-tolylsilyl derivatives exhibit steric hindrance<sup>43, 44</sup>

and a steric effect would explain this slow rate of cleavage. In Eaborn's mechanism<sup>6</sup> for the cleavage reaction, if formation of the intermediate is the rate determining step, the large ortho-methyl groups would prevent the attachment of a proton to the ring carbon atom holding silicon. If destruction of the intermediate by nucleophilic attack is the rate determining step, the silicon atom is shielded by the ortho-methyl groups and this prevents nucleophilic attack by a solvent molecule at silicon. However, it has been recently shown that nucleophilic attack at silicon in the rate determining step is unlikely<sup>30</sup> and therefore it may be concluded that the slow rate of cleavage is due to steric hindrance to formation of the intermediate.



A strong +I effect operates from the  $(CH_3)_3Si$  group when it is transmitted through an insulating methylene group<sup>7</sup>, and the group increased the rate of cleavage more than did p-tolyl. This order of relative rates of cleavage is in agreement with the ionisation constants of substituted benzoic acids,<sup>4,5</sup> the ionisation constant of p- $Me_3SiCH_2C_6H_4COOH$  (0.832) being considerably lower than those of benzoic acid (2.00) and p-toluic acid (1.32).

(b) Trialkyl- and alkylphenyl-silyl groups,  $R_3Si$

Relative rates of cleavage are given in Table VIII.

(i) Trimethyl, and mixed methylphenyl groups.

Trimethyl-p-anisylsilane was considerably more reactive than triphenyl-p-anisylsilane. From the values of its  $\sigma$  constants the  $Ph_3Si$  group functions principally through a -I effect<sup>42</sup> (see Table IX) but the  $Me_3Si$  group usually supplies electrons to the ring<sup>41</sup>,

e.g. trimethylsilylbenzene was nitrated some 1.64 times as fast as benzene by nitric acid in acetic anhydride at  $-10^{\circ}$ <sup>46</sup> and the *p*-Me<sub>3</sub>Si group decreased the strength of benzoic acid.<sup>47</sup> This will account for the observed difference in rates of cleavage.

TABLE VIII

Relative rates of cleavage of trialkyl- and alkylphenyl-*p*-anisylsilanes, R<sub>3</sub>SiC<sub>6</sub>H<sub>4</sub>-OMe-*p*, by perchloric acid.

R <sub>3</sub>	Rate of cleavage relative to <i>p</i> -anisyl SiPh <sub>3</sub>	Rate of cleavage relative to <i>p</i> -anisyl SiMe <sub>3</sub>
Me <sub>3</sub>	60.8	1
Me <sub>2</sub> Ph	18.7	0.31
MePh <sub>2</sub>	3.72	0.061
Ph <sub>3</sub>	1	0.016
Benzyl <sub>3</sub>	5.36	0.088
Me <sub>2</sub> CH <sub>2</sub> Cl	7.34	0.12
Me(CH <sub>2</sub> Cl) <sub>2</sub>	ca 2.6	0.04
Me <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub>	1.15, 0.811	0.019, 0.013

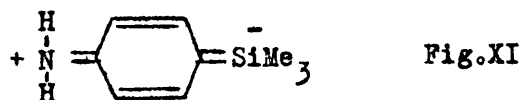
TABLE IX

Hammett  $\sigma$ - constants for the *p*-Ph<sub>3</sub>Si group<sup>42</sup>

Reaction	$\sigma$
Dimethylanilines with methyl iodide	+ 0.27
Sodium phenoxides with ethyl iodide	+ 0.31
Benzoic acids with diphenyldiazomethane	+ 0.10
Benzoyl chlorides with aniline	+ 0.09

However, when substituted para to a strongly electron releasing group<sup>57</sup> e.g. OH, NH<sub>2</sub> or (CH<sub>3</sub>)<sub>2</sub>N the Me<sub>3</sub>Si group functions as an electron withdrawing group. This effect has been interpreted as involving a resonance interaction between the electron-releasing group and the Me<sub>3</sub>Si group in which the silicon atom has expanded its valency shell to accommodate

ten electrons<sup>42,47</sup> and might have structure such as Fig.XI.



Therefore, it is possible that, as the *p*-methoxy group is a strong electron supplier the  $\text{Me}_3\text{Si}-$  group is withdrawing electrons. The presence of the *p*-methoxy group will likewise increase the electron withdrawing power of the  $\text{Ph}_3\text{Si}$  group.

The rate of cleavage decreased with each successive replacement of methyl by phenyl and this must be due to the withdrawal of electrons by the phenyl group. This withdrawal of electrons is shown by the dissociation constants of  $\text{RC}_6\text{H}_4\text{COOH}$ ,<sup>48</sup> (Table X). However, for aliphatic carboxy acids<sup>49</sup> (Table XI) there is a decrease in the dissociation constant, when methyl is replaced by phenyl.

TABLE X.

Thermodynamic Dissociation Constants of  $\text{RC}_6\text{H}_4\text{COOH}$  compounds in 60.1% aqueous ethanol at 25°. <sup>48</sup>

R	H	$\text{Me}_3\text{Si}$	$\text{Me}_2\text{PhSi}$	$\text{MePh}_2\text{Si}$	$\text{Ph}_3\text{Si}$
$10^6 K_A$	1.05	1.11	1.28	1.51	1.81

TABLE XI.

Apparent Dissociation Constants of aliphatic carboxylic acids at 25°. <sup>49</sup>

Acid	$10^5 K_a$
$\text{Me}_3\text{SiCH}_2\text{COOH}$	0.60
$\text{Me}_2\text{PhSiCH}_2\text{COOH}$	0.54

This withdrawal of electrons on replacing methyl by phenyl is also shown by the dissociation constants of amines<sup>50</sup> (Table XII).

TABLE XIIDissociation Constants of aliphatic amines.<sup>50</sup>

Amine	$10^4 K_B$
$\text{Me}_3\text{SiCH}_2\text{NH}_2$	8.5
$\text{PhMe}_2\text{SiCH}_2\text{NH}_2$	2.3

The effect of the phenyl group makes the amine  $\text{PhMe}_2\text{SiCH}_2\text{NH}_2$  markedly weaker than  $\text{Me}_3\text{SiCH}_2\text{NH}_2$  and this has been attributed to a possible steric effect.<sup>50</sup> A similar ratio of relative rates was observed for the acid cleavage of  $\text{PhMe}_2\text{Si-p-anisyl}$  and  $\text{Me}_3\text{Si-p-anisyl}$  and here also steric effects may be operating.

(b) Benzyl

As observed by Gilman and Marshall<sup>4</sup>, tribenzyl-*p*-anisylsilane was cleaved faster than triphenyl-*p*-anisylsilane. This would imply that the tribenzylsilyl group did not withdraw electrons as effectively as a triphenylsilyl- group. In this case a smaller steric effect could be operating as the aromatic ring is now separated from silicon by a methylene group and hence attack by an oxonium ion at C will be facilitated. The presence of the methylene group now separating phenyl and silicon could also have an insulating effect on the withdrawing power of the aromatic nucleus.



(c) Chloromethyl groups

The presence of a chloromethyl group attached to silicon reduced the rate of cleavage. The chlorine atom strongly withdraws electrons from the C atom attached to silicon by the -I effect and thus the  $\text{ClCH}_2$  group will, relative to the  $\text{CH}_3$  group, withdraw electrons from silicon. As a result the positive charge on silicon will be lowered, hence decrease in ease of formation of the intermediate will result from this decrease in polarity of the Si-C (aromatic) bond. The dipole moment of trimethylphenylsilane is 0.42D whereas that of chloromethyldimethylphenylsilane is 1.93D<sup>51</sup> which shows that the chloromethyl group is strongly withdrawing electrons. The presence of a further chlorine atom on a methyl group attached to silicon decreased the rate as would be expected.

(d) Ethylaminomethyl

Using 6.00M perchloric acid an initial fast rate of cleavage was observed and if this was neglected a relative rate of 1.15 was obtained. With 9.48M acid the relative rate was 0.811 but no initial fast rate of cleavage was found. Similar variations in rate of cleavage were shown by p-dimethylaminophenyltrimethylsilane as the rate of cleavage by 0.1M aqueous hydrochloric acid was six times greater than the rate of cleavage by 6M acid.<sup>52</sup> It was thought that in acids of such strengths the compound was largely converted to the ion  $\text{p-Me}_2\text{H}^+\text{NC}_6\text{H}_4\text{SiMe}_3$  which is negligibly reactive and when the acid strength was increased

the increase in rate of reaction of a molecule of a free base,  $p\text{-NMe}_2\text{C}_6\text{H}_4\text{SiMe}_3$ , was slightly more than balanced out by the decrease in the number of such molecules present. Protonation of ethylamino-dimethyl- $p$ -anisylsilane could likewise occur and this would account for its low reactivity. As normal cleavage of  $p$ -dimethylaminophenyl-trimethylsilane occurred at low acid concentration the effect of dilute acid (0.001 - 1.0 M) on ethylaminodimethyl- $p$ -anisylsilane was investigated, but no measurable cleavage was found to occur.

The spectrum of the amine was found to change after being in solution for some time. Variations in the spectrum were also observed when water or perchloric acid (ca. 0.001M and 2.55M) were present.

The protonated base has a spectrum which is separated by about 1.5 $\mu$  from that of the base and the spectrum change would be consistent with the base becoming protonated in the course of a few days in methanol solution but such a slow protonation is unlikely.

#### Acid cleavage of $p$ -anisylethoxysilanes

As it was found that all four groups were cleaved from tetra- $p$ -anisylsilane by acid, it was necessary to prepare tri- $p$ -anisylethoxysilane in order to obtain a synthetic end point. Cleavage of this silane, di- $p$ -anisyl-diethoxysilane and  $p$ -anisyl-triethoxysilane has also been studied and rates of cleavage are given in Table XIII.

TABLE XIII

Cleavage of *p*-anisylethoxysilanes,  $(p\text{-anisyl})_{4-n}\text{Si}(\text{OEt})_n$ ,  
in water/methanol at  $50.00 \pm 0.02^\circ$

n	Concentration of acid, M.	Concentration of silane $\times 10^4$ , M.	Wavelength at which studied $\mu$	Rate of cleavage $\times 10^2$ , $\text{min}^{-1}$	Average rate of cleavage $\times 10^2$ , $\text{min}^{-1}$
1	3.05	1.85	250	1.63 1.62	1.63
2	3.05	2.74	248	1.47 1.48	1.48
2	2.55	3.13	248	1.02 1.01	1.015
2	7.50	3.49	248	17.7 17.9	17.8
3	7.50	10.1	248	3.26 3.26	3.26

Rates of cleavage have been determined by obtaining in each case synthetic end points as described on page 27.

By considering that for tetra-*p*-anisylsilane four *p*-anisyl groups have an equal opportunity of being removed, the actual relative rate of cleavage is the observed rate divided by four. Similar considerations must be made for tri-*p*-anisylethoxysilane and di-*p*-anisyl-diethoxysilane, the observed figures for the relative rate of cleavage having to be divided by 3 and 2, respectively. Relative rates of cleavage are listed in Table XIV. The relative rate of cleavage of di-*p*-diethoxysilane anisyl<sub>A</sub> fell as the acid concentration was increased. This was probably due to experimental error for at high acid concentrations cleavage occurred very rapidly and it was difficult to follow changes in optical density accurately. However, at the higher acid concentrations the compound was possibly hydrolysed to give a siloxane and it was cleavage of this which occurred.

TABLE XIV

Relative rates of cleavage of tetra-*p*-anisyl  
and *p*-anisylethoxy-silanes,  $(p\text{-anisyl})_{4-n}\text{Si(OEt)}_n$ .

n	Rate of cleavage relative to $\text{Ph}_3\text{SiC}_6\text{H}_4\text{OMe-}p$	Rate of cleavage relative to <i>p</i> - anisyltriethoxy- silane	Corrected rate of cleavage relative to <i>p</i> -anisyltriethoxy- silane
0	18.8	9.12	2.28
1	16.2	7.86	2.63
2	14.7	7.13	3.57
2	14.7	7.13	
2	11.3	5.48	2.74
3	2.06	1	1

An increase in rate was observed from  $n=0$  to  $n=2$  but for  $n=3$  a decrease in rate occurred. When  $n=0$  there must be some steric hindrance to attack by an oxonium ion on the ring carbon attached to silicon. Tri-*p*-anisylethoxysilane and di-*p*-anisyl-diethoxysilane will both be hydrolysed in solution to give the silanol and disilanol respectively and it is cleavage of these which occurred. Therefore as would be expected when a *p*-anisyl group is replaced by hydroxyl there is less steric hindrance and consequently the rate of cleavage increased from  $n=0$  to  $n=1$  to  $n=2$ . However, if *p*-anisyltriethoxysilane is hydrolysed to give *p*-anisyltriol, the presence of acid will convert this to a siloxane as triols are notoriously unstable in the presence of acid<sup>53</sup> and it was cleavage of a siloxane containing *p*-anisyl groups which occurred. The steric hindrance to attack by oxonium ion will now be increased and hence decrease in rate of cleavage will be observed. *p*-Anisyltriethoxysilane was cleaved roughly thirty times slowly as *p*-anisyltrimethylsilane. This is expected because of the large -I effect of the -OX grouping (-OX represents the group formed by hydrolysis).

### Quantitative Discussion

#### (a) Triarylsilyl groups, $\text{Ar}_3\text{Si}$

Hammett<sup>37</sup> has shown that the effect of meta- and para-substituents on the rates of many reactions occurring in the side chain of a benzene derivative can be represented by the equation:  $\log k - \log k^\circ = \rho\sigma$   
 $k^\circ$  is the specific rate constant for the unsubstituted derivative,  $k$  is that for the substituted derivative,  $\rho$  is constant for any given type of reaction and  $\sigma$  is constant for any particular substituent. A plot of  $\log k/k^\circ$  against  $\sigma$  will be a straight line of slope  $\rho$ .

This relationship also seems to apply to the reactions at a silicon atom attached to an aromatic ring as a plot of the logarithm of the relative rate of hydrolysis of triarylsilanes in wet piperidine against

$\sigma$  gave what was considered to be a satisfactory linear relationship<sup>54</sup>. However, it has been suggested that  $\sigma$ -constants will not normally apply to aryl-silicon compounds because of  $p_\pi-d_\pi$  bonding between the aryl group and the silicon atom.<sup>97</sup>

For the cleavage of triaryl-*p*-anisylsilanes by perchloric acid a plot of the logarithm of the relative rate of cleavage against  $\sigma$  should also be a straight line and Fig.XII shows that this is reasonably true,  $\rho$  having a value of -2.43.

#### (b) Methylphenylsilyl compounds, $\text{Me}_{4-n}\text{Ph}_{n-1}\text{SiC}_6\text{H}_4\text{-OMe-}p$

The plot of the logarithm of the relative rate of acid cleavage of the compounds  $\text{Me}_{4-n}\text{Ph}_{n-1}\text{SiC}_6\text{H}_4\text{OMe-}p$  (where  $n=1$  to 4) versus the logarithm of thermodynamic dissociation constants,  $K_a$ , of the acids  $p\text{-Me}_{4-n}\text{Ph}_{n-1}\text{SiC}_6\text{H}_4\text{COOH}$ <sup>48</sup> (Table X) can be regarded as showing discontinuity between  $n=2$  and  $n=3$  with points for  $n=4, 3$  and 1 in a straight line or a discontinuity between  $n=1$  and  $n=2$  with points for  $n=4, 3$  and 2 on a straight line (see Fig.XIII).

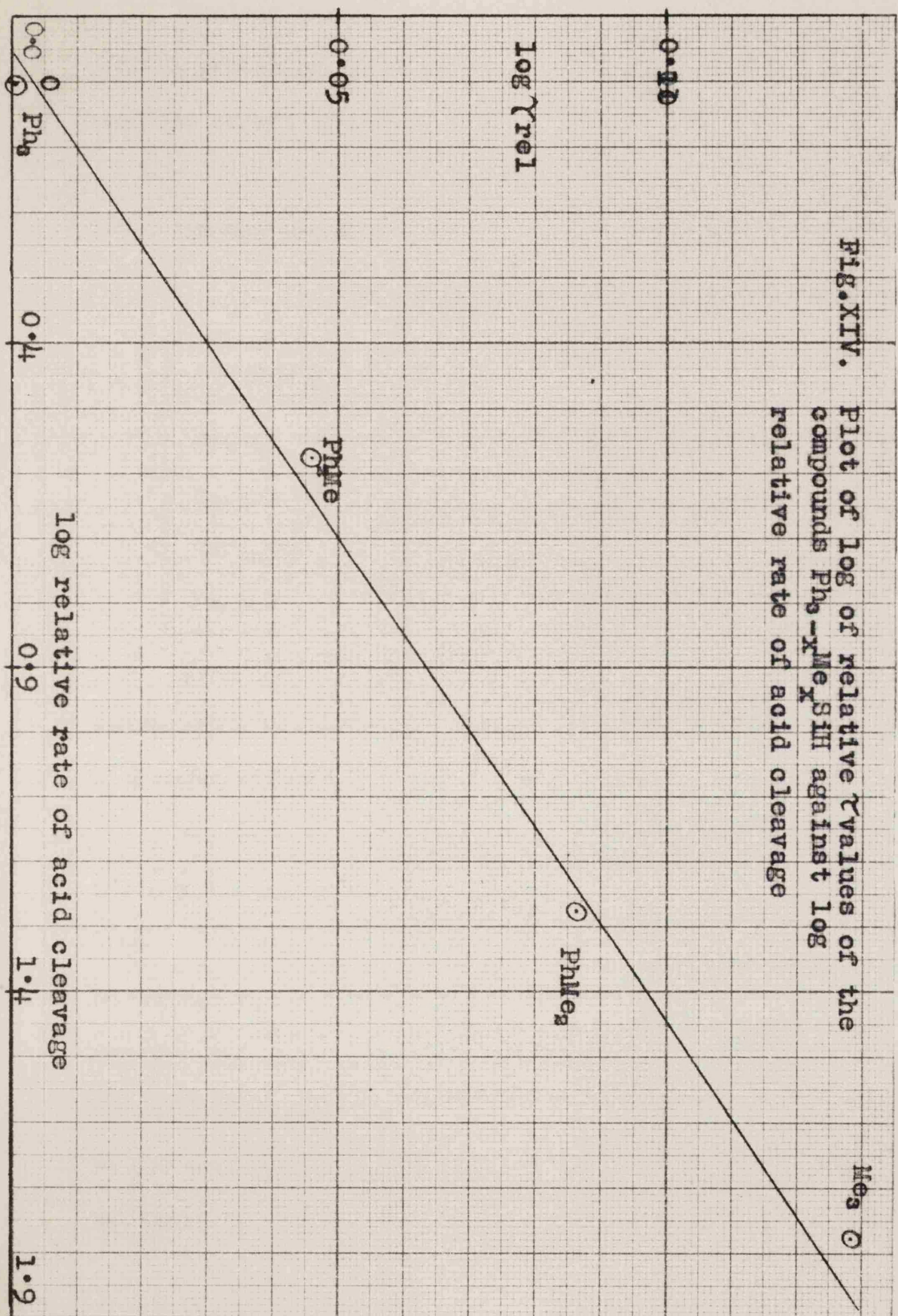
Kimball<sup>58</sup> has predicted that a tetrahedrally co-ordinated atom ( $sp^3$ ) such as silicon can form a maximum of two strong and three weak  $\pi$ -bonds. It would be expected that the average mesomeric effect of the phenyl group would stay roughly constant until two aromatic nuclei were attached to silicon then fall more rapidly as more phenyl groups were introduced.

This would explain the discontinuity between  $n=2$  and  $n=3$ ; however, there should also be a discontinuity between  $n=3$  and  $n=4$  but this was not observed, and therefore the discontinuity probably lies between  $n=1$  and  $n=2$ .

Since the acid strengths of  $p\text{-Me}_4\text{-nPh}_{n-1}\text{SiC}_6\text{H}_4\text{COOH}$  gradually increased with the number of phenyl groups, it was concluded that phenyl groups attached to silicon tend, on balance, to be only slightly more electron attracting than methyl groups i.e. the influence of their inductive effect ( $-I$ ) slightly outweighed their mesomeric effect ( $+M$ ).<sup>48</sup>

It can therefore be considered that this balance of  $+M$  and  $-I$  effects also applies for cleavage of methylphenyl- $p$ -anisylsilanes but here steric effects also occur. The replacement of the first methyl by phenyl causes relatively little steric hindrance to cleavage but successive replacement of methyl by phenyl causes a continuous increase in steric hindrance, and a straight line plot is obtained when  $n=4, 3$  and  $2$ .

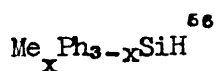
Fig. XIV. Plot of  $\log$  of relative  $\gamma$  values of the compounds  $\text{Ph}_3\text{-Me}_x\text{SiH}$  against  $\log$  relative rate of acid cleavage



Nuclear magnetic resonance shielding values ( $\tau$ ) for the (Si-)H proton of  $R_3SiH$  shows the relative electro-negatives of R and the effect of substituents in R.<sup>56</sup> Values are given in Table XV.

TABLE XV

Proton magnetic shielding values for (Si-)H of



Compound	(p.p.m.)		
Me <sub>3</sub> SiH	6.149	$\pm$	0.014
Me <sub>2</sub> PhSiH	5.574	$\pm$	0.005
MePh <sub>2</sub> SiH	5.083	$\pm$	0.002
Ph <sub>3</sub> SiH	4.579	$\pm$	0.005

Where  $\tau$  (in p.p.m.) =  $10.000 - 10^6 \frac{\nu_{obs} - \nu_{Me_4Si}}{\nu_{Me_4Si}}$  Increasing values of  $\tau$  signify increasing shielding of the proton and decreasing electronegativity.

Fig. XIV shows the plot of log relative  $\tau$  value against the log of relative rate of cleavage and the point for Me<sub>3</sub>Si- lies off the line. For proton resonance of the (Si-)H there was no discontinuity in replacing methyl by phenyl and hence these results agree with those for the dissociation constants of the acids  $p\text{-Me}_4\text{-nPh}_{n-1}\text{SiC}_6\text{H}_4\text{COOH}$ .<sup>48</sup> The deviation from the line must therefore be because of steric effects in the acid cleavage reaction and the explanation given on p. 39 can again be applied.



# CHAPTER V

## Bromine cleavage of triaryl- and trialkyl-p-anisylsilanes.

Bromodesilylation has been carried out in carbon tetrachloride<sup>11</sup> and in glacial acetic acid containing 1.5 wt % water.<sup>12,15</sup> As the kinetics are simpler in the latter solvent it was used in this study.

The primary object here was to show how the variation of R in  $R_3Si-C_6H_4-OMe-p$  affected cleavage of the C-Si bond, hence little emphasis has been placed on the mechanism of the reaction.

However, the order has been determined in typical cases, using the "fractional-life period" method, the equation being:-

$$n = 1 + \frac{\log t_1 - \log t_2}{\log a_2 - \log a_1}$$

where  $a_1$  and  $a_2$  are the initial concentrations of the reactants,  $t_1$  and  $t_2$  are the times required for a specified fraction of the reaction and  $n$  is the reaction order.<sup>58</sup>

For (i) Tri-m-tolyl-p-anisylsilane  $a_1 = 0.000921$  M  $a_2 = 0.000670$  M

n	2.02	2.10	2.11	2.11	2.14	2.14
Percentage reaction	10	20	30	40	50	60

(ii) Diphenylmethyl-p-anisylsilane  $a_1 = 0.000588$  M  $a_2 = 0.000164$  M

n	2.0	2.0	2.1	2.1	2.1	2.1
Percentage reaction	10	20	30	40	50	60

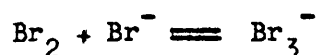
(iii) Chloromethyldimethyl-p-anisylsilane  $a_1 = 0.000164$  M  $a_2 = 0.000372$  M

n	2.1	2.1	2.1	2.1
Percentage reaction	30	40	50	60

(iv) Tri- <u>m</u> -chlorophenyl- <u>p</u> -anisylsilane	$a_1 = 0.00187 \text{ M}$	$a_2 = 0.000841 \text{ M}$
n	2.2	2.2
Percentage reaction	10	20

All values of n are to  $\pm 5\%$ . At these concentrations the increase in order throughout the run is small.

The increase in order of reaction has been attributed to bromine being removed as inactive tribromide ion



during the reaction.<sup>15</sup>

An order between 2 and 3 probably means there are concurrent second and third order reactions and the overall rate equation for bromodetrimethylsilylation has been postulated as

$$\frac{dx}{dt} = k' [\text{ArSiMe}_3] [\text{Br}_2] + k'' [\text{ArSiMe}_3] [\text{Br}_2]^2 \quad 15$$

where  $[\text{ArSiMe}_3]$  is the concentration of silane in solution and  $[\text{Br}_2]$  is the concentration of "free" bromine (i.e. that not complexed as  $\text{HBr}_3$ ) at any given time.

At low concentrations only the second order reaction is operating and the rate equation is

$$\frac{dx}{dt} = k' [\text{ArSiMe}_3] [\text{Br}_2]$$

For a particular bromine concentration the order of reaction was the same for most of the 15 triaryl- and trialkyl-p-anisylsilanes examined and their relative rates of cleavage have been determined by the comparison of times needed for removal of various fractions of

bromine at identical initial concentrations of the two silanes. By overlapping the pairs, the reactivity,  $k_{rel}$ , for each compound relative to triphenyl-*p*-anisylsilane was determined,

Relative rates of cleavage, concentration of bromine, and concentration of silane are listed in Table XVI.

TABLE XVI

Cleavage of *p*-anisyltriaryl- and *p*-anisyltrialkylsilanes,  $R_3SiC_6H_4-OMe-p$  by bromine at  $25.0 \pm 0.02^\circ$  in glacial acetic acid containing 1.5 wt % water.

$R_3$	Concentration of bromine $\times 10^4$ , M.	Concentration of silane $\times 10^4$ , M.	Relative rate of cleavage
$Me_3$ <sup>1</sup>	1.30	1.30	} 17.0
$Me_2CH_2Cl$ <sup>1</sup>	1.30	1.30	
$Me_2CH_2Cl$ <sup>1</sup>	1.64	1.64	} 1.0
$(EtO)_3$ <sup>1</sup>	1.64	1.64	
$MePh_2$ <sup>1</sup>	1.64	1.64	} 0.13
$(p-anisyl)_3$ <sup>1</sup>	1.64	1.64	
$(p-tolyl)_3$ <sup>2</sup>	2.83	2.83	} 0.23
$Me_2EtNHCH_2$ <sup>2</sup>	2.83	2.83	
$[p-(CH_3)_3SiCH_2C_6H_4]_3$ <sup>2</sup>	2.83	2.83	} -
$Benzyl_3$ <sup>2</sup>	2.83	2.83	
$Me_2CH_2Cl$ <sup>1</sup>	3.72	3.72	} 1.0
$(p-anisyl)_3$ <sup>1</sup>	3.72	3.72	

TABLE XVI (Continued)

$R_3$	Concentration of bromine $\times 10^4$ , M.	Concentration of silane $\times 10^4$ , M.	Relative rate of cleavage
$Me_2Ph^1$	4.06	4.06	} 12.0
$(Benzyl)_3^1$	4.06	4.06	
$Ph_2Me^1$	5.88	5.88	} 1.0
$(Benzyl)_3^1$	5.88	5.88	
$[p-(CH_3)_3SiCH_2C_6H_4]_3^1$	6.66	6.17	} -
$(p-tolyl)_3^1$	6.66	6.17	
$Me_2EtNHCH_2^1$	6.66	6.17	} 20 <sup>3</sup>
$(p-tolyl)_3^1$	6.70	6.70	
$[p-(CH_3)_3SiCH_2C_6H_4]_3^1$	6.70	6.70	} -
$(m-tolyl)_3^1$	6.70	6.70	
$(p-tolyl)_3^1$	6.70	6.70	} 1.0
$(m-tolyl)_3^1$	6.70	6.70	
$(p-tolyl)_3^2$	6.80	6.80	} 3.3
$(m-tolyl)_3^2$	6.80	6.80	
$Ph_3^2$	6.80	6.80	} 1.0
$MePh_2^1$	8.21	8.21	
$(p-tolyl)_3^1$	8.21	8.21	} 1.0
$Ph_3^2$	8.99	8.32	

TABLE XVI (Continued)

$R_3$	Concentration of bromine $\times 10^4$ , M.	Concentration of silane $\times 10^4$ , M.	Relative rate of cleavage
$(p\text{-tolyl})_3^2$	8.99	8.32	3.4
$(m\text{-tolyl})_3^2$	9.21	9.21	-
$(m\text{-tolyl})_3^2$	15.4	14.5	1.0
$p\text{-tolylSiMe}_2\text{CH}_2\text{Cl}$	15.4	14.5	0.035
$(p\text{-chlorophenyl})_3^2$	16.1	16.1	0.12
$(m\text{-chlorophenyl})_3^2$	16.1	16.1	0.052
$\text{Ph}_3^2$	16.1	16.1	1.0
$(o\text{-tolyl})_3^2$	16.1	16.1	0.021
$(m\text{-chlorophenyl})_3^2$	18.7	18.7	1.0
$(o\text{-tolyl})_3^2$	18.7	18.7	0.48

<sup>1</sup> Run carried out in fast reaction vessels, denoted "fast run".

<sup>2</sup> Run carried out in 100 ml. flasks, denoted "slow run".

<sup>3</sup> Relative rate taken for first 10% of reaction only.

Qualitative Discussion.(a) Triarylsilyl groups,  $\text{Ar}_3\text{Si}$ 

Relative rates of cleavage are given below.

TABLE XVII

Relative rates of cleavage of triaryl-*p*-anisylsilanes,  
 $\text{Ar}_3\text{SiC}_6\text{H}_4\text{-OMe-}p$  by bromine.

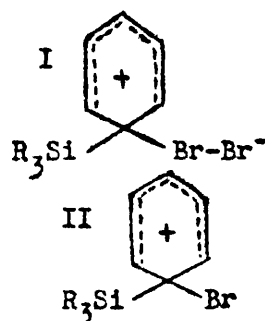
Ar	Relative rate of cleavage
Ph	1
<i>m</i> -tolyl	1.5
<i>p</i> -tolyl	3.4
<i>m</i> -chlorophenyl	0.052
<i>p</i> -chlorophenyl	0.12
<i>p</i> -anisyl	35.4 <sup>a</sup>
$p\text{-(CH}_3)_3\text{SiCH}_2\text{C}_6\text{H}_4$	6.8
<i>o</i> -tolyl	0.021
	0.025

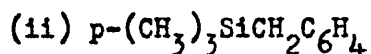
<sup>a</sup> Four *p*-anisyl groups are available to be removed, thus for comparison with other compounds the relative rate is  $\frac{35.4}{4}$   
 i.e. 8.9

As observed for acid cleavage, electron supplying substituents in Ar increased the rate of cleavage and electron withdrawing substituents decreased the rate of cleavage. Here again a supply of electrons increased the polarity of the Si - C (*p*-anisyl) bond and cleavage was facilitated.

(1) o-Tolyl.

The rate was much slower than would be expected when considering the +I effect of an ortho-methyl group. Here again steric hindrance must be occurring. As bromine cleavage is very similar to acid cleavage<sup>12,15</sup> steric hindrance to formation of the intermediate I is probably occurring due to the presence of the large o-tolyl groups attached to silicon. However, the rate of cleavage of tri-o-tolyl-p-anisylsilane relative to that for triphenyl-p-anisylsilane was considerably more for bromine cleavage than for acid cleavage (0.023 : 0.0033). The intermediate II has been postulated to be formed in the bromine cleavage reaction,<sup>15</sup> (see page 19) and formation of this could be involved in the rate determining step. In I interaction would be expected to occur between the o-tolyl groups and the bromine atom not attached to the ring carbon atom. Therefore this bromine atom is probably very easily removed by the electrophile E to form EBr<sup>-</sup>. In effect there is steric hindrance to forming the intermediate I but steric acceleration in forming intermediate II and as a result the overall rate of cleavage was higher than would be expected, when considering the relative rate of acid cleavage of the compound. Increase in the initial concentration of silane had little effect on the relative rate of cleavage.





The  $p-(CH_3)_3SiCH_2$  group strongly supplies electrons and the rate of cleavage of tri-( $p$ -trimethylsilylmethylphenyl)- $p$ -anisylsilane was faster than that of tri- $p$ -tolyl- $p$ -anisylsilane. When the times for removal of different fractions of bromine were compared, the cleavage rate relative to that for tri- $p$ -tolyl- $p$ -anisylsilane did not remain constant throughout the run, being 2.0 times as fast at 10% reaction and increasing to 3.5 times as fast at 70% reaction. This difference in relative rates indicates that some other reaction as well as cleavage was taking place. The orders of reaction calculated as described on page 41 are as follows:

Tri- $p$ -tolyl- $p$ -anisylsilane  $a_1 = 0.000670$  M  $a_2 = 0.000283$  M

Percentage reaction	10	20	30	40	50	60
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n	2.0	2.1	2.1	2.2	2.3	2.5
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Tri( $p$ -trimethylsilylmethylphenyl)- $p$ -anisylsilane  $a_1 = 0.000670$  M

$a_2 = 0.000283$  M

Percentage reaction	10	20	30	40	50	60	70
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n	2.2	2.2	2.2	2.2	2.1	2.1	2.1
---	-----	-----	-----	-----	-----	-----	-----

It is possible that for tri-( $p$ -trimethylsilylmethylphenyl)- $p$ -anisylsilane, as the reaction proceeded both a  $p$ -trimethylsilylmethylphenyl group and a  $p$ -anisyl group were cleaved from silicon.



(b) Trialkylsilyl and alkylphenylsilyl groups,  $R_3Si$ 

Relative rates of cleavage are listed in Table XVIII.

TABLE XVIII

Relative rates of cleavage of trialkyl- and alkylphenyl-p-anisylsilanes,  $R_3SiC_6H_4OMe-p$ , by bromine.

$R_3$	Rate of cleavage relative to p-anisyl $SiPh_3$	Rate of cleavage relative to p-anisyl $SiMe_3$
$Me_3$	1100	1
$Me_2Ph$	355	0.32
$MePh_2$	14.8	0.0135
$Ph_3$	1	0.00091
$(Benzyl)_3$	29.6	0.027
$Me_2CH_2Cl$	64.4	0.0585
$Me_2CH_2NHet$	48, 68	0.044, 0.062
$(OEt)_3$	8.4	0.0076

The rates of cleavage were in the same order as for acid cleavage except in the case of dimethylethylaminomethyl-p-anisylsilane. With bromine cleavage the amine was cleaved at about the same rate as diphenylmethyl-p-anisylsilane but with acid cleavage at about the same rate as chloromethyldimethyl-p-anisylsilane. In bromine cleavage no strong acid was present and the amine would be present largely as the reactive free base, but for acid cleavage little free base probably

existed. Therefore, the rate of cleavage relative to that of triphenyl-p-anisylsilane will be greater for bromine cleavage than for acid cleavage.

The rate of cleavage relative to that of tri-p-tolyl-p-anisylsilane fell from being approximately 17 times as fast at 10% reaction to six times as fast at 70% reaction. It is possible that this decrease in relative rate is because at the start of the reaction, the unprotonated base was rapidly cleaved. As the reaction proceeds, more protonated base was formed due to the presence of hydrogen bromide formed by hydrolysis of the silicon bromide which was obtained as cleavage product. The protonated base was then cleaved more slowly.

As the initial concentrations of bromine and dimethylethylamino-methyl-p-anisylsilane were increased the rate of cleavage relative to that of triphenyl-p-anisylsilane increased. This variation was most probably due to the difficulty in calculating relative rates for the first 10% of reaction.

FIG. XV. Plot of  $\log k_{rel}$  (bromine cleavage) against Hammett's  $\sigma$  constants

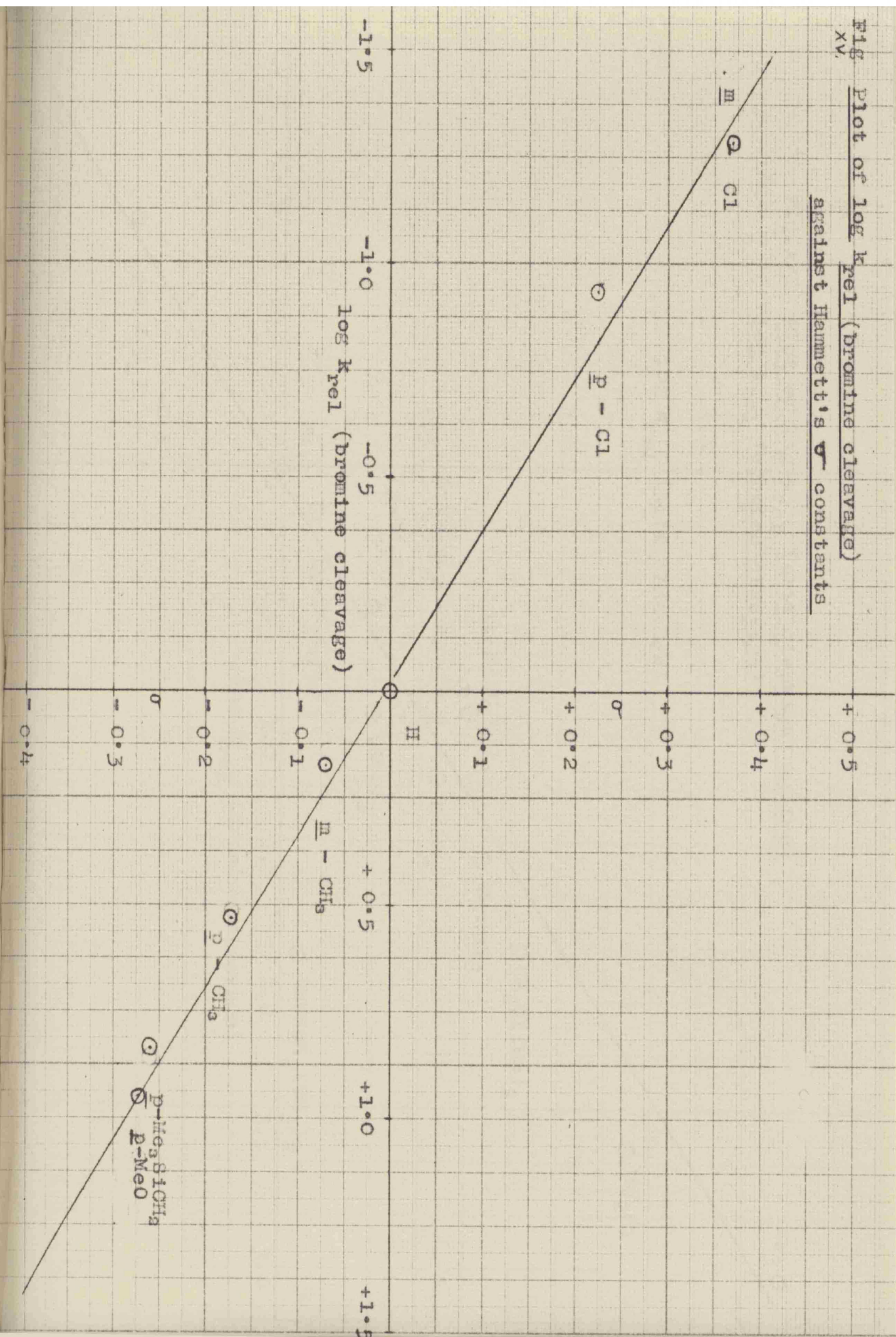
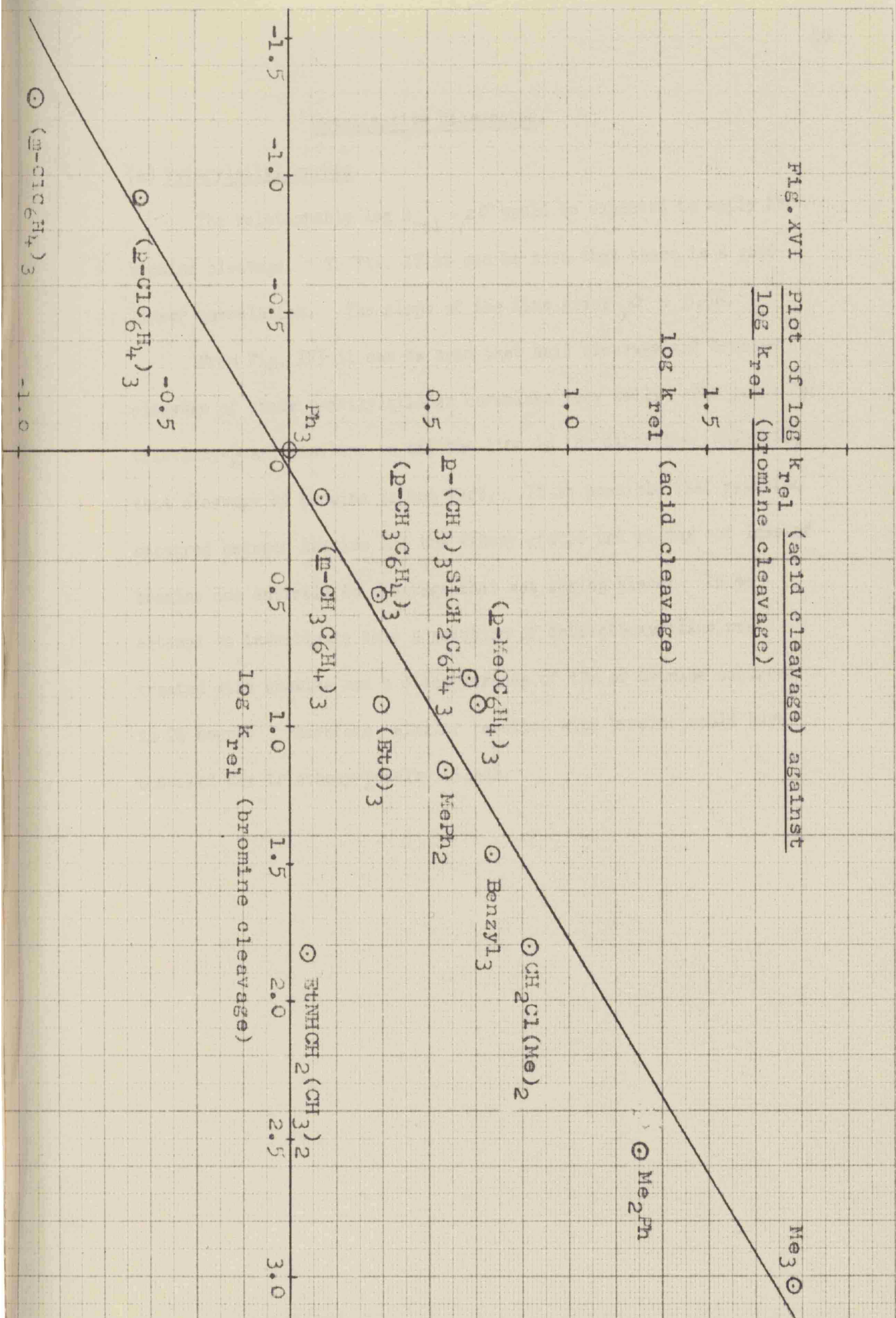




FIG. XVI

Plot of  $\log k_{rel}$  (acid cleavage) against  $\log k_{rel}$  (bromine cleavage)



Quantitative Discussion.

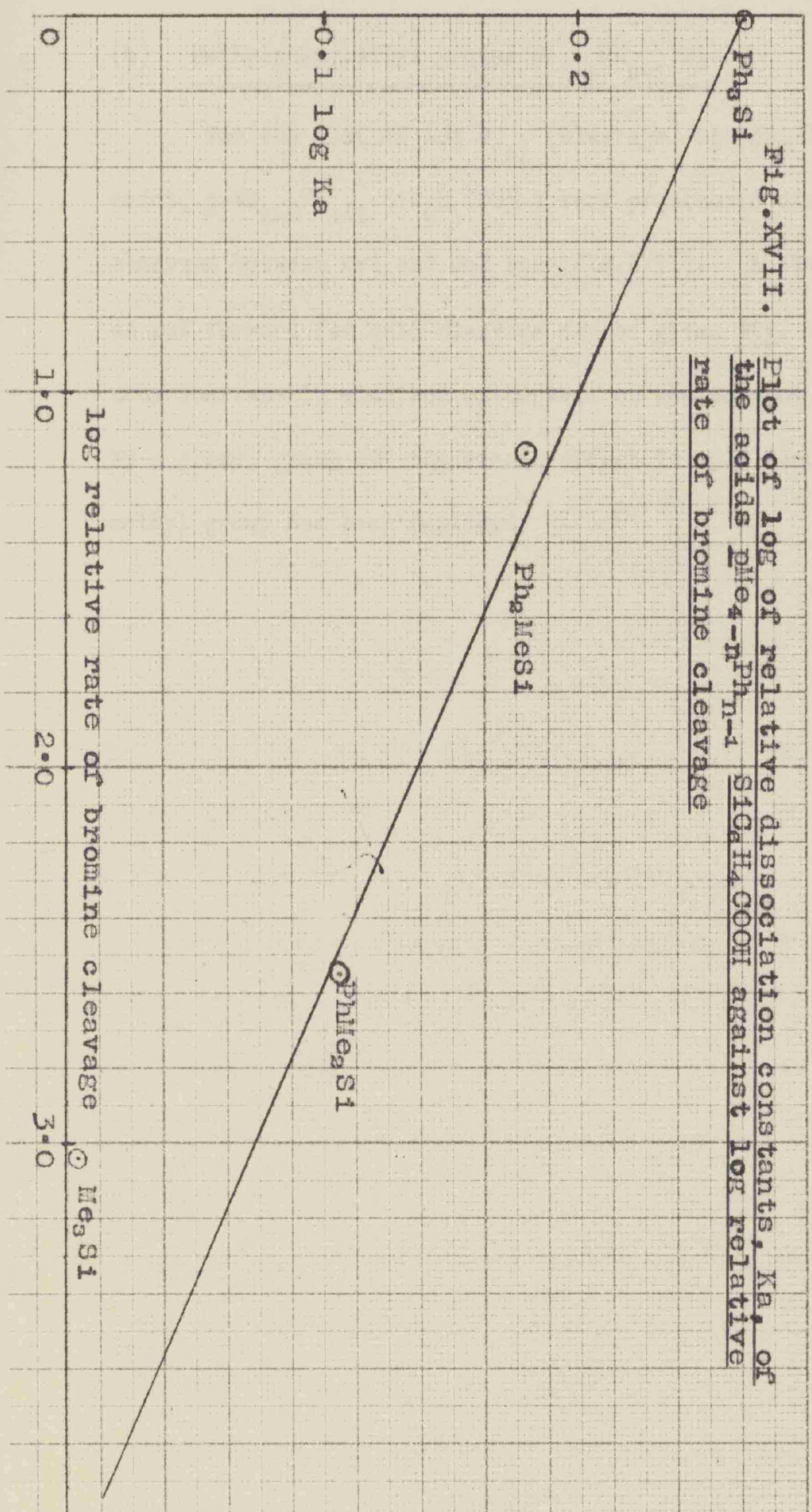
(a) Triarylsilyl groups.

The relationship  $\log k_{\text{rel}} = \rho\sigma$  would be expected to apply for bromine cleavage. In Fig. XV it can be seen that there is a good linear correlation. The slope of the line gives  $\rho = 3.56$ .

From Fig. XVI it can be seen that acid cleavage and bromine cleavage of these *p*-anisylsilanes correlate very well. The point for triethoxy-*p*-anisylsilane is off the line in the direction indicating that cleavage by bromine is too fast. It is possible that reaction occurred between bromine and the ethoxy groups and it was not loss of bromine due entirely to cleavage that was taking place. In an attempt to investigate this a solution of tetraethoxysilane was treated with bromine and a disappearance of 12% of bromine occurred in 24 hours. Therefore, similar reaction with bromine could have occurred for triethoxy-*p*-anisylsilane.

FIG. XVII.

Plot of log of relative dissociation constants,  $K_a$ , of the acids  $\text{PhMe}_4\text{-nPh}_{n-1}\text{SiG}_4\text{H}_4\text{COOH}$  against log relative rate of bromine cleavage



(b) Methylphenylsilyl groups  $\text{Me}_{4-n}\text{Ph}_{n-1}\text{Si}$

For the plot of  $\log k_{\text{rel}}$  (cleavage) against  $\log K_a$  of the acids,  $p\text{-Me}_{4-n}\text{Ph}_{n-1}\text{SiC}_6\text{H}_4\text{COOH}$  a very pronounced discontinuity was observed between  $n=1$  and  $n=2$  (see Fig.XVII). A similar explanation as put forward for acid cleavage may be given viz. there is a continuous increase in electron withdrawal on replacement of a methyl group by a phenyl group but the steric effect is only continuous after one methyl group has been replaced.

## CHAPTER VI

### Mercuric acetate cleavage of triaryl- and trialkyl-p-anisylsilanes.

Cleavage of the aromatic C-Si bond has been carried out by using mercuric acetate in glacial acetic acid<sup>14</sup> and glacial acetic acid containing 20 wt % water.<sup>15</sup> The latter solvent was chosen for this study as (i) most of the silanes were soluble in it (ii) cleavage of the majority of silanes could be followed at a convenient rate (iii) no appreciable reaction occurred between the solvent and mercuric acetate at the temperature used ( $25.00 \pm 0.02^\circ$ ). An attempt was made to follow cleavage at  $75^\circ$  in glacial acetic acid containing 10 wt % water but reaction (equivalent to a loss of 26% of mercuric ions in 18 hours) between the mercuric acetate and the solvent occurred. This has been reported previously and has been attributed to reaction of mercuric ions with acetate ion or acetic acid.<sup>60</sup>

Due to the difficulty in determining an exact end point because of the very dilute solutions used (see Chapter XI) an accuracy greater than 90% should not be attached to the quantitative figures.

Using the fractional life method for determining order, it was found that variation occurred throughout a run. This was most probably due to experimental error as it is likely that the end point observed for one set of runs using a particular mercuric acetate concentration was not the same as that taken for another set of runs (See Chapter XI).



The purpose of this work was to investigate the effect of varying R in  $R_3SiC_6H_4OMe-p$  on the cleavage of the C-Si bond by different electrophilic reagents. Therefore most emphasis has been placed on this aspect of the work.

Relative rates of cleavage and concentration of mercuric acetate are given in Table XIX.

TABLE XIX

Cleavage of triaryl- and trialkyl-*p*-anisylsilanes,  $R_3SiC_6H_4OMe-p$ , by mercuric acetate in glacial acetic acid containing 20 wt % water at  $25.00 \pm 0.02^\circ$ .

$R_3$	Concentration of $Hg(OAc)_2 \times 10^5$ , M.	Relative rate of cleavage
$Ph_3$ <sup>2</sup>	3.86	1
$(p\text{-tolyl})_3$ <sup>2</sup>	3.86	2.53
$(m\text{-tolyl})_3$ <sup>2</sup>	3.86	1.55
$(p\text{-chlorophenyl})_3$ <sup>2</sup>	3.86	0.660
$Me_2Ph$ <sup>1</sup>	3.86	68.7
$Me_3$ <sup>1</sup>	3.86	194
$Me_2Ph$ <sup>1</sup>	8.69	10.19
$MePh_2$ <sup>1</sup>	8.69	1
$(p\text{-anisyl})_3$ <sup>1</sup>	19.4	9.81

TABLE XIX (Continued)

$R_3$	Concentration of $Hg(OAc)_2 \times 10^5$ , M.	Relative rate of cleavage
$MePh_2$ <sup>1</sup>	19.4	1
$Benzyl_3$ <sup>2</sup>	19.4	0.157
$(m\text{-chlorophenyl})_3$ <sup>2</sup>	19.4	0.0217
$MePh_2$ <sup>1</sup>	47.9	1
$Me_2CH_2Cl$ <sup>1,3</sup>	47.9	19.2
$MePh_2$ <sup>1</sup>	80.4	1
$Me_2EtNH_2CH_2$ <sup>1</sup>	80.4	0.434

<sup>1</sup> Runs carried out in 100 ml. flasks - denoted "slow runs"

<sup>2</sup> Runs carried out in sealed tubes - denoted "very slow runs".

<sup>3</sup> Initially reaction was very fast. Relative rate given is that for first 10% of reaction.

Qualitative Discussion(a) Triarylsilyl groups, Ar<sub>3</sub>SiTABLE XX

Relative rates of cleavage of triaryl-p-anisylsilanes,  
Ar<sub>3</sub>SiC<sub>6</sub>H<sub>4</sub>OMe-p, by mercuric acetate.

Ar	Relative rate of cleavage
Ph	1
<u>m</u> -tolyl	1.55
<u>p</u> -tolyl	2.53
<u>m</u> -chlorophenyl	0.146
<u>p</u> -chlorophenyl	0.495
<u>p</u> -anisyl	66.1 <sup>a</sup>

<sup>a</sup> Four p-anisyl groups can be removed ∴ actual  
rate =  $\frac{66.1}{4} = 16.5$

As for both acid and bromine cleavage, electron withdrawing substituents in Ar decrease the rate of cleavage and electron supplying substituents increase the rate of cleavage relative to that of triphenyl-p-anisylsilane.

Trialkyl- and alkylphenylsilyl groupsTABLE XXI

Relative rates of cleavage of trialkyl- and alkylphenyl-*p*-anisylsilanes,  $R_3SiC_6H_4OMe$ -*p*, by mercuric acetate.

$R_3$	Relative rates of cleavage
$Me_3$	194
$Me_2Ph$	68.7
$MePh_2$	6.74
$Ph_3$	1
$Bz_3$	1.06
$Me_2CH_2Cl$	129.5
$Me_2CH_2NHEt$	2.93

A similar order of relative rates as for bromine cleavage was observed except for tribenzyl-*p*-anisylsilane, which now was cleaved at a similar rate to triphenyl-*p*-anisylsilane. If it is considered that the electrical effect of a benzyl group is the same for both bromine and mercuric acetate cleavage, this slower relative rate which has been observed here was probably due to steric effects.

For bromine cleavage it was concluded that steric hindrance due to the tribenzylsilyl group was less than the triphenylsilyl group because of the methylene group separating phenyl and silicon. However, in mercury acetate cleavage, the acetoxymercuri ion is sufficiently large that benzyl groups could also cause considerable steric hindrance to its attack on the ring carbon attached to silicon. From a consideration of the amount of ortho isomer formed in the mercuration of toluene<sup>61</sup> it has been concluded that there is considerable steric

hindrance to the mercuration reaction,<sup>63</sup> but this would not appear to be as great as that for molecular bromination.

The overall spread of rates of cleavage was in the order

bromodesilylation > mercuridesilylation > protodesilylation

This has been attributed to an increase in electron demand from bromodesilylation to mercuridesilylation to protodesilylation.

Fig XVIII Plot of log relative rate of bromine cleavage against log relative rate of mercuric acetate cleavage

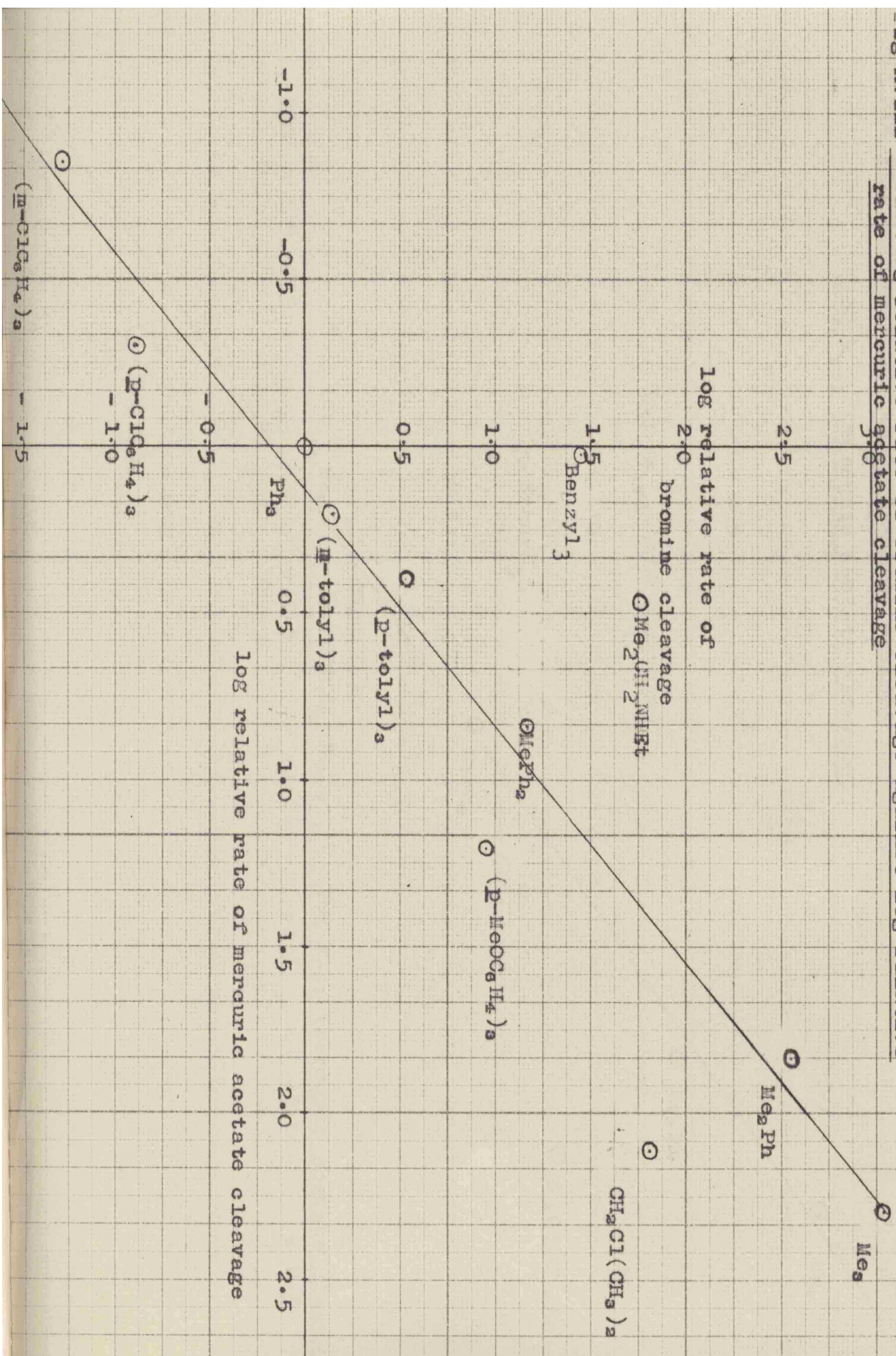




FIG. XIX Plot of  $\log k_{rel}$  (acid cleavage) against  $\log k_{rel}$  (mercuric acetate cleavage)

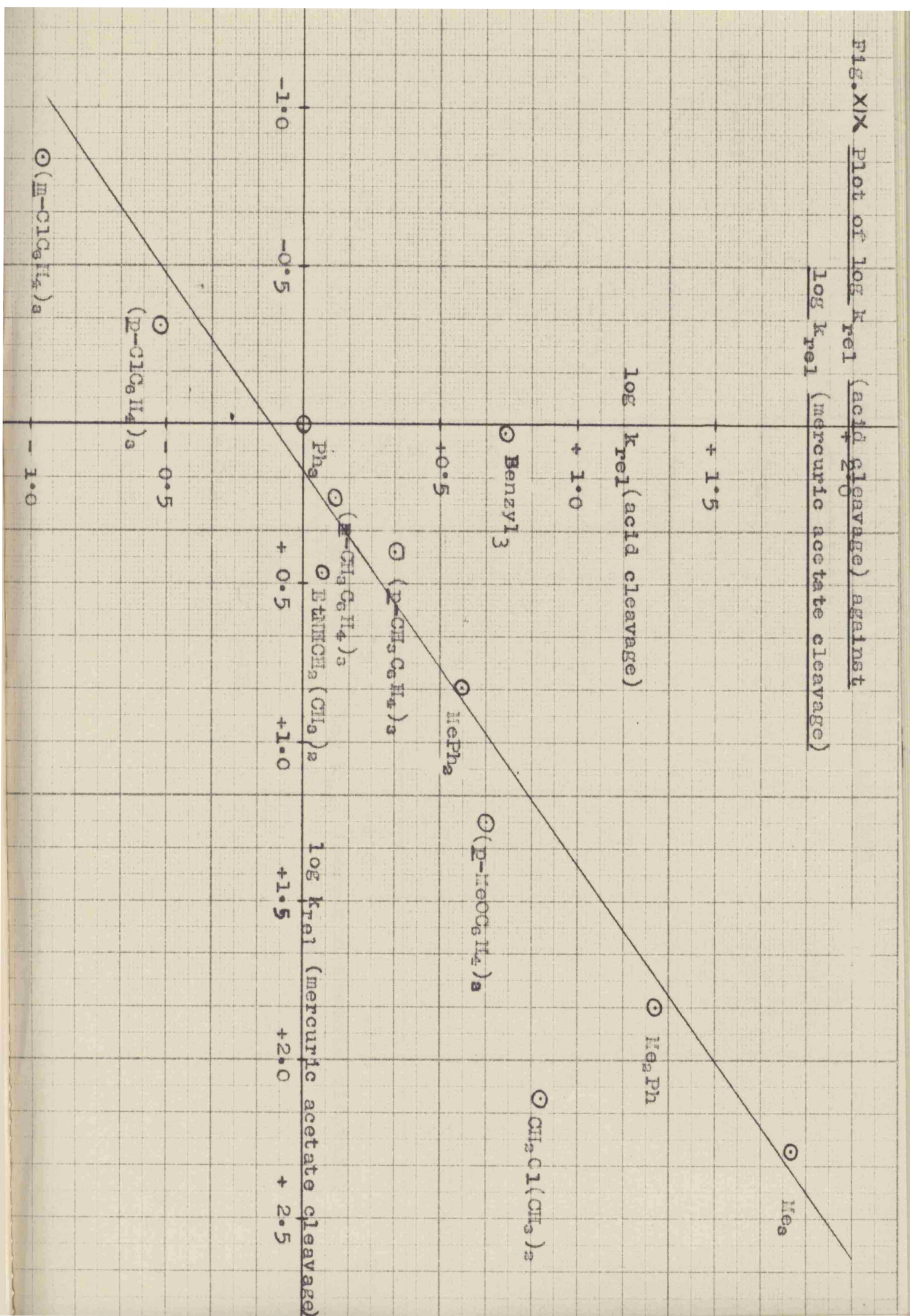
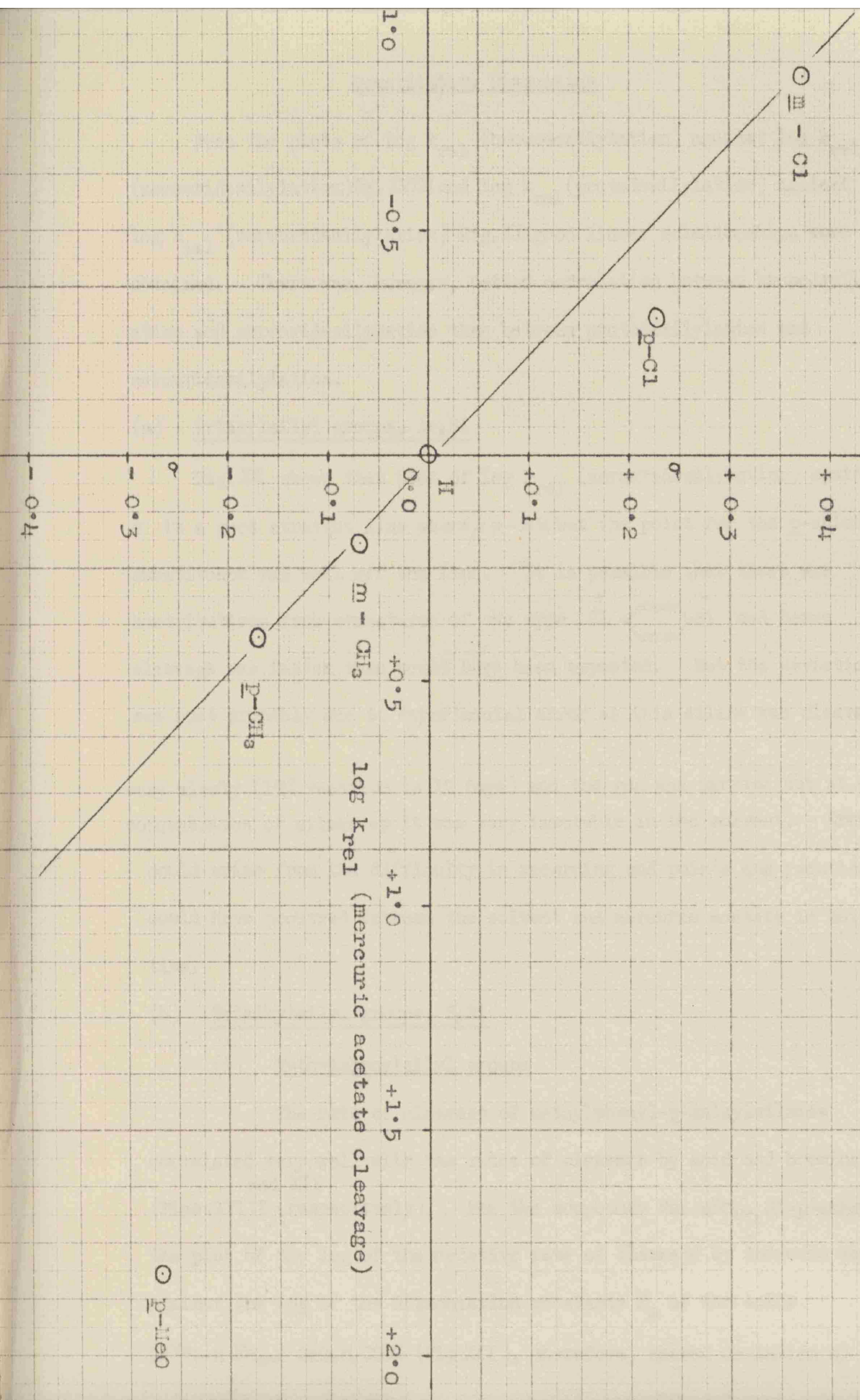




FIG. No. XX Plot of  $\log k_{rel}$  (mercuric acetate cleavage) against Hammett's  $\sigma$  constants





### Quantitative Discussion

From the plots of  $\log k_{\text{rel}}$  (bromodesilylation) against  $\log k_{\text{rel}}$  (mercuridesilylation) Fig. XVIII and  $\log k_{\text{rel}}$  (protodesilylation) against  $\log k_{\text{rel}}$  (mercuridesilylation) Fig. XIX good linear relationships were obtained. There was, however, better correlation between bromodesilylation and mercuridesilylation than between protodesilylation and mercuridesilylation.

(a) Triarylsilyl groups,  $\text{Ar}_3\text{Si}$

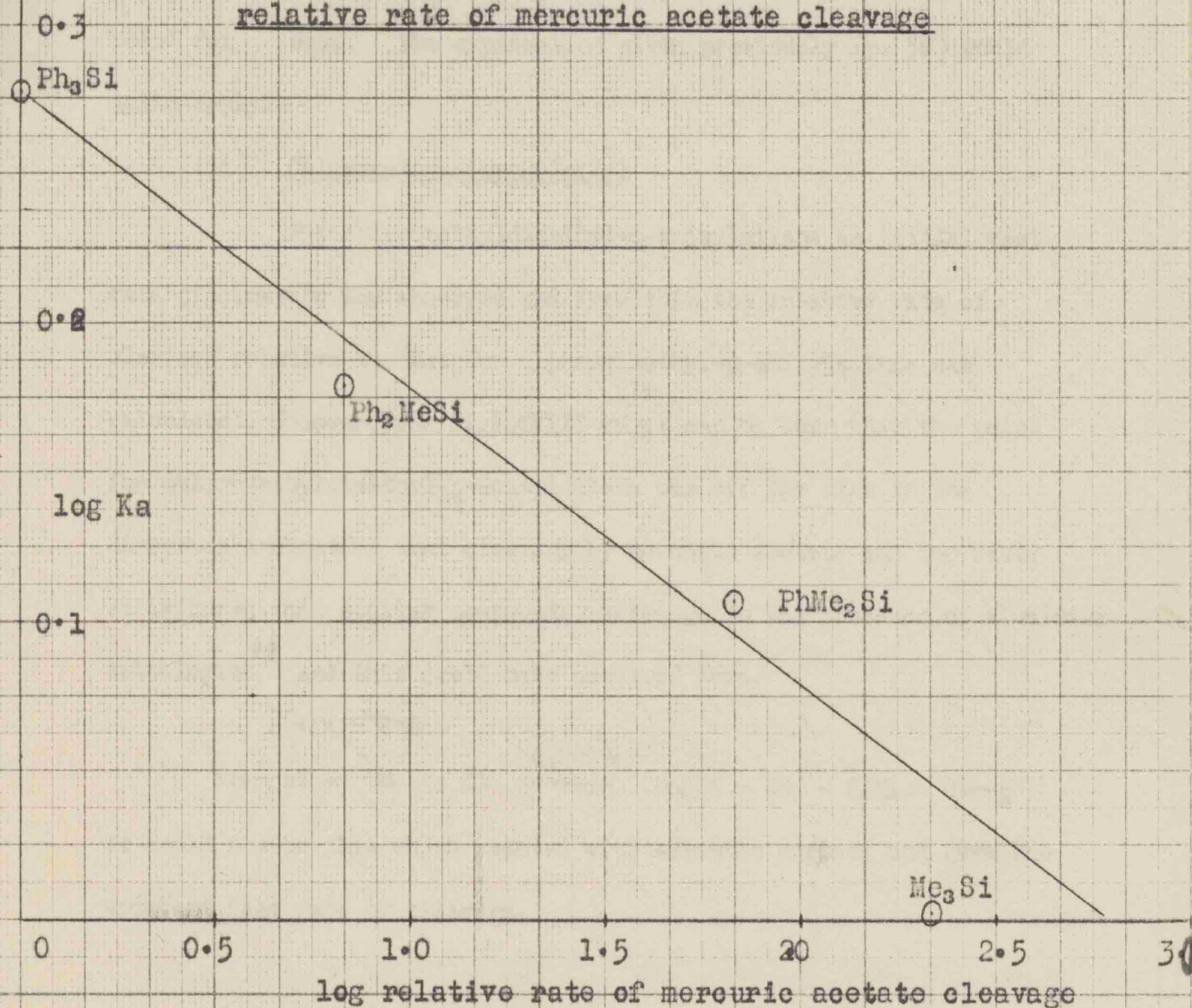
Fig. XX shows that plot of  $\log k_{\text{rel}}$  (mercuridesilylation) against  $\sigma$  is a good straight line where  $\rho = -2.34$  but the point for the *p*-chloro substituent was well off the line. It is possible that there are contributions from structures of the type  $\text{Cl}^+ = \text{C}_6\text{H}_4 = \text{Si}^-$  and hence cleavage was faster than would have been expected. But the deviation was most probably due to experimental error as this silane was cleaved very slowly (12% reaction in 17 days) and the run was carried out at a low concentration of silane as it was very insoluble in the solvent. Errors could arise from the difficulty in recording end points and reaction could have occurred between the solvent and mercuric acetate in this time.

(b) Trialkylsilyl groups,  $\text{R}_3\text{Si}$

(i) Methylphenylsilyl groups

The rate of cleavage of methylphenyl-*p*-anisylsilanes correlated very well with the rates of cleavage by acid and bromine and XIX (Figs. XVIII and XIX respectively). For the compounds  $\text{Me}_{4-n}\text{Ph}_{n-1}\text{Si-p-anisyl}$ , the plot of the log of the relative rate of cleavage by mercuric acetate against the log of the dissociation constants  $K_a$  of the acids  $\text{p-Me}_{4-n}\text{Ph}_{n-1}\text{SiC}_6\text{H}_4\text{COOH}$  (Fig. XXI), therefore, showed deviation by the

Fig.XXI. Plot of log of relative dissociation constants,  $K_a$ , of the acids  $pMe_{4-n}Ph_{n-1}SiC_6H_4COOH$  against log relative rate of mercuric acetate cleavage

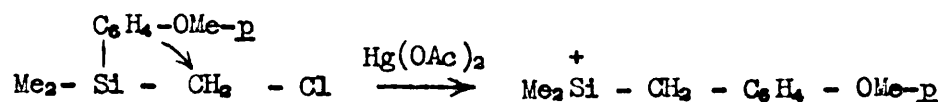




point for  $\text{Me}_2\text{Si}$ . The explanation given previously (p. 39) would again apply.

(ii) Chloromethyldimethylsilyl

For chloromethyldimethyl-*p*-anisylsilane an initial fast rate of cleavage was observed and from this the relative rate of cleavage relative to that for diphenylmethyl-*p*-anisylsilane was calculated. However, from Figs. XVIII and <sup>XIX</sup> it can be seen that the point for chloromethyldimethyl-*p*-anisylsilane was off the line in the direction indicating that cleavage by mercuric acetate was too fast. It is known that similar compounds rearrange in the presence of aluminium trichloride<sup>68</sup> and this could have occurred here.



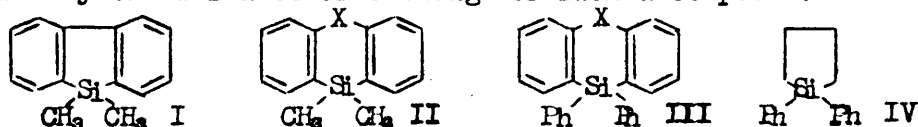
It could now be this which reacted with mercuric acetate and gave the apparent fast rate of cleavage.

As there was some uncertainty as to whether the rate of cleavage of *p*-tolyltrimethylsilane was faster than that of *p*-tertiarybutylphenyltrimethylsilane the rates of cleavage of these two silanes was measured. It was found that *p*-tolyltrimethylsilane was cleaved faster than *p*-tertiarybutylphenyltrimethylsilane.

## CHAPTER VII

### Cleavage of cyclic organosilicon compounds

Cyclic organosilicon compounds have been prepared in which silicon is incorporated into the aromatic ring<sup>64,65,66</sup> but there is only one instance of cleavage of such a compound.



5,5-Diphenyldibenzosilole (I) when treated with formic acid gave biphenyl and an impure silicon-containing fragment.<sup>67</sup> This is similar to the cleavage of 2-biphenyl substituted organosilicon compounds by formic acid.<sup>21</sup>

As cleavage of these compounds was limited to this one example it was proposed to prepare the above compound and a series of cyclic organosilicon compounds of the type II where  $X = \text{SO}_2$ , S, O, NEt, and  $\text{CH}_2$  in order to investigate when silicon was part of the ring and attached to two aromatic nuclei whether increased stability of the C-Si bond resulted and to study how variation of X affected cleavage by acid and bromine.

The corresponding diphenylsilyl compounds III where  $X = \text{O}$ , NH, NEt and S, have been prepared by refluxing diphenylsilane for 3-6 days with the S-containing heterocycles phenoxanthin, phenothiazine, 10-ethylphenothiazine and thianthrene,<sup>64</sup> hydrogen sulphide was evolved and the  $\text{Ph}_2\text{Si}$  group took the place of the sulphur atom in the ring system. Since dimethylsilane is a gas, this method could not be used and consequently other methods of preparation were employed or attempted. The compounds where  $X = \text{O}$ , NEt, and  $\text{SO}_2$  were prepared

but for  $X = S$  and  $CH_2$  the preparations were unsuccessful (see Chapter VIII). 5,5-Dimethyldibenzosilole (I) was also prepared. 1,1-Diphenylsilacyclopentane (IV) was prepared in order to investigate the effect on cleavage when silicon was part of an alicyclic ring.

TABLE XXII

Cleavage of cyclic silicon compounds by perchloric acid  
in water/methanol at  $50.00 \pm 0.02^\circ$

Compound	Concentration of acid, M.	Wavelength at which run carried out $m\mu$	Concentration of silane $\times 10^5$ , M.	Rate of cleavage $\times 10^2$	Average rate of cleavage $\times 10^2$	Rate of cleavage relative to $\text{Me}_3\text{Si-C}_6\text{H}_4\text{OMe-P}$	Rate of cleavage relative to II, $\text{X=O}$
I	12.19	287	0.838	3.25 3.24	3.25	0.00309	1.66
II, $\text{X=O}$	12.19	284	2.24	1.95 1.94	1.95	0.00186	1
II, $\text{X=NEt}$	0.293	282	0.519	21.5 21.6	21.6	97.3	52,300
II $\text{X=SO}_2$	12.19	No cleavage within 6 days					
IV <sup>a, b</sup>	12.19	271	21.3	$\frac{\text{ca}}{7 \times 10} - 2$ $\frac{\text{ca}}{7 \times 10} - 2$	$\frac{\text{ca}}{7 \times 10} - 2$	$\frac{\text{ca}}{0.00007}$	$\frac{\text{ca}}{0.036}$

<sup>a</sup> run carried out in sealed tubes

<sup>b</sup> Both phenyl groups appeared to be cleaved. The value of  $k$  is only approximate and was obtained from the first 30% of the run.

Acid cleavage.

Except for 1,1-diphenylsilacyclopentane straight lines were obtained for the plots of  $\log (D_t - D_{\infty})$  against time.

The spectrum of the cleavage product for 5,5-dimethyldibenzo-silole (I) was removed from that of diphenyl by ca 2  $\mu$  but very similar in shape. This indicates that it probably still has a silicon group attached and that cleavage of only one Si - C(aromatic) bond has occurred.

For 10,10-dimethylphenoxasilin (II, X = O) the spectrum of the cleavage product was the same as that for diphenyl ether and it may be concluded that both Si-C (aromatic) bonds have been broken. Since a straight line was obtained for the plot of  $\log (D_t - D_{\infty})$  against time this meant that the second Si-C bond was probably cleaved very quickly once the first Si - C bond had been broken. If the second bond had been cleaved slowly a straight line would not have been obtained. The value of rate of cleavage was that for cleavage of both Si - C bonds; the rate of cleavage of the first was probably much slower.

Cleavage of the first Si - C bond was slightly faster for 5,5-dimethyldibenzosilole than for 10,10-dimethylphenoxasilin. Once the first bond is broken an ortho-substituted arylsilane would be left; in the latter an o-phenoxy group would strongly supply electrons and this would facilitate cleavage of the second C - Si bond but for the former it would appear that the o-phenyl group does not supply electrons strongly enough for the second Si - C bond to be broken. This would be expected, because in cleavage of nuclear substituted arylsilanes by sulphuric acid/acetic acid/water,<sup>8</sup> the rate of cleavage of 2-biphenyltrimethylsilane is only 6 times faster than that of phenyltrimethylsilane.

In II when  $X = \text{NEt}$  there is a strong supply of electrons from nitrogen, this being more than from oxygen and hence cleavage of this was considerably faster than that of the corresponding oxygen compound. As both bonds of 10,10-dimethylphenoxasilin (II,  $X = \text{O}$ ) were broken by acid it was therefore most probable that both bonds were broken in this case. When the acid concentration was increased from 0.293M to ca 1.0M the rate of cleavage increased. The fall in rate of cleavage as observed for  $p\text{-NMe}_2\text{C}_6\text{H}_4\text{-SiMe}_3$  with increase in acid concentration<sup>7,8</sup> did not occur for this compound.

No cleavage within six days was observed for the compound II( $X=\text{SO}_2$ ) which shows the very large deactivating effect of the sulphone grouping.

In Table XXII are listed the rates of cleavage relative to that of trimethyl- $p$ -anisylsilane. If silicon were not part of the cyclic system an ortho-substituted aryl silane would result. Figures for rates of acid cleavage of such  $o$ -substituted arylsilanes relative to that of trimethyl- $p$ -anisylsilane are listed below

- |       |                     |  |
|-------|---------------------|--|
| (i)   | $o\text{-Ph}^8$     | 0.00594 <sup>a</sup>                           |
| (ii)  | $o\text{-PhO}^{68}$ | 0.00578 <sup>b</sup>                           |
|       | <sup>a</sup>        | cleavage by sulphuric acid/water/acetic acid   |
|       | <sup>b</sup>        | cleavage by aqueous methanolic perchloric acid |
| (iii) | $o\text{-NEtPh}$    | No figure exists for the substituent.          |

It therefore would appear that the stability of the C-Si bond is slightly greater in the cyclic organo-silicon compounds than in the open chain compounds.

For 1,1-diphenylsilacyclopentane, IV, it appeared that both phenyl groups were cleaved as the plot of  $\log (D_t - D_\infty)$  against  $t$



(see p. 95 ) was not a straight line. An approximate value of rate of cleavage was obtained for the first 30% of the reaction and cleavage was much slower than for the other cyclic organosilicon compounds.

Bromine cleavage.

TABLE XXII I

Relative rates of cleavage of cyclic organosilicon compounds  
by bromine in glacial acetic acid containing 1.5 wt % water  
at  $25.00^\circ \pm 0.02^\circ$

Compound	Concentration of bromine $\times 10^4$ , M	Concentration of silane $\times 10^4$ , M	Rate of cleavage relative to $\text{Ph}_3\text{SiC}_6\text{H}_4\text{OMe}$	Rate of cleavage relative to I
I <sup>3</sup>	8.99	8.32	0.009 <sup>a</sup>	1
II, X = O <sup>2</sup>	8.99	8.32	0.110	12
II, X = EtN <sup>1</sup>	2.17	2.17	Cleavage too fast to measure i.e. Complete cleavage occurred in 20 sec.	
II, X = SO <sub>2</sub> <sup>2</sup>	15.6	15.6	No cleavage within 5 days.	

<sup>1</sup> Run carried out in fast reaction vessels ("fast run")

<sup>2</sup> Run carried out in 100 ml. flasks ("slow run")

<sup>3</sup> Run carried out in sealed tubes ("very slow run")

<sup>a</sup> Relative rate figure taken for first 40% reaction.

The rate of cleavage of 10,10-dimethylphenoxasilin relative to that of triphenyl-p-anisylsilane was approximately the same for both cleavage by acid and bromine. However, for cleavage of 5,5-dimethyldibenzosilole, cleavage by bromine was much slower relative

to triphenyl-p-anisylsilane and the rate was slower than for 10,10-dimethylphenoxasilin. From considerations of electrical and steric effects no change in order of cleavage would have been expected. It is possible therefore that it was not in fact cleavage that occurred.

The rate of reaction of I compared to that of triphenyl-p-anisylsilane dropped from 0.0096 at 30% reaction to 0.0078 at 50%. This indicates that the order was higher for the reaction between bromine and I than between bromine and triphenyl-p-anisylsilane.

With II, X = N<sub>2</sub> cleavage occurred too quickly to be measured. This showed the very high reactivity of the Si-C bonds due to a strong supply of electrons by the -N<sub>2</sub> group.

For the compound II, X = SO<sub>2</sub> no cleavage occurred within 5 days and this, once again, showed the unreactivity of the Si - C bond due to the presence of the sulphone grouping.

### SECTION III. Experimental Work

## CHAPTER VIII

### Preparation of Organo-silanes and Intermediates

#### Dimethylphenyl-p-anisylsilane.

Phenylmagnesium bromide was prepared by slowly adding bromobenzene (160 gm, 1.02 mole) in anhydrous ether (400 ml) to magnesium turnings (31 gm, 1.3 mole) and boiling the mixture under reflux for 1 hr. A solution of dimethyldichlorosilane (129 gm, 1.0 mole) in anhydrous ether (400 ml) was rapidly added and the mixture boiled under reflux for a further 5½ hr.

The cooled mixture was then hydrolysed with dilute hydrochloric acid and the ethereal layer separated, washed with water and dried ( $\text{Na}_2\text{SO}_4$ ). The ether was distilled off and the residue was dissolved in approximately fifteen times its volume of alcohol, the total volume of alcohol being about 2 litres. The solution was placed in a 3 litre round-bottomed flask equipped with a reflux condenser and aqueous AnalaR hydrofluoric acid (380 ml)(40% w.w) was added. The flask was warmed in a water bath so that bubbles of gaseous hydrofluoric acid only arose very slowly to the surface. After 10 hr. the bath was switched off and the mixture left overnight. It was then poured into three times its volume of water and the oil which separated out extracted with petroleum ether ( $<40^\circ$ ). The extract was washed with water, dried ( $\text{Na}_2\text{SO}_4$ ) and the solvent was distilled off through a packed column. The residue was fractionally distilled through a packed column to give dimethylphenylfluorosilane (105 gm, 68%) b.p.  $162^\circ$  (reported  $162.4^\circ$  <sup>88</sup> ).

Dimethylfluorosilane (24.6 gm, 0.16 mole) in ether (200 ml) was added to an ethereal solution of p-anisyllithium (ca 0.2 mole). The mixture was stirred for about 2 hr., filtered through glass wool to remove any excess lithium and hydrolysed with dilute hydrochloric acid. The ethereal layer was washed with water and dried ( $\text{Na}_2\text{SO}_4$ ). The ether was distilled off and the residue fractionated at reduced pressure through a Vigreux column to give dimethylphenyl-p-anisylsilane (10 gm, 26%) b.p.  $186^\circ/30$  mm.  $n_D^{20} = 1.5641$

Anal. Calculated for  $\text{C}_{16}\text{H}_{18}\text{SiO}$ : C=74.40 H=7.44

Found: C=74.35 H=7.58

The solution of p-anisyllithium was prepared in the following manner. Lithium (3.18 gm, 0.46 gm.atom) was beaten into thin sheets, cut up into small pieces under a stream of nitrogen and placed in a 1 litre three-necked flask equipped with a dropping funnel, reflux condenser and mechanical stirrer. Ether (150 ml) was added and nitrogen passed through the flask, which was protected from atmospheric moisture by means of bubbles containing concentrated sulphuric acid.

p-Bromo-anisole (37.3 gm, 0.2 mole) in ether (150 ml) was added slowly to the rapidly stirred mixture and the reaction proceeded very readily. When all the p-bromo-anisole had been added the mixture was stirred for about 30 min. In all the preparations of p-anisyllithium a small amount of di-p-anisyl was formed. This was largely precipitated when the ether was distilled off from the final product and was filtered off. However, a small amount always remained and was removed by fractional distillation. Sometimes it sublimed at the same temperature as the boiling point of the wanted silane and it

was necessary to discard the distillate until it remained free from solid. Di-p-anisyl could also be mainly removed by adding petrol (100-120°) to the final product before distillation. The silane dissolved but di-p-anisyl is not very soluble in this solvent and hence can be filtered off.

#### Diphenylmethyl-p-anisylsilane

Phenylmagnesium bromide prepared from bromobenzene (1 mole) in ether as described above was added to methyltrichlorosilane (75 gm, 0.5 mole) in ether (200 ml). The mixture was refluxed for 7 hr. and then hydrolysed with dilute acid. After ether extraction the solvent was distilled off and fluorination of the residue was carried out as before. The product was fractionally distilled at reduced pressure to give <sup>diphenyl</sup> methylsilyl fluoride (42 gm, 39.5%) b.p. 149°/20 mm.

Anal. Calculated for  $C_{13}H_{13}SiF$ : F = 8.80

Found: F = 9.08

Using the above procedure, approximately 0.16 mole of p-anisyllithium was prepared and to it was added diphenylmethylsilyl fluoride (34.6 gm, 0.16 mole), in ether, (200 ml) and the mixture was then boiled under reflux for 2 hr. The usual extraction was followed by removal of the ether. The residue was crystallised from methyl alcohol to give diphenylmethyl-p-anisylsilane (10.3 gm, 21.6%) m.p. 77.5°.

Anal. Calculated for  $C_{20}H_{20}OSi$ : C = 78.94 H = 6.62

Found: C = 78.8 H = 6.78

Tri-(p-tolyl)-p-anisylsilane

p-Tolylmagnesium bromide (ca. 0.33 mole) was prepared by the addition of p-bromo-toluene (67 gm, 0.39 mole) in ether (150 ml) to magnesium turnings (10 gm, 0.42<sup>mole</sup>) followed by 1 hour's refluxing. Silicon tetrafluoride obtained by the slow addition of concentrated sulphuric acid to a mixture of sodium fluoro-silicate (50 gm) and silica (7.5 gm), was bubbled slowly through the solution until two layers separated. The layers were separated, the magnesium salts were washed with ether and these washings added to the ethereal solution. After washing and drying the fluoride was obtained in the usual way to give after recrystallisation from petroleum spirit (60-80°) tri-p-tolylsilyl fluoride (15.5 gm, 43%) m.p. 109.5 - 110.5°.

In the preparation of triarylsilyl fluorides by this method it was later found that after coupling and the two layers had been formed the mixture could be hydrolysed in the usual manner using dilute acid without appreciable loss of product.

Tri(p-tolyl)silyl fluoride (15 gm, 0.047 mole) in ether (50 ml) was treated with p-anisyllithium (ca. 0.05 mole) in the usual way, the mixture refluxed for 5 hr. and the silane isolated. After recrystallising from alcohol it gave tri-(p-tolyl)-p-anisylsilane (4.6 gm, 24%) m.p. 194°.

Anal. Calculated for  $C_{28}H_{28}OSi$ : C = 82.31, H = 6.91

Found: C = 82.04, H = 6.88

Tri-(p-chlorophenyl)-p-anisylsilane

Tri-(p-chlorophenyl)silyl fluoride (20 gm, 47.6%) b.p. 275°/10 mm. was prepared from p-chlorophenyl magnesium bromide (ca. 0.33 mole) using the method described above.

The fluoride (20 gm, 0.052 mole) was dissolved in ether (50 ml) and added to an ethereal solution of p-anisyllithium (ca. 0.06 mole) and refluxed for 5 hr. The product was recrystallised from alcohol to give tri-(p-chlorophenyl)-p-anisylsilane (3.7 gm, 15%) m.p. 160.5°.

Anal. Calculated for  $C_{25}H_{19}Cl_3OSi$ : C = 63.90, H = 4.08

Found: C = 64.23, H = 4.43

Tri(m-chlorophenyl)-p-anisylsilane

m-Chlorophenyl magnesium bromide (ca. 0.33 mole) was converted to tri(m-chlorophenyl)silyl fluoride (15 gm, 36%), b.p. 224°/3 mm. using the method described. This was added to an ethereal solution of p-anisyllithium and gave, after recrystallisation from alcohol, tri-(m-chlorophenyl)-p-anisylsilane (2.5 gm, 13%) m.p. 90-91.5°

Anal. Calculated for  $C_{25}H_{19}Cl_3OSi$ : C = 63.90, H = 4.08

Found: C = 64.09, H = 4.00

In order to obtain this silane it was necessary to prepare the intermediate compound m-chlorobromobenzene. The following method was used:

Preparation of m-chlorobromobenzene

A mixture of 1 mole (127.5 gm) of m-chloroaniline and 48% (w.w.) hydrobromic acid (300 ml, 2.5 mole) were placed in a 2 litre beaker set in an ice-bath and cooled to 0°. A solution of sodium



nitrite (70 gm, 1 mole) in water (125 ml) was added with stirring, the temperature being kept below 10° by addition of ice.

Meanwhile, about 1 mole of cuprous bromide was prepared by addition of a solution of sodium sulphite (80 gm, 0.635mole) in water to a mixture of copper sulphate (300 gm, 1.88mole) and sodium bromide (175 gm, 1.4 mole) in about 1 litre of water. This, together with hydrobromic acid (160 ml), was heated to boiling in a 3 litre round-bottomed three-necked flask.

The diazonium salt solution was added in small quantities (50 ml) over 30 minutes to the cuprous bromide/hydrobromic acid solution which was kept boiling. When addition was complete the mixture was steam distilled and about 1½ - 2 litres of product collected.

The distillate was extracted with ether and washed several times with 2N caustic soda solution to remove any phenolic impurities. The ethereal solution was washed with water and dried over anhydrous sodium sulphate. After distilling off the solvent the residue was fractionally distilled to give m-chlorobromobenzene (160 gm, 84%), b.p. 193°.

#### Tri-(m-tolyl)-p-anisylsilane

m-Bromotoluene (89 gm, 52%) was prepared from m-toluidine, as above. Tri(m-tolyl)fluorosilane b.p. 205-210°/2.5 mm was prepared by the usual method but was not successfully crystallised. 16 gm of the fluoride was added to an ethereal solution of p-anisyllithium (ca. 0.05 mole) and gave after recrystallisation from alcohol

tri(m-tolyl)-p-anisylsilane (3.4 gm, 16.6%) m.p. 111.5 - 112°

Anal. Calculated for  $C_{28}H_{28}OSi$ : C = 82.31, H = 6.91

Found: C = 82.08, H = 6.76

#### Tribenzyl-p-anisylsilane

Benzyl chloride in ether was converted to the corresponding Grignard reagent (ca. 0.33 mole) and silicon tetrafluoride passed into the solution until two layers separated. The gas supply was stopped and the mixture refluxed for 1 hr and left overnight. After hydrolysis with dilute acid, the silane was extracted in the usual way and gave tribenzylfluorosilane (25 gm, 23.4%), m.p. 79°, recrystallisation from petrol (60-80°).<sup>71</sup> Tribenzylsilyl fluoride (20 gm, 0.0625 mole) in ether (50 ml) was added to p-anisyllithium (ca. 0.07 mole) in ether (50 ml) and then refluxed for 4 hr. The product was isolated and after recrystallisation from alcohol gave tribenzyl-p-anisylsilane (10.5 gm, 41.4%) m.p. 84.5° (reported m.p. 83-85°).<sup>4</sup>

#### Tri-(p-trimethylsilylmethylphenyl)-p-anisylsilane

##### Preparation of p-trimethylsilylmethylphenyl chloride.

$\alpha$ -p-Dichlorotoluene (177 gm, 1.1 mole) in ether (450 ml) was added to magnesium (31 gm, 1.3 mole) and the Grignard reagent prepared. Trimethylchlorosilane (108.5 gm, 1 mole) in ether (ca. 400 ml) was added and the mixture refluxed overnight. After hydrolysis the ethereal layer was separated, washed and dried ( $Na_2SO_4$ ). The ether was distilled off and the residue fractionated through a packed column.

The fraction distilling between 226-230° was collected and left to stand and crystalline material was deposited. This was filtered off and had m.p. 75° and was thought to be *p*-chlorobenzyl alcohol (m.p. 75°) and was largely removed by leaving the mixture at 0° for several days when it crystallised out and was filtered off. The remaining liquid was refractionated to give *p*-trimethylsilylmethylphenyl chloride (105 gm, 53%) b.p. 227-229.5°. Any liquid boiling below 227° was discarded.

Preparation of tri-*p*-trimethylsilylmethylphenyl fluorosilane

Attempts to make tri-*p*-trimethylsilylmethylphenyl fluorosilane were as follows:

(i) *p*-Trimethylsilylmethylphenyllithium (ca 0.18 mole) in ether (300 ml) was added to silicon tetrachloride (8.5 gm, 0.05 mole) in ether (50 ml) and refluxed (5 hr). It was then hydrolysed, the product isolated and fluorination carried out in the usual way.

(ii) *p*-Trimethylsilylmethylphenyllithium (ca 0.2 mole) in ether (300 ml) was added to silicochloroform (6.8 gm, 0.05 mole) in ether (100 ml) and stirred for four hours after addition. The product was isolated and treated with dilute aqueous caustic soda solution. After ether extraction, the solvent was removed and the residue treated with aqueous hydrofluoric acid.

In each case tetra-*p*-trimethylsilylmethylphenylsilane m.p. 204-205° (Anal. Calculated for  $C_{40}H_{60}Si_5$ : C=70.53, H=8.88. Found C=70.86, H=9.18) was obtained, in 65.6, 62.3% yield respectively. Recrystallisation was from petrol (100-120°).

A low yield of tri-p-trimethylsilylmethylphenyl fluorosilane (2% and 1.2%) m.p. 122-123.5° was obtained.

Anal. Calculated for  $C_{30}H_{45}Si_4F$ : F = 3.55

Found : F = 3.72

(iii) A Wurtz-Fittig reaction using p-trimethylsilylmethylphenyl chloride (20 gm, 0.1 mole), silicochloroform (4.5 gm, 0.033 mole) and sodium (5 gm, 0.22 gm.at) in petrol (100-120°)(20 ml) gave tetra-(p-trimethylsilylmethylphenyl)silane (14.5 gm, 67%) and a solid (0.5 gm,) m.p. 124.5-125° after recrystallisation from petrol (60-80°). This was treated with dilute alcoholic caustic soda solution, a vigorous effervescence occurred, the product was extracted and recrystallised from petrol (60-80°) to give a solid (0.45 gm) m.p. 136°.

This was fluorinated in the usual manner to give tri-(p-trimethylsilylmethylphenyl)fluorosilane (0.4 gm, 2.4%) m.p. 122.5-124°.

Each of the samples of tri-p-trimethylsilylmethylphenylsilyl fluoride was dissolved in ether and separately treated with an excess of p-anisyllithium in ether. After work up of the products solids m.p. 94.5 - 100.5° were obtained. Yield for each reaction ca 0.3 gm. After recrystallisation from alcohol and methyl alcohol the m.p. range rose to 103 - 108°. The product was a glass and had no crystalline form, and this was taken as an indication that the product was impure.

As the yield of product by all three methods was low p-anisyl-trichlorosilane was prepared and this was treated with p-trimethylsilylmethylphenyllithium.

Preparation of p-anisyltrichlorosilane

p-Anisylmagnesium bromide (ca 0.25 mole) was prepared in the usual way and added to silicon tetrachloride (42.5 gm, 0.25 mole) in ether (120 ml). After addition the mixture was boiled under reflux for 3 hours and then left overnight. The product was not hydrolysed and p-anisyltrichlorosilane (25 gm, 41.4%) b.p.  $131^{\circ}/17$  mm. was distilled off from the magnesium salts.

On further distillation di-(p-anisyl)-dichlorosilane (2 gm) b.p.  $196^{\circ}/5$  mm. was obtained.

Anal. Calculated for  $C_{14}H_{14}Cl_2O_2Si$ : = 22.70

Found : = 22.45

p-Trimethylsilylmethylphenyllithium was prepared from p-trimethylsilylmethylphenyl chloride (10 gm, 0.054 mole) and lithium (1.39, 0.2 gmat) both in ether (40 ml). p-Anisyltrichlorosilane (3 gm, 0.0124) in ether (25 ml) was added and after addition the mixture was refluxed for 3 hr. and then left overnight. The silane was isolated in the usual way and gave an oil which was crystallised from alcohol. After recrystallisation from alcohol and methyl alcohol it gave tri-(p-trimethylsilylmethylphenyl)-p-anisylsilane m.p.  $102.5 - 108^{\circ}$ . (2.65 gm, 34.3%)

Anal. Calculated for  $C_{37}H_{52}OSi_4$ : C = 71.09, H = 8.38

Found : C = 69.47, H = 8.14

This melting point range was a characteristic of the compound and it remained a glass even after baking in an oven at  $80^{\circ}C$  for 14 days.

Tri-(p-anisyl)ethoxysilane

p-Anisylmagnesium bromide (ca 0.2 mole) in ether (100 ml) was prepared and to it was added tetraethoxysilane (14 gm, 0.067M), in ether (50 ml). The mixture was refluxed for 5 hr. and left overnight. The ethereal layer was decanted off and the remaining magnesium salts boiled under reflux with petrol (60 - 80°) for 30 minutes. This was filtered and the petrol solution added to the ethereal solution and the solvents distilled off. The residue was distilled at reduced pressure and gave tri-(p-anisyl)ethoxysilane b.p. 245 - 256°/2.5 mm. This was refractionated and had b.p. 276°/6 mm and crystallised on standing. After recrystallisation from absolute alcohol it gave pure tri-(p-anisyl)ethoxysilane m.p. 81° (6 gm, 23%).

Anal. Caloulated for  $C_{23}H_{26}O_4Si$ : C = 70.01, H = 6.64

Found : C = 70.39, H = 6.57

p-Anisyltriethoxysilane

p-Bromoanisole (80 gm, 0.43 mole) was converted to the Grignard reagent. This was added to tetraethoxysilane (37.6 gm, 0.18 mole) in ether (200 ml) and refluxed for about 18 hours. The ethereal layer was separated from the magnesium salts and the solvent distilled off through a packed column. The residue was distilled through a Vigreux column at reduced pressure to give p-anisyltriethoxysilane (12 gm, 24.7%) b.p.  $131^{\circ}/3\text{mm}$ .

Anal. Calculated for  $\text{C}_{13}\text{H}_{22}\text{O}_4\text{Si}$ : C = 57.73, H = 8.20

Found : C = 57.80, H = 8.17

Di-(p-anisyl)diethoxysilane.

Further fractional distillation gave a liquid (2 gm) b.p.  $195^{\circ}/2.5\text{mm}$  which was contaminated with a solid. The latter was filtered off and recrystallised from alcohol and proved to be di-p-anisyl (m.p.  $173^{\circ}$ ). When no more solid appeared in the distillate the distillation was stopped and the residue in the flask extracted with petrol ( $60-80^{\circ}$ ) in which p-dianisyl is only sparingly soluble. The solution was filtered, the solvent distilled off and the residue distilled at 2.5 mm to give di-(p-anisyl)diethoxysilane (6 gm, 10.4%) b.p.  $198^{\circ}/2.5\text{mm}$ .

Anal. Calculated for  $\text{C}_{18}\text{H}_{24}\text{O}_4\text{Si}$ : C = 65.04, H = 7.28

Found : C = 64.85, H = 7.22

p-Anisyldimethylchloromethylsilane

Preparation of dimethylchloromethylchlorosilane <sup>72, 73</sup>

(i) Trimethylchlorosilane (108.5 gm, 1.0 mole), benzoyl peroxide (1.0 gm) and chlorobenzene (220 ml) were placed in a 2 l.

round bottomed flask equipped with stirrer, dropping funnel containing sulphuryl chloride (125 gm, 0.93 mole) and a reflux condenser surmounted with a "cold finger" condenser filled with powdered dry ice.

The evolved gases were passed through a drying tube containing anhydrous copper sulphate and then through two flasks, the first acting as a trap, the second containing water so that the flow of gas could be observed. The flask was heated so that there was a vigorous reflux at the condenser and gentle reflux at the cold finger. Sulphuryl chloride was added with stirring over a period of 5 hours. The mixture was then refluxed for about 4 hours until gas was only slowly evolved.

It was then fractionally distilled through a packed column and gave a fraction b.p. 45 - 65° which was thought to be a mixture of the reactants and dimethylchloromethylchlorosilane (18 gm, 12.6%) b.p. 113-115°.

(ii) Trimethylchlorosilane (119 gm, 1.1 mole) was placed in a 500 ml flask equipped with dropping funnel, stirrer and reflux condenser and Dry Cold condenser. The flask was cooled in a water bath and illuminated by two 100 watt bulbs placed about two ins. from the flask. Chlorine was passed slowly through the solution until all the air was driven out. A small amount of bromine was added and chlorine passed through solution until the dark red colour of the bromine had almost disappeared. More bromine was added and the process



continued until 46.5 gm (0.58 mole) was added. The gases which were given off were trapped in aqueous alkali.

After all the bromine had been added, more trimethylchlorosilane (15 gm) was added by means of the dropping funnel and chlorine was bubbled through for a further hour. When chlorine was passed too rapidly through the solution explosions occurred which caused charring. The mixture was fractionally distilled and gave dimethylchloromethylchlorosilane (45 gm, 25.4%) b.p. 113-115°.

Dimethylchloromethylchlorosilane (60 gm, 0.42 mole) in ether (200 ml) was added to p-anisylmagnesium bromide (ca 0.5 mole) in ether (200 ml) and refluxed for 6 hours. The product was isolated and fractionally distilled to give p-anisyldimethylchloromethylsilane (62 gm, 68.8%) b.p. 136°/12 mm,  $n_D^{20} = 1.5300$  (reported b.p. 143°/5 mm<sup>74</sup>).

#### Attempted preparation of p-anisyldimethylsilylmethyl alcohol<sup>75</sup>

p-Anisyldimethylchloromethylsilane (21.4 gm, 0.1 mole) was added to anhydrous potassium acetate (11 gm, 0.11 mole) in glacial acetic acid (25 ml) and acetic anhydride (5 ml) was added. This was refluxed for seven days, washed with water, extracted with ether and the solution dried ( $\text{Na}_2\text{CO}_3$ ). After distilling off the solvent, the residue was fractionated at reduced pressure. Two fractions were obtained (i) b.p. 45°/12 mm. anisole (7.5 gm), (ii) 124°/12 mm. 5 gm b.p. at atmospheric pressure 247.5°  $n_D^{20} = 1.4230$ . This was concluded to be the compound  $[(\text{CH}_3)_2\text{SiCH}_2\text{COOCH}_3]_2\text{O}$  (b.p. 252°  $n_D^{25} = 1.4215$ ) formed by cleavage of a p-anisyl group from p-anisyl-Si(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>OOCH<sub>3</sub> which was probably first obtained.

p-Anisyldimethyl(ethylaminomethyl)silane

78

Using the method of Andrianov and Volkova, p-anisyldimethyl-chloromethylsilane (27 gm, 0.126 mole) and anhydrous ethylamine (30 gm, 0.67 mole) were allowed to stand in a stoppered flask for 14 days at 0°, after which time two layers were formed. The upper layer (33 gm) was separated and fractionally distilled to give ethylamine (9 gm), anisole (2 gm) and a solid b.p. 169°/20 mm; a solid and a liquid (11.5 gm) then came over at the same temperature (172°C). The solid was filtered off and was found to be insoluble in petrol (60 - 80°). The filtrate was treated with petrol, filtered and again fractionally distilled to give p-anisyldimethyl(ethylaminomethyl)-silane (9.5 gm, 33.8%) b.p. 152°/18 mm.  $n_D^{20} = 1.5123$ .

Anal. Calculated for  $C_{12}H_{21}NOSi$ : C = 64.51 H = 9.48 N = 6.27

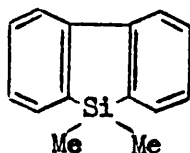
Found: C = 65.08 H = 9.58 N = 6.32

p-Anisyldichloromethylmethylsilane

The high boiling residue obtained from the chlorination of trimethylchlorosilane with sulphuryl chloride and benzoyl peroxide was provided by Mr B. Rushton. This was fractionally distilled and gave di(chloromethyl)methylchlorosilane (24 gm) b.p. 172-4°. Di(chloromethyl)-methylchlorosilane (15 gm, 0.085 mole) was treated with p-anisyllithium (ca 0.1 mole) and boiled under reflux for 6 hours. The wanted silane was isolated in the usual way to give p-anisyldi(chloromethyl)methyl-silane (7.5 gm, 35.7%) b.p. 137°/0.7 mm.  $n_D^{20} = 1.5506$ .

Anal. Calculated for  $C_{10}H_{14}Cl_2O$ : C=48.00 H=5.68

Found: C=48.17 H=5.66

5,5-Dimethyldibenzosilole<sup>77</sup>Preparation of 2,2'-dibromobiphenyl(i) 2,2'-Dinitrobiphenyl<sup>78</sup>

In a 1 litre flask equipped with a mechanical stirrer was placed o-chloronitrobenzene (250 gm, 1.59 mole) and clean dry sand (300 gm). The mixture was heated in an oil bath to 215 - 225° and copper bronze (200 gm) was slowly added (1½ hr). After addition the mixture was stirred for a further 1½ hours and the temperature kept at 215 - 225°. It was then poured whilst hot into a beaker containing sand (300 - 500 gm) and stirred until small lumps were formed. On cooling these were broken up in a mortar and the mixture boiled with alcohol (2 x 1½ litre) and the solid removed by filtration. The filtrates were cooled in ice and 2,2'-dinitrobiphenyl crystallised out and was filtered off. After boiling with charcoal and on recrystallisation 2,2'-dinitrobiphenyl (97 gm, 50%) was obtained as yellow crystals m.p. 123.5 - 124.5.

(ii) 2,2'-Diaminobiphenyl<sup>79</sup>

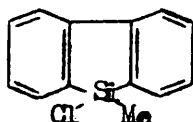
2,2'-Dinitrobiphenyl (97 gm, 0.48 mole) was then reduced by iron filings, water and hydrochloric acid. Reduction proceeded with difficulty and unreduced nitro-compound was obtained on extraction. The base was isolated by pouring the hot iron paste into cold acetone, distilling the ketone from the filtered liquid and extracting the residue with dilute hydrochloric acid. 2,2'-diaminobiphenyl (18 gm, 25%) m.p. 81° was precipitated by addition of aqueous ammonia and recrystallised from alcohol.

(iii) 2,2<sup>1</sup>-Dibromobiphenyl<sup>80</sup> The diazonium salt of 2,2<sup>1</sup>-diamino-biphenyl (12 gm, 0.067 mole) was prepared and the solution added to a solution of mercuric nitrate and potassium bromide, the latter being in excess. The resulting yellow complex salt was filtered off, washed with water and dried by washing with acetone. The salt was mixed with twice its weight of potassium bromide and gently heated in a long hard glass tube equipped with a vertical air condenser. (A sample was previously heated with potassium bromide in a test-tube and if the reaction proceeded too vigorously more potassium bromide was added.) The tube was one third filled, the mixture spread evenly along the tube and the tube heated in a horizontal position. Heating was carried out from the end of the tube carrying the air condenser for otherwise the resulting explosion would have been sufficiently vigorous to blow the reactants out of the tube. When cool, the inorganic material was extracted with water and the organic material extracted with ether. After re-crystallisation from alcohol, it gave 2,2<sup>1</sup>-dibromobiphenyl (15 gm, 72%) m.p. = 81°.

2,2<sup>1</sup>-Dibromobiphenyl (15 gm, 0.048 mole) in ether (50 ml) was added to lithium (2.1 gm, 0.3 gm.at.) in ether (100 ml). The reaction mixture was boiled under reflux (6½ hr) after stirring at room temperature (20 min.). This solution of 2,2<sup>1</sup>-biphenylenedilithium was added to a stirred refluxing solution of methyltrichlorosilane (6.5 gm, 0.0435 mole) in ether (150 ml).

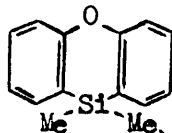
When addition was complete, the mixture was stirred (2 hr.) and left to stand overnight. It was then stirred at room temperature (6 hr.), the ether was distilled off until the temperature rose to 60° and petrol (60-80°) (100 ml) was added. After refluxing (1 hr),

the mixture was filtered whilst hot under an atmosphere of nitrogen. The remaining lithium salts were washed with several portions of petrol, and these washings were combined with the solution. The solvent and any unreacted methyltrichlorosilane were distilled off at atmospheric pressure and the remaining oil distilled at 3.5 mm to give a liquid b.p. 233 - 242°. On standing this crystallised and had a m.p. of 60 - 66°. This was taken to be 5-chloro-5-methyldibenzosilole (4.5 gm, 44.9%) (reported m.p. 63 - 68°C)<sup>77</sup>



Methyl lithium was prepared by dissolving methyl bromide (6.0 gm, 0.063 mole) in ether (25 ml) and adding it to lithium (1 gm. 0.14 gm.at.) in ether (50 ml) and stirring for 30 minutes. The lithium was filtered off and the solution was added to 5-chloro-5-methyldibenzosilole (4.5 gm, 0.0208 mole) in ether (25 ml) and the mixture stirred at room temperature for three hours after addition. The product was isolated in the usual way and was recrystallised from methanol to give 5,5-dimethyldibenzosilole<sup>77</sup> (0.5 gm, 11%) m.p. 60.5°.

10,10-dimethylphenoxasilin<sup>88</sup>



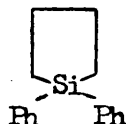
A solution of n-butyllithium<sup>81</sup> (ca. 0.4 mole) was prepared. In a 500 ml three necked flask equipped with stirrer and dropping funnel was placed ether (200 ml) and lithium (8.6 gm, 1.23 gm.at.). By means of the dropping funnel a solution of n-butylchloride (46.25 gm, 0.5 mole) in ether (100 ml) was added whilst the temperature was kept at -30 to -40°. After addition was complete the reaction mixture was allowed to warm up to 0 - 10° and stirred for about 2 hr. The solution was filtered and added to a solution of diphenyl ether (34 gm, 0.2 mole) in ether (100 ml) in a 1 litre flask. The mixture was stirred at ether

reflux temperature for 1 hour.

The solution (ca 400 ml) contained 0.076 mole of 2,2<sup>1</sup>-dilithio-diphenyl ether. About  $\frac{1}{3}$  of this was placed in a litre flask and heated to gentle reflux and stirred whilst the remaining suspension was added over a period of 40 minutes. Simultaneously dimethyldichlorosilane (10 gm, 0.077 mole) in ether (60 ml) was added and this also required 40 minutes. The reaction mixture was stirred at reflux temperature for 4 hours and allowed to stand overnight. It was hydrolysed with water and the two layers separated. The ether layer was dried and chromatographed on activated alumina using ether as eluant and the bands followed using U.V. light. The solvent was distilled from the eluate and the remaining oil distilled at reduced pressure (3 mm), to give 10,10-dimethylphenoxasilin (4.8 gm, 27.6%) b.p. 235°/3 mm. This crystallised on dissolving in alcohol and cooling in a Dry Cold/acetone bath, after further recrystallisation it had a m.p. 74° (reported 74.5 - 77°<sup>82</sup> and 78.5 - 79°<sup>82</sup>)

1,1-diphenylsilacyclopentane<sup>83</sup>

Preparation of 1,4-dibromobutane<sup>84</sup>



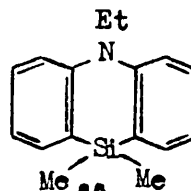
Tetrahydrofuran (72 gm, 1 mole) was added slowly to a cold mixture of 50% hydrobromic acid (972 gm, 6 mole) and concentrated sulphuric acid (50 ml) and the mixture boiled under reflux for 3 hours.

The product was steam distilled and the lower layer dried (CaCl<sub>2</sub> and P<sub>2</sub>O<sub>5</sub>). On distillation it gave 1,4-dibromobutane (141 gm, 64%) b.p. 197°.

Tetramethylenedilithium<sup>85</sup> was prepared by slowly adding 1,4-dibromobutane (37.5 gm, 0.15 mole) in ether (225 ml) to lithium

(7.5 gm, 1.08 gm. atom) in ether (75 ml). The reaction was started by stirring for a few minutes at room temperature and then temperature kept at  $-10^{\circ}$  to  $-20^{\circ}$ . After addition the mixture was stirred for 1 hour at  $-10^{\circ}$  and  $1\frac{1}{2}$  hour at  $10^{\circ}$ . The solution was filtered and added with stirring to diphenyldichlorosilane (38 gm, 0.15 mole) at  $-20^{\circ}$ . The mixture was stirred at this temperature for 1 hour and then stirred at room temperature for 1 hour. After hydrolysis the wanted silane was extracted and the solvent distilled off. The residue was chromatographed on alumina and eluted with petrol (60 -  $80^{\circ}$ ). The eluate after removal of solvent was distilled at reduced pressure to give 1,1-diphenylsilacyclopentane (11.4 gm, 32%) b.p.  $139 - 141^{\circ}/3.5$  mm.

5-Ethyl-5,10-dihydro-10,10-dimethylphenazasiline



Preparation of N-ethyl-2,2'-dibromodiphenylamine

(i) o-Bromoaniline. o-Bromonitrobenzene (140 gm, 0.69 mole) was reduced by tin (153 gm) and concentrated hydrochloric acid (350 ml) and the product steam distilled. After distillation at reduced pressure it gave o-bromoaniline (79 gm, 66%) m.p.  $32^{\circ}$ .

(ii) o-Bromobenzanilide. o-Bromoaniline (79 gm, 0.46 mole) was suspended in 10% sodium hydroxide solution (600 ml) and benzoyl chloride (80 gm, 0.57 mole) slowly added. The mixture was mechanically stirred for 2 hr. After washing thoroughly with water and recrystallisation from alcohol it gave o-bromobenzanilide (123 gm, 97%) m.p.  $115 - 116^{\circ}$ .

(iii) 2,2-Dibromodiphenylamine<sup>87</sup>. Powdered o-bromobenzanilide

(123 gm, 0.44 mole) was then mixed with phosphorus pentachloride (100 gm, 0.48 mole) in a flask through which nitrogen was passed. The reaction began spontaneously and when the vigorous reaction had subsided, the mixture was heated for 10 minutes at 100°. It was distilled at 15 mm to remove phosphorus oxychloride. The residue was distilled at 1 mm and gave *N*-*o*-bromophenylbenzimidoyl chloride  $\text{Br}\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{CClPh}$  (67 gm, 52%) b.p. 137°/1 mm.

*o*-Bromophenol (39 gm, 0.225 mole) was added to a solution obtained by interaction of sodium (4.9 gm, 0.21 gm.at.) and absolute alcohol (200 ml). This was thoroughly stirred and cooled whilst a solution of the imidoyl chloride (67 gm, 0.23 mole) in ether (150 ml) was added. Next day, the greater part of the solvent was removed by distillation and the residue poured into water which precipitated

*o*-bromophenyl *N*-*o*-bromophenylbenzimidate,  $\text{Br}\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{CPh}\cdot\text{OC}_6\text{H}_4\cdot\text{Br}$  as an oil which slowly solidified. Recrystallisation from alcohol gave colourless crystals (61 gm, 63%) m.p. 95°.

The ester (61 gm, 0.14 mole) was heated in an oil-bath at 255 - 260° for 2½ hr. and then after allowing to cool, digested with alcohol and gave *N*-benzoyl-2:2'-dibromodiphenylamine (17 gm, 28%) m.p. 173 - 6°.

This was boiled in a solution of potassium hydroxide (45 gm) in water (45 ml) and ethanol (170 ml) for 8 hr., concentrated by distillation and the residue poured into water. The precipitated oil was extracted with ether, and the dried extract on distillation gave 2,2'-dibromodiphenylamine (10 gm, 78%) <sup>b.p.</sup> 169°/0.7 mm. It crystallised on standing m.p. 57-60°.



(iv) N-Ethyl-2,2<sup>1</sup>-dibromodiphenylamine<sup>86</sup>. Methyllithium

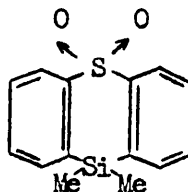
was prepared by addition of methyl bromide (3.6 gm, 0.04 mole) in ether (30 ml) to lithium (0.7 gm, 0.10 gm.at.) in ether (30 ml). The filtered solution was added to 2,2<sup>1</sup>-dibromodiphenylamine (10 gm, 0.0306 mole) in ether (50 ml) which had been cooled in an ice-bath. Freshly distilled ethyl sulphate (7.7 gm, 0.05 mole) in tetrahydrofuran (100 ml) was added and the ether was removed by distillation until the temperature had reached 64°. The solution was heated at reflux temperature for 15 hr. and then hydrolysed by pouring into iced water. The organic product was extracted with ether, dried and the solvent distilled off and gave N-ethyl-2,2<sup>1</sup>-dibromodiphenylamine (2.5 gm, 23%) b.p. 170 - 172°/0.5 mm. After crystallisation from petrol (60 - 80°) m.p. 71 - 73°.

To N-ethyl-2,2<sup>1</sup>-dibromodiphenylamine (2.5 gm, 0.007 mole) in ether (25 ml) cooled in an ice bath was added an ethereal solution of n-butyllithium (ca 0.16 mole). The mixture was stirred for 1 hr. and the solution treated with dimethyldichlorosilane (0.9 gm, 0.007 mole) in ether (50 ml) and stirred for a further 28 hr. at room temperature. It was hydrolysed by pouring into ice water and the organic layer was separated. After drying the ether was removed by distillation and the residue chromatographed on alumina using petrol (60 - 80°) as eluent. A white material was obtained from the first fraction and this was recrystallised from petrol (60 - 80°) to give 5-ethyl-5,10-dihydro-10,10-dimethylphenazasiline (0.25 gm, 14%) m.p. 69.5 - 70.0°.

Anal. Calculated for C<sub>16</sub>H<sub>19</sub>NSi: C = 75.84, H = 7.57 N = 5.53

Found: C = 75.75, H = 7.66 N = 5.45

10,10-dimethylphenothiasilin-5,5-dioxide <sup>88</sup>



Diphenyl sulphone (50 gm, 0.232 mole) was metallated <sup>89</sup> by adding it to ether (2320 ml) and the mixture stirred continuously whilst a solution containing 0.464 mole of n-butyllithium was added over a period of 3½ hr. whilst the temperature was maintained at -25° to -30°.

To the resulting yellow suspension was added a solution of dimethyldichlorosilane (29.2 gm, 0.225 mole) in ether (200 ml). During addition the temperature was maintained at -20°. It was left to stand over night and then stirred at room temperature for a further 8 hr. It was hydrolysed with water, ether extracted and after drying the solvent distilled off and the resulting oil was chromatographed on alumina using ether as eluant. The eluate upon removing solvent gave a white material m.p. 63 - 130°. Several recrystallisations from alcohol and alcohol/petrol (60 - 80°) raised the m.p. to 103 - 130°. Recrystallisations from excess alcohol gave 10,10-dimethylphenothiasilin-5,5-dioxide (2.5 gm, 4%) m.p. 165°.

Attempted preparation of 10,10-dimethylphenothiasilin

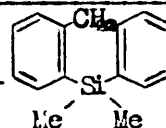


(1) The same procedure as for 10,10-dimethylphenoxasilin was carried out but <sup>from</sup> starting with diphenyl sulphide. <sup>89</sup> No yield of 10,10-dimethylphenothiasilin resulted.

(ii) 10,10-Dimethylphenothiasilin-5,5-dioxide (1 gm, 0.0036 mole) in ether (50 ml) and lithium aluminium hydride (0.5 gm, 0.0143 mole) in ether (25 ml) were refluxed for 48 hr., after which time the product was isolated. The starting material was obtained, neither reduction nor cleavage of the C-Si bond having occurred.

Attempted preparation of 9,9-dimethyl-9,10-dihydro-9-silanthracene

Preparation of 2,2'-dibromodiphenylmethane



(i) m-Nitrobenzyl alcohol

m-Nitrobenzaldehyde (500 gm, 3.31 mole) was added to a solution of potassium hydroxide (250 gm, 4.5 mole) in water (3000 gm). The mixture was left for a further 12 hr. after the aldehyde dissolved, the solution saturated with carbon dioxide then extracted with ether. It was washed with saturated sodium bisulphite solution, 10% carbonate solution and water. After drying the solvent was removed by distillation and the residue distilled at reduced pressure to give m-nitrobenzyl alcohol (205 gm, 81%) b.p. 147°/3.5 mm.

(ii) 3,3'-dinitrodiphenylmethane

m-Nitrobenzyl alcohol (200 gm, 1.31 mole) and nitrobenzene (600 gm, 4.88 mole) were dissolved in concentrated sulphuric acid (4 l.) and the solution heated on a waterbath at 93° for 48 hr. The mixture was poured onto crushed ice, the precipitate was filtered off and re-crystallised from glacial acetic acid to give 3,3'-dinitrodiphenylmethane (305 gm, 90.5%) m.p. 173 - 175°.

(iii) 3,3'-diaminodiphenylmethane

3,3'-Dinitrodiphenylmethane (305 gm, 1.18 mole) was reduced

by mixing with iron dust (640 gm) water (1100 ml) and glacial acetic acid (44 ml), and heated on a water bath with continuous stirring until most of the water had evaporated. The diamine was extracted by refluxing the residue several times with ether. 183 gm (78.3%) of impure diamine was obtained and this was converted to the acetyl compound, by dissolving it in glacial acetic acid (400 ml) and adding acetic anhydride (300 ml) to the solution. After warming to its boiling point the solution was poured into cold water. The product separated out as an oil which slowly crystallised. This was filtered off and recrystallised from alcohol giving 3,3<sup>1</sup>-diacetylaminodiphenylmethane (164 gm, 64%) m.p. 255-8°.

(iv) 3,3<sup>1</sup>-diacetyl-amino-6,6<sup>1</sup>-dibromodiphenylmethane

The diacetyl compound (160 gm, 0.544 mole) was brominated by dissolving it in glacial acetic acid (4 l.) and keeping the solution at 50° with continuous stirring while bromine (68 gm, 0.85 mole) was added, the mixture being heated and stirred for 1/2 hr. after addition. The mixture was allowed to cool and then poured into four times its volume of cold water. It was filtered at the pump and washed with water; purification was by boiling with alcohol; the impurities dissolved and 3,3<sup>1</sup>-diacetyl-amino-6,6<sup>1</sup>-dibromodiphenylmethane (203 gm, 81%) m.p. 276° remained undissolved.

(v) 3,3<sup>1</sup>-diamino-6,6<sup>1</sup>-dibromodiphenylmethane.

The diacetyl compound (180 gm, 0.398 mole) and alcohol (750 ml) were placed in a flask, heated to boiling and concentrated hydrochloric acid (620 ml) slowly added. After 30 min. heating saponification was complete and the hydrochloride of the base was formed. The product was

filtered off and washed with alcohol, which dissolved impurities.

The remaining solid was recrystallised from water. Some hydrochloride dissolved when washed with alcohol and this was recovered by solution to evaporating the alcoholic dryness, adding ammonia and extracting the base with ether. The hydrochloride was precipitated from the ethereal solution by addition of hydrochloric acid. This gave 3,3'-diamino-6,6'-dibromodiphenylmethane dihydrochloride (193 gm, 97%).

(vi) 2,2'-Dibromodiphenylmethane

Deamination was carried out using two procedures.

(a) The hydrochloride (40 gm, 0.094 mole) was made into a paste with water (120 ml) and concentrated hydrochloric acid (40 ml). The diazonium salt was then prepared by addition of a cold saturated solution of sodium nitrite. When the mixture had become entirely homogeneous it was poured into alcohol (4 l.) and a brisk evolution of nitrogen followed. The alcohol was distilled off, the remaining brown oil was taken up with ether, the solution dried and after removal of solvent by distillation, was distilled at 1 mm. It gave 2,2'-dibromodiphenylmethane (12.5 gm, 41%) b.p. 157 - 160°/1 mm. However, this contained impurities which were removed by shaking (12.5 gm, 0.0383 mole) with concentrated sulphuric acid (42 ml) for 3 hr. The insoluble portion rose to the surface and was separated. After washing and drying it gave 9 gm. (29.5%) of product b.p. 149°/0.7 mm.

(b) The hydrochloride (150 gm, 0.35 mole) was mixed with water (450 ml) and concentrated hydrochloric acid (150 ml) and the diazonium salt was prepared as above. This was added to a cold solution of 30% hypophosphorous acid (750 ml) and left at 0° for 24 hr. <sup>92</sup>

and then at room temperature for 2 days. The oil which separated out was extracted with ether, the solution washed with 20% caustic soda solution, water and dried (anhydrous  $K_2CO_3$ ). The solvent was distilled off and the residue distilled at 0.7 mm to give 2,2'-dibromodiphenylmethane (53 gm, 46.5%).

Attempts were made to prepare 9,9-dimethyl-9,10-dihydro-9-silanthracene.

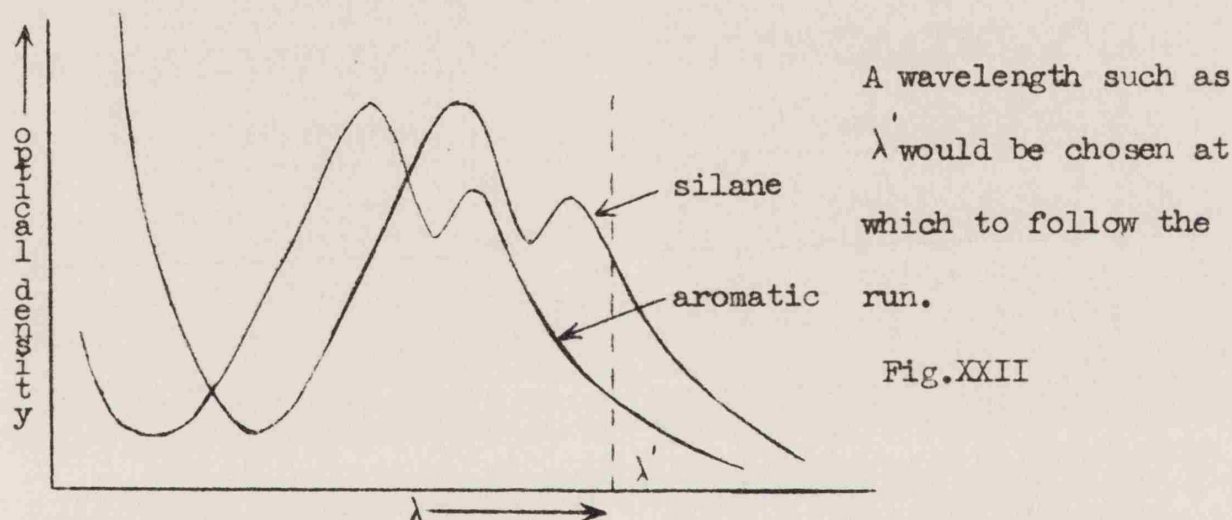
(i) 2,2'-Dibromodiphenylmethane was treated with lithium. Dimethyldichlorosilane in ether was added and after work up of the product gave a crystalline product m.p. 114.5 - 115.5°. (Anal.C=70.78, H=6.78). This was not the required silane.

(ii) 2,2'-Dibromodiphenylmethane was treated with lithium and methyltrichlorosilane in ether was added. The reaction mixture was filtered off under nitrogen, the solvent removed and the residue distilled at reduced pressure to give a liquid (3 gm) b.p. 237 - 242°/1 mm. This in ether was treated with methyllithium but the product could not be crystallised.

## CHAPTER IX

Experimental technique for the kinetic investigation of cleavage  
of the C-Si bond by perchloric acid.

When a trialkylsilyl or triarylsilyl group is removed from a p-anisyltrialkyl- or p-anisyltriaryl- silane, the ultra violet absorption spectra of the products is somewhat different,



from that of the starting material, the spectra usually being similar in shape but separated by about 5  $\mu$  (see Fig.XXII.). Thus change in optical density at a chosen wavelength enables rates to be measured.

With p-anisyltriarylsilanes, it was found that slow cleavage of an aryl group from the triarylsilanol first formed sometimes occurred. It was therefore necessary to carry out runs at a wavelength in the region of 280  $\mu$ , for at this wavelength the difference in optical density of the triaryl silanol and its cleavage products was very small and therefore during a run any change in spectrum due to removal of a further aryl group was negligible.

However, because of this necessity to choose a wavelength of approximately 280  $\mu$  and the low solubility of the p-anisyltriaryl-

silanes in the solvent, very often there was not a large overall change in optical density. In certain cases, particularly for tri-o-tolyl- p-anisylsilane, it was found that the cleavage product was very insoluble and this further necessitated a decrease in concentration of the original silane.

Acid cleavage of the silanes was studied spectrophotometrically using a Unicam S.P.500 spectrophotometer. Various perchloric acid/ aqueous methanol mixtures had to be used in order that the relative rates of cleavage could be studied over a wide range.

A standard kinetic procedure was used whereby 10 ml of aqueous acid was added to 25 ml of a solution of the silane in redistilled "Analar" methanol in a small glass stoppered bottle. After shaking the bubbles were allowed to rise and some of the mixture was transferred by means of a dropper to a 1 cm. stoppered quartz cell fitted with a ground glass stopper. Care was taken not to wet the glass around the stopper as it was found that when this occurred a loss of liquid was caused by capillary attraction and this seriously affected the run.

The cell was placed in the cell-block thermostat of the spectrophotometer which was maintained at a temperature of  $50 \pm 0.02^\circ$  throughout this work. Absorption readings (relative to methanol) were begun after not less than ten minutes and reactions were taken to completion, (approximately ten half-lives) in the cell whenever possible and readings were taken at least as far as 70% reaction.

In other cases infinity values were obtained from samples of the reaction mixture kept in sealed tubes at  $50^\circ$  for a period equivalent



to ten half-lives. Each run was performed in duplicate.

In the case of tri-o-tolyl-p-anisylsilane it was necessary to measure the rate of cleavage over several days. The reaction mixture was made up as usual but then samples were transferred to sealed tubes and kept at 50.0° for different lengths of time, after which some of the contents were placed in the cell and the optical density was measured.

Calculation of rate constants.

The cleavage is a catalytic process, and since the concentration of acid does not change in the presence of excess acid the reaction is pseudo first order.

$$\text{Hence } \frac{dx}{dt} = k_1(a-x) \quad k_1 = \text{rate constant of the reaction}$$

$$a = \text{initial concentration}$$

$$\text{and } x = \text{amount reacted after time } t.$$

$$\therefore \log \frac{a}{a-x} = k_1 t$$

By Beer's Law, at a specified wavelength, the optical density of a solution is proportional to the concentration of the compounds in that solution.

$$\text{Hence } a = D_0 - D_{\infty} \quad x = D_0 - D_t$$

$$D_0 = \text{initial optical density of the kinetic solution}$$

$$D_t = \text{optical density of solution at time } t$$

$$D_{\infty} = \text{optical density of solution at the end point.}$$

$$\therefore \log \frac{D_0 - D_{\infty}}{D_t - D_{\infty}} = k_1 t$$

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

∴ a plot of  $t$  against  $\log_{10}(D_t - D_\infty)$  is a straight line of gradient  $-\frac{2.303}{k_1}$  from which  $k_1$  may be obtained

All rate constants as obtained by acid cleavage have been determined graphically by this method.

#### Preparation of materials.

##### (a) Perchloric acid.

The 60% and 72% aqueous perchloric acids were obtained from Messrs. B.D.H. Ltd. Appropriate quantities of acid were diluted with distilled water as required and the strength of the solution was determined by titration against borax which had been recrystallised.<sup>93</sup>

##### (b) Methanol.

This was dried using the method of Lund and Bjerrum.

##### (c) Aryltrimethylsilanes.

Samples of triphenyl-*p*-anisylsilane, tri-*o*-tolyl-*p*-anisylsilane and tetra-*p*-anisylsilane were supplied by Miss P.M.Greasley. A sample of trimethyl-*p*-anisylsilane was provided by D.M.Walton. Other silanes were prepared as described in Chapter VIII.

#### Weighings

These were carried out on an "Oertling" balance using micro weighing bottles prepared from small ignition tubes of 4 mm. diameter, shortened to a length of 10 - 20 mm. The micro weighing bottle containing a weighed sample was transferred to a 100 ml. graduated flask and made up to the mark with solvent. The volume of the weighing bottle was neglected.

Thermostat

This was a Tecam unit as supplied by Teohne (Cambridge) Ltd., capable of maintaining a temperature of  $50 \pm 0.05^\circ$ .

Reproducibility.

Most runs are reproducible to within 1%; however, in some cases reproducibility was to within 2%.

Error

As a graphical method was used to determine the rate constant, errors must be introduced because of the measurements involved.

This error is at the most ( $\pm 0.5\%$ ).

For several readings of some typical runs, the rate constant has been determined using the formula:

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

$$\therefore t_2 - t_1 = \frac{-2.303}{k} \left[ \log_{10} (D_{t_2} - D_\infty) - \log_{10} (D_{t_1} - D_\infty) \right]$$

(i) Tri-p-chlorophenyl-p-anisylsilane Run No.7

$t_1 = 2 \text{ min.}$

$t_2$	15	20	30	40	50	81	97
$k \times 10^2, \text{min}^{-1}$	1.34	1.34	1.34	1.34	1.34	1.36	1.36

$$k(\text{graphical}) \times 10^2, \text{min}^{-1} = 1.35$$

(ii) Tri-p-chlorophenyl-p-anisylsilane Run No.8
$$t_1 = 0$$

$t_2$	5	10	15	$25\frac{1}{2}$	35	55	75
$k \times 10^2, \text{min}^{-1}$	1.35	1.35	1.35	1.35	1.36	1.36	1.35

$$\underline{k(\text{graphical}) \times 10^2, \text{min}^{-1} = 1.35}$$

(iii) Dimethylphenyl-p-anisylsilane Run No.53

$t_1 = 15 \text{ min.}$

$t_2$	35	40	45	55	60	65	75
$k \times 10^2, \text{min}^{-1}$	1.84	1.88	1.86	1.86	1.87	1.87	1.87

$$k(\text{graphical}) \times 10^2, \text{ min}^{-1} = 1.87$$

(iv) p-Anisyltriethoxysilane Run No.35

$$t_1 = 0$$

$t_2$	18m.20s.	33	$35\frac{1}{2}$	51	52m.15s.	60
$k \times 10^2, \text{min}^{-1}$	3.30	3.27	3.31	3.25	3.28	3.24

$$k(\text{graphical}) \times 10^2, \text{min}^{-1} = 3.26$$

(v) Triphenyl-p-anisylsilane Run No.17

$t_1 = 2 \text{ min.}$

$t_2$	3	9	15	28	37	51	56
$k \times 10^2, \text{min}^{-1}$	3.73	3.72	3.72	3.78	3.74	3.74	3.74
<u><math>k(\text{graphical}) \times 10^2, \text{min}^{-1} = 3.74</math></u>							

(vi) 5,5-Dimethyldibenzosilole      Run No.1 (cyclic)

$t_1 = 0 \text{ min.}$

$t_2$	5	10m.10s.	20	30	50	60	80
$k \times 10^2, \text{min}^{-1}$	3.26	3.27	3.25	3.24	3.24	3.24	3.26
$k(\text{graphical}) \times 10^2, \text{min}^{-1}$	<u>3.25</u>						

Tabulation of Runs

In the following tables of runs a selection of the readings taken during a run are given.

Time unless otherwise stated is in minutes, and optical density of the solution at a particular time is denoted  $D$ .

$\lambda$  = wavelength at which run was followed.

$C$  = the concentration of silane

The concentration of added acid is also given. The rate constant,  $k$ , has been determined graphically in each case from the plot of  $\log (Dt - D_{\infty})$  versus time as described on page 95 .

Run No.1    Tri-m-tolyl-p-anisylsilane
 $\lambda = 282\text{m}\mu$     9.48M     $\text{HClO}_4$      $C = 0.000332\text{M}$ 

Time	0	5	10	20	25	30
D	0.3030	0.2820	0.2660	0.2445	0.2385	0.2330
Time	35	40	50	$\infty$		
D	0.2295	0.2270	0.2235	0.2190		

$$k = 5.88 \times 10^{-2} \text{min}^{-1}$$

Run No.2    (Duplicate)

Time	0	1	3	7	14	16	25
D	0.3090	0.3040	0.2950	0.2795	0.2600	0.2560	0.2420
Time	28	35	40	$\infty$			
D	0.2390	0.2330	0.2305	0.2220			

$$k = 5.88 \times 10^{-2} \text{min}^{-1}$$

Run No.3    Tri-p-tolyl-p-anisylsilane
 $\lambda = 281\text{m}\mu$     9.48M     $\text{HClO}_4$      $C = 0.000725\text{M}$ 

Time	0	$\frac{1}{2}$	1	2	4	6	8	$10\frac{1}{2}$
D	0.4980	0.4920	0.4890	0.4820	0.4665	0.4540	0.4440	0.4335
Time	12	14	16	$\infty$				
D	0.4295	0.4230	0.4180	0.3830				

Run No.4 (Duplicate)

Time	0	2	4	6	8	10m.10sec.	12
D	0.5200	0.5040	0.4880	0.4735	0.4580	0.4505	0.4390
Time	14	16	$\infty$				
D	0.4330	0.4250	0.3830				

Run No.5 Tri-m-chlorophenyl-p-anisylsilane

$\lambda = 282.5\mu$  9.48M  $\text{HClO}_4$  C = 0.000239M

Time	0	60	100 $\frac{1}{2}$	118	150	199	
D	0.3770	0.3530	0.3400	0.3355	0.3285	0.3185	0.2805

$$k = 4.78 \times 10^{-3} \text{min}^{-1}$$

Run No.6 (Duplicate)

Time	11	22	33	45	54 $\frac{1}{2}$	65	117	135
D	0.3790	0.3740	0.3695	0.3645	0.3610	0.3580	0.3400	0.3355
Time	155	181	205	$\infty$				
D	0.3305	0.3245	0.3200	0.2820				

$$k = 4.78 \times 10^{-3} \text{min}^{-1}$$

Run No.7 Tri-p-chlorophenyl-p-anisylsilane.

$\lambda = 281\mu$  9.48M  $\text{HClO}_4$  C = 0.000567M

Time	0	15	20	25	30	40	50	73
D	0.5460	0.5175	0.5090	0.5010	0.4940	0.4810	0.4695	0.4480
Time	81	90min.20sec	97	$\infty$				
D	0.4410	0.4350	0.4310	0.3890				

$$k = 1.35 \times 10^{-2} \text{min}^{-1}$$



Run No.8 (Duplicate)

Time	0	5	10	15	25 $\frac{1}{2}$	35	40	55
D	0.5470	0.5370	0.5270	0.5180	0.5010	0.4870	0.4810	0.4635
Time	60	75	$\infty$					
D	0.4590	0.4460	0.3885					

$$\underline{k = 1.35 \times 10^{-2} \text{ min}^{-1}}$$

Run No.9 Tri-m-chlorophenyl-p-anisylsilane

$$\lambda = 282.5 \mu\text{m} \quad 12.19 \text{M} \quad \text{HClO}_4 \quad C = 0.000238 \text{M}$$

Time	5	10	15 $\frac{1}{2}$	22m.15s.	27	36 $\frac{1}{2}$	52 $\frac{1}{2}$
D	0.3540	0.3475	0.3410	0.3330	0.3290	0.3210	0.3100
Time	68	$\infty$					
D	0.3020	0.2790					

$$\underline{k = 1.87 \times 10^{-2} \text{ min}^{-1}}$$

Run No.10 (Duplicate)

Time	0	5	24	33	34 $\frac{3}{4}$	43	64	71
D	0.3690	0.3620	0.3370	0.3280	0.3270	0.3200	0.3060	0.3037
Time	80 $\frac{1}{2}$	114 $\frac{1}{2}$	$\infty$					
D	0.2990	0.2895	0.2790					

$$\underline{k = 1.85 \times 10^{-2} \text{ min}^{-1}}$$

Run No.11    Triphenyl-p-anisylsilane $\lambda = 281\text{m}\mu$     7.50M  $\text{HClO}_4$      $C = 0.000310\text{M}$ 

Time	0	16	47	57	69	82	98
D	0.2070	0.1950	0.1790	0.1757	0.1717	0.1690	0.1652
Time	121	$\infty$					
D	0.1620	0.1540					

$$\underline{k = 1.57 \times 10^{-2} \text{min}^{-1}}$$

Run No.12    (Duplicate)

Time	0	5	15	24	45	72½	75
D	0.2040	0.1995	0.1920	0.1865	0.1757	0.1665	0.1660
Time	97½	118	$\infty$				
D	0.1607	0.1570	0.1490				

$$\underline{k = 1.58 \times 10^{-2} \text{min}^{-1}}$$

Run No.13    Tri-p-tolyl-p-anisylsilane $\lambda = 281\text{m}\mu$     6.00M  $\text{HClO}_4$      $C = 0.000330\text{M}$ 

Time	0	10	33	45	71	96	115
D	0.2470	0.2380	0.2225	0.2160	0.2035	0.1957	0.1910
Time	129	142	157	$\infty$			
D	0.1885	0.1865	0.1842	0.1745			

$$\underline{k = 1.28 \times 10^{-2} \text{min}^{-1}}$$

Run No.14 (Duplicate)

Time	0	20	31½	43½	52	63½	81½	∞
D	0.2570	0.2360	0.2282	0.2212	0.2155	0.2100	0.2035	0.1755

$$k = 1.27 \times 10^{-2} \text{ min}^{-1}$$

Run No.15 Tri-m-tolyl-p-anisylsilane

$$\lambda = 282\text{m}\mu \quad 9.20\text{M} \quad \text{HClO}_4 \quad C = 0.000233\text{M}$$

Time	0	5	7	12	16	20	25
D	0.2580	0.2350	0.2272	0.2117	0.2015	0.1935	0.1852

Time	30	∞
D	0.1782	0.1550

$$k = 4.98 \times 10^{-2} \text{ min}^{-1}$$

Run No.16 (Duplicate)

Time	0	3	5	12	19	20	30
D	0.2517	0.2380	0.2295	0.2070	0.1902	0.1885	0.1745

Time	35	40	46	∞
D	0.1697	0.1657	0.1620	0.1520

$$k = 4.98 \times 10^{-2} \text{ min}^{-1}$$

Run No.17 Triphenyl-p-anisylsilane

$$\lambda = 281\text{m}\mu \quad 9.20\text{M} \quad \text{HClO}_4 \quad C = 0.000316\text{M}$$

Time	2	3	9	15	28	32	37
D	0.2330	0.2299	0.2137	0.2007	0.1802	0.1757	0.1715

Time	41	51	56	∞
D	0.1685	0.1622	0.1599	0.1487

$$k = 3.74 \times 10^{-2} \text{ min}^{-1}$$

Run No.18 (Duplicate)

Time	0	3	5	10	$22\frac{1}{2}$	$33\frac{1}{2}$	45
D	0.2380	0.2290	0.2230	0.2110	0.1900	0.1760	0.1680
Time	55	$\infty$					
D	0.1630	0.1532					

$$\underline{k = 3.81 \times 10^{-2} \text{ min}^{-1}}$$

Run No.19 Tri-o-tolyl-p-anisylsilane

$$\lambda = 281\text{m}\mu \quad 12.19\text{M} \quad \text{HClO}_4 \quad C = 0.000201\text{M}$$

Time	0	150	270	354	497	603	920
D	0.2382	0.2307	0.2235	0.2199	0.2115	0.2070	0.1965
Time	1000	1128	1257	1410	2480	2595	$\infty$
D	0.1923	0.1883	0.1823	0.1765	0.1560	0.1503	0.1285

$$\underline{k = 5.68 \times 10^{-4} \text{ min}^{-1}}$$

Run No.20 (Duplicate)

Time	0	120	297	520	620	780	885	955
D	0.243	0.239	0.2299	0.2182	0.2125	0.2045	0.2007	0.197
Time	1445	2390	$\infty$					
D	0.1802	0.1575	0.1315					

$$\underline{k = 5.64 \times 10^{-4} \text{ min}^{-1}}$$

Run No.21    Tri-(p-trimethylsilylmethylphenyl)-p-anisylsilane $\lambda = 281\text{m}\mu$     4.26M  $\text{HClO}_4$      $C = 0.0000753\text{M}$ 

Time	0	53	76	89	107	119	132
D	0.1320	0.1020	0.0935	0.0897	0.0847	0.0817	0.0790
Time	140	153	$\infty$				
D	0.0770	0.0745	0.0592				

$$\underline{k = 0.99 \times 10^{-2} \text{min}^{-1}}$$

Run No.22    (Duplicate)

Time	13	70	100	115	134	141 $\frac{1}{2}$	172
D	0.1295	0.1005	0.0902	0.0862	0.0820	0.0801	0.0745
Time	190	208	232	$\infty$			
D	0.0720	0.0698	0.0670	0.0592			

$$\underline{k = 0.98 \times 10^{-2} \text{min}^{-1}}$$

Run No.23    Tetra-p-anisylsilane $\lambda = 281\text{m}\mu$     2.55M  $\text{HClO}_4$      $C = 0.000264\text{M}$ 

Time	0	1	2	4	6	8 $\frac{1}{2}$
D	1.1807	1.1785	1.1765	1.1735	1.1705	1.1670
Time	10	13 $\frac{1}{2}$	15	17 $\frac{1}{2}$		
D	1.1649	1.1590	1.1572	1.1535		

Optical Density of synthetic end point = 1.048

$$\underline{k = 1.30 \times 10^{-2} \text{min}^{-1}}$$

Run No.24 (Duplicate)

Time	0	2	3	5	7	9½	12
D	1.1830	1.1795	1.1768	1.1742	1.1700	1.1670	1.1630
Time	15½	19	20	21			
D	1.1585	1.1530	1.1517	1.1500			

$$k = 1.29 \times 10^{-2} \text{ min}^{-1}$$

Run No.25 Tetra-p-anisylsilane Complete reaction

$$\lambda = 281 \text{ m}\mu \quad 3.05 \text{ M HClO}_4 \quad C = 0.000234 \text{ M}$$

Time	0	12	17	26	33	42½	
D	1.0030	0.9940	0.9850	0.9760	0.9500	0.9410	
Time	54½	69½	85	92½	131	141	
D	0.9340	0.9060	0.8840	0.8720	0.8140	0.7990	
Time	154	171½	180½	191	200	210	
D	0.7820	0.7590	0.7400	0.7380	0.7280	0.7160	
Time	220	232	240	263	287	302	316
D	0.7095	0.6995	0.6905	0.6720	0.6560	0.6455	0.6330
Time	347	367	381½	∞			
D	0.6280	0.6250	0.6230	0.6085			

Run No.26 (Duplicate)

Time	0	13	22½	35½	44½	54
D	1.0145	0.9990	0.9860	0.9650	0.9550	0.9380
Time	67½	79	97½	117	140	160½
D	0.9160	0.8980	0.8720	0.8420	0.8080	0.7810
Time	185	198	214	240	281	303
D	0.7510	0.7390	0.7220	0.6995	0.6710	0.6670

Run No.26 cont. (Duplicate)

Time	369	484	$\infty$
D	0.6430	0.6280	0.6190

Run No.27 Tri-p-anisyl ethoxysilane

$\lambda = 250\text{m}\mu$  3.05M  $\text{HClO}_4$  C = 0.000185M

Time	0	1	2	5	11	18
D	0.9760	0.9660	0.9590	0.9360	0.8840	0.8280
Time	26	34	45	61	86	110
D	0.7610	0.7090	0.6410	0.5480	0.4380	0.3560
Time	130	159	182	218	273	303
D	0.3020	0.2460	0.2120	0.1770	0.1460	0.1370
Time	353	$\infty$				
D	0.1260	0.1165				

Optical density of synthetic end point = 0.395

$$k = 1.63 \times 10^{-2} \text{min}^{-1}$$

Run No.28 (Duplicate)

Time	0	1	2	5	10	18
D	0.890	0.882	0.878	0.858	0.820	0.756
Time	26	45	65	100	159	205
D	0.697	0.585	0.486	0.358	0.233	0.162
Time	308	$\infty$				
D	0.131	0.116				

$$k = 1.62 \times 10^{-2} \text{min}^{-1}$$

Run No.29 Tri-p-anisyl ethoxysilane $\lambda = 250\text{m}\mu$  7.50M  $\text{HClO}_4$  C = 0.000183

Time	0	2	4	6	10	14
D	0.442	0.360	0.2995	0.253	0.194	0.1605
Time	20	26	35	59	$\infty$	
D	0.136	0.125	0.119	0.1147	0.1145	

Run No.30 (Duplicate).

Time	0	3	6	9	12	16
D	0.478	0.353	0.271	0.2185	0.184	0.1555
Time	20	24	30	42	53	$\infty$
D	0.140	0.1315	0.1245	0.1192	0.1180	0.1165

Run No.31 Di-p-anisyl diethoxysilane $\lambda = 248\text{m}\mu$  7.50M  $\text{HClO}_4$  C = 0.000349M

Time	0	$\frac{1}{2}$	1	2	3	4	
D	0.589	0.566	0.526	0.474	0.430	0.390	
Time	$5\frac{1}{2}$	7	11	15	22	37	64
D	0.342	0.306	0.232	0.195	0.1615	0.136	0.1285
Time	$\infty$						
D	0.124						

Optical density of synthetic end point = 0.211

$$\underline{k = 17.7 \times 10^{-2} \text{min}^{-1}}$$



Run No.32 (Duplicate)

Time	0	$\frac{1}{2}$	1	2	3	4	
D	0.686	0.643	0.608	0.548	0.492	0.448	
Time	5	7	11	15	22	39	55
D	0.406	0.341	0.256	0.208	0.167	0.139	0.132
Time	$\infty$						
D	0.1245						

$$\underline{k = 17.9 \times 10^{-2} \text{ min}^{-1}}$$

Run No.33 Di-p-anisyl diethoxysilane

$$\lambda = 248\text{m}\mu \quad 2.55\text{M HClO}_4 \quad C = 0.000313\text{M}$$

Time	0	$\frac{1}{2}$	2	3	4	$5\frac{1}{2}$
D	0.968	0.961	0.946	0.940	0.934	0.924
Time	$6\frac{1}{2}$	$7\frac{1}{2}$	$8\frac{1}{2}$	10	11	12
D	0.918	0.906	0.900	0.892	0.882	0.876

Optical density of synthetic end point = 0.189

$$\underline{k = 1.02 \times 10^{-2} \text{ min}^{-1}}$$

Run No.34 (Duplicate)

Time	0	2	4	5	7	9
D	0.981	0.966	0.951	0.944	0.924	0.914
Time	11	13	15	17		
D	0.897	0.882	0.869	0.856		

$$\underline{k = 1.01 \times 10^{-2} \text{ min}^{-1}}$$

Run No. 35    p-Anisyltriethoxysilane
 $\lambda = 248\text{m}\mu$     7.50M  $\text{HClO}_4$      $C = 0.00101 \text{ M}$ 

Time	0	18m.20s.	31	33	$35\frac{1}{2}$	43	51
D	0.4590	0.4150	0.3980	0.3950	0.392	0.3865	0.3805
Time	52m.15s.	60	$\infty$				
D	0.3795	0.3755	0.3620				

$$k = 3.26 \times 10^{-2} \text{ min}^{-1}$$

Run No. 36    (Duplicate)

Time	2	12	$16\frac{1}{2}$	25	31	49	96
D	0.4500	0.4250	0.4160	0.4015	0.3940	0.3770	0.3620
Time	117	$\infty$					
D	0.3600	0.3580					

$$k = 3.26 \times 10^{-2} \text{ min}^{-1}$$

Run No. 37    p-Anisyltrimethylsilane
 $\lambda = 281\text{m}\mu$     4.26M  $\text{HClO}_4$      $C = 0.000817\text{M}$ 

Time	1	3	4	$5\frac{1}{2}$	7	8	10	$\infty$
D	0.4710	0.4570	0.4510	0.4430	0.4380	0.4345	0.4300	0.4095

$$k = 12.9 \times 10^{-2} \text{ min}^{-1}$$

Run No. 38    (Duplicate)

Time	0	$\frac{1}{2}$	1m.15s.	2	3	4	5
D	0.4830	0.4780	0.471	0.4670	0.4605	0.4545	0.4490
Time	6	$7\frac{1}{2}$	9	$\infty$			
D	0.4450	0.4400	0.435	0.4095			

$$k = 4.04 \times 10^{-2} \text{ min}^{-1}$$

Run No. 39    Dimethylphenyl-p-anisylsilane. $\lambda = 281\text{m}\mu$     4.26M  $\text{HClO}_4$      $C = 0.000814\text{M}$ 

Time	0	11	20	23	$28\frac{1}{2}$	33	$47\frac{1}{2}$
D	0.5160	0.4750	0.4520	0.4460	0.4355	0.4300	0.4170

Time	$55\frac{1}{2}$	64	$\infty$
D	0.4110	0.4080	0.3990

$$\underline{k = 4.04 \times 10^{-2} \text{min}^{-1}}$$

Run No. 40    (Duplicate)

Time	0	7	10	11	20	33	38	$\infty$
D	0.5155	0.4870	0.4760	0.474	0.451	0.4285	0.423	0.3985

$$\underline{k = 4.07 \times 10^{-2} \text{min}^{-1}}$$

Run No. 41    Tribenzyl-p-anisylsilane $\lambda = 281\text{m}\mu$     4.26M  $\text{HClO}_4$      $C = 0.000637\text{M}$ 

Time	0	16	51	$74\frac{1}{2}$	$106\frac{1}{2}$	131	167	$\infty$
D	0.4830	0.4660	0.4380	0.4255	0.4120	0.4060	0.3980	0.3845

$$\underline{k = 1.18 \times 10^{-2} \text{min}^{-1}}$$

Run No. 42    (Duplicate)

Time	0	16	$49\frac{1}{2}$	68	92	113	154	231
D	0.4780	0.4630	0.4380	0.4270	0.4160	0.4100	0.3995	0.3910

Time	$\infty$
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D	0.3840
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$$\underline{k = 1.14 \times 10^{-2} \text{min}^{-1}}$$

Run No.43    Diphenylmethyl-p-anisylsilane. $\lambda = 281\text{m}\mu$     7.50M     $\text{HClO}_4$      $C = 0.000898\text{M}$ 

Time	0	2	8	10	12	18	32	36
D	0.5890	0.5740	0.5380	0.5280	0.5195	0.4995	0.4720	0.4680
Time	$\infty$							
D	0.4515							

$$\underline{k = 5.85 \times 10^{-2} \text{min}^{-1}}$$

Run No.44    (Duplicate)

Time	0	2	7	16	26m.15s.	30m.20s.
D	0.5850	0.5695	0.5380	0.5000	0.4755	0.4690
Time	40	43m.20s.	$\infty$			
D	0.4590	0.4570	0.4460			

$$\underline{k = 5.90 \times 10^{-2} \text{min}^{-1}}$$

Run No.45    Dimethylphenyl-p-anisylsilane. $\lambda = 281\text{m}\mu$     2.55M     $\text{HClO}_4$      $C = 0.000771\text{M}$ 

Time	22	56	107	130	155	163
D	0.4590	0.4315	0.4060	0.4000	0.3935	0.3890
Time	197	199	$\infty$			
D	0.3875	0.3850	0.3792			

$$\underline{k = 1.28 \times 10^{-2} \text{min}^{-1}}$$

Run No.46 (Duplicate)

Time	0	18	40	142	159	192	205
D	0.4950	0.4710	0.4495	0.3972	0.3940	0.3875	0.3865
Time	224	∞					
D	0.3845	0.3787					

$$k = 1.30 \times 10^{-2} \text{ min}^{-1}$$

Run No.47 Chloromethyldimethyl-p-anisylsilane

$$\lambda = 282 \text{ m}\mu \quad 6.00 \text{M HClO}_4 \quad C = 0.000513 \text{M}$$

Time	0	2	11	20	26	41	49	59
Titre	0.5210	0.5065	0.4520	0.4210	0.4045	0.3790	0.3707	0.3640
Time	80	90	∞					
Titre	0.3570	0.3555	0.3525					

$$k = 4.52 \times 10^{-2} \text{ min}^{-1}$$

Run No.48 (Duplicate)

Time	0	12	20m.15s.	31	41	47m.10s.	55
Titre	0.5210	0.4490	0.4180	0.3910	0.3760	0.3695	0.3635
Time	63	∞					
Titre	0.3590	0.3490					

$$k = 4.52 \times 10^{-2} \text{ min}^{-1}$$

Run No.49    Dimethylethylaminomethyl-p-anisylsilane $\lambda = 282\text{m}\mu$     9.48M  $\text{HClO}_4$      $C = 0.000912\text{M}$ 

Time	0	10	15	20	25	30	36	42
D	0.4680	0.4240	0.4100	0.3970	0.3860	0.3770	0.3680	0.3610
Time	50	63	90	$\infty$				
D	0.3530	0.3445	0.3370	0.3300				

$$k = 3.60 \times 10^{-2} \text{min}^{-1}$$

Run No.50    (Duplicate)

Time	2	12	18	36	42	51	60	90
D	0.4040	0.3805	0.3700	0.3500	0.3465	0.3412	0.3372	0.3310
Time	$\infty$							
D	0.3280							

$$k = 3.63 \times 10^{-2} \text{min}^{-1}$$

Run No.51    Dimethylethylaminomethyl-p-anisylsilane $\lambda = 282\text{m}\mu$     6.00M  $\text{HClO}_4$      $C = 0.000640\text{M}$ 

Time	0	3	8	13	16	21	39	49
D	0.3190	0.3120	0.3060	0.3002	0.2990	0.2965	0.2875	0.2825
Time	87	115	162	$\infty$				
D	0.2710	0.264	0.2535	0.2320				

$$k = 0.708 \times 10^{-2} \text{min}^{-1}$$

Run No.52 (Duplicate)

Time	0	1	3	6	10	16	27	44
D	0.3160	0.3130	0.3100	0.3055	0.3010	0.2970	0.3902	0.2835
Time	53	75	100	$\infty$				
D	0.2800	0.2725	0.2655	0.2300				

$$\underline{k = 0.710 \times 10^{-2} \text{ min}^{-1}}$$

Run No.53 Dimethylphenyl-p-anisylsilane

$$\lambda = 281 \text{ m}\mu \quad 3.05 \text{ M } \text{HClO}_4 \quad C = 0.00101 \text{ M}$$

Time	15	35	40	45	50	55	60	65
D	0.6310	0.5900	0.5810	0.5740	0.5680	0.5610	0.5550	0.5500
Time	70	75	89	$\infty$				
D	0.5450	0.5410	0.5305	0.4975				

$$\underline{k = 1.87 \times 10^{-2} \text{ min}^{-1}}$$

Run No.54 (Duplicate)

Time	0	15	20	35	40	55	63	70
D	0.6940	0.6470	0.6340	0.6005	0.5910	0.5680	0.5570	0.5485
Time	78	85 $\frac{1}{2}$	93	$\infty$				
D	0.5405	0.5350	0.5310	0.4960				

$$\underline{k = 1.88 \times 10^{-2} \text{ min}^{-1}}$$

Run No.55    Di-p-anisyl-diethoxysilane    Complete reaction
 $\lambda = 248\text{m}\mu$     3.05M  $\text{HClO}_4$      $C = 0.000274\text{M}$ 

Time	0	3	5	10	15	20
D	0.886	0.865	0.847	0.798	0.749	0.703
Time	25	30	50	69	89	118
D	0.6675	0.628	0.500	0.409	0.334	0.260
Time	145	168	193	252	337	$\infty$
D	0.213	0.1845	0.1625	0.132	0.1155	0.1035

Optical density of synthetic end point = 0.165

$$k = 1.48 \times 10^{-2} \text{min}^{-1}$$

Run No.56    (Duplicate)

Time	0	3	5	10	15	20
D	0.908	0.888	0.853	0.796	0.753	0.7095
Time	25	30	40	70	96	124
D	0.669	0.6315	0.563	0.406	0.317	0.2585
Time	163	196	259	352	$\infty$	
D	0.1915	0.1615	0.132	0.115	0.103	

$$k = 1.47 \times 10^{-2} \text{min}^{-1}$$

Run No.57    p-Anisyltrimethylsilane
 $\lambda = 281\text{m}\mu$     0.293M  $\text{HClO}_4$      $C = 0.000879\text{M}$ 

Time	0	61	85	112	139	167	213
D	0.6085	0.5895	0.5820	0.5740	0.5675	0.5595	0.5490
Time	258	$\infty$					
D	0.5585	0.4510					

$$k = 2.20 \times 10^{-3} \text{min}^{-1}$$



Run No.58 (Duplicate)

Time	0	78	98	118	135	208	260	278
D	0.6095	0.5860	0.5805	0.5735	0.5695	0.5510	0.5400	0.5370
Time	$\infty$							
D	0.4520							

$$\underline{k = 2.24 \times 10^{-3} \text{ min}^{-1}}$$

Run No.59 Dimethylphenyl-p-anisylsilane

$\lambda = 281\text{m}\mu$  7.50M  $\text{HClO}_4$  C = 0.00112M

Time	0	$1\frac{1}{2}$	2	3	4	5	7	12
D	0.5820	0.5690	0.5670	0.5605	0.5580	0.5545	0.5510	0.5475
Time	$\infty$							
D	0.5465							

$$\underline{k = 29.5 \times 10^{-2} \text{ min}^{-1}}$$

Run No.60 (Duplicate)

Time	0	$\frac{1}{2}$	1	2	$2\frac{1}{2}$	3	4m.45s.	$5\frac{1}{2}$
D	0.5890	0.5820	0.5780	0.5695	0.5665	0.5630	0.5560	0.5530
Time	6m.45s.	$\infty$						
D	0.5505	0.5445						

$$\underline{k = 29.5 \times 10^{-2} \text{ min}^{-1}}$$

Run No. 61    Diphenylmethyl-p-anisylsilane $\lambda = 281\text{m}\mu$     6.00M  $\text{HClO}_4$      $C = 0.000602\text{M}$ 

Time	1	9	12	20	34	$48\frac{1}{2}$	74
D	0.4090	0.3915	0.3850	0.3710	0.3520	0.3380	0.3215
Time	139	$166\frac{1}{2}$	$\infty$				
D	0.3045	0.3020	0.2990				

$$\underline{k = 2.24 \times 10^{-2} \text{min}^{-1}}$$

Run No. 62    (Duplicate)

Time	$8\frac{1}{2}$	15	20	25	30	42	49	$\infty$
D	0.3915	0.3780	0.3675	0.3590	0.3507	0.3360	0.3290	0.2900

$$\underline{k = 2.33 \times 10^{-2} \text{min}^{-1}}$$

Run No. 63    Chloromethyldimethyl-p-tolylsilane $\lambda = 276\text{m}\mu$     12.19M  $\text{HClO}_4$      $C = 0.00706\text{M}$ 

Time	0	10	25	$38\frac{1}{2}$	56	76
D	0.3100	0.2897	0.2625	0.2410	0.2170	0.1950
Time	$91\frac{1}{2}$	129	144	162	196	$\infty$
D	0.1800	0.1530	0.1450	0.1360	0.1245	0.0949

$$\underline{k = 1.00 \times 10^{-2} \text{min}^{-1}}$$

Run No.64 (Duplicate)

Time	0	21	35	70	124	172	198
D	0.3020	0.2630	0.2410	0.1980	0.1550	0.1327	0.1240
Time	211	233	272	315	$\infty$		
D	0.1205	0.1155	0.1095	0.1047	0.0957		

$$k = 1.00 \times 10^{-2} \text{ min}^{-1}$$

Run No.65 Di(chloromethyl)methyl-p-anisylsilane

= 248mu 9.20M  $\text{HClO}_4$  C = 0.0006546M

Time	0	$\frac{1}{2}$	1	2	3	4
D	0.314	0.303	0.294	0.277	0.260	0.2445
Time	5	6	10	22	80	$\infty$
D	0.231	0.220	0.186	0.1397	0.1115	0.101

$$k = \text{Ca } 10 \times 10^{-2} \text{ min}^{-1}$$

Run No.66 (Duplicate)

Time	0	1	2	3	5	8
D	0.308	0.286	0.2685	0.2525	0.2252	0.1957
Time	16	25	35	60	95	$\infty$
D	0.152	0.1323	0.1232	0.114	0.1088	0.1005

$$k = \text{Ca } 10 \times 10^{-2} \text{ min}^{-1}$$

Run No.67 p-Anisyltrimethylsilane. $\lambda = 281 \text{ m}\mu$  3.12M  $\text{HClO}_4$  C = 0.000872M

Time	0	2m.3s.	6	7	12	13	15
D	0.4895	0.4700	0.4385	0.4310	0.4020	0.3980	0.3890
Time	17	19	21	23	$\infty$		
D	0.3810	0.3740	0.3675	0.3625	0.3180		

$$k = 5.90 \times 10^{-2} \text{ min}^{-1}$$

Run No.68 (Duplicate)

Time	0	$5\frac{1}{2}$	$6\frac{1}{2}$	10	14	$15\frac{1}{2}$	$19\frac{1}{2}$
D	0.4615	0.4195	0.4130	0.3940	0.3760	0.3700	0.3570
Time	$21\frac{1}{2}$	$29\frac{1}{2}$	$32\frac{1}{2}$	$\infty$			
D	0.3525	0.3375	0.3325	0.3105			

$$k = 5.95 \times 10^{-2} \text{ min}^{-1}$$

Run No.69 Dimethylphenyl-p-anisylsilane. $\lambda = 281 \text{ m}\mu$  3.12M  $\text{HClO}_4$  C = 0.000856M

Time	0	$10\frac{1}{2}$	18	26	29	32	37
D	0.5490	0.5105	0.4865	0.4630	0.4555	0.4485	0.4380
Time	42	67	$147\frac{1}{2}$	$\infty$			
D	0.4280	0.3880	0.3380	0.3210			

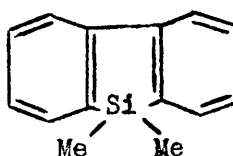
$$k = 1.80 \times 10^{-2} \text{ min}^{-1}$$

Run No.70 (Duplicate)

Time	0	10	17	37	42	46	51	57
D	0.5470	0.5105	0.4880	0.4380	0.4280	0.4205	0.4120	0.4030

Time	71	136 $\frac{1}{2}$	186	$\infty$
D	0.3830	0.3400	0.3290	0.3210

$$\underline{k = 1.79 \times 10^{-2} \text{ min}^{-1}}$$

Cyclic Organosilicon CompoundsRun No.1 5,5-Dimethyldibenzosilole
 $\lambda = 287\text{m}\mu$  12.19M  $\text{HClO}_4$   $C = 0.0000838\text{M}$ 

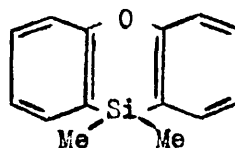
Time	0	5	10m.10s.	20	30	40
D	0.5590	0.4800	0.4115	0.3095	0.2330	0.1785
Time	50	60	70	80	96	$\infty$
D	0.1385	0.1097	0.0899	0.0735	0.0567	0.0347

$$k = 3.25 \times 10^{-2} \text{ min}^{-1}$$

Run No.2 (Duplicate)

Time	10	16	20	28 $\frac{1}{2}$	38	48	59
D	0.3690	0.3105	0.2775	0.2210	0.1732	0.1357	0.1065
Time	72	80	92	$\infty$			
D	0.0835	0.0730	0.0615	0.0387			

$$k = 3.24 \times 10^{-2} \text{ min}^{-1}$$

Run No.3 10,10-Dimethylphenoxasilin
 $\lambda = 284\text{m}\mu$  12.19M  $\text{HClO}_4$   $C = 0.000224\text{M}$ 

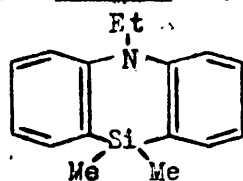
Time	0	20	40m.20s.	69	91	109	128
D	0.3260	0.2425	0.1935	0.1510	0.1315	0.1212	0.1132
Time	147	166 $\frac{1}{2}$	$\infty$				
D	0.1075	0.1037	0.0948				

$$k = 1.94 \times 10^{-2} \text{ min}^{-1}$$

Run No.4 (Duplicate)

Time	0	32	45	60	75m.10s.	92	110
D	0.3140	0.2070	0.1815	0.1599	0.1437	0.1302	0.1200
Time	133	152 $\frac{1}{2}$	188	$\infty$			
D	0.1110	0.1055	0.1000	0.0947			

$$k = 1.95 \times 10^{-2} \text{ min}^{-1}$$

Run No.5 5-Ethyl-5,10-dihydro-10,10-dimethylphenazasiline.

$$\lambda = 282\text{m}\mu \quad 0.293\text{MHClo}_4 \quad C = 0.0000519\text{M}$$

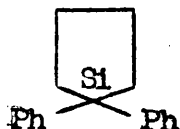
Time	0	35s.	1	2	2 $\frac{1}{2}$	5	7
D	0.2815	0.2695	0.2590	0.2410	0.2330	0.2045	0.1905
Time	8	9	12	$\infty$			
D	0.1855	0.1815	0.1735	0.1650			

$$k = 21.5 \times 10^{-2} \text{ min}^{-1}$$

Run No.6 (Duplicate)

Time	0	1	1m.33s.	2	2m.35s.	5	6
D	0.287	0.2625	0.2515	0.2425	0.2335	0.2045	0.1955
Time	8	10	12	$\infty$			
D	0.1840	0.1755	0.1702	0.1610			

$$k = 21.6 \times 10^{-2} \text{ min}^{-1}$$

Run No.7    1,1-Diphenylsilacyclopentane

$\lambda = 271\text{m}\mu$      $12.19\text{M HClO}_4$      $C = 0.000213\text{M}$

Time	8	100	210	316	467	605
D	0.523	0.494	0.4605	0.429	0.387	0.3497
Time	1020	1320	1590	1710	1460	$\infty$
D	0.2805	0.211	0.179	0.161	0.1005	0.037

Run No.8    (Duplicate)

Time	0	46	120	203	365	486
D	0.528	0.5125	0.4905	0.464	0.418	0.3825
Time	575	990	1635	3060	$\infty$	
D	0.3587	0.271	0.170	0.0645	0.038	

A straight line plot of  $\log (D_t - D_\infty)$  against  $t$  was not obtained.



Optical densities of p-anisylethoxysilanes and anisole in 10% aqueous methanol containing 0.5% of 9.2M perchloric acid.

(i) Anisole  $C = 0.000815$  M.

Wavelength $\mu$	248	250	251	252	281	282	282.5
D	0.158	0.200	0.222	0.250	0.515	0.362	0.3005

(ii) p-Anisyltriethoxysilane  $C = 0.000405$  M.

Wavelength $\mu$	248	250	252	281	282
D	0.2700	0.2785	0.2995	0.351	0.2765

(iii) Di-p-anisyl-diethoxysilane  $C = 0.000300$  M.

Wavelength $\mu$	250	252	281
D	0.826	0.573	0.518

(iv) Tri-p-anisylethoxysilane  $C = 0.000264$  M.

Wavelength $\mu$	252	281
D	1.097	0.779

For runs 3 and 4 a value of rate constant was not given as a straight line plot was not obtained and it appeared that a p-tolyl group was also cleaved.

Spectra of dimethylethylaminomethyl-p-anisylsilane.

1. In methanol (fresh solution)  $C = 0.0000400$  M.

$\lambda$ (m $\mu$ )	283	282	281	280	279	278	277	276
A	0.314	0.368	0.386	0.373	0.359	0.361	0.388	0.426
$\lambda$ (m $\mu$ )	275	274	273	272	270	268		
A	0.453	0.461	0.451	0.434	0.401	0.380		

2. In methanol + 2.55 M HClO<sub>4</sub>  $C = 0.0000623$  M.

of silane  
(25 ml of solution + 10 ml of aqueous acid)

$\lambda$ (m $\mu$ )	284	282	281	280	279	278	277	276
A	0.195	0.3315	0.379	0.401	0.403	0.402	0.414	0.440
$\lambda$ (m $\mu$ )	275	274	273	272	271	270		
A	0.470	0.492	0.506	0.503	0.490	0.474		

3. In methanol + 0.001 M HClO<sub>4</sub> (25 ml of solution of silane + 10 ml of aqueous acid)  $C = 0.0000821$  M

$\lambda$ (m $\mu$ )	284	282	281	280	279	278	277	276
A	0.2675	0.450	0.511	0.5315	0.526	0.519	0.531	0.567
$\lambda$ (m $\mu$ )	275	274	273	272	271	270		
A	0.6195	0.640	0.6475	0.638	0.615	0.591		

4. In methanol (old solution)  $C = 0.0000821$  M

$\lambda$ (m $\mu$ )	284	282	281	280	279	278	277	276
A	0.491	0.670	0.759	0.765	0.730	0.712	0.740	0.807
$\lambda$ (m $\mu$ )	275	274	273	272	271	270		
A	0.880	0.919	0.917	0.886	0.852	0.818		

5. In methanol and water  $C = 0.0000623$  M.

$\lambda$ (m $\mu$ )	284	282	281	280	279	278	277	276
A	0.323	0.545	0.601	0.626	0.619	0.612	0.629	0.669

$\lambda$ (m $\mu$ )	275	274	273	272	271	270
A	0.712	0.745	0.752	0.739	0.711	0.672

Where  $\lambda$  = wavelength

and A = optical density

## CHAPTER X

### Experimental technique for the kinetic investigation of cleavage of the C-Si bond by bromine.

The bromine cleavage of the silane at 25.0°C was followed by determination of residual bromine by titration of sodium thio-  
**sulphate against the iodine** liberated when a solution of the reactants was treated with potassium iodide solution. The dead-stop technique was employed to determine the equivalence point.

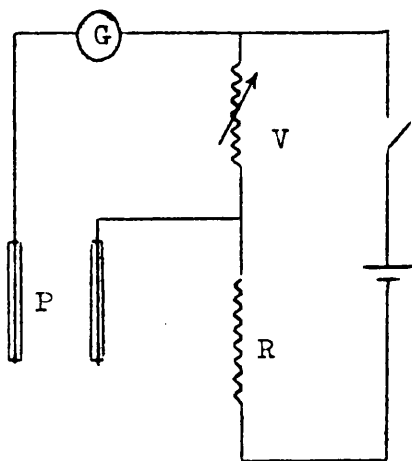
#### Dead-stop technique.

This method was introduced by Foulk and <sup>94</sup>~~Bowden~~.

In the determination of sodium thiosulphate by titration with iodine solution, the thiosulphate acts as an anode depolariser. On adding iodine solution, iodide is formed which also acts as an anode depolariser but immediately the equivalence point is reached, the free iodine acts as a cathode depolariser and current flows. The end point is indicated by the sudden commencement of flow of current, which is shown by permanent deflection of the galvanometer.

In this work the reverse titration i.e. a solution of iodine (which contains iodide) was titrated with a solution of thiosulphate, was carried out. Here, both electrodes are depolarised and until almost to the end point, the galvanometer pointer is deflected off the scale. When equivalence is reached, all the iodine has been removed and the cathode becomes polarised; the galvanometer pointer returns to zero. A difficulty in using this method is that the galvanometer spot remains at zero even after excess of thiosulphate has been added.

Fig. XXIII



The electrical circuit (Fig. XXIII)

consisted of

(a) A pair of platinum electrodes (P)

These were made from platinum wire

sealed in soda-glass and were approx.

$\frac{1}{8}$ " long and  $\frac{1}{4}$ " apart.

(b) A "Cambridge" spot-galvanometer (G)

of resistance 450 ohms and sensitivity

170 mm/ $\mu$ A. It was damped with a 12,500

ohm shunt

(c) A fixed resistance (R) of approx.

100,000 ohms.

(d) A variable resistance (V) of approx.

10,000 ohms.

(e) A battery (E) of approx. 1.5 volts.

#### Apparatus.

A 2 litre stock of sodium thiosulphate solution was connected through a two-way tap to a 10 ml micro-burette read to 0.002 ml.

The titration vessel was that described by Webster.<sup>15</sup> It consisted of an inverted pear-shaped vessel fitted at the top with five openings. These were for addition: of sample, the electrodes, the tip of the burette, a tap for water and a glass tube through which air was passed. By means of the latter the solution in the flask could be thoroughly stirred, the air line consisting of a blower controlled by a switch.

A tap at the bottom of the vessel was closed during titrations and opened to allow the vessel to drain. It was connected to a water-pump for rapid emptying of the flask.

### Preparation of materials

#### (a) Sodium thiosulphate

An approximately 0.001 N solution was prepared from "Analar" sodium thiosulphate and freshly boiled distilled water. About 0.1 ml of chloroform per litre was added in order to stabilise the solution. The solution was kept in brown bottles and standardised once a week with potassium iodate solution prepared from "Analar" potassium iodate dried at 120°C for 1 hour and cooled in a dessicator.

#### (b) Potassium iodide

An approximately 10% solution of potassium iodide was prepared by dissolving "May and Baker" potassium iodide in boiled out distilled water. A fresh solution was made up each day as it was found that decomposition of the potassium iodide solution occurred liberating iodine of a similar concentration as that in the titrations.

#### (c) Acetic acid solvent

"May and Baker" reagent grade acetic acid was purified by the method of ORTON and BRADFELD.<sup>95</sup> Two and a half litres were boiled under reflux for about 1/2 hour with chromium trioxide (60 gm) followed by distillation through a short glass helices packed column (12" long, 1" diameter).

The first 200 ml of distillate was discarded and the next two litres collected. Several distillations were combined and the water

content adjusted to 1.5 wt %.

The water content was found by measuring the freezing point of the acid. Since a depression of  $0.2^{\circ}\text{C}$  is due to 0.1% of water distilled water was added until the solution froze at  $13.6^{\circ}\text{C}$ , the water content then being 1.5 wt %.

(d) Bromine

"May and Baker" bromine was shaken with an equal volume of concentrated sulphuric acid and the acid separated. It was then distilled from potassium bromide in all-glass apparatus.

Method of following kinetic runs.

A fresh solution of halogen in aqueous acetic acid (1.5 wt %) was placed in a long-necked 500 ml flask in the thermostat. It was then left for at least 25 minutes in order to reach thermal equilibrium and a sample (5 ml) standardised with sodium thiosulphate solution.

For most runs the concentrations of silane and bromine were identical. The silane was then weighed out into a 100 ml wide necked graduated flask and about 90 ml of solvent added. This was then placed in the thermostat bath. When the solution had reached thermal equilibrium it was made up to the mark with solvent at the thermostat temperature  $25.0^{\circ} \pm 0.02^{\circ}$  and the solution thoroughly mixed.

(a) Fast runs

Two separate solutions of the silane were made up.

A divided reaction vessel was used and a 5 ml sample

of each reactant was put into separate compartments. The flask was closed with a rubber bung, placed in the bath and left to reach the bath temperature. Whilst still immersed in the bath the contents were thoroughly mixed, the time of mixing being taken as zero time. After a particular time the reaction was stopped by addition of 10 ml of 10% aqueous potassium iodide solution. The contents were then transferred to the reaction vessel with about 100 ml of water. The time of reaction was taken as that from the time of mixing until the time of addition of the potassium iodide solution. A duplicate run was carried out using a different solution of silane.

(b) Slow runs

Only one solution of silane was made up and runs in duplicate were carried out using this solution.

A 25 ml sample of the silane was transferred by means of a pipette equipped with a side arm and a suction bulb to a 100 ml round-bottomed flask equipped with a long neck and fitted with a B.19 ground glass stopper. The flask was well immersed in the bath and the contents allowed to reach bath temperature. 25 ml of bromine solution was added and the flask well shaken. After suitable lengths of time 5 ml samples were withdrawn and added to 10 ml of aqueous potassium iodide solution in the titration vessel. The volume was then made up to about 100 ml with water. The time of reaction was taken as that from half addition of the bromine solution until the time of half addition of the reaction mixture to the potassium iodide solution.



(c) Very slow runs

The method for slow runs was carried out but it was then necessary to transfer samples to sealed tubes and immerse these in the bath. After appropriate lengths of time 5 ml samples were transferred to the reaction vessel, water added and titrations carried out as described above. "Fast runs" in general had about 50% reaction completed in 25 minutes whereas "slow runs" did not. "Very slow runs" had less than 20% reaction completed in 24 hours.

After addition of water the solution was stirred vigorously by means of the air blower, and thiosulphate solution added. Readings were taken as the end point was approached until the galvanometer spot no longer moved. Readings were taken after various times and a time/titre curve was plotted. It was found that a smooth curve could not be obtained if the first part of the run was carried out in fast reaction vessels and the remainder of the run in slow reaction vessels. Whenever it was convenient runs were carried out up to 75% reaction.

Thermostat

All the runs were carried out in a water-filled bath at 25°C, controlled by a mercury-contact toluene regulator and heated by a 60 watt bulb. Stirring was by means of a motor-driven paddle.

The temperature of the bath remained constant within  $\pm 0.02^\circ\text{C}$  of the temperature employed.

### Pipettes

For mixing the reactants a 25 ml pipette fitted with a side-arm and suction bulb was used. Samples were taken with a 5 ml automatic pipette.

### Weighings

These were carried out on an "Oertling" balance using micro-weighing bottles prepared from small ignition tubes of 4 mm diameter shortened to a length of 10-20 mm. The micro weighing bottle containing a weighed sample was placed in a graduated flask and solvent added up to the graduation mark, the volume of the weighing bottle being neglected.

### Calculation of results.

Relative rate figures were obtained by carrying out runs (in duplicate) with two different organosilanes at the same concentration. The times for disappearance of specific fractions of halogen were compared directly.

### Sources of error

#### (a) Reaction of silanes with solvent

The organosilanes were shown spectrophotometrically not to react with the solvent. A solution of *p*-methoxy-phenyltrimethylsilane had the same spectrum after 48 hours as when prepared.

#### (b) Loss of halogen by reaction with solvent or by volatilisation

A solution of bromine in acetic acid solvent was observed to give identical titres over the time of the reactions. The bromine solution was titrated against thiosulphate each day and it was found that the solution lost bromine equivalent to 3% after 3 days.

(c) Reproducibility of the solvent

Two batches (approx. 10 litres) of acetic acid were prepared, and kinetic results of each batch agreed to 3%. Cleavage of tri-p-tolyl-p-anisylsilane and tri-m-tolyl-p-anisylsilane were compared at identical concentrations in both batches of solvent (runs 19 and 21 and runs 22 and 23).

(d) Continued reaction after sampling

Following the addition of or to the aqueous potassium iodide, the organic compound was thrown out of solution and the bromine reacted with potassium iodide to give iodine. These two events effectively stopped reaction.

(e) Reaction between the cleavage product p-bromo-anisole and bromine.

No reaction occurred between p-bromo-anisole and bromine both at a concentration of 0.00156M within 48 hours. Runs with p-anisylsilanes were not carried out for longer than this period.

(f) Ultra-violet catalysis of the reaction

It was found unnecessary to use blackened flasks for reaction vessels as there as no appreciable catalysis of the reaction due to the presence of the light bulb in the thermostat bath which was used for heating purposes.

(g) Accuracy of results

It was not possible at the concentrations used, to record the end point to within  $\pm 0.03$  ml. This led to difficulty in drawing

smooth curves through the points and introduced large errors in calculating relative rates, particularly in the regions 0 - 20% and 60 - 100% reaction. Therefore, in some cases relative rates have been determined only over the range 30 - 60%. Because of the error in determining the end point all relative rate figures are accurate only to 5%. Errors of 5% similarly occur in determinations of order of reaction.

As solutions of bromine could not be kept longer than 3 days because of loss of bromine, many different solutions of bromine had to be made up in order to cover all the compounds. Thus considerable overlapping of pairs of reactants was necessary.

(i) Fast runs

As the run was not continuous and each titration was determined separately, different errors could be introduced in each case, and for this reason it was more difficult to draw a smooth curve through the points of the time against titre plot than for a slow run. Agreement between fast runs was to 3% (from the runs 19 and 21, and runs 22 and 23).

(ii) Slow runs

The run was continuous and errors introduced by taking pipette samples and timing readings were reduced and a good curve could be drawn through the points of the time versus titre plots. Agreement between slow runs and fast runs was 2% (runs 19 and 21, and

runs 27 and 28). Some runs were carried out where the initial concentrations of silane and bromine were not the same, from runs 26 and 28 and 34 and 25 agreement was to within 1% with those in which the initial silane and bromine concentration was the same.

(iii) Very slow runs

No such runs were carried out for the series of p-anisylsilanes. As with the fast runs each titration was determined separately. Further error was introduced for there must have been loss of bromine through reaction with the solvent.

Tabulation of Kinetic Results.

The runs are reported in terms of volume (in ml) of sodium thiosulphate solution (labelled "titre") equivalent to the iodine liberated from potassium iodide solution by the bromine remaining after a specified time (in mins. unless otherwise stated) (labelled "time"). The titration figures are equivalent to the halogen in a measured sample of the solution (5.0 ml). Also given are the concentrations of the solutions of bromine and silane before they were mixed.

Runs were carried out in duplicate and each run and its duplicate were plotted on a time-titre graph, and the times required for removal of various fractions of the bromine were obtained from a smoothed curve through the points. All runs were carried out in 1.5 wt % aqueous acetic acid, using the apparatus described at a temperature of  $25.00 \pm 0.02^\circ$ .

Run No. 1. Triphenyl-p-anisylsilane

[Silane] = [Bromine] = 0.00161 M

Time	Om.	4m. 40s.	14m. 15s.	25m.
Titre	4.640	4.216	3.476	2.938
Time	36m. 40s.	76m. 15s.	116m. 20s.	
Titre	2.526	1.712	1.292	

(Duplicate)

Time	Om.	7m. 20s.	16m. 35s.	27m. 15s.	38m. 30s.
Titre	4.640	3.964	3.300	2.864	2.500
Time	51m. 5s.	58m. 20s.	89m. 40s.	104m. 30s.	119m.
Titre	2.168	1.972	1.540	1.360	1.244

Run No. 2. Tri-p-chlorophenyl-p-anisylsilane

[Silane] = [Bromine] = 0.00161 M

Time	Om.	5m. 15s.	18m. 15s.	35m. 40s.	65m.
Titre	4.640	4.578	4.442	4.250	3.982
Time	204m.	230m.	260m.	293m.	
Titre	2.938	2.812	2.676	2.490	

(Duplicate)

Time	Om.	13m. 25s.	27m.	58m. 30s.	107m.
Titre	4.640	4.548	4.352	4.052	3.550
Time	215m.	243m.	265m.	298m.	
Titre	2.912	2.750	2.644	2.490	

Relative rate Tri-p-chlorophenyl-p-anisylsilane

Triphenyl-p-anisylsilane

Reaction %	10	20	30	40
	0.11	0.12	0.12	0.12

Average = 0.12

Run No. 3. Tri-m-chlorophenyl-p-anisylsilane

[Silane] = [Bromine] = 0.00161 M

Time (min)	0	26	55	122	148	220	270
Titre	4.640	4.500	4.340	4.050	3.938	3.680	3.520
Time (min)	410	478	525	590	672	760	
Titre	3.090	2.970	2.844	2.758	2.644	2.530	

(Duplicate)

Time (min)	0	30	60	165	211	260	348
Titre	4.640	4.498	4.320	3.864	3.730	3.556	3.300
Time (min)	371	431	516	594	676	768	
Titre	3.196	3.040	2.880	2.738	2.646	2.520	

Relative rate Tri-m-chlorophenyl-p-anisylsilane

Triphenyl-p-anisylsilane

Reaction %	10	20	30	40
	0.052	0.052	0.052	0.050

Average = 0.052Run No. 4. Tri-o-tolyl-p-anisylsilane

[Silane] = [Bromine] = 0.00161 M

Time (min)	0	66	152	228	322	408	472
Titre	4.640	4.454	4.290	4.158	3.978	3.840	3.726
Time (min)	538	1215	1345	1449	1645	1815	
Titre	3.638	3.020	2.936	2.844	2.788	2.672	



(Duplicate)

Time (min)	0	73	157	235	327	419
Titre	4.640	4.446	4.282	4.106	3.966	3.834
Time (min)	478	543	1350	1455	1653	1823
Titre	3.758	3.640	2.900	2.842	2.758	2.652

Relative rate Tri-*p*-tolyl-*p*-anisylsilaneTriphenyl -*p*-anisylsilane

Reaction %	10	20	30	40
	0.023	0.022	0.021	0.019

Average = 0.021Run No. 5. Tri-*m*-chlorophenyl-*p*-anisylsilane

[Silane] = [Bromine] = 0.00187 M

Time (min)	0	27	69	111	144
Titre	5.400	5.196	4.880	4.648	4.418
Time (min)	201	248	310	396	469
Titre	4.096	3.940	3.708	3.410	3.246
Time (min)	556	630	693	764	
Titre	3.046	2.896	2.736	2.638	

(Duplicate)

Time (min)	0	19	60	103	135
Titre	5.400	5.204	4.934	4.660	4.472
Time (min)	196	258	321	389	462
Titre	4.154	3.940	3.682	3.446	3.248
Time (min)	548	622	686	758	
Titre	3.058	2.888	2.762	2.638	

Run No. 6. Tri-o-tolyl-p-anisylsilane

[Silane] = [Bromine] = 0.00187 M

Time (min)	0	60	161	198	222	287
Titre	5.400	5.150	4.840	4.742	4.638	4.470
Time (min)	354	440	519	690	1395	
Titre	4.314	4.124	3.946	3.612	2.774	

(Duplicate)

Time (min)	0	76	166	345	433
Titre	5.400	5.098	4.820	4.326	4.118
Time (min)	513	604	695	1400	1594
Titre	3.926	3.746	3.556	2.734	2.590

Relative rate Tri-o-tolyl-p-anisylsilane

Tri-m-chlorophenyl-p-anisylsilane

Reaction %	10	20	30	40	50
	0.47	0.48	0.49	0.50	0.49

Average = 0.48Run No. 7. Tri-p-tolyl-p-anisylsilane

[Silane] = [Bromine] = 0.000283 M

Time	0	3m. 0s.	10m. 45s.	19m. 45s.
Titre	5.480	5.302	4.724	4.274
Time	29m. 3s.	49m. 25s.	107m. 0s.	131m. 0s.
Titre	3.858	3.342	2.530	2.342

## (Duplicate)

Time	0	5m. 15s.	13m. 30s.	23m. 5s.
Titre	5.480	5.058	4.522	3.952
Time	38m. 55s.	117m. 0s.	151m. 0s.	187m. 30s.
Titre	3.588	2.464	2.272	2.040

Run No. 8. Dimethylethylaminomethyl-p-anisylsilane

$$[\text{Silane}] = [\text{Bromine}] = 0.000283 \text{ M}$$

Time	0	1m. 8s.	4m. 45s.	7m. 45s.	10m. 53s.
Titre	5.480	4.504	3.560	3.162	2.826
Time	14m. 28s.	18m. 40s.	23m. 58s.	32m. 50s.	45m. 50s.
Titre	2.544	2.348	2.194	1.974	1.784

## (Duplicate)

Time	0	1m. 4s.	4m. 38s.	7m. 43s.
Titre	5.480	4.502	3.600	3.184
Time	10m. 47s.	14m. 2s.	32m. 25s.	45m. 0s.
Titre	2.896	2.646	1.974	1.894

Relative rate Dimethylethylaminomethyl-p-anisylsilaneTri-p-tolyl-p-anisylsilane

Reaction %	10	20	30	40	50	60
	14.0	12.0	8.8	7.6	7.2	6.5

Run No. 9. Tri-(p-trimethylsilylmethylphenyl)-p-anisylsilane

$$[\text{Silane}] = [\text{Bromine}] = 0.000283 \text{ M}$$

Time	0	1m. 12s.	5m. 33s.	9m. 50s.	13m. 28s.
Titre	5.480	5.316	4.732	4.320	3.932
Time	17m. 35s.	22m. 35s.	28m. 50s.	39m. 30s.	49m. 50s.
Titre	3.600	3.256	2.814	2.188	1.736

(Duplicate)

Time	0	1m. 10s.	4m. 35s.	9m. 12s.
Titre	5.480	5.304	4.824	4.426
Time	15m. 0s.	34m. 30s.	53m. 10s.	67m. 45s.
Titre	3.824	2.530	1.590	1.220

Relative rate Tri-(p-trimethylsilylmethylphenyl)-p-anisylsilane  
Tri-p-tolyl-p-anisylsilane

Reaction %	10	20	30	40	50	60
	1.9	1.9	2.1	2.3	2.9	3.9

Run No. 10. Tribenzyl-p-anisylsilane

[Silane] = [Bromine] = 0.000283 M

Time	0	1m. 7s.	5m. 5s.	9m. 10s.	12m. 54s.
Titre	5.480	4.850	3.410	2.762	2.360
Time	17m. 3s.	22m. 8s.	26m. 30s.	30m. 30s.	38m. 40s.
Titre	2.120	1.932	1.734	1.686	1.328

(Duplicate)

Time	0	1m. 7s.	4m. 15s.	8m. 3s.	11m. 57s.
Titre	5.480	4.864	3.632	2.960	2.486
Time	15m. 35s.	19m. 10s.	22m. 55s.	29m. 33s.	
Titre	2.246	2.042	1.888	1.656	

Relative rate Tribenzyl-p-anisylsilane  
Tri-p-tolyl-p-anisylsilane

Reaction %	10	20	30	40	50	60
	8.7	8.7	8.7	8.7	9.0	9.7

Average = 8.7

Run No. 11. Triethoxy-p-anisylsilane

[Silane] = [Bromine] = 0.000164 M      Blank = 0.236 ml.

Time	0	4m. 30s.	10m. 5s.	15m. 25s.
Titre	3.166	2.920	2.734	2.516
Time	25m. 50s.	54m. 50s.	83m. 0s.	117m. 0s.
Titre	2.168	1.676	1.294	1.086

(Duplicate)

Time	0	1m. 20s.	6m. 50s.	12m. 10s.	24m. 20s.
Titre	3.166	3.190	2.880	2.640	2.238
Time	34m. 35s.	47m. 0s.	66m. 0s.	93m. 0s.	120m. 0s.
Titre	1.968	1.744	1.506	1.214	1.038

Run No. 12. Chloromethyldimethyl-p-anisylsilane

[Silane] = [Bromine] = 0.000164 M      Blank = 0.236 ml.

Time	0	3m. 40s.	6m. 40s.
Titre	3.166	2.100	1.656
Time	9m. 35s.	25m. 30s.	31m. 35s.
Titre	1.450	0.980	0.904

(Duplicate)

Time	0	1m. 2s.	3m. 55s.
Titre	3.166	2.806	2.028
Time	10m. 4s.	13m. 5s.	16m. 3s.
Titre	1.404	1.194	1.130

(Triplicate)

Time	0	1m. 35s.	4m. 5s.	9m. 25s.
Titre	3.166	2.726	2.006	1.464
Time	12m. 35s.	15m. 35s.	31m. 30s.	
Titre	1.280	1.134	0.954	

Relative rate Triethoxy-p-anisylsilane

## Chloromethyldimethyl-p-anisylsilane

Reaction %	10	20	30	40	50	60	70
	0.13	0.12	0.12	0.12	0.13	0.13	0.14

Average = 0.13Run No. 13. Diphenylmethyl-p-anisylsilane

[Silane] = [Bromine] = 0.000164 M      Blank = 0.236 ml.

Time	0	1m. 30s.	5m. 30s.	10m. 25s.
Titre	3.166	3.174	2.670	2.300
Time	22m. 30s.	31m. 0s.	46m. 15s.	
Titre	1.820	1.710	1.502	

(Duplicate)

Time	0	1m. 30s.	6m. 3s.	9m. 50s.
Titre	3.166	3.190	2.708	2.306
Time	39m. 15s.	54m. 30s.	66m. 45s.	
Titre	1.572	1.438	1.256	

(Triplicate)

Time (min)	0	5	12	26
Titre	3.166	2.698	2.224	1.790
Time (min)	33½	43	53	66
Titre	1.620	1.496	1.398	1.300

Relative rate Diphenylmethyl-p-anisylsilane

## Chloromethyldimethyl-p-anisylsilane

Reaction %	10	20	30	40	50	60
	0.23	0.23	0.24	0.24	0.24	0.22

Average = 0.23

Run No. 14. Tetra-p-anisylsilane

[Silane] = [Bromine] = 0.000164 M      Blank = 0.236 ml.

Time	0	1m. 5s.	7m. 35s.	11m. 6s.
Titre	3.166	3.058	2.046	1.610
Time	17m. 50s.	21m. 18s.	25m. 10s.	32m. 0s.
Titre	1.076	0.920	0.870	0.750

(Duplicate)

Time	0	3m. 50s.	7m. 18s.	10m. 31s.
Titre	3.166	2.556	2.084	1.740
Time		13m. 45s.	17m. 8s.	25m. 50s.
Titre		1.458	1.124	0.816

(Triplicate)

Time	0	1m. 3s.	7m. 25s.	10m. 30s.
Titre	3.166	2.510	2.104	1.708
Time	13m. 20s.	16m. 18s.	19m. 3s.	
Titre	1.394	1.272	1.042	

Relative rate Tetra-p-anisylsilaneDiphenylmethyl-p-anisylsilane

Reaction %	10	20	30	40	50	60
	2.1	1.8	1.8	2.0	2.5	3.3

Run No. 15. Chloromethyldimethyl-p-anisylsilane

[Silane] = [Bromine] = 0.000130 M      Blank = 0.236 ml.

Time	0	0m. 30s.	1m. 0s.	1m. 30s.	3m. 0s.
Titre	5.238	4.720	4.432	4.208	3.726
Time	14m. 25s.	18m. 0s.	28m. 0s.	36m. 0s.	
Titre	2.166	1.992	1.764	1.554	

(Duplicate)

Time	0	0m. 45s.	2m. 0s.	3m. 0s.
Titre	5.258	4.640	4.142	3.634
Time	4m. 30s.	8m. 0s.	33m. 30s.	
Titre	3.236	2.698	1.702	

Run No. 16. Trimethyl-p-anisylsilane

$$[\text{Silane}] = [\text{Bromine}] = 0.000130 \text{ M}$$

Time (sec)	0	9 $\frac{1}{2}$	10 $\frac{1}{2}$	15	20
Titre	5.378	3.900	3.792	3.400	3.192
Time (sec)	25	45	60	90	Blank
Titre	2.944	2.404	2.188	1.920	0.356

(Duplicate)

Time (sec)	0	11 $\frac{1}{2}$	15	20	25
Titre	5.722	4.060	3.802	3.554	3.356
Time (sec)	35	45	60	90	Blank
Titre	2.964	2.780	2.462	2.264	0.700

Relative rate    Trimethyl-p-anisylsilane

Chloromethyldimethyl-p-anisylsilane

Reaction %	30	40	50	60	70
	16.0	17.0	17.0	17.0	17.0

Average = 17.0Run No. 17. Tri-p-tolyl-p-anisylsilane

$$[\text{Silane}] = [\text{Bromine}] = 0.000821 \text{ M}$$

Time (min)	0	1 $\frac{3}{4}$	6 $\frac{3}{4}$	17 $\frac{3}{4}$	19 $\frac{3}{4}$
Titre	7.610	6.602	5.684	4.336	4.064
Time	22 $\frac{3}{4}$	38 $\frac{3}{4}$	70 $\frac{3}{4}$	99 $\frac{3}{4}$	
Titre	3.724	2.688	1.504	1.200	



(Duplicate)

Time (min)	0	$\frac{3}{4}$	$5\frac{3}{4}$	$8\frac{3}{4}$	$9\frac{3}{4}$
Titre	7.610	7.230	6.028	5.416	5.252
Time (min)	$15\frac{3}{4}$	$27\frac{3}{4}$	$34\frac{3}{4}$	$72\frac{3}{4}$	
Titre	4.400	3.360	2.930	1.562	

Run No. 18. Diphenylmethyl-p-anisylsilane

[Silane] = [Bromine] = 0.000821 M

Time (min)	0	$\frac{3}{4}$	$1\frac{3}{4}$	$2\frac{3}{4}$	$4\frac{3}{4}$
Titre	7.610	5.810	5.054	4.558	3.654
Time (min)	$7\frac{3}{4}$	$17\frac{3}{4}$	$29\frac{3}{4}$	$55\frac{3}{4}$	$75\frac{3}{4}$
Titre	2.750	1.490	1.000	0.802	0.592

(Duplicate)

Time (min)	0	$\frac{3}{4}$	$2\frac{3}{4}$	$7\frac{3}{4}$	$14\frac{3}{4}$
Titre	7.610	5.864	4.496	2.704	1.682
Time (min)	$35\frac{3}{4}$	$52\frac{3}{4}$	$79\frac{3}{4}$	$99\frac{3}{4}$	
Titre	0.802	0.704	0.548	0.514	

Relative rate Diphenylmethyl-p-anisylsilane

Tri-p-tolyl-p-anisylsilane

Reaction %	20	30	40	50	60	70	80
	5.6	5.2	5.3	5.3	5.1	4.9	4.5

Average (30-70%) = 5.2Run No. 19. Tri-p-tolyl-p-anisylsilane

[Silane] = [Bromine] = 0.000670 M

Time (min)	0	$1\frac{3}{4}$	$2\frac{3}{4}$	$4\frac{3}{4}$
Titre	6.732	6.390	6.088	5.774
Time (min)	$7\frac{3}{4}$	$10\frac{3}{4}$	$27\frac{3}{4}$	$46\frac{3}{4}$
Titre	5.242	4.830	3.212	2.554

(Duplicate)

Time (min)	0	$1\frac{3}{4}$	$4\frac{3}{4}$	$7\frac{3}{4}$	$11\frac{3}{4}$
Titre	6.732	6.424	5.626	5.134	4.654
Time (min)	$14\frac{3}{4}$	$17\frac{3}{4}$	$23\frac{3}{4}$	$31\frac{3}{4}$	$40\frac{3}{4}$
Titre	4.318	4.000	3.632	3.176	2.610

Run No. 20. Tri-(p-trimethylsilylmethylphenyl)-p-anisylsilane $[\text{Silane}] = [\text{Bromine}] = 0.000670 \text{ M}$ 

Time (min)	0	1m. 5s.	$1\frac{3}{4}$	$2\frac{3}{4}$	$4\frac{3}{4}$
Titre	6.732	6.314	5.812	5.510	5.010
Time (min)	$13\frac{3}{4}$	$19\frac{3}{4}$	$31\frac{3}{4}$	$56\frac{3}{4}$	$70\frac{3}{4}$
Titre	3.256	2.280	1.528	0.978	0.844

(Duplicate)

Time (min)	0	$\frac{3}{4}$	$1\frac{3}{4}$	$3\frac{3}{4}$
Titre	6.732	6.494	5.880	5.002
Time (min)	$6\frac{3}{4}$	$15\frac{3}{4}$	$22\frac{3}{4}$	$62\frac{3}{4}$
Titre	4.400	2.970	1.896	0.854

Relative rate Tri-(p-trimethylsilylmethylphenyl)-p-anisylsilane

Tri-p-tolyl-p-anisylsilane

Reaction %	10	20	30	40	50	60
	2.0	2.0	2.0	2.1	2.2	2.4

Run No. 21. Tri-m-tolyl-p-anisylsilane $[\text{Silane}] = [\text{Bromine}] = 0.000670 \text{ M}$ 

Time (min)	0	$1\frac{3}{4}$	$4\frac{3}{4}$	$7\frac{3}{4}$	$11\frac{3}{4}$
Titre	6.732	6.354	6.214	5.910	5.686
Time (min)	$19\frac{3}{4}$	$29\frac{3}{4}$	$40\frac{3}{4}$	$69\frac{3}{4}$	$99\frac{3}{4}$
Titre	4.972	4.642	3.956	3.124	2.374

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(Duplicate)

Time (min)	0	$2\frac{3}{4}$	$5\frac{3}{4}$	$8\frac{3}{4}$	$19\frac{3}{4}$
Titre	6.732	6.270	6.082	5.718	5.040
Time (min)	$30\frac{3}{4}$	$41\frac{3}{4}$	$62\frac{3}{4}$	$98\frac{3}{4}$	
Titre	4.470	2.896	3.274	2.566	

Relative rate Tri-m-tolyl-p-anisylsilane  
Tri-p-tolyl-p-anisylsilane

Reaction %	10	20	30	40	50	60
	0.48	0.47	0.44	0.45	0.46	0.45

Average = 0.46Run No. 22. Tri-p-tolyl-p-anisylsilane[Silane] = [Bromine] = 0.000670 M

Time (min)	0	$1\frac{3}{4}$	$2\frac{3}{4}$	$5\frac{3}{4}$	$9\frac{3}{4}$
Titre	6.728	6.326	6.086	5.522	5.002
Time (min)	$13\frac{3}{4}$	$26\frac{3}{4}$	$35\frac{3}{4}$	$46\frac{3}{4}$	$65\frac{3}{4}$
Titre	4.448	3.358	2.826	2.492	1.802

(Duplicate)

Time (min)	0	$1\frac{3}{4}$	$3\frac{3}{4}$	$6\frac{3}{4}$	$12\frac{3}{4}$
Titre	6.728	6.354	5.750	5.252	4.462
Time (min)	$17\frac{3}{4}$	$25\frac{3}{4}$	$38\frac{3}{4}$	$52\frac{3}{4}$	$74\frac{3}{4}$
Titre	4.006	3.366	2.724	2.200	1.820

Run No. 23. Tri-m-tolyl-p-anisylsilane[Silane] = [Bromine] = 0.000670 M

Time (min)	0	1m. 5s.	$2\frac{3}{4}$	$4\frac{3}{4}$
Titre	6.728	6.502	6.352	6.232
Time (min)	$7\frac{3}{4}$	$11\frac{3}{4}$	$19\frac{3}{4}$	$26\frac{3}{4}$
Titre	5.916	5.636	5.088	4.600
Time (min)	$38\frac{3}{4}$	$56\frac{3}{4}$	$71\frac{3}{4}$	
Titre	4.008	3.454	3.076	

(Duplicate)

Time (min)	0	$1\frac{3}{4}$	$2\frac{3}{4}$	$4\frac{3}{4}$
Titre	8.728	6.498	6.388	6.236
Time (min)	$8\frac{3}{4}$	$16\frac{3}{4}$	$20\frac{3}{4}$	$31\frac{1}{4}$
Titre	5.836	5.272	5.008	4.448
Time (min)	$38\frac{3}{4}$	$45\frac{3}{4}$	$68\frac{3}{4}$	$82\frac{3}{4}$
Titre	4.076	3.822	3.174	2.866

Relative rate Tri-m-tolyl-p-anisylsilane

Tri-p-tolyl-p-anisylsilane

Reaction %	10	20	30	40	50	60
	0.46	0.45	0.45	0.46	0.44	0.43

Average = 0.45Run No. 24. Diphenylmethyl-p-anisylsilane

[Silane] = [Bromine] = 0.000588 M

Time (min)	0	$\frac{3}{4}$	$1\frac{3}{4}$	$2\frac{3}{4}$	$5\frac{3}{4}$
Titre	5.734	4.886	4.230	3.640	3.004
Time (min)	$8\frac{3}{4}$	$15\frac{3}{4}$	$23\frac{3}{4}$	$29\frac{3}{4}$	$43\frac{3}{4}$
Titre	2.512	1.770	1.366	1.88	0.842

(Duplicate)

Time (min)	0	$\frac{3}{4}$	$1\frac{3}{4}$	$4\frac{3}{4}$	$7\frac{3}{4}$
Titre	5.734	4.992	4.208	3.166	2.572
Time (min)	$11\frac{3}{4}$	$18\frac{3}{4}$	$26\frac{1}{4}$	$32\frac{3}{4}$	$42\frac{3}{4}$
Titre	2.128	1.602	1.326	1.112	0.878

Run No. 25. Tribenzyl-p-anisylsilane

[Silane] = [Bromine] = 0.000588 M

Time (min)	0	$\frac{3}{4}$	$1\frac{3}{4}$	$2\frac{3}{4}$	$6\frac{3}{4}$
Titre	5.734	4.362	3.548	3.110	1.968
Time (min)	$11\frac{3}{4}$	$15\frac{3}{4}$	$22\frac{3}{4}$	$29\frac{1}{4}$	$36\frac{1}{4}$
Titre	1.536	1.290	1.020	0.862	0.706

(Duplicate)

Time (min)	0	$\frac{3}{4}$	$2\frac{3}{4}$	$4\frac{3}{4}$	5m. 55s.
Titre	5.734	4.316	3.014	2.372	2.072
Time (min)	$8\frac{3}{4}$	$11\frac{3}{4}$	$17\frac{3}{4}$	$25\frac{3}{4}$	$30\frac{3}{4}$
Titre	1.770	1.578	1.238	0.948	0.870

Relative rate Tribenzyl-p-anisylsilane

Diphenylmethyl-p-anisylsilane

Reaction %	20	30	40	50	60	70
	1.9	2.0	1.9	2.0	2.0	1.9

Average = 2.0Run No. 26. Triphenyl-p-anisylsilane

[Silane] = [Bromine] = 0.000680 M

Time (min)	0	10	35	57	69
Titre	4.635	4.054	3.330	2.834	2.630
Time (min)	96	130	162	194	241
Titre	2.212	1.928	1.696	1.554	1.324

(Duplicate)

Time (min)	0	7	17	29	56
Titre	4.635	4.238	3.846	3.444	2.860
Time (min)	90	128	155	214	
Titre	2.306	1.932	1.726	1.398	

Run No. 27. Tri-m-tolyl-p-anisylsilane

[Silane] = [Bromine] = 0.000680 M

Time (min)	0	7 $\frac{1}{2}$	22 $\frac{1}{4}$	33	46 $\frac{1}{2}$
Titre	4.635	4.216	3.394	3.088	2.714
Time (min)	59	73 $\frac{1}{2}$	90 $\frac{1}{2}$	123	158 $\frac{1}{2}$
Titre	2.388	2.252	1.978	1.666	1.488

(Duplicate)

Time (min)	0	11	23	34	47 $\frac{1}{2}$
Titre	4.635	3.926	3.394	3.064	2.640
Time	63 $\frac{1}{2}$	81 $\frac{1}{2}$	113	148	
Titre	2.346	2.082	1.742	1.456	

Relative rate Tri-m-tolyl-p-anisylsilane  
Triphenyl-p-anisylsilane

Reaction %	10	20	30	40	50	60
	1.4	1.4	1.4	1.4	1.4	1.4

Average = 1.4Run No. 28. Tri-p-tolyl-p-anisylsilane

[Silane] = [Bromine] = 0.000680 M

Time	0	2m. 4s.	6m. 8s.	11m. 2s.	16m. 16s.
Titre	4.635	4.344	3.832	3.360	2.926
Time	24m. 56s.	34m. 51s.	45m. 50s.	59m. 34s.	80m. 38s.
Titre	2.440	2.036	1.742	1.452	1.238

(Duplicate)

Time	0	2m. 15s.	7m. 3s.	11m. 48s.	20m. 18s.
Titre	4.635	4.282	3.600	3.192	2.662
Time	26m. 47s.	36m. 18s.	44m. 48s.	56m. 48s.	70m. 55s.
Titre	2.310	1.966	1.766	1.478	1.370

Relative rate Tri-p-tolyl-p-anisylsilaneTriphenyl-p-anisylsilane

Reaction %	10	20	30	40	50	60
	3.2	3.3	3.3	3.3	3.3	3.4

Average = 3.3

Run No. 29. Tetra-p-anisylsilane

[Silane] = [Bromine] = 0.000372 M

Time (sec)	0	5	10	15	20
Titre	3.634	3.594	3.398	3.316	3.214
Time (sec)	25	30	55	75	165
Titre	3.096	3.050	2.944	2.764	2.174

(Duplicate)

Time (sec)	0	5	10	15	20	25
Titre	3.634	3.566	3.396	3.280	3.196	3.116
Time (sec)	30	55	75			
Titre	3.090	2.950	2.720			

Run No. 30. Chloromethyldimethyl-p-anisylsilane

[Silane] = [Bromine] = 0.000372 M

Time (sec)	0	10	15	25	35
Titre	3.634	3.278	3.100	2.840	2.644
Time (sec)	45	55	85	135	255
Titre	2.548	2.424	2.122	1.756	1.296

(Duplicate)

Time (sec)	0	10	15	25
Titre	3.634	3.254	3.006	2.860
Time (sec)	35	45	65	105
Titre	2.640	2.530	2.324	1.970
Time (sec)	165	285	435	
Titre	1.674	1.300	0.890	

Relative rate Tetra-p-anisylsilane

Chloromethyl-p-anisylsilane

Reaction %	5	10	15
	0.56	0.57	0.53

Average = 0.55Run No. 31. Tri-p-tolyl-p-anisylsilane

[Silane] = 0.000617 M [Bromine] = 0.000666 M

Time (min)	0	$1\frac{3}{4}$	$12\frac{3}{4}$	$20\frac{1}{4}$
Titre	9.066	8.644	6.390	5.498
Time (min)	$34\frac{3}{4}$	$47\frac{3}{4}$	$56\frac{3}{4}$	$72\frac{1}{4}$
Titre	4.282	3.620	3.310	2.804

(Duplicate)

Time (min)	0	$1\frac{3}{4}$	$10\frac{3}{4}$	$18\frac{1}{4}$	$24\frac{3}{4}$
Titre	9.066	8.650	6.668	5.834	5.002
Time (min)	$41\frac{3}{4}$	$58\frac{1}{4}$	$79\frac{1}{4}$	$90\frac{3}{4}$	
Titre	3.812	3.292	2.562	2.358	

Run No. 32. Tri-(p-trimethylsilylmethylphenyl)-p-anisylsilane

[Silane] = 0.000617 M [Bromine] = 0.000666 M

Time (min)	0	$2\frac{3}{4}$	$4\frac{3}{4}$	$8\frac{3}{4}$	$11\frac{3}{4}$
Titre	9.066	7.810	6.916	5.530	4.572
Time (min)	$18\frac{1}{4}$	$23\frac{1}{4}$	$29\frac{3}{4}$	$39\frac{3}{4}$	
Titre	3.182	2.522	1.684	1.354	

(Duplicate)

Time (min)	0	$\frac{3}{4}$	$1\frac{3}{4}$	$3\frac{3}{4}$
Titre	9.066	8.430	7.890	7.234
Time (min)	$5\frac{3}{4}$	$10\frac{1}{4}$	$12\frac{3}{4}$	$28\frac{3}{4}$
Titre	6.322	5.098	4.300	1.714



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Relative rate Tri-(p-trimethylsilylmethylphenyl)-p-anisylsilane  
Tri-p-tolyl-p-anisylsilane

Reaction %	10	20	30	40	50	60	70
	2.0	2.1	2.2	2.4	2.6	2.9	3.5

Run No. 33. Dimethylethylaminomethyl-p-anisylsilane

[Silane] = 0.000617 M      [Bromine] = 0.000666 M

Time (min)	0	$\frac{1}{4}$	$1\frac{3}{4}$	$3\frac{1}{4}$
Titre	9.066	7.904	6.096	5.416
Time (min)	$5\frac{3}{4}$	$7\frac{1}{4}$	$10\frac{3}{4}$	$16\frac{3}{4}$
Titre	4.298	3.774	2.840	2.222

(Duplicate)

Time (min)	0	$\frac{1}{4}$	$1\frac{3}{4}$	$2\frac{3}{4}$	$3\frac{3}{4}$
Titre	9.066	7.910	6.414	5.562	5.072
Time	$5\frac{1}{4}$	$5\frac{3}{4}$	$7\frac{3}{4}$	$10\frac{1}{4}$	$15\frac{3}{4}$
Titre	4.288	4.160	3.614	3.012	2.330

Relative rate Dimethylethylaminomethyl-p-anisylsilane  
Tri-p-tolyl-p-anisylsilane

Reaction %	10	20	30	40	50	60	70
	20.0	12.0	8.7	6.9	6.3	6.1	6.2

Run No. 34. Triphenyl-p-anisylsilane

[Silane] = 0.000832 M      [Bromine] = 0.000899 M

Time (min)	0	7	18	$32\frac{1}{2}$	49
Titre	6.120	5.526	4.732	4.082	3.436
Time (min)	60	83	126	$159\frac{1}{2}$	
Titre	3.140	2.660	2.094	1.866	

(Duplicate)

Time (min)	0	2 $\frac{1}{2}$	13	29	46
Titre	6.120	5.832	5.066	4.154	3.580
Time (min)	62 $\frac{1}{2}$	96	118	143	181
Titre	3.110	2.486	2.208	1.910	1.508

Run No. 35. Tri-p-tolyl-p-anisylsilane

[Silane] = 0.000832 M      [Bromine] = 0.000899 M

Time	0	1m. 51s.	6m. 16s.	10m. 57s.	15m. 18s.
Titre	6.120	5.560	4.616	3.952	3.452
Time	20m. 26s.	29m. 8s.	36m. 44s.	48m. 46s.	63m. 10s.
Titre	3.048	2.544	2.082	1.746	1.462

(Duplicate)

Time	0	1m. 40s.	5m. 44s.	10m. 16s.	14m. 52s.
Titre	6.120	5.656	4.724	4.026	3.484
Time	21m. 13s.	29m. 28s.	41m. 57s.	50m. 3s.	65m. 8s.
Titre	2.966	2.484	1.908	1.640	1.426

Relative rate    Tri-p-tolyl-p-anisylsilane  
                             Triphenyl-p-anisylsilane

Reaction %	10	20	30	40	50	60	70
	3.5	3.4	3.4	3.2	3.2	3.3	3.5

Average = 3.4

Run No. 36. Tri-m-tolyl-p-anisylsilane

[Silane] = [Bromine] = 0.000921 M

Time	0	6m. 15s.	11m. 36s.	17m. 41s.	27m. 8s.
Titre	4.492	3.970	3.522	3.202	2.818
Time	40m. 20s.	55m. 20s.	73m. 9s.	90m. 8s.	123m. 27s.
Titre	2.326	2.038	1.692	1.538	1.222

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(Duplicate)

Time	0	4m. 45s.	10m. 50s.	19m. 10s.	31m. 3s.
Titre	4.492	4.084	3.568	3.112	2.592
Time	43m. 55s.	57m. 30s.	73m. 55s.	89m. 5s.	106m. 34s.
Titre	2.222	1.920	1.638	1.490	1.310

Run No. 37. Chloromethyldimethyl-p-tolylsilane

[Silane] = 0.00145 M      [Bromine] = 0.00156 M

Time (min)	0	98	160	215	312
Titre	19.026	16.266	14.874	13.978	12.780
Time (min)	370	498	622	730	
Titre	12.110	10.608	9.676	8.900	

(Duplicate)

Time (min)	0	90	155	207	305
Titre	19.026	16.310	14.966	14.100	12.830
Time (min)	365	495	615	725	
Titre	12.160	10.540	9.800	8.978	

Run No. 38. Tri-m-tolyl-p-anisylsilane

[Silane] = 0.00145 M      [Bromine] = 0.00156 M

Time (min)	0	2	12	22½	35
Titre	19.026	17.330	12.132	10.038	8.002
Time (min)	46	57	75	180	
Titre	6.924	6.270	5.468	3.010	

(Duplicate)

Time (min)	0	8	18	27
Titre	19.026	12.552	10.788	9.056
Time (min)	41	53	70	175
Titre	7.408	6.526	5.640	3.044

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Relative rate Chloromethyldimethyl-p-tolylsilaneTri-m-tolyl-p-anisylsilane

Reaction %	10	20	30	40	50
	0.035	0.035	0.035	0.035	0.036

Average = 0.035Run No. 39. Dimethylphenyl-p-anisylsilane

[Silane] = [Bromine] = 0.000406 M

Time	0	20s.	30s.	45s.	75s.
Titre	3.960	2.274	2.072	1.646	1.278
Time	1m. 45s.	2m. 45s.	3m. 45s.	10m. 45s.	
Titre	1.080	0.834	0.758	0.574	

(Duplicate)

Time	0	20s.	30s.	45s.	1m. 15s.
Titre	3.960	2.216	1.918	1.620	1.238
Time	1m. 45s.	2m. 45s.	4m. 45s.	5m. 30s.	9m. 15s.
Titre	1.050	0.836	0.726	0.612	0.500

Run No. 40. Tribenzyl-p-anisylsilane

[Silane] = [Bromine] = 0.000406 M

Time	0	$\frac{3}{4}$	$1\frac{3}{4}$	$2\frac{3}{4}$	$4\frac{3}{4}$
Titre	3.960	3.330	2.778	2.518	2.152
Time	$7\frac{3}{4}$	$10\frac{3}{4}$	$16\frac{3}{4}$	$32\frac{3}{4}$	
Titre	1.804	1.518	1.202	0.896	

(Duplicate)

Time (min)	0	$\frac{3}{4}$	$1\frac{3}{4}$	$2\frac{3}{4}$	$3\frac{3}{4}$
Titre	3.960	3.408	2.900	2.586	2.400
Time (min)	$5\frac{3}{4}$	$9\frac{3}{4}$	$15\frac{3}{4}$	$24\frac{3}{4}$	$34\frac{3}{4}$
Titre	2.058	1.618	1.240	1.020	0.902

Relative rate   Dimethylphenyl-p-anisylsilane  
                             Tribenzyl-p-anisylsilane

Reaction %	30	40	50	60	70
	11.0	12.0	12.0	12.0	12.0

Average = 12.0

Run No. 41. Tri-m-chlorophenyl-p-anisylsilane

[Silane] = [Bromine] = 0.000841 M

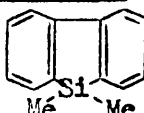
Time (min)	0	68	157	244	347
Titre	4.104	3.930	3.780	3.598	3.414
Time (min)	438	536	606	717	
Titre	3.276	3.138	3.082	2.948	

(Duplicate)

Time (min)	0	53	133	230	423
Titre	4.104	3.994	3.838	3.610	3.294
Time (min)	510	575	639	702	
Titre	3.202	3.110	3.042	2.962	

Runs 1-16 and 22 and 23 were carried out in the second batch of solvent.

Runs 17-21 and 24-41 were carried out in the first batch of solvent.

Cyclic organosilicon compoundsRun No.1    5,5-Dimethyldibenzosilole

[Br<sub>2</sub>] = 0.000899 M.    [Silane] = 0.000832 M

Time (hours)	0	20	44	71	140	165	194	308
Titre	6.120	5.152	4.314	3.844	3.056	2.798	2.516	2.022

(Duplicate)

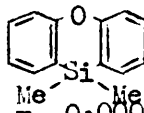
Time (hours)	0	18½	42	69	138	163	192	308
Titre	6.120	5.202	4.346	3.806	3.104	2.796	2.586	2.004

Relative rate    5,5-dimethyldibenzosilole

Triphenyl-p-anisylsilane

Reaction %	10	20	30	40	50
	0.0090	0.0094	0.0096	0.0088	0.0078

Average for first 40% = 0.0092 ± 0.0004

Run No.2    10,10-Dimethylphenoxasilin

[Br<sub>2</sub>] = 0.000899 M    [Silane] = 0.000832 M

Time	0	30	99	163	231	304	361
Titre	6.120	5.806	5.312	4.836	4.358	3.972	3.640
Time	449	557	640				
Titre	3.128	2.742	2.436				

(Duplicate)

Time	0	42	108	173	241	314	372
Titre	6.120	5.672	5.212	4.670	4.276	3.850	3.564
Time	439	546					
Titre	3.192	2.800					

Relative rate    10,10-Dimethylphenoxasilin

Triphenyl-p-anisylsilane

Reaction %	10	20	30	40
	0.104	0.106	0.112	0.119
<u>Average = 0.110</u> $\pm$ 0.005				

## CHAPTER XI

### Experimental Technique for the Kinetic Investigation of Cleavage of the C - Si bond by Mercuric Acetate

Cleavage of silanes by mercuric acetate in acetic acid was followed by the titration of the mercuric ions with potassium thiocyanate in the presence of dilute nitric acid and using ferric alum solution as indicator.

As observed by Kolthoff and Stenger<sup>98</sup> a poor end point was observed in this titration, a colour change to light brown being recorded over 0.2 ml. of thiocyanate solution. For the more concentrated solutions ( $> 0.000869M$ ) it was found that an electrical method could be used for following the titrations.

Using the same electrical circuit as that for titration of bromine, it was observed that as potassium thiocyanate solution was added a deflection occurred of the galvanometer spot. The mercuric acetate solution used for cleavage was first standardised, the end point being determined to a specific colour; the galvanometer deflection to give this colour change was recorded and all subsequent titration readings in the run were taken using this particular deflection. For comparison of runs the same galvanometer deflection was used throughout. This proved to be an easy and accurate method of following kinetic runs.

Unfortunately with dilute solutions this method was no longer sufficiently accurate and here the end point was taken as a particular colour change. This proved a difficult process but the end point could be ascertained within  $\pm 0.075$  ml. Time versus titre was plotted and the best curve drawn through the points.



### Apparatus

This was the same as that described in Chapter X for bromine cleavage. However, in this case a 2 l. stock of potassium thiocyanate solution was connected to the micro-burette.

### Preparation of materials

#### (a) Potassium thiocyanate solution

This was prepared from "Analar" potassium thiocyanate and deionised water. It was kept in brown Winchesters and standardised at regular intervals with silver nitrate solutions prepared from dried solid silver nitrate. For each titration 30 ml. of 10% nitric acid, 70 ml. of water and 1 ml. of ferric alum indicator was added.

#### (b) Ferric alum indicator

The indicator was a cold saturated solution consisting of about 400 g. of "Analar" ferric ammonium sulphate to 1 litre of water and a little concentrated nitric acid.

Thermostat and pipettes were those described in Chapter X. Weighings were carried out as in Chapter X but it was necessary to use larger weighing bottles.

#### (c) Acetic acid solvent.

The 20 wt % aqueous acetic acid was prepared by adding the calculated amount of water to the 1.5 wt % acetic acid.

#### (d) Mercuric acetate

"May and Baker" reagent grade was used without further purification.

### Method of following kinetic runs

A fresh solution of mercuric acetate in aqueous acetic acid (20 wt %)

was placed in the 500 ml. round bottomed flask in the thermostat bath allowed to reach bath temperature and 5 ml. standardised against potassium thiocyanate solution. Solutions of organosilanes were then made up of the same concentration as that of the mercuric acetate solution using the same procedure as that described for bromine cleavage. For most of the triaryl-*p*-anisylsilane it was found that because of their low solubility in the solvent, it was more convenient to dissolve ca 95% of the silane before standardisation of the mercuric acetic solution. Usually it took about 1 week for the silane to dissolve. Runs were slow (completed in a day) or very slow (25% completed in about 10 days). For both sets of runs the procedure for slow and very slow runs for bromine cleavage was used (see page 128).

#### Calculation of Results.

Relative rate figures were obtained by carrying out two runs (in duplicate) with different organosilanes at the same concentration. The times for disappearance of specific fractions of mercuric acetate were compared directly. The titre at 100% cleavage only falls to half the initial figure as titration of the mercuric ions obtained by hydrolysis of the aromatic mercury compound also occurs.

#### Sources of error.

##### (a) Reaction of mercuric acetate with solvent.

At the temperature at which runs were carried out, no reaction occurred between mercuric acetate and 20 wt % aqueous acetic acid after seven days. In an attempt to carry out runs at 75°C it was found that a fall in titre of some 25% was observed after 24 hours for a solution of mercuric acetate in 10 wt % aqueous acetic acid as observed

by Brown and McGary<sup>60</sup> and was therefore not used.

(b) Titration errors

Because of the very dilute solutions used the end point was difficult to establish. For the very dilute solutions ( $< 0.000896M$ ) the end point could only be determined to  $\pm 0.1$  ml; for the rest the end point was determined to  $\pm 0.04$  ml.

Reproducibility.

As the titration errors were considerable the runs were reproducible only to 95%.

Accuracy.

In some cases the relative rate varied as much as 10% throughout a run but in the majority, the variation was not greater than 5%. These are large errors but general conclusions may be made.

### Tabulation of Kinetic Results

The runs are reported in terms of the volume ( in ml.) of potassium thiocyanate solution ( labelled "titre"), equivalent to the mercuric ion concentration remaining at a specified time (in mins. unless otherwise stated). These titration figures are equivalent to the  $\text{Hg}^{++}$  ion concentration in a measured sample of the solution (5.0 ml.).

All runs were carried out in duplicate, and each run and its duplicate were plotted on a time- titre graph and the times for removal of various fractions of the mercuric ions were obtained from a smoothed curve through the points.

The runs were carried out in 20 wt % aqueous acetic acid using the apparatus described at a temperature of  $25.00^\circ \pm 0.02^\circ$ .

For each run, the concentrations of mercuric acetate and silane before mixing the solutions are given.

Run No.1 Triphenyl-p-anisylsilane[Silane] = [Hg(OAc)<sub>2</sub>] = 0.000386 M.

Time (hours)	0	68	114	163	196
Titre	6.550	6.252	6.078	5.934	5.866
	240	337	401		
	5.782	5.700	5.606		

(Duplicate)

Time (hours)	0	48 <sup>1</sup> / <sub>2</sub>	98	130	162
Titre	6.550	6.344	6.080	6.034	5.968
	271	341			
	5.756	5.682			

Run No.2 Tri-p-tolyl-p-anisylsilane[Silane] = [Hg(OAc)<sub>2</sub>] = 0.000386 M.

Time (hours)	0	18	44	67	124	167
Titre	6.550	6.308	6.042	5.896	5.690	5.648
	266	331				
	5.460	5.352				

(Duplicate)

Time (hours)	0	18 <sup>1</sup> / <sub>2</sub>	44 <sup>1</sup> / <sub>2</sub>	89	124	167
Titre	6.550	6.328	6.080	5.816	5.700	5.622
	265	331				
	5.434	5.320				

Relative rate Tri-p-tolyl-p-anisylsilane

			<u>Triphenyl-p-anisylsilane</u>	
Reaction %	16	20	24	28
	2.65	2.50	2.49	2.46
	<u>Average = 2.53 ± 0.06</u>			

Run No.3 Tri-m-tolyl p-anisylsilane[Silane] = [Hg(OAc)<sub>2</sub>] = 0.000386 M.

Time (hours)	0	21	46	94	126
Titre	6.550	6.394	6.260	6.010	5.838
	170	268	334		
	5.762	5.634	5.552		

Run No.4 Tri-p-chlorophenyl-p-anisylsilane

$$[\text{Silane}] = [\text{Hg}(\text{OAc})_2] = 0.000386\text{M.}$$

Time(hours)	0	72	118	168	245	340	416
Titre	6.550	6.392	6.296	6.178	6.082	5.926	5.840

(Duplicate)

Time(hours)	0	72	118	168	245	340	416
Titre	6.550	6.388	6.300	6.162	6.096	5.966	5.882

Relative rate Tri-p-chlorophenyl-p-anisylsilaneTriphenyl-p-anisylsilane

Reaction %	8	12	16	20	24
	0.499	0.495	0.484	0.496	0.504

$$\text{Average} = 0.495 \pm 0.004$$

Run No.5 Dimethylphenyl-p-anisylsilane

$$[\text{Silane}] = [\text{Hg}(\text{OAc})_2] = 0.000386\text{M}$$

Time	0	64	155	281	517	1263	1623
Titre	6.550	6.270	5.932	5.662	5.488	5.102	4.942

Duplicate

Time	0	57	148	271	521	1257	1381	1616
Titre	6.550	6.250	5.968	5.732	5.426	5.096	5.024	4.992

Relative rate Dimethylphenyl-p-anisylsilaneTriphenyl-p-anisylsilane

Reaction %	12	16	20	24
	69.0	66.5	70.3	69.0

$$\text{Average} = 68.7 \pm 1.1$$

Run No.6 Trimethyl-p-anisylsilane

$$[\text{Silane}] = [\text{Hg}(\text{OAc})_2] = 0.000386\text{M}$$

Time	0	1' 25"	4' 30"	14' 30"	29	84	194
Titre	6.550	6.478	6.138	6.058	5.828	5.636	5.442

424      1144  
5.138    4.330

Duplicate

Time	0	53	100	136	232	277	317	362
Titre	6.550	5.780	5.648	5.518	5.352	5.306	5.246	5.182

Relative rate    Trimethyl-p-anisylsilane

Dimethyl-phenyl-p-anisylsilane

Reaction %	32	36	40	44
	2.95	2.82	2.72	2.78

Average = 2.82 ± 0.07

Run No.7    Dimethyl-phenyl-p-anisylsilane

[Silane] = [Hg(OAc)<sub>2</sub>] = 0.000869M

Time	0	15	50	77	125	202	315	600	708
Titre	14.750	12.284	11.542	11.408	11.124	10.800	10.456	10.032	9.890

Duplicate

Time	0	21	55	90	133	260	460	690
Titre	14.750	12.250	11.574	11.342	11.074	10.648	10.216	9.916

Run No.8    Diphenylmethyl-p-anisylsilane

[Silane] = [Hg(OAc)<sub>2</sub>] = 0.000869M

Time	0	87	137	260	330	450	607	730
Titre	14.750	13.134	12.698	12.330	11.986	11.802	11.536	11.444

Duplicate

Time	0	94	145	280	395	495	615	735
Titre	14.750	13.278	12.650	12.162	11.914	11.740	11.520	11.372

Relative rate    Dimethylphenyl-p-anisylsilane

Diphenylmethyl-p-anisylsilane

Reaction %	12	16	20	24	28
	10.2	10.1	10.1	9.95	10.6

Average = 10.24 ± 0.02

Run No.9 Tetra(p-anisyl)silane

$$[\text{Silane}] = [\text{Hg}(\text{OAc})_2] = 0.00194\text{M}$$

Time 0 2m.25s. 6m.55s. 13m.45s. 32 85 134

Titre 5.700 5.344 5.224 5.090 4.962 4.554 4.340

Time 218 362

Titre 4.158 4.068

Duplicate

Time 0 2 6m.30s. 17 33 93 207 336

Titre 5.700 5.404 5.230 5.112 4.952 4.470 4.186 3.934

Run No.10 Diphenylmethyl-p-anisylsilane

$$[\text{Silane}] = [\text{Hg}(\text{OAc})_2] = 0.00194\text{M}$$

Time 0 95 163 223 340 413 479 1180

Titre 5.700 4.874 4.536 4.424 4.190 4.056 4.006 3.250

Duplicate

Time 0 18 38 65 125 168 230 368

Titre 5.700 5.464 5.244 4.994 4.692 4.502 4.420 4.204

Time 418 484

Titre 4.088 4.026

Reaction %	Tetra(p-anisyl)silane				
	Diphenylmethyl-p-anisylsilane				
	10	20	30	40	50
	9.81	3.27	2.33	1.97	1.77

The relative rate was taken as that for the first 10% of reaction

Run No.11 Tri(m-chlorophenyl)-p-anisylsilane

$$[\text{Silane}] = [\text{Hg}(\text{OAc})_2] = 0.00194\text{M}$$

Time (hours) 0 29½ 43 74 91½ 114½ 141 168

Titre 5.700 5.344 5.150 4.886 4.774 4.640 4.498 4.356



Duplicate

Time (hours)	0	29 $\frac{1}{2}$	43	74	91 $\frac{1}{2}$	141	168
Titre	5.700	5.302	5.078	4.850	4.706	4.538	4.380
Relative rate	<u>Tri(m-chlorophenyl)-p-anisylsilane</u>						

	Diphenylmethyl-p-anisylsilane						
Reaction %	10	20	30	40			
	0.0197	0.0206	0.0209	0.0223			

$$\text{Average} = 0.0217 \pm 0.001$$

Run No.12 Tribenzyl-p-anisylsilane

$$[\text{Silane}] = [\text{Hg}(\text{OAc})_2] = 0.00194\text{M}$$

Time (hours)	0	2 $\frac{1}{2}$	6 $\frac{1}{2}$	10 $\frac{1}{2}$	23 $\frac{1}{2}$	32 $\frac{1}{2}$	54 $\frac{1}{2}$
Titre	5.700	5.398	5.030	4.946	4.768	4.700	4.460
Time(hours)	72	121 $\frac{1}{2}$	148 $\frac{1}{2}$				
Titre	4.424	4.224	4.174				

Duplicate

$$[\text{Silane}] = [\text{Hg}(\text{OAc})_2] = 0.00194\text{M}$$

Time(hours)	0	2 $\frac{1}{2}$	6 $\frac{1}{2}$	23 $\frac{1}{2}$	32 $\frac{1}{2}$	54 $\frac{1}{2}$	94 $\frac{1}{2}$
Titre	5.700	5.370	5.050	4.702	4.630	4.544	4.302
Time(hours)	121 $\frac{1}{2}$						
Titre	4.220						

Relative rate Tribenzyl-p-anisylsilane

	Diphenylmethyl-p-anisylsilane				
Reaction %	10	20	30	40	50
	0.152	0.162	0.100	0.061	0.043

The relative rate was taken as that for the first 20%

$$\text{Average} = 0.157 \pm 0.005$$

Run No.13 Diphenylmethyl-p-anisylsilane

$$[\text{Silane}] = [\text{Hg}(\text{OAc})_2] = 0.00479\text{M}$$

Time	0	66	121	229	323	461	581	706
Titre	3.600	3.140	2.940	2.598	2.362	2.280	2.112	2.060

Duplicate

Time	0	57	115	222	313	454	574	708
Titre	3.600	3.238	2.936	2.596	2.448	2.286	2.068	2.022

Run No.14 Dimethylchloromethyl-p-anisylsilane

$$[\text{Silane}] = [\text{Hg}(\text{OAc})_2] = 0.00479\text{M}$$

Time	0	4.45	8.40	26	132	280	365
Titre	3.600	2.958	2.880	2.734	2.514	2.366	2.252

Duplicate

Time	0	6	25	54	112	259	346	488	616
Titre	3.600	2.900	2.708	2.598	2.524	2.396	2.314	2.295	2.118

Relative rate Dimethylchloromethyl-p-anisylsilane

Diphenylmethyl-p-anisylsilane

Reaction %	30	40	50	60
	20.0	18.4	6.84	2.18

The relative rate was taken as that for 30% and 40%.

$$\text{Average} = 19.2 \pm 0.8$$

Run No. 15 p-tolyltrimethylsilane

$$[\text{Silane}] = [\text{Hg}(\text{OAc})_2] = 0.00479$$

Time	0	6	10.15	16.35	35.5	75.15	187	423
Titre	6.170	4.934	4.724	4.640	4.472	4.256	3.766	3.562

Duplicate

Time	0	1.30	5	13	24	47	79	153	381
Titre	6.170	5.276	5.074	6.746	4.648	4.464	4.254	3.830	3.574

Run No.16 p-tertiarybutylphenyltrimethylsilane

$$[\text{Silane}] = [\text{Hg}(\text{OAc})_2] = 0.00479 \text{ M}$$

Time	0	6	16	32	52	70	112	242
Titre	6.170	5.960	5.442	4.968	4.870	4.516	4.294	3.768

Duplicate

Time	0	4	14	25	36	52	216	280
Titre	6.170	5.956	5.486	5.096	4.840	4.692	3.872	3.770

Relative rate p-tolyltrimethylsilane

		<u>p-tertiarybutylbenzenetrimethylsilane</u>					
Reaction %	20	30	40	50	60	70	
	8.83	5.41	5.09	2.75	1.83	1.31	

The relative rate was taken as that for 30% = 5.41

Run No.17 Diphenylmethyl-p-anisylsilane

$$[\text{Silane}] = [\text{Hg}(\text{OAc})_2] = 0.00804 \text{ M}$$

Time	0	23	114	162	224	296	364	546
Titre	5.977	5.518	4.598	4.386	4.080	3.940	3.804	3.498

Duplicate

Time	0	13	39	106	154	216	288	354	537
Titre	5.977	5.700	5.406	6.704	4.356	4.142	3.922	3.764	3.526

Run No.18 Dimethyl(ethylaminomethyl)-p-anisylsilane

$$[\text{Silane}] = [\text{Hg}(\text{OAc})_2] = 0.00804 \text{ M}$$

Time	0	22	108	178	255	380	476	1256
Titre	5.977	5.584	5.260	5.020	4.864	4.658	4.590	4.022

Duplicate

Time	0	77 $\frac{1}{2}$	119	169	240	306	359
Titre	5.997	5.294	5.146	5.070	4.864	4.760	4.634
Time	456	1194					
Titre	4.590	4.068					

Relative rate	<u>Dimethyl(ethylaminomethyl)-p-anisylsilane</u>				<u>Diphenylmethyl-p-anisylsilane</u>		
Reaction %	10	20	30	40			
	0.712	0.585	0.390	0.326			

Relative rate was taken as that from 20 - 40%

Average = 0.434

Run No.19 Dimethylchloromethyl-p-anisylsilane

$[\text{Silane}] = [\text{Hg}(\text{OAc})_2] = 0.00804\text{M}$

Time	0	2	6 $\frac{1}{2}$	68	93	137	215	359
Titre	5.997	4.614	4.558	3.884	3.684	3.584	3.460	3.314

Duplicate

Time	0	2	50	74	105	141	196	339
Titre	5.997	4.620	3.940	3.796	3.664	3.536	3.452	3.326

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