SUPPORTING INFORMATION

Acid-catalyzed Dehydration of Naphthalene *cis*-1,2-dihydrodiols: Origin of Impaired Resonance Effect of 3-Substituents.

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Product analyses.

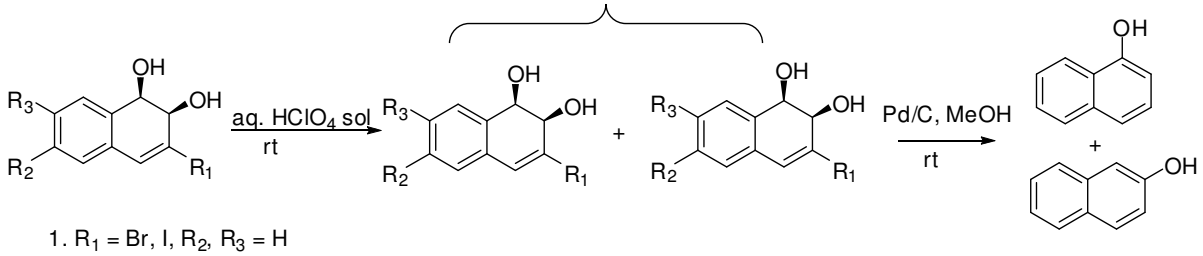
The procedures employed for analysing the products of reaction of substituted naphthalene dihydrodiols were described in the Experimental Section of the paper and for convenience repeated here. The reactants and products of the reactions are summarised in Scheme 1 and details of each analysis are given in Table S1. Two protocols were followed for the analyses.

Protocol A: A substituted dihydrodiol (7-10 mg) in acetonitrile or methanol was treated with dilute perchloric acid for sufficient time for the reaction to go to completion. The acid concentration, acetonitrile volume and reaction time are listed in Table S1. The reaction mixture was neutralized with saturated sodium bicarbonate followed by extraction with ethyl acetate and evaporation of the solvent under reduced pressure. A ^{1}H NMR spectrum of the un-purified reaction mixture was recorded.

In general the 1H NMR spectrum of the two products showed two sets of signals in the region of 6.5-8.5 ppm corresponding to substituted 1-and 2-naphthols. The ratio of the products was measured by integrating non overlapping peaks. The major product was isolated by preparative TLC and the structure was assigned by comparing with the literature or with authentic samples. If the 1H NMR spectrum of one of the expected products did not match that of the isolated product, the alternative structure could be inferred.

Protocol B: This method was applied to bromo and iodo substituted dihydrodiols. These diols were treated with aqueous perchloric acid and the unpurified products converted to simple 1-and 2- naphthols by reductive hydrogenation as shown in Scheme 1. The ratio of concentration of naphthols was determined by HPLC based on comparison with authentic samples

Scheme 1



1. R_1 = Br, I, R_2, R_3 = H
2. R_2 = Br, I, R_1, R_3 = H
3. R_3 = Br, I, R_1, R_2 = H

Product analyses are summarised in Table 1. Details for individual compounds are as follows.

6-MeO. Integration of the methyl peaks gave 98% 6-methoxy-2-naphthol identified by comparison with a reported spectrum.[1]

3-MeO. Integration of the methyl peaks gave 97% 3-methoxy-2-naphthol and 3% 3-methoxy-1-naphthol. The major product was isolated by preparative TLC. Its spectrum did not match that reported for 3-methoxy-1-naphthol[2] and was assigned as its 2-naphthol isomer.

6-Br. Integration of aromatic peaks gave 83% 6-bromo-1-naphthol (8.08 ppm) and 17% 6-bromo-2-naphthol (7.92 ppm). The products were separated by preparative TLC and the spectrum of the minor product identified by comparison with a report in the literature..[3]

3-Br. Reductive hydrogenation of the product mixture gave a mixture of 20% 1-naphthol and 80% 2-naphthol determined by HPLC.

7-Br. A proton NMR spectrum showed formation of only 7-bromo-1-naphthol identified by comparison with a known sample; however, the presence of <1% of the 2-naphthol isomer was detected by GC-MS. the identity of the principal product was ckonfirmed by comparison with the reported spectrum.[4]

7-Me. Integration of protons at 7.38 ppm (7-methyl-1-naphthol) and 7.53ppm (7-methyl-2-naphthol) gave 89% of the 1- and 11% of the 2-naphthol.

3-Me. A product ratio was determined by integration of methyl protons at 2.45 ppm (3-methyl-1-naphthol) and 2.42 ppm (3-methyl-2-naphthol) as 65% of the 1- and 35% of the 2-naphthol. Peaks for the 1-naphthol were identified by comparison with the reported spectrum.[5]

3-I. Reductive hydrogenation of the product mixture gave 30% of the 1- and 70% of the 2-naphthol determined by HPLC.

6-I. A product ratio was determined from integration of the NMR peaks of a mixture of products at 8.2 ppm (6-iodo-1-naphthol) and 8.1 ppm (6-iodo-2-naphthol) to give 80% of the 1- and 20% of the 2-naphthol. The major product was isolated and found not to match the known spectrum of 6-iodo-2-naphthol.[6] By elimination it was assigned as the isomeric 1-naphthol, with which its spectrum was consistent

7-I. A product ratio was determined from integration of peaks of a mixture of products at 8.6 ppm (7-iodo-1-naphthol) and 8.35 ppm (7-iodo-2-naphthol). The product ratio and identity of peaks were confirmed by HPLC analysis of the products of reductive hydrogenation (1- and 2-naphthols).

3-CN. A product ratio was measured from integration of peaks at 7.38 ppm (3-cyano-1-naphthol) and 7.53 ppm (3-cyano-2-naphthol) as 40% of the 1- and 60% of the 2-naphthol.

6-CN. A product ratio was measured from integration of peaks at 7.38 ppm (3-cyano-1-naphthol) and 7.82 ppm (6-cyano-2-naphthol) as 90% of the 1- and 10% of the 2-naphthol. The peaks for the minor component matched the known spectrum of 6-cyano-2-naphthol.[7]

3-F. A product ratio was measured from integration of peaks at 8.13 ppm (3-fluoro-1-naphthol) and 8.03 ppm (3-fluoro-2-naphthol) as 90% of the 1- and 10% of the 2-naphthol.

6-F. A product ratio was measured from integration of peaks at 7.81 ppm (6-fluoro-1-naphthol) and 7.75 ppm (6-fluoro-2-naphthol) as 25% of the 1- and 75% of the 2-naphthol. The principal product was isolated by preparative TLC and its spectrum found to match that reported in the literature.[8]

7-F. An NMR spectrum showed exclusive formation of 7-fluoro-1-naphthol as product with no measurable amount of its 2-naphthol isomer. Identification was based on comparison with a reported spectrum.[9]

Kinetic Measurements. For kinetic measurements stock solutions of concentration ~10^{-2}M substrate in acetonirile or methanol were prepared. Reactions were initiated by injection of between 5 and 25 μL of these solutions into a spectrophotometric cell containing 2 mL of aqueous perchloric acid. For each substrate a 'repetitive scan' of UV-Vis spectra was monitored throughout a reaction. The existence of tight isosbestic points confirmed hat reactants were directly converted to products without accumulation of an intermediate. To determine rate constants reactions were monitored at a single wavelength where a substantial change in absorbance occurred.. In all cases good first order kinetics were observed. Wavelengths of measurement for different substrates were 6-MeO, 229 nm; 3-MeO, 270 nm; 6-Br, 239 nm; 3-Br, 227 nm; 7-Br, 240 nm; 7-Me, 220 nm; 3-Me, 229 nm; 3-I, 281 nm; 6-I, 246 nm; 7-I, 246 nm; 3-CN, 235 nm; 6-CN, 245 nm; 3-F, 222 nm; 6-F, 222 nm; 7-F, 232 nm. To

determine rate constants absorbances A at time t were fitted to the expressions $A = a + be^{-kt}$ or $a + b(1 - e^{-kt})$ depending on whether theabsorbance decreased or in creased.

Table S1 Product analyses for the dehydration of 3- 6- and 7-substituted naphthalene *cis*-1,2-dihydrodoils in aqueous $HClO_4$ with 10% MeCN or MeOH (except as indicated) at 25 °C.

Reactant.	Protons integrated or HPLC analysis	2-naphthol %	1-naphthol %	Product isolated and/or identified[ref]
6-MeO	OCH_3	98	2	6-MeO-2-naphthol[1]
3-MeO	"	97	3	3-MeO-2-naphthol[2]
3-Br[a]	HPLC	80	20	1- and 2-naphthols
6-Br	aromatic (7.8 – 8.1 ppm)	17	83	6-Br-1-naphthol[3]
7-Br[b]	(GC-MS detection of 2-nap)	-	> 99	7-Br-1-naphthol[4]
7-Me	aromatic (7.38 and 7.53 ppm)	11	89	7-Me-1-naphthol
3-Me	CH_3 (2.45 and 2.42 ppm)	35	65	3-Me- 1- and 2-naphthols[5]
3-I[c]	HPLC	70	30	1- and 2-naphthols
6-I	aromatic (8.2 and 8.1 ppm)	20	80	1- and 2-naphthols[6]
7-I[d]	HPLC/aromatic (8.6 and 8.35 ppm)	10	90	1- and 2-naphthols
3-CN	aromatic (7.38 and 7.53 ppm)	60	40	3-CN-1- and 2-naphthols
6-CN[e]	aromatic (7.82 and 8.31 ppm)	10	90	6-CN-2-naphthol[6]
3-F[f]	aromatic (8.03 and 8.13 ppm)	10	90	3-F-2-Naphthol[7]
6-F	aromatic (7.75 and 7.81 ppm)	75	25	6-F-1-naphthol[8]
7-F[g]	aromatic (6.75 ppm)	-	>99	7-F-1-naphthol[9]

[a]Reaction for 24 h in 10 mL 3.0 M $HClO_4$ plus 3 mL MeOH. [b]Reaction for 12 h in 10 mL 1.0 M $HClO_4$ plus 4 mL MeCN. [c]Reaction for 12 h in 15 mL 2.0 M $HClO_4$ plus 5 Ml MeCN. [d]Reaction for 15 h in 10 mL 2.0 M $HClO_4$ plus 3 mL MeCN. [e]Reaction for 10 h in 10 mL 0.5 M $HClO_4$ plus 2 mL meOH or MeCN. [f]Reaction for 20 h in 10 mL 3.0 M $HClO_4$ plus 3 mL MeCN. [g]Reaction for 4 h in 7.0 mL 0.1 M $HClO_4$ plus 3 mL MeCN.

Table S2 First order rate constants for dehydration of 3-, 6- and 7-substituted naphthalene *cis*-1,2-dihhydrodiols to form 1- and 2-naphthols in aqueous $HClO_4$ at 25 °C[a]

$[HClO_4]$ (M)	k (s^{-1})	$[HClO_4]$ (M)	k (s^{-1})	$[HClO_4]$ (M)	k (s^{-1})	$[HClO_4]$ (M)	k (s^{-1})
6-OMe		**3-OMe**		**6-Br**		**3-Br**	
0.02	2.04 x 10^{-3}	0.20	4.45 x 10^{-4}	1.01	0.37x10^{-3}	1.01	0.83 x 10^{-5}
0.04	4.03	0.40	9.93	2.03	1.70	2.05	8.66
0.06	6.42	0.61	17.0	3.05	5.84	3.05	12.3
0.08	8.81	0.81	25.7	4.07	20.9	4.07	53.5
0.10	11.5	1.01	35.9			5.09	185
						5.90	670
7-Br		**7-Me**		**2-Me**		**3-I**	
0.20	9.33 x 10^{-5}	0.02	1.51x10^{-4}	0.20	0.51 x 10^{-3}	1.00	0.16 x 10^{-4}
0.40	21.3	0.04	2.96	0.40	1.19	2.01	0.68
0.61	37.6	0.06	4.71	0.61	2.05	3.00	2.83
0.94	95.1	0.08	6.46	0.94	3.16	4.00	11.4
2.03	399	1..00	8.18	1.01	4.53	5.00	51.3
6-I		**7-I**		**3-CN**		**6-CN**	
1.00	4.45 x 10^{-4}	1.00	0.90 x 10^{-3}	3.00	0.030 x10^{-4}	1.00	0.040 x 10^{-4}
2.00	9.93	2.00	4.65	4.00	0.150	2.00	0.21
3.00	17.0	3.00	17.1	5.00	0.76	3.00	0.84
4.00	25.6	4.00	62.3	7.15	35.2	4.00	3.44
						5.00	13.9
3-F		**6-F**		**7-F**			
2.00	0.71 x 10^{-4}	0.5	0.31 x 10^{-3}	0.50	1.26 x 10^{-3}		
3.00	1.23	1.0	0.92	0.75	2.36		
4.00	2.85	2.0	3.87	1.00	3.86		
5.00	41.3	3.0	15.2	2.00	16.7		

[a]Multipliers of rate constants in the table (10^{-x}) apply to the whole column of which they are at the head.

Table S3. Slopes m* of plots of log$k$/$[H^+]$ against X_o for dehydration of 3-, 6- and 7-substituted naphthalene *cis*-1,2-dihydrodiols in aqueous $HClO_4$ at 25°.

Substit	6-Br	3-Br	3-I	6-I	3-CN	6-CN	3-F	6-F
m*	1.38	1.24	1.47	1.42	1.38	1.46	1.35	1.67

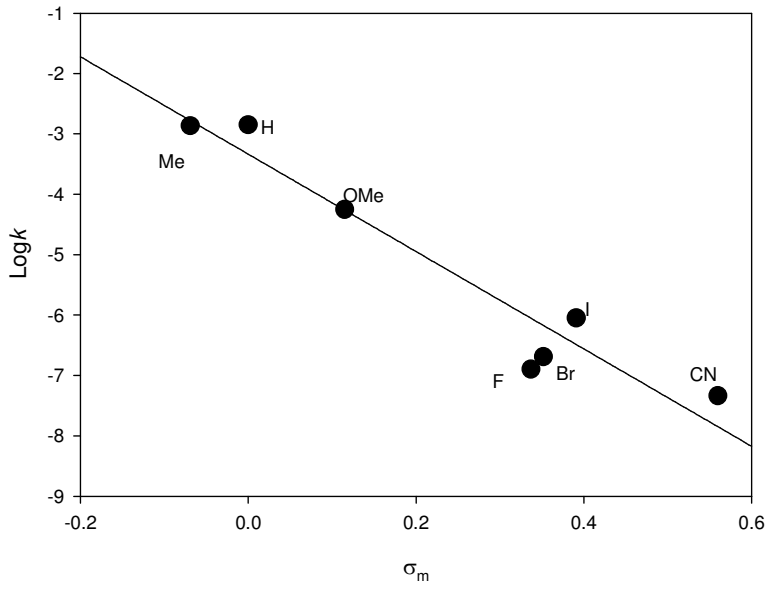


Figure S1. Plot of logs of rate constants for dehydration of 3-substituted naphthalene *cis* 1,2-dihydrodiols with loss of OH at the 2-position against σ_m in aqueous $HClO_4$ at 25 ^oC; log$k$ = -3.33 – 8.06σ_m

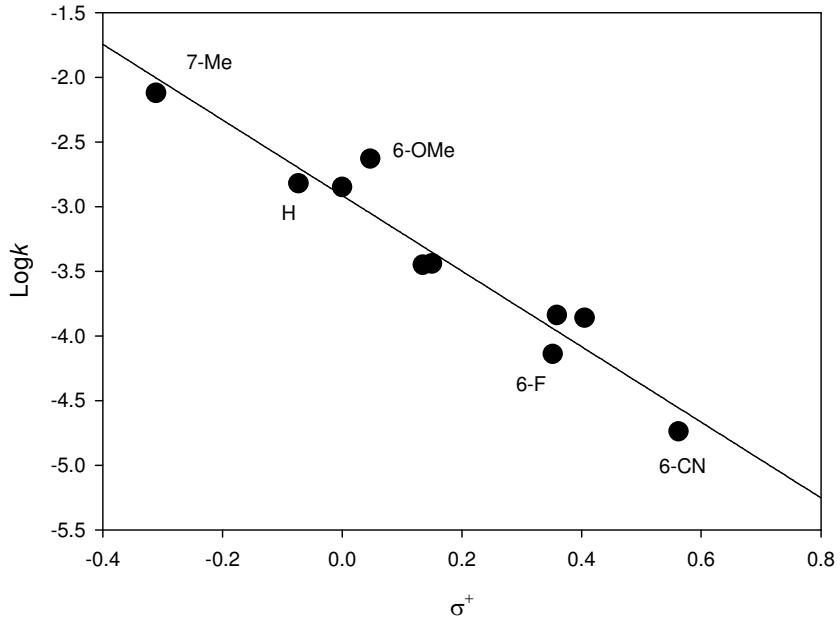


Figure S2. Plot of logs of rate constants for dehydration of 6- and 7-substituted naphthalene *cis* 1,2-dihydrodiols with loss of OH at the 1-position against σ^+ for 7-substituents and σ_m for 6-substituents in aqueous $HClO_4$ at 25 ^oC; log$k$ = -2.91 – 2.92σ

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