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AROMATIC REACTIVITY
LIII* ADDITIVITY OF SUBSTITUENT EFFECTS IN ACID CLEAVAGE OF DISUBSTITUTED PHENYLTRIMETHYLSILANES

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SUMMARY

Rates of cleavage in sulphuric acid/acetic acid mixtures at 50° have been measured for (2-methoxy-5-nitrophenyl)-, (2-methoxy-5-carboxyphenyl)-, (4-methyl-3-nitrophenyl)- and (2-methoxy-5-acetylphenyl)trimethylsilane. In the case of the first two compounds the reactivities are much as expected for additivity of the separate effects of the activating and deactivating substituents, but the 4-methyl-3-nitrophenyl compound is a little less reactive than expected, possibly because of some steric interaction between the adjacent methyl and nitro groups. The reactivity of the 2-methoxy-5-acetylphenyl compound indicates that the deactivating effect of an acetyl group on the *meta*-position is similar to that of a carboxy group.

INTRODUCTION

It has been suggested by de la Mare and Ridd that the principle of additivity of substituent effects tends to underestimate the ease of electrophilic aromatic substitution at a position which is activated by one substituent and strongly deactivated by another[2]. We previously measured the rates of cleavage (desilylation) of some (5-halo-2-methoxyphenyl)trimethylsilanes by aqueous methanolic perchloric acid, and concluded that the the combined effect of the halo and methoxy groups was very little, if at all, different from that expected for simple additivity of the separate effects of the two substituents[3]. We have now examined some disubstituted phenyltrimethylsilanes containing the more strongly deactivating nitro and carbonyl groups along with the activating methyl or methoxy group. The results indicate that any departure from additivity is small.

RESULTS AND DISCUSSION

Results on the cleavage by sulphuric acid/acetic acid/water mixtures are shown in Table 2, which gives the observed first-order rate constant, k, at the acid concentration specified, along with the rate, k_{rel}, relative to that for phenyltrimethyl-

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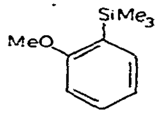
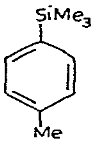
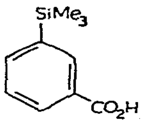
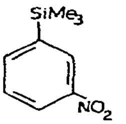
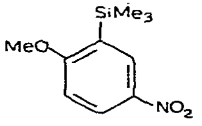
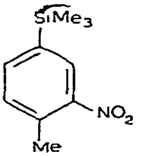
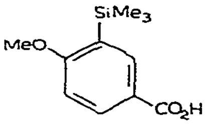
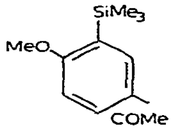
* For Part LII see ref. 1.

TABLE 1

OBSERVED AND CALCULATED VALUES OF k_{rel}[a]

				
k_{rel}	240	18	5.2×10^{-3}	3.7×10^{-4}
				
k_{rel}(obsd.)	6.6×10^{-2}	2.4×10^{-3}	2.3	2.4
k_{rel}(calcd.)	8.9×10^{-2}	6.7×10^{-3}	1.25	
k_{rel}(obsd.)/k_{rel}(calcd.)	0.75	0.36	1.8	

[a] Values from refs. 4 and 5, except that the value for *o*-OMe is derived from that (*viz.* 335) in aqueous methanolic perchloric acid[6] by use of the relationship[4] log k_{rel} ($H_2SO_4/CH_3COOH/H_2O$) = 0.96 log k_{rel} ($HClO_4/MeOH/H_2O$).

silane. In Table 1 the observed values of k_{rel} are compared with those calculated assuming additivity of substituents.

Probably the most significant result, since it reflects the joint action of the most activating group and the most deactivating group studied, is that for (2-methoxy-5-nitrophenyl)trimethylsilane. For this compound the observed value of k_{rel} must be regarded as identical, within the limits of accuracy of the several relative rates involved, with that calculated on the assumption of additivity. Some departure from additivity would not have been surprising in view of the direct resonance interaction which must occur between the electron-releasing methoxy group and the electron-accepting nitro group in the *para*-position to it.

The agreement between actual and calculated values of k_{rel} is not quite as good for (2-methoxy-5-carboxyphenyl)trimethylsilane but the value of the ratio of the observed to the calculated reactivity (*viz.* 1.8) cannot be regarded as a significant departure from additivity. In spite of the uncertainties involved in the calculated rates, the fact that the observed relative rate appears to be slightly higher than that calculated for the carboxy compound whereas it is lower for the nitro compound probably represents a real effect, and such a difference would, indeed, be expected. This is because the carboxyl group undergoes hydrogen-bonding interaction with acidic media[7], and this interaction, which would increase the deactivating influence of the group, would be greater in the more concentrated acid used[5] to measure the value of k_{rel} for (*m*-carboxyphenyl)trimethylsilane than in the more dilute acid used for the more reactive (2-methoxy-5-carboxyphenyl)trimethylsilane, so that the calculated value of k_{rel} in the weaker acid would be somewhat too low.

Since the agreement of calculated and observed values of k_{rel} are so close for the methoxy compound considered above, the 3-fold difference between the actual and calculated values of k_{rel} for the 4-methyl-3-nitro compound must probably be regarded as real at least in part, the departure from additivity being in the opposite direction to that expected from de la Mare and Ridd's suggestion[2]. Departure from additivity would not be surprising in this case since the two substituents are *ortho* to one another, and there could be steric interaction. In the light of the other results, however, it seems very probable that the small differences between the calculated and observed values of k_{rel} for the (5-halo-2-methoxyphenyl)trimethylsilanes were not significant[3], and we must conclude that the principle of additivity holds remarkably well in desilylation. Probably little departure from additivity is to be expected when the influences of two or more substituents on the rate are largely compensatory, so that the overall reactivity (and thus the position of the transition state along the reaction coordinate, and the degree of transfer of positive charge to the aromatic system) is not greatly different from that of the parent phenyltrimethylsilane. However, the additivity principle seems to hold in desilylation even with (2,4,6-trimethoxyphenyl)trimethylsilane, in which the separate substituent influences are all in the one direction and the overall reactivity is more than 10^8 times as great as that of phenyltrimethylsilane[11]. The operation of the additivity principle in desilylation is in marked contrast to some results in nitration; for example, nitration at the 2-position of 1,4-dichlorobenzene in nitric acid/sulphuric acid is 7.3 times as fast as would be expected for additivity of effects[7].

TABLE 2

CLEAVAGE OF (SUBSTITUTED-PHENYL)TRIMETHYLSILANES IN A MIXTURE OF SULPHURIC ACID AND ACETIC ACID AT 50.0°

Substituent(s)	$[H_2SO_4]$[a] (M)	λ[b] (nm)	$10^3 k$ (min^{-1})	k_{rel}
None	7.35	269	24.7	1.00
	8.40	269	38.1	
	10.4	269	244	
3-Cl	15.3	279	255	0.012[c]
4-Me-3-NO_2	15.3	335	51	0.0024
2-MeO-5-NO_2	10.4	350	14.7	0.066
5-HO_2C-2-MeO	8.40	286	86	2.3
5-MeCO-2-MeO	8.40	254	87	2.3
	7.35	254	59	2.4

[a] Concn. of aqueous acid, 3 vol. of which were mixed with 4 vol. of a solution of the arylsilane in anhydrous acetic acid. [b] Wave-length used to follow the progress of reaction. [c] Value from refs. 4 and 5.

The reactivity of (2-methoxy-5-acetylphenyl)trimethylsilane has not been considered above because no reliable figures are available for the influence of the acetyl substituent alone, since in the strength of acid needed to cleave the compound $MeCOC_6H_4SiMe_3$ there is considerable protonation of the acetyl group[8]. In the more dilute acid which can be used with the 2-methoxy-5-acetyl compound, the degree of protonation will be markedly smaller, and the fact that effectively the same value of k_{rel} was found in two media of somewhat different acid concentrations is consistent with this. It is thus likely from the results in Table 2 that the deactivating effect of an *m*-COMe group is rather similar to that of an *m*-CO_2H group, and thus to that of an *m*-CO_2Me group. This is consistent with the fact that the values of the

σ-constants (which normally give a good guide to substituent effects in electrophilic aromatic substitution for *meta*-groups) are very similar for *m*-COMe and *m*-CO_2Me groups, *viz.* +0.38 and +0.39, respectively[9].

EXPERIMENTAL

Preparations of aryltrimethylsilanes

The preparation of (4-methyl-3-nitrophenyl)trimethylsilane has been described previously[10]. Other compounds were prepared as follows:

2,4-Bis(trimethylsilyl)anisole. A mixture of (5-chloro-2-methoxyphenyl)trimethylsilane (18.6 g, 0.087 mole) and chlorotrimethylsilane (10.8 g, 0.10 mole) in toluene (50 ml) was added dropwise to a refluxing mixture of sodium (5.1 g) and toluene (100 ml). The mixture was refluxed for $1\frac{1}{2}$ h, then cooled somewhat and filtered. The filtrate was evaporated, and the residue recrystallized from ethanol then from light petroleum (b.p. 40–60°), to give 2,4-bis(trimethylsilyl)anisole (nc) (18.0 g, 84%), m.p. 55°. (Found: C, 62.1; H, 10.0. $C_{13}H_{24}OSi_2$ calcd.: C, 6.8; H, 9.6%.) The PMR spectrum (in $CDCl_3$) had τ values as follows: Me_3Si, 9.75 (s); MeO, 6.22 (s); ring H's, multiplet centred at 2.82. The integration pattern was as expected.

(2-Methoxy-5-nitrophenyl)trimethylsilane. Nitric, acid (4.5 g, of 70 w/w acid, 0.025 mole) was added dropwise with stirring to acetic anhydride (35 g) maintained at 20°. A mixture (partly an emulsion) of 2,4-bis(trimethylsilyl)anisole (6.3 g, 0.025 mole) and acetic anhydride (15.3 g) was added dropwise with stirring, the temperature being maintained at 20 ± 5°. The mixture was stirred for 1 h, then added to a solution of sodium hydroxide (48 g) in water (150 ml) with strong cooling. Ether extraction, was followed by washing and drying of the ethereal extract, and fractional distillation to give a material of b.p. 118°/ca. 0.2 mm, which solidified in the receiver. Recrystallization from ethanol gave pale-yellow crystals of (2-methoxy-5-nitrophenyl)trimethylsilane (nc) (4.1 g, 74%), m.p. 72°. (Found: C, 53.4; H, 7.0. $C_{10}H_{15}NO_3Si$ calcd.: C, 53.3; H, 6.7%.) The integration pattern in the PMR spectrum (in CCl_4) was as expected, with τ values as follows: Me_3Si, 9.68 (s); MeO, 6.10 (s); 3-H, 3.42 (m); 4- and 6-H, 1.82 (m).

(5-Carboxy-2-methoxyphenyl)trimethylsilane. n-Butyllithium (0.030 mole of a 1.5 *M* solution in hexane) was added to (5-bromo-2-methoxyphenyl)trimethylsilane (5.2 g, 0.020 mole) in ether (40 ml) at −10°, and the mixture was maintained at −10° for 30 min, then allowed to warm to 20° and set aside at that temperature for 30 min. It was then treated with a large excess of powdered solid carbon dioxide, and the usual working-up, involving extraction with aqueous alkali, treatment with acid, and re-extraction with ether, gave (5-carboxy-2-methoxyphenyl)trimethylsilane (nc), m.p. 172–173°. (Found: C, 58.9; H, 7.4. $C_{10}H_{16}O_3Si$ calcd.: C, 58.95; H, 7.15%.) The PMR spectrum (in CCl_4) had the expected integration pattern, with τ values as follows: Me_3Si, 9.76 (s); MeO, 6.11 (s); 3-H, 3.18 (m); 4- and 6-H, 1.88 (m).

(5-Acetyl-2-methoxyphenyl)trimethylsilane. Anhydrous cadmium chloride (6.7 g, 0.060 mole) was added to the Grignard reagent prepared from (5-bromo-2-methoxyphenyl)trimethylsilane (7.8 g, 0.030 mole) in ether. The mixture was stirred under reflux for 3 h, the ether was replaced by benzene (40 ml), and acetyl chloride (2.5 g, 0.032 mole) in benzene (10 ml) was added at 10°. The mixture was stirred at 40° for 2 h, then worked up in the usual way, culminating in fractional distillation, to give a

liquid of b.p. 95°/ca. 0.03 mm, which solidified (2.7 g, 41%). A pure sample for the rate studies and analysis was obtained by preparative GLC on a column of SE 30 on silanized Chromasorb G. (Found: C, 65.3; H, 8.3. $C_{12}H_{18}O_2Si$ calcd.: C, 64.9; H, 8.1%.) The PMR spectrum (in $CDCl_3$) had the expected integration pattern, with τ values as follows: Me_3Si, 9.70 (s); MeO, 6.12 (s); MeCO, 7.46 (s); 3-H, 2.96 (m); 4- and 6-H, 1.96 (m).

Rate Studies

These were carried out as previously described[4,6,8]. Good first-order kinetics were found in all cases.

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