455. *Aromatic Reactivity. Part III.* Cleavage of Substituted Phenyltrimethylsilanes by Sulphuric Acid in Acetic Acid–Water.*

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Use of a sulphuric acid–acetic acid–water medium for rate studies on the cleavage of phenyltrimethylsilanes has permitted measurement of the effects of strongly deactivating substituents. The results provide a detailed picture of the effects of a wide range of substituents on this electrophilic aromatic substitution.

THE effects of some nuclear substituents, X, on the cleavage of a series of aryltrimethylsilanes, $X{\cdot}C_6H_4{\cdot}SiMe_3$, have been studied in aqueous-methanolic perchloric acid.[1] Use of sulphuric acid in acetic acid–water, in which greater variation in acidity is possible, permits a wider range of substituents to be studied, and, in particular, allows the effects of strongly electron-withdrawing groups to be measured. The medium consisted of a mixture of four volumes of acetic acid containing 0·73 wt.-% of water with three volumes of aqueous sulphuric acid; reference to a medium involving, say, 10·1M-sulphuric acid implies that the aqueous sulphuric acid taken was of this normality, not the final mixture.

TABLE 1. *Cleavage of* $X{\cdot}C_6H_4{\cdot}SiMe_3$ *in* H_2SO_4–$CH_3{\cdot}CO_2H$–H_2O *at* 50·18°.

$[H_2SO_4]$ [a] (M)	X	10^2k_1 (min.$^{-1}$)	$k_{rel.}$	$[H_2SO_4]$ (M)	X	10^2k_1 (min.$^{-1}$)	$k_{rel.}$
18·4	*p*-NO_2	1·56	1·22 × 10^{-4}	10·1	*p*-F	15·6	0·95
18·4	*p*-NMe_3^+	4·92	3·84 × 10^{-4}	10·1	H	16·3	1·00
18·4	*p*-CO_2H	18·9	—	10·1	*p*-Ph	46·1 [b]	2·83
16·4	*p*-CO_2H	4·72	1·48 × 10^{-3}	8·75	*p*-Ph	14·1	—
16·4	*m*-Cl	38·3	—	8·75	*o*-Ph	29·1	5·85
12·7	*m*-Cl	1·74	1·20 × 10^{-2}	6·41	*p*-Ph	1·82	—
12·7	*p*-Br	15·1	—	6·41	*p*-Me	11·6	18·0
10·1	*p*-Br	1·70	1·04 × 10^{-1}	5·65	*p*-Me	6·56	—
10·1	*p*-I	1·65	1·01 × 10^{-1}	5·65	(3-C_4H_3S) [c]	41·9	115
10·1	*p*-Cl	3·09	1·90 × 10^{-1}	1·15	(3-C_4H_3S) [c]	7·86	—
10·1	*m*-Ph	5·56	3·3 × 10^{-1}	1·15	*p*-$Me_3Si{\cdot}CH_2$	1·38	202
10·1	*m*-MeO	6·39	3·8 × 10^{-1}	1·15	*p*-MeO	6·93	1010

[a] See text and Experimental section. [b] Calc. from $k_{rel.}$ of 2·83 observed at 40·06°. [c] 3-Thienyltrimethylsilane; these figures are introduced for purposes of overlap and will be discussed later.

The reactions were followed spectrophotometrically. Table 1 lists the first-order rate constants, k_1, observed at 50·18°, and the rate, $k_{rel.}$, of cleavage of each compound relative to that of the unsubstituted compound, $C_6H_5{\cdot}SiMe_3$. These relative rates are obtained by stepwise change in the acidity, some compounds being examined in more than one medium to provide overlap. This procedure largely compensates for the change in the nature of the solvent, but the derived values of $k_{rel.}$ are not necessarily exactly those which would be obtained if all the compounds could be compared directly at one acid concentration.

Effects of some of the substituents in Table 1 have already been discussed;[1] the following are additional: *o*-Ph, *m*-Ph, *m*-MeO, *p*-I, *m*-Cl, *p*-CO_2H, *p*-NMe_3^+, and *p*-NO_2. The outstanding feature is the large deactivation brought about by the *p*-NO_2 group, which is a strong $-I$, $-T$ substituent.[2] The *p*-NMe_3^+ group, in spite of its positive charge which might be expected to repel very strongly the positively-charged attacking species, does not deactivate as strongly as the *p*-NO_2 group. The *para*-halogens deactivate in the order *p*-I = *p*-Br > *p*-Cl > *p*-F, the resultant influence of the *p*-F substituent being very small because its $+T$ effect almost balances out its $-I$ effect. The $+T$ effects of

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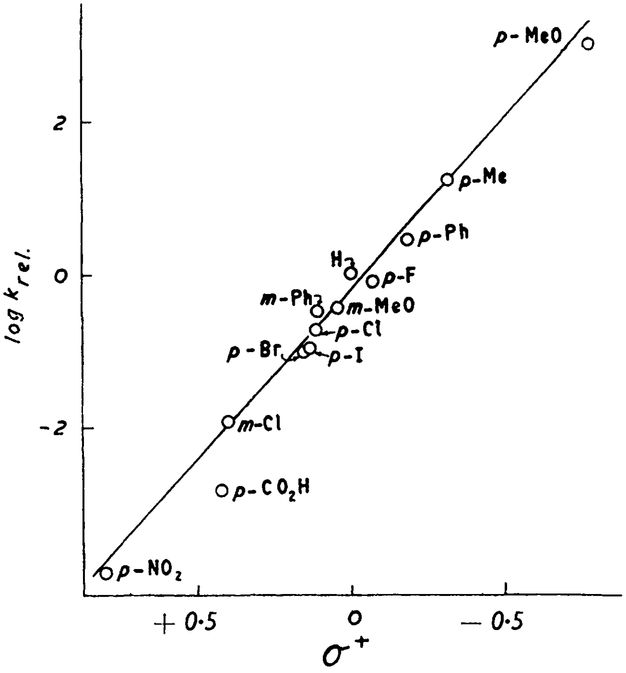
* Part II, *J.*, 1957, 4449.

[1] Eaborn, *J.*, 1956, 4858.

[2] Ingold, "Structure and Mechanism in Organic Chemistry," G. Bell and Sons, Ltd., London, 1953, Chap. VI.

the halogens cannot operate directly to the *meta*-position, and the *m*-Cl compound is about 16 times less reactive than the *p*-Cl compound. For similar reasons the MeO group, which activates strongly from *ortho*- and *para*-positions, deactivates some 2·6 times from the *meta*-position. The effects of phenyl substituents will be discussed in a later paper.

Over the range of substituents common to both studies, the spread of rates is rather smaller in sulphuric acid–acetic acid–water than in aqueous-methanolic perchloric acid; for example, the *p*-MeO group activates 1010 times in the former medium and 1510 times in the latter. However, a plot of values of log $k_{\text{rel.}}$ for the former medium [1] against those of log $k'_{\text{rel.}}$ for the latter is a good straight line (log $k_{\text{rel.}} = 0{\cdot}96$ log k'_{re}.), and the existence of this linear free-energy relation permits conversion of substituent effects observed in aqueous methanolic perchloric acid into those which would be expected in sulphuric acid–acetic acid–water. Thus the *p*-NMe_2 group would activate roughly 10^7 times in the latter medium and the *p*-OH substituent some 6000 times. The activating influence of the *p*-NMe_2 group, whose $+E$ effect may respond to the electron demand during the reaction, is thus much greater than the deactivating influence of the *p*-NO_2 group, whose $-E$ effect cannot come into play.[2]



In the Figure is a plot of the values of log $k_{\text{rel.}}$ against the substituent constants, σ^+, recently proposed for electrophilic aromatic substitutions or electrophilic side-chain reactions and derived from the rates of solvolysis of αα-dimethylbenzyl chlorides in 90% aqueous acetone.[3] With the exception of that for the *p*-CO_2H substituent, the points lie satisfactorily about a straight line, and the success of this use of the σ^+-constants is impressive in view of the range of substituents covered.* It is noteworthy that if the σ^+-constant for the *p*-CO_2Me group (0·49) is used for the *p*-CO_2H group in the Figure in place of the listed value (0·42), a point satisfactorily near the line is obtained, which suggests the possibility that, in spite of some contrary evidence,[4] slight ionization of the compound

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* However, in future Parts attention will be drawn to some defects of the treatment.

[3] Brown and Okamoto, *J. Amer. Chem. Soc.*, 1958, **80**, 4979.

[4] Okamoto, Inukai, and Brown, *ibid.*, p. 4969.

p-$HO_2C{\cdot}C_6H_4{\cdot}CMe_2Cl$ occurs in the aqueous acetone used for measuring σ^+-constants. An alternative explanation, that the compound p-$Me_3Si{\cdot}C_6H_4{\cdot}CO_2H$ is considerably protonated in the cleavage medium, is less likely at the concentration of acid involved.

Activation Energies and Entropies.—In Table 2 are shown the apparent activation energies, E_a, and log A factors for the compounds studied. [log A = log k_1 + ($E_a/2{\cdot}303\boldsymbol{R}T$), with time in minutes.] Reactions were carried out at two temperatures only (50·18° and 40·06°), and the activation energies are probably not accurate in absolute terms to much better than ±1 kcal./mole. Within these limits there is no significant variation in E_a, whereas the effects of the substituents should reveal themselves in the activation-energy term. The reason for this apparent anomaly lies in the considerable change in medium necessary to give convenient rates with all the compounds. For example, the value of E_a for the p-Br compound in a medium involving 12·7M-sulphuric acid is 1·6 kcal./mole lower than that in a medium involving 10·1M-acid, and the difference is probably real, since relative activation energies determined on the same compound in two media are believed to be considerably more accurate than the relative activation energies determined for two compounds in the same medium. If the change from 10·1M- to 12·7M-acid causes the same lowering of the activation energy for all the compounds, then the activation energy for, say, the m-Cl compound in the former medium would be (22 + 1·6), *i.e.*, 23·6 kcal./mole. By this type of procedure it is possible to convert all the E_a values into approximate values of E_a (corr.), the activation energies which would be observed with 10·1M-acid. The rough values of E_a (corr.) show clearly a general fall from the unreactive p-NO_2 compound to the reactive p-MeO compound, as expected.

TABLE 2. *Activation energies and* $\log_{10} A$ *factors for cleavage of* $X{\cdot}C_6H_4{\cdot}SiMe_3$ *in* H_2SO_4–$CH_3{\cdot}CO_2H$–H_2O.

$[H_2SO_4]$ (M)	X	E_a (kcal./mole)	$\log_{10} A$	E_A (corr.) (kcal./mole)	$[H_2SO_4]$ (M)	X	E_a (kcal./mole)	$\log_{10} A$	E_A (corr.) (kcal./mole)
18·4	p-NO_2	20·9	12·30	24·8	10·1	p-F	20·8	13·34	20·8
18·4	p-NMe_3^+	19·3	11·77	23·2	10·1	H	20·7	13·22	20·7
18·4	p-CO_2H	20·5	13·15	—	10·1	p-Ph	20·0	13·06	20·0
16·4	p-CO_2H	20·8	12·72	24·4	8·75	p-Ph	21·2	13·50	—
16·4	m-Cl	20·0	13·11	—	8·75	o-Ph	20·5	13·30	19·3
12·7	m-Cl	22·0	13·10	23·6	6·41	o-Ph	21·8	13·37	—
12·7	p-I	19·3	12·22	20·9	6·41	p-Me	20·8	13·13	18·3
12·7	p-Br	19·5	12·32	—	5·65	p-Me	21·4	13·31	—
10·1	p-Br	21·1	12·49	21·1	5·65	(3-C_4H_3S) [a]	19·0	12·48	—
10·1	p-Cl	21·1	12·76	21·1	1·15	(3-C_4H_3S) [a]	22·2	12·91	—
10·1	m-Ph	21·8	13·45	21·8	1·15	p-$Me_3Si{\cdot}CH_2$	21·6	12·74	15·3
10·1	m-MeO	22·2	13·82	22·2	1·15	p-MeO	20·7	12·50	14·4

[a] See Table 1, footnote [c].

In principle similar corrections could be applied to log A, but Table 2 shows that there is no significant difference between the values determined for any compound in two different media, no doubt because of a fortuitous cancellation of influences. Except for the rather low value for the p-NMe_3^+ compound, log A is thus independent of the substituent present, at least within experimental error.* If it is assumed that a log A factor of 13·0 applies to all the compounds (except the p-NMe_3^+ derivative) in 10·1M-acid, then the values of $k_{rel.}$ in Table 1 would be accounted for by a fall in the activation energy from 27 for the p-NO_2 compound to 16·0 kcal./mole for the p-MeO compound.

The above discussion can profitably be brought to bear on a recent surprising conclusion that in de-deuteration of alkylbenzenes by trifluoroacetic acid–sulphuric acid the effects

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* A low value of log A would be expected for the p-NMe_3^+ compound in reaction with a positively-charged species.[5] One can predict that the deactivating influence of the p-NMe_3^+ group relative to that of the p-NO_2 group would be markedly smaller in a reaction involving a neutral electrophil.

[5] Frost and Pearson, " Kinetics and Mechanism," John Wiley and Sons Inc., New York, 1953, p. 133.

of the alkyl substituents act solely through the entropy term, and not through the activation energy.[6] This conclusion was unjustified, and we believe it to be incorrect. It was reached because absence of effects due to the medium was inferred from the fact that the activation energies found for reaction of $[^2H_1]$-*p*-xylene in trifluoroacetic acid containing 0·1M- and 0·015M-sulphuric acid, respectively, differed by only 1 kcal./mole, *i.e.*, by little more than the estimated standard deviation of $\pm 0{\cdot}6$ kcal./mole. It is more likely that this difference was real, and that considerable effects by the medium on the activation energy were involved over the range of sulphuric acid concentrations (0·015—2M). We suggest that such influences of the medium cancel out the effects of substituents, as in the reaction we have studied.

EXPERIMENTAL

Materials.—Acetic acid, purified by boiling it with chromium trioxide and subsequent fractionation, had m. p. 15·4° (corresponding with a water content of 0·73 wt.-%).

Diphenylyltrimethylsilanes were prepared from the appropriate chlorodiphenyls and trimethylchlorosilane by Wurtz–Fittig condensation in toluene, and had the following properties: 4-isomer, m. p. 55°; 3-isomer, b. p. 158°/10 mm., n_D^{20} 1·5686; 2-isomer, m. p. 38·5—39·0° (from EtOH) (Found: C, 79·6; H, 8·0%. Calc. for $C_{15}H_{18}Si$: C, 79·6; H, 8·0%). The m. p. of the 2-isomer was previously [7] given as 21·7°.

The methiodide of *p*-*NN*-dimethylaminophenyltrimethylsilane was prepared from the base and methyl iodide in methanol, the mixture being kept at 30° for 50 hr. The salt which separated on cooling was recrystallised to constant m. p. (200°, decomp.) from methanol. It was converted into the hydroxide by boiling its aqueous solution with silver oxide, filtering, and drying in a desiccator. The semi-crystalline mass was taken up in methanol, and the solution was filtered through a fine paper to remove particles of silver and silver salts. The methanol was evaporated off, and the residue was dried in a vacuum desiccator (P_2O_5), recrystallized from anhydrous ethanol by addition of dry ether, and stored over phosphoric oxide.

Other $X{\cdot}C_6H_4{\cdot}SiMe_3$ compounds used had the following properties: (X =)*p*-NO_2, m. p. 37°; *p*-CO_2H, m. p. 143°; *m*-Cl, b. p. 206—208°, n_D^{20} 1·5103; *p*-F, b. p. 173°, n_D^{20} 1·4742; H, b. p. 171·6°, n_D^{20} 1·4904; *m*-MeO, b. p. 213°, n_D^{20} 1·5025; *p*-Me, b. p. 191·5°, n_D^{20} 1·4930; *p*-Cl, b. p. 211·5°, n_D^{20} 1·5098; *p*-Br, b. p. 229·5°, n_D^{20} 1·5279. The last-named compound probably contained a little of the compounds *p*-$Br{\cdot}C_6H_4{\cdot}Br$ and *p*-$Me_3Si{\cdot}C_6H_4{\cdot}SiMe_3$, neither of which interferes seriously with the rate studies.[1]

Rate Studies.—The general method is described in ref. 1. To 10 ml. of an acetic acid solution of the aryltrimethylsilane (of concn. shown in Table 3) were added 7·5 ml. of sulphuric acid, ice-cooling being used with 16M- and 18M-acid. Both volumes were delivered from fast-running burettes, the same burettes being used throughout. The mixture was shaken well and a sample was transferred to a 1 cm. stoppered cell in an Adkins's thermostatted cell holder ($\pm 0{\cdot}03°$) in a Unicam S.P. 500 spectrophotometer. Readings of the optical density, relative to a water blank at the wavelengths, λ, shown in Table 3, were begun after 8—10 min. and continued for at least 80% of reaction. Faster reactions were completed in the cell, but for slower runs " infinity " values of the optical density were obtained from samples of the reaction mixture kept in sealed tubes in a thermostat bath. Good first-order kinetics were observed; all rates were reproducible to $\pm 1{\cdot}5\%$, and usually to $\pm 0{\cdot}5\%$.

TABLE 3.

X	Concn. (mM)	λ (mμ)	X	Concn. (mM)	λ (mμ)
p-NO_2	8	360	*m*-MeO	7	290
p-NMe_3^+	7	269	*p*-F	8	272
p-CO_2H	0·5	295, 293	H	10	269
m-Cl	8	279	*p*-Ph	3	294, 296
p-I	7	288, 289	*o*-Ph	7	290, 291
p-Br	8	274	*p*-Me	1·2	271
p-Cl	8	274	*p*-$Me_3Si{\cdot}CH_2$	1	278, 279
m-Ph	4	290, 290·5	*p*-MeO	1·2	282

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[6] Mackor, Smit, and van der Waals, *Trans. Faraday Soc.*, 1957, **53**, 1309.

[7] Clark, Gordon, Young, and Hunter, *J. Amer. Chem. Soc.*, 1951, **73**, 3798.

The possibility of interference by sulphonation or sulphondesilylation (*i.e.*, the reaction $X{\cdot}C_6H_4{\cdot}SiMe_3 + H_2SO_4 \longrightarrow X{\cdot}C_6H_4{\cdot}SO_3H + HO{\cdot}SiMe_3$) was ruled out as follows: (i) The spectrum of a solution of benzene in the medium used for cleaving phenyltrimethylsilane (involving 10·1M-sulphuric acid) did not change during 5 hr. at 50°. A slight change occurred with 18·1M-acid, but so slowly as to make it clear that no significant sulphonation would occur in the case of strongly deactivated rings (*i.e.*, with *p*-CO_2H, *p*-NMe_3^+ and *p*-NO_2 substituents). The spectrum of naphthalene (which is readily sulphonated) did not change in the medium involving 6·41M-acid. (ii) The spectra of the solutions obtained by cleaving the *p*-CO_2H and *p*-Ph compounds in media involving 18·4 and 8·75M-sulphuric acid, respectively, were identical (within 3%) with those of solutions of benzoic acid and diphenyl of corresponding concentrations in the same media. This indicates that significant sulphondesilylation does not occur.

THE UNIVERSITY, LEICESTER. [*Received, February 5th*, 1959.]