949. *Aromatic Reactivity. Part I. Effects of Substituents on the Acid Cleavage of Phenyltrimethylsilanes*
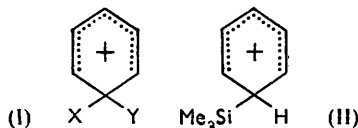
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The acid-catalysed cleavage of some substituted phenyltrimethylsilanes in aqueous-methanolic perchloric acid has been studied spectrophoto-metrically for a range of activating and weakly deactivating substituents. The results provide a detailed picture of the effects of these substituents on electrophilic aromatic reactivity.

THE acid-catalysed solvolytic cleavage of aryl–Si bonds is an electrophilic aromatic substitution in which a proton, initially solvated, is the attacking species.[1] Since removal of a trimethylsilyl group from a benzene ring shifts the ultraviolet absorption spectrum about 3—15 mμ away from the visible region, with little change of shape, the reaction is easily followed spectrophotometrically and may be conveniently used to study the effects of nuclear substituents on aromatic reactivity. The results are free from uncertainties about the position of electrophilic attack which complicate the aromatic substitution processes normally studied.

It is generally accepted that electrophilic aromatic substitutions probably proceed through intermediates (σ-complexes) of type (I) (*e.g.*, in *tert.*-butylation, X = Bu^t, and

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[1] (*a*) Eaborn, *J.*, 1953, 3148; (*b*) Benkeser and Krysiak, *J. Amer. Chem. Soc.*, 1954, **76**, 6353; (*c*) see also Baines and Eaborn, *J.*, 1956, 1436.

Y = H; in nitration, X = NO_2, Y = H),[2] and it is usually considered that in nitration and halogenation the formation of the intermediate is rate-determining,[2,3] but the kinetic isotope-effects on which these beliefs are based are not, in fact, conclusive.[4] The same uncertainty, namely, whether formation or destruction of the intermediate (II) is rate-determining, exists also in protodesilylation; * but this does not reduce the significance of effects of substituents since in all simple electrophilic aromatic substitutions the transition states for formation and destruction of the intermediate are likely to be close in structure to the intermediate and to one another, and effects of substituents will be much the same on both transition states and intermediate.[4]

(I) X Y   Me₃Si H (II)

Table 1 lists first-order rate-constants for removal of the trimethylsilyl group in aqueous-methanolic perchloric acid, and the reactivities of monosubstituted phenyltrimethylsilanes relative to that of phenyltrimethylsilane. We draw attention to some particular features.

TABLE 1. *Cleavage of substituted phenyltrimethylsilanes by aqueous-methanolic* ᵃ *perchloric acid at 51·2°*

Subst.	[HClO₄] (M) ᵇ	$10^3 k_1$ (min.⁻¹)	Relative rate ($k_{rel.}$)	log $k_{rel.}$	Subst.	[HClO₄] (M) ᵇ	$10^3 k_1$ (min.⁻¹)	Relative rate ($k_{rel.}$)	log $k_{rel.}$
p-NMe₂	0·001056	46	—	—	p-Me	4·53	2·72	21·1	1·32(5)
	0·01056	105				9·22	38		
	0·1056	116	ca.	7·5	p-Et	9·22	35	19·5	1·29
			3·0 × 10⁷		o-Me	9·22	32	17·8	1·25
	0·823	105			p-Prⁱ	9·22	31	17·2	1·24
	9·22	53·5			p-Butᵗ	9·22	28	15·6	1·19
2 : 4 : 6-Me₃	0·1056	24·2			m-Me₃Si·CH₂	9·22	11·1	6·2	0·79
	0·440	116	53,600	4·73	p-Ph	9·22	6·4	3·55	0·55
	0·823	258			p-Me₃Si	9·22	4·5	2·5	0·40
p-OH	0·1056	4·91			m-Me	9·22	4·1	2·3	0·36
	0·440	23·5	10,700	4·03	H	9·22	1·80	1	0·0
	0·823	51·2			p-F	9·22	1·35	0·75	−0·12
p-OMe	0·823	7·19	1510	3·18	p-Cl	9·22	0·24	0·13	−0·87
	2·35	39·8			p-Br	9·22	0·18	0·10	−1·0
p-Me₃Si·CH₂	2·35	8·3	315	2·50					
	4·53	40·5							
o-OMe	4·53	43	335	2·53					

ᵃ See Experimental section.   ᵇ Concn. of acid, 2 vol. of which were added to 5 vol. of methanol.

(a) *Alkyl substituents.* The activating effect of an o-Me group ($k_{rel.}$ 18) is close to that of the p-Me group ($k_{rel.}$ 21). This is in line with the closeness of the reactivity of *ortho-* and *para-*positions of toluene in reaction with the Br⁺ or HOBr⁺ ion (partial rate factors, 76 and 59, respectively [5]), and in tritiation in which the *ortho-* and *para-*positions are equally reactive within experimental error.[6] In nitration (partial rate factors, 42 and 58) and molecular halogenation (partial rate factors, 450 and 1990) steric hindrance is said to reduce the reactivity of the *ortho-*position.[5]

The suggestion has been made that *para-*alkyl groups will activate according to the hyperconjugative order (Me > Et > Prⁱ > Butᵗ) when the attack on the ring is by uncharged electrophilic reagents but according to the reverse, inductive order when attack is by a positive entity.[7] However, in protodesilylation,* in which attack is by a positive

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* Removal of a trimethylsilyl group would be described as "detrimethylsilylation" in a suggested systematic nomenclature (*J.*, 1954, 4717), but the less formidable "desilylation" will be used in this series to denote removal of a silicon atom along with the attached groups. The replacing group will normally be specified, as in "bromodesilylation," but "protodesilylation" will often be shortened to "desilylation" when no confusion can arise.

² Ingold, "Structure and Mechanism in Organic Chemistry," G. Bell and Sons, Ltd., London, 1953, Chap. VI.
³ Melander, *Arkiv Kemi*, 1950, **2**, 211; Berglund-Larrson and Melander, *ibid.*, 1953, **6**, 219.
⁴ Hammond, *J. Amer. Chem. Soc.*, 1955, **77**, 334.
⁵ de la Mare and Harvey, *J.*, 1956, 36.
⁶ Olsson and Melander, *Acta Chem. Scand.*, 1954, **8**, 523.
⁷ Robertson, de la Mare, and Swedlund, *J.*, 1953, 782.

entity, the hyperconjugative order is followed, just as it is in molecular halogenation (and also in molecular bromodesilylation). The sole example of the *p*-Bu^t group's activating more than the *p*-Me group in an electrophilic aromatic substitution is in nitration.[8]

(b) *Organosilyl substituents.* Because of the opposition of $+I$ and $-T$ effects the tri-methylsilyl group supplies electrons to the ring or withdraws them according to the demand.[9] Nitration studies have shown the group to be slightly activating and weakly *ortho-para*-directing.[10] Our results show it to activate slightly more from the *para*-position than does the methyl group from the *meta*-position.

The trimethylsilylmethyl group is strongly electron-supplying,[11] and the strong activation of the *para*-positions was expected. We believe that the large difference in activating power of this group in the *para*- and the *meta*-position (the activation ratio is 60 : 1 compared with 10 : 1 for the methyl group) arises from hyperconjugation of the type (A), since this could operate directly only to *ortho*- and *para*-positions.[11] Even so, activation by the *m*-Me$_3$Si·CH$_2$ group is anomalously low in view of its quite large inductive effect,[11] and it is possible that steric hindrance to solvation is important since this bulky group must interfere with solvent approach to both positions *ortho* to itself, on which a substantial portion of the positive charge resides in the transition state.

(c) *Methoxy- and hydroxy-substituents.* The *p*-OH group activates several times more strongly than the *p*-OMe group. This cannot arise from the formation from the phenol of small amount of the highly reactive phenoxide ion, *p*-Me$_3$Si·C$_6$H$_4$·O$^-$, since this would be suppressed by increasing the concentration of acid, whereas the rate of reaction of the

(A)   (B)

phenolic compound shows the same dependence on concentration of acid as that of other compounds (*e.g.*, the ratios of the rate constants for 2-mesityl- and *p*-hydroxyphenyl-trimethylsilane are 5·0, 4·95, and 4·93 for acid concentrations *ca.* 0·8, 0·4, and 0·1M respectively). de la Mare and Robertson have suggested that the activating power of the *p*-OH group is greater than that of the *p*-OMe group because of the hyperconjugation shown in (B), but at least equally important could be hydrogen bonding between the solvent and the hydroxyl group (*i.e.*, $\overset{Me}{\underset{H}{>}}O \colon \cdots H-O-C_6H_4 \cdot SiMe_3$) which increases the electron-release of the latter. (The hydrogen bonding and hyperconjugation would, in fact, interact to reinforce each other.)

The relative activating effects of *p*-OMe and *o*-OMe groups (4·5 : 1), which reflect the stronger operation of the $-I$ effect from the *ortho*-position, agree with those in replacement of deuterium by protium in which *p*-deuteroanisole is 3 times as reactive as *o*-deuteroanisole at 80°.[12]

(d) p-*Dimethylamino-substituent.* The very great activating power of this group is clearly shown in Table 1, and our results confirm the rather indirect deductions from molecular halogenation.[13] The value of $k_{rel.}$ is arrived at in the following way.

p-Dimethylaminophenyltrimethylsilane reacts at an 0·01056M(added)-acid concentration some 4·3 times as fast as mesityltrimethylsilane with 0·1056M-acid, and thus approximately 43 times as fast as the mesityl compound would react in the weaker acid

[8] Cohn, Hughes, Jones, and Peeling, *Nature*, 1952, **169**, 291.
[9] Benkeser and Krysiak, *J. Amer. Chem. Soc.*, 1953, **75**, 2421; Eaborn and Parker, *J.*, 1955, 126; Chatt and Williams, *J.*, 1956, 688.
[10] Speier, *J. Amer. Chem. Soc.*, 1953, **75**, 2930.
[11] Eaborn and Parker, *J.*, 1954, 939.
[12] Lauer and Day, *J. Amer. Chem. Soc.*, 1955, **77**, 1904.
[13] de la Mare, *J.*, 1954, 4450.

(actually rather more, since the rate falls off rather more rapidly than the acid concentration). In the reaction medium, with 0·01056M(added)-acid, 9·6% of NN-dimethylaniline is found spectrophotometrically to be present as free amine, and since the p-trimethylsilyl derivative is a slightly weaker base rather less than 9·6% of it will be present as the free amine. Thus p-dimethylaminophenyltrimethylsilane is at least 430 times as reactive as the mesityl compound, and >2·3 × 10⁷ times as reactive as phenyltrimethylsilane. A similar figure can be deduced from the rate in 0·1056 × 10⁻²M(added)-acid, when 48% of NN-dimethylaniline is present as free base. We believe the figure of 3·0 × 10⁷ in Table 1 to be accurate within 25%.

p-Dimethylaminophenyltrimethylsilane reacts at a maximum rate with ca. 0·1M(added)-acid. At greater concentrations the rate falls slowly, the rates at 0·83M- and 9·2M-acid being 0·90 and 0·46 of that at 0·1056M-acid concentration, whereas rate increases of ca. 10 and 370 respectively would be found for other compounds. This behaviour is to be expected from our previous observation that the rate of desilylation is proportional to the proton-donating power of the medium as measured by the indicator ratio, [BH⁺]/[B], for a neutral base, B, (p-nitroaniline being the base employed).[1a] Since with acid concentration at least 0·1M(added) the p-dimethylaminophenyltrimethylsilane is almost all in the protonated form (which reacts at a negligible rate), the concentration of the latter changes inappreciably, and increasing the acid strength to double the indicator ratio for this base doubles the rate at which the free amine reacts but halves its concentration. The apparent rate would thus be independent of the acid concentration if it were not that (*a*) the variation of rate with the indicator ratio, [BH⁺]/[B], is not completely independent of the base, B,[1c] and (*b*) at a given indicator ratio for a particular base the rate of desilylation falls as the proportion of water in the medium decreases.[1a] Since our method of making up the reaction mixture means that less water is present in the more strongly acidic media, a slight fall in the rate of reaction of p-dimethylaminophenyltrimethylsilane will result from an increase in the concentration of added acid.

Below ca. 0·1M(added)-acid the change in concentration of protonated base can no longer be neglected, and the apparent rate of reaction will begin to fall markedly as the concentration of acid is lowered, since the indicator ratio, [BH⁺]/[B] (and thus the rate of reaction of the free amine), falls more rapidly than the concentration of free amine increases.

Correlation with Other Electrophilic Reactions.—With the figures available in Table 1 it is possible to test proposals that a free energy relation of the Hammett type, log $k_{rel.} = \rho\sigma^+$, may apply to electrophilic aromatic substitutions or to reactions forming carbonium ions adjacent to the ring, σ^+ being characteristic of the substituent for these reactions, and ρ characteristic of the reaction.[14] If the proposals are valid, then log $k'_{rel.}$/log $k_{rel.}$ should be constant for the various substituents where log $k_{rel.}$ refers to desilylation and log $k'_{rel.}$ refers to some other electrophilic reaction. Table 2 gives some values of this ratio for an aromatic substitution involving a molecular reagent and one involving a positive ion, for the migration step of the pinacol rearrangement (which may be looked upon as an electrophilic aromatic substitution in which attack of a carbonium ion breaks a C–C bond), and for two S_N1 solvolysis reactions involving production of carbonium ions adjacent to the ring.

The striking features of this Table are : (*a*) the reasonable constancy of the log $k'_{rel.}$/log $k_{rel.}$ ratios for substituents *m*-Me, *p*-Me, *p*-OMe, *p*-OH, and *p*-MNe₂; and (*b*) the considerable deviations in most cases of the ratios for *p*-Ph and *p*-halogen substituents, the deviations being such that desilylation is several times slower than might have been expected. The strong deactivating effect of a *p*-Cl substituent is not an abnormality to be attributed to some special features of this reaction, since similar deactivation is found in nitration, and it is significant that this is the reaction which most closely resembles desilylation, both being displacements at a ring-carbon atom by a positive reagent. (The deactivating effects of a *p*-F substituent are also similar

¹⁴ (*a*) Pearson, Baxter, and Martin, *J. Org. Chem.*, 1952, **17**, 1511; (*b*) Kochi and Hammond, *J. Amer. Chem. Soc.*, 1953, **74**, 3445; (*c*) Tsurata, *Bull. Inst. Res. Kyoto Univ.*, 1954, **32**, 149; (*d*) McGary Okamoto, and Brown, *J. Amer. Chem. Soc.*, 1955, **77**, 3037; (*e*) Miller, *Austral. J. Chem*, 1956, **9**, 61.

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in the two reactions, whereas a *p*-F substituent activates in molecular halogenation and in brominolysis of benzeneboronic acids,[15] and facilitates the ionization of triphenylmethyl chloride.[16]) It thus appears that while a satisfactory set of σ^+-constants may well be found for some of the substituents listed in Table 1, the influence of some others, such as *p*-Cl and *p*-Ph, will vary too greatly with the electrical demands to be expressed adequately by single σ^+ constants. It is not surprising that the *p*-Ph group should behave abnormally, since this substituent is so sensitive to electron-demand that it is one of only two groups known clearly to activate in both electrophilic and nucleophilic aromatic substitutions.[14b]

TABLE 2. *Substituent effects in desilylation and other electrophilic reactions :*
values of log $k'_{rel.}$/log $k_{rel.}$.

	Mol. halogn.[a]	Pinacol rearr.[b]	Hydrolysis of R·C₆H₄·CH₂·O·Tos [c]	Ethanolysis of (R·C₆H₄)₂CHCl [d]	Nitration [e]
p-NMe₂	2·6	—	—	—	—
p-OH	2·9	—	—	—	—
p-OMe	3·1	0·85	1·36	0·97	—
p-Me	2·5	0·96	1·12	0·92	1·3
p-Alkyl	2·4 [f]	0·78 [g]	—	1·02 [h]	—
m-Me	—	0·78	0·7	0·89	1·1
p-Ph	6·0	1·90	—	1·91	—
p-F	—[i]	—	—	—	0·93
p-Cl	0·46	0·18	—	0·48	1·0
p-Br	0·6	—	0·4	0·33	1·0

[a] Halogenation of R·C₆H₅ in acetic acid.[13] [b] $k'_{rel.}$ is the migratory aptitude of R·C₆H₄ relative to C₆H₅ in rearrangements of [(R·C₆H₄)(C₆H₅)C(OH)]₂ (Bachmann and Ferguson, *J. Amer. Chem. Soc.*, 1934, **56**, 2081). [c] S_N1 hydrolysis of benzyl toluene-*p*-sulphonates in aqueous acetone.[14b] [d] S_N1 reaction (Norris and Banta, *J. Amer. Chem. Soc.*, 1928, **50**, 1804). [e] Ref. 2, p. 247; log $k'_{rel.}$ for *p*-F (− 0·11) is obtained from the rate data on p. 246, and the orientation data on p. 260 of ref. 2. [f] R = Buᵗ. [g] R = Prⁱ. [h] R = Et. [i] log $k'_{rel.}$ = 0·8; log $k_{rel.}$ = − 0·11.

A set of σ^+ constants has recently been proposed by Miller,[14e] but since these are based exclusively on results for molecular halogenation, to test them against our data would yield no information not indicated by the first column of log $k'_{rel.}$/log $k_{rel.}$ ratios in Table 2. A similar argument applies to σ^+ constants derived from solvolysis of benzyl toluene-*p*-sulphonates.[14b] It has recently been suggested that for *meta*-substituents $\sigma^+ = \sigma$ (where σ is the usual Hammett σ constant for nucleophilic side chain reactions [17]), while for *para*-substituents [14d] $\sigma^+ = \sigma − 0.134$. A set of σ^+ constants so derived does not stand up to the test of our data, a plot of log $k_{rel.}$ against σ^+ showing continuous curvature, as indicated by the following values of log $k_{rel.}$/σ^+ :

R	*p*-NMe₂	*p*-OH	*p*-OMe	*p*-Me₃Si·CH₂	*p*-Me	*p*-Ph	*m*-Me	*p*-Cl	*p*-Br
− σ	0·600	0·357	0·268	0·260 [11]	0·170	−0·009	0·069	−0·227	−0·232
− σ^+	0·734	0·491	0·402	0·394	0·304	0·125	0·069	−0·093	−0·098
− log $k_{rel.}$/σ^+ ...	10·3	8·2	7·9	6·3	4·3	4·4	5·2	9·4	10·2

However, we understand from Professor H. C. Brown that he has devised a new set of σ^+ constants based upon the rates of solvolysis of substituted $\alpha\alpha$-dimethylbenzyl halides and that these can be correlated with the data of Table 1 and with those for fifteen other electrophilic reactions at least as well as σ constants are correlated with nucleophilic side-chain reactions. We believe, nevertheless, that with this, and all, sets of σ^+ constants there will inevitably be serious deviations from correlation in the case of certain substituents such as *p*-halogeno and *p*-phenyl, as indicated by the data of Table 2, particularly in substitutions at a ring-carbon atom as distinct from reactions involving electrophilic attack in a side-chain.

Special Features of Desilylation.—Comparisons of effects of substituents in this re-action with those in halogenation and nitration reveal no special features arising from the fact that in the former reaction a C–Si bond is being broken instead of a C–H

[15] Kuivala and Benjamin, *J. Amer. Chem. Soc.*, 1955, **77**, 4834.
[16] Evans, Jones, and Osborne, *Trans. Faraday Soc.*, 1954, **50**, 470.
[17] Jaffé, *Chem. Rev.*, 1953, **53**, 191.

bond. Phenyltrimethylsilanes are stabilized by $d\pi$–$p\pi$ bonding, and this will be most marked when substituents with $+T$ effects are present in the *para*-position [cf. the effects shown in (C)], but since such a substituent will probably stabilize phenyltrimethylsilane in proportion as it stabilizes benzene the effects of substituents relative to one another will not differ much in removal of trimethylsilyl and in the more familiar aromatic substitutions.

(C)   MeO⸺⟨ ⟩⸺SiMe₃
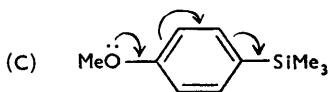
The fact that a C–Si bond is being broken and not a C–H bond seems to decrease the spread of reactivities of substituted compounds (or the slope, ρ, of a plot of log $k_{rel.}$ against σ^+). Thus Melander [6] has shown that in acid-catalysed isotopic exchange, which is also an aromatic substitution by a positive hydrogen ion, the *para*-position of toluene is activated some 32 times as strongly as the *meta*, whereas a ratio of 9 applies in desilylation. This is expected, since the more electropositive the group being removed from the ring the greater will be the fraction of positive charge residing on it in the transition state, and the smaller that on the ring, so that the electrical effects of substituents will have smaller influence.

EXPERIMENTAL

M. p.s and b. p.s are corrected.

Materials.—The compounds employed have been previously described, except p-tert.-*butylphenyltrimethylsilane*, m. p. 78° (from aqueous ethanol) (Found : C, 75·6; H, 10·8. $C_{13}H_{22}Si$ requires C, 75·7; H, 10·4%), and p-iso*propylphenyltrimethylsilane*, b. p. 126—127°/40 mm., 222°/750 mm., n_D^{20} 1·4914 (Found : C, 75·0; H, 10·5. $C_{12}H_{20}Si$ requires C, 74·9; H, 10·5%) which were prepared from trimethylchlorosilane and the appropriate arylmagnesium bromide in ether. In all preparations from aryl bromides care was taken to ensure that no bromide remained unchanged before coupling with the silicon halide, as the bromides boil close to the corresponding trimethylsilyl compounds.

The following physical constants for $R \cdot C_6H_4 \cdot SiMe_3$ compounds are new or are believed to be superior to those in the literature : R = p-Cl, b. p. 211·5°, m. p. 0·0°, n_D^{20} 1·5097 ; p-Ph, m. p. 55·5° (from ethanol) ; p-OH, m. p. 76° (from light petroleum) ; p-NMe₂, m. p. 27·5° ; p-Me₃Si·CH₂, m. p. 16·5°.

p-Bromophenyltrimethylsilane, b. p. 230°, n_D^{20} 1·5284 (prepared from p-bromophenyl-magnesium bromide and trimethylchlorosilane), probably contained small quantities of p-dibromobenzene and p-di(trimethylsilyl)benzene which are very difficult to remove. The former does not interfere in the rate studies (other than by altering the absolute values of the optical density), while the effect of the latter was minimized by neglecting the first 24 hr. of reaction, during which most of the di(trimethylsilyl)benzene is converted into benzene.

Apparatus.—For most of the rate studies a thermostatically controlled cell-holder was used in the Unicam S.P. 500 spectrophotometer. This holder (designed by Dr. N. Macleod) fitted on to the usual movable cell-carrier, and consisted of a block of copper with drilled spaces for two stoppered 1 cm. quartz cells and for the light beam. A heating coil in the block was controlled by a Mullard Temperature Controller Type E7594 actuated by a thermistor in contact with the base of the block between the cells. The absorption cells fitted closely to the metal, so that aqueous methanol in a cell at *ca.* 18° placed in the block reached the temperature of the block (51·2°) in less than 4 min. The subsequent temperature variation could not be detected on a sensitive Anschütz thermometer placed in the liquid, either during a heating–cooling cycle or in the course of a day, and was certainly <0·02°.

Rate Measurements.—The ultraviolet absorptions of solutions of the organosilicon compound, $R \cdot C_6H_4 \cdot SiMe_3$, and the parent compound, $R \cdot C_6H_5$, were examined in methanol, and wavelengths selected for following the removal of trimethylsilyl. Usually two or more wavelengths were employed, and in all reported cases rate constants measured at different wavelengths did not differ by more than 2%. Although rate constants were reproducible to within ±1% and excellent first-order constants were obtained throughout the course of a reaction, often up to 90% completion, the accuracy of spectrometric methods is greatly influenced by impurities, and we believe that the absolute values of the rate constants quoted in Table 1 may be in error by as much as ±3% for liquid aryltrimethylsilanes (possibly ±6% for the p-bromo-compound) but by rather less for solids, which could be obtained pure with certainly. The ratio of the

rate constants for one compound at two acid concentrations, sometimes used in the " overlap " procedure for calculating values of $k_{rel.}$ in Table 1, is more accurate.

For reactions which could be completed in a day, 10 ml. of aqueous acid were added to 25 ml. of a solution of the organosilane in redistilled " AnalaR " methanol, and some of the mixture was transferred to a 1 cm. stoppered quartz cell which was then placed in the cell-block thermostat described above. Absorption readings (relative to methanol) were begun after not less than 8 min. Reactions were taken to completion (*i.e.*, to 10 half-lives) in the cell when the half-life was $< \frac{1}{2}$ hr., but in other cases " infinity " values were obtained from samples of the reaction mixture kept in sealed tubes at 51° for a period equivalent to 10 half-lives, or at 70° for a period equivalent to 1—1·5 half-lives.

For slower reactions (R = *p*-Br, *p*-Cl, *p*-F, H, *m*-Me) 20 ml. of aqueous acid and 50 ml. of methanolic silane derivative were mixed, and samples (*ca.* 3 ml.) were sealed in drawn-out test-tubes which were then placed in a thermostat at 51·2°. " Zero time " readings were taken on samples withdrawn after *ca.* 30 min., quickly cooled to room temperature, and examined in 5 mm. cells.

The first-order rate constants, k_1, are given by the equation, $k_1 t = \ln [(D_0 - D_\infty)/(D_t - D_\infty)]$, where D_t is the optical density at time t, D_0 that at zero-time, and D_∞ that at infinity.

Table 3 shows the wavelengths at which measurements were made and the concentrations of the methanolic solutions of the silanes, $R \cdot C_6 H_5 \cdot SiMe_3$, these usually being such that optical density readings were between 0·9 and 0·05.

TABLE 3.

R	Concn. (M)	λ (mμ)	R	Concn. (M)	λ (mμ)
p-OH	15×10^{-4}	241, 283 [a]	*p*-Pr^i	25×10^{-4}	233·6
,,	,,	241, 284 [b]	*p*-Bu^t	4×10^{-4}	234
,,	,,	240·4, 283 [c]	,,	8×10^{-3}	266
p-NMe$_2$	6×10^{-3}	270 [a, c, d]	*o*-Me	1×10^{-2}	278
,,	7×10^{-4}	268, 274 [e]	,,	1×10^{-3}	230
,,	6×10^{-5}	266 [f]	*m*-Me	12×10^{-3}	270, 277
p-OMe	1×10^{-3}	282	H	14×10^{-3}	264, 231
p-Ph	6×10^{-5}	264, 272	*p*-Me$_3$Si	4×10^{-3}	278 [g]
p-Me$_3$Si·CH$_2$	75×10^{-4}	280	*o*-OMe	2×10^{-4}	228
,,	15×10^{-4}	248	,,	12×10^{-4}	287
m-Me$_3$Si·CH$_2$	3×10^{-3}	283, 275	*p*-F	1×10^{-1}	271·5, 225
p-Me	1×10^{-2}	273	*p*-Cl	1×10^{-2}	238, 239
p-Et	7×10^{-3}	235·4	*p*-Br	1×10^{-2}	275, 250
p-Pr^i	5×10^{-3}	271			

[a] $[HClO_4] = 0·1M$. [b] $[HClO_4] = 0·4M$. [c] $[HClO_4] = 0·8M$. [d] $[HClO_4] = 9·2M$. [e] $[HClO_4] = 0·01M$. [f] $[HClO_4] = 0·001M$. [g] Phenyltrimethylsilane and benzene have low and similar absorptions at this wavelength, so that the change in absorption reflects the disappearance of *p*-trimethylsilyl-phenyltrimethylsilane.

NN-Dimethylaniline in Acidic Aqueous Methanol.—The optical densities, O.D., at 51·2°, of mixtures of 25 ml. methanolic solution of the base, or its methochloride with 10 ml. of aqueous acid (of concn. shown) were determined in 1 cm. stoppered cells at 249 mμ (a maximum for the free base) :

Compound	Concn. (M)	$[HClO_4]$ (M)	O.D.	Ph·NMe$_2$ (%)
Ph·NMe$_2$	7×10^{-5}	0	0·545	100
Ph·NMe$_2$	7×10^{-4}	$1·506 \times 10^{-2}$	0·543	9·6
Ph·NMe$_3^+$Cl$^-$	7×10^{-4}	$1·506 \times 10^{-3}$	0·024	0
Ph·NMe$_2$	7×10^{-5}	$1·506 \times 10^{-3}$	0·259	48
Ph·NMe$_3^+$Cl$^-$	7×10^{-5}	$1·506 \times 10^{-3}$	0·000	0

Some of the compounds used were made by Mr. J. B. Hurd, who also carried out some preliminary reactivity studies.

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