Aromatic Reactivity. Part XXXIX.[1] Effects of *ortho*-Substituents in Protodesilylation

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The compounds *o*-$XC_6H_4{\cdot}SiMe_3$ with X = Br, I, Bu^t, SO_3H, CO_2H, NO_2, Ac, and Bz have been made by appropriate desilylations of *o*-bis(trimethylsilyl)benzene. The rates of cleavage of these compounds, and of those with X = H, F, Cl, and Me_2N, by a mixture of aqueous sulphuric acid (3 vol.) and acetic acid (4 vol.) at 50° have been measured spectrophotometrically. Values of the rates, k_{rel}, relative to that of phenyltrimethylsilane, are as follows: (X=) Bu^t, 8·0; F, 7·3 × 10^{-2}; I, 3·8 × 10^{-2}; Cl, 3·4 × 10^{-2}; Br, 2·5 × 10^{-2}; CO_2H, 5·2 × 10^{-3}; SO_3H, 2·6 × 10^{-3}; NO_2, 6·8 × 10^{-5}; Me_2N, 6·8 × 10^{-5}. (In the last case the effective substituent in the reaction medium is thought to be the protonated Me_2HN^+.)

A plot of log k_{rel} for the *ortho*-substituents against $[\sigma_p + r(\sigma_p^+ - \sigma_p)]$ is a good straight line when $r = 0{\cdot}3$. For the corresponding *para*-substituents, the appropriate value of r is 0·7, and these results are consistent with the view that the inductive are more important relative to the resonance components of the substituent effects for *ortho*- than for *para*-groups. The high reactivity of *o*-bis(trimethylsilyl)benzene is attributed to steric acceleration, but the reactivity of the *o*-fluoro-compound, which is anomalously low in terms of the analysis mentioned, is left unexplained.

Cleavage of the aryl–silicon bond occurs when the amine *o*-$Me_2N{\cdot}C_6H_4{\cdot}SiMe_3$ is treated with methyl iodide in methanol.

Earlier papers in this series have described effects of many *meta*- and *para*-substituents, X, in protodesilylation of substituted phenyltrimethylsilanes, $XC_6H_4{\cdot}SiMe_3$ (for summaries see refs. 2 and 3), but the effects of the corresponding *ortho*-substituents have previously been little studied. We have now synthesised a range of *ortho*-substituted phenyltrimethylsilanes, and have measured spectrophotometrically the rates of their cleavage by acetic acid containing sulphuric acid. The results are listed in Table 1, which shows for each compound the composition of the cleavage medium, the wavelength, λ, used in the measurement, the observed first-order rate constant, k, and the rate, k_{rel}, relative to that for phenyltrimethylsilane. The spread of reactivity is such that the concentration of sulphuric acid had to be varied over a substantial range, and values of k_{rel} are deduced in many cases by an overlap procedure, involving stepwise comparison of compounds of comparable reactivity rather than by direct comparison with phenyltrimethylsilane, an implicit assumption being that the values of k_{rel} do not vary much with the changes in medium. This assumption is probably substantially correct for alkyl, substituted-alkyl, aryl, and halogen substituents, but may be less so for groups such as CO_2H and NO_2, which interact with the solvent through hydrogen-bonding, possibly to an extent which varies somewhat with the acidity of the medium. Results for some *para*-substituted compounds used in the overlap procedure are included in Table 1. Previously determined k_{rel} values for some other *ortho*- and *para*-compounds [4,5] referred to below are given in Table 2.

An important feature of the results is that in a plot of log k_{rel} for the *ortho*-substituted compounds against

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[1] Part XXXVIII, A. R. Bassindale, C. Eaborn, and D. R. M. Walton, preceding paper.

[2] C. Eaborn and R. W. Bott, in 'Organometallic Compounds of the Group IV Elements' (ed. A. G. MacDiarmid), vol. 1, Marcell-Dekker, New York, 1969, ch. 2.

[3] R. O. C. Norman and R. Taylor, 'Electrophilic Substitution in Benzenoid Compounds,' Elsevier, Amsterdam, 1965, ch. 9.

[4] C. Eaborn, *J. Chem. Soc.*, 1956, 4858.

[5] F. B. Deans and C. Eaborn, *J. Chem. Soc.*, 1959, 2299.

TABLE 1

Cleavage of $XC_6H_4{\cdot}SiMe_3$ compounds in H_2SO_4–AcOH–H_2O at 50·02°

X	$[H_2SO_4]$ [a] (M)	10^3k (min.$^{-1}$)	k_{rel}	λ (mμ)
o-$SiMe_3$	8·1	500	8·55 [b]	277
o-Bu^t	8·1	235	8·0	270·5
H	8·1	29·3	1·00	269·5
	10·2	163	—	—
o-F	10·2	11·8	$7{\cdot}3 \times 10^{-2}$	271
	12·2	77·2	—	—
o-I	12·2	40·4	$3{\cdot}8 \times 10^{-2}$	280
o-Cl	12·2	40·0	$3{\cdot}4 \times 10^{-2}$	276·5
o-Br	12·2	26·4	$2{\cdot}5 \times 10^{-2}$	277·5
	16·3	657	—	—
o-CO_2H	16·3	137	$5{\cdot}2 \times 10^{-3}$	291, 292
o-SO_3H	16·3	69·5	$2{\cdot}6 \times 10^{-3}$	277
p-SO_3H	16·3	30·9	$1{\cdot}16 \times 10^{-3}$	276
	19·1	93·4	—	—
p-Me_2HN^+ ...	19·1	94·9	$1{\cdot}18 \times 10^{-3}$	270
p-NO_2	19·1	13·8	$1{\cdot}7 \times 10^{-4}$	360
o-NO_2	19·1	5·44	$6{\cdot}8 \times 10^{-5}$	270
o-Me_2HN^+ ...	19·1	5·42	$6{\cdot}8 \times 10^{-5}$	269·5

[a] Concn. of aqueous acid, 3 vol. of which was added to 4 vol. of acetic acid. [b] The observed reactivity factor of 17·1 has been halved to allow for the availability of two equivalent aryl–$SiMe_3$ bonds.

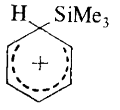
TABLE 2

Relative reactivities of $XC_6H_4{\cdot}SiMe_3$ compounds at 50°

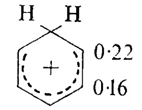
X	k_{rel}	X	k_{rel}
o-OMe	335 [a]	o-Ph	5·85 [b]
p-CH_2SiMe_3	315 [a]	p-SiMe	1·25 [a]
o-CH_2SiMe_3	31 [b]	H	1·00
o-Me	17·8 [b]	p-F	0·95 [b]
p-Bu^t	15·6 [b]	p-NMe_3^+	3×10^{-4} [b]

[a] In $HClO_4$–MeOH–H_2O. [b] In H_2SO_4–AcOH–H_2O.

log k_{rel} for the corresponding *para*-compounds (Figure 1), most of the points lie reasonably well about a straight line.* The existence of even a rough linear free-energy relationship between effects of *ortho*- and *para*-substituents would not be expected if the *ortho*-substituents had serious steric effects. There is evidence that the presence of two methyl groups *ortho*- to a trimethylsilyl group leads to steric acceleration,[6,7] presumably because there is relief of strain as the configuration at the attacked carbon atom changes to tetrahedral, but for single *ortho*-substituents such acceleration is likely to be small for all but the bulkiest groups. It is evident, although as far as we are aware it has not previously been pointed out, that in absence of steric effects (including steric effects on solvation) an exact linear free-energy relationship would be expected between the effects of *ortho*- and *para*-substituents in stabilization of a Wheland-intermediate, of which the ion (I) is an example, since comparable charges are induced by the same electronic mechanism at both *ortho*- and *para*-positions. There is evidence that in the benzenonium ion (actually in the pentamethylcyclopentadienyl cation) the charge distribution is as shown in (II),[7] and if it is generally true that



(I)



(II)

more charge resides at the *para*- than at the *ortho*-position in a Wheland intermediate, then *ortho*- should have a rather smaller effect than *para*-substituents on the stability of the intermediate.[8]

In protodesilylation, as in most electrophilic aromatic substitutions, the highest energy transition-state lies between the initial state and the Wheland intermediate, with the bond to the incoming proton only partly formed, so that a substantial degree of positive charge resides in the neighbourhood of the attacked carbon—mainly, it is to be presumed, on the attacking proton. Groups having large inductive effects can be expected to interact directly with this charge, in part at least by a direct-field electrostatic effect, and groups with large $-I$ effects, such as the halogens, NO_2, and $\overset{+}{N}Me_2H$, would, by virtue of these effects, be expected to deactivate more from the *ortho*- than from the *para*-position, and the observed deviations for these groups from the line of Figure 1 are consistent with this.† That the plot of Figure 1 is as good as it is can be associated with the fact that the transition state in protodesilylation lies more than half-way along the path from the reactants to the Wheland-intermediate.[9]

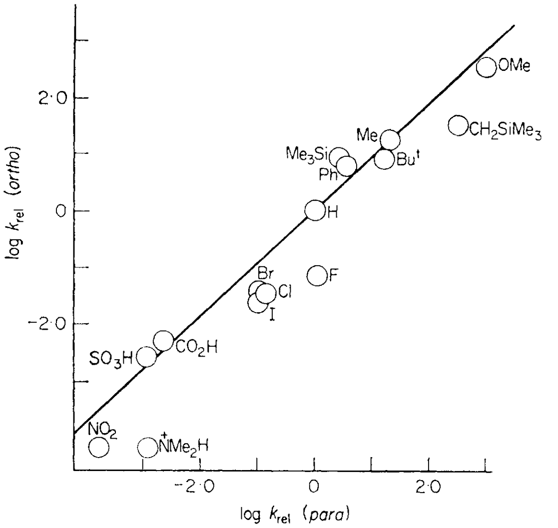


FIGURE 1 Plot of log k_{rel} for o-$XC_6H_4SiMe_3$ against log k_{rel} for p-$XC_6H_4{\cdot}SiMe_3$ compounds

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* For some of the *ortho*-X and *para*-X pairs, the values of k_{rel} used in Figure 1 were measured in $HClO_4$–MeOH–H_2O;[4] there is an excellent linear free-energy relationship between k_{rel} values in this and the H_2SO_4–AcOH–H_2O medium for *m*- and *p*-substituted compounds.

† The line of Figure 1 has been arbitrarily chosen. It will be evident from the discussion below that we could at least equally well draw the line through the point for NO_2 and H substituents and then consider the deviations for those groups with electron-releasing resonance effects.

[6] R. A. Benkeser, R. A. Hickner, D. I. Hoke, and B. H. Thomas, *J. Amer. Chem. Soc.*, 1958, **80**, 5289; C. Eaborn and R. C. Moore, *J. Chem. Soc.*, 1959, 3640.

[7] C. MacLean and E. L. Mackor, *Mol. Phys.*, 1961, **4**, 241; J. P. Colpa, C. MacLean, and E. L. Mackor, *Tetrahedron*, 1963, **19** (Suppl. 2), 65.

[8] Ref. 3, pp. 305—310.

[9] C. Eaborn, P. M. Jackson, and R. Taylor, *J. Chem. Soc.* (*B*), 1966, 613.

Among the halogens the deviations should be greatest for fluorine, as is observed, since it has the largest $-I$ effect, but it is difficult to account for the magnitude of the deviation for this halogen, though we note that in nitration the *ortho* : *para* reactivity ratio is correspondingly smaller for fluorobenzene than for the other halogenobenzenes.[10] (It is noteworthy, too, that the observed deactivation order for the *ortho*-halogens, *viz.* F > I > Cl > Br, agrees with that in detritiation.[11]) Somewhat less satisfactory is the comparison of the *ortho* : *para* reactivity ratio for the nitro-group in protodesilylation and for nitration in sulphuric acid,[12] *viz.* 0·4 and 1·4—1·7 respectively. An explanation advanced for the high *ortho* : *para* reactivity ratio for the nitro-group in nitration depends on the assumption that the transiton state is close to the Wheland intermediate, so that the *ortho*- would be less than the *para*-deactivation,[8] as noted above, but it seems to us unlikely that the transition state is so much further along the reaction co-ordinate than in protodesilylation. (Nitrobenzene is markedly less reactive than the nitrophenyltrimethylsilanes, but, against this, the assumed electrophile in nitration, *viz.* NO_2^+, is very much more reactive than the oxonium ions or other proton-donating species in the acetic acid–sulphuric acid–water mixtures used for protodesilylation.)

The trimethylsilyl group activates in protodesilylation some seven times more from the *ortho*- than from the *para*-position. This could reasonably be ascribed to steric acceleration, since there is undoubtedly serious strain in the initial *o*-bis(trimethylsilyl)benzene. Some such steric acceleration would then be expected with the *o*-tert-butyl substituent, although models suggest that there may be less strain in *o*-tert-butylphenyltrimethylsilane than in *o*-bis(trimethylsilyl)benzene; the *o*-tert-butyl group, in fact, activates only half as effectively as the corresponding *para*-substituent. It is revealing in this connexion to compare the effects of *ortho*-substituents in protodesilylation with those in detritiation in trifluoroacetic acid at 70°, since primary steric effects are believed to be insignificant in the latter reaction.[11] As Figure 2 shows, there is an approximate linear free-energy relationship between the substituents studied in both cases, and this implies that steric effects are fairly small also in protodesilylation, even with the tert-butyl group.

Another large deviation from the line of Figure 1 involves the trimethylsilylmethyl group, which activates 10 times less effectively from the *ortho*- than from the *para*-position. If there were any primary steric effect involved in the protodesilylation of the compound $o\text{-}Me_3SiCH_2{\cdot}C_6H_4{\cdot}SiMe_3$ we should expect it to cause a small acceleration. We shall consider below evidence that the superficially anomalous behaviour of the trimethylsilylmethyl group simply reflects the fact that the electron-supplying inductive effect of this group is small in relation to its electron-supplying resonance effect, but to keep the matter in perspective it is important to note that the deviation for the $o\text{-}Me_3SiCH_2$ group and that, in the other direction, for the $o\text{-}Me_3Si$ group correspond to only 1 kcal./mole or less in the free-energy of activation, and variations in differential solvation between initial and transition states might easily account for this when bulky substituents are involved.

We have assumed above that the compounds *o*- and $p\text{-}Me_2N{\cdot}C_6H_4{\cdot}SiMe_3$ react entirely in the protonated form *o*- and $p\text{-}Me_2H\overset{+}{N}{\cdot}C_6H_4{\cdot}SiMe_3$, and this is justified not only because the *para*-compound was shown to react in this form in a more weakly acidic perchloric acid–water–methanol medium,[4] but also because the value of k_{rel} obtained for this compound is within a factor of three of that found for the compound $p\text{-}Me_3\overset{+}{N}{\cdot}C_6H_4{\cdot}SiMe_3$ in sulphuric acid–acetic acid–water.[5] Significance cannot be attached to the fact that the value of k_{rel} for the $p\text{-}Me_2H\overset{+}{N}{\cdot}C_6H_4{\cdot}SiMe_3$ is larger than that recorded earlier for the $p\text{-}Me_3\overset{+}{N}{\cdot}C_6H_4{\cdot}SiMe_3$ compound, since different overlap compounds were used in the two studies and since any cumulative errors in k_{rel} are largest for the compounds of lowest reactivity. (Thus a k_{rel} value of $1{\cdot}7 \times 10^{-4}$ was obtained for the *para*-nitro-compound in the present work compared with a value of $1{\cdot}2 \times 10^{-4}$ recorded in the earlier study.[5]) However, we note from Table 1 that the $p\text{-}Me_2H\overset{+}{N}{\cdot}C_6H_4{\cdot}SiMe_3$ compound is some 6 times as reactive as the *para*-nitro-compound in a direct comparison, whereas the compound $p\text{-}Me_3\overset{+}{N}{\cdot}C_6H_4{\cdot}SiMe_3$ was only some three times as reactive as the nitro-compound in another direct comparison,[5] so that it seems fairly safe to conclude that the deactivation order $p\text{-}Me_3\overset{+}{N} > p\text{-}Me_2NH$ applies, as it does in nitration.[13]

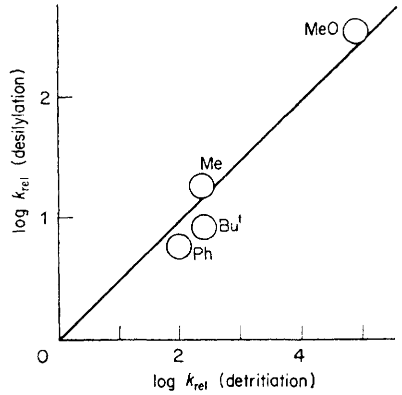

FIGURE 2 Plot of log k_{rel} for protodesilylation of $o\text{-}XC_6H_4{\cdot}SiMe_3$ compounds against log k_{rel} for detritiation of $o\text{-}XC_6H_4{\cdot}[^3H]$ compounds

Correlation with Substituent Constants.—For *para*- and *meta*-substituents in protodesilylation, values of log

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[10] P. B. de la Mare and J. H. Ridd, 'Aromatic Substitution, Nitration and Halogenation, Butterworths,' London, 1959, pp. 82—85.

[11] R. Baker, C. Eaborn, and R. Taylor, *J. Chem. Soc.*, 1961, 4927; C. Eaborn and R. Taylor, *ibid.*, 2388.

[12] A. D. Mesure and J. G. Tillett, *J. Chem. Soc.* (*B*), 1966, 669.

[13] M. Brickman, J. H. P. Utley, and J. H. Ridd, *J. Chem. Soc.*, 1965, 6851.

k_{rel} correlate approximately with σ^+-constants,[14] and better, in terms of the Yukawa–Tsuno equation, with the quantity $[\sigma + r(\sigma^+ - \sigma)]$, where $r = 0{\cdot}7$.[15] In the Yukawa–Tsuno treatment, the value of r is a measure of the contribution from the resonance effects relative to that from the inductive effects of the substituents, and in the light of the discussion above it would be expected that for *ortho*-substituents a rather smaller value of r would apply, corresponding to a greater contribution from inductive effects.* A plot of log k_{rel} against $[\sigma_p + 0{\cdot}3(\sigma_p{}^+ - \sigma_p)]$ is shown in Figure 3,† and it will be seen that the great majority of points fall near the straight line joining the two extreme points and the origin. The only large deviations are that for the trimethylsilyl substituent, which can be attributed to steric acceleration, and that for the fluorine substituent, which we cannot at present explain. It is noteworthy that the point for the trimethylsilylmethyl group lies satisfactorily near the line,‡ indicating that the deviation for this group in the comparison with *para*-substituents shown in Figure 1 may arise less from its bulk than from the importance of its resonance effect relative to that of its inductive effect.

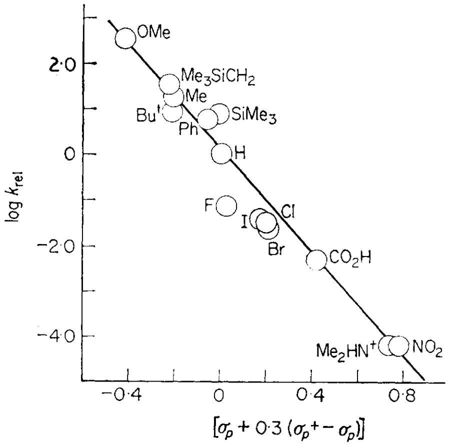

FIGURE 3 Plot of log k_{rel} against $[\sigma_p + 0{\cdot}3(\sigma_p{}^+ - \sigma_p)]$ for protodesilylation of o-$XC_6H_4{\cdot}SiMe_3$ compounds

The slope of the line for *ortho*-substituents (with $r = 0{\cdot}3$), *viz. ca.* 5·5, is rather greater than for the *para*-substituents (with $r = 0{\cdot}7$), *viz., ca.* 4·8, which reflects again the importance of the direct interaction between the polar groups and the incoming proton. It is noteworthy that if the picture we have drawn is correct, negative values of r should be possible for *ortho*-substituents, and it is conceivable that in a reaction involving a highly reactive, positive electrophile, in which the transition state is close to the reactants, the negative value might even exceed 0·53. In this case the *o*-methoxy-group, which has an inductive effect in the opposite direction to its resonance effect, would deactivate. Whether such a case can be demonstrated is doubtful, however, since the value of ρ would be so small that the deactivation would also be very small.

Preparative Methods.—Several of the *ortho*-substituted phenyltrimethylsilanes o-$XC_6H_4{\cdot}SiMe_3$ were made from *o*-bis(trimethylsilyl)benzene by appropriate electrophilic desilylations.[2] Thus the compounds with X = NO_2, Me_3SiOSO_2, Br, I, and Bu^t were made, respectively, from the bis-silyl compound by treatment with (i) nitric acid in acetic anhydride (*cf.* ref. 17), (ii) sulphur trioxide in carbon tetrachloride (*cf.* ref. 18), (iii) bromine in carbon tetrachloride, (iv) iodine in carbon disulphide in presence of aluminium iodide (*cf.* ref. 19), and (v) t-butyl chloride in carbon disulphide in presence of aluminium chloride (cf. ref. 20); the *o*-t-butyl compound was not obtained pure, but the impurity seemed to be *p*-di-t-butyl-benzene, which would not interfere with the cleavage studies. The ester o-$Me_3SiOSO_2{\cdot}C_6H_4{\cdot}SiMe_3$ is hydrolysed very rapidly in the cleavage medium to the sulphonic acid o-$HOSO_2{\cdot}C_6H_4{\cdot}SiMe_3$.

The compounds with X = Ac and Bz were made analogously by treatment of the bis-silyl compound with acetyl or benzoyl chloride in carbon disulphide in presence of aluminium chloride (cf. ref. 20); their protodesilylation was studied, but the results are not used because the change in u.v. absorption accompanying the cleavage was too small to permit accurate rate measurements, and also because there is uncertainty about the extent of protonation of the keto-groups in the media used. (Rough spectrophotometric measurements indicated that such protonation was considerable in media sufficiently acidic to give acceptable cleavage rates.)

When *o*-bromoiodobenzene and chlorotrimethylsilane were brought into reaction with magnesium in diethyl ether, some *o*-chlorophenyltrimethylsilane was produced and biphenylene was obtained in 18% yield. Biphenylene was also obtained along with biphenyl when *o*-chlorophenyltrimethylsilane was used in place of chlorotrimethylsilane, but biphenyl was produced without biphenylene when the *o*-bromoiodobenzene and magnesium were taken alone in ether. Benzyne may be involved as an intermediate.

An unusual aryl–silicon bond cleavage was obtained during an unsuccessful attempt to make the compound o-$Me_3\overset{+}{N}{\cdot}C_6H_4{\cdot}SiMe_3$ by treatment of the amine o-$Me_2N{\cdot}C_6H_4{\cdot}SiMe_3$ with methyl iodide in methanol (the method used for making the isomeric p-$Me_3\overset{+}{N}{\cdot}C_6H_4{\cdot}SiMe_3$), the product obtained being *NNN*-

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* An equivalent analysis in terms of σ_I- and σ_R-constants would no doubt lead to comparable conclusions.

† Values of σ^+- and σ-constants are taken from ref. 16. Values are not available for the Me_2HN^+ group, and those for the Me_3N^+ group are used.

‡ The value of the k_{rel} used for this group refers to a $HClO_4$–MeOH–H_2O medium. A slightly smaller value could be expected in H_2SO_4–AcOH–H_2O, which would bring the point even closer to the line.

[14] L. M. Stock and H. C. Brown, *Adv. in Phys. Org. Chem.*, 1963, **1**, 89.

[15] R. W. Bott and C. Eaborn, *J. Chem. Soc.*, 1963, 2139.

[16] Ref. 3, p. 287.

[17] F. B. Deans and C. Eaborn, *J. Chem. Soc.*, 1957, 498.

[18] R. W. Bott, C. Eaborn, and T. Hashimoto, *J. Organometallic Chem.*, 1965, **3**, 442.

[19] C. Eaborn, *J. Chem. Soc.*, 1950, 3077.

[20] T. Hashimoto, Ph.D. Thesis, University of Leicester, 1962.

trimethylanilinium iodide. That a specific *ortho*-effect was not necessarily involved was shown by the fact that the amine $p\text{-}NH_2\cdot C_6H_4\cdot SiMe_3$ gave the cleavage product methoxytrimethylsilane when heated under reflux with methyl iodide in methanol for 20 hr. This cleavage is worthy of further study; it may involve nucleophilic attack of the solvent or iodide ion on silicon in the positive ions $o\text{-}Me_3\overset{+}{N}\cdot C_6H_4\cdot SiMe_3$ and $p\text{-}MeH_2\overset{+}{N}\cdot C_6H_4\cdot SiMe_3$, with transient formation of the aryl carbanions. Nucleophilic cleavage of $XC_6H_4\cdot SnMe_3$ under more severe conditions, involving aqueous methanolic alkali, has been recently studed;[21] it is known to occur particularly readily when $X = p\text{-}NMe_3^+$, and even more rapid cleavage would be expected when $X = o\text{-}NMe_3^+$.

EXPERIMENTAL

o-Chloro- and o-Fluoro-phenyltrimethylsilane.—*o*-Chloro- [b.p. 95°/18 mm., n_D^{25} 1·5149 (lit.,[22] b.p. 89°/15 mm., n_D^{25} 1·5122)] and *o*-fluoro-phenyltrimethylsilane [b.p. 168°, n_D^{25} 1·4835 (lit.,[22] b.p. 167—168° n_D^{25} 1·4834)] were prepared as previously described.[22]

o-Bis(trimethylsilyl)benzene.—A few drops of a mixture of *o*-chlorophenyltrimethylsilane (18·5 g., 0·10 mole) and chlorotrimethylsilane (15·0 g., 0·14 mole) were added to small lithium strips (2·0 g., 0·28 g.-atom) in tetrahydrofuran (40 ml.) at room temperature. When reaction set in, the temperature was reduced to —45° and the remainder of the mixture was added during 30 min. After 8 hr. at −45° the mixture was filtered through glass wool, and the filtrate was kept at 40° for 30 min. The usual working-up procedure, culminating in fractional distillation, gave *o*-bis(trimethylsilyl)benzene (5·0 g., 23%), b.p. 119°/12 mm., n_D^{25} 1·5097 (lit.,[23], b.p. 135°/20 mm., n_D^{25} 1·5110) (Found: C, 65·0; H, 10·0. Calc. for $C_{12}H_{22}Si_2$: C, 64·8; H, 10·0%).

This compound, b.p. 65°/0·6 mm., n_D^{25} 1·5096, was also made in 58% yield from *o*-chlorophenyltrimethylsilane, chlorotrimethylsilane, and sodium in boiling toluene.[23] Careful fractionation was necessary because the *meta*-isomer (isolated by preparative g.l.c.) was also produced in up to 9% yield. Benzyltrimethylsilane was also formed in about 5% yield (*cf.* ref. 24).

Trimethyl-o-nitrophenylsilane.—A solution (Care! See ref. 25) of 70% nitric acid (6·3 g., 0·07 mole) in acetic anhydride (30 g.) was added slowly to a solution of *o*-bis-(trimethylsilyl)benzene (4·5 g., 0·020 mole) in acetic acid (30 g.) at 100°. The mixture was kept at 100° for 6 hr., then cooled and added to 0·4M-aqueous sodium hydroxide (400 ml.). Ether extraction followed by washing, drying (Na_2SO_4), and fractionation of the extract gave *trimethyl-o-nitrophenylsilane* (3·5 g., 90%), as a straw-coloured liquid, (b.p. 98°/2·3 mm., n_D^{25} 1·5271 (lit.,[26] b.p. 149°/40 mm., n_D^{25} 1·5290) (Found: C, 55·5; H, 7·2; N, 7·15. Calc. for $C_9H_{13}NO_2Si$: C, 55·5; H, 6·7; N, 7·2%).

Derivatives of o-Trimethylsilylbenzenesulphonic Acid.—Freshly distilled sulphur trioxide (1·6 g., 0·020 mole) was added to a well-stirred ice-cooled solution of *o*-bis(trimethylsilyl)benzene (4·5 g., 0·020 mole) in carbon tetrachloride (40 ml.). After 15 min., 15 ml. of the mixture was removed, and volatile liquids were taken off from this portion to leave *trimethylsilyl o-trimethylsilylbenzenesulphonate*., b.p. 295° (decomp.) (Found: C, 47·3; H, 7·2. $C_{12}H_{22}O_3SSi_2$ requires C, 47·6; H, 7·3%).

The remaining reaction mixture was treated with 2M-aqueous sodium hydroxide, and the precipitated solid was crystallized from ethanol to give *sodium o-trimethylsilylbenzenesulphonate*, m.p. 324—327° (Found: C, 42·0; H, 5·1. $C_9H_{13}O_3SSiNa$ requires C, 42·8; H, 5·2%). This gave an *S-benzyl thiuronium salt*, m.p. 170—171° (from aqueous EtOH) (Found: C, 51·4; H, 5·9. $C_{17}H_{22}N_2O_3S_2Si$ requires C, 51·5; H, 6·1%).

A solution of part of the sodium salt in 50% aqueous methanol was passed through a column of acidic Amberlite IR 120 ion-exchange resin, and the eluate was concentrated in a rotary evaporator. The residue was evaporated to dryness in an oven at 60°; the resulting solid was crystallized from benzene to give crystals, m.p. 74—76°, probably of the sulphonic acid trihydrate (Found: C, 38·2; H, 6·8. Calc. for $C_9H_{20}O_6SSi$: C, 38·0; H, 7·1%).

o-Bromophenyltrimethylsilane.—A solution of bromine (3·2 g., 0·020 mole) in carbon tetrachloride (30 ml.) was added during 15 min. to *o*-bis(trimethylsilyl)-benzene (4·45 g., 0·020 mole) in carbon tetrachloride (30 ml.). The mixture was heated under reflux for 2 hr., then fractionated to give *o-bromophenyltrimethylsilane* b.p. 77°/3·5 mm., n_D^{25} 1·5203 (Found: C, 47·4; H, 5·7. $C_9H_{13}BrSi$ requires C, 47·2; H, 5·7%).

o-Iodophenyltrimethylsilane.—A mixture of aluminium powder (0·5 g.), iodine (0·5 g.), and carbon disulphide (20 ml.) was warmed until reaction set in (to produce aluminium iodide), and *o*-bis(trimethylsilyl)benzene (9·0 g., 0·040 mole) was added. A solution of iodine (10·2 g., 0·040 mole) in carbon disulphide (50 ml.) was added during 3 hr., the mixture being kept at −10°. After 12 hr., with stirring, at this temperature the mixture was allowed to warm to room temperature, and then filtered. The filtrate was washed with water, dried (Na_2SO_4), and fractionated to give *o-iodophenyltrimethylsilane* (4 g., 40%), b.p. 82°/1·0 mm., n_D^{25} 1·5707 (Found: C, 39·3; H, 4·6. $C_9H_{13}ISi$ requires C, 39·1; H, 4·7%).

(o-t-Butylphenyl)trimethylsilane (Impure).— t-Butyl chloride (2·3 g., 0·025 mole) in carbon disulphide (15 ml.) was added during 10 min. to *o*-bis(trimethylsilyl)benzene (5·6 g., 0·025 mole) in carbon disulphide (10 ml.) containing aluminium chloride (0·3 g.). The mixture was heated under reflux for 30 min., and was then cooled, filtered, and fractionated to give phenyltrimethylsilane (18%), *o*-bis-(trimethylsilyl)benzene (11%), and a semisolid (1·4 g.), which was recrystallized from methanol to give crystals of m.p. 68—69°. The i.r. spectrum of this solid indicated that t-butyl and aryl-$SiMe_3$ groups were present, but the elemental analysis was not correct for (*o*-t-butylphenyl)-trimethylsilane (Found: C, 80·2; H, 11·0. Calc. for 64 : 36 mixture of $o\text{-}Bu^t\cdot C_6H_4\cdot SiMe_3 : p\text{-}Bu^t_2C_6H_4$: C, 80·2; H, 11·1%).

G.l.c. with a 150 ft. capillary column of tricresyl phosphate gave sufficient resolution into two peaks for the second compound to be identified as *p*-di-t-butylbenzene, but

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attempts to separate the constituents on a preparative scale by sublimation, distillation, crystallization, and chromatography were unsuccessful.

o-*Trimethylsilyl-acetophenone and -benzophenone*.—Acetyl chloride (2·3 g., 0·030 mole) in carbon disulphide (15 ml.) was added to a stirred, ice-cooled suspension of aluminium chloride (4·0 g.) in carbon disulphide (50 ml.) containing *o*-bis(trimethylsilyl)benzene (6·6 g., 0·030 mole). The mixture was heated under reflux for 1 hr., most of the solvent was distilled off, and the residue was added to ice–water (100 ml.). Benzene extraction, followed by washing, drying (Na_2SO_4), and fractionation of the extract gave *o*-trimethylsilylacetophenone (2·8 g., 50%), b.p. 88°/3·3 mm., n_D^{25} 1·5181 (lit.,[27] b.p. 116—117°/14 mm., n_D^{25} 1·5200) (Found: C, 68·4; H, 8·4. Calc. for $C_{11}H_{16}OSi$: C, 68·7; H, 8·4%). The i.r. spectrum showed the very strong band at 1687 cm.$^{-1}$ expected for an aryl carbonyl group. The 2,4-dinitrophenylhydrazone had m.p. 136—137° (lit.,[27] 135—137°).

o-Trimethylsilylbenzophenone, b.p. 106°/0·25 mm., n_D^{25} 1·5714, was prepared analogously in 20% yield (Found: C, 75·5; H, 7·0: $C_{16}H_{18}OSi$ requires C, 75·5; H, 7·1%); the i.r. spectrum showed the very strong band at 1670 cm.$^{-1}$ expected for a diaryl ketone. Treatment with 2,4-dinitrophenylhydrazine gave a yellow solid of m.p. 227—228°, but this did not analyse correctly for the expected 2,4-dinitrophenylhydrazone.

o-*Trimethylsilylbenzoic acid*.—A few drops of a solution of *o*-chlorophenyltrimethylsilane (9·2 g., 0·050 mole) in tetrahydrofuran (15 ml.) were added to lithium strips (1·0 g., 0·14 g.-atom) in tetrahydrofuran (50 ml.) at room temperature. When reaction began the mixture was cooled to −45° and the remaining reactant solution was added during 30 min. The mixture was stirred at −45° for 6 hr. then filtered through glass wool and added to solid carbon dioxide. The usual work up procedure gave *o*-trimethylsilylbenzoic acid (60%), m.p. 99—100° (from aqueous EtOH) (lit.,[27] m.p. 99—100°).

o-*Trimethylsilyl*-NN-*dimethylaniline*.— *o*-Chloro-*NN*-dimethylaniline (6·8 g., 0·044 mole) was added during 30 min. to lithium strips (*ca.* 1 g.) in diethyl ether (25 ml.) kept at −7°. The mixture was kept at −7° for a further 1 hr., and was then heated under reflux for 15 min. Chlorotrimethylsilane (6·5 g., 0·060 mole) was added, and the mixture was heated under reflux for a further 30 min.; it was then set aside overnight, filtered, and fractionated to give o-*trimethylsilyl*-NN-*dimethylaniline* (1·7 g., 30%), 104°/20 mm., n_D^{25} 1·4998 (Found: C, 68·3; H, 10·0; N, 7·4. $C_{11}H_{19}NSi$ requires C, 68·3; H, 9·9; N, 7·25%). The i.r. spectrum showed the expected peaks, including a strong *ortho*-substitution pattern.

Formation of Biphenylene from o-*Bromoiodobenzene*.—*o*-Bromoiodobenzene (28·4 g., 0·10 mole) in diethyl ether (15 ml.) was added during 30 min. to chlorotrimethylsilane (10·8 g., 0·10 mole) and magnesium (3·0 g., 0·13 g.-atom) in ether (100 ml.). Reaction began after addition of the first few drops of the aryl halide. The mixture was heated under reflux for 1·5 hr., then filtered and added slowly to cold aqueous ammonium chloride. Separation, washing, drying (Na_2SO_4), and fractionation of the ethereal layer gave bromobenzene (1%), phenyltrimethylsilane (6·5%), *o*-chlorophenyltrimethylsilane (5·5%), *o*-bromophenyltrimethylsilane (2%), and biphenylene (18%), m.p. 112—114° (from ethanol) (Found: C, 94·6; H, 5·3. Calc. for $C_{12}H_8$: C, 94·7; H, 5·3%); the picrate had m.p. 125—126° (from MeOH) (lit.,[28] m.p. 122°). The identity of the product was confirmed by comparison of u.v., i.r. and n.m.r. spectra with published data.

A similar experiment but with omission of the chlorotrimethylsilane gave bromobenzene (10%), iodobenzene (8·5%), and biphenyl (9%), m.p. 70°.

With *o*-chlorophenyltrimethylsilane in place of chlorotrimethylsilane a mixture of biphenylene (*ca.* 6%) and biphenyl (*ca.* 6%) (analysed by g.l.c.) was obtained, along with 92% of unchanged *o*-chlorophenyltrimethylsilane.

Reaction of o-*Trimethylsilyl*-NN-*dimethylaniline and* p-*Trimethylsilylaniline with Methyl Iodide in Methanol*.—(*a*) A mixture of *o*-trimethylsilyl-*NN*-dimethylaniline (4·1 g., 0·025 mole), methanol (20 ml.), and iodomethane (10 ml.) was maintained at 30° for 24 hr. G.l.c. showed that no reaction had occurred, so the mixture was held at 30° for a further 3 weeks. Volatile materials were then removed under reduced pressure, and the residue was recrystallised from methanol to give phenyltrimethylammonium iodide (5·3 g., 80%), m.p. 226—227° (subl.) [lit.,[29] m.p. 228° (subl.)].

(b) A mixture of *p*-aminophenyltrimethylsilane (1·66 g., 0·01 mole),[30] methanol (15 ml.), and iodomethane (5 ml.) was heated under reflux for 20 hr., during which a deep red colour developed. G.l.c. with toluene as internal standard, showed that methoxytrimethylsilane had been formed quantitatively.

Rate Measurements.—The general spectrophotometric method has been described previously.[4,5] The reaction mixture was prepared by adding 3 vol. of aqueous sulphuric acid, of the concentration shown in Table 1, to 4 vol. of a solution of the arylsilane in anhydrous acetic acid. The spectra after 10 half-lives compared satisfactorily with those of authentic solutions of the expected cleavage products, except in the case of the *o*-t-butyl compound, which was known to contain inert di-t-butylbenzene. In this case also, however, the change in spectrum on cleavage was that expected for formation of t-butylbenzene.

For the measurements on *o*-trimethylsilylbenzene sulphonic acid, the trimethylsilyl ester was used. This is converted rapidly into the free acid in the reaction medium.

o- and *p*-Trimethylsilylaniline were found to be cleaved rapidly by acetic acid alone (no doubt because large proportions of the very reactive free amines were present), and so were dissolved directly in the reaction medium.

Rough values of 10^5k_{rel} of 2·5 and 15 were found for cleavage of the ketones $o\text{-}Me_3Si{\cdot}C_6H_4Ac$ and $o\text{-}Me_3Si{\cdot}C_6H_4Bz$ in a medium containing 19·0M-sulphuric acid. Corresponding rough values of 10^3k_{rel} in a medium containing 16·0M-acid were 1 and 2, respectively, for the *para*-isomers, and 10 and 3·5, respectively, for the *meta*-isomers.

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