# Aromatic Reactivity. Part LIX.[1] Substituent Effects of Groups of Type $CH_2Y$ in Acid Cleavage of *p*-$YCH_2{\cdot}C_6H_4SiMe_3$ Compounds and on the Charge-transfer Maxima of $YCH_2Ph$–Tetracyanoethylene Complexes

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The rates of cleavage of *p*-$YCH_2{\cdot}C_6H_4{\cdot}SiMe_3$ compounds by a mixture of acetic acid (4 vol.) and aqueous sulphuric acid (3 vol.) have been measured in order to provide information about the influence of substituents of the type *p*-$CH_2Y$ in electrophilic aromatic substitution; the rates at 50° relative to that for trimethyl(phenyl)silane, with, in parentheses, the approximate derived values of $\sigma^+$ for $CH_2Y$, are: (Y =) CN, 0·20 (+0·12); Br, 1·35 (−0·06); OH, 0·64 (+0·01); OMe, 1·27 (−0·05); OEt, 0·70 (0·00); $CO_2H$, 0·93 (−0·02); $CO_2Me$, 0·84 (−0·01); $NMe_2H^+$, 0·0043 (+0·50); $NMe_3^+$, 0·0042 (+0·50). The charge-transfer maxima for $YCH_2Ph$–tetracyanoethylene complexes have been determined for the Y groups mentioned above and also for Y = Cl and SH; the effects of the substituents are in accord with those on the cleavage, and the frequencies of the charge-transfer maxima are linearly related to the $\sigma_I$ constants for Y.

In spite of the numerous studies of effects of substituents in electrophilic aromatic substitutions, very little is known of the influences of groups of the type $CH_2Y$.[2] Knowledge of these influences has become more significant in recent years because of the interest in the *ipso*-effects of substituents Y, *i.e.*, the effect of Y on the ease of electrophilic attack at the carbon atom to which it is attached in PhY compounds.[3] The analogy between the stability of the Wheland intermediates of types (I) and (II), which can best be seen from the β-carbonium ion forms (Ia) and (IIa), was first pointed out for Y = $SiMe_3$,[4] but in so far as the stabilities of such intermediates parallel those of the relevant transition states the rates of *para*-substitution in $ArCH_2Y$ systems should provide a general guide to the ease of *ipso*-attack in ArY compounds.

In order to obtain direct information on the influence of $CH_2Y$ groups in an electrophilic aromatic substitution we have measured spectrophotometrically the rates of cleavage (desilylation) of a range of *p*-$YCH_2{\cdot}C_6H_4{\cdot}SiMe_3$ compounds. Furthermore, to provide another, rather

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[1] Part LVIII, B. Bøe, C. Eaborn, and D. R. M. Walton, *J. Organometallic Chem.*, 1974, **82**, 13.

[2] R. O. C. Norman and R. Taylor, 'Electrophilic Substitution in Benzenoid Compounds,' Elsevier, Amsterdam, 1965; R. Taylor in 'Comprehensive Chemical Kinetics,' eds. C. H. Bamford and C. F. H. Tipper, Elsevier, Amsterdam, 1972, vol. 13, ch. 1.

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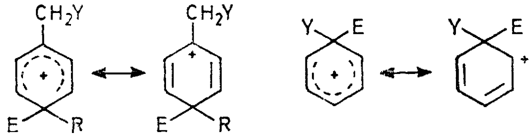
[4] R. W. Bott, C. Eaborn, and P. M. Greasley, *J. Chem. Soc.*, 1964, 4804 (see also H. J. Berwin, *J.C.S. Chem. Comm.*, 1972, 237; C. Eaborn, *ibid.*, p. 1255; C. Eaborn, T. A. Emokpae, V. I. Sidorov, and R. Taylor, *J.C.S. Perkin II*, 1974, 1454).

different, measure of the electronic effects of the groups we have examined the charge-transfer absorption maxima for $PhCH_2Y$-tetracyanoethylene (TCNE) complexes,[5] some of which have been studied previously.[6]



(I) (Ia) (II) (IIa)

A mixture of acetic acid (4 vol.) and aqueous sulphuric acid (3 vol.), was used for the cleavage studies.[7-9] The results are shown in Table 1, which lists the values of the observed first-order rate constants, $k$, and the value of the rate, $k_{rel}$, relative to that for trimethyl(phenyl)-silane. Also shown are the values of $\sigma^+$ derived by use of the relationship $\log k_{rel} + 0{\cdot}135 = -4{\cdot}47\sigma^+$, which applies satisfactorily to a large number of substituents ranging from the strongly electron-withdrawing $p$-$NO_2$ group to the mildly electron-releasing $p$-Me group.[7] (For more strongly electron-releasing groups use of the Yukawa–Tsuno equation is preferable.[9]) The features of the results are as follows. (*a*) The similarity of the rate constants for the compounds with Y = $NMe_2$ and $NMe_3^+$ shows clearly that the results for the former compound refer to the $CH_2NMe_2H^+$ group. (*b*) For Y = Br, OH, OMe, OEt, $CO_2H$, and COMe, electron withdrawal by Y roughly balances out electron release by the $CH_2$ entity, to give rates fairly close to those for trimethyl(phenyl)silane. (*c*) A plot of log $k_{rel}$ against $\sigma_I$[10,11] (not shown) is reasonably linear, except for the point for Y = $SiMe_3$. The $\sigma_I$ value for $SiMe_3$ would not be expected to provide a guide to the effect of the $p$-$CH_2SiMe_3$ group, which releases electrons strongly by a hyperconjugative mechanism.[12]

TABLE 1

Cleavage of $p$-$X{\cdot}C_6H_4{\cdot}SiMe_3$ compounds at 50·1° in a mixture of acetic acid (4 vol.) and 9·15M-aqueous sulphuric acid (3 vol.)

| X | $\lambda$/nm [a] | $10^5k$/s$^{-1}$ | $k_{rel}$ | $\sigma^+$ |
|---|---|---|---|---|
| H | 265 | 109 | 1·0 | −0·03 |
| $CH_2CN$ | 266 | 21·7 | 0·20 | +0·12 |
| $CH_2Br$ | 270 | 147 [b] | 1·35 [b] | −0·06 [b] |
| $CH_2OH$ | 263 | 70 | 0·64 | +0·01 |
| $CH_2OMe$ | 267 | 138 | 1·27 | −0·05 |
| $CH_2OEt$ | 268 | 76 | 0·70 | 0·00 |
| $CH_2CO_2H$ | 267·5 | 101 | 0·93 | −0·02 |
| $CH_2COMe$ | 260 | 92 | 0·84 | −0·01 |
| $CH_2NMe_2H^+$ | 273 | 0·47 | 0·0043 | +0·50 |
| $CH_2NMe_3^+$ | 274 | 0·46 | 0·0042 [c] | +0·50 |
| $CH_3$ | | | 18 [d] | −0·31 |
| $CH_2SiMe_3$ | | | 200 [d] | |

[a] Wavelength used to follow the progress of the reaction. [b] May be less accurate than other values; see Experimental section. [c] A value of 0·0050 was previously recorded.[8] [d] Ref. 7.

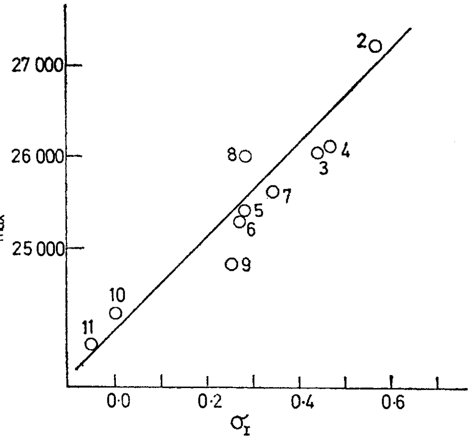
In Table 2 are shown the wavelengths and frequencies of the charge-transfer maxima determined for $PhCH_2Y$–TCNE mixtures in dichloromethane, along with values of $\sigma_p^+$ derived by use of equation (1).[5] However, since equation (1) yields a $\sigma_p^+$ value of −0·05 for H, the derived $\sigma_p^+$ values have been increased by 0·05 to give the 'corrected' values, $\sigma_p^+$ (corr.), listed. Even these values must be regarded as rough approximations, since the procedure gives a value of $\sigma_p^+$ (corr.) of −0·15 for the Me group, compared with the usual $\sigma_p^+$ value of −0·31.

TABLE 2

Charge-transfer maxima for PhX–TCNE complexes in dichloromethane at 30°

| No. | X | $\lambda_{max.}$/nm [a] | $\nu_{max.}$/cm$^{-1}$ | $\sigma_p^+$ [b] | $\sigma_p^+$(corr.) [c] |
|---|---|---|---|---|---|
| 1 | H | 388 | 25,800 | −0·05 | 0·00 |
| 2 | $CH_2CN$ | 368 | 27,200 | +0·11 | +0·16 |
| 3 | $CH_2Br$ | 384 | 26,000 | −0·02 | +0·02 |
| 4 | $CH_2Cl$ | 383 | 26,100 | −0·02 | +0·02 |
| 5 | $CH_2OH$ | 394 | 25,400 | −0·09 | −0·04 |
| 6 | $CH_2OMe$ | 396 | 25,300 | −0·10 | −0·05 |
| 7 | $CH_2CO_2H$ | 390 | 25,600 | −0·06 | −0·01 |
| 8 | $CH_2COMe$ | 385 | 26,000 | −0·02 | +0·03 |
| 9 | $CH_2SH$ | 404 | 24,800 | −0·15 | −0·10 |
| 10 | $CH_3$ | 412 | 24,300 | | |
| 11 | $CH_2CH_3$ | 417 | 24,000 | | |
| 12 | $CH_2SiMe_3$ | 493 [d] | 20,300 | | |

[a] In the cases for which values have been previously reported,[5,6] the agreement is excellent. [b] Values derived by use of equation (1). [c] Values corrected to give $\sigma^+$ 0·00 for H. [d] Ref. 5.



Plot of charge-transfer maxima (in cm$^{-1}$) for $YCH_2Ph$–TCNE complexes against $\sigma_I$ for Y. For the numbering of the points, see Table 2 (X = $CH_2Y$)

Except for Y = $SiMe_3$ (omitted), a plot of $\nu_{max.}$ for the $PhCH_2Y$–TCNE complexes against $\sigma_I$ is a fairly good straight line (see Figure) when the uncertainty in $\sigma_I$ is taken into account, and in view of the ease of measuring

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[5] W. Hanstein, H. J. Berwin, and T. G. Traylor, *J. Amer. Chem. Soc.*, 1970, **92**, 829.

[6] S. Hideki, *J. Org. Chem.*, 1970, **35**, 2807.

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[8] C. Eaborn and J. F. Jaggard, *J. Chem. Soc.* (*B*), 1969, 892.

[9] C. Eaborn and P. M. Jackson, *J. Chem. Soc.* (*B*), 1969, 21.

[10] S. Ehrenson, R. T. C. Brownlee, and R. W. Taft, *Prog. Phys. Org. Chem.*, 1973, **10**, 1.

[11] O. Exner, in 'Advances in Linear Free Energy Relationships,' eds. N. B. Chapman and J. Shorter, Plenum Press, London–New York, 1972, pp. 37—38.

[12] C. E. Eaborn, *J. Chem. Soc.*, 1956, 4858; W. Hanstein, H. J. Berwin, and T. G. Traylor, *J. Amer. Chem. Soc.*, 1971, **93**, 6278; T. G. Traylor, W. Hanstein, H. J. Berwin, N. A. Clinton, and R. S. Brown, *ibid.*, p. 5715; N. C. Cutress, A. R. Katritzky, C. Eaborn, D. R. M. Walton, and R. D. Topsom, *J. Organometallic Chem.*, 1972, **43**, 131; C. G. Pitt, *ibid.*, 1973, **61**, 49, and references therein.

$\nu_{max.}$ this plot offers a simple way of measuring approximate $\sigma_I$ values for Y groups. For a good number of the $CH_2Y$ substituents with which we are concerned a linear relationship between $\nu_{max.}$ and the aliphatic substituent constants $\sigma^*$ has been noted previously.[6]

As would be expected from the several relationships noted above, a plot of log $k_{rel}$ for the cleavage of the $p$-$YCH_2{\cdot}C_6H_4{\cdot}SiMe_3$ compounds against the $\nu_{max.}$ values for the charge-transfer complexes is also reasonably linear if the point for Y = $SiMe_3$ is omitted. The point would be expected to lie off the line, since relative to the balance of inductive and resonance effects reflected in $\sigma_p^+$ values, the charge-transfer frequencies overemphasise the resonance effects [*cf.* the $\sigma_p^+$ value of $-0.63$ derived for the $CH_2SiMe_3$ group by use of equation (1),[5] compared with the directly determined[13] value of $-0.54$], whereas the log $k_{rel}$ values in the cleavage underestimate them (as reflected in the value of 0·65 for $r$ in the Yukawa–Tsuno equation[9]).

TABLE 3

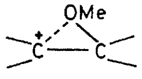
Substituent constants for $CH_2Y$ groups

| Y | $\sigma_I$ [a] | $\sigma_p^+$ (calc) [equation (2)] | $\sigma_p^+$ (calc) [equation (3)] | $\sigma_p^+$ (obs) [Table 1] | $\sigma_p$ (calc) [equation (4)] | $\sigma_p$ (calc) [equation (5)] | $\sigma_p$ (obs) [b] |
|---|---|---|---|---|---|---|---|
| CN | 0·56 | 0·14 | 0·07 | 0·12 | 0·17 | 0·18 | 0·18 |
| Br | 0·44 | 0·04 | 0·01 | −0·06 | 0·11 | 0·00 | |
| OH | 0·28 | −0·09 | −0·07 | 0·01 | 0·04 | 0·07 | |
| OMe | 0·27 | −0·08 | −0·07 | −0·05 | 0·04 | 0·01 | 0·03 |
| OEt | | | | 0·00 | | −0·06 | |
| $CO_2H$ | 0·34 | −0·04 | −0·04 | −0·02 | 0·06 | 0·04 | |
| COMe | 0·28 | −0·09 | −0·07 | −0·01 | 0·03 | 0·05 | |
| $NMe_2H^+$ | | | | 0·50 | | 0·56 | |
| $NMe_3^+$ | 0·99 | 0·48 | 0·29 | 0·50 | 0·39 | 0·56 | |

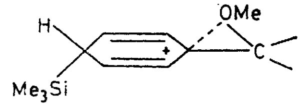
[a] Refs. 10 and 11. [b] Ref. 11, p. 28.

$$\nu_{max.} = (9300\sigma^+ + 26{,}200) \pm 500\ \text{cm}^{-1} \qquad (1)$$

The consistency between the effects of the $CH_2OMe$ group in the cleavage and on the charge-transfer maxima is noteworthy. It was conceivable that bridging, known to stabilise β-carbonium ions, as in (III), might operate to a detectable extent to stabilise the excess of positive charge developed at the *para*-carbon atom in the desilylation, as depicted in (IV). Such an effect cannot operate, however, in the vertical process which determines the charge-transfer maximum, and so it can also be ruled out for the desilylation.



(III)



(IV)

The relationships noted above imply that, except for groups with unusual resonance effects (as for Y = $SiMe_3$), $\sigma_p^+$ values for $CH_2Y$ substituents are linearly related to the $\sigma_I$ values for the groups Y, and the $\sigma_p^+$ values derived from the desilylation are, indeed, fairly consistent with relationships (2) and (2′), as Table 3 shows. The agreement between the observed and calculated $\sigma_p^+$ values for Y = $NMe_3^+$ may be fortuitous, since there is considerable uncertainty in using substituent constants for charged groups.

$$\sigma_p^+(CH_2Y) = \sigma_p^+(Me) + 0.8\sigma_I(Y) \qquad (2)$$

$$\sigma_p^+(CH_2Y) = -0.31 + 0.8\sigma_I(Y) \qquad (2')$$

A conceptually more attractive relationship of the form shown in equation (2) can be derived by assuming that the electronic effect of a $CH_2Y$ group is composed additively of the electron release by the $CH_2$ entity and the inductive effect of Y, as expressed by its $\sigma_I$ constant, attenuated by transmission through a saturated carbon atom. If we assume that the electron release by the $CH_2$ entity is two-thirds that by the $CH_3$ group, while the attenuation factor for the inductive effect is 0·5 (a value at the high end of the range normally assumed), we have equation (3). The $\sigma_p^+$ values derived by use of

$$\sigma_p^+(CH_2Y) = -0.21 + 0.5\sigma_I(Y) \qquad (3)$$

equation (3) are in fair agreement with the observed values except for the case of Y = $NMe_3^+$, and this could be because of the uncertainties attached to applying substituent constants to charged groups.

A reasonable extension of relationship (3) leads to equations (4) and (4′) for $\sigma_p$ constants.* Alternatively,

$$\sigma_p(CH_2Y) = 0.66\sigma_p(Me) + 0.5\sigma_p(Y) \qquad (4)$$

$$\sigma_p(CH_2Y) = -0.11 + 0.5\sigma_p(Y) \qquad (4')$$

more empirically, it can simply be assumed that the difference between the $\sigma_p$ and $\sigma_p^+$ constants for $CH_2Y$ groups is derived entirely from the effects of the C–H bonds, which leads to relationship (5).

$$\sigma_p(CH_2Y) = \sigma_p^+(CH_2Y) + 0.06 \qquad (5)$$

For the only two $CH_2Y$ groups for which $\sigma_p$ constants are available, equations (4) and (5) both lead to values in good agreement with experiment (Table 3). We suggest that, except possibly for the charged groups, the $\sigma_p$ values in Table 3 calculated by use of equation (5) will serve as approximations for analysis of substituent effects of $CH_2Y$ groups until direct experimental values are available.

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* March has proposed the relationship $\sigma_I(CH_2Y) = \sigma_I(Y)/(2.8 \pm 0.5)$.[14] This can easily be shown to be invalid (consider the case of Y = H), and we suspect it is based on a misunderstanding of conclusions reached by Taft and Lewis.[15]

[13] M. A. Cook, C. Eaborn, and D. R. M. Walton, *J. Organometallic Chem.*, 1973, **61**, 49.

[14] J. March, 'Advanced Organic Chemistry,' McGraw-Hill, New York, 1968, pp. 242—243.

[15] R. W. Taft and I. C. Lewis, *J. Amer. Chem. Soc.*, 1958, **80**, 2436.

## EXPERIMENTAL

p-*Trimethylsilylbenzyl Bromide*.—This compound, b.p. 76—80° at 1 mmHg, $n_D^{20}$ 1·5387 (lit.,[16] b.p. 125° at 10 mmHg, $n_D^{20}$ 1·5400), was prepared as described by Severson *et al.*[16] (Found: C, 49·0; H, 6·3. Calc. for $C_{10}H_{15}BrSi$: C, 49·4; H, 6·2%).

p-*Trimethylsilylbenzyl Cyanide*.—*p*-Trimethylsilylbenzyl bromide (12·2 g, 0·05 mol) was refluxed for 6 h with potassium cyanide (3·3 g, 0·05 mol) in ethanol (30 ml)–methanol (30 ml)–water (5 ml). The mixture was cooled and filtered. The filtrate was dried ($MgSO_4$), the solvent evaporated off, and the residual liquid fractionally distilled to give *p*-trimethylsilylbenzyl cyanide (5·7 g, 60%), b.p. 90° at *ca.* 0·2 mmHg, $n_D^{20}$ 1·5018 (lit.,[17] b.p. 125—127° at 5 mmHg) (Found: C, 69·6; H, 7·9; N, 7·2. Calc. for $C_{11}H_{15}NSi$: C, 69·8; H, 8·0; N, 7·4%).

p-*Trimethylsilylphenylacetic Acid and Methyl* p-*Trimethylsilylbenzyl Acetate*.—*p*-Trimethylsilylbenzyl cyanide (2·8 g, 0·014 mol) was refluxed with 20% w/w methanolic sodium hydroxide (20 ml) for 4 h. The solvent was evaporated off, and the residual solid was dissolved in aqueous 2M-sodium hydroxide (5 ml). The solution was evaporated to dryness, and the residual solid washed with ether and dried under vacuum. The solid was then dissolved in water, and the solution was acidified with 2N-hydrochloric acid. Ether extraction followed by drying ($MgSO_4$) and evaporation of the filtrate gave a solid, which was sublimed under reduced pressure to give *p*-trimethylsilylphenylacetic acid (2·5 g, 90%), m.p. 53—54° (lit.,[18] 40°) (Found: C, 63·3; H, 7·5. Calc. for $C_{11}H_{16}O_2Si$: C, 63·4; H, 7·8%).

The acid was treated with diazomethane in the usual way to give *methyl* p-*trimethylsilylphenylacetate* (77%), b.p. 45° at *ca.* 0·1 mmHg, $n_D^{20}$ 1·5001, $\tau$ ($CCl_4$) 2·50 (q, ArH), 6·26 (s, $OCH_3$), 6·35 (s, $CH_2$), and 9·60 (s, $SiMe_3$); $\nu_{max.}$ (liquid film), 1740 (C=O), 1249, 830, and 745 $cm^{-1}$ ($SiMe_3$) (Found: C, 65·1; H, 8·4. $C_{12}H_{18}O_2Si$ requires C, 64·8; H, 8·2%).

p-*Trimethylsilylbenzyl Alcohol*.—A mixture of *p*-trimethylsilylbenzyl bromide (8·0 g, 0·03 mol) in dioxan (150 ml) with sodium hydroxide (1·3 g, 0·03 mol) in water (50 ml) was refluxed for 3 h, the progress of the reaction being monitored by g.l.c. Evaporation of the solvent, followed by filtration and fractionation of the residual liquid, gave *p*-trimethylsilylbenzyl alcohol (3·0 g, 50%), b.p. 72—74° at *ca.* 0·1 mmHg, $n_D^{20}$ 1·5160 (lit.,[16] b.p. 139° at 16 mmHg, $n_D^{20}$ 1·5140) (Found: C, 66·3; H, 8·9. Calc. for $C_{10}H_{16}OSi$: C, 66·6; H, 9·0%).

*Methyl* p-*Trimethylsilylbenzyl Ether*.—Sodium (0·6 g, 0·025 g atom) was dissolved in methanol (100 ml) and *p*-trimethylsilylbenzyl bromide (6·0 g, 0·025 mol) was added. The mixture was refluxed for 1 h, and the solvent taken off at reduced pressure. The residue was extracted with ether, and the extract was dried and fractionated to give *methyl* p-*trimethylsilylbenzyl ether* (2·4 g, 58%), b.p. 50° at *ca.* 0·4 mmHg, $n_D^{20}$ 1·4990, $\tau$ ($CCl_4$) 2·6 (q, ArH), 5·6 (s, $CH_2$), 6·67 (s, $OCH_3$), and 9·79 (s, $SiMe_3$), $\nu_{max.}$ (liquid film) 1099 (C–O–C) and 1249, 838, and 751 $cm^{-1}$ ($SiMe_3$) (Found: C, 67·8; H, 9·1. $C_{11}H_{18}OSi$ requires C, 68·0; H, 9·35%).

p-*Trimethylsilylphenylmethanethiol*.—A mixture of sodium hydrogen sulphide (4·6 g, 0·08 mol) in methanol (50 ml) with *p*-trimethylsilylbenzyl bromide (10 g, 0·04 mol) was stirred at 50° for 4 h and then at room temperature overnight. The mixture was added to water (180 ml), and the solution made alkaline with 20% aqueous sodium hydroxide, then filtered. The filtrate was acidified with concentrated hydrochloric acid which had been precooled to −20°. Ether extraction, followed by drying ($MgSO_4$) and evaporation of the extract left a residue, which was fractionated to give p-*trimethylsilylphenylmethanethiol* (2·3 g, 29%), b.p. 76—78° at 0·5 mmHg, $n_D^{20}$ 1·5396, $\tau$ ($CCl_4$), 2·95 (q, ArH), 6·0 (d, $CH_2$), 7·55 (t, SH), and 10·0 (s, $SiMe_3$), $\nu_{max.}$ (liquid film) 2560 (SH), 1107 (Si–aryl), and 1250, 835, and 740 $cm^{-1}$ ($SiMe_3$) (Found: C, 60·9; H, 8·2. $C_{10}H_{16}SSi$ requires C, 61·2; H, 8·2%).

*Methyl* p-*Trimethylsilylbenzyl Sulphide*.—Methanethiol was passed into a solution of sodium ethoxide (3·4 g, 0·05 mol) in ethanol (30 ml) for 1 h and the solution was then refluxed to remove any excess of the thiol. *p*-Trimethylsilylbenzyl bromide (12 g, 0·05 mol) in ethanol (25 ml) was added during 1 h to the refluxing solution, and refluxing was subsequently continued for 1 h. The mixture was set aside at room temperature overnight, then filtered, and the solvent was evaporated from the filtrate. The residual liquid was fractionated to give *methyl* p-*trimethylsilylbenzyl sulphide* (9·2 g, 88%), b.p. 47° at *ca.* 0·1 mmHg, $n_D^{20}$ 1·4983, $\tau$ ($CCl_4$) 2·31 (q, ArH), 6·13 (s, $CH_2$), 7·85 (s, $SCH_3$), and 9·63 (s, $SiMe_3$) (Found: C, 62·6; H, 8·5. $C_{11}H_{18}SSi$ requires C 62·8; H, 8·65%).

*Phenyl and Ethyl* p-*Trimethylsilylbenzyl Ethers*.—Phenol (2·7 g, 0·03 mol) was dissolved in ethanol (25 ml) containing sodium ethoxide (0·03 mol). *p*-Trimethylsilylbenzyl bromide (6·3 g, 0·03 mol) was added, and the mixture refluxed for 1 h. Filtration, followed by evaporation of the solvent from the filtrate left a mixture of solid and liquid. The solid was filtered off and recrystallised from methanol to give *phenyl* p-*trimethylsilylbenzyl ether* (2 g, 26%), m.p. 104°, $\tau$ ($CCl_4$) 2·71 (m, ArH), 4·85 (s, $CH_2$), and 9·60 (s, $SiMe_3$) (Found: C, 74·95; H, 7·9. $C_{16}H_{20}OSi$ requires C, 74·95; H, 7·9%). The residual liquid was fractionated to give *ethyl* p-*trimethylsilylbenzyl ether* (2·5 g, 40%), b.p. 70° at *ca.* 0·5 mmHg, $n_D^{20}$ 1·4928 (Found: C, 69·4; H, 9·8. $C_{12}H_{20}OSi$ requires C, 69·2; H, 9·7%).

NN-*Dimethyl*-p-*trimethylsilylbenzylamine*.— n-Butyllithium (0·06 mol) in ether (50 ml) was treated with dimethylamine (2·7 g, 0·06 mol) at −10°, and the solution of lithium dimethylamide thus obtained was added dropwise with stirring to *p*-trimethylsilylbenzyl bromide (10 g, 0·06 mol) in ether (25 ml) at −25°. The mixture was allowed to attain room temperature then stirred for 3 h, and 1N-hydrochloric acid (250 ml) was gradually added. The aqueous layer was separated, neutralised with aqueous 2M-sodium hydroxide, and extracted with ether. The extract was dried, the ether evaporated off, and the residue fractionated to give NN-*dimethyl*-p-*trimethylsilylbenzylamine* (3·4 g, 27%), b.p. 50—54° at *ca.* 0·05 mmHg, $n_D^{20}$ 1·4986, $\tau$ ($CCl_4$) 2·65 (q, ArH), 6·62 (s, $CH_2$), 7·81 (s, $NMe_2$), and 9·73 (s, $SiMe_3$) (Found: C, 69·9; H, 10·4; N, 6·7. $C_{12}H_{19}Si$ requires C, 69·6; H, 10·2; N, 6·75%).

*Rate Studies*.—The method used has been described previously;[7-9] runs of half-life $<30$ min were conducted in a thermostatted absorption cell, but sealed ampoules in a thermostat bath were used for slower runs. Good first-order plots were obtained for at least 80% completion of the reaction for the compounds listed in Table 1, and rate constants were reproducible to within 4%. However, for

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[16] R. G. Severson, R. J. Rosscup, D. R. Lindberg, and R. D. Engberg, *J. Amer. Chem. Soc.*, 1957, **79**, 6540.

[17] Lin Tzu-sun, Wu Shih-Leui, Hsu Lin-yuen, and Yu Tung-yin, *Acta Chimica Sinica*, 1960, **26**, 7 (*Chem. Abs.*, 1961, **55**, 18,654).

[18] B.P. 1,108,848/1968 (*Chem. Abs.*, 1968, **69**, 52,283p).

$p$-$Me_3Si{\cdot}C_6H_4{\cdot}CH_2Y$ with Y = Br, the optical density after 10 half-lives drifted slowly (the same effect was observed with a sample of benzyl bromide in the same medium), and so the rate constant for this compound must be regarded as less accurate than the others. For the compounds with Y = SH and SMe, the first-order plots were seriously curved, no doubt because of reactions at the functional groups, and no satisfactory rate constants were derived. (The optical density of a solution of phenylmethanethiol in the reaction medium was found to change gradually.) For the compound with Y = $NMe_2$, an initial rapid rise of optical density in the 260—290 nm region occurred on mixing the sulphuric acid with the acetic acid solution of the organosilane, but this was followed by the gradual fall on which the reported rate constant is based. For measurements on the system with Y = $NMe_3^+$ the iodide $p$-$Me_3Si{\cdot}C_6H_4{\cdot}CH_2{\cdot}NMe_3^+I^-$ was used.

*Charge-transfer Spectra.*—Appropriate volumes of the PhX compound were added from a microsyringe to 0·05M solutions of triply sublimed tetracyanoethylene in dichloromethane. The charge-transfer maxima did not change on variation of the concentration of the aromatic compounds.

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