ORGANOSILICON COMPOUNDS
XXXIII[*]. ADDITIONAL SUBSTITUENT EFFECTS IN ALKALI CLEAVAGE OF BENZYLTRIMETHYLSILANES

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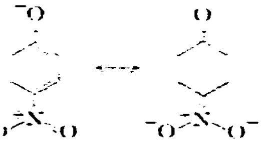
INTRODUCTION

The cleavage of some benzyltrimethylsilanes, $\mathrm{XC_6H_4CH_2SiMe_3}$, by sodium hydroxide in 39 wt-% water in methanol [eqn. (1), M = H or Me] was examined by Eaborn and Parker[1], who found that the effects of the substituents studied correlated

$$\mathrm{MOH} + \mathrm{XC_6H_4CH_2SiMe_3} \longrightarrow \mathrm{XC_6H_4CH_3} + \mathrm{MOSiMe_3} \qquad (1)$$

well with the Hammett substituent constants, provided that the σ^--constant was used for the p-$\mathrm{NO_2}$ group, the one substituent used for which this constant differs significantly from the σ-constant. Since there are few types of reaction in which use of σ^--constants are required, it was of interest to extend the range of substituents studied, and a number of new $\mathrm{XC_6H_4CH_2SiMe_3}$ compounds have been prepared and subjected to cleavage in the medium used by Eaborn and Parker.

Use of σ^--constants was originally proposed to cover the effects on strengths of phenols, $\mathrm{XC_6H_4OH}$, or anilines, $\mathrm{XC_6H_4NH_2}$, of some *para*-substituents such as p-$\mathrm{NO_2}$ and p-CN which can interact conjugatively with the lone-pairs of electrons on the oxygen and nitrogen atom [*cf.* (I) and (II)][2,3]. It is not surprising that use of σ^--constants should also be necessary in analysing the rates of cleavage of benzyltrimethylsilanes, because the large value of ρ (*viz.*, 4.9) indicates that the benzylic carbon atom has substantial carbanion character in the rate-determining transition state[1,4], and resonance interactions of the type indicated by structures (III) and (IV) could be expected. It has since been shown that σ^--constants can be applied satis-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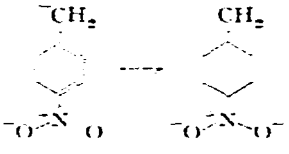
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factorily to nucleophilic aromatic substitutions[5], for many of which the values of ρ are similar to that in the cleavage under discussion[3]. For those reactions, however, it seems that some electron-releasing *para*-substituents such as *p*-Me and *p*-OMe, have rate-retarding effects much greater than expected from the σ-constants, and special constants, σ^{--}-constants, have been proposed in these cases for use in nucleophilic aromatic substitutions[5].

RESULTS AND DISCUSSION

The results are shown in Table 1 as specific first-order rate constants, k_s ($k_s = k/[\text{NaOH}]$ where k is the observed first-order rate constant at the alkali concentration used); as previously observed[1], values of k_s are independent of the alkali concentration except for charged substituents. It should be noted that the temperature of the measurements, *viz.*, 50.4°, was somewhat higher than that used in the earlier work[1], (*viz.*, 49.7°) but this difference would not significantly alter the plots or the conclusions below, and is ignored in subsequent discussions.

TABLE 1

CLEAVAGE OF $XC_6H_4CH_2SiMe_3$ BY ALKALI IN 39 WT-% WATER–METHANOL AT 50.4°.

X	$10^5 k_s$[a] (*min*$^{-1}$·*mole*$^{-1}$·*l*)	λ[b] (*mµ*)	*X*	$10^5 k_s$[a] (*min*$^{-1}$·*mole*$^{-1}$·*l*)	λ[b] (*mµ*)
H	3.25[c]	274.5	*m*-CF_3	3.33×10^2	279
o-F	5.1×10	275	*o*-SO_2NH^-	3.62×10^2	280
m-SO_2NH^-	9.8×10	283	*o*-I	4.5×10^2	282.5
p-I	1.19×10^2	250	*p*-SO_2NH^-	1.74×10^3	257
m-SO_3^-	1.20×10^2	281.5	*p*-SO_3^-	2.14×10^3	250
m-F	1.29×10^2	273	*m*-SO_2NMe_2	3.08×10^3	284
o-SO_3^-	1.36×10^2	281	*p*-SO_2NMe_2	1.71×10^5	260.5
m-Cl	1.86×10^2[d]	279.5	*p*-COMe	3.45×10^5	313
m-I	2.23×10^2	283	*p*-SO_2Ph	4.9×10^5	280
m-Br	2.26×10^2	272.5	*p*-COPh	5.3×10^5	320
o-Br	3.16×10^2	280			

[a] Measured at [NaOH] = 0.98 *M*, except for (X =) *p*-SO_3^- (0.96 *M*); *p*-COPh, *p*-COMe, *p*-SO_2Ph (0.0098 *M*); and *p*-SO_2NMe_2 (0.098 *M*). [b] Wave-lengths used in rate measurements. [c] Previously recorded[1], $10^5 k_s = 2.90$ min^{-1}·mole^{-1}·l at 49.7°. [d] Previously recorded[1], $10^5 k_s = 1.83 \times 10^2$ min^{-1}·mole^{-1}·l at 49.7°.

Figure 1 shows a plot of log k_s against σ and σ^-; some results from the earlier work[1] are included. It will be seen that σ-constants give an excellent plot for *meta*-substituents and for X = H, *p*-Cl, *p*-Br, *p*-I, and *p*-Me, but points for substituents with —*T* effects fall badly off the line*. When σ^--constants are used for such substituents a greatly improved plot is obtained. The points for the *p*-SO_2Ph and *p*-SO_2NMe_2 groups, for which the σ^--constants are derived from nucleophilic aromatic substitutions[5], fall reasonably close to the line, but the points for all three *p*-COX substituents, for which the σ^--values were similarly derived, fall away from the line

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* No points are included for charged substituents, since the rates depend on the ionic strength (*cf.* ref. 6), and also since low log *A* factors would be expected for reactions between anions.

The values of σ used for the *m*-CONHPh and *p*-SO_2Ph groups are actually those for *m*-$CONH_2$ and *p*-SO_2Me, respectively[2,7].

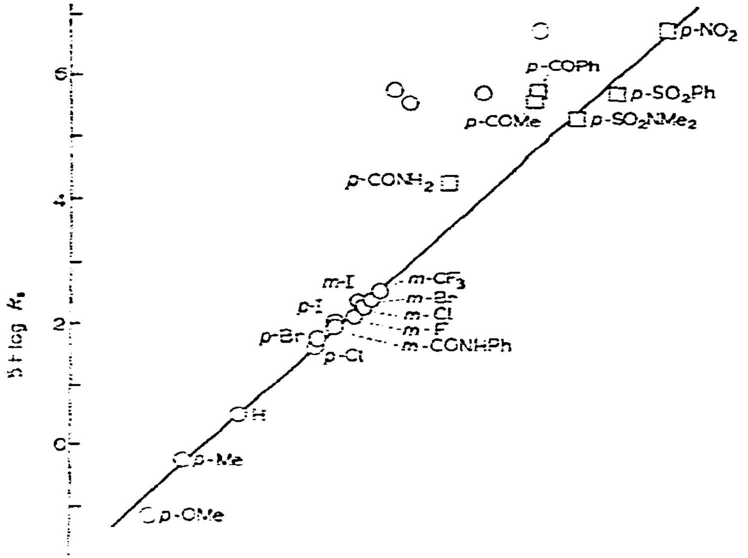

Fig. 1. Plot of log k_s *vs.* σ (circles) or σ^- (squares).

in the direction indicating that their —*T* effects operate more strongly than in nucleophilic aromatic substitution. (The *p*-CO_2^- group also activates much more than would be expected from its influence in nucleophilic aromatic substitution, even after generous allowance has been made for the ionic strength effect; a low log *A* factor for the substituent would be common to the cleavage and the aromatic substitutions.) Possibly the effects of the *p*-COX group are more sensitive to electron demand than those of *p*-SO_2X and *p*-NO_2 groups, but there is no evidence for this from the influence of the *p*-CHO group on the strength of phenols and amines and in nucleophilic aromatic substitutions (*cf.* Table XVI, ref. 3). The orders of activation by *p*-COX and *p*-SO_2X groups, *viz.*, $CO_2^- < CONH_2 < CONHPh < COMe < COPh$, and $SO_2NH^- < SO_3^- < SO_2NMe_2 < SO_2Ph$, are in accord with those noted and explained by Heppolette and Miller for nucleophilic aromatic substitution[5]. (Although, in fact, they found the order $SO_2NH^- > SO_3^-$, they noted that this was anomalous, and suggested that it might arise from incomplete ionization of the sulphonamide in their medium.)

It is noteworthy that use of the σ-constant is satisfactory for the *p*-Me group, contrary to what was found for nucleophilic aromatic substitution[5]. While the rate constant for the compound with X = *p*-OMe is only approximate, it is likely that the rate is somewhat lower than would be expected from the σ-constant for the group but much greater than that expected from the σ^--constant ($\sigma^- = -0.6$)*.

Values of σ^--constants calculated from the relationship, $\log k_s = 4.88\,\sigma^- - 4.49$, are given in Table 2.

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* It is significant that the *p*-F group deactivates in the cleavage of the benzyltrimethylsilanes[9], as in the analogous cleavage of benzyltrimethylstannanes[4]. This accords with its effect in nucleophilic aromatic substitution. It is difficult to see by what mechanism the *p*-F and *p*-OMe groups, and possibly the *p*-Me group, supply electrons more strongly than normal in reactions with a strong electron demand.

TABLE 2

SOME VALUES OF σ AND σ^-

X	σ	σ^-	σ^- (*calcd.*)
p-NO_2	0.778	1.27^a	—
p-$CONH_2$	—	0.627	0.765
p-CONHPh	—	—	0.78
p-COMe	0.502	0.874	1.03
p-COPh	0.459	$0.879^{b,c}$	1.07
p-SO_2NMe_2	—	0.995^b	0.965
p-SO_2Ph	—	1.117^b	1.06
(p-OMe)	(−0.268)	$(-0.6)^b$	(−0.35)

[a] Ref. 2. [b] Value from nucleophilic aromatic substitution[5]. [c] A value of 0.95 has been derived from NMR chemical shifts of amino protons in anilines[10].

TABLE 3

VALUES OF σ FOR *ortho*-SUBSTITUENTS

X	σ (*calcd.*)	σ^a	σ^b
o-F	0.245	0.06	0.24
o-Cl	0.38	0.21	0.20
o-Br	0.41	0.20	0.21
o-I	0.44	—	0.21
o-NO_2	1.15^c	0.76	0.80
o-CONHPh	0.55^c	—	—

[a] From ionization constants of o-substituted benzoic acids[12]. [b] Derived from $[\log (k_X/k_H)_B - \log (k_X/k_H)_A]$, where the k's are rate constants for base- and acid-catalysed hydrolyses of o-substituted ethyl benzoates[13]. [c] Presumably values of σ_0^-.

All the *ortho*-substituents activate more than would be expected from the σ_0-constants for the substituents for which they are available (*cf.* ref. 11), which supports the view[1] that steric hindrance by *ortho*-substituents must be relatively small. In reactions such as the cleavage under consideration, "exalted" constants, σ_0^-, would presumably be required for substituents such as o-NO_2. Values of σ_0 calculated for the cleavage using the ρ-value of Fig. 1 are given in Table 3, and compared where possible with values derived from some other selected reactions[11–13]. (For a more complete list see ref. 11, 12, 13.)

The activating effect of *ortho*- and *para*-halogen atoms is in the order F < Cl < Br < I: the same order applies to the *meta*-halogens, except that in this case the effects of bromine and iodine are indistinguishable.

Analogy to base-catalysed α-hydrogen exchange in toluenes

Streitwieser and Koch recently studied hydrogen exchange in the methyl group of various mono-substituted toluenes[14] catalysed by cyclohexylcarboxamide in cyclohexylamine. They found that rates correlated well with σ-constants, and suggested that the large value of ρ, *viz.*, 4.0, is consistent with a substantial formation of the benzyl carbanion in the transition state.

There is a close analogy between cleavages of C–H bonds and those of C–Si bonds[15], and it is not surprising to find that there is a marked similarity between the alkali cleavage of benzyl–silicon and that of benzyl–hydrogen bonds, and that for the few substituents in common there is a good linear free energy relationship between the two reactions. At first sight it might seem surprising that the value of ρ for the hydrogen exchange is smaller than that for the cleavage. In a given medium, ρ would be expected to be larger for the exchange, which is much the slower reaction, and for which carbanion separation would be expected to have progressed further in the transition state. An explanation of the lower ρ in the exchange is that a very much stronger base was employed than in the cleavage, and because of the high reactivity of the nucleophile the transition state is closer to the reactants than it is for the cleavage.

The *p*-F group deactivates in the exchange[14], as was to be expected from the results for cleavage of benzyltrimethyl-silanes and -stannanes[4,9]. It can be predicted with some confidence that σ^--constants would be needed to interpret effects on the hydrogen exchange of *para*-substituents to which such constants are applicable.

The relative rates of base-catalysed hydrogen exchange at R–H bonds are rightly taken to provide a measure of the relative acidities of the R–H compounds[14]. The rates of alkali-cleavage of the analogous R–SiMe$_3$ or R–SnMe$_3$ bonds, usually much easier to determine, can probably also be taken to be a rough measure of the acidity of the RH compounds, in the sense that they are a measure of the stabilities of the carbanion R$^-$ (*cf.* refs. 1, 4, 16, 17).

EXPERIMENTAL

Preparation of substituted benzyltrimethylsilanes

m- and p-XSO$_2$C$_6$H$_4$CH$_2$SiMe$_3$ and XCOC$_6$H$_4$CH$_2$SiMe$_3$ compounds. With the exceptions noted below, these were prepared by T. HASHIMOTO[18].

(o-, m- and p-Iodobenzyl)trimethylsilane. To the organolithium reagent made from (*p*-chlorobenzyl)trimethylsilane (82 g, 0.415 mole) and lithium (7 g, 1.0 g-atom) in ether, and subsequently filtered, a solution of iodine in ether (105 g, 0.415 mole, in 500 ml) was added dropwise until the brown colour persisted. (About 35 ml of solution remained unused.) The mixture was added to ice–water and the ether layer was washed with aqueous sodium sulphite and then water, and was dried (Na$_2$SO$_4$) and fractionated, to give (*p*-iodobenzyl)trimethylsilane (96 g, 79 %), b.p. 93–94°/1 mm, n_D^{25} 1.5598. (Found: C, 41.6; H, 5.3. C$_{10}$H$_{15}$ISi calcd.: C, 41.4; H, 5.2 %.)

Similarly prepared in 76 and 28 % yield, respectively, were the *meta*-isomer, b.p. 99°/3 mm, n_D^{25} 1.5566 (Found: C, 41.8; H, 5.1 %.), and *ortho*-isomer, b.p. 103°/4 mm, n_D^{25} 1.5600. (Found: C, 41.0; H, 5.2 %.)

(o- and m-Bromobenzyl)trimethylsilane. By a method analogous to that used for the iodo-compounds, above, but with use of a solution of bromine in light petroleum, were obtained (*o*-bromobenzyl)trimethylsilane (5 %), b.p. 80–81°/3.5 mm. n_D^{25} 1.5275 (Found: C, 50.1; H, 6.1. C$_{10}$H$_{15}$BrSi calcd.: C, 49.4; H, 6.2 %.), and its *meta*-isomer (70 %), b.p. 79°/2 mm, n_D^{25} 1.5250. (Found: C, 50.1; H, 6.0 %.)

(o- and m-Fluorobenzyl)trimethylsilane. Chlorotrimethylsilane (56.0 g, 0.52 mole) in ether (100 ml) was added dropwise during 45 min to the Grignard reagent from *o*-fluorobenzyl bromide (81.3 g, 0.43 mole) and magnesium (11.5 g, 0.47 g-atom) in ether (150 ml), and the residue was refluxed for 18 h. Saturated aqueous ammonium

chloride was added, and the ethereal layer was separated, washed, dried (Na_2SO_4), and fractionated to give (*o*-fluorobenzyl)trimethylsilane (56 g, 72 %), b.p. 75°/15 mm, n_D^{25} 1.4789. (Found: C, 66.3; H, 8.3. $C_{10}H_{15}FSi$ calcd.: C, 65.9; H, 8.3 %.)

The *meta*-isomer, b.p. 83°/18 mm, n_D^{25} 1.4770, was prepared analogously in 80 % yield. (Found: C, 66.5; H, 8.2 %.)

[m-(Trifluoromethyl)benzyl]trimethylsilane. A mixture of chlorotrimethylsilane (47 g, 0.40 mole) in ether (50 ml) and the Grignard reagent from *m*-(trifluoromethyl)-benzyl bromide (82 g, 0.34 mole) and magnesium (9.7 g, 0.40 g-atom) in ether (250 ml), was refluxed for 27 h. The usual working up, as above, gave [*m*-(trifluoromethyl)-benzyl]trimethylsilane (56.5 g, 71 %), b.p. 63.5/5 mm, n_D^{25} 1.4455. (Found: C, 57.0; H, 6.2, F, 24.5. $C_{11}H_{15}F_3Si$ calcd.: C, 56.8; H, 6.5; F, 24.5 %.)

N,N-Dimethyl-x-[(trimethylsilyl)methyl]benzenesulphonamide. A mixture of *m*-[(trimethylsilyl)methyl]benzenesulphonyl chloride (13.2 g, 0.05 mole), 25 % aqueous dimethylamine (50 ml, 0.3 mole of amine), and benzene (50 ml) was shaken for 5 min. The benzene layer was separated, washed with water, and dried (Na_2SO_4), and the benzene was evaporated to leave N,N-dimethyl-*m*-[(trimethylsilyl)methyl]benzenesulphonamide (13.5 g, 100 %), m.p. 98–102°. Recrystallisation from aqueous ethanol, then from light petroleum gave material of m.p. 108–109°. (Found: C, 52.9; H, 8.0; N, 5.3. $C_{12}H_{21}NO_2SSi$ calcd.: C, 53.1; H, 7.8; N, 5.2 %.)

The *para*-isomer, m.p. 112–112.5°, was prepared analogously. (Found: C, 53.1; H, 7.5; N, 4.9 %.)

p-[(Trimethylsilyl)methyl]benzenesulphon-amide and -anilide. The amide, m.p. 81°, and anilide, m.p. 124–125°, were prepared by Bygden's method[19].

Cleavage products

Cleavage products were identified by examination of the ultraviolet spectra after 10 half-lives, and also, in some selected cases, by isolation as follows.

(*a*) A solution of [*m*-(trifluoromethyl)benzyl]trimethylsilane (15 g, 0.065 mole) and potassium hydroxide (20 g) in 95 % ethanol (100 ml) was boiled for 14 h. The mixture was added to water, and ether extraction followed by washing, drying (Na_2SO_4), and fractionation of the ethereal layer gave *m*-(trifluoromethyl)toluene (8 g, 78 %), b.p. 128°, n_D^{25} 1.4235 (lit.[20] b.p. 127°, n_D^{25} 1.4254).

(*b*) Analogously, from (*o*- and *m*-iodobenzyl)trimethylsilane, respectively, *o*-iodotoluene, b.p. 82°/10 mm, n_D^{25} 1.6031, and *m*-iodotoluene, b.p. 87°/13 mm, n_D^{25} 1.6000, were obtained in 74 and 78 % yield.

(*c*) A solution of 4-[(trimethylsilyl)methyl]diphenyl sulphone (2.0 g) in 4 *M* ethanolic potassium hydroxide (25 ml) was refluxed for 2.5 h then added to water. After some hours in a refrigerator the mixture was filtered, and the solid obtained was recrystallised from ethanol to give 4-methyldiphenyl sulphone (1.1 g, 73 %), m.p. 128° (lit.[21] m.p. 124.5°).

Rate measurements

The methods previously employed[1] were used, except that (*a*) for runs of half-life less than 6 h reaction samples were contained in a stoppered cell in a thermostatted holder in the spectrophotometer, and (*b*) "infinity" values of the optical density were experimental values, taken after 10 half-lives, rather than values measured on synthetic mixtures of cleavage products.

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SUMMARY

We have prepared a range of new substituted benzyltrimethylsilanes, XC_6H_4-CH_2SiMe_3, and measured the rates of their cleavage by alkali in 39 wt-% water in methanol at 50.4°. The results for the *meta*-substituents, and for $X = p$-Cl, *p*-Br and *p*-I, correlate well with the Hammett substituent constants, σ, but for the groups, *p*-NO_2, *p*-SO_2Ph, *p*-SO_2NMe_2, *p*-COMe, and *p*-COPh, σ^--values must be used. There is a similarity between the observed substituent effects and those in nucleophilic aromatic substitution.

An analogy between the cleavage and the base-catalysed hydrogen exchange at the α-position of substituted toluenes is discussed.

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