Organosilicon Compounds. Part XI. The Alkali-catalysed Cleavage of Substituted Benzyltrimethylsilanes.*

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The kinetics of the alkali-catalysed cleavage of substituted benzyltrimethylsilanes in aqueous methanol have been studied spectrophotometrically. The reaction is markedly facilitated by electron-withdrawing substituents in the benzyl group, and the effects of substituents agree well with their Hammett σ constants. The simplest mechanism consistent with the experimental facts is of the synchronous bimolecular (S_N2) type.

There are several examples in the literature of the breaking of $Si{-}CH_2{\cdot}C_6H_4X$ bonds by aqueous or aqueous-alcoholic alkali (*e.g.*, Kipping, *J.*, 1908, **93**, 457; Kipping and Steele, *J.*, 1928, 1431; Bygdén, *J. prakt. chem.*, 1917, **96**, 86; Benkeser and Brumfield, *J. Amer. Chem. Soc.*, 1951, **73**, 4770). The benzyl group itself is cleaved from silicon less readily than triphenylmethyl, 9-fluorenyl, and diphenylmethyl groups but markedly more readily than phenyl and alkyl groups (Hauser and Hance, *ibid.*, p. 5846; Gilman, Brook, and Miller, *ibid.*, 1953, **75**, 4531). We now report the first kinetic study of the alkaline cleavage of C–Si bonds, having examined spectrophotometrically the cleavage of seventeen benzyltrimethylsilanes, $X{-}C_6H_4{\cdot}CH_2{\cdot}SiMe_3$, by aqueous-methanolic alkali (*i.e.*, $X{\cdot}C_6H_4{\cdot}CH_2{\cdot}SiMe_3 + HOY \xrightarrow{OY^-} X{\cdot}C_6H_4{\cdot}CH_3 + YO{\cdot}SiMe_3$, where $Y = H$ or Me).

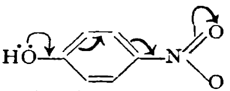
Kinetic Results.—The cleavages are of first order within a run since the concentration of alkali remains constant, and the rate-constant, k_1, at a fixed alkali concentration is independent of the initial concentration of silane. The reaction is also of first order in alkali, since the specific rate constant k_s ($= k_1/[MOH]$) is independent of the alkali concentration [MOH], as the following example shows. The figures refer to the cleavage of *p*-(trimethylsilylmethyl)benzanilide (initially 10^{-3}M) in 39 wt.-% aqueous methanol at 49·7°.

$10^3 \times$ [NaOH], (M)	971	728	486	243	121	60·7
10^4k_1 (min.$^{-1}$)	1970	1430	990	496	233	123
10^3k_s (min.$^{-1}$ mole^{-1} l.)	203	196	204	204	193	203

However, the cleavage of the anions $Me_3Si{\cdot}CH_2{\cdot}C_6H_4{\cdot}CO_2^-$ involves reaction between two negative ions, and the first-order specific rate constant rises markedly with increasing ionic strength, as shown by the following data for the *para*-isomer in 5 wt.-% water–methanol at 49·7°:

[NaOH] (M)	1·023	0·869	0·767	0·526	0·396	0·130
10^3k_s (min.$^{-1}$ mole^{-1} l.)	3·26	3·02	2·83	2·53	2·23	1·67

Table 1 shows the specific rate constants k_s for a particular alkali concentration, the Arrhenius activation energies E, and the log A factors, where $k_s = A\exp(-E/\boldsymbol{R}T)$.

para- *and* meta-*Substituents*.—The order of ease of cleavage of the *m*- and *p*-$X{\cdot}C_6H_4{\cdot}CH_2{\cdot}SiMe_3$ compounds may be seen from Table 1, and the reaction is very clearly facilitated by electron-withdrawal in X. The following table of deviations shows that when log k_s is plotted against the Hammett σ constants for the substituents (Jaffé, *Chem. Reviews*, 1953, **53**, 191) the points lie well about a straight line of slope 4·88 through the point for $X = p\text{-}NO_2$, provided that the σ^* constant is used for the p-NO_2 group. The σ^* constant (see Jaffé, *loc. cit.*) represents the effect of a substituent *para* to a phenolic or amino-group, when resonance interaction of the type  enables the substituent to withdraw electrons more effectively than the simple σ constant would require.

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* Part X, *J.*, 1954, 4266.

Neglecting the *p*-MeO point, for which the rate constant used is only approximate (see p. 131), the standard deviation from the line of the σ value for the six substituents with well-established σ constants (H, *p*-Me, *p*-Cl, *p*-Br, *m*-Cl, *p*-NO$_2$) is only 0·014 (mean deviation, 0·009), and if all the points (except X = *p*-CO·NH$_2$, see below) are included for which Jaffé lists σ or, where appropriate, σ* values the standard deviation is still only 0·045. The high value of the Hammett ρ constant, given by the slope of the line, reflects the high sensitivity of the reaction to polar influences in the benzyl group.

TABLE 1. *Cleavage of* X·C$_6$H$_4$·CH$_2$·SiMe$_3$ *by alkali in* 39 *wt.-% water–methanol at* 49·7°.

X	λ (mμ)	[NaOH] (M)[a]	k_s[b]	E (cal.)	log A[i]
p-NO$_2$	315	7·4 × 10^{-3}	52·6[c]	13·7[e]	8·84
o-NO$_2$	330	7·4 × 10^{-3}	14·1[c]	13·7[e]	8·30
p-CO·NHPh	301	0·13	0·201	18·4[f]	11·72
p-CO·NH$_2$	256	0·13	0·183	—	—
o-CO·NHPh	305	0·98	1·53 × 10^{-2}	23·9[f]	14·37
p-CO$_2^-$	255	0·97	9·40 × 10^{-3}	19·7[f]	11·32
o-Cl	230	0·97	2·26 × 10^{-3}	—	—
m-Cl	230	0·97	1·83 × 10^{-3}	28·2[d, g]	16·5[d]
m-CO·NHPh	221	0·97	9·1 × 10^{-4}[d]	—	—
p-Br	240	1·0	5·61 × 10^{-4}	—	—
p-Cl	230	0·97	4·03 × 10^{-4}	25·9[g]	14·14
p-Me$_3$Si	235	1·0	2·80 × 10^{-4}	29·3[g]	16·25
o-CO$_2^-$	285	0·97	1·39 × 10^{-4}	22·9[h]	11·61
m-CO$_2^-$	292·5	0·98	5·95 × 10^{-5}	21·5[h]	10·32
H	275	0·96	2·90 × 10^{-5}	29·5[g, d]	15·43[d]
p-Me	230	1·0	5·6 × 10^{-6}[d]	—	—
p-MeO	234	1·0	~7 × 10^{-7}[d]	—	—

[a] Approximate alkali concentration at which listed specific rate was measured. [b] Specific rate constant (k_1/[NaOH]) in min.$^{-1}$ mole^{-1} l. [c] By extrapolation from measurements at 25° (k_s = 8·7 and 2·34 min.$^{-1}$ mole^{-1} l. for the *p*- and the *o*-compound, respectively) and 35°. [d] Less accurate than other data. [e] From measurements at 25° and 35°. [f] From measurements at 50°, 40°, and 30°. [g] From measurements at 50° and 40°. [h] From measurements at 53°, 45°, and 40°. [i] Calc. on basis of time in minutes.

TABLE 2. *Deviations from Hammett* log k_s–σ *plot* (ρ = 4·88).

X	*p*-NO$_2$	*p*-CO·NHPh	*p*-CO·NH$_2$	*p*-CO$_2^-$	*m*-Cl	*m*-CO·NH$_2$Ph	*p*-Br
− log k_s	−1·721	0·697	0·738	2·027	2·737	3·041	3·251
σ, calc.	1·270	0·786	0·766	0·50	0·357	0·294	0·250
σ (or σ*)	1·270	—	(0·627)	—	0·373	0·280[a]	0·232
σ (calc.) − σ	0·000	—	(+0·139)	—	−0·016	+0·014	+0·018

X	*p*-Cl	*p*-Me$_3$Si	*m*-CO$_2^-$	H	*p*-Me	*p*-MeO
− log k_s	3·395	3·553	4·225	4·538	5·252	6·155
σ, calc.	0·222	0·190	0·051	0·015	−0·159	−0·344
σ (or σ*)	0·227	0·09[b]	0·104	0·000	−0·170	−0·268
σ (calc.) − σ	−0·005	+0·10	−0·053	+0·015	+0·011	−0·076

[a] Is actually σ for *m*-CO·NH$_2$. [b] σ* value, from Benkeser and Brumfield (*J. Amer. Chem. Soc.*, 1953, **75**, 2421).

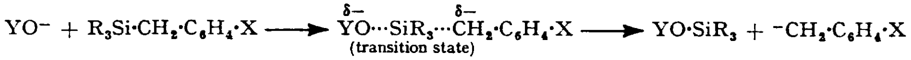
The deviation of the *p*-CO·NH$_2$ point from the line is only apparent since the σ* value for this group is derived from only one reaction and is subject to a standard deviation of 0·201. Our results indicate σ* values for *p*-CO·NH$_2$ and *p*-CO·NHPh of 0·766 and 0·786, respectively (the rates of cleavage are very close for these two substituents, with that for *p*-CO·NHPh slightly the greater, as expected in view of the electron-withdrawing effect of the phenyl group). The σ* value used for the *m*-CO·NHPh group is actually that for *m*-CO·NH$_2$; no doubt the σ* value for *m*-CO·NHPh should be slightly greater than this, and our results indicate a value of +0·29.

There is no σ* value for the *p*-CO$_2^-$ group, and use of the σ value (+0·132) gives a point well away from the line. Undoubtedly this group requires a σ* value, and our figures indicate one of *ca.* 0·50, but this cannot be regarded as accurate because our data do not allow extrapolation of the rate constant to zero ionic strength, which is strictly required for reaction of this negatively charged entity. This uncertainty applies also to the *meta*-carboxylate-ion compound. (Other difficulties in applying the Hammett equation to charged substituents are discussed by Jaffé, *loc. cit.*)

Of particular interest is the ten-fold increase in rate, relative to that of benzyltrimethylsilane, caused by a *p*-Me_3Si substituent, which confirms that this group, in spite of its $+I$ effect, can effectively withdraw electrons from the ring by expansion of the valency shell of the silicon atom (d_π–p_π bonding). The *p*-Me_3Si group here withdraws electrons more strongly than its σ^* value of +0·09 would indicate (Benkeser and Brumfield, *loc. cit.*). Our results suggest a σ^* value of +0·19 for *p*-Me_3Si, and it may be that the group responds to the very strong demand for electron-withdrawal in the cleavage reaction.

The activating influence of a *p*-NO_2 group is so great that *p*-nitrobenzyltrimethylsilane is cleaved readily by 39 wt.-% aqueous alcohol alone ($k_1 = 6{\cdot}43 \times 10^{-5}$ at 49·7°).

The Mechanism of the Cleavage.—The simplest mechanism consistent with experimental observations is one of a synchronous bimolecular (S_N2) type :

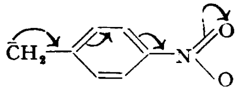


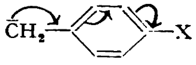
$$YO^- + R_3Si{\cdot}CH_2{\cdot}C_6H_4{\cdot}X \longrightarrow \underset{\text{(transition state)}}{\overset{\delta-}{Y}O\cdots SiR_3\cdots \overset{\delta-}{C}H_2{\cdot}C_6H_4{\cdot}X} \longrightarrow YO{\cdot}SiR_3 + {}^-CH_2{\cdot}C_6H_4{\cdot}X$$

(followed by the rapid reaction $X{\cdot}C_6H_4{\cdot}CH_2^- + HOY \longrightarrow X{\cdot}C_6H_4{\cdot}CH_3 + OY^-$), where Y = H or Me. Electron-withdrawal in X aids reaction partly by facilitating the approach of the OY^- ion to silicon but mainly by increasing the ease of separation of the benzyl group with the electrons of the Si–C bond. We have seen that where a *para*-substituent has a σ^* as well as a σ value the former must be used to represent its effect in the cleavage, and we suggest that this is because the separating benzyl anion has a lone-pair of electrons conjugated with the *p*-substituent (just as have *p*-substituted phenols and amines), and will be stabilized by resonance interaction, such as, *e.g.*, (I). Any effect stabilizing the separating anion will also stabilize the transition state, and it is understandable that σ^* constants must be used to relate structure and reactivity.

Electron withdrawal by a substituent, whether by $-I$ or $-T$ effects or both, will stabilize the separating anion (II) and the greater is the lowering of the activation energy

(I)





(II)

by such stabilization the greater will be the amount of double-bond character of the CH_2–aryl bond in the transition state, and the more rigid will be the transition state and the lower its entropy, and hence the lower the A factor. Table 1 shows that, in general, increase in E is accompanied by increase in A. Plot of log A against E, in fact, gives points lying well about a straight line. [The greatest deviations are for X = *o*- and *m*-CO_2, when the log A factors are relatively low as expected for reaction between negative ions (Laidler, " Chemical Kinetics," McGraw-Hill Book Co., New York, 1950, pp. 132—135) but this effect is not present when X = *p*-CO_2^-, possibly because of the greater separation of the charges.] The Hammett equation can be applied to the cleavage reaction, not because of the constancy of the entropy terms, but because these terms are proportional to the enthalpy terms (cf. Brown and Hudson, *J.*, 1953, 883; Jaffé, *loc. cit.*).

We have found that benzyltriphenylsilane is more readily cleaved by aqueous-ethanolic alkali than is benzyltri-*p*-tolylsilane, so that electron-release in R hinders the cleavage of R_3Si–$CH_2{\cdot}C_6H_5$ compounds. This is consistent with the above mechanism if in the transition state the Si–OY bond is formed to a slightly greater extent than the Si–benzyl bond is broken, so that the silicon atom is slightly negatively charged in the transition state relative to the ground state. (This may not be true for, say, the *p*-nitrobenzyl compounds, in which bond-breaking may be more important than bond-making.) Benzyltriphenylsilane is more readily cleaved than benzyltrimethylsilane, in accord with the more rapid alkaline hydrolysis of triphenylsilane than of trialkylsilanes, which also involves predominant nucleophilic attack on silicon (Price, *J. Amer. Chem. Soc.*, 1947, **69**, 2600; Gilman and Dunn, *ibid.*, 1951, **73**, 3404).

Reaction by the above mechanism should be sterically hindered by large R groups, and benzyl-*n*-propyl-di*iso*propylsilane, is much less reactive than benzyltrimethylsilane, though this may in part be due to the additional electron release to silicon.

The facts are equally consistent with a mechanism in which a quinquecovalent-silicon intermediate is rapidly formed and then decomposes in the rate-determining step :

$$YO^- + R_3Si{\cdot}CH_2{\cdot}C_6H_4{\cdot}X \overset{\text{Fast}}{\rightleftharpoons} YO\text{–}R_3\overset{-}{Si}\text{–}CH_2{\cdot}C_6H_4{\cdot}X \xrightarrow{\text{Slow}} YO{\cdot}SiR_3 + {}^-CH_2{\cdot}C_6H_4{\cdot}X$$

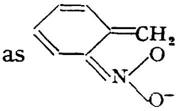
The ground state must be taken as the trialkylbenzylsilane whether or not the intermediate has real existence, and relative to this ground state the effects of electron-withdrawal in X, of electron release in R, and of steric hindrance will be in the same direction in both mechanisms. Analogous intermediates have been proposed for the cleavage of Si–C bonds by alkali (Gilman, Brook, and Miller, *loc. cit.*) and by lithium amide (Hauser and Hance, *loc. cit.*), and also for the alkaline hydrolysis of triarylsilanes (Gilman, Dunn, and Hammond, *J. Amer. Chem. Soc.*, 1951, **73**, 4499) but in no case are there theoretical or experimental grounds for rejecting the synchronous bimolecular (S_N2) type of attack. In the neutral hydrolysis of organofluorosilanes the evidence that the silicon atom is more negative in the transition state than in the ground state, which Swain, Esteve, and Jones (*ibid.*, 1949, **71**, 965) interpret as proving the existence of intermediate $H_2\overset{+}{O}\text{–}R_3\overset{-}{Si}\text{–}F$ is equally consistent with a modified S_N2 mechanism (Hughes, *Quart. Reviews*, 1951, **5**, 268; see also Sommer and Rockett, *J. Amer. Chem. Soc.*, 1951, **73**, 5130). Until there is evidence to the contrary it seems reasonable to accept the simple S_N2 mechanism for alkaline cleavage of Si–C and for other reactions involving nucleophilic attack on silicon. It is of interest that in nucleophilic reactions of Z_2POCl compounds (Z = alkyl or alkoxy) the balance of evidence is in favour of a synchronous S_N2 mechanism rather than an initial attachment of the nucleophilic reagent with expansion of the valency shell of the phosphorus atom (Dostrovsky and Halman, *J.*, 1953, 502, 505, 511, 516).

Effects of Change of Medium.—The following figures for the three cases studied show that in 39 wt.-% water–methanol the reaction is faster by roughly the same factor in each case than in 5 wt.-% water–methanol.

X in $Me_3Si{\cdot}CH_2{\cdot}C_6H_4X$	*p*-CO·NHPh		*o*-CO·NHPh		H	
Wt.-% of H_2O	39	5	39	5	39	5
10 × [NaOH] (M)	4·86	4·91	9·70	9·78	9·66	9·81
$10^4 \times k_s$ (min.$^{-1}$ mole^{-1} l.)	2040	1240	153	88·0	0·290	0·176
Ratio of specific rates	1·65 : 1		1·74 : 1		1·65 : 1	

Both mechanisms proposed above involve dispersal of charge in the transition state, and increasing polarity of the medium as the water content is increased should lower the reaction rate (Ingold, " Structure and Mechanism in Organic Chemistry," Bell and Sons, London, 1953, p. 347). However, addition of water also moves the equilibrium $MeO^- + H_2O \rightleftharpoons MeOH + OH^-$ towards the right, and we suggest that hydroxide ion is more nucleophilic towards silicon than methoxide ion, although the opposite order holds for attack on carbon (Bunnett and Davis, *J. Amer. Chem. Soc.*, 1954, **76**, 3011).

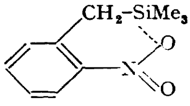
Increase in ionic strength would also be expected to lower the reaction rate (except for the reactions of the carboxylate ion compounds which will be discussed in a later paper). We have not, however, observed significant change in specific rate constant for cleavage of *p*-(trimethylsilylmethyl)benzanilide over a range of high alkali concentrations (see p. 126) or of trimethyl-*p*-nitrobenzylsilane over a range of much lower alkali concentrations (0·003—0·02M).

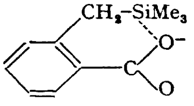
ortho-*Substituents.*—Since the reaction site is separated from the ring by a methylene group, *ortho*-substituents probably have inappreciable primary steric effects, but they may have significant secondary steric effects by interference with mesomeric stabilization of the transition state. For example, steric interference will suppress contributions to the stability of the forming *o*-nitrobenzyl anion from structures such as  which require coplanarity of the methylene and nitro-groups. Electrostatic repulsion between the forming negative charge and the nearby existing negative charge will undoubtedly raise the energy of the transition state in the case of the *o*-CO_2^- substituent.

However, the order of ease of cleavage of *o*-$X{\cdot}C_6H_4{\cdot}CH_2{\cdot}SiMe_3$ compounds is (X =)NO_2>CO·NHPh>Cl>CO_2^->H, which is explicable in terms of polar effects alone. The NO_2 and CO·NHPh groups (relative rates for *p*- and *o*-compounds are 3·8 : 1 and 13 : 1 respectively) withdraw electrons by both $-I$ and $-T$ effects, and thus activate strongly from the *ortho*-position, but less so than from the *para*-position from which the $-T$ effect is most powerful (Ingold, *op. cit.*, pp. 267—269). The Cl substituent has a $-I$ and a weaker $+T$ effect, and since the former is most effective from the *ortho*-position this substituent activates more from here than from the *para*-position, and even than from the *meta*-position (relative rates of *p*-, *m*-, and *o*-compounds, 1 : 4·5 : 5·5). The CO_2^- group has a strong $+I$ effect opposed by a $-T$ effect, and the powerful operation of the $+I$ effect from the *ortho*-position markedly reduces activation by this group relative to its influence in the *para*-position (relative rates of *p*-, *m*-, and *o*-compounds, 69 : 0·4 : 1).

The small difference in reactivity between *o*- and *p*-nitrobenzyltrimethylsilane is not such that the " enhanced stability " of the *o*-compound requires any special explanation, such as the chelation (III) suggested by Benkeser and Brumfield (*J. Amer. Chem. Soc.*, 1951, **73**, 4770). However, the analogous chelation (IV) provides an alternative explanation for the relative stability of the *o*-(trimethylsilylmethyl)benzoate ion. The comparative weakness of the *o*-(trimethylsilylmethyl)benzoic acid [chelation (IV) would be acid-strengthening] and the absence of unusual features in the ultra-violet absorption of the *o*-(trimethylsilylmethyl)benzoate ion (Eaborn and Parker, *J.*, 1954, 939) are arguments against chelation existing to an extent which would have detectable kinetic consequences.

(III)





(IV)

EXPERIMENTAL

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

Preparation of Benzylsilane Derivatives.—Preparations of *o*-, *m*-, and *p*-$X{\cdot}C_6H_4{\cdot}CH_2{\cdot}SiMe_3$ compounds in which X = Cl, CO_2H, and CO·NHPh have been described previously (Eaborn and Parker, *loc. cit.*).

Interaction of excess of benzylmagnesium chloride in ether and fluorotriphenylsilane, fluorotri-*p*-tolylsilane, and difluorodi*iso*propylsilane gave, respectively, benzyl-triphenylsilane (50%), m. p. (from EtOH) 99° (Found : C, 85·6; H, 6·5. Calc. for $C_{25}H_{22}Si$: C, 85·7; H, 6·5%), -*tri*-p-*tolylsilane* (70%), m. p. (from light petroleum) 105° (Found : C, 85·7; H, 7·2. $C_{28}H_{28}Si$ requires C, 85·6; H, 7·2%), and -*fluorodi*iso*propylsilane* (70%), b. p. 256°, n_D^{25} 1·4874 (Found : C, 70·3; H, 9·5%; equiv., 230. $C_{13}H_{21}FSi$ requires C, 69·6; H, 9·4%; equiv., 224).

Interaction of chlorotrimethylsilane in ether with the *p*-methylbenzylmagnesium bromide and *p*-methoxybenzylmagnesium chloride and with the lithium aryl from *p*-chlorobenzyltrimethylsilane gave, respectively, p-*methylbenzyltrimethylsilane* (45%), b. p. 211·5°, n_D^{25} 1·4917 (Found : C, 73·8; H, 10·0. $C_{11}H_{18}Si$ requires C, 74·1; H, 10·2%), p-*methoxybenzyltrimethylsilane* (10%), b. p. 142°/44 mm., 238°/760 mm., n_D^{25} 1·5002 (Found : C, 67·4; H, 9·2. $C_{11}H_{18}OSi$ requires C, 67·4; H, 9·3%), and *trimethyl*-p-*trimethylsilylbenzylsilane* (53%), b. p. 151·5°/45 mm., 250°/760 mm., n_D^{25} 1·4915 (Found : C, 66·1; H, 10·4. $C_{13}H_{24}Si_2$ requires C, 66·0; H, 10·2%).

Benzylfluorodi*iso*propylsilane and *n*-propyl-lithium in ether (initially at −20°, and then at the b. p. for 2 hr.) gave *benzyl*-n-*propyldi*iso*propylsilane* (80%), b. p. 187°/46 mm., 292°/760 mm., n_D^{25} 1·5050 (Found : C, 77·4; H, 11·4. $C_{16}H_{28}Si$ requires C, 77·4; H, 11·4%).

Nitration of Benzyltrimethylsilane.—Benzyltrimethylsilane (82 g.) was added during 45 min. to a well-stirred solution of fuming (95%) nitric acid (53 g.) in acetic anhydride (23 g.), kept below 10°. After being allowed to warm to room temperature during 24 hr. the mixture was added cautiously to a stirred slurry of ice and aqueous ammonia. Ether-extraction was followed by washing and drying (Na_2SO_4) of the ethereal extract and removal of the ether. The residue was fractionated in a column equivalent to *ca.* 30 plates, to give unchanged benzyltrimethylsilane (2 g.), trimethyl-*o*-nitrobenzylsilane (66·5 g., 65·3%), b. p. 124°/10 mm., n_D^{25} 1·5258, and the *p*-isomer (11·5 g., 11·2%), b. p. 146—147°/10 mm., n_D^{25} 1·5395. The physical constants agree with those given by Benkeser and Brumfield (*loc. cit.*).

Kinetic Measurements.—Methanol–water mixtures of s.g. (15·6°) 0·896 (39 wt.-% water) or 0·810 (5 wt.-% water) were used as solvents. Alkali solutions were carbonate-free.

Equal volumes of organosilane and alkali solutions (pre-warmed for fast runs) were mixed in a glass-stoppered vessel which was placed in a thermostat (constant to ±0·02°). Samples were withdrawn at intervals and diluted with the same solvent at room- or ice-temperature, and the optical density (at the wave-length, λ, given in Table 1) was measured with a Unicam S.P. 500 spectrophotometer. For reactions of half-life >60 hr. sealed tubes were used. Reactions were followed to >70% completion in most cases but for X = H, Me, and MeO the rate constants are based on the first 40, 20, and 5%, respectively, of reaction.

The rate-constant k_1 is given by:

$$k_1(t_2 - t_1) = 2{\cdot}303 \log (D_1 - D_\infty)/(D_2 - D_\infty)$$

where D_1, D_2, and D_∞ are the optical densities at times t_1, t_2, and infinity. For fast reactions D_∞ was obtained from reaction mixtures after more than ten times the half-life, but usually it was obtained by use of the appropriate solution of the substituted toluene, $X{\cdot}C_6H_4{\cdot}CH_3$. Values of k_1 were obtained from the slope of the straight-line plot of log $(D_t - D_\infty)$ against t.

The following typical run involved 39 wt.-% water–methanol at 49·7°:

X = *o*-CO·NHPh. [NaOH] = 0·971M.

Time (min.)	10	20	30	45	65	90	120	160	—
10^3D	609	564	526	475	429	378	343	313	279 *
10^5k_1 (min.$^{-1}$)	—	147	145	149	143	150	149	152	—

* Obtained from solution of *o*-toluanilide.

k_1 from graph, $1{\cdot}49 \times 10^{-2}$ min.$^{-1}$.

Reaction Products.—The identities of these were confirmed by isolation (in the case of solids) and by their ultra-violet absorption spectra. Hydrolysis of C–N bonds of anilides and amides seemed negligible under reaction conditions. The products were not investigated for X = Me or MeO.

Cleavage of Triarylbenzylsilanes.—A solution of benzyltriphenylsilane (2·5 g.) and potassium hydroxide (7·5 g.) in 95% aqueous ethanol (75 ml.) was boiled for 4 hr. and then added to water. Ether-extraction was followed by drying (Na_2SO_4) of the ethereal layer and removal of the ether. The solid left was dried in a vacuum-desiccator, and shown to contain 86% of triphenylsilanol by use of the Karl Fischer reagent (Gilman and Miller, *J. Amer. Chem. Soc.*, 1951, **73**, 2367). Benzyltri-*p*-tolylsilane similarly gave a solid containing 47% of tri-*p*-tolylsilanol.

A solution of benzyltriphenylsilane (5·0 g.) and potassium hydroxide (8·0 g.) in 95% ethanol (75 ml.) was boiled for 4 hr. and then added to water. The solid which separated was washed with water, and dried. It had m. p. and mixed m. p. of 154—156° and was almost pure triphenylsilanol (3·7 g., representing a minimum of 94% cleavage).

Cleavage of Trialkylbenzylsilanes.—A solution of trimethylbenzylsilane (16·4 g.) and potassium hydroxide (20 g.) in 95% aqueous ethanol (100 ml.) was boiled for 8 hr. and then added to water. Ether-extraction followed by drying (Na_2SO_4) and fractionation of the ethereal extract gave toluene (6·0 g., representing 65% of cleavage) and unchanged trimethylbenzylsilane (3·5 g., a 21% recovery).

Similar treatment of benzyl-*n*-propyldi*iso*propylsilane led to 94% recovery of unchanged material. No cleavage products were observed.

We thank Mr. H. R. Allcock who prepared *p*-bromobenzyltrimethylsilane and *p*-(trimethylsilylmethyl)benzamide and examined their cleavage reactions.

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