Further Studies of Solvent Isotope Effects in the Cleavage of Substituted Benzyltrimethylsilanes by Methanolic Sodium Methoxide. Intermediate Kinetic Isotope Effects for Reactions of Carbanions with Methanol

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Product isotope effects (p.i.e.), given by the product ratio RH : RD obtained in 1 : 1 MeOH–MeOD, have been determined for cleavages of some substituted benzyltrimethylsilanes by methanolic sodium methoxide; values (with estimated uncertainties of ±20%) given in the sequence of decreasing ease of cleavage, are: (X or XY in XC_6H_4– or $XYC_6H_3CH_2$–$SiMe_3$ =) *p*-NO_2, 2-Me-4-NO_2, or *o*-NO_2, 10 (25 °C); *p*-COPh, 7 (50 °C); *p*-SO_2Ph, 2.9 (50 °C); 2-Me-6-NO_2, 10 (25 °C); *p*-CN, 2.0 (50 °C); 3,5-Cl_2, 1.3 (50 °C); *m*-NO_2, 1.3 (25 °C); *m*-CN, *m*-CF_3, or H, 1.2 (50 °C). These values are believed to represent the kinetic isotope effects for interactions of the carbanions R^- with MeOH and MeOD; as expected, except when there is unusual steric hindrance, they show an overall increase with increasing reactivity of the $RSiMe_3$ compound, and thus with the pK_a of the carbon acid RH, but remain effectively constant over a large pK_a range before increasing steeply over a small pK_a range. The p.i.e. values (at 50 °C) for the compounds $Ph_2CHSiMe_3$ and Ph_3CSiMe_3 have been redetermined, and found to be *ca.* 1.3 ± 0.2, consistent with the values for substituted benzyl compounds of comparable reactivity. The value for the triphenyl compound is incompatible with a reported value of the kinetic isotope effect for proton abstraction from triphenylmethane by sodium methoxide in methanol.

We previously demonstrated that the cleavage by methanolic sodium methoxide of an R–$SiMe_3$ bond, where R is an organic group of the benzylic type, *e.g.* $XC_6H_4CH_2$, Ph_2CH, Ph_3CH, or fluoren-9-yl, probably involves formation of the carbanion, R^-, which then rapidly acquires a proton from the solvent to give the carbon acid RH (see Scheme).[1] The formation of the carbanion may proceed through an Si^V intermediate, as in mechanism *B*, or by a synchronous process, mechanism B_s, in which the transition state for the carbanion formation is close in structure to that in mechanism *B*. (The diagrammatic representations of the transition states in the Scheme are not meant to imply anything about the stereochemistry of the processes.) For simplicity we shall assume in the subsequent discussion that the type *B* mechanism applies, but we emphasize that we cannot exclude the type B_s mechanism.[1]

Type *B*

$$MeO^- + Me_3SiR \rightleftharpoons [MeOSiMe_3R]^-$$

$$[MeOSiMe_3R]^- \longrightarrow \underset{\text{transition state}}{[MeO{-}SiMe_3 \cdots R]^-} \longrightarrow MeOSiMe_3 + R^-$$

$$R^- + MeOH \longrightarrow RH + MeO^- \quad \text{(fast)}$$

Type B_s

$$MeO^- + Me_3SiR \longrightarrow \underset{\text{transition state}}{[MeO{-}{\cdot}SiMe_3 \cdots{\cdot}R]^-} \longrightarrow MeOSiMe_3 + R^-$$

$$R^- + MeOH \longrightarrow RH + MeO^- \quad \text{(fast)}$$

SCHEME Mechanisms of base cleavage of Me_3Si–R bonds by methanolic sodium methoxide

The view that the reactions generate carbanions is based mainly on two features of the cleavages of a range of such $RSiMe_3$ compounds, *viz.* (*a*) the ratio of the specific rate constant k_s (the observed pseudo-first-order constant *k* divided by the concentration of sodium methoxide) in methanol to that in MeOD, which we refer to as the overall rate isotope effect (r.i.e.), has a value in the range 0.4—0.5, and (*b*) for some readily cleaved compounds $RSiMe_3$, *e.g.* R = *p*-$NO_2C_6H_4CH_2$, fluoren-9-yl, and inden-1-yl, which would give stabilized carbanions, large values were observed for the product isotope effect (p.i.e.), the RH : RD product ratio obtained on cleavage in 1 : 1 MeOH–MeOD.[1] If our view of the mechanism is correct, the p.i.e. values represent the kinetic isotope effects for the interactions of the carbanions with methanol,† and provide the only measures for those effects for anions of such weak carbon acids.

For the substituted benzyl compounds, $XC_6H_4CH_2SiMe_3$, we observed p.i.e. values only at the extremes of the range, *viz. ca.* 1.2 for X = H and *m*-CF_3, and >10 for X = *o*- and *p*-NO_2.[1] Intermediate values would be expected for X groups of intermediate electron-withdrawing power (and thus $XC_6H_4CH_2SiMe_3$ compounds of intermediate reactivity), and we have now observed such values. (In the light of the results we have also re-examined the p.i.e. values we reported for cleavage of the compounds $Ph_2CHSiMe_3$ and Ph_3CSiMe_3,[1] and found them to be in error.) We have also looked into the possibility that increase in steric hindrance around the reaction centre might, by enhancement of tunnelling, lead to especially high p.i.e. values,[1] but have found no evidence for such an effect.

RESULTS AND DISCUSSION

The results of our studies of the cleavages of $XC_6H_4CH_2SiMe_3$ and $XYC_6H_3CH_2SiMe_3$ compounds are shown in Tables 1 and 2. As an easy guide to reactivities, Table 2 includes approximate values (at 25 °C) of k_{rel}, the specific rate constant relative to that for the parent benzyltrimethylsilane; since k_s increases with the sodium

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† For the time being we are using the simplest picture of the interaction, and neglecting secondary complications, such as the possibility that the carbanion might acquire its proton either before or after being fully (symmetrically) solvated. For other possible complications see ref. 1.

[1] C. Eaborn, D. R. M. Walton, and G. Seconi, *J.C.S. Perkin II*, 1976, 1857.

methoxide concentration above *ca.* 0.5M, for calculation of k_{rel} values the observed k_s values have been roughly corrected by a factor of 0.8 for 1M- and 0.5 for 2M-sodium methoxide.

TABLE 1

Rates and solvent isotope effects in cleavages of substituted benzyltrimethylsilanes by sodium methoxide in methanol at 25 or 50 °C

		In MeOH [b]		In MeOD [b]		
Substituent(s)	λ/nm [a]	[NaOMe]/M	$10^5 k_s$ l mol^{-1} s^{-1}	[NaOMe]/M	$10^5 k_s$ l mol^{-1} s^{-1}	R.i.e.
o-NO_2	330	0.0155	2 340	0.015	4 800	0.49
m-NO_2	330	0.85	3.22	0.84	7.6	0.42
p-NO_2 [c]	310	0.010	11 500	0.010	23 000	0.50
2-Me-4-NO_2	340	0.030	4 300	0.031	8 550	0.50
2-Me-6-NO_2	330	0.030	320	0.031	670	0.48
m-CN	290	1.05	1.72	1.0	4.00	0.43
p-CN	270	0.51	315	0.52	705	0.45
p-SO_2Ph	280	0.067	470	0.068	1 120	0.42
p-COPh	320	0.067	640	0.068	1 300	0.49
3,5-Cl_2	274	0.50 [d]	66 [d]	0.50 [d]	137 [d]	0.48

[a] Wavelength used for rate measurements. [b] At 25.0 °C unless otherwise indicated. [c] Values of $10^5 k_s$ of 7 600 and 15 100 l mol^{-1} s^{-1} previously reported [1] for this compound in MeOH and MeOD, respectively, referred to reaction at 20.0 °C. [d] At 50.0 °C

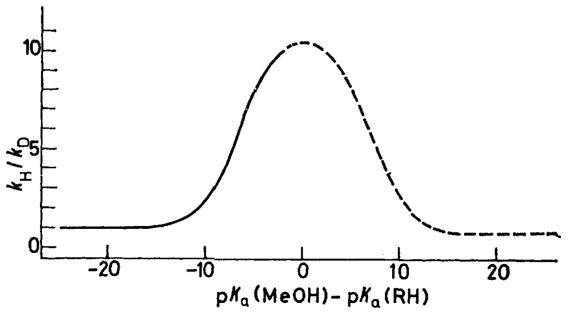
TABLE 2

Product isotope effects in cleavage of substituted benzyltrimethylsilanes by sodium methoxide in methanol

Substituent(s)	MeOH : MeOD	[NaOMe]/M	*T*/°C	*t*/h	RH : RD	P.i.e.	k_{rel}[a]
p-NO_2	1 : 4	0.03	25	3	2.6	10	2.3×10^7
2-Me-4-NO_2	1 : 4	0.03	25	4	2.5	10	8.6×10^6
o-NO_2	1 : 4	0.03	25	4	2.6	10	4.7×10^6
p-COPh	1 : 4	0.03	25	9	1.7	7	1.3×10^6
p-SO_2Ph	1 : 4	0.03	25	9	0.72	2.9	9.4×10^5
2-Me-6-NO_2	1 : 4	0.03	25	24	2.5	10	6.4×10^5
p-CN	1 : 4	0.3	25	3	0.50	2.0	6.3×10^5
3,5-Cl_2	1 : 1	0.4	50	9	1.3	1.3	8.2×10^3
m-NO_2	1 : 3	0.8	25	48	0.44	1.3	5.2×10^3
m-CN	1 : 1	0.8	50	30	1.2	1.2	2.8×10^3
m-CF_3	1 : 1				1.2	1.2 [b]	
p-Cl	1 : 1				1.1	1.1 [b]	
H	1 : 1				1.2	1.2 [b]	1.0

[a] Approximate values at 25 °C; rough allowance has been made, as described in the text, for the dependence of k_s on [NaOMe]. [b] From ref. 18.

The main features of the results, with their implications are as follows. (i) The expected intermediate p.i.e. values are observed, and there is a general tendency for the p.i.e. to increase with the rate of cleavage. However, there is little, if any, variation in the p.i.e. over the large range of reactivity from the benzyl to the 3,5-dichlorobenzyl derivative (k_{rel} 8.2×10^3). For the monosubstituted compounds $XC_6H_4CH_2SiMe_3$, the increase in the p.i.e. sets in at a k_{rel} value in the region of 10^4—10^5, being 2.0 for X = *p*-CN (k_{rel} 6.3×10^5) (but see below for a comment on the results for the cyano-compounds), and 2.9 for X = *p*-SO_2Ph (k_{rel} 9.4×10^5), and then rises steeply to 7 for X = *p*-COPh (k_{rel} 1.3×10^6) and *ca.* 10 for X = *o*- (k_{rel} 4.7×10^6) and *p*-NO_2 (k_{rel} 2.3×10^7). The large difference in p.i.e. between the compound with X = *p*-SO_2Ph and that with X = *p*-COPh is associated with only a small increase in reactivity, revealing that the ease of cleavage provides only a general rather than a quantitative guide to the kinetic isotope effects for the proton abstraction by the relevant carbanion. The results imply, however, that a plot of the isotope effects for the various R^- carbanions against the acidity difference pK_a (MeOH) − pK_a(RH) has the form shown in the Figure (which is not meant to have quantitative significance). The shape of the central portion of the curve with ΔpK_a between −10 and +10 is consistent with that of curves observed for some stronger acids in such a ΔpK_a range (see, *e.g.* ref. 2), and the rapid levelling off outside this range is to be expected. This shape is wholly inconsistent with the k_H/k_D value of 4.2



Diagrammatic representation of the variation of the isotope effect k_H/k_D with the acidity difference pK_a (MeOH) − pK_a (RH) for interaction of the carbanions R^- with MeOH or MeOD

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[2] R. A. More O'Ferrall in ' Proton Transfer Reactions ', eds. E. F. Caldin and V. Gold, Chapman and Hall, London, 1975, p. 224.

reported by Streitwieser and his co-workers for proton abstraction from triphenylmethane by sodium methoxide in methanol at 98 °C (see below),[3] since the relevant ΔpK_a is *ca.* 15 units.

We note that while the observed sharp onset of the increase in p.i.e. would be consistent with a change in *mechanism* between say, the *m*-nitro- and cyano-compound, this can be ruled out by the existence of excellent linear correlations between log k_{rel} values and (*a*) the (σ^-) constants for the X groups in $XC_6H_4CH_2SiMe_3$ compounds,[4] and (*b*) the pK_a values of the acids RH for a series of $RSiMe_3$ compounds (covering the same range of k_{rel} values) in which R varies from benzyl to, for example, diphenylmethyl, to fluoren-9-yl and inden-1-yl.[5]

(ii) The p.i.e. values for the various nitrobenzyl compounds are high, in the region of 10, but the very high approximate p.i.e. values of 15.6 and 14.2 for the *o*- and *p*-nitrobenzyl compounds indicated by our earlier p.i.e. determinations,[1] which were recognised as being subject to large errors, are not substantiated. We previously suggested that steric hindrance around the reaction centre, as for example with the *o*-nitrobenzyl compound, might enhance proton tunnelling and lead to high p.i.e. values,[1] but the values now observed for the 2-methyl-4- and -6-nitro-compounds are not significantly different from that for the 4-nitro-compound. Steric hindrance can account for the fact that the bis-*ortho*-substituted 2-methyl-6-nitro- is *ca.* 7.3 times less reactive than the *o*-nitro-compound while the 2-methyl-4-nitro- is only 2.6 times less reactive than the 4-nitro-compound. It is noteworthy that the 2-methyl-6-nitro-compound provides the one case in which the p.i.e. value falls outside the sequence of k_{rel} values, and this is readily understood since the steric effect reduces the rate of the cleavage but not the reactivity of the carbanion.

(iii) In spite of the large variations in the p.i.e. values, all the r.i.e. values fall in the range 0.42—0.50. There is no apparent order in the variations in r.i.e., and probably all the values could better be expressed as 0.46 ± 0.04 taking into account the maximum possible errors in the specific rate constants. This constancy of r.i.e. value is as expected for the type *B* (or B_s) mechanism.[1,5-7]

(iv) The results for the *m*- and *p*-cyanobenzyl derivatives require some special consideration because these compounds must be converted to some extent into the corresponding imidates during the reaction,[8] and these would be cleaved much less readily. However, even at equilibrium only *ca.* 15% of imidate would be present, and observed individual specific rate constants are unlikely to be as much as 10% below the true values. The p.i.e. values are unlikely to be significantly affected, and the r.i.e. values are probably also fairly reliable since the proportionate effect on the rate is likely to be much the same in MeOD as in MeOH.

Correction of the P.i.e. Values for Di- and Tri-phenylmethyl(trimethyl)silane.—Our previously reported[1] p.i.e. values of 2.2 and 2.3, respectively, for cleavage of the compounds $Ph_2CHSiMe_3$ and Ph_3CSiMe_3 looked abnormally high in the light of the values for the substituted benzyl compounds of comparable reactivity. For example, the 3,5-dichlorobenzyl compound, which is about twice as reactive as the diphenylmethyl compounds, gives a p.i.e. of only 1.3. A reinvestigation revealed that the p.i.e. values for the $Ph_2CHSiMe_3$ and Ph_3CSiMe_3 compounds are, in fact, both in the region of 1.3, a value consistent with the reactivities. The previous error arose from previously unsuspected limitations in the determination of H : D ratios by the microwave plasma discharge (m.p.d.) method.[9] (Our colleagues who carry out the determinations suspect that compounds which give unusually stable ions may not be wholly fragmented.[10]) Especially careful work with diphenylmethane gave seemingly reliable values (*e.g.* the theoretical H : D ratio of 11.0 was observed for the product of cleavage of $Ph_2CHSiMe_3$ in 100% MeOD), and the p.i.e. value of 1.4 thus obtained was in reasonable agreement with that of 1.2 ± 0.2 obtained by an n.m.r. method of analysis (see Experimental section). With triphenylmethane no reliable results could be obtained by the m.p.d. method (variable and clearly incorrect H : D ratios were recorded for the product of cleavage in 100% MeOD), but the n.m.r. method gave a p.i.e. of *ca.* 1.3. Mass spectrometry can be used to give an approximate value of RH : RD, and this also leads to a p.i.e. of *ca.* 1.3, but fragmentation rules out this method for diphenylmethane.

The corrected p.i.e. values for $Ph_2CHSiMe_3$ and Ph_3CSiMe_3 are consistent with those for the benzyl compounds of comparable reactivity, but the new value for Ph_3CSiMe_3 means that there is an even greater discrepancy than we previously noted[1] between the deuterium isotope effect for the protonation of the anion Ph_3C^- and that for the reverse reaction, the proton abstraction from Ph_3CH by methoxide ion. The $k_H : k_D$ ratio for the latter reaction was reported by Streitwieser and his co-workers to be 4.2 at 97.7 °C,[3] which is equivalent to *ca.* 5.4 at 50 °C. This, by Schowen's approximate treatment[7] (temperature effects between 25 and 50° being neglected), indicates a C–H bond order of 0.24 in the transition state for the ionization of triphenylmethane, and this implies a deuterium isotope effect of *ca.* 8.1 for the reverse reaction, compared with our p.i.e. value of 1.3. We offer no explanation for this serious discrepancy.

In view of the errors in our previous p.i.e. values for the di- and tri-phenylmethyl compounds we redetermined

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[3] A. Streitwieser, W. B. Hollyhead, A. H. Pudjatamaka, P. H. Owens, T. C. Kruger, P. A. Rubinstein, R. A. MacQuarrie, M. L. Brokaw, W. K. C. Chu, and H. M. Niemeyer, *J. Amer. Chem. Soc.*, 1971, **93**, 5088.

[4] C. Eaborn and S. H. Parker, *J. Chem. Soc.*, 1955, 126; R. W. Bott, C. Eaborn and T. W. Swaddle, *ibid.*, 1963, 2342; R. W. Bott, C. Eaborn, and B. M. Rushton, *J. Organometallic Chem.*, 1965, **3**, 448.

[5] C. Eaborn, G. Seconi, and D. R. M. Walton, *J.C.S. Chem. Comm.*, 1975, 937.

[6] J. R. Jones, 'The Ionization of Carbon Acids', Academic Press, London and New York, 1971, pp. 205—207.

[7] R. L. Schowen, *Progr. Phys. Org. Chem.*, 1972, **9**, 275.

[8] F. C. Schaefer and G. A. Peters, *J. Org. Chem.*, 1964, **26**, 412.

[9] J. J. Etherton and C. F. Simpson, *Analyst.*, submitted for publication.

[10] J. J. Etherton and C. F. Simpson, personal communication.

the values for fluoren-9-yl- and 9-methylfluoren-9-yl-trimethylsilane. The new values are somewhat lower than those previously recorded,[1] but not significantly so, and no amendment of our earlier discussion is necessary in this case. We now estimate that the p.i.e. values for both fluoren-9-yl- and 9-methylfluoren-9-yl-trimethylsilane are best expressed as 9 ± 2, and, as previously obobserved,[1] such values are consistent with Streitwieser's results [3] for the reverse reaction.

Activation Energies and Entropies.—We have determined the activation energies (from measurements at three or four temperatures), and hence the log A values and entropies of activation, for cleavages of a selection of the compounds discussed above, and included cleavage of an aryltrimethylsilane (*cf.* ref. 11) for comparison. The results, shown in Table 3, reveal a similar pattern to that noted for cleavages of $XC_6H_4CH_2SiMe_3$ compounds in aqueous methanolic alkali,[4] *viz.* as the rate of reaction falls, the increase in activation energy is accompanied by a compensating fall in log A; it is noteworthy that the cleavage of the arylsilicon compound fits normally into this pattern. While an apparent compensation of this kind is often the misleading result of error in the activation energies, the overall consistency of the pattern for cleavages in both methanol and aqueous methanol suggests that in this case it is probably a real effect. However, the results for the compound Ph_3CSiMe_3 fall outside the general pattern; the values E_a and log A are markedly lower than those for the compounds $Ph_2CHSiMe_3$ and $3,5\text{-}Cl_2C_6H_3CH_2SiMe_3$, which do not differ much from it in reactivity. Repeated measurement has failed to reveal any experimental error in the values for the triphenyl derivative.

In a process of type B (or B_S) the higher reactivities will tend to be associated with a smaller degree of separation of the carbanion, and thus increased crowding, in the transition state,[12] which would lead to lower log A values. However the dominant influence on the activation entropy is almost certainly the degree of restriction of solvent molecules, the liberation of the molecules which initially solvate the methoxide ion being especially important.

Synthetic Methods.—Two new preparative procedures are noteworthy. First, the previously elusive *m*-nitrobenzyltrimethylsilane was made by interaction of *m*-nitrobenzyl bromide and hexamethyldisilane in the presence of $[Pd(PPh_3)_4]$,[13] an extension of the valuable route to arylsilicon compounds discovered by Matsumoto and his colleagues.[14] Second, *m*- and *p*-cyanobenzyltrimethylsilane were obtained by metallation of the appropriate cyanotoluene at low temperature [15] followed by coupling with chlorotrimethylsilane; these products can also be made by the catalytic method used for the *m*-nitro-compound.[13]

TABLE 3

Activation parameters for cleavages of $RSiMe_3$ compounds by sodium methoxide in methanol

R	T/°C	[NaOMe]/M	$10^5 k_s$/l mol^{-1} s^{-1}	E_a/l mol^{-1} [a]	log A/l mol^{-1} s^{-1}	$\Delta S^‡$/cal mol^{-1} K^{-1}
Fluoren-9-yl	20	0.01	7 350	13.6	9.1	−19
	25		10 850			
	30		16 350			
	40		33 150			
Ph_3C	25	1.0	4.74	17.2	8.3	−23
	40		18.8			
	50		45			
Ph_2CH	25	1.0	2.93	18.8	9.2	−18
	35		7.95			
	40		14.1			
	50		34.4			
$3,5\text{-}Cl_2C_6H_3CH_2$	30	0.50	7.5	21.2	11.1	−9.5
	40		22.2			
	50		66			
2-Benzo[*b*]thienyl	30	1.0	1.22	22.4	11.2	−9.5
	35		2.17			
	40		4.15			
	50		12.0			
m-$ClC_6H_4CH_2$	40	2.0	0.66	22.6	10.6	−12
	50		2.03			
	55		3.46			
$C_6H_5CH_2$	40	2.0	0.0085	26.1	11.2	−9.5
	50		0.0327			
	55		0.058			

[a] Estimated maximum error *ca.* 1 kcal mol^{-1}

EXPERIMENTAL

Materials.—Previously known $XC_6H_4CH_2SiMe_3$ compounds, *viz.* (X =) *o*- or *p*-NO_2,[16] *p*-SO_2Ph,[4] and *p*-COPh,[4] were made by published methods. o-*Methylbenzyltrimethylsilane*, b.p. 98 °C at 25 mmHg (Found: C, 73.9; H, 10.3. $C_{11}H_{17}Si$ requires C, 74.1; H, 10.2%), was made

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[11] C. Eaborn and G. Seconi, *J.C.S. Perkin II*, 1976, 925.

[12] C. Eaborn, K. L. Sinnitambe, and D. R. M. Walton, *J.C.S. Perkin II*, 1975, 380.

[13] D. Azarian, S. J. Dua, C. Eaborn, and D. R. M. Walton, *J. Organometallic Chem.*, 1976, **117**, C55.

[14] H. Matsumoto, S. Nagashima, K. Yoshihiro, and Y. Nagai, *J. Organometallic Chem.*, 1975, **85**, Cl.

[15] E. M. Kaiser and J. D. Petly, *J. Organometallic Chem.*, 1976, **107**, 219.

[16] E. A. Chernyshev, M. E. Dolgaya, and A. D. Petrov, *Bull. Acad. Sci. U.S.S.R., Chem. Section*, 1960, 1323.

from *o*-methylbenzyl chloride by treatment of the Grignard reagent with chlorotrimethylsilane (for the general procedure see ref. 3), and 3,5-*dichlorobenzyltrimethylsilane*, b.p. 75 °C at 1 mmHg (Found: C, 51.2; H, 5.9. $C_{10}H_{14}Cl_2Si$ requires C, 51.5; H, 6.05%), was made analogously from 3,5-dichlorobenzyl chloride.[17]

m-*Nitrobenzyltrimethylsilane* was made in good yield on a *ca.* 2 g scale by treatment of *m*-nitrobenzyl bromide with hexamethyldisilane in the presence of tetrakistriphenylphosphinepalladium(0),[13] and was separated and purified by g.l.c., b.p. 94 °C at 0.5 mmHg (Found: C, 57.0; H, 7.4; N, 6.9. $C_{10}H_{15}NO_2Si$ requires C, 57.4; H, 7.2; N, 6.7%).

The *m*- and *p*-cyanobenzyltrimethylsilanes were made by low temperature metallation of the appropriate cyanotoluene in tetrahydrofuran–hexamethylphosphoric triamide,[15] followed by treatment at −78 °C with chlorotrimethylsilane with stirring. The mixture was allowed to warm to room temperature overnight with stirring, the solvent was evaporated off, and the residue extracted with ether. The ethereal extract was shaken with cold saturated aqueous ammonium chloride and then several times with water. Drying and fractional distillation gave m-, b.p. 118 °C at 6 mmHg (Found: C, 69.4; H, 8.0; N, 7.5. $C_{11}H_{15}NSi$ requires C, 69.8; H, 8.0; N, 7.4%), and p-*cyanobenzyltrimethylsilane*, b.p. 108 °C at 4 mmHg (Found: C, 69.2; H, 7.8; N, 7.4%).

Nitration of *o*-methylbenzyltrimethylsilane, by the method used for nitration of benzyltrimethylsilane,[16] gave 2-*methyl*-4-, b.p. 93 °C at 0.2 mmHg, δ ($CDCl_3$), 0.03 (9 H, s, $SiMe_3$), 2.24 (2 H, s, CH_2), 2.31 (3 H, s, ArMe), and 7.11—8.0 (3 H, m, ArH) (Found: C, 59.6; H, 7.7; N, 6.6. $C_{11}H_{17}NO_2Si$ requires C, 59.15; H, 7.7; N, 6.3%), and 2-*methyl*-6-*nitrobenzyltrimethylsilane*, b.p. 80 °C at 0.3 mmHg, δ ($CDCl_3$), 0.02 (9 H, s, $SiMe_3$), 2.32 (3 H, s, ArMe), 2.50 (2 H, s, CH_2), and 6.8—7.8 (3 H, m, ArH) (Found: C, 59.0; H, 7.7; N, 6.4%). Spectroscopic data for the products were as expected, but did not distinguish the second product from the 2-Me-3-NO_2-isomer. The latter would not be expected to be produced in substantial amount in the nitration, however, and would be cleaved at a much lower rate than that observed.

Rate Measurements.—These were determined spectrophotometrically, at the wavelengths shown in Table 1, as previously described.[11] No departure from first-order kinetics was noted for *m*- or *p*-cyanobenzyltrimethylsilane, and g.l.c. and n.m.r. analysis revealed no aromatic product of the cleavage other than the expected cyanotoluene. Base concentrations refer to mixtures at 25 °C, and no correction has been made in calculating k_s values for expansion of the medium in runs at higher temperatures.

Product Isotope Effects.—(a) Unless otherwise indicated, these were calculated from product H : D ratios determined, as previously described,[11] with the aid of an Applied Chromatography Systems Organic Analyzer MPD 850 linked to a Pye model 64 gas chromatograph. The following H : D ratios, with theoretical values in parentheses, were observed for cleavages of $RSiMe_3$ compounds in '100%' MeOD: (R =) *m*-$NO_2C_6H_4CH_2$, 6.04 (6.0); 2-Me-4-$NO_2C_6H_3CH_2$, 8.1 (8.0); 2-Me-6-$NO_2C_6H_3CH_2$, 8.05 (8.0); *p*-$PhCOC_6H_4CH_2$, 11.0 (11.0); *m*- and *p*-$NO_2C_6H_4CH_2$, 6.1 (6.0); 3,5-$Cl_2C_6H_3CH_2$, 5.05 (5.0); Ph_2CH, 11.0 (11.0); fluoren-9-yl, 9.1 (9.0) (a synthetic mixture of [9-^{2}H]fluorene and fluorene corresponding to a H : D ratio of 21.2 gave 21.0). (Incorrect observed and theoretical values were previously given [1] for the last compound as a result of typographical errors.)

Separate experiments confirmed that for the various cleavage products, RH, no hydrogen exchange occurred under the conditions used for cleavage.

(b) The p.i.e. value for the compound Ph_3CSiMe_3 was obtained by mass spectroscopic [18] and n.m.r. analysis of the $Ph_3CH : Ph_3CD$ mixture. For cleavage in 1 : 1 MeOH : MeOD the mass relative intensities of the M^+ and $M^+ + 1$ peaks, after correction for ^{13}C,[18] corresponded with a $Ph_3CH : Ph_3CD$ ratio of 1.3 : 1. (The mass spectrum of the product from cleavage of Ph_3CSiMe_3 in 100% MeOD indicated the absence of any significant quantity of Ph_3CH.)

For p.i.e. determinations by n.m.r. analysis (*cf.* ref. 19) a mixture of weighed amounts of Ph_3CSiMe_3 and Ph_2CH_2 (internal standard) was treated with sodium methoxide in 1 : 1 MeOH–MeOD (4 cm^3). Subsequently, tetrachloromethane (2 cm^3) was added to give a clear solution, which was added to cold water. Further tetrachloromethane (2 cm^3) was added, and the mixture well shaken. The organic layer was washed three times with cold water (2 cm^3), then dried (Na_2SO_4). Measurement of the peak heights for signals from the methine protons then (in the light of calibrations) gave the Ph_3CH content of the $Ph_3CH : Ph_3CD$ mixture as 1.3 ± 0.2. A similar procedure for cleavage of $Ph_2CHSiMe_3$ (with Ph_3CH as internal standard) was less reliable (because of the additional methanic hydrogen), but in repeated measurements gave p.i.e. values between 1.0 and 1.3, with a mean value of 1.1 ± 0.2.

We thank the Dow Corning Co. Ltd., for gifts of organosilicon chemicals, and Mr. C. F. Simpson and Mrs. J. J. Etherton for measurement of the deuterium content of cleavage products by use of the MPD 850 Organic Analyzer.

[7/1921 *Received, 2nd November*, 1977]

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