Cleavage of Diphenylmethyl-, Triphenylmethyl-, Fluoren-9-yl-, and Substituted Benzyl-trialkylstannanes by Methanolic Sodium Methoxide. Evidence for a Duality of Mechanism

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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 measured for cleavage of $RSnMe_3$ compounds by methanolic sodium methoxide; values (with estimated uncertainties of ±20%) are: (R =) p-$NCC_6H_4CH_2$, m-$NCC_6H_4CH_2$, or 3,5-$Cl_2C_6H_3CH_2$, 2.1; Ph_2CH, 1.5; Ph_3C, 1.3; fluoren-9-yl, 8.4; 9-methylfluoren-9-yl, 8.4. (For the compounds with R = fluoren-9-yl, change to Et_3Sn or $Pr^i{}_3Sn$ groups has no significant effect on the p.i.e. value, but for R = Ph_2CH this change may be accompanied by a small fall in the p.i.e. value.) Values of the ratio of the rate in MeOH to that in MeOD are: p-$NCC_6H_4CH_2$, 0.57 (25 °C); m-$NCC_6H_4CH_2$, 0.85 (25 °C); 3,5-$Cl_2C_6H_3CH_2$, 0.82 (50 °C); Ph_2CH, 0.59; Ph_3C, 0.47; fluoren-9-yl, 0.46; 9-methylfluoren-9-yl, 0.50. Approximate ratios of the rates for tin to those of corresponding silicon compounds are: $C_6H_6CH_2$, 27.5 (50 °C); m-$ClC_6H_4CH_2$, 13.5 (50 °C); m-$CF_3C_6H_4CH_2$, 9 (50 °C); 3,5-$Cl_2C_6H_3CH_2$, 10.5 (50 °C); m-$NCC_6H_4CH_2$, 9.5 (25 °C); p-$NCC_6H_4CH_2$, 24 (25 °C); Ph_2CH, 190 (25 °C); Ph_3C, 40 000 (25 °C); fluoren-9-yl, 19 000 (25 °C). It is suggested that for the benzyl compounds, except perhaps the p-cyano derivative, the rate-determining step involves proton transfer to the separating R group, but for the triphenylmethyl and fluoren-9-yl compounds it involves separation of the carbanion R^-; the diphenylmethyl and p-cyanobenzyl compounds may react by a mixture of the two mechanisms.

IT was previously shown that for some benzyltrimethylstannanes the mechanism of cleavage by methanolic sodium methoxide appears to differ from that for the corresponding benzyltrimethylsilanes.[1] Whereas cleavage of the silicon compounds, $RSiMe_3$ seems to generate carbanions R^- in a mechanism of type B or B_s (see Scheme)[1-4] with the tin compounds $RSnMe_3$ the R group apparently acquires a proton from the solvent as it separates, in a type A or A_s mechanism.† The main evidence for the distinction is that for some $XC_6H_4CH_2SnMe_3$ compounds of relatively low reactivity (X = H, p-Me, p-Cl, m-CF_3), the product isotope effect (p.i.e.), the product ratio RH : RD obtained on cleavage in 1 : 1 MeOH–MeOD, has values in the region of 2.1, whereas the values for comparable silicon compounds fall in the region of 1.1—1.3. Furthermore, the ratios of the rate isotope effect (r.i.e.) [the ratio, k_s(MeOH) : k_s(MeOD), of the specific rate constant for cleavage in MeOH to that for cleavage in MeOD] to the p.i.e. for m-$CF_3C_6H_4CH_2SnMe_3$ was 0.46,[1] which would be consistent with a process in which the readier nucleophilic attack by MeO^- in MeOD is countered by the readier proton transfer from MeOH.[1,5] (The evidence for a type A or A_s mechanism is even more complete for cleavage of aryl–$SnMe_3$ bonds, which give rise to even larger p.i.e. values, and thus r.i.e. values substantially greater than unity.[5])

(1) type A

$$MeO^- + Me_3MR \rightleftharpoons [MeOMMe_3R]^-$$

$$[MeOMMe_3R]^- + MeOH \longrightarrow \underset{\text{transition state}}{[MeO\text{——}MMe_3\cdots R\cdots H\cdots OMe]^-} \longrightarrow MeOMMe_3 + RH + MeO^-$$

(2) type A_s

$$MeO^- + Me_3MR + MeOH \longrightarrow \underset{\text{transition state}}{[MeO\text{——}\cdot MMe_3\cdots R\cdots H\cdots OMe]^-} \longrightarrow MeOMMe_3 + RH + MeO^-$$

(3) type B

$$MeO^- + Me_3MR \rightleftharpoons [MeOMMe_3R]^-$$

$$[MeOMMe_3R]^- \longrightarrow \underset{\text{transition state}}{[MeO\text{——}MMe_3\cdots R]^-} \longrightarrow MeOMME_3 + R^-$$

$$R^- + MeOH \text{——} RH + MeO^- \qquad \text{(fast)}$$

(4) type B_s

$$MeO^- + Me_3MR \longrightarrow \underset{\text{transition state}}{[MeO\text{——}\cdot MMe_3\cdots R]^-} \longrightarrow MeOMMe_3 + R^-$$

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

SCHEME Mechanisms of base cleavage of Me_3M–R bonds by methanolic sodium methoxide

If our proposals are correct, there should be a possibility that the mechanism of cleavage of the benzyltin compounds would change from the A (or A_s) type (the 'electrophically-assisted' mechanism) to the B (or B_s) type (the 'ionization' mechanism) as the stability of the carbanion R^- is increased. In seeking such a mechanistic change we have now examined the behaviour of some more readily cleaved tin compounds, *viz.* m- and p-cyano- and 3,5-dichloro-benzyl-, and diphenylmethyl-, triphenylmethyl-, fluoren-9-yl-, and 9-methylfluoren-9-yl-trimethylstannane. Some corresponding triethyl and tri-isopropyl compounds have also been studied.

RESULTS AND DISCUSSION

Observed rate constants and r.i.e. values are shown in Table 1, and p.i.e. values in Table 2. In Table 3 are shown the reactivity ratios for corresponding tin and silicon compounds (referred to below as Sn : Si reactivity ratios) derived after rough correction for the variation of k_s with the concentration of sodium methoxide, and also the values, k_{rel}, of the reactivities of $RSiMe_3$ compounds relative to that of benzyltrimethylsilane.

Before discussing the results, we first note that the m- and p-cyanobenzyltrimethylstannanes must be converted

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† If attention is focused on the carbon atom of the breaking R–M bond, the A and A_s mechanisms represent nucleophilically-assisted S_E2 processes and the B and B_s mechanisms nucleophilically-assisted S_E1 processes.

to some extent into the much less readily cleaved imidates in the cleavage medium. However, the conversions are probably slower than the cleavages, and even at equilibrium only *ca.* 15% of the imidate would be present.[6] Thus while the observed rate constants may be up to 10% below their true values, this will not significantly affect the p.i.e. or r.i.e. values (*cf.* ref. 2).

TABLE 1

Rates and solvent isotope effects in cleavage of the compounds $R_3'SnR$ by sodium methoxide in methanol at 25 or 50 °C

			In MeOH [a]		In MeOD [a]		
R′	R	λ/nm	[NaOMe]/M	10^5k_s/l mol^{-1} s^{-1}	[NaOMe]/M	10^5k_s/l mol^{-1} s^{-1}	R.i.e.
Me	*p*-$NCC_6H_4CH_2$	270	0.05	7 500	0.05	13 200	0.57
	m-$NCC_6H_4CH_2$	300	0.50	11.0	0.52	13.0	0.85
	3,5-$Cl_2C_6H_3CH_2$	280	0.50	575 [b]	0.50	700 [b]	0.82 [b]
	Ph_2CH	240	0.10	450	0.10	760	0.59
			0.50	460	0.50	780	
Et	Ph_2CH	245	0.10	182	0.10	335	0.54
Pr^i	Ph_2CH	245	0.50	7.3	0.50	13.9	0.53
Me	Ph_3C	276	0.001	152 × 10^3	0.001	325 × 10^3	0.47
			0.10 [c]	~160 × 10^3	0.10 [c]	~400 × 10^3	
Me	Fluoren-9-yl	307	0.002 [c]	21 × 10^7	0.002 [c]	46 × 10^7	0.46
Et	Fluoren-9-yl	307	0.002 [c]	78 × 10^6	0.002 [c]	16 × 10^7	0.49
Pr^i	Fluoren-9-yl	307	0.001	73 × 10^4	0.001	104 × 10^4	0.70
			0.002 [c]	64 × 10^4	0.002 [c]	90 × 10^4	0.71
Me	9-Methylfluoren-9-yl	307	0.002 [c]	89 × 10^7	0.002 [c]	176 × 10^7	0.50

[a] At 25 °C unless otherwise indicated. [b] At 50.0 °C. [c] By stopped-flow technique.

TABLE 2

Product isotope effects in cleavage of the compounds $R_3'SnR$ by sodium methoxide in methanol

R′	R	MeOH : MeOD	[NaOMe]/M	θ/°C	*t*/h	RH : RD	P.i.e.	R.i.e. : p.i.e.
Me	*p*-$NCC_6H_4CH_2$	1 : 4	0.3	25	3	0.53	2.1	0.27
	m-$NCC_6H_4CH_2$	1 : 1	0.8	25	30	2.1	2.1	0.40
	3,5-$Cl_2C_6H_3CH_2$	1 : 1	0.4	50	5	2.1	2.1	0.39
	Ph_2CH	1 : 1	0.1	50	24	1.5 [a,b]	1.5	0.39
Et	Ph_2CH	1 : 1	0.1	50	24	1.3 [a,b]	1.3	0.42
Pr^i	Ph_2CH	1 : 1	0.2	50	48	1.2 [a,c]	1.2	0.44
Me	Ph_3C	1 : 1	0.1	50	10	1.3 [a,d]	1.3	0.36
Me	Fluoren-9-yl	1 : 4	0.01	22	0.5	2.1	8.4	0.055
Et	Fluoren-9-yl	1 : 4	0.01	22	0.5	2.3	9.2	0.053
Pr^i	Fluoren-9-yl	1 : 4	0.01	22	1	2.1	8.4	0.083
Me	9-Methylfluoren-9-yl	1 : 4	0.1	22	2	2.1	8.4	0.060
			0.01	22	2	2.1	8.4	

[a] By n.m.r. analysis. [b] Analysis by the MPD organic analyser gave 1.6. [c] Analysis by the MPD organic analyser gave 1.3. [d] Mass spectrometry gave 1.3.

TABLE 3

Derivation of reactivity ratios for corresponding tin and silicon compounds, and of reactivities, k_{rel}, of $RSiMe_3$ compounds relative to that of $PhCH_2SiMe_3$ at 25 °C

		$RSnMe_3$			$RSiMe_3$				
R	θ/°C	[NaOMe]/M	10^5k_s/l mol^{-1}s^{-1}	10^5k_s(corr)/l mol^{-1} s^{-1} [a]	[NaOMe]/M	10^5k_s/l mol^{-1} s^{-1}	10^5k_s(corr)/l mol^{-1} s^{-1} [a]	React. ratio Sn : Si	k_{rel}(Si)
$PhCH_2$	50	2.0	0.52	0.44	2.0	0.033	0.016	27.5	
	25				2.0	0.0010 [b]	0.0005		1.0
m-$ClC_6H_4CH_2$	50	1.0	13.7	13.7	2.0	2.03	1.01	13.5	
	25				2.0	0.10 [b]	0.05		100
m-$CF_3C_6H_4CH_2$	50	2.0	76	65	2.0	6.8	3.4	19	
3,5-$Cl_2C_6H_3CH_2$	50	0.5	575	690	0.5	66	66	10.5	
	25	0.5	39	47	0.5	4.1 [b]	4.1	11.5	8 200
m-$NCC_6H_4CH_2$	25	0.5	11	13	1.0	1.72	1.38	9.5	2 800
p-$NCC_6H_4CH_2$	25	0.05	7 500	7 500	0.5	315	315	24	630 000
Ph_2CH	25	0.1	450	450	1.0	2.93	2.3	190	4 700
	50	0.05	7 250	7 250	1.0	34	27	260	
Ph_3C	25	0.01	152 000	152 000	1.0	4.74	3.8	40 000	7 600
Fluoren-9-yl	25	0.002	21 × 10^7	21 × 10^7	0.01	11 200	11 200	19 000	22 × 10^6
9-Methylfluoren-9-yl	25	0.002	89 × 10^7	89 × 10^7	0.02	197	197	45 × 10^5	39 × 10^4

[a] Values of k_s vary with the methoxide concentration. In the light of results for the *m*-$ClC_6H_4CH_2MMe_3$ compounds at 50 °C (F. M. S. Mahmoud, personal communication), observed values of k_s are roughly corrected for M=Si by a factor of 0.8 for 1M- and 0.5 for 2M-NaOMe, and for M=Sn by a factor of 1.2 for 0.5M- and 0.85 for 2M-NaOMe. [b] Approximate value obtained by extrapolation from values at higher temperatures.

Some important features of the results for the substituted benzyl compounds, with their implications, are as follows.

(a) For the benzyltin compounds the p.i.e. values are in the range 2.1—2.3, while for the corresponding silicon compounds they are in the range 1.2—1.3, except for the *p*-cyano compound, which gives a value of 2.0. The difference (except for the *p*-cyano compounds) between the two sets of values implies that the tin and the silicon cannot both be cleaving by generation of a free carbanion, since corresponding compounds would then give the same p.i.e. values. If it is accepted that the silicon compounds do react by such a mechanism, it follows that the tin compounds do not.

(b) Except for the *p*-cyano compounds, the r.i.e. values for the tin compounds, *ca.* 0.82—0.87, are markedly higher that those for the silicon compounds, and too high for the B (or B_s) mechanism. The r.i.e. : p.i.e. ratios fall in the range 0.39—0.46, which is consistent with the electrophilically-assisted type A (or A_s) mechanism.[1,5] For the *p*-cyano compounds the r.i.e. value, *viz.* 0.57, while larger than that for the corresponding silicon compound, is distinctly lower than that for the other tin compounds, and moreover the r.i.e. : p.i.e. ratio, 0.26, is well outside the range for the other compounds.

(c) When the point for the *p*-cyano derivative is omitted, a plot of log k_s for the tin compounds against log k_s for the corresponding silicon compounds is an excellent straight line (correlation coefficient 0.998; slope 0.93). The Sn : Si reactivity ratio falls progressively with the reactivity from the parent benzyl compounds to the *m*-cyano derivatives (Table 3), but it rises for the *p*-cyano compound to 24, rather than falling to the value of *ca.* 7 which would be expected by extrapolation of the line for the other compounds.

Overall the results for the benzyltin compounds are wholly consistent with operation of the A (or A_s) mechanism except for the most reactive compound, the *p*-cyano derivative, and we consider below the possibility that cleavage of this compound proceeds partly by the ionization B (or B_s) mechanism.

The results for the fluoren-9-yl and di- and triphenylmethyl compounds present a very different picture. For the fluoren-9-ylSnR_3' compounds, with $R' =$ Me, Et, or Pr^i, for which the k_s values vary over a 300-fold range, the p.i.e. values are very high, and, within the experimental uncertainty, are the same as one another and as that for the silicon compound fluoren-9-yl$SiMe_3$. Furthermore, the r.i.e. : p.i.e. ratios fall in a range, *viz.* 0.05—0.08, wholly inconsistent with the operation of a type A (or A_s) mechanism (*cf.* refs. 2 and 4), and it seems clear that a type B (or B_s) carbanion mechanism is operating.* The very large Sn : Si reactivity for the fluoren-9-ylMMe_3 compounds, *viz.* 19 000, is very much larger than the ratios noted above for $XC_6H_4CH_2MMe_3$ compounds, adding further support to our view that a change in mechanism has occurred on going from the benzyl to the fluoren-9-yl compounds.

The difficulty of determining H : D ratios for $R =$ Ph_3C or Ph_2CH (see ref. 2) blurs the picture somewhat for the di- and tri-phenylmethyltin compounds, but the p.i.e. value for Ph_3CSnMe_3, *viz. ca.* 1.3, is clearly smaller than that for the range of $XC_6H_4CH_2SnMe_3$ compounds; it is also effectively the same as that for the corresponding silicon compound, Ph_3CSiMe_3. Furthermore, the Sn : Si reactivity ratio for the Ph_3CMMe_3 compounds is extremely large, *viz.* 40 000, and while, as we shall show, this ratio is probably exaggerated by steric hindrance for $M = Si$, it is probable that Ph_3CSnMe_3 resembles fluoren-9-yl$SnMe_3$ in reacting by a B (or B_s) mechanism.

It is necessary at this point to consider the influence of steric hindrance on the rates of reaction of the silicon compounds. We have previously estimated that steric hindrance renders 9-phenylfluoren-9-yltrimethylsilane *ca.* 60—100 times less reactive, when compared with fluoren-9-yltrimethylsilane, than would be expected on the basis of the acidities of 9-phenylfluorene and fluorene.[8,†] The increase in the bulk of the R group on going from $PhCH_2SiMe_3$ to Ph_3CSiMe_3 is markedly greater; however, although, other things being equal, steric hindrance seems to be less important the lower the reactivity of the $RSiMe_3$ compound (see ref. 8), it seems reasonable to suggest that Ph_3CSiMe_3 could be as much as 100 times less reactive than would be expected on the basis of the stability of the Ph_3C^- anion alone. This would remove two anomalies: (a) the greater Sn: Si reactivity ratio observed for the triphenylmethyl- than for the fluoren-9-yl-MMe_3 compounds (since the ratio after correction, for steric hindrance would be reduced to *ca.* 400 for the Ph_3CMMe_3 compounds), and (b) the fact that Ph_3CSnMe_3 seems to follow the B (or B_s) mechanism while $3,5\text{-}Cl_2C_6H_4CH_2SnMe_3$ retains the A (or A_s) mechanism, whereas, since Ph_3CSiMe_3 and $3,5\text{-}Cl_2C_6H_4CH_2SiMe_3$ have comparable reactivities[2] the same mechanism would be expected for both if the choice between the two types of mechanism were governed solely by the stability of the carbanion R^-, and if this stability were accurately indicated by the ease of cleavage of the $RSiMe_3$ compound.‡

In the case of $Ph_2CHSnMe_3$, while the p.i.e. value of 1.5 is distinctly lower than that for benzyltin compounds of comparable reactivity, it is probably significantly higher than that, *viz.* 1.1 + 0.2, observed for the corresponding silicon compound,[2] although the experimental uncertainty prevents a definite conclusion about this. The Sn : Si reactivity ratio of *ca.* 190 observed for the Ph_2CHMMe_3 compounds argues in favour of a differ-

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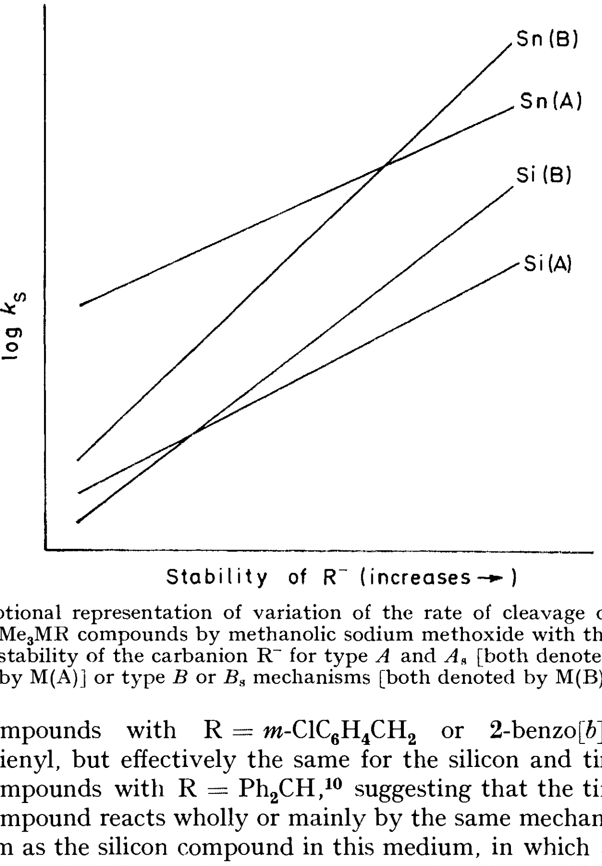
* Even after allowing for the rather large possible error in k_s values for these very rapid reactions, the r.i.e. value for fluoren-9-yl$SnPr^i_3$, *viz.* 0.70, seems significantly above the usual range for the carbanion mechanism, but we have observed a value of 0.71 for the compound *o*-$O_2NC_6H_4CH_2SiPh_3$;[7] perhaps bulky R' groups tend to give rise to large r.i.e. values, a possibility we are investigating.

† It is noteworthy that whereas 9-methylfluoren-9-yltrimethylsilane is less readily cleaved than the fluoren-9-yl compound, probably because of steric hindrance,[8] 9-methylfluoren-9-yltrimethylstannane is more reactive than the fluoren-9-yl compound, in line with the higher equilibrium acidity[9] of 9-methylfluorene than of fluorene.

‡ If steric hindrance is, indeed, responsible for a 100-fold rate lowering for Ph_3CSiMe_3, it follows that the excellence of the straight line plot of log k_{rel} for $RSiMe_3$ compounds against the pK_a values of the corresponding carbon acids RH^4 is to this extent fortuitous, and that pK_a values estimated by use of this plot in the range *ca.* 27—32 may be too high by up to *ca.* 2 pK_a units. We plan to investigate this.

ent mechanism for $Ph_2CHSnMe_3$ than for $XC_6H_4CH_2SnMe_3$ compounds of similar reactivity, but again steric hindrance probably operates to give the silicon compound $Ph_2CHSiMe_3$ a lower reactivity than would be expected from the acidity of diphenylmethane; if this caused, say, a five-fold reduction in reactivity, then the 'corrected' Sn : Si ratio would be only *ca.* 40. The facts are reasonably consistent with concurrent operation of both an *A* (or A_S) and a *B* (or B_S) mechanism for cleavage of $Ph_2CHSnMe_3$, which would thus lie at the point of mechanistic crossover. It is thus noteworthy that for cleavage of $RMMe_3$ compounds by Me_2SO–MeOH–MeONa, the slopes of the plots of log *k* against the acidity function H_- are markedly lower for tin than for silicon compounds with R = *m*-$ClC_6H_4CH_2$ or 2-benzo[*b*]-thienyl, but effectively the same for the silicon and tin compounds with R = Ph_2CH,[10] suggesting that the tin compound reacts wholly or mainly by the same mechanism as the silicon compound in this medium, in which a higher basicity and a lower proton-donating ability compared with MeOH–MeONa would be conducive to a carbanion mechanism. If the apparent fall in the p.i.e. for the Ph_2CHSnR_3' compounds as R′ is varied from Me to Pr^i is accepted as real, it could be taken to indicate a movement towards the carbanion mechanism, but we note that just such a fall in p.i.e. values accompanies the same change of R′ groups for cleavages of some $arylSnR_3'$ compounds which seem clearly to involve *A* (or A_S) type mechanisms.[5]



Notional representation of variation of the rate of cleavage of Me_3MR compounds by methanolic sodium methoxide with the stability of the carbanion R^- for type *A* and A_s [both denoted by M(A)] or type *B* or B_s mechanisms [both denoted by M(B)]

In the light of the above discussion there seems a distinct possibility that the slightly anomalous results for *p*-cyanobenzyltrimethylstannane are associated with a contribution by the ionization, *B* (or B_S) mechanism for cleavage of this compound; all the features, *viz.* a p.i.e. effectively the same as that for the corresponding silicon compound, a relatively low r.i.e. value, a distinctly low r.i.e. : p.i.e. ratio, and a somewhat high Sn : Si reactivity ratio are consistent with this possibility. That the crossover point for the $XC_6H_4CH_2SnMe_3$ series should lie near the compound with X = *p*-CN would be satisfactorily consistent with the fact that if the allowance suggested above for steric hindrance is made for Ph_3CSiMe_3, then the 'corrected' reactivity of the latter, which would be related to the stability of the Ph_3C^- carbanion, would be fairly similar to that of *p*-$CNC_6H_4CH_2SiMe_3$. Furthermore, the stability of the separating carbanion and steric effects are not the only relevant factors; the ease of electrophilic attack by the solvent on the separating R group, will be important. Such electrophilic attack will be especially favoured for aryl and allyl compounds, and the *A* (or A_s) mechanism thus markedly favoured for a given stability of the carbanion R^-, and so it is significant that results for cleavage of phenylallyltrimethylsilane point to an electrophilically-assisted mechanism.[11]

In the Figure we suggest a possible notional representation of the dependence of the rate constants for the type *A* (or A_S) and type *B* (or B_S) mechanisms for cleavage of silicon and tin compounds in methanol upon the stability of the carbanion R^-, all other factors being ignored. The scheme implies that the silicon compounds might react by an electrophilically-assisted mechanism at very low R^- stabilities in MeOH–MeONa, and at rather higher R^- stabilities in cases in which electrophilic attack would be especially easy.*

The relative positions and slopes of the several lines would, of course, be different in other media. We can envisage a line for tin crossing a line for silicon (*e.g.* with the *B* mechanism lines) at a very low carbanion stability, to accommodate the fact that in Me_2SO–H_2O–NaOH media of very low water content, in which electrophilic assistance may be much reduced, the tin compound $PhSnMe_3$ is cleaved *less* readily than its silicon analogue, $PhSiMe_3$.[13] While a considerable body of results can be rationalized in terms of the tentative scheme, it must be regarded as a considerable over-simplification. In particular, there is no certainty that any of the lines are straight, and we have noted above that a curve may be more appropriate even for the cleavages of the $RSiMe_3$ compounds in MeOH–MeONa.

In the light of the discussion above, for Me_3SnR compounds derived from carbon acids RH of high acidity, *e.g.* R = fluoren-9-yl, a mechanism involving self-ionization to the ion pair ($Me_3Sn^+R^-$) has to be considered in view of the conclusion by Beletskaya and her colleagues that such ionization is rate-determining in the cleavages of such compounds by iodine in Me_2SO–CCl_4.[14]

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* Because of the unusual pattern of substituent effects, it was previously suggested that a type *A* (or A_s) mechanism might operate in cleavage of $XC_6H_4SiMe_3$ compounds by hydroxide ion in Me_2SO–H_2O.[12] However, calculations on the relative stabilities of $XC_6H_4^-$ anions (C. Eaborn, J. G. Stamper, and G. Seconi, *J. Organometallic Chem.*, 1978, **150**, C23) reveal that the substituent effects are consistent with free carbanion formation.

Such a mechanism can be ruled out for the cleavages we have studied, since if it applied base catalysis would be unnecessary, and we find that while fluoren-9-yltrimethylstannane is cleaved by neutral methanol, a trace of acid, which suppresses autoprotolysis to methoxide ion, completely inhibits the reaction. It is noteworthy that if the ionization observed by Beletskaya *et al.* actually occurred under the influence of a dimethyl sulphoxide molecule fully or partly co-ordinated to tin, and we see no evidence against this, then the overall process would be precisely analogous to our A or A_S mechanism, with dimethyl sulphoxide replacing methoxide ion as the nucleophile and iodine replacing methanol as the electrophile.

Activation Parameters.—Activation parameters for some tin compounds are listed in Table 4, which also, for comparison, shows the corresponding data for analogous silicon compounds and for some aryl compounds (*cf.* ref. 2). We thought that the difference in mechanism found between most tin and corresponding silicon compounds might reveal itself in low log A factors (*i.e.* less favourable entropies of activation) for the tin compounds since the rate-determining step for the A (or A_S) mechanism involves covalent involvement of an additional solvent molecule in the rate-determining transition state. The results show no such differences, however, except for the 2-benzo[*b*]thienyl compounds, and direct comparison is not justified in this case because the tin is much more reactive than the silicon compound. Two reasons can be offered for this negative result: (*a*) any such inherent effect may be obscured by the variation of the log A values with changing reactivity even within a series of silicon compounds for which the B (or B_S) mechanism operates throughout (see refs. 3 and 15); and (b) even within the type B (or B_S) mechanism, a solvent molecule (or more than one) may be partly hydrogen-bonded to the separating carbanion in the rate-determining transition state, and this would blur the distinction in entropy effects between the two mechanisms. There are two minor features of interest. (a) The two aryltrimethyltin compounds examined are *ca.* 40 times less reactive than (triphenylmethyl)trimethylstannane, in spite of having much smaller activation energies, because of their very low log A factors; these effects are consistent with operation of a type A (or A_S) mechanism for the aryl compounds and a type B (or B_S) mechanism for the triphenylmethyl compound. (b) The low reactivities of the compounds Ph_3CSiMe_3 and $Ph_2CHSiMe_3$ compared with those of the tin analogues appear to be associated with low log A values; the steric effects discussed above could contribute to this.

TABLE 4

Activation parameters for cleavages of Me_3MR compounds by sodium methoxide in methanol

	M = Sn					M = Si	
	θ/°C	[NaOMe]/M	10^5k_s/l mol^{-1}s^{-1}	E_{act}[a]	log A[b]	E_{act}[a]	log A[b]
$C_6H_5CH_2$	40	2.0	0.168	23.8	10.7	26.1	11.2
	50		0.52				
	55		0.88				
m-$ClC_6H_5CH_2$	30	1.0	1.57	21.6	10.7	22.6	10.6
	40		4.98				
	50		13.7				
3,5-$Cl_2C_6H_3CH_2$	25	0.5	39	20.6	11.6	21.2	11.1
	35		125				
	50		575				
Ph_2CH	25	0.05	450	21.1	13.1	18.8	9.2
	35		1 390				
	50		7 250				
Ph_3C	18	0.001	80 700	17.0	12.7	17.2	8.3
	25		159 000				
	30		261 000				
	35		409 000				
2-Benzo[*b*]thienyl	25	0.01	4 200	13.4	8.4	22.4	11.2
	35		9 100				
	50		24 000				
2-Furyl	25	0.01	4 050	12.1	7.5		
	40		10 600				
	50		19 600				

[a] In kcal mol^{-1}. [b] In l mol^{-1} s^{-1}.

EXPERIMENTAL

Materials.—(a) *Trialkylfluoren-9-ylstannanes.* A solution of n-butyl-lithium (0.18 mol) in ether (100 cm^3) was added to a solution of fluorene (0.17 mol) in ether (200 cm^3) and the mixture was boiled under reflux for 3 h. The appropriate trialkylchlorostannane (0.20 mol) in ether (150 cm^3) was added dropwise, and the mixture was subsequently boiled under reflux for 2 h. After filtration, ether was evaporated from the filtrate and the residue was extracted with benzene. Benzene was evaporated and the residue distilled (for the triethyl compound) or recrystallized from light petroleum (b.p. 40—60°) to give *trimethyl-*, m.p. 89—90 °C (Found: C, 58.8; H, 5.5. $C_{16}H_{18}Sn$ requires C, 58.4; H, 5.5%); triethyl-, b.p. 128 °C at 0.005 mmHg (lit.,[6] 151 °C at 0.15 mmHg); and *tri-isopropylfluoren-9-ylstannane*, m.p. 68—69 °C (Found: C, 64.0; H, 7.2 $C_{22}H_{30}Sn$ requires C, 63.95; H, 7.3%). *9-Methylfluoren-9-yltrimethylstannane*, m.p. 132—133 °C (Found: C, 59.5; H, 6.1. $C_{17}H_{20}Sn$ requires C, 59.5; H, 5.9%), was prepared analogously from 9-methylfluorene.

(b) *Trialkyl(diphenylmethyl)stannanes.* A solution of n-butyl-lithium (0.11 mol) in ether (150 cm^3) was added to a solution of diphenylmethane (16.8 g, 0.10 mol) and tetramethylethylenediamine (11.6 g, 0.10 mol) in ether (300 cm^3) and the mixture was boiled under reflux for 4 h. The appropriate trialkylchlorostannane (0.10 mol) in ether (100 cm^3) was added, and the mixture was boiled under reflux for 20 h. Work-up as in (a) gave *trimethyl-*, m.p. 68—69 °C (Found: C, 57.8; H, 6.2. $C_{16}H_{20}Sn$ requires C, 58.05; H, 6.1%), *triethyl-*, b.p. 108 °C at *ca.* 0.001 mmHg (Found: C, 61.3; H, 6.9. $C_{19}H_{26}Sn$ requires C, 61.2; H, 7.0%), or *tri-isopropyl-diphenylmethylstannane*, b.p. 123 °C at *ca.* 0.003 mmHg (Found: C, 63.7; H, 7.7. $C_{22}H_{32}Sn$ requires C, 63.6; H, 7.8%).

(c) *Cyanobenzyltrimethylstannanes.* Starting from the appropriate cyanotoluene and chlorotrimethylstannane, the procedure used for the corresponding silicon compounds,[2] gave *m-*, b.p. 94 °C 0.5 mmHg (Found: C, 47.6; H, 5.4; N, 5.2. $C_{11}H_{15}NSn$ requires C, 47.2; H, 5.4; N, 5.0%) and *p*-cyanobenzyltrimethylstannane, b.p. 95 °C at 0.3 mmHg (Found: C, 47.6; H, 5.4; N, 5.1%).

(d) 3,5-*Dichlorobenzyltrimethylstannane.* This *compound*, b.p. 90 °C at 0.6 mmHg (Found: C, 37.1; H, 4.2. $C_{10}H_{14}Cl_2Sn$ requires C, 37.1; H, 4.4%), was made from 3,5-dichlorobenzylmagnesium chloride and chlorotrimethylstannane by the usual procedure.[15]

Other benzyl compounds [15] and triphenylmethyl(trimethyl)stannane [16] were made as previously described.

For all trialkylSnR compounds, careful g.l.c. analysis was carried out to confirm that none of the parent RH compound was present, since this would vitiate the p.i.e. determinations.

Rate Measurements.—These were carried out spectrophotometrically as previously described.[4] The stopped-flow technique (Durrum model D-110 stopped-flow spectrometer) had to be used for the very reactive fluoren-9-yltin compounds, and the solutions of these compounds were made immediately before use because cleavage by neutral methanol is quite rapid. Base concentrations refer to the solutions at 25 °C, and no allowance has been made for expansion of the medium for runs at higher temperature. The kinetic behaviour of the cyanobenzyl compounds was normal, and corresponding cyanotoluenes were the only detectable aromatic products.

Product Isotope Effects.—Conditions for the cleavages used in p.i.e. determinations are shown in Table 2. The RH : RD product ratio was usually determined by use of the ARL MPD 850 organic analyser linked to a Pye model 64 gas chromatograph; [3,4] the measurements for corresponding silicon and tin compounds were made on the same day and after satisfactory results had been obtained for the RH : RD ratio of the product of cleavage of the appropriate $RMMe_3$ compound in ' 100% ' MeOD (see ref. 2); cleavage of the compounds Ph_2CHSnR_3' with R′ = Me, Et, or Pr^i in ' 100% ' MeOD all gave the theoretical product H : D ratio of 11.0 ($\pm$0.1). For the Ph_2CHSnR_3' compounds, RH : RD ratios were also determined by the n.m.r. spectroscopic method used for the corresponding silicon compounds.[2] This method was also applied for Ph_3CSnMe_3, for which mass spectrophotometric analysis [2] was also used.

Checks showed that no hydrogen exchange occurred in the RH compounds under the conditions used for cleavage.

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