Aromatic Reactivity. Part LXI.[1] Reactivities and Solvent Isotope Effects in the Base Cleavage of Triorgano-silicon, -germanium, and -tin Groups from Furan, Thiophen, Benzofuran, and Benzothiophen Rings †

By **Colin Eaborn,*** School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ
Giancarlo Seconi,* Laboratorio dei composti del carbonio contenenti eteroatomi e loro applicazioni, C.N.R., Via Tolara di Sotto 89, 40064, Ozzano Emilia (Bologna), Italy

First-order constants have been measured for the cleavage of some heterocyclic $\mathrm{ArMR_3}$ compounds by methanolic sodium methoxide at 50 °C, along with the values, p.i.e., of the product ratio ArH : ArD obtained on cleavage in 1 : 1 MeOH–MeOD, and in some cases the values, r.i.e., of the ratio of the rates of cleavage in MeOH and MeOD, respectively. The values of the specific rate constants, k_s, increase with base concentration, especially at higher concentrations. For $\mathrm{ArSnMe_3}$ compounds the values of 10^2k_s ([MeONa] = 0.001 5M) p.i.e. and r.i.e. are (Ar =) 2-furyl, 18.0, 4.3, 2.0; 2-thienyl, 11.4, 3.95, 1.90; 2-benzofuryl, 41, 3.5, 1.46; and 2-benzothienyl, 23.8, 3.6, —. The corresponding values of 10^6k_s ([NaOMe] = 1M), p.i.e. and r.i.e. for $\mathrm{SiMe_3}$ compounds are (Ar =) 2-furyl, 2.75, 1.20, 0.495; 2-thienyl, 7.5, 1.05, —; 2-benzofuryl, 98, 1.2, 0.46; and 2-benzothienyl, 117, 1.2, 0.46. The r.i.e. : p.i.e. ratios fall in the range 0.40—0.49. The $\mathrm{ArSiMe_3}$ are *ca.* 130—190 times as reactive as the $\mathrm{ArSiEt_3}$ compounds. For $\mathrm{ArSnR_3}$ compounds the corresponding ratios lie in the range 22—32, while the ratio for R = Me and $\mathrm{Pr^i}$ is *ca.* 16 000 for Ar = 2-thienyl and 8 000 for Ar = 2-benzothienyl. For 2-benzothienyltrimethylgermane the values of k_s ([MeONa] = 2M) and p.i.e. are 0.017 and 1.19, and the germanium compound is estimated to be *ca.* 1 300 times less reactive than its silicon analogue. The results are consistent with substantial electrophilic assistance by proton transfer to the leaving carbon atom in the rate-determining step of the cleavage of the $\mathrm{ArSnR_3}$ and little, if any, such assistance in cleavage of the $\mathrm{ArSiR_3}$ and $\mathrm{ArGeMe_3}$ compounds.

An earlier paper in this series was concerned with the solvent isotope effects in the cleavage of some $\mathrm{XC_6H_4{-}SnMe_3}$ bonds by methanolic sodium methoxide.[2] Measurements were made of (a) the ratio $k_{\mathrm{MeOH}} : k_{\mathrm{MeOD}}$, denoted r.i.e. (rate isotope effect), of the rate constants for cleavage in MeOH and MeOD, respectively, and (b) the ratio of the products ArH : ArD, denoted p.i.e. (product isotope effect) obtained on cleavage of the $\mathrm{ArSnMe_3}$ compound in 1 : 1 MeOH–MeOD. It was shown that the values of the p.i.e. were substantially greater than unity (falling in the range 3.8—5.2), implying that the reaction does not give a free carbanion $\mathrm{Ar^-}$, since this would not discriminate to this extent between MeO–H and MeO–D bonds. It was also shown that in the two representative cases for which it was measured, the ratio r.i.e. : p.i.e. fell in the range 0.46—0.50, which implies that the rate of the reaction and the composition of the products are probably determined in the same step of the reaction, the reasoning being as follows. Methoxide ion is, in effect, 2.0—2.5 times as readily available in MeOD as in MeOH if it becomes effectively free from at least one molecule of solvation in the transition state.[3] Thus if the rate-determining step involved, say, the formation of a substrate–methoxide ion complex, $\mathrm{[MeOMMe_3Ar]^-}$, the reaction would be 2.0—2.5 times as fast in MeOD as in MeOH (*i.e.* r.i.e. 0.50—0.40) provided the O–M bond were considerably formed in the transition state and the methoxide ion thus effectively freed from its solvation shell. If the rate-determining step involved dissociation of the $\mathrm{M^V}$ complex to a carbanion $\mathrm{Ar^-}$, an overall rate ratio, r.i.e., of 0.50—0.40 would again be expected, and the product ratio, the p.i.e., would be determined in a subsequent step and thus not necessarily be related to the r.i.e. On the other hand, if the rate-determining (and product-determining) step is the reaction of the $\mathrm{M^V}$ complex with the solvent, then the kinetic isotope effect for this step, which is also the product isotope effect, p.i.e., will tend to counterbalance that on the first step, so that the overall ratio of rates, r.i.e., will be (0.50—0.40) × p.i.e., *i.e.* the r.i.e. : p.i.e. ratio will fall in the range 0.50—0.40.

The rather complex effects of the substituents X on the rates of the cleavage of the $\mathrm{XC_6H_4SnMe_3}$ compounds are consistent with a rate-determining step in which there is electrophilic attack (involving proton transfer) by solvent molecules on the carbon atom of the Ar–Sn bond within the $\mathrm{Sn^V}$ complex $\mathrm{[MeOSnArMe_3]^-}$.[4] (However, neither the substituent nor the isotope effects completely rule out a concerted attack of methoxide ion at tin and methanol at carbon provided the transition state resembles fairly closely that associated with the rate-determining step of the stepwise process.) The substituent effects in cleavage of the silicon compounds $\mathrm{XC_6H_4SiMe_3}$ in a more basic medium, $\mathrm{Me_2SO{-}H_2O{-}OH^-}$, were consistent with a rate-determining step involving electrophilic assistance to the leaving carbanion, though the contribution by this assistance appeared to be smaller than with the tin compounds.[4] On the other hand, a comparative study of the base cleavage of $\mathrm{XC_6H_4Me_2Si{-}CH_2C_6H_4Cl}$-*p* and 2-$\mathrm{(XC_6H_4Me_2Si){-}C_8H_5O}$ bonds ($\mathrm{C_8H_5O}$ = benzofuryl) indicated that very similar degrees of charge were developed on the silicon atom in the (rate-determining) transition state in these comparably reactive systems,[5] suggesting that the Ar–Si cleavage resembled the

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† No reprints available.

[1] Part LX, C. Eaborn, R. Eidenschink, and D. R. M. Walton, *J. Organometallic Chem.*, 1975, **96**, 83.

[2] R. Alexander, W. A. Asomaning, C. Eaborn, I. D. Jenkins, and D. R. M. Walton, *J.C.S. Perkin II*, 1974, 304.

[3] J. R. Jones, 'The Ionization of Carbon Acids,' Academic Press, London and New York, 1973, pp. 205—207; R. A. More O'Ferall, *Chem. Comm.*, 1969, 114; C. G. Mitton, M. Gresser, and R. L. Schowen, *J. Amer. Chem. Soc.*, 1969, **91**, 2045; K. O'Donnell, R. Bacon, K. L. Chellapa, R. L. Schowen, and J. K. Lee, *ibid.*, p. 2500; R. L. Schowen, *Progr. Phys. Org. Chem.*, 1972, **9**, 275; V. Gold and S. Grist, *J. Chem. Soc.* (*B*), 1971, 2282.

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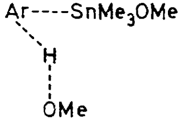
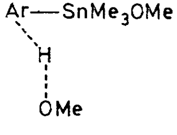
benzyl–Si cleavages[6] in involving little, if any, electrophilic assistance.

For the $ArSnMe_3$ compounds, there are two possibilities for the rate-determining destruction of the intermediate $[MeOSnArMe_3]^-$. In the first (which corresponds to that favoured for cleavage of $XC_6H_4CH_2SnMe_3$ compounds), proton transfer to the separating carbon is concerted with breaking of the Ar–Sn bond, as in transition state (I). In the second, the proton transfer, through transition state (II), gives the Wheland-intermediate (III)


(I)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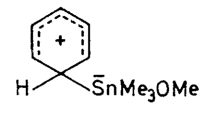
(III)

(with subsequent rapid loss of Me_3SnOMe). Substituent effects within the $XC_6H_4SnMe_3$ series led us marginally to favour a transition state of type (II), with proton transfer more than half complete at the transition state.[2]

We have now extended the solvent isotope effect studies to $ArMR_3$ compounds in which M = Sn or Si, Ar = 2-furyl, 2-thienyl, 2-benzofuryl, or 2-benzothienyl, and R = Me (usually), Et, or Pr^i. The objectives were (i) to see whether the conclusions tentatively reached for the $XC_6H_4SnMe_3$ compounds were valid for the more reactive heterocyclic $ArSnR_3$ compounds, and (ii) to provide corresponding information on cleavage of aryl–silicon bonds, since $XC_6H_4SiMe_3$ compounds are not sufficiently reactive towards methanolic sodium methoxide. For comparison, a single germanium compound, 2-benzofuryltrimethylgermane, was also examined.

The results are shown in Table 1, in which appear (i) the observed first-order rate constants, k, at the specified concentration of sodium methoxide, (ii) the value of the specific rate constant, k_s, (iii) the value of k_{rel}, the estimated reactivity (see below) relative to that of the corresponding $PhCH_2MMe_3$ compounds (which are arbitrarily used as reference points in our papers on base cleavage), (iv) the ratio, r.i.e., of the rate constants in MeOH and MeOD, (v) the value, p.i.e., of the product ratio ArH : ArD, and (vi) the ratio r.i.e. : p.i.e. The values of k_s are almost independent of the concentration of base at low concentrations but increase markedly with the concentration at higher concentrations, apparently more than they do for reactions in aqueous methanol.[7] Table 2 shows that the value of k_s for 2-benzofuryltriethylstannane is effectively constant for sodium methoxide concentrations of 0.001 6—0.04M, but that the value for 2-benzothienyltrimethylsilane increases by almost a factor of 4 over the range 0.27—4.3M-base. We are studying such medium dependancy in some detail and preliminary results indicate that it may vary from compound to compound and may be less marked for tin than for silicon compounds; in the meantime we have derived the rough values of k_{rel} in Table 1 by halving the k_s values observed for benzyltrimethyl-stannane and -silane at 2M-base concentration to make them roughly equivalent to the k_s values for the aryl–tin compounds at base concentrations below 0.25M and for the aryl–silicon com-

TABLE 1

Rate constants and solvent isotope effects in the cleavage of R^1–MR^2_3 bonds by sodium methoxide in methanol at 50 °C

		In MeOH				In MeOD					
M = Sn R^1	R^2	10^2[MeONa]/M	$10^5k/s^{-1}$ [a]	10^5k_s [b] l mol^{-1} s^{-1}	k_{rel} [c]	10^2[MeONa]/M	$10^5k/s^{-1}$ [a]	10^5k [b]/ l mol^{-1} s^{-1}	R.i.e.	P.i.e.	R.i.e./p.i.e.
$PhCH_2$	Me	198	1.05	0.53	1.0				2.1		
2-Thienyl	Me	0.153	17.5	11 400	43 000	0.217	13.0	6 000	1.90	3.95	0.48
	Et	3.94	14.2	360	1 360	2.72	7.4	270	1.33	3.2	0.42
	Pr^i	23.8	0.167	0.70	2.6					1.95	
		55.6	0.42	0.75							
2-Furyl	Me	0.153	28.2	18 000	68 000	0.217	19.3	8 900	2.02	4.3	0.47
	Et	3.94	21.5	540	2 100					3.7	
2-Benzothienyl	Me	0.153	36.4	23 800	90 000					3.6	
	Et	3.94	37.5	950	3 580					2.9	
	Pr^i	159	4.75	3.00	11.3	203	6.80	3.34	0.90	1.75	0.51
2-Benzofuryl	Me	0.153	62.6	41 000	155 000	0.217	61	28 000	1.46	3.5	0.42
	Et	2.62	51.60	1 970	7 400	2.72	40	1 490	1.32	3.1	0.43
M = Si											
$PhCH_2$	Me	198	0.069	0.0348	1.0					1.17	
2-Thienyl	Me	100	0.75	0.75	43					1.05	
	Et	100	0.004 25	0.004 25	0.24						
2-Furyl	Me	100	0.275	0.275	15.8	137	0.75	0.55	0.50	1.19	0.42
2-Benzothienyl	Me	102	12.2	12.0	690	100	25.4	25.4	0.47	1.18	0.40
	Et	100	0.096	0.096	5.5					1.12	
2-Benzofuryl	Me	102	10.0	9.8	560	100	20.6	20.6	0.46	1.15	0.40
	Et	100	0.057	0.057	3.3	137	0.017	0.125	0.46	1.08	0.43
M = Ge											
2-Benzofuryl	Me	200	0.034	0.017						1.19	

[a] Observed first-order rate constant. [b] k[/MeONa]. [c] Approximate values (see text); the ratio of k_s for the compound concerned relative to that for the appropriate $PhCH_2MMe_3$ has been doubled to take account of the high base concentration used for the latter

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[6] R. Alexander, W. A. Asomaning, C. Eaborn, I. D. Jenkins, and D. R. M. Walton, *J.C.S. Perkin II*, 1974, 490.

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

pounds at 1M-base concentration. The validity of the discussion below is not affected by the uncertainty in the k_s values.

The main features of the results, and some comments, are as follows.

(a) The heterocyclic $ArSnMe_3$ compounds are much more reactive than previously studied $XC_6H_4SnMe_3$ compounds.[8] A value of 10^5k_s of 95 s^{-1} was observed for *p*-nitrophenyltrimethylstannane with 1.0M-sodium methoxide and we roughly estimate that the value would be *ca.* 1.5 times smaller with, say, 0.1M-sodium methoxide, *i.e.* 65. Thus 2-thienyltrimethylstannane is *ca.* 180 times as reactive as the *p*-nitrophenyl compound. The latter is 31 times as reactive as phenyltrimethylstannane in 3 : 2 v/v $MeOH-H_2O$ (see Experimental section), and assuming that the relative reactivities are not greatly affected by the medium change the 2-thienyl$SnMe_3$: $PhSnMe_3$ reactivity ratio is, very roughly, 5 500. The corresponding ratios for the other heterocyclic aryl$SnMe_3$ compounds are shown in Table 2, and the most reactive, the 2-benzofuryl compound, is seen to be *ca.* 20 000 times as reactive as the phenyl compound.

TABLE 2

Variation of observed first-order rate constant, k, and specific constant, k_s, with base concentration for cleavage in methanol at 50 °C

Compound	10^2[MeONa]/ M	$10^5k/s^{-1}$	$10^5k/$ l mol^{-1} s^{-1}
2-Benzofuryl$SnEt_3$	3.94	75	1 900
	2.62	52	1 970
	0.158	2.9	1 835
2-Benzothienyl$SiMe_3$	27	2.4	8.9
	102	12.2	12.0
	112	14.1	12.6
	187	32.5	17.4
	282	67	23.8
	429	138	32.8

(b) In comparison with compounds of the benzyl–tin type, *e.g.* $Ph_xH_{(3-x)}CSnMe_3$ with $x = 1$—3, the heterocyclic aryl–tin compounds are much more reactive than would be expected from the acidities of the corresponding hydrocarbons, ArH, and thus from the stabilities of the carbanions Ar^-. For example, 2-thienyl- is more reactive than (diphenylmethyl)-trimethylstannane, although the (ion-pair) pK_a of thiophen is 5 units higher than that of diphenylmethane (see Table 3).[9] This is inconsistent with rate-determining formation of the carbanions in both types of compound, but is readily understandable if the proton attack occurs in the rate-determining step, since the electrophilic attack will be much easier at the aromatic centres.

The reactivities within the set of heterocyclic $ArSnMe_3$ compounds follow the sequence of pK_a values for three compounds for which the latter are known (Table 3). This is consistent with either of the transition states (I) and (II). In (I) the proton transfer would have to be substantially less complete than the Ar–Sn bond breaking (*cf.* refs. 2 and 6). In (II), the dominant effect would be the stabilization of the intermediate $[MeOSnArMe_3]^-$ by inductive electron withdrawal by the Ar group (as suggested for the $XC_6H_4SnMe_3$ compounds [2]), and this can reasonably be expected to run parallel to the acidities of the ArH compounds since the stabilization of the carbanions does not involve conjugative delocalization of the lone pair of electrons.

Significantly, the sequence of reactivities for the $ArSnMe_3$ compounds is quite different from that recorded for the base-catalysed hydrogen exchange at the 2-positions of the corresponding hydrocarbons, ArH, in ethanolic potassium ethoxide[10] (Table 3). (It is also different from that for the silicon compounds, as discussed below.) The most marked difference is that the furan system is the most reactive for the tin compounds, whereas in the hydrogen exchange it is *ca.* 200 and 600 times less reactive than the thiophen and benzothiophen systems, respectively.* This difference can reasonably be associated with the fact that furan is the most reactive of the aromatic compounds towards electrophilic attack at the 2-position, since this factor will be very important for the reactions of the tin compounds, in which electrophilic assistance appears to make a major contribution. It is noteworthy that the relative reactivities in the

TABLE 3

Comparison of relative reactivities of $RMMe_3$ compounds at 50 °C with pK_a values and relative rates, f_{rel}, of hydrogen exchange at 90 °C for the corresponding RH compounds

R	RH pK_a [a]	RH 10^3f_{rel} [b]	$RSnMe_3$ k_{rel} [c]	$RSnMe_3$ k'_{rel} [d]	$RSiMe_3$ k_{rel} [c]
$PhCH_2$	41		1.0		1.0
Ph_2CH	33.4		17 000 [e]		1 900 [f]
Ph	43		(8) [g]	1.0	
2-Furyl		5.4	68 000	8 700	15.8
2-Thienyl	38.4	1 000	43 000 [h]	5 500	23
2-Benzofuryl	36.8	720	155 000	19 800	630
2-Benzothienyl	37	3 290	90 000 [i]	11 500	710

[a] Ion-pair acidities in $CsNHC_6H_{11}-H_2NC_6H_{11}$.[9] [b] Relative rates of 2-deuteriation in KOEt–EtOD at 90 °C derived from rate constants at various temperatures.[10] [c] Rates of cleavage relative to appropriate $PhCH_2MMe_3$ at 50 °C. [d] Rough value (see text) of rates relative to that of $PhSnMe_3$. [e] Approximate value based on unpublished work by G. Seconi. [f] Approximate value based on k_s 34 × 10^{-5} l mol^{-1} s^{-1} for $Ph_2CHSiMe_3$ with 1.0M-NaOMe and allowing roughly for higher base concentration used for $PhCH_2SiMe_3$. [g] Rough value derived from the k'_{rel} and k_{rel} values for the heterocyclic compounds. [h] A value of 23 000 was found in 5 : 1 $MeOH-H_2O$, no allowance being made for variation of the specific first-order rate constant with the base concentration (see Experimental section). [i] 50 000 in 5 : 1 $MeOH-H_2O$ [see note (*h*)].

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* The 2-position of thiophen is also reported to be *ca.* 500 times as reactive as that of furan towards hydrogen exchange in $Me_2SO-MOBu^t$ (M = Li or K).[11]

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[11] A. I. Shatenshtein, A. G. Kamrad, I. O. Shapiro, Yu. I. Ranneva, and E. N. Zvyagintseva, *Doklady Akad. Nauk S.S.S.R.*, 1966, **168**, 364.

hydrogen exchange, the ' kinetic acidities ', are not consistent with the equilibrium ion-pair acidities.

(c) The p.i.e. values for the heterocyclic $ArSnMe_3$ compounds fall in the range established for $XC_6H_4SnMe_3$ compounds,[2] and confirm that the products do not arise from interaction of the carbanion Ar^- with the solvent. Within the range of $XC_6H_4SnMe_3$ compounds the value of the p.i.e. appeared to increase with increasing ease of electrophilic attack at the corresponding position of the ArH compound. The p.i.e. values cannot depend only on this factor, since if they did they would be larger for 2-furyl- than for *p*-methoxyphenyl-trimethylstannane, and, indeed, the change in the degree of stabilization of the Sn^V intermediate in process (II), or in the stability of the (notionally) separating carbanion in process (I) can be expected to obscure any such simple relationship on passing from the phenyl to the very different heterocyclic aryl systems.

(d) For all the $ArSnR_3$ compounds the r.i.e. : p.i.e. ratios fall in the range 0.42—0.51, which is consistent with the mechanisms (I) and (II) proposed for the $XC_6H_4SnMe_3$ compounds, as described in the Introduction.

(e) For the $ArSnR_3$ compounds there is a substantial fall in reactivity on going from R = Me to Et (though this is markedly smaller than the corresponding effect with the silicon compounds) and a much bigger fall on going to R = Pr^i The change from (R =) Me to Et to Pr^i is also accompanied by a clear fall in the p.i.e. value. In terms of processes (I) and (II), the fall in reactivity with increasing bulk of R can be mainly associated with increasing compression in the transition state. In discussing the p.i.e. values it is necessary to consider separately transition states (I) and (II). For (I), the lower p.i.e. would be associated with greater compression in the Sn^V intermediate, which would lead to more rapid expulsion of the SnR_3 group, thus to a transition state (I) closer to this intermediate, and so to a smaller degree of proton transfer at the transition state. For (II), the compression for large R groups in the first Sn^V intermediate would be compounded on going to the Wheland intermediate, and the transition state would be further removed from the first Sn^V intermediate, the proton transfer would be more complete, and the p.i.e. would be lower, provided, as previously suggested,[2] that the proton transfer is more than half complete at the transition state.

(f) The heterocyclic $ArSiMe_3$ compounds are much less readily cleaved than the corresponding $ArSnMe_3$ compounds, which is in keeping with the much lower reactivity of phenyltrimethylsilane than of phenyltrimethylstannane towards aqueous methanolic alkali.[8] In comparison with compounds of the benzylMMe$_3$ type, the reactivities of the heterocyclic $ArSiMe_3$ compounds accord much more closely with the pK_a values of the ArH compounds (Table 3), and the log k_{rel} values for Ar = 2-C_4H_3S, 2-C_8H_5O, and 2-C_8H_5S, fall between those of the compounds $PhCH_2SiMe_3$ and $Ph_2CHSiMe_3$, in line with the relevant pK_a values. In 5 : 1 v/v $MeOH-H_2O$ at 50° (*cf.* ref. 13), 2-benzothienyl- was found to be cleaved *ca.* 510 times as readily as benzyl-trimethylsilane (see Experimental section). On the assumption that the relative reactivities of the several arylsilanes are approximately the same in the two media, the derived values of k_{rel} in 5 : 1 $MeOH-H_2O$ for Ar = 2-C_4H_3O, 2-C_4H_3S, and 2-C_8H_5O would be 11.5, 16.5, and 450. The corresponding log k_{rel} values lie only 0.2—1.2 units above the line of the log k_{rel}-pK_a plot [12] for compounds of the benzyltrimethylsilane type. These results are consistent with the view that if electrophilic assistance operates at all for the arylsilicon compounds, it is much less important than for the tin compounds, so that the stability of the Ar^- carbanion is the greatly dominant effect.

(g) The sequence of reactivities for the silicon compounds differs significantly from that for the tin compounds in that the two oxygen heterocycles are less reactive than their sulphur analogues. This can be associated with the fact that the higher susceptibility of the oxygen systems to electrophilic attack is less important for the reactions of the silicon compounds. The sequence of reactivity for the $ArSiMe_3$ compounds is the same as that of the kinetic acidities, but the very low kinetic acidity of furan is not reflected in the reactivities of the silicon compounds. The reactivity pattern for the silicon compounds shows a very minor deviation from the pattern of pK_a values (Table 3), but the deviation is much less than that for the hydrogen exchange, in which benzofuran is less reactive than thiophen even though the pK_a of the latter is 1.4 units higher.

(h) The p.i.e. values for the silicon are markedly smaller than those for the tin compounds, and are consistent with a carbanion mechanism. The similarity in the p.i.e. values for the $ArSiMe_3$ and $XC_6H_4CH_2SiMe_3$ compounds accords with the observation that similar degrees of charge are developed at silicon in the highest energy transition states for cleavage of $XC_6H_4SiMe_2$-$CH_2C_6H_4Cl$-*p* and $XC_6H_4SiMe_2C_8H_5O$ compounds.[5]

(i) There are quite large differences in reactivity between the $ArSiMe_3$ and $ArSiEt_3$ compounds. The Me_3Si : Et_3Si reactivity ratios fall in the range 130—190, which compares with a value of 5.5 for *p*-$^-O_2CC_6H_4CH_2$-SiR_3, *ca.* 280 for $PhC{\equiv}CSiR_3$, and *ca.* 1 000 for 9-fluorenyl-SiR_3 compounds. This result is in accord with our view that, other things being equal, the magnitude of the steric hindrance rises with the reactivity of the $RSiMe_3$ compound, probably as the rate-determining transition state moves closer in structure to that of the Si^V intermediate. (In addition, specific steric effects associated with structural changes around the reaction centre can also be observed.[13])

(j) When allowance is made for the base concentrations, 2-trimethylgermylbenzofuran appears to be *ca.* 1 300 times less readily cleaved than its silicon analogue. Such a difference is not unusual for base cleavage of

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corresponding $RSiMe_3$ and $RGeMe_3$ compounds,[7] and suggests that electrophilic assistance plays a relatively small part, if any, in the cleavages of the germanium as of the silicon derivatives of benzofuran. (Any electrophilic assistance would be expected to be slightly more important for germanium than for silicon compounds in the light of the slightly greater ease of acid cleavage of $ArGeMe_3$ than of $ArSiMe_3$ compounds.[14])

Conclusions.—The picture which emerges is one of distinct difference between the mechanism of the cleavage of the R–$SnMe_3$ bond on the one hand and that of the R–$SiMe_3$ (and R–$GeMe_3$) bond on the other. Within the range of $ArSnR_3$ compounds considered there appears to be substantial contribution by electrophilic assistance involving proton transfer to the leaving aryl group from the solvent, which is greater than that in cleavage of $XC_6H_4CH_2SnMe_3$ compounds. For the $ArSiR_3$ compounds, the isotope effects are consistent with separation of the carbanion or with a very small contribution from electrophilic assistance (involving, say, a 10% degree of proton transfer at the highest energy transition state). It may be possible to decide between these alternatives by use of Ar groups derived from much more acidic heterocyclic ArH compounds, since the more stable Ar^- carbanions could discriminate significantly between MeO–H and MeO–D and thus give rise to p.i.e. values substantially greater than unity.

TABLE 4

Elemental analyses and b.p.s of $ArMR_3$ compounds, and wavelengths used in rate studies

Ar	MR_3	λ/nm	B.p./°C (mmHg)	Found (%) C	Found (%) H	Found (%) S	Required (%) C	Required (%) H	Required (%) S
2-Furyl	$SiMe_3$ [a]	230	127—130 (760)						
	$SiEt_3$ [b]	230	55 (2.5)						
	$SnMe_3$	230	65 (15)	36.9	5.25		36.4	5.2	
	$SnEt_3$	230	105 (15)	43.8	6.5		44.0	6.65	
2-Thienyl	$SiMe_3$ [c]	245	165—167 (760)						
	$SiEt_3$	245	92 (3)	60.0	9.2		60.55	9.1	
	$SnMe_3$	245	89 (15)	34.2	5.1		34.05	4.9	
	$SnEt_3$	245	104 (3)	41.8	6.3	11.4	41.6	6.3	11.1
	$SnPr^i_3$	245	72 (0.1)	47.2	7.5		47.15	7.3	
2-Benzofuryl	$SiMe_3$	259	92 (6)	69.3	7.3		69.4	7.4	
	$SiEt_3$	260	74 (0.01)	71.8	8.4		72.3	8.7	
	$SnMe_3$	260	92 (1.2)	47.1	4.9		47.0	5.0	
	$SnEt_3$	255	88 (0.015)	52.3	6.2		52.1	6.2	
	$GeMe_3$	286.5	115 (9)	56.4	6.3		56.3	6.0	
2-Benzothienyl	$SiMe_3$	241	123 (7) [c]						
	$SiEt_3$	241	102 (0.01)	67.9	7.9	13.1	67.5	8.1	13.1
	$SnMe_3$	240	124 (1)	44.6	4.6	10.6	44.4	4.7	11.0
	$SnEt_3$	240	118 (0.02)	49.7	5.9	9.5	49.5	5.9	9.6
	$SnPr^i_3$	245	108 (0.005)						

[a] See Ref. 15. See Ref. 16. [c] See D. Shopov, S. S. Dyankov, and N. S. Nametkin. *Doklady Akad. Nauk S.S.S.R.*, 1965, **161**, 1106.

A Note on the Reactivity of p-*Nitrophenyltrimethylstannane.*—We previously suggested that the *p*-NO_2 group might activate significantly less in cleavage of *p*-nitrophenyltrimethylstannane in MeOH–H_2O than would be expected on the basis of the σ constant of the group.[4] The value of k_{rel} of 31 we have now observed for this compound relative to phenyltrimethylstannane corresponds with a log k_{rel} value of 1.49, compared with a value of 1.70 which would be expected on the basis of the correlation line (ρ 2.18) established for *meta*-substituents.[8] The deviation is thus comparable with that noted for the *p*-CF_3 substituent.[8]

EXPERIMENTAL

Preparations of $ArMR_3$ *Compounds.*—The parent heterocyclic compounds were metallated with n-butyl-lithium in ether and the resulting aryl-lithium compounds were treated with the appropriate R_3MCl compound (*cf.* refs. 15 and 16). After addition of saturated aqueous ammonium chloride, the ethereal layer was separated, washed, dried (Na_2SO_4), and fractionated. The b.p.s, and analyses in the case of new compounds, are shown in Table 4. The compounds gave the expected ^1H n.m.r. spectra (with correct integration ratios) and mass spectra. G.l.c. analyses were carried out in every case; where impurities were detected samples for kinetics were finally purified by preparative g.l.c. Special care was taken to ensure the absence of the parent ArH compound.

In the case of 2-benzothienyltri-isopropylstannane preparative g.l.c. was not practicable, and a small amount of inert impurity (not benzothiophen) remained; a satisfactory elemental analysis was not obtained, although the spectra were as expected. This impurity seemed not to interfere with the rate and p.i.e. measurements.

Solvent.—Methanol and [^{2}H]methanol were dried by boiling with magnesium turnings and a crystal of iodine followed by fractionation. [^{2}H]Methanol was initially prepared by treatment of dimethyl carbonate with deuterium oxide,[17] but later similar treatment of purified tetramethoxysilane was found to be very satisfactory. Deuterium oxide (>99%) (2 mol) was added dropwise with cooling and stirring to tetramethoxysilane (1 mol), containing one drop of 98% deuteriosulphuric acid contained in a flask with a reflux condenser. After a few minutes the mixture appeared to solidify. The condenser was replaced by a fractionating column and [^{2}H]methanol (>99% [^{2}H]) was distilled out in 94% yield. It was treated with a few grams

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[16] C. Eaborn and J. A. Sperry, *J. Chem. Soc.*, 1961, 4921.

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of sodium, then redistilled before being treated with magnesium.

Methanolic Sodium Methoxide.—Concentrations of sodium methoxide in the range 0.05—4M were determined by acid titration after dilution with water. Solutions in the concentration range 10^{-2}—10^{-4}M were made by appropriate dilution of a more concentrated solution with pure methanol.

Rate Measurements.—The general procedures have been described.[7,8] For the less reactive compounds, appropriate mixture of a methanolic solution of the organometallic compound with methanolic sodium methoxide was placed in a closed vessel contained in a thermostat at 50.0 °C. At appropriate intervals, 1 ml samples were taken and diluted to 25 ml with methanol, and the optical density was measured at the relevant wavelength (Table 4) by means of a Unicam SP 500 spectrophotometer.

For the more reactive compounds, the reaction mixture was contained in the thermostatted (50 ± 0.1 °C) absorption cell of a Unicam SP 1700 spectrophotometer, and variation with time of the optical density at the selected wavelength was automatically recorded. In a few cases, rate constants were determined by both the sampling and direct method, and were in good agreement (within $\pm 1\%$).

In all cases the spectra of the cleavage products agreed with those of the expected ArH compounds.

Product Isotope Effects.—For the silicon compounds 1M methanolic sodium methoxide in 1 : 1 MeOH–MeOD was used; this was made by mixing 2.0M-sodium methoxide in MeOH–MeOD,[2] with an equal volume of 1 : 1 MeOH–MeOD. The $ArSiR_3$ compound (100 µl) was dissolved in 4 ml of this medium, and the solution kept in a sealed ampoule at 50° for 24 (Ar = C_4H_3S, C_8H_5S) or 48 h (Ar = C_4H_3O, C_8H_5O). Cleavage was not complete with the less reactive compounds, notably the triethyl derivatives, but this is of no consequence.

For the one germanium compound examined, 2.0M-methoxide in 1 : 1 MeOH–MeOD [2] was used with a reaction time of 50 h. For the tin compounds, the medium consisted of a mixture of 1 : 1 MeOH–MeOD with an equal volume of 0.2M-NaOMe in 1 : 1 MeOH–MeOD. Cleavages were carried out as before for 48 h at 50°.

In all cases the mixtures were subsequently added to water (5 ml) and extracted with n-pentane (2 × 3 ml), except that for the furan derivatives n-decane was used. The organic layer was washed with water (3 × 2 ml), dried (Na_2SO_4), and samples were taken for the deuterium analyses. The latter were carried out with an Applied Research Laboratories Organic Analyzer MPD 850 linked to a Pye Model 64 gas chromatograph. In most cases the deuterium content was also determined by use of an Edwards E606 fast scanning mass spectrometer linked to the same chromatograph,[2,6] and the results from the two methods were in very good agreement.

The linked g.l.c.–deuterium analyses showed that no significant amount of deuterium was incorporated into any exchanged $ArMR_3$. Separate experiments showed that no significant amount of deuterium was incorporated into the parent hydrocarbon under the cleavage conditions in the case of the compounds listed in Table 1, but p.i.e. values could not be determined for 2-furyl- or 2-thienyl-triethylsilane because in these cases such hydrogen exchange is significant in the time needed for cleavage. A detectable amount of exchange occurs with benzofuran under the conditions used for cleavage of 2-benzofuryltrimethylgermane, but not enough to affect the p.i.e. value significantly.

Cleavage of p-*Nitrophenyltrimethylstannane in* 3 : 2 v/v $MeOH–H_2O$.—In a mixture of methanol (3 vol) and aqueous 2.0M-sodium hydroxide (2 vol) at 50 °C (*cf.* ref. 8), pseudo-first-order rate constants of 2.33×10^{-3} and 0.61×10^{-3} s^{-1}, respectively, were observed for *p*-nitro- and *m*-chlorophenyltrimethylstannane. Since the k_{rel} value for the *m*-chloro-compound relative to phenyltrimethylstannane in this medium is 8.1,[8] that for the *p*-nitro-compound is thus *ca.* 31.

Cleavage of $2\text{-}C_8H_5S\text{-}SiMe_3$ *and* $\text{-}SnMe_3$ *and of* $2\text{-}C_4H_3SnMe_3$ *in* 5 : 1 $MeOH–H_2O$.—Rates were measured in a mixture of methanol (5 vol) with aqueous NaOH (1 vol).[13] Base concentrations in the mixture were 0.343, 0.001 66, and 0.016 6M for $2\text{-}C_5H_8SiMe_3$, $2\text{-}C_5H_8SSnMe_3$, and $2\text{-}C_4H_3SnMe_3$, respectively, and the corresponding observed first-order rate constants were 6.1×10^{-5}, 83×10^{-5}, and 380×10^{-5} s^{-1}, and the values of 10^5 k_s were thus 17.8, 50 000, and 23 000 l mol^{-1} s^{-1} respectively. The k_{rel} values are thus 510, 50 000, and 23 000, respectively, based on values of 10^5 k_s for $PhCH_2SiMe_3$ and $PhCH_2SnMe_3$ of 0.035 and 1.01 l mol^{-1} s^{-1}, any variation of k_s with the base concentration being neglected (see ref. 7).

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