433. *Alkali-cleavage of Some Carbon–Silicon, –Germanium, and –Tin Bonds.*

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The benzyl–silicon bond is cleaved by alkali in 80% methanol much more readily than the benzyl–germanium bond, but rather less readily than the benzyl–tin bond. The approximate relative reactivities of the m-$Cl·C_6H_4·CH_2·MR_3$ compounds are: (M =) Ge, 1×10^{-3}; Si, 1·0; Sn, 17. The cleavage of benzyltrimethylstannanes shows close similarity to cleavage of benzyltrimethylsilanes.

The ease of cleavage of Y–MR_3 bonds increases in the order (Y =) benzyl, diphenylmethyl, triphenylmethyl, and fluorenyl. Diphenylmethyltrimethylsilane is 125 times as reactive as the analogous germane, but the factor is only 23 with the triethyl compounds, and triphenylmethyltrimethylsilane is 21 times as reactive as the analogous germane. With the fluorenyl compounds, the trimethylsilyl derivative is only 2·5 times as reactive as its germanium analogue, and the triethylsilyl derivative is less reactive than its germanium analogue.

Steric hindrance may be mainly responsible for the large difference in cleavage rates between (i) trimethyl- and triethyl-silyl derivatives (factors of 440 and 960 apply in the case of diphenylmethane and fluorene derivatives, respectively), and (ii) the trimethylsilyl and trimethylstannyl derivatives of fluorene (the tin compound is 10^7—10^9 times the more reactive).

THE ease of acid cleavage of aryl–MR_3 bonds, in which the predominant attack is by an electrophile on carbon, increases in the order (M =) Si < Ge ⩽ Sn.[1] We have now examined the ease of alkali-cleavage of some bonds between a saturated carbon atom and an MR_3 group, specifically $Ph·CH_2$–MR_3, Ph_2CH–MR_3, Ph_3C–MR_3, and fluorenyl–MR_3 bonds; in this reaction nucleophilic attack on M predominates.

Cleavage of $Ph·CH_2·MR_3$ *Compounds*.—We first tried to study spectrophotometrically the cleavage of a series of benzyltrimethylgermanes by aqueous-methanolic alkali under conditions used for benzyltrimethylsilanes,[2] but the rates were much lower—too low for measurement by our technique. In the case of 3-chlorobenzyltrimethylgermane, the most reactive benzylgermane examined, a change in absorption consistent with 4% of cleavage took place in three months in a mixture of methanol (5 vol.) and 0·635M-aqueous sodium hydroxide (1 vol.) at 50·0°; this corresponds with a specific rate constant k_s of *ca.* 1×10^{-6} l. mole^{-1} min.$^{-1}$ (compared with $1·22 \times 10^{-3}$ l. mole^{-1} min.$^{-1}$ for the corresponding silicon compound).* This value could be considerably in error because of the instability of the reaction medium and the small change in optical density; the correct value could be much

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* For simplicity we refer throughout to the base anion as hydroxide, although there is actually an equilibrium mixture of hydroxide and alkoxide ion.

[1] Eaborn and Pande, *J.*, 1960, 1566.

[2] Eaborn and Parker, *J.*, 1955, 126.

smaller; but it could not be as much as five times greater, otherwise we should have observed a much greater spectral change.

The low reactivity of benzylgermanes was confirmed by experiments on a small preparative scale. For example, after a solution of 4-chlorobenzyltrimethylgermane in *ca.* 2M-aqueous-ethanolic alkali had been refluxed for 44 hr., 86% of the organogermane was recovered unchanged, and no *p*-chlorotoluene could be isolated, whereas 4-chlorobenzyltrimethylsilane after 38 hr. under the same conditions gave *p*-chlorotoluene in 97% yield. Again, after a solution of 4-carboxybenzyltrimethylgermane in 2·3M-aqueous sodium hydroxide had been boiled for 50 min., 95% of the acid was recovered unchanged, whereas the corresponding silicon compound would be completely cleaved under these conditions.[3] Of the benzyl-trimethyl- and -triethyl-germanes studied, only 3-chlorobenzyltrimethylgermane was observed to undergo cleavage; after a solution in *ca.* 2M-aqueous-ethanolic sodium hydroxide had been boiled for 45 hr., 74% of it was recovered unchanged, along with *m*-chlorotoluene in 4% yield (the total recovery was low because of the small scale), whereas under the same conditions the analogous silicon compound gave *m*-chlorotoluene in 62% yield and no unchanged starting material.

3-Chlorobenzyltrimethylstannane, on the other hand, was found to be 17 times more reactive in the cleavage than 3-chlorobenzyltrimethylsilane (see below). The relative ease of alkali-cleavage of m-Cl·C_6H_4·CH_2–MMe_3 bonds, *viz.*, (M =) Ge $\sim 10^{-3}$, Si 1, Sn 17, is thus very different from that of acid cleavage of Ph·MEt_3 bonds,[1] *viz.*, Ge 36, Si 1, Sn $3{\cdot}5 \times 10^5$.

It seems clear that nucleophilic attack is easier on silicon than on germanium, probably because of increased nuclear shielding,[4] the germanium atom having a filled *M* shell without being much larger. Nuclear shielding is probably greater in tin than in silicon (though in this case the increase in the number of inner-shell electrons is partly offset by the increase in covalent radius), but the effect of this seems to be more than balanced out by the lower strength and greater polarisability of bonds to tin.* The results accord with the observations that the ease of hydrolysis of Ph_3MCl compounds[6] and of alkaline solvolysis in aqueous ethanol of R_3MH compounds[7] increases in the order (M =)Ge < Si < Sn; both reactions involve predominant nucleophilic attack at the metal.

Benzyltrimethylstannanes, X·C_6H_4·$SnMe_3$, were cleaved at convenient rates by hydroxide ion in methanol containing 20% of water (for the exact composition see the Experimental section), and results for a series of compounds are given in Table 1 as values of specific rate constants, k_s (the observed pseudo-first-order rate constants divided by the alkali concentration [OH^-]) and of k_{rel}, the rates relative to that for benzyltrimethylstannane. For comparison, rates for a few benzyltrimethylsilanes were measured in the same medium, since the more extensive studies of cleavage of such compounds[2] involved a more aqueous solvent.

Some features of the results, and some comments are as follows:

(i) Over the small range of alkali concentration used for any one compound, the value of k_s is independent of the alkali concentration, as in cleavage of benzyltrimethylsilanes.[2] Values of k_s may thus be compared directly.

(ii) For the benzylsilicon compounds the effects of substituents are slightly smaller

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* Since the ease of forming 6-co-ordinated complexes seems to increase in the order Si<Ge<Sn, Eaborn and Pande[1] suggested that, as a result of some undetermined combination of factors, energetic eccessibility of *d*-orbitals increased in this order. Since *d*-orbital participation is probably important in nucleophilic attack,[5] the ease of such attack might have been expected to increase in the same order, but presumably some factors, particularly steric, which determine the ease of complex formation, do not outbalance the effects of nuclear screening in nucleophilic substitution.

[3] Eaborn and Parker, *J.*, 1957, 955.

[4] Hughes, *Quart. Rev.*, 1951, **5**, 245.

[5] Eaborn, "Organosilicon Compounds," Butterworths Scientific Publ., London, 1960, pp. 103—113.

[6] Chipperfield and Prince, *Proc. Chem. Soc.*, 1960, 385; see also Prince, *J.*, 1959, 1783.

[7] Schott and Harzdorff, *Z. anorg. Chem.*, 1960, **307**, 105.

than in cleavage in 39 wt.%-aqueous methanol. A plot of $k_{\rm rel}$ against σ for the three points available (*viz.*, X = H, *m*-Cl, and *p*-Cl) has a slope, ρ, of 4·7 compared with one of 4·88 established [2] for a much larger number of points in the more aqueous system.

(iii) The effects of substituents are somewhat smaller for the benzyltin than for the benzylsilicon compounds. For two sets of analogous compounds reacting by the same mechanism it is normal for substituent effects to be smaller in the more reactive set.

(iv) A plot of log $k_{\rm rel}$(Sn) for the benzylstannanes against log $k_{\rm rel}$(Si) for the benzylsilanes in 39 wt.%-aqueous methanol is a good straight line. Since a plot of log $k_{\rm rel}$(Si) against σ-constants is a straight line (except for the *p*-fluoro-substituent as mentioned below),[2] it follows that a plot of log $k_{\rm rel}$(Sn) against σ is also a straight line. (Probably σ^- constants would have to be used for substituents to which they apply, as with the silicon compounds.[2]) The slope, ρ, of 4·23, is somewhat smaller than that (~4·7) for the benzylsilanes in the same medium, and extrapolation indicates that the compound $X{\cdot}C_6H_4{\cdot}CH_2{\cdot}SnMe_3$ would be less reactive than the analogue $X{\cdot}C_6H_4{\cdot}CH_2{\cdot}SiMe_3$ for substituents with values of σ (or σ^-) greater than about +3·0 (for example, the $-{}^{+}N{\equiv}N$ group,[8] which has a σ^- constant of 3). It would be interesting to see if the extrapolation is valid.

(v) The fairly large slope of the log $k_{\rm rel}$–σ plot suggests, as for cleavage of benzyltrimethylsilanes, that there is considerable negative charge on the separating benzyl group in the rate-determining transition state. This step is thus unlikely to involve co-ordination of the hydroxide (or alkoxide) ion to the metal atom; it could involve either the breakdown of the complex $[HO{\cdot}\overset{-}{S}nMe_3{\cdot}CH_2Ar]$, or the simultaneous formation of the HO–Sn bond and breaking of the $Sn{-}CH_2Ar$ bond.

TABLE 1.

Cleavage of $Me_3M{\cdot}CH_2{\cdot}C_6H_4{\cdot}X$ compounds by a mixture of methanol (5 vol.) and aqueous sodium hydroxide (1 vol.) at 50·0°.

X	$[HO^-]$ (M)	10^4k_s (l. mole^{-1} min.$^{-1}$)	$k_{\rm rel}$	X	$[HO^-]$ (M)	10^4k_s (l. mole^{-1} min.$^{-1}$)	$k_{\rm rel}$
		M = Tin				M = Tin	
H	0·961	6·05	1	*m*-Me	0·961	4·41	0·73
	0·706	6·04	—		0·706	4·39	—
m-Cl	0·833	198	32·8	*p*-Me	0·961	1·29	0·213
	0·332	198	—		0·669	1·29	—
p-Br	0·961	77·1	12·8				
	0·669	77·2	—			M = Silicon	
p-Cl	0·961	47·8	7·9	H	0·961	0·212	1
	0·706	47·6	—	*p*-Cl	0·706	2·50	11·7
p-F	0·961	3·35	0·55	*m*-Cl	0·833	12·2	57·3
	0·669	3·30	—		0·556	12·3	—

(vi) The *p*-fluoro-substituent was not included in the original study of the benzyltrimethylsilanes, but has since been found to lower the reactivity,[9] as in the stannanes (Table 1). The rate-retarding effect is not in accord with the σ-constant (0·062) of the group, but is consistent with its deactivating influence in nucleophilic aromatic substitution.[10] It is an unexplained anomaly that, whether a reaction is assisted or retarded by electron-supply, a *p*-fluoro-substituent seems to function as an electron-supplying group when the general spread of rates (or the numerical value of ρ) is large, but as an electron-withdrawing substituent when the spread is small. (For consideration of the effects of the substituent in electrophilic aromatic substitution see, for example, ref. 11.)

Cleavage of $Ph_2CH{\cdot}MR_3$ and $Ph_3C{\cdot}MR_3$ *Compounds*.—To compare quantitatively the

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[8] Lewis and Johnson, *J. Amer. Chem. Soc.*, 1959, **81**, 2070.

[9] Allcock and Eaborn, unpublished work.

[10] Bunnett and Zahler, *Chem. Rev.*, 1951, **49**, 273.

[11] de la Mare and Ridd, " Aromatic Substitution. Nitration and Halogenation," Butterworths Scientific Publ., London, 1959, pp. 139, 238; Eaborn and Taylor, *J.*, 1961, 2388.

ease of alkaline cleavage of corresponding C–Ge and C–Si bonds, we examined some diphenylmethyl and triphenylmethyl compounds, with results shown in Table 2. The features are as follows:

(i) For diphenyl- but not triphenyl-methyl compounds, the specific rate appears to increase slightly with increasing alkali concentration. [It should be noted, however, that our method of making up the reaction medium, involving mixing of the aqueous alkali (1 vol.) with the methanol (5 vol.), results in small change in the water and methanol ratio with changing alkali concentration.] This effect is insignificant for our purposes, but nevertheless rate ratios considered below are based on measurements at similar alkali concentrations.

TABLE 2.

Rates of cleavage of $Ph_2CH\cdot MR_3$ and $Ph_3C\cdot MR_3$ compounds in methanol (5 vol.) containing aqueous sodium hydroxide (1 vol.) at 50·0°.

Compound	$[OH^-]$ (M)	10^5k_s (l. mole^{-1} min.$^{-1}$)	Compound	$[OH^-]$ (M)	10^5k_s (l. mole^{-1} min.$^{-1}$)
$Me_3Si\cdot CHPh_2$	0·961	2950	$Et_3Ge\cdot CHPh_2$	0·961	0·32
	0·817	2930		0·706	0·29
	0·706	2910			
	0·389	2700	$Me_3Si\cdot CPh_3$	0·817	3770
				0·389	3780
$Me_3Ge\cdot CHPh_2$	0·706	24·1			
	0·373	20·8	$Me_3Ge\cdot CPh_3$	0·961	177
				0·373	181
$Et_3Si\cdot CHPh_2$	0·706	6·6			
	0·373	6·4	$Et_3Ge\cdot CPh_3$	0·961	0·98

(ii) For some pairs of $Ph_2CH\cdot MR_3$ compounds, the reactivity quotients are: Me_3Si/Me_3Ge, 120; Et_3Si/Et_3Ge, 23; Me_3Si/Et_3Si, 440; Me_3Ge/Et_3Ge, 83. For $Ph_3C\cdot MR_3$ compounds ratios are: Me_3Si/Me_3Ge, 21; Me_3Ge/Et_3Ge, 180.

The difference between the reactivities of corresponding germanes and silanes decreases considerably from benzyl to diphenylmethyl compounds, and then again, less markedly, to triphenylmethyl compounds. Such a decrease would be expected for increasing reactivity of the M–C bond (that is, with increasing stability of the separating carbanion), but we believe that steric effects play a large part, as indicated below.

9-Fluorenyl–MR_3 *Compounds, and a Discussion of Steric Effects.*—The rates of alkali-cleavage of some fluorenyl compounds are shown in Table 3, along with some values of the apparent activation energies, E, and of log A [where $k_s = A \exp(-E/\boldsymbol{R}T)$]. Reactivity ratios (at 50·0°) of various $9\text{-}R_3M$–fluorene pairs are: Me_3Si/Et_3Si, 960; Me_3Ge/Et_3Ge, 131; Me_3Si/Me_3Ge, 2·5; Et_3Si/Et_3Ge, 0·34.

TABLE 3.

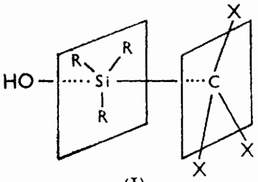
Cleavage of $9\text{-}R_3M$-fluorenes by methanol (5 vol.) containing aqueous sodium hydroxide (1 vol.).

R_3M	Temp.	$10^2[OH^-]$ (M)	k_s (l. mole^{-1} min.$^{-1}$)	E (k. cal./mole)	log A
Me_3Si	50·0°	0·334	41·1	13·25	10·6
	50·0	0·223	41·1	—	—
	25·0	1·63	7·29	—	—
Me_3Ge	50·0	0·334	16·6	17·3	12·9
	25·0	2·05	1·74	—	—
	25·0	1·02	1·72	—	—
Et_3Si	50·0	56·3	0·0425	—	—
	50·0	42·6	0·0432	17·0	10·2
	36·2	96·1	0·0135	—	—
Et_3Ge	50·0	42·6	0·127	16·9	10·5
	50·0	20·5	0·127	—	—
	36·2	96·1	0·0394	—	—

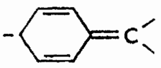
9-Triethylstannylfluorene could not be compared directly with its silicon and germanium analogues, partly because it is very reactive, being cleaved rapidly even by neutral anhydrous methanol, and also because it is insoluble in the medium used for the other rate studies reported. However, the rate of cleavage by slightly-aqueous methanolic alkali was measured approximately at 25°, and it corresponds with a value of k_s of *ca.* 3×10^4 l. mole^{-1} min.$^{-1}$. The rate would probably be greater in a more aqueous medium, and we can assign a rough value of 10^7—10^9 for the reactivity of 9-triethylstannyl- relative to that of 9-triethylsilyl-fluorene. The magnitude of this factor contrasts sharply with the ratio of only 28 observed for the benzyltrimethyl compounds.

A striking feature of the results for the fluorenyl compounds is the $Me_3Si : Et_3Si$ ratio of 960, which is markedly greater than for the less reactive diphenylmethyl and triphenylmethyl compounds, and much greater than for benzyl compounds (for example, 4-carboxybenzyltrimethylsilane is 5·5 times more reactive than the triethyl compound[9]).* It is unlikely that the small difference in electron-release by the methyl and the ethyl group would give rise to such a large factor, particularly since one would normally expect such polar effects to be smaller in a highly reactive system than in a much less reactive one, and we suggest that steric influences are mainly responsible.

The existence of a large steric effect can be understood if the structure of the rate-determining transition state is closer to that of the (possibly hypothetical) intermediate (I) than to that of the reactants.† In this intermediate the Si–R bonds are at right angles to the HO–Si–C line, and there is thus the possibility of interference between the R groups and the *ortho*-hydrogen atoms in any X groups which are aromatic. Any stretching of the Si–C bond in the transition state will not lower the hindrance much, because the R groups will move over towards the leaving group as stretching occurs and, furthermore, resonance stabilisation of the separating anion, involving contributions from structures such as (II), will tend to bring the C–X bonds into a plane at right angles to the Si–C bond, and thus closer to the R groups.



(I)



(II)

Such hindrance would increase steeply with the number of phenyl groups, particularly when the third phenyl group is added, and would counteract the increasing stabilisation of the separating anion. This may be why, in the trimethylsilyl series, change from the diphenylmethyl to the triphenylmethyl compound is accompanied by only a 1·3-fold increase in reactivity although that from the benzyl to the diphenylmethyl compound is accompanied by a 1400-fold increase. The hindrance would be greatest with the fluorenyl compounds, because in this case the aromatic rings are held coplanar, whereas in the other cases they are free to rotate about the C–Ar bonds to relieve strain.

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* The largest reactivity ratio previously reported for trimethyl- and triethyl-silyl compounds is that of 160 in alkaline solvolysis of trialkylphenoxysilanes.[12]

† For simplicity we ignore the possibility that the hydroxide ion may approach at right angles to the Si–C bond to be broken [*e.g.*, the HO group would take the place of an R group in the intermediate (I)] or at 120° to it [*i.e.*, the HO and the leaving organic group would take the place of two R groups in the intermediate (I)], because in all cases there could be considerable crowding in the rate-determining transition state. The stereochemistry of the displacement may possibly change as the leaving organic group is varied, and certainly could vary from one metal to another, but since we have at present no information which could throw light on this we assume the situation to be the simplest consistent with our results.

[12] Åkerman, *Acta Chem. Scand.*, 1956, **10**, 298.

The steric effects seem to be markedly smaller in the germanium than in the silicon compounds, and are probably absent in the tin compounds. It might at first seem surprising that the hindrance is markedly smaller for the germanium than for the silicon compounds since there is little difference in C–Si and C–Ge bond lengths (1·93 and 1·98 Å, respectively, in Me_4M compounds), but it is characteristic of steric effects that they can change sharply with small changes in dimensions, and there is, for example, a markedly lower barrier to rotation about the carbon–metal bond in tetramethylgermane (400 cal./mole) than in tetramethylsilane (1100—1500 cal./mole).[13] We suggest that, in the cases of fluorenyltrimethyl-silane and -germane, steric hindrance results in the silicon compound's being only 2·5 times as reactive as the germanium compound, while with the triethyl compounds the considerable increase in hindrance with the silicon compound causes it to be 3 times *less* reactive than its germanium analogue. The very large difference in reactivity between triethylfluorenylstannane and the corresponding silane is, we think, a result of steric hindrance with the silicon compound rather than a reflection of the relative inherent ease of cleavage of the C–Sn and C–Si bonds.

Steric hindrance such as we postulate can be expected to affect both the energy and the entropy of activation. If there were no serious atomic compressions in the transition state but only restriction of rotations there could be a marked increase in the entropy of activation without increase in the energy of activation. Possibly fluorenyltrimethylsilane is only a little more reactive than the corresponding germane because of such restriction of rotation, the values of E and log A being consistent with this. With fluorenyltriethylsilane the additional bulk of the alkyl groups seems to result in atomic compression in the transition state, so that there is a marked increase in activation energy, and the compound is less reactive than its germanium analogue.

EXPERIMENTAL

Substituted Trialkylbenzylgermanes.—A mixture of bromotriethylgermane (0·027 mole) with the Grignard reagent from α-bromo-*p*-xylene (0·054 mole) and magnesium (1·3 g.) in ether (80 ml.) was refluxed for 18 hr. Addition of dilute hydrochloric acid followed by ether-extraction and separation, drying, and fractionation of the extract gave *triethyl-4-methylbenzylgermane* (5·3 g., 73%), b. p. 118—119°/4 mm., 95°/0·9 mm., n_D^{20} 1·5167 (Found: C, 63·4; H, 9·0. $C_{14}H_{24}Ge$ requires C, 63·5; H, 9·1%).

The following new $X{\cdot}C_6H_4{\cdot}CH_2{\cdot}SiEt_3$ *compounds* were similarly prepared: (X =) *o*-Cl (84%), b. p. 118°/30 mm., n_D^{20} 1·5321 (Found: C, 54·9; H, 7·6. $C_{13}H_{21}ClGe$ requires C, 54·7; H, 7·4%); *m*-Cl (86%), b. p. 114°/1·8 mm., n_D^{20} 1·5297 (Found: C, 55·0; H, 7·4%); *p*-Cl (68%), b. p. 129·5°/3·5 mm., n_D^{20} 1·5310 (Found: C, 54·4; H, 7·2%); *m*-Br (71%), b. p. 130°/2·2 mm., n_D^{20} 1·5440 (Found: C, 47·4; H, 6·4. $C_{13}H_{21}BrGe$ requires C, 47·3; H, 6·4%); *p*-Br (60%), b. p. 133°/2·0 mm., n_D^{20} 1·5459 (Found: C, 47·6; H, 6·2%). (In preparation of the bromo-compounds, magnesium was used in 10% deficiency to avoid reaction of the aromatic bromine.)

The *p*-fluoro-compound (88%), b. p. 91·5°/1·7 mm., n_D^{20} 1·5030, prepared in this way did not give a good analysis (Found: C, 58·7; H, 7·9. Calc. for $C_{13}H_{21}FGe$: C, 58·05; H, 7·9%).

From bromotrimethylgermane by the same method was prepared *3-chlorobenzyltrimethylgermane*, b. p. 101°/7·2 mm., n_D^{20} 1·5280 (Found: C, 49·5; H, 6·2. $C_{10}H_{15}GeCl$ requires C, 49·4; H, 6·2%).

Substituted Trialkylbenzylstannanes.—By a method similar to that described above for organogermanes, but with use of saturated aqueous ammonium chloride in place of dilute hydrochloric acid, the following new *benzyltrimethylstannanes*, $X{\cdot}C_6H_4{\cdot}CH_2{\cdot}SnMe_3$ were prepared from bromotrimethylstannane: (X =) *m*-Me (69%), b. p. 62°/0·70 mm., n_D^{25} 1·5384 (Found: C, 49·1; H, 6·6. $C_{11}H_{18}Sn$ requires C, 49·1; H, 6·7%); *p*-Me (52%), b. p. 69°/1·0 mm., n_D^{25} 1·5383 (Found: C, 49·1; H, 6·7%); *m*-Cl (82%), b. p. 89·5°/1·2 mm., n_D^{23} 1·5569 (Found:

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[13] Rasmussen and French, *J. Chem. Phys.*, 1946, **14**, 389.

C, 41·6; H, 5·2. $C_{10}H_{15}ClSn$ requires C, 41·6; H, 5·2%); *p*-Cl (80%), b. p. 96·0°/2·0 mm., n_D^{25} 1·557 (Found: C, 41·9; H, 5·4%); *p*-F (64%), b. p. 69°/1·8 mm., n_D^{25} 1·5261 (Found: C, 43·7; H, 5·6. $C_{10}H_{15}FSn$ requires C, 44·0; H, 5·5%).

Diphenylmethane Derivatives.—Diphenylmethylpotassium was prepared from freshly made potassium amide (0·092 mole) and diphenylmethane (0·096 mole) in ether (100 ml.).[14] A solution of bromotriethylgermane (0·041 mole) in ether (50 ml.) was added and the mixture was refluxed for 18 hr. Dilute hydrochloric acid was added until the solids dissolved, and the ethereal layer was separated, washed, dried (Na_2SO_4), and fractionated to give some chlorotriethylgermane, diphenylmethane (12 g.), and *(diphenylmethyl)triethylgermane*, 5·3 g., 40%), b. p. 148°/0·9 mm., n_D^{20} 1·5685 (Found: C, 70·1; H, 8·1. $C_{19}H_{26}Ge$ requires C, 69·8; H, 8·0%).

Similarly, from triethylfluorosilane, was obtained *(diphenylmethyl)triethylsilane* (7%), b. p. 140°/0·52 mm., n_D^{20} 1·5574 (Found: C, 80·5; H, 9·3. $C_{19}H_{26}Si$ requires C, 80·8; H, 9·3%).

Similarly, from bromotrimethylgermane, but with recrystallisation of the product from ethanol, was obtained *(diphenylmethyl)trimethylgermane* (35%), m. p. 73·5° (Found: C, 67·5; H, 7·2. $C_{16}H_{20}Ge$ requires C, 67·2; H, 7·1%).

Triphenylmethane Derivatives.—Potassium (0·049 g.-atom) was dissolved in liquid ammonia (150 ml.) containing a little ferric nitrate, triphenylmethane (0·045 mole) in ether (200 ml.) was added, and the mixture was refluxed for 4 hr. Bromotriethylgermane (0·036 mole) in ether (100 ml.) was added and the mixture was refluxed for 1·5 hr. Working-up in the way described for diphenylmethane derivatives gave *triethyl(triphenylmethyl)germane* (3·4 g., 26%), b. p. 206—208°/0·23 mm., n_D^{20} 1·5915 (Found: C, 74·4; H, 7·6. $C_{25}H_{30}Ge$ requires C, 74·5; H, 7·5%).

Triphenylmethylsodium was made from triphenylmethyl chloride (0·032 mole) in ether (250 ml.) by Renfrow and Hauser's method,[15] and bromotrimethylgermane (0·030 mole) was added. After 18 hr. at room temperature, the mixture was treated with dilute sulphuric acid and the ethereal layer was washed, dried, filtered, and evaporated to dryness. The residue was recrystallised from benzene and then from benzene–methanol to give *trimethyl(triphenylmethyl)germane* (40%), m. p. 180·5—181° (Found: C, 72·9; H, 6·9. $C_{22}H_{24}Ge$ requires C, 73·2; H, 6·7%).

Similarly from chlorotrimethylsilane, but with recrystallisation from benzene only, was obtained trimethyl(triphenylmethyl)silane, m. p. 172·5—173·5° (lit.,[14] 169·5—170·5°).

Fluorene Derivatives.—A mixture of bromotriethylgermane (0·032 mole) and 9-lithiofluorene [prepared from fluorene (10·0 g., 0·060 mole) and n-butyl-lithium (0·050 mole)] in ether (200 ml.) was refluxed for 3 hr. and then set aside for 18 hr. Addition of dilute acid followed by separation, washing, drying, and evaporation of the ethereal layer left a residue which was distilled at low pressure to give fluorene (5·3 g.), and a higher-boiling liquid, which was fractionated to give 9-*triethylgermylfluorene* (6·7 g., 63·5%), b. p. 170°/1·0 mm., n_D^{20} 1·6060 (Found: C, 70·3; H, 7·3. $C_{19}H_{24}Ge$ requires C, 70·2; H, 7·4%).

Similarly from bromotrimethylgermane and chlorotriethylsilane, respectively, were made 9-*trimethylgermyl-* (73%) b. p. 147—150°/2·2 mm., m. p. 92° (from ethanol) (Found: C, 67·9; H, 6·6. $C_{16}H_{18}Ge$ requires C, 67·9; H, 6·4%), and 9-*triethylsilyl-fluorene* (60%), b. p. 167·5°/1·2 mm., n_D^{20} 1·5960 (Found: C, 81·6; H, 8·6. $C_{19}H_{24}Si$ requires C, 81·3; H, 8·6%).

Similarly from chlorotriethylstannane, but with treatment of the mixture with water in place of dilute acid, there was obtained 9-*triethylstannylfluorene* (47%), b. p. 151°/0·15 mm., n_D^{20} 1·6229 (Found: C, 61·8; H, 6·5. $C_{29}H_{24}Sn$ requires C, 61·5; H, 6·5%). This compound slowly gave fluorene and triethyltin hydroxide on exposure to the atmosphere.

Isolation of Cleavage Products.—In Table 4 are shown the results of some cleavages carried out on a preparative scale. The organometallic compound (3—6 g.) was boiled with a mixture (*ca.* 50 ml.) of ethanol (7 vol.) and 50 wt.% aqueous sodium hydroxide (1 vol.) (the mixture being *ca.* 2M in alkali). The mixture was added to water, and ether-extraction was followed by separation, washing, drying, and fractionation (in a precision-made Vigreux column of *ca.* 15 theoretical plates) of the ethereal layer. The substituted toluenes were identified from their b. p.s and refractive indices, and by conversion into the corresponding benzoic acids. The relatively low recovery of some of the starting materials in cases in which no cleavage seemed to occur probably arose from mechanical losses, particularly in the column hold-up.

9-Triethylsilyl- and 9-triethylgermyl-fluorene (1·5 g.) both gave fluorene in 100% yield when boiled for 1·5 hr. in the medium specified above. 9-Trimethylgermylfluorene (0·8 g.) gave

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[14] Hauser and Hance, *J. Amer. Chem. Soc.*, 1951, **73**, 5846; Yost and Hauser, *ibid.*, 1947, **69**, 2325.

[15] Renfrow and Hauser, *Org. Synth.*, Coll. Vol. II, 1943, 607.

fluorene in 100% yield when boiled with a mixture of ethanol (25 ml.) and 5% aqueous sodium hydroxide (3·5 ml.) for 0·5 hr. 9-Triethylstannylfluorene (1·3 g.) gave fluorene (85%) when boiled for 1 hr. with a mixture of methanol (25 ml.) and water (5 ml.).

TABLE 4.

Cleavage of $R'{\cdot}MR_3$ compounds by aqueous-ethanolic alkali.

Compound	Reflux time (hr.)	Products * and yield (%)	Compound	Reflux time (hr.)	Products * and yield (%)
$C_6H_5{\cdot}CH_2{\cdot}GeEt_3$	44	s.m., 88	*p*-$Cl{\cdot}C_6H_4{\cdot}CH_2{\cdot}SiMe_3$	38	*p*-$Cl{\cdot}C_6H_4{\cdot}Me$, 98
p-$Cl{\cdot}C_6H_4{\cdot}CH_2{\cdot}GeEt_3$	44	s.m., 92	*m*-$Cl{\cdot}C_6H_4{\cdot}CH_2{\cdot}SiMe_3$	45	*m*-$Cl{\cdot}C_6H_4{\cdot}Me$, 62
m-$Cl{\cdot}C_6H_4{\cdot}CH_2{\cdot}GeEt_3$	44	s.m., 85	*p*-$Cl{\cdot}C_6H_4{\cdot}CH_2{\cdot}SiEt_3$	38	s.m., 30; *p*-$Cl{\cdot}C_6H_4{\cdot}Me$, 47
p-$Me{\cdot}C_6H_4{\cdot}CH_2{\cdot}GeEt_3$	44	s.m., 75			
m-$Br{\cdot}C_6H_4{\cdot}CH_2{\cdot}GeEt_3$	44	s.m., 88	*m*-$Cl{\cdot}C_6H_4{\cdot}CH_2{\cdot}SnMe_3$	52	*m*-$Cl{\cdot}C_6H_4{\cdot}Me$, 85
p-$Cl{\cdot}C_6H_4{\cdot}CH_2{\cdot}GeMe_3$	44	s.m., 86	$Ph_3C{\cdot}GeMe_3$	10	Ph_3CH, 88 †
m-$Cl{\cdot}C_6H_4{\cdot}CH_2{\cdot}GeMe_3$	45	s.m., 74 *m*-$Cl{\cdot}C_6H_4{\cdot}Me$, 4	$Ph_2CH{\cdot}SiEt_3$	19	s.m., 3; Ph_2CH_2, 81
			$Ph_2CH{\cdot}GeEt_3$	37	s.m., 44 ‡

* Recovered starting material denoted s.m. † The product was recrystallised, not fractionated. ‡ The cleavage products could not be satisfactorily separated.

A solution of 4-carboxybenzyltriethylgermane (0·2 g.) in 2·3M-aqueous sodium hydroxide was boiled for 50 min. Acidification gave the unchanged acid in 95% yield.

Rate Studies.—Rates of cleavage were determined spectrophotometrically by the general method previously described.[2,3] The organometallic products of the cleavages do not absorb significantly above about 230 mμ, and thus the optical density changed from that of the $Y{\cdot}MR_3$ compound to that of the $Y{\cdot}H$ compound (where Y is, for example, $Ph{\cdot}CH_2$). The reaction medium consisted (unless otherwise stated) of a mixture of aqueous alkali (1 vol.) and a methanolic solution (5 vol.) of the organometallic compound. The strength of the aqueous alkali was 5·84 times that listed in the various Tables and typical runs, which give the strength of the alkali in the mixture, titration having established this dilution factor for some of the mixtures. (The factor must vary slightly with the strength of the alkali, but this is unimportant.)

In normal runs, some of the mixture was placed in a 1 cm. stoppered cell which was placed in a thermostat, kept at 50·0° ± 0·03°, in a Unicam S.P. 500 spectrophotometer, and the optical density at a suitable wavelength was recorded at appropriate times, the value of the optical density, D_∞, at " infinite " time being measured on the mixture kept for 10 half-lives either in the thermostat-controlled cell or in sealed glass tubes contained in a thermostat-bath at 50·0°.

For slower runs, samples of the mixture were sealed under nitrogen in small hard-glass tubes which were placed in a thermostat-bath at 50·0° ± 0·02° and withdrawn at suitable intervals so that the optical densities of the solutions could be determined in 1 cm. cells kept at 25·0°. Sometimes in the longer runs a fine suspension of solid, formed by attack of the alkali on the glass, had to be removed by centrifugation before the optical-density measurements. Values of D_∞ were usually measured on samples kept for 10 times the half-life, but for the slowest runs they were measured on synthetic solutions of the expected reaction products. (Such values are referred to below as " synthetic.")

No correction has been made in listed specific rate constants for expansion of the reaction medium between room temperature and 50°; the correction involves multiplying the listed constants by 1·03.

Rate constants could be duplicated within ±1·5%. In runs involving experimental D_∞ values, rate constants are probably accurate within ±3%, unless otherwise specified, but in those involving synthetic D_∞ values rate constants could be in error by ±10% because of the possible effect of impurities in the reaction mixture, though even in these cases the rate constants, usually based on the first 60% of the reaction, could be duplicated to ±2%. These errors could be even larger in the very slow runs involving (diphenylmethyl)- and (triphenylmethyl)-triethylgermane since only the first 40% of the reaction was studied; the possible errors are not, however, large enough to affect the above discussion of the results.

In the following sample runs, all at 50·0°, the first was taken to completion in the cell, the second involved a value of D_∞ measured on samples kept in sealed tubes, and the third utilised a synthetic D_∞ value. First-order rate constants were determined graphically, but they are here, for convenience, calculated for some points throughout the run.

(i) [m-Cl·C_6H_4·CH_2·$SnMe_3$], 1·7 × 10^{-3}M; [NaOH], 0·332M; λ 286 mμ.

Time (min.)	0	10	21	40	50	70	102	175	288	357	∞
10^3D	840	785	734	652	612	541	448	291	158	110	34
10^5k (min.$^{-1}$)	—	691	669	662	663	661	652	653	650	661	—

(ii) [Ph_3C·$GeMe_3$], 6·4 × 10^{-5}M; [NaOH], 0·961M; λ 240 mμ.

Time (min.)	0	210	465	690	840	1020	1410	∞
10^3D	820	627	461	360	319	275	213	148
10^5k (min.$^{-1}$)	—	161	164	167	163	163	165	—

(iii) [Ph_2CH·$GeMe_3$], 2·1 × 10^{-3}M; [NaOH], 0·373M; λ 275·5 mμ.

Time (hr.)	0	45·5	93	131	203	264	323	432	∞
10^3D	838	688	571	486	360	286	230	166	60
10^7k (min.$^{-1}$)	—	784	755	768	783	781	785	769	—

9-Triethylstannylfluorene underwent cleavage rapidly in freshly distilled, boiled-out methanol at 25·0°. Good first-order kinetics were observed during a run, a wavelength of 325 mμ being used, but the mean rate constant varied from run to run, probably because of impurities, particularly traces of base. The values lay around 9 × 10^{-2} min.$^{-1}$. In a mixture of methanol (5 vol.) and water (1 vol.), the solvolysis was roughly twice as fast.

In measurement of the rate of the alkali-catalysed cleavage of this compound, a drop (0·033 ml.) of 0·0195M-aqueous sodium hydroxide was added to a methanolic solution (2·60 ml.) of the organostannane contained in an absorption cell kept at 25·0°, the optical density of the solution being noted just before the drop was added. The mixture was shaken quickly, the cell was replaced in its thermostat, and optical density measurements were begun. This was done three times with the results shown below.

(i) λ 326 mμ.

Time (sec.)	0	16	27	38	∞
10^3D	1060	247	168	152	147
k (min.$^{-1}$)	—	8·3	8·5	7·8	—

(ii) λ 328 mμ.

Time (sec.)	10	26	40	55	∞
10^3D	1140	312	207	188	185
k (min.$^{-1}$)	—	7·6	7·6	8·0	—

(iii) λ 331 mμ.

Time (sec.)	30	46	54	67	∞
10^3D	980	340	282	254	248
k (min.$^{-1}$)	—	7·8	7·5	8·0	—

The value of k was taken to be 8 min.$^{-1}$. The concentration of alkali in the reaction mixture was *ca.* 2·5 × 10^{-4}M, and thus k_S is 3·2 × 10^4 l. mole^{-1} min.$^{-1}$. The rate of concurrent neutral solvolysis was negligible in comparison.

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