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EFFECTS OF VARYING THE MEDIA FOR BASE CLEAVAGE OF SOME BENZYL-SILICON AND -TIN COMPOUNDS IN ALCOHOLS *

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Summary

The effects on the rates of cleavage of $3\text{-ClC}_6H_4CH_2MMe_3$ and $3,5\text{-Cl}_2C_6H_3\text{-}CH_2MMe_3$ compounds with M = Si and Sn have been examined for (a) various concentrations of NaOMe-MeOH; (b) various concentrations of H_2O in NaOH-H_2O-MeOH; and (c) variation of R from Me to Et, i-Pr and t-Bu for metal alkoxide-ROH mixtures. Rates have also been measured for cleavages in $NaOCH_2CF_3$-$HOCH_2CF_3$-Me_2SO. In all cases there are differences in behaviour between the silicon and tin compounds which are consistent with the postulated difference in the mechanisms of their reactions.

Introduction

Extensive studies have been made of base cleavage of R—MMe_3 bonds, where M = Si or Sn and R is an organic group, usually of the aryl or benzyl (including, e.g. diphenylmethyl or 9-fluorenyl) type [1—9]. The medium NaOMe-MeOH has been most frequently used, and in it the cleavages of the silicon and tin compounds have been shown to differ in mechanism; for the silicon compounds the rate-determining step involves the separation of the carbanion R^-, whereas for most tin compounds the breaking of the Sn—R bond is accompanied by proton transfer ("electrophilic assistance") from the solvent to the separating carbon centre [5—8]. (The exceptions for tin compounds arise in the case of the very reactive species, for example, with R = 9-fluorenyl, which appear to undergo cleavage without electrophilic assistance [8].)

Some studies have been carried out in various MeOH-H_2O mixtures containing NaOH [1—4], and there is no reason to doubt that the mechanism in such media is the same as that in MeONa-MeOH. However, for cleavages of benzyl-silicon compounds, whereas in a medium of fairly high water content (39 wt %,

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* No reprints available for distribution.

equal to ca. 36 vol.%) the value of the specific rate constant, k_s, given by the observed first-order rate constant divided by the base concentration, is fairly constant over a wide range of base concentration [1], in MeOH it depends markedly on the NaOMe concentration.

We have now examined the cleavages of some representative silicon and tin compounds, $RMMe_3$, in various media in order (a) to provide for $MeOH$-H_2O systems a set of data which can be used to make more accurate comparisons between results reported for different media, and (b) to see how far the observed effects can be interpreted in terms of the mechanistic difference between the silicon and tin compounds, and at the same time to provide a body of information which could be used in future to help to decide between the carbanion and the electrophilically-assisted processes in cleavages of other types of compound (see, for example, ref. 10).

Results and discussion

1. Variation of the concentration of base in methanol

The effects on the specific rate constant, k_s, (given by the stoichiometric concentration of base) of varying the base concentration in methanol for cleavages of the compounds $3\text{-}ClC_6H_4CH_2MMe_3$, with M = Si or Sn, are shown in Table 1, and illustrated in Figure 1.

Perhaps the most important feature is that, in keeping with the existence of a difference in mechanism, there is a clear difference in behaviour between the silicon and the tin compounds. For the silicon compound, above 0.26 *M* base there is a progressive rise in k_s with increasing [NaOMe], the rise being sharp above about 1 *M* base, so that the k_s in 3.6 times as large in 3 *M* as in 0.26 *M* NaOMe. In contrast, for the tin compound, as the base concentration is increased there is an initial small but definite decrease in k_s followed by moderate increase; in consequence, k_s at 1.5 *M* is similar to that at 0.1 *M* base, while at 3 *M* base it is 1.5 times as large. If the reasonable approximation is made that the dependence of k_s on [NaOMe] will not vary much from one

TABLE 1

RATES OF CLEAVAGE OF $3\text{-}ClC_6H_4CH_2MMe_3$ COMPOUNDS IN NaOMe-MeOH AT 50.0°C

$RSiMe_3$			$RSnMe_3$		
[NaOMe] (*M*)	10^5k_s ($l\ mol^{-1}\ s^{-1}$)	k_M/k_0 [a]	[NaOMe] (*M*)	10^5k_s ($l\ mol^{-1}\ s^{-1}$)	k_M/k_0 [a]
0.0	0.87 [b]	1.00	0.0	17.8 [b]	1.0
0.26	0.90	1.03	0.10	17.3	0.97
0.51	1.02	1.17	0.23	16.4	0.92
1.02	1.20	1.38	0.51	14.8	0.83
1.52	1.68	1.93	1.07	15.4	0.87
1.98	1.98	2.27	1.49	17.5	0.98
2.52	2.75	3.16	2.00	20.5	1.15
3.00	3.26	3.75	2.50	23.5	1.32
			3.11	26.4	1.48

[a] Ratio k_s at specified base concentration to that very low concentration. [b] Estimated by extrapolation.

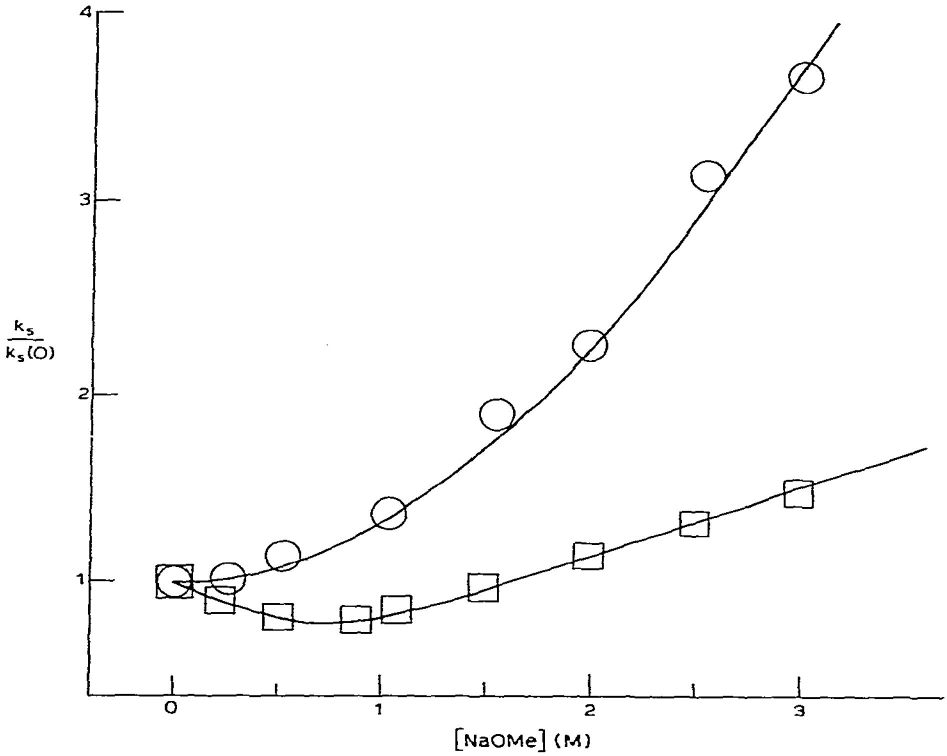


Fig. 1. Plot against [NaOMe](*M*) of the ratio of the k_s value at the relevant base concentration to that, $k_s(0)$, (given by extrapolation) at very low base concentration, for the compounds 3-$ClC_6H_4CH_2SiMe_3$ (circles) and 3-$ClC_6H_4CH_2SnMe_3$ (squares).

silicon compound to another, or from one tin compound to another within the same mechanistic group, the data in Table 1 can be used to make comparisons between the reactivities of compounds examined at different base concentrations; for example, for silicon compounds the k_s values observed at 1 *M* and 2 *M* base must be multiplied by factors of ca. 0.71 and 0.42, respectively, to make them comparable with values measured at low base concentration (approximate factors of 0.8 and 0.5 have previously been used — cf. refs. 7 and 8), while for most tin compounds the variation in k_s can usually be neglected up to about 1.5 *M* base, and a factor of 0.85 used to adjust values measured at 2.0 *M* base. (For the very reactive tin compounds which seem to go by the carbanion mechanism [8], any adjustment would presumably be similar to that made for silicon compounds, but in practice this does not arise because the reactive compounds are normally studied at very low base concentrations [6,8].)

The log k_s values for *m*-$ClC_6H_4CH_2SiMe_3$ at various concentrations of NaOMe show a good linear correlation with the H_- acidity function [11] (corrln. coeff., 0.993; 7 points), as expected from the analogy between proton abstraction by base from an indicator acid and base cleavage of an R—$SiMe_3$ bond. For the tin compound, however, the effective activity of the base is not the only important factor, because of the need for electrophilic assistance; the initial small decrease

TABLE 2

RATES OF CLEAVAGE OF $3\text{-}ClC_6H_4CH_2MMe_3$ COMPOUNDS BY BASE (NaOH AND/OR NaOMe) IN H_2O-MeOH AT 50.0°C

$[H_2O]$ (vol-%)	[Base] (M)	$10^5 k_s$ (l mol^{-1} s^{-1})	$[H_2O]$ (vol-%)	[Base] (M)	$10^5 k_s$ (l mol^{-1} s^{-1})
M = Si			M = Si		
0	1.00	1.20	20	0.51	1.77
2	0.50	1.08		1.00	2.00
	1.00	1.46		1.53	2.35
	1.53	2.04		2.04	2.67
	2.05	2.35		2.51	3.07
	2.55	2.66		3.11	3.38
	3.11	3.00	25	1.99	2.64
5	1.00	1.60	30	1.00	2.72
10	0.27	1.33		1.53	3.13
	0.51	1.34		2.00	3.31
	1.02	1.71		2.52	3.51
	1.52	2.04		3.03	3.80
	2.02	2.44	35	2.00	3.82
	2.54	2.93			
	3.02	3.07	M = Sn		
15	1.02	1.81	0	1.07	15.4
			2.9	0.93	19.5
			5.8	0.96	21.6
			11.6	0.93	26.5

in k_s and subsequent slow rise as the base concentration is increased can be rationalized in terms of a balance between the effects of the increasing H_- of the medium and the decreasing proton availability as more methanol molecules are engaged in solvation of methoxide ions through hydrogen-bonding.

2. *Variation of proportion of water in H_2O-MeOH mixtures*

Values of k_s for $3\text{-}ClC_6H_4CH_2SiMe_3$ determined at various concentrations of base in several H_2O-MeOH mixtures are shown in Table 2, which also includes a

TABLE 3

EFFECTS ON RATE OF CLEAVAGE OF $3\text{-}ClC_6H_4CH_2MMe_3$ COMPOUNDS OF VARYING THE PROPORTION OF WATER IN AQUEOUS METHANOLIC BASE AT 50.0°C

M	$[H_2O]$ (vol-%)	$k_s(3\ M)/k_s(0.5\ M)$	$k_s(3\ M)/k_s(1\ M)$	k_s/k_s (MeOH) [a]
Si	0	3.2	2.7	1.0
	2	2.7	2.0	1.22
	5			1.33
	10	2.3	1.8	1.42
	15			1.51
	20	1.85	1.65	1.67
	30		1.4	2.27
Sn	0			1.0
	2.9			1.26
	5.8			1.40
	11.6			1.72

[a] At ca. 1 M base.

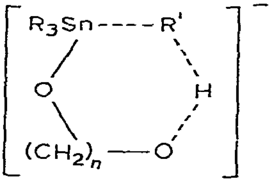
few k_s values for the tin compound 3-$ClC_6H_4CH_2SnMe_3$ in some H_2O-MeOH mixtures at (effectively) a single base concentration. The data were used to derive the ratios shown in Table 3, namely: (a) the ratio k_s/k_s(MeOH) of the value of k_s for 3-$ClC_6H_4CH_2SiMe_3$ at 1 *M* base in each H_2O-MeOH mixture to that in MeOH; (b) the corresponding ratio for 3-$ClC_6H_4CH_2SnMe_3$ at 0.94 *M* base; (c) the ratio of k_s in 3.0 to that in 0.5 *M* base for 3-$ClC_6H_4CH_2SiMe_3$ with various proportions of water, and (d) the similar ratio for 3 and 1 *M* base.

It will be seen that added water has only a small effect on the rate of cleavage of 3-$ClC_6H_4CH_2SiMe_3$, the value of k_s at 1 *M* base being increased only 2.3 fold on going from MeOH to 30 vol.% H_2O-MeOH. A practical implication of this is that the presence of a little water in cleavages intended to be in anhydrous MeOH will not have any significant effect on the observed rate constant. The influence of added water seems to be slightly greater for the tin compound 3-$ClC_6H_4CH_2SnMe_3$, possibly because increase in the proportion of water increases the availability of protons to provide electrophilic assistance.

The data for the silicon compound also confirms that the increase in k_s with the base concentration becomes smaller as the proportion of water is raised, but the effect is still significant even with 30 vol.% of water present.

Reactions in $NaO(CH_2)_nOH$-$HO(CH_2)_nOH$ media

We decided to examine the diols $HO(CH_2)_nOH$ (n = 2—6) as solvents for the cleavages in place of MeOH because of the possibility that they might have substantially different effects on the rates for the tin and silicon compounds as a result of the difference in mechanism. We had especially in mind the possibility that in the case of the tin compounds, after (or synchronous with) the attachment of an $HO(CH_2)_nO^-$ ion to the tin atom, a proton might be transferred internally to the separating carbon centre in the rate determining step, as depicted in I.



I

Making the reasonable assumption that the mechanism for the silicon compound is unchanged on going to the diol media, the rates for suitable silicon compounds in the various media can be taken as indicating, at least approximately, the effective nucleophilicity (and probably the basicity) of the system, so that any additional effect for tin compounds might reflect the change in proton availability for the rate-determining step.

The results for the 3-$ClC_6H_4CH_2MMe_3$ and 3,5-$Cl_2C_6H_3CH_2MMe_3$ compounds are shown in Table 4, which also includes data for MeOH-diol mixtures. The k_s values for such mixtures fall between those for MeOH and the neat diol, and no special effects arise which require discussion. In Table 5 are listed the ratios, k_s(diol)/k_s(MeOH) of the specific rate constant in each diol to that in MeOH at a comparable base concentration (Figure 1 and the data in Table 1 being used

TABLE 4

RATES OF CLEAVAGE OF $RMMe_3$ COMPOUNDS BY SODIUM ALKOXIDE IN $HO(CH_2)_nOH$ OR $HO(CH_2)_nOH$-MeOH AT 50.0° C

R	n	Medium (mol-% diol)	$RSnMe_3$		$RSiMe_3$	
			[Base] (M)	10^5k_s ($l\ mol^{-1}\ s^{-1}$)	[Base] (M)	10^5k_s ($l\ mol^{-1}\ s^{-1}$)
$3,5\text{-}Cl_2C_6H_3CH_2$		0	0.32	600	0.32	71
	2	73.4	0.35	540	0.87	36
		100	0.25	560	0.25	26
	3	15.0	0.32	600		
		67.2	0.30	1240		
		100	0.19	1570	0.86	92
	4	63.8	0.30	1810	0.31	135
		100	0.20	2960	0.86	157
	5	100	0.22	4800	0.66	187
	6	100	0.15	6200	0.16	210
$3\text{-}ClC_6H_4CH_2$		0	0.78	15.2	1.0	1.20
	2	73.4	0.84	15.4		
		100	0.78	14.9		
	3	15.0	0.78	18.5		
		67.9	0.78	36.4		
		100	0.87	42.8	1.36	2.10
	4	63.8	0.70	39.3	1.42	3.1
		100	0.87	59	1.16	4.2
	5	100	0.46	112	0.96	4.2
	6	100	0.54	143	0.56	4.5

TABLE 5

RATIO OF RATE CONSTANT FOR CLEAVAGE OF $RMMe_3$ COMPOUNDS IN $NaO(CH_2)_nOH$-$HO(CH_2)_2OH$ TO THAT IN NaOMe-MeOH AT 50° C

$RMMe_3$	n	[Base] (M)	k_s(diol)/k_s(MeOH)	R(Sn)/R(Si)[a]
$3\text{-}ClC_6H_4CH_2SiMe_3$	3	1.36	1.45	2.0
	4	1.16	3.1	1.3
	5	0.96	3.6	2.1
	6	0.56	4.5	2.2
$3\text{-}ClC_6H_4CH_2SnMe_3$	2	0.78	0.98	
	3	0.87	2.9	
	4	0.87	4.0	
	5	0.46	7.5	
	6	0.54	9.7	
$3,5\text{-}Cl_2C_6H_3CH_2SiMe_3$	2	0.25	0.37	2.5
	3	0.86	1.00	2.5
	4	0.31	1.9	2.5
	5	0.66	2.4	3.2
	6	0.16	3.0	3.2
$3,5\text{-}Cl_2C_6H_3CH_2SnMe_3$	2	0.25	0.93	
	3	0.19	2.5	
	4	0.20	4.7	
	5	0.22	7.6	
	6	0.15	9.7	

[a] Ratio of quantity k_{diol}/k_{MeOH} for tin compound to that for the corresponding silicon compound.

to derive k_s values in MeOH at the appropriate base concentrations where necessary). For the silicon compound 3,5-$Cl_2C_6H_3CH_2SiMe_3$ there is a clear (2.7 fold) fall in k_s on going from MeOH to $HOCH_2CH_2OH$ (a fall would be expected from the values of $H\_$ in various $NaOCH_2CH_2OH$-$HOCH_2CH_2OH$-MeOH mixtures [11]), then for this compound and 3-$ClC_6H_4CH_2SiMe_3$ the rates in the diols $HO(CH_2)_nOH$ rise as the value of n is increased. For the tin compounds there is almost no change on going from MeOH to $HOCH_2CH_2OH$, then a rise on going to the diols of higher n values, the rise being more marked than that for the silicon compounds. In fact, with the anomalous exception of the 3-Cl compounds in $HO(CH_2)_4OH$ which may reflect some undetected experimental error, the value of the ratio, R(Sn)/R(Si), of the quantity k_s(diol)/k_s(MeOH) for a tin compound to that for the corresponding silicon compound falls in the range 2—3.2. If the change in k_s for a silicon compound on going to a diol solvent is assumed to reflect the changes in all the other relevant properties of the medium (and especially the basicity), it is attractive to associate the values in the region of 2 for this ratio with the availability of two hydroxyl groups per solvent molecule to assist the cleavage of the tin compounds, but the actual stoichiometric concentration of hydroxyl groups for the diols $HO(CH_2)_nOH$ varies in the sequence $n = 2 > n = 3 >$ MeOH $> n = 4 > n = 5 > n = 6$, with a factor of almost 2 between the extremes. The effects observed are too small to be taken as evidence for intramolecular proton transfer in the case of the tin compounds, such as that depicted in I, though such a process cannot be ruled out. Once again, however, the differences between the behaviour of the silicon and tin compounds is consistent with the assumed difference in mechanism.

Reactions in NaOR'-R'OH (R' = Me, Et, i-Pr) and KOBu^t-Bu^{t}OH

The rates of cleavage of 9-fluorenyl$SiMe_3$ (the high reactivity of which permits the use of low base concentrations) were measured in various alkoxide-R'OH media, with the results shown in Table 6. It will be seen that the value of k_s falls progressively on going from (R' =) Me to Et to i-Pr, then rises slightly on going to (R' =) t-Bu, the relative k_s values being Me, 1.0; Et, 0.50; i-Pr, 0.27;

TABLE 6

RATES OF CLEAVAGE OF $RMMe_3$ COMPOUNDS BY NaOR'-R'OH (R = Me, Et, i-Pr) OR KOR'/R'OH (R' = t-BuOH) AT 50°C

Compound	R'	[NaOR'](*M*)	$10^5 k_s$(l mol^{-1} s^{-1})
9-fluoroenyl$SiMe_3$	Me	0.003	74 000
	Et	0.004	37 000
	i-Pr	0.005	20 100
	t-Bu	0.008 [a]	23 800
3,5-$Cl_2C_6H_3CH_2SiMe_3$	Me	0.32	71
	t-Bu	0.144 [a]	215
3-$ClC_6H_4CH_2SnMe_3$	Me	0.10	17
	t-Bu	0.144 [a]	64
3,5-$Cl_2C_6H_3CH_2SnMe_3$	Me	0.32	600
	t-Bu	0.144 [a]	2150

[a] Base was KOBu^t.

t-Bu, 0.32. This sequence can be accounted for in terms of the opposing effects of the increases in the basicity of the medium (as indicated by the H_- values [11]) and in steric hindrance to the attack of the alkoxide ion, which will be especially large for 9-fluorenyl$SiMe_3$. (The importance of steric hindrance with this compound is apparent from the near 1000-fold fall in rate on going to the corresponding triethyl compound, 9-fluorenyl$SiEt_3$ [3]).

In agreement with this interpretation, the much less hindered $3\text{-}ClC_6H_4CH_2SiMe_3$ and $3,5\text{-}Cl_2C_6H_3CH_2SiMe_3$ are cleaved some 3.0 and 3.8 times, respectively, as readily in $KOBu^t\text{-}Bu^tOH$ as in MaONa-MeOH; the increases in k_s are still very small, however, when viewed against the large increase in H_- [11], and steric hindrance to the attack by the $t\text{-}BuO^-$ ion is no doubt considerable even with these benzyl compounds.

Interestingly, the rate increase for the tin compound $3,5\text{-}Cl_2C_6H_3CH_2SnMe_3$ on going from R = Me to R = t-Bu, involving a factor of 3.6, is very similar to that for the analogous silicon compound even though for tin the steric hindrance to the attack by the bulky $t\text{-}BuO^-$ is likely to be much smaller. That the rate increase is not larger for the tin compound can be associated with the need for electrophilic assistance in the rate-determining step, the lower acidity of t-BuOH than of MeOH implying a lower proton availability for this assistance.

Reactions in $NaOCH_2CF_3\text{-}CF_3CH_2OH\text{-}Me_2SO$ media

We thought we might be able to demonstrate the importance of the acidity of the alcohol in the cleavage of the tin compounds by using $NaOCH_2CF_3\text{-}CF_3CH_2OH$ media. Because of the higher acidity of CF_3CH_2OH ($pK_a \sim 12$) the electrophilic assistance should be especially large, and so while all the rates could be expected to be low (because of the low basicity and nucleophilicity of the anion $CF_3CH_2O^-$) a very high rate ratio might be obtained for reactions of corresponding tin and silicon compounds. Unfortunately even with the $3,5\text{-}Cl_2C_6H_3CH_2MMe_3$ compounds cleavage did not occur at a detectable rate in CF_3CH_2OH containing 1 *M* $NaOCH_2CF_3$.

We were able to obtain satisfactory rates of cleavage by adding Me_2SO to the $NaOCH_2CF_3\text{-}CF_3CH_2OH$ systems, but the amount of the Me_2SO needed was so large that we can reach no conclusions about any special influence of the alcohol, the molecules of which must be very strongly hydrogen-bonded to the sulphoxide. The interesting feature of the results, shown in Table 6 (in which observed first-order rate constants not k_s values are given) is that in the presence of 90 mol-% of Me_2SO the tin compound $3\text{-}ClC_6H_4CH_2SnMe_3$ is ca. 10.5 times less reactive than its silicon analogue, whereas in NaOMe-MeOH the tin compound is the more reactive by a factor of 11. This can be attributed to the low availability in the presence of Me_2SO of protons for electrophilic assistance [8], and the results are in keeping with earlier observations of inversion in the usually reactivity sequence for corresponding tin and silicon compounds for base cleavages on going from MeOH or $MeOH\text{-}H_2O$ solvents to $MeOH\text{-}Me_2SO$ or $H_2O\text{-}Me_2SO$ solvents of high Me_2SO content [4,12] *.

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* Related inversions of the normal reactivity sequence for tin and silicon compounds have been noted for cleavages in another basic medium [13].

TABLE 7

RATES OF CLEAVAGE OF $RMMe_3$ COMPOUNDS BY $NaOCH_2CF_3$-CF_3CH_2OH-Me_2SO at 50° C

R	CF_3CH_2OH (mol-%)	$[NaOCH_2CF_3]$ (M)	$RSnMe_3$ $10^5k(s^{-1})$ [a]	$RSiMe_3$ $10^5k(s^{-1})$ [a]
3,5-$Cl_2C_6H_3CH_2$	10.0	0.023	850	790
	20.8	0.021	118	71
3-$ClC_6H_4CH_2$	10.0	0.78	31	320
	20.8	0.075	6.9	17.5
Ph_2CH	10.0	0.011		120
	20.8	0.011		17.2

[a] Observed first-order rate constant.

Lowering the Me_2SO content of the Me_2SO-CF_3CH_2OH mixtures to 79% causes a smaller rate decrease for the tin compound 3-$ClC_6H_4CH_2SnMe_3$ than for the silicon analogues, so that the latter is only 2.6 times the more reactive, and this can reasonably be attributed to the fact that for the tin compound the greater proton availability counteracts the fall in basicity. Presumably at very high Me_2SO contents the tin compounds will react by the carbanion mechanism, without electrophilic assistance, and as the Me_2SO content is lowered, at some point both mechanisms can be expected to operate concurrently.

With the more reactive 3,5-$Cl_2C_6H_3CH_2MMe_3$ compounds, the tin is still slightly more reactive than the silicon derivative even in 90% Me_2SO. If the tin compounds are assumed to react by the carbanion mechanism in this medium, the difference between the behaviour of 3-$ClC_6H_4SnMe_3$ and 3,5-$Cl_2C_6H_3CH_2$-$SnMe_3$ (relative to their silicon analogues) can be understood in terms of the relative slopes (which can be associated with corresponding ρ values) of the lines Sn(B) and Si(B) in the Figure in ref. 8, with these lines actually crossing as envisaged in the text of ref. 8.

Experimental

Purification of solvents

Methanol was dried by distillation from magnesium methoxide. The diols $HO(CH_2)_nOH$ with $n = 5$ and 6 were purified by fractional distillation at reduced pressure, and the other alcohols and Me_2SO by standard procedures [14].

Reaction media

Solutions of metal alkoxides in the corresponding alcohols were made by dissolving sodium or potassium in the alcohol (with warming where necessary) under dry nitrogen and the centrifuging. Before rate studies the base concentration was determined by titration.

For the H_2O-MeOH media, the procedure depended on the required concentration of base. For those of low water content (<vol-%), NaOH was dissolved in the H_2O-MeOH mixture of appropriate v/v ratio. For those of higher water content, a solution of sodium hydroxide in water was mixed with MeOH in the appropriate v/v ratio. The difference in procedure means that the vol-% of wa-

ter specified in Table 2 has a slightly different meaning for mixtures of low and high water content, but this is of no significant consequence.

Rate measurements

Rate constants were determined spectrophotometrically by the general procedures used in much earlier work [1—10]. A Unicam SP1700 spectrometer fitted with a thermostatted cell holder (±0.1°C) was used.

In H_2O-MeOH, x vol-% of H_2O denotes a mixture of x volumes of H_2O with $(100 - x)$ of MeOH.

A sample of the organometallic compound was dissolved in the appropriate volume of the relevant basic medium, some of the solution was then transferred to the absorption cell (1 cm), and the change in absorption at the selected wave-length with time was automatically recorded. For slow reactions samples of the reaction mixture were sealed into ampoules which were kept in a thermostat bath; these were opened at appropriate intervals and the contents transferred to the absorption cell. For the faster reactions in methanolic media, a solution of the organometallic compound in methanol, preheated to the reaction temperature, was mixed in appropriate volume ratio with a preheated solution of the base.

The following wave-lengths were used in the rate studies: 3-$ClC_6H_4CH_2SiMe_3$, 279.5; 3,5-$Cl_2C_6H_3CH_2SiMe_3$, 283.5; 3-$ClC_6H_4CH_2SnMe_3$, 286; 3,5-$Cl_2C_6H_3CH_2$-$SnMe_3$, 280; 9-fluorenyl$SiMe_3$, 290 nm. The UV spectrum of the reaction mixture was determined in each case after 10 half-lives, and found to be identical with that of the expected cleavage product.

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