Substituent Effects in Formation of Aryl Carbanions. Base Cleavage of Aryltrimethylstannanes in Dimethyl Sulphoxide–Water

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The rates of cleavage of some $XC_6H_4SnMe_3$ compounds by 9:1 or 100:3 v/v Me_2SO–aqueous KOH at 40 °C have been measured; the values of k_{rel} (the rate for X = X relative to that for X = H) in 9:1 v/v Me_2SO–H_2O, with those for 100:3 v/v Me_2SO–H_2O in parentheses, are (X =) *p*-NMe_2, 0.22 (0.089); *p*-OMe, 0.78 (0.65); *p*-Me, 0.66 (0.44); *m*-Me, 0.59 (0.58); *p*-SMe, 3.2 (3.4); *p*-Cl, 15.8 (25); *m*-Cl, 70 (144); *m*-CF_3, 115 (240), *p*-NMe_3I, 192 (530); *p*-NO_2, 950 (3 370). Correlations of the log k_{rel} values with the calculated energies for the conversion $XC_6H_5 \longrightarrow XC_6H_4^-$ and with the log k_{rel} values for cleavage of the corresponding $XC_6H_4SiMe_3$ compounds in 9:1 v/v Me_2SO–aqueous KOH indicate that the electrophilic assistance to cleavage of the tin compounds falls with the proton availability in the medium, and is absent or slight in 100:3 v/v Me_2SO–H_2O.

We have previously shown that the effects of substituents X on the ease of cleavage of XC_6H_4–$SiMe_3$ bonds by KOH in 6:1 or 9:1 v/v Me_2SO–H_2O are consistent with rate-determining separation of the aryl carbanions, $XC_6H_4^-$, as are those for protodedeuteriation of $XC_6H_4{}^2H$ compounds in KNH_2–NH_3.[1,2] In contrast, the substituent effects in cleavage of the tin compounds $XC_6H_4SnMe_3$ in NaOMe–MeOH (in which both electron-withdrawing and certain electron-releasing groups, such as *p*-NMe_2, cause activation [3]) are consistent with the view that in this case electrophilic assistance is provided by proton-transfer from the solvent to the separating group synchronous (though by no means fully concerted) with the breaking of the aryl–tin bond.[1,4] Data for the cleavage by KOH in 6:1 v/v Me_2SO–H_2O show an intermediate pattern, consistent with a markedly smaller but still significant degree of electrophilic assistance in this medium, in which protons are much less readily available.[1] If the previous analysis was correct, it was to be expected that on lowering the proportion of water in Me_2SO–H_2O the pattern of substituent effects in cleavage of the tin compounds would move progressively closer to that consistent with rate-determining separation of the aryl anion without electrophilic assistance, and thus we have measured the rates of cleavage by KOH in 9:1 and 100:3 v/v Me_2SO–H_2O at 40 °C. The results are shown in the Table, which lists the observed pseudo-first-order rate constants, *k*, and the values of k_{rel}, the rate for a substituted

Rates of cleavage of $XC_6H_4SnMe_3$ compounds by Me_2SO–aqueous KOH (9:1 or 100:3 v/v) at 40.0 °C

				9:1 Me_2SO–H_2O		100:3 Me_2SO–H_2O	
No.	X	λ/nm [a]	[KOH]/M [b]	10^5 *k*/s^{-1}	k_{rel}	10^5 *k*/s^{-1}	k_{rel}
1	*p*-NMe_2	270	0.50	0.39	0.22		
		270	0.20			0.16	0.089
2	*p*-OMe	274	0.50	1.37	0.78		
		287	0.20			1.18	0.65
3	*p*-Me	273.5	0.50	1.15	0.66		
		273.5	0.20			0.79	0.44
4	*m*-Me	273.5	0.50	1.03	0.59		
		272	0.20			1.04	0.58
5	H	264	0.50	1.75	1.00		
		264	0.20			1.80	1.00
6	*p*-SiMe	292	0.50	5.6	3.2		
		292	0.20			6.1	3.4
7	*p*-Cl	278	0.50	27.7	15.8		
		278	0.20			45	25
		278	0.10	6.1			
8	*m*-Cl	274	0.20			260	144
		274	0.10	27.2	70		
9	*m*-CF_3	270	0.20			430	240
		270	0.10	44.6	115		
			0.05			97	
10	*p*-$NMe_3{}^+I^-$	269	0.20			960	530
		269	0.10	74	192		
11	*p*-NO_2	302	0.01	37			
		302	0.05			1 550	
		302	0.10	370			
		302	0.20		950	6 070	3 370

[a] Wavelength used to monitor reaction. [b] Concentration of aqueous KOH, 1 vol. of which was mixed with 9 vol. of Me_2SO.

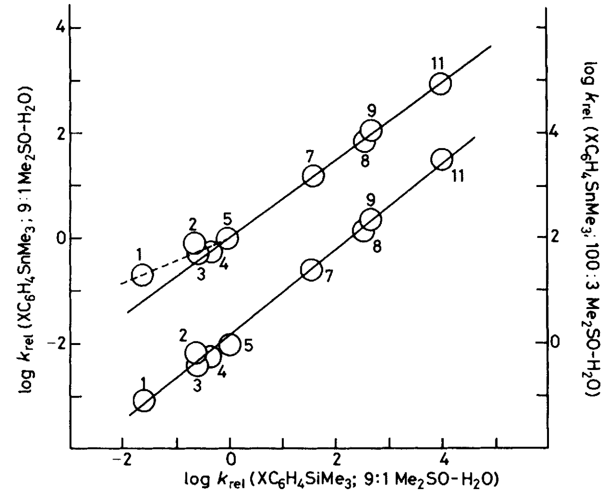

Figure 1. Plot of log k_{rel} for cleavage of $XC_6H_4SnMe_3$ compounds by KOH in (a) 9 : 1 Me_2SO-H_2O (upper line) or (b) 100 : 3 Me_2SO-H_2O (lower line) against log k_{rel} for cleavage of $XC_6H_4SiMe_3$ compounds by KOH in 9 : 1 Me_2SO-H_2O. The numbering of the points is shown in the Table

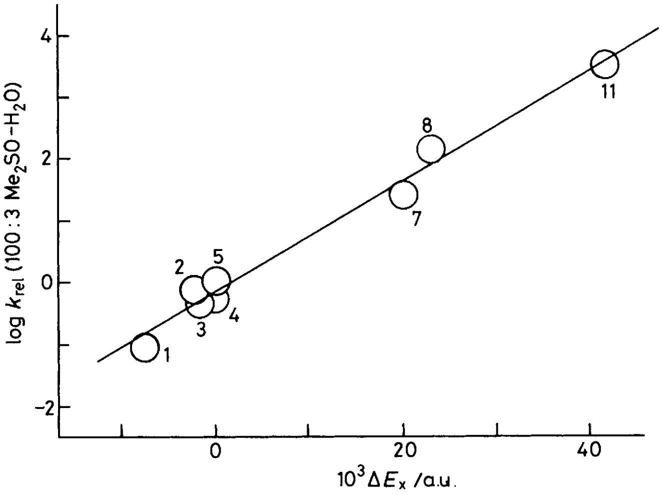

Figure 2. Plot of log k_{rel} for cleavage of $XC_6H_4SnMe_3$ compounds by KOH in 100 : 3 v/v Me_2SO-H_2O against 10^{-3} ΔE_x, where ΔE_x is the difference between the deprotonation energy for XC_6H_5 and that for C_6H_6

compound $XC_6H_4SnMe_3$ relative to that for the parent compound with X = H.

Plots of log k_{rel} for the cleavages in the two media against the corresponding values [2,5] of log k_{rel} for cleavage of the analogous silicon compounds by KOH in 9 : 1 Me_2SO-H_2O are shown in Figure 1. It will be seen that for the cleavage of the tin compounds in 9 : 1 Me_2SO-H_2O (upper plot in Figure 1) there is an excellent linear correlation with the data for the silicon compounds in the case of the electron-withdrawing groups and the weakly electron-releasing *m*-Me group, all the points being effectively on a straight line through the origin (*r*, 0.999; slope 0.740; intercept 0.014; 6 points), while the points for the more strongly electron-releasing groups *p*-NMe_2, *p*-OMe, and *p*-Me fall around a separate line through the origin, the point for the *p*-NMe_2 group lying 0.5 log k_{rel} units above the line through the majority of the points; this pattern is consistent with a still significant degree of electrophilic assistance to cleavage of the tin compounds in this medium. Such assistance is also in accord with the fact that the sensitivity to substituent effects is smaller for the tin than for the silicon compounds (the main line in the upper plot of Figure 1 has a slope of 0.74), since an electron-withdrawing group will reduce the ease of the proton attachment at the same time as it stabilizes the forming negative charge in the aryl group (*cf.* ref. 5), so that the overall activation is smaller than it would otherwise have been, as correspondingly, is the deactivation by electron-releasing groups. The $(p \longrightarrow d)_\pi$ bonding effect considered below could also contribute to the observed difference in sensitivity to substituent effects in the tin and silicon systems.

For cleavage of the tin compounds in 100 : 3 Me_2SO-H_2O (lower plot in Figure 1) all the points can be regarded as falling very satisfactorily about a single line, which, however, misses the origin by a small but significant amount (*r* 0.998; slope 0.82; intercept 0.146; 9 points), but once again the points for the *p*-NMe_2, *p*-OMe, and *p*-Me groups lie slightly above the excellent line which effectively passes through the origin and all the other points (*r* 0.999; slope 0.86; intercept 0.021; 6 points). The point for *p*-NMe_2 lies *ca.* 0.2 log k_{rel} units above the latter line, and if significance is attached to such a small deviation it can be accounted for in two ways. First, there may be a residual small degree of electrophilic assistance in the cleavage of the tin compounds even in this unfavourable medium, so that $XC_6H_4SnMe_3$ compounds with X = *p*-NMe_2, *p*-OMe, and *p*-Me are slightly more reactive than would otherwise be expected. Second there may be a significant loss of stabilization by $(p \longrightarrow d)_\pi$ bonding on going from the reactant to the transition state; this would be more important for the silicon than for the tin compounds, and the initial stabilization especially large for X = *p*-NMe_2, *p*-OMe, and *p*-Me, so that the $XC_6H_4SiMe_3$ compounds containing these substituents would be slightly *less* reactive than would otherwise be expected.

The small deviations from exact correlation between the substituent effects in the two systems lead to the interesting observation that a plot (Figure 2) of log k_{rel} for the $XC_6H_4SnMe_3$ compounds in 100 : 3 v/v Me_2SO-H_2O against values [1] of $10^{-3}\Delta E_x^-$, the relative deprotonation energies for the 1-position of XC_6H_5 species (data for *m*-CF_3 being omitted as usual [1]) is a satisfactory straight line (*r* 0.993; slope 0.090; intercept −0.166; 8 points), seemingly somewhat better than the corresponding plot for the cleavage of the silicon compounds in 9 : 1 v/v Me_2SO-H_2O, which showed two distinct lines through the origin, one for X = *p*-NMe_2, *p*-OMe, and *p*-Me, and the other for all the remaining substituents.[1] It was suggested that such a two-line plot originated in the fact that the aryl carbanion is far from fully formed in the transition state of cleavage, and the better single-line plot for the tin compounds could thus be taken to indicate that the transition state for their cleavage is closer to the aryl carbanion (as it is thought to be in the hydrogen-exchange of $XC_6H_4{}^2H$ compounds in KNH_2-NH_3, which also gives a single-line plot [1]). This would, indeed, be consistent with the fact that in the medium involved the tin are several times less reactive than the silicon compounds,[5,6] but the difference in reactivity seems to us not to be large enough to give rise to the effect observed, and, moreover, if the transition state were closer to the aryl carbanion for the tin compounds the sensitivity to substituent effects should be greater for them than for the silicon compounds, contrary to observation. It is rather more likely than the contrast between the two-line plot for the silicon compounds and the single-line plot for the tin compounds is due to a small residual degree of electrophilic assistance in the cleavage of the latter [1] or to $(p \longrightarrow d)_\pi$ stabilization of the initial state, as discussed above.

As would be expected[1] from the nature of the correlation noted above, fairly satisfactory correlations with σ^0 constants[7] are found for the $XC_6H_4SnMe_3$ compounds in both media. (For the 9 : 1 medium: *r* 0.987; slope 3.53; intercept 0.28; 10 points. For the 100 : 3 medium: *r* 0.992; slope 4.32; intercept 0.253; 10 points) The higher slope in the 100 : 3 medium is probably primarily associated with poorer solvation of the forming aryl carbanion in this medium, but the greater degree of electrophilic assistance in the 9 : 1 medium must make some contribution

The main conclusion from these studies is that in 100 : 3 Me_2SO-H_2O there is very little if any residual electrophilic assistance to base cleavage of the $XC_6H_4SnMe_3$ compounds, in line with expectations based on our previous proposals.[1,4] It is noteworthy that whereas in NaOMe–MeOH phenyltrimethylstannane is much more readily cleaved than phenyltrimethylsilane, in 6 : 1 v/v Me_2SO-H_2O the two compounds show almost the same reactivity,[3] while in 9 : 1 and 100 : 3 v/v Me_2SO-H_2O the silicon is cleaved about twice and nine times, respectively, as readily as the tin compound.[5,6] The much greater ease of base cleavage of the aryltin compounds in methanol[3] can thus be largely associated with the very effective electrophilic assistance in that medium, cleavage of the silicon compounds becoming increasingly favoured as the proton availability in the medium is lowered.

Experimental

Organotin Compounds.—These were made by standard methods as previously described.[3]

Rate Measurements.—These were carried out as described for cleavage of arylsilicon compounds,[2] but rate constants were usually obtained by the Swinbourne method,[8] since in some cases the ordinary first-order plots showed some curvature after about three or four half-lives as a result of some secondary reactions. Rate constants were reproducible to ±3%

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References

1 C. Eaborn, J. G. Stamper, and G. Seconi, *J. Organomet. Chem.*, 1981, **204**, 27.
2 G. Seconi, M. Taddei, C. Eaborn, and J. G. Stamper, *J. Chem. Soc., Perkin Trans. 2*, 1982, 643.
3 C. Eaborn, H. L. Hornfeld, and D. R. M. Walton, *J. Chem. Soc. B*, 1967, 1036.
4 C. Eaborn and G. Seconi, *J. Chem. Soc., Perkin Trans. 2*, 1979, 203.
5 A. R. Bassindale, C. Eaborn, R. Taylor, A. R. Thompson, D. R. M. Walton, J. Cretney, and G. J. Wright, *J. Chem. Soc. B*, 1971, 1155.
6 C. Eaborn, A. A. Najam, and D. R. M. Walton, *J. Organomet. Chem.*, 1972, **46**, 255.
7 O. Exner in ' Correlation Analysis in Chemistry,' eds. N. B. Chapman and J. Shorter, Plenum Press, New York and London, 1978, ch. 10.
8 E. S. Swinbourne, ' Analysis of Kinetic Data,' Nelson, London, 1971, pp. 83—84.

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