

Preliminary communication

The question of the intermediacy of carbanions in base-catalyzed cleavage of benzyl-silicon, benzyl-tin, and aryl-tin bonds

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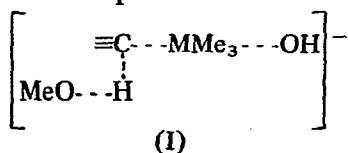
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Studies of the base cleavages of benzyl-MR₃ and aryl-MR₃ bonds, where M = Si, Ge, or Sn previously left unanswered the question of whether a carbanion is formed and an intermediate^{1,2}. We have now shown that free carbanions are not involved in base-catalyzed cleavage of XC₆H₄CH₂-SiMe₃, XC₆H₄CH₂-Me₃, and XC₆H₄-SnMe₃ bonds in methanol.

This conclusion was reached by using combined gas chromatographic-mass spectrometric analysis to establish the isotopic content of the aromatic products, XC₆H₄CH₃ + XC₆H₄CH₂D, or XC₆H₅ + XC₆H₅ + XC₆H₄D, formed by cleavage in a MeOH-MeOD mixture. (Separate experiments showed that no hydrogen-exchange occurred in these products under the reaction conditions.) A free carbanion will not discriminate significantly between the isotopes, and thus if the products are determined in a fast reaction of the carbanion with the solvent the H/D ratio in the products should be the same as that in the hydroxyl groups of the MeOH-MeOD mixture. (The benzene produced by addition of ethereal phenyllithium to the reaction medium showed such a ratio within the experimental error.) If, on the other hand, the transfer from the solvent to the carbon atom is synchronous with the breaking of the C-M bond, as in a transition state such as (I), the product can be expected to contain a lower proportion of deuterium. The results for



cleavage of XC₆H₄CH₂MMe₃ and XC₆H₄SnMe₃ compounds by 1M NaOH in an equimolar MeOH-MeOD mixture at 50° are expressed in Table 1 as *k_H*/*k_D* ratios (which would be unity for reaction of a free carbanion), and it is clear that in no case is the carbanion ever free. The (notional) carbanion is substantially less free in the cleavage of the aryl-tin than that of the benzyl-tin bonds and is somewhat less free in the cleavage of the benzyl-tin than in that of the benzyl-silicon bonds. Because of the rather large uncertainty in the

TABLE 1

PRODUCT ISOTOPE RATIOS IN THE CLEAVAGE OF $\text{XC}_6\text{H}_4\text{CH}_2\text{MMe}_3$ AND $\text{XC}_6\text{H}_4\text{SnMe}_3$ COMPOUNDS BY 1M NaOH IN MeOH-MeOD AT 50°

$\text{XC}_6\text{H}_4\text{CH}_2\text{MMe}_3$			$\text{XC}_6\text{H}_4\text{SnMe}_3$		
M	X	$k_{\text{H}}/k_{\text{D}}$	X	$k_{\text{H}}/k_{\text{D}}$	
		(± 0.3) ^a		(± 0.2) ^a	
Si	H	1.4	H	4.4	
	<i>p</i> -Me	1.5	<i>p</i> -Me	3.4	
	<i>m</i> -Cl	1.6	<i>m</i> -Cl	3.8	
	<i>m</i> -CF ₃	1.6	<i>m</i> -CF ₃	4.6	
Sn	H	2.8	<i>p</i> -OMe	3.8	
	<i>p</i> -Me	2.5	<i>p</i> -Br	4.0	
	<i>m</i> -Cl	2.4			
	<i>m</i> -CF ₃	2.0			

^aThe estimated uncertainties mainly indicate the degree of reproducibility.

measured $k_{\text{H}}/k_{\text{D}}$ ratios (which reflects the limitations of the linked gas chromatography-mass spectrometry systems employed), we cannot be sure that there is a significant variation with the substituent X within the separate sets of $\text{XC}_6\text{H}_4\text{CH}_2\text{SiMe}_3$ and $\text{XC}_6\text{H}_4\text{CH}_2\text{SnMe}_3$ compounds. There does seem to be a real variation in $k_{\text{H}}/k_{\text{D}}$ with X for the $\text{XC}_6\text{H}_4\text{SnMe}_3$ series, but we await more precise measurements before attempting to interpret it; there is probably significance, however, in the fact that the lowest value of the ratio is associated with the least reactive ($\text{X} = \textit{p}-Me) and the highest value with the most reactive ($\text{X} = \textit{m}-CF₃) substrate².$$

The observation that there is a substantial element of electrophilic attack at carbon by solvent in the cleavage of the aryl-SnMe₃ bonds means that a new analysis must be made of the influences of the substituents X, which, for simplicity were previously discussed in terms of production of substantially free carbanion in the rate-determining step². A full discussion to be submitted later will show that the unusual substituent pattern can, in fact, be largely accounted for by taking the electrophilic attack into account.

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