Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

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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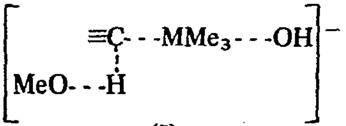
(Received January 9th, 1970)

Studies of the base cleavages of benzyl—MR_3 and aryl—MR_3 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 $XC_6H_4CH_2$—$SiMe_3$, $XC_6H_4CH_2$—Me_3, and XC_6H_4—$SnMe_3$ bonds in methanol.

This conclusion was reached by using combined gas chromatographic—mass spectrometric analysis to establish the isotopic content of the aromatic products, $XC_6H_4CH_3$ + $XC_6H_4CH_2D$, or XC_6H_5 + XC_6H_5 + XC_6H_4D, 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



$$\left[\begin{array}{ll} & \equiv\!\!\underset{\vdots}{C}\text{- - }MMe_3\text{- - -}OH \\ MeO\text{- - } & \!\!H \end{array}\right]^-$$

(I)

cleavage of $XC_6H_4CH_2MMe_3$ and $XC_6H_4SnMe_3$ compounds by 1*M* 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 $XC_6H_4CH_2MMe$ AND $XC_6H_4SnMe_3$ COMPOUNDS BY 1*M* NaOH IN MeOH-MeOD AT 50°

$XC_6H_4CH_2MMe_3$			$XC_6H_4SnMe_3$	
M	X	k_H/k_D	X	k_H/k_D
		(±0.3)[a]		(±0.2)[a]
Si	H	1.4	H	4.4
	p-Me	1.5	*p*-Me	3.4
	m-Cl	1.6	*m*-Cl	3.8
	m-CF_3	1.6	*m*-CF_3	4.6
Sn	H	2.8	*p*-OMe	3.8
	p-Me	2.5	*p*-Br	4.0
	m-Cl	2.4		
	m-CF_3	2.0		

[a] The estimated uncertainties mainly indicate the degree of reproducibility.

measured k_H/k_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 $XC_6H_4CH_2SiMe_3$ and $XC_6H_4CH_2SnMe_3$ compounds. There does seem to be a real variation in k_H/k_D with X for the $XC_6H_4SnMe_3$ 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 (X = *p*-Me) and the highest value with the most reactive (X = *m*-CF_3) substrate[2].

The observation that there is a substantial element of electrophilic attack at carbon by solvent in the cleavage of the aryl–$SnMe_3$ 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 step[2]. 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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