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THE MECHANISM OF THE REACTION OF ARYLOXYTRIMETHYLSTANNANE WITH METHANESULFONYL CHLORIDE

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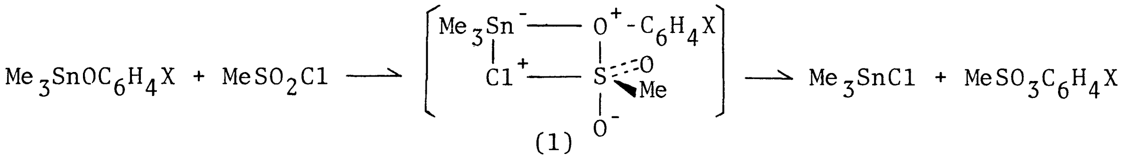
A kinetic study has been conducted for the reaction of aryloxytrimethylstannane with methanesulfonyl chloride. Substituent effect was found to be dependent on the solvent and obscure solvent effect was observed. A mechanism has been suggested involving nearly concerted four-center transition state.

The reaction of alkoxytrimethylsilane with benzenesulfinyl chloride had been considered to involve non-ionic four-center transition state.[1] The mechanism, however, was suspected and a nucleophilic attack of alkoxy-oxygen has been suggested.[2] On the contrary, we have found that the reaction of aryloxytrimethylstannane with methanesulfonyl chloride seems to involve the four-center mechanism although it involves ionic character (1). The preliminary aspects of the reaction will be described.



$$Me_3SnOC_6H_4X + MeSO_2Cl \longrightarrow \left[\begin{array}{ccc} Me_3Sn^- & \text{——} & O^+\text{-}C_6H_4X \\ | & & | \\ Cl^+ & \text{——} & S(=O)Me \\ & & | \\ & & O^- \end{array}\right] \longrightarrow Me_3SnCl + MeSO_3C_6H_4X$$

(1)

Trimethylphenoxystannane (0.92g) was heated with methanesulfonyl chloride (0.40g) in carbon tetrachloride (reflux 5h). Phenyl methanesulfonate was isolated from the solution and identified (0.55g, 91%).

The rate of the reaction was measured by ^{1}H NMR spectra. Second order rate constant was obtained by the relative intensities of the methyl signals of the sulfonate and the sulfonyl chloride (δ3.03 and 3.58) at time. Solvent and substituent effects were examined. The results are given in Table 1.

As shown in Table 1, a complicated solvent effect was observed. Although the polar solvents accelerate the reaction, the rate enhancements are quite small and the enhancements were also observed in nonpolar solvents. The substituent effects are also complicated. A small negative ρ value was observed in carbon tetrachloride solution. This might suggest a nucleophilic process for the reaction. The mechanism, however, is inconsistent with the substituent effect in benzonitrile and also with the small and obscure solvent effect. Thus, if such ionic process was operative even in the most nonpolar solvent, it should be facilitated more in the other polar solvents. The ρ value observed in the polar solvent would appear clearly negative and more enhanced solvent effect is expected as were observed for the analogous nucleophilic reactions.[2,3] The actual observations are against these considerations.

Table 1. Second Order Rate Constants for the Reaction of $Me_3SnOC_6H_4X(p)$ [0.242mol dm^{-3}] with $MeSO_2Cl$ [0.175mol dm^{-3}] at 130°C

X	Solvent	(ε)[a]	k $dm^3mol^{-1}s^{-1}$(X10^4)	Remarks
H	CCl_4	(2.23)	3.74 ± 0.12	k_{rel} = 1.00, $\Delta H^{\ddagger}$ = 10.6, $\Delta S^{\ddagger}$ = -48[b]
H	$CHCl_2CHCl_2$	(8.2)	2.93 ± 0.11	k_{rel} = 0.78
H	CH_2Cl_2	(8.9)	1.20 ± 0.06	k_{rel} = 0.32
H	PhCN	(25.2)	7.56 ± 0.29	k_{rel} = 2.0
H	CH_3CN	(36.2)	37.8 ± 2.28	k_{rel} = 10
OCH_3	CCl_4		5.37 ± 0.51	
CH_3	CCl_4		3.99 ± 0.29	$\rho_{(\sigma)}$ = -1.03, γ = 0.967 in CCl_4
Cl	CCl_4		2.81 ± 0.15	
NO_2	CCl_4		0.417 ± 0.009	
OCH_3	PhCN		17.3 ± 1.50	
CH_3	PhCN		9.67 ± 0.59	No linearity to any σ constant
Cl	PhCN		6.18 ± 0.23	in PhCN
NO_2	PhCN		7.58 ± 0.91	

a) Dielectric constant. b) Activation parameters in Kcal mol^{-1} and e.u., respectively (400°K, 1 cal = 4.184 J).

An alternative mechanism to explain the present result is a four-center process. The process is profitable especially to the substituent effect observed in benzonitrile and also to the small and unusual solvent effect. The activation parameters are consistent with the process. The features of the substituent effects in the different solvents, however, may suggest that the character of the transition state would dependent on the solvent. Namely, the mechanism does not involve a fully concerted transition state but involves a charge separated one (1) as like as that of the associative mechanism suggested for the unimolecular rearrangement of β-ketosilanes.[4] The timings of the bond formings and the breakings may dependent on the polarity of the solvents. The O-S bond forming would mark the nature of the transition state in carbon tetrachloride. On the other hand, both the O-S and the Sn-Cl bond creations characterize the transition state in benzonitrile.

The detailed study of the reaction is now in progress in this laboratory.

References

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