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A KINETIC STUDY FOR THE REACTION OF ARYLOXYTRIMETHYLSILANE WITH METHANESULFINYL CHLORIDE GIVING ARYL METHANESULFINATE

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Abstract: A nucleophilic attack of phenoxy-oxygen has been suggested as the mechanism of the reaction of aryloxytrimethylsilane with methanesulfinyl chloride.

Recently, Harpp et al. performed some kinetic studies for the reactions of methoxy and ethoxytrimethylsilanes with benzenesulfinyl chloride.[1)] A non-ionic four-centered mechanism has been suggested for the reaction based on the results that the rate of the reaction was found to be rather insensitive to the solvent polarity and sensitive to the steric effect of the alkoxy group. This is the only one report to the best of our knowledge, suggesting a four-centered mechanism for the cleavage reaction of IVb-VIb bond supported by kinetic evidence. The substituent effect on the rate of this reaction would be of interest.

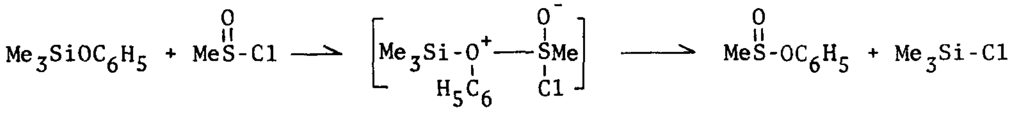
The reaction of trimethylphenoxysilane with methanesulfinyl chloride was chosen for our study instead of the reaction of alkoxytrimethylsilane with arenesulfinyl chloride because of the difficulty to prepare substituted-arenesulfinyl chlorides in pure form. The reaction was found to give phenyl methanesulfinate and chlorotrimethylsilane in nearly quantitative yield. Kinetic experiments were carried out in benzonitrile as the solvent. The rate was measured by monitoring ^{1}H NMR trimethyl signals of the starting silane and the product and found that the reaction obeyed a second order rate equation. The results are shown in Table 1.

Unexpectedly, a clear negative ρ value was observed for the reaction in almost the same magnitude with those of the analogous reactions of (arylthio)tri-

Table 1. Rates of the Reaction: $Me_3SiOC_6H_4X$-p (0.19 mol/dm^3) + MeS(O)Cl (0.23 mol/dm^3) $\longrightarrow$ $MeS(O)OC_6H_4X$ + Me_3SiCl at 36°C in C_6H_5CN.

X	k (dm^3 mol^{-1} s^{-1})	
OMe	2.96 X 10^{-3}	Hammett plot
Me	1.39 X 10^{-3}	
H	1.03 X 10^{-3}	ρ = -1.44
Cl	6.60 X 10^{-4}	(γ = 0.984)
Br	6.30 X 10^{-4}	
NO_2	7.04 X 10^{-5}	

methylstannanes with haloalkane (-1.40)$^{2)}$ and with benzoyl chloride (-1.6)$^{3)}$ in which nucleophilic attacks of the sulfur atoms have been suggested as the mechanisms based on kinetic and stereochemical studies. As an analogy, the reaction presently studied could not be explained by a non-ionic mechanism but would involve a nucleophilic attack of the phenoxy-oxygen atom on the sulfinyl group.



$$Me_3SiOC_6H_5 + Me\overset{\overset{O}{\|}}{S}-Cl \longrightarrow \left[Me_3Si-\underset{H_5C_6}{\underset{|}{\overset{+}{O}}}-\underset{Cl}{\underset{|}{\overset{O^-}{\overset{|}{S}}}}Me\right] \longrightarrow Me\overset{\overset{O}{\|}}{S}-OC_6H_5 + Me_3Si-Cl$$

More detailed study is now in progress in order to clarify whether this nucleophilic mechanism is also applicable to the reaction reported by Harpp et al. i.e., the reaction of alkoxytrimethylsilane with benzenesulfinyl chloride.$^{1)}$

References

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