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Kinetic Study for the Reaction of (Arylthio)trimethylstannane with Benzoyl Chloride Giving *S*-Aryl Thiobenzoate.

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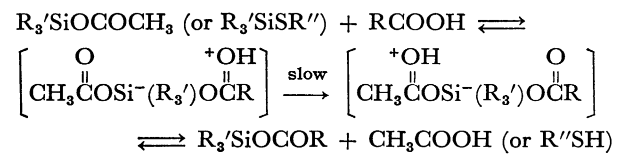
A kinetic study has been conducted on the reaction of (arylthio)trimethylstannane with benzoyl chloride giving chlorotrimethylstannane and *S*-aryl thiobenzoate. The reaction has been found to obey a second order kinetic equation. A mechanism involving bimolecular nucleophilic attack of the sulfur atom on the acyl carbon has been suggested for the reaction based on the substituent effects of arylthio and benzoyl moieties.

Several different mechanisms are conceivable for the cleavage reactions of group IVb–VIb bonds with various reagents as expressed by the following general formula. Namely, the IVb element can form a coordinated

$$\equiv\text{M–Y–} + \text{E–Nu} \longrightarrow \equiv\text{M–Nu} + \text{E–Y–}$$

$$\text{M=Si, Ge, Sn } etc.\text{, Y=O, S, Se } etc.$$
$$\text{E–Nu}=\text{H}_2\text{O, ROH, RCOOH, RX, RCOX, RS(O)X } etc.$$

intermediate and the complex has been suggested as the reaction intermediate in the reactions of silyl ether hydrolysis,[1)] acetoxysilane[2)] and thiosilane[3)] with carboxylic acids on the basis of kinetic results. Assuming the nucleophilicity of the VIb element



$$\text{R}_3'\text{SiOCOCH}_3 \text{ (or R}_3'\text{SiSR}'') + \text{RCOOH} \rightleftharpoons \left[\text{CH}_3\overset{\text{O}}{\overset{\|}{\text{C}}}\text{OSi}^-(\text{R}_3')\text{O}\overset{^+\text{OH}}{\overset{\|}{\text{C}}}\text{R}\right] \xrightarrow{\text{slow}} \left[\text{CH}_3\overset{^+\text{OH}}{\overset{\|}{\text{C}}}\text{OSi}^-(\text{R}_3')\text{O}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{R}\right] \rightleftharpoons \text{R}_3'\text{SiOCOR} + \text{CH}_3\text{COOH (or R}''\text{SH)}$$

played an important role in the course of reaction, a nucleophilic reaction involving an onium intermediate would result instead of the 5-coordination of the IVb element. The reaction of thiostannane with haloalkane is a typical reaction of this type.[4)]

$$\text{R}_3'\text{SnSR}'' + \text{RX} \xrightarrow{\text{slow}} [\text{R}_3'\text{SnS}^+(\text{R}'')\text{R X}^-] \longrightarrow \text{R}_3'\text{SnX} + \text{RSR}''$$

Another possible mechanism for the reaction is a 4-centered cyclic process.[5)] Thus, different mechanisms would be expected for individual reactions based on the coordination ability of the group IVb element, nucleophilicity of the group VIb atom and also the nature of the reactant, E–Nu. In this paper, the mechanism of the reaction of (arylthio)trimethylstannane with benzoyl chloride will be reported.

Results and Discussion

Product Analysis. The reactions of (arylthio)-trimethylstannanes with benzoyl chlorides have been found to give *S*-aryl thiobenzoate and chlorotrimethylstannane quantitatively. No other product in the reaction mixture was found by NMR analysis. The products were isolated and identified. The reaction

$$\text{Me}_3\text{SnSC}_6\text{H}_4\text{-X-}p + p\text{-Y-C}_6\text{H}_4\text{COCl} \longrightarrow \text{Y-C}_6\text{H}_4\text{COSC}_6\text{H}_4\text{-X} + \text{Me}_3\text{SnCl}$$
$$\text{X, Y=H, CH}_3\text{, Cl, OCH}_3$$

thus appeared to be similar to analogous reactions of this type.[6)] This reaction provides a novel route to prepare thiocarboxylic acid *S*-esters.

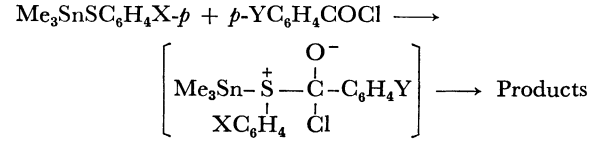
Kinetics and Mechanism. Rate of reaction of (arylthio)trimethylstannanes with benzoyl chlorides in carbon tetrachloride solutions were measured by monitoring the relative ratio of ^{1}H-NMR trimethyl signals of the thiostannane (δ 0.33—0.38 ppm) and chlorostannane (δ 0.63 ppm) with time. Second order rate constants were obtained with good reproducibility, the results of which are summarized in Table 1.

TABLE 1. RATE CONSTANTS FOR THE REACTION OF p-$\text{XC}_6\text{H}_4\text{SSnMe}_3$ (0.48 mol/dm^3) WITH p-$\text{YC}_6\text{H}_4\text{COCl}$ (0.57 mol/dm^3) IN CCl_4

Substituent		Temp	$k_2 \times 10^5$	Remarks
X	Y	°C	dm^3 mol^{-1} s^{-1}	
MeO	H	34.0	6.6±0.2	$\rho_{\text{X}(\sigma)}=-1.6$
Me	H	34.0	4.5±0.1	$\gamma=0.999$
H	H	34.0	2.3±0.1	
Cl	H	34.0	1.2±0.02	
H	H	42.9	5.2±0.4	$\Delta H^{\neq}=14.0$ kcal/mol
H	H	50.7	10 ±0.1	$\Delta S^{\neq}=-34.0$ e.u.
H	H	61.9	20 ±2.0	
H	MeO	34.0	1.3±0.05	$\rho_{\text{Y}(\sigma)}=+1.1$
H	Me	34.0	1.5±0.1	$\gamma=0.996$
H	Cl	34.0	4.6±0.1	

The large negative entropy value observed in the present study is in accordance with those of reactions of this type.[2–5a)] This may be recognized in terms of an ionic reaction which is conducted in a nonpolar solvent, rather than pπ-dπ bonding[1)] since the large negative value observed for the reaction of thiostannane with haloalkane in a nonpolar solvent has been shown to fall in a normal magnitude for a bimolecular reaction when conducted in a polar solvent.[4)]

The Hammett plot of the rates of reaction of substituted arylthiostannanes (substituent X) gave a straight line with a negative ρ value which is reasonable in magnitude for a reaction involving sulfonium ion formation positioned α- to the phenyl ring bearing the substituent.[7)] A quite comparable ρ value was also observed for the reaction of the same thiostannane with haloalkane and the reaction has been suggested to proceed *via* a sulfonium intermediate.[4)] As an analogy, the mechanism of the reaction of the thiostannane with acyl halide can be formulated as following, involving a nucleophilic attack of the sulfur atom on the acyl



$$\mathrm{Me_3SnSC_6H_4X}\text{-}p + p\text{-}\mathrm{YC_6H_4COCl} \longrightarrow \left[\mathrm{Me_3Sn}\text{-}\underset{\displaystyle \mathrm{XC_6H_4}}{\overset{+}{\mathrm{S}}}\text{—}\underset{\displaystyle \mathrm{Cl}}{\overset{\displaystyle \mathrm{O^-}}{\mathrm{C}}}\text{-}\mathrm{C_6H_4Y}\right] \longrightarrow \text{Products}$$

carbon. The positive and smaller ρ value due to the substituent Y on the benzoyl moiety is consistent with the mechanism since the negative charge in the intermediate is localized in the β-position to the aryl ring bearing the substituent.

Experimental

Materials. Preparation of the thiostannanes have previously been reported.[4] All solvents and benzoyl chlorides were purified prior to use.

Product Analysis. Trimethyl(phenylthio)stannane (1.40 g) and benzoyl chloride (0.70 g) were dissolved in CCl$_4$ (10 cm^3) and heated at 60 °C for 16 h in a sealed tube. NMR analysis confirmed the presence of only chlorotrimethylstannane and *S*-phenyl thiobenzoate. Chlorotrimethylstannane was obtained by distillation (65%, bp 59 °C/18 mmHg; 1 mmHg=133.322 Pa) and *S*-phenyl thiobenzoate was isolated from the residue by recrystallization (72%, mp 55 °C from CHCl$_3$–C$_6$H$_{14}$, lit,[8] 56 °C, IR $\nu_{\mathrm{C=O}}$ 1662 cm^{-1}). Other thiol esters were isolated similarly: C$_6$H$_5$COSC$_6$H$_4$Cl-*p*, 70%, mp 75—76 °C, lit,[8] 74—75 °C; *p*-ClC$_6$H$_4$COSC$_6$H$_5$, 72%, mp 80—82 °C, lit,[9] 81.5—83 °C; C$_6$H$_5$COSC$_6$H$_4$OCH$_3$-*p*, 66%, mp 93—94 °C, lit,[9] 93—95 °C; *p*-CH$_3$OC$_6$H$_4$COSC$_6$H$_5$, 75 %, mp 99—100 °C, lit,[8] 99—100 °C. All the yields are based on the isolated compound in pure form.

Kinetic Procedure. The procedure is essentially the same as that employed for the acyloxy exchange reaction of acetoxysilane.[2] Trimethyl(phenylthio)stannane (40 mm^3, 59 mg) and benzoyl chloride (30 mm^3, 36 mg) were dissolved in CCl$_4$ (370 mm^3) and the reaction monitored by following the ^{1}H-NMR trimethyl signals of the starting material and the product with time. The second order rate constant was obtained with an experimental error of 5%.

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