The Mechanism of the Reaction of (Aryloxy)trimethylstannane with Benzyl Bromide giving Aryl Benzyl Ether

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Synopsis. A kinetic study has been performed for the reaction of (aryloxy)trimethylstannane with benzyl bromide giving aryl benzyl ether and bromotrimethylstannane. Bimolecular nucleophilic attack of the aryloxy-oxygen on the benzyl-carbon has been suggested for the reaction based on the substituent effect.

Recently, we have reported kinetic and stereochemical results of the reactions of (alkylthio and arylthio)trimethylstannanes with haloalkanes.[1] A bimolecular nucleophilic attack of the sulfur atom on

$$Me_3SnSR + R'X \rightarrow [Me_3SnS^{\delta+}(R)\cdots R'\cdots X^{\delta-}] \rightarrow Me_3SnX + RSR'$$

the alkyl-carbon has been suggested for the reaction. A similar reaction has been known for the alkoxy analogue of the (alkylthio)stannane *i.e.*, the reaction of alkoxystannane with haloalkane.[2]

$$Bu_3SnOMe + BuI \rightarrow Bu_3SnI + BuOMe$$

Since the nucleophilicity of oxygen atom is much weaker than that of sulfur, it is doubtful whether the mechanism suggested for the reactions of (alkylthio and arylthio)stannanes is also applicable for that of alkoxystannane. We have extended our mechanistic study to the reaction of alkoxystannane with haloalkane.

The reaction of trimethyl(phenoxy)stannane with benzyl bromide was examined in the present study and found that the reaction gave bromotrimethylstannane and benzyl phenyl ether. The bromostannane was detected by GLC analysis of the reaction solution and the ethereal product was isolated and characterized.

$$Me_3SnOPh + PhCH_2Br \xrightarrow{120\,^\circ C,\ 24\,h} Me_3SnBr + PhCH_2OPh$$

The reaction, however, was found to proceed much slower than that of the (arylthio)stannane with benzyl bromide.[1] Almost no reaction was found under the same reaction conditions used for the reaction of the (arylthio)stannane. Accordingly, the rate of the reaction was measured in a polar solvent at higher temperature with high concentration of the substrate in order to increase the observed rate. A good pseudo-first-order plot was obtained. The results are given in Table 1. Hammett plot of the rates given in Table 1 gave apparently negative ρ value [$\rho_{(\sigma)} = -0.78$] with fair linearity ($\gamma = 0.982$). This would reveal that the nucleophilicity of aryloxy-oxygen played an important role during the reaction although the magnitude of the value appeared somewhat smaller than that obtained for the analogous reaction of (arylthio)stannane.[1] A charge separated 4-center mechanism could not be ruled out by the rather small ρ value alone but is unlikely considering the lower reactivity of the (aryloxy)stannane. The relative reactivity of (aryloxy)stannane toward (arylthio)stannane is consistent with relative nucleophilicities of oxygen and sulfur atoms.[3] Furthermore, the four-center mechanism has recently been ruled out for the bimolecular reaction of this type.[4] Thus, the most plausible mechanism is the nucleophilic attack of the

$$Me_3SnOPh + PhCH_2Br \rightarrow [Me_3Sn{-}O^{\delta+}(Ph)\cdots CH_2(Ph)\cdots Br^{\delta-}] \rightarrow \text{Products}$$

oxygen atom similar to that suggested for the reactions of analogous (alkylthio and arylthio)stannanes with haloalkane.[1] The reaction of alkoxystannane with haloalkane[2] would proceed *via* the same process, that is nucleophilic attack of oxygen atom, since this mechanism has been suggested in the present study even for the less nucleophilic (aryloxy)stannane.

Table 1. Pseudo-first-order rate constants for the reaction of $Me_3SnOC_6H_4X$-*p* + $C_6H_5CH_2Br$ in PhCN at 120 °C

X	k_{obsd}/s^{-1}
OCH_3	2.70×10^{-4}
CH_3	1.63×10^{-4}
H	1.15×10^{-4}
Cl	9.05×10^{-5}
NO_2	3.47×10^{-5}

Experimental

(Aryloxy)trimethylstannane. The compounds were prepared either by the reaction of sodium aryl oxide with bromotrimethylstannane in liquid ammonia[5] or by a modified alkoxyl exchange reaction[6] of methoxytrimethylstannane with appropriate phenol. The latter mathod gave better yields with simple procedure. Substituent X of $Me_3SnOC_6H_4X$-*p*, yield, physical properties, and elemental analysis were as follows: H, 36%, 109 °C/8 mmHg (1 mmHg = 133.322 Pa), δ_{CDCl_3} 0.53 ppm (Me_3); CH_3, 21%, mp 87—88 °C (from hexane-chloroform), δ_{CDCl_3} 2.22 (*p*-Me), 0.50 ppm (Me_3). Found: C, 44.06, H, 5.68%. Calcd for $C_{10}H_{16}OSn$: C, 44.33; H, 5.95; OCH_3, 34%. Mp 65—66 °C, bp 137 °C/3 mmHg, δ_{CDCl_3} 3.70 (OCH_3), 0.49 ppm (Me_3). Found C, 41.91; H, 5.25%. Calcd for $C_{10}H_{16}O_2Sn$: C, 41.86; H, 5.62; Cl, 65% (by exchange). Bp 137 °C/3 mmHg, δ_{CDCl_3} 0.53 ppm (Me_3). Found C, 36.60; H, 4.34%. Calcd for $C_9H_{13}ClOSn$: C, 37.10; H, 4.50; NO_2, ≈100% (by exchange). Mp 83.5—84 °C (from hexane–benzene), δ_{CDCl_3} 0.67 ppm (Me_3). Found C, 36.16; H, 4.33%. Calcd for $C_9H_{13}NO_3Sn$: C, 35.81, H, 4.34%.

Product Analysis. Trimethylphenoxystannane (1.2 g, 4.5 mmol) and benzyl bromide (3.8 g, 9.0 mmol) were dissolved in benzonitrile (5 cm^3) and the solution was heated

at 120 °C for 24 h in a sealed tube. The solvent and volatile product were evapolated under reduced press. Bromotrimethylstannane was detected in the volatile components by GLC analysis and benzyl phenyl ether was isolated from the residue by recrystallization, mp 40 °C (from hexane), 68% yield.

Kinetics. In a polar solvent, both the trimethyl signals of trimethylphenoxystannane (δ 0.53 ppm) and bromotrimethylstannane (δ 0.77 ppm) are submerged into one signal due to exchange reaction and the rate could not be measured by integration of those two signals. Accordingly, (aryloxy)-trimethylstannane (1.8×10^{-3} mol) and benzyl bromide (1.8×10^{-2} mol) were dissolved in benzonitrile (total 5 cm^3) with the addition of dichloromethane (5.4×10^{-4} mol) as the internal standard. The solution was devided into ten portions and sealed in glass tubes. The tubes were dipped in a constant temperature bath (120±0.1 °C). The tubes were picked up at time intervals and the amount of benzyl phenyl ether at the time was measured by integration of the benzyl proton signal (δ 4.98 ppm) relative to the internal standard (CH_2Cl_2, δ 5.21 ppm). Rate constant was obtained by least square calculation. The reaction of the (aryloxy)-stannane with dichloromethane was found to be negligible under the reaction conditions used.

References

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3) Trimethylphenoxystannane is less reactive than trimethyl(phenylthio)stannane by a factor of *ca.* 10^4 which is estimated by inspection of the present result and that reported in Ref. 1.

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