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The Reaction of (Arylthio)trimethylstannanes with 1-Aryl-1-bromoethanes: Effect of Substituent on the Process Shifting from Unimolecular to Bimolecular Substitution

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A kinetic study has been conducted on the reaction of (arylthio)trimethylstannanes with 1-aryl-1-bromoethanes. The reaction of the arylbromoethane bearing an electron-donating substituent was found involving unimolecular ionization of the arylbromoethane. The other reactions, however, were found to be second-order reactions. The nature of the second-order reactions was shifted from one involving unimolecular ionization as the minor process, to a clear bimolecular nucleophilic reaction, according to the electron-withdrawing nature of the substituents on the arylbromoethanes.

The mechanisms of the reactions of (arylthio)trimethylgermanes have been known to be dependent on the nature of the substrates regardless of their quite similar aspects in the products. Namely, the reaction with benzoyl chloride was found to proceed by five-coordination of the germanium atom (Eq. 1).[1] The reaction with benzyl bromides, on the other hand, involved nucleophilic attack of the sulfur atom on the benzyl moiety (Eq. 2).[2]

$$(CH_3)_3GeSC_6H_4X + YC_6H_4COCl \xrightarrow{\text{5-Co. of Ge}} (CH_3)_3GeCl + YC_6H_4CO\text{-}SC_6H_4X \quad (1)$$

$$(CH_3)_3GeSC_6H_4X + YC_6H_4CH_2Br \xrightarrow{\text{Nu. attack of S}} (CH_3)_3GeBr + YC_6H_4CO\text{-}SC_6H_4X \quad (2)$$

The difference of those two reactions in their mechanisms has been rationalized in terms of different steric requirements of the individual substrates. The benzyl moiety provides enough room to be attacked by the sulfur atom of the bulky thiogermane. On the other hand, a similar attack of the sulfur of the thiogermane on the carbon atom of benzoyl functional group would be difficult by steric hindrance. Formation of the tetrahedral addition intermediate bearing four heavy atoms, including the sulfur with bulky trimethylgermyl group, would be difficult since they require much space around the central carbon atom. Hence, the reaction proceeds by five-coordination process when forced to proceed.

In this connection, it is quite natural that the analogous thiostannane could attack not only on benzyl[3] but also on benzoyl[4] substrates (Eq. 3). The bulky trimethylstannyl group does not inhibit the nucleophilic attack of the sulfur atom because the stannyl–sulfur bond is long enough providing a room around the reaction center of the sulfur atom.[2]

$$(CH_3)_3SnSC_6H_5X + YC_6H_4COCl \text{ (or } YC_6H_4CH_2Br) \xrightarrow{\text{Nu. attack of S}} (CH_3)_3GeCl \text{ (or Br)} + YC_6H_4CO\text{-}SC_6H_4X \text{ (or } YC_6H_4CH_2\text{-}SC_6H_4X) \quad (3)$$

On the other hand, the sulfur atom in the shorter silyl-sulfur linkage could not act as a nucleophile. The bulky trimethylsilyl group nearby the nucleophile of the sulfur, disturbs the reactivity by steric hindrance. Thus, the reaction of (arylthio)trimethylsilane with a haloalkane, phenacyl bromide, was found to proceed by another process i.e., five-coordination of the silicon atom (Eq. 4)[5]

$$(CH_3)_3SiSC_6H_4X + RBr \xrightarrow{\text{5-Co. of Si}} (R{=}PhCOCH_2) \qquad (CH_3)_3SiBr + RSC_6H_4X \quad (4)$$

Standing on these results, an increment of steric hindrance on benzyl moiety would disturb the bimolecular nucleophilic attack. The reaction of (arylthio)trimethylgermanes with 1-aryl-1-bromoethanes (1-arylethyl bromides) was examined expecting mechanism shift from bimolecular nucleophilic to five-coordination process.

Unexpected unimolecular ionization of 1-aryl-1-bromoethanes was found as the mechanism. The result was also unexpected in view of the reaction conditions used, since the reaction was carried out under typical second order reaction conditions, with nearly equal amount of diluted nucleophile. The solvent was also unusual for the process because the reactions were carried out in aprotic solvents. The unexpected mechanism was undoubtedly due to the nature of the starting arylbromoalkane. The arylbromoalkane was a secondary alkyl bromide bearing an α-phenyl group which gives much stabilized carbenium ion on ionization (Eq. 5).[6]

$$(CH_3)_3GeSC_6H_4X + YC_6H_4CH(CH_3)Br \rightarrow [YC_6H_4C^+HCH_3\ Br^-] \rightarrow (CH_3)_3GeBr + YC_6H_4CH(CH_3)\text{-}SC_6H_4X \quad (5)$$

We have now extended our study to the reaction of (arylthio)trimethylstannane with 1-aryl-1-bromoethanes. The longer stannyl–sulfur bond may provide enough space for a bimolecular nucleophilic attack of the sulfur atom on the particular haloalkane, regardless of its facile unimolecular ionization. Preliminary aspects of

the reaction have been communicated recently.[7]

Results and Discussion

Trimethyl(phenylthio)stannane (1 g) was heated with an equimolar amount of 1-bromo-1-phenylethane at 110 °C for 24 h in a sealed tube. Only phenyl 1-phenylethyl sulfide and bromotrimethylstannane were found by ^{1}H NMR analysis of the resulting mixture. The products were isolated by fractional distillation and identified (Eq. 6).

$$(CH_3)_3SnSC_6H_5 + C_6H_5CH(CH_3)Br \xrightarrow{110\,^\circ C,\ 24\ h} (CH_3)_3SnBr + C_6H_5CH(CH_3)\text{-}SC_6H_5 \quad (6)$$

Rate of the reaction was measured by ^{1}H NMR analysis observing ratio of the trimethyl signals of the starting and the product stannanes at time. There were several limitations on the choice of the kinetic conditions. Some of the target trimethyl signals of the stannanes with certain substituents, could be observed separately under any reaction conditions. While, the signals of the other stannanes usually submerged into one signal by ligand-exchange reaction in common solvents. Pseudo-first-order kinetic conditions in less polar solvent of chloroform were chosen for the present study. Under these reaction conditions, the target signals could be observed separately for all the reactions of the stannanes bearing various substituents. Polar solvents and second-order reaction conditions could not be used for the present study.

A good linear pseudo-first-order kinetic plot was obtained up to 60% completion of the reaction in chloroform with 10-fold excess of 1-aryl-1-bromoethanes. A slight upward deviation of the plot was observed above 60% completion of the reaction. The deviation might due to the acceleration of the reaction by the products. In fact, additions of the products into the reaction solutions resulted noticeable acceleration of the rates of the reactions. Accordingly, rate constants for the reactions were obtained less than 60% completion of the reactions where such acceleration was nearly negligible.

Rate dependency on the concentration of 1-bromo-1-phenylethane was observed employing different concentrations of the arylbromoethane (Table 1, Entries 1, 2, and 3). Plot of the results gave a straight line of slope 1.1. Thus, first-order dependency on the concentration of the arylbromoethane was confirmed within experimental error. The result revealed total second-order reaction, dependent on both the concentrations of trimethyl(phenylthio)stannane and 1-bromo-1-phenyl-

Table 1. Pseudo-First-Order Rate Constants for the Reactions of $(CH_3)_3SnSC_6H_4$–X (SnS) with Y–$C_6H_4CH(CH_3)Br$ (PhEBr) in Chloroform

Entry	[SnS]×10² / mol dm⁻³	X	[PhEBr]×10 / mol dm⁻³	Y	Temp / °C±0.1	k×10⁵ / s⁻¹
1	6.0	H	3.0	H	100	5.17±0.41[a]
2	6.0	H	6.0	H	100	11.8±0.7[a,b]
3	6.0	H	7.5	H	100	15.7±0.9[a]
4	6.0	H	6.0	H	90	5.82±0.44[b,c,e]
5	6.0	H	6.0	H	80	2.55±0.24[b]
6	6.0	*p*-OCH_3	6.0	H	90	7.13±0.28[c]
7	6.0	*p*-CH_3	6.0	H	90	6.71±0.24[c]
8	6.0	*p*-Cl	6.0	H	90	5.01±0.26[c]
9	6.0	*m*-Cl	6.0	H	90	4.55±0.14[c]
10	6.0	H	6.0	*p*-CH_3	90	167[d,e]
11	6.0	H	6.0	*p*-CH_3	30	1.84±0.10
12	6.0	H	6.0	*p*-CH_3	40	3.98±0.25
13	6.0	H	6.0	*p*-CH_3	50	10.6±0.6[f]
14	6.0	H	6.0	*p*-Cl	90	4.00±0.35[e]
15	6.0	H	6.0	*m*-Cl	90	0.95±0.04[e]
16	6.0	H	6.0	*p*-NO_2	90	0.75±0.02[e,g,h]
17	4.62	H	6.0	*p*-CH_3	50	11.1±0.5[f]
18	8.58	H	6.0	*p*-CH_3	50	10.1±0.6[f]
19	4.62	H	6.0	*p*-NO_2	90	0.50±0.05[g]
20	8.58	H	6.0	*p*-NO_2	90	0.99±0.03[g]
21	6.0	*p*-OCH_3	6.0	*p*-NO_2	90	1.35±0.06[h]
22	6.0	*p*-CH_3	6.0	*p*-NO_2	90	1.10±0.10[h]
23	6.0	*p*-Cl	6.0	*p*-NO_2	90	0.43±0.01[h]
24	6.0	*m*-Cl	6.0	*p*-NO_2	90	0.29±0.02[h]

a) First-order dependency on [PhEBr](slope 1.1) for the reactions X=Y=H, (Entry 1, 2, and 3). b) $\Delta H^{\neq}_{400}$=84.8 kJ mol^{-1}, $\Delta S^{\neq}_{400}$=−95.2 J K^{-1} mol^{-1}, correlation coefficient (γ)= 0.9999, (2, 4, and 5). c) Effect of X for the reactions Y=H: $\rho_{X(\sigma)}$=−0.31, γ=0.9991, (4, 6 to 9). d) Estimated value (11, 12, and 13). e) No linear plot for the effect of Y, when X=H, (4, 10, and 14 to 16). f) No dependency on [SnS] for the reaction of Y=*p*-CH_3 (13, 17, and 18). g) First-order dependency on [SnS] (slope 1.1) for the reactions: X=H, Y=*p*-NO_2 (16, 19, and 20). h) Effect of X for the reactions Y=*p*-NO_2: $\rho_{X(\sigma)}$=−1.04, γ=0.999, (16, 21 to 24).

ethane.

Rates were measured for the reactions with (substituted arylthio)trimethylstannanes with 1-bromo-1-phenylethane. A small negative ρ_x value due to the effect of the substituent (X) was thus obtained (Table 1, $\rho_{X(\sigma)}=-0.31$, Entries 4, 6 to 9), with a straight Hammett plot. The second-order kinetic behavior together with the negative Hammett plot, would suggest a bimolecular nucleophilic attack of the sulfur atom on 1-bromo-1-phenylethane. The reaction, however, seems to be not fully consisted by the mechanism. The absolute ρ_x value appeared too small. There would be another contributing process, that might be an unimolecular ionization of 1-bromo-1-phenylethane, in view of the small absolute ρ_x value. The contribution of unimolecular process was confirmed by the reaction of the arylbromoethane having electron-withdrawing substituent. The detailed results of the unimolecular reaction will be described below. The results would suggest the contribution of the unimolecular process for the reaction of the unsubstituted 1-bromo-1-phenylethane at least in some extent.

Definitely, no dependency of the rate of the reaction on the concentration of the thiostannane was observed for the reaction of 1-bromo-1-(*p*-tolyl)ethane (Table 1, Y=*p*-CH_3, Entries 13, 17, and 18). The reaction with the arylbromoethane bearing an electron-donating substituent (Y=*p*-CH_3) would involve an unimolecular ionization of the arylbromoethane as the mechanism. The reaction of another arylbromoethane having more powerful electron-donating substituent (*p*-OCH_3) would proceed by the same manner. The arylbromoethane bearing *p*-OCH_3 as the substituent, Y could not be prepared in pure form due to its instability. The substituents, X effect would not be expected for the reactions when the 1-aryl-1-bromoethanes possesses electron-donating substituents.

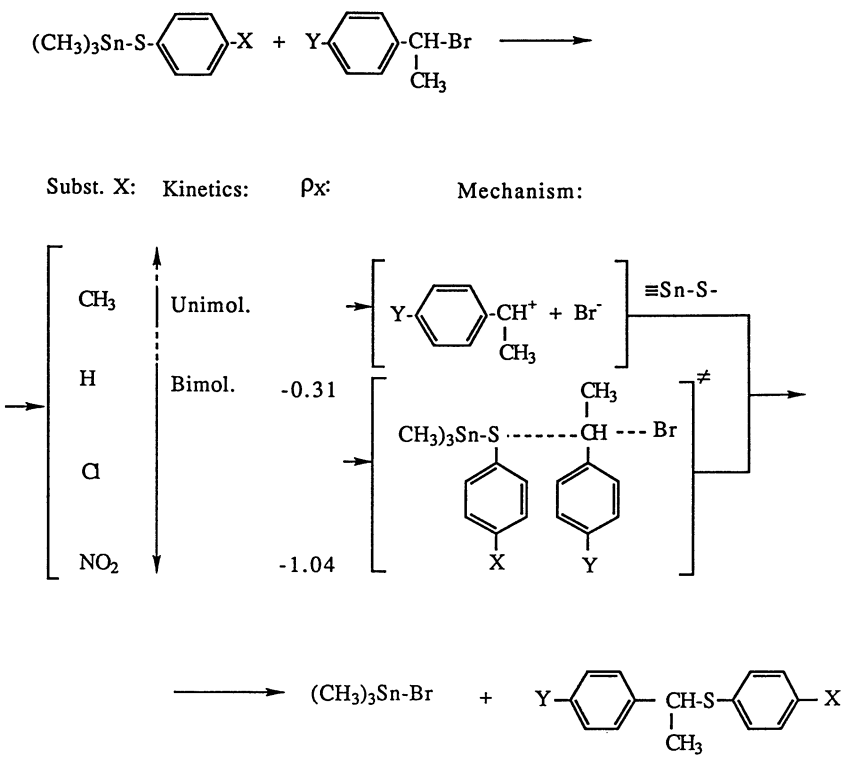
On the contrary, another electronic nature of the 1-aryl-1-bromoethanes, that is the arylbromoethane bearing nitro group on the aryl ring, gave clearly contrasted result in the substituent (X) effect. Appreciable negative ρ_x value was observed for the reactions of the arylbromoethane bearing nitro group as the substituent, Y (Table 1, Y=*p*-NO_2, $\rho_{X(\sigma)}=-1.04$, Entries 16, 21 to 24). Rate dependency on the concentration of the thiostannane was examined for the reaction with the arylbromoethane bearing nitro group. A clear first-order dependency was observed on the concentration of the thiostannane within experimental error (Table 1, Entries 16, 19, and 20, slope=1.1). These results would clearly suggest a bimolecular nucleophilic attack of the sulfur atom as the mechanism for the reaction of 1-bromo-1-(*p*-nitrophenyl)ethane.

The expected mechanism shift from bimolecular nucleophilic to five-coordination, has not been observed. The present study, however, revealed that the nature of the arylbromoethanes effects dramatically on the course of the reaction. The process of the reactions clearly changed from first-order unimolecular ionization to second-order bimolecular nucleophilic attack.

The substituent effect on the benzylic substrates for bimolecular nucleophilic reactions usually gives complicated Hammett plots, although negative tendency appears as a whole.[8] A similar bent plot with a negative tendency was also observed for the analogous reaction of benzyl bromides with (arylthio)trimethylgermanes.[2] A particular electronic effect was discussed by Hudson et.al., explaining the bent plot.[8] On the other hand, slightly bent upwards, but almost linear and clearly large negative Hammett plots have been observed for the unimolecular reactions of benzylic substrates.[9] The upward deviations of Hammett plots for the unimolecular reactions have been rationalized by considering minor contribution of a bimolecular process.[6,9] A bent plot can be drawn in the present study for the effect of the substituent Y. However, the acceleration due to the *p*-methyl group appeared abnormally too much in comparison with that commonly observed for bimolecular reactions of benzylic substrates. Neither σ nor σ^+ constants gave linear correlations (Entries 4, 10, and 14 to 16). The abnormal acceleration due to *p*-methyl group was rationalized, as discussed above, by considering shift of the reaction mechanism.

The shift of the process would undoubtedly be dependent on the nature of the 1-aryl-1-bromoethanes. The easier ionize arylbromoethane, especially bearing electron-donating substituent, exclusively facilitated the unimolecular pathway. The opposite nature of the substituent, on the other hand, brought in exclusive contribution of the bimolecular process, as shown in Scheme 1.

It is interesting to note here, the similarities and differences of the present reactions to those of the analogous thiogermanes with the same substrates.[6] Unimolecular ionization of the arylbromoethanes was found as the mechanism for the reaction of (arylthio)-trimethylgermanes with all the substituted arylbromoethanes. Clear bimolecular nucleophilic substitution was not observed, although minor contribution of the process could not be ruled out for the reaction with the thiogermane.[6] On the contrary, the arylbromoethanes bearing electron-withdrawing substituents (Y=*p*-NO_2) have been found exclusively to accept bimolecular nucleophilic attack of the sulfur atoms of various (arylthio)trimethylstannanes in the present study. Difference in nucleophilicity of the sulfur atoms of the thiogermanes and the thiostannanes may be a factor accounting for the difference in the mechanisms of those two reactions. On the other hand, different bond lengths between germyl–sulfur and stannyl–sulfur bonds would be the important factor controlling the mechanism, in view of the steric control of the mechanisms in analogous reactions, as discussed previously.[2] The longer stannyl–sulfur bond pushes off the bulky trimethylstan-



Scheme 1.

nyl group and provides a room around the sulfur allowing to act it as a nucleophile even toward a secondary carbon atom.

Experimental

Materials. (Arylthio)trimethylstannanes were prepared from bromotrimethylstannane and appropriate arenethiol as described previously.[3] Substituted 1-aryl-1-bromoethanes were prepared by reduction of the corresponding acetophenone followed by bromination.[10] Substituent (Y), yield of the arylbromoethane, and its bp were as follows: *p*-CH_3, 65%, 73 °C/mmHg (1 mmHg=133.322 Pa), *p*-Cl, 70%, 120 °C/28 mmHg, *m*-Cl, 70%, 100 °C/2 mmHg, *p*-NO_2, 76%, 120 °C/2 mmHg. Kinetic solvent, chloroform was dried over magnesium sulfate and simply distilled before use without removal of ethanol of the stabilizer.

Product Analysis. (Phenylthio)trimethylstannane (1.00 g, 3.68 mmol) was heated at 110 °C for 24 h in a sealed tube in the presence of an equimolar amount of 1-bromo-1-phenylethane. ^{1}H NMR Analysis of the resulting mixture showed signals corresponding to bromotrimethylstannane and phenyl 1-phenylethyl sulfide. The products were separated by distillation obtaining bromotrimethylstannane, bp 59 °C/26 mmHg, 50% yield, and the sulfide, bp 120 °C/1 mmHg, 52% yield. The isolated products were characterized by their physical properties and spectra.

Kinetics. The procedure was essentially the same to that reported previously.[3] Concentrations and temperature for the kinetic experiments are recorded in the Table. Addition of 2.3×10^{-2} mol dm^{-3} of either bromotrimethylstannane or phenyl 1-phenylethyl sulfide resulted ca. 5% acceleration of the reaction of trimethyl(phenylthio)stannane with 1-bromo-1-phenylethane.

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