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Mechanism of the Reaction of (Arylthio)trimethylgermanes with 1-Aryl-1-bromoethanes—Kinetic and Stereochemical Studies—

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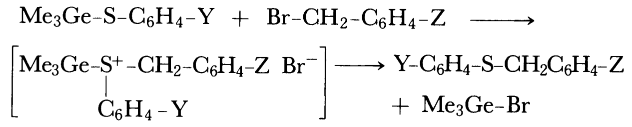
Kinetic and stereochemical studies have been conducted on the reaction of (arylthio)trimethylgermanes with 1-aryl-1-bromoethanes. The reaction has been found to obey a first-order kinetic equation. The rates of the reaction of the substituted arylethanes were well-correlated with σ^+ constants. Optically active 1-bromo-1-phenylethane gave racemic phenyl 1-phenylethyl sulfide by the reaction with trimethyl(phenylthio)germane. An $\mathrm{S_N1}$ ionization of 1-aryl-1-bromoethanes has been suggested as the reaction mechanism.

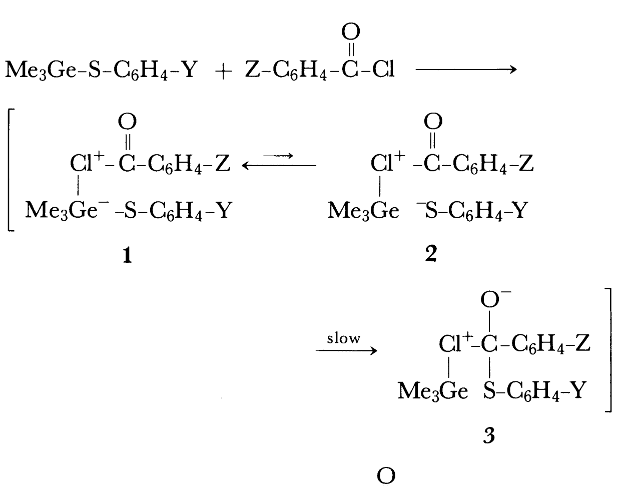
We have reported a kinetic study on the reaction of (arylthio)trimethylgermanes with benzyl bromides giving aryl benzyl sulfides and bromotrimethylgermane.[1] The reaction obeyed a second-order kinetic equation and gave apparently negative ρ value due to the substituents on the arylthio group. Accordingly, a nucleophilic attack of the sulfur atom on the benzylic carbon atom has been suggested as the reaction mechanism (Scheme 1).



$$\mathrm{Me_3Ge\text{-}S\text{-}C_6H_4\text{-}Y + Br\text{-}CH_2\text{-}C_6H_4\text{-}Z} \longrightarrow \left[\begin{array}{l}\mathrm{Me_3Ge\text{-}S^+\text{-}CH_2\text{-}C_6H_4\text{-}Z\ Br^-} \\ \qquad\ \ |\\ \qquad\mathrm{C_6H_4\text{-}Y}\end{array}\right] \longrightarrow \begin{array}{l}\mathrm{Y\text{-}C_6H_4\text{-}S\text{-}CH_2C_6H_4\text{-}Z} \\ \mathrm{+\ Me_3Ge\text{-}Br}\end{array}$$

Scheme 1.

A quite different kinetic aspect was observed for the reaction of (arylthio)trimethylgermanes with aroyl chlorides.[2] The reaction also obeyed a second-order kinetic equation, however, quite different in the substituent effects. Namely, positive ρ values were observed for both due to the substituents on the arylthio moiety and to the substituents on the aroyl group. These substituent effects together with the observed large solvent effects on the rate of the reaction were well-rationalized in terms of 5-coordinated process involving unfavorable equilibrium formation of the intermediate **2** which was followed by rate-determining attack of the arenethiolate ion on the carbonyl carbon atom (Scheme 2).[2]



$$\mathrm{Me_3Ge\text{-}S\text{-}C_6H_4\text{-}Y + Z\text{-}C_6H_4\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}Cl} \longrightarrow$$

$$\left[\begin{array}{l}\mathrm{Cl^+\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}C_6H_4\text{-}Z} \\ \ \ | \\ \mathrm{Me_3Ge^-\text{-}S\text{-}C_6H_4\text{-}Y}\end{array} \rightleftarrows \begin{array}{l}\mathrm{Cl^+\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}C_6H_4\text{-}Z} \\ \ \ | \\ \mathrm{Me_3Ge\ \ {}^-S\text{-}C_6H_4\text{-}Y}\end{array} \xrightarrow{\text{slow}} \begin{array}{l}\mathrm{Cl^+\text{-}\overset{\displaystyle O^-}{\overset{|}{C}}\text{-}C_6H_4\text{-}Z} \\ \ \ |\quad\ | \\ \mathrm{Me_3Ge\ \ S\text{-}C_6H_4\text{-}Y}\end{array}\right]$$

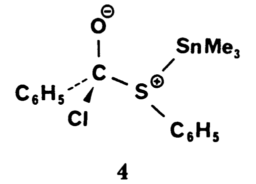
$$\qquad\qquad\mathbf{1}\qquad\qquad\qquad\qquad\mathbf{2}\qquad\qquad\qquad\qquad\mathbf{3}$$

$$\xrightarrow{\text{fast}} \mathrm{Me_3Ge\text{-}Cl + Y\text{-}C_6H_4\text{-}S\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}C_6H_4\text{-}Z}$$

Scheme 2.

The difference in their mechanisms of those two reactions was explained in terms of different steric requirements of the reactants. Benzyl bromide can accept a bimolecular nucleophilic attack even by such bulky nucleophiles as (arylthio)trimethylgermanes. On the other hand, aroyl halides involve addition intermediates during the course of a nucleophilic addition-elimination process and hence hardly accept attack of a bulky nucleophile like the arylthiogermanes. Thus, the reaction with aroyl chlorides proceeds by another process, i.e., 5-coordination of the metal atom.[1]

The same concept can be applied to rationalizing mechanistic difference in the analogous reactions. It is quite natural that the reaction of (arylthio)trimethylstannanes, a compound bearing longer metal-sulfur bond than that of germanium-sulfur, with benzyl halides proceeds by a nucleophilic attack.[3] The longer stannyl-sulfur bond provides a room for a bimolecular nucleophilic process in the reaction even with aroyl chlorides which demands more space for the nucleophilic attack forming an intermediate **4**, than that required for benzylic substrate.[4] On the contrary, (arylthio)trimethylsilanes can only undergo the 5-coordination process in the reaction even with phenacyl bromide which has been known as one of the most reactive substrates for $\mathrm{S_N2}$ reactions.[5]



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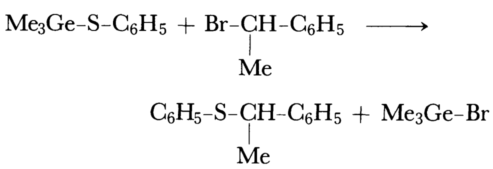
Based on these considerations, the length of germanium-sulfur bond in (arylthio)trimethylgermanes is critical which allows to proceed a bimolecular nucleophilic process in the reaction with benzyl halides.

An increment of some steric hindrance on benzyl halides may cause the change of the reaction mechanism from the bimolecular nucleophilic process to another, i.e., 5-coordination process. Thus, we have tried the reaction of (arylthio)trimethylgermanes with benzyl bromides bearing a methyl group at the α-position, that is 1-aryl-1-bromoethanes. Another possible mechanism would be the S_N1 process since the bromoalkane undergoes a facile unimolecular ionization.

Results and Discussion

Trimethyl(phenylthio)germane (247 mg, 1.27 mmol) was allowed to react with an equimolar amount of 1-bromo-1-phenylethane (235 mg, 1.27 mmol) at 100 °C for 41 h. The ^{1}H NMR spectrum of the reaction mixture showed signals only corresponding to the products although prolonged heating after completion of the reaction resulted in formation of some amount of unidentified side-product which might form from thermolysis of the product. Bromotrimethylgermane and phenyl 1-phenylethyl sulfide were isolated from the reaction mixture and characterized. Thus, the present reaction appeared to be a quite similar reaction in the type of the products with those of the reaction with benzyl halides[3] as shown in Scheme 3.



$$Me_3Ge\text{-}S\text{-}C_6H_5 + Br\text{-}\underset{\substack{|\\ Me}}{CH}\text{-}C_6H_5 \longrightarrow C_6H_5\text{-}S\text{-}\underset{\substack{|\\ Me}}{CH}\text{-}C_6H_5 + Me_3Ge\text{-}Br$$

Scheme 3.

The reaction was carried out in a solvent with a small excess amount of the bromide. This is typical kinetic conditions for second-order reactions. The reaction was monitored by observing ^{1}H NMR trimethyl signals of the starting germane (δ=0.47) and the product, bromotrimethylgermane (δ=0.85). The rate constant was obtained by least-squares calculation of relative intensity of the trimethyl signals at time intervals. The second-order kinetic equation, each first-order in respective to the two reactants, failed to reveal linear kinetic plot. On the other hand, the first-order equation in respective to the concentration of the bromoethane gave a satisfactory result up to more than 90% completion. The result suggests the first-order reaction dependent only on the concentration of the bromoethane. The first-order dependency was also confirmed by the kinetic experiments with various concentrations of the phenylthiogermane. The rate constants thus obtained were nearly identical regardless of the different concentrations of the phenylthiogermane. Thus, the reaction was found to be of a first-order dependent only on the concentration of 1-bromo-1-phenylethane even under typical second-order reaction conditions. Accordingly, it is quite natural that the effect of the substituents (Y) of the arylthio group on the rate of the reaction appeared insignificant. These results are shown in Table 1.

Table 1. First-Order Rate Constants for the Reaction of $Me_3GeSC_6H_4$-Y with $C_6H_5CH(Me)Br$

[GeS][a]	[RBr][a]	[GeS]/[RBr]	Y	Solvent	Temp /°C	k_1×10^5 /s^{-1}	γ[b]
0.131	0.318	0.4	H	C_6H_5CN	110	6.39±0.18	0.999
0.262	0.318	0.8	H	C_6H_5CN	110	7.00±0.31	0.999
0.380	0.318	1.2	H	C_6H_5CN	110	7.22±0.70	0.998
0.262	0.318	0.8	H	C_6H_5CN	100	2.99±0.03	0.999
0.262	0.318	0.8	H	C_6H_5CN	120	15.6 ±0.64	0.999
0.262	0.318	0.8	*m*-Cl	C_6H_5CN	110	4.57±0.16	0.998
0.262	0.318	0.8	*p*-Cl	C_6H_5CN	110	5.89±0.16	0.999
0.262	0.318	0.8	*p*-Me	C_6H_5CN	110	6.14±0.25	0.999
0.262	0.318	0.8	*p*-OMe	C_6H_5CN	110	5.18±0.13	0.999
0.262	0.318	0.8	*m*-Cl	C_6H_5OMe	120	0.77±0.14	0.993
0.262	0.318	0.8	*p*-Cl	C_6H_5OMe	120	0.73±0.10	0.996
0.262	0.318	0.8	H	C_6H_5OMe	120	0.91±0.05	0.999
0.262	0.318	0.8	*p*-Me	C_6H_5OMe	120	0.83±0.05	0.998
0.262	0.318	0.8	*p*-OMe	C_6H_5OMe	120	0.75±0.02	0.999
0.262	0.318	0.8	H	C_6H_5OMe	110	0.39±0.07	0.994
0.262	0.318	0.8	H	C_6H_5OMe	130	2.06±0.18	0.997
0.262	0.318	0.8	H	C_6H_5Me	130	0.27±0.03	0.986
0.262	0.318	0.8	H	C_6H_5Me	140	0.68±0.04	0.988
0.262	0.318	0.8	H	C_6H_5Me	150	1.23±0.14	0.986

$\Delta H^{\neq}_{400}$=101.0 kJ mol^{-1}, $\Delta S^{\neq}_{400}$=−63.2 J K^{-1} mol^{-1}, in C_6H_5CN 0.999.[b]
$\Delta H^{\neq}_{400}$=106.4 kJ mol^{-1}, $\Delta S^{\neq}_{400}$=−73.1 J K^{-1} mol^{-1}, in C_6H_5OMe 0.999.
$\Delta H^{\neq}_{400}$=107.0 kJ mol^{-1}, $\Delta S^{\neq}_{400}$=−87.8 J K^{-1} mol^{-1}, in C_6H_5Me 0.999.
k_{rel} in C_6H_5Me : C_6H_5OMe : C_6H_5CN=1 : 7.6 : 125 at 130 °C.

a) Concentrations: mol dm^{-3}. b) Correlation coefficient.

Table 1 also contains activation parameters and the solvent effects on the rates of the reaction. The observed entropy of activation values are negative but these results do not contradict with the unimolecular ionization mechanism. The values observed for the analogous reactions of this type involving bimolecular nucleophilic or 5-coordination process as their mechanisms have been known much more negative than those observed for the present study in various solvents.[6] The values presently observed suggest looser transition state for the reaction than those proceeding bimolecular mechanisms. The smaller negative entropy of activations in absolute values in more polar solvents, shown in Table 1, are in accordance with the unimolecular ionization although it is difficult to explain why they are still negative. Substantially smaller enthalpy values observed in polar solvents suggest an ionic process for the present reaction and is in line with the large solvent effect.

Contrary to insignificant substituent effect of the arylthio group (Y), the substituents on 1-aryl-1-bromoethanes (Z) affect largely the rates of the reaction. The results are given in Table 2. Linear Hammett plots were obtained with σ^+ constants giving large negative ρ values for both the reactions in benzonitrile and anisole, although they are slightly curved upward as shown in Fig. 1. The effects of Z in both the solvents are nearly comparable with those of the unimolecular ionization of benzylic substrate.[7] The small upward deviations of the plots for the electron-withdrawing substituents may be explained by the minor contribution of a bimolecular nucleophilic substitution. The unimolecular ionization would become more unfavorable with the electron-withdrawing substituents and the bimolecular nucleophilic process would contribute more.

Table 2. First-Order Rate Constants for the Reaction of $Me_3GeSC_6H_5$ (0.262 mol dm^{-3}) with Z-$C_6H_4CH(Me)Br$ (0.318 mol dm^{-3})

Solvent	Temp/°C	Z	$k_1 \times 10^5$/s^{-1}	γ[a]
C_6H_5CN	70	*p*-Me	5.27±0.49	0.998
C_6H_5CN	80	*p*-Me	13.64±0.47	0.999
C_6H_5CN	110	H	7.00±0.31	0.999
C_6H_5CN	110	*p*-Cl	3.36±0.27	0.999
C_6H_5CN	110	*n*-Cl	0.47±0.06	0.998
C_6H_5OMe	80	*p*-Me	1.30±0.34	0.979
C_6H_5OMe	90	*p*-Me	2.96±0.21	0.998
C_6H_5OMe	130	H	2.06±0.18	0.997
C_6H_5OMe	130	*p*-Cl	1.52±0.02	0.999
C_6H_5OMe	130	*m*-Cl	0.30±0.03	0.992

a) Correlation coefficient of the kinetic plot.

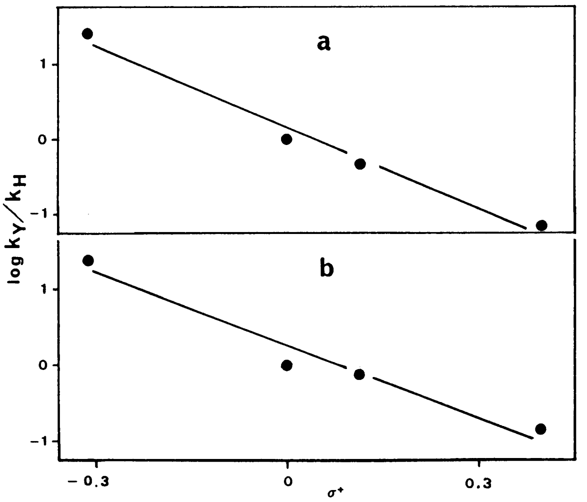


Fig. 1. Plots of the rate constants of the reactions of $Me_3GeSC_6H_5$ with Z-$C_6H_4CH(Me)Br$ against σ^+ constants, (a) in benzonitrile, (b) in anisole.

In a control experiment, 1-bromo-1-phenylethane was heated in the presence of 2,6-lutidine, instead of the thiogermane, in benzonitrile under the same reaction conditions used for the kinetic experiments. Styrene was obtained in about 70% yield which is quite comparable with the conversion of the reaction with the thiogermane under the same reaction conditions (65%) as shown in Scheme 4. The unimolecular ionization of the bromoethane has been confirmed under the kinetic conditions.

$$\underset{(318\ \text{mmol dm}^{-3})}{C_6H_5CH(Me)Br} \xrightarrow[110\,^{\circ}\text{C, 3.75 h, in benzonitrile}]{\text{2,6-lutidine (382 mmol dm}^{-3})} C_6H_5CH{=}CH_2\ (70\%\ \text{yield})$$

Scheme 4.

Optically active (+)-1-bromo-1-phenylethane was allowed to react with an equimolar amount of trimethyl(phenylthio)germane. Phenyl 1-phenylethyl sulfide thus obtained was found to be racemized nearly completely (Scheme 5). This is conclusive evidence supporting a unimolecular ionization of the bromoethane.

$$Me_3GeSC_6H_5 + \underset{(40\%\ \text{ee})}{(+)\text{-}C_6H_5C^*H(Me)Br} \xrightarrow[100\,^{\circ}\text{C, 41 h}]{} C_6H_5C^*H(Me)SC_6H_5\ (51\%\ \text{yield, }1.2\%\ \text{ee})$$

Scheme 5.

All the results obtained in the present study suggest a mechanism involving unimolecular ionization of 1-aryl-1-bromoethanes at the rate-determining step (rds) for the reaction (Scheme 6). The present study, however, does not rule out minor contribution of a bimolecular nucleophilic process especially for the reaction with the 1-aryl-1-bromoethanes bearing electron-withdrawing substituents.

Among the three possible mechanisms mentioned earlier, the unimolecular ionization of 1-bromo-1-phenylethane has been confirmed in the present reaction. Although our hypothesis of the steric control

Table 3. Mechanism of the Reactions: $Me_3{\equiv}IVb{-}VIb{-}R' + R{-}X \longrightarrow Me_3{\equiv}IVb{-}X + R{-}VIb{-}R'$

IVb-VIb	R′	R-X	Mechanism	Ref.
Ge-S	Aryl	Aryl-CH(CH_3)-Br	S_N1	This work
Ge-S	Aryl	Aryl-CH_2-Br	S_N2	1
Ge-S	Aryl	Aryl-C(O)-Cl	5-Coordination	2
Si-S	Aryl	Aryl-C(O)CH_2-Br	5-Coordination	5
Si-S	Aryl	Aryl-C(O)-Cl	5-Coordination	12
Si-O	Alkyl, Aryl	Alkyl, Aryl-S(O)-Cl	S_N2[a]	13
Sn-S	Alkyl, Aryl	Alkyl, Aryl-CH_2-Cl, Br, I	S_N2	1, 3
Sn-S	Aryl	Aryl-C(O)-Cl	S_N2[a]	4
Sn-O	Aryl	Aryl-CH_2-Br	S_N2	14
Sn-O	Aryl	Alkyl-S(O_2)-Cl	4-Center	15

a) Bimolecular nucleophilic addition-elimination.

$$C_6H_5CH(Me)Br \xrightarrow{rds} [C_6H_5C^+H(Me)\ Br^-] \xrightarrow{Me_3GeSC_6H_5} C_6H_5CH(Me)SC_6H_5 + Me_3GeBr$$

Scheme 6.

on the reaction mechanism could not be clarified by the present study, this study revealed a first example of an S_N1 reaction for the reaction of the compounds bearing IVb atom-VIb atom bonds as summarized in Table 3. The particular mechanism is undoubtedly due to the nature of the substrate, 1-aryl-1-bromoethanes which easily undergoes unimolecular ionization. The present reaction is also an example of S_N1 reaction under unusual reaction conditions for the process. Most of the S_N1 reactions have been known to proceed with large excess of nucleophiles in polar media, or nucleophiles as the solvents.

It is interesting to note here, the halogen-exchange reaction of 1-bromo-1-phenylethane with mercury(II) thiocyanate in dibutyl ether at 0 °C giving thiocyanate. The mechanism has been suggested as the unimolecular ionization standing on the racemization of optically active 1-phenylethyl moiety during the reaction.[8] This is another unimolecular nucleophilic reaction under abnormal reaction conditions for the process. The reaction, however, may better be explained by initial association of 1-bromo-1-phenylethane with the salt followed by ionization of the formed complex or mercury(II) salt-assisted ionization of the reactant. 1-Bromo-1-phenylethane is fairly stable in nonpolar media below room temperatures in the absence of the salt. Kinetic study on the halogen-exchange reaction is desired to clarify the possible complexation of the bromoethane with mercury(II) salts. However, it is difficult to determine kinetic order of the salts because of their limited solubility in the solvent. On the other hand, no dependency of concentration of the nucleophile on the rate of the reaction has been confirmed in the present study. In this connection, the present reaction is not only a first example of S_N1 reaction of the compounds bearing IVb atom-VIb atom bonds with haloalkanes but also a unique unimolecular nucleophilic substitution proceeding with a small amount of nucleophile in nonpolar media.

Experimental

Materials. Solvents were dried and distilled. Substituted 1-bromo-1-phenylethanes were prepared by reduction of the corresponding acetophenones.[9] Commercially available optically active (−)-1-phenylethanol was brominated with PBr_3 obtaining (+)-1-bromo-1-phenylethane.[10] Preparation of (arylthio)trimethylgermanes was reported previously.[2]

Product Analysis. Trimethyl(phenythio)germane (0.25 g, 1.3×10^{-3} mol) was heated with an equimolar amount of 1-bromo-1-phenylethane (0.24 g, 1.3×10^{-3} mol) in a sealed tube at 100 °C for 41 h. ^{1}H NMR analysis of the reaction mixture showed only signals due to bromotrimethylgermane (δ 0.85, s, 9H) and phenyl 1-phenylethyl sulfide (δ 1.60, d, 3H; 4.30, q, 1H; 7.20, broad, 10H) and small amounts of the remaining reactants. The conversion was 85%. Bromotrimethylgermane was isolated by distillation (bp 113—114 °C, 84.2% yield). Phenyl 1-phenylethyl sulfide was isolated from the residue by column chromatography on silica gel with hexane as the eluent (0.14 g, 51.4% yield). The reaction of optically active compound was carried out similarly. Rotations ($[\alpha]_D$) of the starting 1-bromo-1-phenylethane and obtained phenyl 1-phenylethyl sulfide were, +69.0° (ethanol, *c* 2.35, 40.3% ee) and −9.04° (ethanol, *c* 0.55), respectively. Optical purity of the sulfide was determined by converting to the corresponding sulfone,[11] −1.14° (methanol, *c* 0.39, 1.2% ee).

Kinetics. The kinetic procedure was essentially the same to that previously reported.[1] Initial concentrations were 0.262 and 0.318 mol dm^{-3} for the thiogermane and the bromoethane, respectively.

The Reaction of 1-Bromo-1-phenylethane in the Absence of the Thiogermane. A mixture of 1-bromo-1-phenylethane (0.294 g, 0.318 mol dm^{-3}) and 2,6-lutidine (0.204 g, 0.382 mol dm^{-3}) in benzonitrile (0.50 cm^3) was sealed in a glass tube and heated at 110±0.1°C for 3.75 h. After heating, the precipitated salt was filtered off. Styrene was identified by the pattern of its olefinic protons in the ^{1}H NMR spectrum of the filtrate and the yield was estimated by intensity of the signals relative to that of the remaining 1-bromo-1-phenylethane.

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