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The Mechanism of the Reaction of (Arylthio)trimethylgermanes with Benzyl Bromides Giving Aryl Benzyl Sulfides. A Kinetic Study

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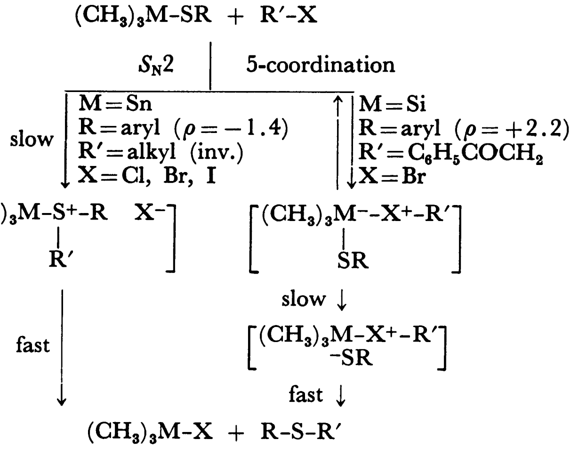
A kinetic study has been conducted on the reaction of (arylthio)trimethylgermanes with benzyl bromides. The reaction was found to be second order and the rate was largely accelerated in polar solvents. Both ρ values due to substituents on arylthio and benzyl groups revealed nucleophilic attack of the sulfur atom on benzylic carbon atom as the reaction mechanism. Rates of the reactions of trimethyl(*p*-tolylthio)stannane with substituted benzyl chlorides were also examined to compare the substituent effects. Steric crowd around the sulfur atom has been found as an important factor to control the reaction mechanism.

Different kinetic aspects have been observed for the reactions of aroyl chlorides with a series of organometallic sulfur compounds. Individually different mechanisms have been suggested for the reactions of (arylthio)trimethylstannanes,[1] germanes,[2] and silanes,[3] regardless of quite similar outcomes of the reaction products. The difference has also been observed between the reactions of haloalkanes with (arylthio)trimethylstannanes[4] and analogous silanes.[5] Namely, a negative ρ value due to the substituents on the arylthio group and inversion of the carbon atom of the haloalkane were observed for the reaction of the arylthiostannanes. Accordingly, a nucleophilic attack of the sulfur atom has been suggested for the reaction. Relative reactivity of the haloalkanes also supported the mechanism.[4] On the other hand, a large positive ρ value was observed for the reaction of (arylthio)trimethylsilanes with a reactive haloalkane of phenacyl bromide.[5] Initial formation of a 5-coordinated intermediate followed by rate-determining cleavage of the silicon-sulfur bond has been claimed for the reaction (Scheme 1). In this connection, a kinetic study is of interest on the reaction of germanium analogue with haloalkanes.



Scheme 1.

We have conducted a kinetic study on the reaction of (arylthio)trimethylgermanes with benzyl bromides.

Results and Discussion

The reaction of trimethyl(phenylthio)germane with benzyl bromide was found to give bromotrimethylgermane and benzyl phenyl sulfide in quantitative yields. No other product was found in the reaction mixture. Products were isolated and characterized.

$$(CH_3)_3Ge\text{-}SC_6H_5 + C_6H_5CH_2\text{-}Br \xrightarrow{100\,°C,\ 30\,h} (CH_3)_3Ge\text{-}Br + C_6H_5S\text{-}CH_2C_6H_5$$

The reaction was monitored by observing ^1H NMR trimethyl signals of the starting germane (δ=0.47) and the product (δ=0.85). The rate constant, k_2, was obtained by least-squares calculation of relative intensities of the trimethyl signal at time intervals. The reaction was found to obey second order rate equation. Kinetic experiments were done at various temperatures in several solvents to observe activation parameters and solvent effect. The results are given in Table 1.

Dichloromethane used as a solvent was observed to react with the arylthiogermane. However, the rate of this reaction was found to be much smaller than that of the reaction with benzyl bromide under the same reaction conditions and the solvent reaction can be neglected. No reaction was found with the other solvents.

Activation parameters given in Table 1 are quite similar to those of the analogous reactions which proceed by ionic processes.[4,5] Solvent effect on the rate of the reaction also supports ionic mechanism for the present reaction since large acceleration in polar solvent was observed.

Effects of the substituents both in the arylthio (X) and the benzyl (Y) moieties were examined to clarify the reaction mechanism. The results are shown in Tables 2 and 3. A clear negative ρ value due to the substituents of the arylthio moiety (ρ_X=−1.41) was

Table 1. Activation Parameters and Solvent Effects on the Rates of the Reactions of $(CH_3)_3GeSC_6H_5$ (0.262 mol dm^{-3}) with $C_6H_5CH_2Br$ (0.318 mol dm^{-3})

Solvent(ε)$^{a)}$	Temp °C	$k_2 \times 10^4$ dm^3 mol^{-1} s^{-1}	$\Delta H^{\neq}_{400}$ kJ mol^{-1}	$\Delta S^{\neq}_{400}$ JK^{-1} mol^{-1}	k_{rel} at 140 °C
C_6H_6(2.28)	130	0.0870±0.0031	65.8	−181	1.00
C_6H_6	140	0.151±0.022	$\gamma=0.996$$^{b)}$		
C_6H_6	150	0.225±0.017			
$C_6H_5OCH_3$(4.33)	130	0.446±0.021	70.6	−155	5.0
$C_6H_5OCH_3$	140	0.757±0.024	$\gamma=0.999$		
$C_6H_5OCH_3$	150	1.23 ±0.02			
CH_2Cl_2(8.9)	130	3.48 ±0.20	67.2	−147	41
CH_2Cl_2	140	6.17 ±0.56	$\gamma=0.995$		
CH_2Cl_2	150	9.24 ±0.89			
C_6H_5CN(25.2)	110	2.19 ±0.16	80.8	−106	110
C_6H_5CN	120	4.61 ±0.45	$\gamma=0.998$		
C_6H_5CN	130	7.72 ±0.43			

a) Dielectric constants. b) Correlation coefficient.

Table 2. Rate Constants for the Reactions of $(CH_3)_3GeSC_6H_4X$ (0.262 mol dm^{-3}) with $C_6H_5CH_2Br$ (0.318 mol dm^{-3})

Solvent	Temp °C	X	k_2 dm^3 mol^{-1} s^{-1}	ρ_X (γ)$^{a)}$
C_6H_6	150	*p*-OCH_3	$6.29\pm0.37\times10^{-5}$	
C_6H_6	150	*p*-CH_3	$3.66\pm0.43\times10^{-5}$	
C_6H_6	150	H	$2.25\pm0.17\times10^{-5}$	−1.41
C_6H_6	150	*p*-Cl	$1.02\pm0.19\times10^{-5}$	(0.994)
C_6H_6	150	*m*-Cl	$7.66\pm0.76\times10^{-6}$	
C_6H_5CN	130	*p*-OCH_3	$1.33\pm0.07\times10^{-3}$	
C_6H_5CN	130	*p*-CH_3	$1.07\pm0.07\times10^{-3}$	
C_6H_5CN	130	H	$7.72\pm0.43\times10^{-4}$	−0.76
C_6H_5CN	130	*p*-Cl	$5.32\pm0.67\times10^{-4}$	(0.998)
C_6H_5CN	130	*m*-Cl	$4.28\pm0.18\times10^{-4}$	

a) Correlation coefficient.

Table 3. Rate Constants for the Reactions of $(CH_3)_3GeSC_6H_5$ (0.262 mol dm^{-3}) with $YC_6H_4CH_2Br$ (0.318 mol dm^{-3})

Solvent	Temp/°C	Y	k_2/dm^3 mol^{-1} s^{-1}
C_6H_6	150	*p*-CH_3	$3.97\pm0.37\times10^{-5}$
C_6H_6	150	H	$2.25\pm0.17\times10^{-5}$
C_6H_6	150	*p*-Cl	$2.37\pm0.28\times10^{-5}$
C_6H_6	150	*p*-Br	$2.22\pm0.14\times10^{-5}$
C_6H_5CN	130	*p*-CH_3	$1.36\pm0.12\times10^{-3}$
C_6H_5CN	130	H	$7.72\pm0.43\times10^{-4}$
C_6H_5CN	130	*p*-Cl	$7.20\pm0.38\times10^{-4}$
C_6H_5CN	130	*p*-Br	$6.53\pm0.32\times10^{-4}$

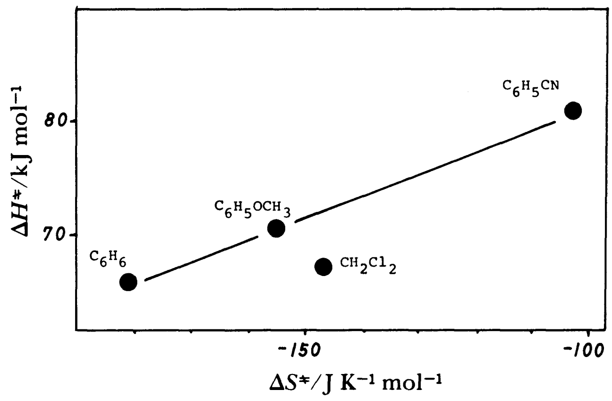


Fig. 1. Plot of ΔH^{*} vs. ΔS^{*} in various solvents.

observed in benzene solution. This result together with the large solvent effect supports a nucleophilic attack of the sulfur atom as the mechanism for the reaction carried out even in a nonpolar solvent. The effect, on the other hand, appeared substantially smaller in a polar solvent like benzonitrile (ρ_X= −0.76). However, it does not necessarily suggest another mechanism for the reaction in benzonitrile. Rather, the observed linear isokinetic relationship shown in Fig. 1 suggests similarity in the mechanism for the reactions in these solvents, although the plot for the reaction in dichloromethane appeared somewhat deviated. One possible explanation for the small absolute ρ value observed in benzonitrile is to consider the greater stabilization of the polar transition state in the polar solvent and hence stabilization or destabilization by the substituent becomes less important. This interpretation, however, contradicts with the results observed for the analogous reaction in which an enhanced substituent effect was observed in a polar solvent.6) Thus, the smaller negative ρ value observed in benzonitrile is difficult to explain but it is clearly negative anyway in accordance with the nucleophilic mechanism.

The substituent (Y) effect due to the benzyl group (ρ_Y) appeared somewhat obscure. Rate acceleration by electron donating substituent was observed in all the solvents examined. Almost no effect, on the other

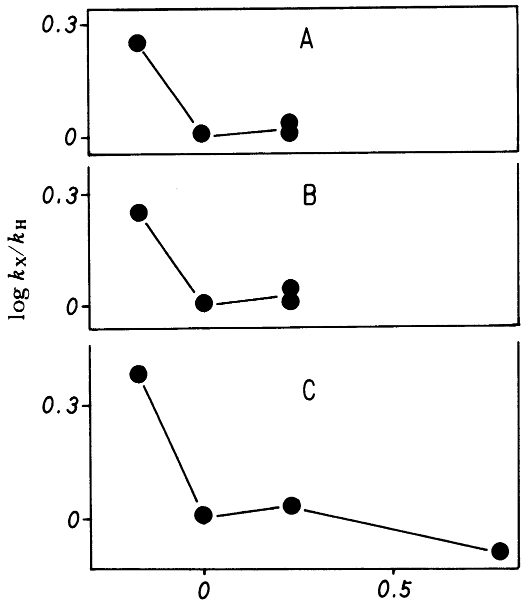


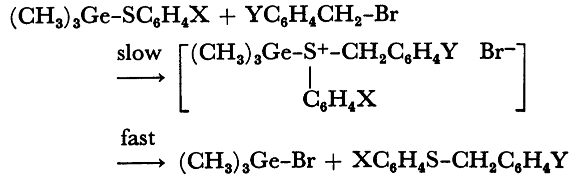
Fig. 2. Hammett plots for the reactions of $(CH_3)_3GeSC_6H_5+YC_6H_4CH_2Br$: A, in C_6H_6; B, in C_6H_5CN and $(CH_3)_3SnSC_6H_4CH_3$-*p*$+YC_6H_4CH_2Cl$: C, in $CHCl_3$.

hand, was observed by electron-withdrawing substituents. Thus, bent or curved Hammett plots were obtained as shown in Fig. 2. The bent plots do not contradict with the nucleophilic mechanism. Indeed, a quite similar bent plot has also been reported for the nucleophilic reaction of benzenethiol with substituted benzyl bromides.[7]

Moreover, rate of the reaction of trimethyl(*p*-tolylthio)stannane with substituted benzyl chlorides was measured in order to make sure the mechanism, since a nucleophilic mechanism has been accepted conclusively for such reaction by many evidences.[4] The plot is shown in Fig. 2. A similar bent plot was obtained. The observed bent or curved plot is quite common for the nucleophilic reactions with the substituted benzyl halides.

Thus, all the results obtained by the present study support a mechanism involving nucleophilic attack of the sulfur atom on the benzylic carbon atom (Scheme 2). The formation of the sulfonium intermediate would be the rate-determining step and the salt would decompose rapidly. Neither any precipitation was formed even in a nonpolar solvent nor signals corresponding to the salt were observed during the reaction. A stannylsulfonium salt of this type had once been reported as an isolable product[8] but we later found that the structure of the isolated product was wrong and concluded that the salt cannot be isolated.[9]

The mechanism for the present reaction which has thus been suggested, is quite different from that of the reaction of the same arylthiogermanes with benzoyl chloride.[2] The kinetic aspects observed in the present study are quite similar with those of the reaction of the arylthiostannanes with haloalkanes[4] and different from those of the reaction of the arylthiosilanes with phenacyl bromide.[5]



$$(CH_3)_3Ge\text{-}SC_6H_4X + YC_6H_4CH_2\text{-}Br \xrightarrow{\text{slow}} \left[(CH_3)_3Ge\text{-}\underset{\displaystyle C_6H_4X}{\overset{+}{S}}\text{-}CH_2C_6H_4Y \quad Br^- \right] \xrightarrow{\text{fast}} (CH_3)_3Ge\text{-}Br + XC_6H_4S\text{-}CH_2C_6H_4Y$$

Scheme 2.

There are several factors which may control the course of the reaction. Nucleophilicity of the sulfur atom and 5-coordination ability of the germanium atom might be important factors. However, the difference in the mechanisms of the present reaction and that of the reaction with benzoyl chloride[2] cannot be explained in terms of those factors since the same arylthiogermanes were used.

On inspection of the present results and those of the previously reported, the reactivity of benzoyl chloride[2] is appeared smaller than expected.[10] In other words the reactivity of the arylthiogermanes seems to be restricted toward aroyl chlorides and the restriction may change the mechanism. Namely, the reaction of the arylthiogermanes with benzoyl chloride proceeds only slightly faster than the reaction with benzyl bromide and these two reactions proceed by different mechanisms. Aroyl chlorides would be expected to have much higher reactivity than benzyl bromides for the reaction with nucleophiles. In fact, much faster reaction of benzoyl chloride was observed than that of benzyl bromide with the arylthiostannanes and the reactions have been known to proceed by a common mechanism i.e., nucleophilic attack of the sulfur atom.[11]

The restricted reactivity of the arylthiogermanes toward benzoyl chloride can also be recognized by comparing the rates of the reactions of the arylthiogermanes and the stannanes with these two halides.[1,2,4] The arylthiogermanes are substantially less reactive than the arylthiostannanes for the reactions with benzoyl chloride. On the other hand, no such substantial difference in their reactivities was observed for the reactions with benzyl bromide.[12] Only the reaction of the arylthiogermanes with benzoyl chloride, among these four reactions, has been known to involve a 5-coordinated intermediate.[2]

There should be a special factor to restrict the reactivity of the arylthiogermanes toward aroyl chlorides. The mechanism of the reaction seems to be closely related to the reactivity as has hither been discussed. The facile reaction involves a nucleophilic attack of the sulfur atom, while 5-coordinated intermediate is formed when the nucleophilic reaction was disturbed. The factor to control the reactivity together with the mechanism would be a steric effect. The aroyl halides may have more steric requirements than that of benzyl halides upon nucleophilic attacks. Thus, benzyl bromide accepts a facile nucleophilic attack even by a bulky nucleophile like the arylthiogermanes. On the other hand, benzoyl chloride cannot be attacked by a bulky nucleophile and the reaction proceeds by forming a 5-coordinated intermediate when forced to proceed.[2]

The same concept can also be applied to the other reactions of this type. The loger metal–sulfur bond would reduce the steric crowd around the sulfur atom and hence allows the sulfur atom to act as a nucleophile. The reaction of the arylthiostannanes of the longer metal–sulfur bond, with aroyl chlorides has been known to proceed by the nucleophilic process.[1] On the other hand, the shorter metal–sulfur bond increases the steric crowd and restricts the nucleophilic attack. The reaction of the arylthiogermanes with benzoyl chloride proceeds via 5-coordinated intermediate as mentioned above.[2] In this connection, it is quite natural that the reaction of the arylthiosilanes having the shortest metal–sulfur bond with benzoyl chloride involves 5-coordinated intermediate.[3] The borderline bond length lies between the tin–sulfur and the germanium–sulfur bonds for the reaction with aroyl chlorides in changing the mechanism from nucleophilic reaction to the 5-coordination process.

The difference in the mechanisms of the reactions of a series of metal–sulfur compounds with benzyl bromide can also be rationalized by their different bond lengthes. The reaction of the arylthiostannanes with benzyl bromide undergoes by a nucleophilic attack of the sulfur atom on the benzylic carbon.[4] In the present study, the shorter metal–sulfur bond like the arylthiogermanes has been found to attack on the benzyl bromide in a similar way due to less steric requirements of the halide. The 5-coordination process suggested for the reaction of the arylthiosilanes with phenacyl bromide[5] can be understood in terms of the steric crowd due to the shortest metal–sulfur bond length. Among the reactions with primary haloalkanes, only the reaction of the arylthiosilanes would involve a 5-coordinated intermediate although any kinetic evidence with a common haloalkane like benzyl bromide has not been obtained yet.[13]

The steric effect has thus been found to be an important factor to control the course of the reaction. Other factors such as the nucleophilicity and the 5-coordination ability dependent on the individual metals cannot be ruled out but seem to be not important at least for the reactions discussed here.

Experimental

Materials. Solvents were dried and distilled. Substituted benzyl bromides and chlorides were purified by distillation or recrystallization before use. The preparations of (arylthio)trimethylgermanes were reported previously.[2]

Product Analysis. Trimethyl(phenylthio)germane (1.10 g, 5.6×10^{-3} mol) was heated with an equimolar amount of benzyl bromide (0.94 g) in a sealed tube at 100 °C for 30 h. ^{1}H NMR analysis of the reaction mixture showed only signals due to bromotrimethylgermane and benzyl phenyl sulfide. Bromotrimethylgermane was isolated by distillation (bp 113—114 °C, 65%). Benzyl phenyl sulfide was obtained from the residue and was purified by recrystallization, mp 41—43 °C (from hexane, 98%, lit,[14] 41—43.5 °C).

Kinetics. The rates of the reactions of the arylthiogermanes (0.262 mol dm^{-3}) with benzyl bromides (0.318 mol dm^{-3}) were measured by the procedure reported recently.[2] The rates of the reactions of trimethyl(*p*-tolylthio)stannane (0.06 mol dm^{-3}) with benzyl chlorides (0.6 mol dm^{-3}) were measured by the previous method.[4] Pseudo-first-order rate constants k_1 for the reactions of $(CH_3)_3SnSC_6H_4CH_3$-*p* with $ClCH_2C_6H_4Y$-*p* in chloroform at 130 °C are as follows: Y=CH$_3$, 2.36×10^{-5} s^{-1}; H, 9.96×10^{-6} s^{-1}; Cl, 1.05×10^{-5} s^{-1}; NO$_2$, 7.86×10^{-6} s^{-1}.

The Reaction of (Arylthio)trimethylgermanes with the Solvents. Dichloromethane solution of trimethyl(phenylthio)germane (0.262 mol dm^{-3}) was heated at 150 °C for 110 min. The reaction conditions correspond to more than 75% completion of the reaction of the germane with benzyl bromide. Small amount of chlorotrimethylgermane was found in the mixture by ^{1}H NMR analysis (δ=0.72). Pseudo-first-order rate constant was estimated based on the conversion: $k_1=1.2\times1.0^{-5}$ s^{-1}. Thus, the reaction with the solvent was negligible under the conditions used for the kinetics. No reaction was found with the other solvents.

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5) S. Kozuka, T. Higashino, and T. Kitamura, *Bull. Chem. Soc. Jpn.*, **54**, 1420 (1981).

6) A more enhanced substituent effect, ρ_X=+2.32, was observed in benzonitrile than in tetrachloromethane (ρ_X=+1.46) although the signs are opposite and hence a different machanism has been suggested.[2]

7) R. F. Hudson and G. Klopman, *J. Chem. Soc.*, **1962**, 1062.

8) E. W. Abel and D. B. Brady, *J. Chem. Soc.*, **1965**, 1192.

9) S. Kozuka and S. Ohya, *J. Organomet. Chem.*, **149**, 191 (1978).

10) For instance, extrapolation of the present result and comparing with that reported[2] gives $k_2(C_6H_5COCl)/k_2(C_6H_5CH_2Br)$ is only 9 in CH_2Cl_2 at 100 °C.

11) The reaction of $(CH_3)_3SnSC_6H_4CH_3$-*p* with benzyl

bromide in nonpolar solvent proceeds only at elevated temperatures (k_1=2.65×10^{-4} s^{-1} at 115 °C in $CHCl_3$)[4] while that with benzoyl chloride proceeds at around room temperature (k_2=4.5×10^{-5} mol^{-1} dm^{3}s^{-1} at 34 °C in CCl_4).[1] These reactions proceed by nucleophilic mechanisms.

12) The retes of the reactions are as follows: $(CH_3)_3GeSC_6H_5+C_6H_5COCl$; k_2=3.45×10^{-4} dm^3 s^{-1} at 130 °C in CCl_4,[2] and $(CH_3)_3SnSC_6H_5+C_6H_5COCl$; k_2=5.2×10^{-5} dm^3 mol^{-1} s^{-1} at 43 °C in CCl_4.[1] Extraporations of their Arrhenius plots gave relative reactivity of the phenylthiogermane and the phenylthiostannane with benzoyl chloride: k_2(GeS)/k_2(SnS)=ca. 0.025 at 100 °C in CCl_4. On the other hand, direct comparison of their reactivity toward benzyl bromide is difficult due to difference in their reaction conditions. However the rate of the reaction of $(CH_3)_3SnSC_6H_4CH_3$-*p* + $C_6H_5CH_2Br$[4,11] is only slightly faster than that in nonpolar solvents as shown in Table 1.

13) Kinetic study on the reaction of the arylthiosilanes with benzyl halides was failed due to facile decomposition of the reactant.[5] However, the reaction with phenacyl bromide has been found to proceed via 5-coordinated intermediate.[5]

14) "Beilstein Handbuch der Organischen Chemie," **6**, p. 454.