September, 1978] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (9), 2651—2653 (1978) 2651

Kinetic and Stereochemical Studies of the Reaction of Trialkyl(alkylthio and arylthio)stannanes with Haloalkanes

Seizi Kozuka* and Sadamu Ohya
Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sugimoto-cho, Sumiyoshi-ku, Osaka 558

(Received January 28, 1978)

A kinetic study has been conducted on the reaction of arylthio(trimethyl)stannane with haloalkanes giving halotrimethylstannane and alkyl aryl sulfide. The reaction has been found to obey second order kinetics. Substituent effects of the arylthio group, solvent effects, relative reactivities of the leaving halogens and steric effects of the haloalkanes have been investigated. Optically active (+)-1-methylheptyl bromide gives an inverted product *i.e.*, (−)-methyl 1-methylheptyl sulfide by the reaction with trimethyl(methylthio)stannane. A mechanism involving bimolecular nucleophilic attack of the sulfur atom on the haloalkane has been confirmed for the reaction.

The reactions of methylthiostannanes with iodomethane have been known to give iodostannane and

$$R_2Sn(SMe)_2 \xrightarrow{MeI} R_2SnI_2 + 2Me_3S^+I^-$$

$$R_3SnSMe \xrightarrow{MeI} R_3SnI + Me_3S^+I^-$$

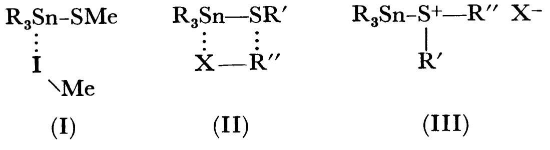
$$R = Me,\ Et,\ \text{and}\ n\text{-}Bu$$

trimethylsulfonium iodide.[1] Recently, the reactions of trialkyl(arylthio)stannanes with various haloalkanes have been examined and it has been found that the reactions proceed in a way similar to those of methylthiostannanes but give alkyl aryl sulfides, instead of sulfonium salts.[2]

$$R_3SnSAr \xrightarrow{R'X} R_3SnX + R'SAr$$

$$R = Me,\ n\text{-}Bu,\ R' = Me,\ Et,\ 2\text{-}Pr,\ \text{and benzyl.}$$

Several different mechanisms have been forwarded for the reaction: Five-coordination of the tin atom to iodine (I) has been suggested by Balcombe *et al.*[1] Four-centered reaction (II) is another plassible process in view of the analogous reaction of stannanes.[3] Contrary to these mechanisms, formation of a transient sulfonium salt (III) by a nucleophilic attack of the sulfur atom has been suggested based on the observations that the reaction of trimethyl(phenylthio)stannane with iodomethane proceeds much slower than that of trimethyl(methylthio)stannane.[2] The salt III had been accepted as the final product of the reaction of trimethyl(methylthio)stannane with iodomethane[4] but recently it has been shown to be a non-isolable intermediate.[2] In this paper, the kinetic and stereochemical studies of the reaction are reported and the reaction mechanism discussed.



(I) (II) (III)

Results and Discussion

Kinetics. The rate of the reaction of trimethyl(*p*-tolylthio)stannane with a 10-fold excess of iodomethane in chloroform solution at 100 °C was measured by following the decrease and rise of the ^{1}H NMR of the starting trimethyl signal and product. A pseudo-first-order kinetic plot was obtained up to nearly completion of the reaction. First order dependency of the rate was observed on the concentration of iodomethane. Thus, the reaction was found to be second order, first order with respective to thiostannane and haloalkane.

Activation parameters were observed for the reactions of the tolylthiostannane and trimethyl(phenylthio)stannane with iodomethane. Remarkably large negative entropy values were obtained for the reactions in non-polar solvents. These results indicate tight transition states for the reactions but do not suggest a 4-centered reaction since the rate is markedly accelerated in better solvents for ionic reaction (PhCN). Also the entropy vales appeares to be reasonable in magnitude for a bimolecular reaction. The tight transition state may be rationalized in terms of an ionic reaction which is forced to proceed in non-polar solvents.

Clear evidence was obtained in the present study supporting nucleophilic attack as the mechanism. Hammett plots of the rates of reactions for *p*-substituted phenylthiostannanes gave a significant negative ρ values (−1.4) against σ parameters. This result does not support the mechanism involving 5-coordination of the tin atom to the halogen since the mechanism would result in a positive ρ value of moderate magnitude. The reactions of more efficient nucleophiles, such as trimethyl(methylthio)stannane and other alkylthiostannanes with haloalkanes would proceed by the same mechanism to that of arylthio(trimethyl)stannane, since the nucleophilic reaction has been confirmed for the reaction of a less efficient nucleophile *i.e.*, arylthiostannane.

The kinetics of the reactions with various haloalkanes were also performed to elucidate steric and electronic effects on the rate of reaction. The steric effect observed for the reactions with iodomethane, iodoethane and 2-iodopropane (k_{rel} : 1.00, 0.125, and 0.014, respectively) appears smaller than that for standard S_N2 reactions[5] but consistent with that observed with the benzenethiolate ion as the nucleophile.[6] The small steric retardation is undoubtedly due to the longer length of the forming carbon–sulfur bond. Relative reactivity of benzyl chloride, bromide and iodide (k_{rel}: 0.023, 1.2, and 5.9, respectively) was observed in the present study and is in good agreement with that of S_N2 reactions.[5,7] These results obtained by the kinetic studies are shown in the Table 1.

Table 1. Rate constants for the reactions of arylthio(trimethyl)stannanes with haloalkanes

Me_3SnS-C_6H_4Y-p[a] Y	RX	Mole ratio RX/SnS	Solvent	Temp °C	$k_{obsd} \times 10^4$	Remark
CH_3	CH_3I	10.0	$CHCl_3$	115	2.24	1.00[b]
CH_3	CH_3I	10.0	$CHCl_3$	100	1.03	13.4, −41.2[c]
CH_3	CH_3I	10.0	$CHCl_3$	85	0.480	
CH_3	CH_3I	15.1	$CHCl_3$	100	1.67	
CH_3	CH_3I	20.3	$CHCl_3$	100	2.04	
H	CH_3I	10.0	$CHCl_3$	115	1.45	
H	CH_3I	10.0	$CHCl_3$	100	0.637	13.4, −42.0[c]
H	CH_3I	10.0	$CHCl_3$	90	0.413	
H	CH_3I	10.0	PhCN	100	10.3[d]	16.8, −27.6[c]
H	CH_3I	10.0	PhCN	75	1.85	
H	CH_3I	10.0	PhCN	60	0.513	
H	CH_3I	10.0	PhCN	50	0.263	
CH_3	CH_3I	10.0	C_6H_6	130	0.734	
CH_3	CH_3I	10.0	C_6H_6	120	0.397	
CH_3	CH_3I	10.0	C_6H_6	100	0.154	14.5, −42.1[c]
OCH_3	CH_3I	10.0	$CHCl_3$	100	1.16	
Cl	CH_3I	10.0	$CHCl_3$	100	0.204	
NO_2	CH_3I	10.0	$CHCl_3$	100	0.0457	−1.40[e]
CH_3	C_2H_5I	10.0	$CHCl_3$	115	0.281	0.125[b]
CH_3	2-C_3H_7I	10.0	$CHCl_3$	115	0.0321	0.014[b]
CH_3	$C_6H_5CH_2I$	10.0	$CHCl_3$	115	13.3	5.9[b]
CH_3	$C_6H_5CH_2Br$	10.0	$CHCl_3$	115	2.65	1.2[b]
CH_3	$C_6H_5CH_2Cl$	10.0	$CHCl_3$	115	0.0515	0.023[b]

a) 6.0×10^{-2} mol/l as the initial concentration. b) Relative rate. c) Activation parameters, ΔH^{*}(kcal/mol) and ΔS^{*}(e. u.), respectively. d) Estimated value. e) ρ value against σ constants.

Stereochemistry. Inversion of configuration of the alkyl group of the haloalkane would be expected by the bimolecular nucleophilic attack of the sulfur atom on the haloalkane. Retention or partial racemization, on the other hand, may result if the reaction proceeded by 5-coordination of the tin atom or by a 4-centered process.

Optically active (+)-1-methylheptyl bromide was allowed to react with the thiostannane in order to confirm the mechanism. Trimethyl(methylthio)stannane, instead of arylthio(trimethyl)stannane, was employed for the reaction with the optically active bromide since the sterically hindered secondary bromide is less reactive. The reaction was stopped at about half completion. The product, methyl 1-methylheptyl sulfide did not undergo sulfonium salt formation with the remaining bromide probably due to steric hindrance of the bulky 1-methylheptyl groups. The stereochemical result is shown below. This result indicates inversion of configuration of the alkyl carbon atom

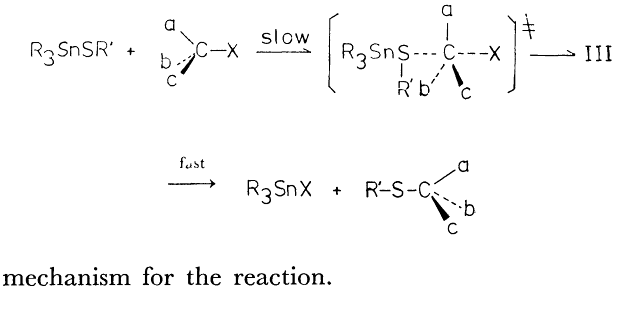
$$(CH_3)_3SnSCH_3 + (+)\text{-}n\text{-}C_6H_{13}CH(CH_3)Br \xrightarrow{120\,^{\circ}\mathrm{C},\ 115\,\mathrm{h}}$$
$$[\alpha]^{30}_{D}\ +36.4^{\circ}$$

$$(CH_3)_3SnBr + (-)\text{-}n\text{-}C_6H_{13}CH(CH_3)\text{-}S\text{-}CH_3$$
$$[\alpha]^{30}_{D}\ -9.7^{\circ}$$

$$+\ \text{recov. } (+)\text{-}n\text{-}C_6H_{13}CH(CH_3)Br$$
$$[\alpha]^{30}_{D}\ +24.3^{\circ}$$

during the reaction since S_N2 reaction of optically active 1-methylheptyl bromide with sodium methanethiolate in ethanol has been shown to give optically active methyl 1-methylheptyl sulfide of opposite sign.[8] The starting bromide underwent partial racemization during the reaction and consequently, the stereospecificity of the reaction could not be determined. However, high stereospecific inversion may be assumed for the present reaction in comparison with the optical activities of the bromide and sulfide with stereochemical results obtained by the S_N2 reaction.[8]

Mechanism. All the results are consistent with a mechanism involving bimolecular nucleophilic attack of the sulfur atom on the haloalkane to form the sulfonium salt III as a transient intermediate. No evidence was found to support the 5-coordination or 4-centered



mechanism for the reaction.

Experimental

Materials. Preparation of the thiostannanes have previously been reported.[2,9] Solvents for the kinetic studies were dried and distilled before use. Commercial haloalkanes except for benzyl iodide were used for the kinetic studies after distillation. Benzyl iodide was prepared from benzyl bromide by the halogen exchange reaction with sodium iodide.

Kinetic Procedure. The general procedure was as follows: arylthio(trimethyl)stannane (3×10^{-4} mol) and haloalkane (3×10^{-3} mol) were dissolved in the solvent using a 5 ml volumetric flask. The solution was divided into 10 portions and sealed in glass tubes of *ca.* 0.7 ml volume. The tubes were heated in a constant temperature bath (100 °C) and samples taken at appropriate intervals. Each sample of the solution was analyzed by ^{1}H NMR with 5-repeated integrations of the starting trimethyl signal (δ 0.38 ppm, Me_3SnSPh) and that of the product (δ 0.88 ppm, Me_3SnI). Pseudo-first-order rate constant was obtained by a least square calculation of the relative intensities of the signals at the time intervals.

Preparation of (+)-1-Methylheptyl Bromide. The bromide was prepared from L-(−)-2-octanol and phosphorus tribromide by the usual procedure,$^{10)}$ bp 82 °C/16 mmHg, $[\alpha]^{30}_{D}$ +36.4° (c=2.00, acetone).

Reaction of (+)-1-Methylheptyl Bromide with Trimethyl(methylthio)stannane. The stannane (300 mg, 1.42 mmol) and the bromide (277 mg, 1.42 mmol) were mixed and heated at 120 °C for 115 h in a sealed tube. Bromotrimethylstannane, methyl 1-methylheptyl sulfide and the remaining 1-methylheptyl bromide were identified in the reaction mixture by GLC analysis (Silicon SE-30, 2 m, 70 °C). Among these, methyl 1-methylheptyl sulfide, $[\alpha]^{30}_{D}$ −9.7° (c=0.65, acetone), and 1-methylheptyl bromide, $[\alpha]^{30}_{D}$ +24.3° (c=0.07, acetone), were isolated by GLC and the rotations measured. No appreciable racemization of 1-methylheptyl bromide was found when the bromide was heated alone or with bromotrimethylstannane in chloroform under the reaction conditions (120 °C, 115 h).

References

1) C. I. Balcombe, E. C. Macullin, and M. E. Peach, *J. Inorg. Nucl. Chem.*, **37**, 1353 (1975).

2) S. Kozuka and S. Ohya, *J. Organomet. Chem.*, **149**, 161 (1978).

3) For example, R. C. Paul, K. K. Soni, and S. P. Narula, *J. Organomet. Chem.*, **40**, 355 (1972).

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

5) T. H. Lowry and K. S. Richardson, "Mechanism and Theory in Organic Chemistry," Harper & Row, New York (1976), p. 179.

6) H. M. R. Hoffmann, *J. Chem. Soc.*, **1965**, 6753.

7) E. M. Kosower, "An Introduction to Physical Organic Chemistry," John Wiley & Sons, Inc., New York (1968), p. 81.

8) H. Matsuyama, H. Minato, and M. Kobayashi, *Bull. Chem. Soc. Jpn.*, **48**, 3287 (1975).

9) J. L. Wardell and D. W. Grant, *J. Organomet. Chem.*, **20**, 91 (1969).

10) R. L. Shriner and J. H. Young, *J. Am. Chem. Soc.*, **52**, 3337 (1930).