Journal of Organometallic Chemistry, 149 (1978) 161—165

THE REACTIONS OF TRIMETHYL(METHYLTHIO)- AND TRIALKYL(ARYLTHIO)STANNANES WITH ALKYL HALIDES

SEIZI KOZUKA * and SADAMU OHYA

Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sugimoto-cho, Sumiyoshi-ku, Osaka 558 (Japan)

(Received July 19th, 1977)

Summary

The reaction of trimethyl(methylthio)stannane with methyl iodide was reinvestigated. Trimethylsulfonium iodide and iodotrimethylstannane were the products which were isolated. Trialkylhalostannanes and alkyl aryl sulfides were obtained in nearly quantitative yield by the reaction of trialkyl(arylthio)stannanes with alkyl halides. The rate of the reaction of the trialkyl(arylthio)stannanes with an alkyl iodide was much slower than that of trimethyl(methylthio)stannane under the same reaction conditions. Nucleophilic attack of the stannyl sulfur atom on the alkyl halide is suggested as the first step of the reaction.

Few reactions of the organotin—sulfur linkage with alkyl halides have been reported [1—3]. We have reinvestigated the reaction of trimethyl(methylthio)stannane with methyl iodide. The reactions of arylthiostannane with alkyl halides also were examined in order to obtain a better understanding of the chemical reactivity of the tin—sulfur bond. Both reactions have been found to proceed in similar manner.

The reactions of trimethyl(methylthio)stannane

The reaction of organotin alkanethiolates of the type $R_2Sn(SR')_2$ with an excess of methyl iodide is known to give diorganotin diiodides (eq. 1) [1]. A similar reaction has been reported to occur with R_3SnSR' compounds (eq. 2) [1].

$$R_2Sn(SMe)_2 \xrightarrow{\text{excess MeI}} R_2SnI_2 + 2\ Me_3S^+I^- \quad (1)$$

R = Me, Et and Bu

$$Bu_3SnSMe \xrightarrow{MeI} Bu_3SnI + Me_3S^+I^- \quad (2)$$

All these reactions proceed with fission of the tin—sulfur bond. A notable exception is the reaction of trimethyl(methylthio)stannane with an equimolar amount of methyl iodide, which was reported to give the sulfonium salt without the cleavage of the Sn—S bond (eq. 3) [2]. It may be that the retention of the Sn—S bond is due to the different reaction conditions used. Thus, the reaction with an equimolar amount of methyl iodide may result in formation of the sulfonium salt I as the initial product, and an excess of methyl iodide then serves to decompose this species, giving the iodostannane and dimethyl sulfide. The latter then is converted further to trimethylsulfonium iodide.

$$Me_3SnSMe + MeI \rightarrow \underset{(I)}{Me_3SnS^+Me_2\ I^-} \qquad (3)$$

In order to clarify this possibility, we have repeated the reaction shown in eq. 3. Trimethyl(methylthio)stannane was warmed at 50°C for 3.5 h with an equimolar amount of methyl iodide in a sealed tube. The solids formed were collected and identified as trimethylsulfonium iodide (30% yield) rather than I*. The structure of the product was confirmed by comparison of the physical properties with those of an authentic sample prepared from dimethyl sulfide and methyl iodide. The reaction was carried out under different reaction conditions in attempts to obtain the salt I, but only trimethylsulfonium iodide was obtained. The same product was obtained in 85% yield by the reaction with two equivalents of methyl iodide with the methylthiostannane at 80°C for 40 min. The reaction in chloroform solution with an excess of methyl iodide gave the same product, and PMR analysis of the reaction solution showed that iodotrimethylstannane was the only chloroform-soluble product. The only evidence cited by Abel et al. in support of their salt I formulation was the elemental analysis for carbon and hydrogen. However, the postulated product and trimethylsulfonium iodide have very similar carbon and hydrogen values**. We conclude that the product of Abel et al. was trimethylsulfonium iodide.

The reactions of trialkyl(arylthio)stannanes

To date, only one reaction of an arylthiostannane with an alkyl halide has been reported: the reaction of tetrakis(*p*-*N*,*N*-dimethylaminophenylthio)stannane with an excess of methyl iodide (eq. 4) [3]. However, no reaction has been reported to occur between tri-n-butyl(phenylthio)stannane and methyl iodide [1]. We have tried the reaction again and found a result similar to that observed with the methylthiostannane.

$$Sn(SC_6H_4NMe_2)_4 \xrightarrow{\text{excess MeI}} SnI_4 + 4[(Me_3NC_6H_4SMe)^+I^-] \qquad (4)$$

---

* Abel et al. [2] only mentioned that they "warmed" an equimolar mixture of Me_3SnSMe (14.5 g, 0.069 mol) and MeI (9.8 g, 0.069 mol) and that they obtained $Me_3SnS^+Me_2I^-$ (15.0 g, 62%). Correcting the product as $Me_3S^+I^-$, the maximum yield should be 50% based on the tin compound.

** Calcd. for Me_3SI: C, 17.7; H, 4.4%; for Me_3SnSMe_2I: C, 17.0; H, 4.3%; Found by Abel et al., C, 17.5; H, 5.2% [2].

TABLE 1

REACTION OF TRIALKYL(ALKYLTHIO AND ARYLTHIO)STANNANES WITH ALKYL HALIDES

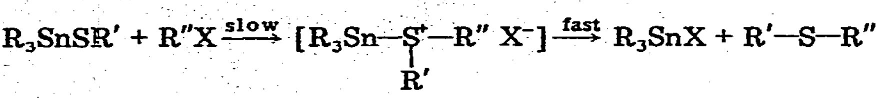
R_3SnSR'			$R''X$		Solvent[a]	Temp. (°C)	Time (h)	Yield (%)	
R	R'	mmol	$R''X$	mmol				R_3SnX	$R'SR''$
CH_3	CH_3	0.7	CH_3I	0.7	none	50	3.5	[b]	30[c]
CH_3	CH_3	0.7	CH_3I	1.4	none	80	0.67	[b]	85[c]
CH_3	C_6H_5	0.7	CH_3I	1.4	none	80	0.67	26[d]	28[d]
CH_3	CH_3	0.7	CH_3I	7.0	$CHCl_3$	75	2.0	72	84[c]
CH_3	C_6H_5	0.7	CH_3I	7.0	$CHCl_3$	120	15	85	89
CH_3	p-$CH_3C_6H_4$	0.7	CH_3I	7.0	$CHCl_3$	120	15	94	98
CH_3	p-ClC_6H_4	0.7	CH_3I	7.0	$CHCl_3$	100	40	64	87
CH_3	p-$NO_2C_6H_4$	0.7	CH_3I	7.0	$CHCl_3$	100	40	100	88
CH_3	C_6H_5	0.7	C_2H_5I	7.0	$CHCl_3$	120	15	74	74
CH_3	p-$CH_3C_6H_4$	0.7	C_2H_5Br	7.0	$CHCl_3$	120	20	100	100
CH_3	C_6H_5	0.7	i-C_3H_7I	7.0	$CHCl_3$	120	20	[b]	69[d]
CH_3	C_6H_5	0.7	$C_6H_5CH_2Br$	0.7	$CHCl_3$	120	20	76	99
CH_3	C_6H_5	5.5	$C_6H_5CH_2Br$	17	none	100	10	86[e]	63[e]
CH_3	C_6H_5	0.7	p-$CH_3C_6H_4CH_2Cl$	0.7	$CHCl_3$	120	40	[b]	100[f]
n-C_4H_9	C_6H_5	0.7	CH_3I	7.0	$CHCl_3$	90	40	[b]	100
n-C_4H_9	C_6H_5	4.3	CH_3I	32	none	100	20	89[e]	87[e]

[a] 1 ml. [b] Not analyzed. [c] $(CH_3)_3S^+I^-$, dimethyl sulfide was not detected. [d] Incomplete reaction, conversion was not determined. [e] Isolated by distillation. [f] Incomplete reaction, yield was obtained based on 66% conversion.

Trimethyl(phenylthio)stannane was allowed to react with an excess of methyl iodide in chloroform solution. No reaction (or only a very slow reaction) was observed at room temperature, as reported [1]. The reaction was found to proceed on heating, but much more slowly than that of trimethyl(methylthio)stannane under the same reaction conditions (80°C, 40 min). Upon heating at higher temperatures for longer periods (120°C, 15 h), the reaction was found to give iodotrimethylstannane and methyl phenyl sulfide in nearly quantitative yield. No other products were detected. Reactions of other trialkyl(arylthio)stannanes, including tri-n-butyl(phenylthio)stannane, with various alkyl halides were carried out similarly. The results are given in Table 1 together with that of the methylthiostannane under comparable reaction conditions in order to show the different reactivities of arylthio and methylthiostannanes.

These observations indicate that the reactions of the arylthiostannanes proceed in a manner similar to that of the methylthiostannane but differ in the relative reactivities and in the sulfur-containing product isolated. The alkyl aryl sulfides did not undergo sulfonium salt formation.

These differences can be explained in terms of the lesser nucleophilicity of the arylthio group. Thus, nucleophilic attack of the sulfur atom on the carbon atom of the alkyl halide is the most plausible mechanism of the reaction.



$$R_3SnSR' + R''X \xrightarrow{\text{slow}} [R_3Sn{-}\underset{\displaystyle R'}{\overset{+}{S}}{-}R''\ X^-] \xrightarrow{\text{fast}} R_3SnX + R'{-}S{-}R''$$

when $R' =$ alkyl: $R'{-}S{-}R'' \xrightarrow{R''X} R'R''_2S^+\ X^-$

Experimental

Materials

Trialkyl(alkylthio and arylthio)stannanes were prepared from trialkylhalostannane and the appropriate thiol [4].

The reaction of trimethyl(methylthio)stannane with methyl iodide

Using the procedure of Abel et al. [2], the stannane (145 mg, 0.69 mmol) was warmed with methyl iodide (98 mg, 0.69 mmol) in a sealed tube at 50°C for 3.5 h. The solids which formed were collected and washed with hexane. The physical properties of the solids were identical to those of authentic trimethylsulfonium iodide and the yield was 30%, based on the tin compound used. Warming the reaction mixture at 50°C for 1 h gave the same product in 17% yield.

The reaction with two equimolar amounts of methyl iodide at 80°C for 40 min gave trimethylsulfonium iodide in 85% yield. Iodotrimethylstannane was detected by PMR analysis of the reaction solution in chloroform when an excess of methyl iodide was used. The results are shown in Table 1.

The reaction of trialkyl(arylthio)stannane with alkyl halide

Trimethyl(phenylthio)stannane (0.7 mmol) and a 10-fold excess of methyl iodide in $CHCl_3$ (1 ml) were heated at 120°C for 15 h. Subsequently, dichloromethane (40 µl) was added and the whole solution was subjected to PMR analysis. Yields of iodotrimethylstannane (δ 0.88 ppm) and methyl phenyl sulfide

($\delta(CH_3)$, 2.43 ppm) were determined by integration of the signals relative to that of the added dichloromethane. No other signal was detected in the clear reaction solution. Other reactions were carried out similarly. The products were isolated by GLC (SE-30, 90°C) and the structures were identified by IR and PMR analyses. Some reactions were carried out on a preparative scale and the products were isolated by distillation. Reaction conditions and the yields of the products are given in Table 1.

References

1 C.I. Balcombe, E.C. Macullin and M.E. Peach, J. Inorg. Nucl. Chem., 37 (1975) 1353.
2 E.W. Abel and D.B. Brady, J. Chem. Soc., (1965) 1192.
3 H. Wuyts and A. Vangindertaelen, Bull. Soc. Chem. Belg., 30 (1921) 323.
4 J.L. Wardell and D.W. Grant, J. Organometal. Chem., 20 (1969) 91.