Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

REACTIONS OF INDIUM COMPOUNDS WITH TRIMETHYLSTIBINE SULFIDE

TAKAYOSHI MAEDA, GOHEI YOSHIDA and ROKURO OKAWARA
Department of Applied Chemistry, Osaka University, Yamadakami, Suita, Osaka (Japan)

(Received May 15th, 1972)

SUMMARY

Reactions of R_2InX and CH_3InCl_2 with $(CH_3)_3SbS$ gave stibonium salts $R(CH_3)_3SbX$ and $(CH_3)_4SbCl$, respectively ($R=CH_3$ and C_2H_5, $X=Cl$, Br and I). $(CH_3)_3SbCl_2$ was obtained from the reaction of $InCl_3$ with $(CH_3)_3SbS$.

The complexes, $R_2InX \cdot (CH_3)_3SbS$, $CH_3InCl_2 \cdot (CH_3)_3SbS$ and $InCl_3 \cdot (CH_3)_3SbS$ ($X=Cl$, $R=CH_3$ and C_2H_5; $X=Br$, $R=C_2H_5$) were isolated. On the basis of IR spectra, it was found that $(CH_3)_3SbS$ coordinates to the indium through the sulfur atom.

INTRODUCTION

Most studies concerning the reactions of In–C bonds have been limited to those of trialkylindium[1]. It has been suggested[2,3] recently that in dialkyl compounds containing the In–S bond, the indium atom interacts strongly with sulfur. On the other hand, the Sb–S bond in trimethylstibine sulfide has been found to be quite reactive[4–6]. In this paper, reactions of dialkylindium halides, methylindium dihalide and indium trihalide with trimethylstibine sulfide are described.

EXPERIMENTAL

General comments

All the following reactions and physical measurements were carried out under a dry nitrogen atmosphere, and nitrogen was bubbled into solvents before use.

Starting materials

$(CH_3)_3SbS$[7], $(C_2H_5)_2InX$[8] ($X=Cl$, Br and I), CH_3InCl_2[9], and $CH_3In[SSCN(CH_3)_2]_2$[10] were prepared according to the directions in the literature. $(CH_3)_2InX$ ($X=Cl$, Br and I) were obtained almost quantitatively from the reactions of $(CH_3)_3In$[11] with $(CH_3)_2SnCl_2$, $CHBr_3$ and CH_2I_2, respectively, in the manner similar to that used to prepare $(C_2H_5)_2InX$[8]. IR spectra of these halides were identical with those of authentic specimens[12] of the respective compounds.

TABLE 1

PROPERTIES AND ANALYTICAL DATA OF THE COMPLEXES

Complex	*M.p.*[a] (°C)	*Analysis found (calcd.) (%)*		*IR in Nujol mulls* (cm^{-1})				*PMR in* CH_2Cl_2[b]	
		C	*H*	$\nu(Sb-C)$	$\nu(In-C)$	$\nu(Sb-S)$	$\nu(In-S)$ *or* $\nu(In-Cl)$	$\tau(CH_3-Sb)$[c]	$\tau(CH_3-In)$[c]
L = $(CH_3)_3SbS$				555 531		431		8.49	
$(CH_3)_2InCl \cdot L$	65–69	16.13 (15.83)	4.07 (3.99)	564 531	561 483	404	261 242	8.20	10.00
$(C_2H_5)_2InCl \cdot L$[d]	78–80	20.54 (20.64)	4.76 (4.70)	559 530	496 460	407	250 230	8.20	
$(C_2H_5)_2InBr \cdot L$[e]	70–73	18.37 (18.61)	4.42 (4.24)	558 528	492 456	407	247	8.19	
$CH_3InCl_2 \cdot L$	102–104	12.02 (12.02)	3.31 (3.03)	567 535	515	395	296, 285 275	8.03	9.65
$InCl_3 \cdot L$	155–158	8.48 (8.58)	2.40 (2.16)	564 530		393	322 338	7.92	

[a] Decomposition point. [b] At 3–5 wt.%. [c] With reference to internal tetramethylsilane (10.00 ppm). [d] Mol.wt. in benzene at 2.51 wt.%; found 487 (calcd. 407). [e] Mol.wt. in benzene at 2.47 wt.%; found 530 (calcd. 452).

Preparations of the complexes of $(CH_3)_3SbS$ *with* R_2InX $(X=Cl, R=CH_3$ *and* C_2H_5; $X=Br, R=C_2H_5)$, CH_3InCl_2 *and* $InCl_3$

Equimolar amounts of the indium compound and trimethylstibine sulfide in methanol were mixed at 0°. The solvent was removed under reduced pressure, and the residual solid was recrystallized quickly from dichloromethane/petroleum ether to give the complex quantitatively. Properties and analytical data of the prepared complexes are shown in Table 1. These compounds decompose slowly in benzene solution and rapidly in methanol.

An attempted preparation of the complexes, $R_2InX\cdot(CH_3)_3SbS$ $(X=Br, R=CH_3$; $X=I, R=CH_3$ *and* $C_2H_5)$

When the R_2InX compounds were treated with $(CH_3)_3SbS$ in a manner similar to the above, viscous oily materials resulted. Crystallization and identification of these materials were unsuccessful.

Reactions of $(CH_3)_3SbS$ *with indium compounds*

The reaction conditions and the yields of the products are shown in Table 2. Quite similar results were also obtained starting with the corresponding complex.

(*i*). *With* R_2InX $(R=CH_3$ *and* C_2H_5, $X=Cl$, *Br and I*). A methanol solution containing equimolar amounts of $(CH_3)_2InCl$ and $(CH_3)_3SbS$ was refluxed with stirring for 4 h. CH_3InS, m.p. >270°, was precipitated. (Found: C, 7.73; H, 1.92. CH_3InS calcd.: C, 7.42; H, 1.87%.) Methanol was removed from the filtrate, and the

TABLE 2

REACTIONS OF INDIUM COMPOUNDS WITH $(CH_3)_3SbS$ (1/1 MOLE RATIO IN METHANOL)

Indium compounds (mmol)	*Reflux time (h)*	*Products (yield) (%)*	
$(CH_3)_2InCl$ (4.53)	4	CH_3InS (65)	$(CH_3)_4SbCl$ (31)
$(CH_3)_2InBr$ (4.53)	4	CH_3InS (85)	$(CH_3)_4SbBr$ (67)
$(CH_3)_2InI$ (4.76)	4	CH_3InS (97)	$(CH_3)_4SbI$ (77)
$(C_2H_5)_2InCl$ (2.92)	4	C_2H_5InS (54)	$C_2H_5(CH_3)_3SbCl$ (31)[a]
$(C_2H_5)_2InBr$ (2.63)	4	C_2H_5InS (88)	$C_2H_5(CH_3)_3SbBr$ (66)
(3.18)	70[b]	(80)	(61)
(2.25)	70[c]	(42)	(25)
$(C_2H_5)_2InI$ (2.38)	4	C_2H_5InS (98)	$C_2H_5(CH_3)_3SbI$ (64)
CH_3InCl_2 (3.38)	6	InSCl and In_2S_3	$(CH_3)_4SbCl$ (33)[a]
$InCl_3$ (1.14)	6[d]	InSCl and In_2S_3	$(CH_3)_3SbCl_2$ (25)

[a] Determined as the tetraphenylborate salt. [b] Reaction at room temperature. [c] Reaction in CH_2Cl_2 at room temperature. [d] Reaction in refluxing ethanol.

residual solid was recrystallized from methanol/dichloromethane/petroleum ether to give $(CH_3)_4SbCl$[13], m.p. 90–140° (decompn.). (Found: C, 21.81; H, 5.51. $C_4H_{12}ClSb$ calcd.: C, 22.11; H, 5.56%.) The other tetramethylstibonium halides shown in Table 2 were obtained quite similarly. $(CH_3)_4SbBr$[13] m.p. >280°. (Found: C, 18.25; H, 4.95. $C_4H_{12}BrSb$ calcd.: C, 18.35; H, 4.62%.) $(CH_3)_4SbI$[13] m.p. >280°. (Found: C, 15.58; H, 4.01. $C_4H_{12}ISb$ calcd.: C, 15.56; H, 3.92%.) $(CH_3)_4SbB(C_6H_5)_4$ m.p. >280°. (Found: C, 67.10; H, 6.47. $C_{28}H_{32}BSb$ calcd.: C, 67.11; H, 6.43%.) $C_2H_5(CH_3)_3SbBr$ m.p. 223–236° (decompn.). (Found: C, 21.86; H, 5.34. $C_5H_{14}BrSb$ calcd.: C, 21.77; H, 5.12%.) $C_2H_5(CH_3)_3SbI$ m.p. >280°. (Found: C, 18.51; H, 4.63. $C_5H_{14}ISb$ calcd.: C, 18.61; H, 4.37%.) $C_2H_5(CH_3)_3SbB(C_6H_5)_4$ m.p. 293–295°. (Found: C, 67.48; H, 6.81. $C_{29}H_{34}BSb$ calcd.: C, 67.61; H, 6.65%.)

(ii). With CH_3InCl_2. Formation of a pale yellow precipitate was observed on refluxing a methanol solution of the reactants. This precipitate was assumed to be a mixture of InSCl and In_2S_3 from the analysis (found: S, 23.56; In, 67.36. InClS calcd.: S, 17.59; In, 62.97%. In_2S_3 calcd.: S, 29.52; In, 70.48%) and its IR spectrum, in which no bands attributable to the In–C or Sb–C stretching vibrations were found. It was confirmed by the IR spectrum that the filtrate contained the starting materials and $(CH_3)_4SbCl$. The yield of the stibonium chloride was determined from the weight of the white precipitate, $(CH_3)_4SbB(C_6H_5)_4$, formed by adding an excess of $NaB(C_6H_5)_4$ in methanol.

(iii). With $InCl_3$. A mixture of InSCl and In_2S_3 precipitated from an ethanol solution of the reactants. From the filtrate, ethanol was removed under reduced pressure to give a white solid, which was found by its IR spectrum to be a mixture of the starting materials and $(CH_3)_3SbCl_2$. $(CH_3)_3SbCl_2$ was separated by subliming *in vacuo* at 60°. (M.p. 224°, reported[7] m.p. 224°).

An attempted reaction of $CH_3In[SSCN(CH_3)_2]_2$ with $(CH_3)_3SbS$

The starting materials were recovered almost quantitatively after a benzene solution of $CH_3In[SSCN(CH_3)_2]_2$ and $(CH_3)_3SbS$ was refluxed for 6 h. An IR spectrum indicated that when toluene was used as the refluxing solvent, a decomposition of $(CH_3)_3SbS$ occurred and the indium compound remained unchanged.

Physical measurements

Molecular weights were determined cryoscopically in benzene. The PMR spectra were measured using a Japan Electron Optics JNM-3H-60 spectrometer. The IR spectra were obtained using a Hitachi Model 225 spectrophotometer equipped with gratings.

RESULTS AND DISCUSSION

Properties of the complexes

As shown in Table 1, trimethylstibine sulfide formed 1/1 complexes with R_2InX ($X=Cl$, $R=CH_3$ and C_2H_5; $X=Br$, $R=C_2H_5$), CH_3InCl_2 and $InCl_3$. Their IR spectra indicate that coordination of trimethylstibine sulfide occurs through the sulfur atom in all of these complexes, because the Sb–S stretching frequencies are shifted to lower energy by about 30 cm^{-1} from that for the free ligand. The values of these shifts increase in the following order, which parallels the expected order of increase in acceptor strength of the indium atom.

$$R_2InX < CH_3InCl_2 < InCl_3$$

The proton resonances of the methyl groups attached to antimony (Table 1) are also shifted to lower field in the above order. These results suggest that in the $InCl_3$ complex, the interaction of the indium with the sulfur atom is the strongest and the contribution of the semi-polar structure of $(CH_3)_3Sb^+{-}S^-$ [4,14] is the largest.

Reactions of indium compounds with trimethylstibine sulfide

As shown in Table 2, the reactions of R_2InX and $(CH_3)_3SbS$ gave RInS and the corresponding stibonium salts, $R(CH_3)_3SbX$. These reactions proceed more smoothly in a polar solvent such as methanol, and the yield of the products increases in the order, $X = Cl < Br < I$. Monomethylindium dichloride also reacts with $(CH_3)_3SbS$ to give $(CH_3)_4SbCl$. This alkyl migration from indium to antimony is considered to occur via the corresponding complex, since in some cases the complex was isolated. The failure of the reaction of monomethylbis(*N*,*N*-dimethyldithiocarbamato)indium is ascribed to the poor complexing ability of this compound, which contains pentacoordinate indium[10]. This alkyl migration reaction has not been observed in the reactions of organotin(IV) halides with trimethylstibine sulfide, in which only halogen–sulfur exchange reaction occurs[7]. It is similar to the pyrolysis reaction of diethylindium thiobenzoate which give stable monoethylindium sulfide and the alkylation product, propiophenone[3]. It is interesting that our reaction gives the stibonium halides* very smoothly; these compounds except the iodide, are difficult to obtain from the reaction[16] of trimethylstibine and alkyl halides.

ACKNOWLEDGEMENT

Thanks are due to Prof. D. G. White of The George Washington University for improving our manuscript.

REFERENCES

1 K. Yasuda and R. Okawara, *Organometal. Chem. Rev.*, 2 (1967) 255.
2 G. E. Coates and R. A. Whitcombe, *J. Chem. Soc.*, (1956) 3351.
3 H. Tada and R. Okawara, *J. Organometal. Chem.*, 28 (1971) 21.
4 J. Otera and R. Okawara, *J. Organometal. Chem.*, 16 (1969) 335.
5 J. Otera and R. Okawara, *J. Organometal. Chem.*, 17 (1969) 353.
6 J. Otera, T. Kadowaki and R. Okawara, *J. Organometal. Chem.*, 19 (1969) 213.
7 M. Shindo, Y. Matsumura and R. Okawara, *J. Organometal. Chem.*, 11 (1968) 299.
8 T. Maeda, H. Tada, K. Yasuda and R. Okawara, *J. Organometal. Chem.*, 27 (1971) 13.
9 H. C. Clark and A. L. Pickard, *J. Organometal. Chem.*, 13 (1968) 61.
10 T. Maeda and R. Okawara, *J. Organometal. Chem.*, 39 (1972) 87.
11 F. Runge, W. Zimmermann, H. Pfeiffer and I. Pfeiffer, *Z. Anorg. Allg. Chem.*, 267 (1951) 39.
12 H. C. Clark and A. L. Pickard, *J. Organometal. Chem.*, 8 (1967) 427.
13 H. Landolt, *Ann. Chem.*, 78 (1851) 91.
14 J. Otera and R. Okawara, *Inorg. Nucl. Chem. Lett.*, 6 (1970) 855.
15 Y. Takashi and I. Aishima, *J. Organometal. Chem.*, 8 (1967) 209.
16 G. O. Doak and L. D. Freedman, *Organometallic compounds of arsenic, antimony, and bismuth*, 1970, p. 336.

---

* It has been reported[15] that the reaction of $(C_2H_5)_2AlCl$ with $(C_2H_5)_3SbCl_2$ gives the complex $[(C_2H_5)_4Sb]^+[C_2H_5AlCl_3]^-$.