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STUDIES ON SOME ASYMMETRIC ORGANOANTIMONY COMPOUNDS

1974

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論文目録

佐藤眞一

主論文 Studies on Some Asymmetric Organoanyimony Compounds
(不斉有機アンチモン化合物に関する研究)

(主論文のうち印刷公表したもの)

1. Preparation of asymmetrical tertiary stibines, $(C_6H_5)(CH_3)RSb$ and $[(C_6H_5)(CH_3)Sb]_2(CH_2)_n$.
(不斉第3スチビン、フェニルメチルアルキルスチビンおよびビス(フェニルメチルスチビン)アルカンの合成)

Journal of Organometallic Chemistry
43巻2号
昭和47年10月1日

1. Alkyl cleavage of tertiary phenylalkylstibines with sodium.
(第3フェニルアルキルスチビンのナトリウムによるアルキル基開裂)

Inorganic and Nuclear Chemistry Letters
8巻9号
昭和47年9月

1. Optically active stibonium iodide.
(光学活性ヨウ化スチボニウム)

Journal of Organometallic Chemistry
60巻1号
昭和48年10月16日

（主論文のうち未公表のもの）

1. Preparation and properties of PhMeSbSR.
（フェニルメチルチオスチビンの合成と性状）

執筆中
Inorganic and Nuclear Chemistry Letters
投稿予定

1. Preparation and configurational isomerism of ditertiary stibine sulfides, $(C_6H_5)(CH_3)(S)\text{-}SbCH_2Sb(CH_3)(C_6H_5)$ and $[(C_6H_5)(CH_3)(S)Sb]_2\text{-}(CH_2)_3$.
（ビス（フェニルメチルスチビノ）メタンモノスルフィドおよびビス（フェニルメチルスチビノ）プロパンジスルフィドの合成と立体配置異性化現象）

執筆中
Journal of Organometallic Chemistry
投稿予定

STUDIES ON SOME ASYMMETRIC ORGANOANTIMONY COMPOUNDS

1974

SHIN-ICHI SATO

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CHAPTER I

Introduction

Stereochemical aspects of organophosphorous and arsenic compounds have been much developed by making use of asymmetric compounds. However, asymmetric organoantimony compounds have been limited to some triarylstibines ArAr'Ar''Sb, which are tedious to prepare and inconvenient to PMR spectral investigations, and therefore the stereochemistry of organoantimony compounds has been little studied.

The main purpose of this study is to clarify the stereochemical properties of organoantimony compounds. I have prepared several types of hitherto unknown alkyl-substituted asymmetric organoantimony compounds and investigated their properties.

In chapter II, asymmetric tertiary stibines are prepared and the existence of the stable invertomers of the stibines is shown by PMR data. In addition, an interesting alkyl cleavage reaction found in tertiary phenylalkylstibines with sodium in liquid ammonia, which was performed in connection with the preparation of asymmetric tertiary stibines, is also described.

In chapter III, asymmetric ditertiary stibine sulfides are prepared and their configurational isomerization in solution is discussed. A possibility of configurational lability of tertiary stibine sulfide is suggested. The preparation and properties of asymmetric thiostibines are also described.

In chapter IV, the first preparation of two optically active stibonium iodides is described.

The content of this thesis is mainly composed of the following papers.

1) Preparation of asymmetrical tertiary stibines, $(C_6H_5)(CH_3)RSb$ and $[(C_6H_5)(CH_3)Sb]_2(CH_2)_n$.
   S. Sato, Y. Matsumura and R. Okawara,
   J. Organometal. Chem., 43, 333 (1972).
2) Alkyl cleavage of tertiary phenylalkylstibines with sodium.
   S. Sato, Y. Matsumura and R. Okawara,
   Inorg. Nucl. Chem. Lett., 8, 837 (1972).
3) Optically active stibonium iodide.
   S. Sato, Y. Matsumura and R. Okawara,
   J. Organometal. Chem., 60, C9 (1973).
4) Preparation and configurational isomerism of ditertiary stibine sulfides, $(C_6H_5)(CH_3)(S)SbCH_2Sb$-

$(CH_3)(C_6H_5)$ and $[(C_6H_5)(CH_3)(S)Sb]_2(CH_2)_3$.

S. Sato, Y. Matsumura and R. Okawara, to be published.

5) Preparation and properties of PhMeSbSR.

S. Sato, Y. Matsumura and R. Okawara, to be published.

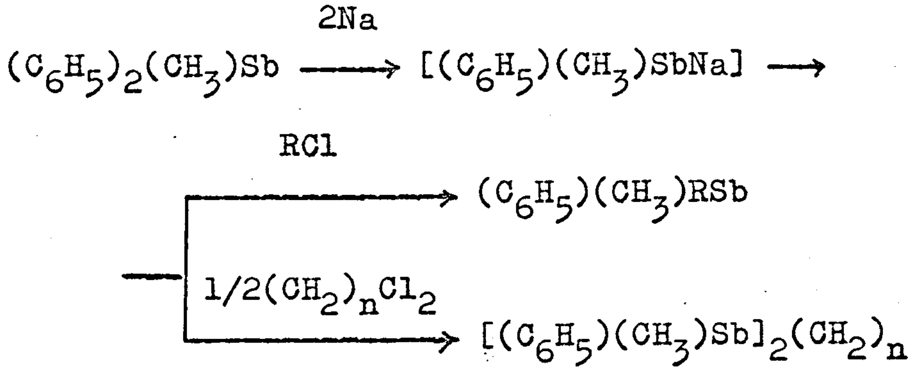
CHAPTER II . Asymmetric tertiary stibines.

II-1. Preparation of asymmetric tertiary stibines, $(C_6H_5)(CH_3)RSb$ and $[(C_6H_5)(CH_3)Sb]_2(CH_2)_n$.

II-1-1. Introduction

Some asymmetric triarylstibines[1,2] have been prepared by the reaction of phenylmagnesium halides with diarylchlorostibines R'R''SbCl, which were obtained by the diazonium reaction. However, alkyl-substituted analogues are not known[3].

Here I wish to report on the preparation of asymmetric tertiary stibines, $(C_6H_5)(CH_3)RSb$ (R=alkyl) and $[(C_6H_5)(CH_3)Sb]_2(CH_2)_n$ (n=1, 3 and 4) via the cleavage reaction of $(C_6H_5)_2(CH_3)Sb$ with sodium in liquid ammonia as shown below.



$$(C_6H_5)_2(CH_3)Sb \xrightarrow{2Na} [(C_6H_5)(CH_3)SbNa] \longrightarrow$$

$$\xrightarrow{RCl} (C_6H_5)(CH_3)RSb$$

$$\xrightarrow{1/2(CH_2)_nCl_2} [(C_6H_5)(CH_3)Sb]_2(CH_2)_n$$

PMR data are submitted to show the existence of the stable invertomers of these asymmetric tertiary stibines.

II-1-2. Experimental

All the reactions were carried out under a dry nitrogen atmosphere, and nitrogen was bubbled into the solvents just before use. Since essentially the same procedure was used to prepare all of the tertiary stibines, only typical experiments will be described. Since all the tertiary stibines except $[(C_6H_5)_2Sb]_2-(CH_2)_3$ are easily oxidized in air, analyses were performed on the dihalides obtained by adding sulfury chloride or bromine to the stibines in dichloromethane at 0°. The PMR spectra were measured in $CDCl_3$ using Japan Electron Optics JNM-3H-60 or JNM-PS-100 spectrometers, and the data (δ) are given in ppm downfield from TMS.

Preparation of $(C_6H_5)_2(CH_3)Sb$ and $[(C_6H_5)_2Sb]_2(CH_2)_3$

$(C_6H_5)_2(CH_3)Sb$. To a solution of $(C_6H_5)_3Sb$ (75 g, 0.21 mol) in liquid ammonia (1 l), sodium (9.7 g, 0.42 mol) was added with stirring, and the stirring was continued for 6 h. After ammonium chloride (11.2 g, 0.21 mol) was added to consume the phenylsodium, methyl chloride gas was bubbled into the dark red solution of $(C_6H_5)_2SbNa$[4,5]. The reaction took place immediately. After the ammonia was allowed to boil off, water (200 ml), THF (200 ml) and benzene (70 ml) were added to dissolve the residue. The organic layer was separated and dried with anhydrous sodium sulfate. The solvent was removed under reduced pressure and the residual liquid was distilled to give 36.5 g (60 %) of colorless $(C_6H_5)_2(CH_3)Sb$: b.p. 115-120/1 mmHg (lit[6]. b.p. 98-105.5/5×10^{-5} mmHg); PMR 1.11 (s, $SbCH_3$), 7.10-7.50 (m, aromatic).

$(C_6H_5)_2(CH_3)SbBr_2$. This compound was recrystallized from dichloromethane/petroleum ether; m.p. 147-148°. (Found: C, 34.81; H, 3.02. $C_{13}H_{13}Br_2Sb$ calcd.: C, 34.64; H, 2.91 %.) PMR 2.99 (s, $SbCH_3$), 7.40-7.60 and 8.00-8.23 (m, aromatic).

$[(C_6H_5)_2Sb]_2(CH_2)_3$. This compound was prepared in 60 % yield by the reaction of $(C_6H_5)_2SbNa$ with a 0.5 molar amount of $(CH_2)_3Cl_2$ and recrystallized from acetone, m.p. 52-53°. (Found: C, 54.69; H, 4.62. $C_{27}H_{26}Sb_2$ calcd.:

C, 54.60; H, 4.41 %.) PMR 1.94 [s, $Sb(CH_2)_3Sb$], 7.00-7.60 (m, aromatic).

$[(C_6H_5)_2Cl_2Sb]_2(CH_2)_3$. This compound was recrystallized from dichloromethane/methanol; m.p. 137-137.5°. (Found: C, 43.83; H, 3.50. $C_{27}H_{26}Cl_4Sb_2$ calcd.: C, 44.07; H, 3.56 %.) PMR 3.00-3.50 [m, $Sb(CH_2)_3Sb$], 7.45-7.65 and 7.97-8.30 (m, aromatic).

Preparation of asymmetric tertiary stibines $(C_6H_5)(CH_3)$-RSb [R= C_2H_5, $(CH_3)_2CH$, $C_6H_5CH_2$, $(CH_2)_nSb(CH_3)(C_6H_5)$ (n= 1, 3, 4)]

All the compounds were obtained in ca. 60 % yields from the reaction of the corresponding alkyl chloride or dichloroalkane with $(C_6H_5)(CH_3)SbNa$ prepared in 14 h from $(C_6H_5)_2(CH_3)Sb$ and sodium. $[(C_6H_5)(CH_3)Sb]_2(CH_2)_3$ was prepared also from the reaction of $[(C_6H_5)_2Sb]_2(CH_2)_3$ with sodium and CH_3Cl.

Properties and the PMR data of the asymmetric stibines and their dihalides thus obtained are listed in Table 1 and 2, respectively. The PMR spectrum of the methylene group in $[(C_6H_5)(CH_3)Sb]_2CH_2$ is shown in Fig. 1.

Table 1

Table 2

Fig. 1

TABLE 1

PROPERTIES OF ASYMMETRICAL TERTIARY STIBINES AND THEIR DERIVATIZED DIHALIDES

Tertiary stibines	*B.p. (°C/mmHg)*	*Derivatized dihalides*	*M.p. (°C)*	*Analysis found (calcd.) (%)*	
				C	H
$(C_6H_5)(CH_3)RSb$		$(C_6H_5)(CH_3)RSbX_2$			
$R=C_2H_5$	74–75/2.5	X=Br	44–45	27.11 (26.89)	3.34 (3.26)
$(CH_3)_2CH$	84–85/4	Br	62–63	29.02 (28.82)	3.43 (3.63)
$C_6H_5CH_2$	135–136/2	Br	132–133	36.35 (36.18)	3.21 (3.25)
$[(C_6H_5)(CH_3)Sb]_2(CH_2)_n$[a]		$[X_2(C_6H_5)(CH_3)Sb]_2(CH_2)_n$			
$n=1$	130–168/10^{-2}	X=Cl	163	30.89 (30.87)	3.14 (3.11)
		F[b]	120–121	35.05 (34.79)	3.34 (3.50)
3	130–180/10^{-2}	Cl	148.5–149.5	33.41 (33.38)	3.71 (3.63)
4	100–157/10^{-2}	Cl	198.5–199.5	34.54 (34.55)	3.94 (3.87)

[a] A yellow color could not be removed by repeated distillations (See ref. 5).
[b] Obtained from the reaction of $[Cl_2(C_6H_5)(CH_3)Sb]_2CH_2$ with AgF in moist acetone.

TABLE 2

PMR DATA[a] OF ASYMMETRICAL TERTIARY STIBINES AND THEIR DERIVATIZED DIHALIDES

Tertiary stibines	*δ (ppm)*	*J (Hz)*	*Derivatized dihalides*	*δ (ppm)*	*J (Hz)*	*Assignment*
$(C_6H_5)(CH_3)RSb$			$(C_6H_5)(CH_3)RSbX_2$			
$R=C_2H_5$	0.90 (s)		X=Br	2.71 (s)		$SbCH_3$
	1.30 (m)			1.71 (t)	7.5[b]	SbC_2H_5
				3.23 (q)	7.5[b]	
$(CH_3)_2CH$	0.95 (s)		Br	2.73 (s)		$SbCH_3$
	1.21 (d)	7.5[c]		1.75 (d)	6.8[c]	$C(CH_3)_2$
	1.26 (d)	7.5[c]				
	1.90 (m)			3.85 (m)	6.8[c]	SbCH
$C_6H_5CH_2$	0.95 (s)		Br	2.49 (s)		$SbCH_3$
	2.96 (d)	12.0[d]		4.61 (s)		$SbCH_2$
	3.06 (d)	12.0[d]				
$[(C_6H_5)(CH_3)Sb]_2(CH_2)_n$[f]			$[X_2(C_6H_5)(CH_3)Sb]_2(CH_2)_n$			
$n=1$[g]	0.91 (s)		X=Cl	2.83 (s)		$SbCH_3$
	1.45 (d)	11.3[d]		4.20 (s)		$SbCH_2Sb$
	1.50 (d)	11.3[d]				
	1.50 (S)					
			F[g]	2.00 (m)		$SbCH_3$
				2.90 (qui)	6.0[e]	$SbCH_2Sb$
3	0.83 (s)		Cl	2.48 (s)		$SbCH_3$
	1.64 (m)			3.00 (m)		$Sb(CH_2)_3Sb$
4	0.84 (s)		Cl[h]			$SbCH_3$
	1.63 (m)					$Sb(CH_2)_4Sb$

[a] In $CDCl_3$ at 23°; δ ppm downfield from internal TMS. Aromatic protons were observed at about 7.0–7.6 ppm in tertiary stibines and at about 7.3–7.7 and 8.0–8.3 ppm in derivatized dihalides. Multiplicity: (s), singlet; (d), doublet; (t), triplet; (q), quartet; (qui), quintet; (m), multiplet. [b] $J(CH_3–CH_2)$. [c] $J(CH_3–CH)$. [d] $J(H_A–H_B)$. [e] $J(CH_2–F)$. [f] The yellow liquids showed a small broad singlet at 1.00–1.12 ppm due to an impurity. The peak scarcely appeared in the pale yellow liquid of $[(C_6H_5)(CH_3)Sb]_2CH_2$ obtained by reduction from $[Cl_2(C_6H_5)(CH_3)Sb]_2CH_2$ (see ref. 5). [g] At 100 MHz. [h] Not measured because of the limited solubility in $CDCl_3$.

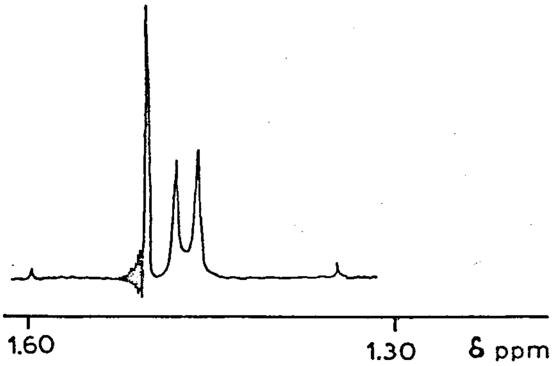
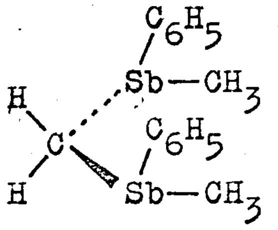


Fig. 1. PMR Spectrum of methylene group in $[(C_6H_5)(CH_3)Sb]_2CH_2$ (b.p. 130–168°/10^{-2} mmHg) in $CDCl_3$ solution at 23°.

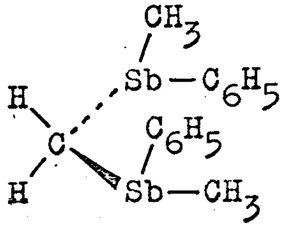
II-1-3. Results and Discussion

The asymmetric tertiary stibines, $(C_6H_5)(CH_3)RSb$ and $[(C_6H_5)(CH_3)Sb]_2(CH_2)_n$ were obtained in fairly good yields via cleavage of a phenyl group in $(C_6H_5)_2(CH_3)Sb$ with sodium.

As shown in Table 2, the PMR spectra of phenylmethylbenzylstibine and phenylmethylisopropylstibine in $CDCl_3$ at room temperature showed an AB quartet for the benzyl methylene group and two doublets for the isopropyl methyl groups, which are expected for asymmetric compounds. In methylene bis(phenylmethylstibine) a singlet and an AB quartet for the methylene group were observed as shown in Fig. 1. These are reasonably assigned to the racemic and the meso forms, respectively.



meso



racemic

The above observations, which are consistent with the calculations* of both Weston[7] and Keopple et al.[8],

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* The calculated barrier to the pyramidal inversion

suggest that the rates of the pyramidal inversion of our asymmetric tertiary stibines are very slow on the PMR time scale.

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for trimethylstibine was reported to be 26.7 (ref. 7) and 25 Kcal/mol (ref. 8). A lower limit to the barrier for diisopropyl-p-tolylstibine was determined[9] to be 26 Kcal/mol from its PMR spectrum.

II-2. Alkyl cleavage of tertiary phenylalkylstibines with sodium.

II-2-1. Introduction

In the previous section, I have found that one phenyl group in diphenylmethylstibine was cleaved with sodium in liquid ammonia, and subsequent treatment with alkyl chlorides gave asymmetric tertiary stibines $(C_6H_5)(CH_3)RSb$ (R=alkyl) in fairly good yields. Here I wish to describe an interesting alkyl cleavage reaction found in tertiary phenylalkylstibines with the same reagent*.

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* With lithium in THF, one phenyl group was cleaved in diphenylalkylphosphines, and in phenyldialkylphosphines a complex reaction took place but characterizable products were not obtained[10]. Similarly, with potassium in dioxane, one aryl group was cleaved in diarylalkylarsines but in aryldialkylarsines no reaction occurred[11].

II-2-2. Experimental

All the reactions were carried out under a dry nitrogen atmosphere and nitrogen was bubbled into the solvents just before use. The tertiary stibines prepared here are easily oxidized in air, and analyses were performed on their derivatized dibromides obtained by adding bromine in dichloromethane at 0°. The PMR spectra were measured on a Japan Electron Optics JNM-3H-60 spectrometer, and the data (δ) are given in ppm downfield from TMS.

Starting materials

All the starting materials were prepared in a similar manner to that described in the previous section from $(C_6H_5)_3Sb$ or $(C_6H_5)_2(CH_3)Sb$, sodium and the corresponding alkyl chlorides in 50-70 % yields.

$(C_6H_5)_2(C_2H_5)Sb$: b.p. 123-124°/0.5 mm; PMR 1.03-2.06 (m, SbC_2H_5), 7.05-7.61 (m, aromatic).

$(C_6H_5)_2(C_2H_5)SbBr_2$: m.p. 156-157° [m.p. 158° (12)]. (Found: C, 36.34; H, 3.34. $C_{14}H_{15}Br_2Sb$ calcd.: C, 36.18; H, 3.25%.) PMR 1.80 [t, C-CH_3; J(CH_2-CH_3) 7.5 Hz], 3.48 (q, $SbCH_2$), 7.27-7.72 and 7.88-8.32 (m, aromatic).

$(C_6H_5)_2[(CH_3)_2CH]Sb$: b.p. 127-128°/0.5 mm [b.p. 167-169°/6-7 mm (13)]. PMR 1.27 [d, $(CH_3)_2C$; J(CH-CH_3) 7.5 Hz], 2.25 (m, SbCH), 7.00-7.51 (m, aromatic).

$(C_6H_5)_2[(CH_3)_2CH]SbBr_2$: m.p. 155-156°. (Found: C, 37.62; H, 3.64. $C_{15}H_{17}Br_2Sb$ calcd.: C, 37.62; H, 3.58 %.) PMR 1.78 [d, $(CH_3)_2C$; J(CH-CH_3) 6.8 Hz], 3.96 (m, SbCH), 7.15-7.50 and 7.77-8.10 (m, aromatic).

$(C_6H_5)_2(C_6H_5CH_2)Sb$: b.p. 179-180°/0.5 mm [b.p. 224-225°/ 15-17 mm (14)]. PMR 3.10 (s, $SbCH_2$), 6.80-7.50 (m, aromatic).

$(C_6H_5)_2(C_6H_5CH_2)SbBr_2$: m.p. 121-122°. (Found: C, 43.24; H, 3.28. $C_{19}H_{17}Br_2Sb$ calcd.: C, 43.31; H, 3.25 %.) PMR 4.86 (s, $SbCH_2$), 7.15-7.50 and 7.60-7.95 (m, aromatic).

$(C_6H_5)(CH_3)_2Sb$: b.p. 74-75°/3.5 mm [b.p. 95-97°/10 mm (15)]. PMR 0.95 (s, $SbCH_3$), 7.10-7.60 (m, aromatic).

$(C_6H_5)(CH_3)_2SbBr_2$: m.p. 108-109°. (Found: C, 24.60; H, 2.93. $C_8H_{11}Br_2Sb$ calcd.: C, 24.72; H, 2.85 %.) PMR 2.80 (s, $SbCH_3$), 7.10-7.60 and 7.85-8.15 (m, aromatic).

Cleavage of tertiary phenylalkylstibines

All the reactions were carried out by the practically same procedure to that of the preparation of the starting materials. The results are summarized in Table 3. The products and the derivatized bromides were identified by comparison of the PMR and IR spectra with the authentic samples. The two stibines obtained from $(C_6H_5)_2(C_2H_5)Sb$ were separated by distillation. However, the products from $(C_6H_5)(CH_3)(C_2H_5)Sb$ and benzylchloride were not separated by distillation, and the yields were assumed by the PMR spectrum of the brominated mixture.

Table 3. Cleavage reaction of tertiary phenylalkylstibines.

Starting material	Reaction time* (h)	Alkyl chloride	Product stibine	Product % yield
Ph_2EtSb	15	MeCl	Ph_2MeSb PhMeEtSb	30 25
$Ph_2{}^iPrSb$	15	MeCl	Ph_2MeSb	58
Ph_2BzSb	15	MeCl	Ph_2MeSb	30
$(Ph_2Sb)_2CH_2$	3.5	MeCl	Ph_2MeSb	29
$PhMe_2Sb$	5	BzCl	PhMeBzSb	43
PhMeEtSb	10	BzCl	PhMeBzSb PhEtBzSb	29 24
$PhMe{}^iPrSb$	10	BzCl	PhMeBzSb	58
PhMeBzSb	10	${}^iPrCl$	$PhMe{}^iPrSb$	56

Me= CH_3, Et= C_2H_5, ${}^iPr$= $(CH_3)_2CH$, Bz= $C_6H_5CH_2$ and Ph= C_6H_5.

* Time required to react with sodium.

II-2-3. Results and Discussion

As shown in Table 3, the cleavage of the alkyl group was found in the diphenylalkylstibines, $(C_6H_5)_2R$-Sb [$R=C_2H_5$, $(CH_3)_2CH$ and $C_6H_5CH_2$], and $[(C_6H_5)_2Sb]_2CH_2$*, and the cleavage of the phenyl group was also observed in $(C_6H_5)_2(C_2H_5)Sb$. It is worth noting that the alkyl cleavage was found to occur in all the phenyldialkylstibines listed. The results suggest that the cleavage of the isopropyl (or benzyl) group is preferred to those of the phenyl and methyl groups, and the phenyl group in phenyldialkylstibines is difficult to be cleaved.

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* In $[(C_6H_5)_2Sb]_2(CH_2)_3$ and $[(C_6H_5)_2E]_2(CH_2)_n$ [E= P (16), As (17)], only one of the phenyl groups attached to each metal atom was cleaved with sodium in liquid ammonia.

II-3. Summary

Six asymmetric tertiary stibines, $(C_6H_5)(CH_3)RSb$ [$R=C_2H_5$, $(CH_3)_2CH$ and $C_6H_5CH_2$] and $[(C_6H_5)(CH_3)Sb]_2(CH_2)_n$ (n=1, 3 and 4) were prepared in about 60 % yields by the reaction of $(C_6H_5)_2(CH_3)Sb$ with sodium in liquid ammonia and the subsequent reaction with RCl and $(CH_2)_nCl_2$, respectively. $[(C_6H_5)(CH_3)Sb]_2(CH_2)_3$ was also prepared by the reaction of $[(C_6H_5)_2Sb]_2(CH_2)_3$ with sodium and CH_3Cl in the same solvent. The cleavage of alkyl-antimony bond by sodium was observed in the reaction of some other tertiary stibines, such as $(C_6H_5)_2RSb$ and $(C_6H_5)(CH_3)RSb$ (R=alkyl). The existence of the stable invertomers of newly prepared asymmetric tertiary stibines was shown by PMR data.

II-4. References

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CHAPTER III. Asymmetric organoantimony compounds containing Sb-S bond.

III-1. Preparation and configurational isomerism of ditertiary stibine sulfides, $(C_6H_5)(CH_3)(S)Sb{-}CH_2Sb(CH_3)(C_6H_5)$ and $[(C_6H_5)(CH_3)(S)Sb]_2(CH_2)_3$.

III-1-1. Introduction

It has been reported that configuration of tertiary stibines is stable[1-5]. Thus, for example, bis(phenylmethylstibino)methane exists as meso and racemic forms without any mutual interconversion at least on the PMR time scale[1]. On the other hand, the Sb-S bond in trimethylstibine sulfide has been known to be quite reactive[6-9], and it is therefore of great interest to study the configurational stability of tertiary stibine sulfides. In the course of the study on the stereoisomers derived from the asymmetric ditertiary stibines, I have found that monosulfide $(C_6H_5)(CH_3)(S)SbCH_2Sb(CH_3)(C_6H_5)$ and $[(C_6H_5)(CH_3)(S)Sb]_2(CH_2)_3$ are configurationally labile as found from their time dependent PMR spectra.

III-1-2. Experimental

$[(C_6H_5)(CH_3)SbCl_2]_2(CH_2)_n$ (n=1 and 3) and $(C_6H_5)(CH_3)(i\text{-}C_3H_7)SbBr_2$ were synthesized in a manner similar to that described in our previous paper[1]. The PMR spectra were measured using a Japan Electron Optics JNM-PS-100 spectrometer, and the data (δ) are given in ppm downfield from internal TMS. Molecular weights were measured in chloroform solution using a Mechrolab vapor pressure osmometer Model 302. The IR spectra were recorded using a Hitachi 225 spectrometer equipped with gratings.

Preparation of asymmetric tertiary stibine sulfides

Since these sulfides were prepared by essentially the same procedure, only typical experiments will be described.

$(C_6H_5)(CH_3)(S)SbCH_2Sb(CH_3)(C_6H_5)$ [I]. To a mixture of $[(C_6H_5)(CH_3)SbCl_2]_2CH_2$ (9.7 g, 16.6 mmol) and $Na_2S \cdot 9H_2O$ (8.0 g, 33.3 mmol), methanol (80 ml) was added and the solution was stirred for 5 h under a nitrogen atmosphere. From the filtrate, the solvent was removed in vacuo, and the residual solid was extracted with dichloromethane (60 ml). After removal of the solvent, the residual solid was recrystallized several times from ethanol to give 3.2 g (40 %) of colorless crystals of [I]: m.p.

89-90°. (Found: C, 37.89; H, 3.93. $C_{15}H_{18}Sb_2S$ calcd.: C, 38.02; H, 3.83 %.) Mol. wt. found: 480, 490 at concentrations 0.62, 0.23 % W(sample)/W(solvent), respectively. Calcd. for monomer 474. IR: ν(Sb-S) 430 (in Nujol mull), 435 cm^{-1} (in CH_2Cl_2).

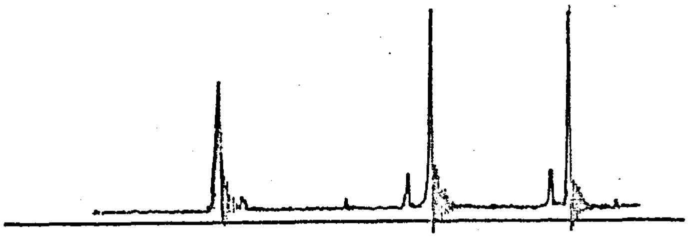
$[(C_6H_5)(CH_3)(S)Sb]_2(CH_2)_3$ [II]. This compound was prepared in 85 % yield from $[(C_6H_5)(CH_3)SbCl_2]_2(CH_2)_3$ and $Na_2S \cdot 9H_2O$, and was recrystallization from dichloromethane/methanol: m.p. 141-142°. (Found: C, 38.05; H, 4.19. $C_{17}H_{32}Sb_2S_2$ calcd.: C, 38.24; H, 4.15 %.) Mol. wt. found: 528, 506 at concentrations 0.72, 0.45 %, respectively. Calcd. for monomer 534. IR: ν(Sb-S) 435 (in Nujol mull), 440 cm^{-1} (in CH_2Cl_2).

The time dependent PMR spectra of [I] and [II] in dichloromethane at room temperature are shown in Fig. 1 and 2, respectively.

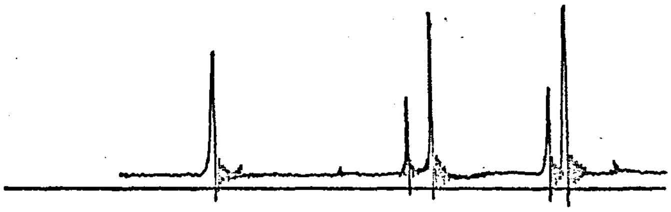
Fig. 1 Fig. 2

$(C_6H_5)(CH_3)(i\text{-}C_3H_7)SbS$. This compound was prepared in 90 % yield from $(C_6H_5)(CH_3)(i\text{-}C_3H_7)SbBr_2$ and Na_2S $9H_2O$, and recrystallized from ethanol under a nitrogen atmosphere: m.p. 74-75°. (Found: C, 41.24; H, 5.17. $C_{10}H_{15}SbS$ calcd.: C, 41.55; H, 5.23 %.) PMR: 1.42 and

Immediately after dissolving



After 5 min



After 15 min

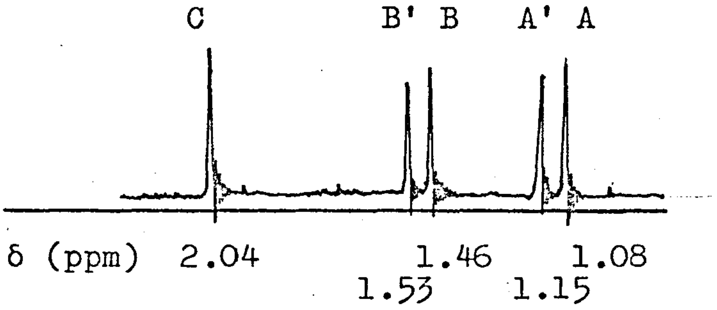
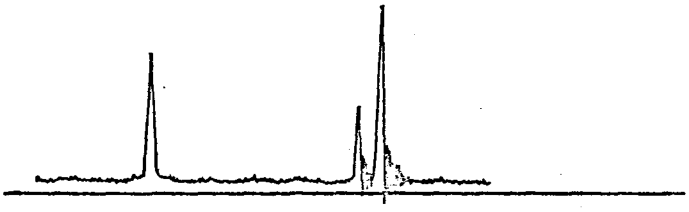


Fig. 1. PMR spectra of $(C_6H_5)(CH_3)(S)SbCH_2Sb(CH_3)(C_6H_5)$ in dichloromethane (12 %) at room temperature.

Immediately after dissolving

After 1 h



After 3 h

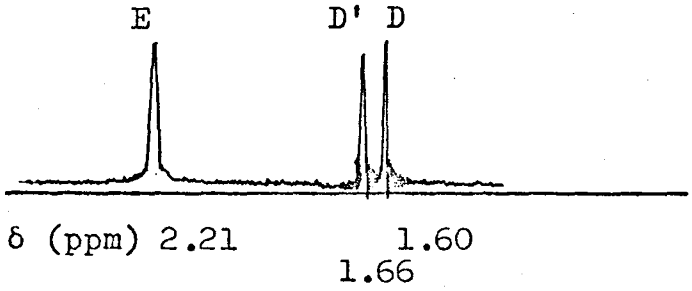


Fig. 2. PMR spectra of $[(C_6H_5)(CH_3)(S)Sb]_2(CH_2)_3$ in dichloromethane (2.7 %) at room temperature.

1.45 [d, $C(CH_3)_2$; J($CH-CH_3$) 7.5 Hz], 1.64 (s, $SbCH_3$), 2.60 (m, SbCH).

Reaction of triphenylphosphine with ditertiary stibine sulfides

All the reactions described below were carried out in PMR tubes under a nitrogen atmosphere. The reaction products were identified by comparison of their PMR spectra with those reported for the authentic samples[1]. The reactions were found to be complete in several minutes.

With [I].

A solution of triphenylphosphine (0.38 mmol) in dichloromethane (0.5 ml) was added to [I] (0.10 mmol). The PMR spectrum of this solution showed the formation of the racemic and very small amount of the meso forms of $[(C_6H_5)(CH_3)Sb]_2CH_2$. However, when triphenylphosphine (0.30 mmol) in dichloromethane (0.3 ml) was added to [I] in the same solvent (0.2 ml), which had been kept for 1.5 h, almost equal amounts of the both isomers were formed.

With [II].

To a mixture of triphenylphosphine (0.35 mmol) and [II] (0.09 mmol), dichloromethane (0.5 ml) was added. The PMR spectrum of the solution showed that $[(C_6H_5)(CH_3)Sb]_2(CH_2)_3$ was formed.

III-1-3. Results and Discussion

It is interresting that the reduction of one antimony(V) in $[(C_6H_5)(CH_3)SbCl_2]_2CH_2$ occurred easily on treatment with sodium sulfide, affording stable monosulfide $(C_6H_5)(CH_3)(S)SbCH_2Sb(CH_3)(C_6H_5)$ [I], while an expected product, $[(C_6H_5)(CH_3)(S)Sb]_2(CH_2)_3$ [II] was obtained from a similar reaction of $[(C_6H_5)(CH_3)SbCl_2]_2$-$(CH_2)_3$. The sulfides [I] and [II] are monomeric in solution and their Sb-S stretching frequencies both in the solid and in solution are very similar to those of $(CH_3)_3SbS$[11]. These data suggest that each sulfur atom in [I] and [II] is bound to one antimony atom in both states*, and in [I] therefore two diastereomers, each of which has a pair of enantiomers, are expected to exist.

As shown in Fig. 1, the PMR spectrum of [I] immediately after dissolving in dichloromethane at room

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* Although the IR data of [I] suggest the existence of a trivalent antimony atom in the molecule, this compound is fairly stable in air.

temperature showed three main signals at δ 1.08 (A), 1.46 (B) and 2.04 ppm (C) with very weak ones at 1.15 (A') and 1.53 ppm (B'). The intensity of A' and B' increased gradually with time, and after the intensity ratio A'/A (or B'/B) had reached almost unity, further spectral change was not observed. The removal of the solvent and the subsequent recrystallization from ethanol gave crystals, which showed a similar spectral change. On the basis of the chemical shifts of these peaks the signals A and B are reasonably assigned to the methyl groups of $(C_6H_5)(CH_3)Sb-$ and $(C_6H_5)(CH_3)(S)Sb-$ moieties, respectively, in one of the two possible diastereomers of [I] and A' and B' to those in the other isomer. The signal C may be due to the methylene groups in the both isomers*

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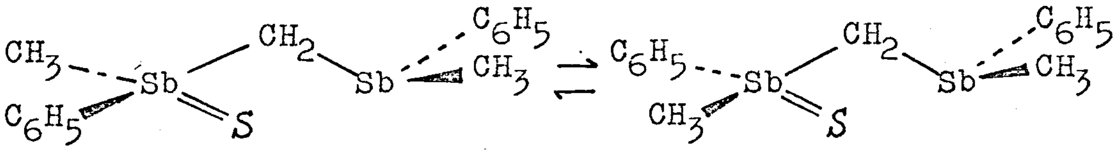
* The methylene groups are diastereotopic in the both isomers and are expected to appear as two AB quartets. Since the singlet C showed no measurable change on lowering the temperatures even to ca. -90°, the appearance of only one singlet for the methylene groups may be regarded as being due to an accidental coincidence of the chemical shifts.

On the basis of this assignment, it is concluded that one form of the two diastereomers which exists exclusively in the crystals isomerizes gradually to the other and reaches the equilibrium in solution as shown below.



A further support for this isomerization was obtained from the sulfur abstraction reaction of [I] with $(C_6H_3)_3P$. An addition of [I] into the solution of $(C_6H_5)_3P$ in dichloromethane gave almost exclusively the racemic form of $[(C_6H_5)(CH_3)Sb]_2CH_2$, while an addition of $(C_6H_5)_3P$ into the dichloromethane solution of [I], which had been kept for 1.5 h, gave almost equal amounts of the racemic and meso forms of the ditertiary stibine. This observation shows that the isomerization of [I] in solution is slower than the sulfur abstraction, and the abstraction reaction is stereospecific, although no information is available about the stereospecificity (inversion or retention).

The fact that the rate of the isomerization was accelerated either by increasing the concentration of [I] or addition of $(CH_3)_3SbS$, suggests the isomerization (inversion of configuration) proceeds through an intermolecular pathway*. A reasonable mechanism for this intermolecular process is associative sulfur exchange between the two or more $(C_6H_5)(CH_3)(S)Sb$-moieties through pentacoordinate intermeadiate, in which antimony bonded to sulfur is expected to invert the configuration**.

With raising temperatures up to ca. 100° under a nitrogen atmosphere the four signals (A, A', B and B') in 1,1,2,2-tetrachloroethane gradually broadened, this spectral change being reversible. However, as the pattern of such spectral change with temperatures was independent of the concentration, there must be another fluxionality in the molecule with an intramolecular mechanism. We may attribute such process to a rapid migration of sulfur between the two antimony atoms with different oxidation states (III and V). Further this

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* The first half-lives were found to be ca. 5 min for a concentration of 12 wt. %, ca. 15 min for that of 3.5 % and ca. 2 min for that of 4.0 % containing 4.4 times moles of $(CH_3)_3SbS$.

** A bimolecular halogen exchange has been suggested to be responsible for configurational lability of R_3SnX[12,13].

intramolecular migration of sulfur is more rapid than the intermolecular sulfur exchange accompanied by inversion of configuration, and seems to proceed through retention of configuration. The sulfur migration between Sb(III) and Sb(IV) was also observed between $(C_6H_5)(CH_3)$-$(i-C_3H_7)Sb$ and $(C_6H_5)(CH_3)(i-C_3H_7)SbS$. In the PMR spectra of a mixture of these two compounds in o-dichlorobenzene (ca. 7 %, respectively) at ca. 100°, broadenings of signals, which were reversible with temperature, were observed for the isopropyl-methyl groups and methyl groups bonded to antimony [Sb(III) and Sb(IV)], and these broadenings are reasonably regarded as being due to an intermolecular migration of sulfur.

As shown in Fig. 2, the PMR signals (D and D') assigned to the methyl groups of the two diastereomers in [II] showed a change with time similar to those of [I]. The signal E, which is assigned to the three methylene groups in the both isomers, did not show any change. The removal of the solvent and the subsequent recrystallization from dichloromethane/methanol gave crystals, which showed a similar spectral change. Although the dependence of the rate of inversion at antimony on concentration of [II] in dichloromethane was not determined because of its limited solubility, a remarkable effect of an addition of $(CH_3)_3SbS$ on that rate was again observed*. These findings suggest that one of the two diastereomers (meso and racemic), which exists in the crystals, gradually isomerizes to the other form in solution and the isomerization proceeds through sulfur exchange.

Finally it should be noted that the PMR spectral behaviour of monotertiary stibine sulfide $(C_6H_5)(CH_3)$-(i-C_3H_7)SbS does not tell whether this compound is configurationally stable or the rate of inversion is very slow on the PMR time scale, since the spectra in dichloromethane at room temperature showed two doublets for the diastereotopic isopropyl-methyl groups invariably over a wide range of concentrations (from 3.2 to 25 wt. %), and the two doublets were also observed at ca. 100° in o-dichlorobenzene, above which a decomposition occurred predominantly. Thus our observation about the isomerization of both [I] and [II] seems to suggest, for the first time, a possibility of configurational lability of tertiary stibine sulfides.

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* The first half-lives were found to be ca. 1 h for a solution of 2.7 wt. %, ca. 5 min for that of 1.8 % of [II] containing 5.6 times moles of $(CH_3)_3SbS$.

III-2. Preparation and properties of $(C_6H_5)(CH_3)SbSR$

III-2-1. Introduction

Among diorganostibines of the type RR'SbX, which are expected to be useful for deriving asymmetric compounds, only diarylchlorostibines ArAr'SbCl have been known[2,3]. These chlorostibines have been prepared in low yields by the diazonium reaction. I have now found that $(C_6H_5)(CH_3)(i\text{-}C_3H_7)Sb$[1] reacts with RSH in refluxing benzene in the presence of AIBN to give $(C_6H_5)(CH_3)SbSR$ (R= $i\text{-}C_3H_7$, $C_6H_5CH_2$ and C_6H_5), as a sole isolable product in fairly good yields. A similar homolytic substitution reaction of R_3Sb with phenylthio radical to give $R_nSb(SC_6H_5)_{3-n}$, in which n varies with R, has been reported[14].

III-2-2. Experimental

All the procedures were carried out under a nitrogen atmosphere.

Preparation of $(C_6H_5)(CH_3)SbSR$ [R= $CH(CH_3)_2$, $C_6H_5CH_2$, C_6H_5]

To a solution of $(C_6H_5)(CH_3)(i\text{-}C_3H_7)Sb$[1] in benzene, a small amount of azobisisobutyronitrile and an excess of the corresponding mercaptan were added, and the solution was refluxed for 3-6 hours. After the removal of the solvent under reduced pressure, the residual liquid was distilled to give the compounds in ca. 60 % yields. The compounds thus obtained decomposed gradually in air.

Properties and the PMR data of the thiostibines are shown in Table 1.

Table 1 Properties and PMR data of $(C_6H_5)(CH_3)SbSR$

Compounds	B.p. (°C/mmHg)	Analysis found(calcd.)(%) C	H	PMR[a] δ (ppm)	Assignment
$(C_6H_5)(CH_3)SbSR$					
R= $CH(CH_3)_2$	81-82/0.1	41.67 (41.56)	5.33 (5.23)	1.03(s)	$SbCH_3$
				1.22(d)[b] 1.24(d)[b]	$C(CH_3)_2$
				3.00(m)[b]	SCH
$CH_2C_6H_5$	130-131/0.1	50.09 (49.88)	4.49 (4.49)	0.09(s)	$SbCH_3$
				3.70(s)	SCH_2
C_6H_5[c]	142-143/0.5	48.55 (48.33)	4.13 (4.06)	1.16(s)	$SbCH_3$

[a] In benzen [R= $CH(CH_3)_2$, $CH_2C_6H_5$] and in $CDCl_3$ (R= C_6H_5) at 23°. ; δ ppm downfield from internal TMS. [b] $J(CH-CH_3)$ 7.0 Hz.
[c] This compound shows yellow color.

III-2-3. Results and Discussion

The preferential leaving of the isopropy group in the present displacement reaction is quite similar to that found in reductive cleavage reaction of $(C_6H_5)(CH_3)$-$(i\text{-}C_3H_7)Sb$ with sodium in liquid ammonia[15] and that of $(C_6H_5)(CH_3)(C_2H_5)(i\text{-}C_3H_7)SbI$[10] with sodium benzophenone ketyl in THF[16].

As shown in Table 1, the PMR spectrum of (isopropylthio)phenylmethylstibine in benzene at room temperature showed two doublets for the isopropyl methyl groups. In dichloromethane, however, the isopropyl methyl protons appeared as one doublet (δ 1.37 ppm J 7 Hz), and the PMR spectra of (benzylthio)-phenylmethylstibine showed a singlet for the benzyl methylene group both in benzene (see Table 1) and in dichloromethane (δ 3.80). All these spectra did not show any measurable change on dilution from about 1 to 7×10^{-2} mol/l, or on lowering the temperatures to below -60°. These observations can be explained by assuming that the rate of inversion at antimony is very slow on the PMR time scale, which is similar to the configurational stability of triorganostibines[1,4,5], and that the appearance of a singlet and one doublet for the benzylic (in both benzene and dichloromethane) and the isopropyl methyl protons (in dichloromethane), may be due to an accidental coincidence of the chemical shifts of each pair of the diastereotopic protons.

III-3. Summary

Asymmetric ditertiary stibine sulfides $(C_6H_5)(CH_3)(S)SbCH_2Sb(CH_3)(C_6H_5)$ and $[(C_6H_5)(CH_3)(S)Sb]_2(CH_2)_3$ were prepared. It was found that these sulfides exist as only one of two possible diastereomers in crystals, however isomerization to the other form takes place in solution resulting in an equilibrium mixture. A possibility of configurational lability of tertiary stibine sulfide was suggested for the first time. Asymmetric thiostibines $(C_6H_5)(CH_3)SbSR$ [R= $CH(CH_3)_2$, $C_6H_5CH_2$ and C_6H_5] were prepared by the reaction of $(C_6H_5)(CH_3)(i\text{-}C_3H_7)Sb$ with RSH in the presence of AIBN. From PMR data configuration of these thiostibines was suggested to be stable.

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CHAPTER IV. Optically active stibonium iodides.

IV-1. Introduction

Optically active quartenary phosphonium and arsonium salts are well known and their reactions have been much studied. The preparation of asymmetric stibonium iodide $(CH_3)(C_2H_5)(C_3H_7)(C_4H_9)SbI$ has been described recently[1], but no optical resolution of an asymmetric quarternary stibonium salt has been reported[2]. I describe in this chapter the first preparation of two optically active stibonium iodides $(C_6H_5)(CH_3)(C_2H_5)$-$RSbI$ (R= i-C_3H_7 and n-C_3H_7).

IV-2. Experimental

$(C_6H_5)(CH_3)RSb$ [R= i-C_3H_7(3) and n-C_3H_7] and $(C_6H_5)(CH_3)(i\text{-}C_3H_7)SbS$ were synthesized in a manner similar to that described in chapter II and III, respectively.

$\underline{(C_6H_5)(CH_3)(n\text{-}C_3H_7)Sb}$. b.p. 86/1 mm.

$\underline{(C_6H_5)(CH_3)(n\text{-}C_3H_7)SbBr_2}$. oily liquid. (Found: C, 29.37; H, 3.66. $C_{10}H_{15}SbBr_2$ calcd.: C, 28.82; H,3.63 %.) PMR($CDCl_3$)(δ): 1.14 (m, CCH_3), 2.18 (m, CCH_2C), 2.70 (s, $SbCH_3$), 3,23 (m, $SbCH_2$).

Preparation of asymmetric stibonium iodides $(C_6H_5)(CH_3)(C_2H_5)RSbI$ (R= i-C_3H_7 and n-C_3H_7)

$(C_6H_5)(CH_3)(C_2H_5)(i\text{-}C_3H_7)SbI$ [I]. This compound was prepared in two different ways.

(i) $(C_6H_5)(CH_3)(i\text{-}C_3H_7)Sb$ (30.7 g, 0.12 mol) was added to $(C_2H_5)_3OBF_4^4$ (22.8 g, 0.12 mol) in dichloromethane (120 ml) under a nitrogen atmosphere, and the solution was stirred for 12 h. After the removal of the solvent, potassium iodide (21.6 g, 0.13 mol) and methanol (100 ml) were added, and the solution was stirred for 3 h. The removal of the solvent from the filtrate gave solid, which was extracted with dichloromethane (100 ml). After the distillation of the solvent in vacuo, the residual solid was recrystallized from dichloromethane/ benzene or acetone/ether to give 23.7 g (47.8 %) of colorless crystals of [I]: m.p. 117-118°. (Found: C, 34.78; H, 5.17. $C_{12}H_{20}SbI$ calcd.: C, 34.90; H, 4.88 %.) PMR($CDCl_3$)(δ): 1.56 and 1.58 [d, $C(CH_3)_2$; J(CH-CH_3) 7.5 Hz], 1.54 [t, $SbCH_2C\underline{H}_3$; J(CH_2-CH_3) 7.5 Hz], 2.19 (s, $SbCH_3$), 3.13 (m, $SbCH_2$), 3.98 (m, SbCH).

(ii) To a mixture of $(C_6H_5)(CH_3)(i\text{-}C_3H_7)SbS$ (26.2 g, 90.6 mmol) and $(C_2H_5)_2InI^5$ (27.3 g, 90.1 mmol), methanol (50 ml) was added under a nitrogen atomosphere, and the solution was stirred for 10 h at 60°. After the removal of the solvent from the filtrate, the residual solid was recrystallized to give 15.7 g (38 %) of [I].

$\underline{(C_6H_5)(CH_3)(C_2H_5)(n\text{-}C_3H_7)SbI}$ [II]. This compound was prepared in 70 % yield from $(C_6H_5)(CH_3)(n\text{-}C_3H_7)Sb$ and $(C_2H_5)_3OBF_4$ in a manner similar to (i) described above, and was recrystallized from acetone/ether: m.p. 83.5-84°. (Found: C, 34.69; H, 4.98. $C_{12}H_{20}SbI$ calcd.: C, 34.90; H, 4.88 %.) PMR($CDCl_3$)(δ): 2.44 (s, $SbCH_3$).

Resolution of [I] and [II].

[I]. To a solution of [I] (14.5 g, 35 mmol) in methanol (50 ml), silver-(-)-dibenzoylhydrogentartrate (DBHT)[6] (16.3 g, 35 mmol) was added, and the solution was stirred for 10 h. After the removal of the solvent from the filtrate, the residual solid was recrystallized several times from ethyl acetate to give 1.37 g (12 %) of $(C_6H_5)(CH_3)(C_2H_5)(i\text{-}C_3H_7)Sb$-(-)-DBHT of $[\alpha]_D^{18}$ -66.5° (c 1.023 in methanol); m.p. 115-116°. (Found: C, 55.78; H, 5.28. $C_{30}H_{33}O_8Sb$ calcd.: C, 56.01; H, 5.17 %.)

To a solution of the dibenzoylhydrogentartrate (0.48 g, 0.75 mmol) in methanol (10 ml), potassium iodide (0.5 g) was added, and the solution was stirred for 2 h.

After the removal of the solvent under reduced pressure, the residual solid was extracted with dichloromethane (10 ml). The solid obtained from the filtrate was recrystallized from dichloromethane/benzene or acetone/ether to give 0.097 g (31 %) of dextrorotatory stibonium iodide [(+)-I] of $[\alpha]_D^{26}$ +4.10° (c 0.634 in methanol); m.p. 107°. (Found: C, 34.66; H, 5.00. Calcd.: C, 34.90; H, 4.88 %.)

In a quite similar manner levorotatory stibonium iodide [(-)-I] was obtained by using Ag-(+)-DBHT.

$(C_6H_5)(CH_3)(C_2H_5)(i\text{-}C_3H_7)Sb$-(+)-DBHT. $[\alpha]_D^{21}$+65.7° (c 1.43 in methanol), m.p. 112-113°. (Found: C, 55.79; H, 5.16. Calcd.: C, 56.01; H, 5.17 %.)

[(-)-I]. $[\alpha]_D^{21}$ -2.9° (c 2.26 in methanol), m.p. 109-110°. (Found: C, 34.88; H, 4.99. Calcd.: C, 34.90; H, 4.88 %.)

<u>[II]</u>. This compound was resolved by practically the same procedure to that for [I] except that stibonium dibenzoylhydrogentartrate was recrystallized from dichloromethane/ethyl acetate.

$(C_6H_5)(CH_3)(C_2H_5)(n\text{-}C_3H_7)Sb$-(-)-DBHT. $[\alpha]_D^{21}$ -70° (c 0.779 in methanol), m.p. 119-120°. (Found: C, 55.62; H, 5.01. $C_{30}H_{33}O_8Sb$ calcd.: C, 56.01; H, 5.17 %.)

[(-)-II]. $[\alpha]_D^{21}$ -0.85° (c 12.3 in methanol), m.p. 85-85.5°. (Found: C, 34.68; H, 4.91. Calcd.: C, 34.90;

H, 4.88 %.)

$(C_6H_5)(CH_3)(C_2H_5)(n\text{-}C_3H_7)Sb\text{-}(+)\text{-}DBHT$. $[\alpha]_D^{21}$ +68.3° (c 1.87 in methanol), m.p. 120°. (Found: C, 56.07; H, 5.22. Calcd.: C, 56.01; H, 5.17 %.)

[(+)-II]. $[\alpha]_D^{21}$ +2.2° (c 8.18 in methanol), m.p. 85-85.5°. (Found: C, 34.96; H, 4.89. Calcd.: C, 34.90; H, 4.88 %.)

IV-3. Results and Discussion

Asymmetric stibonium iodides $(C_6H_5)(CH_3)(C_2H_5)RSbI$ [R= $i\text{-}C_3H_7$ [I] and $n\text{-}C_3H_7$ [II]] were prepared by the reaction of $(C_6H_5)(CH_3)RSb$[3] with triethyloxonium fluoroborate[4] in methylene chloride, followed by treatment with potassium iodide in methanol. Compound [I] was also obtained from $(C_6H_5)(CH_3)(i\text{-}C_3H_7)SbS$ and $(C_2H_5)_2InI$, which has been reported to react with $(CH_3)_3SbS$ to give $(CH_3)_3(C_2H_5)SbI$[5].

The stibonium iodides were optically resolved via their dibenzoylhydrogentartrate (DBHT). By using Ag-(-)-DBHT as a resolving agent, dextrorotatory stibonium iodide [(+)-I] was obtained for [I], while levorotatory iodide [(-)-II] was obtained for [II].

By using Ag-(+)-DBHT as a resolving agent, their enantiomers [(-)-I] and [(+)-II] were obtained, respectively. These optically active stibonium iodides were found to be stable as a solid and in solution.

IV-4. References

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V. Summary

Several types of alkyl-substituted asymmetric organoantimony compounds, tertiary stibines, tertiary stibine sulfides, thiostibines and quarternary stibonium iodides have been prepared and their stereochemical properties were clarified.

1) Asymmetric tertiary stibines $(C_6H_5)(CH_3)RSb$ (R= alkyl) were prepared in fairly good yields via cleavage of one phenyl group in $(C_6H_5)_2(CH_3)Sb$ with sodium in liquid ammonia, followed by the treatment with alkyl chlorides. In the reaction of other tertiary phenylalkylstibines with sodium, however, the cleavage of alkyl-antimony bond occurred. The configuration of the asymmetric stibines was found to be stable from the PMR data.

2) From the observation of isomerization of asymmetric ditertiary stibine sulfides, a possibility of configurational lability of tertiary stibine sulfide was suggested for the first time. On the other hand, the configuration of asymmetric thiostibines was suggested to be stable from the PMR data.

3) Optically active stibonium iodides were prepared for the first time and found to be stable as a solid and in solution.

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