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PREPARATION AND CONFIGURATIONAL ISOMERISM OF DITERTIARY STIBINE SULFIDES, $(C_6H_5)(CH_3)(S)SbCH_2Sb(CH_3)(C_6H_5)$ AND $[(C_6H_5)(CH_3)(S)Sb]_2(CH_2)_3$

SHIN-ICHI SATO* and YOSHIO MATSUMURA

Department of Petroleum Chemistry, Osaka University, Yamadakami, Suita, Osaka 565 (Japan)

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Summary

Asymmetric ditertiary stibine sulfides $(C_6H_5)(CH_3)(S)SbCH_2Sb(CH_3)(C_6H_5)$ and $[(C_6H_5)(CH_3)(S)Sb]_2(CH_2)_3$ have been prepared. It was found that they exist as only one of two possible diastereomers in the crystalline state. 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.

Introduction

It has been reported that the 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.

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. IR spectra were recorded using a Hitachi 225 spectrometer equipped with gratings.

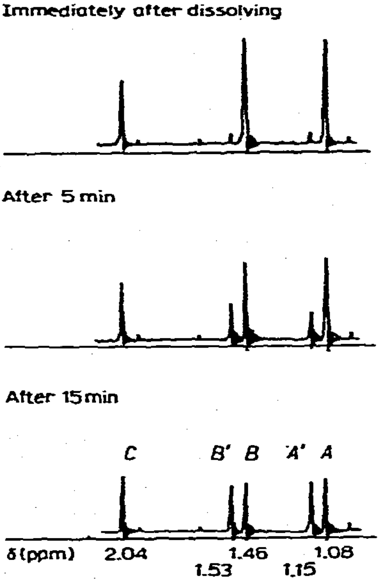
Preparation of asymmetric tertiary stibine sulfides

The sulfides described below were obtained by the reaction [11] in methanol of $Na_2S \cdot 9H_2O$ (2 mol) with $[(C_6H_5)(CH_3)SbCl_2]_2(CH_2)_n$ ($n = 1$ and 3) (1 mol) or $(C_6H_5)(CH_3)(i\text{-}C_3H_7)SbBr_2$ (2 mol). In the reaction with $[(C_6H_5)(CH_3)SbCl_2]_2CH_2$, the expected formation of $[(C_6H_5)(CH_3)(S)Sb]_2CH_2$ was not observed.

$(C_6H_5)(CH_3)(S)SbCH_2Sb(CH_3)(C_6H_5)$ (I). Methanol (80 ml) was added 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), and the solution was stirred for 5 h under a nitrogen atmosphere. The solvent was removed in vacuo from the filtrate, and the residual solid was extracted with dichloromethane (60 ml). Evaporation of the extracts left a solid which was recrystallized several times from ethanol to remove the liberated sulfur. Colorless crystals of I were obtained in 40% yield (3.2 g); 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 recrystallized from dichloromethane/methanol; m.p. 141-142° (85% yield). (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 Figs. 1 and 2, respectively.



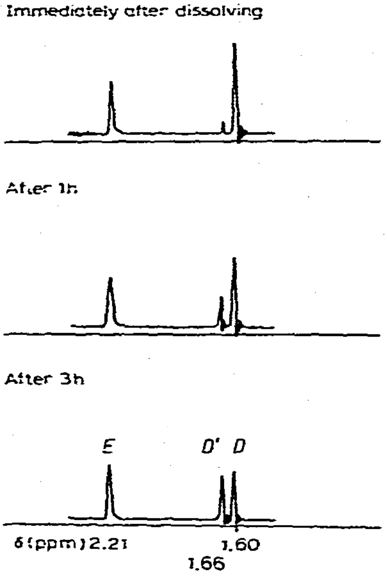


Fig. 1. PMR spectra of $(C_6H_5)(CH_3)(S)SbCH_2Sb(CH_3)(C_6H_5)$ in dichloromethane (12 wt. %) at room temperature.

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

$(C_6H_5)(CH_3)(i\text{-}C_3H_7)SbS$. (90% yield.) The properties and the PMR data of this compound have been described in our preliminary report [10].

Reaction of triphenylphosphine with ditertiary stibine sulfides

All 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 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 form and a very small amount of the *meso* form of $[(C_6H_5)(CH_3)Sb]_2CH_2$. However, when a solution of triphenylphosphine (0.30 mmol) in dichloromethane (0.3 ml) was added to a dichloromethane solution (0.2 ml) of I (0.17 mmol), which had been prepared 1.5 h earlier, almost equal amounts of both isomers were formed.

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

Results and discussion

It is interesting that the reduction of one antimony(V) in $[(C_6H_5)(CH_3)\text{-}SbCl_2]_2CH_2$ occurred easily on treatment with sodium sulfide, affording the stable monosulfide $(C_6H_5)(CH_3)(S)SbCH_2Sb(CH_3)(C_6H_5)$ (I), while $[(C_6H_5)(CH_3)\text{-}(S)Sb]_2(CH_2)_3$ (II) was obtained from a similar reaction of $[(C_6H_5)(CH_3)SbCl_2]_2\text{-}(CH_2)_3$. The sulfides I and II are monomeric in solution and their Sb—S stretching frequencies both in solution and in the solid are very similar to those of $(CH_3)_3\text{-}SbS$ [11]. These data suggest that the sulfur atom in I and each sulfur atom in II are 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 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 changes were not observed. The removal of the solvent and 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 both isomers***.

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

** The observed value of the intensity ratio A'/A (or B'/B) was 1.0 (or 1.05).

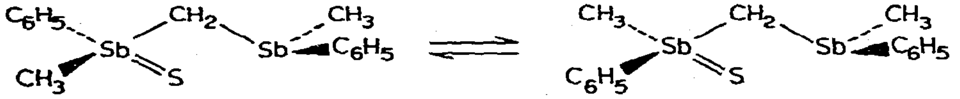
*** The methylene groups are diastereotopic in both isomers and are expected to appear as two AB quartets. Since the signal C did not change on lowering the temperatures even to ca. —90°, the appearance of only one singlet for the methylene groups may be regarded as being due to an accidental coincidence of the chemical shifts of the protons.

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 that equilibrium is reached in solution.

Further support for this isomerization was obtained from the sulfur abstraction reaction of I with $(C_6H_5)_3P$. 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 prepared 1.5 h before, 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 $(CH_3)_3$SbS* suggests the isomerization (inversion of configuration) proceeds through an intermolecular pathway. A reasonable mechanism for this intermolecular process is associative sulfur exchange between two or more $(C_6H_5)(CH_3)(S)$Sb moieties through a pentacoordinate intermediate, in which antimony bonded to sulfur is expected to invert the configuration**. Thus we may illustrate the isomerization of I as shown in eqns. 1 and 2.

(1)



(2)

On raising the temperature 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 changes with temperature was independent of the concentration, there must be another fluxionality in the molecule with an intramolecular mechanism. We may attribute such a process to a rapid migration of sulfur between the two antimony atoms with different oxidation states (III and V). Further, as this process is more rapid than the intermolecular sulfur exchange (inversion), the intramolecular sulfur migration seems to proceed through retention of configuration. The sulfur migration between Sb^{III} and Sb^{V} was also observed between $(C_6H_5)(CH_3)$-$(i\text{-}C_3H_7)$Sb and $(C_6H_5)(CH_3)(i\text{-}C_3H_7)$SbS. In the PMR spectra of a mixture of these two compounds in *o*-dichlorobenzene (ca. 7%, respectively) at ca. 100°,

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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% of I, all solutions containing 4.4 times moles of $(CH_3)_3$SbS.

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

broadenings of signals, which were reversible with temperature, were observed for the isopropyl-methyl groups and the methyl groups bonded to the antimony atoms [Sb^{III} and Sb^{V}]. These broadenings are reasonably regarded as being due to a sulfur migration between the two antimony atoms with different oxidation states.

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, while the signal E, which is assigned to the three methylene groups in both isomers, did not show any change. Removal of the solvent and subsequent recrystallization from dichloromethane/methanol gave crystals which showed a similar spectral change. Although the dependence of the rate of inversion at antimony on the concentration of II in dichloromethane was not determined because of the limited solubility of II, a remarkable effect of an addition of $(CH_3)_3SbS$ on that rate again was 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 that the isomerization proceeds through sulfur exchange.

Finally it should be noted that the PMR spectral behavior of monotertiary stibine sulfide $(C_6H_5)(CH_3)(i\text{-}C_3H_7)SbS$ does not tell whether this compound is configurationally stable or the rate of inversion is very slow on the PMR time scale, since the spectrum showed two doublets for the diastereotopic isopropylmethyl groups invariably over a wide range of concentrations in dichloromethane (from 3.2 to 25 wt. %) at room temperature and in *o*-dichlorobenzene at ca. 100°, above which 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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* When equilibrium was reached, the intensity ratio D'/D was found to be 1.06.

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