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DIASTEREOMERIC ISOMERS OF FIVE-COORDINATE ORGANOANTIMONY COMPOUNDS

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SUMMARY

A series of unsymmetrical diarylantimony trichlorides of the type $PhArSbCl_3$, where Ar is a substituted phenyl group have been prepared. An attempt was then made to convert these to the oxides $(PhArSbCl_2)_2O$. In addition to the known compound $(Ph_2SbCl_2)_2O$, only bis(phenyl-*p*-tolyldichloroantimony) oxide was obtained in pure form. An impure sample of bis(phenyl-*p*-fluorophenyldichloroantimony) oxide was also obtained. PMR spectra of the tolyl compound and ^{19}F spectra of the fluoro compound revealed the presence of two diastereomeric forms for both compounds at low temperature.

Molecules which contain a five-coordinate non-transition element usually exhibit trigonal bipyramidal geometry in both the solid state and in solution, although exceptions to this generalization are known[1]. Since in a trigonal bipyramidal molecule atoms attached to the two apical positions are in a different chemical environment from those attached to the three equatorial positions, even such a simple molecule as Ma_4b could theoretically exist in two isomeric forms. When all five groups are different but symmetric (Mabcde) twenty isomers (ten enantiomeric pairs) are possible. The fact that only a few examples of isomeric trigonal bipyramidal molecules are known has usually been attributed to two phenomena, ligand exchange by a process first suggested by Berry[2] (termed Berry pseudorotation*), and the tendency of the more electronegative groups to seek the apical positions of the trigonal bipyramid (the Muetterties polarity rule)[3].

In 1966 Hellwinkel[4] reported the preparation of both *d* and *l* isomers of the spiro compound I in optically pure states. As far as the authors are aware this is the only reported example of an optically active molecule in which the asymmetry can be ascribed to the five-coordinate central atom. There is considerable evidence for the existence of diastereomeric molecules containing asymmetric five-coordinate atoms[5]. For example, the two compounds IIa and IIb were identified by low temperature NMR studies as occurring in unequal amounts in the product obtained by the reaction of dimethyl phenylphosphonite and 3-benzylidene-2,4-pentanedione[5a,b].

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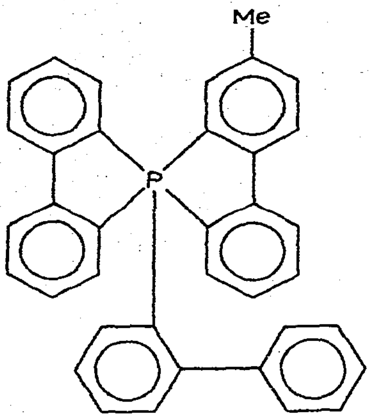
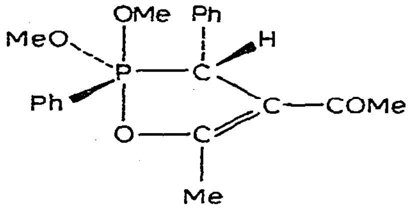
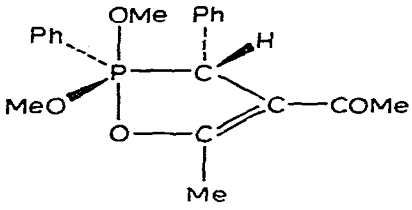
* For reviews on Berry pseudorotation see ref. 14 and 9. For alternative concepts see ref. 6 and 15.



(I)

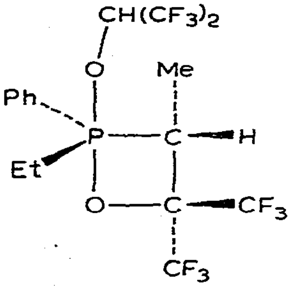


(IIa)

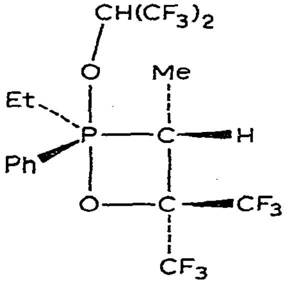


(IIb)

At room temperature there was a rapid equilibrium between the two isomers due to pseudorotation around the five-coordinate phosphorus atom. Ramirez and coworkers[6] have separated the two 1,2-oxaphosphetanes (IIIa and IIIb) by careful fractional crystallization. The two isomers possessed different melting points, and different NMR spectra, but addition of $(CF_3)_2CHOH$ converted either isomer to an equilibrium mixture of both isomers. Ramirez and coworkers[7] have also reported on a rigid and stable dioxaphosphorane which the authors believe "is essentially incapable of pseudorotation".



(IIIa)



(IIIb)

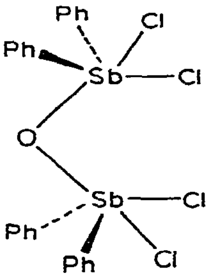
In spite of the paucity of stereoisomers based on trigonal bipyramidal geometry, NMR data suggests that certain suitably substituted acyclic five-coordinate molecules may be rigid at room temperature. Thus Muetterties and coworkers[3] have reported that such molecules as Me_2PF_3, Et_2PF_3, Ph_2PF_3 and $PhMePF_3$ gave two distinct ^{19}F NMR signals which they attributed to equatorial and apical fluorine atoms. The barrier to rearrangement in the molecule H_2NPF_4 is quite large and there is no evidence of intramolecular rearrangement at room temperature; the higher rearrangement barrier in this molecule as compared with the dialkylamino derivatives is probably due to intramolecular hydrogen bonding effects. Schmutzler has summarized the work of several authors on the pseudorotation of molecules of the type RPF_4, R_2PF_3 and R_3PF_2[9]*.

The present paper reports on NMR evidence for the existence of compounds containing five-coordinate antimony atoms in diastereomeric forms. In 1962 Kolditz and coworkers[10] prepared bis(dichlorodiphenylantimony) oxide $(Ph_2Cl_2Sb)_2O$. The compound was obtained in crystalline form when a solution of diphenylantimony trichloride in methanol was allowed to stand at room temperature:

$$2Ph_2SbCl_3 \xrightarrow[H_2O]{MeOH} (Ph_2SbCl_2)_2O + 2HCl$$

Diphenylantimony trichloride usually occurs with one mole of water of crystallization and it is not clear from Kolditz's report whether the anhydrous or the hydrated form was used. In repeating Kolditz's synthesis we have used $Ph_2SbCl_3 \cdot H_2O$; however, the hydrated form is unnecessary for the reaction to proceed. Apparently sufficient water is present in the methanol to effect the hydrolysis.

Bis(dichlorodiphenylantimony) oxide probably occurs as a combination of two trigonal bipyramidal antimony atoms linked through oxygen. If the Muetterties polarity rule is followed the oxygen should occupy one apical position and the molecule should possess structure IV. If one of the Ph groups on each antimony atom is exchanged for other groups the two antimony atoms become asymmetric centers and in the absence of pseudorotation, the molecule should exist in *dl* and *meso* forms. In order to test this possibility and also to gain further insight into the interesting reaction reported by Kolditz we have prepared a series of unsymmetrical diaryl-



(IV)

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* There is a discrepancy between Schmutzler's conclusions that the two compounds Me_3PF_2 and Me_2PF_3 do not undergo ligand exchange at room temperature as based on ^{19}F NMR spectra and a more recent report by Furtsch *et al.*[16] that both compounds undergo fast intermolecular exchange of fluorine atoms at 30°.

TABLE 1

UNSYMMETRICAL DIARYLANTIMONY TRICHLORIDES

Compound *$PhArSbCl_3$*	*M.p.* (°C)	*Yield* (%)	*Analyses found (calcd.)* (%)		
			C	*H*	*Loss at 100°*
p-$CH_3C_6H_4$	153–155[a]	25	39.6 (39.4)	3.32 (3.05)	
p-$NO_2C_6H_4$	161–162	43	33.4 (33.7)	2.48 (2.12)	
p-$ClC_6H_4 \cdot H_2O$	115–118[b]	31	33.3 (33.2)	2.60 (2.54)	4.01 (4.14)
m-ClC_6H_4	134–137	5	34.6 (34.6)	2.76 (2.16)	
p-$FC_6H_4 \cdot H_2O$	155–157	38	34.8 (34.6)	2.81 (2.65)	4.57 (4.30)

[a] Lit. 150–151.5°; 153.5–154°. [b] Lit. 121°.

antimony trichlorides of the type $PhArSbCl_3$ (where Ar was a substituted phenyl group) and have studied their hydrolysis in methanol solution. The trichlorides prepared are given in Table 1. Both the phenyl-*p*-tolyl- and phenyl-*p*-chlorophenylantimony trichlorides have been previously reported[11]; the remaining compounds are new.

In the procedure of Kolditz for preparing bis(dichlorodiphenylantimony) oxide, diphenylantimony trichloride is dissolved in methanol and allowed to stand for 1 h. The yield of oxide which crystallizes from solution was stated to be 36%. Duplication of this procedure in our laboratory gave somewhat lower yields (16–23%). With the crystalline trichlorides listed in Table 1 no crystalline precipitate separated after 1 h in methanol solution but with the phenyl-*p*-tolyl- and phenyl-*p*-fluorophenylantimony trichlorides crystalline precipitates started to form after several hours and precipitation was complete after 1 week. The yields of oxides were approximately 21 and 23%, respectively. None of the other compounds gave crystalline precipitates on prolonged standing nor did the addition of small amounts of water affect the result. In the case of phenyl-*p*-chlorophenylantimony trichloride the starting material was recovered essentially unchanged after removal of the methanol. With both the diphenyl- and phenyl-*p*-tolylantimony trichlorides, some starting material was also recovered after removal of the oxide and evaporation of the methanol. It would appear therefore that the procedure of Kolditz results in an equilibrium:

$$2Ar_2SbCl_3 + H_2O \rightleftharpoons (Ar_2SbCl_2)_2O + 2HCl$$

and that this equilibrium lies partially or almost completely to the left, depending on the nature of the aryl groups. In an attempt to shift the equilibrium to the right various bases were added to the methanol solution of the trichlorides. With pyridine or triethylamine a white precipitate separated immediately, but this precipitate did not contain any bis(diaryldichloroantimony) oxide as judged by IR spectra, and the precipitate was not further investigated. The yield of bis(dichlorodiphenylantimony) oxide was materially increased (84%) by refluxing a solution of diphenylantimony trichloride in a Soxhlet apparatus and removing the HCl by allowing the condensate from the reflux to drip through solid sodium carbonate in the Soxhlet cup. Unfortunately this procedure was not successful with the unsymmetrical diarylantimony trichlorides. The most successful procedure was to add sodium methoxide to the methanol solution of the diarylantimony trichloride. When these solutions were allowed to stand for 24 to 48 hours maximum yields of several of the oxides were obtained. It was also possible to increase the yields by first following Kolditz's procedure and then adding sodium methoxide to the filtrate after removal of the precipitated oxide. By either procedure the yields of the diphenyl, phenyl-*p*-tolyl and phenyl-*p*-fluorophenyl compounds were increased substantially. The results with these three compounds are given in Table 2.

TABLE 2

BIS(DIARYLDICHLOROANTIMONY) OXIDES

Compound $(PhArSbCl_2)_2O$	*Yield* (%)	*Analyses found(calcd.)* (%)	
		C	*H*
C_6H_5	100	40.7 (40.6)	2.91 (2.84).
p-$CH_3C_6H_4$	93	41.9 (42.3)	3.28 (2.94)
p-FC_6H_4	83.5	38.9 (38.7)	2.43 (2.71)

Somewhat different results were obtained with phenyl-*p*-nitrophenyl- and phenyl-*p*-chlorophenylantimony trichloride. With the nitro compound a crystalline precipitate formed on standing when sodium methoxide was added to a methanol solution of the trichloride. The material, after several recrystallizations from carbon tetrachloride, proved to be bis(diphenyldichloroantimony) oxide as judged both by analyses and by infrared spectra. With phenyl-*p*-chlorophenylantimony trichloride in methanol in the presence of sodium methoxide no precipitate formed even on prolonged standing. After removal of the methanol, the gummy residue was extracted with carbon tetrachloride leaving a residue of sodium chloride. We were unable to obtain a pure sample of bis(phenyl-*p*-chlorophenyldichloroantimony) oxide from the carbon tetrachloride solution. It would appear that both in the case of the phenyl-*p*-nitrophenyl- and phenyl-*p*-chlorophenylantimony trichlorides disproportionation had occurred. Because of the limited amount of phenyl-*m*-chlorophenylantimony trichloride available no attempts were made to prepare the corresponding oxide.

In previous papers from this laboratory[12] it has been noted that compounds which contain the Sb–O–Sb linkage give an intense, broad absorption band in the 750–775 cm^{-1} region of the infrared spectra. The infrared spectra of the compounds listed in Table 2 showed this strong band occurring between 770 and 785 cm^{-1}. Other than this band the infrared spectra of these compounds were almost identical with the spectra of the corresponding diarylantimony trichlorides. The 770–785 band has proved to be of great value in determining the formation (or lack of formation) of the bis(diaryldichloroantimony) oxides during the course of this work.

The two compounds bis(phenyl-*p*-tolyldichloroantimony) oxide and bis(phenyl-*p*-fluorophenylantimony) oxide should lend themselves to NMR investigations of the existence of stereoisomerism in this class of compound. The ^{1}H NMR spectrum of bis(phenyl-*p*-tolyldichloroantimony) oxide at 27° in deuterochloroform showed a single sharp peak for the methyl group at τ 7.6. As the temperature was lowered (in methylene dichloride solution) the signal broadened and at $-90°$ was split so that the presence of two peaks was discernible (Fig. 1). The separation, however, was only 10 Hz at 100 MHz. The fact that the two peaks are of unequal heights (the ratio is approximately 1/2.5) strongly suggests that we are dealing with the two diastereomeric forms of bis(phenyl-*p*-tolyldichloroantimony) oxide which are undergoing stereomutation at room temperature, presumably by Berry pseudorotation. Somewhat different results were obtained with bis(phenyl-*p*-fluorophenyldichloroantimony) oxide. Here the ^{19}F spectrum showed evidence of splitting into two peaks at room temperature (Fig. 2). The separation between peaks is approximately 100 Hz at 94.1 MHz. Accordingly an attempt was made to separate the mixture by fractional crystallization from carbon tetrachloride solution. The actual course of the separation could be followed by ^{19}F spectra on successive fractions. Eventually two fractions were obtained each of which gave a single ^{19}F peak. The more soluble fraction gave a sharp signal at δ 105 ppm (referred to CFCl$_3$); the less soluble fraction gave a signal at δ 106.2

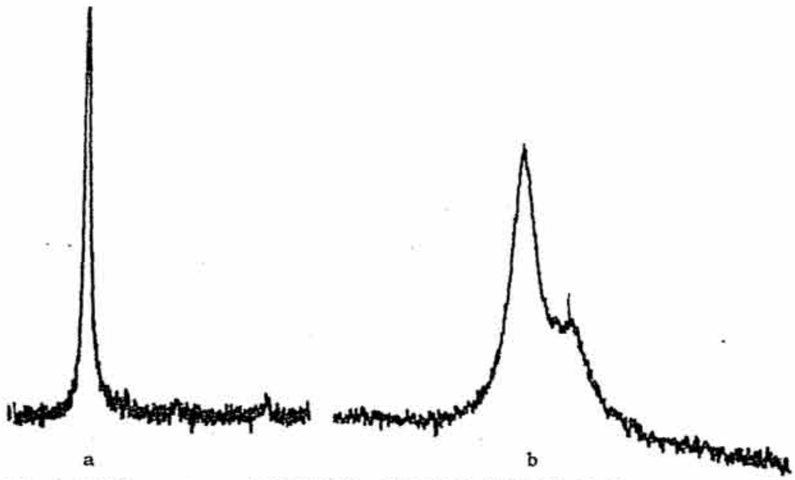

Fig. 1. PMR spectrum of $[(C_6H_5)(p\text{-}CH_3C_6H_4)SbCl_2]_2O$, (a) at room temperature; (b) at $-90°$.

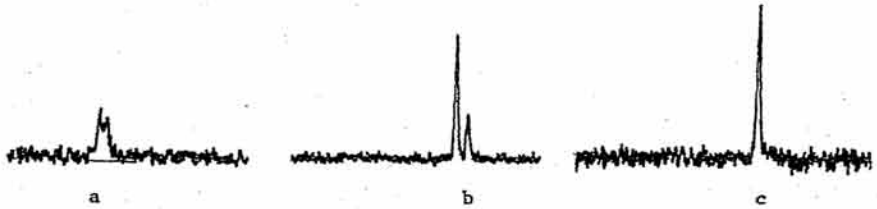

Fig. 2. ^{19}F spectrum of $[(C_6H_5)(p\text{-}FC_6H_4)SbCl_2]_2O$, (a) uncrystallized product; (b) the more soluble fraction after partial fractional crystallization; (c) the pure more-soluble product showing a single ^{19}F peak.

ppm, (again referred to $CFCl_3$). The melting points of the two fractions were 135–138° and 167–168°, respectively; the mixture of the two compounds melted over a wide range from 130 to 150°. The infrared spectra of the two compounds are fairly similar but not identical. In the lower melting material the Sb–O–Sb stretching frequency appears about 770 cm^{-1}, whereas with the higher melting material this band is closer to 780 cm^{-1}.

Although these results are consistent with the existence of the oxide in *dl* and *meso* forms, there is also the possibility that in the preparation of bis(phenyl-*p*-fluorophenyldichloroantimony) oxide some disproportionation had occurred and that the product was a mixture of the desired oxide with some bis(diphenyldichloroantimony) oxide and bis(di-*p*-fluorophenyldichloroantimony) oxide. If the latter two compounds were present in equal amounts elemental analysis of the original material would not distinguish between the two possibilities. Furthermore the ^{19}F spectrum would show the presence of two fluorine peaks*. However, elemental analysis of the two materials obtained after fractional crystallization should distinguish clearly between the two possibilities. Indeed, elemental analysis of the more soluble fraction confirmed the fact that this was essentially pure bis(di-*p*-fluorophenyldichloroantimony) oxide (Found: C, 36.45; H, 2.39. $C_{24}H_{16}F_4Cl_4OSb_2$ calcd.: C, 36.92; H, 2.10%). The compound gave a single ^{19}F NMR signal (δ 106.6 ppm referred to $CFCl_3$) which was not broadened when the temperature was lowered to −60°. Elemental analysis of the less soluble fraction suggested that it was a mixture of bis(diphenyldichloroantimony) oxide and bis(phenyl-*p*-fluorophenyldichloroantimony) oxide (Found: C, 39.93; H, 2.65; F, 3.88. $C_{24}H_{18}F_2Cl_4OSb_2$ calcd.: C, 38.65; H, 2.43; F, 5.09%). Based on the fluorine analysis and assuming the presence of only the two compounds mentioned above these results would be in agreement with a mixture of 77% of bis(phenyl-*p*-fluorophenyldichloroantimony) oxide and 23% bis(diphenyldichloroantimony) oxide. It is surprising that this mixture melted over such a narrow range (167–168°). The ^{19}F NMR spectrum of this mixture in methylene chloride gave a single signal at room temperature which broadened as the temperature was lowered and was split into two peaks (δ 106.2 and 113.2 referred to $CFCl_3$) when the temperature was cooled to −60°. In view of the fact that repeated fractional crystallization had not effected complete separation of the two compounds and after preliminary experiments with separation by chromatography did not appear promising, no further attempt to separate the mixture was made.

We conclude, however, that both bis(phenyl-*p*-tolyldichloroantimony) oxide and bis(phenyl-*p*-fluorophenylantimony) oxide exist in *dl* and *meso* forms at low temperature but that these forms undergo rapid stereomutation at room temperature.

EXPERIMENTAL

Nesmeyanov and coworkers[11a] prepared a series of unsymmetrical diarylantimony trichlorides by the reaction of aryldichlorostibines with diazonium salts of the type $[ArN_2][SbCl_4]$ in acetone solution:

$$ArSbCl_2 + [Ar'N_2][SbCl_4] \rightarrow ArAr'SbCl_3 + SbCl_3 + N_2$$

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* The authors gratefully acknowledge the suggestions of one of the referees in this regard.

Actually the diarylantimony trichlorides were usually not isolated but were characterized as the so-called diazonium double salts $[Ar'N_2][ArAr'SbCl_4]$. We have employed a somewhat similar reaction in the present study, namely the reaction of an arenediazonium tetrafluoroborate with phenyldichlorostibine. Ethanol was used as the solvent and cuprous bromide as a catalyst. The preparation of phenyl-*p*-fluorophenylantimony trichloride is illustrative of the method used.

Phenyl-p-fluorophenylantimony trichloride

Phenyldichlorostibine (101 g) was dissolved in 350 ml of absolute ethanol and added to a suspension of 79 g of *p*-fluorobenzenediazonium tetrafluoroborate in 50 ml of absolute ethanol. Cuprous bromide (5 g) was added. The reaction was stirred during the vigorous evolution of nitrogen and for 1 h after nitrogen was no longer evolved. The alcohol was then removed *in vacuo* by means of a rotary evacuator. The resulting solid was then extracted several times with 5 *N* NaOH until a few drops of the extracting fluid gave no precipitate upon acidification. The alkaline solution was filtered and acidified to pH 6.2 with acetic acid, whereupon a dense precipitate of phenyl-*p*-fluorophenylstibinic acid separated from solution. (The pH for maximum precipitation varies with different stibinic acids and since the acids redissolve on the acid side care must be taken to reach the desired pH for maximum precipitation). The precipitated acid was then dissolved in the minimum amount of boiling 5 *N* HCl. Upon cooling $(C_6H_5)(p\text{-}FC_6H_4)SbCl_3 \cdot H_2O$ crystallized from solution. The compound may be recrystallized from 5 *N* HCl to give a 38% yield of the trichloride.

Diphenylantimony trichloride

This compound was prepared from diphenylstibinic acid which in turn was prepared from triphenylstibine by oxidative cleavage of one phenyl group. This method was first proposed by Schmidt[13] but no yields were given. In this laboratory Schmidt's method gave poor and variable results. As a consequence the reaction was carried out under a variety of conditions in an attempt to improve the yield. The following procedure gives diphenylstibinic acid in over 90% yield. Triphenylstibine (80 g) was dissolved in 250 ml of acetone and added dropwise to 1.5 liter of an aqueous solution containing 500 g of NaOH and 600 ml of 6% hydrogen peroxide. The mixture was then heated to boiling and boiled for 8 h. During the heating process 120 ml of 30% H_2O_2 were added in 40 ml increments every 2 h. The dark solution was filtered through sintered glass and the alkaline solution acidified to Congo-red paper whereupon a 96% yield of crude diphenylstibinic acid separated from solution. The acid may then be converted into the trichloride, $Ph_2SbCl_3 \cdot H_2O$, by crystallizing from 5 *N* HCl. The yield on this last step is usually about 65%.

Bis(phenyl-p-tolyldichlorantimony) oxide

To a solution of 4.0 g (0.01 mole) of phenyl-*p*-tolylantimony trichloride in 100 ml of methanol 0.6 g of sodium methoxide was added and the solution allowed to stand for 48 h. The crystalline precipitate which formed was removed by filtration, washed with methanol and dried. It can be readily recrystallized from benzene.

Determination of spectra

Infrared spectra were determined between 4000 and 250 cm^{-1} on a Perkin–Elmer 521 infrared spectrophotometer. The spectra were run as Nujol mulls. The NMR spectra were determined on a Varian HA-100 high resolution spectrophotometer, with methylene dichloride as the solvent for the fluorine spectra and deuterochloroform as the solvent for the proton spectra at room temperatures.

Analyses

Elemental analyses were done by Galbraith Laboratories, Inc., Knoxville, Tennessee. Melting points were determined on a Mel-Temp melting point apparatus and are uncorrected.

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