

# STUDIES ON ORGANOMETALLIC COMPOUNDS. I.

## Dialkyl and Diphenyl-*p*-chlorophenylantimony and Their Dibromides<sup>1)</sup>

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As a part of a study on organometallic compounds, several of tervalent organoantimony compounds, dimethyl- (II), diethyl- (III), di-*n*-propyl- (V), and cyclopentamethylene-*p*-chlorophenylantimony (VI), were synthesized by the coupling reaction of *p*-chlorophenyldiiodoantimony (I) with the corresponding Grignard reagent. The bromination of II-VI gave the corresponding pentavalent dibromides (VII-XI).

The structures of the tervalent and pentavalent organoantimony compounds are discussed on the basis of their spectral data.

### 1. INTRODUCTION

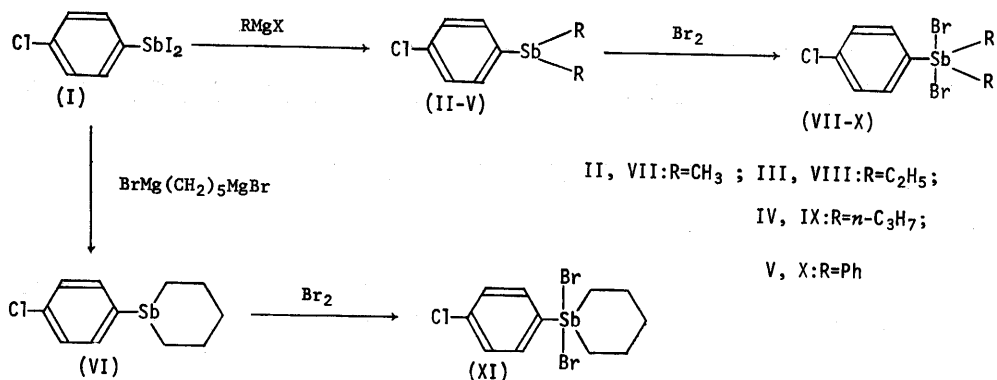
A wide variety of tervalent and pentavalent organoantimony compounds which possess the same substituents such as trialkyl- and triarylantimony and their dihalides have been synthesized and studied by several investigators,<sup>2-9)</sup> while the synthesis and investigation of chemical and physical properties or the structures of the  $R'R_2Sb$  and  $R'R_2SbX_2$  type compounds, where  $R'$  is aryl,  $R$  is alkyl, and  $X$  is halogen atom, have not been satisfactorily carried out as yet. This paper deals with the synthesis of dialkyl-, and cyclopentamethylene-*p*-chlorophenylantimony and their dibromides.

### 2. RESULTS AND DISCUSSION

*p*-Chlorophenyldiiodoantimony (I) was prepared from trichloroantimony and *p*-chloroaniline according to the method described by Campbell.<sup>10)</sup> The coupling reaction between I and methylmagnesium iodide, ethyl, *n*-propyl, and phenylmagnesium bromides or double Grignard reagent of 1,5-dibromopentane gave the corresponding dimethyl- (II), diethyl- (III), di-*n*-propyl- (IV), diphenyl- (V), and cyclopentamethylene-*p*-chlorophenylantimony (VI), respectively. Among these tervalent antimony compounds, only V is stable in air, while the other compounds are oxidized very easily so that they must be kept in a nitrogen atmosphere.

Dimethyl- (VII), diethyl- (VIII), di-*n*-propyl- (IX), diphenyl- (X), and cyclopentamethylene-*p*-chlorophenylantimony dibromide (XI) were respectively obtained by the bromination of II-VI in ether or in carbon tetrachloride at room temperature under an atmosphere of nitrogen.

In the IR spectra, each of the compounds (I-XI) showed the characteristic



Scheme 1. Preparation and Bromination of II-VI.

absorption bands due to *p*-chlorophenyl group, that is, the C-H stretching absorption bands appeared in the 3080-3000 cm<sup>-1</sup> region and the ring skeletal vibrations both in the 1569-1563 cm<sup>-1</sup> and 1482-1474 cm<sup>-1</sup> regions. The C-H in-plane and out-of-plane deformation vibration bands were also observed in the 1100-1000 and 810-803 cm<sup>-1</sup> region respectively. In the compounds II-IV, VI-IX, and XI. the absorption bands due to the C-H stretching vibration of the methyl and/or methylene group appeared in the general 3000-2845 cm<sup>-1</sup> region.

Table 1. Characteristic bands in the IR spectra of I-XII (cm<sup>-1</sup>).

	C-H stretching	C-H out-of-plane deformation	X-sensitive
I		804	486
II	2988, 2915	807	483
III	2955, 2921, 2865	804	480
IV	2957, 2929, 2900, 2869	805	482
V		809, 730, 694	488, 454
VI	2913, 2845	803	481
VII	3000, 2921	809	484
VIII	2955, 2922, 2860	805	482
IX	2965, 2924, 2865	810	485
X		806, 727, 677	484, 449
XI	2920, 2854	808	482
XII		730, 680	453

Long *et al.*<sup>7)</sup> assigned the absorption band at 1387 cm<sup>-1</sup> in the IR spectrum of trimethylantimony dibromide to the C-H asymmetric deformation vibration of the methyl group. In II and VII, the bands assignable to the asymmetric deformation of the Sb-CH<sub>3</sub> were observed at 1404 and 1390 cm<sup>-1</sup> respectively, while those of III, IV, VIII, and IX shifted to the general region and appeared at 1456,

1456, 1452, and 1454  $\text{cm}^{-1}$  respectively.

The bands at 2913 and 2845  $\text{cm}^{-1}$  in the spectrum of VI, were assignable to the C-H stretching and the band at 1441  $\text{cm}^{-1}$  to the C-H deformation vibrational frequency of the methylene groups. Bands corresponding those of XI also appeared at the same frequencies (2920, 2854, and 1446  $\text{cm}^{-1}$  respectively).

In the KBr region (650-400  $\text{cm}^{-1}$ ), all the compounds (I-XI) showed a strong absorption band at 488-480  $\text{cm}^{-1}$  region, which may be assignable to the X-sensitive band. On the other hand, X-sensitive bands were observed at 454  $\text{cm}^{-1}$  in V, at 449  $\text{cm}^{-1}$  in X, and at 453  $\text{cm}^{-1}$  in triphenylantimony dichloride (XII)<sup>4a</sup>, respectively.

The NMR spectral data are shown in Tables 2 and 3, from which the structures of all of the compounds (I-XII) were confirmed. In relation to the NMR spectral difference between trivalent (II-VI) and pentavalent antimony compounds (VII-XI), for example, the proton chemical shift of III was comparable to that of VIII. Compound III indicated signals at higher magnetic fields of 0.77 ppm for the *ortho*-proton and of 0.26 ppm for the *meta*-proton than those corresponding to VIII. In general, the proton chemical shift of the pentavalent compound shifted to a lower magnetic field than that of the corresponding trivalent com-

Table 2. NMR data of II, III, IV, VII, VIII, and IX. ( $\delta$  value, at 60 MHz)<sup>a)</sup>

	II	VII	III	VIII	IV	IX
Cl-C <sub>6</sub> H <sub>4</sub> Sb protons						
<i>ortho</i> -position to Sb	7.33 (2H, d, $J=8.3$ Hz)	7.54 <sup>b)</sup> (2H, d, $J=8.3$ Hz)	7.32 (2H, d, $J=8.3$ Hz)	8.09, 7.53 <sup>b)</sup> (2H, d, $J=8.3$ Hz)	7.31 (2H, d, $J=8.3$ Hz)	8.13 (2H, d, $J=8.3$ Hz)
<i>meta</i> -position to Sb	7.18 (2H, d, $J=8.3$ Hz)	7.07 <sup>b)</sup> (2H, d, $J=8.3$ Hz)	7.17 (2H, d, $J=8.3$ Hz)	7.43, 7.06 <sup>b)</sup> (2H, d, $J=8.3$ Hz)	7.15 (2H, d, $J=8.3$ Hz)	7.42 (2H, d, $J=8.3$ Hz)
Alkyl protons						
Sb-CH <sub>3</sub> proton	0.87 (6H, s)	2.39 <sup>b)</sup> (6H, s)				
$\begin{array}{c}   \\ -\text{C}-\text{CH}_3 \text{ proton} \\   \end{array}$				1.58, 1.22 <sup>b)</sup> (6H, t, $J=7.5$ Hz)	0.91 (6H, t, $J=7.5$ Hz)	1.05 (6H, t, $J=7.5$ Hz)
Sb-CH <sub>2</sub> - $\begin{array}{c}   \\ -\text{C}- \\   \end{array}$			1.67-0.95 (10H, m)	3.07, 2.75 <sup>b)</sup> (4H, q, $J=7.5$ Hz)	1.70-1.40 (8H, m)	3.07 (4H, t, $J=7.5$ Hz)
$\begin{array}{c}   \\ -\text{C}-\text{CH}_2-\text{C}- \\   \end{array}$						2.05 (4H, sextet, $J=7.5$ Hz)

a) The spectra were measured at 60°C in carbon tetrachloride with hexamethyldisiloxane (HMDS) as the internal reference, the sample concentration was maintained at 1/30 (mol/mol).

b) Trichloroacetic acid was used as the solvent.

Table 3. NMR data of I, V, VI, X, XI, and XII ( $\delta$  value, at 60 MHz)<sup>a)</sup>

	I <sup>b)</sup>	V	X	XII	VI	XI <sup>c)</sup>
Ring protons						
<i>ortho</i> -position to Sb	7.84 (2H, d, $J=8.3$ Hz)		8.15-7.99 (6H, m)	8.33-8.06 (6H, m)	7.30 (2H, d, $J=8.3$ Hz)	7.49 (2H, d, $J=8.3$ Hz)
<i>meta</i> -position to Sb	7.32 (2H, d, $J=8.3$ Hz)	7.20 (14H, s)			7.17 (2H, d, $J=8.3$ Hz)	7.00 (2H, d, $J=8.3$ Hz)
<i>para</i> -position to Sb			7.44-7.32 (8H, m)	7.46-7.30 (9H, m)		
Cyclopentamethylene protons						
$\alpha$ -position to Sb						2.95 (4H, t, $J=6.3$ Hz)
$\beta$ -and $\gamma$ -position to Sb					1.59 (10H, s)	2.20-1.40 (6H, m)

a) The spectra were measured at 60°C in carbon tetrachloride with HMDS as the internal reference, and the sample concentration was maintained at 1/30 (mol/mol).

b) Measured at 69°C. c) Measured at 66°C in trichloroacetic acid.

pound, although in the case of II and VII, strict comparison was not possible because the NMR data were obtained in different solvents. This lower shift of the proton signal in pentavalent compounds can be explained by increase in the electronegativity of Sb with change in valency from trivalent to pentavalent. Some comments on this explanation are given in the discussion of the methyl proton shift in the NMR spectra of dimethyl-*p*-chlorophenylantimony dihalides.<sup>11)</sup>

The structures of the pentavalent antimony compounds such as trialkyl and triarylantimony dihalides have been established by the work of several investigators. Wells,<sup>8)</sup> on the basis of X-ray diffraction method, confirmed that trimethylantimony dihalides are in the form of a trigonal bipyramid structure with the three methyl groups in the plane of antimony atom and two halogen atoms at the apices. Jensen<sup>12)</sup> obtained the dipole moment values for triphenylantimony dihydroxide and XII, and assigned trigonal bipyramid structure to these compounds. This structure was later confirmed for XII by Polynova *et al.*<sup>9)</sup> by means of X-ray diffraction technique.

From the facts mentioned above and the Muetterties rule, X can be assumed to take the trigonal bipyramid structure, similar to XII. The NMR spectra of VII, VIII, and IX supported that the *p*-chlorophenyl group, two of the same alkyl groups, two bromine atoms, and an antimony atom compose a similar trigonal bipyramid molecule. For example, as shown in Fig. 1. the protons of two

methyl groups showed the signal as a singlet at the same position and each of the two protons in the *ortho*- and *meta*-positions on the ring revealed the corresponding doublet in the spectrum of VII, indicating that the protons of two methyl groups are equivalent nuclei. Similarly, VIII and IX showed excellent symmetry of the proton signals of two methyl groups and the *p*-chlorophenyl ring in the NMR spectra.

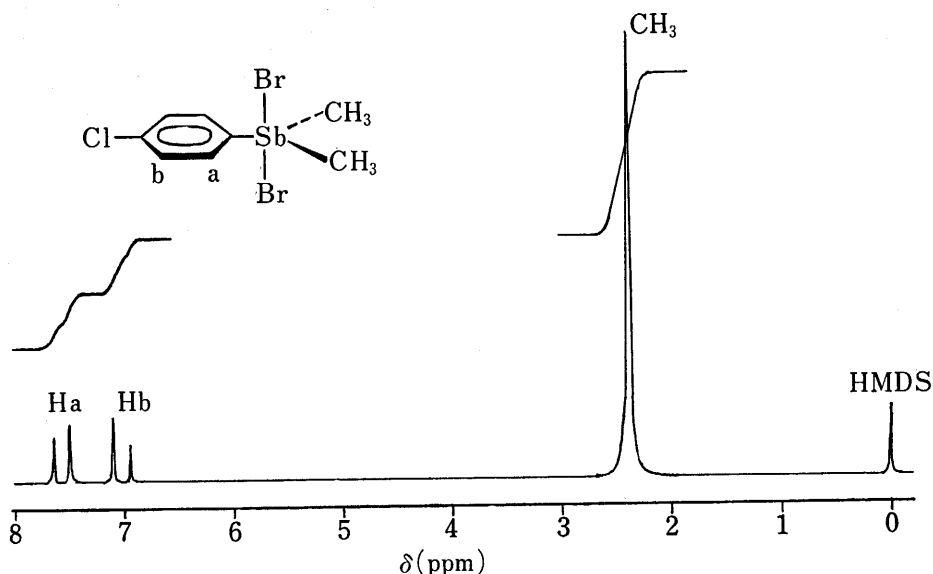


Fig 1. NMR NMR spectrum of VII (in  $\text{CCl}_3\text{COOH}$ ).

### 3. EXPERIMENTAL

The melting and boiling points are uncorrected. The elemental analyses were carried out with a Yanagimoto CHN Corder, MT-2 type. The infrared absorption (IR) spectra were taken on a JASCO Model IRA-2 grating infrared spectrophotometer. The nuclear magnetic resonance (NMR) spectra were measured with a Japan Electron Optics Lab. Co. spectrometer, JNM-C-60HL, at 60 MHz with hexamethyldisiloxane as the internal reference and the chemical shifts are expressed in  $\delta$ -values. The mass spectra were taken on a Hitachi RMU-6L mass spectrometer at 70 eV.

***p*-Chlorophenyldiiodoantimony (I).** This compound was prepared according to a method described by Campbell.<sup>10)</sup> A solution of *p*-chlorophenyldiazonium chloride which was prepared by the diazotization of *p*-chloroaniline (127.6 g, 1.0 mol) with sodium nitrite (69.0 g, 1.0 mol) in 10% hydrochloric acid (750 ml) was added dropwise to a solution of antimony trichloride (228.1 g, 1.0 mol) in 35% hydrochloric acid (800 ml) at  $-10^\circ$  to  $-5^\circ\text{C}$ . The precipitated cream-colored double salt was filtered, washed with cold ethanol, and dried in air. This double salt was

suspended in a mixture of ethanol (850 ml) and 35 % hydrochloric acid (90 ml), and copper powder (2-3 g) was added in several portions to this suspension and then heated at 30-35°C for 3 hr. After cooling, the insoluble material was filtered off, and the filtrate was poured into cold water (1.5 l) with cooling, subsequently the precipitated white stibonic acid was filtered and washed thoroughly with water.

To a solution of the above moist stibonic acid in 20 % hydrochloric acid (1.3 l) was added dropwise a solution of stannous chloride dihydrate (180 g, 0.8 mol) in 35 % hydrochloric acid (300 ml) at -10° to -5°C and stirring was continued for 1 hr. The insoluble material was filtered out and an aqueous solution of potassium iodide (265.6 g, 1.6 mol in 200 ml of water) was added to the filtrate at -10° to -5°C. The precipitated yellow crystals were collected, dried, and recrystallized from carbon tetrachloride to obtain 267.9 g (55 % based on *p*-chloroaniline) of I as yellow needles which melted at 89°C. Mass *m/e* (%): 490 (4.1)/488 (16.8)/486 (16.7) (M<sup>+</sup>), 363 (22.2)/361 (100)/359 (89.8) (M-I)<sup>+</sup>.

Found: C, 14.80; H, 0.83 %. Calcd for C<sub>6</sub>H<sub>4</sub>ClI<sub>2</sub>Sb: C, 15.04; H, 0.84 %.

**Dimethyl-*p*-chlorophenylantimony (II).** Compound I (121.7 g, 0.25 mol) was added in several portions to an ethereal solution of methyl-magnesium iodide (prepared from 0.6 mol of methyl iodide and 0.6 g-atom of magnesium turnings in 1 l of dry ether) in a stream of dry nitrogen, and the reaction mixture was heated under reflux for 1 hr. Water (50 ml) was added gradually to the resulting mixture with cooling and the ether layer was separated. The aqueous layer was extracted with 50 ml portions of ether 2-3 times. The ether extracts were combined with the ether layer and washed with a small amount of water. After concentration of the ether solution, subsequent vacuum distillation gave 51g (77.5 %) of II as a colorless clear liquid; bp 81°C/0.2 mmHg. Mass *m/e* (%): 266 (10.4)/264 (40.1)/262 (39.6) (M<sup>+</sup>), 251 (25.3)/249 (100)/247 (96.6) (M-CH<sub>3</sub>)<sup>+</sup>.

Found: C, 36.26; H, 3.83 %. Calcd for C<sub>8</sub>H<sub>10</sub>ClSb: C, 36.48; H, 3.83 %.

**Diethyl-*p*-chlorophenylantimony (III).** This compound was prepared in the same way as II, but using I (48.7 g, 0.1 mol), ethyl bromide (27.2 g, 0.25 mol), and magnesium turnings (6.1g, 0.25 g-atom). 15.3g (52.5%) of III was obtained as a colorless clear liquid, bp 124.5°C/0.42 mmHg, by the same procedure described above.

Found: C, 41.53; H, 4.64 %. Calcd for C<sub>10</sub>H<sub>14</sub>ClSb: C, 41.22; H, 4.85 %.

**Di-*n*-propyl-*p*-chlorophenylantimony (IV).** The procedure outlined above for II was followed using I (48.7 g, 0.1 mol), *n*-propyl bromide (28.3 g, 0.25 mol), and magnesium turnings (6.1 g, 0.25 g-atom). 16.1 g (50.4 %) of IV was obtained as colorless clear liquid; bp 100°C/0.1 mmHg.

Found: C, 45.31; H, 5.47 %. Calcd for C<sub>12</sub>H<sub>18</sub>ClSb: C, 45.11; H, 5.69 %.

**Diphenyl-*p*-chlorophenylantimony (V).** The method used here was virtually identical with that described for II, but I (243.6 g, 0.5 mol), a few drops of methyl

iodide, bromobenzene (188.4 g, 1.2 mol), and magnesium turnings (29.2 g, 1.2 g-atom) were used; 171.6 g (88.6 %) of V was obtained as a pale yellow oil. Bp 179°C/0.08 mmHg.

Found: C, 55.97; H, 3.69%. Calcd for  $C_{18}H_{14}ClSb$ : C, 55.79; H, 3.65%.

**Cyclopentamethylene-*p*-chlorophenylantimony (VI).** The procedure outlined above for II was employed using I (146.1 g, 0.3 mol), 1,5-dibromopentane (120 g, 0.4 mol), and magnesium turnings (19.4 g 0.8 g-atom). The yield of VI was 66.5 g (73 %), colorless liquid, bp 124°C/0.09 mmHg.

Found: C, 43.63; H, 4.64%. Calcd for  $C_{11}H_{14}ClSb$ : C, 43.52; H, 4.66%.

**Dimethyl-*p*-chlorophenylantimony Dibromide (VII).** To a stirred solution of II (2.63 g, 10 mmol) in dry ether (100 ml) was added dropwise an ethereal solution of bromine at room temperature in a nitrogen stream, until bromine was no longer absorbed. The resulting solution was concentrated and the precipitated crystals were collected, washed with a small amount of ether then dried. Recrystallization from methanol afforded 3.86 g (91.2 %) of VII as colorless micro needles which melted at 157-159°C. Mass *m/e* (%):  $M^+$  was not observed, 347 (11.9)/345 (59.6)/343 (100)/341 (49.3) (M-Br)<sup>+</sup>.

Found: C, 22.75; H, 2.48%. Calcd for  $C_6H_{10}ClBr_2Sb$ : C, 22.70; H, 2.39%.

**Diethyl-*p*-chlorophenylantimony Dibromide (VIII).** A solution of bromine in carbon tetrachloride was added dropwise to a stirred solution of III (4.51 g, 10mmol) in carbon tetrachloride (100 ml) at room temperature in a nitrogen stream until a slight trace of bromine remained. The resulting solution was concentrated to about 20 ml and diluted with cold methanol to crystallize the product. After cooling, the precipitated product was filtered, washed with cold methanol, and dried to give 3.6 g (79.8 %) of VIII as colorless granules; mp 85-86°C.

Found: C, 26.28; H, 3.36%. Calcd for  $C_{10}H_{14}ClBr_2Sb$ : C, 26.62; H, 3.13%.

**Di-*n*-propyl-*p*-chlorophenylantimony Dibromide (IX).** The procedure outlined above for VIII was employed using IV (3.16 g, 10 mmol). The resulting solution was dried *in vacuo* and the oily residue was left standing for several days to solidify. 4.4 g (92 %) of IX was obtained as colorless solid and as this product was pure enough for elementary analysis, further purification was not carried out. Mp 37-41°C

Found: C, 29.99; H, 3.57%. Calcd for  $C_{12}H_{18}ClBr_2Sb$ : C, 30.07; H, 3.79%.

**Diphenyl-*p*-chlorophenylantimony Dibromide (X).** To a stirred, refluxing, solution of V (3.87 g, 10 mmol) in ether (100 ml) was added dropwise to a solution of bromine in ether until the reddish-brown color of bromine disappeared. The resulting solution was concentrated to about 20 ml of the volume and diluted with cold methanol. After cooling, the product was separated, filtered, washed with cold methanol and dried. 3.8 g (69.4 %) of a faint cream-colored powder (X) which melted at 103-106°C was obtained, and although recrystallization from solvents was

not possible, this product was sufficiently pure for elemental analysis.

Found: C, 39.64; H, 2.58 %. Calcd for  $C_{18}H_{14}ClBr_2Sb$ : C, 39.49; H, 2.56 %.

**Cyclopentamethylene-*p*-chlorophenylantimony Dibromide (XI).** The procedure outlined above for VIII was followed using VI (3.03 g, 10 mmol). Work-up as VII described above gave 3.1g (66.9%) of XI as colorless granules; mp 155°C (decomp) (from methanol).

Found: C, 28.75; H, 3.11 %. Calcd for  $C_{11}H_{14}ClBr_2Sb$ : C, 28.52; H, 3.05 %.

**Triphenylantimony Dichloride (XII).** This product was prepared according to the method by Nesmeyanov *et al.*<sup>4a)</sup> from aniline and antimony trichloride. Colorless needles (from ethanol); mp 142-143°C. The yield was 12 %.

Found: C, 51.06; H, 3.80 %. Calcd for  $C_{18}H_{15}Cl_2Sb$ : C, 50.99; H, 3.57 %.

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