

## PENTACHLOROPHENYL-ARSENIC, -ANTIMONY AND -BISMUTH COMPOUNDS

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### Summary

$(C_6Cl_5)_3Sb$  and  $(C_6Cl_5)_3Bi$  have been isolated from  $SbCl_3$  or  $BiCl_3$  and  $C_6Cl_5Li$ .  $AsCl_3$  gives only  $(C_6Cl_5)_2AsCl$  even with a large excess of  $C_6Cl_5Li$ . Treatment of  $(C_6Cl_5)_3Sb$  with halogens gives  $(C_6Cl_5)_3SbX_2$  ( $X = Cl, Br$ ).  $Br_2$  does not react with  $(C_6Cl_5)_2AsCl$  whereas  $Cl_2$  gives an intractable residue which is rapidly hydrolysed to  $[(C_6Cl_5)_2As]_2O$ . Treatment of  $(C_6Cl_5)_3Bi$  with halogens cleaves the C—Bi bonds to give  $C_6Cl_5X$  and unidentified oxohalobismuth(III) derivatives.

### Introduction

We recently described pentafluorophenyl-arsenic [1] and -antimony [2] compounds. The comparative stability of  $C_6F_5-M$  and  $C_6Cl_5-M$  bonds prompted us to extend our research to the preparation and study of the behaviour of similar  $C_6Cl_5$  derivatives. We report here the preparation of arsenic, antimony and bismuth(III) compounds and the results obtained in their reactions with halogens.

### Results and discussion

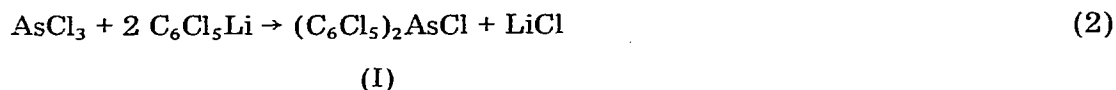
#### (a) Preparative results

Reaction 1 takes place when solutions of  $SbCl_3$  or  $BiCl_3$  in diethyl ether are treated with a solution of  $C_6Cl_5Li$  [3] in a 1/3 molar ratio.



(II, X = Sb;  
 III, X = Bi)

When the same ratio is used in the reaction of  $\text{AsCl}_3$ , only two of the chlorine atoms are substituted, as in eq. 2 and the same result is obtained even with a large excess of  $\text{C}_6\text{Cl}_5\text{Li}$  (molar ratio 1/6).



The different behaviour observed for arsenic may be attributed to the greater strength of the As—Cl bond rather than to the smaller size of the atom since other transition metal derivatives containing four  $\text{C}_6\text{Cl}_5$  groups have been obtained [4].

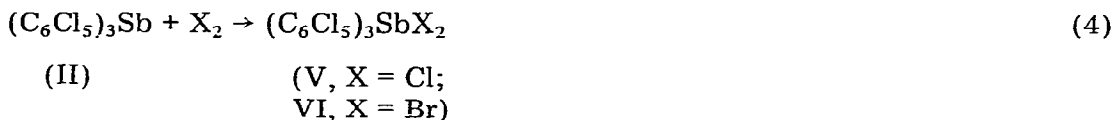
Compounds I—III are insoluble in water so that the  $\text{C}_6\text{Cl}_5\text{—X}$  bonds are not hydrolyzed by water alone; with the pentafluorophenyl species, only  $(\text{C}_6\text{F}_5)_3\text{As}$  [5] resists hydrolysis,  $(\text{C}_6\text{F}_5)_3\text{Sb}$  and  $(\text{C}_6\text{F}_5)_3\text{Bi}$  being partially or totally hydrolyzed. Compounds I and II are stable even in hydrochloric acid, but compound III reacts to give  $\text{C}_6\text{Cl}_5\text{H}$  and  $\text{BiCl}_3$ .

When a suspension of I is treated with a solution of  $\text{Cl}_2$  in  $\text{CCl}_4$ , a colorless solution is obtained which probably contains an arsenic(V) derivative, but this could not be isolated by evaporation. The addition of diethyl ether produces crystals of  $[(\text{C}_6\text{Cl}_5)_2\text{As}]_2\text{O}$  (IV). The reaction must proceed through the formation of the arsenic(V) derivative which must be hydrolysed to give a hydroxyarsenic(V) compound, which spontaneously decomposes to the organoarsenic(III) derivative, because decomposition with elimination of chlorine would give I, which is not hydrolyzed by water.

The reaction of IV with aqueous hydrochloric acid gives I (eq. 3). The same



behaviour is observed for  $[(\text{C}_6\text{F}_5)_2\text{As}]_2\text{O}$  [6]. The addition of chlorine and bromine to II gives organoantimony(V) halides according to eq. 4.



In contrast, chlorine or bromine react with III with cleavage of C—Bi bonds to give unidentified decomposition products containing oxohalobismuth(III) derivatives. Similar behaviour was observed for  $(\text{C}_6\text{F}_5)_3\text{Bi}$  [2].

All the compounds are indefinitely stable at room temperature in the air as solids. They are thermally stable, and melt without decomposition. I—III are soluble in nitromethane but insoluble in most organic solvents. IV—VI are soluble in carbon tetrachloride, chloroform and THF. The molar conductivities of all the compounds in nitromethane indicate that they are non-conductors in this solvent [7].

#### (b) IR spectra

The absorptions due to the pentachlorophenyl group appear in all the compounds at 1515—1505 $\text{cm}^{-1}$ , 1330—1320 $\text{cm}^{-1}$ , 1298—1293 $\text{cm}^{-1}$ , 1270 $\text{cm}^{-1}$ , 1230—1225 $\text{cm}^{-1}$ ,

1200w, 1170–1160m, 1080–1075m, 855–830 (one or two bands) s, 725–720w, 705w, 690–675vs, 625–615w, 580–565w and 350–310w  $\text{cm}^{-1}$ . The spectrum of I shows a band at 360w  $\text{cm}^{-1}$  assignable to  $\nu(\text{As}-\text{Cl})$ , consistent with that known for  $(\text{C}_6\text{H}_5)_2\text{AsCl}$  [8]. The stretching vibration  $\nu(\text{As}-\text{O}-\text{As})$  of compound IV is observed at 930vs  $\text{cm}^{-1}$ . The stretching vibration  $\nu(\text{Sb}-\text{Cl})$  of compound V appears at 300s  $\text{cm}^{-1}$ , as in  $(\text{C}_6\text{F}_5)_3\text{SbCl}_2$  [9].

## Experimental

IR spectra were recorded on a Perkin–Elmer 457 spectrophotometer at 4000–250  $\text{cm}^{-1}$  using Nujol mulls between CsI plates. Conductivities were measured with a Phillips PW9501/01 Conductimeter. C and H analyses were carried out on a Perkin–Elmer 240 microanalyzer, and the results are shown in Table 1.

$(\text{C}_6\text{Cl}_5)_3\text{X}$  (II, X = Sb; III, X = Bi) and  $(\text{C}_6\text{Cl}_5)_2\text{AsCl}$  (I)

A solution of  $\text{SbCl}_3$  (1 g; 4.38 mmol) in diethyl ether (25 ml) was added to a freshly prepared solution of  $\text{LiC}_6\text{Cl}_5$  (13.14 mmol) in the same solvent (50 ml) at  $-78^\circ\text{C}$  under nitrogen and an insoluble colorless solid was produced. The suspension was stirred for 4 h after which it was allowed to warm to room temperature. The mixture was then treated with water (75 ml) containing a few drops of HCl. The organic layer, which contained the precipitate, was decanted and the solvent removed under reduced pressure. The residue was dried over  $\text{P}_2\text{O}_5$ . Recrystallization from hot nitrobenzene gave white crystals of II, which were repeatedly washed with warm hexane and finally dried for several hours under vacuum. Yield ca. 60%. The same method was used to prepare compounds I and III. Compound I was also obtained when a large excess 6/1 of  $\text{LiC}_6\text{Cl}_5$  was used.

$(\text{C}_6\text{Cl}_5)_2\text{As}-\text{O}-\text{As}(\text{C}_6\text{Cl}_5)_2$  (IV)

5.94 ml of a 0.55 N solution of  $\text{Cl}_2$  (0.116 g; 1.64 mmol) in  $\text{CCl}_4$  were added

TABLE 1  
ANALYTICAL DATA FOR PENTACHLOROPHENYL COMPOUNDS

Compound	Molecular formula	Analysis (found (calcd.) (%))		
		C	Cl	Br
I	$\text{C}_{12}\text{AsCl}_{11}$	24.20 (23.66)	64.16 (64.03)	
II	$\text{C}_{18}\text{SbCl}_{15}$	24.80 (24.86)	61.02 (61.14)	
III	$\text{C}_{18}\text{BiCl}_{15}$	22.17 (22.59)	55.72 (55.57)	
IV	$\text{C}_{24}\text{As}_2\text{Cl}_{20}\text{O}$	25.29 (24.78)	60.65 (60.96)	
V	$\text{C}_{18}\text{SbCl}_{17}$	22.38 (22.98)	64.12 (64.07)	
VI	$\text{C}_{18}\text{SbCl}_{15}\text{Br}_2$	21.02 (21.00)	51.82 (51.65)	15.45 (15.52)

dropwise to a suspension of I (1 g; 1.64 mmol) in chloroform (50 ml). After stirring for 30 min at room temperature a colorless solution was obtained. The solution was concentrated and treated with a few drops of diethyl ether to give white crystals of IV, which were washed with ether and dried under vacuum. Yield ca. 70%.

$(C_6Cl_5)_3SbX_2$  ( $X = Cl, V; Br, VI$ )

4.18 ml of a 0.55 *N* solution of  $Cl_2$  (0.082 g; 1.15 mmol) or  $Br_2$  (0.184 g, 1.15 mmol) in  $CCl_4$  were added to a suspension of II in chloroform (50 ml). The mixture was stirred for 30 min at room temperature giving a colorless solution. The solutions were concentrated by evaporation and crystals were formed on cooling. Solids were filtered, washed with hexane or diethyl ether, and dried under vacuum. Yields ca. 75%.

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