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Tetrachloropyridylstibines

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Abstract

Three tertiary stibines containing tetrachloropyridyl groups, tris(2,3,5,6-tetrachloro-4-pyridyl)stibines, phenyl- and tolylbis(2,3,5,6-tetrachloro-4-pyridyl)stibines and their dibromides, were synthesized. The compounds were characterized by elemental analysis, vapour pressure osmometry, thermogravimetry, IR, far IR, ^{1}H and ^{13}C NMR spectroscopy. IR and NMR data indicate that the tetrachloropyridyl group is attached to antimony through the fourth position.

Keywords: Tertiary stibines; Tetrachloropyridyl stibines; ^{13}C NMR spectra

1. Introduction

Tertiary stibines R_3Sb (where R is alkyl, aryl or polyhalogenated aryl) are known in the literature, but information concerning tertiary stibines containing heterocyclic aromatic groups is very limited [1–3].

There appears to be no report on the synthesis of organoantimony derivatives of polyhalogenated nitrogen-containing heterocycles, though there are some reports on the synthesis of organo- mercury, sulphur, phosphorus, titanium, and silicon derivatives containing tetrachloropyridyl groups or tetrafluropyridyl groups [4–9]. Polychloropyridyl derivatives are now finding applications in pharmaceuticals and agrochemicals [10,11]. Thus it appeared worthwhile to synthesize and characterize the tetrachloropyridyl derivatives of antimony.

2. Experimental details

All the reactions were carried out in nitrogen atmosphere. Carbon, hydrogen and nitrogen analyses of these compounds were carried out using a Perkin-Elmer 240 C elemental analyser and antimony was determined iodometrically. Molecular weights of the derivatives were determined in benzene using a Knauer vapour pressure osmometer. IR spectra in the range 400–4000 cm^{-1} were recorded in KBr on a Nicolet 5-DX FTIR spectrometer. Far IR spectra were recorded in polyethylene in the range 700–30 cm^{-1} on a Perkin-Elmer 1700 X FT far IR spectrometer. The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Jeol JNM FX-100 FT NMR spectrometer. Thermogravimetric study up to 800°C with a heating rate of 10°C min^{-1} was carried out using an STA-780 series recording thermobalance under nitrogen and also in static air.

2.1. Tris(tetrachloro-4-pyridyl)antimony(III) $(Tcp)_3Sb$

This compound was synthesized by two routes, either through Grignard reagent of pentachloropyridine or through lithium derivative of pentachloropyridine.

2.1.1. Method A (Grignard reagent route)

A solution of pentachloropyridine (20 mmol) and ethylenedibromide (2–3 drops) in THF was added dropwise to magnesium turnings (20 mmol) in THF with stirring at −10°C. After the addition of pentachloropyridine solution, the mixture was stirred for about 4 h at −10°C. During the course of the reaction, the reaction mixture became cherry red in colour. A solution of $SbCl_3$ (7 mmol) in THF was added dropwise to the above coloured mixture with stirring. Stirring was continued for 2 h at room temperature. The reaction mixture was poured slowly with stirring into 200 ml ice and water. Most of the tris(tetrachloropyridyl)stibine dis-

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solved in THF and the THF layer was separated. The rest was filtered through a Buchner funnel and the residue was extracted with ether. On evaporation of combined ether extract and THF solution, tris(tetrachloro-4-pyridyl)stibine appeared as a light brown solid, which was recrystallized from ether–hexane mixture.

2.1.2. Method B (lithium derivative route)

BuLi (10 ml of 2.2 M solution in hexane) was added dropwise to a solution of pentachloropyridine (20 mmol) in diethyl ether at −60°C. Then the solution was allowed to warm to −20°C and stirred for 1 h. A solution of $SbCl_3$ in ether (7 mmol) was added dropwise and stirred for a further 2 h. The reaction mixture was then hydrolysed by pouring it into ice–water. The ether layer was collected and evaporated under vacuum to obtain tris(tetrachloro-4-pyridyl)stibine, which was recrystallized from ether–hexane mixture.

2.2. Arylbis(tetrachloro-4-pyridyl)antimony(III) [R(Tcp)$_2$Sb], R = phenyl or tolyl

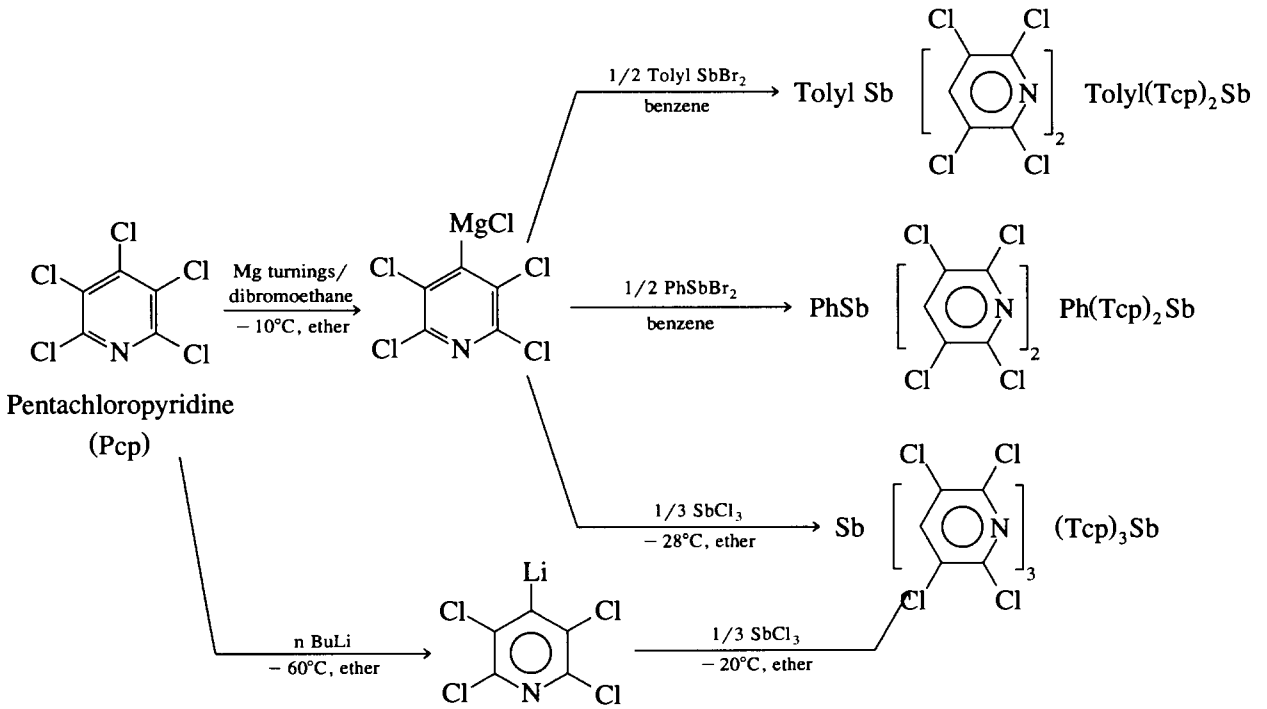
A solution of $PhSbBr_2$ or tolyl$SbBr_2$ (10 mmol) in benzene (20 ml) was added dropwise to the solution of Grignard reagent of pentachloropyridine (20 mmol) in THF (40 ml) at −10°C and stirred for 2 h. This mixture was then hydrolysed by pouring into ice–water. The THF–benzene layer was separated and the residue was extracted with THF two times. The combined THF–benzene mixture was then concentrated by evaporating under vacuum, on which phenylbis(tetrachloro-4-pyridyl)antimony(III) or tolylbis(tetrachloro-4-pyridyl)antimony(III) separated out. The compound was recrystallized from methanol–ether mixture.

2.3. Tris(tetrachloro-4-pyridyl)stibine dibromide [(Tcp)$_3$SbBr$_2$]

To a stirred solution of $(Tcp)_3Sb$ (10 mmol) in dichloromethane (40 ml), bromine (10 mmol) in the same solvent (20 ml) was added dropwise at 0°C. The reaction mixture was stirred for 1 h after which it was concentrated under low pressure yielding light-brown coloured product of $(Tcp)_3SbBr_2$. This was then recrystallized from dichloromethane.

2.4. Arylbis(tetrachloro-4-pyridyl)stibine dibromide [R(Tcp)$_2$SbBr$_2$], R = phenyl or tolyl

These dibromides were prepared by bromination of the corresponding $[R(Tcp)_2Sb]$ in an analogous way as above.



$$(Tcp)_3Sb \xrightarrow[\text{dichloromethane}]{Br_2} (Tcp)_3SbBr_2$$

$$Ph(Tcp)_2Sb \xrightarrow[\text{dichloromethane}]{Br_2} Ph(Tcp)_2SbBr_2$$

$$Tolyl(Tcp)_2Sb \xrightarrow[\text{dichloromethane}]{Br_2} Tolyl(Tcp)_2SbBr_2$$

Scheme 1.

Table 1
Elemental analysis and physical properties of tetrachloro-4-pyridyl derivatives

Number	Compound	Formula	Yield(%) Colour	Melting point (°C)	C(%)	H(%)	N(%)	Sb(%)	Total X [a]	Molecular weight
1	$(Tcp)_3Sb$	$C_{15}Cl_{12}N_3Sb$	28 Light brown	160–162	22.78 [b] (23.40) [c]	— —	4.93 (5.46)	16.27 (15.75)	54.28 (55.39)	744 (769)
2	$Ph(Tcp)_2Sb$	$C_{15}C_5Cl_8N_2Sb$	32 Yellowish brown	229	29.82 (30.47)	1.02 (0.79)	4.28 (4.44)	20.48 (19.20)	44.35 (45.07)	612 (630)
3	p-Tolyl$(Tcp)_2Sb$	$C_{17}H_7Cl_8N_2Sb$	30 Yellowish brown	142(d)	30.73 (31.67)	0.92 (1.08)	3.20 (4.34)	19.39 (18.78)	43.01 (44.09)	629 (644)
4	$(Tcp)_3SbBr_2$	$C_{15}Cl_{12}N_3SbBr_2$	82 Light brown	148	19.32 (19.37)	— —	4.37 (4.52)	14.78 (13.02)	60.37 (63.07)	902 (929)
5	$Ph(Tcp)_2SbBr_2$	$C_{16}H_5Cl_8N_2SbBr_2$	85 Light brown	193	23.71 (24.30)	0.88 (0.63)	2.86 (3.54)	17.20 (15.31)	55.13 (56.22)	758 (790)
6	p-Tolyl$(Tcp)_2SbBr_2$	$C_{17}H_7Cl_8N_2SbBr_2$	80 Light brown	227	24.63 (25.37)	1.08 (0.87)	3.47 (3.48)	16.76 (15.04)	53.85 (55.23)	784 (804)

[a] X ≡ Cl or Cl + Br. [b] Observed value; [c] Calculated value in parentheses.

3. Results and discussion

The reactions involved in the synthesis of the tertiary stibines, and their dibromo derivatives are shown n Scheme 1.

All the compounds are microcrystalline solids. $(Tcp)_3Sb$, $Ph(Tcp)_2Sb$ and/or tolyl$(Tcp)_2Sb$ are insoluble in water and remain unaffected by water. Thus Sb–C bonds in the above compounds are not hydrolysed by water alone. These compounds are found to be quite stable in air and are reasonably soluble in common organic solvents, i.e. benzene, THF, ether, dichloromethane etc. $(Tcp)_3Sb$ and $Ph(Tcp)_2Sb$ are thermally stable and melt without decomposition while tolyl-$(Tcp)_2Sb$ decomposes before melting.

Dibromides of these stibines, namely $(Tcp)_3SbBr_2$, $Ph(Tcp)_2SbBr_2$ and tolyl$(Tcp)_2SbBr_2$, are also soluble in organic solvents such as chloroform, benzene and THF but insoluble in ether and hexane. These compounds are stable and melt without decomposition (Table 1). The observed molecular weights of stibines and their dibromides indicate that they exist as monomers in benzene.

The positions of the important IR and far IR bands along with the assignments of the tertiary stibines and dibromides are listed in Table 2. On the basis of the structures of other tertiary stibines [12,13] a pyramidal structure may be assigned to $(Tcp)_3Sb$.

For monosubstituted pyridines ($X\text{-}C_5H_4N$) there are five X-sensitive vibrations [14,15]. In the present case, for $(Tcp)_3Sb$ also, five X-sensitive vibrations for tetrachloropyridyl group are expected which may be assigned to Sb–C vibrations. Thus the bands observed at 1052, 627, 471, 243 and 153 cm^{-1} in the IR spectrum of $(Tcp)_3Sb$ may be assigned to Sb–C vibrations. These values are comparable with those assigned to Sb–C vibrations in triphenylstibine or tris(pentafluorophenyl)-stibine [16,17].

It is interesting to note that the values of the Sb–C vibrational frequencies in $(Tcp)_3Sb$ are lower than the corresponding values in $(C_6F_5)_3Sb$ but higher than the corresponding values in $(C_6H_5)_3Sb$. This may be explained on the basis of the increasing trend in electronegativity H < Cl < F. In the compounds containing both Tcp and phenyl or tolyl groups it has not been possible to differentiate between the Sb–C vibrations due to Sb–phenyl or Sb–tolyl and those due to Sb–(Tcp) because these are very close in value.

The planar ring vibration occurs at 660 cm^{-1} in four-substituted pyridines whereas in two- or three-substituted pyridines it appears at 615 cm^{-1} [14,15], thus the band observed at 656 cm^{-1} in $(Tcp)_3Sb$ indicates that the tetrachloropyridyl group is attached to antimony at the fourth position. In the dibromo derivatives of $(Tcp)_3Sb$ this vibration occurs at 649 cm^{-1}.

For $(Tcp)_3SbBr_2$ the stretching vibrations of the Sb–

Table 2
Important IR and far IR bands (cm^{-1}) of tetrachloro-4-pyridylstibines and dibromides

Number	Compound	ν_{Sb-Br}	ν_{Sb-C} vibration	ν_{CH}	Planar ring
1	$(Tcp)_3Sb$	—	1052, 672, 471, 243, 153	—	656
2	$Ph(Tcp)_2Sb$	—	1070, 1044, 659, 653, 490, 478, 262, 250, 170, 149	3068	650
3	Tolyl$(Tcp)_2Sb$	—	1068, 1048, 666, 485, 460, 261, 262, 238	3061	655
4	$(Tcp)_3SbBr_2$	218	1043, 619, 492, 462, 287, 245, 151	—	649
5	$Ph(Tcp)_2SbBr_2$	202	1065, 1044, 658, 649, 482, 465, 260, 170	3060	650
6	Tolyl$(Tcp)_2SbBr_2$	198	1066, 1037, 652, 480, 456, 273, 238, 179	3066	650

Table 3
^{1}H NMR data of tetrachloro-4-pyridyl derivatives in chloroform at room temperature

Number	Compound	Methyl protons	Aromatic protons
1	$Ph(Tcp)_2Sb$	—	7.36–8.22 (m,5H)
2	p-Tolyl$(Tcp)_2Sb$	2.36 (s,3H)	7.33–8.18 (m,4H)
3	$Ph(Tcp)_2SbBr_2$	—	7.54–8.34 (m,5H)
4	p-Tolyl$(Tcp)_2SbBr_2$	2.38 (s,3H)	7.34–8.36 (m,4H)

Br bond occur at higher frequencies than for the corresponding phenyl derivative Ph_3SbBr_2. The replacement of the phenyl group by the highly electron withdrawing tetrachloropyridyl group leads to an increase in partial positive charge on the antimony atom [16] and strengthens the Sb–Br band.

The UV–visible spectra of $(Tcp)_3Sb$ and tolyl-$(Tcp)_2Sb$ show an absorption maximum at 296 nm and 289 nm respectively. These bands can be assigned to $\pi-\pi^*$ transition and are red shifted compared with Ph_3Sb. Similar observation has been recorded in the case of phosphorus derivatives where the $\pi-\pi^*$ transition in Ph_3P at 260 nm is red shifted to 317 nm in $(Tcp)_3P$ [6]. The N-heterocyclic molecules contain non-bonded electron pairs in addition to π-electrons giving rise to $n-\pi^*$ transition etc. This transition could not be observed in these compounds.

The chemical schift data obtained from ^{1}H NMR spectra of some of the compounds are shown in Table 3. In the spectrum of $Ph(Tcp)_2Sb$ a multiplet is observed owing to the phenyl protons which appears downfield compared with the phenyl protons of Ph_3Sb. This downfield shift is indicative of the deshielding of phenyl protons in $Ph(Tcp)_2Sb$ because of the presence of the tetrachloropyridyl group.

The ^{1}H NMR spectrum of tolyl$(Tcp_2)Sb$ shows two doublets in the aromatic region due to the $-C_6H_4$ group of the tolyl group and a singlet due to methyl protons of the tolyl group which appear downfield compared with the protons in $(tolyl)_3Sb$.

It may be further noted that the multiplet due to phenyl protons in $Ph(Tcp)_2Sb$ shifts downfield in $Ph(Tcp)_2SbBr_2$. A similar situation exists in the case of tolyl$(Tcp)_2Sb$ and tolyl$(Tcp)_2SbBr_2$. This observation is as expected owing to the introduction of electronegative bromine atoms. A similar trend has been reported in the case of Ph_3Sb and Ph_3SbBr_2 [17].

^{13}C NMR spectra of $(Tcp)_3Sb$ and $(Tcp)_3SbBr_2$ were recorded and for the compounds containing phenyl or tolyl group the ^{13}C NMR spectra (protons completely decoupled) and off resonance decoupled ^{13}C spectra were recorded; values of the chemical shifts are shown in Table 4.

$(Tcp)_3Sb$ shows three chemical shifts at 131.1 ppm, 146.3 ppm and 147.9 ppm from which it may be inferred that the attachment of antimony to the tetrachloropyridyl ring is through the fourth position and not through the two or three position, because in the latter situation five different chemical shifts ought to have been observed.

It is possible to assign the three chemical shifts observed for $(Tcp)_3Sb$ to three different kinds of carbon atom of the chloropyridine ring on the basis of the reported ^{13}C spectra of pentachloropyridine and related compounds [18,19]. In pentachloropyridine the ^{13}C chemical shifts are observed at 146.2 (C_2 and C_6), 144.7 (C_4) and 129.7 (C_3 and C_5) [18]. In $(Tcp)_3Sb$ the most affected carbon atom of tetrachloropyridyl group is C_4 which is directly attached to antimony and the other carbon atoms will be very slightly affected. Thus the signal at 147.9 in $(Tcp)_3Sb$ may be assigned to C_4, the signal at 146.3 may be assigned to C_2 and C_6, and the signal at 131.1 may be assigned to C_3 and C_5.

The ^{13}C NMR spectrum of $Ph(Tcp)_2Sb$ with the protons completely decoupled exhibits three peaks for tetrachloropyridyl groups and four for the phenyl group

Table 4
^{13}C NMR data of tetrachloro-4-pyridyl stibines and their dibromides

Number	Compound	C_{12}	C_3 and C_5	C_1	C_4	C_{11}	C_2 and C_6	C_9 and C_{10}	C_7 and C_8
1.	$(Tcp)_3Sb$	—	131.1	—	147.9	—	146.3	—	—
2.	$Ph(Tcp)_2Sb$	—	129.51	136.8	149.72	128.97	147.22	127.4	135.4
3.	p-Tolyl$(Tcp)_2Sb$	25.9	129.6	134.92	147.7	143.65	144.93	126.98	132.14
4.	$(Tcp)_3SbBr_2$	—	131.7	—	148.53	—	146.87	—	—
5.	p-Tolyl$(Tcp)_2SbBr_2$	24.3	129.2	133.1	146.7	142.7	144.0	128.4	131.0

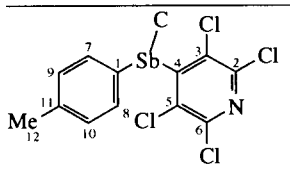


Table 5
Thermogravimetric analysis data of tetrachloro-4-pyridylstibines

Number	Compound	First step decomposition		Second step decomposition		Residue	Sb/Sb_2O_3 (%)
		$T_b - T_e$ (°C)	Weight loss (%)	$T_b - T_e$ (°C)	Weight loss (%)		
1	$(Tcp)_3Sb$	188–269	51	269–466	33.5	15.5	15.75
2	$Ph(Tcp)_2Sb$	229–259	45.5	259–517	35.0	19.5	19.20
3	p-Tolyl$(Tcp)_2Sb$	162–320	42.5	320–616	35.5	22.0	22.4

T_b temperature at the begining of decomposition;
T_e temperature at the end of decomposition.

(Table 4) as expected for the tetrachloropyridyl group attached to antimony at C_4 and for the phenyl group. In the off resonance spectrum of this compound, proton bearing carbons of the phenyl group split into two signals owing to residual $^{13}C\{^1H\}$ coupling.

In addition to seven ^{13}C signals (three for tetrachloropyridyl group carbons and four for phenyl carbons) another signal is observed for methyl group carbon at 25.9 ppm in the completely decoupled spectrum of tolyl$(Tcp)_2Sb$. The chemical shift value for the methyl carbon is 4.6 ppm downfield in comparison with tritolyl stibine, again indicating the effect of the tetrachloropyridyl groups. The off resonance decoupled spectrum of this compound shows that proton-bearing ring carbons in the tolyl group split into two signals and the signal due to methyl carbon splits into a quartet because of residual coupling. It has been possible to assign the ^{13}C NMR signals to the individual carbon atoms in this compound (Table 4). However, there may be some ambiguity in the assignments of the signals at 143.65 and 144.93 since the values are rather close. The off resonance spectrum is of no help since the carbon atoms giving rise to these signals (C_{11} of the tolyl group and C_2 and C_6 of the tetrachloropyridyl group) do not have any attached proton.

$(Tcp)_3Sb$ and $Ph(Tcp)_2Sb$ were subjected to thermogravimetric analysis in nitrogen atmosphere, while for tolyl$(Tcp)_3Sb$ thermogravimetric analysis was carried out in air. Thermogravimetric data are shown in Table 5. The thermograms are similar and show that these compounds decompose in two steps.

For $(Tcp)_3Sb$ and $Ph(Tcp)_2Sb$, in the first decomposition step, the weight loss corresponds to the loss of all the chlorine atoms, while in the second decomposition step the compounds lose all the organic groups and the end product (residue) in both cases is antimony. $Ph(Tcp)_2Sb$ appears to be more stable as it starts decomposing later than $(Tcp)_3Sb$.

The decomposition of tolyl$(Tcp)_2Sb$ in air also takes place in two steps but the end product (residue) in this case is antimony trioxide.

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