

Available online at www.sciencedirect.com



Journal of Fluorine Chemistry 122 (2003) 165-170



www.elsevier.com/locate/jfluchem

# Some reactions and spectroscopic studies of tris(pentafluorophenyl)arsenic and -antimony(III and V) derivatives

Sanjeev K. Shukla, Ashok Ranjan, A.K. Saxena<sup>\*</sup>

Defence Materials and Stores, Research and Development Establishment, G.T. Road, Kanpur 208013, India Received 19 September 2002; received in revised form 9 December 2002; accepted 24 February 2003

## Abstract

The reactions of tris(pentafluorophenyl)arsenic(III) with iodine monochloride, iodine monoazide, and dithiocyanogen yielded corresponding oxidative-addition products of the type ( $C_6F_5$ )<sub>3</sub>As(V)XY (X = I, Y = Cl, N<sub>3</sub>; X = Y = NCS). The elemental sulphur also added oxidatively with tris(pentafluorophenyl)arsenic(III) yielding tris(pentafluorophenyl)arsine(V) sulphide. Some displacement reactions were also carried out to synthesize mixed pseudohalide derivatives of the type ( $C_6F_5$ )<sub>3</sub>M(N<sub>3</sub>)NCS (M = As and Sb) and their insertion reactions were studied with phenyl isothiocyanate which yielded the corresponding 1,2-cycloaddition products, i.e. tetrazole-5-thiones. The compounds were characterized by elemental analysis, molar conductance, UV, IR and <sup>19</sup>F NMR spectroscopic studies. © 2003 Elsevier Science B.V. All rights reserved.

Keywords: Pentafluorophenyl; Arsenic; Antimony; Synthesis; Spectroscopy

# 1. Introduction

Despite a considerable interest in the chemistry of hydrocarbon derivatives of arsenic and -antimony(III and V) [1–3], very few studies have been devoted to the corresponding fluorocarbon analogous [4–13]. Furthermore, compared to perfluorophenylantimony(III and V) derivatives not much attention has been given to similar perfluorophenylarsenic(III and V) derivatives [14–16]. As an electronic character of aromatic rings is markedly changed by the replacement of five nuclear hydrogen atoms for fluorine atoms, the chemical and physical properties of the compounds are also changed [14]. Thus, very striking differences have been observed in phenyl and pentafluorophenyl substituted compounds just as perfluoroalkyl groups alter the chemistry of alkyl groups [17]. Such intricacies always kindled interest of researchers to study pentafluorophenyl derivatives of group 15 elements.

Thus, keeping our mind on the synthesis, reactions and spectroscopic studies of perfluorophenyl group 15 derivatives [6–13], it is considered worthwhile to investigate some hitherto unstudied reactions (oxidative-addition, displacement and insertion reactions) of tris(pentafluorophenyl)arsenic and -antimony(III and V) derivatives.

# 2. Results and discussion

In general, compared to organoantimony(III and V) derivatives organoarsenic(III and V) derivatives have been less studied due to a highly toxic nature of the arsenic element [18]. In chemical reactivity there is also marked difference in both these two elements which may be due to an atomic size difference between As and Sb elements. As our general interest lies in the study of synthesis and reactions of group 15 derivatives, we thought to study some reactions, which were already carried out by us with organoantimony derivatives [6]. Thus, some oxidative-addition, displacement and insertion reactions of  $(C_6F_5)_3$ As(III and V) derivatives were studied herein along with some unstudied reactions of  $(C_6F_5)_3$ Sb(III and V) derivatives for comparison.

## 2.1. Oxidative-addition reaction

Oxidative-addition reactions are well known to synthesize higher-valent derivatives of those compounds in which a central metal atom has variable valency. Thus, a series of oxidative-addition reactions of tris(pentafluorophenyl)-arsenic(III) with ICl,  $IN_3$ ,  $(SCN)_2$  and  $S_n$  have been carried out.

An iodine monochloride solution in acetonitrile was added to  $(C_6F_5)_3As$  at -10 °C with stirring under nitrogen

<sup>&</sup>lt;sup>\*</sup> Corresponding author. Tel.: +91-512-2451759–78 Ext. 215 (O), 2402228 (R); fax: +91-512-2450404.

E-mail address: sanshukla@lycos.com (A.K. Saxena).

atmosphere, which yielded a corresponding oxidative-addition product:

$$(C_6F_5)_3As + ICl \rightarrow (C_6F_5)_3AsICl$$
(1)

The reaction of  $(C_6F_5)_3As$  with IN<sub>3</sub> (prepared from NaN<sub>3</sub> and ICl) [19] and (SCN)<sub>2</sub> (prepared by the reaction between Pb(SCN)<sub>2</sub> and Br<sub>2</sub>) [20] yielded corresponding oxidative-addition products as shown below:

$$(C_6F_5)_3As + IN_3 \rightarrow (C_6F_5)_3AsIN_3$$
(2)

$$(C_6F_5)_3As + (SCN)_2 \rightarrow (C_6F_5)_3As(SCN)_2$$
(3)

Reactions with dithiocyanogen  $(SCN)_2$  were performed in the dark to circumvent the  $(SCN)_2$  polymerization in the light.

Elemental sulphur was also found to add oxidatively to  $(C_6F_5)_3As$  in a refluxing benzene solution under dry nitrogen atmosphere to give corresponding sulphides.

$$(C_6F_5)_3As + S_n \to (C_6F_5)_3AsS \tag{4}$$

 $(C_6F_5)_3AsS$  has also been obtained by passing a H<sub>2</sub>S gas in an alcoholic ammonia solution of  $(C_6F_5)_3AsCl_2$  in the presence of triethylamine.

The molecular weight of the sulphide derivative determined cryoscopically in nitrobenzene indicated that it existed in monomeric form. It may be worth mentioning that tris(perfluoroalkyl)antimony and sulphur did not react each other [21].

In these reactions no cleavage of the M–C bond has been noticed compared to tetraorganometallic derivatives of Group 14 (M = Ge, Sn and Pb), where ICl and IN<sub>3</sub> behaved as electrophilic reagents and cleaved the metal–carbon bond(s) [22].

#### 2.2. Displacement reaction

Tris(pentafluorophenyl)arsenic and -antimony azidoisothiocyanates were prepared by a displacement reaction of the corresponding metal iodoazides with freshly prepared AgNCS (prepared by reaction of AgNO<sub>3</sub> and NH<sub>4</sub>NCS) as shown below:

$$(C_6F_5)_3MIN_3 + AgNCS \underset{M = As(5)orSb(6)}{\rightarrow} (C_6F_5)_3M(N_3)NCS + AgI$$

In the present investigation it has been observed that the iodine was replaced by an isothiocyanate group, which is in contrast to our previous studies, where the iodine invariably remained bonded to antimony, irrespective of the nature of the metallic salt used [6].

## 2.3. Insertion reaction

Insertion reactions were carried out with the corresponding triaryl M(V) iodoazides and -azidoisothiocyanates (M = As and Sb) with PhNCS, yielding corresponding 1,2-cycloaddition products, i.e. tetrazole 5-thiones.



$$X = I, M = As(7); X = NCS, M = As(8), Sb(9)$$

The consistency in the melting points of these cycloaddition products obtained after several crystallization, excluded the possibility of mixtures of reactants. The molar conductance values of the compounds were evaluated in methanol  $(10^{-3} \text{ M solution})$ , which were in the range of  $16-29 \text{ cm}^2 \Omega^{-1} \text{ mol}^{-1}$ , showing their non-conducting behaviour in solution [23]. The molecular weights and the van't Hoff factor '*i*' (0.97–1.04) determined cryoscopically in nitrobenzene showed their monomeric nature. The elemental analysis were also found satisfactory and within permissible limits (Table 1).

# 2.4. IR spectra

IR spectra were recorded in KBr/CsI pellets in the range of  $4000-200 \text{ cm}^{-1}$  and some of the characteristic absorption bands of these derivatives are given in Table 2.

In pentafluorophenylantimony derivatives (**6** and **9**) characteristic v(C-C) bands of  $C_6F_5$  group were found as reported for other pentafluorophenylantimony compounds and appeared at 1641 ± 7 (s), 1519 ± 6 (vs) and 1480 ± 5 (vs) cm<sup>-1</sup> as well as v(C-F) absorption bands appeared at 1385 ± 4 (s), 1289 ± 3 (m), 1083 ± 5 (vs) and 979 ± 6 (vs) cm<sup>-1</sup> [5].

In pentafluorophenylarsenic derivatives (1–5, 7 and 8) characteristic v(C-C) bands of  $C_6F_5$  group appeared comparatively at lower frequency, i.e. at  $1620 \pm 6$  (s),  $1516 \pm 7$  (vs) and  $1473 \pm 7$  (vs) cm<sup>-1</sup> and v(C-F) absorption bands appeared at  $1380 \pm 3$  (s),  $1279 \pm 5$  (m),  $1078 \pm 4$  (vs) and  $969 \pm 8$  (vs) cm<sup>-1</sup>.

The most prominent absorption in the infrared spectra of the pentafluorophenylarsenic azide derivative **2** is the asymmetric stretching frequency which was observed at 2133 cm<sup>-1</sup>. Though the asymmetric absorptions appeared at a higher frequency as compared to Ph<sub>3</sub>Sb(N<sub>3</sub>)<sub>2</sub>, other modes of vibrations, i.e. symmetric and bending, were not significantly changed, suggesting the covalent nature of the derivative [24]. The corresponding symmetric band which has been reported to appear as a weak band (at ~1275 cm<sup>-1</sup>) in triorganoantimony azides (R = alkyl or aryl) was observed at 1282 cm<sup>-1</sup> [24]. Moreover, a weaker band observed at 663 cm<sup>-1</sup> is assigned to the bending mode of the –N<sub>3</sub> group.

The isothiocyanate group in compound **3** gives three fundamental modes of vibrations due to v(C=N), v(C-S) and  $\delta(NCS)$  at 2058, 775 and 461 cm<sup>-1</sup>, respectively.

In the compounds **5** and **6** asymmetric stretching absorption bands of v(NCS) and  $v(N_3)$  could not be observed separately due to close proximities of both frequencies

 Table 1

 Some physical and analytical data of tris(pentafluorophenyl)arsenic and -antimony(V) compounds

Compound no.	Empirical formula	mp (°C)	Yield (%)	$\Lambda_{\rm M}  ({\rm cm}^2  \Omega^{-1}  {\rm mol}^{-1})  10^{-3}  {\rm M}$	Analysis: found (%) (calc.) (%)		
	(molecular weight)			solution in methanol	С	Н	Ν
1	C <sub>18</sub> F <sub>15</sub> IClAs (738.44)	138-139	68	28.37	29.31 (29.28)	_	_
2	C <sub>18</sub> F <sub>15</sub> IN <sub>3</sub> As (745.01)	170 (d)	62	22.09	29.00 (29.02)	_	5.66 (5.64)
3	C <sub>20</sub> F <sub>15</sub> S <sub>2</sub> N <sub>2</sub> As (692.26)	255 (d)	58	17.36	34.72 (34.70)	_	4.07 (4.05)
4	C <sub>18</sub> F <sub>15</sub> SAs (608.16)	128	75	16.08	35.53 (35.55)	_	-
5	C <sub>19</sub> F <sub>15</sub> N <sub>4</sub> SAs (676.19)	179-180	74	25.80	33.78 (33.75)	_	8.27 (8.29)
6	C <sub>19</sub> F <sub>15</sub> N <sub>4</sub> SSb (723.02)	188	79	26.79	31.54 (31.56)	_	7.76 (7.75)
7	C <sub>25</sub> H <sub>5</sub> F <sub>15</sub> IN <sub>4</sub> SAs (880.20)	198	62	23.31	34.12 (34.11)	0.60 (0.57)	6.35 (6.36)
8	C <sub>26</sub> H <sub>5</sub> F <sub>15</sub> N <sub>5</sub> S <sub>2</sub> As (811.38)	209	65	21.86	38.50 (38.49)	0.64 (0.62)	8.60 (8.63)
9	$C_{26}H_5F_{15}N_5S_2Sb\;(858.21)$	264 (d)	69	22.06	36.41 (36.39)	0.60 (0.59)	8.17 (8.16)

Table 2 Characteristic IR absorption bands (cm<sup>-1</sup>) for tris(pentafluorophenyl)arsenic and -antimony(V) compounds

2	3	5	6	7	8	9	Assignments
2133	_	_	_	_	_	_	$v_{\rm asym}(N_3)$
-	2058	2079	2080	_	2064	2068	$v_{asym}(NCS)$
-	_	_	_	1380	1376	1352	Exocyclic(C=S)
1282	_	1284	1281	_	-	_	$v_{\rm sym}(N_3)$
_	_	_	_	1261	1265	1240	Cyclic N=N-N
-	_	_	_	1025	1018	1021	Ring skeletal
_	775	785	781	_	784	786	$v_{\rm sym}(\rm NCS)$
663	_	-	-	-	_	-	$\delta(N_3)$
-	461	485	482	-	479	476	$\delta(NCS)$

and appeared as a broad band at  $\sim 2080 \text{ cm}^{-1}$ . A symmetric IR absorption band due to  $v(N_3)$  appeared in such derivatives at  $1282 \pm 2 \text{ cm}^{-1}$ . The v(CS) band also appeared at  $783 \pm 2 \text{ cm}^{-1}$  (w) in these derivatives.

The nature of N- or S-bonded thiocyanato derivatives (3, 5 and 6) is better elucidated by the energy of bending modes,  $\delta$ (NCS), which occur in regions 490–450 and 440–400 cm<sup>-1</sup>, respectively [24]. In these derivatives  $\delta$ (NCS) bands appeared at 461–485 cm<sup>-1</sup>, while no band was observed between 440 and 400 cm<sup>-1</sup>, thereby excluding any possibility of the presence of a S–Sb bond.

In the cycloaddition product **7** the absorption due to  $N_3$  group disappeared  $[v_{asym}(N_3) \sim 2133 \text{ cm}^{-1}, v_{sym}(N_3) \sim 1281]$  [24] and new absorption bands appeared due to cyclic N=N-N at 1261–1255 cm<sup>-1</sup> and exocyclic (C=S) at 1380–1365 cm<sup>-1</sup>, respectively, [10] thus confirming the formation of a tetrazole ring. The formation of azido adducts with PhNCS through N- or S-centres also has been ruled out due to the absence of  $v_{asym}$ (NCS) absorption at ~2060 cm<sup>-1</sup>. But in the case of cycloaddition compounds **8** and **9** when both –NCS and –N<sub>3</sub> groups were present, after the insertion reaction a strong band still persisting at 2066 ± 2 cm<sup>-1</sup>, which may be attributed due to Sb–NCS group, [10] but

disappearance of  $v_{sym}(N_3)$  band at ~1280 cm<sup>-1</sup> and appearance of other IR absorption bands due to tetrazole ring (cyclic N<sub>3</sub> at 1265–1240 cm<sup>-1</sup> and exocyclic v(C=S) at 1376–1352 cm<sup>-1</sup>), [10] confirmed the formation of insertion products. Invariably in all insertion products a new band of medium intensity appeared at 1021 ± 4 cm<sup>-1</sup>, which may be assigned to the skeletal vibrations of the tetrazole ring [25].

In pentafluorophenylarsenic sulphide derivative **4** stretching vibration v(As-S) appeared at 498 cm<sup>-1</sup>, which appeared at a higher field compared to alkylarsenic sulphide derivatives [v(As-S) at 484 cm<sup>-1</sup>] [24].

# 2.5. UV spectra

The UV absorption spectra of the cyclic derivatives **7–9** in methanol solutions exhibited absorption in the region  $\lambda$  260–290 nm, similar to that exhibited by an authentic sample of 1-phenyl tetrazole-5-thione **10** and thus supported the formation of tetrazole derivatives [26].

An additional support for the formation of the tetrazole ring, acid hydrolysis of the compound 7 gave 1-phenylte-trazole-5-thione **10** and  $(C_6F_5)_3AsICl$ , mp 138–139 °C as shown below:



# 2.6. <sup>19</sup>F NMR spectra

The <sup>19</sup>F NMR spectra of the compounds **1–9** were recorded in CDCl<sub>3</sub> using CF<sub>3</sub>COOH as a reference at 400 MHz. In all pentafluorophenylarsenic compounds (**1–5**, **7** and **8**) the signals due to F<sub>4</sub>, F<sub>2,6</sub> and F<sub>3,5</sub> appeared at  $\delta$  –145.7 ± 1.5, -128 ± 3 and -156.9 ± 1 ppm, respectively and pentafluorophenylantimony compounds (**6** and **9**) showed the signals due to F<sub>4</sub>, F<sub>2,6</sub> and F<sub>3,5</sub> at  $\delta$  –149.4 ± 1.3, -126.6 ± 0.7 and -157.2 ± 1.8 ppm, respectively. The F<sub>3,5</sub> signals appeared at higher field as compared to the F<sub>2,6</sub> and F<sub>4</sub> signals indicating the donation of electron from *ortho* and *para* positions towards carbon attached to antimony atom [11].

# 3. Conclusion

The oxidative-addition reactions of interhalogen (ICl), halopseudohalogen (IN<sub>3</sub>) and pseudohalogen  $[(SCN)_2]$  proceeded in the similar way as the analogous phenyl derivatives of arsenic and antimony.

The tris(pentafluorophenyl)arsenic(V)sulphide formation is not so smooth and easy compared to triphenylarsine derivatives, which further indicated that due to  $C_6F_5$  ring the central metal atom, i.e. arsenic feels more electron density which slower down the reaction.

Insertion reactions of tris(pentafluorophenyl)arsenic and antimony with PhNCS proceeded easily and gave quantitative yields compared to the analogous phenyl derivatives, which may be attributed to the electron donor behaviour of  $C_6F_5$  rings compared to  $C_6H_5$  rings.

## 4. Experimental

#### 4.1. General experimental procedures

Solvents (AR Grade) were purified, dried and distilled before use as per the literature methods [27].  $(C_6F_5)_3As$  [6],  $(C_6F_5)_3Sb$  [6], and  $(C_6F_5)_3SbIN_3$  [6] were synthesized by the reported methods. Silver thiocyanate was prepared by the reaction of silver nitrate and ammonium thiocyanate. Iodine azide and thiocyanogen were prepared by standard methods and used when freshly prepared. Iodine monochloride (Fluka) and phenyl isothiocyanate were used as received.

IR spectra were recorded on a Pye Unicam SP3-300 spectrophotometer in the range 4000–200 cm<sup>-1</sup> in the solid state using KBr/CsI Pellets. <sup>19</sup>F NMR spectra were recorded on a JEOL JNM-400 NMR spectrometer in CDCl<sub>3</sub> using CF<sub>3</sub>COOH as a reference. UV spectra were recorded on a Varian Cary-1000 spectrophotometer ( $\lambda = 220$ –400 nm) in methanol. Molecular weights were determined cryoscopically in nitrobenzene using a Beckman thermometer of ±0.01 accuracy. The molar conductance of a

 $10^{-3}$  M solution of the compounds was determined at 25 °C with a Khera DC610 Digital conductivity meter in methanol.

# 4.2. Representative synthetic procedures

# 4.2.1. Reaction of $(C_6F_5)_3As$ and ICl

A solution of iodine monochloride (0.325 g, 2 mmol) in acetonitrile (50 ml) was added dropwise to a stirred solution of (C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>As (1.15 g, 2 mmol) in the same solvent (50 ml) at -10 °C during 1 h. The reaction mixture was allowed to attain room temperature and stirred further for 30 min to ensure the completion of the reaction. Concentration of the solution followed by the addition of petroleum-ether (40– 60 °C) afforded off-white crystalline solid (C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>AsICl (1), mp 138–139 °C; yield ~1.0 g (68%); <sup>19</sup>F NMR (400 MHz):  $\delta = -130.90$  (d, F<sub>2,6</sub>) [ $J_{2,3}$ (Hz) = 20.54], -144.13 (t, F<sub>4</sub>), -157.83 ppm (t, F<sub>3,5</sub>) [ $J_{3,4}$ (Hz) = 19.53].

## 4.2.2. Reaction of $(C_6F_5)_3As$ and $IN_3$

A freshly generated solution of iodine azide (0.338 g, 2 mmol) in acetonitrile (50 ml) at -10 °C was added to a precooled (-10 °C) vigorously stirred solution of ( $C_6F_5$ )<sub>3</sub>As (1.15 g, 2 mmol) in the same solvent (50 ml) during 15 min under nitrogen atmosphere. The reaction mixture was stirred for 1 h at initial temperature and then allowed to come at room temperature. The solution was distilled under reduced pressure (1.00 mm) and cooled overnight after adding petroleum-ether (40–60 °C) (10 ml). A pale yellow crystalline solid thus obtained was characterized as ( $C_6F_5$ )<sub>3</sub>AsIN<sub>3</sub> (**2**), mp 170 °C (d); yield 0.93 g (62%); <sup>19</sup>F NMR (400 MHz):  $\delta = -130.21$  (d,  $F_{2,6}$ ) [ $J_{2,3}$ (Hz) = 20.54], -144.90 (t,  $F_4$ ), -157.32 ppm (m,  $F_{3,5}$ ) [ $J_{3,4}$ (Hz) = 19.53].

## 4.2.3. Reaction of $(C_6F_5)_3As$ and $(SCN)_2$

A freshly prepared solution of thiocyanogen (0.25 g, 2 mmol) in CCl<sub>4</sub> (30 ml) was added to a stirred solution of (C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>As (1.15 g, 2 mmol) in the same solvent at -10 °C during 15 min under nitrogen atmosphere. The reaction mixture was subsequently stirred for 1 h and warmed to room temperature. Removal of the volatiles under reduced pressure (1.0 mm) afforded a pale yellow solid. After recrystallization from ethanol it was characterized as (C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>-As(NCS)<sub>2</sub> (**3**), mp 255 °C (d); yield 0.80 g (58%); <sup>19</sup>F NMR (400 MHz):  $\delta = -130.12$  (d, F<sub>2,6</sub>) [ $J_{2,3}$ (Hz) = 20.53], -145.31 (t, F<sub>4</sub>), -157.20 ppm (m, F<sub>3,5</sub>) [ $J_{3,4}$ (Hz) = 19.54].

# 4.2.4. Reaction of $(C_6F_5)_3$ As with elemental sulphur

A solution of  $(C_6F_5)_3As$  (1.15 g, 2 mmol) in benzene (50 ml) was refluxed with elemental sulphur (0.064 g, 2 mmol) for 8 h under nitrogen atmosphere. The solution was concentrated and cooled overnight to afford an off white crystalline solid  $(C_6F_5)_3AsS$  (4), mp 128 °C; yield 0.91 g (75%);<sup>19</sup>F NMR (400 MHz):  $\delta = -130.00$  (d, F<sub>2,6</sub>)  $[J_{2,3}(Hz) = 20.54]$ , -145.10 (t, F<sub>4</sub>), -157.00 ppm (t, F<sub>3,5</sub>)  $[J_{3,4}(Hz) = 19.53]$ .

## 4.2.5. Synthesis of $(C_6F_5)_3Sb(N_3)NCS$ (6)

A solution of  $(C_6F_5)_3$ SbIN<sub>3</sub> (1.98 g, 2.5 mmol) and freshly prepared AgNCS (0.58 g, 3.5 mmol) in acetonitrile (100 ml) was stirred vigorously for 4 h at room temperature (~25 °C) and further refluxed for 1 h. The solution was filtered to remove AgI and unreacted AgNCS and the filtrate was concentrated to 25 ml under vacuum (0.01 mm). To the concentrated solution, petroleum-ether (40–60 °C) (15 ml) was added and the mixture was cooled overnight to afford white, moisture sensitive crystals identified as (C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>Sb(N<sub>3</sub>)NCS (**6**), mp 188 °C; yield 1.43 g (79%); <sup>19</sup>F NMR (400 MHz):  $\delta = -126.00$  (d, F<sub>2,6</sub>) [ $J_{2,3}$ (Hz) = 20.63], -148.13 (t, F<sub>4</sub>), -155.40 ppm (m, F<sub>3,5</sub>) [ $J_{3,4}$ (Hz) = 19.60].

Similarly (C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>As(N<sub>3</sub>)NCS (**5**) was prepared by the reaction of (C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>AsIN<sub>3</sub> with AgNCS, <sup>19</sup>F NMR (400 MHz):  $\delta = -125.28$  (d, F<sub>2,6</sub>) [ $J_{2,3}$ (Hz) = 20.53], -144.90 (t, F<sub>4</sub>), -156.00 ppm (m, F<sub>3.5</sub>) [ $J_{3,4}$ (Hz) = 19.53].

These compounds (5 and 6) were also prepared without separating iodoazide derivatives and in situ converted into azidoisothiocynato derivatives.

## 4.2.6. Insertion reaction of $(C_6F_5)_3AsIN_3$ with PhNCS

An equimolar mixture of  $(C_6F_5)_3AsIN_3$  (0.745 g, 1.0 mmol) and PhNCS (0.135 g, 1.0 mmol) was heated at 110 °C for 4 h. The resulting brown viscous mass was extracted with sodium dried *n*-hexane to afford 1-phenyl-4-[tris(pentafluorophenyl)arsenic] iodo tetrazole-5-thione 7, mp 198 °C; yield 0.55 g (62%); <sup>19</sup>F NMR (400 MHz):  $\delta = -125.90$  (d, F<sub>2,6</sub>) [ $J_{2,3}$ (Hz) = 20.54], -147.20 (t, F<sub>4</sub>), -155.90 ppm (m, F<sub>3,5</sub>) [ $J_{3,4}$ (Hz) = 19.54].

# 4.2.7. Insertion reaction of $(C_6F_5)_3Sb(N_3)NCS$ with PhNCS

An equimolar molar mixture of  $(C_6F_5)_3Sb(N_3)NCS$ (0.723 g, 1 mmol) and PhNCS (0.135 g, 1 mmol) was heated at 90 °C for 2 h. The resulting brown viscous mass was extracted with sodium dried *n*-hexane to afford 1-phenyl-4-[tris(pentafluorophenyl)antimony isothiocyanato] tetrazole-5-thione **9**, mp 264 °C (d); yield 0.59 g (69%); <sup>19</sup>F NMR (400 MHz):  $\delta = -127.30$  (d,  $F_{2,6}$ ) [ $J_{2,3}$ (Hz) = 20.60], -150.60 (t,  $F_4$ ), -159.00 ppm (m,  $F_{3,5}$ ) [ $J_{3,4}$ (Hz) = 19.61].

Similar reaction of  $(C_6F_5)_3As(N_3)NCS$  (0.676 g, 1 mmol) with PhNCS (0.135 g, 1 mmol) resulted in the formation of 1-phenyl-4-[tris(pentafluorophenyl) arsenic isothiocyanato] tetrazole-5-thione **8**, <sup>19</sup>F NMR (400 MHz):  $\delta = -125.00$  (d,  $F_{2,6}$ ) [ $J_{2,3}$ (Hz) = 20.54], -145.00 (t,  $F_4$ ), -157.42 ppm (m,  $F_{3,5}$ ) [ $J_{3,4}$ (Hz) = 19.53].

# 4.2.8. Hydrolysis of 1-phenyl-4-[tris(pentafluorophenyl)arsenic] iodo tetrazole-5-thione (7) with hydrochloric acid

The compound 7 (0.88 g, 1.0 mmol) in 40 ml diethyl ether was stirred with 3N hydrochloric acid (25 ml) at room temperature for 5 h. The ether layer was separated, washed with water, dried over anhydrous MgSO<sub>4</sub> and distilled to leave an off-white solid which subsequently was washed with cold ethanol (25 ml). After rinsing with a little *n*-hexane, the remaining solid was recrystallized with hot ethanol and characterized as 1-phenyltetrazole-5-thione **10**, yield 0.1 g (56%), mp 148–149 °C ([10] mp 150 °C). UV:  $\lambda$  276 nm ([10]  $\lambda$  276 nm).

The ethanol solution on slow evaporation yielded  $(C_6F_5)_3$ AsICl, mp 138–139 °C.

#### Acknowledgements

One of the authors (SKS) is thankful to DRDO, New Delhi for the award of Senior Research Fellowship. We are thankful to the Director, DMSRDE, Kanpur for providing laboratory facilities and permission to publish the work.

## References

- G.O. Doak, L.D. Freedman, Organometallic Compounds of Arsenic, Antimony and Bismuth, Wiley/Interscience, New York, 1970.
- [2] J.P. Crow, W.R. Cullen, Organic compounds of arsenic, antimony and bismuth, in: H.J. Emeleus, B.J. Aylett (Eds.), Inorganic Chemistry, M.T.P. International Review of Science, Ser. 1, vol. 4, Butterworths, London, 1972, p. 383.
- [3] Y.Z. Huang, Z.L. Zhou, Antimony and bismuth, in: A. Mckillop (Ed.), Comprehensive Organometallic Chemistry-II, vol. 11, Elsevier, Oxford, 1995, pp. 487–513, and references therein.
- [4] A. Otero, P. Royo, J. Organomet. Chem. 154 (1978) 13-19.
- [5] B.A. Nevett, A. Perry, Spectrochim. Acta Part A 31A (2) (1975) 101–106.
- [6] P. Raj, A.K. Saxena, K. Singhal, A. Ranjan, Polyhedron 4 (2) (1985) 251–258, and references therein.
- [7] P. Raj, A.K. Aggarwal, A.K. Saxena, J. Fluorine Chem. 42 (1989) 163–172.
- [8] A. Ranjan, A.K. Saxena, P.S. Venkataramani, Indian J. Chem. 33A (1994) 948–951.
- [9] A.K. Saxena, A. Ranjan, P.S. Venkataramani, J. Fluorine Chem. 64 (1993) 107–115.
- [10] A.K. Saxena, A. Ranjan, Synth. React. Inorg. Met.-Org. Chem. 29 (9) (1999) 1579–1591.
- [11] A.K. Saxena, A. Ranjan, K. Misra, P.S. Venkataramani, Indian J. Chem. 37A (1998) 736–738.
- [12] S.K. Shukla, A. Ranjan, A.K. Saxena, Synth. React. Inorg. Met.-Org. Chem. 30 (50) (2000) 909–919.
- [13] S.K. Shukla, A. Ranjan, A.K. Saxena, J. Fluorine Chem. 113 (2002) 155–159.
- [14] M. Fild, O. Glemser, Phosphorus, arsenic and antimony pentafluorophenyl compounds, in: P. Tarrant (Ed.), Fluorine Chemistry Reviews, vol. 3, Marcel Dekker, New York, 1969, pp. 129–144.
- [15] A. Otero, P. Royo, J. Organomet. Chem. 149 (1978) 315–320.
- [16] J.L. Wardell, Arsenic, antimony and bismuth, in: G. Wilkinson, F.G.A. Stone (Eds.), Comprehensive Organometallic Chemistry-I, vol. 2, Elsevier, Oxford, 1982, pp. 681–707, and references therein.
- [17] H.P. Braendlin, E.T. McBee, in: M. Stacey, J.C. Tatlow, A.G. Sharpe (Eds.), Advances in Fluorine Chemistry, vol. 3, Butterworths, Washington, DC, 1963.
- [18] G.O. Doak, L.D. Freedman, Arsenicals, antimonicals and bismuthicals, in: Burger (Ed.), Medicinal Chemistry, Wiley/Interscience, New York, 1973.
- [19] F.W. Fowler, A. Hassner, L.A. Levy, J. Am. Chem. Soc. 89 (1967) 2077–2082.
- [20] R. Adams (Ed.), Org. React., vol. 3, 1947, p. 255.

- [21] R.E. Banks, R.N. Haszeldine, Polyfluoroalkyl derivatives of metalloids and non-metals, in: H.J. Emeleus, A.G. Sharpe (Eds.), Advances in Inorganic Chemistry and Radiochemistry, vol. 3, Academic Press, New York, 1961, p. 367.
- [22] S.N. Bhattacharya, P. Raj, R.C. Srivastava, J. Organomet. Chem. 87
   (3) (1975) 279–283;
   S.N. BL # 105

S.N. Bhattacharya, P. Raj, R.C. Srivastava, J. Organomet. Chem. 105 (1) (1976) 45–49.

[23] W.J. Geary, Cord. Chem. Rev. 7 (1) (1971) 81–122.

- [24] E. Maslowsky Jr., Vibrational Spectra of Organometallic Compounds, Wiley/Interscience, New York, 1977.
- [25] Z. Grzonka, B. Liberek, Z. Palacz, Zesz. Nauk. Wydz. Mat., Fiz. Chem., Uniw. Gdanski, Chem. 2 (1972) 914; Chem. Abstr. 81 (1974) 120998a.
- [26] E. Lieber, J. Ramachandran, C.N.R. Rao, C.N. Pillai, Can. J. Chem. 37 (1959) 563–574.
- [27] A.I. Vogel, Practical Organic Chemistry, 3rd ed., Longman, London, 1971.