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Synthesis and Characterization of Some New Triorganophosphorus, -Arsenic and -Antimony(V) Amido Derivatives

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SYNTHESIS AND CHARACTERIZATION OF SOME NEW TRIORGANOPHOSPHORUS, -ARSENIC AND -ANTIMONY(V) AMIDO DERIVATIVES

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(Received August 2, 2002)

A number of triorganophosphorus, -arsenic, and -antimony(V) amido derivatives of the general formula $R_2R'ML_2$ [where $R = C_6F_5$, C_6H_5 ; $R' = C_6F_5$, $C_6H_4CH_3$ -p; M = P, As or Sb and L =imidazole, benzimidazole, 2-methyl benzimidazole, indazole, and 1,2,3,4-tetrahydrocarbazole] have been synthesized by the metathetical reaction of triorganophosphorus, -arsenic, and -antimony(V) halides and the corresponding imidazoles in the presence of triethyl amine. These compounds have been characterized by elemental analysis, IR and NMR (¹H and ¹⁹F) spectroscopy, conductance, and molecular weight data. The Van't Hoff factor "i" and molar conductance data of the compounds revealed them to be monomeric and nonionic in nature. On the basis of spectroscopic studies, a tentative trigonal bipyramidal structure has been assigned for these amido derivatives.

Keywords: Imidazole; NMR spectroscopy; pentafluorophenyl; synthesis; trigonal bipyramidal

In comparison to the well-documented hydrocarbon based organoarsenic and -antimony(III and V) amido derivatives, $^{1-4}$ corresponding perfluorophenyl derivatives are scarcely reported.⁵ As the electronic character of aromatic ring is markedly changed by the replacement

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Address correspondence to A. K. Saxena, Defence Materials and Stores, Research and Development Establishment, Joint Director, DMSRDE PO, G.T. Road, Kanpur 208013, India. of five nuclear hydrogen atoms by fluorine, the chemical and physical properties of the compounds also are changed. Thus, most of the time, very striking differences have been observed in phenyl and pentafluorophenyl substituted compounds just as perfluoroalkyl groups alter the chemistry of alkyl groups.⁶ Such intricacies always kindled interest of researchers to study pentafluorophenyl derivatives of group 15 elements.

Thus, keeping in view our continued interest in the synthesis, reactions, and spectroscopic studies of fluorophenyl group 15 derivatives⁷⁻¹⁰ and also to study the effect of pentafluorophenyl group on coordination behaviour of group 15 organometallic compounds,^{11–14} it is considered worthwhile to synthesize and characterize some new triaryl M(V) amido derivatives (M = As and Sb) along with some hydrocarbon based triorganophosphine(V) amido derivatives for the shake of spectral comparison.

RESULTS AND DISCUSSION

A number of hitherto unreported triorganophosphorus, -arsenic, and -antimony(V) amido derivatives were synthesized by metathetical reaction using triorganophosphorus, -arsenic, and -antimony halides and imidazoles in the presence of Et_3N as shown below:

 $R_{2}R'MCl_{2} + 2 HL \xrightarrow{\text{Benzene}} R_{2}R'ML_{2} + Et_{3}N.HCl$ $L = \sqrt[4]{1}{N}^{2} R = R' = C_{6}F_{5}, M = As (I), Sb (V);$ $R = C_{6}H_{5}, R' = C_{6}H_{4}CH_{3}-p, M = P (X)$ $L = \sqrt[4]{1}{1}^{3}N^{2} R = R' = C_{6}F_{5}, M = As (II), Sb (VI);$ $R = C_{6}H_{5}, R' = C_{6}H_{4}CH_{3}-p, M = P (XI)$ $L = \sqrt[5]{1}{1}^{3}N^{2} R = R' = C_{6}F_{5}, M = As (III), Sb (VI);$ $R = C_{6}H_{5}, R' = C_{6}H_{4}CH_{3}-p, M = P (XI)$ $L = \sqrt[5]{1}{1}^{3}N^{2} CH_{3} R = R' = C_{6}F_{5}, M = As (III), Sb (VII);$ $R = C_{6}H_{5}, R' = C_{6}H_{4}CH_{3}-p, M = P (XII)$



The reactions were carried out under inert atmosphere in benzene offering high yields of the products in general. Physical and analytical details of the compounds are given in Table I. All the compounds are sharp melting and soluble in common organic solvents and are stable to air and moisture. The melting points of compound (**II**) and (**VI**) do not change even after stirring 1.5 h with water and methanol at room temperature. The molar conductance values for 10^{-3} M solution in methanol of these derivatives were found in range of $14-22 \ \Omega^{-1}$ mol⁻¹ cm², which showed the absence of ionic species in solution.¹⁵ From the molecular weight determination, it has been concluded that the derivatives are monomeric in nature.

IR Spectra

The formation of imidazole derivatives was identified by the disappearance of $\nu(NH)$ absorption band at 3404 \pm 6 cm⁻¹ present in the ligands invariably. Further, the appearance of characteristic absorptions for C₆F₅, C₆H₅, C₆H₄CH₃-*p* group and imidazole ring in the respective derivatives confirmed the formation of the derivatives.^{16,17}

As the absorption bands of $\nu(C-C)$ of $C_6F_5 \operatorname{ring}^{16}$ at 1645–1465 cm⁻¹, ring stretching vibration $\nu(C-C)$ of $C_6H_5 \operatorname{ring}^{17}$ at 1584–1446 cm⁻¹, and $\nu(C=N)$ of imidazoles at 1640–1527 cm⁻¹ appear in close proximities, hence could not be assigned separately in these derivatives. Similarly, $\nu(CN)$ [at 1307–1274 cm⁻¹], $\delta(CN)$ [at 1170–1068 cm⁻¹] absorptions of imidazoles¹⁷ and $\nu(C-F)$ of C_6F_5 group (at 1385–1088 cm⁻¹) also appear very close, hence not assignable separately (Table II).

In pentafluorophenylarsenic and -antimony derivatives [compounds (I)–(IX)] characteristic aromatic stretching vibrations ν (C–H) and bending vibrations out of plane δ (C–H) appeared at 3087–3010 cm⁻¹ and 767–713 cm⁻¹ respectively.

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(5.65)(6.91)(89.9) (6.91)(7.40)(6.54)(6.33)6.56(6.54)13.65)10.97)10.40)10.97)7.86 (7.89) 6.936.897.366.536.355.6210.42Analysis: found (%) (calc.) (%) 6.71 13.6710.9410.94z $\begin{array}{c} 0.84\\ (0.85)\\ 1.26\\ (1.24)\\ 1.69\\ (1.68)\\ 1.68\\ 1.68\\ 0.82\\ 0.82\\ 0.80\\ 0.80\\ \end{array}$ $\begin{array}{c} 1.17\\ (1.18)\\ 1.57\\ 1.59)\\ 1.17\\ 1.17\\ 1.18\\ 1.18\\ 1.18\\ 2.46\\ 2.46\\ 2.46\\ 5.63\\ 5.63\\ 5.65)\end{array}$ 5.36 5.33) 5.78 5.80) 5.35 (5.33) Η (50.88) 73.18 (47.43)(46.13)(44.84)(73.16)40.5947.4048.7448.71) 47.4147.43)38.1038.08) 44.81(44.84)46.1544.8150.8677.6577.63) 78.10 (78.05)77.6577.66) 40.57C ${\Lambda_{
m M} \over (\Omega^1 \ {
m mol}^{-1} \ {
m cm}^2)}$ 10^{-3} M solution in methanol 19.01 18.9521.8314.6215.0421.1616.2219.0314.0715.2414.8714.8917.61 Yield (%) 74 86 85 6578 79 85 76 69 77 7279 81 m.p. (°C) 135 - 136109-111 105 - 10798 - 10094 - 96122140112138141 111 104117 Emperical formula (molecular weight) $\rm C_{34}H_{14}F_{15}N_{4}As$ $\rm C_{42}H_{24}F_{15}N_4Sb$ $C_{32}H_{10}F_{15}N_4As$ $C_{32}H_{10}F_{15}N_4As$ $\rm C_{32}H_{10}F_{15}N_4Sb$ $\rm C_{34}H_{14}F_{15}N_4Sb$ $\rm C_{32}H_{10}F_{15}N_{4}Sb$ $\mathrm{C}_{24}\mathrm{H}_{6}\mathrm{F}_{15}\mathrm{N}_{4}\mathrm{As}$ $\mathrm{C}_{24}\mathrm{H}_{6}\mathrm{F}_{15}\mathrm{N}_{4}\mathrm{Sb}$ $\mathrm{C}_{25}\mathrm{H}_{23}\mathrm{N}_{4}\mathrm{P}$ $C_{33}H_{27}N_4P$ $C_{35}H_{31}N_4P$ $\lambda_{33}H_{27}N_4P$ (857.179)(885.23)(857.18)(991.40)(838.41)(810.35)(757.06)(710.23)(810.35)(410.46)(510.58)(538.63)(510.58)Comp. No. (IIIX) (IIIIA) (III) (IIX) E S E X Ê S 8 Ξ

TABLE I Some Physical and Analytical Data of Amido Derivatives

TABLE	II Characteristic IR Al	osorption Bands (cm ⁻¹) of Ar	nido Derivatives	
Comp. No.	$\nu(C-H)$	$\nu(C-C)/\nu(C=N)$	$\nu(C-N)/\nu(C-F)/\delta(C-N)$	δ(C-H)
(I)	3020, 2929	1638 (s), 1514 (vs), 1470 (vs)	1376 (m), 1274 (m), 1191 (s), 1080 (vs), 968 (vs), 943 (m)	758 (m), 740 (m)
(I)	3082, 2980, 2604	1639 (s), 1616 (m), 1515 (vs), 1471 (vs)	1376 (w), 1205 (s), 1251 (m), 1080 (vs), 968 (vs)	746 (s), 713 (m)
(III)	3059, 2930	1638 (s), 1521 (vs), 1485 (vs)	1375 (s), 1281 (s), 1072 (s), 981 (vs)	1356 (m), 767 (m), 718 (s)
(V)	3075, 2941	1001 (s), 1637 (vs), 1515 (s),	1381 (s), 1290 (m), 1091 (vs), 977 (vs),	1355 (s), 746 (s), 719 (m)
		1483 (vs)	1201 (m)	
\mathbf{v}	3010, 2995	1644 (s), 1599 (s), 1522 (s),	1397 (w), 1353 (m), 1287 (m), 1200 (vs),	760 (s), 749 (m)
		1489 (vs)	1084 (s), 978 (vs)	
(IA)	3087, 2982	1642 (s), 1611 (s), 1495 (vs),	1346 (m), 1299 (m), 1201 (vs), 1091 (m),	746 (s), 720 (m)
		1519(s)	979 (vs)	
(III)	3060, 2926	1637 (s), 1512 (vs), 1472 (vs)	1387 (m), 317 (m), 1272 (s), 1258 (m),	1416 (m), 743 (s), 715 (m)
			1080 (vs), 969 (vs)	
(IIIIA)	3085, 2972	1635 (s), 1514 (s), 1473 (vs),	1375 (s), 1360 (m), 1272 (w), 1229 (m),	743 (m), 721 (m)
		1559 (w)	1081 (s), 970 (s), 951 (m)	
(X 1)	3050, 2935, 2846	1637 (s), 1513 (s), 1474 (vs),	1376 (m), 1080 (vs), 971 (vs), 1302 (s),	743 (s), 725 (m)
		1585 (s), 1444 (s)	1234 (m)	
(X)	3030, 2925, 2844	1601 (s), 1525 (m), 1483 (m),	1307 (m), 1255 (vs), 1176 (vs), 1118 (vs),	1407 (m), 1395 (m), 748 (vs),
		1437 (s)	1061 (s)	730 (vs)
(X)	3061, 2968, 2862	1601 (s), 1588 (m), 1458 (m),	1301 (m), 1273 (s), 1245 (vs), 1185 (vs),	1409 (vs), 1364 (m), 751 (vs),
		1438(s)	1120 (vs)	725 (vs)
(XII)	3051, 2990, 2918, 2848	1622 (m), 1601 (s), 1556 (s),	1271 (m), 1185 (vs), 1119 (vs), 1070 (m)	1417 (s), 1387 (s), 1361 (m),
		$1484 ({ m m}),1438 ({ m s})$		751 (s), 726 (vs), 704 (s)
(IIIX)	3089, 3053, 2919	1621 (s), 1601 (s), 1503 (s),	1312 (m), 1248 (m), 1185 (vs), 1120 (vs),	1382 (m), 1355 (s), 743 (s),
		1483 (s), 1437 (s)	1075 (s)	722 (vs), 705 (s)

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In diphenyl(*p*-tolyl)phosphine derivatives [compounds (**X**)–(**XIII**)] characteristic aromatic and aliphatic stretching vibrations ν (CH) appeared at 3089–2844 cm⁻¹ and bending vibrations δ (C–H) appeared¹⁷ at 1417–705 cm⁻¹. In these derivatives the imidazole ring showed the stretching and bending vibrations ν (CN) and δ (CN) at 1312-1245 cm⁻¹ and 1185–1070 cm⁻¹ respectively.¹⁷

¹H NMR Spectra

The signals due to N–H protons invariably disappeared in all the phosphorus, arsenic, and antimony imidazole derivatives, which may be attributed to the formation of the derivatives. In diphenyl(*p*-tolyl)phosphine derivatives [compound (**X**)–(**XIII**)] the aromatic protons of C_6H_5 , $C_6H_4CH_3$ -*p* and aromatic ring of imidazole ligands appeared in close proximities as multiplet in the range δ 7.14–7.31 ppm thus could not be assigned separately whereas the CH₃ protons of *p*-tolyl group appeared at $\sim \delta$ 2.35 ppm (Table III).

In the triarylarsenic and -antimony imidazole derivatives [compound (I) and (V)] the C₂ and C_{4,5} protons of the ligands appeared at $\sim \delta$ 7.85 ppm (s, 2H) and $\sim \delta$ 7.33 ppm (s, 4H) respectively.

Benzimidazole derivatives of triorganoarsenic and -antimony(V) [compounds (II) and (VI)] showed the protons of C₂, C_{5,6}, and C_{4,7} at $\sim \delta 8.13$ (s, 2H), $\delta 7.68$ (q, 4H), and $\delta 7.32$ ppm (q, 4H) respectively.

In the compound (**III**) and (**VII**) the C_{5,6} and C_{4,7} protons of 2methyl benzimidazole ligand appeared at $\sim \delta$ 7.49 (q, 4H) and 7.19 ppm (q, 4H) respectively. The C_{4,7} protons in the ligand appeared at δ 7.15 ppm as hexet due to coupling of NH and C_{5,6} protons which in the derivatives appeared as a quartet at δ 7.19 ppm due to loss of -NH proton. The CH₃ proton due to ligand in these derivatives appeared at $\sim \delta$ 2.6 ppm (s, 6H). The single peak of CH₃ further showed that ligands are present in one plane. In the compound (**XII**), CH₃ protons of the *p*-tolyl group and ligand appeared at δ 2.32 (s, 3H) and 2.60 ppm (s, 6H), respectively, which further confirmed that the *p*-tolyl group and the ligand are present separately in one plane.

Indazole derivatives (**IV**) and (**VIII**) showed the C₃, C₄, C₅, C₆, C₇ protons in usual manner at $\sim \delta$ 8.62 (s, 2H), 7.45 (d, 2H), 7.13 (t, 2H), 7.35 (t, 2H), and 7.73 ppm (d, 2H) respectively.

Compound (**IX**) showed the proton signals of 1,2,3,4tetrahydrocarbazole in usual manner at δ 7.6 (C₂, t, 2H), 7.4 (C₄, t, 2H), 7.16 (C_{3.5}, Q, 4H), 2.75 (C_{6.9}, Q, 4H), 1.96 ppm (C_{7.8}, m, 4H).

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TABLE III ¹H and ¹⁹F NMR Data of Amido Derivatives

		1	9 F NMR δ (ppm)	
Comp. No.	¹ H NMR & (ppm)	${ m F}_{3,5}$ $[{ m J}_{3,4}~({ m Hz})]$	${ m F}_{2,6}$ $[{ m J}_{2,3}({ m Hz})]$	${ m F}_4$
(I)	7.85 (s, 2H) protons at C_2 , 7.33 (s, 4H) protons at $C_{4,5}$	-156.18 (t) $[19.54]$	–129.39 (d) [20.55]	-143.61 (t)
(II)	8.13 (s, 2H) protons at C_2 , 7.68 (q, 4H) protons at $C_{5,6}$, 7.32 (q, 4H)	-157.00 (t) [19.53]	-130.00 (d) $[20.54]$	-143.81 (t)
(III)	protons at $O_{4,7}$ 7.49 (q, 4H) protons at $C_{5,6}$, 7.19 (q, 4H) protons at $C_{4,7}$, 2.6 (s, 6H)	-156.92 (t) $[19.54]$	-131.21 (d) $[20.54]$	-144.07 (t)
	CH ₃ protons			
(V I)	8.62 (s, 2H) protons at C_3 , 7.45 (d, 2H) protons at C_4 , 7.13 (t, 2H)	-157.35 (t) [19.54]	-130.93 (d) [20.53]	-143.92 (t)
	protons at C_5 , 7.35 (t, 2H) protons at C_6 , 7.73 (d, 2H) protons at C_7			
S	7.83 (s, 2H) protons at C_2 , 7.30 (s, 4H) protons at $C_{4,5}$	-160.81 (t) [19.53]	-135.00 (d) $[20.54]$	-143.72 (t)
(M)	8.14 (s, 2H) protons at C_2 , 7.66 (q, 4H) protons at $C_{5,6}$, 7.34 (q, 4H)	-159.26 (t) [19.54]	-135.86 (d) [20.53]	-143.00(t)
	protons at $C_{4,7}$			
(III)	7.47 (q, 4H) protons at $C_{5,6}$, 7.16 (q, 4H) protons at $C_{4,7}$, 2.5 (s, 6H)	-160.57 (t) $[19.55]$	-134.91 (d) [20.54]	-144.21 (t)
	CH ₃ protons			
(IIII)	8.61 (s, 2H) protons at C ₃ , 7.46 (d, 2H) protons at C ₄ , 7.13 (t, 2H)	-158.35 (t) [19.54]	-134.23 (d) $[20.55]$	-143.96 (t)
	protons at C_5 , 7.35 (t, 2H) protons at C_6 , 7.71 (d, 2H) protons at C_7			
(X I)	$7.6(t, 2H)$ protons at C_2 , $7.4(t, 2H)$ protons at C_4 , $1.96(m, 4H)$ protons	-161.00 (t) $[19.53]$	-135.76 (d) $[20.53]$	-143.57 (t)
	at $C_{7,8}$, 7.16 (q, 4H) protons at $C_{3,5}$, 2.75 (q, 4H) protons at $C_{6,9}$			
(X)	$7.16-7.313$ (m) aromatic protons of C_6H_5 , $C_6H_4CH_3$ and imidazole	I	I	
	ring, 2.35 (s, $3H$) CH_3 protons			
(X)	$7.14-7.317$ (m) aromatic protons of C_6H_5 , $C_6H_4CH_3$ and	I	Ι	
	imidazole ring, 2.34 (s, $3H$) CH ₃ protons			
(IIX)	$7.15-7.312$ (m) aromatic protons of C_6H_5 , $C_6H_4CH_3$ and	Ι	Ι	I
	imidazole ring, 2.32 (s, 3H) CH ₃ protons of p -tolyl group and			
	2.6 (s, 6H) CH3 protons of ligand			
(XIII)	$7.14-7.318$ (m) aromatic protons of C_6H_5 , $C_6H_4CH_3$ and	Ι	Ι	
	imidazole ring, 2.35 (s, $3H$) CH_3 protons			

¹⁹F NMR Spectra

Pentafluorophenylarsenic derivatives [compound (I)–(IV)] showed F_{2,6}, F₄ and F_{3,5} signals at $\sim \delta$ –129, –143, and –156 ppm, respectively and pentafluorophenyl antimony derivatives [compound (V)–(IX)] showed F_{2,6}, F₄, and F_{3,5} signals at $\sim \delta$ –135, –143, and –160 ppm respectively. The F₄ signals were easily identified due to half intensity compared to F_{2,6} and F_{3,5}. The F₄ signals appeared as a triplet due to F_{3,5} coupling. The F_{2,6} and F_{3,5} signals appeared as doublet and triplet respectively. The F_{3,5} chemical shifts were observed at higher field compared to the F_{2,6} and F₄ chemical shifts, indicating that the donation of electron from *o*- and *p*-positions takes place toward carbon attached to antimony atom and this observation is in accordance with the previous studies that the C₁ carbon of perfluorinated benzene ring feels high electron density due to the diminished inductive effect of the fluorine atom and donation of electron density from the unshared p electron of fluorine to the system of the ring (*p*- π interaction).^{18,19}

In view of the spectroscopic data of these compounds, the metal (P, As, and Sb) in such cases is assumed to be in pentacoordinated state and the structure of the compounds (I)–(XIII) may be tentatively assigned as trigonal bipyramidal (Figure 1) in which aryl rings are in one plane and thus imidazole ligands attained apical position.



where $R = R' = C_6F_5$, M = As or Sb

 $R = C_6 H_5, R' = C_6 H_4 C H_3 - p, M = P$

L = Imidazole Ligands

 $\label{eq:FIGURE1} FIGURE1 \quad Configuration of triorganophosphorus, \mbox{-}arsenic, \mbox{and -}antimony(V) \\ amido \ derivatives.$

EXPERIMENTAL

All solvents (AR Grade) were purified, dried, and distilled before use by the standard methods.²⁰ The reactants, viz. imidazole, benzimidazole, 2-methyl benzimidazole, indazole, and 1,2,3,4-tetrahydrocarbazole (all Lancaster) were used as such. Triethylamine (E. Merck, AR Grade) was used after drying over potassium hydroxide. Tris(pentafluorophenyl)arsenic and -antimony(V) dichlorides were prepared by the reported methods.^{21,22}

IR spectra were recorded on a Pye Unicam SP3-300 spectrophotometer over the spectral range 4000–200 cm⁻¹in the solid state using KBr/CsI Pellets.¹H and ¹⁹F NMR spectra were recorded on Jeol JNM-400 NMR spectrometer using TMS and CF₃COOH as references respectively. Molecular weights were determined cryoscopically in nitrobenzene using a Beckman thermometer of ± 0.01 accuracy. The molar conductance of 10^{-3} M solution of the compounds was determined at 25°C with a Khera DC610 digital conductivity meter in methanol. Some representative synthesis procedures follow.

Synthesis of Diphenyl(*p*-tolyl)phosphine Dichloride [(C₆H₅)₂(C₆H₄CH₃-*p*)PCl₂]

Dry chlorine gas (generated by reaction of KMnO₄ and conc. HCl) was bubbled in a solution of $Ph_2(p\text{-Tol})P(13.82 \text{ g}, 0.05 \text{ mmol})$ in petroleumether (60–80°C) at room temperature under moisture free and nitrogen atmosphere with constant stirring. White precipitate was started to settle down, after 15 min bubbling of Cl_2 gas was stopped and the reaction mixture was further stirred for 30 min at room temperature, and then the solvent was decanted. The residue was washed three times with petroleum-ether (60–80°C) to remove unreacted $Ph_2(p\text{-Tol})P$. The residue was characterized as $Ph_2(p\text{-Tol})PCl_2$, yield 12.50 g (72%), m.p. 93°C, (found: C, 65.79; H, 5.00%; calcd. for $C_{19}H_{17}Cl_2P$; C, 65.72; H, 4.93%).

Reaction of Tris(pentafluorophenyl)arsenic Dichloride $[(C_6F_5)_3AsCl_2]$ with Imidazole

Tris(pentafluorophenyl)arsenic dichloride (1.294 g, 2 mmol), imidazole (0.272 g, 4 mmol) and Et₃N (1 ml) were stirred together in 75 ml of benzene at room temperature for 6 h, followed by 3 h of refluxing to ensure the completion of the reaction. Et₃N · HCl [m.p. 261°C(d)] formed was filtered off and the filtrate on concentration and addition of petroleum-ether (40–60°C) afforded the product $C_{24}H_6F_{15}N_4As$ (I), yield 1.05 g (74%), m.p. 122°C.

Similarly, other reactions of $(C_6F_5)_3AsCl_2$ with benzimidazole, 2-methyl benzimidazole, and indazole were carried out.

Reaction of Tris(pentafluorophenyl)antimony Dichloride [(C₆F₅)₃SbCl₂] with Benzimidazole

Tris(pentafluorophenyl)antimony dichloride (1.388 g, 2 mmol), benzimidazole (0.472 g, 4 mmol) and Et_3N (1 ml) were stirred together in 75 ml of benzene at room temperature for 6 h, followed by 1 h of refluxing to ensure the completion of the reaction. $Et_3N \cdot HCl$ [m.p. $261^{\circ}C(d)$] formed was filtered off and the filtrate on concentration and addition of petroleum-ether (40–60°C) afforded the product $C_{32}H_{10}F_{15}N_4Sb$ (VI), yield 1.457 g (85%), m.p. 109–111°C.

In a similar way, other reactions of $(C_6F_5)_3SbCl_2$ with imidazole, 2-methyl benzimidazole, indazole, and 1,2,3,4-tetrahydrocarbazole were carried out.

Reaction of Diphenyl(p-tolyl)phosphine Dichloride [(C₆H₅)₂(C₆H₄CH₃-p)PCl₂] with 2-Methylbenzimidazole

Diphenyl(*p*-tolyl)phosphine dichloride (1.389 g, 4 mmol), 2-methyl benzimidazole (1.057 g, 8 mmol) and Et_3N (1 ml) were stirred together in 75 ml of benzene at room temperature for 6 h, followed by 3 h of refluxing to ensure the completion of the reaction. $Et_3N \cdot HCl$ [m.p. 261°C(d)] formed was filtered off and the filtrate on concentration and addition of petroleum-ether (40–60°C) afforded the product $C_{35}H_{31}N_4P$ (**XII**), yield 1.71 g (79%), m.p. 104°C.

Similarly, other reactions of $Ph_2(p-Tol)PCl_2$ with imidazole, benzimidazole, and indazole were carried out. Some products were viscous, which could be crystallized only after scratching with a glass rod.

Reaction of (II) and (IV) with Water and Methanol

The diamides (II) and (IV) were stirred with excess of water and methanol respectively for 1.5 h at room temperature and subsequently refluxed for 1 h. After removal of the solvent the residue showed no change in melting point or IR spectra.

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