TRIPHENYLPNICTOGEN CHALCOGENIDES: A PREPARATIVE AND MASS-SPECTROMETRIC STUDY

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Summary

Oxidative-addition reactions of triphenylpnictogens, Ph_3M (M = N, P, As, Sb, Bi), with selenium(IV) oxide, sulphur dichloride, disulphur dichloride, diselenium dichloride, lead(IV) acetate and potassium selenocyanate have been studied. Mass spectra are described of Ph_3M (M = N, P, As, Sb, Bi), Ph_3MO (M = P, As), Ph_3MS (M = P, As, Sb), Ph_3PSe, $Ph_3Sb(OH)_2$ and $Ph_3M(OCOCH_3)_2$ (M = Sb, Bi).

Introduction

As part of a general study of phosphorus(V) derivatives [1—4], we have investigated the preparative routes to and mass spectrometry of, a number of triphenylpnictogen chalcogenides, Ph_3MX (M = N, P, As, Sb, Bi; X = O, S, Se, $(OH)_2$, $(OCOCH_3)_2$). A number of preparative routes to these compounds are recorded only in the earlier literature; thus Mel'nikov and Rokitskaya claimed [5] that reaction of Ph_3M (M = P, As, Sb) with selenium(IV) oxide yielded a mixture of Ph_3MO and Ph_3MSe, which for M = As or Sb represents the only reported preparation of Ph_3MSe. Zuckerkandl and Sinai described [6] an addition compound of stoichiometry $Ph_3As \cdot S_2Cl_2$ which they regarded as containing five-coordinate arsenic $Ph_3As(SSCl)Cl$. We have investigated the reactions of Ph_3M (M = N, P, As, Sb, Bi) with SeO_2, S_2Cl_2 and SCl_2, as well as with lead(IV) acetate [7—9] and report here the results of this work.

Results and discussion

A. Reactions

Triphenylphosphine and triphenylarsine both react with disulphur dichloride, S_2Cl_2, to yield the corresponding sulphide in high yield (eq. 1). By contrast the

$$Ph_3M + S_2Cl_2 \rightarrow Ph_3MS + SCl_2 \tag{1}$$
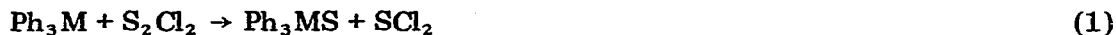
(M = P, As)

antimony and bismuth analogues react to give the triphenylpnictogen dichloride and sulphur, (eq. 2). Triphenylamine does not react; Zuckerkandl and Sinai [6]

$$Ph_3M + S_2Cl_2 \rightarrow Ph_3MCl_2 + \tfrac{1}{4} S_8 \tag{2}$$

(M = Sb, Bi)

reported that a 1 : 1 adduct was formed when M = As, but we have found no evidence for this. The reaction to give Ph_3MCl_2 was reported by Challenger [10] for M = Bi.

Similarly, no adduct formation was found with sulphur dichloride SCl_2; for M = P, As, the products were Ph_3MS and chlorine (eq. 3), while triphenyl-

$$Ph_3M + SCl_2 \rightarrow Ph_3MS + Cl_2 \tag{3}$$

(M = P, As)

antimony and -bismuth again abstracted chlorine (eq. 4). As with S_2Cl_2, triphenylamine showed no reaction.

$$Ph_3M + SCl_2 \rightarrow Ph_3MCl_2 + \tfrac{1}{4} S_8 \tag{4}$$

(M = Sb, Bi)

For the equilibrium 5 a simple thermochemical calculation indicates that the

$$Ph_3MS + SCl_2 \rightleftharpoons Ph_3MCl_2 + \tfrac{1}{4} S_8 \tag{5}$$

$\Delta H^{\ominus}$ term strongly favours elemental sulphur and triphenylpnictogen dichloride. Any attempt to rationalise the observed products must therefore be in mechanistic terms.

Mel'nikov and Rokitskaya [5] reported that reaction of selenium(IV) oxide with Ph_3M (M = P, As, Sb) gave a mixture of Ph_3MO and Ph_3MSe. Zingaro and Merijanian [11] found no evidence for the formation of Ph_3AsSe in this reaction, nor from the reaction of Ph_3As and elemental selenium, nor from the reaction of triphenylarsine dihalides with hydrogen selenide, despite other claims to the contrary [12]. We have studied the reaction of selenium(IV) oxide with Ph_3M (M = N, P, As, Sb, Bi); no reaction occurs when M = N or Bi and when M = P or Sb the sole products, other than red selenium, are Ph_3PO and $Ph_3Sb(OH)_2$, respectively. However, there is some evidence for the transient formation of a selenide in the case of Ph_3As; from the reaction of the arsine with SeO_2, a colourless oil can be obtained which rapidly deposits red selenium and triphenylarsine. Although no characterisation of the seleniferous species was achieved, it seems probable that it is indeed the thermodynamically unstable triphenylarsine selenide. That red selenium is deposited, may be taken as evidence that this allotrope does not react with triphenylarsine: Zingaro has shown [11] that the less reactive grey allotrope does not react.

Although triphenylphosphine reacts very rapidly with potassium selenocyanate, KNCSe, in warm acetonitrile to give the selenide [13], reflux of a mixture of the selenocyanate and triphenylarsine for 18 h gave no triphenylarsine selenide, nor was any selenium deposited, suggesting that no transfer of selenium from carbon to arsenic took place. Observing that Ph_3M (M = P, As) are converted to the corresponding sulphides by reaction with disulphur dichloride the analogous reactions with diselenium dichloride Se_2Cl_2 were attempted; in

each case, copious deposition of selenium took place, with no formation of Ph$_3$MSe. From the present work, and that of Zingaro [11], it is concluded that triphenylarsine selenide is thermodynamically unstable under ambient conditions.

The reaction of lead(IV) acetate with triphenylbismuth to give triphenylbismuth diacetate, first reported by Kocheskov [8] was later extended first to triphenylantimony [7] and then subsequently to triphenylarsine [9]. We have now studied the action of lead(IV) acetate on triphenylphosphine and triphenylamine. Although no solid triphenylphosphine diacetate was isolated, a concentrated solution in dichloromethane was obtained whose spectroscopic properties (see Experimental section) accord with its being the diacetate. The IR spectrum is very similar to that of the arsenic analogue [9]. Since the apicophilicity of acetate is higher than that of phenyl, it is probable that the structure of each of the triphenylpnictogen diacetates is a *trans* diaxial trigonal bipyramid. The thermal stability shows a marked increase from phosphorus to bismuth, thus P < As < Sb $\approx$ Bi. The antimony and bismuth derivatives can be stored at room temperature unchanged for many months and give ions containing phenyl and acetate groups bound to M in their mass spectra. The thermal stability of the arsenical is much lower; all attempts to record a mass spectrum give only Ph$_3$AsO$^+$, (CH$_3$CO)$_2$O$^+$ and their decomposition products, while attempts to isolate the phosphorus compound yield only triphenylphosphine oxide and acetic anhydride.

Although the C—M—C angles in triphenylphosphine [14], tri-*p*-tolyl arsine [15] and triphenylbismuth [16] are 103°, 102° and 94° respectively, the C—N—C angle in triphenylamine [17] is 116°, i.e. the NC$_3$ fragment is almost planar. Consequently it was thought possible that two acetate groups might be oxidatively added, without significant change to the Ph$_3$N geometry, to the nitrogen atom to give five-coordinate nitrogen. On reaction with lead(IV) acetate in dichloromethane triphenylamine yields a blue-green solution (λ_{max} 650 nm); this most probably contains the radical-cation Ph$_3$N$^+$, since the absorption maximum for this species has been reported as occurring at wavelengths between 660 nm [18] and 640 nm [19], depending on its environment. This species is subsequently replaced by a red species (λ_{max} 480 nm), probably the radical-cation of *N,N,N',N'*-tetraphenylbenzidine, (Ph$_2$NC$_6$H$_4$)$_2^+$ [18—20].

Hydrolysis of triphenylarsine diacetate [9] and of triphenylphosphine diacetate yields Ph$_3$MO (M = P, As): hydrolysis of triphenylantimony diacetate gives the dihydroxide Ph$_3$Sb(OH)$_2$, while hydrolysis of the bismuth compound in dichloromethane solution yields metallic bismuth, biphenyl, diphenylbismuth acetate and chlorobenzene. The presence of chlorobenzene is suggestive of the free-radical intermediate C$_6$H$_5$ which abstracts chlorine from the solvent. Challenger postulated [21] the formation of diphenylbismuth hydroxide in the decomposition of triphenylbismuth dihydroxide; it was suggested that this bismuth(III) species underwent a redistribution reaction (eq. 6).

$$3 \, Ph_2BiOH \rightarrow 2 \, BiPh_3 + Bi(OH)_3 \qquad (6)$$

In the diacetate hydrolysis we observe formation of Ph$_2$BiOCOCH$_3$, consistent with this suggestion; we observe neither triphenylbismuth nor bismuth(III)

hydroxide, again lending support to Challenger's suggestion for their mode of formation. Thiolysis of triphenylantimony diacetate with sodium sulphide and hydrogen sulphide yielded triphenylantimony sulphide; the thiolysis of triphenylbismuth diacetate was not attempted.

B. Mass spectrometry

In Table 1 are recorded the mass spectra of Ph_3M (M = N, P, As, Sb, Bi). Triphenylphosphine has been the subject of a very careful study by Williams and his colleagues, in which assignments of the structures of fragment ions were derived from the spectra of selectively deuterated samples [22], their work provides the basis for assignment in the spectra of the remaining Ph_3M compounds. In triphenylamine and triphenylphosphine, the molecular ion is the base peak of the spectrum, and $(Ph_3M - H)^+$ is also prominent: in triphenylarsine and triphenylantimony the base peak is PhM^+ and the molecular

TABLE 1

MASS SPECTRA OF Ph_3M (M = N, P, As, Sb, Bi)

Ion	M				
	N (m/e)[a]	P (m/e)	As (m/e)	Sb [b] (m/e)	Bi (m/e)
Ph_3M^+	245(100)	262(100)	306(22)	352(3.3)	440(0.4)
$(Ph_3M-H)^+$	244(26)	261(23)	305(0)	351(0)	439(0)
$(Ph_3M-2H)^+$	243(9.7)	260(0)	304(0)	350(0)	438(0)
Ph_2M^+	168(4.4)	185(15)	229(6.4)	275(4.9)	363(1.1)
$(Ph_2M-H)^+$	167(16)	184(20)	228(4.5)	274(0.7)	362(0)
$(Ph_2M-2H)^+$	166(8.5)	183(73)	227(25)	273(3.7)	361(0)
PhM^+	91(1.8)	108(66)	152(100)	198(100)	286(58)
$(PhM-H)^+$	90(0)	107(30)	151(13)	197(4.9)	285(0)
M^+	14(—)	31(0.1)	75(1.4)	121(6.2)	209(100)
Ph_2^+	154(2.6)	154(2.6)	154(13)	154(27)	154(4.1)
$(Ph_2-H)^+$	153(2.1)	153(1.9)	153(5.9)	153(6.1)	153(2.0)
$(Ph_2-2H)^+$	152(15)	152(12)	152(11)	152(5.5)	152(2.1)
PhH^+	78(5.0)	78(2.8)	78(3.8)	78(3.5)	78(4.1)
Ph^+	77(18.8)	77(5.0)	77(5.8)	77(16)	77(3.9)

Doubly charged ions:

Ph_3M^{2+}	122.5(17)				
$(Ph_3M-2H)^{2+}$	121.5(5)				
$(Ph_3M-4H)^{2+}$	120.5(6)				
$(Ph_3M-6H)^{2+}$	119.5(2)				

Metastable peaks, M*

Process	N	P	As	Sb [b]	Bi
$Ph_3M^+ \rightarrow PhM^+$	33.8	44.5	75.5	111.4	n.o.
$Ph_3M^+ \rightarrow (Ph_2-M-H)^+$	n.o.	129.2	n.o.	n.o.	n.o.
$Ph_2M^+ \rightarrow M^+$	n.o.	n.o.	n.o.	n.o.	120.3
$PhM^+ \rightarrow M^+$	n.o.	n.o.	n.o.	n.o.	152.7
$Ph_2M^+ \rightarrow Ph_2^+$	n.o.	128.2	103.6	86.2	n.o.

[a] Relative intensities in parentheses. [b] m/e value given [121]Sb only, relative intensity given for ([121]Sb + [123]Sb).

ion is weak. The spectrum of triphenylbismuth is dominated by the Bi^+ ion; the only other ion whose intensity exceeds 5% of the base peak is $PhBi^+$ (58%). On descending the group from phosphorus to bismuth, ions of the types $(Ph_3M - nH)^+$ and $(Ph_2M - nH)^+$ decrease in abundance, indicating that formation of heterocycles such as I is decreasing. The spectrum of triphenyl-
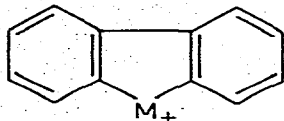
(I)

M = N, P, As, Sb, Bi

amine contains a series of doubly charged ions $(Ph_3M - nH)^{2+}$ (n = 0, 2, 4, 6) for which in the n = 6 case the symmetrical structure II is postulated. It is tempting to suppose that the two electrons lost in these ions are the two non-
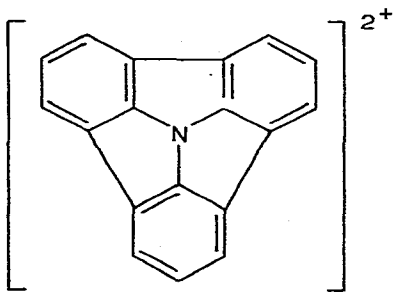
(II)

bonding electrons on the nitrogen atom, in which case the configuration about nitrogen would be strictly planar. Support for this, as opposed to loss of electrons from the arene groups, is derived from the observation that the first ionisation energy, 7.8 eV, in N,N-dimethylaniline is substantially lower than the first ionisation energy, 9.3 eV, of benzene [23].
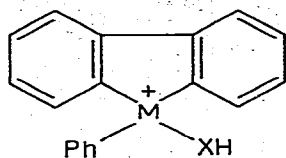
Table 2 contains the mass spectra of compounds Ph_3MX (M = P; X = O, S, Se: M = As; X = O, S: M = Sb; X = S). As with Ph_3M, structural assignments for fragment ions are based on the study [22] of triphenylphosphine oxide and its deuterated analogues. Although all the spectra in Table 2 contain biphenylene ions $C_{12}H_8^+$ and heterocyclic ions of type I, only the spectra of triphenylphosphine oxide and sulphide contain the quasi-onium ions $(Ph_2MX - 2H)^+$ (III). All
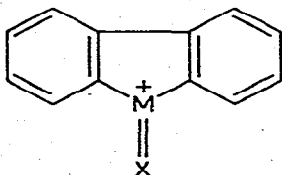
(III)

M = P; X = O, S

except those of triphenylarsine sulphide and triphenylantimony sulphide however contain the onium ions $(Ph_3MX - H)^+$, (IV), although the abundance of such

(IV)

$M = P; X = O, S, Se$

$M = As; X = O$

ions decreases not only with increasing atomic number of M, but also with increasing atomic number of X.

Table 3 contains the mass spectra of triphenylantimony dihydroxide and of the diacetates of triphenylantimony and triphenylbismuth. Observation of a molecular ion $Ph_3SbO_2H_2^+$ is strong evidence that this antimonial is a true dihydroxide, rather than an oxide hydrate, as is the case for the arsenic analogue. An X-ray structure of this compound reveals it to be a hydrated oxide $Ph_3AsO \cdot H_2O$ [24], and analytically pure samples of triphenylarsine oxide and its monohydrate give identical mass spectra. As in triphenylantimony and triphenylantimony sulphide, the base peak of the dihydroxide spectrum is $C_6H_5Sb^+$. Other

TABLE 2

MASS SPECTRA OF Ph_3MX (M = P, X = O, S, Se: M = As: X = O, S: M = Sb: X = S)

Ion	M					
	Ph_3PO (m/e) [a]	Ph_3PS (m/e)	Ph_3PSe [b] (m/e)	Ph_3AsO (m/e)	Ph_3AsS (m/e)	Ph_3SbS [c] (m/e)
Ph_3MX^+	278(37)	294(84)	342(100)	322(2.4)	338(1.7)	384(3.2)
$(Ph_3MX-H)^+$	277(100)	293(56)	341(18)	321(8.4)	337(0)	383(0)
Ph_3M^+	262(0)	262(6.4)	262(53)	306(2.2)	306(10)	352(7.1)
Ph_2MX^+	201(23)	217(12)	265(1.4)	245(0)	261(0.2)	307(0.4)
$(Ph_2MX-2H)^+$	199(17)	215(81)	263(0)	243(0)	259(0)	305(0)
Ph_2M^+	185(11)	185(81)	185(77)	229(12)	229(8.2)	275(9.1)
$(Ph_2M-2H)^+$	183(17)	183(100)	183(91)	227(13)	227(15)	273(12)
$PhMH^+$	109(0.5)	109(13)	109(2.7)	153(11)	153(0.4)	199(11)
PhM^+	108(1.3)	108(36)	108(35)	152(97)	152(5.7)	198(100)
$C_6H_4M^+$	107(3.5)	107(32)	107(24)	151(69)	151(100)	197(2.7)
M^+	31(7.2)	31(1.6)	31(1.9)	75(3.3)	75(0)	121(14)
Ph_2^+	154(7.7)	154(2.9)	154(1.9)	154(49)	154(1.4)	154(47)
$(Ph_2-H)^+$	153(5.6)	153(0)	153(2.4)	153(36)	153(8.3)	153(1.2)
$(Ph_2-2H)^+$	152(17)	152(17)	152(10)	152(63)	152(4.3)	152(12)
PhH^+	78(8.0)	78(9.5)	78(8.4)	78(100)	78(1.8)	78(6.4)
Ph^+	77(51)	77(9.6)	77(8.6)	77(31)	77(3.2)	77(1.9)

[a] Relative intensities in parentheses. [b] m/e value given only for ^{80}Se: relative intensity given for $(^{74}Se + ^{76}Se + ^{77}Se + ^{78}Se + ^{80}Se + ^{82}Se)$. [c] m/e value given only for ^{121}Sb: relative intensity given for $(^{121}Sb + ^{123}Sb)$.

TABLE 3

MASS SPECTRA OF $Ph_3Sb(OH)_2$ AND $Ph_3M(OCOCH_3)_2$ (M = Sb, Bi)

Ion	$Ph_3Sb(OH)_2$ [b] (m/e) [a]	Ion	$Ph_3Sb-(OCOCH_3)_2$ [b] (m/e)	$Ph_3Bi-(OCOCH_3)_2$ (m/e)
$Ph_3SbO_2H_2^+$	386(1.8)	$Ph_3M(OCOCH_3)_2^+$	470(0)	558(0)
$Ph_3SbOH_2^+$	370(2.7)	—	—	—
Ph_3SbOH^+	369(2.0)	$Ph_3M(OCOCH_3)^+$	411(12)	499(11)
—	—	$Ph_2M(OCOCH_3)_2^+$	393(5.2)	481(6.0)
Ph_3Sb^+	352(2.7)	Ph_3M^+	352(4.2)	440(0)
Ph_2Sb^+	275(7.3)	Ph_2M^+	275(5.5)	363(3.0)
$(Ph_2-2H)^+$	273(8.6)	$(Ph_2M-2H)^+$	273(5.8)	361(0)
—	—	$PhM(OCOCH_3)^+$	257(10)	345(4.1)
—	—	$M(OCOCH_3)_2^+$	239(0)	327(3.9)
$PhSbOH^+$	215(3.2)	$PhMOH^+$	215(13)	303(2.3)
$PhSb^+$	198(100)	PhM^+	198(100)	286(43)
$SbOH^+$	138(8.9)	$MOCOCH_3^+$	180(23)	268(47)
SbO^+	137(3.9)	—	—	—
Sb^+	121(12)	M^+	121(6.4)	209(100)
Ph_2^+	154(56)	Ph_2^+	154(53)	154(15)
$(Ph_2-2H)^+$	152(16)	$(Ph_2-2H)^+$	152(0)	152(0)
—	—	$PhOCOCH_3^+$	136(0)	136(18)
$PhOH^+$	94(0)	$PhOH^+$	94(4.8)	94(67)
PhH^+	78(0)	PhH^+	78(13)	78(25)
Ph^+	77(58)	Ph^+	77(39)	77(26)

[a] Relative intensities in parentheses. [b] m/e value given for ^{121}Sb only, relative intensity given for $(^{121}Sb + ^{123}Sb)$.

noteworthy ions in this spectrum are SbO^+ and $SbOH^+$, whose intensities are 3.9 and 8.9% respectively of the base peak.

Neither of the diacetates gives a molecular ion, but both spectra contain the onium ions $Ph_3M(OCOCH_3)^+$ and $Ph_2M(OCOCH_3)_2^+$: the ion $M(OCOCH_3)_2^+$ occurs only for M = Bi, but both spectra contain $MOCOCH_3^+$. The bismuth species also has the radical cation of phenyl acetate $PhOCOCH_3^+$ in its spectrum. As with the spectrum of triphenylbismuth itself, Bi^+ is the base peak and there are few

SCHEME 1
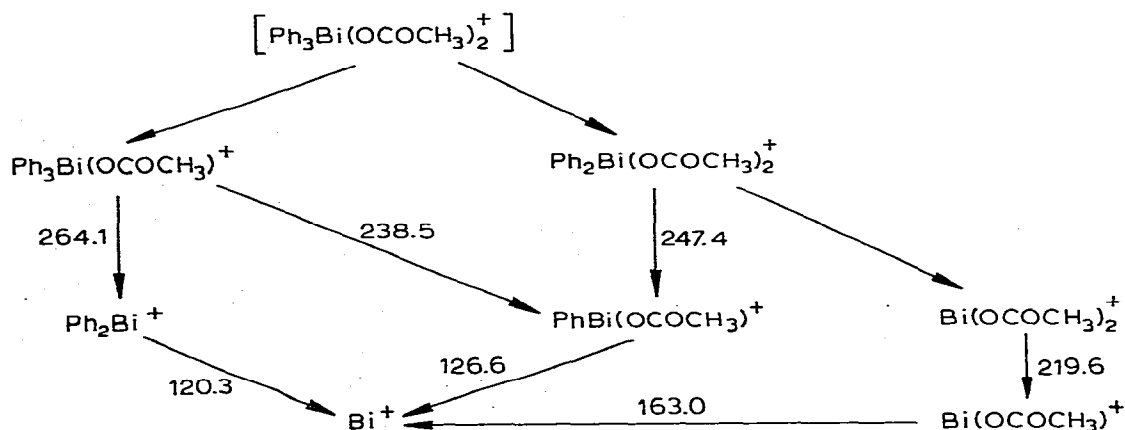
heavy ions of high intensity. The redox stability of the Bi^+ ion is such that in the presence of suitable counter ions it can be trapped in crystalline solids, as in Bi^+ $(Bi_9^{5+})(HfCl_6^{2-})_3$ [25]. Of the mass spectra herein reported, only that of triphenylbismuth diacetate contains a large number of metastable peaks: fragmentation pathways, with metastable-supported transitions are shown in Scheme 1.

Experimental

Compounds Ph_3M (M = N, P, As, Sb, Bi) and Ph_3PO were commercial products and were recrystallised from methylene chloride before use. Ph_3PS was prepared by reaction of Ph_3P and sulphur in refluxing benzene solution. Ph_3PSe was prepared by reaction of Ph_3P and KNCSe in acetonitrile solution [31], and had $\delta(P)$ +35.19 ppm, $^1J(^{31}P—^{77}Se)$ 736.2 Hz. Oxidation of Ph_3As with potassium permanganate in aqueous acetone gave $Ph_3AsO \cdot H_2O$, which was converted to Ph_3AsS by the action of hydrogen sulphide in ethanolic solution [6]. Ph_3SbS was prepared by reaction of hydrogen sulphide with Ph_3SbBr_2 in ethanol [26].

Reactions of Ph_3M with SeO_2

Equimolar quantities of Ph_3M and SeO_2 (0.01 M) were stirred in dry benzene (100 ml) for 1 week at room temperature. Unreacted SeO_2 and, for M = P, As, Sb, red selenium were removed by centrifugation and the solvent evaporated. When M = N, Bi, the starting triphenyl was recovered unchanged; for M = P, the sole phosphorus-containing product was Ph_3PO. When M = As, the products were Ph_3AsO and a colourless oil which rapidly (<1 min) solidified, depositing copious amounts of red selenium; extraction of the solid mass with hot benzene, followed by removal of the solvent yielded Ph_3As. When M = Sb, the sole antimony-containing product was $Ph_3Sb(OH)_2$.

Reactions of Ph_3M with S_2Cl_2

(a) Ph_3N. The amine (1.22 g, 0.5×10^{-3} mol) was dissolved in anhydrous diethyl ether (100 ml) and S_2Cl_2 (0.67 g, 5×10^{-3} mol) was added dropwise. After 50 h, the volatiles were removed to yield the unchanged amine.

(b) Ph_3P. S_2Cl_2 (1.35 g, 1.0×10^{-2} mol) was added to a solution of the phosphine (2.62 g, 1.0×10^{-2} mol) in anhydrous ether (100 ml). After 1 h at room temperature, triphenylphosphine sulphide (2.41 g, 9.2×10^{-3} mol, 92%) was removed by filtration.

(c) Ph_3As. Equimolar quantities (5.0×10^{-3} mol) of the arsine and S_2Cl_2 were allowed to react as above. After stirring for 1 h at room temperature, triphenylarsine sulphide (1.45 g, 4.3×10^{-3} mol, 86%) was collected by filtration.

(d) Ph_3Sb. Equimolar quantities (2.0×10^{-3} mol) of S_2Cl_2 and triphenylantimony were stirred in ether (100 ml) for 0.5 h at room temperature. Sulphur (0.12 g, 0.46×10^{-3} mol, 90%) was filtered off, and the filtrate reduced to small volumes when triphenylantimony dichloride (0.63 g, 1.48×10^{-3} mol, 74%) was precipitated and collected by filtration.

(e) Ph_3Bi. The bismuthine and S_2Cl_2 were stirred together in equimolar quantities (2×10^{-3} mol) in ether (100 ml) for 2 h. After removal of sulphur,

the filtrate was reduced in volume and triphenylbismuth dichloride was filtered off (0.83 g, 1.62 × 10^{-3} mol, 81%).

Reactions of Ph$_3$M with SCl$_2$

(a) Ph$_3$P. To a stirred solution of the phosphine (2.6 g, 1.0 × 10^{-2} mol) in diethyl ether (150 ml) was added dropwise SCl$_2$ (1.03 g, 1.0 × 10^{-2} mol). Chlorine was evolved in copious amounts and after 1 h at room temperature, triphenylphosphine sulphide was removed by filtration in almost quantitative yield.

(b) Ph$_3$As. The arsine (1.53 g, 5.0 × 10^{-3} mol) and the sulphur chloride (0.52 g, 5 × 10^{-3} mol) were stirred together in ether (150 ml) for 1 h at room temperature. Chlorine was again evolved, leaving triphenylarsine sulphide (1.01 g, 3 × 10^{-3} mol, 60%) which was filtered off.

(c) Ph$_3$Sb. SCl$_2$ (0.20 g, 2.0 × 10^{-3} mol) was added dropwise to a solution of triphenylantimony (0.71 g, 2.0 × 10^{-3} mol) in ether (50 ml). After removal of sulphur, triphenylantimony dichloride (0.72 g, 1.7 × 10^{-3} mol, 85%) was obtained on evaporation of the solvent.

(d) Ph$_3$Bi. Equimolar quantities of SCl$_2$ and triphenylbismuth (2 × 10^{-3} mol) were stirred together in anhydrous ether, to yield sulphur and triphenyl-bismuth dichloride (0.65 g, 1.28 × 10^{-3} mol, 64%).

Reaction of Ph$_3$M (M = P, As) with Se$_2$Cl$_2$

To a solution of the triphenylpnictogen (1.0 × 10^{-2} mol) in anhydrous ether (100 ml) was added dropwise Se$_2$Cl$_2$ (2.29 g, 1.0 × 10^{-2} mol). Red selenium was precipitated exceedingly rapidly and copiously, after filtration, and evaporation of the solvent, no triphenylpnictogen selenide was detected mass spectrometrically.

Reaction of triphenylarsine with KNCSe

Triphenylarsine (3.06 g, 1.0 × 10^{-2} mol) and KNCSe (1.25 g, 1.0 × 10^{-2} mol) were refluxed in anhydrous acetonitrile (100 ml) during 18 h. After removal of the solvent, washing of the residual solid with water and recrystallisation from nitromethane, triphenylarsine was recovered unchanged; no selenium was precipitated at any stage.

Reactions of lead(IV) acetate with Ph$_3$M (M = N, P)

(a) Ph$_3$M. To a stirred solution of Ph$_3$N (2.45 g, 1.0 × 10^{-2} mol) in dichloromethane (50 ml), was added portionwise lead(IV) acetate, (4.43 g, 1.0 × 10^{-2} mol). Lead(II) acetate was immediately precipitated with concurrent development of a blue-green colouration (λ_{max} 650 nm): during 1 h, this absorption maximum was replaced by another band (λ_{max} 480 nm), as the blue-green turned to red.

(b) Ph$_3$P. To a solution of Ph$_3$P (5.24 g, 2.0 × 10^{-2} mol) in dichloromethane (100 ml) was added in portions lead(IV) acetate (8.86 g, 2.0 × 10^{-2} mol). After 0.5 h, lead(II) acetate (6.18 g, 1.9 × 10^{-2} mol, 95%) was removed and the solution evaporated to small volume. The NMR parameters (δ, ppm) aside from CH$_2$Cl$_2$, were δ(C$_6$$\underline{\text{H}}$$_5$) 7.2—8.1, δ(C$\underline{\text{H}}$$_3$) 2.16 (doublet, J(H···P) 10.1 Hz), δ(C$\underline{\text{H}}$$_3$) 21.64, δ(C$\underline{\text{O}}$) 174.62, δ($\underline{\text{P}}$) −30.80. IR (cm^{-1}), 3088m, 2924m, 2601w,

1830s, 1759s, 1724vs, 1592w, 1486m, 1440vs, 1371s, 1252s, 1170(br)s, 1126vs, 1095m, 1030m, 1002s, 900(br)m, 750s, 729vs, 699vs. All attempts to isolate a solid product from this concentrated solution yielded only triphenylphosphine oxide and acetic anhydride.

Hydrolysis of $Ph_3M(OCOCH_3)_2$ (M = Sb, Bi)

(a) M = Sb. Triphenylantimony diacetate (2.35 g, 5.0×10^{-3} mol) was dissolved in dichloromethane (100 ml), and the solution shaken with 4×50 ml aliquots of water. The combined aqueous fraction was extracted with 4×25 ml of dichloromethane, and the organic fractions were combined and dried. Evaporation of the solvent yielded triphenylantimony dihydroxide.

(b) M = Bi. Treatment of triphenylbismuth diacetate in an identical manner caused precipitation of metallic bismuth. Evaporation of the organic layer gave an oil, mass spectrometric examination of which suggested the presence of diphenylbismuth acetate, phenyl acetate, chlorobenzene and biphenyl. No evidence was found for the formation of triphenylbismuth dihydroxide.

Thiolysis of $Ph_3Sb(OCOCH_3)_2$

Triphenylantimony diacetate (2.35 g, 5.0×10^{-3} mol) was dissolved in dry ethanol (50 ml) and sodium sulphide (0.78 g, 1.0×10^{-2} mol) added. Hydrogen sulphide was bubbled through the solution during 1 h. After filtration and evaporation of the solvent to small volume, trituration with anhydrous ether gave triphenylantimony sulphide (1.19 g, 3.1×10^{-3} mol, 62%).

Mass spectra were recorded at 70 eV using an AEI MS-902 instrument, fragments of the same nominal m/e value, such as $C_{12}H_8^+$ and $C_6H_5As^+$ with nominal m/e 152, were readily distinguished under conditions of high resolution. Known compounds were identified by microanalysis and mass spectrometry. Diethyl ether and benzene were dried over sodium, acetonitrile over phosphoric oxide, and ethanol and dichloromethane over flamed-out molecular sieve.

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