OXIDE AND NITRATE DERIVATIVES OF TRIPHENYL-ARSINE AND -PHOSPHINE

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(Received November 20th, 1967)

SUMMARY

Triphenylarsine dinitrate can be prepared from the dibromide both by metathesis with silver nitrate and by reaction with dinitrogen tetroxide. In contrast to the oxygen bridged compound, $(Ph_3SbNO_3)_2O$, formed on hydrolysis of the analogous stibine dinitrate, a 1:1 adduct of nitric acid with triphenylarsine oxide results from hydrolysis of triphenylarsine dinitrate. Nitrato–phosphorus compounds did not result from reactions of triphenylphosphine dibromide with silver nitrate, dinitrogen tetroxide or dinitrogen pentoxide.

INTRODUCTION

Organometallic compounds of antimony[1-3] and bismuth[4] with the general formula $R_3M(NO_3)_2$ are well known, and the infrared spectra of the methyl-[2,3] and phenylantimony[1] derivatives have been interpreted in terms of a trigonal bipyramidal structure. Covalently bonded nitrate groups occupy the axial positions. A similar structure with axial halogens is found for triphenyl-antimony[5] and -bismuth[6] dichloride, and the zero dipole moment for triphenylarsine dichloride and analogous compounds[7] is also in agreement with this type of molecular structure.

Trialkylarsine dinitrates are not known and the only triaryl compound reported, $Ph_3As(NO_3)_2$, was not characterized[8,9]. In view of this and since no nitrato-complexes of phosphorus are known, the reactions of Ph_3AsBr_2 and Ph_3PBr_2 with both nitrogen oxides and silver nitrate in acetonitrile have been investigated.

EXPERIMENTAL

Reaction of triphenylphosphine dibromide with dinitrogen tetroxide

The dibromide was prepared by adding the stoichiometric amount of bromine in carbon tetrachloride dropwise with stirring over a two h period to a solution of triphenylphosphine in carbon tetrachloride cooled in ice. Triphenylphosphine dibromide (1 g) dissolved readily in liquid dinitrogen tetroxide (10 ml). After one h the excess dinitrogen tetroxide and other volatiles were removed under vacuum leaving a pale yellow solid. After further pumping under vacuum the product turned white and was identified as triphenylphosphine oxide by its melting point (154°) and IR spectrum.

If moisture was present during this reaction, a different product resulted. Recrystallization from a mixture of carbon tetrachloride and petrol (80–100°) gave $Ph_3PO \cdot HNO_3$ as colourless diamond-shaped crystals, m.p. 79–81°. (Found: C, 63.9; H, 4.3; N, 4.1; mol.wt. 302. $C_{18}H_{16}NO_4P$ calcd.: C, 63.4; H, 4.4; N, 4.1%; mol.wt. 341.) The compound is unaffected by moisture and is soluble in acetonitrile, ethyl acetate and carbon tetrachloride.

Reaction of triphenylphosphine dibromide with dinitrogen pentoxide

Excess dinitrogen pentoxide (5 g) was condensed on to triphenylphosphine dibromide (1.9 g) at −78°. On shaking at 0° the mixture rapidly turned dark red and liquefied. After one and a half h at 0°, the unreacted dinitrogen pentoxide and gaseous products were removed under vacuum leaving a bright yellow, moisture-insensitive solid. An IR spectrum showed bands attributed to aromatic nitro groups [1533 s, 1348 s and 850 m (sh) cm^{-1}] and coordinated nitric acid (1660 s, 1420 m, 1272 s and 948 s cm^{-1}). The product is thus a nitric acid adduct of a nitrophenylphosphine oxide. A similar product resulted when the temperature was held below −15°.

An attempt to moderate the reaction by adding a solution of two moles of dinitrogen pentoxide (1.8 g) in carbon tetrachloride (50 ml) to a stirred mixture of the dibromide (3.5 g) in carbon tetrachloride (10 ml) lead to the isolation of triphenylphosphine oxide only. If moisture is present during this reaction mixtures of triphenylphosphine oxide and the adduct between nitric acid and triphenylphosphine oxide are obtained.

Reaction of triphenylphosphine dibromide and silver nitrate

The reaction between triphenylphosphine dibromide and 2 moles of silver nitrate in acetonitrile was incomplete; only 35% of the calculated amount of silver bromide was precipitated in two h.

Reaction of triphenylphosphine and nitric acid

Concentrated nitric acid was added to triphenylphosphine and the mixture heated to just below the boiling point until evolution of brown fumes ceased. On cooling, a reddish brown oil separated which solidified on trituration with crushed ice. Recrystallization from a mixture of carbon tetrachloride and petrol (80–100°) gave $Ph_3PO \cdot HNO_3$.

Triphenylarsine dinitrate

(*i*) *From triphenylarsine dibromide and silver nitrate.* Triphenylarsine dibromide was prepared from triphenylarsine as described for the phosphorus analogue. A solution of silver nitrate (2.0 g) in dry acetonitrile (30 ml) was added dropwise with stirring to triphenylarsine dibromide (2.7 g) in 130 ml of the same solvent. An immediate precipitate was formed and after 30 min filtration yielded the quantitative amount of silver bromide. The filtrate was concentrated under vacuum to approximately 30 ml and white crystals of the dinitrate separated on cooling. Further concentration of the filtrate and cooling yielded a second crop; m.p. (in sealed tube) 161–162° decompn. (Found: C, 49.6; H, 3.9; N, 6.5. $C_{18}H_{15}AsN_2O_6$ calcd.: C, 50.2; H, 3.5; N, 6.5%.) The compound is extremely hygroscopic and rapidly liquefies on exposure to traces of moisture.

(ii) *From triphenylarsine dibromide and dinitrogen tetroxide*. The white residue obtained after removal of the gaseous products from the reaction of the dibromide with liquid dinitrogen tetroxide was recrystallized from an ethyl acetate/light petrol (40–60°) mixture yielding $Ph_3As(NO_3)_2$.

Hydrolysis of triphenylarsine dinitrate

The dinitrate was dissolved in moist acetone and light petrol (60–80°) was added. The white crystalline solid which precipitated was not affected by moisture; m.p. 104°. (Found: C, 55.9; H, 4.2; N, 3.6; mol.wt., 435. $C_{18}H_{16}AsNO_4$ calcd.: C, 56.1; H, 3.9; N, 3.6%; mol.wt., 385.) The product, $Ph_3AsO \cdot HNO_3$, is soluble in acetonitrile and ethyl acetate but is insoluble in carbon tetrachloride and petrol.

Reaction of triphenylarsine and nitric acid

Concentrated nitric acid reacted vigorously with triphenylarsine forming a green solution and liberating oxides of nitrogen. The yellow oil which separated on diluting the solution with two volumes of water was dissolved in a small volume of ethanol. On cooling to $-78°$, $Ph_3AsO \cdot HNO_3$ separated as white crystals which were recrystallized from ethyl acetate containing a small amount of acetonitrile.

Triphenylstibine dinitrate

This compound can be prepared from the reaction between triphenylstibine dichloride and an excess of dinitrogen tetroxide. The product separates on cooling the concentrated reaction mixture to 0°; m.p. 144–146° (lit.[1] 143–145°). (Found: C, 46.8; H, 3.6; N, 5.0. $C_{18}H_{15}N_2O_6Sb$ calcd.: C, 45.3; H, 3.1; N, 5.9%.)

Oxybis(triphenylstibine) dinitrate

This was prepared from triphenylstibine dichloride and silver nitrate using moist acetonitrile, in place of alcohol as solvent. Recrystallization from acetonitrile yielded white needles; m.p. 224° decompn. (lit.[1] 237–240° and[10] 224–225°). (Found: C, 50.6; H, 3.6; N, 3.5. $C_{36}H_{30}N_2O_7Sb_2$ calcd.: C, 51.1; H, 3.3; N, 3.3%.)

Infrared spectra

The region between 4000 cm^{-1} and 250 cm^{-1} was scanned using a Perkin–Elmer 521 spectrometer. Below 450 cm^{-1}, the samples were examined as Nujol mulls between cesium iodide windows protected with thin sheets of polyethylene and above 450 cm^{-1} as Nujol and halocarbon oil mulls between silver chloride windows.

Conductance measurements

A Mullard conductivity bridge and a dipping cell were used. All measurements were carried out in a dry box on 10^{-2} M solutions in acetonitrile at 22°. The solvent, purified by several distillations from phosphorus(V) oxide and finally from potassium carbonate, had a specific conductance of $< 1 \times 10^{-6}$ ohm^{-1}.

RESULTS AND DISCUSSION

Preparative methods

Compounds with the general formula $R_3M(NO_3)_2$, where M is a group V element, are expected to result from reactions such as:

(*a*) the action of dinitrogen tetroxide or dinitrogen pentoxide on the dihalide, R_3MX_2;
(*b*) metathesis between silver nitrate and the dihalide in a solvent such as acetonitrile or ethanol;
(*c*) oxidation of the trivalent compound, R_3M, with concentrated nitric acid.

The reaction with dinitrogen tetroxide is the most convenient and dinitrates in quantitative yields are obtained from triphenylstibine dichloride and triphenylarsine dibromide. Although both dinitrates are stable in the absence of moisture, recrystallization is only possible from dried solvents. The arsine dinitrate is particularly hygroscopic and it should be handled with rigorous exclusion of moisture.

Recrystallization of the stibine dinitrate from moist acetonitrile or moist alcohol gives an oxygen bridged compound, oxybis(triphenylstibine) dinitrate[1] $(Ph_3SbNO_3)_2O$, which was previously considered to be a stibine hydroxynitrate[10]. Partial hydrolysis of the arsine dinitrate on the other hand does not yield the corresponding oxygen bridged species, $(Ph_3AsNO_3)_2O$, but a compound with the composition of a hydroxynitrate results. Although this may be a hydroxynitrate, an alternative formulation as a hydrogen bonded nitric acid adduct of triphenylarsine oxide is more likely. The absence of an oxygen bridged species here probably reflects the decreased resistance to hydrolysis of M–O–M bridges with the lighter members of group V and the increase in base strength of the oxide.

Treatment of triphenylphosphine dibromide with dinitrogen tetroxide does not produce a nitrate; triphenylphosphine oxide only was isolated as a stable product when the reaction was carried out with rigorous exclusion of moisture. The product obtained after removing the excess dinitrogen tetroxide in a vacuum was pale yellow and contained occluded dinitrogen tetroxide (absorption in the infrared at $1727\ cm^{-1}$). Although an adduct, $(Ph_3PO)_2 \cdot N_2O_4$, has been claimed[11], the product above developed an atmosphere of dinitrogen tetroxide on standing at room temperature. This was removed by further treatment in vacuum leaving pure triphenylphosphine oxide.

When the reaction was carried out at $0°$ in an attempt to isolate any less stable intermediate product, red crystals precipitated. These were separated and kept at $0°$. The solid contained both dinitrogen tetroxide and bromine and is perhaps related to the adduct[11], $(Ph_3PO)_2 \cdot Br_2$. On pumping in vacuum at room temperature, most of the bromine was lost leaving substantially triphenylphosphine oxide. This reaction is very sensitive to moisture and unless rigorous precautions are taken the triphenylphosphine oxide product is contaminated with the nitric acid adduct, $Ph_3PO \cdot HNO_3$.

In the case of some metal halides, *e.g.* titanium and zirconium, the use of dinitrogen pentoxide gives pure nitrato compounds[12,13] whereas oxide nitrates result from reactions with the tetroxide[14,13]. However, with triphenylphosphine dibromide, only the phosphine oxide was obtained when two moles of dinitrogen pentoxide in carbon tetrachloride were used. A large excess of the pentoxide in the absence of solvent leads to nitration of the phenyl groups in addition to replacement of the bromine atoms. Nitric acid is thus produced and adducts between the acid and nitrophenylphosphine oxides are formed.
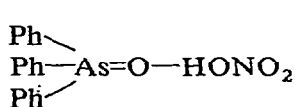
Substitution of the halogen atoms in Ph_3MX_2 by silver nitrate [method (*b*)] is very susceptible to traces of moisture, but the arsine dinitrate can be obtained from reactions in acetonitrile in which water is rigorously excluded. On the other hand, there was incomplete precipitation of silver bromide in the reaction with triphenyl-

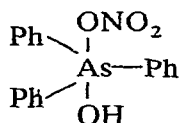phosphine dibromide and this was not examined further.

Method (c) can be used for preparing triphenylstibine dinitrate if fuming nitric acid is used[15]. Isolation of the corresponding arsine dinitrate from the oxidation of triphenylarsine is not expected in view of the ready hydrolysis of the dinitrate, and the nitric acid adduct, $Ph_3AsO \cdot HNO_3$ is obtained. The dinitrate with a melting point of 100° is said to be obtained from nitric acid and either triphenylarsine oxide[8] or triphenylarsine dihydroxide[9]. This melting point is close to that found for Ph_3-$AsO \cdot HNO_3$ (104°) and it is probable that even if the hygroscopic dinitrate were obtained initially, it would hydrolyse before it could be characterized. A hydroxynitrate, $Ph_3As(OH)NO_3$, melting at 84°[16], 160–161°[9] or 165°[17], has been claimed from the reaction between triphenylarsine dihydroxide and dilute nitric acid.

The oxidation of triphenylphosphine with nitric acid may proceed through nitrato species but none was isolated. The product of this reaction was the nitric acid adduct of triphenylphosphine oxide.
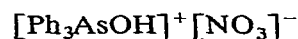
It seems clear that none of the methods employed yield stable nitrato–phosphorus species but triphenylarsine dinitrate can be obtained. On hydrolysis, the latter gave a product that can be formulated as: a nitric acid adduct of triphenylarsine oxide (I), a covalent hydroxynitrate (II) or an ionic hydroxynitrate (III).

$$\begin{array}{ccc}
\begin{array}{l}
Ph \\
Ph-As{=}O{-}HONO_2 \\
Ph
\end{array}
&
\begin{array}{l}
\quad\ ONO_2 \\
Ph\ | \\
\quad As{-}Ph \\
Ph\ | \\
\quad OH
\end{array}
&
[Ph_3AsOH]^+[NO_3]^-
\\[1em]
(I) & (II) & (III)
\end{array}$$

Formulations (I) and (III) differ essentially only in the strength of the bond between the oxygen of the arsine oxide and the nitric acid molecule. In one extreme, this is a relatively weak hydrogen bond, while in (III) the proton has been completely transferred to the arsine oxide. Similar considerations apply to the formulation of the corresponding phosphorus compound.

Conductance measurements

The data in Table 1 are molar conductances of $10^{-2}\ M$ solutions in acetonitrile; the value for a strong electrolyte[18] at a similar concentration is in the region of 140 $ohm^{-1} \cdot cm^2 \cdot mole^{-1}$. The increased conductivity of solutions of triphenylarsine dinitrate over the corresponding antimony compound parallels the trend in the

TABLE 1

MOLAR CONDUCTANCES OF $10^{-2}\ M$ SOLUTIONS IN ACETONITRILE

Compound	$\Lambda_M(ohm^{-1} \cdot cm^2 \cdot mole^{-1})$
$Ph_3As(NO_3)_2$	12
$Ph_3Sb(NO_3)_2$	<1
$Ph_3PO \cdot HNO_3$	6
$Ph_3AsO \cdot HNO_3$	24
$(Ph_3SbNO_3)_2O$	3
$Ph_3As(OH)Br$[20]	20

analogous dichlorides and dibromides[19] and can be accounted for if ionization such as:

$$Ph_3As(NO_3)_2 \rightleftharpoons Ph_3As(NO_3)^+ + NO_3^-$$
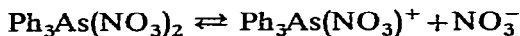
takes place to a small extent. The nitric acid adduct of triphenylphosphine oxide is a non-electrolyte but the higher conductance for the arsenic analogue implies partial ionization and ionic character in the $H-O(NO_2)$ bond. The molar conductance is similar to that found for the compound formulated as $Ph_3As(OH)Br^{20}$.

Infrared spectra

The IR spectrum of triphenylarsine dinitrate includes strong bands at 1550, 1285, 925 and 783 cm^{-1}, which by analogy with the spectrum of trimethylstibine dinitrate[2], are assigned respectively to the v_4, v_1, v_2 and v_6 modes of covalently bonded, unidentate nitrate. The separation of the v_4 and v_1 vibrations is considerably greater than 100 cm^{-1}, the suggested criterion for covalent bonding[21]. Other nitrate absorptions are difficult to identify because of interference from phenyl group vibrations. A strong band at 260 cm^{-1} is tentatively assigned as the asymmetric $As-O(NO_2)$ stretching vibration. Other absorption bands are associated with the phenylarsine moiety and will be discussed later.

The IR spectrum of the triphenylarsine oxide–nitric acid adduct is similar in many respects to that of the corresponding phosphine oxide adduct[22]. There is a 68 cm^{-1} decrease in the frequency of the As–O stretching vibration from the value in the free arsine oxide (888 cm^{-1}), compared with a drop of 135 cm^{-1} for the phosphorus analogue[22]. Broad bands associated with the asymmetric and symmetric NO_2 vibrations occur at 1630 and 1318 cm^{-1}. A broad absorption on the high frequency side of a phenyl vibration at 1445 cm^{-1} compares with a band at 1420 cm^{-1} in the phosphine oxide adduct and is similarly assigned to the NOH in-plane bend. This vibration occurs at 1330 cm^{-1} in free nitric acid and moves to higher energy on hydrogen bonding.

The region between 3000 and 2000 cm^{-1} contains only weak, diffuse absorption ($\sim$2260 cm^{-1}). This is in strong contrast to the spectra of compounds which, although similar in composition, are formulated as five-coordinate hydroxy compounds. The spectrum of $Ph_3As(OH)Br$, for example, contains strong bands at 2490 and 2310 cm^{-1}. In the nitric acid adducts, stretching vibrations involving the hydrogen atom probably occur close to the asymmetric NO_2 stretch. Hadzi[22], for example, has observed that the band at 1640 cm^{-1} for the triphenylphosphine oxide complex moves to lower energy on deuteration.

In all these compounds, the majority of bands above 800 cm^{-1} not already discussed are associated with the monosubstituted phenyl groups and agree with those adequately documented[23]. Vibrations of the phenyl group, which also involve motion of the substituent (Whiffen's[24] mass-sensitive vibrations q, r, t, u, x and y), except for vibration q occur at energies below 800 cm^{-1}. When more than one phenyl group is attached to a central atom M, vibrations which involve M will couple. As $Ph_3As(NO_3)_2$ is probably trigonal bipyramidal with equatorial phenyl groups, each mass-sensitive vibration will give a doubly degenerate IR active, asymmetric component and inactive symmetric component. For the nitric acid adducts, two infrared active components would be expected. The extent of coupling in each mass-sensitive

mode ·will, however, depend on the proportion of C–M stretching character in that vibration. Table 2 summarizes values for vibration q and the bands below 800 cm^{-1} for the arsine dinitrate. Also included are data for $Ph_3AsO \cdot HNO_3$, the phosphine oxide analogue and two related antimony compounds.

TABLE 2

INFRARED SPECTRA IN THE REGION 250–800 CM^{-1}

$Ph_3Sb(NO_3)_2$	$(Ph_3SbNO_3)_2O$	$Ph_3As(NO_3)_2$	$Ph_3AsO \cdot HNO_3$	$Ph_3PO \cdot HNO_3$	Assignment
1069 m ⎫ 1060 m ⎬	1067 s	1075 s	1078 s	1118 s	q
789 m		783 m		783 m	$v_6(NO_3)$
		748 (sh) ⎫	757 (sh) ⎫	755 (sh) ⎫	
730 s	a	740 s ⎬	742 vs ⎭	748 s ⎭	f
		730 (sh) ⎭			
	738 vs				v(Sb–O–Sb)
708 w	708 w				v_3 or $v_5(NO_3)$
		698 m	694 sh	723 s	r
684 s	685 s	682 m	687 s	691 s	v
				650 s ⎫ 645 (sh) ⎬	HNO_3
612 w	612 w	610 w	611 w	613 w	s
458 s ⎫	455 s ⎫	481 s ⎫	477 s ⎫	545 (sh) ⎫	
450 s ⎬	448 (sh) ⎬	476 s ⎬	457 s ⎭	535 s ⎬	y
		463 (sh) ⎭		506 m ⎭	
				466 m	t_{asym}
				447 m	t_{sym}
395 w	394 w			407 m	w
	389 s(br)				δ(Sb–O–Sb)
300 s ⎫	301 s ⎫	371 s ⎫	362 m ⎫		t_{asym}
292 s ⎬	290 m ⎭	362 s ⎭	348 s ⎭		
270 m		322 vw	319 m		t_{sym}
			293 s	348 m(br)	$HNO_3(?)$
				325 (sh)	
				292 m	u
		260 s			v(As–ONO$_2$)

a Obscured by other bands.

Vibration r is sometimes difficult to identify unambiguously because f and v also occur in this region of the spectrum. Vibration y has been identified as a strong band at 458 cm^{-1} in triphenylstibine dinitrate and at 455 cm^{-1} in the corresponding oxygen bridged compound. In triphenylarsine dinitrate it occurs as a strong complex band at 476 cm^{-1} and as two strong bands at 476 and 457 cm^{-1} in the arsine oxide-nitric acid adduct. Identification of y in $Ph_3PO \cdot HNO_3$ is more difficult but it has been assigned to the complex band at 535 cm^{-1}. By analogy with the halobenzene this is abnormally high, but in silicon compounds the frequency of y increases with the number of phenyl groups attached and reaches 515 cm^{-1} in tetraphenylsilane[25]. It is therefore possible that with smaller atoms such as phosphorus and silicon coupling could bring about an increase in the frequency of y.

The vibration closest to being a Ph–M stretch for heavier central atoms is t.

The complex band at approximately 290 cm^{-1} in the spectra of the two antimony compounds is assigned as the asymmetric component of vibration t by analogy with the band at 266 cm^{-1} in iodobenzene. Doak et al.[1] have previously assigned this as the Ph–Sb bend and have considered the absorption at approximately 450 cm^{-1} to be the stretching vibration. The absorption spectra of phenyltin and phenylantimony compounds are expected to be very similar and Poller[26] has assigned bands at approximately 250 cm^{-1} in phenyltin compounds as vibration t which he considers to be the Ph–Sn stretch. In the arsenic compounds absorption between 350 and 370 cm^{-1} is assigned to t, in agreement with similar assignments for di- and tri-phenylarsonium compounds[27]. The spectrum of $Ph_3PO \cdot HNO_3$ contains no strong band below 500 cm^{-1}, but by analogy with chlorobenzene[24] and di- and tri-phenylsilicon compounds[25], vibration t is assigned to the medium intensity absorptions in the 450 cm^{-1} region.

ACKNOWLEDGEMENTS

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