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NOTE

PREPARATION AND SOME REACTIONS OF DIPHENYLANTIMONY AZIDE AND DIPHENYLBISMUTH AZIDE

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In Group Va only the diphenyl azides of phosphorous[1] and arsenic[2] have been prepared and characterized. The former is a very labile compound which decomposes at its melting point (13.7°) to diphenylphosphonitride polymers and nitrogen; the latter has an impressive stability, it decomposes at 180–200° to nitrogen and diphenylarsenonitride tetramer*. Both of the other members of this series have now been prepared. Prior to this there was only one report in the literature[4] which claimed the preparation of diphenylbismuth azide. Organometallic azides have recently been reviewed[5].

EXPERIMENTAL**

Preparation of diphenylantimony azide

Diphenylantimony chloride (0.01 mole), finely ground and dry sodium azide (0.15 mole) were reacted in dry pyridine (50 ml) under nitrogen for the time and temperature indicated in Table 1. The solvent was then evaporated on a rotary evaporator and the residue extracted three times with 15 ml benzene. This clear solu-

TABLE 1

PREPARATIVE CONDITIONS AND ANALYSES OF DIPHENYLANTIMONY AZIDE

Run	Temp.	Time	Yield[c]	Analyses, found (calcd.) (%)			
No.	(°C)	(h)	(%)	C	H	N	Cl
1[a]	116	2	98	50.09	3.78	10.21	0.0
2[a]	25	18	93.5	46.58	3.38	11.12	0.26
3[b]	25	[b]	85	49.19	3.53	6.08	0.47
				(45.30)	(3.15)	(13.20)	(0.00)

[a] Pyridine reaction medium, 0.01 mole $(C_6H_5)_2SbCl$, 0.15 mole NaN_3. [b] 0.15 mole NaN_3 in 50 ml H_2O added to 0.01 mole $(C_6H_5)_2SbCl$ in 30 ml ethanol, stirred 5 min, extracted with CCl_4, dried over $MgSO_4$, pumped dry 25°/0.01 mm, 24 h. Infrared shows strong azide absorption, strong 790 cm^{-1} band (Sb–O). [c] For purposes of yield calculation it was assumed that the products were the pure azides.

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* The structure of this compound has been determined[3].

** Although these azides appear to be stable, the usual precautions should be observed (face shield, etc.).

tion was pumped to dryness at 25°/0.01 mm, 24 h. The residue was a light tan, viscous liquid which could not be induced to crystallize. The infrared spectrum showed the usual phenyl group absorptions[6] and additionally had the intense asymmetric azide absorption[7] at 2060 cm^{-1}. The corresponding symmetric band could not be located with certainty; there are a number of medium to weak bands in the 1200–1300 cm^{-1} region. The spectrum of triphenyltin azide also does not show the symmetrical azide absorption[7].

Preparation of P,P,P-triphenyl-N-(diphenylantimony) phosphine imide

The diphenylantimony azide (0.50 g) was heated with triphenylphosphine (0.42 g) in an oil bath. At 60–80° gas evolution started. The mixture was brought to 135° and kept there for 2 min. The infrared of the gross product showed the presence of an intense 1150 cm^{-1} band and the absence of the asymmetrical azide band. The product was crystallized twice from hot cyclohexane yielding colorless crystals (0.1 g), m.p. 123.5–124.0°. The infrared had intense, sharp P=N absorptions at 1140, 1110, 1090 cm^{-1} in line with Lehn's observations[8] and none in the 1250 cm^{-1} region[7]. (Found: C, 65.04; H, 5.46; N, 2.59. $C_{30}H_{25}NPSb$ calcd.: C, 65.25; H, 4.52; N, 2.53%.)

Thermal decomposition of diphenylantimony azide

Diphenylantimony azide (run 1, Table 1, 1.3255 g) was placed into a 7 × 0.5 cm glass tube and heated in a 220° oil bath. Within 0.5 min the material turned hazy, a precipitate appeared and gas evolved. Total gas evolution after 1 hour was 80 ml (STP; 93 ml theory), wt. loss 0.1218 g (0.117 g theory for 1.0 N_2). The residue was a brown viscous oil and a solid. The infrared spectrum had only a very weak azide band. Gas chromatographic analysis of the residue showed it to contain much triphenylantimony, no benzene or biphenyl. One g of this residue was extracted with benzene and the clear solution evaporated to dryness. The dry solubles weighed 0.78 g. (Found: C, 60.73; H, 4.67; N, 0.39. $C_{18}H_{15}Sb$ calcd.: C, 61.20; H, 4.35%.)

The dry, insoluble residue weighed 0.22 g. (Found: C, 9.35; H, 1.64; N, 7.51%.)

Preparation of diphenylbismuth azide

Diphenylbismuth chloride (0.020 mole, recrystallized from chloroform; (Found: C, 35.57; H, 2.39; Cl, 9.00. $C_{12}H_{10}BiCl$ calcd.: C, 36.12; H, 2.51; Cl, 8.90%.), sodium azide (0.185 mole fine dry powder) were stirred at room temp. for 60 h in pyridine (100 ml). The pyridine was removed under vacuum and the residue extracted three times with 50 ml of cold benzene. The clear benzene liquors quickly turned hazy. The solvent was removed at 25°/0.01 mm, 60 h; yield 6.2 g of an opaque gum. Attempted crystallization from a variety of solvents was unsuccessful. The infrared spectrum showed a very intense asymmetrical azide vibration at 2020 cm^{-1}. (Found: C, 37.34; H, 2.85; N, 7.05; Cl 0.19. $C_{12}H_{10}BiN_3$ calcd.: C, 35.55; H, 2.57; N, 10.38%.)

This gum was left standing at 25° for several weeks; following this 3.0 g were extracted with chloroform. The dry insolubles (1.05 g) had a strong azide band at 2040 cm^{-1}. (Found: C, 21.48, H, 1.55, N, 8.21%.) The dry liquors weighed 1.80 g and had a weak azide band at 2030 cm^{-}1. (Found: C, 45.76; H, 3.02; N, 3.01. $C_{18}H_{15}Bi$ calcd.: C, 48.65; H, 3.41%.)

No triphenylphosphine reaction product with diphenylbismuth azide could be isolated.

Attempted preparation of diphenylbismuth azide by the procedure of Challenger and Richards[4]

This procedure was followed in detail. A compound, m.p. 160.5–162°, was isolated (their m.p. 168°) which had no asymmetric azide absorption in the infrared spectrum. (Found: C, 29.52; H, 2.25; N, 0.34. $C_{12}H_{10}BiN_3$ calcd.: C, 35.55; H, 2.57; N, 10.38%.)

Challenger and Richards did not carry out a nitrogen analysis on their compound although they indicated that on treatment with hydrochloric acid hydrazoic acid, benzene and bismuth chloride were formed.

RESULTS AND DISCUSSION

The preparation of diphenylantimony azide is best carried out in a pyridine slurry at 25°. Elevated temperatures are definitely not desirable; it appears that the starting material or the product disproportionates to triphenylantimony, etc. (always high % C, low % N in product). The use of an aqueous ethanol medium at room temperature appears to involve the same problems as well as partial hydrolysis of the starting material or product. The diphenylantimony azide is a clear, viscous liquid which does not crystallize. It readily forms the phosphine imide without the problems

$$(C_6H_5)_2SbN_3+(C_6H_5)_3P \rightarrow (C_6H_5)_2Sb\text{-}N{=}P(C_6H_5)_3+N_2$$

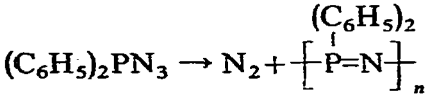
encountered in the triphenyltin azide/triphenyl phosphine reaction[8]. The diphenylantimony azide decomposes upwards of 135°; initially the liquid becomes hazy at 120–130° probably due to disproportionation.

$$2\,(C_6H_5)_2SbN_3 \rightarrow (C_6H_5)_3Sb+C_6H_5Sb(N_3)_2$$

Following this it is then probably the phenylantimony diazide or even the antimony triazide which finally decomposes quite smoothly at 220°. The actual thermal decomposition of diphenylantimony azide is therefore preceded by disproportionation; the gross decomposition product here gave a high yield of triphenylantimony.

The preparation of diphenylbismuth azide can again be carried out at 25° in pyridine medium using sodium azide. The product shows a strong tendency to disproportionate, high carbon, low nitrogen content. This amorphous product was left standing at 25° for several weeks. On extraction, a soluble portion, evidently very rich in triphenylbismuth, was isolated. The diphenylbismuth azide is unstable to disproportionation even at 25°. A triphenylphosphine adduct could not be prepared probably for the same reason.

These results are in contrast to the Group IVa triphenyltin and -lead azides. The tin azide is hydrolytically stable (it can be prepared from aqueous ethanolic sodium azide and the chloride). It does not decompose till a fairly high temperature is reached, but then disproportionation takes place (69% tetraphenyltin recovered[9]). The triphenyllead azide undergoes catastrophic decomposition at about 200° to yield biphenyl and some tetraphenyllead. The group IVa triphenyl azides are therefore much more stable than the corresponding group Va diphenylantimony and -bismuth azides. Neither of these two compounds seems to yield antimony or bismuth analogs of the phosphonitrides



$$(C_6H_5)_2PN_3 \rightarrow N_2 + \left[\overset{(C_6H_5)_2}{\overset{|}{P}}{=}N \right]_n$$

$n=3, 4$ (cyclic) or polymeric or arsenonitride tetramer, $[(C_6H_5)_2As{=}N]_4$[2].

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