

DIPHENYL NITRIDES OF ANTIMONY, ARSENIC AND PHOSPHORUS

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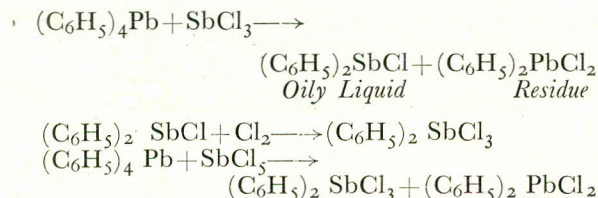
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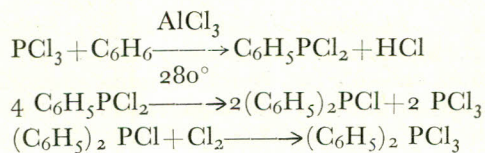
Diphenyl phosphinic nitrides (trimer and tetramer) have been synthesised by two different methods and their yields have been worked out. Similarly arsenic and antimony nitridic compounds have been prepared, but by different methods. Their preparations have been made in the medium of liquid ammonia. Properties of all these compounds have been studied and their structures with the magnetic susceptibilities measurements have been determined. The composition of various compounds in this category already known, have also been determined and the previous findings supported.

Introduction

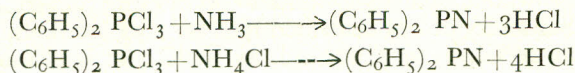
Preparation of diphenyl nitrides is based on the preparation of diphenyl trihalides, for which the use of tetraphenyl lead has been found most convenient. Tetraphenyl lead was prepared by Calingart¹ by the action of lead chloride of phenyl magnesium bromide in dry ether. A.E. Groddard² prepared diphenyl trichloride of antimony and arsenic by heating tetraphenyl lead with SbCl₃ and AsCl₃, respectively, under reflux in toluene when the oily product obtained was chlorinated. Pentachloride can also be used:-



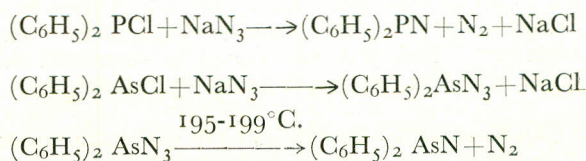
Analogous phosphorus compound was prepared by W.T. Dye, Jr.³ by applying Freidal and Crafts reaction, and heating the product formed in sealed tube. The oily substance obtained was chlorinated.



Diphenyl phosphinic nitride was prepared by C.P. Haber, D.L. Herring and E.A. Lawton⁴ by the action of liquid ammonia on diphenyl phosphorus trichloride firstly at -200°C., then agitating at -40°C. for two hours. They prepared this compound by the action of ammonium chloride on (C₆H₅)₂PCl₃ in inert organic solvent.



D.L. Herring⁵ converted (C₆H₅)₂PCl to (C₆H₅)₂PN by heating the (C₆H₅)₂PCl with alkali azide in pyridine under reflux. Walter T. Reichle⁶ prepared arsenic compound by using the above method.



Diphenyl phosphinic nitride and diphenyl arsenic nitride have got the tendency to get polymerised, so trimer and tetramers were obtained by the above methods. In contrast to phosphorus and arsenic, antimony nitridic compound has no tendency to polymerise.

Experimental

During this work tetraphenyl lead, diphenyl antimony trichloride, diphenyl arsenic trichloride and diphenyl phosphorus trichloride were prepared. Methods of their preparation in brief are as described below:-

Tetraphenyl Lead.—To the freshly prepared phenyl magnesium bromide (1.657 moles) in ether was added 207 g. of PbCl₂ slowly with constant shaking. When whole of the PbCl₂ had been added, the reaction mixture was heated on water-bath for two hours. The product was cooled in ice-bath and decomposed with water carefully. Tetraphenyl lead was extracted by adding benzene in the above. After the removal of benzene white crystals of tetraphenyl lead melting at 222°C. were obtained.

Diphenyl Antimony Trichloride.—32.7 g. of lead tetraphenyl and 14.4 g. of antimony trichloride were heated under reflux with 50 ml. of toluene for half an hour, when a solid mass resulted, which was further treated with 150 ml.

of toluene and heated again. After cooling and filtering, a residue was obtained which was identified to be diphenyl lead chloride. Filtrate after the removal of toluene gave 16.0 g. of an oily substance. This was dissolved in dry ether and was chlorinated. The whole mass was crystallized from 1:1 HCl.

Diphenyl arsenic trichloride was prepared in the same manner as the corresponding antimony compound mentioned above. In this case the mass obtained was crystallized from benzene.

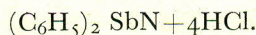
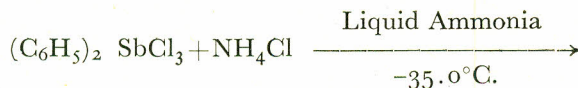
Diphenyl Phosphorus Trichloride.—0.1 mole of PCl_3 , 71 ml. benzene and 0.5 mole of AlCl_3 were refluxed in a three-necked flask for 3 hours. Then 1.5 mole of water was added. Benzene layer was removed. After the removal of benzene $\text{C}_6\text{H}_5_2\text{PCl}_2$ was obtained. This was heated in a sealed tube at 280°C . when $(\text{C}_6\text{H}_5)_2\text{PCl}$ was obtained. This was chlorinated in ether and the mass obtained was crystallised from benzene.

These diphenyl trichlorides are white crystalline substances and are resistant to light and atmosphere. Their melting points are:—

$(\text{C}_6\text{H}_5)_2\text{SbCl}_3 = 175^\circ\text{C}$.; $(\text{C}_6\text{H}_5)_2\text{AsCl}_3 = 171^\circ\text{C}$.;
 $(\text{C}_6\text{H}_5)_2\text{PCl}_3 = 194 - 198^\circ\text{C}$. They are soluble in concentrated HCl.

Preparation of Diphenyl Antimony Nitride.—19.1 g. of diphenyl antimony trichloride and 2.65 g. of ammonium chloride were taken in a wide tube fitted with a three-way adaptor. To one of them was fixed a condenser, to the central one mercury sealed stirrer, while third one was stoppered. From the bottom of the condenser a glass tube was dipped in dilute H_2SO_4 .

The wide tube containing the material was dipped in ice-bath containing CaCl_2 for maintaining temperature at -35°C . 50 ml. of liquid ammonia was added and the reaction mixture was constantly agitated for about two hours. The ammonia evolved was absorbed in dilute H_2SO_4 . After so much cooling, temperature was allowed steadily to rise and the ammonia slowly escaped. When the whole of ammonia had been removed, the contents of the tube were put into water and stirred well. On filtration it was washed with water in order to remove ammonium chloride completely. The mass was dried and then crystallized from methylene dichloride. 12.6 g. of diphenyl antimony nitride was obtained. Yield 66%.



Assembly of the apparatus is shown below.

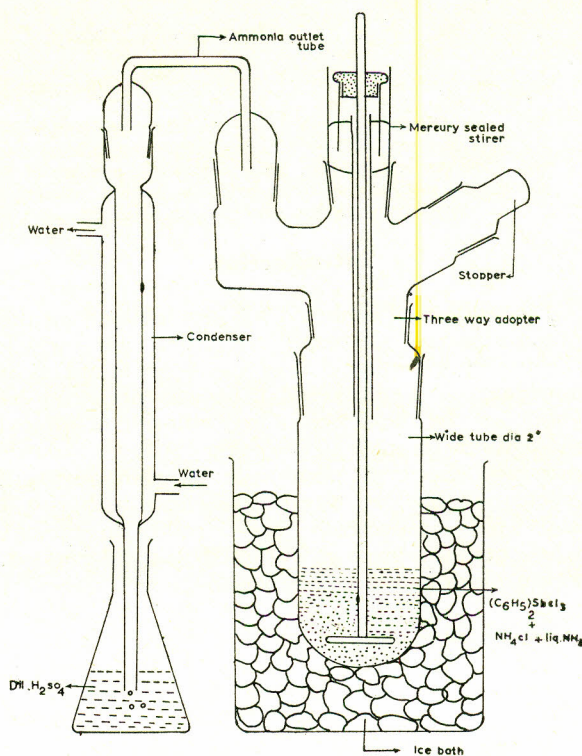


Fig. 1.

Diphenyl Arsenic Nitride.—16.75 g. of diphenyl arsenic trichloride, 2.65 g. of ammonium chloride and 50 ml. of liquid ammonia were made to react in the same manner as described already. The product was crystallized from excess of benzene. 9.85 g. of diphenyl arsenic nitride was obtained. Yield 59%.

Diphenyl Phosphorus Nitride.—15.07 g. of diphenyl phosphorus trichloride, 2.65 g. of ammonium chloride and 50 ml. of liquid ammonia were made to react in the same manner as described in the case of antimony. The product was crystallized from benzene. 8.85 g. of diphenyl phosphorus nitride was obtained. Yield 59%.

Properties

I. Diphenyl Antimony Nitride.—It is a white crystalline powder melting at 282°C . When heated strongly with concentrated HCl it changes to diphenyl antimony trichloride. It is insoluble in water, sparingly soluble in organic solvents. Solubility in concentrated HCl is: 1.11 g./100 ml. at 40°C ., 1.42 g./100 ml. at 80°C . It is stable

upto 300°C; decomposes slowly between 350–420°C. Diphenyl antimony nitride is diamagnetic; specific susceptibility is -0.609×10^{-6} . Effective magnetic moment = $0.20732i$ Bohrmagneton.

Analysis:

Antimony: 41.855% [found] 41.666% [Calculated]
Nitrogen: 4.992% [found] 4.861% [Calculated]

II. Diphenyl Arsenic Nitride.—Diphenyl arsenic nitride crystallizes in colourless crystals melting at 320°C. When heated strongly with concentrated HCl it changes to diphenyl arsenic trichloride. It is generally tetramer. It is insoluble in water, sparingly soluble in organic solvents, solubility in concentrated HCl is 1.30./100 ml. at 32°C., 2.5 g./100 ml. at 70°C. It is stable upto 360°C., then decomposes abruptly near 420°C. Diphenyl arsenic nitride is diamagnetic; specific susceptibility is -0.487×10^{-6} . Effective magnetic moment = $1.0741i$ Bohrmagneton.

Analysis:

Arsenic: 30.717% [found] 30.85% [Calculated]
Nitrogen: 5.716% [found] 5.77% [Calculated]

III. Diphenyl Phosphorus Nitride.—Diphenyl phosphorus nitride crystallizes as white needles, melting at 318–319°C. It is hygroscopic. When heated strongly with concentrated HCl it changes to diphenyl phosphorus trichloride. It is also a tetramer. It is insoluble in water, sparingly soluble in HCl and organic solvents. It is fairly soluble in benzene and ethylene dichloride. The solubility in benzene is: 2.8 g./100 ml. at 30°C. 10.6 g./100 ml. at 70°C. 4.5 g./100 ml. at 32°C. in ethylene dichloride. It is stable upto 300°C. then it decomposes upto 460°C. Diphenyl phosphorus nitride is diamagnetic. Specific susceptibility = -0.6204×10^{-6} . Effective magnetic moment = $1.0914i$ Bohrmagneton.

Analysis:

Phosphorus: 15.434% [found] 15.6% [Calculated]
Nitrogen: 7.185% [found] 7.0% [Calculated]

Discussion

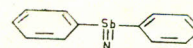
Previously they were prepared by the reaction of diphenyl trichlorides and liquid ammonia, but this method required low temperature upto -200°C . They were also prepared by the reaction of diphenyl trichlorides with ammonium chloride in inert organic solvent, but yield was very low.

Later on alkali azide and diphenyl trichloride were made to react under reflux in pyridine and yield was 48%. Arsenic and phosphorus com-

pounds were thus prepared, but antimony compound could not be obtained.

In the present investigations, due to greater reactivity of ammonium salts in liquid ammonia, the diphenyl trichlorides, ammonium chloride and liquid ammonia were agitated at -35°C . for about two hours. This method proved equally effective for obtaining all the three compounds.

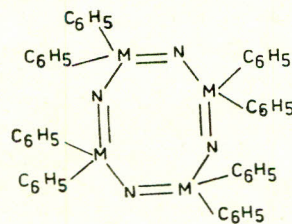
Under magnetic field they behave as diamagnetic substances. Magnetic susceptibility provided sufficient information regarding the structure of the compounds. P, As and Sb have 2 electrons in s-level, 3 electrons in p-level of their outermost orbit. These elements are in pentavalent state in all these compounds. So all the five electrons are shared with groups attached. Since the compounds are non-ionizable the bonding must be of covalent type. Moreover, "effective magnetic moment" comes out to be in negative value showing the presence of planar structure. In case of diphenyl antimony nitride the proposed structure is:



From the observed magnetic susceptibility -0.609×10^{-6} , the molar susceptibility is $X_m = -176.51 \times 10^{-6}$. The calculated value is -176.49×10^{-6} , thus supporting the above structure. In case of arsenic and phosphorus compounds.

$[(C_6H_5)_2AsN]_4$	$X = -0.487 \times 10^{-6}$
	$X_m = -473.38 \times 10^{-6}$ (found)
	$X_m = -473.68 \times 10^{-6}$ (calculated)
$[(C_6H_5)_2PN]_4$	$X = -0.6204 \times 10^{-6}$
	$X_m = -489.1 \times 10^{-6}$ (found)
	$X_m = -494.88 \times 10^{-6}$ (calculated).

These values support the structure of diphenyl phosphorus nitride tetramer and diphenyl arsenic nitride tetramer proposed by Walter T. Reichle,⁶ which is:



Where M=As or P.

References

1. Calingart, Chem. Rev., **2**, 43 (1926).
2. A.E. Groddard, J.N. Ashley and R.B. Evans, J. Chem. Soc., **121**, 978 (1922).
3. W.T. Dye, Jr., J. Am. Chem. Soc., **70**, 2595 (1948).
4. C.P. Haber, D.L. Herring and E.A. Lawton, J. Am. Chem. Soc., **80**, 2116 (1958).
5. D.L. Herring, Chem. Ind. (London), **25**, 717 (1960).
6. Walter, T. Reichle, Tetrahedron Letters 513 (1962).
7. H. Bode and R. Thamer, Chem. Ber. **76**, 121 (1943).
8. D.P. Craige, J. Chem. Soc., 997 (1959).
9. L.W. Daasch, J. Am. Chem. Soc., **76**, 3403 (1954).
10. Scott, Standard Methods of Chem. Anal., (Technical Press Ltd., London, 1945), vol. 1, p. 67.
11. Scott, *Ibid.*, 693—65.
12. M.H. Hashmi, Ehsan Elahi and Mohammad Umar, Anal. Chem., **34**, 988 (1962).
13. Sellwood, *Magneto Chemistry* (Interscience Publishers Inc., New York, 1956).
14. Bhatnager and Mathur, *Physical Principles of Magneto Chemistry* (MacMillan and Company Ltd., London, 1935).