A Bicyclic Hydrazodiphosphine

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ALTHOUGH a few examples of aminophosphine ring compounds are known only one example of a polycyclic, or cage, compound is reported, namely, $P_4(NMe)_6$.[1,2] Recently the arsenic analogue[3-6] and another cage structure, $As_2(NMe)_6$,[7] in which 1,2-dimethylhydrazino-groups separate the arsenic atoms have been described. We now report the preparation of the phosphorus analogue of this latter compound.

Tris-(1,2-dimethylhydrazino)diphosphine (2,3,5,-6,7,8-hexamethyl-1,4-diphospha-2,3,5,6,7,8-hexaaza[2,2,2]bicyclo-octane] (I) is conveniently

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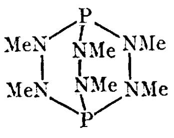
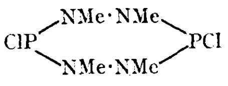
[1] R. R. Holmes and J. A. Forstner, *J. Amer. Chem. Soc.*, 1960, **82**, 5509.
[2] R. R. Holmes, *J. Amer. Chem. Soc.*, 1961, **83**, 1334.
[3] H. Nöth and H. J. Vetter, *Naturwiss.*, 1961, **48**, 553.
[4] D. Hass, *Z. anorg. Chem.*, 1963, **325**, 139.
[5] R. R. Holmes and J. A. Forstner, *Inorg. Chem.*, 1963, **2**, 377.
[6] H. J. Vetter, H. Nöth, and W. Jahn, *Z. anorg. Chem.*, 1964, **328**, 144.
[7] H. Nöth and W. Regnet, *Z. Naturforsch.*, 1965, in the press.

prepared by heating together tris(dimethylamino)-phosphine and 1,2-dimethylhydrazine hydrochloride in benzene under reflux for 64 hours. The resulting dimethylamine hydrochloride is separated by filtration and the required compound isolated by removing the solvent and purified by sublimation at 70—80°/1 mm. to give needles, m.p. 116—117°. Treatment of an alcoholic solution with 100-vol. hydrogen peroxide gives a white dioxide, $OP(NMe{-}NMe)_3PO$, m.p. 320—325° (darkening at m.p.). Reaction with sulphur in xylene affords a crystalline disulphide m.p. >360° (with darkening). Reaction of (I) with diborane in tetrahydrofuran yields $H_3BP(NMe{-}NMe)_3PBH_3$ m.p. ~250° (decomposition to red liquid). Several attempts to make alkyl iodides react were made before a 1 : 1 methyl iodide adduct of (I) was obtained under forcing conditions. The identity of compound (I) was established by analysis and determination of molecular weight, as well as by treatment with hydrogen chloride in benzene solution to give 1,2-dimethylhydrazine hydrochloride in quantitative yield. By reaction with phosphorus trichloride a solid ring-compound (II) was obtained in quantitative yield. With the exception of the apparent difficulty of preparing the quaternary salt the chemical behaviour of (I) is typical of a diphosphine. It reacts readily with bromine, molybdenum hexacarbonyl, and nickel(II) salts.



(I)

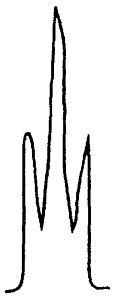


(II)

The infrared spectrum of the free base is comparatively simple and has similarities to the arsenic analogue.[7] The n.m.r. spectra at 60 and 100 Mc./sec. measured in deuterochloroform with tetramethylsilane as internal standard consisted of a triplet at τ7·26 of the form shown in Figure 1, with ratios close to 1 : 1 : 1 (J = 14·9 c./sec.). The dioxide and disulphide, under similar conditions, gave 1 : 2 : 1 triplets of the form shown in Figure 2 (τ7·08, J = 10·6 c./sec., τ7·05, J = 6·5 s./sec., respectively), whereas the simple ring-compound (II) gave the expected doublet, τ6·98, J = 16·5 c./sec. The n.m.r. spectrum of the other aminophosphine cage,[2] $P_4(NMe)_6$, is also a triplet with, however, a broad central peak (τ7·05, J 16·7 ± 0·6 c./sec.). Somewhat similar n.m.r. spectra have been observed in the complexes of metal carbonyls with tris(dimethylamino)phosphine[8] and with tetramethyldiphosphine[9] and can be tentatively explained in terms of additional phosphorus–proton coupling. In the case of this bicyclic compound the same type of coupling may operate but in addition there is the possibility of direct methyl or methyl–lone-pair interactions and/or of the presence of several conformations. The stereochemistry at the nitrogen is important in determining the overall symmetry of the molecule. If the nitrogen is sp^2 hybridized, the molecule will be of simple D_{3h} symmetry, but this requires an N–P–N bond angle of about 97°. However if the nitrogen is sp^3 the corresponding angle would be about 110°, so that the phosphorus would also be sp^3 hybridized. The ready formation, and the

$P_2(NMe)_6\,{}^1H$ spectrum
at 60 and 100 Mc./sec.

FIGURE 1



$(XP)_2\,(NMe)_6$ where X=O,S
at 60 and 100 Mc./sec.

FIGURE 2

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[8] R. B. King, *Inorg. Chem.*, 1963, **2**, 936.

[9] R. G. Hayter, *Inorg. Chem.*, 1964, **3**, 711.

apparent chemical stability of the molecule suggests that the molecule may be substantially strain-free, and supports the idea of sp^3 hybridized nitrogen. If this were so the molecule would have a number of possible conformations depending on the relative locations of the methyl groups of the nitrogens.

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