2,5-Dihydro-1,3,2-oxazaphosph(v)oles. Preparation and Properties

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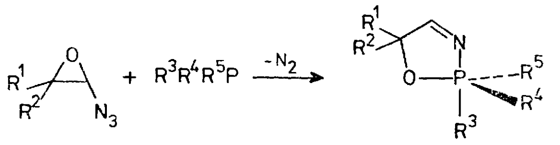
Summary 2,5-Dihydro-1,3,2-oxazaphosph(v)oles, prepared by reaction of 2-azido-oxirans with trico-ordinated phosphorus compounds, exhibit a trigonal bipyramidal structure with the sp^2 nitrogen atom apical and the oxygen atom equatorial.

The chemistry of pentacovalent phosphorus compounds has received a great deal of attention in recent years.[1] We now report the synthesis and some properties of the substituted 2,5-dihydro-1,3,2-oxazaphosph(v)oles (**3a**—**g**).† Reaction of the 2-azido-oxirans (**1**)[2] with the trico-ordinated phosphorus derivatives (**2**) in pentane or ether (0—25 °C) for 1 h resulted in the evolution of nitrogen and the formation of (**3**) in high yields. A similar reaction, involving the intramolecular reaction of ω-epoxy Wittig reagents has recently been reported.[3]



(1) (2) (3)

Although most of the compounds (**3**) were oils,‡ (**3a**) (Table) was crystalline, m.p. 158—162 °C (decomp.) (from hexane—chloroform), and preliminary *X*-ray diffraction results show the trigonal bipyramidal structures as depicted in (**3a**).§ The nitrogen atom would normally be expected to be in the equatorial position,[4] but presumably because of the 'equatorial lone pair effect,'[5] the oxygen atom is situated equatorially, since the sp^2 nitrogen atom does not have a lone pair of electrons which can lie in the equatorial plane.

Table. Selected n.m.r. data for compounds (**3**).[a]

	R^1	R^2	R^3	R^4	R^5	δ (^{31}P)[b]	δ (4-H)[c]	$^3J_{P-H}$/Hz[d]
(**3a**)	Ph	Ph	Ph	Ph	Ph	24·8	8·31	61
(**3b**)	Ph	Ph	MeO	Ph	Ph	9·2	8·41	52
(**3c**)	Bu^t	Me	MeO	Ph	Ph	15·2	8·04	52
(**3d**)	Ph	Ph	MeO	MeO	Ph	15·9	8·35	61
(**3e**)	Bu^t	Me	MeO	MeO	Ph	18·9	7·92	61
(**3f**)	Ph	Ph	MeO	MeO	MeO	30·5	8·32	78
(**3g**)	Bu^t	Me	MeO	MeO	MeO	32·7	7·96	79

[a] $CDCl_3$ solutions (*ca.* 10%). [b] ^{1}H decoupled; chemical shifts given are upfield from external 85% H_3PO_4 reference. [c] Spectra were determined at 100 MHz using Me_4Si as internal standard. [d] Coupling between 4-H and phosphorus.

The Table shows selected n.m.r. data for (**3**). The ^{31}P chemical shifts are in the range expected for valence-expanded phosphorus compounds,[6] but no trends are apparent in these data. Of interest, however, are the three-bond coupling constants which are about a factor of two larger than any previously reported,[1,6] indicating ideal orbital arrangement for three-bond coupling. Preliminary studies indicate that some members of (**3**) are fluxional. Thus (**3d**) exhibited a single methoxy doublet at room temperature which showed a coalescence temperature of −100 °C (in Freon 12), but owing to insolubility problems, the spectrum of the static structures was unobtainable. It was clear, however, that a pair of doublets was arising as the temperature was lowered from −100 °C. This presumably indicates that (**3d**) is in fact a mixture of readily interconvertible pseudorotamers in equilibrium, which averages the methoxy environments at higher temperatures. At low temperatures two methoxy (apical and equatorial) signals are observed owing to the retardation of MeO exchange.¶ It is interesting that even at the methoxy resonance coelescence temperature, the $^3J_{P-H}$ value was unchanged (61 Hz) from that at room temperature.

Our studies thus far indicate that the chemistry of the oxazaphospholes (**3**) is rather complex. Thus reaction of (**3a**) in dichloromethane with water (two-phase system) at room temperature gave high yields of triphenylphosphine oxide, and *ca.* 20% of benzophenone along with smaller amounts of three other, as yet unidentified, components (by g.l.c. analysis).

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† To the best of our knowledge, the 2,5-dihydro derivatives have not been reported previously.

‡ All compounds exhibited spectroscopic properties [i.r. (ν_{CN} 1650—1655 cm^{-1}), n.m.r. (^{1}H, ^{31}P), and m.s. (M^+ observed)] in accord with the postulated structures. Compound (**3a**) gave the correct microanalytical data. The others, as oils, were difficult to purify, and even Kugelrohr distillation at temperatures < 50 °C led to extensive decomposition. High resolution mass spectra, however, gave elemental compositions in agreement with postulated structures.

§ Only one angle in this structure deviates from an idealized trigonal bipyramid by 6°, the rest deviate by less than 4°. Detailed *X*-ray crystallographic results will be published elsewhere by L. K. Liu and R. A. Davis of the University of Texas at Austin.

¶ We thank a referee for pertinent comments in this regard.

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