1,3,2λ^5-Oxazaphosphinan-4-ones: Synthesis and *X*-Ray Analysis of a New Type of Phosphorus-containing Heterocycle

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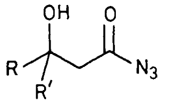
Reaction of 3-hydroxycarboxylic acid azides with phosphorus(III) reagents yields 3-hydroxyacyl iminophosphoranes or 1,3,2λ^5-oxazaphosphinan-4-ones depending upon the nature of the phosphorus reagent.

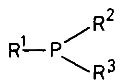
Azides of carboxylic acids lacking additional reactive sites are known to react with phosphorus(III) compounds to yield acyliminophosphoranes.[1] Therefore we expected that hydroxycarboxylic acid azides should give the corresponding hydroxyacyl iminophosphoranes; the latter might cyclize to λ^5-phosphoranes, provided that the OH group is in a suitable position. The resulting novel heterocycles are interesting not only from a theoretical point of view, but also with regard to synthesis: by analogy with the synthesis of aziridines *via* 1,3,2λ^5-oxazaphospholidines,[2] these compounds could possibly be converted into azetidinones under proper conditions. We report here the reaction of β-hydroxycarboxylic acid azides with phosphorus(III) reagents, which, depending upon the phosphorus compound used, yields 3-hydroxyacyl iminophosphoranes or 1,3,2λ^5-oxazaphosphinan-4-ones.

The 3-hydroxy-3-phenylpropionyl azide (**1**) reacted with triphenylphosphine, trimethylphosphite, or 2-phenylphospholane in CH_2Cl_2 to give the 3-hydroxyacyl iminophosphoranes (**2**), (**3**), and (**4**)† respectively in almost quantitative yields. In contrast, the acyliminophosphorane resulting from the reaction of (**1**) with 2-phenyl-1,3,2-dioxaphospholane exhibits the expected high tendency of the phosphorus to achieve the pentaco-ordinate state (known as the phospholane effect[3]): thus, the acyliminophosphorane, which to a smaller extent also dimerizes reversibly, is converted into the acylamino-λ^5-phosphorane (**5**), yielding a 3:1 mixture of the diastereoisomers (**5a**) and (**5b**). This was evidenced by monitoring the course of the reaction by ^{31}P n.m.r. spectroscopy, showing signals at 32.0 (s), −37.0 (br), −45.0 (**5a**) and −43.6 (**5b**) p.p.m. (in $CDCl_3$). The isomer (**5a**) crystallizes from the mixture as a pure compound. Both diastereoisomers are stable at room temp.; at 100 °C they interconvert within 40 min, presumably by permutation on phosphorus, giving a 4:3 ratio of (**5a**):(**5b**). Structural proof of these novel heterocyclic compounds is given mainly by their ^{31}P n.m.r. signals at high field and by a single crystal *X*-ray analysis carried out on (**5a**).‡

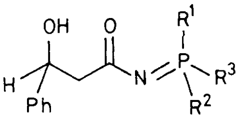
This *X*-ray analysis represents the first complete example of a spirophosphorane with an isolated six-membered ring.§ Particularly interesting is the nearly ideal trigonal bipyramidal geometry on phosphorus: the sum of angle deviations, calculated with the Holmes and Deiters method[5] is 11.1° and thus the smallest value for any pentaco-ordinate phosphorane in which the phosphorus is incorporated in a six-membered ring with carbon, nitrogen, or oxygen as neighbours. The shape of the 1,3,2-oxazaphosphinanone ring is closely related



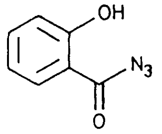
	R	R'
(**1**)	H	Ph
(**6**)	Ph	Ph
(**7**)	—[CH$_2$]$_5$—	
(**8**)	—[CH$_2$]$_4$—	
(**9**)	Me	Me



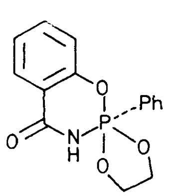
$R^1 = R^2 = R^3 = Ph$
$R^1 = R^2 = R^3 = OMe$
$R^1 = Ph,\ R^2,R^3 = -[CH_2]_4-$
$R^1 = Ph,\ R^2,R^3 = -O[CH_2]_2O-$



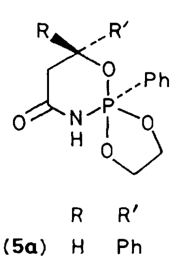
(**2**) $R^1 = R^2 = R^3 = Ph$
(**3**) $R^1 = R^2 = R^3 = OMe$
(**4**) $R^1 = Ph,\ R^2,R^3 = -[CH_2]_4-$



(**14**)



(**15**)



	R	R'
(**5a**)	H	Ph
(**5b**)	Ph	H
(**10**)	Ph	Ph
(**11**)	—[CH$_2$]$_5$—	
(**12**)	—[CH$_2$]$_4$—	
(**13**)	Me	Me

All chiral substances were produced as racemic mixtures; a single enantiomer is shown for simplicity.

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† All new compounds gave satisfactory i.r., n.m.r., and mass spectral data in agreement with the assigned structure. In addition, satisfactory elemental analyses were obtained for crystalline compounds.

‡ *Crystal data:* $C_{17}H_{18}NO_4P$, $M = 331.13$, monoclinic, space group $P2_1/n$, $a = 11.043(2)$, $b = 10.714(2)$, $c = 13.694(2)$ Å, $\beta = 98.8(8)°$, $Z = 4$, $D_{calc.} = 1.373$ g cm^{-3}. Intensity measurements were made at room temp. with a diffractometer using Mo-K_α-radiation which led to 2837 independent reflections with $2\theta \leq 50°$. The structure was refined by blocked and full-matrix least-squares analyses using 2186 observed reflections with $I \geq 3\sigma(I)$. The final value of $R(F)$ was 0.036. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

§ In a search of the Cambridge Crystallographic Data File, 5-(*p*-bromophenoxy)-10-methyl-2,2,3,3-tetrakis(trifluoromethyl)-1,4,6-trioxa-10-aza-5-phosphaspiro[4.5]decane was found as the only related structure; however, the reported single crystal *X*-ray data are incomplete (ref. 4).

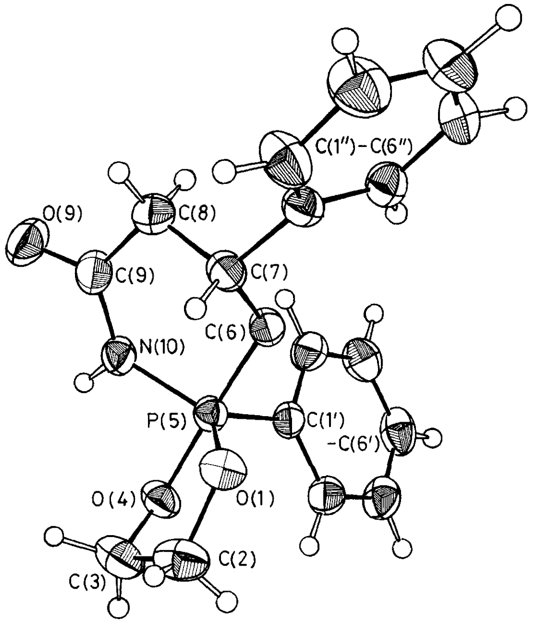

Figure 1. ORTEP drawing of the molecule (**5a**) with thermal vibration ellipsoids at the 50% probability level.

to that of a cyclohexene unit in a half-twist conformation, in which, as the most remarkable feature, the endocyclic angle at the planar nitrogen atom is enlarged up to 132°; the dioxaphospholane ring exhibits the usual envelope conformation.

By analogy with the reaction of (**1**) with 2-phenyl-1,3,2-dioxaphospholane, the hydroxycarboxylic acid azides (**6**), (**7**), (**8**), and (**9**) afforded the 1,3,2λ^5-oxazaphosphinan-4-ones (**10**), (**11**), (**12**), and (**13**) respectively. These compounds gave essentially the same spectroscopic data as (**5a**), but could not be isolated in crystalline form. Further application of this reaction led to another novel phosphorane: starting from salicylic acid azide (**14**), the crystalline 1,3,2λ^5-benzoxazaphosphinan-4-one (**15**) was synthesized.

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