# 2-Azidoallylphosphonates: Synthesis and Application to Formation of 4-Amino-2-ethoxy-1,2-oxaphosphol-3-ene 2-Oxides

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2-Azidoallylphosphonates (**1**) have been synthesised from allenic phosphonates and converted to 2-azirinylmethylphosphonates (**2**) photochemically; the latter are readily transformed into stable primary enamines, (4-amino-2-ethoxy-1,2-oxaphosphol-3-ene 2-oxides) (confirmed by *X*-ray crystallography) by warming in the presence of catalytic amounts of $PdCl_2(PhCN)_2$.

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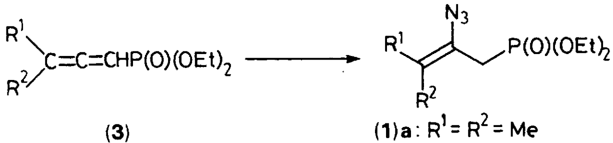
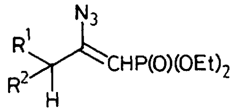
Vinyl azides have received a great deal of attention for a number of years and have found much use in the generation of azirines, vinylnitrenes, and nitrilium ylides, and thence a large variety of heterocycles.[1] Combining the vinyl azide functionality with that of potential Wittig–Horner–Emmons reagents should lead to very useful synthons. We now report the synthesis of 2-azidoallylphosphonates (**1**), their transformation to 2-azirinylmethylphosphonates (**2**), and the rearrangement of the latter to novel 4-amino-2-ethoxy-1,2-oxaphosphol-3-ene 2-oxides.

It has been shown[2] that allenic phosphonates (**3**), readily accessible from 1-alkyn-3-ols, add diethylamine or ethanol to give α-phosphonato-enamines and -enol ethers, respectively. When (**3a,b**) were treated with $NaN_3$ in ethanol a mixture of the desired vinyl azides (**1a,b**) and the corresponding enol ethers[2] was obtained. The azides were obtained cleanly by the addition of tetramethylguanidinium azide in dry $CH_2Cl_2$ at room temperature [(**1a**) 79.4%; (**1b**) 90%]. That these had the expected structure (**1**) and not that of tautomer (**1′**) was confirmed by their $^1H$ NMR spectra.† Conformation of the geometry shown for (**1b**) came from the fact that no NOE enhancement in the Me group was observed when the allylic $CH_2$ was irradiated. On the other hand, the azide obtained (36%) from (**3**; $R^1 = R^2 = H$)[3] had structure (**1′**; $R^1 = R^2 = H$).

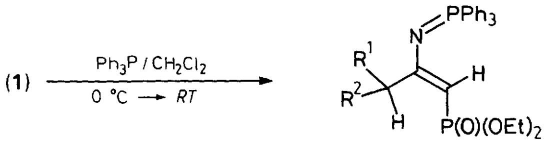


(**3**)

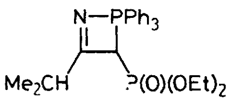
(**1**)**a**: $R^1 = R^2 = Me$
**b**: $R^1 = Me$; $R^2 = Ph$



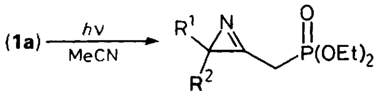
(**1′**)



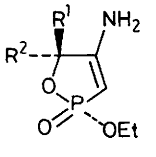
(**4**)



(**5**)



(**2**)

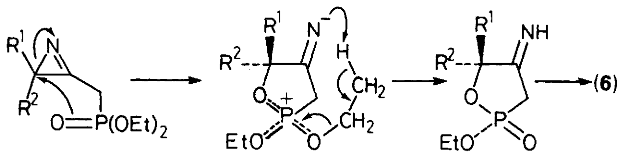


(**6**)**a**; $R^1 = R^2 = Me$
**b**; $R^1 = Ph$, $R^2 = Me$
**c**; $R^1 = Me$, $R^2 = Ph$

The vinyl azides were unstable and decomposed even when analytically pure and stored at room temperature. Azides (**1**) were converted to the stable phosphinimines (**4**) in virtually quantitative yields. Interestingly, (**4a**) now exhibited a 6H doublet at δ 1.22 [$(CH_3)_2CH$], a 1H multiplet at δ 3.35 [MeC*H*] and a 1H vinylic proton multiplet at δ 4.07, while (**4b**) exhibited a doublet for the $CH_3(Ph)CH$ group. The $^{31}P$ absorptions were also shifted to δ 25.98 and 25.17 p.p.m., respectively. This suggested that a 1,3-H shift had accompanied phosphinimine formation, which was confirmed by a single crystal *X*-ray structure determination on (**4a**) [thus ruling out a 1,2-phosphazetine structure (**5**)].

Azirines (**2a,b**) were obtained in high yield (96 and 97%) by photolysis (3500 Å) of (**1a,b**) in acetonitrile. When azide (**1a**) was boiled in dry benzene for 4 h the product was a mixture of (**2a**) (62%) and a compound (**6**) (23.5%) ($C_7H_4NO_3P$), m.p. 199—200 °C, whose spectral properties indicated the presence of a primary amino group and of one ethoxy group. Its structure was confirmed to be primary enamine (**6a**) by single crystal *X*-ray analysis. A number of 3-halo-,[4a] 3-thio-,[5] and 3-unsubstituted[6] 1,2-oxaphosphol-3-ene 2-oxides have been prepared. Some of the thio-substituted compounds exhibited herbicidal and cytokynin activity. 4-Amino-derivatives, such as (**6**), had not been reported up to now.

Similar thermolysis of (**1b**) (single stereoisomer) gave (**2b**) (40%) and a mixture of stereoisomers [(**6b**), m.p. 163—164 °C and (**6c**), m.p. 157 °C (18 and 13.8%)] whose individual geometries could not be established unambiguously by IR or NMR spectroscopies. Isomer (**6b**) was shown to have the



(**2**)

**Scheme 1**

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† (**1a**) $^1H$ NMR (90 MHz, $CDCl_3$) δ 2.84 [2H, d, $^2J_{PH}$ 20.75 Hz, $=CCH_2P(O)R_3$], 1.76 (3H, s), 1.71 [3H, s, $(CH_3)_2C=$]; $^{31}P$ (36.19 Hz, $CDCl_3$) δ 23.56 p.p.m. (**1b**) $^1H$ NMR (90 MHz, $CDCl_3$) δ 2.85 (2H, d, $^2J_{PH}$ 21.25 Hz), 2.04 (3H, brd, $J_{PH}$ 5.6 Hz, $CH_3C=$); $^{31}P$ δ 23.96 p.p.m. (**1′**) $^1H$ NMR (90 MHz, $CDCl_3$) δ 5.2 [1H, d, $J_{PH}$ 24.6 Hz, $=CHP(O)(OEt)_2$], 2.2 (3H, d, $J$ 2.7 Hz, $CH_3C=$). The vinyl azides gave no $M^{+\cdot}$ ion in EI MS, only an $(M - N_2)^+$ ion. They did give the parent ions in the CI MS.

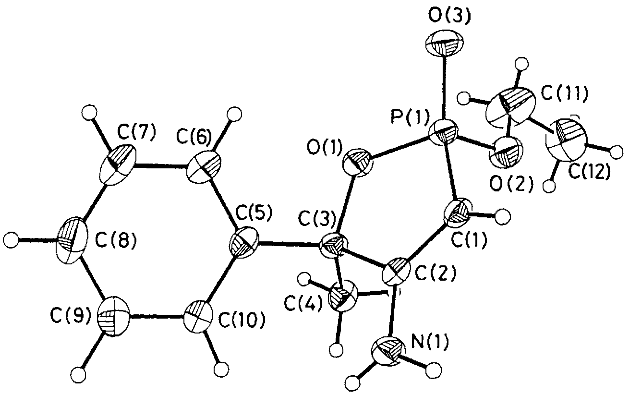

**Figure 1.** A view of (**6b**) showing the atomic numbering and thermal ellipsoids (35% probability). Selected bond lengths (Å): P(1)–O(1) = 1.590(2), P(1)–O(2) = 1.578(2), P(1)–O(3) = 1.465(2), P(1)–C(1) = 1.729(3), O(1)–C(3) = 1.465(3), N(1)–C(2) = 1.344(4), C(1)–C(2) = 1.339(4), C(2)–C(3) = 1.540(3). Selected bond angles (°): O(1)–P(1)–O(2) = 106.8(1), O(1)–P(1)–O(3) = 112.4(1), O(1)–P(1)–C(1) = 97.0(1), O(2)–P(1)–O(3) = 111.9(1), O(2)–P(1)–C(1) = 104.1(1), O(3)–P(1)–C(1) = 122.8(1), P(1)–O(1)–C(3) = 113.2(1), P(1)–C(1)–C(2) = 108.9(2), N(1)–C(2)–C(1) = 126.6(3), N(1)–C(2)–C(3) = 118.9(2), C(1)–C(2)–C(3) = 114.5(2), O(1)–C(3)–C(2) = 105.2(2), O(1)–C(3)–C(5) = 107.6(2), C(2)–C(3)–C(5) = 111.8(2).

stereochemistry shown (phenyl and oxide group *cis*) in Figure 1 by single crystal *X*-ray analysis.‡ That (**2**) was an intermediate in the formation of (**6**) was established by its thermolysis under the same conditions as used for (**1**). [Formation of (**6**) by intramolecular cyclisation of (**1**) would require an unfavourable 5-*endo-trig*[8] geometry.] Indeed, (**2a,b**) could be converted smoothly and in good yield to [(**6**)**a**; 63.8%, **b** and **c**; 37.4, 34.1%] by warming a toluene solution (50 °C) with a catalytic amount of $PdCl_2(PhCN)_2$. In the case of (**2b**), no indole formation[7] was ever observed. A possible pathway for the thermal formation of (**6**) is illustrated in Scheme 1. Ring-opening would be assisted by complexing at N by the metal catalyst, which may also be involved in other roles.

We thank Mrs. Peggy Kotun for the NOE experiments, and the Petroleum Research Fund for support of this work.

*Received, 9th October 1989; Com. 9/04317I*

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‡ *Crystal data*: $C_{12}H_{16}NO_3P$, $M = 253.26$, parallelepiped, space group $P2_1/n$, $a = 8.435(6)$, $b = 13.473(9)$, $c = 11.745(6)$ Å, $\beta = 107.92(4)°$, $U = 1270(1)$ Å$^3$, $D_c = 1.32$ g cm$^{-3}$, $F(000) = 536$, $\mu(\text{Mo-}K_\alpha) = 2.06$ cm$^{-1}$, Nicolet R3mV diffractometer, 1842 reflections ($1.0 \leqslant 2\theta \leqslant 45.0°$), 1401 observed [$I > 3\sigma(I)$]. The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located by standard difference Fourier techniques and were refined isotropically. The final residual values were $R = 0.041$, $R_w = 0.055$, and $S = 1.44$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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