

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

Rudolph A. Abramovitch,* Marek Konieczny, William Pennington, Suseela Kanamathareddy, and Murugapa Vedachalam

Department of Chemistry, Clemson University, Clemson, S.C. 29634-1905, U.S.A.

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 $\text{PdCl}_2(\text{PhCN})_2$.

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.

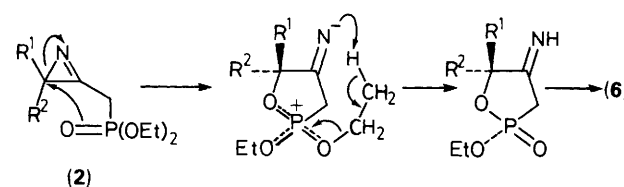
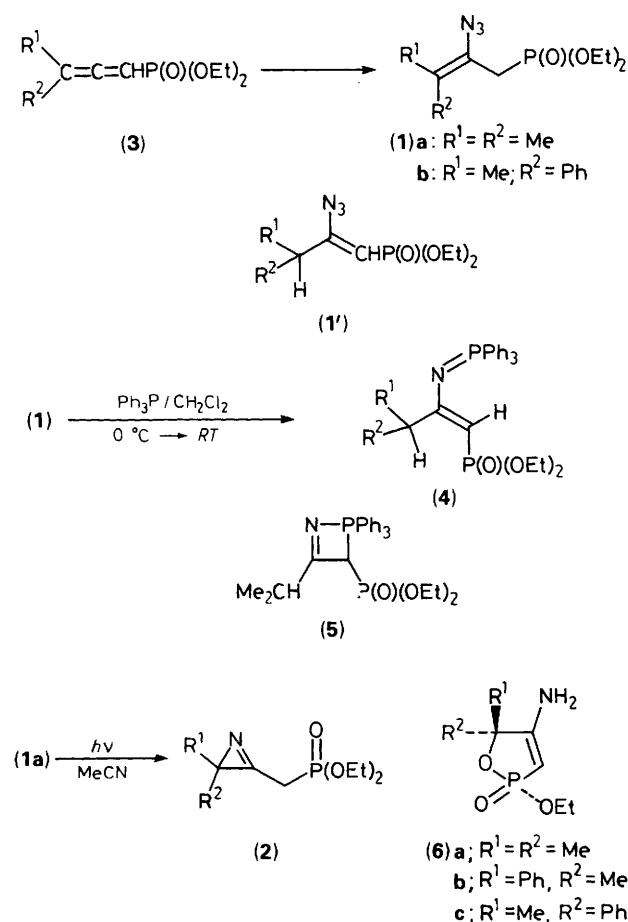
It has been shown² that allenic phosphonates (**3**), readily accessible from 1-alkyn-3-ols, add diethylamine or ethanol to give α -phosphonato-enamines and -enol ethers, respectively. When (**3a,b**) were treated with NaN_3 in ethanol a mixture of the desired vinyl azides (**1a,b**) and the corresponding enol ethers² 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**; $\text{R}^1 = \text{R}^2 = \text{H}$)³ had structure (**1'**; $\text{R}^1 = \text{R}^2 = \text{H}$).

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 [$(\text{CH}_3)_2\text{CH}$], a 1H multiplet at δ 3.35 [MeCH] and a 1H vinylic proton multiplet at δ 4.07, while (**4b**) exhibited a doublet for the $\text{CH}_3(\text{Ph})\text{CH}$ 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-phosphazetene 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%) ($\text{C}_7\text{H}_4\text{NO}_3\text{P}$), 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-unsubstituted⁶ 1,2-oxaphosphol-3-ene 2-oxides have been prepared. Some of the thio-substituted compounds exhibited herbicidal and cytokinin 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



Scheme 1

[†] (**1a**) ^1H NMR (90 MHz, CDCl_3) δ 2.84 [2H, d, $^2J_{\text{PH}}$ 20.75 Hz, $=\text{CCH}_2\text{P}(\text{O})\text{R}_3$], 1.76 (3H, s), 1.71 [3H, s, $(\text{CH}_3)_2\text{C}=\text{C}$]; ^{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, $^2J_{\text{PH}}$ 21.25 Hz), 2.04 (3H, brd, J_{PH} 5.6 Hz, $\text{CH}_3\text{C}=\text{C}$); ^{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, $=\text{CHP}(\text{O})(\text{OEt})_2$], 2.2 (3H, d, J 2.7 Hz, $\text{CH}_3\text{C}=\text{C}$). The vinyl azides gave no M^+ ion in EI MS, only an $(\text{M} - \text{N}_2)^+$ ion. They did give the parent ions in the CI MS.

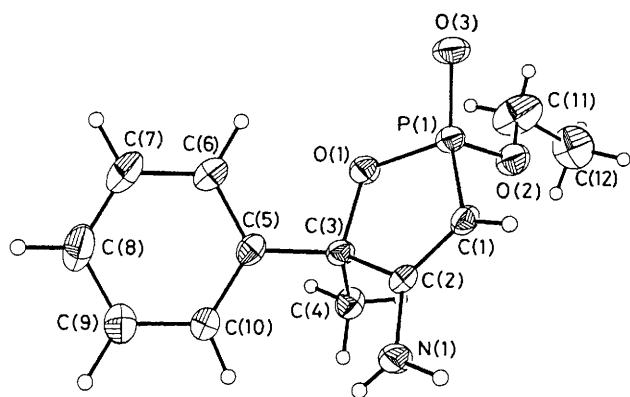


Figure 1. A view of (**6b**) showing the atomic numbering and thermal ellipsoids (35% probability). Selected bond lengths (Å): P(1)–O(1) = 1.590(2), P(1)–O(2) = 1.578(2), P(1)–O(3) = 1.465(2), P(1)–C(1) = 1.729(3), O(1)–C(3) = 1.465(3), N(1)–C(2) = 1.344(4), C(1)–C(2) = 1.339(4), C(2)–C(3) = 1.540(3). 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 inter-

‡ *Crystal data:* C₁₂H₁₆NO₃P, *M* = 253.26, parallelepiped, space group *P*2₁/*n*, *a* = 8.435(6), *b* = 13.473(9), *c* = 11.745(6) Å, β = 107.92(4)°, *U* = 1270(1) Å³, *D*_c = 1.32 g cm⁻³, *F*(000) = 536, μ(Mo-*K*α) = 2.06 cm⁻¹, Nicolet R3mV diffractometer, 1842 reflections (1.0 ≤ 2θ ≤ 45.0°), 1401 observed [*I* > 3σ(*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.

mediate 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 [(**6a**); 63.8%, **b** and **c**; 37.4, 34.1%] by warming a toluene solution (50 °C) with a catalytic amount of PdCl₂(PhCN)₂. In the case of (**2b**), no indole formation⁷ 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. 9/043171

References

- 1 A. Hassner in, 'Azides and Nitrenes: Reactivity and Utility,' ed. E. F. V. Scriven, Academic Press, New York, 1984, ch. 2, pp. 35–94; A. Padwa and Per H. J. Carlsen in, 'Reactive Intermediates,' ed. R. A. Abramovitch, Plenum, New York, 1982, vol. 2, ch. 2.
- 2 H.-J. Altenbach and R. Korff, *Tetrahedron Lett.*, 1981, **22**, 5175; *Angew. Chem. Suppl.*, 1982, 777.
- 3 A. N. Pudovik, J. M. Aladzheva, and L. N. Yakovenko, *J. Gen. Chem. USSR*, 1965, **35**, 1214.
- 4 Kh. M. Angelov, D. Enchev, and M. Kirilov, *J. Gen. Chem. USSR*, 1983, 1766; V. K. Brel, V. Ya. Komarov, B. I. Ionin, and A. A. Petrov, *ibid.*, 1983, **53**, 52.
- 5 Kh. M. Angelov and K. V. Vachkov, *Phosphorus & Sulfur*, 1984, **21**, 237; O. G. Prudnikova, V. K. Brel, and B. I. Ionin, *Zh. Obshch. Khim.*, 1987, **56**, 764.
- 6 R. S. Macomber, I. Constantinides, and G. Garrett, *J. Org. Chem.*, 1985, **50**, 4711.
- 7 K. Isomura, K. Uto, and H. Taniguchi, *J. Chem. Soc., Chem. Commun.*, 1977, 664.
- 8 J. E. Baldwin, *J. Chem. Soc., Chem. Commun.*, 1976, 734.