

N-Phosphinoyl Oxaziridines; A New Class of Oxaziridines

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Novel stable N-phosphinoyl oxaziridines have been prepared and characterised by n.m.r. and mass spectrometry; they function as oxidants towards phosphines, sulphides, and alkenes.

Phosphinoyl oxaziridines appear to be a previously unreported class of compound, though structure (1) has recently been tentatively proposed for an unstable cytotoxic oxidised derivative of the antitumour drug cyclophosphamide.¹ It could be inferred that the presence of an energy rich and

reactive P–N bond on the highly strained oxaziridine ring might produce an unstable molecule. However we now report the synthesis of N-phosphinoyl oxaziridines which are remarkably stable in air at ambient temperature.

In a typical reaction, 2-naphthaldehyde oxime, when mixed with chlorodiphenylphosphine and triethylamine in dichloromethane at –40 °C under nitrogen (according to the general conditions of Krzyzanowska and Stec²), afforded the N-phosphinoyl imine (2a), m.p. 178–180 °C, in 45% yield; δ_{H} (CDCl₃) 9.47 (1H, d, $^3J_{\text{PH}}$ 31.9 Hz) and 7.2–8.4 (17H, m, aromatic); ν 1614 cm^{–1} (C=N). Two-phase oxidation of (2a) in chloroform at 0 °C with *m*-chloroperoxybenzoic acid (MCPBA) (2 equiv.) for 20 min in the presence of aqueous sodium hydrogen carbonate gave the N-phosphinoyl oxaziridine (3a) as the main product. Several other N-phosphinoyl oxaziridines were similarly prepared (Table 1). The oxaziridines were purified by flash column chromatography on silica gel (230–400 mesh) using diethyl ether–dichloromethane (4:1) as eluant, though preparative t.l.c. was also successful for small quantities. Isolated yields of oxaziridines from imines after flash chromatography were 30–50%. Structures were confirmed by spectroscopic analysis (Table 1). In

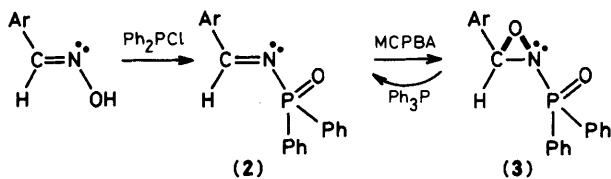
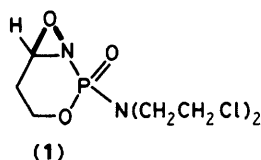


Table 1. N.m.r. and mass spectral data for N-(diphenylphosphinoyl) oxaziridines.

Compound	Ar	M.p./°C ^a	δ_{H}^b	$^3J_{\text{PH}}/\text{Hz}$	δ_{C}^c	$^2J_{\text{PC}}/\text{Hz}$	$\delta_{\text{P}}/\text{p.p.m.}^d$	M^+ (M calc.) ^e
(3a)	2-naphthyl	118–120	5.86	8.8	76.7	3.8	34.9	371.1074 (371.1075)
(3b)	4-BrC ₆ H ₄	136–141	5.65	8.8	75.7	4.2	34.9	399.0020 (399.0026)
(3c)	4-CF ₃ C ₆ H ₄	163–168	5.76	8.8	75.4	3.7	35.0	389.0787 (389.0794)
(3d)	Ph	138–141	5.65	9.0	76.0	4.5	34.8	321.0908 (321.0918)

^aDecomp. ^bChemical shift of the oxaziridine ring hydrogen atom in CDCl₃ relative to internal SiMe₄. ^cChemical shift of the oxaziridine ring carbon atom in CDCl₃ relative to internal SiMe₄. ^dMeasured in CDCl₃ downfield from 85% H₃PO₄ as external reference.

^eMolecular ion relative abundance 5–10%.

particular the chemical shifts of the heterocyclic ring carbon³⁻⁵ and hydrogen^{5,6} atoms lie in the region characteristic of oxaziridines, and the doublet splitting of these signals together with the ³¹P n.m.r. data indicates the presence of the *N*-phosphinoyl group. Electron impact mass spectra showed, in addition to the expected molecular ions (Table 1), strong fragment ions at *m/z* 201 and 202 corresponding to Ph₂P(O)⁺ and Ph₂P(O)H⁺ arising from cleavage of the P–N bond. Additionally, (3a)–(3d) liberated iodine spontaneously from aqueous potassium iodide and are rapidly converted back into the imines (2a)–(2d) by adding triphenylphosphine to a chloroform solution of the oxaziridine. These reactions are characteristic of oxaziridines,⁷⁻⁹ and together with the n.m.r. data enable isomeric structures (*e.g.* *N*-phosphinoyl nitrones or amides) to be excluded.

Most oxaziridines are very weak oxidants,⁷⁻¹⁰ but Davis and coworkers¹¹ have recently shown that *N*-sulphonyl oxaziridines are capable of a variety of oxidations. A preliminary investigation into the reactivity of *N*-phosphinoyl oxaziridines indicate that their oxidising ability resembles *N*-sulphonyl oxaziridines rather than *N*-alkyl derivatives. Thus the *N*-phosphinoyl compounds readily oxidise thioethers to sulfoxides and disulphides to thiosulphinates, and also convert cyclohexene into the epoxide.

These oxaziridines offer scope for the preparation of chiral oxidants, for example by incorporating an optically active *N*-phosphinoyl group.

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