# Imines and Derivatives. Part 20.[1] *N*-Phosphinoyloxaziridines: Synthesis and Structural Characterisation by Nuclear Magnetic Resonance Spectroscopy and a Crystal Structure of 3-(4-Chlorophenyl)-2-(diphenylphosphinoyl)oxaziridine

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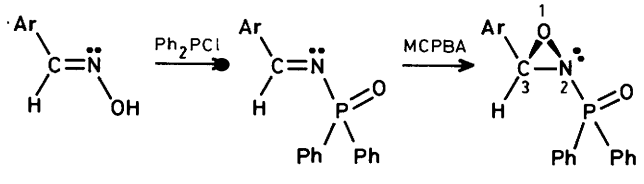
The preparation of a new class of oxaziridines containing an *N*-phosphinoyl group is described. The compounds were obtained by peroxyacid oxidation of *N*-phosphinoyl imines under basic or neutral conditions, and characterised by n.m.r. spectroscopy. Relevant $^2J_{PC}$, $^3J_{PH}$, and $^1J_{CH}$ coupling constants are reported. An *X*-ray structure analysis of the title compound establishes that the 2-diphenylphosphinoyl group is *trans* to the 3-aryl ring. The P–N bond length (1.76 Å) is abnormally high for an aminophosphorus(v) compound and the nitrogen atom is pyramidal ($\Sigma$ N̂ = 280°). This geometry is interpreted in terms of an unusually low degree of π-bonding between nitrogen and phosphorus due to the high *s*-character of the nitrogen lone pair.

Oxaziridines have been known for thirty years following pioneering investigations by Emmons,[2] Horner and Jurgens,[3] and Krimm.[4] Most of the early examples contained an *N*-alkyl group, though some oxaziridines containing N–H,[5] *N*-acyl,[6] or *N*-aryl[7] groups have also been reported.[8] More recently Davis and co-workers[9] have synthesised a range of stable oxaziridines containing an *N*-arenesulphonyl group. Although the oxidising properties of oxaziridines has been long established,[2] the *N*-sulphonyl substituent was found to impart more synthetically useful oxidising properties on this class of heterocycle.[10]

In this paper, which follows a preliminary communication,[11] we report the preparation and characterisation of *N*-phosphinoyl-oxaziridines. These oxaziridines are the first stable examples of this ring system where a phosphorus atom is bonded to the ring nitrogen atom, though a structure of this type has been tentatively assigned to an unstable cytotoxic intermediate isolated at −20 °C from a preparation of 4-hydroperoxycyclophosphamide.[12]

## Results and Discussion

*Synthesis.*—The synthetic route (Scheme 1) involves the reaction of aldoximes (**1**) with chlorodiphenylphosphine at




(1) (2) (3)

**Scheme 1.**

low temperature under inert anhydrous conditions to afford *N*-phosphinoyl aldimines (**2**) as described by Krzyzanowska and Stec.[13] It was found that under appropriate two-phase basic or neutral conditions the *N*-phosphinoyl imines could be oxidised by *meta*-chloroperoxybenzoic acid (MCPBA) to give *N*-phosphinoyloxaziridines (**3**).

The *N*-phosphinoyl imines (**2**) often tended to decompose either on standing or during attempted purification, but the corresponding *N*-phosphinoyloxaziridines (**3**) proved to be much more stable and could be readily purified by flash column chromatography on silica gel. Accordingly, we adopted the procedure of performing the oxidation on crude, freshly prepared, *N*-phosphinoyl imine (**2**). The crude imines (**2a—j**), obtained from the oxime, were characterised and assayed for purity by $^1$H n.m.r. spectroscopy, using the highly characteristic imino proton doublet resonance at δ 9.2—9.9 (Table 1) split by a large three-bond coupling to phosphorus (*ca.* 32 Hz). The purity of the crude *N*-phosphinoyl imine was typically 40—70% by n.m.r. analysis, though lower yields (15—20%) were obtained in the case of the 4-fluoro and 4-nitro derivatives [(**2d**) and (**2f**)]. In some cases several batches of the *N*-phosphinoyl imines were prepared, and on occasions the reaction unexpectedly failed to yield any imine despite the disappearance of the oxime. These failures could not readily be related to experimental technique or to the reagents used, and generally a repeated reaction under apparently identical conditions was successful.

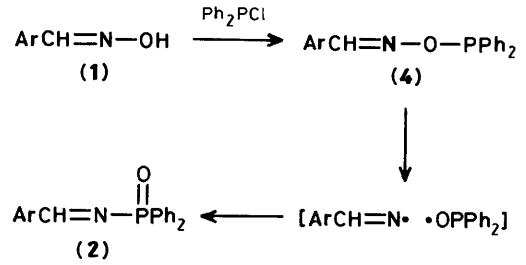
**Table 1.** $^1$H N.m.r. data for *N*-phosphinoyl imines

| Imine | Ar | $\delta_H$[a] | $^3J_{PH}$/Hz |
|---|---|---|---|
| (**2a**) | Ph | 9.29 | 32.4 |
| (**2b**) | 4-$BrC_6H_4$ | 9.27 | 31.7 |
| (**2c**) | 4-$ClC_6H_4$ | 9.28 | 31.7 |
| (**2d**) | 4-$FC_6H_4$ | 9.18 | 31.9 |
| (**2e**) | 4-$CF_3C_6H_4$ | 9.38 | 31.5 |
| (**2f**) | 4-$NO_2C_6H_4$ | 9.40 | 31.3 |
| (**2g**) | 1-Naphthyl | 9.91 | 33.3 |
| (**2h**) | 2-Naphthyl | 9.47 | 31.9 |
| (**2i**) | 2,4-$Cl_2C_6H_3$ | 9.65 | 32.0 |
| (**2j**) | 2,6-$Cl_2C_6H_3$ | 9.70 | 33.0 |

[a] Chemical shift of the characteristic HC= signal in deuteriochloroform.

The problems could possibly be due either to the instability of the *N*-phosphinoyl imines or to side-reactions from the proposed free radical nature (Scheme 2) of the rearrangement of the initially formed *O*-diphenylphosphino-oxime (**4**).[14,15]

Direct oxidation of the *N*-phosphinoyl imines with MCPBA in dichloromethane was unsuccessful, but in most cases the desired *N*-phosphinoyloxaziridines (**3a—j**) (see Table 2) were obtained in acceptable yields (typically 40—70% based upon the purity of the crude imine reactant estimated by n.m.r. analysis) using MCPBA at 0 °C in the presence of aqueous sodium



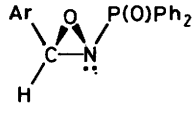

Scheme 2.

hydrogen carbonate. In some cases phase-transfer catalysis was found to be successful. The two-phase procedure failed in the case of imines (**2c**), (**2d**), (**2f**), and (**2g**). However, an alternative oxidation procedure, using the MCPBA–KF complex devised by Camps and co-workers[16] for sensitive alkene epoxidation, proved to be successful in the more difficult cases, giving isolated yields of oxaziridines (**3c**), (**3d**), (**3f**), and (**3g**) (10—30%). Experiments on some of the other *N*-phosphinoyl imines indicate that the MCPBA–KF oxidation procedure avoids the risk of imine hydrolysis present in the two-phase method and tends to give improved yields of oxaziridine. The mechanism for the oxidation of (**2**) to (**3**) is not known with certainty, but by analogy with the reaction of peroxyacids with *N*-alkyl imines,[17,18] a two-step process is likely involving nucleophilic attack on the *N*-phosphinoyl imine.

With the exception of the 4-fluoro compound (**3d**) the oxaziridines were sufficiently stable to be purified by flash column chromatography. However, in common with other types of oxaziridines, prolonged adsorption on chromatographic silica gel may cause decomposition. 3-Phenyloxaziridines tend to be thermally destabilised by the presence of π-donor (+*M*) substituents at the *para* position,[9,19] and the instability of (**3d**) may be associated with this effect.

*Spectra.*—$^1$H and $^{13}$C n.m.r. spectral data for the oxaziridines are given in Table 2, and representative spectra are shown in Figures 1 and 2.

The chemical shifts of the 3-H proton fall in the narrow range δ 5.65—5.86 for most compounds, extending to δ 6.39 for derivatives with an *ortho* substituent. *N*-Alkyloxaziridines derived from *para*-substituted benzaldehydes have 3-H chemical shifts of *ca.* δ 4.6 or δ 5.4 for *trans* or *cis* isomers respectively.[20,21] This does not necessarily imply that *N*-phosphinoyloxaziridines exist in the *cis* configuration (**5**) since the diphenylphosphinoyl group could deshield the adjacent 3-H in the *trans*-configuration (**3**). *N*-Sulphonyloxaziridines[9] have 3-H chemical shifts in the region δ 5.4—5.6 which is close to the values obtained for *N*-phosphinoyloxaziridines, and the *trans* configuration has been determined by *X*-ray crystallography on five separate examples.[22–25]




(**5**)

A three-bond coupling of 8.7 ± 0.3 Hz between the 3-H and phosphorus (Table 2) is also evident in these *N*-phosphinoyloxaziridines. This compares well with the reported PNCH couplings of 10.2 Hz in $Ph_2P(O)NMe_2$[26] and 8.8 Hz in tris(aziridino)phosphine oxide, $[(CH_2)_2N]_3PO$.[27]

The $^{13}$C n.m.r. signal of the oxaziridine ring carbon (C-3) of (**3a—j**) is a characteristic doublet in the range δ 73—77 which is comparable to C-3 shifts previously reported for *N*-alkyl- and *N*-sulphonyl-oxaziridines containing a 3-aryl substituent, *viz.* δ 72—74 and δ 75—78 respectively.[9,28] The two-bond coupling to phosphorus is essentially constant along the series (4.0 ± 0.4 Hz) and is close to the $^2J_{PC}$ value of 4.9 Hz reported for tris(aziridino)phosphine oxide.[27] The aromatic carbon signals of (**2a—j**) are not reported as this region is very complex due to the presence of three aryl rings. The situation is further complicated by the fact that the *P*-phenyl groups are diastereotopic owing to the absence of a molecular σ-plane containing the prochiral phosphorus atom.[29]

The presence of only a single set of n.m.r. signals in the $^1$H and $^{13}$C n.m.r. spectra of (**3a—j**) indicates that these oxaziridines exist in solution as a single isomeric form, *viz. cis* (**5**) or *trans* (**3**). *N*-Alkyloxaziridines are configurationally stable at nitrogen at ambient temperature with large barriers to inversion (100—140 kJ mol$^{-1}$).[30] Accordingly the *cis*:*trans* isomer distribution of oxaziridines produced by the oxidation of *N*-alkyl imines is

**Table 2.** $^1$H N.m.r. data for *N*-phosphinoyloxaziridines[a]

| Oxaziridine | Ar | $\delta_H$[b] | $^3J_{PH}$/Hz[b] | $\delta_C$[c] | $^2J_{PC}$/Hz[c] | $^1J_{CH}$/Hz[d] |
|---|---|---|---|---|---|---|
| (**3a**) | Ph | 5.65 | 9.0 | 76.0 | 4.3 | 183.5 |
| (**3b**) | 4-$BrC_6H_4$ | 5.71 | 8.8 | 75.7 | 4.2 | 183.8 |
| (**3c**) | 4-$ClC_6H_4$ | 5.71 | 8.8 | 75.8 | 3.8 | 184.2 |
| (**3d**) | 4-$FC_6H_4$ | 5.68 | 8.8 | *e* | *e* | *e* |
| (**3e**) | 4-$CF_3C_6H_4$ | 5.76 | 8.8 | 75.4 | 3.7 | 185.2 |
| (**3f**) | 4-$NO_2C_6H_4$ | 5.77 | 8.7 | 75.1 | 4.4 | 186.4 |
| (**3g**) | 1-Naphthyl | 6.39 | 8.8 | 76.0 | 4.4 | 183.1 |
| (**3h**) | 2-Naphthyl | 5.86 | 8.8 | 76.7 | 3.8 | 184.1 |
| (**3i**) | 2,4-$Cl_2C_6H_3$ | 6.05 | 8.6 | 73.2 | 4.2 | 188.9 |
| (**3j**) | 2,6-$Cl_2C_6H_3$ | 5.99 | 8.4 | 74.4 | 4.2 | 190.0 |

[a] Recorded in deuteriochloroform solution. [b] Oxaziridine ring hydrogen atom (3-H) resonance; resolution <0.3 Hz. [c] Oxaziridine ring carbon (C-3) resonance; digital resolution <0.3 Hz. [d] Determined from the separation of the $^{13}$C satellite lines in the $^1$H spectrum (3-H resonance); digital resolution <0.3 Hz. [e] Not recorded owing to the instability of this oxaziridine.

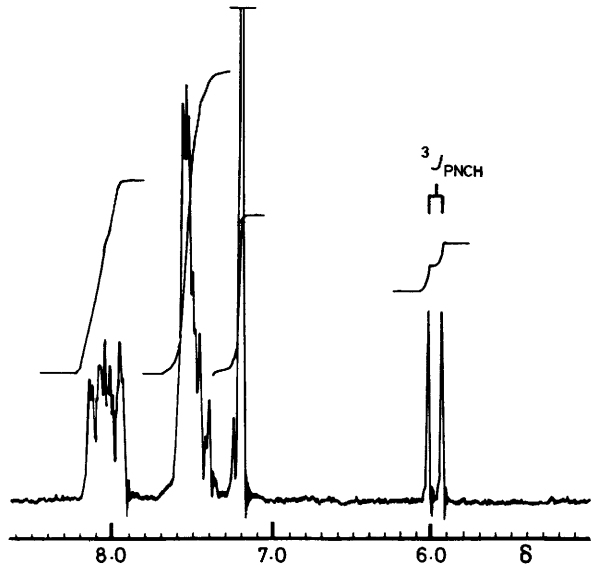



**Figure 1.** 100 MHz $^1$H N.m.r. spectrum of oxaziridine (**3j**) in deuteriochloroform; the three protons on the dichlorophenyl ring are accidentally isochronous at δ 7.2

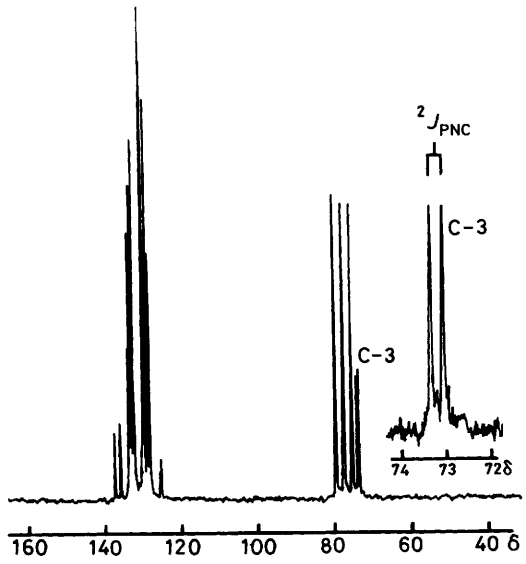



**Figure 2.** 15 MHz $^{13}C$ N.m.r. spectrum of oxaziridine (**3i**) in deuteriochloroform; the inset shows an expansion of the C-3 doublet which lies close to the solvent signals

usually under kinetic control. However, the diphenylphosphinoyl group is very effective at lowering the barrier to inversion at a directly bonded nitrogen atom.[31,*] Hence it is likely that the *cis* and *trans* forms of oxaziridines (**3a—j**) would equilibrate during the reaction and work-up, and the exclusive observation of one stereoisomer of (**3a—j**) probably reflects a marked thermodynamic preference. Steric interactions between the diphenylphosphinoyl group and the substituents at C-3 are minimised in the *trans* configuration (**3**).

It has been shown previously that in *N*-alkyloxaziridines the one-bond $^{13}C$–H coupling constant for the ring hydrogen atom is indicative of the *cis*:*trans* configuration. A larger coupling (*ca.* 184 Hz) was observed when the nitrogen lone pair is *cis* to the hydrogen at C-3 as compared with $^1J_{CH}$ *ca.* 179 Hz in the *trans* isomer.[32] The values of $^1J_{CH}$ at C-3 in (**3a—j**) fall in the range 183—190 Hz (Table 2). This might be taken as evidence for the *cis* geometry in (**3a—j**). However, the base value of $^1J_{CH}$ could well be altered by replacing an *N*-alkyl group with *N*-diphenylphosphinoyl, and it would be premature to conclude that the *cis* configuration predominates. Indeed, the *X*-ray analysis of the representative compound (**3c**), see below, shows that the *trans* geometry is adopted, at least in the solid state. $^1J_{CH}$ coupling constants vary appreciably according to the nature of the 3-aryl group (Table 2). This is unlikely to be indicative of any change in configuration along the series as $^3J_{PH}$ and $^2J_{PC}$ couplings, which are also likely to depend on the geometry, do not change significantly along the series. It would seem much more likely that *ortho* chloro substitution, and to a lesser extent an electron-withdrawing *para* substituent, increases $^1J_{CH}$ by electronic effects. Literature data indicate that the introduction of a *para*-chloro substituent in 2-arylsulphonyl-3-phenyloxaziridines also increases $^1J_{CH}$ at C-3 by *ca.* 1 Hz (no data were reported for *ortho*-substituted compounds).[9]

*X-Ray Crystal Structure.*—The atomic co-ordinates and principal molecular dimensions of oxaziridine (**3c**) are given in Tables 3 and 4. The crystallographic numbering scheme used in the Tables is indicated in Figure 3 which shows a projection of the molecule.

The relative configuration was found to be *trans* (*R,R*/*S,S*) as depicted in (**3**). This configuration is favoured on steric grounds as it avoids non-bonded interactions between the diphenylphosphinoyl group and the 3-aryl ring. The bond lengths and angles in the heterocyclic ring are similar to those found in *N*-alkyl- and *N*-sulphonyl-oxaziridines.[22–25] Although the standard deviations are large, it is clear that the P–N bond length in (**3c**) (1.76 Å) is abnormal being *ca.* 0.10 Å longer than P–N bonds in standard diphenylphosphinamides of the type $Ph_2P(O)NRR'$ (R,R′ = H or alkyl) which lie in the range 1.63—1.68 Å based on four separate crystal structure determinations.[33–35] The estimated length[33] of a pure single P(O)–N bond is *ca.* 1.80 Å, and the shortening to *ca.* 1.66 Å in normal diphenylphosphinamides is generally considered to be indicative of strong π-bonding between nitrogen and phosphorus. Traditionally this has been represented as $p_\pi$–$d_\pi$ bonding, but it may be better considered in terms of a non-classical $n$–σ* bond[36] involving overlap of the nitrogen lone pair orbital with a vacant antibonding σ*-orbital on phosphorus. Clearly, the unusually long P–N bond in (**3c**) suggests only a very small degree of π-bonding. The highly pyramidal nitrogen atom in

**Table 3.** Atomic fractional co-ordinates ( × $10^4$) for (**3c**)

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| P(1) | 2 236(3) | −130(6) | 8 194(5) |
| Cl(1) | 4 722(4) | −7 804(7) | 7 692(5) |
| O(1) | 3 702(8) | −705(15) | 8 902(12) |
| O(2) | 2 458(6) | 296(12) | 9 540(9) |
| N(1) | 2 891(8) | −1 253(16) | 7 934(12) |
| C(1) | 3 439(11) | −2 229(27) | 9 029(19) |
| C(2) | 3 785(11) | −3 513(25) | 8 703(19) |
| C(3) | 4 084(11) | −3 469(24) | 7 883(17) |
| C(4) | 4 373(11) | −4 696(28) | 7 579(17) |
| C(5) | 4 350(12) | −6 119(28) | 8 065(19) |
| C(6) | 4 085(10) | −6 354(22) | 8 924(18) |
| C(7) | 3 775(10) | −5 022(26) | 9 176(16) |
| C(8) | 2 117(5) | 1 576(16) | 7 225(9) |
| C(9) | 1 938(5) | 3 053(16) | 7 548(9) |
| C(10) | 1 877(5) | 4 408(16) | 6 823(9) |
| C(11) | 1 994(5) | 4 285(16) | 5 774(9) |
| C(12) | 2 173(5) | 2 807(16) | 5 451(9) |
| C(13) | 2 234(5) | 1 453(16) | 6 176(9) |
| C(14) | 1 394(7) | −1 351(11) | 7 392(10) |
| C(15) | 864(7) | −1 380(11) | 6 064(10) |
| C(16) | 245(7) | −2 452(11) | 5 558(10) |
| C(17) | 155(7) | −3 496(11) | 6 380(10) |
| C(18) | 685(7) | −3 467(11) | 7 708(10) |
| C(19) | 1 304(7) | −2 395(11) | 8 214(10) |

**Table 4.** Selected bond lengths (Å) and bond angles (°) for (**3c**)

| Bond lengths (Å) | | Bond angles (°) | |
|---|---|---|---|
| P(1)–N(1) | 1.764(14) | O(2)–P(1)–N(1) | 118.8(7) |
| P(1)–O(2) | 1.483(9) | O(2)–P(1)–C(8) | 112.6(6) |
| P(1)–C(8) | 1.778(13) | O(2)–P(1)–C(14) | 113.8(6) |
| P(1)–C(14) | 1.779(12) | N(1)–P(1)–C(8) | 100.2(6) |
| N(1)–O(1) | 1.510(15) | N(1)–P(1)–C(14) | 100.6(6) |
| N(1)–C(1) | 1.460(19) | C(8)–P(1)–C(14) | 109.4(5) |
| O(1)–C(1) | 1.416(18) | P(1)–N(1)–O(1) | 107.9(9) |
| C(1)–C(2) | 1.436(21) | P(1)–N(1)–C(1) | 115.1(12) |
| C(5)–Cl(1) | 1.756(19) | O(1)–N(1)–C(1) | 56.9(9) |
| | | N(1)–O(1)–C(1) | 59.8(9) |
| | | N(1)–C(1)–O(1) | 63.3(10) |
| | | N(1)–C(1)–C(2) | 114.8(18) |
| | | O(1)–C(1)–C(2) | 112.8(17) |

* N.m.r. studies of symmetrically 3-disubstituted 2-phosphinoyloxaziridines indicate that inversion at nitrogen occurs rapidly at ambient temperature (half-life < 1 s).[31b]

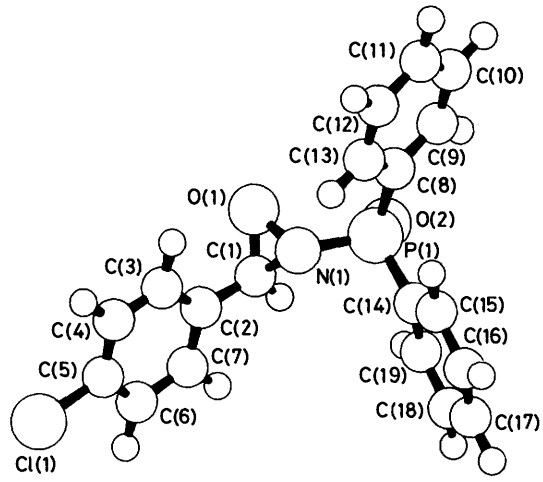
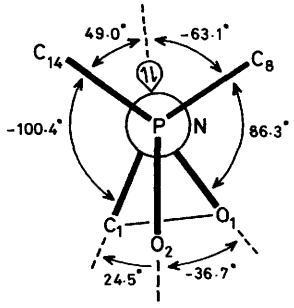



**Figure 3.** Crystal structure of oxaziridine (**3c**)

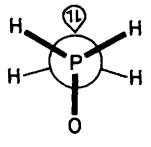
(**3c**) will have its lone pair electrons in an orbital of high *s*-character which will overlap poorly with vacant σ* antibonding (or *d*) orbitals on phosphorus. The P–N σ-bond will also have increased *p*-character in (**3c**) as compared with standard acyclic diphenylphosphinamides. Both these factors, together with possible changes in coulombic interactions, could contribute to the lengthening of the P–N bond in (**3c**).

The pyramidal geometry at the nitrogen atom as shown by the sum of the three bond angles. $\Sigma\hat{N} = 279.9°$, is similar to the situation in other oxaziridines where $\Sigma\hat{N}$ lies between 278 and 285°.[22–25] This contrasts markedly with the 'flattened' nitrogen geometry found in normal diphenylphosphinamides where $\Sigma\hat{N}$ lies in the range 337—352° (three structures).[33–35] The highly pyramidal nature of the nitrogen results from the geometrical constraints of the three-membered ring combined with the presence of the electronegative oxygen atom directly bonded to nitrogen (Walsh-Bent rules).[37]

The 4-chlorophenyl ring is orientated with its plane intersecting the oxaziridine ring as shown by torsion angles C(3)–C(2)–C(1)–O(1) −25.7° and C(3)–C(2)–C(1)–N(1) +44.3° (using the atom numbering scheme shown in Figure 3).




(**6**)




(**7**)

The conformation around the P–N bond in the crystal is depicted in projection (**6**), together with the relevant torsion angles. The nitrogen lone pair may be assumed to lie formally on the bisector of the projected CNO, although, as discussed above, the lone pair orbital will have a high *s*-character in oxaziridine (**3c**). Accordingly in conformation (**6**) the lone pair is directed essentially antiperiplanar to the P–O bond (torsion angle 173.9°). The crystal structures of diphenylphosphinamides, $Ph_2P(O)NR_2$, also reveal a similar antiperiplanar conformation, though the nitrogen is flattened.[33,35] Furthermore, an *ab initio* molecular orbital calculation on $H_2P(O)NH_2$ using an STO-3G basis set also indicates that the *anti* conformation (**7**) is the preferred geometry.[38] Although this conformation may well minimise steric interactions in the diphenylphosphinoyl compounds, the *anti* arrangement is consistent with an *n*–σ* bonding model. The nitrogen lone pair is directed *anti* to the most polar bond at phosphorus (here P–O) in order to maximise overlap with the rear-directed lobe of the σ* orbital.[36] Much weaker N–P *n*–σ* bonding in (**3c**) should, in principle, result in a slight shortening of the P–O bond in this molecule compared with diphenylphosphinamides. However, the precision of the bond length data does not allow any conclusion to be reached on this aspect.

## Experimental

All work involving potentially toxic phosphorus compounds was performed in a good fume hood, wearing protective gloves where appropriate. N.m.r. spectra were recorded on Jeol GX-270, Jeol FX-60, Varian XL-100, Bruker WH-250, or Bruker WH-90 spectrometers.

Oximes were prepared by standard methods from the aldehyde, hydroxylamine hydrochloride, and sodium hydroxide, and recrystallised from non-aqueous solvents. The oximes were thoroughly dried *in vacuo* before use. Potassium fluoride was activated by heating for 1 h at 120 °C under reduced pressure (0.1 mmHg). The MCPBA–KF mixture was obtained by dissolution of MCPBA and KF (2 equiv.) in dry dichloromethane followed by the removal of the solvent under reduced pressure.

N-(*Arylmethylene*)*diphenylphosphinamides* (**2a—j**).—These *N*-diphenylphosphinoyl imines were generated *in situ* using the method reported by Brzyzanowska and Stec.[13] Typically, chlorodiphenylphosphine (7.0 mmol) in dry dichloromethane (20 $cm^3$) was added dropwise over *ca.* 15 min to a stirred solution of the dried oxime (7.0 mmol) and triethylamine (dried over KOH) (9.0 mmol) in dry dichloromethane (120 $cm^3$) under nitrogen at −40 to −45 °C. The mixture was stirred at this temperature for 3 h and then allowed to warm to ambient temperature with stirring for a further 2 h. The reaction mixture was washed rapidly with ice-cold water (twice), dried ($MgSO_4$), and the solvent removed to give the crude imine which was immediately assayed for purity by $^1H$ n.m.r. spectroscopy (Table 1). This crude product (typically 40—70% pure) was used immediately in the subsequent oxidation step. In our hands several unexplained failures of this reaction occurred but a repeated preparation under apparently identical conditions was successful. Low yields of the *N*-phosphinoyl imine (15—20% by $^1H$ n.m.r.) were obtained for the 4-fluoro (**2d**) and 4-nitro (**2f**) compounds.

3-*Aryl*-2-(*diphenylphosphinoyl*)*oxaziridines* (**3a—j**).—The oxaziridines were obtained by oxidising the *N*-phosphinoyl imines with MCPBA under non-acidic conditions. In most cases biphasic conditions were employed [method (a)], similar to the procedure used to convert *N*-sulphonyl imines into oxaziridines.[9] In a few cases [(**2d**), (**2f**), and (**2g**)] this procedure failed to produce oxazirdine, and an alternative procedure [method (b)] involving the MCPBA–KF complex[16] was used successfully. This procedure also appears to be applicable to the oxidation of other imines.

*Method* (a). Sodium hydrogen carbonate (0.8 g, 9.5 mmol) dissolved in ice-cold water (35 $cm^3$) was rapidly added to a magnetically stirred solution of the crude *N*-phosphinoyl imine (4.8 mmol) in chloroform (80 $cm^3$) pre-cooled to 0 °C. Immediately, MCPA (1.6 g, 9.3 mmol) in chloroform (40 $cm^3$) was

added dropwise over 5 min with rapid stirring. The reaction mixture was stirred at 0 °C for a further 15 min, then the chloroform layer was separated and dried ($K_2CO_3$). Removal of the solvent gave the crude oxaziridine which was purified by flash chromatography using silica gel (Merck no. 9385) as stationary phase and diethyl ether–dichloromethane (*ca.* 4:1) or dichloromethane–ethyl acetate (*ca.* 95:5) as eluant. In some cases the oxaziridine was further purified by recrystallisation from tetrachloromethane or light petroleum (b.p. 40—60 °C) containing diethyl ether, avoiding prolonged heating. In some oxidations a phase-transfer catalyst, benzyltriethylammonium chloride (BTEAC),[39] was added.

*Method* (b). Freshly prepared, vacuum dried, MCPBA–KF complex prepared from MCPBA (5.0 g, 29.0 mmol) and activated potassium fluoride (3.39 g, 58.0 mmol) was added to the *N*-phosphinoyl imine (11.6 mmol) dissolved in dry dichloromethane (150 $cm^3$). The reaction mixture was stirred at ambient temperature for 15 min, filtered, and the filtrate dried ($MgSO_4$). Removal of the dichloromethane gave the crude oxaziridine which was purified by flash chromatography as in method (a).

2-(*Diphenylphosphinoyl*)-3-*phenyloxaziridine* (**3a**) prepared by method (a) in 48% yield had m.p. 138—141 °C (decomp.) (Found: $M^+$, 321.0908. $C_{19}H_{16}NO_2P$ requires *M*, 321.0918).

3-(4-*Bromophenyl*)-2-(*diphenylphosphinoyl*)*oxaziridine* (**3b**) prepared by method (a) in 42% yield had m.p. 136—138 °C (decomp.) (Found: C, 56.9; H, 3.9; N, 3.3. $C_{19}H_{15}BrNO_2P$ requires C, 57.0; H, 3.8; N, 3.5%).

3-(4-*Chlorophenyl*)-2-(*diphenylphosphinoyl*)*oxaziridine* (**3c**) prepared by method (b) in 32% yield had m.p. 137—139 °C (Found: C, 64.0; H, 4.5; N, 3.7. $C_{19}H_{15}ClNO_2P$ requires C, 64.1; H, 4.3; N, 3.9%).

2-(*Diphenylphosphinoyl*)-3-(4-*fluorophenyl*)*oxaziridine* (**3d**) prepared by method (b) in 21% yield had m.p. 130—132 °C (decomp.). The thermal instability of this compound precluded a meaningful microanalysis.

2-(*Diphenylphosphinoyl*)-3-(4-*trifluoromethylphenyl*)*oxaziridine* (**3e**) prepared by methods (a) and (b) in 60% yield had m.p. 166—168 °C (Found: C, 61.3; H, 3.8; N, 3.6. $C_{20}H_{15}F_3NO_2P$ requires C, 61.7; H, 3.9; N, 3.6%).

2-(*Diphenylphosphinoyl*)-3-(4-*nitrophenyl*)*oxaziridine* (**3f**) prepared by method (b) in 12% yield [not obtained by method (a)] had m.p. 160—162 °C (Found: C, 62.0; H, 4.0; N, 7.6. $C_{19}H_{15}N_2O_4P$ requires C, 62.3; H, 4.1; N, 7.7%).

2-(*Diphenylphosphinoyl*)-3-(1-*naphthyl*)*oxaziridine* (**3g**) prepared by method (b) in 11% yield [not obtained by method (a)] had m.p. 106—107 °C (Found: C, 74.1; H, 4.8; N, 3.6. $C_{23}H_{18}NO_2P$ requires C, 74.4; H, 4.9; N, 3.8%).

2-(*Diphenylphosphinoyl*)-3-(2-*naphthyl*)*oxaziridine* (**3h**) prepared by method (a) in 27% yield and method (b) in 52% yield had m.p. 118—120 °C (Found: C, 3.8; H, 4.7; N, 3.8%).

3-(2,4-*Dichlorophenyl*)-2-(*diphenylphosphinoyl*)*oxaziridine* (**3i**) prepared by method (a) in 64% yield had m.p. 96—98 °C (Found: C, 59.0; H, 3.7; N, 3.9. $C_{19}H_{14}Cl_2NO_2P$ requires C, 58.5; H, 3.6; N, 3.6%).

3-(2,6-*Dichlorophenyl*)-2-(*diphenylphosphinoyl*)*oxaziridine* (**3j**) prepared by method (a) in 51% yield had m.p. 146—148 °C (decomp.) (Found: C, 58.5; H, 3.9; N, 3.9%).

*Crystal Data for* (**3c**).—$C_{19}H_{15}ClNO_2P$, $M$ = 355.8. Monoclinic, $a$ = 20.02(2), $b$ = 8.36(1), $c$ = 11.99(1) Å, $\beta$ = 120.5(1)°, $U$ = 1 729.2 Å$^3$, $\lambda$ = 0.710 69 Å, space group $P2_1/a$, $Z$ = 4, $D_c$ = 1.37 g cm$^{-3}$, $F(000)$ = 736, $\mu$(Mo-$K_\alpha$) = 2.75 cm$^{-1}$.

*Structure Analysis and Refinement.*—Crystals were small, colourless, well formed tablets. The lattice was characterised by preliminary photographic study (oscillation and Weissenberg, Cu-$K_\alpha$ radiation). A crystal of dimensions 0.32 × 0.25 × 0.08 mm was mounted with the unique axis (*b*) coincident with the ω axis of a Stöe STADI-2 two-circle diffractometer. Using the ω-scan technique and graphite-monochromated Mo-$K_\alpha$ radiation 867 independent diffraction intensities ($2\theta < 40°$) were recorded, of which the 745 with $I > 0$ were employed in the structure determination. The structure was solved using the direct methods of SHELX.[40] Hydrogen atoms were included in positions calculated from the geometry of the molecule (C–H = 1.08 Å) and the two benzene rings attached to the phosphorus atom were constrained as regular hexagons (C–C = 1.395 Å). Least-squares refinement with allowance for anisotropic vibrations for non-hydrogen atoms and a common refined isotropic temperature factor for all hydrogens gave a final conventional $R$ of 0.088, when only the 592 data with $I > 2\sigma(I)$ were used. The final weighting scheme was $w = 1.55/[\sigma^2(F) + 0.000\,072\,F^2]$. The atomic co-ordinates for non-hydrogen atoms are given in Table 3, and selected bond lengths and angles in Table 4. A projection of the molecule is shown in Figure 3.*

* *Supplementary data* (see Instructions for Authors in the January issue). Full lists of atomic co-ordinates, bond lengths, bond angles and torsion angles, hydrogen-atom co-ordinates, and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre.

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