Structure and Bonding in 3,3-Dialkyl-2-phosphinoyloxaziridines by X-Ray Diffraction and Nuclear Magnetic Resonance Spectroscopy

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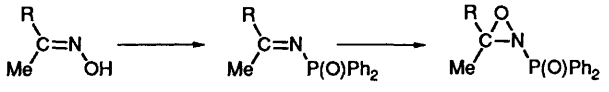
X-ray crystal structure determinations are reported for 2-diphenylphosphinoyl-3,3-dimethyl- and 3-ethyl-3-methyloxaziridines, **2a** and **2b**, prepared from acetone and butanone *via* the oximes. The P–N bond lengths, 1.722(3) and 1.702(5) Å, and the conformation about this bond, are consistent with an n–σ* π-bonding interaction. Steric interactions appear to influence the bond angles at the pyramidal nitrogen. Oxaziridine **2b** is a mixture of *cis* and *trans* isomers (ratio *ca.* 1:3) in the crystal and in solution. The ^{1}H, ^{13}C and ^{31}P NMR spectra are discussed. The barriers to nitrogen inversion, $\Delta G^{\ddagger}$ 12.6–13.2 kcal (52.7–55.2 kJ) mol^{-1} by dynamic ^{13}C NMR, are the lowest yet reported for an oxaziridine.

2-Phosphinoyloxaziridines derived from aromatic aldehydes have recently been prepared and characterised.[1,2] These compounds are closely related to the better established 2-sulphonyloxaziridines[3] and appear to show similar interesting oxidising properties.[2] We now report on the preparation and structure determination of 2-diphenylphosphinoyl-3,3-dialkyloxazirdines (**2**) derived from simple dialkyl ketones.[4]

Results and Discussion

Synthesis.—*N*-Phosphinoylimines (**1**), the precursors of 2-phosphinoyloxaziridines, were prepared *in situ* by the reaction of acetone or butanone oximes with chlorodiphenylphosphine and triethylamine at *ca.* −50 °C.[1,5]



1 **2a** R = Me **2b** R = Et

An alternative preparation of *N*-phosphinoylimines from the ketone, phosphinic amide and titanium tetrachloride is unsuitable for enolisable ketones.[6] The crude imines were then oxidised in hexane–dichloromethane solution with a suspension of the 2:1 complex of potassium fluoride and *m*-chloroperoxybenzoic acid (MCPBA)[1,7] to give the corresponding oxaziridines **2a** and **2b** in 63% yield. The compounds, which were colourless crystalline solids, were subjected to X-ray diffraction and NMR spectral analysis.

X-Ray Crystal Structures.—The atomic coordinates and molecular dimensions of oxaziridines **2a** and **2b** are given in Tables 1–4.* The crystallographic numbering scheme is indicated in Fig. 1 which shows comparable views of the molecules. Only the major *trans* isomer of ethylmethyloxaziridine **2b** is depicted. The X-ray result, 71% *trans*, 29% *cis* isomer present in the crystal, is in excellent agreement with the results of line shape analysis of the ^{13}C NMR signals at 3.5 °C, which yield the rates of nitrogen inversion of the *trans* and *cis* isomers, 252 and 681 s^{-1}, respectively, indicating the presence in solution of 73% *trans* and 27% *cis* forms and also with the integrated ratios of the alkyl signals corresponding to the two invertomers (see below). In the minor *cis* isomer the terminal carbon atom C(16′) of the ethyl substituent points away from the P=O moiety, torsion angles C(16′)–C(14)–C(13)–N(1) and C(16′)–C(14)–C(13)–O(2), 160 and 85°, respectively, thus avoiding any unfavourable steric interactions. In contrast, the major isomer has the comparable torsion angles C(16)–C(15)–C(13)–N(1) = −26.4° and C(16)–C(15)–C(13)–O(2) = 43.9°.

Bond lengths, bond angles and torsion angles in the two molecules are in good agreement, and are compared in Table 5 with those determined[1] for 3-(4-chlorophenyl)-2-(diphenylphosphinoyl)oxaziridine (**3**) by X-ray crystallography. Apart from the orientation of one of the phenyl rings, the conformation of **3** is similar to those of **2a** and **2b**. The agreement is closest with **2b**, corresponding torsion angles differing by less than 10°. The maximum difference between torsion angles in **2a**

Table 1 Fractional atomic coordinates (×10^4) with esd's in parentheses and equivalent isotropic temperature factors (Å^2 × 10^3) for the dimethyl derivative **2a**

Atom	*x*	*y*	*z*	U_{eq}[a]
P	8 323(1)	184(1)	9 623(1)	35
N	8 380(4)	1 191(2)	10 478(2)	44
O(1)	9 309(3)	−824(2)	9 675(2)	49
O(2)	10 050(4)	1 509(3)	10 694(2)	59
C(1)	8 753(4)	1 010(3)	8 617(3)	38
C(2)	9 706(6)	557(4)	7 933(3)	57
C(3)	10 038(7)	1 168(4)	7 119(3)	71
C(4)	9 410(7)	2 186(4)	6 993(3)	65
C(5)	8 457(6)	2 630(4)	7 652(3)	68
C(6)	8 121(6)	2 064(3)	8 464(3)	55
C(7)	6 277(4)	−120(3)	9 654(3)	36
C(8)	5 855(5)	−1 255(3)	9 550(3)	42
C(9)	4 285(5)	−1 557(4)	9 541(3)	52
C(10)	3 149(5)	−754(4)	9 641(3)	60
C(11)	3 559(5)	362(4)	9 725(4)	60
C(12)	5 107(5)	667(3)	9 738(3)	52
C(13)	9 043(6)	1 061(4)	11 396(3)	54
C(14)	9 499(7)	−53(4)	11 778(3)	78
C(15)	8 459(8)	1 918(5)	12 074(4)	85

[a] $U_{eq} = \frac{1}{3}$ (trace of the orthogonalized U_{ij} tensor)

* Anisotropic temperature factors and hydrogen atom co-ordinates have been deposited at the Cambridge Crystallographic Data Centre. For details of the deposition scheme see Instructions for Authors: *J. Chem. Soc., Perkin Trans. 2*, 1991, issue 1.

Table 2 Fractional atomic coordinates ($\times 10^4$) with esd's in parentheses and equivalent isotropic temperature factors ($Å^2 \times 10^3$) for the ethylmethyl derivative **2b**

Atom	*x*	*y*	*z*	U_{eq}[a]
P	8 656(1)	181(1)	9 552(1)	50
N	8 685(5)	1 096(4)	10 410(3)	69
O(1)	9 719(4)	−753(3)	9 537(3)	64
O(2)	10 338(5)	1 433(4)	10 645(3)	100
C(1)	8 923(6)	1 048(4)	8 587(4)	55
C(2)	9 702(9)	612(6)	7 850(4)	80
C(3)	9 867(11)	1 221(8)	7 064(5)	106
C(4)	9 321(12)	2 255(8)	7 043(7)	113
C(5)	8 570(11)	2 683(6)	7 784(7)	114
C(6)	8 356(8)	2 081(5)	8 558(5)	90
C(7)	6 639(5)	−207(4)	9 612(3)	49
C(8)	6 302(6)	−1 304(4)	9 534(4)	60
C(9)	4 747(6)	−1 628(5)	9 552(4)	74
C(10)	3 573(6)	−910(5)	9 624(5)	75
C(11)	3 870(7)	161(6)	9 704(5)	84
C(12)	5 424(6)	518(4)	9 698(4)	67
C(13)	9 395(9)	878(8)	11 297(5)	103
C(14)	9 870(16)	−243(10)	11 612(6)	166
C(15)	8 807(16)	1 538(14)	12 040(7)	161
C(16)	8 183(24)	2 578(15)	11 832(11)	164[b]
C(16′)	11 014(48)	27(47)	12 349(27)	248(34)[c]

[a] $U_{eq} = \frac{1}{3}$ (trace of the orthogonalized U_{ij} tensor). [b] Site occupation 0.71(3). [c] Site occupation 0.29(3); U_{iso} refined.

Table 3 Bond lengths (Å) and bond angles (°) with esd's in parentheses for the dimethyl derivative **2a**

P–N	1.722(3)	C(4)–C(5)	1.357(7)
P–O(1)	1.477(3)	C(5)–C(6)	1.376(6)
P–C(1)	1.787(4)	C(7)–C(8)	1.418(5)
P–C(7)	1.788(3)	C(7)–C(12)	1.382(5)
N–O(2)	1.510(5)	C(8)–C(9)	1.391(5)
N–C(13)	1.439(5)	C(9)–C(10)	1.376(6)
O(2)–C(13)	1.428(5)	C(10)–C(11)	1.391(6)
C(1)–C(2)	1.384(6)	C(11)–C(12)	1.374(6)
C(1)–C(6)	1.394(6)	C(13)–C(14)	1.497(6)
C(2)–C(3)	1.406(6)	C(13)–C(15)	1.500(6)
C(3)–C(4)	1.348(7)		
N–P–O(1)	121.5(2)	C(4)–C(5)–C(6)	121.2(5)
N–P–C(1)	100.2(2)	C(1)–C(6)–C(5)	120.0(4)
O(1)–P–C(1)	112.2(2)	P–C(7)–C(8)	116.3(3)
N–P–C(7)	98.8(2)	P–C(7)–C(12)	124.8(3)
O(1)–P–C(7)	113.0(2)	C(8)–C(7)–C(12)	118.8(3)
C(1)–P–C(7)	109.6(2)	C(7)–C(8)–C(9)	119.8(4)
P–N–O(2)	110.5(2)	C(8)–C(9)–C(10)	119.9(4)
P–N–C(13)	125.8(3)	C(9)–C(10)–C(11)	120.4(4)
O(2)–N–C(13)	57.9(2)	C(10)–C(11)–C(12)	120.1(4)
N–O(2)–C(13)	58.6(2)	C(7)–C(12)–C(11)	121.0(4)
P–C(1)–C(2)	118.2(3)	N–C(13)–O(2)	63.6(2)
P–C(1)–C(6)	123.4(3)	N–C(13)–C(14)	122.2(4)
C(2)–C(1)–C(6)	118.3(4)	O(2)–C(13)–C(14)	115.8(4)
C(1)–C(2)–C(3)	120.0(4)	N–C(13)–C(15)	112.6(4)
C(2)–C(3)–C(4)	120.3(5)	O(2)–C(13)–C(15)	113.4(4)
C(3)–C(4)–C(5)	120.2(5)	C(14)–C(13)–C(15)	117.6(4)

Table 4 Bond lengths (Å) and bond angles (°) with esd's in parentheses for the ethylmethyl derivative **2b**

P–N	1.702(5)	C(5)–C(6)	1.378(10)
P–O(1)	1.471(3)	C(7)–C(8)	1.396(7)
P–C(1)	1.800(5)	C(7)–C(12)	1.376(7)
P–C(7)	1.787(4)	C(8)–C(9)	1.385(7)
N–O(2)	1.509(6)	C(9)–C(10)	1.344(8)
N–C(13)	1.468(9)	C(10)–C(11)	1.358(9)
O(2)–C(13)	1.431(9)	C(11)–C(12)	1.396(8)
C(1)–C(2)	1.385(8)	C(13)–C(14)	1.521(14)
C(1)–C(6)	1.370(8)	C(13)–C(15)	1.457(13)
C(2)–C(3)	1.393(9)	C(14)–C(16′)	1.499(30)
C(3)–C(4)	1.365(12)	C(15)–C(16)	1.429(20)
C(4)–C(5)	1.375(12)		
N–P–O(1)	121.9(2)	C(1)–C(6)–C(5)	119.1(6)
N–P–C(1)	100.9(2)	P–C(7)–C(8)	117.1(4)
O(1)–P–C(1)	112.4(2)	P–C(7)–C(12)	123.4(4)
N–P–C(7)	99.0(2)	C(8)–C(7)–C(12)	119.4(4)
O(1)–P–C(7)	112.3(2)	C(7)–C(8)–C(9)	118.5(5)
C(1)–P–C(7)	108.8(2)	C(8)–C(9)–C(10)	121.4(5)
P–N–O(2)	111.7(3)	C(9)–C(10)–C(11)	121.1(5)
P–N–C(13)	123.2(5)	C(10)–C(11)–C(12)	119.1(6)
O(2)–N–C(13)	57.4(4)	C(7)–C(12)–C(11)	120.4(5)
N–O(2)–C(13)	59.8(4)	N–C(13)–O(2)	62.7(4)
P–C(1)–C(2)	116.7(4)	N–C(13)–C(14)	123.4(6)
P–C(1)–C(6)	122.6(5)	O(2)–C(13)–C(14)	119.7(8)
C(2)–C(1)–C(6)	120.7(6)	N–C(13)–C(15)	115.2(8)
C(1)–C(2)–C(3)	119.4(6)	O(2)–C(13)–C(15)	115.4(9)
C(2)–C(3)–C(4)	119.7(8)	C(14)–C(13)–C(15)	112.0(9)
C(3)–C(4)–C(5)	120.3(8)	C(13)–C(14)–C(16′)	101.0(24)
C(4)–C(5)–C(6)	120.8(7)	C(13)–C(15)–C(16)	118.3(12)

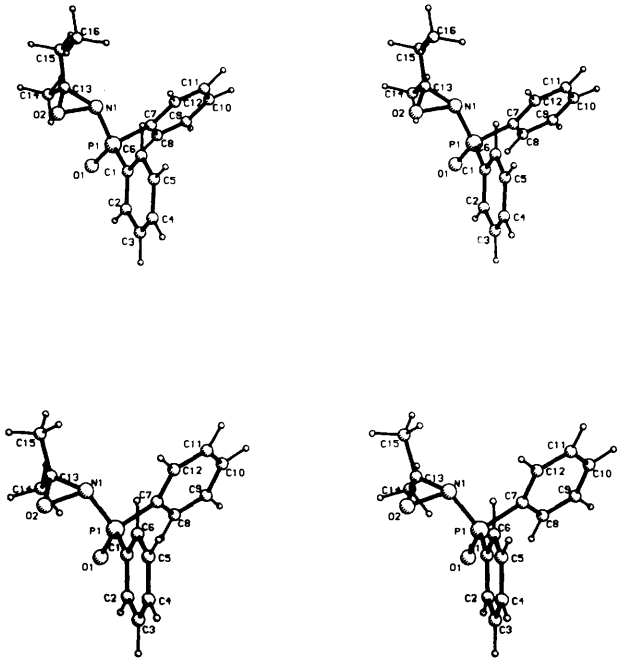


Fig. 1 Stereoscopic view of **2a** (lower diagram) and **2b** (upper diagram)

and **2b** is 9.3° with respect to the orientation of the C(1)–C(6) phenyl ring.

Corresponding bond lengths generally agree well amongst the three structures. However, a statistically significant difference occurs in the P–N bond length which is some 0.04–0.06 Å longer in the chlorophenyl derivative (**3**). The 1.764(14) Å length of this bond in **3** was noted[1] as being longer than P–N bonds in acyclic diphenylphosphinic amides of type $Ph_2P(O)NRR'$ (R,R′ = H or alkyl) which have been found to lie in the range 1.63–1.68 Å. This difference was attributed to a smaller degree of π-bonding in the P–N bond of **3** than apparently occurs in the diphenylphosphinic amides. It was considered[1] that this was associated with the nitrogen atom forming part of a three-membered ring. Thus its bonds have high p-character and consequently its lone pair of electrons is in an orbital of high s-character which will overlap only poorly with vacant orbitals on phosphorus.

The present results for molecules **2a** and **2b**, however, are less supportive of these arguments. While the geometry about the P–N bond is quite similar (see Table 5), the shorter P–N bond lengths of 1.722(3) and 1.702(5) Å would seem to indicate an appreciable degree of π-electron delocalization, more compar-

Table 5 Selected bond lengths (Å), bond angles and torsion angles (°) for the dimethyl (**2a**), ethylmethyl (**2b**), and 4-chlorophenyl (**3**) derivatives. Esd's of the torsion angles are *ca.* 0.4, 0.5 and 1.5°, respectively, for the three structures.

	2a	**2b**	**3**
P–N	1.722(3)	1.702(5)	1.764(14)
P–O	1.477(3)	1.471(3)	1.483(9)
N–O	1.510(5)	1.509(6)	1.510(15)
N–C(13)	1.439(5)	1.468(9)	1.460(19)
O–C(13)	1.428(5)	1.431(9)	1.416(18)
P–N–O	110.5(2)	111.7(3)	107.9(9)
P–N–C(13)	125.8(3)	123.2(5)	115.1(12)
O–N–C(13)	57.9(2)	57.4(4)	56.9(9)
O–P–N	121.5(2)	121.9(2)	118.8(7)
C(1)–P–N–O	−75.4	−79.2	−86.3
C(1)–P–N–C(13)	−139.9	−143.6	−147.5
C(7)–P–N–O	172.7	169.6	161.6
C(7)–P–N–C(13)	108.2	105.2	100.4
O–P–N–O	48.7	46.1	36.7
O–P–N–C(13)	−15.8	−18.3	−24.5
C(2)–C(1)–P–N	141.4	149.3	151.6
C(6)–C(1)–P–N	−41.8	−32.5	−25.7
C(8)–C(7)–P–N	−141.1	−137.0	−95.8
C(12)–C(7)–P–N	41.3	45.3	81.5
C(1)–P–N–ee[a]	74.9	70.6	63.1
C(7)–P–N–ee[a]	−37.0	−40.7	−49.0
O–P–N–ee[a]	−161.0	−164.2	−173.9

[a] ee denotes the probable position of the lone pair orbital.

able to that in the acyclic diphenylphosphinamides than in the chlorophenyloxaziridine **3**. The possibility that the difference in bond lengths between **2a** and **2b** on the one hand, and **3** on the other, might be due to the electronic effects of replacing alkyl substituents on the oxaziridine ring by an aromatic group seems unlikely, since the intervening N–C and N–O bond lengths appear to be unaffected in any systematic manner by the change. It is, nevertheless, noteworthy that in **2a** and **2b**, the nitrogen atom is somewhat less pyramidal (sum of bond angles 294.2 and 292.3°, respectively) than in **3** (sum of angles at N 279.9°). P–N orbital overlap is thus more favoured in **2a** and **2b**, entirely consistent with the bond length variation being due to variations in P–N orbital overlap. Also consistent is the geometry found[8] in the crystal structure of *N*-(diphenylphosphinoyl)aziridine. The conformation about the P–N bond is similar to those in the three oxaziridines **2a**, **2b** and **3**. Thus the O–P–N–C torsion angles are 42.3 and −26.5°, compared with values of 36.7–48.7 and −24.5 to −15.8°, respectively, for the corresponding torsion angles in the oxaziridines. The P–N bond length in the aziridine is 1.672 Å and the sum of angles at nitrogen, 295.9°. Over the four structures (in all of which the nitrogen atom forms part of a three-membered ring) there is, in fact, a moderately strong inverse correlation ($r = -0.89$) between P–N bond length and the nitrogen bond angle sum.

The bond angle variation at nitrogen may be rationalised by considering steric interactions between the P=O moiety and certain neighbouring groups. Thus in **2a** and **2b** there is some steric interaction with the *cis* methyl group, P···C(14), 3.26 Å in both cases, and the P–N–C(13) angles, the magnitudes of which determine the P···C(14) distances, are some 8–10° greater in **2a** and **2b** than in **3**, where the *cis* position of the oxaziridine carbon is occupied by hydrogen (see Table 5). In the aziridine all the ring substituents are hydrogen atoms, so that, as in oxaziridine **3**, the interaction between the phosphinoyl moiety and the ring substituents is less important, and the corresponding P–N–C angle is relatively small at 118.2°. Here, however, the oxygen (van der Waals radius 1.50 Å) of the oxaziridine ring is replaced by carbon (van der Waals radius 1.65 Å), thus increasing the non-bonded repulsive interaction with phosphorus. Accordingly, the P–N–C angle of the aziridine, 117.9°, is 6–10° larger than the corresponding P–N–O angles in oxaziridines **2a**, **2b** and **3**. The variation in the endocyclic angle at nitrogen is much smaller, only 2.9° over the four molecules. A relatively minor steric interaction between the phosphinoyl oxygen atom of **2a** and **2b** and the *cis* methyl group [O(1)···C(14) distances 3.15 and 3.13 Å] might account for the slightly greater O–P–N angles in these molecules than in **3** and the aziridine.

The P–N bond length variation can thus be attributed to variations in certain steric interactions involving the phosphorus moiety. The greater the steric crowding, the greater will be the bond angle sum at nitrogen, thus facilitating P–N orbital overlap and leading to shorter P–N bonds. Shortening of the P–N bond would, of course, tend to counteract the steric relief brought about by the increase in bond angles at nitrogen. However, the bond length variation amounts to no more than 0.09 Å, quite small compared with the effect of the angular variations at nitrogen on the position of the phosphorus atom relative to the crowding groups.

In all four molecules the probable orientation of the lone pair of electrons on nitrogen is approximately antiperiplanar to the polar P–O bond, consistent with an n–σ* bonding model[1] for the P–N bond.

NMR Spectra.—Both oxaziridines gave ^{31}P NMR signals at δ 28.7 (**2a**) and 28.2 (**2b**) downfield from external 85% phosphoric acid. Diphenylphosphinic amides, $Ph_2P(O)NR_2$, give ^{31}P NMR signals in the range δ 15–30.[9]

^{1}H NMR spectra recorded at ambient temperature in deuteriochloroform solution displayed broadened α-methyl or methylene signals, typical of exchange broadening effects. On cooling to −45 °C well resolved alkyl signals were observed for both oxaziridines. At this temperature compound **2a** showed two methyl signals at δ 1.65 and 2.04, the former being resolved into a doublet ($J_{P,H}$ 1.7 Hz) due to a four-bond coupling to phosphorus. Clearly inversion at nitrogen is slow on the NMR time-scale at −45 °C.

The ^{1}H NMR spectrum of **2b** at −55 °C in deuteriochloroform solution showed two sets of alkyl signals in the integrated ratio 78.22, assigned to the two diastereoisomeric invertomers of this unsymmetrically 3-substituted oxaziridine. The upfield ring-methyl signal of the minor invertomer at δ 1.63 was a doublet ($^4J_{P,H}$ 1.7 Hz) whereas the corresponding signal of the major invertomer at δ 1.99 was a singlet. The X-ray crystallographic analysis and the ^{13}C NMR data (see below) establish that the major invertomer of **2b** has the ring methyl group *cis* to the diphenylphosphinoyl moiety, hence the upfield ring-methyl signal in **2b**, (and by analogy in **2a**) which shows the four-bond coupling to phosphorus, is located *trans* to the diphenylphosphinoyl moiety. The geminal methylene protons of the prochiral ethyl group in **2b** are diastereotopic[10] and exhibit in the major invertomer at 270 MHz an AMX_3 system with δ_A 1.74, δ_M 1.92, δ_X 0.92, $^2J_{A,M}$ 14.5 Hz, $^3J_{A,X}$ 7.4 Hz and $^3J_{M,X}$ 7.4 Hz (first-order analysis). An additional small splitting of 2.7 Hz observable on the downfield H_M multiplet of the major invertomer is ascribed to a four-bond *trans* coupling to phosphorus. Since only one of the diastereotopic geminal methylene protons of the major (*trans*) invertomer shows coupling to phosphorus, this coupling must be dependent on the preferred conformation about the CH_2–ring bond. The phosphorus-coupled methylene proton may be the one which in solution has an approximately W-shaped H–C–C–N–P relationship. The methylene protons of the minor invertomer were accidentally isochronous giving a quartet at δ 2.39 ($^3J_{H,H}$ 7.7 Hz) at −55 °C with no evidence of coupling to phosphorus.

The ^{13}C NMR spectra of **2a** and **2b** showed one set of exchange-broadened alkyl resonances at ambient temperature in deuteriochloroform. The oxaziridine ring carbon gave a characteristic doublet signal at δ 87.0 (**2a**) or a δ 89.1 (**2b**) due to coupling with phosphorus ($^2J_{P,C}$ 6.6 Hz).[1] At −40 °C, where nitrogen inversion is slow on the NMR time-scale, two equally intense methyl signals were observed for **2a** at δ 20.5 and δ 26.2. At this temperature compound **2b** showed signals for two invertomers with intensity ratios of *ca.* 78:22 (as in the ^1H NMR spectra). The principal chemical shifts at −40 °C are as follows: Major invertomer (*trans*): δ 8.6 (CH_2*Me*), 18.3 (Me, ring), 32.1 (CH_2), 90.0 (C–O). Minor invertomer (*cis*): δ 10.6 (CH_2*Me*), 22.7 (Me, ring), 27.3 (CH_2), 91.7 (C–O).

It is known from ^{13}C NMR studies on other types of oxaziridine that 3-alkyl α-carbons located *trans* to the nitrogen lone pair electrons experience a substantial upfield shift from a similar carbon located *cis* to the lone pair.[11] On this basis, the major invertomer with the upfield α-methyl signal and the downfield α-CH_2 signal has the *seq.-trans* configuration as indicated by the X-ray crystallographic study.

The inversion rates were determined by computer assisted analysis of the lineshapes of the α-methyl (and α-methylene in **2b**) ^{13}C resonances at the coalescence temperature. **2a**: k = 750 s^{-1} at 18.5 °C, $\Delta G^{\ddagger}$ = 13.2 kcal (55.2 kJ) mol^{-1}; **2b**: $k_{t\rightarrow c}$ = 252 s^{-1} at 3.5 °C, $\Delta G^{\ddagger}_{t\rightarrow c}$ = 13.1 kcal (54.8 kJ) mol^{-1}; $k_{c\rightarrow t}$ = 681 s^{-1} at 3.5 °C, $\Delta G^{\ddagger}_{c\rightarrow t}$ = 12.6 kcal (52.7 kJ) mol^{-1}.

Steric interactions between the ethyl group and the diphenylphosphinoyl moiety accelerate the *cis* ⟶ *trans* interconversion relative to the reverse process, and destabilise the *cis* isomer.

The barriers to pyramidal nitrogen inversion in these *N*-phosphinoyloxaziridines are considerably lower than those reported previously for *N*-alkyloxaziridines ($\Delta G^{\ddagger}$ 25–34 kcal mol^{-1}) or *N*-sulphonyloxaziridines ($\Delta G^{\ddagger}$ 20–21 kcal mol^{-1}). The phosphinoyl group is highly efficient at facilitating inversion of a directly bonded trivalent nitrogen. This can be attributed to N–P π-bonding of the n–σ*, and possibly p_π–d_π, type, which lowers the energy of the trigonal transition state for nitrogen inversion. Indeed, the inversion barriers in phosphinic amides are normally far too low to measure by dynamic NMR methods, and it is only the remarkable barrier enhancing effect of the oxaziridine moiety that renders a measurable barrier in **2a** and **2b**. Previously described *N*-phosphinoyloxaziridines derived from aromatic aldehydes[1] do not exhibit dynamic NMR effects, because they exist essentially exclusively in the much less hindered *seq.-trans* configuration.

Experimental

All synthetic work involving those phosphorus compounds was performed in a good fume hood, wearing protective gloves. ^1H and ^{13}C NMR spectra were recorded at 270 or 67.8 MHz on a JEOL GX-270 spectrometer and ^{31}P NMR spectra were obtained at 22.5 MHz on a JEOL FX-90Q instrument. Probe temperatures were calibrated using a standard methanol sample.[12] The ^{13}C NMR lineshapes near coalescence were analysed on the University of Birmingham Honeywell computer using the iterative dynamic NMR programme INMR.[13] All coupling constants are in Hz.

Syntheses.—2-Diphenylphosphinoyl-3,3-dimethyloxaziridine (**2a**). Under a stream of dry nitrogen, in a flask equipped with an alcohol thermometer, freshly distilled chlorodiphenylphosphine (1.26 g, 5.7 mmol) in hexane–dichloromethane (2:1) (15 cm^3) was rapidly added to a stirred solution of dry acetoxime (0.42 g, 5.7 mmol) and triethylamine (0.58 g, 5.7 mmol) in the same solvent (75 cm^3) cooled to *ca.* −50 °C. A copious amount of white precipitate was formed and a temperature rise of *ca.* 10 °C was observed. Stirring was maintained and the reaction mixture was allowed to return to room temperature (*ca.* 1 h). The reaction mixture was filtered under nitrogen into an ice-cooled rapidly stirred suspension of 2:1 potassium fluoride/MCPBA complex (prepared from finely powdered activated potassium fluoride [1.32 g, 22.8 mmol] and MCPBA [1.90 g, 11.4 mmol]) in dichloromethane (40 cm^3) in a flask purged with dry nitrogen.[7] Stirring was maintained under a nitrogen atmosphere at *ca.* 5 °C for 2 h and the solid complex was removed by suction filtration through Celite. Rotary evaporation of the filtrate gave the crude oxaziridine as a pale green solid which on washing with hexane–diethyl ether (2:1) gave a colourless powder (1.26 g). This crude product was dissolved in diethyl ether and filtered through a 1 cm silica gel bed to afford, after rotary evaporation of the solvent, the oxaziridine as a colourless powder (1.00 g, 63%). Recrystallization of this material from hexane–chloroform afforded the pure oxaziridine as colourless crystals, m.p. 148–151 °C (decomp.). (Found: C, 65.6; H, 5.7; N, 5.0. $C_{15}H_{16}NO_2P$ requires C, 65.93; H, 5.90; N, 5.13%). $\delta_H(CDCl_3)$ 1.77 (6 H, broad, 3-CH_3), 7.27–7.70 (6 H, m, *m* + *p*-Ph), 7.70–8.20 (4 H, m, *o*-Ph). $\delta_C(CDCl_3)$ 22.4 (broad, 3-CH_3), 87.0 (d, $^2J_{C,P}$ 6.7, C–O), 127.7–133.6 (aromatic). $\delta_P(CDCl_3)$ 28.7 [N–*P*(O)Ph_2].

2-Diphenylphosphinoyl-3-ethyl-3-methyloxaziridine (**2b**). Following the above procedure, butanone oxime (0.50 g, 5.7 mmol) gave the crude oxaziridine as a colourless powder (1.05 g 64%). Recrystallization of this material from hexane–chloroform afforded the pure oxaziridine as colourless crystals, m.p. 132–136 °C (decomp.) (Found: C, 67.1; H, 6.4; N, 4.8. $C_{16}H_{18}NO_2P$ requires C, 66.89; H, 6.31; N, 4.88%). $\delta_H(CDCl_3$, 270 MHz) 0.92 (3 H, t, *J* 7.5, CH_3CH_2), 1.68–2.30 (5 H, broad, CH_3CH_2 and 3-CH_3), 7.45–7.60 (6 H, m, *m* + *p*-Ph), 7.91–8.10 (4 H, m, *o*-Ph). $\delta_C(CDCl_3)$ 8.7 (CH_3CH_2) 19.6 (broad, 3-CH_3), 30.9 (broad, CH_3CH_2), 89.1 (d, $^2J_{C,P}$ 6.6, C–O), 128.3–134.2 (aromatic). $\delta_P(CDCl_3)$ 28.2 (N–*P*(O)Ph_2).

X-Ray Structure Determinations.—Cell dimensions and reflection intensities were measured with graphite-monochromated Mo-Kα radiation on an Enraf–Nonius CAD-4 diffractometer operating in the ω-2θ scan mode. Three standard reflections were monitored at regular intervals to check the stability of the system. Lorentz and polarization corrections were applied; no corrections were made for absorption or extinction effects. Details of crystal and experimental parameters are given in Table 6.

Both structures were solved[14] by direct methods and refined[15] by least squares. The non-hydrogen atoms were

Table 6 Crystal and experimental parameters

	2a	**2b**
Molecular formula	$C_{15}H_{16}NO_2P$	$C_{16}H_{18}NO_2P$
M	273.3	287.3
Crystal size (mm)	0.5 × 0.4 × 0.2	0.7 × 0.7 × 0.4
a (Å)	8.554(3)	8.519(3)
b (Å)	12.007(4)	12.409(5)
c (Å)	14.310(6)	14.772(7)
U (Å^3)	1469.7	1561.6
Space group	$P2_12_12_1$	$P2_12_12_1$
Z	4	4
F(000)	576	608
D_c(g cm^{-3})	1.24	1.22
μ (mm^{-1})	0.18	0.17
Data collection range, θ (°)	2–27.5	2–25
Unique data measured	3359	1971
Significant data [$I > 2.5\sigma(I)$]	2198	1407
Least-squares weights *K* in $w = [\sigma^2(F) + KF^2]^{-1}$	0.0007	0.0035
Final *R*	0.051	0.052
Final *wR*	0.063	0.076

refined with anisotropic thermal parameters; H atoms were placed in calculated postions and allowed to 'ride' on their respective carbon atoms. The carbon–carbon bond length of the ethyl group, C(15)–C(16), refined initially to an abnormally low value, and in further refinements its length was constrained to 1.50(1) Å.

The ethylmethyloxaziridine **2b** has the ethyl group *trans* to the diphenylphosphinoyl moiety (see Fig. 1), and refinement had apparently converged satisfactorily at $R = 0.058$, $wR = 0.082$. However, closer inspection of a difference map showed the presence of a small residual peak of 0.66 eÅ^{-3} at a distance of 1.24 Å from the methyl carbon atom [C(14)]. This distance was too great for this peak to be a hydrogen atom and it was considered to indicate the presence of a carbon atom corresponding to the isomer with the ethyl group *cis* to the diphenylphosphinoyl moiety. This peak was designated C(16′) and its coordinates, isotropic thermal parameter and site occupation factor included in the least-squares refinement [site occupation of terminal carbon atom of original ethyl group C(16) was taken as 1 − that of C(16′)]. The occupation factor of C(16′) converged to a value of 0.29(3). The X-ray results thus indicate the presence in the solid state of *ca.* 29% of the nitrogen invertomer with the ethyl group *cis* to the phosphinoyl group, the two forms of the molecule packing in such a way that the positions of all the other atoms apparently coincide and the disorder manifests itself only with respect to the terminal carbon atom of the ethyl group. Thermal parameters are, however, considerably higher than in the dimethyloxaziridine **2a** (cf. U_{eq} values in Tables 1 and 2), which may be an indication of not quite perfect coincidence of the atoms in the packing arrangement.

The refinements were terminated when all calculated shift/error ratios were less than 0.05. The residual electron densities in final difference maps were within the ranges ±0.35 and ±0.45 eÅ^{-3} for the ethylmethyl and dimethyl structures, respectively. In each case the inverse structures gave virtually identical values of R and wR.

On completion of the analyses it became apparent that the crystals of the two compounds were nearly isostructural; the refined atomic parameters of the dimethyloxaziridine **2a** could be obtained simply by using the parameters of the corresponding atoms of the ethylmethyl derivative **2b** as initial values in least-squares refinement.

Complex neutral-atom scattering factors were employed. Computations were carried out on the University of Birmingham Honeywell and IBM 3090 computers. Molecular diagrams were prepared with PLUTO[16] at the Manchester Computer Centre.

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