

Photochemistry of Azole *N*-Oxides. Facile Photoisomerisation
of 2*H*-Imidazole *N*-Oxides to 1,3-Diaza-6-oxabicyclo[3.1.0]hex-3-enes
and Synthesis of a 1,3-Diaza-4,7-dioxatricyclo[4.1.0.^{1,6,3,5}0]heptane

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Ultraviolet irradiation of a series of 2*H*-imidazole *N*-oxides **2** has been shown to effect a clean isomerisation to derivatives of the new ring system, 1,3-diaza-6-oxabicyclo[3.1.0]hex-3-ene, **7**. Epoxidation of a representative **7** has given access to the hitherto inaccessible *trans*-fused 1,3-diaza-4,7-dioxatricyclo[4.1.0.^{1,6,3,5}0]heptane ring system **9**.

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Introduction.

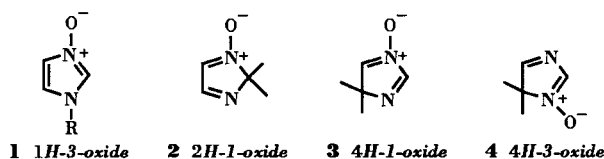
In the photochemistry of the few reported azole *N*-oxides, the intermediacy of fused oxaziridines as primary photoproducts is assumed [1-7] in precisely the same manner it is in the well established photochemistry of aromatic azine *N*-oxides [8,9]. Despite the fact that no such intermediates from either class have been isolated this assumption is not unreasonable given the allowedness of the 4π electrocyclicisation process.

The feature common to the incipient bicyclic oxaziridines derived from both classes of *N*-oxide is the presence on an "N-vinyl" residue, whether it is part of a contiguous aromatic ring or not. In fact, to our knowledge there are no known examples of acyclic oxaziridines bearing unsaturation α to the ring nitrogen atom.

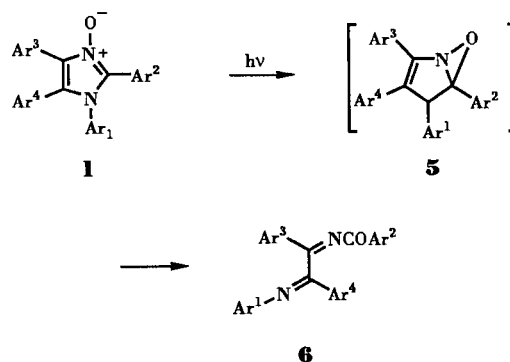
On the other hand, the non-aromatic azole *N*-oxides so far reported (3*H*-indole *N*-oxide [10], 3*H*-isoindole *N*-oxide [11], 2*H*-benzimidazole *N,N*-dioxide [12], 4*H*-pyrazole *N*(2)-oxide [13] and 2*H*-pyrrole *N*-oxide [14] all afford stable oxaziridines that do not contain this linkage.

As part of a study designed to investigate the photochemistry of azole *N*-oxides and to evaluate the influence of unsaturation α to the putative oxaziridine, we have undertaken a study of the imidazole *N*-oxide ring system. Of the four members of this system **1-4** we have so far shown that the *N*-oxide **1** isomerises cleanly, more than likely *via* the fused bicycle **5**, to the *Z,Z*-benzil diimine system **6** [6,7]. In continuation of these studies we report here our findings on the photochemical behaviour of representatives of the next member of the series, namely, the non-aromatic 2*H*-imidazole *N*(1)-oxide system **2**.

Scheme 2



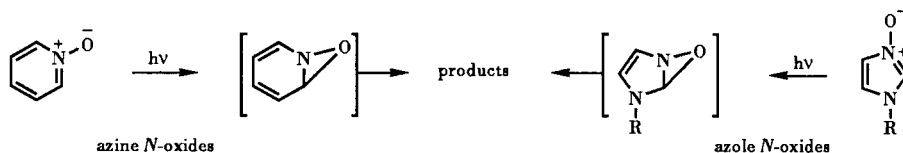
Scheme 3



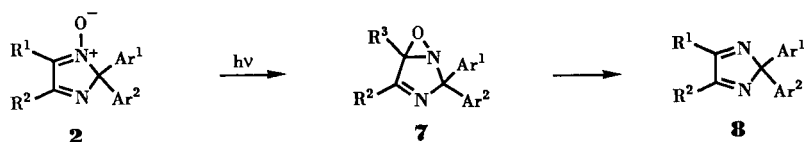
Results and Discussion.

Derivatives of the 2*H*-imidazole *N*-oxide system **2a-k** were synthesised by the acid-catalysed condensation of diarylmethyleneamines [15] with various α-hydroxyiminoketones as described by Clark *et al* [16]. Brief exposure (0.5-1.5 hour) of degassed benzene solutions of each of the *N*-oxides to pyrex-filtered ultraviolet light caused a rapid consumption of *N*-oxide with the concomitant appearance of a single product. Isolation of the products - members of the hitherto unknown 1,3-diaza-6-oxabicyclo[3.1.0]hex-3-

Scheme 1



Scheme 4



- a**, $R^1 = H, R^2 = Me, Ar^1 = Ar^2 = Ph$
b, $R^1 = H, R^2 = Ph, Ar^1 = Ar^2 = Ph$
c, $R^1 = R^2 = Me, Ar^1 = Ar^2 = Ph$
d, $R^1 = R^2 = Me, Ar^1 = p\text{-anisyl}, Ar^2 = Ph$
e, $R^1 = COMe, R^2 = Me, Ar^1 = Ar^2 = Ph$
f, $R^1 = R^2 = Me, Ar^1 = Ph, Ar^2 = p\text{-tolyl}$
g, $R^1 = Me, R^2 = Ph, Ar^1 = Ar^2 = Ph$
h, $R^1 = Ph, R^2 = Me, Ar^1 = Ar^2 = Ph$
i, $R^1 = R^2 = Ar^1 = Ar^2 = Ph$
j, $R^1 = R^2 = Ar^1 = Ph, Ar^2 = p\text{-tolyl}$
k, $R^1 = R^2 = Ar^1 = Ph, Ar^2 = p\text{-anisyl}$

ene heterocyclic system **7** - was achieved either by chromatography or by trituration of the concentrated photolysate solution with cold ether.

Combustion analyses and spectral data recorded for each of the colourless, crystalline photoproducts confirmed the isomeric nature of each with respect to its *N*-oxide precursor and that the isomerisation was not deep-seated. Active oxygen assays performed by iodometric titration [17] were consistent with expectation of the bicyclic oxaziridine ring system; under identical conditions the corresponding *N*-oxides were inert. These assays were found to be difficultly reproducible but were consistently $\geq 70\%$. Treatment of the oxaziridine with triethylphosphite was shown, as expected, to give the corresponding *2H*-imidazole **8**. Under similar conditions the *N*-oxides were much slower to react but did give the same deoxygenation product.

Confirmation of this simple ring closure to the diazoxabicyclo[3.1.0]hex-3-ene system was deduced from ^{13}C - and 1H -nmr data. Consistent with the change in hybridisation ($sp^2 \rightarrow sp^3$) the C5 resonance in the *N*-oxide (126-138 ppm) demonstrated an upfield shift of *ca* 45 ppm to 81-92 ppm in the oxaziridine. Similarly the C2 resonance showed an upfield shift of 7-8 ppm from 106-109 ppm in the *N*-oxide to 99-102 ppm in **7**. In like manner the C5 proton resonances in **2a,b** showed the anticipated shifts from the aromatic region to 5.2 and 5.5 δ , respectively.

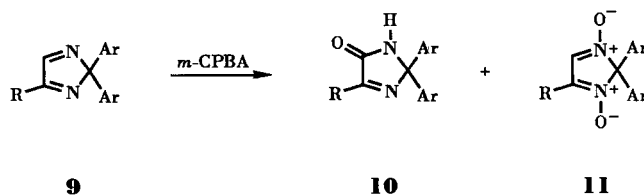
Epoxidation of the remaining imine moiety in a representative oxaziridine **7c** under standard conditions gave a single oxygenated product (mp 187-188 $^\circ$) which was shown by the spectral simplicity of the ^{13}C -nmr spectrum to be a bisoxaziridine, a member of the new 1,3-diaza-4,7-dioxatricyclo[4.1.0. 1,6,3,5 .0]heptane ring system **9**. In particular, only a single methyl signal was observed at 13.9 ppm (1H -nmr 1.76 δ) in addition to the two sp^3 quaternary car-

Scheme 5



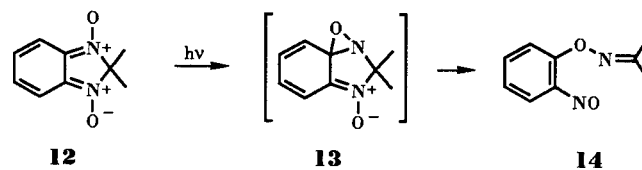
bon resonances at 91.9 and 93.4 ppm attributable to C5/C6 and C2, respectively. This result is to be contrasted with that reported by Clark *et al* [16] who demonstrated that epoxidation of the *2H*-imidazole system (*e.g.* **9**) does not proffer access to the bis oxaziridine; instead the corresponding imidazolones **10** ($R = Me, Ar = Ph$) are isolated as the major products together with traces of the bis *N*-oxide **11**. Furthermore, an account of the photochem-

Scheme 6



istry of a bis *N*-oxide (*2H*-benzimidazole *N,N*-dioxide **12**) suggests that access to the tricyclic bis oxaziridine ring system is unlikely to be gained by a photoinduced isomerisation [12]. Here, a deep-seated rearrangement through an intermediate oxaziridine **13** to give the *O*-(2-nitrosophenyl)hydroxylamine **14** was postulated.

Scheme 7



The final assignment of configuration to this tricyclic species was achieved by X-ray crystallography and shown (Figure 1) to be all-*trans* fused. Crystal data: $C_{17}H_{16}N_2O_2$; M_r 283.4, triclinic, space group $P\bar{1}$, a 8.081 (4), b 8.854 (5), c 12.23 (3) Å; α 94.91 (16)°, β 110.29 (16)°, γ 116.91 (38)°. The conventional residuals R and R_w were 0.097 and 0.112 for 641 reflections (see Experimental).

Figure 1. X-ray crystal structure of **9**.

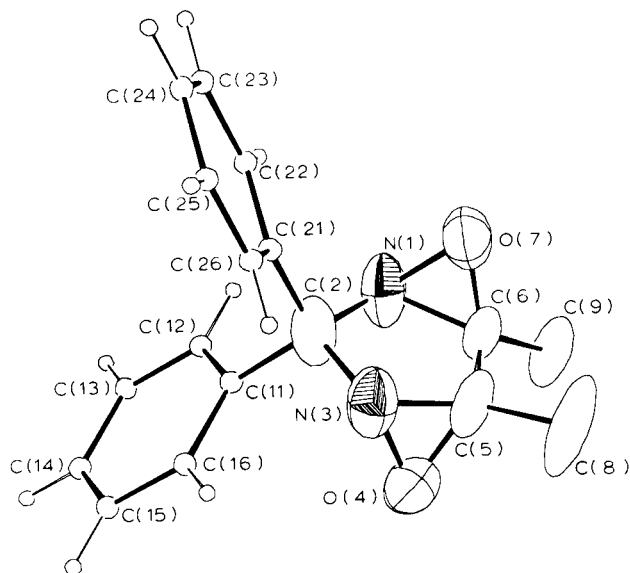


Figure 1 is a computer-generated diagram [23] illustrating the independent molecule and the atom labelling scheme with 50% probability ellipsoids except for the phenyl rings which have arbitrary radii for clarity.

Certain features of the crystal structure determination are worthy of comment. The structure consists of discrete *trans* units with atom numbering as shown in Figure 1. Parameters are presented in Table 1 and selected bond lengths in Table 2. The discrete units occur with orientational disorder in the crystal, the major being that depicted in Figure 1 and the minor being that obtained by an approximate two-fold rotation about an axis through C2 and the midpoint of C5-C6. Crystal packing contacts ensure that the two conformers are not identical through the operation of the crystallographic inversion centre; because of the similarity, only the atoms O(4), C(8), C(9), and O(7) were able to be refined in the two conformers. In the crystal studied, the refinement indicated a ratio of *ca.* 70, major:30, minor. Within the lower structural resolution, bond lengths and angles are normal [23].

EXPERIMENTAL

Microanalyses were performed by Professor A. D. Campbell and Associates, University of Otago, and high resolution mass spectra were recorded at 70 eV on an A.E.I. MS30 spectrometer. Infrared spectra were recorded as mulls in paraffin on a Perkin-Elmer 397 spectrophotometer and ultraviolet spectra with a Beckman Acta CV spectrophotometer. The 1H -nmr spectra were

measured at 60 MHz on Varian EM 360 and FT-80A spectrometers and ^{13}C -nmr spectra on the latter instrument. Preparative ultraviolet irradiations were performed with a water-cooled 450W Hanovia medium pressure immersion arc equipped with interchangeable filters and with a 100W Hanovia PCR 1L medium pressure reactor. Keisegel PF₂₅₄ was employed for preparative tlc and prepared to a thickness of 1.25 mm. Melting points were determined on a Reichert Kofler Hot Stage microscope and are uncorrected.

Syntheses of 2,2-Diaryl-2*H*-imidazole *N*-oxides **2a-k**.

Solutions containing equimolar proportions of the α -hydroxyimino ketone and the diarylmethyleneamine in either toluene or toluene/xylene mixtures (1:1), also containing several drops of methanesulphonic acid, were refluxed for 20 hours. Water formed was removed by azeotropic distillation. After cooling the solution was in each case washed once with saturated sodium bicarbonate solution and once with water before being dried and concentrated. Trituration of the resulting oil with either ether or cold ethanol afforded the 2*H*-imidazole *N*-oxide as a colourless, crystalline solid. The physical properties of compounds **2a-e,i** are in agreement with those previously reported by Clark *et al* [16], however, all attempts to effect the condensation of ethyl 2-hydroxyiminoacetate with diphenylmethyleamine, to give 2,2-diphenyl-5-ethoxycarbonyl-4-methyl-2*H*-imidazole *N*-oxide, were unsuccessful. For the *N*-oxide **2d** a melting point of 124-125° (lit mp 178-179°) was recorded for a sample which furnished a satisfactory combustion analysis. New 2*H*-imidazole *N*-oxides possessing different patterns of ring substitution, which were synthesized by the above method, are detailed as follows.

4,5-Dimethyl-2-phenyl-2-*p*-tolyl-2*H*-imidazole *N*-Oxide (**2f**).

From the reaction of biacetyl monooxime with phenyl *p*-tolylmethyleamine the *N*-oxide **2f** (72%) was obtained. Recrystallisation of the crude product from benzene/ether furnished **2f** as light yellow prisms, mp 153-155°; ir: ν max 1605, 1525, 1510, 1490, 1350, 1305, 1180, 1140, 1115, 925, 915, 825, 800, 760, 700, 660, 630 and 545 cm^{-1} ; uv (acetonitrile): λ max 300 ($\log_{10} \epsilon$ 3.61); 1H -nmr (deuteriochloroform): δ 2.15 (s, CH_3), 2.32 (s, CH_3), 2.39 (s, CH_3), 6.95-7.59 (m, aromatic); ms: m/z 278 (M^+), 221, 180 (100%), 165.

Anal. Calcd. for $C_{18}H_{18}N_2O$: C, 77.7; H, 6.5; N, 10.1. Found: C, 77.9; H, 6.6; N, 10.0.

5-Methyl-2,2,4-triphenyl-2*H*-imidazole *N*-Oxide (**2g**).

From the reaction of *anti*-2-hydroxyimino-propiofenone with diphenylmethyleamine the *N*-oxide **2g** (79%) was isolated. A single recrystallisation from benzene/ether gave **2g** as shiny, colourless prisms, mp 184-185°; ir: ν max 1590, 1565, 1515, 1490, 1450, 1360, 1315, 1190, 1175, 1045, 1030, 935, 775, 770, 755, 705, 695, 675, 660 and 620 cm^{-1} ; uv (acetonitrile): λ max 242 (4.18), 275 (3.94), 308 (3.62); 1H -nmr (deuteriochloroform): δ 2.39 (s, CH_3) 6.96-8.05 (m, aromatic); ms: m/z 326 (M^+), 269, 166, 165 (100%).

Anal. Calcd. for $C_{22}H_{18}N_2O$: C, 80.9; H, 5.6; N, 8.6. Found: C, 80.8; H, 5.5; N, 8.5.

4-Methyl-2,2,5-triphenyl-2*H*-imidazole *N*-Oxide (**2h**).

From the reaction of *anti*-1-hydroxyimino-1-phenylacetone with diphenylmethyleamine the *N*-oxide **2h** was obtained. Recrystallisation from benzene/ether gave **2h** (70%) as off-white needles, mp 177-178°; ir: ν max 1595, 1520, 1485, 1450, 1385, 1375, 1190, 1160, 990, 910, 845, 770, 755, 700, 690, 670, 655 and

650 cm^{-1} ; uv (acetonitrile): λ max 245 (4.27), 320 (3.83); $^1\text{H-nmr}$ (deuteriochloroform): δ 2.58 (s, CH_3), 7.02-8.08 (m, aromatic); ms: m/z 326 (M^+), 296, 207, 166 (100%), 165, 115, 103, 77.

Anal. Calcd. for $\text{C}_{22}\text{H}_{18}\text{N}_2\text{O}$: C, 81.0; H, 5.6; N, 8.6. Found: C, 81.0; H, 5.4; N, 8.6.

2-*p*-Tolyl-2,4,5-triphenyl-2*H*-imidazole *N*-Oxide (**2j**).

From the reaction of α -benzil monooxime with phenyl *p*-tolyl methyleneamine the *N*-oxide **2j** was obtained. Recrystallisation from benzene/ether of ethanol gave **2j** (64%) as colourless prisms, mp 176-177 $^\circ$; ir: ν max 1585, 1555, 1440, 1380, 1175, 1115, 1025, 1005, 930, 780, 760, 750, 725, 705, 695 and 545 cm^{-1} ; uv (acetonitrile): λ max 257 (4.36), 325 (3.77); $^1\text{H-nmr}$ (deuteriochloroform): δ 2.41 (s, CH_3), 7.13-7.93 (m, aromatic); ms: m/z 402 (M^+), 386, 372, 283 (100%), 180, 165, 119, 103, 77.

Anal. Calcd. for $\text{C}_{28}\text{H}_{22}\text{N}_2\text{O}$: C, 83.6; H, 5.5; N, 7.0. Found: C, 83.6; H, 5.4; N, 6.9.

2-*p*-Anisyl-2,4,5-triphenyl-2*H*-imidazole *N*-Oxide (**2k**).

From the reaction of a α -benzil monooxime with *p*-anisyl phenyl methyleneamine the *N*-oxide **2k** (58%) was isolated. A single recrystallisation from ethanol gave **2k** as colourless prisms, mp 156-158 $^\circ$; ir: ν max 1610, 1585, 1560, 1510, 1490, 1480, 1445, 1380, 1255, 1180, 1175, 1035, 830, 780, 750, 700, 690 and 545 cm^{-1} ; uv (acetonitrile): λ max 256 (4.37), 320 (3.82); $^1\text{H-nmr}$ (deuteriochloroform): δ 3.77 (s, OCH_3), 6.78-7.80 (m, aromatic), 6.83 (d, $J = 9.4$ Hz, upper branch of AB quartet due to *p*-anisyl protons); ms: m/z 418 (M^+), 402, 401, 299 (100%), 196, 181, 149.5, 98, 77.

Anal. Calcd. for $\text{C}_{28}\text{H}_{22}\text{N}_2\text{O}_2$: C, 80.4; H, 5.3; N, 6.7. Found: C, 80.2; H, 5.2; N, 6.5.

Preparation and Isolation of Oxaziridines.

The general photochemical procedure described below for the preparation and isolation of 1,3-diaza-2,2-diphenyl-4-methyl-6-oxabicyclo[3.1.0]hex-3-ene (**2a**) was that utilised for the synthesis of all fused oxaziridines.

Photolysis of 2,2-diphenyl-4-methyl-2*H*-imidazole *N*-Oxide (**2a**).

The *N*-oxide (0.8 g) was dissolved in dry, de-aerated benzene (450 ml) and irradiated through pyrex for periods ranging between 0.5-1.5 hours. Evaporation of the benzene under reduced pressure (such that the temperature of the solution remained below 30 $^\circ$) afforded a clear yellow oil to which cold ether (5 ml) was added. Trituration with several drops of *n*-pentane generally furnished a colourless solid which was removed by filtration and recrystallised from ether to give 1,3-diaza-2,2-diphenyl-4-methyl-6-oxabicyclo[3.1.0]hex-3-ene (**7a**) (0.5 g, 64%) as fine colourless needles, mp 117 $^\circ$; ir: ν max 1650, 1490, 1450, 1385, 1230, 1210, 1000, 925, 860, 765, 745, 730, 700, 695, 660, 595 and 525 cm^{-1} ; uv (acetonitrile): λ max 249 (2.80); $^1\text{H-nmr}$ (acetone- d_6): δ 2.40 (s, CH_3), 5.18 (s, oxaziridinyl-H), 7.13-7.67 (m, aromatic); ms: m/z 250 (M^+), 209, 207, 180, 166 (100%), 165, 131, 104.

Anal. Calcd. for $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}$: C, 76.8; H, 5.6; N, 11.2. Found: C, 76.8; H, 5.8; N, 11.3.

1,3-Diaza-6-oxa-2,2,4-triphenylbicyclo[3.1.0]hex-3-ene (**7b**).

This compound was obtained as colourless prisms, mp 138-140 $^\circ$; ir: ν max 1615, 1575, 1490, 1445, 1275, 1230, 1200, 1045, 1020, 975, 910, 860, 780, 760, 750, 705, 695, 630 and 535 cm^{-1} ; uv (acetonitrile): λ max 256 (4.27); $^1\text{H-nmr}$ (deuteriochloroform): δ 5.46 (s, oxaziridinyl-H), 7.07-8.20 (m, aromatic); ms: m/z

312 (M^+), 296, 269, 203, 180, 166, 165 (100%), 104, 77.

Anal. Calcd. for $\text{C}_{21}\text{H}_{16}\text{N}_2\text{O}$: C, 80.8; H, 5.2; N, 9.0. Found: C, 80.7; H, 5.1; N, 9.1.

1,3-Diaza-4,5-dimethyl-2,2-diphenyl-6-oxabicyclo[3.1.0]hex-3-ene (**7c**).

This compound was obtained as colourless prisms, mp 148-150 $^\circ$; ir: ν max 1650, 1490, 1450, 1395, 1325, 1210, 1160, 1000, 950, 920, 835, 770, 750, 705, 675, 665, 625, 605 and 530 cm^{-1} ; uv (acetonitrile): λ max 254 sh (2.84), 259 (2.89), 262 sh (2.84); $^1\text{H-nmr}$ (deuteriochloroform): δ 1.71 (s, oxaziridinyl- CH_3), 2.29 (s, vinylic- CH_3), 7.10-7.69 (m, aromatic); ms: m/z 264 (M^+), 207, 180, 166 (100%), 165, 77.

Anal. Calcd. for $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}$: C, 77.3; H, 6.1; N, 10.6. Found: C, 77.2; H, 6.1; N, 10.8.

2-*p*-Anisyl-1,3-diaza-4,5-dimethyl-6-oxa-2-phenylbicyclo[3.1.0]hex-3-ene (**7d**).

This compound was obtained after preparative tlc as colourless prisms, mp 95-96 $^\circ$; ir: ν max 1650, 1610, 1510, 1465, 1445, 1395, 1325, 1295, 1250, 1205, 1175, 1150, 1105, 1035, 990, 950, 930, 915, 830, 790, 760, 750, 730, 695, 590 and 535 cm^{-1} ; uv (acetonitrile): λ max 270 (3.31), 280 sh (3.25); $^1\text{H-nmr}$ (acetone- d_6): δ 1.68 (s, CH_3), 2.27 (s, CH_3), 3.70 (s, $-\text{OCH}_3$), 6.86-7.73 (m, aromatic); ms: m/z 294 (M^+), 278, 277, 237, 210, 196 (100%), 181, 165, 152, 98, 77.

Anal. Calcd. for $\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_2$: C, 73.5; H, 6.2; N, 9.5. Found: C, 73.6; H, 6.0; N, 9.7.

5-Acetyl-1,3-diaza-2,2-diphenyl-4-methyl-6-oxabicyclo[3.1.0]hex-3-ene (**7e**).

This compound was obtained as massive colourless prisms (83%), mp 109-110 $^\circ$; ir: ν max 1720, 1645, 1490, 1445, 1380, 1365, 1245, 1190, 1185, 1060, 900, 870, 760, 740, 700, 690, 675, 665 and 630 cm^{-1} ; uv (acetonitrile): λ max 260 (2.95); $^1\text{H-nmr}$ (deuteriochloroform): δ 2.21 (s, CH_3), 2.45 (s, COCH_3), 7.03-7.74 (m, aromatic); ms: m/z 292 (M^+), 250, 233, 209, 207, 180 (100%), 166, 165, 104, 77.

Anal. Calcd. for $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_2$: C, 74.0; H, 5.5; N, 9.6. Found: C, 74.1; H, 5.6; N, 9.7.

1,3-Diaza-4,5-dimethyl-6-oxa-2-phenyl-2-*p*-tolylbicyclo[3.1.0]hex-3-ene (**7f**).

This compound was obtained as shiny colourless plates, mp 116-117 $^\circ$; ir: ν max 1650, 1515, 1490, 1450, 1390, 1325, 1205, 1160, 1000, 990, 915, 840, 810, 760, 740, 720, 700, 665 and 530 cm^{-1} ; uv (acetonitrile): λ max 259 (2.96), 264 (2.95), 296 sh (2.09); $^1\text{H-nmr}$ (deuteriochloroform): δ 1.75 (s, CH_3), 2.20 (s, CH_3), 2.33 (s, CH_3), 6.87-7.68 (m, aromatic); ms: m/z (M^+), 237, 221, 194, 180 (100%), 165.

Anal. Calcd. for $\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}$: C, 77.7; H, 6.5; N, 10.1. Found: C, 77.7; H, 6.6; N, 10.1.

1,3-Diaza-5-methyl-6-oxa-2,2,4-triphenylbicyclo[3.1.0]hex-3-ene (**7g**).

This compound was obtained as colourless needles, mp 159-160 $^\circ$; ir: ν max 1625, 1495, 1450, 1390, 1320, 1205, 1070, 1040, 1025, 775, 765, 750, 705, 695, 640, 575 and 535 cm^{-1} ; uv (acetonitrile): λ max 244 (4.23), 312 sh (3.36); $^1\text{H-nmr}$ (deuteriochloroform): δ 1.87 (s, oxaziridinyl- CH_3), 6.98-8.01 (m, aromatic); ms: m/z 326 (M^+), 312, 298, 269 (100%), 180, 166, 165, 118, 104, 103, 77.

Table 1

Atomic Coordinates with Standard Deviations [a]

Atom	X	Y	Z
C(11)	-0.1129(19)	-0.0640(18)	0.7383(9)
C(12)	-0.2261(19)	-0.1565(18)	0.6307(9)
C(13)	-0.4027(19)	-0.3019(18)	0.6189(9)
C(14)	-0.4661(19)	-0.3547(18)	0.7148(9)
C(15)	-0.3529(19)	-0.2622(18)	0.8224(9)
C(16)	-0.1763(19)	-0.1168(18)	0.8342(9)
C(21)	0.0406(15)	0.2537(19)	0.7446(11)
C(22)	-0.0261(15)	0.2791(19)	0.6381(11)
C(23)	-0.0624(15)	0.4179(19)	0.6288(11)
C(24)	-0.0320(15)	0.5312(19)	0.7260(11)
C(25)	0.0348(15)	0.5057(19)	0.8324(11)
C(26)	0.0711(15)	0.3669(19)	0.8417(11)
N(1)	0.1561(15)	0.0681(19)	0.6508(11)
N(3)	0.2131(18)	0.1307(21)	0.8613(12)
C(2)	0.0738(20)	0.0987(22)	0.7500(13)
C(5)	0.3704(23)	0.1208(30)	0.8335(17)
C(6)	0.3476(20)	0.0930(27)	0.7083(17)
O(7) [b]	0.3454(18)	0.2370(21)	0.6664(13)
O(4) [b]	0.2423(23)	-0.0255(22)	0.8712(13)
C(8) [b]	0.5805(30)	0.2312(42)	0.9147(21)
C(9) [b]	0.4309(41)	-0.0039(47)	0.6548(27)
O(7') [c]	0.1670(48)	-0.0958(50)	0.6637(30)
O(4') [c]	0.3801(52)	0.2846(54)	0.8555(31)
C(8') [c]	0.4649(81)	0.0386(82)	0.9021(50)
C(9') [c]	0.5039(88)	0.1726(85)	0.6406(50)
H(12)	-0.181	-0.119	0.562
H(13)	-0.484	-0.368	0.542
H(14)	-0.593	-0.459	0.706
H(15)	-0.398	-0.300	0.891
H(16)	-0.095	-0.051	0.911
H(22)	-0.048	0.198	0.568
H(23)	-0.110	0.436	0.552
H(24)	-0.058	0.631	0.719
H(25)	0.056	0.587	0.902
H(26)	0.119	0.349	0.918
H(91) [b]	0.573(24)	0.061(24)	0.688(17)
H(92) [b]	0.427(26)	-0.103(25)	0.701(17)
H(93) [b]	0.478(40)	0.074(33)	0.624(22)

[a] The value in parentheses following any parameter is the estimated standard deviation in the least significant quoted digit(s), as derived from the appropriate least squares inversion matrix. [b] Occupancy refined to 0.713(16). [c] Occupancy refined to 1.0 - b (see Experimental).

Anal. Calcd. for $C_{22}H_{18}N_2O$: C, 80.2; H, 5.6; N, 8.6. Found: C, 81.2; H, 5.6; N, 8.7.

1,3-Diaza-4-methyl-6-oxa-2,2,5-triphenylbicyclo[3.1.0]hex-3-ene (7h).

This compound was obtained after preparative tlc (20% ether/hexane) as colourless needles (72%), mp 114-115°C; ir: ν max 1645, 1490, 1450, 1380, 1365, 1290, 1205, 1185, 1170, 1050, 1030, 1010, 975, 900, 780, 760, 750, 740, 700, 690 and 650 cm^{-1} ; uv (acetonitrile): λ max 263 (4.18); 1H -nmr (deuteriochloroform): δ 2.17 (s, CH_3), 7.14-7.86 (m, aromatic); ms: m/z 326 (M^+), 310, 309,

Table 2(a)

Interatomic Distances (Å) [a]

N(1)-C(2)	1.54(2)	N(1)-C(6)	1.49(2)
N(1)-O(7)	1.55(2)	N(1)-O(7')	1.51(4)
C(2)-N(3)	1.52(2)	C(2)-C(11)	1.51(2)
C(2)-C(21)	1.52(3)	N(3)-C(5)	1.41(2)
N(3)-O(4)	1.52(2)	N(3)-O(4')	1.44(4)
C(5)-C(6)	1.49(2)	C(5)-O(4)	1.42(2)
C(5)-O(4')	1.42(4)	C(5)-C(8)	1.60(3)
C(5)-C(8')	1.48(6)	C(6)-O(7)	1.42(2)
C(6)-C(9)	1.48(3)	C(6)-O(7')	1.60(4)
C(6)-C(9')	1.56(7)	C(9)-H(91)	1.0(2)
C(9)-H(92)	1.1(2)	C(9)-H(93)	0.8(3)

Distances between atoms of different conformers (e.g. C(9)-C(9')) have been omitted for clarity.

Table 2(b)

Selected Bond Angles (degrees)

C(21)-C(2)-C(11)	110.8(10)	N(3)-C(2)-C(11)	110.6(13)
N(3)-C(2)-C(21)	109.0(12)	N(1)-C(2)-C(11)	106.2(11)
N(1)-C(2)-C(21)	110.6(14)	N(1)-C(2)-N(3)	109.6(10)
N(3)-C(5)-C(6)	111.2(14)	N(1)-C(6)-C(5)	109.3(13)
C(2)-C(11)-C(12)	119.7(7)	C(2)-C(21)-C(26)	122.1(8)
C(2)-N(3)-C(5)	106.3(12)	C(2)-N(1)-C(6)	103.4(12)
O(4)-N(3)-C(2)	110.1(13)	O(4)-N(3)-C(2)	102.4(20)
O(7)-N(1)-C(2)	104.2(12)	O(7)-N(1)-C(2)	103.9(18)
O(4)-N(3)-C(5)	58.0(11)	O(4)-N(3)-C(5)	59.6(16)
O(7)-N(1)-C(6)	55.8(9)	O(7)-N(1)-C(6)	64.6(16)
O(4)-C(5)-N(3)	64.7(11)	O(4)-C(5)-N(3)	61.2(16)
O(7)-C(6)-N(1)	64.1(11)	O(7)-C(6)-N(1)	58.5(15)
O(4)-C(5)-C(6)	113.5(17)	O(4)-C(5)-C(6)	101.7(25)
O(7)-C(6)-C(5)	109.6(18)	O(7)-C(6)-C(5)	103.7(19)
O(7)-C(6)-C(9)	120.6(19)	O(7)-C(6)-C(9')	121.9(29)
C(8)-C(5)-C(6)	119.0(17)	C(8)-C(5)-C(6)	118.7(26)
C(9)-C(6)-C(5)	120.6(19)	C(9)-C(6)-C(5)	128.5(28)
C(8)-C(5)-N(3)	120.8(16)	C(8)-C(5)-N(3)	119.8(28)
C(9)-C(6)-N(1)	119.5(19)	C(9)-C(6)-N(1)	114.1(29)
O(4)-C(5)-C(8)	116.0(2)	O(4)-C(5)-C(8')	131.2(30)
C(6)-O(7)-N(1)	60.0(10)	C(6)-O(7)-N(1)	56.9(16)
C(5)-O(4)-N(3)	57.3(10)	C(5)-O(4)-N(3)	59.2(18)

296, 269, 207, 166 (100%), 165, 105, 77.

Anal. Calcd. for $C_{22}H_{18}N_2O$: C, 81.0; H, 5.6; N, 8.6. Found: C, 81.1; H, 5.5; N, 8.6.

1,3-Diaza-6-oxa-2,2,4,5-tetraphenylbicyclo[3.1.0]hex-3-ene (7i).

This compound was obtained after preparative tlc as large colourless prisms, mp 114-116°C; ir: ν max 1605, 1570, 1490, 1445, 1350, 1235, 1200, 1025, 1000, 995, 960, 780, 770, 760, 750, 695, 630, 595 and 550 cm^{-1} ; uv (acetonitrile): λ max 255 (4.20); 1H -nmr (deuteriochloroform): δ 6.97-7.95 (m, aromatic); ms: m/z 388 (M^+), 372, 360, 285, 269, 180, 166, 165, 105, 103, 77 (100%); m^+ 186.9 (388 - 269).

Anal. Calcd. for $C_{27}H_{20}N_2O$: C, 83.5; H, 5.2; N, 7.2. Found: C, 83.6; H, 5.3; N, 7.1.

1,3-Diaza-6-oxa-2-*p*-tolyl-2,4,5-triphenylbicyclo[3.1.0]hex-3-ene (7j).

This compound was isolated after preparative tlc (68%) as

Table 2(c)
Selected Torsion Angles (degrees)

C(5)-N(3)-C(2)-N(1)	0.0(7)	C(5)-N(3)-C(2)-C(11)	116.8(13)
O(4)-N(3)-C(2)-N(1)	-61.2(13)	C(5)-N(3)-C(2)-C(21)	-121.2(13)
O(4')-N(3)-C(2)-N(1)	61.6(13)	O(4)-N(3)-C(2)-C(11)	55.6(13)
C(4)-N(3)-C(2)-C(21)	177.6(13)	O(4')-N(3)-C(2)-C(21)	-59.6(15)
C(6)-N(1)-C(2)-C(11)	-122.5(13)	C(6)-N(1)-C(2)-C(21)	117.2(11)
O(7)-N(1)-C(2)-C(11)	179.9(10)	O(7)-N(1)-C(2)-C(21)	59.6(8)
C(22)-C(21)-C(2)-N(3)	158.2(13)	C(12)-C(11)-C(2)-N(3)	-153.2(13)
C(22)-C(21)-C(2)-N(1)	37.6(6)	C(12)-C(11)-C(2)-N(1)	-34.4(7)
C(2)-N(3)-C(5)-C(6)	3.1(7)	N(3)-C(5)-C(6)-N(1)	-5.2(6)
C(5)-C(6)-N(1)-C(2)	4.8(7)	C(6)-N(2)-C(2)-N(3)	-3.0(6)
C(2)-N(3)-C(5)-C(8)	149.7(15)	O(4)-C(5)-C(6)-N(1)	-65.5(13)
C(2)-N(3)-C(5)-C(8')	-141.5(15)	O(4')-C(5)-C(6)-N(1)	-68.6(15)
O(7)-N(1)-C(2)-N(3)	-60.6(8)	C(2)-N(3)-O(4)-C(5)	97.2(13)
O(7')-N(1)-C(2)-N(3)	63.8(12)	C(2)-N(1)-C(6)-C(9)	149.6(15)
N(1)-O(7)-C(6)-C(9)	110.4(18)	C(2)-N(1)-C(6)-C(9')	-146.8(22)
N(1)-O(7')-C(6)-C(9')	-100.5(22)	N(3)-C(5)-C(6)-O(7)	63.4(10)
O(4)-C(5)-C(6)-C(9)	-78.9(18)	N(3)-C(5)-C(6)-O(7')	-66.2(13)
O(4')-C(5)-C(6)-C(9')	77.7(23)	O(7)-C(6)-C(5)-C(8)	-83.9(13)
C(8)-C(5)-C(6)-C(9)	63.1(14)	O(7')-C(6)-C(5)-C(8')	78.9(22)
C(8')-C(5)-C(6)-C(9')	-73.8(26)	C(2)-N(1)-O(7)-C(6)	96.7(11)
N(3)-C(5)-C(6)-C(9)	-149.6(18)	N(1)-C(6)-C(5)-C(8)	-152.5(16)
N(3)-C(5)-C(6)-C(9')	141.1(23)	N(1)-C(6)-C(5)-C(8')	139.8(23)

colourless plates, mp 157-158°; ir: ν max 1605, 1495, 1445, 1345, 1195, 1180, 985, 810, 785, 755, 705, 695 and 600 cm^{-1} ; uv (acetonitrile): λ max 252 (4.24); $^1\text{H-nmr}$ (deuteriochloroform): δ 2.31 (s, CH_3), 6.88-7.91 (m, aromatic); ms: m/z 402 (M^+), 374, 283 (100%), 194, 180, 165, 105, 103, 77.

Anal. Calcd. for $\text{C}_{28}\text{H}_{22}\text{N}_2\text{O}$: C, 83.6; H, 5.5; N, 6.9. Found: C, 84.1; H, 5.4; N, 6.6.

Iodometric Titrations.

Active oxygen assays were performed by the method detailed by Siggia [17] and were consistently greater than 70%. The variable iodometric assays have been attributed to the instability of some of the oxaziridines in hot alcoholic solvents. In some cases to be described this reaction could be used 'preparatively'; the resulting 2*H*-imidazoles could be removed by filtration and purified by crystallisation.

Deoxygenation of Oxaziridines 7. Syntheses of 2,2-Diaryl-2*H*-imidazoles.

To a stirred solution of the fused oxaziridine (0.2 g) in anhydrous chloroform (10 ml) was added freshly distilled triethyl phosphite (0.4 ml). After an initial exothermic reaction, the solution was stirred for 1 hour and then concentrated. Trituration with ether gave, in each case, a crystalline solid in practically quantitative yields, which was removed by filtration and recrystallised.

2,2-Diphenyl-4-methyl-2*H*-imidazole (8a).

This compound was obtained from **7a** as colourless needles after a single recrystallisation from hexane, mp 106-107° (lit [16] mp 106-107°); $^1\text{H-nmr}$ (deuteriochloroform): δ 2.39 (s, CH_3), 7.20-7.70 (m, aromatic), 7.98 (s, =CH).

2,2,4-Triphenyl-2*H*-imidazole (8b).

This compound was obtained from **7b** as colourless needles after recrystallisation from hexane, mp 113-114° (lit [16] mp 113-114°); $^1\text{H-nmr}$ (deuteriochloroform): δ 6.96-8.11 (m, aromatic), 8.50 (s, =CH).

4,5-Dimethyl-2,2-diphenyl-2*H*-imidazole (8c).

This compound was obtained by recrystallisation from methanol as colourless needles, mp 197°; ir: ν max 1650, 1585, 1485, 1445, 1435, 1315, 1205, 1190, 1000, 960, 920, 900, 765, 740, 700, 650 and 640 cm^{-1} ; uv (acetonitrile): λ max 231 (3.65), 259 sh (2.87), 266 sh (2.81); $^1\text{H-nmr}$ (deuteriochloroform): δ 2.38 (s, CH_3), 6.92-7.74 (m, aromatic); ms: m/z 248 (M^+), 247, 207, 166, 165 (100%), 139. This compound could also be obtained in like manner from the $\text{P}(\text{OEt})_3$ -induced deoxygenation of the *N*-oxide precursor (**2c**).

Anal. Calcd. for $\text{C}_{17}\text{H}_{16}\text{N}_2$: C, 82.2; H, 6.5; N, 11.3. Found: C, 82.3; H, 6.8; N, 11.3.

2-*p*-Anisyl-4,5-dimethyl-2-phenyl-2*H*-imidazole (8d).

This compound was obtained as pale yellow prisms, mp 113-114°; ir: ν max 1645, 1605, 1580, 1510, 1465, 1455, 1445, 1380, 1300, 1255, 1185, 1170, 1035, 1000, 930, 910, 830, 790, 760, 725, 700, 655 and 645 cm^{-1} ; uv (acetonitrile): λ max 264 (3.30), 274 sh (3.29), 280 sh (3.21); $^1\text{H-nmr}$ (deuteriochloroform): δ 2.33 (s, CH_3), 3.71 (s, OCH_3), 6.70-7.68 (m, aromatic); ms: m/z 278 (M^+), 237, 196 (100%), 181, 165, 153, 152, 98.

Anal. Calcd. for $\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}$: C, 77.7; H, 6.5; N, 10.1. Found: C, 77.6; H, 6.7; N, 10.3.

4-Acetyl-2,2-diphenyl-5-methyl-2*H*-imidazole (8e).

This compound was obtained as colourless needles, mp 120-121°; ir: ν max 1705, 1610, 1600, 1555, 1495, 1450, 1375, 1370, 1235, 1075, 935, 910, 765, 760, 700, 650 and 610 cm^{-1} ; uv (acetonitrile): λ max 230 (3.58), 242 sh (3.31), 256 sh (3.18), 265 sh (3.13); $^1\text{H-nmr}$ (deuteriochloroform): δ 2.56 (s, CH_3), 2.70 (s, CH_3), 7.01-7.77 (m, aromatic); ms: m/z 276 (M^+), 261, 233 (100%), 207, 193, 166, 165, 130, 103, 77, 43.

Anal. Calcd. for $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}$: C, 72.8; H, 5.8; N, 10.2. Found: C, 78.3; H, 5.8; N, 10.4.

4,5-Dimethyl-2-phenyl-2-*p*-tolyl-2*H*-imidazole (8f).

This compound was obtained as colourless plates, mp 134-135°; ir: ν max 1650, 1580, 1485, 1445, 1375, 1315, 1205, 1185, 1040, 1030, 930, 910, 810, 760, 715, 700, 655, 590 and 530 cm^{-1} ; uv (acetonitrile): λ max 231 (3.84), 253 sh (3.05), 265 sh (3.00); $^1\text{H-nmr}$ (deuteriochloroform): δ 2.28 (s, CH_3), 2.33 (s, CH_3), 6.97-7.69 (m, aromatic); ms: m/z 262 (M^+), 221 (100%), 180, 165; m^* 151.3 (180-165).

Anal. Calcd. for $\text{C}_{18}\text{H}_{18}\text{N}_2$: C, 82.4; H, 6.9; N, 10.7. Found: C, 82.5; H, 7.1; N, 10.8.

4-Methyl-2,2,5-triphenyl-2*H*-imidazole (8g).

This compound was obtained from the reactions of oxaziridines **2g** and **2h** as colourless needles, mp 153-155°; ir: ν max 1635, 1605, 1595, 1560, 1490, 1450, 1380, 1330, 1230, 1205, 1045, 1025, 910, 905, 775, 765, 750, 705, 700, 650, 590 and 535 cm^{-1} ; uv (ethanol): λ max 262 (3.96); $^1\text{H-nmr}$ (deuteriochloroform): δ 2.57 (s, CH_3), 7.20-8.03 (m, aromatic); ms: m/z 310 (M^+), 269, 207, 166 (100%), 165, 103. From 'active' oxygen assays on both of these oxaziridines the crude 2*H*-imidazole could be almost completely precipitated by the addition of water.

Anal. Calcd. for $\text{C}_{22}\text{H}_{18}\text{N}_2$: C, 85.1; H, 5.9; N, 9.0. Found: C, 85.3; H, 5.9; N, 9.1.

2,2,4,5-Tetraphenyl-2*H*-imidazole (8i).

This compound was obtained as colourless plates, mp 198-200° (lit [18] mp 199-201°); ms: m/z 372 (M^+), 269 (100%), 166,

165, 103.

2-*p*-Tolyl-2,4,5-triphenyl-2*H*-imidazole (**8j**).

This compound was obtained as colourless plates, mp 162–163°; ir: ν max 1605, 1555, 1490, 1445, 1270, 1045, 1025, 1015, 935, 815, 770, 755, 695, 670, 610 and 545 cm^{-1} ; uv (acetonitrile): λ max 260 (3.97); $^1\text{H-nmr}$ (deuteriochloroform): δ 2.30 (s, CH_3), 7.00–7.91 (m, aromatic); ms: m/z 386 (M^+), 283 (100%), 180, 165; m^* 151.25 (180–165).

1,3-Diaza-5,6-dimethyl-4,7-dioxa-2,2-diphenyltricyclo[4.1.0.^{1,6,3,5}0]heptane (**9**).

To a solution of oxaziridine **7c** (0.30 g, 1.13 mmoles) in methylene chloride (10 ml) cooled to 0° was added *m*-chloroperbenzoic acid (0.27 g, 1.56 mmoles) in a single portion. After complete consumption of **7c**, the filtrate was concentrated and the product purified by preparative tlc (R_f 0.20% ethyl acetate/toluene). Recrystallisation of the resulting solid from an ether-hexane mixture furnished 1,3-diaza-5,6-dimethyl-4,7-dioxa-2,2-diphenyltricyclo[4.1.0.^{1,6,3,5}0]heptane (**9**) (0.23 g, 72%) as colourless prisms, mp 187–188°; ir: ν max 1490, 1450, 1395, 1320, 1210, 1145, 870, 755, 712, 700, 635 and 550 cm^{-1} ; uv (ethanol): λ max 225 (3.91), 262 sh (2.67); $^1\text{H-nmr}$ (deuteriochloroform): δ 1.76 (s, CH_3), 7.06–7.77 (m, aromatic); ms: m/z 280 (M^+).

Anal. Calcd. for $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2$: C, 72.8; H, 5.8; N, 10.0. Found: C, 73.1; H, 6.1; N, 9.8.

Crystal Data.

Collection and Reduction of X-ray Diffraction Data.

Colourless irregular crystals of **9** were grown and a tabular crystal of dimensions 0.25 x 0.25 x 0.10 mm selected. Cell dimensions were determined using 20 reflections ($7 < 2\theta < 20$ degrees) centred automatically on a Nicolet R3M diffractometer using $\text{MoK}\alpha$ radiation ($\lambda = 0.7170 \text{ \AA}$). A total of 1772 reflections ($\pm h \pm k l$) including standards (1718 unique) were measured within the limits $2 < 2\theta < 42$ degrees at 20°, using graphite-monochromatized $\text{MoK}\alpha$ radiation. Equivalent reflections were averaged and the 641 reflections with intensities 3.0 times their standard deviations (from counting statistics) were corrected for Lorentz and polarization factors. No absorption correction was applied.

Solution and Refinement of Structure.

The structure was solved by direct methods [RANT] [19] and successive difference Fourier syntheses. Refinement [20] was *via* full matrix least-squares minimizing wD^2 , where $D = |F_o| - |F_c|$ and $w = (\alpha F_o)^2 + .0006 |F_o|^2)^{-2}$ and $|F_o|, |F_c|$ are the calculated and observed structure factors.

The phenyl groups were refined as rigid groups (C–C 1.395 Å, C–H 1.0 Å); the hydrogen atoms H(22)... H(26) had fixed temperature factors of 0.17²; the remaining phenyl hydrogen atoms, and the atoms O(4'), O(7'), C(8'), C(9'), H(91), H(92) and H(93), were refined with isotropic thermal parameters in two groups. All other atoms were refined with anisotropic thermal parameters. The

common occupancy factor for two groups of atoms, O(4), O(7), C(8), C(9), H(91), H(92), H(93) (major) and O(4'), O(7'), C(8'), C(9') (minor), were refined so their total was 1.0. Scattering factors for non-hydrogen and hydrogen atoms were taken from references [21] & [22] respectively. Final residuals R, R_w were 0.097, 0.112 respectively. The final occupancy factor for the major conformation was 0.713(16).

Listings of structure factors, bond angles, torsion angles and thermal parameters are available from the authors.

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