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3,3-DIALKYL-2-PHOSPHINOYLOXAZIRIDINES: SYNTHESIS AND DETERMINATION OF THE BARRIER TO NITROGEN INVERSION

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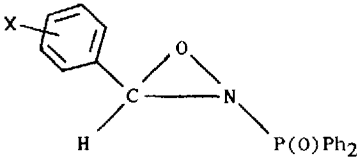
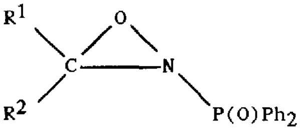
Summary: 3,3-Dialkyl-2-diphenylphosphinoyloxaziridines, prepared by the oxidation of N-diphenylphosphinoyl imines with the 3-chloroperoxybenzoic acid-KF complex, have very low barriers to inversion at nitrogen ($\Delta G^{\ddagger}$ 12.6-13.3 kcal mol^{-1}).

The preparation and characterization of 2-phosphinoyloxaziridines has recently been described.[1] Thus far these compounds, which show interesting oxidising properties, have been limited to examples of type (1) bearing a 3-aryl group. In this respect the situation was similar to that in 2-sulphonyloxaziridines[2] which, until recently,[3] were largely restricted to 3-aryl substituted compounds. We now report the preparation of 3,3-dialkyl-2-phosphinoyloxaziridines (2) and the first quantitative assessment of the configurational stability at nitrogen in the N-phosphinoyl oxaziridine system.



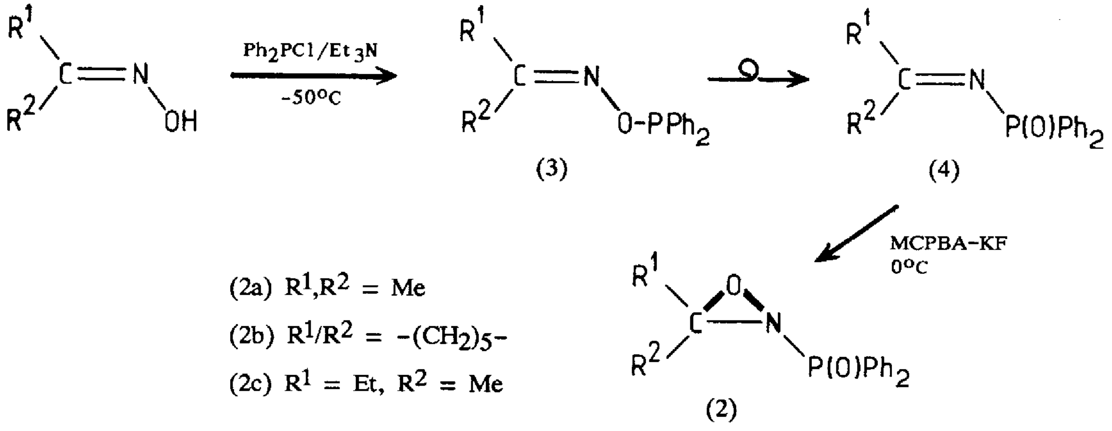
(1)



(2)

Although 3-aryl-2-phosphinoyloxaziridines can be prepared by biphasic (3-chloroperoxybenzoic acid/$CHCl_3$/H_2O/$NaHCO_3$) oxidation of N-benzylidenephosphonamides,[1] our investigations have found that this procedure is unsatisfactory for the oxidation of the hydrolytically sensitive N-phosphinoyl imines deriving from dialkyl ketones. However, oxidation of these imines with the 2:1 potassium fluoride/3-chloroperoxybenzoic acid (MCPBA) complex devised by Camps et al.[4] for alkene epoxidation affords 3,3-dialkyl-phosphinoyloxaziridines (2) in good yield. This oxidation regime is performed under anhydrous conditions.

SCHEME 1



(2a) R^1,R^2 = Me
(2b) R^1/R^2 = $-(CH_2)_5-$
(2c) R^1 = Et, R^2 = Me

TABLE 1

N.m.r. data and barriers to nitrogen inversion for 3,3-dialkyl-2-diphenylphosphinoyloxaziridines.[a]

Compd.	$\delta(C\text{-}3)^b$ p.p.m.	$^2J(PNC)^b$ Hz	$\delta(^{31}P)^b$ p.p.m.	$\delta(R^1)^c$ p.p.m.	$\delta(R^2)^c$ p.p.m.	T^d °C	k s^{-1}	$\Delta G^{\ddagger}$ kcal mol^{-1}
(2a)	87.0	6.7	28.7	26.2^e	20.5^e	18.5	750	13.2 ± 0.1
(2b)	91.5	6.6	27.7	36.1^f	30.5^f	22.5	937	13.3 ± 0.1
(2c)	89.1	6.6	28.2	32.1(<u>t</u>)^{f,g}	18.3^e	3.5	252	13.1 ± 0.1(<u>t</u>→<u>c</u>)^g
				22.7(<u>c</u>)^{e,g}	27.3^f		681	12.6 ± 0.1(<u>c</u>→<u>t</u>)^g

[a] Recorded in deuteriochloroform solution at 67.8 MHz (^{13}C) or 36.2 MHz (^{31}P) using internal TMS and external H_3PO_4 references. [b] Recorded at ambient temperature. [c] Chemical shift of the 3-alkyl substituents recorded at -40°C where nitrogen inversion is slow on the n.m.r. time-scale; R^1 and R^2 are <u>trans</u> and <u>cis</u> respectively to the $P(O)Ph_2$ group. [d] Coalescence temperature. [e] α-Methyl signal. [f] α-Methylene signal. [g] <u>c</u> and <u>t</u> refer to nitrogen invertomers in which the 3-ethyl and 2-phosphinoyl moieties are <u>cis</u> and <u>trans</u> respectively.

<u>N</u>-Phosphinoyl imines (4) were obtained by rearrangement of <u>O</u>-diphenylphosphino-oximes (3) prepared by reaction of equimolar quantities of oxime, chlorodiphenylphosphine and triethylamine at <u>ca</u>. -50°C (Scheme I).[5] The dichloromethane solution containing the crude imine was filtered under nitrogen onto a rapidly stirred suspension of a 100% excess of the KF/MCPBA complex in dichloromethane. After stirring for <u>ca</u>. 2h, filtration and rotary evaporation afforded the crude oxaziridines. Subsesquent trituration with hexane/ether 2:1 and filtration through a 1 cm silica gel bed gave oxaziridines (2a-c) in 55-65% overall yield.

Compounds (2a-c) afforded satisfactory elemental analyses and spectral data in accord with the oxaziridine structure, quaternary ^{13}C resonances (which exhibited a coupling to phosphorous) in the region δ 87-92 being particularly characteristic. In addition, oxaziridines (2a-c) displayed ^{31}P NMR resonances in the region of δ 28 (Table 1).[1] In contrast to their 2-sulphonyl counterparts, the ambient temperature n.m.r. spectra of oxaziridines (2a-c) indicate a rapidly

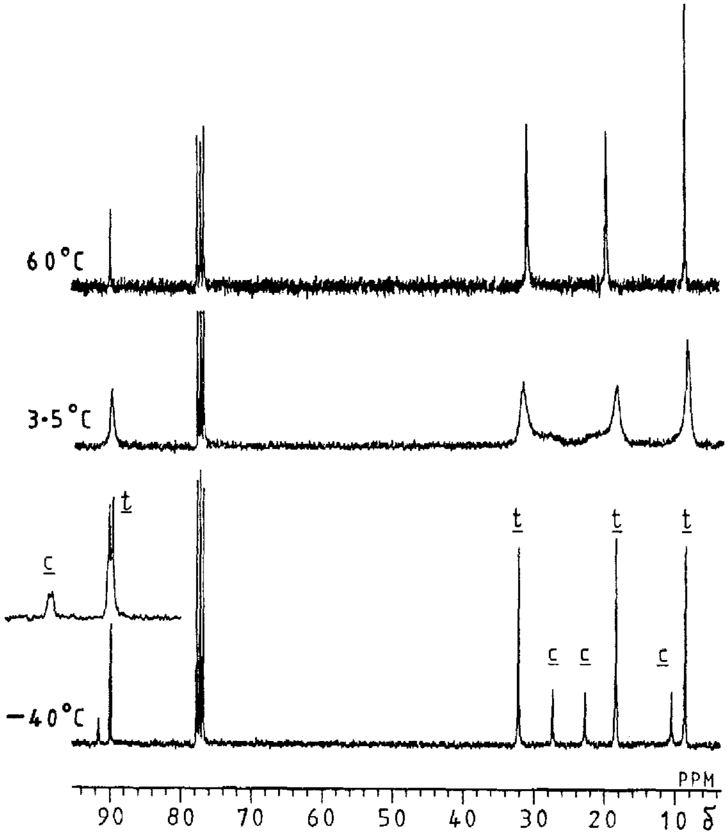


Figure 1 67.8 MHz ^{13}C n.m.r. spectra of (2c) in deuteriochloroform at various temperatures showing the dynamic coalescence of cis (c) and trans (t) isomers

inverting nitrogen atom, for example ^{1}H and ^{13}C n.m.r. spectra of (2a) showed one discrete (exchange broadened) 3-Me resonance. On cooling below 10°C the 3-alkyl resonances of oxaziridines (2a) and (2b) split into two equally intense sets of signals indicative of slow inversion at nitrogen on the NMR time-scale. At -40°C the alkyl signals of the asymmetrically 3,3-disubstituted compound (2c) were split into two components of unequal intensity (Figure 1). On the basis that 3-alkyl α-carbons located trans to an oxaziridine nitrogen lone pair experience an upfield shift,[6] the major and minor components can be assigned to the nitrogen invertomers in which the 3-ethyl group resides respectively trans and cis to the diphenylphosphinoyl moiety.

Line shape analysis[7] of the α-carbon signal of (2a-c) at coalescence afforded the rates of nitrogen inversion (Table 1). The barrier to nitrogen inversion in these oxaziridines (12.6-13.3 kcal mol^{-1}) is much lower than that obtaining in 2-sulphonyloxaziridines (20-21 kcal mol^{-1})[3,8] and reflects a much stronger conjugative interaction between nitrogen and phosphorus than between nitrogen and sulphur in the trigonal transition state for nitrogen inversion. A similar trend has been observed previously in N-phosphinoyl and N-sulphonyl aziridines,[9] though the magnitude of the effect is much greater in the oxaziridines. The absence of configurational stability at nitrogen in N-phosphinoyl oxaziridines, as compared with N-alkyl oxaziridines where the inversion barrier is 25-34 kcal mol^{-1}, [10,11] has important consequences for stereochemical work involving these compounds.

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