Photoracemization at a Chiral Pyramidal Nitrogen Centre

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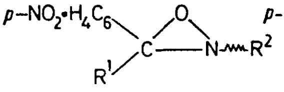
Summary The absorption of u.v. light by chiral oxaziridines having a stable pyramidal nitrogen configuration results in photoracemization *via* a mechanism involving C–O bond cleavage and a nitrone intermediate.

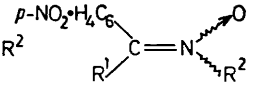
TABLE

Oxaziridine (**1**)[a]	R^1	R^2	$[\alpha]_D$[b]	Yield of nitrone (**2**)/%[c]
(**1a**)	p-$NO_2 \cdot C_6H_4$	Bu^t	−60·2 → 0·0° (74)	34 (7)
(**1b**) *trans*	H	Me	−17·2 → −12·8° (11)	10 (17)[d]
(**1c**) *trans*	H	Pr^i	−12·0 → − 9·7° (8)	21 (14)[d]
(**1d**) *trans*	H	Bu^t	−44·8 → −28·1° (8)	34 (12)[d]
(**1e**) *trans*	Me	Bu^t	+ 8·5 → + 1·6° (20)	27 (21)[e]
			+11·8 → + 6·2° (20)	
(**1f**) *cis*	Me	Bu^t	−40·1 → −22·8° (8)	27 (26)[e]
			−32·7 → −23·7° (6)	

[a] *cis* and *trans* refer to the relative positions of the *N*-alkyl and *C*-aryl groups. [b] Change in specific optical rotations (in $CHCl_3$) after irradiation and chromatographic purification (hours of irradiation). [c] Maximum yield obtained by n.m.r. analysis and chromatographic separation (hours of irradiation, 0·75 M in $CDCl_3$). [d] *trans*-Nitrone. [e] *cis*- and *trans*-Nitrone mixture which on thermal equilibration gave *cis* and *trans* isomers in the ratio of 4 : 1. p-$NO_2 \cdot C_6H_4 \cdot CONMeBu^t$ was also detected as a minor product.

PHOTOCHEMICAL stereomutation of a pyramidal molecule, previously reported for a sulphur atom (sulphoxide[1]), is now found to occur also with an optically active nitrogen pyramid (oxaziridine). Pyramidal inversion occurs in the thermal racemization of oxaziridines[2,3] and in the photochemical racemization of several sulphoxides.[1]


(1)


(2)

Optically active oxaziridines (**1**) were obtained by asymmetric oxidation of the corresponding imines[2—4] and were irradiated (low pressure u.v. lamp, 2537 Å) in a quartz vessel (CH_2Cl_2 solvent) at ambient temperature. Racemization of oxaziridines (**1a**—**f**, Table) occurred during irradiation and was accompanied by nitrone (**2**) formation. The synthesis of nitrones by a photochemical method, to our knowledge, is without precedent; photochemical rearrangement in the reverse direction[5] or to amide[6] is widely reported, however. Rearrangement of these nitrones back to the original oxaziridines also occurs under the present experimental conditions and thus provides a mechanism for photochemical racemization.

The *trans*-oxaziridines (**1b**—**d**) on irradiation yielded only *trans*-nitrones and partially racemized *trans*-oxaziridines (Table). Under identical experimental conditions the *cis*-oxaziridines (**1b**) and (**1c**) ($[\alpha]_D$ −1·6 and −7·4° respectively) gave *trans*-nitrone, *cis*-oxaziridine (unchanged optical rotation), and *trans*-oxaziridine (racemic). The latter results constitute a stereoselective photoepimerization sequence (*cis*-oxaziridine $\xrightarrow{h\nu}$ *trans*-nitrone $\overset{h\nu}{\rightleftarrows}$ *trans*-oxaziridine).

Stereochemical interpretation of the results of irradiation of the optically active oxaziridines *cis*- and *trans*-(**1f**) is more complex since photoracemization, photoepimerization, and photorearrangement to *cis*- and *trans*- nitrones occur. *C*-Alkyl aryl nitrones had previously been found to exist only in the *cis* isomeric form.[7] The present procedure provides a simple synthetic method to a range of previously inaccessible hindered nitrones, *e.g.*, (**1a**) and (**1f**).

Photoracemization of oxaziridines may involve either bond cleavage (A) or pyramidal nitrogen inversion (B). While mechanism (A) must account for the racemization of oxaziridines (**1b**—**d**) and *cis*- and *trans*-(**1f**), it is probable that the same pathway will apply to other oxaziridines since nitrone is present in each case. Photoepimerization of *cis*-(**1f**) ($[\alpha]_D$ −40·1 and −32·7°) to *trans*-(**1f**) ($[\alpha]_D$ + 0·2 and 0·0°) thus shows a marked preference for (A). In contrast however the photochemical isomerization of *trans*-(**1f**) ($[\alpha]_D$ + 8·5 and +11·8°) to *cis*-(**1f**) ($[\alpha]_D$ −1·7 and −8·0°) may be explained by a significant contribution from mechanism (B). A similar sign inversion was previously noted for the thermal epimerization of *cis*-(**1f**) $\rightleftarrows$ *trans*-(**1f**) which must proceed by a pyramidal inversion path.[4]

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