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OPTICALLY ACTIVE OXAZIRIDINES

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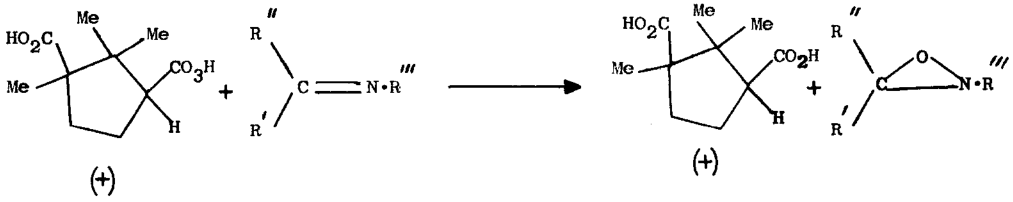
A general method for obtaining oxaziridines involves reaction between imines and peracetic (1) or m-chloroperbenzoic acid (2). When optically active peracids are used to oxidize certain sulphides and olefins, dissymmetric sulphoxides (3) and epoxides (4,5) are formed. Imines have now been shown to give optically active products on treatment with (1S)-(+)-percamphoric acid (at 3°C. in dichloromethane solution) cf. Table I.

TABLE I

	Imine	Oxaziridine $[\alpha]_D^{22}$	Oxaziridine physical properties b.p. and n_D^{22}	Oxaziridine literature (1) physical properties b.p. and n_D^{20}
(i)	$Ph{\cdot}CH{=}N{\cdot}Bu^t$	-12.7° *	$58-60^\circ/0.3$ mm., 1.5078	$61-63^\circ/0.2$ mm., 1.5081
(ii)	$\alpha{-}C_5H_4N{\cdot}CH{=}N{\cdot}Bu^t$	-4.3° *	$62-63^\circ/0.4$ mm., 1.5000	$68-70^\circ/0.4$ mm., 1.5010
(iii)	$Pr^i{\cdot}CH{=}N{\cdot}Bu^t$	-3.3° *	$67-69^\circ/38$ mm., 1.4152	$68-70^\circ/39$ mm., 1.4152
(iv)	$(Bu^i)Me{\cdot}CH{=}N{\cdot}Pr$	-9.0° *	$69-71^\circ/11-12$ mm., 1.4265	$61^\circ/8$ mm., 1.4267
(v)	$p{-}NO_2{\cdot}C_6H_4{\cdot}CH{=}N{\cdot}Bu^t$	-11.3°	$62-63^\circ$ **	$65-66^\circ$ **
(vi)	$p{-}NO_2{\cdot}C_6H_4{\cdot}CH{=}N{\cdot}Pr^i$	-12.0°	$47-48^\circ$ **	$46-48^\circ$ **
		-1.3°	$102-103^\circ$**	
(vii)	$p{-}NO_2{\cdot}C_6H_4{\cdot}CH{=}N{\cdot}Et$	-11.0°	$42-43^\circ$ **	$34-35^\circ$ **
		-2.7°	$80-81^\circ$ **	

* neat liquids corrected for density

** melting points



The physical properties (m.p., b.p., n_D, and $[\alpha]_D$) allied to microanalytical (C,H determination and accurate M.W.), spectral (i.r., u.v., n.m.r. and mass spectra), and chemical properties (active oxygen content) leave no doubt that the optically active products are oxaziridines. Most of these oxaziridines have been described before in optically inactive forms (1).

Yields in the imine-(+)-percamphoric acid reactions are generally good (47 to 80%) and this oxidant has the advantage, shared by m-chloroperbenzoic acid, of being soluble in dichloromethane whilst the resultant carboxylic acid separates during the reaction. This solubility factor can be helpful in the synthesis of relatively unstable oxaziridines (2).

One optically active oxaziridine ($[\alpha]_D$ -3.94°) has been obtained before, by asymmetric removal of an enantiomer from the racemate by treatment with brucine (1). The present method, starting from the imine (iv) gives this oxaziridine with a higher optical activity ($[\alpha]_D$ -9.0°). If inversion at the nitrogen atom is slow in oxaziridines (6), this product may consist of enantiomers and diastereomers. Three of the imines (v), (vi) and (vii) gave solid oxaziridines on reaction with (+)-percamphoric acid. Oxidation of imine (v) gave a single optically active product after crystallisation, but the other two imines each gave a separable mixture of two oxaziridines (with different optical rotations). The racemic forms of each of these compounds were obtained by oxidizing the imines with m-chloroperbenzoic acid.

The optical purity of each of the oxaziridines in Table I will not be known until the rotation of a pure enantiomer has been determined. The results shown in Tables II and III indicate that the degree of stereoselectivity in the imine-(+)-percamphoric acid reaction depends on the reaction temperature and on the solvent used. Choice of conditions may therefore be of some assistance in obtaining one or more optically pure oxaziridines by this general procedure.

TABLE II

Temperature Effects in Oxidation of N-*p*-nitrobenzylidene-t-butylamine (v) with (+)-Percamphoric Acid in Dichloromethane.

Temperature °C	+ 29°	+ 3°	- 18°	- 40°	- 72°
Oxaziridine $[\alpha]_D^{22}$ (c 5, $CHCl_3$)	- 3.2°	-11.3°	-13.2°	-36.5°	-62.7°

TABLE III

Solvent Effects in Oxidation of N-benzylidene-t-butylamine (1) with (+)-Percamphoric Acid at 3°C.

Solvent	$CHCl_3$	CH_2Cl_2	CCl_4	C_6H_6	$(C_2H_5)_2O$	C_2H_5OH
Oxaziridine $[\alpha]_D^{22}$ (neat)	-17.1°	-12.7°	-10.9°	-10.0°	+1.5°	+6.5°

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