Oxaziridine Synthesis by Asymmetric Induction

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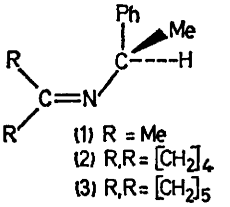
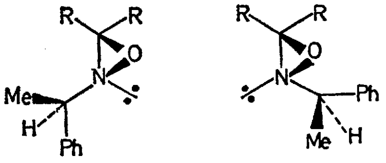
Summary Chiral substituents on nitrogen in Schiff bases induce oxidation to give oxaziridines with a high degree of stereospecificity when the bases are treated with organic peroxy-acids.

So far optically active oxaziridines containing a stable chiral nitrogen atom have been prepared by oxidation of imines with optically active peroxy-acids.[1,2] As for cases involving the C=C bond, the optical yield of this synthesis is rather low (*ca.* 10%).



(1) R = Me
(2) R,R = $[CH_2]_4$
(3) R,R = $[CH_2]_5$



Diastereoisomers (A) and (B)

We recently found that oxaziridines, which contain a stable chiral nitrogen atom, can be obtained in a very stereospecific fashion by an asymmetric synthesis starting with Schiff bases carrying a chiral substituent on nitrogen.

The Schiff bases,[3] with *R*-(+)-methylbenzylamine as starting material, were oxidized with *m*-chloroperoxybenzoic acid in CH_2Cl_2, at 0—5 °C (yield 75—85%); the resulting diastereoisomeric mixtures were resolved either by column chromatography (silica gel, hexane–ether 9 : 1) or by high-pressure chromatography (h.p.c.). We cannot ascribe the *RR* or *SR* configurations to the diastereoisomers (A) and (B) without knowing the absolute configuration at the chiral nitrogen atom.

Table

Starting imine	% Oxaziridine diastereoisomers (A)	(B)	$[\alpha]^{22}_{436}$ (A)	(*c* 1, $CHCl_3$) (B)
(**1**)	82	18	+ 98·5	+271·9
(**2**)	87	13	+ 66·0	+295·4
(**3**)	97	3	+118·5	+205·4

The diastereoisomers resolved by column chromatography were estimated iodometrically; those resolved by h.p.c. were also compared by their u.v. absorption at 254 nm.

For compound (**1**) the composition of the reaction mixture can be determined by integration of the methyl n.m.r. signals. The diastereotopic $Me_2C=$ groups give signals as follows: (A), δ 1·32 and 1·40; (B), δ 1·43 and the PhCH*Me* group gives a doublet at δ 1·47 for (A) and 1·32 for (B).

The absolute configuration at the chiral nitrogen atom in oxaziridines is still debatable; this problem is connected with the mechanism of oxidation of imines with organic peracids. Madan and Clapp[4] postulated an epoxidation type (one-step) mechanism *via* a nucleophilic reaction of π-electrons. The kinetic results of Ogata and Sawaki[5] suggested that oxaziridines are formed *via* a two-step (Baeyer-Villiger-type) mechanism. Boyd[6] considered that the imines may exist as a rapid equilibrium of *Z* and *E* forms, leading to two diastereoisomeric oxidation products.

The ketimines investigated by us are derivatives of symmetrical ketones. The formation of two diastereoisomeric oxaziridines with high stereospecificity can be explained by either a one-step or an ionic mechanism.

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