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THE SYNTHESIS OF N-UNSUBSTITUTED KETIMINES FROM OXAZIRIDINES

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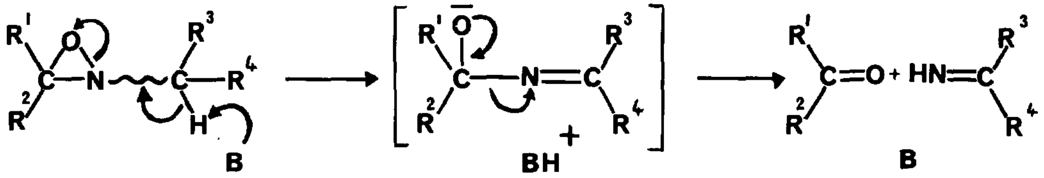
Summary. N-Unsubstituted diaryl, alkyl aryl and dialkyl ketimines are prepared in good yield at ambient temperature by the reaction of $KOBu^t$ on oxaziridines having an α-hydrogen atom on the N-alkyl substituent; the mechanism and stereochemistry of the reaction are discussed.

The base-catalysed elimination reaction of oxaziridines to form[1-6] aldehydes and ketones has recently been examined in depth by several groups. While N-unsubstituted imines were proposed as transient intermediates in these earlier reports, they were not detected and thus the first unequivocal evidence for their formation was provided by the observation (by n.m.r. in $C_6D_5CD_3$ solution at -70°C) of highly unstable N-unsubstituted aldimines which decomposed spontaneously at room temperature.[7] The present report indicates that a range of more stable N-unsubstituted ketimines can be isolated in good yield by base treatment of a range of readily available oxaziridines.

The oxaziridines 1-9 were prepared by the normal MCPBA oxidation route from N-alkyl imines derived from fluorenone or benzaldehydes.[8]



	R^1	R^2	R^3	R^4
1.	- Fl^a -		-Ph	-Ph
2.	- Fl^a -		- Fl^a -	
3.	- Fl^a -		-Ph	-Me
4.	- Fl^a -		-Et	-Et
5.	-Ph	-H	-Ph	-Ph
6.	-NP^b	-H	-Ph	-Ph
7.	-Ph	-H	- Fl^a -	
8.	-NP^b	-H	-Ph	-Me
9.	-NP^b	-H	-Et	-Et

a Fl = fluorenyl b NP = 4-nitrophenyl

In a typical reaction, oxaziridine 5 (0.37g) was stirred with a suspension of $KOBu^t$ (0.15g) in dry THF (10ml) for 8 h at ambient temperature to give benzophenone imine. This N-unsubstituted ketimine was isolated as the insoluble hydrochloride (0.25g, 90%) after dilution of the THF solution with ether and passage of dry HCl. Under similar conditions oxaziridines 1, 2, 6-9 gave the corresponding N-unsubstituted ketimine hydrochlorides with yields in the range 52-90%. These imine hydrochlorides, and the parent imines (generated from the hydrochlorides by treatment with dry NH_3), were identified by spectral comparison with authentic samples. This synthetic route to N-unsubstituted imines such as the less stable dialkylketimine 3-pentanone imine (obtained from 9), or the cyclic ketimine fluorenone imine (obtained from 2 or 7) has advantages over the previously reported routes.

The base-catalysed reaction of oxaziridines to form aldehydes and ketones has been assumed[1-3,5,7] or shown[6] to proceed *via* the mechanism indicated in the equation. An alternative mechanism involving nucleophilic attack at the ring nitrogen atom of oxaziridines has recently been proposed.[4] The latter mechanism can however be excluded in the present reactions of oxaziridines 1-9 from the following evidence:

(i) Oxidation of the corresponding aldimines ($MCPBA/CH_2Cl_2/5^oC$) yielded oxaziridines 5-9 as a mixture of configurationally stable[8] *cis* (25-50%) and *trans* (75-50%) isomers. The rate of attack of the *trans* isomer by tertiary butoxide anion was faster than for the *cis* form. Thus the ratio of rate constants (k_{trans}/k_{cis}) for oxaziridines 6 (in $C_6D_5.NO_2$) and 9 (in $(CD_3)_2SO$) was 21.0 and 2.5 respectively. This stereoselectivity is in marked contrast with the only previous reports [4,9] on the differential reactivity of similar *cis* and *trans* oxaziridines, where the *cis* isomer reacted faster with nucleophiles (including triethylamine) at the oxaziridine ring nitrogen atom.

(ii) The rate of reaction appeared to be related to the acidity of the α-hydrogen atom and thus oxaziridines 1, 2, 5, 6 and 7 generally reacted faster than 3, 8 or 9 while 4 appeared to be totally unreactive at ambient temperature.

(iii) Substitution of D for H at the α-position in oxaziridine 6 allowed the primary kinetic isotope effect for the reaction to be determined (k_H/k_D ~6 in $C_6D_5.NO_2$). This indicates that the initial proton abstraction process is rate determining.

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