Stereochemical and Mechanistic Aspects of the Base-catalysed Decomposition of *N*-Alkyloxaziridines to form NH Ketimines

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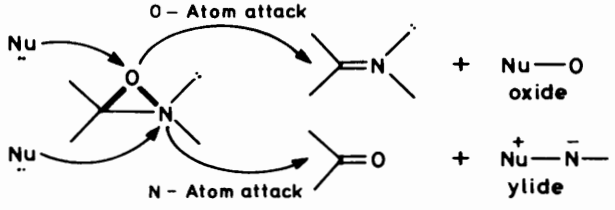
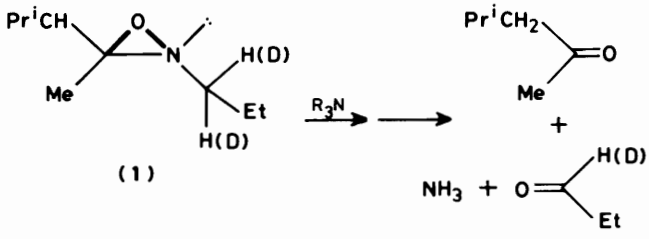
The synthesis of a new range of oxaziridines (**18**)—(**23**), (**30**)—(**35**) by peracid oxidation of diaryl ketimines and aryl aldimines is reported. Relatively stable NH ketimine products (**24**)—(**27**) have been isolated from base-catalysed decomposition of the oxaziridines (**18**)—(**20**), (**30**)—(**35**) and a primary kinetic isotope effect (*ca.* k_H/k_D 6.0) was observed during decomposition of the oxaziridine *trans*-(**31**). The *trans*-oxaziridines (**31**)—(**35**) were found to decompose at a faster rate than the corresponding *cis* isomers. The relative rates of base-catalysed decomposition of oxaziridine stereoisomers are consistent with a mechanism involving an α-C–H proton abstraction mechanism.

The reaction of oxaziridines with nucleophiles and bases was first reported in 1957[1] and has recently been examined in a more comprehensive manner.[2–17] In the earlier studies[1,5] which were carried out with a range of *N*-alkyloxaziridines, tertiary phosphines were initially used as nucleophilic reagents (O atom attack). While *N*-alkyloxaziridines were also found to oxidize sulphides to sulphoxides[2,6] *N*-sulphonyl-[7–10] and *N*-phosphinyl-oxaziridines[11] proved to be much stronger oxidants which were able to oxidize phosphines (to phosphine oxides), sulphides (to sulphoxides), and olefins (to epoxides). Nucleophilic attack can occur at either the oxaziridine ring oxygen (oxide formation) or nitrogen atom (ylide formation). Oxygen atom attack was preferred when bulky substituents were present on the oxaziridine ring.[4] Conversely, nucleophilic attack at the nitrogen atom (N atom attack) to yield unstable intermediates was facilitated by less bulky *N*-alkyl substituents.



Base-catalysed attack on the *N*-alkyl substituent of oxaziridines bearing an α-H atom to yield ammonia and two carbonyl (aldehyde or ketone) products has been reported by several groups.[1,12,13] This reaction, which may be regarded as an example of C-atom attack, and as a model system for enzyme catalysed oxidative deamination,[12] has been found to occur with a range of bases including tertiary amines,[13–16] and hydroxide or alkoxide anions.[1,12,17] The mechanism of this base-catalysed decomposition of oxaziridines was assumed to proceed *via* initial abstraction of an α-H atom followed by formation of an NH imine intermediate which decomposed[1,12] *in situ*

Evidence for the α-atom abstraction mechanism was recently obtained by Rastetter *et al.*[13,14] who found a primary kinetic isotope effect (k_H/k_D 4.25) for decomposition of the oxaziridine (**1**) with tertiary amines into an aldehyde, ketone, and ammonia.

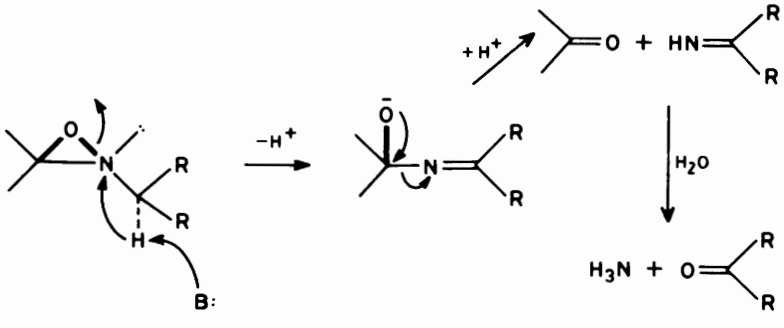


(**1**)

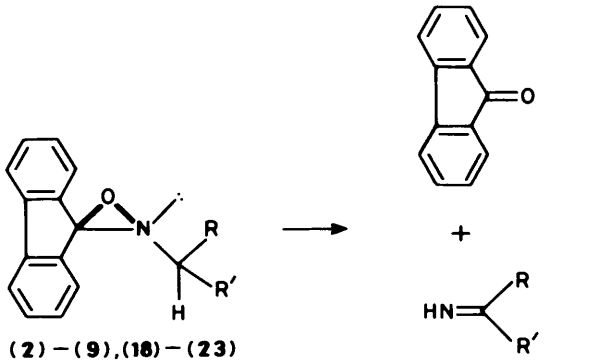
This result indicated that the propionaldehyde product could only have been formed by a mechanism involving an initial rate-determining proton-abstraction step and probably occurred *via* spontaneous decomposition of an NH aldimine intermediate. The latter compound (propionaldimine) was assumed to be unstable under the reaction conditions and has since been shown to decompose at temperatures > −120 °C.[18]

Based upon these ^{2}H-labelling studies,[13,14] a mechanism involving nucleophilic attack of a oxaziridine to yield an ylide intermediate (analogous to the ylide intermediates proposed by Hata *et al.*[2–4]), which decomposed to propionaldimine and finally to carbonyl products and ammonia, was excluded.

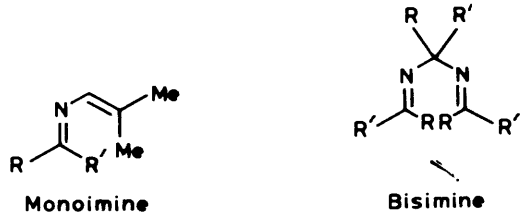
Detection of the slightly more stable conjugated NH aldimine products (by n.m.r. spectroscopy) from the base-catalysed decomposition of oxaziridines[15,16] provided further support for the α-H atom abstraction mechanism. Thus, the base-catalysed



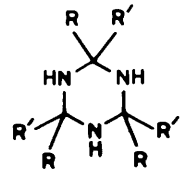
decomposition of a series of oxaziridines (2)—(9) derived from fluorenone initially gave the corresponding NH aldimines (10)—(17). Only the conjugated aldimines (15)—(17) were however detected (low temperature n.m.r. analysis) while the non-conjugated NH aldimines (11)—(13) decomposed to hexahydro-1,3,5-triazines [from (11) and (12)], mono- [from (13)] and bis-[from (12)—(14)] *N*-alkyl imines before they could be detected.



(2)—(9),(18)—(23) (10)—(17),(24)—(29)



Monoimine Bisimine

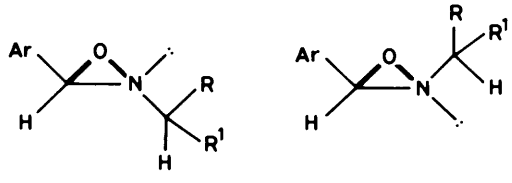


Hexahydro-1,3,5-triazine

R	R'	Oxaziridine	NH Imine	R	R'	Oxaziridine	NH Imine
H	H	(2)	(10)	Ph	Ph	(18)	(24)
H	Me	(3)	(11)	Fluorenyl		(19)	(25)
H	Et	(4)	(12)	Ph	Me	(20)	(26)
H	Pr^i	(5)	(13)	Et	Et	(21)	(27)
H	Bu^t	(6)	(14)	Ph	Bu^t	(22)	(28)
H	$CH{=}CH_2$	(7)	(15)	Mesityl	Me	(23)	(29)
H	$C(Me){=}CH_2$	(8)	(16)				
H	Ph	(9)	(17)				

In the present studies (and the preliminary report[17]) a wider range of oxaziridines derived from fluorenone (18)—(23) has been examined, the initially formed NH ketimine products (24)—(29) being sufficiently stable to be isolated.

Previous studies of base-catalysed decomposition of the oxaziridines (1)—(9) were carried out using amine bases and a range of solvents under mild conditions. Potassium t-butoxide was selected for decomposition studies on the oxaziridines (18)—(23) in order to simplify the isolation of the NH ketimine hydrochloride products (24)—(29). Thus, decomposition of the oxaziridines (18) and (19) at ambient temperature using KOBu^t as a suspension in tetrahydrofuran (THF) solvent gave the NH diaryl ketimines (24) and (25) which were readily separated from the fluorenone product as the insoluble hydrochlorides after passage of dry HCl. The free NH diaryl ketimine products (24)—(25) were liberated by treatment with base. The oxaziridine (20) gave no comparable decomposition products under identical reaction conditions (after 60 h). The NH ketimine (26) was formed however using dimethyl sulphoxide as solvent (KOBu^t was totally soluble in DMSO). The oxaziridines (21)—(23) did not react with KOBu^t in either THF or dimethyl sulphoxide (DMSO) solvent at ambient temperature. These results are in accord with the mechanism suggested[1,12-14] since the α-H atom acidity would be expected to decrease across the series (19) > (18) > (20) > (21). The low reactivity of oxaziridines (22) and (23) may be attributed to steric inhibition of attack by the base. The *peri*-hydrogen atoms on the fluorenyl ring system may also exert a sterically inhibiting effect on the rate of base-catalysed decomposition of oxaziridines (18)—(23). In view of the latter consideration a less hindered range of oxaziridines (30)—(35) were synthesized from the corresponding C-aryl aldimines (Table 1).



trans *cis*

(30) Ar = R = R^1 = Ph
(31) Ar = *p*-$NO_2C_6H_4$, R = R^1 = Ph
(32) Ar = 4-$MeOC_6H_4$, R = R^1 = Ph
(33) Ar = Ph, R—R^1 = fluorenyl
(34) Ar = *p*-$NO_2C_6H_4$, R = Ph, R^1 = Me
(35) Ar = *p*-$NO_2C_6H_4$, R = R^1 = Et

The oxaziridines (30)—(35), unlike the oxaziridines (18)—(23), were obtained as a *cis–trans* mixture of isomers from *m*-chloroperoxybenzoic acid (MCPBA) oxidation of the corresponding aldimines in CH_2Cl_2. The relative ratios of *cis–trans* isomers obtained in each case are not directly comparable however since standard conditions (concentration, temperature *etc.*) were not used. The decreased steric interactions about the *N*-alkyl group of oxaziridines (30)—(35), relative to compounds (18)—(23), can account for their faster rate of base-catalysed decomposition (KOBu^t in THF). The NH diaryl ketimines (24) and (25) were sufficiently stable to be isolated as hydrochloride salts and free bases. A direct spectral comparison of the imines (24) and (25) with authentic samples provided unequivocal evidence for the involvement of NH imine intermediates during base-catalysed decomposition of oxaziridines. The NH alkyl aryl ketimine (26) and NH dialkyl ketimine (27) were also isolated as their hydrochloride salts. Neither the free bases (26) and (27) nor their hydrochlorides proved to be sufficiently stable for acceptable elemental analyses to be obtained and these compounds were thus characterized only by n.m.r. spectroscopy.

A crude n.m.r. analysis of the relative rates of decomposition of oxaziridines (30)—(35) appeared to follow the sequence (33) > (31) > (30) > (32) > (34) > (35). The results thus obtained appeared to parallel the earlier sequence of reactivity for oxaziridines (18)—(23), *i.e.* oxaziridines bearing the more acidic α-H atom reacted faster. The isolated yields of NH ketimine hydrochlorides obtained from the oxaziridines (33) (88%), (30) (90%), (34) (60%), and (35) (52%) were not optimized and probably reflect the relative rates of decomposition to NH ketimines or other products.

Table 1. Relative ratios of *cis*- and *trans*-oxaziridines (**31**)—(**35**) and relative rates of their base-catalysed decomposition

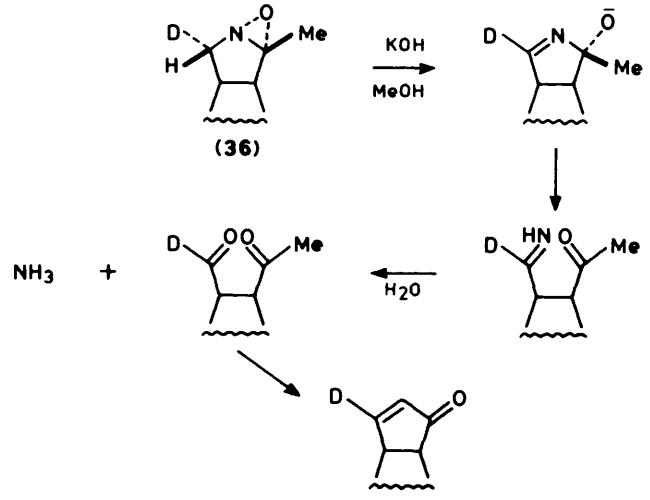
Ar	R	R'	Oxaziridine	NH Ketimine	%cis[a]	%trans[a]	k_t'/k_c'[b]
Ph	Ph	Ph	(**30**)	(**24**)	50	50	
p-$NO_2C_6H_4$	Ph	Ph	(**31**)	(**24**)	51	49	20[c,d]
p-$MeOC_6H_4$	Ph	Ph	(**32**)	(**24**)	38	62	80[c]
Ph	Fluorenyl		(**33**)	(**25**)	74	26	1 000[c]
p-$NO_2C_6H_4$	Ph	Me	(**34**)	(**26**)	38	62	
p-$NO_2C_6H_4$	Et	Et	(**35**)	(**27**)	39	61	2.5[e]

[a] Oxaziridine ratio obtained directly after synthesis. [b] Relative rates of disappearance of *trans* (k_t') and *cis* (k_c') isomers by n.m.r. analysis. [c] DABCO–$CDCl_3$. [d] Bu^{t}OK–$C_6D_5NO_2$. [e] Bu^{t}OK–$(CD_3)_2SO$.

Further evidence for the importance of the α-C–H bond cleavage step during base-catalysed decomposition of oxaziridines derived from benzaldimines was obtained by synthesis of the oxaziridine (**31**). Reduction of benzophenone NH imine (**24**) [derived from the oxaziridine (**30**)] with $LiAlD_4$ gave deuteriated benzhydrylamine which was condensed with *p*-nitrobenzaldehyde. The monodeuteriated aldimine (>98% ^2H) product (**49**) was oxidized to [α-^2H]-2-benzhydryl-3-(*p*-nitrophenyl)oxaziridine (**31**; >98%D) using MCPBA. Base-catalysed decomposition of unlabelled and ^2H-labelled samples of *trans*-(**31**) using Bu^{t}OK in $C_6D_5NO_2$ was monitored by n.m.r. analysis under identical conditions. A primary kinetic isotope effect (k^1_H/k^1_D) of *ca.* 6.0 was obtained. The slightly larger value obtained for oxaziridine *trans*- (**31**) (k^1_H/k^1_D 5.95) compared with that previously reported for oxaziridine **1** (k^1_H/k^1_D 4.3) may be accounted for by the difference in oxaziridines, bases, and solvents. Despite these differences, the mechanism of base-catalysed decomposition of the oxaziridines (**1**) and (**31**) appeared to be similar, *i.e.* α-C–H bond cleavage was involved in the rate-determining initial step.

The stereochemistry of the base-catalysed decomposition of oxaziridines was assumed[1,12,13,14,17] to be directly analogous to that established for the E_2 elimination mechanism for alkene formation.

Thus it was expected that the appropriate N–O and α-CH bonds should adopt an antiperiplanar conformation before elimination could occur. The only previously reported evidence for this preferred geometry was obtained by base-catalysed decomposition of a stereospecifically deuteriated steroidal oxaziridine (**36**) to yield a cyclopentenone product containing 100% of the original deuterium.[19] Exclusive removal of the α-H atom (which was 'locked' into the preferred antiperiplanar conformation) was observed.

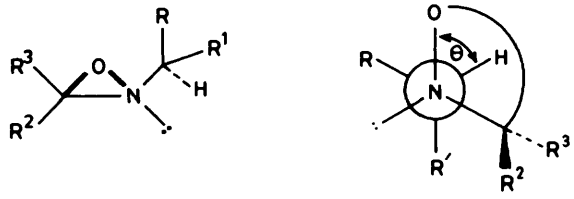


Unfortunately neither the NH aldimine nor the aldehyde intermediates were detected during decomposition of the steroidal oxaziridine (**36**). In order to provide further information on the stereochemistry of the base-catalysed decomposition reaction of oxaziridine, the relative rates of decomposition of *cis* and *trans* isomers of the oxaziridines (**30**)—(**36**) were determined by n.m.r. methods. Perdeuteriated DMSO (Bu^{t}OK), nitrobenzene (Bu^{t}OK), and chloroform (DABCO) were found to be convenient solvents for n.m.r. analysis of the base-catalysed decomposition pathway. It proved to be very difficult to obtain highly accurate and reproducible kinetic data by the n.m.r. method using a single base or solvent due to the relatively poor solubility of KOBu^t and some dark decomposition products. The most reliable values for the relative rates of decomposition of *cis* and *trans* oxaziridines present in the same sample are given in Table 1. Since three different solvent systems were used (DABCO/$CDCl_3$, Bu^{t}OK/$C_6D_5NO_2$, Bu^{t}OK/$(CD_3)_2SO$) direct rate comparisons between these systems cannot be made. Despite these limitations the following conclusions may be drawn. (*a*) In all cases the *cis* isomer reacted more slowly than the *trans* isomer when a mixture of isomers was used. (*b*) The rate difference between *cis* and *trans* isomers was optimal where the R and R' groups had the largest steric requirements.

These results can be rationalized in terms of steric hindrance and conformational preference. Approach of the base to the α-C–H atom will thus be easier if the Ar substituent on the oxaziridine ring is *trans* to the *N*-alkyl group due to lower degree of steric congestion. This faster rate of decomposition of the *trans* isomer contrasts with the earlier observations of Hata *et al.*[2-4] who found that *cis* oxaziridines (having less bulky *N*-alkyl groups) reacted faster with nucleophiles. These observations are consistent with the view that C-atom attack is occurring in the present study while N-atom attack was obtained previously.[2-4]

The preferred conformation of the *N*-alkyl substituent in oxaziridines (**30**—(**35**) also appears to determine the relative rates of decomposition of *cis* and *trans* isomers. The results obtained from four independent *X*-ray crystallographic studies of oxaziridines (**37**)—(**40**)[20-24] (Table 2) indicate that the dihedral angle (θ) between the N–O and α-C–H bond is generally less than 50° in the crystalline state. A comparison of the observed dihedral angle in the crystalline state with the preferred dihedral angle obtained from calculations using molecular mechanics (Chemgraf) has been made (Table 2). The results obtained indicate that the observed (39—50°) and calculated (−18—45°) dihedral angles both deviate markedly from the optimal value (180°) required for the E_2 type of base-catalysed elimination mechanism in oxaziridines. These results can be extrapolated to the *cis* isomers of the oxaziridines (**30**)—(**35**) which may be considered as stereochemically analogous to the oxaziridines (**37**)—(**39**), *i.e.* *C*-aryl and *N*-alkyl oxaziridine ring substituents *cis*. Similarly, the *trans* isomers of oxaziridines

Table 2. Observed and calculated optimal dihedral angle (θ) in the oxaziridines (37)—(40)



Oxaziridine	R	R^1	R^2	R^3	Dihedral[a] angle (θ)°	Calculated[b] dihedral angle (θ)°
(37)[20]	Me	Me	H	p-$NO_2C_6H_4$	40.5	40.5
(−)—(38A)[21]	Me	Ph	Ph	Ph	39.5	15.3
(+)—(38B)[21]	Ph	Me	Ph	Ph	44.7	44.7
(39)[22]	Me	Mesityl	Ph	Ph	50.1	38.1
(40)[23,24]	Me	Ph	p-BrC_6H_4	H	42.2	−18.2

[a] In crystalline state. [b] Calculated using the CHEMGRAF method.

Table 3. Physical properties and microanalytical data for the oxaziridines (18)—(23), (30)—(35) and the imines (41)—(52)

	R	R^1	R^2	R^3	M.p. (°C)	Found (%) C	H	N	Formula	Required (%) C	H	N
(18)	Ph	Ph	Fluorenyl		178—182	86.4	5.2	4.0	$C_{26}H_{19}NO$	86.4	5.3	3.9
(19)	Fluorenyl		Fluorenyl		131—135	87.2	4.7	3.65	$C_{26}H_{17}NO$	86.9	4.8	3.9
(20)	Ph	Me	Fluorenyl		118—120	84.0	5.6	4.6	$C_{21}H_{17}NO$	84.3	5.7	4.7
(21)	Et	Et	Fluorenyl		*a*	(*M*, 265.146 64)			$C_{18}H_{19}NO$	(*M*, 265.146 79)		
(22)	Ph	Bu^t	Fluorenyl		89—91	84.1	6.7	3.9	$C_{24}H_{23}NO$	84.4	6.8	4.1
(23)	Mesityl	Me	Fluorenyl		149	(lit.,[22] m.p. 149 °C)						
(30)	Ph	Ph	Ph	H	90—91[b]	83.4	5.9	4.8	$C_{20}H_{17}NO$	83.6	6.0	4.9
(31)	Ph	Ph	p-$NO_2C_6H_4$	H	100—101[b]	72.0	5.0	8.4	$C_{20}H_{16}N_2O_3$	72.3	4.9	8.4
(32)	Ph	Ph	p-$MeOC_6H_4$	H	101—107[b]	79.1	6.0	4.4	$C_{21}H_{19}NO_2$	79.5	6.0	4.4
(33)	Fluorenyl		Ph	H	117—119[b]	84.0	5.4	4.8	$C_{20}H_{15}NO$	84.2	5.3	4.9
(34)	Ph	Me	p-$NO_2C_6H_4$	H	134—136[b]	66.9	5.4	10.2	$C_{15}H_{14}N_2O_3$	66.7	5.2	10.4
(35)	Et	Et	p-$NO_2C_6H_4$	H	*a,b*	61.1	6.6	11.7	$C_{12}H_{16}N_2O_3$	61.0	6.8	11.9
(41)	Ph	Ph	Fluorenyl		163—165	90.0	5.5	5.5	$C_{26}H_{19}N$	90.4	5.5	4.1
(42)	Fluorenyl		Fluorenyl		194—200	90.3	3.9	5.0	$C_{26}H_{17}N$	90.9	4.1	5.0
(43)	Ph	Me	Fluorenyl		65—67	(lit.,[c] b.p. 165/0.01 mmHg)						
(44)	Et	Et	Fluorenyl		67—70/0.005 mmHg	(*M*, 249.151 62)			$C_{18}H_{19}N$	(*M*, 249.151 73)		
(45)	Ph	Bu^t	Fluorenyl		115—118	88.7	7.3	4.1	$C_{24}H_{23}N$	88.6	7.1	4.3
(46)	Mesityl	Me	Fluorenyl		190—195/0.01 mmHg	(lit.,[22] 190—195/0.01 mmHg)						
(47)	Ph	Ph	Ph	H	95	(lit.,[d] m.p. 98—99 °C)						
(48)	Ph	Ph	p-$NO_2C_6H_4$	H	134—135	75.9	4.9	8.8	$C_{20}H_{16}N_2O_2$	75.9	5.1	8.9
(49)	Ph	Ph	p-$MeOC_6H_4$	H	104—107	83.5	6.4	4.6	$C_{21}H_{19}NO$	83.7	6.4	4.7
(50)	Fluorenyl		Ph	H	138—139	(lit.,[e] m.p. 141 °C)						
(51)	Ph	Me	p-$NO_2C_6H_4$	H	144—148/0.02 mmHg	70.6	5.6	11.0	$C_{15}H_{14}N_2O_2$	70.9	5.6	11.0
(52)	Et	Et	p-$NO_2C_6H_4$	H	93/0.1 mmHg	65.6	7.2	12.7	$C_{12}H_{16}N_2O_2$	65.4	7.3	12.7

[a] High b.p. liquid decomposing during distillation. [b] Isomeric mixture. [c] D. R. Boyd and D. C. Neill, *J. Chem. Soc., Perkin Trans. 1*, 1977, 1308. [d] E. Linow, *Chem. Ber.*, 1893, **26**, 2169. [e] J. Schmidt and H. Stützel, *Chem. Ber.*, 1908, **41**, 1243.

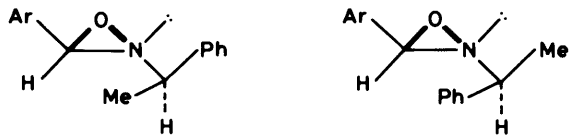
(30)—(35) have comparable stereochemical requirements to the oxaziridine (40).

Based upon application of computer graphics (CHEMGRAF) and an inspection of molecular models of the *cis* and *trans* forms of the oxaziridines (37)—(40), it is evident that much more energy is required to achieve the required 180° dihedral angle in the *cis* isomer. The largest rate differences for *cis* and *trans* isomers of the oxaziridines (30)—(35), were found when the most bulky R, R^1 groups were present. Thus, the energetic requirements for alignment of the oxaziridine N-substituent to the optimal dihedral angle (θ) for an E_2 type base-catalysed elimination (180°) will be less for compound (35; R = R^1 = Et) compared with (33; R,R^1 = fluorenyl). This effect may thus account for the marked rate differences (k^1_{trans}/k^1_{cis}) observed for decomposition of oxaziridines (35) (2.5) and (33) (1 000).

The oxaziridine (34) was found to consist of a mixture of two *cis* [*cis*-(34A) and *cis*-(34B)] and two *trans* diastereoisomers [*trans*-(34A) and *trans*-(34B)]) after synthesis by the imine–peracid route. The individual isomers of the oxaziridine (34) were tentatively assigned the stereochemistry indicated by comparison of the relative proportions formed (from the imine–peracid route) and of their n.m.r. spectral characteristics with the corresponding isomers of the oxaziridine (40). The configurations of the directly comparable stereoisomers of the oxaziridine (40) had previously[23,24] been unequivocally established by rigorous n.m.r. and *X*-ray crystallographic studies and thermal isomerizations.

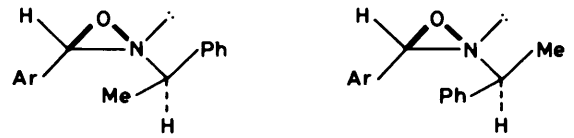
The oxaziridine diastereoisomers [*trans*-(34A), *trans*-(34B), *cis*-(34A) and *cis*-(34B)] are shown in the preferred conformation for a base-catalysed elimination to occur, *i.e.* with the N–O and α-C–H bonds in an antiperiplanar arrangement.

Owing to the formation of reaction products which reduced



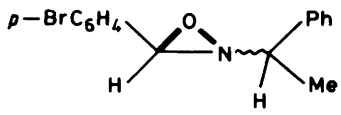
trans—(34A)

trans—(34B)



cis—(34A)

cis—(34B)



(40)

the homogeneity of the sample, it was possible to obtain only an approximate estimate of the relative rates of disappearance of particular isomers (DABCO/$CDCl_3$) which indicated a similar trend to that observed previously, *i.e.* $k_{trans} > k_{cis}$. The observed differential in rates appeared to be in the sequence $k_{trans\text{-}(34A)} > k_{trans\text{-}(34B)} > k_{cis\text{-}(34A)}, k_{cis\text{-}(34B)}$.

In conclusion, the results obtained from base-catalysed decomposition of compounds (**30**)—(**35**) provide clear evidence of the influence of oxaziridine stereochemistry upon reactivity in accord with the α-C–H proton abstraction (E_2 type) mechanism. Further evidence for this mechanism is available from the primary kinetic isotope effect found with the oxaziridine *trans*-(**31**) and from the isolation of NH ketimines (**24**)—(**27**).

Experimental

^{1}H Magnetic resonance spectra were obtained using Jeol model JNM-PMX60 (60 MHz), Hitachi-Perkin Elmer model R-24B (60 MHz), Bruker model WH90 (90 MHz) and WH250 (250 MHz) instruments. Unless specified otherwise all n.m.r. spectra were obtained with $CDCl_3$ solvent and tetramethylsilane as reference. Mass spectra were obtained using an AEI MS-902 instrument operating at 70 eV. Accurate mass measurements were obtained using the peak matching method. Molecular mechanics calculations were carried out using the CHEMGRAF Suite: Program Model, (E. K. Davies: CHEMGRAF User Manual, Chemical Crystallography Laboratory, University of Oxford, Oxford, UK 1984) with a Sigma 5688 monitor and a VAX 11/780 Computer.

The imine precursors of the oxaziridines (**18**)—(**23**) and (**30**)—(**35**) were synthesized by previously reported condensation methods[25,26] from the corresponding amine and aldehyde or ketone. The physical properties and n.m.r. spectral data for the oxaziridines (**18**)—(**23**) and (**30**)—(**35**) and the corresponding imines (**41**)—(**52**) are given in Tables 3 and 4.

Oxaziridines were synthesized by MCPBA oxidation of the corresponding imines in CH_2Cl_2 solution at temperatures in the range 0—5 °C as reported previously.[27] The *cis–trans* mixture of oxaziridines obtained by oxidation of the imines (**47**)—(**52**) was not separated. Microanlaytical data was obtained on the purified mixture after recrystallization, chromatography, or distillation. A sample of [α-^{2}H]benzhydrylamine was prepared by reduction of benzophenone imine (obtained from the oxaziridine (**30**) or by the literature method[28]) using lithium aluminium deuteride in refluxing diethyl ether (12 h), 87% yield, b.p. 89—92 °C/0.15 mmHg, >98%^{2}H (lit.,[29] b.p. 295 °C).

Table 4. N.m.r. spectral data for the imines (**41**)—(**52**) and the oxaziridines (**18**)—(**23**) and (**30**)—(**35**) (δ_H, $CDCl_3$)

(**18**)	5.38 (1 H, s, NCH), 7.0—7.7 (18 H, m, ArH)
(**19**)	5.29 (1 H, s, NCH), 6.4—8.0 (16 H, m, ArH)
(**20**)	1.79 (3 H, d, *J* 6.5 Hz, Me), 4.34 (1 H, q, *J* 6.5 Hz, NCH), 7.0—7.6 (13 H, m, ArH)
(**21**)	0.46 (3 H, t, *J* 7.6 Hz, Me), 1.14 (3 H, t, *J* 7.5 Hz, Me), 1.32 (2 H, m, CH_2), 1.86 (2 H, m, CH_2), 2.93 (1 H, m, NCH), 7.2—7.8 (8 H, m, ArH)
(**22**)	0.68 (9 H, s, Bu^t), 3.89 (1 H, s, NCH), 7.1—7.9 (13 H, m, ArH)
(**23**)[22]	1.67 (3 H, d, *J* 7 Hz, α-Me), 2.00 (3 H, s, *p*-Me), 2.20 (6 H, s, *o*-Me), 3.90 (1 H, m, α-H), 6.53 (2 H, s, *m*-H), 7.1—7.7 (8 H, m, ArH)
trans-(**30**)	4.38 (1 H, s, α-H), 4.84 (1 H, s, 3-H), 6.60—7.56 (15 H, m, ArH)
cis-(**30**)	4.38 (1 H, s, α-H), 5.58 (1 H, s, 3-H), 6.60—7.56 (15 H, m, ArH)
trans-(**31**)	4.42 (1 H, s, α-H), 4.82 (1 H, s, 3-H), 7.0—8.3 (7 H, m, ArH)
cis-(**31**)	4.20 (1 H, s, α-H), 5.44 (1 H, s, 3-H), 7.0—8.3 (7 H, m, ArH)
trans-(**32**)	3.72 (3 H, s, OMe), 4.32 (1 H, s, α-H), 4.66 (1 H, s, 3-H), 6.60—7.56 (14 H, m, ArH)
trans-(**33**)	4.56 (1 H, s, α-H), 4.92 (1 H, s, 3-H), 6.80—8.00 (13 H, m, ArH)
cis-(**33**)	4.48 (1 H, s, α-H), 5.56 (1 H, s, 3-H), 6.80—8.00 (13 H, m, ArH)
trans-(**34A**)	1.68 (3 H, d, *J* 6.4 Hz, α-Me), 4.68 (1 H, s, 3-H), 3.33 (1 H, q, *J* 6.5 Hz, α-H), 6.8—8.4 (9 H, m, ArH)
trans-(**34B**)	1.54 (3 H, d, *J* 6.9 Hz, α-Me), 4.74 (1 H, s, 3-H), 3.46 (1 H, q, *J* 6.9 Hz, α-H), 6.8—8.4 (9 H, m, ArH)
cis-(**34A**)	1.60 (3 H, d, *J* 6.5 Hz, α-Me), 5.32 (1 H, s, 3-H), 3.18 (1 H, q, *J* 6.4 Hz, α-H), 6.8—8.4 (9 H, m, ArH)
cis-(**34B**)	1.09 (3 H, d, *J* 6.8 Hz, α-Me) 5.50 (1 H, s, 3-H), 3.20 (1 H, q, *J* 6.7 Hz, α-H), 6.8—8.4 (9 H, m, ArH)
trans-(**35**)	0.94 (3 H, t, *J* 7.3 Hz, Me), 1.03 (3 H, t, *J* 7.3 Hz, Me), 4.63 (1 H, s, 3-H), 1.45—2.15 (5 H, m, CH_2, α-H), 7.59—8.43 (4 H, m, ArH)
cis-(**35**)	0.58 (3 H, t, *J* 7.3 Hz, Me), 0.91 (3 H, t, *J* 7.3 Hz, Me), 5.34 (1 H, s, 3-H), 1.45—2.15 (5 H, (5 H, m, CH_2, α-H), 7.59—8.43 (4 H, m, ArH)
(**41**)	6.77 (1 H, s, NCH), 7.8—8.1 (18 H, m, ArH)
(**42**)	6.73 (1 H, s, NCH), 7.0—8.3 (16 H, m, ArH)
(**43**)[a]	1.73 (3 H, d, *J* 6.6 Hz, Me), 5.73 (1 H, q, *J* 6.6 Hz, NCH), 7.2—7.9 (13 H, m, ArH)
(**44**)	0.95 (6 H, t, *J* 7.4 Hz, Me), 1.72 (4 H, m, CH_2), 4.37 (1 H, m, NCH), 7.2—7.9 (8 H, m, ArH)
(**45**)	1.05 (9 H, s, Bu^t), 5.16 (1 H, s, CH), 7.1—8.1 (13 H, m, ArH)
(**46**)[22]	1.87 (3 H, d, *J* 7 Hz, α-Me), 2.37 (3 H, s, *p*-Me), 2.70 (6 H, s, σ-Me), 6.25 (1 H, q, α-H), 7.03 (2 H, s, *m*-H), 7.37—8.15 (8 H, m, ArH)
(**47**)	5.70 (1 H, s, α-H), 7.17—8.06 (15 H, m, Ph), 8.50 (1 H, s, HC=N)
(**48**)	5.67 (1 H, s, α-H), 7.33 (10 H, br s, Ph), 8.06 (4 H, m, ArH), 8.43 (1 H, s, HC=N)
(**49**)	3.80 (3 H, s, OMe), 5.50 (1 H, s, α-H), 6.84 (2 H, d, *m*-H, $J_{\alpha,m}$ 8 Hz), 7.27 (10 H, m, ArH), 7.68 (2 H, d, σ-H), 8.24 (1 H, s, HC=N)
(**50**)	5.44 (1 H, s, α-H), 7.16—7.94 (13 H, m, ArH), 8.80 (1 H, s, HC=N)
(**51**)	1.76 (3 H, d, *J* 6 Hz, Me), 4.62 (1 H, 1, α-H), 7.3 (5 H, m, Ph), 7.8 (2 H, d, *J* 8 Hz, σ-H), 8.2 (2 H, d, *J* 8 Hz, *m*-H), 8.4 (1 H, s, HC=N)
(**52**)	0.85 (6 H, t, *J* 7 Hz, Me), 1.70 (4 H, m, CH_2), 3.00 (1 H, m, *J* 6 Hz, *J* 7 Hz, α-H), 8.05 (4 H, m, ArH), 8.35 (1 H, s, HC=N)

[a] See footnote *c* in Table 3.

General Procedure for the Reactions of Oxaziridines with Bases.—The oxaziridine (0.5 mmol) was stirred with a suspension of KOBu^t (0.5 mmol) in dry THF (10 ml) at room temperature for 15 h. The mixture was diluted with dry diethyl

ether (15 ml), filtered, and the NH ketimine isolated either as the free base or as the hydrochloride salt by passing dry HCl through the solution. Yields of hydrochlorides were in the range 50—90%.

Fluorine imine (**25**), m.p. 120—122 °C (lit.[30] m.p. 124 °C), yield 88%.

Benzophenone imine (**24**), oil, yield 90%. Spectrally identical with an authentic sample prepared by a literature method.[28]

Acetophenone imine hydrochloride (**26**), m.p. 126 °C (decomp.), yield 59%; δ 3.0 (3 H, s, Me) and 7.4—8.4 (5 H, m, Ph).

Pentan-3-one imine hydrochloride (**27**), m.p. 170 °C (decomp.), yield 52%; δ 1.07 (6 H, t, *J* 7.4 Hz, Me) and 1.76 (4 H, q, *J* 7.4 Hz, CH_2).

Kinetic Analysis of the Base-catalysed Decomposition of Oxaziridines.—(*a*) The oxaziridine (0.2 mmol) was dissolved in $CDCl_3$ (0.4 ml) and the tertiary amine base (15 μl, satd. solution of DABCO in $CDCl_3$) was added to form a homogeneous solution. The sample was prepared in a standard n.m.r. tube and immediately analysed by the n.m.r. method (60 or 250 MHz) at the specified probe temperature.

(*b*) The oxaziridine (0.2 mmol) was dissolved in [$^2H_5$]-nitrobenzene or $(CD_3)_2SO$ (0.4 ml) in an n.m.r. tube and potassium t-butoxide (0.2 mmol) was added to form a suspension. The rate of decomposition was followed by n.m.r. (60 or 250 MHz) analysis at normal probe temperature.

A plot of ln [oxaziridine concentration] *vs. t* was used to obtain the pseudo-first-order rate constants (k^1). The primary kinetic isotope effect observed ($k^1_H/k^1_D \simeq 6$) during base-catalysed decomposition of *trans*-(**31**) at 34 °C using Bu^{t}OK in $C_6D_5NO_2$ was thus estimated for rate constants of $k^1_H = 5.7 \times 10^{-3}$ and $k^1_D = 0.9 \times 10^{-3} s^{-1}$. Relative rate constants for the decomposition of both *cis* and *trans* isomers of the oxaziridines (**31**)—(**33**) and (**35**) are given in Table 2. In general, accurate rate constants were not obtained and the relative rates were of a more qualitative nature, *i.e.* n.m.r. analysis of the relative proportions of *cis* and *trans* isomers observed initially and after a suitable interval of time.

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