Dynamic Stereochemistry of Imines and Derivatives. Part VI.[1] Stereochemistry of the Peroxyacid–Imine Route to Oxaziridines

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The stereochemistry of the peroxyacid oxidation of *N*-alkyl-aldimines and -ketimines to oxaziridines containing a stable nitrogen pyramid is considered over a range of reaction conditions. The possible relevance of reactant and product molecular geometry in distinguishing between the concerted and stepwise mechanisms is discussed. A comparison is made between rate constants of several peroxyacid oxidation reactions in different solvents. The concerted mechanism appears to be less attractive on the basis of stereochemical and solvent effect data.

THE peroxyacid epoxidation of olefins can be classified as a stereospecific oxygen atom transfer process.[2] Thus, where the barrier to *t*–*c*-olefin † isomerization is high, reactant and product stereochemistry will be identical.[3] In a preliminary communication[4] it was reported that stereospecificity was not a general feature of the analogous imine–peroxyacid synthesis of oxaziridines. In the present report this stereochemical investigation has been enlarged to cover the oxidation of both *C*-alkyl- and *C*-aryl-substituted aldimines and ketimines over a range of experimental conditions.

While the peroxyacid–imine reaction provides a

† Throughout this paper *cis* or *trans* stereochemistry (abbreviated to *c* and *t*) is assigned in accordance with the Sequence Rule, *i.e.* c = *seqcis* and t = *seqtrans* (for double bonds $c = Z$ and $t = E$).

[1] Part V, W. B. Jennings, S. Al-Showiman, M. S. Tolley, and D. R. Boyd, *J.C.S. Perkin II*, 1975, 1535.

[2] B. M. Lynch and K. H. Pausacker, *J. Chem. Soc.*, 1955, 1525.

[3] R. D. Bach, U. Mazur, I. Hamama, and S. K. Lauderback, *Tetrahedron*, 1972, **28**, 1955.

[4] D. R. Boyd, W. B. Jennings, R. Spratt, and D. M. Jerina, *Chem. Comm.*, 1970, 745.

convenient and generally applicable synthetic route to oxaziridines,[5–10] reference to the detection and separation of configurationally stable *t*- and *c*-oxaziridines after oxidation of acyclic imines appears to have been generally[11–13] omitted. The development of synthetic routes and techniques for stereochemical analysis which are applicable to a wide range of *t*–*c*-imines[14–16] and oxaziridines[4,17,18] has now facilitated a systematic study of imine oxidation.

Oxidation with *m*-chloroperbenzoic acid (MCPBA) under controlled conditions (in dichloromethane solution at 20°) was carried out on a range of aldimines (Table 1).

TABLE 1

Oxaziridine isomer ratios from oxidation of *C*-arylaldimines

Compd.	R^1	R^2	% *c*-Imine [a]	% *c*-Oxaziridine [b]
(1)	4-$NO_2C_6H_4$	Me	<1 [c]	54
(2)	4-$NO_2C_6H_4$	Et	<1	52
(3)	4-$NO_2C_6H_4$	Bz	<1	45
(4)	4-$NO_2C_6H_4$	Pr^i	<1	39
(5)	4-$NO_2C_6H_4$	Bu^t	<1	<1
(6)	Ph	Me	<1	51
(7)	1-$C_{10}H_7$	Me	<1	75
(8)	2,6-$Me_2C_6H_3$	Me	6	74 [d]
(9)	2,4,6-$Me_3C_6H_2$	Me	8	73 [d]
(10)	Et	Me	<1	<1
(11)	n-Pr	Me	<1	<1
(12)	Bu^t	Me	<1	<1

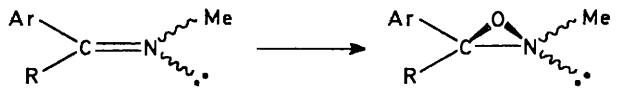
[a] Proportion of the total *t* : *c* equilibrium ratio at room temperature, estimated by n.m.r. integration in $CDCl_3$ solution (±2%). [b] Proportion of the total *t* : *c* product after complete imine oxidation in CH_2Cl_2 at +20°, estimated by n.m.r. integration in $CDCl_3$ solution (±2%). [c] <1 Signifies that no *c*-isomer could be detected using n.m.r. methods. [d] Accompanied by nitrone, 36 and 45% respectively from imines (8) and (9). Decomposition products in other examples generally <5%.

Arenecarbaldehyde derived imines (1)—(5) and (7) were utilized as crystalline *t*-isomers whereas the liquid imines (6), (8), and (9) existed only as an equilibrium mixture; oxidation of all *C*-arylaldimines gave both *t*- and *c*-oxaziridines with the exception of the *N*-t-butyl compound (5). The proportion of *c*-oxaziridine formed was consistently larger than the initial equilibrium proportion of *c*-aldimine. The influence of non-bonded interactions during oxygenation is evident from the decreasing proportion of *c*-oxaziridine with increasing steric size of the *N*-substituent [(1)—(5)]. The highest percentage *c*-oxaziridine was formed from imines containing an *ortho*-substituted aryl ring; these imines generally also possessed the highest proportion of *c*-isomer. No *c*-oxaziridines were detected after oxidation of the *C*-alkylaldimines (10)—(12) although it is possible that the *c*-form could have been formed in a very low concentration, further diminished by rapid decomposition (<5% aldehyde resulting from decomposition was detected).

The oxaziridine distribution from the oxidation of *C*-arylketimines is given in Table 2. The proportion of *c*-oxaziridine increases with increasing steric bulk of the *C*-alkyl group [(13)—(16)]. Indeed when these data are considered in conjunction with those for the analogous aldimine (6) it can be seen that the oxaziridine product

TABLE 2

Oxaziridine isomer ratios from oxidation of *C*-arylketimines



Compd.	Ar	R	% *c*-Imine [a]	% *c*-Oxaziridine [b]
(13)	Ph	Me	7	68
(14)	Ph	Et	26	83
(15)	Ph	Pr^i	95	91
(16)	Ph	Bu^t	100	100
(17)	1-$C_{10}H_7$	Me	77	84
(18)	4-$NO_2C_6H_4$	Ph	35	39 [c]

[a,b] See Table 1. [c] Stereochemistry uncertain.

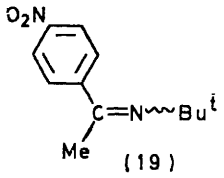
ratio in PhC(R) = NMe changes from 51 to 100% *c*-isomer along the series R = H, Me, Et, Pr^i, and Bu^t. This compares with a much more marked change in the equilibrium ratio of the corresponding imines (0—100% *c*-imine).

The product distribution in the imine–peroxyacid reaction is kinetically controlled as oxaziridine interconversion is slow at ambient temperature with barriers of *ca.* 33 kcal mol^{-1}. In addition, pure samples of both *c*- and *t*-oxaziridines derived from imine (1) remained unchanged when treated with peroxyacid under standard reaction conditions. Unfortunately the position of equilibrium of the diastereoisomeric oxaziridines could generally not be ascertained owing to thermal instability and the high barriers to interconversion. However, heating oxaziridine (1*c*) at 115° in tetrachloroethylene

[5] W. D. Emmons in 'The Chemistry of Heterocyclic Compounds,' ed. A. Weissberger, Interscience, New York, 1964, vol. 19, p. 630.
[6] W. D. Emmons, *J. Amer. Chem. Soc.*, 1957, **79**, 5739.
[7] H. Krimm, *Chem. Ber.*, 1958, **91**, 1057.
[8] L. Horner and E. Jurgens, *Chem. Ber.*, 1957, **90**, 2184.
[9] R. G. Pews, *J. Org. Chem.*, 1967, **32**, 1628.
[10] V. Madan and L. B. Clapp, *J. Amer. Chem. Soc.*, 1969, **91**, 6078; 1970, **92**, 4902.
[11] D. R. Boyd, *Tetrahedron Letters*, 1968, 4561.
[12] D. R. Boyd, R. Spratt, and D. M. Jerina, *J. Chem. Soc.* (*C*), 1969, 2650.
[13] A. Mannschreck, J. Linss, and W. Seitz, *Annalen*, 1969, **727**, 224.
[14] H. J. C. Yeh, H. Ziffer, D. M. Jerina, and D. R. Boyd, *J. Amer. Chem. Soc.*, 1973, **95**, 2741.
[15] J. Bjørgo, D. R. Boyd, C. G. Watson, and W. B. Jennings, *J.C.S. Perkin II*, 1974, 757.
[16] J. Bjørgo, D. R. Boyd, C. G. Watson, W. B. Jennings, and D. M. Jerina, *J.C.S. Perkin II*, 1974, 1081.
[17] J. F. Cannon, J. Daly, J. V. Silverton, D. R. Boyd, and D. M. Jerina, *J.C.S. Perkin II*, 1972, 1137.
[18] W. B. Jennings, D. R. Boyd, C. G. Watson, E. D. Becker, R. B. Bradley, and D. M. Jerina, *J. Amer. Chem. Soc.*, 1972, **94**, 8501.
[19] D. R. Boyd and W. B. Jennings, unpublished data.

solution led to both decomposition and formation of (1*t*) whereas heating (1*t*) resulted in decomposition without detection of (1*c*). This suggests that oxaziridines derived from aldimines may be more stable in the *t*-configuration as would be expected on steric grounds and by analogy with the corresponding imines. The oxaziridines derived from the *N*-t-butylketimine (19) were found to be thermally more stable but configurationally less stable and equilibration proceeded with no observable decomposition in C_2Cl_4 solution at 70° to afford a *c* : *t* ratio of 65 : 35.[19]

The equilibrium preference of this oxaziridine for the *c*-configuration might suggest that the 4-nitrophenyl ring [which is probably twisted out of the Me–C–N plane as shown in (20)] is 'smaller' than a methyl group. Additional factors including possibly attractive and repulsive (*e.g.* n-π repulsion between the nitrogen lone pair of electrons and the aromatic π-cloud) interactions favouring the *c*-isomer may also operate in conjunction with the classical type of steric effect. The equilibrium distribution of this oxaziridine differs considerably from the



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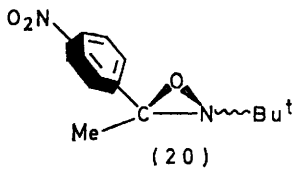


(20)

corresponding imine equilibrium ratio (2% *c*, 98% *t*) and also from the kinetically controlled oxaziridine ratio obtained on oxidation (78% *c*, 22% *t*). The marked preference of the imine for the *E*-configuration can be attributed mainly to steric effects and to the stabilization of this isomer (relative to the more hindered *c*-isomer) by conjugation between the *p*-nitrophenyl ring and the imino-system.

Experiments were carried out with aldimine (1) to determine the sensitivity of the product oxaziridine distribution to changes in the reaction conditions. It was found that a five-fold increase in the molar concentration of both imine and MCPBA had no significant effect on the *c* : *t* oxaziridine ratio. However, alteration of the relative proportion of imine (1) to MCPBA significantly changed the oxaziridine distribution from

TABLE 3

Temperature dependence of *c* : *t* product ratio on oxidation of (1)

Temperature (°C)	−73	−10	+20	+41
(1*c*) (%)	18	46	54	57

45% *c* using imine: MCPBA 10 : 1 to 60% *c* using imine: MCPBA 1 : 2. Further increase in the proportion of MCPBA did not produce a corresponding increase in the *c*-oxaziridine concentration. Similarly the proportion of *c*-oxaziridine produced could be decreased by slowing down the rate of addition of MCPBA solution (a reduction to 30% *c* was observed). Under standard reaction conditions the proportion of *c*-oxaziridine showed a small but reproducible decrease as oxidation proceeded; 62% *c* at 13% imine oxidized compared to 54% *c* at 94% conversion. The final (100% imine oxidation) oxaziridine product ratio was markedly temperature dependent (Table 3).

The effect of solvent upon the oxidation of (1) is given in Table 4. Alcoholic and ethereal solvents had the most marked effect on the product distribution, and altered the ratio in favour of the *t*-isomer.

While the accessibility of oxaziridines in a particular *t* : *c* ratio according to the reaction conditions [3—65% (1*c*)], and the stereospecific formation of one oxaziridine isomer [(5), (10)—(12), (16)] may be of some synthetic value, the present results are of greater interest when considered in conjunction with possible mechanisms of the imine–peroxy acid reaction.

TABLE 4

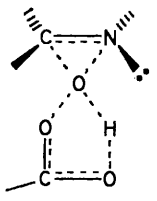
Solvent dependence of *c* : *t* product ratio on oxidation

Solvent	% (1*c*)	Solvent	% (1*c*)
Dichloromethane	53	Dioxan	26
Benzene	50	Ether	24
Carbon tetrachloride	48	Ethyl acetate	22
Cyclohexane	46	t-Butyl alcohol	14
1,2-Dichloroethane	41	Ethanol	3
Chloroform	39		

Oxidations in 0.1% w/v solution at 20°. Aldehyde <12% in all cases.

Emmons [5,6] originally proposed that the oxaziridine synthesis might proceed *via* either (a) a concerted electrophilic attack of the peroxyacid on the imine to form a 'butterfly-type' transition state (21) analogous to that widely accepted for the peroxyacid epoxidation of olefins or (b) a two-step nucleophilic attack of the peroxyacid on the imine by an analogous type of mechanism to that found in the Baeyer–Villiger peroxyacid oxidation of ketones, involving an intermediate of the type (22).

Kinetic studies were conducted by Madan and Clapp [10] and their interpretation was in agreement with the



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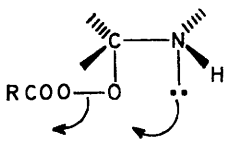


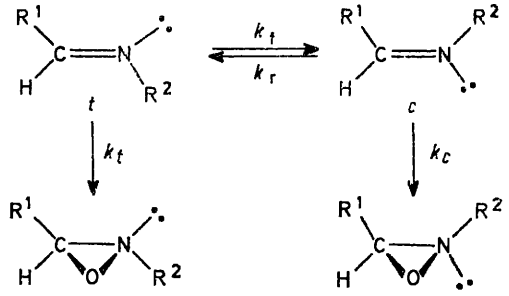
(22)

preference shown by Emmons [5,6] for mechanism (a) but in addition they assumed the peroxyacid to be in dimer form (RCO_3H-HA, HA = solvent, carboxylic acid, or peroxyacid). A recent report by Ogata and Sawaki [20] confirmed and extended these earlier kinetic results but proposed instead a modification of the original two-step mechanism involving reversible protonation of the imine

prior to reversible nucleophilic attack of the peroxyacid. In view of (i) the conflicting interpretations which have been placed upon the complex kinetic data obtained,[10,20] (ii) the additional information which has recently become available about the stereochemistry of imines and oxaziridines,[14-18] and (iii) the reservations expressed about the compatibility of earlier stereochemical studies with a concerted mechanism [4] it is considered timely to re-examine the presently available stereochemical data.

Interpretation of Stereochemical Results on the Basis of a Concerted Mechanism.—As a result of the high *t–c* isomerization barriers in olefins ($\Delta G^{\ddagger}$ *ca.* 65 kcal mol^{-1}) and the nature of the transition state during the peroxyacid epoxidation of olefins, stereospecificity will obtain. The barrier to isomerization of *N*-methylimines is normally in the range $\Delta G^{\ddagger}$ *ca.* 24—27 kcal mol^{-1} but addition of a trace of carboxylic acid has been shown to cause a marked lowering of this barrier.[1] Under the conditions of oxidation carboxylic acid is always present and thus the barrier to isomerization in imines will be lower than the above value. The relatively high barrier to inversion which has been reported for *N*-methyloxaziridines ($\Delta G^{\ddagger}$ *ca.* 33 kcal mol^{-1}) is apparently unaffected by the presence of acid and thus the oxaziridines isolated after synthesis will not have been equilibrated.

In order to account for the large proportion of *c*-oxaziridine found on oxidation of aldimines (1)—(4) and (6)—(9) (Table 1) by a concerted mechanism it is necessary to assume that (a) *c*-aldimine is initially present, (b) crystalline *t*-aldimines equilibrate with the *c*-isomer very much faster than the rate of oxidation, and (c) the rate of oxidation of the *t*-aldimine (k_t) is slower than the corresponding rate for the *c*-isomer (k_t) (Scheme).

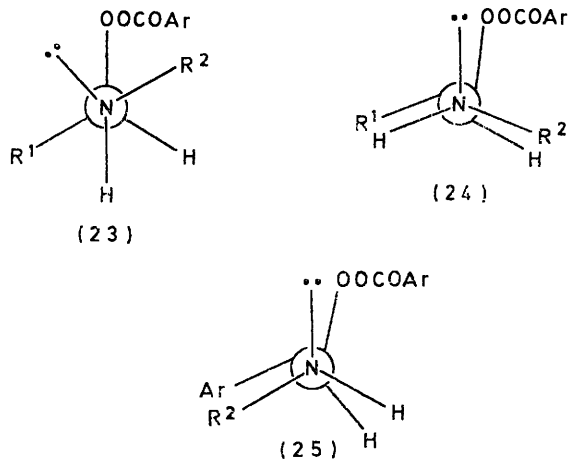


SCHEME k_t and $k_r \gg k_c > k_t$

N.m.r. studies on *t*-aldimines before and immediately after u.v. irradiation showed discrete *N*-methyl signals for (6*c*) and (7*c*) as transient photoproducts which rapidly disappeared on thermal equilibration at ambient temperature; [14] thus the n.m.r. method is capable of distinguishing between *t*- and *c*-aldimines. At thermal equilibrium the proportion of *c*-aldimines in compounds (1)—(7) and (10)—(12) was too low to be detected even in concentrated solution. The concentration of *c*-aldimine at equilibrium could be increased however by introduction of *ortho*-substituents [(8) and (9)].

It is difficult to obtain information on the relative rates of equilibration and oxidation of aldimines in the presence of MCPBA. However, n.m.r. studies on ketimine (18) have shown that imine isomerization occurs *ca.* 8 times faster than oxidation to the oxaziridine.[1] Therefore, on this basis, the possibility of a concerted mechanism for the aldimine–peroxyacid reaction cannot be completely excluded.

Some precedent for a small differential in the rate of oxidation of *t*- and *c*-isomers may be found for the peroxyacid epoxidation of stilbene.[2] The small rate enhancement (*ca.* 2) is found to favour the *c*-olefin, possibly due to a decrease in conjugation between the olefinic and phenyl groups in the *c*-isomer. A smaller rate enhancement might be expected for the imines in Tables 1 and 2 which are less conjugated than the corresponding stilbene isomers. If a significant difference were found in k_t and k_c then the higher initial proportion of *c*-aldimine found in (8) and (9) should lead to an almost complete preference for the *c*-oxaziridine. The relatively small increase in the proportion of *c*-oxaziridine isomer of (8) and (9) (73—74%) over the *c*-oxaziridines (1), (2), (6), (7) (51—75%) is difficult to rationalize by the concerted mechanism. It should be noted however that imines (8) and (9) contain *ortho*-substituents which could lead to some change in the preferred conformation of the aryl ring and could thus conceivably affect the magnitude of the differential between k_t and k_c.



Interpretation of Stereochemical Results on the Basis of a Two-step Mechanism.—In the two-step mechanism the intermediacy of conformers of structure (22) is assumed. According to the Curtin–Hammett Principle the product ratio will depend upon the relative energy levels of the transition states. The ground-state conformational preference for intermediates in the peroxyacid oxidation of imines (based upon non-bonded interactions) may be close to the staggered conformation (23). By the same rationale the transition state preference would thus be similar to the eclipsed conformation (24). A total prefer-

[20] Y. Ogata and Y. Sawaki, *J. Amer. Chem. Soc.*, 1973, **95**, 4687.

ence for the latter conformation might be deduced from the isolation of *t*-oxaziridines alone after oxidation of the *C*-alkylaldimines (10)—(12).

The introduction of a C-aryl substituent previously resulted in a deviation from the expected *t* : *c* equilibrium ratio of *N*-alkylaldimines [15,16] and ketimines [and *N*-alkyloxaziridines (20) [19]]. Thus other factors may be involved in addition to non-bonded interactions. The preferred conformation in the transition state during oxidation of *C*-arylaldimines would be close to that shown in (24; R^1 = Ar) as a result of steric factors alone; other effects however (*e.g.* solvent, hydrogen-bonding, polar, *etc*) may combine to lower the energy level of the alternative conformation (25) and thus give a significant proportion of the *c*-oxaziridine product.

In conclusion it should be emphasised that it is not possible from these stereochemical results alone to provide an unequivocal distinction between the two mechanisms. However, on the basis of all the currently available data the balance would appear to be slightly in favour of the stepwise imine–peroxyacid mechanism.

A recent study [21] of the relative rate constants for the oxidation of (a) sulphides to sulphoxides, (b) nitroso- to nitro-compounds, and (c) sulphoxides to sulphones in a wide range of solvents has been used to distinguish between the concerted [reactions (a) and (b)] and stepwise mechanisms [reaction (c)]. A further comparison of the latter observations with the kinetic data obtained from the olefin–peroxyacid [22] (d) and the imine–peroxy acid reaction [10] (e) now shows that the solvent effects during imine oxidation bear little similarity to the characteristic results associated with a concerted mechanism [reactions (a), (b), and (d)] *i.e.* a fast rate in 'non-basic' [21] solvents (dichloromethane, chloroform, carbon tetrachloride, benzene) and a much slower rate in ' basic ' solvents [dioxan, t-butyl alcohol (Table 5)]. Thus the literature data on solvent effects would again appear to *favour* the stepwise imine–peroxyacid reaction.

TABLE 5

Peroxyacid oxidation rate constants

	(10^2k) [a]	(10^2k) [b]	(10^2k) [c]	(10^4k) [d]	(10^3k) [e]
CH_2Cl_2				225	5.01
$CHCl_3$	146.0	3.60	2.40	472	4.31
CCl_4	63.4	1.31	7.60	77.2	3.36
C_6H_6	134.0	1.99	5.60	156	
Dioxan	13.1	0.28	3.83	9.8	4.83
Bu^tOH	7.3	0.20	1.60	*	1.35

[a] Sulphide ⟶ sulphoxide.[21] [b] Nitroso ⟶ nitro.[21]
[c] Sulphoxide ⟶ sulphone.[21] [d] Olefin ⟶ epoxide.[22]
[e] Imine ⟶ oxaziridine.[10]

* The rate of epoxidation in Bu^tOH is extremely slow (N. N. Schwartz and J. H. Blumbergs, *J. Org. Chem.*, 1964, **29**, 1976) *i.e.* *k* is lower than for other solvents in Table 5.

TABLE 6

Physical properties and microanalytical data

		Found (%)				Required (%)			
Oxaziridines	M.p. (°C)	C	H	N	Formula	C	H	N	NR τ ($CDCl_3$)
(1*t*)	80—81	53.3	4.5		$C_8H_8N_2O_3$	53.3	4.5		7.16 (3H, s)
(1*c*)	94—96	53.5	4.6		$C_8H_8N_2O_3$	53.3	4.5		7.57 (3H, s)
(2*t*)	42—43 (lit.,[6] 42—43)								6.93 (1H, m), 7.20 (1H, m), 8.70 (3H, t)
(2*c*)	81 (lit.,[6] 80—81)								7.47 (1H, m), 7.56 (1H, m), 8.93 (3H, t)
(3*t*)	108	64.8	4.7	10.9	$C_{14}H_{12}N_2O_3$	65.6	4.7	10.9	6.32 (1H, d), 6.44 (1H, d)
(3*c*)	110	65.4	4.7	11.1	$C_{14}H_{12}N_2O_3$	65.6	4.7	10.9	6.93, (1H, d), 6.96 (1H, d)
(4*t*)	101—102 (lit., [6]102—103)								
(4*c*)	42—44 (lit.,[6] 47—48)								
(5*t*)	62—63 (lit.,[6] 62—63)								
(6*t*/*c*) [a]	48 (0.1) [b] [lit.,[10] 45 (0.07)]								
(7*t*/*c*) [a]	*c*	77.2	5.6		$C_{12}H_{11}NO$	77.8	5.9		7.03 (3H, s), 7.63 (3H, s)
(8*t*/*c*)	31 (0.001) [b]	73.9	8.1	8.6	$C_{10}H_{13}NO$	73.6	8.0	8.6	7.12 (3H, s), 7.61 (3H, s)
(9*t*/*c*)	56	74.3	8.3	7.7	$C_{11}H_{15}NO$	74.5	8.5	7.9	7.11 (3H, s), 7.54 (3H, s)
(10*t*)	22 (10)	*M* 87.0685 ± 0.0002			C_4H_9NO	*M* 87.0684			7.25 (3H, s)
(11*t*)	19 (6)	*M* 101.0840 ± 0.0003			$C_5H_{11}NO$	*M* 101.0840			7.25 (3H, s)
(12*t*)	22 (6)	*M* 115.0997 ± 0.0003			$C_6H_{13}NO$	*M* 115.0997			7.20 (3H, s)
(13*t*/*c*) [a]	40—42 (0.05) [b]	72.5	7.4	9.4	$C_9H_{11}NO$	72.5	7.4	9.4	7.10 (3H, s), 7.64 (3H, s)
(14*t*/*c*) [a]	46—48 (0.05) [b]	73.7	8.2	8.3	$C_{10}H_{13}NO$	73.6	8.0	8.6	7.07 (3H, s), 7.63 (3H, s)
(15*t*/*c*) [a]	47—49 (0.05) [b]	74.4	8.5	8.0	$C_{11}H_{15}NO$	74.6	8.5	7.9	7.00 (3H, s), 7.64 (3H, s)
(16*c*)	53—55 (0.05) [b]	75.5	9.0	7.5	$C_{12}H_{17}NO$	75.4	8.9	7.3	7.67 (3H, s)
(17*t*/*c*) [c]	51—56	78.2	6.8	7.0	$C_{13}H_{13}NO$	78.4	6.5	7.0	6.97 (3H, s), 7.60 (3H, s)
(18*t*/*c*) [a,d]	71—72	65.5	4.8	11.0	$C_{14}H_{12}N_2O_3$	65.5	4.7	10.9	7.42 (3H, s), 7.44 (3H, s)

[a] Product mixture containing both *t*- and *c*-isomers. [b] B.p. (*p*/mmHg). [c] High boiling gum which decomposed at elevated temperatures. [d] Stereochemical assignment uncertain.

[21] K. M. Ibne-Rasa, J. O. Edwards, M. T. Kost, and A. R. Gallopo, *Chem. and Ind.*, 1974, 964.
[22] P. Renolen and J. Ugelstad, *J. Chim. phys.*, 1960, **57**, 234.

EXPERIMENTAL

The synthesis and stereochemistry of imines has been previously reported.[15,16] Physical properties, microanalytical data, and accurate molecular weights are recorded in Table 6. The instability of *C*-alkyloxaziridines precluded normal purification techniques and elemental composition was based upon accurate molecular weight determination (sample purity >95% by n.m.r. analysis) using an A.E.I. MS 902 mass spectrometer. N.m.r. spectra were obtained using Varian A-60 and HA-100 instruments and deuteriochloroform as solvent. N.m.r. integration is considered to be accurate to ±2%.

Thermal equilibration of oxaziridines were carried out using purified tetrachloroethylene solvent in n.m.r. tubes sealed *in vacuo* and heated at 130° in a thermostatically controlled oil-bath (±0.1°). Product analysis revealed the presence of aldehyde (major decomposition product), imine, and a trace of hexamethylenetetramine in addition to oxaziridine.

The oxidation of imines to the corresponding oxaziridines was carried out according to the following standard procedure. The imine (0.1 g) was dissolved in dichloromethane (50 ml) and stirred magnetically in a thermostatically controlled bath (+20°). *meta*-Chloroperbenzoic acid (25% excess; 85% active oxygen content; Aldrich) was added instantaneously (no temperature change observed) in dichloromethane (50 ml). The mixture was stirred for 30 min and the oxaziridine product was isolated after washing with 2N-Na_2SO_3, 2N-Na_2CO_3, and drying ($MgSO_4$). Dichloromethane was removed at room temperature under reduced pressure and the product mixture was analysed by n.m.r. The reproducibility of results was verified by duplicate experiments and the relative concentrations of *t*- and *c*-oxaziridines were deduced from multiple integration of the n.m.r. signals.

The stereochemistry of the aldimine-derived oxaziridines (1)—(7) and (12) has previously been established.[12,17,18] The other oxaziridines were assigned stereochemistry on the basis of n.m.r. chemical shift positions, the *N*-alkyl group being further upfield when adjacent to the *C*-aryl group. The stereochemistry of the diaryloxaziridines (18*t* and *c*) is assumed to be analogous to that deduced for the parent ketimine (upfield *N*-methyl signal associated with the *c*-isomer); however this assignment should be considered as tentative.

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