Asymmetric Synthesis at Nitrogen by Oxidation of Imines with *m*-Chloroperbenzoic Acid in the Presence of Optically Active Carbinols. Absolute Stereochemistry of Chiral Alcohol–Imine–Peracid Solvates

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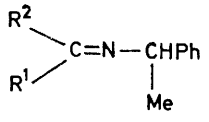
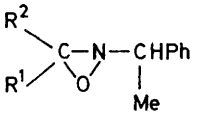
Optically active oxaziridines, stable at the asymmetric nitrogen atom, have been obtained by oxidation of imines with *m*-chloroperbenzoic acid in the presence of chiral carbinols. The optical purity of the reaction products increases on decreasing the temperature and depends on the starting imine and on the nature and relative amount of the chiral solvent. The absolute stereochemistry of the oxaziridines obtained is correlated with the chirality of the alcohol used. Specific carbinol–imine solvation models are discussed in the light of enantiomeric ^{1}H n.m.r. non-equivalence and asymmetric reaction results, obtained by using chiral trifluoromethylcarbinols, imine substrates, and oxaziridine products of well established configuration.

ASYMMETRIC syntheses may be effected by using optically active media in reactions involving prochiral substrates and achiral reagents.[1] As a rule, these reactions are characterized by a low extent of induced stereoselectivity (at best 3—5%).[1] Fairly large asymmetric inductions can be obtained when optically active alcohols are used as the chiral media; for instance, oxidation of sulphides [2] in the presence of chiral alcohols has recently been reported to give enantiomeric excesses of, in some cases, 10—40%.[2]

Previously [3] we observed that oxidation of *N*-methyl- and *N*-t-butyl-imines of type (5) with *m*-chloroperbenzoic acid (MCPBA) gives the corresponding optically active oxaziridines (8a) and (8b) in quite low optical yields (*ca.* 1.5%) when the reactions are carried out in the presence of acyclic or cyclic aliphatic alcohols; the optical purity of the reaction products increases (to *ca.* 9%) when aromatic chiral carbinols are used, and maximum values are achieved (*ca.* 19%) for both oxaziridines (8a) and (8b) with (+)-2,2,2-trifluoro-1-phenylethanol (13).[3] Moreover, in all the cases examined the absolute configuration of the oxaziridines (8) depends on the chirality of the alcohol used.[3] In the present work, oxidation of a variety of ketimines and aldimines of types (1), (2), and (5)—(7) was carried out in the presence of chiral alicyclic and aromatic trifluoromethyl- and methyl-carbinols (12)—(16), in order to study in detail the factors which can influence the extent and stereochemistry of asymmetric reactions involving chiral alcohol–imine–peracid systems and also to develop



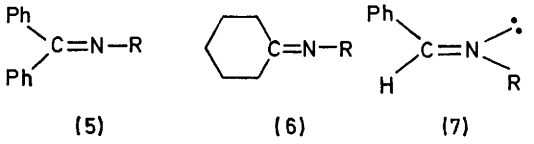
(1) $R^1 = R^2 = Ph$
(2) $R^1 = R^2 = Me$



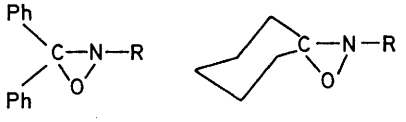
(3a and b) $R^1 = R^2 = Ph$
(4a and b) $R^1 = R^2 = Me$

correlation models which might help to rationalize the results in terms of the absolute configuration at the chiral nitrogen atom of the optically active oxaziridines.

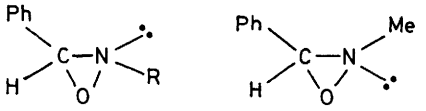
N-(Diphenylmethylene)-α-methylbenzylamine (1) and *N*-(isopropylidene)-α-methylbenzylamine (2) were used as starting imine substrates since (*i*) the conformational behaviour of the diastereoisomeric chiral alcohol–imine solvates, which quite probably is largely responsible for



(5) (6) (7)



(8) (9)



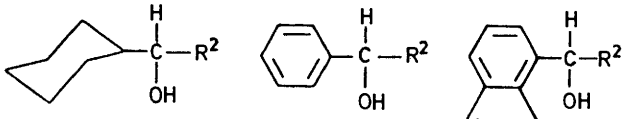
(10) (11)

a; R = Me
b; R = Bu^t

the asymmetric induction results, may be investigated by ^{1}H n.m.r. enantiomeric non-equivalence techniques,[4] by use of mixtures of chiral trifluoromethylcarbinols of type (12)—(14) and partially optically active imines (1) and (2) of known absolute configuration; (*ii*) oxidation of the racemic forms of (1) and (2) in the presence of a chiral alcohol can give not only different amounts of diastereoisomeric oxaziridines (3a and b) and (4a and b), but also a predominance of one enantiomeric species in both (a) and (b) stereoisomers, providing that the reaction is carried out under controlled kinetic conditions (for instance, by using an insufficient amount of the peracid); [5] (*iii*) the absolute configuration of the optically active forms of the diastereoisomeric oxaziridines, which can be obtained in this way, has been well estab-

lished by *X*-ray crystal-structure analysis,[6] and by configurational correlation on the basis of changes in molecular rotation;[7] and (*iv*) the stereochemical information obtained by using the imines (1) and (2) can reasonably be extended to the asymmetric oxidation of imines (5)—(7) in the presence of the same optically active carbinols, owing to the similar aromatic or aliphatic skeleton at the carbon of the C=N bond.

N-Methyl- (5a) and *N*-t-butyl-diphenylmethylenamine



(12) $R^2 = CF_3$
(15) R^2 = Me

(13) $R^2 = CF_3$
(16) R^2 = Me

(14) $R^2 = CF_3$

(5b) were used to study the difference between the asymmetric inducing power of (*R*)-(+)-1-cyclohexyl-2,2,2-trifluoroethanol (12), (*S*)-(+)-2,2,2-trifluoro-1-phenylethanol (13), and (*R*)-(−)-2,2,2-trifluoro-1-(1-naphthyl)-ethanol (14) and that of the defluorinated alcohols (*S*)-(+)-1-cyclohexylethanol (15) and (*S*)-(−)-1-phenylethanol (16). Oxidation of *N*-methyl- (6a) and *N*-t-butyl-cyclohexylideneamine (6b) was carried out in the presence of (*R*)-(+)-(12) and (*R*)-(−)-(14), whereas oxidation of *N*-methyl- (7a) and *N*-t-butyl-benzylideneamine (7b) was effected only with (*R*)-(−)-(14).

^{1}H N.m.r. spectra of partially optically active (*R*)-(1) and (*R*)-(2) were recorded for solutions in CCl_4, at +20 °C and in the presence of a 2—3 fold excess of (*R*)-(+)-(12), (*S*)-(+)-(13), and (*R*)-(−)-(14). The asymmetric oxidations of racemic (1) and (2) were carried out in dichloromethane solution at +20 °C, with 0.5 molar equivalents of MCPBA and in the presence of a 2 molar excess of chiral (12)—(14). Oxidations of the imines (5)—(7) were all carried out in dichloromethane solution at −40 °C and with a 5 molar excess of chiral alcohol. The effects of temperature (+20 and −40 °C) and concentration of carbinol (5 or 2 molar excess) on the extent of the asymmetric oxidations, was studied only with the imines (1), (2), and (5), and by using (*S*)-(+)-(13) as the chiral solvating agent.

RESULTS AND DISCUSSION

In rationalizing the quantitative and qualitative aspects of the present work in terms of conformational behaviour of transient diastereoisomeric chiral alcohol–imine–peracid solvates, it is convenient to analyse in the first instance those results which should depend only on interactions between the chiral solvent and the imine solute. Accordingly, we discuss first the ^{1}H n.m.r. non-equivalence results obtained with the imines (1) and (2) in the presence of the trifluoromethyl chiral solvating agents (12)—(14) (Table 1 and Figure 1), and subsequently the asymmetric induction results observed by oxidation of the imines (1), (2), and (5)—(7) in the presence of the optically active carbinols (12)—(16) (Tables 2—3).

^{1}H *N.m.r. Results.*—Doubling of the methyl resonances is observed when the n.m.r. spectrum of partially optically active (*R*)-(−)-(1) is recorded in the presence of cycloalkyl- (12) as well as aryl- (13) and (14) -trifluoromethylcarbinols. When (*R*)-(+)-(12) is used as the chiral solvating agent, the non-equivalence of the Me signals is very low (0.6 Hz), as expected;[8] it increases to 2.5 and 5.7 Hz with phenyl- (13) and α-naphthyl- (14) carbinols, respectively. The field position of the Me signal of (*R*)-(−)-(1), relative to the field position of the Me signal of (*S*)-(+)-(1) is correlated to the absolute configuration of the alcohol used.

The enantiotopic CH_3 groups of (*R*)-(+)-enriched (2) show no detectable chemical shift difference at 60 MHz, when optically pure (*S*)-(+)-(13) is used as solvent, and Me^1 and Me^2 signals show high-field senses of non-equivalence † with Δν 2.7 and 3.7 Hz, respectively. In

† As high- or low-field sense of non-equivalence, we mean the field position of the (*R*)-enantiomer of both (1) and (2) imines, relative to the field position of (*S*)-(1) and (*S*)-(2).

TABLE 1

^{1}H N.m.r. non-equivalence and asymmetric oxidation induced by optically active trifluoromethylcarbinols (12), (13), and (14) and relative to (*R*)-enriched or racemic imines (1) and (2), respectively

Alcohol	Imine	Δν [a]/Hz [b] (field position) [c]			Oxaziridine							
					Diastereoisomer (a)				Diastereoisomer (b)			
		R¹	R²	Me	% [d]	$[\alpha]_{436}^{20}$ (°) [e]	Optical [f] yield	Absol. [f] config.	% [d]	$[\alpha]_{436}^{20}$ (°) [e]	Optical [f] yield	Absol. [f] config.
(*R*)-(+)-(12) [g]	(1)			0.6 (L)	(3) [h] 88	−9.7	4.9	(2*S*, α*R*)	12	−42.1	7.7	(2*S*, α*S*)
(*S*)-(+)-(13) [g]	(1)			2.5 (H)	(3) [h] 86	+18.3	9.2	(2*R*, α*S*)	14	+67.8	12.4	(2*R*, α*R*)
(*S*)-(+)-(13) [g]	(1)				(3) [i] >95	+48.7	24.5	(2*R*, α*S*)				
(*R*)-(−)-(14) [j]	(1)			5.7 (L)	(3) [h] 87	−19.1	9.6	(2*S*, α*R*)	13	−77.7	14.2	(2*S*, α*S*)
(*S*)-(+)-(13) [g]	(2)	2.7 (H)	3.7 (H)	0	(4) [i] >95	+3.0	3.1	(2*S*, α*R*)				
(*R*)-(−)-(14) [j]	(2)	5.3 (L)	11.5 (L)	2.7 (H)	(4) [h] 80	−0.4	0.4	(2*R*, α*S*)	20	+14.8	5.4	(2*R*, α*R*)

[a] Non-equivalence (Δν) was caused by adding 2- or 3-fold excess of chiral carbinol to a solution composed of 1 : *ca.* 3 mol. ratio of 50% (*R*)-enriched imine and CCl_4. [b] At 60 MHz and 20 °C. [c] Field position of the anisochronous R^1, R^2, and Me groups of (*R*)-imine with respect to (*S*)-imine; H refers to high field and L to low field position. [d] ±4%; values obtained by separation of optically active oxaziridine diastereoisomers through column chromatography. [e] Optical rotations in chloroform solution. [f] Based on the optical value and on the absolute configuration established for optically pure (3a and b) (ref. 6) and (4a and b) (ref. 7). [g] Optically pure trifluoromethylcarbinol was used. [h] Oxaziridine obtained from reaction carried out at 20 °C and with mixture composed of 1 : 2 : 0.5 : *ca.* 38 mol. equiv. ratios of imine–carbinol–MCPBA–CH_2Cl_2. [i] Oxaziridine obtained from reaction carried out at −40 °C and with mixture composed of 1 : 5 : 0.5 : *ca.* 38 mol. equiv. ratios of imine–alcohol–MCPBA–CH_2Cl_2. [j] (*R*)-(−)-(14) 86% optically pure was used; the values reported are corrected to optically pure alcohol.

(*R*)-(—)-(14) the Me^1 and Me^2 groups show low-field senses of non-equivalence ($\Delta\nu$ 5.3 and 11.5 Hz), whereas the signal for the CH_3 group is located at higher field ($\Delta\nu$ 2.7 Hz) with respect to the corresponding signal of (*S*)-(—)-(2). Thus, in the presence of the same chiral solvating agent, the opposite trend of n.m.r. non-equivalence is observed for the resonances of the CH_3 groups of (1) with respect to the corresponding CH_3 groups of (2) (Figure 1)

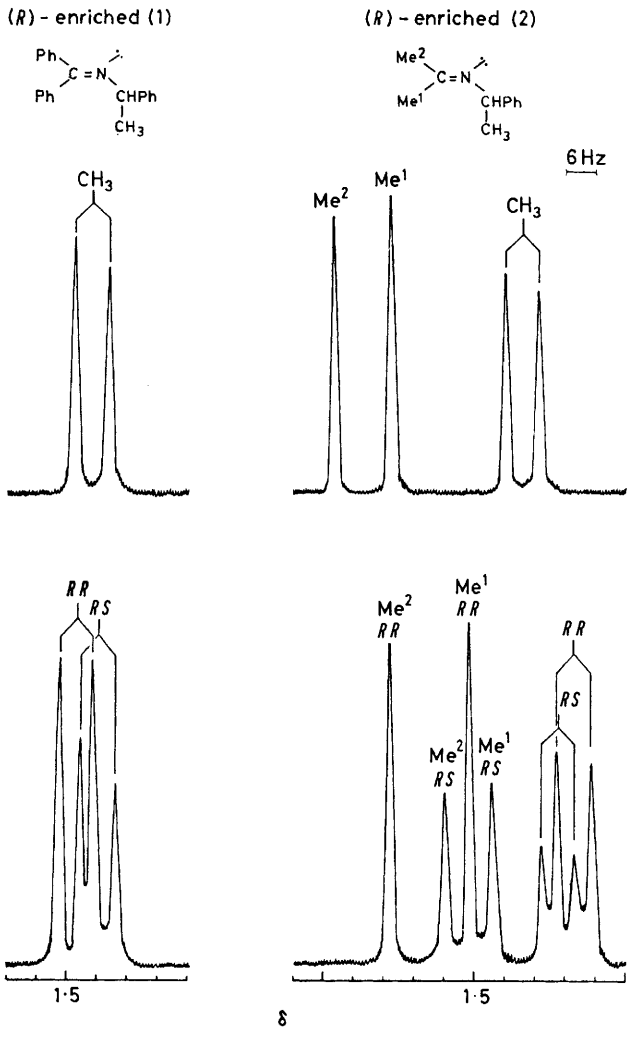


FIGURE 1 60 MHz N.m.r. spectrum of (*R*)-enriched (1) and (2) in the absence (top) and in the presence (bottom) of (*R*)-(—)-(14)

Details of interactions between optically active trifluoromethylcarbinols and a variety of enantiomeric solutes are frequently described by means of solvation models which take into account the ability of the hydroxy-hydrogen of the chiral alcohol to form primary bonding interactions with basic sites of the solute molecule, and the ability of the other substituents of the interacting molecules to form secondary attractive forces.[4] The n.m.r. non-equivalences reported in Table 1 and in Figure 1, for the imines (1) and (2), can be accounted for by the same type of approach, *i.e.* by assuming that short-lived chiral alcohol–imine diastereoisomeric solvates may originate by rapid and reversible hydrogen-bonding between the hydroxy-group of the solvent and the lone pair of the nitrogen atom of both imines (1) and (2), such bonding being chiefly responsible for the life-time of the solvates, while secondary interactions between the other substituents of the solvent and the solute molecules are a major factor in the formation of the conformers believed to be responsible for the observed stereochemical behaviour.

Depending on the nature and the structural features of these primary and secondary factors, one may depict solvation models (Figures 2 and 3) which account for the n.m.r. results reported in Table 1 and Figure 1.

(i) *Chiral trifluoromethylcarbinol–imine* (1) *solvation models.* When the imine (1) is used, secondary interactions can arise between the acidic [9] carbinyl hydrogen of the trifluoromethylcarbinols (12)—(14) and the basic π-electron cloud of the phenyl group *cis* to the lone pair of the nitrogen atom of (1), leading to the conformations of Figure 2.* In this type of conformation, the (*R*) · · · (*R*) diastereoisomer A, arising from interaction between the (*R*)-trifluoromethylcarbinol and (*R*)-(1), has the CH_3 group of the *N*-methylbenzylamine substituent *trans* to the diamagnetically anisotropic R^1 substituent of the chiral solvating agent, causing it to experience a deshielding effect relative to the reversed *cis* position of the same CH_3 group in the (*R*)-trifluoromethylcarbinol · · · (*S*)-imine (1) diastereoisomer B. Accordingly, the resonances of this group should appear at lower field for the (*R*) · · · (*R*) solvate than for the (*R*) · · · (*S*) solvate. The opposite trend should be observed when the (*S*)-trifluoromethylcarbinol is used as the chiral solvent. Moreover, the magnitude of the observed non-equivalence should follow an order linked to the expected cyclohexyl < phenyl < α-naphthyl diamagnetic anisotropic characters.[8]

(ii) *Chiral trifluoromethylcarbinol–imine* (2) *solvation models.* Conformations A and B of Figure 2 do not successfully correlate the n.m.r. results of Table 1 and Figure 1 for the Me^1, Me^2, and CH_3 groups of imine (2). These results are better rationalized by models of type C, C′, and D of Figure 3, in which it is assumed that the conformational behaviour of the chiral trifluoromethylcarbinol–imine (2) solvate is controlled, on the one hand, by weak secondary attractive forces which can arise between the electron rich R^1 (cyclohexyl, phenyl, α-naphthyl) ring of the carbinol and a positively charged site of the imine (2) and, on the other, by a repulsive interaction between the CF_3 group of the carbinol and the Ph ring of the *N*-methylbenzylamine substituent of (2).

* As emphasised in many of such cases, it should be stated that we do not claim A–B and C–D models of Figures 2 and 3 to be preferred ground-state conformations of the molecules under consideration, even if they successfully correlate the results found. On the other hand, we must also realize that these conformations might be effective indeed in the ground state behaviour of the present solvated species, as equilibrium studies of *E–Z* ketimines [10] and space filling molecular models seem to suggest.

Both these types of interaction have been well documented. For instance, asymmetric induction [11] and spectroscopic studies [12] have shown that electronic repulsion between the CF_3 and Ph groups may be

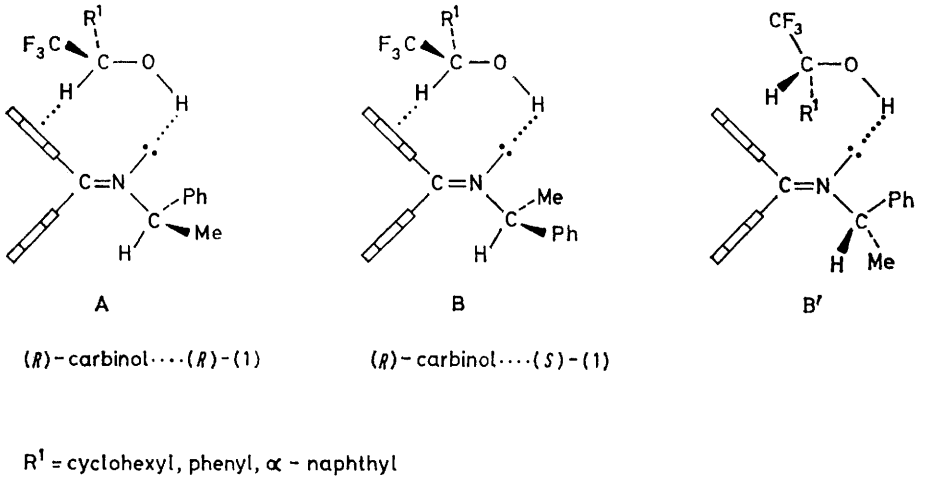


FIGURE 2 Configurational correlation models for (*R*)-(1) · · · (*R*)-trifluoromethylcarbinol A and (*S*)-(1) · · · (*R*)-trifluoromethylcarbinol B solvate

especially large when these two groups are directly juxtaposed as, for example, in models B and C of Figures 2 and 3, respectively. On the other hand, an attractive interaction between the hydrogen atom or the alkyl groups of a variety of polar molecules and the π-electron system of the benzene molecule has been established by

between the imine (2) and the benzene solvent was obtained in our laboratory by means of measurements of the n.m.r. behaviour of the H, CH_3, Me^1, and Me^2 groups of (2), performed in carbon tetrachloride and benzene solutions. The solvent shifts [$\Delta\nu = \nu(CCl_4) - \nu(C_6H_6)$] observed for the signals of the H and of the CH_3 group were −1.8 (for the signal at δ 4.44 in CCl_4) and −5.2 Hz (for the signal at δ 1.34 in CCl_4) respectively. The shifts corresponding to the resonances of the methyl groups at the carbon site of the C=N group were

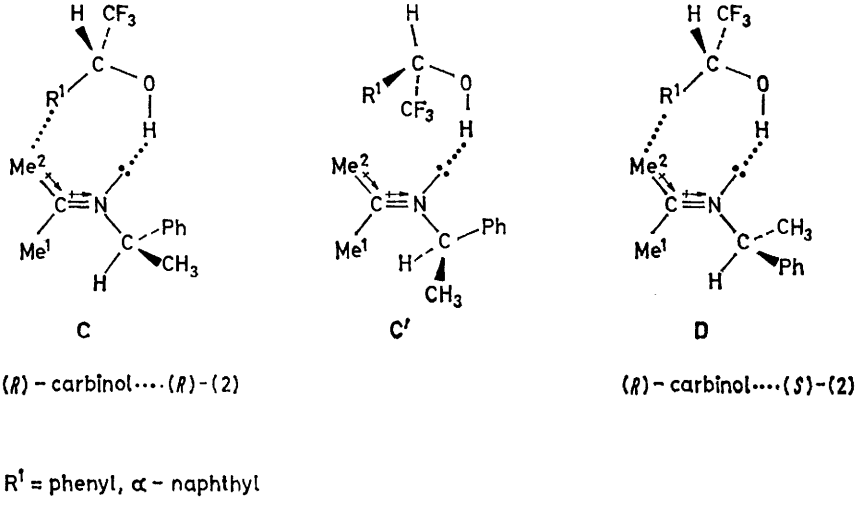


FIGURE 3 Configurational correlation models for (*R*)-(2) · · · (*R*)-trifluoromethylcarbinol C and (*S*)-(2) · · · (*R*)-trifluoromethylcarbinol D solvate

n.m.r. spectroscopy.[13] In these cases, a very similar geometric type of collision complex is assumed, with the dipole axis of the solute molecule located along the six-fold symmetry axis of the benzene nucleus, and with the positive end of the dipole nearest and the negative end farthest away from it.[13]

Evidence for the formation of a collision complex +8.5 and +24.4 Hz, for the signals at δ 1.97 and 1.78 in CCl_4. On the basis of similar structural studies on imines,[14] we assign the considerably larger upfield shift on dilution with benzene to the *cis*-Me^1 group, and the smaller shift to the *trans*-Me^2 substituent.

Depending on the relative importance of these attractive and repulsive forces, the R^1 substituent of the

chiral carbinol should occupy different spatial positions in the two conformations C and D. More particularly, in the solvate C, the R^1 of the solvent should be forced into the pro-(*S*) space by means of rotation and/or distortion of the carbon–oxygen bond of the solvent, and by effect of the electronic repulsion of the CF_3 and Ph groups placed on the same pro-(*R*) face of the C=N bond (model C'), whereas in conformation D the substituents on each side of the pro-(*R*) and pro-(*S*) faces of the C=N should not strongly interact with each other, and the R^1 ring can stay directly superimposed on both Me^2 (the nearest group) and Me^1 of (2). Consequently, the Me^1 and Me^2 substituents of (*R*)-(2) of model C' will experience a weaker (low-field position) and the CH_3 group a stronger (high-field position) shielding effect than the corresponding Me^1, Me^2, and CH_3 groups of (*S*)-(2) (model D), when the n.m.r. spectrum of the imine (2) is recorded in the presence of chiral (*R*)-trifluoromethylcarbinols of type (12)—(14).*

Asymmetric Reaction Results.—Oxidation of racemic (1) and (2) with MCPBA in the presence of the chiral trifluoromethylcarbinols (12)—(14) and under conditions of kinetic control, yields optically active oxaziridines (3a and b) and (4a and b) which exhibit the stereochemical properties shown in Table 1. The (a) or (b) diastereoisomeric configuration and the (*S*) or (*R*) absolute chirality at the asymmetric nitrogen atom of the oxaziridines (3) and (4) were established by comparing their n.m.r. spectra and optical rotation at 436 nm with those reported for the same optically active compounds of well established configuration.[6,7]

In all the cases examined, a large excess (>80%) of the diastereoisomer (a) was obtained, and the oxaziridines (3b) and (4b) were recovered more optically pure than (3a) and (4a). Nevertheless, apart from these similarities, oxidations of the imines (1) and (2) in the presence of the chiral carbinols (12)—(14), provided quite different quantitative and qualitative results. As shown in Table 1, the optical yield and the absolute stereochemistry of the oxaziridines (3a and b) and (4a and b) depend not only on the carbinol used as chiral solvating agent, but also on the structure of the imine substrate; in reactions carried out at 20 °C, the best results [9.6 and 14.2% optical yield for (3a) and (3b), respectively] were obtained with the α-naphthylcarbinol (*R*)-(−)-(14) and with the imine (1), which contains the two Ph substituents at the carbon of the C=N bond, whereas the imine (2), which bears the two Me groups, provided (4a) and (4b) 0.4 and 5.4% optically pure, respectively. Moreover, oxidation of (1) gives predominantly the oxaziridines (3a) and (3b) with (*S*) absolute configuration at the nitrogen atom, whereas oxidation of (2) yields the oxaziridines (4a) and (4b) with the inverted (*R*) configuration, when the reactions are carried out in the presence of the (*R*)-trifluoromethylcarbinols (12) or (14). This contrasting stereochemical behaviour between the oxidations of (1) and (2) is confirmed by the results obtained with the carbinol (*S*)-(13), where the oxaziridines (3a and b) and (4a and b) with (*R*) and (*S*) absolute chirality at nitrogen, respectively, have been obtained (see Table 1 and Figures 2 and 3).

The results reported in Tables 2 and 3 show the following interesting aspects of the asymmetric oxidation of the imines (5)—(7) in the presence of the chiral trifluoromethyl- or methyl-carbinols (12)—(16).

(*a*) Trifluoromethylcarbinols exhibit an inducing power which is 3 to 15 times higher than the corresponding power of methylcarbinols. More particularly, the optical purity of the oxaziridines (8) is relatively low (1—9%) when the oxidation of the imines (5) is carried out at −40 °C in the presence of the methylcarbinols (15) and (16). It reaches higher values (12—34%) when the inducing chiral alcohol contains the trifluoromethyl group (Table 2).

TABLE 2

Asymmetric oxidation of imines (5a) and (5b) with MCPBA in the presence of chiral alcohols at −40 °C [a]

Alcohol [b]	Oxaziridine (8a) $[\alpha]_D^{20}$ (°) [c]	(8a) Optical [d] yield	(8b) $[\alpha]_D^{20}$ (°) [c]	(8b) Optical [e] yield
(*R*)-(+)-(12) [f]	−31.1 [g]	33.0	−32.1	12.4
(*S*)-(+)-(13) [f]	+20.9 [h]	22.2	+49.6 [h]	19.2
(*S*)-(+)-(13) [f]	+16.1 [i]	17.1	+32.2 [i]	12.5
(*S*)-(+)-(13) [f]	+12.8 [h,l]	13.6	+19.4 [h,l]	7.5
(*R*)-(−)-(14)	−23.8	25.3	−71.7 [m]	27.8
(*S*)-(+)-(15) [f]	−2.5	2.6	−5.4	2.0
(*S*)-(−)-(16) [f]	−1.5 [h]	1.6	−23.6 [h]	9.1

[a] Reaction mixture composed of 1 : 5 : 1.1 : 38 mol. ratios of imine–alcohol–MCPBA–CH_2Cl_2. [b] Alcohols of 80—100% optical purity were used. [c] Data for chloroform solutions values corrected for optically pure alcohols. [d] ±2%; enantiomeric excess estimated from the relative peak heights of the enantiotopic Me singlets which appear anisochronous when ^1H n.m.r. spectrum of (8a) is registered with samples composed of 2 : 1 : *ca.* 3 mol. ratios of (*R*)-(−)-(13) : partially optically active (−)-(8a) : CCl_4; in these conditions, the relative chemical shifts (δ) and intensities of the resonances of the Me group are 2.36 (highest peak), 2.34 (lowest peak). [e] Calculated from maximum reported, ref. 15. [f] (*R*)-(12) and (*R*)-(13) trifluoromethylcarbinols are configurationally related to (*S*)-(15) and (*S*)-(16) methylcarbinols, respectively. [g] $[\alpha]_{436}^{20}$ −64.2°. [h] Data from ref. 3. [i] Reaction mixture composed of 1 : 2 : 1.1 : 38 mol. ratios of imine–alcohol–MCPBA–CH_2Cl_2. [l] At +25 °C. [m] $[\alpha]_{436}^{20}$ −152.3°.

Taking into account that the best conditions so far tried may well be improved upon, the enantiomeric excesses observed with (+)-(12), (+)-(13), and (−)-(14) carbinols compare favourably with the best results reported for asymmetric oxidations of the imines (5) by chiral peracids,[15,16] and by photochemical rearrangement in (−)- and (+)-(13) of the nitrone isomer of (8b).[17]

(*b*) Methyl- or trifluoromethyl-cyclohexylcarbinols are more effective inducing solvents than methyl- or trifluoromethyl-arylcarbinols, when used in the oxidation

* Electronic repulsion between the CF_3 and the Ph groups may be effective also in model B and should lead to conformation B' of Figure 2. In this case, however, the relative *cis* position of the CH_3 and R^1 groups is not greatly modified with respect to B. Therefore, at least the qualitative non-equivalence n.m.r. behaviour of the CH_3 of B' should be only slightly modified with respect to the behaviour of the CH_3 of B. Conformation B' seems to play quite an important role in the control of the asymmetric induction results, as is discussed below.

of *N*-methyl ketimine (5a). Opposite results are found for the oxidation of the *N*-t-butyl ketimine (5b) (Table 2).

(*c*) The stereoselectivity of the present type of asymmetric reaction largely depends on the nature of the starting imine: the optical yields of the oxaziridines (9)—(11) are generally quite low (3—8%) and the best results, obtained in these cases for both *N*-methyl and *N*-t-butyl derivatives when the α-naphthyl-(—)- (14) alcohol was used, are still 3 to 6 times lower than the corresponding results reported in Table 2 for the ketimines (1) and (5), on the one hand, and with the *C*-dimethyl-ketimine (2) and the cyclohexyl-imine (6), on the other, must reflect also a uniformity of conformational pattern of the relative diastereoisomeric chiral

TABLE 3

Oxidation of imines (6) and (7) with MCPBA in the presence of (*R*)-(+)-(12) and (*R*)-(—)-(14) at −40 °C [a]

Alcohol	Oxaziridine			
	R = Me		R = Bu^t	
	$[\alpha]_D^{20}$ (°) [b]	Optical yield	$[\alpha]_D^{20}$ (°) [b]	Optical yield
(*R*)-(+)-(12)	(9a) −1.3 [c]	3.4 [d]	(9b) −0.5 [c]	
(*R*)-(—)-(14)	(9a) −3.1	8.0 [d]	(9b) −2.8 [c]	
(*R*)-(—)-(14)	(10a) [f]	7.0 [g]	(10b) −4.1 [c]	4.8 [d]
(*R*)-(—)-(14)	(11) [f]	6.5 [g]		

[a] As Table 2. [b] Values corrected to optically pure alcohols. [c] Rotations taken in CCl_4 using concentration of *ca.* 7%. [d] Based on the maximum reported optical value, ref. 27. [e] In chloroform solution. [f] Obtained as 6.7 : 1 mixture of *trans*-(10a)–*cis*-(11) isomers. [g] ±3%; enantiomeric excess estimated by ^{1}H n.m.r. analysis of the (10a) and (11) mixture of isomers, diluted with CCl_4, and in the presence of (*R*)-(—)-(14). The non-equivalence of the Me-signals ($\Delta\nu$/Hz), and the relative field position of the more intense peak were: 0.99 (high-field position), and 4.06 (low-field position) for (10a) and (11), respectively.

(*d*) The absolute stereochemistry of the oxidation depends on the configuration of the chiral solvent used; the laevorotatory oxaziridines (8), (9), and (10b) are obtained when (*R*)-trifluoromethylcarbinols [or (*S*)-methylcarbinols] are used. Oxaziridines having opposite (+) optical activity are obtained when the oxidations are induced by (*S*)-trifluoromethyl- or (*R*)-methyl-carbinols (Tables 2 and 3).

(*e*) The stereochemical information regarding the prevalent enantiomers of the oxaziridines (10a) and (11), obtained as a *trans–cis* mixture *via* oxidation of the aldimine (7a), was obtained using n.m.r. spectroscopy. In the presence of (*R*)-(—)-(14), *i.e.* of the same trifluoromethylcarbinol used to induce the asymmetric reaction, the prevalent enantiomer of the *trans*-oxaziridine (10a) shows a methyl resonance at high field, whereas the corresponding signal of the prevalent *cis*-oxaziridine (11) shows a low degree of non-equivalence (Table 3).

The data in Tables 2 and 3 closely resemble the trends seen for asymmetric oxidation of the imines (1) and (2). More particularly, the findings of points (*c*) and (*d*), which indicate uniformity of stereochemical behaviour between the reactions carried out with the *C*-diphenyl-imines (5), which contain two Ph substituents at the carbon site of the C=N bond (Table 3).

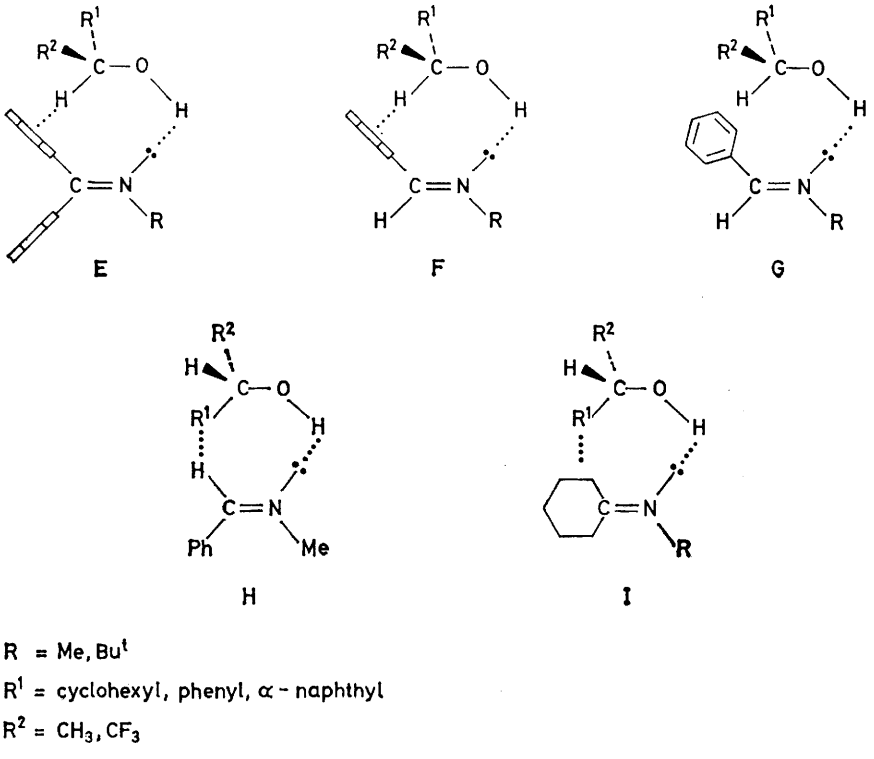


FIGURE 4 Conformational structures of (*R*)-trifluoromethylcarbinol [or (*S*)-methylcarbinol] · · · imine (5)—(7) solvates

alcohol–imine–peracid transition states. Therefore, these results should be of importance when used in connection with the problem of the absolute configuration at the asymmetric nitrogen atom of optically active oxaziridines, or with the more general aspects which characterize the stereochemistry of solvent–solute interactions.

Rationalization of the results of asymmetric induction is in principle difficult, owing to the great dependence of the reactions on minimal and subtle changes of the stereochemical properties of the interacting species. For instance, addition of an achiral peracid to the chiral alcohol–imine system should create very complex stereochemical problems; in fact, among other things, one has to consider the possibility that in the presence of alcohols the oxidizing agent can be hydrogen-bonded to the solvent, thus effectively producing, when the alcohol used is optically active, a ' chiral peracid-form ' which may significantly affect the stereochemical behaviour of the reagents.

Nevertheless, in our opinion, any attempt to reconcile the asymmetric reaction results of the present work with knowledge of the factors underlying such complex chiral alcohol–imine–peracid systems has to take into account the following points: (*i*) experimental [5,18,19] as well as theoretical evidence [20] has been accumulated recently in favour of a two-step mechanism for the oxidation of imines with peracids; (*ii*) stereochemical results seem to indicate that the qualitative and quantitative aspects of asymmetric syntheses of oxaziridines of the type (3), (4), and (8)—(11) are controlled by non-bonded interactions between the reagents during the initial approach of the peracid at the imine carbon atom,[5] the transition state for the formation of the imine–peracid adduct being considered more reactant-like, with that for the second step being more product-like; [5,20] (*iii*) kinetic studies have shown that oxidation of acyclic imines with perbenzoic acid is strongly accelerated by addition of alcohols, this result having been explained in terms of a two-step mechanism, by assuming that the catalysis is due to hydrogen bonding between the imine nitrogen and the protic solvent, with formation of a hydrogen-bonded peracid-alcohol dimer being excluded.[19]

These assumptions are of importance when applied to the systems in the present work, since they may signify that, in the presence of a 2—5 molar excess of optically active alcohols, the results of Tables 1—3 do not depend on the chiral peracid–carbinol dimer, but most probably on the chiral alcohol–imine solvate which, very possibly, interacts with the intramolecularly bonded achiral form [20,21] of MCPBA. Therefore, we shall attempt to rationalize the results observed with the oxaziridines (3), (4), and (8)—(11) by means of the same factors underlying models A—D of Figures 2 and 3, and by assuming that the optical yields and configurational correlations reported in Tables 1—3 are essentially controlled by the strength and nature of the same primary and secondary interactions between the chiral carbinol and the imine as have been discussed and used to account for the n.m.r. results of Table 1 and of Figure 1, and also by differences in non-bonded steric and electronic interactions between the approaching peracid and the substituents of the chiral solvent and of the solute on either side of the two prochiral faces of the C=N bond.

(i) *Optical yields of oxaziridines.* The assumption that the strength of the primary bonding should play a major role in the control of the life-time of solvates arising from interaction of the alcoholic solvent and basic solute is well demonstrated by the findings of Table 2 [point (*a*)], where the optical yields of the oxaziridines (8a) and (8b) follow the order of the trifluoromethyl- $\gg$ methyl-carbinol acidic power.

The strength of the primary bonding, which involves the proximate surrounding of the nitrogen site of the C=N, should not depend only on the acidic character of the hydroxy-group of the solvent, but also on the extent of steric hindrance to the approach of the solvent offered by the substituent at the nitrogen atom. The results of Table 2 described in point (*b*) seem to indicate that when the imine (5a) is dissolved in the chiral alcohol the relatively small bulk of the *N*-methyl group does not hinder the primary bonding between the solvent and the imine; consequently, the life-time of the solvate should not depend on variations of the acidic strength of methylcyclohexyl- *versus* methylaryl- or trifluoromethylcyclohexyl- *versus* trifluoromethylaryl-carbinols, and the observed stereochemical results should be a consequence of structural behaviour of solvates of type E (Figure 4) in which the steric requirements of aryl groups (R^1 = phenyl, α-naphthyl) in a particular conformation may be lower than the requirements of a cyclic methylene-group (R^1 = cyclohexyl) with respect to CH_3 or CF_3 (R^2 substituent). On the contrary, when the imine (5b) is solvated by the chiral alcohol, the large *N*-t-butyl group interacts with the approaching solvent and the life-time of the solute–solvent complex should depend on the α-naphthyl > phenyl > cyclohexyl-carbinol relative hydrogen-bonding power, as indicated by the relative order of the optical yields of (8b).

Some interesting conclusions about the role played by secondary interactions between the substituents of the chiral solvent and of the imine solute on the extent of the asymmetric inductions of the present work can be reached, on the one hand, by comparing the results of the asymmetric syntheses of the oxaziridines (3) and (8) with the results of the oxaziridines (4), (9), and (11) [point (*c*)], and, on the other, by analysing the results of the same compounds (3) and (8) with respect to the results of the oxaziridines (10a) and (10b) of Table 3. In the first case, the quite higher optical yields observed for (3) and (8) when compared with those of (4), (9), and (11) indicate that the attractive interaction between the carbinyl hydrogen of trifluoromethylcarbinols and the basic phenyl site of imines (1) and (5), which should stabilize models of type A–B and E, is considerably stronger than the interaction between the R^1 group of the solvent and the cycloalkyl, methyl, or hydrogen substituents of the polar imines of models C–D and H

and I. In the second case, the (8) ⩾ (10) trend of the optical yields seems to indicate that the strength of the conformational control of chiral alcohol–imine solvates, when dependent on secondary carbinyl–hydrogen bonding, does implicate also a proper time-averaged conformational preference of the basic groups of the molecule potentially involved in the secondary attractive force. As anticipated in the preceding discussion, in models A and B and in the solvate E, interaction between the *gem*-phenyl groups of the imines (1) and (5) should oblige these rings to be twisted from the C=N plane and, consequently, to present suitable geometry for an attractive interaction with the carbinyl hydrogen of the solvent to be strongly effective; on the contrary, in the *trans*-aldimines (7a) and (7b), the twisted conformational preference of the phenyl ring will be opposed by the resonance energy which favours the coplanar conformation of the phenyl-imine group depicted in model G of Figure 4, and which essentially acts to reduce the life-time of conformation F and, of consequence, the extent of the optical yields of the oxaziridines (10a) and (10b).

(ii) *Absolute configuration at nitrogen of the oxaziridines.* Problems of configurational assignment from asymmetric induction results are conventionally looked at in terms of electronic and/or steric requirements of the substituents of the reacting species. Electronic interactions between the phenyl- or α-naphthyl-ring or between the trifluoromethyl group and MCPBA, *i.e.* between the electronegative substituents of the solvent and of the solute on either one or the other side of the C=N prochiral faces (see models A–B, C–D, and E–I of Figures 2, 3, and 4, respectively) and the oxidative agent, seem to be ineffective in the present systems, as shown by the observation that oxidations in the presence of cyclohexyl- or methyl-carbinols provide oxaziridines with the same sign of rotation as oxidations in the presence of phenyl- and α-naphthyl-carbinols or trifluoromethyl-carbinols, respectively. It is therefore on steric grounds alone that we shall attempt to rationalize the qualitative aspects of Tables 1—3, by considering, in particular, the size properties of cyclohexyl, phenyl, α-naphthyl, trifluoromethyl, methyl, and hydrogen groups of the chiral solvent and of the imine solute.

Taking into account the established absolute configuration of the oxaziridines (3) [6] and (4),[7] we can realize that the trend of the optical yields and of the absolute stereochemical correlations of Table 1 can be predicted on the basis of the models of Figures 2 and 3, with the assumption that the stereochemical behaviour of the chiral trifluoromethylcarbinol–imine (1) or –imine (2) solvate towards the preferred attack of the peracid depends first, on the relative steric requirements of the H, Me, and Ph substituents at nitrogen more than on size properties of the groups of the carbinol, the ligands at the imine C=N bond being more proximate to the reaction site; secondly, on conformations B′ and C′, which can be stabilized by the electronic repulsion of the CF_3 and Ph groups directly juxtaposed in B and C; and finally, on the $R^1 > R^2 > H$ relative order of steric bulk.*

Accordingly, from solvates A and D we should expect preferred *pro*-(*S*)-(3a) and *pro*-(*R*)-(4a) direction of attack of the peracid, respectively, and from conformations B′ and C′, a *much* preferred *pro*-(*S*)-(3b) and *pro*-(*R*)-(4b) reaction, as were observed when the oxidations of racemic (1) and (2) were carried out in the presence of the (*R*)-trifluoromethylcarbinols (12) and (14).

Solvates E—I of Figure 4 do not present the complex conformational possibilities inherent in the solvates A–B and C–D. Electronic interaction between Me and Bu^t substituents at nitrogen and the electronegative groups of the chiral solvent should be ineffective in these adducts; moreover, the Me and Bu^t groups possess C_{3v} symmetry and can be considered to offer approximately the same steric interaction on both faces of the C=N bond, regardless of the specific orientation proximate to the prochiral reaction site.

From the rationalization of the configurational correlations reported in Tables 2 and 3 with models E, F, and I, and the assumption that the preferred direction of the peracid attack at C=N depends on the $R^1 > R^2 >$ carbinyl-H steric relation of the substituents of the chiral solvent, we conclude that oxidations of the imines (5)—(7) in the presence of chiral carbinols with the depicted stereochemistry of Figure 4 should provide the oxaziridines (8)—(10) with the *same* (−)-(*S*) absolute configuration at the chiral nitrogen, whereas oxidations with carbinols having opposite (*S*)-trifluoromethyl or (*R*)-methyl configuration, should give oxaziridines with the *same* (+)-(*R*) chirality at nitrogen.

The results obtained with the imine (7a) and described in point (*e*), need more discussion. In fact, configurational assignment with model H of Figure 4 to oxaziridine (11), which has been obtained together with the *trans*-(10a) isomer by oxidation of the *trans*-aldimine (7a), should imply that the observed stereochemical behaviour of (11) depends on interaction between the chiral alcohol and the *cis*-isomer of the *N*-methylbenzylideneamine, and not from isomerization of the optically active *trans*-oxaziridine (10a) to the *cis*-isomer (11). Stereochemical studies have shown that isomerization of *trans*-*N*-methyl aldimines of type (7a) to the *cis*-derivatives is catalysed by peracids and, even more, by carboxylic acids, and that in these cases *trans*–*cis* equilibria are reached faster that the reaction of imines with peracids.[24] Therefore, we can reasonably postulate that oxidation with MCPBA of the *trans*-imine (7a), obtained by condensation of benzaldehyde with *N*-methylamine,[10] does involve in effect both *E*- and *Z*-isomers of *N*-methylbenzylideneamine and, from the solvates F and H, we can assign to the prevalent enantiomers of oxaziridines (10a) and (11), which exhibit

* It should be noted that the reported steric preference, which in models A—D signifies (cyclohexyl, phenyl, α-naphthyl) > (CF_3, CH_3) > H, is not so obvious as it would appear, owing to the complexity of the group-size concept,[22] and to the suggestion that, in some cases, the size of the aryl group is similar to or perhaps slightly less than the methyl or trifluoromethyl group.[23]

the properties of point (*e*) (Table 3), the *same*-(*S*) configuration at nitrogen.

The absolute configuration of oxaziridines of the type (8)—(11) is a long standing problem, which has been only recently treated and solved, even if not unequivocally, by means of reasonable stereochemical [5] and spectroscopic [25-27] correlations. For instance, configurational assignments for the oxaziridines (8) have been reported based on a dynamic stereochemistry investigation of the chiral peracid–imine reaction [5] and by c.d. spectroscopy,[25] and the absolute chirality of the oxaziridines (9a), (10), and (11) has been postulated on the basis of n.m.r. enantiomeric non-equivalence registered in the presence of trifluoromethylcarbinols.[26,27]

All the configurational assignments made in the present work by means of models of Figure 4 are in good accord with the previously reported structures of the chiral oxaziridines (8)—(11).[5,25-27] This result, together with the quantitative aspects of Tables 1—3, strongly suggests that chiral methyl- and trifluoromethyl-carbinols represent powerful solvating agents for the study of the absolute stereochemistry of asymmetric reactions of a variety of basic and polar prochiral substrates, and also indicates the relative importance of the factors which commonly underlie the stereochemical behaviour of short-lived solvent–solute complexes.

EXPERIMENTAL

Optical rotations were measured with a Perkin-Elmer 141 polarimeter with cells of 1 or 10 cm path length. Quantitative i.r. measurements were made with a Perkin-Elmer 257 instrument, for weighed solutions of sample–CCl_4 (0.1—0.5% ratio), and following the 'base line density' method.[28] N.m.r. spectra were registered in CCl_4 (Me_4Si as internal standard) with a JEOL C-60-HL spectrometer. For the ^1H n.m.r. spectra registered in optically active solvent, mixtures of 50% enantiomerically enriched imines (1) or (2), or of optically active oxaziridines, chiral alcohol, and CCl_4 (1 : 2—3 : 3 molar ratios) were used, at +20 °C. ^1H N.m.r. quantitative data are considered to be accurate to ±3%. Mass spectra were determined with a Varian MAT-112 instrument.

Starting Materials.—Optically active and racemic imines (1) [5] and (2),[18] *N*-methyl and *N*-t-butyl ketimines (5) [29] and (6),[30] and aldimines (7) [31] were prepared by condensation of the carbonyl compound and amine. The physical properties of these compounds are consistent with those reported in the literature.

The chiral alcohols (12), (14), and (15) were obtained by reduction of the corresponding ketones by actively fermenting yeast.[32] They showed the following properties: (*R*)-(+)-1-cyclohexyl-2,2,2-trifluoroethanol (12), b.p. 73—74° at 15 mmHg, $[\alpha]_D^{25}$ +17.8° (*c*, 4.1 in $CHCl_3$), n_D^{20} 1.423 4, *m/e* 182 (M^+) and 164 ($M^+ - H_2O$); (*R*)-(−)-2,2,2-trifluoro-1-(1-naphthyl)ethanol (14), b.p. 160° at 2 mmHg, $[\alpha]_D^{25}$ −22.1° (*c*, 2.8 in ethanol), n_D^{20} 1.558 0, *m/e* 226 (M^+) {lit.,[33] m.p. 51.6—53.2°, $[\alpha]_D^{25\cdot3}$ −25.7° (ethanol)}; (*S*)-(+)-1-cyclohexylethanol (15), b.p. 86—87° at 16 mmHg, $[\alpha]_D^{25}$ +5.3° (neat), n_D^{20} 1.466 7 {lit.,[34] b.p. 82—83° at 12 mmHg, $[\alpha]_D^{25}$ ±5.6° (neat), n_D^{25} 1.463 5}.

(*S*)-(+)-2,2,2-Trifluoro-1-phenylethanol (13) was obtained by fractional crystallization of the esters of the racemate with (−)-ω-camphanic acid,[35] b.p. 83—85° at 14 mmHg, $[\alpha]_D^{20}$ +41.2 (neat) {lit.,[35] b.p. 100—110° at 0.6 mmHg, $[\alpha]_D^{20}$ +41.3 (neat)}.

(*S*)-(−)-1-Phenylethanol (16) was obtained by optical resolution of the racemate, as described in the literature,[36] b.p. 88° at 12 mmHg, $[\alpha]_D^{25}$ −43.3° (neat), n_D^{20} 1.527 3 {lit.,[37] b.p. 93° at 14 mmHg, $[\alpha]_D$ −43.6° (neat)}.

Oxaziridine Syntheses.—Mixtures of imine (1 mmol) and chiral alcohol (2 or 5 mmol) were diluted with CH_2Cl_2 (0.4 ml) and treated at +20 or −40° with a solution of 1.1 mmol of *m*-chloroperbenzoic acid (MCPBA) in CH_2Cl_2 (2 ml) [racemic imines (1) and (2) were oxidized with 0.5 mmol of MCPBA]. The reaction mixture was kept 6 h at the selected temperature and then repeatedly extracted with saturated aqueous sodium hydrogencarbonate, washed with water, dried (Na_2SO_4), and evaporated. In every case, the crude mixture of the reactions contained more than 80% of oxaziridines [more than 40% from reactions with imines (1) and (2)], and less than 5% of product of decomposition (the original carbonyl compound, as determined by quantitative i.r. measurements).

The optically active diastereoisomers (3a and b) and (4a and b) were separated and purified, and the optically active oxaziridines (8), (9), and (10b) were recovered as pure compounds by column chromatography on silica [CH_2Cl_2–hexane (70 : 30 v/v)], or alumina [CH_2Cl_2–hexane (90 : 10 v/v)], prior to optical rotation measurements. ^1H N.m.r. and i.r. spectroscopy as well as t.l.c. showed that the oxaziridines obtained were completely free from traces of chiral carbinol.

The relative (a) and (b) amounts of diastereoisomeric oxaziridines (3a) and (3b), and (4a) and (4b) were determined by integration of the n.m.r. resonances of the diastereotopic Me group, whereas the (a) and (b) configuration and the absolute stereochemistry of the non-racemic oxaziridines obtained were assigned by their n.m.r. spectra and by the sign of the optical rotation of the eluates, and by comparison of the results obtained with the previously reported n.m.r. spectra and optical activities of (−)-(2*S*,α*R*)- and (+)-(2*R*,α*S*)-(3a) with (−)-(2*S*,α*S*)- and (+)-(2*R*,α*R*)-(3b),[6] and (+)-(2*S*,α*R*)- and (−)-(2*R*,α*S*)-(4a) with (−)-(2*S*,α*S*)- and (+)-(2*R*,α*R*)-(4b).[7]

Oxidation of the aldimine (7a) provided a crude reaction product which, after the removal of *m*-chlorobenzoic acid and of the solvent, was essentially composed of the chiral alcohol and of a mixture of *trans*-(10a) and *cis*-2-methyl-3-phenyloxaziridine (11). In this case, the rotations of pure (10a) and (11) were not determined, but the unrefined reaction product was diluted with CCl_4 and directly analysed by n.m.r. spectroscopy. The presence in the crude reaction mixture of (*R*)-(−)-(14), employed as chiral solvent for the asymmetric oxidation of (7a), allowed contemporaneous determination of the proportion of the total (10a) : (11) oxaziridine product, as well as of the enantiomeric composition of the *trans*-(10a) and *cis*-(11) isomers. The diastereotopic pattern of the n.m.r. signals has been clearly and unambiguously observed only in correspondence of the resonances of the Me-groups of (10a) and (11). The relative results are reported in Table 3.

The oxaziridines (8)—(11) have previously been reported in the literature.[15,16,38]

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