Dynamic Stereochemistry of Imines and Derivatives. Part IX.[1] The Mechanism of *E–Z* Isomerization in *N*-Alkylimines

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Rates of *E–Z* isomerization in *N*-alkylimines have been determined by direct thermal stereomutation and by dynamic n.m.r. spectroscopy. Thermal racemization rates of optically active *para*-disubstituted 2-t-butyl-3,3-diphenyloxaziridines have also been measured, and show a small but consistent correlation with Hammett σ_p. Comparison of the activation parameters for imine isomerization with data for nitrogen inversion in oxaziridines indicates that *N*-alkylimines isomerize by a planar inversion (lateral shift) mechanism. Barriers determined for an aldimine under optimal conditions are higher than previously reported for imines (*ca.* 30 kcal mol^{-1}).

THE process of isomerization or topomerization about a carbon–nitrogen double bond has aroused considerable interest and has been the subject of several recent reviews.[2,3] Imines, as the parent structure of molecules containing a C=N bond, have received most attention. Two mechanisms have been considered for thermal *E–Z* isomerization *viz.* rotation through 180° around the imino-bond or planar inversion through 120° at the nitrogen atom (a lateral shift);[2] an intermediate itinerary has also been postulated.[4,5] The barrier to interconversion of *N*-alkylimines may be lowered by reversible acid catalysis[6] or by reversible imine–enamine tautomerism.[7]

Systematic experimental investigations of *E–Z* isomerization in imines have to date been mainly concerned with *N*-aryl compounds. The balance of evidence for *N*-arylimines appears to favour a nitrogen inversion mechanism on the basis of steric and electronic substituent effects. The latter conclusions are complicated by the conformation dependent steric and electronic interactions of the *N*-aryl group.[3] Furthermore, the above mechanistic conclusions for *E–Z* isomerization of *N*-arylimines cannot *a priori* be extended to *N*-alkylimines since *N*-aryl substituents generally facilitate the nitrogen inversion process, *e.g.* $\Delta G^{\ddagger}$ 11.7 and 22.3 kcal mol^{-1} respectively for pyramidal inversion in *N*-phenyl- and *N*-methyl-aziridine.[3]

Studies of *E–Z*-*N*-alkylimine isomerization appear to have been largely neglected and so prompted our preliminary report on the interconversion of *E–Z* isomers of *N*-alkylketimines by dynamic n.m.r. spectroscopy.[7]
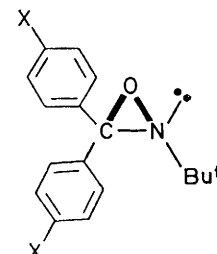
The most relevant of the earlier isomerization data for *N*-alkyl imines has been reported by Curtin and Hausser.[8]
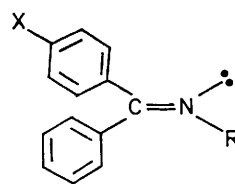
E		*Z*
(1) X = NMe$_2$;	R = Me	
(2) X = OMe;	R = Me	
(3) X = Cl ;	R = Me	
(4) X = Br;	R = Me	
(5) X = NO$_2$;	R = Me	
(6) X = NO$_2$;	R = CH$_2$CMe$_3$	
(7) X = NO$_2$;	R = Bu^t	
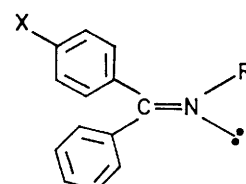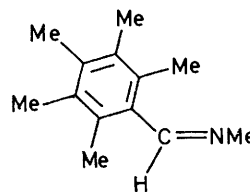
(8)

(9) X = Me
(10) X = H
(11) X = Br
(12) X = NO$_2$

Using u.v. spectroscopy and two substituted *N*-(α-phenylbenzylidene)methylamines they were able to

[1] Part VIII, W. B. Jennings, D. R. Boyd, and L. C. Waring, *J.C.S. Perkin II*, 1976, 610.

[2] H. O. Kalinowski and H. Kessler, *Topics Stereochem.*, 1973, 7, 295.

[3] J. M. Lehn, *Fortschr. chem. Forsch.*, 1970, 15, 311.

[4] D. Y. Curtin, E. J. Grubbs, and C. G. McCarty, *J. Amer. Chem. Soc.*, 1966, 88, 2775.

[5] M. Raban, *Chem. Comm.*, 1970, 1415; M. Raban and E. Carlson, *J. Amer. Chem. Soc.*, 1971, 93, 685.

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

[7] W. B. Jennings and D. R. Boyd, *J. Amer. Chem. Soc.*, 1972, 94, 7181.

[8] D. Y. Curtin and J. W. Hausser, *J. Amer. Chem. Soc.*, 1961, 83, 3474.

obtain kinetic data for isomerization, and to show a *para*-substituent effect on the E_a values.

In the majority of cases where entropies of activation have been obtained for isomerization around a double bond the values are small.[2,3] However, we have previously noted that *N*-alkylaldimines show large negative $\Delta S^{\ddagger}$ values for *E-Z* isomerization which are difficult to rationalize in terms of either a rotation or an inversion type of mechanism.[9] Large negative activation entropies are characteristic of a bimolecular acid-catalysed isomerization process.[6]

NBu^t signals. The rate constants for isomerization were also determined at a much higher temperature using the dynamic n.m.r. technique. Application of these two kinetic methods to the same sample enabled the rate constants to be precisely determined over a range of ca. 10^6. This procedure has been used in previous stereodynamic investigations [10] of other systems and allows the enthalpy and entropy of activation to be determined to high precision (within the approximations of absolute rate theory).

Previous work has shown that the rate of imine isomerization is very sensitive to the presence of trace amounts of acidic material.[6] Accordingly, samples for kinetic study

TABLE 1

Kinetic data and activation parameters for imine isomerization

Imine	Solvent ^{a}	Temp. (°C)	k_{E-Z}/s^{-1}	k_{Z-E}/s^{-1}	$\Delta G^{\ddagger}_{E-Z}$ ^{b}/ kcal mol^{-1}	$\Delta G^{\ddagger}_{Z-E}$ ^{b}/ kcal mol^{-1}	$\Delta H^{\ddagger}_{E-Z}$ ^{c}/ kcal mol^{-1}	$\Delta H^{\ddagger}_{Z-E}$ ^{c}/ kcal mol^{-1}	$\Delta S^{\ddagger}_{E-Z}$ ^{d}/ cal mol^{-1} K^{-1}	$\Delta S^{\ddagger}_{Z-E}$ ^{d}/ cal mol^{-1} K^{-1}
(1)	DPE	35	1.12×10^{-6}	2.36×10^{-6}	26.45	26.0				
	DPE	208	6.65	11.1	26.8	26.3	25.8	25.4	-2.1	-1.9
	TBU	34.8	0.16×10^{-6}	0.36×10^{-6}	27.6	27.1				
(2)	DPE	35	2.26×10^{-6}	3.69×10^{-6}	26.0	25.7				
	DPE	205	7.43	11.3	26.5	26.1	25.1	25.0	-3.0	-2.5
(3)	DPE	35	3.11×10^{-6}	5.07×10^{-6}	25.8	25.5				
	DPE	176	0.99	1.76	26.7	26.15	24.0	24.1	-6	-4
(4)	DPE	35	2.11×10^{-6}	3.44×10^{-6}	26.1	25.8				
	DPE	171	0.43	0.78	27.1	26.6	23.7	23.9	-8	-6
(5) ^{e}	DPE	35	2.17×10^{-6}	4.19×10^{-6}	26.05	25.65				
	DPE	201	8.32	15.7	26.2	25.6	25.7	25.6	-1.0	$+0.2$
(6)	DPE	35	0.869×10^{-5}	1.67×10^{-5}	25.2	24.8				
	DPE	191	13.7	24.4	25.2	24.6	25.3	25.1	$+0.2$	$+1.1$
(7)	TOL	-9.5	0.55×10^{-4}	1.14×10^{-4}	20.5	20.1				
	TOL	91	4.91	10.24	20.3	19.8	21.0	21.0	$+2.0$	$+3.5$
(8)	TBU	60	1.75×10^{-7}	3.89×10^{-7}	29.9	29.3				
	TBU	80	2.58×10^{-6}	5.74×10^{-6}	29.8	29.3	28.5	28.9	-4	-1
	TBU	120	1.52×10^{-4}	3.70×10^{-4}	30.1	29.4				
	DPE	202	0.80	3.20	28.5	27.2				

^{a} DPE = diphenyl ether, TOL = [$^2H_8$]toluene, TBU = t-butyl alcohol containing 0.095M-potassium t-butoxide. ^{b} $\Delta G^{\ddagger}$ Values are ± 0.1 kcal mol^{-1} with the exception of imines (3) and (4) where the error may be larger (± 0.3 kcal mol^{-1}) due to the very small separation of the *N*-methyl signals. ^{c} $\Delta H^{\ddagger}$ Values are ± 0.6 kcal mol^{-1} for (1), (2), and (5)—(7),¦and ± 1.5 kcal mol^{-1} for (3), (4), and (8). ^{d} $\Delta S^{\ddagger}$ Values are ± 1.5 cal mol^{-1} K^{-1} for (1), (2), and (5)—(7), and ± 4 cal mol^{-1} K^{-1} for (3), (4), and (8). ^{e} Data taken from ref. 6.

In an attempt to gain further insight into the mechanism of interconversion of *N*-alkylimines a range of *E-Z-C*-arylimines has been synthesized. The rates of isomerization have been determined (by direct thermal stereomutation and by dynamic n.m.r. measurement), and the effect of imine substituent (steric and electronic) and solvent upon these barriers under acid-free conditions have been interpreted. Data for enantiomerization of some related oxaziridines has also been obtained to assess the effect of *para*-substituents in the *C*-aryl ring on the nitrogen inversion process.

RESULTS

Imines (1)—(8) exist in solution as an equilibrium mixture of geometric isomers which generally show anisochronous *N*-alkyl signals in the n.m.r. spectrum. In each case a single isomer was obtained by recrystallization of the equilibrium mixture from a suitable solvent (as shown by the n.m.r. spectrum obtained immediately after dissolution). The kinetics of equilibration were determined by observing the change in integrated intensities of the NMe, NCH$_2$, or

were recrystallized several times from dry ethanol or pentane solution containing a trace of sodium ethoxide. The sample was then washed with pure solvent to minimize any possibility of base catalysis. In several cases, sublimation of the base recrystallized material was carried out but this did not increase the half-life for isomerization. The isomerization was followed at 35° [$-9.5°$ in the case of (7)] on 3—5 different samples of imine, including one containing traces of calcium hydride as an additional acid scavenger.*

In most cases some difference in isomerization rates at 35° were observed even for purified samples. However, samples generally exhibited identical coalescence temperatures, even in cases where the rates at 35° differed by a factor of two. The catalysed route for isomerization is less favourable at high temperature due to the large negative $\Delta S^{\ddagger}$ term and can apparently only compete with the intramolecular process at 200° in the presence of relatively high concentrations of acid. Activation parameters shown in Table 1 were determined from the sample with the longest half-life at 35° and it is assumed that these correspond with the intramolecular process. It must however be emphasized

* Curtin and Hausser [8] had previously noted the rather variable rate of isomerization for imines (3) and (5), and reported that reproducible data were obtained in the presence of traces of calcium hydride. We have found in this study that the effect of calcium hydride was rather variable.

[9] D. R. Boyd, C. G. Watson, W. B. Jennings, and D. M. Jerina, *J.C.S. Chem. Comm.*, 1972, 183.
[10] See for example A. Jaeschke, H. Muensch, H. G. Schmid, H. Friebolin, and A. Mannschreck, *J. Mol. Spectroscopy*, 1969, **31**, 14; M. Raban and E. Carlson, *J. Amer. Chem. Soc.*, 1971, **93**, 685.

that catalysis is a major problem in these studies (particularly at ambient temperature) and even with highly purified material it is impossible to guarantee that all catalytic effects have been completely eliminated. Catalysis is particularly acute with the aldimine (8) and it was not possible to eliminate these effects in purified diphenyl ether solution at 35°. Thus, samples of aldimine (8) purified by sublimation gave half-lives for isomerization <1 min at 35°. Prior purification of the imine by dissolution in ethanol containing traces of sodium ethoxide, followed by sublimation, increased the half-life to *ca.* 45 min; several treatments of this type eventually raised the half-life to *ca.* 80 min.

Nevertheless, when the latter value is combined with the dynamic n.m.r. data at 202° the resulting activation entropy is large and negative, indicative of a catalysed process. In deuteriomethanol the half-life for this aldimine at 35° was *ca.* 15 min, increasing to *ca.* 2.5 h in the presence of traces of sodium deuteriomethoxide. However, the latter result also may not refer to the uncatalysed process as methanol could add reversibly to the C=N bond and catalyse the isomerization. Indeed, it has recently been reported [11] that methanol can add to some ketimines, and aldimines might be expected to react more readily. The half-life for the equilibration of (8) at 35° in anhydrous t-butyl alcohol was observed to be 4.0 h. A remarkable retarding effect was observed in the presence of potassium t-butoxide. Indeed, no isomerization of (8E) was detected even after 26 days at 35° in t-butyl alcohol containing t-butoxide, and the temperature had to be raised to 60° in order to follow the kinetics (see Table 2).

TABLE 2

Kinetic data for oxaziridine racemization

Compound	X	$t/°C$	$10^6 k/s^{-1}$	$\Delta G^{\ddagger a}/$ kcal mol^{-1}
(9)	Me	4.0	34.67, 34.68	26.34
(10)	H	54.4	37.29	26.33
		54.2	37.82	26.30
		54.0	37.75	26.31
(11)	Br	54.2	50.30	26.12
		54.1	48.20	26.14
		54.0	46.75	26.15
(12)	NO$_2$	54.4	67.80	25.94
		54.2	69.41	25.91
		54.0	71.64	25.87

a The quoted $\Delta G^{\ddagger}$ values refer to enantiomerization [the rate of enantiomerization is half the rate (k) for racemization].

Optically active oxaziridines (9)—(12) were obtained by asymmetric oxygenation of the parent imines with (+)-peroxycamphoric acid. Although the N-t-butyl group tends to enhance the stability of oxaziridines, compounds which contained strong electron-donating substituents proved to be too unstable for characterization by kinetic measurements. The *para*-methyl compound (9) slowly decomposed into ketone and other achiral products in the neat state at ambient temperature but it was sufficiently stable in solution for racemization studies to be carried out. While all the racemizing solutions were monitored for decomposition by n.m.r., only in compound (9) was a significant proportion observed (mainly to ketone). This decomposition was taken into account in the derivation of

the rate constant for racemization. The rate constants for racemization and the derived $\Delta G^{\ddagger}$ values for enantiomerization are given in Table 2. Several experiments were performed on each compound to establish the reproducibility of the results.

DISCUSSION

Imines (1)—(8) cannot isomerize *via* tautomerization to the enamine, and conditions have been chosen to minimize isomerization by the catalysed addition–elimination route. It is noteworthy that the activation entropies for these imines are small (Table 1). Values of $\Delta S^{\ddagger}$ of $<ca.$ 5 cal mol^{-1} K^{-1} are characteristic of a stereodynamic process proceeding by an intramolecular route (in the absence of a highly polar transition state in a polar medium where solvation entropies could be important).[3,12] Imines (3) and (4) do show slightly larger negative $\Delta S^{\ddagger}$ values which might indicate some residual catalytic effect. However, the activation parameters for (3) and (4) are also less accurate than those obtained for the other imines on account of the small chemical shift separations [13] between the N-methyl signals for the E- and Z-isomers.
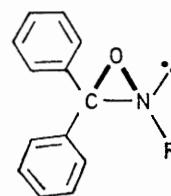

(13)

Increasing the bulk of the nitrogen substituent is known to lower the barrier to pyramidal inversion. Thus in the diphenyloxaziridines (13) the barriers to inversion ($\Delta G^{\ddagger}$) are 32.2, 31.6, and 26.2 kcal mol^{-1} for R = Me, Pr^i, and Bu^t respectively.[12,14] The results for the nitro-substituted imines (5)—(7) indicate that the barrier to isomerization also decreases along the N-alkyl series Me, CH$_2$Bu^t, Bu^t. This N-alkyl steric effect is therefore consistent with an inversion mechanism, but the steric effect would be expected to operate in the same direction for a rotational process. The entropy of activation increases slightly (in the positive sense) along the same series [imines (5)—(7)]. This entropy effect may be due to decreased libration of the bulkier N-alkyl groups in the more hindered ground state.

It is of interest to compare the magnitude of the barriers ($\Delta G^{\ddagger}_{E-Z}$) for the N-methylketimines (1) and (14) and the N-methylaldimine (8) (26.8, 26.2,[7] and 30.1 kcal mol^{-1} respectively). The similarity of $\Delta G^{\ddagger}_{E-Z}$ values for imines (1) and (14) are consistent with the steric influence of C-methyl and C-aryl substituents being rather similar.[13] If a rotational mechanism were operative one would have expected C-aryl substituents to considerably stabilize the dipolar transition state.

[11] H. Iwamura, M. Tsuchiomoto, and S. Nishimura, *Bull. Chem. Soc. Japan*, 1974, **47**, 143.
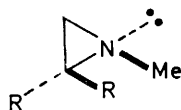[12] J. Bjørgo and D. R. Boyd, *J.C.S. Perkin II*, 1973, 1575.
[13] J. Bjørgo, D. R. Boyd, C. G. Watson, and W. B. Jennings, *J.C.S. Perkin II*, 1974, 757.
[14] F. Montanari, I. Moretti, and G. Torre, *Gazzetta*, 1973, **103**, 681.

The difference in $\Delta G^{\ddagger}_{E-Z}$ for (14) and (8) of *ca.* 4 kcal mol⁻¹ is similar to that found experimentally for analogous steric effects on pyramidal nitrogen inversion, *cf.* aziridines (15) and (16).[3]

(14)
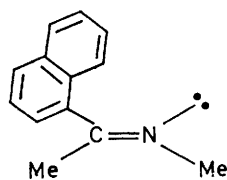
(15) R = H ($\Delta G^{\ddagger}$ 24·2 kcal mol⁻¹)
(16) R = Me ($\Delta G^{\ddagger}$ 20·2 kcal mol⁻¹)

In contrast with the marked steric effect on the imine isomerization process, only a very small electronic effect was observed on changing the *para*-substituent on the C-aryl ring along the series NMe_2, OMe, Cl, Br, and NO_2 (Table 1). A large substituent effect would be expected for a rotational mechanism, and indeed the barrier to C=C bond rotation in aryl-substituted ethylenes is very sensitive to the nature of the *para*-substituent.[2] Electron donating substituents (*e.g.* NMe_2) should considerably stabilize the dipolar transition state (17) for rotation about the C=N bond.
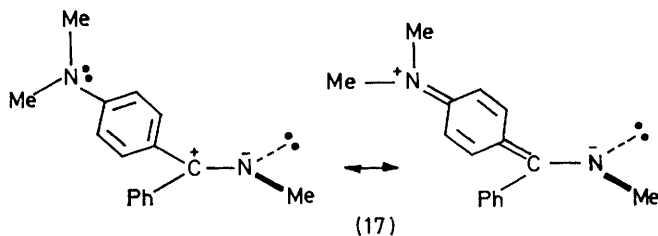
(17)

However, the effect of *para*-substituents in the C-aryl ring on the barrier to nitrogen inversion is difficult to

TABLE 3

Linear regression data for $-\Delta G^{\ddagger}$ on Hammett σ_p

Stereodynamic process	Slope (ρ) [a]	Standard deviation	Correlation coefficient
Oxaziridine enantiomerization at 54°	0.47	0.02	0.99
Imine isomerization at 35° (E-Z)	0.25	0.15	0.68
Imine isomerization at 35° (Z-E)	0.22	0.10	0.76
Imine isomerization at *ca.* 200° (E-Z) [b]	0.24 (0.37)	0.27 (0.03)	0.43 (0.99)
Imine isomerization at *ca.* 200° (Z-E) [b]	0.32 (0.46)	0.27 (0.03)	0.54 (0.99)

[a] The slope (ρ) is in units of kcal mol⁻¹ per σ unit. [b] Open figures were obtained using data for imines (1)—(5); values in parentheses were obtained by omitting the results for the halogen substituted compounds (3) and (4).

predict *a priori* and there appeared to be little information in the literature on this subject. Accordingly we have obtained data for racemization in a series of *para*-disubstituted 3,3-diphenyloxaziridines (9)—(12) (Table

[15] J. Bjørgo, D. R. Boyd, R. M. Campbell, N. J. Thompson, and W. B. Jennings, *J.C.S. Perkin II*, 1976, 606.

2). The results show that the *para*-substituent exerts a small but consistent effect on the process. The rate constant for racemization increases with the electron-withdrawing character of the substituent and correlates well with Hammett σ_p (Table 3).

It has been previously established[12,15] that oxaziridines racemize by an intramolecular nitrogen inversion process. *para*-Substituent effects on nitrogen inversion have also been studied in N-arylaziridines (18).[16]

Thus $\Delta G^{\ddagger}$ was observed to be diminished by *ca.* 3 kcal mol⁻¹ on changing X from H to NO_2 in (18). This large effect is due to stabilization of the trigonal transition state for nitrogen inversion by direct conjugation between the *para*-substituent and the nitrogen lone pair. The effect in the CC-diaryloxaziridines is smaller by an
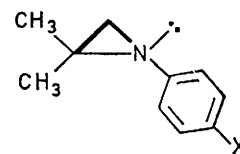
(18)

order of magnitude, but is in the same direction. Presumably there is weak conjugation between the C-aryl rings and the oxaziridine ring which affects the nitrogen inversion process. A purely σ inductive effect would not appear to account for the trend since electronegative substituents generally *raise* the barrier to nitrogen inversion.[3] This nitrogen isomerization process in oxaziridines is free from the problem of sensitivity to acid catalysis which hampers accurate measurement of barriers to interconversion of E-Z-imines.

While the present relationship between the barrier to racemization and Hammett σ values in oxaziridines may be interpreted as a long range electronic effect, it should be emphasized that it is frequently difficult to treat steric and electronic effects in isolation. The bulk of the *para*-substituents would not be expected to affect the barriers to racemization; however, the electron-withdrawing or -donating character of these substituents may alter the preferred conformation and steric requirements of the aryl rings to a minor degree.

The free energy barriers to isomerization of imines (1)—(5) have also been examined for a Hammett correlation; linear regression data are given in Table 3. Although the correlation of $-\Delta G^{\ddagger}$ with σ_p is much poorer than that shown by the oxaziridines, it is noteworthy that all four sets of data show a positive ρ value of similar magnitude. The ρ values for the imines appear to be slightly lower than for the oxaziridines, but the latter compounds possessed two *para*-substituents as compared with a single substituent in the imine series. The observation that the *para*-substituent effect for N-alkylimine isomerization is of similar magnitude to, and is in the same direction as that for nitrogen inversion in oxaziridines, is strong evidence for an inversion

[16] J. D. Andose, J. M. Lehn, K. Mislow, and J. Wagner, *J. Amer. Chem. Soc.*, 1970, **92**, 4050.

mechanism in the former. Furthermore, the effect operates in an opposite direction to that expected for a rotational process. Wettermark et al.[17] have previously reported that isomerization rate constants for N-benzylideneanilines correlated with the σ values of para-substituents in the C-aryl ring. The ρ value was again observed to be positive, though the effect was somewhat more marked than in the present series of N-alkyl compounds. It would therefore appear that a common isomerization mechanism (nitrogen inversion) obtains in N-alkyl- and N-aryl-imines.

It has previously been noted that protic solvents often increase the barrier to nitrogen inversion by hydrogen bonding to the lone pair.[3] The $\Delta G^{\ddagger}$ values found for imines (1) and (8) are higher in t-butyl alcohol than in diphenyl ether by 1—2 kcal mol^{-1} (Table 1). This observation would again be consistent with a planar nitrogen inversion mechanism for N-alkylimines.

The activation parameters for the aldimine (8) in t-butyl alcohol are noteworthy since (i) the value of $\Delta G^{\ddagger}_{E \rightarrow Z}$ (30 kcal mol^{-1}) represents to our knowledge the highest measured barrier for imines devoid of hetero-atomic substituents and (ii) the $\Delta S^{\ddagger}$ values are close to zero in contrast with the large negative values observed in other media and noted previously[9] for a related aldimine. The acid-catalysed mechanism for imine isomerization is associated with large negative activation entropies and shortened half-lives at ambient temperature.[6,18] Catalysis was particularly acute with the aldimine (8) and we were unable to eliminate these effects at 35° with base purified samples in diphenyl ether solution (see Results section). Potassium t-butoxide in t-butyl alcohol was found to minimize catalytic effects and gave long half-lives at ambient temperature together with small $\Delta S^{\ddagger}$ values. Presumably the bulky t-butyl alcohol molecule cannot readily add across the C=N bond, and the t-butoxide ion removes any traces of acidic impurity.

The small bulk of the proximate CH and NMe groups in the E-isomer of the aldimine (8) is probably responsible for the large E–Z barrier in this compound. This result suggests that the barrier to nitrogen inversion in CH$_2$=NMe or CH$_2$=NH should lie in the region 28.5—30.0 kcal mol^{-1}. This estimate is in good agreement with the calculated potential barriers to inversion in the latter compound using CNDO/2, and ab initio molecular orbital methods (31 and 28 kcal mol^{-1} respectively).[19,20] MINDO/1 calculations on CH$_2$=NMe and CH$_2$=NH have afforded lower estimates of the inversion barrier (13.0 and 14.7 kcal mol^{-1}).[21] The CNDO/2 and ab initio calculations also indicated that the barrier to rotation around the C=N bond was about a factor of two higher than the calculated barrier to inversion. However, the CNDO/2 method appears to seriously overestimate the

C=N rotational barrier in nitrones.[1] Similarly, ab initio calculations overestimate the barrier to rotation around the C=C bond in ethylene, particularly when configuration interaction is not taken into account.[22] Accordingly, the energy of the rotational transition state in imines may be closer to that for inversion than the calculations appear to indicate. Thus, experimental underestimates of imine isomerization barriers combined with possible theoretical overestimates of the rotational barriers means that the molecular orbital analogy (which has frequently been used to support the inversion mechanism) should be used only with caution. Nevertheless, the alternative experimental data presented in this paper strongly supports an inversional mechanism for N-alkylimines.

EXPERIMENTAL

Materials.—Diphenyl ether (99%) was washed several times with aqueous sodium carbonate, dried over potassium carbonate, and distilled *in vacuo*. Anhydrous t-butyl alcohol was obtained by refluxing over sodium under nitrogen followed by distillation. [$^2H_8$]Toluene was dried over molecular sieves or calcium hydride. All glassware used to contain purified solvents and kinetic samples was rinsed with dilute ammonium hydroxide, distilled water, and oven dried.

Ketimines were prepared by condensation of the ketone and amine in the presence of titanium tetrachloride.[23,24] E-N-(α-*Phenyl-4-nitrobenzylidene*)-2,2-*dimethylpropylamine* (6) had m.p. 98—99° (Found: C, 72.9; H, 6.8; N, 9.3. C$_{18}$H$_{20}$N$_2$O$_2$ requires C, 73.0; H, 6.7; N, 9.5). E-N-(α-*Phenyl-4-nitrobenzylidene*)-t-*butylamine* (7) had m.p. 113—114° (Found: C, 72.2; H, 6.5; N, 9.8. C$_{17}$H$_{18}$N$_2$O$_2$ requires C, 72.3; H, 6.4; N, 9.9%). N-[*Bis*-(4-*methylphenyl*)*methylene*]-t-*butylamine* had m.p. 115—116° (Found: C, 86.0; H, 8.7; N, 5.3. C$_{19}$H$_{23}$N requires C, 86.1; H, 8.8; N, 5.1%). N-[*Bis*-(4-*bromophenyl*)*methylene*]-t-*butylamine* had m.p. 146—148° (Found: C, 51.7; H, 4.4; N, 3.7. C$_{19}$H$_{17}$Br$_2$N requires C, 51.7; H, 4.3; N, 3.5%). N-[*Bis*-(4-*nitrophenyl*)*methylene*]-t-*butylamine* had m.p. 210—212° (Found: C, 62.2; H, 5.2; N, 12.7. C$_{17}$H$_{17}$N$_3$O$_4$ requires C, 62.4; H, 5.2; N, 12.8%).

Imines (1)—(5) and (8) had physical data in accord with those reported previously.[13,18]

Oxaziridines were prepared [using (+)-peroxycamphoric acid as oxidant] from the corresponding imines in dichloromethane at −72° as reported previously.[25] 3,3-*Bis*-(4-*methylphenyl*)-2-t-*butyloxaziridine* (9) had [α]$_{589}$ −66° (chloroform) but decomposition precluded meaningful microanalytical data (Found: M, 281.177 5 ± 0.000 7. C$_{19}$H$_{23}$NO requires M, 281.177 9). 3,3-Diphenyl-2-t-butyloxaziridine (10) had m.p. 110° (lit., 102°), [α]$_{589}$ −194°. 3,3-*Bis*-(4-bromophenyl)-2-t-butyloxaziridine (11) had m.p. 145—147°, [α]$_{589}$ −84° (Found: C, 49.7; H, 4.2; N, 3.4. C$_{17}$H$_{17}$Br$_2$NO requires C, 49.6; H, 4.1; N, 3.4%). 3,3-*Bis*-(4-nitrophenyl)-2-t-butyloxaziridine (12) had m.p. 143°, [α]$_{589}$ −17° (Found:

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C, 59.6; H, 4.9; N, 12.2. $C_{17}H_{17}N_3O_5$ requires C, 59.5; H, 4.9; N, 12.2%).

Kinetic Studies.—Imine samples for kinetic investigation were recrystallized several times from ethanol or pentane containing traces of sodium ethoxide. The equilibration of imine (7) was carried out in the probe of a Varian XL-100 spectrometer maintained at $9.5 \pm 0.5°$. All other stereomutations were followed in n.m.r. tubes placed in a thermostatically controlled bath ($\pm 0.2°$). The sample was periodically removed for assay in the probe of an adjacent n.m.r. spectrometer at 35° (Perkin-Elmer R12B, R14, or Varian XL-100). Rate constants were determined from a plot of $\ln(x_e/x_e - x)$ *vs.* time. Ketimine solutions were generally 0.33M and solutions of the aldimine (8) were 0.5M. Dynamic n.m.r. studies were carried out as described previously,[6] and the temperature dependence of all n.m.r. parameters were taken into account. Rate constants for degenerate stereomutation were determined from the exchange broadened bandshape using the program INMR and the University ICL-1906A computer. In the case of

aldimine (8) in diphenyl ether the coalescing N-methyl signals were doublets [$^4J_{HCNOH}$ 2.2 (Z) and 1.8 Hz (E)]. This coupling was taken into account in the lineshape analysis by treating the doublet components as separate sites.

Racemization experiments on the oxaziridines were performed using a thermostatically controlled polarimeter cell ($\pm 0.1°$) and a Perkin-Elmer 141 automatic polarimeter. Rotations were averaged over several readings in chloroform solution. The racemizing samples were also monitored for decomposition by ^1H n.m.r. under the same conditions (using hexamethylbenzene or 1,4-dimethoxybenzene as standards).