Dynamic Stereochemistry of Imines and Derivatives. Part V.[1] Acid Catalysis of *E–Z* Imine Interconversion

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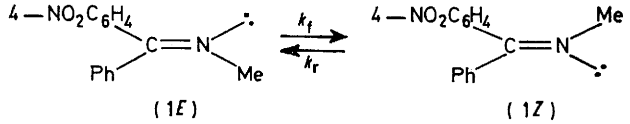
The rate of *E–Z* isomerization in *N*-(α-phenyl-4-nitrobenzylidene)methylamine at 35° is shown to be markedly increased by trace amounts of benzoic acid. Dynamic n.m.r. experiments at higher temperature show that the isomerization rate is proportional to the acid concentration and enable activation parameters to be determined.

CNDO/2 Calculations performed on the benzylideneammonium ion suggest that the $C{=}\overset{+}{N}$ rotational barrier is *ca.* 46 kcal mol^{-1}, and high temperature n.m.r. studies on a related immonium perchlorate also indicate a high rotational barrier. It is suggested that benzoic acid promotes imine isomerization by nucleophilic addition to the $C{=}\overset{+}{N}$ bond in the conjugate acid. The relevance of the rate of imine isomerization to the mechanism of the imine–peroxyacid reaction is discussed.

THE mechanism of *E–Z* isomerization in imines is the subject of considerable debate and is generally considered in terms of either rotation around the C=N bond or planar inversion at nitrogen.[2] Intermediate mechanisms have also been suggested.[3] In the case of simple alkyl or aryl substituted imines, experimental evidence and MO calculations indicate that nitrogen inversion usually provides the lower energy path for isomerization.[2] Other mechanisms may operate in particular circumstances. Thus *C*-alkylimines that possess an α-hydrogen atom can isomerize *via* a reversible tautomerization to the enamine followed by rapid rotation around the C–N single bond.[1a] It has also been suggested that in 1,3-dienoid solvents, imino-compounds might isomerize by a reversible [4 + 2] cycloaddition followed by rapid



(1*E*) (1*Z*)

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[1] The following are considered to constitute earlier parts of this series: (*a*) Part I, W. B. Jennings and D. R. Boyd, *J. Amer. Chem. Soc.*, 1972, **94**, 7187; (*b*) Part II, J. Bjørgo and D. R. Boyd, *J.C.S. Perkin II*, 1973, 1575; (*c*) Part III, J. Bjørgo, D. R. Boyd, C. G. Watson, and W. B. Jennings, *ibid.*, 1974, 757; (*d*) Part IV, J. Bjørgo, D. R. Boyd, C. G. Watson, W. B. Jennings, and D. M. Jerina, *ibid.*, p. 1081.

[2] For recent reviews see H. O. Kalinowski and H. Kessler, *Topics Stereochem.*, 1973, **7**, 295; H. Kessler, *Tetrahedron*, 1974, **30**, 1861.

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

nitrogen inversion in the tetrahydropyridine adduct.[4] Quantitative results are now presented suggesting that yet another mechanism may obtain in the presence of acid.

In a preliminary investigation of aldimine equilibria we noted that the rate of *E*–*Z* isomerization was unexpectedly fast at 35° and was possibly associated with a large negative entropy factor.[5] It was suggested [1d] that the process was being catalysed by trace amounts of acid impurity. Previous results from the literature suggest that the rate of imine isomerization may be affected by acid. Curtin *et al.*[6] reported that it was necessary to add calcium hydride to isomerizing diarylimine solutions in order to obtain reliable kinetic data, and it has also been noted that acetic acid–sodium acetate buffer catalyses *Z*–*E* isomerization in anils after flash photolysis.[7] Kessler *et al.*[4] have also reported recently that *E*–*Z* isomerization in hydrazones is accelerated by trifluoroacetic acid.

In addition to the considerable interest in the imine isomerization mechanism, the rate of this process has implications regarding the controversy over the mechanism of the imine–peroxyacid reaction.[5,8-10] Reported isomerization barriers are generally in the range 24—27 kcal mol^{-1} corresponding to a half-life of several hours or days at ambient temperature. Since the imine–peroxyacid reaction is rapid at ambient temperature [8-10] it might be expected that this reaction is very much faster than the imine isomerization. Imine (1), derived from 4-nitrobenzophenone and methylamine, is available in the pure *E*-configuration by crystallisation of the isomer mixture from ethanol [1c,6] (involving a second-order diastereomeric transformation [11]). Although the half-life * of isomerization for this compound has been reported to be 17 h at 40.2° in cyclohexane solution,[6] we found that in the presence of carboxylic acid (or peroxycarboxylic acid) equilibration occurred rapidly as revealed by n.m.r. This imine was also found to show a variable half-life for isomerization (followed by n.m.r. at 35°) depending on the sample chosen. These observations can again be rationalised in terms of catalysis by carboxylic acid present in the peroxyacid reaction or as an impurity in equilibrating imine solutions.

Imine (1) was chosen for quantitative investigation since (i) it is available in crystalline form as the pure *E*-configuration and shows an appreciable proportion of the other isomer at equilibrium; (ii) this imine cannot isomerize by tautomerization to the enamine,[1a] thus avoiding a further potential complication; (iii) the isomers show separate singlet *N*-methyl signals enabling isomerization to be readily monitored by n.m.r. spectroscopy; (iv) the stereochemistry of the *E*- and *Z*-isomers had previously been established; [1c,6] and (v) this imine was found to be thermally stable at temperatures >200°.

Samples of (1*E*) in several solvents were found to show a range of half-lives for equilibration (of the order of a few hours) as followed by n.m.r. spectroscopy at 35°. The half-life could be increased by recrystallising the imine from ethanol containing a trace of sodium ethoxide.† Using this procedure and acid-free diphenyl ether as solvent the half-life was increased to 30 h at 35°.‡ A plot of log $x_e/(x_e - x)$ *versus* time gave k_f 2.17 × 10^{-6} s^{-1} and k_r 4.19 × 10^{-6} s^{-1} at 35°. These data are considered to refer to interconversion by an uncatalysed intramolecular process (probably nitrogen inversion [2]), and the faster rates observed for untreated samples are due to interconversion by an acid-catalysed route (see below). The catalytic effect is very pronounced as equilibration of base purified (1*E*) (15 mg) in diphenyl ether (0.5 ml) containing benzoic acid (1 mg) reduced the half-life to <1 min. In the presence of only 0.049 mg of benzoic acid the half-life was *ca.* 7.5 min. Reduction in the amount of benzoic acid by 50% increased the half-life to *ca.* 13 min. The great sensitivity of imine equilibration to acid catalysis makes accurate kinetic studies difficult at ambient temperature. However, degenerate isomerization of imines can be investigated at higher temperature by the dynamic n.m.r. method.[1a] On warming the equilibrated sample of purified (1*E*) (>180°) in diphenyl ether solution the *N*-methyl signals of both isomers broadened and then coalesced at 201°, where interconversion is fast on the n.m.r. time-scale. Computer analysis of the exchange broadened spectrum gave k_f 8.3 s^{-1} and k_r 15.7 s^{-1} at 201°. Combination of these data with those obtained for the same sample at 35° gave $\Delta H_f^\ddagger$ 25.7 kcal mol^{-1}, $\Delta H_r^\ddagger$ 25.6 kcal mol^{-1}, $\Delta S_f^\ddagger$ −1.0 cal K^{-1} mol^{-1}, and $\Delta S_r^\ddagger$ +0.2 cal K^{-1} mol^{-1}. The near zero entropies of activation are quite consistent with an intramolecular planar inversion process.[12] The activation parameters are comparable with those obtained previously by Curtin and Hausser [6] under different conditions.

The solution containing benzoic acid (0.049 mg) showed the same coalescence temperature (201°) as the previous sample. However, addition of larger amounts of benzoic acid lowered the coalescence temperature (Table 1). A quantitative study of the effect of benzoic acid on the rate of degenerate isomerization was carried

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* The half-life for the equilibration process is $0.693/(k_f + k_r)$.

† The crystals were washed with ethanol to minimise any possibility of base catalysis of the isomerization.

‡ The same half-life was obtained by adding a trace of calcium hydride to a solution of (1*E*) in acid-free diphenyl ether.

[4] H. O Kalinowski, H. Kessler, D. Leibfritz, and A. Pfeffer, *Chem. Ber.*, 1973, **106**, 1023.

[5] D. R. Boyd, C. G. Watson, W. B. Jennings, and D. M. Jerina, *J.C.S. Chem. Comm.*, 1972, 183.

[6] D. Y. Curtin and J. W. Hausser, *J. Amer. Chem. Soc.*, 1961, **83**, 3474; D. Y. Curtin, E. J. Grubbs, and C. G. McCarty, *ibid.*, 1966, **88**, 2775.

[7] (*a*) G. Wettermark, J. Weinstein, J. Sousa, and L. Dogliotti, *J. Phys. Chem.*, 1965, **69**, 1584; (*b*) G. Wettermark, *Arkiv Kemi*, 1967, **27**, 159.

[8] D. R. Boyd, D. G. Neill, C. G. Watson, and W. B. Jennings, *J.C.S. Perkin I*, 1975, in the press.

[9] V. Madan and L. B. Clapp, *J. Amer. Chem. Soc.*, 1969, **91**, 6078; 1970, **92**, 4902.

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

[11] E. Carlson, F. B. Jones, and M. Raban, *Chem. Comm.*, 1969, 1235.

[12] See refs. 1*b* and 2, and J. M. Lehn, *Fortschr. Chem. Forsch.*, 1970, **15**, 311.

out at 167° on a solution of the purified imine in diphenyl ether. Isomerization rates were derived from the exchange broadened spectra by complete lineshape analysis (Table 2). The effect on the lineshape of adding increasing amounts of benzoic acid is similar to that more usually obtained by increasing the temperature (Figure 1). Thus the *N*-methyl signals coalesced on addition of acid (5.12 mg) and collapsed to a single Lorentzian signal after addition of acid (20.1 mg) (Figure 1). A plot of the isomerization rate *versus* acid concentration (Figure 2) is linear, and affords the catalytic rate constants k_f^{cat} 77.1 l mol^{-1} s^{-1} and k_r^{cat} 145 l mol^{-1} s^{-1} at 167°. It is worth noting that the effect of benzoic acid is much less marked at higher temperature, thus acid (0.049 mg) had no detectable effect on the rate at 201° whereas it reduced the half-life at 35° from 30 h to 7.5 min (a factor of 240). This is due to a large negative entropy of activation for the bimolecular acid catalysed process as compared to the near zero value for the intramolecular inversion process. The catalytic rate constants determined at 167° (see above) can be combined with those calculated from the half-life (7.5 min) obtained at 35° in the presence of 8.08×10^{-4}M-benzoic acid to give $\Delta S_f^‡$ −30.2 cal K^{-1} mol^{-1} and $\Delta S_r^‡$ −29.0 cal K^{-1} mol^{-1}.

TABLE 1

Variation of coalescence temperature with added benzoic acid

Benzoic acid (mg) per 0.5 ml diphenyl ether	0	5.12	25.2
Coalescence temperature (°C)	201	167	126

TABLE 2

Effect of benzoic acid on the rate of *E–Z* isomerization of *N*-(α-phenyl-4-nitrobenzylidene)methylamine (1) at 167° in diphenyl ether solution

Benzoic acid[a] (10^{-3} g)	k_f[b] (s^{-1})	k_r[b] (s^{-1})
0.0	0.94[c]	1.8[c]
0.958	1.50	2.84
2.50	4.16	7.85
5.12	7.56	14.3
8.09	11.3	21.3
12.0	15.3	28.9
16.1	21.8	41.1
20.1	25.8	48.7
25.2	31.3	59.0

[a] Amount of benzoic acid added to a solution containing imine (30.0 mg) dissolved in diphenyl ether (0.50 ml). [b] Isomerization rates were derived from the exchange-broadened n.m.r. spectrum using a digital computer (see text). [c] Calculated at 167° from the activation parameters derived at 35 and 201° in the same solvent.

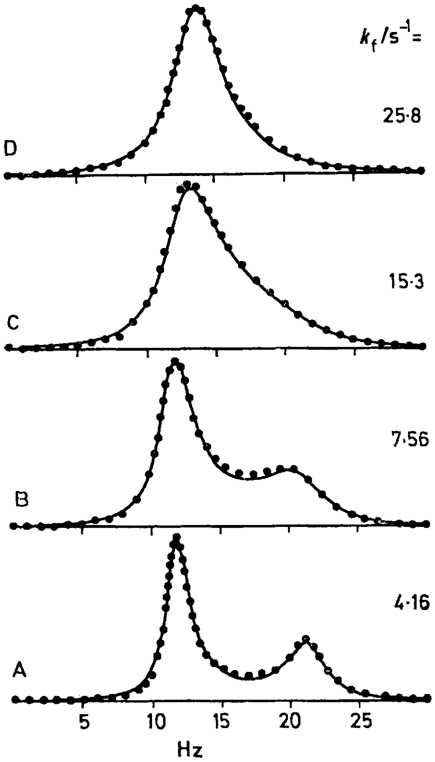


FIGURE 1 Experimental (●) and 'best fit' computed (solid line) dynamic n.m.r. spectra of imine (1) at 167° in diphenyl ether containing varying amounts of added benzoic acid: (A) 2.50×10^{-3} g; (B) 5.12×10^{-3} g; (C) 12.0×10^{-3} g; (D) 20.1×10^{-3} g

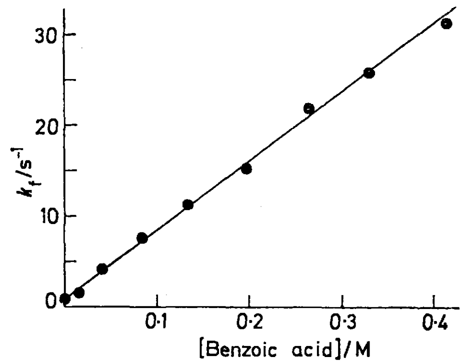
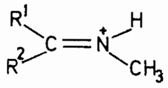


FIGURE 2 Variation of k_f with concentrations of added benzoic acid

Mechanism.—The carboxylic acid may protonate the imine to generate the immonium ion (2), and it has been suggested [7b] that rotation around the immonium double bond may be ready enough to interconvert the *E* and *Z*-forms. Only a small fraction of imine (1) appears to be protonated even in the presence of equimolar amounts of benzoic acid since the *E–Z* isomer ratio remains unchanged and only small effects are observed on the position of the *N*-methyl signals. Both of these parameters should alter on conversion of the imine to the immonium salt. Similarly, it has been reported that u.v. spectra of *N*-benzylidene-t-butylamine in the presence of benzoic acid show no indication of significant conversion to the conjugate acid in organic solvents.[10] However, if rotation around the $C{=}\overset{+}{N}$ bond in (2) is sufficiently fast, it would only require a very small fraction of imine molecules to be protonated in order to effect isomerization. Rotational barriers around isolated double bonds are usually very high, thus the measured barrier in 1,2-dideuterioethylene is 65 kcal mol^{-1}, and the C=N rotational barrier in imines has been calculated to be *ca.* 60 kcal mol^{-1} by CNDO/2 and *ab initio* MO methods.[2] Nevertheless, using a simple valence-bond picture, it might be considered that the rotational barrier in protonated imines is lowered by a contribution from the resonance canonical (3). However, the barrier to E–Z isomerization of the CC-dialkylimmonium perchlorate (4) has been found to be >30 kcal mol^{-1} at 80°, and degenerate isomerization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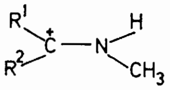
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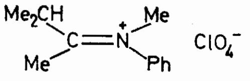
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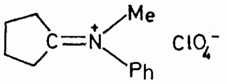
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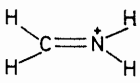
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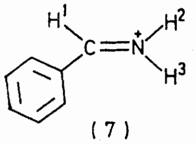
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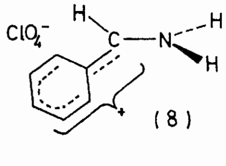
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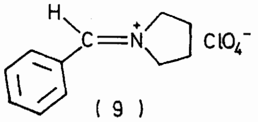
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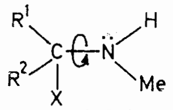
(10)

of (5) was slow on the n.m.r. time-scale at 150°.[13,14] Extrapolation of results for partial C=$\overset{+}{\mathrm{N}}$ bonds in guanidinium salts suggest a barrier of *ca.* 45 kcal mol^{-1} for rotation around a ' pure ' C=$\overset{+}{\mathrm{N}}$ double bond.[2] Recent MO calculations on the methyleneammonium ion (6) appear to support this view as the rotational barrier is predicted to be 76 kcal mol^{-1} by CNDO/2 and 72 or 87 kcal mol^{-1} by *ab initio* methods (depending on the basis set chosen). On the other hand, MINDO/2–SCF–MO calculations on ethylidene- and benzylidene-ammonium ions gave a much lower rotational barrier (27.9 and 27.3 kcal mol^{-1} respectively).[15b]

It might be argued that the presence of C-phenyl groups in imine(1) might lower the rotational barrier in the conjugate acid by stabilising the carbonium ion (3; R^1 = Ph). To investigate this possibility some CNDO/2[16] MO calculations were carried out on the C-phenyl substituted immonium ion (7). Standard geometry was used for the phenyl ring (assumed to be coplanar with the HCN system), and the bond lengths and angles of the imino-system were taken from the optimised geometry[15] of the methyleneammonium ion (see Experimental section). The CN bond lengths in the planar ground state and orthogonal transition state were varied in steps of 0.02 Å to minimise the total energy, and the results are given in Table 3. The torsional barrier is calculated to be 46 kcal mol^{-1} which is considerably lower than that calculated[15] by the same method for methyleneammonium (76 kcal mol^{-1}). The charge distributions (Table 3) indicate that the phenyl system stabilises the molecule by delocalising the charge, and this effect appears to be greater in the transition state. The electron density at nitrogen is also greater in the transition state, and the latter shows a lengthening of the C–N bond. These observations give some support for the valence bond representation (8) of the transition state.

TABLE 3

Results of CNDO/2 MO calculations on the planar ground state (G.S.) and the orthogonal transition state (T.S.) for rotation around the CN bond in the benzylideneammonium ion (7)

	G.S.	T.S.
CN bond length (Å)	1.32	1.36
Total energy (a.u.)	−67.0805	−67.0067
CN π-bond order	0.78	0.40
Dipole moment (D)	3.62	5.14
Atomic charge N	−0.10	−0.30
C	+0.28	+0.38
H^1	+0.07	+0.04
H^2	+0.20	+0.23
H^3	+0.21	+0.23
Phenyl ring (total)	+0.34	+0.42

We have also investigated the variable temperature n.m.r. spectra of N-benzylidenepyrrolidinium perchlorate (9). At ambient temperature in nitrobenzene solution this compound shows two broadened triplets at τ 5.52 and 5.25 [both, ^3J(HCCH) *ca.* 6.5 Hz] ascribed to the two sets of NCH$_2$ protons. These signals did not coalesce up to 204°, hence $\Delta G^{\ddagger} > 27$ kcal mol^{-1} at 204° for rotation around the C=N$^+$ bond (based on a maximum signal broadening of 1 Hz).

It seems unlikely that the additional 4-nitrophenyl substituent present in (1) would significantly lower the rotational barrier in the conjugate acid, particularly as steric interactions would force the aryl rings out of plane and reduce the conjugation (*cf.* benzophenone[17]). Accordingly, we suggested that benzoic acid might catalyse the imine isomerization by adding reversibly across the C=N bond to form the unstable intermediate (10; X = PhCO$_2$). It would also be possible for traces of water or amine to act as the nucleophile (X = OH or NH$_2$) in the presence of benzoic acid to generate the conjugate acid of the imine. Addition of nucleophiles to C=N$^+$ bonds is well established,[18] and indeed this was the reason for studying the perchlorate (9) as other anions might add to the immonium bond. Addition of sodium benzoate (1 mg) to a solution of (9) in nitrobenzene at 204° caused considerable decomposition of the sample, but in addition the two residual NCH$_2$ signals of the immonium salt collapsed to one signal at the mean position (broad triplet). This would tend to support the view

[13] A. Krebs and J. Breckwoldt, *Tetrahedron Letters*, 1969, 3797.

[14] H. Kessler and D. Leibfritz, *Chem. Ber.*, 1971, **104**, 2158.

[15] (*a*) P. A. Kollman, W. F. Trager, S. Rothenberg, and J. E. Williams, *J. Amer. Chem. Soc.*, 1973, **95**, 458; (*b*) M. Shansal, *Tetrahedron*, 1972, **28**, 61.

[16] J. A. Pople and G. A. Segal, *J. Phys. Chem.*, 1966, **44**, 3289.

[17] E. B. Fleischer, N. Sung, and S. Hawkinson, *J. Chem. Phys.*, 1968, **72**, 4311.

[18] K. Koehler, W. Sandstrom, and E. H. Cordes, *J. Amer. Chem. Soc.*, 1964, **86**, 2413.

that even the weakly nucleophilic benzoate anion may add to the immonium bond.

Relevance to the Imine–Peroxyacid Synthesis of Oxaziridines.—The peroxyacid oxidation of imines to oxaziridines has been shown to be non-stereospecific in contrast to alkene epoxidation which proceeds with retention of configuration.[8] In connection with the mechanism of the former reaction it is of interest to determine whether imine isomerization is faster or slower than reaction with the peroxyacid. Imine (1*E*) provides an opportunity to investigate the relative rates of these processes by n.m.r. spectroscopy. In solutions of the concentration usually employed in n.m.r. studies (*ca.* 0.3M) both these processes were found to be too rapid to study. Since both reactions are bimolecular it was possible to render them just slow enough for study by using very dilute solution in 10 mm n.m.r. tubes. Isomerization of (1*E*) in dichloromethane was followed by observing the imine *N*-methyl signals (τ_E 6.71; τ_Z 6.79) and conversion into the oxaziridines was concurrently monitored by observing the appearance of the oxaziridine *N*-methyl signals at τ 7.45 and 7.48. Solutions were 6.25×10^{-3}M in (1*E*) and 9.28×10^{-3}M in 3-chloroperbenzoic acid. The half-life ($t_{\frac{1}{2}}$) for imine equilibration at the probe temperature (30°) was *ca.* 0.7 min and the half-life for oxaziridine formation was *ca.* 6.0 min. The imine equilibrium ratio in dichloromethane was (1*E*) : (1*Z*) = 63 : 35 and the oxaziridine product ratio was 61 : 39 (latter stereochemical assignment is uncertain [8]). In carbon tetrachloride solution of the same concentration $t_{\frac{1}{2}}$ *ca.* 0.5 and 4.5 min for imine equilibration and oxaziridine formation respectively with an imine *E*–*Z* equilibrium ratio = 71 : 29, and oxaziridine product ratio = 66 : 34. Similarly in benzene solution $t_{\frac{1}{2}}$ *ca.* 0.9 and 5.9 min respectively with an imine *E*–*Z* equilibrium distribution = 60 : 40 and oxaziridine distribution = 57 : 43; imine *N*-methyl signals at τ 6.87 (*E*) and 7.01 (*Z*) and oxaziridine *N*-methyl signals at τ. 7.75 and 7.85. Therefore, equilibration of imine (1) proceeds about eight times faster than oxidation. Furthermore, the oxaziridine product distribution does not reflect the imine *E* : *Z* ratio (particularly for the oxidation of *C*-arylaldimines).[8] Although these results are probably best rationalised in terms of a stepwise mechanism for the imine–peroxyacid reaction, the observation that imine (1*E*) equilibrates more rapidly than it is converted into the oxaziridines does not rigorously exclude the alternative concerted mechanism.

Isomerization of (1*E*) in the presence of 3-chloroperbenzoic acid could occur by reversible addition of the peroxyacid across the C=N bond to give (10; X = 3-$ClC_6H_4CO_3$). Indeed this is the first step in the proposed stepwise mechanism for oxidation.[10] Alternatively, isomerization could take place by reaction with 3-chlorobenzoic acid which is initially present as an impurity in the peroxyacid and subsequently generated in the oxidation reaction. Equilibration of (1*E*) in benzene solution (6.25×10^{-3}M) in the presence of 3-chloroperbenzoic acid (3.2×10^{-3}M) at 30° occurred with a half-life of *ca.* 3.2 min whereas the same process showed a half-life of *ca.* 0.9 min in the presence of 3-chlorobenzoic acid 3.0×10^{-3}M. Thus the carboxylic acid appears to be a better catalyst for imine isomerization than the peroxyacid. Indeed, part of the isomerization observed in peroxyacid solution may be due to the carboxylic acid present, and the peroxyacid adds more slowly to the imine followed by rapid [10] cyclisation to the oxaziridines.

EXPERIMENTAL

N-(α-Phenyl-4-nitrobenzylidene)methylamine (1) was prepared from 4-nitrobenzophenone and methylamine in the presence of titanium tetrachloride.[19,20] Several recrystallisations from dry ethanol containing a trace of sodium ethoxide were performed until the material was shown to be the pure *E*-isomer by n.m.r., m.p. 126—127° (lit.[6] 127—128°). *N*-Benzylidenepyrrolidinium perchlorate (9) was prepared by standard procedures [21] and purified by recrystallisation from dry acetonitrile–ether and then several times from dry ethanol, m.p. 150—151° (lit.,[21] 156—159°). The compound was extremely hygroscopic and samples for n.m.r. spectroscopy were prepared in a dry-box. Diphenyl ether (99%) was purified by washing several times with aqueous sodium carbonate followed by drying over potassium carbonate and distillation under reduced pressure in a dry apparatus that had been rinsed with dilute ammonium hydroxide. N.m.r. tubes used in kinetic studies were rinsed in dilute ammonium hydroxide solution followed by distilled water and then baked in an oven.

Rate Measurements.—Kinetic studies on (1*E*) (0.33M in diphenyl ether) were carried out in a thermostatically controlled bath at 35 ± 0.2°. The sample was periodically transferred to an adjacent Perkin-Elmer R12B n.m.r. spectrometer (permanent magnet maintained at 35.0°) and the proportions of *E*- and *Z*-isomers determined by integration. Dynamic n.m.r. studies were carried out on a Varian XL-100 spectrometer. Probe temperatures were measured on a Doric digital thermocouple thermometer by inserting the copper–constantan thermocouple into the solution. The *N*-methyl signal separation and the equilibrium constants near coalescence were determined by graphical extrapolation of values observed at lower temperatures. Solutions used to investigate the effect of benzoic acid at 167° were 0.25M in imine. The concentration of benzoic acid was found to have no effect on the equilibrium constant, but it did slightly reduce the *N*-methyl signal separation. The latter effect was taken into account when analysing the spectra. Site exchange rates were determined directly from the digitised spectra using the program INMR [22] and the University ICL–1906A computer.

MO Calculations.—The program used was a modified version of QCPE–91 with standard parameters. The molecular geometry used was as follows: bond lengths (A°) N–H 1.09, C–H 1.11, aryl C–H 1.08, C-phenyl 1.45, C-C 1.40; bond angles (°) H–N–H 115, H–N–C 122.5, H–C–phenyl 116, H–C–N 122, aryl ring 120.

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