# Influence of Steric Factors on the Rates of Thermal Racemisation of *N*-Alkyl-oxaziridines. Isolation of an Enantiomer whose Optical Activity is due solely to a Tercovalent Asymmetric Nitrogen Atom

By F. MONTANARI*
(*Istituto di Chimica Industriale dell'Università, Milano, Italy*)

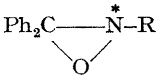
and (Miss) I. MORETTI and G. TORRE
(*Istituto di Chimica Organica dell'Università, Modena, Italy*)

*Summary* The influence of steric factors on the optical stability of *N*-alkyl-diphenyloxaziridines is proved by an 8000-fold higher rate of racemisation of the t-butyl as compared with the methyl derivative; the optically active t-butyl derivative is the first example of a highly pure enantiomer whose optical activity is due solely to a tercovalent non-bridgehead nitrogen.

---

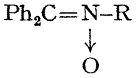
THE energy barrier to pyramidal inversion of tercovalent nitrogen is much increased because of ring strain when nitrogen is in a three-membered ring.[1] A further increase in the energy barrier is due to the repulsion between the unshared electron pairs of nitrogen and of an adjacent hetero-atom.[1] This has recently been confirmed by the isolation of stable invertomers of *N*-halogeno-aziridines,[2] -diaziridines,[3] and -oxaziridines.[4,5] The influence of other factors (steric, conjugative, or solvation effects) has not yet been adequately defined.

We have found that the optical stability of *N*-alkyl-diphenyloxaziridines (I) is very dependent upon steric factors. Optically active compounds (I) are obtained by oxidation of the corresponding imines with (+)-peroxycamphoric acid[6] at −60°.



(Ia) R = Me

(Ib) R = Buᵗ



(II)

The rate constants and the activation parameters of racemisation of the methyl and t-butyl derivatives (Ia) and (Ib) in tetrachloroethylene are reported in the Table. The loss of optical activity of (Ia) in the range 100—123° is due both to racemisation and to conversion into the nitrone (II), while the loss of optical activity of (Ib) is due solely to racemisation, at least in the range 60—80°. These results suggest that racemisation occurs through pyramidal inversion at nitrogen, not through ring opening, which should lead to nitrone formation. Decrease of optical activity has been followed polarimetrically; conversion into nitrone by $^1$H n.m.r. spectroscopy.

TABLE

| R | $T$(°c) | $k \times 10^6$ (sec.$^{-1}$) | $\Delta H^\ddagger$ (kcal./mole) | $\Delta S^\ddagger$((100·5°) e.u.) | $E_a$ (kcal./mole) |
|---|---|---|---|---|---|
| Me[a] | 100·5 | 1·1 | 34·1 | +5 | 34·8 |
| | 111·5 | 4·5 | | | |
| | 123·0 | 15·6 | | | |
| Buᵗ | 60·0 | 83·3 | 27·7 | +6 | 28·4 |
| | 70·0 | 284·0 | | | |
| | 80·0 | 956·0 | | | |
| | 100·5 | 7850·0[b] | | | |

[a] First-order rate constants and activation parameters for the conversion into nitrone: $k \times 10^6$ = 0·64, 1·8, and 6·2 (sec.$^{-1}$) at 100·5, 111·5, and 123·0°, respectively; $\Delta H^\ddagger$ 29·0 kcal./mole, $\Delta S^\ddagger$ −10 e.u. (100·5°), $E_a$ 29·7 kcal./mole; [b] extrapolated value.

The importance of steric factors on the optical stability of oxaziridines (I) is proved by the fact that the rate of racemisation of the t-butyl derivative (Ib) exceeds that of the methyl derivative (Ia) by a factor of 8000 at 100°. The activation parameters seem to indicate that a predominant role is played by the decrease of nonbonding interactions on going from the ground state to the planar transition state. Entropy factors connected with an increase of rotational freedom of the alkyl group should play a minor role.

The t-butyl-oxaziridine (Ib) gives a racemate much more soluble in ethyl ether than the corresponding enantiomers. Thus the (−)-enantiomer can easily be isolated by fractional crystallisation of the adduct ($[\alpha]_D^{25}$ − 54°, $CHCl_3$) obtained *via* asymmetric synthesis with (+)-peroxycamphoric acid. It shows m.p. 117·5—118·5°, $[\alpha]_D^{25}$ − 258°, $CHCl_3$. Since the specific rotatory power remains constant after further crystallisations, and the crystals appear to be homogeneous at the polarising microscope, it seems likely that compound (Ib) is optically pure. To the best of our knowledge, this is the first example of isolation of an enantiomer whose optical activity is due solely to a tercovalent asymmetric non-bridgehead nitrogen atom.

This work was supported by a grant from the Consiglio Nazionale delle Ricerche, Rome.

(*Received, July 28th*, 1969; *Com.* 1156.)

[1] J. F. Kincaid and F. C. Henriques, *J. Amer. Chem. Soc.*, 1940, **62**, 1474; A. T. Bottini and J. D. Roberts, *ibid.*, 1958, **80**, 5203; F. A. L. Anet, R. D. Trepka, and D. J. Cram, *ibid.*, 1967, **89**, 357.

[2] S. J. Brois, *J. Amer. Chem. Soc.*, 1968, **90**, 508; D. Felix and A. Eschenmoser, *Angew. Chem. Internat. Edn.*, 1968, **7**, 224; R. G. Kostyanovsky, Z. E. Samojlova, and I. I. Tchervin, *Tetrahedron Letters*, 1969, 719.

[3] A. Mannschreck and W. Seitz, *Angew. Chem. Internat. Edn.*, 1969, **8**, 212.

[4] D. R. Boyd, *Tetrahedron Letters*, 1968, 4561.

[5] A. Mannschreck, J. Linss, and W. Seitz, *Annalen*, in the press.

[6] F. Montanari, I. Moretti, and G. Torre, *Chem. Comm.*, 1968, 1694.