# Compounds with Molecular Asymmetry due solely to a Tercovalent Non-bridgehead Nitrogen Atom: Optically Active *N*-Chloro-2,2-diphenylaziridine

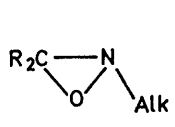
By (Miss) R. ANNUNZIATA, R. FORNASIER, and F. MONTANARI*

(*C.N.R. Centro di studio sulla sintesi e stereochimica di speciali sistemi organici, Istituto di Chimica Industriale dell'Università Via Saldini* 50, 20133 *Milano, Italy*)

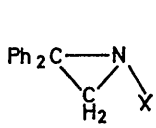
*Summary* Optically active *N*-chloro-2,2-diphenylaziridine, whose asymmetry is due solely to the chiral nitrogen atom, has been obtained by asymmetric chlorination of 2,2-diphenylaziridine by (1*R*; 2*R*)-(−)-isobornyl hypochlorite and (*S*)-(+)-(*N*-chloro)methylphenylsulphoximide.

FACTORS that affect the magnitude of barriers to pyramida inversion of the trico-ordinate nitrogen atom have been widely investigated recently, mainly by dynamic n.m.r. spectroscopy.[1] Although many nitrogen invertomers which are stable at room temperature have been identified and many pairs of diastereoisomers have been isolated, *N*-alkyl-

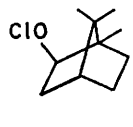
oxaziridines (I) seem to be the only compounds hitherto obtained in optically active form,[2] whose asymmetry is due solely to a tercovalent non-bridgehead nitrogen atom.



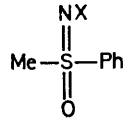
(I)



(II) X = H
(III) X = Cl



(IV)



(V) X = H
(VI) X = Cl

In *N*-halogeno-aziridines barriers to pyramidal inversions are generally high enough to allow the isolation of diastereoisomeric species.[3] Reaction of 2,2-diphenylaziridine (II)[4] with asymmetric halogenating reagents gave optically active *N*-chloro-2,2-diphenylaziridine (III).

Reaction of the aziridine (II) with (1*R*:2*R*)-(−)-isobornyl hypochlorite (IV),[5] 87% optically pure, for 3 h at −60° in pentane gave *N*-chloroaziridine (III) (chromatography on silica, ether–n-hexane 1:9 as eluant; 65%), m.p. 60—61°, $[\alpha]_D^{25}$ + 3·4°, $[\alpha]_{436}^{25}$ + 6·8° (*c* 0·4 in acetone).† The same compound (III), m.p. 60—61°, $[\alpha]_D^{25}$ +4·3°, $[\alpha]_{43}^{25}$ +8·6° (*c* 0·4 in acetone), was obtained by reaction of (II) with the (+)-(*S*)-sulphoximide (VI),‡ $[\alpha]_D^{25}$ + 195·0° (*c* 0·2 in acetone), for 12 h at −78° in chloroform (chromatography on alumina, ether–n-hexane 3:7 as eluant; 60%).§ The presence of optically active impurities in the optically active samples of (III) was excluded by i.r., n.m.r., t.l.c., and/or g.l.c. analysis.

Independent of an electrophilic or homolytic mechanism for halogenation, a higher optical yield would perhaps be expected from the *N*-chlorosulphoximide (VI), both because of the larger differences in the relative size of groups bonded to the chiral centre, and the closer proximity of the latter to chlorine. Since *N*-chloroaziridine (III) was completely racemized after four days at 0°, the similar degree of stereoselectivity with the two reagents (IV) and (VI), although repeatable, may depend on a fortuitous combination of different asymmetric inductions and of different losses of optical activity during the isolation of (III).

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† Racemic (III) has m.p. 61° (EtOH); τ ($CDCl_3$): 2·65 (10H, d) and 7·12 (2H, q).

‡ Prepared from (*S*)-methylphenylsulphoximide (V), $[\alpha]_D^{25}$ +25·0 (*c* 10 in acetone, 72% optically pure, lit.,[6] $[\alpha]_D^{25}$ +35·4°) and *N*-chlorobenzotriazole in chloroform at −20°.

§ The possible use of *N*-chlorosulphoximides as chiral chlorinating reagents was suggested by A. Scarset, University of Clermont-Ferrand.

[1] A. Rauk, L. C. Allen, and K. Mislow, *Angew. Chem. Internat. Edn.*, 1970, **9**, 400; J. M. Lehn, *Fortschr. Chem. Forsch.*, 1970, **15**, 311; J. B. Lambert, *Topics Stereochem.*, 1971, **6**, 19.
[2] F. Montanari, I. Moretti, and G. Torre, *Chem. Comm.*, 1968, 1694; 1969 ,1086; D. R. Boyd and G. Graham, *J. Chem. Soc.* (*C*), 1969, 2648.
[3] S. J. Brois, *J. Amer. Chem. Soc.*, 1968, **90**, 506, 508; D. Felix and A. Eschenmoser, *Angew. Chem. Internat. Edn.*, 1968, **7**, 224; J. M. Lehn and J. Wagner, *Chem. Comm.*, 1968, 148; R. G. Kostyanovsky, Z. E. Samojlova, and I. I. Tchervin, *Tetrahedron Letters*, 1969, 719; R. G. Kostyanovsky, I. I. Tchervin, A. A. Formichov, Z. E. Samojlova, C. N. Makarov, Yu. V. Zeifman, and B. L. Dyatkin, *ibid.*, 1969, 4021; R. G. Kostyanovsky, V. I. Markov, and I. M. Gella, *ibid.*, 1972, 1301, and references therein; A. Padwa and A. Battisti, *J. Org. Chem.*, 1970, **36**, 230.
[4] A. Hassner and J. E. Galle, *J. Amer. Chem. Soc.*, 1970, **92**, 3733.
[5] H. Dieckmann and W. Lüttke, *Angew. Chem. Internat. Edn.*, 1968, **7**, 388.
[6] R. Fusco and F. Tenconi, *Chimica e Industria*, 1965, **47**, 61; E. U. Jonsson and C. R. Johnson, *J. Amer. Chem. Soc.*, 1971, **93**, 5308.