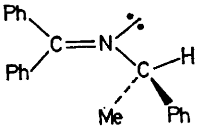
Absolute Configuration at the Chiral Nitrogen Atom in an Optically Active Oxaziridine. *X*-Ray Structure of (2*S*)-(—)-*N*-(*R*)-α-Methylbenzyldiphenyloxaziridine

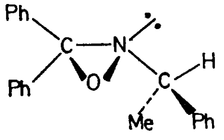
By MARIA BUCCIARELLI, IRENE MORETTI, and GIOVANNI TORRE*
(*Istituto di Chimica Organica dell'Universita', via Campi* 183, 41100 *Modena, Italy*)
and GIOVANNI DARIO ANDREETTI,* GABRIELE BOCELLI, and PAOLO SGARABOTTO
(*Istituto di Strutturistica Chimica dell'Universita' di Parma, C.N.R. Centro di Studio per la Strutturistica Diffrattometrica, via M. D'Azeglio* 85, 43100 *Parma, Italy*)

Summary (*R*)-(—)-(Diphenylmethylene)-α-methylbenzylamine reacts with organic peroxy-acids in chloroform solution to give stereospecifically (2*S*)-(—)-*N*-(*R*)-α-methylbenzyldiphenyloxaziridine; *X*-ray crystal structure analysis shows that the absolute configuration at the configurationally stable chiral nitrogen atom is (*S*).

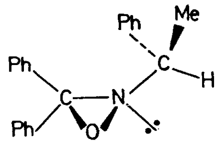
THE problem of the absolute configuration at the chiral nitrogen atom in optically active oxaziridines is still unresolved. This question is especially concerned with the asymmetric synthesis of chiral oxaziridines with optically active peroxy-acids,[1,2] and also with the more general problem of the mechanism of oxidation of imines.[3] The synthesis of optically active oxaziridines with a high degree of stereospecificity has been reported recently[4] and we now report our own results.†



(I)



(Va)



(Vb)

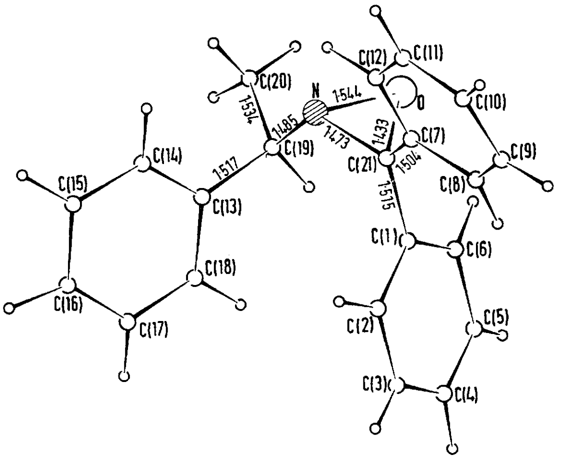


FIGURE. *X*-Ray structure of the (—)-*N*-methylbenzyldiphenyloxaziridine (Va). Bond distances are given in Å, standard deviations are 0·004Å.

The (*R*)-(—)-ketimine (I), prepared from benzophenone and (*R*)-(+)-α-methylbenzylamine as previously described for other ketimines,[5] was oxidised in chloroform solution at −20 °C with *m*-chloroperoxybenzoic acid (II), (1*S*)-(+)-peroxycamphoric acid (III), and (*R*)-(—)-2-phenylperoxypropionic acid (IV). Optical rotation value, n.m.r. spectral data, mixed m.p.s., as well as t.l.c. analysis showed that in every case the product recovered from the unchanged imine

---

† Taken in part from the Thesis of Vaifro Fiaccadori, University of Modena, 1972–1973.

in 80–90% yield (preparative t.l.c. on silica, CH_2Cl_2–n-hexane, 70:30, as eluant) consists of one diastereoisomer which is the same whether the achiral reagent (II) or the more complex peroxy-acids (III) and (IV) of opposite chirality are used as oxidant. This diastereoisomer crystallises from ether solution at −50 °C giving orthorombic prisms which are stable at room temperature; m.p. 78–79 °C, $[\alpha]_{\mathrm{D}}^{25}$ − 95·52° ($CHCl_3$); δ (CCl_4) 7·19 (m, ArH), 3·11 (q, CH), and 1·55 (d, Me). Analytical and spectroscopic data of the compound are in close agreement with structure (V); its stereochemistry was determined unambiguously by an *X*-ray structure analysis.

Crystal Data: $C_{21}H_{19}NO$, M = 301·4, orthorhombic, space group $P2_12_12_1$, a = 23·754(8), b = 8·778(5), c = 8·358(5) Å, Z = 4, D_c = 1·15 g cm^{-3}, U = 1742·7 Å^3, Cu-K_α radiation, λ = 1·5418 Å. 1924 intensities, of which 1561 were used in the crystal analysis, were measured diffractometrically. The structure was solved by direct methods and refined by anisotropic block-diagonal least-squares to a conventional R factor of 0·051. The hydrogens were located in the final ΔE map and refined isotropically.

Since the (*R*) chirality of the asymmetric carbon atom of (V) was known, and the *X*-ray analysis showed that the absolute configuration at the nitrogen atom (2) is (*S*), we can assign the (2*S*,α*R*) structure (Va) to our diastereoisomer. To the best of our knowledge, this is the first example of an optically active oxaziridine of known absolute chirality at the tercovalent asymmetric nitrogen atom.

The extremely high degree of stereoselectivity shown by the stereospecific synthesis of the (2*S*,α*R*)-(−)-diastereoisomer (Va) and the lack of correlation between the chirality of the optically active peroxy-acids and the chirality of the oxaziridine are not found in the oxidation of other similar achiral ketimines,[1] but are in very good agreement with the results of Bełżecki and Mostowicz.[4] It seems reasonable therefore to extend our configurational assignment to the results of the Polish authors.[4] We believe that knowledge of the stereochemistry of the predominant diastereoisomer from the ketimine (I) upon peroxy-acid oxidation [*i.e.* the (*S*,*R*) or (*R*,*S*) structures of (V) much more favoured than the (*S*,*S*) or (*R*,*R*) forms] can probably be used as a starting point for a more detailed study of the asymmetric inductions at tercovalent nitrogen in oxaziridine syntheses.

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

(*Received*, 28*th October* 1975; *Com.* 1217.)

---

[1] F. Montanari, I. Moretti, and G. Torre, *Gazzetta*, 1973, **103**, 681.

[2] D. R. Boyd and R. Graham, *J. Chem. Soc.* (*C*), 1969, 2648.

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

[4] C. Bełżecki and D. Mostowicz, *J.C.S. Chem. Comm.*, 1975, 244.

[5] I. Moretti and G. Torre, *Synthesis*, 1970, 141.