

Enantioselective Photocyclization of Nitrones into Oxaziridines
 in a Crystalline Inclusion Complex with Optically Active
 1,6-Di(o-chlorophenyl)-1,6-diphenylhexa-2,4-diyne-1,6-diol

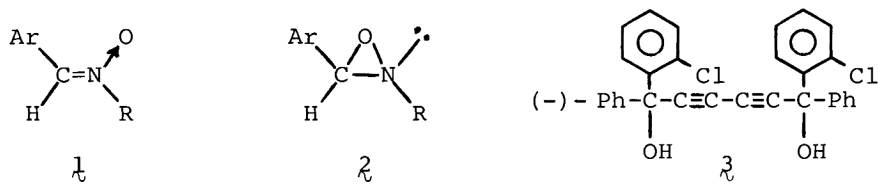
Fumio TODA* and Koichi TANAKA

Department of Industrial Chemistry, Faculty of Engineering,
 Ehime University, Matsuyama 790

Irradiation of complexes of nitrones with the title host compound in the solid state gave optically active oxaziridines in 100% enantiomeric excess.

Optically active oxaziridines are useful reagents for an enantioselective oxidation of olefin,¹⁻³⁾ and the following three preparative methods of the reagent have been reported: enantioselective oxidation of imine by (-)-peroxycamphoric acid,^{1,2)} photocyclization of nitrone which has a chiral substituent,³⁾ and photocyclization of nitrone in an optically active solvent.³⁾ In any case, however, optically active oxaziridine of more than 30% ee has not been obtained. We report on the preparation of 100% ee oxaziridines (**2**) by enantioselective photocyclization of nitrones (**1**) in a crystalline inclusion complex with (-)-1,6-di(o-chlorophenyl)-1,6-diphenylhexa-2,4-diyne-1,6-diol (**3**).

A 1:1 complex of **1** and **3** (**4**) was prepared by mixing **1** with an equimolar amount of **3** in benzene-hexane. For example, when a solution of **1a** (0.65 g, 4.1 mmol) and **3**⁴⁾ (2.0 g, 4.1 mmol) in benzene-hexane (1:1) (20 ml) was kept at room temperature for 12 h, a 1:1 complex of **1a** and **3** (**4a**) was obtained as colorless crystals in almost quantitative yield. Melting points of all the complex (**4a-g**) prepared are shown in Table 1. Powdered **4** was irradiated by a high pressure Hg-lamp, and the reaction mixture was chromatographed on silica gel (benzene) to give **2** and recovered **3**. Irradiation time and yield, $[\alpha]_D$ value, and % ee of **2** are summarized in Table 1. Optical purity of **2a-f** was determined by HPLC using a column containing an optically active solid phase, Chiralcel OC of Daicel Chemical Industries, Ltd. Optical

Table 1. Melting points of 1 , irradiation time, and yield, $[\alpha]_D$ value, and % ee of 2

	1		Mp of 1	Irradiation	Yield	$[\alpha]_D$	% ee
	Ar	R	$\theta_m/^\circ\text{C}$	time/h	%	$^\circ$ (c , CHCl_3)	%
$2a$	Ph	iPr	124-126	24	56	+40.7 (0.31)	---
$2b$	Ph	tBu	135-136	36	41	+8.2 (0.55)	9.5
$2c$		tBu	112-115	32	74	+16.0 (0.61)	30
$2d$		tBu	108-110	12	51	-4.3 (0.83)	100
$2e$		iPr	95-103	16	63	+20.0 (0.21)	28
$2f$		tBu	104-111	21	52	+78.5 (0.38)	94
$2g$	Ph	iPrMeCH	126-128	24	40	+53.9 (0.50)	100

purity of $2g$ was determined by NMR spectroscopy using chiral shift reagent, $\text{Eu}(\text{hfc})_3$. However, optical purity of $2a$ could not be determined.

Enantioselectivity in the formation of $2d$, $2f$, and $2g$ is high, but that of $2b$, $2c$, and $2e$ is low. This suggests that the selectivity is sensitive to the kind of substituent. Complexation of racemic $1g$ with 3 gave $(-)-1g$ of 100% ee in 31% yield ($[\alpha]_D -66.8^\circ$ (c 0.22, CHCl_3)).⁴⁾ Irradiation of a 1:1 complex of $1g$ of 100% ee and 3 gave $2g$ of 100% ee (Table 1). This is not due to a chiral induction by the optically active alkyl group, because irradiation of $1g$ of 100% ee in benzene gave $2g$ of only 12% de.

References

- 1) A. Forni, I. Moretti, and G. Torre, *J. Chem. Soc., Perkin Trans. 2*, **1987**, 699.
- 2) F. A. Davis, J. P. McCauley, Jr., S. Chattopadhyay, M. E. Harakal, J. C. Towson, W. H. Watson, and I. Tavanaiepour, *J. Am. Chem. Soc.*, **109**, 3370 (1987).
- 3) D. R. Boyd, R. M. Campbell, P. B. Coulter, J. Grimshaw, D. C. Neill, and M. B. Jennings, *J. Chem. Soc., Perkin Trans. 1*, **1985**, 849.
- 4) F. Toda, K. Tanaka, T. Omata, K. Nakamura, and T. Ōshima, *J. Am. Chem. Soc.*, **105**, 5151 (1983).

(Received September 5, 1987)