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ORBITAL SYMMETRY CONTROL IN THE NITRONE-OXAZIRIDINE SYSTEM. NITRONE PHOTOSTATIONARY STATES

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Orbital Symmetry Control in the Nitrone-Oxaziridine System.

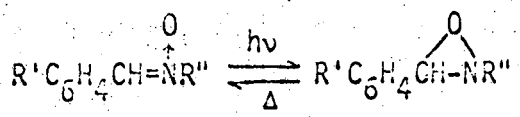
Nitrone Photostationary States

Sir:

Recently the orbital symmetry rules[1] have been shown to apply to hetero-atom systems such as nitrone thermal cycloaddition reactions[2] and the thermal and photochemical aziridine ring cleavage at the C-C bond.[3] The concerted photocyclization is disrotatory and the reverse thermal cleavage is conrotatory in these molecules with four π electrons.[1]

In contrast to the azomethine ylide - aziridine system, the stereochemistry of the nitrone photocyclization to oxaziridine can only be observed on carbon and nitrogen atoms because the oxygen atom has lone pair electrons instead of substituents. For the reverse thermal ring opening of oxaziridine to the nitrone, the two possible conrotatory motions of C-O bond cleavage should result in a mixture of the cis and trans-isomers of the nitrone,[4] in contrast to the photoclosure which should be stereospecific.

Boyd et al.[5] recently reported the formation of mixtures of cis and trans oxaziridines from the irradiation of trans-nitrones. However, there has been some evidence for the stereospecific formation of oxaziridine from nitrones.[6] We wish to report our results obtained from the photolysis of several nitrones at -60°C,[7] including IIIA and IVA which were studied by Boyd, et al.[5] at room temperature, and the thermolysis of IB at -8°C. Under these conditions thermal isomerization of the oxaziridine and nitrone isomers was suppressed.



A B

I, R' = $(CH_3)_2N$, R" = CH_3

II, R' = H, R" = CH_3

III, R' = NO_2, R" = CH_3

IV, R' = NO_2, R" = CH_2CH_3

The nmr spectra of these nitrones at -60° indicated the presence of only one nitrone isomer, the trans configuration as discussed by Koyano and Suzuki.[8] Irradiation of trans-IA and IIA at -60° in CD_3OD and $CDCl_3$ yielded exclusively trans-oxaziridines,[9] as observed by nmr at -60°. However, under the same conditions in CD_3OD, trans-IIIA and IVA yielded a mixture of 69% cis: 31% trans oxaziridines, which was in contrast to the predominantly trans-oxaziridines found by Boyd, et al.[5] With successive partial irradiations of trans-IVA at -60°, the presence of cis-IVA was demonstrated by nmr,[10] and a photostationary state of 37% cis: 63% trans-IVA was reached at approximately 15% conversion to oxaziridines. The cis-IVA rapidly isomerized thermally to trans-IVA at room temperature. The thermal stability of cis-IIIA and IVA was found to be concentration dependent. They were relatively stable when formed by irradiation at room temperature in alcoholic solvents in 10^{-4} M ($t_{1/2}$ ~24 hours). The UV spectrum of the photostationary mixture of IVA was similar to that obtained by dilution of the concentrated solution irradiated in the nmr tube to the photostationary state at -60°. The uv spectrum of cis-IVA[11] was determined from the photoequilibrium composition and the isosbestic point for cis → trans thermal isomerization.

The ratio of cis and trans-IVA at the photostationary state is very different from the ratio of cis and trans-IVB formed at the end of the photocyclization reaction. For this reason the quantum yields of the photoreactions for each isomer were determined at 23° (10^{-4} M) and are

reported in Table I. From the quantum yields of formation of trans and

Table I. Quantum Yields for Products at 23° [a]

Reaction	Solvent	ϕ
trans-IA → trans-IB	isopropanol	0.26
trans-IVA → IVB[b]	methanol	0.02
trans-IVA → cis-IVA[c]	"	0.22
cis-IVA → trans-IVA[d]	"	0.57
cis-IVA → IVB[b]	"	0.11

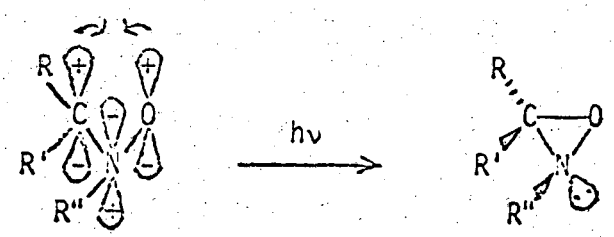
[a]Wavelength, 366 nm; concentration, 10^{-4} M; ferrioxalate actinometry. [b]Determined by decrease in optical density at 327 nm, isosbestic point of the nitrone isomers. [c]Determined by change in ratio of optical density at 357 nm and 317 nm. [d]Calculated from the photostationary state relation, $\phi_{t\to c}\varepsilon_t X_t^{\infty} = \phi_{c\to t}\varepsilon_c X_c^{\infty}$, where X_t^{∞} and X_c^{∞} are the mol fractions of the isomers at photoequilibrium.

cis-IVA[12] and of IVB formation from cis and trans-IVA, the calculated ratio of IVB isomers formed after the photostationary state was reached, assuming stereospecificity is 68% cis: 32% trans. After the IVA photostationary state was reached on irradiation at -60°, the ratio of IVB isomers found by nmr was 71% cis: 29% trans. Therefore, these results indicate stereospecificity in the nitrone photocyclization reaction.

For the reverse thermal cleavage of oxaziridine to nitrone, IB in CD_3OD gave a 50:50 mixture of cis and trans-IA with a first order rate constant, 6.8×10^{-4} sec^{-1} at -8°, by nmr spectroscopy.[13] The first order rate constant for the cis → trans-IA under these conditions was 2.9×10^{-5} sec^{-1} at 23°. Only in alcoholic solvents was the rate of

the thermal cis → trans-IA isomerization slower than the rate of the IB ring opening reaction.[14] The photostationary state composition of IA was confirmed to be 100% trans-IA.

The trans-IB thermal cleavage to cis and trans-IA is clearly in accordance with the predictions of the orbital symmetry rules. The observed stereospecificity in the nitrone photocyclization is consistent with the symmetry of the nitrone antibonding molecular orbital. As the carbon-oxygen σ bond forms in disrotatory motion, the nitrogen π orbital rehybridizes to a lone pair sp^3 hybridized orbital in the opposite direction, giving an oxaziridine with the same configuration as the initial nitrone.



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(5) D. R. Boyd, W. Jennings, and R. Spratt, Chem. Commun., 745 (1970).

(6)(a) H. Ono, Ph.D. Dissertation, Univ. of California, Berkeley, Calif., 1969;

(b) G. G. Spence, E. C. Taylor, and O. Buchardt, Chem. Rev., 70, 231 (1970).

(7) Solutions (10^{-2} M) were irradiated in the nmr tube in the presence of oxygen with a Hanovia 450 watt medium pressure mercury lamp, Pyrex filter. The oxaziridines remained unchanged under these conditions of irradiation. Nmr spectra were recorded on a Varian 220 MHz spectrophotometer; uv spectra on a Cary 14 spectrophotometer.

(8) K. Koyano and H. Suzuki, Tetrahedron Lett., 1859 (1968); Bull. Chem. Soc. Jap., 42, 3306 (1969). These authors presented nmr evidence which was used to distinguish cis and trans-nitrone isomers.

(9) According to the assignment of D. Jerina, D. Boyd, L. Paolillo, and E. Becker, Tetrahedron Lett., 1483 (1970).

(10) Trans-IVA: α-CH, τ 1.82; $-CH_3$, τ 8.49(t)

cis -IVA: α-CH, τ 1.75; $-CH_3$, τ 8.46(t)

(11) Trans-IVA: λ_{max}^{MeOH} 338 nm (ε 14,800)

cis -IVA: λ_{max}^{MeOH} 325 nm (ε 13,750)

Although the uv of the IIIA photostationary state was similar to that of IVA, the photostationary state composition could not be determined because of the lesser solubility of IIIA in CD_3OD.

(12) The combined $\phi_{t\to c}$ and $\phi_{c\to t}$ suggest, in addition to oxaziridine formation, the efficient formation of a common twisted state analogous to the twisted state in the stilbene direct photoisomerization. (a) D. Gegiou, K. A. Muszkat, and E. Fischer, J. Amer. Chem. Soc., 90, 3907 (1968); (b) J. Saltiel and E. D. Megarity, ibid., 91, 1265 (1969); 90, 4759 (1968).

(13) Trans-IA: α-CH, τ 2.19; N-CH_3, τ 6.27.

Cis -IA: α-CH, τ 1.94; N-CH_3, τ 6.15.

No cis-IA was detected in the partial irradiation of trans-IA.

(14) At 23° in isopropanol (10^{-4} M) the ring cleavage rate was 3.4×10^{-4} sec^{-1}; the cis → trans-IA thermal rate was 4.0×10^{-7} sec^{-1}.

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