

Figure 1. Comparative CD spectra of ApA (\cdots) (J. Brahms, A. M. Michelson, and K. E. Van Holde, *J. Mol. Biol.*, **15**, 467 (1966)), thymidine ($---$), adenosine ($- \cdot -$), **3** ($—$), and **4** ($---$). The following abbreviations are used: Ad, aden-9-yl; Th, thym-1-yl; C₃, *n*-propyl; ApA, adenylyl-(3'-5')-adenosine.

The uv spectra of **3** and **4** both exhibit a blue shift and hypochromicity compared to their components (Table I). It is of interest to note that the extinction coefficients of **3** and **4** have approximately the same magnitude as the extinction coefficients of Ad(CH₂)₃Ad and Ad(CH₂)₃Th reported by Browne, Eisinger, and Leonard. Presumably similar base-base interactions could exist in both cases. The CD spectra of **3** and **4** (Figure 1) reflect significant changes from the spectra of adenosine (disregarding the 2'-deoxy) and thymidine. The absorption band near 257, in a similar manner as does that of ApA, in both **3** and **4** gives rise to two intense CD bands of opposite sign indicative of interaction between the two bases. It is interesting to note that compounds **3** and **4** exhibit *negative* CD bands at the longer wavelength as opposed to ApA where the long-wavelength CD band is *positive*.

The synthesis of other "double-headed" ribonucleosides and a comparison of their interaction with polynucleotides are in progress.

(9) To whom all inquiries should be addressed.

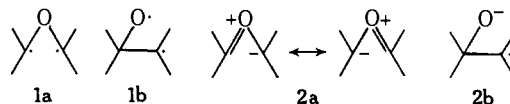
R. Fecher, K. H. Boswell, J. J. Wittick, T. Y. Shen⁹
Merck Sharp and Dohme Research Laboratories
Rahway, New Jersey 07065
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Low-Temperature Photochemistry of Oxiranes. II. The Formation of Carbonyl Ylides and Their Stereospecific Interconversion with Oxiranes

Sir:

Low-temperature photolyses of aryloxiranes in rigid glasses have recently been reported to produce highly

colored materials, carbenes, and carbonyl compounds.^{1,2} While the mechanism of carbene formation has been discussed,^{1,2} little information is available regarding the nature of these colored compounds. Becker, *et al.*,² without excluding the possibility of an ionic intermediate, suggested diradical **1b** resulting from a C-O cleavage. In our earlier report we favored zwitterions **2a** or **2b** formed directly or rapidly from short-lived diradicals **1a** or **1b**. We now present evidence that the



colored intermediates are most probably carbonyl ylides **2a** and that their photochemical interconversion with oxiranes is consistent with an allowed electrocyclic process.

The stereospecific ring opening and recyclization of *cis*- and *trans*-stilbene oxides is typical of these photolyses. Irradiation of *trans*-stilbene oxide in ethanol glass at 77°K produced an orange material (λ_{\max} 490 nm, $\epsilon > 10^4$) along with small amounts of benzaldehyde, phenylmethylene, and desoxybenzoin.³ Irradiation of the *cis* isomer gave similar products, but the colored intermediate was a deep red compound (λ_{\max} 510 nm). Near 140°K, both colorations disappeared (the bleaching occurring somewhat faster in the *trans* sample than in the *cis*) and gave benzaldehyde and phenylmethylene. The amount of fragmentation products formed by this photolysis-warm-up procedure was estimated to be 20–25 times more than that originally produced by photolysis.³ The rate of fading on warming was noticeably greater if norbornadiene or dimethyl acetylenedicarboxylate were present. Significantly both reagents are efficient dipolarophiles.⁴ Irradiation in the visible (450-W Hanovia medium pressure arc, Pyrex filter) caused rapid fading and regenerated the original oxirane with little fragmentation.⁵ In no case could *cis-trans* isomerization be detected in the recovered oxirane which had undergone repeated double photolysis cycles or photolysis-warm-up resulting in 15% conversion to fragmentation products.⁵

The photochemical ring opening of stilbene oxides to isomeric intermediates and the stereospecific recyclization of the latter to oxiranes suggest structures of the type **2a**, rather than **2b**, **1a**, or **1b** which do not possess double bonds or double bond character.⁶ The overall

(1) A. M. Trozzolo, W. A. Yager, G. W. Griffin, H. Kristinsson, and I. Sarkar, *J. Amer. Chem. Soc.*, **89**, 3357 (1967).

(2) R. S. Becker, J. Kolc, R. C. Bost, H. Dietrich, P. Petrellis, and G. W. Griffin, *ibid.*, **90**, 3292 (1968). For a more recent interpretation, see R. S. Becker, *et al.*, *ibid.*, **92**, 1302 (1970).

(3) Solutions of the oxiranes (0.5–1 mg/ml) in quartz tubes at 77°K were irradiated for 15–30 sec with 2537-Å light from a Rayonet reactor (New England Ultraviolet Co.) equipped with low-pressure mercury lamps. Benzaldehyde was identified by its luminescence spectrum using an Aminco-Kiers spectrophotofluorometer, phenylmethylene was trapped as benzyl ethyl ether, and desoxybenzoin was identified by comparison with an authentic sample.

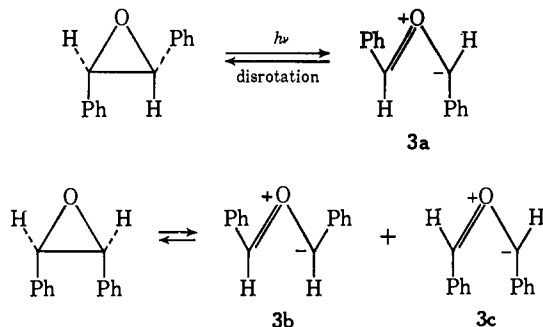
(4) R. Huisgen, *Angew. Chem. Intern. Ed. Engl.*, **2**, 565 (1963).

(5) Benzaldehyde and phenylmethylene formed in the first photolysis were not appreciably increased when the colored intermediates were bleached by a second photolysis with visible light. *cis*- and *trans*-stilbene oxides and other products were separated by a 5-ft Carbowax 20 M column using the analytical Beckman GC-5.

(6) The formation of desoxybenzoin may be rationalized by a rearranged diradical or dipole of the type **1b** or **2b**. However, the fact that styrene oxide gave phenylacetaldehyde, but did not give phenylmethylene or any low-temperature colored intermediate, suggests that **1b** or **2b** is unlikely to be responsible for the observed colorations.

process may be envisioned as an electrocyclic reaction which interconverts oxiranes and open-chained carbonyl ylides by a conrotatory or disrotatory course. Three possible ylides may be derived from stilbene oxides as depicted in Scheme I (3a-c). It is evident for stereo-

Scheme I



electronic reasons that the order of stability is $3b > 3a \gg 3c$. Since $3c$ can only be formed in conjunction with $3b$ regardless of the mode of rotation, its formation is highly improbable. This is supported by the recent results of Huisgen and coworkers on the isoelectronic aziridine-azomethine ylide system. Only the two ylides having structures corresponding to $3a$ and $3b$ could be found as cycloadducts⁷ and the equilibrium at 100° between the two forms was substantially in favor of the *cis-exo* isomer. From the relative stability and absorption spectrum it is possible to assign the *cis-exo*-ylide $3b$ to the more stable, red-shifted intermediate from *cis*-stilbene oxide, and the *trans*-ylide $3a$ to the one from *trans*-stilbene oxide. Consequently, the electrocyclic reaction very probably involves a disrotatory course, and in the case of *cis*-stilbene oxide, an "outward" disrotation. This is further supported by the photochromic behavior of bicyclic oxiranes whose special geometry permits only an outward disrotatory course. Thus irradiation of 1,2-diphenylcyclopentene oxide or 1,2-diphenylcyclohexene oxide yielded bright red intermediates (λ_{max} 525 and 538 nm, respectively) which, upon further irradiation with visible light, quantitatively reverted to oxiranes.⁸ The facile photochromism is attributed to the fact that ylides from these ring systems are rigidly maintained in the proper geometry for cyclization.⁹

Carbonyl ylide intermediates also are suggested by evidence that excludes alternative structures. The absorption spectra of the colored materials do not agree with those of known anions,¹⁰ cations,^{10,11} or radicals¹² having structures related to **1a**, **1b**, or **2b**. Model compounds such as 1,2-diphenylcyclopropane and styrene oxide, which may be photochemical precursors for

(7) R. Huisgen and H. Mader, *Angew. Chem. Intern. Ed. Engl.*, **8**, 604 (1969).

(8) No loss of oxirane or appearance of products was detected (Beckman GC-5, Carbowax 20 M) from repeated double photolyses, except when the photolysis-warm-up cycles were followed.

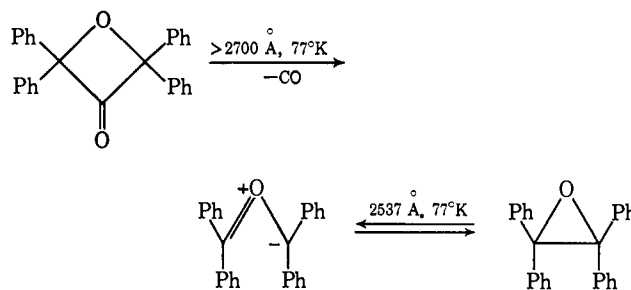
(9) Dr. D. Arnold has kindly called our attention to his work on 1,2-diphenylcyclobutene oxide from which the carbonyl ylide ($\lambda_{\text{max}}^{\text{EtOH}}$ 22° 550 nm) was intercepted by various dipolarophiles. His observations and interpretation are consistent with and complementary to ours (see accompanying communication: D. R. Arnold and L. A. Karnischky, *J. Amer. Chem. Soc.*, **92**, 1404 (1970)).

(10) S. F. Mason, *Quart. Rev.* (London), **15**, 335 (1961).

(11) H. H. Jaffé and M. Orchin, "Theory and Application of Ultraviolet Spectroscopy," John Wiley & Sons, Inc., New York, N. Y., 1966.

(12) A. M. Trozzolo and W. A. Gibbons, *J. Amer. Chem. Soc.*, **89**, 239 (1967).

analogous of **1a** and **1b** or **2b**, respectively, failed to give colored intermediates at 77°K. The absence of an epr signal in the temperature range of 77–140°K, where the colored intermediates are stable, indicates that a triplet diradical is not formed as a stable species. Significantly, *cis*-2,3-diphenylaziridine upon irradiation in low-temperature glasses formed a yellow compound ($\lambda_{\text{max}}^{\text{EtOH}}$ 473 nm), presumably an azomethine ylide of the type **3b**. Finally, in confirmation of a C-C cleavage in the ring opening of oxiranes, irradiation of tetraphenyl-oxetanone¹³ with wavelengths which would not affect the photolysis of tetraphenyl-oxirane (450-W Hanovia arc, Corex filter) gave a blue intermediate spectroscopically identical with the one from tetraphenyl-oxirane irradiated with shorter wavelengths ($\lambda_{\text{max}}^{\text{EtOH}}$ 318, 420, 585 nm).



Cyclopropyl anions are predicted by Woodward and Hoffmann to open photochemically to allyl anions by a disrotatory course.¹⁴ Recently this prediction has been demonstrated convincingly by Huisgen and coworkers for the isoelectronic aziridine-azomethine ylide system.¹⁵ By analogy, isoelectronic oxiranes might be expected to interconvert photochemically with carbonyl ylides by a disrotation. On the other hand, conrotation is a thermally allowed process. Thus, if ring closure were to take place during warm-up, *cis-trans* isomerization would have been expected. The absence of isomerization indicates that fragmentation is the more important reaction pathway.

Although carbonyl ylides have been postulated in the addition of carbenes to carbonyl compounds and the thermolysis of 1,3-dioxolan-4-ones, these polar compounds have not been observed directly.⁴ The stereospecific interconversion between oxiranes and carbonyl ylides described here provides the first such observation and is consistent with the principle of conservation of orbital symmetry.¹⁴

Acknowledgments. We wish to thank Dr. E. A. Chandross for several stimulating discussions and W. A. Yager for the epr experiments.

(13) J. L. Harper and C. T. Lester, *J. Org. Chem.*, **26**, 1294 (1961). We thank Miss Ingrid Fuss for technical assistance in preparing this compound.

(14) R. B. Woodward and R. Hoffmann, *Angew. Chem. Intern. Ed. Engl.*, **8**, 781 (1969); R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968).

(15) R. Huisgen, W. Scheer, and H. Huber, *ibid.*, **89**, 1753 (1967).

Thap Do-Minh, A. M. Trozzolo
Bell Telephone Laboratories
Murray Hill, New Jersey 07974

G. W. Griffin
Louisiana State University
New Orleans, Louisiana 70122

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