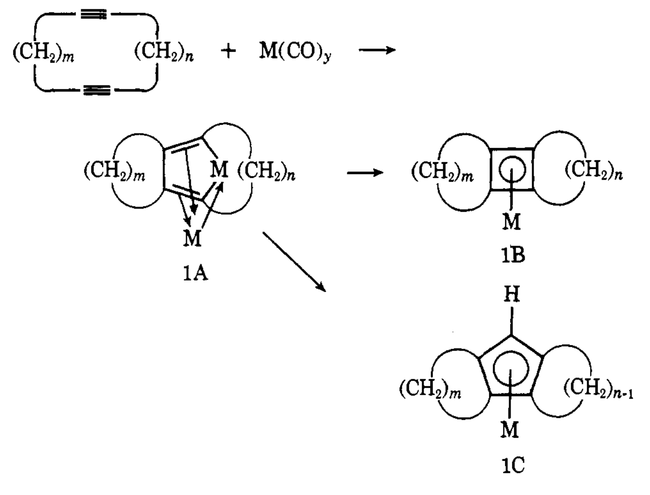
Scheme I. Proposed Scheme for the Intramolecular Transannular Cyclization of Macrocyclic Alkadiynes with Metal Carbonyls



M = Fe(CO)$_x$ or C_5H_5Co

$(C_6H_5C_2C_6H_5)_2P(C_6H_5)_3$ (VII) to be an intermediate in the formation of the tetraphenylcyclobutadiene complex $C_5H_5CoC_4(C_6H_5)_4$ from the alkyls $C_5H_5CoR_2P(C_6H_5)_3$ (R = isopropyl, etc.) and diphenylacetylene. The metallacyclopentadiene derivative 1A in Scheme I can undergo loss of one of the two metal atoms with carbon–carbon bond formation to form a four-membered central ring giving the tricyclic cyclobutadiene derivative 1B in Scheme I. Alternatively the metallacyclopentadiene derivative 1A in Scheme I can undergo hydrogen migration and hydrogen loss along with loss of one of the two metal atoms with carbon–carbon bond formation to form a five-membered central ring giving the tricyclic cyclopentadienyl derivative 1C in Scheme I. Whether the end product is the tricyclic cyclobutadiene derivative 1B (Scheme I) or the tricyclic cyclopentadienyl derivative 1C (Scheme I) will depend upon the available coordination sites on the transition metal atom and on the sizes of the two outer rings in the final tricyclic system.

In the reactions of the macrocyclic alkadiynes I with $C_5H_5Co(CO)_2$ the complete loss of both carbonyl groups from the cobalt atom provides sufficient free coordination sites for the four-electron donor cyclobutadiene ring in a tricyclic cyclobutadiene derivative (1B in Scheme I) but not for the five-electron donor cyclopentadienyl ring in a tricyclic cyclopentadienyl derivative (1C in Scheme I). Therefore the reactions of $C_5H_5Co(CO)_2$ with the macrocyclic alkadiynes of type I are relatively simple[1,2] and in all cases proceed relatively efficiently to give the tricyclic cyclobutadiene derivatives II.

The reactions of the macrocyclic alkadiynes I with iron carbonyls are considerably more complex since the $Fe(CO)_3$ groups in the intermediate metallacyclopentadiene derivative (1A in Scheme I) either have enough free coordination sites for the four-electron donor cyclobutadiene ring in a tricyclic cyclobutadiene derivative (1B in Scheme I) or can generate enough free coordination sites for the five-electron donor cyclopentadienyl ring in a tricyclic cyclopentadienyl derivative (1C in Scheme I) by losses of a carbonyl ligand to form $Fe(CO)_2$ groups. The following principles account for the observations summarized in this and the previous[3] communication on the reactions of macrocyclic alkadiynes with iron carbonyls.

(1) The presence of a bridge of exactly five CH_2 groups (*i.e.*, either *m* or *n* or both = 5) is necessary for the transannular cyclization forming a tricyclic cyclopentadienyl derivative of type III (*i.e.*, 1C in Scheme I). Such a five CH_2 group bridge would give a six-membered outer ring upon cyclization to a cyclopentadienyl derivative but a seven-membered outer ring upon cyclization to a cyclobutadiene derivative (*i.e.*, 1B in Scheme I). In 1,8-cyclotetradecadiyne (I, *m* = *n* = 5) with two bridges of five CH_2 groups the tendency for formation of a tricyclic cyclopentadienyl derivative (1C in Scheme I) is particularly high.

(2) A bridge of four CH_2 groups is sufficient for formation of a tricyclic cyclobutadiene derivative (1B in Scheme I) but a bridge of more than four CH_2 groups is necessary for the conversion of the intermediate metallacyclopentadiene derivative (1A in Scheme I) to the tricyclic cyclobutadiene derivative (1B in Scheme I) to take place at a significant rate.

Acknowledgment. We are indebted to the National Science Foundation for partial support of this work under Grant GP-31347X.

(7) Permanent staff member of the Department of Chemistry, Babeş Bolyai University, Cluj, Romania, on leave during 1971–1972 in the Department of Chemistry, University of Georgia.

R. B. King,* Ionel Haiduc[7]
Department of Chemistry, University of Georgia
Athens, Georgia 30601

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Photochromic Aziridines. I. The Mechanism of Photochromism in 1,3-Diazabicyclo[3.1.0]hex-3-enes and Related Aziridines

Sir:

The synthesis of a series of photochromic bicyclic aziridines has been described by Heine and coworkers.[1] We present evidence that the colored species produced in these photoinduced reversible reactions are 1,3 dipoles (azomethine ylides). In addition, structural requirements for the photochromism are outlined, and the suggestion is made that the formation of the colored intermediate may involve vibrationally excited ground-state species.

Typical of the compounds investigated (Table I)

Table I. Photochromic Bicyclic Aziridines

Colored intermediate	$\lambda_{max}^{77° K}$, nm	Glass	$\lambda_{max}^{KBr; 25°}$, nm	Color
1a[a]	605	MTHF	625,580 (sh)	Blue
1b[b]	512,485 (sh)	EtOH	526,495 (sh)	Pink
1c[c]	610,570 (sh)	MTHF	645,600 (sh)	Green

[a] Heine, *et al.*[1a] [b] A. Padwa, S. Clough, and E. Glazer (*J. Amer. Chem. Soc.*, **92**, 1778 (1970)) isolated **1b** when preparing the exo-trans isomer according to the Heine procedure. [c] Mp 166–167°; we prepared **1c** and its exo-trans isomer (mp 175–176°) using Heine–Padwa methods.

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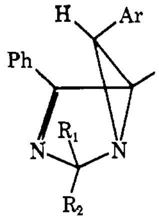
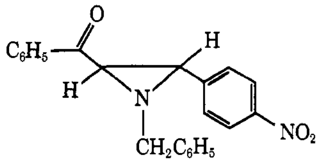
(1) (a) H. W. Heine, R. H. Weese, R. A. Cooper, and A. J. Durbetaki, *J. Org. Chem.*, 32, 2708 (1967); (b) H. W. Heine, A. B. Smith, III, and J. D. Bower, *ibid.*, 33, 1097 (1968); (c) H. W. Heine and R. P. Hanzel, *ibid.*, 34, 171 (1969).



1a, $R_1 = R_2 =$ Me;
Ar = *p*-nitrophenyl
b, R_1 = Ar = Ph;
R_2 = H (exo-cis)
c, R_1 = Ph; R_2 = H;
Ar = $PhNO_2$(p)(exo-cis)

is **1a**, which is a colorless crystalline material: mp 182–190°; λ_{max}^{EtOH} 250 nm (ϵ 3.0 × 10^4), 283 (ϵ 2.3 × 10^4). Crystals of **1a** or its glassy solutions at 77°K upon exposure to light ($\lambda < 450$ nm) rapidly developed an intense blue color ($\lambda_{max}^{MTHF, 77°K}$ 605 nm, $\epsilon \simeq 5 \times 10^4$). The color can be erased by irradiation in the visible region ($\lambda > 550$ nm) or by heat. In the dark at room temperature, the color faded in 12 hr (3 min at 110°) in a first-order kinetic process and the coloration–erasure cycle could be repeated several hundred times with no apparent sign of decomposition. The quantum efficiency for color formation in 2-methyltetrahydrofuran (MTHF) at 77°K was estimated to be 0.85.[2] In solution, the lifetime of the colored intermediates was much shorter (several minutes at room temperature) and their formation was not entirely reversible due to a competing reaction leading to enediimines.[3,4] In an earlier report, we showed that the enediimine was formed *via* transient colored intermediates which were 1,3 dipoles (azomethine ylides).[4] Now, we have found that these same colored intermediates were obtained when the aziridines were irradiated in the crystalline state. Their absorption spectra in KBr, except for a small red shift, closely parallel those taken in rigid glasses at 77°K, and undoubtedly are due to the same species. The red shift in the KBr spectra at 25°K can be attributed to a matrix and temperature effect.

In agreement with the proposed 1,3-dipolar structure, the stability of the colored intermediates is strongly influenced by both electronic and steric changes in the structure of the aziridines. Thus, removal of the nitro group, or shifting it to a meta position, markedly reduced the photochromic sensitivity of the aziridines and blue-shifted the absorption spectrum of the colored species (Table I). A second fused ring, especially with 2 substituents, appears to stabilize the ylide relative to the aziridine. When this added ring strain was eliminated as in **2**,[5] irradiation produced a purple coloration which was stable only at 77°K ($\lambda_{max}^{MTHF, 77°K}$ 580 nm) and faded instantly on warming to room temperature. Compound **3**,[1c] with an unsubstituted fused 6 ring, exhibited intermediate sensitivity ($\lambda_{max}^{MTHF, 77°K}$ 605 nm, lifetime 15 min at 25°, blue color readily erased by visible light). Interestingly, irradiated single crystals of the aziridines were found to be highly dichroic. The blue monoclinic crystals of **1a** absorbed strongly along one axis and were essentially transparent in the perpendicular when observed under a a polarizing microscope. The anisotropy presumably reflects a highly stereospecific ring opening of the aziridines. Irradiation of the powder of **1a** in an electric field produced a significant increase (~1%) of the total capacitance which we ascribe to the formation of the dipolar intermediate.[6] The internal reflection ir spectrum of the irradiated solid of **1a** revealed new bands at 1400, 1320, and 1270 cm^{-1}; the latter two bands may be attributed to an extensively conjugated nitro group[7] in the colored intermediate.



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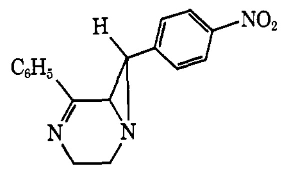
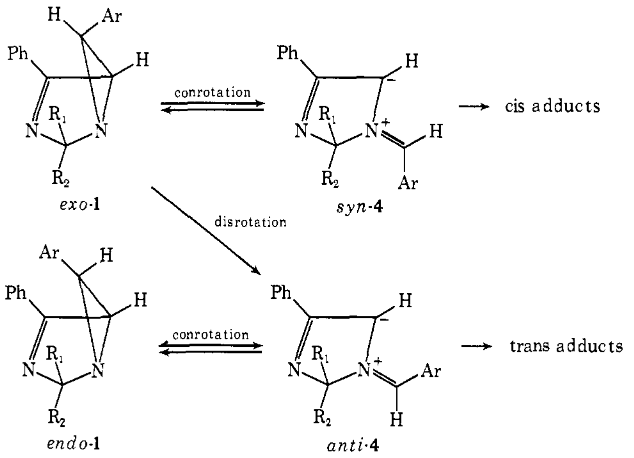


3

Orbital symmetry considerations[8] suggest that aziridines interconvert with azomethine ylides by a conrotatory process in the ground state. A disrotatory course is predicted from the excited state. This prediction has been verified recently by Huisgen and coworkers for a simpler aziridine–azomethine ylide system.[9] The two possible ylides derived from **1a** are *syn-* and *anti*-**4** (Scheme I). Earlier, in our study on the mechanism of enediimine formation,[4] we assigned a cis configuration to the cycloadduct with dimethyl acetylenedicarboxylate on the basis of the nmr spectrum and a facile catalytic dehydrogenation of the adduct to form a pyrrole. From the stereochemistry of the adduct, the *syn*-**4** structure was given to the colored intermediate. Consequently, the ring opening of the aziridine appears to involve a conrotation which is a

Scheme I



a, $R_1 = R_2$ = Me; Ar = *p*-nitrophenyl
b, R_1 = Ar = Ph; R_2 = H
c, R_1 = Ph; R_2 = H; Ar = *p*-nitrophenyl

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(2) Glassy 10^{-3} *M* solutions of **1a** were irradiated for 20–30 sec with 3500-Å light from a Bausch-Lomb grating monochromator. Light intensity was measured by an Eppley thermopile and the reaction was monitored by a Cary 15 spectrophotometer.

(3) See Padwa, *et al.*, Table I, footnote *b*.

(4) T. DoMinh and A. M. Trozzolo, *J. Amer. Chem. Soc.*, **92**, 6997 (1970).

(5) Mp 133–135°.

(6) We thank Mr. G. E. Johnson for technical assistance in this experiment.

(7) L. J. Bellamy, "Infrared Spectra of Complex Molecules," Wiley, New York, N.Y., 1960, p 297.

(8) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(9) (a) H. Hermann, R. Huisgen, and H. Mäder, *J. Amer. Chem. Soc.*, **93**, 1779 (1971); (b) R. Huisgen, S. Scheer, and H. Huber, *ibid.*, **89**, 1753 (1967).

symmetry-allowed concerted process in the *ground state.* The photoinduced reaction may be only a dark reaction in which electronically excited states internally convert to vibrationally excited ground states. Support for this view is found in the thermochromic behavior of **1a**. Thus, heating crystals of **1a**, up to 150°, developed the same blue color. Furthermore, thermal cycloaddition with TCNE or dimethyl acetylenedicarboxylate in toluene at 100° for 3 hr gave 60–70% yields of cycloadducts[10] having identical stereochemistry with the corresponding photoproducts. On the other hand, if the photochemical ring opening were to take a disrotatory course to form *anti*-**4** (Scheme I) thermal ring closure would be expected to take an opposite course to give the new *endo*-**1**. Such an exo–endo isomerization has not been observed to date. Examination of scale models suggests that the endo isomer of **1** is sterically unfavorable in general and impossible in the case of **1a** and **1c**. Indeed, our attempts to detect *endo*-**1a** in the synthesis[1a] of *exo*-**1a** or in its base-catalyzed epimerization[11] have been so far unsuccessful. To the extent that the formation of *endo*-**1a** appears unfeasible, a ground-state conrotatory course to and from *exo*-**1a** may be a more favored process. Complementary evidence for this view is found in the very low quantum yields of luminescence ($<10^{-3}$) from these photochromic aziridines or their colored intermediates even at 77°K. (The photocoloration can also be sensitized by triplet sensitizers of $E_T > 70$ kcal/mol.) Vibrationally excited ground states have been suggested by Ullman and Henderson[12] for the thermophotochromic system of indenone–benzopyrylium oxide which provides an excellent analogy to ours.

Acknowledgment. We thank Professor H. W. Heine for a generous supply of **1a** and for stimulating and timely discussions.

[10] Heine, *et al.*,[1b] reported a similar reaction with diethyl acetylenedicarboxylate.

[11] A. B. Turner, H. W. Heine, J. Irving, and J. B. Bush, Jr., *J. Amer. Chem. Soc.*, **87**, 1050 (1965).

[12] E. F. Ullman and W. A. Henderson, *ibid.*, **86**, 5050 (1964).

Thap DoMinh, Anthony M. Trozzolo*
Bell Laboratories
Murray Hill, New Jersey 07974
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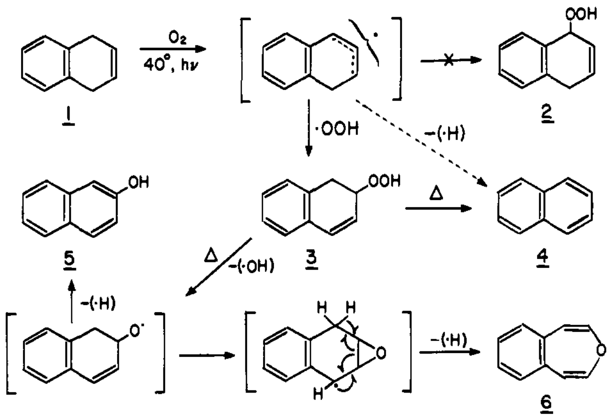
Autoxidation of 1,4-Dihydronaphthalene. Formation of 3-Benzoxepin *via* Pyrolysis of 1,2-Dihydronaphthalene 2-Hydroperoxide

Sir:

The considerable current interest in the chemistry[1a,b] and biochemistry[1c,d] of arene oxides and oxepins has prompted us to report a novel and convenient synthesis[2] of 3-benzoxepin (**6**). The route was discovered in the course of an attempt to prepare 1,4-dihydronaphthalene 1-hydroperoxide (**2**) by the reported autoxidation of 1,4-dihydronaphthalene (**1**). The latter reaction did not proceed as described,[3a,b] but led instead to 1,2-dihydronaphthalene 2-hydroperoxide (**3**) together with naphthalene (**4**), 2-naphthol (**5**), a polymeric mixture, and, quite unexpectedly, 3-benzoxepin (**6**) (Scheme I).

Scheme I



In a typical experiment, 5 g of **1**[4] was maintained at 45° and irradiated with a 60-W fluorescent lamp while oxygen was passed through the liquid. After 48 hr, the mixture became too viscous for oxygenation to be continued. Dilution of the reaction mixture with 5 ml of ether was followed by precipitation of the polar components (3.2 g) with isopentane (50 ml), providing a preliminary separation. A small amount of **6** along with **1**, **4**, and **5** was found in the yellow isopentane solution. The hydroperoxide **3**, the major component in the viscous precipitate, was obtained as a colorless oil[5] by tlc on silica gel.[6] The mass spectrum of **3** shows a weak molecular ion (*m/e* 162, 3%) with fragments resulting from the loss of 16 (18%), 18 (42%), and 34 (100%) mass units. The nmr spectrum of **3** (1 $H_{1,ax}$ 2.95, 1 $H_{1,eq}$ 3.27, 1 H_2 4.73, 1 H_3 5.98, 1 H_4 6.75, and four aromatic protons 7.0–7.25; $^2J_{1,1} = 17.3$, $^3J_{1ax,2} = 6.1$, $^3J_{1eq,2} = 4.7$, $^3J_{2,3} = 4.4$, $^4J_{2,4} = 0.7$, and $^3J_{3,4} = 9.5$ Hz)[7] indicates a 3,4 double bond and quasiaxial substitution by oxygen at the 2 position. The structure of **3** was established by its chemical reactions. Decomposition by 20% Na_2CO_3 (100°, 5 min) gave **5** with only a trace of 1-naphthol, which presumably arose from a minor contaminant of **2**. Similarly, reduction of **3** with Pd and hydrogen gave 2-tetralol with only a trace of the 1 isomer.[8]

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[1] (a) C. H. Foster and G. A. Berchtold, *J. Amer. Chem. Soc.*, **93**, 3831 (1971); (b) L. A. Paquette and T. McCreadie, *J. Org. Chem.*, **36**, 1402 (1971); (c) B. R. Brodie, W. D. Reid, A. K. Cho, G. Sipes, G. Krishna, and J. R. Gillette, *Proc. Nat. Acad. Sci. U. S.*, **68**, 160 (1971); (d) P. L. Grover, P. Sims, E. Huberman, H. Marquardt, T. Kuroki, and C. Heidelberger, *ibid.*, **68**, 1098 (1971).

[2] For earlier syntheses, see K. Dimroth, G. Pohl, and H. Follmann, *Chem. Ber.*, **99**, 634 (1966); E. Vogel and H. Günther, *Angew. Chem., Int. Ed. Engl.*, **6**, 385 (1967); and G. R. Ziegler, *J. Amer. Chem. Soc.*, **91**, 446 (1969).

[3] (a) H. Hock and F. Depke, *Chem. Ber.*, **83**, 327 (1950); (b) M. Martan, J. Mangssen, and D. Votsi, *Israel J. Chem.*, **7**, 751 (1969).

[4] No differences in yield or distribution of products were observed with **1** purified *via* its mercuric acetate complex; H. Donaldson, "The Chemistry and Technology of Naphthalene Compounds," E. Arnold and Co., London, 1958, pp 456–457. Also, autoxidation conditions identical with those used in ref 3 caused no change in products.

[5] Elemental analysis within 0.2% of theory. Low peroxide content (76% of theory) by the method of V. R. Kokatnur and J. Murray, *J. Amer. Chem. Soc.*, **63**, 1432 (1941), seemed due to acid-catalyzed decomposition of **3** during analysis.

[6] The plates were developed twice with benzene–toluene (9:1) at 4° in the dark, and the hydroperoxide was localized by uv fluorescence and acidic KI spray.

[7] All nmr spectra were run at 100 MHz in $CDCl_3$ and are reported with line positions in δ relative to TMS and coupling constants in hertz. Subscripts on hydrogens designate their position in the molecule.

[8] Analysis by vpc on 15% SE-30 at 130–140°; less than 2% 1-tetralol or 1-naphthol (as the trimethylsilyl ether) was present in the samples.