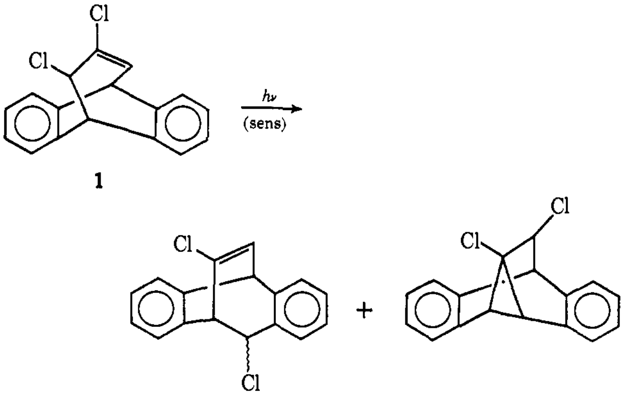
Bridged Polycyclic Compounds. LV. Photoisomerization *via* Carbonium Ion Intermediates[1]

Sir:

The nonphotochemical interconversions of 3,4-dichlorodibenzobicyclo[3.2.2]nonatriene-2,6,8 (**1**) with its isomers **2** and **3** have been reported.[2] The equilibrium mixture contains 41% **1**, 10% **2**, and 49% **3**. We report now that photoinduced rearrangement of **1** gives predominantly the thermodynamically unstable **2**. Similar photochemical rearrangements have not previously been reported.[3] Irradiation[4] of **1** (0.5 *M*) in benzonitrile gave a mixture[5] containing 53% **1**, 21% **2a**, 23% **2b**, and 3% **3** after 68 hr.



2a, *exo* **3**
b, *endo*

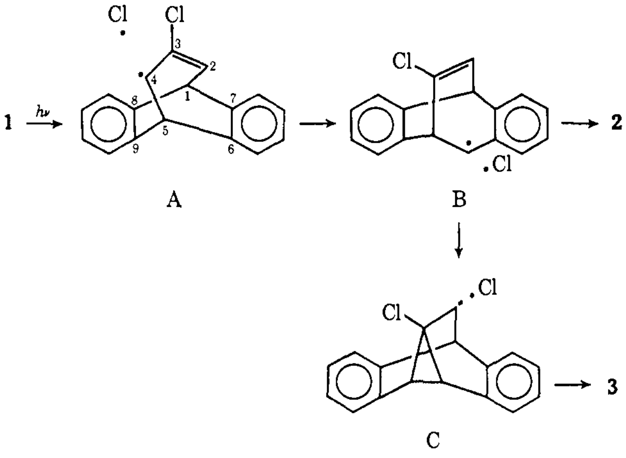
1 and **3** have previously been characterized.[2] Isomers **2** were prepared from 7-chloro-*exo*-2-dibenzobicyclo[3.2.2]octa-3,6,8-trienol[2] with thionyl chloride. Pmr analysis of the resulting product, mp 103.5–106° (satisfactory analysis for $C_{17}H_{12}Cl_2$), revealed a 1.2:1 mixture of **2b**:**2a**.

Attempts to obtain pure samples of either **2a** or **2b** by synthesis or separation failed, apparently due to rapid epimerization at C_4. **2** and **3** were stable when subjected to photolysis conditions. **1** was photoactive, but inert in the dark in an otherwise similar environment. Very severe conditions were required for dark displacement or rearrangement reactions.

Photoisomerization of **1** was sensitized by benzene, acetone, and benzonitrile, but not by acetophenone and benzophenone. The absence of rearrangement by direct irradiation of **1** in cyclohexane without photosensitization suggests that a triplet state (of energy 77–74 kcal/mol[6]) is involved.

Mechanistic interpretation of these results presents some interesting possibilities. Light-induced homolytic cleavage of the C_4–Cl bond in **1** would result in an allylic free radical which could suffer benzo migration (Scheme I). Ample precedence exists[7] for the initial formation of A, but the radical rearrangements indicated in Scheme I have not been observed by us.[8] In the acetone-sensitized reaction, the lack of formation of chloroacetone, which is observable in miniscule amounts (lachrymator), may argue against this path.

Scheme I



Another possible pathway, closely related to Zimmerman's benzo-vinyl bridging mechanism,[13] is shown in

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(1) Previous paper in this series: S. J. Cristol and R. W. Gleason, *J. Org. Chem.*, in press. This work was supported by the National Science Foundation.

(2) S. J. Cristol, R. M. Sequeira, and G. O. Mayo, *J. Amer. Chem. Soc.*, 90, 5564 (1968).

(3) B. B. Jarvis (University of Maryland, private communication, 1968) has noted the photochemical allylic rearrangement of 7-trichloromethyldibenzobicyclo[2.2.2]octatriene to 8-chloro-(7-dichloromethylene)dibenzobicyclo[2.2.2]octadiene [*J. Org. Chem.*, **33**, 4075 (1968)].

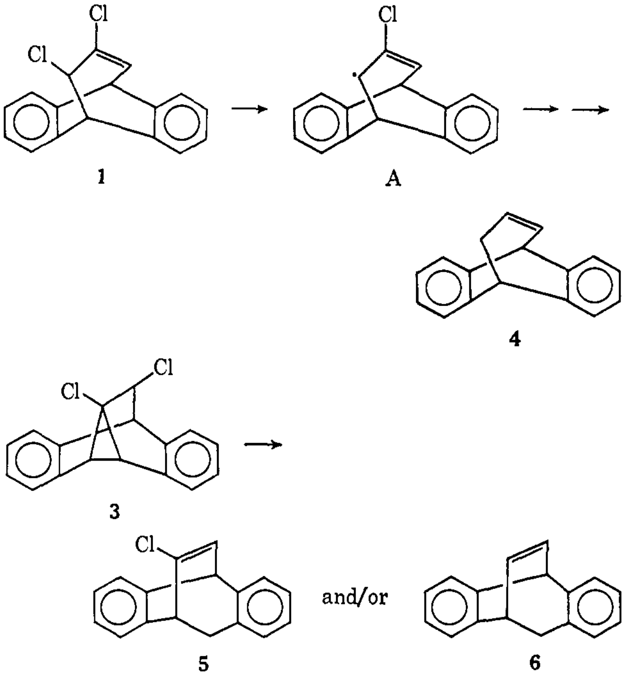
(4) Rayonet reactor, 2527 Å.

(5) Percentages based on pmr analysis (Varian A-60A spectrometer).

(6) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, p 132.

(7) H. L. Benson, Jr., and J. E. Willard, *J. Amer. Chem. Soc.*, **88**, 5689 (1966), and references cited therein.

(8) Reduction of **1** by biphenyl radical anion[9] gave unrearranged **4**, while reduction of **3** with biphenyl radical anion or triphenyltin hydride[10] led to the rearranged products **5** and **6**.



Both kinds of reductions are known to proceed *via* free radical intermediates.[9,10] Where rearrangements have been observed with radical anion reductions it has been shown that carbon radicals, not carbanion intermediates, undergo isomerization.[9] Although A apparently does not undergo aryl migration in ground-state reactions, such migrations are not uncommon.[11,12]

(9) S. J. Cristol and R. V. Barbour, *J. Amer. Chem. Soc.*, **88**, 4262 (1966); **90**, 2832 (1968).

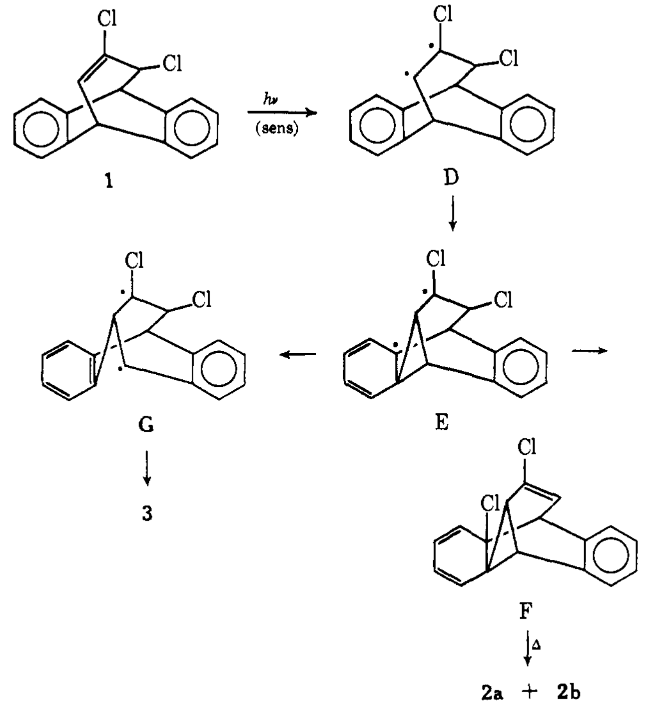
(10) H. G. Kuivila, L. W. Menapace, and C. R. Warner, *ibid.*, **84**, 3584 (1962); H. G. Kuivila and L. W. Menapace, *J. Org. Chem.*, **28**, 2165 (1963); L. W. Menapace and H. G. Kuivila, *J. Amer. Chem. Soc.*, **86**, 3047 (1964).

(11) W. A. Pryor, "Free Radicals," McGraw-Hill Book Co., Inc., New York, N. Y., 1966, pp 266–273.

(12) S. J. Cristol and G. W. Nachtigall, *J. Org. Chem.*, **32**, 3727 (1967).

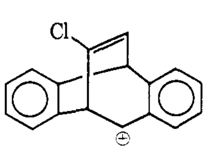
(13) H. E. Zimmerman, R. S. Givens, and R. M. Pagni, *J. Amer. Chem. Soc.*, **90**, 4191 (1968)

Scheme II

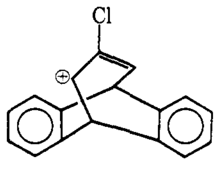


Scheme II. While benzo–vinyl bridging may account for the formation of **3**, it appears less likely for the formation of intermediate F, precursor of **2**.[14] Further, since **2** is the initially formed and predominant product (**3** being formed only to a small extent late in the reaction), it appears that this pathway is at best of minor importance.

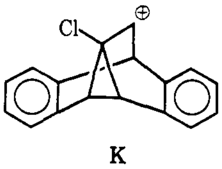
It seems to us that the data compel a new mechanism for this reaction. A path in which photosensitization leads to a triplet state of **1** which then ionizes to a triplet carbonium ion–chloride ion ion pair seems energetically unattractive. However, the triplet state of **1** could decay to a vibrationally excited singlet[15–17] which then dissociates to a [R^+Cl^-] ion pair. This ion pair could recombine to give the thermodynamically unstable **2** isomers. It was shown[2] that cation H is more stable than J or K, and that kinetic products formed from this ion manifold are derived largely from H, while thermodynamic products are formed from J and K. It is reasonable that the ion manifold produced photochemically should be similar to that produced in solvolytic reactions and that capture from this manifold should lead to the **2** epimers rather than to **1** or **3**.



H



J



K

Reports of photochemical reactions involving ionic intermediates (rather than zwitterions) are now beginning to appear.[18–20] In the present case one may speculate that the twisted aliphatic double bond (striving to become orthogonal in its π,π^* state) may aid the heterolytic departure of chloride ion.

We are investigating other cases to test predictions based upon the ionic mechanism.

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(14) Preliminary work on the photorearrangement of the methanesulfonate of 3-chloro-6,7:8,9-dibenzobicyclo[3.2.2]nona-3,6,8-trienol-2 vitiates this mechanism.

(15) Reference 8, pp 186–190.

(16) D. I. Schuster, B. R. Sckolnick, and F. H. Lee, *J. Amer. Chem. Soc.*, **90**, 1300 (1968).

(17) O. L. Chapman and J. D. Lassila, *ibid.*, **90**, 2449 (1968).

(18) P. J. Kropp and H. J. Krauss, *ibid.*, **89**, 5199 (1967).

(19) J. A. Marshall and R. D. Carroll, *ibid.*, **88**, 4092 (1966).

(20) E. E. van Tamelen, T. M. Cole, R. Greeley, and H. Schumacher, *ibid.*, **90**, 1372 (1968).

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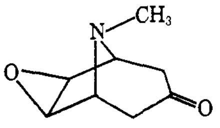
4,5-Homotropone

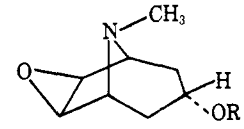
Sir:

Substantial interest has been shown recently in the chemistry of homoaromatic systems[1] and in the facile Cope rearrangements of *cis*-1,2-divinylcyclopropanes.[2] We wish to report the synthesis of 4,5-homotropone which is both a homoaromatic system and a *cis*-divinylcyclopropane. The synthesis of 2,3-homotropone has been described by Holmes and Pettit.[3]

Our approach to the synthesis of 4,5-homotropone was based on the observation by Meinwald, *et al.*, that base-catalyzed degradation of tropinone methiodide gave a mixture of cycloheptadienones.[4] This approach takes advantage of the plane of symmetry in the final product and provides the first route to derivatives of scopinone, scopine, and scopolamine in which the oxirane oxygen has been replaced by a methylene group. Success in our pilot synthesis of 4,5-trimethylenetropone[5] and the availability of *cis*-cyclopropane-1,2-dicarboxaldehyde[6] encouraged us to undertake the synthesis of 4,5-homotropone *via* amino ketone **1**.



scopinone



R = H, scopine

$\mathrm{R = CO\overset{\overset{\textstyle CH_2OH}{|}}{C}HC_6H_5}$, scopolamine

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(1) For a review see S. Winstein, "Aromaticity," Special Publication No. 21, The Chemical Society, London, 1967, p 5.

(2) (a) W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963); (b) W. von E. Doering and W. R. Roth, *Angew. Chem. Intern. Ed. Engl.*, **2**, 115 (1963); (c) G. Schröder, *Angew. Chem.*, **75**, 722 (1963); (d) M. Saunders, *Tetrahedron Letters*, 1699 (1963); (e) R. Merenyi, J. F. M. Oth, and G. Schröder, *Chem. Ber.*, **97**, 3150 (1964); (f) J. B. Lambert, *Tetrahedron Letters*, 1901 (1963); (g) J. M. Brown, *Chem. Commun.*, 226 (1965); (h) E. Vogel, R. Erg, G. Lenz, and A. Bothner-by, *Ann. Chem.*, **682**, 1 (1965); (i) M. Simonetta, G. Favini, C. Mariani, and P. Gramaccioni, *J. Amer. Chem. Soc.*, **90**, 1280 (1968); (j) O. L. Chapman and J. D. Lassila, *ibid.*, **90**, 2449 (1968).

(3) J. D. Holmes and R. Pettit, *ibid.*, **85**, 2531 (1963).

(4) J. Meinwald, S. L. Emmerman, N. C. Yang, and G. Büchi, *ibid.*, **77**, 4401 (1955).

(5) O. L. Chapman and T. H. Koch, *J. Org. Chem.*, **31**, 1042 (1966).

(6) G. Maier and T. Sayrac, *Chem. Ber.*, **101**, 1354 (1968).