Numerical integration[8] of the differential kinetic equations (14 rate constants) using these trial values then generates a set of reactant and product concentrations as functions of time. The approximate rate constants are adjusted until a satisfactory fit to the experimental data is obtained. Scheme I shows the refined values of the rate constants ($\times 10^5$ sec) obtained. The values without and with parentheses are for the tCT–cCT and tCC–cCC systems, respectively.

The most significant findings are that the rate constants for the direct stereodistal Cope rearrangements, tCT or tCC → **6** and **7**, are extremely small and, within the limitations of the method, indistinguishable from zero. In the CC series, the rate constants for the reaction cCC → **6** and **7** depend on measurements of a small component of the total reaction and therefore are rather rough,[7] whereas in the CT series, the rate constants for cCT[7] (and hence for tCT) → **6** and **7** are more reliable. In both cases, however, it is clear that the indirect pathway predominates heavily.

The product ratios **6**/**7**, 94.7/5.3 from tCT and 99.5/0.5 from tCC, correspond exactly to those found[7] from cCT and cCC, respectively, and hence are also consistent with the indirect mechanism.

The absence of the direct mechanism leading to **6** and **7** may be associated with a strain barrier to closure of a diradical intermediate, similar to the barrier postulated[6] to oppose the formation of **5**. However, another factor unique to the present system operates in the same direction. In order to form **6** or **7** by the direct mechanism, it would be necessary for both propenyl groups of tCT or tCC to be in the "in" conformation shown in Scheme I, which would produce one methyl-ring repulsive interaction in the case of tCT and two in the case of tCC. These interactions retard the rate of the ordinary stereoproximal Cope rearrangement of cDV by factors of 2×10^2 each[7] and could similarly affect the direct stereodistal process. It remains to be seen whether, when this feature is absent, as in tDV or other systems that might be devised, the direct stereodistal process can occur.

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(8) This is effected with a computer program RUNGG for numerical integration by the Runge–Kutta method[9] written for the PDP-10 computer by Professor Martin Saunders, whom we thank for making it available. We also thank Dr. John Weiner for instruction in its use and the Yale Department of Computer Sciences for access to their facilities.

(9) *Cf.* H. Margenau and G. M. Murphy, "The Mathematics of Physics and Chemistry," 2nd ed, D. Van Nostrand Co., Princeton, N. J., 1956, p 486 ff.

(10) National Institute of General Medical Sciences Predoctoral Fellow (No. 5-FO1-GM-40662), 1968–1971.

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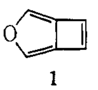
3,6-Dehydrooxepin, a Furocyclobutadiene

Sir:

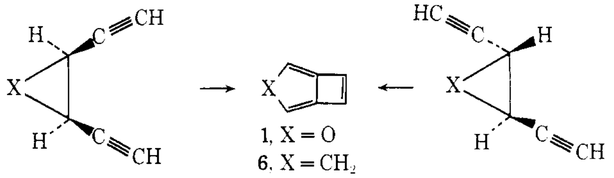
We wish to report the first synthesis and isolation of a completely planar, unsubstituted cyclic 8π-electron molecule, 3,6-dehydrooxepin (a furocyclobutadiene, **1**).



1

Treatment of *meso*-3,4-dihydroxyhexa-1,5-diyne (**2**)[1] with 1 equiv of *p*-toluenesulfonyl chloride in pyridine at −20° for 3 days gave a mixture of mono- and ditosylates from which *erythro*-3-hydroxy-4-*p*-toluenesulfonyloxyhexa-1,5-diyne (**3**) could be separated by fractional crystallization. Reaction with 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) in dry ether solvent led to a mixture of *cis*- and *trans*-1,2-diethynyloxiranes (**4c** and **4t**, 53% yield, 1:16 ratio) which were separated by preparative vapor chromatography.[2]

Epoxides **4c** and **4t** are thermally quite stable compared with their cyclopropane analogs[3] **5c** and **5t**. A 15-sec half-life for rearrangement of **5c** to bicyclo[3.2.0]hepta-1,4,6-triene (**6**) is obtained[3] at 198°, whereas **4c** requires ∼15 sec at 270° to produce half-conversion to **1**. Similarly, **5t** is half-rearranged[3] in 15 sec at 286°, whereas the same half-life for **4t** is observed only at 370°. No interconversion of **4c** and **4t** is observed during thermolysis of either isomer.



4c, X = O
5c, X = CH$_2$

1, X = O
6, X = CH$_2$

4t, X = O
5t, X = CH$_2$

Complete pyrolysis of **4c** or **4t** was conducted in a nitrogen flow system (400°, contact time ∼20 sec) connected to a vacuum line. The pyrolysate, condensed at −196°, was a white crystalline solid which was stable at low temperature but could be warmed to room temperature long enough to allow vacuum transfer into an nmr tube attached to the line. Degassed carbon tetrachloride was distilled onto this material, the nmr tube was sealed off under vacuum, and the solution was warmed to room temperature. Inspection of the proton nmr spectrum of material prepared in this way revealed the presence of a 10% yield of dehydrooxepin **1** as the product ($\geqslant$95% pure), which showed an AA′-BB′ pattern with resonances centered at δ 6.33 and 6.11 ($J \cong 0.4, 0.3$ Hz) ppm. The uv spectrum shows major absorptions at 265, 271, 277, 284, 297, 316, 323, 331, 341, 363, 373, and 387 nm.

Although stable for several days in solution (*vide infra*), compound **1** is extremely sensitive. It polymerizes instantaneously on exposure to oxygen, and does not survive either vapor phase or thin-layer chromatography. It reacts immediately with cyclopentadiene, forming an air-sensitive adduct whose structure is tentatively assigned[4] as **7**. Confirmation of the structure of **1** was afforded by its mass spectrum,[5] which

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(1) H. P. Figeys and M. Gelbcke, *Tetrahedron Lett.*, 5139 (1970).

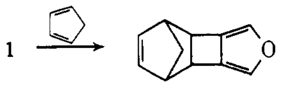
(2) Nmr (CDCl$_3$) of **4c**, δ 3.58 (d, 2 H, $J \cong 0.8$ Hz), 2.47 (d, 2 H, $J \cong 0.8$ Hz) ppm; of **4t**, δ 3.51 (d, 2 H, $J \cong 1$ Hz), 2.35 (d, 2 H, $J \cong 1$ Hz) ppm.

(3) (a) R. G. Bergman and M. B. D'Amore, *J. Amer. Chem. Soc.*, **91**, 5694 (1969); (b) M. B. D'Amore, R. G. Bergman, M. Kent, and E. Hedaya, *Chem. Commun.*, 49 (1972).

(4) Nmr (CCl$_4$) of **7**: δ 6.72 (s, 2 H, furan), 5.75 (d of d, 2 H, J = 2, 2 Hz, olefinic), 4.64 (d of d, 2 H, J = 3, 2 Hz, cyclobutane), 2.97 (m, 2 H, bridgehead), 1.91 (d, 1 H, bridge, $J \cong 9$ Hz), 1.53 (d, 1 H, bridge, $J \cong 9$ Hz).

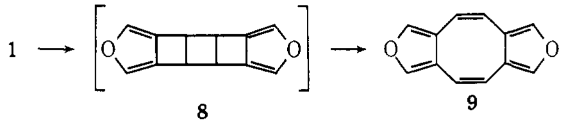
(5) Obtained on a CEC-21-013C mass spectrometer. Compound **1** was condensed directly from the pyrolysis line into a tube with a break-seal and then sealed off under vacuum at low temperature. The tube was transferred to the inlet line of the spectrometer, the break-seal destroyed, and the sample allowed to warm to room temperature.

showed a parent peak at m/e 92 and base peak at m/e 64 ($M^+ - CO$), and by the fact that when allowed to stand in acetone solution, **1** slowly formed the known[6]



7

cyclic 16π-bisfurocyclooctatetraene **9**, presumably *via* 2 + 2 dimer **8**.



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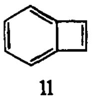
Compound **1** is of theoretical interest for a number of reasons. It can be viewed as a heterocyclic analog of benzocyclobutadiene (**11**), which (unlike **1**) has been



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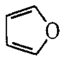
generated only in transient form.[7] Of major concern also is its stability compared with that of furan (**12**) and oxepin (**13**). Thermodynamic data on **1** will be difficult to obtain; clearly, however, it is reluctantly formed (despite the often similar thermal reactivity of oxiranes and cyclopropanes,[8] **4** is converted to **1** much less readily than **5** goes to **6**) and more reactive[9] than either **12** or **13**. This is undoubtedly partially due to a high strain energy, but its sensitivity compared even to triene **6** suggests that its apparent instability has a substantial electronic component as well. The nmr spectrum of **1** is ambiguous with regard to the presence of a ring current; clearly the paramagnetic component[10] in **1** (α-hydrogen chemical shift at δ 6.28 ppm) is much greater than that in furan (α-hydrogen chemical shift at δ 7.40 ppm), but whether one should consider **1** to be "nonaromatic" or "antiaromatic" on the basis of ring current effects is still open to question[11] (*e.g.*, compare[9] α hydrogens in **13**, δ 5.7; **7**, 6.72; **9**, 7.27 ppm). In any case, both the four- and five-ring protons appear at relatively high field, indicating the absence of a large polarization of charge in **1**.



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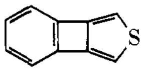

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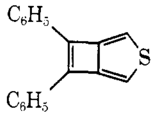

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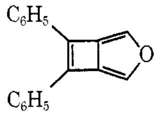

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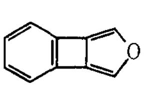

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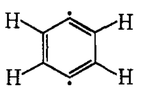

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Compounds **14** and **15**, which are substituted analogs of **1**, are considerably less reactive substances.[12,13] Attempts to prepare oxygen analogs **16** and **17** have failed,[14] undoubtedly because their sensitivity approaches that of **1**. Finally, the contrast between the structures of 1,4-dehydrobenzene (**18**)[15] and 3,6-dehydrooxepin is striking; apparently these compounds lie on opposite sides of the energetic borderline that determines whether the "dehydro" bond is open,[15] as in **17**, or closed, as it is in **1**.

Acknowledgments. We are grateful to the National Science Foundation for financial support and to Professor Sara Jane Rhoads for providing us with data prior to publication.

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(6) J. A. Elix, M. V. Sargent, and F. Sondheimer, *J. Amer. Chem. Soc.*, **89**, 5080 (1967); **92**, 973 (1970).

(7) M. P. Cava and M. J. Mitchell, "Cyclobutadiene and Related Compounds," Academic Press, New York, N. Y., 1967, Chapter 6.

(8) (a) It is not clear whether one should *a priori* expect cyclopropanes to have greater or similar thermal reactivity compared with oxiranes. For example, *cis*-1,2-divinyloxirane rearranges[8b] to 4,5-dihydrooxepin at temperatures below 100° with E_a = 24.6 kcal/mol and $\Delta S^{\ddagger}$ = 0.4 eu, whereas *cis*-1,2-divinylcyclopropane rearranges to 1,5-cycloheptadiene so quickly that numerous attempts to isolate it have been unsuccessful.[8c] However, *trans*-1,2-divinyloxirane and *trans*-1,2-divinylcyclopropane have very similar reactivities (E_a = 36 and 35 kcal/mol, $\Delta S^{\ddagger}$ = 0.4 and 2.0 eu, respectively[8b,8c]), suggesting that **4t**, at least, may be unusually unreactive since it rearranges so much more slowly than does **5t**. (b) E. Vogel and H. Günther, *Angew. Chem., Int. Ed. Engl.*, **6**, 385 (1967); (c) S. J. Rhoads, private communication; (d) for related examples, see R. J. Crawford and T. R. Lynch, *Can. J. Chem.*, **46**, 1457 (1968); (e) H. H. J. MacDonald and R. J. Crawford, *ibid.*, **50**, 428 (1972); (f) L. B. Rodewald and C. H. DePuy, *Tetrahedron Lett.*, 2951 (1964).

(9) E. Vogel, W. A. Böll, and H. Günther, *ibid.*, 609 (1965).

(10) F. Baer, H. Kuhn, and W. Regel, *Z. Naturforsch. A*, **22**, 103 (1967).

(11) Perhaps the term "schizoantiaromatic" would be consistent with an earlier suggestion: *cf.* E. Heilbronner, as quoted by D. Ginsburg, as quoted by J. F. Stoddart, *Chem. Brit.*, **250**, 490 (1971).

(12) P. J. Garratt and K. P. C. Vollhardt, *Chem. Commun.*, 109 (1970).

(13) P. J. Garratt and K. P. C. Vollhardt, *J. Amer. Chem. Soc.*, **94**, 1022 (1972).

(14) P. J. Garratt and K. P. C. Vollhardt, private communication.

(15) R. R. Jones and R. G. Bergman, *J. Amer. Chem. Soc.*, **94**, 660 (1972).

(16) (a) Alfred P. Sloan Foundation Fellow, 1970–1972; Camille and Henry Dreyfus Foundation Teacher-Scholar, 1970–1975.

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Mechanism of the Photochemical Transformation of a 1,3,5-Hexatriene to a Bicyclo[3.1.0]hex-2-ene[1]

Sir:

The photoinduced rearrangement of conjugated 1,3,5-trienes to bicyclo[3.1.0]hex-2-ene ring systems has been the focus of much research[2] since the process was first reported in 1958.[3] This two-bond forming reaction has been looked upon as a photochemical Diels–Alder reaction and has been designated as a concerted $[_\pi 4 + {}_\pi 2]$ cycloaddition.[4] While data have been presented that appear to substantiate the proposed concerted nature of the rearrangement,[2,5] other recent studies have indicated that a related reaction process may in fact proceed *via* a nonconcerted

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(1) This work was supported in part by the National Institute of Arthritis and Metabolic Diseases, U. S. Public Health Service, Grant No. AM-00709.

(2) A. Padwa and S. Clough, *J. Amer. Chem. Soc.*, **90**, 5803 (1970), and references cited therein.

(3) W. G. Dauben, I. Bell, T. W. Hutton, G. F. Laws, A. Rheiner, Jr., and H. Urscheler, *ibid.*, **80**, 4116 (1958); W. G. Dauben and P. Baumann, *Tetrahedron Lett.*, 565 (1961).

(4) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.

(5) A. Padwa, L. Brodsky, and S. Clough, *Chem. Commun.*, 417 (1971).