The structure of **7** was confirmed by oxidation with ceric ammonium nitrate in 80% acetone–20% H_2O, a reagent known[2] to cleave methoxycarbene complexes to methyl esters, which gave a 2:1 mixture of methyl 2-acetoxy-2-butenoate (**8**). The nmr (CCl_4) of the major isomer of **8** had resonances at δ 1.98 (d, J = 1.1 Hz, 3 H, $CH_3C{=}C$), 2.15 (s, 3 H, CH_3CO_2), 3.62 (s, 3 H, OCH_3), and 5.58 (m, 1 H), while the minor isomer had resonances at δ 2.10 (s, 3 H, CH_3CO_2), 2.32 (br s, 3 H, $CH_3C{=}C$), 3.67 (s, 3 H, OCH_3), and 5.60 (m, 1 H, $HC{=}C$).[6] The major isomer of **8** obtained from ceric oxidation is assigned the *E* structure on the basis of the greater downfield chemical shift of the vinyl proton of the major isomer.[5]

The results presented here indicate that anions α to the carbene carbon atom of transition metal–carbene complexes are versatile intermediates for the synthesis of a wide variety of transition metal–carbene complexes.

Acknowledgment. This work was supported by the National Science Foundation (Grant No. GP-32160).

(6) An authentic sample of **8** was prepared from methyl acetoacetate and isopropenyl acetate and was shown by gas chromatography to be a 1:24 mixture of the major and minor isomers obtained above.

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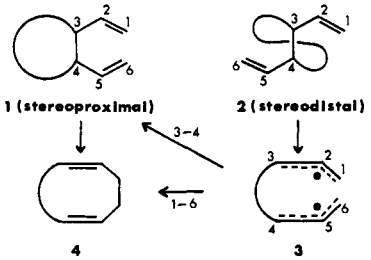
The Stereodistal Cope Rearrangement of *trans*-1,2-Dialkenylcyclobutanes[1]

Sir:

Although stereoproximity of the ends (C_1 and C_6) of the biallyl system (schematically shown as **1**) is required in the ordinary Cope rearrangement, there are a number of cases in which the process occurs despite a stereodistal relationship (**2**) imposed by the geometry of the reactant.[2a,b] A major mechanistic question is does the stereodistal[2c] reaction occur by an indirect mechanism requiring prior epimerization to the stereoproximal reactant, perhaps by way of a diradical intermediate **3**, or can it occur directly, for example by closure of **3** at C_1 and C_6, to give Cope rearrangement product **4**?

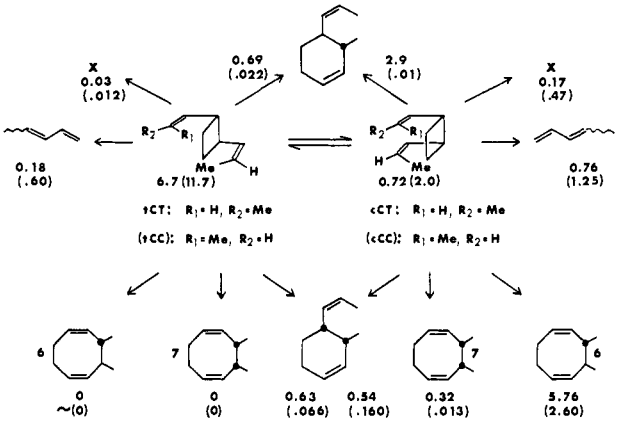


In one previously discussed example of this problem, the thermal rearrangement of *trans*-1,2-divinylcyclobutane (tDV) to cycloocta-1,5-diene (**5**),[3-6] evaluation of the indirect mechanism on energetic grounds does not seem to be straightforward. There are two conflicting thermochemical estimates ($\sim$0[5] and $\geq$7.6[6] kcal/mol) of the activation energy for cyclization of the octa-1,7-diene-3,6-diyl diradical, the hypothetical precursor of **5**. Moreover, the question is difficult to test experimentally with tDV because the stereoproximal intermediate, *cis*-1,2-divinylcyclobutane (cDV), rearranges to **5** too rapidly.[3]

This paper reports a circumvention of this difficulty in two related stereodistal systems, *trans*-1,2-*cis*,*trans*- and *trans*-1,2-*cis*,*cis*-dipropenylcyclobutanes (tCT and tCC, Scheme I). These are especially well suited for the detection of the indirect mechanism because the Cope rearrangements of the corresponding stereoproximal compounds, cCT and cCC, are known[7] to be much slower (factors of 2×10^{-3} and 5×10^{-6}, respectively) than that of cDV. In fact, we now find that cCT and cCC accumulate during pyrolyses of tCT and tCC, respectively, at 146.5°, and both reactions are reversible. Although consistent with the indirect mechanism, these observations do not exclude contributions from the direct one. The relative importance of the two paths, however, can be evaluated by a kinetic analysis of the tCT–cCT and tCC–cCC systems.

Scheme I shows the products formed (capillary

Scheme I



vapor chromatographic analysis) in the reactions at 146.5° of degassed neat liquid samples of each of these four compounds. With the exception of the 1–6% of unidentified components (X, Scheme I), all of the products are stable under the reaction conditions.

Because of trans $\rightleftharpoons$ cis reversibility, the pyrolyses do not follow first-order kinetics, but the kinetic scheme can be solved numerically. Early points in the kinetic runs provide approximate values of the rate constants.

(1) We thank the National Science Foundation (Grant No. GP-33909X) and the Hoffmann-La Roche Foundation for partial support of this work.

(2) (a) For an early example, see *trans*-divinylcyclopropane → cyclohepta-1,4-diene: E. Vogel, *Angew. Chem.*, 72, 4 (1960). (b) See also C. Ullenius, P. W. Ford, and J. E. Baldwin, *J. Amer. Chem. Soc.*, **94**, 5410 (1972). (c) Stereodistal and stereoproximal Cope reactants are related by configurational inversion at C_3 or C_4 of the biallyl system.

(3) G. S. Hammond and C. D. DeBoer, *J. Amer. Chem. Soc.*, **86**, 899 (1964).
(4) D. J. Trecker and J. P. Henry, *ibid.*, **86**, 902 (1964).
(5) S. W. Benson, *J. Chem. Phys.*, **46**, 4920 (1967).
(6) W. von E. Doering, M. Franck-Neumann, D. Hasselmann, and R. L. Kaye, *J. Amer. Chem. Soc.*, **94**, 3833 (1972).
(7) J. A. Berson and P. B. Dervan, *ibid.*, **94**, 7597 (1972).

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.

(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

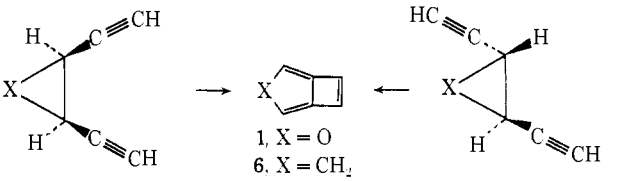
Sir:

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



4c, X = O
5c, X = CH_2
4t, X = O
5t, X = CH_2

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.

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 (≥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

(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.