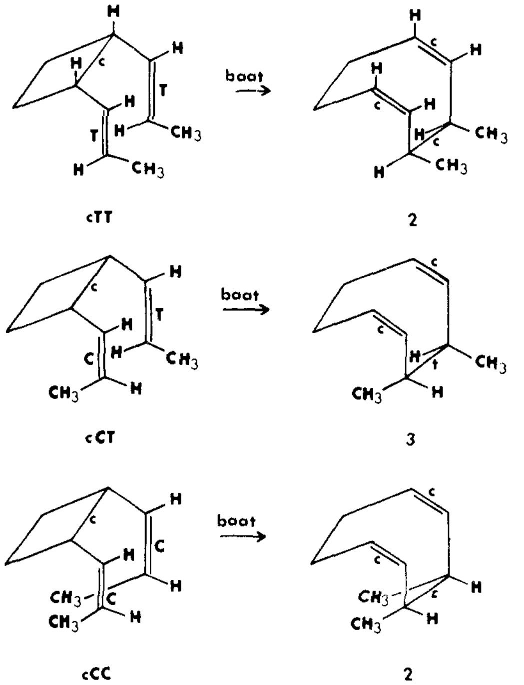
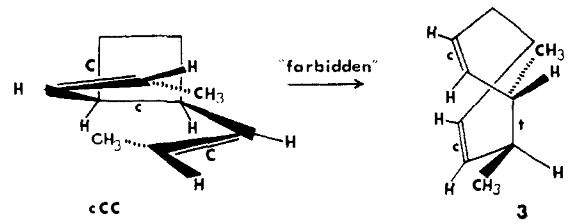
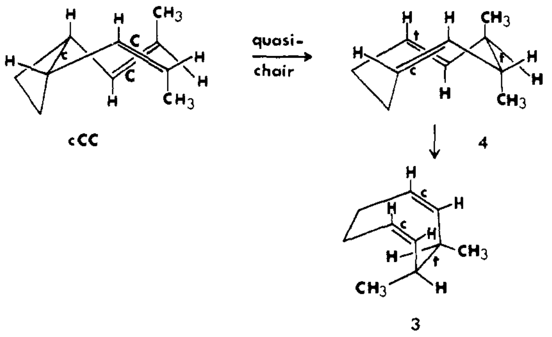


transformation, for example, cCC → 3, by way of a



transition state geometry corresponding to that of an orbital symmetry "forbidden" concerted process.[10] The second is a two-step reaction involving a quasi-chair transition state in a preliminary rearrangement, cCC → *trans*-3,4-dimethyl-*cis,trans*-cycloocta-1,5-diene (4), followed by geometric isomerization of the trans double bond of 4 to give the *cis,cis*-diene 3.[12]



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(10) It is conceivable but not necessary that this reaction be nonconcerted.[11]

(11) J. A. Berson and L. Salem, submitted for publication in *J. Amer. Chem. Soc.*

(12) (a) Analogy to results in an accompanying paper[12b] suggests the possibility that the first step in the hypothetical two-step crossover mechanism might well be reversible. This precludes a simple ascription of the energy gap $F^{\ddagger}_{\text{crossover}} - F^{\ddagger}_{\text{boat}} \gtrsim 4.4$ kcal/mol (product ratio < 1:200) in the pyrolysis of cTT. (b) J. A. Berson, P. B. Dervan, and J. A. Jenkins, *ibid.*, 94, 7598 (1972).

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

Jerome A. Berson,* Peter B. Dervan[13]
Department of Chemistry, Yale University
New Haven, Connecticut 06520

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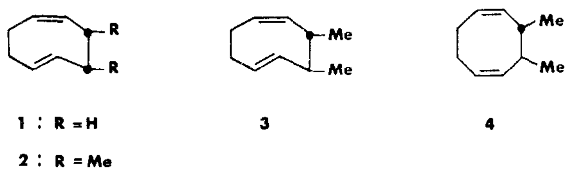
Stereospecific Double Rearrangement of *trans*-3,4-Dimethyl-*cis,trans*-cycloocta-1,5-diene to *cis*-3,4-Dimethyl-*cis,cis*-cycloocta-1,5-diene[1]

Sir:

The chemistry of the highly strained *cis,trans*-cycloocta-1,5-diene ring system[2] (1) is largely unexplored. Because there is a possibility that the corresponding 3,4-dimethyl derivatives 2 and 3 may be involved in the thermal nonboat, "crossover" rearrangement of *cis*-1,2-*cis,trans*- and *cis*-1,2-*cis,cis*-dipropenylcyclobutanes (cCT and cCC, respectively),[3] we have carried out a study of the pyrolysis of *trans*-3,4-dimethyl-*cis,trans*-cycloocta-1,5-diene (3). The present paper reports a new thermal rearrangement of this compound.

In a procedure modeled after that used to invert *cis,cis*-cycloocta-1,5-diene to the cis,trans isomer 1,[4] pure *trans*-3,4-dimethyl-*cis,cis*-cycloocta-1,5-diene (4)[3] reacts with *m*-chloroperbenzoic acid to give the monoepoxide, which successive treatments with lithium diphenyl phosphide in tetrahydrofuran and then with CH_3I convert to the *cis,trans*-diene 3.



Compound 3 can be purified by vpc on an ammonia-purged column, but only with severe losses. The substance shows an infrared (ir) spectrum indicating[5] both trans (λ_{max} 990 cm^{-1}) and cis (λ_{max} 720 cm^{-1}) double bonds. Concentrated solutions or neat samples deposit a solid (dimer or polymer) upon standing a few hours at room temperature. Treatment with I_2–$CHCl_3$ converts 3 to 4.

Attempts to carry out vpc on 3 with the dibutyl tetrachlorophthalate capillary column used in the study of the Cope rearrangements of *cis*-1,2-dialkenylcyclobutanes[3] give a complex trace of peaks with retention times intermediate between those of decane (internal standard) and *trans*-3,4-dimethyl-*cis,cis*-cycloocta-1,5-diene (4).[6] This would have precluded the detection of small amounts of 3 under our previous analytical conditions,[3] so that 3 cannot be ruled out as a possible intermediate in the Cope rearrangement of cCC.

Pyrolysis of a 0.7 *M* solution of 3 in decane at 146.5° for 1000 sec gives a substantial amount of polymer and an identifiable material balance (vpc against internal standard) of 35%. Aside from 4, which probably is not formed by pyrolysis,[6] there are only two volatile products, which appear in the ratio 12:1. The major product is *cis*-3,4-dimethyl-*cis,cis*-cycloocta-1,5-diene (5), in which there has been formal geometric isomeriza-

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(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. C. Cope, C. F. Howell, J. Bowers, R. C. Lord, and G. M. Whitesides, *J. Amer. Chem. Soc.*, 89, 4024 (1967).

(3) J. A. Berson and P. B. Dervan, *ibid.*, 94, 7597 (1972).

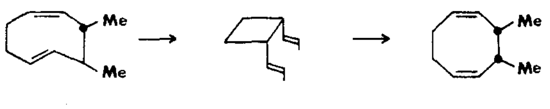
(4) E. Vedejs and P. L. Fuchs, *ibid.*, 93, 4070 (1971).

(5) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Wiley, New York, N. Y., 1958, pp 45–49.

(6) Compound 4 appears in the vpc trace of the original solution of 3, and it probably is present as a contaminant in the sample, rather than as a product of pyrolysis during vpc, since its concentration does not depend upon whether the 3 is heated before vpc analysis (9.6 ± 0.6% in three pyrolysis samples, 8.6 ± 0.4% in two unheated samples).

tion about one double bond as well as formal inversion of configuration at one of the asymmetric carbon atoms of **3**.

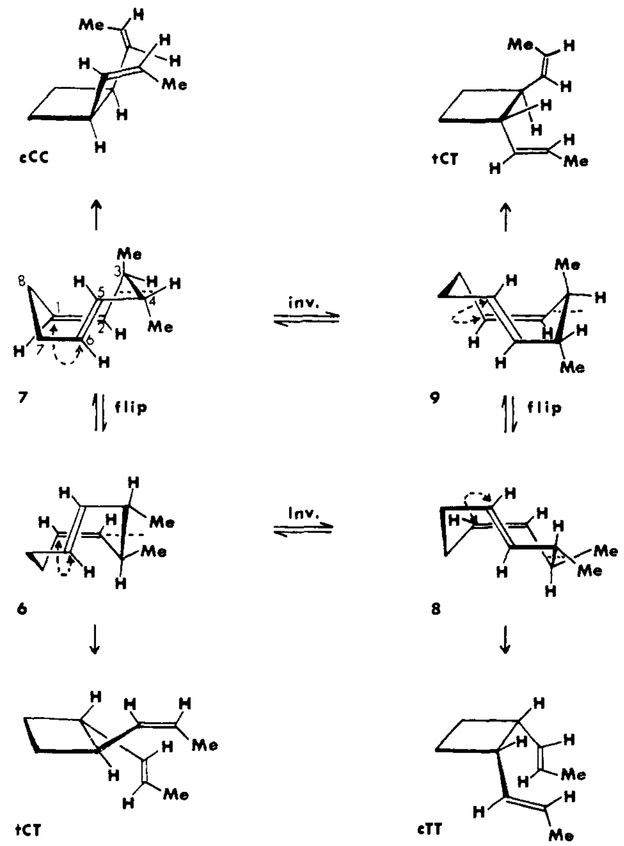
The mechanistic puzzle created by this result is solved by the identification of the minor product as *cis*-1,2-*trans*,*trans*-dipropenylcyclobutane (cTT), pyrolysis of which is known to give **5** exclusively.[3] In accord with the mechanism **3** → cTT → **5**, we find that shorter pyrolysis of **3** (500 sec) permits the detection of a higher proportion of the intermediate (**5**:cTT = 2.7:1). Again, polymer formation limits the yield of volatiles to 30%, but no other pyrolysis products appear. The overall process thus consists of two successive highly stereospecific Cope rearrangements, the first chair-like and the second boat-like.



3 **cTT** **5**

Two diastereomers of *trans*-3,4-dimethylcycloocta-1,5-diene (**3**) can exist which differ in the axial dissymmetry element associated with the ring. In principle, they should be thermally interconvertible by rotations about the bonds C_6–C_7 and C_4–C_5 (**6** ⇌ **8** and **7** ⇌ **9**), by analogy to the racemization of *trans*-cyclooctene.[7] Moreover, just as in the parent *cis*,*trans*-cycloocta-1,5-diene (**1**)[2], ring flips should rapidly interconvert conformational isomers (**6** ⇌ **7** and **8** ⇌ **9**, Scheme I).

Scheme I



It is not known whether **3** prepared by the present method contains one or both of the diastereomers. However, although the inversion barrier is undoubtedly much higher than the conformational one,[2] it might be surmounted at 146.5°. Therefore, even if only one diastereomer results from synthesis, the other might be accessible under the conditions of pyrolysis. In any case, the chair-like Cope rearrangement leading to cTT evidently proceeds from **8**.

It might appear that Scheme I provides a potential mechanism for the frequently observed[3,8,9] thermal racemization and trans ⇌ cis interconversion of 1,2-dialkenylcyclobutanes. In detail, however, this seems unlikely. Although the racemization [(*RR*)-tCT ⇌ (*SS*)-tCT)] cannot be formally ruled out, Scheme I requires that a trans → cis transformation of the relationship of the propenyl groups be coupled with a T → C inversion of one of the olefinic geometric configurations. This conflicts with the experimental observations[3] of the reactions tCC ⇌ cCC and tCT ⇌ cCT.

In the absence of a stereochemical labeling experiment such as that described here, caution would be advisable in the mechanistic interpretation of the thermal isomerization of the parent compound, *cis*,*trans*-cycloocta-1,5-diene, to the cis,cis isomer.

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(7) *Cf.* A. C. Cope and B. A. Pawson, *J. Amer. Chem. Soc.*, **87**, 3649 (1965).

(8) G. S. Hammond and C. D. DeBoer, *ibid.*, **86**, 899 (1964).

(9) D. J. Trecker and J. P. Henry, *ibid.*, **86**, 902 (1964).

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

(11) National Science Foundation Postdoctoral Fellow (No. 40014), 1970–1971.

Jerome A. Berson,* Peter B. Dervan,[10] Jerry A. Jenkins[11]
Department of Chemistry, Yale University
New Haven, Connecticut 06520

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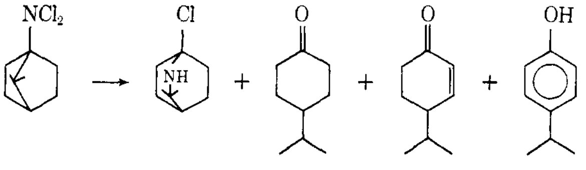
Rearrangement of 1-*N*,*N*-Dichloroaminoapocamphane with Aluminum Chloride, and Solvolytic Behavior of the 1-Chloro-3,3-dimethyl-2-azabicyclo[2.2.2]octane Product

Sir:

Exposure of *N*,*N*-dihaloamines to aluminum chloride has recently been shown to result in products, after hydrolysis, which derive from alkyl migration to electron-deficient nitrogen.[1] We wish to report that a similar reaction of 1-*N*,*N*-dichloroaminoapocamphane (**1**) with aluminum chloride, in addition to following the expected rearrangement route to **2**, yielded products **3**, **4**, and **5** (*ca.* 40% yield total) arising from *β* scission.



1 2 3 4 5

1, obtained by chlorination of 1-aminoapocamphane[2] with *tert*-butyl hypochlorite in cyclopentane, on treatment with 2 mol of aluminum chloride in methylene chloride at *ca.* −75° provided 1-chloro-3,3-dimethyl-2-

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(1) P. Kovacic, J.-H. Liu, E. M. Levi, and P. D. Roskos, *J. Amer. Chem. Soc.*, **93**, 5801 (1971); T. A. Kling, M. B. Nazareno, and P. Kovacic, *ibid.*, **94**, 2157 (1972); P. Kovacic, M. K. Lowery, and P. D. Roskos, *Tetrahedron*, **26**, 529 (1970); S. J. Padegimas and P. Kovacic, *J. Org. Chem.*, **37**, 2672 (1972).

(2) D. N. Kursanov and S. V. Vitt, *J. Gen. Chem. USSR*, **25**, 2401 (1955).