(Grant No. GP-30589X) for partial support of this research.

(11) Alfred P. Sloan Fellow, 1972–1974.

Arthur J. Ashe, III,*[11] Michael D. Gordon
Department of Chemistry, University of Michigan
Ann Arbor, Michigan 48104

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Incremental Substituent Effects Leading to Steric Blockade of the Boat-Like Six-Center Cope Rearrangement of *cis*-1,2-Dialkenylcyclobutanes[1]

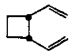
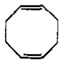
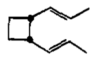
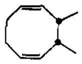
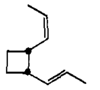
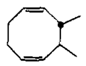
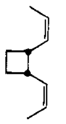
Sir:

Although the rate of the chair-like, four-center Cope rearrangement of acyclic biallyls is faster than that of the boat-like, six-center one by a factor greater than exp((6000 cal/mol)/RT),[2] there are several cases in the literature in which the order of preference is qualitatively reversed. Among the earliest examples so interpreted are the thermal transformations of *cis*-1,2-dialkenylcyclobutanes to *cis,cis*-cycloocta-1,5-dienes.[3,4] The normal preference for the chair-like pathway in these systems should be diminished because of the high strain energy[5] of the product, a *cis,trans*-cycloocta-1,5-diene. Although the transient intermediacy of that substance cannot be excluded on purely energetic grounds,[6] the present results strongly support the formulation[3,4,6] of the rearrangement of *cis*-1,2-divinylcyclobutane to *cis,cis*-cycloocta-1,5-diene as a direct process *via* a boat-like transition state. Moreover, they show how *cis*-1,2-dialkenylcyclobutanes, already deprived of the normal chair-like pathway by product strain, can be subjected to incremental steric effects that gradually deny access even to the "second-best" boat-like reaction.

Successive treatments of dimethyl *cis*-1,2-cyclobutanedicarboxylate with $NaAlH_2(OCH_2CH_2OCH_3)_2$ and $CH_3CH{=}PPh_3$, followed by gas chromatographic (gc) separation on a $AgNO_3$–Carbowax 200 column, give *cis*-1,2-*trans,trans*-, *cis*-1,2-*cis,trans*-, and *cis*-1,2-*cis,cis*-dipropenylcyclobutanes (cTT, cCT, and cCC).[7] These substances are identified by nuclear magnetic resonance (nmr) and especially by infrared (ir) spectroscopy ($\lambda\lambda_{max}$ cTT, 965 cm^{-1}; cCC, 740 and 695 cm^{-1}; cCT, 965 and 715 cm^{-1}).

Table I records the rates and products observed on pyrolysis of these three reactants and of *cis*-1,2-divinylcyclobutane[3] (cDV) at 146.5° in the liquid phase.

Table I. Rates and Products of Pyrolyses of *cis*-1,2-Dialkenylcyclobutanes

	Boat		Crossover	
Reactant	Product	k_b, rel	Product	k_c, rel
 cDV	 1	181,000[a]		
 cTT	 2	41,800[b]	**3**	
 cCT	 3	435[c]	**2**	24[c]
 cCC	**2**	1[c,d]	**3**	200[c]

[a] Calculated from published activation parameters.[3] [b] Measured directly. [c] Calculated as the product of the observed overall first-order rate constant for disappearance of cCT (or cCC) and the fraction of the indicated 3,4-dimethylcycloocta-1,5-diene in the product mixture, which also contains *trans*-1,2-*cis,trans*- (respectively, *cis,cis*)-dipropenylcyclobutanes from cCT and cCC, as well as piperylene and 3-methyl 4-propenylcyclohexenes. [d] k_b(abs) = 1.3 × 10^{-7} sec^{-1}.

The data show that methyl substitution at the terminal carbons of the vinyl groups of cDV produces a regular decline in the rate of the boat-like rearrangement. In the transition state of cTT → **2**, the major steric difference as compared to the case of cDV → **1** is the methyl–methyl interaction, MM. The same conformation in the case of cCT → **3** replaces this with two methyl–hydrogen interactions, MH, but also introduces a methyl–ring interaction, MR. Finally, the reaction cCC → **2** has one MM and two MR interactions. On the assumption that the interaction free energies remain constant in the series, the relative rate data of Table I for the boat-like reactions can be expressed in the form of the following parameters (in kcal/mol): $\Delta\Delta F_{MH}{}^{\ddagger} = 0.29$; $\Delta\Delta F_{MM}{}^{\ddagger} = 1.22$; $\Delta\Delta F_{MR}{}^{\ddagger} = 4.43$. These steric effects, when combined with the observed stereochemistry of the products (both double bonds cis, methyl configurations cis from cTT and cCC, trans from cCT), strongly suggest boat-like transition states for the Cope rearrangements of cDV, cTT, and the major portion of cCT.

By far the largest steric effect is the methyl–ring interaction,[8] which comes into play in the boat-like transition states from the reactants having cis propenyl groups (cCT and cCC). Not only does this depress strongly the rate of the unperturbed boat-like reaction of cDV, but by doing so, it permits the observation of a much slower "crossover" process which gives a different product. The crossover and boat-like reactions are distinguished by the configuration of the methyl groups in the product 3,4-dimethylcycloocta-1,5-diene.[9] Undetectable in the Cope rearrangement of cTT, crossover begins to emerge in the cCT case (95% boat-like, 5% crossover) and becomes dominant in cCC (0.5% boat-like, 99.5% crossover).

Two mechanisms for the crossover reaction are presently under consideration. The first is a direct

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[1] We thank the National Science Foundation (Grant No. GP11017X) and the Hoffmann-La Roche Foundation for partial support of this work.

[2] W. von E. Doering and W. Roth, *Tetrahedron*, **18**, 67 (1962).

[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).

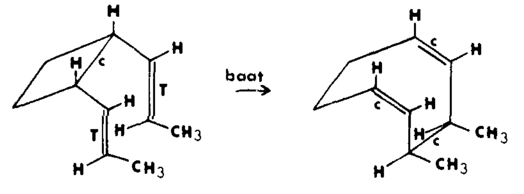
[5] A. C. Cope, C. F. Howell, J. Bowers, R. C. Lord, and G. M. Whitesides, *ibid.*, **89**, 4024 (1967).

[6] For a discussion, see W. von E. Doering, M. Franck-Neumann, D. Hasselmann, and R. L. Kaye, *ibid.*, **94**, 3833 (1972), ref 45.

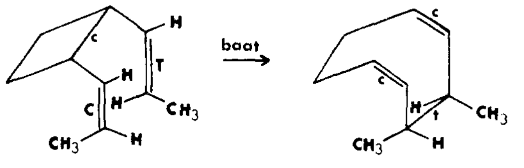
[7] Elemental analysis confirms the composition.

[8] Qualitative evidence for a large retarding effect of this type has been provided recently by W. Grimme, *J. Amer. Chem. Soc.*, **94**, 2525 (1972).

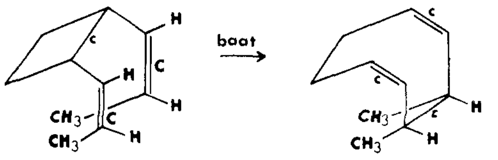
[9] Ozonolyses of **2** and **3** give succinic acid and (respectively) *meso*- and *rac*-2,3-dimethylsuccinic acids.



cTT 2

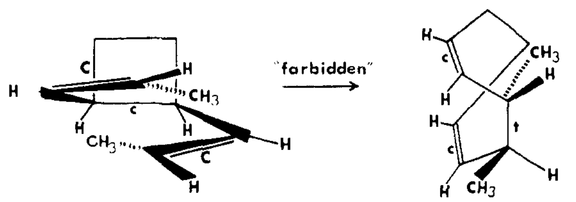


cCT 3



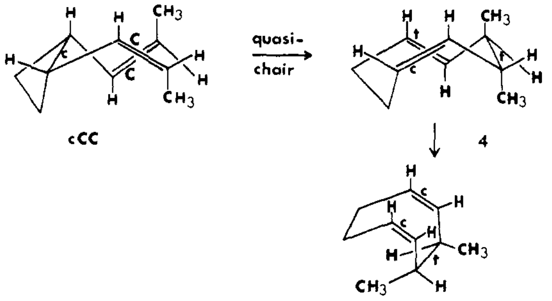
cCC 2

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



cCC 3

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]



cCC 4 3

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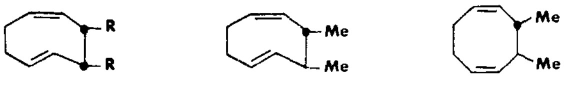
Stereospecific Double Rearrangement of *trans*-3,4-Dimethyl-*cis,trans*-cycloocta-1,5-diene to *cis*-3,4-Dimethyl-*cis,cis*-cycloocta-1,5-diene[1]

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.



1 : R = H
2 : R = Me
3
4

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).