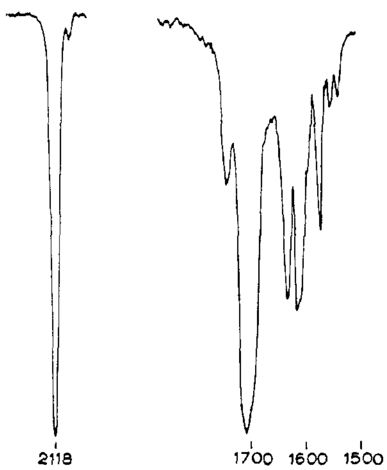
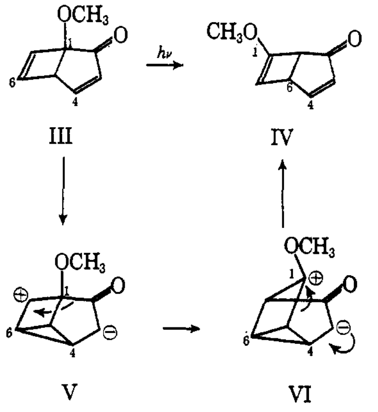


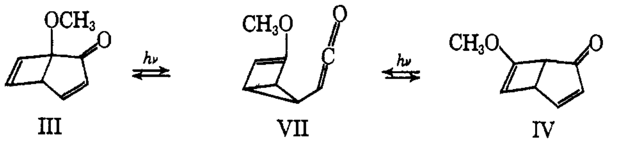
Figure 2. Low-temperature infrared spectrum of the carbonyl region after 50-min irradiation[4] of 1-methoxybicyclo[3.2.0]hepta-3,6-dien-2-one (III).

ketene carbonyl band at 2118 cm^{-1} (Figure 2)[5,8] which could be observed after 2-min irradiation and which reached a maximum at 1-3 hr. The intermediate was stable in the dark for 12 hr at $<-180^\circ$. Above -70° the intermediate disappeared rapidly in the dark. The only products observed by infrared analysis, gas chromatography, and nmr spectra were III and IV.[9] Analysis of the low-temperature infrared spectra and the behavior of the various bands during warm-up to room temperature permit assignment of bands at 1620 (enol ether double bond) and 825 cm^{-1} and tentative assignment of bands at 1320, 1280, and 1223 cm^{-1} to the intermediate.



The ketene intermediate is also formed on irradiation of IV. In fact, a steady state involving III, IV, and the intermediate can be approached from either III or IV.

The intermediate possesses a ketene carbonyl group and an enol ether double bond and it is thermally unstable at temperatures above -70°. The thermal rearrangement leads predominantly to IV. These considerations lead us to assign structure VII to the intermediate. The thermal instability of VII has excellent analogy in the apparent thermal isomerization of *cis*-1,2-divinylcyclopropane generated *in situ* below -40° to 1,4-cycloheptadiene[10,11] and in the degenerate valence isomerizations of tricyclo[3.3.2.0^{4,6}]deca-2,7,9-triene (bullvalene),[10–14] tricyclo[3.3.1.0^{4,6}]nona-2,7-dien-9-one (barbaralone),[11,15] and tricyclo[3.3.2.0^{4,6}]deca-2,7-diene[14] which are not frozen out at -50°. Formation of VII from either III or IV is easily understood as an example of the well-known α-cleavage reaction of n,π^* excited stages.



Ketene intermediates analogous to VII can be considered for many photochemical reactions. These possibilities are under active investigation.

Acknowledgment. This investigation was supported by Grant 14305 from the National Institute of General Medical Sciences, National Institutes of Health. Samples of III and IV were provided by Mr. R. L. Reierson.

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[8] The possibility that the 2118-cm^{-1} band might be due to carbon monoxide was excluded by irradiation of a freeze–thaw degassed glass of I followed by warm-up and mass spectrometric examination of the gaseous products. A trace of residual nitrogen could be detected but no carbon monoxide.

[9] After prolonged (12 hr) irradiation of the intermediate some absorption in the 1720–1780-cm^{-1} region was observed.

(10) W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963).

(11) W. von E. Doering and W. R. Roth, *Angew. Chem. Intern. Ed. Engl.*, **2**, 115 (1963).

(12) G. Schröder, *Angew. Chem.*, **75**, 722 (1963).

(13) M. Saunders, *Tetrahedron Letters*, 1699 (1963).

(14) R. Merenyi, J. F. M. Oth, and G. Schröder, *Ber.*, **97**, 3150 (1964).

(15) J. B. Lambert, *Tetrahedron Letters*, 1901 (1963).

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Conformational Analysis in Multisulfur Heterocycles. II. Isolation of the Conformationally Pure Twist-Boat Form of Duplodithioacetone

Sir:

Although many studies have dealt with the measurement of the rate of very fast conformational equilibrations[1] in solution, little effort has been expended to isolate conformers in solution when the barrier ($\Delta F^{\ddagger}$) to conformational interconversion is about 16 kcal/mole or less.[2] Once the barrier to conformational equilibration has been measured, *e.g.*, by variable-temperature nuclear magnetic resonance (nmr) spectroscopy, appropriate low temperatures can be selected at which the half-life of a given conformer is many hours.

Recently, the unusual observation was made that the twist-boat conformer of duplodithioacetone (tetramethyl-*s*-tetrathiane) was more stable than the chair form ($\Delta F^\circ = -0.8$ kcal/mole at 0° in CS$_2$).[3]

Examination of the nmr spectrum[4] of duplodithioacetone at 35° reveals a set of two broadened resonances of unequal intensities at δ 2.00 and 1.66 ppm. Upon

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(1) J. E. Anderson, *Quart. Rev.* (London), **19**, 426 (1965); F. G. Riddell, *ibid.*, **21**, 364 (1967).

(2) F. R. Jensen and C. H. Bushweller, *J. Am. Chem. Soc.*, **88**, 4279 (1966).

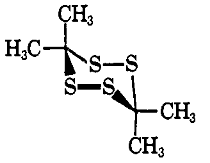
(3) C. H. Bushweller, *ibid.*, **89**, 5978 (1967).

(4) The nmr spectra were recorded on a Varian Associates A-60 nmr spectrometer using a V-6040 temperature controller. Temperature was measured using a methanol sample.

lowering the temperature, these resonances sharpened in the usual manner into a set of three peaks consisting of two resonances of equal area at δ 1.53 and 2.03 ppm and a larger sharp singlet at δ 1.68 ppm. When the sample temperature was raised, the spectrum showed kinetic broadening characteristic of an intermediate exchange rate on the nmr time scale, and at 80° the two broad resonances observed at 35° had coalesced into a singlet at δ 1.73 ppm. Upon again lowering the temperature, an identical sequence of spectral transitions was observed.

The large, sharp singlet (δ 1.68 ppm) observed at −30° is assigned to the twist-boat conformer of duplodithioacetone (I), and the two smaller peaks of equal intensity at δ 1.53 and 2.03 ppm are assigned to the axial and equatorial methyl resonances of the chair conformers (II). If the diamagnetic anisotopy of the sulfur–sulfur bond is analogous to that proposed for carbon–carbon bonds in cyclohexane,[5] the resonance at δ 1.53 ppm may be assigned to the axial methyl group of the chair form and the resonance at δ 2.03 ppm to the equatorial methyl.

I



II

The temperature dependence of the nmr spectrum of duplodithioacetone indicates that the barrier ($\Delta F^{\ddagger}$) to chair–boat isomerism is approximately 16 kcal/mole.[3]

Thus, it would be expected that at about −80° the half-life of the chair or twist-boat conformer would be many hours and either conformer could be isolable by some technique. Indeed, by cooling a sample of crystalline duplodithioacetone to −80° and then slowly adding carbon disulfide until the sample was completely dissolved at −80°, the pure ($\sim$100%) twist-boat form of duplodithioacetone was isolated *in solution.* An nmr spectrum of the resultant solution at −80° revealed one sharp singlet at δ 1.70 ppm (Figure 1) and no indication of the two resonances at δ 1.53 and 2.03 ppm of the chair conformers. Upon warming to −30°, the two resonances at δ 2.03 and 1.53 ppm appeared and grew very rapidly in intensity.

The result reported above substantiates the observation of Fredga[6] using X-ray crystallography that duplodithioacetone exists in a boat conformation. It is apparent that crystalline duplodithioacetone exists in a conformationally pure state. The sharp singlet (δ 1.70 ppm) observed for the nmr spectrum of the twist-boat form of duplodithioacetone is consistent with a symmetrical, nonpseudo-rotating twist-boat form (I) in which all methyl groups are in equivalent environments *or* a very rapidly pseudo-rotating twist-boat. If pseudo-rotation is slow on the nmr time scale, the presence of a true boat form proposed by Fredga (III) for crystalline duplodithioacetone is not consistent with a singlet nmr resonance in solution as a chemical shift between the axial and equatorial methyl resonances would be expected. Clearly, studies at much lower temperatures than employed here might give additional evidence concerning the identity of the conformers present.

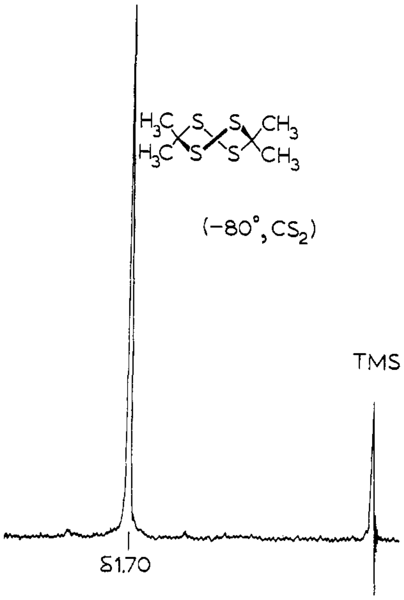
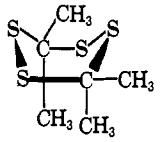


Figure 1. The nmr spectrum (60 MHz) of the conformationally pure twist-boat form of duplodithioacetone (−80°, CS_2).

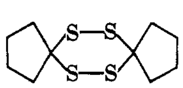


III

The isolation of the pure twist-boat conformer of duplodithioacetone makes possible the measurement of accurate rates of chair–boat equilibration at various temperatures and should give a meaningful enthalpy and entropy of activation for the rate processes involved.

It is apparent that the long carbon–sulfur and sulfur–sulfur bonds play an important role in minimizing lone-pair repulsions and rendering the twist-boat of duplodithioacetone more stable than the chair conformation. It would appear likely that entropy would favor the flexible twist-boat conformer over the rigid chair. Indeed, a preliminary study of the temperature dependence of the equilibrium constant (K = [boat]/[chair]) between twist-boat and chair conformers indicates that the twist-boat is favored by an entropy term ($\Delta S° \cong +1$ eu) as well as an enthalpy term ($\Delta H° \cong -0.5$ kcal/mole).[7]

A preliminary study of the temperature dependence of the nmr spectrum of 3,3:6,6-bis(tetramethylene)-*s*-tetrathiane (IV) indicates conformational equilibra-



IV

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(5) A. A. Bothner-By and C. Naar-Colin, *Ann. N. Y. Acad. Sci.*, 70, 833 (1958).

(6) A. Fredga, *Acta Chem. Scand.*, 12, 891 (1958).

(7) The sample studied was 0.8 *M* duplodithioacetone in carbon disulfide and the temperature range was 40°.

tion of some type. A preliminary X-ray crystallographic study indicates that IV exists in a chair form.[8]

(8) D. S. Breslow and H. Skolnik, "Multi-Sulfur and Sulfur and Oxygen Five- and Six-Membered Heterocycles," Part Two, Interscience Publishers, Inc., New York, N. Y., 1966, p 629.

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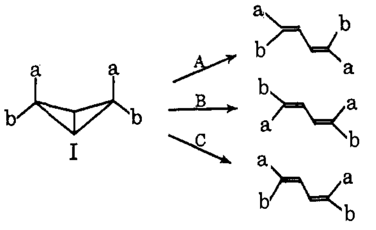
The Steric Course of the Thermal Rearrangements of Methylbicyclobutanes[1]

Sir:

Two problems arise from the observed thermal rearrangement of bicyclobutane to butadiene.[2] First, the detailed stereochemistry of the ring opening is as yet unknown, and second, no evidence exists either proving or disproving the existence of an intermediate in this reaction.[3] Answers to both questions are of considerable importance to an understanding of thermal rearrangements in general.

Considering a symmetrically labeled bicyclobutane, I, three sterically different modes of ring opening can be envisioned. In modes A and B reactants and products have a common symmetry element (C_2), but the rotations required to bring the substituents at carbon atoms 2 and 4 of the bicyclobutane into the molecular plane of butadiene are of opposite sense in the two modes. Mode C gives a product which shares no symmetry element with the reactant. A more detailed analysis shows that in a concerted reaction to *s-trans*-butadiene mode A corresponds to a quasi-disrotatory opening of both rings while B requires quasi-conrotatory motions. In mode C one ring is opened disrotatory and the other conrotatory.[4] If one assumes a concerted mechanism, it follows that correlation diagrams can be constructed with symmetry orbitals only for A and B but not for C.[5] Furthermore, the results of such correlations predict high activation energies for A and B because the ground state of I correlates with $\Psi_1{}^2\Psi_4{}^2$ and $\Psi_2{}^2\Psi_3{}^2$ of butadiene, respectively.[6,7] The results of a previous attempt to determine the stereochemistry of ring opening of bicyclobutane-2-d_1 were ambiguous because the product analysis was compatible with either path C, or product formation by both A and B, or the occurrence of all three reaction modes.[8]



To gain information on these questions we have synthesized *exo,exo*- and *exo,endo*-2,4-dimethylbicyclobutanes (III and IV) *via* the cuprous cyanide catalyzed decomposition of *trans*-1-diazo-2-methylpent-3-ene (II), and *exo*- and *endo*-2-methylbicyclobutanes (VII and VIII) from *trans*- and *cis*-1-diazopent-3-enes (V and VI), respectively.[9] The product analyses of the vapor-phase pyrolysis (200°) are shown in Tables I and II.[10] The results obtained for the dimethyl derivatives can be summarized by stating that: (i) diene formation is stereoselective but not completely specific; (ii) the predominantly formed dienes are those expected from the unsymmetrical mode C; (iii) minor side products are *trans*-1-methyl-2-vinylcyclopropane and *cis*-1,4-hexadiene, a known rearrangement product of *cis*-1-methyl-2-vinylcyclopropane.[11] In contrast, the product distribution of the pyrolysis of the monomethyl derivatives VII and VIII is very similar for both isomers and consists mostly of *trans*-1,3-pentadiene.

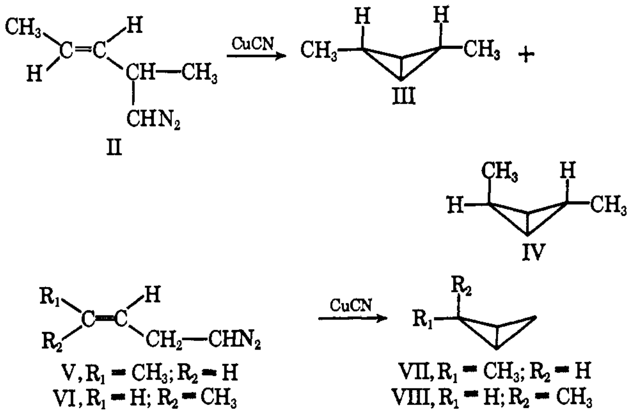


Table I. Pyrolysis Products of 2,4-Dimethylbicyclobutanes

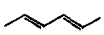
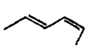
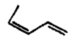
	Products, %			
Reactant				
III	3.9	93.2	2.9	. . .
IV	95.0	1.2	2.2	1.6

Table II. Pyrolysis Products of 2-Methylbicyclobutane

	Products, %		
Reactant			
VII	91.0	6.2	2.8
VIII	90.5	7.5	2.0

These observations eliminate the concerted symmetrical mechanisms A and B. Also, the unsymmetrical

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[1] Supported by National Science Foundation Grants GP-4212 and GP-7043.

[2] H. M. Frey and I. D. R. Stevens, *Trans. Faraday Soc.*, **61**, 90 (1965); W. von E. Doering and J. F. Coburn, Jr., *Tetrahedron Letters*, 991 (1965).

[3] See, however, I. A. D'yakonov, V. V. Razin, and M. I. Komendantov, *ibid.*, 1127, 1135 (1966), on the rearrangements of 1,3-diphenyl-2,4-dicarbomethoxybicyclobutanes.

[4] Actually each of the three modes corresponds to two different pathways, one in which the initial product is *s-trans*-butadiene and another in which *s-cis*-butadiene is formed first. However none of the conclusions drawn in this communication is effected by this degeneracy.

[5] *Cf.* R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, 1, 17 (1968).

[6] This correlation neglects the "noncrossing" rule of levels of identical symmetry.

[7] A previous discussion of orbital correlation in the ring opening of bicyclobutane[8] should be disregarded because it was erroneously based on a *trans*-fused bicyclobutane.

[8] K. B. Wiberg and J. M. Lavanish, *J. Am. Chem. Soc.*, **88**, 5272 (1966).

[9] The bicyclobutanes were fully characterized by complete analyses of their nmr spectra and by mass spectra.

[10] The reactions were carried out in quartz flasks because pyrolyses in Pyrex vessels gave irreproducible results due to surface effects.

[11] W. R. Roth and J. König, *Ann.*, **688**, 28 (1965).