terface. Since the rate constant is independent of the compression and rather insensitive to the nature of the acyl group, the enzymatic reaction most likely occurs at the interface without penetration of the enzyme.

Orientation of diglycerides dominated by the polar hydroxyl group should make the primary ester group more inaccessible at the interface than in the case of triglycerides, and this is reflected by a large rate difference observed between dioctanoin and trioctanoin.

We believe that this simple experimental technique, which is sensitive, convenient, reproducible, and amenable to quantitative analysis, opens the way to rigorous quantitative studies on the behavior and mechanism of pancreatic lipase. The method can undoubtedly be adapted to the study of the action of enzymes at interfaces, such as biological membranes.

[7] Predoctoral trainee of the National Aeronautics and Space Administration.

James W. Lagocki,[7] Norman D. Boyd
John H. Law, Ferenc J. Kézdy
Departments of Biochemistry and Chemistry, University of Chicago
Chicago, Illinois 60637

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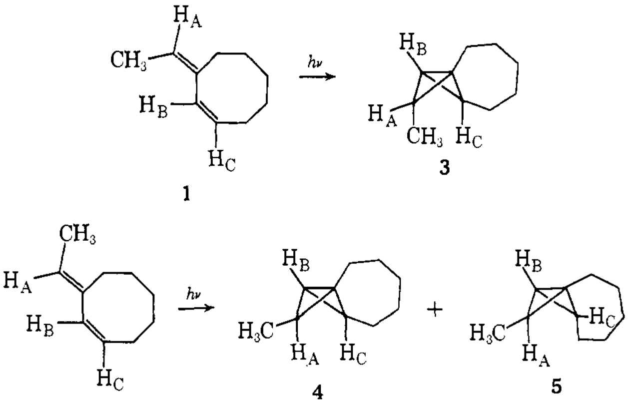
Photochemistry of Ethylidenecyclooctenes. Mechanism of Bicyclobutane Formation.[1]

Sir:

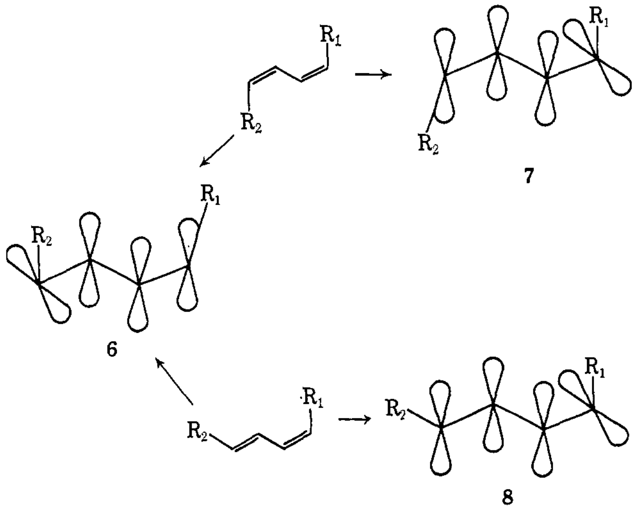
We wish to report the stereochemistry of bicyclobutanes formed from *cis*- and *trans*-3-ethylidenecyclooctene (**1** and **2**) and the mechanistic implications to the photocyclization of butadienes to bicyclobutanes.



Ethylidenetriphenylphosphorane upon reaction with 2-cycloocten-1-one afforded a mixture of two isomeric dienes (**1**:**2**, 40:60), readily separable by vpc:[2] nmr (δ, CCl$_4$) **1**, 6.27 (H$_B$, d, J = 12 Hz), 5.49 (H$_C$, d of t, J = 12, 8 Hz), 5.20 (H$_A$, q, J = 7 Hz); **2**, 6.03 (H$_B$, d, J = 12 Hz), 5.42 (H$_A$, q, J = 7 Hz), 5.24 (H$_C$, d of t, J = 12, 8 Hz). Isomer **2** was assigned the *trans* configuration since the H$_A$ of **2** is at lower field due to the greater deshielding by the endocyclic double bond and the H$_B$ and H$_C$ of **1** are at lower field due to deshielding by the methyl group.[3]

Typical of *s-trans* dienes,[4a,b] irradiation[5] of **1** and **2** gave bicyclobutanes **3**–**5**. Concentration studies showed that **3** was derived from **1**, and **4** and **5** (3:1) from **2**: nmr (δ, CCl$_4$) **3**, 1.10 (H$_C$, br d, J = 6 Hz), 0.77 (3 H, d, J = 6 Hz); **4**, 0.93 (5 H, m); **5**, 0.92 (4 H, m). In **3**, an *endo*-methyl group is indicated by its chemical shift (δ 0.77), and its almost symmetrical doublet pattern requires H$_A$ to be at much lower field ($\Delta\nu \gg J$)[6] and thus *exo*. The presence of the high-field broad doublet indicates that H$_C$ has the *endo* configuration.[7] Hence, **3** is *endo*-9-methyl-*cis*-tricyclo[6.1.0.0^{1,7}]nonane. In **4** and **5**, the multiplet patterns agree well with the calculated[6] AB$_3$ spectra for $\Delta\nu/J = 1$. The presence of 5-H above δ 1.1 permits assignment of **4** as the *exo*-9-methyl-*cis* isomer and the 4-H above δ 1.1 in **5** confirms the *exo*-9-methyl-*trans* structure.

The orbital symmetry concept of the cyclization proceeding in a concerted manner beginning with two planar double bonds and following *cis–cis* or *trans–trans* (2 + 2) cycloaddition[8] requires any pair of bicyclobutanes produced from a *single* diene such as **1** or **2** to be epimeric at *two* centers. This prediction is incompatible with our results which show that a single diene, **2**, yields two bicyclobutanes epimeric at only *one* center. This result is, however, easily accommodated by considering the cyclization to be initiated from the vibrationally relaxed (nonplanar or orthogonal) first excited singlet state.[9] If two epimeric dienes are excited to their first excited electronic level, vibrational relaxation can lead to identical (**6**) or to epimeric species (**7** and **8**).



In the present study, it has been found that isomerization about the endocyclic double bond in ethylidenecyclooctenes occurs faster by a factor of 3–5 than exocyclic bond isomerization though, indeed, the product of the dominant path is highly strained. Hence, vi-

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[1] This work was supported in part by PHS Grant No. AM 00709, National Institute of Arthritis and Metabolic Diseases, U. S. Public Health Service.

[2] 5% Carbowax 20M, 5% KOH on Chromosorb G.

[3] C. G. Cárdenas, *Tetrahedron Lett.*, 4013 (1969).

[4] (a) W. G. Dauben and C. D. Poulter, *ibid.*, 3021 (1967); (b) W. G. Dauben and W. T. Wipke, *Pure Appl. Chem.*, **9**, 539 (1964); (c) W. G. Dauben, *Chem. Weekbl.*, **29**, 381 (1964).

[5] A 0.5–1.0% solution in cyclohexane was irradiated with a mercury resonance lamp (Vycor filter).

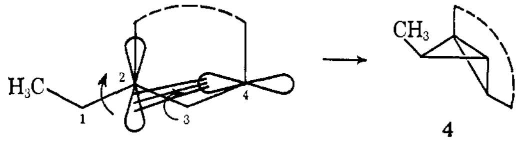
[6] K. B. Wiberg and B. J. Nist, "The Interpretation of NMR Spectra," W. A. Benjamin, Inc., New York, N. Y., 1962.

[7] (a) K. B. Wiberg, G. M. Lampman, R. P. Ciula, D. S. Connor, P. Schertler, and J. Lavanish, *Tetrahedron*, **21**, 2749 (1965); (b) K. B. Wiberg, *Advan. Alicyclic Chem.*, **2**, 185 (1968).

[8] R. B. Woodward and R. Hoffmann, *Angew. Chem. Int. Ed. Engl.*, **8**, 781 (1969).

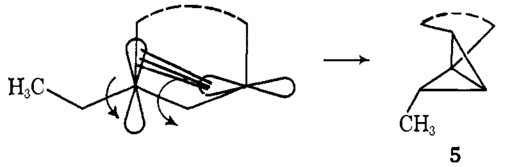
[9] (a) L. Burnelle, *J. Chem. Phys.*, **43**, S29 (1965); (b) R. Hoffmann, *Tetrahedron*, **22**, 521 (1966).

brational relaxation with twisting of the internal double bond must be highly preferred. Assuming that the cyclization is initiated from this twisted species, *i.e.*, **7** or **8**, R_1 = ring, R_2 = Me, one expects and finds retention of the stereochemical integrity of the methyl group. However, because the fourth p orbital is orthogonal there are no orbital symmetry requirements for 2,4 bonding. Thus, for example, clockwise rotation in



(1)

4

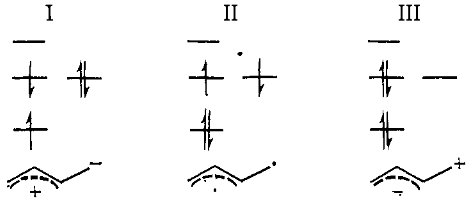


(2)

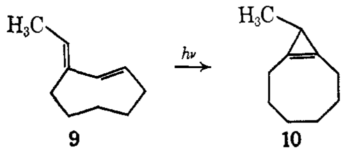
5

a conrotatory closure of the allyl system (eq 1) (with 2,4 closure as indicated to avoid a *trans*-bicyclobutane) would give **4**, while counterclockwise rotation (eq 2) (requiring use of the alternate lobe at C-2) would produce **5**. Given free rotation about the 3,4 bond, both pathways should be of equal probability. In the system under study, the restraint induced by the eight-membered ring accounts for the preferential *cis* stereochemistry of the fused ring (eq 1).

From the stereochemistry found for the methyl group, the 1,3 closure of the allyl system is conrotatory as suggested above, thus requiring that the orthogonal singlet have one of the following three electronic configurations.[10]



To evaluate further these possible electronic configurations some additional experimental results must be considered: first, cyclopropene **10** [ir (CCl_4) 1880 cm^{-1}; nmr (δ CCl_4) 0.96 (3 H, d, J = 4.5 Hz), 2.4 (4 H, m)] is formed (10%) during the irradiation of **2** and it arises from the subsequent irradiation of the initially formed *endo-trans* isomer **9**.[11] Second, direct, but *not* sensitized excitation of 3-methylenecycloalkenes in methanol yields methyl ethers.[12]



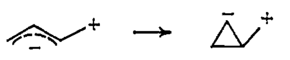
9 **10**

Considering now the three possible electronic configurations of the orthogonal singlet, the first, the excited allyl cation–methyl anion, is rejected as being too high in energy to be formed from the spectroscopic singlet of a diene and as not accounting for cyclopropene formation and the observed direction of solvent addition.

The second species, the diradical, besides having a high activation energy for closure,[10,13] does not account for the observed type of solvent addition.

The third species, allyl anion–methyl cation, is consistent with cyclopropene formation occurring *via* a 1,2-hydride shift during the ring closure and also correctly predicts the position and direction of solvent addition. Such a species does not require the excited state to be fully 90° nonplanar to remove 2,4 orbital symmetry bonding requirements.

The next question to consider is whether the cyclization to bicyclobutanes is a concerted or two-step process. One can envision a cyclopropyl anion–carbinyl cation (eq 3), analogous to the diradical postulated by Srinivasan[14] for a two-step process. Analogous to the cyclization of butadiene to cyclobutene,[4b,c] cyclization cannot proceed from the $S_1{}^0$ state of butadiene to the $S_1{}^0$ state of bicyclobutane because of the high endothermicity. In a two-step cyclization, internal conversion could occur during the second closure; however, this requires that the first closure produce an excited state of bicyclobutane, an unlikely endothermic process. Both the diradical and zwitterion two-step closures must be rejected on this basis.



(3)

In a concerted cyclization of the third species, it is possible that electrostatic interaction between the methyl cation and the developing anion might lower the energy of the transition state and allow progress along the reaction path to a point of *facile internal conversion* and collapse to ground-state bicyclobutane, such as has been calculated for the butadiene–cyclobutene closure.[15] We suggest that bicyclobutane formation from conjugated dienes occurs in a concerted fashion from a vibrationally relaxed singlet having an allyl anion–methyl cation electronic configuration,[16] that orbital symmetry controls the stereochemistry of the allylic system cyclization, and that internal conversion occurs during the closure.

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[10] H. C. Longuet-Higgins and E. W. Abrahanson, *J. Amer. Chem. Soc.*, **87**, 2045 (1965).

[11] The *endo-trans* isomer is assigned an *s-cis* configuration (**9**) since photolysis of this isomer produces as the major product a cyclobutene; bicyclobutane **3** is also formed, consistent with our predicted stereochemistry.

[12] W. G. Dauben and C. D. Poulter, unpublished observations.

[13] O. P. Strausz, P. J. Kozak, G. N. C. Woodall, A. G. Sherwood, and H. E. Gunning, *Can. J. Chem.*, **46**, 1317 (1968).

[14] R. Srinivasan, *J. Amer. Chem. Soc.*, 90, 4498 (1968).

[15] (a) W. Th. A. M. van der Lugt and L. J. Osterhoff, *ibid.*, **91**, 6042 (1969); (b) G. Feler, *Theor. Chim. Acta*, **12**, 412 (1968).

[16] Extended Hückel calculations[8b] on singlet diene also support this configuration. We thank Professor Hoffmann for communicating this result to us.

[17] National Science Foundation Predoctoral Fellow, 1966–present.

William G. Dauben, James S. Ritscher[17]
Department of Chemistry, University of California
Berkeley, California 94720

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Multiple Chromium(II)–Chromium(II) and Rhodium(II)–Rhodium(II) Bonds

Sir:

It has been noted elsewhere[1] that the binuclear, carboxylato-bridged species, I, (where the end groups,

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[1] F. A. Cotton, *Rev. Pure Appl. Chem.*, **17**, 25 (1967).