of activation for the various isomers can be estimated with much greater precision, however. Values of $\Delta\Delta V^{\ddagger}_0$, calculated by extrapolating the slopes of relatively linear plots of ln k_x/k_2 against pressure, are independent of any errors in absolute rate measurements and are apparently accurate to within approximately 1 cm^3/mol. These agree as well as can be expected with differences in $\overline{\Delta V}^{\ddagger}$ or $\Delta V^{\ddagger}_0$. There has been considerable controversy[7] previously over attempts to compare an *absolute* value for *one* observed process to absolute values predicted for the two processes from theory. This difficulty is not relevant in the present case where the *difference* between the *two* processes is observable.

If, as proposed, diradical and electrocyclic reactions are usually comparable in energy in diene dimerizations, similar pressure effects should be observable in other systems. At least one trend in the appropriate direction can be seen in the data of Walling and Peisach[8] on the dimerization of isoprene, where the proportion of cyclooctadiene dimers was found to decrease with increasing pressure. Because the cyclooctadienes are presumably secondary products resulting from decomposition of initially formed cyclobutanes (comparable to formation of **5** from **1a** and **1b**), and because additional amounts of cyclohexenes can be formed similarly as well as by the electrocyclic process, quantitative interpretation is hazardous, but the apparent activation volume is about 3 cm^3/mol less negative for these "diradical" products than for the predominant methylisopropenylcyclohexenes.

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(7) See, for example, S. W. Benson and J. A. Berson, *J. Amer. Chem. Soc.*, **86**, 259 (1964); C. Walling and D. D. Tanner, *ibid.*, **85**, 612 (1963).

(8) C. Walling and J. Peisach, *ibid.*, **80**, 5819 (1958).

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Mechanisms of Photochemical Reactions in Solution. LXXI.[1] Photochemistry of 1,3-Cyclohexadiene at Long Wavelength

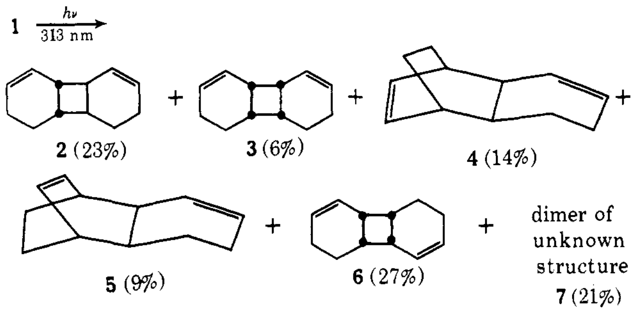
Sir:

The long wavelength absorption of conjugated dienes is of interest in view of uncertainty regarding the position of the 0–0 level of the first excited singlet state.[2,3] In addition, the nature of the absorbing species at wavelengths too low in energy to be reasonably assigned to excitation to S_1 has not been determined. The characterization of photochemical processes at these wavelengths, as distinct from those at energies in the region of the first absorption maximum, might be a useful approach to the resolution of these questions. We wish to report the occurrence of such unique photochemical processes in 1,3-cyclohexadiene (**1**), an *s-cis*-diene, during direct 313-nm (91 kcal mol^{-1}) irradiation.

Schenck and coworkers[4] first studied the photoreactivity of neat **1** at long wavelengths, which they designated as >330 nm. They reported that the same three dimers **2–4** formed by triplet sensitization[4,5] were produced, although in different proportion. Based on this result the suggestion was made that the long wavelength dimerization was due to direct singlet–triplet absorption by ground-state collision aggregates, followed by formation of the triplet dimers.

Our own studies, conducted at 313 nm, show that irradiation of neat **1** or its pentane or cyclohexane solutions at >1 *M* leads to the formation of three further dimers **5–7** in amounts comparable to those of the triplet dimers, together with trace amounts of several other presumably dimeric constituents. The composition of the dimer fraction obtained on irradiation of neat **1** is given in Scheme I. Dimers **2**, **4**, and **6** and a mixture of dimers **3**, **5**, and **7** were isolated by chromatography on a 10% silver nitrate–alumina column;[6] dimer **7** was isolated, although not in analytical purity,[7] by preparative gas–solid partition chromatography on Porasil D.

Scheme I



Dimer **5** (*endo*-dicyclohexadiene) is the major dimer produced thermally;[4,5] it is also formed by γ irradiation[4,8,9] and, in trace amounts, by the sensitized irradiation of **1**.[5]

Dimer **6**[10] (*cis,syn,cis*-tricyclo[6.4.0.0^{2,7}]dodeca-3,9-diene) is cleanly converted by catalytic hydrogenation to a tricyclic hydrocarbon[10] (*cis,syn,cis*-tricyclo[6.4.0.0^{2,7}]dodecane), which is identical with the compound produced by catalytic hydrogenation of **3** but differs from that produced[5] on hydrogenation of dimer **2**. The structure and stereochemistry of dimers **2** and **3** have been assigned previously.[4,5]

Compounds **2**, **6**, and **7**, collectively, constitute *ca.* 70% of the mixture of dimers produced on irradiation of neat (10.4 *M*) **1** at 313 nm. On dilution with pentane or cyclohexane, the relative contribution of dimers **5–7** decreases uniformly until, at 1.0 *M*, they comprise only *ca.* 25% of the mixture; the relative distribution of dimers **2–4** successively approaches the 3:1:1 ratio obtained on sensitized irradiation of **1** as the solutions are diluted. This change in product distribution on

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(1) Part LXX: J. W. Meyer and G. S. Hammond, *J. Amer. Chem. Soc.*, in press.

(2) R. Srinivasan, *Advan. Photochem.*, **4**, 113 (1966).

(3) R. Srinivasan and F. I. Sonntag, *J. Amer. Chem. Soc.*, **87**, 3778 (1965).

(4) G. O. Schenck, S.-P. Mannsfeld, G. Schomburg, and C. H. Krauch, *Z. Naturforsch.*, *B*, **19**, 18 (1964).

(5) D. Valentine, N. J. Turro, Jr., and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 5202 (1964).

(6) L. R. Chapman and D. F. Kuemmel, *Anal. Chem.*, **37**, 1598 (1965).

(7) The mass spectrum of dimer 7 shows contamination by tri- and tetrameric materials which presumably form on standing.

(8) R. Schutte and G. R. Freeman, *J. Amer. Chem. Soc.*, **91**, 3715 (1969).

(9) T. L. Penner, D. G. Whitten, and G. S. Hammond, *ibid.*, **92**, 2861 (1970).

(10) Satisfactory microanalytical and spectral data were obtained for this compound.

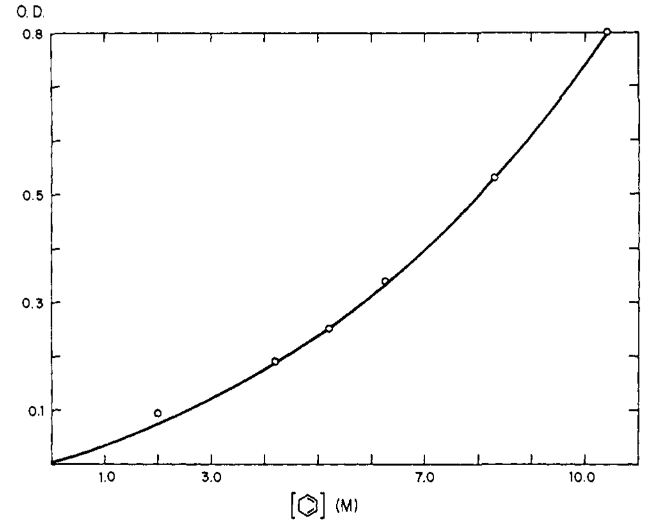

Figure 1. Beer's law plot for **1** at 313 nm.

dilution is accompanied by a dramatic decrease in initial quantum yield for dimer formation ($\phi_{10.4M} = 0.14$; $\phi_{1.0M} = 0.03$). The quantum yields and dimer distributions are independent of the amount of light absorbed up to 10^{-5} einstein cm^{-3}, which indicates that the dimers must be primary photoproducts. On prolonged irradiation *cis*-1,3,5-hexatriene, the major primary product at 313 nm ($\phi_{10.4M} = 0.45$; $\phi_{1.0M} = 0.82$), competes with **1** on an increasingly successful basis for the light.[11]

Irradiations were also performed at 254 nm, near the maximum of the first absorption band of **1**. At this wavelength the quantum yield for dimer formation in neat diene is very low (6×10^{-3}) and the only dimers detected are traces of **2**, **4**, and **5**. As at 313 nm, the major primary product is the *cis*-triene ($\phi_{10.4M} = 0.46$; $\phi_{1.0M} = 0.56$).[12]

The completely different photochemistry observed at 254 and 313 nm demonstrates that the diene excited singlet state is not involved in the dimerizations at the longer wavelength, and the presence of comparatively major amounts of new dimers at 313 nm indicates that precursors other than the lowest triplet excited state of **1**[14] must be responsible for the formation of these products.

A plausible explanation of these results is that absorption by ground-state aggregates of **1** occurs at 313 nm. That such complex formation does occur is indicated by the observation that the Beer's law plot for rigorously degassed solutions of **1** in cyclohexane shows substantial curvature at 313 nm; the apparent ϵ's range from 0.05 at 1.0 *M* to 0.08 at 10.4 *M* (*cf.* Figure 1).

We suggest that excited dimeric or polymeric species are formed by direct excitation and that their decay to new chemical products does not duplicate paths open to excimers which are formed by diffusive encounter of excited monomers with ground-state monomers. The phenomenon, absoption of light by weakly interacting pairs of neighboring molecules followed by unusual photoreaction, may be fairly common when systems containing very high concentrations of chromophoric species are exposed to light of wavelengths longer than that absorbed by monomeric species. The mechanism may be involved in degradation of some materials on exposure to sunlight.

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[11] For this reason, the chemical yield of dimers from preparative irradiations of neat 1 at 313 nm is extremely low (0.6%).

[12] The original designation[13] of the *trans*-triene as the primary photoproduct was in error: unpublished results from this laboratory and private communication from Professor E. Havinga.

[13] R. J. DeKock, N. G. Minnaard, and E. Havinga, *Recl. Trav. Chim. Pays-Bas*, 79, 922 (1960).

[14] E_{T_1} = 54 kcal mol^{-1}: D. T. Evans, *J. Chem. Soc.*, 1735 (1960).

[15] NATO Postdoctoral Fellow, 1970–1971.

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Theoretical Investigations of the Trimethylene Biradical[1]

Sir:

There is currently much interest in establishing the mechanisms and potential surfaces involved in the geometric and structural isomerizations of small cyclic compounds such as cyclopropane.[2–8] We report here the results of *ab initio* calculations on several configurations of trimethylene (open cyclopropane) using the generalized valence bond (GVB) method.[9]

We will use the following notation in describing the trimethylene configurations: θ is the central CCC angle; (90,90) indicates that the plane of each terminal CH$_2$ group is perpendicular to the CCC plane; (0,0) indicates that both terminal CH$_2$ groups are in the CCC plane; (0,90) is the obvious combination; a subscript c [*e.g.*, (0,90$_c$)] indicates that the terminal group is canted from planar to the nearest staggered configuration[7,8] (with respect to the bonds of the central carbon).

The geometric isomerizations of cyclopropane involve breaking of one C–C bond [in the (90$_c$,90$_c$) configuration] followed by rotation of one (path I) or both (path II) terminal CH$_2$ groups. If the shape of each CH$_2$ group is kept fixed as one CH$_2$ group is rotated, there would occur three relative maxima in each of which both bonds of this group would eclipse the bonds of the central carbon; in between would be two points [both (0$_c$,90$_c$)] at which the bonds would be staggered,

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[1] Partially supported by a grant (PF-013) from the President's Fund of the California Institute of Technology and by a grant (GP-15423) from the National Science Foundation.

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[4] H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, **72**, 1866 (1968).

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[6] A. K. Q. Siu, W. M. St. John III, and E. F. Hayes, *ibid.*, **92**, 7249 (1970). This work used CC bond lengths of 1.30 Å, somewhat shorter than the 1.54 Å we used. They carried out a 2×2 CI calculation, starting with the Hartree–Fock triplet orbitals. This procedure corresponds to the first iteration in the GVB method and should be adequate for $\theta > 100°$.

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