

The effect of experimental variables, such as dilution, wavelength, temperature, state of aggregation, etc., is being further investigated and a more detailed discussion of the results will be delayed until this additional information is obtained. It may be mentioned at this time that the observation of the stereospecific photochemical cyclodimerization of 2-butene in the liquid phase may be of considerable interest in connection with the recent spectroscopic and theoretical discussions concerning the low-lying electronic states of olefins.³ It may also be of importance as the simplest model of photochemical cyclodimerization and in general cycloaddition with cyclobutane ring formation. Cyclobutane ring formation in more complex systems is observed, for example, in the photochemistry of nuclei acids⁴ and in the photochemical cycloadditions to steroids.⁵ Detailed studies of numerous other photochemical cycloadditions of this type have been made.^{6,7} The noteworthy feature of the present case is the retention of the original geometric configuration of both fragments in the cycloadduct although energies in excess of 5 eV are absorbed.

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(3) M. B. Robin, H. Basch, N. A. Kuebler, B. E. Caplan, and J. Meinwald, *J. Chem. Phys.*, **48**, 5037 (1968).

(4) R. B. Setlow, *Science*, **153**, 379 (1966).

(5) P. H. Nelson, J. W. Murphy, J. A. Edwards, and J. H. Fried, *J. Am. Chem. Soc.*, **90**, 1307 (1968).

(6) R. O. Kan, "Organic Photochemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1966, Chapters 5 and 6.

(7) N. J. Turro "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, Chapter 8.

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Photosensitized Cope Rearrangements of 1,2,6-Trienes¹

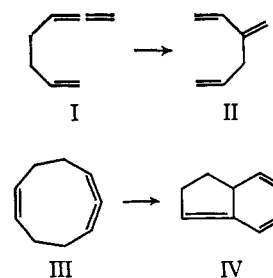
Sir:

The Cope rearrangement² of 1,5-dienes is one of the better known examples of valence isomerization. The unimolecular reaction is relatively insensitive to changes in solvent or to catalysis and consequently occurs with facility in both gas phase and solution. Although the Cope rearrangement is predicted to proceed with thermal

(1) This research was supported by the National Aeronautics and Space Administration.

(2) A. C. Cope and E. M. Hardy, *J. Amer. Chem. Soc.*, **62**, 441 (1940); review on thermal isomerizations: W. von E. Doering and W. R. Roth, *Angew. Chem. Intern. Ed. Engl.*, **2**, 115 (1963).

and with photochemical activation, only the thermal mode has been thoroughly documented by experiment.³ Two specific examples of the thermal Cope rearrangement are the isomerizations of 1,2,6-heptatriene (I) and 1,2,6-cyclononatriene (III).⁴



We have observed that the benzene-sensitized photolysis (2537 Å) of I in the vapor phase⁵ gives 3-methylene-1,5-hexadiene (II),⁶ identical with the products of pyrolysis. At low intensity and very short irradiation time, II is the only product formed, and a plot of per cent conversion *vs.* time gives a straight line with zero intercept. The quantum yield for the formation of II is 0.24 based on a benzene-*cis*-butene actinometer.^{7,8} When II is irradiated under identical conditions several isomeric products are formed; these same compounds appear when the triene I is photolyzed to higher conversion (>0.2%).⁹ The photorearrangement is not reversible; the photolysis of II does not yield I. Compound II is formed as a major photoproduct of the direct vacuum ultraviolet photolysis¹⁰ of I along with

(3) A referee has called our attention to a report of the photorearrangements of 1-cyano-1,5-dienes which give the Cope product, accompanied in some cases by other products of allyl rearrangements: R. C. Cookson, V. N. Gogte, J. Hudec, and N. A. Mirza, *Tetrahedron Letters*, 3955 (1965).

(4) E. Vogel, W. Grimme, and E. Dinne, *Angew. Chem.*, **75**, 1103 (1963); L. Skattebøl and S. Solomon, *J. Amer. Chem. Soc.*, **87**, 4506 (1965).

(5) All 2537-Å photolyses were done in a cylindrical Vycor cell at ambient temperature (21–23°), with triene/benzene ≈ 7, and total pressures of 10–20 torr.

(6) Identification of the photoproducts was made on the basis of retention times and mass spectra, which are identical with those of authentic materials (obtained by the thermal rearrangement of I and III). Retention times relative to benzene: 10% Ucon 50H (50°), 0.87; 15% TCEP (50°), 0.53; 15% squalane (50°), 1.4. The pyrolysis products were identified by their nmr and ir spectra.⁴

(7) M. Tanaka, M. Kato, and C. Sato, *Bull. Chem. Soc. Japan*, **39**, 1423 (1966).

(8) The Cundall technique (photosensitized olefin isomerization) has been criticized as a general method for determining the quantum yield for triplet formation (E. K. C. Lee, H. O. Denschlag, and G. A. Haninger, *J. Chem. Phys.*, **48**, 4547 (1968); W. A. Noyes, Jr., and C. S. Burton, *Ber. Bunsenges. Phys. Chem.*, **72**, 146 (1968)). The uncertainties that give rise to these criticisms do not affect the utility of the benzene-*cis*-butene system as a very convenient way to measure the amount of light absorbed by benzene in the photosensitized triene rearrangements. All that is required is to replace the triene with *cis*-butene (at a pressure known to completely quench ³B_{1u} benzene), keeping all other parameters unchanged and consonant with those used by Tanaka,⁷ and to measure the amount of *trans*-butene formed at low conversions. This method does not require that the energy transfer to the trienes I or III necessarily be from the ³B_{1u} state, although this appears to be the most likely process. The transfer from ¹B_{2u} to the trienes II and IV (which contain a 1,3-diene system) may well contribute to the very efficient secondary photolyses (A. Morikawa and R. J. Cvetanović, *Can. J. Chem.*, **46**, 1813 (1968)).

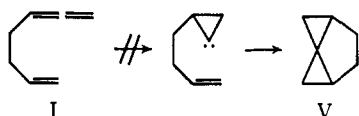
(9) Direct photolysis of II in solution gives a single product, 1-(prop-2-enyl)cyclobut-1-ene: J. L. Charlton, P. deMayo, and L. Skattebøl, *Tetrahedron Letters*, 4679 (1965).

(10) The vacuum ultraviolet lamp and wavelength distribution are described in J. S. Wishnok, Ph.D. Thesis, Brown University, 1968.

numerous minor products and a considerable amount of polymer.

The photochemistry of III is less complex and less efficient. Both the benzene-sensitized and the vacuum ultraviolet photolyses yield IV¹¹ as a primary product.⁶ Compound IV can itself be photoisomerized, but does not revert to III. The quantum yield for the benzene-sensitized conversion of III \rightarrow IV is 0.02.

We recently reported¹² that the benzene-sensitized photolysis of 1,2-cyclononadiene yields tricyclo[2.2.0.0^{2,9}]nonane. A mechanism involving the closing of the allene to a cyclopropylidene and subsequent transannular insertion into a C-H bond was proposed. If triene I followed the same reaction pathway, the expected product, resulting from the addition of the cyclopropylidene to the terminal double bond, would be tricyclo[4.1.0.0^{4,6}]heptane (V). By comparison of



the spectra and chromatographic properties of an authentic sample¹³ of V with those of the photoproducts, we have established that V is not formed in either the benzene-sensitized or the vacuum ultraviolet photolyses of I. Clearly the photo-Cope rearrangement of the 1,5-diene system takes precedence over the allene \rightarrow cyclopropylidene mutation when both are possible.

The most reasonable mechanism for these photochemical rearrangements is the concerted intramolecular process by which the thermal Cope rearrangements are known to proceed. A four-center chair-like transition state for the thermal Cope has been demonstrated by a classic experiment¹⁴ and ratified by orbital symmetry considerations.¹⁵ The six-center boat-like transition state should be preferred by an excited-state reactant and may also be available to sterically stressed systems in thermal rearrangements.¹⁵ Both conformations are available to I, while III can comfortably assume the six-center transition state, but appears from models to be severely strained in the four-center arrangement.¹⁶ However, the ease of reaching the thermally preferred four-center conformation does not fully control the reaction rates in this system. Vapor-phase pyrolyses in a flow system with short contact time show that III \rightarrow IV is more facile than I \rightarrow II, at least at temperatures above 300°. (At 340°, (III \rightarrow IV)/(I \rightarrow II) = 1.5.)

Although it is not yet possible to choose between the reasonable alternatives for the electronic state of the

triene leading to rearrangement (the first excited singlet, the lowest triplet, or a vibrationally excited ground electronic state), it is interesting to note that the photochemical isomerization shows the reverse proclivity ((III \rightarrow IV)/(I \rightarrow II) = 0.1) of the thermal process.

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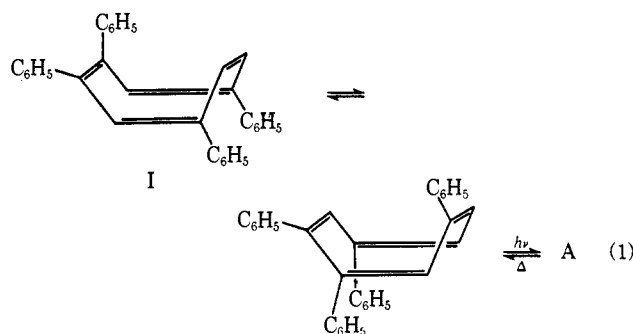
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A Probable *trans*-Cyclooctatetraene

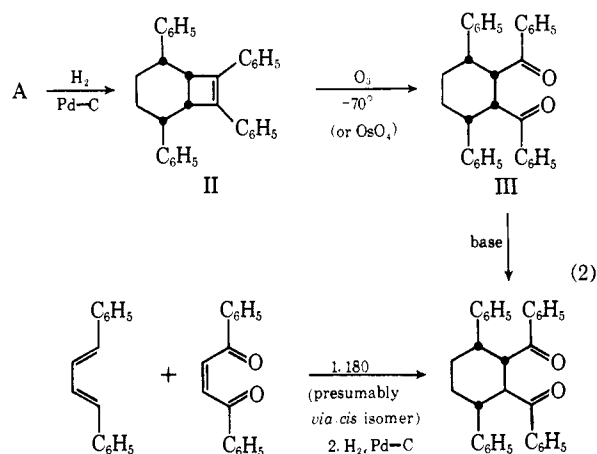
Sir:

The irradiation of 1,2,4,7-tetraphenylcyclooctatetraene (I)¹ in hexane yields a photoisomer (A), mp 121–



122° dec, to which we assign structure VII.² The photoisomer reverts quantitatively to cyclooctatetraene (I) very slowly in the solid state and with a half-life of 18 hr in solution at 25° (first-order rate constant).

Hydrogenation of isomer A yielded only a tetrahydro derivative, assigned structure II. The ultraviolet spec-



(11) Retention times relative to benzene: 10% Carbowax 20M (70°), 2.7, 15% squalane (80°), 6.0, 15% TCEP (80°), 1.6.

(12) H. R. Ward and E. Karafiath, *J. Amer. Chem. Soc.*, **90**, 2193 (1968).

(13) L. Skattebøl, *Chem. Ind. (London)*, 2146 (1962).

(14) W. von E. Doering and W. R. Roth, *Tetrahedron*, **10**, 67 (1962).

(15) R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, **87**, 4389 (1965).

(16) If III could be obtained as a single enantiomeric form whose configuration could be related to that of the product IV, then it would be possible to distinguish between the two reaction routes (provided that neither III or IV racemizes prior to or after the rearrangement). The formidable difficulties inherent in meeting these conditions have discouraged us from attempting these experiments.

(1) (a) E. H. White and H. C. Dunathan, *J. Am. Chem. Soc.*, **86**, 453 (1964); (b) E. H. White and R. L. Stern, *Tetrahedron Letters*, 193 (1964).

(2) Because of its lability, the photoisomer could not be freed of solvent; e.g., when recrystallized from a toluene-hexane mixture, analysis gave C 93.46, and H 6.19 (*Anal.* calcd for C₃₂H₂₄: C, 94.08; H, 5.92); when recrystallized from ethyl ether, C 92.82, H 6.19 (*Anal.* calcd for C₃₂H₂₄·0.25C₄H₁₀O: C, 92.81; H, 6.25). The molecular weight by two methods on four trials averaged 450 (theory 408). Correct analyses were obtained for all other compounds, and molecular weights were determined for key compounds.