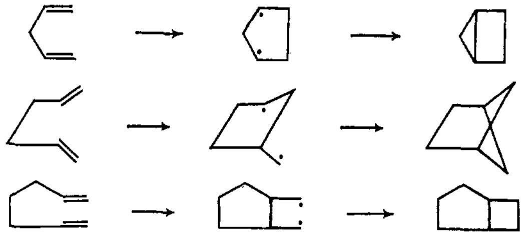
molecular isomerization of a molecule in a thermal system. In the latter case, with increasing complexity of the molecule, at any given pressure, the rate of unimolecular isomerization will correspond more nearly to its value at infinite pressure. In the present case, since the system involves the stabilization of a "hot" molecule, an increase in the complexity of the molecule at a given pressure reduces its isomerization (to a cyclopropyl compound) rate more nearly to zero which would be its value at infinite pressure. Thus, both 2-methyl-1,4-pentadiene and 1,5-hexadiene, which are isomers, give the same yield of cyclopropyl products. Both 2-methyl-1,5-hexadiene and 1,6-heptadiene, which form another isomeric pair, give very little cyclopropyl products at 1 atm, although at lower pressures they do isomerize to such compounds to a significant extent.[14,15]

Perhaps the most interesting result of this work is the change in the stereochemistry of the cycloaddition reaction as the chain length increases. Cross addition to parallel addition is seen to be highly selective in the pentadienes, a feature which is more emphasized by methyl substitution. In the hexadienes the importance of the two modes inverts itself and becomes less selective, although in 1,5-cyclooctadiene the process is very selective. In 1,6-heptadiene the process inverts its importance once again and is also quite selective. These results can be explained by assuming that the cycloaddition is a two-step process and that the initial step is the formation of a five-membered ring. These reactions can be written as follows.



(13)

(14)

(15)

The formation of the alternative cycloadducts cannot go through similar five-membered rings. This hypothesis can be tested by the examination of other systems which incorporate these dienes as well as by placing substituent(s) at the unsaturated carbons to see if the intermediates in steps 13–15 allow free rotation at the radical sites. Such investigations are now in progress.

Acknowledgment. The assistance of Mr. Fred W. Hetzel of Ohio State University in recording the nmr spectra is gratefully acknowledged.

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(15) R. Srinivasan, unpublished work.

Photosensitized Internal Addition of Dienes to Olefins

Robert S. H. Liu[1] and George S. Hammond

Contribution No. 1331 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898, and Contribution No. 3481 from The Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California. Received May 4, 1967

Abstract: When irradiated in the presence of photosensitizers, myrcene cyclizes to give 5,5-dimethyl-1-vinylbicyclo[2.1.1]hexane (**1**). 3-Methylene-1,5-hexadiene, 3-methylene-1,6-heptadiene, and 6-methyl-3-methylene-1,5-heptadiene cyclize under similar conditions to the corresponding bicyclo[2.1.1]hexanes. The geometric isomers of 3-methylene-1,5-heptadiene give identical mixtures of 5-methyl-2-methylenebicyclo[2.1.1]hexanes. The result indicates that cyclization involves formation of long-lived diradical intermediates. Preferential cyclization by way of intermediates containing five-membered rings is noted and discussed.

Conjugated dienes dimerize efficiently when irradiated in the presence of photosensitizers.[2,3] Cross-additions between dienes under similar conditions have also been reported.[4,5] Scattered reports have also appeared on the intermolecular cycloaddition of diene triplets to olefins.[6,7] Although the reactions often lead to fairly complex product mixtures, some selectivity is normally observed. For example, in the dimerization of butadiene, 1,3-disubstituted cyclobutanes were not observed.[2] Examination of the product structures has led to the hypothesis that exclusion of certain products is a result of selective formation of diradical intermediates.[2,6,8]

There is also a commonly held opinion that addition of a triplet to a singlet *must* involve formation of an intermediate.[9] This premise is usually known as "the Wigner spin-conservation rule" and states that processes involving changes in the multiplicity of systems will be relatively slow.[10] Application to addition reactions of the type under discussion leads to formulation of the spin inversion that *must* occur at some stage as a

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(1) To whom inquiries should be addressed, E. I. du Pont de Nemours and Co., Wilmington, Del.

(2) G. S. Hammond, N. J. Turro, and R. S. H. Liu, *J. Org. Chem.*, **28**, 3297 (1963).

(3) D. Valentine, N. J. Turro, and G. S. Hammond, *J. Am. Chem. Soc.*, 86, 5202 (1964).

(4) G. Sartori, V. Turba, A. Valvasson, and M. Riva, *Tetrahedron Letters*, 211, 4777 (1966).

(5) R. S. H. Liu, C. D. DeBoer, and G. S. Hammond, manuscript in preparation.

(6) N. J. Turro and P. D. Bartlett, *J. Org. Chem.*, **30**, 1849 (1965).

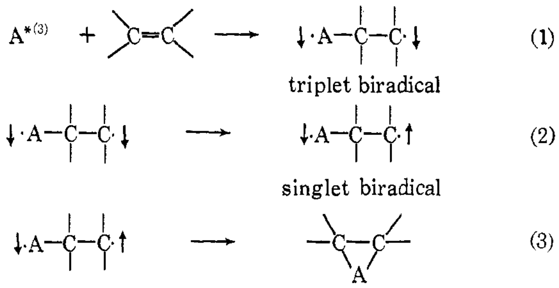
(7) R. S. H. Liu and G. S. Hammond, *J. Am. Chem. Soc.*, 86, 1892 (1964).

(8) G. S. Hammond and N. J. Turro, *Science*, **142**, 1547 (1963).

(9) See, for example, P. S. Skell and R. C. Woodworth, *J. Am. Chem. Soc.*, 78, 4496 (1956).

(10) K. J. Laidler, "Chemical Kinetics," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1965, pp 166–167.

separate step, independent of bond-making and bond-breaking reactions.



Results of stereochemical studies generally tend to be consistent with the implications of the Wigner rule. However, theoretical justification is far from quantitatively rigorous. The rate constants for addition of butadiene triplets to diene ground-state molecules are probably no greater than 10^6 l. mole^{-1} sec^{-1},[11] and activation energies for such steps are very small.[12] Obviously the preexponential factors in the rate constants are small enough to be easily compatible with incorporation of spin inversion in the rate-limiting step. Consequently, there is good reason to seek direct evidence for the intervention of an intermediate having a finite lifetime.

A rather obvious stereochemical approach to the problem is inapplicable to the study of diene dimerization because the substrates undergo concurrent *cis–trans* isomerization. In this paper, we wish to report a study of photosensitized cycloaddition reactions[7,13] in which there is no competitive photoisomerization of the unsaturated unit to which the diene triplet is added.

Results

To avoid dimerization reactions, we found it necessary to carry out the photosensitized cyclization reactions with solutions containing 2%, or less, of the trienes. The nature of the product is, in general, insensitive toward variation of sensitizer and solvent. In preparative runs, we have, therefore, adopted the general procedure of irradiating a 2% ether solution of triene with β-acetonaphthone as sensitizer.

3-Methylene-7-methyl-1,6-octadiene (Myrcene). When myrcene is irradiated in the presence of a variety of photosensitizers (acetophenone, benzophenone, triphenylene, β-acetonaphthone, benzil, 9-fluorenone), the formation of a single new product is observed. The reaction proceeds with reasonable efficiency with all the sensitizers used. With benzophenone as sensitizer, the quantum yield for the reaction has been determined to be 0.023. The photoproduct can easily be isolated and purified by fractional distillation under vacuum or by preparative gas chromatography method. For reasons outlined below, the product has been assigned the structure 5,5-dimethyl-1-vinylbicyclo[2.1.1]hexane (**1**).

Elemental analyses and molecular weight measurements show that **1** is an isomer of myrcene. Its structure is clearly indicated by the nmr spectrum (Figure 1a). The low-field signals are multiplets of ABC patterns and are characteristic of a vinyl group (relative area 3). The two high-field singlets (0.75 and 1.14 ppm) have relative areas of 3 each, obviously belonging to two isolated methyl groups. The chemical shifts are virtually identical with those of the corresponding methyl groups in **2** (0.70 and 1.11 ppm).[14] The doublet centered at 0.97 ppm (J = 8.0 cps) corresponds to one proton. This high-field signal for one proton is most unusual but is also most indicative of the structure. Structures **1** and **1a** are the only ones resulting from internal cyclization of myrcene which retain intact vinyl groups.

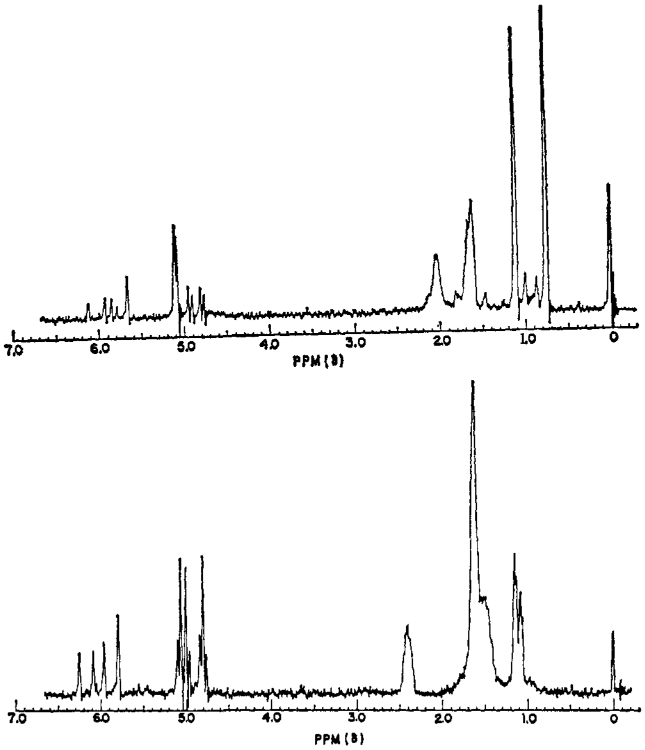
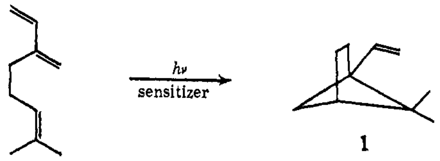
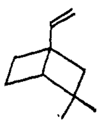


Figure 1. 60-Mc nmr spectra (in carbon tetrachloride with TMS as internal standard) of (a) 5,5-dimethyl-1-vinylbicyclo[2.1.1]hexane (**1**) (upper) and (b) 1-vinylbicyclo[2.1.1]hexane (**13**) (lower).



1

2



1a

There is no precedent for the expectation that either of the single protons in **1a** would absorb at exceptionally high field. On the other hand, the spectra of bicyclo[2.1.1]hexane[15] and its derivatives[16] show high-field signals attributed to the *endo* protons on methano bridges. One such proton is present in **1**. Absorptions of the ethano-bridge protons appear as the distorted

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(11) R. S. H. Liu, N. J. Turro, and G. S. Hammond, *J. Am. Chem. Soc.*, 87, 3406 (1965).

(12) G. F. Vesley and G. S. Hammond, unpublished observations.

(13) R. S. H. Liu, *Tetrahedron Letters*, 2159 (1966).

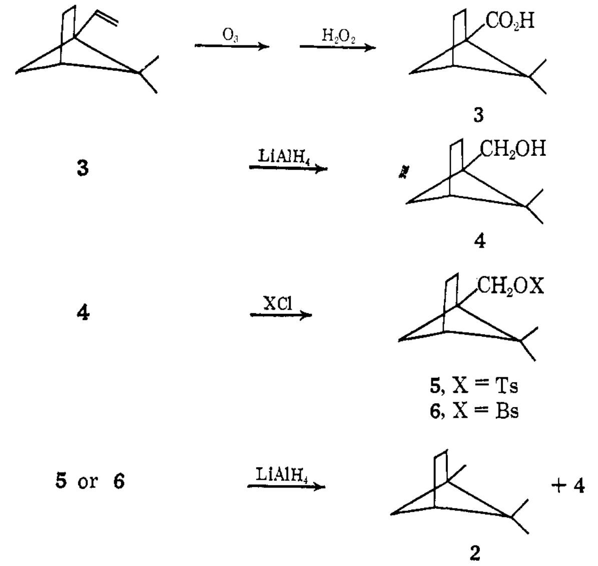
(14) R. Srinivasan, *J. Am. Chem. Soc.*, 83, 4923 (1961).

(15) R. Srinivasan, *ibid.*, 85, 819 (1963).

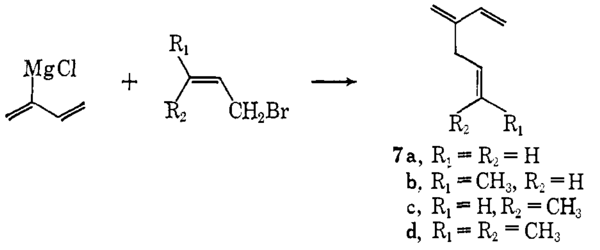
(16) See ref 7 and J. Meinwald and A. Lewis, *ibid.*, 83, 2769 (1961); J. Meinwald and R. A. Schneider, *ibid.*, 88, 5218 (1966); T. Thomas and W. F. Erman, *J. Org. Chem.*, 31, 3028 (1966).

A_2B_2 group centered at 1.62 ppm. The remaining high-field absorption must include the protons at the bridgeheads and the *exo* position on the methano bridge.

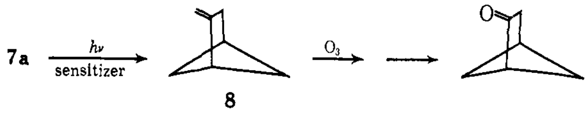
The assignment is confirmed by chemical degradation of the photoproduct. Ozonolysis of **1** with oxidative work-up yielded a low-melting solid. The spectra of the acidic product are consistent with those expected of **3**, which has been prepared recently by oxidation of 5,5-dimethylbicyclo[2.1.1]hexane-1-carboxaldehyde.[17] The acid was further reduced by lithium aluminum hydride to give another low-melting solid with a strong camphor-like odor. Its spectroscopic data agree with the structure **4**. From alcohol **4** both the tosylate, **5**, and brosylate, **6**, were prepared. Reaction of **5** or **6** with lithium aluminum hydride followed by hydrolysis gave a mixture of two compounds in a ratio of 5:1. The minor product is identical with **4**. The nmr spectrum of the major product agrees with that reported for **2**.[14]



3-Methylene-1,5-hexadiene (7a). The triene was prepared by reaction of 2-butadienylmagnesium chloride[18] with allyl bromide. The product had spectra identical with those reported for **7a**.[19]

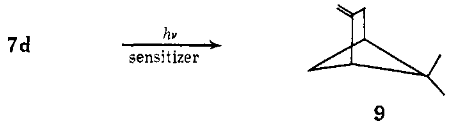


Irradiation in the presence of a variety of photosensitizers converts the triene quantitatively to a single product, **8**. Although the quantum yield was not determined, the reaction appears to proceed with efficiency comparable to that of the myrcene reaction. Analyses and molecular weight determination indicate that the photoproduct is isomeric with **7a**. The nmr spectrum of **8** (Figure 2a) is consistent with the structure 2-methylenebicyclo[2.1.1]hexane. The high-field quartet (integrated area 2) is assigned to the two *endo*-methano-bridge protons and the multiplets centered at 1.80 and 2.17 ppm (2 H each), to the *exo*-methano-bridge and allylic methylene protons, respectively. The two multiplets, centered at 2.54 and 2.89 ppm (1 H each), are coupled to each other (J = 7.0 cps). These are due to the two bridgehead protons. The alternative structure, also possessing two vinyl protons, is 2-methylenebicyclo[2.2.0]hexane. However, none of the protons in **8a** should give signals at field as high as 1.15 ppm; furthermore, because of the lack of symmetry, a more complicated spectrum would be expected. On oxidative ozonization, **8** yielded a ketone having an infrared spectrum identical with that reported for bicyclo[2.1.1]hexan-2-one.[20]



This cyclization reaction has also been reported by Charlton, De Mayo, and Skattebol.[21] They have carried out a more extensive degradative structure proof leading to the assignment of the same structure to **8**.

5-Methylene-6-methyl-1,5-heptadiene (7d). The triene was prepared by reaction of 2-butadienylmagnesium chloride with 1-bromo-3-methyl-2-butene. When irradiated in the presence of a sensitizer, the triene is converted quantitatively to an isomer, which is believed to have the structure **9**. Its nmr spectrum is shown in Figure 2b. The high-field signals closely resemble those of **1**. Therefore, the two singlets at 0.78 and 1.28 ppm are probably due to the *endo*- and *exo*-methyl groups and the high-field doublet is due to the *endo*-methylene proton. The remaining signals are also in agreement with the structure 5,5-dimethyl-2-methylenebicyclo[2.1.1]hexane.



***trans*- and *cis*-3-Methylene-1,5-heptadienes (7b and 7c).** A mixture of trienes obtained from the reaction of butadienylmagnesium chloride with an isomeric mixture of 1-bromo-2-butene contains 75% *trans* isomer and 25% *cis*. The isomers could be separated only by preparative vapor chromatography, and even then with some difficulties. The purest samples that we obtained were 98% *trans* and 85% *cis;* in each case the impurity was the isomeric triene. These samples were used in mechanistic studies.

Upon photosensitized irradiation, each of the isomeric trienes gives two new products. The composition of the product mixture appears to be independent of the composition of the starting triene mixture, so the original 75:25 mixture was used in preparative runs. The two products, **10** and **11**, were formed in a ratio of 5.8 to 1 and were separated by preparative gas chromatography. Their nmr spectra are shown in Figures

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[17] K. Ebisu, L. B. Batty, J. M. Higaki, and H. U. Larson, *J. Am. Chem. Soc.*, **88**, 1995 (1966).

[18] C. Aufdermarsh, *J. Org. Chem.*, **29**, 1994 (1964). Isochloroprene, for the preparation of the Grignard, was generously supplied by Dr. C. Aufdermarsh.

[19] L. Skattebøl, *J. Am. Chem. Soc.*, **87**, 4506 (1965).

[20] F. T. Bond, H. L. Jones, and L. Scerbo, *Tetrahedron Letters*, 4685 (1965).

[21] J. L. Charlton, P. De Mayo, and L. Skattebøl, *ibid.*, 4679 (1965).

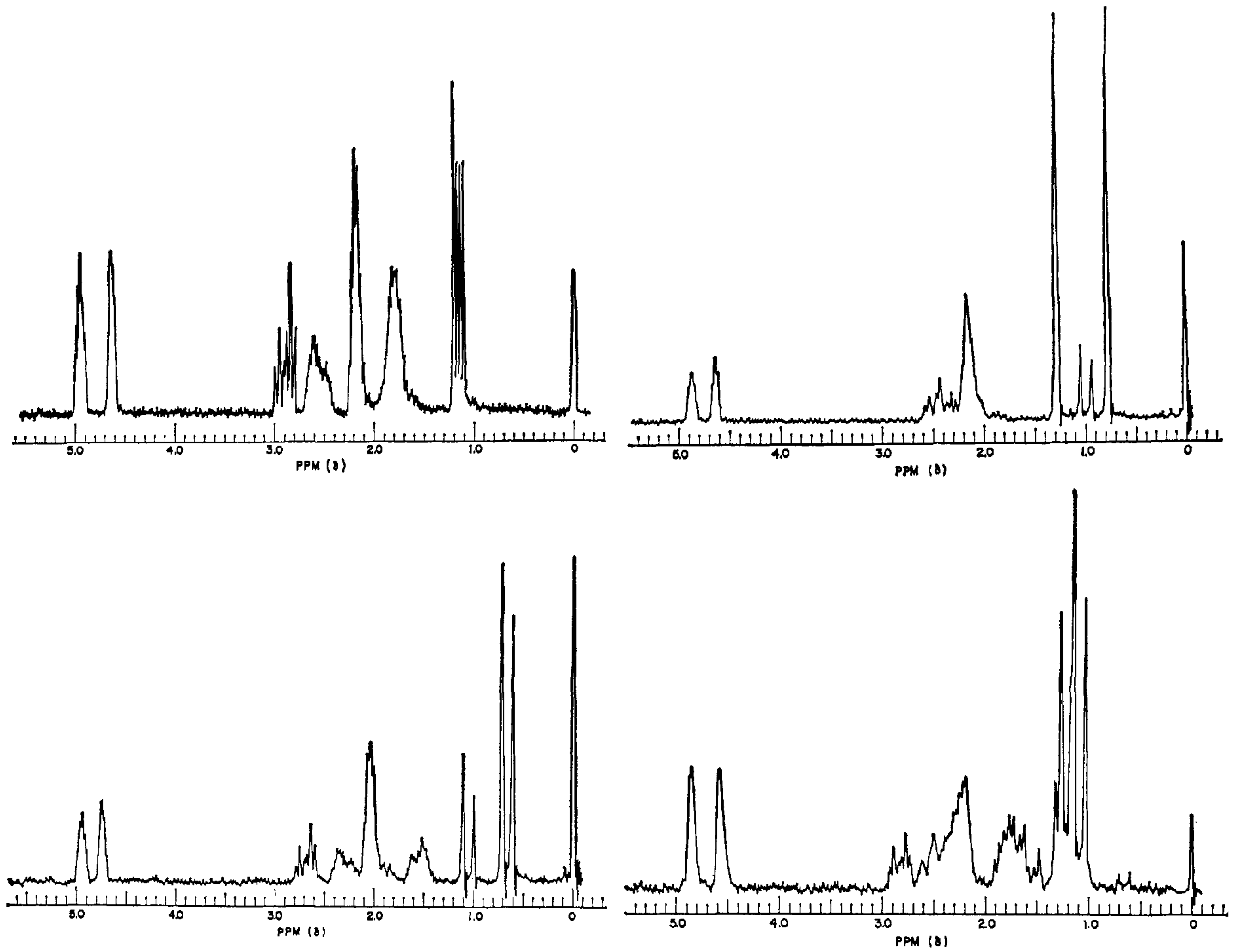
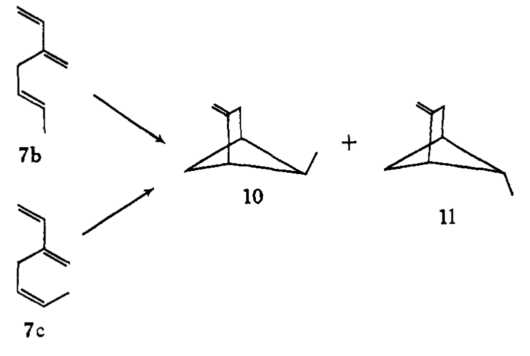


Figure 2. 60-Mc nmr spectra (solvent, CCl_4 with tetramethylsilane as internal standard) of (a) 2-methylenebicyclo[2.1.1]hexane (**8**) (upper left), (b) 5,5-dimethyl-2-methylenebicyclo[2.1.1]hexane (**9**) (upper right), (c) 5-*endo*-methyl-2-methylenebicyclo[2.1.1]hexane (**10**) (lower left), and (d) 5-*exo*-methyl-2-methylenebicyclo[2.1.1]hexane (**11**) (lower right).

2c and 2d. Comparison with the spectra of compounds **8** and **9** indicates immediately that the products are the two isomeric 5-methyl-2-methylenebicyclo[2.1.1]-hexanes, with the *endo* isomer being the major product. The spectrum of **10** shows the characteristic high-field *endo*-methyl group (doublet at 0.65 ppm) and the high-field *endo*-methano-bridge proton (doublet at 1.05 ppm). The nmr spectrum of **11** is expectedly more complex with the signal of the methyl group overlapping those of the high-field *endo*-methano-bridge protons.



We have made a study of the distribution of the products **10** and **11** as a function of relative concentration of the two trienes. Results are summarized in Table I. Obviously, the two isomeric trienes do not interconvert during irradiation. The data also indicate that there is no measurable selectivity in the competition between **7b** and **7c** as energy acceptors. Furthermore, there was no noticeable variation in the initial rates of reaction with mixtures of different initial composition, implying equivalence of efficiencies of cyclization of triplets derived from the isomeric starting materials.

Table I. Relative Amounts of Reactants and Products during Sensitized Irradiation[a]

Conversion	Percentage of		Percentage of	
%	**7b**	**7c**	**10**	**11**
0	97	2.9	..	..
45	98	2.4	86	14
84	*b*		85	15
100	..	...	86	14
0	13	87	..	..
50	13	87	85	15
54	13	87	85	15
100	..	...	86	14

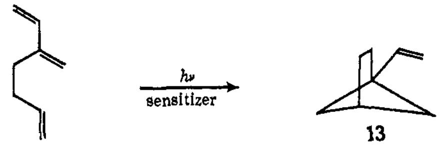
[a] Degassed methanol solution of 2% triene with triphenylene as sensitizer, irradiated with AH-3 lamp with Pyrex vessels. [b] Concentration of **7c** too low for accurate measurements.

Direct irradiation of dilute solutions of trienes **7b** and **7c** leads to formation of two major products, which together account for 89% of the product mixture. Both products, however, have gas chromatographic retention times different from those of the products from the sensitized reactions. Four minor products are also formed, two of which have retention times identical with **10** and **11**. However, the **10**:**11** ratio is distinctly different from that observed in the sensitized reaction (see Table II).

Table II. Relative Amounts of Products from Irradiation

Condition	Starting triene mixture **7b**:**7c**	**10**:**11**
Sensitized	97:2.9	5.8
Sensitized	13:87	5.8
Direct	97:2.9	2.3
Direct	13:78	1.4

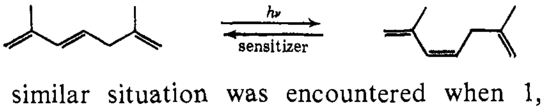
3-Methylene-1,6-heptadiene (12). The triene was prepared by reaction of vinylmagnesium bromide with 1-hexen-5-one followed by dehydration of the alcohol over potassium acid sulfate. When irradiated in the presence of benzophenone, the triene is converted quantitatively to an isomeric olefin. The nmr spectrum of the product (Figure 1b) is consistent with the structure 1-vinylbicyclo[2.1.1]hexane (**13**). The high-field quartet (relative area 2) is assigned to the *endo*-methano-bridge protons. The singlet at 1.63 ppm together with the band at 1.52 ppm accounts for the four ethano-bridge and the two *exo*-methano-bridge protons. The bridgehead proton appears at 2.40 ppm. The low-field signals are typical of a vinyl group. The infrared spectrum, molecular weight, and elemental analysis are consistent with the assigned structure. The quantum yield of the reaction was found to be 0.021.



13

12

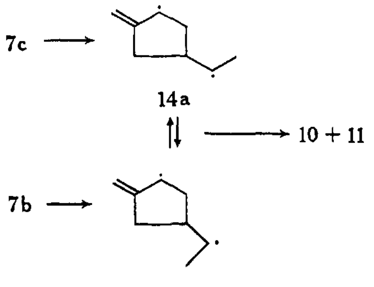
Other Trienes. Several other trienes were studied under similar conditions. When *trans*-2,6-dimethyl-1,3,6-heptatriene was irradiated in the presence of a photosensitizer, rapid formation of a new product was detected. However, the system appeared to reach a photostationary state after irradiation for 1 day, and no other new products could be detected even if irradiation was continued for 1 week. The new product was isolated by preparative vapor chromatography. It was shown to be *cis*-2,6-dimethyl-1,3,6-heptatriene. Therefore, sensitized irradiation in this case leads only to the establishment of a photostationary state containing approximately equal amounts of the two geometric isomers.



A similar situation was encountered when 1,3,6-heptatriene was irradiated. A photostationary mixture of stereoisomers resulted without formation of any new product. In the case of 5-methyl-1,3,6-heptatriene, *cis–trans* isomerization was observed and, in addition, two new products were formed in amounts too small to encourage attempts to isolate them.

Discussion

The Biradical Intermediate. The identity of the product mixtures formed from the two isomers of 3-methylene-1,6-heptadiene is presumptive evidence that cyclization of the two compounds involves formation of a common intermediate. Therefore, the reaction probably involves the initial cyclization at 1,5 positions of the two trienes to give a rapidly interconverting mixture of the stereoisomeric biradicals, **14a** and **14b**. The results indicate that rotation is more rapid than cyclization.



14b

Although the result is inherently reasonable, complete stereochemical equilibration of the intermediate biradical is actually exceptional in comparison with formally analogous cases. Biradicals have often been suggested as intermediates in nonstereospecific cycloaddition[22,23] and in ring-contraction[24,25] reactions. However, it has usually been necessary to postulate incomplete rotational equilibration of intermediates. There are two obvious reasons for expecting the intermediates in the present cases to have relatively slow rates of cyclization. First, the Wigner hypothesis suggests that the biradicals should inherit triplet character because of the spin characteristics of their precursors. It is quite possible that the time required to effect spin inversion is long compared with the time required for rotation about single bonds. This effect alone could be sufficient to account for the difference between reactions in which four-membered rings are formed by thermal[22] and photochemical reactions. However, cyclization of triplet biradicals to form three-membered rings appears to be competitive with rotation rates.[23–25] There is also a classical stereochemical reason for anticipating that the rates of ring closure of **14a** and **14b** will be slow compared with rates of cyclization of acyclic 1,4-biradicals; to bring the spin centers close enough to permit bond formation must involve development of some of the exceptional ring strain found in the [2.1.1]bicyclohexane system.

Preference for Formation of Five-Membered Rings. Remarkably high selectivity is shown in these photocyclization reactions. Thus far, we have found only products that would be derived from *biradicals contain-*

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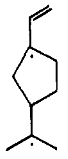
[22] L. K. Montgomery, K. Schueller, and P. D. Bartlett, *J. Am. Chem. Soc.*, 86, 622 (1964), and earlier papers in the series.

[23] K. Kopecky, P. Leermakers, and G. S. Hammond, *ibid.*, 84, 1015 (1962).

[24] P. Scheiner, *ibid.*, 88, 4759 (1966).

[25] C. D. DeBoer, unpublished results.

ing five-membered rings. Competition with other possible first steps seems to be insensitive to the relative stabilities of the various possible intermediates. Each of the cyclizations observed could have taken other courses in which six-membered rings are formed initially. In general, one expects the latter to be more stable than the cyclopentane derivatives.[26] In the specific case of the intermediates formed from myrcene, one might be able to muster a rationalization of the view that **15** is more stable than **16** since the allylic radical unit in **15** has one tertiary terminal whereas **16** has one secondary and one primary end, but no such rationalization can account for the fact that cyclization of 3-methylene-1,6-heptadiene (**12**) takes the same course despite the fact that the intermediate biradical, **17**, would contain an unconjugated, primary spin center.



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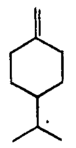

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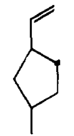
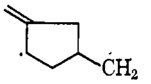
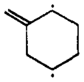


17

The same preference with respect to ring size of the intermediate can be seen in the cyclization of 3-methylene-1,5-hexadiene (**7a**) and its homologs. On any grounds that we can think of, **19**, the precursor to 2-methylenebicyclo[2.2.0]hexane, should be more stable than **18**, the probable precursor to the observed product.



18



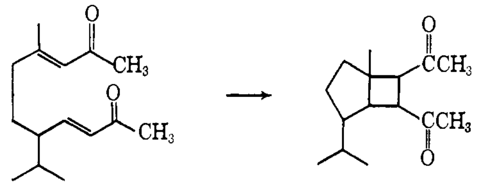
19

Intermediates such as **15** and **17** could conceivably be formed reversibly so that the failure of the mechanism occurs in the second step. Two lines of evidence argue against this view, although the evidence is not unequivocal. First, the failure of **7b** and **7c** to be interconverted during cyclization indicates that **14a** and **14b** do not revert to acyclic trienes. Furthermore, some of the intermediates containing six-membered rings can potentially undergo ring-opening to structural isomers of the starting materials. For example, **19** could open to give 1,2,6-heptatriene. Such isomerization reactions are not observed.[27]

The selectivity probably reflects kinetic control of the first addition step. The triplet states of conjugated dienes are endowed with large amounts of excitation energy.[11] Consequently, the course of chemical reactions of such species is controlled by the relative probabilities of various paths for conversion of the electronic excitation to other forms of energy.[28] The preference for formation of five-membered rings may merely reflect the fact that the carbon atoms that become bonded are, on the average, closer together than those that would have to interact to form a six-membered ring.

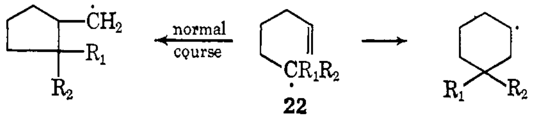
Preferential reaction by way of five-membered rings may also be indicated by the reported course of photocyclization of the unsaturated ketones **20**[19] and **21**;[29] other examples are also known.[30] A less clear-cut preference is shown in intramolecular oxetane formation.[31]

20



21

The common tendency of 5-hexenyl free radicals to cyclize to cyclopentylmethyl radicals[32–37] is probably a closely related phenomenon and again indicates that kinetic factors of geometric origin are probably a dominant influence on the course of reaction. Only with highly substituted systems ($R_1 = CO_2R$; $R_2 = CN$ in **22**) does product stability exert a sufficiently strong influence on the course of internal addition to make cyclohexyl radicals the principal products.[38]



22

Comparison with Direct Excitation. Crowley first reported that direct irradiation of myrcene gives at least seven products.[39] Two major products were identified, and a third product was shown by Dauben's group[40] to be identical with the product of the sensitized reaction. Only a cyclobutene derivative is reported to be formed by direct irradiation of 3-methylene-1,5-hexadiene.[21] The contrast between direct and sensitized reactions is striking and indicates that there may be significant differences between the chemical properties of excited singlets and triplets.[41] It also indicates that intersystem crossing from the lowest excited

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(26) J. D. Roberts and M. C. Caserio, "Basic Principles of Organic Chemistry," W. A. Benjamin, Inc., New York, N. Y., 1964, p 112.

(27) Additional negative evidence can be adduced from the failure to observe formation of new products when the reaction is carried out at low temperatures. We are grateful to Professor P. De Mayo for communication of these unpublished results.

(28) Discussion of the view that photochemical reactions are special cases of the internal conversion process will be developed elsewhere in more detail.

(29) M. Brown, *Chem. Commun.*, 340 (1965).

(30) W. L. Dilling, *Chem. Rev.*, **66**, 355 (1966).

(31) N. C. Yang, M. Nussim, and D. R. Coulson, *Tetrahedron Letters*, 1525 (1965).

(32) R. C. Lamb, P. W. Agers, and W. K. Toney, *J. Am. Chem. Soc.*, **85**, 3483 (1963).

(33) C. Walling and M. S. Pearson, *ibid.*, **86**, 2262 (1964).

(34) H. Pines, N. Sih, and D. B. Rosenfield, *J. Org. Chem.*, **31**, 2255 (1966).

(35) N. O. Brace, *ibid.*, **31**, 2879 (1966).

(36) Photochemical cyclization of 1,5-hexadiene and 1,5-cyclooctadiene are probably examples of photoinitiated radical chain reactions.[37]

(37) R. Srinivasan, *J. Am. Chem. Soc.*, **88**, 5084 (1966), and literature cited therein.

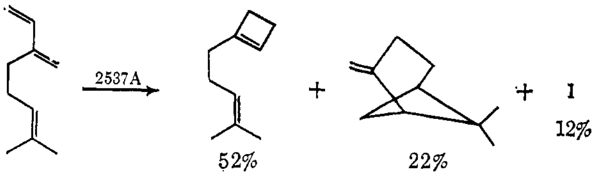
(38) M. Julia and O. Maumy, *Bull. Soc. Chim. France*, 434 (1966).

(39) K. J. Crowley, *Proc. Chem. Soc.*, 245, 334 (1962).

(40) W. G. Dauben, R. L. Cargill, R. M. Coates, and J. Saltiel, *J. Am. Chem. Soc.*, **88**, 2742 (1966).

(41) Cisoid conjugated dienes are known to absorb in the longer wavelengths; therefore, it is not surprising that using light of 2537 A, the product mixture consists predominantly of the cyclobutene. On the other hand, the sensitized reaction is probably predominantly a reaction of transoid triplets. We believe, however, that the comparison is meaningful, since the nature of the product in the sensitized reaction is invariant under conditions where selective population of transoid or the cisoid triplets is possible,[11] *i.e.*, independent of sensitizer.

singlet states of dienes to the triplet manifold must be inefficient.



Experimental Section

5,5-Dimethyl-1-vinylbicyclo[2.1.1]hexane. (1). The commercial sample of myrcene (Aldrich Chemical, technical grade) is only 80–85% pure, containing impurities with boiling point close to that of myrcene. However, the impurities were found not to undergo photochemical reactions. For preparative runs, the once distilled sample (90–95% pure) can be used. Initially, myrcene purified by preparative gas chromatography was used.

In a typical run, a solution of myrcene (2.8 g) and β-acetonaphthone (0.04 g) in 120 ml of ether was irradiated in a Pyrex immersion apparatus with a 200-w Hanovia medium-pressure mercury lamp for 8 hr for complete conversion. Ether was removed by distillation through a short Vigreux column; the product was distilled under vacuum. The fraction boiling at 56–57° (20 mm) was collected (2.1 g, 75% yield). The colorless liquid contains pure **1** (by gas chromatography).

Its nmr spectrum is shown in Figure 1a. The infrared spectrum showed the following absorptions: 3105, 2950, 2910, 1830, 1635, 1465, 1448, 1416, 1388, 1360, 1278, 1240, 1191, 990, 907, 887, and 694 cm^{-1}; $n^{19.2}\text{D}$ 1.4641.

Anal. Calcd for $C_{10}H_{16}$: C, 88.16; H, 11.84; mol wt, 136. Found: C, 87.96; H, 11.91; mol. wt, 136.[42]

The reaction apparently proceeded with comparable efficiency with other hydrocarbon solvents (benzene, *n*-hexane). However, when irradiation was carried out with higher concentrations of myrcene (up to 10% was attempted), side reactions, possibly dimerization, took place.

5,5-Dimethylbicyclo[2.1.1]hexane-1-carboxylic Acid (3). Ozone was passed into a methylene chloride (200 ml) solution of the photoproduct **1** (11.0 g) at −78°. At the end of reaction, the solution turned purple. Methylene chloride was removed under reduced pressure and replaced by 60 ml of ethyl acetate. To this solution 50 ml of water, 3 ml of concentrated sulfuric acid, and 22 ml of 30% hydrogen peroxide (0.2 mole) were added. The solution was refluxed overnight. Another 50 ml of water was added, and the solution was extracted with four 100-ml portions of ether. The combined ether extracts were extracted with 5% sodium hydroxide solution. Acidification of the basic extract followed by extraction with ether and evaporation of solvent yielded a colorless, viscous liquid. The crude product was sublimed, giving 2.4 g (19.3% yield) of a white, fluffy solid with melting point range 53–59°. The nmr spectrum of the solid showed[43] a group of overlapping peaks between 1.4 and 2.5, two singlets at 1.30 and 0.93, and a doublet (J = 8 cps) centered at 1.18 ppm and another low-field singlet at 10.66 ppm. These features are identical with those described for the carboxylic acid **3**.[17]

5,5-Dimethylbicyclo[2.1.1]hexane-1-methanol (4). An ether solution of the once sublimed acid **3** (3.3 g, 0.0214 mole) was added to a suspension of lithium aluminum hydride (0.76 g, 0.02 mole) in ether in a three-necked, 100-ml, round-bottomed flask at a rate so that mild reflux persisted. The solution was then refluxed for 2 hr and allowed to cool to room temperature. Water was added slowly to remove the unreacted metal hydride, followed by addition of 10% sulfuric acid. The ether layer was washed and dried. After evaporation of ether, a viscous, colorless liquid with strong camphor-like odor was obtained. On sublimation, a white, fluffy solid (1.90 g, 68%) of low melting point was obtained. The oily residue in the sublimator weighed 0.20 g; its nmr spectrum suggested that it contains a mixture of alcohols. The nmr spectrum of the solid shows singlets at 3.56, 1.17, and 0.77 ppm of relative areas 2:3:3, respectively, a doublet (J = 2.5 cps) centered at 1.08 ppm (1 H), a group of multiplets between 2.15 and 1.40 ppm (6 H), and another singlet of relative area 1, the chemical shift or which is dependent upon the concentration of the compound.

5,5-Dimethylbicyclo[2.1.1]hexane-1-methane Tosylate (5a). The tosylate was prepared by reaction of the alcohol **4** with tosyl chloride in pyridine. The tosylate is a viscous oil. Attempts to crystallize it failed.

5,5-Dimethylbicyclo[2.1.1]hexane-1-methane Brosylate (5b). The brosylate was supplied by Dr. A. Fry. It was prepared by reaction of the alcohol **4** with brosyl chloride in pyridine. When supplied the material had been recrystallized once from *n*-heptane, mp 67.2–67.7°. For analysis the brosylate was recrystallized once more from *n*-hexane.

Anal. Calcd for $C_{15}H_{19}OBrS$: C, 50.14; H, 5.33; Br, 22.24; S, 8.93. Found: C, 50.08; H, 5.31; Br, 22.29; S, 8.88.

1,5,5-Trimethylbicyclo[2.1.1]hexane (2). The tosylate **5a** was refluxed in ether with excess lithium aluminum hydride for 48 hr. After conventional work-up, a poor yield of crude product was obtained. The colorless liquid was obviously a mixture of the title hydrocarbon and the alcohol **4** in approximate ratio of 3:1 (by nmr spectroscopy). Positions of the three strong singlets (τ 8.89, 9.04, and 9.30) in the nmr spectrum are identical with the chemical shifts of the three methyl groups in **2** as reported by Srinivasan.[14] The hydrocarbon has not been isolated.

Quantum Yield Determination of the Sensitized Reaction of Myrcene. Benzene solutions of myrcene (1%) and benzophenone (0.1 *M*) in previously constricted Pyrex test tubes (13 × 100 mm) were degassed, and the tubes were sealed. Irradiation was carried out simultaneously with benzophenone–benzhydrol actinometer[44] tubes in the "merry-go-round" apparatus.[45] The reaction was allowed to reach approximately 10% conversion before the tubes were opened for analysis. Vapor phase chromatography (Apiezon J column, 6 ft, 14%, 90°) was used for analysis of samples. In calculations it was assumed that the bicyclic compound was the only product from myrcene; quantum yield found is 0.023 ± 0.01 (average value of three runs).

3-Methylene-1,5-hexadiene (7a). Butadienylmagnesium chloride was prepared as described by Aufdermarsh by reaction of 1-chloro-2,3-butadiene (58 g, 0.65 mole) with 16.0 g of magnesium turnings in 500 ml of ether. A solution of 82.0 g of allyl bromide in ether (60 ml) was then added at a rate such that mild reflux persisted. The solution was then refluxed for an additional 0.5 hr. At 0°, 200 ml of saturated NH_4Cl solution was added. The ether layer was washed with water and then dried over anhydrous sodium sulfate. The solution was concentrated to approximately 40 ml by evaporation. The colorless product mixture was fractionated by distillation through a spinning-band column. The fraction boiling at 53–54° (214 mm) was chromatographically pure and weighed 15.8 g (26% yield). Its nmr spectrum shows absorption at 2.80–3.00 (doublet, 2 H), 4 80–5.35 (multiplet, 6 H), 5.48–6.08 (multiplet, 1 H), and 6.1–6.62 ppm (quartet, 1 H). The infrared spectrum shows absorptions at 905, 990, and 1810 (terminal double bond), 1600 (conjugated double bond), and 1643 cm^{-1} (unconjugated double bond). These spectroscopic data agree with those reported for **7a**.[19]

Anal. Calcd for C_7H_{10}: C, 89.28; H, 10.72. Found: C, 88.28; H, 10.96.

3-Methylene-1,5-heptadienes (7b and 7c). A procedure similar to the preparation of **7a** was used. The 1-bromo-2-butene obtained from the Pierce Co. contained a mixture of *trans* and *cis* isomers in 70:30 ratio and was used without further purification. In a preparative run, 50 g (0.55 mole) of 1-chloro-2,3-butadiene was used to prepare butadienylmagnesium chloride, which was allowed to react with equal moles of 1-bromo-2-butene. The product mixture was vacuum distilled. A fraction boiling at 39–40° (110 mm) (21.0 g, 35% yield) was obtained. Gas chromatographic analysis (20% TCEP column, 70°, 6 ft) showed that the distillate contained a mixture of two compounds in a 3:1 ratio with respective retention times of 5.95 and 6.68 min. The mixture was partially separated into its components by repeated preparative gas chromatography. The major product was obtained in 98% purity, with the minor

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[42] Mass spectroscopy was used for the determination of molecular weights reported in this paper.

[43] The nmr spectra reported in this paper were all taken on a 60-Mc spectrometer with tetramethylsilane as internal standard and carbon tetrachloride as solvent, unless otherwise stated.

[44] G. S. Hammond and R. P. Foss, *J. Phys. Chem.*, 68, 3739 (1964).

[45] For a description of the apparatus, see G. S. Hammond, *et al.*, *J. Am. Chem. Soc.*, 86, 3197 (1964).

product as the only contamination. The nmr spectrum of the major product shows a complex structure of four groups of signals centered at 1.65, 2.87, 5.20, and 6.32 ppm of relative intensities 3:2:6:1. Its infrared spectrum shows absorptions due to conjugated double bond, 1600 cm^{-1}, unconjugated double bond, 1648 cm^{-1}, terminal vinyl group, 895, 987, and 1815 cm^{-1}, and *trans*-disubstituted double bond, 965 cm^{-1}. The ultraviolet spectrum (in methanol) showed λ_{max} 2230 A (ϵ 10,800). These data are in agreement with the structure *trans*-3-methylene-1,6-heptadiene.

Anal. Calcd for C_8H_{12}: C, 88.83; H, 11.17. Found: C, 89.29; H, 11.24.

The minor product was isolated in 87% purity with the major product as the only contamination. Its nmr spectrum also shows four groups of signal with complex structures and of relative intensities 3:2:6:1. The infrared spectrum also resembles that of the major compound (absorptions at 1600, 1632, 894, 985, and 1805 cm^{-1}) with the exception of an additional absorption band at 686 cm^{-1}, characteristic of a *cis*-disubstituted double bond. The spectra, therefore, agree with the structure *cis*-3-methylene-1,6-heptadiene.

2-Methyl-5-methylene-2,6-heptadiene (7d). The compound was prepared by a procedure similar to that described before and was obtained in 25% yield. The nmr spectrum of the triene shows two singlets (3 H each) at 1.55 and 1.68 ppm, a doublet (1 H) at 1.91 ppm, and a group of signals, 4.6–6.0 ppm, corresponding to six vinyl protons. The infrared spectrum shows absorptions at 914, 1002, and 1830 (terminal vinyl groups), 1640 and 1680 (conjugated and unconjugated double bonds), and 1362, 1380, 1416, and 1450 cm^{-1} (methyl groups).

Anal. Calcd for C_9H_{14}: C, 88.52; H, 11.48. Found: C, 88.02; H, 11.36.

Photosensitized Cyclization of 3-Methylene-1,5-hexadiene. 2-Methylenebicyclo[2.1.1]hexane (8). A solution of **7a** (10.0 g) and β-acetonaphthone (0.1 g) in 600 ml of ether was irradiated with high-pressure mercury lamps in a Sylvania photoreactor. Reaction was followed by gas chromatographic analysis (20% TCEP, 6 ft). Formation of only one product could be detected. After 48 hr of irradiation, conversion of the triene was complete. The reaction apparently proceeded without significant side reactions. The solution remained colorless after irradiation. The product was isolated by distillation through a 2-ft spinning-band column. The fraction boiling at 91–92° (750 mm) (6.8 g) was homogeneous as shown by gas chromatography. The product is **8**. The nmr spectrum is shown in Figure 2a. The infrared spectrum (in CCl_4) shows absorptions at 872, 945, and 1776 (terminal double band), and 1048, 1070, 1140, 1194, 1232, 1269, 1442, 2880, 2960, 3000, and 3090 cm^{-1}.

Anal. Calcd for C_7H_{10}: C, 89.28; H, 10.72; mol wt, 94. Found: C, 88.87; H, 10.66; mol wt, 94.

Several other sensitizers (acetophenone, benzophenone, triphenylene, and 9-fluorenone) were equally effective in sensitizing the reactions. To ensure good yield of the product, initial concentrations of the triene should be $\leq 2\%$ to minimize side reactions such as dimerization.

Reductive Ozonolysis of 8. Ozone was directed into a solution of 0.50 g of **8** in 25 ml of methanol at −78°. The solution turned slightly purple by the end of the reaction. The methanol solution of the ozonide was hydrogenated with Pd–charcoal as catalyst. The solution was treated with 2,4-dinitrophenylhydrazine without isolation of the ketone. A first crop of 0.45 g of orange crystals, mp 151–158°, was obtained. After one recrystallization from 95% ethanol, the solid melted at 176–178°.

Anal. Calcd for $C_{12}H_{12}N_4O_4$: C, 52.15; H, 4.38; N, 20.28. Found: C, 52.27; H, 4.54; N, 20.14.

In a separate run a pure sample of the ketone was obtained by preparative gas chromatography (20% TCEP column, 6 ft, 125°). Its infrared spectrum shows carbonyl absorptions at 1755 cm^{-1}, in agreement with the recently reported value for bicyclo[2.1.1]-hexan-2-one prepared by a different route.[20]

2-Methylene-5,5-dimethylbicyclo[2.1.1]hexane (9). Irradiation of a 2% ether solution of **7d** with β-acetonaphthone yielded one product, which was isolated by preparative gas chromatography (TCEP column, 57°, 6 ft). The compound is a colorless liquid. Its nmr spectrum is shown in Figure 2b (integrations: 1:1:5:3:1:1 going upfield). The infrared spectrum (film) shows absorptions at 873, 907, 1730, and 1760 cm^{-1} (terminal double bond), and 782 820, 1071, 1171, 1248, 1370, 1389, 1456, and 1473 cm^{-1}.

Anal. Calcd for C_9H_{14}: C, 88.52; H, 11.48; mol wt, 126. Found: C, 87.84; H, 11.59; mol wt, 126.

***endo*- and *exo*-2-Methylene-5-methylbicyclo[2.1.1]hexanes (10 and 11).** Irradiation of a 1% ether solution of the 3-methylene-1,5-heptadiene mixture (*trans:cis*, 3:1) prepared previously with β-acetonaphthone yielded two products in the ratio of 5.8 to 1. They were separated by preparative gas chromatography (TCEP column, 6 ft, 70°). The nmr spectrum of the major product, assigned the structure 2-methylene-*endo*-5-methylbicyclo[2.1.1]hexane, is shown in Figure 2c. Its infrared spectrum (film) shows absorptions at: 721, 868, 1022, 1064, 1139, 1220, 1264, 1370, 1435, 1670, 2890, 2990, 3090 cm^{-1}.

Anal. Calcd for C_8H_{12}: C, 88.88; H, 11.12; mol wt, 108. Found: C, 89.29; H, 11.24; mol wt, 108.

The nmr spectrum of the minor product, assigned the structure 2-methylene-*exo*-5-methylbicyclo[2.1.1]hexane, is shown in Figure 2d. Its infrared spectrum shows absorptions at: 772, 805, 823, 830, 869, 927, 1043, 1070, 1141, 1190, 1200, 1262, 1359, 1440, 1635, 1665, 2890, 2990, and 3090 cm^{-1}; mol wt found: 108.

Product Distribution. Solutions of 98% pure **7b** and 85% pure **7c** were irradiated to determine the product distribution throughout the reaction period. The samples were prepared by introducing 2 ml of a 2% solution of the triene in methanol with 1×10^{-2} *M* triphenylene into constricted Pyrex test tubes. The tubes were degassed and sealed, and then irradiated with an AH-3 high-pressure Hg lamp. Results are shown in Table I.

Direct Irradiation. Degassed ether solutions of 1% triene isomers were irradiated in sealed quartz tubes with a low-pressure Hg lamp. Reactions were followed by gas chromatography (6 ft TCEP column). Two major products (in total yields up to 89%) with retention times longer than those of the two bicyclohexanes were found. Four minor products were also formed, two of which had retention times identical with those of the isomers of bicyclohexanes. Results of analysis are shown in Table II.

2,6-Dimethyl-1,3,6-heptatriene. The triene, as obtained commercially (Aldrich Chemical), was found to contain the *trans* isomer only. When a 2% ether solution of the triene was irradiated with β-acetonaphthone as described before, rapid formation of one new product was detected by gas chromatography analysis (Carbowax column). The new product reached a maximum concentration of approximately 50% after 2 days of irradiation. When irradiation was continued for 5 additional days, no other new products were detected, and the solution composition remained constant. The new product was isolated by preparative gas chromatography, and identified as *cis*-2,6-dimethyl-1,3,6-heptatriene. Its nmr spectrum is identical with the *trans* isomer, consisting of two singlets at 1.73 and 1.85 ppm (3 H each), a doublet (2 H) centered at 2.90, and a complex group of signals between 4.64 and 6.10 ppm accounting for six vinyl protons. The infrared spectrum also resembles that of the *trans* isomer except for the additional absorption peak at 762 cm^{-1} for the *cis*-substituted double bond, instead of the strong peak at 965 cm^{-1} observed for the *trans* isomer.

3-Methylene-1,6-heptadiene (12). 3-Methyl-1,6-heptadien-3-ol was prepared by reaction of vinylmagnesium bromide with 1-hexen-5-one. The alcohol, bp 41–42° (3 mm), was obtained in 75% yield. Spectral data show expected features for the dienol.

Potassium acid sulfate was used for dehydration of the alcohol. To a flask containing 1.0 g of powdered potassium acid sulfate heated to 220°, was added dropwise 15.5 g of the dienol. The collected distillate, dried over Na_2SO_4, weighed 4.2 g. The mixture was found to contain three major components in relative ratio 4:1:3. They could be separated only by gas chromatography (Silicon 200, 20%, 5-ft, 100°). The major fraction was identified as the desired 3-methylene-1,6-heptadiene; nmr spectrum: a doublet centered at 2.25 (4 H), a complex group of peaks between 4.75 and 6.65 ppm (8 H); ultraviolet (MeOH): λ_{max} 2300 A (ϵ 1.0×10^4).

Anal. Calcd for C_8H_{12}: C, 90.50; H, 9.50; mol wt, 108. Found: mol wt, 108.

The two minor products were also isolated. They are the two isomeric 3-methyl-1,3,6-heptatrienes.

1-Vinylbicyclo[2.1.1]hexane (24). Irradiation of a 1% solution of **12** with β-acetonaphthone gave a single product as shown by gas chromatography. The compound was isolated by preparative gas chromatography. The nmr spectrum is shown in Figure 1b; molecular weight (C_8H_{12}): 108 (calcd), 108 (found).

The quantum yield of the reaction was determined by using the myrcene reaction as standard. Pyrex test tubes containing solutions of 0.100 *M* triene and 1.1×10^{-2} *M* benzophenone in *n*-hexane were degassed and sealed. The tubes were placed around a rotating table and irradiated with 3500-A light. Irradiation was stopped after approximately 20% calculated conversions were reached. The tubes were analyzed by gas chromatography. The relative quantum of formation of **24** to that of **1** was found to be 0.90. Since the quantum yield of the myrcene reaction has been determined (0.023), the quantum yield of formation of **24** is calculated to be 0.021.

Acknowledgment. The part of the work carried out at the California Institute of Technology was supported by a grant from the National Science Foundation.[46]

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[46] This paper has been assigned no. XLV in the series, "Mechanisms of Photochemical Reactions in Solution." Paper XLIV is E. Y. Lam, D. Valentine, and G. S. Hammond, *J. Am. Chem. Soc.*, **89**, 3482 (1967).

Photochemistry of Cyclopentenone in Various Media

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Contribution from the Department of Chemistry, Wesleyan University, Middletown, Connecticut 06457. *Received April 7, 1967*

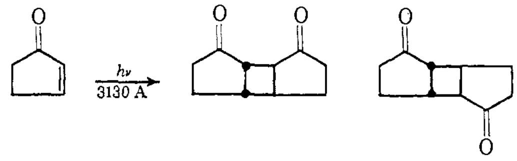
Abstract: Cyclopentenone at various concentrations in several solvents, and in a silica gel–cyclohexane slurry, has been irradicated yielding the *trans syn-* and *anti*-photodimers as well as other products. The excited state responsible for dimerization is the triplet, formed in high quantum efficiency, and lying at about 61 kcal/mole. The ratio of dimers is highly concentration and solvent dependent. On silica gel, photodimerization appears to be virtually completely suppressed; that dimer which does form is apparently formed in the supernatent solvent. An interesting side reaction in cyclohexane solvent, which becomes important when certain sensitizers are used (and also when the medium contains silica gel), is addition of cyclohexane to the carbon–carbon double bond of cyclopentenone.

The photochemistry of conjugated cyclic enones has been the subject of considerable recent activity.[1–4] From these studies a fairly consistent picture of the reaction mechanism appears. Cyclopentenone and cyclohexenone behave in a similar fashion, and it is relatively well established that (1) photodimerization occurs in the triplet state; (2) of the four possible cycloadducts, only the *trans syn* and *anti* are of major importance; and (3) the ratio of *anti* to *syn* is concentration and solvent dependent, with *anti* becoming increasingly important at higher concentrations of enone and with increasing solvent polarity.

Our original purpose in this investigation was to study the effect of physical adsorption (on silica gel) in photodimerization reactions; we felt that physical constraint on a surface could lead either to measurably more efficient cycloaddition, or to drastically reduced efficiency, depending upon the nature of the surface interaction and the chemical mechanism. We chose the cyclopentenone system because previous work[5] had been done on it in solution, and because there existed the possibility that the system might be perturbed enough by adsorption on silica gel so that *cis* as well as *trans* stereochemistry might be observed in the dimerization. Before very long it became apparent that the reaction in solution was complex enough to warrant additional investigation in its own right; in this paper we will attempt to digest the work of others and ourselves on the photochemistry of cyclic enones in solution, and to discuss briefly our results in a somewhat different medium, namely, a cyclohexane–silica gel matrix.

Results

Cyclopentenone undergoes photodimerization at 3130 A as indicated in eq 1, the efficiency of which depends upon several variables. The ratio dimer II/dimer I has been studied as a function of concentration in a variety of solvents: cyclohexane, isopropyl alcohol, ethanol, and methanol. The data are given in Table I.



I II

Table I

	Cyclopentenone concn, *M*			
	Neat	6.2	1.2	0.12
Solvent	Dimer II/dimer I			
(Neat)	1.1			
Cyclohexane		2.0	4.3	6.4
Isopropyl alcohol		1.6	2.2	2.1
Ethanol		1.4	1.7	4.3
Methanol		1.9	1.9	1.9

A. Multiplicity of the Excited Intermediate. In order to investigate the possibility of participation by an excited triplet state intermediate, attempts were made to quench (*i.e.*, inhibit) the dimerization with the triplet quencher *cis*-piperylene (Table II). *cis*-Pieryl-

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[1] J. L. Ruhlen and P. A. Leermakers, *J. Am. Chem. Soc.*, **88**, 5671 (1966).

[2] P. E. Eaton and W. S. Hurt, *ibid.*, **88**, 5038 (1966).

[3] P. De Mayo, J. Pete, and M. Tchir, private communication.

[4] E. Y. Lam, D. Valentine, and G. S. Hammond, *J. Am. Chem. Soc.*, **89**, 3482 (1967).

[5] P. E. Eaton, *ibid.*, **84**, 2344 (1962).