from τ 8.6 to 9.0 (1), and a complex cyclopropyl absorption from τ 9.26 to 9.74 (2). On the basis of these spectra, and a comparison with the spectra of authentic 1,1-dimethyl-2-vinylcyclopropane (**17**), this compound was identified as 1,1-pentamethylene-2-vinylcyclopropane.

The second major photoproduct, **19**, showed infrared (CCl_4) absorption maxima at 3.22 (w), 3.42 (s), 5.45 (w), 5.98 (w), 6.10, 6.93, (s), 7.42, 10.10, and 11.00 (s) μ. The nmr spectrum showed olefinic proton absorption from τ 3.8 to 5.25 (4), a triplet centered at τ 7.30 (w), a broad singlet centered at τ 7.90 (4), and another broad singlet centered at τ 8.47 (6). On the basis of these spectra and a comparison with the spectra of an authentic sample of 5-methyl-1,4-hexadiene (**16**), this product was identified as 1,1-pentamethylene-1,4-pentadiene.

Mercury ($^3P_1$) Photosensitized Internal Cycloaddition Reactions in 1,4-, 1,5-, and 1,6-Dienes

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Abstract: The mercury ($^3P_1$) photosensitized internal cycloaddition reactions of 1,4-pentadiene, 2-methyl-1,4-pentadiene, 2,4-dimethyl-1,4-pentadiene, 1,5-hexadiene, 2-methyl-1,5-hexadiene, 1,5-cyclooctadiene, and 1,6-heptadiene have been studied at 1-atm pressure at the boiling points of the respective compounds. With the exception of 1,5-cyclooctadiene, all the compounds gave a parallel adduct of the general formula bicyclo[*n*.2.0]alkane and a crossed adduct of the formula bicyclo[*n*.1.1]alkane. In all of the 1,4-pentadienes the former predominated, in the 1,5-hexadienes the latter predominated, while in 1,6-heptadiene the former once again predominated. A mechanism is proposed to explain this. With an increase in the complexity of the molecule the isomerization to give cyclopropyl derivatives decreased in importance, and internal cycloaddition accounted for as much as 60% of the diene. A dimerization reaction is proposed to account for the remaining diene that reacted.

In earlier work we had shown that in the vapor phase, on sensitization by mercury ($^3P_1$) atoms, nonconjugated dienes such as 1,5-hexadiene,[2] 1,5-cyclooctadiene,[3] and 1,6-heptadiene[4] undergo isomerization with migration of hydrogen to give cyclopropyl derivatives, internal cycloaddition leading to bicyclic compounds with a cyclobutane ring, and decomposition to free radicals. It had also been demonstrated that the relative importance of these reactions was a sensitive function of the total pressure in the system. The quantitative aspects of these earlier results will be considered in the Discussion. The aims of the present study were to extend these results to the 1,4-pentadienes, and to investigate the stereochemistry of the cycloaddition reaction as a function of alkyl substitution in both the 1,4-pentadienes and the 1,5-hexadienes.

Experimental Section

Materials. 2-Methyl-1,4-pentadiene, 2,4-dimethyl-1,4-pentadiene, 2-methyl-1,5-hexadiene, and 1,6-heptadiene of >99% purity were obtained from Chemical Samples Co., Columbus, Ohio, and used without further purification. 1,4-Pentadiene, 1,5-hexadiene, and 1,5-cyclooctadiene of 98% purity were obtained from K & K Laboratories, Plainview, N. Y. These were fractionated before use in quantitative studies and used as such in preparative work.

Apparatus. A cylindrical quartz cell of 80-mm diameter and 1.5-l. volume was mounted vertically along the axis of a circular bank of mercury resonance lamps. The total output of the source was 64 w at 2537 A.[5] The lower end of the cell was connected by a ground joint to a flask in which the diene, along with 2 g of mercury, was placed. The top end of the cell was attached to an efficient condenser whose exit was plugged with glass wool.

Procedure. On heating the contents of the flask, vapors of the diene and mercury ascended the cell, condensed at the cold surface at the top, and dropped back into the flask. The heat from the lamps was sufficient to prevent any condensation on the walls of the cell. In any case, all of the dienes that were used had negligible, if any, absorption at 2537 A. This arrangement permitted the irradiation of 1 mole of the reactant at a time.

In quantitative studies, 25 ml of the diene and 1 g of mercury were used. The progress of the reaction was followed continuously by gas chromatographic analysis.

Isolation of the products (in preparative work) required a preliminary distillation in a spinning-band column (18 in. long) followed by separation of the saturated material in each cut f om the unsaturated materials by passage through a silver nitrate column.

It is interesting to note that the cross adduct from a given diene always boiled at a lower temperature than the corresponding parallel adduct[6] in every one of the six pairs that were observed. The properties of the new compounds that were isolated are listed in Table I.

Quantitative analyses for the products was carried out on a Ucon-oil 550X column, 2 m long, at temperatures which ranged from 26 to 50°. A Perkin-Elmer 154D vapor fractometer was used. The ratio of the two types of cycloadducts was measured on a silver nitrate column which readily separated the saturated materials from the unsaturates, and the cycloadducts from each other. The Ucon-oil column was found to have the same sensitivity for isomeric hydrocarbons while the silver nitrate column had identical sensitivities for each of a pair of saturated products.

Results

All of the results reported here were obtained at the boiling points of the respective dienes at a pressure of 1 atm. These conditions were chosen in order to optimize the yield of the cycloaddition products.

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[1] Author to whom inquiries may be addressed: IBM Watson Research Center, Yorktown Heights, N. Y. 10598.

[2] R. Srinivasan, *J. Phys. Chem.*, 67, 1367 (1963).

[3] R. Srinivasan, *J. Am. Chem. Soc.*, **85**, 819 (1963); I. Haller and R. Srinivasan, *ibid.*, **88**, 5084 (1966).

[4] R. Srinivasan and K. A. Hill, *ibid.*, **87**, 4988 (1965).

[5] A photochemical reactor of this design with twice the output of ultraviolet light at 2537 A is manufactured by the Southern New England Ultraviolet Co., Middletown, Conn.

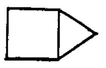
[6] The terms "parallel addition" and "cross addition" are used in this article to indicate the intramolecular equivalents of "head-to-head" and "head-to-tail" addition in dimerization to cyclobutane derivatives.

Table I. Properties of Internal Photocycloaddition Products

	Compound				
	1-Methylbicyclo[2.1.0]pentane (**1**)	1,4-Dimethylbicyclo[2.1.0]pentane (**2**)	1,3-Dimethylbicyclo[1.1.1]pentane (**3**)	1-Methylbicyclo[2.1.1]hexane (**4**)	1-Methylbicyclo[2.2.0]hexane (**5**)
Bp, °C	60–61	74	71–72	81–82	88
Refractive index (23.5°)	1.4131	1.4108	. . .	1.4233	. . .
C, calcd,[a] %	87.74	87.44	87.44	87.44	87.44
H, calcd, %	12.26	12.58	12.58	12.58	12.58
C, found, %	87.87	87.09	87.47	87.68	87.70
H, found, %	12.23	12.94	12.61	12.40	12.60
Infrared[b] spectrum, cm^{-1}	3115 (s), 2985 (vs), 1431 (s), 1372 (w), 1264 (s), 1049 (s), 1009 (s), 935 (s), 846 (s)	3125 (w), 3021 (vs), 2933 (s), 1451 (s), 1439 (s), 1383 (w), 1300 (w)	2985 (vs), 1639 (w), 1447 (s), 1370 (s), 1266 (vs), 1070 (w)	2941 (vs), 1439 (vs), 1368 (s), 1304 (vs), 1279 (s), 1203 (s), 1015 (s), 881 (s), 821 (s)	2959 (vs), 1435 (s), 1368 (w), 1297 (w)
Nmr spectrum[c]	9.15 to 9.70 (2H), 8.78 (3H), remaining protons from 7.9 to 9.0	9.89 (1H), 9.38 (1H), 8.83 (6H), rest from 8.1 to 8.8	8.48 (3H), 8.86 (3H)	7.65 (1H), 8.80 (3H), rest from 8.2 to 9.1	8.87 (3H), rest from 7.4 to 8.5

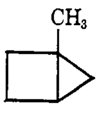
[a] Microanalyses by Micro-Tech Laboratories, Skokie, Ill. [b] The infrared spectra of **3** and **5** were run as gas samples (l = 10 cm; pressure = 30–40 mm); of **4** as pure liquid in 0.1-mm path; the remaining two were run in solution in CCl_4. Spectra were obtained on a Perkin-Elmer Infracord spectrometer. [c] Spectra were run on a Varian A-60 spectrometer using 10–20% solutions in carbon tetrachloride or pure liquids. Tetramethylsilane was used as internal standard. Peak positions in τ units.

Products. In the mercury-photosensitized reaction of 1,4-pentadiene the C_5 products were 1-pentene, vinylcyclopropane, bicyclo[2.1.0]pentane (**6**), and bicyclo[1.1.1]pentane (**7**). The last two, which are the cycloaddition products, have been described before.[7,8] They were identified by their infrared and nmr spectra.

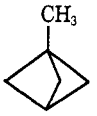

6


7

In the mercury-photosensitized reaction of 2-methyl-1,4-pentadiene, the C_6 products were 2-methylvinylcyclopropane (*cis* and *trans*?), isopropenylcyclopropane, 1-methylbicyclo[2.1.0]pentane (**1**), and 1-methylbicyclo[1.1.1]pentane (**8**). Of the cycloaddition products, **8** has been described before.[8] 1-Methylbicyclo[2.1.0]pentane (**1**), analyzed correctly for the formula C_6H_{10}, showed no unsaturation in its infrared or nmr spectra. The presence of a methyl group was indicated by an absorption in the infrared at 1372 cm^{-1}. A sharp unsplit absorption due to three protons at τ 8.78 in the nmr spectrum showed that the methyl group was on a carbon bearing no protons. The formula demands that the compound be bicyclic. Of the two possible structures (**1** and **8**), since **8** was known, the compound on hand was identified as **1**. The rest of the nmr spectrum (Table I) was consistent with this identification.

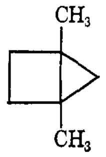


1

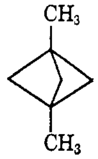


8

In the mercury-photosensitized reaction of 2,4-dimethyl-1,4-pentadiene there were two C_7 products. Both compounds analyzed for C_7H_{12}, and showed no unsaturation in their infrared or nmr spectra. The major product had infrared absorptions at 3125 (cyclopropyl C–H) and 1383 (CH_3) cm^{-1}. The nmr spectrum showed the presence of two cyclopropyl protons at τ 9.89 and 9.38, a sharp singlet due to six protons at τ 8.83 which could be attributed to two identical methyl groups, and the remaining four protons in a series of sharp absorptions centered at τ 8.4 (cyclobutyl protons).[9] The structure, 1,4-dimethylbicyclo[2.1.0]pentane (**2**) would account for all of these observations.



2



3

The minor product had an infrared absorption at 1370 cm^{-1} attributable to a methyl group(s). The nmr spectrum consisted of merely two sharp singlets of equal intensity at τ 8.48 and 8.86. For the formula C_7H_{12}, if the compound has two methyl groups, as has the starting material, the only possible saturated structures are **2** and **3**. In bicyclo[1.1.1]pentane, which is the parent ring system for **3**, the six protons in the three methylene groups occur at τ 8.16, while in 1-methylbicyclo[1.1.1]pentane (**8**) the same protons are at τ 8.23.[8] It is reasonable to conclude that the minor product is 1,3-dimethylbicyclo[1.1.1]pentane (**3**) and that the absorption at τ 8.48 is due to the six equatorial protons while the absorption at τ 8.86 is due to the six protons in the two methyl groups.

The products from the mercury-photosensitized isomerization of 1,5-hexadiene at 1-atm pressure have been described.[10]

In the mercury-photosensitized irradiation of 2-methyl-1,5-hexadiene, there were two C_7 products, both of which analyzed for C_7H_{12}. The minor product showed no unsaturation in its infrared or nmr spectra.

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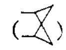
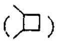
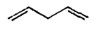
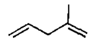
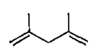
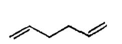
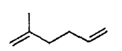
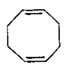
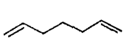
(7) R. Criegee and A. Rimmelin, *Chem. Ber.*, **90**, 414 (1954).

(8) K. B. Wiberg and D. S. Connor, *J. Am. Chem. Soc.*, **88**, 4437 (1966).

(9) A detailed analysis of the nmr spectrum is being carried out by Drs. G. Fraenkel and N. Wilson, Ohio State University, and will be published later.

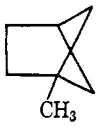
(10) R. Srinivasan and F. I. Sonntag, *J. Am. Chem. Soc.*, **89**, 407 (1967).

Table II. Cycloaddition Reactions of Diolefins Sensitized by Hg($^3P_1$)[a]

Compd	Bp, °C	Rate, μmoles/min: Disappearance of diene	Rate, μmoles/min: Formation of isomers	Relative rates of formation of products ▷—	□	Other[b]	Cross adduct  / Parallel adduct 
	26.0	334	89	83.0	9.1	7.9	0.10
	56.0	161	57	60.7	16.7	22.5	0.11
	81.6	87	50	22.1	77.9	0	0.03
	59.6	104	61	40.0	60.0	0	2.53
	88.5	80	40	0	100.0	0	2.12
	150.9	40	13	0	100.0	0	>40[c]
	90.0	106	64	0	100.0	0	0.04

[a] At 1-atm pressure; temperature equaling boiling point of diene; incident intensity = 64 w at 2537 A. [b] Includes reduction products with same number of carbons. [c] No parallel adduct observed.

An absorption at 1368 cm^{-1} in the infrared spectrum indicated the presence of a methyl group. In the nmr spectrum a sharp singlet at τ 8.87 due to three protons could also be attributed to this methyl group which was presumably on a carbon bearing no protons. The rest of the nmr spectrum consisted of a complex series of lines from τ 7.4 to 8.5. The resemblance to the spectrum of bicyclo[2.2.0]hexane[11] was noteworthy. By analogy to 1,5-hexadiene, it can be expected that internal cycloaddition of 2-methyl-1,5-hexadiene would give rise to 1-methylbicyclo[2.1.1]hexane (**4**) and 1-methylbicyclo[2.2.0]hexane (**5**).[10] The minor product was hence identified as **5**.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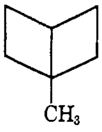
5

The major product was also saturated and had an absorption at 1368 cm^{-1} which could be attributed to a methyl group. In the nmr spectrum, a sharp singlet due to three protons at τ 8.80 was assigned to this methyl group. In bicyclo[2.1.1]hexane, the parent hydrocarbon, the absorption due to the bridgehead protons occurs at τ 7.47 and shows considerable broadening.[12] In the major product at hand, there was a broad absorption due to one proton at τ 7.65. Since the compound showed no absorption above τ 9.1, the bicyclo[3.1.0]hexane structure is excluded. The most likely structure is **4** in which the methyl group is on one bridgehead carbon atom. The cycloaddition products that are formed on sensitization of 1,5-cyclooctadiene[3] and 1,6-heptadiene[4] have been described.

Quantitative Studies. The results of quantitative studies are given in Table II. These values were not corrected for the slight fluctuations in barometric pressure and corresponding variations in the boiling point during the course of an experiment.

The reactants that have been used in this study are all nonconjugated dienes ranging from C_5 to C_8 as well as from linear to branched to cyclic compounds. The cross sections for the quenching of mercury ($^3P_1$) atoms by these molecules are not available. The values in the literature[13] for propylene, 1-butene, 2-butene, and 1,3-butadiene fall within such a narrow range that it seems unlikely that the cross sections for the compounds used here vary by more than 30%. At constant intensity of the incident radiation, since the primary absorbing species is the Hg($^1S_0$) atom, it can be assumed that the rates of disappearance of the diene (Table II) are proportional to their quantum yields. This statement does not take into account the disappearance of the diene by secondary (free radical) processes. As a result the rates of disappearance of 1,4-pentadiene and 2-methyl-1,4-pentadiene (both of which showed evidence for a considerable amount of free-radical products) were anomalously high. The next three, as well as 1,6-heptadiene, are the same within ±15%. It is not clear whether 1,5-cyclooctadiene is another exception, or the higher operating temperature caused a significant reduction in the photon intensity due to pressure broadening of the resonance line.

From the data in Table II the following distinct patterns can be discerned in the sensitized photoprocesses among the dienes that were studied. (i) At a given pressure, as the complexity of the molecule increases, the trend is from free-radical processes to cyclopropyl products to cycloaddition products. (ii) In a given series, *e.g.*, 1,4-pentadiene, the pattern of cycloaddition (the ratio of cross-addition to parallel addition) does not reverse itself with substitution. The extreme example is 1,5-cyclooctadiene which gives exclusively the cross-adduct even if its ground-state structure may appear to favor the parallel adduct. (iii) In the most com-

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

(12) K. B. Wiberg, B. R. Lowry, and B. J. Nist, *ibid.*, **84**, 1594 (1962).

(13) H. E. Gunning and O. P. Strausz, *Advan. Photochem.*, **1**, 248 (1963).

plex molecules, the yield of the cycloadduct seems to reach a limiting value which is between 40 and 60%.

Discussion

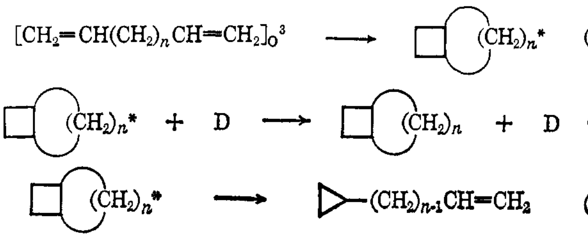
It has been proposed[4] that the formation of free radicals, cycloaddition products, and cyclopropyl derivatives in the mercury-sensitized decomposition of nonconjugated dienes proceeds through the following mechanisms

$$\mathrm{Hg}(^1\mathrm{S}_0) + h\nu \longrightarrow \mathrm{Hg}(^3\mathrm{P}_1) \qquad (1)$$

$$\mathrm{CH_2{=}CH(CH_2)}_n\mathrm{CH{=}CH_2} + \mathrm{Hg}(^3\mathrm{P}_1) \longrightarrow [\mathrm{CH_2{=}CH(CH_2)}_n\mathrm{CH{=}CH_2}]_\mathrm{m}{}^3 + \mathrm{Hg}(^1\mathrm{S}_0) \qquad (2)$$

$$[\mathrm{CH_2{=}CH(CH_2)}_n\mathrm{CH{=}CH_2}]_\mathrm{m}{}^3 \longrightarrow \text{free radicals} \qquad (3)$$

$$\mathrm{CH_2{=}CH(CH_2)}_n\mathrm{CH{=}CH_2}]_\mathrm{m}{}^3 + \mathrm{D} \longrightarrow [\mathrm{CH_2{=}CH(CH_2)}_n\mathrm{CH{=}CH_2}]_0{}^3 + \mathrm{D} \qquad (4)$$



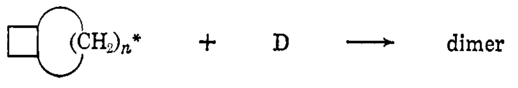
(5)

(6)

(7)

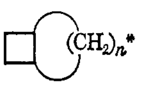
where the superscripts refer to the multiplicities, m and 0 indicate vibrational levels, and D is a diene molecule in its ground state. A reaction similar to 5 which would give the "hot" crossed adduct has been left out as only one mode of cycloaddition dominates in each system. The chemical difference between the excited species that participates in (3) and (5) is a matter for speculation. Since an increase in pressure markedly diminishes the free-radical path, these two species may differ in vibrational energy content as postulated earlier.[4]

The scheme, consisting of steps 1–7, is obviously incomplete as it would require that at sufficiently high pressures the photocycloaddition product be the only ultimate product. In the present set of experiments, particularly with C_7 and C_8 dienes, the cyclopropyl derivatives which are from (7) are hardly detectable. Yet the photocycloaddition products never accounted for all of the diene that disappeared. The third possible route to the consumption of the diene, *i.e.*, secondary reactions (additions) of the free radicals that were formed in (3) no doubt accounted for a small portion of the diene.[14] However, the disappearance of nearly 40% of the diene as high-boiling material with 2,4-dimethyl-1,4-pentadiene, 1,5-hexadiene, 2-methyl-1,5-hexadiene, and 1,6-heptadiene suggests an additional step. This is probably the formation of a dimer some of the time in (6). Thus



(8)

It is first of all necessary to analyze the present data (at 1 atm) to see if these are consistent with earlier data obtained at a lower pressure for the isomerization process in the instances in which these are available. From (6) and (7) and inserting [Cy*] for the concentration of



$$\frac{\text{rate of cycloadduct formation}}{\text{rate of cyclopropane formation}} = \frac{k_6[\mathrm{Cy}^*][\mathrm{D}]}{k_7[\mathrm{Cy}^*]} = \frac{k_6[\mathrm{D}]}{k_7} \qquad (9)$$

Hence

$$\frac{\text{rate of cycloadduct formation}}{\text{rate of cyclopropane formation} \times \text{pressure}} = \text{constant} \qquad (10)$$

In the case of 1,5-hexadiene, the values for this ratio at 120 and 200 mm^2 are 1.83 and 1.60 $\times 10^{-3}$, while from this study at 760 mm the value is 1.97 $\times 10^{-3}$. The agreement may be considered reasonable when it is borne in mind that in this range of pressure the relative importance of these two products is completely inverted. In 1,5-cyclooctadiene[3] and 1,6-heptadiene[4] at pressures of 3.6 and 65 mm, the ratios were 0.036 and 0.035, respectively. At 760 mm, the ratio of cycloadduct to cyclopropane would be 27.4 and 26.4, respectively. This would explain the failure to find any cyclopropyl product in these two systems in the present study.

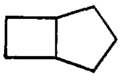
From steps 1–8 using the usual stationary state assumptions for the reactive intermediates, it is possible to derive that

$$\text{rate of cycloadduct formation} = k_6[\mathrm{D}]\{I - k_3[\mathrm{D_m}{}^3]\}/k_7 + (k_6 + k_8)[\mathrm{D}] \qquad (11)$$

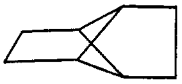
Substituting for $[\mathrm{D_m}{}^3]$ and noting that in the region in which free-radical reactions are minor, $k_4[\mathrm{D}] \gg k_3$

$$\text{rate of cycloadduct formation} = k_6I[\mathrm{D}]/k_7 + (k_6 + k_8)[\mathrm{D}] \qquad (12)$$

where I is the absorbed photon intensity. In instances in which $k_7 \ll (k_6 + k_8)[\mathrm{D}]$, *i.e.*, when cyclopropyl products are not important (12) reduces to $k_6I[\mathrm{D}]/(k_6 + k_8)[\mathrm{D}]$. $(k_6 + k_8)$ is simply the collision rate between any given molecule and all other molecules in the system. This value should change very little among the reactants studied here. The magnitude of k_6, the rate of stabilization of the cycloadduct, should be an inverse function of the strain involved in the bicyclic system that is formed. The last three compounds in Table II do not yield a detectable amount of cyclopropyl products. The relative yields for cycloaddition are: 1,6-heptadiene:2-methyl-1,5-hexadiene:1,5-cyclooctadiene::0.61:0.50:0.33. The cycloaddition products are **9**, **4**, and **10** in which the strain energies (by adding the strain in the component rings) can be estimated to be 32, 33, and 37 kcal/mole. The two sets of values are seen to show the same trend.



9



10

In a given series, the effect of increasing substitution can be explained by the increased number of vibrational modes that become available for "cooling" the "hot" cycloadduct (Cy*) that is formed in step 5. As a result, the yield of the cycloadduct increases chiefly due to a decrease in the magnitude of k_7. The pair of reactions 6 and 7 correspond *inversely* to the activation and uni-

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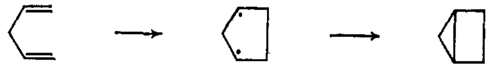
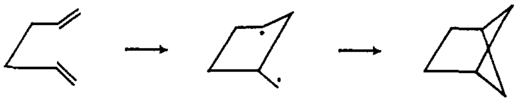
[14] Although **2** itself is subject to pressure quenching, such free radical + diene → adduct reactions would be promoted by an increase in pressure.

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.

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(15) R. Srinivasan, unpublished work.

Photosensitized Internal Addition of Dienes to Olefins

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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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