(6.4%), and recrystallized from hexane, mp 67–69°; ν^{KBr}: ν^{KBr} 3085, 1740 (d), 1100, and 1000 cm^{-1}; nmr: τ 6.37 (s, CH_2), 6.31 (s, CH_3), 5.98 (s, C_5H_5), 5.70–5.38 (2t, C_5H_4), and 2.56–2.93 (m, C_6H_4).

Anal. Calcd for $C_{19}H_{18}FeO_2$: C, 68.29; H, 5.43. Found: C, 68.14; H, 5.53.

Methyl *p*-Ferrocenylphenylacetate. The free acid was prepared by the previous route from 8 g of methyl *p*-aminophenylacetate[41,44,49] [bp 240–250° (17 mm)] (0.053 mole) with hydrolysis of the ester in the reaction medium yielding 3.94 g (19.4%). Recrystallization from 1:1 CH_2Cl_2–methylcyclohexane gave *p*-ferrocenylphenylacetic acid, mp 160.5–161.5°; ν^{KBr}: 3500–2500, 1710, 1100, and 1000 cm^{-1}; nmr: τ 6.40 (s, CH_2), 5.97 (s, C_5H_4), 5.70–5.32 (2t, C_5H_4), and 2.63 (ABd, C_6H_4).

Anal. Calcd for $C_{19}H_{18}FeO_2$: C, 67.52; H, 5.04. Found: C, 67.37, 67.36; H, 5.14, 5.09.

A mixture of 1.00 g of *p*-ferrocenylphenylacetic acid (3.0 mmoles), 10 ml of methanol, and then 2.3 ml of $BF_3 \cdot Et_2O$ was stirred under nitrogen at room temperature for 2 hr and poured into saturated $NaHCO_3$. The ester was filtered off, washed with water (0.75 g, 72%), dissolved in benzene, washed through a plug of alumina, and recrystallized from hexane, mp 87.0–87.7°; ν^{KBr}: 3095, 1737, 1100, and 1000 cm^{-1}; nmr: τ 6.40 (s, CH_2), 6.30 (s, CH_3), 5.97 (s, C_5H_5), 5.71–5.37 (2t, C_5H_4), and 2.70 (ABd, C_6H_4).

Anal. Calcd for $C_{19}H_{18}FeO_2$: C, 68.29; H, 5.43. Found: C, 68.27; H, 5.50.

***o*-Ferrocenylphenylacetic acid** was prepared by saponification of 200 mg of methyl *o*-ferrocenylphenylacetate (0.6 mmole) yielding 170 mg (89%); recrystallized from methylcyclohexane, mp 100–103°; ν^{KBr} 3300–2200, 1700, 1100, and 995 cm^{-1}; nmr: τ 6.14 (s, C_5H_4), 5.40–5.90 (m, C_6H_4), and 2.00–3.00 (m, C_6H_4).

Anal. Calcd for $C_{18}H_{16}FeO_2$: C, 67.52; H, 5.04. Found: C, 67.53; H, 4.89.

Trideuteriomethyl *o*-Ferrocenylphenylacetate. To 1.4 ml of trideuteriomethyl alcohol was added 102 mg of *o*-ferrocenylphenylacetic acid (0.32 mmole) and 0.4 ml of $BF_3 \cdot EtO$. The solution was stirred at room temperature for 2 hr and worked up as before, yielding 83.2 mg (77.5%); recrystallized from hexane, mp 42.44°.

***o*-Ferrocenylacetophenone** was prepared from 10 g of *o*-aminoacetophenone (Aldrich, $n^{20}D$ 1.6101) (0.329 mole) yielding 3.75 g (17.5%), and was recrystallized from hexane, mp 90–91° or 75–77° (crystalline modifications interconvertible by seeding); ν^{KBr}: 3090, 1678, 1100, and 1000 cm^{-1}; nmr: τ 7.91 (s, CH_3), 5.96 (s, C_5H_5), 5.70–5.57 (2t, C_5H_4), and 2.05–2.85 (m, C_6H_4).

Anal. Calcd for $C_{18}H_{16}FeO$: C, 71.07; H, 5.32. Found: C, 70.98; H, 5.35.[49a]

***m*-Ferrocenylacetophenone** was prepared from 5.8 g of *m*-aminoacetophenone (Aldrich) (mp 98–99°; lit.[50] 99.5°) (0.016 mole) yielding 2.03 g (14.5%) and after recrystallization from hexane melted at 73–75.5°; ν^{KBr}: 3085, 1680, 1100, and 997 cm^{-1}; nmr: τ 7.41 (s, CH_3), 5.9 (s, C_5H_5), 5.25–5.85 (m, C_5H_4), and 1.80–2.70 (m, C_6H_4).

Anal. Calcd for $C_{18}H_{16}FeO$: C, 71.07; H, 5.32. Found: C, 70.78; H, 5.37.[49a]

***p*-Ferrocenylacetophenone** was prepared from 10 g of *p*-aminoacetophenone (Aldrich) (mp 106–107°; lit.[51] mp 105–106°) (0.027 mole) yielding 4.65 g (21.5%); recrystallized from hexane, mp 174.0–174.5° (lit.[42] 176–178°).

***o*-Ferrocenylacetophenone-2,2,2-d_3.** To a mixture of 0.50 g of clean Na, 0.400 g of *o*-ferrocenylacetophenone (0.0013 mole), and 40 ml of dry peroxide-free dioxane was added 20 ml of D_2O with stirring.[52] The solution was maintained at 70° under nitrogen for 5 hr. The dioxane was removed under reduced pressure and the product isolated by extraction with ether. A single treatment gave 91% of the d_3 and 9% of the d_2 species.

Acknowledgments. We thank Mr. Laurence R. Dusold for recording many of the spectra. D. T. R. thanks E. I. du Pont de Nemours and Company, Inc., for a DuPont Teaching Fellowship and the American Enka Corporation for an Enka Summer Fellowship.

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[49] Prepared from *p*-nitrophenylacetic acid (mp 153–155°) as in ref 46.

[49a] NOTE ADDED IN PROOF. Analytical data correspond to those of T. G. Traylor and J. C. Ware, *J. Am. Chem. Soc.*, **89**, 2304 (1967).

[50] H. Rupe, A. Braun, and K. von Zembruzski, *Chem. Ber.*, **34**, 3522 (1901).

[51] J. Klingel, *ibid.*, **18**, 2687 (1885).

[52] E. Lund, H. Budzikiewicz, J. M. Wilson, and C. Djerassi, *J. Am. Chem. Soc.*, **85**, 1528 (1963).

Mercury-Photosensitized Reactions of 1,4-Dienes[1]

Jerrold Meinwald and G. Warren Smith[2]

Contribution from the Department of Chemistry, Cornell University, Ithaca, New York 14850. Received March 2, 1967

Abstract: The gas-phase, mercury-photosensitized reactions of four 1,4-dienes (**1**, **9**, **15**, and **18**) have been found to yield vinylcyclopropanes (**2**, **10**, **17**, and **20**) as the major monomeric products. Accompanying these cyclization reactions, carbon skeleton rearrangements which yield isomeric 1,4-dienes, cycloadditions to form bicyclo[2.1.0]pentanes, and partial reductions to give monoolefins were detected. All of these reactions were accompanied by polymer formation. A variety of mechanisms compatible with vinylcyclopropane and rearranged diene formation are considered.

While there has long been interest in the physical aspects of mercury-photosensitized reactions,[3] the synthetic potential of these reactions has only recently been made apparent, especially as a result of the excellent work of Lemal and of Srinivasan.[4-8] Several years ago, we initiated a study of the mercury-photosensitized reactions of 1,4-dienes, in part in the hope that a route to the then unknown bicyclo[1.1.1]pentanes[9,10] might result. In fact, this particular mode of

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[1] The partial support of this research by a National Science Foundation research grant and by the Chevron Research Co. is gratefully acknowledged.

[2] National Institutes of Health Predoctoral Fellow, 1963–1966.

[3] For a review of mercury-photosensitized reactions, see J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, Chapter 2; H. E. Gunning and O. P. Strausz, *Advan. Photochem.*, **1**, 209 (1963); R. J. Cvetanović, *Progr. Reaction Kinetics*, **2**, 39 (1964).

[4] D. M. Lemal and K. S. Shim, *J. Am. Chem. Soc.*, **86**, 1550 (1964).

[5] R. Srinivasan, *ibid.*, **84**, 4141 (1962).

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

[7] R. Srinivasan, *J. Am. Chem. Soc.*, **85**, 819 (1963).

[8] R. Srinivasan, *ibid.*, **86**, 3318 (1964).

[9] The first successful synthesis of bicyclo[1.1.1]pentane was reported by K. B. Wiberg, D. S. Connor, and G. M. Lampman, *Tetra-*

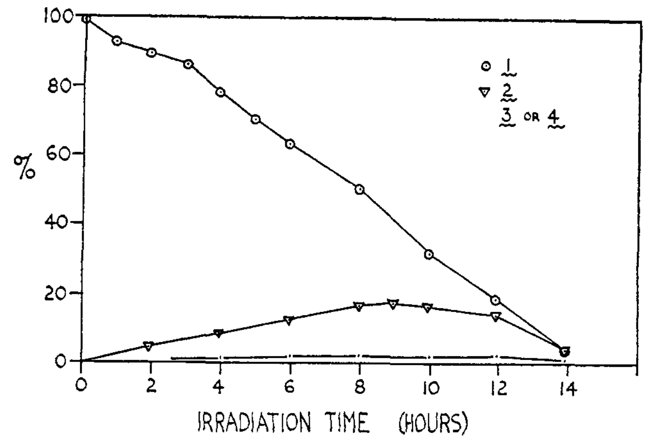

Figure 1. Irradiation at 1 mm initial pressure.

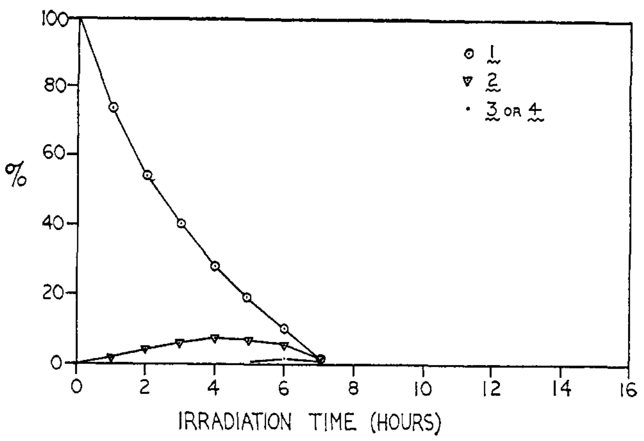

Figure 2. Irradiation at 100 mm initial pressure.

cyclization was not observed under the experimental conditions we employed.[11] However, other novel reactions were observed, and we should like to present our findings in this relatively unexplored area of photochemistry.

Results

Initial studies were carried out with the simplest 1,4-diene, 1,4-pentadiene (**1**), which is commercially available. A mixture of the diene and mercury was irradiated in a 500-ml round-bottomed quartz flask which was evacuated initially to a low pressure (under an argon or nitrogen atmosphere) while the contents were frozen in a liquid nitrogen bath. The flask was then isolated from the vacuum system and allowed to warm to ambient temperature. A circular bank of germicidal lamps (with chiefly 2537-A output) was used as the ultraviolet light source. The progress of the irradiation was followed by periodic sampling of the reaction mixture and subsequent glpc analysis.

The vapor-phase reaction showed a slightly greater yield of monomeric products using nitrogen rather than argon. The pressure of the inert gas relative to the amount of hydrocarbon in the vapor phase was found to influence the results as shown in Figures 1 and 2. All the C_5 products were found to increase at a rate apparently independent of the concentration of inert gas, and attained a maximum yield when **1** was *ca.* 70% consumed. However, the rate of disappearance of **1**, and the rate of polymer formation, was significantly greater with a higher pressure of inert gas. This resulted in an over-all decrease in the maximum yield of volatile photoproducts. The enhanced rate of polymer, but not of monomeric product, formation in those experiments involving a higher pressure of foreign gas (nitrogen or argon) may be due to collisional deactivation of an excited intermediate to give a lower energy state which leads only to polymer.

The major volatile photoproduct (18% over-all) formed from **1** was found to be vinylcyclopropane (**2**). Its nmr spectrum showed typical vinyl group absorption (τ 4.32 to 5.30; 3 H) and cyclopropyl proton absorption (τ 9.17 to 9.80, 4 H), with a downfield absorption by the single allylic cyclopropyl proton (τ 8.42 to 8.90, 1 H). The infrared and nmr spectra of **2** were identical with those of an authentic sample of vinylcyclopropane prepared by the dehydration of methylcyclopropylcarbinol.[12]

1 **2** **3** **4**

Two additional photoproducts obtained were bicyclo[2.1.0]pentane (**3**, 3%) and 1-pentene (**4**, 2%). Both of these were identified by comparison of their infrared and nmr spectra, and glpc retention volumes, with those of authentic samples. The nmr spectrum of bicyclo[2.1.0]pentane showed cyclopropyl proton absorption (complex multiplet centered at τ 9.4, 2 H), cyclobutyl proton absorption (complex multiplet centered at τ 8.48, 4 H), and bridgehead proton absorption (complex multiplet centered at τ 7.88, 2 H).

Three additional components of the reaction mixture, present in only trace amounts, were identified on the basis of their glpc retention volumes. They are cyclopentene (**5**), *trans*-1,3-pentadiene (**6**), and *cis*-1,3-pentadiene (**7**). Several even less abundant components were not identified.

Experiments discussed in the Experimental Section were performed in order to determine whether any of these products were formed as a result of irradiation in the liquid phase. We were able to conclude that this was not the case, and that gas-phase reactions were responsible for the observed transformations.

Several of the photoproducts were themselves subjected to mercury-sensitized irradiation in order to determine whether any of the observed products from **1** might, in fact, be formed in secondary reactions by a photosensitized transformation of one of the primary products. When the irradiation of vinylcyclopropane (**2**) was carried out under exactly the same conditions as the irradiation of **1**, most of **2** was recovered unchanged at the end of 14 hr, the length of a typical irradiation of **1**. The major photoreaction appeared to be

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hedron Letters, 531 (1964); K. B. Wiberg and D. S. Connor, *J. Am. Chem. Soc.*, **88**, 4437 (1966).

[10] A convenient, alternate synthesis of bicyclo[1.1.1]pentane *via* decarbonylation of bicyclo[2.1.1]hexan-2-one has just been reported by J. Meinwald, W. Szkrybalo, and D. R. Dimmel, *Tetrahedron Letters*, 731 (1967).

[11] In a similar study using somewhat different experimental conditions, however, the formation of small amounts of bicyclo[1.1.1]-pentanes, as well as of bicyclo[2.1.0]pentanes, has been observed independently by Professor R. Srinivasan. We are grateful to Professor Srinivasan for discussing his results with us prior to publication.

[12] V. A. Slabey, *J. Am. Chem. Soc.*, **74**, 4930 (1952).

slow polymer formation. Less than 1% of **3** and **1** was detected by glpc analysis.

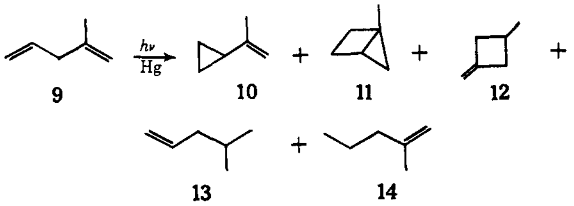
The irradiation of **5**, carried out under exactly the same conditions as the irradiation of **1**, resulted in the formation of two C_5 photoproducts and *ca.* 25% polymer. Vinylcyclopropane (**2**, 15% of the C_5 components in the reaction mixture) had been previously observed by Gunning, *et al.*,[13] in an earlier study of the mercury-photosensitized decomposition of **5**. The other product (10% of the C_5 components) was found to be cyclopentane (**8**). Unchanged cyclopentene made up the remaining 75% of the C_5 mixture.

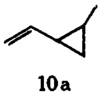
5 **2** **8**

Irradiation of a commercial mixture of the 1,3-pentadienes (**6** and **7**; 70% **6**, 30% **7**) indicated that they underwent no significant reaction other than very slow polymer formation. The ratio of *cis* to *trans* isomer did not vary over 16 hr of irradiation. Over-all, it would appear from these observations that the chief products isolated from the 1,4-pentadiene experiment were direct products of the reaction.

Further experiments were carried out with the aim of learning how substituted 1,4-dienes would react. Irradiation of 2-methyl-1,4-pentadiene (**9**) produced most of the products which might be anticipated from a knowledge of the products of the irradiation of **1**. The major photoproduct (13% of the total liquid hydrocarbon mixture remaining after 14 hr of irradiation) was identified as 2-cyclopropylpropene (**10**) by comparison of its infrared and nmr spectra, and its glpc retention volume, with those of an independently prepared authentic sample. Its nmr spectrum showed olefinic proton absorption (a singlet at τ 5.38, 2 H), a sharp singlet corresponding to an allylic methyl group (τ 8.38, 3 H), and a complex series of upfield peaks indicating cyclopropyl proton absorption (τ 8.5 to 9.7, 2 H). No evidence for the formation of the isomeric 1-methyl-2-vinylcyclopropane (**10a**) was found.

The previously unknown intramolecular cycloaddition product, 1-methylbicyclo[2.1.0]pentane (**11**), also formed in significant amount (6% of the liquid mixture) from **9**. The structure of this compound was deduced from its infrared and nmr spectra, and from its very short retention volume on a glpc column (silver nitrate–ethylene glycol) which is highly selective and predictable in its separation of olefinic and isomeric C_5 compounds.[14] In support of this structural assignment, the analogous 1,5-dimethylbicyclo[2.1.0]pentane-5-carboxylic acid, which has been described recently,[15] has an nmr spectrum which corresponds closely to that of **11**. The nmr spectrum of **11** showed a sharp methyl singlet (τ 8.74, 3 H) superimposed upon a complex series of peaks due to bridgehead and cyclobutyl proton absorption (τ 7.94 to 8.89, 5 H), and cyclopropyl proton absorption (τ 9.34 to 9.6, 2 H).



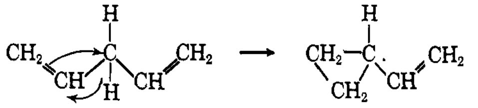


10a

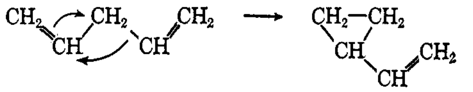
The remaining C_6H_{10} component formed from **9** (**12**, 2.6%) was found to have no analog in the irradiation of **1**. It was identified as 1-methyl-3-methylenecyclobutane on the basis of a comparison of its infrared and nmr spectra with those of an authentic sample.[16] The nmr spectrum of **12** exhibited olefinic proton absorption (τ 5.23 to 5.45, 2 H), a complex series of cyclobutyl proton absorption peaks (τ 6.9 to 8.0, 5 H), and a methyl proton doublet (centered at τ 8.84, 3 H, $J = 6$ cps).

Both of the expected methylpentenes, **13** and **14**, presumably resulting from the scavenging of hydrogen atoms in the system, were formed. However, the more highly substituted double bond of **9** was found to be reduced preferentially. The resulting 4-methyl-1-pentene (**13**) made up *ca.* 3% of the liquid mixture, while the isomeric 2-methyl-1-pentene (**14**) amounted to only *ca.* 0.2%. Both of these olefins were identified by comparison of their infrared and nmr spectra, and their glpc retention volumes, with those of authentic samples.

Our initial results with **1** and **9** show that vinylcyclopropane formation is an important process in both of these mercury photosensitized reactions. Independent of the detailed nature of the reaction mechanisms, two fundamentally different types of pathway which might be invoked to rationalize these transformations are given in eq 1 and 2. The first of these involves a hydrogen atom migration, with retention of the integrity of the carbon skeleton, while the second involves a vinyl group migration, but maintains the integrity of all the carbon–hydrogen bonds. In order to test the hypothesis that the hydrogen atom rearrangement pathway 1 might be required for the observed isomerizations, two 3,3-disubstituted 1,4-pentadienes, for which such a mechanism cannot occur, were prepared and studied.



(1)



(2)

Mercury-sensitized irradiation of 3,3-dimethyl-1,4-pentadiene (**15**)[17,18] was found after 24 hr to give two major volatile photoproducts, along with 15–20% of polymer. The more abundant product (*ca.* 35% overall, after 24 hr of irradiation) was shown to be 5-methyl-1,4-hexadiene (**16**) by comparison of its nmr and infrared spectra with those of an authentic sample. The nmr spectrum showed complex vinyl and olefinic proton absorption (τ 3.9 to 5.24, 4 H), an allylic proton triplet

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[13] W. A. Gibbons, W. F. Allen, and H. E. Gunning, *Can. J. Chem.*, **40**, 568 (1962).

[14] J. Shabtai, J. Herling, and E. Gil-Av, *J. Chromatog.*, **11**, 32 (1963).

[15] M. J. Jorgenson, *J. Am. Chem. Soc.*, **88**, 3463 (1966).

[16] We are indebted to Dr. Jean-Louis Ripoll for providing these data.

[17] L. Schmerling and J. P. West, *J. Am. Chem. Soc.*, **74**, 2885 (1952).

[18] R. Ciola and R. L, Burwell, Jr., *J. Org. Chem.*, **23**, 1063 (1958).

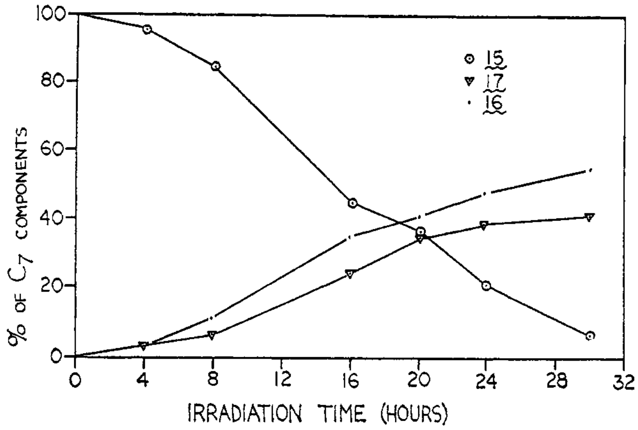
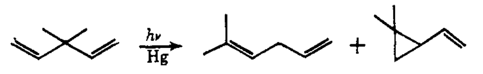


Figure 3. Irradiation of 3,3-dimethyl-1,4-pentadiene.

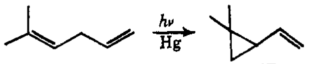
(centered at τ 7.30, J = *ca.* 6 cps, 2 H), and two allylic methyl absorptions at τ 8.33 and 8.43.



15 **16** **17**

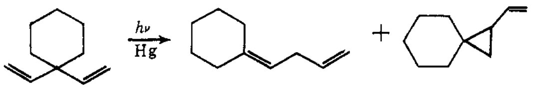
The second photoproduct (*ca.* 30% over-all) was identified as the previously unknown 1,1-dimethyl-2-vinylcylopropane (**17**). It exhibited an nmr spectrum with vinyl group absorption (τ 4.28 to 5.23, 3 H), and a sharp pair of methyl absorptions (τ 8.90 and 8.97, each 3 H) superimposed upon a complex cyclopropyl proton absorption region (τ 8.60 to 9.80, 3 H). The structure of **17** was proved by a Lemieux oxidation, which gave the well-characterized 2,2-dimethylcyclopropanecarboxylic acid,[19,20] identified by a comparison of infrared and nmr spectra with those of an authentic sample. This result demonstrates that vinylcyclopropane formation *can* entail carbon-skeleton rearrangement, but it leaves unanswered the question of whether a direct rearrangement of type 2 is involved, or whether **15** rearranges first to **16**, which then cyclizes *via* a type 1 reaction. The qualitative progress of this irradiation may be seen in Figure 3.

In an attempt to clarify this point, a sample of **16** was collected by preparative glpc and irradiated under the same conditions. The sensitized irradiation of **16** in fact gave **17** as the sole product, but no clear-cut answer to the mechanistic question can be obtained without a more careful analysis of the relative rates of the reactions concerned.



16 **17**

The final 1,4-diene to be prepared and irradiated was 1,1-divinylcyclohexane (**18**). This compound was synthesized in a manner analogous to that used to prepare **15**. Commercially available 3,3-pentamethylene-1,5-pentanediol reacted with phosphorus tribromide to give an intermediate 1,5-dibromo compound which was subsequently dehydrohalogenated. The mercury-sensitized irradiation of **18** also gave only two monomeric products, which were found to be analogous to those obtained from **15**. The reaction, however, was found to be considerably slower than was the case with **15**. Thus, a typical run took 70 hr at room temperature, possibly because of the much lower volatility of **18**. One of the products (comprising 5% of the liquid hydrocarbon mixture) was assigned structure **19** on the basis of its infrared and nmr spectra, and by a comparison of these spectra with those of the closely related **16**. The nmr spectrum of **19** showed olefinic and vinyl proton absorption (τ 3.8 to 5.25, 4 H), a doubly allylic proton triplet (centered at τ 7.30, 2 H), a broad allylic proton absorption (τ 7.90, 4 H), and a broad absorption (τ 8.47, 6 H) corresponding to expectations for the remaining six alicyclic protons.

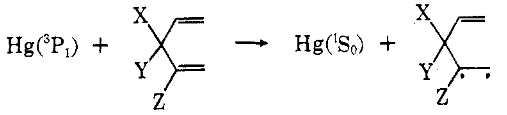


18 **19** **20**

The second product (comprising 9% of the liquid hydrocarbon mixture) was assigned structure **20** on the basis of the following evidence. Its nmr spectrum showed vinyl group proton (τ 4.00 to 5.20, 3 H), a sharp singlet for the absorption of all ten alicyclic protons (τ 8.52, 10 H) superimposed upon a complex multiplet arising from the single allylic cyclopropyl proton (τ 8.6 to 9.0, 1 H), and a complex cyclopropyl proton absorption (τ 9.26 to 9.74, 2 H). The infrared and nmr spectra of **20** were very similar to the corresponding spectra of the analogous 1,1-dimethyl-2-vinylcyclopropane (**17**), characterized earlier in this work. Unfortunately, the amounts of material available in this series were too small to permit a study of the possible role of **19** as a precursor to **20**.

Discussion

Taking into account the results of earlier studies on mercury-photosensitized rearrangements of some simple olefins,[3] it would appear that the most likely initial step in the reactions of 1,4-dienes would involve diene excitation by an excited Hg atom, raising one of the double bonds to a vibrationally excited triplet state (eq 3).



(3)

It would be desirable to determine whether the initial excited state of the olefin is, in fact, produced through the quenching of the $Hg(^3P_1)$ state (with 112.2 kcal of electronic excitation energy), or, alternatively, by the quenching of the much longer lived metastable $Hg(^3P_0)$ state (with 107.2 kcal of electronic excitation energy). The fact that the $^3P_0$ state has a significantly longer lifetime than the $^3P_1$ state[21] suggests that it might possibly play a role in mercury-photosensitized reactions, if it were produced in sufficient concentration to be utilized.

Callear and Norrish[22] have studied the production of the metastable $^3P_0$ state in a variety of systems. They found that the metastable atoms were not produced in the flash irradiation of mercury vapor in the presence of

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[19] R. S. Bly and R. T. Swindell, *J. Org. Chem.*, **30**, 10 (1965).

[20] D. J. Patel, M. E. H. Howden, and J. D. Roberts, *J. Am. Chem. Soc.*, **85**, 3218 (1963).

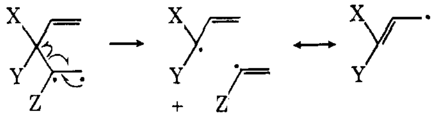
[21] See Calvert and Pitts, ref 3, p 80.

[22] A. B. Callear and R. G. W. Norrish, *Proc. Royal Soc.* (London), **A266**, 299 (1962).

H_2, C_2H_6, C_2H_4, NO, or N_2O. These gas mixtures were studied with added argon, and it was found that in no case could the $^3P_0$ state be detected. A more recent study by Gunning, *et al.*,[23] has shown that with low molecular weight alkanes in general, no significant amount of the metastable state was produced.

It has been determined that small quantities of nitrogen may quench the $^3P_1$ state to the metastable state. However, in the light of the insignificant difference between the irradiation of **1** in an argon atmosphere and in an atmosphere of nitrogen, it seems likely that the metastable $^3P_0$ state does not play an important role in the presently reported reactions of 1,4-dienes,

Focusing on the necessity of rationalizing the carbon skeleton rearrangements illustrated by **15** → **16**, and **18** → **19**, the initial excitation of one of the double bonds of the 1,4-diene to a vibrationally excited triplet state may be imagined, as one possibility, to be followed by the cleavage of an allylic C–C bond to give a vinyl radical and an allyl radical (eq 4). In accord with known trends in radical reactions, when Z represents an alkyl group, the bond cleavage leading to the more substituted vinyl radical should be preferred. On the basis of the experimental results, it must be assumed that the resultant radical pairs undergo further reaction without separating, since there is no evidence for cross-coupling products. Recombination of the radical fragments to regenerate the starting material (eq 5) is one possible sequel which leads to no net change. Since an allylic radical is a resonance hybrid, however, it may undergo recombination with the vinyl radical at its opposite end (eq 6). If both X and Y are H atoms, the product of this transformation will be indistinguishable from the starting material. However, if X and/or Y should be alkyl groups, then a new, terminally substituted 1,4-diene is obtained. This mechanism could account for the isomerization of **15** (X, Y = CH_3; Z = H) and **18** (X, Y = pentamethylene; Z = H) to **16** and **19**.



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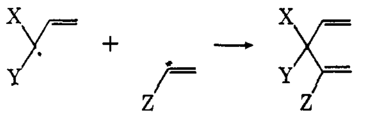

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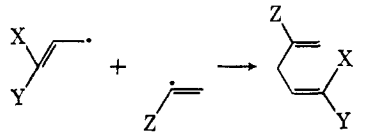
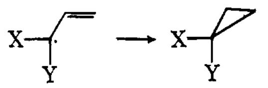


(6)

Another sequel to radical-pair formation might involve isomerization of the allylic radical to a cyclopropyl radical prior to recombination with the vinyl radical (eq 7 and 8). These transformations would account for the formation of **2** (X = Y = Z = H), **10** (X, Y = H; Z = CH_3), **17** (X, Y = CH_3; Z = H), and **20** (X, Y = pentamethylene; Z = H) from **1** (X = Y = Z = H), **9** (X, Y = H; Z = CH_3), **15** (X, Y = CH_3; Z = H), and **18** (X, Y = pentamethylene; Z = H), respectively.



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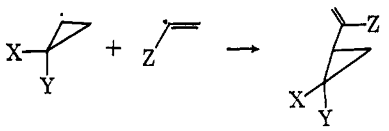
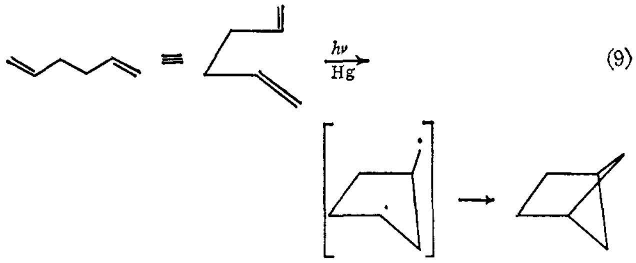
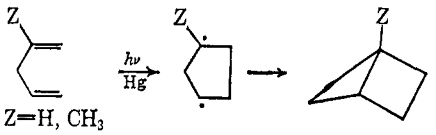


(8)

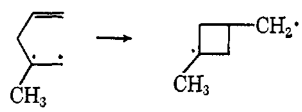
Thus far we have been able to rationalize both the formation of vinylcyclopropanes and of rearranged 1,4-dienes by assuming that the excited dienes can undergo carbon–carbon bond fission. Since the formation of bicyclo[2.1.0]pentanes is also significant in the reactions of **1** and **9**, a path must also be sought for this previously unobserved mode of cycloaddition. The intramolecular addition of one olefinic group to another in a photochemical reaction is well known.[5–7,24] This may either occur in a head-to-head or in a head-to-tail manner, and many examples of these processes may be found in the literature. It has been suggested[7] that in a molecule such as 1,5-hexadiene, where two olefinic groups have the freedom to twist with respect to each other, the preferred orientation is head-to-tail rather than head-to-head (eq 9). In the present study of 1,4-dienes, head-to-head addition adducts (the bicyclo[2.1.0]pentanes **3** and **11**) appear to be favored (eq 10), and there was no evidence for the formation of the head-to-tail addition products (bicyclo[1.1.1]pentanes).[11] Our observations seem to point to a preference for forming a secondary cyclopentyl radical, rather than a more highly strained primary cyclobutylcarbinyl radical. In this context, however, the formation of **12** from **9** takes on special interest, since it may be the result of an incomplete intramolecular head-to-tail addition. The triplet derived from **9** might undergo ring closure to form the diradical shown in eq 11, which might go on to **12** by means of an intramolecular hydrogen atom transfer as shown in eq 12.



(9)



(10)



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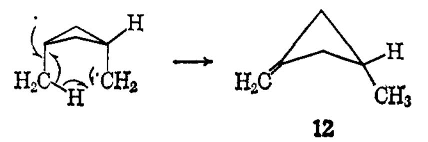

12

(12)

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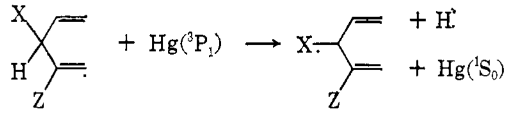
[23] S. Penzes, A. J. Yarwood, O. P. Strausz, and H. E. Gunning, *J. Chem. Phys.*, **42**, 4524 (1965).

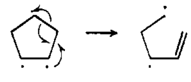
[24] For a very convenient summary, see W. L. Dilling, *Chem. Rev.*, **66**, 373 (1966).

That atomic hydrogen is an important intermediate in some of these reactions may be seen in the fact that monoolefins, presumably resulting from the scavenging of hydrogen atoms, are important products. The most likely reaction leading to the formation of atomic hydrogen is the rupture of the allylic C–H bond of the starting material in a primary decomposition step (eq 13). Polymer formation, which is important for each of these diene reactions, could result from subsequent reactions of the resultant radicals. In the case where the central carbon atom is fully substituted (**15** and **18**) no hydrogenated products would be anticipated, and none were found.



(13)

The formation of cyclopentane and vinylcyclopropane from the mercury-photosensitized decomposition of cyclopentene may also proceed *via* initial cleavage of allylic C–C and C–H bonds of the excited olefin (eq 14 and 15). The diradical formed in eq 14 may recyclize to give the vinylcyclopropane (eq 16). The atomic hydrogen produced in eq 15 would be scavenged by cyclopentene to give the cyclopentyl radical which may then scavenge another hydrogen atom and form cyclopentane, or initiate polymer formation (as would the cyclopentenyl radical).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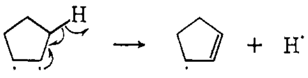

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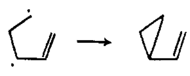
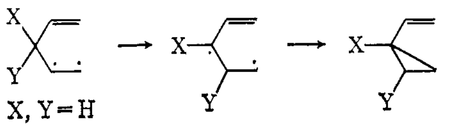
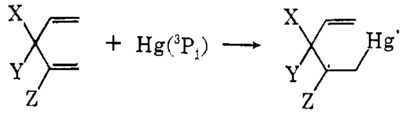

(16)

A distinctive feature of the above mechanisms (eq 7, 8, 14, and 16) for vinylcyclopropane formation is that they retain the integrity of all C–H bonds, but require carbon skeleton rearrangement. An entirely different pathway can be imagined in which hydrogen atom migration would play a key role. The possibility of a 1,2-hydrogen transfer mechanism for the formation of the vinylcyclopropane photoproducts is shown in eq 17. It is perhaps a less attractive alternative, since it necessitates the postulation of a reaction pathway entirely separate from that required for the production of a rearranged 1,4-diene (eq 6). In addition, the work of Placzek and Rabinovitch[25] on the photochemical decomposition of 1-pentene indicated that 1,2-hydrogen transfers of the sort shown in eq 17 are not preferred mechanisms. Further work needs to be carried out, however, in order to determine conclusively whether a 1,2-hydrogen shift occurs in our cases.

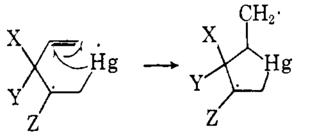


(17)

An intriguing alternative to the initial *cleavage* of either the allylic C–C or C–H bonds of the starting materials, and one which is more speculative, would involve formation of a transient, excited mercury compound by a radical *addition* mechanism (eq 18). This organometallic diradical could then undergo cyclization to form a five-membered ring intermediate (eq 19). There is an analogy for this type of reaction found in the rearrangement of the 5-hexenyl radical to the cyclopentylmethyl radical.[26,27] The heterocyclic ring could then open to form an excited allyl vinyl mercury intermediate (eq 20). This intermediate might subsequently decompose into mercury and two free-radical fragments which could then combine to form a rearranged (or unrearranged) diene (eq 21). A similar process has in fact been postulated in the thermal decomposition of diallylmercury into mercury and 1,5-hexadiene.[28] Independent experiments aimed at evaluating the possible role of organomercury intermediates in the diene reactions under discussion would appear to be desirable.



(18)



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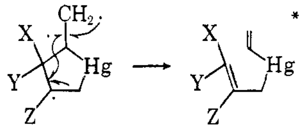

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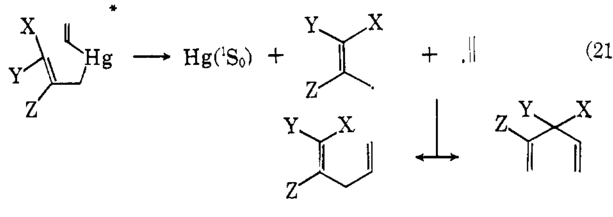
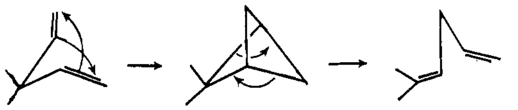


(21)

Finally, it should be pointed out that a unique and attractive mechanism for the formation of rearranged 1,4-dienes (but not the other products) could involve the previously discussed head-to-tail ring closure to give a transient bicyclo[1.1.1]pentane, followed by ring opening in an alternate direction (eq 22). If the postulated bicyclo[1.1.1]pentane shown in this mechanism returned to its ground state before going on, this hypothesis might be tested by examining the mercury-sensitized photochemistry of **21**. However, if an excited **21** is formed which goes directly to **16**, this simple test would not be significant.


9 **21** **16**
(22)

In summary, our studies have revealed the generality of vinylcyclopropane formation from 1,4-dienes, un-

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(25) D. W. Placzek and B. S. Rabinovitch, *Can. J. Chem.*, **43**, 820 (1965).

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

(27) A. S. Gordon and S. R. Smith, *J. Phys. Chem.*, **66**, 521 (1962).

(28) K. V. Vijayaraghavan, *J. Indian Chem. Soc.*, **20**, 318 (1943).

covered the cycloaddition to form bicyclo[2.1.0]pentanes, and detected the novel transformation of 1,4-dienes to isomeric 1,4-dienes. This work raises a number of mechanistic questions, and we hope to pursue some of these problems in a continuation of this study.

Experimental Section

All boiling points are uncorrected. Microanalyses were performed by the Galbraith Laboratories, Knoxville, Tenn.

Infrared Spectra. Infrared spectra were generally recorded on a Perkin-Elmer Infracord, Model 137 B. The double bond stretching frequency of olefin **12** was measured on a Perkin-Elmer grating infrared spectrometer, Model 337.

Nuclear Magnetic Resonance Spectra. Nmr spectra were taken on a Varian A-60 spectrometer in carbon tetrachloride, using tetramethylsilane as an internal standard.

Gas-Liquid Partition Chromatography (glpc). Analytical determinations were carried out on an Aerograph Model 600 Hy-Fl chromatograph and a Beckman GC-2 chromatograph. Stainless steel columns with the following liquid phases were used: 6 ft × 1/8 in. of 20% 1,2,3-tris(2-cyanoethoxy)propane (TCEP) on 40–60 mesh Firebrick, A; 14 ft × 1/4 in. of 20% TCEP on 40–60 mesh Firebrick, B; 8 ft × 1/8 in. of silver nitrate–ethylene glycol[29] on acid-washed 60–80 mesh Chromosorb P, D: and 6 ft × 1/8 in. of 5% SE-30 on acid-washed 60–80 mesh Chromosorb W, F.

The Beckman GC-2 chromatograph was used for preparative glpc. The following columns were used: 14 ft × 1/4 in. of 20% TCEP on 40–60 mesh Firebrick, B; 15 ft × 1/2 in. of 20% TCEP on 40–60 mesh Firebrick, C; 11 ft × 1/4 in. of silver nitrate–ethylene glycol on acid-washed 60–80 mesh Chromosorb P, E; and 9 ft × 1/4 in. of 20% Nitrile Silicone XF-1150 on 80–100 mesh Firebrick, G.

Flow rates were determined by the use of a soap bubble flowmeter and a stopwatch. Retention data is expressed in terms of the relative retention volume ($V'_R/V'_{R(\text{diene starting material})}$, where $V'_R = V_{R(\text{obsd})} - V_{R(\text{air})}$) and the corrected retention time ($t' = t_{\text{obsd}} - t_{\text{air}}$) of the diene starting material, unless otherwise noted. Mixture compositions are expressed in terms of the gas chromatogram peak areas. They are uncorrected for any differences in thermal conductivity.

Irradiation of 1,4-Pentadiene (1). A mixture of 1,4-pentadiene (3.4 g, 0.0515 mole; Aldrich Chemical Co., 98%) and mercury (*ca.* 3 g) was frozen in a 500-ml round-bottomed quartz flask by immersion into liquid nitrogen. The flask was twice evacuated to less than 1 mm pressure using a standard vacuum system from which stopcock grease was not excluded, and refilled with prepurified nitrogen. The nitrogen pressure was then reduced to *ca.* 0.5 mm, after which the flask was isolated from the vacuum system by a stopcock and the contents allowed to warm to room temperature. Irradiation was carried out with a bank of eight germicidal lamps (General Electric G15T8) arranged in a circle with their long axis vertically inclined. During the irradiation the temperature of the reaction mixture rose to *ca.* 35° as determined by an external thermometer in the proximity of the reaction vessel. The progress of the irradiation was followed by shutting off the lamps, cooling the reaction mixture in a Dry Ice–acetone bath, filling the reaction vessel with prepurified nitrogen to atmospheric pressure, and removing a small (*ca.* 0.05 ml) aliquot for glpc analysis. After 8 hr of irradiation, three photoproducts had been formed in significant amounts and the ratio of **1** to major photoproduct **2** was estimated to be 7:2 by glpc (column B at 25°). The liquid portion of the reaction mixture (3.25 g) was then decanted from the mercury and solid polymer in the reaction flask, and separated by preparative glpc (column C at 25°). The individual components were collected in Dry Ice-acetone-cooled receivers and subsequently identified. Polymeric products were retained on the preparative glpc column (at 25°) and were later analyzed through the use of temperature-programmed glpc (column A from 25 to 135°; rate of temperature increase, 10°/min). Further irradiation of the reaction mixture did not result in appreciably more of the monomeric products, but rather in higher molecular weight products and less **1**.

Characterization of the Photoproducts Derived from 1. The major product **2** (18% over-all, estimated by glpc) was shown to be identical with an authentic sample of vinylcyclopropane, prepared by a modification of the previously reported dehydration of methylcyclopropylcarbinol over alumina.[12] The nmr spectrum of each showed three separate complex groups from τ 4.32 to 5.30 (3), 8.42 to 8.90 (1), and 9.17 to 9.80 (4). The infrared spectra of both samples were superimposable and were identical with the published spectrum of vinylcyclopropane.[12] Relative retention volumes on two glpc columns (column B at 25°: $V'_2/V'_1 = 2.8$, $t'_1 = 6.4$ min; column D at 25°: $V'_2/V'_1 = 0.92$, $t'_1 = 25.8$ min) also showed the two compounds to be identical.

Vinylcyclopropane (2). Dehydration of methylcyclopropylcarbinol was achieved by injection of the carbinol (20 g, 0.232 mole) into a nitrogen carrier stream through a 30 × 1/2 in. coiled aluminum tube packed with alumina chips and heating in a glpc oven to 245°. A nitrogen inlet pressure of 50 psi resulted in the optimum yield of the olefin. The crude yellow product (7.0 g) was collected in a Dry Ice–acetone cooled trap. Purification by preparative glpc (column C at 25°) gave the clear, colorless vinylcyclopropane (3.3 g, 21%), $n^{20}\text{D}$ 1.4143 (lit.[12] $n^{20}\text{D}$ 1.4138).

Bicyclo[2.1.0]pentane (3). In addition to vinylcyclopropane, two other products were formed in significant amounts during the mercury-photosensitized irradiation of **1**. Compound **3** was formed in *ca.* 3% yield. Its infrared spectrum (CCl_4) showed absorption maxima at 3.25, 3.48, 6.07, 6.85, 6.95, 7.85, 9.52, 9.75, 10.08, 10.35, and 11.00 μ. The nmr spectrum showed three complex groups of peaks centered at τ 7.88 (2), 8.58 (4), and 9.4 (2).

Comparison of the nmr and infrared spectra of **3** with those of an authentic sample of bicyclo[2.1.0]pentane obtained from Professor P. G. Gassman indicated that the two compounds were identical. This was confirmed by their having identical glpc relative retention volumes on two columns (column B at 25°: $V'_3/V'_1 = 2.0$; column D at 25°: $V'_3/V'_1 = 0.039$).

1-Pentene (4). A second minor product **4** was formed in *ca.* 2% yield. A comparison of its nmr and infrared spectra, as well as glpc relative retention volumes on two columns (column B at 25°: $V'_4/V'_1 = 0.59$; column D at 25°: $V'_4/V'_1 = 0.15$), with those of a 99.95% (mole) sample of 1-pentene supplied by the Phillips Petroleum Co. proved the two compounds to be identical.

Trace Products from the Irradiation of 1. Three components of the photoreaction mixture present in *ca.* 0.1% were identified on the basis of their glpc relative retention volumes on two columns at 25°. These were cyclopentene (**5**) (column B: $V'_5/V'_1 = 1.9$; column D: $V'_5/V'_1 = 0.78$), *trans*-1,3-pentadiene (**6**) (column B: $V'_6/V'_1 = 2.3$; column D: $V'_6/V'_1 = 0.35$), and *cis*-1,3-pentadiene (**7**) (column B: $V'_7/V'_1 = 2.5$; column D: $V'_7/V'_1 = 0.50$). In the same manner, it was shown that neither isoprene nor spiropentane was present. Data for the spiropentane was acquired from an authentic sample obtained from Professor D. E. Applequist.

Irradiation of Vinylcyclopropane (2). Vinylcyclopropane (3.1 g, 0.045 mole) and mercury (*ca.* 3 g) were irradiated in a manner similar to that described for the irradiation of **1**. The flask was isolated from the vacuum system at a nitrogen pressure of 40 mm and the irradiation carried out for 14 hr. The reaction mixture was sampled hourly by cooling the reaction vessel in a Dry Ice–acetone bath, introducing nitrogen to atmospheric pressure, and removing a small sample for glpc analysis (columns B and D at 25°). The contents of the flask was then frozen in liquid nitrogen and the system reevacuated to a nitrogen pressure of 40 mm. Most of the vinylcyclopropane was recovered unchanged at the end of 14 hr. A few higher molecular weight products were formed, as well as less than 1% of bicyclo[2.1.0]pentane and 1,4-pentadiene, as determined by glpc analysis (columns B and D at 25°).

Irradiation of Cyclopentene (5). Cyclopentene (3.85 g, 0.056 mole) and mercury (*ca.* 3 g) were irradiated using a procedure identical with that described for the irradiation of **2**. At the end of 14 hr, two photoproducts had been formed in significant amounts. The first was shown to be vinylcyclopropane (15% of the C_5 components) by direct comparison of its glpc retention data (columns B and D) and its infrared and nmr spectra with those of an authentic sample of vinylcyclopropane synthesized previously. Cyclopentane (**8**) (10% of the C_5 components) was also identified in the product mixture by direct comparison of its glpc retention data on two columns at 25° (column B: $t' = 6.9$ min; column D: $t' = 0.5$ min) and its infrared and nmr spectra with those of an authentic sample (Aldrich Chemical Co.). Unchanged cyclopentene made up 75% of the C_5 component mixture. Nearly a quarter of the irradiation mixture consisted of higher molecular weight materials.

Irradiation of 1,3-Pentadiene (6 and 7). A commercial mixture of *cis*-1,3-pentadiene (**6**, 30%) and *trans*-1,3-pentadiene (**7**, 70%)

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[29] Stationary phase: 30 g of silver nitrate/100 ml of ethylene glycol in a weight ratio of solid support to liquid phase of 3:1.

(3.4 g, 0.05 mole; Aldrich Chemical Co.) and mercury (*ca.* 3 g) was irradiated using the procedure given for the irradiation of **2**. The relative amount of *cis* and *trans* isomers was determined by preparative glpc separation (column C at 25°) and by their nmr spectra. After 16 hr of irradiation, most of the 1,3-pentadiene was recovered unchanged. Trace amounts of 1,4-pentadiene (*ca.* 0.1%) and some higher molecular weight products were found. There was no significant change in the proportions of the *cis* and *trans* isomers as determined by glpc (columns B and D at 25°).

Irradiation of 2-Methyl-1,4-pentadiene (9). A mixture of a commercial sample of **9** (2.85 g, 0.035 mole; Aldrich Chemical Co.) and mercury (*ca.* 3 g) was irradiated under a nitrogen atmosphere at reduced pressure in the same manner as was described for the irradiation of **1**. The reaction mixture was sampled at intervals by cooling the reaction vessel in a Dry Ice–acetone bath, introducing nitrogen to atmospheric pressure, and removing a small sample for glpc analysis (column A and column B at 50°). At the end of 18 hr, the reaction was stopped. From the glpc data (column B at 25°), it was apparent that the optimum length of irradiation time, in terms of low molecular weight product yield, was *ca.* 14 hr under the conditions used. Longer irradiations resulted in a decreased yield of all low molecular weight products.

Characterization of the Major Photoproduct 10 from the Irradiation of 9. The liquid portion of the reaction mixture (2.4 g) was decanted from the mercury and solid polymer in the reaction vessel after 14 hr of irradiation. This was then separated into three fractions by preparative glpc (column C at 25°). These fractions were collected in Dry Ice–acetone-cooled receivers, and exhibited the following glpc (column B at 25°; t'_9 = 7.8 min) relative retention data: V'/V'_9 = 0.45 (3% of the total liquid mixture), 1.0 (84%), and 2.44 (13%). Through the use of glpc (columns B and D at 25°), the first and last fractions were shown to contain only a single component, while the middle fraction was found to be composed of several components, the chief one being the starting material, **9**. The fraction with the largest retention volume, the major photoproduct **10**, showed infrared absorption maxima (CCl$_4$) at 3.22, 3.36, 6.10, 6.92, 7.25, 9.56, 9.80, 10.42, and 11.2 μ. Its nmr spectrum exhibited olefinic proton absorption as a singlet at τ 5.38 (2), a sharp singlet corresponding to an allylic methyl group at τ 8.38 (3), and a complex series of peaks from τ 8.5 to 9.7 (5). Compound **10** was proven to be 2-cyclopropylpropene by direct comparison of its glpc behavior and spectral properties with those obtained for an authentic sample, prepared by the dehydration of dimethylcyclopropylcarbinol.

2-Cyclopropylpropene. The dehydration of dimethylcyclopropylcarbinol was carried out as described by Boord, *et al.*[30] In a 50-ml flask equipped with a short Vigreux distillation column was placed the carbinol (12.2 g, 0.12 mole), sulfuric acid (four drops), and several boiling chips. The mixture was heated to a slow boil (bath temperature 120°) and the dehydration product collected as it distilled through the column. The temperature at the head of the column was not allowed to rise above 65°. The distillate was washed with water, dried over molecular sieves, and fractionally distilled through a micro (8 in.) spinning-band column at 68.5 to 69.5° (atmospheric pressure) to give pure 2-cyclopropylpropene (5.25 g, 53%), n^{20}D 1.4200 [lit.[30] bp 70.41° (760 mm), n^{20}D 1.4254]. The nmr and infrared spectra, as well as the glpc retention volume were identical with those obtained for the photoproduct **10**.

Characterization of the Minor Photoproducts from the Irradiation of 9. The product with the smallest retention volume (column B at 25°) exhibited infrared absorption maxima (CCl$_4$) at 3.40, 6.11, 6.87, 7.22, 7.30, 10.10, and 11.00 μ. The nmr spectrum showed olefinic proton absorption from τ 4.0 to 5.4 (3), a complex multiplet from τ 7.9 to 9.0 (3), and a doublet (J = *ca.* 6 cps) centered at τ 9.1 (6). This compound was proven to be 4-methyl-1-pentene (**13**) by direct comparison of its infrared and nmr spectra, as well as its glpc retention volume (columns B and D at 25°), with those obtained from an authentic sample of 99.82% (mole) 4-methyl-1-pentene supplied by the Phillips Petroleum Co.

The middle fraction was further separated into four additional components by preparative glpc (column E at 40°). These components showed glpc relative retention volumes (column E at 40°; t'_9 = 12.9 min) of 0.11, **11** (6% of the total liquid portion of the reaction mixture after 14 hr of irradiation); 0.25, **14** (0.2%); 0.77, **12** (2.6%); and 1.0, **9** (75%). The component with the largest retention volume was shown to be pure starting material, **9**, by direct comparison of its infrared and nmr spectra, and its glpc retention volumes (column B at 25°).

Compound **11** exhibited infrared absorption maxima (CCl$_4$) at 3.45 (s), 6.92 (s), 7.22, 7.40, 8.30, 9.02, 9.45, 9.74, 10.6, and 10.7 μ. The nmr spectrum showed a sharp singlet at τ 8.74 (3) superimposed upon a complex multiplet from τ 7.94 to 8.89 (5), and a complex cyclopropyl proton absorption from τ 9.34 to 9.6 (2). This spectrum is similar to the recently reported nmr spectrum of 1,5-dimethylbicyclo[2.1.0]pentane-5-carboxylic acid.[15] Compound **11** was identified as 1-methylbicyclo[2.1.0]pentane on the basis of these infrared and nmr spectra and its glpc retention volumes on two columns (column E at 40°; column B at 25°) which are highly selective and predictable in their retention of small ring and olefinic compounds.[14]

The second component to be eluted, **14**, showed infrared absorption maxima (CCl$_4$) at 3.45, 6.1, 6.9, 7.3, 10.95, and 11.2 μ. The nmr spectrum showed olefinic proton absorption at τ 5.36 (2), a singlet methyl at τ 8.33 (3), and a complex series of peaks from τ 7.8 to 9.3 (7). A comparison of its nmr and infrared spectra, as well as glpc retention volumes on two columns (column E at 40°; column B at 25°), with those of a 99.89% (mole) sample of 2-methyl-1-pentane supplied by the Phillips Petroleum Co., proved the two compounds identical.

The remaining component, **12**, showed infrared absorption maxima (CCl$_4$) at 3.43, 5.96 (1675 cm^{-1}), 6.90, 7.04, 7.23, and 7.46 μ. Its nmr spectrum showed olefinic proton absorption from τ 5.23 to 5.45 (2), a complex series of peaks from τ 6.9 to 8.0 (5), and a methyl doublet (J = *ca.* 6 cps) centered at 8.84 (3). Comparison of the above spectra with those obtained from an authentic sample of 1-methyl-3-methylenecyclobutane prepared by Dr. J. L. Ripoll, showed the two compounds to be the same.

1,3-Dibromo-3-methylbutane (21). Isoprene (88.0 g, 1.42 moles) was placed in a water-cooled gas-bubbling apparatus (40 × 2 cm) and hydrogen bromide bubbled through it at room temperature for a period of 8 hr at a moderate rate. Analysis of the reaction mixture for production of **21** by glpc (5% SE-30 at 100°) at frequent intervals showed the reaction to be virtually complete by the end of 6 hr, with the desired dibromide formed in nearly quantitative yield. The crude **21** was allowed to stand uncovered in a wide-mouth vessel for several hours to allow the dissolved hydrogen bromide to escape. The impure **21** was poured into a separatory funnel, and water and ether were added. The ethereal layer was washed four times with water, four times with saturated sodium bicarbonate, twice more with water, and was finally dried over anhydrous magnesium sulfate. The ether was removed from the dibromide on a rotary evaporator after filtration from the drying agent, and the residue was fractionally distilled through a short Vigreux column at 76° (16 mm) to give pure **21** (262 g, 81%), n^{25}D 1.5045 [lit.[11] bp 54–55° (4 mm), n^{20}D 1.5065]. The infrared spectrum (neat) of this compound showed absorption maxima at 3.45, 6.92, 7.30, 7.46, 7.72, 8.10, 8.47, 8.72, 9.15, and 11.92 μ. The nmr spectrum showed an unsymmetrical triplet centered at τ 6.54 (2), an unsymmetrical quartet centered at τ 7.72 (2), and a sharp singlet at τ 8.26 (6).

1,5-Dibromo-3,3-dimethylpentane (22). This compound was prepared following the procedure by Schmerling and West.[17] To a sample of **21** (43.4 g, 0.174 mole) cooled to −50° was added aluminum trichloride (1.5 g, 0.011 mole). Ethylene was then bubbled into the magnetically stirred mixture and the temperature allowed to rise to from −20 to −10°, at which temperature absorption of the olefin began. Ethylene was bubbled through the mixture at a rate at least as fast as it was absorbed, as determined by the difference in bubbling rate in an inlet and exit bubbler. The temperature of the mixture was kept at *ca.* −15° for 1.5 hr, at which time the absorption of olefin had nearly ceased. The dark gummy mixture was filtered and fractionally distilled at 89–90° (2 mm) giving pure **22** (23 g, 51%), n^{25}D 1.5058 [lit.[17] bp 98–99° (3 mm), n^{20}D 1.5091]. The infrared spectrum (neat) showed absorption maxima at 3.40, 6.72, 7.21, 7.31, 7.51, and 8.10 μ. The nmr showed a complex triplet centered at τ 6.72 (4), a complex triplet centered at τ 8.18 (4), and a sharp singlet at τ 9.05 (6). This product had a tendency to turn lavender color when allowed to stand at room temperature.

3,3-Dimethyl-1,4-pentadiene (15). The dehydrohalogenation of **22** was achieved by utilizing the procedure developed by Ciola and Burwell[18] for the dehydrohalogenation of 1,5-dichloro-3,3-dimethylpentane. A mixture of **22** (23 g, 0.089 mole), 2-methylquinoline (55 g, 0.4 mole), and sodium iodide (3 g, 0.02 mole) was refluxed in a small distillation assembly. The reflux rate was maintained so that the temperature at the head of the Vigreux distillation column never rose above 60°. Reaction was slow and

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(30) R. Van Wolkenburgh, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *J. Am. Chem. Soc.*, **71**, 172 (1949).

several hours were necessary before **15** began to distil out of the mixture. The entire reaction took 8 hr. The distillate was dried and redistilled through a micro (8 in.) spinning-band column at 69.5–70° (atmospheric pressure) to give pure **15** (4.0 g, 47%) [lit.[18] bp 70.2° (750.5 mm)]. The infrared spectrum (neat) showed absorption maxima at 3.18, 3.3, 5.4, 6.08, 6.8, 7.07, 7.25, 7.33, 8.57, 9.5, 9.98, and 10.90 μ. The nmr spectrum exhibited a typical vinyl group absorption with an unsymmetrical quartet centered at τ 4.17 (2) and a complex multiplet centered at τ 5.08 (4) as well as a singlet at τ 8.90 (6).

Irradiation of 3,3-Dimethyl-1,4-pentadiene (15). A mixture of **15** (7.4 g, 0.077 mole) and mercury (*ca.* 3 g) was frozen in a 500-ml quartz flask equipped with a magnetic stirrer, by immersion into liquid nitrogen. The irradiation was carried out under a nitrogen atmosphere at reduced pressure in the same manner as was described in the irradiation of **1.** The reaction mixture was sampled at intervals by cooling the reaction vessel in a Dry Ice–acetone bath, introducing nitrogen to atmospheric pressure, and removing a small sample for glpc analysis (columns A and B at 50°). At the end of 24 hr the reaction was stopped. The products were separated by preparative glpc (column C at 25°) and subsequently identified as described below.

Characterization of the Photoproducts Derived from 15. The glpc analyses (column B at 25°) indicated that the reaction mixture contained three major components with relative retention volumes of 1.0, 1.8, and 2.7 (t'_{15} = 10.8 min). The component with the smallest retention volume was shown to be starting material **15** by direct comparison of the infrared and nmr spectra of a collected sample with those of authentic material. The component with the greatest retention volume, **16**, n^{22}D 1.4252, exhibited infrared absorption maxima (CCl_4) at 3.3, 3.4, 5.45, 6.08, 6.9, 7.26, 9.0, 10.1, and 11.0 μ. The nmr spectrum showed a complex multiplet from τ 3.9 to 5.25 (4), a triplet (J = *ca.* 6 cps) centered at τ 7.30 (2), and a doublet (J = *ca.* 6 cps) centered at τ 8.34 (6). These spectra were identical with the infrared and nmr spectra of an authentic sample of 5-methyl-1,4-hexadiene prepared and measured by Cywinski,[31] and supplied by the Phillips Petroleum Co.

Anal. Calcd for C_7H_{12}: C, 87.42; H, 12.58. Found: C, 87.33; H, 12.60.

The remaining photoproduct, **17**, n^{22}D 1.4222, showed infrared absorption maxima (CCl_4) at 3.32, 3.39, 5.55, 6.13, 6.9, 7.27, 8.37, 8.93, 9.76, 10.13, 10.98, 11.17, and 11.75 μ. The nmr spectrum consisted of a complex multiplet from τ 4.28 to 5.23 (3) and a pair of sharp methyl peaks at τ 8.97 (3) and 8.91 (3) superimposed on a complex multiplet from τ 8.60 to 9.80 (3).

Anal. Calcd for C_7H_{12}: C, 87.42; H, 12.58. Found: C, 87.51; H, 12.74.

Lemieux Oxidation of 17. A solution of potassium metaperiodate (4.14, g, 18 mmoles) and potassium permanganate (60 mg, 9.38 mmoles) in distilled water (650 ml) was brought to a pH of *ca.* 8 by dropwise addition of aqueous potassium carbonate. To this was added a solution of **17** (210 mg, 2.18 mmoles) in *t*-butyl alcohol (50 ml). The reaction mixture was stirred for 4 days at room temperature by a magnetic stirrer. The solution was then acidified with hydrochloric acid and decolorized by the addition of saturated sodium metabisulfite solution. Acidic and neutral products were extracted with ether, after which the acidic product was extracted from the ethereal solution with potassium carbonate solution. The aqueous fraction was evaporated to dryness using a rotary evaporator to eliminate traces of *t*-butyl alcohol. The solid residue was redissolved in dilute hydrochloric acid and the acidic product extracted with ether, washed, and dried over anhydrous magnesium sulfate. The ether was then removed by a rotary evaporator leaving the carboxylic acid (80 mg, 33%). Both the infrared and nmr spectra of this product were in agreement with the published data for 2,2-dimethylcyclopropanecarboxylic acid.[19,20]

Irradiation of 5-Methyl-1,4-hexadiene (16). A mixture of **16** (1.6 g, 0.017 mole) and mercury (*ca.* 3 g) was irradiated following the procedure for the irradiation of **15.** At the end of 9 hr the reaction was stopped and analyzed by glpc. The only product which appeared in significant amounts was shown to be 1,1-dimethyl-2-vinylcyclopropane by glpc retention data on two columns (columns B and D at 25°) and by comparison of infrared and nmr spectra.

Irradiation of 1,1-Dimethyl-2-vinylcyclopropane (17). A mixture of **17** (0.65 g, 0.0068 mole) and mercury (*ca.* 1 g) was irradiated following the procedure for the irradiation of **15** for a period of 9 hr. Analysis of the reaction mixture by glpc (columns B and D at 25°) indicated that no low molecular weight products were formed and that **17** undergoes only slow polymerization under these conditions.

3,3-Pentamethylene-1,5-dibromopentane (23). Phosphorus tribromide (16.3 g, 0.06 mole) in a 50-ml, round-bottomed flask equipped with a reflux condenser and a magnetic stirrer was cooled by immersion into an ice–salt bath. 3,3-Pentamethylene-1,5-pentanediol (10.0 g, 0.058 mole; Aldrich Chemical Co.) was slowly added with magnetic stirring. The ice–salt bath was removed and the mixture was stirred for 5 hr at room temperature, followed by heating to *ca.* 125° for an additional hour. After the solution had cooled, it was poured into a separatory funnel containing water (50 ml) and ether (50 ml). The layers were separated, and the aqueous layer extracted was twice with ether (25 ml). The combined ether layers were washed twice with water, twice with saturated sodium carbonate solution, and twice more with water and dried over anhydrous magnesium sulfate. The ether was removed on a rotary evaporator leaving the extremely viscous slightly yellow, crude **23** (13.7 g, 80%), n^{24}D 1.5310. Fractional distillation through a short Vigreux column gave **23**, bp 94–96° (0.25 mm), n^{24}D 1.5352. The infrared spectrum (neat) showed absorption maxima at 3.37 (s), 3.44, 5.68, 6.85 (s), 7.42, 7.79 (w), 7.89 (w), 8.12, 8.34 (w), 8.46 (w), 9.05 (w), 9.68 (w), 10.18 (w), 10.70 (w), 11.26 (w),and 11.72 (w) μ. The nmr spectrum showed an unsymmetrical triplet (J = *ca.* 8 cps) centered at τ 6.78 (4) with the middle peak split into a complex multiplet, an unsymmetrical triplet (J = *ca.* 8 cps) centered at τ 8.17 (4) with the middle peak split into another complex multiplet, and a sharp singlet at τ 8.66 (10).

Anal. Calcd for $C_{10}H_{18}Br_2$: C, 40.38; H, 6.08; Br, 53.62. Found: C, 41.20; H, 6.24; Br, 52.57.

1,1-Divinylcyclohexane (18). To a mixture of quinaldine (40 g, 0.28 mole) and sodium iodide (2.0 g, 0.013 mole) in a 100-ml, round-bottomed flask equipped with a short Vigreux distillation column was added **23** (13.7 g, 0.046 mole). The resulting mixture was heated to reflux (bath temperature 200°) at a reduced pressure (*ca.* 110 mm). After several hours the yellow product, **18**, began to distil out of the reaction mixture and was collected in an ice-cooled trap. The temperature at the head of the distillation column was kept below 95°. The impure distillate was washed once with dilute hydrochloric acid and once with water and dried over anhydrous calcium chloride (4 mesh). Of the resulting **18** (4.5 g, 73%), a small sample was further purified by preparative glpc (column G at 130°), n^{25}D 1.4670, and the rest was irradiated without purification. The infrared spectrum (neat) of **18** showed absorption maxima at 3.20 (w), 3.39 (s), 3.48 (w), 6.22, 6.90, 7.07 (w), 10.04, and 11.00 μ. Its nmr spectrum exhibits a typical vinyl group absorption from τ 4.0 to 5.22 (6) and a sharp singlet at τ 8.48 (10). The analytical sample of this compound was broken in transit.

Irradiation of 1,1-Divinylcyclohexane (18). A mixture of **18** (2.3 g, 0.017 mole) and mercury (*ca.* 2 g) was irradiated following the procedure for the irradiation of **15.** After *ca.* 20 hr, the liquid portion of the reaction mixture had to be decanted into a clean quartz irradiation vessel, as a dark brown polymer formed on the walls of the flask during the irradiation. This transfer was necessary at about 20-hr intervals for the photoreaction to progress. At the end of 70 hr of irradiation, the reaction was stopped, and the liquid hydrocarbon portion of the reaction mixture (1.6 g) was decanted from the mercury and solid polymer in the flask and was analyzed by glpc (column G at 130°; t'_{18} = 12.8 min). The glpc analysis indicated that the reaction mixture contained three components in significant amounts, with relative retention volumes of 1.0 (85% of the total recovered liquid hydrocarbon mixture), 1.18 (**20**, 8.6%), and 1.33 (**19**, 5.3%). These products were separated by preparative glpc (column G at 130°), collected in an ice-cooled trap, and subsequently identified as described below. A minor photoproduct with a relative retention volume of 0.89 (1.1%) was not identified.

Characterization of the Photoproducts Derived from 18. The major component of the above photolysate showing the smallest retention volume was shown to be starting material **18** by glpc analysis and direct comparison of the infrared and nmr spectra of a collected sample with those of authentic material. The first of the two major photoproducts to be eluted, **20**, exhibited infrared (CCl_4) absorption maxima at 3.25 (w), 3.45 (s), 5.55 (w), 6.12 (s), 8.26, 8.93, 9.48, 9.68, 10.29, and 10.58 μ. The nmr spectrum showed a typical vinyl group absorption from τ 4.00 to 5.20 (3), a sharp singlet at τ 8.52 (10) superimposed upon a complex multiplet

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[31] N. F. Cywinski, *J. Org. Chem.*, **30**, 36 (1965).

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

R. Srinivasan[1] **and Karen Hill Carlough**

Contribution from the IBM Watson Research Center,
Yorktown Heights, New York 10598, and the Evans Chemical Laboratory,
Ohio State University, Columbus, Ohio 43210. *Received March 4, 1967*

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).

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(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.