Photoequilibria between 1,3-Cyclohexadienes and 1,3,5-Hexatrienes. Photochemistry of 3-Alkyl-6,6,9,9-tetramethyl-$\Delta^{3,5(10)}$-hexalins[1]

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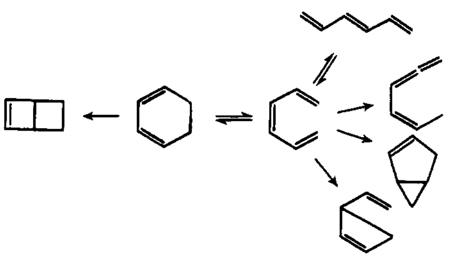
Abstract: The overall photochemical transformations of 3-alkyl-6,6,9,9-tetramethyl-$\Delta^{3,5(10)}$-hexalins have been determined. In addition, the relative quantum yields of disappearance of the diene and the relative rates of reaction of the related trienes have been determined. By evaluation of all these data, it was established that the photostationary state between diene and triene was controlled by the conformation of the triene. A triene with a preferred *s*-cis,*s*-cis conformation is less favored in the photostationary state than a triene with an *s*-cis,*s*-trans conformation. The preferred conformation of the triene was determined by the steric size of the 3-alkyl group of the original diene. It was also shown that a triene with an *s*-cis,*s*-cis conformation was transformed to a vinylcyclobutene whereas a triene with an *s*-cis,*s*-trans conformation was transformed to a bicyclo[3.1.0]hexene.

Part A

The 1,3-cyclohexadiene chromophore, one of the first groupings studied photochemically in detail due to its role in the *in vivo* formation of vitamin D,[4a] is the starting point for a wide variety of photochemical reactions. Many types of compounds containing this grouping have been studied[4b] and a general summary of the results obtained is given in eq 1. To date, no single compound has been reported to exhibit all these reactions and 1,3-cyclohexadiene is used in eq 1 simply as an example.



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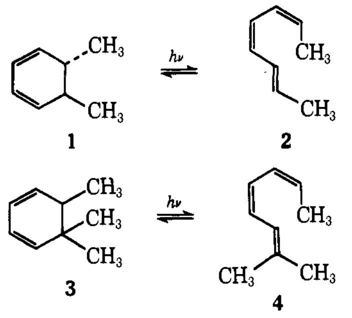
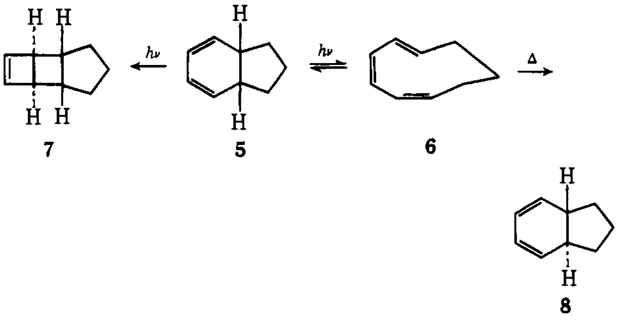
In this overall photochemical reaction scheme there are both reversible and irreversible processes. In general, the quantum yields for the reversible processes, at the wavelength of light employed (λ >220 nm), are higher than those for the irreversible reactions and, thus, at the early stages of the photochemical process a temporary photostationary state between the 1,3-cyclohexadiene and the 1,3,5-hexatriene is found. The composition of this photostationary state is dependent upon the substitution pattern of the diene system. For example, the photostationary state of *trans*-5,6-dimethyl-1,3-cyclohexadiene (**1**) and *trans,cis,cis*-2,4,6-octatriene (**2**) has been reported to be 95% triene.[5] With the related 5,5,6-trimethyl derivative **3**, 80–90% of the triene **4** has been found to be present in the photostationary state.[5,6]



In a more complex case, it has been found that at 254 nm the photostationary state between **5** and **6** is 40 and 60%, respectively.[7] At 300 nm, the photostationary state is shifted back toward diene **5** and the irreversible formation of tricyclo[4.3.0.0^{2,5}]non-3-ene (**7**) becomes the favored reaction. The ring closure of **6** to **8** is thermally induced and thus can be controlled; the facile photo-induced ring closure of **6** to **5** is due to the geometrical constraints of the cyclic triene which places the terminal carbon atoms of the conjugated system in a



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[2] Postdoctoral Fellow, Stiftung für Stipendien auf dem Gebiete der Chemie.

[3] National Science Foundation Predoctoral Fellow, 1967–1971.

[4] (a) For reviews pertaining to photochemistry related to vitamin D, see L. F. Fieser and M. Fieser, "Steroids," Reinhold, New York, N. Y., 1959, Chapter 4; H. H. Inhoffer and K. Irmscher, *Fortschr. Chem. Org. Naturst.*, 17, 70 (1959); G. M. Sanders, J. Pot, and E. Havinga, *ibid.*, 27, 129 (1969); (b) for reviews pertaining to general photochemistry of dienes see K. J. Crowley, *Photochem. Photobiol.*, 7, 775 (1968); R. N. Warrener and J. B. Bremmer, *Rev. Pure Appl. Chem.*, **16**, 118 (1966); G. J. Fonken in "Organic Photochemistry," Vol. 1, O. L. Chapman, Ed., Marcel Dekker, New York, N. Y., 1967, pp 197–246.

[5] G. J. Fonken, *Tetrahedron Lett.*, 549 (1962).

[6] K. J. Crowley, *J. Org. Chem.*, **33**, 3679 (1968).

[7] W. G. Dauben and M. S. Kellogg, *J. Amer. Chem. Soc.*, **93**, 3805 (1971).

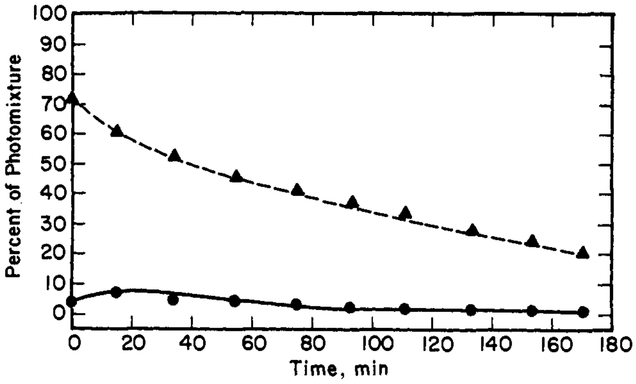


Figure 1. The photoreaction of **12a** (● = **11a**, ▲ = **12a**). The remainder of the photomixture exists as secondary photoproducts and polymer.

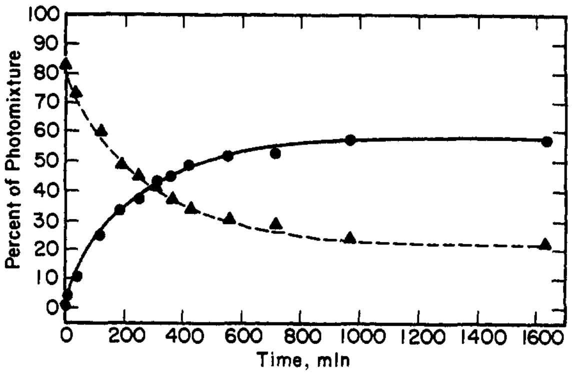
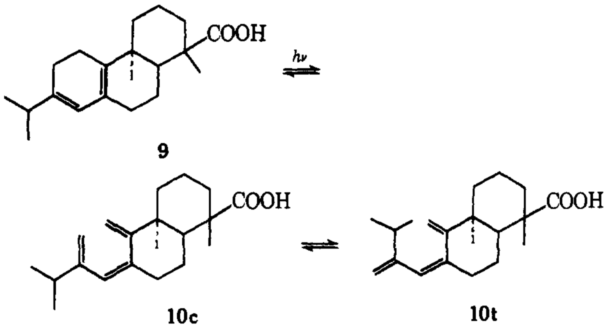


Figure 2. The photoreaction of **12c** (● = **11c**, ▲ = **12c**). The remainder of the photomixture exists as secondary products and polymer.

position conducive to conrotatory ring closure in the excited state and is so arranged that the conformation has a maximized absorption at 290 nm.

The conformation of the newly formed triene apparently is of importance in this reversible reaction. It has been found that a photostationary state of 50:50 exists between palustric acid **9** and the trienes **10c** and **10t**.[8] This enhanced ring closure has been explained on conformational grounds, noting that the isopropyl group destabilized the transoid rotamer **10t** and hence increases the concentration of the cisoid rotamer **10c** which has the correct geometry for efficient ring closure.

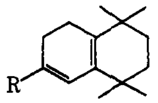


9

10c

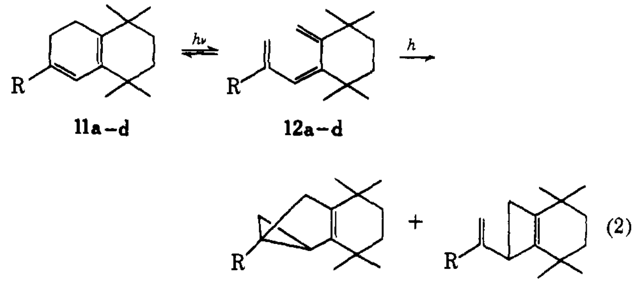
10t

In view of the importance of the photostationary state between the diene and triene in the photochemistry of the 1,3-cyclohexadiene chromophore, a systematic investigation into some factors controlling the photostationary state was undertaken. The system chosen for this study, 3-alkyl-6,6,9,9-tetramethyl-$\Delta^{3,5(10)}$-hexalin (**11a–d**), is analogous to palustric acid and is a good probe into the effects of conformation on the reversibility of the photoreaction.



11a, R = H
b, R = Me
c, R = *i*-Pr
d, R = *t*-Bu

The hexalins **11a–d** were synthesized (see Part B) and each diene upon irradiation showed the same type of major products (shown in eq 2). Although the course of the photoreactions was the same in each case, the rate of disappearance of the starting material and the ratio of products **13** and **14** changed with the substituent. These rate data and composition data are summarized in Table I. In these four dienes, the shapes of the absorption curves were practically superimposable and, as reported in the Experimental Section, the absorption maxima followed the expected substituent trend. Over the wavelength range of the light source used in this study, the absorption coefficients of all four dienes were within 20% of each other. The striking feature of these data is that the rates of disappearance of starting material dropped as the bulk of the substituent increased and as the rate became slower the ratio of products **13**/**14** decreased.



11a–d

12a–d

13a–d

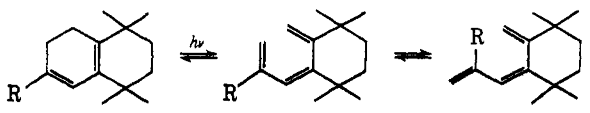
14a–d

(2)

Table I. Relative Rates and Product Composition

R	$t_{1/2}$, hr	13/14
H	0.4	2.3/1
Me	2.1	1/1
i-Pr	8.5	0.3/1
t-Bu	43.5	0.2/1

The cyclization to a diene is limited to a triene with a cisoid conformation and considering the equilibria shown in eq 3, it is evident that as the bulk of the alkyl substituent increases, the concentration of the cisoid conformation (*cis*-**12**) should increase relative to



11

cis-**12**

trans-**12**

(3)

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[8] W. G. Dauben and R. M. Coates, *J. Amer. Chem. Soc.*, **86**, 2490 (1964).

the concentration of the transoid rotamer (*trans*-**12**). Such a change in concentration (assuming that the spectra of *cis*-**12** and *trans*-**12** are independent of the substituent) should increase the efficiency of the photo-induced reclosure to diene **11** and, thus, decrease the rate of disappearance of the diene.[9]

This hypothesis requires that more diene **11** should be observed upon irradiation of triene **12** as the bulk of the substituent increases. The trienes **12a** and **12c** with the substituents being hydrogen and isopropyl were prepared by irradiation of dienes **11a** and **11c**. The results obtained upon irradiation of these two trienes are shown in Figures 1 and 2 and from these results the differences in the photochemistry of the two trienes are immediately apparent. When the substituent was hydrogen, the most efficient process was the formation of photoproducts **13a** and **14a**; a minor process yielded less than 5% of diene **11a**, indicating that a photostationary state between **11a** and **12a** exists. When the substituent was isopropyl, however, the major reaction of the triene **12c** was to reclose to diene **11c**. Thus, these data show that the efficiency of reclosure of triene **12** to diene **11** is enhanced by increasing the bulk of the alkyl substituent, a result predicted by conformational analysis (see eq 3).

All the results obtained supported the concept that the effect of changing the alkyl group was due to steric factors. However, there remains the possibility that the effect is electronic in nature. For example, the substituent being on the chromophore could act as a free rotor and enhance the efficiency of the radiationless transition of the diene from the excited state to the ground state. This interpretation would require that the triene **12**, in all cases, reclosed to diene with similar efficiency and that the efficiency of the initial opening of the diene **11** decreased as the bulk of the substituent became larger. To test this hypothesis the relative quantum yields for ring opening of **11a** and **11c** (R = H and *i*-Pr, respectively) were determined. The observed ratio of the quantum yields (extrapolated to zero time) was unity. Since a rotor effect of the substituent in the ring opening of the diene required a ratio much larger than unity, it can be concluded that the substituent effect must be in the **12** to **11** conversion.

The control of the conformation of the triene by the 3-alkyl substituent was also reflected in the change in ratio of photoproducts **13** and **14**. As shown in Table I, when the preference of the triene to adopt a transoid conformation (*trans*-12) diminished, the efficiency of the formation of **13** in respect to **14** also diminished; the electrocyclic closure of the two double bonds exocyclic to the cyclohexane ring to give **14** would be expected to be independent of the orientation of the acyclic terminal group. Thus, these results indicate that the formation of the bicyclo[3.1.0]hexene structure **13** proceeds from the *s*-cis, *s*-trans conformation of a triene. If this latter ring system is formed by a concerted process, the cycloaddition must be either $[{}_{\pi}4_{s} + {}_{\pi}2_{a}]$ or $[{}_{\pi}4_{a} + {}_{\pi}2_{s}]$,[10] there being no inherent conformational preference for either process. However, if there is some coupling of the two basis sets, secondary effects due to orbital symmetry of the excited state of the triene could favor one allowed process over the other. Using this concept, the $[{}_{\pi}4_{s} + {}_{\pi}2_{a}]$ cycloaddition must originate from the *s*-cis, *s*-trans conformation of the triene **12**. In the case of acyclic trienes, such as **12**, where there has been sufficient substitution to differentiate between these two processes, only the $[{}_{\pi}4_{s} + {}_{\pi}2_{a}]$ reaction has been observed.[11-13] The present findings are in line with these conformational requirements but further evidence is required before the concerted nature of the process can be established.

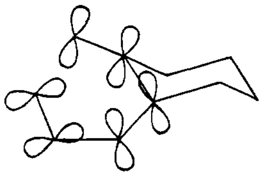

Figure 3. Conformation of triene **12c**.

The ultraviolet absorption spectra of the two trienes **12a** and **12c** provide further information about the conformation of the chromophore. The absorption maximum of triene **12a** with no alkyl substituent (R = H) is at 241 nm (ν 15,000). This maximum is at a considerably lower wavelength (higher energy) than would be expected for a 1,3,5-hexatriene.[14] Knowing that the two exocyclic double bonds of 1,2-dimethylenecyclohexene are skewed to a considerable extent,[14,15] the spectrum of **12a** can be interpreted as a transoid diene with some interaction with the adjacent exocyclic methylene group.

The absorption spectrum of the isopropyl-substituted triene **12c** is quite different, there being no maximum at a wavelength above 200 nm. The spectrum shows a shoulder at 223 nm (ε 4950) and intense end absorption. This spectrum is reminiscent of that showed by 1,2-dimethylenecyclohexene[15] which has a maximum at 220 nm (ε 5500). Thus, the spectral properties of triene **12c** are consistent with a conformation where the terminal vinyl group is nonplanar to the adjacent double bond of the 1,2-dimethylenecyclohexane moiety. As is shown in Figure 3, this conformation places the terminal vinyl group in perfect geometry for an orbital symmetry allowed closure to the diene **11c**.

The photochemistry and spectral data of the trienes **12c–d** are consistent with a postulate that the conformation of the triene system controls the efficiency of the various photoreactions arising from it.

Part B

The dienes employed in this investigation were prepared by similar processes and the procedures are outlined in Scheme I. The reaction of 2,5-dichloro-2,5-dimethylhexane (**16**)[16] with anisole (**15**) under Friedel-Craft conditions gave 3-methoxy-6,6,9,9-tetramethyltetralin (**17**). Reduction of **17** under Birch reaction conditions (Li–NH_3–ROH) gave a mixture of 3-me-

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[9] Due to the difference in the ultraviolet spectra of each conformer and due to the Franck–Condon principle, the usual concept of the ground state Curtin–Hammett rule does not apply.

[10] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, p 79.

[11] W. G. Dauben and P. Baumann, *Tetrahedron Lett.*, 565 (1961).

[12] J. Meinwald, A. Eckell, and K. Erickson, *J. Amer. Chem. Soc.*, **87**, 3532 (1965).

[13] A. Padwa and S. Clough, *ibid.*, **92**, 5803 (1970).

[14] A. J. Scott, "Interpretation of the Ultraviolet Spectra of Natural Products," Macmillan, New York, N. Y., 1964.

[15] A. T. Blomquist and D. T. Longone, *J. Amer. Chem. Soc.*, **79**, 3916 (1957).

[16] H. A. Bruson and J. W. Kroeger, *ibid.*, **62**, 36 (1960).

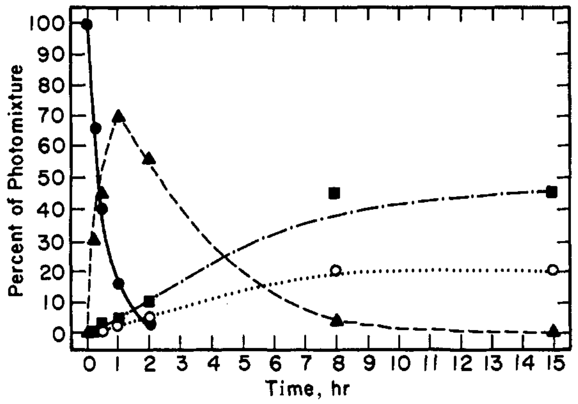
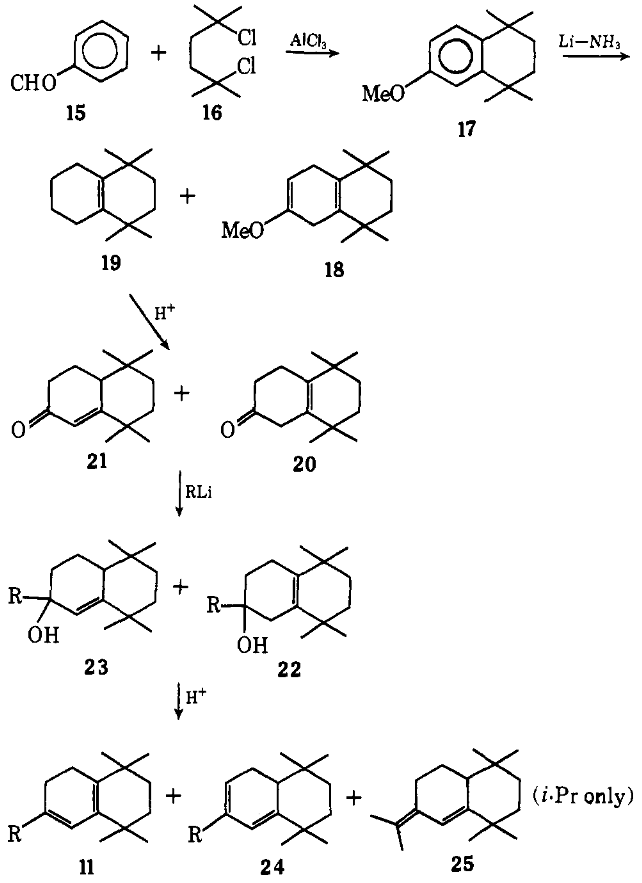


Figure 4. The photoreaction of 6,6,9,9-tetramethyl-$\Delta^{3,5(10)}$-hexalin (● = **11a**, ▲ = **12a**, ■ = **13a**, ○ = **14a**). Remainder of photomixture exists as an unidentified photoproduct X and polymer.

Scheme I. Synthesis of Substituted 3,5(10)-Hexalins



thoxy-6,6,9,9-tetramethyl-$\Delta^{2,5(10)}$-hexalin (**18**) and 6,6,-9,9-tetramethyl-$\Delta^{5(10)}$-octalin (**19**).[17] This mixture was not separated on a preparative scale but an analytical sample of **18** was collected by glpc and characterized. The reduction mixture was hydrolyzed in aqueous methanolic hydrochloric acid; the olefin **19** precipitated and it was collected by filtration. The enone mixture of **20** and **21** in the filtrate was separated by a combination of fractional distillation and glpc. The pure enones **20** and **21** upon reaction with the appropriate lithium reagent (using $LiAlH_4$ when R = H) yielded substituted allylic alcohols **22** and **23**. Each alcohol when allowed to react with *p*-toluenesulfonic acid gave the same mixture of 3-alkyl-6,6,9,9-tetramenthyl-$\Delta^{3,5(10)}$-hexalin (**11**) and the isomeric $\Delta^{2,4}$-diene **24**; in all cases except when the substituent was an isopropyl group, the desired $\Delta^{3,5(10)}$-hexalin derivative comprised over 90% of the product. With the isopropyl group present, the *s*-trans diene **25** was a major product (30%). The purity of the dienes was increased by preparative glpc when needed.

The dienes **11a–d** were individually irradiated in pentane using a Corex filter. From **11a** (R = H) four major volatile products were formed. The first formed product, triene **12a**, reached a maximum concentration of 70% (determined by uv spectrum) after which time three secondary photoproducts built-in. The results are shown graphically in Figure 4. The primary photoproduct **12a** and the major secondary photoproduct **13a** had the same retention time on a 10-ft Carbowax column (~0.7 that of diene). These products were separable on a 500 ft × 0.03 in. capillary column (OV-101) but this method could not be used to follow the reaction. Thus, uv spectroscopy was used to follow the formation and the disappearance of triene **12a**.

The primary photoproduct **12a** was isomeric with diene, as measured by mass spectroscopy and combustion analysis. Its absorption spectrum showed two maxima at 205 nm (ϵ 11,200) and 241 nm (15,600); its nmr spectrum displayed absorptions for six vinyl hydrogens as a multiply split broad signal from δ 4.5 to 6.8, for four methylene hydrogens as a broad singlet at δ 1.47, and for 12 methyl hydrogens as a singlet at δ 1.03. The infrared spectrum showed bands indicative of a terminal vinyl group (995 and 906 cm^{-1}) and of a terminal methylene group (900 cm^{-1}). These spectral data establish the structure of triene **12a**. As discussed earlier this triene is viewed as being in the extended *s*-trans conformation.

Two of the three secondary photoproducts, **13a** and **14a**, were isolated by glpc; a third product was formed in minor amounts and had a retention time too close to **13a** to permit its isolation and characterization. The major secondary photoproduct **13a** was found to be isomeric with diene **11a** and triene **12a** by mass spectrometry and analysis. The uv maximum at 204 nm (ϵ 10,500) was indicative of a cyclopropylene chromophore.[12,18] The nmr spectrum contained a one hydrogen broad singlet at δ 0.5–0.8 and a one hydrogen multiplet at δ −0.25 for the two cyclopropyl methylene hydrogens, a two hydrogen multiplet at δ 1.4–1.7 for the remaining two cyclopropyl hydrogens, and a two hydrogen multiplet at δ 2.0–2.5 for the two allylic hydrogens. These resonances are characteristic of a bicyclo[3.1.0]hexene.[19]

The lesser of the secondary photoproducts **14a** had the shortest glpc retention time (0.3 that of starting diene) and by high resolution mass spectrometry was also found to be isomeric with starting material. Its

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(17) The loss of the methoxy group in such a reductive process has been found to occur with mono and dialkoxybenzenes; see M. Smith in "Reduction," R. L. Augustine, Ed., Marcel Dekker, New York, N. Y., 1968, p 123.

(18) W. G. Dauben, I. Bell, T. W. Hutton, G. F. Laws, A. Rheiner, and H. Urscheler, *J. Amer. Chem. Soc.*, **80**, 4116 (1958); C. H. Heathcock and S. R. Poulter, *ibid.*, **90**, 3766 (1968).

(19) (a) W. G. Dauben and W. T. Wipke, *J. Org. Chem.*, **32**, 2967 (1967); (b) J. Meinwald and P. H. Mazzocchi, *J. Amer. Chem. Soc.*, **89**, 1755 (1967); (c) *ibid.*, **88**, 2850 (1966).

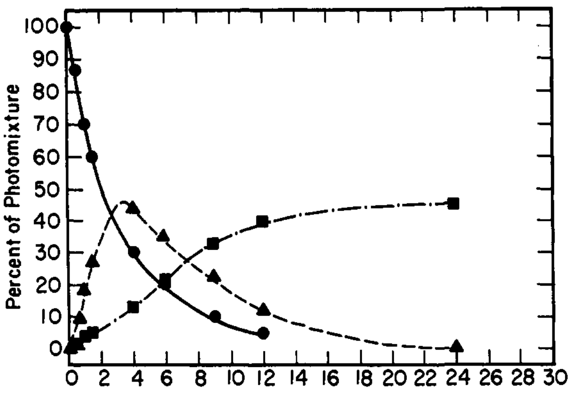

Figure 5. The photochemistry of 3,6,6,9,9-pentamethyl-$\Delta^{3,5(10)}$-hexalin (● = **11b**, ▲ = **12b**, ■ = **13b** and **14b**). The remainder of the photomixture exists as polymer. Both **13a** and **14a** build in at identical rates.

uv absorption spectrum showed no maximum above 190 nm but did display a strong end absorption (ϵ 10,900 at 200 nm). The infrared spectrum showed bands characteristic of a terminal vinyl grouping (990 and 906 cm^{-1}). The nmr spectrum showed two singlets characteristic of aliphatic hydrogens, one singlet of four hydrogen at δ 1.43 (methylene hydrogens), and one at δ 0.92 representing the four methyl groups. There were resonances for three vinyl hydrogens in a typical pattern of a terminal vinyl group between δ 4.8 and 6.2, for one diallylic hydrogen as a doublet of doublets at δ 3.25 (J_{AB} = 4.0 Hz, J_{AC} = 9.0 Hz), and for two allylic hydrogens, one at δ 2.58 (doublet of doublets, J_{AB} = 4.0 Hz, J_{BD} = 12.5 Hz) and one at δ 2.0 (a doublet, J_{BD} = 12.5 Hz). The chemical shifts and the coupling patterns of the three signals make it clear that the product is a vinylcyclobutene which has a tetrasubstituted double bond in the cyclobutene ring. Furthermore, these vinyl, allylic, and diallylic signals match those reported for 3-vinyl-1-cyclobutene, itself.[19c]

The photochemical behaviors of the 3-alkyl-6,6,9,9-tetramethyl-$\Delta^{3,5(10)}$-hexalins are shown in Figures 5–7. Irradiation of 3,6,6,9,9-pentamethyl-$\Delta^{3,5(10)}$-hexalin (**11b**, Figure 5), in pentane gave an initial product (retention time = 0.62 that of diene) which was gradually replaced by equal amounts of two secondary photoproducts (retention times = 0.50 and 0.45, respectively). The initial photoproduct had an absorption maximum at 245 nm, indicating that it was triene **12b**. The spectrum of the photomixture after all **11b** and **12b** has been consumed indicated that the two photoproducts were **13b** and **14b**, respectively.

The irradiation of 3-isopropyl-6,6,9,9-tetramethyl-$\Delta^{3,5(10)}$-hexalin (**11c**, Figure 6) first formed a product with glpc retention time of 0.7 that of the starting diene; the isolated product exhibited spectral characteristics (nmr, ir, uv) consistent with structure **12c**. Upon continued irradiation, this product disappeared and was replaced by two products of shorter retention times (0.65 and 0.45, respectively, of diene). The compound with the shorter retention time was the major product. The spectra of the final reaction mixture contained signals characteristic of a bicyclo[3.1.0]hexene derivative **13c** and a vinylcyclobutene derivative **14c**. From the retention times and the relative strength of the nmr signals, the major product was assigned the structure **14c** and the minor product the structure **13c**.

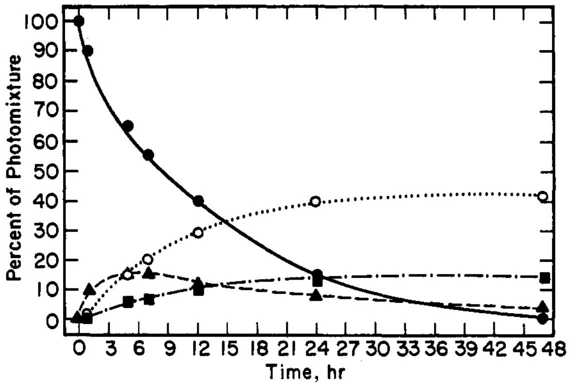

Figure 6. The photoreaction of 3-isopropyl-6,6,9,9-tetramethyl-$\Delta^{3,5(10)}$-hexalin (● = **11c**, ▲ = **12c**, ■ = **13c**, ○ = **14c**). The remainder of the photomixture exists as polymer.

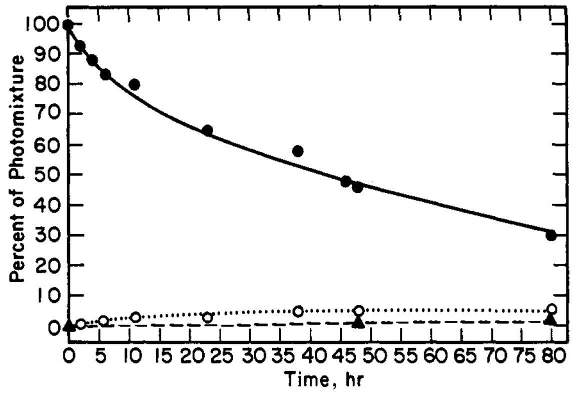

Figure 7. The photoreaction of 3-*tert*-butyl-6,6,9,9-tetramethyl-$\Delta^{3,5(10)}$-hexalin (● = **11d**, ▲ = **12d** and **13d**, ○ = **14d**). The remainder of the photomixture exists as polymer. **12c** and **13a** build in at identical rates.

The irradiation of 3-*tert*-butyl-6,6,9,9-tetramethyl-$\Delta^{3,5(10)}$-hexalin (**11d**, Figure 7) gave a large amount of polymer and a small amount of photoproducts. The glpc analysis showed three products with retention times of 0.68, 0.57, and 0.38, respectively, relative to that of the diene. A time averaged nmr spectrum of the photomixture showed signals characteristic of the triene **12d**, the bicyclo[3.1.0]hexene **13d**, and the vinylcyclobutene **14d**. Further identification was not possible.

By comparison of spectral characteristics and glpc retention times, it was evident that the photoproducts of the four hexalins studied were the same. However, as shown in Figures 4–7, the reaction half-times and yields of secondary photoproducts do change with substituent.

To measure the efficiency of the closure of triene **12** to diene **11**, the trienes with hydrogen (**12a**) and isopropyl (**12c**) as the 3-substituent were collected and irradiated. As noted before, the triene **12a** could not be separated from bicyclo[3.1.0]hexene **13a** and consequently was irradiated as a mixture. The mixture was analyzed by glpc using a 500 ft × 0.03 in. capillary column. A solution of triene **12a** in pentane was irradiated in a quartz flask with a 100-W Hanovia lamp; the results are shown in Figure 1. A solution of triene

12c was irradiated in a Vycor tube with a mercury 254-nm resonance lamp; the results are shown in Figure 2. The difference on time of irradiation was due primarily to the change of apparatus, a change necessitated by the small amount of **12c** available.

The relative quantum yields for the disappearance of dienes **11a** and **11c** were determined in a merry-go-round apparatus equipped with a mercury resonance lamp. Three pentane solutions, all of which contained hexadecane as an internal standard, were placed in Vycor tubes and irradiated. These tubes contained diene **12a**, diene **12c**, and both dienes, respectively. The disappearance of starting material was monitored by glpc and the relative quantum yields calculated from these data. The calculations, when extrapolated to zero time, gave a ratio of quantum yields equal to one.

Experimental Section

Analytical Procedures. The combustion analyses were performed by the Microanalytical Laboratory, University of California, Berkeley. The glpc analyses were conducted with an Aerograph Hy-Fi Model 600D using a 10 ft × 1/8 in. 10% Carbowax 20M–10% KOH (or 10% Carbowax 4M) column at temperatures of 80 to 150° and with a custom-made Teranishi gas chromatograph apparatus using a 500 ft × 0.03 in. capillary column coated with OV-101 at similar temperatures. Preparative glpc was conducted with an Aerograph Model A-700 using a 5 ft × 0.5 in. 10% Carbowax 20M or 10 ft × 3/8 in. 10% Carbowax–10% KOH column at similar temperatures. The spectroscopic data were obtained on the following instruments. The infrared spectra were taken on Perkin-Elmer 137 and 237 spectrophotometers, the ultraviolet spectra on a Perkin-Elmer 202 and a Beckman DK-2, the nmr spectra on Varian A60, T60, and HA100 spectrometers, and the mass spectra on Consolidated Electrodynamics Corp. Type 21-103C and Type 21-110A high resolution spectrometers.

3-Methoxy-6,6,9,9-tetramethyltetralin (17). To a stirred solution of 88.5 g (0.82 mol) of anisole, 154 g (0.84 mol) of 2,5-dichloro-2,5-dimethylhexane,[16] and 150 ml of spectral grade heptane was added 10 g of anhydrous aluminum chloride (0.08 mol). The mixture was stirred at room temperature for 1 hr and was heated under reflux for 2 hr. The mixture was cooled, 5 g of anhydrous aluminum chloride was added, the red solution was refluxed for 2 hr, and the solution was stirred overnight at room temperature. There was added 75 ml of 10% aqueous HCl; the heptane layer was separated, washed 3 times with 50 ml of water, and dried. The extract was rotary evaporated and the residue distilled (bp 112–113° (0.5 mm)) to give 162 g (90%) of 3-methoxy-6,6,9,9-tetramethyltetralin (**17**), which crystallized after a few days, mp 39.5–40.0°: ir (CCl_4) 2850 (m), 1460 (m), 1366 (m), 1240 (s), and 1040 (m) cm^{-1}; nmr (CCl_4) δ 1.23 (s, 3, methyl), 1.26 (s, 9, methyl), 1.67 (s, 4, methylene), 3.76 (s, 3, methoxyl), and 6.6–7.4 (m, 3, aromatic); mass spectrum (70 eV) *m/e* 218 (parent ion).

Anal. Calcd for $C_{15}H_{22}O$: C, 82.52; H, 10.16. Found: C, 82.25; H, 9.94.

Birch Reduction of 3-Methoxy-6,6,9,9-tetramethyltetralin (17). To 1 l. of liquid ammonia there was added, dropwise, a solution of 75 g (0.34 mol) of **17** in 250 ml of anhydrous tetrahydrofuran and 250 ml of anhydrous methanol. A total amount of 38 g of lithium wire was added over a period of 30–40 min (the solution remained blue after the addition of 25 g), the solution was stirred for 2 hr, and 125 ml of methanol added. The reaction was processed in the usual manner to yield 66 g (61%) of crude 3-methoxy-5,5,8,8-tetramethyl-1,4,5,6,7,8-hexahydronaphthalene (65–70% pure, glpc collected for analytical purposes): uv (EtOH) no maximum above 210 nm; ir (CCl_4) 1698 (m), 1387 (m, doublet), 1362 (m), 1217 (s), and 1172 (m) cm^{-1}; mass spectrum (70 eV) *m/e* 220 (parent ion).

Anal. Calcd for $C_{15}H_{24}O$: C, 81.76; H, 10.98. Found: C, 81.47; H, 10.72.

The material was not purified at this stage. When the same operation was done with only 30 g of lithium and the reaction mixture allowed to reflux under stirring for 30 min, only 50% of the starting material was reduced and 50% remained unchanged.

3-Keto-6,6,9,9-tetramethyl-Δ^4-octalin (21) and 3-Keto-6,6,9,9-tetramethyl-$\Delta^{5(10)}$-octalin (20). A solution of 69 g of the crude enol ether **18** + **19**, 700 ml of methanol, 65 ml of concentrated HCl, and 35 ml of water was stirred for 2 hr under nitrogen. A solid material formed rapidly and was removed by filtration upon completion of the reaction. The precipitate (6.9 g, 16%) was 6,6,9,9-tetramethyl-$\Delta^{5(10)}$-octalin (**19**): mp 57.5–58.5°; nmr (CCl_4) δ 0.95 (s, 12, methyl), 1.46 (s, 4, methylene), and 1.9–2.1 (m, 4, allyl); mass spectrum (70 eV) *m/e* 192 (parent ion). The filtrate was neutralized with saturated aqueous sodium bicarbonate and extracted 3 × 250 ml with chloroform. The chloroform extracts were dried and rotary evaporated to give 50 g of a liquid residue. This residue (containing the enones **20** and **21** and hydrocarbon **19**) was distilled under reduced pressure to give 33.1 g (51%) of a mixture of two enones. Glpc collected material gave the following spectral characteristics for 3-keto-6,6,9,9-tetramethyl-Δ^4-octalin (**21**), bp 100–105° (1 mm): ir (CCl_4) 3030 (w), 1684 (vs), 1605 (m), and 883 cm^{-1}; nmr (CCl_4) δ 0.79 (s, 3, methyl), 1.06 (s, 3, methyl), 1.15 (s, 6, methyl), 1.2–2.6 (m, 9, methylene and allyl), and 6.05 (d, 1, J = 2 Hz, vinyl); mass spectrum (70 eV) *m/e* 206 (parent ion).

Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.26; H, 10.82.

Spectral characteristics of 3-keto-6,6,9,9-tetramethyl-$\Delta^{5(10)}$-octalin (**20**) showed ir (CCl_4) 1715 (vs) cm^{-1}; mass spectrum (70 eV) *m/e* 206 (parent ion).

Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.44; H, 10.55.

6,6,9,9-Tetramethyl-$\Delta^{3,5(10)}$-hexalin (11a, R = H). To a vigorously stirred solution of 0.38 g of lithium aluminum hydride (0.010 mol) was added, dropwise, 5.56 g (0.027 mol) of the mixture of enones **20** and **21**. This solution was stirred for 2.5 hr. At the end of this time, water was *very* carefully added with a 10 μl syringe until just enough had been added to neutralize the lithium aluminum hydride (0.72 ml). This solution was stirred for 1 hr and filtered. The solvent was rotary evaporated to give 5.0 g (89%) of a mixture of enols (3-hydroxy-6,6,9,9-tetramethyl-Δ^4-octalin, **23a**, and 3-hydroxy-6,6,9,9-tetramethyl-$\Delta^{5(10)}$-octalin (**22a**). This material was not purified at this point, but glpc collection gave a sample of pure 3-hydroxy-6,6,9,9-tetramethyl-Δ^4-octalin (**22a**): ir (CCl_4) 3400 (m, OH) cm^{-1}; nmr (CCl_4) δ 0.66 (s, 3, methyl), 0.93 (s, 3, methyl), 1.04 (s, 3, methyl), 1.08 (s, 3, methyl), 2.30 (s, 1, OH), 5.56 (d, 1, vinyl).

A solution of 3.4 g (0.016 mol) of the enol mixture, 100 ml of acetone, and 0.18 g of *p*-toluenesulfonic acid was refluxed under nitrogen for 2 hr. The solution was neutralized with solid sodium bicarbonate, filtered, and rotary evaporated to give 2.8 g of dienes and some oxygenated materials. This mixture was chromatographed on 90 g of silica gel with pentane as the eluant to give 1.5 g (48%) of 91% pure 6,6,9,9-tetramethyl-$\Delta^{3,5(10)}$-hexalin (**11a**, R = H): uv$_{max}$ (heptane) 257 nm (ϵ 6250); ir (CCl_4) 3030 (s), 1639 (w), 1587 (w), 900 (m), and 676 (m, cis –CH=CH–) cm^{-1}; nmr (CCl_4) δ 1.00 (s, 12, methyl), 1.47 (s, 4, methylene), 2.00 (d, 4, J = 2 Hz, allyl), 5.7–6.1 (m, 2, vinyl); mass spectrum (70 eV) *m/e* 190 (parent ion).

Anal. Calcd for $C_{14}H_{22}$: C, 88.35; H, 11.65. Found: C, 88.62; H, 11.35.

3,6,6,9,9-Pentamethyl-$\Delta^{3,5(10)}$-hexalin (11b, R = Me). To 6.18 g (0.030 mol) of the enone mixture (**20** and **21**) in 200 ml of dry pentane cooled to 0° was added 60 ml of 1.6 *M* methyllithium (0.076 mol, Alfa Inorganic Inc.). The reaction was stirred for 15 min at 0° and refluxed for 30 min, and processed in the standard fashion to give a solid residue (6.1 g, 92%) containing the two enols (**22b** and **23b**). This crude residue was dissolved in 200–250 ml of acetone, 200 mg of *p*-toluenesulfonic acid was added and the solution stirred for 15 min at room temperature under nitrogen and then refluxed for 30 min. Solid $NaHCO_3$ was added, the acetone solution filtered, and the filtrate rotary evaporated gave 5.4 g of an oil (containing the diene and other material). This crude material was chromatographed on a silica gel column (90 g) with pentane as the eluant to give 2.8 g (45%) of 95% pure 3,6,6,9,9-tetramethyl-$\Delta^{3,5(10)}$-hexalin (**11b**, R = Me): uv$_{max}$ (cyclohexane) 265 nm (ϵ 8500); ir (CCl_4) 2960 (s), 1650 (w), 1470 (m), 1357 (w), and 860 (m) cm^{-1}; nmr (CCl_4) δ 1.03 (s, 6, methyl), 1.04 (s, 6, methyl), 1.50 (s, 4, methylene), 1.82 (s, 3, vinyl methyl), 1.97 (s, 4, allyl), and 5.68 (s, 1, vinyl); mass spectrum (70 eV) *m/e* 204 (parent ion).

Anal. Calcd for $C_{15}H_{24}$: C, 88.23; H, 11.77. Found: C, 88.26; H, 11.54.

3-Isopropyl-6,6,9,9-tetramethyl-$\Delta^{3,5(10)}$-hexalin (11c, R = *i*-Pr). To a stirred solution of 6.18 g (0.030 mol) of the mixture of enones (**21** and **22**) in 200 ml of pentane, was added dropwise, under nitrogen, 25 ml of a 2.1 *M* solution of isopropyllithium (0.0735 mol) in pentane. The reaction mixture was worked up as above to give 5.6 g (76%) of the crude enols (**22** and **23**). Treated as before with *p*-toluenesulfonic acid in acetone, the mixture of enols gave rise to three dienes (4.7 g). The mixture of crude dienes was chromatographed on an 80-g silica gel column and gave upon elution with pentane 2.7 g (39%) of a mixture of the $\Delta^{3,5(10)}$-diene (60%), of the $\Delta^{2,4}$-diene (5–10%) and of the transoid diene (30%). Collection from glpc for analysis and photolysis gave pure 3-isopropyl-6,6,9,9-tetramethyl-$\Delta^{3,5(10)}$-hexalin (**11c**, R = H): uv$_{max}$ (heptane) 262 nm (ϵ 5000); ir (CCl_4) 3030 (w), 1650 (m), 1387 (m), 1362 (m), and 694 (m) cm^{-1}; nmr (CCl_4) δ 1.00 (s, 12, methyl), 1.03 (d, 6, J = 6.5 Hz, $CH(CH_3)_2$), 1.45 (s, 4, methylene), 1.91 (s, 4, allyl), 2.20 (m, 1, J = 6.5 Hz, $CH(CH_3)_2$), and 5.60 (s, 1, vinyl); mass spectrum (70 eV) *m/e* 232 (parent ion).

Anal. Calcd for $C_{17}H_{28}$: C, 87.86; H, 12.14. Found: C, 88.04; H, 11.99.

3-*tert*-Butyl-6,6,9,9-tetramethyl-$\Delta^{3,5(10)}$-hexalin (11d, R = *tert*-Bu). A solution of 6.18 g (0.030 mol) of the mixture of enones in 200 ml of pentane and 35 ml of 2.2 *M* *tert*-butyllithium, (0.077 mol) in pentane were allowed to react, with vigorous stirring under nitrogen for 15 min at 0° (ice bath) and 45 min at reflux. The reaction mixture worked up as before gave 5.5 g (70%) of the crude enols (**22c** and **23d**). The crude enols, treated with *p*-toluenesulfonic acid in acetone as before, gave 5.0 g of the crude $\Delta^{3,5(10)}$-diene (and other unidentified products). This mixture was chromatographed on a silica gel column (80 g) and eluted with pentane. Evaporation of the pentane gave 2.7 g of an oily residue and it was dissolved in a small amount of pentane and an excess (about 200 ml) of methanol was added. A pasty precipitate formed and was filtered. The filtrate was evaporated and the residue was treated a second time in the same manner. The new filtrate was again evaporated and the residue, left in the refrigerator, solidified after 10 to 20 hr and consisted of 1.7 g (23%) of 94% pure 3-*tert*-butyl-6,6,9,9-tetramethyl-$\Delta^{3,5(10)}$-hexalin (**11d**, R = *tert*-Bu), mp 32–33°: uv$_{max}$ (cyclohexane) 261 nm (ϵ 7000); ir ($CHCl_3$) 3020 (w), 2950(s), 1645 (m), 1450 (s), 1350 (m), 1375 (m), 1250 (m), 1275 (m), 1100 (w), 885 (w), and 867 (s) cm^{-1}; nmr (CCl_4) δ 0.98 (s, 9, *tert*-butyl), 1.05 (s, 12, methyl), 1.46 (s, 4, methylene), 1.94 (s, 4, allyl), and 5.72 (s, 1, vinyl); mass spectrum (70 eV) *m/e* 246 (parent ion).

Anal. Calcd for $C_{18}H_{30}$: C, 87.80; H, 12.20. Found: C, 87.60; H, 12.09.

General Irradiation Procedure. Unless otherwise noted, all irradiations were done in solutions of irradiation grade pentane or cyclohexane (see ref 3e for preparation), which were placed in Pyrex irradiation vessels (125 or 350 ml) fitted with a quartz probe, 450-W Hanovia lamp, Corex filter, gas inlet, magnetic stirrer, and rubber serum stopper. The solutions were degassed with nitrogen in the irradiation vessel for at least 1 hr prior to irradiation, and the nitrogen was passed slowly through the solution throughout the irradiation.

Irradiation of 6,6,9,9-Tetramethyl-$\Delta^{3,5(10)}$-hexalin (11a, R = H). Short Irradiation. A solution of 0.39 g of diene **11a** in 340 ml of pentane was degassed and irradiated in the standard manner for 1 hr. At the end of that time, glpc and ultraviolet analysis showed four photoproducts, one of which accounted for 70% of the photomixture. The pentane was rotary evaporated to yield the photomixture as a slightly yellow oil. The major product (retention time = 0.70 that of the diene **11a**), isolated by preparative glpc, was the triene **12a** (R = H): uv$_{max}$ (cyclohexane) 241 nm (ϵ 15,600), 205 nm (11,200); ir (CCl_4) 3077 (w), 3094 (w), 1631 (m, C=C), 995 (m, CH=CH$_2$), 906 (s, CH=CH$_2$), 900 (s, terminal =CH$_2$), and 658 (m) cm^{-1}; nmr (CCl_4) δ 1.03 (s, 12, methyl), 1.47 (s, 4, methylene), 4.5–5.3 (m, 4, vinyl), and 5.8–6.8 (m, 2, vinyl); mass spectrum (70 eV) *m/e* 190 (parent ion), 175, 119, 105, 91 (base).

Anal. Calcd for $C_{14}H_{22}$: C, 88.35; H, 11.65. Found: C, 88.13; H, 11.43.

Prolonged Irradiation. A solution of 0.35 g of diene **11a** (R = H) in 340 ml of cyclohexane was degassed and irradiated in the standard manner for 15 hr. At the end of this time, glpc and ultraviolet analysis (see Figure 4) showed three photoproducts, the two major ones accounting for 45 and 20% of the photomixture. The cyclohexane was rotary evaporated and the remaining thick yellow oil was distilled using a small Hickman still (0.1 mm, 50–60°). The distillate (0.1 g, 29%) contained only the two major photoproducts, which were separated by preparative glpc. The major product (retention time = 0.70 that of the diene **11a**) was assigned the structure of the bicyclo[3.1.0]hexene **13a** (R = H): uv$_{max}$ (heptane) 204 nm (ϵ 10,500); ir (CCl_4) 3040 (m), 3021 (m), 1381 (s), 1360 (s), and 1030 (m) cm^{-1}; nmr (CCl_4) δ −0.25 (m, 1, cyclopropyl), 0.7 (m, 1, cyclopropyl), 0.83 (s, 3, methyl), 0.98 (s, 3, methyl), 1.03 (s, 6, methyl), 1.43 (s, 4, methylene), 1.55 (m, 2, cyclopropyl), and 2.25 (m, 2, allyl); mass spectrum (70 eV) *m/e* 190 (parent), 175 (base), 133, 119, 105, and 91.

Anal. Calcd for $C_{14}H_{22}$: C, 88.35; H, 11.65. Found: C, 88.54; H, 11.38.

The minor product (retention time = 0.30 that of the diene **11a**), which rearranged to the triene **12a** if the glpc column temperature was greater than 120°, was assigned the structure of the vinyl cyclobutane **14a** (R = H): uv (cyclohexane) no maximum above 190 nm, end absorption at 200 nm (ϵ 10,900); ir (CCl_4) 3058 (w), 1634 (w), 1383 (w), 990 (m, CH=CH$_2$), and 906 (m, CH=CH$_2$) cm^{-1}; nmr (CCl_4) δ 0.93 (s, 12, methyl), 1.43 (s, 4, methylene), 2,00 (d, 1, J = 12.5 Hz, allyl), 2.59 (d of d, 1, J_1 = 12.5 Hz, J_2 = 4.0 Hz, allyl), 3.26 (d of d, 1, J_1 = 4.0 Hz, J_2 = 9.0 Hz, diallyl), 4.92 (m, 2, vinyl), and 5.79 (m, 1, J = 9.0 Hz, vinyl); mass spectrum (70 eV) *m/e* 190 (parent ion), 175 (base), 133, 119, 105, and 91; high resolution mass spectrum 190.1720. (190.1721, calcd for $C_{14}H_{22}$); sample glpc collected, greater than 99% pure.

The fourth photoproduct (retention time = 0.75 that of the diene **11c**) could not be purified by glpc and was not identified.

Irradiation of 3,6,6,9,9-Pentamethyl-$\Delta^{3,5(10)}$-hexalin (11b, R = Me). A solution of 0.9 g of diene **11b** in 340 ml of cyclohexane was degassed and irradiated in the standard manner for 24 hr. The reaction (see Figure 5) was followed by glpc and uv spectroscopy. The first formed product, triene **12b** (R = Me; established from glpc retention time, 0.62 that of the diene **11b**, and ultraviolet maximum, 245 nm), slowly was transformed to two secondary photoproducts, each of which was formed in 45% yield. The cyclohexane was rotary evaporated to give a yellow oil containing the two photoproducts (retention time = 0.45 and 0.50, respectively), which proved inseparable by preparative glpc. However, the spectra of the mixture showed the presence of the vinyl cyclobutene **14b** (R = Me) and the bicyclo[3.1.0]hexene **13b** (R = Me). The photomixture exhibited the following spectral characteristics: uv$_{max}$ (cyclohexane) 212 nm; ir (CCl_4) 3060 (**14b**), 3040 (**13b**), 3020 (**13b**), 1635 (**14b**), 995 (CH=CH$_2$), and 906 (CH=CH$_2$) cm^{-1}; nmr (CCl_4) δ −0.25 (m, cyclopropyl, **13b**), 0.7 (m, cyclopropyl, **13b**), 0.9–1.1 (methyl singlets), 1.4–1.5 (methylene singlets), 1.66 (s, methyl on vinyl, **14b**), 2.0–2.8 (m, allyl), 3.41 (m, diallyl, **14b**), and 4.72 (d, J = 8.0 Hz, vinyl, **14b**).

Irradiation of 3-Isopropyl-6,6,9,9-tetramethyl-$\Delta^{3,5(10)}$-hexalin (11c, R = *i*-Pr). Short Irradiation. A solution of 0.102 g of diene **11c** in 125 ml of pentane was degassed and irradiated in the standard manner for 3.75 hr. At the end of this time glpc and ultraviolet analysis showed about 15% of the initial photoproduct. The pentane was rotary evaporated to give a yellow photomixture, and a small amount of the major photoproduct was isolated by preparation glpc. This product was assigned the structure of the triene **12c** (R = *i*-Pr): uv (pentane) no maximum, shoulder at 223 nm (ϵ 4950); nmr (CCl_4) 0.9–1.1 (18, methyl singlets), 1.45 (s, 4, methylene), 3.33 (m, 1, allyl), 4.5–5.0 (m, 4, vinyl), 5.83 (m, 1, vinyl); mass spectrum (70 eV) *m/e* 232 (parent ion), 217 (base), 160, 137, 119, 105, and 91; high resolution mass spectrum 232.2191 (232.2191, calcd for $C_{17}H_{28}$); sample glpc collected, greater than 99% pure.

Prolonged Irradiation. A solution of 0.212 g of diene **11c** (R = *i*-Pr) in 125 ml of cyclohexane was degassed and irradiated in the standard manner for 27 hr. The reaction (see Figure 6) was followed by glpc and ultraviolet spectroscopy which showed three photoproducts at the end of irradiation in 4, 14, and 42% yield (based on diene **11c**). One of these, the 4% product, was identified as the triene **12c** by its glpc retention time. The cyclohexane was rotary evaporated to give the yellow photomixture. The spectra of this mixture showed that the major product (retention time = 0.45 that of the diene) was the vinyl cyclobutene **14c** (R = *i*-Pr) and the minor product (retention time = 0.68 that of the diene) was the bicyclo[3.1.0]hexene **13c** (R = *i*-Pr): uv (cyclohexane) no maximum above 210 nm; nmr (CCl_4) δ 0.7 (m, cyclopropyl, **13c**), 0.9–2.1 (m, methyl, methylene, and allyl), and 4.8 (m, vinyl, **14c**).

Irradiation of 3-*tert*-Butyl-6,6,9,9-tetramethyl-$\Delta^{3,5(10)}$-hexalin (11d, R = *tert*-Bu). A solution of 0.400 g of the diene **11d** in 340 nm of cyclohexane was degassed and irradiated in the standard manner for 81 hr. The reaction (see Figure 7) was followed by glpc and ultraviolet spectroscopy, which showed that at the end of the irradiation there was 30% of the original diene and minor amounts of photoproducts. The cyclohexane was rotary evaporated to give the yellow photomixture. No attempt was made to separate the mixture, but a time averaged nmr indicated that the products probably were the vinyl cyclobutene **14c** (R = *tert*-Bu; retention time = 0.38 that of the diene **11d**), the bicyclo[3.1.0]hexene **13d** (R = *tert*-Bu; retention time = 0.57 that of the diene), and the triene **12d** (R =

tert-Bu; retention time = 0.68 that of the diene): nmr (CCl_4) δ 0.7 (m, cyclopropyl, **13d**), 0.9–2.1 (m, methyl, methylene, and allyl), and 4.8 (m, vinyl, **14d**).

Irradiation of Triene 12a (R = H). A solution of 76.6 mg of a mixture of the triene **12a** and the bicyclo[3.1.0]hexene **13a** (71.6% triene, 16.7% bicyclo[3.1.0]hexene, 4% diene **12a**, and 8% isomer X) in 28 ml of pentane was placed in a 28-ml quartz irradiation flask fitted with a 100-W Hanovia lamp, a gas inlet, and a rubber serum stopper. The solution was degassed in the standard manner and irradiated for 170 min. The reaction was followed by glpc. The final mixture (65 mg, 85% yield), isolated by rotary evaporation of the pentane, contained 20% triene **12a**, 49% bicyclo[3.1.0]hexene **13a**, 1% diene **11a**, 10% vinyl cyclobutene **14a**, and 20% isomer X. Data for intermediate times are shown on Figure 1.

Irradiation of Triene 11c (R = *i*-Pr). A solution of 5.8 mg of the triene **12c** (83% triene, less than 1% diene **11c**, and 16% bicyclo[3.1.0]hexene **13c**, and vinyl cyclobutene **14c**) in 4 ml of pentane was placed in a 6-ml Vycor tube which was held in a merry-go-round apparatus. This solution was irradiated for 1630 min with a 254-nm mercury resonance lamp (Nester/Faust UV-300). The reaction was followed by glpc. The final solution contained 21% triene **13c**, 57% diene **11c**, and 22% bicyclo[3.1.0]hexene **13c** and vinyl cyclobutene **14c**. Data for intermediate times are shown in Figure 2.

Relative Quantum Yields of 11a and 11c. Three solutions, 6.9 mg of diene **11a** in 4 ml of pentane, 6.9 mg of diene **11c** in 4 ml of pentane, and 1.7 mg of both dienes in 4 ml of pentane (all solutions contained hexadecane as an internal standard), were placed in a 6-ml Vycor tubes and irradiated for 640 min with a 254-nm mercury resonance lamp in a merry-go-round apparatus. The disappearance of the dienes **11a** and **11c** was followed by glpc. The data up to 10% conversion were used to calculate the ratio of the quantum yields.

Photochemistry of Bicycloalkyl Phenyl Ketones[1a]

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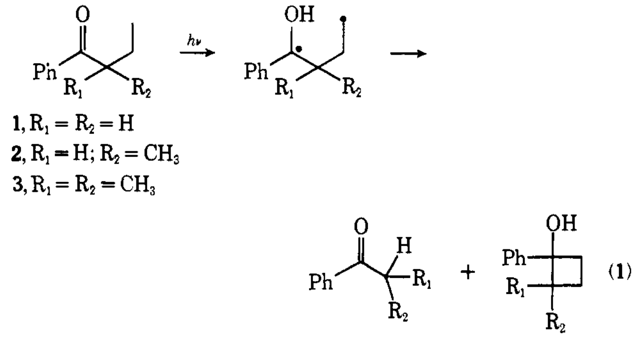
Abstract: The photochemistry of several bicycloalkyl and cyclopentyl phenyl ketones has been investigated. The quantitative and stereoselective photochemical syntheses of a tricyclo[$3.2.1.0^{3,6}$]octane and tricyclo[$3.3.1.0^{2,7}$]nonane are described. α-Methyl substituents are found to increase greatly the ratio of photocyclization to photoelimination products and to affect the reactivity of the carbonyl excited state toward γ-hydrogen abstraction. The large variation in the rate constants for secondary γ-hydrogen abstraction (2.5×10^6 to 1×10^{10} sec^{-1}) for the ketones studied is attributed primarily to conformational factors.

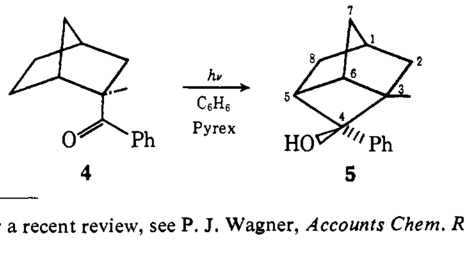
Recently we have described a marked enhancement of the ratio of photocyclization to photoelimination products from alkyl phenyl ketones upon α substitution.[2,3] For example, α-methyl (**2**) and α,α-dimethyl (**3**) substitution of butyrophenone (**1**) increases the percentage of cyclization from 10 to 29 and 89%, respectively (eq 1).[2] Both cyclization and elimination products are formed from a common 1,4-biradical intermediate, which can also undergo reversion to ground state ketone. The effects of substituents upon the behavior of the 1,4-biradical intermediates have been attributed to small nonbonded interactions in the conformations of the biradical necessary for cyclization and elimination.[2,4] These observations led to the prediction[2] that by proper choice of substituent some degree of control over product composition and stereochemistry might be obtained. The present investigation of the photochemistry of several bicycloalkyl and cyclopentyl phenyl ketones provides support for this supposition. High yield, stereoselective syntheses of several novel bridged polycyclic cyclobutanols are reported. In addition, excited state reactivity toward γ-hydrogen abstraction is found to be highly dependent upon conformational factors for both rigid (bicycloalkyl) and nonrigid (cyclopentyl and acyclic) phenyl ketones.



1, $R_1 = R_2 = H$
2, $R_1 = H$; $R_2 = CH_3$
3, $R_1 = R_2 = CH_3$

Results

Product Studies. The ketones studied were synthesized from the corresponding carboxylic acids by reaction with phenyllithium (see Experimental Section). Product studies were carried out on dilute ($\lesssim 1\%$) benzene solutions irradiated under nitrogen or argon with a 450-W, medium-pressure mercury lamp



4 **5**

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[2] (a) F. D. Lewis and T. H. Hillard, *J. Amer. Chem. Soc.*, **92**, 6672 (1970). (b) F. D. Lewis and T. Hillard, *ibid.*, in press.

[3] For a preliminary communication of a portion of this work, see F. D. Lewis and R. A. Ruden, *Tetrahedron Lett.*, 715 (1971).

[4] For a recent review, see P. J. Wagner, *Accounts Chem. Res.*, **4**, 168 (1971).