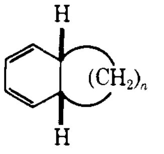
Photochemistry of Cis-Fused Bicyclo[4.*n*.0]-2,4-dienes. Ground State Conformational Control[1a]

William G. Dauben* and Michael S. Kellogg[1b]

Contribution from the Department of Chemistry, University of California, Berkeley, California 94720. *Received August 31, 1979*

Astract: The photochemistry of a series of simple cis-fused bicyclo[4.*n*.0]-2,4-dienes (*n* = 3, 4, 5) which possess flexible conformations in the ground state has been studied. The bicyclo[4.3.0]nona-2,4-diene system gave rise to cyclic trienes (ring-opened products) and cyclobutenes (ring-closed products) depending upon the wavelength of the excitation light and upon the temperature of the reaction. The bicyclo[4.4.0]deca-2,4-diene yielded materials which are viewed as secondary photoproducts; the expected initial photoproducts could not be detected. The bicyclo[5.4.0]undeca-8,10-diene yielded both a triene and cyclobutene as primary photoproducts. No wavelength dependency was observed. The results indicate ground state conformational control of the photoreactions.

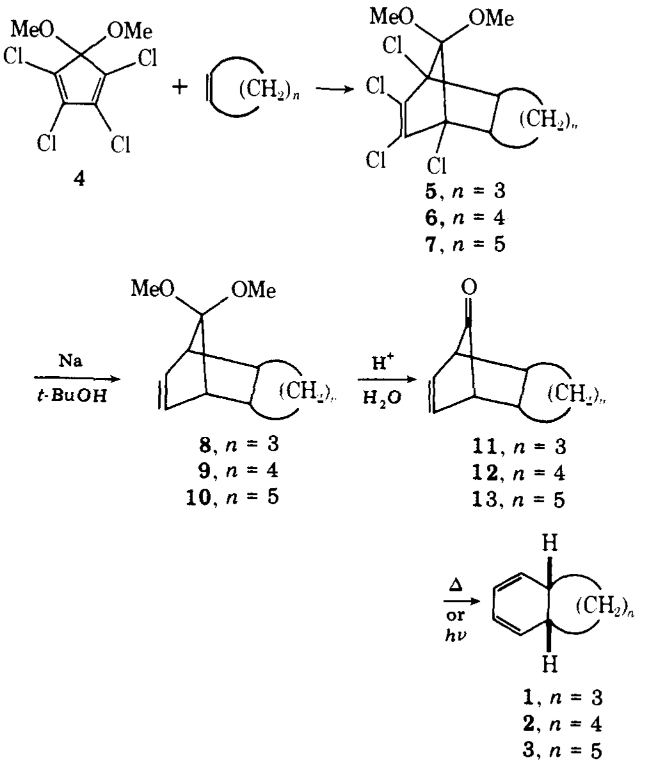
Homoannular conjugated cyclohexadienes have available two major modes of rearrangement upon direct photoexcitation, ring opening to a 1,3,5-hexatriene derivative or ring closure to a bicyclo[2.2.0]hex-2-ene derivative.[2] Rarely have the two processes been observed from the same molecule upon photochemical excitation.[3] A thorough investigation of the photochemistry of the $\Delta^{2,4}$-hexalin nucleus and several peripherally substituted analogues has led to the concept that the ground-state conformation of the chromophore controlled the primary photochemical reaction.[4] This concept of ground-state conformational control also has been evaluated in a selected group of 1,3-hexalin compounds and related steroids.[5] The generality of this concept has now been extended by a study of a series of simple cis-fused bicyclo[4.*n*.0]-2,4-dienes (1,3-hexalin analogues) which possess flexible conformations in the ground state.



1, *n* = 3
2, *n* = 4
3, *n* = 5

The synthetic approach to the desired irradiation substrates is outlined in Scheme I. The initial chlorinated tricyclic derivatives **5–7** were prepared by the Diels–Alder addition of the appropriate cyclic olefin to tetrachlorocyclopentadienone dimethyl ketal (**4**).[6] The product was dechlorinated with sodium and *tert*-butyl alcohol to give ketals **8–10** which, in turn, were hydrolyzed to the ketones **11–13**. These latter compounds were decarbonylated either thermally[7] or photochemically[8] to yield the desired dienes **1–3**.

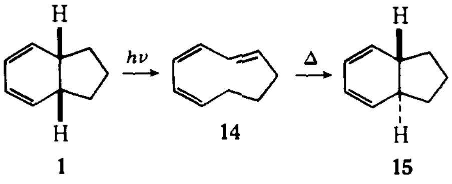
Scheme I



Results and Discussion

Irradiation of *cis*-Bicyclo[4.3.0]nona-2,4-diene (1). It has been reported that *cis*-bicyclo[4.3.0]nona-2,4-diene (**1**) on irradiation in methanol with a low-pressure mercury lamp at -20 °C yielded *cis,cis,trans*-1,3,5-cyclononatriene (**14**).[9] The triene was isolated via its silver nitrate complex and, after regeneration from the complex, it was shown to have a UV maximum at 290 nm (ϵ 2050). Thermally, **14** rearranged quantitatively to *trans*-bicyclo[4.3.0]nona-2,4-diene (**15**).

In an experiment similar to that reported by the earlier workers, a 1.5×10^{-2} M solution of **1** in pentane was irradiated through Vycor (λ >210 nm) at 254 nm in a Rayonet reactor. Under these conditions a photoequilibrium was reached between **1** and **14**; analysis by UV and by VPC indicated about 30% of **1** and 70% of **14**; the UV displayed isosbestic points at 235 and 283 nm and under the VPC conditions **14** was converted to **15**, the product expected on the basis of orbital-symmetry considerations (disrotatory). Another photoproduct **16** (of short retention time) was slowly formed at the expense of **1** and **14**. An experiment run at -20 °C in pentane utilizing a low-pressure mercury resonance lamp gave essentially the same results.



However, when **1** was irradiated through Vycor with RPR 300-nm lamps (λ, 270–330 nm) in a Rayonet reactor, no significant amount of **14** could be detected by UV or VPC, but photoproduct **16** slowly was formed. Solutions of **1** in pentane also gave **16** as the major product when irradiated with a Ha-

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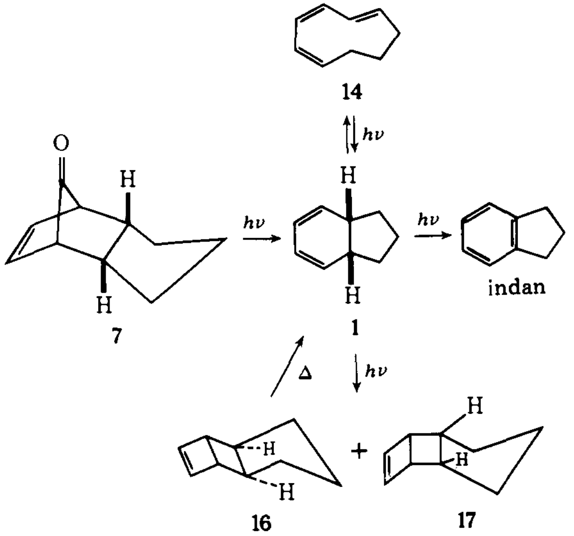
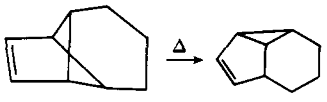
novia 450-W medium-pressure lamp through Corex (λ >220 nm) in an immersion well apparatus. For preparative runs, it was found most convenient to irradiate *cis,endo*-tricyclo[5.2.1.$0^{2,6}$]dec-8-en-10-one (**11**) utilizing the photochemical decarbonylation of the β,γ-unsaturated ketone[8] to prepare and irradiate **1** directly, in situ.



In the preparative runs, the new photoproduct **16** was formed in 28% yield, amounting to 48% of the volatile irradiation products, and was easily purified by preparative VPC. Spectral analysis (see Experimental Section) indicated a bicyclo[2.2.0]hexene structure and the compound was characterized as *anti,cis*-tricyclo[4.3.0.$0^{2,5}$]non-3-ene (**16**). Further evidence supporting the assigned structure was obtained by pyrolysis at 150°C in a sealed tube or in the injection port of a gas chromatograph to yield **1**, and by hydroboration and oxidation to obtain a compound exhibiting a carbonyl stretch at 1780 cm^{-1} in the IR.

At high conversions another presumably primary photoproduct of **1** could be obtained. This compound had the same retention time as **1** on nonpolar VPC columns and close to the same retention time as trans diene **15** on polar columns; thus its appearance could not easily be monitored during the course of the reaction. Isolation could be effected by preparative VPC in the high-conversion runs. The photoproduct **17** formed in yield (12% of overirradiation mixture) was characterized, spectrally, as *syn,cis*-tricyclo[4.3.0.$0^{2,5}$]non-3-ene. When **17** was heated at 150 °C for 1 h in a sealed tube, it rearranged to **1**. Hydroboration of **17** followed by oxidation yielded a ketone with a carbonyl stretch at 1790 cm^{-1}.

The spectral data presented for **16** and for **17** are reasonable for either the proposed structure or for tricyclo[4.3.0.$0^{5,9}$]non-7-ene (**18**). Thermal rearrangement of the photoproducts rules out **18** as a possibility since the bicyclo[2.1.1]hexene grouping leads exclusively to bicyclo[3.1.0]hexene structures when pyrolyzed.[10] Furthermore, ketones generated from **18** would not be expected to exhibit a carbonyl stretch with a frequency as high as 1780 cm^{-1}.[11] The syn stereochemistry for **17** was suggested by the high degree of splitting of the bridgehead protons in the NMR. Larger coupling constants are expected for the vicinal bridgehead protons in the syn isomer since the dihedral angle between them should be about 0°, whereas in the anti isomer the dihedral angle between the bridgehead protons of different chemical shift should be close to 90°.[11]



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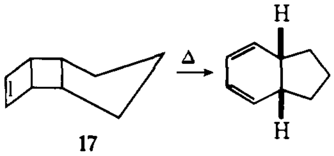

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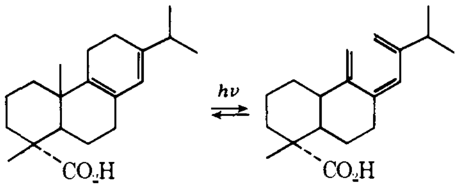
One possible explanation for the wavelength-dependent behavior of this system could be a very efficient photochemical closure of **14** back to **1**. Photochemical cyclizations of hexatrienes to cyclohexadienes are symmetry-allowed processes[12] and have been reported in the literature by several workers.[4a,13-15] In some instances, the reported photoproduct composition was also found to be dependent on the excitation wavelength.[14] With most systems studied, photoequilibrium highly favors the triene, indicating inefficient cyclization as compared to ring opening. Palustric acid, however, approaches a photostationary state that is about 50% diene and 50% triene.[15] The rationale given for this observation was inhibition of rotation of the terminal methylene by the isopropyl side chain, keeping the triene in a conformation amenable to cyclization.



palustric acid

Since at 254 nm the extinction coefficient of **1** is about four times that of **14** ($\epsilon^{254}_{\text{diene}}$ 3800, $\epsilon^{254}_{\text{triene}}$ 1000), the quantum yield for closure of **14** must be 1.6 times that for the opening of **1**, assuming that the quantum yield for triene reversal is independent of wavelength. At 300 nm the ratio of extinction coefficients drops to about 0.02 ($\epsilon^{300}_{\text{diene}}$ 50, $\epsilon^{300}_{\text{triene}}$ 2000), so the photostationary state is greatly changed to favor **1**, thus allowing the less efficient bicyclo[2.2.0]hexene structure formation to proceed from the diene.[16] Such a reaction profile can be viewed as effects due to secondary photoreactions by primary photoproducts.

Evidence that the cyclization does readily proceed at 300 nm was obtained by irradiating a solution of **1** in pentane at 254 nm in a Rayonet reactor until a quasi-photoequilibrium was reached; the irradiation vessel was then cooled to −78 °C to prevent thermal cyclization while the lamps in the reactor were changed, and the solution containing **14** was irradiated with the 300-nm lamps through Pyrex (λ >280 nm). The reaction was monitored by UV spectroscopy and VPC and the rapid reversion to **1** was established. The photostationary state at 254 nm is 30% of **1** and 70% of **14**; the photostationary state at 300 nm is 99% of **1** and 1% of **14**.

In addition to the wavelength effect upon the composition of the quasi-photochemical stationary state, it has previously been reported that another ground-state effect which plays a role in photochemical reactions of this type of diene series is the conformational equilibrium of the starting 1,3-cyclohexadiene chromophore.[4] Such an equilibrium should be temperature dependent, and the NMR spectrum of **1** exhibited a distinct, although uninterpretable, change upon cooling, especially in the vinyl region, indicating an effect of temperature upon the conformational equilibrium. Inspection of models of **1** suggested that the skew form of the cyclohexadiene moiety would be favored over the planar form. Assuming this to be the case, the temperature-dependent photochemistry of **1** was studied.

Dilute solutions of **1** in hexane were irradiated at 254 nm in a Rayonet reactor using a modification of the quartz Dewar apparatus. All irradiations were done to approximately 15%

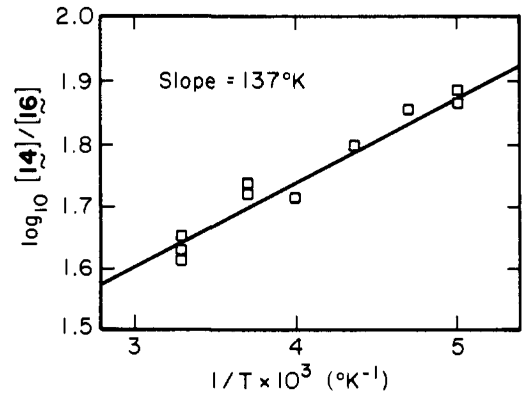


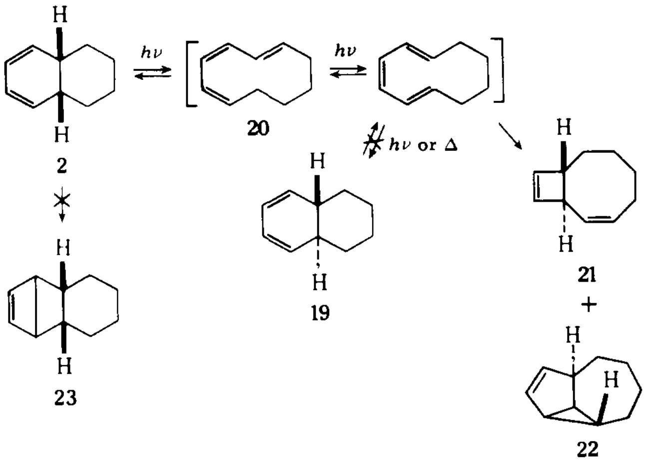
Figure 1. Plot of products **14** and **16** formation vs. temperature.

conversion to minimize spurious results due to the diene–triene photoequilibrium. Analysis was effected by VPC and the areas under the peaks were measured by an electronic integration device. The very small amount of **16** formed under these conditions led to considerable uncertainty in the ratio at each temperature but the ratios were reproducible to a satisfactory degree. A plot of the logarithm of the ratio of **14** to **16** against the reciprocal of the temperature results in a straight line with a slope of 135 K (Figure 1).

These results show that, as the temperature decreases, the efficiency of the ring-opening process increases; such a result is in agreement with the previous postulate that the skew form of the 1,3-cyclohexadiene moiety prefers to follow the ring-opening pathway. These results add further support to the concept of ground-state control of photochemical reactions.[4,5]

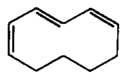
The multiplicity of the excited state involved in the observed rearrangements was determined by triplet sensitization studies. When a solution of **1** (1×10^{-2} M) in benzene was irradiated at 350 nm in the presence of 0.3 M acetophenone (E_t = 74 kcal/mol),[20] no monomeric products were observed while the starting diene **1** rapidly disappeared. Thus, the triplet excited state of **1** is not responsible for the isomerizations upon direct irradiation.

Irradiation of *cis*-Bicyclo[4.4.0]deca-2,4-diene (2). In a study of the photochemistry of *cis*- and *trans*-bicyclo[4.4.0]deca-2,4-diene (**2** and **19**, respectively) it was reported that these materials eventually led to the same photoproduct mixture **21** and **22**, presumably through the intermediacy of the corresponding cyclodeca-1,3,5-trienes.[21] A very approximate steady state between cis and trans dienes in which the trans isomer predominated was also reported, but insufficient evidence was available to warrant this deduction.[21] Both isolated photoproducts were considered to have the intermediate triene (**20**) as their immediate precursor and there was no mention of a bicyclo[2.2.0]hexene isomer **23**.



In a similar series of experiments, dilute solutions of *cis*-bicyclo[4.4.0]deca-2,4-diene (**2**) were irradiated under various conditions; again, two major photoproducts were found and they were shown to be **21** and **22**.[22] Changes in solvent and wavelength did not seem to affect the course of the reaction, and in no case was any bicyclo[2.2.0]hexene or any cyclodeca-1,3,5-triene isomer detected. If any such materials had been formed, they must not have amounted to much more than 1% of the reaction products. Furthermore, *trans*-bicyclo[4.4.0]deca-2,4-diene (**19**), which had been reported to exist in photoequilibrium with **2**, could not be detected. The only materials formed were products that could be formed only feasibly from trienes, and a small amount of tetralin.

The presumed intermediate, *cis,cis,trans*-cyclodeca-1,3,5-triene (**20**), was expected to be detectable since it had been reported to be thermally stable up to temperatures of 220 °C.[22] Subsequently, it has been found[23] that the material used in the thermal study actually was the cis,trans,cis isomer **24** and, thus, the ready ring closure of the expected triene intermediate could have occurred. The product of such a ring closure would be the trans diene **19**.[12] This diene could not be found in the reaction mixture, although it is readily detectable by VPC when externally introduced. Thus, thermally induced transformation of a triene intermediate must be ruled out.



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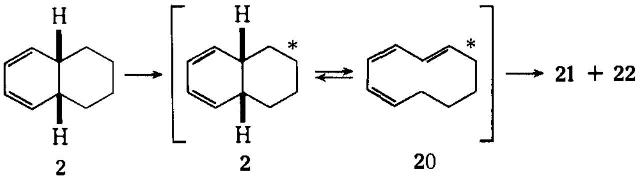
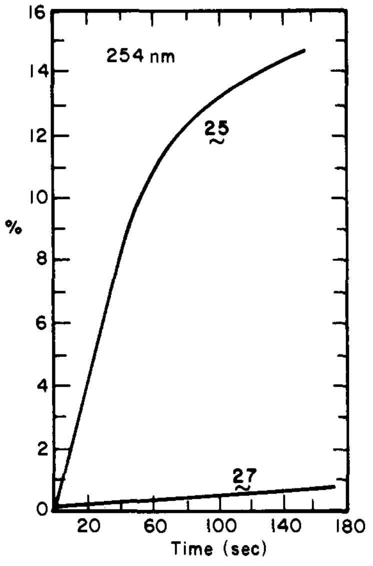
Another possible reason for the absence of triene **20** is a very facile photochemical closure to diene **2**, much in the same fashion as *cis,cis,trans*-cyclonona-1,3,5-triene (**14**) closes to *cis*-bicyclo[4.3.0]nona-2,4-diene (**1**).[16] The fact that no wavelength dependence was observed in this system can be explained if the diene **2** and the triene **19** have their UV absorptions in the same spectral region. To test the possibility of facile photochemical reclosure of triene **20** to diene **2**, the quantum yields for the disappearance of starting diene and the formation of the "overirradiation" product **22** were measured, assuming that they were direct photoproducts of **2**. At low conversions mass balance remains quite good in this system, and a quantum yield of 0.07 for disappearance of diene was found. While this is a relatively low efficiency for a one-photon process, it is relatively high for a two-photon process in competition with triene reclosure, and the proposed facile photochemical closure of triene **20** cannot be definitively proven by these data.

A third possible reason for the absence of ground-state triene in this reaction process is that there is a direct formation of triene excited state from diene excited state, a reaction course which is theoretically possible but which has rarely been found.[24] Further studies related to triene **20** are needed in order to evaluate these various suggestions.



Irradiation in the presence of acetophenone at 350 nm resulted in the disappearance of starting material with no buildup of monomeric photoproducts. The indication is, therefore, that the observed unimolecular photoprocesses of **4** emanate from an electronically excited singlet state.

Irradiation of *cis*-Bicyclo[5.4.0]undeca-8,10-diene (3). Direct irradiation of *cis*-bicyclo[5.4.0]undeca-8,10-diene (**3**) with

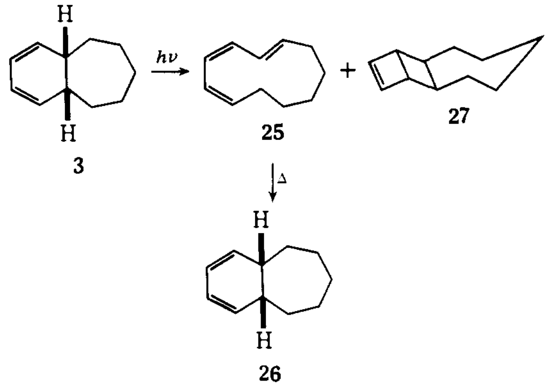


Time (sec)	10	30	60	90	150
[27]/[25]	0.02	0.03	0.03	0.03	0.04

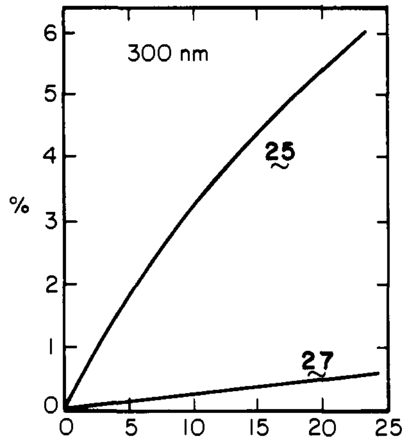
Figure 2. Plot of products **25** and **27** formation vs. time at 254 nm.

a 450-W Hanovia lamp in pentane through Corex (λ >220 nm) produced two primary photoproducts in a ratio of about 1:30 at low conversions, as determined by VPC analysis. Monitoring the course of rearrangement by VPC and by UV spectroscopy showed rapid disappearance of starting diene while the UV maximum of the reaction mixture shifted toward shorter wavelength. The photoproducts were isolated by preparative VPC or by a combination of chromatography on silver nitrate impregnated alumina and preparative VPC. Examination of spectra before and after VPC collection indicated that no thermal rearrangements occurred under the conditions used for product isolation.

When diene **3** was irradiated to about 70% conversion, the major photoproduct *cis,cis,trans*-1,3,5-cycloundecatriene (**25**) was formed in about 25% yield and was the only photoproduct detected at this point that underwent further photoisomerization to expected tricyclic product. The structure of **25** was established by spectral analysis (see Experimental Section) and by its stereospecific thermal conversion to the trans diene **26**.



The minor primary photoproduct, *anti,cis*-tricyclo[5.4.0.0^{8,11}]undec-9-ene (**27**), was formed in about 3% yield upon extended irradiation. The structure was determined by spectral analysis and by its stereospecific conversion to the cis diene **3** at 220 °C, the product predicted by orbital symmetry considerations (disrotatory). Assignment of the anti stereochemistry was based on the very small NMR coupling of the bridgehead allylic protons.



Time (min)	3	5	8	12	12
[27]/[25]	0.06	0.06	0.07	0.07	0.08

Figure 3. Plot of products **25** and **27** formation vs. time at 300 nm.

Table I

column symbol	column support and coating
A	10 ft × ⅛ in. 1% 20M on 100-120 G
B	10 ft × ⅛ in. 10% Carbowax 6000, 10% KOH on 60-80 S
C	15 ft × ⅛ in. 1% OV-1
D	10 ft × ⅛ in. 4% SF-96 (50) on 70-80 G
E	6 ft × ⅛ in. 10% SE-30 on 80-100 G
F	5 ft × ⅛ in. 5% 20M on 60-80 G
G	10 ft × ⅛ in. 10% 20M on 60-80 G
H	10 ft × ⅜ in. 5% SE-30 on 60-80 W
I	6 ft × ¼ in. 10% SE-30 on 60-80 W
J	10 ft × ⅜ in. 15% 20M, 15% KOH on 60-80 G
K	6 ft × ¼ in. 5% 20M, 5% KOH on 60-80 G

The course of the photoreaction of **3** was not as dependent upon the wavelength of the exciting light as that of the related *cis*-bicyclo[4.3.0]nona-2,4-diene (**1**), but the results did reveal an interesting trend as displayed in Figures 2 and 3. It is readily apparent that more triene **25** is formed relative to the bicyclohexene **27** at the lower wavelength. Similar results were obtained at low and at high conversions.

Quantum yields for the observed primary rearrangement processes were measured in the wavelength range 260-310 nm using the black box apparatus. Ring opening to **25** exhibited a quantum yield of 0.13 while ring closure to **27** proceeded with an efficiency of 0.003. The multiplicity of the unimolecular rearrangement processes was examined by irradiation of dilute benzene solutions of **3** in the presence of acetophenone at 350 nm. Under these conditions **3** rapidly disappeared while no isomeric rearrangement products were observed.

Experimental Section

Infrared and NMR spectra were run with carbon tetrachloride as solvent unless otherwise noted. Melting points were determined in open capillary tubes and are uncorrected. Combustion analyses were performed by the Microanalytical Laboratory, College of Chemistry, University of California, Berkeley.

The columns indicated in Table I were used for vapor phase chromatography.

Quantum-Yield Determination. A modification of the "Wisconsin Black Box Apparatus"[17] was used for most runs. The usual three-filter solution (nickel sulfate, cobalt sulfate, and bismuth trichloride)[25] was used to provide a transmission window 260-305 nm, with maximum intensity at 290 nm (25% transmittance). Potassium ferrioxalate actinometry was used.[17]

General Procedure for Preparative Irradiations. A dilute solution of starting material (0.1-0.2%) in spectroquality solvent was placed with a magnetic stir bar in a three-neck immersion well irradiation vessel fitted with inert gas inlet, reflux condenser with U-tube bubbler, and a ground-glass stopper. The system was purged with inert gas (nitrogen or helium) for at least 20 min prior to irradiation and at a slower rate for the duration. A Hanovia 450-W medium-pressure lamp acted as light source, and cylindrical filters of appropriate glass [Vycor (λ >210 nm), Corex (λ >220 nm), Pyrex (λ >280 nm)] were used to limit the energy of radiation impinging on the sample. Often the course of irradiation was monitored by VPC and UV by removing small aliquots at various time intervals. When irradiation was completed, solvent was removed by rotary evaporation to give the photoproduct mixture. Yields reported for formation of photoproducts were determined by VPC with an internal standard.

General Procedure for Dechlorination. The procedure of Gassman and Marshall for the preparation of 7,7-dimethoxynorbornene was followed.[6] To a vigorously stirred, gently refluxing mixture of tetrahydrofuran, sodium spheres, and *tert*-butyl alcohol, under nitrogen, a solution containing the tetrachloro adduct in tetrahydrofuran was added, dropwise, over a period of 3 h. The mixture was heated at reflux for an additional 12 h. After the excess sodium had fused into a solid lump, the mixture was allowed to cool to room temperature and passed through a fine wire screen and filter paper (grade 202) into crushed ice. This mixture was extracted with ether. The ethereal extracts were washed twice with saturated NaCl and once with water, dried, concentrated, and distilled.

***endo*-10,10-Dimethoxy-1,7,8,9-tetrachlorotricyclo[5.2.1.0^{2,6}]dec-8-ene (5).** Into the glass liner of a 1-L bomb were placed 40 g of cyclopentene (0.59 mol) and 132 g (0.5 mol) of 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene (4).[6] The bomb was heated to 200 °C in 15 min and maintained at this temperature, with shaking, for 1 h. The bomb was allowed to cool to 50 °C (6.5 h) and opened. The blackish product mixture was distilled to yield **5**, bp 135 °C (0.5 mm), as a colorless, viscous liquid which was crystallized from 95% ethanol to give 144 g (86%) of the product as a white, crystalline solid: mp 86.0-87.0 °C; NMR δ 3.55 (s, 3), 3.49 (s, 3), 3.07 (m, 2) 1.55 (m, 6); IR 2900, 1600, 1185 cm^{-1}; mass spectrum (70 eV) *m/e* 301, 299, 297, 295.

Anal. Calcd for $C_{12}H_{14}Cl_4O_2$: C, 43.41; H, 4.25; Cl, 42.71. Found: C, 43.15; H, 4.27; Cl, 42.92.

***endo*-10,10-Dimethoxytricyclo[5.2.1.0^{2,6}]dec-8-ene (8).** The general procedure for dechlorination was followed. To a vigorously stirred, gently refluxing mixture of 800 mL of tetrahydrofuran, 87 g of sodium spheres (3.8 mol), and 128 mL of *tert*-butyl alcohol (1.33 mol) under nitrogen was added 200 mL of a solution containing 83 g (0.25 mol) of the tetrachloro adduct **5** in tetrahydrofuran. The usual workup gave 31.5 g (65%) of clear, colorless ketal **8**: bp 70-75 °C (0.3 mm); IR 2900, 1440, 1260, 1120, 1080, 1050 cm^{-1}; NMR δ 6.00 (t, 2, J = 2 Hz), 3.10 (s, 3), 3.00 (s, 3), 2.70 (m, 2), 1.90-0.90 (m, 6); mass spectrum (70 eV) *m/e* 194 (100%), 179, 163, 151, 119.

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 73.89; H, 9.26.

***endo*-Tricyclo[5.2.1.0^{2,6}]dec-8-en-10-one (11).** To 150 mL of a 10% sulfuric acid solution was added 19.4 g (0.1 mol) of tricyclic ketal **8**. The mixture was stirred vigorously for 12 h and extracted with pentane. The combined pentane extracts were washed with 5% $NaHCO_3$, dried ($MgSO_4$), and concentrated. The residue was crystallized from pentane (−15 °C) to yield 7.3 g (50%) of the ketone **11**: mp 60.0-61.0 °C; IR 2900, 1780 (C=O), 710 cm^{-1}; NMR δ 6.40 (t, 2, J = 2 Hz), 2.88 (quintet, 2, J = 2 Hz), 2.57 (m, 2), 2.0-0.9 (m, 6); mass spectrum (70 eV) *m/e* 120, 105, 92, 91 (100%), 78.

Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 81.03; H, 8.01.

***cis*-Bicyclo[4.3.0]nona-2,4-diene (1).** A neat sample of 1.53 g (10.3 mmol) of ketone **11** was heated under nitrogen with stirring at 180-195 °C (bath temperature). When the evolution of carbon monoxide had ceased, the product was distilled at 70 Torr pressure and 90 °C with a Büchi Kugelrohr apparatus to yield 953 mg (76%) of the diene **1**, greater than 97% pure by VPC (columns A and C) which had identical spectral properties with those reported by Alder[26] and by Winstein:[27] bp 155-157 °C; UV max (pentane) 261 nm (ϵ 4200); IR 3030, 2900, 1700, 1640, 1590, 690 cm^{-1}; NMR δ 5.65 (m, 4), 2.62 (m, 2), 1.97 (m, 2), 1.45 (m, 4).

***endo*-11,11-Dimethoxy-1,8,9,10-tetrachlorotricyclo[6.2.1.0^{2,7}]-undec-9-ene (6).** Following the procedure of Hoch,[28] 132 g (0.5 mol) of diene **4** and 81 g (1 mol) of cyclohexene were heated at reflux to yield, after recrystallization (95% ethanol), 122 g (70%) of **6**, mp 81.5-83.5 °C (lit.[28] mp 81.5-82.3 °C).

***endo*-11,11-Dimethoxytricyclo[6.2.1.0^{2,7}]undec-9-ene (9).** The general procedure for dechlorination was followed. To a vigorously stirred, gently refluxing mixture of 1 L of tetrahydrofuran, 108 g (4.7 mol) of sodium spheres, and 160 mL (1.7 mol of *tert*-butyl alcohol under nitrogen was added 300 mL of a solution containing 104 g (0.3 mol) of the tetrachloro adduct **6** in tetrahydrofuran. The usual workup gave 44.3 g (71%) of the clear, colorless ketal **9**: bp 75-87 °C (0.5 mm); IR 2900, 1450, 1270, 1120, 1090, 1070, 1050 cm^{-1}; NMR δ 5.99 (t, 2, J = 2 Hz), 3.10 (s, 3), 3.00 (s, 3), 2.62 (quintet 2, J = 2 Hz), 2.12 (m, 2), 1.8-1.0 (m, 8); mass spectrum (70 eV) *m/e* 208 (100%), 177, 133, 105, 91.

Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.74; H, 9.68.

***endo*-Tricyclo[6.2.1.0^{2,7}]undec-9-en-11-one (12).** To 100 mL of an aqueous 10% sulfuric acid solution was added 20.8 g (0.1 mol) of tricyclic ketal **9**. The mixture was stirred vigorously for 32 h and extracted with pentane. The combined pentane extracts were washed with 5% $NaHCO_3$, dried ($MgSO_4$), and concentrated. The product was crystallized from pentane (−78 °C) to yield 10.5 g (65%) of the ketone **12**: mp 28-31 °C; bp 60-65 °C (0.3-0.4 mm); IR 2900, 1780 (C=O), 725 cm^{-1}; NMR δ 6.42 (t, 2 J = 2 Hz), 2.75 (quintet, 2, J = 2 Hz), 2.20 (m, 2), 1.55 (m, 4), 1.32 (m, 4); mass spectrum (70 eV) *m/e* 134, 119, 105, 91 (100%).

Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.50; H, 8.70.

***cis*-Bicyclo[4,4,0]deca-2,4-diene (2). A.** A neat sample of 2.2 g (13.5 mmol) of ketone **12** was heated under nitrogen with stirring at 180-195 °C (bath temperature). When the evolution of carbon monoxide had ceased, the product was bulb to bulb distilled with a Büchi Kugelrohr apparatus to yield 1.4 g (78%) of diene **2**, of greater than 97% purity by VPC (columns A and C), which had identical spectral properties with those reported by Mehrohta:[20] bp 90-110 °C (30 mm); UV max (95% ethanol) 261 nm (ϵ 4050); IR 3030, 2900, 1705, 1640, 1570, 690 cm^{-1}; NMR δ 5.70 (m, 4), 2.28 (m, 2), 1.40 (m, 8); mass spectrum (70 eV) *m/e* 134, 119, 105, 91 (100%).

B. Alternatively, **2** was prepared by passage of **12** through a tube packed with glass helices heated to 200 °C. From a 50-mL pressure-equalizing dropping funnel, 10.4 g (0.064 mol) of carefully melted ketone **12** was passed, dropwise, through the hot column with a continuous flow of nitrogen. The pyrolysate was collected in an ice-cooled receiver and passed through a short silica gel column with pentane to remove unreacted starting material, and the pentane removed to yield 7.63 g (87%) of diene (**2**) of greater than 97% purity by VPC (columns A and E).

***endo*-12,12-Dimethoxy-1,9,10,11-tetrachlorotricyclo[7.2.1.0^{2,8}]-dodec-10-ene (7).** Following the procedure of Hoch,[28] 132 g (0.5 mol) of diene **4** and 64 g (0.67 mol) of cycloheptene were heated at reflux for 2 h to yield after crystallization (95% ethanol) 131 g (73%) of **7** as a white solid: mp 98.5-99.5 °C; IR 2900, 1600, 1185 cm^{-1}; NMR δ 3.54 (s, 3), 3.47 (s, 3), 2.57 (m, 2), 1.93 (m, 5), 1.1 (m, 5); mass spectrum (70 eV) *m/e* 327, 325, 323.

Anal. Calcd for $C_{14}H_{18}Cl_4O_2$: C, 46.71; H, 5.01; Cl, 39.39. Found: C, 46.56; H, 5.14; Cl, 39.54.

***endo*-12,12-Dimethoxytricyclo[7.2.1.0^{2,8}]dodec-10-ene (10).** The general procedure for dechlorination was followed. To a vigorously stirred, gently refluxing mixture of 800 mL of tetrahydrofuran, 87 g (3.8 mol) of sodium spheres, and 128 mL (1.33 mol) of *tert*-butyl alcohol under nitrogen was added 200 mL of a solution containing 86.4 g (0.25 mol) of the tetrachloro adduct **7** in tetrahydrofuran. The usual workup gave 42.9 g (80%) of the slightly yellow ketal **10**: bp 95-105 °C (0.2-0.5 mm); IR 2900, 1650, 1570, 1440, 1050, 720 cm^{-1}; NMR δ 5.99 (t, 2, J = 2 Hz), 3.14 (s, 3), 3.01 (s, 3), 2.58 (quintet, 2, J = 2 Hz), 2.25 (m, 2), 2.0-0.9 (m, 10); mass spectrum (70 eV) *m/e* 222 (100%), 208, 191, 151, 147, 133, 119, 91.

Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.82; H, 9.85.

***endo*-Tricyclo[7.2.1.0^{2,8}]dodec-10-en-12-one (13).** To 100 mL of an aqueous 10% sulfuric acid solution was added 22.2 g (0.1 mol) of tricyclic ketal **10**. The mixture was stirred vigorously for 28 h and extracted with pentane. The combined pentane extracts were washed with 5% $NaHCO_3$, dried ($MgSO_4$), and concentrated. The product was crystallized from pentane (−15 °C) to yield 9.9 g (56%) of ketone **13**: mp 42.0-43.5 °C; bp 75-78 °C (0.5 mm); IR 2900, 1780 (C=O), 725 cm^{-1}; NMR δ 6.41 (t, 2, J = 2 Hz), 2.75 (quintet, 2, J = 2 Hz), 2.37 (m, 2), 1.80 (m, 5), 1.13 (m, 5); mass spectrum (70 eV) *m/e* 148, 105, 91 (100%).

Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.65; H, 9.42.

***cis*-Bicyclo[5.4.0]undeca-8,10-diene (3).** A neat sample of 2.74 g (15.5 mmol) of ketone **13** was heated under nitrogen with stirring at 180-195 °C (bath temperature). When the evolution of carbon monoxide had ceased, the product was distilled at 20 Torr pressure and 100 °C with a Büchi Kugelrohr apparatus to yield 1.53 g (67%) of diene **3**, 90% pure by VPC (columns A and E), the main impurity being benzosuberane: bp 115-120 °C (30 mm); UV max (hexane) 262 nm (ϵ 3900); IR (neat) 3020, 2850, 1770, 1700, 1580, 725 cm^{-1}; NMR δ 5.51 (m, 4), 2.50 (m, 2), 1.55 (m, 10); mass spectrum (70 eV) *m/e* 148, 146, 133, 131, 105, 92, 91 (100%).

Anal. Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 89.29; H, 11.04.

Irradiation of *cis*-Bicyclo[4.3.0]nona-2,4-diene (1) at 254 nm and −20 °C. In a refrigerated room (−10 °C), 339 mg (2.8 mmol) of diene **1** was dissolved in 75 mL of pentane, placed in an irradiation vessel, and deaerated by nitrogen purge. The irradiation vessel was further cooled to −20 °C with a dry ice-acetone bath. Irradiation was effected with a coil low-pressure mercury resonance lamp. The reaction was monitored by VPC (Column F) and allowed to proceed for 13 h until an apparent photoequilibrium was reached. The solution was filtered to remove polymer and rotary evaporated at room temperature to yield 257 mg (75%) of a liquid. Preparative VPC (column J, 120 °C) resulted in the isolation of **1** as the longer retention time product (40% of photoequilibrium products) and *trans*-bicyclo[4.3.0]nona-2,4-diene (**15**) (60% of photoequilibrium products). Compounds **1** and **15** were identified by their spectral data, which matched those reported in the literature.[9,26,27]

Irradiation of *cis*-Bicyclo[4.3.0]nona-2,4-diene (1) with a Medium-Pressure Lamp. A solution of 845 mg (7.04 mmol) of diene **1** was irradiated in 125 mL of pentane according to the general irradiation procedure through Corex (λ >220 nm) for 30 h. The course of the reaction was monitored by UV and there was a monotonic decrease in the intensity of the diene absorption. VPC (80-150 °C at 4 °C/min) indicated the slow formation of five photoproducts (columns A, B, C, and E). The polymeric precipitate was filtered and the filtrate rotary evaporated to give 600 mg (71%) of a yellow oil still containing polymer. No one VPC column was found capable of separating all five photoproducts and starting diene effectively. Photoproducts were separated and purified by preparative VPC (columns I and K) at 100 °C, and are discussed in order of relative retention time on column E. Photoproduct **16**, formed in about 28% yield (48% of volatile products), was characterized as *anti,cis*-tricyclo-[4.3.0.0^{2,5}]non-3-ene and displayed the following spectral properties: IR 3050, 3010, 2930, 2850, 1550, 1450, 1300, 1050, 960, 900, 725, 700 cm^{-1}; NMR δ (CCl_4) 6.20 (m, 2, cyclobutene vinyl protons), 2.67 (sh, m, 2, allylic bridgehead protons), 2.43 (sh, m, 2, bridgehead protons), 1.63-1.60 (m, 6, methylene protons); mass spectrum (70 eV) *m/e* 120, 105, 92, 91, 78.

Photoproduct **17** exhibited the same retention time as diene **1** on nonpolar VPC columns and the same retention time as a triene overirradiation photoproduct on polar VPC columns. The isolated material was one peak on columns A, C, D, and E. Formed in yield (12% of the volatile photoproducts), compound **17** was designated *syn,-cis*-tricyclo[4.3.0.0^{2,5}]non-3-ene: IR 3030, 2910, 2850, 1460, 1440, 1370, 1290, 1270, 1130, 930, 700 cm^{-1}; NMR δ 6.23 (m, 2, cyclobutene vinyl protons), 3.13 (m, 2, allylic bridgehead protons), 2.83 (m, 2, bridgehead protons), 1.63 (m, 6); mass spectrum (70 eV) *m/e* 120, 105, 92, 91, 78.

Indan and two products attributed to overirradiation of the triene **14** accounted for the remaining material.

Irradiation of *endo*-Tricyclo[5.2.1.0^{2,6}]deca-8-en-10-one (11). A solution of 2.0 g of ketone **11** was irradiated in 250 mL of pentane according to the general irradiation procedure through Corex for 120 h. Analysis by VPC indicated the same product mixture as that obtained from direct irradiation of diene **1**. The precipitate was filtered and the filtrate evaporated to give 955 mg (59%) of a yellow oil which displayed the same spectral properties as the crude photoproduct mixture of **1**.

Hydroboration and Oxidation of *anti,cis*-Tricyclo[4.3.0.0^{2,5}]non-3-ene (16). A solution of 10 mg (0.083 mmol) of tricyclic photoproduct **16** in 4 mL of tetrahydrofuran was treated with 0.3 mL of 1 M borane in tetrahydrofuran, and after 3 h with 0.3 mL of 3 N NaOH and 0.3 mL of 30% hydrogen peroxide. The usual workup gave 10 mg of an alcohol which without further characterization was oxidized with chromium trioxide-pyridine complex.[29] The usual workup gave 5 mg (44%) of a mixture of compounds, one of which displayed a strong carbonyl absorption at 1780 cm^{-1}, indicating the presence of a cyclobutanone.[11]

Pyrolysis of *anti,cis*-Tricyclo[4.3.0.0^{2,5}]non-3-ene (16). A solution of 20 mg of tricyclic photoproduct **16** in 1 mL of hexane (0.17 M) was placed in a thick-walled Pyrex tube, deaerated by nitrogen purge, and sealed. The sealed tube was heated at 150 °C in an oil bath for 1.5 h, cooled, and opened. The solvent was rotary evaporated to give 20 mg (100%) of a slightly yellow liquid which was identical in all respects with *cis*-bicyclo[4.3.0]nona-2,4-diene (**1**).

Pyrolysis of *syn,cis*-Tricyclo[4.3.0.0^{2,5}]non-3-ene (17). A solution of 3 mg of tricyclic hydrocarbon **17** in 1 mL of hexane (0.025 M) was placed in a thick-walled Pyrex tube, deaerated by nitrogen purge, and sealed. The tube was immersed in an oil bath at 150 °C for 1 h, cooled, and opened. Analysis by VPC (columns A, C, and E) showed disappearance of **17** and formation of *cis*-bicyclo[4.3.0]nona-2,4-diene (**1**), identified by coinjection on all three columns and by its ultravioldet spectrum.

Hydroboration and Oxidation of *syn,cis*-Tricyclo[4.3.0.0^{2,5}]non-3-ene (17). Following the general procedure for hydroboration and oxidation used for **16**, 10 mg (0.83 mmol) of tricyclic photoproduct **17** gave 4 mg (35%) of a mixture of compounds, one of which displayed a strong carbonyl absorption at 1780 cm^{-1} indicating the presence of a cyclobutanone.[11]

Irradiation of *cis*-Bicyclo[4.3.0]nona-2,4-diene (1) at 300 nm. A 4-mL solution of **1** in pentane (1.6 × 10^{-2} M) was placed in a Vycor tube, deaerated by helium purge, capped with a rubber septum, and irradiated at 300 nm in a Rayonet reactor (wavelength range 270-330 nm). The course of reaction was monitored by VPC (column B). No triene was observed, except possibly 1-2% early in the reaction. Prolonged irradiation gave the same photoproduct mixture found when diene **1** was irradiated with a medium-pressure lamp.

Irradiation of *cis*-Bicyclo[4.3.0]nona-2,4-diene (1) at 254 nm and Irradiation of *cis,cis,trans*-Cyclonona-1,3,5-triene (14) at 300 nm. A 4-mL solution of **1** in pentane was placed in a Vycor tube, deaerated by helium purge, capped with a rubber septum, and irradiated at 254 nm in a Rayonet reactor. The course of the irradiation was monitored by UV and by VPC (column B) until the photoequilibrium between **1** and **14** was reached (about 30% **1** and 70% **14**). The UV displayed isosbestic points at 235 and 283 nm; subtraction of the absorption due to diene **1** gave the spectrum for triene **14**. When photoequilibrium was established, the irradiation vessel was removed from a Rayonet reactor and cooled rapidly to −78 °C to prevent thermal isomerization of triene **14**. The lamps were changed to 300 nm. The irradiation vessel was warmed under cold water, replaced in the Rayonet reactor with a Pyrex filter (λ >280 nm), and irradiated. Rapid reversion to diene **1** was monitored by UV and by VPC. No bicyclo[2.2.0]hexene isomer **16** buildup was detected. The presence of triene **14** was measured on VPC as its thermal valence tautomer **15**. That **15** was not a photoproduct of **1** was evidenced by the observed disappearance of the VPC peak due to the trans diene **15** under conditions where **15** would not absorb light.

Temperature-Dependent Irradiation of *cis*-Bicyclo[4.3.0]nona-2,4-diene (1). A solution of diene **1** (1.58 × 10^{-2} M) in spectral-grade hexane was placed in the special quartz-tipped vessel and deaerated by nitrogen purge. The irradiation vessel was then placed in the quartz Dewar in which a cooling solution had been placed. Approximately one-half of the quartz tip was immersed in the coolant. About 15 min was allowed for thermal equilibration. Agitation was accomplished by a slow stream of precooled nitrogen saturated at that temperature with solvent vapor. Irradiation at 254 nm in the Rayonet reactor to about 15% conversion gave *cis,cis,trans*-cyclonona-1,3,5-triene (**14**) and *anti,cis*-tricyclo[4.3.0.0^{2,5}]non-3-ene (**16**). The ratio of **14** to **16** was determined by VPC (column B) and the peak areas were measured with a Hewlett-Packard Model 7123A electronic integrator recorder. The results are presented in Figure 1.

Quantum Yields. Irradiation of *cis*-Bicyclo[4.3.0]nona-2,4-diene (1). A. Black Box Apparatus (260-305 nm). The quantum yield was determined according to the general procedure with decane as internal standard.

Starting diene (201 mg, 1.67 mmol); 450 mL of hexane; 23 °C; 2.69 mE; 0.014 mmol of tricyclic photoproduct (**16**); 0.093 mmol of triene

(**14**); 12% conversion; $\varphi_{\text{triene}} = 0.035$, $\Phi_{2.2.0} = 0.005$.

B, Merry-Go-Round Apparatus (254 nm). A stock solution of diene **1** in spectral-grade hexane (1.58×10^{-2} M) with decane as an internal standard was deaerated by nitrogen purge. A 4-mL aliquot of this solution was transferred by pipet to a Vycor tube, purged again by nitrogen for 2 min, capped with a rubber septum, and placed in a merry-go-round apparatus. At least three sample tubes and two actinometer tubes were irradiated in each run. Actinometry was accomplished using 0.15 M potassium ferrioxalate solutions and, in one run, by photoisomerization of *anti,cis*-tricyclo[6.2.1.0^{2,7}]undeca-3,5-diene which using the black box technique had been found to have a quantum yield for isomerization to *anti,exo*-tetracyclo-[6.2.1.0^{2,7}0^{3,6}]undec-4-ene of 0.035 and had also been shown not to change its photochemistry as a function of wavelength. This run served to compare the compatibility of analysis by the black box and the merry-go-round techniques. Both sample and actinometer solutions absorbed greater than 99% of the incident light at 254 nm. A 10% correction factor was employed in those runs using potassium ferrioxalate as actinometer since the low-pressure mercury lamp used emits only about 90% of its radiation at 254 nm. Analysis of the photoproducts was by VPC (column B), and triene **14** was analyzed as *trans*-bicyclo[4.3.0]nona-2,4-diene (**15**).

Run 1. *anti,cis*-Tricyclo[6.2.1.0^{2,7}]undeca-3,5-diene was used as actinometer. Starting diene **1** (7.60 mg, 0.063 mmol); 4.0 mL of hexane; 23 °C; 0.031 mE; 0.000 31 mmol of tricyclic photoproduct **16**; 0.0099 mmol of triene (**14**); 21% conversion; $\Phi_{\text{triene}} = 0.32$, $\Phi_{2.2.0} = 0.01$.

Run 2. Ferrioxalate actinometry was used. Starting diene (7.60 mg, 0.063 mmol); 4.0 mL of hexane; 23 °C; 0.0089 mE; 0.000 10 mmol of tricyclic photoproduct **16**; 0.0031 mmol of triene **14**; 8% conversion; $\Phi_{\text{triene}} = 0.35$, $\Phi_{2.2.0} = 0.01$.

Triplet-Sensitized Irradiation of *cis*-Bicyclo[4,3.0]nona-2,4-diene (1). A 4-mL benzene solution containing diene **1** (1.0×10^{-2} M), acetophenone (0.3 M), and *n*-decane as internal standard was placed in a Vycor tube, deaerated, capped with a rubber septum, and irradiated for 1 h at 350 nm in the Rayonet reactor through a Pyrex sleeve (λ >280 nm). Analysis of the resulting mixture by VPC (columns A and C) showed the disappearance of diene **1** and no monomeric photoproduct formation.

Irradiation of *cis*-Bicyclo[4,4,0]deca-2,4-diene (2). A solution of 1.0 g of diene **2** (7.5 mmol) in 125 mL of anhydrous ether was irradiated according to the general procedure through a Corex filter for 5 h. The course of the reaction was monitored by VPC (column G) and the disappearance of starting material and the formation of two photoproducts in a ratio of about 4:3 were indicated. The reaction mixture was filtered to remove polymeric precipitate and rotary evaporated to give 860 mg (86%) of a yellow oil. The UV spectrum of the crude reaction mixture showed intense end absorption and the infrared spectrum had a band at 1950 cm^{-1} indicating the presence of a vinyl allene. The photoproducts were separated and purified by preparative VPC (columns J and H). No triene **20** or bicyclo[2.2.0]hexene products were observed; only materials mainly **21** and **22** from triene isomerization were obtained. Their chemistry will be presented in a later paper.

Irradiation of *cis*-Bicyclo[4.4.0]deca-2,4-diene (2). Wavelength Dependency. A 4-mL solution of diene **4** (1.4×10^{-2} M) in hexane with hexadecane as internal standard was placed in a Vycor tube and deaerated by nitrogen purge. The tube was capped with a rubber septum and irradiated in the Rayonet reactor. Irradiation at 254 and 300 nm resulted in the same overirradiation product mixture as analyzed by VPC (columns A and C). No triene **20** or bicyclo[2.2.0]-hexene product **23** were observed. The course of the reaction was monitored at both wavelengths by UV and there was a monotonic decrease in the absorbance of the starting material with no new strongly absorbing chromophores being formed.

Triplet-Sensitized Irradiation of *cis*-Bicyclo[4.4,0]deca-2,4-diene (2). The experiment was performed exactly as described for **1**. Analysis of the resulting mixture by VPC (columns A and C) showed the disappearance of diene **2** and no monomeric photoproduct formation.

Quantum Yields. Irradiation of *cis*-Bicyclo[4.4.0]deca-2,4-diene (2). The quantum yields for formation of the overirradiation products and for disappearance of diene **2** were determined according to the general procedure with hexadecane as internal standard.

Run 1. Starting diene (348 mg, 2.6 mmol); 450 mL of hexane; 23 °C; 1.78 mE; 0.051 mmol of overirradiation product **22**; 4% conversion; $\Phi_{22} = 0.029$, $\Phi_{\text{dis}} = 0.07$.

Run 2. Starting diene (139 mg, 1.04 mmol); 450 mL of hexane; 23 °C; 2.12 mE; 0.04 mmol of overirradiation product **22**; 11% conversion; $\Phi_{22} = 0.031$, $\Phi_{\text{dis}} = 0.07$.

Run 3. Starting diene (221 mg, 1.64 mmol); 450 mL of hexane; 23 °C; 3.1 mE; 0.105 mmol of overirradiation product **22**; 20% conversion; $\Phi_{22} = 0.034$, $\Phi_{\text{dis}} = 0.08$.

Irradiation of *cis*-Bicyclo[5.4.0]undeca-8,10-diene (3). A solution of 1.69 g of diene **3** (11.4 mmol) in 125 mL of pentane was irradiated according to the general procedure through a Corex filter. The course of the reaction was monitored by VPC (column A) and the reaction stopped when 70% of the starting material had been converted to three new compounds. The solvent was rotary evaporated to give 1.3 g of a yellow oil containing substantial polymeric material. The infrared spectrum of the crude product mixture had a distinct absorption at 1950 cm^{-1}, indicative of an allene. The components of the reaction mixture could be separated by preparative VPC (column K) at 120 °C, and are discussed in order of relative retention times.

The first photoproduct, formed in about 3% yield at 70% conversion, was *anti,cis*-tricyclo[5.4.0.0^{8,11}]undec-9-ene (**27**): IR 3000, 2900, 2820, 1540, 725 cm^{-1}; NMR δ 6.22 (m, 2, cyclobutene protons), 2.67 (m, 2, allylic bridgehead protons), 2.3–0.95 (m, 12, bridgehead and methylene protons); mass spectrum (70 eV) *m/e* 148, 146, 133, 131, 105, 92, 91, 79, 78, 77; high-resolution mass spectrum 148.1253 (calcd for $C_{11}H_{16}$, 148.1252).

The next compound eluted was a triene overirradiation product (13% yield, 17% of the volatile product mixture).

The starting diene **3** was next isolated and accounted for 40% of the volatile product mixture.

Photoproduct **25**, formed in 25% yield (33% of the volatile product mixture), was *cis,cis,trans*-cycloundeca-1,3,5-triene (**25**): UV max (hexane) 254 nm (ε 5000); IR 3000, 2900, 2800, 1450, 980, 680 cm^{-1}; NMR δ 6.2–5.1 (m, 6, vinyl protons), 2.3–1.9 (m, 4, allylic protons), 1.5 (m, 6, methylene protons); mass spectrum (70 eV) *m/e* 148, 146, 133, 131, 105, 92, 91; high-resolution mass spectrum 148.1255 (calcd for $C_{11}H_{16}$, 148.1252).

A small amount of benzosuberane was the final photoproduct.

Irradiation of *endo*-Tricyclo[7.2.1.0^{2,8}]dodec-3-en-12-one (13). A solution of 2.0 g of the tricyclic ketone **13** (11.4 mmol) in 125 mL of pentane was irradiated through Corex according to the general irradiation procedure for 13 h. The VPC chromatogram was identical with that observed in the irradiation of diene **3** except that the amounts of the various materials present were slightly different. The solvent was rotary evaporated to give 1.5 g of a yellow oil. The spectral data for the crude reaction products were also identical with those obtained from the irradiation of diene. Chromatography on neutral alumina impregnated with 25% silver nitrate, using successively as eluant 1 L of 5% ethyl acetate in hexane and 2 L of 12%, 1 L of 25%, 1 L of 35%, and 500 mL of 50% ethyl acetate in hexane, gave a total recovery of 1.0 g of material in 70-mL fractions. The first 12 fractions contained 300 mg of a material that polymerized on removal of solvent and of benzosuberane. Fractions 13–17 contained 378 mg of a mixture of tricyclic cyclobutene isomer **27** and the triene overirradiation product. Fractions 21–32 contained 187 mg of diene **3**, and fractions 58–75 contained 146 mg of triene **25**.

Irradiation for a longer period of time resulted in a product mixture containing the tricyclic cyclobutene **27** (4% yield), the tricyclic overirradiation product (30% yield), and benzosuberane (about 4% yield).

Pyrolysis of *anti,cis*-Tricyclo[5.4.0.0^{8,11}]undec-9-ene (27). A solution of 20 mg (0.135 mmol) of the tricyclic cyclobutene **27** in 20 μL of hexane was pyrolyzed at 220 °C on a gas chromatograph (column I). About 10 mg of pyrolysate was collected and shown by NMR to contain a 2:1 mixture of diene **3** and tricyclic cyclobutene **27**. No other materials were detected.

Pyrolysis of *cis,cis,trans*-Cycloundeca-1,3,5-triene (25). A 1-mL hexane solution containing 7 mg of the triene **25** (0.05 mmol), 5 mg of the overirradiation product, and 2 mg of benzosuberane was deaerated by nitrogen purge and sealed under vacuum. The sealed tube was immersed in an oil bath at 150 °C for 1 h. Control experiments showed the other components of the mixture to be stable under these conditions and they served as convenient internal standards. After cooling, the tube was opened and the resulting solution was analyzed by VPC (column A). No triene remained and a new material had been quantitatively formed. The reaction solution was rotary evaporated to give 15 mg of a clear, colorless liquid. The pyrolysis product was isolated by preparative VPC (column K) to give 4 mg of *trans*-bicyclo[5.4.0]undeca-8,10-diene (**26**), greater than 95% pure by analytical VPC (column A): UV max (hexane) 264 nm (ϵ 2500); IR 3010, 2900, 2850, 1700, 690 cm^{-1}; NMR δ 5.53 (q, 4, $\delta_A - \delta_B = 0.25$ ppm, $J_{AB} = J_{A'B'} = 10$ Hz, vinyl protons), 2.17 (m, 2, allylic protons), 1.62 (m, 10, methylene protons).

Irradiation of *cis*-Bicyclo[5.4.0]undeca-8,10-diene (3). Wavelength Dependency. Into Vycor tubes were placed 4-mL solutions of diene **3** in hexane (1.4×10^{-2} M) with hexadecane as internal standard. The solutions were deaerated by nitrogen purge, capped with a rubber septum, and irradiated in the Rayonet reactor equipped with RPR 254-nm or RPR 300-nm lamps. The progress of photorearrangement was monitored by VPC (column A) and by UV spectroscopy. The ultraviolet spectrum in all irradiations showed a shift of the maximum to shorter wavelength and finally only end absorption. The composition of the reaction mixture was determined as a function of time by determination of the area under the VPC peaks (triangulation) relative to internal standard. Plots of composition vs. time are illustrated in Figures 2 and 3 at low conversions. At both wavelengths, the ratio of products [**27**/**25**] remained fairly constant between 20 and 80% conversion.

Quantum Yields. Irradiation of *cis*-Bicyclo[5.4.0]undeca-8,10-diene (3). The quantum yields for formation of tricyclic cyclobutene isomer **27** and for formation of triene **25** were determined according to the general procedure with hexadecane as internal standard.

Run 1. Starting diene (293 mg, 1.98 mmol); 390 mL of hexane; 23 °C; 0.612 mE; 0.0018 mmol of tricyclic cyclobutene **27**; 0.069 mmol of triene **25**; 5% conversion; $\Phi_{2.2.0} = 0.003$, $\Phi_{\text{triene}} = 0.11$.

Run 2. Starting diene (175 mg, 1.18 mmol); 390 mL of hexane; 23 °C; 0.431 mE; 0.0014 mmol of tricyclic cyclobutene **27**; 0.0598 mmol of triene **25**; 5% conversion; $\Phi_{2.2.0} = 0.003$, $\Phi_{\text{triene}} = 0.14$.

Triplet-Sensitized Irradiation of *cis*-Bicyclo[5.4.0]undeca-8,10-diene (3). The experiment was performed exactly as described for **1**. Analysis of the reaction mixture by VPC (columns A and C) showed the disappearance of diene **3** and no monomeric photoproduct formation.

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References and Notes

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(2) For general reviews see: Dauben, W. G.; McInnis, E. L.; Michno, D. M. In "Rearrangements in Ground and Excited States", de Mayo, P., Ed.; Academic Press: New York, in press. Havinga, E. *Experientia* **1973**, *29*, 1181. Courtot, P.; Rumin, R.; Salaum, J-Y. *Pure Appl. Chem.* **1977**, *49*, 312.
(3) (a) Fonken, G. J.; Mehrotra, K. *Chem. Ind.* (*London*) **1964**, 1025. (b) Dauben, W. G.; Kellogg, M. S. *J. Am. Chem. Soc.* **1971**, *93*, 3805.
(4) (a) Dauben, W. G.; Rabinowitz, J.; Vietmeyer, N. D.; Wendschuh, P. H. *J. Am. Chem. Soc.* **1972**, *94*, 4285. (b) Dauben, W. G.; Kellogg, M. S.; Seeman, J. I.; Vietmeyer, N. D.; Wendschuh, P. H. *Pure Appl. Chem.* **1973**, *33*, (197. (c) Seeman, J. I. Ph.D. Thesis, University of California, Berkeley.
(5) Dauben, W. G.; Williams, R. G.; McKelvey, R. D. *J. Am. Chem. Soc.* **1973**, *95*, 3932.
(6) Gassman, P. G.; Marshall, J. L. *Org. Synth.* **1968**, *48*, 68.
(7) Buson, J. A.; Davis, R. F. *J. Am. Chem. Soc.* **1972**, *94*, 3658.
(8) Shuster, D. I.; Lee, F. H.; Padwa, A.; Gassman, P. G. *J. Org. Chem.* **1965**, *30*, 2262.
(9) Vogel, E.; Grimme, W.; Dinne, E. *Tetrahedron Lett.* **1965**, 391.
(10) (a) Roth, W. R.; Friedrich, A. *Tetrahedron Lett.* **1969**, 2607. (b) Frey, H. M.; Hopkins, R. G.; Oneal, H. E. *Chem. Commun.* **1969**, 1069. (c) Meinwald, J.; Schmidt, D. *J. Am. Chem. Soc.* **1969**, *91*, 5877. (d) Meinwald, J.; Tsuruta, H. *Ibid.* **1969**, *91*, 5877. (e) Zimmerman, H. E.; Robbins, J. D.; Schantl, J. *Ibid.* **1969**, *91*, 5878. (f) Roth, R. R.; Katz, T. J. *Ibid.* **1972**, *94*, 4771.
(11) Williams, D. H.; Fleming, I. "Spectroscopic Method in Organic Chemistry"; McGraw-Hill: New York, 1966.
(12) Woodward, R. B.; Hoffman, R. "The Conservation of Orbital Symmetry"; Academic Press: New York, 1970.
(13) (a) Fonken, G. J. *Tetrahedron Lett.* **1962**, 549. (b) Crowley, K. J. *J. Org. Chem.* **1968**, *33*, 3679.
(14) (a) Havinga, E.; de Kock, R. J.; Rappoldt, M. P. *Tetrahedron* **1960**, *11*, 276. (b) Pfoertner, K.; Weber, J. P. *Helv. Chim. Acta* **1972**, *55*, 921. (c) Pfoertner, K. *Ibid.* **1972**, *55*, 937.
(15) Dauben, W. G.; Coates, R. M. *J. Org. Chem.* **1964**, *29*, 2761.
(16) A preliminary publication of the wavelength dependency of this photoreaction has been published; see ref 3b.
(17) As the discussed reactions would indicate, the reactions should appear relatively inefficient at the longer wavelength range where photoequilibrium in favor of **1** is rapidly established. At 260–305 nm and 12% conversion, the apparent quantum yield[18,19] for the formation of **14** was 0.035 and for **16** was 0.005. Studies at 254 nm to the same degree of conversion indicated that the quantum yield for the triene **14** was at least 0.3 and for the bicyclo[2.2.0]hexene was 0.01. These gross quantum yields are in accord with the concept of the photoequilibrium dependence upon excitation wavelength.
(18) (a) Zimmerman, H. E. *Mol. Photochem.* **1971**, *3*, 281. (b) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A* **1956**, *235*, 518.
(19) Calvert, J. G.; Pitts, J. N., Jr. "Photochemistry"; Wiley: New York, 1966; p 371.
(20) Turro, N. J. "Molecular Photochemistry"; W. A. Benjamin: New York, 1967; p 132.
(21) Mehrotra, K. N. *Diss. Abstr.* **1967**, *66*, 7353.
(22) The stereochemistry previously postulated for these two products was incorrect; proof of the structures of **21** and **22** will be published in a later paper.
(23) Radlich, P.; Fenical, W. *Tetrahedron Lett.* **1967**, 4801.
(24) (a) Dauben, W. G.; Michno, D. M., submitted for publication. (b) Baldwin, J. E.; Kaplan, M. S. *J. Am. Chem. Soc.* **1971**, *93*, 3969.
(25) The direct conversion of a diene to a triene excited state has been proposed to account for isomeric triene formation (Ramamurthy, V.; Liu, R. S. H. *Tetrahedron Lett.* **1973**, 1393). Also, a similar proposal has been given for the photochemistry of olefins at 185 nm (Srinivasan, R.; Ors, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 3411).
(26) Zimmerman, H. E.; Pratt, A. C. *J. Am. Chem. Soc.* **1970**, *92*, 6259.
(27) Alder, K.; Dortmann, H. *Chem. Ber.* **1954**, *87*, 1905.
(28) (a) Winstein, S.; Watthey, J. W. H. *J. Am. Chem. Soc.* **1963**, *85*, 3715. (b) Glass, D. S.; Watthey, J. W. H.: Winstein, S. *Tetrahedron Lett.* **1965**, 377.
(29) Hoch, P. E. *J. Org. Chem.* **1961**, *26*, 2066.
(30) (a) Collins, J. C.; Hess, W. W.; Frank, F. J. *Tetrahedron Lett.* **1968**, 3363. (b) Radcliffe, R.; Rodehorst, R. *J. Org. Chem.* **1970**, *35*, 4000.