Reaction of *endo*-Bicycloocteneboronic Acid with Mercuric Chloride. The boronic acid from 4.5 g of 98.8% *endo*-dibutyl bicyclo[2.2.2]oct-2-ene-5-boronate was stirred with 4.6 g of mercuric chloride, 3.0 g of calcium carbonate, and 72 ml of acetone under reflux and nitrogen atmosphere for 7 days. Addition of 400 ml of water precipitated 0.34 g (5.8%) of *exo*-bicyclo[2.2.2]oct-2-enyl-5-mercuric chloride. The unreacted boronic acid recovered from the solution weighed 1.90 g (73%), identity checked by infrared.

Bromo-Demercurations.[10] A solution of 3.90 g of *exo*-bicyclo[2.2.2]oct-2-enyl-5-mercuric chloride (IV) in 35 ml of anhydrous pyridine (distilled from *p*-toluenesulfonyl chloride) was stirred at −40° under nitrogen during the dropwise addition of 1.8 g of bromine in 15 ml of pyridine over a period of 15 min. The solution was stirred 1 hr at −40°, mixed with 40 ml of cold hexane, and treated with 100 ml of cold water. The pyridine–mercuric bromide complex was filtered; yield 4.5 g (100%). The hexane solution was purified by further washings with water, acid, and sodium bicarbonate, and the hexane was distilled through an efficient column. The oily residue of bicyclooctenyl bromide was refluxed 3 days with 1.0 g of lithium carbonate in 50 ml of water and 4 ml of dioxane. Ether extraction yielded tricyclo[2.2.2.0^{2,6}]octan-3-ol, sublimed twice at 55° (0.1 mm), 0.38 g (28%), mp 122–123° (lit.[11] mp 125–127.1°), correct carbon and hydrogen analyses. Similar attempts to obtain tricyclooctanol from tricyclooctylmercuric chloride led to a small amount of oil which showed infrared absorption characteristic of the tricyclic alcohol.

Demercurations with Lithium Aluminum Hydride. A solution of 5.0 g of bicyclo[2.2.2]oct-2-enyl-5-mercuric chloride in 75 ml of ether was stirred under nitrogen at 0° during the dropwise addition of 2.2 g of lithium aluminum hydride in 50 ml of ether, then stirred at room temperature overnight. The mixture was cooled with an ice bath, the excess hydride decomposed with water, and the solid removed by filtration and washed with ether. The combined ether phase was distilled, and the residue sublimed at 15 mm to yield 0.40 g (26%) of bicyclo[2.2.2]octene, mp 114–115° (lit. mp 113–114.5°,[11] 116.4–117.5°[16]). Similar treatment of 4.0 g of tricyclo[2.2.2.0^{2,6}]octyl-3-mercuric chloride with 5 g of lithium aluminum hydride, improved in the work-up stages by the use of sodium hydroxide to dissolve the aluminum hydroxide and by careful fractionation of the ether, yielded 0.56 g (45%) of bicyclo[2.2.2]octene, mp 114–115.5°. The nmr spectrum showed a multiplet at τ 3.6–4.1 which integrated to 2.0/12 of the total proton signal.

***exo*-5-Chlorobicyclo[2.2.2]oct-2-ene (V).** Heating 5.7 g of bicyclo[2.2.2]oct-2-enyl-5-mercuric chloride to its melting point (150°) in air led to decomposition to metallic mercury and a yellow oil in a few minutes. The mixture was triturated with ether and filtered. Concentration of the filtrate and sublimation of the residue at 50° (14 mm) yielded 1.05 g (45%) of *exo*-5-chlorobicyclo[2.2.2]oct-2-ene, mp 39–40° with prior softening. Evidence for the unsaturated group appeared in the infrared at 3.27 and 6.20 μ (in CS_2) and in the nmr at τ 3.5–4.4, integral 2.0/11 of total. Infrared fingerprint bands appeared at 10.35, 10.93, 11.44, 12.20, 12.43, 13.93 (vs), and 14.81 μ.

Anal. Calcd for $C_8H_{11}Cl$: C, 67.36; H, 7.78; Cl, 24.86. Found: C, 67.13; H, 7.80; Cl, 24.88.

Heating tricyclooctylmercuric chloride on the steam bath led to rapid decomposition to *exo*-5-chlorobicyclo[2.2.2]oct-2-ene in similar yield, infrared spectrum identical, nmr integral at τ 3.5–4.4 was 1.8/11 of total. Storage of the mercury compound at room temperature under nitrogen for 5 days led to similar decomposition.

Solvolysis of *exo*-5-chlorobicyclo[2.2.2]oct-2-ene (V) was accomplished by refluxing 1.03 g of the compound in 60 ml of water and 4 ml of dioxane with 1.5 g of lithium carbonate under nitrogen for 3 days. Extraction with ether, concentration, and sublimation led to 0.76 g (85%) of tricyclo[2.2.2.0^{2,6}]octan-3-ol. Gas chromatography indicated this alcohol to be 95% pure with 1–2% each of compounds having identical retention times with *exo*- and *endo*-bicyclo[2.2.2]oct-2-en-5-ol plus a similar amount of an unidentified impurity, probably *exo*-bicyclo[3.2.1]oct-6-en-2-ol.[6]

Isomerization of Tricyclooctylmercuric Chloride (III). A solution of 1.0 g of tricyclo[2.2.2.0^{226}]octyl-3-mercuric chloride and 4.0 g of mercuric chloride in 80 ml of acetone was stirred with 1.5 g of calcium carbonate under nitrogen at room temperature for 26 hr. Filtration followed by addition of 300 ml of water precipitated 0.82 g of *exo*-bicyclo[2.2.2]oct-2-ene-5-mercuric chloride (IV), mp 148–149° dec, identity checked by infrared.

Isomerization of Tricyclooctanol (VI). A solution of 0.50 g of 95% tricyclo[2.2.2.0^{2,6}]octan-3-ol (VI) in 28 ml of water, 12 ml of acetone, and 0.023 ml of hydrochloric acid was refluxed 24 hr, then saturated with sodium chloride and extracted with ether. The ether extracts yielded 0.45 g (90%) of a sublimed mixture of alcohols, mainly *exo*-bicyclo[2.2.2]oct-2-en-5-ol according to the infrared and nmr spectra. Gas chromatography showed 76% *exo*-bicyclooctenol, 10.5% unchanged tricyclooctanol, less than 1% *endo*-bicyclooctanol, and 13% of an unidentified component presumed to be *exo*-bicyclo[3.2.1]oct-6-en-2-ol.[6] Similar treatment of tricyclooctanol under reflux for 7 days yielded 75% of a mixture of alcohols containing 86% *exo*-bicyclooctenol, 2% *endo*-bicyclooctanol, 0.15% tricyclooctanol, and 12% of the unidentified compound.

---

(16) H. L. Goering and M. F. Sloan, *J. Am. Chem. Soc.*, **83**, 1397 (1961).

The Photochemistry of (+)-2-Carene-4α-methanol

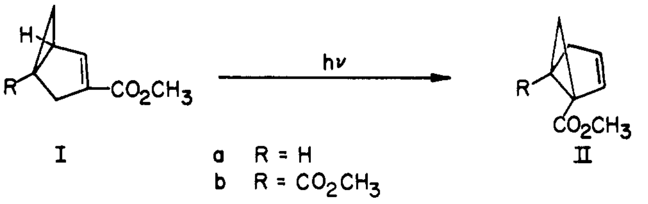
Paul J. Kropp

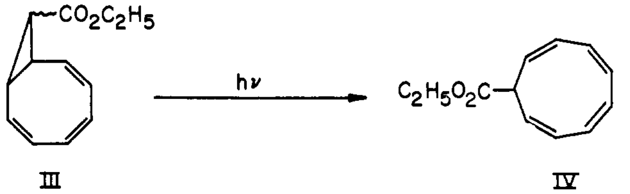
Contribution from The Procter & Gamble Company, Miami Valley Laboratories, Cincinnati, Ohio 45239. Received October 13, 1966

Abstract: In order to gain additional insight into the photochemical behavior of conjugated cyclopropyl systems, the light-induced behavior of the vinylcyclopropane **2**, a 2-carene derivative, was investigated. On irradiation in the presence of photosensitizers having $E_T \geq 74$ kcal/mole, **2** underwent selective isomerization involving the internal 1,6-cyclopropyl bond, to afford, as the only detectable photoproducts, a mixture of two bicyclo[3.2.0]hept-2-enes, to which are given the *cis,endo* and *cis,exo* assignments **3** and **4**, respectively. The behavior of **2** on direct irradiation was found to be more complex; the principal photoproducts were **3** and **4** and the menthene **24**, a product resulting from fission of the external 1,7-cyclopropyl bond. Thermal treatment of the photoproduct **4** did not effect any detectable reversion to **2**, but gave instead the bicyclo[2.2.1]heptane **20** by way of the endocyclic olefin **19**. Mechanistic implications of these results are discussed.

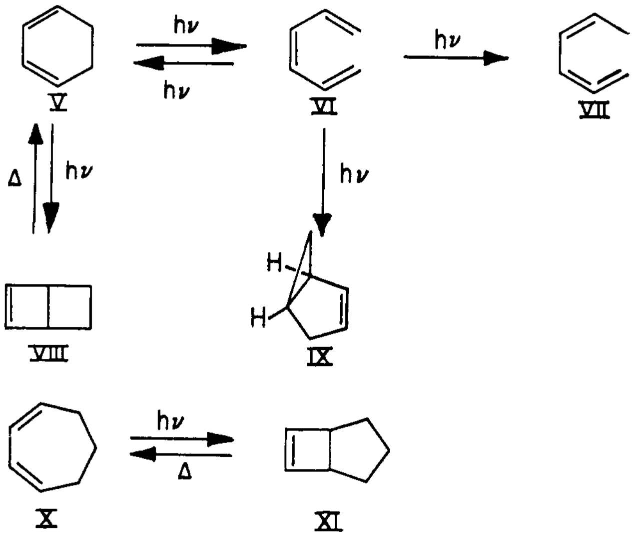
The cyclopropane ring has played an enigmatic role throughout the history of organic chemistry. Being labile and exhibiting many of the reactions characteristic of double bonds, it has, nevertheless, often displayed an ostensibly capricious behavior which has fostered long-standing controversies concerning, among other properties, its ability to transmit or extend conjugation[1] and its geometrical requirements, if any, for conjugation.[2] The general lack of understanding of the fundamental properties of conjugated cyclopropyl systems is perhaps nowhere more poignant than in the area of photochemistry.[3] With the intention of delineating more clearly the role of the cyclopropyl chromophore in the photochemistry of vinylcyclopropyl systems, an investigation of the 2-carene **2**[4] was initiated.

Although the thermal transformations of cyclic vinylcyclopropanes has been rather well investigated,[5] relatively little is known of their photochemical behavior. The fact that they have been obtained as photoisomerization products from various polyene systems[6–8] might seem to imply that they are photochemically stable. However, several examples of light-induced rearrangement of vinylcyclopropanes have been noted. For example, it is reported that the esters Ia and b undergo photorearrangement to IIa and b.[6c,8] The photochemistry of the ester III has also been pursued, and it has been suggested that in this case the primary photochemical process involves ring opening to the nonatetraene IV.[9,10]

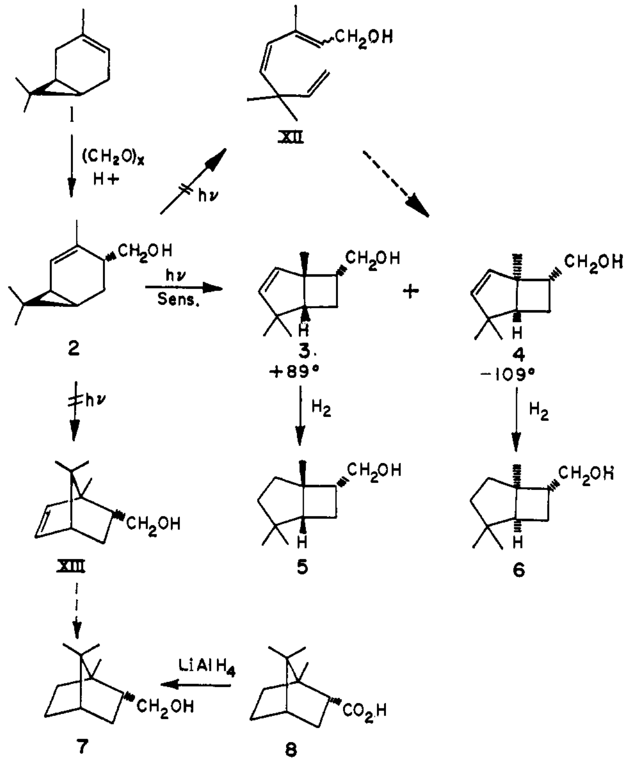




On the other hand, the photochemical isomerization of conjugated cyclic dienes has been the subject of extensive investigation,[6] and is characterized by two general modes of rearrangement. The principal photochemical pathway for 1,3-cyclohexadienes (V) involves ring cleavage to an acyclic triene VI, which can undergo further isomerization to an allene VII or a bicyclo[3.1.0]hexene (IX). In a few cases, principally those in which isomerization to the triene VI is structurally inhibited, the primary course of rearrangement is a bond-crossing process to give a bicyclo[2.2.0]hexene (VIII). In the case of 1,3-cycloheptadienes (X) (and larger ring systems) triene formation is precluded and bond switching to give a bicyclo[3.2.0]heptene (XI) is the sole course of rearrangement.



The 2-carene **2** was chosen for study because of its easy accessibility from 3-carene (**1**) through the Prins reaction.[4,11] This reaction is not only a convenient route to the conjugated 2-carene system, but it also provides a substituent at C-4 which can serve as both a positional



---

(1) See, for example, the discussion by E. N. Trachtenberg and G. Odian, *J. Am. Chem. Soc.*, **80**, 4018 (1958).

(2) See (a) E. M. Kosower and M. Ito, *Proc. Chem. Soc.*, 25 (1962); (b) A. L. Goodman and R. H. Eastman, *J. Am. Chem. Soc.*, **86**, 908 (1964), and references cited therein.

(3) See, for example, the discussion by P. J. Kropp, *Org. Photochem.*, **1**, 1 (1967).

(4) G. Ohloff, H. Farnow, and W. Philipp, *Ann.*, **613**, 43 (1958).

(5) See, for example, the review by W. von E. Doering and W. R. Roth, *Angew. Chem. Intern. Ed. Engl.*, **2**, 115 (1963).

(6) For recent reviews of the photochemistry of conjugated dienes see (a) W. G. Dauben, *Chem. Weekblad*, **60**, 381 (1964); (b) W. G. Dauben and W. T. Wipke, *Pure Appl. Chem.*, **9**, 539 (1964); (c) H. Prinzbach, H. Hagemann, J. H. Hartenstein, and R. Kitzing, *Chem. Ber.*, **98**, 2201 (1965).

(7) See, for example (a) K. J. Crowley, *Tetrahedron Letters*, 2863 (1965); (b) W. R. Roth and B. Peltzer, *Ann.*, **685**, 56 (1965); (c) J. Meinwald, A. Eckell, and K. L. Erickson, *J. Am. Chem. Soc.*, **87**, 3532 (1965); (d) J. Meinwald and P. H. Mazzocchi, *ibid.*, **88**, 2850 (1966).

(8) H. Prinzbach and E. Druckrey, *Tetrahedron Letters*, 2959 (1965).

(9) G. J. Fonken and W. Moran, *Chem. Ind.* (London), 1841 (1963); see ref 7b for a possibly related example.

(10) The photochemistry of several monocyclic vinylcyclopropanes has also received recent attention. See J. Wiemann, N. Thoai, and F. Weisbuch, *Tetrahedron Letters*, 2983 (1965), and M. J. Jorgenson, *J. Am. Chem. Soc.*, **88**, 3463 (1966). In these cases either simple cleavage or ring expansion of the cyclopropane ring was observed. For several recent reports of bond switching in homovinylcyclopropyl systems, see H. Prinzbach, W. Eberbach, and G. von Veh, *Angew. Chem.*, **77**, 454 (1965), and P. K. Freeman, D. G. Kuper, and V. N. M. Rao, *Tetrahedron Letters*, 3301 (1965).

(11) To facilitate clarity, Arabic numerals have been used to designate compounds encountered experimentally and Roman numerals to indicate other compounds introduced by way of discussion.

and a stereochemical point of reference in the photoproducts.[12] Rearrangement of **2** was investigated under both photosensitized and direct irradiation conditions.

Results

Photosensitized Rearrangement. As summarized in Table I, irradiation of benzene or toluene solutions of **2** with the broad spectral emission of a medium-pressure mercury arc effected a somewhat slow, but nonetheless clean, isomerization to a mixture of two photoproducts. The elemental analyses and mass spectra indicated that the photoproducts were isomeric with **2**, while the nmr spectra (outlined in Table II) revealed that the hydroxymethyl substituent had remained intact in each case. Also observable in the nmr spectra for both products were quartets attributable to the protons of a disubstituted double bond and singlets arising from three methyl groups, but no evidence for the continued presence of any cyclopropyl or allylic protons could be detected.

Table I. Photosensitized Rearrangement of (+)-2-Carene-4α-methanol (**2**)[a]

Sensitizer	E_T,[b] kcal/mole	Solvent	Time, hr	Yield, %[c] **3**	**4**	**2**
Benzene	84	..	14	10	57	13[d]
Benzene	84	MeOH	3	7	35	53
Benzene	84	HOAc	6	13	66	15
Toluene	83[e]	..	16	5	30[d]	..
Aniline	77	MeOH	12	6	30	36
Xanthone[f]	74	C_6H_6	16	1	4	90
Dibenzofuran[f]	70[g]	MeOH	16	..	..	98
Triphenylene[f]	67	MeOH	21	..	..	97

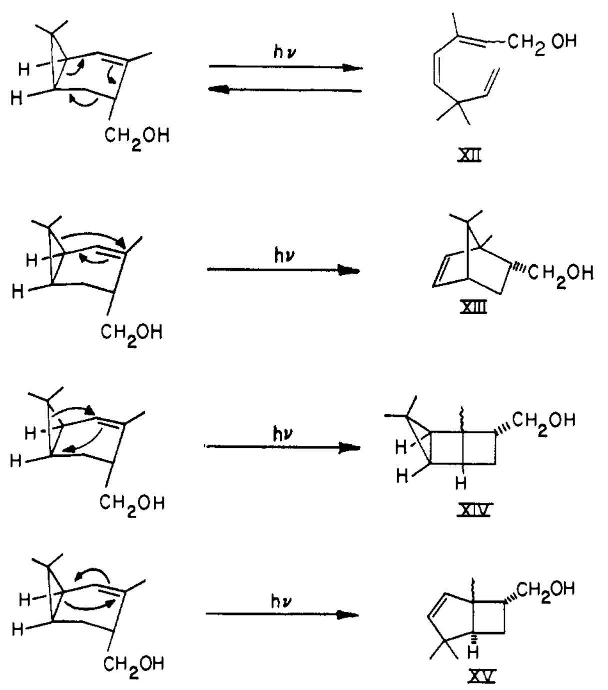
[a] Irradiations were conducted using a 450-w mercury lamp and a Vycor immersion well. Further details are outlined in the Experimental Section. [b] Data taken from N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, p 132. [c] Determined by gas chromatographic analysis of crude irradiation product unless otherwise indicated. [d] Determined by gas chromatographic analysis of distilled product mixture. [e] D. F. Evans, *J. Chem. Soc.*, 2753 (1959). [f] A Pyrex filter was employed. [g] W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 4537 (1964).

Table II. Nuclear Magnetic Resonance Data for Photoproducts **3** and **4**

Assignment	**3** τ	Integ	Pattern[a]	**4** τ	Integ	Pattern[a]
CH=CH	4.56 4.64	2	AB	4.62 4.70	2	AB
CH_2OH	6.52	2	A_2X[b]	6.32	2	ABX[b]
CH_3	8.76	3	s	8.88	3	s
	9.04	6	s	9.00	3	s
				9.03	3	s

[a] s, singlet. [b] The X proton is not distinguishable.

In analogy with the well-established photochemical behavior of cyclohexadienes,[6] two principal modes of rearrangement might be anticipated for **2**: (a) ring cleavage to the acyclic triene XII or (b) bond switching to one of the photoproducts XIII–XV, depending upon which cyclopropyl bond participates. Although the spectral data for the two photoproducts are clearly inconsistent with the structures XII and XIV, they are not incompatible with that expected for either of the olefins XIII or XV. However, the structure XIII was easily eliminated from further consideration for either photoproduct by the observation that hydrogenation of each of the two photoproducts gave dihydro derivatives which were quite different from a specimen of (+)-bornan-2-*endo*-methanol (**7**)[14] obtained by lithium aluminum hydride reduction of (+)-bornan-2-*endo*-carboxylic acid (**8**). There remained then only the bicyclo[3.2.0]heptene structure (XV); additional data substantiated the assignment of this basic skeleton and permitted the specific stereochemical assignments **3** and **4**, respectively, for the minor and principal photoproducts and **5** and **6** for their dihydro derivatives.



Oxidation of the major photoproduct **4** with 2 equiv of chromic acid provided a carboxylic acid (**11**). Reduction of the corresponding methyl ester **12** with lithium aluminum hydride regenerated **4**, confirming that no epimerization had occurred during the oxidation process. Treatment of the methyl ester **12** with methanolic sodium methoxide gave an epimeric methyl ester [(−)-**10**], which on reduction afforded the *optical antipode* (−)-**3** of the minor photoproduct (+)-**3**. When the isomerization was conducted in deuteriomethanol, the resulting alcohol (−)-**3** contained a single deuterium atom, which was located adjacent to the hydroxymethyl substituent.[15] This interconvertibility of the two systems indicates that the photoproducts possess the same basic structural skeleton, but with an antipodal relationship at each asymmetric center other than the one bearing the hydroxymethyl group.

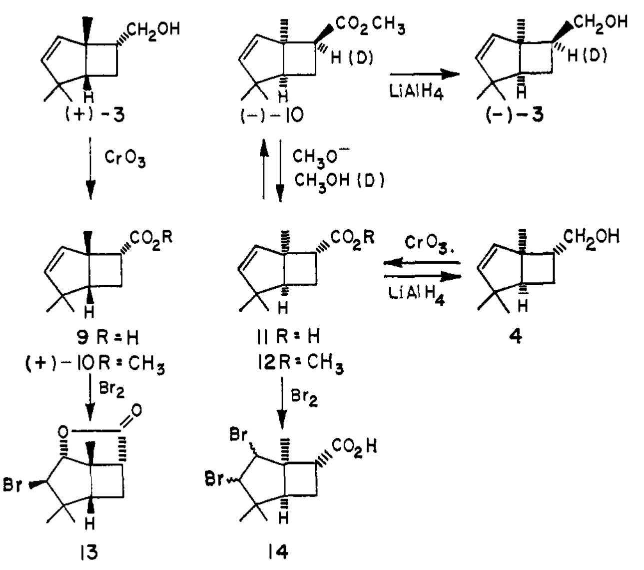
---

[12] Evidence for an α orientation of the hydroxymethyl substituent will be forthcoming: P. J. Kropp and D. C. Heckert, in preparation. This stereochemistry for **2** has been depicted previously,[4,13] but without any supporting comment.

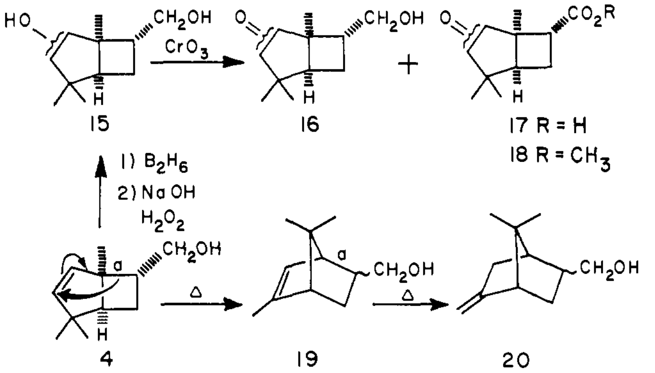
[13] (a) G. Ohloff, *Chem. Ber.*, **93**, 2673 (1960); (b) *Tetrahedron Letters*, 3795 (1965).

[14] (a) C. Rivière, *Ann. Chim.* (Paris), **1**, 157 (1946); (b) H. H. Zeiss and F. R. Zwanzig, *J. Am. Chem. Soc.*, **79**, 1733 (1957).

[15] With the introduction of the deuterium substituent at C-7 of **3**, the A_2X doublet of the hydroxymethyl group collapsed to a singlet.

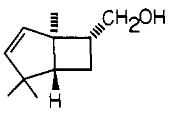


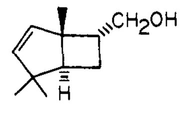
Hydroboration of the major photoproduct **4** followed by oxidative cleavage gave a 1:1 mixture of diols **15**. Partial oxidation with chromic acid afforded a mixture of keto alcohols **16** and keto acids **17**, which were characterized as the keto esters **18**. The ketones **16** and **17** exhibited intense infrared absorption at 5.76 μ characteristic of cyclopentanones, affording clear evidence for the presence of a cyclopentene moiety in each of the two photoproducts.[16]

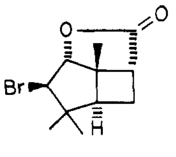


Oxidation of the minor photoproduct (+)-**3** gave the carboxylic acid derivative **9**. The acids **9** and **11** proved useful in delineating the precise stereochemical assignments for the photoproducts. Treatment of **9** with bromine resulted in the formation of a monobromo derivative **13** which possessed a γ-lactone ring, as evidenced by the presence of strong infrared absorption at 5.64 μ. By contrast, the acid **11** gave only a dibromo acid **14** which could not be induced to lactonize on prolonged heating in basic media.[17] The ability to form a γ-lactone indicates that in the acid **9** and, likewise, in the alcohol (+)-**3** the substituent must be *endo* oriented. In the epimer **11**, an *exo* relationship must therefore exist, and lactone formation is precluded, as observed.

The assignment of the bicyclo[3.2.0]hept-2-ene structure to the photoproducts **3** and **4** is completely consistent with all of the foregoing chemical and spectral data as well as with the thermal behavior of **4**, described below. The *cis*-ring fusion is assigned primarily on the basis of the facile formation of the γ-lactone **13**, although the possibility of having the pair of *trans* isomers XVI and XVII, with XVII giving rise to the exceptionally strained lactone XVIII, cannot be rigorously excluded. *trans*-Fused bicyclo[3.2.0]heptane derivatives have been synthesized,[18] but there are apparently no known *trans*-bicyclo[3.2.0]hept-2-enes, which should be much more highly strained than their saturated analogs.[19]


XVI


XVII

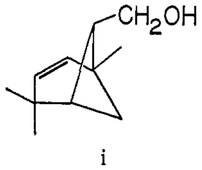

XVIII

As can be seen in Table I, the addition of methanol or acetic acid to a benzene solution of **2** had no observable effect on the photorearrangement to **3** and **4**. It is probable that the rearrangement is a photosensitized process in the presence of benzene or toluene since irradiation in solvents not capable of serving as photosensitizers led to much more complex results (see below). Moreover, a control experiment conducted at 2537 A led to no observable rearrangement of **2** in methanol under conditions in which substantial rearrangement occurred in benzene. Rearrangement to **3** and **4** also occurred with aniline or xanthone but completely failed using dibenzofuran or triphenylene as the photosensitizer. Irradiation of the major photoisomer **4** in benzene solution resulted in no detectable reversal to the starting carene **2** or rearrangement to the isomer **3**.

Thermal Rearrangement of Photoproduct 4. In contrast with the bond-switching process in cyclic dienes (V → VIII or X → XI),[6] the formation of the photoproduct **4** from the carene **2** is not thermally reversible. Treatment of **4** in a sealed tube at 300–325° generally afforded a single rearranged product which was neither the carene **2** nor the menthadiene **21**, to which **2** is known to isomerize at such temperatures.[13] An alternative rearrangement pathway available to **2** would be cleavage of bond a and recombination at the allylic position to give **19**—a process which might be either stepwise or concerted.[20] In agreement with this, a minor product isolated from one run conducted at precisely 300° exhibited nmr absorptions consonant with the principal structural features of **19**, including

---

[16] The mechanistically improbable structure i for the photoproduct, which is not rigorously excluded by the preceding data, is incompatible with the formation of a cyclopentanone.



i

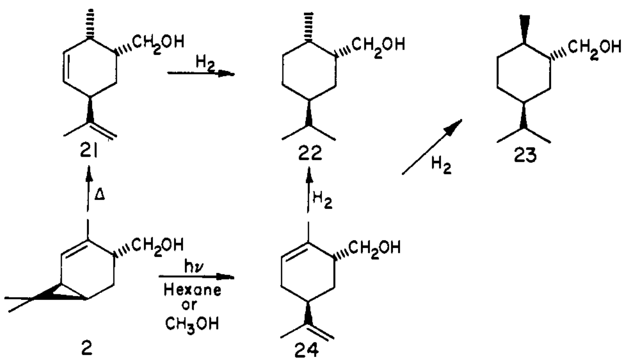
[17] Because of the proclivity of **14** for undergoing dehydrobromination, good analytical data could not be obtained.

[18] J. Meinwald, J. J. Tufariello, and J. J. Hurst, *J. Org. Chem.*, **29**, 2914 (1964).

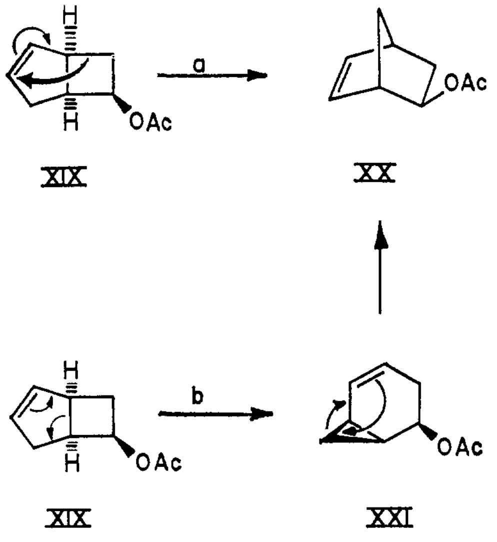
[19] In the stereochemical assignments **3** and **4**, it has been assumed that the orientation of the hydroxymethyl substituent remains unchanged from that in the starting 2-carene **2**. Should either this assumption or the α assignment for the hydroxymethyl group in **2** be invalid, the structures **3** and **4** are antipodal representations of the photoproducts.

[20] A third possibility of an intermolecular rearrangement involving dissociation to 2,5,5-trimethylcyclopentadiene and allyl alcohol followed by Diels–Alder recombination is not precluded by the present data.

one vinylic methyl group (τ 8.32) and a single vinylic proton (4.42) which were mutually coupled and two additional methyl groups (singlet at 9.02) located at a tetrasubstituted position. However, the major product from this run and the only product detected in all other experiments was clearly an exocyclic olefin, as evidenced by the appropriate infrared (6.02 and 11.32 μ) and nmr absorptions (one-proton multiplets at τ 5.12 and 5.32). Apparently the initial product **19** undergoes a facile secondary transformation to the exocyclic isomer **20**, in complete analogy with the previously observed thermal rearrangement of 2-methyl-2-norbornene to 2-methylenenorbornane.[21]



The conversion of **4** to **19** has direct analogy in the previously reported rearrangement of the bicyclo[3.2.0]hept-2-ene XIX to the norbornene XX,[22a] for which two possible pathways have been proposed:[22] (a) a one-step formal allylic rearrangement and (b) a two-step process involving a preliminary cyclopentene → vinylcyclopropane isomerization (XIX → XXI) followed by conversion of XXI to XX. In the present case the latter route can clearly be ruled out since the rearrangement product from **4** analogous to XXI would be the 2-carene **2**, which unquestionably is not formed.[23]



Direct Irradiation. When a hexane solution of **2** was irradiated at 2537 A, a very slow, but nonetheless clean, rearrangement of **2** to **3** and **4** occurred. However, when the monochromatic light source was replaced with the broad spectral emission of a high-pressure mercury arc, a substantially more complex reaction mixture was obtained. At least 24 photoproducts were observable by gas chromatographic analysis. Similar mixtures having only slightly different product ratios were obtained in methanol or *t*-butyl alcohol.

As shown in Table III, two of the principal photoproducts were again **3** and **4**, which were formed in ratios similar to those observed in the photosensitized rearrangement of **2**. The only other major product which could be isolated in pure form was identified as the menthadiene **24**.[24] This assignment was initially based on nmr and infrared absorptions attributable to the structural features $CH{=}C(CH_3)-$ and $-(CH_3)\text{-}C{=}CH_2$, along with the obvious absence of a cyclopropane ring. (See Experimental Section for details.) The basic structure was confirmed by the formation of two tetrahydro derivatives (**22** and **23**) on hydrogenation, one of which, **22**, was identical in all respects with the known tetrahydro derivative of the pyrolysis product **21**.[13a]

Table III. Direct Photochemical Rearrangement of (+)-2-Carene-4α-methanol (**2**)[a]

Solvent	Wave-length, A	Time, hr	Yield, % 3	4	24	2
Hexane	2537	72	9	41	. .	45
Hexane[b]	>2100[c]	16.5	3	21	19	1
Hexane[d]	>2100[c]	7	. .	. .	19	12
MeOH[b]	>2100[c]	7	2	12	35	5
MeOH	>2600[e]	48	. .	. .	. .	96
t-BuOH	>2100[c]	6	1	6	26	5

[a] See Experimental Section for details. [b] Typical results; similar yields were obtained in five or more runs. [c] Vycor apparatus employed with 450-w mercury lamp. [d] Naphthalene added. [e] Corex filter employed with 450-w mercury lamp.

Discussion

The data of Table I indicate that the lowest triplet of **2** lies within the range 74–77 kcal/mole[25]—well above the energy required to cleave a cyclopropyl bond.[26] The exclusive formation of the photoproducts **3** and **4** indicates that, of the three available cyclopropyl bonds, the internal 1,6 bond reacts selectively. However, the fact that two stereoisomeric *cis*-fused photoproducts are formed rules out the possibility of a concerted bond-switching process, at least as an exclusive reaction pathway. Apparently excitation of **2** to its lowest triplet state effects 1,6-bond cleavage to a cyclo-

---

(21) K. Alder and H.-J. Ache, *Chem. Ber.*, **95**, 511 (1962).

(22) (a) J. A. Berson and J. W. Patton, *J. Am. Chem. Soc.*, **84**, 3406 (1962); (b) J. A. Berson and E. S. Hand, *ibid.*, **86**, 1978 (1964).

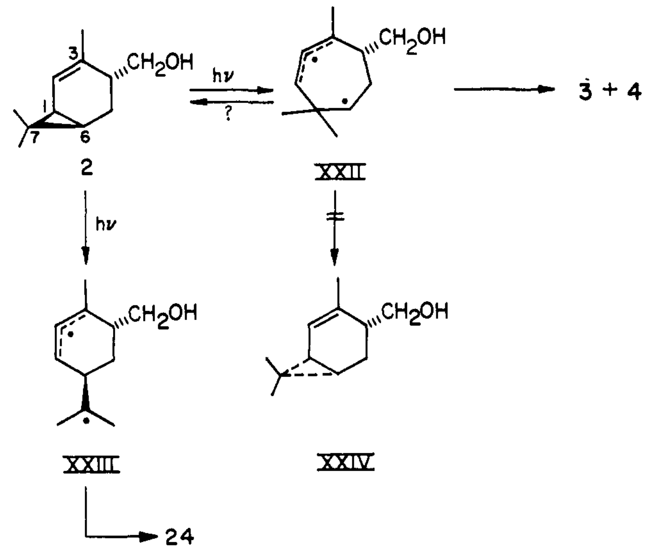
(23) A similar conclusion has recently been reached for the conversion of XIX to XX on the basis of deuterium labeling studies; see R. S. Wood, Ph.D. Dissertation, University of Wisconsin, 1966.

(24) J. Colonge and J. Crabalona, *Bull. Soc. Chim. France*, 102 (1960), have reported a (−)-*p*-mentha-1,8-diene-6-methanol of unspecified stereochemistry as a Prins reaction product from (+)-limonene. The physical properties reported for this material do not agree with those observed for the photoproduct **24**.

(25) It is assumed that the photosensitized rearrangements proceed *via* triplet energy transfer to **2**. For a recent demonstration of the transfer of triplet energy from excited benzene to cyclohexene, see R. B. Cundall and P. A. Griffiths, *Chem. Commun.*, 194 (1966). Transfer of singlet energy from aromatic hydrocarbons to dienes has recently been reported, but apparently occurs only at high diene concentrations; see L. M. Stephenson, D. G. Whitten, G. F. Vesley, and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 3665 (1966). Transfer of triplet energy by xanthone has also been previously reported; see V. L. Ermolaev, *Usp. Fiz. Nauk*, **80**, 3 (1963).

(26) F. H. Seubold, Jr., *J. Chem. Phys.*, **21**, 1616 (1953), has calculated the carbon–carbon bond dissociation energy for cyclopropane to be 50 kcal/mole.

heptenyl intermediate XXII followed by nonstereospecific 3,6 rebonding to form **3** and **4**.[27]



The possibility that the intermediate undergoes reversal to the starting 2-carene **2**, in addition to cyclization to **3** and **4**, is indeterminate from the present data. Also possible would be recyclization to the isomer XXIV, but comparison with an independently prepared specimen[12] revealed no evidence for the presence of XXIV at any stage of reaction.[28] An alternative route to **3** and **4** involving ring opening to the acyclic triene XII followed by subsequent intramolecular cyclobutane-type closure might also be considered. However, no evidence for such an intermediate could be detected. Moreover, the fact that **3** and **4** are generated in optically active form is not consistent with the intervention of a symmetrical intermediate such as XII.

By contrast, the direct irradiation of **2** with the broad mercury spectrum leads to a complex mixture of products, which includes, however, the photoproducts **3** and **4**. That **3** and **4** are again formed *via* a triplet intermediate is suggested by the fact that the formation of these two products can be selectively quenched by the addition of naphthalene (E_T 60 kcal/mole; see Table III, third entry). The failure of the other products to be either quenched by naphthalene or generated by photosensitizers suggests the intervention of singlet species in their formation.[29] A control experiment with **4** revealed that it is not a precursor to any of the other photoproducts formed by direct irradiation of **2**. Apparently **24** arises directly from **2** *via* cleavage of the external 1,7-cyclopropyl bond (see XXIII),[27] a reaction pathway not observed in the photosensitized rearrangements.

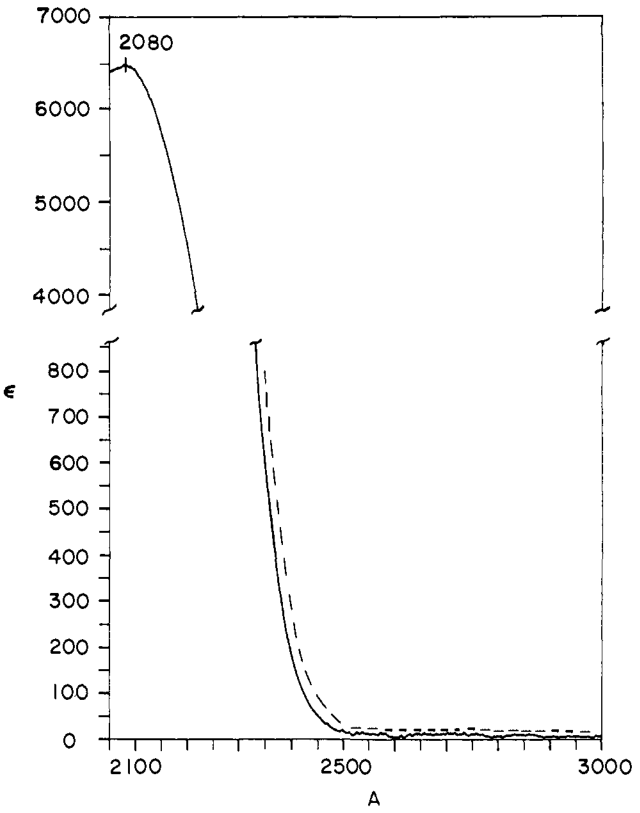


Figure 1. Ultraviolet absorption spectrum of 2-carene-4α-methanol (**2**) in methanol, ———; and hexane, – – – –.

A question which at once arises is whether the exclusive 1,6-bond scission by photosensitized irradiation, in contrast to concurrent 1,6- and 1,7-bond fission by direct irradiation, is merely attributable to a basic difference in behavior of singlet and triplet excited species. That this is perhaps not the complete explanation was indicated by the observation that direct irradiation of **2** in hexane at 2537 A gave only the photoproducts **3** and **4**, in complete analogy with the photosensitized rearrangements. From the ultraviolet absorption spectrum of **2** shown in Figure 1, it can be seen that 2537 A is about the longest wavelength at which absorption occurs. If the absorption spectrum of **2** consists of two or more unresolved bands, irradiation at 2537 A should effect a selective transition to the lowest available excited singlet state. Apparently excitation of **2** to this state results in selective 1,6 cleavage and rearrangement to **3** and **4**, possibly *via* intersystem crossing to the same low-lying triplet which is attained by energy transfer from photosensitizers.[30] On the other hand, irradiation at lower wavelengths could effect excitation to one or more additional excited singlet species.[33] This apparently results in less selective

---

(27) The representation of intermediates XXII and XXIII as radical species is not necessarily intended to have mechanistic significance.

(28) However, light-induced *cis–trans* isomerization of cyclopropanes is well known in other systems. See, for example, W. von E. Doering and M. Jones, Jr., *Tetrahedron Letters*, 791 (1963); G. W. Griffin, E. J. O'Connell, and H. A. Hammond, *J. Am. Chem. Soc.*, **85**, 1001 (1963); R. C. Cookson, M. J. Nye, and G. Subrahmanyam, *Proc. Chem. Soc.*, 144 (1964); and M. Jones, Jr., and K. R. Rettig, *J. Am. Chem. Soc.*, **87**, 4013 (1965).

(29) Previous experience with photosensitized reactions has shown that triplet-state reactions are often much more highly selective than their excited singlet-state counterparts; see, for example, R. S. H. Liu, *Tetrahedron Letters*, 2159 (1966), and references cited therein.

(30) It is of interest that the preferred mode of cleavage involves the 1,6 bond. The degree of substitution is obviously not a controlling factor since the 1,6 bond is only disubstituted whereas the 1,7 and 6,7 bonds are trisubstituted. Likewise, the order of photoreactivity does not parallel the degree of orbital overlap available in the ground state, since it is the orbitals of the 1,7 bond which come closer to being parallel and coplanar with the π orbitals of the double bond. This latter factor is apparently reflected, for example, in the acid-catalyzed[31] and other cationic cleavages[32] of **2** and related carenes, which generally involve rupture of the 1,7- or 6,7-cyclopropyl bonds.

(31) For a recent review of the chemistry of carane derivatives, see J. Verghese, *Perfumery Essent. Oil Record*, **56**, 438 (1965).

(32) See P. J. Kropp, *J. Am. Chem. Soc.*, **88**, 4926 (1966).

(33) It has been suggested that in systems containing a cyclopropane ring and an adjacent conjugating group, low-lying excited states might arise from excitation from the degenerate pair of highest occupied molecular orbitals of cyclopropane to the antibonding π* orbital; see R.

behavior and 1,7-bond cleavage.[34] Thus the identity of the initial electronic transition apparently plays a principal role in determining which cyclopropyl bond of a conjugated cyclopropyl system undergoes reaction. Any truly incisive understanding of the photochemical behavior of conjugated cyclopropyl systems must await a more precise characterization of the various excited states available to these systems.

Experimental Section[35]

Photosensitized Rearrangement of (+)-2-Carene-4α-methanol (2). A. In Benzene. A solution containing 628 mg of **2**[4] in 130 ml of benzene was irradiated for 14 hr using a Hanovia Type L 450-w, high-pressure mercury lamp and the apparatus previously described.[36] Removal of the solvent at atmospheric pressure followed by short-path distillation of the resulting residue at 105–110° (0.2 mm) gave 428 mg (79% recovery) of a colorless liquid which was shown by gas chromatography to consist solely of photoproducts **3** (12%) and **4** (72%) and recovered starting material (17%). The yields of **3** and **4** were thus 10 and 57%, respectively, or 11 and 65% based on recovered starting material.

Isolation by gas chromatography followed by short-path distillation at 104–105° (6.5 mm) gave **(+)-1,4,4-trimethyl-*cis*-bicyclo[3.2.0]hept-2-ene-7-*endo*-methanol (3)** as a colorless liquid, $[\alpha]^{27}\text{D}$ +89° (c 1.53); λ_{max} 2.98 and 12.88 μ; λ_{max} (0.02 M CCl_4) 3636 and 3620 cm^{-1}; nmr spectrum: τ 4.56, 4.64 (q, 2, J = 5.0 cps, CH-2 and -3), 6.52 (m, 2, CH_2O), 8.76 (s, 3, CH_3), and 9.04 (s, 6, $2CH_3$);[37a] *m/e:* 135, 133, 119, and 108;[37b] 3,5-dinitrobenzoate, long colorless needles from hexane, mp 76–77°.

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.25; H, 10.65.

Anal. Calcd for $C_{18}H_{20}N_2O_6$: C, 59.99; H, 5.59; N, 7.77. Found: C, 60.0; H, 5.6; N, 7.8.

Similar isolation by gas chromatography followed by short-path distillation at 90–90.5° (0.8 mm) gave **(−)-1,4,4-trimethyl-*cis*-bicyclo[3.2.0]hept-2-ene-7-*exo*-methanol (4)** as a colorless liquid, $[\alpha]^{27}\text{D}$ −109° (c 2.64); λ_{max} 2.98 and 13.00 μ; λ_{max} (0.02 M CCl_4) 3640 and 3620 cm^{-1}; nmr spectrum: τ 4.62, 4.70 (q, 2, J = 5.0 cps, CH-2 and -3), 6.32 (m, 2, CH_2O), 8.88 (s, 3, CH_3), and 9.00 and 9.03 (2s, 6, CH_3); *m/e:* 166, 134, 132, 119, and 108; 3,5-dinitrobenzoate, colorless needles from ethanol–hexane, mp 77–78°.

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.6; H, 10.9.

Anal. Calcd for $C_{18}H_{20}N_2O_6$: C, 59.99; H, 5.59; N, 7.77. Found: C, 60.3; H, 5.8; N, 7.9.

Irradiation of a solution of 503 mg of **2** in 103 ml of 3:1 benzene–methanol for 3 hr as described above gave, after removal of the solvent, 504 mg of a yellow oil shown by gas chromatography to consist of the photoproducts **3** (7% yield) and **4** (35%) and recovered starting material (53%).

Irradiation of a solution of 508 mg of **2** in 150 ml of 9:1 benzene–acetic acid for 6 hr as described above gave, after isolation by neutralization and extraction with ether, an amber liquid which was shown by gas chromatography to consist of the photoproducts **3** (13% yield) and **4** (66%) and recovered starting material (15%).

Irradiation of a solution of 521 mg of **2** in 125 ml of benzene for 5 hr with a low-pressure mercury lamp (2537 A) resulted in approximately 15% conversion to a mixture of the photoproducts **3** and **4**. Repetition of the experiment using methanol as the solvent failed to result in the formation of any detectable photoproducts.

B. In Toluene. Irradiation of a solution consisting of 1.00 g of **2**[4] in 150 ml of toluene for 16 hr as described above using benzene gave, after removal of the solvent and short-path distillation at 105–110° (0.2 mm), 382 mg of a colorless liquid which was shown by gas chromatography to be composed solely of photoproducts **3** (30% yield) and **4** (5%).

C. With Dibenzofuran. A solution containing 1.00 g of **2** and 50 mg of dibenzofuran in 150 ml of benzene was irradiated in a Pyrex vessel with a Hanovia 450-w, high-pressure mercury lamp for 16 hr. Removal of the solvent gave 1.10 g of an amber oil which was shown by gas chromatography to contain only recovered starting material and no detected photoproducts.

D. With Triphenylene. A solution containing 1.01 g of **2** and 50 mg of triphenylene in 150 ml of benzene was irradiated for 21 hr as described above with dibenzofuran. Removal of the solvent gave 1.15 g of a pale amber oil which was shown by gas chromatography to consist only of recovered starting material and no detectable photoproducts.

E. With Aniline. A solution containing 1.02 g of the carene **2** and 15 ml of freshly distilled aniline in 135 ml of methanol was irradiated for 12 hr as described above. The methanol was removed by distillation at atmospheric pressure, and the resulting residue was diluted with ether, exhaustively washed with 10% hydrochloric acid followed by saturated sodium bicarbonate solution and water, dried over saturated sodium chloride solution followed by anhydrous sodium sulfate, and concentrated by distillation at atmospheric pressure to give 1.76 g of a brown oil. Short-path distillation at 105–110° (0.2 mm) gave 743 mg (73% recovery) of a colorless liquid which was shown by gas chromatography to contain the photoproducts **3** (8.5%) and **4** (40%), as well as recovered starting material (49%) and an unidentified minor product. Gas chromatographic isolation of the first two components gave colorless liquids which exhibited infrared spectra identical with those of the two photoproducts described above.

F. With Xanthone. A solution of 1.01 g of **2** and 102 mg of xanthone in 150 ml of benzene was irradiated for 16 hr as described above except for the inclusion of a Pyrex filter. Removal of the solvent gave 1.10 g of an amber oil which was shown by gas chromatography to consist principally of **3** (1% yield), **4** (4%), and recovered **2** (90%). No rearrangement was observed under identical conditions except for the absence of xanthone.

Irradiation of (−)-1,4,4-Trimethyl-*cis*-bicyclo[3.2.0]hept-2-ene-7-*exo*-methanol (4). A solution of 102 mg of **4** in 125 ml of benzene was irradiated for 70 min as described above. Removal of the solvent at atmospheric pressure gave 103 mg of a colorless liquid which was shown by gas chromatography to consist solely of recovered starting material and to contain none of the other photoproducts usually obtained by irradiation of **2** in sensitizing or nonsensitizing media.

(−)-1,4,4-Trimethyl-*cis*-bicyclo[3.2.0]heptane-7-*endo*-methanol (5). A solution of 35 mg of **3** in 5 ml of absolute ethanol was stirred with 10 mg of 10% palladium on charcoal in the presence of hydrogen at atmospheric pressure until absorption ceased (0.9 molar equiv). Isolation in the usual manner followed by short-path distillation at 78° (2 mm) gave **7** as a colorless liquid which crystallized on cooling, mp 35–36°; $[\alpha]^{27}\text{D}$ −1° (c 1.06); λ_{max} (0.02 M CCl_4) 3635 and 3625 cm^{-1}; nmr spectrum: τ 6.42 (m, 2, CH_2O), 8.71 (s, 3, CH_3), and 9.09 (s, 6, CH_3); *m/e:* 168, 166, 153, 151, 150, 148, 137, 136, 135, 133, 131, 125, 123, 122, 121, and 119.

Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.55; H, 11.85.

(−)-1,4,4-Trimethyl-*cis*-bicyclo[3.2.0]heptane-7-*exo*-methanol (6). A solution of 77 mg of **4** in 20 ml of absolute ethanol was stirred with 10 mg of 10% palladium on charcoal in the presence of hydrogen at atmospheric pressure until absorption ceased (1.1 molar equiv). Removal of the catalyst by filtration and removal of the solvent by distillation at atmospheric pressure gave **6** as a colorless liquid which was further purified by short-path distillation at 84.5–86°

Hoffmann, *Tetrahedron Letters*, 3819 (1965). Such transitions should weaken cyclopropyl bonding in the excited state. Any such states for **2** would be in addition to the (π, π^*) excited states.

(34) A similar, but less decisive, wavelength dependence on the mode of cyclopropyl bond cleavage in two bicyclo[3.1.0]hexenones, with irradiation at the longest wavelength absorption favoring involvement of the internal cyclopropyl bond, has recently been reported by J. Frei, C. Ganter, D. Kägi, K. Kocsis, M. Miljković, A. Siewinski, R. Wenger, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **49**, 1049 (1966).

(35) Optical rotations were measured in absolute ethanol, and infrared spectra were obtained on neat samples with a Perkin-Elmer Infracord spectrophotometer unless otherwise indicated. Melting points were determined on a micro hot stage and are calibrated and corrected. Gas chromatographic analyses were performed on an Aerograph Model A-90P instrument using 10 ft × 0.25 in. columns packed with 20% Carbowax 20M on 60–80 mesh Firebrick or 20% SE-30 on 60–80 mesh Chromosorb W. The elution order used in column chromatography was hexane, benzene, ether, and ethyl acetate. Nuclear magnetic resonance spectra were determined in deuterated chloroform soultion with a Varian Model A-60 or HA-100 spectrometer, using tetramethylsilane as an internal standard. Mass spectra were obtained using an Atlas CH-4 spectrometer. Microanalyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Mich.

(36) P. J. Kropp and W. F. Erman, *J. Am. Chem. Soc.*, **85**, 2456 (1963).

(37) (a) Indicates multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; and m, unresolved multiplet), integration, coupling constant (cps), and assignment. (b) *m/e* values reported include the parent ion peak, if present, and other significantly large peaks appearing above the lowest value listed.

(2.1 mm); $[\alpha]^{27}_{\mathrm{D}}$ −56° (c 1.76); λ_{max} (0.02 M CCl_4) 3638 and 3625 cm^{-1}; nmr spectrum: τ 6.62 (m, 2, CH_2O), 8.82, 9.06, and 9.14 (3s, 9, CH_3); m/e: 168, 166, 153, 151, 150, 137, 135, and 110.

Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.8; H, 11.95.

(+)-1,4,4-Trimethyl-*cis*-bicyclo[3.2.0]hept-2-ene-7-*endo*-carboxylic Acid (9). A. Preparation. A solution of 109 mg of **3** and 10 ml of acetone was titrated with 2 molar equiv of chromic acid reagent.[38] Isolation in the usual manner followed by chromatography of the resulting crude product on 3 g of silica gel gave, on elution with benzene, 98 mg (83% yield) of acid **9** as a colorless liquid which was further purified by short-path distillation at 78° (0.15 mm); $[\alpha]^{27}_{\mathrm{D}}$ +47.5° (c 1.28); λ_{max} 5.72 (m), 5.88, and 12.26 μ; nmr spectrum: τ 4.52 and 4.62 (2d, 2, J = 6 cps, CH-2 and -3), 7.12 (m, 1, CH-7), and 8.68, 9.01, and 9.04 (3s, 9, CH_3).

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.7; H, 9.05.

Treatment with diazomethane followed by short-path distillation at 96–97° (3 mm) gave the **methyl ester 10** as a colorless liquid, $[\alpha]^{27}_{5461}$ +150° (c 1.64); λ_{max} 5.74 μ; nmr spectrum: τ 4.56 and 4.74 (2d, 2, J = 5 cps, CH-2 and -3), 6.42 (s, 3, OCH_3), 7.18 (m, 1, CH-7), 8.02 (m, 3, CH-5 and CH_2-6), and 8.70, 9.02, and 9.06 (3s, 9, CH_3).

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.5; H, 9.35.

B. Bromolactonization. To a solution of 135 mg (0.749 mmole) of acid **9** in 7 ml of carbon tetrachloride was added dropwise 2.8 ml of a carbon tetrachloride solution containing 120 mg (0.749 mmole) of bromine. The resulting colorless solution was taken up in ether, washed with water and saturated sodium bicarbonate solution, dried over saturated sodium chloride solution followed by anhydrous sodium sulfate, and concentrated to dryness at atmospheric pressure. Chromatography of the resulting residue on 6 g of silica gel gave, on elution with benzene, 178 mg (91% yield) of **(−)-3-*exo*-bromo-2-*endo*-hydroxy-1,4,4-trimethyl-*cis*-bicyclo[3.2.0]heptane-7-*endo*-carboxylic acid lactone (13)** as colorless crystals. Recrystallization from hexane gave large colorless prisms, mp 80.5–81°; $[\alpha]^{27}_{5461}$ −106° (c 1.01, $CHCl_3$); λ_{max} (5% CH_2Cl_2) 5.64 μ; nmr spectrum: τ 5.30 and 5.86 (2d, 2, J = 6 cps, CH-2 and -3), 7.40 (m, 1, CH-7), and 8.60, 8.86, and 9.06 (3s, 9, CH_3); m/e: 260, 258, 191, 189, 178, 177, and 161.

Anal. Calcd for $C_{11}H_{15}O_2Br$: C, 50.97; H, 5.83; Br, 30.83. Found: C, 50.7; H, 6.1; Br, 30.8.

(+)-1,4,4-Trimethyl-*cis*-bicyclo[3.2.0]hept-2-ene-7-*exo*-carboxylic Acid (11). A. Preparation. A solution of 973 mg of alcohol **4** in 25 ml of acetone was treated with 2 molar equiv of chromic acid solution. Isolation in the usual manner followed by chromatography of the resulting crude product on 30 g of silica gel gave, on elution with 1:3 and 1:1 benzene–hexane, the acid **11** as colorless crystals. Purification of comparable material by sublimation gave long colorless needles, mp 57–58°; $[\alpha]^{25}_{\mathrm{D}}$ +18° (c 1.10); λ_{max} (5% CH_2Cl_2) 5.72 (m), 5.88, and 12.90 μ; nmr spectrum: τ 4.50 (t, 2, CH-2 and -3), 7.18 (t, 1, CH-7), and 8.76, 8.94, and 8.98 (3s, 9, CH_3); m/e: 180, 165, 147, 135, 119, and 108.

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.55; H, 9.0.

Treatment with diazomethane followed by short-path distillation at 80–81° (0.8 mm) gave the **methyl ester 12** as a colorless liquid, $[\alpha]^{27}_{5461}$ −20° (c 1.56); λ_{max} 5.76 and 12.88 μ; nmr spectrum: τ 4.56 (t, 2, CH-2 and -3); 6.36 (s, 3, CH_3O-), 7.26 (t, 1, CH-7), and 8.92, 9.00, and 9.04 (3s, 9, CH_3).

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.4; H, 9.45.

B. Bromination. To a solution of 138 mg of acid **11** in 5 ml of carbon tetrachloride was added dropwise with stirring under an atmosphere of nitrogen a carbon tetrachloride solution containing 122 mg of bromine. After an additional 3 hr of stirring the solution still contained an excess of bromine. Removal of solvent gave 240 mg of yellow blades, mp 131–149°; λ_{max} (5% CH_2Cl_2) 5.70 (m) and 5.82 μ. Repeated recrystallization from ether–hexane gave long colorless needles, mp 141–142°; λ_{max} (5% CH_2Cl_2) 5.72 (m) and 5.84 μ.[17]

Anal. Calcd for $C_{11}H_{16}O_2Br_2$: C, 38.85; H, 4.74; Br, 47.00. Found: C, 40.85; H, 4.7; Br, 45.45.

Treatment of 178 mg of crystalline bromo acid **14** in 50 ml of ether with an excess of sodium hydride under reflux for 16 hr followed by acidification with 10% hydrochloric acid, extraction with ether, and drying and concentration of the combined extracts in the usual fashion gave 178 mg of a yellow oil which crystallized on standing and displayed an infrared spectrum unchanged from that of the starting material.

Epimerization of Ester 12. A solution containing 432 mg of ester **12** and a small piece of sodium in 1 ml of methanol was heated under reflux under an atmosphere of nitrogen for 3 days. Acidification with concentrated hydrochloric acid followed by extraction with ether, drying over saturated sodium chloride solution and then anhydrous sodium sulfate, and removal of solvent gave 390 mg of a yellow oil which was shown through the infrared spectrum to be a mixture of ester and carboxylic acid. Reduction with 164 mg of lithium aluminum hydride followed by isolation in the usual manner gave 332 mg of a yellow liquid which was shown by gas chromatography to consist of only two components present in a ratio of 43:57. Isolation of the first component followed by short-path distillation at 86° (0.9 mm) gave alcohol (−)-**3** as a colorless liquid, $[\alpha]^{27}_{\mathrm{D}}$ −97° (c 1.43). The infrared and nmr spectra of this material were identical with those described above. Isolation of the larger component gave a colorless liquid which exhibited infrared and nmr spectra identical with those described above for alcohol **4**.

In a second experiment 145 mg of ester **12** was treated as described above for 2 days with an excess of sodium in 5 ml of deuteriomethanol. Acidification with deuterioacetic acid and isolation as described above gave 178 mg of a yellow liquid, which was reduced with 70 mg of lithium aluminum hydride. The resulting colorless liquid (127 mg) was shown by gas chromatography to consist solely of two components present in a ratio of 32:68. Isolation of the minor component by gas chromatography followed by short-path distillation at 85° (0.9 mm) gave alcohol (−)-7-*d*-**3**, $[\alpha]^{27}_{\mathrm{D}}$ −90° (c 1.84); λ_{max} 2.95 and 12.90 μ; nmr spectrum identical with that described above except for the triplet at τ 6.52, which now appeared as a singlet, and the region from τ 7.5 to 8.5 which now appeared less complex; m/e: 167, 165, 149, 136, and 134 (94% D_1, 6% D_0). Gas chromatographic isolation of the major component gave a colorless liquid which exhibited infrared, nmr, and mass spectra identical with those described above for alcohol **4**.

Hydroboration of 4. To a solution of 522 mg of **4** in 10 ml of tetrahydrofuran was added dropwise with ice-bath cooling 10 ml of a 1 M solution of diborane in tetrahydrofuran. After standing 21 hr at 25°, the reaction mixture was again cooled with an ice bath, and 5 ml of 3 N sodium hydroxide followed by 5 ml of 30% hydrogen peroxide was added dropwise. After a 1-hr period the resulting solution was neutralized with 15% hydrochloric acid, saturated with sodium chloride, and thoroughly extracted with ether. The combined ether extracts were washed with saturated sodium bicarbonate solution, followed by saturated sodium chloride solution, and dried over anhydrous sodium sulfate. Removal of the solvent gave a colorless liquid which exhibited no infrared or nmr absorptions characteristic of an olefinic system. Oxidation with chromic acid solution gave 842 mg of a yellow oil which was chromatographed on 25 g of silica gel. Elution with 1:19 ether–benzene gave 110 mg of a mixture of **1,4,4-trimethyl-*cis*-bicyclo[3.2.0]hept-2- and -3-one-7-*exo*-carboxylic acid (17)** as a colorless, partially crystalline oil λ_{max} (1% CH_2Cl_2) 5.76 (s, >C=O and CO_2H) and 5.86 μ (m, CO_2H, dimer); nmr spectrum: no absorption below τ 7. Treatment with diazomethane followed by short-path distillation at 79.5–81° (0.2 mm) gave the mixture of **methyl esters 18** as a partially crystalline oil which exhibited two poorly resolved peaks of approximately equal area on gas chromatographic analysis; λ_{max} 5.76 μ.

Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63. Found: C, 68.75; H, 8.45.

Elution with 1:9 ether–benzene followed by short-path distillation at 110–112° (0.15 mm) gave 88 mg of the mixture of **1,4,4-trimethyl-*cis*-bicyclo[3.2.0]hept-2- and -3-one-7-*exo*-methanol (16)** as a colorless oil, λ_{max} 2.85, 5.76, and 5.82 μ (sh); nmr spectrum: τ 6.28 [m, 2 (rel to OH), CH_2O].

Thermal Isomerization of Alcohol 4. In a typical run 115 mg of alcohol **4** was maintained at 300° for a 4-hr period in a sealed tube under an atmosphere of nitrogen. Gas chromatographic analysis revealed the presence of three major components which were present in 39, 8, and 41% yields, respectively. Isolation of the first component by gas chromatography gave a colorless oil which was shown by the infrared and nmr spectra to be recovered starting material. Isolation of the second component gave 6 mg of **(+)-2,7,7-trimethyl-2-norbornene-5-methanol (19)** as colorless needles; nmr spectrum: τ 4.42 (m, 1, CH-3), 6.18 (d, 2, J = 7 cps, CH_2O), 8.32 (d, 3, CH_3-2), and 9.02 (s, 6, CH_3-7). Isolation of the major component followed by short-path distillation at 85–86° (0.1 mm)

---

[38] K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).

gave **(+)-7,7-dimethyl-2-methylenenorbornane-5-methanol (20)** as long colorless needles, mp 39.5–40.5°; $[\alpha]^{27}{}_{5461}$ +71° (*c* 1.74), $[\alpha]^{27}{}_{D}$ +61° (*c* 1.04); λ_{max} (5% CH_2Cl_2) 2.75, 6.02, and 11.32 μ; nmr spectrum: τ 5.12 and 5.32 (2m, 2, $=CH_2$), 6.36 (m, 2, CH_2O), and 8.98 and 9.02 (2s, 6, CH_3-7).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.3; H, 10.8.

(+)-Bornan-2-*endo*-methanol (7). Reduction of 197 mg of (+)-bornan-2-*endo*-carboxylic acid (**8**), mp 91–92.5°,[39] with 41 mg of lithium aluminum hydride in 15 ml of ether at 25° for 24 hr followed by isolation in the usual manner gave 215 mg of a pale yellow oil. Isolation by gas chromatography followed by sublimation gave alcohol **7** as long colorless needles, mp 84–85.5°; nmr spectrum: τ 6.30 (m, 2, CH_2O) and 9.12 (s, 9, CH_3-1 and -7); *m/e:* 168, 153, 150, 137, 135, and 107 (lit.[14] mp 77.5–79° for (±)-**7**, 88° for (+)-**7**).

Direct Irradiation of (+)-2-Carene-4α-methanol (2). A. In Methanol. In a typical experiment a solution containing 433 mg of **2**[4] in 150 ml of methanol was irradiated for 7 hr using a Hanovia Type-L 450-w, high-pressure mercury lamp and the apparatus previously described. Removal of the solvent at atmospheric pressure followed by short-path distillation of the resulting residue at 140–150° (0.2 mm) gave 324 mg (75% recovery) of a colorless liquid which was shown by gas chromatography to consist of at least 24 components, including recovered **2** (5%) and the olefins **3** (2%), **4** (12%), and **24** (35%). The first three were initially identified through their retention times, and the assignments were confirmed by the identity of the infrared spectra of collected material with those of authentic specimens obtained as described above.

Gas chromatographic isolation of the major component followed by short-path distillation at 85° (0.25 mm) gave **(+)-*p*-mentha-1,8-diene-6-methanol (24)** as a colorless liquid $[\alpha]_{D}^{27}$ +85° (*c* 1.76); $n^{25}{}_{D}$ 1.4968; λ_{max} 2.95, 6.06, and 11.26 μ; nmr spectrum: τ 4.54 (m, 1, CH-2), 5.38 (s, 2, CH_2-9), 6.42 (m, 2, CH_2O), and 8.32 (s, 6, CH_3-7 and -10); *m/e:* 166, 160, 151, 148, 135, and 133; 3,5-dinitrobenzoate, long colorless needles from ethanol, mp 78.5–79.5°, $[\alpha]^{27}{}_{D}$ +54° (*c* 1.40).[24]

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.2; H, 10.8.

B. In Hexane. In a typical experiment a solution containing 1.02 g of **2**[4] in 150 ml of hexane was irradiated as described above for 16.5 hr. Removal of the solvent at atmospheric pressure followed by short-path distillation of the resulting residue at 140–150° (0.1–0.2 mm) gave 721 mg (72% recovery) of a colorless liquid which displayed a complex gas chromatogram similar to that obtained from irradiations conducted in methanol, including peaks corresponding to recovered **2** (1%) and to photoproducts **3** (3%), **4** (21%), and **24** (19%). Each of these was further identified by isolation of the pure component and comparison of the infrared spectra with those of the specimens obtained by irradiation of **2** in methanol as described above.

C. In *t*-Butyl Alcohol. A solution of 509 mg of **2** in 125 ml of *t*-butyl alcohol was irradiated for 6 hr as described above. The resulting residue (512 mg) from removal of the solvent at atmospheric pressure gave a complex gas chromatogram similar to that obtained by conducting the irradiation in methanol, showing the presence of **2** (5% recovery) and of photoproducts **3** (1% yield), **4** (6%), and **24** (26%).

D. With a Corex Filter. A solution of 509 mg of **2**[4] in 125 ml of methanol was irradiated for 48 hr as described above. The resulting residue (520 mg) from removal of the solvent at atmospheric pressure gave a gas chromatogram identical with that of the starting material and showed no evidence for the formation of any photoproducts.

E. In the Presence of Naphthalene. A solution containing 520 mg of **2**[4] and 40 mg of naphthalene in 150 ml of hexane was irradiated for 7 hr as described above. Removal of the solvent at atmospheric pressure gave 593 mg of an amber oil which gave a gas chromatogram almost identical with that obtained by irradiation of **2** in hexane except for the absence of peaks corresponding to photoproducts **3** and **4**, including **2** (12% recovery) and photoproduct **24** (19% yield).

F. At 2537 A. A solution of 1.01 g of **2**[4] in 150 ml of hexane contained in a quartz flask was irradiated at 2537 A with low-pressure mercury lamps in a Rayonet photochemical reactor for 72 hr. Removal of the solvent gave 1.10 g of a pale amber oil which was shown by gas chromatography to consist of **2** (45% recovery) and photoproducts **3** (9% yield) and **4** (41%). None of the other photoproducts obtained by irradiation of **2** in hexane with a high-pressure mercury lamp could be detected. By contrast, irradiation under identical conditions except for the substitution of methanol as solvent afforded a mixture of photoproducts similar to that obtained with a 450-w lamp as described above, including **3** (2%), **4** (13%), **24** (36%), and recovered **2** (8%).

G. Control Run. A solution of 500 mg of photoproduct **4** in 150 ml of hexane was irradiated for 4 hr as described in part A. Removal of the solvent by distillation gave 510 mg of a pale yellow oil which was shown by gas chromatography to consist solely of starting material; no evidence for the presence of any of the other photoproducts obtained by irradiating **2** in hexane could be detected.

Hydrogenation of (+)-*p*-Mentha-1,8-diene-6-methanol (24). A solution containing 93 mg of photoproduct **24** in 5 ml of glacial acetic acid was stirred with 10 mg of platinum oxide under an atmosphere of hydrogen. Absorption ceased at 2 molar equiv. Isolation of the product by neutralization and extraction with ether followed by drying of the combined ether extracts over sodium chloride solution followed by anhydrous sodium sulfate, and subsequent removal of the solvent at atmospheric pressure gave 94 mg of a colorless liquid which was found by gas chromatography to consist of an approximately 1:1 mixture of alcohols **22** and **23**. Isolation of one of the components gave **22** as a colorless liquid which was identified by comparison of its gas chromatographic retention time and infrared and nmr spectra with those of an authentic specimen prepared by hydrogenation of (+)-*p*-mentha-2,8-diene-6-methanol (**21**);[13a] 3,5-dinitrobenzoate, fine colorless needles from ether–hexane, mp 100–101° which was unchanged upon admixture with similar material obtained from the authentic specimen (lit.[13a] mp 96.5°).

Gas chromatographic isolation of the second component followed by short-path distillation at 79–80° (0.3 mm) gave the tetrahydro alcohol **23** as a colorless liquid λ_{max} 2.95 μ; nmr spectrum: τ 6.42 (m, 2, CH_2O) and 9.16 (d, 9, $J = 6$ cps, CH_3CH).

Anal. Calcd for $C_{11}H_{22}O$: C, 77.58; H, 13.02. Found: C, 77.8; H, 12.7.

Acknowledgments. The able technical assistance of Messrs. H. J. Krauss and T. R. Walker is gratefully acknowledged. A generous supply of (+)-3-carene was provided by the Waldorf-Hoerner Corp., Missoula, Mont.

---

[39] Generously supplied by Dr. W. F. Erman.