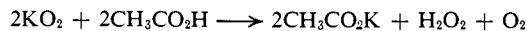


manually controlled gas buret. Potassium superoxide was analyzed³⁸ by the addition of diethyl phthalate (50 vol. %) followed by an equal volume of acetic acid at 0°. A vigorous evolution of oxygen occurred. The temperature was brought to room temperature and after shaking for 100 min the oxygen evolution was measured. The yield of potassium superoxide was calculated from the equation



Azobenzene was isolated from the oxidates after acidification with hydrochloric acid by the addition of 300 ml of water for 20 ml of the initial oxidate. After standing for 24 hr, the precipitated azobenzene was removed by filtration. The crystals were dissolved in methylene chloride and transferred to a tared flask. The solvent was removed under vacuum and the azobenzene, mp 67–68°, evacuated for 4 hr before weighing. Recovery tests indicated a loss of 20 mg of azobenzene in this procedure, and this correction has been applied to yields given in the text.

Photochemical Transformations of Unsaturated Bicyclic Ketones. Verbenone and Its Photodynamic Products of Ultraviolet Irradiation¹

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Contribution from The Procter & Gamble Company, Miami Valley Laboratories, Cincinnati, Ohio 45239. Received August 15, 1966

Abstract: Irradiation of verbenone (**1**) in cyclohexane or acetic acid with a light source with principal emission $>300\text{ m}\mu$ or a Pyrex filter afforded chrysanthenone (**2**) of high optical purity as the principal product (37–67%). In contrast, irradiation of **1** in cyclohexane with a broad-spectrum mercury arc lamp using a quartz or Vycor filter afforded as many as six products: the two decarbonylation products **9** (1–2%) and **10** (6–13%) and the rearranged ketones **8** (9–20%), **2** (6–16%), **11a** (4–6%), and **12** (2–3%). Three other ketones, **13**, **14**, and **15**, were produced in small amounts. Each of the compounds **2**, **8**, and **12**, from the latter irradiation, though optically active, showed appreciable loss of activity depending upon the length and conditions of irradiation. When alcohols were employed as solvent for the irradiation of **1** using the broad-spectrum lamp, the major products were the ketone **2** (12–20%) and the ester **3** (21%). Irradiation of **2** or **8** with the broad-spectrum lamp led to a photostationary state in which the ratio of **2** to **8** was approximately 1.5:1. The ketone **14** on exposure to ultraviolet light in methanol solution afforded the three acetals **19** (3%), **20** (2%), and **21** (11%) and the ester **3** (5%). Irradiation of **14** in cyclohexane afforded the hydrocarbon **10** (12%) as the principal isolable product and only trace quantities of **2** (1.8%) and **8** (2.1%). The above results are discussed in terms of the dual mechanisms proposed by Hurst and Whitham for the formation of chrysanthenone (**2**) from verbenone (**1**).

The photochemical conversion of verbenone (**1**) to chrysanthenone (**2**)² is one of two recorded examples in which α,β -unsaturated ketones undergo photoinduced rearrangement resulting in an ultimate 1,3-alkyl shift.³ Whitham and Hurst, in their investigation of this transformation, showed that ultraviolet irradiation of verbenone in cyclohexane afforded chrysanthenone with partial optical retention while irradiation in the presence of alcohol or amines yielded, besides ketone **2**, derivatives related to geranic acid (e.g., the ester **3b** or **4b**⁴ and the esters **5b** and **6b** resulted from irradiation of **1** in ethanol). They further showed that irradiation of chrysanthenone **2** in ethanol produced the same esters **3b**, **4b**, **5b**, and **6b**, while irradiation of optically active **2** for long periods in inert media afforded **2** with considerable loss of optical activity depending upon the period of irradiation.

(1) Paper presented in part before the Division of Organic Chemistry, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, Abstracts, p 29S.

(2) J. J. Hurst and G. H. Whitham, *J. Chem. Soc.*, 2864 (1960).

(3) A second example has been provided recently by Zimmerman and Sam, who reported the production of 2-(*cis*-styryl)-3-phenylcyclobutanone in 8–9% yield from the ultraviolet irradiation of 4,5-diphenylcyclohexenone in *t*-butyl alcohol: H. E. Zimmerman and D. J. Sam, *J. Am. Chem. Soc.*, **88**, 4905 (1966).

(4) Although two geometric isomers of the β,γ -unsaturated ester, i.e., **3** and **4**, could be produced in this reaction, Hurst and Whitham did not separate the isomers or assign stereochemistry to the predominant isomer.

All of these observations were consistent with a two-path mechanism for the formation of chrysanthenone (Chart I): path a, a fast process involving an ultimate 1,3-alkyl migration, and path b, cleavage of **1** to the ketene **7**, an optically inactive species, which undergoes an intramolecular thermal or photolytic cyclization to **2**. Photochemical racemization of chrysanthenone by cleavage to ketene **7** and recyclization to **2** (path c) would account for part of the loss in optical activity of **2** during the irradiation process.

In an over-all program directed toward the utilization of this reaction in sesquiterpene synthesis, we reinvestigated the photochemistry of verbenone with the hope of (1) effecting the rearrangement with minimal racemization, and (2) discovering other products of the irradiation (by varying reaction conditions) which might shed further light on the mechanism of product formation.

Results

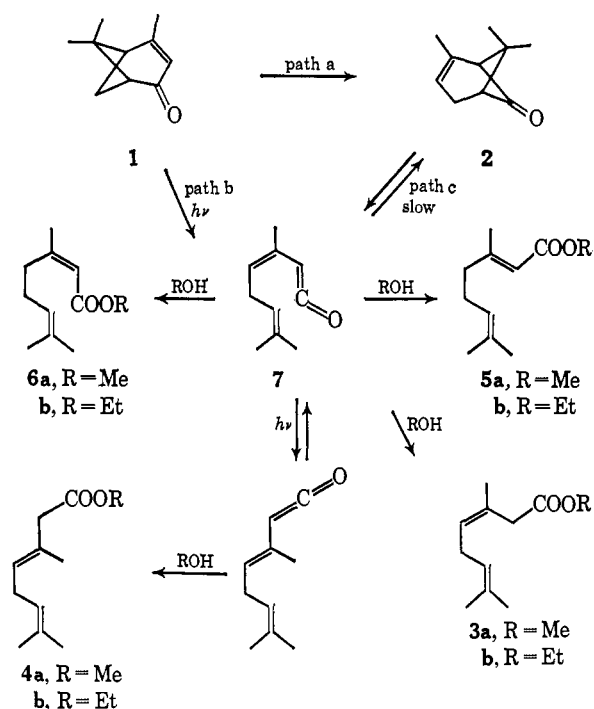
(–)-Verbenone (**1**) was irradiated under a variety of conditions using light sources with broad spectrum emission in quartz or Vycor vessels, using light sources with limited emission in the 280–300-m μ region, and using filters which diminish transmission of light below 300 m μ . The results of these experiments are listed in Table I.

Table I. Irradiation of (-)-Verbenone, $[\alpha]^{26D} -256^\circ$

Run	Lamp	Time, hr	Temp, $^\circ\text{C}$	Jacket	Solvent	% un-reacted	Yield, %					[α] 26D , deg							
							1	9	10	14	13	8	2	11	12	15	3	7	2
1	450 Hanovia	1.0	20	Vycor	Cyclohexane	0.4	1.5	9	0.1	0.2	20	16	4	2	0.4	...	+24	-28	+19
2	450 Hanovia	1.0	20	Quartz	Cyclohexane	Trace	1	6	0.3	0.5	19	11	6	3	0.5
3	450 Hanovia	3.0	20	Quartz	Cyclohexane	0	2	12	0.1	0.1	13	9	4	2	1.0	...	+14	-16	...
4	450 Hanovia	3.0	70	Quartz	Cyclohexane	0	2	13	1.1	0.8	9	6	3	2	1.0	-9 $^\circ$...
5 ^b	450 Hanovia	1.0	20	Vycor	Benzene	0	0.8	5	Trace	Trace	14	10	2	1	0
6	450 Hanovia	1.0	20	Pyrex	Cyclohexane	0	0.1	0.4	Trace	Trace	7	54	3	1.5	0	-36	...
7	450 Hanovia	1.0	20	Pyrex	Acetic acid	0	Trace	Trace	Trace	Trace	5	67	1.4	1.0	0	-76	...
8	450 Hanovia	0.16	20	Vycor	Acetic acid	17	0	0	0.3	0.5	2	38	0	0.5	0	-69	...
9	450 Hanovia	0.5	20	Vycor	Acetic acid	0	Trace	Trace	0.5	0.3	8	42	1	0	0
10	450 Hanovia	1.0	20	Vycor	Acetic acid	0	1	5	0.5	0.3	23	15	1	0	0
11 ^b	450 Hanovia	0.5	20	Vycor	Methanol	1	0	0	Trace	Trace	4	21	2	0.2	0	21
12 ^b	450 Hanovia	1.0	20	Vycor	Methanol	0	0	0	0.3	0.9	10	8	3	0	0	23
13	2537 A Rayonet	6.0	27	Quartz	Cyclohexane	8	0	0	0	2	7	42	Trace	7	Trace	-52	+41
14	3500 A Rayonet	6.0	27	Quartz	Cyclohexane	10	0	0	0	Trace	2	38	Trace	2	0	-50	...
15	3500 A Rayonet	6.0	27	Quartz	Acetic acid	5	0	0	0	Trace	2	43	Trace	0	0	-85	...

^a Solutions of 1.50 g of verbenone (1) in 150 ml of solvent were irradiated in runs 1-12; solutions of 1.00 g of 1 in 100 ml of solvent were irradiated in runs 13-15. ^b 1,5-Dimethyl-5-carbomethoxymethylcyclohex-1-ene (16) was also produced from run 11 in 2-3% yield and from run 12 in 4% yield. An unidentified ester was also produced in 2-3% yield from each run, 11 and 12. ^c The difference in rotation of 2 at 70 and 20 $^\circ$ may be explained by the fact that chrysanthenone undergoes slow thermal isomerization at these temperatures.

Chart I

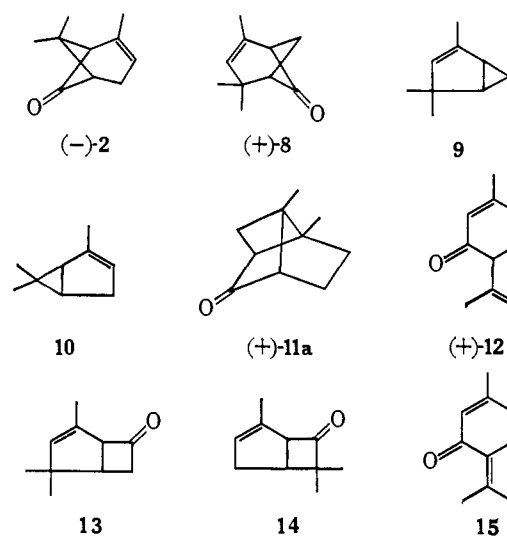


When a broad-spectrum, 450-w Hanovia mercury arc lamp and an inert solvent, cyclohexane, were employed for these irradiations, as many as six products (2, 8-12) were isolated even when we attempted to duplicate the conditions of Hurst and Whitham (*i.e.*, run 4, Table I):⁵ (-)-2,7,7-trimethylbicyclo[3.1.1]hept-2-

(5) The apparent anomalies between our results and those of Hurst and Whitham are, to a large extent, explained by differences in spectral properties of the specific lamps employed. Indeed, with our system,

en-6-one (chrysanthenone, 2), (+)-2,4,4-trimethylbicyclo[3.1.1]hept-2-en-6-one (8), 2,4,4-trimethylbicyclo[3.1.0]hex-2-ene (9), 2,6,6-trimethylbicyclo[3.1.0]hex-2-ene (10), (+)-1,2-dimethyltricyclo[3.3.0.0^{2,7}]octan-6-one (11a), and (+)-isopiperitenone (12) (Chart II). Three

Chart II



other compounds were formed in small quantities: 2,4,4-trimethylbicyclo[3.2.0]hex-2-en-7-one (13), 2,6,6-

complete consumption of 1.25 g of verbenone as a 1% solution in cyclohexane was observed after an irradiation period of less than 30 min compared to the 3-hr period reported by Hurst and Whitham. Exactly the same quantities of verbenone (1.25 g) and cyclohexane (125 ml) were employed in our initial runs in order to compare results with those of Hurst and Whitham. Subsequent experiments listed in Table I employed 1.5 g of verbenone in 150 ml of cyclohexane.

trimethylbicyclo[3.2.0]hex-2-en-7-one (**14**), and piperitenone (**15**).

An infrared spectrum of the crude reaction product showed the presence of ketene (4.72 μ) even when the irradiation was terminated after 5 min. The ketene could not be isolated as such from the reaction mixture but was trapped as the ester **3a** by addition of methanol to the reaction mixture after irradiation was complete. The compounds **2** and **8-12** accounted for 30–74% of the product in each run while polymer and possibly ketene dimers accounted for the remaining 26–70%. Each of the ketones **2** and **8** from irradiations with the broad spectrum lamp, though optically active, showed appreciable loss of activity depending upon the period or irradiation. Thus irradiation of verbenone, $[\alpha]^{26D} -256^\circ$, for a period of 1 hr (run 1) produced ketone **2**, $[\alpha]^{26D} -28^\circ$, and ketone **8**, $[\alpha]^{26D} +24^\circ$ (27% retention), while irradiation for a period of 3 hr yielded **2** and **7** with $[\alpha]^{26D} -16$ and $+14^\circ$ (15% retention), respectively. The isopiperitenone (**12**) isolated from the same 1-hr run was racemized to about the same extent as ketones **3** and **7**, $[\alpha]^{26D} +19^\circ$ (23% retention). Surprisingly, the tricyclic ketone **11a** from run 1, $[\alpha]^{26D} +158^\circ$ (61% retention), showed considerably greater retention of optical activity than its immediate precursor, isopiperitenone (**12**).⁶

In contrast to the above experiments with the broad-spectrum lamp, chrysanthenone (**2**) was almost the exclusive product when a light source with principal emission in the 2537- or 3500-A region⁷ or a Pyrex vessel which filters >90% of light of wavelength below 300 m μ was employed for the irradiations. The rearrangement proceeded with somewhat greater optical retention in the latter instances (compare runs 6, 13, and 14 to run 1, Table I).

When the irradiation was performed in methanol (runs 11 and 12) the principal products were chrysanthenone (**2**, 8–21%) and the *seqcis*- β,γ -unsaturated ester **3** (21–23%).⁸ A small quantity (2–3%) of a second ester, 1,5-dimethyl-5-carbomethoxymethylcyclohex-1-ene (**16**),⁹ was isolated from irradiation of **1** in methanol, but not even trace quantities of the *trans*- β,γ -unsaturated ester **4a** and the conjugated geranate **5a** and nerate **6a** esters were observed in the product mixture.¹⁰

When the irradiations were performed in acetic acid using a Pyrex filter or the 3500-A lamps, chrysanthenone of high optical purity relatively free of side products was isolated in 76 and 43% yields, respectively. That acetic acid is the preferred solvent for limiting racemization is indicated by comparing the rotation of ketone **2** isolated from run 6 ($[\alpha]^{26D} -36^\circ$,

cyclohexane) and run 7 ($[\alpha]^{26D} -76^\circ$, acetic acid). It should be emphasized that temperature is a critical factor in ruling the course of reaction in acetic acid. For example, when a 33% solution of (+)-verbenone (+253°) in acetic acid was irradiated at 40–50° for a period of 66 hr with the 3500-A lamp, the ketone **14**, $[\alpha]^{25D} -210^\circ$, was a major product (22%),¹¹ while the chrysanthenone (30%) was highly racemized, $[\alpha]^{25D} +14^\circ$.¹¹

In order to determine the role played by the ketones **2**, **8**, **12**, **14**, and **15** in the production or photochemical equilibrium of products, each was exposed to ultraviolet irradiation with the 450-w mercury arc lamp.

Chrysanthenone (**2**, 273 mg) when irradiated for a period of 20 min produced four major products: **9** (2%), **10** (13%), **8** (52%), and **2** (33%). When the irradiation was terminated after a shorter period, the ratio of ketone **2** to **8** was greater; however, longer periods of exposure did not alter this ratio appreciably.

Irradiation of the ketone **8** for periods identical with that used for chrysanthenone afforded the same products in almost identical yield (40%) and relative composition: **9** (4%), **10** (13%), **8** (56%), and **2** (27%). Further irradiation gave little change in ratio of products but considerable decrease in yields. Thus an apparent photostationary state between **8** and **2** is reached after about 20-min irradiation. Our many photochemical studies on verbenone suggest that the ratio of **8**:**2** is approximately 1.5–1.6:1 when this photostationary state is attained (see Table I).¹² If ketene **7** were involved as an intermediate in the photochemical transformation of verbenone to products, one might anticipate that optically inactive ketone **14** would be produced in significant quantities from this reaction. Since racemic **14** was not produced photochemically in significant quantity from any of these runs, we considered the possibility that **14**, though formed initially, was converted rapidly to the other observed products of the reaction. For this reason the photochemical behavior of **14** was investigated in some detail.

Based on documented examples of the photolytic behavior of 7,7-dimethylbicyclo[3.2.0]hex-2-en-6-one^{13b} or -bicyclo[3.2.0]hex-2-en-7-one,^{13a,c} one might predict that the ketone **14** could undergo photochemical cleavage *via* either or both paths a or b (Chart III). If path b proceeded at a rate faster than a, one might further predict that the ketone **14**, once formed from verbenone, would be in a photodynamic equilibrium with chrysanthenone **2** *via* the ketene intermediate **7**. In order to determine if the ketene **7** was produced to any extent, the irradiation of **14** was first performed in methanol in order to trap at least a minimal quantity of the ketene as the ester derivative **3a**.

(6) If the rearrangements proceeded with complete optical integrity the products would have been expected to possess the following estimated optical rotations (see Configurational Assignments): **2**, $\sim 108^\circ$; **8**, $\sim 105^\circ$; **11a**, $\sim 254^\circ$; **12**, $\sim 83^\circ$.

(7) For these experiments a Rayonet photochemical reactor was employed using lamps with principal emission in the region of 2537 and 3500 Å, respectively. With the former, bands of about 0.01 the intensity of the principal emission occur in the 280–300-m μ or $n \rightarrow \pi^*$ region of chrysanthenone (296 m μ). The 3500-Å lamp shows principal intensity above 310 m μ with maximum emission at 350 m μ .

(8) The *seqcis* and *seqtrans* terminology are used in accordance with the rules suggested by R. S. Cahn, C. Ingold, and V. Prelog, *Angew. Chem. Intern. Ed. Engl.*, **5**, 385 (1966).

(9) Structure proof of this ester will be presented in a separate communication by W. F. Erman and T. W. Gibson, to be submitted.

(10) Hurst and Whitham isolated, as the major product, ethyl geranate (**3**), as well as the nonconjugated isomer **4b**, from the irradiation of verbenone in ethanol. However, irradiations in the presence of amines produced only the nonconjugated isomers.

(11) It should be emphasized that chrysanthenone (**2**) is converted to ketone **14** on treatment with acetic acid under essentially the same conditions in the absence of light. We have also found that chrysanthenone undergoes thermal racemization on extended exposure to temperatures employed here. A description of the photochemical, thermal, and acid-catalyzed rearrangements of chrysanthenone and the mechanistic implications with regard to the photochemical rearrangement of verbenone will be reserved for a separate communication by W. F. Erman, to be published.

(12) For a further discussion of this and related photochemical reactions of β,γ -unsaturated ketones, see W. F. Erman and H. C. Kretschmar, *J. Am. Chem. Soc.*, **89**, 3842 (1967).

(13) (a) D. I. Schuster, M. Axelrod, and J. Auerbach, *Tetrahedron Letters*, 1911 (1963); (b) H. U. Hostettler, *ibid.*, 687 (1965); (c) G. O. Schenck and R. Steinmetz, *Chem. Ber.*, **96**, 520 (1963).

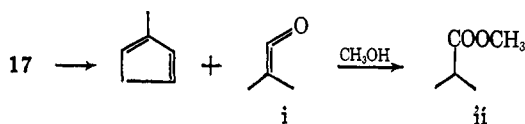
Irradiation of **14** in methanol, in fact, did produce the *cis*- β,γ -unsaturated ester **3a** in small but significant yield (5%). (As in the photolysis of verbenone, only the *cis* isomer was formed; not even trace quantities of the *trans* ester **4a**, nerate ester **6a**, or geranate ester **5a** were observed in the reaction mixture.) The principal products of the reaction, however, were an aldehyde (14%), which we were unable to identify because of its apparent lability, and the three acetals, 2,6,6-trimethyl-7-*endo*-methoxy-8-oxabicyclo[3.3.0]oct-2-ene (**19**, 3%), 2,6,6-trimethyl-7-*exo*-methoxy-8-oxabicyclo[3.3.0]oct-2-ene (**20**, 2%), and 2,6,6-trimethyl-8-*exo*-methoxy-7-oxabicyclo[3.3.0]oct-2-ene (**21**, 11%).¹⁴

Irradiation of **14** in cyclohexane afforded only trace quantities of the two ketones **8** (2.1%) and **2** (1.8%) (which could arise by intramolecular cyclization of the ketene **7**), along with a number of minor products including the unidentified aldehyde **22** (1.1%). The principal isolable product, however, was the hydrocarbon **10** (12%). The total absence from the reaction mixture of the hydrocarbon **9**, trace amounts of which could be detected easily by gas chromatography, certainly confirms that the latter hydrocarbon **9** is not formed *via* **10** (see Discussion) in the irradiation of verbenone. Even when the irradiation was performed in benzene as a photosensitizer, the cyclopropane **9** was not detected in the product mixture.¹⁵

It seemed obvious at first glance that isopiperitenone (**12**) was the photochemical precursor of the ketone **11a**. Indeed, irradiation of racemic isopiperitenone in cyclohexane with a broad-spectrum lamp and Vycor filter did produce as one product **11a** but in very poor yield (~3%). On the other hand, irradiation of **12** using a Pyrex filter afforded **11a** in 36% yield.¹⁶

It is quite surprising that the ketone **15** is absent from many runs when **12** is present in significant quantities.¹⁸ The reports of Yang on the isomerization

(14) We were unable to detect even trace quantities of methyl α -methylpropionate (ii) which would have arisen from the anticipated ketene fragmentation product i of the diradical **17**.¹³



(15) Prinzbach and Druckrey, on the other hand, have found that the closely related cyclopropane **iii** is transformed cleanly to **iv** on ultraviolet irradiation. The ester **iii** is thermally more stable, however, since **iv** is converted back to **iii** at 220°: H. Prinzbach and E. Druckrey, *Tetrahedron Letters*, 2959 (1965).

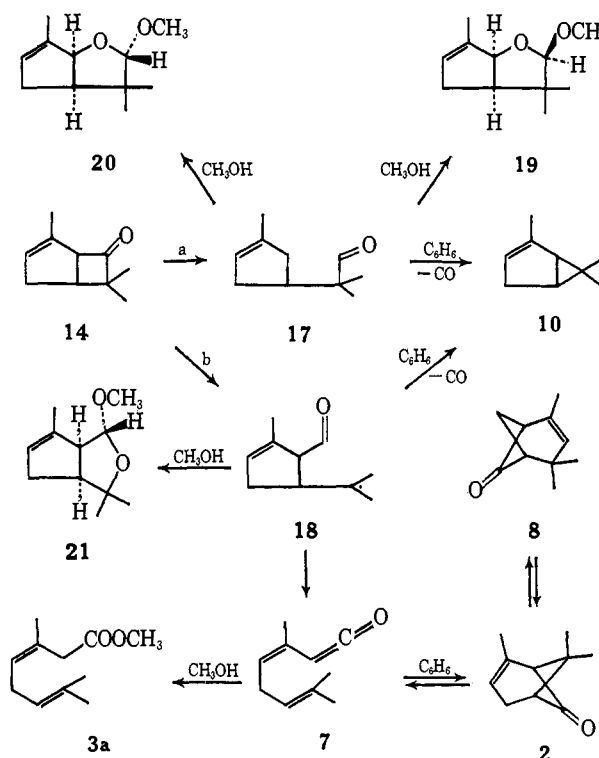


(16) It also should be emphasized that the analogous photoinduced cyclization of carvone to carvoncamphor is best performed in ethanol as solvent using sunlight¹⁷ or a light source with principal emission above 310 m μ . We are investigating the photochemical behavior of isopiperitenone in further detail. These studies, including irradiations in alcohol solvents, will be reported in a separate communication.⁹

(17) (a) G. Büchi and I. M. Goldman, *J. Am. Chem. Soc.*, **79**, 4741 (1957); (b) J. Meinwald and R. A. Schneider, *ibid.*, **87**, 5218 (1965); (c) T. W. Gibson and W. F. Erman, *J. Org. Chem.*, **31**, 3028 (1966).

(18) In fact, piperitenone may well be formed from isopiperitenone (**12**) during work-up exclusively. Thus **12** is converted to **15** by mild acid or base conditions including column chromatography separations on alumina or silica gel.

Chart III



of acyclic α,β -unsaturated ketones to the β,γ position¹⁹ prompted us to consider the possibility of photochemical rearrangement of piperitenone (**15**) to isopiperitenone (**12**). If such a photochemical conversion did occur, then this would account for the absence of piperitenone in these runs and also make available a convenient synthesis of isopiperitenone. Unfortunately, irradiation of piperitenone (**15**) for as long as 6.5 hr in cyclohexane or ethanol afforded only polymeric materials and unchanged **12**.²⁰

Structure Proof of Products. The structures of the two hydrocarbons **9** and **10** were easily deciphered by infrared and nmr spectroscopy. The infrared spectrum of **9** showed absorption at 6.11 and 12.0 μ typical of a trisubstituted olefin and at 9.75 μ , a characteristic band for cyclopropane.²¹ The nmr spectrum was well resolved in benzene (100 Mc). Since chemical shifts and spin-coupling constants are recorded in the Experimental Section, only two aspects of the spectrum which clearly define the structure as **9** will be discussed here. Since the *endo*-cyclopropyl methylene proton lies directly over the π orbitals of the olefin, a strong diamagnetic chemical shift²² of this proton to τ 9.74 is observed. The *exo* proton is well separated from the *endo* at τ 9.39. That these are the correct assignments for the *endo* and *exo* protons is confirmed by the spin-coupling patterns of each with the H-1 and H-5

(19) N. C. Yang and M. J. Jorgenson, *Tetrahedron Letters*, 1203 (1964).

(20) Photocyclodimerization of ethanolic or acetic acid solutions of the closely related piperitenone occurs in sunlight [W. Treibs, *Chem. Ber.*, **63**, 2738 (1930); H. Ziffer, N. E. Sharpless, and R. O. Kan, *Tetrahedron*, **22**, 3011 (1966)]. Indeed, photodimerization may be the principal course of reaction with piperitenone.

(21) Unless otherwise stated, infrared interpretations are derived from L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958.

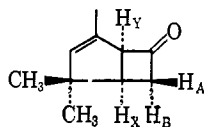
(22) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, p 129.

protons.²³ The *exo* proton is *cis* to the H-1 and H-5 protons and should exhibit greater coupling (6–8 cps) than the *endo* proton *trans* to H-1 and H-5 (3–5 cps).²⁴ Indeed, the methylene coupling pattern was that of an ABX₂ system with J (H-6-*endo*, H-6-*exo*) \cong 4.0 cps, J (H-1 and -5, H-6-*exo*) \cong 6.0 cps, and J (H-1 and -5, H-6-*endo*) \cong 3.0 cps, as anticipated.

One other distinguishing feature of the nmr spectrum of **9** is the vinyl C-3 proton signal which displays coupling of less than 1 cps. In contrast the vinyl C-3 proton exhibits considerably greater splitting in the nmr spectrum of **10**. This observation is consistent with the presence of the *gem*-dimethyl function at C-4 in **9** and a methylene at C-4 in structure **10**.

The same difference in chemical shift for the *endo*- and *exo*,*gem*-dimethyl protons in the nmr spectrum of **10** is observed as for the methylene protons of **9**. This observation plus the well-defined but broadened AB quartet exhibited by the allyl protons (centered at τ 7.85) serve to define the second hydrocarbon **10**.

The infrared, nmr, and mass spectra of compounds **13** and **14** were strikingly similar. The two compounds were resolved only with difficulty by gas chromatography. Since the structure of **14** was readily identified by comparison of the nmr, mass, infrared, and ultraviolet spectra with an authentic sample of **14** prepared by the method of Beereboom,²⁵ we were encouraged to propose the structure **13** for the second compound. The compound **13** showed strong absorption in the infrared spectrum for a cyclobutanone at 5.62 μ ,²⁴ a *gem*-dimethyl doublet at 7.25 μ ,²¹ and a trisubstituted olefin at 6.11 and 11.9 μ .²¹ The distinguishing feature of the nmr spectra of both **14** and **13** was the heavily coupled C-1 proton which occurred at τ 6.0 in both isomers. Final confirmation of structure **13** was presented by analysis of the nmr spectrum and spin decoupling experiments. The C-4 *gem*-dimethyl and C-2 vinyl methyl signals were readily apparent and are detailed in the Experimental Section. The C-6 protons appear as part of an ABXY system with the AB portion centered at τ 6.98 with $J_{AB} = 17.6$ cps, $J_{BX} = 8.1$ cps, $J_{AX} = 6.0$ cps, $J_{BY} = 4.0$ cps, and $J_{AY} = 2.4$ cps as anticipated for a slightly puckered four-membered ring. The C-5 (H_X) proton appears as a multiplet centered at τ 7.44. However, irradiation of the C-1 (H_Y) proton with a frequency of 2717 cps resolved the H_X spectrum into a simple quartet of $J_{BX} = 8.1$ cps and $J_{AX} = 6.0$ cps.²⁶



13

The principal features of the mass, nmr, infrared, and ultraviolet spectra of compounds **2** and **8** were mark-

(23) The numbering system for bicyclic structures as accepted by *Chemical Abstracts* is used throughout this paper.

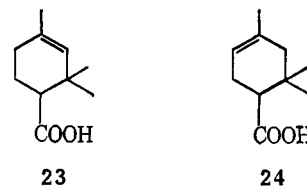
(24) (a) H. Weitkamp and F. Korte, *Tetrahedron*, **20**, 2125 (1964); (b) P. G. Gassman and F. V. Zalar, *Tetrahedron Letters*, 3251 (1964).

(25) J. J. Beereboom, *J. Am. Chem. Soc.*, **85**, 3525 (1963). We have assumed that the ketone isolated under the rather drastic conditions of heat and acid by Beereboom would equilibrate to the more stable *cis*-fused structure **14**.

(26) The ketone **13** is also produced from acid-catalyzed rearrangement of ketone **8**. Chemical confirmation of structure will be reported later.¹¹

edly similar. Since comparison of the infrared and ultraviolet spectra of the first isomer with that published for natural chrysanthenone²⁷ isolated from the essential oil *Chrysanthemum indium* established the structure **2** for this ketone, we were prompted to assign structure **8** to the second isomer.

Confirmation of structure **8** is apparent from the following arguments. The infrared spectrum of **8**, like that of chrysanthenone, showed strong carbonyl absorption at 5.62 μ suggestive of a cyclobutanone.²¹ The ultraviolet spectrum was that of a typical β,γ -unsaturated ketone with λ_{\max} 297 m μ (ϵ 180). Both ketones **2** and **8** were cleaved by alcoholic potassium hydroxide to a mixture of the two carboxylic acids, 2,2,4-trimethylcyclohex-3-enylcarboxylic acid (**23**) and 2,2,4-trimethylcyclohex-4-enylcarboxylic acid (**24**); the former (**2**) afforded **23** and **24** in the ratio 18:13 (55% yield), while the latter (**8**) gave **23** and **24** in the ratio 55:45 (52%).²⁸ Since β,γ -unsaturated cyclobutanones are known to be susceptible to attack by base with α cleavage occurring at the position allyl to the double bond,^{12,25,27,28} structure **8** must be assigned to the second isomer.



Final confirmation of structure **8** was given by the nmr spectrum (see Experimental Section), the most striking feature of which is the previously unreported long-range coupling (6.0 cps) between the H-1 and H-5 protons in the bicyclo[3.1.1]heptane system.²⁹ These protons occur as overlapping triplets centered at τ 7.1 with J (H-7-*exo*, H-1) \cong J (H-7-*exo*, H-5) = 6.0 cps, J (H-1, H-5) = 6.0 cps and J (H-1, H-7-*endo*) = J (H-5, H-7-*endo*) \cong 0 cps (some broadening). The 7-*exo* proton appears as a multiplet centered at τ 8.0 and superimposed with the C-2 methyl at τ 8.19 while the 7-*endo* proton appears as a doublet centered at τ 8.30, J (7-*endo*, 7-*exo*) = 9.0 cps. Irradiation of the bridgehead protons at τ 7.1 converted the C-7-*exo* proton at τ 8.1 into a doublet, $J = 9.0$ cps. Examination of Dreiding models of **8** reveals dihedral angles between the H-7-*endo* proton and the H-1 and H-5 protons of $\sim 85^\circ$; the result should be virtually no coupling between these protons as observed. The dihedral angle between the H-7-*exo* proton and the H-1 and

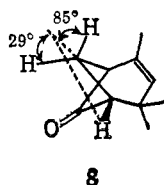
(27) J. de Pascual Teresa, H. Sanchez Bellido, and I. Sanchez Bellido, *Anales Real Soc. Espan. Fis. Quim.* (Madrid), *Ser. B*, **58**, 339 (1962).

(28) The base cleavage of chrysanthenone and the ketone **8** and the mechanistic implications of these cleavages will be discussed in another communication.

(29) The spin coupling between the bridgehead protons of the bicyclo[2.2.1]heptane system has been recorded as 1.5 cps^{30a} while that of the bicyclo[1.1.1]pentane system is reported as 18 cps.^{30b} Spin coupling between the bridgehead protons of the bicyclo[2.1.1]hexane system is as yet unrecorded.^{30c,d}

(30) (a) R. W. King and P. E. Butler, Abstracts, 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1962, p 84Q; (b) K. B. Wiberg, G. M. Lampman, R. P. Ciula, D. S. Connor, P. Schertler, and J. Lavanish, *Tetrahedron*, **21**, 2749 (1965); (c) J. Meinwald and A. Lewis, *J. Am. Chem. Soc.*, **83**, 2769 (1961); (d) K. B. Wiberg, B. R. Lowry, and B. J. Nist, *ibid.*, **84**, 1594 (1962).

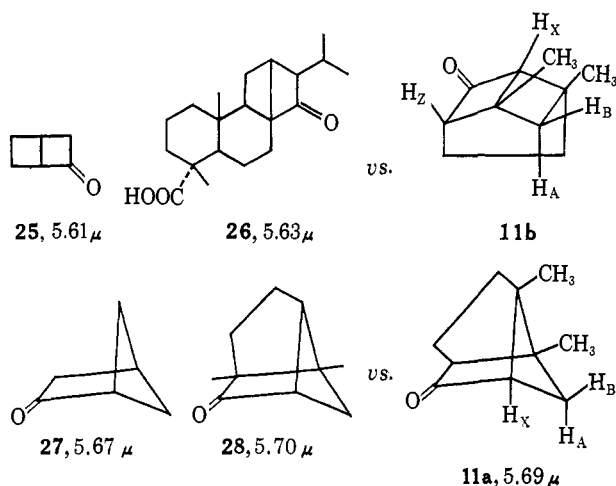
H-5 protons is $\sim 29^\circ$. The observed coupling of 6.0 cps is that predicted from the Karplus equation.³¹



The structure of piperitenone (**15**) was authenticated by comparison with a specimen of **15** prepared by the method of Schinz³² and the structure of isopiperitenone confirmed by comparison with an authentic sample prepared by the method of Schenck.³³

Compound **11**, described by the empirical formula $C_{10}H_{14}O$ (molecular weight and elemental analyses) was a crystalline solid, mp 136–138°, which possessed an unusually large optical rotation, $[\alpha]_D +158^\circ$. The infrared spectrum was that of a four-membered ring ketone or a strained five-membered ring, 5.69 μ . The compound was not affected by hydrogen in the presence of 10% palladium-on-charcoal catalyst; vinyl protons were conspicuously absent from the nmr spectrum. The structure must therefore be tricyclic. The nmr spectrum disclosed only two methyl groups (τ 8.96 and 9.06) and these were uncoupled. That these methyl groups were not located geminate to each other was indicated by the infrared spectrum which showed only a single sharp peak at 7.25 μ instead of the typical *gem*-dimethyl doublet.

These data are consistent with only two structures, **11a** and **b** below. That isopiperitenone yields the same ketone on irradiation in cyclohexane (see Results) strongly supports this assignment. Careful examination of the infrared carbonyl absorption prompted us to assign structure **11a** to this ketone. Thus the 4/4 fused ketones **25**³⁴ and **26**³⁵ exhibit carbonyl absorptions of 5.61 and 5.63 μ , respectively. In compari-



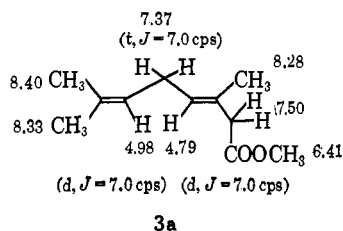
son, the bicyclo[2.1.1]hexanone (**27**)³⁶ absorbs at 5.67 μ in the infrared and the closely related 3,8-cyclocamphor (**28**)³⁷ at 5.70 μ comparable to the value for our tricyclic ketone (5.69 μ).

Absolute confirmation of structure was made by careful examination of the nmr spectrum and by double resonance experiments. The spectrum (in τ values) of **11** revealed an eight-peak ABX multiplet consisting of a doublet at 7.50 ($J = 3.0$ cps), a quartet at 7.80 ($J_1 = 8.5$ cps; $J_2 = 3.0$ cps) and a doublet at 8.33 ($J = 8.5$ cps), a broad peak at 7.77, and a very complex A_2B_2C pattern in the region of 7.8–8.8. (The doublet at τ 8.33 essentially bisects and does not appreciably overlap the A_2B_2C pattern.) Irradiation of the doublet at τ 7.50 with a frequency of 2701 cps converted the quartet at τ 7.80 into a doublet, $J = 8.5$ cps, but had no effect upon the doublet at τ 8.33. Irradiation of the quartet at τ 7.80 with a frequency of 2668 or 2701 cps converted both peaks at τ 8.33 and 7.50 into singlets.

Examination of a molecular model of **11a** indicates that the four-membered ring is partially puckered and that the angle between the protons H_A and H_X is approximately 80° ; thus the coupling constant J_{AB} should be less than 1 cps. The angle H_BH_X is approximately 34° and should exhibit coupling in the order of 3–5 cps. The geminate coupling J_{AB} in similar four-membered rings is reported to be in the order of 7–10 cps.^{17b,c} Since H_A is located at the apex of the π orbital of the ketone, this proton would be expected to occur at higher field than H_B . Furthermore, the proton located *exo* to the two-carbon bridge is paramagnetically shielded relative to the protons *endo* to this bridge in similarly substituted bicyclo[2.1.1]hexanes.^{17c} Thus the spectrum is completely consistent with structure **11a** with H_A at τ 8.33, H_B at τ 7.80, and H_X at τ 7.50.

In contrast the structure **11b** would not exhibit a simple ABX pattern as observed in the nmr spectrum of **11**. Although a secondary coupling of 3 cps between the H_X, H_B protons is possible, H_X would also show at least equal coupling with H_Z . Thus the H_X signal would be expected to occur as a triplet (or quartet) which should become a doublet on irradiation of H_B . The fact that the H_X signal degenerates into a singlet clearly precludes structure **11b** from consideration.

That the ester product from irradiation of verbenone (**1**) or the ketone **14** in methanol was the nonconjugated isomer **3a** or **4a** was suggested from the infrared carbonyl absorption, 5.73 μ , and the completely resolved nmr spectrum outlined below.



(31) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Inc., New York, N. Y., 1959, p 87.

(32) Ch. Balant, Ch. A. Vodoz, H. Kappeler, and H. Schinz, *Helv. Chim. Acta*, **34**, 722 (1951).

(33) G. O. Schenck, O.-A. Neumüller, G. Ohloff, and S. Schroeter, *Ann.*, **687**, 26 (1965).

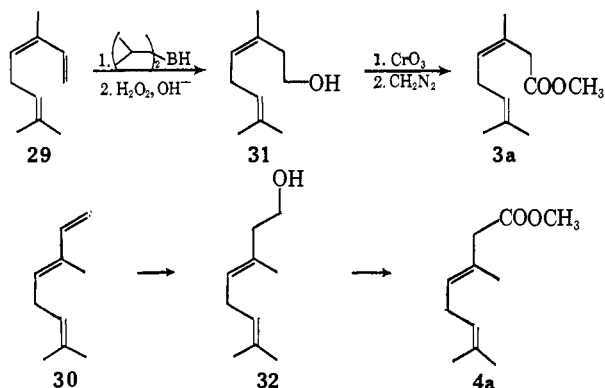
(34) R. N. McDonald and C. E. Reineke, *Tetrahedron Letters*, 2739 (1966).

(35) W. G. Dauben and R. M. Coates, *J. Am. Chem. Soc.*, **86**, 2490 (1964).

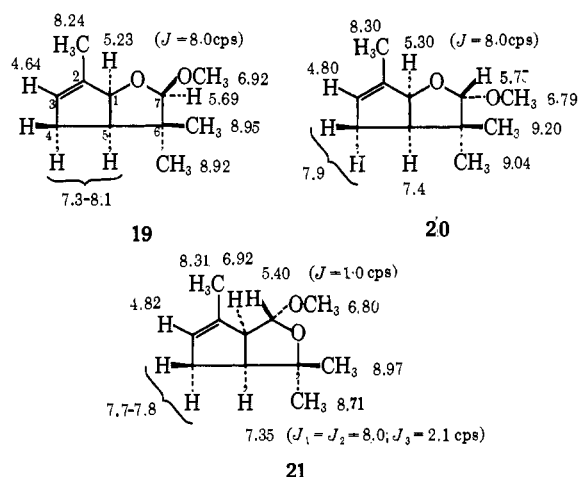
(36) J. Meinwald and P. G. Gassman, *ibid.*, **85**, 57 (1963).

(37) E. J. Corey, M. Ohno, S. W. Chow, and R. A. Scherrer, *ibid.*, **81**, 6305 (1959).

of **29** with disiamylborane,³⁸ subsequent Jones³⁹ oxidation, and diazomethane methylation afforded the *cis* ester **3a**. Repetition of the same sequence starting with *trans*-ocimene (**30**) produced the *trans* ester **4a** which was well separated from **3a** by gas chromatography.



The structures of the three acetals **19**, **20**, and **21** from irradiation of ketone **14** in methanol were described by the infrared spectra, which showed strong absorption in the 9–10- μ region, characteristic of ether functions, and by their well-resolved nmr spectra outlined below.



The C-7 methoxyl group is assigned the *endo* stereochemistry in **19** and the *exo* stereochemistry in **20** on the basis of the chemical shift of the methoxyl methyl protons and the C-7 protons of the two isomers. The C-7 proton in **20** lies over the π orbital of the C-2 carbon and should be diamagnetically shielded relative to the C-7 proton in **19**. Indeed, the C-7 proton in **20** occurs at 0.06 ppm higher field than the same proton in **19**. Similarly, the C-7 methoxyl protons in **19** occur at 0.13 ppm higher field than the C-7 methoxyl protons in **20**, a consequence of the former being situated almost directly over the double bond in **19**.

The stereochemistry of the third acetal **21** is defined by the spin-coupling pattern of the C-8 proton α to the methoxyl group. This proton, which occurs at τ 5.40, shows only small coupling (<1.0 cps) with the C-1 proton. Such small coupling would occur only if these protons were *trans* to each other. In this orientation the dihedral angle between the two protons is $\sim 107^\circ$. If the protons were *cis* oriented the resulting

(38) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **82**, 3223 (1960).

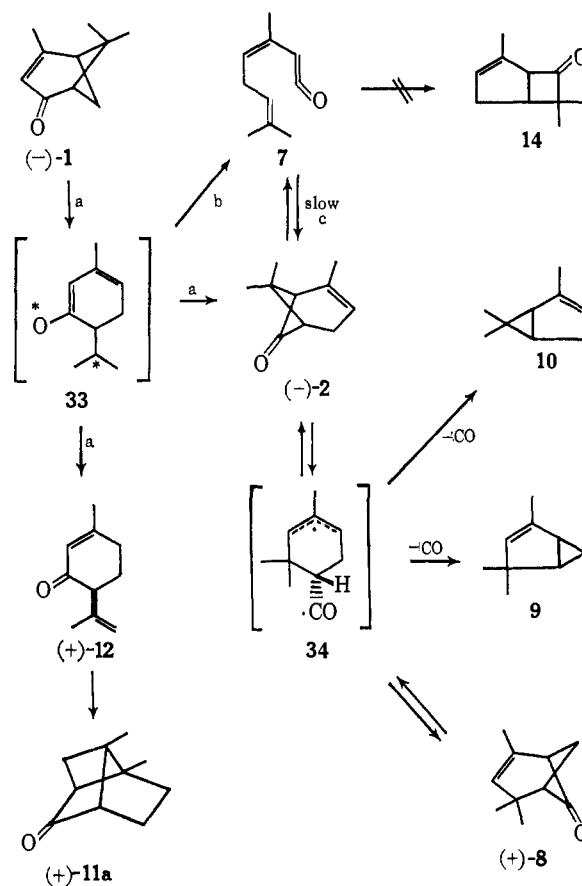
(39) K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).

dihedral angle (0°) would require spin interaction of at least 8–10 cps.

Absolute Configuration and Rotation of Products. The following arguments and experiments were employed to assess the absolute configuration and estimated optical rotations of compounds isolated or utilized in these reactions.

The preparation of verbenone (**1**) from pinene inherently proceeds with optical retention. Since the pinene utilized in this work possessed a rotation of -55° (chloroform) (-48° , neat) approaching that of optically pure pinene,⁴⁰ the rotation of -256° for verbenone approximates that of the optically pure compound. The absolute configuration of (–)-verbenone is deduced from the known configuration of (–)-pinene⁴¹ and is shown by structure **1** in Chart IV.

Chart IV



The absolute configuration and approximate maximum rotation of chrysanthenone were determined by interrelation with pinene. Wolff–Kishner reduction⁴² of **2** ($+13.8^\circ$) afforded pinene (-7°). Thus the absolute configuration of (–)-chrysanthenone is the same as (+)-pinene and is that shown by structure **2** in Chart IV. Based on the rotation of starting pinene ($+55^\circ$), the rotation of optically pure chrysanthenone is estimated at -108° .

The absolute configuration of (+)-isopiperitenone³³ has been related to (+)-limonene³⁸ and is that shown

(40) Optically pure pinene is reported to have a specific rotation of $\sim 51^\circ$ (neat): F. H. Thurber and R. C. Thielke, *J. Am. Chem. Soc.*, **53**, 1030 (1931).

(41) For appropriate references see A. J. Birch, *Ann. Rept. Progr. Chem.* (Chem. Soc. London), **47**, 191 (1950).

(42) D. J. Cram, M. R. V. Sahyun, and G. R. Knox, *J. Am. Chem. Soc.*, **84**, 1734 (1962).

by structure **12**, Chart IV. Although the rotation of optically pure isopiperitenone has not been determined, **12** of $[\alpha]_D +83^\circ$ has been prepared from limonene of high optical purity ($+123^\circ$) by a process which should proceed with optical retention.

Since irradiation of isopiperitenone, $+48^\circ$, produces **11a**, $+148^\circ$, the rotation of optically pure (+)-**11a** is estimated to be at least $+254^\circ$. The absolute configuration and maximum optical rotation of **7** are inferred from the mode of formation of (see Discussion) and the similarity in structure to **2**, respectively.

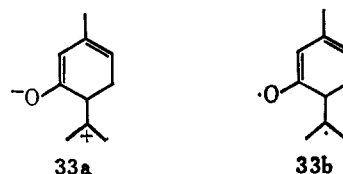
Discussion

Each of the major products isolated from irradiation of **1** with the 450-w mercury arc lamp can be depicted as emanating from two sources: the optically inactive ketene **7** and an optically active intermediate which, for the purpose of discussion, is represented by the species **33**. It will be shown subsequently in this discussion that the primary products of irradiation are ketene **7** and the ketones **2** and **12**, while the remaining photochemical products are derived from each of the initially produced ketones as outlined in Chart IV. In a separate communication¹¹ we will show that the minor products **13**, **14**, and **15** are also generated from ketones **8**, **2**, and **12**, respectively, by nonphotochemical processes. This latter observation and the fact that each of the ketones **13**, **14**, and **15** are produced in relatively small quantities from irradiation of **1** discourages us from discussing the exact mode of formation of these products at this time.

Primary Products of Irradiation. That both paths a and b are involved in the formation of ketones **2** and **12** is indicated by the fact that each ketone is partially racemized regardless of the conditions employed in the irradiation. Under our optimum conditions (run 15) approximately 80% of the chrysanthenone (-85°) from verbenone (-256°) is formed *via* path a. That further racemization of chrysanthenone occurs *via* path c (Chart IV) is suggested by the loss in rotation of **2** and **7** in going from a 1-hr to a 3-hr period of irradiation and by Hurst and Whitham's observations that chrysanthenone is racemized on extended irradiation.⁴³ Further evidence for path c is suggested by the fact that chrysanthenone of higher optical rotation is isolated from runs when a Pyrex filter or when light sources with principal emission above the $n \rightarrow \pi^*$ region of absorption for chrysanthenone are employed.

No attempt will be made in the present discussion to define the exact nature of the intermediate **33**. Chapman has suggested that the conversion of **1** to **2** proceeds *via* dipolar species; *i.e.*, **33** is depicted as the species **33a**.⁴⁴ On the other hand, Zimmerman presents ample evidence from his study of the photochemistry of 4,5-diphenylcyclohexanone³ and other cyclo-

hexenones⁴⁵ which would suggest that **33** is better represented by the species **33b** or, better, by a species in which the migrating isopropyl group is not completely disrupted from the π system.^{46,47}



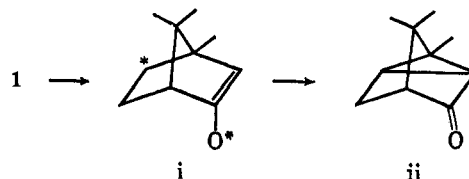
Path b. Whether the ketene **7** is generated directly from **1** by initial cleavage of the C-4,5 carbon or if **33** is an intermediate in the production of **7** is a matter of speculation at this point. However, cleavage of the bond α to the carbonyl of an α,β -unsaturated ketone is a highly inefficient process.⁴⁹ Furthermore, since studies on the thermal cleavage of **2** suggest that a diradical of type **33b** undergoes cleavage to ketene **7** at temperatures as low as 70° ,¹¹ a more reasonable hypothesis at this stage is that **33** is an intermediate in the production of **7**.

That the ketene **7** is formed on irradiation of verbenone in the presence of nucleophilic reagents is suggested by Hurst and Whitham's irradiation experiments (see introductory section) and from our results using alcohols as solvent. One point worthy of speculation is the observed generation of only ester **3a** from the irradiation in methanol. Apparently the ketene **7**, once formed, undergoes solvolysis with the alcohol solvent at a faster rate than photochemical *cis-trans* isomerization can occur. Formation of only the *cis*-nonconjugated ester from **7** is consistent with the idea of a kinetically controlled protonation at the position of highest electron density of the enol ester or incipient carbanion⁵⁰ generated initially from nu-

(45) For other references pertinent to this proposal see (a) H. E. Zimmerman, R. G. Lewis, J. J. McCullough, A. Padwa, S. W. Staley, and M. Semmelhack, *J. Am. Chem. Soc.*, **88**, 1965 (1966); (b) *ibid.*, **88**, 159 (1966).

(46) If a nondissociated species is the proper representation, then scrambling of the *gem*-dimethyl groups in the ensuing product should not occur. Work currently underway in our laboratories on the irradiation of π -substituted verbenone derivatives should shed light on this aspect of the rearrangement:^{47,48} T. W. Gibson, unpublished work.

(47) Regardless of the exact nature of the photochemical process, it is noteworthy that the cyclopropyl ketone ii, which would be generated *via* the species i, is not produced from irradiation of **1**. Thus, on ultraviolet irradiation, related 4,4- and 3,4-disubstituted cyclohexanones yield cyclopropyl ketones analogous to ii.^{3,44,45,48} As shown by Zimmerman, the course of rearrangement of cyclohexanones is greatly influenced by substituent effects.^{3,45} The stereochemical relationship of the migrating function to the π system may also play a role in influencing the course of reaction, although such stereochemical arguments are entirely speculative at this stage.



(48) (a) W. W. Kwie, B. A. Shoulders, and P. D. Gardner, *J. Am. Chem. Soc.*, **84**, 2268 (1962); (b) B. Nann, D. Gravel, R. Schorta, H. Wehrli, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **46**, 2473 (1963); (c) O. L. Chapman, J. B. Sieja, and W. J. Welstead, Jr., *J. Am. Chem. Soc.*, **88**, 161 (1966).

(49) P. J. Wagner and G. S. Hammond, *ibid.*, **88**, 1245 (1966).

(50) For pertinent references to observations about the protonation of allylic systems see C. D. Broaddus, *ibid.*, **87**, 3706 (1965), footnotes 3, 4, 23, and 24.

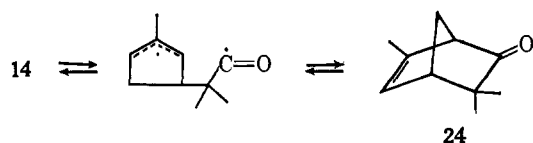
(43) It should be emphasized, however, that Whitham and Hurst's photochemical experiments were conducted at temperatures which lead to thermal racemization of chrysanthenone.¹¹ We should also interject that the loss in optical activity observed by these authors may have been due, in part, to the formation of ketone **8** which has a rotation almost equal and opposite to **2**.

(44) For a discussion of how such an intermediate may arise see (a) O. L. Chapman, *Advan. Photochem.*, **1**, 361 (1963); (b) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, pp 169-170; (c) O. L. Chapman, T. A. Rettig, A. A. Griswold, A. I. Dutton, and P. Flitton, *Tetrahedron Letters*, 2049 (1963).

cleophilic attack of methanol on the ketene carbonyl.⁵¹

Although the production of ketene **1** from irradiation of **7** seems indisputable, no direct evidence was obtained that the ketene **7** is reconverted to **1** by a photochemical process. One isolated attempt to prepare the ketene **7** generated *in situ* from geranoyl chloride was unsuccessful. Geranoyl chloride in cyclohexane was irradiated simultaneously with dropwise addition of triethylamine,⁵² but even after 3 hr no monomeric ketenes were observed in the reaction mixture.

Since irradiation of ketone **14** in methanol afforded a significant quantity of ester **3a**, the production of **2** and **8** in greater yield from the irradiation of **14** in cyclohexane might have constituted some evidence for the cyclization of **7** to **2**. Since the yields of **2** and **8** from this reaction were relatively minute, this experiment serves only to verify that ketone **14** is not produced initially from **7** in the photochemical process and does not play a role in the production of products from **1**. Although the principal products from irradiation of **14** in cyclohexane were not isolable, the course of photochemical reaction was clearly evident from the irradiation results in methanol. That α cleavage occurs almost equally at the 1,7- and the 1,8-carbon bonds of **14** is evident from the fact that the acetals **19** and **20** clearly proceed from the diradical **17**⁵³ and the acetal **21** from



the diradical **18** (Chart III). The mechanism by which the diradicals interact with methanol to form the acetals now seems well documented and undoubtedly proceeds through the carbenes **35** and **36**.⁵⁴ If the carbene mechanism is assumed, formation of two acetals from **17** and only one from **18** is readily explained by an examination of Dreiding models of each carbene. Regardless of the conformation of the five-membered ring containing the carbene function, the C-7 position of **35** is sterically unimpeded by the fused five-membered ring. Thus, formation of almost equimolar quantities of both epimers **19** and **20** from the intermediate **35** is not unexpected. In contrast, the C-8 position of the carbene **36** is hindered to approach by solvent from the *endo* side of the molecule by the C-2 vinyl methyl

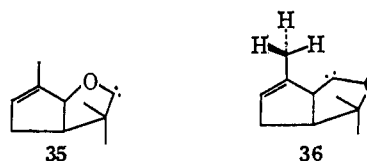
(51) Such a process is consonant with the observation of Cram that *cis*- and *trans*-allylic anions undergo protonation in *t*-butyl alcohol at a much faster rate than interconversion of the two geometric anionic forms: D. H. Hunter and D. J. Cram, *J. Am. Chem. Soc.*, **86**, 5478 (1964). The hypothesis is also in accord with the observation of Ozeki and Kusaka that treatment of crotonyl chloride with amines in alcohol solvent produces as the major product (as high as 97%) the β,γ -unsaturated vinyl acetic acid ester, probably *via* the unsaturated ketene: T. Ozeki and M. Kusaka, *Bull. Chem. Soc. Japan*, **39**, 1995 (1966). We thank Dr. C. D. Broadus for calling our attention to the latter reference.

(52) Ketenes are generally prepared *in situ* by treatment of acid chlorides with trialkylamines: H. H. Wasserman and E. Dehmlow, *Tetrahedron Letters*, 1031 (1962).

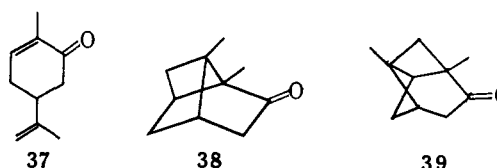
(53) In view of the photochemical behavior of other β,γ -unsaturated bicyclic ketones which undergo initial cleavage of the α -carbon allyl to the double bond,¹¹ it is somewhat surprising that a significant quantity of 3,3,6-trimethylbicyclo[2.2.1]hept-5-en-2-one is not produced when the irradiation of **10** is performed in cyclohexane.

(54) Carbene intermediates for similar type reactions were first postulated by Yates and Kilmurry and have now received excellent experimental verification by the same workers: P. Yates and L. Kilmurry, *Tetrahedron Letters*, 1739 (1964); *J. Am. Chem. Soc.*, **88**, 1563 (1966).

hydrogens. Consequently, only the *exo* epimer **21** would be anticipated from this isomer.



Secondary Products of Irradiation. The formation of the tricyclic ketone **11** is of itself a most intriguing subject and will be discussed in detail in a subsequent communication.⁹ It should be emphasized here that the proposed structure **11a**, though structurally the same, is "mechanistically" antipodal to the photocycloaddition product of carvone (**37**), *i.e.*, carvonecamphor (**38**).¹⁷ Corey has shown that the principal product from photoaddition of isobutylene to cyclohexenone is the adduct in which the more nucleophilic carbon of the olefin adds to the α -carbon of the α,β -unsaturated ketone. He suggested that the major product arises *via* a donor-acceptor complex of the nonexcited olefin and the $n \rightarrow \pi^*$ excited ketone.⁵⁵ Since the β -carbon of the α,β -unsaturated ketone in the $n \rightarrow \pi^*$ excited state is the position of greater electron density relative to the α -carbon,^{55,56} the major products from the intermolecular photoaddition reaction of isobutylene to cyclohexenone and of isopiperitenone are the products anticipated by this mechanistic course. On the other hand, ketone **39**, rather than carvonecamphor (**38**), would be the favored product from irradiation of carvone if such mechanistic arguments are invoked. Isomers **39** and **11b** may be too strained to permit their formation or, once formed, may be thermally unstable and not isolable. On the other hand, regardless of how the isopropenyl group of isopiperitenone or carvone in the reacting pseudo-boat conformation is rotated, the π orbital of the C-8 carbon of each is better oriented for overlap with the C-1 than with the C-2 orbital. Thus production of isomers **11a** and **38** from **12** and **37**, respectively, may simply be a consequence of relative stereochemistry of the interacting π -electron clouds.



The known susceptibility of bicyclic β,γ -unsaturated ketones to undergo rearrangement¹² and the observation that ketone **2** is readily converted to **8** on ultraviolet irradiation suggested that **8** is produced principally from **2** *via* the diradical species **34** (Chart IV). The fact that there is a slow buildup of ketone **8** until an apparent steady state between **2** and **8** is reached substantiates this conclusion. The limited production of **8** when the Rayonet 3500- and 2537-A lamps or Pyrex filter are utilized for these irradiations further implicates ketone **2** as an intermediate in the production of **8**. Since the Rayonet lamps show only limited emission of light in the region of $n \rightarrow \pi^*$ absorption (290 $m\mu$) of chrysanthenone, production of **8** from **2**

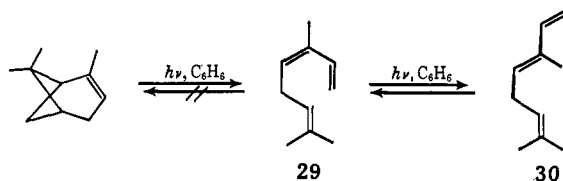
(55) E. J. Corey, J. D. Bass, R. LeMahieu, and R. B. Mitra, *ibid.*, **86**, 5570 (1964).

(56) H. E. Zimmerman and J. S. Swenton, *ibid.*, **86**, 1436 (1964).

would be impeded under these conditions. We, of course, cannot eliminate the possibility that part of **8** is produced directly from **1** by ultimate migration of the methylene, rather than the isopropylene bridge. However, the above evidence certainly implicates **2** as an intermediate in the production of the major portion of **8**.

Considering the fact that there are comparatively equal quantities of **8** and **2** when the photostationary state is reached, it is somewhat surprising that the ratio of the decarbonylated hydrocarbons **10** and **9** is so great (ca. 6:1) regardless of which ketone, **1**, **2**, or **8**, is irradiated. We have already indicated that **9** and **10** are not photochemically interconverted under our irradiation conditions (see Results). The predominance of **10** in the product mixture, then, is most likely a reflection of hyperconjugative stabilization rendered to the conjugated cyclopropyl-olefin system in the transition state in its production.⁵⁷

Finally, it was of interest to see if pinene itself might undergo photosensitized rearrangement in benzene solution *via* a process similar to verbenone.⁵⁸ Indeed irradiation of 1.5 g of pinene as a 1% solution in benzene with the 450-w broad spectrum lamp for a period of 1.0 hr afforded *seqcis*- and *seqtrans*-ocimene (among other products) in 13% yield in the ratio 1.5:1. However, the recovered pinene (20%) showed no loss of optical activity indicating that a 1,3-alkyl migration did not occur and that the resulting ocimenes are not recycled to pinene. Furthermore, irradiation of a mixture of *seqcis*- or *seqtrans*-ocimene in benzene did not afford pinene but rather led to a photochemical equilibrium of 47% *seqcis*-ocimene (**29**) and 53% *seqtrans*-ocimene (**30**).⁵⁹



Experimental Section

General. Melting points were determined on a Thomas-Hoover capillary melting point apparatus or on a micro hot stage and are corrected; boiling points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Infracord spectrophotometer as 5% solutions in carbon tetrachloride unless otherwise stated and ultraviolet spectra were obtained on a Perkin-Elmer Model 202 spectrophotometer using ethanol as solvent. Nuclear magnetic resonance spectra were run as 10% solutions in carbon tetrachloride (unless stated otherwise) on a Varian A-60 or HA-100 spectrometer using tetramethylsilane as an internal reference. Chemical shifts are recorded as parts per million on the τ scale, coupling constants as cycles per second. Nuclear magnetic resonance data are re-

(57) The mechanism of photoinduced decarbonylation reactions in the gas phase is discussed by R. Srinivasan, *Advan. Photochem.*, **1**, 83 (1963), and in the liquid phase most recently by D. I. Schuster, F.-T. Lee, A. Padwa, and P. G. Gassman, *J. Org. Chem.*, **30**, 2262 (1965).

(58) The nonsensitized irradiation of pinene has been reported to yield a gross mixture of products including *cis*-ocimene (3%), *trans*-ocimene (5%), dipentene (7%), and cyclofenchene (7%): R. Mayer, K. Bochow, and W. Zieger, *Z. Chem.*, **4**, 348 (1964). The irradiation of pinene in the presence of other photosensitizers is being studied in further detail by Dr. P. J. Kropp of these laboratories.

(59) The photochemical behavior of the ocimenes is in direct contrast to that of myrcene which undergoes nonsensitized photocycloaddition to a mixture of β -pinene (9%) and 1-(3-methylpent-2-enyl)cyclobutene^{59a} and in the presence of photosensitizers to 5,5-dimethyl-1-vinylbicyclo-[2.1.1]hexane:^{59b} (a) K. J. Crowley, *Proc. Chem. Soc.*, **245**, 334 (1962); (b) R. S. H. Liu and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 1892 (1964).

corded in the order: chemical shift (multiplicity, where s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet; coupling constant; interpretation). Molecular weights were determined on a Bendix Model 12-100 Time-of-Flight mass spectrometer. Gas chromatography separations were made on one of three columns: column 1, a 10 ft \times 0.25 in. stainless steel column packed with 20% DC-200 silicone oil on 70-80 mesh Anakrom ABS; column 2, a 10 ft \times 0.25 in. stainless steel column packed with 20% Reoplex 400 on 60-80 mesh Anakrom ABS 300; column 3, a 10 ft \times 0.25 in. stainless steel column packed with 20% GE-SF-96 silicone oil on Anakrom ABS-300.

Specific rotations were obtained using a Rudolph Model 70 precision polarimeter with chloroform as solvent. Microanalyses were performed by T. Atanovich and associates of these laboratories and by Spang Microanalytical Laboratories, Ann Arbor, Mich.

The petroleum ether used in this work was purified by distillation, bp 30-60°.

Preparation of Verbenone (1). Verbenone was prepared from *trans*-verbenol⁶⁰ by Jones oxidation.³⁹ From 53.214 g (0.35 mole) of *trans*-verbenol there was isolated 19.874 g (38%) of verbenone, bp 89-91° (6.0 mm), n_D^{25} 1.4940, λ_{max} 252 m μ (ϵ 6790) (ethanol), $[\alpha]_D^{25}$ -256° (c 0.0094, chloroform); infrared: 5.95 (carbonyl) and 6.18 μ (olefin); nmr: 4.35 (m, C-3 vinyl), 7.0-8.0 (m, C-7, methylene and C-1, C-5 methyne), 8.0 (d, J = 2.0, C-2 methyl), 8.48 (s, *exo*-C-6 methyl), and 8.98 (s, *endo*-C-6 methyl) [lit.² bp 102-105° (12 mm), n_D^{18} 1.4957, λ_{max} 253 m μ (ϵ 6730)].

Irradiation of Verbenone. A. General Procedure. Irradiations were performed with a Hanovia 450-w, high-pressure mercury arc lamp placed in a quartz or Vycor water jacket as previously described⁶¹ or with a Rayonet reactor employing lamps with maximum emissions at 2537 and 3500 Å, respectively. Solutions of verbenone in a suitable solvent were flushed with nitrogen for 1 hr previous to irradiation; a steady stream of nitrogen was passed through the solution during all irradiations. The yields and relative composition of products under different reaction conditions were determined by irradiating 1.5 g of verbenone in 150 ml of solvent, and these results are listed in Table I. The relative composition of products was determined by gas chromatographic analysis of the product before and after distillation. A typical example (B) is described below. All products from each run were isolated by preparative gas chromatography and were identified by infrared and nmr spectroscopy. Larger quantities of each product were isolated for further characterization and structure elucidation as described in subsequent experiments (C-G) below.

B. Specific Example. A solution of 1.506 g of verbenone in 150 ml of cyclohexane (Matheson Spectroquality reagent) was irradiated with a Hanovia 450-w lamp using a Vycor vessel as described above for a period of 1.0 hr. The cyclohexane was removed by careful distillation under reduced pressure to afford 1.7434 g of light yellow liquid. The infrared spectrum of this liquid showed a strong band at 4.72 μ for ketene which remained even after storage overnight at 0°. The ketene band disappeared when the crude product was stored at room temperature, adsorbed on alumina or silica gel, or distilled under high vacuum so that the ketene could not be isolated from the reaction mixture. Analysis of this liquid by gas chromatography on column 1 at 60 cc/min helium flow and 100° showed 11 components (besides cyclohexane) listed here, in the order of emission from the column [at higher temperatures (150-175°) essentially the same ratio of products was observed except for chrysanthenone which undergoes partial thermal decomposition at temperatures much above 100°]: **9**, 3%; **10**, 17%; **14**, 0.2%; **13**, 0.4%; **8**, 37%; **2**, 30%; **11**, 7%; **1**, 1%; **12**, 4%; **15**, 0.5%. The product was rectified on a modified Hickman still into three fractions: (1) 0.1275 g, bp 135-144° (755 mm), consisting of **8**, 86%, and **10**, 14%; (2) 0.5871 g, bp 88-126° (10-12 mm), consisting of **14**, 0.2%; **13**, 0.6%; **8**, 49%; **2**, 40%; **11**, 10%; and (3) 0.0472 g, bp 126-155° (6-10 mm), consisting of **8**, 30%; **2**, 20%; **11**, 5%; **1**, 14%; **12**, 75%; **15**, 11%. The yields of products **2** and **8-15** based upon starting verbenone are extrapolated: **9**, 1.5%; **10**, 9.1%; **14**, 0.1%; **13**, 0.2%; **8**, 20%; **2**, 16%; **11**, 4%; **1**, 0.4%; **12**, 2%; **15**, 0.4%. The relative ratio compares favorably with the values obtained by gas chromatography of the crude reaction mixture. Relative yields in all reactions were determined in this manner and are listed in Table I. Each component from each run was collected and the nmr and infrared spectra were compared with the products isolated and characterized below

(60) G. H. Whitham, *J. Chem. Soc.*, 2232 (1961).

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

under the specific conditions indicated. In order to isolate sufficient quantities of compounds for spectral data, material from several runs was combined.

C. Preparation of 2,4,4-Trimethylbicyclo[3.1.0]hex-2-ene (9) and 2,6,6-Trimethylbicyclo[3.1.0]hex-2-ene (10). From 1.504 g of verbenone irradiated as described above for a period of 3.0 hr there was isolated 0.1694 g of the hydrocarbon mixture, bp 135–144° (752 mm), consisting of **9**, 85%, and **10**, 15%. The two peaks were isolated by preparative gas chromatography on column 2 at 75° and 60 cc/min helium flow.

2,4,4-Trimethylbicyclo[3.1.0]hex-2-ene (**9**), peak 1, separated as a colorless liquid; infrared spectrum (5% in CCl₄): λ 6.11, 12.0 (trisubstituted olefin), 9.75 μ (cyclopropane); nmr spectrum (10% in benzene): 5.16 (broad s, C-3-vinyl), 8.16 (s, C-2 methyl), 8.0–8.4 (m, C-1), 8.57–8.8 (m, C-5), 8.76 and 8.64 (s, C-4 *gem*-dimethyl), 9.39 [ABX₂ pattern: J (H-6-*exo*, H-1) = J (H-6-*exo*, H-5) = 6.0, J (H-6-*exo*, H-6-*endo*) = 4.0, C-6-*exo* proton], and 9.74 [ABX₂ pattern, J (C-6-*endo*, H-1) = J (C-6-*endo*, H-5) = 3.0, J (H-6-*endo*, H-6-*exo*) = 4.0, C-6-*endo* proton]; mol wt, 122.

Anal. Calcd for C₉H₁₄: C, 88.45; H, 11.55. Found: C, 88.64; H, 11.31.

2,6,6-Trimethylbicyclo[3.1.0]hex-2-ene (**10**), peak 2, separated as a colorless liquid; infrared spectrum (5% in CCl₄): λ 6.10 and 11.90 μ (trisubstituted olefin); nmr spectrum (10% in benzene): 5.02 (broad s, C-3-vinyl), 7.85 (AB q, broad peaks, J = 9.0, C-4-allyl), 8.34 (broad s, C-2-methyl coupling with C-3 protons), 8.56 (q, J_1 = 3.5, J_2 = 1.0, C-1), 8.79 (m, C-5), 8.98 (s, *exo*-C-6 methyl), and 9.22 (s, *endo*-C-6 methyl); mol wt, 122.

Anal. Calcd for C₉H₁₄: C, 88.45; H, 11.55. Found: C, 88.21; H, 11.73.

D. Preparation of 2,7,7-Trimethylbicyclo[3.1.1]hept-2-en-6-one, Chrysanthenone (2), Isopiperitenone (12), Piperitenone (15), and 2,4,4-Trimethylbicyclo[3.2.0]hept-2-en-7-one (13). Although chrysanthenone was one of the principal products from irradiation of verbenone under all conditions studied, this compound was the major constituent when verbenone was irradiated with either the 2537- (run 13) or 3500-A (run 14) Rayonet lamps or when a Pyrex filter (run 6) was employed. For maximum yields of pure chrysanthenone of high optical purity, irradiations should be performed in acetic acid (runs 7 and 15, Table I). The ketones **12**, **13**, and **15** were most easily isolated from the runs employing the 2537-A lamps. In order to accumulate enough of the latter ketones **12**, **13**, and **15**, the following procedure was repeated several times.

Irradiation in Cyclohexane. A solution of 1.016 g of verbenone in 100 ml of cyclohexane was irradiated with the 2537-A Rayonet lamps using a quartz vessel as described in the general procedure above for a period of 6.2 hr. Removal of cyclohexane under reduced pressure afforded 1.467 g of liquid. Rectification of the liquid at 105–170° (0.9 mm) (oil-bath temp) afforded 725 mg of colorless liquid which, when analyzed by gas chromatography on column 2 at 100°, was shown to contain six major components: **13**, 3%; **8**, 10%; **2**, 60%; **1**, 11%; **12**, 10%; and **15**, 0.5% (conversion to yields are listed in Table I, run 13). Compounds **13**, **12**, and **15** were isolated by preparative gas chromatography on column 2 under the conditions described above.

The ketone assigned the structure 2,4,4-trimethylbicyclo[3.2.0]hept-2-en-7-one (**13**) was isolated from several combined runs as a colorless liquid; infrared spectrum (5% in CCl₄): λ 5.62 (cyclobutanone), 6.11 and 11.9 μ (trisubstituted olefin); nmr spectrum (10% in CCl₄): 4.78 (m, C-3), 6.0 (m, C-1), 6.98 [AB portion of ABXY-16 lines: J (H-6-*exo*, H-6-*endo*) = 17.6, J (H-6-*exo*, H-5) = 8.1, J (H-6-*endo*, H-5) = 6.0, J (H-6-*exo*, H-1) = 4.0, J (H-6-*endo*, H-1) = 2.4], 7.44 [multiplet which is resolved into a quartet, J (H-5, H-6-*endo*) = 8.1, J (H-5, H-6-*exo*) = 6.0 when H-1 is irradiated with a frequency of 2717 cps], 8.29 (broad s, C-2 vinyl methyl), 8.85 and 8.9 (singlets, C-6 *gem*-dimethyls). When the vinyl proton (τ 4.78) was irradiated with a frequency of 3019 cps there was no observable change in the multiplet pattern at τ 7.44.

Anal. Calcd for C₁₀H₁₄O: C, 79.95; H, 9.39. Found: C, 79.53; H, 9.47.

Isopiperitenone (12) was isolated as a colorless liquid, $[\alpha]_D +41^\circ$ (c 0.0135, ethanol); ultraviolet: λ_{max} 233 m μ (ϵ 9400); infrared: λ 5.95 (C=O), 6.08, 11.12, and 11.32 μ (R₂C=CH₂); nmr: 4.25 (s, fine splitting, C-2), 5.16 and 5.32 (s, R₂C=CH₂), 7.20 (t, J = 8.0, C-4), 7.70 (m, C-6 protons), 7.8–8.1 (m, C-5 protons), 8.06 (s, C-1 methyl), and 8.26 (s, C-7 methyl).

Anal. Calcd for C₁₀H₁₄O: C, 79.95; H, 9.39. Found: C, 79.24; H, 9.28.

The nmr and infrared spectra and gas chromatography retention time of the isopiperitenone isolated from this reaction were identical

in every respect with the *dl*-isopiperitenone prepared from geranic acid by the method of Schinz³² below and with *d*-isopiperitenone, $[\alpha]_D +49^\circ$, prepared from *d*-limonene by the method of Schenck.³³

Chrysanthenone and piperitenone were most readily isolated from the same reaction by column chromatography. From 999 mg of verbenone, irradiated as above, there was isolated 1.315 g of liquid residue after removal of solvent. The liquid was dissolved in 50 ml of petroleum ether and adsorbed on 15.026 g of Davison 100–200 mesh silica gel. Elution with petroleum ether afforded 0.031 g of a mixture of **13**, **8**, and **2**. Elution with 3% ether in petroleum ether removed 0.311 g of a mixture of **8**, 8%, and **2**, 92%. Further elution with the same solvent afforded 255 mg of almost pure, but slightly colored chrysanthenone. Filtration through 2.014 g of 1:1 Celite-activated charcoal gave a colorless liquid which was distilled from a modified Hickman to yield 151 mg of chrysanthenone (**2**), bp 99–100° (10.5 mm), which was purified for analysis by preparative gas chromatography on column 1 at 100°, $[\alpha]_D -52^\circ$ (c 0.1445, chloroform); infrared: λ 5.62 (C=O) and 6.05 μ (olefin); ultraviolet: λ_{max} 295 m μ (ϵ 126); nmr: 4.60 (m, vinyl C-3), 7.4 (m, C-1, C-4, C-5 protons), 8.20 (s, with fine splitting, C-2 methyl), and 8.70 and 8.72 (s, bridgehead *gem*-dimethyls); mol wt, 150.

Anal. Calcd for C₁₀H₁₄O: C, 79.95; H, 9.39. Found: C, 80.28; H, 9.44.

The infrared spectrum of the chrysanthenone isolated here was identical with the infrared spectrum published by Teresa, Bellido, and Bellido²⁷ for chrysanthenone isolated from the essential oil *Chrysanthemum indicum*.

Elution with 25% ether–petroleum ether and 100% ether removed 271 mg of a mixture of verbenone (**1**, 15%), isopiperitenone (**12**, 25%), and piperitenone (**15**, 60%). The piperitenone (**15**) was isolated by preparative gas chromatography on column 2 at 175° as a colorless liquid; infrared: λ 6.01 (C=O) and 6.20 μ (C=C); nmr: 4.24 (s, fine splitting, C-2 vinyl), 7.36 (m, C-6), 7.75 (m, C-5), 7.92 (s, fine splitting, C-1 methyl), and 8.09 and 8.16 (s, C-7 vinyl methyls). The nmr and infrared spectra and the gas chromatography retention time of the piperitenone isolated here were identical with those of a sample of **15** prepared by the method of Schinz.³²

Chrysanthenone from Irradiation in Acetic Acid. A solution of 1.009 g of verbenone, $[\alpha]_D -256^\circ$, in 100 ml of glacial acetic acid was irradiated for a period of 10 hr with the 3500-A lamp. The mixture was diluted with 200 ml of water and extracted with 500 ml of ether. The ethereal layer was washed with two 100-ml portions of water, three 100-ml portions of saturated potassium carbonate, and three 100-ml portions of water and dried over magnesium sulfate. Evaporation of solvent afforded 855 mg of liquid which was dissolved in 50 ml of petroleum ether and adsorbed on 14.99 g of Davison 100–200 mesh silica gel. Elution with 3% ether–petroleum ether afforded 620 mg of light yellow liquid which was filtered through 5.69 g of 1:1 Celite-activated charcoal to afford 517 mg of colorless liquid. Short-path distillation afforded 300 mg (30%) of chrysanthenone, bp 110° (10 mm), $[\alpha]_D -85^\circ$. Similar irradiation of verbenone, $[\alpha]_D +253^\circ$, afforded 258 mg (26%) of chrysanthenone, $[\alpha]_D +89^\circ$. When the crude product was distilled directly without purification by column chromatography, chrysanthenone was isolated in 43% yield along with a small quantity (2%) of ketone **8** (see Table I).

E. Preparation of 2,4,4-Trimethylbicyclo[3.1.1]hept-2-en-6-one (8) and 1,2-Dimethyltricyclo[3.3.0.0^{2,7}]octan-6-one (11). The ketones **8** and **11** were isolated by preparative gas chromatography on column 1 at 110° after distillation of the product as described in procedure B. From 0.587 g of fraction 2, bp 88–126° (10 mm), there was isolated 153 mg of 2,4,4-trimethylbicyclo[3.1.1]hept-2-en-6-one (**8**) as a colorless liquid, $[\alpha]_D +24.4^\circ$ (c 0.0381 in ethanol); infrared: 5.61 (C=O), 6.03 and 11.9 (trisubstituted C=C), 7.25 and 7.33 (*gem*-dimethyl), and 9.41 and 9.59 μ (characteristic sharp strong bands); ultraviolet: λ_{max} 297 m μ (ϵ 180); nmr: 4.99 (broad s, C-3 vinyl), 7.1 [two superimposed triplets, J (H-1, H-7-*exo*) = J (H-5, H-7-*exo*) = J (H-1, H-5) = 6.0, C-1, C-5], 8.0 (multiplet, C-7-*exo*), 8.19 (d, J = 0.3, C-2 methyl), 8.30 (d, J = 9.0, C-7-*endo*), and 8.86 and 8.89 (s, C-4 methyls); irradiation of the peak at τ 7.1 with a frequency of 2703 cps converted the multiplet at τ 8.1 to a doublet, J = 9.0; mol wt, 150.

Anal. Calcd for C₁₀H₁₄O: C, 80.0; H, 9.4. Found: C, 79.8; H, 9.4.

The tricyclic ketone **11**, was isolated by preparative gas chromatography as above. From 587 mg of fraction 2, bp 88–126° (10 mm), there was isolated 43 mg of **11** as a crystalline solid, mp 136–138°, $[\alpha]_D +158.5^\circ$ (c 0.0099, chloroform); infrared: λ 5.69 (C=O) and 7.25 μ (sharp singlet, absence of *gem*-dimethyl), absence

of olefin in the 6.0–6.25- μ region; nmr: described in detail under Results; mol wt, 150.

Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 80.02; H, 9.36.

The infrared and nmr spectra and gas chromatography retention time of this material and the ketone isolated from the irradiation products of isopiperitenone below were identical.

F. Preparation of 2,6,6-Trimethylbicyclo[3.2.0]hept-2-en-7-one (14). The ketone **14** was isolated by irradiation of larger quantities of verbenone for relatively shorter periods of irradiation according to the procedure of Hurst and Whitham.² A solution of 4.759 g (0.0309 mole) of verbenone in 125 ml of cyclohexane was irradiated at reflux with the 450-w lamp using a quartz jacket for a period of 3 hr. After removal of solvent under reduced pressure, the residue was dissolved in petroleum ether and adsorbed on 20.04 g of Woelm activity II alumina. Elution with petroleum ether afforded 1.971 g of a mixture of **14** (9%), **13** (2%), **8** (48%), and **2** (41%), bp 97–101° (7.0 mm). The ketone **14** was isolated as a colorless liquid by preparative gas chromatography on column 2 at 150° and 60 cc/min helium flow. The infrared, mass, and nmr spectra and gas chromatography retention time of this ketone and that of 2,6,6-trimethylbicyclo[3.2.0]hept-2-en-7-one prepared according to the procedure of Beereboom²⁵ were identical.

In another experiment, irradiation of 9.999 g of verbenone (+253°) in 300 ml of glacial acetic acid with the 3500-A lamp for 66 hr at 45–55° afforded, after column chromatography on 147 g of silica gel and fractional distillation through an 18-in. spinning-band column, 2.166 g (22%) of ketone **14**, bp 54–57° (8.50–8.75 mm) and 3.072 g (31%) of liquid, bp 60–63° (8.0–8.5 mm), containing chrysanthenone (96%) and the ketone **8** (4%). A fraction of chrysanthenone (>99% pure), bp 57° (5.75 mm), had $[\alpha]_D^{25} +13.75^\circ$ (*c* 0.024, $CHCl_3$). The ketone **14**, collected by preparative glpc on column 1 at 100° and 60 cc/min helium flow, possessed $[\alpha]_D^{25} -210^\circ$ (*c* 0.0158, $CHCl_3$).

G. Irradiation in Methanol. Isolation of Methyl *seqcis*-3,7-Dimethylocta-3,6-dienoate (3a). A solution of 1.011 g of verbenone in 100 ml of absolute methanol was irradiated with the 450-w mercury arc lamp for a period of 30 min. Careful removal of methanol afforded 872 mg of residual liquid which, on analysis by programmed gas chromatography on column 1 (75–150°), indicated the presence of **8** (6%), **2** (40%), **11** (3%), **16** (3%), **3** (21%), **12** (4%), and **16** (3%). The glpc spectrum was devoid of peaks in the region of the retention times for methyl veronate, methyl geranate, and the *trans* ester **4**, all of which were well separated from **3a** on the same column. Short-path distillation afforded 516 mg of colorless liquid, bp 100–131° (5.0 mm), consisting of **8** (6%), **2** (40%), **11** (3%), **16** (4%), **3a** (42%), and an unidentified ester (5%). Redistillation afforded two fractions, 186 mg, bp 100–110° (6.0 mm), consisting of **8**, **2**, **11**, and **16** and 331 mg, bp 110–131° (5.0 mm), consisting of **39** (92%) and unidentified ester (8%). The ketones **8**, **2**, **11**, and **12** were isolated as in previous runs. The ester **3a** was isolated on column 1 at 140° and 60 cc/min helium flow as a colorless liquid; infrared spectrum: λ 5.73 μ ; nmr spectrum: 4.79 (t, *J* = 7.0, C-4 vinyl); 4.98 (t, *J* = 7.0, C-6 vinyl), 6.41 (s, ester methyl), 7.50 (s, C-2 methylene), 7.37 (broad t, *J* = 7.0, C-5 methylene), 8.28 (s, fine splitting of \sim 1.0 cps, C-3 methyl), and 8.33 and 8.40 (s, fine splitting, C-7 methyls). The spectral properties and glpc retention time of the ester isolated in this manner was identical with the ester **3a** prepared from *cis*-ocimene described below.

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.5; H, 10.0. Found: C, 72.4; H, 10.0.

The ester **16** was isolated by preparative gas chromatography on column 2 at 125° and 70 cc/min helium flow. The spectral properties of this ester were identical with those of an authentic sample of 1,5-dimethyl-5-carbomethoxymethylcyclohex-1-ene (**16**).⁹

Irradiation in Ethanol. Preparation of Ethyl 3,7-Dimethylocta-3,6-dienoate (3b). Irradiation of 1.50 g of verbenone in 150 ml of absolute ethanol afforded 843 mg of liquid, bp 105–160°, consisting of unreacted **1** (2%), **8** (8%), **2** (25%), **11** (3%), **3b** (53%), and an unidentified ester (8%). The ester **3b** was isolated in the same manner as the methyl ester; infrared spectrum: λ 5.73 μ ; nmr spectrum: 4.79 (t, *J* = 7.0, C-4 vinyl proton), 4.97 (t, *J* = 7.0, C-6 vinyl proton), 5.95 (q, *J*₁ = *J*₂ = 6.0, methylene of ethyl ester), 7.08 (s, C-2 protons), 7.35 (t, *J* = 7.0, C-5 methylene), 8.27 (s, C-3 methyl), 8.36 and 8.41 (s, C-7 methyl groups), and 8.79 (t, *J* = 6.5, methyl of ethyl ester).

Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.4; H, 10.3. Found: C, 73.1; H, 10.1.

Irradiation of Chrysanthenone (2). A solution of 273 mg (0.0018 mole) of chrysanthenone, isolated by gas chromatography as above,

in 100 ml of cyclohexane was irradiated with the 450-w lamp using a Vycor water jacket for a period of 20 min. After careful removal of solvent and rectification there was isolated 95.6 mg (35%) of liquid, oil-bath temperature 134 (755 mm) to 144° (10 mm), which was analyzed by gas chromatography on column 1 at 100° and 60 cc/min helium flow: **9**, 2%; **10**, 13%; **8**, 52%; **2**, 33%. Each of the four products **9**, **10**, **8**, and **2** was isolated by preparative gas chromatography. The infrared spectra and gas chromatography retention times of each compound were identical with the respective compounds isolated from the irradiation of verbenone above. Irradiation for longer periods did not alter the ratio of **8** to **2** but led to a decrease in yield of the two ketones. In a separate experiment, irradiation of 6.577 g of **2** in 400 ml of cyclohexane afforded the relative compositions of **8:2** as shown in Table II.

Table II

Irradiation time, min	Ratio 8:2	Irradiation time, min	Ratio 8:2
15	1.0:4.9	70	1.0:1.0
45	1.0:1.5	120	1.56:1.0
60	1.0:1.1	440	1.58:1.0

Irradiation of 2,4,4-Trimethylbicyclo[3.1.1]hept-2-en-6-one (8). A solution of 88 mg (0.0006 mole) of the ketone **8** was irradiated in the same manner as chrysanthenone above for a period of 10 min. Careful evaporation of solvent and rectification afforded 35 mg (40%) of light yellow liquid, oil-bath temperature 130 (755 mm) to 126° (9 mm), which was analyzed by gas chromatography: **9**, 4%; **10**, 13%; **8**, 56%; **2**, 27%. The infrared spectrum and retention times of each of the four products **9**, **10**, **8**, and **2** isolated by preparative column chromatography (column 1, 100°, 60 cc/min helium flow) were identical with the corresponding products isolated from the verbenone irradiation.

Irradiation of 2,6,6-Trimethylbicyclo[3.2.0]hept-2-en-7-one (14). The ketone **14** was irradiated in the same manner as verbenone (**1**) using the 450-w lamp and Vycor jacket at 20° in cyclohexane and benzene solvents; the results of these experiments are listed in Table III.

Table III. Irradiation of Ketone 14^a

Time, min	Solvent	Yield, %					Aldehyde
		1	9	10	8	2	
15	Cyclohexane	20	0	5	1.0	0.9	0.5
30	Cyclohexane	8	0	10	2.1	1.8	1.1
60	Cyclohexane	0	0	12	Trace	Trace	Trace
30	Benzene	10	0	8	0.8	1.0	Trace

^a Ketone **14** (2.00 g) in 150 ml of solvent.

Each of the products **1**, **10**, **8**, and **2** were isolated by preparative gas chromatography on column 1 at 110° and 60 cc/min helium flow and were identified by comparison with samples isolated in previous runs. The aldehyde was not characterized except for the infrared spectrum: λ 3.73 ($HC=O$), 5.80 ($C=O$), 6.01, 11.10, and 11.25 μ ($R_2CH=CH_2$).

Irradiation of 2,6,6-Trimethylbicyclo[3.2.0]hept-2-en-7-one (14) in Methanol. A solution of 1.000 g (0.007 mole) of the ketone **14** in 125 ml of absolute methanol was irradiated with the 450-w lamp (Vycor filter) for a period of 30 min. Evaporation of methanol afforded 704 mg of yellow liquid which, on gas chromatographic analysis on column 2 at 125° and 125 cc/min helium flow, was shown to consist of six components: peak 1, acetal **19**, relative retention time 8.46 min, 9%; peak 2, acetal **20**, relative retention time 9.13 min, 5%; peak 3, ketone **14**, relative retention time 10.07 min, 12%; peak 4, acetal **21**, relative retention time 11.50 min, 25%; peak 5, unknown aldehyde **22**, relative retention time 16.80 min, 32%; peak 6, ester **3a**, relative retention time 27.0 min, 17%.

Short-path distillation afforded 257 mg of colorless liquid, bp 94–105° (10.5–12.0 mm), which showed the same relative ratio of peaks except for the aldehyde **22** which underwent almost complete decomposition during the distillation: acetal **19**, 9%; acetal **20**,

5%; ketone **14**, 12%; acetal **21**, 30%; aldehyde **22**, 6%; ester **23**, 17%.

Each of the peaks 1–6 was isolated by preparative gas chromatography on column 2 at 100° and 100 cc/min helium flow.

1,6,6-Trimethyl-7-endo-methoxy-8-oxabicyclo[3.3.0]oct-2-ene (19). The acetal **19** (3% yield) was isolated as a colorless liquid; infrared spectrum: (absence of carbonyl bands) λ 6.05 (olefin), 9.05, and 9.82 μ (acetal); nmr spectrum: 4.64 (m, C-3 vinyl proton), 5.23 (d, $J = 8.0$, C-1 proton), 5.69 (s, C-7 proton) 6.92 (s, C-7 methoxy protons), 7.3–8.1 (m, C-4 allyl and C-5 protons), 8.24 (s, fine splitting, C-2 vinyl methyl), and 8.92 and 8.95 (s, C-6 gem-dimethyls).

Anal. Calcd for $C_{11}H_{16}O_2$: C, 72.49; H, 9.96. Found: C, 71.57; H, 9.71.

2,6,6-Trimethyl-7-exo-methoxy-8-oxabicyclo[3.3.0]oct-2-ene (20). The acetal **21** (2% yield) was isolated as a colorless liquid; infrared spectrum: λ 6.05 (olefin), 9.16, and 8.5–10.0 μ (acetal); nmr spectrum: 4.80 (m, C-3 vinyl proton), 5.30 (d, $J = 8.0$, C-1 proton), 5.75 (s, C-7 proton), 6.79 (s, C-7 methoxy protons), 7.4 (m, C-5 proton), 7.9 (m, C-4 allyl protons), 8.30 (broad s, fine splitting, C-2 vinyl methyl), 9.04 (s, C-6 exo-methyl), and 9.20 (s, C-6 endo-methyl).

Anal. Calcd for $C_{11}H_{16}O_2$: C, 72.49; H, 9.96. Found: C, 71.88; H, 10.04.

2,6,6-Trimethylbicyclo[3.2.0]hept-2-en-7-one (14). The ketone **14** (4% recovery), peak 3, was isolated as a colorless liquid by gas chromatography and identified by comparison of the infrared spectrum and gas chromatography retention time with that of the starting material.

2,6,6-Trimethyl-8-exo-methoxy-7-oxabicyclo[3.3.0]oct-2-ene (21). The acetal **21** (11%) was isolated as a colorless liquid; infrared spectrum: λ 6.05 (olefin), 9.15, 9.45, 9.7, broad absorption (acetal); nmr spectrum: 4.82 (m, C-3 vinyl proton), 5.40 (s, 1.0 cps, C-8-endo proton), 6.80 (s, C-8 exo-methoxy), 6.92 (m, C-1 proton), 7.35 (sextet, $J_{H-1, H-5} = 8.0$, $J_{H-4-endo, H-5} = 2.1$, $J_{H-4-exo, H-5} = 8.0$), 7.7–7.8 (m, C-4 allyl protons), 9.31 (m, C-2 vinyl methyl), 8.71 (s, C-6 exo-methyl), and 8.97 (s, C-6 endo-methyl).

Anal. Calcd for $C_{11}H_{16}O_2$: C, 72.49; H, 9.96. Found: C, 72.42; H, 9.88.

Unknown Aldehyde 22. The aldehyde **22** (2%) was isolated as a colorless liquid; infrared spectrum: 3.70 (CH=O), 4.80 (aldehyde carbonyl), and 6.18 and 11.25 μ ($R_2C=CH_2$). The aldehyde was too unstable for further characterization.

Methyl *seqcis*-3,7-Dimethylocta-3,6-dienoate (3a). The ester **3a** (5%) was isolated as a colorless liquid, the infrared and nmr spectra and gas chromatography retention time of which were identical with that of the authentic material prepared below from ocimene.

Preparation of 1,2-Dimethyltricyclo[3.3.0.0^{2,7}]octan-6-one (11). **Irradiation of Isopiperitenone.** A. **Pyrex Filter.** A solution of 499 mg of isopiperitenone,³³ $[\alpha]_D^{25} +53.7^\circ$, in 50 ml of cyclohexane was placed in a Pyrex flask, flushed with nitrogen, and irradiated under a stream of nitrogen for a period of 80 min. The cyclohexane was removed under reduced pressure and the residual liquid distilled from a modified Hickman apparatus to yield 177 mg (35%) of ketone **11**, bath temperature 110–119° (10.75–9.75 mm), and 133 mg (27%) of isopiperitenone, bath temperature 130–160° (1.75 mm). The ketone **11** was purified by preparative gas chromatography on column 2 at 150° and 70 cc/min helium flow, mp 134–137°, $[\alpha]_D^{26} +152^\circ$. The ketone **11** isolated from this run was spectroscopically and gas chromatographically identical with the tricyclic ketone **11** isolated from the irradiation products of verbenone, above.

B. **Vycor Jacket.** A solution of 105 mg (0.006 mole) of *dl*-isopiperitenone, isolated below by the procedure of Schinz,³² in 100 ml of cyclohexane was irradiated with the 450-w lamp using a Vycor jacket at 20° for 30 min. Removal of cyclohexane afforded 103 mg of oil which showed three principal products by gas chromatography on column 1 at 100° and 60 cc/min helium flow in the ratio 43:44:14. The three components were isolated by preparative gas chromatography as above. From 103 mg of the product mixture above there was isolated 0.6 mg of peak 1 (unidentified ketone; infrared: λ , 5.80 μ), 2.0 mg (2%) of peak 2 as a colorless liquid (infrared: λ 5.86 μ) and 2.7 mg of *dl*-diketone **12** as a crystalline solid, mp 116–117°. The infrared and nmr spectra and gas chromatography retention time of this material collected from several runs and those of ketone **12** from irradiation of verbenone were identical. No further characterization of the other products of irradiation of isopiperitenone was made.

Preparation of *dl*-Isopiperitenone (12), Piperitenone (15), and 2,6,6-Trimethylbicyclo[3.2.0]hept-2-en-7-one (14). The exact procedure of Beereboom²⁵ was followed for the preparation of the

ketone **14**. From 50.0 g (0.3 mole) of geranic acid there was isolated by careful fractionation on an 18-in. spinning-band column, 4.725 g of a mixture of **14** and 4-methyl- α -methylstyrene, bp 53–85° (18 mm), 3.269 g of pure ketone **14**, bp 85° (18 mm), 4.285 g of liquid, bp 85–93° (2.8 mm), containing four compounds including isopiperitenone (26%; 2% yield based on starting geranic acid) and piperitenone (57%), and 6.320 g of piperitenone (97% pure), bp 98–100° (0.5 mm). The isopiperitenone was isolated by preparative gas chromatography on column 1 at 150° and 60 cc/min helium flow as a colorless liquid, the infrared and nmr spectra and gas chromatography retention time of which were identical with those of ketone **13** isolated from irradiation of verbenone above and with isopiperitenone prepared by the method of Schenck.³³

Alkaline Cleavage of Chrysanthenone (2) and 2,4,4-Trimethylbicyclo[3.1.1]hept-2-en-6-one (8). These experiments will be detailed in a separate communication.²⁸

Attempted Irradiation of 2-Methylhepta-2,5-dienylketene (7). A solution of 2.0 g (0.01 mole) of geranyl chloride [prepared by treatment of the sodium salt of geranic acid with oxalyl chloride at 0°, bp 101–103° (2.8 mm); infrared: λ_{max} 5.62 (carbonyl) and 6.20 μ (olefin)] was flushed for 1 hr with a stream of nitrogen maintained throughout irradiation. The solution of geranyl chloride was irradiated with the 450-w Hanovia mercury arc lamp using a quartz jacket for a period of 3 hr simultaneously with dropwise addition of 4.0 g (0.04 mole) of triethylamine (addition time of triethylamine, 30 min). After removal of triethylamine hydrochloride by filtration, the cyclohexane was removed under reduced pressure and the resulting residue distilled from a modified Hickman still. Only traces of material boiled below 150° (10 mm). Gas chromatographic analysis of the crude product on columns 1 and 2 at 100° showed no appreciable quantities of material with retention times in the region of the ketones **2**, **8**, and **14**.

Irradiation of Piperitenone (15). A solution of 1.000 g (0.006 mole) of piperitenone (**15**)³² dissolved in 100 ml of cyclohexane was irradiated with the 450-w lamp using a Vycor filter for a period of 6.5 hr. Aliquots were removed after 0.5-, 1.0-, 2.0-, and 4.0-hr periods and analyzed by gas chromatography. Although the piperitenone was 75% consumed after 4 hr, only traces of monomeric products were observed; the principal course of reaction was formation of polymeric or dimeric materials which were not investigated further. Similar results were observed when the reaction was conducted in ethanol solvent.

Conversion of Chrysanthenone (2) to Pinene. The procedure of Cram⁴² was employed for reductive removal of the carbonyl from ketone **2**. A mixture of 1.765 g (0.012 mole) of chrysanthenone (**2**), $[\alpha]_D^{25} +13.8^\circ$, 25 ml of absolute ethanol, 15.0 g (13.55 ml; 0.0471 mole) of anhydrous hydrazine, and 0.704 g (0.0117 mole) of glacial acetic acid was heated at reflux for 3 hr under a nitrogen atmosphere. The mixture was allowed to cool to 26°, the bulk of the ethanol removed under reduced pressure, and the mixture diluted with 100 ml of ether. The ethereal layer was partitioned, washed with 10 ml of 10% sodium hydroxide saturated with sodium chloride solution and four 10-ml portions of saturated sodium chloride, and dried over sodium sulfate. Evaporation of solvent afforded 1.859 g of viscous yellow hydrazone; infrared spectrum: 2.9–3.1 (NH stretching), 5.85, and 6.0–6.2 μ (C=N); absence of carbonyl at 5.62 μ .

To a solution of 1.550 g of potassium *t*-butoxide (MSA Research Corp.) in 10 ml of dimethyl sulfoxide (freshly distilled over calcium hydride) was added a solution of 1.858 g of the above hydrazone in 5 ml of dimethyl sulfoxide over a 15-min period; the mixture was stirred at 26° for 17 hr. The mixture was poured into 50 ml of water (0–5°) and acidified with 13 ml of 10% hydrochloric acid. The water layer was extracted with three 50-ml portions of ether and the ethereal layer washed with 10 ml of 3% hydrochloric acid, four 10-ml portions of water, and 10 ml of saturated sodium chloride and dried over magnesium sulfate. Evaporation of solvent afforded 686 mg of liquid residue which, on short-path distillation, afforded 422 mg (27%) of α -pinene, bp 155–156° (752.9 mm), $[\alpha]_D^{25} -6.5^\circ$ (*c* 0.020, $CHCl_3$). Further purification by glpc on column 2 at 75° and 60 cc/min helium flow gave $[\alpha]_D^{25} -7.0^\circ$. The glpc retention time and infrared spectrum of the above isolated pinene and that of an authentic specimen from Aldrich Chemical Co. were identical.

Irradiation of (+)- α -Pinene. A solution of 1.502 g of α -pinene, $[\alpha]_D^{25} +48^\circ$ (neat), $+54.8^\circ$ (*c* 0.0237, $CHCl_3$), in 150 ml of benzene was irradiated with the 450-w mercury arc lamp (Vycor filter) for a period of 60 min. After removal of benzene under reduced pressure, the residual oil, 1.644 g, was subjected to short-path distillation to afford 495 mg (33%) of colorless liquid, bp 140–170° (110

mm), consisting of α -pinene (60%), *seqcis*-ocimene (17%), and *seqtrans*-ocimene (23%). Longer periods of irradiation did not increase the yield of the ocimenes but changed the ratio of **29** to **30**. After 3-hr irradiation there was isolated 356 mg (24%) of a mixture of α -pinene (50%), *seqcis*-ocimene (23%), and *seqtrans*-ocimene (27%).

The three compounds were isolated by preparative glpc on column 3 at 85° and 60 cc/min helium flow. The recovered α -pinene, glpc retention time 10.4 min, had $[\alpha]_D^{25} +54.6^\circ$ (*c* 0.015, CHCl₃).

seqcis-Ocimene was isolated as a colorless liquid; glpc retention time, 18.7 min; infrared spectrum: λ 6.08 (nonconjugated olefin), 6.25 (conjugated olefin), 10.15, and 11.08 μ (RCH=CH₂); nmr spectrum: 3.35 (q, $J_{trans-C-1, C-2} = 17$, $J_{cis-C-1, C-2} = 14$, C-2 proton), 4.6–5.1 (m, C-1, C-4, C-6 vinyl protons), 7.22 (t, $J_1 = J_2 = 6.7$, C-5 methylene protons), 8.24, 8.34, and 8.40 (singlets, vinyl methyl groups). The glpc retention time and infrared and nmr spectra of this material and those of an authentic sample, kindly supplied by International Flavors and Fragrances, Inc., New York, N. Y.,⁶² were identical.

seqtrans-Ocimene was isolated as a colorless liquid; glpc retention time, 20.4 min; infrared spectrum: 6.10 (nonconjugated olefin), 6.22 (conjugated olefin), and 1.14 and 10.19 μ (RCH=CH₂); nmr spectrum: 6.10 (nonconjugated olefin), 6.22 (conjugated olefin), and 10.14 and 10.19 μ (RCH=CH₂); nmr spectrum: 3.80 (q, $J_1 = 17.0$, $J_2 = 12.0$, C-2 vinyl proton), 4.7–5.2 (m, C-1, C-4 protons), 7.25 (t, $J_1 = J_2 = 7.0$, C-5 allyl protons), and 8.31, 8.35, and 8.41 (s, vinyl methyls).

The glpc retention time and infrared and nmr spectra were identical with an authentic specimen of **30** obtained from International Flavors and Fragrances, Inc., New York, N. Y.⁶⁸

Preparation of *seqcis*-1,7-Dimethylocta-3,6-dienol (31). Essentially the procedure of Brown and Zweifel³⁸ was employed for the hydroboration step. To a solution of disiamylborane (prepared by adding 3.68 ml of a 1 *M* solution of diborane in tetrahydrofuran to 5.96 mg of 2-methyl-2-butene in 5.5 ml of tetrahydrofuran) maintained at 0–5° under a nitrogen atmosphere was added, dropwise over a 35-min period, 504 mg of *seqcis*-ocimene.⁶⁸ The mixture was stirred an additional 90 min at 26°, then cooled to 0°. To the cooled mixture was added 4.4 ml of 30% hydrogen peroxide followed by 4.4 ml of 3 *N* sodium hydroxide solution at such a rate as to maintain the temperature below 15°. This mixture was stirred at 26° for 16 hr. The mixture was diluted with 25 ml of water and extracted with 150 ml of ether. The ethereal layer was separated, washed with three 10-ml portions of water and 10 ml of saturated sodium chloride, dried over magnesium sulfate, and evaporated to yield 650 mg of colorless liquid, which on short-path distillation afforded 138 mg of the alcohol **31** as a colorless liquid, bp 88–90° (3.1 mm). Gas chromatographic analysis on column 1 at 125° and 60 cc/min helium flow showed that the distilled liquid was 87% alcohol **31** (21% yield). The remaining 13% product consisted of a mixture of at least six different materials. Final purification was effected by preparative gas chromatography on the same column; infrared: λ^{film} 2.95 and 9.5 μ (OH), absence of terminal olefin; nmr spectrum: 4.85 (m, vinyl protons), 6.45 (t, $J_1 = J_2 = 6.9$, C-1 protons), 7.35 (broad t, $J_1 = J_2 = 6.2$, C-5 protons), 7.7 (m, C-2 protons), and 8.3 (broad overlapping multiplets, C-3, C-7 vinyl methyl protons).

Anal. Calcd for C₁₀H₁₈O: C, 77.86; H, 11.76. Found: C, 77.04; H, 11.72.

Preparation of Methyl *seqcis*-1,7-Dimethylocta-3,6-dienoate (3a). Essentially Jones³⁹ oxidation conditions were employed for conversion of **31** to **3a**. To a solution of 622 mg (0.004 mole) of alcohol **31** in 25 ml of acetone was added dropwise, over a 5-min period,

1.5 ml of standard chromate reagent.³⁷ The excess chromic acid was destroyed by addition of 0.5 ml of 2-propanol, the mixture filtered, the bulk of the acetone removed under reduced pressure, and the product extracted with 100 ml of ether. The ethereal layer was washed with three 10-ml portions of water and dried over magnesium sulfate and the solvent removed under reduced pressure to afford 417 mg of acid product as a yellow liquid; infrared: λ^{film} 6.85 μ (carbonyl). Treatment of the above acid with 125 ml of a 2% solution of diazomethane in 100 ml of ether at 26° for 15 min, work-up, and short-path distillation afforded 85 mg (13%) of liquid ester **3a**, bp 112–114° (5.5 mm). Final purification by preparative gas chromatography on column 2 at 125° afforded **3a** as a colorless liquid, the gas chromatography retention time and spectral properties of which were identical with the ester **3a** isolated from the irradiation of verbenone in methanol. The glpc retention time of this *seqcis* isomer (26.8 min) was markedly different from that of the *seqtrans* isomer prepared below (33.5 min).

Preparation of *seqtrans*-1,7-Dimethylocta-3,6-dienol (32). Essentially the same procedure was employed for preparation of the *seqtrans* alcohols **32** as for the *seqcis* isomer **31**, above. From 6.806 g (0.050 mole) of a mixture of 70% *seqtrans*-ocimene and 30% *seqcis*-ocimene, hydroborated with disiamylborane [prepared from 8.24 g (0.118 mole) of 2-methyl-2-butene and 50 ml of 1 *M* diborane in tetrahydrofuran (0.05 mole)] and subsequently oxidized with 30% hydrogen peroxide, there was obtained, after short-path distillation, 4.055 g (52%) of colorless liquid, bp 137–140° (3.1–4.0 mm). Analysis of this liquid by gas chromatography on column 1 at 125° showed two peaks: peak 1 (22%), relative retention time 19.2 min, identical with the *seqcis* alcohol **31** prepared above; peak 2 (88%), relative retention time 20.5 min, *seqtrans* alcohol **32**. The *trans* isomer was collected in pure form by preparative gas chromatography; infrared: λ^{film} 2.95 and 9.60 μ (OH), absence of terminal olefin bands; nmr spectrum (10% in CDCl₃): 4.85 (m, vinyl protons), 6.45 (t, $J_1 = J_2 = 6.0$, C-1 protons), 7.37 (broad t, $J_1 = J_2 = 6.2$), 7.85 (m, C-2 protons), and 8.4 (three vinyl methyl groups superimposed).

Preparation of Methyl *seqtrans*-1,7-Dimethylocta-3,6-dienoate (3a). The procedure was the same as that employed for preparation of the *cis* isomer **3a**. Treatment of 3.001 g (0.019 mole) of the alcohol **32** in 60 ml of acetone with 10 ml of standard chromate reagent³⁷ afforded, after work-up, 2.260 g of acid; infrared: λ^{film} 5.85 μ (carbonyl). Treatment of the crude acid with excess diazomethane afforded, after work-up and short-path distillation, 980 mg (27%) of colorless liquid, bp 112–114° (5.5 mm). Analysis of the liquid on column 2 at 125° showed two peaks: peak 1 (19%), relative retention time 26.8 min, identical with ester **3a**; peak 2 (81%), relative retention time 33.5 min. Both compounds were separated by preparative gas chromatography on column 2 as above. The spectral properties of the compound represented by peak 1 were identical with the ester **3a** prepared from *seqcis*-ocimene.

The compound, relative retention time 33.5 min, was isolated as a colorless liquid; infrared: λ^{CCl_4} 5.75, and 8.6–8.7 μ (ester carbonyl); nmr spectrum: 4.9–5.05 (m, C-4, C-6 vinyl protons), 6.45 (s, ester methyl), 7.18 (s, C-2 methylene), 7.39 (t, $J_1 = J_2 = 6.8$, C-5 protons), 8.37 (s, C-7 methyl protons superimposed), and 8.42 (s, C-3 methyl protons).

Anal. Calcd for C₁₁H₁₈O₂: C, 72.5; H, 10.0. Found: C, 72.7; H, 9.8.

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(62) For preparation of these compounds see B. M. Mitzner, E. T. Theimer, and S. K. Freeman, *Appl. Spectry.*, **19**, 169 (1965); B. M. Mitzner, S. Lemberg, and E. T. Theimer, *Can. J. Chem.*, **44**, 1090 (1966).