Novel Photochemical Rearrangements of Citral and Related Compounds at Elevated Temperatures

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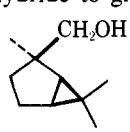
Abstract: Photolysis of citral (**1**) at temperatures ≥80 °C gave **5** and **6**, products whose formation requires 1,2 migration of the formyl group, in addition to **2–4**, which are previously known products obtained at 30 °C. Similar temperature-dependent rearrangements were observed with **22**, forming **31**, and with **34**, giving **39** and **40**, but not with **42**. Nitrile **49** afforded **53**, apparently the result of a 1,3 shift of the nitrile group in biradical **56c**. The structures of both expected and novel products were secured by a combination of chemical and spectroscopic evidence. Biradical mechanisms are suggested for these rearrangements.

The inter- and intramolecular photocyclization of olefins with α,β-unsaturated chromophores has been the subject of a great number of synthetic and mechanistic investigations.[1] These studies have demonstrated that the photoreaction can tolerate a wide variation in substrate structure and that, in contrast with many other photochemical reactions, its course is generally predictable. Anomalous results in [2 + 2] photocyclizations are rarely observed; novel examples of aberrant pathways, namely, the formation of rearranged products when the irradiation is carried out at elevated temperature, were described in two of our recent preliminary communications.[2,3] There are only a limited number of studies that deal with temperature effects on this reaction.[4] Indeed there have been rather few investigations of photochemical processes in solution at elevated temperature, and those reported generally concern processes already known at lower temperature[5] or thermal transformation of photoproducts available at lower temperature.[6] We now provide an account of our investigation of temperature-dependent photochemical transformations of citral and related compounds.

The irradiation of citral (**1**) in cyclohexane to afford a ~2:1 mixture of photocitral A (**3**) and photocitral B (**2**) in moderate yield is one of the first modern examples of intramolecular [2 + 2] photocyclization.[7] These products are thought to arise from disproportionation and closure of biradical intermediate **15t** (vide infra).[7a] We obtained similar results in benzene at 30 °C, except that a third product identified as epiphotocitral A[7b] (**4**) was obtained in 5% yield (see Table I).[8]

Photolysis of citral in benzene at reflux (80 °C) gave **2–4** and, in a combined yield of 5–10%, what was ultimately identified as a mixture of **5** and **6**. Greater quantities of these new compounds were obtained by photolysis in refluxing solvents with higher boiling points, as will be discussed later. Direct separation of this mixture was not achieved on any VPC column. Rather, the two aldehydes were reduced with lithium aluminum hydride to give corresponding alcohols **7** and **8**,



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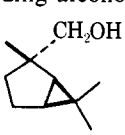

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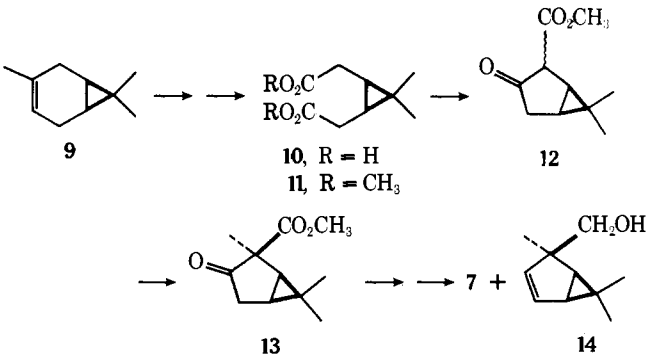
which were readily separable. These alcohols were fully characterized (see Experimental Section), and each was converted back to the aldehyde by treatment with chromium trioxide–pyridine complex.[9] Spectroscopic data for each compound indicated that the formyl group and the three methyl groups were bonded to quaternary carbon atoms and that there were no carbon–carbon double bonds; these data also suggested the presence of a three-membered ring and an epimeric relationship between the two compounds. These insights and the mechanistic considerations discussed later led us to entertain structures **5** and **6** for the new photoproducts. In addition, the stereochemistry as depicted could be assigned on the basis of ^{1}H NMR spectra of **7** and **8** in the presence of the shift reagent Eu(fod)$_3$ [tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)europium], since in **8** the doublet at 0.80 ppm, attributed to a cyclopropyl methine, was shifted downfield at a greater rate than the analogous signal in **7**.

These proposals were rigorously confirmed by independent synthesis of the major isomer **5** from bishomocaronic acid (**10**), readily available from 3-carene (**9**) by oxidation.[10] The derived diester (**11**) underwent Dieckmann condensation with sodium in benzene to give β-keto ester **12** as a mixture of epimers.



9 **10**, R = H; **11**, R = CH$_3$ **12** **13** **14**

Methylation of **12** was achieved with sodium hydride and iodomethane in benzene–dimethylformamide, giving a single product whose stereochemistry was assigned as shown since the substituted cyclopropane ring is expected to disfavor endo alkylation. The derived tosylhydrazone was reduced with lithium aluminum hydride[11] to give authentic **7**, identical in all respects with the alcohol obtained from **5**; hydroxy olefin **14**, the product of a Bamford–Stevens reaction,[11] was also obtained in this reduction.

Note must be made of several interesting features of these photolyses at temperatures above ambient. The yields of **5** and **6** are temperature dependent, increasing at the expense of the other products as the temperature of the reaction is raised. Yield data for a range of temperatures is presented in Table II, where it may be seen that at 190 °C the dominant product is **5** and that the combined yield of the novel products is 60% of the total. Using these data for the temperature range 80–177 °C, all products gave linear Arrhenius plots (see Figure 1), from which approximate relative activation energies, shown in Table III, were calculated. The rate of formation of all the products is also increased at higher temperatures by factors of 2–10, an effect also observed with all substrates described below. These photochemical rearrangements were sensitized by acetophenone at 30 and 132 °C, and the products were

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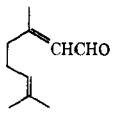
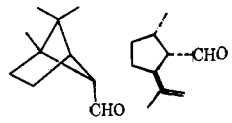
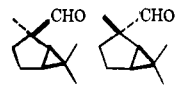
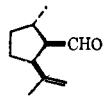
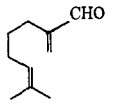
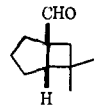
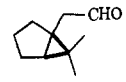
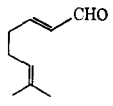
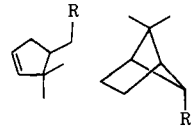
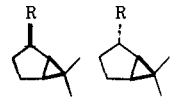
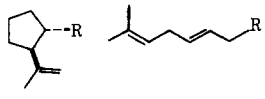
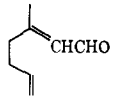
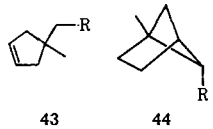
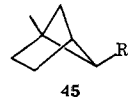
Table I. Products of Photolysis of Aldehydes

substrate	products: at ambient temp	products: at elevated temp[a]
 1	 2, 3	 5, 6
	 4	
 22	 28	 31
 34[b]	 35, 36	 39, 40
	 37, 38[c]	
 42[b]	 43, 44	
	 45	

a, R = CHO
b, R = CO_2CH_3

[a] Products obtained at ambient temperature usually accompany these. [b] Photolysis products characterized as methyl esters. [c] This compounds was not present in the photolysis at elevated temperature.

Table II. Photoisomerization of Citral at Various Temperatures

product	yield, % 30 °C	80 °C	111 °C	165 °C	190 °C
2	25	23	22	15	13
3	42	40	28	16	10
4	5	8	8	6	6
5	0	4	9	26	36
6	0	1	2	7	7
total	72	76	69	70	72

found in the same yields and relative amounts upon sensitized and direct irradiation. Photolysis of citral in neat 2,3-dimethylbutadiene (8.85 M) at 30 °C caused a 25% decrease in the yield of **2–4** with no observable effect on their ratio. These results suggest a common triplet precursor for all products, with the lifetime of the quenchable species ~0.1 ns. Experiments with geranial and neral [(*E*)- and (*Z*)-citral] indicated that photochemical equilibration of these geometric isomers is relatively rapid, but that, at the beginning of the photolysis before a steady state is achieved, all products are formed in approximately the same ratio from each isomer.

A stepwise mechanism for the formation of **5** and **6** from the triplet excited state of citral is shown in Scheme I. This is

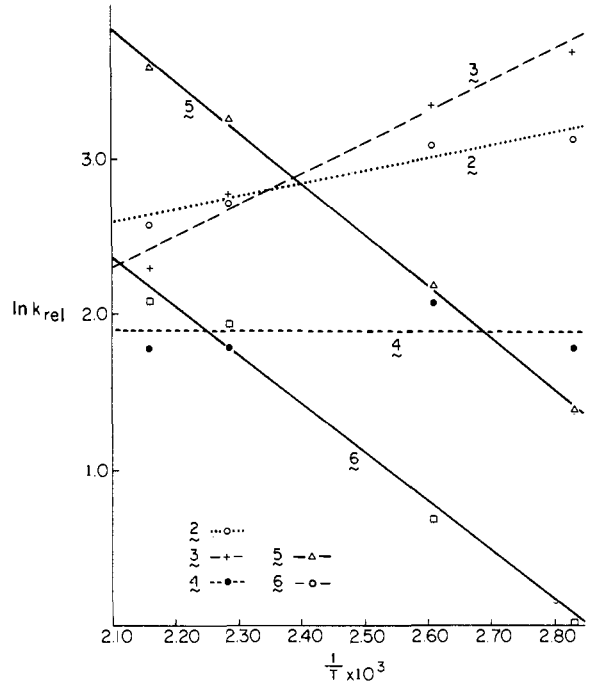


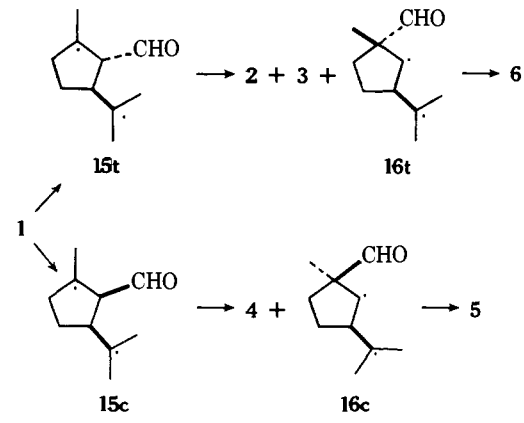
Figure 1. Plot of ln k_{rel} vs. $1/T$ for the photoproducts of citral.

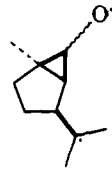
Table III. Relative Activation Energies

product	E_a, kcal/mol	product	E_a, kcal/mol
2	$E_3 + 2$	**5**	$E_3 + 10$
3	E_3	**6**	$E_3 + 10$
4	$E_3 + 3.5$		

compatible with the proposal,[7a] mentioned previously, of the intermediacy of biradical **15t** in the reaction at room temperature and with the role of five-membered-ring biradicals in intramolecular [2 + 2] photocyclizations.[12] Also pointed out in the earlier work on citral[7b] was the fact that the formation of **15t**, rather than **15c**, should be favored on steric grounds, thus accounting for the observed stereochemistry of **2** and **3**. The mechanism presented in Scheme I not only incorporates these elements but also implies that, when the temperature of the photolysis is raised, greater amounts of the more congested biradical **15c** are produced and that activation for the 1,2 migration of the formyl group, yielding **16t** and **16c**, is provided. Whether a cyclopropyloxy radical such as **17** is a discrete intermediate in the migration step is problematic. Although we prefer the biradical mechanism, other pathways leading to **5** and **6** can be envisioned; these include insertion of carbene **18**, generated by a shift of the formyl group, into the trisubstituted double bond—a process which has precedent[13] in the photo-

Scheme I





17

18

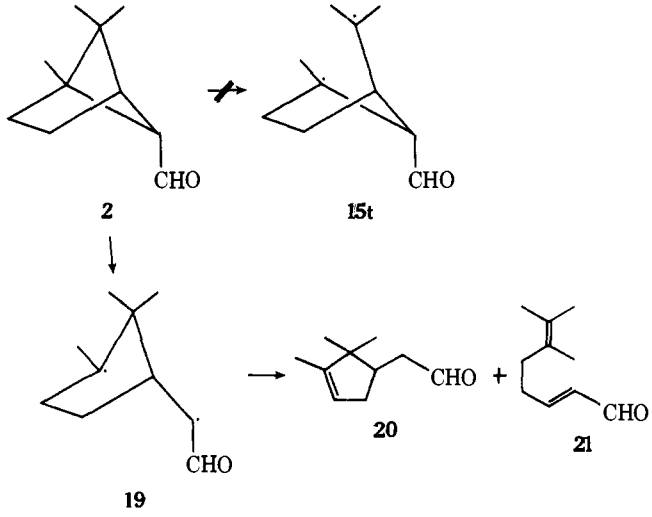
chemistry of alkenes, but not enones—and a symmetry-allowed $[_{\pi}2_s + _{\pi}2_s + _{\sigma}2_a]$ process.[14]

An attempt to generate **15t** alternatively by pyrolysis of **2** was unsuccessful. As shown in Scheme II, exclusive cleavage of the C(1)-C(5) bond occurred, giving α-campholenic aldehyde (**20**)[15] and **21** by disproportionation and fragmentation, respectively, of **19.**

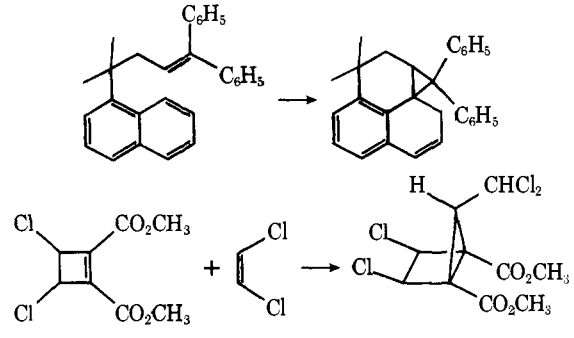
If the mechanism in Scheme I is valid, then the ordering of the relative activation energies given in Table III is in accord with what one would expect on an intuitive basis. The unimpeded transfer of a hydrogen atom from a methyl group of the isopropyl radical in **15t** should require a lower E_a than closure of the two tertiary radicals to form **2** or disproportionation of **15c.** Since the E_a's for **5** and **6** are about the same, the stereochemistry of the isopropyl radical does not appear to be a factor in the migration step; i.e., in **15t,** the shift of the formyl group apparently is not simultaneous with the formation of the final three-membered ring. Obviously, more complicated interpretations of these data are possible.

In free-radical chemistry, 1,2 migrations of acyl groups are rare;[16] to our knowledge, there are no examples specifically involving a formyl group. Two examples of photochemical transformations that take place at room temperature and can be interpreted mechanistically as the formation of a 1,4 biradical, followed by a 1,2 shift and then finally closure of the resulting 1,3 biradical, are shown in Scheme III.[17,18]

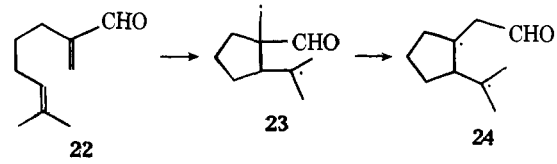
Scheme II



Scheme III

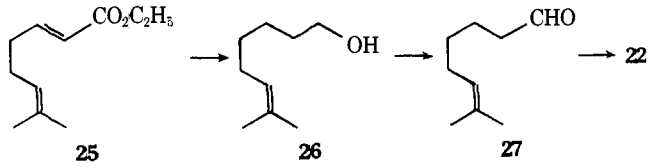


The question of whether this rearrangement is unique for citral prompted us to study the photochemistry of some other aldehydes at high temperature. Since, in the mechanism proposed for the transformation of citral (Scheme I), the formyl group migrates to a tertiary radical and generates a secondary radical, we thought that the shift perhaps would be facilitated if the migration terminus were a primary radical and the migration origin became a tertiary radical. α-Methylene aldehyde **22** appeared to be an appropriate precursor for a biradical having these features. We expected **22** to furnish **23** upon photolysis since 1,6-heptadienes generally undergo straight cycloaddition yielding bicyclo[3.2.0]heptanes via five-membered-ring biradicals.[19] Migration of the aldehyde group in **23** would give the more stable **24.**



22 23 24

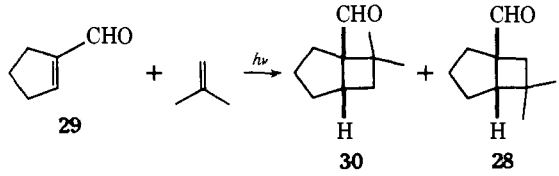
Synthesis of **22** was straightforward. Reduction of α,β-unsaturated ester **25**[20] with lithium aluminum hydride gave largely **26.**[21] Without purification, **26** was oxidized to **27** using



25 26 27

the chromium trioxide–pyridine complex.[9] The final carbon atom was introduced using standard Mannich reaction conditions,[22] formaldehyde and diethylamine hydrochloride, giving desired **22.**

Photolysis of **22** in benzene at 30 °C gave **28** in 30% yield and three minor products whose combined yields totaled 13%[23] (see Table I). Independent synthesis of **28** established its structure to be the result of straight, not crossed, cycloaddition. Irradiation of formylcyclopentene **29** in the presence of excess isobutylene gave **30** and **28** in a ratio of 3:1. In the NMR

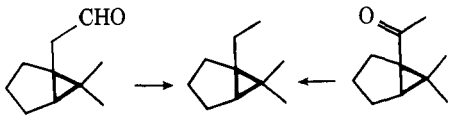


29 30 28

spectrum of **30** there is one distinct proton at lower field, a broad multiplet between 3.23 and 2.83 ppm, attributed to the bridgehead methine proton. The corresponding proton in its isomer **28** cannot be discerned, being shielded presumably by the methyl group at C(6). IR and NMR spectra of **28** obtained from this independent synthesis were identical with those of the photoproduct from **22.**

Irradiation of **22** in benzene or chlorobenzene at reflux permitted the isolation of another photoproduct, **31.** This product, formed in 2–3% yield at room temperature, became increasingly important at higher temperatures, 30% of the product mixture at 80 °C and 49% at 132 °C. Initial assignment of the structure was made on the basis of its spectroscopic properties: an IR band at 2995 cm^{-1} and a one-proton doublet at 0.89 ppm in the NMR spectrum point to the presence of a three-membered ring, and an aldehyde triplet together with a two-proton doublet at 2.52 ppm, each having a coupling constant of 2 Hz, indicate partial structure $-CH_2CHO$ bonded to a quaternary carbon atom. These data suggest **31.** Rigorous confirmation of this structure was provided by converting **31**

to the corresponding hydrocarbon (**32**) by Wolff-Kishner reduction and preparing **32** independently by similar reduction of **33**, obtained by the procedure of Engel and Schexnayder.[25]



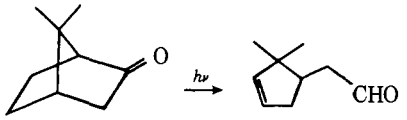
31 **32** **33**

Photolysis of **22** in benzene at reflux in the presence of acetophenone as a triplet sensitizer afforded **28** and **31** in the same ratio as upon direct irradiation; no other products were formed.

Thus the photochemistry of **22** followed the desired pathway and can be rationally interpreted employing biradicals **23** and **24.** The former species is formed from the triplet excited state of **22,** and this intermediate, upon closure, gives **28** at room temperature. At elevated temperature, migration of the formyl group is activated, generating **24,** from which **31** is derived by closure. Observation of trace amounts of **31** even at 30 °C and the greater proportion of rearranged product at higher temperature, relative to that formed from citral, are in accord with our speculation that migration of the formyl group from a quaternary to a primary center might be favored.

We were also curious to learn whether the rearrangement would occur in molecules analogous to citral but lacking some of its methyl groups. Aldehydes **34** and **42** were prepared from the corresponding unsaturated esters, readily available using the phosphonate ester modification of the Wittig reaction.[26]

Results of the photolyses of **34** and **42** are shown in Table I. At 30 °C, disappearance of the substrates, especially **42,** was slower than reaction of citral. Increases in the rate of reaction at temperatures above 30 °C were observed. Direct separation of the photoproducts from each aldehyde could not be accomplished under any VPC conditions tried. Rather, the crude photolysate was oxidized and treated with diazomethane to give methyl esters, which were separated and characterized as such. Structures **36b–38b** were apparent from their spectral data. The structure of **35a,** formed in only 3% yield at 30 °C, was confirmed by preparation of an authentic sample of it and the derived methyl ester. The known Norrish type I cleavage of apocamphor (**41**) furnished **35a,**[27] and conversion to the

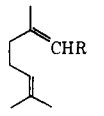
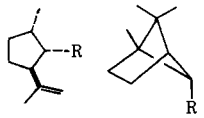
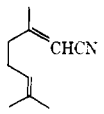
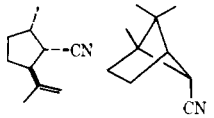
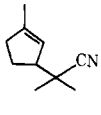
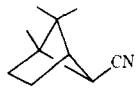


41 **35a**

corresponding methyl ester **35b** gave a product identical with that obtained from **34.**

Irradiation of **34** in refluxing *p*-xylene (138 °C) caused the formation of **39a** and **40a** (see Table I). The assigned structures are based on analogy with citral, spectral data, and base-catalyzed equilibration. The ^{13}C NMR spectrum of **39b,** the ester derived from the major novel photoisomer, indicates the absence of olefinic carbon atoms; the high-field signals at 15.3 and 19.7 ppm are characteristic of three-membered rings.[28] Additional support for this structural element is furnished by a weak stretching band at 3005 cm^{-1} in the IR spectrum and high-field signals at 1.29 and 1.06 ppm in the ^1H NMR spectrum. Evidence for the isomeric nature of the two products was obtained upon treatment of **39b** with sodium methoxide in warm methanol affording a 1:1 mixture of **39b** and **40b.** The latter, isolated from the epimerization reaction, was identical with photochemically derived material. Spectral data for **40b,** in particular the ^{13}C NMR spectrum, were similar to those for **39b.** A major difference in the ^1H NMR spectra is the chemical shift of the proton at C(2), appearing 0.47 ppm upfield in **40b,** where it is shielded by the three-membered ring.

Table IV. Products of Photolysis of Functional Group Analogues of Citral

substrate	products: at ambient temp	products: at elevated temp[a]
 **46**	 **47** **48** a, R = $COCH_3$ b, R = CO_2CH_3	
 **49**	 **50** **51**	 **53**
	 **52**	

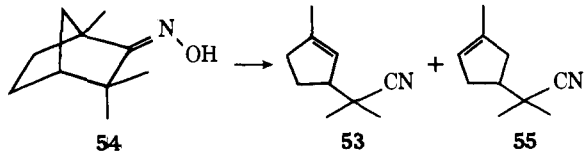
[a] Products obtained at ambient temperature are also formed.

The photochemistry of **34** obviously parallels that of citral at elevated temperature, and an analogous mechanism can be proposed. Since the methyl group at C(3) is no longer present, the migration terminus in the biradical resulting from C(2)–C(6) bonding is a secondary radical and, as seen with **22,** a greater proportion of rearranged material is formed at comparable temperatures.

In contrast to the photochemistry of **34,** there was little evidence for the formation of novel products in greater than 5% yield when **42** was irradiated at elevated temperature. The structures of **43b–45b** follow from spectra[29] and the formation of the bicyclo[2.1.1]hexanes is well precedented. Cyclopentenacetaldehydes **35a** and **43a** apparently arise from disproportionation of biradicals resulting from C(1)–C(5), rather than C(2)–C(6), cyclization of **34** and **42.** The increasing yield of this type of product, from 0 to 3 and finally 5% from citral, **34,** and **42,** respectively, can be correlated in simple fashion with the difference in stability between the two biradicals resulting in each case from these alternative modes of cyclization.[31]

In further extending this study, we examined the photochemistry of analogues of citral containing other functional groups capable of being transferred in free-radical reactions.[32,33] At 30 °C, direct photolysis of **46a**[35] and propiophenone-sensitized irradiation of methyl geranate (**46b**) gave the unexceptional products **47a,b** and **48a,b.**[36] In striking contrast to citral, there was absolutely no indication of the formation of products other than **47a** and **48a** when **46a** was irradiated in refluxing *p*-xylene (138 °C) or *p*-cymene (177 °C). Sensitized photolysis of **46b** at elevated temperature gave greatly reduced yields of **47b** and **48b** and ~1% of a third product. Under these conditions, the sensitizer apparently causes the destruction of the ester without formation of volatile products.

Finally we examined geranonitrile (**49**), whose room temperature, acetone-sensitized photolysis to give **51** and **52** has been described by Cookson.[39] In our hands, with propiophenone as sensitizer, photolysis of **49** in benzene at 30 or 80 °C gave both bicyclic nitriles and **50,** the product of disproportionation.[40] Sensitized irradiation of **49** in refluxing chlorobenzene gave in addition to **50–52** varying yields of a fourth compound, identified as **53** initially on the basis of its spectral properties. This assignment was confirmed by comparison of the new photoproduct with an authentic sample of **53,** prepared by the known[41] acid-catalyzed Beckmann fragmentation of α-fenchone oxime (**54**).



54 53 55

A stepwise mechanism for the transformation of geranonitrile is presented in Scheme IV. Disproportionation and closure of **56t** and **56c** give **50–52.** Interaction of the isopropyl radical with the cyano group (possible only in cis biradical **56c**) forms bicyclic iminium species **57,** and cleavage of the cyclobutane bond affords **53.** The mechanism in Scheme IV is obviously generally similar to the proposal for citral, the difference being the 1,3 rather than the 1,2 shift of the nitrile group. The 1,2 transfer may require an intermediate with an sp^2-hydridized carbon atom in a three-membered ring, as shown in **58,** which would be considerably more strained than the putative cyclopropyloxy radical **17.** We are unaware of any example of a 1,3 transfer of a nitrile in free-radical chemistry, although there is ample precedent for 1,4 transfer involving intermediates similar to **57.**[42]

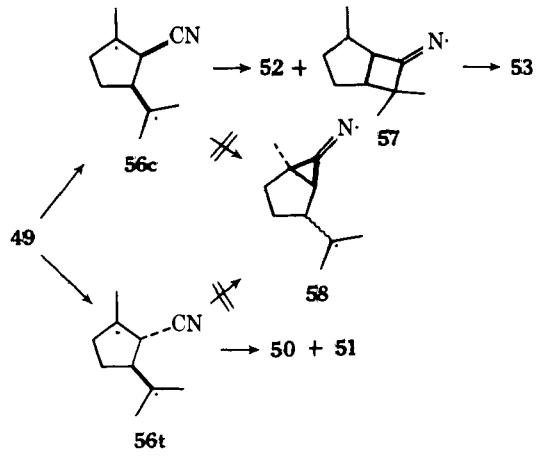
Summary

The promotion of unusual photochemical transformations via thermal activation has been demonstrated. Rearrangement reactions that compete with [2 + 2] photocyclization have been discovered in a number of aldehydes and a nitrile; it remains to be learned why the rearrangement does not occur with other functional groups. These results suggest investigation of other photochemical reactions at high temperature to see whether processes unobserved at ambient temperature can be made to occur.

Experimental Section

Materials and Equipment. These have been previously described.[43] All VPC was carried out using a Varian Aerograph Model 700 or 920 gas chromatograph with one of the following columns: A, 25% EGSP-A, 10 ft; B, 25% QF-1, 10 ft; C, 25% cyclohexanedimethanol adipate, 20 ft; D, 25% EGA, 10 ft; E, 25% QF-1, 25 ft; F, 25% EGA, 20 ft; G, 25% Carbowax 20M, 10 ft; H, 25% tetramethylcyclobutanediol adipate, 10 ft; I, 25% Carbowax 20M, 5 ft; J, 25% QF-1, 5 ft; K, 25% EGA, 25 ft; L, 25% DEGS, 5 ft; M, 25% DEGS, 25 ft. All columns were packed in 0.25-in. aluminum tubing using 45/60 Chromosorb W, except column I, which employed 45/60 Chromosorb P. Unless otherwise noted all pure compounds were obtained as colorless oils. Solutions were irradiated under a nitrogen atmosphere in toroidal vessels fitted with a side arm and standard taper 14/20 joint with a Hanovia 450-W medium-pressure mercury lamp in either a quartz or Pyrex immersion well using either Pyrex 7740 or uranium glass (Corning no. 3320) as filter. For irradiations above 30 °C, the vessels were wrapped with heating tape and fitted with a reflux condenser; the solutions were heated to reflux prior to irradiation.

Scheme IV



Photolysis of Citral (1). A. At 30 °C. A solution of citral (1.004 g) in benzene (50 mL) was irradiated for 18.5 h through uranium glass. VPC analysis on column K (150 °C) indicated the formation of two products in the ratio 26:74 and a 1:1 mixture of geranial and neral. The first eluted component was identified as 1,6,6-trimethylbicyclo[2.1.1]hexane-5-carboxaldehyde (photocitral B, **2**): IR 2940 (s), 2780 (w), 2680 (m), 1725 (s), 1460 (m), 1388 (m), 1380 (m), 1370 (m), 1175 (m) cm^{-1}; NMR (60 MHz) δ 9.62 (d, J = 1 Hz, 1 H), 2.50 (br s, 1 H), 2.35 (m, 1 H), 2.0–1.33 (m, 4 H), 1.10 (s, 6 H), 0.72 (s, 3 H). The second, major peak consisted of a 10:1 mixture of **3** and **4.**

B. At 80 °C. Citral (0.50 g) in benzene (50 mL) was heated to reflux and irradiated as above for 18 h. VPC analysis on column D (150 °C) showed three product peaks in the ratio of 9:33:58 in addition to small amounts of residual (E)- and (Z)-citral. The first eluted peak did not correspond in retention time to any product formed at 30 °C. The second was **2,** and the third, a mixture of **3** and **4.**

C. At 132 °C. Citral (0.50 g) in chlorobenzene (50 mL) was heated to reflux and irradiated as before for 18 h. VPC analysis indicated no remaining citral and the same three-component product mixture now in a ratio of 33:26:41. An NMR spectrum of the first component after preparative VPC showed two new aldehydes in the ratio of 4:1. This mixture was reduced with $LiAlH_4$ in ether at 0 °C following standard methods. The derived alcohols were separated on column I (180 °C). The major, first eluted alcohol was identified as **7:** IR 3625 (w), 3550–3200 (br w), 3000 (w), 2945 (s), 2855 (s), 1460 (w), 1450 (w), 1375 (w), 1020 (s) cm^{-1}; ^1H NMR (220 MHz) δ 0.72 (d, J = 7 Hz, 1 H), 0.92 (s, 3 H), 1.04 (s, 3 H), 1.07 (m, 1 H), 1.12 (s, 3 H), 1.28–1.39 (m, 2 H), 1.57–1.71 (m, 1 H), 1.84–2.03 (m, 1 H), 3.36 (s, 1 H), 3.38 (d, J = 15 Hz, 1 H), 3.44 (d, J = 15 Hz, 1 H). Anal. ($C_{10}H_{18}O$) C, H.

The second eluted alcohol was **8:** IR 3625 (w), 3550–3200 (br w), 3000 (w), 2940 (s), 2855 (s), 1460 (w), 1445 (w), 1370 (w), 1030 (s), 1020 (w) cm^{-1}; ^1H NMR (220 MHz) δ 0.80 (d, J = 6.5 Hz, 1 H), 0.95 (s, 3 H), 0.99 (m, 1 H), 1.02 (s, 3 H), 1.17 (s, 3 H), 1.56–1.69 (m, 3 H), 1.79–1.94 (m, 2 H), 3.23 (s, 3 H). Anal. ($C_{10}H_{18}O$) C, H.

Addition of 0.2 equiv of $Eu(fod)_3$ to $CDCl_3$ solutions of **7** and **8** shifted the one-proton doublet at C(1)—initially at 0.72 and 0.80, respectively—to 2.45 and 3.13 ppm.

Each alcohol was converted back to the corresponding aldehyde using the chromium trioxide–pyridine complex according to the method of Ratcliffe and Rodehorst.[9] Alcohol **7** gave **5:** IR 3000 (w), 2950 (s), 2925 (s), 2860 (s), 2800 (w), 2700 (w), 1730 (s), 1450 (w), 1370 (w), 910 (w) cm^{-1}; ^1H NMR (60 MHz) δ 0.98 (s, 3 H), 1.07 (s, 3 H), 1.15 (s, 3 H), 0.86–1.33 (m, 2 H), 1.50–2.26 (m, 4 H), 9.57 (s, 1 H); ^{13}C NMR δ_{Me_4Si} 16.7, 20.8, 23.5, 24.7, 28.7, 31.5, 33.9, 40.0, 56.1. Anal. ($C_{10}H_{16}O$) C, H.

Aldehyde **6** was obtained from minor alcohol **8:** IR 3000 (w), 2950 (s), 2925 (s), 2860 (s), 2800 (w), 2700 (w), 1730 (s), 1455 (w), 1445 (w), 1370 (w), 890 (w) cm^{-1}; ^1H NMR (60 MHz) δ 1.02 (s, 3 H), 1.15 (s, 3 H), 1.22 (s, 3 H), 0.93–1.30 (m, 2 H), 1.36–2.26 (m, 4 H), 9.38 (s, 1 H); ^{13}C NMR δ_{Me_4Si} 17.0, 17.8, 21.6, 26.3, 29.4, 32.2, 34.8, 37.3, 56.3. Anal. ($C_{10}H_{16}O$) C, H.

For photolyses at other temperatures, solutions of citral (1.0 g) in the appropriate solvent (50 mL), heated to reflux, were irradiated in the same fashion for 0.5 h. Yields were determined by calibrated VPC and are based on converted starting material.

Photolysis of Geranial and Neral [(E)- and (Z)-Citral]. Solutions of each isomer (1.0 g) in mesitylene (50 mL) were heated to reflux and irradiated through Pyrex. VPC analysis on column K of aliquots obtained after 2, 4, 6, 8, 10, 20, 30, 60, and 120 min indicated that before complete photochemical equilibration of the isomers the same ratio of products was formed in the two cases.

Sensitized Photolysis of Citral. Benzene solutions of citral (0.066 M) and citral with acetophenone (0.066 and 0.55 M, respectively) were flushed with N_2 for 10 min and irradiated in a merry-go-round device through Pyrex for 1.5 h. Analysis by VPC on column K (150 °C) indicated the same extent of conversion and ratio of products in the two cases. A similar experiment at 132 °C in refluxing chlorobenzene gave similar results.

Photolysis of Citral in 2,3-Dimethylbuta-1,3-diene. Two solutions of citral (0.066 M), one in benzene, the other in neat diene, were degassed and irradiated at 30 °C through uranium glass in a merry-go-round apparatus for 17 h. VPC analysis as above indicated about

30% less conversion using the diene as solvent. Attempts to quench the photolysis in benzene using naphthalene as quencher were unsuccessful.

Pyrolysis of *endo*-1,6,6-Trimethylbicyclo[2.1.1]hexane-5-carboxaldehyde (2). A solution of **2** (~100 mg) in chlorobenzene (1.2 mL) in an evacuated sealed tube was heated at 250 °C for 5 h. Analysis by VPC on column K (155 °C) indicated the formation of two products in the ratio of 64:36. The first eluted component was identified as α-campholenic aldehyde (**20**) on the basis of identical NMR and IR spectra.[15] The second component was identified as (*E*)-6,7-dimethylocta-2,6-dienal (**21**): IR 2975 (w), 2910 (m), 2850 (w), 2800 (w), 2720 (w), 1690 (s), 1630 (w), 1370 (w), 1140 (w), 1125 (w), 1100 (w), 965 (m) cm^{-1}; ^1H NMR (60 MHz) δ 1.67 (s, 9 H), 2.25 (m, 4 H), 5.97 (dd, *J* = 16, 8 Hz, 1 H), 6.70 (m, 1 H), 9.47 (d, *J* = 8 Hz, 1 H). Anal. ($C_{10}H_{16}O$) C, H.

Methyl 6,6-Dimethyl-3-oxobicyclo[3.1.0]hexane-2-carboxylate (12). Bishomocaronic acid[10] (**10**) was prepared from 3-carene as previously described and converted to the dimethyl ester by esterification with acidic methanol. The distilled diester **11** (4.0 g) in benzene (20 ml) was treated with freshly cut sodium (950 mg). Methanol (1 mL) was added and the mixture was heated to reflux. The heat was removed as a vigorous reaction ensued; then the mixture was heated at reflux for 3.5 h. Excess sodium was removed, the solution was acidified with 10% HCl, the benzene layer was separated, and the aqueous layer was extracted with benzene. The organic layers were combined and washed with saturated $NaHCO_3$, H_2O, and brine. After drying and removal of solvent, distillation of the residue yielded 2.3 g (67%). A small portion was purified on column J. Both epimers were present: NMR (60 MHz) δ 3.73, 3.70 (s, 3 H), 3.0–1.4 (m, 5 H), 1.13, 1.07 (s, 3 H), 0.9–0.83 (s, 3 H); IR 3025 (w), 2950 (s), 2850 (w), 1750 (s), 1730 (s), 1660 (m), 1605 (m), 1440 (m), 1425 (m), 1370 (w), 1325 (m), 1260 (m), 1220 (s), 1190 (m), 1160 (m), 1140 (m), 1050 (w), 1035 (w), 1000 (w), and 850 (w) cm^{-1}.

Methyl *exo*-2,6,6-Trimethyl-3-oxobicyclo[3.1.0]hexane-2-carboxylate (13). Keto ester **12** (2.3 g, 12.6 mmol) was added to a solution of NaH (700 mg, 53%, 14.6 mmol) dissolved in benzene (24 mL) and dimethylformamide (16 mL). The solution instantly turned yellow and was heated to reflux for 0.5 h and then cooled to 25 °C. Methyl iodide (2.73 g, 19.3 mmol) was added dropwise, and after addition was completed the reaction mixture was heated at reflux overnight. Water (50 mL) was added, and the aqueous layer was extracted with ethyl ether. Organic layers were combined and washed with water and brine. Drying and removal of solvent followed by bulb-to-bulb distillation yielded 1.716 g (8.75 mmol, 69%). An analytical sample was obtained on column I: IR 3025 (w), 2950 (s), 1768 (m), 1738 (s), 1450 (m), 1430 (m), 1275 (m), 1250 (m), 1190 (m), 1155 (m), 1070 (m), 1045 (w) cm^{-1}; ^1H NMR (60 MHz) δ 0.90 (s, 3 H), 1.07 (s, 3 H), 1.13–1.27 (m, 2 H), 1.37 (s, 3 H), 2.12 (dd, *J* = 20, 0.5 Hz, 1 H), 2.63 (ddd, *J* = 20, 3, 3 Hz, 1 H), 3.67 (s, 3 H). Anal. ($C_{11}H_{16}O_3$) C, H.

Formation and Reduction of the of Tosylhydrazone of Methyl *exo*-2,6,6-Trimethyl-3-oxobicyclo[3.1.0]hexane-2-carboxylate (13). Keto ester **13** ((500 mg, 2.55 mmol) and *p*-toluenesulfonylhydrazine (525 mg, 3.05 mmol) were dissolved in absolute ethanol (1 mL) with 2 drops of acetic acid and heated to reflux overnight. The product was recrystallized from ethanol with a trace of H_2O. After drying in vacuo over P_2O_5, off-white flakes (300 mg, 0.82 mmol, 32%) were recovered, mp 146–149 °C: NMR (60 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8 Hz, 2 H), 7.53 (br s, 1 H), 7.20 (d, *J* = 8 Hz, 2 H), 3.63 (s, 3 H), 2.40 (s, 3 H), 2.36 (br s, 2 H), 1.40 (s, 3 H), 1.20 (br s, 2 H), 0.97 (s, 3 H), 0.66 (s, 3 H); IR ($CDCl_3$) 3005 (m), 2940 (m), 2860 (w), 1725 (s), 1595 (w), 1450 (m), 1390 (m), 1335 (m), 1260 (m), 1160 (s), 1085 (m), and 1025 (w) cm^{-1}. Anal. ($C_{18}H_{24}O_4N_2S$) C, H, N.

The tosylhydrazone (300 mg, 0.82 mmol) was dissolved in 5 mL of THF and added dropwise to a solution of $LiAlH_4$ (1.5 g, 45 mmol) suspended in 50 mL of THF cooled to 0 °C. After addition was complete, the reaction mixture was heated to reflux for 1.5 days. After cooling, the remaining $LiAlH_4$ was destroyed with saturated Na_2SO_4 and then filtered. The filtrate was washed with 5% HCl, saturated $NaHCO_3$, and brine and dried, and most of the solvent was removed. Two components were found upon VPC analysis on column E. Preparative VPC yielded 45 mg (0.30 mmol) of **14** and 15 mg of **7**. The latter component had identical 220-MHz NMR spectrum and VPC retention time on columns E and I with the product of reduction of **5**. The first eluted component (**14**) had the following spectral characteristics: NMR (60 MHz) δ 5.48 (br s, 2 H), 3.52 (d, *J* = 10 Hz, 1 H), 3.34 (d, *J* = 10 Hz, 1 H), 1.68 (br d, *J* = 7 Hz, 1 H), 1.07 (s, 3 H), 1.03 (s, 3 H), 1.00 (s, 3 H), 0.93 (s, 1 H), 0.88 (br d, *J* = 7 Hz, 1 H); IR 3625 (w), 3550–3150 (br w), 3045 (w), 3000 (**m**), 2950 (s), 2860 (s), 1590 (vw), 1450 (m), 1440 (m), 1370 (m), 1040 (w), and 1020 (s) cm^{-1}.

7-Methyl-6-octen-1-ol (26). To a suspension of $LiAlH_4$ (0.75 g) in anhydrous ether (100 mL), magnetically stirred under a N_2 atmosphere, was added dropwise ethyl (*E*)-7-methylocta-2,6-dienoate (**25**,[20] 1.094 g, 6 mmol) in ether (25 mL) over a period of 0.5 h. After completion of the addition, the reaction mixture was heated to reflux for 0.5 h. Excess $LiAlH_4$ was destroyed with saturated Na_2SO_4, the inorganic salts were removed by filtration, and the organic phase was washed twice with water and saturated NaCl solution and dried over $MgSO_4$. Removal of solvent in vacuo gave 0.881 g of a colorless oil which was shown to consist of three components by VPC analysis on column A (150 °C). The first eluted compound (10%) was identified as **27**. The second component (78%) was **26**: IR 3625 (w), 3330 (br), 2920 (s), 2850 (s), 1450 (m), 1375 (m), 1050 (m) cm^{-1}; NMR (60 MHz) δ 5.08 (br t, *J* = 7 Hz, 1 H), 3.55 (t, *J* = 6 Hz, 2 H), 2.67–1.00 (br m with s at 1.68 and 1.60, 15 H); mass spectrum *m/z* 147.1357 (M^+, calcd for $C_9H_{18}O$, 147.1357). The third component (12%) was 7-methyl-2,6-octadien-1-ol.

7-Methyl-6-octen-1-al (27). The crude alcohol **26** (9.78 g, 68.8 mmol) was oxidized with the complex prepared from CrO_3 (41.25 g, 0.4125 mmol) and pyridine (65.3 g, 0.825 mmol) in CH_2Cl_2 according to the procedure of Ratcliffe and Rodehorst.[9] After solvent was removed by distillation through a Vigreux column, short-path distillation of the residue gave **27** (4.24 g, 44%), bp 87–92 °C (18 mm). An analytical sample was obtained by preparative VPC on column A (150 °C): IR 2930 (s), 2855 (s), 2815 (m), 2720 (m), 1727 (s), 1450 (m), 1375 (m) cm^{-1}; NMR (60 MHz) δ 9.78 (t, *J* = 2 Hz, 1 H), 5.05 (br t, *J* = 6 Hz, 1 H), 2.53–1.05 (br m with s at 1.68 and 1.60, 14 H). Anal. ($C_9H_{16}O$) C, H.

7-Methyl-2-methylene-6-octen-1-al (22). A mixture of **27** (1.0 g, 7.13 mmol), diethylamine hydrochloride (0.782 g, 7.13 mmol), and 37% aqueous formaldehyde (579 mg, 7.14 mmol) was heated at 75 °C for 3 h under a nitrogen atmosphere. The resulting solution was destructively distilled and the distillate was purified following the procedure of Cormier et al.[22] After removal of solvent, preparative VPC on column B (140 °C) gave **22** (349 mg, 32%): IR 3075 (w), 2960 (m), 2920 (s), 2850 (m), 2685 (w), 1700 (s), 1625 (w), 1448 (m), 1375 (m), 935 (s) cm^{-1}; NMR (60 MHz) δ 9.60 (s, 1 H), 6.22 (br s, 1 H), 5.95 (br s, 1 H), 5.12 (br t, 1 H), 2.55–1.08 (br m with s at 1.70 and 1.62, 12 H). Anal. ($C_{10}H_{16}O$) C, H.

Direct Photolysis of 7-Methyl-2-methylene-6-octen-1-al (22). A. At 30 °C. A solution of **22** (100 mg) in benzene (60 mL) was photolyzed for 72 h using an uranium glass filter. VPC analysis on column A (148 °C) indicated the formation of four products in the ratio 70:6:12:12 (overall yield 43%). The first eluted component was **28**, identical with material independently synthesized as described below. The retention time of the second component was identical with that of **31**, but the component was formed in quantities that precluded identification. The NMR and IR spectra of the third and fourth components suggested that they were isomeric 3-(3,3-dimethylallyl)cyclobutane-1-carboxaldehydes, but contaminated with an unknown substance(s), and they were not investigated further.

B. At 80 °C. A solution of the aldehyde (100 mg) in benzene (75 mL) was heated to reflux and irradiated as above for 22 h (100% conversion). VPC analysis showed the presence of the same four compounds in the ratio 49:30:10:10.

C. At 132 °C. Conversion of **22** (100 mg) in chlorobenzene heated to reflux in 56% yield to a mixture of four products in a ratio of 32:49:10:9 was completed by irradiating for 10 h. The second component was isolated by preparative VPC and identified as **31**: IR 2995 (w), 2948 (s), 2865 (s), 2800 (w), 2700 (w), 1727 (s), 1450 (w), 1380 (w), 1368 (w) cm^{-1}; NMR (220 MHz) δ 9.69 (t, *J* = 2 Hz, 1 H), 2.52 (d, *J* = 2 Hz, 2 H), 2.05–1.27 (br m, 6 H), 1.05 (s, 3 H), 1.01 (s, 3 H), 0.89 (d, *J* = 5.5 Hz, 1 H); mass spectrum *m/z* 152.1199 (M^+, calcd for $C_{10}H_{16}O$, 152.1201).

Sensitized Photolyses of 22. A benzene (25 mL) solution of **22** (10^{-2} M) and acetophenone (10^{-1} M) was irradiated at 30 °C for 4 h. VPC analysis on column A indicated that no products had been formed. Similar concentrations of **22** and acetophenone in chlorobenzene were heated to reflux and photolyzed. Analysis showed that only **28** and **31** in a ratio of 38:62 were produced.

Wolff–Kishner Reduction of 31. Aldehyde **31** (86 mg) was treated with anhydrous hydrazine (0.5 mL) and KOH (1 g) in di(ethylene

glycol) (3 mL) for 0.5 h at 110 °C and 3 h at 180 °C.[44] The reaction mixture was diluted with water, extracted with pentane, and dried. Solvent was removed by distillation and the residue was chromatographed on alumina (2.5 g, activity I) with pentane. Concentration of the eluent afforded a residue which VPC analysis on column G (123 °C) indicated to consist of one component. This was collected and identified as **32:** IR 2990 (m), 2960 (s), 2865 (s), 1450 (m), 1382 (w), 1368 (m), 1112 (w) cm^{-1}; NMR (220 MHz) δ 1.96–1.31 (m, 8 H), 1.05 (s, 3 H), 0.94 (s, 3 H), 0.91 (t, J = 7 Hz, 3 H), 0.66 (d, J = 5 Hz, 1 H); mass spectrum m/z 138.1408 (M^+, calcd for $C_{10}H_{18}$, 138.1408).

Wolff–Kishner Reduction of 33. Following the procedure described above, **33**[25] (~135 mg) was treated with anhydrous hydrazine (0.75 mL) and KOH (1 g) in di(ethylene glycol) (3 mL). The residue obtained after similar workup and chromatography consisted of two components (ratio 73:27) upon VPC. The major first eluted component had identical NMR and IR spectra and VPC retention time with those given above for **32**. The second compound was identified as *trans*-1-ethyl-2-isopropenylcyclopentane: IR 3065 (w), 2950 (s), 2870 (m), 1642 (m), 1455 (m), 1372 (m), 880 (s) cm^{-1}; NMR (220 MHz) δ 4.63 (m, 2 H), 2.03–1.41 (m with s at 1.65, 10 H), 1.24–0.94 (m, 3 H), 0.88 (t, J = 7 Hz, 3 H); mass spectrum m/z 138.1415 (M^+, calcd for $C_{10}H_{18}$, 138.1408).

Photolysis of 1-Cyclopentene-1-carboxaldehyde (29) and Isobutylene. A mixture of **29** (522 mg) and isobutylene (~22 mL) in benzene (40 mL) was irradiated for 72 h (>95% conversion). Solvent was removed by distillation and the residue was bulb-to-bulb (130 °C, 8 mm) distilled to give 594 mg (72%) of a mixture of three products in a ratio of 26:57:17. These were separated by preparative VPC on column F (143 °C). The first eluted component was identified as **28**: IR 2950 (s), 2855 (m), 2795 (w), 2700 (w), 1715 (s), 1462 (m), 1442 (m), 1430 (m), 1377 (m), 1360 (m), 1168 (m), 1000 (m), 868 (m) cm^{-1}; NMR (220 MHz) δ 9.58 (s, 1 H), 2.37 (br d, J = 9.5 Hz, 1 H), 2.31 (dd, J = 12, 2 Hz, 1 H), 2.05–1.16 (br m, 7 H), 1.07 (s, 3 H), 0.92 (s, 3 H); mass spectrum m/z 152.1205 (M^+, calcd for $C_{10}H_{16}O$, 152.1201).

The second and major component was identified as 7,7-dimethylbicyclo[3.2.0]heptane-1-carboxaldehyde (**30**): IR 2950 (s), 2870 (m), 2860 (m), 2800 (w), 2700 (w), 1710 (s), 1465 (w), 1440 (m), 1375 (w), 1361 (m), 1190 (w) cm^{-1}; NMR (60 MHz) δ 9.77 (s, 1 H), 3.23–2.83 (m, 1 H), 2.23–1.27 (m, 8 H), 1.20 (s, 3 H), 1.05 (s, 3 H); mass spectrum m/z 152.1192 (M^+, calcd for $C_{10}H_{16}O$, 152.1201). The last component was not identified, but appeared to be one or more of the products of disproportionation: IR 3070 (w), 2955 (s), 2870 (s), 2805 (w), 2705 (m), 1725 (s), 1645 (m), 1440 (m), 1370 (m), 880 (s) cm^{-1}.

(*E*)-7-Methylocta-2,6-dien-1-ol. To a solution of ethyl (*E*)-7-methylocta-2,6-dienoate (**25**,[20] 5.94 g, 37.8 mmol) in hexane (100 mL), magnetically stirred under a nitrogen atmosphere and cooled to between −25 and −35 °C, was added diisobutylaluminum hydride (61.0 g of a 20% solution in hexane, 81.5 mmol) over a period of 1 h. The reaction mixture was stirred for 1 h and then allowed to warm to 0 °C during 1 h. Methanol (10 mL) was added, then water (5 mL) and dilute HCl to acidify the reaction mixture. The organic phase was separated and the aqueous phase was extracted twice with ether. The organic phases were combined and washed with dilute HCl, saturated $NaHCO_3$, and saturated NaCl and dried over $MgSO_4$. After removal of solvent in vacuo, a quantitative yield of the dienol was obtained. An NMR spectrum indicated that virtually no **26** (<5%) had been formed.

(*E*)-7-Methylocta-2,6-dienal (34). Oxidation of the above alcohol (4.64 g, 33.1 mmol) with the complex prepared from chromium trioxide (19.85 g, 198.5 mmol) and pyridine (31.4 g, 397 mmol) in CH_2Cl_2 (500 mL)[9] gave **34** (3.901 g, 85%), bp 98–104 °C (20 mm). An analytical sample was obtained by preparative VPC on column H (180 °C): IR 2965 (s), 2930 (s), 2908 (s), 2850 (m), 2810 (m), 2800 (m), 2730 (w), 1690 (s), 1635 (m), 1440 (w), 1370 (w), 1118 (s), 968 (s) cm^{-1}; NMR (60 MHz) δ 9.45 (d, J = 8 Hz), 6.73 (dt, J = 15, 6 Hz, 1 H), 6.00 (ddd, J = 15, 8, 1 Hz, 1 H), 5.07 (br t, 1 H), 2.60–1.87 (m, 4 H), 1.72 (s, 3 H), 1.63 (s, 3 H). Anal. ($C_9H_{14}O$) C, H.

Photolysis of (*E*)-7-Methylocta-2,6-dienal (34). A. At 30 °C. A solution of **34** (374 mg) in benzene (65 mL) was photolyzed through a uranium glass filter until <5% of the enal remained. Attempts to separate directly by VPC each component of the mixture of aldehydes failed. Most of the benzene was removed by distillation and the residue was taken up in acetone (35 mL) and treated with an excess of Jones reagent[45] at ~15 °C. The reaction mixture was concentrated in vacuo, diluted with water, and extracted with ether. After the mixture was dried over $MgSO_4$, diazomethane was added to the solution. Bulb-to-bulb distillation (to 130 °C, 8 mm), afforded 191 mg of an oil which comprised four products upon VPC analysis on column C (161 °C). The first eluted component (3%) was identified as **35b** on the basis of identical IR and NMR spectra with an authentic sample whose preparation is described below. The second component (18%) was *trans*-2-isopropenylcyclopentanecarboxylic acid methyl ester (**37b**): IR 3072 (w), 2950 (s), 2860 (m), 1735 (s), 1645 (m), 1448 (m), 1430 (s), 1372 (m), 1260 (m), 1190 (s), 1160 (s), 890 (s) cm^{-1}; NMR (60 MHz) δ 4.73 (br s, 2 H), 3.65 (s, 3 H), 2.92–2.28 (br m, 2 H), 2.28–1.25 (br m with s at 1.73, 9 H); mass spectrum m/z 168.1152 (M^+, calcd for $C_{10}H_{16}O_2$, 168.1150).

The third constituent was 6,6-dimethylbicyclo[2.1.1]hexane-5-carboxylic acid methyl ester (**36b**, 6%): IR 2960 (s), 1735 (s), 1430 (m), 1372 (m), 1260 (m), 1215 (s), 1205 (s), 1030 (s) cm^{-1}; NMR (60 MHz) δ 3.60 (s, 3 H), 2.96 (br s, 1 H), 2.28 (d, J = 2.5 Hz, 2 H), 1.65 (s, 4 H), 1.28 (s, 3 H), 0.82 (s, 3 H); mass spectrum m/z 168.1155 (M^+, calcd for $C_{10}H_{16}O_2$, 168.1150).

The last eluted compound was identified as (*E*)-7-methylocta-3,6-dienoic acid methyl ester (**38b**, 20%): IR 3030 (w), 2975 (m), 2950 (m), 2930 (m), 1742 (s), 1428 (s), 1320 (m), 1245 (m), 1155 (s), 1010 (w), 962 (w) cm^{-1}; NMR (60 MHz) δ 5.53 (t, J = 5 Hz, 2 H), 5.12 (br t, J = 6.5 Hz, 1 H), 3.68 (s, 3 H), 3.05 (d, J = 5 Hz, 2 H), 2.88–2.52 (m, 2 H), 1.72 (s, 3 H), 1.65 (s, 3 H); mass spectrum m/z 168.1144 (M^+, calcd for $C_{10}H_{16}O_2$, 168.1150).

B. At 138 °C. Irradiations of the aldehyde (275–460 mg) in refluxing *p*-xylene (90–100 mL) using a uranium glass filter were completed in 18–24 h. After careful removal of *p*-xylene by distillation in vacuo the residue was oxidized and esterified as above. VPC analysis of the ester mixture (55–67%) on column C (160 °C) indicated four components. The first was **35b** (2%). The second proved to be a mixture of **39b** (36%) and **37b** (6%). The latter was removed by treatment with osmium tetroxide in pyridine for 3–4 h, addition of aqueous $NaHSO_3$, dilution with water, and extraction with ether. Only **39b** was isolated upon VPC: IR 3005 (m), 2945 (s), 2925 (s), 2860 (s), 1740 (s), 1445 (w), 1427 (m), 1310 (m), 1190 (s), 1150 (m), 1022 (m) cm^{-1}; ^1H NMR (220 MHz) δ 3.63 (s, 3 H), 3.14–3.03 (m, 1 H), 2.01–1.70 (m, 4 H), 1.29 (dd, J = 6, 6 Hz, 1 H), 1.08 (br t, J = 6 Hz, 1 H), 0.977 (s, 3 H), 0.970 (s, 3 H); ^{13}C NMR δ_{Me_4Si} 15.3, 19.7, 24.8, 28.1, 28.4, 30.7, 32.4, 44.8, 51.2, 175.8; mass spectrum m/z 168.1148 (M^+, calcd for $C_{10}H_{16}O_2$, 168.1150).

The third component was **36b** (6%). The last eluted compound was identified as **40b** (11%): IR 3005 (w), 2945 (m), 2860 (m), 1732 (s), 1428 (m), 1370 (w), 1312 (w), 1185 (m), 1162 (s) cm^{-1}; ^1H NMR (220 MHz) δ 3.63 (s, 3 H), 2.62 (dd, J = 9, 4 Hz), 2.23–1.95 (m, 2 H), 1.73–1.51 (m, 2 H), 1.31 (d, J = 6.5 Hz, 1 H), 1.20 (dd, J = 6.5, 6 Hz, 1 H), 1.01 (s, 3 H), 0.96 (s, 3 H); ^{13}C NMR δ_{Me_4Si} 14.0, 19.4, 24.9, 27.6, 31.6, 32.1, 34.5, 43.9, 51.5, 176.7; mass spectrum m/z 168.1129 (M^+, calcd for $C_{10}H_{16}O_2$, 168.1150).

Treatment of **39b** with $NaOCH_3$ in warm methanol (50 °C) gave a ~1:1 mixture of **39b** and **40b**.

Photolysis of Apocamphor (41). A solution of apocamphor (76 mg) in benzene (55 mL) was irradiated for 18 h through Pyrex to give the known aldehyde **35a**.[27] This was treated with Jones reagent[45] and diazomethane as described above to give 2,2-dimethyl-3-cyclopentene-1-acetic acid methyl ester (**35b**): IR 3040 (w), 2950 (s), 2860 (m), 1740 (s), 1610 (w), 1427 (m), 1357 (m), 1287 (m), 1190 (m), 1140 (m), 705 (m) cm^{-1}; NMR (60 MHz) δ 5.53 (br s, 2 H), 3.67 (s, 3 H), 2.87–1.33 (br m, 5 H), 1.10 (s, 3 H), 0.85 (s, 3 H); mass spectrum m/z 168.1144 (M^+, calcd for $C_{10}H_{16}O_2$, 168.1150).

(*Z*)- and (*E*)-3-Methylhepta-2,6-dienal (42). A ~1:1 mixture of the cis and trans unsaturated esters was prepared from 5-hexen-2-one (14.72 g, 0.15 mol), triethyl phosphonoacetate (37.9 g, 0.169 mol), and NaH (8.11 g of a 50% dispersion, 0.169 mol) in dimethoxyethane in 43% yield (bp 99–103 °C, 20 mm), according to the method of Wadsworth and Emmons.[26] The ester mixture was reduced with diisobutylaluminum hydride to the cis and trans alcohols in 92% yield as described above for **25** and oxidized with the chromium trioxide–pyridine complex[9] in 81% yield (bp 90–100 °C, 10 mm). The products were separated and purified further by preparative VPC on column E (165 °C). The cis isomer was eluted first: IR 3060 (m), 2960 (m), 2915 (m), 2840 (m), 2745 (m), 1675 (s), 1640 (s), 1612 (m), 1437 (m), 1390 (m), 1370 (m), 1175 (m), 1125 (m), 985 (m), 912 (s), 850 (w), 830 (w) cm^{-1}; NMR (60 MHz) δ 9.94 (d, J = 8 Hz, 1 H),

6.13–5.56 (br m, 1 H), 5.81 (d of q, J = 8, 2 Hz, 1 H), 5.23–4.81 (m, 2 H), 2.84–2.11 (m, 4 H), 1.98 (d, J = 2, Hz, 3 H). Anal. ($C_8H_{12}O$) C, H.

The major component was the trans isomer: IR 3070 (**m**), 2987 (m), 2940 (m), 2845 (m), 2760 (m), 1675 (s), 1640 (m), 1615 (m), 1440 (m), 1377 (m), 1188 (m), 1122 (m), 985 (m), 913 (s), 852 (w) cm^{-1}; NMR (60 MHz) δ 10.00 (d, J = 7.5 Hz, 1 H), 6.12–5.38 (br m, 1 H), 5.80 (br d, J = 7.5 Hz, 1 H), 5.22–4.75 (m, 2 H), 2.28 (d, J = 3.5 Hz, 4 H), 2. 17 (d, J = 2 Hz, 3 H). Anal. ($C_8H_{12}O$) C, H.

Photolysis of 3-Methylhepta-2,6-dienal. A. At 30 °C. A solution of *Z*- and *E*-**42** (ratio 1.0:3.6, 344 mg) in benzene (70 mL) was irradiated until VPC analysis on column B (140 °C) indicated 90% conversion (240 h). Benzene was removed by distillation and the residue was oxidized and esterified as described for **34.** Bulb-to-bulb distillation gave 81.4 mg of a mixture of esters which were separated on column C (140 °C). The first component was 1-methylbicyclo[2.1.1]hexane-*endo*-5-carboxylic acid methyl ester (**44b,** 13%): IR 2950 (s), 2880 (m), 1733 (s), 1448 (m), 1427 (m), 1375 (w), 1310 (m), 1227 (s), 1200 (s), 1180 (s), 1085 (w), 1030 (s) cm^{-1}; NMR (220 MHz) δ 3.56 (s 3 H), 2.59 (sym 7-line m, 1 H), 2.07 (br s, 1 H), 1.89–1.75 (m, 1 H), 1.66–1.49 (m, 2 H), 1.39–1.32 (m, 1 H), 1.28 (s, 3 H), 1.17 (m, 1 H), 0.94 (d, J = 6 Hz, 1 H); mass spectrum m/z 154.0974 (M^+, calcd for $C_9H_{14}O_2$, 154.0994).

The second component was the exo isomer **45b** (1%): IR 2945 (s), 2860 (m), 1735 (s), 1430 (m), 1360 (m), 1277 (m), 1165 (s), 1133 (m), 1103 (m) cm^{-1}; NMR (220 MHz) δ 3.62 (s, 3 H), 2.61 (m, 1 H), 2.23 (br d, J = 8 Hz, 1 H), 2.11 (d, J = 7 Hz, 1 H), 1.74–1.51 (m, 4 H), 1.19 (s, 3 H), 1.06 (dd, J = 7, 7 Hz, 1 H); mass spectrum m/z 154.0984 (M^+, calcd for $C_9H_{14}O_2$, 154.0994).

The last eluted constituent was identified as 1-methylcyclopent-3-en-1-acetic acid methyl ester (**43b,** 5%): IR 3050 (w), 2950 (s), 2925 (m), 2840 (m), 1740 (s), 1430 (m), 1195 (s), 1152 (m), 1108 (m), 1010 (m), 666 (m) cm^{-1}; NMR (60 MHz) δ 5.58 (s, 2 H), 3.63 (s, 3 H), 2.40–2.67 (m with s at 2.34, 6 H), 1.15 (s, 3 H); mass spectrum m/z 154.1007 (M^+, calcd for $C_9H_{14}O_2$, 154.0994).

B. At 130 °C. A solution of the *E* and *Z* aldehydes (329 mg) in *p*-xylene (90 mL) was heated to reflux and irradiated through uranium glass for 20 h (100% conversion). Xylene was removed by distillation at reduced pressure (aspirator) and the residue was oxidized and esterified as described above. VPC analysis indicated a five-component mixture in the ratio 47:13:24:9:7 (overall yield ~25%). The first three components had retentions time which corresponded to **44b, 45b,** and **43b.** The two minor components eluted last were not investigated.

Photolysis of 4,8-Dimethylnona-3,7-dien-2-one (46a). A. At 30 °C. A solution of the trans ketone[35] (165 mg) in benzene (50 mL) was irradiated through Pyrex for 0.33 h, in which time VPC analysis on column E (183 °C) indicated that a photostationary state consisting of a cis to trans ratio of 58:42 had been reached. A uranium glass filter was added and the photolysis was continued until no unsaturated ketone remained (~100 h). After removal of solvent by distillation, preparative VPC on column F (175 °C) gave two components. The first eluted was *endo*-5-acetyl-1,6,6-trimethylbicyclo[2.1.1]hexane (**48a,** 16%): IR 2950 (s), 1705 (s), 1452 (w), 1375 (m), 1367 (m), 1347 (m), 1202 (w) cm^{-1}; NMR (60 MHz) δ 2.52 (br s, 1 H), 2.25 (d, J = 3 Hz, 1 H), 2.08–1.42 (m with s at 1.89, 7 H), 1.08 (s, 6 H), 0.70 (s, 3 H); mass spectrum m/z 166.1360 (M^+, calcd for $C_{11}H_{18}O$, 166.1358).

The second component was *r*-1-acetyl-*t*-2-isopropenyl-*c*-5-methylcyclopentane (**47a,** 48%): IR 3070 (w), 2955 (s), 1710 (s), 1640 (w), 1447 (w), 1375 (w), 1348 (m), 1160 (w), 882 (w) cm^{-1}; NMR (60 MHz) δ 4.63 (s, 2 H), 3.18–1.25 [m with s at 2.07 and d (J = 1 Hz) at 1.67, 13 H], 0.84 (d, J = 7 Hz, 3 H); mass spectrum m/z 166.1350 (M^+, calcd for $C_{11}H_{18}O$, 166.1358).

B. At 138 °C. A solution of the trans ketone (269.1 mg) was photolyzed through uranium glass in *p*-xylene (55 mL) heated to reflux for 18 h at which time no **46** remained. Only **47a** and **48a** (~1:1) were formed in an overall yield of 78%.

C. At 177 °C. The cis ketone (187 mg) was dissolved in *p*-cymene (65 mL) and irradiated to reflux for 16 h. Preparative VPC afforded only **47a** and **48a,** again in a ratio of ~1:1.

Photolysis of Methyl Geranate (46b). A. At 30 °C. A mixture of methyl geranate (~1:3 ratio of cis and trans isomers, 52.7 mg) and propiophenone (27.5 mg) in benzene (25 mL) was irradiated through Pyrex at 30 °C for 17 h. VPC analysis on column D (160 °C) indicated that 58% of the sensitizer was destroyed and 93% of **46b** was consumed to yield two products. The first was 1,6,6-trimethylbicyclo[2.1.1]hexane-*endo*-5-carboxylic acid methyl ester (**48b,** 18%): IR 2950 (s), 1733 (s), 1426 (m), 1375 (m), 1365 (m), 1218 (s), 1022 (s) cm^{-1}; NMR (60 MHz) δ 3.56 (s, 3 H), 2.57 (s, 1 H), 2.22 (br d, J = 1 Hz, 1 H), 1.98–1.27 (m, 4 H), 1.10 (s, 3 H), 1.04 (s, 3 H), 0.73 (s, 3 H). Anal. ($C_{11}H_{18}O_2$) C, H. The second product was *c*-2-methyl-*t*-5-isopropenylcyclopentane-*r*-1-carboxylic acid methyl ester (**47b,** 35%): IR 3070 (w), 2960 (s), 2945 (s), 2870 (m), 1735 (s), 1642 (m), 1427 (s), 1373 (m), 1360 (w), 1187 (s), 1155 (s), 882 (s) cm^{-1}; NMR (60 MHz) δ 4.65 (q, J = 1 Hz, 2 H), 3.62 (s, 3 H), 3.05–1.13 (m, with d, J = 1 Hz, at 1.68, 9 H), 0.89 (d, J = 7 Hz, 3 H). Anal. ($C_{11}H_{18}O_2$) C, H.

Similar results were obtained in acetone as solvent, although the reaction was slower and side products apparently derived from the solvent were formed.

B. At 80 and 132 °C. A mixture of the esters (254 mg) and propiophenone (135 mg) in benzene (80 mL) was heated at reflux and irradiated overnight. Products **48b** (31%) and **47b** (35%) were obtained, and half the sensitizer was destroyed. A similar experiment at 132 °C in refluxing chlorobenzene gave small amounts of the same two products with very little destruction of sensitizer. About 1% of a third unidentified component was noted.

Photolysis of Geranonitrile (49). A. At 30 and 80 °C. A benzene (25 mL) solution of *cis*- and *trans*-**49** (50.3 mg) containing propiophenone (31.1 mg) was irradiated through Pyrex for 40 h. VPC analysis on column D indicated ~95% conversion and the formation of one major and at least two minor products. The major, first eluted compound was identified as **51:** IR 2965 (s), 2915 (s), 2885 (s), 2865 (m), 2235 (m), 1475 (m), 1440 (m), 1388 (m), 1376 (m), 1368 (m), 1300 (m), 1280 (m) cm^{-1}; NMR (60 MHz) δ 2.75–2.58 (m, 1 H), 2.4–2.25 (m, 1 H), 2.07–1.40 (m, 4 H), 1.15 (s, 3 H), 1.10 (s, 3 H), 0.825 (s, 3 H). The second component, a wax, was identified as **52:** IR 2960 (s), 2920 (s), 2885 (s), 2238 (m), 1450 (m), 1422 (m), 1387 (m), 1375 (m), 1368 (m), 1310 (w), 1275 (w), 1182 (w), 1130 (w), 1085 (w) cm^{-1}; NMR (60 MHz) δ 2.45 (m, 1 H), 2.05 (s, 1 H), 1.90–1.40 (m with s at 1.52, 7 H), 1.15 (s, 3 H), 0.75 (s, 3 H). The ratio of **51** to **52** was 4:1. The third component was *c*-2-methyl-*t*-5-isopropenylcyclopentane-*r*-1-carbonitrile (**50**): IR 3080 (w), 2960 (s), 2865 (m), 2238 (m), 1645 (m), 1445 (w), 1378 (m), 890 (m) cm^{-1}; NMR (60 MHz) δ 4.82 (s, 2 H), 2.90–1.03 (br m with m at 1.78 and d (J = 7 Hz) at 1.19). Anal. ($C_{10}H_{15}N$) C, H, N. Similar results were obtained when the benzene was heated to reflux or when acetone was used as solvent and sensitizer.

B. At 132 °C. A mixture of *trans*-geranonitrile (72.1 mg), propiophenone (33.9 mg), and sodium bicarbonate (364 mg) in chlorobenzene (33 mL) was heated to reflux and irradiated through Pyrex for 10 h. VPC analysis as above indicated the formation of a new, more rapidly eluted component in addition to **50–52.** This was identified as **53** on the basis of identical NMR and IR spectra and retention time with an authentic sample prepared as described below. The ratio of **53** to **51** varied between 7:3 and 1:10; low ratios were obtained when the concentration of either geranonitrile or propiophenone was increased.

Beckmann Fragmentation of α-Fenchone Oxime. Treatment of **54** (3.0 g) with H_2SO_4 (0.5 g) and water (10 mL) as described previously[41] afforded 2.43 g [91%, bp 92–95 °C (10 mm)] of a 1:1 mixture of **53** and **55.** The former was eluted first on column F (175 °C): IR 3040 (w), 2975 (s), 2940 (s), 2870 (s), 2850 (s), 2238 (m), 1658 (w), 1465 (m), 1432 (m), 1382 (m), 1373 (m), 1362 (m), 978 (m) cm^{-1}; NMR (60 MHz) δ 5.35–5.17 (m, 1 H), 2.88–1.70 (m with br s at 1.80, 8 H), 1.30 (s, 3 H). Spectral data for the other isomer (**55**): IR 3040 (w), 2970 (s), 2975 (s), 2840 (s), 2830 (m), 1660 (w), 1465 (m), 1435 (m), 1382 (m), 1374 (m), 1362 (m), 1010 (m) cm^{-1}; NMR (60 MHz) δ 5.22 (br s, 1 H), 2.30 (s, 5 H), 1.88 (br s, 3 H), 1.33 (s, 6 H).

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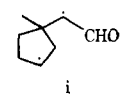
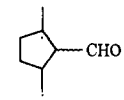


i



ii

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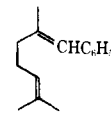

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