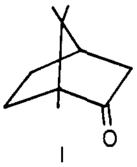
The Solution Photolysis of Camphor[1a]

William C. Agosta and David K. Herron[1b]

*Contribution from the Laboratories of The Rockefeller University,
New York, New York 10021.* *Received May 27, 1968*

Abstract: Irradiation of camphor (**1**) in 95% ethanol and/or in *n*-heptane gives rise to α-campholenic aldehyde (**2**), enol ether **5**, and acetal **6** as primary products. Three additional substances, cyclobutanols **14** and **15** and oxetane **21**, result from secondary photolysis of initially formed **2**. No other products are present above the 1–2% level. Ketone **3**, previously regarded as a major but anomalous product of this reaction, has been synthesized and shown to be absent. Deuterium labeling demonstrates that oxycarbene **8** is an intermediate in the formation of acetal **6** and enol ether **5**.

Over half a century ago Ciamician and Silber showed[2] that irradiation of camphor (**1**) in solution yielded α-campholenic aldehyde (**2**) as a major product in a reaction later recognized as typical of saturated ketones.[3] There has been substantial agreement[4] that a second major product of this photolysis is 3,3,4-trimethyl-4-acetylcyclopentene (**3**), and that the proportion of this ketone formed is markedly solvent dependent.[5] While **3** is formally the result of a Norrish type II cleavage, the cyclic mechanism[3] of this well-studied transformation is sterically excluded in camphor, and to account for these observations Srinivasan has proposed[5] a mechanism involving hydrogen abstraction from solvent by excited camphor. We have now examined the solution photolysis of camphor in some detail in the hope of studying the novel reaction leading to **3**. Below we present results pertinent to this matter, as well as details of the isolation and identification of other primary and secondary photolytic products of the reaction.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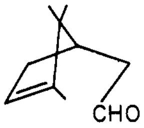
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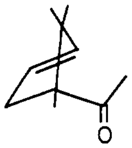
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We have irradiated camphor under nitrogen with Pyrex filtered light both in *n*-heptane and in 95% ethanol and isolated by vapor phase chromatography (vpc) all products forming at least 1–2%[6,7] of the total. With the exception concerning **5** and **6** noted below, the variation of solvent had no significant effect on the distribution of products. In each case α-campholenic aldehyde (**2**) accounted for 70–80%[8] of the mixture. Controlled photolytic conditions gave similar results. Irradiation of camphor in degassed *n*-heptane to 0.5% conversion with 3100–3180-Å light led to α-campholenic aldehyde (**2**) as the only observable product.[9] In duplicate experiments under these carefully controlled conditions the quantum yield for production of **2** was 0.12 ± 0.04. These findings must be contrasted with those of Srinivasan, who reported[5] that the ratio of aldehyde **2** to ketone **3** changed from 3:2 in ethanol to 1:10 in *n*-heptane, and that the quantum yield for production of all nonvolatile products was 0.06 and invariant with solvent.

Our observations thus fail to corroborate the reported striking effect of solvent on the course of this photolysis; further, the results to be recounted indicate that none of the other products which we have isolated from the reaction is ketone **3**. We have therefore synthesized an authentic sample of this substance for comparison of its properties with those reported[2,5] for the anomalous irradiation product.[10] Reaction of camphonenic acid (**4**)[11] with methyllithium[12] in ether solution gave **3** without difficulty. Its structure is supported by mass, infrared (ir), ultraviolet (uv), and nuclear magnetic resonance (nmr) spectra, as well as elemental analysis and its unambiguous mode of

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[1] (a) This investigation was supported in part by National Science Foundation Grant GB-137; (b) National Science Foundation Graduate Fellow.

[2] G. Ciamician and P. Silber, *Atti Reale Accad. Lincei*, [1], **19**, 532 (1910); *Ber.*, **43**, 1340 (1910).

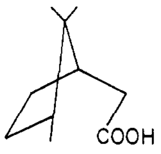
[3] *Cf.* J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, Inc., New York, N. Y., 1966, Chapter 5.

[4] *Cf.*, for example, R. Srinivasan, *Advan. Photochem.*, **1**, 83 (1963); J. N. Pitts, Jr., and J. K. S. Wan in "The Carbonyl Group," S. Patai, Ed., John Wiley & Sons, Inc., London, 1966, p 880 ff; ref 3, p 411; R. O. Kan, "Organic Photochemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1966, p 89.

[5] R. Srinivasan, *J. Am. Chem. Soc.*, **81**, 2604 (1959).

[6] This figure is only approximate and is high. Secondary photolysis of α-campholenic aldehyde (**2**) to form unisolated 1,5,5-trimethylcyclopentadiene and acetaldehyde (*cf.* ref 29 and 30) lowers the observed amount of **2** and consequently raises the apparent amount of all others.

[7] Quinkert has shown that an acid, presumably *trans*-campholanic acid (*i*) and derived from the related ketene, is formed in no more than 1% yield in this reaction: G. Quinkert, E. Blanke, and F. Homburg, *Ber.*, **97**, 1799 (1964).


i

[8] Note in this regard ref 6.

[9] The conditions and equipment used are fully described in the Experimental Section. Apart from a 25% higher beam intensity, they are the conditions reported by Srinivasan.[5]

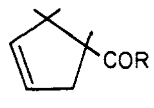
[10] The early Italian workers used (+)-camphor, while Srinivasan irradiated (±)-camphor. For the comparisons to be made (see below) it was appropriate to have optically active **3**, and we have accordingly prepared the enantiomer of **3** related to (+)-camphor. In our own photolytic experiments both racemic and dextrorotatory camphor have been used (see Experimental Section).

[11] We have prepared this long-known camphor derivative by a new and more convenient procedure. Details, along with physical constants previously unreported, are given in the Experimental Section. Earlier work is summarized by J. L. Simonsen in "The Terpenes," Vol. II, The University Press, Cambridge, 1957, p 509.

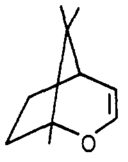
[12] C. Tegner, *Acta Chem. Scand.*, **6**, 782 (1952).

preparation. This ketone, mp 77–78°, shows carbonyl absorption at 1699 cm^{-1} (CHCl$_3$, typical of a pinacolone) in the ir and 286 mμ (ϵ 22, EtOH) in the uv; it forms a semicarbazone, mp 191–193° dec. These data are at considerable variance with those found previously. Ciamician and Silber stated[2] their ketone to be an oil yielding a semicarbazone, mp 151–152°. Srinivasan gave[5] for his ketone (physical state unreported) carbonyl absorption at 1715 cm^{-1} (CHCl$_3$) and 280 mμ (ϵ 60, EtOH).

With authentic **3** in hand we were readily able to demonstrate that it would survive the irradiation and that as little as 0.2% of this ketone would have been detected among the products. From these various results we conclude that it is most unlikely that 3,3,4-trimethyl-4-acetylcyclopentene (**3**) is obtained on solution photolysis of camphor.[13]



3, R=CH$_3$
4, R=OH



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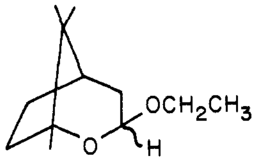

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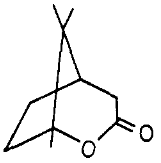
Turning now to other substances formed in this reaction, we describe the isolation and identification of five new compounds as well as the pathways of their formation. The first two of these are enol ether **5** and acetal **6**. The enol ether is a quite volatile, crystalline solid, the structure of which is deduced from its elementary composition and spectral data. In particular, the ir spectrum has strong absorption at 1638 cm^{-1}, typical of an enol ether, and the nmr spectrum shows two vinylic hydrogen signals (δ 4.78 ppm (triplet, 1 H) and 5.92 (doublet, 1 H)). Finally structure **5** was confirmed by chromic acid oxidation of the enol ether in acetone[14] to the known lactone **7**.[15] The acetal (**6**) is a colorless oil which decomposes on standing at 4°. On vpc **6** undergoes partial thermolysis to **5** (inlet temperature 235°), and on Jones oxidation[14] it also yields lactone **7**. In its nmr spectrum the presence of two sets of signals for the ethoxyl protons reveals **6** to be an approximately equal mixture of isomers epimeric about the acetal carbon atom. The proton on this carbon atom appears as a doublet at 4.64 ppm. These two related substances, **5** and **6**, make up about 15%[6] of the product mixture from irradiation of camphor in ethanol; the reaction in *n*-heptane gives no acetal **6** and about 10%[6] enol ether **5**.

The simplest pathway for the formation of **5** and **6** from camphor is through the oxycarbene **8**, which might be expected to insert into the O–H bond of solvent ethanol to give **6** or suffer internal insertion (1,2 shift of hydrogen) to give **5**. Such carbene intermediates from photolysis of saturated ketones have been suggested on several occasions in the recent past, particularly to account for formation of acetals incorporating a molecule of solvent.[16–18] Transformation of an oxycarbene to enol ether, however, seems not to have been previously observed. At the time of this work the only evidence independent of product analysis that these reactive species had a role in ketone photolysis was the isolation in two instances of cyclopropanes formed by oxycarbene addition to olefinic solvent.[16] To explore the intermediacy of **8** in the formation of **5** and **6** we undertook two different deuterium-labeling experiments.



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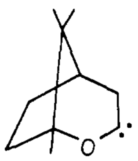

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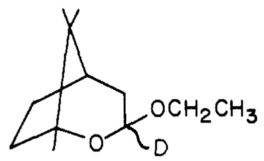

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Photolysis of camphor (**1**) in 95% ethanol-*d* (95% EtOD–5% D$_2$O) yielded acetal and enol ether as before. The nmr spectrum of recovered camphor indicated no incorporation of deuterium, while the spectrum of the acetal showed a single difference from that of **6** obtained earlier. The acetal proton signal at 4.64 ppm was absent, indicating that this hydrogen atom was now present as deuterium (*cf.* **9**). It is then clear that both hydrogen and ethoxyl of **6** come from solvent, most simply by insertion of oxycarbene **8** into ethanol.[19] The nmr spectrum of enol ether from this photolysis was also informative; the signal at 5.92 ppm was absent, showing the compound to be monodeuterated (*cf.* **10**). This could not occur *via* intramolecular insertion from **8**, but is easily explained by thermal cracking of **9** during vpc isolation. In ethanol then, enol ether **5** arises simply as a secondary thermal product, and carbene **8** is completely trapped by solvent.

With this result in hand we were particularly interested in the origin of enol ether **5** in heptane solution, since here no acetal is formed to serve as precursor. This question was investigated by photolysis in *n*-heptane of camphor-3,3-d_2 (**11**).[20] Deuterium levels were determined in this case by a combination of nmr data and parent peak measurements in mass spectra. These indicated starting camphor to be 91% d_2, 7% d_1, and 2% deuterium free, and camphor recovered after

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(13) With the advantages of hindsight it is not difficult to construct a credible explanation of the original observations (ref 2). Ciamician and Silber separated their reaction mixture into two portions. From one portion they isolated α-campholenic aldehyde, but only as the corresponding hydroxamic acid. They treated the other portion with sodium bisulfite to remove α-campholenic aldehyde and subjected the remaining material to purification by distillation. This procedure yielded pure liquid "ketone," characterized as its semicarbazone (mp 151–152°), and oxidized by permanganate to a ketodicarboxylic acid, C$_{10}$H$_{16}$O$_5$ (mp 133–134°). Unfortunately the then accepted melting point for the semicarbazone of α-campholenic aldehyde (prepared from α-pinene oxide) was 137–138°, an error that was neither discovered nor corrected until 1961. It is now known that pure α-campholenic aldehyde forms a semicarbazone, mp 154–155°, and yields on oxidation a ketodicarboxylic acid C$_{10}$H$_{16}$O$_5$ (isoketocamphoric acid), mp 130–131° (*cf.* L. C. King and H. Farber, *J. Org. Chem.*, **26**, 326 (1961)). It appears most probable then that in the early Italian work sodium bisulfite treatment had failed to remove entirely the aldehyde present, and that distillation simply furnished a pure sample of α-campholenic aldehyde.

(14) A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lemin, *J. Chem. Soc.*, 2548 (1953).

(15) (a) R. R. Sauers, *J. Am. Chem. Soc.*, **81**, 925 (1959); (b) R. R. Sauers and G. P. Ahearn, *ibid.*, **83**, 2759 (1961).

(16) P. Yates and L. Kilmurry, *ibid.*, **88**, 1563 (1966); H. A. Staab and J. Ipaktschi, *Tetrahedron Letters*, 583 (1966).

(17) H. U. Hostettler, *ibid.*, 687 (1965); R. F. C. Brown and R. C. Solly, *ibid.*, 169 (1966); G. Quinkert, G. Cimbollek, and G. Buhr, *ibid.*, 4573 (1966).

(18) N. J. Turro and R. M. Southam, *ibid.*, 545 (1967).

(19) In similar, but completely independent and more extensive experiments, Turro has shown that α-methoxytetrahydrofurans are formed on photolysis of cyclobutanones by carbene insertion into solvent methanol.[18]

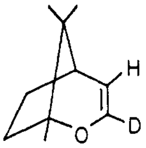
(20) Camphor was deuterated according to the procedure of D. S. Weinberg and C. Djerassi, *J. Org. Chem.*, **31**, 115 (1966).

Table I. Nmr Spectra of Cyclobutanones **16**, **17**, and **18**

16		**17**[d]		**18**[e]	
Position[a]	Signal,[b] δ	Position[a]	Signal,[b] δ	Position[a]	Signal,[b] δ
C(2)-H	5.15 (broad s, 1 H)	C(3)-H	5.22 (m, 1 H)	C(3)-H	5.46 (m, 1 H)
C(1)-H	4.0 (m, 1 H)	C(1)-H	4.0 (m, 1 H)	C(1)-H	4.03 (m, 1 H)
C(6)-H,H	2.9 (m, 2 H)	C(6)-H,H	3.02 (m, 2 H)		
C(5)-H	2.6 (m, 1 H)	C(5)-H	2.56 (m, 1 H)	C(4)-H,H; C(5)-H	2.55 (m, 3 H)
C(3)-CH_3	1.68 (t,[c] 3 H)	C(2)-CH_3	1.71 (broad s, 3 H)	C(2)-CH_3	1.75 (m, 3 H)
C(4)-CH_3	1.12 (s, 3 H)	C(4)-CH_3	1.15 (s, 3 H)	C(6)-CH_3	1.19 (s, 3 H)
C(4)-CH_3	1.07 (s, 3 H)	C(4)-CH_3	1.1 (s, 3 H)	C(6)-CH_3	1.12 (s, 3 H)

[a] Compounds are numbered as derivatives of bicyclo[3.2.0]hept-2-en-7-one. [b] **16** and **17** in CCl_4, **18** in $CDCl_3$. [c] An apparent triplet, J_{app} = 1.5 Hz. [d] See ref 24. [e] See ref 26.

photolysis to be unchanged. From mass spectra the enol ether formed was 19% d_2, 74% d_1, and 7% deuterium free. Nmr measurements in the vinyl proton region were in accord with this result; they further identified the monodeuterated species as **12** and the dideuterated species as **13**. The enol ether obtained from camphor-d_2 (**11**) is then 19% **13**, 7% **5**, and 74% **12**. About 19% of this compound must arise through **8** *via* intramolecular insertion,[21] while the remainder is formed by some other process(es). We suggest that this latter probably involves as a first-step hydrogen abstraction from solvent heptane by **8**[22] and are currently investigating this point in systems leading to more convenient amounts of oxycarbene intermediates. For the present these data do demonstrate that 1,2 insertion is an observable, but not particularly favorable, mode of reaction for oxycarbene **8**.[23]



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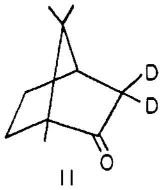

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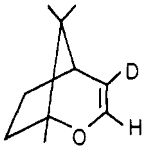

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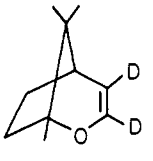

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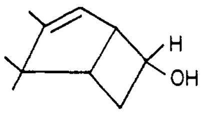
The next two photolytic products to be described are the epimeric cyclobutanols **14** and **15**, which are formed in a ratio of approximately 4:1, and account for some 7%[6] of the isolated products in ethanol and about 19%[6] in heptane. Their structures are derived from the following considerations. Jones oxidation[14] of each alcohol leads to ketone **16**, which from ir carbonyl absorption is a cyclobutanone (1781 cm^{-1}). Careful study of the nmr spectrum of this oxidation product suggested that it was either **16** or its position isomer **17**. The latter is a known product of the photolysis of verbenone, and its nmr spectrum has been analyzed in considerable detail.[24] While direct comparison of the nmr and ir spectra of our oxidation product with those of **17**[25] revealed that the compounds are not identical, they are obviously quite similar. In Table I are collated the nmr spectra of **16** and **17** along with the spectrum of **18**,[26] another isomer available originally from cyclization of geranic acids[26] and also from photolysis of verbenone.[24] We believe that these data uniquely establish **16** as the structure of the ketone in question. This conclusion is supported by the uv absorption of the ketone, which shows the expected complex spectrum;[27] in further agreement with **16** are nmr data for the cyclobutanols (**14** and **15**) detailed in the Experimental Section, as well as double resonance experiments described below. Reduction of cyclobutanone **16** with sodium borohydride leads quantitatively to a mixture of **14** (98%) and **15** (2%).



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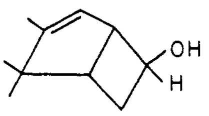

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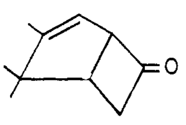

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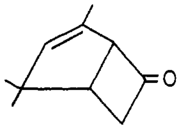

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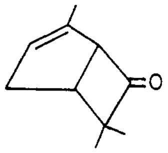

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(21) If there operates a deuterium isotope effect on the intramolecular insertion reaction, this percentage should be somewhat higher in the undeuterated series. While we know of no relevant data for oxycarbenes, carbene itself and simple alkylcarbenes have k_D/k_H in the range 1.2–1.8 for insertion into C–H bonds. *Cf.* J. P. Chesick and M. R. Willcott, *J. Phys. Chem.*, **67**, 2850 (1963); W. Kirmse, H.-D. von Scholz, and H. Arold, *Ann.*, **711**, 22 (1968); and M. J. Goldstein and S. J. Baum, *J. Am. Chem. Soc.*, **85**, 1885 (1963). If k_D/k_H for this reaction of 8 is 1.5, and if any deuterium isotope effect on the alternative pathway(s) is neglected, intramolecular insertion rises from 19 to 26% for the undeuterated carbene.

(22) To our knowledge the recorded examples of intermolecular hydrogen abstraction by carbene species in solution involve either methylene itself (a trivial side reaction; W. von E. Doering and H. Prinzbach, *Tetrahedron*, **6**, 24 (1959)) or diarylcarbenes (W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 4675 (1952); W. Kirmse, L. Horner, and H. Hoffmann, *Ann.*, **614**, 19 (1958); V. Franzen and H.-I. Joschek, *ibid.*, **633**, 7 (1960); G. L. Closs and L. E. Closs, *Angew. Chem.*, **74**, 431 (1962)). Such abstraction is the major reaction of diarylcarbenes with hydrocarbons.

(23) The reactive species formed by α elimination from α-halo ethers undergo efficient addition to olefins to yield cyclopropyl ethers but give no C–H insertion products. Whether or not these intermediates are oxycarbenes, however, remains an open question. *Cf.* U. Schöllkopf and H. Gorth, *Ann.*, **709**, 97 (1967), and references cited therein.

(24) W. F. Erman, *J. Am. Chem. Soc.*, **89**, 3828 (1967).

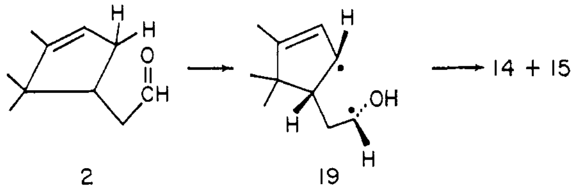
(25) These data were courteously provided by Dr. William F. Erman, The Procter and Gamble Co.

(26) J. J. Beereboom, *J. Am. Chem. Soc.*, **85**, 3525 (1963).

(27) $\lambda\lambda_{max}$ 287 mμ (sh) (ϵ 96), 298 (150), 307 (160), and 316 (110) in isooctane. *Cf.* A. Moscowitz, K. Mislow, M. A. W. Glass, and C. Djerassi, *ibid.*, **84**, 1945 (1962). The unsubstituted parent bicyclo[3.2.0]hept-2-en-7-one has $\lambda\lambda_{max}$ 284 mμ (sh) (ϵ 73), 297 (142), 306 (160), and 317 (112) in isooctane (D. I. Schuster, M. Axelrod, and J. Auerbach, *Tetrahedron Letters*, 1911 (1963)).

Approach to the carbonyl from the shielded and concave side of the molecule appears severely hindered in models, and we conclude that the major product in this reduction results from *exo* attack by hydride. Cyclobutanol **14** is then the *endo*-alcohol.[28]

Since structures **14** and **15** could be derived without consideration of the origin of these alcohols, it is particularly satisfying that these are the cyclobutanols mechanistically most simply reached on photolysis of camphor. Separate irradiation experiments with α-campholenic aldehyde (**2**) have confirmed that, as expected, the alcohols are actually derived from this substance rather than directly from camphor. Allylic hydrogen abstraction in excited **2** followed by rotation about the carbon–carbon single bond and collapse of the diradical **19** can easily lead to **14** and **15**. This collapse must be rapid, since there is available an alternative and energetically more favorable pathway, α,β cleavage to 1,5,5-trimethylcyclopentadiene and acetaldehyde enol. Such cleavage is known to be the principal fate of α-campholenic aldehyde on photolysis.[29,30] A similar conclusion follows from the observed preferential formation of the thermodynamically less stable cyclobutanol (**14**). Creation of the carbinyl asymmetric center is under kinetic control, and cyclization of **19** must be rapid with respect to rotation about the carbon–carbon single bond. These requirements are most simply satisfied by the geometry specifically illustrated in **19**, an arrangement sterically favorable for hydrogen abstraction and also allowing subsequent collapse to **14** with little motion.



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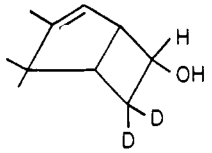

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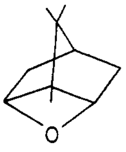
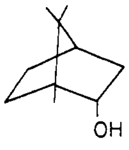
From the above considerations the more abundant cyclobutanol formed on irradiation of camphor-3,3-d_2 (**11**) should be the dideuterated alcohol **20**. The material isolated from photolysis of **11** gave an nmr spectrum fully compatible with this prediction; in the deuterated sample complex absorption for two protons in the 1.8–2.4-ppm region was absent and spin–spin splitting was reduced, while the spectrum was otherwise virtually identical with that of undeuterated **14**. Furthermore, spin–spin decoupling measurements[31] on this deuterated alcohol (**20**) thoroughly supported the structure deduced above (**14**) and also disclosed the coupling constants for the three pairs of adjacent protons and for the long-range interactions of the methyl group at C(3). These methyl protons show both allylic coupling to the vinyl proton at C(2) (1.5 Hz) and homoallylic coupling to the bridgehead proton at C(1) (2.0 Hz).[32]

We describe finally a third product of secondary photolysis. The oxetane **21** forms about 1%[6] of the isolated product from camphor photolysis and some 7% of that from α-campholenic aldehyde. Examination of the nmr spectrum of this photoproduct furnished the most significant clues to its structure. The simplicity of this spectrum, particularly the presence of a single sharp signal for the six protons of the geminal methyl groups, suggested structure **21**; this possibility was substantiated chemically. Reaction of **21** with lithium aluminum hydride[33] in boiling *n*-butyl ether brought about quite slow reductive cleavage of the cyclic ether and formation of racemic borneol (**22**). The known photolytic cycloaddition[34] of carbonyl groups to olefins provides an attractive and simple pathway to the oxetane; intramolecular addition of the aldehyde carbonyl group to the double bond in α-campholenic aldehyde (**2** = **23**) leads directly to **21**.

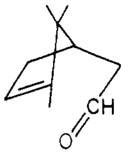
In summary, solution photolysis of camphor leads predominately to α-campholenic aldehyde (**2**), with competing formation of only a small amount of oxycarbene **8**, which is trapped as **5** or **6**. Subsequent photolysis of **2** leads to cyclobutanols **14** and **15** and to oxetane **21**.



21



22



23

Experimental Section

Materials and Equipment. Eastman White Label (±)-camphor was further purified by vapor phase chromatography (vpc) and then showed less than 0.05% impurities on vpc analysis. Eastman White Label (+)-camphor was used without further purification and showed less than 0.05% impurities on vpc analysis. Phillips 99% pure grade *n*-heptane was further purified[35] by shaking successively with (1) small portions of concentrated H_2SO_4 until the

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[28] Effort failed to substantiate this conclusion by thermodynamically controlled reduction with sodium in alcohol. The reaction gave in almost quantitative yield a mixture of **14** (84%) and **15** (16%). The failure of thermodynamic control in dissolving metal reductions of strained and of grossly hindered ketones has previously received attention: H. O. House, H. C. Müller, C. G. Pitt, and P. P. Wickham, *J. Org. Chem.*, 28, 2407 (1963), and references cited therein. In an earlier study reduction of the related but less hindered bicyclo[3.2.0]hept-2-en-6-one (ketene–cyclopentadiene adduct) yielded an *endo*-:*exo*-alcohol ratio of 3:1 with sodium borohydride and 3:7 with sodium in alcohol, while stereochemical equilibration of the alcohols in benzene using fluorenone and aluminum *t*-butoxide gave a 45:55 mixture. *Cf.* J. A. Berson and J. W. Patton, *J. Am. Chem. Soc.*, 84, 3406 (1962).

[29] The photolysis of 2 has been studied in some detail by J. Meinwald and R. A. Chapman, who have isolated and identified 1,5,5-trimethylcyclopentadiene and also isolated cyclobutanol **14**. These investigators have independently derived the explanation outlined in ref 13 above for the observations of Ciamician and Silver: private communication from Professor Jerrold Meinwald, Cornell University; J. Meinwald and R. A. Chapman, *J. Am. Chem. Soc.*, **90**, 3218 (1968).

[30] In both earlier investigations of the photolysis of camphor[2,5] acetaldehyde was detected.

[31] These experiments were kindly performed by Dr. L. A. Wilson, Varian Associates, Union, N. J., using a Varian HA-100 spectrometer.

[32] *Cf.* S. Sternhell, *Rev. Pure Appl. Chem.*, **14**, 15 (1964); for examples with similar geometry, see S. Toki, K. Shima, and H. Sakurai, *Bull. Chem. Soc. Japan*, 38, 760 (1965).

[33] *Cf.* S. Searles, Jr., K. A. Pollart, and E. F. Lutz, *J. Am. Chem. Soc.*, 79, 948 (1957).

[34] This cycloaddition reaction is reviewed by S. Searles, Jr., in "Heterocyclic Compounds with Three- and Four-Membered Rings," John Wiley & Sons, Inc., New York, N. Y., 1964, Part 2, pp 1045 ff.

[35] D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, "Purification of Laboratory Chemicals," Pergamon Press, Oxford, 1966, p 177.

acid layer remained colorless, (2) H_2O, (3) 10% aqueous Na_2CO_3 until CO_2 evolution ceased, (4) H_2O, and then drying over Na_2SO_4 followed by distillation. Ethanol (95%) was distilled before use.

All vpc was done using a Varian Aerograph Model 700 Autoprep with a 20 ft × 0.25 in. stainless steel column packed with 30% FFAP on Chromosorb W. Unless otherwise noted the column oven temperature was 205 ± 5° and the helium carrier gas flow rate was 100 cc/min. Unless otherwise noted both ir and nmr spectra were obtained for CCl_4 solutions, the former on a Perkin-Elmer 237 B spectrophotometer and the latter on a Varian A-60 spectrometer. A Varian C-1024 time averaging computer was employed for multiple-scan nmr spectra.

A Hanovia Model L mercury lamp with quartz immersion well and Pyrex filter was used in all photolyses except the quantum yield determinations. Photolyses were carried out at about 15°, in magnetically stirred solutions.

In the quantum yield determinations the light source was a Hanovia 1000-W compact mercury–xenon lamp. The desired wavelengths were selected using a Bausch and Lomb No. 33-86-25-01 monochromator and Corning 7-54 filter. The beam spectrum was analyzed, and beam intensity monitored during the photolyses, using a Czerny-Turner No. 1800 spectrometer in conjunction with a Hamamatsu R106 photomultiplier tube. Irradiations were carried out at about 25°.

Photolysis of (±)-Camphor in *n*-Heptane. A solution of (±)-camphor (700 mg) in 350 ml of *n*-heptane was flushed with dry nitrogen for 45 min and irradiated under nitrogen for 10 hr. An aliquot of the resulting solution was examined by vpc and found to contain enol ether **5** (retention time 5.5 min), minor component A (8 min), oxetane **21** (9.2 min), α-campholenic aldehyde (**2**) (11 min), unreacted camphor (**1**) (14 min), cyclobutanol **14** (18 min), and cyclobutanol **15** (22 min). The ratios **5**:A:**21**:**2**:**14**:**15** were 10:1:1.5:69:15:4. The solution was concentrated by distillation through a Vigreux column under nitrogen at aspirator pressure, and the concentrated solution was subjected to preparative vpc.

1,8,8-Trimethyl-2-oxabicyclo[3.2.1]oct-3-ene (5). The enol ether **5** is a volatile, white, crystalline solid at room temperature: ir 3060, 1638 (s), 1245 (s), 1050 (s), 835, 720 cm^{-1}; nmr δ 5.92 (d, J = 6 Hz, 1 H), 4.78 (t, J = 6 Hz, 1 H), 1.6–2.2 (m, 5 H), 1.13 (s, 3 H), 1.05 (s, 3 H), 0.97 (s, 3 H); mass spectrum (intensity values from low-resolution spectrum, elemental composition from high-resolution spectrum) *m/e* 152.1204 (M^+, 70%, calcd for $C_{10}H_{16}O$, 152.1201), 137 (M − CH_3, 55%), 109 (M − C_2H_3O and M − C_3H_7, 45%), 96 (M − C_4H_8, 90%), 83 (M − C_4H_5O, 100%).

Minor Component A. The infrared spectrum showed bands at 1721, 1450, and 1375 cm^{-1}. From its nmr spectrum this material appeared to be a mixture; it was not further examined.

α-Campholenic Aldehyde (2). A. By Photolysis. The infrared spectrum showed bands at 3039, 2710, 1728, and 1690 (w) cm^{-1}; nmr δ 9.74 (t, J = 1.5 Hz, 1 H), 5.22 (broad, 1 H), 2.7–1.7 (m, 5 H), 1.60 (m, J < 1 Hz, 3 H), 0.97 (s, 3 H), 0.75 (s, 3 H); mass spectrum *m/e* 152 (M^+, 3%), 109 (M − 43, 24%), 108 (m − 44, 100%), 95 (M − 57, 29%), 93 (M − 59, 55%).

B. From α-Pinene Oxide. The aldehyde was also prepared from α-pinene oxide the method of Meinwald and Chapman[29] and purified by preparative vpc (>99% pure). Retention time on vpc and ir spectrum were identical with those of aldehyde produced photolytically.

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 79.10; H, 10.52.

***endo*-3,4,4-Trimethylbicyclo[3.2.0]hept-2-en-7-ol (14).** The cyclobutanol **14** was obtained as a colorless oil: infrared 3595, 3400 (broad), 3015, 1635, 1110 (s), 1080 (s), 825, 710 cm^{-1}; nmr δ 5.27 (broad, 1 H), 4.0 (m, 1 H), 3.40 (broad, 1 H), 2.4–1.8 (m, 3 H), 1.66 (t, J = 1.5 Hz, 3 H), ~1.6 (s, 1 H, shifted upfield on dilution; exchanges with D_2O), 0.95 (s, 3 H), 0.92 (s, 3 H).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 79.21; H, 10.76.

***exo*-3,4,4-Trimethylbicyclo[3.2.0]hept-2-en-7-ol (15).** The minor hydroxylic photoproduct is a colorless oil: infrared 3620, 3350 (broad), 3030, 1635, 1050 (s), 850 cm^{-1}; nmr δ 5.24 (broad, 1 H), 3.85 (m, 1 H), 3.34 (s, 1 H, shifted upfield on dilution), 3.0–1.6 (4 H), 1.62 (t, J = 1.5 Hz, 3 H), 0.96 (s, 3 H), 0.91 (s, 3 H).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 79.11; H, 10.91.

Photolysis of (±)-Camphor in 95% Ethanol. A solution of (±)-camphor (416 mg) in 450 ml of 95% ethanol was flushed with nitrogen for 45 min and irradiated under nitrogen for 10 hr. The solution was diluted with 1 l. of distilled water and extracted with ether. The ether extracts were back-extracted with water, dried over Na_2SO_4, and concentrated to a small volume by distillation through a Vigreux column. The resulting solution was examined by vpc and found to contain the same compounds found after the photolysis in *n*-heptane, except that the acetal **6** was eluted in the place of minor component A and oxetane **21**. The ratios **5**:**6**:**2**:**14**:**15** were 6:8:79:5.5:1.5. Photoproducts were isolated by preparative vpc.

3-Ethoxy-1,8,8-trimethyl-2-oxabicyclo[3.2.1]octane (6). A mixture of epimeric acetals (**6**) was obtained as a colorless oil which decomposes on standing, even at 4°: infrared 1295, 1215, 1180, 1150, 1125 (s), 1074 (s), 1050, 1015 (vs), 985, 933, 906 (s), 858, 833 cm^{-1}; nmr (parts per million downfield from external $(CH_3)_4Si$): 4.64 (d, 0.8 H), 3.0–3.92 (m, 1.6 H), 1.58–2.33 (m, 6.8 H), 0.67–1.33 (m, 12.9 H); mol wt (mass spectrum), *m/e* 198.1583 (M^+, calcd for $C_{12}H_{22}O_2$: 198.16197).

Quantum Yield for α-Campholenic Aldehyde Formation. A solution of (±)-camphor (0.77 g in expt no. 1 and 0.83 g in expt no. 2) in 3.5 ml of *n*-heptane in a quartz cell fitted with a capillary bubbler and stopcock was flushed with nitrogen for 45 min. The cell was cooled to −70°, evacuated to 0.1 mm, allowed to warm to room temperature, and then irradiated for 26 hr with 3100–3180-Å light. The beam intensity was monitored and found to increase by about 10% in the course of the 26-hr irradiation. The average beam intensity was used in the quantum yield calculations, and was found to be $4.0 \pm 0.6 \times 10^{14}$ quanta/(sec ml) by potassium ferrioxalate actinometry[36] in a separate experiment. A single photoproduct was observed and identified as α-campholenic aldehyde by vpc retention time and mass spectrum. The amount of aldehyde produced was measured by calibrated vpc and found to be 0.50% in expt no. 1 and 0.38% in expt no. 2, corresponding to quantum yields of 0.14 ± 0.04 and 0.11 ± 0.03 mol/einstein.

Photolysis of (+)-Camphor in 95% Ethanol-*d*. A solution of 2.5 g of (+)-camphor in 225 ml of 95% ethanol-*d* was irradiated and the products were isolated as described above with suitable precautions to avoid contamination with water. Preparative vpc yielded 42 mg of acetal-*d* (**9**), 17 mg of enol ether-*d* (**10**), and 270 mg of camphor. The nmr spectrum of **9** was as above for **6**, but had no signal at 4.64 ppm; integrals from computer-summed spectra indicated <0.08 H at ~4.64 ppm. The nmr spectrum of **10** showed the following signals: 4.78 (d, J = 6 Hz, 1 H), 1.6–2.2 (m, 5 H), 1.13 (s, 3 H), 1.05 (s, 3 H), 0.97 (s, 3 H) ppm. Integrals from computer summed spectra indicated <0.03 H at ~5.92 ppm. The nmr spectrum of recovered camphor indicated no incorporation of deuterium.

Photolysis of (±)-Camphor-3,3-d_2 in *n*-Heptane. A solution of 1.09 g of (±)-camphor-3,3-d_2[20] in 220 ml of *n*-heptane was photolyzed and the products were isolated exactly as described above. Calculations from the parent peak region of mass spectra indicated the following deuterium contents: camphor used and camphor recovered, 91% d_2, 7% d_1, and 2% deuterium free; enol ether **5** isolated, 19% d_2, 74% d_1, and 7% deuterium free. The nmr spectrum of recovered camphor was identical with that of starting material. The nmr spectrum of enol ether **5** showed bands at 5.92 (s, 0.74 H), 5.0–4.6 (0.1 H), 1.5–2.3 (m, 5.0 H), 1.13, 1.05, 0.97 (three singlets, 8.8 H); α-campholenic aldehyde, δ 9.74 (sharp s, 1 H), 5.22 (broad, 1 H), 2.7–1.7 (m, 3 H), 1.60 (m, J small, 3 H), 0.97 (s, 3 H), 0.75 (s, 3 H); cyclobutanol **14**-d_2 = **20** (100 Mc, couplings indicated were determined by double resonance experiments[31]); δ 5.20 (H_A, broad, $J_{A,Me}$ = 1.5 Hz, $J_{A,B}$ = 2 Hz, 1 H), 4.02 (H_C, d, $J_{B,C}$ = 7 Hz, 1 H), 3.40 (H_B, broad m, $J_{B,Me}$ = 2 Hz, 1 H), 1.95 (H_D, broad d, $J_{B,D}$ = 5 Hz, 1 H), 1.89 (sharp s, exchanges with D_2O, 1 H), 1.65 (Me, t, $J_{A,Me}$ = 2 Hz, $J_{B,Me}$ = 1.5 Hz, 3 H), 0.93 (s, 3 H), 0.89 (s, 3 H); cyclobutanol **15**-d_2, δ 5.21 (broad, 1 H), 3.84 (s, 1 H), 2.58–3.07 (m, 2 H), 2.32 (s, 1 H, shifted upfield on dilution, exchanges with D_2O), 1.61 (t, J = 1.5 Hz, 3 H), 0.96 (s, 3 H), 0.92 (s, 3 H).

2,2,3-Trimethyl-3-hydroxycyclopentane-1-acetic Acid Lactone (7). A. By Oxidation of Acetal 6. A solution of 30 mg of acetal **6** in 6 ml of acetone was oxidized at room temperature by adding dropwise 0.30 ml of chromic acid solution[14] (2.67 g of CrO_3, 2.3 ml of concentrated H_2SO_4, diluted to 50 ml with water). The solution was then diluted with water and extracted with ether. The ether extracts were back-extracted with water, dried over Na_2SO_4, and evaporated to dryness to yield 30 mg of oily semisolid material. This was taken up in ether and purified by vpc (215°, 170 cc/min). The vpc retention time and ir spectrum of the white, crystalline product were identical with those of authentic lactone **7**.[15]

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[36] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.* (London), **235A**, 518 (1956).

B. By Oxidation of Enol Ether 5. A solution 25 mg of enol ether **5** in 6 ml of acetone was oxidized and worked up as described above for the acetal **6**. The vpc retention time and ir spectrum of the white, crystalline product were identical with those of authentic lactone **7**.[15]

C. Authentic Sample. The lactone was prepared as described by Sauers,[15] except that final purification of the lactone was effected by vpc (215°, 175 cc/min): mp 163–164° (lit.[15a] mp 172–174°); $[\alpha]^{25}{}_D$ ($CHCl_3$) −47° (lit.[15a] −37°); ir 1742 (s), 1470, 1445, 1420, 1390, 1375, 1335, 1315 (doublet), 1260 (doublet), 1240, 1215, 1142 (s), 1095, 1045, 1015, 955 cm^{-1} (lit.[15a] 1745 cm^{-1} ($CHCl_3$)); nmr δ 2.58 (q, J = 2 Hz, 1 H), 2.37 (d, J = 1 Hz, 1 H), 2.25–1.67 (m, 5 H), 1.25 (s, 3 H), 1.05 (s, 3 H), 0.99 (s, 3 H). (In our hands, Sauers's procedure[15a] gave a crude product shown by vpc to contain **7**, α-campholide, and camphor. Two recrystallizations from petroleum ether (bp 30–60°) gave material, mp 175–177°, shown by vpc to be a 7:3:1 mixture of these components. These results are in general agreement with Sauers's latter report.[15b])

3,4,4-Trimethylbicyclo[3.2.0]hept-2-en-7-one (16). A. By oxidation of Cyclobutanol 14. A solution of 19 mg of cyclobutanol **14** in 7 ml of acetone was oxidized as described for acetal **6**. The product was purified by vpc: infrared 3045, 1781 (s), 1105 (m) cm^{-1}; nmr δ 5.15 (s, 1 H), 4.0 (m, 1 H), 2.9 (m, 2 H), 2.6 (m, 1 H), 1.68 (t, J = 1.5 Hz, 3 H), 1.12 (s, 3 H), 1.07 (s, 3 H); uv $\lambda\lambda_{max}$ 287 mμ (sh) (ϵ 96), 298 (150), 307 (160), 316 (110) (isooctane); mass spectrum m/e 150.1038 (M$^+$, 2.9%, calcd for $C_{10}H_{14}O$: 150.1045), 108 (M − 42, 100%), 93 (M − 57, 59%).

B. By Oxidation of Cyclobutanol 15. A solution of 16 mg of cyclobutanol **15** in 6 ml of acetone was oxidized as above. The product was shown by identity of vpc retention time and ir spectrum to be cyclobutanone **16**.

Reduction of Cyclobutanone 16 with Sodium Borohydride. A solution of $NaBH_4$ (14 mg) in 4.0 ml of dry isopropyl alcohol was added to a solution of the cyclobutanone (17 mg) in 1 ml of isopropyl alcohol and the resulting solution stirred at room temperature under nitrogen. After 12 hr 1 ml of water was added and the solution refluxed for 1 hr, then cooled and extracted with ether. The ether extracts were washed with water and brine, dried over Na_2SO_4, and analyzed by calibrated vpc. This showed the product, formed in >99% yield, to be a mixture of 98% cyclobutanol **14** and 2% cyclobutanol **15**. Compound **14** was identified by vpc retention time and ir spectrum, and **15** by vpc retention time only.

Reduction of Cyclobutanone 16 with Sodium in Ethanol. Sodium (168 mg) was added over 1 hr to a solution of cyclobutanone **16** (26 mg) in 1 ml of 95% ethanol under nitrogen at room temperature. The reaction mixture was diluted with water, acidified with concentrated HCl, and extracted with ether. The ether extracts were washed with water and brine, dried over Na_2SO_4, and analyzed by calibrated vpc. The product, formed quantitatively, was a mixture of 84% cyclobutanol **14** and 16% cyclobutanol **15**. The cyclobutanols were identified by vpc retention times and ir spectra.

Photolysis of α-Campholenic Aldehyde. A solution of α-campholenic aldehyde (1.07 g, prepared from α-pinene oxide) in 220 ml of n-heptane was flushed with dry nitrogen for 45 min and irradiated under nitrogen for 9 hr. An aliquot of the resulting solution was examined by vpc (column temperature 200 ± 5°) and found to contain components A (retention time 4.5 min), B (5.5 min), C (8 min), the oxetane **21** (9.5 min), α-campholenic aldehyde (**2**) (12 min), F (14 min), cyclobutanol **14** (19.5 min), and cyclobutanol **15** (24 min). The ratios of peak areas A:B:C:**21**:**2**:F:**14**:**15** were 10:12:11:7:29:6:22:3.[6] The solution was concentrated by distillation through a Vigreux column under nitrogen at aspirator pressure, and the concentrated solution was subjected to preparative vpc. Compounds **2**, **14**, and **15** were identified by vpc retention times and ir spectra.

6,6,7-Trimethyl-2-oxatricyclo[3.2.1.0^{3,7}]octane (21). The oxetane **21** is a volatile, white, crystalline solid at room temperature: ir 2950, 2855, 1448, 1380, 1360, 1270, 1143, 1073, 988, 955 (s), 898, 838, 820 cm^{-1}; nmr δ 4.10 (broad, 2 H), 2.14 (m, 1 H), 1.90 (broad, 4 H), 1.38 (s, 3 H), 0.78 (s, 6 H); mass spectrum m/e 152.1186 (M$^+$, calcd for $C_{10}H_{16}O$: 152.1201).

Lithium Aluminum Hydride Reduction of Oxetane 21. Pure oxetane **21** (17 mg) was dissolved in 2 ml of di-n-butyl ether, $LiAlH_4$ (80 mg) was added, and the mixture was refluxed under nitrogen for 96 hr. The reaction was quenched with water, acidified with dilute hydrochloric acid, and extracted with ether. The ether extracts were washed with water and brine, dried over Na_2SO_4, and concentrated. Vpc analysis showed at least 95% of the oxetane had been converted to a mixture of products. The major product (about 65% of the mixture) was purified by vpc and identified as borneol by comparison of its vpc retention time, and infrared and mass spectra, with those of an authentic sample (Aldrich technical borneol purified by vpc).

In a separate experiment it was found that refluxing a solution of borneol in di-n-butyl ether with $LiAlH_4$ for 48 hr gave a product mixture quite similar to that derived from the oxetane.

3-Dimethylamino-1,2,2-trimethylcyclopentane-1-carboxylic Acid Hydrochloride. 3-Amino-1,2,2-trimethylcyclopentane-1-carboxylic acid hydrochloride was derived from (+)-camphoric anhydride by the methods of Faigle and Karrer.[37] A solution of this hydrochloride (5.0 g) in 20 ml of 37% formaldehyde and 10 ml of 88% formic acid was heated for 12 hr at 95° and then evaporated to dryness under reduced pressure. The residue was dissolved in dilute HCl and the solution evaporated to dryness. The last step was repeated twice to give 5.63 g of white solid (about 93%). This was recrystallized twice from methanol: mp 322–323° dec; ir (KBr disk) 3000–2500 (broad), 2655 (s), 1722 (s), 1405, 1235, 1205, 1145, 1110 cm^{-1}.

Anal. Calcd for $C_{11}H_{22}NO_2Cl$: C, 56.04; H, 9.41; N, 5.94. Found: C, 55.81; H, 9.46; N, 5.81.

1,2,2-Trimethylcyclopent-3-ene-1-carbocylic Acid (4). A solution of 472 mg of the above amine hydrochloride and 336 mg of $NaHCO_3$ in water was evaporated to dryness and the residue treated with 3 ml of 30% H_2O_2 and then heated 11 hr at 44–45°. Another 3 ml of H_2O_2 was added and heating continued for another 14 hr. Evaporation to dryness gave a residue which was pyrolyzed at 145–150° (15 mm) for 30 min. The residue was dissolved in water, extracted twice with ether, acidified with concentrated HCl, and extracted twice with ether. The latter ether extracts were dried over Na_2SO_4 and evaporated to dryness to yield 125 mg (41%) of yellowish, crystalline material which was purified by vpc: mp 157–159.5° (lit.[38] 152–154°); ir (KBr disk) 3400–2500, 1700 (s), 1620, 1280, 715 cm^{-1}; nmr 12.3 (s, 1 H), 5.52 (m, 1 H), 5.30 (m, 1 H), 3.18 (d, J = 16 Hz, 1 H), 1.27 (s, 3 H), 1.15 (s, 3 H), 1.02 (s, 3 H).

Anal. Calcd for $C_9H_{14}O_2$: C, 69.70; H, 9.10. Found: C, 70.05; H, 8.95.

1,2,2-Trimethylcyclopent-3-enyl Methyl Ketone (3). A solution of **4** (114 mg) in 5 ml of dry ether under nitrogen was treated with 2.0 ml of 1.88 M methyllithium in ether.[12] After 3.5 hr at room temperature the reaction was quenched with water. The phases were separated and the ether layer was extracted twice with water and then dried over Na_2SO_4. Analysis of the ether solution by vpc indicated no unreacted acid and a single major product. Removal of solvent gave 70 mg of oily, crystalline material which was purified by vpc. The pure ketone forms volatile, soft, white crystals that look and smell like camphor: mp 77–78°; ir (CCl_4) 3050, 1701 (s), 1616, 1455, 1350 (multiplet), 712 cm^{-1}; ir ($CHCl_3$) 3010, 1698 (s), 1620, 1455, 1350 (multiplet) cm^{-1}; uv (95% ethanol) λ_{max} 2855 Å (ϵ 22); nmr δ 5.55 (m, 1 H), 5.27 (m, 1 H), 3.11 (broad d, J = 17 Hz, 1 H), 2.09 (s, 3 H), 1.91 (broad d, J = 17 Hz, 1 H), 1.16 and 1.14 (overlapping s, 6 H), 0.86 (s, 3 H); mass spectrum m/e 152 (M$^+$, 28%), 137 (12%), 109 (100%), 95 (14%), 81 (15%), 67 (34%), 56 (14%), 43 (62%).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.78; H, 10.45.

A semicarbazone was prepared, mp 191–193°, from methanol.

Anal. Calcd for $C_{11}H_{17}N_3O$: C, 63.12; H, 9.15; N, 20.08. Found: C, 63.36; H, 9.12; N, 20.22.

Using the synthetic ketone as standard it was shown that this compound could have been detected among camphor photolysis products at the level of 0.2% of the total product in n-heptane or 0.6% in 95% ethanol. It was not found in either case.

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