air oxidation of I$^-$ in the Kokatnur, *et al.*, quench was inhibited by addition of *ca.* 1 g of KOAc. In acetic acid, the total peroxide concentration was determined by the Kokatnur, *et al.*, method, and the HOOH concentration by the technique reported by Greenspan and MacKellar[20] which uses ceric sulfate standard solution to titrate HOOH directly with ferroin indicator; the peroxyacetic acid concentration was then calculated by difference. The stock HOOH solutions in AcOH were made, standardized immediately, used in kinetic runs, and then restandardized to determine the concentration change of either HOOH or AcOOH; no detectable change occurred during the extent of the kinetic runs when KOAc was present. For the kinetic experiments in all solvents a blank was run on the reagents used in the quench for the same period of time as that occurring between the quenching and the titration of the first aliquot; the blank was negligible or zero for all reported data.

For each solvent used the extent of hydroperoxide decomposition was determined, in independent experiments, at the highest hydroperoxide concentration adopted for any given series of kinetic runs. Generally all runs were finished before any peroxide decomposition could be detected in the solvent, except for the case of N-methylacetamide; in this solvent, consequently, no run was extended over a time which would allow more than 1% peroxide autodecomposition.

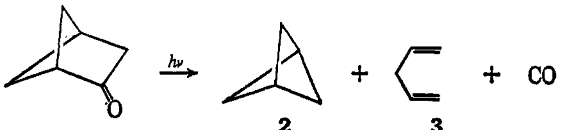
The Solution Photochemistry of Some Bicyclic Ketones[1]

Jerrold Meinwald[2] and Ralph A. Chapman[3]

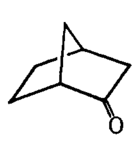
Contribution from the Department of Chemistry, Cornell University, Ithaca, New York 14850. *Received December 15, 1967*

Abstract: Irradiation of pentane solutions of bicyclo[2.1.1]hexan-2-one (**1**), bicyclo[2.2.1]heptan-2-one (**4**), and camphor (**5**) leads to the formation of cycloolefinic aldehydes (**7, 17,** and **25**) which react further under continued irradiation. In the case of **7** and **17**, photocycloadditions of possible synthetic utility are observed, leading to the tricyclic oxetanes **10** and **18**. Analogous oxetane formation from campholenic aldehyde (**25**), followed by thermolysis, provides a new rationalization of earlier reports of an abnormal photoproduct derived from camphor. Under the experimental conditions chosen for the present work, however, this product was not detected. In diethyl ether, all three excited aldehydes (**7, 17,** and **25**) attack solvent to give α-hydroxy ethers, while in methanol partial conversion to dimethylacetals is observed.

We recently described an elementary, synthetic application of ketone photochemistry:[4] the *gas-phase* irradiation of bicyclo[2.1.1]hexan-2-one (**1**) to give bicyclo[1.1.1]pentane (**2**), along with 1,4-pentadiene (**3**).[5] We now wish to report on the *solution* photochemistry of **1**, and of the closely related bridged ketones norcamphor (**4**) and camphor (**5**).



1 **2** **3**



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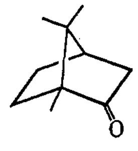
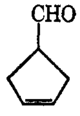


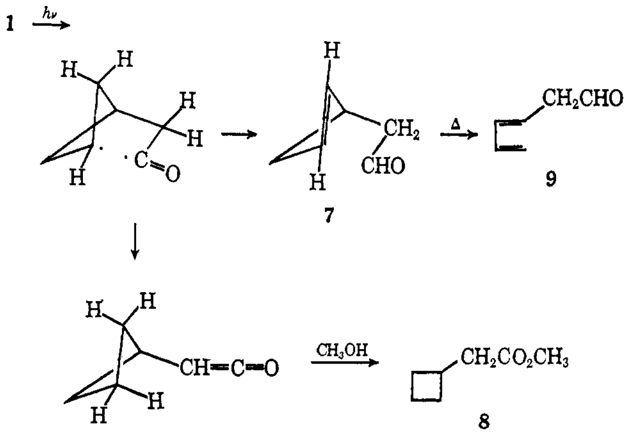
5

Bicyclo[2.1.1]hexan-2-one (1). In an exploratory experiment involving the irradiation of a dilute pentane solution of **1**, a product which appeared to be the isomeric unsaturated aldehyde **6** on the basis of infrared and nmr spectral evidence was isolated by preparative glpc. While one of the best known photochemical reactions of alicyclic ketones involves ring fission to give an acyl–alkyl diradical, followed by hydrogen atom transfer to give an unsaturated aldehyde (or ketene),[4,6] expectations for **1** based on this type of process, as outlined in Chart I, lead to **7** rather than to **6**. Since



6

Chart I



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[1] The partial support of this research by the National Science Foundation and by the Chevron Research Company is acknowledged with pleasure.

[2] National Institutes of Health Special Postdoctoral Fellow, and Visiting Scholar at Stanford University, 1967–1968.

[3] Recipient of a National Research Council of Canada Scholarship, 1965–1967.

[4] For comprehensive reviews, see (a) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965; (b) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966; (c) R. O. Kan, "Organic Photochemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1966; (d) D. O. Neckers, "Mechanistic Organic Photochemistry," Reinhold Publishing Corp., New York, N. Y., 1967.

[5] J. Meinwald, W. Szkrybalo, and D. R. Dimmel, *Tetrahedron Letters*, 731 (1967).

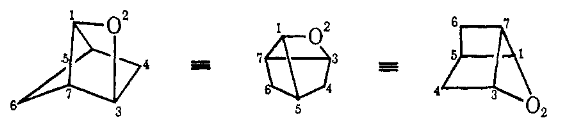
[6] For leading references, see J. Meinwald, R. A. Schneider, and A. F. Thomas, *J. Am. Chem. Soc.*, **89**, 70 (1967); G. Quinkert, *Angew. Chem.*, 77, 229 (1965).

the aldehyde isolated in this initial experiment was not the anticipated **7**, and since no methyl ester corresponding to **8** could be detected when **1** was irradiated in methanol, the photolysis of **1** was examined more closely.

On repeating our initial experiment, we found that *prolonged* irradiation of **1** in pentane did not, in fact, yield **6** as a *primary* product, but rather gave a 60% yield of an isomer devoid of carbonyl (or hydroxylic) absorption in its infrared spectrum. This photoproduct was thermally labile, however, and was converted to **6** even on an 8-ft Carbowax column at 90°. More careful monitoring of the photolysis of **1** showed that this labile product was itself formed by irradiation of another intermediate, whose spectral properties were in good accord with expectations for Δ^2-cyclobutenylacetaldehyde (**7**). Glpc collection of **7** resulted in its partial conversion to 3,5-hexadienal (**9**), as indicated by its spectral characteristics.

Thus, irradiation of **1** brings about the sequence

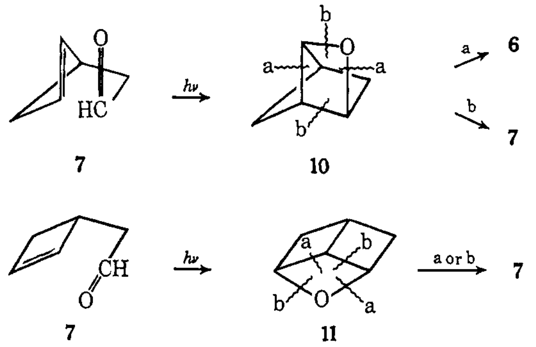
$$\mathbf{1} \xrightarrow{h\nu} \mathbf{7} \xrightarrow{h\nu} \text{unknown isomer} \xrightarrow{\Delta} \mathbf{6}$$



10 **10a**

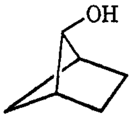
Thus **10** appeared most likely for the unknown precursor of **6**. The formation of this bridged oxetane (2-oxatricyclo[3.2.0.0^{3,7}]heptane) would correspond to an intramolecular Paterno–Büchi reaction,[7] and the pyrolysis of **10** to form **6** has ample precedent,[8] if we presume that especially strained oxetanes should pyrolyze at lower than normal temperatures. It should be noted that the intramolecular photocycloaddition of **7** could be imagined to occur in two directions, as shown in Chart II, giving **10** or **11**. While **10** might be expected to give **6** or **7** on pyrolysis, **11** can give only **7**. Thus, the formation of **6** from the unknown requires that the oxetane have structure **10**.

Chart II

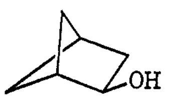


Further chemical confirmation of this conclusion was obtained by reducing the tricyclic oxetane with lithium aluminum hydride. In contrast to the usual sluggishness of such oxetane reductions,[8] this reaction proceeded well in refluxing ether; the enhanced reactivity of **10** undoubtedly reflects the additional driving force provided by increased relief of steric strain in the transition state for ring opening. The resultant alcohol proved to be *endo*-bicyclo[2.1.1]hexan-5-ol (**12**).[9] Assuming that no molecular rearrangement had occurred,[10] this transformation alone would serve to establish structure **10** for the oxetane.

While lithium aluminum hydride reduction of **10** might have led to either of two unrearranged alcohols, **12** or **13**, the exclusive formation of **12** can be rationalized on the basis of greater steric hindrance offered by the C_6 methylene group to hydride donor attack at C_1, compared to attack at C_3 (see formula **10a**). A Brown *I*-strain argument would also predict preferential SN2 attack at the wider $C_4C_3C_7$ angle rather than at the more acute $C_5C_1C_7$ angle.



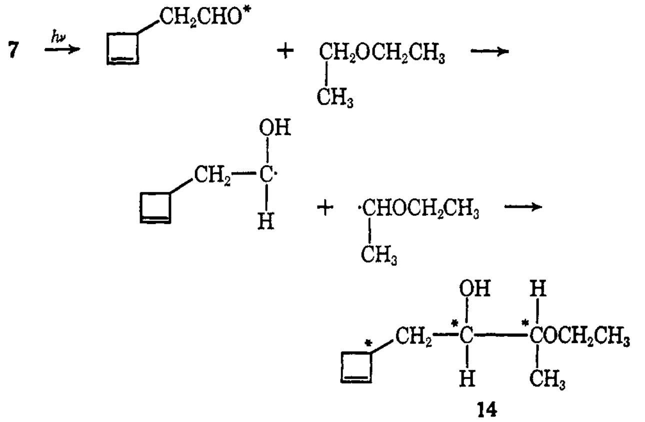
12



13

While the aldehyde **7** and oxetane **10** were both formed on irradiation of **1** in diethyl ether, glpc analysis showed that these were accompanied by *ca.* 35% of a mixture of two less volatile components in comparable amounts. It was apparent from spectral evidence that these components were hydroxy ethers, resulting from substrate attack on solvent. Their formation is rationalized *via* the excited aldehyde **7** abstracting an α-hydrogen atom from the diethyl ether, followed by radical coupling, as shown in Chart III. The intramolecular version of this mechanism for photochemical carbon–carbon bond formation is, of course, well known.[11] (While **14** corresponds to four racemic mixtures, we assume that the two glpc peaks correspond to the *erythro*- and *threo*-glycol derivatives, and that isomers differing at the third asymmetric center were not separated.)

Chart III



Irradiation of **1** in methanol for a short time resulted in the formation of **7** (isolated as its crystalline semicarbazone), accompanied by its dimethyl acetal, **15**. (The formation of acetals or ketals during the irradia-

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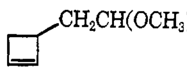
[7] For a leading reference concerned with the mechanistic aspects of this type of reaction, see N. C. Yang, R. Loeschen, and D. Mitchell, *J. Am. Chem. Soc.*, **89**, 5465 (1967).

[8] An extensive review of oxetane chemistry is provided by S. Searles, Jr., in "The Chemistry of Heterocyclic Compounds with Three- and Four-membered Rings," Part II, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, pp 983–1068.

[9] K. B. Wiberg, B. R. Lowry, and B. J. Nist, *J. Am. Chem. Soc.*, **84**, 1594 (1962).

[10] In fact, even had carbonium ion rearrangements accompanied this reduction, **11** would not be expected to give rise to **12**.

[11] For a more detailed discussion, see ref 4d, p 177 ff.



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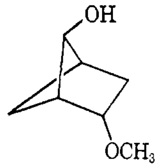
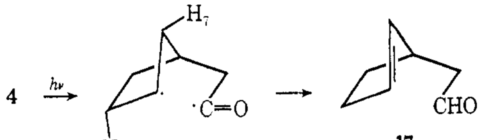


16

tion of carbonyl compounds has been observed previously.[12,13] It appears that this involves inadvertent acid catalysis.[13]) The **7** produced suffered subsequent cycloaddition followed by methanolysis, giving a product, isolated in *ca.* 30% yield, which we assume to be *anti*-2-methoxy-*endo*-bicyclo[2.1.1]hexan-2-ol (**16**) on the basis of nmr spectral evidence and mechanistic reasoning. Through Pyrex, the dimethyl ketal of **1** was the major product.

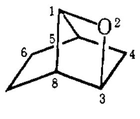
From a synthetic point of view, we consider the most interesting aspect of these findings to be the over-all conversion of **1**, *via* a monocyclic intermediate, to the tricyclic oxetane **10**. Combined with subsequent transformations, this permits *transfer* of an oxygen atom from C_2 to C_5 in a bicyclo[2.1.1]hexane, it provides a new route to bifunctional bicyclo[2.1.1]hexanes, and it uncovers a new synthesis of the bicyclo[2.1.1]hexanes from cyclobutenes.

Bicyclo[2.2.1]heptan-2-one (4). With the above results in hand, we considered it relevant to explore the photochemistry of bicyclo[2.2.1]heptan-2-one (**4**). A single unsaturated aldehyde was found to be the major initial product in pentane, ether, or methanol, and in sharp contrast to our experience with **1** and **7**, subsequent cycloaddition was sufficiently slow to permit a clean separation of the two photochemical steps. Chapman and Garin,[14] as well as Yates,[13] had also observed the formation of a single aldehyde from **4**, and had demonstrated rigorously that this product possesses structure **17**, corresponding to preferential *syn*-7 (rather than *endo*-2) hydrogen atom transfer.

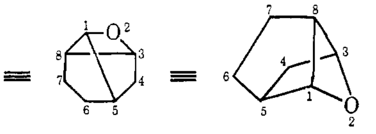


17

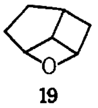
Prolonged irradiation of **17** gave a tricyclic oxetane, this time in *ca.* 30% yield, accompanied by a considerable amount of polymer. Once more, oxetane formation, which could proceed to give **18** or **19**, went selectively to 2-oxatricyclo[3.3.0.0^{3,8}]octane (**18**), as proved by lithium aluminum hydride reduction which yielded pure bicyclo[2.2.1]heptan-7-ol (**20**). The cyclizations of both **7** and **17** involve a preference for cyclopentane over cyclobutane ring formation. The opening of **18** to **20** is closely analogous to the opening of **10** to **12**, and is easily rationalized on the basis of formula **18a**.



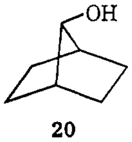
18



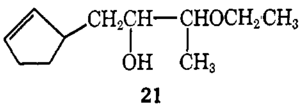
18a



19

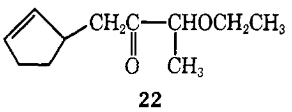


20



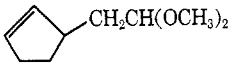
21

In ether, **18** was accompanied by a mixture of stereoisomeric hydroxy ethers (**21**), isolable in *ca.* 40% yield. Chromium trioxide oxidation gave an inseparable mixture of keto ethers with spectral properties in good accord with structure **22**. The formation of these ether-incorporating products is again interpreted as resulting from α-hydrogen atom abstraction by the oxygen atom of the excited aldehyde, followed by coupling of the two resultant radicals.

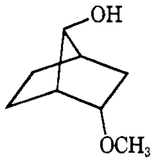


22

Irradiation of **4** in methanol once more gave rise to an acetal, identified as **23** by direct comparison with an independently prepared sample. No methyl ester, resulting from ketene formation, was detected. In place of the tricyclic oxetane **18**, its methanolysis product, **24**, was obtained. This structure assignment rests on spectral evidence, the observation that a 5.60-μ carbonyl absorption, characteristic of 7-ketobicyclo[2.2.1]heptanes,[15] is developed upon chromic acid–pyridine oxidation, and the demonstration that the identical material is formed from acid-catalyzed methanolysis of isolated **18**. The direction of the postulated acid-catalyzed oxetane opening appears reasonable on mechanistic grounds, and it has been assumed that displacement at C_2 would proceed with inversion to give a 2-*endo*-methoxy substituent. The *photochemical* addition of methanol to **18** remains unexplained. In a control experiment, **18** was found to give no appreciable amount of **24** on refluxing in methanol for 3 days, while the same solution, when irradiated for 1 day, gave significant conversion to **24**. The simplest explanation would be that acidic catalysts are developed, as postulated earlier to rationalize "photochemical" acetal formation. An alternate possibility is that we are observing a photosensitized oxetane opening.



23



24

Camphor (5). In the case of camphor, a brief review of the earlier work in this area is important, in order to place our own experiments in their proper context. In contrast to ketones **1** and **4**, camphor had been the subject of at least two earlier photochemical studies, and these led to some unexpected findings. The pioneer photochemists Ciamician and Silber reported the exposure of a rather concentrated aqueous alcoholic

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[12] *Cf.* E. Bamberger and F. Elger, *Ann.*, **371**, 319 (1910); H. Mauser and H. Heitzer, *Z. Naturforsch.*, **21B**, 109 (1966).

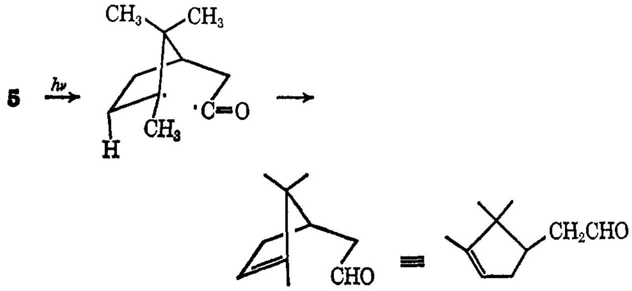
[13] Professor P. Yates, talk presented at the Second IUPAC Symposium on Photochemistry in Enschede, Holland, June 1967.

[14] We are indebted to Professor O. L. Chapman for making this unpublished information available to us.

[15] P. Wilder, Jr., and A. Winston, *J. Am. Chem. Soc.*, **78**, 868 (1956).

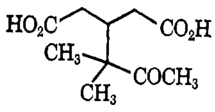
solution of camphor to sunlight for 7 months.[16] This resulted in the partial conversion of the camphor into an oily mixture, believed to contain an unsaturated aldehyde and an unsaturated ketone, both isomeric with the starting material. Acetaldehyde was detected by its characteristic odor. The unsaturated aldehyde was separated from the mixture as a sodium bisulfite adduct, and was carefully shown to be campholenic aldehyde (**25**). Chart IV shows the straightforward rationale for this reaction.

Chart IV

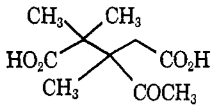


25

The "ketonic" product was isolated from that portion of the oily photolysate which was recovered after sodium bisulfite extraction. It yielded a semicarbazone, mp 151–152°, from which a liquid, unsaturated carbonyl compound, could be regenerated. Permanganate oxidation of this liquid, followed by treatment with potassium chromate and sulfuric acid, yielded a dibasic acid ($C_{10}H_{16}O_5$), mp 133–134°, which Ciamician and Silber considered to be either isoketocamphoric acid (**26**), mp 129–130.5°, or β-acetyl-α,β,β-trimethylglutaric acid (**27**), mp 125–140°.[16] Because of the ambiguity in the structure of this acid, Ciamician and Silber did not postulate a structure for their ketone.

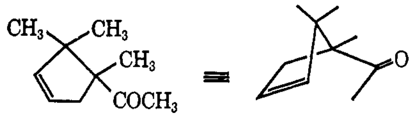


26



27

In a reinvestigation of camphor photochemistry, Srinivasan was able to add both spectral and chemical data to the earlier observations, and concluded that the second product was an unsaturated methyl ketone, tentatively assigned structure **28** on the assumption that the dibasic acid was **27**. The ratio of quantum yields of **25** to **28** varied from 0.1 in hydrocarbon solvent to 1.5 in methanol. On the basis of these studies, the mechanism given in Chart V was postulated for the formation of **28**.[17]



28

In view of the lack of rigorous proof that structure **28** is correct for the Ciamician product, as well as the novelty of the mechanistic scheme, we were tempted to suggest an alternate hypothesis based on analogy with our above described findings, as shown in Chart VI. Thus, if campholenic aldehyde were to undergo the Paterno–Büchi reaction to give oxetane **29**, pyrolysis could yield **30**, which is an acceptable structure for Ciamician's ketone. Oxidation of **30** should produce **26**, again a result compatible with the experimental data.

Chart V

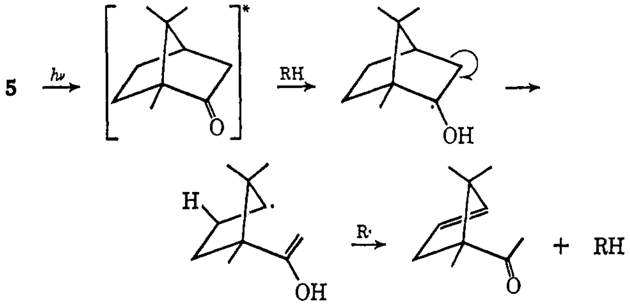
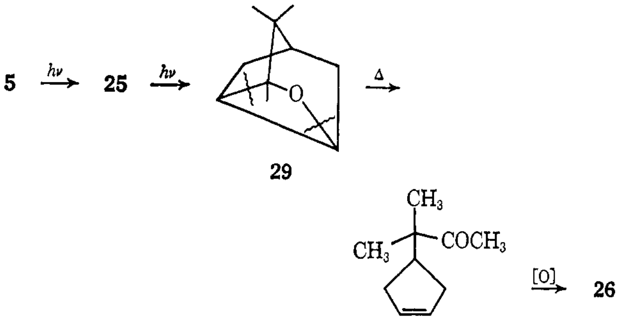


Chart VI



30

Unfortunately, we were unable to test the validity of this conjecture, since under our experimental conditions we could neither isolate nor detect any material corresponding to Ciamician's ketone.[18,19] Instead, we found that **25** (identified by direct comparison with an authentic sample, prepared independently) was the chief primary product produced by irradiation of **5** in pentane, diethyl ether, methanol, or aqueous methanol. Because of the instability of **25** to light, however, other products were also isolated.

One important process leading to the disappearance of **25** was a Norrish type II cleavage,[4] leading to 1,5,5-trimethylcyclopentadiene (**31**), identified by comparison with an authentic sample.[21] Irradiation of **25** itself also gave **31**, but we were unable to observe oxetane formation. It may be significant that the Norrish type II cleavage of **25** involves abstraction of an *allylic* hydrogen atom, and this fact may increase the likelihood of the cleavage process in competing with

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(16) G. Ciamician and P. Silber, *Ber.*, **43**, 1340 (1910).

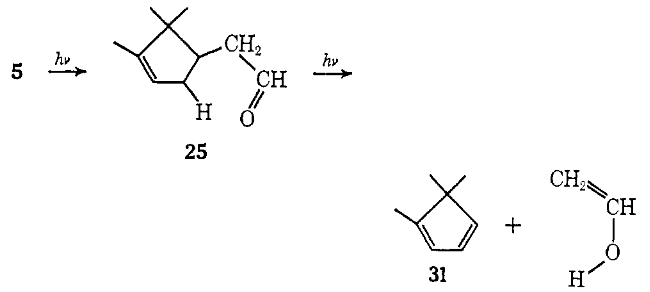
(17) R. Srinivasan, *J. Am. Chem. Soc.*, **81**, 2604 (1959).

(18) Following the completion of our work, we learned that three other groups (Dr. Agosta at Rockefeller University, Dr. Hudek at the University of Southampton, and Dr. Yates at the University of Toronto) were unable to detect this elusive component. It is, of course, quite possible that the course of this photolysis is very sensitive to some subtle difference in experimental conditions.

(19) We have also entertained the hypothesis that Ciamician's ketonic product might actually have been a sample of campholenic aldehyde (**25**) which had failed to react completely with sodium bisulfite. It is pertinent to note that campholenic aldehyde semicarbazone has a reported melting point of 154–155° [20] (*cf.* 151–152° for the "ketone"), and that **25** would also be expected to yield isoketocamphoric acid (**26**) upon vigorous oxidation. Because of these coincidences, and the ambiguity discussed in ref 18, we do not regard this particular problem as solved. In fact, we have now two hypotheses in search of a problem.

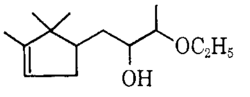
(20) L. C. King and H. Faber, *J. Org. Chem.*, **26**, 326 (1961).

(21) This sample was prepared in this laboratory by Dr. Albrecht Eckell.

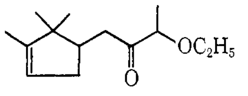


photocycloaddition, when compared with the similar competition in the case of **17**. (In the case of **7**, an allylic hydrogen atom is available, but the product would be cyclobutadiene.) It may also be significant that both **7** and **17**, which gave oxetanes, are γ,δ-unsaturated aldehydes, while **25** is a δ,ϵ-unsaturated aldehyde.

In diethyl ether, a great number of short retention time products were observed, all of which corresponded to materials produced simply by irradiating a saturated ethereal solution of cuprous chloride. In addition, stereoisomeric hydroxy ethers (**32**), analogous to **14** and **21**, were isolated and characterized on the basis of spectral evidence. Again, Sarett oxidation gave a ketonic product (λ_{max} 5.82 μ) considered to be **33**.



32



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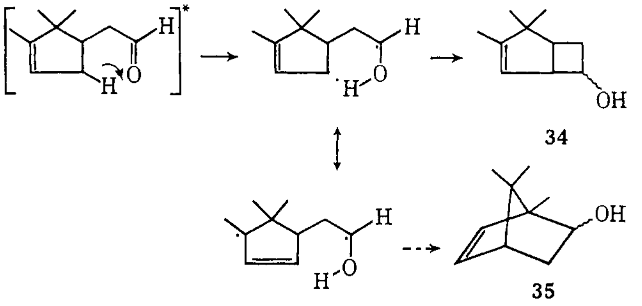
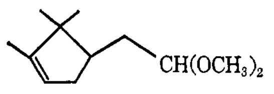
A less important component also found at long retention times is thought to be 3,4,4-trimethylbicyclo[3.2.0]hept-2-en-7-ol (**34**), a product whose formation is easily rationalized as shown in Chart VII.[22] Structure **34** is favored over the bridged alternative **35**,

Chart VII



since the nmr spectrum of this material suggests the presence of an allylic methyl group. Oxidation of crude **34** gave a ketone with carbonyl absorption at 5.61 μ, again favoring structure **34** over **35**.

In methanol, irradiation of **5** gave **25**, perhaps protected as its hemiacetal, quite cleanly. Once more, prolonged irradiation gave the acetal **36**, identified by comparison with a sample prepared by the acid-catalyzed reaction of **25** with methanol.



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In summary, we have observed that the bridged ketones **1**, **4**, and **5** all suffer initial Norrish type I cleavages when irradiated in solution, that the resultant species all undergo hydrogen atom transfer to produce aldehydes (**7**, **17**, and **25**) in preference to ketenes, and that these aldehydes upon further irradiation undergo either Paterno–Büchi cycloadditions to form tricyclic oxetanes (**10** and **18**) or Norrish type II cleavage. In diethyl ether, the aldehydes attack and combine with the solvent, producing α-hydroxy ethers, and it would appear that this coupling reaction should be of quite general significance. In methanol, acetal formation occurs. The photocycloadditions leading to **10** and **18** suggest synthetic utility, and we hope to pursue this aspect of our findings in a continuation of this work.

Experimental Section

Irradiations were carried out using Hanovia 450- and 550-W, medium-pressure mercury lamps with water-cooled quartz or Pyrex immersion wells. For small-scale reactions, a quartz flask (*ca.* 30-ml capacity) containing the solution to be irradiated was placed adjacent to the immersion well and was cooled with running water.

The solvents used were Fisher Certified Reagent *n*-pentane and Mallinckrodt AR diethyl ether and methanol. Eastman White Label *d*-camphor and norcamphor from Aldrich Chemical Co. were used. Both appeared homogeneous to glpc analysis and had infrared spectra identical with those published.

Gas–liquid partition chromatographic analyses and preparative separations (glpc) were carried out using an Aerograph A-90P-3 instrument equipped with 9 ft × 1/8 in. 10% Carbowax 20M on 60–80 Firebrick and 8 ft × 0.25 in. 20% Carbowax 20M on 60–80 Chromosorb P columns. Infrared spectra were recorded on a Perkin-Elmer Model 137 Infracord spectrophotometer either in carbon tetrachloride or as neat films. Nuclear magnetic resonance spectra (nmr) were recorded on a Varian A-60 spectrometer in carbon tetrachloride with tetramethylsilane as external standard. Mass spectra were determined using a CEC Model 21-103A instrument equipped with a MicroTek heated inlet system. Melting points and boiling points are uncorrected.

Bicyclo[2.1.1]hexan-2-one (1). A solution of 1,5-hexadien-3-ol[23] in 150 ml of acetone was cooled to 15°. A solution of Jones reagent[24] was added rapidly, keeping the temperature at 10–20°, until the solution maintained a permanent brown color, at which time glpc analysis of an aliquot showed that no alcohol remained. The excess oxidant was destroyed by the addition of a minimum of sodium bisulfite suspended in a small amount of water, and the mixture was allowed to stand in the cold until separation of the green lower layer was complete, *ca.* 5–10 min. (The addition of excess reducing agent can produce a gelatinous lower layer which makes subsequent extraction difficult.) The aqueous acetone was decanted and the lower layer was diluted with water and extracted quickly with pentane. Addition of the first extract to the aqueous acetone caused the separation of an aqueous layer, which was recombined with the original lower layer before continuing the extraction. The combined extracts and aqueous acetone were washed with 20-ml portions of saturated aqueous sodium chloride and saturated aqueous sodium bicarbonate until neutral, followed by saturated aqueous sodium chloride. After drying the extract over anhydrous magnesium sulfate, the solvent was evaporated at *ca.* 10° (140 mm) (with a slight loss of product as determined by glpc analysis) to yield crude allyl vinyl ketone.

A solution of 13.5 g of the above product in 1 l. of pentane was irradiated using a 550-W lamp and a quartz immersion well. After 9 hr, glpc analysis of an aliquot showed that most of the dienone had disappeared, and a major new component had formed at longer retention time. The solvent was evaporated at *ca.* 10° (140 mm) to yield a 75-ml residue which, when distilled *in vacuo* through a Vigreux column, yielded 2.57 g of bicyclo[2.1.1]hexan-2-one, bp 54–56° (20 mm). The infrared spectrum of this product (neat) had bands at 5.69, 7.05, 7.90, 8.19, 8.69, 9.85, 11.55, 12.40, and 13.20 μ. The nmr spectrum (τ values) had signals at 7.60 (multiplet, two

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[22] Dr. W. Agosta (private communication) is presently engaged in a more thorough study of these aspects of camphor photochemistry. *Cf.* W. C. Agosta and D. K. Herron, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, P164.

[23] J. C. H. Hwa and H. Sims, *Org. Syn.*, **41**, 49 (1961).

[24] R. G. Curtis, I. Heilbron, E. R. H. Jones, and G. F. Woods, *J. Chem. Soc.*, 457 (1953).

protons), 8.1 and 8.22 (two multiplets partially overlapped, four protons), and 8.74 (doublet of doublets, two protons).

The preparation of large quantities of **1** was accomplished by oxidizing several 20-g portions of 1,5-hexadien-3-ol and extracting the product as described. The extract was then diluted to 1 l. with pentane (making a *ca.* 30:1 pentane–acetone mixture) and was irradiated for two 5-hr periods with an intermission to remove polymeric material from the surface of the immersion well. (Glpc analysis of the solution before photolysis indicated that it contained considerably less than 20 g of allyl vinyl ketone.) It was advantageous to irradiate several batches of **1** before distillation, to minimize losses due to the volatility of the product.

Irradiation of 1 in Pentane. a. Analytical. A solution of 0.50 g of **1** in 25 ml of pentane was irradiated using a 450-W lamp through quartz. Aliquots were removed at intervals for glpc analysis. Two new components were easily observable after 1 hr. The concentration of one of these increased steadily while the other reached a maximum concentration and then gradually decreased along with the starting ketone as irradiation proceeded. Prolonged irradiation (2–3 days) produced a solution containing a single volatile component in a concentration only slightly less than that of the starting ketone, and containing no less volatile material observable by glpc analysis at high temperatures.

The infrared and nmr spectra of the mixture after 25 hr were obtained by evaporating most of the pentane from an aliquot and examining the residue. The infrared spectrum had characteristic bands (neat) at 3.60, 5.65, 5.80, 6.08, 6.82, 7.24, 9.8–9.9, 10.8, and 11.1 μ, and the nmr (τ values) showed signals at *ca.* 0.6 (triplet, J = 2 cps), 4.3 (multiplet), 5.6–6.0 (multiplet), 6.9–7.4 (multiplet), and 7.5–7.9 (multiplet), with the remainder of the sweep being obscured by signals from residual pentane.

A similar irradiation through a Pyrex immersion well for 8 days produced a solution which contained starting ketone in addition to the two components described above.

b. Preparative: 2-Oxatricyclo[3.2.0.0^{3,7}]heptane (10). A solution of 10.0 g of **1** in 1 l. of pentane was irradiated using a 550-W lamp through quartz. Aliquots were examined periodically by glpc. After 3.5 days, glpc analysis showed the new photostable component to be the only major component present. The pentane was evaporated through a Vigreux column and the residue was distilled to yield 5.78 g of 2-oxatricyclo[3.2.0.0^{3,7}]heptane (**10**), bp 71–74° (120 mm). It had infrared bands (neat) at 6.8–6.9 (broad), 7.70, 7.80, 8.08, 8.20, 8.54, 8.96, 9.80, 9.90, 10.15, 10.30, 10.80, 10.90, 11.10, 12.0, and 13.0 μ. Its nmr spectrum (τ values) had signals centered at 5.45 (unsymmetrical doublet, J = 6 cps, each part of which was further coupled to produce a multiplet, one proton), 5.51 (complex multiplet, one proton), 6.8 (complex multiplet, one proton), 7.3 (multiplet, one proton), 8.17 (an unsymmetrical doublet, J = 10 cps, further split to a multiplet, one proton), 8.42 (an unsymmetrical doublet, J = 10 cps, one proton), 8.55 and 8.72 (complex unsymmetrical doublet, J = 9 cps, one proton), and 9.15 and 9.30 (unsymmetrical doublet, J = 9 cps, one proton).

Δ^2-Cyclobutenylacetaldehyde (7) and 3,5-Hexadienal (9). The pentane was removed from a 6-hr aliquot through an 8-in. spinning-band column, and samples of the three major components (**1**, the photoreactive intermediate, and **10**) present were separated from the residual mixture by preparative glpc. The reactive intermediate was collected by glpc and showed characteristic infrared bands (CCl_4) at 3.28, 3.96, 5.80, 5.90, 6.05, 6.20, 10.0, and 11.0 μ, and nmr signals (τ values) at 0.35 (triplet, J = 2 cps), 0.45 (triplet, J = 2 cps), 4.05 (multiplet), 4.80, 4.95, and 5.10 (parts of multiplets), 6.95 (doublet, J = 7 cps, with further small coupling), 7.29 (doublet of doublets, J = 14 and J = 4 cps), 7.50 (doublet, J = 2 cps), and 7.74 (doublet, J = 14 cps). The material was thermally unstable as indicated by the fact that the 5.9-μ band (attributed to a small amount of the dienal **9** having isomerized to a conjugated isomer) increased in intensity at the expense of the 5.80-μ band, even when the sample was stored under refrigeration. The collected material was obviously a mixture which contained at least one thermally produced aldehydic component not present in the original photochemical reaction mixture.

Δ^3-Cyclopentenecarboxaldehyde (6). The glpc peak corresponding to oxetane **10**, when collected, gave **6** with characteristic infrared bands (CCl_4) at 3.21, 3.69, 5.80, 6.15, 6.80, 7.40, 8.50, and 9.30 μ. The nmr spectrum (τ values) had signals at 0.6 (doublet, J = 2 cps), 4.6, 7.60, 7.70, and 7.89. It was unstable even when stored in solution under refrigeration. The nmr spectrum of this material definitely showed that it was not a component of the original photolysis mixture.

The starting ketone **1** could be collected by glpc without decomposition. It had a retention time and infrared spectrum identical with those of an authentic sample.

Irradiation of a Mixture of 7 and 9 in Pentane. A mixture of these components (collected from glpc) was dissolved in 1.5 ml of pentane and irradiated using a 550-W lamp through quartz. A component with a retention time identical with that of 2-oxatricyclo[3.2.0.0^{3,7}]heptane formed steadily until the major part of the starting material had disappeared. Some polymer was also produced.

Lithium Aluminum Hydride Reduction of 10. A 0.21-g sample of **10** was dissolved in 5 ml of ether and added to a mixture of 0.20 g of lithium aluminum hydride in 5 ml of ether at reflux. After stirring and refluxing for 2.5 hr, the mixture showed (glpc analysis) that no **10** remained; a single new component appeared at longer retention time. The mixture was cooled and hydrolyzed with 2 ml of water; the salts were filtered and washed with ether. The ether was separated, and the aqueous portion was extracted with ether. After drying over anhydrous magnesium sulfate, the ether was evaporated to yield 0.20 g of an oil which crystallized when the last traces of solvent were removed. The infrared spectrum of the crude reduction product (CCl_4) had characteristic bands at 3.00, 7.61, 7.75, 8.00, 8.90 (broad), 10.00, 11.68, and 11.79 μ. The nmr spectrum was identical with that of *endo*-5-bicyclo[2.1.1]hexanol.[9]

Irradiation of 1 in Diethyl Ether. a. Analytical. A solution of 0.50 g of **1** in 25 ml of ether was irradiated for 17 hr using a 550-W lamp through quartz. Glpc analysis of the mixture at that time showed that the oxetane **10** was the major component. The mixture was contaminated by numerous minor components, and analysis at high temperature revealed the presence of two less volatile components present in approximately equal concentration.

b. Preparative. A solution of 10.0 g of **1** in 1 l. of ether was irradiated for 8 hr, using a 550-W lamp through quartz. The solvent was evaporated through a Vigreux column and the residue was distilled and separated into six arbitrary fractions, bp 25 (120 mm)–122° (28 mm), to yield a total of 9.8 g of distillate.

Fractions 1–5 (7.0 g) were found to be mixtures of the photoproducts of ether and oxetane **10** by glpc analysis. Fraction 6 (bp 120–122° (28 mm), 2.0 g) comprised mostly the less volatile hydroxy ethers **14** as determined by glpc analysis. The infrared spectrum of the mixture (neat) had characteristic bands at 2.90, 6.10, 6.28, 9.10 (strong), 9.92, 11.15, and 14.2 μ. The nmr spectrum (τ values) of the mixture had signals at 3.8–4.2 (multiplet), 4.9–5.3 (multiplet), 6.3–7.0 (multiplet), 7.45 (singlet, broad), 7.7–8.1 (multiplet), 8.3–8.7 (multiplet), 8.90 (triplet, J = 6.5 cps), 8.92 (triplet, J = 6.5 cps), and 8.98 (doublet, J = 6 cps).

Irradiation of 1 in Methanol. a. Analytical. A solution of 0.65 g of **1** in 25 ml of methanol was irradiated using a 550-W lamp through quartz. Analysis of aliquots by glpc showed the presence of aldehyde **7** and an unknown component at retention times shorter than that of **1**, as well as a single less volatile component. No peak corresponding to **10** was observed. After 2.5 hr, most of **1** had disappeared. Continued irradiation resulted in a decrease in the concentration of **7** and the volatile unknown, with a corresponding increase in the concentration of the less volatile unknown.

A solution of 0.50 g of **1** in 25 ml of methanol was irradiated using a 550-W lamp through Pyrex. After 51 hr, glpc analysis showed that little of **1** remained. The photoproducts from irradiation through quartz were present in low concentration and the major product in this experiment was not a product of that photolysis. An attempt to remove the methanol from a portion of the photolysis mixture by distillation through an 8-in. spinning-band column with a bath temperature up to 110° resulted in the almost complete destruction of the photoproduct and the re-formation of **1** as observed by the retention time of the major component, then observed by glpc analysis, and the appearance of bands at 5.70, 7.70, 7.85, 8.10, 11.50, 12.34, and 13.10 μ in the infrared spectrum (neat), characteristic of **1**. The photoproduct could be isolated by diluting the remaining mixture with 50 ml of ether and washing the resulting solution free of methanol with water. After drying over anhydrous magnesium sulfate, the solvent was evaporated to yield a residue in which the photoproduct was still the major component observable by glpc analysis. This residue had infrared bands at 3.50, 5.65, 5.75, 6.85, 6.95, 7.58, 8.70, 9.00, 9.35, 9.50, 10.35, 11.25, and 11.48 μ. A sample was collected by glpc. The collected material had infrared bands (CCl_4) at 3.50, 6.75–6.95, 7.58, 8.50, 8.65, 9.00, 9.32, 9.50, 10.35, 11.28, and 11.48 μ. It had a retention time identical with that of the dimethyl ketal of **1** prepared by refluxing **1** in methanol with a catalytic amount of ammonium chloride.

b. Preparative: Δ^2-Cyclobutenylacetaldehyde Dimethylacetal (15) and the Semicarbazone of 7. A solution of 6.0 g of **1** in 1 l. of methanol was irradiated using a 550-W lamp through quartz for 2 hr. The mixture was diluted with 2 l. of saturated aqueous sodium chloride solution and was extracted with ether. After drying over anhydrous magnesium sulfate and evaporating the ether through a Vigreux column, the residue was distilled into three arbitrary fractions (bp 25 (30 mm)–80° (10 mm), 3 g).

Glpc analysis of fractions 1 and 2 (bp 25 (30 mm)–55° (42 mm), 2.4 g) showed they consisted mostly of **7** and **15**. Fraction 1, *ca.* 1 g, was dissolved in 10 ml of methanol, and 1.1 g of semicarbazide hydrochloride and 1.5 g of sodium acetate were added. The mixture was refluxed overnight. After dilution with an equal volume of water, the mixture was extracted with ether, and the extract was dried over anhydrous magnesium sulfate. The solvent was evaporated, and the residue was distilled to yield *ca.* 0.2 g of **15** as a colorless liquid, bp 55–60° (42 mm). The infrared spectrum (CCl_4) had bands at 3.28, 3.55, 6.8–7.0, 7.25, 7.35, 8.40, 8.90, and 9.45 μ. The nmr spectrum (τ values) had signals at 4.1 (quartet, J = 2 cps, two protons), 5.80 (triplet, J = 5.5 cps, one proton), 6.85 (singlet, six protons), 7.3 (multiplet, one proton), 7.50 and 7.57 (part of a doublet of doublets the other part of which is partially obscured by the 7.3 multiplet, one proton), 7.92 and 8.13 (doublet, J = 13 cps, one proton), 8.30, 8.39, 8.41, and 8.51 (parts of a doublet of doublets, two protons).

The aqueous alcohol solution from above was evaporated to dryness and the residue was recrystallized from methanol to yield 0.1 g of the semicarbazone of **7** as a colorless crystalline solid, mp 109–110°.

Anal. Calcd for $C_7H_{11}N_3O$: C, 54.88; H, 7.24. Found: C, 54.60; H, 7.35.

The nmr spectrum (τ values) of the solid had signals at 2.35 (triplet, J = 5 cps, one proton), 3.95 (quartet, J = 3 cps, two protons), and 4.0 (multiplet, three protons). The integral of the high-field portion of the spectrum corresponded to five protons and had signals centered at 7.18 and 7.40 (doublet of doublets), 7.60 (doublet, J = 5 cps), and 7.87 (doublet, J = 13 cps).

***endo*-2-Methoxybicyclo[2.1.1]hexan-*syn*-5-ol (16).** A solution of 10.0 g of **1** in 1 l. of methanol was irradiated under the conditions described above for 8 hr. Glpc analysis showed that **16** was the *only volatile product. The solvent was evaporated and the residue* was distilled to yield 3.4 g of **16** as a liquid, bp 100–105° (10 mm). The infrared spectrum had bands at 2.95, 6.80, 6.90, 7.40, 8.05, 9.00, 9.65, and 10.23 μ. The nmr spectrum (τ values) had signals at 6.15 and 6.25 (doublet, J = 6.5 cps, one proton), 6.45 (multiplet, one proton), 6.81 (singlet, three protons), 7.04 (singlet, one proton), 7.60 (multiplet, two protons), 7.89, 7.99, 8.08, and 8.19 (doublet of doublets, one proton), 8.71 and 8.89 (doublet, J = 11 cps, further coupled by *ca.* 2 cps, one proton), 8.84 and 8.96 (doublet, J = 7.5 cps, one proton), and 9.15 and 9.28 (doublet, J = 7.5 cps, further coupled by *ca.* 2 cps, one proton).

Reaction of 10 with Methanol. A solution of 0.060 g of **10** in 2.5 ml of methanol was heated under reflux. After 1 hr, glpc analysis showed the presence of a component having a retention time identical with that of **16**. After 5 days, about half of the oxetane had been converted to this material. The solvent and remaining oxetane were evaporated. The infrared spectrum of the residue was identical with that of **16**.

A similar reaction with 0.012 g of ammonium chloride present as catalyst also produced **16**, but caused other modes of reaction of **10** to compete with the formation of **16**, as the mixture turned dark and less **16** was formed in this reaction than in the noncatalyzed one.

Attempted Oxidation of 16. A slurry of 0.66 g of chromium trioxide in 6 ml of pyridine was prepared. A solution of 0.50 g of **16** in 6 ml of pyridine was added, and the mixture was stirred for a day at room temperature. Glpc analysis of an aliquot showed no new component, and no carbonyl band was observable in the infrared spectrum of an aliquot.

A solution of 0.1 g of **16** in 2.5 ml of acetone was cooled in ice and was treated with Jones reagent. The color of the oxidizing agent disappeared quickly; however, the infrared spectrum of an aliquot showed only a very broad band at *ca.* 5.90 μ after careful removal of the acetone.

Irradiation of Bicyclo[2.2.1]heptan-2-one (4) in Pentane. a. Analytical. A solution of 0.50 g of **4** in 25 ml of pentane was irradiated using a 550-W lamp through quartz. Glpc analysis of an aliquot after 2 hr showed that most of the **4** had disappeared, and a single new component had formed. The infrared spectrum of an aliquot had bands at 3.21, 3.62, and 5.80 μ characteristic of **17**.[14] Continued irradiaton led to the appearance of another component, formed at the expense of the aldehyde which had completely disappeared after 3 days of irradiation. The new component had infrared bands (CCl_4) at 5.80 (very weak), 8.45, 8.75, 9.50, 10.30, 10.45, 10.73, 11.00, 11.28, and 11.75 μ, and nmr signals (τ values) at 5.4–5.7 (multiplet), 7.0–7.3 (multiplet), and 7.5–7.8 (multiplet) in the ratio of 2:1:1 with the region from 8.0 to 9.0 being a complex multiplet.

b. Preparative: 2-Oxatricyclo[3.3.0.0^{3,8}]octane (18). A solution of 20.0 g of **4** in 1 l. of pentane was irradiated for 14 days using a 550-W lamp through quartz. The surface of the immersion well was cleaned daily. The solvent was distilled through a 10-in. Vigreux column, and the residue was distilled to yield 8.42 g of distillate in six arbitrary fractions, bp 30 (30 mm)–130° (0.5 mm). There was a nondistillable residue of 2.0 g, and the total polymer coating the immersion well and walls of the vessel amounted to *ca.* 6 g.

Glpc analysis showed that fractions 3 and 4 (bp 65–75° (31 mm), 6.09 g) were mostly **18**. By cooling the fractions in Dry Ice–acetone, a quantity of this material crystallized, and 1.10 g of a solid could be obtained by rapid filtration. This material could be sublimed (60° (760 mm)) to yield **18** as a volatile, crystalline solid, mp 96–98° (sealed capillary).

Anal. Calcd for $C_7H_{10}O$: C, 76.32; H, 9.15. Found: C, 76.11; H, 9.06.

It had characteristic infrared bands (CCl_4) at 6.81, 6.91, 7.80, 8.45, 8.75, 9.32, 9.50, 10.30, 10.45, 10.73, 11.00, 11.28, and 11.75 μ. The nmr spectrum (τ values) had signals at 5.5 (multiplet, two protons), 7.1 (multiplet, one proton), 7.65 (multiplet, one proton), 8.0–8.6 (complex multiplet, four protons), and 8.6–9.0 (complex multiplet, two protons). The residual liquid from fraction 3 had an infrared spectrum (neat) identical with that of the solid **18** except for additional weak bands at 5.80 and 7.20 μ, while the infrared spectrum of fraction 4 had all the bands of fraction 3 with additional broad bands at 2.9 and 9.10 μ.

The solid **18** was unstable to glpc analysis; two minor peaks were always observed following a large one. Attempted glpc isolation of **18** produced an aldehydic material having additional bands at 3.25, 3.62, 5.75, and 6.0 μ in its infrared spectrum, and signals at τ 0.6 and 4.25 in the nmr spectrum.

Lithium Aluminum Hydride Reduction of 18. A slurry of 0.40 g of lithium aluminum hydride in 20 ml of ether was prepared and to it was added 0.5 g of **18** in a small amount of ether. The mixture was stirred and refluxed for 5 hr. At that time, glpc analysis showed that none of the oxetane remained; a single new component appeared at longer retention time. The mixture was cooled, hydrolyzed with 2 ml of water, and the solvent was decanted. The salts were washed with ether and, after drying the combined solvent and washings, the solvent was evaporated to yield 0.44 g of a partially solid product. Sublimation of this material (80–85° (760 mm)) gave 7-norbornanol (**20**) as a colorless crystalline solid, mp 155–157° (sealed capillary). This material had a glpc retention time, infrared spectrum, and nmr spectrum identical with those of an authentic sample of 7-norbornanol, mp 151–152.5°.

Irradiation of 4 in Diethyl Ether. a. Analytical. The irradiation of 0.10 g of **4** in 5 ml of ether was observed (glpc analysis) to take the same course as irradiation in pentane. In addition photoproducts of ether were produced, and, as in the case of ketone **1**, two longer retention time components were formed in almost equal amount.

b. Preparative. A solution of 20.0 g of **4** in 1 l. of ether was irradiated for 2.5 hr using a 550-W lamp through quartz. The solvent was distilled through a 10-in. Vigreux column, and the residue was collected in five arbitrary fractions from 68 (32 mm) to 135° (32 mm) to yield 17.2 g of distillate and 2.8 g of nondistillable residue.

Glpc analysis of fractions 1–3 (bp 76–78° (32 mm), 13.5 g) showed they contained **17** contaminated by traces of **4**. The infrared spectrum of **17** (neat) had characteristic bands at 3.21, 3.62, and 5.80 μ. It had nmr signals (τ values) at 0.4 (triplet, J = 2 cps, one proton), 4.15 (multiplet, two protons), 6.4–6.7 (multiplet, one proton), 7.09 (doublet, J = 2 cps, two protons), 7.22 (unsymmetrical doublet of doublets, two protons) with the remaining two protons in a complex multiplet about 8.0. The semicarbazone of **17** showed mp 115–116° (lit.[14] mp 115–117°).

(A similar 2-day irradiation, worked up in the same way, yielded 21.5 g of distillate in 13 fractions collected between 30 (32 mm) and 160° (0.4 mm). Glpc analysis showed that fractions 1–4 (bp 30–80° (32 mm), 5.7 g) were a mixture of ether photoproducts. Fractions 5 and 6 (bp 80–100° (32 mm), 1.9 g) contained most of the **18** formed.)

Fractions 9–11 (bp 133–137 (32 mm) and 71–115° (0.4 mm), 8.5 g) consisted mostly of the hydroxy ethers **21** observed as two components in the analytical experiment. Samples of the two materials separated by glpc were collected. They had almost identical infrared and nmr spectra with bands (CCl_4) at 2.75, 3.29 (5.80, 6.09, and 6.22 all very weak), 6.90, and 9.0–9.1 μ, and signals in the nmr (τ values) at 4.42 and 4.49 (broadened singlets, two protons), 6.2–7.3 (complex multiplet, four protons), 7.58 (singlet), 7.87 (unsymmetrical doublet, $J = 4$ cps), and a multiplet under the last two signals (all together four protons). The region from 8.5 to 9.2 was complex but displayed assignable signals at 8.90 (triplet, $J = 7$ cps) and 9.02 (doublet, $J = 6$ cps) and all corresponded to ten protons.

No cyclopentadiene could be detected by glpc analysis of the distilled solvent under conditions where 1 mg/l. was detectable. No dicyclopentadiene was detected by glpc examination of the distillation fractions or crude product under conditions where it was known to be stable.

Oxidation of 21. A slurry of 0.66 g of chromium trioxide in 6 ml of pyridine was prepared at room temperature. A solution of 0.5 g of the mixture **21** in 6 ml of pyridine was added. The mixture was stirred at room temperature for 24 hr. Glpc analysis of an aliquot at that time showed no starting material remained. The solution was diluted with *ca.* 50 ml of water and extracted with ether. The ether extracts were washed with water, 10% hydrochloric acid, and water and were dried over anhydrous magnesium sulfate. The solvent was evaporated and the residue was distilled, bp 85–90° (10 mm), to yield **22** as a colorless oil. The infrared spectrum (CCl_4) of the distillate had strong bands at 5.83, 9.0, and 13.9 μ. The nmr spectrum (τ values) had signals at 4.45 (multiplet, two protons), 6.40 (quartet, $J = 7$ cps, one proton), 6.60 (quartet, $J = 7$ cps, two protons), 7.2–8.2 (multiplet, five protons), 8.85 (triplet, $J = 7$ cps), 8.84 (doublet, $J = 7$ cps), the latter two signals being superimposed on other signals and all integrating for eight protons.

Irradiation of 4 in Methanol. a. Analytical. A 0.5-g sample of **4** in 25 ml of methanol was irradiated using a 550-W lamp through quartz. Glpc analysis showed the ketone was rapidly converted to the aldehyde **17**. Continued irradiation led to the disappearance of the aldehyde and the appearance of two new components. No **18** was observed. The more volatile of the new components was destroyed when an attempt was made to remove the methanol by distillation.

b. Preparative. A solution of 20.0 g of **4** in 1 l. of methanol was irradiated for 10 days. Half of the mixture was diluted with 750 ml of saturated aqueous sodium chloride solution. The resulting solution was extracted with ether. The extract was dried over anhydrous magnesium sulfate and the solvent was distilled through a Vigreux column. The residue was distilled to yield 3.0 g of distillate, bp 60 (30 mm)–115° (10 mm).

Fractions 2 and 3 (bp 60 (30 mm)–108° (10 mm), 1.4 g) contained **23** as the major constituent. The infrared spectrum and glpc retention time of this component were identical with those of authentic dimethyl acetal of **17** (see below).

Fractions 4 and 5 (bp 108–115° (10 mm), 1.9 g) contained *endo*-2-methoxybicyclo[2.2.1]heptan-*syn*-7-ol (**24**) as the major constituent. It had characteristic infrared bands at 2.95, 8.75, 8.92, 9.10, and 9.25 (broad) μ. The infrared spectrum and glpc retention time were identical with those of **24** prepared by the acid-catalyzed addition of methanol to **18**.

Δ^2-Cyclopentenylacetaldehyde Dimethyl Acetal (23). The following is a procedure patterned after that described by Hickenbottom.[25] A 0.54-g sample of **17** in 5 ml of methanol containing 0.6% ammonium chloride was refluxed gently for a day. After cooling, the mixture was neutralized with alcoholic sodium methoxide. The solvent was evaporated *in vacuo*, and the residue was treated with saturated aqueous sodium bisulfite containing sodium carbonate. The mixture was filtered, and the organic material was extracted from the aqueous portion with ether. The extract was dried over anhydrous magnesium sulfate, and the solvent was evaporated to an oily residue which yielded **23**, bp 78–80° (32 mm), on distillation. Glpc analysis showed some aldehyde contaminant. The infrared spectrum (neat) had characteristic bands at 5.72 (weak), 7.25, 7.35, 8.40, 8.48, 8.88, 9.40, 10.30, and 13.9 μ. The nmr spectrum (τ values) had signals at 4.45 (singlet, broad, two protons), 5.75 (triplet, $J = 6$ cps, one proton), 6.85 (singlet, six protons), 7.89 (unsymmetrical doublet with further small coupling, $J = 4$ cps, two protons) superimposed on a 7.3–8.0 multiplet for one proton, 8.45 (doublet with further small coupling, $J = 6$ cps, two protons) superimposed on an 8.3–9.0 multiplet for two protons.

Reaction of 18 with Methanol. A 0.050-g sample of **18** was refluxed in 2.5 ml of methanol for 3 days. Glpc analysis showed that only a small amount of **24** had formed at that time. When this mixture was further treated with 10 mg of ammonium chloride and refluxed for 2 hr, a large amount of **24** had formed. After 24-hr reflux, the methanol was evaporated, and the ammonium chloride was removed by filtration. The filtered salts were washed with ether and a small amount of alcohol. The solvent was evaporated from the washings, and the residue was kept at 0.1 mm for several minutes to remove the last traces of solvent. The infrared spectrum of the residual oil was identical with that of photochemically produced **24**.

Oxidation of 24. A slurry of 0.66 g of chromium trioxide in 6 ml of pyridine was prepared. A solution of 0.50 g of **24** in 6 ml of pyridine was added, and the mixture was stirred at room temperature. After 24 hr, a carbonyl band was readily observable at 5.60 μ in the infrared spectrum (CCl_4) of an aliquot.

Irradiation of Camphor (5) in Pentane. a. Analytical. A solution of 0.50 g of camphor in 25 ml of *n*-pentane was irradiated using a 450-W lamp through quartz. Aliquots were removed at 0.5-hr intervals (2-hr intervals after most of the camphor had disappeared) and were analyzed by glpc. After the first 0.5-hr period, four components with retention times of 1.1, 4.5 (minor), 9.4 (minor), and 14.5 min, respectively (retention time of camphor, 16.9 min), had appeared. The concentration of the fourth passed through a maximum at about this time and decreased along with camphor as irradiation proceeded. At about 3.5 hr, the first component reached a maximum concentration and then slowly decreased. Prolonged photolysis led to the disappearance of all but the (minor) second and third components. The nmr spectrum (τ values) of an aliquot after 4 hr had signals at 0.3 (triplet, $J = 1.5$ cps), 4.3 (doublet, $J = 2$ cps), 4.6 (multiplet), and 4.8 (multiplet) with no other discernible features in the region not obscured by residual pentane.

A similar irradiation through Pyrex produced the same components at a much slower rate. A 24-hr aliquot had about the same composition (glpc) as the 3.5-hr aliquot described above. The nmr spectrum of the residual material also showed that the same components were present.

b. Preparative. A solution of 20.0 g of camphor in 1 l. of pentane was irradiated using a 550-W lamp through quartz for 3 days. The pentane was evaporated through a 10-in. Vigreux column, and the residue was distilled to yield 17.2 g of distillate in 13 arbitrary fractions, bp 25 (90 mm)–124° (0.4 mm). There was a nondistillable residue of 3.5 g.

Glpc analysis of fractions 2 and 3 (bp 25–30 (90 mm) and 25° (10 mm), 3.55 g) showed one major component contaminated with traces of pentane and other minor products. The retention time of the major component was identical with that of an authentic sample of 1,5,5-trimethylcyclopentadiene (**31**). Fraction 3 had nmr signals (τ values) at 3.98 (doublet, $J = 2$ cps, two protons), 4.3 (multiplet, one proton), 8.36 (doublet, $J = 2$ cps, three protons), and 9.05 (singlet, six protons) characteristic of this diene.

The two minor components (4.5 and 9.4 min) could not be characterized; it is even possible that these were decomposition products of other components injected. A 0.5-g sample of a mixture (distillation fraction 5) whose glpc showed mostly these two components was treated with 0.27 g of lithium aluminum hydride in refluxing ether for 45 hr. Glpc analysis showed no detectable change in the concentration of these components, excluding any carbonyl or strained oxetane containing structures.

Glpc analysis of the original distillate showed that fractions 5–8 (bp 55–72° (10 mm), 5.14 g) contained traces of the fourth component and residual camphor. Quantities of each were collected from preparative glpc. The retention time and infrared spectrum of the fourth component were identical with those of an authentic sample of campholenic aldehyde (**25**). The infrared spectrum of the camphor collected was identical with that of an authentic sample.

Irradiation of Campholenic Aldehyde (25) in Pentane. Campholenic aldehyde was prepared from α-pinene epoxide by a procedure patterned after that reported.[26] A 3.9-g sample of α-pinene epoxide in 10 ml of anhydrous benzene was treated with 50 mg of

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(25) W. J. Hickenbottom, "Reactions of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1957, p 238.

(26) B. A. Arbuzov, *Ber.*, **68**, 1430 (1935).

freshly fused zinc chloride and heated at 95–100° for 1.5 hr. After work-up the residue yielded 2.7 g of colorless oil, bp 76° (8.5 mm). It had characteristic infrared bands (neat) at 3.29, 3.69, 5.78, 6.02 (very weak), 6.80, 6.90, 7.20, 7.30, and 12.4 μ, and nmr signals (τ values) at 0.35 (triplet, $J = 1.5$ cps, one proton), 4.9 (multiplet, one proton), 7.70 (multiplet, two protons), 8.40 (multiplet, three protons), 9.05 (singlet, three protons), and 9.25 (singlet, three protons). Glpc analysis showed one major component (**25**) with about 10% of an impurity of similar retention time.[20]

A 0.10-g sample of **25** in 5 ml of pentane was irradiated using a 550-W lamp through quartz. After 1.75 hr, glpc analysis showed the presence of 1,5,5-trimethylcyclopentadiene, the two uncharacterized minor components from the photolysis of camphor in pentane, as well as the starting aldehyde and its original impurity.

Irradiation of 1,5,5-Trimethylcyclopentadiene (31) in Pentane. A solution of 0.14 g of **31** in 6 ml of pentane was irradiated for 23 hr using a 450-W lamp through quartz. A large amount of polymer deposited on the sides of the vessel. Glpc analysis indicated that the concentration of diene had decreased by more than 50%. No new products stable to glpc were observed even at temperatures as low as 50°. The infrared spectrum of the polymer was similar to that of the high-boiling material from the photolyses of camphor.

Irradiation of Camphor (5) in Diethyl Ether. a. Analytical. The irradiation of 0.10 g of **5** in 5 ml of ether took the same course as irradiation in pentane. In addition, photoproducts of ether were produced, and, as in the case of ketone **1**, two longer retention time components were formed in almost equal amounts. Similar behavior was observed on irradiation through Pyrex, but with a decrease in rate.

b. Preparative. A solution of 25.0 g of camphor in 1.25 l. of ether was irradiated using a 550-W lamp through Pyrex for 4.5 days. The solvent was removed through a 24-in. spinning-band column, and the residue was distilled to yield 23.2 g of distillate in 14 arbitrary fractions, bp 60 (760 mm)–140° (0.3 mm). There was a large nondistillable residue.

Fractions 10 and 11 (bp 50–70° (0.5 mm), 4.9 g) contained **35** as a major constituent. A sample of this material isolated by glpc showed characteristic infrared bands (CCl_4) at 2.70, 6.10, 6.80–7.00, 7.10–7.30, 9.00, 9.24, 9.82, and 10.62 μ. The nmr spectrum (τ values) showed signals at 4.8 (multiplet), 6.1 (multiplet), 6.7 (multiplet), 8.0–8.3 (multiplet), and 8.45 (multiplet, $J = 1.5$ cps) in the ratio of 1:1:1:1:5:3. The high-field region was complex, probably due to the presence of impurities, but singlets at 9.08 and 9.11 were easily discernible.

Glpc analysis of fraction 12 (bp 70–95° (0.45 mm), 3.07 g) showed that it consisted almost entirely of two components, corresponding to isomers of **32**, in about equal amount. Samples of these two components collected from glpc had almost identical infrared spectra. A collected mixture of the components had infrared bands (CCl_4) at 2.70, 5.6–5.8 (weak), and 9.1 (strong) μ, and nmr signals (τ values) at 5.02, 8.51, 9.11, and 9.35 assignable to vinyl, allylic, methyl, and *gem*-dimethyl protons, respectively. A mass spectrum showed a large parent peak at m/e of 226 with important fragments at M − 45 and M − 72, and smaller fragments at M − 18 and M − 28.

Irradiation of Campholenic Aldehyde (25) in Diethyl Ether. A 0.10-g sample of **25** in 5 ml of ether was irradiated using a 550-W lamp through quartz for 21 hr. Glpc analysis showed the same components present as were observed from the photolysis of **5** in ether.

Oxidation of 32. A solution of 0.5 g of distillation fraction 12 from the photolysis of camphor in ether in 6 ml of pyridine was added to a slurry of 0.66 g of chromium trioxide in 6 ml of pyridine at room temperature. The mixture was stirred for 24 hr. Glpc analysis showed the two major components had disappeared and a single new major component had appeared at shorter retention time. After work-up, 0.45 g of a liquid, bp 66–70° (0.2 mm), was obtained. The infrared spectrum (neat) had bands at 5.61, 5.82, 6.18, and 9.00 μ. The nmr spectrum (τ values) had signals at 4.9 (multiplet, one proton), 6.45 (quartet, $J = 7$ cps, one proton), 6.60 (quartet, $J = 7$ cps, two protons), 7.5–8.6 (complex multiplet, five protons), 8.42 (multiplet, three protons), 8.87 (triplet, $J = 7$ cps), 8.96 (doublet, $J = 7$ cps), and two singlets at 9.05 and 9.25 with the integral of the last four signals corresponding to a total of 12 protons. The major impurity in distillation fraction 12 was the component of shorter retention time, assigned structure **35**. The infrared band at 5.61 μ in the oxidation product from this fraction is the chief evidence for the presence of a four-membered ring in this material.

Irradiation of Camphor in Methanol. A solution of 20.0 g of camphor in 1 l. of methanol was irradiated using a 550-W lamp through quartz. After 9.5 hr, glpc analysis showed only a small component at the retention time of camphor and a major component with a retention time identical with that of campholenic aldehyde. The concentration of this component was of the same order of magnitude as that of the starting material originally. Several minor components were observed at shorter retention times. After 48 hr, a large part of the aldehyde had disappeared and a component with about the same retention time as camphor had appeared along with increased amounts of short retention time components. After 6 days, most of the aldehyde had disappeared leaving the material with a retention time approximately equal to that of camphor as the major component. The solvent was evaporated on a rotary evaporator *in vacuo* at *ca.* 30°. The residue was distilled to give 17.8 g of distillate in ten arbitrary fractions, bp 30 (90 mm) to 120° (0.1 mm), and a 2.5-g nondistillable residue. No 1,5,5-trimethylcyclopentadiene could be detected (by nmr or glpc) in the solvent or more volatile fractions.

Glpc analysis showed that fractions 6–8 (bp 90–100° (10 mm), 8.22 g) contained mostly a single component. The infrared spectrum (neat) of fraction 8 had bands at 2.8 (weak), 5.70 (very weak), 6.00, 6.80, 6.90, 7.20, 7.30, 8.90, 9.45, 9.80, 10.30, and 12.50 μ. The nmr spectrum (τ values) had signals at 4.9 (multiplet), 5.70 (triplet, $J = 5$ cps), 6.80 (two barely resolved singlets), 8.42 (multiplet), 9.04 (singlet), and 9.28 (singlet) in the ratio of 1:1:6:3:3:3. The retention time of this major component was identical with that of a sample of the dimethyl acetal of campholenic aldehyde (**36**) which also had infrared and nmr signals corresponding to the major ones of fraction 8.

Campholenic Aldehyde Dimethyl Acetal (36). A 0.1-g sample of **25** was treated as described for the preparation of **23** from **18**. The oil produced had infrared bands at 6.80, 6.90, 7.20, 7.30, 8.90, 9.45, 9.80, 10.30, and 12.50 μ. The nmr spectrum (τ values) had signals at 4.8 (multiplet, one proton), 5.70 (triplet, $J = 5$ cps, one proton), 6.80 (two barely resolved singlets, six protons), 8.42 (multiplet, three protons), 9.04 (singlet, three protons), and 9.28 (singlet, three protons). The other five protons appeared as a multiplet between 7.5 and 8.5.

Irradiation of Camphor (5) in Aqueous Methanol. A solution of 0.62 g of **5** in 3 ml of methanol and 2 ml of water was irradiated using a 550-W lamp through Pyrex. After about 5 hr, a component with a retention time identical with that of campholenic aldehyde (**25**) was detectable by glpc. Irradiation for 4 days produced a mixture containing about equal amounts of **5** and **25**. The mixture was diluted with 50 ml of water and extracted with pentane. The pentane extract was washed free of alcohol with water and dried over magnesium sulfate. The residue from evaporation of the solvent contained only the components which had been observed previously in this work.