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I. SOLUTION PHOTOCHEMISTRY OF CAMPHOR
II. SYNTHESIS AND SOLUTION PHOTOCHEMISTRY OF 2,2-DIMETHYLCYCLOBUTANONE

A thesis submitted to the Faculty of The Rockefeller University
in partial fulfillment of the requirements
for the degree of Doctor of Philosophy

by

David Kent Herron
III

*Approved for publication
Mr. C. Agosta
Associate Professor*

1 April 1969
The Rockefeller University
New York, New York

PREFACE

I could not have done the work described in this thesis without the help of many people. I owe special thanks to my research advisor, Dr. William C. Agosta, for introducing me to exciting areas of organic chemistry and for guiding me wisely in the course of my thesis research. I would also like to thank Dr. Lyman C. Craig for giving me the opportunity to work in his laboratory, and for teaching me some of his beautiful techniques for handling small amounts of material.

The mass spectrometric measurements which made this work feasible were performed by the Perkin-Elmer Corp., Norwalk, Conn.; Hoffmann-LaRoche, Inc., Nutley, N.J.; and Dr. R. L. Autrey, Harvard University. I am grateful to them for their generous help.

The spin-decoupling experiments described were kindly performed by Dr. L. A. Wilson, Varian Associates, Union, N. J., using a Varian HA-100 spectrometer.

Finally, I would like to thank the National Science Foundation for a graduate fellowship.

ABSTRACT

I. Solution Photochemistry of Camphor

Irradiation of camphor in solutions of 95% ethanol or n-heptane produces mainly α -campholenic aldehyde (2). In ethanol a bicyclic acetal (10) is also formed, while in n-heptane a bicyclic enol ether (8) is formed instead of the acetal. Deuterium labelling experiments indicate that the acetal is formed by reaction of a bicyclic oxycarbene (18) with ethanol, and that the enol ether is formed from this oxycarbene in part by reaction with n-heptane and in part by an intramolecular rearrangement.

Two cyclobutanols (34 and 35) and an oxetane (26) which are also produced on irradiation of camphor arise by secondary photolysis of α -campholenic aldehyde.

1,2,2-Trimethylcyclopent-3-enyl methyl ketone (5), previously thought to be a major product of the solution photolysis of camphor, has been synthesized and shown to be absent from our product mixtures.

II. Synthesis and Solution Photochemistry of 2,2-Dimethylcyclobutanone

2,2-Dimethylcyclobutanone has been synthesized by a new and convenient route which gives the desired product in 49% overall yield from commercially available materials.

Irradiation of 2,2-dimethylcyclobutanone in methylene chloride or in pentane produced little or no 2,3-dihydro-2,2-dimethylfuran. This observation is contrasted with the results of our study of camphor photochemistry.

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I. SOLUTION PHOTOCHEMISTRY OF CAMPHOR¹

INTRODUCTION

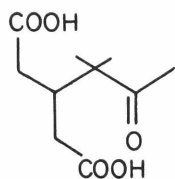
The first study of the photochemistry of camphor (1) was reported by Ciamician and Silber in 1910 as part of their pioneering studies of photochemical reactions. They showed that exposing a solution of camphor in aqueous ethanol to sunlight for six months produced a crude oil from which α -campholenic aldehyde (2) could be isolated as the corresponding hydroxamic acid or as a bisulfite adduct². Ciamician and Silber had shown earlier³ that irradiation



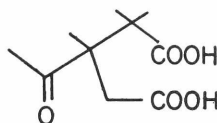
of cyclohexanone derivatives produces unsaturated aldehydes, and that the bond from carbonyl carbon to the more substituted α -carbon is broken preferentially. Now this reaction is recognized as typical of saturated cyclic ketones^{4,5}, and is believed to proceed by way of a diradical⁵ produced by breaking the bond between the α -carbon and the carbonyl group.

When Ciamician and Silber's crude oil mentioned above was extracted with aqueous bisulfite to remove all of the aldehyde present and then was treated with semicarbazide, two crystalline semicarbazones were isolated. One of these was identified as camphor semicarbazone, while the other, which had mp (melting point) 151-152° and was isomeric with camphor semicarbazone, was considered to be the semicarbazone of some other $C_{10}H_{16}O$ ketone. Hydrolysis of this semicarbazone gave a pure sample of the $C_{10}H_{16}O$ compound as an oil. When this oil was oxidized with permanganate and then with chromic acid, a dibasic $C_{10}H_{16}O_5$ acid was produced which had mp 133-134°.

Ciamician and Silber did not identify this acid, but pointed out that its mp was near those reported for isoketocamphoric acid (3, mp⁶ 129-130.5°), and β -acetyltrimethylglutaric acid (4, mp⁷ 125-140°).



3



4

Another study of camphor photochemistry was not reported until 1959, when Srinivasan described his experiments⁸. Srinivasan irradiated camphor with light from a mercury lamp in five different solvents, removed the solvents in vacuo, and analyzed the remaining material by vpc (vapor phase chromatography). He found that the same two main products were always formed, and that they could be separated on a preparative scale by chromatography on neutral alumina. One of these products, which he found to be the main product of the irradiation of camphor in aqueous ethanol, was identified as an aldehyde by its ir (infrared) absorption at 1735, 1620, 1445, 1385, 1370, and 1360 cm^{-1} and was taken to be α -campholenic aldehyde. The other main product was identified as a ketone on the basis of its ir absorption at 1715, 1615, 1440, 1360, and 1375 cm^{-1} , uv (ultraviolet) absorption at 280.0 nm (ϵ 60), mass spectrum base peak at m/e 43, and the fact that it gave a positive iodoform test. Assuming that this ketone was the same one Ciamician and Silber isolated as a product of their camphor photolysis, Srinivasan suggested that the ketone may be acetyl 1,2,2-trimethylcyclopent-3-ene (5), and noted that oxidation of 5 with permanganate and chromic acid should give 4.



The transformation of camphor into 5 is formally a Norrish Type II elimination. This well known⁹ cleavage of ketones and aldehydes possessing γ -hydrogens is believed to proceed through a six-membered ring transition state by abstraction of a γ -hydrogen by carbonyl oxygen and collapse to an olefin and the enol of a ketone or an aldehyde (as shown in figure 1). Such a six-membered

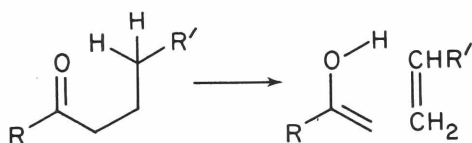


Figure 1

ring transition state leading from camphor to 5 appears inordinately strained in models. This reasoning led Srinivasan to consider that 5 must be produced by some other, hitherto unknown, pathway.

From the melting point depression of the camphor recovered after irradiations with a 313 nm source were carried out to low conversions and the solvents removed in vacuo, Srinivasan calculated a quantum yield for the formation of non-volatile products. For irradiations in 3-methylpentane, diethyl ether, and methanol this quantum yield was found to be 0.06. The ratio of ketone to aldehyde

produced, however, varied from 10 in n-heptane and 3-methylpentane to 0.67 in ethanol (see table I). Since the reaction leading from cyclic ketones to unsaturated aldehydes was known to be intramolecular

TABLE I

EFFECT OF SOLVENT ON RATIO KETONE/ALDEHYDE PRODUCED⁸

<u>Solvent</u>	<u>Ratio</u>
<u>n</u> -heptane	10
3-methylpentane	10
diethyl ether	1
ethanol	0.67

and relatively independent of solvent⁴, this striking variation of the product ratio and invariance of the quantum yield with changes in solvent led Srinivasan to propose the mechanism shown in figure 2 for the conversion of camphor into 5. According to this mechanism changes in the ratio of ketone to aldehyde with solvent would be due⁸ to the ease with which solvent molecules participate in steps 2 and 4.

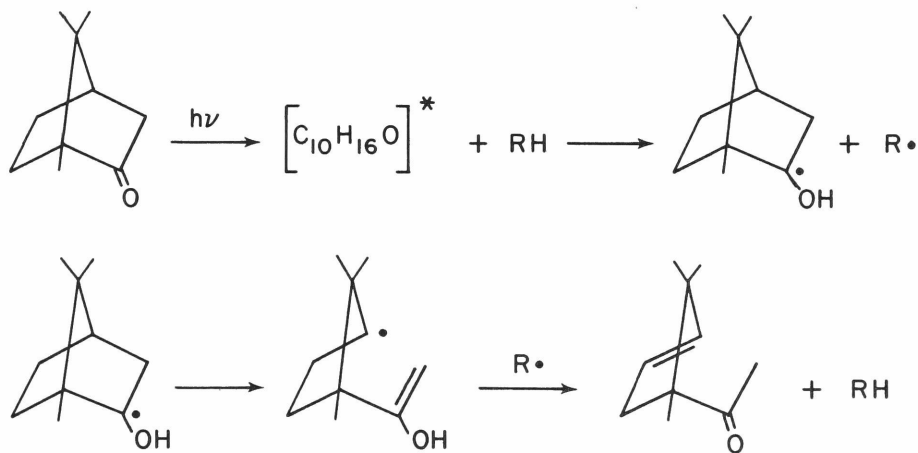


Figure 2

Thus the photochemistry of camphor stood for a number of years. It was widely accepted¹⁰ that irradiation of camphor gave α -campholenic aldehyde and an "anomalous" product, the ketone 5. Yet the assignment of structure 5 rested on very little evidence, and the mechanism proposed by Srinivasan for its formation from camphor was unprecedented.

The behavior of the rigid, strained carbon skeleton of camphor in ionic ground state reactions has puzzled organic chemists for over a hundred years¹¹. It has recently led to the development of new concepts¹², and still has no completely satisfactory theoretical interpretation¹³. In the hope that the photochemistry of this system would also be distinctive and interesting, we set out to study the formation of the anomalous camphor photoproduct.

RESULTS AND DISCUSSION

Formation of α -Campholenic Aldehyde

We first attempted to duplicate the experiments of Ciamician and Silber², and of Srinivasan⁸. We irradiated pure camphor in 95% ethanol and in *n*-heptane with Pyrex-filtered light from a high-pressure mercury lamp* and analyzed the resulting mixtures by vpc. Representative chromatograms are shown in figure 3. The material corresponding to each lettered peak was collected by preparative vpc and examined spectroscopically. Peaks D and e consisted of unchanged camphor

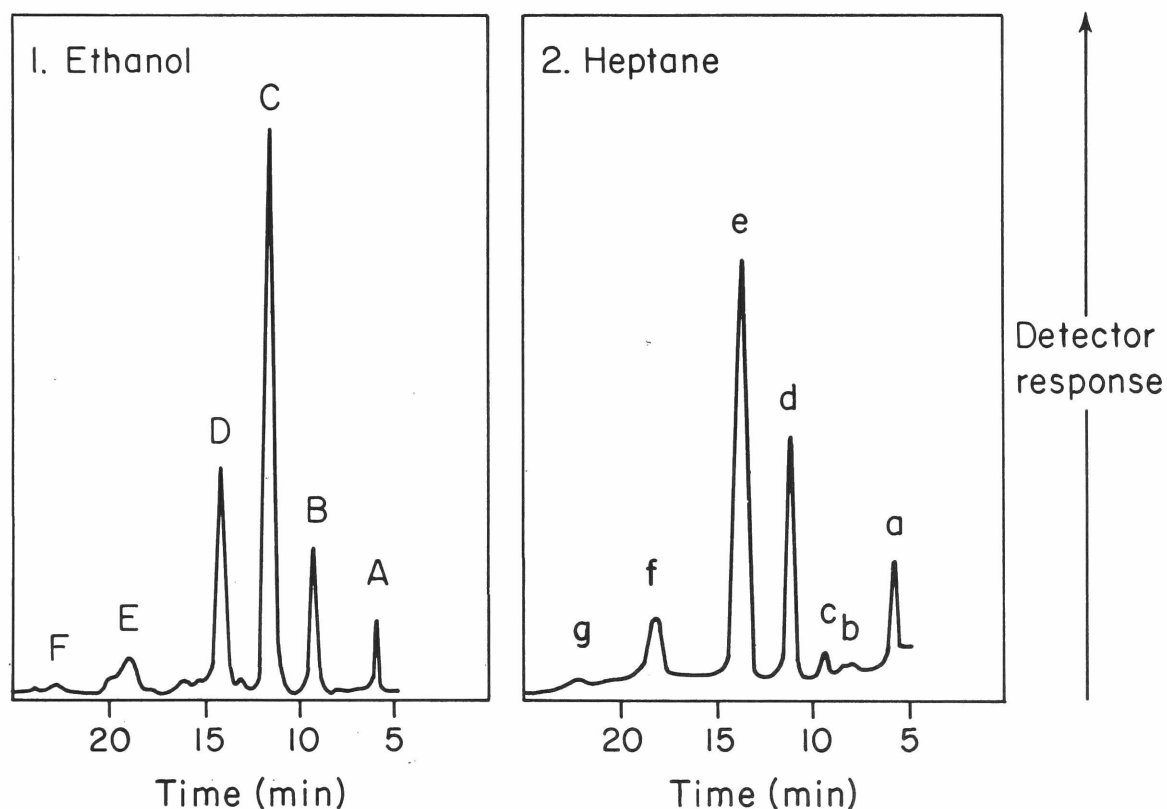


Figure 3

*We also irradiated an aqueous ethanol solution of camphor with sunlight for six months, and found qualitatively the same result produced by our mercury lamp.

which showed no impurities in its nmr (nuclear magnetic resonance) spectrum. Peaks C and d each consisted of a compound whose elemental analysis and ir, nmr, and mass spectra suggested that it was α -campholenic aldehyde. The identity of this compound was proven by comparing its vpc retention time and ir spectrum with those of an authentic sample of α -campholenic aldehyde prepared by the acid-catalyzed rearrangement of α -pinene oxide¹⁴.

The "Anomalous" Photoproduct

Thus although we had expected the anomalous product to predominate in heptane, α -campholenic aldehyde was the main product formed on irradiating camphor either in ethanol or in heptane. Furthermore the spectroscopic properties of the materials corresponding to the other vpc peaks indicated that none of these contained the anomalous product.

We considered that this product might have been formed in heptane and decomposed photochemically during our photolysis. To test this possibility we repeated the photolysis in heptane taking aliquots for vpc analysis frequently, especially early in the reaction, but no peaks other than those shown in figure 3 appeared.

We also considered that some impurity in our solvent might be quenching the reaction leading to the anomalous product. In this case the quantum yield for α -campholenic aldehyde formation in our experiments should be less than 0.06. Under conditions which differed from those reported by Srinivasan⁸ only in our use of a 25% more intense source, we irradiated camphor to very low conversions. In these experiments α -campholenic aldehyde was the only product detectable by vpc, and its quantum yield was found to be 0.12 ± 0.04 . We concluded from this result that our failure to observe the anomalous product was not due to quenching by impurities.

We finally synthesized the ketone 5 by the unambiguous route outlined in figure 4. Since Ciamician and Silber used (+)-camphor in their experiments, we used camphoric anhydride (6) derived from (+)-camphor as our starting material. Camphonic acid (7), which had been prepared before by less convenient routes¹⁵, reacted with methyllithium¹⁶ to give a single product, which was assigned structure 5. The elemental analysis and ir, uv, nmr, and mass spectra of this

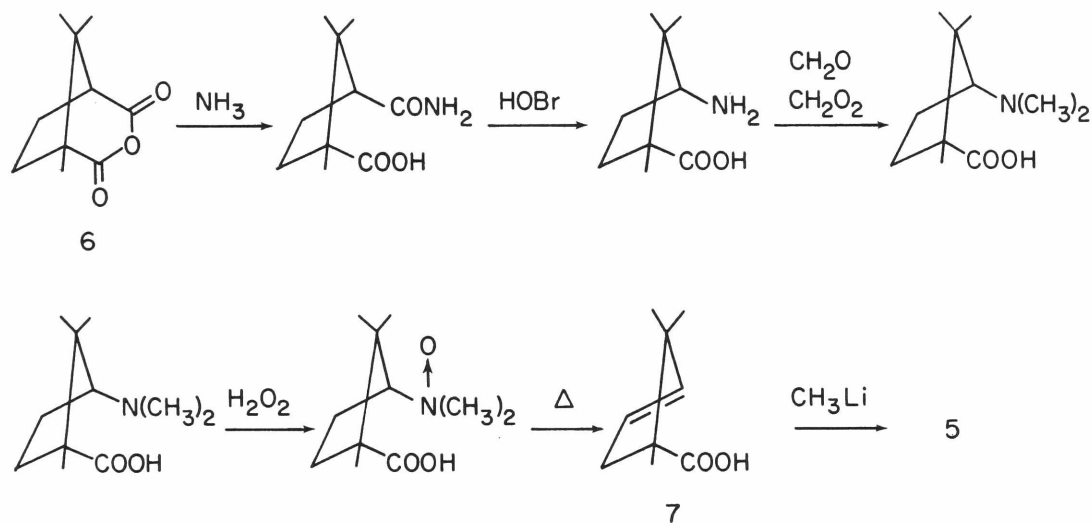



Figure 4

product fully supported this structure assignment. The ir spectrum showed C=C stretching at 1620 cm^{-1} and C=O stretching characteristic¹⁷ of a pinacolone at 1698 cm^{-1} . The uv spectrum showed only the weak $n-\pi^*$ transition characteristic¹⁸ of saturated ketones. The nmr spectrum consisted of multiplets for each of two vinyl protons, broad doublets ($J=17\text{ Hz}$) for each of two allylic protons, a singlet for

the methyl group of a methyl ketone, and singlets for each of three methyl groups on saturated carbon. The base peak in the mass spectrum occurred at m/e 109, corresponding to loss of acetyl radical from the parent ion.

The reported properties of the compounds isolated by Ciamician and Silber², and by Srinivasan⁸, are compared with the corresponding properties of ketone 5, in table II. These data indicate that the earlier workers had not isolated 5.

TABLE II

		Ciamician and Silber ²	Srinivasan ⁸
Physical state	Crystalline, m.p. 77-78°	oil	unreported
Infrared spectrum	1699 cm ⁻¹	—	1715 cm ⁻¹
Ultraviolet spectrum	286 mμ (22, EtOH)	—	280 mμ (60, EtOH)
Semicarbazone	m. p. 191-193° (dec.)	m. p. 151-152°	—

The vpc retention time of 5 fell between those of components A and B of chromatogram 1 (figure 3), and coincided with that of component b of chromatogram 2. After determining the minimum amount of 5 that could be detected under our vpc conditions it was possible to say that less than 0.6%* of the mixture of photolysis products from camphor in ethanol could have been 5. Component b appeared from its ir and nmr spectra to be a mixture. The vinyl signals of

*This percentage is only approximate and is high. Meinwald and Chapman have shown¹⁴ that photolysis of α -campholenic aldehyde under conditions similar to ours produces mainly 1,5,5-trimethylcyclopentadiene. We did not attempt to measure the amount of this product formed in our experiments, and so the sum of the products observed in our vpc analysis is less than the true total product. Percentages of the photolysis product mixtures calculated on the basis of the sum of the observed products will then be larger than corresponding percentages of the actual total product.

5 were missing from the nmr spectrum of component b, in which 20% of 5 should have been detected easily. Since this vpc component made up only 1%* of the products from the photolysis in heptane, less than 0.2%* of this product mixture could have been 5. Thus it is clear that 5 was not produced on irradiation of camphor in our experiments.

It is possible to construct a believable explanation for the isolation of a "ketone" photoproduct by Ciamician and Silber on the basis of experiments reported by King and Farber in 1961¹⁹. Using vpc these workers were able to show that the aldehyde product of acid-catalyzed rearrangement of α -pinene oxide, previously considered to be α -campholenic aldehyde, was actually a mixture of aldehydes forming a semicarbazone mixture of mp 137-139^o. They found that pure α -campholenic aldehyde forms a semicarbazone of mp 154-155^o, and can be oxidized to isoketocamphoric acid (3), mp 130-131^o. If Ciamician and Silber's bisulfite extractions had failed to remove all of the α -campholenic aldehyde from their crude oil, their semicarbazone of mp 151-152^o could have been α -campholenic aldehyde semicarbazone**. Hydrolysis of this semicarbazone would have given α -campholenic aldehyde, which is an oil; and oxidation of this oil would have given isoketocamphoric acid.

It is not clear what the material assigned structure 5 by Srinivasan⁸ might have been.

Formation of Products by Way of a Carbene Intermediate

Thus frustrated in our attempt to study the mechanism of formation of 5 from camphor, we set out to determine the structures of the other photoproducts indicated in the chromatograms of figure 3.

**This interpretation of Ciamician and Silber's data was suggested independently by Meinwald and Chapman¹⁴.

The components A and a were shown to be identical by comparison of their vpc retention times and ir, nmr, and mass spectra. The ir spectrum of this material showed vinyl C-H stretching and the very characteristic²⁰ intense C=C stretching of an enol ether. The nmr spectrum showed a one-proton doublet at $\delta 5.92$ ($J=6$ Hz) and a one-proton triplet at 4.78 ($J=6$ Hz) which fit the characteristic chemical shift pattern²¹ of an enol ether with one proton on the oxygen-bearing vinyl carbon and one proton on the adjacent vinyl carbon. The ir and nmr data together suggest the part structure shown in figure 5. The rest of the nmr spectrum consisted of

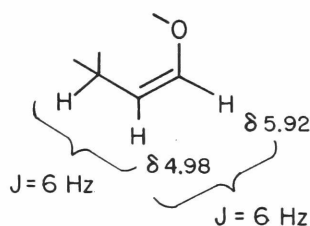


Figure 5

three singlets for methyl groups on saturated carbon and a five-proton multiplet between $\delta 1.6$ and 2.2, suggesting the part structure present in camphor and shown in figure 6. Combining these two part structures we arrive at the structure 8 for this photoproduct. The high-resolution

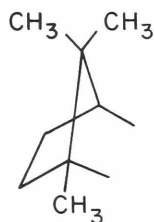
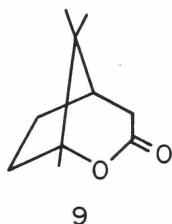


Figure 6

mass spectrum of this material was completely consistent with the proposed structure.

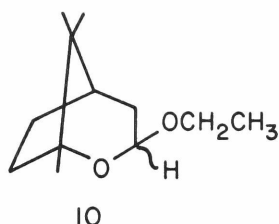


This structure assignment was confirmed chemically by oxidation of the enol ether with chromic acid in aqueous acetone (Jones oxidation²²) to the lactone 9, which was identified by comparison of its vpc retention time and ir spectrum with those of authentic 9 prepared by peracetic acid oxidation of camphor²³.



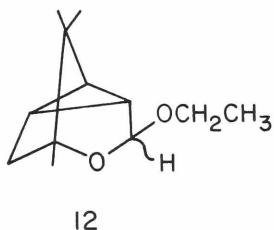
Component B was formed only when the photolysis was carried out in ethanol. The ir spectrum of this material showed no vinyl C-H, C=C, or C=O stretching. The strong bands in the spectrum occurred where the C-O-C stretching bands of ethers are usually observed. The high-resolution mass spectrum of this material was particularly informative, showing a small parent peak at m/e 198.1583 corresponding to the composition $C_{12}H_{22}O_2$ (camphor + ethanol). The mass spectrum also showed large peaks corresponding to loss of ethoxyl and loss of ethanol from the parent ion. The nmr spectrum was consistent with the rest of the data in suggesting structure 10 for this material, and could be interpreted most easily by assuming that only

one diastereomer of 10 was present and that one signal in the methyl region belonged to an impurity (about 10%) not separated from 10 by vpc*. The stereochemistry about the acetal carbon could not be determined from the nmr spectrum.



The assignment of structure 10 was confirmed chemically by Jones oxidation²² of the acetal to lactone 9 in high yield.

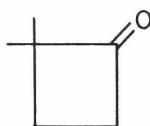
Formation of a ring-expanded acetal by irradiating a cyclic ketone in alcohol was first reported by Yates and Kilmurry²⁴ in 1964. They found that irradiation of cyclocamphanone (11) in ethanol produced mainly 12, and they proposed that the oxycarbene 13 might be an intermediate in the reaction. These workers later provided



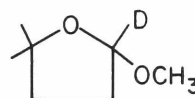
support²⁵ for their proposal by irradiating 11 in cyclohexene and isolating a 1:1 adduct of cyclohexene and 13, which was shown to have the expected²⁶ cyclopropane structure.

* We would like to acknowledge correspondence with Dr. Robert Hutchins, Drexel Institute of Technology, which was helpful in interpreting this nmr spectrum.

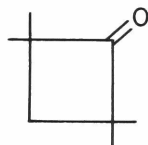
The other known examples of this kind of ring expansion in saturated ketones all involve conversions of cyclobutanones to α -alkoxytetrahydrofurans²⁷⁻³⁰. The evidence that these reactions proceed through oxycarbene intermediates is that irradiation of 14 in methanol-O-d²⁷ gave 15, the carbene insertion product; and that irradiation of 16 in benzene²⁷ in the presence of oxygen gave 17, again the product expected³¹⁻³² to arise from a carbene.



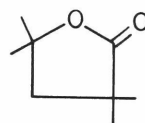
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15



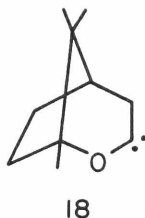
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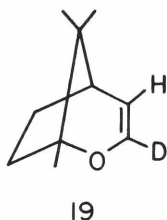
Previous attempts to generate oxycarbenes³³ involved treating α -haloethers with strong bases, and probably produced organometallic reagents rather than free carbenes³⁴. These photochemical ring expansions, which apparently provide a route to free oxycarbenes, offered the first opportunities to observe oxycarbene reactivity.

The acetal 10 could arise from camphor by way of the oxycarbene 18 analogous to 13. The origin of the enol ether 8, however, was not so clear. It might arise by thermal elimination of ethanol

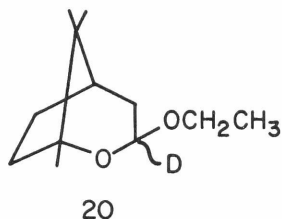


from the acetal, or it might arise directly from the carbene. Thermal eliminations of alcohols from acetals are well known³⁵, and 1,2-hydrogen shifts in carbenes to give olefins have often been observed³⁶, although not specifically in an oxycarbene.

To determine the origin of 8 we irradiated camphor in 95% ethanol-O-d (95% EtOD, 5% D₂O). If the enol ether arises from the acetal the deuterated enol ether 19 should be isolated from this photolysis, while if it arises by a 1,2-hydrogen shift in 18 the undeuterated enol ether 8 should be produced.

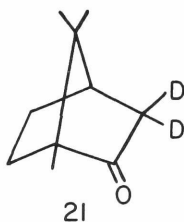


When the photolysis was carried out in 95% ethanol-O-d, the chromatogram of the product mixture looked like that of the products from the photolysis in ordinary ethanol (figure 3). The enol ether, acetal, and camphor peaks were isolated by preparative vpc and examined by nmr. The spectrum of the acetal was very similar to that of 10, but showed no signal for the acetal proton, indicating the structure 20. The spectrum of the enol ether was like that of 8 except that the low-field vinyl doublet was missing and the higher-field vinyl triplet was replaced by a doublet ($J=6$ Hz),



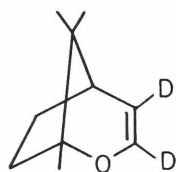
indicating that the enol ether formed was 19. The spectrum of the recovered camphor showed that camphor had incorporated no deuterium during the photolysis. Therefore the enol ether does not arise by a 1,2-hydrogen shift in 18, but probably arises exclusively from thermal decomposition of the acetal during vpc. This conclusion is consistent with the observation that vpc-purified acetal always gave comparable amounts of acetal and enol ether when it was resubjected to vpc (injector block at 235°).

In view of this result we were all the more interested in knowing the origin of the enol ether in heptane, where no acetal can be formed. To discover this we irradiated camphor-3,3-d₂ (21)³⁷ in heptane. The chromatogram of the product mixture looked the same as that from the irradiation of ordinary camphor in heptane (figure 3),

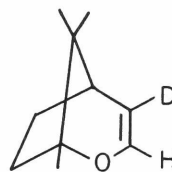


and the peaks a, c, and d-g were collected by preparative vpc. The deuterium content of the starting camphor and of the recovered camphor was determined by mass spectrometry to be 91% d₂, 7% d₁, 2% d₀. The mass spectrum of the enol ether showed that it was 16% d₂, 75% d₁,

and 9% \underline{d}_0 . The nmr spectrum of this enol ether was like that of 8 except that the low-field vinyl doublet of 8 was replaced by a singlet integrating for only 0.73 proton, and the higher-field vinyl signal of 8 was almost undetectable--integrating for 0.05 proton. Thus the enol ether must be a mixture of about 19% 22, 74% 23, and 7% 8.



22



23

The formation of 23 may occur as shown in figure 7. The oxycarbene 24 abstracts hydrogen from solvent, and the solvent radical then abstracts deuterium from the radical 25. In unlabelled camphor the net change is a 1,2-hydrogen migration. Hydrogen abstraction of the sort postulated in figure 7 is a well-known reaction of some carbenes, especially diarylcarbenes, but the observed products in these cases are results of radical coupling reactions³⁸ instead of apparent 1,2-hydrogen migrations.

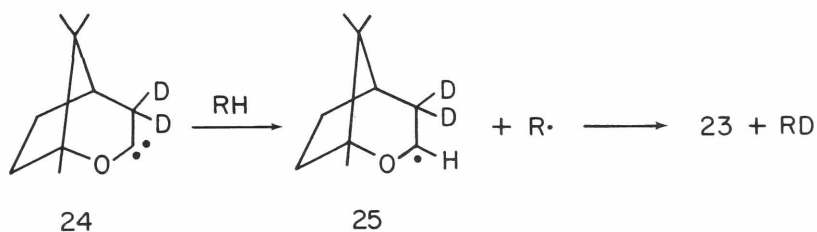


Figure 7

In view of the reactivity of oxycarbene 18 in hydrogen abstraction, we cannot rule out the possibility that some of the deuterated enol ether 19 formed when camphor was irradiated in ethanol-0-d might also have arisen by the kind of mechanism outlined in figure 7, with carbene 18 abstracting deuterium from ethanol-0-d. However this possibility seems unlikely because free radicals are known to abstract the carbinyl hydrogen of an alcohol rather than the hydroxyl hydrogen³⁹.

The dideuterated enol ether might arise by a 1,2-deuterium shift in the carbene 24, or it might arise by the kind of pathway suggested for the formation of 23, with carbene abstracting deuterium from camphor-d₂ instead of from the solvent. The 1,2-deuterium shift is by far the more likely of these two possibilities, however. In the photolysis of camphor-3,3-d₂ the concentration of n-heptane was 74 times that of camphor-d₂. Since each molecule of heptane has 16 abstractable hydrogens while each molecule of camphor-d₂ has only two deuteriums, and since about 20% of the enol ether formed was dideuterated, if the dideuterated enol ether were formed by the kind of pathway shown in figure 7 the carbene would have to abstract deuterium from camphor-d₂ about 230 times faster than it abstracts hydrogen from heptane (on a per hydrogen basis) in spite of the fact that a primary deuterium isotope effect would be expected to slow the deuterium abstraction somewhat*. This selectivity might be compared with the selectivity of a free radical in abstracting similar types of hydrogen atoms. The phenyl radical reacts very much as the methyl radical does, and is moderately selective in hydrogen abstraction

*Deuterium isotope effects for carbene insertions into C-H bonds fall in the range^{40,41} 1.2-1.8. For free radical hydrogen abstractions the isotope effect falls in a range⁴² from slightly over 1 to about 8. Deuterium isotope effects for hydrogen abstractions of carbenes have not been determined.

reactions⁴³, but it abstracts hydrogen from the α -positions of acetone only 0.47 times as fast as from n-heptane (on a per hydrogen basis)⁴⁴. That is, the phenyl radical actually abstracts hydrogen from acetone less readily than from n-heptane, although the selectivity is slight. Yet in general, carbenes are less selective in their reactions than are free radicals⁴⁵. Thus the demand that 24 must show great selectivity in abstracting deuterium from camphor-d₂ seems unreasonable, and it follows that 22 probably does not arise by deuterium abstraction from camphor-d₂.

Assuming that the dideuterated enol ether arises from camphor-d₂ by a 1,2-deuterium shift, we can calculate how much of the enol ether from ordinary camphor arises by a 1,2-hydrogen shift. If the deuterium isotope effect is the same as that measured⁴¹ for the same reaction in ethylcarbene ($k_H/k_D=1.4$), it follows that 29% of the enol ether produced on irradiation of camphor in heptane arises by a 1,2-hydrogen shift in oxycarbene 18.

The Oxetane Product

When camphor was irradiated in heptane the minor component c (figure 3) was found in the product mixture. Even though this component made up only about 1% (see footnote on p. 10) of the product mixture, and was therefore available only in small quantities, its structure could be deduced readily because of the simplicity of its ir and nmr spectra. The nmr spectrum consisted of a sharp six-proton singlet at 0.78 ppm, a three-proton singlet at 1.38, a broad four-proton signal at 1.90, a one-proton multiplet at 2.14, and a broad two-proton signal at 4.10. The equivalence of two methyl groups suggested a molecule with a plane of symmetry. This plane could be either the one which includes all three carbon atoms of the gem-dimethyl group, or the one perpendicular to this and passing through the central carbon atom of the gem-dimethyl group. The ir spectrum contained no absorption for vinyl C-H,

C=C, or C=O stretching, but showed absorption in the ether C-O-C stretching region and strong absorption at 955 cm^{-1} which is characteristic of oxetanes⁴⁶. The high-resolution mass spectrum of this compound showed a parent peak at m/e 152.1186 corresponding to the composition $\text{C}_{10}\text{H}_{16}\text{O}$. The structure 26 met the exacting requirements of these data, and was a satisfying solution to the problem since photochemical addition of the carbonyl group of α -campholenic aldehyde to its neighboring carbon-carbon double bond as shown in figure 8 would give 26 in an intramolecular case of the well-known Paternò-Büchi reaction⁴⁷.

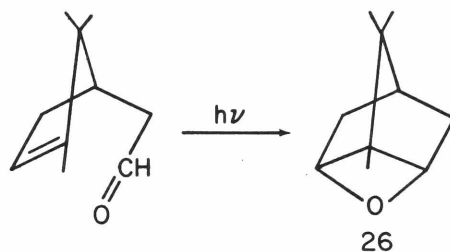
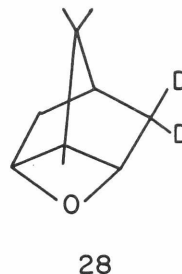
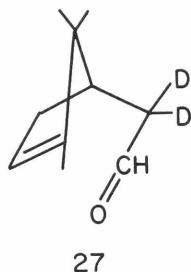
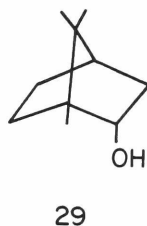


Figure 8

Some support for the assignment of structure 26 and for the assumption that 26 is derived from α -campholenic aldehyde came from the photolysis of camphor- d_2 . The nmr spectrum of the α -campholenic aldehyde isolated from this reaction showed clearly that it had structure 27. The oxetane derived from this aldehyde would be expected to have structure 28, and in fact the nmr spectrum of the oxetane isolated was consistent with the structure 28. The spectrum was virtually the same as that of 26 except that the four-proton signal of 26 at 1.90 ppm was replaced by a two-proton signal.



The assignment of structure 26 was confirmed by reducing the oxetane to borneol (29) with lithium aluminum hydride in boiling di-n-butyl ether⁴⁸.

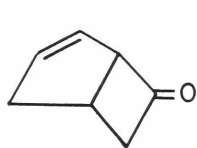


Formation of Cyclobutanols

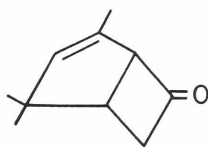
The components E and f, and F and g (figure 3), were found to be identical by comparisons of their vpc retention times and ir and nmr spectra. Microanalyses indicated that both compounds were isomeric with camphor. The ir spectra of these compounds were very similar, each showing O-H, vinyl C-H, and C=C stretching bands. The nmr spectra were also remarkably similar, each showing one vinyl proton, a three-proton triplet ($J=1.5$ Hz) at about δ 1.6, two methyl singlets, and one proton which exchanged readily with D_2O . These data indicated that the compounds were closely related alcohols having a methyl group and a hydrogen on a double bond.

Jones oxidation²² of each of these alcohols gave the same compound, whose ir spectrum showed that it was a cyclobutanone and

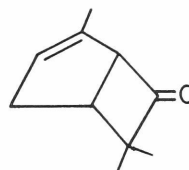
still had a carbon-carbon double bond. The uv spectrum of this compound showed the characteristic $n-\pi^*$ absorption of β,γ -unsaturated ketones in which the two double bonds interact^{49,50} and was virtually identical with the spectrum of bicyclo 3.2.0 hept-2-en-7-one (30)⁵¹. Chemical shift data from the nmr spectrum were quite similar to the corresponding data published^{30,52} for cyclobutanones 31 and 32, as shown in table III. We considered the possibility that our cyclobutanone and 31 were identical,



30



31

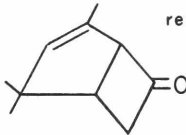
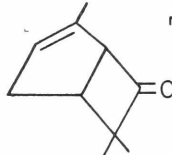


32

but when we compared the actual nmr and ir curves* for 31 with those of our cyclobutanone, we found the two sets of spectra to be significantly different. The signal at $\delta 4.0$ in the spectra of 31 and 32 seems to be characteristic of the proton which is both allylic and α - to the cyclobutanone carbonyl group, and the signal a $\delta 4.0$ in the spectrum of our cyclobutanone probably belongs to this type of proton. The one-to-one correspondence between the nmr signals of 31 and those of our cyclobutanone is quite striking, and strongly suggests that the two compounds differ only slightly in structure. In particular both compounds appear to have one vinyl proton and one methyl group on a carbon-carbon double bond,

* We would like to thank Dr. William F. Eрман, The Proctor and Gamble Co., for providing us with copies of these spectra.

TABLE III

Cyclobutanone from Jones Oxidations	 ref. 30		 ref. 52		
	Position *	Signal, δ (CCl ₄)	Position *	Signal, δ (CDCl ₃)	
C(2)-H	5.15 (broad s, 1H)	C(3)-H	5.22 (m, 1H)	C(3)-H	5.46 (m, 1H)
C(1)-H	4.0 (m, 1H)	C(1)-H	4.0 (m, 1H)	C(1)-H	4.03 (m, 1H)
C(6)-H, H	2.9 (m, 2H)	C(6)-H, H	3.02 (m, 2H)		
C(5)-H	2.6 (m, 1H)	C(5)-H	2.56 (m, 1H)	C(4)-H, H; C(5)-H	2.55 (m, 3H)
C(3)-CH ₃	1.68 (t [†] , 3H)	C(2)-CH ₃	1.71 (broad s, 3H)	C(2)-CH ₃	1.75 (m, 3H)
C(4)-CH ₃	1.12 (s, 3H)	C(4)-CH ₃	1.15 (s, 3H)	C(6)-CH ₃	1.19 (s, 3H)
C(4)-CH ₃	1.07 (s, 3H)	C(4)-CH ₃	1.1 (s, 3H)	C(6)-CH ₃	1.12 (s, 3H)

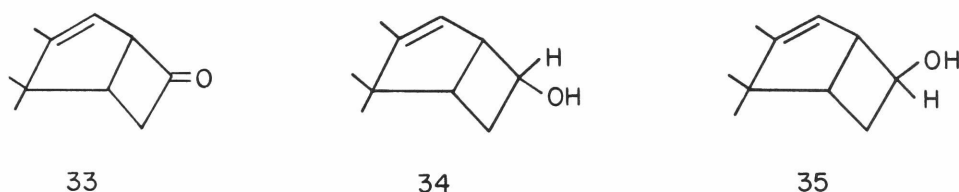
* Compounds are numbered as derivatives of bicyclo[3.2.0]hept-2-en-7-one

† An apparent triplet, $J_{app} = 1.5$ Hz

an allylic proton α - to the carbonyl group, a methylene group α - to the carbonyl group, and a gem-dimethyl group. The high-resolution mass spectrum of our cyclobutanone showed a parent peak at m/e 150.1038 corresponding to the expected composition $C_{10}H_{14}O$, and the base peak was at $M-42$ corresponding to loss of ketene from the parent ion and confirming that our cyclobutanone has a methylene group adjacent to its carbonyl group.

The requirements that our cyclobutanone have the composition $C_{10}H_{14}O$, that it be a β,γ -unsaturated ketone with a methyl group and a hydrogen on its carbon-carbon double bond, that it have a methylene group on one side of its carbonyl group and an allylic proton on the other side, and that it have two methyl groups

on saturated carbon which show singlets in the nmr spectrum, allow only 31 and 33 as possible structures. Since structure 31 was already ruled out, our cyclobutanone must be 33. The cyclobutanols from which 33 was derived then have structures 34 and 35. These alcohols could easily arise from α -campholenic aldehyde by a well known⁵³ route, involving abstraction of γ -hydrogen by the carbonyl



oxygen, followed by collapse of the resulting diradical to the two cyclobutanols (as shown in figure 9).

Our photolyses always produced 4 to 5 times more of one cyclobutanol than of the other. We could assign the stereochemistry of these compounds by reducing 33 with sodium borohydride. Examination of models indicated that the concave (bottom) side of 33 should

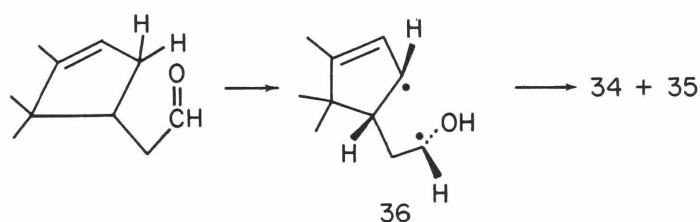
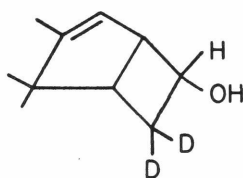


Figure 9

be much more crowded than the convex (top) side, and since hydride should be delivered to the less crowded side of the carbonyl group⁵⁴, the major product of this reduction should be 34. In fact the reduction gave a 98% yield of the alcohol produced in greater

amounts in the photolyses and a 2% yield of the other alcohol. Therefore in the photolyses the endo-alcohol 34 is produced in greater amounts than the exo-alcohol 35 in spite of the fact that 34 is probably the less stable of the two isomers because of the more crowded environment of its hydroxyl group. This probably means that collapse of the initially formed diradical 36 to 34, which requires very little motion, is faster than the rotation about a carbon-carbon bond required to give the diradical which can collapse to 35. This reasoning has been used before to rationalize stereoselectivity in photochemical cyclobutanol formation⁵³.

The nmr spectra of the cyclobutanols isolated from the photolysis of camphor- d_2 supported the assignment of structures 34 and 35 and the assumption that these compounds were formed from α -campholenic aldehyde. If dideuterated α -campholenic aldehyde (27) were to undergo cyclobutanol formation as described, 6,6-dideutero-34 (37) and 6,6-dideutero-35 should be formed instead of 34 and 35. In fact the deuterated alcohol with the retention time of 34 gave an nmr spectrum very similar to that of 34

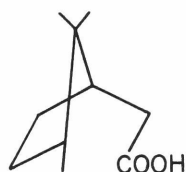


37

itself except that signals for two protons between $\delta 2.4$ and 1.8 were missing and spin-spin splitting was reduced in the deuterated alcohol. Similarly the deuterated alcohol corresponding to 35 gave an nmr spectrum very similar to that of 35 itself, but with

signals for two protons between δ 3.0 and 1.6 missing and spin-spin splitting reduced in the deuterated alcohol. Spin-decoupling experiments on 37 revealed the reason for the characteristic methyl triplets in the nmr spectra of 33, 34, 35, 37, and 6,6-dideutero-35. The methyl group is coupled both to the vinyl proton ($J=1.5$ Hz), and to the allylic bridgehead proton⁵⁵ ($J=2$ Hz), and the resulting two overlapping doublets appear as a triplet.

Thus we have identified all of the products making up more than 1-2% (see footnote on p. 10) of the photolysis product mixtures. Irradiation of camphor might also have been expected⁵⁶ to produce the ketene corresponding to trans-campholanic acid (38), but Quinkert has shown⁵⁷ that less than a 1% yield of 38 is produced when camphor



38

is irradiated in aqueous dioxane. In our irradiation of camphor in ethanol the ethyl ester of 38 may have been produced, but its vpc retention time would have been long, and the resulting small, broad peak could have been missed.

Irradiation of α -Campholenic Aldehyde

We also irradiated α -campholenic aldehyde in 95% ethanol and in n-heptane. The photolysis in ethanol gave mostly a very volatile product (presumably 1,5,5-trimethylcyclopentadiene¹⁴) and also materials with the vpc retention times of 34 and 35. The acetal 10 and the enol ether 8, however, were not produced.

When the aldehyde was irradiated in n-heptane a number of products were detected by vpc (see figure 10). The peaks lettered in figure 10 had the same retention times as the correspondingly

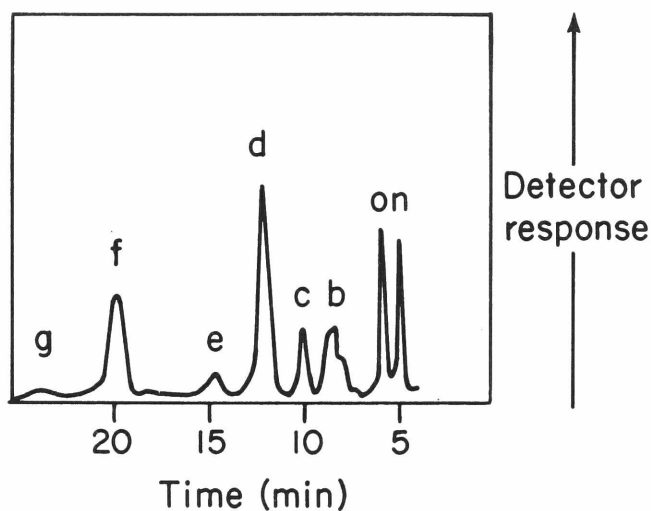


Figure 10

lettered peaks in figure 3. Peaks c, d, f, and g were collected and shown to be the oxetane 36, α -campholenic aldehyde, and the cyclobutanols 34 and 35, respectively. The retention time of enol ether 8 falls between those of peaks o and b, and so this compound would have been seen if it had been present in the product mixture.

These results fully support the conclusion that in our camphor photolyses only α -campholenic aldehyde, enol ether 8, and acetal 10 arise directly from camphor. Oxetane 26 and the cyclobutanols 34 and 35 arise by secondary photolysis of α -campholenic aldehyde.

CONCLUSION

In summary, irradiation of camphor in 95% ethanol or in *n*-heptane produced mainly α -campholenic aldehyde. The oxycarbene 18 was also produced, and reacted with solvent to give the acetal 10 in ethanol and the enol ether 8 in heptane. The formation of an unsaturated aldehyde from camphor is an example of a common ketone photoreaction⁴, while oxycarbene formation has not been observed often^{24, 27-30}

Meinwald and Chapman have shown¹⁴ that photolysis of nor-camphor (39) gives the aldehyde 40 and not the aldehyde 41 analogous to α -campholenic aldehyde. Thus abstraction of γ -hydrogen through a five-membered ring transition state must be more favorable than



39



40



41

abstraction of δ -hydrogen through a six-membered ring transition state. Presumably this would be true in camphor as well, but the γ -hydrogens in camphor are replaced by methyl groups and so the less favorable mechanism can operate to give α -campholenic aldehyde¹⁴

Since Norrish type II cleavage and cyclobutanol formation do not occur in camphor, presumably for steric reasons already discussed, and since aldehyde formation must proceed by a slow mechanism, the oxycarbene formation can be observed.

The oxycarbene could of course be formed by cyclization of the same diradical that forms α -campholenic aldehyde, but it could

also arise by a different route. Wagner has reported⁵⁸ that most of the formation of α -campholenic aldehyde from camphor is not affected by triplet quenchers, and presumably occurs by way of excited singlet camphor. On the other hand our oxycarbene (18) inserts into the O-H bond of ethanol and abstracts hydrogen from n-heptane--reactions previously observed only in triplet diphenylcarbene⁵⁹, triplet benzoylcarbene⁶⁰, and an unspecified state of methylene⁶¹. It seems likely then that triplet oxycarbene 18 is reacting in our experiments. If this is the case then it might be formed from triplet camphor, or alternatively singlet carbene might form from excited singlet camphor and then undergo intersystem crossing to triplet carbene. If 18 does undergo a 1,2-hydrogen shift, this reaction could proceed through singlet 18, since in the case of methylphenylcarbene, it has been shown that³² the singlet is mainly responsible for the 1,2-hydrogen shift observed. Singlet 18 could be imagined to arise either directly from excited singlet camphor or from triplet camphor by way of triplet 18. It may be then that both a singlet and a triplet oxycarbene 18 are reacting in our experiments, but it is not clear how the singlet and triplet 18 are related energetically or what excited state of camphor produces each of them.

Thus a number of questions have been raised by the camphor experiments. What excited state of camphor produces the oxycarbene 18? Does 18 really undergo a 1,2-hydrogen shift? What is the multiplicity of the oxycarbene that produces each of the observed products? What is the ground state of 18?

We hoped to be able to answer some of these questions by studying the photochemistry of 2,2-dimethylcyclobutanone (14). In work mentioned earlier Turro and Southam showed²⁷ that irradiation of 14 in methanol-O-d gave mainly acetal 15, presumably by way of an

oxycarbene analogous to 18. Since 18 was formed in comparable amounts whether camphor was irradiated in ethanol or in heptane, we expected that irradiation of 14 in a hydrocarbon solvent would produce mainly an oxycarbene, just as it had⁷ in methanol. It would be much more convenient to study this oxycarbene than to study 18 itself since 18 is only a minor product of the photolysis of camphor, and so we turned to the work described in part II of this thesis.

EXPERIMENTAL SECTION

Materials and Equipment

Eastman white label (\pm)-camphor was further purified by 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 purified⁶² by shaking successively with: 1) small portions of conc. H_2SO_4 until the acid layer remained colorless, 2) H_2O , 3) 10% aq. 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' x 1/4" stainless steel column packed with 30% FFAP on Chromosorb W. Unless otherwise noted the column oven temperature was $205 \pm 5^\circ$ and the helium carrier gas flow rate was 100 ml/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 watt 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 hrs. An aliquot of the resulting solution was examined by vpc and found to contain enol ether 8 (retention time 6.1 min), minor component b (8.5 min), oxetane 26 (10.0 min), α -campholenic aldehyde (2) (12.0 min), unreacted camphor (1) (14.7 min), cyclobutanol 34 (19.7 min), and cyclobutanol 35 (23.6 min). The ratios 8:b:26:2:34:35 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 (8) The enol ether 8 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, 1H), 4.78 (t, $J=6$ Hz, 1H), 1.6-2.2 (m, 5H), 1.13 (s, 3H), 1.05 (s, 3H), 0.97 (s, 3H); 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 b Infrared: 1721, 1450, 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, ir: 3039, 2710, 1728, 1690 (w) cm^{-1} ; nmr: δ 9.74 (t, $J=1.5$ Hz, 1H), 5.22 (broad, 1H), 2.7-1.7 (m, 5H), 1.60 (m, $J=1$ Hz, 3H), 0.97 (s, 3H), 0.75 (s, 3H); 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 by the method of Meinwald and Chapman¹⁴ 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 (34) The cyclobutanol 34 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, 1H), 4.0 (m, 1H), 3.40 (broad, 1 H), 2.4-1.8 (m, 3H), 1.66 (t, $J=1.5$ Hz, 3H), 1.6 (s, 1H, shifted upfield on dilution; exchanges with D_2O), 0.95 (s, 3H), 0.92 (s, 3H).

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 (35) The minor hydroxylic photoproduct is a colorless oil. Infrared: 3620, 3350 (broad), 3030, 1635, 1050 (s), 850 cm^{-1} ; nmr: δ 5.24 (broad, 1H), 3.85 (m, 1H), 3.34 (s, 1H, shifted upfield on dilution), 3.0-1.6 (4H), 1.62 (t, $J=1.5$ Hz, 3H), 0.96 (s, 3H), 0.91 (s, 3H).

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 10 hours. 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 10 was eluted in the place of minor component b and oxetane 26. The ratios

8:10:2:34:35 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 (10) The acetal 10 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 (ppm downfield from external tetramethylsilane in CCl_4): 4.64 (d, $J=5$ Hz, 0.8H), 3.0-3.92 (XY part of A_3XY system, $J_{AX}=7$ Hz, $J_{BX}=10$ Hz, 1.6H), 1.58-2.33 (m, 6.8H), 0.67-1.33 (m, 12.9H); mass spectrum: m/e 198.1583 (M^+ , 0.5%, calcd for $C_{12}H_{22}O_2$: 198.16197), 153 ($M-45$, 6%), 152 ($M-46$, 16%), 137 ($M-61$, 17%), 109 ($M-89$, 42%), 108 ($M-90$, 100%).

Photolysis of ($^+$)-Camphor in Aqueous Ethanol Using Sunlight

A solution of ($^+$)-camphor (125 g) in 625 ml 95% ethanol and 460 ml distilled water was left in a soft glass flask in full Manhattan sunlight from May 4 until October 19, 1966. The resulting solution was worked up as described for the photolysis of ($^+$)-camphor in 95% ethanol with our mercury lamp. The vpc retention times and relative amounts of the components of the product mixture were the same in this case as those observed in the mercury lamp photolysis. The conversion of camphor to products, however, was only about 3%.

Quantum Yield for α -Campholenic Aldehyde Formation

A solution of ($^+$)-camphor (0.77 g in experiment No. 1 and 0.83 g in experiment 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 hrs 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 actionometry⁶³ 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 experiment No. 1 and 0.38% in No. 2, corresponding to quantum yields of 0.14 ± 0.04 and 0.11 ± 0.03 mole / einstein.

Photolysis of (+)-Camphor in 95% Ethanol-O-d

A solution of 2.5 g of (+)-camphor in 225 ml of 95% ethanol-O-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 (20), 17 mg of enol ether-d (19), and 270 mg of camphor. The nmr spectrum of 20 was as above for 10, 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 19 showed the following signals: δ 4.78 (d, $J=6$ Hz, 1H), 1.6-2.2 (m, 5H), 1.13 (s, 3H), 1.05 (s, 3H), 0.97 (s, 3H). 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-d₂ in n-Heptane

A solution of 3.10 g of (+)-camphor-3,3-d₂³⁷ in 220 ml of n-heptane was photolyzed and the products 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% d₂, 7% d₁, and 2% d₀; enol ether isolated, 16% d₂, 75% d₁, and 9% d₀. The nmr spectrum of recovered camphor was identical to that of starting material. Enol ether nmr spectrum: δ 5.92 (s, 0.73H), 5.0-4.6 (0.05H), 1.5-2.3 (m, 5.0H), 1.13, 1.05, 0.97 (3 singlets, 8.9H). α -Campholenic aldehyde-d₂ (27) nmr spectrum: δ 9.74 (sharp s, 1H), 5.22 (broad, 1H), 2.7-1.7 (m, 3H), 1.60 (m, J

small, 3H), 0.97 (s, 3H), 0.75 (s, 3H). Oxetane- d_2 (28) nmr (ppm downfield from external tetramethylsilane in CCl_4): 4.12 (broad, 2H), 2.12 (m, 1H), 1.88 (broad, 2H), 1.36 (s, 3H), 0.76 (s, 6H). Cyclobutanol $34-d_2$ = 37 nmr (100 Mc, couplings indicated were determined by double resonance experiments): δ 5.20 (H_A , broad, $J_{A,Me} = 1.5$ Hz, $J_{A,B} = 2$ Hz, 1H), 4.02 (H_C , d, $J_{B,C} = 7$ Hz, 1H), 3.40 (H_B , broad m, $J_{B,Me} = 2$ Hz, 1H), 1.95 (H_D , broad d, $J_{B,D} = 5$ Hz, 1H), 1.89 (s, 1H, exchanges with D_2O), 1.65 (Me, t, $J_{A,Me} = 2$ Hz, $J_{B,Me} = 1.5$ Hz, 3H), 0.93 (s, 3H), 0.89 (s, 3H). Cyclobutanol $35-d_2$ nmr: δ 5.21 (broad, 1H), 3.84 (s, 1H), 2.58-3.07 (m, 2H), 2.32 (s, 1H, shifted upfield on dilution, exchanges with D_2O), 1.61 (t, $J = 1.5$ Hz, 3H), 0.96 (s, 3H), 0.92 (s, 3H).

2,2,3-Trimethyl-3-hydroxycyclopentane-1-acetic Acid Lactone (9)

A. By Oxidation of Acetal 10. A solution of 30 mg of acetal 10 in 6 ml of acetone was oxidized at room temperature by adding dropwise 0.30 ml of chromic acid solution²² (2.67 g CrO_3 , 2.3 ml conc. 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 $^\circ$, 170 ml/min). The vpc retention time and ir spectrum of the white, crystalline product were identical to those of authentic lactone 9²³.

B. By Oxidation of Enol Ether 8. A solution of 25 mg of enol ether 8 in 6 ml of acetone was oxidized and worked up as described above for the acetal 10. The vpc retention time and ir spectrum of the white, crystalline product were identical to those of authentic lactone 9²³.

C. Authentic Sample. The lactone was prepared as described by Sauers²³, except that final purification of the lactone was

effected by vpc (215°, 175 ml/min); mp 163-164° (reported^{23a} 172-174°), $[\alpha]_D^{25}$ (CHCl₃) = -47° (reported^{23a} -37°); ir: 1742 (s), 1470, 1445, 1420, 1390, 1375, 1335, 1315 (doublet), 1260 (doublet), 1240, 1215, 1142 (s), 1095, 1045, 1015, 955 cm⁻¹ (reported^{23a} 1745 cm⁻¹ (CHCl₃)); nmr: δ 2.58 (q, J=2 Hz, 1H), 2.37 (d, J=1 Hz, 1H), 2.25-1.67 (m, 5H), 1.25 (s, 3H), 1.05 (s, 3H), 0.99 (s, 3H). In our hands Sauers' procedure^{23a} gave a crude product shown by vpc to contain 9, α -campholide, and camphor. Two recrystallizations from petroleum ether 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' latter report^{23b}.

3,4,4-Trimethylbicyclo [3.2.0] hept-2-en-7-one (33)

A. By Oxidation of cyclobutanol 34. A solution of 19 mg of cyclobutanol 34 in 7 ml of acetone was oxidized as described for acetal 10. The product was purified by vpc. Infrared: 3045, 1781 (s), 1105 (m) cm⁻¹; nmr δ 5.15 (s, 1H), 4.0 (m, 1H), 2.9 (m, 2H), 2.6 (m, 1H), 1.68 (t, J=1.5 Hz, 3H), 1.12 (s, 3H), 1.07 (s, 3H); uv: λ_{\max} 287nm (sh) (ϵ 96), 298 (150), 307 (160), 316 (110) (isooctane); mass spectrum: m/e 150.1038 (M⁺, 2.9%, calcd for C₁₀H₁₄O: 150.1045), 108 (M-42, 100%), 93 (M-57, 59%).

B. By Oxidation of cyclobutanol 35. A solution of 16 mg of cyclobutanol 35 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 33.

Reduction of Cyclobutanone 33 with Sodium Borohydride

A solution of NaBH₄ (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 hrs 1 ml of water was

added and the solution refluxed for 1 hr, the 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 34 and 2% cyclobutanol 35. Compound 34 was identified by vpc retention time and ir spectrum, and 35 by vpc retention time only.

Reduction of Cyclobutanone 33 with Sodium in Ethanol

Sodium (168 mg) was added over an hour to a solution of cyclobutanone 33 (26 mg) in 1 ml of 95% ethanol under nitrogen at room temperature. The reaction mixture was diluted with water, acidified with conc. 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 34 and 16% cyclobutanol 35. The cyclobutanols were identified by vpc retention times and ir spectra.

Photolysis of α -Campholenic Aldehyde in 95% Ethanol

A solution of ($^+$)- α -campholenic aldehyde (360 mg) in 450 ml 95% ethanol was irradiated under nitrogen for 10 hrs, worked up as described for the photolysis of camphor in 95% ethanol, and the product mixture was analyzed by vpc. Peaks with the retention times of cyclobutanols 34 and 35 were observed, but no enol ether 8 or acetal 10 could be detected. It is estimated that 15-20% of the amount of 8 or 10 produced when 416 mg of ($^+$)-camphor was irradiated under nitrogen for 10 hrs could have been detected.

Photolysis of α -Campholenic Aldehyde in n-Heptane

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 hrs. An aliquot of the resulting solution was examined by vpc and found

to contain components n (retention time 4.8 min), o (5.6 min), b (8.2 min), the oxetane 26 (9.8 min), α -campholenic aldehyde (2) (11.9 min), e (14.4 min), cyclobutanol 34 (19.4 min), and cyclobutanol 35 (23.5 min). The ratios of peak areas n:o:b:26:2:e:34:35 were 10:12:11:7:29:6:22:3. 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, 34, and 35 were identified by vpc retention times and ir spectra.

6,6,7-Trimethyl-2-oxatricyclo [3.2.1.0^{3,7}] octane (26) The oxetane 26 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 (ppm downfield from external tetramethylsilane in CCl_4): 4.10 (broad, 2H), 2.14 (m, 1H), 1.90 (broad, 4H), 1.38 (s, 3H), 0.78 (s, 6H); mass spectrum: m/e 152.1186 (M^+ , 3%, calcd for $\text{C}_{10}\text{H}_{16}\text{O}$: 152.1201), 109 (M-43, 31%), 108 (M-44, 100%).

Lithium Aluminum Hydride Reduction of Oxetane 26

Pure oxetane 26 (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 hrs. The reaction was quenched with water, acidified with dilute HCl, 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 ir 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 hrs 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 Karrer⁶⁴. 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 hrs 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): 3000-2500 (broad), 2655 (s), 1722 (s), 1405, 1235, 1205, 1145, 1110 cm⁻¹.

Anal. Calcd for C₁₁H₂₂NO₂Cl: 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-carboxylic Acid (7)

A solution of 472 mg of the above amine hydrochloride and 336 mg of NaHCO₃ in water was evaporated to dryness and the residue treated with 3 ml of 30% H₂O₂ and then heated 11 hrs at 44-45°. Another 3 ml of H₂O₂ was added and heating continued for another 14 hrs. Evaporation to dryness gave a residue which was pyrolyzed at 145-150°/15mm for 30 min. The residue was dissolved in water, extracted twice with ether, acidified with conc. HCl, and extracted twice with ether. The latter ether extracts were dried over Na₂SO₄ and evaporated to dryness to yield 125 mg (41%) of yellowish, crystalline material which was purified by vpc, mp 157-159.5° (reported⁶⁵ 152-154°); Infrared (KBr): 3400-2500, 1700 (s), 1620, 1280, 715 cm⁻¹; nmr δ12.3 (s, 1H), 5.52 (m, 1H), 5.30 (m, 1H), 3.18 (d, J=16 Hz, 1H), 1.27 (s, 3H), 1.15 (s, 3H), 1.02 (s, 3H).

Anal. Calcd for C₉H₁₄O₂: C, 69.70; H, 9.10. Found: C, 70.05; H, 8.95.

1,2,2-Trimethylcyclopent-3-enyl Methyl Ketone (5)

A solution of 7 (114 mg) in 5 ml of dry ether under nitrogen was treated with 2.0 ml of 1.88 M methyllithium in ether¹⁶. After 3.5 hrs at room temperature the reaction was quenched with water. The phases were separated and the ether layer 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 $77-78^\circ$; ir (CCl_4): 3050, 1701 (s), 1616, 1455, 1350 (multiplet), 712 cm^{-1} ; (CHCl_3): 3010, 1698 (s), 1620, 1455, 1350 (multiplet) cm^{-1} ; uv (95% ethanol): λ_{max} 285.5 nm (ϵ 22); nmr: δ 5.55 (m, 1H), 5.27 (m, 1H), 3.11 (broad d, $J=17\text{ Hz}$, 1H), 2.09 (s, 3H), 1.91 (broad d, $J=17\text{ Hz}$, 1H), 1.16 and 1.14 (overlapping singlets, 6H), 0.86 (s, 3H); mass spectrum: m/e 152 (M^+ , 28%), 137 (12%), 109 (100%), 95 (14%), 81 (15%), 67 (34%), 56 (14%), 43 (62%).

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

A semicarbazone was prepared, mp $191-193^\circ$ (dec), from methanol.

Anal. Calcd for $\text{C}_{11}\text{H}_{17}\text{N}_3\text{O}$: 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.

Methyl 3-Dimethylamino-1,2,2-trimethylcyclopentane-1-carboxylate Methiodide

Methyl 3-Amino-1,2,2-trimethylcyclopentane-1-carboxylate was

prepared by Fischer esterification of 3-amino-1,2,2-trimethylcyclopentane-1-carboxylic acid hydrochloride as described by Faigle and Karrer⁶⁴. The aminoester and methyl iodide (2 equiv) were heated at reflux in methanol⁶⁶ for 30 min and then cooled. Sodium methoxide (1 equiv) was added and refluxing was resumed for 30 min before the solution was cooled again. Addition of methyl iodide (2 equiv) again, refluxing 30 min, addition of sodium methoxide (1 equiv), refluxing for 1 hr, and evaporation of the solvent gave a residue which was extracted several times with boiling CHCl_3 . Evaporation of the extracts gave a 95% yield of crude methiodide which was recrystallized from acetone, mp $260-261^\circ$ (dec); ir (KBr): 1720 (s), 1280, 1245 cm^{-1} ; nmr (D_2O , ppm downfield from external tetramethylsilane): 3.92 (m, 1H), 3.72 (s, 3H), 3.20 (s, 9H), 2.48-1.53 (m, 4H), 1.47 (s, 3H), 1.24, 1.12 (two s, 6H).

Anal. Calcd for $\text{C}_{13}\text{H}_{26}\text{NO}_2\text{I}$: C, 43.95; H, 7.38; N, 3.95. Found: C, 44.02; H, 7.30; N, 4.09.

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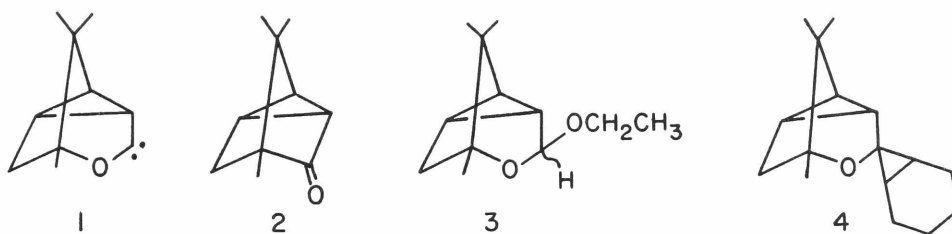
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II. SYNTHESIS AND SOLUTION PHOTOCHEMISTRY OF 2,2-DIMETHYLCYCLOBUTANONE

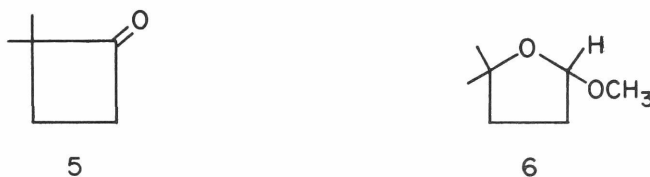
INTRODUCTION

In 1964 Yates and Kilmurry reported¹ the first case of photochemical formation of an oxycarbene (1) from a saturated cyclic ketone. Irradiation of cyclocamphanone (2) in ethanol gave 3 as the major product. The intermediacy of the oxycarbene 1 was inferred



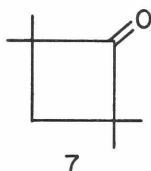
from the structure of 3 and was supported by the results of a later experiment² in which 2 was irradiated in cyclohexene. This reaction yielded a 1:1 adduct of 1 and cyclohexene which was shown to have the expected³ cyclopropane structure 4.

During the following three years it was found that a number of cyclobutanones undergo a reaction analogous to the transformation of 2 into 3⁴⁻⁷. Irradiation of 2,2-dimethylcyclobutanone (5) in methanol, for instance, gave a 41% yield of the α -alkoxytetrahydrofuran 6^{*}. An extensive study by Turro and Southam showed⁴ that

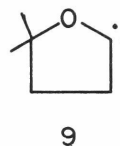
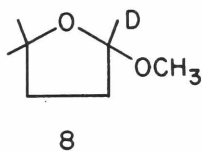


* Under these conditions 5 also underwent fragmentation to isobutylene and ketene in 32% yield, and to 1,1-dimethylcyclopropane in 7% yield⁴.

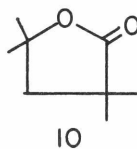
cyclobutanones generally yield products of this type on irradiation in methanol, and that this reaction is favored by increasing alkyl substitution on the α -carbon atoms. For example cyclobutanone itself gives only an 8% yield of an α -alkoxytetrahydrofuran while 2,2,4,4-tetramethylcyclobutanone (7) gives a 68% yield of this type of product.



Turro and Southam found⁴ that irradiation of 2,2-dimethylcyclobutanone (5) in methanol- $O\text{-}d$ gave the acetal 8, which can be viewed as the product of insertion⁸ of carbene 9 into the $O\text{-}D$ bond of methanol- $O\text{-}d$. They also found⁴ that irradiation of the cyclobutanone 7 in benzene in the presence of oxygen produced the lactone 10--the product

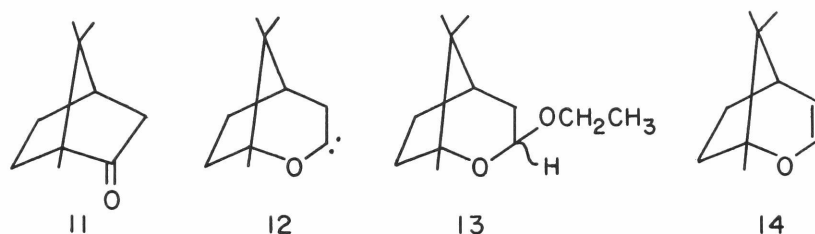


expected⁹ if the carbene analogous to 9 were formed from 7 and reacted with oxygen. These observations supported the idea that



the acetals produced on irradiation of cyclobutanones in alcohols are formed by way of carbenes analogous to 1.

In part I of this thesis we showed that camphor (11) also undergoes a reaction analogous to the conversion of cyclocamphanone into the acetal 3. Irradiation of 11 in ethanol produced a small amount of the oxycarbene 12, which was trapped by ethanol as the acetal 13. We also found that irradiation of camphor in heptane yielded the enol ether 14 instead of 13, and our deuterium



labelling experiments indicated that 14 was formed from 12 by two distinct mechanisms as shown in figure 1. About 29% of the enol ether was apparently formed from 12 by the expected¹⁰ 1,2-hydrogen shift, but the rest was formed by a mechanism involving hydrogen abstraction from the solvent.

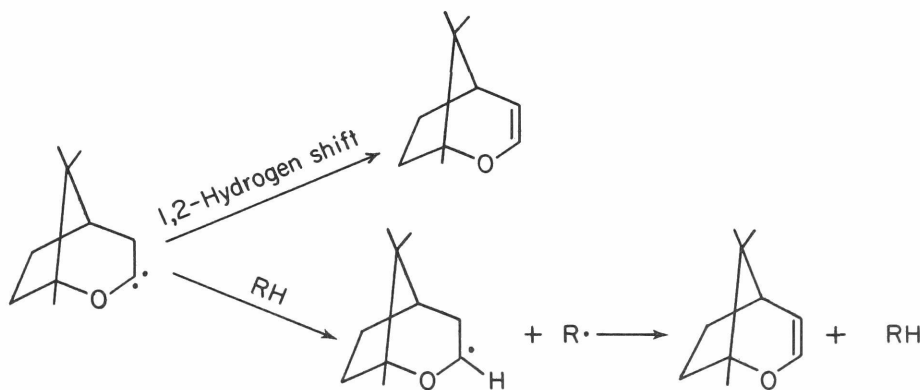
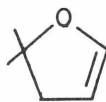


Figure 1

Neither formation of an enol ether from an oxycarbene nor duality of mechanism in olefin formation by a carbene had been observed before our work with camphor, and we were interested in studying these reactions in more detail. The small amounts of enol ether formed on irradiation of camphor in heptane made studies of its formation quite laborious, however, and so we hoped to carry out our experiments in a more convenient system.

The requirements for such a system are that irradiation of a saturated, cyclic ketone in a hydrocarbon solvent give an oxycarbene as the major product, and that the oxycarbene have at least one α -hydrogen so that an enol ether can be formed.

2,2-Dimethylcyclobutanone (5) appeared to satisfy these requirements. The photochemistry of 5 in hydrocarbon solvents had not been reported, but since irradiation of camphor in ethanol or in heptane gave comparable amounts of oxycarbene 12, and irradiation of 5 in methanol produced mainly oxycarbene 9, it seemed reasonable to expect that irradiation of 5 in a hydrocarbon solvent would also produce mainly 9. If 9 were formed in a hydrocarbon solvent, and if it reacted in the same way as 12, the enol ether 15 would be formed. A simple synthesis of this compound is known¹¹, and so it would be straightforward to determine whether or not it were formed on irradiation of 5.



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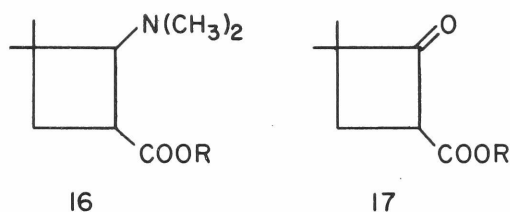
The only apparent shortcoming of our plan to study the photochemistry of 5 was that this compound was not commercially available and the only reported syntheses of it^{12,13} were inconvenient. One of these involves¹² addition of dimethylketene to ethylene and requires special equipment to carry out the reaction at 200 atmospheres pressure, while the other involves¹³ addition of diazomethane to dimethylketene and gives a difficultly separable mixture of the major product, 3,3-dimethylcyclobutanone, and the desired minor product 5.

The following section will describe our development of a new and convenient synthesis of 2,2-dimethylcyclobutanone (5), and the results of irradiating 5 in pentane and in methylene chloride.

RESULTS AND DISCUSSION

Synthesis of 2,2-Dimethylcyclobutanone¹⁴

The cycloaddition of isobutyraldehyde dimethylenamine to methyl acrylate is known¹⁵ to produce the aminoester 16a. We reasoned that if the amino function of 16a could be oxidized to produce the β -ketoester 17a, this ester could then be hydrolyzed to the corresponding β -ketoacid and then decarboxylated to the desired product, 2,2-dimethylcyclobutanone (5). Alternatively, the



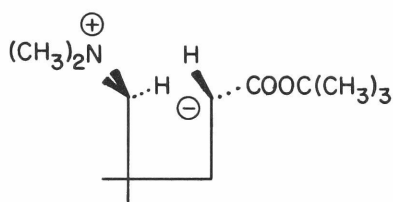
a, R = CH₃

b, R = C(CH₃)₃

cycloaddition of isobutyraldehyde dimethylenamine to t-butyl acrylate should give the aminoester 16b. Oxidation of the amino group to give 17b followed by thermal elimination of isobutylene and decarboxylation¹⁶, would also give 5. In fact the latter route is highly successful. It requires four steps to convert commercially available materials into 5, but the steps can be carried out with little purification of intermediates, and the overall yield is quite good (49%). This synthesis requires no special equipment, and a simple distillation of the crude product gives pure 5.

Heating t-butyl acrylate and isobutyraldehyde dimethylenamine together in acetonitrile, gave a 63% yield of 16b without difficulty.

The ir spectrum and microanalytical data for this compound were consistent with the assigned structure. The nmr spectrum showed sharp singlets for the N,N-dimethyl group, the *t*-butoxyl group, and each of the methyl groups on the four-membered ring, indicating that only one stereoisomer of 16b had been formed. If this cycloaddition proceeds in two steps as other additions of enamines to α,β -unsaturated carbonyl compounds are thought to do¹⁷, the zwitterion 18 would be formed initially and then would cyclize to 16b. If the bulky carbo-*t*-butoxy and N,N-dimethylamino groups of

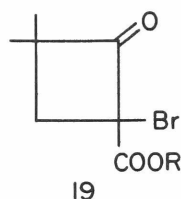


18

18 remained as far as possible from one another as the four-membered ring closed (as shown in 18), the trans isomer of 16b would be produced. In fact the repulsion of the two bulky groups is apparently great enough to cause the exclusive formation of trans 16b.

With 16b in hand we turned to the problem of converting this tertiary amine to the ketoester 17b. Zimmerman and coworkers have synthesized several ketones by oxidizing the corresponding tertiary amines with sodium tungstate and hydrogen peroxide¹⁸, but long reaction times were required and the yields were only about 50%. An alternative to this method was suggested by the results of a general study by Deno and Fruit¹⁹ showing that some simple tertiary amines, dissolved in an acetate buffer, can be oxidized to carbonyl compounds in good yield with bromine. This method,

which had not been used synthetically before*, served our purposes beautifully. Addition of bromine to a solution of 16b in an acetate buffer (pH 6) gave an 88% yield of the bromoketoester 19b. The assignment of structure 19b to the product of this reaction is supported



a, $R = \text{CH}_3$

b, $R = \text{C}(\text{CH}_3)_3$

by its elemental analysis, ir absorption at 1798 cm^{-1} (α -bromocyclobutanone²²) and 1725 cm^{-1} (t-butyl ester²³), and its very simple nmr spectrum showing only a singlet for the t-butoxyl group, two singlets for the methyl groups on the four-membered ring, and an AB quartet ($J=13.5 \text{ Hz}$) for the protons of the methylene group.

The conversion of 19b into the desired ketoester 17b was effected quantitatively by treatment with zinc dust in acetic acid. The structure of 17b was also clear from its elemental analysis, ir absorption at 1780 cm^{-1} (cyclobutanone²²) and 1724 cm^{-1} (t-butyl ester²³), and its very simple nmr spectrum showing a doublet of doublets at $\delta 4.10$ for the proton α to both of the carbonyl groups, a multiplet at $2.40\text{--}1.7$ for the methylene group, a singlet for the t-butoxyl group, and a fortuitous singlet for the methyl groups on the four-membered ring.

When 17b was heated to 138° with a catalytic amount of p-toluenesulfonic acid¹⁶, a single product distilled out of the reaction

*Other methods which have been reported for converting tertiary amines to the corresponding²⁰ carbonyl compounds are oxidations with neutral permanganate²⁰ and with nitrous acid²¹. These methods have not yet found synthetic applications.

mixture in 91% yield. This product was shown to be 2,2-dimethylcyclobutanone (5) by the identity of its ir and nmr spectra and the mp of its 2,4 dinitrophenylhydrazone with those reported^{12,13} for 5.

We also attempted to convert the aminoester 16a to 2,2-dimethylcyclobutanone by the route suggested earlier. The bromine oxidation¹⁹ of 16a gave the bromoketoester 19a in acceptable yield. The structure of this product was apparent from its microanalysis and ir and nmr spectra. Since the spectra are very similar to those of 19b, they will not be discussed here. In contrast to the oxidation of 16b to 19b, however, the oxidation of 16a to 19a produced variable amounts (usually 5-15%) of a side product. The side product was purified and its structure was proved to be 20 by Agosta¹⁴. This compound probably arises by hydrolysis of 19a

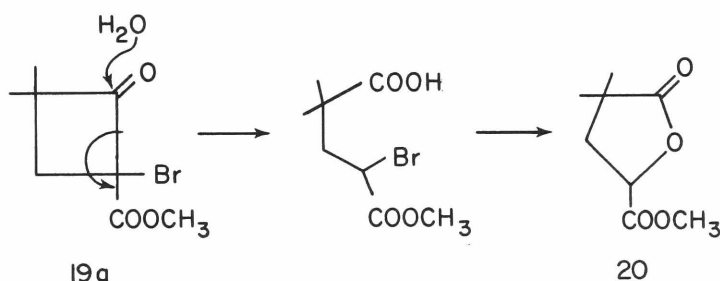


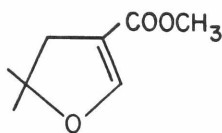
Figure 2

(as shown in figure 2) under the reaction conditions. The formation of 20 in this reaction, below room temperature and in only slightly acidic solution, illustrates the readiness of this four-membered ring system to open.

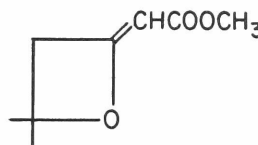
Treatment of crude 19a from the bromine oxidation of 16a with zinc dust in acetic acid produced 17a in about 46% yield. The ir and nmr spectra of this product, which are very similar to those already discussed for 17b, fully support the assignment of structure 17a. In addition, the 2,4-dinitrophenylhydrazone gave the correct microanalysis, and its melting point agreed with that reported²⁴ for this derivative prepared directly from the dimethylenamine of 17a.

Unlike the reduction of the corresponding *t*-butyl bromoketoester this reduction of crude 19a gave about 10% of a side product, which was purified by vpc. The elemental analysis of the side product indicated the empirical formula $C_8H_{12}O_3$, and the ir spectrum showed C=O stretching at 1710 cm^{-1} and the strong C=C stretching characteristic of an enol ether²⁵ at 1625 cm^{-1} . The uv spectrum showed a maximum at 253.5 nm ($\epsilon\ 1.1 \times 10^3$), which²⁶, combined with the position of the C=O stretching frequency in the ir spectrum suggested that the compound is an α,β -unsaturated ester. The nmr spectrum revealed still more of the structure. There was only one vinyl proton signal, which appeared as a triplet ($J=1.5\text{ Hz}$) at quite low field (6.98 ppm). Two protons which appeared as a doublet ($J=1.5\text{ Hz}$) at 2.53 were clearly coupled to the vinyl proton since the only other signals in the spectrum were two singlets -- one for methoxyl at 3.56 and one for a pair of methyl groups at 1.32. The chemical shift of the protons at 2.53 is consistent with their being allylic protons²⁷, and the 1.5 Hz coupling constant is of the usual magnitude for allylic coupling²⁷. Thus the data suggest our side product to be an enol ether and an α,β -unsaturated ester. A methylene group is allylic to the sole vinyl proton, and the molecule contains two methyl groups on carbon which are probably equivalent.

The only structures that meet these requirements are 21 and 22. However any structure proposed for the side product must account for the appearance of the vinyl proton in its nmr spectrum at 6.98 ppm. In 21 the vinyl proton could be at such low field because it is the β -vinyl proton of an α,β -unsaturated ester²⁸ and



21



22

the α -proton of a vinyl ether²⁹. On the other hand it is unlikely that the vinyl proton of 22 would occur at such low field. The β -protons of vinyl ethers actually appear at higher field than simple vinyl protons²⁹, while the α -vinyl proton of an α,β -unsaturated ester usually appears at about 5.8 ppm²⁸.

This analysis of the data favored structure 21 for the side product, and in fact the vpc retention time and ir, uv and nmr spectra of the side product were found to be identical with those of an authentic sample* of 21.

Neither pure bromoketoester 19a nor pure lactone 20 produced any 21 on treatment with zinc dust in acetic acid, so some other product of the bromine oxidation of 16a must be converted into 21.

*We thank Professor Friedhelm Korte and Dr. Heinrich Wamhoff, University of Bonn, for generous samples of both 21 and the corresponding carboxylic acid.

We have not isolated this precursor of 21, but suggest that if 23 were formed in the bromine oxidation it is plausible that it would be converted into 21 by zinc and acetic acid as shown in figure 3.

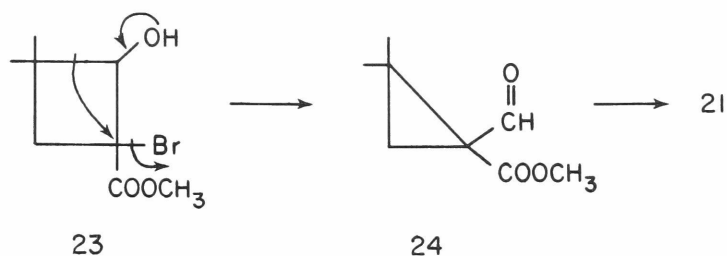
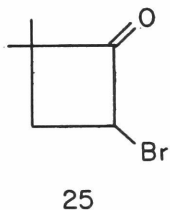
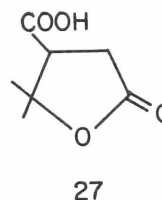
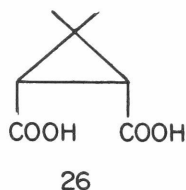


Figure 3

Ring contraction of 23 to give 24 could occur easily in view of the readiness of the parent bromoketone 25 to undergo the analogous Favorskii rearrangement¹³. The acid catalyzed rearrangement of 24



to give 21 is mechanistically reasonable, and has precedent in the acid catalyzed rearrangement³¹ of 26 to 27. The aldehyde 24 itself is probably not the precursor of 21 which forms in the bromine oxidation, since the nmr spectrum of a fraction of the bromine oxidation product which gave a 10% yield of 21 showed no signal for an aldehyde proton.



Our plans to convert the methyl ketoester 17a into 2,2-dimethylcyclobutanone required that mild hydrolysis of 17a give the corresponding carboxylic acid, but in fact the cyclobutane ring opened faster than the ester could be hydrolyzed. When 17a was treated with one equivalent of sodium bicarbonate in aqueous methanol at room temperature, only the dimethyl and monomethyl esters of 2,2-dimethylglutaric acid were produced. Similarly, treatment of 17a with 6 M hydrochloric acid, under conditions which according to an early report³² caused simple ester hydrolysis and decarboxylation of a carbethoxycyclobutanone, gave only ring opening. This result is consistent with a report in the more recent literature²⁴.

Thus our experiments with the methyl esters 16a, 19a, and 17a did not provide a convenient route to 2,2-dimethylcyclobutanone, but did provide useful information about the reactivity of these compounds. The greater success of our experiments with the corresponding t-butyl esters is probably due to two factors. First, of course, the troublesome ester hydrolysis step could be omitted altogether in the t-butyl series. Second, the bromine oxidation of the t-butyl ester 16b did not give side products such as those observed in the methyl series. This result can be understood by considering that formation of either the lactone side product 20 or the presumed alcohol side product 23 requires attack by water on the cyclobutane ring. The t-butyl group would sterically hinder

this attack more than the methyl group, and would also make the t-butyl compounds less accessible to water by decreasing their water solubility.

Photolysis of 2,2-Dimethylcyclobutanone

The enol ether 15 was prepared without difficulty by an established procedure¹¹, and vpc conditions were chosen which cleanly separated 2,2-dimethylcyclobutanone (5), enol ether 15, and each of the solvents in which photolyses were carried out.

When a solution of 5 in pentane was irradiated until 74% of the starting material had been destroyed, none of the enol ether 15 was produced. The only products detected by vpc were much more volatile than 15, being eluted very near pentane. It is likely that these volatile products are isobutylene, ketene, and 1,1-dimethylcyclopropane, since Turro and Southam observed⁴ the formation of these compounds when 5 was irradiated in methanol.

A very similar result was obtained when a solution of 5 in methylene chloride was irradiated until 53% of the starting material had been destroyed. In this case the only products detected by vpc were three which were eluted very rapidly, and a small amount (about 3% conversion) of material with the retention time of enol ether 15.

CONCLUSION

Although irradiation of 2,2-dimethylcyclobutanone (5) in methanol yields⁴ mainly the acetal derived from oxycarbene 9, irradiation of 5 in pentane or in methylene chloride yields little or none of the enol ether 15. There are two possible explanations for this result. If appreciable yields of 9 are simply not produced when 5 is irradiated in pentane or methylene chloride, then the change in solvent from pentane to methanol must increase the quantum efficiency of oxycarbene formation relative to that of the fragmentation reactions of 5. If on the other hand appreciable yields of 9 are produced on irradiation of 5 in pentane or methylene chloride then 9 does not react to form enol ether 15.

A scheme illustrating the second possibility is shown in figure 4. If the diradical 28 and the oxycarbene 9 were rapidly interconvertible, and if fragmentation of the diradical were much

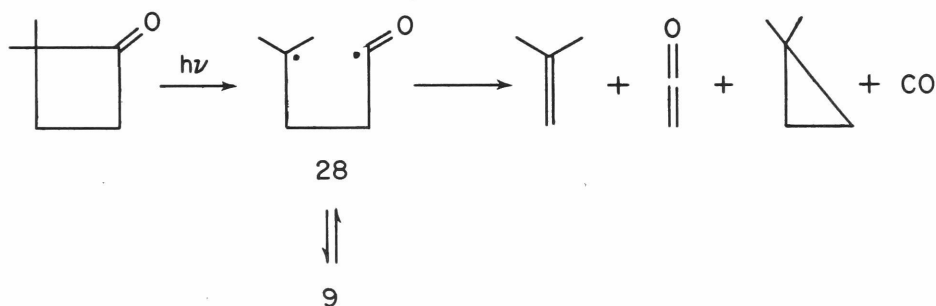
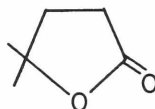


Figure 4

faster than reaction of the carbene with pentane, only the very volatile fragmentation products would be observed on irradiating 5 in pentane. On the other hand if fragmentation of the diradical were not so fast as reaction of the carbene with methanol, irradiation of 5 in methanol would produce mainly the acetal derived from oxycarbene 9. We have not yet done an experiment to test this scheme, but one such experiment which could be done involves irradiating 5 in pentane in the presence of some trapping agent which would react with 9 very rapidly but would not greatly change the polarity of the solvent. Oxygen is an attractive candidate for this trapping agent, since it is known to react rapidly with a number of carbenes⁹ to give the corresponding carbonyl compounds. Reaction of oxycarbene 9 with oxygen would be expected⁹ to give the lactone 29, which could be prepared independently by Jones



29

oxidation³³ of enol ether 15. If the quantum yield for formation of 29 from 5 in pentane saturated with oxygen were higher than the quantum yield for formation of 15 from 5 in pentane saturated with nitrogen, the scheme outlined in figure 4 would be supported. Unfortunately failure of the experiment to give this result would not be very informative. Oxygen might simply quench some excited species on its way to 9. There is also evidence that⁹ only triplet carbenes react with oxygen, so 9 might even be formed and fail to react with oxygen. Since Turro

and Southam did observe⁴ formation of lactone 10 on irradiation of cyclobutanone 7 in the presence of oxygen, however, there is some reason to expect a positive result in this experiment.

Whether or not this experiment indicates that the oxycarbene 9 is actually formed on irradiation of 2,2-dimethylcyclobutanone (5) in pentane, the photochemistry of 5 contrasts sharply with that of camphor. If 9 is produced in pentane then it fails to form enol ether 15, while the oxycarbene 12 derived from camphor forms enol ether 14 in heptane. On the other hand if 9 is not produced in pentane then its formation from 5 is much more sensitive to a change of solvent than is the formation of 12 from camphor.

Thus instead of providing us with an opportunity to study hydrogen abstraction and hydrogen shift reactions similar to those of the oxycarbene derived from camphor, our experiments with 2,2-dimethylcyclobutanone have challenged us to explain an unexpected contrast between the photochemistry of 5 and that of camphor.

EXPERIMENTAL SECTION

Materials and Equipment

Isobutyraldehyde dimethylenamine (N,N-dimethylisobutenylamine, K and K Laboratories), methyl acrylate (practical, Matheson, Coleman, and Bell) and t-butyl acrylate (Borden Chemical Co., Monomer-Polymer Laboratories) were used without further purification. Pentane and methylene chloride used for the photolyses were Matheson, Coleman, and Bell Spectroquality solvents. Vpc was carried out using a Varian Aerograph Model 700 Autoprep with a 20 ft. x 0.25 in stainless steel column packed with 30% FFAP on Chromosorb W, and unless otherwise noted operated at 180° with a helium carrier gas flow rate of 100 ml/min. Irradiations were carried out using a Hanovia model L 450 watt high pressure mercury lamp with a Pyrex filter. Unless otherwise noted both ir and nmr spectra were obtained for CCl₄ solutions, the former on a Perkin-Elmer 237B spectrophotometer and the latter on a Varian A-60 spectrometer. Distillations were carried out under nitrogen.

t-Butyl 2-(Dimethylamino)-3,3-dimethylcyclobutanecarboxylate (16b)

t-Butyl acrylate (16.25 g), isobutyraldehyde dimethylenamine (34.10 g), and 40 ml acetonitrile were heated at reflux under nitrogen for 54 hrs. Acetonitrile and excess enamine were removed by distillation at atmospheric pressure and the remainder was distilled at reduced pressure to give 18.06 g (63%) of product, bp 45-47°/0.08mm; ir 2855, 2805, 2760, 1725 (s), 1365, 1145 cm⁻¹; nmr δ 2.72-2.18 (m, 3H), 2.02 (s, 6H), 1.70 (m, 1H), 1.41 (s, 9H), 1.12, 1.06 (two s, 6H).

Anal. Calcd for C₁₃H₂₅O₂N: C, 68.68; H, 11.08; N, 6.16. Found C, 68.54; H, 11.37; N, 6.05.

Methyl 1-Bromo-2-oxo-3,3-dimethylcyclobutanecarboxylate (19a)

Amino ester 16a¹⁵ (21.7 g) was dissolved in 600 ml of 2.0 M acetate buffer (pH 6). Bromine (43 g) was added dropwise with mechanical stirring and cooling below room temperature. Excess bromine was destroyed with solid NaHSO_3 about 15 min after bromine addition was complete, and the reaction mixture was extracted with ether. The ether extracts were washed with 0.5 M HCl, 0.6 M NaHCO_3 , water, and brine, and dried over Na_2SO_4 . Evaporation of ether gave 17.3g (63%) crude product, which was distilled; bp $46-48^\circ/0.1\text{mm}$; mp $31-33^\circ$; ir 1801 (s), 1730 (s), 1430, 1250 (s), 1120, 1000 cm^{-1} ; nmr δ 3.80 (s, 3H), 3.00 (d, $J=13\text{ Hz}$, 1H), 2.28 (d, $J=13\text{ Hz}$, 1H), 1.44 (s, 3H), 1.26 (s, 3H).

Anal. Calcd for $\text{C}_8\text{H}_{11}\text{O}_3\text{Br}$: C, 40.87; H, 4.72. Found C, 41.13; H, 4.78.

t-Butyl 1-Bromo-2-oxo-3,3-dimethylcyclobutanecarboxylate (19b)

t-Butyl aminoester 16b (32.9 g) was oxidized as described above for 16a to give 35.13 g (88%) crude product, which from nmr analysis contained very little impurity (no absorption below 3.1 ppm). Distillation gave an analytical sample: bp $71-73^\circ/0.5\text{ mm}$; ir 1798 (s), 1775 (m), 1725 (s), 1370 (s), 1255 (s), 1160 (s); nmr δ 2.92 (d, $J=13.5\text{ Hz}$, 1H), 2.22 (d, $J=13.5\text{ Hz}$, 1H), 1.48, 1.42 (two s, 12H), 1.25 (s, 3H).

Anal. Calcd for $\text{C}_{11}\text{H}_{17}\text{O}_3\text{Br}$: C, 47.66; H, 6.18. Found: C, 47.76; H, 6.24.

Methyl 3,3-Dimethyl-2-oxocyclobutanecarboxylate (17a)

A solution of slightly impure bromoketoester 19a (671 mg, bp $72-87^\circ/2.0\text{mm}$) in 25 ml glacial acetic acid was chilled in an ice bath. Zinc dust (1.0 g) was added with vigorous stirring and the mixture was allowed to come to room temperature as the stirring continued for 30 min. The mixture was filtered and the excess zinc washed

with ether and water. The resulting solution was extracted with ether, and the ether extracts washed with water, 0.6M NaHCO_3 , water, brine and were dried over Na_2SO_4 . Evaporation of ether gave 340 mg (76%) of crude ketoester contaminated with about 5% of dihydrofuran 21; ir 1795 (s), 1735 (s), 1315, 1205, 1170 cm^{-1} ; nmr (ppm downfield from external tetramethylsilane in CCl_4): 4.12 (dd, $J_1=10$ Hz, $J_2=6.5$ Hz, 1H), 3.68 (s, 3H) 2.30-1.75 (m, 2H), 1.20 (s, 6H). When analytically pure bromoketoester was reduced, no 21 was formed.

A 2,4-dinitrophenylhydrazone was prepared for analysis; mp $132-133^\circ$ from methanol (lit mp²⁴ $128.5-130^\circ$); nmr (CDCl_3 ; ppm downfield from external tetramethylsilane in CHCl_3): 11.4 (broad s, 1H), 8.95 (d, $J=2$ Hz, 1H), 8.20 (dd, $J_1=9$ Hz, $J_2=2$ Hz, 1H), 7.80 (d, $J=9$ Hz, 1H), 4.23 (dd, $J_1=10$ Hz, $J_2=6$ Hz, 1H), 3.84 (s, 3H), 2.24-1.93 (m, 2H), 1.33 (s, 6H).

Anal. Calcd for $\text{C}_{14}\text{H}_{16}\text{O}_6\text{N}_4$: C, 49.99; H, 4.80; N, 16.66. Found: C, 49.80; H, 4.97; N, 16.91.

Methyl 4,5-Dihydro-5,5-dimethyl-3-furoate (21)

Reduction of crude bromoketoester 19a with zinc dust always gave 5-15% of dihydrofuran 21. Preparative vpc destroyed the ketoester but gave pure 21 (ret. time 24 min.); ir 1710 (s), 1625 (s), 1175, 1090 cm^{-1} ; nmr (ppm downfield from external tetramethylsilane in CCl_4): 6.98 (t, $J=1.5$ Hz, 1H), 3.56 (s, 3H), 2.53 (d, $J=1.5$ Hz, 2H), 1.32 (s, 6H); uv (CH_3OH) λ_{max} 253.5 nm (ϵ 1.1×10^3).

Anal. Calcd for $\text{C}_8\text{H}_{12}\text{O}_3$: C, 61.52; H, 7.74. Found: C, 61.61; H, 7.56.

The vpc retention time and ir, uv, and nmr spectra of this material were identical with those of an authentic sample³⁰.

Hydrolysis of Methyl 3,3-Dimethyl-2-oxocyclobutanecarboxylate (17a)

A. Basic Hydrolysis Ketoester 17a (4.74 g) was stirred at room temperature under nitrogen for 23 hr with 20 ml of methanol, 60 ml of water, and 2.90 g (1.1 equiv) NaHCO_3 . The reaction mixture was diluted with water and extracted with ether. The ether extracts were washed with water, dried over Na_2SO_4 , and evaporated to give 2.04 g of colorless oil, ir and nmr spectra identical with those of authentic dimethyl 2,2-dimethylglutarate. Acidification of the reaction mixture followed by ether extraction gave 2.70 g of colorless oil; ir 3300-2700 (broad), 1740 (s), 1701 (s); nmr (ppm downfield from external tetramethylsilane in CCl_4): 10.4 (s, 1H), 3.57 (s, 3H), 2.47-1.67 (m, 4H), 1.17 (s, 6H). Esterification of this material with diazomethane gave dimethyl 2,2-dimethylglutarate.

B. Acidic Hydrolysis The ketoester 17a (820 mg) was heated at reflux with 1.6 ml of 6 M HCl for 1.5 hr and the reaction mixture extracted with ether. The ether extracts were washed with water and brine and dried over Na_2SO_4 . Evaporation of ether gave 746 mg of crude brown oil; ir 3400-2400 (broad), 1735 (w), 1710 (s). There was no cyclobutanone carbonyl absorption.

t-Butyl 3,3-Dimethyl-2-oxocyclobutanecarboxylate (17b)

t-Butyl bromoketoester 19b (5.93 g) was reduced as described above for 19a to give 4.31 g (100%) of crude product which showed no impurities in its nmr spectrum. Distillation gave analytically pure material; bp $80.2^\circ/2.8$ mm; ir 1780 (s), 1724 (s), 1365 (m), 1150 (s); nmr δ 4.05 (dd, $J_1=10$ Hz, $J_2=7$ Hz, 1H), 2.40-1.75 (m, 2H), 1.41 (s, 9H), 1.22 (s, 6H).

Anal. Calcd for $\text{C}_{11}\text{H}_{18}\text{O}_3$: C, 66.63; H, 9.15. Found: C, 66.81; H, 9.33.

2,2-Dimethylcyclobutanone (5)

t-Butyl ketoester 17b (9.86 g) and p-toluenesulfonic acid monohydrate (40 mg) were heated with an oil bath in a distillation apparatus under nitrogen. Smooth gas evolution began at a bath temperature of 138°, and product began to distill. The reaction was complete in 15 min, during which time bath temperature increased to 152° and 4.31 g (91%) very slightly impure product distilled. Redistillation through a short Vigreux column gave pure material; bp 113.5-114°/760 mm. The spectroscopic properties of this material were in complete agreement with literature values¹³.

A 2,4-dinitrophenylhydrazone was prepared; mp 140.5-141.5° from methanol (lit mp¹² 140-141°).

2,3-Dihydro-2,2-dimethylfuran (15)

A mixture of 15 (✓ 60%) and 2,5-dihydro-2,2-dimethylfuran (A, ✓ 40%) was prepared by the method of Colonge and Garnier¹¹. Preparative vpc (column 75-80°, helium flow 133 ml/min) gave pure 15 (ret. time 10 min): ir 3090 (w), 1620 (s), 1170 (m), 1120 (m), 1055 (s), 975, 880, 700 (m) cm⁻¹; nmr (ppm downfield from external tetramethylsilane in CCl₄): 6.02 (q, 1H), 4.58 (q, 1H), 2.28 (m, 2H), 1.22 (s, 6H). Pure A (ret. time 13 min) had ir 3070 (w), 1625 (w), 1170 (m), 1080 (s), 1035 (s), 930, 860, 705 (m) cm⁻¹; nmr (ppm downfield from external tetramethylsilane in CCl₄): 5.65 (s, 2H), 4.50 (s, 2H), 1.17 (s, 6H).

Photolysis of 2,2-Dimethylcyclobutanone (5) in Pentane

A solution of 5 (2.08 g; > 99% pure by vpc) in 250 ml pentane was cooled with an ice bath while nitrogen was bubbled through the solution for 45 min. The solution was irradiated for 8 hrs. under nitrogen with aliquots being taken at 0, 1, 3, 5, and 8 hrs for vpc analysis. No peak with the retention time of 15 developed during this

time. After 8 hrs 74% of the starting ketone had been destroyed and no 15 was detectable by vpc. Conversion of 1% of 5 to 15 could have been detected.

Photolysis of 2,2-Dimethylcyclobutanone (5) in Methylene Chloride

A solution of 5 (2.09 g: >99% pure by vpc) in 240 ml methylene chloride was cooled with an ice bath while nitrogen bubbled through the solution for 30 min. The solution was irradiated for 6 hrs, after which 53% of the starting ketone had been destroyed, and a small peak with the retention time of 15 had appeared. The area of this peak was about 3% that of the 5 peak before irradiation.

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