

## ORGANIC AND BIOLOGICAL CHEMISTRY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER, ROCHESTER 20, N. Y.]

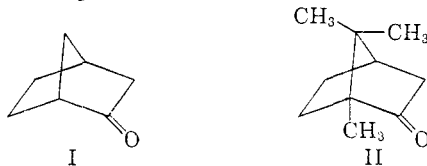
Mercury Photosensitized Decomposition of Norcamphor and *d*-Camphor<sup>1a</sup>BY R. SRINIVASAN<sup>1b</sup>

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The mercury photosensitized decomposition of norcamphor has been found to lead to carbon monoxide, three hydrocarbons of formula  $C_6H_{10}$  and a polymer as the major products. The three hydrocarbons have been identified as 1,5-hexadiene, allylcyclopropane and bicyclo[2.1.1]hexane, respectively. The minor products included bicyclo[2.2.0]hexane and nortricycylene. The formation of 1,5-hexadiene and bicyclo[2.1.1]hexane along with CO is analogous to the formation of ethylene cyclobutane and CO in the photolysis of cyclopentanone. The mechanism of the formation of allylcyclopropane was traced by the use of norcamphor deuterated in the  $\alpha$ -methylene group. The process probably involves a symmetric intermediate which can rearrange in one of two equivalent ways to give allylcyclopropane. Mercury sensitized decomposition of *d*-camphor gave carbon monoxide, 1,5,5-trimethylbicyclo[2.1.1]hexane, 5,6-dimethylheptadiene-1,5 and a polymer as products. The bicyclic hydrocarbon was found to be optically active. The mercury sensitized decomposition of ketones derived from bicyclo[2.2.1]heptane may be a useful route to the synthesis of hydrocarbons derived from bicyclo[2.1.1]hexane.

## Introduction

A great deal of information exists in the literature on the mercury photosensitized decomposition of simple organic compounds.<sup>2</sup> The use of mercury photosensitization as a preparative method in organic chemistry has hardly been explored. This is unfortunate since intense sources of the mercury resonance lines are readily and cheaply available and sensitized decomposition caused by  $Hg^3P_1$  atoms appears to lead to interesting products. In this work, the mercury photosensitized decomposition of norcamphor (I) and *d*-camphor (II) have been studied from a qualitative aspect and as a possible method of preparation of some of the hydrocarbon products.

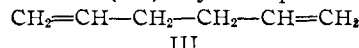


## Results

Photolysis of cyclopentanone vapor is known to lead to cyclobutane and carbon monoxide<sup>3</sup> and the reaction has preparative value. It was considered possible that the vapor phase photolysis of ketones derived from bicyclo[2.2.1]heptane may lead to hydrocarbons derived from bicyclo[2.1.1]hexane. Direct photolysis did lead to the formation of such products,<sup>4</sup> but the necessity to work at temperatures above 120° to obtain a high enough vapor pressure of the ketone cut down the yield of bicyclic hydrocarbon products. The use of mercury photosensitization was then attempted and it was found that in the case of norcamphor (I), 40% of

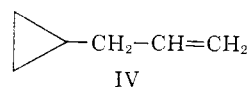
the hydrocarbon fraction was made up of bicyclic compounds. The total yield of all hydrocarbon products with respect to the ketone that was consumed depended on the degree of conversion and ranged from 60% of the theoretical value at low conversions to 23% at 75% conversion.

The important products of the mercury sensitized decomposition of norcamphor (I) were carbon monoxide, a multicomponent hydrocarbon fraction (boiling range -78° to +110°), a small fraction of high boiling products (b.p. 110-150°) and a liquid polymer. Apart from the polymer, the hydrocarbon fraction constituted the major liquid product. It was made up of  $C_3$ - and  $C_4$ -hydrocarbons which were not identified, four  $C_6$ -hydrocarbons (three of which accounted for 80% of this fraction) and one  $C_7$ -hydrocarbon. All four of the  $C_6$ -hydrocarbons gave analysis for the formula  $C_6H_{10}$  and had a molecular weight of 82. In photolysis to low conversions it was found that the carbon monoxide yield was equal ( $\pm 10\%$ ) to the yield of these products. The lowest boiling isomer was identified as 1,5-hexadiene (III) by comparison with an



III

authentic sample. The isomer which boiled at 59.6° showed infrared absorption at 11.0, 10.1 and 6.1  $\mu$  (indicative of  $-CH=CH_2$ ) and other absorptions at 9.87 and 3.32  $\mu$  which may be due to a cyclopropane ring. The n.m.r. spectrum (Fig. 1) showed a multiplet at 4.17  $\tau$  (one proton) and a triplet at 4.98  $\tau$  (two protons) which confirmed the presence of a  $-CH=CH_2$  group. A complex absorption from 8.67 to 10.00  $\tau$  (5 protons) could be attributed to protons on a cyclopropane ring. The position of the protons on the sixth carbon in the compound was indicated by the peak at 8.05  $\tau$  which was split into three, so that these protons probably were allylic and placed in between two other protons. Of the possible structures, only allylcyclopropane (IV) would explain all these



IV

observations. The infrared spectrum of the compound showed similarity to the published spectrum of vinylcyclopropane.<sup>5</sup>

(1) (a) This research was supported in part by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under Contract No. AF 18(600)1528 presently AF 49(638)679. Reproduction in whole or in part is permitted for any purpose by the United States Government. (b) IBM Research Center, P.O. Box 218, Yorktown Heights, N.Y.

(2) (a) W. A. Noyes, Jr., and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publishing Corp., New York, N. Y., 1941, Chapter V; (b) A. R. Knight and H. E. Gunning, *Can. J. Chem.*, **39**, 1231 (1961), and earlier references; (c) R. F. Pottier, A. G. Harrison and F. P. Lossing, *ibid.*, **39**, 102 (1961), and earlier references.

(3) S. W. Benson and G. B. Kistiakowsky, *J. Am. Chem. Soc.*, **64**, 81 (1942); F. E. Blacet and A. Miller, *ibid.*, **79**, 4327 (1957); R. Srinivasan, *ibid.*, **81**, 1546 (1959); **83**, 4348 (1961).

(4) R. Srinivasan, *ibid.*, **83**, 2590 (1961).

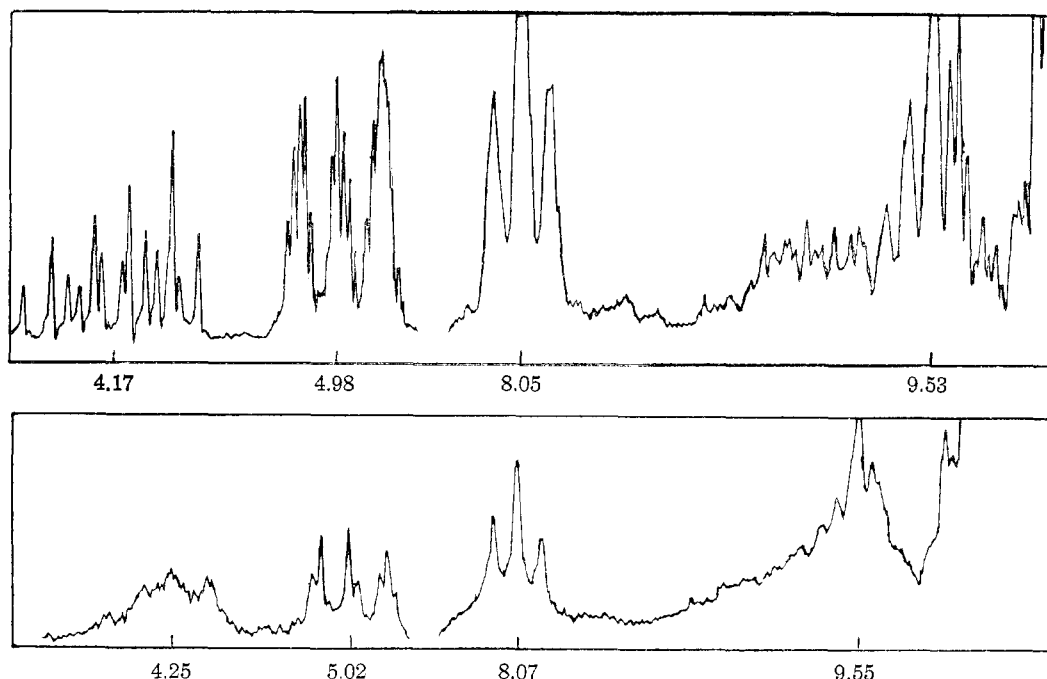
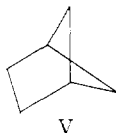


Fig. 1.—N.m.r. spectra: top, allylcyclopropane (concn. 8%); bottom, allylcyclopropane- $d_2$  (concn. 4%) (peak positions in  $\tau$  units; 60 mc.; solvent carbon tetrachloride; internal standards chloroform and tetramethylsilane).

The isomer which boiled at  $70.9^\circ$  showed no evidence of unsaturation in its ultraviolet and infrared spectra so that the formula demands the presence of two rings. Of the possible bicyclohexanes, bicyclo[2.2.0]hexane<sup>6</sup> has a different n.m.r. spectrum from the compound at hand, while bicyclo[3.1.0]hexane would show the presence of the cyclopropane ring in its spectra. Such was not the case with this isomer, which was hence identified as bicyclo[2.1.1]hexane (V). The n.m.r.



spectrum (Fig. 2) consisted of three peaks. The first of these at  $7.47 \tau$  (broad) represented two protons. It could be ascribed to the two bridgehead protons in accordance with the spectra reported by Meinwald and Lewis<sup>7</sup> for substituted bicyclo[2.1.1]hexanes. The peak at  $8.41 \tau$  (6 protons) showed fine structure under high resolution. It probably was made up of 4 protons from the two-carbon bridge, superimposed on two protons in the *exo* position in the one-carbon bridges. In substituted bicyclo[2.1.1]hexanes, it has been noted<sup>7</sup> that the proton in the *exo* position appears at lower fields than a proton in the *endo* position on the same carbon bridge, other things being equal. The quartet centered at  $9.13 \tau$  (2 protons) is due to the *endo* protons in the one carbon bridges.

The isomer which boiled at  $85.3^\circ$  was found to be identical with bicyclo[2.2.0]hexane (VI) in its

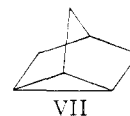
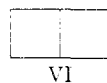
(5) R. Van Volkenburgh, K. W. Greenlee, J. M. Derfer and C. E. Boord, *ibid.*, **71**, 3595 (1949).

(6) S. Cremer and R. Srinivasan, *Tetrahedron Letters*, No. 21, 24 (1960).

(7) J. Meinwald and A. Lewis, *J. Am. Chem. Soc.*, **83**, 2769 (1961).

n.m.r. and mass spectra<sup>6</sup> and also in its retention time on a vapor phase chromatograph.

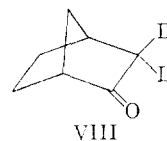
The  $C_7H_{10}$  hydrocarbon was a low melting solid whose infrared spectrum agreed with the published spectrum<sup>8</sup> of nortricyclene (VII). The n.m.r. spectrum showed a broad peak at  $8.09 \tau$  (one pro-



ton) due to the lone proton at the bridgehead. A singlet at  $8.78 \tau$  (six protons) may be due to the six methylene protons which are equivalent, while the singlet at  $9.00 \tau$  (three protons) may be from the three cyclopropyl protons. The coupling between the latter and the methylenic protons probably is very small.

In the high boiling fraction only one compound predominated. This was found to be an aldehyde (carbonyl peak at  $5.82 \mu$ , C-H at  $3.73 \mu$ , one proton (triplet) at  $0.4 \tau$ ), unsaturated (two protons at  $4.33 \tau$ ) and isomeric to norcamphor (molecular weight 110). It was not identified as a sufficient quantity was not available.

In order to get some insight into the formation of allylcyclopropane, the mercury sensitized decomposition of norcamphor-3,3- $d_2$  (VIII) was under-



taken. The deuterium atom content of the norcamphor- $d_2$  used, as determined by mass spec-

(8) J. D. Roberts, E. R. Trumbull, Jr., W. Bennett and R. Armstrong, *ibid.*, **72**, 3116 (1950).

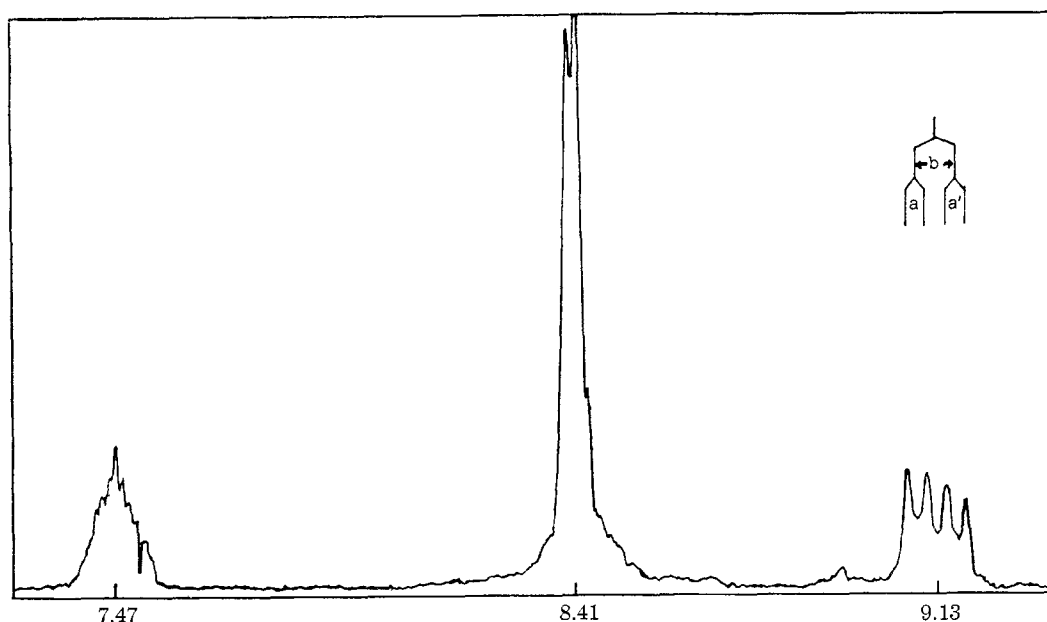
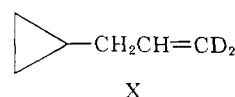
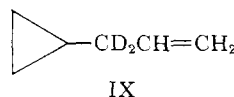


Fig. 2.—N.m.r. spectrum of bicyclo[2.1.1]hexane (peak positions in  $\tau$  units; 60 mc.; solvent carbon tetrachloride; concn. 8%; internal standards chloroform and tetramethylsilane;  $a = a' = 2.2$  cycles;  $b = 5.0$  cycles).

trometry, was 1.93 atoms/molecule instead of the possible 2.00 atoms/molecule. The deuterium atom content of the bicyclo[2.1.1]hexane formed by the photosensitized decomposition was 1.88 atoms/molecule. Since the mass spectrometer that was used had poor resolving power above an  $m/e$  value of 100, these two values may be taken to be in agreement. The n.m.r. spectrum of the 1,5-hexadiene- $d_2$  that was obtained by the decomposition of norcamphor- $d_2$  showed peak positions and splittings similar to that of the undeuterated material, but the peak intensities which were in the ratio 2:4:4 for the peaks at 4.32, 5.02 and 7.87  $\tau$  in the undeuterated material had the ratio 2:2.1:4 in the deuterated compound. The peak at 5.02  $\tau$  may be attributed to the four protons at the ends of the molecule, and it is seen that in the deuterated compound two of these have been replaced by deuterium.

In the infrared spectrum of allylcyclopropane- $d_2$ , which was obtained by photosensitized decomposition of norcamphor- $d_2$ , C-D stretching absorptions at 4.62–4.83  $\mu$  were present indicating the presence of deuterium atoms. The absorption corresponding to C-H stretching of cyclopropyl protons at 3.32  $\mu$  was more intense compared to the main C-H stretching absorption at 3.40–3.50  $\mu$ , than in the undeuterated compound. The absorptions at 11.0, 10.1 9.90 and 6.12  $\mu$  were also present as in the undeuterated compound. The n.m.r. spectrum of the compound (Fig. 1) was similar to that of the undeuterated compound in the number, position and multiplicity of the peaks (except the multiplet at 4.25  $\tau$  which showed minor changes). But the intensities of the peaks showed that instead of one-half of the protons absorbing above 8.6  $\tau$ , the deuterated compound had  $5/8$  of its protons in this region. This indicated that the deuterium atoms were not located on the cyclopropane ring. The protons in the three-carbon chain gave rise to peaks at 4.25, 5.02 and 8.07  $\tau$  of almost identical

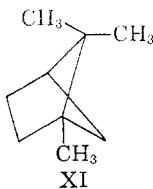
intensities. These results can best be interpreted to mean that the allylcyclopropane- $d_2$  was made up of two compounds which had structures IX and X. The presence of both compounds would explain the fact that the deuterated allylcyclopropane showed all of the absorption peaks of the undeuterated compound in its infrared and n.m.r. spectra. Both IX and X have five protons in the cyclopropane ring but only IX may have the peak at 5.02  $\tau$  and only X may have the peak at 8.07  $\tau$ . The equivalence in the intensities of these two peaks suggests that IX and X were present in equal amounts.



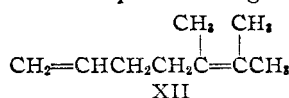
In the mercury photosensitized decomposition of *d*-camphor, the important products were carbon monoxide, a  $C_9$ -hydrocarbon fraction and a polymer. From the hydrocarbon fraction two major components were separated by vapor phase chromatography. Both compounds gave analyses for the formula  $C_9H_{16}$  and had a molecular weight of 124.

The lower boiling isomer showed no evidence of unsaturation in its spectra. The presence of two equivalent peaks at 7.25 and 7.38  $\mu$  and a shoulder at 7.31  $\mu$  in the infrared spectrum indicated that the three methyl groups in camphor were present in the product. The n.m.r. spectrum showed three singlet peaks of three protons each at 8.89, 9.04 and 9.30  $\tau$ , respectively, which may be due to the three methyl groups in the molecule. The rest of the n.m.r. spectrum showed a similarity to the spectrum of bicyclo[2.1.1]hexane (V). Based on this and on the mode of formation, it was concluded that this compound was 1,5,5-trimethylbicyclo[2.1.1]hexane (XI). The observed optical activity

of the compound also supports this asymmetric structure.



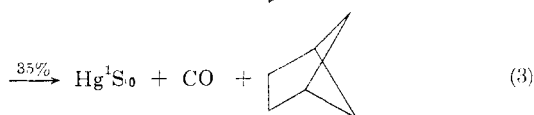
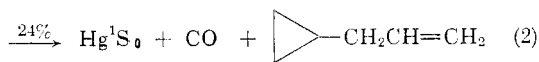
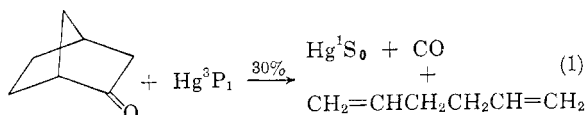
The higher boiling isomer showed peaks at 6.12, 10.15 and 11.05  $\mu$  in its infrared spectrum which indicated the presence of a  $-\text{CH}=\text{CH}_2$  group. There was a single methyl peak at 7.31  $\mu$ . In the n.m.r. spectrum there were three olefinic protons and 13 aliphatic protons. By analogy with the decomposition of norcamphor and by inference from the direct photolysis of *dl*-camphor<sup>4</sup> in which this compound was a major product, it was deduced that this compound was 5,6-dimethylheptadiene-1,5 (XII). The n.m.r. spectrum agreed with this



structure in that there was a multiplet peak at 4.33  $\tau$  (one proton) and a triplet at 5.11  $\tau$  (two protons) due to the protons on the terminal double bond. The three methyl groups on the other double bond gave rise to a single peak at 8.38  $\tau$ . A doublet (?) at 7.94  $\tau$  (4 protons) was attributed to the four methylene protons. There was a small amount of diffuse absorption at *ca.* 9.0  $\tau$  which suggested that even after purification on a vapor phase chromatograph, the compound might have contained a small amount of an isomer.

### Discussion

The formation of the  $\text{C}_8\text{H}_{10}$  isomers can be represented by the following equations<sup>9</sup> in which the numbers on the arrows indicate the probability of each process under the experimental conditions.

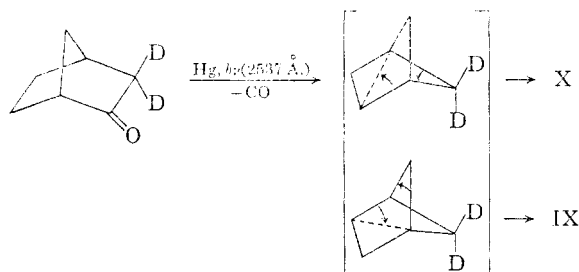


(1) and (3) were observed in the direct photolysis of norcamphor and correspond to the production of ethylene and carbon monoxide and cyclobutane and carbon monoxide, respectively, in the photolysis of cyclopentanone. It is hard to explain the formation of allylcyclopropane and bicyclo[2.2.0]hexane, which involve a rearrangement of the

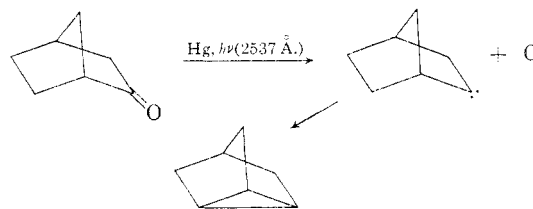
(9) These equations merely indicate the stoichiometry of these processes and not the mechanism.

carbon skeleton in norcamphor. The former, which is quite important in the mercury photo-sensitized reaction, is hardly detectable in the direct photolysis.<sup>4</sup> It was established that it was not a secondary product as its yield relative to that of the other hydrocarbons was unchanged with the conversion.

An idea of the mechanism of the formation of allylcyclopropane is given by the location of the deuterium atoms in the allylcyclopropane-*d*<sub>2</sub> that was obtained in the mercury sensitized decomposition of norcamphor-*d*<sub>2</sub>. Since the deuterium atom content of the bicyclo[2.1.1]hexane-*d*<sub>2</sub> that was formed in this experiment was the same as that of the starting ketone, intermolecular exchange of deuterium atoms does not seem to be important in reactions 1 to 4. Since the 1,5-hexadiene-*d*<sub>2</sub> that was formed had the structure that could be expected if reaction 1 is not accompanied by an intramolecular reshuffling of hydrogen (and deuterium atoms), it can be assumed that this is true in the formation of all of the  $\text{C}_8\text{H}_{10}$  hydrocarbons.<sup>10</sup> The formation of IX and X in equal amounts suggests that a symmetric intermediate that can decompose in one of two equivalent ways is important in the production of allylcyclopropane. A reasonable possibility is



The formation of nortricyclene, although in small amount, is an unusual reaction as it involves the net loss of an oxygen atom *alone* from a carbonyl compound. Many mechanisms may be visualized to account for this, but the simplest process appears to be a direct split of an oxygen atom followed by an internal abstraction of a hydrogen from the 6-position and bonding.



The reaction is seen to be analogous to the carbene reactions described in other bicyclic systems which also lead to tricyclic products.<sup>11</sup> A photon at 2537 Å. corresponds to 112 kcal./mole so that one photon of energy when transferred to a norcamphor

(10) The n.m.r. spectrum of the bicyclo[2.1.1] hexane-*d*<sub>2</sub> that was obtained from norcamphor-3,3-*d*<sub>2</sub> consisted of three peaks located at 7.52, 8.44 and 9.19  $\tau$  of intensities 2, 5 and 1, respectively, which further supports this assumption.

(11) W. R. Moore, H. R. Ward and R. F. Merritt, *J. Am. Chem. Soc.*, **83**, 2019 (1961).

molecule by sensitization would not be sufficient to break the carbon-oxygen bond. Two photons may contribute to the decomposition of each molecule. Since the  $^3P_0$  state of mercury is relatively long lived, such a possibility, especially at high intensities, is reasonable.<sup>12</sup> Alternately the presence of an appreciable amount of 1849 Å. radiation from the light source may also contribute to the process.

From the present work it is suggested that the mercury sensitized photodecomposition of bicyclo[2.2.1]heptanones may be a general method for the preparation of bicyclo[2.1.1]hexanes. Although the yields obtained were only of the order of 10% when the reaction was carried to completion, the improved yields that were obtained at lower conversions indicate that better irradiation apparatus can be devised in which the ketone may be flowed past the light source. Work on the development of such a system is in progress. The 1-2% yield of bicyclo[2.2.0]hexane that was obtained in the mercury sensitized photolysis of norcamphor makes this a much better method for the synthesis of this hydrocarbon than the photolysis of bicyclo[3.2.0]heptanone-3<sup>6</sup> which can be obtained only by a tedious synthetic procedure.

**Acknowledgment.**—The author wishes to thank Professor W. Albert Noyes, Jr., for his advice and encouragement during the course of this work. He is indebted to the members of the Organic Chemistry Section for helpful suggestions, criticism and encouragement.

### Experimental

**Materials.**—Norcamphor (Columbia Organic Chemicals, Inc.) and *d*-camphor (Eastman Kodak Co., white label) were used as obtained. Norcamphor-*d*<sub>2</sub> was prepared by successive exchange with 99.5% deuterium oxide (Stuart Oxygen Co.) in the presence of anhydrous potassium carbonate. After six exchanges the ketone corresponded to C<sub>7</sub>H<sub>8</sub>. or D<sub>1.98</sub>O.

**Apparatus.**—Mercury sensitized decomposition on a small scale (100 mg.) was carried out in a 4.4 × 5.0 cm. quartz cell wound with heating tape to avoid condensation of the solid material on the walls and windows. The temperature during a run was 80°. The light source was an Ottawa-style mercury resonance lamp operated from a GE luminous tube transformer (51G 274).

Sensitized decomposition on a larger scale (1-5 g.) was carried out in a 2-liter quartz bulb. The light source was a bank of 12 GE G8T5 germicidal lamps<sup>13</sup> arranged in a circle around the bulb at a minimum distance of 10 mm. The heat from the lamps maintained the bulb at 75°. The bulb was connected to a mechanical pump through a mercury cut-off which also served as the manometer.

**Procedure.**—In any run the desired amount of ketone and 5 g. of mercury were introduced in the quartz bulb, which was then sealed to the glass lead tube to the pump. Air pressure inside the bulb was reduced to 3 mm. after which the bulb was isolated from the pump. The dead space in the system was heated electrically to prevent the distillation of the ketone from the bulb to the cooler parts. Progress of the sensitized decomposition was followed by

the change in pressure—about 100 min. of irradiation was sufficient to decompose 1 g. of the ketone. The large amount of polymer formed is believed to be in part due to direct absorption of light by the liquid ketone and also due to secondary decomposition of the products.

At the end of the irradiation all of the volatile material was distilled over in a vacuum to a trap cooled to -195° while at the same time the carbon monoxide was pumped off. The liquid photolysate which collected in the trap was redistilled at atmospheric pressure to give one fraction (b.p. 50-110°) made up of all the C<sub>6</sub> and some C<sub>7</sub>-hydrocarbons, a second fraction (b.p. 110-170°) which was mostly norcamphor and a residue which was rejected. The first fraction was passed through a vapor phase chromatograph at 60° fitted with a 2-meter column of diisodecyl phthalate when the following products were separated: (melting points uncorrected; infrared spectra obtained in CCl<sub>4</sub>; n.m.r. spectra obtained in CCl<sub>4</sub> on a Varian V-4311 spectrometer, 60 Mc.; concentration 8-20%; chloroform and tetramethylsilane as internal standards. Mass spectra were obtained on a Consolidated Engineering Co. type 21-620 instrument, microanalyses by Micro-Tech Laboratories, Skokie, Ill.

1. Hexadiene-1,5 (III), b.p. 57° (lit.<sup>14</sup> 59.6°), infrared spectrum as published<sup>15</sup>; retention time on chromatograph agreed with that of authentic sample.<sup>16</sup>

2. Allylcyclopropane (IV), b.p. 59.6°; infrared spectrum 3.32(shoulder), 3.55(s), 6.10(s), 6.90, 7.05, 7.32, 7.85, 9.62, 9.88(s), 10.10(s), 11.00(v.s) μ.

*Anal.* Calcd. for C<sub>6</sub>H<sub>10</sub>: C, 87.74; H, 12.26; mol. wt., 82. Found: C, 87.33; H, 12.40; mol. wt., 82.

3. Bicyclo[2.1.1]hexane (V), m.p. 22°, b.p. 70.9°; infrared spectrum: 3.54(s), 6.14, 6.90(s), 7.00, 7.83(s), 8.35(s), 8.92(s), 9.33, 11.05 (shoulder), 11.20 μ; mass spectrum: most intense peak was at 67, strong peaks at 54, 41 and 39.

*Anal.* Calcd. for C<sub>6</sub>H<sub>10</sub>: C, 87.74; H, 12.26; mol. wt., 82. Found: C, 87.70; H, 12.25; mol. wt., 82.

4. Bicyclo[2.2.0]hexane (VI), b.p. 85.3°; n.m.r. spectrum: continuous absorption from 7.01 to 8.56 τ with peaks at 7.96τ (doublet 0.1τ apart) and 8.34 τ; mass spectrum: most intense peak at 41; peaks of equal intensities at 67, 54 and 39.

*Anal.* Calcd. for C<sub>6</sub>H<sub>10</sub>: C, 87.74; H, 12.26; mol. wt., 82. Found: C, 87.82; H, 12.44; mol. wt., 82.

5. Nortricyclene (VII), m.p. 50.5-51.0° (lit.<sup>8</sup> 56°). *Anal.* Calcd. for C<sub>7</sub>H<sub>10</sub>: C, 89.32; H, 10.68; mol. wt., 94. Found: C, 89.33; H, 10.86; mol. wt., 94.

Sensitized decomposition of *d*-camphor was conducted similarly. The C<sub>6</sub>H<sub>10</sub> products were separated by a simple distillation at room temperature in a vacuum. Separation of the individual products was carried out in a vapor phase chromatograph on a 2-meter diisodecyl phthalate column at 95°, when the following compounds were obtained:

6. 1,5,5-Trimethylbicyclo[2.1.1]hexane (XI), m.p. 56.5-57.0°, b.p. 130.5°; infrared spectrum: 3.52(s), 6.77-(shoulder), 6.85(shoulder), 6.90(s), 7.25(s), 7.31(shoulder), 7.34(s), 7.64, 7.81; n.m.r. spectrum: 8.01τ (1 H); 8.48τ (5 H), 8.89, 9.04 and 9.30τ (3 H each), 9.11τ (1 H); [α]<sub>D</sub><sup>25</sup> +3.71° (CCl<sub>4</sub>, 8).

*Anal.* Calcd. for C<sub>9</sub>H<sub>16</sub>: C, 87.04; H, 12.98; mol. wt., 124. Found: C, 87.07; H, 12.90; mol. wt. (mass spectrum), 124.

7. 5,6-Dimethylheptadiene-1,5 (XII), b.p. 140.2°. *Anal.* Calcd. for C<sub>9</sub>H<sub>16</sub>: C, 87.04; H, 12.98; mol. wt., 124. Found: C, 87.04; H, 12.94; mol. wt., 124.

(14) "Handbook of Chemistry and Physics," C. D. Hodgman, Editor, Chemical Rubber Publishing Co., Cleveland, O., 1960, p. 1030.

(15) American Petroleum Institute Research Project 44, Infrared Spectrum No. 1654.

(16) The author wishes to thank Professor W. D. Walters for kindly furnishing this sample.

(12) A similar mechanism has been proposed in other systems; see ref. 2, p. 227.

(13) According to the manufacturer's specifications lamp input is 8 watts; average ultraviolet output is 0.98 watt/lamp.