state of a cyclohexanone molecule before the ring structure is disrupted. If a similar mechanism is assumed to be operative in the photoisomerization of 2-methylcyclohexanone to 5-heptenal, then the production of only one geometric isomer in the process, if established, supports the idea that the carbon atoms in the ring are not appreciably disarranged before the shift of a hydrogen atom occurs.[16]

In cyclohexanone, the photoisomerization appears to be a more efficient process than in cyclopentanone. This may be determined by the shorter distance over which a hydrogen atom is moved in the former instance in going from the cyclic ketone to the unsaturated aldehyde and by the degree of strain necessary for the change. It may be of interest to study the photochemistry of cyclobutanone and cycloheptanone to see whether isomerization occurs in these ketones and, if so, with what efficiency.

Acknowledgment.—The author wishes to thank Professor W. Albert Noyes, Jr., for advice and encouragement during the course of this work.

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(16) There is an assumption made here that the photoisomerization in these ketones proceeds by the same mechanism in the gas phase and in the liquid phase.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

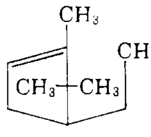
Photoisomerization Processes in Cyclic Ketones. III. *dl*-Camphor[1]

BY R. SRINIVASAN

RECEIVED DECEMBER 24, 1958

It has been found that *dl*-camphor, as a solution in air-free organic solvents, isomerizes under the influence of radiation of 3130 Å., to α-campholenic aldehyde (A) and a ketone (B). B has been identified as 1:2:2-trimethylcyclopent-3-enyl methyl ketone. Quantum yields for the formation of carbon monoxide and non-volatile products have been obtained in three solvents. The ratio Φ_A/Φ_B appears to be influenced by the nature of the solvent. It is suggested that the formation of B from an excited camphor molecule proceeds in several steps involving one or more solvent molecules.

Ciamician and Silber[2] photolysed camphor in an aqueous-alcoholic solution using sunlight as the source of radiation and obtained an aldehyde (A) and a ketone (B) both isomeric with camphor as the major products. A was identified by them as α-campholenic aldehyde



A

The nature of the isomerization of camphor to A is analogous to the photoisomerization of five and six-membered cyclic ketones in the liquid phase and in solution.[3,4] On the other hand, the formation of an isomeric ketone under the influence of light is not known in the latter instances. The present work was undertaken to study the photolysis of *dl*-camphor in air-free non-aqueous solvents, identify the products and determine the efficiency of these processes.

Experimental

Materials.—*dl*-camphor from Eastman Kodak Co. (white label) was used without purification. Its vapor chromatogram showed no impurities. The solvents used were diethyl ether, methanol (reagent grade), ethanol, 3-methylpentane and *n*-heptane. The last two were purified by repeated agitation with concentrated sulfuric acid. Chromatographic separations were made on neutral alumina, activity grade 1 (supplied by F. Woelm Eschwege).

Apparatus.—Photolyses on a preparatory scale were carried out in a hemispherical Pyrex cell irradiated from the center by a Hanovia S-100 lamp. A solution of camphor in a suitable solvent was allowed to circulate through the cell by convection. The cell was cooled by water.

Quantitative experiments were conducted in a Pyrex cell 2.0 cm. diameter and 1.0 cm. thick and a quartz cell 3.0 cm. diameter and 0.05 cm. thick. The light source was a Hanovia S-100 mercury arc lamp filtered by a combination of Corning 0–53 and 9863 filters and 5.0 cm. length of a solution containing 60 g./l. of $NiSO_4 \cdot 6H_2O$ and 11.3 g./l. of $CoSO_4 \cdot 7H_2O$. The useful radiation was the group of lines at 3130 Å. The intensity of the radiation at 3130 Å., as calibrated by a diethyl ketone actinometer was 3.0×10^{14} quanta/sec./cc.

Procedure.—The cell filled with solution was degassed in a high vacuum system and sealed. After irradiation, the products could be admitted to the vacuum line by breaking a capillary seal on the cell. Carbon monoxide, which was found to be the only gaseous product, was removed from the solution at liquid nitrogen temperature. The residual solution was evaporated at room temperature *in vacuo*, and the melting point of the camphor mixed with the non-volatile products was determined. From the lowering in the melting point as compared to pure camphor, the total number of moles of non-volatile products could be calculated. Less than 3% of the camphor was decomposed. Analysis could be made either by vapor phase chromatography using a Perkin–Elmer Vapor Fractometer Model 154 and column "A," or by the infrared spectrum, using a Perkin–Elmer Model 21 spectrometer. In the presence of a large excess of undecomposed camphor, neither method was found to be sensitive. Acceptable analysis could be made under conditions where more than one product was formed, only when at least 20% of the camphor was decomposed. For this reason, the ratios of non-volatile products given in Table I should be considered to be merely indicative of the relative rates of production.

Results

Photolysis of camphor in solution gave carbon monoxide as the only volatile product. After prolonged photolysis in ethanol solution, acetaldehyde also was observed to be formed.[5] The

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(1) This research was supported in part by Contract AF18(600) 1528 with the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command. Reproduction in whole or in part is permitted for any purpose by the United States Government.

(2) G. Ciamician and P. Silber, *Ber.*, **43**, 1341 (1910).

(3) M. S. Kharasch, J. Kuderna and W. Nudenberg, *J. Org. Chem.*, **18**, 1225 (1953).

(4) R. Srinivasan, THIS JOURNAL, **81**, 1546, 2601 (1959).

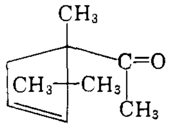
(5) Ciamician and Silber[2] have observed the formation of acetaldehyde in the photolysis of camphor in an aqueous-alcoholic solution.

TABLE I

QUANTUM YIELDS IN THE PHOTOLYSIS OF CAMPHOR AT 3130 Å.

Solvent	Concn., moles/l. × 10^3	Time, min.	Φ_{CO}	$\Phi_{non\text{-}vol}$	Φ_A/Φ_B
3-Methylpentane	40	1050	0.007	0.06	0.1
Diethyl ether	40	803	0.005	.06	1
Methanol	40	1080	...	.06	..
n-Heptane	1731	1545	...	..	0.1
Ethanol	55	2400	...	..	1.5

non-volatile products along with the undecomposed camphor were chromatographed on a column of neutral alumina and these various substances were separated: (i) an unsaturated aldehyde which had in its infrared spectrum (chloroform solvent) peaks at 1735(s), 1620, 1445, 1385, 1370 and 1360 cm.$^{-1}$. Since this product was formed in good yield on photolyzing camphor in an aqueous-alcoholic solution, it was taken to be α-campholenic aldehyde (A). (ii) An unsaturated ketone with peaks in its infrared spectrum at 1715(s), 1615, 1440, 1360 and 1375 cm.$^{-1}$. The ultraviolet spectrum in ethanol showed a maximum at 2800 Å. with a molar extinction coefficient of about 60. It gave the iodoform test, and its mass spectrum had its highest peak at an *m/e* value of 43, which is characteristic of methyl ketones. Since this substance was also a major product in the photolysis of camphor in an aqueous-alcoholic solution, it is probably the ketone B described by Ciamician and Silber.[2] They found that B was isomeric with camphor and that on oxidation it gave a dibasic acid of formula $C_{10}H_{16}O_5$, m.p. 133–134°. They suggested that this could be β-acetyltrimethylglutaric acid, m.p. 125–140°. From this evidence, the structure of B may be



(iii) a compound with a strong absorption peak in the infrared spectrum at 1660 cm.$^{-1}$. Its ultraviolet spectrum in ethanol showed a maximum at 2330 Å. with a minimum estimated value for the molar absorption coefficient of 3800. This evidence suggests that the compound may be an unsaturated ketone with a double bond conjugated with the carbonyl group and substituted in the α and β, and β-positions.[6] However, since this substance was formed in poor yield (about $^1/_{30}$th of the total non-volatile products), it could not be purified and identified positively.

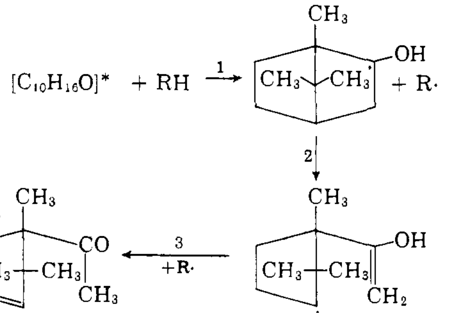
Quantum yields for the production of carbon monoxide and non-volatile products from camphor in three solvents are listed in Table I. The nonvolatile products were mainly A and B. The ratios Φ_A/Φ_B in these solvents and in two others also are listed. In one experiment on the photolysis of camphor in the vapor phase at room temperature, the value of Φ_{CO} was estimated to be greater than 0.1. This value is subject to a large uncertainty since the vapor pressure of camphor at 28° is only 0.31 mm.[7] The decrease in Φ_{CO} in going from the vapor phase to solution may be attributed to the collisional deactivation of the excited camphor molecules by the solvent.

Discussion

The structure of B is such that it can be formed from camphor by transferring a hydrogen atom from the γ-carbon atom in the ring to the unsubstituted α-carbon atom and breaking the bond between the α- and β-carbon atoms. This is analogous to the type II process that is observed to take place in simple aliphatic ketones with at least one hydrogen atom on the γ-carbon.[8] In these cases, the process is supposed to occur through a ring intermediate. But such an intermediate definitely can be excluded in the isomerization of camphor to B, as it would involve an impossibly strained structure. Further no analog of the type II process has been detected in the six-membered cyclic ketones.[3,4]

The fact that the solvent is an important factor in determining the ratio Φ_A/Φ_B, while the quantum yield for the formation of non-volatile products (essentially $\Phi_A + \Phi_B$) appears to be independent of the solvent indicates that the solvent may participate in the formation of A or B. It is known that the formation of 4-pentenal from cyclopentanone and 5-hexenal from cyclohexanone proceed intramolecularly from an excited state of these ketone molecules.[4] Hence it is likely that it is the formation of the ketone B that is influenced by the solvent.

A simple mechanism through which camphor could isomerize to B would be



where $[C_{10}H_{16}O]^*$ indicates a camphor molecule in an excited state, and RH, the solvent. Reactions similar to (1) have been postulated in many instances[9] where light induced reactions between ketones and solvents occur. Usually, the radicals formed from reactions such as (1) are believed to disproportionate to give stable products. In this instance, due to the structure of camphor, (2) can occur easily by an electron shift. The radical so formed may subsequently lose a hydrogen atom to another free radical, which may

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(6) R. B. Woodward, THIS JOURNAL, **63**, 1123 (1941); **64**, 76 1942).

(7) This value was calculated from the vapor pressure data listed in the "International Critical Tables," Vol. III, McGraw-Hill Book Co., New York, N. Y., p. 208.

(8) For a general discussion and references, see J. N. Pitts, *J. Chem. Educ.*, **34**, 112 (1957).

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not necessarily be the one formed in (1). No doubt some of the radicals disproportionate to give oxidation products, as indicated by the formation of small amounts of acetaldehyde during photolysis in ethanol solution. The change in Φ_A/Φ_B with the nature of the solvent would be due to the ease with which the solvent molecules participate in (1) and (3).

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ROCHESTER, NEW YORK

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, STANDARD OIL COMPANY (INDIANA)]

Organic Ions in the Gas Phase. VII. Tropylium Ion from Benzyl Chloride and Benzyl Alcohol

BY SEYMOUR MEYERSON, PAUL N. RYLANDER, ERNEST L. ELIEL[1] AND JOHN D. MCCOLLUM

RECEIVED OCTOBER 13, 1958

The $C_7H_7^+$ ion present in the mass spectra of benzyl chloride and benzyl alcohol appears not to be the benzyl ion. The spectra of variously deuterated species show that the seven hydrogens have completely lost identity. The structure of the $C_7H_7^+$ ion is better represented as tropylium, just as in toluene and ethylbenzene, although its formation and further decomposition are not entirely clear. The appearance potentials of this ion from benzyl chloride, benzyl bromide and benzyl iodide are somewhat lower than the values expected for benzyl ion and suggest that rearrangement occurred before or during dissociation. These appearance potentials lead to an upper limit of 207 to 210 kcal./mole for the heat of formation of the tropylium ion.

Evidence has been presented that the $C_7H_7^+$ ion found in great abundance in the mass spectrum of toluene, as well as in the spectra of higher alkylbenzenes and cycloheptatriene, is the symmetrical tropylium (cycloheptatrienylium) ion rather than the benzyl ion.[2,3] This finding was surprising, and implicit in it was the question of how general such behavior might be. In particular, do non-hydrocarbon benzyl compounds give rise to benzyl ions, or do they likewise rearrange to give tropylium?

The appearance potentials of the $C_7H_7^+$ ion from benzyl halides[4] show clearly that the energetics of $C_7H_7^+$ formation from these compounds are different than those from toluene, ethylbenzene, propylbenzene, dibenzyl and cycloheptatriene.[2,3] Whereas the values for the hydrocarbons all exceed those expected for a benzyl ion by about 16 kcal./mole, those from the benzyl halides were found to be 3 to 5 kcal./mole lower than the expected values.[4] Recent estimates of the bond-dissociation energies $D(C_6H_5CH_2–Cl)$[5] and $D(C_6H_5CH_2–I)$[6] increase the apparent discrepancy in the halide measurements to 6 to 10 kcal./mole. The pertinent data for the halides are summarized in Table I.

TABLE I

ENERGETICS OF $C_7H_7^+$ FORMATION FROM BENZYL HALIDES

X in $C_6H_5CH_2X$	D-($C_6H_5CH_2$–X), kcal./mole	Ref.	Calcd. A-($C_6H_5CH_2^+$),[a] kcal./mole	Obsd. $A(C_7H_7^+)$,[b] kcal./mole
Cl	68	5	247	239
Br	50.5	7	229	223
	48.5	8	227	
I	43.2	6	222	213
	36.5	8	215	
	39	9	218	

[a] The sum of $D(C_6H_5CH_2–X)$ and $I(C_6H_5CH_2)$, the ionization potential of the benzyl radical, 179 kcal./mole, ref. 10. [b] See ref. 4.

To obtain more evidence on the nature of the $C_7H_7^+$ ion formed by electron impact from non-hydrocarbon benzyl compounds, we studied the mass spectra of deuterated benzyl chlorides and benzyl alcohols. We prepared both compounds labeled with a single deuterium atom in the *ortho*, *meta* and *alpha* positions, and with two alpha deuteriums. The *para*-deuterated species were omitted because the three ring-deuterated isomers of every benzene derivative studied previously[2,3,11,12] have given indistinguishable spectra; even if the $C_7H_7^+$ ion proved to be a benzyl ion, one would expect to find spectral differences between the *ortho* and other ring deuterated species, but not between the *meta* and *para*.[2] Benzyl alcohol deuterated in the hydroxyl group was omitted because hydrogen exchange with water on the walls of the spectrometer inlet system would greatly reduce the isotopic purity of such a sample and, consequently, the likelihood of obtaining a useful spectrum.

To establish the decomposition processes at work, the spectra of these compounds were examined for both metastable peaks[13] and distri-

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[1] 1956 summer research participant from Department of Chemistry, University of Notre Dame.

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