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Photoisomerization Processes in Cyclic Ketones. II. Cyclohexanone and 2-Methylcyclohexanone[1]

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5-Hexenal has been identified as one of the products of the vapor phase photolysis of cyclohexanone at 3130 Å. Quantum yields for the formation of 5-hexenal have been obtained as a function of temperature and pressure and in the presence of oxygen or carbon dioxide. The photoisomerization also occurs in the pure liquid phase and in methylpentane solution. The photolysis of 2-methylcyclohexanone as a pure liquid apparently gives rise to only one isomeric product, which is most probably *trans*-5-heptenal. The photoisomerization of these two ketones closely resembles the corresponding process in cyclopentanone and probably proceeds by the same mechanism.

Introduction

The vapor phase photolysis of cyclohexanone has been investigated by Saltmarsh and Norrish,[2] Bamford and Norrish,[3] Benson and Kistiakowsky[4] and more recently by Blacet and Miller.[5] The products of the photolysis are carbon monoxide, ethylene, propylene, 1-pentene, cyclopentane and possibly a polymer. These products can be explained by the steps[5]

$$\mathrm{O\overline{C\ CH_2CH_2CH_2CH_2C}H_2} + h\nu \longrightarrow$$

$$\mathrm{O\dot{C}\ CH_2CH_2CH_2CH_2\dot{C}H_2} \quad (1)$$

$$\longrightarrow \mathrm{\dot{C}H_2CH_2CO\ CH_2CH_2\dot{C}H_2} \quad (2)$$

$$\mathrm{O\dot{C}\ CH_2CH_2CH_2CH_2\dot{C}H_2} \longrightarrow$$

$$\mathrm{CO + C\overline{H_2CH_2CH_2CH_2C}H_2} \quad (3)$$

$$\longrightarrow \mathrm{CO + CH_2{=}CHCH_2CH_2CH_3} \quad (4)$$

$$\mathrm{\dot{C}H_2CH_2CO\ CH_2CH_2\dot{C}H_2} \longrightarrow$$

$$\mathrm{CO + CH_2{=}CH_2 + CH_2{=}CHCH_3} \quad (5)$$

$$\mathrm{COCH_2CH_2CH_2CH_2CH_2} \longrightarrow$$

$$\mathrm{CO + \cdot CH_2CH_2CH_2CH_2CH_2\cdot} \quad (6)$$

$$\mathrm{X{\cdot}CH_2CH_2CH_2CH_2CH_2 + Y\ C_{\mathit{n}}H_{2\mathit{n}}} \longrightarrow \text{polymer} \quad (7)$$

Cyclohexenyl cyclohexanone and water were also detected in the products by Benson and Kistiakowsky,[4] and these could be formed by a direct condensation of two molecules of the ketone. Dunn and Kutschke[6] studied the effect of oxygen and carbon dioxide on the photolysis.

The present study was undertaken to see if in addition to these products which can be explained on the basis of a primary split to give a diradical, there are other product(s) formed by a direct rearrangement under the influence of light. Such a rearrangement has been found to occur in cyclopentanone vapor and leads to the formation of 4-pentenal.[7] On the basis of results obtained in that study it seemed promising to carry out the photolysis of cyclohexanone at room temperature and analyze the products by gas chromatography in order to detect the hypothetical product of any photorearrangement reaction.

Photoisomerization of cyclohexanone is known to occur in solution. Ciamician and Silber[8] who studied the effect of sunlight on aqueous and aqueous-alcoholic solutions of the ketone found caproic acid and unsaturated aldehydes to be among the products. Kharasch, *et al.*,[9] who studied the action of radiation from a mercury arc on cyclohexanone reported that the pure liquid apparently does not

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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] O. D. Saltmarsh and R. G. W. Norrish, *J. Chem. Soc.*, 455 (1935).

[3] C. H. Bamford and R. G. W. Norrish, *ibid.*, 1521 (1938).

[4] S. W. Benson and G. B. Kistiakowsky, THIS JOURNAL, **64**, 80 (1942).

[5] F. E. Blacet and A. Miller, *ibid.*, **79**, 4327 (1957).

[6] J. R. Dunn and K. O. Kutschke, *Can. J. Chem.*, **32**, 725 (1954).

[7] R. Srinivasan, THIS JOURNAL, **81**, 2604 (1959).

[8] G. Ciamician and P. Silber, *Ber.*, **41**, 1071 (1908); **46**, 3077 (1913).

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

decompose or react in 24 hr., but in 1-octene solution several products are formed, one of these being 5-hexenal. Since it has been found that cyclopentanone rearranges under the influence of light to 4-pentenal both in pure liquid phase[7] and in hexane solution[10] it was considered relevant to study the photolysis of cyclohexanone in solution and as a pure liquid.

The photolysis of 2-methylcyclohexanone has been studied in the vapor phase by Bamford and Norrish[3] and in aqueous solution by Ciamician and Silber.[8] In the latter case hydrolysis and oxidation accompanied photolysis.

Experimental

Materials.—Cyclohexanone (white label) obtained from Eastman Kodak Co. was fractionated at atmospheric pressure. The middle cut was distilled twice *in vacuo*, degassed and stored at Dry Ice temperature. Analysis by gas chromatography showed no impurities. 2-Methylcyclohexanone obtained from K. and K. laboratories was used without purification. Its purity as checked by gas chromatography was better than 98%. Oxygen and carbon dioxide from Airco were used as obtained. 3-Methylpentane supplied by Phillips Petroleum Co. was stirred with concentrated sulfuric acid, repeatedly washed with water and dried before use.

Procedure.—Gas phase photolyses were carried out in a quartz cell 20.0 cm. long and 3.9 cm. diameter. It was surrounded by a metal jacket through which steam was passed for experiments at 100°. In experiments in which foreign gases were added to the ketone vapor, thorough mixing of the sample was ensured by alternately compressing and expanding the mixture into a large volume. The light source was a Hanovia S-100 mercury arc filtered by 2 mm. of Corning 0-53 glass. The useful radiation was essentially the group of lines around 3130 Å. The intensity of the source as calibrated by a diethyl ketone actinometer at 100° ($\Phi_{CO} \sim 1$) was 1.1×10^{16} quanta/sec. The logarithm of the molar absorption coefficient of cyclohexanone vapor at 3130 Å. was taken as 0.80 on the basis of the data of Benson and Kistiakowsky.[4] Photolyses were carried out to less than 3% decomposition.

The photolysis of cyclohexanone at room temperature was found to cause a solid to be deposited on the window of the cell. Heating to 100° and pumping the cell did not remove this deposit completely. Hence it was found impractical to perform an extended series of experiments. The results reported here are on the basis of experiments which were sandwiched between calibration runs. If the deposit formed during any run changed the nature of the wall of the cell, it was not found to affect the results.

Liquid Phase Photolysis.—Photolyses of cyclohexanone in the liquid phase were carried out in a Pyrex cell 1.5 cm. diameter and 1.0 cm. deep and a quartz cell 2.0 cm. diameter and 3.0 cm. deep. Before irradiation, the liquid samples were degassed at Dry Ice–ether temperature and the cell was sealed. After irradiation, the carbon monoxide formed could be admitted to the vacuum line by breaking a capillary seal on the cell. In the case of pure cyclohexanone, absorption of the useful radiation was essentially 100%. Photolyses of cyclohexanone in methylpentane solution were carried out at a concentration such that 57.8% of the radiation at 3130 Å. was absorbed and the decomposition was carried to 7.2%.

The photolysis of 2-methylcyclohexanone was studied with the sole purpose of identifying the isomeric product. Hence the experiment was conducted in the liquid phase in a bell-shaped Pyrex cell which was irradiated from the center by a mercury arc. The cell was cooled by a water jacket.

Results

Photolysis of cyclohexanone vapor gave carbon monoxide, ethylene, propylene, 1-pentene, cyclopentane and an unknown product A which was characterized by its retention time on a gas chromatographic column and its mass spectrum. The peak with the highest *m/e* value on the mass spectrum (excluding isotope peaks) was 98. The infrared spectrum of A as a dilute solution in carbon disulfide showed peaks at 1725 (s), 986 and 908 cm.$^{-1}$. It was found that A was formed in the liquid phase photolysis of cyclohexanone too. In this way milligram quantities of A were prepared and purified by gas chromatography. As a solution in chloroform its infrared spectrum showed these peaks at 2820, 2700 (aldehydic C–H), 1725 (C=O), 1641, 992 and 915 ($CH_2{=}C{<}$), 1450 and 1408 ($-CH_2-$ adjacent to C=O). The spectrum showed a strong similarity to that of 4-pentenal.[7] On the basis of this evidence, it was concluded that A is 5-hexenal.

The quantum yields for carbon monoxide and 5-hexenal in the photolysis of cyclohexanone vapor are given in Table I. Carbon monoxide was separated from the photolysis products at liquid nitrogen temperature. 5-Hexenal was separated from undecomposed cyclohexanone by gas chromatography using a Perkin–Elmer Model 154 Vapor Fractometer and column "A" and estimated by both the area under the trace made by the recorder under standard conditions and by mass spectrometry (using a Consolidated Engineering Co. type 21–620 mass spectrometer).

TABLE I

PHOTOLYSIS OF CYCLOHEXANONE AT 3130 Å.

Pressure, mm.	Time, min.	Temp., °C.	Φ_{CO}	Φ_{hexena}	Remarks
		Vapor phase			
4.8	120	28.9	0.04_6	0.16	
3.7	60	25.8	...	.17	P_{Oxygen} = 21.0 mm.
4.7	120	28.8	$.02_2$	.19	P_{CO_2} = 18.0 mm.
5.0	120	100.0	$.10_8$	.12	
25.5	30	100.0	$.08_7$	.16	
47.0	30	100.0	$.06_1$	> .12	
Concn., moles/l.	Time, min.	Temp., °C.	Φ_{CO}	Φ_{hexena}	
		Liquid phase			
	2400	28	0.01_9	0.27	Pure liquid
5.94×10^{-2}	1000	28	0.01_3	0.11	Solvent: 3-methylpentane

Hexenal production was 3.7 times as important as the production of carbon monoxide at room temperature. With increasing temperature and constant pressure, $\Phi_{hexenal}$ decreased and Φ_{CO} increased. The effect of temperature on Φ_{CO} is known already from the work of Blacet and Miller.[5] Addition of oxygen did not suppress the production of hexenal but actually increased it. At the same time, in accordance with the results of Dunn and Kutschke,[6] it was found that the production of 1-pentene and cyclopentane was diminished but not eliminated. Similarly, their results on the effect of carbon dioxide on the production of carbon monoxide were also confirmed. With respect to $\Phi_{hexenal}$, addition of carbon dioxide acted the same way as oxygen, but more efficiently. The action of foreign gases can be attributed to their quenching effect on excited cyclohexanone molecules. Since such a quenching of the vibrational energy leads to an increased yield of hexenal at the expense of carbon monoxide, it appears that the diradical

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[10] R. Srinivasan, unpublished results, Kharasch, *et al.*,[9] noted the formation of 4-pentenal when the solvent was 1-octene.

which leads to the latter in the reaction scheme of Blacet and Miller[5] may originate from the higher vibrational levels of an electronically excited cyclohexanone molecule and the hexenal from the lower vibrational levels of the same electronic state. The electronic state involved is probably an upper singlet, as oxygen does not suppress it even at 21.0 mm. pressure. Using the superscript 1 to represent the upper singlet state and subscripts to indicate the vibrational levels, *some* of the primary processes in this system may be written as

$$[C_6H_{10}O] + h\nu \longrightarrow [C_6H_{10}O]_n^1 \qquad (8)$$

$$[C_6H_{10}O]_n^1 \longrightarrow CH_2CH_2CH_2CH_2CH_2\dot{C}O \qquad (9)$$

$$[C_6H_{10}O]_n^1 + M \longrightarrow [C_6H_{10}O]_0^1 + M \qquad (10)$$

$$[C_6H_{10}O]_0^1 \longrightarrow CH_2{=}CH\ CH_2CH_2CH_2CHO \qquad (11)$$

Steps to indicate deactivation by collision and internal conversion also should be included in the scheme. The action of added gases is to facilitate reaction 10. It follows that the molecule M can be cyclohexanone itself, and the experiments at 100° at increasing pressures of the ketone show the self-quenching effect.[11] It was found difficult to perform experiments at even higher pressures of the ketone than those given in Table I, as the separation of the small quantity of hexenal formed from the unreacted cyclohexanone proved troublesome.

On the basis of this picture it is possible to explain the temperature independence of Φ_{CO} at shorter wave lengths as well as its larger value compared to that at 3130 Å.[5] At 3130 Å., the temperature dependence of Φ_{CO} may be due to a small activation energy requirement for steps 3, 4, 5 and 6 in all of which a diradical splits off carbon monoxide.

In experiments in the liquid phase, the small quantity of hexenal formed during photolysis could not be separated efficiently from the large amount of pure cyclohexanone or solvent present. Hence in the two experiments reported here, Φ_{hexenal} is subject to greater uncertainty than the values in the gas phase photolysis. In general it can be said that in the condensed phase at 3130 Å., Φ_{CO} is only a third of its value in the vapor phase at room temperature while Φ_{hexenal} is not appreciably affected by the change of phase. It also was found that at this wave length in 3-methylpentane solution practically all the cyclohexanone that was used up could be accounted for as hexenal (90%) and carbon monoxide (10%). But when the photolysis was carried out in a quartz cell with the unfiltered radiation from the same light source, only about 16% of the cyclohexanone was isomerized to hexenal and products of higher boiling point than the ketone were produced. The gaseous products were still minor. It is known[12] that cyclohexanone in cyclohexanol solution on irradiation with a mercury arc gives rise to cyclohexanonepinacol as one of the products. So it is likely that a reaction between the ketone and the solvent, similar to that known in the cases of simple aliphatic ketones,[13] predominates in the photolysis at short wave lengths.

The photolysis of 2-methylcyclohexanone in the liquid phase gave rise to an unknown product B. In the mass spectrum of B, the peak with the highest *m/e* value was at 112, neglecting isotope peaks. B had these various peaks in its infrared spectrum: (solvent: chloroform from 5000 to 900 cm.$^{-1}$; carbon disulfide from 900 to 650 cm.$^{-1}$). 1725(s)(C=O); 2900, 2700 (aldehyde C–H); 1415, 1375, 1210, 1012, 967(s), 756(s). Since the spectrum did not indicate a double bond conjugated with the carbonyl group, or located terminally, B probably was hepten(3 or 4 or 5)-al(1). The peak at 756 cm.$^{-1}$ was taken to indicate a chain of three methylene groups[14] so that the double bond may be in the 5-position. This structure would be in keeping with the results of Ciamician and Silber[8] and also can be predicted from the photoisomerization of cyclohexanone if substitution of a methyl group does not alter the nature of the process. 5-Heptenal can exist in two geometric forms, and an attempt was made to establish the configuration of the product that was obtained. The infrared spectrum had a strong peak at 967 cm.$^{-1}$ and none in the region below 725 cm.$^{-1}$ This suggested the presence of a *trans*-isomer alone.[15] The product obtained was also run through a gas chromatographic column under conditions which were favorable for good resolution. Even under the best conditions the product gave only one, fairly symmetric peak. It appears reasonable to conclude that the product is mainly *trans*-5-heptenal.

A few experiments were made on the vapor phase photolysis of 2-methylcyclohexanone. A product which had the same retention time on a chromatographic column as 5-heptenal and a similar mass spectrum was observed to be formed. But attempts to obtain its infrared spectrum in solution were unsuccessful. In the absence of this evidence, it is not possible to decide whether one or both geometric isomers are formed.

Discussion

The photoisomerization of cyclohexanone to 5-hexenal conceivably can occur by several different mechanisms. In examining these, it is necessary to bear in mind the results previously obtained[7] on the photoisomerization of cyclopentanone, since the two processes seem to be very similar.

The possibility of the formation of 5-hexenal from smaller radical fragments is excluded by the non-inhibition of the process by oxygen. The diradical $\cdot CH_2CH_2CH_2CH_2CH_2CO\cdot$ which gives rise to carbon monoxide can lead to 5-hexenal, too, by an internal abstraction of a hydrogen atom by the carbonyl group, or by some other manner of rearrangement.[9] In that case, it is unlikely that addition of foreign gases would affect Φ_{CO} and Φ_{hexenal} in opposite ways. One is led to conclude that the transfer of a hydrogen atom to the carbonyl group from a β-carbon occurs in the excited

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[11] These experiments could not be performed at room temperature, as the vapor pressure of cyclohexanone at 25° is only 5.18 mm.[4]

[12] Ch. Weizmann, E. Bergmann and Y. Hirshberg, THIS JOURNAL, **60**, 1530 (1938).

[13] N. C. Yang and D. D. H. Yang, *ibid.*, **80**, 2913 (1958), and earlier references therein.

[14] L. J. Bellamy, "Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 26.

[15] L. J. Bellamy, ref. 14, p. 40.

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.

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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

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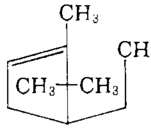
It has been found that *dl*-camphor, as a solution in air-free organic solvents, isomerizes under the influence of radiation of 3130 Å., to α-campholenic aldehyde (A) and a ketone (B). B has been identified as 1:2:2-trimethylcyclopent-3-enyl methyl ketone. Quantum yields for the formation of carbon monoxide 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.