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

Photoisomerization Processes in Cyclic Ketones. IV. Cycloheptanone[1]

BY R. SRINIVASAN

RECEIVED JUNE 2, 1959

6-Heptenal has been identified as one of the products of the vapor phase photolysis of cycloheptanone at 3130 Å. The other products were carbon monoxide, propylene (both of which have been reported before), traces of ethylene, 1-hexene and cyclohexane. Quantum yields for the formation of carbon monoxide and 6-heptenal have been obtained. The mechanism of the photochemical decomposition of cycloheptanone appears to be similar to that of cyclopentanone and cyclohexanone.

Introduction

The photolysis of cycloheptanone vapor has been studied by Saltmarsh and Norrish,[2] and by Bamford and Norrish.[3] The products found by them were carbon monoxide, small quantities of propylene, and a hydrocarbon C_6H_{12} which might have been a hexene or cyclohexane. The experimental arrangement used by these workers for irradiation has been criticised by Benson and Kistiakowsky[4] on the ground that a part of the liquid was also exposed to the radiation.

The present work was undertaken as an extension of the previous studies on the photoisomerization of five- and six-membered ring ketones[5] to a seven-membered ring ketone. At the same time, since reliable results on the free radical photodecomposition products of this ketone have not hitherto been published, the identity of these products was established, and quantitative data on their production have been obtained.

The results of a few experiments on the photoisomerization process in cyclobutanone have also been included.

Experimental

Materials.—Cycloheptanone from K and K laboratories was fractionated at atmospheric pressure. A small middle fraction was collected, dried over "Drierite," distilled once *in vacuo* and used. By gas chromatography, it was found to be essentially free from impurities. Oxygen from Airco and cyclohexane (spectrograde) from Eastman Kodak Co. were used as obtained. Cyclobutanone from K and K laboratories was distilled repeatedly *in vacuo* before use. The final product was only 98% pure.

Apparatus.—The photolysis cell and light source have been described.[5] The intensity of the useful radiation (the group of lines at 3130 Å.) was 3.3×10^{15} quanta/sec. The logarithm of the molar absorption coefficient of the ketone at 3130 Å. was taken as 0.86 on the basis of the data of Biquard.[6] The extent of the decomposition in all experiments was 2% or less.

Results

The products of the photolysis were separated into different fractions by distillation and analyzed by gas chromatography with a Perkin–Elmer Model 154 Vapor Fractometer and column "A." Where necessary, products were identified by mass spectroscopy. The fraction removed at −195° was essentially carbon monoxide. The fraction at −130° was mostly propylene with about 12% of ethylene. The fraction at −10° consisted of two compounds, both of which had their highest peak at an *m/e* of 84 in their mass spectrum. These were identified as 1-hexene (infrared spectrum in chloroform showed peaks at 908, 990, 1638 and 2810 cm.$^{-1}$) and cyclohexane (by comparison of the retention time on a chromatographic column with authentic cyclohexane). The residue, which contained unreacted cycloheptanone and an unknown product A restored the color to Schiff's reagent, indicating the presence of an aldehyde. The peak with the largest *m/e* value in the mass spectrum of A was at 112. Its infrared spectrum (solvent, chloroform) showed peaks at 1720 (C=O), 2800, 2690 (-CHO), 1640, 990 and 910 cm.$^{-1}$ (CH_2=CH-). On the basis of this evidence, A was identified as 6-heptenal.

An attempt was made to detect other photoisomeric products formed by processes analogous to those reported in cyclodecanone[7] and γ-tropolone methyl ether[8] but no evidence for the formation of such a product under the present experimental conditions was found.

Quantum yields for the production of carbon monoxide and 6-heptenal in the photolysis of cycloheptanone vapor are given in Table I. 6-Heptenal was separated from undecomposed cycloheptanone by vapor phase chromatography and estimated from the area under the trace made by the recorder under standard conditions. For calibration, cycloheptanone was used, since pure 6-heptenal was not available.[9]

TABLE I

PHOTOLYSIS OF CYCLOHEPTANONE VAPOR AT 3130 Å.

P_{ketone}, mm.	T, °C.	Time, min.	P_{oxygen}, mm.	Φ_{CO}	Φ_{heptenal}
11.7	70	110	..	0.12	0.17
10.5	100	120	..	0.14	.15
9.3	100	120	3.2	Not determined	.14

In the limited temperature range from 70–100°, 6-heptenal is a more important product than carbon monoxide. The ratio of 1-hexene to cyclohexane

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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] R. Srinivasan, *ibid.*, **81**, 1546, 2601 (1959).

[6] D. Biquard, *Bull. soc. chim. France*, **8**, 55 (1941).

[7] M. Barnard and N. C. Yang, *Proc. Chem. Soc.*, 302 (1958).

[8] O. L. Chapman and D. J. Pasto, THIS JOURNAL, **80**, 6685 (1958).

[9] Since the detecting element in the chromatograph used was sensitive only to the thermal conductivity of the components, use of cycloheptanone for calibrating the sensitivity of the instrument to the isomeric 6-heptenal is a reasonable approximation. This was tested by using cyclohexanone and 5-hexenal, when no difference in sensitivity was found within the accuracy of the calibration procedure which was 0.8%.

was 1:4.7. Ethylene and propylene amounted to 0.3 and 2.3%, respectively, of the total hydrocarbon ($C_2 + C_3 + C_6$) products. The mass balance, *i.e.*, propylene/2 + 1-hexene + cyclohexane = CO, was satisfactory to within 10%. The addition of 3.2 mm. of oxygen did not suppress the production of either 6-heptenal or the C_6 hydrocarbons.

The photolysis of cyclobutanone led to the formation of carbon monoxide, ethylene, propylene and cyclopropane, all of which have been reported in earlier studies.[4,10] The only peak in the gas chromatogram of the products that was not accounted for was found to be due to a compound of mass 70 and hence isomeric to cyclobutanone. It was not positively identified as it was produced in very small yields, the efficiency being 1/86 of that of carbon monoxide. Assuming that this compound was 3-butenal, which would be the predicted product of the photoisomerization of cyclobutanone, the quantum yield for this process can be estimated to be less than 0.004 using the value for Φ_{CO} at 3130 Å. of 0.35[11] found by Blacet and Miller.[10]

Discussion

The mechanism of the photolysis of cycloheptanone appears to follow from those of the unsubstituted four, five and six-membered cyclic ketones.[5,10] The steps that may be important are

$$\overline{CH_2(CH_2)_5CO} + h\nu \longrightarrow \dot{C}H_2(CH_2)_5\dot{C}O \qquad (1)$$

$$\longrightarrow \dot{C}H_2CH_2CH_2COCH_2CH_2\dot{C}H_2 \qquad (2)$$

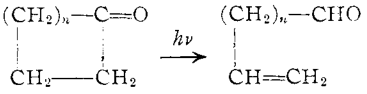
$$\longrightarrow CH_2{=}CH(CH_2)_4CHO \qquad (3)$$

$$\dot{C}H_2(CH_2)_5\dot{C}O \longrightarrow \overline{CH_2(CH_2)_4CH_2} + CO \qquad (4)$$

$$\longrightarrow CH_2{=}CH(CH_2)_3CH_3 + CO \qquad (5)$$

$$\dot{C}H_2CH_2CH_2COCH_2CH_2\dot{C}H_2 \longrightarrow 2C_3H_6 + CO \qquad (6)$$

The photoisomerization processes in cyclopentanone, cyclohexanone and cycloheptanone resemble one another in that (a) in every instance the product involves the net transfer of a β-hydrogen atom to the carbon of the carbonyl group. The reaction can be formulated in the general case as



$$\begin{array}{ccc} (CH_2)_n\text{—}C{=}O & & (CH_2)_n\text{—}CHO \\ | \qquad\quad | & \xrightarrow{h\nu} & | \\ CH_2\text{——}CH_2 & & CH{=}CH_2 \end{array} \qquad (7)$$

(b) the process is only slightly temperature dependent when radiation of 3130 Å. is used, and (c) the process is not suppressed by the addition of oxygen. A comparison of Φ_{CO} and the quantum yield for photoisomerization under approximately identical conditions for the various cyclic ketones is made in Table II.

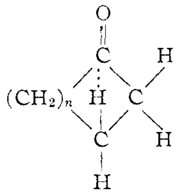
TABLE II

Φ_{CO} and $\Phi_{CH_2=CH(CH_2)_nCHO}$ for the ketone $\overline{CH_2CH_2(CH_2)_nCO}$ at 3130 Å. and 100°

	n = 1	2	3	4
Φ_{CO}	0.35[a]	0.18[b]	0.11[b]	0.14
$\Phi_{CH_2=CH(CH_2)_nCHO}$	<0.004	<0.04[b]	0.12[b]	0.15

[a] Reference 10. [b] Reference 5.

Earlier results on the photoisomerization of cyclopentanone and cyclohexanone[5] indicated that the transfer of the hydrogen atom occurred in an excited state of the ketone molecule before the ring structure had been disrupted. Extending this concept to the four and seven-membered ring ketones as well, it can be postulated that in general, reaction 7 proceeds through the intermediate



In the four-membered ring ketone (n = 1), the carbon atoms are presumably planar, or nearly so, with the hydrogen atoms extending above and below this plane. Since the freedom to turn around the carbon–carbon bonds is severely restricted, the formation of an intermediate as pictured above would involve the spanning of a considerable distance between the carbonyl carbon and a β-hydrogen. Further, cyclobutanone has only two β-hydrogen atoms, which may also be a factor in tending to limit this type of process.[12] In view of this, the low quantum efficiency of the photoisomerization process in this instance is not surprising. With increasing ring size, the freedom to turn around the individual C–C bonds increases and the efficiency of the photoisomerization process may be expected to increase. But when $n>4$, other processes may compete with this particular type of isomerization as indicated by the work of Barnard and Yang on cyclooctanone.[7] It is interesting to note that the quantum yields in cyclohexanone and cycloheptanone are about the same.

A test of the above theory may lie in determining the efficiency of the photoisomerization in substituted five-, six- and seven-membered ring ketones. In general, substitution in positions other than β should not affect the quantum yield, provided the substituent is a small group or atom and not strongly polar.

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

ROCHESTER, NEW YORK

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(10) F. E. Blacet and A. Miller, THIS JOURNAL, **79**, 4327 (1957).

(11) This value was obtained over the range 100–300°. It was found in the present study that the value for Φ_{CO} was the same at room temperature and at 100°.

(12) In the type II process in simple aliphatic ketones which also involves the net transfer of a hydrogen atom (from the γ to the α carbon atom) under the influence of light, the quantum efficiency of the process increases with the number of γ-hydrogen atoms available. J. W. Kraus and J. G. Calvert, THIS JOURNAL, **79**, 5921 (1957).