Intramolecular Rearrangements. III. Formation of 1-Methylcyclobutanol in the Photolysis of 2-Pentanone[1]

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1-Methylcyclobutanol has been isolated as a product in the vapor-phase photolysis of 2-pentanone. The yield of the alcohol diminishes with decrease in pressure and wave length. Oxygen and nitric oxide reduce the yields of acetone, ethylene and 1-methylcyclobutanol. In the photochemical decomposition of the liquid phase, the ratio acetone/1-methylcyclobutanol is independent of wave length and only slightly dependent on temperature.

Introduction

Recently Yang and Yang[2] reported the formation of 1-methylcyclobutanol in the liquid-phase photolysis of 2-pentanone.

Although the vapor-phase photochemical decomposition of ketones containing one or more γ-hydrogen atoms has been extensively investigated, cyclic alcohols have never been reported as products. It is clear, however, that the presence of these compounds among the products might eventually lead to an explanation of the fact that the apparent quantum yields of decomposition observed in the photolysis of ketones containing γ-hydrogen atoms were less than unity.[3]

Experimental

(a) **Apparatus.**—The vapor-phase quartz cell (10 cm. in length, 5 cm. in diameter) and liquid-phase quartz cell (0.05 cm. in length, 3.0 cm. in diameter) were provided with two outlets, one for sealing after filling and one with a breakseal. The cells were immersed in a Pyrex Dewar flask having double quartz windows. A water bath was used for experiments performed above 0°, and cold ethanol was the refrigerant for those conducted at temperatures below 0°. In a few vapor-phase experiments the quartz cell was enclosed in an aluminum furnace provided with double quartz windows.

A low-pressure mercury arc in conjunction with a Corning filter 9–54 was used in the Hg($^3P_1$)-sensitized experiments. An Osram 200 lamp was used in all other experiments. The 3130 Å. group of lines was obtained with a combination of Corning filters 0–54 and 7–54. A diphenylbutadiene solution,[4] in combination with a Corning filter 7–54, was used to isolate the 2537–2650 Å. group of lines. In the vapor-phase experiments, the quantum yields were determined at 3131 Å. by using 3-pentanone as an actinometer.

(b) **Analysis.**—After irradiation the liquid products of the reaction vessel were analyzed with a Perkin–Elmer Vapor Fractometer, equipped with a 2-meter column "A" (diisodecyl phthalate). A thermal-conductivity and flame-ionization detector were used simultaneously. In a few experiments ethylene and propane were determined quantitatively by combining low-temperature fractionation with mass spectrometric analysis.

(c) **Materials.**—2-Pentanone was obtained from Eastman Kodak Co. and carefully distilled on a spinning-band column. Only those fractions were used which contained less than 0.05% of impurity. 2-Pentanone-1,1,1,3,3-d_5 was obtained from Merck and Company. Mass-spectrometric analysis indicated that the sample contained only 3% of 2-pentanone-d_4 and was deuteriated only in the α-position.
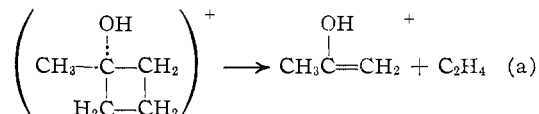
Results and Discussion

(a) **Identification of 1-Methylcyclobutanol.**—A product of the vapor- and liquid-phase photolysis which had a retention time on the Perkin–Elmer column "A" somewhat greater than that for 2-

pentanone was trapped out at −195° and subsequently analyzed on the mass spectrometer. The relatively simple cracking pattern given in Table I

TABLE I
MASS SPECTRAL PATTERN OF 1-METHYLCYCLOBUTANOL
Ionizing voltage, 70 volts

m/e	Relative intensity	m/e	Relative intensity
26	3.6	44	4.2
27	13.2	45	6.9
28	12.3	53	2.2
29	11.6	55	2.6
30	2.9	57	7.4
31	5.3	58	100.0
37	1.2	59	3.7
38	2.1	67	1.8
39	9.8	68	1.0
40	4.5	69	2.0
41	11.3	71	4.5
42	5.2	86	0.5
43	67.6		

indicates the major contribution comes from mass 58. No peaks were observed for masses greater than 86. It should be pointed out that the mass spectral pattern of 2-pentanone differs considerably from the spectrum given in Table I. For instance, the parent peak is higher than the peak of mass 58. It was thus tentatively concluded that the compound in question was 1-methylcyclobutanol,[5] the ion of which decomposes mainly according to the process

$$\left(\begin{array}{c} OH \\ | \\ CH_3-C-CH_2 \\ |\ \ \ \ | \\ H_2C-CH_2 \end{array} \right)^+ \longrightarrow \begin{array}{c} OH \\ | \\ CH_3C=CH_2 \end{array}^+ + C_2H_4 \quad (a)$$

In order to verify this identification, 2-pentanone-1,1,1,3,3-d_5 was photolyzed and the products analyzed by the same procedure as that described above. The mass spectrum cracking pattern of the product corresponding to a peak with a retention time the same as that for the one trapped out in the case of 2-pentanone could be ascribed to the cyclic alcohol in view of the presence of two major peaks of masses 61 and 63. These two peaks were of the same height and can only be explained by the decomposition of the cyclic alcohol ion according to two different routes having equal probability (b), (c). In the mass spectrum of 2-pentanone 1,1,1,3,3-d_5, only one peak corresponding to mass 63 has been observed.[6]

(1) This research was supported by a grant from the U. S. Public Health Service, Department of Health, Education, and Welfare.

(2) N. C. Yang and D-D. H. Yang, *J. Am. Chem. Soc.*, **80**, 2913 (1958).

(3) For a review see J. N. Pitts, Jr., *J. Chem. Educ.*, **34**, 112 (1957).
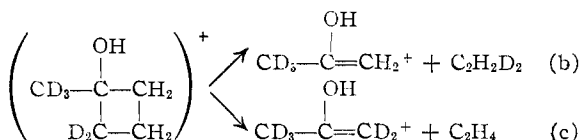
(4) M. Kasha, *J. Opt. Soc. Am.*, **38**, 929 (1948).

(5) The mass spectral pattern given in Table I agrees very well with that obtained from a prepared sample of 1-methylcyclobutanol received from N. C. Yang.

(6) P. Ausloos and E. Murad, *J. Am. Chem. Soc.*, **80**, 5929 (1958).

<div align="center">

Table II

Vapor-phase Photolysis. Effect of Pressure

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Wave length, Å.	Temp., °C.	P	$I_{abs.}$ quanta/cc./ sec. $\times 10^{-14}$	C_2H_4 Φ	Acetone Φ	n-Hexane Φ	1-Methyl-cyclobutanol Φ	1-Methyl-cyclobutanol/ acetone
3130	28	3.2	3.0	0.30	0.317	0.084	0.108	0.335
3130	28	2.5	3.0	..	.310	.087	.090	.291
		1.5	3.0	..	.300	.084	.075	.250
		1.5	0.2	..	.310	.075	.067	.213
		0.63	3.0	..	.318	.087	.0545	.171
		.30	3.0	...	.290	.087	.0348	.120
		.13	3.0	0.31	.318	.099	.0282	.088
	150	1.5	3.0	..	.310	...	.044	.141
2537–2650	28	1.5	..	..	...	...	....	.115
2537[a]	28	1.5	..	..	...	...	....	.09

[a] $Hg(^3P_1)$ sensitized.

$$\left(\begin{array}{c} \text{OH} \\ | \\ CD_3—C—CH_2 \\ | \quad | \\ D_2C—CH_2 \end{array}\right)^+ \nearrow \begin{array}{l} CD_3—\overset{\text{OH}}{\underset{|}{C}}=CH_2{}^+ + C_2H_2D_2 \quad (b) \\[2mm] \searrow CD_3—\overset{\text{OH}}{\underset{|}{C}}=CD_2{}^+ + C_2H_4 \quad (c) \end{array}$$

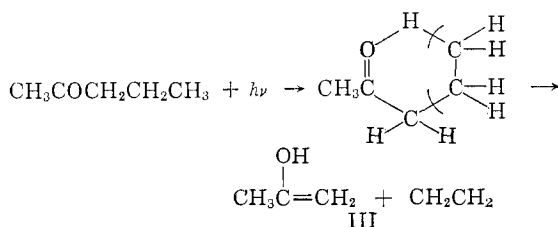**(b) Vapor-phase Photolysis.**—At 3130 Å., 28° and relatively high intensities, the major products are ethylene, acetone, biacetyl, n-hexane and 1-methylcyclobutanol. In agreement with the results reported earlier,[6] the products: CO, CH_4, C_2H_6, C_3H_6, C_3H_8 and C_4H_{10} also are formed, but at rates which are not more than 5% of the rate of formation of ethylene. The formation of biacetyl, n-hexane and the minor products can be explained by the dissociative processes

$$CH_3COCH_2CH_2CH_3 + h\nu \longrightarrow$$
$$CH_3CO + CH_2CH_2CH_3 \quad I$$
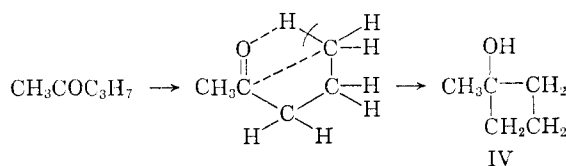$$\longrightarrow CH_3 + COCH_2CH_2CH_3 \quad II$$
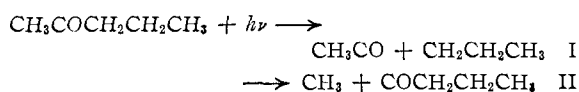
followed by subsequent secondary reactions of the radicals thus produced. The formation of ethylene, acetone and 1-methylcyclobutanol in the presence of efficient radical scavengers such as oxygen and nitric oxide indicates that these products are most likely formed by molecular rearrangements. A process analogous to

$$CH_3COCH_2CH_2CH_3 + h\nu \rightarrow CH_3C\underset{\substack{\\ }}{\overset{\text{O}}{\diagdown}}\begin{array}{c}H\diagdown C\diagup H \\ | \\ C—H \\ H\diagup \diagdown H\end{array}\begin{array}{c}C—H \\ | \\ C—H \\ \diagdown H\end{array} \rightarrow$$

$$\underset{\text{III}}{CH_3\overset{\text{OH}}{\underset{|}{C}}=CH_2 + CH_2CH_2}$$

has been proposed several times before to explain the formation of olefins in the photochemical decomposition of ketones containing γ-hydrogen atoms. Indirect evidence for the formation of the enol form of acetone has been obtained[7] recently in a photochemical investigation of 2-hexanone-5,5-d_2. It is reasonable to assume that the formation of 1-methylcyclobutanol occurs through a similar six-membered intermediate, where instead of the rupture of the α–β carbon bond, a linkage is formed between the carbonyl carbon and the γ-carbon

(7) R. Srinivasan. *J. Am. Chem. Soc.*, **81**, 5061 (1959).

$$CH_3COC_3H_7 \rightarrow CH_3C\underset{\substack{\\ }}{\overset{\text{O}}{\diagdown}}\begin{array}{c}H\diagdown C\diagup H \\ | \\ C—H \\ H\diagup \diagdown H\end{array}\begin{array}{c}C—H \\ | \\ C—H \\ \diagdown H\end{array} \rightarrow CH_3\overset{\text{OH}}{\underset{|}{C}}—CH_2 \atop \underset{CH_2CH_2}{|} \atop IV$$

1. Effect of Wave Length, Pressure and Temperature.—The results given in Table II show that the quantum yield for the formation of 1-methylcyclobutanol decreases with decrease in pressure and wave length and with an increase in temperature.

Three alternative interpretations must be considered.

(i) 1-Methylcyclobutanol produced in process IV may retain excess vibrational energy and may undergo a decomposition by reactions analogous to (b) and (c) unless the molecule is stabilized by collision. However, in the wave length range 2537–3130 Å. no CH_2CD_2 could be detected in the photochemical decomposition of 2-pentanone-1,1,1,3,3-d_5 at pressures as low as 0.05 mm. Also, yields of ethylene and acetone are within experimental error independent of pressure.

(ii) An intermediate diradical may be formed which unless stabilized may decompose according to

$$CH_3—\overset{\text{OH}}{\underset{|}{C}}—CH_2CH_2CH_2 \longrightarrow CH_3\overset{\text{OH}}{\underset{|}{C}}=CH_2 + CH_2CH_2$$
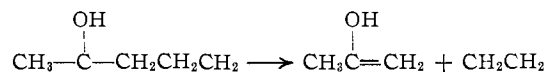
This possibility can be excluded on the basis of the pressure independence of the quantum yields of ethylene and acetone.

(iii) The alcohol may only be formed when the electronically excited ketone molecule is in a low vibrational level. This hypothesis is consistent with the observed effects of pressure, temperature and wave length. The data do not show that the non-occurrence of process IV under certain conditions is compensated by other modes of decomposition. In view of the low total primary quantum yields observed in the photolysis of ketones containing γ-hydrogens. it is reasonable to assume that the excited molecule may return to the ground state. It is also conceivable that the non-occurrence of process IV is compensated by process I. The quantum yield of this process is, however, difficult to measure under conditions where process IV is important.

2. Effect of Additives.—The data presented in Table III clearly indicate that oxygen and nitric oxide reduce the quantum yields of ethylene, acetone and 1-methylcyclobutanol, while a chemically inert compound such as carbon monoxide shows no effect.

Oxygen and nitric oxide inhibit the formation of 1-methylcyclobutanol to a considerably greater extent than the formation of acetone. This difference probably can be attributed to the observation made above that 1-methylcyclobutanol is formed only from a ketone molecule in a low-lying vibrational level which has a longer dissociative lifetime.

The quenching effect of oxygen on process III has not been reported previously. It should be pointed out, however, that the 20% decrease in the quantum yield of propylene observed by Brunet and Noyes[8] in the photolysis of 2-hexanone in the presence of 230 mm. oxygen may actually have been due to a genuine quenching effect and not to an incomplete condensation as suggested by the authors. The results presented in this paper indicate that the effect of oxygen is not a very pronounced one, and it is conceivable that the inhibition is even less important in the case of 2-hexanone. It is well-known that traces of oxygen quench the phosphorescence of acetone effectively and reduce the quantum yield of decomposition.[9] As pointed out by Noyes,[9] the fact that in the 3-pentanone–oxygen system no such decrease in quantum yield has been observed may be related to the very weak phosphorescence emitted by 3-pentanone, which in turn is probably

TABLE III

VAPOR-PHASE PHOTOLYSIS. EFFECT OF ADDITIVES

P additive, cm.	Φ C$_2$H$_4$	Φ Acetone	Φ 1-Methyl-cyclobutanol	1-Methyl-cyclobutanol/acetone
None	0.310	0.307	0.078	0.252
[CO] 4.5	.302	.310	.081	.260
[O$_2$] 0.3	.240	.252	.047	.185
1.5	.212	.225	.033	.144
9.8	.183	.198	.021	.107
[NO] 4.5	...	.205	.028	.129

related to a shorter lifetime of the dissociative excited-triplet state, and not necessarily to the absence of it. The high phosphorescence yield of biacetyl observed in the 3-pentanone-biacetyl system[10] clearly indicates the presence of triplet excited 3-pentanone. 2-Pentanone is similar to 3-pentanone in that no phosphorescence has been observed.[11] The moderate effect of oxygen in the case of 2-pentanone could thus either be due to an interaction of oxygen with a short-lived triplet state responsible for processes III and IV or to quenching of the upper singlet state.

(c) Liquid-phase Photolysis.—The data presented in Table IV confirm the findings of Yang

(8) V. Brunet and W. A. Noyes. Jr., *Bull. Soc. Chim. France*, 121 (1958).

(9) For a review see: W. A. Noyes, Jr., "Festschrift Arthur Stoll," Birkhäuser AG., Basel, 1958.

(10) D. S. Weir, *J. Am. Chem. Soc.*, **83**, 2629 (1961).

(11) P. Ausloos and E. Murad, *J. Phys. Chem.*, 1519 (1961).

and Yang[2] that 1-methylcyclobutanol is a major product in the liquid-phase photochemical decomposition of 2-pentanone. In contrast with the gas-phase studies, experiments performed at 2537 Å. gave values for the ratio alcohol/acetone which are the same as those obtained at 3130 Å. (Table IV). Also, addition of cyclohexane up to 90 mole % did not alter this ratio.
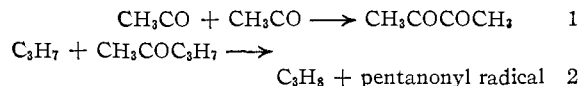
TABLE IV

LIQUID-PHASE PHOTOLYSIS[a]

Temp., °C.	−65	0	76
Products in mole/cc./sec. × 10^{10}			
Ethylene	n.d.	n.d.	3.0
Propane	<0.005	0.10	2.0
Acetone	1.26	2.7	2.9
Biacetyl	<0.005	0.05	0.60
1-Methylcyclobutanol	0.53	1.30	1.30
1-Methylcyclobutanol/acetone	0.42	0.48	0.45

[a] λ, 3130 Å.; n.d., not determined; I_{abs} 8 × 10^{14} quanta/cc./sec.

The relatively high yield of 1-methylcyclobutanol is consistent with the pressure trends observed in the gas-phase photolysis. The absence of a wave length effect in the liquid-phase clearly indicates that vibrational deactivation is very effective under these conditions.

A change in temperature from −65 to +75° has only a small effect on the ratio alcohol/acetone but may have an effect on the rates of formation of these compounds.[12] The relative yields of propane and biacetyl are negligibly small at −65°, but increase sharply at higher temperatures. Carbon monoxide, methane, propylene, acetaldehyde and n-hexane were less than 10% of the propane at all temperatures. The formation of propane and biacetyl are explained readily by the occurrence of process I followed by the secondary reactions

$$CH_3CO + CH_3CO \longrightarrow CH_3COCOCH_3 \qquad 1$$

$$C_3H_7 + CH_3COC_3H_7 \longrightarrow$$
$$C_3H_8 + \text{pentanonyl radical} \qquad 2$$

The pentanonyl radical produced in reaction 2 may further react with a similar radical or with acetyl. In the condensed phase, and at the intensities and temperatures used in this work, the propyl radical may be expected to react mainly according to reaction 2. Propane may thus be considered as a measure of the yield of decomposition according to process I. The observed temperature effect may be due either to an energy barrier to process I, or to a cage recombination. The only argument against the latter possibility is the absence of any evidence of a disproportionation reaction between the original partners, as indicated by the absence of propylene and acetaldehyde among the products at −65°.

(12) All experiments listed in Table IV were performed at constant absorbed intensity and are for 0.2% conversion. It was found that the rates of formation of acetone, and to a much lesser extent those of 1-methylcyclobutanol. decrease with increase in conversion. The lower the temperature the more pronounced the effect of conversion. The rates of formation of biacetyl and propane were not appreciably affected by a change in conversion.