JOURNAL
OF THE AMERICAN CHEMICAL SOCIETY

VOLUME 89, NUMBER 9 APRIL 26, 1967

Physical and Inorganic Chemistry

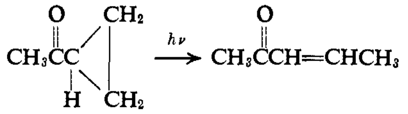
Structure and Reactivity in the Vapor-Phase Photolysis of Ketones. IV. Cyclopropyl and Olefinic Cyclic Ketones[1]

L. D. Hess[2] and J. N. Pitts, Jr.

Contribution from the Department of Chemistry, University of California, Riverside, California. *Received November 21, 1966*

Abstract: Vapor-phase irradiation of bicyclo[3.1.0]hexan-3-one (I) and 3-cyclopentenone (III) at 3130 and 2380–2654 A results in the formation of carbon monoxide and hydrocarbon products with high quantum efficiencies, $\Phi_{CO} = 0.77$ and 0.87 for I and III, respectively, under a variety of experimental conditions. The hydrocarbon products from I are 1,4-pentadiene (major), vinylcyclopropane, and 1,3-butadiene, while III gives almost exclusively butadiene ($\Phi = 0.88$) over a wide range of temperatures. In contrast, irradiation of bicyclo[3.1.0]hexan-2-one (II) and 2-cyclopentenone (IV) under identical conditions produces only trace amounts of CO and no detectable hydrocarbons. However, compound II does undergo a photoinduced rearrangement to form 3-methyl-2-cyclopentenone. The cyclopropyl and double-bond groups were found to exhibit similar effects on the modes of photoreactivity of these four cyclic ketones. Either of these groups conjugated with the carbonyl chromophore stabilize the ketone, whereas their location in the homoallylic position greatly facilitates photodecomposition.

In an earlier study of this series relating molecular structure and modes of photodecomposition of ketones,[3] it was observed that the major primary process in the vapor-phase irradiation of methyl cyclopropyl ketone at 2537–2654 A is an intramolecular rearrangement to methyl propenyl ketone.[4]



The efficiency of this interesting, temperature-independent (25–120°) rearrangement ($\Phi = 0.3$) compared to the relative lack of free radical and carbon monoxide production ($\Phi < 0.1$) led to the idea that the incorporation of a cyclopropyl group into α and β positions of a series of ketones might serve as a "structural probe" indicating the degree of intramolecular energy transfer from the C=O chromophore to the relatively weak C—C bonds in the cyclopropyl ring.

Studies of physical properties, particularly spectra, place the cyclopropyl group between a vinyl and a saturated group in ability to conjugate with adjacent unsaturation.[5] Further, cyclopropyl and olefinic groups have similar effects on rates of reactions involving carbonium ions. To determine whether these correlations apply to vapor-phase photochemical reactions was an additional objective of this investigation.

We report here detailed studies of the vapor-phase photoreactivity of two cyclopropyl (I and II) and two

---

[1] Presented in part at the Fourth International Conference on Photobiology, Oxford, 1964 (see "Recent Progress in Photobiology," E. J. Bowen, Ed., Blackwells, 1965, p 30); for reviews of earlier vapor-phase studies relating to the structure and reactivity of ketones, see (a) W. A. Noyes, Jr., G. A. Porter, and J. E. Jolley, *Chem. Rev.*, **56**, 49 (1956); (b) J. N. Pitts, Jr., *J. Chem. Educ.*, 34, 112 (1957).

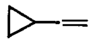
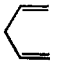
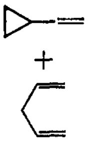
[2] This paper is taken from Ph.D. dissertation of L. D. H., University of California, Riverside, Calif., 1965.

[3] The photochemistry of ketones has been reviewed by several authors: (a) R. Srinivasan, *Advan. Photochem.*, 1, 83 (1963); (b) O. L. Chapman *ibid.*, 1, 323 (1963); (c) K. Schaffner, *Fortschr. Chem. Org. Naturstoffe*, **22**, 1 (1964); (d) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965; (e) J. N. Pitts, Jr., and J. K. S. Wan, in "Chemistry of the Carbonyl Group," S. Patai, Ed., John Wiley and Sons, Inc., London, 1965; (f) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966; (g) E. W. Abrahamson, J. G. F. Littler, and K. P. Vo, *J. Chem. Phys.*, **44**, 4082 (1966).

[4] J. N. Pitts, Jr., and I. Norman, *J. Am. Chem. Soc.*, **76**, 4815 (1954).

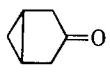
[5] E. Vogel, *Fortschr. Chem. Forsch.*, **3**, 431 (1955).

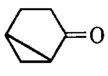
Table I. Effect of Temperature on the Photolysis of Bicyclo[3.1.0]hexan-3-one (I) at 3130 A

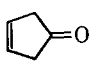
				Quantum yields, Φ^a				
Temp, °C	Incident quanta/sec × 10^{-14}, I_0	Fraction abs, Q_m	Time, sec × 10^{-4}					CO
77.9	2.39	0.420	1.15	0.019	0.07	0.67	0.74	0.77
77.6	2.48	0.420	1.03	0.023	0.08	0.67	0.75	0.80
77.8	2.53	0.390	1.08	0.020	0.08	0.64	0.72	0.77
118	2.63	0.392	1.50	0.016	0.10	0.58	0.68	0.75
118	2.71	0.388	0.93	0.017	0.10	0.62	0.72	0.76
154	2.48	0.420	1.14	0.016	0.12	0.70	0.82	0.83
155	2.48	0.418	1.00	0.014	0.12	0.66	0.78	0.82
196	2.82	0.569	1.08	0.009	0.13	0.58	0.71	0.75
196	2.78	0.393	0.96	nd	nd	nd		nd
196	2.75	0.384	1.08	0.013	0.14	0.63	0.77	0.79
241	2.51	0.430	1.02	0.012	0.17	0.72	0.89	0.83
240	2.49	0.416	1.02	0.009	0.16	0.64	0.80	0.85
			Average	0.015	0.11	0.65	0.76	0.79

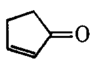
[a] nd = not determined.

olefinic (III and IV) cyclic ketones with the double bond and cyclopropyl groups located in analogous positions with respect to the carbonyl chromophore.[6]


I


II


III


IV

Experimental Section

Apparatus and Procedures. The photochemical apparatus used is similar to the type first developed by Blacet and Heldman.[7] The basic parts of the apparatus consisted of a medium pressure mercury arc, a set of interference filters, a quartz reaction cell and and optical system, a phototube for relative radiant energy measurements, and a conventional high-vacuum system.

The light source was a Hanovia Type A lamp which was mounted in a water-cooled housing and operated by an inductance-stabilized 165-v output transformer operating at 2.8 amp (460 w). The input voltage to the transformer was obtained from a Sola 1000-w ac voltage stabilizer. This arrangement yielded very stable operation of the lamp after an initial break-in period of 24 hr.

Interference filters obtained from Jena Gaswerk, Schott and Gen., Mainz, Germany (distributed by Fish-Schurman Corp., New Rochelle, N. Y.) were used to isolate the 3130-A mercury emission line. A 3-cm layer of chlorine gas at 1 atm pressure in a quartz filter cell and a Corning red-purple Chlorex glass filter (9863) were used to isolate the group of lines in the region 2380–2654 A. The quartz-lens system formed a parallel homogeneous light beam which completely illuminated the reaction cell. A water-cooled detector housing was attached to the exit of a heated masonite chamber and contained an RCA 935 phototube for relative light intensity measurements.

The quartz reaction cell (2.5 × 25 cm) was placed inside a cylindrically shaped aluminum block furnace which could be heated to 300° and automatically controlled at any temperature in the range 30–300° with an accuracy of 1% at a specific point. The temperature variation along the cell was also about 1% as determined by three thermocouples placed at the center and ends of the cell. The furnace was heated by an 800-w heating tape to which the power was regulated by a Brown potentiometer pyrometer. The furnace and high-vacuum manifold were located inside an air-thermostated chamber which could be heated to 100°. This chamber was heated by two conical 1000-w heating elements which were controlled by a second Brown potentiometer.

The analytical section of the vacuum system utilized a small down-draft diffusion pump to assist in transferring gaseous products to a calibrated gas buret attached directly to the output side of a 2-l. Toepler pump. A second Toepler pump was used to transfer the gaseous products from the buret to either a stopcock sample holder, a micro-infrared gas cell, or a chromatograph "crusher tube." Samples were subsequently analyzed by gas chromatography and infrared and mass spectroscopy. Condensable products not volatile at Dry Ice temperatures were sealed in a 3-mm Pyrex tube and introduced into a gas chromatograph where the sample was admitted to the helium flow stream by means of a heated stainless steel tubing-crusher.[2] Samples were routinely trapped from the chromatography for spectroscopic analysis. Several column packings were employed for identification, purification, and quantitative analyses. A 0.25-in. by 15-ft 20% Carbowax 20M on 60–80 HMDS Chromosorb and an $^1/_8$-in. by 25-ft 20% hexadecane on 30–42 firebrick were the most useful columns. Quantitative analysis of hydrocarbons not volatile at −196° could be obtained without previous separation from the parent ketone when these two columns were used in series. The chromatograph used was an Aerograph A-350-B with a thermal conductivity detector. Calibrations of detector response for each compound were made in terms of peak area units per micromole of component admitted. The precision of each sensitivity plot was better than 2%. Permanent gases were analyzed on a separate system utilizing a molecular sieve column and also by mass spectrometry.

3-Methyl-2-cyclopentenone was analyzed spectrophotometrically at 3380 A after quantitative transfer from the reaction vessel to a measured quantity of cyclohexane (*in vacuo*). The extinction coefficient for this ketone at 3380 A determined from a Beer's law plot is 23.3 ± 0.8 ml mmole^{-1} cm^{-1}.

Acetone[8,9] (Φ_{CO} = 1.00) and diethyl ketone[8,10] (Φ_{CO} = 0.97) at 120° were used as internal actinometers. The value of Φ_{CO} for diethyl ketone was determined using Φ_{CO} = 1.00 for acetone. The experimental value obtained, 0.97, is in good agreement with literature values.[8,10] Dark runs for ketones I–IV at the highest temperatures employed in the photolyses were carried out for time periods longer than photolysis times; each of the ketones was found to be thermally stable under these conditions. In addition the amount of ketone remaining unreacted was at least 95% in all of the quantitative experiments.

Synthesis and Ultraviolet Data of Ketones I–IV. The cyclopropyl groups of compounds I[11] and II[12] were formed by a Simmons-Smith reaction[13,14] of methylene iodide with 3-cyclopen-

---

(6) Quantum yields of CO for I and II are reported in ref 1 and in J. N. Pitts, Jr., L. D. Hess, E. J. Baum, E. A. Schuck, J. K. S. Wan, P. A. Leermakers, and G. Vesley, *J. Photochem. Photobiol.*, 4, 305 (1965).

(7) F. E. Blacet and J. D. Heldman, *J. Am. Chem. Soc.*, 64, 889 (1942).

(8) E. W. R. Steacie, "Atomic and Free Radical Reactions," Vol. 1 and 2, 2nd ed, American Chemical Society Monograph No. 125, Reinhold Publishing Corp., New York, N. Y., 1954.

(9) D. S. Herr and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **62**, 2052 (1940).

(10) K. D. Kutschke, M. H. J. Wijnen, and E. W. R. Steacie, *ibid.*, **74**, 714 (1952).

(11) S. Winstein and J. Sonnenberg, *ibid.*, **83**, 3235 (1961).

(12) N. A. Nelson and G. A. Mortimer, *J. Org. Chem.*, **22**, 1146 (1957).

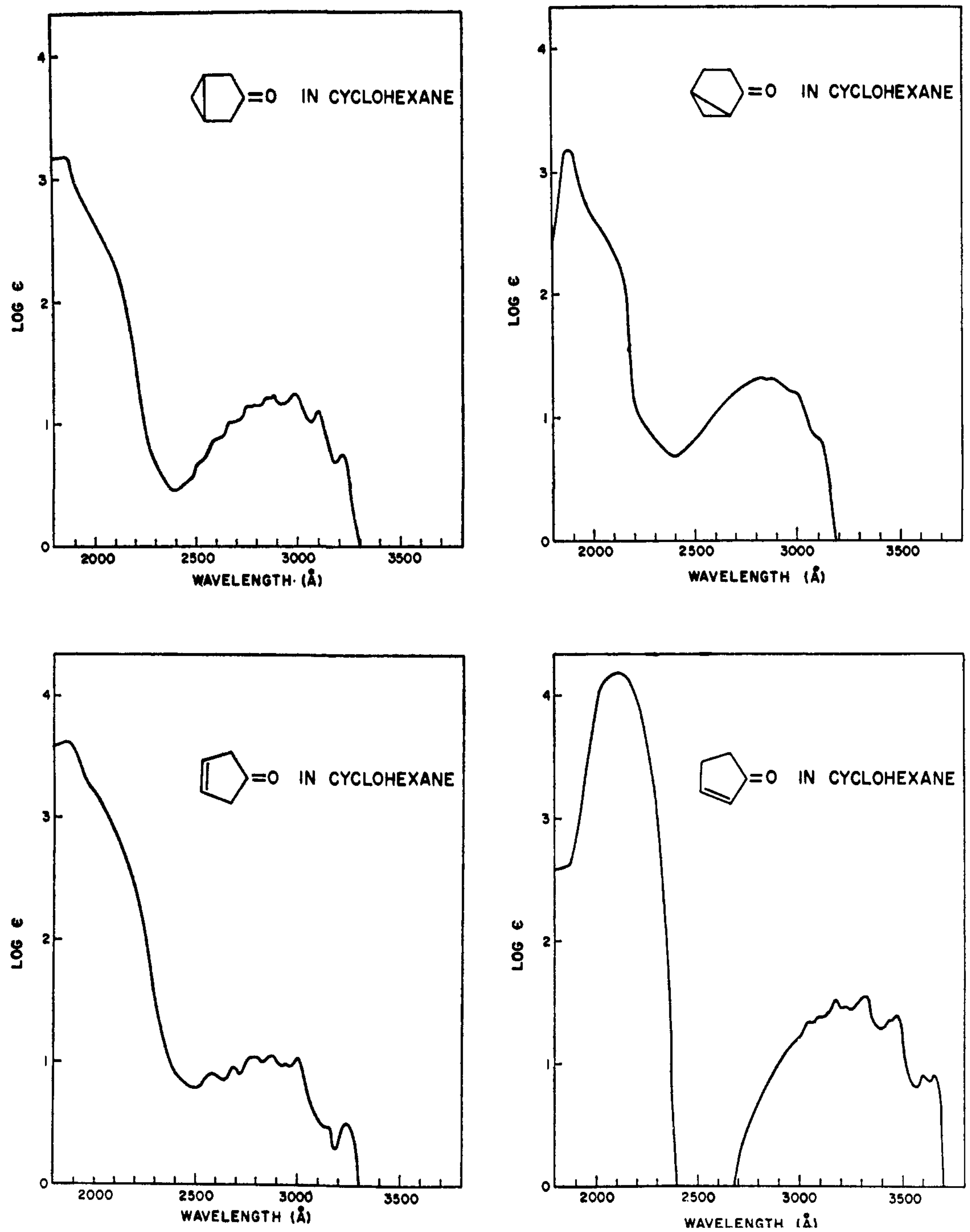


Figure 1. Ultraviolet spectra of ketones I–IV dissolved in cyclohexane (Cary 15 spectrophotometer).

tenol[15] and 2-cyclopentenol,[16] respectively. Oxidation of the resulting cyclopropyl alcohols as well as 3-cyclopentenol and 2-cyclopentenol using the Jones reagent[17] gave the corresponding ketones I, II, III,[16] and IV, respectively. Identification of reaction intermediates and the ketones was accomplished by infrared, ultraviolet (for ultraviolet spectra see Figure 1), nmr, and mass spectroscopy as well as gas chromatography.

Results

Bicyclo[3.1.0]hexan-3-one (I). The products formed from the vapor-phase photolysis of compound I are carbon monoxide, 1,4-pentadiene, vinylcyclopropane,[18] and 1,3-butadiene. Quantum yields of these compounds, obtained from a series of photolyses at several temperatures (80–240°) and 35 mm pressure with light of wavelength 3130 A, are shown in Table I (see also Figure 2).

In another set of experiments the ketone pressure was varied nearly 20-fold, and the effect of added nitrogen (up to 400 mm) and oxygen (50 mm) on the hydrocarbon quantum yields was also determined. These results are given in Table II. An additional series of experiments with the ketone at 118° and 5 to 40 mm pressure were conducted with light of shorter wave-

---

(13) H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **81**, 4256 (1959).

(14) E. LeGoff, *J. Org. Chem.*, **29**, 2048 (1964).

(15) S. Winstein, E. L. Allred, and J. Sonnenberg, *ibid.*, **25**, 26 (1960).

(16) K. Alder and F. H. Flock, *Chem. Ber.*, **89**, 1732 (1956).

(17) K. Bowden, I. M. Heilbron, E. H. R. Jones, and B. L. C. Weedon, *J. Chem. Soc.*, 39 (1946); 2548 (1953).

(18) H. M. Frey (private communication) also reports CO, 1,4-pentadiene, and vinylcyclopropane as the major vapor-phase photolysis products from compound I.

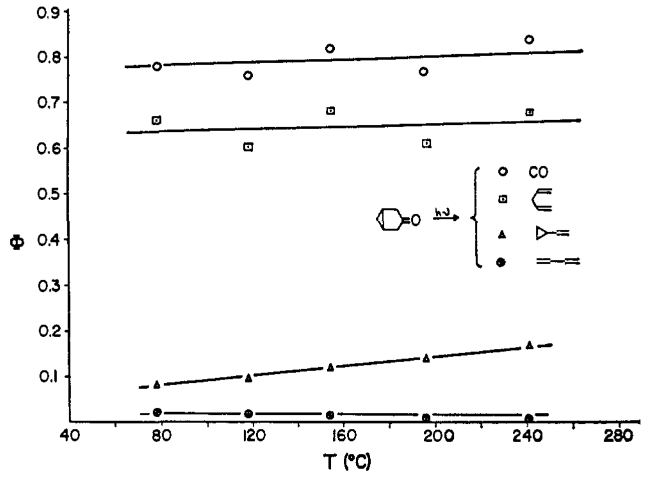


Figure 2. Temperature dependence of quantum yields of products from the photolysis of bicyclo[3.1.0]hexan-3-one (I) at 3130 A and 30 mm pressure (see also Table I).

lengths (2380–2654 A); the results are tabulated in Table III. Care was taken to ensure that the light intensities absorbed at the two spectral regions are similar.

Table II. Effect of Pressure on Photolysis of Bicyclo[3.1.0]hexan-3-one (I) at 118°, 3130 A

P, mm Ketone	N₂	Time, sec × 10^{-4}	Quantum yields, Φ[a] =—=	▷—=		▷—= + 	CO
7.5	187	1.69	0.024	0.12	0.84	0.96	nd
9.7	411	3.99	0.033	0.10	0.79	0.89	nd
35.5		0.536	0.018	0.10	0.64	0.74	0.76
35.5		0.539	0.018	0.10	0.64	0.74	0.76
24.3		0.914	0.018	0.11	0.66	0.77	0.76
24.5		0.904	0.018	0.11	0.68	0.79	0.77
15.0		0.903	0.018	0.11	0.65	0.76	0.77
15.1		0.720	0.019	0.12	0.72	0.84	0.80
5.0		1.71	0.023	0.12	0.73	0.85	0.84
5.0		0.732	nd	nd	nd		0.74
5.0		0.760	0.021	0.12	0.71	0.83	0.81
2.0		0.865	0.021	0.12	0.70	0.82	0.83
2.3		0.902	0.024	0.14	0.72	0.86	0.80
		Average	0.021	0.11	0.71	0.82	0.79

[a] nd = not determined.

Table III. Effect of Ketone Pressure on the Photolysis of Bicyclo[3.1.0]hexan-3-one (I) at 118°, 2380–2654 A

Fraction abs, Q_m	P, mm	Time, sec	Quantum yields, Φ =—=	▷—=		▷—= + 	CO
0.069	5	3608	0.012	0.10	0.72	0.82	0.83
0.079	5	4920	0.012	0.11	0.85	0.96	0.95
0.078	5	4819	0.010	0.10	0.73	0.83	0.87
0.069	5	4821	0.010	0.10	0.73	0.83	0.84
0.123	14	2430	0.011	0.11	0.82	0.93	0.92
0.152	15	1914	0.013	0.12	0.84	0.96	0.88
0.175	24	1651	0.011	0.12	0.82	0.94	0.99
0.279	40	2037	0.010	0.12	0.80	0.92	0.93
		Average	0.011	0.11	0.79	0.90	0.90

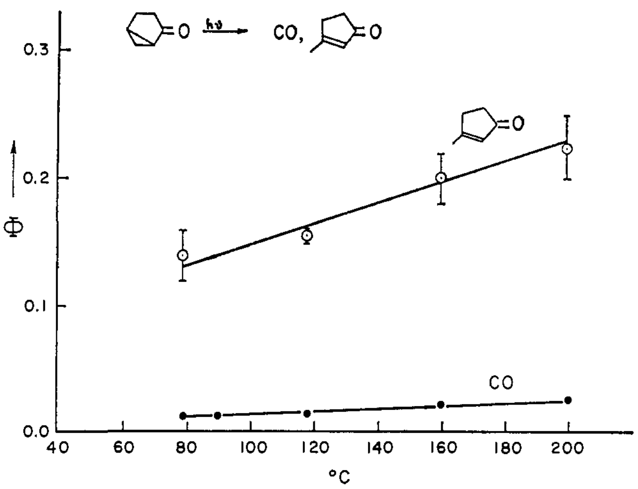


Figure 3. Effect of temperature on the photolysis of bicyclo[3.1.0]hexan-2-one (II) at 3130 A (see also Table IV).

Bicyclo[3.1.0]hexan-2-one (II). The major product from vapor-phase photolysis of this bicyclic ketone is 3-methyl-2-cyclopentenone. Small amounts of carbon monoxide and trace amounts of two other conjugated isomers, 2-methyl-2-cyclopentenone and 2-cyclohexenone, were also observed. Quantum yields of 3-methyl-2-cyclopentenone and carbon monoxide obtained from photolyses at different temperatures are shown in Table IV (see also Figure 3).

Table IV. Effect of Temperature on the Photolysis of Bicyclo[3.1.0]hexan-2-one (II) at 3130 A

Temp, °C	Time, sec × 10^{-3}	Incident quanta/sec × 10^{-15}, I_0	Fraction abs, Q_m	3-Me-2-CP,[a] μmoles	Quantum yields, Φ 3-Me-2-CP[a]	CO
79	7.20	2.88	0.180		0.12	0.012
79	7.20	2.82	0.116	0.63	0.16	nd[b]
90	14.0	2.27	0.162	1.19	0.14	0.013
118	7.20	2.57	0.222	1.02	0.15	0.013
118	7.20	2.57	0.226	1.09	0.16	0.014
160	7.20	3.00	0.210	1.63	0.22	0.020
160	7.20	2.59	0.220	1.22	0.18	0.021
200	5.40	2.81	0.224	1.42	0.25	0.023
200	8.80	2.47	0.190	1.35	0.20	0.024

[a] 3-Me-2-CP = 3-methyl-2-cyclopentenone. [b] nd = not determined.

The data for 3-methyl-2-cyclopentenone are not completely satisfactory since the experimental error is as high as 20% in some cases. This was due, at least in part, to the analytical methods employed. Experimentation with gas chromatographic conditions showed that quantitative product separation was not feasible. 3-Methyl-2-cyclopentenone has either an identical or a slightly greater retention volume than bicyclo[3.1.0]hexan-2-one on a variety of chromatograph columns. 2-Methyl-2-cyclopentenone and 2-cyclohexenone are easily separated from each other and from 3-methylcyclopentenone and bicyclo[3.1.0]hexan-2-one on a Carbowax 20M column.

It was, however, possible to obtain a linear Beer's law plot in the same concentration region as that required for analysis of photolysis products by diluting concentrated solutions of 3-methylcyclopentenone.

(The precision of this calibration was 3%.) Nevertheless, it was not possible to obtain product analyses with a reasonable degree of precision (5–10%). One reason for this is probably the fact that the amounts of product obtained under quantitative photochemical conditions necessitated use of the ultimate sensitivity of the spectrophotometer (full-scale absorbance range of 0–0.1).

3-Cyclopentenone (III). This ketone photodecomposes very cleanly to yield only carbon monoxide and 1,3-butadiene. As shown by the results in Table V, the quantum efficiency for formation of these products is near unity and is constant over the temperature range of 60–190°.

2-Cyclopentenone (IV). The quantum yield for the formation of carbon monoxide from ketone IV under the same conditions as described above for compounds I–III is about 0.004. No other products were detectable from the vapor-phase photolysis of this conjugated ketone.

Table V. Effect of Temperature on the Photolysis of 3-Cyclopentenone (III) at 3130 A and 35 mm

Temp, °C	Time, sec	Incident quanta/sec × 10^{-15}, I_0	Fraction abs, Q_m	Quantum yields, Φ	
				=−=	CO
60	1810	1.25	0.200	0.92	0.92
60	2230	1.25	0.200	0.76	0.89
90	1800	1.25	0.185	0.88	0.83
90	2100	1.25	0.200	0.94	0.83
120	1800	1.25	0.240	0.91	0.87
150	1800	1.25	0.240	0.87	0.87
195	1800	1.25	0.290	0.86	0.88
			Average	0.88	0.87

Discussion

Bicyclo[3.1.0]hexan-3-one (I). Under all conditions there is equivalence between the molecules of carbon monoxide and the hydrocarbon products, 1,4-pentadiene and vinylcyclopropane. The relationship

$$\Phi_{CO} = \Phi_{1,4\text{-pentadiene}} + \Phi_{\text{vinylcyclopropane}}$$

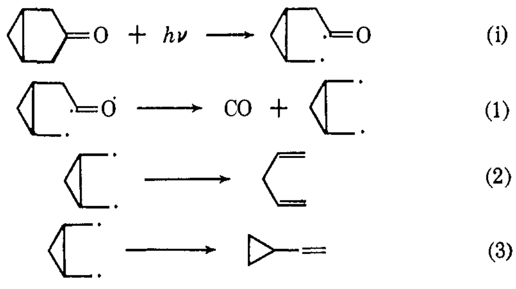
is valid within experimental error over a wide range of pressures and temperatures at 3130 A (Tables I and II and Figure 2) and over a pressure range of 35 mm at 2380–2654 A (Table III).

The simplest explanation, and perhaps the most reasonable, for these results at both 3130 and 2380–2654 A is afforded by a single mechanism which includes one primary photochemical process followed by several very fast reactions. This sequence of events is quite efficient, *e.g.*, the average over-all quantum yield is 0.80 at 3130 A and 0.90 at 2380–2654 A.

The small amounts of butadiene found in all runs appear to arise from another primary process, possibly a β cleavage. The resulting species could lead to the formation of butadiene and ketene. Detection of traces of ketene under the reaction conditions employed was not possible. Since the average over-all quantum yield of this decomposition mode of ketone I is only 0.02 at 3130 A and 0.01 at 2380–2654 A, we shall not consider it further.

The pressure and temperature independence of product quantum yields, Φ_{CO} and $\Phi_{1,4\text{-pentadiene}}$, and the small variation of $\Phi_{\text{vinylcyclopropane}}$ with temperature indicate that the reactive state(s) of I must be short lived. In fact, the significant increase of the average over-all quantum yields at the shorter wavelengths indicate that the reaction competes effectively with vibrational relaxation of the electronically excited species. A more specific determination of the nature and lifetime of the excited state(s) involved requires detailed spectroscopic and quenching data. Further discussion of this point awaits these data.

In view of the nature of the principal photoproducts arising from ketone I, primary process (i) followed by the formal sequence of reactions 1–3 are postulated to account for the major pathway of vapor-phase photochemical decomposition. Primary process i, photochemical α cleavage,[3a,19,20] also has been proposed as the predominant reaction of saturated cyclic ketones.



The existence of the biradical precursor, cyclopropylenedimethyl, is speculative but is postulated because it is a logical intermediate for both 1,4-pentadiene and vinylcyclopropane and since several concerted decompositions of the ketone seem unlikely. Moreover, experimental evidence supports the existence of hydrocarbon biradicals in the photolysis of cyclic ketones.[21–26] In the photolysis of cyclohexanone and cyclopentanone, an important reaction pathway for the hydrocarbon biradicals resulting from primary process i is ring closure.[19,20] The corresponding product from ketone I would be bicyclo[2.1.0]pentane[27] which was not observed among the photoproducts even in runs at high pressures of added nitrogen. The failure of the proposed biradical to cyclize may be due to the very high degree of ring strain[27] present in the bicyclic structure.

The independence of Φ_{CO} and $\Phi_{1,4\text{-pentadiene}}$ of temperature (see Figure 2) suggests that both the decarbonylation (reaction 1) and the isomerization of the resulting biradical to 1,4-pentadiene (reaction 2) proceed very rapidly and possess small, if any, activation

---

(19) S. W. Benson and G. B. Kistiakowsky, *J. Am. Chem. Soc.*, **64**, 80 (1942).

(20) F. E. Blacet and A. Miller, *ibid.*, **79**, 4327 (1957).

(21) M. C. Flowers and H. M. Frey, *J. Chem. Soc.*, 2758 (1960).

(22) G. Quinkert, *Pure Appl. Chem.*, **9**, 607 (1964).

(23) B. Rickborn, R. L. Alumbaugh, and G. O. Pritchard, *Chem. Ind.* (London), 1951 (1964).

(24) A. Singh and G. R. Freeman, *J. Phys. Chem.*, **69**, 666 (1965).

(25) R. L. Alumbaugh, G. O. Pritchard, and B. Rickborn, *ibid.*, **69**, 3225 (1965).

(26) H. M. Frey, *Chem. Ind.* (London), 947 (1966).

(27) For pertinent data on bicyclo[2.1.0]pentane, see R. Criegee and A. Rimmelin, *Chem. Ber.*, **90**, 414 (1957); R. B. Turner, "Kékulé Symposium on Theoretical Organic Chemistry," Butterworth & Co. (Publishers), Ltd., London, 1959, p 57; M. L. Halberstadt and J. P. Chesick, *J. Am. Chem. Soc.*, 84, 2688 (1962); C. Steel, *J. Phys. Chem.*, **67**, 1779 (1963).

energies. Thus one can write

$$d(\text{1,4-pentadiene})/dt = k_2(\text{cyclopropylenedimethyl}) = \Phi_{\text{1,4-pentadiene}}I_a$$

$$d(\text{vinylcyclopropane})/dt = k_3(\text{cyclopropylenedimethyl}) = \Phi_{\text{vinylcyclopropane}}I_a$$

$$\Phi_{\text{1,4-pentadiene}}/\Phi_{\text{vinylcyclopropane}} \simeq (A_2/A_3)\exp(E_3/RT)$$

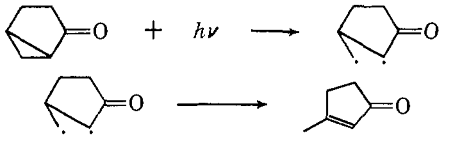
with $E_2 \sim 0$. A plot of $\log(\Phi_{\text{1,4-pentadiene}}/\Phi_{\text{vinylcyclopropane}})$ *vs.* $1/T$ was a straight line whose slope is determined by E_3. A value of $E_3 = 0.7$ kcal/mole, which was calculated from the slope, approximates the activation energy of reaction 3. Extrapolation of the plot yields the ratio of the frequency factors, $A_3/A_2 = 1.14$.

These kinetic data are fully compatible with valence tautomeric rearrangements of the intermediate biradical to the products, 1,4-pentadiene and vinylcyclopropane.

Bicyclo[3.1.0]hexan-2-one (II). In contrast to I, compound II yields only small amounts of gaseous products, but rearranges relatively efficiently to 3-methyl-2-cyclopentenone. Trace amounts of two other conjugated isomers, 2-methyl-2-cyclopentenone and 2-cyclohexenone, were also identified; however, they were formed in such small amounts ($\Phi << \Phi_{CO}$) that they need not be considered further.

The predominant rearrangement of ketone II to 3-methyl-2-cyclopentenone is paralleled by the analogous efficient photochemical conversion of methyl cyclopropyl ketone to methyl propenyl ketone in the vapor phase.[4] Also yields of carbon monoxide from II are of the same order of magnitude as those from methyl cyclopropyl ketone. One important difference in the experimental conditions under which these two cyclopropyl ketones were studied is the wavelength of light used. Methyl cyclopropyl ketone was irradiated with light of wavelengths 2380–2654 A, whereas bicyclo[3.1.0]hexan-2-one (II) was photolyzed at 3130 A. The difference in energy of the quanta at these two wavelength regions (approximately 20 kcal/einstein) could be sufficient to explain the observation that the quantum yield of methyl propenyl ketone was found to be practically independent of temperature, whereas the quantum yield of 3-methyl-2-cyclopentenone is temperature dependent (see Figure 3).

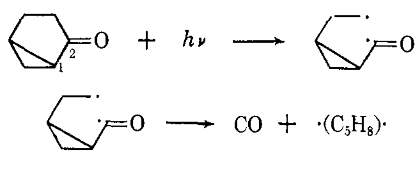
With both ketones initial bond rupture of the cyclopropyl ring is followed by a 1,2-hydrogen shift (assuming the postulated biradical mechanism[4]). This could account for the small activation energy required when II was irradiated at 3130 A. Consequently, the following reaction scheme is proposed for the vapor-phase photoisomerization of bicyclo[3.1.0]hexan-2-one (II) to 3-methyl-2-cyclopentenone.



(ii)

(4)

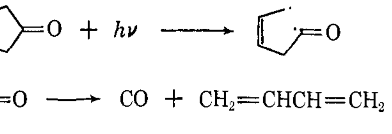
The relatively small amounts of carbon monoxide formed are explicable in terms of process iii followed by decomposition of the resulting acyl–alkyl biradical (reaction 5). A small activation energy for (5) could be responsible for the observed temperature dependence of Φ_{CO}. There is no direct experimental evidence favoring process iii over a similar reaction resulting in the alternative cleavage of the 1,2 bond. The latter seems less probable, however, on the basis that the resulting species, an acyl–cyclopropyl biradical, would be less stable. Since no hydrocarbon products were observed, it is assumed that the biradicals from (5) react to form undetected polymeric products.



(iii)

(5)

3-Cyclopentenone (III). Irradiation of compound III in its n → π* absorption band with light of wavelength 3130 A resulted solely in a highly efficient temperature-independent conversion to 1,3-butadiene and carbon monoxide. Primary photochemical process iv followed by the fast reaction 6 affords a reasonable mechanism.



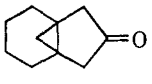
(iv)

(6)

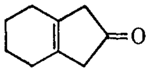
No experimental evidence was obtained for the intermediacy of biradicals. In fact, a concerted process circumventing step iv in the formal sequence given above can be envisaged as well. In such a case, butadiene could be produced *via* its intermediate triplet form depending on the multiplicity of the reacting excited state of ketone III.

2-Cyclopentenone (IV). Contrary to its photodimerization in the liquid phase at room temperature with light of wavelengths greater than 3000 A,[28] ketone IV is stable to photoreaction at 50 mm pressure, 120°, and 3130 A. The quantum yield for the formation of carbon monoxide under these experimental conditions is about 0.004.

Comparison with Studies on Related Systems. It is interesting to note that a number of similar photochemical decompositions and rearrangements have been observed in solution studies with derivatives of the model compounds I–IV. For example, the photodecarbonylation in the vapor phase of compounds I and III is paralleled by the liquid-phase reactions of analogous tricyclic ketones V and VI reported by Eastman and co-workers.[29]



V



VI

A number of other β,β′-unsaturated cyclic ketone systems have been investigated in solution and found to undergo similar photochemical decarbonylations. The resulting intermediate hydrocarbon biradicals either cyclize, dimerize, or form conjugated systems.[30]

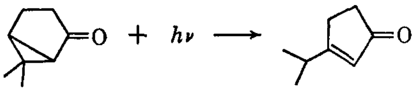
---

[28] P. E. Eaton, *J. Am. Chem. Soc.*, 84, 2344 (1962).

[29] (a) J. E. Starr and R. H. Eastman, *J. Org. Chem.*, 31, 1393 (1966); (b) see also R. H. Eastman, J. E. Starr, R. St. Martin, and M. K. Sakatal, *ibid.*, 28, 2162 (1963).

[30] O. L. Chapman, D. J. Pasto, G. W. Bordon, and A. A. Griswold, *J. Am. Chem. Soc.*, 84, 1220 (1962); K. Mislow and A. J. Gordon, *ibid.*, 85, 3521 (1963); G. Quinkert, K. Opitz, W. W. Wiersdorff, and J. Weinlich, *Tetrahedron Letters*, 1863 (1963).

The photoinduced rearrangements of bicyclo[3.1.0]-hexan-2-one derivatives to the corresponding 3-substituted 2-cyclopentenones, analogous to II, had also been observed in solutions. For example Chapman and co-workers report the isomerization of VII to VIII.[31]


VII VIII

The reactivity of 2-cyclopentenone in the liquid and gas phases can also be considered "similar," *i.e.*, in both phases it is remarkably stable to unimolecular photochemical processes. The observed photodimerization in liquid solution is an intermolecular process and as such would be expected to be formed in a condensed medium.

We should note that although the quantum yields of the photoreactions in solutions have not been reported, these processes appear to be the major photochemical conversions which occur.

Cyclopentanone is known to decompose to carbon monoxide + hydrocarbons and to isomerize to 4-pentenol, with a total efficiency at 3103 A and 124° of about 0.7, independent of pressure.[32] These reactions result from α cleavage in one or more primary processes. The photochemistry of a number of cyclopentenone derivatives in which a cyclopropyl group or a double bond is introduced in the β position can also be explained *on a formal basis* solely in terms of α-bond cleavage. This is reasonable because the radicals formed are readily stabilized by the allylic double bond and by homolytic fission of the adjacent cyclopropyl ring, respectively.

The over-all efficiency of photodecomposition for the modified cyclopentanones I and III is similar to the efficiency of formal α cleavages in cyclopentanone itself [Φ_{CO} = 0.8 and 0.9 for I and III, respectively]. However, there is a pronounced qualitative difference in that compounds I and III show no sign of forming aldehydic isomers, a process which is common to simple cycloalkanones. This observation is compatible with the assumption that aldehyde formation from cycloalkanones proceeds *via* an acyl–alkyl biradical which undergoes an intramolecular hydrogen shift. Such a rearrangement would appear to be unfavorable on the basis of structural considerations in the case of ketones I and III. In the former it would involve the shift of a cyclopropane hydrogen. With compound III the most likely hydrogen shift would lead to an unsaturated ketene, $CH_3CH{=}CHCH{=}C{=}O$. Such a product would probably not have been detected by the analytical techniques employed, but its quantum yield could not be more than 0.1.

In the isomers II and IV where the cyclopropyl group and the double bond, respectively, are in the α position to the ketone group, photodecarbonylation becomes negligible. This seems due to the fact that the α bond between carbonyl and cyclopropyl group and double bond, respectively, is significantly strengthened, and that the cleavage of the alternate α bond leads to a primary alkyl radical in both cases. In compound II, however, β cleavage of the relatively weak cyclopropyl bond leads to the stable 3-methyl-2-cyclopentenone as the major product.

Finally we may note that our results with these simple modified cyclopentanones are paralleled by those obtained with the corresponding aliphatic cyclopropyl and olefinic ketones[2,3e,f] which will be published in a subsequent paper.

Acknowledgment. The authors wish to thank Dr. P. A. Leermakers and Mr. G. Vesley for synthesis of the bicyclic ketones and collaborative discussions in the initial phase of this work.[6] We are grateful to Drs. Phillip Radlick and John Vernon for the synthesis of 3-methyl-2-cyclopentenone and 3-cyclopentenone and to Messrs. Gerald Brem and Jerry Jacobson for skillful technical assistance. Finally, we are indebted to Dr. Kurt Schaffner for stimulating discussions and his critical review of the manuscript. This research was supported by Grant AP 00109, Division of Air Pollution, Bureau of State Services, Public Health Service. L. D. H. also wishes to acknowledge financial support from a National Defense Graduate Fellowship, 1962–1965.

---

(31) O. L. Chapman, T. A. Rettig, A. A. Griswold, A. I. Button, and P. Fitton, *Tetrahedron Letters*, 2049 (1963); see also H. Bohrer, D. Gravel, K. Schaffner, and O. Jeger, cited by K. Schaffner, *Advan. Photochem.*, 4, 81 (1966); H. E. Zimmerman and J. W. Wilson, *J. Am. Chem. Soc.*, **86**, 4036 (1964).

(32) R. Srinivasan, *ibid.*, **83**, 3444 (1961).