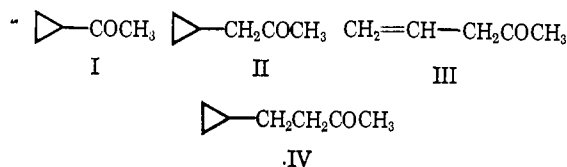# Structure and Reactivity in the Vapor-Phase Photolysis of Ketones. V. Aliphatic Cyclopropyl and Olefinic Ketones[1]

L. D. Hess,[2] J. L. Jacobson, K. Schaffner,[3] and J. N. Pitts, Jr.

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Abstract: Vapor-phase irradiations of the aliphatic cyclopropyl and olefinic ketones c-$C_3H_5COCH_3$ (I), c-$C_3H_5CH_2COCH_3$ (II), c-$C_3H_5CH_2CH_2COCH_3$ (IV), and CH_2=$CHCH_2COCH_3$ (III) at 3130 A and 120° have been carried out. Quantum yields of carbon monoxide from the type I split are 0.04 for ketone I, 0.88 for ketone II, 0.71 for ketone IV, and 0.60 for ketone III. Other primary photochemical processes in these ketones are cyclopropane isomerized in compounds I and II to yield CH_3CH=$CHCOCH_3$ (Φ = 0.3 at 2537–2654 A and 120° as reported previously) and CH_2=$CHCH_2CH_2COCH_3$ (Φ = 0.05), respectively, and the type II split in compound IV to give acetone and methylenecyclopropane (Φ = 0.06). These data, together with previously reported results, provide the basis for a coherent evaluation of the relationship between structure and photoreactivity in the vapor phase at 3130 A and 120° of two series of closely related aliphatic and cyclic ketones which possess cyclopropyl and double bonds, respectively, in the α, β, and γ positions to the carbonyl group.

In the previous paper of this series[1a] we considered structure and reactivity relationships in the vapor-phase photochemistry of several cyclic cyclopropyl and olefinic ketones at 3130 A and elevated temperatures ($\geq 120°$).[4] This paper deals with the extension of our studies to the related aliphatic ketones I–IV.

$$\text{[structures I, II, III]} \quad \triangleright\!\!-\!COCH_3 \qquad \triangleright\!\!-\!CH_2COCH_3 \qquad CH_2\!=\!CH\!-\!CH_2COCH_3$$

$$\text{I} \qquad\qquad \text{II} \qquad\qquad\qquad \text{III}$$

$$\triangleright\!\!-\!CH_2CH_2COCH_3$$

$$\text{·IV}$$

Experimental Section

Apparatus and Procedures. The apparatus and experimental techniques employed have been described previously.[1a] The light source was a medium-pressure Hanovia Type A dc lamp (460 w); 3130-A radiation was isolated by interference filters. Relative light intensities were determined photometrically, and acetone (Φ_{CO} = 1.00) and diethyl ketone (Φ_{CO} = 0.97) at 120° were used as internal actinometers. No significant dark reactions were observed under the conditions employed during photolysis of ketones I–IV.

Synthesis of Ketones. 1-Cyclopropyl-2-propanone (II), 1-penten-4-one (III),[5] and 1-cyclopropyl-3-butanone (IV) were prepared by oxidation of the corresponding alcohols using the Jones reagent.[6] The cyclopropyl groups were formed by the Simmons–Smith reaction[7] of methylene iodide with the appropriate alcohols, 1-penten-4-ol (Aldrich) and 1-hexen-5-ol, respectively. The latter was obtained by reduction of 1-hexen-5-one[8] with lithium aluminum hydride. Analytical, infrared, ultraviolet, and nmr data of ketones II–IV are listed in Table I.

(1) (a) Paper IV: L. D. Hess and J. N. Pitts, Jr., *J. Am. Chem. Soc.*, **89**, 1973 (1967); (b) presented in part at the Fourth International Photobiology Congress, Oxford, July 1964 (see "Recent Progress in Photobiology," E. J. Bowen, Ed., Blackwell Scientific Publications, Oxford, 1965, p 30); (c) see also 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).

(2) This paper is taken from the Ph.D. dissertation of L. D. Hess, University of California, Riverside, 1965.

(3) Visiting Professor from the Eidg. Technische Hochschule, Zurich, fall quarter 1966.

(4) For references to the literature in this field see paper IV of this series.[1a]

(5) Ketone III has been repeatedly reported in the literature; e.g., R. Paul and S. Tchelitcheff, *Bull. Soc. Chim. France*, 417 (1953).

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

(7) H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **81**, 4265 (1959); E. LeGoff, *J. Org. Chem.*, **29**, 2048 (1964).
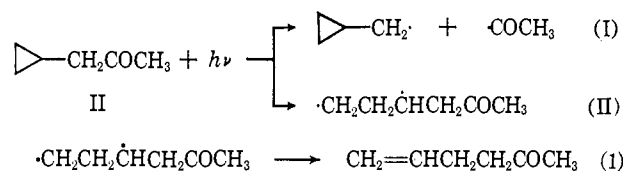
(8) E. M. La Combe and B. Stewart, *J. Am. Chem. Soc.*, **83**, 3457 (1961).

Results

Irradiations were carried out at 3130 A, 120°, and approximately 25 mm pressure. The products and their modes of formation are discussed separately below for each ketone. Additional experiments with compounds II–IV were run at 50°. Biacetyl was produced in all three cases. Its formation at low temperatures is indicative of the intermediacy of acetyl radicals and hence of predominantly selective type I splits according to eq I, III, and IV, respectively.[9] At 120° acetyl radical is known[10] to decompose in these systems quantitatively to carbon monoxide and a methyl radical.

Methyl Cyclopropyl Ketone (I). This ketone had been irradiated previously[11] at 2537–2654 A and 120° (see Discussion). The present experiments at 3130 A verify its stability toward photodecarbonylation at the longer wavelengths, the quantum yield for carbon monoxide being only 0.04.

1-Cyclopropyl-2-propanone (II). Carbon monoxide (Φ = 0.88), 1-hexen-5-one ($\Phi \sim 0.05$), methane, ethane, 1-butene, 1-pentene, and 1,7-octadiene are the only observed products. Their formation can be adequately explained on the basis of primary processes I and II.

$$\triangleright\!\!-\!CH_2COCH_3 + h\nu \longrightarrow \begin{cases} \triangleright\!\!-\!CH_2\cdot + \cdot COCH_3 & \text{(I)} \\ \\ \cdot CH_2CH_2\dot{C}HCH_2COCH_3 & \text{(II)} \end{cases}$$

$$\text{II}$$

$$\cdot CH_2CH_2\dot{C}HCH_2COCH_3 \longrightarrow CH_2\!=\!CHCH_2CH_2COCH_3 \quad \text{(1)}$$

As no cyclopropyl derivatives could be detected among the photoproducts in the runs at 120°, direct evidence for the cyclopropylmethyl radicals as intermediates formed in process I is lacking. However, the cyclopropylmethyl radical is known to isomerize rapidly to the more stable 1-butenyl radical, CH_2=CH-

(9) The primary photochemical cleavage of methyl alkyl ketones to an alkyl radical and an acetyl radical is generally much more efficient than the alternative process which produces a methyl radical and the corresponding acyl radical; see, e.g., J. N. Pitts, Jr., and F. E. Blacet, *ibid.*, **72**, 2810 (1950), for results with methyl ethyl ketone at 100° and 3130 A.

(10) See J. A. Kerr and J. G. Calvert, *J. Phys. Chem.*, **69**, 1022 (1965), and references therein.

(11) J. N. Pitts, Jr., and I. Norman, *J. Am. Chem. Soc.*, **76**, 4815 (1954).
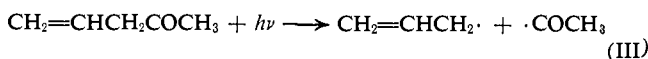
Table I

Compound	C, % Obsd	C, % Calcd	H, % Obsd	H, % Calcd	Mol wt[a]	Infrared,[b] cm⁻¹	Nmr,[b,c] δ	Ultraviolet[d] λmax, A	εmax
II	73.2	73.5	10.5	10.2	98	1017, 1720, 3090	0.0–1.2 (m) (5 H) 2.07 (s)(3 H) 2.20 (d), $J = 7$ (2 H)	2840	34
III	...	...	...	...	84	920, 990, 1637, 1718, 3088	2.08 (s) (3 H) 3.12 (d), $J = 6$ (2 H) 5.01 (b d), $J \sim 6$ (1 H) 5,23 (b s) (1H) 5.6–6.3 (m) (1 H)	2845	32
IV	75.3	75.0	11.0	10.7	112	1027, 1722, 3090	−0.1 (b)(2 H) 0.3 (b)(3 H) 1.33 (b q), $J \sim 7$ (2 H) 1.96 (s)(3 H) 2.35 (t), $J = 7$ (2 H)	2810	28

[a] Molecular weight determined by mass spectrometry. [b] In CCl₄. [c] s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; b, broad signal; J in cps. [d] In cyclohexane.

$CH_2\dot{C}H_2$,[12] and the hydrocarbon products can reasonably be explained as the result of typical secondary reactions of the primary 1-butenyl and methyl radicals.

Primary process II and a subsequent rapid 1,2-hydrogen shift in the resulting ketone diradical (reaction 1) account for the isomerization of ketone I to 1-hexen-5-one. The secondary reaction (eq 1) has a formal analogy in the rearrangement that was proposed for the vapor-phase photoisomerization of the cyclopropyl ketones I (eq 3)[11] and V (eq 4).[1a] An alternative mode of formation of 1-hexen-5-one, radical recombination of $CH_3CO\cdot + \cdot CH_2CH_2CH=CH_2$, is precluded by the instability of the acetyl radical at 120°. We should note the possibility that the 1-hexen-5-one could have been formed by a concerted reaction, without a diradical intermediate. Products resulting from a type II process (vide infra), i.e., acetone and cyclopropene, were not detected.

1-Penten-4-one (III). The major products were carbon monoxide ($\Phi = 0.6$), methane, ethane, propylene, 1-butene, and 1,5-hexadiene. This result is clearly due to primary photochemical process III and to secondary thermal reactions which are known to occur with acetyl and allyl radicals when produced in the vapor phase at elevated temperatures.[14]

$$CH_2=CHCH_2COCH_3 + h\nu \longrightarrow CH_2=CHCH_2\cdot + \cdot COCH_3$$
(III)

1-Cyclopropyl-3-butanone (IV). The results of four irradiations (runs A–D) are summarized in Table II. The nature and stoichiometry of the products suggest primary processes IV and V.
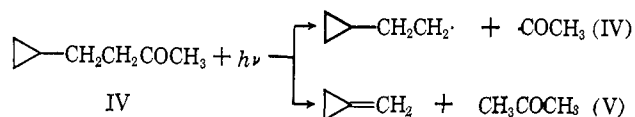
Carbon monoxide, vinylcyclopropane, and the saturated hydrocarbons represent products that are

(12) Precedent for this isomerization may be found in the work of Roberts and co-workers:[13] photochlorination of methylcyclopropane in the vapor phase at 50° gave cyclopropylmethyl chloride and 1-chloro-3-butene in approximately equal quantities. At the temperature employed in our work (120°), the primary 1-butenyl radical should be greatly favored over the cyclopropylmethyl radical.

(13) J. D. Roberts and R. H. Mazur, J. Am. Chem. Soc., 73, 2509 (1951); E. Renk, P. R. Shafer, W. H. Graham, R. H. Mazur, and J. D. Roberts, ibid., 83, 1987 (1961).

(14) M. Szwarc, B. N. Ghosh, and A. H. Sehon, J. Chem. Phys., 18, 1142 (1950).

expected from the type I split of ketone IV (process IV) and subsequent secondary reactions of the resulting cyclopropylethyl and acetyl radicals. A consideration of the mass balance supports this over-all reaction scheme; i.e., $\Phi_{CO} \simeq \Phi_{c\text{-}C_3H_5CH_2CH_2} \simeq \Phi_{CH_3}$, if allowance is made for appropriate amounts of nonobserved products resulting from cross combination of cyclopropylethyl and methyl radicals with radicals generated by hydrogen abstraction from the starting ketone IV.

The primary decomposition of ketone IV to methylenecyclopropane and acetone (eq V) is characteristic of the Norrish type II cleavage of ketones with γ-hydrogens. Presumably this photocycloelimination occurs through a six-membered cyclic transition state (eq 2).
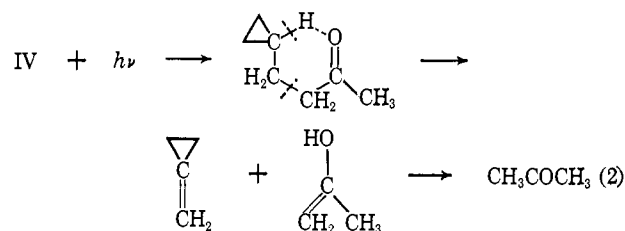
Reaction V seems to be the first example of this type of primary process in which a cyclopropyl hydrogen participates.[15]

Discussion

The results reported in this paper complement the data on the vapor-phase photochemistry at 3130 A and 120° of two series of closely related aliphatic and cyclic ketones which possess cyclopropyl groups and double

(15) Additional evidence for primary process V is provided by the mass spectrometric cracking pattern of ketone IV which shows a rearrangement peak at m/e 58 that persists at low-electron-beam energies (ca. 10 ev). Such a peak has been generally observed with methyl ketones that undergo the photochemical Norrish type II cleavage to yield acetone and an olefin. This correlation between the type II cycloelimination mode of carbonyl compounds with alkyl γ-hydrogen atoms under the influence of ultraviolet light and under electron impact has been noted previously.[16]

(16) A. J. C. Nicholson, Trans. Faraday Soc., 50, 1067 (1954); T. W. Martin and J. N. Pitts, Jr., J. Am. Chem. Soc., 77, 5465 (1955), presented at the Conference on Photochemistry, University of Rochester, Rochester, N. Y., Sept 1954; J. N. Pitts, Jr., and A. D. Osborne, "Symposium on Chemical Reactions in the Upper and Lower Atmosphere," John Wiley and Sons, Inc., New York, N. Y., 1961, p 128; S. Meyerson and J. D. McCollum, Advan. Anal. Chem. Instr., 2, 179 (1963); S. Meyerson, J. Phys. Chem., 68, 968 (1964); J. N. Pitts, Jr., J. K. Foote, and J. K. S. Wan, J. Photochem. Photobiol., 4, 323 (1965); see also the papers of F. W. McLafferty summarized in "Interpretation of Mass Spectra," W. A. Benjamin, Inc., New York, N. Y., 1966.

Table II. Quantum Yields of Products from the Photolysis of 1-Cyclopropyl-3-butanone (IV) at 120°, 3130 A, and 25 mm

Run	CO	CH₄	C₂H₆	▷◁	▷◁	▷=	▷◁	▷=	CH₃COCH₃
A	0.74	0.25	0.086	0.15	0.27	0.021	0.065	0.060	0.058
B	0.72	0.26	0.084	0.17	0.25	0.032	0.068	0.055	0.057
C	0.70	0.24	0.088	0.14	0.26	0.019	0.064	0.062	0.060
D	0.71	0.27	0.085	0.16	0.24	0.025	0.066	0.058	0.059
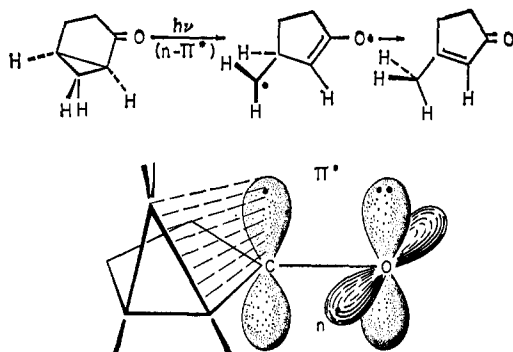
Figure 1.

bonds, respectively, in the α, β, and γ positions to the carbonyl group. The pertinent results are summarized in Table III.
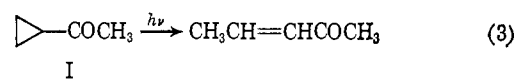
Table III. Correlation of Photochemical Reactivity of Cyclopropyl and Olefinic Ketones at 3130 A and 120°

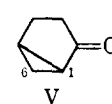| Compound	Type I split, Φ_{CO}	Other photoprocesses	Ref
I	0.04	…ᵃ	This work
II	0.88	Eq II, $\Phi_{CH_2=CH(CH_2)_2COCH_3}$ = 0.05	This work
IV	0.71	Eq 2, $\Phi_{type\ II\ split}$ = 0.06	This work
V	0.014	Eq 4,	1a
		Φ (⬠=O) = 0.16	
		Φ (⬡=O) + Φ (⬡=O) < 0.01	
XI	0.76	$\Phi_{CH_2=CHCH=CH_2}$ = 0.017	1a
VI	0.00	Eq 5, cis–trans isomerization	17
III	0.60	…	This work
XIII	0.005	Eq 8, $\Phi_{oxetane}$ = 0.006	b
⬠=O	0.004	…	1a
XII	0.87	…	1a

ᵃ $\Phi_{CH_3CH=CHCOCH_3}$ = 0.3, eq 3, at 2537–2654 A and 120°.[11] ᵇ Results by R. Srinivasan, *J. Am. Chem. Soc.*, **82**, 775 (1960): Φ_{CO} ∼ 0.005 at 3130 A and 120° confirmed in this work.

It is apparent that the cyclopropyl group and the double bond, when conjugated with the carbonyl chromophore, stabilize aliphatic and cyclic ketones toward the type I split and photodecarbonylation in the vapor phase.[1a] In the cyclopropyl ketones I[11] and V[1a] a rearrangement to olefinic isomers occurs instead with quantum yields of 0.3 (at 2537–2654 A and 120°), reaction 3, and 0.16 (at 3130 A and 118°), reaction 4, respectively. The only significant reaction of 3-penten-2-one
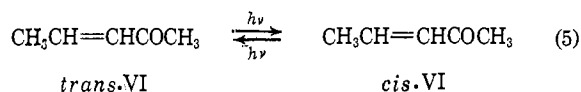
(VI) was found to be *cis–trans* isomerization (eq 5),[17] while 2-cyclopentenone remains virtually unchanged.[1a]

$$\text{▷—COCH}_3 \xrightarrow{h\nu} \text{CH}_3\text{CH}=\text{CHCOCH}_3 \quad (3)$$
I

$$\text{⬡=O} \xrightarrow{h\nu} \text{⬠=O} \quad (4)$$
V

$$\text{CH}_3\text{CH}=\text{CHCOCH}_3 \underset{h\nu}{\overset{h\nu}{\rightleftharpoons}} \text{CH}_3\text{CH}=\text{CHCOCH}_3 \quad (5)$$
$$trans\text{-VI} \qquad\qquad cis\text{-VI}$$

The orbital overlap in the ketones I and V between the π^* system of the n,π^*-excited carbonyl group and the vicinal cyclopropyl bond provides an attractive picture for the primary photochemical process in reactions 3 and 4, i.e., π^*-assisted cyclopropane fission. If it is assumed that the geometry of the reactive n,π^*-excited keto group deviates only slightly from a planar arrangement,[18] the external 1,6-cyclopropyl bond in the sterically rigid bicyclic ketone V will have maximum overlap with the π^* orbital (see Figure 1).[18a] The highly selective fission of this bond in reaction 4 is in accord, therefore, with a stereoelectronic control as required by this mechanism. In order to account at least in part for the relatively low quantum yields observed, reclosure of the resulting diradical to starting material is considered to compete effectively with the ensuing 1,2 migration of hydrogen to yield the unsaturated isomers.

Since the first demonstration of this photochemical isomerization process of cyclopropyl ketones in the vapor phase,[11] numerous analogous photochemical transformations have been found in solution.[19] Similar modes of π^*-assisted cyclopropane opening appear to be operative in α,β-unsaturated carbonyl systems possessing a three-membered ring in the γ position, partial structure c-C₃H₅CH=CHCO–.[20,21] Experi-

(17) R. S. Tolberg and J. N. Pitts, Jr., *J. Am. Chem. Soc.*, **80**, 1304 (1958).

(18) Formaldehyde has been found to adopt a pyramidal form in the n,π^* excited states, with the angle between the CO axis and the CH₂ plane ranging from 20.7° in the singlet to 37° in the triplet. For a discussion of the excited-state geometry and references, see E. W. Abrahamson, J. G. F. Littler, and K.-P. Vo, *J. Chem. Phys.*, **44**, 4082 (1966).

(18a) Note Added in Proof. *Cf.* R. Hoffmann, *Tetrahedron Letters*, 3819 (1965), for the possible contribution of the cyclopropane group to the excited state of cyclopropyl ketones.

(19) (a) O. L. Chapman, T. A. Rettig, A. A. Griswold, A. J. Dutton, and P. Fitton, *ibid.*, 2049 (1963); C. H. Robinson, O. Gnoj, and F. E. Carlson, *Tetrahedron*, **21**, 2509 (1965); R. Beugelmans, *Bull. Soc. Chim. France*, 3087 (1965); H. Borer, D. Gravel, K. Schaffner, and O. Jeger, cited in ref 21a.

(20) (a) B. Nann, H. Wehrli, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **48**, 1680 (1965); (b) M. Jorgenson and C. H. Heathcock, *J. Am. Chem. Soc.*, **87**, 5264 (1965); (c) *cf.* also J. Pfister, H. Wehrli, and K. Schaffner, *Helv. Chim. Acta*, **50**, 166 (1967).

(21) See also the photochemical transformations of bicyclo[3.1.0]-hex-3-en-2-one derivatives: (a) K. Schaffner, *Advan. Photochem.*, **4**, 81 (1966); (b) H. E. Zimmerman, R. Keese, J. Nasielski, and J. S. Swenton, *J. Am. Chem. Soc.*, **88**, 4895 (1966).

mental evidence for the previously suggested[11] reversal of the cyclopropane fission has been obtained for both saturated[22] and unsaturated ketones.[19a] Also, additional examples of selective bond cleavage support the concept of a π^*-assisted, stereoelectronically controlled process.[19,20c]

The exclusive photoisomerization of the *gem*-dimethylcyclopropyl ketone VII to 1-hexen-2-methyl-5-one (X) in solution[23] may represent a different mode of ring opening in an n,π^*-excited cyclopropyl ketone. The presently available data permit no distinction between a π^*-assisted ring cleavage to VIII with a subsequent methyl hydrogen shift and a primary intramolecular hydrogen transfer from methyl to oxygen, either through the intermediate diradical IX or through a six-membered cyclic transition state generally ascribed to type II split processes.[24]
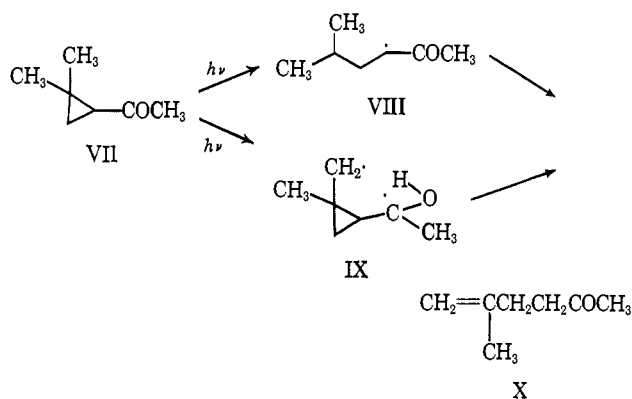
Finally we may note that the cyclopropane fission in saturated and unsaturated ketones has at least a *formal* parallel in the numerous cases other than type II splits (of saturated ketones) or intramolecular hydrogen transfers (photoenolization of α,β-unsaturated ketones) in which bonds α,β to the chromophore are photochemically cleaved. Representative examples are the photoelimination of a chlorine atom from chloroacetone in the vapor phase[25] and similar heterolytic and homolytic fissions of bonds attached to the α position of saturated and the γ position of conjugated carbonyl chromophores in solution.[26] An elegant demonstration of the stereoelectronic control governing such π^*-assisted eliminations was recently provided by Hlavka.[27]

With the insertion of one or two methylene group(s) between the carbonyl and the cyclopropyl group or double bond, the type I split, and hence decarbonylation, becomes the major if not exclusive photochemical process. Thus, quantum yields for carbon monoxide at 3130 A and 120° are 0.60 for 1-penten-4-one (III),

(22) H. E. Zimmerman and J. N. Wilson, *J. Am. Chem. Soc.*, **86**, 4036 (1964).

(23) (a) R. M. Roberts and R. G. Landolt, *ibid.*, **87**, 2281 (1965); (b) G. Hüppi, G. Eggart, S. Iwasaki, H. Wehrli, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **49**, 1986 (1966); (c) for the corresponding benzoyl analog see W. G. Brown, *U. S. Govt. Res. Rept.*, **38** (22), 25 (1963).

(24) A joint investigation of both the vapor-phase and the solution photochemistry of compound VII and related systems is in progress in this laboratory and at ETH, Zürich. The photochemistry of simple methylcyclopropyl ketones in solution also is currently being investigated by Professor W. G. Dauben, University of California, Berkeley: private communication.

(25) A. N. Strachan and F. E. Blacet, *J. Am. Chem. Soc.*, **77**, 5254 (1955).

(26) For key references see, *e.g.*, ref 20c, 21a, and 23.

(27) J. J. Hlavka and P. Bitha, *Tetrahedron Letters*, 3843 (1966).

reaction III, and approach unity for cyclopropyl-2-propanone (II), 1-cyclopropyl-3-butanone (IV), bicyclo[3.1.0]hexan-3-one (XI),[1a] and 3-cyclopentenone (XII),[1a] reactions I, IV, 6, and 7, respectively.
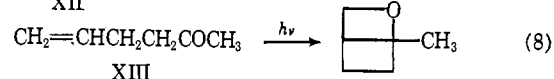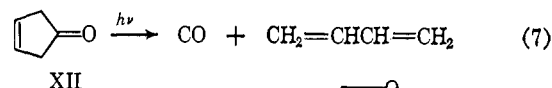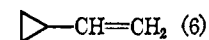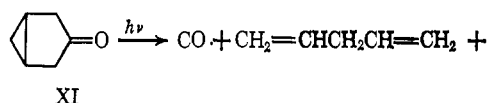
In striking contrast, 1-hexen-5-one (XIII) was found to be exceptionally stable in the temperature range from 27 to 139° at 3130 A. Decarbonylation and intramolecular oxetane formation (reaction 8) are very minor photochemical processes.[28]

One explanation for this apparent photochemical inertness of compound XIII would be an efficient intramolecular triplet energy transfer from the carbonyl group to the double bond, although other nonchemical modes of conversions of electronic energy are possible. Such a competing intramolecular photosensitization would tend to reduce the type I split, otherwise the most likely photodissociative process in this ketone. A closely related precedent for this internal energy transfer has been established in the solution photochemistry of the methyl homolog of XIII, *trans*-$CH_3CH=CHCH_2$-CH_2COCH_3,[29a] which undergoes *trans* $\rightarrow$ *cis* isomerization of the double bond on selective excitation of the keto group. A similar observation has been reported for the methyl homolog of ketone III, *trans*-$CH_3CH=$ $CHCH_2COCH_3$.[29b] The latter result suggests that internal quenching of the type I dissociation by the double bond might also occur in ketone III, $CH_2=$ $CHCH_2COCH_3$, which has a value of $\Phi_{CO} = 0.60$, intermediate between those of 3-cyclopentenone (XII, 0.87) and $CH_2=CHCH_2CH_2COCH_3$ (XIII, 0.005). Transfer could compete with the enhancement of the decarbonylation process by the allylic double bond. In short, the observed quantum efficiencies of molecular decomposition in these olefinic ketones may be expected to reflect primarily the competition between primary processes leading to decarbonylation[30] and internal energy transfer processes. An evaluation of the relationship between structure and efficiency of this postulated internal triplet energy transfer is presently impeded by the lack of sufficient information on both the donor and acceptor triplet energies in the compounds involved, and on the requirement of specific steric conditions for the transfer mechanism.[31] It is important to note, however, that the postulated competition between

(28) See R. Srinivasan, footnote *b*, Table III.

(29) (a) H. Morrison, *J. Am. Chem. Soc.*, **87**, 932 (1965); (b) *Tetrahedron Letters*, 3653 (1964).

(30) The available data[1a] for 3-cyclopentenone (XII) do not distinguish between a concerted elimination of carbon monoxide and a stepwise sequence including a primary type I split.

(31) See R. L. Cargill, J. R. Damewood, and M. M. Cooper, *J. Am. Chem. Soc.*, **88**, 1330 (1966), for an internal carbonyl $\rightarrow$ β,γ double bond sensitization in a rigid cyclic system where the fixation of ketonic and olefinic double bond approximates a linear arrangement on orthogonal planes as contrasted by 3-cyclopentenone (XII).

type I splits from either electronically excited state and singlet–triplet intersystem crossing followed by intramolecular energy transfer is much more efficient for the γ,δ-unsaturated ketone XIII than for the β,γ-unsaturated analog III.

Similar conclusions have already been drawn by Yang and co-workers from photochemical results obtained in solution. Specifically, in pentane solution a β,γ-unsaturated ketone with allylic γ hydrogens, $CH_2=C(CH_3)CH_2COCH_3$, was found to be decarbonylate with a quantum efficiency of 0.33 and to form a cyclobutanol to an appreciable extent.[32] In the case of 1-hexen-5-one (XIII), only oxetane formation occurred; cf. reaction 8. No photodecarbonylation was reported.[33]

The cyclopropane triplet state of approximately 87 kcal/mole[34] appears too high to allow a similar energy transfer mechanism to operate to any significant extent in the corresponding cyclopropyl ketones, cyclopropyl-2-propanone (II), 1-cyclopropyl-3-butanone (IV), and bicyclo[3.1.0]hexan-3-one (XI). Accordingly, exclusive photophysical energy degradation is relatively un-

important. The isomerization of ketone II to 1-hexen-5-one, though quite inefficient ($\Phi = 0.05$), would therefore result from a mechanism other than electronic energy transfer from the keto group. This may be related to the mode of formation of traces of 2-cyclohexenone and 2-methyl-2-cyclopentenone from compound V;[1a] π^* assistance as postulated above for the ring cleavage in methyl cyclopropyl ketone (I) and bicyclo[3.1.0]hexan-2-one (V), reactions 3 and 4, seems unlikely from structural considerations. On the other hand, conversion of the photoexcited ketones to vibrationally excited ground-state molecules could account more reasonably for these low efficiency, random cyclopropane cleavages.

(32) N. C. Yang and D. M. Thap, *Tetrahedron Letters*, 3671 (1966).
(33) N. C. Yang, M. Nussim, and D. R. Coulson, *ibid.*, 1525 (1965).
(34) J. A. Bell, *J. Am. Chem. Soc.*, 87, 4966 (1965).

The Thermal Intramolecular Rearrangement of 7-Methyl-1,3,5-cycloheptatriene in the Gas Phase. I. The Kinetics of the Unimolecular Positional Isomerization *via* a 1,5 Hydrogen Transfer

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Abstract: Rate constants (k_1) for the unimolecular thermal isomerization of 7-methyl-1,3,5-cycloheptatriene to 3-methyl-1,3,5-cycloheptatriene have been measured in the gas phase over the temperature range 128.7–226.0°. The reaction is first order in the pressure range studied (13 to 170 torr) and homogeneous, as shown by the insensitivity toward a 13-fold change in the surface-to-volume ratio of the reaction vessels and toward added nitric oxide. The least-squares fit of the measured rate constants to the Arrhenius equation yields (with standard errors) $\log k_1$ (sec^{-1}) $= (12.60 \pm 0.09) - (33.25 \pm 0.19)/2.303RT$. Comparing this value with the transition-state formulation for unimolecular reactions results in -3.6 cal/deg mole for the entropy of activation. These results are in line with corresponding gas-phase kinetic data on linear 1,3-diene systems reported in the literature and they further substantiate the postulated six-center hydrogen-bridged cyclic transition state formed in this type of internal rearrangement reactions.

The internal 1,5-hydrogen-shift reaction has been postulated to account for a number of thermally induced intramolecular isomerization reactions in cyclic and acyclic cisoid 1,3-diene and in vinylcyclopropane systems.[1] Despite the fact that 1,5-hydrogen-transfer reactions have been studied for a number of accessible systems, only very few reliable kinetic parameters are available for reactions in the gas phase. The

bulk of the literature data is based on pmr studies of liquid-phase reactions, carried out over narrow temperature ranges only. Arrhenius parameters derived from these data have relatively large error limits attached.

Frey, et al.,[2] reported the kinetic parameters for the gas-phase interconversion of the following systems: cis-2-methyl-1,3-pentadiene–cis-4-methyl-1,3-pentadi-

(1) For a summary of the available literature data, compare D. S. Glass, R. S. Boikess, and S. Winstein, *Tetrahedron Letters*, 10, 999 (1966).

(2) (a) H. M. Frey and R. J. Ellis, *J. Chem. Soc.*, 4770 (1965); (b) R. J. Ellis and H. M. Frey, *ibid.*, *Suppl. I*, 5578 (1964); (c) H. M. Frey and B. M. Pope, *ibid.*, *Sect. A*, 1701 (1966).