dence either for or against this proposition. However, biradical intermediates have been postulated by other workers on similar systems on the basis of chemical evidence.[10–15]

Acknowledgment. The authors wish to thank Drs. J. Coomber, O. Buchardt, and K. Schaffner for helpful discussions. We acknowledge the support of this research by Grant No. AP 00109, Research Grants Branch, National Air Pollution Control Administration, Consumer Protection and Environmental Health Service, U. S. Public Health Service.

(10) G. W. Griffin, E. J. O'Connell, and H. A. Hammond, *J. Amer. Chem. Soc.*, **85**, 1001 (1963).

(11) G. W. Griffin, J. Covell, R. C. Peterson, R. M. Dodson, and G. Klose, *ibid.*, **87**, 1410 (1965).

(12) J. K. Crandall, J. P. Arrington, and R. J. Watkins, *Chem. Commun.*, 1052 (1967).

(13) W. G. Dauben and G. W. Schaffer, *Tetrahedron Lett.*, **45**, 4415 (1967).

(14) A. Padwa, E. Alexander, and M. Niemcyzk, *J. Amer. Chem. Soc.*, **91**, 456 (1969).

(15) A. Padwa and D. Eastman, *ibid.*, **91**, 462 (1969).

Photolysis of Cyclopropyl Ketones in the Vapor Phase and in Solution[1,2]

Dana G. Marsh, J. N. Pitts, Jr.,*[3a] Kurt Schaffner,[3b] and Albert Tuinman[3b]

Contribution from the Department of Chemistry,
University of California, Riverside, California 92502,
and Laboratorium für Organische Chemie der Eidg. Technischen Hochschule, 8006
Zürich, Switzerland. *Received April 24, 1970*

Abstract: The vapor-phase (at 120°) and solution photochemistry of dicyclopropyl ketone (I), methyl 2,2-dimethylcyclopropyl ketone (II), cyclopropyl 2,2-dimethylcyclopropyl ketone (III), propyl cyclopropyl ketone (IV), 3-butenyl cyclopropyl ketone (V; in the vapor phase), and 3-methyl-3-butenyl cyclopropyl ketone (VI; in solution) has been investigated. Dicyclopropyl ketone (I), when irradiated in the vapor phase in its $n \rightarrow \pi^*$ band at 2537–2654 Å, yields cyclopropyl *cis*-propenyl ketone, cyclopropyl *trans*-propenyl ketone, allyl cyclopropyl ketone, and carbon monoxide as major products with quantum yields of 0.125, 0.025, 0.01, and 0.01, respectively. These quantum yields are temperature and pressure independent. Carbon monoxide is formed *via* a Norrish type I elimination, whereas the photoisomers result from a π^*-assisted cyclopropane fission reaction. On irradiation of ketone I at 2537 and at 3130 Å in isooctane and benzene solutions, no photochemical reaction is observed. In isopropyl alcohol, however, irradiation leads to reductive cleavage of one ring to yield propyl cyclopropyl ketone (IV). The reaction is presumably due to hydrogen abstraction from the solvent by the excited carbonyl in the primary photochemical process. Ketones II and III, when photolyzed in their $n \rightarrow \pi^*$ bands at 2537–2654 Å in the vapor phase and at 2537 or 3130 Å in isooctane, benzene, or ethanol solutions, undergo Norrish type II processes to yield 5-methyl-5-hexen-2-one (VII) and 3-methyl-3-butenyl cyclopropyl ketone (VI), respectively. The quantum yields in the vapor phase are 0.30 and 0.25, respectively, and they are independent of pressure. On the basis of experiments with nitric oxide and 2,3-dimethyl-2-butene in the vapor phase, the Norrish type II process for ketones II and III presumably proceeds through their first excited *singlet* state. Infrared spectroscopy evidence for an enol intermediate as the primary photoproduct of II in the vapor phase is presented. Ketones IV and V proved to be quite stable to irradiation in the vapor phase at 2537–2654 Å. Similar photostabilities were observed for ketone IV in isopropyl alcohol and for ketone VI in ethanol solution using 3130-Å light.

In the photolysis of the cyclopropyl ketones I–VI the competition among several intramolecular primary photochemical processes has to be envisaged *a priori:* Norrish type I splits and π^*-assisted cyclopropane fissions in all six compounds, Norrish type II processes in ketones II, III, and IV, and oxetane formation (and/or intramolecular energy transfer from the carbonyl group to the double bond) in ketones V and VI. In solution, the intervention of photoreductive processes by intermolecular hydrogen abstraction from appropriate solvent molecules can be expected as well. This study was undertaken to gain some insight into the competition of such processes in each case. Special emphasis was laid on obtaining evidence regarding the mechanistic differentiation between the cyclopropyl ring fission of ketones I, II, and III in the vapor phase

The vapor-phase photochemistry of dicyclopropyl ketone (I) has been investigated previously by Pitts and Woolfolk[4] and Pitts and Hess.[5] In these two studies, the major products, *cis-* and *trans*-propenyl cyclopropyl ketone, had not been isolated and characterized satisfactorily, the quantum yield determination of product formation required further experimental scrutiny, and the nature of the excited state(s) responsible for the reaction had not been investigated.

---

(1) Part XVI of the series Structure and Reactivity in the Vapor Phase Photolysis of Ketones [for part XV, see D. G. Marsh and J. N. Pitts, Jr., *J. Amer. Chem. Soc.*, **93**, 326 (1971)], and part LXI of the series Photochemical Reactions [for part LX, see S. Domb, and K. Schaffner, *Helv. Chim. Acta*, **53**, 1765 (1970)].

(2) Taken in part from the doctoral dissertation of D. G. Marsh, University of California, 1969.

(3) (a) University of California, Riverside; (b) Eidg. Technische Hochschule, Zürich.

(4) J. N. Pitts, Jr., and R. W. Woolfolk, Abstracts, 133rd National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, p 4-Q.

(5) J. N. Pitts, Jr., and L. D. Hess, unpublished results.

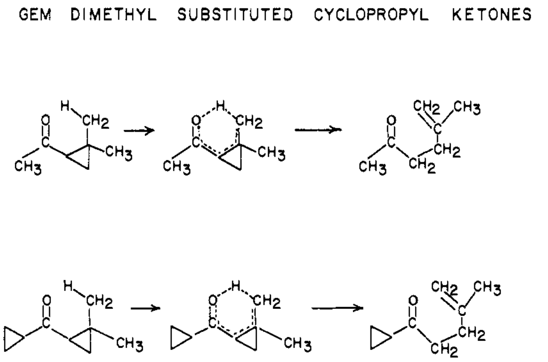
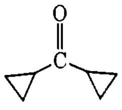
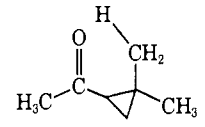


Figure 1. The bridged Norrish type II process in *gem*-dimethyl-substituted cyclopropyl ketones.

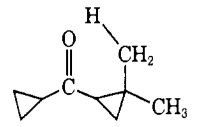
The exclusive isomerization of methyl 2,2-dimethylcyclopropyl ketone (II) to 5-methyl-5-hexen-2-one upon irradiation in solution has been reported previously by Roberts and Landolt[6] and by Schaffner, Jeger, and collaborators.[7]



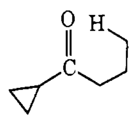
I



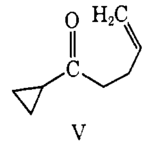
II



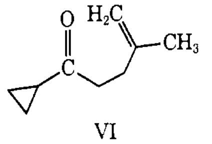
III



IV



V



VI

Experimental Section

Materials. Dicyclopropyl ketone (I) is available commercially. This ketone was purified immediately before each photolysis by glpc using a 20 ft × 0.25 in. 1,2,3-tris(2-cyanoethoxy)propane 20% loaded on 60–80 Chromosorb P column at 120°. A dual-column Aerograph 202-2B thermocouple detector gas chromatograph was used for all preparative and analytical studies. Ketone I purified in this way showed no detectable impurities by analytical glpc.

For the synthesis of **methyl 2,2-dimethylcyclopropyl ketone** (II) and **cyclopropyl 2,2-dimethylcyclopropyl ketone** (III), 5-methyl-1,4-hexadien-3-one[8] was prepared from mesityl oxide *via* a Mannich condensation using formaldehyde, diethylamine hydrochloride, and concentrated hydrochloric acid, and subsequent pyrolysis of the anhydrous crude product at 10 Torr and 170° in the presence of hydroquinone. The resulting distillate, consisting of *ca.* 30% unreacted mesityl oxide and 70% dienone, was directly converted to a mixture of II and III according to Corey's[9] method, using dimethylsulfonium methylide in dimethyl sulfoxide. The products II and III were separated by glpc on a 10 ft × $^3/_8$ in. SR-96 20% column at 150°.

Propyl cyclopropyl ketone (IV) was synthesized *via* a Grignard reaction using cyclopropyl cyanide and *n*-propyl bromide, and a Grignard reaction using cyclopropyl cyanide and 1-bromo-3-butene gave **3-butenyl cyclopropyl ketone** (V). Ketones II–V were purified in the same manner as I before photolysis.

5-Methyl-5-hexen-2-one (VII) and **3-methyl-3-butenyl cyclopropyl ketone** (VI) were accessible by pyrolysis of ketones II and III, respectively, *in vacuo* at 175°.[10]

3-Pentanone was used for actinometric determinations. This ketone was purified by distillation on a Nester/Faust Teflon spinning band distillation column. A middle cut was determined to be 99.9% pure by glpc.

2,3-Dimethyl-2-butene was obtained commercially and purified by glpc.

Ultraviolet, infrared, nmr, and mass spectrometry were used to analyze all these materials and to determine the structures of the products formed during photolyses.

Apparatus and Procedures. Vapor-Phase Photolyses. A conventional high-vacuum system was used. It was connected *via* a small down-draft mercury-vapor diffusion pump to a combination Toepler pump–gas buret adapted such that small samples could be transferred from the gas buret to a removable sample bulb for subsequent analyses.

The quartz reaction vessel (2.5 × 20 cm) was contained within an aluminum cylindrical furnace which could be heated from room temperature to 350° and controlled to within 2% at any temperature. The reactor vessel was equipped with a closed loop containing an all-glass pumping device which continuously circulated the reactor contents. Secondary reactions were minimized by irradiating to low conversions as well as by the continuous pumping. The reaction vessel was completely illuminated with the collimated emission from a Hanovia Type A medium-pressure mercury arc. The arc was operated at 500 W (150 V and 3.3 A) using an inductance-stabilized 165-V output transformer with input voltage provided by a Sola 1000-W ac voltage stabilizer. Using this arrangement, the light intensity varied less than 3% over a period of months. Light of 2537–2654 Å was isolated using a 4.5-cm-path chlorine vapor filter (1 atm) in series with a 2-mm-path Corning 7-54 filter.

Absorbed light intensities were determined by using two RCA 945 photodiodes employed in a Wheatstone bridge circuit. A portion of the incident light was reflected off a quartz plate set at 45° into one of the photodiodes. The remainder of the light (about 90%) passed through the reactor vessel and into the other photodiode. With the cell evacuated, the bridge circuit was balanced, and any addition of sample that absorbed radiation unbalanced the bridge. Using a high-sensitivity galvanometer in the bridge allowed the measurement of small fractions of absorbed light with an uncertainty of less than 2%. Light intensities were checked at least every four runs using 3-pentanone as an actinometer. At 25 Torr and at temperatures above 120°, $\Phi_{CO} = 0.97$.[11] Pressure in the reaction vessel was measured with a Statham PA707-TC5-350 pressure transducer which had a linear response from 0 to 250 Torr.

After irradiation, everything condensable at −197° was trapped and analyses for CO and other gases were performed on the Toepler pump–gas buret assembly. The condensable fraction was then removed and analyzed by glpc. Products were collected from the exit port of the gas chromatograph and subjected to spectrometric analyses.

An experiment was performed using a cylindrical aluminum tank having a diameter of 26 cm and a volume of 60 l. It enclosed the 1-m mirror support beam of the "long-path" attachment to a Perkin-Elmer Model 621 infrared spectrophotometer. Folded optics were employed such that a 20-m path length (of irradiation) was achieved. Six quartz windows, 6.4 × 6.4 cm, in the reaction tank admitted radiation from a 1200-W Hanovia Type S medium-pressure mercury arc, held in a quartz water-cooled condenser. Experiments were carried out at 24°.

Solution-Phase Photolyses. The irradiations were carried out in a merry-go-round assembly, with the *ca.* 10% sample solutions placed in tubes of 10-mm diameter, at room temperature. A Hanau NK 6/20 low-pressure mercury lamp was used with quartz sample tubes for experiments at 2537 Å, and a Hanau Q81 medium-pressure mercury lamp, which was placed in a water-cooled Pyrex jacket (principal emission in the ketone n → π* absorption region at 3130 Å) with Pyrex sample tubes for experiments using 3130-Å light. During the irradiations, the ground-glass stoppered sample tubes were closed air tight. Test runs with degassed samples (freeze–thaw cycling technique) indicated no differences from those carried out in the presence of air.

Glpc analyses of the irradiated solutions were performed using 20 ft × 0.25 in. 1,2,3-tris(2-cyanoethoxy)propane (at 150°) and 5 ft × 0.25 in. SF-96 columns (at 130°). For additional identi-

---

[6] R. M. Roberts and R. G. Landolt, *J. Amer. Chem. Soc.*, **87**, 2281 (1965).

[7] G. Hüppi, G. Eggart, S. Iwasaki, H. Wehrli, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **49**, 1986 (1966).

[8] G. S. Mironov, M. I. Faberov, and I. M. Orlova, *Zh. Obshch. Khim.*, **33**, 1512 (1963).

[9] E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **87**, 1353 (1965).

[10] See also ref 6 for the pyrolysis of ketone II.

[11] L. D. Hess and J. N. Pitts, Jr., *J. Amer. Chem. Soc.*, **89**, 1973 (1967).

Table I. Data Table for Dicyclopropyl Ketone (I) Vapor-Phase Photolysis at 2537–2654 Å

					Quantum yields			
Pressure, Torr	Temp, °C	Time, sec × 10^3	$I_0 \times 10^9$ einsteins/sec	Q_m	CO	*cis*-Propenyl cyclopropyl ketone	*trans*-Propenyl cyclopropyl ketone	Allyl cyclopropyl ketone
9.0	250	1.0	5.60	0.380	0.01	0.125	0.020	
27.0	250	1.9	5.60	0.570	0.01	0.125	0.025	
5.8	250	3.65	5.60	0.262			0.026	0.008
21.5	120	68.8	5.60	0.545		0.13	0.033	0.001
7.7	120	1.1	5.60	0.365	0.035	0.11	0.019	

fication purposes, sufficient amounts of each compound were collected by glpc and subjected to spectrometric comparisons with authentic materials.

Results

Vapor-Phase Photolyses. The results of the photolyses of **dicyclopropyl ketone** (I) are given in Table I. Four major products are formed: namely, carbon monoxide, cyclopropyl *cis*-propenyl ketone, cyclopropyl *trans*-propenyl ketone, and allyl cyclopropyl ketone. The quantum yields reported are for the *direct* photolysis of ketone I. Mercury-sensitized reactions are unimportant in this system. The quantum yields of formation are about 0.12 and 0.025 for the cis and the trans isomers, respectively, and are independent of temperature and pressure. The quantum yield for formation of carbon monoxide is about 0.01, and that for allyl cyclopropyl ketone less than 0.01.

Data from the photolyses of **methyl 2,2-dimethylcyclopropyl ketone** (II) are presented in Table II. The average quantum yield for formation of 5-methyl-5-hexen-2-one (VII) in the presence of quenchers is 0.306. In the presence of 2,3-dimethyl-2-butene (up to 7.8 Torr) the quantum yield is 0.307, and in the presence of 4.6 Torr of nitric oxide, 0.310. With 360 Torr of carbon dioxide present, the quantum yield of VII is 0.19. The average quantum yield for formation of VII from ketone II at various pressures of II is 0.304. Clearly, the quantum yield is independent of pressure and quencher concentration. It is significant that VII is the *only* photoproduct observed in the photolysis of methyl 2,2-dimethylcyclopropyl ketone (II).

Table II. Data Table for Methyl 2,2-Dimethylcyclopropyl Ketone (II) Vapor-Phase Photolysis[a]

Pressure, Torr	Q_m	CO_2, Torr	NO, Torr	2,3-Dimethyl-2-butene, Torr	Φ[b]
4.7	0.282				0.300
15.0	0.49				0.287
7.3	0.36			2.0	0.303
8.0	0.373			1.0	0.298
7.4	0.362				0.318
7.4	0.362			4.0	0.318
7.3	0.362			7.8	0.310
20.7	0.587				0.320
1.8	0.165				0.294
15.0	0.48	360			0.190
4.0	0.275		4.6		0.310

[a] Wavelength, 2537–2654 Å; temperature, 120°; $I_0 = 5.4 \times 10^{-9}$ einstein/sec; photolysis time, 1000 sec. [b] Quantum yield for 5-methyl-5-hexen-2-one (VII).

Data from the photolysis of ketone II in the long-path attachment to the infrared spectrophotometer are shown in Table III. A background between 3450 and 3800 cm^{-1} (the enolic hydroxyl stretch region) was run. Three peaks were observed in this region at 3780, 3650, and 3535 cm^{-1}. Upon irradiation, the 3535-cm^{-1} peak grew rapidly and within 13 min had reached a constant value. The base line of this peak was about 93.5% T. The 3535-cm^{-1} peak was then monitored and the irradiation by ultraviolet light stopped. The 3535-cm^{-1} wavelength began to decrease, and after 20 min the pen returned to 85% T. The peak disappeared by first-order kinetics and a half-life of 167 sec was calculated.

Table III. Data Table for the Methyl 2,2-Dimethylcyclopropyl Ketone (II) Photolysis in the "Long-Path" Attachment to the Infrared Spectrophotometer

Time, min	% T[a]
0.0	87.5
3.6	38.5
8.6	18.8
12.6	12.0
16.6	11.0
19.6	11.6

[a] Per cent transmittance values for 3535-cm^{-1} absorption due to hydroxyl stretch of an enol intermediate.

Cyclopropyl 2,2-dimethylcyclopropyl ketone (III) was photolyzed at 120° at pressures below 5 Torr. The major photoproduct is 3-methyl-3-butenyl cyclopropyl ketone (VI) with a quantum yield of 0.25. Carbon monoxide is formed with a quantum yield of 0.03. Trace amounts of some unidentified products are also formed. These trace products are formed with quantum estimated to be at least a factor of 10 smaller than that of the principal product.

Propyl cyclopropyl ketone (IV), when irradiated at 120° in the 2537–2564-Å region, formed no detectable products at pressures less than 10 Torr and short irradiation periods.

3-Butenyl cyclopropyl ketone (V) also proved to be quite stable to irradiation at 120° using 2537- or 3130-Å light. Again no photoproducts were observed.

Solution-Phase Photolyses. Ketone I did not react on irradiation with 2537- or 3130-Å light in isooctane and benzene solutions. A single photoproduct, propyl cyclopropyl ketone (IV), resulted when ketone I was photolyzed in isopropyl alcohol using 2537- and 3130-Å radiation.

The ***gem*-dimethylcyclopropyl ketones** II and III isomerized readily to 5-methyl-5-hexen-2-one (VII) and 3-methyl-3-butenyl cyclopropyl ketone (VI), respectively, on photolysis in isooctane, benzene, and ethanol solutions with 2537- and 3130-Å light.

Even when the photoconversions of ketones I (in isopropyl alcohol) and III (in isooctane, benzene, and ethanol) were run to completion, no further photolytic transformations of the products IV and VI, respectively, could be observed.

Discussion

Vapor-Phase Photolyses. Dicyclopropyl Ketone (I). The products formed in the vapor-phase photolysis of I are analogous to those formed during the photolysis of methyl cyclopropyl ketone.[12] In methyl cyclopropyl ketone vapor-phase photolyses, methyl *cis*-propenyl ketone, methyl *trans*-propenyl ketone, methyl allyl ketone, and carbon monoxide are formed in primary photochemical steps from vibrational levels in the first excited singlet state. Carbon monoxide is formed in a Norrish type I elimination. Methyl cyclopropyl ketone can split on either side of the carbonyl group to yield acetyl and cyclopropyl radicals, or alternately to yield cyclopropylcarbonyl and methyl radicals. The acetyl radical (at temperatures above 120°) decomposes immediately into carbon monoxide and methyl radicals.[13] The fate of the cyclopropyl carbonyl radical is less certain. It can be expected that some of these radicals will decompose to yield carbon monoxide and cyclopropyl radicals. However, Thynne has found that ▷-CO· decomposed only 40% of the time in a similar system.[14] Also, there was evidence in the methyl cyclopropyl ketone study that the

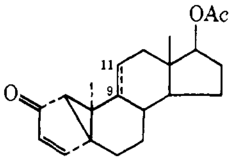
▷—CO·

radical was involved in reactions other than decomposition to carbon monoxide and cyclopropyl radicals.[12] The stability of the cyclopropyl carbonyl radical is further illustrated in the data presented in Table IV.

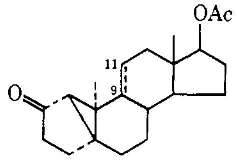
Table IV. Norrish Type I Split at 2537–2654 Å and 20 Torr of Pressure

Temp, °C	Quantum yield of CO from CH_3CO—◁	Quantum yield of CO from ▷—CO—◁
120	0.13	0.01
170	0.17	
183	0.19	
200		0.05
227	0.21	
283	0.22	

Clearly, dicyclopropyl ketone (I) is more photostable with respect to the type I process than is methyl cyclopropyl ketone. This increased photostability may be rationalized in terms of the stability of the cyclopropyl carbonyl radical. In methyl cyclopropyl ketone an acetyl radical may be formed at least part of the time, whereas in ketone I only the cyclopropyl carbonyl radical is formed. An alternate explanation for the reduced reactivity of ketone I and of methyl cyclopropyl ketone compared to the dialkyl ketones is that the excitation energy initially absorbed by the carbonyl group in the n → π* band is delocalized into the cyclopropyl rings, thereby reducing α cleavage (the Norrish type I process). The exact manner by which the energy is transferred is not clear. It has been suggested that an appreciable overlap exists between the π system of the carbonyl group and diffuse sp^5 cyclopropane orbitals.[15] This concept of overlap has been used by Hess, *et al.*,[16] to explain results of the photolyses of bicyclo[3.1.0] systems, and by Dauben[17] and Zimmerman[18] for related cases of cyclopropyl ketone photoisomerizations. The suggestion that a cyclopropyl ring can accept energy from an adjacent carbonyl group has support from observations that, in certain cases (presumably where favorable orbital overlap is enforced sterically), a cyclopropyl ring has been found capable of transmission of conjugation. An illustrative example of this is represented, *e.g.*, by the uv data (λ_{max}, nm; ε) of the following two pairs of steroidal compounds[19]



9,11 saturated (238; 5500)
9,11 unsaturated (280; 7600)



9,11 saturated (212; 6300)
9,11 unsaturated (241; 8300)

In order to explain a decrease in the Norrish type I elimination, Padwa, *et al.*,[20] have called upon delocalization into an adjacent phenyl group of energy absorbed in the carbonyl group n → π* band. Clearly then, dicyclopropyl ketone (I), having two cyclopropyl groups into which excitation energy may be delocalized, should have little tendency toward α cleavage, and this is observed experimentally.

In all photolyses of dicyclopropyl ketone (I), the quantum yield for formation of cyclopropyl *cis*-propenyl ketone exceeds that of the trans isomer, which in turn exceeds the quantum yield for the formation of the allyl isomer. The quantum yields for the formation of the allyl isomer and for carbon monoxide are approximately equal. The photoreactivity of methyl cyclopropyl ketone may be compared to the reactivity of acetone by comparing the quantum yields for carbon monoxide formed in their photolyses. For temperatures above 120° the quantum yield for CO formed in the photolysis of acetone is 1.0. At the same temperature and at lower pressures where collisional deactivation is small, the quantum yield for formation of CO in the photolysis of methyl cyclopropyl ketone is 0.25. The photoreactivities of methyl cyclopropyl ketone and dicyclopropyl ketone (I) may be compared by examining the quantum yield sums for all the products formed in primary steps. For methyl cyclopropyl

---

[12] D. G. Marsh and J. N. Pitts, Jr., *J. Amer. Chem. Soc.*, 93, 326 (1971).

[13] J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966.

[14] G. Greig and J. C. J. Thynne, *Trans. Faraday Soc.*, 62, 3338 (1966).

[15] W. A. Bernett, *J. Chem. Educ.*, 44, 17 (1967), and references therein.

[16] L. D. Hess, J. L. Jacobson, K. Schaffner, and J. N. Pitts, Jr., *J. Amer. Chem. Soc.*, 89, 3684 (1967).

[17] W. G. Dauben and G. W. Shaffer, *Tetrahedron Lett.*, 4415 (1967).

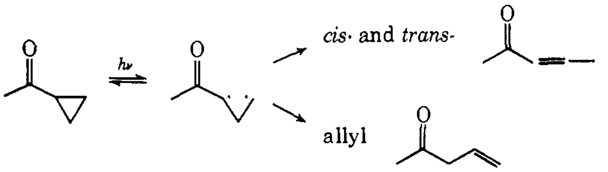
[18] H. E. Zimmerman, K. G. Hancock, and G. C. Licke, *J. Amer. Chem. Soc.*, 90, 4892 (1968), and references therein.

[19] Lj. Lorenc, M. Miljković, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, 49, 1183 (1966).

[20] A. Padwa, E. Alexander, and M. Niemcyzk, *J. Amer. Chem. Soc.*, 91, 456 (1969); A. Padwa and D. Eastman, *ibid.*, 91, 462 (1969).

ketone, the sum is about 0.60[12] at 120° and *ca.* 20 Torr. For I, the sum of the quantum yields is about 0.17 under similar conditions. These data show that substitution of a cyclopropyl group for a methyl group in simple ketones lowers the reactivity by a factor of approximately 4.

The term π^*-assisted cyclopropane fission has been applied to the process in which energy absorbed by a carbonyl group in its $n \rightarrow \pi^*$ band is delocalized into a cyclopropyl group α to the carbonyl, with subsequent β bond fission to produce photoproducts similar to the ones observed in the photolysis of I[16] (and of methyl cyclopropyl ketone). A biradical intermediate has been postulated for this mechanism by Pitts and Norman.[21] Several other workers have postulated biradical intermediates in similar systems on the basis of chemical evidence.[16–18,22–24] The biradical intermediate may then undergo a 1,2 hydrogen shift to yield the three possible photoisomers.



An alternate mechanistic pathway for the photochemical isomerization of cyclopropyl ketones to unsaturated aliphatic ketones is a symmetry-allowed concerted [$\sigma^2_{\text{cyclopropyl}} + \sigma^2_{\text{C-H}}$] addition involving an α,β-cyclopropane C–C bond which would lead again to all three isomers formed from methyl cyclopropyl ketone and from ketone I: bonding of the α methylene carbon to an adjacent methylene hydrogen would give the propenyl ketones. Bonding between the methine carbon and an adjacent methylene hydrogen would furnish the allyl products.[23,25] Experimental support for a concerted process has been found in the photoisomerization of a cyclopropyl ketone in solution phase.[23a]

Methyl 2,2-Dimethylcyclopropyl Ketone (II). The vapor-phase photolysis of II in the $n \rightarrow \pi^*$ band using 2537–2654-Å light yields only one product, 5-methyl-5-hexen-2-one (VII). There is no evidence of carbon monoxide being formed even after lengthy exposures. The gas chromatograms shows no trace of other products. Data for the photolyses of II are shown in Table II.

The product, 5-methyl-5-hexen-2-one (VII), may be formed by one of two possible mechanisms. A π^*-assisted cyclopropane fission reaction could conceivably lead to the product. An alternate possibility is a Norrish type II process. The latter involves the abstraction by the excited carbonyl group of a γ hydrogen with subsequent formation of a ketone and an olefin moiety.[26] It was first suggested by Rice and Teller[27] that a six-membered transition state was formed followed by primary production of an enol intermediate. McMillan, Calvert, and Pitts[28] observed an infrared absorption in a long-path ir cell during the photolysis of 2-pentanone which was attributed to the hydroxyl stretch of the enol form of acetone. The observation of an enol intermediate in the isomerization of ketone II would serve to distinguish between the two mechanisms considered. An experiment was performed, therefore, using the long-path attachment to a Perkin-Elmer Model 621 infrared spectrophotometer.

We attribute the 3535-cm^{-1} absorption to the hydroxyl stretch of the enol intermediate (half-life, 167 sec) formed during the photolysis of II; see Table III. Formation of a transient enol suggests strongly that the formation of 5-methyl-5-hexen-2-one (VII) in the photolysis of II occurs *via* a Norrish type II process. This mechanism is illustrated in Figure 1.

The evidence presented in Table II suggests that the "bridged" Norrish type II process of ketone II occurs in the first excited *singlet* state. Triplet quenching experiments were carried out by adding 1.0–7.8 Torr of 2,3-dimethyl-2-butene and 4.6 Torr of nitric oxide, respectively. Nitric oxide can act both as a quencher of triplet states and as a radical scavenger. Neither additive has any significant effect, however, on the quantum yield of 5-methyl-5-hexen-2-one (VII). The addition of 360 Torr of carbon dioxide causes more than a 30% decrease in the quantum yield for formation of VII. This is indicative of collisional deactivation of higher vibrational levels of the excited singlet state, which are amply populated with 2537–2654-Å light. One may conclude, therefore, that the bridged Norrish type II process of ketone II occurs more efficiently from a higher vibrational level(s).

The striking fact that photochemical isomerization of ketone II to the γ,δ-unsaturated ketone VII predominates (to the mutual exclusion of all other processes) may be attributed to the constrained geometry of II which forces the *cis*-methyl of the *gem*-dimethyl group, and with it, concurrently, the necessary γ hydrogen for the type II process, into close proximity with the carbonyl group.

Cyclopropyl 2,2-Dimethylcyclopropyl Ketone (III). This compound undergoes the expected bridged Norrish type II process quite analogously to ketone II. The major photoproduct is cyclopropyl 3-methyl-3-butenyl ketone (VI) (Φ 0.25) at 120° and pressures less than 5 Torr using 2537–2654-Å light. In addition, CO (Φ 0.03) and trace amounts of other products were formed. Ketone III differs from II in that there is another cyclopropane ring adjacent to the carbonyl group. Therefore, in competition with the predominant bridged type II process and to the less important type I eliminations, the unsubstituted ring might undergo π^*-assisted cyclopropane fission reactions. The glpc retention times of the trace unidentified products suggest that they may be cis, trans, and allyl isomers corresponding to just such reactions.

Propyl Cyclopropyl Ketone (IV) and 3-Butenyl Cyclopropyl Ketone (V). These ketones were studied in

---

(21) J. N. Pitts, Jr., and I. Norman, *J. Amer. Chem. Soc.*, **76**, 4815 (1954).

(22) (a) G. W. Griffin, E. J. O'Connell, and H. A. Hammond, *ibid.*, **85**, 1001 (1963); (b) C. H. Robinson, O. Gnoj, and F. E. Carlon, *Tetrahedron*, 21, 2509 (1965); (c) R. E. K. Winter and F. R. Lindauer, *Tetrahedron Lett.*, 2345 (1967); (d) W. G. Dauben and G. W. Shaffer, *J. Org. Chem.*, **34**, 2301 (1969).

(23) (a) R. Beugelmans, *Bull. Soc. Chim. Fr.*, 244 (1967); (b) D. Belluš, D. R. Kearns, and K. Schaffner, *Helv. Chim. Acta*, **52**, 971 (1969).

(24) W. G. Dauben, L. Schutte, and R. E. Wolf, *J. Org. Chem.*, **34**, 1849 (1969).

(25) *Cf.* R. Hoffmann and R. B. Woodward, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(26) R. G. W. Norrish and M. E. S. Appleyard, *J. Chem. Soc.*, 874 (1934); C. H. Bamford and R. G. W. Norrish, *ibid.*, 1504 (1935).

(27) F. O. Rice and E. Teller, *J. Chem. Phys.*, **6**, 489 (1938); W. D. Davis, Jr., and W. A. Noyes, Jr., *J. Amer. Chem. Soc.*, **69**, 2153 (1947).

(28) G. R. McMillan, J. G. Calvert, and J. N. Pitts, Jr., *ibid.*, **86**, 3602 (1964).

order to answer the question of whether aliphatic cyclopropyl ketones, having available either γ hydrogens or γ,δ double bonds, will undergo Norrish type II processes and oxetane formation, respectively, in competition with π^*-assisted cyclopropane fission reactions. Photolysis of ketone IV did not yield any methyl cyclopropyl ketone, the expected product for the Norrish type II process, in the vapor phase. In the vapor-phase photolysis of both ketones IV and V, trace amounts of other products were detected by glpc, which suggest that other processes, possibly π^*-assisted cyclopropane fission in IV and V, and oxetane formation on V, were occurring. These products were, however, not identified. At the very least, delocalization of the excitation energy into the ring, whatever the subsequent mode of deactivation, eliminates the Norrish type II process for the propyl cyclopropyl ketone studied. This has some analogy with the reduction or exclusion of the Norrish type I elimination (to yield carbon monoxide) by substitution of cyclopropane rings adjacent to the carbonyl group. The failure of ketone IV to yield methyl cyclopropyl ketone upon irradiation also lends further support to the idea that it is the constrained geometry of the gem-disubstituted cyclopropyl compounds II and III that permits the bridged Norrish type II process to predominate over competitive reactions.

Solution-Phase Photolyses of Ketones I–IV and VI. Ketone I is strikingly resistant toward phototransformations in solvents that are relatively poor hydrogen donors (isooctane, benzene), with the result that no reaction is observed after photolysis times that suffice to effect total conversion of ketones II and III under comparable irradiation conditions. At least in part, this apparent low reactivity could well be due to reversible π^*-assisted cyclopropane fission *via* a biradical[29] with the reclosure to I over hydrogen 1,2 shifts being more favored in solution than in the vapor-phase experiments. This is in contrast to the rapid conversion of ketone I to propyl cyclopropyl ketone (IV) in isopropyl alcohol. This transformation may be attributed to hydrogen abstraction from the solvent by the excited carbonyl group, followed by cyclopropane opening in the intermediate α-hydroxydicyclopropylcarbinyl radical[30] and the subsequent addition of a second hydrogen to the terminal methylene radical. An alternate mechanism, *i.e.*, trapping of the intermediate biradical product of the photochemical ring fission, would also be possible and cannot be ruled out on the basis of available experimental evidence. The behavior of ketone I in isooctane, benzene, and isopropyl alcohol is quite analogous to that of methyl cyclopropyl ketone[31] and differs from that of ketones II and III in a similar way as in the vapor-phase photolysis. The efficient and largely solvent-independent photorearrangement of ketones II[6,7] and III in isooctane, benzene, and ethanol to 5-methyl-5-hexen-2-one (VII) and cyclopropyl 3-methyl-3-butenyl ketone (VI), respectively, as the only detectable primary photoproducts, is again attributable to bridged Norrish type II processes. This conclusion is substantiated by the findings of Dauben, *et al.*,[24] that *cis*-2-methylcyclopropyl methyl ketone in similar solvents yielded a single product, 5-hexen-2-one, whereas the trans isomer reacted analogously to ketone I and methyl cyclopropyl ketone.[29]

The reasons for the relatively low reactivity of ketones IV *in isopropyl alcohol* and VI in ethanol as the solvents are difficult to assess at present, and further experimentation on this point is desirable. Thus, it is not immediately obvious why, particularly in the case of propyl cyclopropyl ketone (IV), intermolecular hydrogen abstraction is distinctly less efficient than the corresponding process of dicyclopropyl ketone (I).

Acknowledgments. The authors wish to thank Drs. John Coomber and Ole Buchardt for stimulating discussions. The support of this research by Grant No. AP 00109, Research Grants Branch, National Air Pollution Control Administration, Consumer Protection and Environmental Health Service, U. S. Public Health Service (to J. N. P.), by Grant No. 4700, Schweizerischer Nationalfonds zur Förderung der Wissenschaftlichen Forschung and the J. R. Geigy AG., Basel (to K. S. and A. T.), and a Public Health Service Special Predoctoral Fellowship, is gratefully acknowledged.

---

[29] For a discussion and literature references pertaining to reversible π^*-assisted fission of cyclopropyl ketones see ref 16 and 18. Experimental evidence for such a process in an acyclic compound, *i.e.*, *trans*- $+ h\nu \rightarrow$ *cis*-2-methylcyclopropyl methyl ketone, has been described recently by Dauben, *et al.*[24]

[30] Ring opening in thermally generated α-hydroxycyclopropylcarbinyl radicals has been investigated by D. C.Neckers, A. P. Schaap, and J. Hardy, *J. Amer. Chem. Soc.*, **88**, 1265 (1966).

[31] Unpublished results by A. Tuinman and K. Schaffner; *cf.* also the discussion in ref 12. In benzene and in isooctane, methyl cyclopropyl ketone photoisomerizes, but very slowly, to *cis*- and *trans*-propenyl methyl ketone, and 2-pentanone is the major product in isopropyl alcohol. Similar findings have been reported by Dauben.[24] *Cf.* also W. G. Dauben, L. Schutte, R. E. Wolf, and E. J. Deviny, *J. Org. Chem.*, **34**, 2512 (1969), on the photoreduction of cyclic cyclopropyl ketones in isopropyl alcohol.