Structure and Reactivity of Small Ring Compounds. IV.[1) Photochemistry of Spirocyclopropyl Ketones[2)

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The photochemical transformations of a series of spriocyclopropyl ketones (**1**—**4**) have been investigated in dilute *n*-hexane solutions. Spirocyclopropyl ketones **1** and **2** give mainly the 'Type I' photoproducts of cycloalkanones, *i.e.*, 1-(2'-propenyl)cyclopropanecarboxaldehyde (**5**, 34%) and 1-(3'-butenyl)cyclopropanecarboxaldehyde (**7**, 37%), respectively, in marked contrast to the usual photochemical cleavage of cyclopropyl ketones. Ethylidenecycloalkanones are not detected, but their hydrogenated derivatives, 2-ethylcycloalkanones, are produced in a small amount.

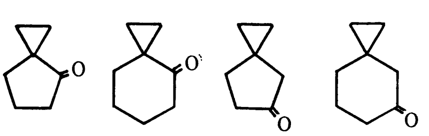
The photoreaction of **1** has been found to be quenched by piperylene, so that it is highly probable that the reaction products are derived from the n-π^* triplet states of the ketones.

The irradiations of nonconjugated spiroketones **3** and **4** afford ring-enlarged 4-methylenecycloalkanones, **9** and **10**, respectively.

The preferential photoisomerization of conjugated cyclopropyl ketones to enones has been extensively studied both in gas and liquid phases.[3) It has been thought that in this characteristic photoisomerization, transfer of the excitation energy absorbed by the carbonyl chromophore to a highly strained cyclopropane ring through a conjugative interaction causes the homolytic ring fission to give the enones.[4)

In order to elucidate this interesting photochemical process on the basis of conformational aspect, we have investigated the photochemistry of some spirocyclopropyl ketones (**1**—**4**). In compounds **1** and **2** bearing a cyclopropane ring in an adjacent position to a carbonyl group, the cyclopropane ring and carbonyl group are fixed to permit the maximum conjugative interaction from their geometry.[5) On the other hand, compounds **3** and **4** are nonconjugated.

In a preliminary paper,[2) we reported the unusual photochemical behaviors of these spiroketones. Recently, Crandall and Seidewand[6), and Turro *et al.*[7) also reported the photoreactions of **1** and **2** in different solvents. In the present paper, we describe the detailed results and discuss the photochemistry of cyclopropyl ketones.

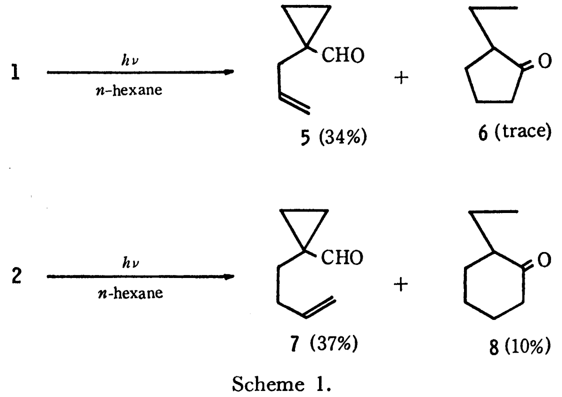


1 **2** **3** **4**

Fig. 1.

Results

*Photochemistry of Spiro[2.4]heptan-4-one (**1**).* Irradiation of a *n*-hexane solution of **1** (0.11 mol/*l*) by a high pressure mercury lamp gave 1-(2'-propenyl)-cyclopropanecarboxaldehyde (**5**) and a trace amount of 2-ethylcyclopentanone with a considerable amount of polymeric materials. The prolonged irradiation caused the polymerization. Under optimized reaction conditions (40 hr irradiation) the aldehyde **5** was isolated in 34% yield by means of preparative vpc. The structure of **5** was determined by elemental analysis, IR, and NMR spectra. 2-Ethylcyclopentanone which was obtained in too small a quantity to be isolated was assigned by comparison of its retention times of vpc with an authentic sample.[8)



Scheme 1.

Oxygen Effect and Quenching Experiments. On irradiation of ketone **1**, the presence of oxygen caused marked retardation of the photoconversion. In addition, piperylene quenched the photochemical reaction of **1**. These results are shown in Table 1.

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1) Part III: This bulletin, **40**, 2334 (1967).

2) Presented at the 22nd annual meeting of the Chemical Society of Japan, Tokyo, April, 1969. Preliminary communication has been given; *Tetrahedron Lett.*, **1969**, 3189.

3) a) J. N. Pitts, Jr. and I. Norman, *J. Amer. Chem. Soc.*, **72**, 4815 (1954). b) L. D. Hess and J. N. Pitts, Jr., *ibid.*, **89**, 1973 (1967). c) W. G. Dauben and G. W. Shaffer, *Tetrahedron Lett.*, **1967**, 4415. d) H. E. Zimmerman, K. G. Hancock, and G. C. Licke, *J. Amer. Chem. Soc.*, **90**, 4892 (1968). e) W. G. Dauben L. Schutte, R. E. Wolf, and E. J. Deviny, *J. Org. Chem.*, **34**, 2512 (1969). f) W. G. Dauben, G. W. Shaffer, and E. J. Deviny, *J. Amer. Chem. Soc.*, **92**, 6273 (1970).

4) R. Hoffmann, *Tetrahedron Lett.*, **1965**, 3819; Ref. 3c.

5) E. M. Kosower and M. Ito, *Proc. Chem. Soc.* (London), **1962**, 25.

6) J. K. Crandall and R. J. Seidewand, *J. Org. Chem.*, **35**, 697 (1970).

7) D. R. Morton, E. Lee-Ruff, R. M. Southam, and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 4349 (1970).

8) F. H. Cose and E. E. Reid, *ibid.*, **50**, 3062 (1928).

9) Prepared by the method reported by G. W. Baily and M. Mandoff, *J. Amer. Chem. Soc.*, **76**, 2707 (1954).

Table 1. Quenching experiments of the photoreaction of spiro[2.4]heptan-4-one (**1**)[a)]

Quencher	Irradiarion time (min)	Analytical data[b)]	
		1 (recovered)	**5**
None (N_2 bubbling)	60	65%	35%
	120	35	65
O_2 (bubbling)	60	96	4
	120	91	9
Piperylene[c)]	60	100	trace
	150	99.5	0.5
	300	99	1
	400	98	2

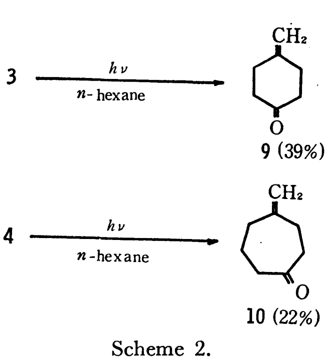
a) Irradiated by means of 3130 Å using potassium chromate filter solution ($5\times10^{-4}M$, path length 5 cm).
b) Determined by the relative area of vpc.
c) In concentration of 0.16 mole/*l* *n*-hexane.

*Photochemistry of Spiro[2.5]octan-4-one (**2**).* Irradiation of ketone **2** in *n*-hexane under the conditions similar to those employed in the photolysis of **1** afforded 1-(3′-butenyl)cyclopropanecarboxyaldehyde (**7**) and 2-ethylcyclohexanone (**8**) in 37% and 10% yields, respectively. The structure of **7** was established by elemental analysis, NMR, and IR spectra. The minor product **8** was identified by comparisons of its IR and NMR spectra with those of an authentic sample.[9)]

Irradiation of **2** in diethyl ether for 50 hr also gave **7** and **8** in 23% and 16% yields, respectively. The irradiation through a Pyrex filter did not affect the reaction (after 50 hr, **7** and **8** were produced in 17% and 9% yields, respectively).

*Photochemistry of Spiro[2.4]heptane-5-one (**3**) and Spiro[2.5]octan-5-one (**4**).* Irradiation of a *n*-hexane solution of **3** in a quartz vessel gave only polymeric materials after 20 hr. On irradiation through a Pyrex filter, the ring-enlarged product, 4-methylenecyclohexanone (**9**) was obtained in 39% yield after 3 hr. The structure of **9** was established by the comparison with an authentic sample.[10)]

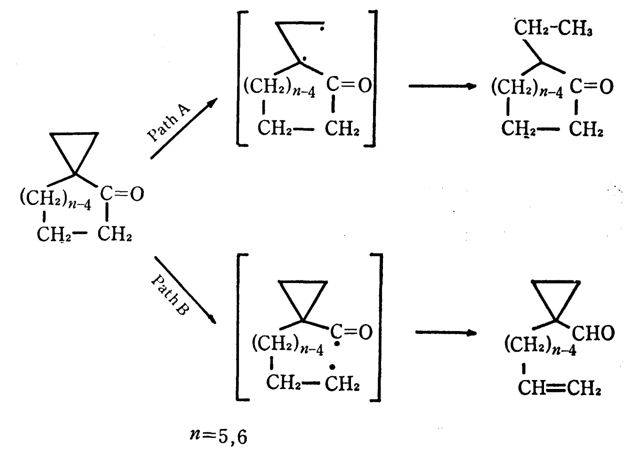
Irradiation of **4** in *n*-hexane produced 4-methylenecycloheptanone (**10**) in 22% yield after 20 hr. The structure of **10** was also confirmed by IR and NMR spectra and elemental analysis. Hydrogenation of **10** gave 4-methylcycloheptanone.[11)]



Scheme 2.

Discussion

The photochemistry of **1** and **2** has been studied by three research groups.[2,6,7)] Although their results are slightly different in detail according to the reaction conditions, the most important observation in these studies is that the cyclopropane cleavage (Path A) is not the major path, but the α-cleavage of the bond away from the cyclopropyl group (Path B) is actually the preferred process.[12)]



Scheme 3.

Accordingly, it can be concluded that the retention of cyclopropane ring is characteristic for the photoconversions of conjugated spirocyclopropyl ketones. This is a striking contrast to the predominant photocleavage of a cyclopropane ring observed in numbers of cyclopropyl ketones.[3)]

The present investigation showed that the irradiation of **1** in *n*-hexane gives 1-(2′-propenyl)cyclopropanecarboxaldehyde (**5**) almost exclusively, whereas the irradiation of **2** in the same solvent produced 1-(3′-butenyl)cyclopropanecarboxaldehyde (**7**, 37%) accompanied by a considerable amount of 2-ethylcyclohexanone (**8**, 10%). The latter compound might be formed *via* a diradical followed by abstraction of hydrogen atoms from the solvent (Scheme 3). This is supported by the fact that the yield of **8** is substantially increased (16%), when **2** is treated in diethyl ether. It becomes apparent that the cyclopropane cleavage is hardly found in the photolysis of **1**, but in **2** it competes with 'Type I'[13)] cleavage.

The photochemical cleavage of cyclopropyl ketones to enones is rationalized by the concept that photoexcitation energy is transferred to the cyclopropyl group through conjugative interaction and the strained ring is cleaved by its excess energy.[4)] However, this concept would not be able to explain the difference in the photochemical behavior between

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[10)] T. Tsuji, Ph. D. Thesis (1967) Osaka University.

[11)] C. Djerassi, B. F. Burrows, G. G. Overberger, T. Takekoshi, C. D. Gutsche, and C. T. Chang, *J. Amer. Chem. Soc.*, **85**, 949 (1963).

[12)] In addition to **1** and **2**, Turro *et al.*[7)] reported that 1,1-dimethylspiro[2.3]hexan-4-one gives cyclopropane ring-retained acetals as exclusive photoproducts in methanol.

[13)] J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, Inc., New York, N. Y. (1966), p. 368—427.

spiroketones and other cyclopropyl ketones. According to Kosower and Ito,[5] the spiroketone **1** has higher degree of conjugation between the cyclopropyl and carbonyl groups than bicyclo[3.1.0]hexan-2-one. This would lead that the spiroketone suffers the cyclopropane cleavage more efficiently than the bicyclic ketone. However, the reverse is true in our case.

We determined the π–π^* absorption maxima of **1** and **2** in ethanol, and compared them with those of corresponding methylene- and dimethyl-cycloalkanones and nonconjugated spiroketones **3** and **4** (Table 2). The result indicates that the spiroketones **1** and **2** have similar conjugative interaction. Again this cannot help to understand the difference in their photochemical transformations.

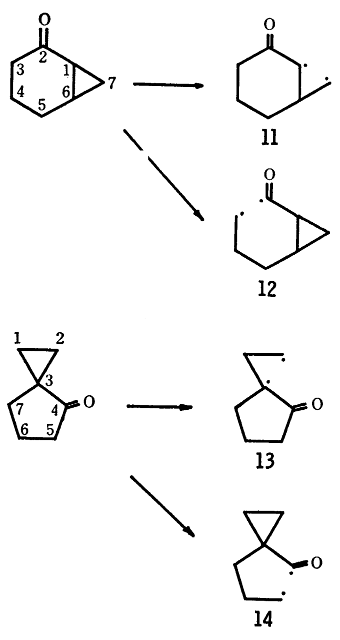
Table 2. UV data of spiro[2.n]alkanones (n=4, 5) and related ketones

Compounds	$\lambda_{\max}$ (ethanol) nm	$\varepsilon_{\max}$
2-Methylenecyclopentanone[a]	231[a]	7550[a]
1	203	3360
3	<200	—
2,2-Dimethylcyclopentanone[b]	<200	—
2-Methylenecyclohexanone[a]	230[a]	7400[a]
2	205	3440
4	<200	—
2,2-Dimethylcyclohexanone[c]	<200	—

a) Ref. 14
b) Prepared by the known method.[15]
c) Prepared by the known method.[9]

In the photochemistry of bicyclo[4.1.0]heptan-3-ones, Dauben and his coworkers[3c,f] showed that only when a methyl group is substituted at C-3 position, the α-cleavage away from the cyclopropyl group (C-2—C-3) becomes a predominant reaction path. However, this substituent effect to stabilize the radical generated in the photolysis cannot also be the factor controlling the direction of bond fission in these spiroketones. In the bicyclic ketones, the diradical **11**, which is primary–secondary, is proposed to be more stable than diradical **12**.[3c,f] The diradical **13** expected from the cyclopropane cleavage of spiroketone **1** is a primary-tertiary one. The α-cleavage of **1** will give **14**, which may be comparable in its stability with **12**. There will be no reason to expect that the diradical **13** is less stable than **11**, and hence **13** is less stable than **14**.

Crandall and Seidewand[6] have suggested that the apparent resistance of the cyclopropyl group to photochemical ring fission is due to the reversible recombination to the ring. Actually, the cyclopropane ring fission is reversible in several instances,[16] but there may be no reason why such a recombination process is particularly important only in the spiroketones and not so in other cyclopropyl ketones such as bicyclo[n.1.0]alkanones. Therefore, we believe that this explanation is not sufficient enough to account for the present results.



Scheme 4.

It was demonstrated that the photolysis of **1** using Pyrex-filtered light (>280 nm) proceeds similarly to the direct photolysis, and the photoreaction is quenched by piperylene. These results strongly indicate that the photoreaction of **1** as well as **2** proceeds *via* the n–π^* triplet state.[17] In many cases, the cleavage of cyclopropane ring proceeds through the triplet state.[18]

We would like to propose a hypothesis to rationalize the features of the photochemical behavior of spiroketones of **1** and **2**. Since the present photoreactions are regarded as a triplet reaction, the photoexcitation of these spiroketones leads to their triplet diradical state, where both the carbonyl carbon and the oxygen atoms may behave as a radical-like species.[19] The cyclopropane cleavage would subsequently occur through merely a dark reaction of the cyclopropylcarbinyl radical. Thus, the radical-like carbonyl-carbon would attack the cyclopropyl bond in an intramolecular S_H2 fashion to cleave the cyclopropyl ring giving an enolic diradical which is

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14) R. L. Erskin and E. S. Waight, *J. Chem. Soc.*, **1960** 3425.

15) Part I in this series: This Bulletin **40**, 2338 (1967).

16) G. W. Griffin, E. J. O'Connell, and H. A. Hammond, *J. Amer. Chem. Soc.*, **85**, 1001 (1963); G. W. Griffin, J. Covell, R. C. Petterson, R. M. Dodson, and G. Klose, *ibid.*, **87**, 1410 (1965); R. C. Cookson, M. J. Nye, and G. Subrahmanyan, *Proc. Chem. Soc.* (London), **1964**, 144; W. G. Brown and J. F. Neumer, *Tetrahedron*, **22**, 473 (1966); Ref. 3d.

17) Although the measurement of the phosphorescence spectrum of **1** was attempted in M-P-Matrix with an Aminco Bowman Spectrofluorometer, there obtained no well-defined spectrum allowing to calculate the precise E_T value, but a broad peak (350—500 nm, $\lambda_{\max}$ 430 nm) was observed.

18) A. Padwa, Organic "Photochemistry," edited by O. L. Chapman, Marcel Dekker, Inc., New York, N. Y. (1967), Vol. 1, Chapter 2; D. I. Schuster and D. J. Petal, *J. Amer. Chem. Soc.*, **90**, 5145 (1968); Ref. 16a.

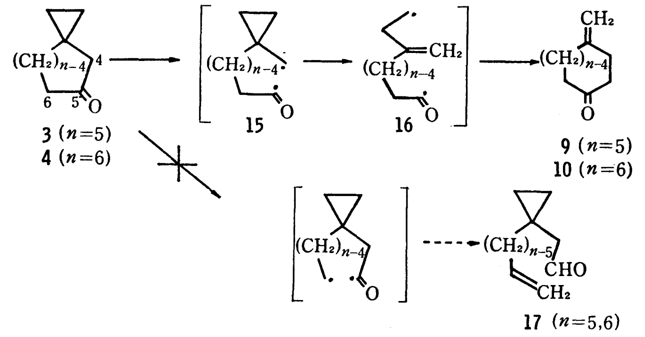
19) N. J. Turro, "Energy Transfer and Organic Photochemistry" edited by P. A. Leermakers and A. Weissberger, Interscience Publisher, New York, N. Y. (1969), p. 192.

followed by abstraction or migration of hydrogen atoms. In the S_H2 process[20], the attack would take place from the backside of the dissociating cyclopropyl bond, and hence the relative geometry between the cyclopropyl bond and *p*-orbital at the carbonyl carbon will be important.

The examination of the molecular models of these spiroketones indicates that in ketone **2**, the overlapping of the backside bond of the cyclopropyl bond and *p*-orbital of the carbonyl carbon in a *p*-σ manner might be possible to some extent, whereas in ketone **1**, the two orbitals are so arranged spacially as not to allow significant overlapping because of the rigid conformation of the cyclopentanone structure. The flexibility of the cyclohexane-ring structure in ketone **2** makes this sort of *p*-σ overlapping possible to a certain degree, but not fully as those of acyclic and bicyclic cyclopropyl ketones. Therefore, in the photolysis of **2**, the cyclopropane cleavage would compete with the α-cleavage.

Irradiation of nonconjugated spiroketones, **3** and **4**, afforded the ring-enlarged products, 4-methylenecycloalkanones, **9** and **10**, respectively. The cyclopropane ring was cleaved in these ketones. The reaction could be explained in a following way. The diradical **15** formed by the α-cleavage at C-4—C-5 gives the second diradical **16** *via* the induced ring opening of the cyclopropylcarbinyl radical, and finally the diradical cyclize intramolecularly to afford the reaction product. The ring-opening of the cyclopropylcarbinyl radical to form the second cyclic compound has been demonstrated in the photoreaction of several β-cyclopropyl cyclic ketones[21].

In the reaction of **3** and **4**, the formation of aldehyde **17** expected from the cleavage at C-5—C-6 could not be detected. This fact may suggest that the C-4—C-5 bond fission forming cyclopropylcarbinyl radicals occurs in preference to the C-5—C-6 cleavage.



Scheme 5.

Experimental

The IR spectra were recorded on a Hitachi EPI-S2 spectrophotometer. The UV spectra were obtained with a Hitachi EPS-2U spectrophotometer. The NMR spectra were obtained with a JEOLCO JNM-MH-60 or JNM-4H-100 spectrometer at 60 MHz and 100 MHz, respectively, using TMS as an internal standard. The analytic and preparative vpc were carried out using a Yanagimoto GCG-5DH gas chromatograph. All irradiations were conducted with a Eikosha PIH-500 (High pressure mercury lamp, 500 W). All temperatures are uncorrected.

Materials. Spiro[2.4]heptan-4-one (**1**) and spiro-[2.5]octan-4-one (**2**) were prepared by sodium dichromate oxidation of the corresponding carbinols[22] as described previously.[1]

Spiro[2.4]heptan-5-one (**3**) was prepared by the known method[23] from spiro[2.4]heptan-5-ol. Bp 58°C/18 mmHg, IR (liquid film): 1743 cm^{-1} (C=O), UV (ethanol): λ_{max} 290 nm (ε=35), NMR (60 MHz, CCl_4): 7.86 τ (2H, s, methylene of cyclopentanone), 7.5—8.3 τ (4H, m, methylenes of cyclopentanone), and 9.43 τ (4H, s, cyclopropane). Found: C, 76.08; H, 9.26%. Calcd for $C_7H_{10}O$: C, 76.32; H, 9.15%.

Spiro[2.5]octane-5-one (**4**) was prepared by the oxidation of spiro[2.5]octan-5-ol which was reported previously.[24] IR (liquid film): 1718 cm^{-1} (C=O). UV (ethanol): λ_{max} 288 nm (ε=35). NMR (60 MHz, CCl_4): 7.91 τ (2H, s, methylene of cyclohexanone), 7.5—8.5 τ (6H, m, methylenes of cyclohexanone), and 9.69 τ (4H, s, cyclopropane).

The spiroketones, starting materials, were purified by either fractional distillation or preparative vpc. Solvent *n*-hexane was purified by treating with fuming sulfuric acid followed by distillation. Diethyl ether and 2-propanol were purified by fractional distillation before use.

Irradiation of **2** *in* n-*hexane.* A solution of 15.0 g of **2** in 450 m*l* of *n*-hexane was irradiated through a quartz vessel under continuous slow bubbling of pure nitrogen. The reaction was monitored periodically by removing aliquots and then analyzing by vpc (Apiezon L at 130°C). When about the half of the starting ketone had been consumed, irradiation was stopped (40 hr). After solvent was evaporated through a short column, the residual oil (14.4 g) was subjected to fractional distillation under reduced pressure. The distillate (11.8 g) was separated by vpc (Apiezon L) into three components. The first compound (2.75 g) was characterized as an aldehyde **7** (37% yield based on consumed **2**) by the analysis, functional tests and the spectral data. IR (liquid film): 2730 cm^{-1} (C–H, aldehyde) 3070, 1025 cm^{-1} (C–H, cyclopropane), 1705 cm^{-1} (C=O), 1635, 900 cm^{-1} (terminal olefin). UV (ethanol): λ_{max} 211 nm (ε=2400), and 280 nm (ε=67). NMR (100 MHz, CCl_4): 1.4 τ (1H, s, aldehyde), 4.25 and 5.05 τ(1H, and 2H, ABC pattern of vinyl), 7.86 τ (2H, q, methylene), 8.35 τ (2H, overlapped d, methylene), and 8.93 and 9.12 τ (2H+2H, AA′BB′ pattern of cyclopropane). Found: C, 77.03; H, 9.79%. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74%. Bp. 60—61°C/7 mmHg. n_D^{20} 1.4612. Olefin test (Br_2, $KMnO_4$) positive. 2,4-Dinitrophenylhydrazone; mp 133—134°C.

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20) W. A. Pryor, "Free Radicals," McGraw Hill Book Co., Inc., New York, N. Y., (1966), Chapter 13.

21) L. D. Hess, J. L. Jacobson, K. Schaffner, and J. N. Pitts, Jr., *J. Amer. Chem. Soc.*, **89**, 3684 (1967); D. C. Hechert and P. J. Kropp, *ibid.*, **90**, 4911 (1968); R. H. Eastman, J. E. Starr, R. St. Martin, and M. K. Sakata, *J. Org. Chem.*, **28**, 2162 (1963); J. E. Starr and R. H. Eastman, *ibid.*, **31**, 1393 (1966).

22) Prepared by the procedure reported by W. G. Dauben and G. H. Berezin, *J. Amer. Chem. Soc.*, **85**, 468 (1963).

23) W. G. Dauben and T. L. Chitwood, *ibid.*, **90**, 3835 (1968).

24) S. Nishida, I. Moritani, K. Ito, and K. Sakai, *J. Org. Chem.*, **32**, 959 (1967).

The second product (0.76 g, 10% yield) was identified to be 2-ethylcyclohexanone (**8**) by comparisons of IR, retention times of vpc (Apiezon L and Carbowax 6000) with an authentic sample.9) IR (liquid film): 1710 cm^{-1} (C=O), and 1382 cm^{-1} (CH_3). NMR (100 MHz, CCl_4): 9.20 τ (3H, t, methyl). Found: C, 75.75; H, 11.03%. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18%. Bp 51—52°C/8 mmHg. Semicarbazone, mp 157—157.5°C. The mixed mp of the semicarbazone with an authentic sample showed no depression.

The last component was unchanged **2** (7.58 g).

Irradiation of **2** in diethyl ether using a Pyrex reaction vessel for 50 hr afforded a volatile reaction mixture which was composed of **7** (24%), **8** (12%) and **2** (64%).

Irradiation of ***1*** *in* n-*hexane.* A solution of **1** (7.0 g) in *n*-hexane (500 m*l*) was similarly irradiated for 40 hr. The volatile reaction mixture (4.3 g) was separated with a preparative vpc (Apiezon L) into two components. The first eluted product (1.23 g, 34% yield) was characterized as an aldehyde **5**. Bp 34°C/7 mmHg. n_D^{20} 1.4608. UV (ethanol): λ_{max} 211 nm (ε=2700), 260 nm (ε=82). IR (liquid film): 3080, 1030 cm^{-1} (cyclopropane), 2725, 1690 cm^{-1} (aldehyde), 1630, 1410, 995, and 910 cm^{-1} (terminal olefin). NMR (100 MHz, CCl_4): 1.35 τ (1H, s, aldehyde), 4.3 τ (1H, m, vinyl), 4.99 and 5.12 τ (2H, two multiplet peaks, vinyl), 7.68 τ (2H, d, J=6.5 Hz, methylene), and 9.03 τ (4H, AA'BB' pattern, cyclopropane). Found: C, 76.09; H, 9.16%. Calcd for $C_7H_{10}O$: C, 76.32; H, 9.15%. 2,4-Dinitrophenylhydrazone, mp 139—139.5°C. Found: C, 53.96; H, 5.13; N, 19.26%. Calcd for $C_{13}H_{14}O_4N_4$: C, 53.79; H, 4.86; N, 19.26%. The second component was **1** unchanged (3.4 g). The existence of **6** was observed in vpc, but **6** was not isolated. The structure of **6** was confirmed by the identity of retention time (Apiezon L, diglycerol and Carbowax 20 M) with that of authentic 2-ethylcyclopentanone.8) The yield of **6** was estimated to be less than 0.5%. The photolyses of **1** in diethyl ether, 2-propanol, benzene, and *n*-hexane, respectively, with a Pyrex filter afforded almost the same results as above.

Quenching of photoreaction of **1**. Three *n*-hexane solution of **1**; (A: **1**, 0.16 M), (B: **1**, 0.16 M and piperylene, 0.16 M) and (C: **1**, 0.16 M and piperylene 1.6 M) were degassed by the freeze-thaw method and irradiated in quartz tubes under nitrogen on a round table (5 cm from 500 W mercury lamp) immersed in an aqueous K_2CrO_4 filter solution (5×10^{-4} M). Periodical sampled aliquots of these solutions were subjected to the vpc analysis. While **1** converted to **5** in solution A (16% of **5** formed after 5 hr), in solution B there was observed marked quenching effect as shown in Table 1. In solution C, the photolysis of **1** was found to be completely quenched.

Irradiation of **3** *in* n-*hexane.* A solution of **3** (0.200 g) in *n*-hexane (10 m*l*) was irradiated for 3 hr in a Pyrex tube. After careful removal of the solvent, reaction mixture was subjected to a preparative vpc. Besides unreacted **3** (0.094 g), compound **9** was separated from several minor products. The compound **9** was characterized to be 4-methylenecyclohexanone (0.042 g, 39% yield). IR (liquid film): 1715 cm^{-1} (C=O), 1650, 895 cm^{-1} (olefinic). NMR (60 MHz, CCl_4): 5.15 τ (2H, s, vinyl), 7.55 τ (8H, m, methylene). UV (ethanol): λ_{max} 210 nm (ε=2800) and λ_{max} 283 nm (ε=30). Found: C, 76.44; H, 9.18%. Calcd for $C_7H_{10}O$: C, 76.32; H, 9.15%. The comparisons of **9** with an authentic sample which was prepared by the oxidation of 4-methylenecyclohexanol showed good identity in retention times of vpc (Apiezon L and Carbowax 6000) and in the mixed mp test of the 2,4-dinitrophenylhydrazones (mp 154—155°C).

Irradiation of ***4*** *in* n-*hexane.* A solution of **4** (0.572 g) in *n*-hexane (15 m*l*) was irradiated in a quartz tube for 20 hr. After the reaction mixture was treated as usual, 0.18 g of **4** and 0.086 g of **10** were isolated by vpc (Carbowax 6000). Compound **10** was characterized as 4-methylenecycloheptanone (22% yield). IR (liquid film): 1710 cm^{-1} (C=O), 1640, 890 cm^{-1} (olefinic). UV (ethanol): λ_{max} 286 nm (ε=20). NMR (60 MHz, CCl_4): 5.18 τ (2H, s, vinyl), 7.55 τ (8H, m, methylene) and 8.20 τ (2H, m, methylene). Found: C, 77.01; H, 10.09%. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74%. The 2,4-dinitrophenylhydrazone, mp 148—149°C.

Compound **10** (0.020 g) was hydrogenated in methanol on Pd-black (0.005 g). The hydrogenated product was identified as 4-methylcycloheptanone by the comparisons of the IR spectra and retention times of vpc (Apiezon L and Carbowax 6000) with an authentic sample.9)