Molecular Photochemistry. XXVII. Photochemical Ring Expansion of Cyclobutanone, Substituted Cyclobutanones, and Related Cyclic Ketones[1a–c]

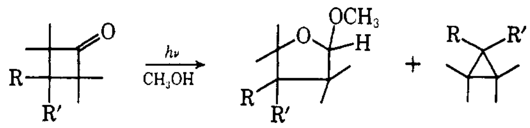
Douglas R. Morton,[1d] Edward Lee-Ruff,[1e] Richard M. Southam, and Nicholas J. Turro[1f]

Contribution from the Chemistry Department, Columbia University, New York, New York 10027. *Received October 27, 1969*

Abstract: The photochemical reactions of several substituted cyclobutanones in methanol are reported with particular emphasis being given to the nature and scope of the photochemical ring expansion reaction. Cyclobutanone (**1**), for example, yields the ring-expanded product, 2-methoxytetrahydrofuran (**2**). The results are interpreted in terms of initial α-cleavage to give the most stable 1,4-acyl alkyl biradical which undergoes subsequent or concerted rearrangement and rebonding to the corresponding oxacarbene intermediate. Evidence is presented which supports the proposition that oxacarbenes are intermediates in these photolyses, and comparison is made with related systems which undergo ring expansion (*e.g.*, benzocyclobutene-1,2-dione, cyclocamphanone, and spiroheptanone **31**).

In ground-state chemistry, it is observed that molecules possessing excessive ring strain quite often undergo unusual and sometimes unexpected chemical transformations to species of lower energy content. Similarly, it might be anticipated that ring strain would also have a pronounced effect upon the reactivity of molecules in an electronically excited state. In an attempt to assess the importance of this effect, we have studied the photochemical transformations of variously substituted cyclobutanones.

Early work on the vapor phase photolysis of cyclobutanone by Blacet and Miller[2] and Klemm and coworkers,[3] and the recent work by Lee and Denschlag[4,5a] have demonstrated the existence of two primary photochemical processes: (a) a photocycloelimination[5b] yielding ethylene and ketene and (b) a photodecarbonylation yielding carbon monoxide, cyclopropane, and propene. In the liquid phase photolysis of cyclobutanones, a third primary photoprocess, photo ring expansion,[1b,6–8] has been detected in addition to photodecarbonylation and photocycloelimination. Thus, Hostettler[6] observed that irradiation of methanolic solutions of 2,2,4,4-tetramethylcyclobutanone derivatives afforded 30–73% yields of the 2-methoxy-3,3,5,5-tetramethyltetrahydrofurans as well as cyclopropane products derived from photodecarbonylation. Pacifici and Diebert[8] have recently reported that photo ring expansion and photodecarbonylation also occur for 4,4,6,6-tetramethyl-1-thiaspiro[2.3]hexan-5-one, when irradiations are carried out in methanol at wavelengths greater than 2800 Å. Finally, Quinkert and coworkers[7] have demonstrated that photo ring expansion also occurs for the epimeric C-13 D-nor-16-keto steroids.



While attempting to elucidate the nature of the excited state(s) involved in the liquid phase photolyses of cyclobutanones we have found that the photo ring expansion reaction is general for cyclobutanones with few exceptions (*vide infra*). In addition the ring expansion reaction shows promise as a convenient synthetic route to 2-alkoxytetrahydrofurans.

Results and Discussion

The products derived from the photolyses of variously substituted cyclobutanones in methanol are illustrated in Scheme I, while the respective yields of these products are set forth in Table I. Thus, in a typical experiment, irradiation of cyclobutanone (**1**) in methanol afforded a 48% yield of methyl acetate and an 8% yield of 2-methoxytetrahydrofuran (**2**), which was characterized by its spectral properties (nmr, ir, and mass spectrum) and also by its independent synthesis from 2,3-dihydrofuran and methanol in the presence of p-toluenesulfonic acid. The nmr spectrum of **2** revealed a broad, one proton singlet at τ 5.02 corresponding to the acetal proton[9] and a three-proton singlet at τ 6.70 for the methoxyl protons. The methylene protons α to the ring oxygen were observed as a multiplet at τ 6.12 while the remaining four methylene protons were grouped in a multiplet centered at 8.10. The infrared spectrum of **2** revealed strong bands between 1000 and 1200 cm^{-1} and the mass spectrum

---

[1] (a) Part XXVI: F. S. Wettack, G. D. Renkes, M. G. Rockley, N. J. Turro, and J. C. Dalton, *J. Amer. Chem. Soc.*, **92**, 1793 (1970); (b) for preliminary reports, see N. J. Turro and R. M. Southam, *Tetrahedron Lett.*, 545 (1967), and N. J. Turro, E. Lee-Ruff, D. R. Morton, and J. M. Conia, *ibid.*, 2991 (1969); (c) the authors at Columbia gratefully acknowledge the generous support of this work by the Air Force Office of Scientific Research (Grant AFOSR-68-1381); (d) National Institutes of Health Predoctoral Fellow, 1968–present; (e) National Research Council of Canada Fellow, 1967–1969; (f) Alfred P. Sloan Fellow, 1966–1970.

[2] F. E. Blacet and A. Miller, *J. Amer. Chem. Soc.*, **79**, 4327 (1957).

[3] R. F. Klemm, D. N. Morrison, P. Gilderson, and A. T. Blades, *Can. J. Chem.*, **43**, 1934 (1965).

[4] E. K. C. Lee, G. A. Hanniger, and H. O. Denschlag, *Ber. Bunsenges. Phys. Chem.*, **72**, 302 (1968).

[5] (a) H. O. Denschlag and E. K. C. Lee, *J. Amer. Chem. Soc.*, **90**, 3628 (1968); (b) J. N. Pitts, Jr., F. Wilkinson, and G. S. Hammond, *Advan. Photochem.*, **1**, 1 (1963).

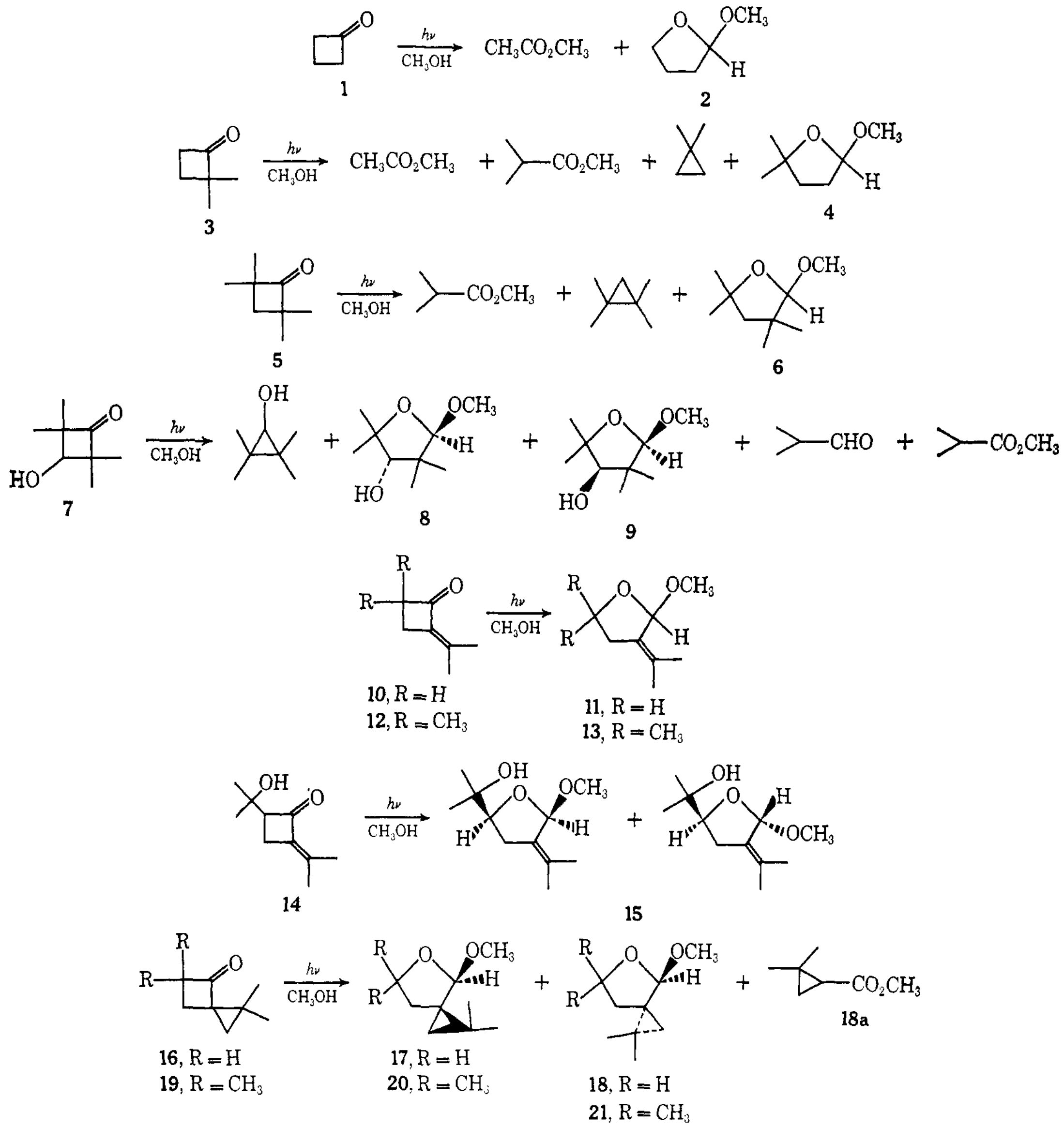
[6] H. U. Hostettler, *Helv. Chim. Acta*, **49**, 2417 (1966).

[7] G. Quinkert, G. Cimbollek, and G. Buhr, *Tetrahedron Lett.*, 4573 (1966).

[8] J. G. Pacifici and C. Diebert, *J. Amer. Chem. Soc.*, **91**, 4595 (1969).

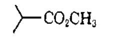
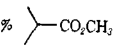
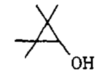
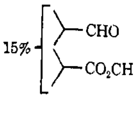
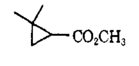
[9] Analogous acetal protons (ref 6) have been observed in the range τ 6.0–5.2 downfield from TMS.

Scheme I. Photolyses of Substituted Cyclobutanones in CH_3OH

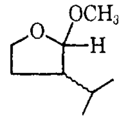


displayed a very weak parent ion at *m/e* 102. The cyclic acetals **4**, **6**, **8**, and **9** also displayed similar absorptions in their respective nmr spectra between τ 5.6 and 5.1, and strong bands between 1000 and 1200 cm^{-1} in their infrared spectra. In addition, all cyclic acetals revealed very weak parent ions in their mass spectra.

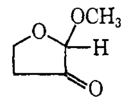
Table I. Per Cent Yields of Products Derived from Photolyses of Cyclobutanones in CH_3OH

Compd	Photo ring expansion (%)	Photo-decarbonylation	Photo-cycloelimination
1	2 (8)		48% $CH_3CO_2CH_3$
3	4 (41)	8% 	32% $CH_3CO_2CH_3$
			3% 
5	6 (68)	11% 	13% 
7	8 (36) 9 (31)	17% 	15% 
10	11 (100)		
12	13 (100)		
14	15 (100)		
16	17 (44) 18 (44)		12% 
19	20 (50) 21 (50)		

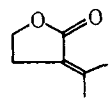
The structures of the cyclic acetals derived from 2-isopropylidene ketones **10**, **12**, and **14** and those derived from spirohexanones **16** and **19** were also determined from spectral properties (see Experimental Section). Additional support for compound **11** was obtained by its hydrogenation over Pd to **22**, its ozonolysis to **23**, and by its oxidation[10] to **24**. As with the saturated acetals described above, the 3-isopropylidene acetals all revealed one-proton singlets in their nmr spectra between τ 4.8 and 5.0 downfield from TMS.



22



23



24

---

[10] W. C. Agosta and D. K. Herron, *J. Amer. Chem. Soc.*, **90**, 7025 (1968).

Further, their infrared spectra revealed strong ether absorptions between 1000 and 1200 cm^{-1} and their mass spectra revealed very weak parent ions, and strong peaks at *m/e* values corresponding to $M^+ - CH_3OH$.[11]

The stereochemistries of 5-oxaspiro[4.2]heptanes **17**, **18**, **20**, and **21** were assigned on the basis of differences in chemical shifts in their respective nmr spectra. Thus, for *cis* isomer **20** (see Figure 1a) steric interaction between the methoxyl group and a cyclopropyl methyl would be expected to force the tetrahydrofuran ring to pucker in such a manner as to cause the cyclopropane ring to prefer a conformation in which it is essentially below the five-membered ring. In such a conformation, H^2 is suspended above the cyclopropane ring while H^1 is outside this ring. Consequently, H^2 would be expected to absorb at a higher chemical shift than H^1. In addition, $\Delta\nu_{AB}$ for H^1 and H^2 in **20** should be greater than that in **21** (see Figure 1b) where H^1 and H^2 should now be in similar environments with respect to the cyclopropane ring. This difference has been observed. For **20**, $\Delta\nu_{AB}$ = 61.4 Hz and for **21**, $\Delta\nu_{AB}$ = 12.0 Hz. Similar arguments with respect to stereochemical assignment may be made based on $\Delta\nu_{AB}$ for the cyclopropyl methylene protons and the chemical shifts of the acetal protons, both arguments being consistent with the stereochemistry assigned.

Irradiation of ketones **1** and **10** in methanol-0-*d*, again, afforded the expected tetrahydrofuran ethers which were each shown (nmr) to possess one deuterium atom exclusively at the 2 position of the tetrahydrofuran ring.

The quantum yields for cyclic acetal formation in methanol at 3130 Å have been determined. Cyclobutanone, upon photolysis, yields cyclic acetal **2** with a quantum yield of 0.02. This value and those for other cyclobutanones have been listed in Table II.

Table II. Quantum Yields for Cyclic Acetal Formation

Ketone	Acetal	ϕ
1	**2**	0.02[a]
5	**6**	0.14[b]
7	**8** + **9**	0.16[b]
10	**11**	0.11[c]

[a] Irradiation at 3130 Å. Potassium ferrioxalate actinometry: C. A. Parker, *Proc. Roy. Soc.* (London), **A220**, 104 (1953); C. G. Hatchard and C. A. Parker, *ibid.*, **A235**, 518 (1956). [b] Irradiation at 3140 Å (Bausch and Lomb monochromator). Potassium ferrioxalate actinometry. [c] Irradiation at 3130 Å. Benzophenone–benzhydrol actinometry: W. M. Moore and M. Ketchum, *J. Amer Chem. Soc.*, **84**, 1386 (1962).

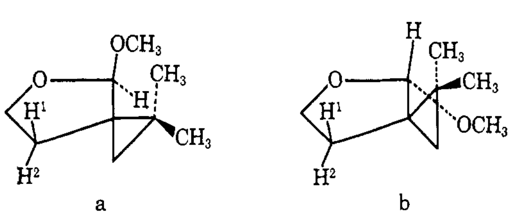
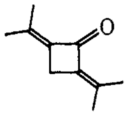
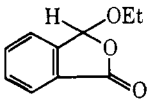


Figure 1. Stereochemistries of spirocyclic acetals derived from the photolyses of sprio[2.3]hexan-4-ones in methanol.

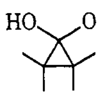
Although the photo ring expansion reaction appears to be general for cyclobutanones,[12] we have noted one exception.[13a] Ketone **25** has been shown to be inert to photolysis in alcoholic solvents, even when irradiation is conducted through quartz apparatus. On the other hand, there are related systems which do undergo ring expansion reactions. Irradiation of benzocyclobutene-1,2-dione in ethanol at 80°[14] affords the cyclic acetal **26**; however, irradiation of tetramethyl-1,3-cyclobutanedione in methanol at wavelengths greater than 3000 Å[15] affords only hemiketal **27** and methyl isobutyrate.[13b] Irradiations of cyclocamphanone[12] and camphor[10] in ethanol afford cyclic acetals **28** and **29**, respectively, the latter being formed in approximately 15% yield together with enol ether **30**.



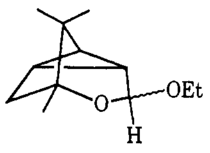
25



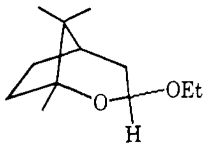
26



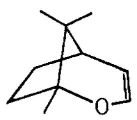
27



28

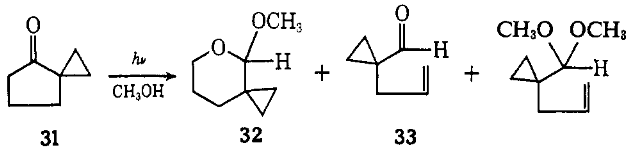


29



30

Recently we have found that irradiation of spiroketone **31** in methanol affords cyclic acetal **32**, aldehyde **33**[16] and its methanol acetal, cyclic acetal **32** being the major product. A similar irradiation of cyclopentanone, 2,2,5,5-tetramethylcyclopentanone and ketones **34** and **35** revealed no evidence for ring expansion products. Spiroketone **34** afforded ketal **36** while ketone **35** appeared to be unchanged after 24 hr of irradiation.[13a] The photolyses of the saturated cyclopentanones resulted in aldehyde and methanol acetal formation only. Irradiation of ketone **37** in methanol yielded aldehyde **38** and it methanol acetal.[16]



---

(11) In agreement with our results, we were informed by Professor J. K. Crandall (Indiana University) that 2-isopropylidene-3,3,4,4-tetramethylcyclobutanone affords a quantitative yield of 2-methoxy-3-isopropylidene-4,4,5,5-tetramethyltetrahydrofuran when irradiated in methanol.

(12) P. Yates, *Pure Appl. Chem.*, **16**, 93 (1968).

(13) (a) E. Lee-Ruff, unpublished results. (b) The ring-expanded product expected, 2-methoxy-3,3,5,5-tetramethyl-4-oxotetrahydrofuran, was independently synthesized by hydrolysis of 2-methoxy-3,3,5,5-tetramethyl-4-phenyliminotetrahydrofuran[6] and appeared to be stable under the photolysis conditions.[13a]

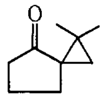
(14) H. A. Staab and J. Ipaktsehi, *Tetrahedron Lett.*, 583 (1966).

(15) N. J. Turro, P. A. Leermakers, J. P. Wilson, D. C. Neckers, G. W. Byers, and G. F. Vesley, *J. Amer. Chem. Soc.*, **87**, 2613 (1965).

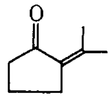
(16) Identical aldehydes have recently been reported as arising from ketones **31** and **37** when photolyses are conducted in *n*-hexane.[16a,17]

(16a) NOTE ADDED IN PROOF. The photochemistry of **31** has recently been studied: J. K. Crandall and R. J. Seidewald, *J. Org. Chem.*, **35**, 697 (1970).

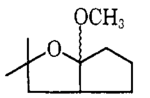
(17) A. Sonoda, I. Moritani, J. Miki, and T. Tsuji, *Tetrahedron Lett.*, 3187 (1969).



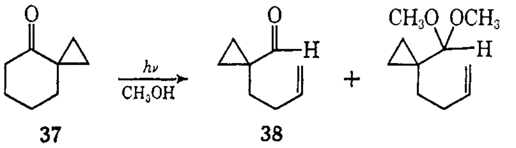
34



35



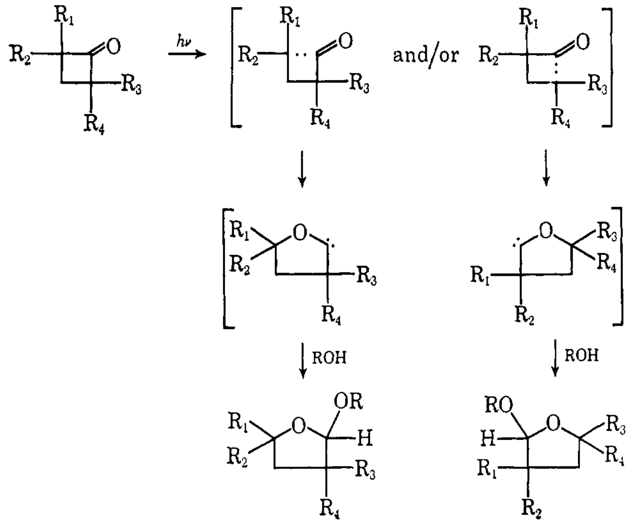
36

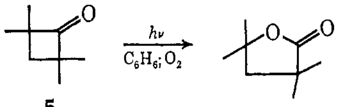


37 38

The mechanism of the photo ring expansion reaction has been postulated to involve an oxacarbene intermediate[1b,6-8,10,12] (see Scheme II). In the presence of alcoholic solvents, this intermediate is efficiently trapped yielding the expected cyclic acetal. To date, an oxacarbene originating from a cyclobutanone has not been trapped by other typical carbene reagents such as olefins;[18,19] however, we have obtained other evidence which supports its existence. Thus, when photolyses are conducted in methanol-0-*d*, deuterium incorporation occurs exclusively at the 2 position of the product acetal. Further, irradiation of 2,2,4,4-tetramethylcyclobutanone in aerated benzene affords lactone **39** and a similar irradiation of ketone **10** in oxygen saturated pentane affords lactone **24**. Similar results have been reported for cyclocamphanone.[12] In addition, Bartlett and Traylor[20] have reported that irradiation of diphenyldiazomethane in the presence of oxygen affords a symmetric tetroxalane which subsequently yields benzophenone upon thermal decomposition.

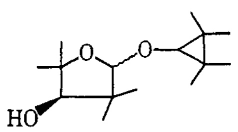
Scheme II



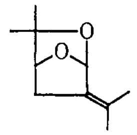


5 39

Irradiation of cyclobutanone **7** in benzene yields the isomeric cyclic acetals, **40**, the formation of which requires prior photodecarbonylation to a cyclopropanol which then reacts with the oxacarbene. Irradiation of ketone **14** in benzene yields bicyclic acetal **41** in 60% yield, presumably by intramolecular trapping of the postulated oxacarbene intermediate. Treatment of **41** with methanol *in the dark* produces cyclic acetal **15**. Finally, irradiation of 2-isopropylidenecyclobutanone (**10**) in benzene affords an unstable intermediate which, when treated with methanol *in the dark*, produces cyclic acetal **11** as the major product. Attempts to isolate this intermediate by gas chromatography resulted in the isolation of diene **42**. Previously, we believed the intermediate to be cyclopropene **44**, formed by intramolecular addition of the oxacarbene to the carbon-carbon double bond. Subsequent acid catalyzed addition of methanol with rearrangement would then afford acetal **11**. We now have evidence, however, that this intermediate is an equilibrium mixture of hemiacetal **43** and its hydroxyaldehyde **43a** (see Scheme III), formed by insertion of the oxacarbene into an O-H bond of water present in the benzene. Acid-catalyzed acetal formation with methanol (or methanol-0-*d*) then results in the formation of **11**. In support of this mechanism are the following observations: (a) irradiation of ketone **10** in benzene saturated with water affords only **43** and **43a** based on nmr analysis (see Experimental Section). Treatment of this equilibrium mixture with excess methanol causes the disappearance of all peaks attributable to aldehyde **43a** and the appearance of an nmr spectrum identical with that obtained for pure acetal **11**. (b) Treatment of **43** $\rightleftharpoons$ **43a** with excess methanol-0-*d* results in *no* deuterium incorporation, a result which would not be expected if the intermediate were cyclopropene **44**. (c) Irradiation of ketone **10** in rigorously dried benzene, followed by treatment with excess methanol, affords <5% acetal **11**. Although we cannot completely rule out formation of **44** from the oxacarbene followed by reaction with water to produce **43** $\rightleftharpoons$ **43a**, we favor, at present, direct formation of **43** $\rightleftharpoons$ **43a** from the oxacarbene and water.

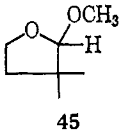


40

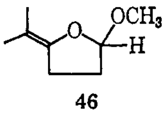


41

The photo ring expansion reaction appears to be general for cyclobutanones and, in addition, appears to demonstrate good selectivity with respect to the direction of initial α cleavage. Examination of the nature of cyclic acetals derived from ketones **3**, **10**, **12**, **14**, **16**, and **19** demonstrates that only one of two possible oxacarbenes is generated—that which is derived from the most stable 1,4-acyl alkyl biradical (see Scheme II). Ketone **3** ($R_1 = R_2 = H$; $R_3 = R_4 = CH_3$), for example, yields only cyclic acetal **4** and α,β-unsaturated ketone **10** yields only cyclic acetal **11**. No evidence was found for the existence of acetals **45** and **46** in these photolyses. The *trans*-fused cyclobutanone, **47**, however, appears to be the only reported exception[7]



45



46

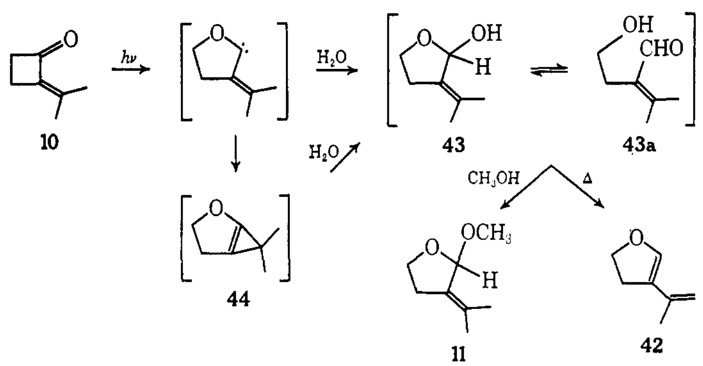
---

(18) A similar situation has been reported for nucleophilic carbenes: N. D. Hartzler, Abstracts, 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, paper 97 ORGN.

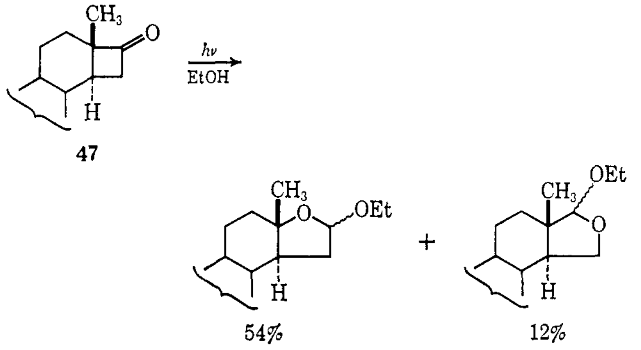
(19) T. R. Oakes, H. G. David, and J. J. Nagel, *J. Amer. Chem. Soc.*, **91**, 4761 (1969).

(20) P. D. Bartlett and T. G. Traylor, *ibid.*, **84**, 3408 (1962).

Scheme III



to this selectivity, yielding 12% of the acetal derived from the less stable 1,4-acyl alkyl biradical. Of additional interest is the effect of substitution on the relative yields of photo ring expansion products. On



going from cyclobutanone (**1**) to its 2,2-dimethyl derivative, **3**, there is a fivefold increase observed in cyclic acetal yield, while further stabilization of the 1,4-acyl alkyl biradical, as in ketones **10**, **12**, **14**, **16**, and **19**, results in quantitative yields of the respective acetals.[21]

Yates[12] has speculated that the photo ring expansion reaction for cyclic ketones appears to occur only when the efficiencies of the other reactions are greatly diminished. For cyclobutanones, there are three primary photoprocesses which compete for the intermediary acyl alkyl biradical. Saturated cyclobutanones partition among all three processes, while 2-unsaturated cyclobutanones and spiro[2.3]hexan-4-ones appear to undergo only photo ring expansion. Examination of the quantum yields for cyclic acetal formation in Table II demonstrates that the variation of substitution on the cyclobutanone alters the efficiency with which the ketone undergoes photo ring expansion. Putting four methyl substituents α to the carbonyl increases the efficiency by a factor of 7, yet a further increase in stability of the intermediary 1,4-acyl alkyl biradical (*e.g.*, as in **10**) affects the efficiency of photo ring expansion only slightly. It is conceivable that increasing biradical stability not only increases the efficiency of cyclic acetal formation, but lowers the efficiencies of competing processes.

Experimental Section

All commercial chemicals employed were of reagent or spectrophotometric quality, and unless specified, were used without further purification. Irradiations were carried out in internally water cooled reactors (quartz) at 15–25° with a Hanovia 450-W medium-pressure mercury lamp, and photolysis vessels were constructed of quartz unless otherwise specified. Infrared spectra were taken on a Perkin-Elmer Models 137 and 621 grating spectrophotometers. Nuclear magnetic spectra were taken on a Varian A-60 or A-60A analytical high-resolution nmr spectrometer. Chemical shifts are reported in τ units from internal or external tetramethylsilane (τ 10.00), or, in the case of spirocyclopropyl compounds, in τ units from internal chloroform (τ 2.75). Mass spectra were taken on a Hitachi Perkin-Elmer RMU-6D mass spectrometer. Vpc analyses and separations were performed on Aerograph Model 1200 and Model A-90P gas chromatographs. The following liquid phases were employed: Carbowax 20M (CWX 20M), SE-30, FFAP, and 1,2,3-tris(cyanoethoxy)propane ($\beta\beta\beta$). Chromosorb P (Chrom P), Chromosorb W (Chrom W), and firebrick were employed as supports. Elemental analyses were performed by Schwartzkopf Microanalytical Laboratory, Woodside, N. Y., and Galbraith Laboratories, Knoxville, Tenn. Product yields were determined by either vpc or nmr. Interpretation of vpc results was accomplished by standard calibration techniques, product yields being corrected for variance in detector response.

Ketene was prepared by the pyrolysis of acetone by the method of Williams and Hurd.[22]

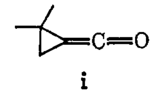
Diazomethane was prepared as a solution in ether or CH_2Cl_2 from N-methyl-N-nitrosourea[23] and 50% aqueous KOH by the method of Arndt.[24]

Cyclobutanone (1) was prepared from diazomethane and ketene by the method of Kaarsemaker and Coops.[25] Purification was effected on a spinning band column or by vpc (10 ft × 0.25 in. 20% CWX 20M on Chrom P; column temperature 100°).

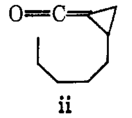
Irradiation of Cyclobutanone in CH_3OH. A 5-ml solution of 0.238 g (3.4 mmol) of cyclobutanone in CH_3OH was irradiated in a quartz tube and monitored by vpc (10 ft × 0.25 in. 20% CWX 20M; column temperature 103°). Photolysis was carried to 88.5% conversion (200 min) and extrapolation of product percentages to 100% reaction gave methyl acetate, 48%, and 2-methoxytetrahydrofuran (2), 8%. The methyl acetate formed had the same nmr, ir, and vpc retention time as commercially available material. The structure of **2** was deduced from spectral data: nmr (TMS external standard, CCl_4) τ 8.10 (m, 4), 6.70 (s, 3, $-OCH_3$), 6.12 (m, 2), 5.02 (broad s, 1); ir $\nu_{max}^{CCl_4}$ cm^{-1} 2980, 2945, 2890, 2825, 1435, 1355, 1200, 1090, 1105, 1040 (vs), 955, 920; mass spectrum (70 eV) m/e (relative intensity) 102 (M^+, 4.7), 101 (9.3), 72 (15.2), 71 (100.0), 61 (39.8), 43 (78.5), 42 (85.5), 41 (96.0).

---

(21) It is interesting to note that a 12% yield of ester **18a** is obtained from the photolysis of **16** in methanol, presumably *via* ketene i formed from cycloelimination. In a related example, L. A. Paquette and R. F. Eizember [*J. Amer. Chem. Soc.*, **91**, 7108 (1969)] appear to have trapped ketene ii as its *t*-butyl ester. These appear to be the first successful trappings of dimethyleneketenes, although previous attempts have been made: (a) H. Staudinger, H. Schneider, P. Schutz, and P. M. Strong, *Helv. Chim. Acta*, **6**, 294, (1923); (b) H. M. Walborsky, *J. Amer. Chem. Soc.*, **74**, 4962 (1952); (c) F. T. Williams, Abstracts of Research (Petroleum Research Fund), 44 (1964); (d) F. E. Collins, *Dissertation Abstr.*, **26**, 4231 (1966).



i



ii

(22) J. W. Williams and C. D. Hurd, *J. Org. Chem.*, **5**, 122 (1940).

(23) F. Arndt, "Organic Syntheses," Coll. Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1943, p 461.

(24) See ref 23, p 165.

(25) S. Kaarsemaker and J. Coops, *Rec. Trav. Chim.*, **70**, 1033 (1951).

2-Methoxytetrahydrofuran (2). To 1.00 g (0.014 mol) of 2,3-dihydrofuran[26] was added 10 ml of CH_3OH. To this mixture (stirred with cooling) was added one crystal of *p*-toluenesulfonic acid which initiated a rapid exothermic reaction. The reaction was allowed to proceed for 6 hr, following which 0.100 g (0.007 mol) of anhydrous K_2CO_3 was added. The resulting mixture was stirred at room temperature for 15 hr. Decantation of the liquid layer and distillation afforded 1.70 g of a colorless liquid. Preparative vpc (5 ft × 0.25 in. 22% CWX 20M on Chrom P; column temperature 125°) gave pure **2**, 0.78 g (53.5%). The nmr, ir, and mass spectrum were identical with those given for the photolytically derived **2**.

Irradiation of Cyclobutanone in CH_3OD. To 0.648 g (0.009 mol) of cyclobutanone in a quartz tube was added 2.5 ml of CH_3OD (93.5% CH_3OD by nmr). The sample was strapped to a quartz immersion well and irradiated. Vpc (5 ft × 0.25 in. 22% CWX 20M on Chrom P; column temperature 125°) showed the reaction to be essentially complete after 28 hr. Isolation of products by preparative vpc (10 ft × 0.25 in. 25% on Chrom P; column temperature 135°) afforded methyl 2-deuterioacetate and 2-deuterio-2-methoxytetrahydrofuran. Using the $-OCH_3$ peak at τ 6.70 as an internal standard, nmr integration of the acetal proton region (5.02) revealed that deuterium incorporation had occurred to an extent of 93.5% (6.5% CH_3OH impurity in the CH_3OD was taken into account). Mass spectral analysis of the residual cyclobutanone after photolysis showed that less than 1.4% deuterium incorporation had occurred in the starting material.

Irradiation of 2,2-Dimethylcyclobutanone (3). To 0.304 g (0.0037 mol) of **3**[27] was added 5.0 ml of CH_3OH. The sample was photolyzed in all quartz apparatus for 148 min (*ca.* 100% conversion). Vpc analysis (20 ft × 0.25 in. 20% SE-30 on Chrom P; column temperature 118°) of the photolysate revealed the following major products: 2-methoxy-5,5-dimethyltetrahydrofuran (**4**), 41%, and methyl acetate, 32%. In addition, methyl isobutyrate, 3%, and 1,1-dimethylcyclopropane,[28] *ca.* 8%, were detected. Methyl acetate and methyl isobutyrate were identified by comparison of vpc retention times with authentic materials, while **4** was characterized by its spectral properties: nmr (TMS external standard, CCl_4) τ 8.77 (s, 3), 8.65 (s, 3), 8.17 (m, 2), 8.0 (m, 2), 6.73 (s, 3, $-OCH_3$), 5.10 (t, 1); ir $\nu_{max}^{CCl_4}$ cm^{-1} 1380–1365, 1098–1040; mass spectrum (75 eV) *m/e* (relative intensity) 130 (M^+, vw), 115 (17.4), 99 (13.8), 98 (48.0), 83 (56.2), 81 (15.8), 72 (13.8), 70 (26.5), 69 (48.5), 59 (10.7), 57 (22.0), 56 (13.3), 55 (65.4), 53 (13.3), 43 (59.2), 42 (28.6), 41 (100.0), 39 (52.0), 31 (49.0).

2,2,4,4-Tetramethylcyclobutanone (5) was prepared by the method of Herzog and Buchman[29] from the disemicarbazone of 2,2,4,4-tetramethylcyclobutane-1,3-dione.[30]

Irradiation of 2,2,4,4-Tetramethylcyclobutanone (5) in CH_3OH. To 0.0406 g (0.0032 mol) of **5** in a quartz tube was added 5 ml of CH_3OH. The sample was strapped to a quartz immersion well and irradiated. Loss of starting material was monitored by vpc (20 ft × 0.25 in 20% SE-30 on Chrom P; column temperature 150°) which showed the reaction to be complete after 119 min. Analysis of the photolysate by vpc revealed the following major products: 2-methoxy-3,3,5,5-tetramethyltetrahydrofuran (**6**, 68%), methyl isobutyrate (13%), and 1,1,2,2-tetramethylcyclopropane[28] (11%). Methyl isobutyrate was identified by comparison of vpc retention time with authentic material. For **6**, nmr (TMS external standard, CCl_4) τ 8.74 (s, 3), 8.68 (s, 3), 8.48 (s, 6), 8.22, 7.98 (AB, J = 12 Hz), 6.49 (s, 3), 5.50 (s, 1); ir $\nu_{max}^{CCl_4}$ cm^{-1} 1382, 1377, 1364, 1359, 1094, 1032; mass spectrum (75 eV) *m/e* (relative intensity) 158 (M^+, vw), 143 (27.1), 127 (25.1), 111 (14.5), 98 (34.8), 97 (25.1), 85 (35.8), 83 (92.6), 73 (35.3), 70 (60.0), 69 (35.3), 57 (13.0), 56 (16.4), 55 (100.0), 44 (23.2), 43 (65.5), 42 (10.6), 41 (55.0), 39 (27.1), 31 (58.0).

Irradiation of 3-Hydroxy-2,2,4,4-tetramethylcyclobutanone (7) in CH_3OH. To 0.940 g (0.0066 mol) of **7**[31] in a quartz tube was added 10 ml of CH_3OH. The sample was irradiated in all-quartz apparatus for 130 min (93.1% conversion). Periodic analysis by vpc (4 ft × 0.25 in. 20% *βββ* on Chrom P; column temperature 132°) of the photolysate (extrapolated to 100% reaction) revealed the following major products: 2,2,3,3-tetramethylcyclopropanol (17%), *cis*-2-methoxy-4-hydroxy-3,3,5,5-tetramethyltetrahydrofuran (**9**, 31%), and *trans*-2-methoxy-4-hydroxy-3,3,5,5-tetramethyltetrahydrofuran (**8**, 36%). For **9**, nmr (TMS external standard, CCl_4) τ 8.76, 8.68, 8.45 (each a three-proton singlet), 7.64 (s, 1), 6.50 (overlapping one- and three-proton singlets), 5.48 (s, 1); ir $\nu_{max}^{CCl_4}$ cm^{-1} 3572 (intramolecular OH), 1389, 1380, 1370 (*gem*-dimethyl), 1090, 1035; mass spectrum (15 eV) *m/e* (relative intensity) 174 (M^+, vw), 173 (w), 159 (5.1), 143 (30.6), 142 (w), 117 (8.2), 116 (95.0), 114 (45.0), 101 (16.3), 99 (36.8), 91 (10.0), 88 (24.5), 85 (14.3), 84 (100.0), 72 (12.3), 71 (18.4), 59 (22.5), 56 (47.0). For **8**, nmr (TMS external standard, CCl_4) τ 8.89, 8.83, 8.71, 8.59 (each a three-proton singlet), 7.68 (s, 1), 6.60 (s, 3), 6.09 (s, 1), 5.59 (s, 1); ir $\nu_{max}^{CCl_4}$ cm^{-1} 3638, 3465 (polymeric OH), 1380, 1368 (*gem*-dimethyl), 1090, 1030; mass spectrum (14 eV) *m/e* (relative intensity) 174 (M^+, vw), 173 (w), 159 (6.9), 143 (29.2), 142 (w), 117 (7.9), 116 (100.0), 114 (30.2), 101 (7.9), 99 (23.3), 91 (8.4), 88 (20.8), 85 (8.9), 84 (63.5), 72 (12.4), 71 (10.0), 70 (7.9), 59 (15.8), 56 (36.6). The minor product, 2,2,3,3 tetramethylcyclopropanol, was tentatively characterized by the similarity of its vpc behavior and nmr with authentic material.

In a separate photolysis, 0.940 g (0.0066 mol) of starting ketol in 10 ml of CH_3OH was photolyzed for 159 min (96% conversion). Periodic analysis by vpc (20 ft × 0.25 in. 20% SE-30 on Chrom P; column temperature 100°) followed by extrapolation to 100% reaction, revealed the following volatile products in addition to those described above: isobutyraldehyde, 14%, and methyl isobutyrate, 16%. Both compounds were identified by comparison of their respective vpc retention times with authentic materials.

2-Isopropylidenecyclobutanone (10) and 4-(1-Hydroxyisopropyl)-2-isopropylidenecyclobutanone (14). Both compounds were prepared by a modified method of Conia and Sandre.[32] Thus, to a mixture of 2.1 g (0.03 mol) of cyclobutanone and 5.2 g (0.09 mol) of acetone was added, with stirring, 20 ml of 1 *N* NaOH. The reaction was maintained at room temperature for 24 hr, during which time a pale yellow organic layer was formed. Neutralization of the reaction mixture with HCl, extraction of the organic layer with ether and drying of the latter over $MgSO_4$ afforded a pale yellow oil after the ether was removed. Distillation of this liquid afforded **10** (bp 71–72° (21 mm)) whose spectral properties were identical with those previously reported.[32] A subsequent distillation of the remaining oil afforded a mixture of **14** and 2,4-diisopropylidenecyclobutanone (**25**) (bp 85–100° (2 mm)). Repeated chromatography over alumina (petroleum ether solvent) afforded pure **14**: nmr (TMS internal standard, CCl_4) τ 8.72 (two singlets, 6), 8.24 (s, 3), 7.94 (s, 3, allylically coupled to τ 7.4, $-CH_2-$), 7.4 (broad m, 2), 7.26 (s, 1, $-OH$ from D_2O exchange), 6.90 (t, 1, J = 7 Hz); ir $\nu_{max}^{CCl_4}$ cm^{-1} 3450, 1735, 1665, 1110; mass spectrum (75 eV) *m/e* (relative intensity) 168 (M^+, 47.8), 153 (17.4), 150 (36.6), 135 (11.13), 125 (16.1), 123 (18.7), 122 (12.2), 112 (13.0), 111 (11.3), 110 (100.0), 107 (50.9), 95 (23.0), 85 (12.2), 84 (10.9), 83 (17.4), 82 (56.6), 81 (26.0), 79 (10.9), 71 (30.8), 70 (54.3), 69 (44.7), 68 (18.3), 67 (72.1), 59 (20.8), 58 (31.8), 56 (15.2), 55 (10.4), 44 (56.9), 43 (33.5).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.43; H, 9.52. Found: C, 71.22; H, 9.44.

Irradiation of 2-Isopropylidenecyclobutanone (10) in CH_3OH. To 0.200 g (0.002 mol) of **10** in a Pyrex tube was added 20 ml of of CH_3OH. The sample was irradiated in quartz apparatus through a Pyrex filter for 6 hr. Analysis of the photolysis by vpc (6 ft × 0.25 in. 20% CWX 20M on Chrom P; column temperature 140°) revealed the reaction to be essentially complete. Removal of the CH_3OH by rotary evaporation yielded 0.24 g (*ca.* 90%) of 2-methoxy-3-isopropylidenetetrahydrofuran (**11**): nmr (TMS internal standard, CCl_4) τ 8.35 (s, 6), 7.67 (t, 2, J = 7 Hz, allylically coupled to τ 8.35 methyls), 6.80 (s, 3), 6.20 (t, 3, J = 7 Hz), 4.99 (s, 1); ir $\nu_{max}^{CCl_4}$ cm^{-1} 1706 (w), 1439 1370, 1351, 1326, 1189, 1155, 1075 (s), 1058 (s), 1029 (s), 973, 935; mass spectrum (75 eV) *m/e* (relative intensity) 142 (M^+, vw), 110 (100.0), 109 (10.0), 95 (26.2), 83 (10.0), 81 (27.7), 79 (21.5), 67 (67.6), 65 (26.2), 55 (14.6), 54 (12.3), 53 (28.5). 51 (10.0), 44 (36.2), 43 (10.0), 41 (43.1), 40 (37.0), 39 (41.5).

Anal. Calcd for $C_8H_{14}O_2$: C, 67.61; H, 9.86. Found: C, 67.75; H, 9.93.

In a separate photolysis, 0.100 g of **10** was dissolved in 0.4 ml of CH_3OH and placed in a sealed nmr tube. The sample was irradiated through Pyrex and periodically analyzed by nmr. The tetrahydrofuran, **11**, was the only detectable product after 6 hr of irradiation (>95% conversion).

---

(26) We thank Professor R. W. Hoffmann (University of Heidelberg, Germany) for a sample of 2,3-dihydrofuran.

(27) J. M. Conia and J. Salaun, *Bull. Soc. Chim. Fr.*, 1957 (1964).

(28) Tentatively assigned on the basis of observed high-field resonances (τ 9.7) in the nmr of the photolysate.

(29) H. L. Herzog and E. R. Buchman, *J. Org. Chem.*, **16**, 99 (1951).

(30) E. Wedekind and W. Weisswange, *Chem. Ber.*, **39**, 1631 (1906).

(31) R. H. Hasch, E. H. Elam, J. C. Martin, and R. G. Nations, *J. Org. Chem.*, **26**, 700 (1961).

(32) J. M. Conia and J.-P. Sandre, *Bull. Soc. Chim. Fr.*, 744 (1963).

Irradiation of 2-Isopropylidenecyclobutanone (10) in CH_3OD. To 0.110 g (1.0 mmol) of **10** in a Pyrex tube was added 5 ml of CH_3OD (Diaprep, 99% -OD) and 15 ml of C_6H_6. The sample was irradiated for 6 hr with the standard 450-W apparatus (Pyrex filter sleeve). The C_6H_6 and CH_3OD were removed by rotary evaporation, yielding 0.127 g (*ca.* 90%) of 2-deuterio-2-methoxy-3-isopropylidenetetrahydrofuran. An nmr analysis of the product revealed that deuterium incorporation was >95%.

Catalytic Hydrogenation of 11. To 50 mg of **11** was added 3 ml of ethyl acetate and 10 mg of 10% Pd/C. The reaction mixture was stirred under 1 atm of H_2 for 5 hr. Removal of catalyst and the solvent afforded 45 mg of an oil whose nmr and ir suggest structures **22**: nmr (TMS internal standard, CCl_4) τ 9.14 (m, 6), 7.86–8.89 (m, 4), 6.74 (s, OCH_3, 3), 6.25 (m, 2), 5.41 (m, 1). The infrared spectrum shows bands for *gem*-dimethyl at 1374 and 1359 cm^{-1} and strong ether bands at 1096, 1053, and 1018 cm^{-1}.

Jones Oxidation of 2-Methoxy-3-isopropylidenetetrahydrofuran (11). To 0.100 g (0.0007 mol) of **11** in 30 ml of acetone was added (with stirring) 1.56 ml of Jones reagent[10] (2.67 g of CrO_3, 2.3 ml of concentrated H_2SO_4, diluted to 50 ml with H_2O). The mixture was allowed to react for 10 min, following which 30 ml of distilled H_2O was added. The mixture was extracted with ether and the latter layer washed with H_2O and dried over $MgSO_4$. The ether was removed by rotary evaporation and the remaining oil subjected to preparative vpc (5 ft × 0.25 in. 20% FFAP on Chrom P; column temperature 164°) yielding 0.008 g (*ca.* 8%) of 2-isopropylidene-γ-butyrolactone (**24**), whose nmr and ir were identical with those reported below.

Ozonolysis of 11. Approximately 2.38 mmol of acetal **11** were photolytically generated from ketone **10** as described above. The methanol photolysate was cooled to −78° and treated with ozone (Welsbach ozone generator) until the blue color of excess ozone appeared. This excess was removed by a stream of O_2 and the reaction mixture was then treated with 10 ml of dimethyl sulfide–H_2O (1:1), diluted with 20 ml of H_2O, extracted with ether, washed with H_2O, and dried over anhydrous Na_2SO_4. Preparative vpc 12 ft × 0.25 in. 20% FFAP on Chrom W; column temperature (100°) afforded a single volatile product, **23**: nmr (TMS internal standard, CCl_4) τ 7.64 (t, J = 7 Hz, 2), 6.63 (s, 3), 5.81 (t, J = 7 Hz, 2), 5.61 (s, 1); ir $\nu_{\max}^{CCl_4}$ cm^{-1} 2825, 1783 (C═O), 1410, 1195, 1165, 1095, 1064, 1033, 951, 916; mass spectrum (75 eV), *m/e* (relative intensity) 116 (M^+, vw), 88 (63.0), 85 (9.0), 61 (100.0), 43 (8.5), 33 (17.0), 32 (8.0), 31 (29.0), 29 (65.0), 28 (71.0).

Irradiation of 4,4-Dimethyl-2-isopropylidenecyclobutanone (12) in CH_3OH. To 0.115 g (0.0008 mol) of **12**[33] in a quartz tube was added 3 ml of CH_3OH. After a stream of N_2 was bubbled through the sample for 5 min, it was photolyzed through Pyrex for 3 hr. Removal of the CH_3OH under vacuum yielded 2-methoxy-3-isopropylidene-5,5-dimethyltetrahydrofuran (**13**) as the only product (isolated yields *ca.* 90%): nmr (TMS internal standard, CCl_4) τ 8.78 (s, 3), 8.69 (s, 3), 8.32 (broad s, 6), 7.69 (broad s, 2), 6.74 (s, 3), 4.83 (s, 1); ir $\nu_{\max}^{CCl_4}$ cm^{-1} 1709, 1374, 1361, 1075, 1028; mass spectrum (75 eV) *m/e* (relative intensity) 170 (M^+, vw), 139 (9.7), 138 (84.2), 123 (100.0), 120 (14.5), 109 (28.4), 105 (36.7), 96 (10.3), 95 (19.0), 94 (10.3), 93 (16.7), 91 (14.6), 82 (12.1), 81 (29.2), 79 (41.7), 77 (21.7), 67 (18.8), 65 (13.3), 55 (36.3), 53 (25.0), 51 (13.3), 43 (51.6), 39 (56.6).

Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.59; H, 10.59. Found: C, 70.57; H, 10.66.

Irradiation of 4-(1-Hydroxyisopropyl)-2-isopropylidenecyclobutanone (14) in CH_3OH. To 0.210 g (0.0013 mol) of **14** in a quartz tube was added 20 ml of CH_3OH. After the sample was irradiated for 1.5 hr and the CH_3OH was removed by a slow stream of N_2, a single product was obtained (a mixture of isomers) which was identified as 2-methoxy-3-isopropylidene-5-(1-hydroxyisopropyl)-tetrahydrofuran (**15**): nmr (TMS internal standard, CCl_4) τ 8.95, 8.91, 8.79 (three singlets, 6), 8.32 (s, 6, allylically coupled to 7.70, $-CH_2-$), 7.70 (m, 2), 6.92 (s, 1, -OH by D_2O exchange), 6.70, 6.60 (two singlets, 3, $-OCH_3$ from *cis* and *trans* isomers), 6.05 (t, 1, J = 8 Hz), 4.80 (s, 1); ir $\nu_{\max}^{CCl_4}$ cm^{-1} 3344 (OH), 1453, 1435, 1366, 1182, 1159, 1073, 1019, 962; mass spectrum (75 eV) *m/e* (relative intensity) 200 (M^+, vw), 180 (4.6), 168 (37.4), 153 (18.1), 135 (12.9), 110 (61.4), 109 (30.4), 95 (44.5), 81 (38.0), 72 (53.1), 71 (39.1), 70 (38.1), 69 (43.3), 67 (41.0), 59 (68.4), 43 (100.0), 41 (78.9), 39 (58.5).

Anal. Calcd for $C_{11}H_{20}O_3$: C, 66.00; H, 10.00. Found: C, 65.92; H, 9.96.

1,1-Dimethylspiro[2.3]hexan-4-one (16). Spiroketone **16** was prepared from **10** by a Simmons–Smith reaction, according to the method of Shank and Shechter.[34] For **16**, nmr ($CHCl_3$ internal standard, CCl_4) τ 7.03 (m, 2), 7.86 (m, 2), 8.60, 9.03 (two doublets, AB, 2, J_{AB} = 4.0 Hz, $\Delta\nu_{AB}$ = 25.7 Hz), 8.73, 8.81 (two singlets, 6); ir $\nu_{\max}^{CCl_4}$ cm^{-1} 3030, 1757, 1453, 1439, 1376, 1362, 1239, 1167, 1148, 1116, 1079, 1043, 1037; mass spectrum (75 eV) *m/e* (relative intensity) 124 (M^+, 31.5), 109 (14.5), 96 (30.6), 82 (27.0), 81 (87.1), 79 (12.0), 68 (55.0), 67 (100.0), 53 (48.7), 41 (55.0).

Irradiation of 16 in CH_3OH. To 0.087 g (0.70 mmol) of **16** in a quartz tube was added 6 ml of CH_3OH. The sample was irradiated through Pyrex and monitored by vpc (12 ft × 0.25 in. 20% FFAP on Chrom W; column temperature 105°). After 8 hr, the photolysis was complete. Isolation of the products by vpc afforded spiroacetals **17** (44%) and **18** (44%) and methyl 2,2-dimethylcyclopropane carboxylate (**18a**, 12%). For **17**, nmr ($CHCl_3$ internal standard, CCl_4) τ 9.55 (AB, 2, J_{AB} = 4.5 Hz, $\Delta\nu_{AB}$ = 20.0 Hz), 8.85 (s, 6), 8.50 (m, 1), 7.65 (m, 1), 6.73 (s, 3), 6.00 (complex t, 2), 5.66 (s, 1); ir $\nu_{\max}^{CCl_4}$ cm^{-1} 3012, 2809, 1447, 1404, 1379, 1346, 1310, 1189, 1094, 1035, 967; mass spectrum (75 eV) *m/e* (relative intensity) 156 (M^+, vw), 124 (100.0), 109 (38.0), 95 (29.5), 83 (55.9), 81 (88.3), 79 (34.5), 67 (43.0), 55 (65.5). For **18**, nmr ($CHCl_3$ internal standard, CCl_4) τ 9.43 (AB, 2, J_{AB} = 4.5 Hz, $\Delta\nu_{AB}$ = 24.6 Hz), 8.90 (s, 6), 7.6–8.5 (m, 2), 6.71 (s, 3), 6.07 (m, 2), 5.47 (s, 1); ir $\nu_{\max}^{CCl_4}$ cm^{-1} 3012, 2809, 1451, 1381, 1200, 1160, 1096, 1086, 1040; mass spectrum (75 eV) *m/e* (relative intensity) 156 (M^+, vw), 124 (100.0), 109 (36.9), 95 (29.0), 83 (53.6), 81 (92.0), 79 (33.6), 67 (46.9), 55 (71.5).

Structure **18a** was confirmed by its identity (ir and nmr) with an authentic sample prepared by the method of Bly and Swidell.[35]

Irradiation of 1,1,5,5-Tetramethylspiro[2.3]hexan-4-one (19) in CH_3OH. To 0.095 g (0.62 mmol) of **19**[33] in a quartz tube was added 5 ml of CH_3OH. The sample was irradiated through Pyrex and monitored by vpc (12 ft × 0.25 in. 20% FFAP on Chrom W; column temperature 130°). After 10 hr, isolation of the products afforded **20** (50%) and **21** (50%). For **20**, nmr ($CHCl_3$ internal standard, CCl_4) τ 9.60 (AB, 2, J_{AB} = 4.5 Hz, $\Delta\nu_{AB}$ = 19.5 Hz), 8.97 (s, 6), 8.80 (s, 3), 8.70 (s, 3), 8.27 (AB, 2, J_{AB} = 12.0 Hz), $\Delta\nu_{AB}$ = 61.4 Hz), 6.82 (s, 3), 5.77 (s, 1): ir $\nu_{\max}^{CCl_4}$ cm^{-1} 3021, 1451, 1381, 1368, 1178, 1106, 1093, 1038, 1030, 990; mass spectrum (75 eV) *m/e* (relative intensity) 184 (M^+, vw), 153 (12.5), 152 (100.0), 137 (28.4), 124 (17.6), 119 (20.5), 109 (52.3), 95 (39.8), 93 (25.0), 91 (21.0), 81 (85.3), 79 (36.4), 67 (46.6), 55 (57.4), 43 (79.5). For **21**, nmr ($CHCl_3$ internal standard, CCl_4) τ 9.51 (AB, 2, J_{AB} = 5.0 Hz, $\Delta\nu_{AB}$ = 31.6 Hz), 8.99 (s, 6), 8.81 (s, 3), 8.69 (s, 3), 8.30 (AB, 2, J_{AB} = 12.0 Hz, $\Delta\nu_{AB}$ = 12.0 Hz), 6.78 (s, 3), 5.50 (s, 1): ir $\nu_{\max}^{CCl_4}$ cm^{-1} 3021, 1451, 1381, 1366, 1104, 1093, 1032, 1018: mass spectrum (75 eV) *m/e* (relative intensity) 184 (M^+, vw), 153 (10.8), 152 (100.0), 137 (30.0), 123 (17.5), 119 (20.0), 109 (50.9), 95 (38.4), 81 (78.4), 79 (31.6), 67 (40.0), 55 (38.4), 43 (46.6).

Irradiation of Spiro[2.4]heptan-4-one (31) in CH_3OH. To 0.500 g (4.5 mmol) of spiroketone **31**[36] in a quartz tube was added 15 ml of CH_3OH. The sample was irradiated through Corex for 6 hr. Analysis by vpc (8 ft × 0.25 in. 20% FFAP on Chrom W; column temperature 135°) revealed two products, one of which was converted into a third product following evaporation of solvent. The major product appeared from its spectral data to be cyclic acetal **32**: nmr ($CHCl_3$ internal standard, CCl_4) τ 9.73 (A_2B_2, cyclopropyl, 4), 9.2 (m, 1), 8.2 (m, 3), 6.81 (s, OCH_3, 3), 6.4 (m, 3); ir $\nu_{\max}^{CCl_4}$ cm^{-1} 3049 (cyclopropyl), 1449, 1404, 1351, 1212, 1190, 1109 (s), 1054 (s), 988, 943, 915, 891, 885; mass spectrum (9 eV) *m/e* (relative intensity) 142 (M^+, 7.3), 141 (vw), 115 (6.4), 114 (100.0), 111 (14.2), 110 (9.0), 84 (34.2). In the 75-eV spectrum, *m/e* 114 is still the base peak; however, *m/e* 141 is now twice as intense as *m/e* 142. The second and third products were aldehyde **33** and its methanol acetal. For aldehyde **33**, nmr (TMS internal standard, CCl_4) τ 9.03 (A_2B_2, 4), 7.64 (d, J = 7 Hz, 2), 5.14, 4.92 and 4.55–3.81 (three one-proton multiplets characteristic of vinyl absorption), 1.50 (s, 1), ir $\nu_{\max}^{CCl_4}$ cm^{-1} 3049 (cyclopropyl), 2793, 2710 (CHO), 1724 (C═O), 1653 (vinyl), 1431, 1342, 1242, 1064, 1037, 1008, 920, 909. Upon addition of CH_3OH to aldehyde **33**, the methanol acetal was formed whose vpc retention time was identical with that observed in the photolysate.

---

[33] We thank Professor M. Bertrand (La Faculte des Sciences de Marceille, France) for generous samples of 4,4-dimethyl-2-isopropylidenecyclobutanone and 1,1,5,5-tetramethylspiro[2.3]hexan-4-one.

[34] R. S. Shank and H. Shechter, *J. Org. Chem.*, **24**, 1825 (1959).

[35] R. S. Bly and R. T. Swidell, *ibid.*, **30**, 10 (1965).

[36] W. G. Dauben and G. H. Berezin, *J. Amer. Chem. Soc.*, **85**, 468 (1963); **89**, 3449 (1967).

Irradiation of Spiro[2.5]octan-4-one (37) in CH_3OH. To 0.500 g (4.03 mmol) of **37**[36] in a quartz tube was added 15 ml of CH_3OH. The sample was irradiated through Corex for 6 hr. Isolation of the volatile products by vpc (8 ft × 0.25 in. 20% FFAP on Chrom W; column temperature 160°) afforded only aldehyde **38** and its methanol acetal. For **38**, nmr (TMS internal standard, CCl_4) τ 9.02 (A_2B_2, 4), 8.55–8.17 (m, 2), 8.07–7.62 (m, 2), 5.20, 4.98, and 4.56–3.87 (three one-proton multiplets characteristic of vinyl absorption), 1.45 (s, 1); ir $\nu_{max}^{CCl_4}$ cm^{-1} 3030, 2809, 2695, 1709 (C=O), 1642 (C=C), 1447, 1429, 1357, 1333, 1068, 992, 915, 903. Addition of excess methanol to this aldehyde reversibly forms the methanol acetal.

Irradiation of 1,1-Dimethylspiro[2.4]heptan-4-one (34) in CH_3OH. To 3.300 g (2.18 mmol) of ketone **34**[37] in a quartz tube was added 15 ml of CH_3OH. The sample was irradiated through Corex for 8 hr and monitored by vpc (5 ft × 0.25 in. 20% CWX 20M on KOH washed Chrom P; column temperature 130°). Only one major volatile product, acetal **36**, was detected: nmr (TMS internal standard, CCl_4) τ 8.97–7.20 (broad m, 9), 8.74 (s, 6), 6.84 (s, 3); ir $\nu_{max}^{CCl_4}$ cm^{-1} 2785, 1466, 1374, 1359, 1225, 1190, 1147, 1124, 1081, 972; mass spectrum (75 eV) *m/e* 170 (M^+), 155 ($M^+ - CH_3$), 139 ($M^+ - OCH_3$), 138 ($M^+ - CH_3OH$).

Irradiation of 5 in C_6H_6. Ketone **5** (0.500 g, 4.0 mmol) in 10 ml of C_6H_6 was irradiated in all quartz apparatus for 6 hr. Separation of the products by vpc (5 ft × 0.25 in. 20% $\beta\beta\beta$ on Chrom P; column temperature 145°) afforded isobutylene, tetramethylcyclopropane, and 2,2,4,4-tetramethyl-γ-butyrolactone (**39**): nmr (TMS external standard, CCl_4) τ 8.46 (s, 6), 8.31 (s, 6), 7.78 (s, 2); ir $\nu_{max}^{CCl_4}$ cm^{-1} 1770, 1762, 1382, 1370, 1095; mass spectrum (13 eV) *m/e* (relative intensity) 142 (M^+ vw), 127 (66.4), 98 (100.0), 83 (64.0). A fourth unidentified product was also detected.

Irradiation of 2-Isopropylidenecyclobutanone in *n*-C_5H_{12} in the Presence of O_2. A solution of 1.210 g (0.011 mol) of **10** and 800 ml of dry *n*-C_5H_{12} was emptied into a 1-l. immersion well jacket possessing a gas inlet. After inserting a quartz immersion well containing a Pyrex filter sleeve, O_2 was bubbled through the solution for 10 min prior to photolysis. The solution was then irradiated for 4 hr, following which the *n*-C_5H_{12} was removed by rotary evaporation. The remaining oil was subjected to preparative vpc (5 ft × 0.25 in. 20% FFAP on Chrom W; column temperature 163°) and collection of the major fraction afforded pure 2-isopropylidene-γ-butyrolactone (**24**) (*ca.* 10%): nmr (TMS internal standard, CCl_4) τ 8.14 (s, 3), 7.82 (s, 3, allylically coupled to 7.16 -CH_2-), 7.16 (t, 2, J = 10 Hz), 5.81 (t, 2, J = 10 Hz); ir $\nu_{max}^{CCl_4}$ cm^{-1} 1748, 1672, 1439, 1368, 1264, 1183, 1044, 1033; mass spectrum (75 eV) *m/e* (relative intensity) 126 (M^+, 100.0), 111 (17.4), 97 (31.3), 83 (14.8), 81 (26.1), 80 (18.3), 79 (34.8), 69 (25.2), 68 (59.1), 67 (66.1), 65 (13.0), 59 (11.3), 58 (12.2), 55 (18.3), 54 (10.4), 53 (35.6), 51 (13.0), 43 (66.8), 42 (13.9), 41 (79.0), 40 (20.8), 39 (60.9); uv $\lambda_{max}^{C_6H_{14}}$ nm (log ϵ) 224 (4.15).

Anal. Calcd for $C_7H_{10}O_2$: C, 66.67; H, 7.94. Found: C, 64.89; H, 7.87.

Irradiation of Cyclopentanone in CH_3OH. A 5% solution of cyclopentanone in CH_3OH was irradiated in all quartz apparatus for 5 hr. Concentration at atmospheric pressure of the photolysate followed by preparative vpc (5 ft × 0.25 in. 22% CWX 20M on Chrom P; column temperature 105°) yielded only 4-pentenal and its methanol acetal. Less than 1% of the ring expanded product, 2-methoxytetrahydropyran (independently synthesized by the method of Woods and Kramer[38]), could have been detected.

Irradiation of 2,2,5,5-Tetramethylcyclopentanone in CH_3OH. To 0.5 g (0.0037 mol) of 2,2,5,5-tetramethylcyclopentanone[39] in a quartz tube was added 10 ml of CH_3OH. The sample was photolyzed in an all-quartz apparatus for 78 min. Periodic analysis by vpc (10 ft × 0.25 in. 22% CWX 20M on Chrom P; column temperature 120°) revealed that one major product, 2,2,5-trimethyl-4-hexenal,[40] was formed and that further photolysis led to disappearance of this product. Three other minor products were formed in amounts less than 1% relative to the major hexenal, and consequently were not characterized.

Irradiation of 7 in C_6H_6. Ketone **7** (0.500 g, 3.5 mmol) in 15 ml of C_6H_6 was irradiated in an all-quartz apparatus for 2 hr. Vpc (5 ft × 0.25 in. 20% $\beta\beta\beta$ on Chrom P; column temperature 155°) afforded two compounds. The major product was the *cis*-cyclic acetal **40**: nmr (TMS internal standard, CCl_4) τ 8.93, 8.87, 8.81 (three singlets, 18), 8.64, 8.58 (two singlets, 6), 7.87 (OH by D_2O exchange), 7.00 (s, 1), 6.63 (broad s, 1), 5.56 (s, 1); ir $\nu_{max}^{CCl_4}$ cm^{-1} 3521, 1471, 1449, 1372, 1103, 1075, 1057, 1026, 971; mass spectrum (12 eV) *m/e* (relative intensity) 256 (M^+, no observed), 114 (70.5), 99 (100.0), 96 (18.6), 84 (41.3), 73 (14.6), 72 (49.2), 71 (28.8), 70 (28.8). The other major product was the *trans*-cyclic acetal **40**: nmr (TMS internal standard, CCl_4) τ 8.97, 8.93, 8.88 (three singlets, 18), 8.79, 8.61 (two singlets, 6), 8.15 (OH by D_2O exchange), 7.07 (s, 1), 6.11 (s, 1), 5.62 (s, 1); ir $\nu_{max}^{CCl_4}$ cm^{-1} 3571, 3425, 1466, 1377, 1362, 1215, 1104, 1057, 1026, 980; mass spectrum (14 eV) *m/e* (relative intensity) 256 (M^+, not observed), 143 (<10.0), 142 (<10.0), 114 (47.2), 99 (100.0), 84 (18.2), 73 (29.0), 72 (61.4), 71 (68.2), 70 (58.0).

Irradiation of 4-(1-Hydroxyisopropyl)-2-isopropylidenecyclobutanone (14) in C_6H_6 and Treatment of 41 with CH_3OH. To 0.050 g (0.0003 mol) of **14** in a quartz tube was added 3 ml of C_6H_6. The sample was photolyzed for 8 hr, the solvent was evaporated, and the residue dissolved in cyclohexane. After 2 days, 0.030 g of a white crystalline compound, 2,7-dioxo-3,3-dimethyl-6-isopropylidenebicyclo[2.2.1]heptane (**41**), was isolated (60%): nmr (TMS internal standard, CCl_4) τ 8.98 (s, 3), 8.82 (s, 3), 8.43 (s, 3), 8.35 (s, 3), 7.69 (d, 2, J = 8 Hz), 5.97 (t, 1, J = 8 Hz), 4.20 (s, 1); ir $\nu_{max}^{CCl_4}$ cm^{-1} 1692 (vw), 1447, 1370, 1340, 1287, 1253, 1233, 1161, 1149, 1062, 1039, 998, 962, 877; mass spectrum (9 eV) *m/e* (relative intensity) 168 (M^+, 100.0), 167 (10.0), 150 (14.5), 122 (10.0), 109 (15.5), 108 (10.0), 94 (16.7), 80 (12.2), 70 (12.2), 68 (11.7), 58 (23.9), 42 (28.9), 40 (18.4).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.43; H, 9.52. Found: C, 70.26; H, 10.13.

To 0.060 g (0.0036 mol) of **41** was added 1 ml of CH_3OH. The reaction was allowed to proceed for 3 days at room temperature, following which the CH_3OH was removed by a slow stream of N_2. The remaining oil was shown by nmr to be essentially pure **15**.

Irradiation of 2-Isopropylidenecyclobutanone (10) in C_6H_6 and the Dark Reaction with CH_3OH. To 0.115 g (0.001 mol) of **10** in a quartz tube was added 20 ml of reagent grade C_6H_6 (undried). The sample was photolyzed through Pyrex for 4 hr and the C_6H_6 was blown off by a slow stream of N_2. The photolysate was then injected into 20 ml of CH_3OH, and kept for 10 hr at 0° in the dark. The sample was allowed to come to room temperature and the C_6H_6 and CH_3OH were removed. An nmr of the remaining liquid revealed that the major product was the cyclic acetal, **11**.

Irradiation of 10 in Water-Saturated C_6H_6. A solution of 0.329 g (3.0 mmol) of **10** in 20 ml of C_6H_6 was treated with 1 ml of distilled H_2O. The sample was photolyzed through Pyrex for 7 hr after which the products were taken up in ether, washed with H_2O, and dried over K_2CO_3. Removal of ether and C_6H_6 afforded a clear oil whose nmr suggests that it is an equilibrium mixture of hemiacetal **43** and hydroxyaldehyde **43a**: nmr (TMS internal standard, CCl_4) τ 8.33 (s, 6, hemiacetal -CH_3), 8.01, 7.81 (two singlets, 6, aldehyde -CH_3), 7.6 (m, 2, hemiacetal -CH_2- α to C=C), 7.52 (t, 2, J = 7 Hz, aldehyde -CH_2- α to C=C), 6.61 (q, 2, J = 7 Hz, aldehyde -CH_2- α to -OH), 6.15 (t, 2, J = 7 Hz, hemiacetal -CH_2- α to ring oxygen), 4.86 (s, 1, hemiacetal proton), 4.40 (m, 1, aldehyde -OH), −0.32 (s, 1, -CHO). Treatment of the **43** ⇌ **43a** nmr solution with excess CH_3OH resulted in the disappearance of all aldehyde resonances and the exclusive formation of acetal **11**. In a subsequent experiment, excess CH_3OD was added to the **43** ⇌ **43a** nmr solution. No evidence for deuterium incorporation was observed in the acetal, **11**, produced.

Thermolysis of C_6H_6 Photolysate. To 0.096 g (0.87 mmol) of **10** in an nmr tube was added 0.4 ml of C_6H_6. The sample was photolyzed through Pyrex for 6 hr and the solvent was removed by a slow stream of N_2. Preparative vpc (4 ft × 0.25 in. 20% CWX 20M on Chrom P; column temperature 140°) of the photolysate resulted in the isolation of starting material, **10** (18%), diene **42** (4%), and an unidentified crystalline dimer (21%). For **42**, nmr (TMS internal standard, CCl_4) τ 8.10 (s, 3), 7.29 (t, 2, J = 10 Hz), 5.62 (t, 2, J = 10 Hz), 5.42 (two singlets, 2), 3.62 (s, 1); ir $\nu_{max}^{CCl_4}$ cm^{-1} 3058, 1634, 1112, 1104, 867, 850; mass spectrum (75 eV) *m/e* (relative intensity) 110 (M^+, 92.1), 95 (33.0), 81 (36.6), 79 (28.9), 69 (20.0), 67 (100.0), 55 (28.0), 53 (41.5), 44 (22.5), 43 (28.0), 42 (90.0), 39 (75.1).

Quantum yields were determined for nondegassed solutions of ketone in methanol, concentrations being adjusted so that the ketone absorbed >99% of the light at 3130 Å (filter solution of potassium chromate in aqueous potassium bicarbonate). Potas-

---

[37] D. H. Marr and J. B. Stothers, *Can. J. Chem.* **45**, 225 (1967).

[38] G. F. Woods and D. N. Kramer, *J. Amer. Chem. Soc.*, **69**, 2246 (1947).

[39] J. M. Conia, *Ann. Chim.*, **8** [12], 748 (1953).

[40] P. Cresson, *Bull. Soc. Chim. Fr.*, 2618 (1964).

sium ferrioxalate[41] or benzophenone–benzhydrol[42] actinometers were employed as indicated in Table II. For ketones **1**, **5**, and **7**, the quantum yields for cyclic acetal formation were determined directly by vpc. For ketone **10**, the quantum yield for formation of **11** was equated to the quantum yield for disappearance of **10** since the reaction appears to be quantitative. The latter quantum yield was determined by the decrease in absorption of **10** at 3230 Å following irradiation.

---

[41] See Table II, footnote *a*.

[42] See Table II, footnote *b*.

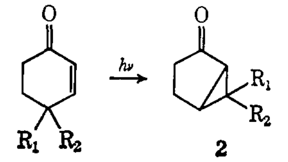
The Mechanism of Photoisomerization of Cyclohexenones. 10-Hydroxymethyl-$\Delta^{1,9}$-2-octalone. The Question of Hydrogen Abstraction from Benzene by Ketone Triplets[1-3]

David I. Schuster[4] and Donald F. Brizzolara[5]

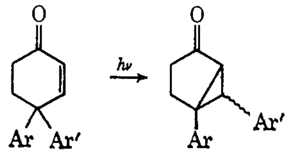
Contribution from the Department of Chemistry, New York University, University Heights, New York, New York 10453. *Received October 14, 1969*

Abstract: The photochemistry of 10-hydroxymethyl-$\Delta^{1,9}$-2-octalone (**10**) has been studied in detail. Irradiation through Pyrex in *t*-butyl alcohol gives solely and inefficiently lumiketone **11**. In chloroform, toluene, cumene, and benzene, a novel fragmentation reaction occurs in addition to give $\Delta^{9,10}$-2-octalone (**12**) and $\Delta^{1,9}$-2-octalone (**13**) and other products derived from them, as well as products derived from solvent radicals. Quenching and sensitization results indicate that all products are derived from the same radical-like triplet excited state, which is concluded to be the n,π^* triplet. It is concluded that zwitterion intermediates are not involved in any of the photochemical reactions of **10**. Solvent effects on quantum yields are attributed to stabilization of a higher π,π^* triplet and/or to complexing with the hydroxyl group of **10**. A comparison with results obtained by others with other model cyclohexenones is made, and differences in mechanistic conclusions are indicated. The inefficiency of these photochemical reactions is emphasized, and an explanation is proposed involving formation of a biradical intermediate which can regenerate the starting ketone in its ground electronic state. The results in benzene would seem to indicate that hydrogen abstraction is occurring with the same rate constant as in toluene. However, the results are shown to be consistent with an alternative mechanism involving initial addition of the triplet to benzene to form a diradical, followed by fragmentation and coupling reactions. Such a scheme is considered to be energetically more reasonable than the abstraction reaction, and consistent with results of pulse radiolysis studies in benzene and studies of hydrogen donor reactivities.

The light-induced photoisomerization (type A rearrangement) of cyclohexenones **1** to bicyclo[3.1.0]-hexanones **2** is well documented.[6-11] There are also numerous examples of a second type of structural rearrangement which occurs with 4,4-diaryl- and 4,5-diarylcyclohexenones, where reaction is accompanied by migration of an aryl group (**3** → **4**).[12] Detailed mechanistic studies of the type A rearrangement have been very limited, while the aryl migration route has been elucidated in minute detail.[12] The rearrangements in *t*-butyl alcohol of phenanthrone **5** and octalone **7** to lumiketones **6** and **8**, respectively, have low quantum efficiencies; these reactions could be effected by triplet sensitization without appreciable increase in quantum efficiency, and could be quenched by piperylene, naphthalene, and di-*t*-butyl nitroxide in low concentrations.[9,10] In isopropyl alcohol, **5** gave pinacol **9** in



1 **2**



3 **4**

---

[1] Part XXII of a series on the photochemistry of unsaturated ketones in solution. Part XXI: D. I. Schuster and N. K. Lau, *Mol. Photochem.*, **1**, 415(1969).

[2] Supported by the U. S. Army Research Office (Durham) and in initial stages by an Institutional Grant from the National Science Foundation.

[3] Portions of this work were communicated earlier: D. I. Schuster and D. F. Brizzolara, *Chem. Commun.*, 1158 (1967).

[4] Fellow of the Alfred P. Sloan Foundation, 1967–1969.

[5] National Science Foundation Summer Fellow, 1966, and Graduate Trainee, 1967–1968.

[6] W. W. Kwie, B. A. Shoulders, and P. D. Gardner, *J. Amer. Chem. Soc.*, **84**, 2268 (1962).

[7] O. L. Chapman, T. A. Rettig, A. A. Griswold, A. I. Dutton, and P. Fitton, *Tetrahedron Lett.*, 2049 (1963).

[8] B. Nann, D. Gravel, R. Schorta, H. Wehrli, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **46**, 2473 (1963).

[9] H. E. Zimmerman, R. G. Lewis, J. J. McCullough, A. Padwa, S. W. Staley, and M. Semmelhack, *J. Amer. Chem. Soc.*, **88**, 1965 (1966).

[10] O. L. Chapman, J. B. Sieja, and W. J. Welstead, Jr., *ibid.*, **88**, 161 (1966).

[11] W. G. Dauben, G. W. Shaffer, and N. D. Vietmeyer, *J. Org. Chem.*, **33**, 4060 (1968).

[12] H. E. Zimmerman and J. W. Wilson, *J. Amer. Chem. Soc.*, **86**, 4036 (1964); H. E. Zimmerman, R. C. Hahn, H. Morrison, and M. C. Wani, *ibid.*, **87**, 1138 (1965); H. E. Zimmerman and D. J. Sam, *ibid.*, **88**, 4905 (1966); H. E. Zimmerman, R. D. Rieke, and J. R. Scheffer, *ibid.*, **89**, 2033 (1967); H. E. Zimmerman and J. O. Grunewald, *ibid.*, **89**, 5163 (1967); H. E. Zimmerman and R. L. Morse, *ibid.*, **90**, 954 (1968); H. E. Zimmerman and K. G. Hancock, *ibid.*, **90**, 3749 (1968); H. E. Zimmerman and N. Lewin, *ibid.*, **91**, 879 (1969); H. E. Zimmerman and W. R. Elser, *ibid.*, **91**, 887 (1969).