difference from ketones) that thiobenzophenone and presumably other thiones are excellent radical traps.[19] We have observed the same phenomenon on long wavelength irradiation of the thiobenzophenone–acrylonitrile system,[5c] and there are indications[5a] that the same may be true for alicyclic thiones also.

[19] G. Tsuchihashi, M. Yamauchi, and A. Ohno, *Bull. Chem. Soc. Jap.*, **43**, 968 (1969).

Photochemical Ring Expansion of Cyclic Aliphatic Ketones. Cyclobutanones and Cyclopentanones[1a]

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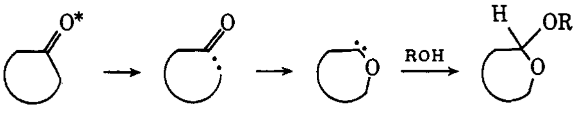
Abstract: The solution phase photochemical transformations of several substituted cyclobutanones and cyclopentanones are described with emphasis placed on the mechanism and scope of the photochemical ring expansion reaction. For cyclobutanone, ring expansion appears to be a singlet state reaction, and the extent to which it occurs is found to depend upon the nature and position of substituents on the four-membered ring (Table I). For example, the following yields of ring-expanded acetals are obtained from the designated ketones in methanol: 2,2-bis(trifluoromethyl)-3-phenylcyclobutanone (0%); cyclobutanone (8%); 2,2-dimethyl-3-phenylcyclobutanone (82%); 2-isopropylidenecyclobutanone (100%). The results can be interpreted in terms of an intermediary oxacarbene in equilibrium with a singlet biradical (Scheme II). For monocyclic cyclopentanones, ring expansion is only observed for spiro[2.4]heptan-4-one (**56**). Quantum yield and kinetic and product analyses demonstrate that ring expansion for **56** is a triplet state reaction. These results suggest that substituents capable of stabilizing the oxacarbene intermediate favor ring expansion.

During the past several years, considerable research effort has been directed toward an understanding of the chemistry of electronically excited aliphatic ketones, both acyclic and alicyclic.[2] Analysis of the data obtained from this research has revealed that aliphatic ketones are capable of undergoing four general types of reactions in condensed media:[3] (1) photoreduction, (2) cycloaddition to olefins, (3) intramolecular photoreduction or type II cleavage,[4] and (4) α cleavage or type I cleavage. The latter two processes are unimolecular reactions of electronically excited ketones and. as such, are capable of producing isomeric and fragmentation products. For cyclic aliphatic ketones, in particular, the α-cleavage reaction is known to give rise to products of decarbonylation in addition to products of intramolecular disproportionation (acyclic aldehydes and ketenes). In the case of cyclobutanones, β cleavage (fragmentation to form olefin and ketene products) is a commonly observed reaction. In special cases, another type of reaction, photochemical ring expansion, is also observed, and it is this reaction upon which we focus our attention in the present investigation.

Perhaps because of the rarity of its occurrence, the photochemical ring expansion reaction is one of the least studied excited state transformations of cyclic aliphatic ketones. Nevertheless, it has been shown to be a general reaction of cyclobutanones[5] and tricyclo[2.1.0^{2,6}]heptan-3-ones.[6] At the initiation of this work, the commonly accepted mechanism was that initially suggested by Yates and Kilmurry.[6,7] This mechanism involves initial α cleavage of the excited cyclic ketone (*e.g.*, **1**) to an acyl alkyl biradical intermediate **2** which then undergoes electronic rearrangement and rebonding to afford an oxacarbene intermediate **3**. Studies have revealed that **3** is most efficiently trapped by alcohols to afford ring expanded acetals **4** as isolable products.[5–7]



1 2 3 4 (1)

In this report, we present additional results from our investigation of the photochemical ring expansion reaction of cyclic aliphatic ketones and suggest a somewhat modified mechanism which is capable of explaining a variety of reported results.

Results and Discussion

Photochemical Ring Expansion of Cyclobutanones. It has been observed that electronically excited cyclobutanones rearrange in alcoholic media to yield products of decarbonylation (carbon moxoxide and cyclopropanes), β cleavage (ethylenes and ketenes), and ring expansion (2-alkoxytetrahydrofurans).[3,5,8–10] Al-

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[1] (a) The authors at Columbia gratefully acknowledge the generous support of this work by the Air Force Office of Scientific Research (Grant AFOSR-70-1848). (b) National Institutes of Health Predoctoral Fellow, 1968–1971.

[2] For a review, see J. C. Dalton and N. J. Turro, *Annu. Rev. Phys. Chem.*, **21**, 499 (1970).

[3] N. J. Turro, J. C. Dalton, K. Dawes, G. Farrington, R. Hautala, D. Morton, M. Niemczyk, and N. Schore, *Accounts Chem. Res.*, **5**, 92 (1972), and references cited therein.

[4] P. J. Wagner, *ibid.*, **4**, 168 (1971).

[5] D. R. Morton, E. Lee-Ruff, R. M. Southam, and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 4349 (1970), and references cited therein.

[6] P. Yates, *Pure Appl. Chem.*, **16**, 93 (1968), and references cited therein.

[7] (a) P. Yates and L. Kilmurry, *Tetrahedron Lett.*, 1739 (1964); (b) P. Yates and L. Kilmurry, *J. Amer. Chem. Soc.*, **88**, 1563 (1966).

[8] N. J. Turro and D. M. McDaniel, *ibid.*, **92**, 5727 (1970).

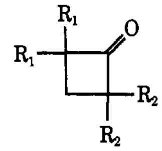
[9] N. J. Turro and D. R. Morton, *ibid.*, **93**, 2569 (1971).

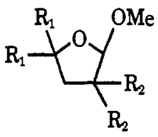
[10] N. J. Turro, D. R. Morton, E. Hedaya, M. E. Kent, P. D'Angelo, and P. Schissel, *Tetrahedron Lett.*, 2535 (1971).

Table I. Products Derived from the Irradiation of Cyclobutanones in Methanol Solutions at 25°

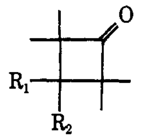
Ketone	$\Phi_K{}^a$	Cyclic acetal (%)	Other products (%)	Ref
5	0.30	**10** (8)	Methyl acetate (48), cyclopropane (?)	5
6		**11** (41)	Methyl acetate (32), methyl isobutyrate (3) 1,1-Dimethylcyclopropane (8)	5
7	0.20	**12** (68)	Methyl isobutyrate (13) 1,1,2,2-Tetramethylcyclopropane (11)	5
8		**13** (67)^b	Isobutyraldehyde (15) Methyl isobutyrate (15) 1,1,2,2-Tetramethyl-3-hydroxycyclopropane (17)	5
9	0.24	**14** (86)^b	2,2,3,3-Tetramethylcyclobutanone (14)	*c*, 10
15		**19** (88)^b	1,1-Dimethyl-2-carbomethoxycyclopropane (12)	5
16		**20** (100)^b		5
17	0.27	**21** (89)	1,1,2,2-Tetramethylmethylenecyclopropane and 1,1-dimethyl-2-isopropylidenecyclopropane (total *ca.* 11%)	*c*
18	0.11 (0.07)^d	**22** (100)		5
27 or **28**	0.14^e	**29** + **30** (100)		*c*

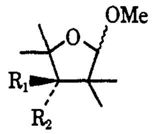
^{a} For nondegassed solutions of ketone in methanol at 313 nm. ^{b} Yield for both isomers. ^{c} Reference made to this work; see Experimental Section for details. ^{d} Quantum yield for disappearance of **18** in cyclohexane. ^{e} Quantum yield for disappearance of both **27** and **28**.



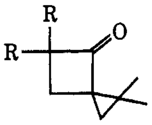


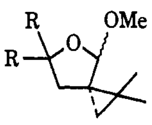
5 $R_1 = R_2 = H$ **10**
6 $R_1 = Me; R_2 = H$ **11**
7 $R_1 = R_2 = Me$ **12**

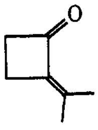


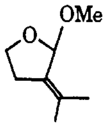


8 $R_1 = OH; R_2 = H$ **13**
9 $R_1R_2 = -OCH_2-$ **14**
17 $R_1R_2 = CH_2{=}$ **21**

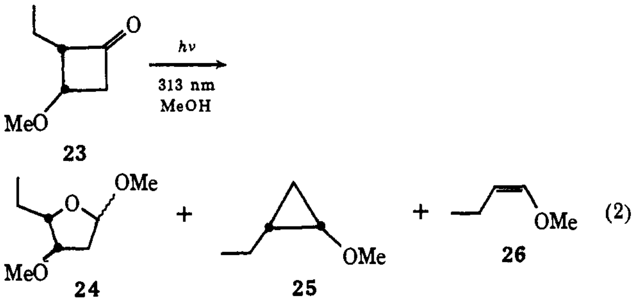








15 R = H **19**
16 R = Me **20**
18
22



23 **24** **25** **26** (2)

though only one or two of these rearrangements may be realized for any given cyclobutanone, the above three reactions are usually the only types detected. A summary of selected previous results in addition to some new results is presented in Table I. Inspection of the table reveals the following trends: (a) increasing α-alkyl substitution on the ketone progressively increases the importance of the ring expansion reaction (compare **5**, **6**, **7**, and **8** and **15** and **16**), (b) factors which *a priori* tend to increase the ring strain of the cyclobutanone favor decomposition by way of ring expansion (compare **9** and **15**–**18** with **5**–**8**), (c) 2-alkylidenecyclobutanones (*e.g.*, **18**, **27**, and **28**) only undergo ring expansion, (d) ring expansion appears to be regiospecific (*e.g.*, only **11** is formed from **6** and not the isomer where $R_1 = H$; $R_2 = Me$), (e) in no case is a quantum yield for ketone disappearance above 0.30 obtained. In addition to these observations, we should point out that, in general, (f) photochemical reactions of cyclobutanones appear to be stereoselective or stereospecific (*e.g.*, **23** → **24**–**26**).[8,11] Most of these observations can be accommodated by the mechanism $\mathbf{1} \rightarrow \mathbf{2} \rightarrow \mathbf{3} \rightarrow \mathbf{4}$. In particular, observation e is understood by postulating the intermediacy of a biradical such as **2** which could undergo ring closure to regenerate the starting ketone. Further, biradical **2** serves as a common intermediate for the β cleavage and decarbonylation reactions. Unfortunately, the mechanism in its present form does not satisfactorily explain observations a, b, and c, and f, and is therefore of questionable validity. Further, while the intermediacy of oxacarbenes (*e.g.*, **3**) in the ring expansion reaction has received reasonable support,[5,7b] the nature of the cyclobutanone excited state (*e.g.*, **1**) has remained a mystery.

In an attempt to clarify the excited state transformations of cyclobutanones and in particular the ring expansion reaction, we have examined the photochemistry of the 2-*sec*-butylidenecyclobutanones **27** and **28**. These ketones were synthesized by base-catalyzed condensation of cyclobutanone (**5**) with 2-butanone[12] and have been characterized by spectral analysis and literature analogy (see Experimental Section). Our original reasons for choosing these compounds were twofold. (1) Since both compounds are α,β-unsaturated ketones, both should have triplet energies on the order of 60–70

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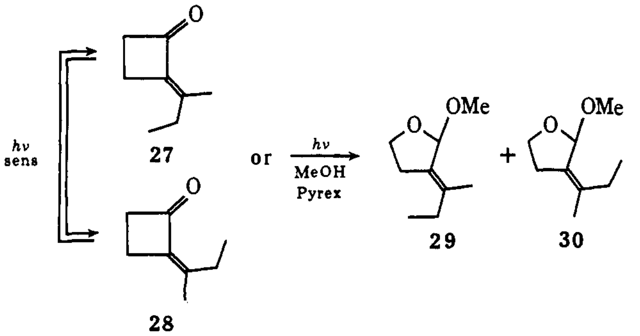
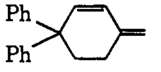
(11) G. Quinkert, G. Cimbollek, and G. Buhr, *Tetrahedron Lett.*, 4573 (1966).

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

kcal/mol.[13] This would enable their triplet states to be selectively populated by a variety of readily accessible sensitizers and allow an evaluation of their triplet state photoreactivity to be made. (2) Ketones **27** and **28**, in analogy with **18**, should only rearrange by way of ring expansion, thereby simplifying analysis. Indeed, irradiation of either **27** or **28** in methanol resulted in the formation of isomeric acetals **29** and **30**. The quantum yield for total enone disappearance was 0.14, and, when irradiation was terminated prior to the total disappearance of enone, glpc analysis of the reaction mixture revealed that significant isomerization of **27** to **28** (or *vice versa*) had occurred ($\Phi = 0.1$). This isomerization process is reminiscent of the "free-rotor effect" postulated to account for the low reactivity of the excited triplet state of diene **31**.[14] For diene **32**, on the other hand, free rotation about a carbon-carbon double bond has a higher energy barrier, and, as a result, the excited triplet state of this species undergoes a di-π-methane rearrangement.





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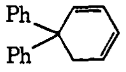


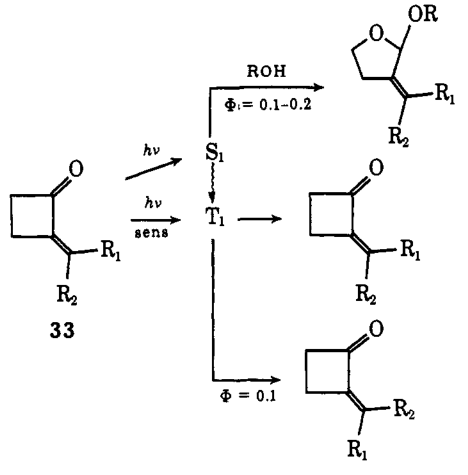
32

To confirm that the excited triplet state of enone **27** (or **28**) was responsible for syn–anti isomerization about the carbon–carbon double bond, benzene solutions of **27** containing xanthone (E_T = 74 kcal/mol) and acetophenone (E_T = 69 kcal/mol) were prepared, degassed, and excited with 313-nm radiation. In each instance the concentration of the sensitizer was adjusted so that it absorbed >93% of the incident radiation at 313 nm. Analysis by glpc confirmed that syn–anti isomerization had occurred in all three cases, and parallel irradiation and analysis of a control sample containing no sensitizer demonstrated that the triplet sensitized isomerization was approximately four to five times more efficient than that induced by direct irradiation. Interestingly, syn–anti isomerization was the only detectable photoprocess in the samples containing sensitizer. To eliminate the possibility that isomerization was not the result of a Schenck mechanism,[15] a similar sensitization experiment was successfully performed using triphenylene (E_T = 67 kcal/mol) as sensitizer, with concentrations being adjusted to minimize singlet–singlet energy transfer from the aromatic hydrocarbon to enone.[16] Attempts to quench the triplet state syn–anti isomerization reaction in methanol under excitation at 313 nm with 1,3-pentadiene (0.0–1.0 *M*) proved difficult and yielded a Stern–Volmer slope of only 0.05 M^{-1}.

Since it was concluded that the triplet states of **27** and **28** could be populated by sensitizers with $E_T \geq 67$ kcal/mol, it was of interest to determine if ring expansion to **29** and **30** was a triplet state reaction. To this end, an nmr experiment was performed using a methanol–benzene solution of *anti*-enone **27** containing benzophenone as sensitizer and following reaction progress by monitoring the appearance or disappearance of the allylic methyl resonances of **27–30**. Irradiation of this solution (degassed) at 313 nm in parallel with a control sample containing no sensitizer demonstrated that syn–anti isomerization was the only reaction to occur under the triplet sensitized conditions. Further, nmr analysis of the control sample (no sensitizer) at low conversion suggested that *anti*-enone **27** ring expanded exclusively, within the limits of detection, only to *anti*-acetal **29**.

These results demonstrate that the ring expansion reaction of 2-alkylidenecyclobutanones (*e.g.*, **33**) is a singlet state reaction (Φ = 0.1–0.2) while triplet state reactivity is manifested by isomerization about the carbon–carbon double bond (Scheme I). For the case where $R_1 = R_2$, the triplet isomerization process provides a mechanism for energy loss without net chemical reaction.

Scheme I



While it is tempting to extend the mechanism of photochemical ring expansion for the 2-alkylidenecyclobutanones to the variety of saturated cyclobutanones (*e.g.*, **5–9**, **15**, **16**) studied, the chromophoric difference involved, in addition to the occurrence of the two additional processes, β cleavage and decarbonylation, makes this extension difficult. There exists, however, a significant amount of data which indirectly supports the cyclobutanone S_1 state as that which is responsible for ring expansion. Attempts to quench the photoreactions of saturated cyclobutanones with 1,3-dienes, for example, have met with failure in every reported instance.[17–19] In addition, attempts to sensitize these same reactions have also been unsuccessful.[17,20] It is interesting to note that when irradia-

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[13] N. J. Turro in "Energy Transfer and Organic Photochemistry," A. A. Lamola and N. J. Turro, Ed., Wiley-Interscience, New York, N. Y., 1969, p 234.

[14] J. S. Swenton, J. A. Hyatt, T. J. Walker, and A. L. Crumrine, *J. Amer. Chem. Soc.*, **93**, 4808 (1971), and references cited therein.

[15] (a) N. J. Turro, *Photochem. Photobiol.*, **9**, 555 (1969); (b) N. C. Yang, J. I. Cohen, and A. Shani, *J. Amer. Chem. Soc.*, **90**, 3264 (1968).

[16] A. B. Smith and W. C. Agosta, *Chem. Commun.*, 466 (1970).

[17] P. J. Wagner, C. A. Stout, S. Searles, and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 1242 (1966).

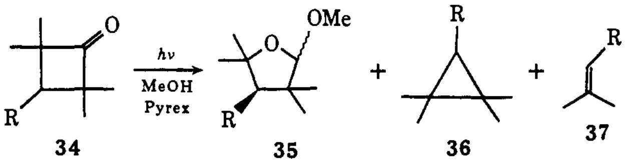
[18] N. J. Turro and D. M. McDaniel, *ibid.*, **92**, 5727 (1970).

[19] R. F. Klemm, *Can. J. Chem.*, **48**, 3320 (1970).

[20] N. J. Turro and D. M. McDaniel, *Mol. Photochem.*, **2**, 39 (1970).

tion of cyclobutanone is carried out in the presence of 1,3-dienes, no evidence has been found for diene dimer formation, nor has cis–trans isomerization of the diene been observed.[19] Both of these processes are known reactions of 1,3-diene T_1 states.[21]

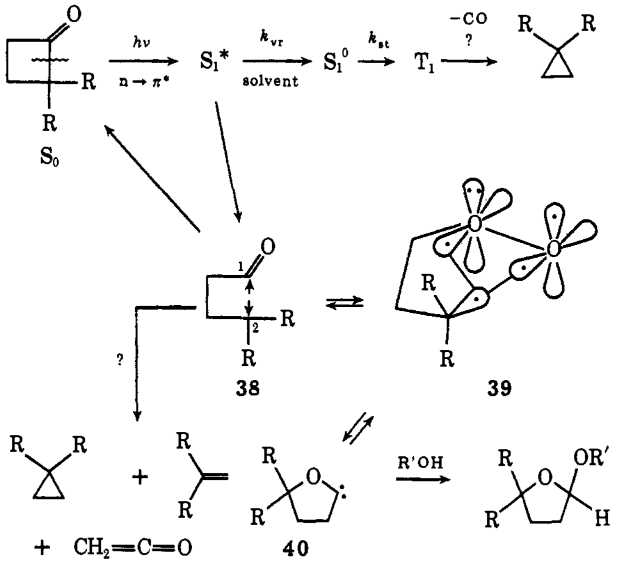
The photoreactivity of the cyclobutanone S_1 state also receives support from spectroscopic studies.[22,23] Comparison of the vapor phase fluorescence quantum yield (Φ_f) values for cyclobutanone, cyclopentanone, cyclohexanone, and acetone (310–320-nm excitation) suggests that all four ketones have the same rate of intersystem crossing to T_1 ($k_{st} \sim 1\text{–}4 \times 10^8$ sec^{-1}). For cyclobutanones, however, Φ_f drops drastically at excitation wavelengths ≤ 313 nm while a more gradual drop occurs at <280 nm for cyclopentanone. The corresponding Φ_f values for cyclohexanone appear to be independent of exciting wavelength. Lee and coworkers[22,23] have interpreted the sharp decrease in Φ_f for cyclobutanone to be due to a competing ring strain facilitated predissociation mechanism from vibrationally excited S_1. This facile predissociation is described as α cleavage of the vibronically excited ketone to form a singlet acyl alkyl biradical which subsequently decomposes to products. From the variation of Φ_f with excitation wavelength, predissociation will effectively compete with intersystem crossing in cyclobutanone when S_1 has ≥ 4 kcal/mol excess vibrational energy. In solution, a similar dependence of Φ_f on excitation wavelength has also been observed.[24] All this evidence for the photoreactivity of the cyclobutanone S_1 state, however, is not totally satisfying since reaction could still occur from a short-lived, unquenchable T_1 state. Further, sensitization in solution results may be ambiguous since suitable triplet sensitizers with $E_T >$ 78 kcal/mol are rare.



R = OTHP

In an attempt to obtain more direct experimental support for the intermediacy of the cyclobutanone S_1 state in the ring expansion reaction, we have examined the sensitized and direct photolyses of the tetrahydropyranyl ketone **34**. A preparative scale direct photolysis afforded the three expected photoproducts **35–37** in analogy with hydroxycyclobutanone **8**.[5] The photoproducts were characterized by spectroscopy and, in the case of cyclic acetals **35**, by independent synthesis from the isomeric acetals **13**. The choice of a suitable triplet sensitizer with $E_T > 78$ kcal/mol to ensure exothermic triplet–triplet energy transfer to **34** precluded the use of commonly employed carbonyl sensitizers (*e.g.*, xanthone and acetophenone). In addition, the ideal sensitizer should have an intersystem crossing quantum yield, Φ_{st}, near unity and a short excited singlet state lifetime (τ_S). As a compromise, *m*-xylene ($\Phi_f = 0.17$ and $\tau_s = 30.8$ nsec in cyclohexane for excitation at 265 nm;[25] $E_T \sim 82\text{–}83$ kcal/mol[26]) was selected as an appropriate sensitizer. In view of a recent report[16] describing the possible interference of singlet–singlet energy transfer with relatively long-lived aromatic hydrocarbon sensitizers, a Stern–Volmer experiment was performed by quenching the fluorescence of *m*-xylene (at 286 nm) in methanol with **34**. This analysis afforded a value of $k_q\tau_s \sim 110\ M^{-1}$. Under the conditions of sensitized photolysis ($1.32 \times 10^{-3}\ M$ in **34**), it can be calculated that singlet–singlet energy transfer will only occur to an extent of 12–13%. Irradiation (254 nm) of methanol solutions of **34** with and without *m*-xylene was performed. Although in both cases all three photoproducts were detected (glpc), quantitative analysis clearly revealed that the extent of decarbonylation to **36** is definitely increased relative to ring expansion to **35** in the presence of *m*-xylene. Specifically, the ratio of **36** to **35** was increased by approximately a factor of 4. Nothing conclusive can be said with regard to the formation of β-cleavage product **37** since it could not be accurately determined under the conditions of analysis. These results lend experimental support to the variety of indirect evidence for S_1 photoreactivity in the ring expansion reactions of saturated cyclobutanones.

Scheme II



Any attempt to put forth a reasonable mechanism to describe the excited state transformations of cyclobutanones, therefore, must account for observations a–f (*vide supra*) and the apparent reactivity of the cyclobutanone S_1 state. For these reasons, we prefer the mechanism in Scheme II. Excitation ($n \rightarrow \pi^*$) of the cyclobutanone ground state (S_0) would initially produce an excited singlet state with excess vibrational energy (S_1^*). From this level the molecule could either be deactivated to the lowest vibrational level of S_1 (*i.e.*, S_1°) by solvent molecules or undergo ring strain facilitated predissociation to a spin-conserved singlet biradical (*i.e.*, **38**). Intersystem crossing from S_1° would produce T_1 which is probably the precursor of decar-

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[21] A. A. Lamola in ref 13, p 86.

[22] J. C. Hemminger and E. K. C. Lee, *J. Chem. Phys.*, **54**, 1405 (1971).

[23] R. G. Shortridge, C. F. Rusbult, and E. K. C. Lee, *J. Amer. Chem. Soc.*, **93**, 1863 (1971).

[24] J. C. Hemminger, C. F. Rusbult, and E. K. C. Lee, *ibid.*, **93**, 1867 (1971).

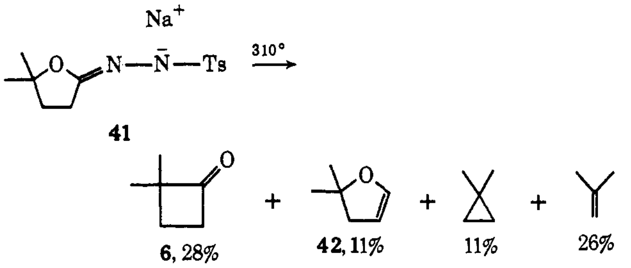
[25] I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," 2nd ed, Academic Press, New York, N. Y., 1971, p 152.

[26] J. B. Birks, "Photophysics of Aromatic Molecules," Wiley-Interscience, New York, N. Y., 1970, p 256.

bonylation products. Consideration of α cleavage to a singlet biradical as the primary photochemical reaction explains the observed photoreactions as logical stabilization paths of **38**. In addition, recyclization of **38** to the ground state ketone nicely accounts for the nonunit quantum efficiencies generally observed. Finally, it should be mentioned that Dowd and coworkers[27] have reported trapping of an intermediate which seemingly supports the intermediacy of a 1,4-acyl alkyl biradical (spin multiplicity unspecified) in the low temperature (−78°) photolyses of cyclobutanone in 1,3-butadiene.

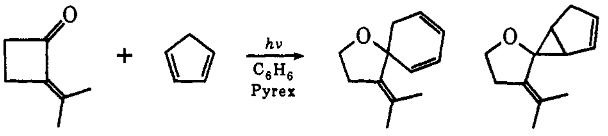
Migration of the γ carbon atom to the electron-deficient acyl oxygen atom (*vide infra*) as suggested by transition state **39** would afford ring expanded oxacarbene **40**, the precursor of the isolated cyclic acetals. Alternatively, **38** could decompose to β cleavage and/or decarbonylation products. Intermediate **38** is perhaps best characterized as a "vitual biradical" or a biradical with a partial bond order between C1–C2 since all photochemical reactions appear to be (1) regiospecific with respect to α cleavage[28] and (2) stereoselective or stereospecific. In addition, partial bonding between C1–C2 would maintain **38** in a favorable conformation for stereoselective ring expansion, stereospecific β cleavage, and recyclization to starting cyclobutanone with minimal nuclear reorganization and without loss of stereochemistry. Alternatively, many of the experimental observations may be explained by a mechanism involving competing, concerted reactions from S_1^*. This mechanism, by avoiding the intermediacy of **38**, however, forces one to consider more primary photochemical steps than are necessary and it still does not adequately account for all observations.

In Scheme II, the transition from **38** to oxacarbene **40** is depicted as an equilibrium. In the absence of suitable carbene trapping agents, this would imply that **40** would revert to **38** or perhaps directly to the cyclobutanone ground state (S_0). Indeed, Agosta and coworkers[29] have observed that the tosylhydrazone salt **41** undergoes thermolysis to afford cyclobutanone **6**, dihydrofuran **42**, isobutylene, and 1,1-dimethylcyclopropane. Presumably, oxacarbene **40** (R = Me) is the precursor of **6** and **42**. Further evidence for an equilibrium between **38** and **40** derives from solvent dependent quantum yield studies. For 2-isopropylidenecyclobutanone (**18**), a ketone which yields only ring expanded carbene derived products in alcoholic media, a substantial decrease in the quantum yield for disappearance of ketone is effected on going from methanol to a hydrocarbon solvent (Table I). That ring expansion does not *require* the presence of an alcohol solvent is demonstrated by the detection and isolation of 1-oxaspiro[4.5]deca-6,8-diene (**43**) from the photolysis of **18** in 1:1 benzene–cyclopentadiene. Product **43**, which was characterized by nmr, ir, and mass spectroscopy (see Experimental Section), is presumably formed from spirocyclopropyl ether **44** during work-up.



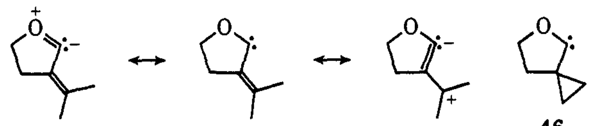
41

6, 28% **42**, 11% 11% 26%



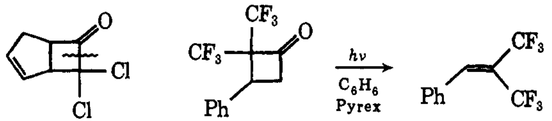
18 **43** **44**

The mechanism presented in Scheme II is also capable of explaining certain substituent effects. If comparisons of ketone **9** with **16** and of **17** with **18** are made with respect to the extent of ring expansion products produced in methanol (Table I), it is readily apparent that a spirocyclopropyl or carbon–carbon double bond substituent attached at an α-carbon position of cyclobutanone causes a greater enhancement of ring expansion. This enhancement may be interpreted as stabilization of the carbene center by way of electron interaction (*e.g.*, **45**), and its overall effect may be to shift the proposed equilibrium between **38** and **40** toward **40**. Similar resonance structures can be written for carbene **46** since it is known that divalent carbon centers interact with adjacent cyclopropane rings.[30]



45 **46**

One final point should be made concerning certain cyclobutanones which do not undergo photochemical ring expansion and their relation to the mechanism in Scheme II. For example, neither tetramethylcyclobutane-1,3-dione,[31] dichloro ketone **47**[32] (α cleavage as indicated), nor 2,2-bis(trifluoromethyl)-3-phenylcyclobutanone (**48**) appears to yield ring expanded products upon photolysis in methanol. Ketone **48**, in fact, undergoes essentially quantitative β cleavage to styrene **49** when irradiated in benzene.[33] In contrast, the dimethyl ketone **50**[34] (α cleavage as indicated) and 2,2-dimethyl-3-phenylcyclobutanone (**51**) undergo ring expansion in yields of 50 and 87%, respectively. These



47 **48** **49**, 94–96%

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[27] P. Dowd, A. Gold, and K. Sachdev, *J. Amer. Chem. Soc.*, **92**, 5724 (1970).

[28] For an exception to this generalization, see R. D. Miller and V. Y. Abraitys, *ibid.*, **94**, 663 (1972); R. D. Miller, D. Dolce, and V. Y. Merritt, Abstracts, IVth IUPAC Symposium on Photochemistry, Baden-Baden, Germany, July 1972.

[29] (a) A. M. Foster and W. C. Agosta, *J. Amer. Chem. Soc.*, **94**, 5777 (1972); (b) A. B. Smith, A. M. Foster, and W. C. Agosta, *ibid.*, **94**, 5100 (1972); (c) A. M. Foster and W. C. Agosta, *ibid.*, **95**, 608 (1973).

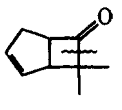
[30] L. Friedman and H. Shechter, *ibid.*, **82**, 1002 (1960).

[31] N. J. Turro, P. A. Leermakers, H. R. Wilson, D. C. Neckers, G. W. Byers, and G. F. Vesley, *ibid.*, **87**, 2613 (1965).

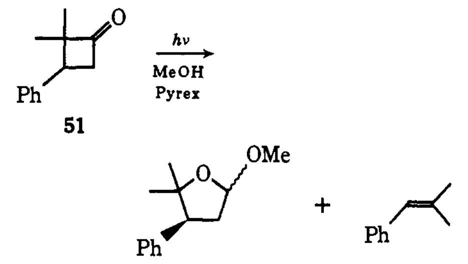
[32] B. E. Kaplan and L. T. Turner, Abstracts, 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, No. ORGN-40.

[33] See footnote 16, ref 9.

[34] H. U. Hostettler, *Tetrahedron Lett.*, 687 (1965).



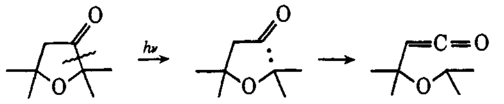
50



51

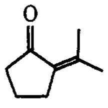
results can be understood if recourse is made to the simple but effective model of the carbonyl n,π^* excited state.[3,35] In this excited state, the model predicts an electron-rich (nucleophilic) region above and below the carbonyl plane and an electron-deficient (electrophilic) and radical-like region in the plane of the carbonyl group. For intermediate **38**, therefore, the migrating center is capable of undergoing migration and concomitant nucleophilic attack on the half-vacant n orbital when R = H or Me, while for R = Cl or CF_3, a corresponding nucleophilic attack on the acyl oxygen atom is not feasible. Instead, **38** appears to be stabilized by β cleavage and/or decarbonylation.

Photochemical Ring Expansion of Cyclopentanones. Our previous attempts to observe ring expanded products from the photolysates of monocyclic cyclopentanones (*e.g.*, cyclopentanone and 2,2,5,5-tetramethylcyclopentanone) were unsuccessful.[5] Only when the five-membered ring is incorporated into a strained tricyclo[2.2.1.0^{2,6}]heptane[6] or bicyclo[2.21]heptane[36] ring system have such products been reported. Yates[6] has suggested that the ring expansion reaction is an inherently inefficient reaction and that structural changes in a molecule which lead to ring expansion do so by rendering competing reactions unfavorable. In an attempt to verify this reasoning, Yates, Joullié, and coworkers have recently reported the results of an investigation of the photochemistry of dihydrofuranone **52**.[37] Previous studies[2] suggested that initial α cleavage would occur exclusively as indicated to produce acyl alkyl biradical **53**. Since aldehyde formation is not possible from **53**, and ketene formation from cyclopentanones has been shown to be inefficient,[38] it was anticipated that **53** would undergo ring expansion. However, no cyclic acetals were detected in the product mixture, and, in fact, all products could be explained as arising from the initially formed ketene **54**.

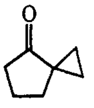


52 **53** **54**

To determine if photochemical ring expansion could be made to occur from specially designed monocyclic cyclopentanones, we have investigated the excited state transformations of 2-isopropylidenecyclopentanone (**55**) and spiro[2.4]heptan-4-one (**56**). It should be emphasized that these molecules are analogous to cyclobutanones **18** and **15** for which ring expansion was found to be significantly enhanced.

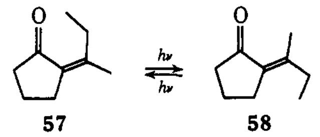


55



56

Irradiation of a methanolic solution of **55** with the full emission from a mercury arc resulted in no observable reaction after 36 hr as determined by glpc and nmr.[39] In analogy with cyclobutanones **27** and **38**, it was felt that rapid rotation about the exocyclic C=C was responsible for facile excited state deactivation. This hypothesis was confirmed by observing the photochemical interconversion of *syn*- and *anti*-2-*sec*-butylidenecyclopentanones **57** and **58**, respectively. Interestingly, the total disappearance of **57** and **58**, during a time interval of irradiation sufficient to cause significant isomerization of initially pure **57** to **58**, was negligible. In the presence of the triplet sensitizers acetophenone (E_T = 74 kcal/mol) or benzophenone (E_T = 69 kcal/mol), isomerization of **57** to **58** occurred with approximately the same efficiency as in the direct photolysis. If it is assumed that the triplet lifetime of benzophenone is 1.9×10^{-6} sec[40] in benzene solution at ambient temperatures, then under the conditions of sensitization (*i.e.*, concentration of **57** = 5.48×10^{-2} *M*; $k_q = 5 \times 10^9$ M^{-1} sec^{-1}) it can be calculated from the standard Stern–Volmer equation[2] that >99% of all benzophenone triplets would be quenched by **57**. Consequently, the fact that the quantum yield for sensitized isomerization is approximately equal to that for direct excitation suggests that Φ_{st} for **57** (and presumably **58**) is close to unity. This high value for Φ_{st} is consistent with the observed unreactivity of ketones **55**, **57**, and **58** toward ring expansion since previous results suggest that triplet state isomerization about exocyclic double bonds in conjugated systems is probably extremely rapid relative to the rates of unimolecular rearrangements.[14,41] The absence of significant ring strain in these ketones in comparison to their cyclobutanone counterparts probably precludes predissociation or α cleavage from their respective S_1 states. Instead, intersystem crossing to the triplet manifold is the predominant, if not exclusive mode of S_1 deactivation.



57 **58**

Having failed to obtain ring expansion products from **55**, **57**, and **58**, the photochemistry of spiro[2.4]heptan-4-one (**56**) was investigated. Unlike the photochemically inert 2-alkylidenecyclopentanones, **56** was cleanly photolyzed to aldehyde **59** and its dimethyl acetal **60** and to cyclic acetal **61**.[5] Although the relative yields of the three products were sensitive to the experimental conditions, cyclic acetal **61** was consistently the major product. These results are also in

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(35) N. J. Turro, J. C. Dalton, G. Farrington, M. Niemczyk, and D. M. Pond, *J. Amer. Chem. Soc.*, **92**, 6978 (1970), and references cited therein.

(36) W. C. Agosta and D. K. Herron, *ibid.*, **90**, 7025 (1968).

(37) G. Hagens, J. P. Wasacz, M. Joullié, and P. Yates, *J. Org. Chem.*, **35**, 3682 (1970).

(38) J. D. Coyle, Ph.D. Thesis, Oxford, 1969, p 73.

(39) An analogous observation has recently been made for 2-cyclopentylidenecyclopentanone: R. C. Cookson and N. R. Rogers, *J. Chem. Soc., Chem. Commun.*, 809 (1972).

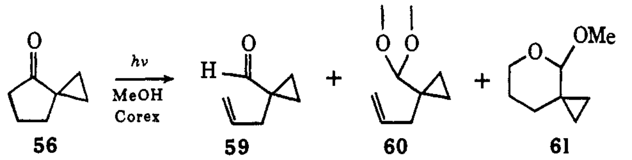
(40) J. G. Calvert and J. N. Pitts, "Photochemistry," Wiley, New York, N. Y., 1966, p 349.

(41) E. F. Ullman and N. Baumann, *J. Amer. Chem. Soc.*, **90**, 4158 (1968).

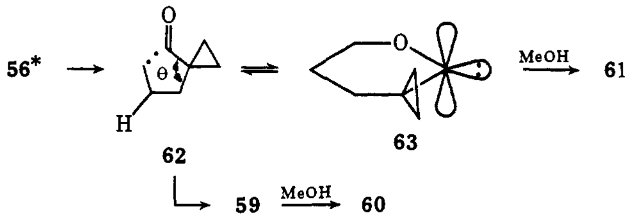
Table II. Quantum Yields[a] and Quenching Data[b] for Cyclopentanones in Methanol[c]

Ketone	Aldehyde	Acetal	$k_q\tau_t$,[d] M^{-1}	$k_q\tau_t$,[e] M^{-1}	τ_t^{-1},[d,f] sec^{-1}	τ_t^{-1},[e,f] sec^{-1}	Φ^d	Φ^e
64a	**65a**		45		4.0×10^8		0.23	
56	**59**	**61**	39	37	4.5×10^8	4.8×10^8	0.16	0.12
64b	**65b**		<0.50		$>3.6 \times 10^{10}$		0.30	
64c	**65c**		0.44		4.0×10^{10}		0.29	

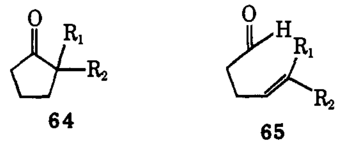
[a] Measured at 313 nm for degassed solutions of ketone (*ca.* 0.1 M) in methanol using benzophenone–benzhydrol actinometry (see Experimental Section). Generally the average of two determinations. Per cent conversion <10%. [b] Determined at 313 nm using purified 1,3-pentadiene as quencher. [c] All samples contained *ca.* 100 mg of anhydrous sodium bicarbonate per 1.75 ml of solution to prevent ketal and acetal formation from carbonyl compounds. [d] For formation of aldehyde. [e] For formation of ring expanded cyclic acetal. [f] Assumes k_q for methanol at 25° is 1.8×10^{10} M^{-1} sec^{-1}.



agreement with the independently reported results of Crandall and Seidewand.[42] In analogy with cyclobutanone and its derivatives, the formation of cyclic acetal **61** from ketone **56** is most satisfactorily explained by a photochemical ring expansion reaction by way of oxacarbene **63**, while the formation of **59**, on the other hand, is a typical reaction of acyl alkyl biradicals (*e.g.*, **62**).[2] Although the formation of **59** does not in itself confirm the intermediacy of biradical **62**, recent results of Cooke and Lyon[43] strongly implicate the existence of such intermediates in the solution phase photochemistries of monocyclic cyclopentanones.



The occurrence of photochemical ring expansion from ketone **56** represents the first example of this rearrangement from a monocyclic cyclopentanone. Initially, it was felt that the formation of acetal **61** provided support for the theory of Yates[6] that ring expansion is an inherently inefficient reaction. Specifically, microwave studies[44] have revealed that the angle between geminal substituents on a cyclopropane ring (*e.g.*, angle θ in **62**) is approximately 116°, and this increase of 7° over the normal tetrahedral angle would increase the separation between the acyl radical portion of **62** and the hydrogen atom on the γ carbon. The expected overall effect of this increased separation would be a decrease in the quantum yield for aldehyde formation from **56** relative to cyclopentanone. This quantum yield decrease was *a priori* expected to be significant since the supposedly inefficient ring expansion reaction is a major reaction from excited **56**, whereas it is not detected to occur at all from cyclopentanone. In addition, it follows from the preceding argument that the quantum yield for formation of acetal **61** should be quite low. Interestingly, kinetic and quantum yield analyses (Table II) reveal that the photochemical ring expansion reaction from **56** is not as inefficient or slow as originally presumed. Although the quantum yield for aldehyde formation from **56** is somewhat smaller than that from the parent ketone **64a**, this decrease in quantum yield is not as large as would be expected if the ring expansion reaction were inherently inefficient. Perhaps even more striking is the observation that the quantum yield for ring expansion of **56** to cyclic acetal **61** is not appreciably smaller than that for formation of aldehyde **59**. Since <1% of 2-methoxytetrahydropyran (the expected ring expansion product from cyclopentanone) could have been detected in the methanol photolysate of **64a**, an upper limit for the quantum yield of ring expansion from **64a** can be set at ≤0.001. While Yates' theory (*vide supra*) may be applicable to the bi- and tricyclic cyclopentanones, the results presented in Table II provide evidence that such is not the case with monocyclic cyclopentanones. Indeed, the incorporation of a spirocyclopropyl group at the α-carbon atom of **64a** (*i.e.*, **56**) *enhances* the photochemical ring expansion reaction to the point where it competes effectively with aldehyde formation.



a, $R_1 = R_2 = H$
b, $R_1 = R_2 = Me$
c, $R_1 = R_2 = -(CH_2)_3-$

Analysis of the rate data presented in Table II provides further evidence that ring expansion is not an inherently inefficient or slow reaction. The results for spiro[3.4]octan-5-one, **64c**, and 2,2-dimethylcyclopentanone, **64b**, are also given for comparison, In addition, the formation of all photoproducts from the cyclopentanone systems studied could be quenched by 3.0 M 1,3-pentadiene, a result which implicates the ketone T_1 states as the reactive precursors of all products.

These findings suggest that the presence of the α-spirocyclopropyl group in **56** *facilitates* bonding between the carbonyl oxygen atom and the alkyl radical center in the hypothetical biradical intermediate **62**. Possible explanations for this enhancement are (1) the larger magnitude of θ in **62** relative to the normal tetrahedral angle, (2) cyclopropylcarbinyl resonance stabilization of the acyl radical portion of **62**, and/or (3) resonance stabilization of oxacarbene intermediate

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(42) J. K. Crandall and R. J. Seidewand, *J. Org. Chem.*, 35, 697 (1970). A recent example of the ring expansion reaction for a bicyclo-[3.2.1]hexanone has been reported: W. G. Dauben, L. Schutte, G. W. Shaffer, and R. B. Gagosian, *J. Amer. Chem. Soc.*, 95, 468 (1973).

(43) R. S. Cooke and G. D. Lyon, *J. Amer. Chem. Soc.*, 93, 3840 (1971).

(44) (a) J. P. Friend and B. P. Dailey, *J. Chem. Phys.*, 29, 577 (1958); (b) R. G. Ford and R. A. Beaudet, *ibid.*, 48, 4671 (1968); (c) F. M. K. Lam and B. P. Dailey, *ibid.*, 49, 221 (1968).

63 which, in analogy to the cyclobutanones, may be in equilibrium with biradical **62**.[29a] It is not immediately obvious that stabilization of the acyl radical portion of **62** would facilitate rearrangement to **63**, nor is it reasonable to assume that the slightly larger value of θ in **62** over the normal tetrahedral angle by itself is responsible for the enhancement in ring expansion observed for **56**. Rather, the results presented in Table II are best explained by the third alternative, *i.e.*, resonance stabilization of oxacarbene intermediate **63**. Electron density donation from the cyclopropane bent bonds to the vacant p orbital on the carbene center in **63** would stabilize the oxacarbene[30] and perhaps favor its formation in equilibrium with **62**. This argument also implies that ring expansion should be the preferred mode of reaction from the 2-alkylidenecyclopentanones, where the cyclopropane ring in **63** is replaced by a double bond. In this case, however, an additional and very much faster reaction occurs, *i.e.*, T_1 deactivation by rotation about the exocyclic double bond prior to α cleavage.

In conclusion, it has been shown that (1) photochemical ring expansion is not an inherently inefficient or slow reaction; (2) ring expansion may occur from monocyclic cyclopentanones as evidenced by the transformation **56** → **61**; (3) ring expansion from **56** occurs by way of T_1, in contrast to analogous cyclobutanones where S_1 is reactive; (4) stabilization of the ring expanded oxacarbene intermediate by an adjacent cyclopropane ring (and presumably an adjacent double bond) appears to be an important driving force in the rearrangement; and (5) ring expansion is not observed for 2-alkylidenecyclopentanones where T_1 is rapidly deactivated.

Experimental Section

Part of the results described in this report have already been published in complete form (see ref 5).

General. All commercial chemicals employed were of reagent or spectrophotometric quality and unless specified were used without further purification. Methanol was refluxed over and distilled from magnesium methoxide. Benzene was washed with concentrated sulfuric acid until discoloration of the acid layer ceased, and it was then refluxed over and distilled from phosphorus pentoxide.

Irradiations for preparative scale reactions were carried out in internally water-cooled reactors (quartz) at 15–25° with a Hanovia Type L-679A-36, 450-W medium-pressure mercury arc. In most cases, irradiations did not utilize the full wavelength range of the mercury arc, and the filter sleeve employed has been designated: Pyrex ($\lambda \geq 300$ nm); Corex ($\lambda \geq 280$ nm); Vycor ($\lambda \geq 220$ nm).

Infrared spectra were recorded on Perkin-Elmer Models 137 and 621 grating spectrophotometers. Nuclear magnetic resonance spectra were taken on Varian A-60A or T-60 spectrometers, and chemical shifts are reported in τ units from internal TMS (τ 10.00). Mass spectra were recorded on a Hitachi Perkin-Elmer RMU-6D mass spectrometer, and ultraviolet spectra were recorded on Cary 14 and Unicam SP 800 spectrophotometers.

Glpc analyses and separations were performed on Aerograph Model 1200 and Model A-90P gas chromatographs and a Hewlett-Packard F&M Model 5750 research gas chromatograph. The following liquid phases were employed: Carbowax 20M (CWX 20 M), XF-1150, FFAP, DC-710, and UC-W98. Chromosorb P (Chrom P), Chromosorb W (Chrom W), firebrick, Anakrom AB, and Diatoport S were employed as supports. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Product yields were determined by either glpc or nmr. Interpretation of glpc results was accomplished by standard calibration techniques; product yields were corrected for variance in detector response.[45]

2,2,4,4-Tetramethyl-3-methylenecyclobutanone (17) was prepared by a modification of the method of Hamon and Lee-Ruff.[46] To 210 g (1.5 mol) of 2,2,4,4-tetramethylcyclobutane-1,3-dione and 140 g (1.5 mol) of aniline in 500 ml of benzene was added 0.5 g of toluenesulfonic acid monohydrate. The solution was stirred at reflux with separation of water for 17 hr. After removal of benzene by atmospheric pressure distillation, reduced pressure distillation afforded 151 g (0.7 mol, 47%) of 2,2,4,4-tetramethyl-3-phenyliminocyclobutanone, bp 85° (0.45 nm), whose infrared spectrum was identical with that reported by Hasek, *et al.*[47] Nmr (CCl$_4$) τ 8.87 (s, 6), 8.60 (s, 6), 3.37–2.56 (m, 5); ir $\nu_{\max}^{\text{film}}$ 1805, 1701, 1600, 1381, 1362 cm^{-1}.

A three-necked, 1000-ml, round-bottom flask equipped with magnetic stirrer, reflux condenser, and N$_2$ inlet was charged with 16.8 g (0.15 mol) of potassium *tert*-butoxide, 100 ml of *tert*-butyl alcohol, and 400 ml of anhydrous ether. After dissolution of the base, 53.6 g (0.15 mol) of methyltriphenylphosphonium bromide was added all at once. The mixture was stirred for 1 hr at ambient temperature under N$_2$. To this yellow mixture was added 16.8 g (0.078 mol) of the above ketophenylimine all at once and stirred for 17 hr at ambient temperature under N$_2$. Excess ether was removed at reduced pressure and the residue was dissolved in 200 ml of *n*-pentane. After the pentane solution was washed with 50% aqueous methanol (2 × 200 ml) and saturated aqueous sodium chloride (2 × 100 ml) and dried over magnesium sulfate, the pentane layer was concentrated and distilled under reduced pressure to afford 13.25 g (0.063 mol, 80%) of 2,2,4,4-tetramethyl-3-phenylimino-1-methylenecyclobutane: bp 66–68° (0.55 mm); mp 46–47.8°: nmr (CCl$_4$) τ 8.91 (s, 6), 8.63 (s, 6), 5.19 (s, 1), 5.08 (s, 1), 3.47–2.67 (m, 5); ir $\nu_{\max}^{\text{film}}$ 1733, 1667 cm^{-1}.

To 37.3 g (0.175 mol) of the above methylenephenylimine was added 300 ml of 60% aqueous acetic acid. The mixture was refluxed for 2 hr, cooled to room temperature, and neutralized with sodium carbonate. The aqueous solution was extracted with ether (3 × 150 ml), and the combined ether fractions were washed successively with 10% aqueous HCl, saturated aqueous sodium bicarbonate, and saturated aqueous NaCl. After the solution was dried over MgSO$_4$ and concentrated at atmospheric pressure, cold crystallization (−78°) afforded 17.5 g (0.127 mol, 72%) of crude ketone **17**. Purification was effected by atmospheric pressure sublimation. The spectral data for **17** agree with published data:[48] nmr (CCl$_4$) τ 8.87 (s, 12), 5.03 (s, 2); ir $\tau_{\max}^{\text{CCl}_4}$ 3040, 1789, 1672, 1453, 1000, 885 cm^{-1}.

4,4,6,6-Tetramethyl-1-oxaspiro[2.3]hexan-5-one (9). To 10.0 g (0.0725 mol) of ketone **17** in 200 ml of methylene chloride was added 20.4 g (0.087 mol) of 85% *m*-chloroperbenzoic acid. The solution was stirred at room temperature for 20 hr. The precipitated *m*-chlorobenzoic acid was removed by filtration, and the filtrate was washed with 10% aqueous Na$_2$SO$_3$ (2 × 200 ml), saturated aqueous sodium bicarbonate (1 × 200 ml), and water (2 × 100 ml). After the filtrate was dried over potassium carbonate, excess methylene chloride was removed by distillation at atmospheric pressure. Cold crystallization (−78°) afforded 6.95 g (0.045 mol; 62%) of crude product, and sublimation at atmospheric pressure (oil bath temperature 75°) gave a pure sample of **9**: mp 66.7–67.9°; nmr (CCl$_4$) τ 8.84 (s, 6), 8.82 (s, 6), 7.14 (s, 2, $J_{^{13}\text{C}-\text{H}}$ = 176 Hz); ir $\nu_{\max}^{\text{CCl}_4}$ 3012, 1783 cm^{-1}; mass spectrum (75 eV) *m/e* (rel intensity) 154 (M$^+$, vw), 110 (21.0), 96 (15.9), 95 (38.4), 81 (89.9), 79 (10.6), 70 (42.1), 56 (50.1), 43 (25.1), 42 (51.1), 41 (100.0), 39 (63.1); uv $\lambda_{\max}^{\text{CH}_3\text{OH}}$ 313 nm (ϵ 21.8).

Anal. Calcd for C$_9$H$_{14}$O$_2$: C, 70.10; H, 9.15. Found: C, 69.84; H, 8.95.

Photolysis of 4,4,6,6-Tetramethyl-1-oxaspiro[2.3]hexan-5-one (9) in Methanol. A 0.31 *M* solution of epoxy ketone **9** in methanol (5 ml) was irradiated for 6 hr (Pyrex filter sleeve). Analysis by glpc (6 ft × 0.25 in. 20% Carbowax 20M on Chromosorb P at 120°) indicated the presence of *cis*- and *trans*-4,4,7,7-tetramethyl-6-methoxy-1,5-dioxaspiro[2.4]heptane (**14**) and 2,2,3,3-tetramethylcyclobutanone. Preparative glpc gave a pure sample of each product. For *cis*-**14** (epoxide and methoxyl oxygen atoms cis): nmr (CCl$_4$) τ 9.34 (s, 3), 8.99 (s, 3), 8.96 (s, 3), 8.82 (s, 3), 7.53 (s, 2), 6.75 (s, 3), 5.61 (s, 1); ir $\nu_{\max}^{\text{CCl}_4}$ 1379, 1366, 1100 (s), 1030 cm^{-1} (s); mass spectrum (75 eV) *m/e* (rel intensity) 186 (M$^+$, vw), 155

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(M^+ − OCH_3, 33.8), 126 (73.0), 96 (64.1), 86 (53.7), 81 (100.0), 71 (42.2), 43 (96.4).

Anal. Calcd for $C_{10}H_{18}O_3$; C, 64.49; H, 9.74. Found: C, 64.72; H, 9.86.

For *trans*-**14**: nmr (CCl_4) τ 9.13 (s, 3), 8.97 (s, 3), 8.90 (s, 3), 8.79 (s, 3), 7.32 (AB quartet, 2), 6.64 (s, 3), 5.57 (s, 1); ir $\nu_{max}^{CCl_4}$ 1376, 1364, 1096 (s), 1029 (s) cm^{-1}; mass spectrum (75 eV) *m/e* (rel intensity) 186 (M^+, vw), 155 (M^+ − OCH_3, 14.9), 154 (M^+ − CH_3OH, 18.1), 126 (43.6), 81 (57.2), 70 (100.0), 43 (75.4).

Anal. Calcd for $C_{10}H_{18}O_3$: C, 64.49; H, 9.74. Found: C, 64.71; H, 9.53.

The third photoproduct, 2,2,3,3-tetramethylcyclobutanone, was characterized by the identity of its infrared spectrum with that of authentic material.[49]

In a separate photolysis employing *trans*-decalin as an internal standard, glpc analysis (6 ft × $^1/_8$ in. 20% UC-W98 on Diatoport S at 80°) indicated the following yields: *cis*-**14** (55%), *trans*-**14** (31%), and 2,2,3,3-tetramethylcyclobutanone (12–14%).

Photolysis of 2,2,4,4-Tetramethyl-3-methylenecyclobutanone (17) in Methanol. A 0.23 *M* solution of methylene ketone **17** in methanol (5 ml) was irradiated (Pyrex filter sleeve) for 6 hr (100% conversion). Glpc analysis (10 ft × $^1/_8$ in. 20% Carbowax 20M on firebrick at 80°) indicated the presence of one major and two minor products. Isolation of the major product by preparative glpc (8 ft × $^3/_8$ in. 20% Carbowax 20M on Chromosorb W at 110°) gave 3,3,5,5-tetramethyl-4-methylene-2-methoxytetrahydrofuran (**21**): nmr (CCl_4) τ 8.93 (s, 3), 8.89 (s, 3), 8.69 (s, 6), 6.72 (s, 3), 5.59 (s, 1), 5.30 (s, 1), 5.25 (s, 1); ir ν_{max}^{film} 3058, 1645, 1468, 1361, 1193, 1096 (s), 1034 (s), 976, 889 cm^{-1}.

Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.65. Found: C, 70.73; H, 10.74.

The two minor products could not be isolated in pure form since they eluted at approximately the same retention time as the solvent (see following experiment). In a separate experiment, a glpc mass balance determination revealed that acetal **21** was formed in 89% yield.

Photolysis of 2,2,4,4-Tetramethyl-3-methylenecyclobutanone (17) in Diethyl Ether. A 0.71 *M* solution of ketone **17** in ether (1.0 ml) was irradiated (Pyrex filter sleeve) for 3 hr (50% conversion). Glpc analysis (6 ft × $^1/_8$ in. 20% UC-W98 on Diatoport S at 100°) indicated the formation of two major products of short retention time, which coinjected with the two minor products of the methanol photolysis (see above experiment). Preparative glpc (6 ft × 0.25 in. 20% UC-W98 on Chromosorb W at 50°) purification of both products (collected as a mixture) gave 1,1,2,2-tetramethyl-3-methylenecyclopropane and 1,1-dimethyl-2-isopropylidenecyclopropane: nmr (CCl_4) τ 9.23 (m, 2, cyclopropyl), 8.88 and 8.86 (2 singlets, 18), 8.28 (m, 6, allylic methyl groups), 4.91 (s, 2, exo methylene). The peaks at τ 9.23, 8.86, and 8.28 agree with the published nmr spectrum of 1,1-dimethyl-2-isopropylidenecyclopropane:[50] ir $\nu_{max}^{CCl_4}$ 3059 (w), 3027 (w), 1783 (w), 1741 (w), 1370, 890 cm^{-1}.

syn- **and** *anti*-**2**-*sec*-**Butylidenecyclobutanones, 28 and 27,** were prepared by a modification of the method of Conia and Sandré.[12] Reaction of 4.35 g (0.062 mol) of cyclobutanone,[6] 17.47 g (0.243 mol) of 2-butanone, and 45 ml of 1 *N* aqueous NaOH for 42 hr was carried out with stirring at room temperature in a closed vessel. Following neutralization with concentrated HCl, the yellow-orange organic phase was decanted and the aqueous phase extracted with ether (2 × 100 ml). The combined organic fractions were washed with H_2O (2 × 100 ml), dried over $MgSO_4$, and concentrated at reduced pressure. Fractional distillation at reduced pressure gave 2.45 g (0.020 mol, 32%) of a 1:1 mixture of ketones **27** and **28**, bp 80–85° (11 mm). Purification was effected by preparative glpc (8 ft × 0.25 in. 20% FFAP on Chromosorb W at 140°). For **27** (anti isomer): nmr (CCl_4) τ 8.92 (t, 3, J = 7 Hz), 7.99 (t, 3, J = 1.5–2 Hz), 7.93 (q, 2, J = 7 Hz), 7.36 (m, 4); ir $\nu_{max}^{CCl_4}$ 1748, 1736, 1667, 1095 cm^{-1}; mass spectrum (75 eV) *m/e* (rel intensity) 124 (M^+, 60.5), 81 (100.0), 67 (64.0), 53 (30.9); uv spectrum $\lambda_{max}^{n\text{-}C_6H_{14}}$ 347 nm (ϵ 72.5), $\lambda_{max}^{C_6H_6}$ 342 nm (ϵ 71.3), $\lambda_{max}^{CH_3OH}$ 329 nm (ϵ 77.1).

Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 76.77; H, 9.76.

For **28** (syn isomer): nmr (CCl_4) τ 8.98 (t, 3, J = 7.5 Hz), 8.27 (t, 3, J = 1 Hz), 7.4 (m, 6); ir $\nu_{max}^{CCl_4}$ 1754, 1739, 1667, 1099 cm^{-1}; mass spectrum (75 eV) *m/e* (rel intensity) 124 (M^+, 69.0), 81 (100.0), 67 (80.0), 53 (37.5); uv spectrum $\lambda_{max}^{n\text{-}C_6H_{14}}$ 347 nm (ϵ 66.5), $\lambda_{max}^{C_6H_6}$ 342 nm (ϵ 66.5), $\lambda_{max}^{CH_3OH}$ 330 nm (ϵ 69.7).

Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 76.90; H, 9.92.

The assignment of syn and anti configurations was determined by nmr precedent.[51]

Photolysis of *syn*- **and** *anti*-**2**-*sec*-**Butylidenecyclobutanones, 28 and 27, in Methanol.** A 2.5% solution of a 1:1 mixture of ketones **27** and **28** in methanol (20 ml) was irradiated (Pyrex filter sleeve) for 4 hr (100% conversion). The crude photolysate was concentrated under reduced pressure and subjected to preparative glpc (8 ft × 0.25 in. 20% FFAP on Chromosorb W at 131°). Only two products, *syn*- and *anti*-3-*sec*-butylidene-2-methoxytetrahydrofuran, were detected and collected with partial decomposition. For **29** (anti acetal): nmr (CCl_4) τ 9.00 (t, 3, J = 7 Hz), 8.33 (t, 3, J = 2 Hz), 7.97 (q, 2, J = 7 Hz), 7.61 (t, 2, J = 6–6.5 Hz), 6.73 (s, 3), 6.11 (t, 2, J = 6–6.5 Hz), 4.92 (s, 1); ir ν_{max}^{film} 1704 (w), 1381, 1359, 1332, 1114, 1086, (s), 1075 (s), 1063 (s), 1036 (s), 986, 974, 957, 939 cm^{-1}. For **30** (syn acetal): nmr (CCl_4) τ 9.02 (t, 3, J = 7 Hz), 8.35 (broad s, 3), 7.97 (q, 2, J = 7 Hz), 7.63 (t, 2, J = 6–6.5 Hz), 6.74 (s, 3), 6.13 (t, 2, J = 6–6.5 Hz), 4.89 (s, 1); ir ν_{max}^{film} 1704 (w), 1379, 1351, 1332, 1114 (s), 1085 (s), 1064 (s), 1036 (s), 975, 953, 938 cm^{-1}.

In a separate experiment, photolysis of a 1:1 mixture of **27** and **28** in methanol was carried out in a sealed nmr tube. Only peaks corresponding to **29** and **30** were detected. Microdistillation of the methanol photolysates at 20 mm gave >90% isolated yields of **29** and **30**.

Photolysis of 2,2,4,4-Tetramethyl-3-(tetrahydropyran-2′-yloxy)cyclobutanone (34). A 0.22 *M* solution of ketone **34**[52] in methanol (20 ml) was irradiated (Pyrex filter) for 2 hr (100% conversion). Three major volatile products, 2-methyl-1-(tetrahydropyran-2′-yloxy)propene (**37**), 2,2,3,3-tetramethyl-1-(tetrahydropyran-2′-yloxy)cyclopropane (**36**), and *cis*- and *trans*-3,3,5,5-tetramethyl-2-methoxy-4-(tetrahydropyran-2′-yloxy)tetrahydrofuran (**35**), were detected and collected by preparative glpc (6 ft × 0.25 in. 20% UC-W98 on Chromosorb W at 180°). For **37**: nmr (CCl_4) τ 8.35 (m, 12), 5.23 (m, 1, acetal H), 4.08 (m, 1, vinyl H); ir ν_{max} 1695, 1160, 1040, 976 cm^{-1}. For **36**: nmr (CCl_4) τ 9.03, 9.00, 8.96 (3 s, 12), 8.36 (m, 6), 7.17 (s, 1), 5.86–6.79 (m, 2), 5.53 (s, 1); ir ν_{max} 1372, 1351, 1143, 1130, 1087 (s), 1035 (s), 966 (s), 911, (s) cm^{-1}. For **35** (both cis and trans isomers eluted as a single peak): nmr (CCl_4) τ 9.08, 9.01, 8.98, 8.94, 8.88, 8.83, 8.75, 8.72., 8.70 (10, s, 12 H total); 8.36 (bd m, 6 H); 6.75 (s, OCH_3 *cis*-**35**); 6.73 (s, OCH_3 *trans*-**35**) (3, H total); 6.51 (bd m), 6.21 (s); 6.12 (s), 6.9–5.9 (bd m) (3 H total), 5.78, 5.75 (2s, 1 H, THF acetal (proton); 5.48 (bd m, 1 H, THP acetal proton); ir ν_{max} 1379, 1362, 1135, 1121, 1096 (s), 1079 (s), 1030 (vs), 972 (s) cm^{-1}. The structures of acetals **35** were confirmed by independent synthesis (see following experiment).

cis- **and** *trans*-**3,3,5,5-Tetramethyl-2-methoxy-4-(tetrahydropyran-2′-yloxy)tetrahydrofuran (35).** To 0.0974 g (0.56 mmol) of *trans*-3,3,5,5-tetramethyl-2-methoxy-4-hydroxytetrahydrofuran[5] was added 0.3 ml of 2,3-dihydropyran and a single small crystal of *p*-toluenesulfonic acid monohydrate. After 2 hr at room temperature, the reaction mixture was neutralized with solid sodium bicarbonate. Purification by preparative glpc (6 ft × 0.25 in. 20% UC-W98 on Chromosorb W at 180°) gave *trans*-**35** as the only detectable product: nmr (CCl_4) τ 9.01, 8.98, 8.94, 8.88, 8.83, 8.70 (6 s, 12 H total), 8.36 (bd m, 6), 6.73 (s, 3, OCH_3), 6.9–5.9 (bd m, 2), 6.21 and 6.12 (2 s, 1 H total), 5.78 (s, 1, THF acetal proton), 5.48 (bd m, 1, THP acetal proton); ir ν_{max} 1381, 1364, 1098 (s), 1080 (s), 1031 (vs), 978 (s) cm^{-1}. This material had the same glpc retention time (above conditions) as the mixture of *cis*- and *trans*-**35** from the photolysis of ketone **34** in methanol (see previous experiment).

An identical reaction was carried out with an authentic sample of *cis*-3,3,5,5-tetramethyl-2-methoxy-4-hydroxytetrahydrofuran.[5] Preparative glpc (above conditions) gave a mixture of *cis*- and *trans*-**35**, the nmr spectrum and glpc retention time of which were identical with those for the photochemically derived isomer mixture with the exception that the cis:trans ratio was different. Acid-catalyzed epimerization prevented the isolation of pure *cis*-**35** in this instance.

Photolysis of 2-Isopropylidenecyclobutanone (18) in Cyclopen-

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tadiene–Benzene. A 0.138 *M* solution of **18** in cyclopentadiene–benzene (1:1, 20 ml) was irradiated (Pyrex filter sleeve) for 6 hr. The photolysate was concentrated at reduced pressure and purified by preparative tlc on silica gel (methylene chloride) to afford two major products. The higher R_f product appeared to undergo silica gel catalyzed decomposition and was not characterized. The lower R_f fraction was obtained in a pure state and characterized as 4-isopropylidene-1-oxaspiro[4.5]deca-6,8-diene (**43**): nmr (CCl_4) τ 8.43 (s, 3), 8.27 (s, 3), 7.55 (t, J = 7 Hz, 2), 7.12 (s, 2), 6.23 (t, J = 7 Hz, 2), 4.88 (s, 1), 3.7–3.8 (m, 3); ir $\nu_{max}^{CCl_4}$ 3039–3030, 1372, 1364, 1050 (s), 677 (s) cm^{-1}; mass spectrum (75 eV) *m/e* (rel intensity) 176 (M^+, 66.4), 161 (100.0), 135 (39.4), 134 (25.6), 133 (48.4); uv spectrum $\lambda_{max}^{n\text{-}C_6H_{14}}$ 221 nm (ϵ 1980), 253 (ϵ 2440).

Photolysis of 2,2-Bis(trifluoromethyl)-3-phenylcyclobutanone (48) in Benzene. A 0.147 *M* solution of **48**[53] in benzene (5 ml) was irradiated for 4 hr. Analysis by glpc (6 ft × 1/8 in. 20% UC-W98 on Diatoport S at 96° for 10 min, then temperature programmed to 120° at 20°/min) indicated the formation of β,β-bis(trifluoromethyl)styrene (**49**), as the single major product: nmr (CCl_4) τ 2.62 (s, 5), 2.41 (bd, s, 1); $\nu_{max}^{CCl_4}$ 1664, 1403, 1299, 1280, 1236, 1192, 1163, 975 cm^{-1}; mass spectrum (75 eV) *m/e* (rel intensity) 240 (M^+, 100.0), 171 ($M^+ - CF_3$, 34.8), 151 ($M^+ - CF_3 - HF$, 72.1); metastable peaks at *m/e* 122 (240 → 171) and 133.5 (171 → 151).

A separate experiment utilizing *trans*-decalin as a glpc internal standard indicated that styrene **49** was formed in 94–96% yield. Photolysis of **48** in methanol is complicated by a competing dark reaction;[54] however, control experiments show that styrene **49** is still the single major photoproduct formed.

Photolysis of 2,2-Dimethyl-3-phenylcyclobutanone (51) in Methanol. A 0.08 *M* solution of **51**[55] in methanol (5 ml) was irradiated (Pyrex filter sleeve) for 12 hr (100% conversion). Purification by preparative glpc (6 ft × 0.25 in. 20% DC-710 on Anakrom AB at 180°) gave *cis*- and *trans*-5,5-dimethyl-4-phenyl-2-methoxytetrahydrofuran as an inseparable mixture of isomers and β,β-dimethylstyrene. For the 2-methoxytetrahydrofurans: nmr (CCl_4) τ 9.28 and 8.60 (2s, 3 H each, methyl groups on trans isomer), 9.06 and 8.76 (2s, 3 H each, methyl groups on cis isomer), 7.33–8.00 (m, 2), 6.69 (s, 3, OMe of trans isomer), 6.66 (s, 3, OMe of cis isomer), 5.02 (m, 2, acetal protons of both isomers), 2.84 (s, 5, aryl protons of trans isomer), 2.80 (s, 5, aryl protons of cis isomer); ir ν_{max}^{film} 1451, 1364, 1099 (s), 1035 (s), 978 (s), 757, 698 cm^{-1}.

Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.79. Found: C, 75.85; H, 8.72.

For β,β-dimethylstyrene: nmr (CCl_4) τ 8.18 (d, J = 1.5 Hz, 3), 8.12 (d, J = 2 Hz, 3), 6.27 (m, 1), 2.8 (s, 5). These values are in excellent agreement with the reported spectrum of this compound.[56]

In a separate experiment, a mass balance determination was performed by nmr. Since all products contained one phenyl substituent, integration of the methyl group signals for each product relative to the entire aromatic region allowed the percentage of each product to be determined: cis acetal (32%), trans acetal (50%), β,β-dimethylstyrene (15%).

***syn*- and *anti*-2-*sec*-Butylidenecyclopentanones, 57 and 58.** A 1000-ml flask was charged with cyclopentanone (42 g, 0.5 mol), 2-butanone (108 g, 1.5 mol), 1 *N* aqueous sodium hydroxide (300 ml), and enough ethanol to make the reaction mixture homogeneous. After the mixture was stirred in a closed vessel at room temperature for 48 hr, the reaction mixture was neutralized with concentrated HCl. The organic fraction was separated and the aqueous fraction extracted with ether (2 × 100 ml). The combined organic fractions were washed with water, dried over $MgSO_4$, and concentrated at reduced pressure. Distillation at reduced pressure gave 6.5 g (0.047 mol, 10%) of a 1:1 mixture of syn and anti ketones **57** and **58**, bp 102–104° (25 mm), which could be purified by preparative glpc (20 ft × 0.25 in. 20% XF-1150 on Chromosorb W at 150°). For **57**: nmr (CCl_4) τ 9.01 (t, J = 7 Hz, 3), 8.5–7.1 (complex m, 8), 8.21 (t, J = 1 Hz, 3); ir $\nu_{max}^{CCl_4}$ 1707, 1628 cm^{-1}; uv spectrum $\lambda_{max}^{C_6H_6}$ 338 nm (ϵ 47), 350 (47).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.16; H, 10.27.

For **58**: nmr (CCl_4) τ 8.95 (t, J = 7 Hz, 3), 8.5–7.1 (complex m, 8), 7.87 (t J = 2 Hz, 3); ir $\nu_{max}^{CCl_4}$ 1709, 1626 cm^{-1}; uv spectrum $\lambda_{max}^{C_6H_6}$ 338 nm (ϵ 54), 350 (56).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.27; H, 10.16.

Photolysis of *syn*-2-*sec*-Butylidenecyclopentanone (57) in Methanol. A 0.626 *M* solution of **57** in methanol (10 ml) containing *trans*-decalin (glpc internal standard) was irradiated at 313 nm. Periodic analysis by glpc (6 ft × 1/8 in. 20% UC-W98 on Diatoport S at 107°) revealed that extensive isomerization of **58** had occurred after 3 hr and that conversion of **57** + **58** to products was negligible.

In a separate experiment, photolysis of **57** (Pyrex filter sleeve) for 36 hr resulted only in isomerization to **58**. No other products were detected.

Photolysis of 2,2-Dimethylcyclopentanone (64b) in Methanol. A 5% solution of **64b**[57] in methanol (10 ml) containing *ca.* 200 mg of anhydrous sodium bicarbonate was irradiated (Pyrex filter sleeve) for 6 hr. Isolation of the single major photoproduct by preparative glpc (6 ft × 0.25 in. 20% CWX 20M on Chromosorb P at 130°) gave 5-methyl-4-hexenal (**65b**): nmr (CCl_4) τ 8.38 (s, 3), 8.33 (s, 3), 7.7 (m, 4), 4.98 (broad s, 1), 0.26 (s, 1); ir $\nu_{max}^{CCl_4}$ 2825, 2725, 1736 cm^{-1}. These values are in good agreement with the reported spectra.[58]

Photolysis of Spiro[3.4]octan-5-one (64c) in Methanol. A 2.7% solution of **64c**[59] in methanol (1.85 ml) containing *ca.* 100 mg of anhydrous sodium bicarbonate was irradiated (Pyrex filter sleeve) for 7 hr. Analysis of glpc (10 ft × 1/8 in. 20% CWX 20M on Chromosorb P at 150°) indicated the formation of 4-cyclobutylidenebutanal (**65c**) as the only detectable photoproduct: nmr (CCl_4) τ 8.65–7.13 (m, 10), 5.01 (m, 1), 0.29 (t, J = 1 Hz, 1); ir $\nu_{max}^{CCl_4}$ 2801, 2717, 1730 cm^{-1}; mass spectrum (75 eV) *m/e* (rel intensity) 124 (M^+, 20.4), 96 (50.0), 95 (50.0), 81 (45.7), 79 (71.8), 68 (52.4), 67 (100.0), 53 (55.0), 41 (69.2), 39 (74.4).

Apparatus Utilized in Quantum Yield, Sensitization, and Kinetic Analyses. A merry-go-round apparatus and a 313-nm filter solution were employed in all studies which required the simultaneous monochromatic irradiation of several samples to ensure that each was exposed to the same light intensity. This apparatus has been previously described.[60]

Samples were made up in 5- or 10-ml volumetric flasks and 1.75-ml aliquots of these solutions were transferred to 10 × 75 mm Pyrex test tubes. For irradiations where it was not necessary to degas, the samples were stoppered with serum caps. For irradiations where it was necessary to degas the samples, each 10 × 75 mm test tube was fused to a 10/30 male joint, attached to a mercury-free vacuum line (oil diffusion pump), and degassed by the freeze–pump–thaw procedure at pressures near 5 μ. Three such degassing cycles were performed before the sample tube was sealed.

Actinometry. To measure the number of quanta of radiation absorbed by the sample solutions, the benzophenone–benzhydrol chemical actinometer was used.[61] A standard solution *ca.* 0.0500 *M* in benzophenone and *ca.* 0.1000 *M* in benzhydrol was prepared in purified benzene. Six samples were then prepared by transferring 1.75-ml aliquots of this solution to each of six 10 × 75 mm Pyrex test tubes. All six tubes were then degassed by five freeze–pump–thaw cycles (*vide supra*) and sealed at liquid nitrogen temperature with the stopcocks open to the vacuum. Following irradiation (*ca.* 15–20 min for intensities of 2–6 × 10^{17} quanta/min), each actinometer sample was diluted 1 to 10 with benzene and the optical density at 343 nm was measured. Comparison with unphotolyzed samples allows the number of moles of benzophenone consumed to be calculated. The quantum yield for consumption of benzophenone (Φ_{-B}) is determined from eq 3[61] where $[BH_2]$ is

$$\Phi_{-B} = (1 + 0.033/[BH_2])^{-1} \tag{3}$$

the average concentration of benzhydrol. The latter quantity is calculated by assuming that each mole of benzophenone reduced corresponds to 1 mol of benzhydrol consumed. Substitution of Φ_{-B} from eq 3 into eq 4[61] allows the lamp intensity (I) to be calculated.

$$I = (\Delta B)(6.02 \times 10^{23})/(t)(\Phi_{-B}) \tag{4}$$

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[53] We thank Dr. C. G. Krespan (E. I. du Pont de Nemours and Co.) for a generous sample of this compound.

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In this equation, ΔB is the number of moles of benzophenone consumed and t is the time interval of irradiation.

General Procedure for Quantum Yield Analyses. To ensure that the sample and actinometer solutions absorbed equal amounts of the 313-nm radiation, solutions of ketone (1.75 ml) were made up such that the optical densities of the solutions at 313 nm were >2.0 (>99% of the light at 313 nm absorbed). In some instances, these optical densities were <2.0 at 313 nm, and, as a result, the final quantum yields were corrected to 100% absorption. All samples were irradiated to low conversion (<10%).

The quantum yield for product formation (Φ_P) was determined from eq 5 where ΔP is the number of moles of product formed, and t

$$\Phi_P = (\Delta P)(6.02 \times 10^{23})/(t)(I) \qquad (5)$$

and I are irradiation time and source intensity (*vide supra*). The quantity ΔP was determined by uv, nmr, or glpc, and the limits of error on quantum yield calculations are estimated at ±10–20%.

General Procedure for Sensitization Reactions. Solutions of sensitizer and ketone were prepared such that the sensitizer absorbed >90–100% of the incident radiation at 313 nm. In most cases, a second solution was prepared containing ketone but with no sensitizer. For each solution the total optical density was >2.0.

For most experiments, samples were transferred to 10 × 75 mm Pyrex test tubes and thoroughly degassed by three freeze–pump–thaw cycles and sealed. Samples were then irradiated in parallel at 313 nm and analyzed for product formation by glpc, uv, or nmr. For the sensitized irradiation of ketone **34** with *m*-xylene, irradiation was carried out at 254 nm with low-pressure mercury lamps.

General Procedure for Quenching Experiments. Solutions of ketone in an appropriate solvent were prepared as described above for quantum yield determinations except that varying amounts of 1,3-pentadiene (purified by bulb-to-bulb distillation on a vacuum line) were added to the solutions. Four to six solutions containing different concentrations of quencher were usually prepared, in addition to blanks containing no quencher. Equal aliquots of each solution were transferred to 10 × 75 mm Pyrex test tubes which were stoppered and irradiated in parallel. Product formation was measured by glpc and the Stern–Volmer analyses were repeated at least once to afford averaged values of $k_q\tau_t$. The limits of error for $k_q\tau_t$ are estimated at ±10%. Fluorescence quenching experiments were carried out in similar fashion except that fluorescence intensities were measured with a Hitachi Perkin-Elmer MPF-2A spectrofluorimeter.

Photochemical Reactivity of Keto Imino Ethers. IV.[1] Type I and Type II Reactions

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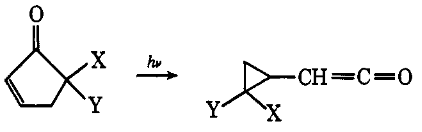
Abstract: The photochemical reactivity of 2-ethoxypyrrolin-5-one (**1**), 6-ethoxy-4,5-dihydro-2(3*H*)-pyridone (**2a**), and 6-propoxy-4,5-dihydro-2(3*H*)-pyridone (**2b**) is described. Irradiation of **1** in *tert*-butyl alcohol solvent gave 2-methyl-2-propyl *N*-(ethoxycyclopropyl)carbamate (**3**). When the irradiation was conducted in tetrahydrofuran solvent, a precursor, ethoxycyclopropyl isocyanate, was isolated. A mixture of glutarimide (**7**) and (*Z*)-2-methyl-2-propyl *N*-(ethoxyethylidene)carbamate (**5a**) was obtained from the irradiation of **2a** in *tert*-butyl alcohol solvent. With **2b**, glutarimide, (*Z*)-2-methyl-2-propyl *N*-(propoxyethylidene)carbamate (**5b**), and (*E*)-2-methyl-2-propyl *N*-(propoxyethylidene)carbamate (**6b**) were formed. Neither **2a** nor **2b** reacted with dimethoxyethene or cyclohexene in the 2 + 2 cycloaddition reaction. Formation of carbamates **3**, **5a**, **5b**, and **6b** is discussed in terms of the Norrish type I mechanism, and formation of glutarimide, in terms of the Norrish type II mechanism. Evidence is presented which suggests that **1** and **2a** react from the n,π* singlet state.

The Norrish type I reaction[2] or α cleavage is a common photochemical reaction of saturated ketones. Cleavage of medium ring alkanones gives enals and/or ketenes *via* intermediate biradicals. The reaction occurs predominantly from the triplet excited state, although the first excited singlet has also been implicated.[3] For cyclic α,β-unsaturated ketones, photocycloaddition is generally so competitive that α cleavage is not observed.[4] 2-Cyclopentenones substituted in the 5 position, however, have recently been shown to preferentially α-cleave in dilute solution giving cyclopropyl ketenes among other products.[5] These reactions have been shown to occur under sensitized conditions; however, the details of the mechanism are still unknown. In this report we will describe



X = Y = Ph
X = Y = CH_3
X = C_2H_5; Y = H
X = n-C_3H_7; Y = H
X = OC_2H_5; Y = H

the photochemical type I cleavage of cyclic keto imino ethers which structurally resemble 2-cyclopentenone and 2-cyclohexenone. In these examples, α cleavage occurs to the complete exclusion of photodimerization or cycloaddition to olefins.

While Norrish type II photoreactions[2] have been reported for aliphatic,[6] aromatic,[6] and α,β-unsaturated

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