THE PHOTOCHEMICAL RING EXPANSION OF CYCLIC KETONES*

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Summary

The photochemical conversion of cyclic ketones in alcoholic solution to ring-expanded cyclic acetals was first observed in the cases of cyclocamphanone and nortricyclanone. This reaction has subsequently been shown to be general for cyclobutanones. It has not been observed for simple cyclopentanones, but occurs with some, but not all, bicyclo [2.2.1]-heptan-2-ones and with cyclopentanones having a α-cyclopropyl ring. It has not been observed for any carbocyclic ketone with a six-membered or larger ring. The reaction is considered to proceed *via* a cyclic oxacarbene, which is formed in the case of five-membered cyclic ketones by α-cleavage followed by carbon–oxygen bond formation in the resulting alkyl acyl biradical. It is proposed that the ring expansion of cyclic ketones to cyclic acetals is dependent upon structural features that either facilitate oxacarbene formation, *e.g.*, an α-cyclopropyl ring, and/or inhibit competing reactions, *e.g.*, enal formation.

Introduction

The photolysis of cyclocamphanone (I) in hydroxylic solvents was investigated by Yates and Kilmurry more than a decade ago. The reasons for this undertaking are lost in the mists of history, but we were fortunate to observe a novel photochemical reaction of a cyclic ketone-ring expansion to a cyclic acetal (II)** [1].
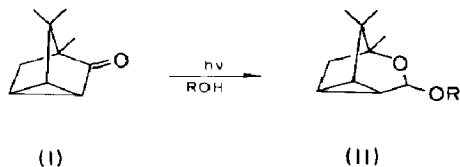

(I)   (II)

**A mixture of anomeric acetals was obtained; such mixtures are here depicted by single structures without designation of configuration at the anomeric carbon atom.

Since most of the photochemical reactions of cyclic ketones observed theretofore had involved α-cleavage (Norrish type 1 reaction) as the primary chemical step [2], we were led to postulate that II arises *via* α-cleavage of I to form III followed by rebonding to give the oxacarbene IV, which reacts with the solvent to give II [1, 3]. We then corroborated this view by the demonstration that photolysis of I in cyclohexene gives V [3].
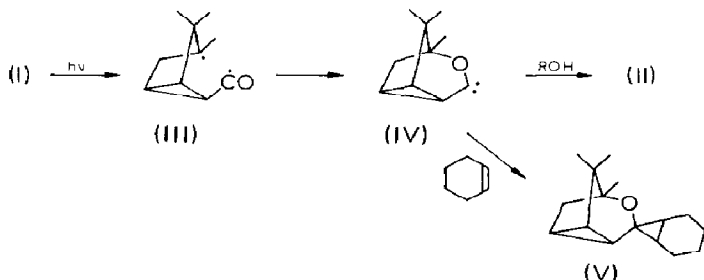

A similar photochemical reaction was observed in the case of nortricyclanone (VI) in ethanolic solution; however, in methanolic solution the ketal VII is formed [4]. This was shown to result from the formation of an acidic product during the photolysis [5], since irradiation in the presence of sodium carbonate gives the acetal VIII, analogous to II*:
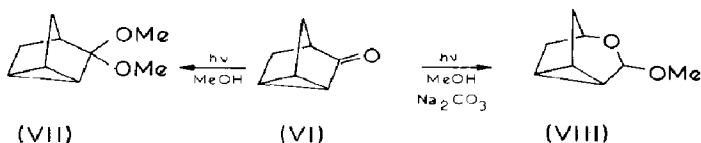

Structural requirements

Shortly after the publication of our observations on the photo-chemistry of I, a number of other cases of photochemical ring expansion of cyclic ketones in alcoholic solution to cyclic acetals were reported; most of these involved cyclobutanones, for which this reaction is general [6 - 8]. Thus, Turro and coworkers [9] have observed the following transformations:
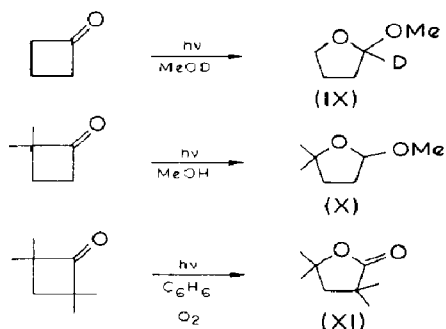

*Many of the photolyses in methanolic solution described in the sequel were carried out in the presence of sodium carbonate or bicarbonate in order to inhibit ketalization.

Irradiation of cyclobutanone in methanol gives a cyclic acetal together with cleavage and decarbonylation products. Reaction in methanol-*d* gives IX, lending support to the intermediacy of an oxacarbene and excluding the possibility that the acetal is formed *via* a vinyl ether. Irradiation of 2,2-dimethylcyclobutanone in methanol gives the acetal X illustrating the fact that ring expansion of unsymmetrically substituted ketones usually occurs regiospecifically, carbon–carbon bond cleavage occurring at the more highly substituted α-carbon atom. Irradiation of 2,2,4,4-tetramethylcyclobutanone in benzene in the presence of oxygen gives XI, which is also considered to be formed *via* an oxacarbene; an analogous product is formed from I [4].

Quinkert and coworkers [10] have thrown further light on the photochemical ring expansion of cyclobutanones by the demonstration of retention of configuration at the α-carbon atom at which cleavage occurs (cf. [9]). They have observed that XII and XIII give XIV and XV, respectively; these products are formed without allylic rearrangement whereas the formation of the decarbonylation products XVI and XVII involves such rearrangement.
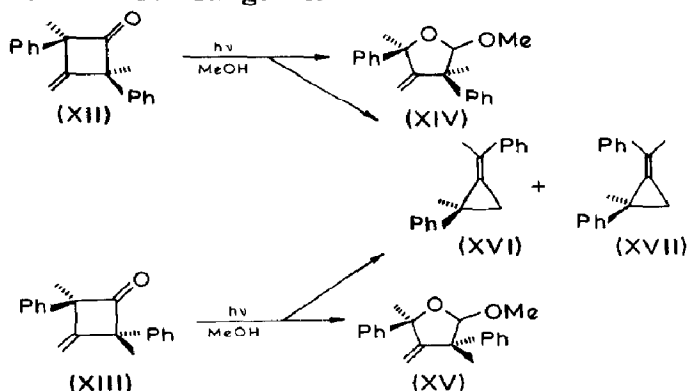

We have investigated the photochemistry of two bridged cyclobutanones. Irradiation of XVIII gives the products shown below [11]:
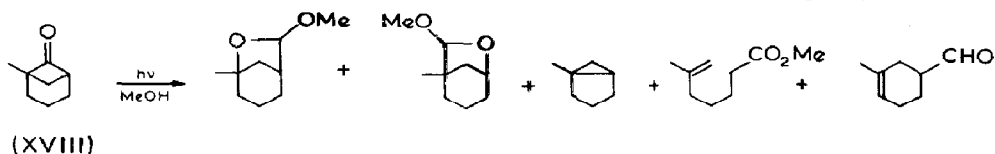

As usual, the products include cyclic acetals; however, this represents an unusual case where ring expansion is not regiospecific [12]. Irradiation of XIX gives products that include the expected cyclic acetal and also the unsaturated ketone XX, whose formation may possibly involve a rare β-cleavage to form XXI followed by intramolecular hydrogen transfer [13].

(XXI)
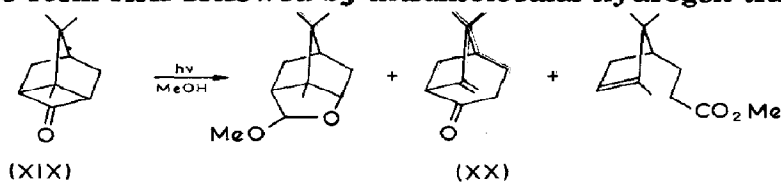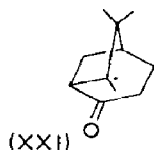
Although the photochemical ring expansion reaction has been found to be common for cyclobutanones, no five-membered or larger *monocarbo-cyclic* ketone has been observed to undergo this reaction. We have re-examined the photolysis in methanol of several such ketones, *e.g.*, cyclopentanone and cyclohexanone, but have failed to obtain any evidence for the formation of cyclic acetals by examination of the ^{1}H n.m.r. spectra of the crude photolyzates [14].

We then turned to an investigation of the photochemistry of various bicyclo[2.2.1]heptan-2-ones in methanol [14]. 2-Norbornanone (XXII) and 1-methyl-2-norbornanone (XXIII) give only the enals XXIV and XXV, respectively, arising *via* α-cleavage of the C(1)–C(2) bond followed by intramolecular hydrogen transfer of the *syn*-C(7) hydrogen atom rather than the *endo*-C(6) hydrogen atom (*vide infra*). The 3-*endo*- and 3-*exo*-methyl-2-norbornanones (XXVI and XXVII) undergo both C(2)–C(3) bond cleavage, leading to their interconversion, and also C(1)–C(2) bond cleavage, giving a diastereomeric mixture of enals XXVIII.

(XXII). R = H   (XXIV). R = H
(XXIII). R = Me   (XXV). R = Me

(XXVI)   (XXVII)

(XXVIII)
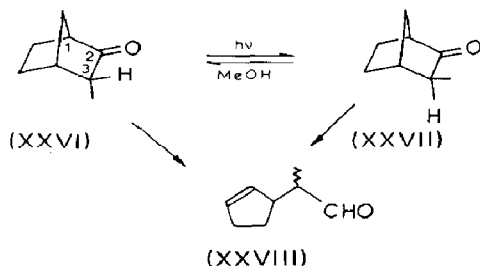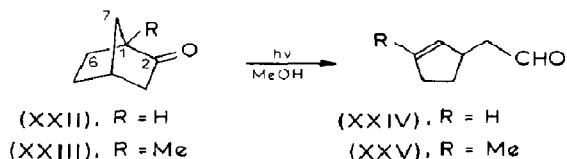
Our first observation of the ring expansion of a 2-norbornanone came in the case of camphenilone (XXIX), which gives the acetal XXX, the enal XXXI, and the ether XXXII. Compound XXXII is considered to arise from XXXI in a dark reaction. All of these products arise *via* cleavage of the C(2)–C(3) bond, a process that also leads to epimerization at C(3), as demonstrated by the interconversion of XXXIII and XXXIV:

(XXIX)   (XXX)   (XXXI)   (XXXII)

(XXXIII)   (XXXIV)
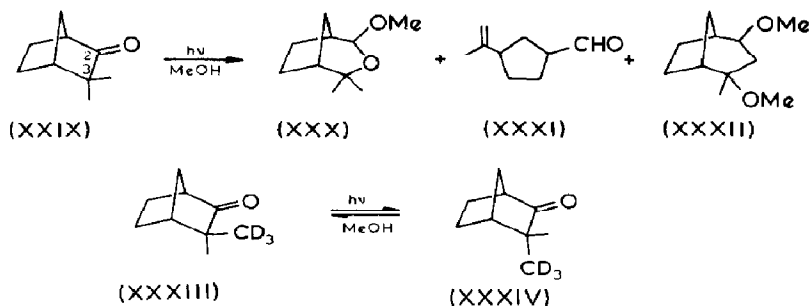
In the case of fenchone (XXXV) cleavage of both C(2)–C(3) and C(1)–C(2) bonds occurs; the former leads to products XXXVI - XXXVIII analogous to those obtained from camphenilone (we had previously shown that a diol analogous to XXXVIII is formed in the irradiation of XXXV in water [15], while the latter gives only the enal XXXIX, an analogue of XXIV, XXV and XXVIII.

(XXXV)   (XXXVI)   (XXXVII)   (XXXVIII)

(XXXIX)
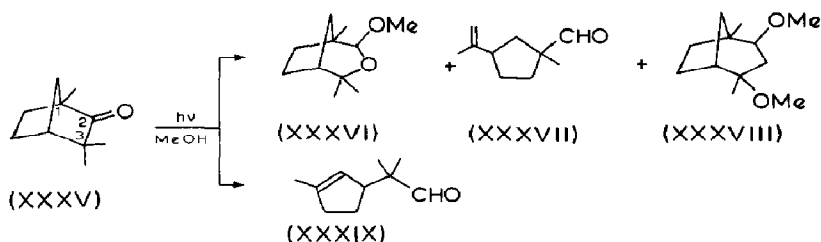
Agosta and Herron [16] have examined the photochemistry of camphor (XL) in ethanol and have shown that the acetal XLI and vinyl ether XLII are formed together with the enal XLIII; compound XLII was shown to arise *via* a secondary, thermal reaction of XLI. We have also found that apocamphor (XLIV) gives both a cyclic acetal and enal on irradiation in methanol [14]. Here as in the cases of XXX and XXXVI the ring-expansion products represent minor products.

(XL), R = Me
(XLIV), R = H   (XLI)   (XLII)   (XLIII)
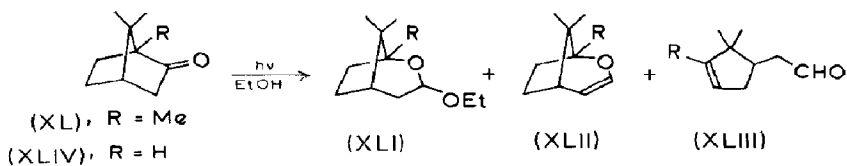
Other bridged ketones that we have investigated in the search for further examples of photochemical ring expansion include the tricyclic ketone XLV [17] and the bicyclo [2.2.2] octanones XLVI - XLVIII [18]. These give the products shown below; in no case was the formation of ring-expansion products detected*.
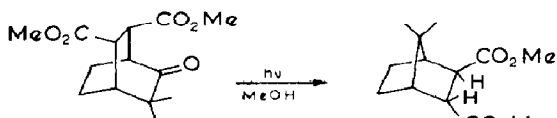
*The occurrence of such extensive photodecarbonylation in solution is unusual and is under further investigation.
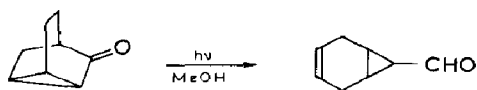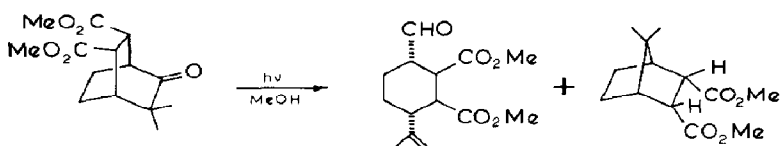
(XLV)
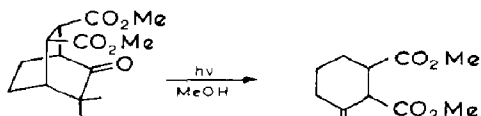
(XLVI)

(XLVII)

(XLVIII)

The only other instances of which we are aware in which carbocyclic ketones other than cyclobutanones have been observed to undergo photochemical ring expansion to acetals involve cyclopentanones with a cyclopropane ring bonded to the α-position. Thus Turro and Crandall and their coworkers [9, 19] have shown that the spiro-ketone IL gives the acetal L as a major product, together with the enal LI, while Dauben an coworkers [20] have found that bicyclo [3.1.0] hexan-2-one (LII) gives the acetal LIII as a minor product accompanying the ketene-derived product LIV. The cyclohexanone analogue of IL and LII give no ring expansion products.
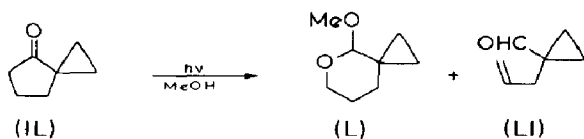
(IL)   (L)   (LI)
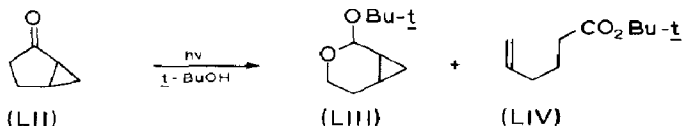
(LII)   (LIII)   (LIV)

Our knowledge to this point of the structural requirements for the photochemical ring expansion of carbocyclic ketones to cyclic acetals

may thus be summarized as follows: (i) the reaction is general for cyclo-
butanones; (ii) it has not been observed for simple cyclopentanones, but
occurs as a minor pathway with some, but not all, bicyclo[2.2.1]heptan-
2-ones and with bicyclo[3.1.0]hexan-2-one (LII), and as a major pathway
with the spiro ketone IL and the tricyclic ketones, cyclocamphanone (I)
and nortricyclanone (VI); (iii) it has not been observed for cyclohexanones
or larger ring ketones.

Mechanism

The proposal that the photochemical ring expansion of cyclic ketones
to cyclic acetals proceeds *via* cyclic oxacarbenes has been generally ac-
cepted. In addition to the trapping experiment with cyclohexene in the
case of cyclocamphanone referred to earlier, related trapping experiments
have been carried out with benzocyclobutenedione (LV) and 2-isopropyl-
idenecyclobutanone (LVII). Staab and Ipaktschi [21] irradiated LV in
the presence of several alkenes and obtained products of type LVI, while
Turro and Morton [9] on irradiation of LVII in the presence of cyclo-
pentadiene obtained LIX, which is considered to arise *via* LVIII.
Furthermore, Quinkert and coworkers [22] have attributed transient
ultra-violet absorption ($\lambda_{max} \sim 360$ nm) observed after irradiation of cyclo-
butanones in glasses at -186 °C to the corresponding cyclic oxacarbenes.

(LV)   (LVI)

(LVII)   (LVIII)   (LIX)
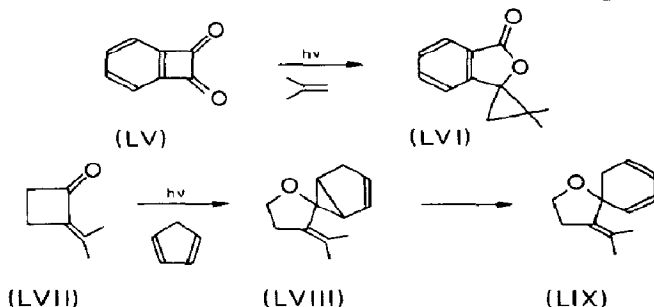
Agosta and coworkers [23] have examined the reactions of thermally
generated cyclic oxacarbenes. Pyrolysis of the lactone tosylhydrazone salt
LX, for example, gives the following products, which are considered to arise
from the oxacarbene LXI:


(LX)   (LXI)   (LXII)   (LXIII)
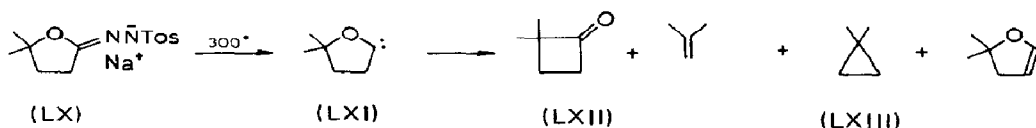
The formation of the cyclobutanone LXII suggests that photochemically
generated cyclic oxacarbenes may revert to their parent cyclic ketones,

accounting for the frequently observed inefficiency of formation of oxacarbene-derived products. The formation of the cyclopropane LXIII suggests further that photochemical decarbonylation of cyclobutanones may proceed, at least in part, *via* oxacarbenes.

Although there appears to be general agreement on the intermediacy of oxacarbenes in the photochemical ring expansion of cyclic ketones, the details of their pathways of formation from the excited ketones are less certain. Quinkert and coworkers [6, 10] have proposed that in the case of cyclobutanones the oxacarbene is formed from the singlet $n{\to}\pi^*$ excited state of the ketone by a concerted process that does not involve cleavage to an alkyl acyl biradical. They consider that such a concerted process best accounts for the retention of configuration in the ring expansion of cyclobutanones with chiral α-carbon atoms (*vide supra*). They have also advanced theoretical arguments [24] for the view that concerted oxacarbene formation in the case of cyclobutanones is favored over α-cleavage as a result of through-bond coupling, while in the case of larger ring ketones α-cleavage is the primary chemical step. However, the stereochemical evidence is not compelling since it cannot be excluded that an intermediate alkyl acyl biradical formed by α-cleavage could close more rapidly than it rotates, resulting in retention of configuration [25].

In the case of the cyclopentanone IL, Turro and Morton [9] have shown by quenching experiments that both ring expansion product L and the enal LI are formed *via* the triplet $n{\to}\pi^*$ excited state of IL. They consider that this undergoes α-cleavage to the alkyl acyl biradical LXIV which closes to the oxacarbene LXV, *i.e.*, that the formation of the oxacarbene is stepwise rather than concerted.


(IL)   (LXIV)   (LXV)
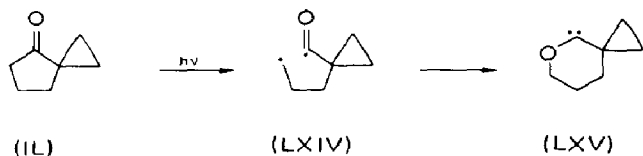
It thus seems reasonable to consider the photochemical ring expansion of cyclopentanones separately from that of cyclobutanones, a view that is strengthened by the circumstance that ring expansion of the latter is general while that of the former has very special structural requirements. Turro and Morton [9] have advanced a very plausible interpretation of the occurrence of oxacarbene formation in the case of IL in terms of stabilization of the transition state for the formation of the oxacarbene LXV by delocalization of two of the carbon—carbon bonds of the cyclopropyl ring. They have shown that the quantum yield for the formation of the ring expansion product L is comparable to that for the formation of the enal LI, which itself is not greatly different from the quantum yield for the formation of enal from cyclopentanone. Thus, in accord with their interpretation, the cyclopropyl ring here facilitates oxacarbene formation and makes it competitive with enal formation. A related interpretation can be invoked to account for oxacarbene formation in the case of LII.

However, no such interpretation appears to apply in the case of the bicyclo[2.2.1]heptan-2-ones discussed earlier. Here we consider that oxacarbene formation occurs when structural features make competing reactions unfavorable [2, 26]. In this series the only important competing reaction is enal formation, and the parent member of the series, 2-norbornanone (XXII), gives the enal XXIV exclusively. It is, we believe, important to note that of the two enals XXIV and LXVII that could be formed by cleavage of the C(1)–C(2) bond followed by intramolecular hydrogen transfer in the biradical LXVI, only XXIV is formed. It is perhaps possible to rationalize this observation in terms of the geometries of the two transition states involved (cf. LXVIII vs. LXIX); in any event, the result establishes that abstraction of *syn*-C(7)-H is greatly favored over abstraction of *endo*-C(6)-H. We attribute the formation of oxacarbene-derived products from camphor (XL) and apocamphor (XLIV) to the fact that enal formation here must involve the less favorable abstraction of hydrogen from C(6) because of the presence of a *syn*-C(7) substituent, thus permitting some competition from oxacarbene formation.
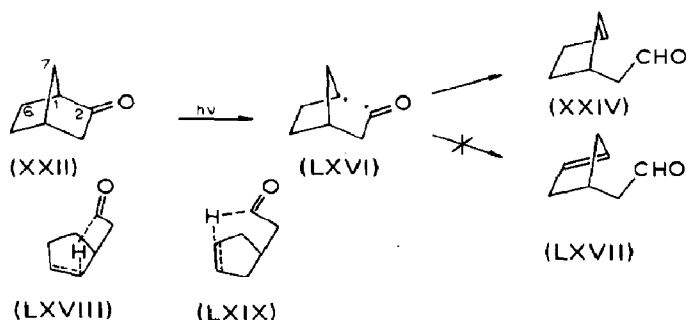
Camphenilone (XXIX) also gives both enal and an oxacarbene-derived product; this is interpreted as due to increased difficulty of enal formation both because it involves abstraction of a hydrogen atom from a methyl group and because the cyclic transition state for the hydrogen transfer is seven membered. Similarly, cleavage of the C(2)–C(3) bond of fenchone (XXXV) gives both enal and oxacarbene-derived product. However, cleavage of the C(1)–C(2) bond of XXXV results only in enal formation as expected in terms of the above interpretation.
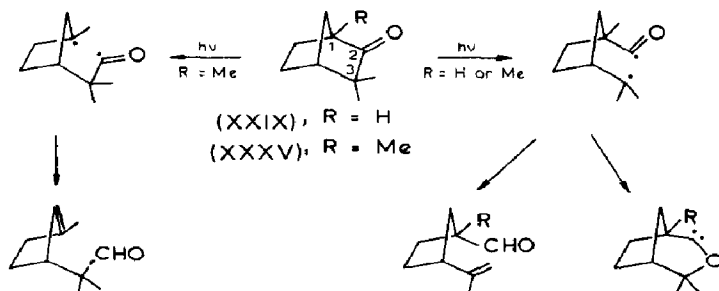
It follows from this interpretation that if enal formation is completely inhibited in a bicyclo[2.2.1]heptan-2-one, conversion to an oxacarbene should become the major pathway of photochemical reaction. We tested this conclusion by the synthesis of *endo*-6-carbomethoxycamphor (LXX) and examination of its photolysis in methanol. As predicted, the major product is the oxacarbene-derived product LXXI, accompanied by ~5% of the diester LXXII. The latter must arise from the ketene LXXII, a type of intermediate that is rarely formed from bicyclo [2.2.1] heptan-2-ones. Its formation here must again reflect the suppression of the normally facile process of enal formation.

(LXX)   (LXXI)   (LXXII)
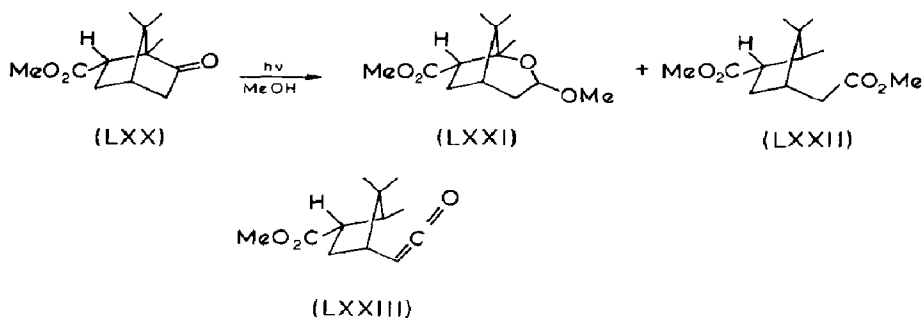
(LXXIII)

A corollary to our interpretation of the formation of LXXI as the major photochemical product from LXX is that the efficiency of the formation of the oxacarbene intermediate remains low, although the chemical yield of LXXI is high. We have confirmed this circumstance by the demonstration that the quantum yield for the formation of LXXI is low, *viz.*, 0.03 [26]*.

Further confirmation of the dual nature of the effect of substituents comes from the photolysis of LXXIV, which gives LXXV as the major product. This result is interpreted as being due to both facilitation of oxacarbene formation by the spirocyclopropyl substituent and diminution of enal formation by the *syn*-C(7) substituent. A similar interpretation can be advanced for the formation of II as the major product from cyclo-camphanone (I). Finally, the case of LXXIV may be compared with that of LXXVI, where enal LXXVIII is the major product since the C(7) position is unsubstituted, but is accompanied by the oxacarbene-derived product LXXVII unlike the case of 2-norbornanone (XXII), because of facil-itation of oxacarbene formation by the cyclopropyl ring.

(LXXIV), R = Me   (LXXV), R = Me   (LXXVIII)
(LXXVI), R = H   (LXXVII), R = H
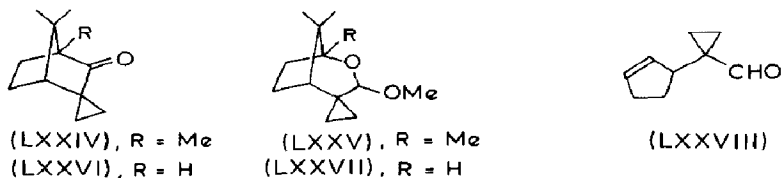
*Cf. the quantum yield for the formation of L from IL: 0.12 [9].

Heterocycloalkanones

Thus far we have concerned ourselves with carbocyclic ketones. Turning to heterocycloalkanones, we find that there are two classes that have been observed to undergo photochemical ring expansion to cyclic acetals. Brook has found that 2-silacycloalkanones give such products [27] as exemplified by the photoconversion of LXXIX to LXXX, which is accompanied by the decarbonylation product LXXXI.
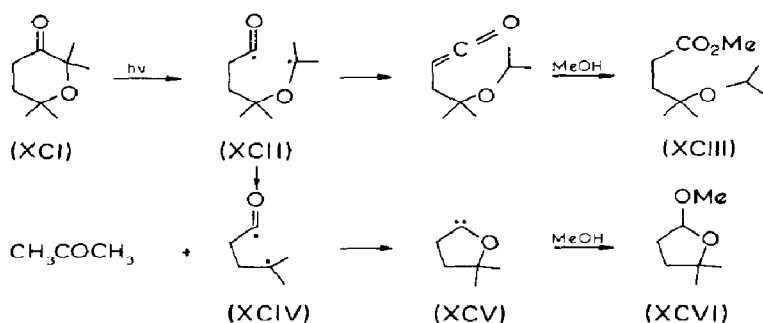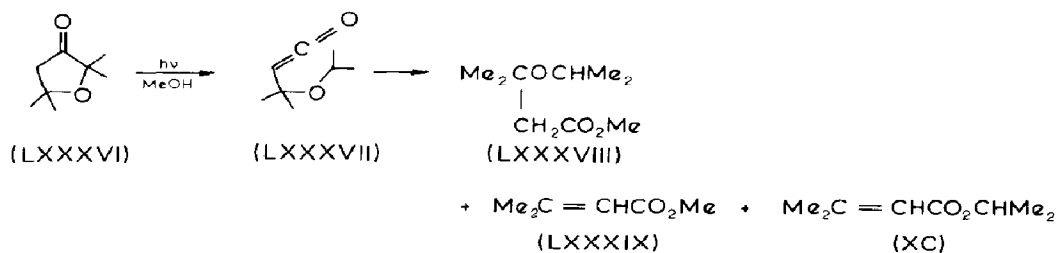

(LXXIX)   (LXXX)   (LXXXI)
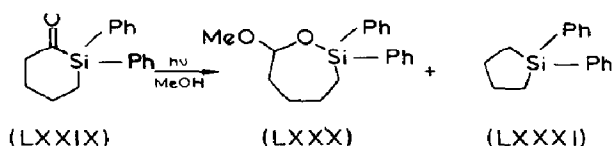
This case is of particular interest, since it involves a six-membered cyclic ketone; no carbocyclic ketones of this ring size have been reported to undergo ring expansion. It may be suggested that the case of the 2-silacyclo-alkanones is *sui generis* both because of the ability of silicon to utilize its *d*-orbitals in transition states and because of the unusually high bond energy of the Si—O bond.
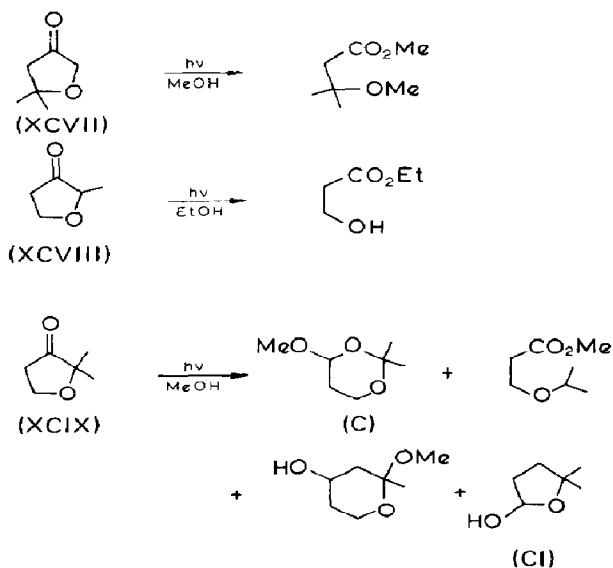
Collins and coworkers [28] have recently reported the photochemical ring expansion of the two 3-oxacycloalkanones LXXXII and LXXXIV to give LXXXIII and LXXXV respectively. The latter irradiation was conducted at − 70 °C to inhibit competitive decarbonylation. Again the unusual formation of an oxacarbene-derived product from a six-membered ring cyclic ketone may be noted.

(LXXXII)   (LXXXIII)

(LXXXIV)   (LXXXV)
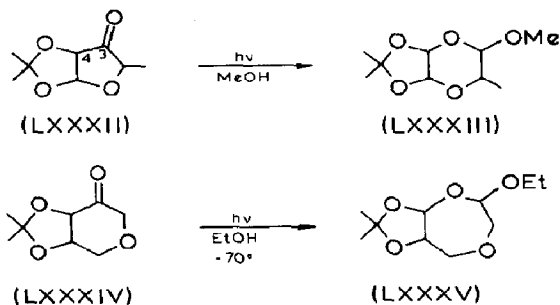
Earlier investigations of the photochemistry of 3-oxacycloalkanones had not led to observation of the formation of oxacarbene-derived products. Thus LXXXVI on irradiation gives LXXXVIII - XC all of which are considered to be derived from the ketene LXXXVII [29]. Photolysis of XCI gives the ketene-derived product XCIII together with the ring-contracted cyclic acetal XCVI, acetone, and isopropyl alcohol [30]. The formation of XCVI can be interpreted in terms of loss of acetone from biradical XCII to give the biradical XCIV, which cyclizes to XCV, a process that provides further evidence for the formation of cyclic oxacarbenes from alkyl acyl biradicals.

(LXXXVI) → (LXXXVII) → Me$_2$COCHMe$_2$ | CH$_2$CO$_2$Me (LXXXVIII)

+ Me$_2$C $=$ CHCO$_2$Me + Me$_2$C $=$ CHCO$_2$CHMe$_2$

(LXXXIX)   (XC)

(XCI) → (XCII) → (XCIII) MeOH

CH$_3$COCH$_3$ + (XCIV) → (XCV) MeOH → (XCVI)

We have initiated a study of the photochemistry of 3-oxacyclopentan-ones [31] in an attempt to define which of the structural features of LXXXII are associated with oxacarbene formation. This study is as yet incomplete, but the results obtained thus far are shown below:

(XCVII) $\xrightarrow[\text{MeOH}]{\text{hv}}$ CO$_2$Me / OMe

(XCVIII) $\xrightarrow[\text{EtOH}]{\text{hv}}$ CO$_2$Et / OH

(XCIX) $\xrightarrow[\text{MeOH}]{\text{hv}}$ (C) + CO$_2$Me

+ (CI)

Of the three oxacyclopentanones XCVII - XCIX only the last gives an oxacarbene-derived product (C). This, furthermore, is formed only in minor amount, whereas in the case of LXXXII, the ring expansion product LXXXIII is the only product reported. The formation of the other

photoproducts from XCVII - XCIX has intrinsic interest, particularly CI, but clearly the photochemistry of these ketones is different from that of LXXXII, and further work is required to define the pertinent structural features that lead to the predominant oxacarbene formation in the case of LXXXII*.


Oxacarbene vs. ketene formation

We conclude by returning to consider the photolysis of LXX, which led to the formation of the oxacarbene-derived product LXXI as the major product together with the ketene-derived product LXXII as a minor product. These processes do not occur in the case of 2-norbornanone but are considered to occur *faute de mieux* in the case of LXX. However, this result stands in interesting contrast to the observation by Meinwald and Erman and co-workers [32] that photolysis of carvonecamphor (CIV) gives the ketene-derived compound CVI as the major product but no oxacarbene-derived product**.
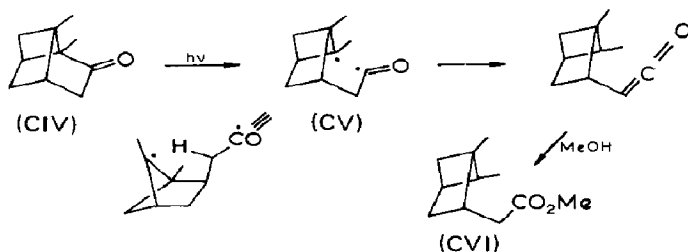

We interpret this difference in terms of facilitation of the hydrogen transfer process in the biradical CV derived from CVI because of the geometrical restrictions imposed by the additional one-carbon bridge. In order to examine whether the cyclobutane ring as such plays any role in the formation of CVI we undertook an investigation of the photochemistry of CVIII [33], which was synthesized by the route shown below:

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*Our present view is that the formation of the oxacarbene (CII) from LXXXII involves stabilization of the transition state by interaction of an unshared pair on the annular oxygen atom with the developing carbene center (cf. CIII). This implies that the structural requirements comprise both the annular oxygen atom and a substitution pattern that results in α-cleavage of the C(3)–C(4) bond.
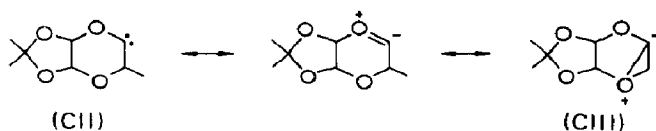
**We have re-examined this reaction but have failed to obtain any evidence for the formation of a ring-expanded cyclic acetal [33].
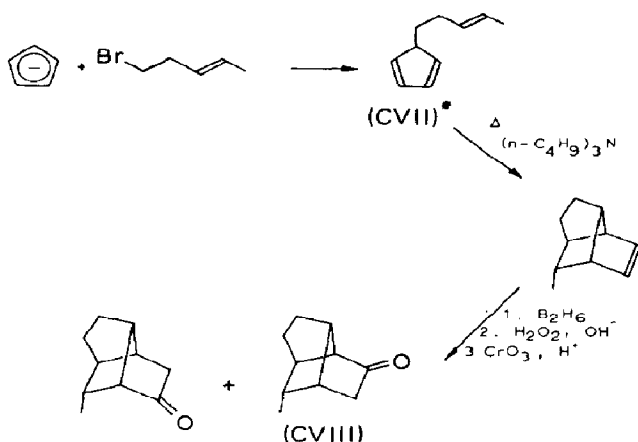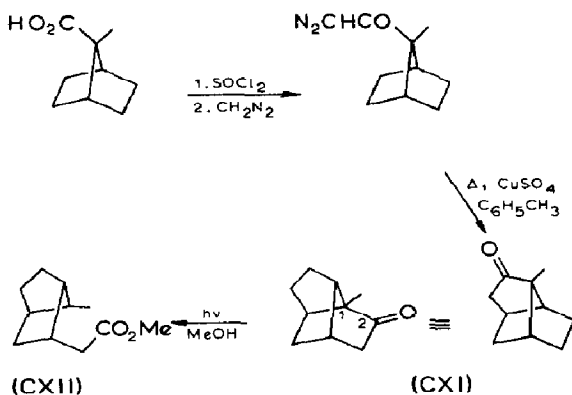
Irradiation of CVIII in methanol gives CIX as the major product together with a low yield of CX. The former product arises *via* cleavage of the C(2)–C(3) bond and oxacarbene formation; the latter *via* cleavage of the C(1)–C(2) bond and ketene formation. The unexpected predominance of cleavage at the less substituted α-position is attributed to the circumstance that the secondary alkyl radical formed by cleavage of the C(1)–C(2) bond is destabilized by virtue of its situation at the C(7) position of a norbornyl system [34]. The formation of CIX as the product from C(2)–C(3) cleavage is in excellent accord with our views, since here enal and ketene formation cannot occur. The formation of a ketene-derived product but not oxacarbene-derived product from C(1)–C(2) cleavage is analogous to the case of CIV, indicating that the cyclobutane ring as such is not the determining factor in the formation of ketene to the exclusion of oxacarbene. This demonstration, however, was less than satisfying since C(1)–C(2) cleavage represented only a minor pathway in the photolysis of CVIII.
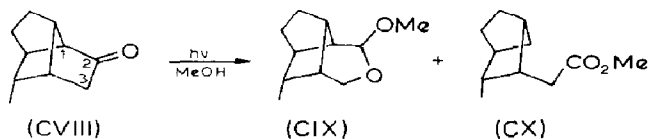
We therefore examined the photolysis of CXI [33] in the expectation that the presence of the C(1) methyl substituent would result in cleavage of the C(1)–C(2) bond as the major photolytic process, as for the similarly substituted carvonecamphor (CIV). Compound CXI was prepared by the route shown below:

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*Product CVII is obtained as a tautomeric mixture consisting largely of the 1- and 2-substituted cyclopentadienes; only the 5-substituted isomer undergoes cyclization.

(CXII)   (CXI)

Irradiation of CXI in methanol gives only XII derived by C(1)–C(2) bond cleavage followed by ketene formation. Thus we conclude that the formation of ketene-derived products from the tricyclic ketones CIV, CVIII, and CXI is attributable to the geometrical restrictions imposed on the intermediate alkyl acyl biradical by the additional one- or two-carbon bridges*.

Acknowledgements

References

1 P. Yates and L. Kilmurry, Tetrahedron Lett., (1964) 1739.
2 P. Yates, Pure Appl. Chem., 16 (1968) 93.
3 P. Yates and L. Kilmurry, J. Am. Chem. Soc., 88 (1966) 1563.
4 L. Kilmurry, Ph.D. Thesis, University of Toronto (1966).
5 G. Roussi and R. Beugelmans, Tetrahedron Lett., (1972) 1333.
6 W.-D. Stohrer, P. Jacobs, K. H. Kaiser, G. Wiech and G. Quinkert, Fortschr. Chem. Forsch., 46 (1974) 181.
7 N. J. Turro and D. R. Morton, Adv. Photochem., 9 (1974) 197.
8 P. Yates and R. O. Loutfy, Acc. Chem. Res., 8 (1975) 209.
9 N. J. Turro and R. M. Southam, Tetrahedron Lett., (1967) 545; D. R. Morton, E. Lee-Ruff, R. M. Southam and N. J. Turro, J. Am. Chem. Soc., 92 (1970) 4349; N. J. Turro and D. R. Morton, J. Am. Chem. Soc., 93 (1971) 2569; D. R. Morton and N. J. Turro, J. Am. Chem. Soc., 95 (1973) 3947.
10 G. Quinkert, G. Cimballek and G. Buhr, Tetrahedron Lett., (1966) 4573;

*Oxacarbene formation is subject to related factors, but these factors are expected to be considerably more decisive in the case of the five-membered transition state involved in ketene formation.

G. Quinkert, P. Jacobs and W.-D. Stohrer, Angew. Chem. (Int. Edn), 13 (1974) 197; G. Quinkert and P. Jacobs, Chem. Ber., 107 (1974) 2473.

11 H. W. Yeung, Ph.D. Thesis, University of Toronto (1971).
12 Cf. ref. 10; A. G. Fallis, Tetrahedron Lett., (1972) 4573.
13 J. C. L. Tam, Ph.D. Thesis, University of Toronto (1974).
14 R. G. R. Hagens, Ph.D. Thesis, University of Toronto (1970).
15 P. Yates and A. G. Fallis, Tetrahedron Lett., (1967) 4621.
16 W. C. Agosta and D. K. Herron, J. Am. Chem. Soc., 90 (1968) 7025.
17 A. G. Fallis, Ph.D. Thesis, University of Toronto (1967); P. Yates and D. N. Butler, unpublished results.
18 K. E. Stevens, M.Sc. Thesis, University of Toronto (1975).
19 J. K. Crandall and R. J. Seidewand, J. Org. Chem., 35 (1970) 697.
20 W. G. Dauben, L. Schutte, G. W. Schaffer and R. B. Gagosian, J. Am. Chem. Soc., 95 (1973) 468.
21 H. A. Staab and J. Ipaktschi, Tetrahedron Lett., (1966) 583; Chem. Ber., 101 (1968) 1457.
22 G. Quinkert, K. H. Kaiser and W.-D. Stohrer, Angew. Chem. (Int. Edn), 13 (1974) 198.
23 A. B. Smith III, A. M. Foster and W. C. Agosta, J. Am. Chem. Soc., 94 (1972) 5100; A. M. Foster and W. C. Agosta, J. Am. Chem. Soc., 94 (1972) 5777; 95 (1973) 608.
24 W.-D. Stohrer, G. Wiech and G. Quinkert, Angew. Chem. (Int. Edn), 13 (1974) 199, 200.
25 P. J. Wagner, personal communication.
26 P. Yates and J. C. L. Tam. J.C.S., Chem. Commun., (1975) 737.
27 A. G. Brook, R. Pearce and J. B. Pierce, Can. J. Chem., 49 (1971) 1622; J. M. Duff and A. G. Brook, Can. J. Chem., 51 (1973) 2869; A. G. Brook, Acc. Chem. Res., 7 (1974) 77.
28 P. M. Collins, N. N. Oparaeche and B. R. Whitton, J.C.S., Chem. Commun., (1974) 292.
29 G. Hagens, J. P. Wasacz, M. Joullié and P. Yates, J. Org. Chem., 35 (1970) 3682.
30 J. P. Wasacz and M. M. Joullié, Tetrahedron Lett., (1970) 2501.
31 P. Yates and J. C. L. Tam, unpublished results.
32 J. Meinwald and R. A. Schneider, J. Am. Chem. Soc., 87 (1965) 5218; T. Gibson and W. F. Erman, J. Org. Chem., 31 (1966) 3028; J. Meinwald, R. A. Schneider and A. F. Thomas, J. Am. Chem. Soc., 89 (1967) 70.
33 J. C. L. Tam and P. Yates, J.C.S., Chem. Commun., (1975) 739.
34 C. Rüchardt, Angew. Chem. (Int. Edn), 9 (1970) 830.