

PHOTOCHEMISTRY OF CYCLIC KETONES IN SOLUTION

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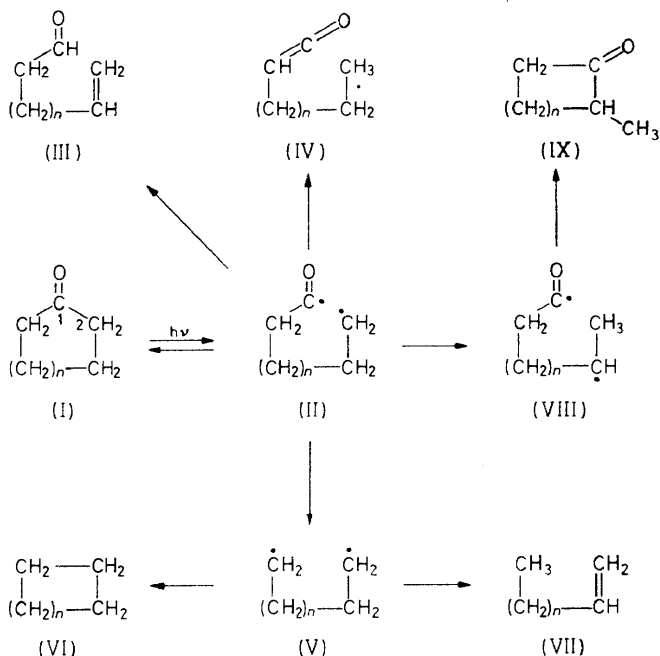
INTRODUCTION

In the course of the recent renaissance of organic photochemistry the photochemical reactions of ketones have received more attention than those of any other type of compound. These investigations have both revealed hitherto unknown modes of reaction and provided a wealth of information regarding the scope and mechanism of reactions which have long been known. I should like to discuss work of our own and of other workers which falls in the first of these categories. In our own work emphasis has been placed on the structural rather than the physicochemical aspects of the problem.

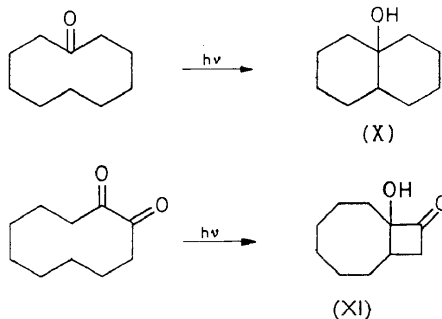
The discussion concerns a novel type of photochemical reaction of non-conjugated cyclic ketones. The investigation of the photochemical reactions of such ketones spans sixty years, having been initiated by Ciamician, the father of organic photochemistry¹. The field has been ably reviewed by investigators²⁻⁴ who have themselves made important contributions to its development, and it will suffice here to summarize previous work briefly.

GENERAL TYPES OF PHOTOCHEMICAL REACTION OF NON-CONJUGATED CYCLIC KETONES

The course of one of the two major groups of these reactions can be rationalized in a *formal sense* in terms of $n \rightarrow \pi^*$ excitation of the cyclic ketone (I) followed by a Norrish Type I cleavage to give the acyl-alkyl diradical (II). Reclosure can return the ketone (I), or, when C-2 is asymmetric, the epimer of (I). Intramolecular hydrogen abstraction in (II) can give either the unsaturated aldehyde (III) or the ketene (IV). Loss of carbon monoxide from (II) can lead via the diradical (V) to the cyclic hydrocarbon (VI) or the alkene (VII). Hydrogen migration in (II) followed by closure can lead via (VIII) to the ring-contracted cyclic ketone (IX). The formal nature of this scheme must be emphasized since there is evidence in certain instances that cleavage of the C-1—C-2 bond is concerted with the further processes leading to products and that the diradical (II) either does not intervene or is very short-lived. This aspect of the detailed description of the reaction pathways is still a matter of controversy⁵. In structural terms, the important observation has been made that in the case of cyclic ketones with differing degrees of alkyl substitution on the carbon atoms adjacent to the carbonyl group cleavage normally occurs exclusively at the more highly substituted position. This corresponds to the formation of the more stable diradical of type (II), although photo-induced reactions would not necessarily have been expected to show this selectivity³.

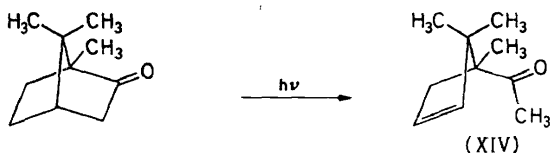
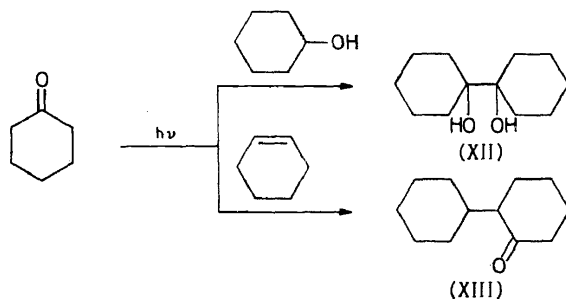


The course of the other major group of photochemical reactions of non-conjugated cyclic ketones can be interpreted in terms of $n \rightarrow \pi^*$ excitation followed by hydrogen abstraction by the oxygen atom of the excited carbonyl group. This abstraction may be either intramolecular or intermolecular. Examples of reactions probably proceeding by the former route are the formation of a mixture of *cis*- and *trans*-9-decalol (X) and the α -ketol (XI) on irradiation of cyclodecanone^{6,7} and 1,2-cyclodecanedione⁷, respectively. The photochemical reaction of cyclohexanone with cyclohexanol to give the pinacol (XII)⁸ is an example of an intermolecular abstraction reaction,



while its reaction with cyclohexene to give the ketone (XIII) has also been suggested to involve such abstraction⁹. Of particular relevance to the present discussion is the proposal that the methyl ketone (XIV) is formed on irradiation of camphor by a pathway involving hydrogen abstraction from the solvent¹⁰.

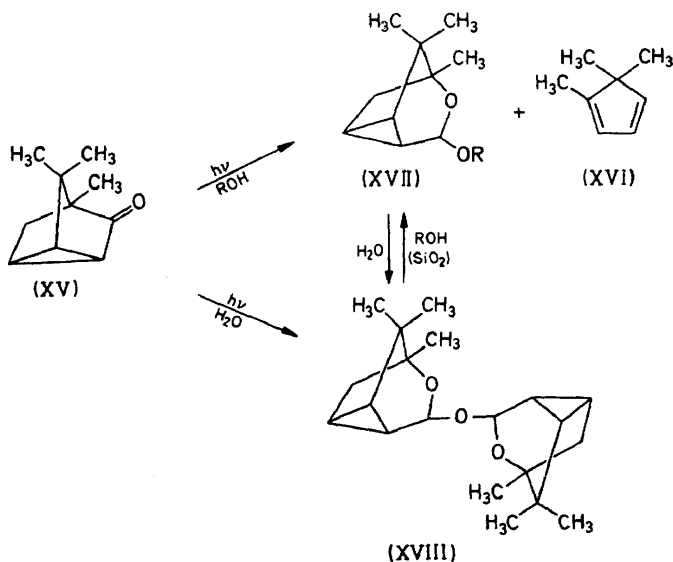
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FORMATION OF CYCLIC ACETALS BY IRRADIATION OF CYCLIC KETONES IN HYDROXYLIC SOLVENTS

Irradiation of cycloamphanone

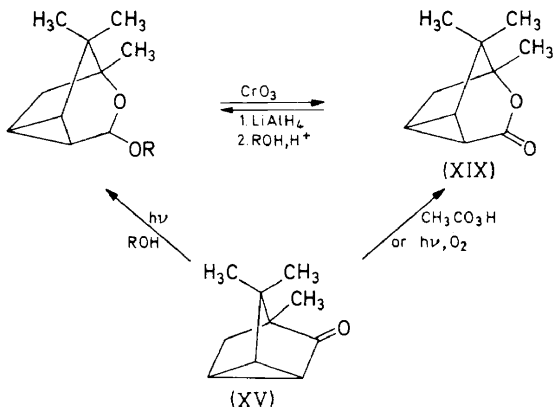
Our own interest in this field stemmed from a study of the products formed when cycloamphanone (XV) is irradiated in hydroxylic solvents. In methanol or ethanol the major product is an oil corresponding in composition to a 1:1 adduct of the ketone and the alcohol. A second, minor product was detected by ultraviolet spectroscopy in the distillate obtained on removal



of solvent from the major product. A maximum at 255 $m\mu$ suggested the presence of a cyclopentadiene derivative; this minor product was shown to be 1,5,5-trimethylcyclopentadiene (XVI) by direct comparison of its adduct with *N*-phenylmaleimide with an authentic sample.

The major products were considered to have structures of type (XVII) on the basis of infrared and n.m.r. spectroscopic data. They were very readily hydrolyzed to a crystalline, bimolecular product, considered to have structure (XVIII), which was obtained as the major product on irradiation of cyclocamphanone in the presence of water. Chromatography of (XVIII) on silica with elution by alcohols gave (XVII).

These structural assignments were confirmed in two ways. Oxidation of (XVIII) with chromic acid gave a lactone, which was also formed when cyclocamphanone was irradiated in solution in the presence of air. This was shown to be (XIX) by its synthesis from cyclocamphanone by Baeyer-Villiger oxidation with peracetic acid. Similar oxidation of nortricyclanone, the analogue of cyclocamphanone lacking methyl groups, has previously been shown to give an analogous lactone¹¹. That migration of the tertiary carbon atom rather than the secondary, cyclopropyl carbon atom had occurred, as expected¹², was demonstrated by the absence of a signal in the

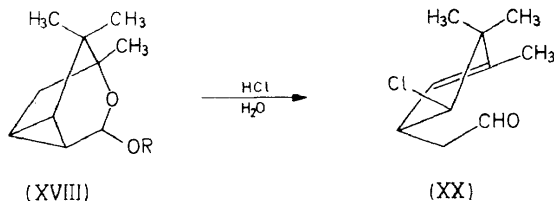


n.m.r. spectrum of (XIX) associated with a proton on a carbon bearing an oxygen atom. The absence of rearrangement in the conversion of the photochemical product (XVIII) to the lactone (XIX) was shown by reduction of the latter with lithium aluminium hydride; work-up in the presence of water gave (XVIII), while in the presence of ethanol the alkoxy compound (XVII) was obtained.

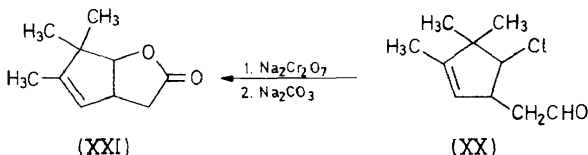
Treatment of (XVIII) with hydrochloric acid in dioxane gave a chloro aldehyde which is assigned structure (XX) on the basis of its spectroscopic properties. Oxidation to the corresponding carboxylic acid followed by lactone formation gave a product whose properties were in excellent accord with expectation for compound (XXI).

The formation of (XX) can be interpreted in general terms as involving opening of the cyclopropane ring of the aldehyde formed on hydrolysis of the acetal group of (XVIII). However, such opening could occur in two different ways to give either (XX) or (XXII); further, preponderant or

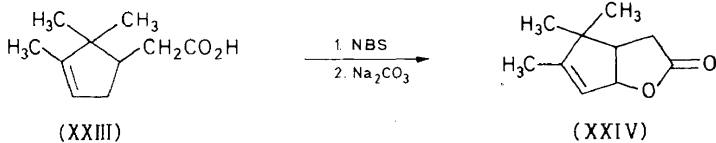
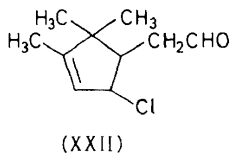
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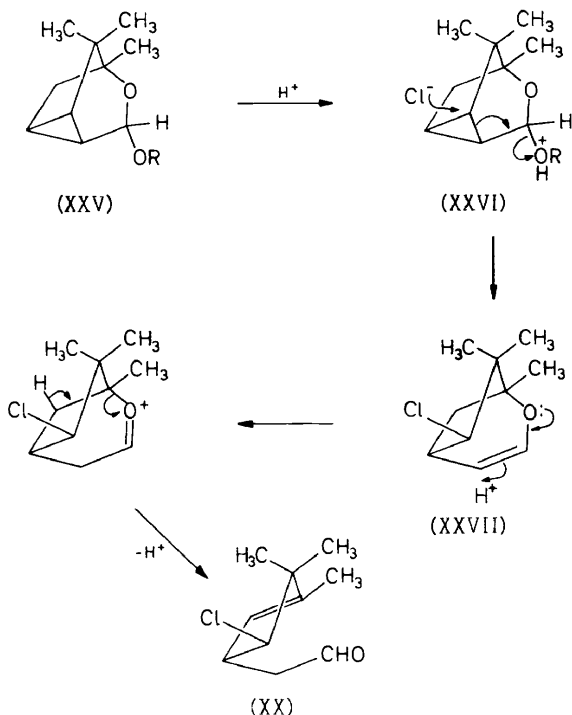
perhaps exclusive formation of the latter might have been expected on steric grounds. The assignment of structure (XX) rather than (XXII) to the chloro aldehyde is based on a detailed analysis of its n.m.r. spectrum and that of the lactone (XXI). In order to provide additional evidence for the choice between structures (XX) and (XXII), the lactone (XXIV) was synthesized by allylic bromination of α -campholenic acid (XXIII) with *N*-bromosuccinimide followed by lactonization. Had (XXII) been the structure of the chloro aldehyde derived from (XVIII), the product obtained by oxidation followed by lactonization would have had structure (XXIV). The two



lactones were not identical and indeed their n.m.r. spectra differed in just those respects which had led originally to the choice of structure (XXI) for the lactone obtained from the chloro aldehyde. The assignment of structure (XX) to the chloro aldehyde is thus secure. A possible explanation of its preferential formation is based on the assignment of stereochemistry for the photoproduct shown in (XXV), which appears likely on other grounds. Concerted opening of the protonated species (XXVI) could then account for attack of chloride ion as shown to give the enol ether (XXVII), which could serve as the source of (XX).

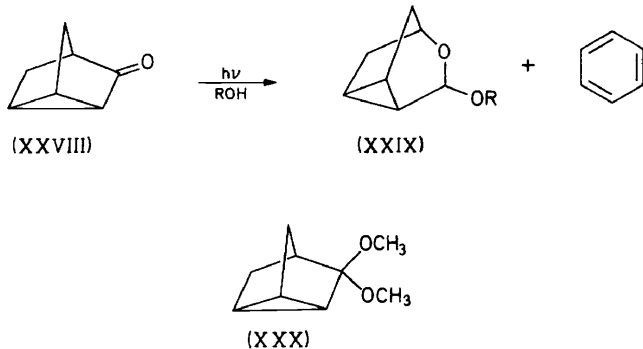
Irradiation of nortricyclanone

Irradiation of nortricyclanone (XXVIII) in methanol or ethanol has been found to give cyclic acetals (XXIX) which are analogous to those



obtained from cyclocamphanone. Their structures were assigned on the basis of their spectroscopic properties and their oxidation to the corresponding lactone, prepared independently by Baeyer-Villiger oxidation of (XXVIII)¹¹. A minor product was again detected in the distillate from the reaction mixture; this was shown by its ultraviolet spectrum to be benzene. Lemal and Shim¹³ have previously studied the mercury-photo-sensitized, vapour phase photolysis of nortricyclanone; they also obtained benzene, together with the tricyclic hydrocarbon derived by decarbonylation, which was the major product.

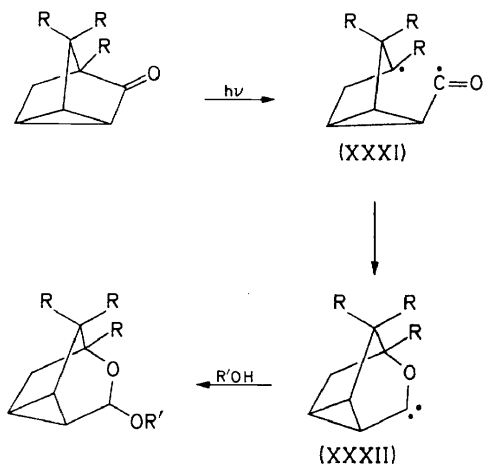
An interesting feature of the photoreaction of nortricyclanone in methanol was the very ready formation of the ketal (XXX). In fact, in early experi-



ments this was obtained to the exclusion of the acetal (XXIX), even when the methanol was freed of acidic impurities by distillation over magnesium. However, when solid sodium carbonate was present in the reaction mixture during the irradiation, formation of (XXX) was suppressed and (XXIX) was obtained as the major product. It appears, therefore, that the formation of the ketal is catalyzed by traces of acid formed by irradiation.

Mechanism of cyclic acetal formation

This new photoreaction of cyclic ketones can be interpreted in terms of the intermediacy of the acyl-alkyl diradical (XXXI) formed by Norrish Type I cleavage, in like manner to the interpretation of the several other types of reaction discussed previously in terms of the intermediacy of (II). On the basis of the empirical observation referred to earlier that cleavage occurs at the more highly substituted α -carbon atom, the preferred mode of cleavage in the case of cycloamphanone would be that corresponding to the formation of (XXXI). If in fact this choice of cleavage pathway is dependent

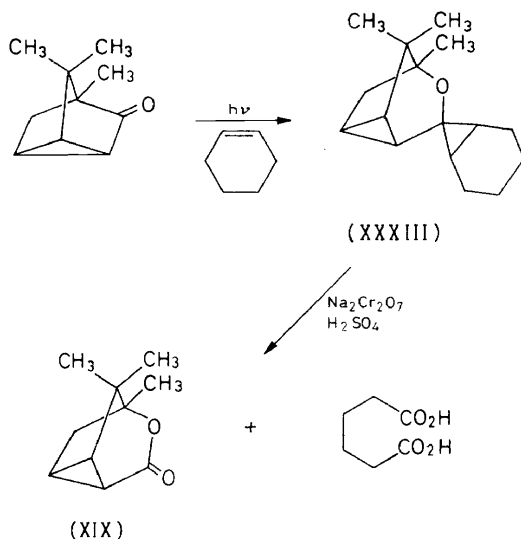


on the relative stability of the alkyl radical centre, the preferred mode of cleavage in the case of nortricyclanone would also be expected to be that corresponding to the formation of (XXXI), since, although the alternative mode of cleavage would also give rise to a secondary alkyl radical, this would be a cyclopropyl radical, which is known to be less stable than other cycloalkyl radicals¹⁴.

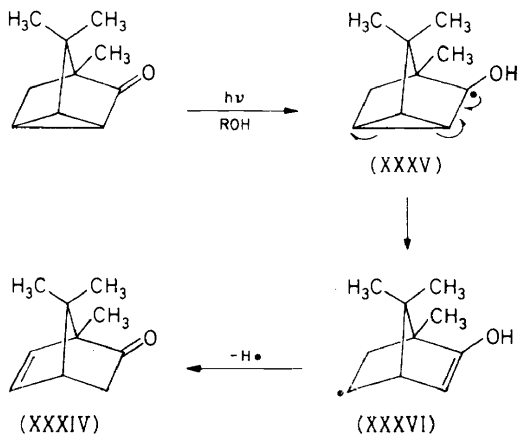
Rebonding in (XXXI) could lead to the formation of the oxacarbene (XXXII), whose reaction with alcohols would be expected to give rise to the observed photoproducts. As in the case of the reactions interpreted in terms of the acyl-alkyl diradical (II), the possibility exists that a discrete intermediate (XXXI) is not formed but that the carbon-oxygen bond formation is concerted with the carbon-carbon bond cleavage.

The postulation of the intervention of a carbenoid intermediate carries with it the responsibility of attempting to trap the carbene. Irradiation of cycloamphanone in cyclohexene gave a crystalline 1:1 adduct in low

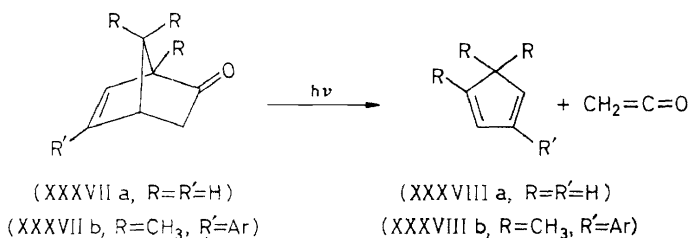
yield, together with a liquid having very similar spectroscopic properties to those of the solid product. Oxidation with sodium dichromate gave the lactone (XIX) and adipic acid. On the basis of the degradative and spectral evidence the adduct is considered to have the structure (XXXIII), and to be formed by addition of the oxacarbene (XXXII) to the double bond of cyclohexane. The crystalline material is considered to be one of the two stereoisomers corresponding to structure (XXXIII), and the liquid product to be a mixture of the two.



Before proceeding with discussion of the formation of cyclic acetals by irradiation of cyclic ketones, attention will be given to the path of formation of the minor product, 1,5,5-trimethylcyclopentadiene (XVI), in the photo-reaction of cyclocamphanone. It seems likely that this product arises via dehydrocamphor (XXXIV), which may itself be formed via hydrogen



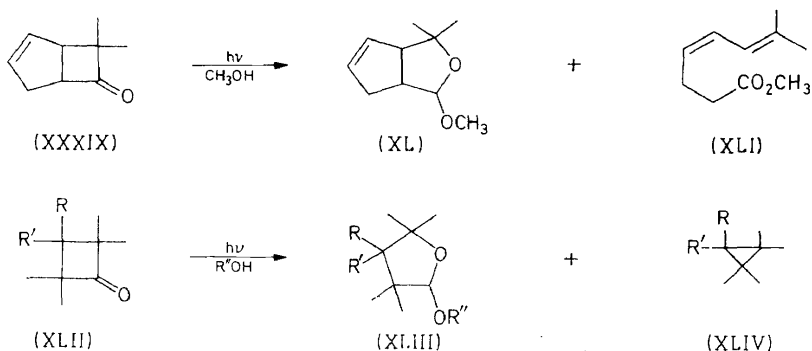
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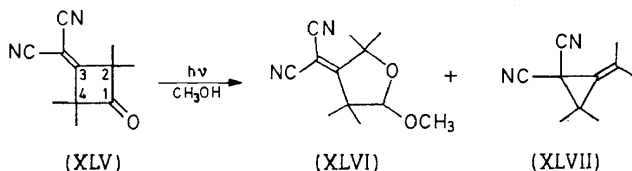
abstraction from the solvent by the excited cycloamphanone to give (XXV), cleavage of the cyclopropane ring to give (XXXVI), and hydrogen atom transfer and ketonization. This postulated route for the isomerization of cycloamphanone to (XXXIV) is based on the proposal by Srinivasan for the route of isomerization of camphor to the ketone (XIV)¹⁰. The photolysis of (XXXIV) to give (XVI) finds close analogy in work on the photolysis of dehydronorcamphor (XXXVII a) which has shown that cleavage occurs to give cyclopentadiene and ketene¹⁵. A similar reaction has also been observed in the case of dehydrocamphor with a 5-aryl substituent (XXXVII b) which gives a 3-aryl-1,5,5-trimethylcyclopentadiene (XXXVIII b)¹⁶.

Formation of cyclic acetals by irradiation of other cyclic ketones

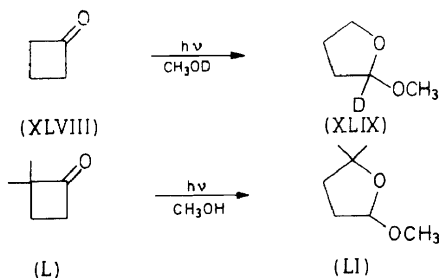
Since our original preliminary report on the novel photochemical ring expansion of cyclic ketones to cyclic acetals¹⁷ many other examples have come to light. Hostettler¹⁸ found that irradiation of the bicyclic ketone (XXXIX) gave two major products. One of these is the cyclic acetal (XL), which is the analogue of the acetals obtained from cycloamphanone and nortricyclanone. The other is the ester (XLI), which is considered to be formed from the corresponding ketene, itself formed by photocleavage of the four-membered ring in a well-known fashion that was first observed in the vapour phase photolysis of cyclobutanone itself¹⁹. Hostettler²⁰ has also observed cyclic acetal formation in the photochemical reactions of a series of 3-substituted-2,2,4,4-tetramethylcyclobutanones (XLII). Irradiation in alcohols gave a mixture of the corresponding ring-expanded cyclic acetal



(XLIII) and the decarbonylation product (XLIV). Of particular interest is the case of compound (XLV) in which the acetal (XLVI) is formed by bonding of oxygen to the site at which cleavage occurred, while the decarbonylation product (XLVII) is formed by rebonding at an allylic position with respect to the original cleavage site. It is possible that this difference reflects a concerted reaction in the case of the cyclic acetal formation or that the lifetime of an acyl-alkyl diradical intermediate of type (II) is too short to permit rotation about the C-2(4)—C-3 bond.



Turro and Southam²¹ have also investigated the photochemistry of simple cyclobutanones in methanol and have found that formation of ring-expanded cyclic acetals is a general reaction for such compounds. They observed in addition in each case the formation of decarbonylation products and of products derived by cleavage to an alkene and ketene. In the case of cyclobutanone itself (XLVIII) the corresponding cyclic acetal was obtained in 8 per cent yield together with 48 per cent of methyl acetate, derived by reaction of ketene with the solvent[†]. Irradiation of (XLVIII) in CH₃OD was shown to give the deuterium-labelled acetal (XLIX). This provided evidence that, if an oxacarbene is an intermediate, this gives the acetal by direct reaction with methanol rather than by hydrogen migration to give dihydrofuran followed by reaction with methanol. In the case of the unsymmetrically substituted cyclobutanone (L) it was shown that the only acetal formed was (LI), with none of the isomer which would be derived from the alternative α -cleavage process. This was attributed to exclusive cleavage of the more α electron-rich α -carbon-carbon bond; it can also be

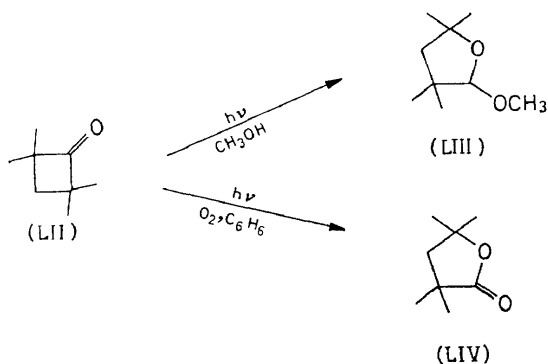


looked upon, of course, as involving the formation of the more stable acyl-alkyl radical (*vide supra*). Another analogy with the case of cyclo-camphanone is seen in the photoreaction of 2,2,4,4-tetramethylcyclobutanone (LII); this gave the acetal (LIII) on irradiation in methanol, while in benzene in the presence of air it gave the corresponding lactone (LIV).

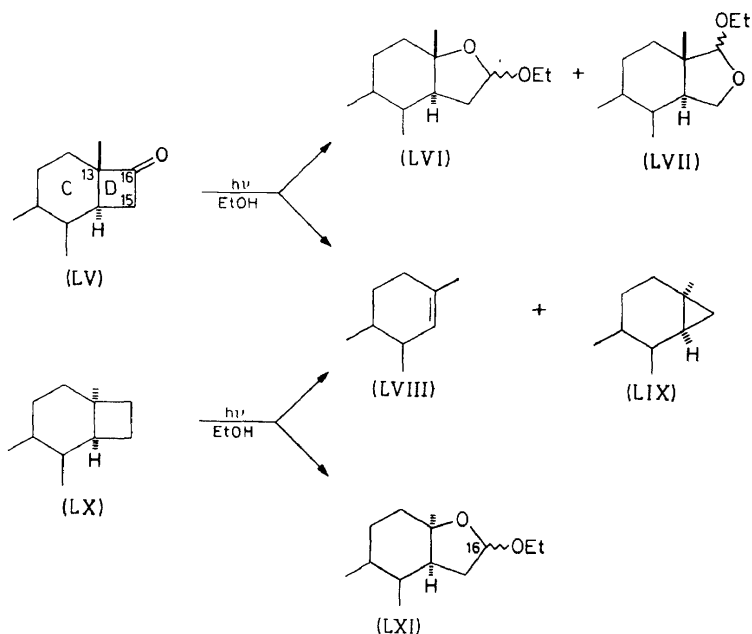
Quinkert and coworkers²³ have made important contributions to our

[†] We have independently observed a very similar ratio of these products²².

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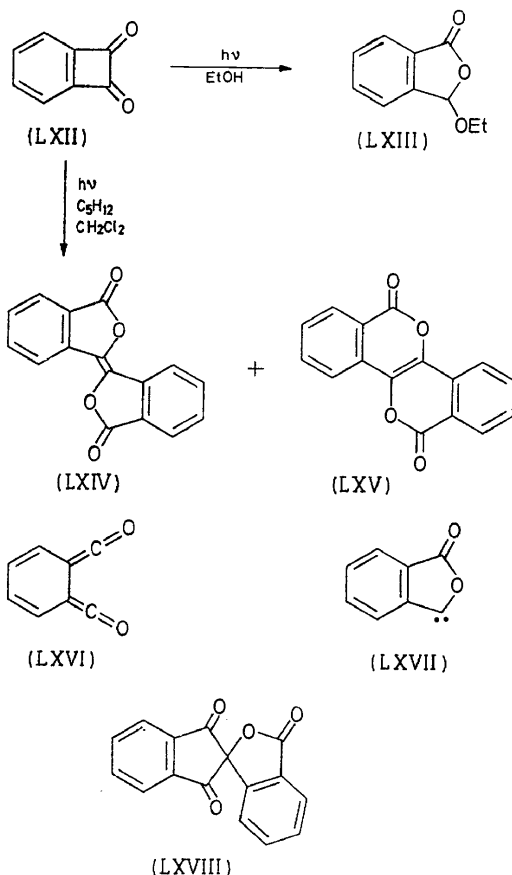
knowledge of photochemical cyclic acetal formation from cyclobutanones by their work on *D*-nor-16-keto-steroids. Irradiation of a *C/D-trans* compound (LV) in ethanol gave the cyclic acetals (LVI) and (LVII) together with the alkene (LVIII) and the cyclopropane (LIX) derived by loss of ketene and carbon monoxide, respectively. Irradiation of the corresponding *C/D-cis* steroid (LX) in ethanol gave, in addition to (LVIII) and (LIX), two acetals, both of which have structure (LXI), but are epimeric at C-16.



C/D-cis compound the acetals are formed by exclusive cleavage of the bond corresponding to formation of the more stable acyl-alkyl diradical as in

previous instances. It is clearly probable that the reduced discrimination in the case of (LV) is associated with the very high ring strain of the C/D-*trans*-fused system. Of great further interest is the observation that acetal formation is stereospecific in the sense that the C/D-*trans* compound (LV) gives C/D-*trans*-fused products only, while the C/D-*cis* compound (LX) gives C/D-*cis*-fused products only. This result demonstrates that in these cases carbon-oxygen bond formation is concerted with carbon-carbon bond cleavage and no acyl-alkyl diradical intermediate is formed.

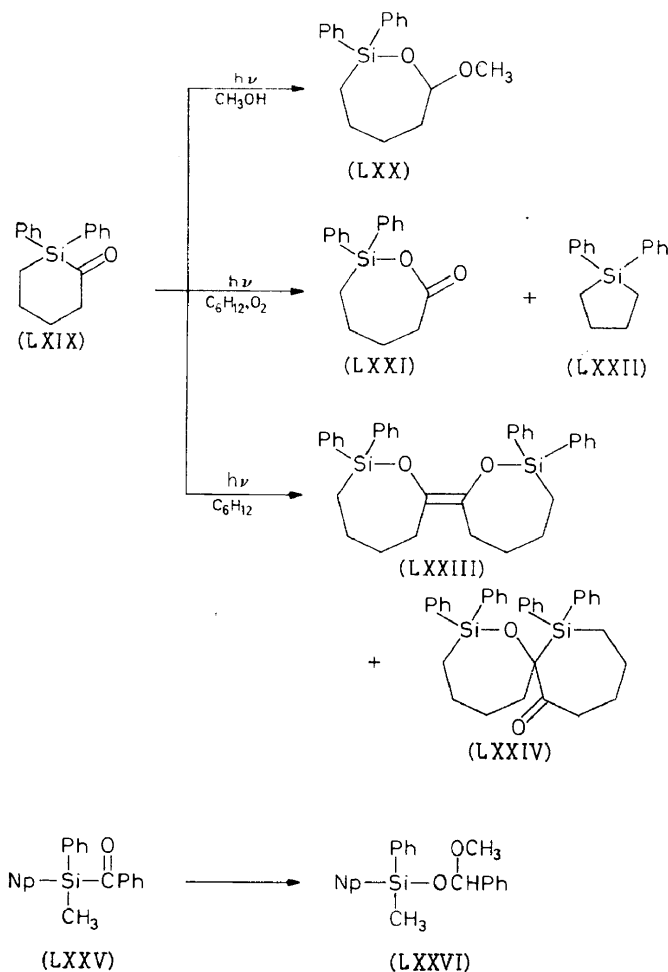
Related to these reactions of cyclobutanones are the photoreactions of 1,2-benzocyclobutenedione (LXII) which have been investigated by two groups of workers. Staab and Ipaktschi²⁴ found that on irradiation in ethanol it gives the lactol ether (LXIII), the analogue of the acetals formed from the tricyclic ketones and cyclobutanones discussed previously. On irradiation in pentane/dichloromethane (LXII) gave *trans*-biphthalyl (LXIV) as the major product together with its *cis*-isomer and a third dimer (LXV); the latter was also formed as a minor product on irradiation in ethanol. The formation of these products was interpreted in terms of



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cleavage of (LXII) to the bisketene (LXVI) (a process which can be considered as involving a Norrish Type I reaction) and conversion of this to the oxacarbene (LXVII). Evidence for the intermediacy of both (LXVI) and (LXVII) was obtained by trapping them with dienophiles and alkenes, respectively. Brown and Solly²⁵ have observed the formation of (LXIV) on irradiation of (LXII) in cyclohexane and have also postulated the intermediacy of (LXVI) and (LXVII). Under their conditions the major product obtained was a dimer assigned structure (LXVIII); however, it is not excluded that this product is identical with the product which Staab and Ipaktschi consider to be *cis*-biphthalyl.

One other type of ketone has been reported to undergo photochemical ring expansion to a cyclic acetal. Brook and Pierce²⁶ have found that irradiation of 1,1-diphenylsila-2-cyclohexanone (LXIX) in methanol gave the acetal (LXX). The corresponding lactone (LXXI) was obtained on irradiation in cyclohexane in the presence of air together with the decar-



bonylation product (LXXII). Irradiation in cyclohexane in the absence of air gave two dimers considered to have most probably structures (LXXIII; stereochemistry undefined) and (LXXIV). They interpreted the formation of these products in terms of the intermediacy of an oxacarbene of the type postulated previously. On the basis of analogy with other reactions of organosilicon compounds having oxygen atoms α or β to the silicon atom they suggested that in the formation of the oxacarbene, silicon-oxygen bond formation occurs either before or in concert with the cleavage of the silicon-carbon bond. Evidence on this score was adduced from an analogous reaction of the optically active acyclic α -sila ketone (LXXV) which on photolysis in methanol gave the optically active acetal (LXXVI) with retention of configuration²⁷.

Thus the categories of cyclic ketones which have been observed to undergo photochemical ring expansion to cyclic acetals are the tricyclic ketones, cycloamphanone and nortricyclanone, in which the carbonyl group is situated in a five-membered ring, cyclobutanones, and the six-membered silacyclohexanone (LXIX). It may be noted that the last probably represents a special case both because of the possibility of bonding between the oxygen and silicon prior to carbon-carbon bond cleavage; due to the availability of *d* orbitals on silicon, and the unusual strength of the silicon-oxygen bond.

A question clearly arises in the case of carbocyclic compounds as to the nature of the structural requirements for the formation of cyclic acetals or other products derived from an oxacarbene. The photoreactions of many five- and six-membered ring cyclic ketones in solution had been examined prior to our own work but there appears to have been no previous report of the formation of such products. In order to determine whether cyclic acetals might be formed even as minor products in the photochemical reactions of such ketones we have submitted the photoproducts obtained from several simple cycloalkanones on irradiation in methanol to v.p.c. and n.m.r. analysis²². Detection of cyclic acetal formation would readily be effected by n.m.r. spectroscopy by virtue of the occurrence of both a peak due to methoxyl protons in the δ 3-3.5 ppm region and one due to the single proton on the acetal carbon atom in the δ 4.5-5.0 ppm region.

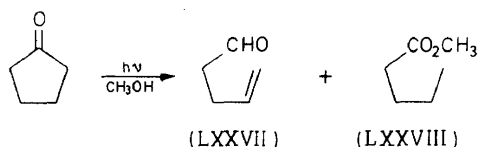
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Irradiation of monocyclic ketones

Irradiation of cyclopentanone in methanol gave the unsaturated aldehyde (LXXVII) [cf. (I) \rightarrow (II) \rightarrow (III)] as the major product detectable by vapour phase chromatography[†]; this product has been obtained previously in the vapour phase photolysis of cyclopentanone and the mechanism of its formation has been investigated by Srinivasan². A minor product, methyl valerate (LXXVIII), was detected by vapour phase chromatography. This latter product may be assumed to be derived from the corresponding ketene [cf. (I) \rightarrow (II) \rightarrow (IV)]; the preponderance of (LXXVII) over

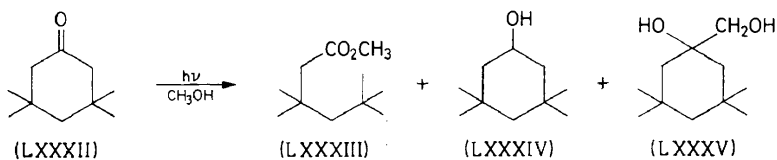
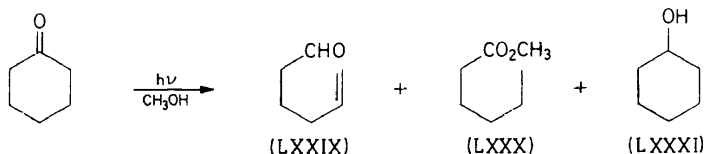
[†] In this and related cases, the aldehyde was accompanied by its dimethyl acetal; if irradiation is conducted in acidic methanol all of the aldehyde is converted to its acetal, providing a potentially useful preparative procedure.

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(LXXVIII) is in accord with earlier observations by Quinkert³, who has found in general that aldehyde formation takes precedence over ketene formation in the case of five-membered cyclic ketones and has interpreted this in terms of the geometries of the transition states for the alternative modes of hydrogen transfer in an acyl-alkyl diradical of type (II). V.p.c. and n.m.r. analysis failed to indicate the presence of any cyclic acetal analogous to that obtained from cyclocamphanone. Turro and Southam²¹ have also reported recently that irradiation of cyclopentanone in methanol gives (LXXVII) but no cyclic acetal; they made a corresponding observation for 2,2,5,5-tetramethylcyclopentanone.

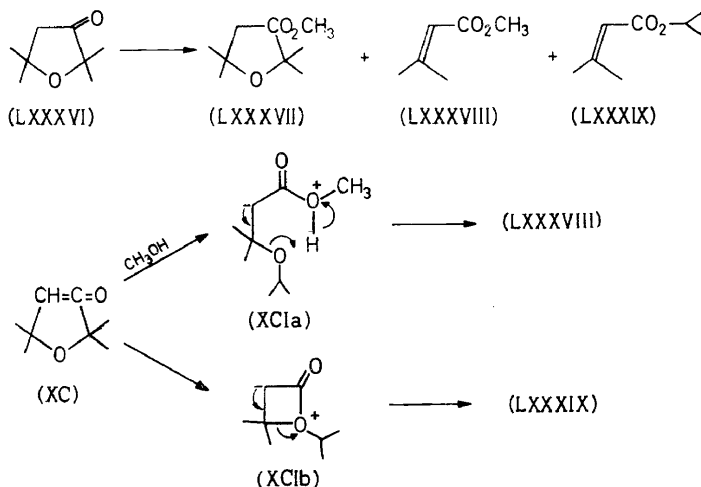
Irradiation of cyclohexanone in methanol gave the aldehyde (LXXIX) and the ester (LXXX) with the latter predominating, in accord with expectation³. In addition the reduction product, cyclohexanol (LXXXI) was formed. No cyclic acetal could be detected by v.p.c. and n.m.r. analysis of the cyclohexanone reaction mixture.



3,3,5,5-Tetramethylcyclohexanone (LXXXII) was next investigated since it was expected that unsaturated aldehyde formation would be inhibited in this case. Irradiation of (LXXXII) in methanol fulfilled this expectation, but gave only the ketene-derived product (LXXXIII) and the reduction products (LXXXIV) and (LXXXV). Again no cyclic acetal formation could be detected. The reduction product (LXXXV) is of interest; it corresponds to a mixed pinacol reduction product involving methanol and finds precedent in the early work on aliphatic ketones²⁸ and in the photoreduction of acetophenone in methanol²⁹.

Having failed to detect cyclic acetal formation in the case of these simple ketones, we turned to the study of the dihydrofuranone derivative (LXXXVI)²². This was chosen because (i) the lack of β -hydrogen atoms

should make aldehyde formation unlikely, (ii) the five-membered ring should make ketene formation unfavourable, and (iii) the ether oxygen should facilitate Norrish Type I cleavage. In the event, irradiation of (LXXXVI) in methanol gave the esters (LXXXVII), (LXXXVIII), and (LXXXIX); no cyclic acetal could be detected. Product (LXXXVII) clearly arises from the ketene (XC), which may also serve as the source of the other two products, as indicated in (XCI a) and (XCI b). It is also possible that (XXXVIII) arises from (LXXXVII). It is noteworthy that even in the case of this five-membered cyclic ketone ketene-derived products are formed to the exclusion of any ring-expanded cyclic acetal.

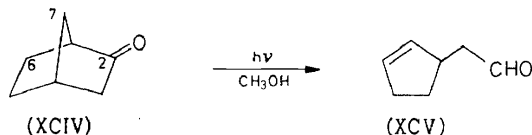
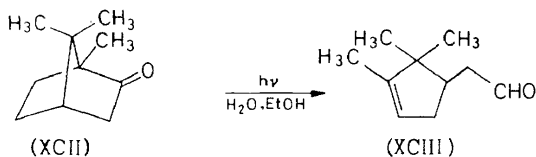


Irradiation of bridged cyclic ketones

Having failed to uncover cyclic acetal formation in the photolysis of these monocyclic ketones, we turned our attention to bridged bicyclic ketones^{22, 30}. The irradiation of camphor (XCII) in aqueous ethanol is reported to give two major products to which have been assigned structures (XIV) and (XCIII)¹⁰. We find that irradiation of norcamphor (XCIV) in methanol gives the aldehyde (XCV)[†] and its dimethyl acetal as the only major products; no evidence was obtained for the formation of a cyclic acetal. The position of the ethylenic double bond in this aldehyde is of interest; none of the isomeric 3-cyclopenteneacetaldehyde analogous to (XCIII) appears to be formed. Clearly in the case of camphor, the analogue of (XCV) cannot be formed; however, in the case of norcamphor, while aldehyde formation can occur by transfer of a hydrogen atom from either C-6 or C-7 to C-2, the latter process occurs to the exclusion of the former. This can be rationalized in terms of a more favourable geometry for hydrogen transfer either subsequent to or in concert with the cleavage of the C-1—C-2 bond. Preliminary results indicate that the aldehyde obtained by irradiation of 3-methylnorcamphor in methanol also is the Δ^2 - rather than the Δ^3 -cyclopentene derivative.

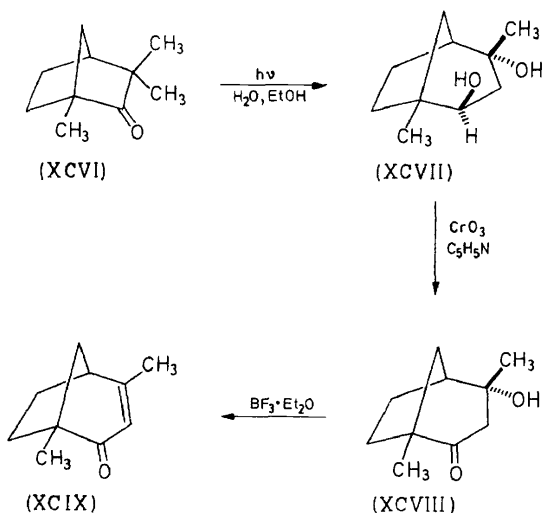
[†] The formation of this aldehyde by irradiation of norcamphor in solution has also been observed by Srinivasan and by Chapman³¹.

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Of particular interest in relation to the possible formation of cyclic acetals from bicyclic ketones was the early report³² that prolonged irradiation of fenchone (XCVI) in aqueous ethanol gave a crystalline diol corresponding in composition to a 1:1 adduct of fenchone and water. We now assign structure (XCVII) to this product³⁰.

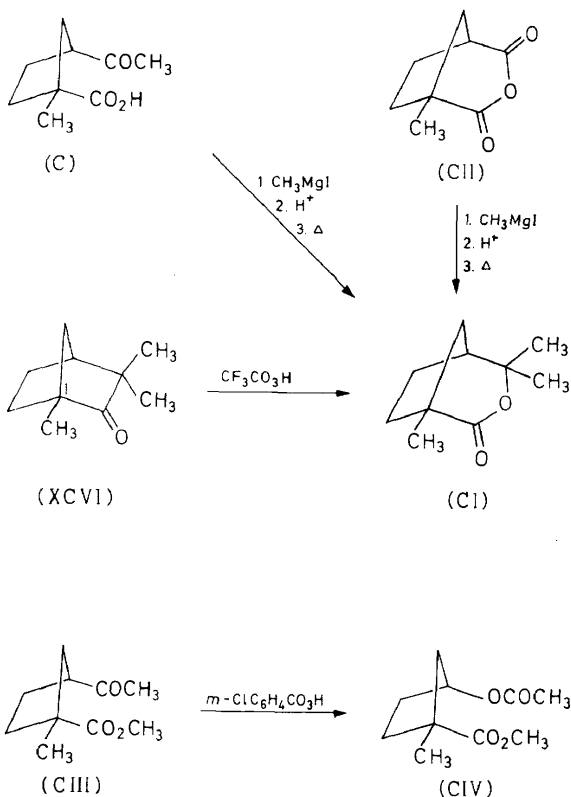
It was obtained in 14 per cent yield (based on unrecovered starting material) after exposure of fenchone in aqueous ethanol in a Pyrex vessel to intermittent sunlight for six months. The same product could be obtained



more rapidly and in somewhat higher yield by irradiation of the solution in a quartz vessel with a medium-pressure mercury arc lamp; however, reaction remains slow since only 30 per cent of the fenchone had been consumed in seven weeks. Its spectra confirmed that it is a diol and showed that the hydroxyl groups are secondary and tertiary. Oxidation with chromium trioxide and pyridine gave the hydroxy ketone (XCVIII), which on dehydration with boron trifluoride etherate gave the α,β -unsaturated ketone (XCIX); the spectra of these products were in accord with expectation. Ozonolysis of (XCIX) followed by oxidative work-up gave the keto

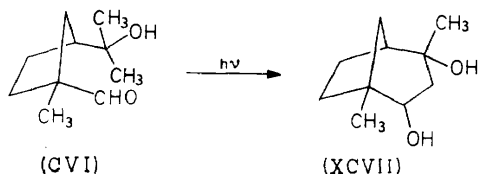
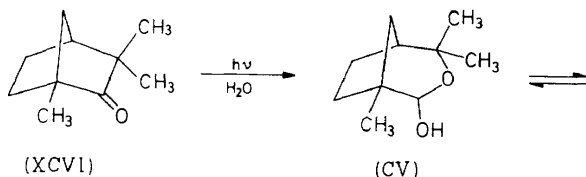
acid (C), whose structure was confirmed by its conversion to the lactone (CI) by treatment with methylmagnesium iodide followed by hydrolysis and heating in boiling benzene. The identity of this lactone was established by its independent synthesis from the anhydride (CIII); it was also obtained by the action of trifluoroacetic acid on fenchone, together with the isomeric lactone derived by migration of C-1 to oxygen³³. The relative disposition of the acetyl and carboxylic acid groups in (C) and thus of the secondary and tertiary hydroxyl groups in (XCVII) was confirmed by methylation of (C) to give (CIII) followed by Baeyer-Villiger oxidation to give (CIV), whose structure was confirmed by n.m.r. spectral data.

The stereochemistry assigned in structure (XCVII) is based on n.m.r. spectral evidence that the secondary hydroxyl group is axial, and infrared spectral evidence that intramolecular hydrogen bonding is absent.



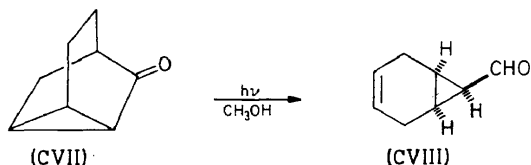
The diol represents a novel type of product from the photochemical reaction of cyclic ketones in hydroxylic media. Several pathways for its formation can be envisaged: we suggest that this may involve the intermediacy of the cyclic hemiacetal (CV), the direct analogue of the cyclic acetals obtained previously. Conversion to the diol could then occur via the aldehyde tautomer (CVI) of the hemiacetal. [Added in proof: Recent results show that (CV) is not an intermediate in the formation of (XCVII)³⁰, and suggest that (XCVII) arises from 3-isopropenyl-1-methy-

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licyclopentancarboxaldehyde, formed by cleavage of the C-2—C-3 bond of (XCVI) and hydrogen transfer from one of the *gem*-methyl groups²².]

We have also examined the products obtained on irradiation of the tricyclic ketone (CVII) in methanol. This was chosen, of course, because of its close relationship to nortricyclanone. However, v.p.c. and n.m.r. analysis



of these products failed to indicate the presence of any cyclic acetal. The major products were the unsaturated aldehyde (CVIII) and its dimethyl acetal^{30, 34}.

CONCLUSION

What then can be deduced with respect to the structural requirements for photochemical cyclic acetal formation from cyclic ketones? The reaction appears to be a general one for cyclobutanones. In the case of cyclopentanones, it has not been observed with simple monocyclic derivatives, but occurs with the tricyclo[2.2.1.0^{2,6}]heptan-2-ones, cyclocamphanone and nortricyclanone. [Added in proof: It does not occur with various methyl-substituted 2-norbornanones, nor with norcamphor.]† It has not been observed with cyclohexanones, with the single exception of the α -sila ketone (LXIX), where, as has already been pointed out, the presence of the silicon atom may well introduce a special driving force.

The occurrence of the reaction in the case of cyclobutanones and the tricycloheptanones initially suggested to us that entropy might be an important factor. On this view rebonding to oxygen in an acyl-alkyl diradical intermediate of type (II) formed by Norrish Type I cleavage would

† The formation of cyclic acid anhydrides on irradiation of five-membered cyclic α -diketones in the presence of air³⁵ could be a related reaction²¹, however the formation of lactol ethers of type (LXIII) has not been reported in these cases.

be favoured in those cases where the opportunity for separation of the two reaction sites by rotation about carbon-carbon single bonds is reduced. However, the work of Quinkert²² and his colleagues makes it appear likely that a diradical of type (II) is not involved.

It is possible that this type of reactivity of cyclic ketones is associated with unusually high ring strain. However, we now suggest that those compounds which undergo the reaction do so, not because their structural features necessarily make the reaction more ready, but rather because these features are unfavourable for competing intramolecular reactions, which normally occur to the exclusion of cyclic acetal formation. On this view the transition states for both ketene formation and unsaturated aldehyde formation are unfavourable in the case of cyclobutanones and tricyclo[2.2.1.0^{2,6}]heptan-2-ones. That the former is the case follows from the considerations of Quinkert³ relating to the difficulty of ketene formation in the case of cyclopentanones relative to cyclohexanones. That the latter could be the case follows from examination of the geometry of the transition states. The reluctance with which cyclic ketones undergo cyclic acetal formation is indicated by the fact that the dihydrofuranone (LXXXVI), which cannot undergo aldehyde formation, gives only products derived from the corresponding ketene, although formation of ketenes from five-membered cyclic ketones is normally an unfavourable process.

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References

- ¹ G. Ciamician and P. Silber. *Ber. dtsh chem. Ges.* **41**, 1071, 1928 (1908).
- ² R. Srinivasan. *Adv. Photochem.* **1**, 83 (1963).
- ³ G. Quinkert. *Pure Appl. Chem.* **9**, 607 (1964); *Angew. Chem. Intern. Ed. Engl.* **4**, 211 (1965).
- ⁴ J. G. Calvert and J. N. Pitts, Jr. *Photochemistry*, p. 389, John Wiley and Sons, Inc., New York (1966).
- ⁵ R. L. Alumbaugh, G. O. Pritchard, and B. Rickborn. *J. Phys. Chem.* **69**, 3225 (1965).
- ⁶ M. Barnard and N. C. Yang. *Proc. Chem. Soc.* 302 (1958).
- ⁷ W. H. Urry, D. J. Trecker, and D. A. Winey. *Tetrahedron Letters* 609 (1962).
- ⁸ C. Weizmann, E. Bergmann, and Y. Hirshberg. *J. Am. Chem. Soc.* **60**, 1530 (1938).
- ⁹ P. de Mayo. *Adv. Org. Chem.* **2**, 378 (1960).
- ¹⁰ R. Srinivasan. *J. Am. Chem. Soc.* **81**, 2604 (1959).
- ¹¹ R. R. Sauers. *Tetrahedron Letters* 1015 (1962).
- ¹² R. R. Sauers and R. W. Ubersax. *J. Org. Chem.* **30**, 3939 (1965).
- ¹³ D. M. Lemal and K. S. Shim. *J. Am. Chem. Soc.* **86**, 1550 (1964).
- ¹⁴ D. I. Schuster and J. D. Roberts. *J. Org. Chem.* **27**, 51 (1962).
- ¹⁵ G. O. Schenck and R. Steinmetz. *Chem. Ber.* **96**, 520 (1963);
D. I. Schuster, M. Axelrod, and J. Auerbach. *Tetrahedron Letters* 1911 (1963).
- ¹⁶ D. E. Bays and R. C. Cookson. *J. Chem. Soc. (B)*, 226 (1967).
- ¹⁷ P. Yates and L. Kilmurry. *Tetrahedron Letters* 1739 (1964); *J. Am. Chem. Soc.* **88**, 1563 (1966).
- ¹⁸ H. U. Hostettler. *Tetrahedron Letters* 687 (1965).
- ¹⁹ S. W. Benson and G. B. Kistiakowsky. *J. Am. Chem. Soc.* **64**, 80 (1942).
- ²⁰ H. U. Hostettler. *Helv. Chim. Acta* **49**, 2417 (1966).
- ²¹ N. J. Turro and R. M. Southam. *Tetrahedron Letters* 545 (1967).
- ²² P. Yates and G. Hagens, unpublished results.
- ²³ G. Quinkert, G. Cimbollek, and G. Buhr. *Tetrahedron Letters* 4573 (1966).

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- ²⁴ H. A. Staab and J. Ipaktschi. *Tetrahedron Letters* 583 (1966).
²⁵ R. F. C. Brown and R. K. Solly. *Tetrahedron Letters* 169 (1966).
²⁶ A. G. Brook and J. B. Pierce, private communication.
²⁷ A. G. Brook and J. M. Duff. *J. Am. Chem. Soc.* **89**, 454 (1967).
²⁸ G. Ciamician and P. Silber. *Ber. dtsh chem. Ges.* **44**, 1280 (1911).
²⁹ P. Yates and A. G. Szabo, unpublished results.
³⁰ P. Yates and A. G. Fallis, unpublished results.
³¹ R. Srinivasan, private communication.
³² G. Ciamician and P. Silber. *Ber. dtsh chem. Ges.* **43**, 1340 (1910).
³³ R. R. Sauers and G. P. Ahearn. *J. Am. Chem. Soc.* **83**, 2759 (1961).
³⁴ P. Yates and D. N. Butler, unpublished results.
³⁵ J. Meinwald and H. O. Klingele. *J. Am. Chem. Soc.* **88**, 2071 (1966).
J. Rigaudy and N. Paillous. *Tetrahedron Letters* 4825 (1966).