PHOTOCHEMISTRY OF DIENES[1]

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In the past few years the photochemical transformation of a molecule possessing olefinic bonds has been the subject of many investigations[2]. Before considering the chemical transformations which have been observed, it is worthwhile to look at the various transitions and states which can be involved in the excitation of an olefinic bond. Direct excitation[3] of an isolated carbon–carbon double bond occurs at a wavelength between 1800–2000 Å. The singlet (S_1) so produced thus possesses an energy between 140–160 kcal/mole above the ground state (S_0) (*Figure 1*). The direct formation of the triplet (T_1) is highly forbidden but it can be formed by direct irradiation in the presence of a high pressure of oxygen. Evans[4] has found that for ethylene the triplet has an energy about 80 kcal/mole above the ground state (S_0). For preparative photochemistry, the triplet is most efficiently produced by the indirect manner of sensitization or triplet transfer from a preformed triplet. In the case of the isolated olefin, the sensitizer normally used is mercury, its readily available tripler state having an energy of 113 kcal/mole. In the case of the olefin, as mentioned above, the intersystem crossing from a singlet to a triplet is apparently forbidden and access to the triplet from the singlet formed in direct excitation is not possible. Thus, in all direct excitations of olefins the reaction must occur either in the electronically excited singlet S_1 or in a vibrationally excited ground state formed by internal conversion of S_1 to S_0. This latter process can be illustrated by consideration of the over-simplified energy diagram shown in *Figure 2.*

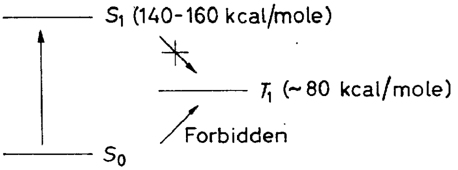


Figure 1

The initial excitation results in a singlet–singlet transition, *i.e.*, $S_0 \rightarrow S_1$. According to the Franck-Condon principle, the geometry of the excited state, S_1, resulting from the most probable electronic transition will be like that of the ground state, S_0. However, vibrational relaxation can produce an excited state with a different equilibrium geometry and different energy.

From the excited state S_1, internal conversion can occur and the molecule will return to a ground state. In so doing, the geometry of the molecule at the time it undergoes this internal conversion can be such that it is similar to two different ground state molecules, S_0 and S_0'. In this highly vibrational excited ground state, downward vibrational cascade to either S_0 or S_0' is possible, that is, the molecule can choose a pathway leading to starting material S_0 or to a new product S_0'. If this latter new product possesses a chromophore which cannot be re-excited by the incident light, the downward cascade to this new material is an irreversible process. Such is not the case when the state S_0 is formed for it was from this state the original photo-excitation occurred. It should be noted that S_0' possesses more potential energy than S_0. However, the crossover point between S_0 and S_0' can be sufficiently above the minimum of S_0' that it cannot be reached thermally at moderate temperatures. In the vast majority of the cases studied, the actual mechanistic details are not known. However, in many of the intramolecular transformations the intervention of the vibrationally excited ground state is indicated.

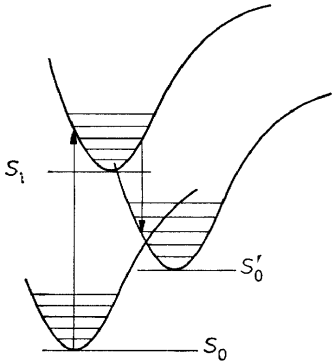
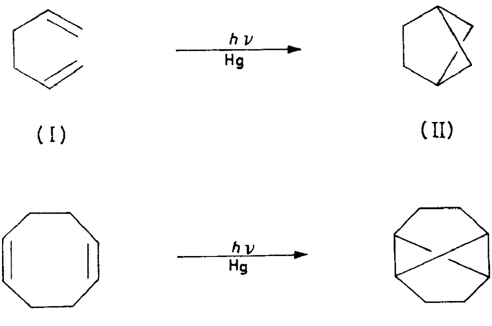
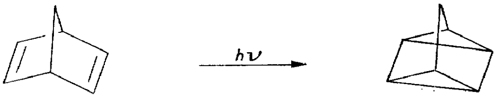


Figure 2

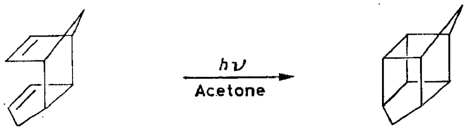
As pointed out previously, the wavelength required to excite an isolated olefinic bond is between 180–200 mμ and such wavelengths cannot be reached with preparative scale lamp sources. Thus, only the sensitization method can be used and a typical example is the conversion of 1,5-hexadiene (I) to bicyclo[2,1,1]hexane (II)[5]. A similar reaction occurs with



1,5-cyclo-octadiene (III) to yield tricyclo-[3,3,0,0^{2,6}]octane (IV)[5]. This bond crossing reaction to form 1,3-substituted cyclobutanes appears to be preferred when not strongly prohibited by strain. When the compound is held in a *cis* conformation, the bond addition to form a 1,2-substituted cyclobutane occurs as in the conversion[6, 7] of bicycloheptadiene (V) to

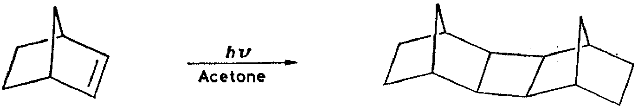


(V) (VI)



(VII) (VIII)

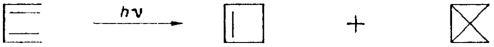
quadricyclene (VI) and dicyclopentadiene (VII) to the valence isomeric cage compound (VIII)[8]. The intermolecular equivalent of this reaction, that is, dimerization, can also occur and a typical example is the sensitized dimerization of bicyclo[2,2,1] heptene(IX) to a mixture[9] of two isomeric dimers (X). In general, there are many dimeric reactions similar to the



(IX) (X)

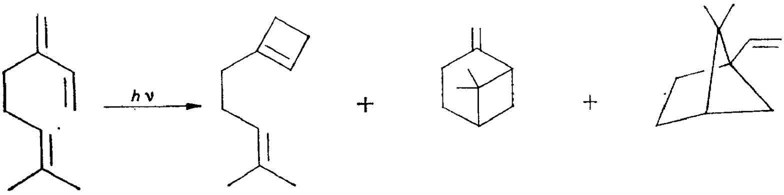
intramolecular monomeric processes but such dimerizations will not be considered in this paper.

When the two olefinic bonds are conjugated, excitation of the molecule by direct irradiation is possible but similar reactions to those described above occur. In such cases, as with 1,3-butadiene (XI), the simple bond addition gives rise[10] both to cyclobutene (XII) and bicyclo[1,1,0]butene (XIII),

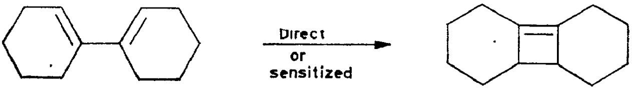


(XI) (XII) (XIII)

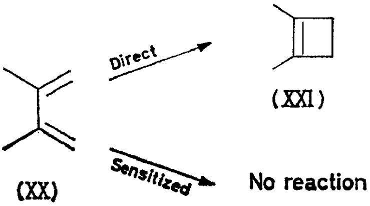
products apparently arising from the *cisoid* and *transoid* conformations of the starting material. If another double bond is so placed in the molecule that it can react with the diene, the analogous reactions to the non-conjugated dienes occur. In the case of myrcene (XIV), direct irradiation gives rise to two direct addition products, the cyclobutene (XV) and α-pinene (XVI), the former being the predominant product[11, 12]. Although the bicyclobutane has not yet been obtained, a small amount of bicyclo-[2,1,1]hexane (XVII) resulting from the bond crossing addition reaction is formed[12]. Recently, it has been found that when myrcene is activated by a ketone sensitization, only (XVII) is formed[13]. This result is of interest since it shows that the directly excited diene during its various processes to rid itself of excess energy to return to ground state has at least one pathway, albeit inefficient, which crosses a pathway from the downward cascade of the triplet; this crossing is most likely at a vibrationally excited ground state. The crossing can change in efficiency with a change in structure of the diene in that it has been found that conversion of 1,1′-bicyclohexenyl (XVIII) to its valence isomer (XIX) goes in high yield either by direct irradiation[11, 12] or by sensitized irradiation[12]. With 2,3-dimethyl-1,3-butadiene (XX), however, direct irradiation[12] gives the valence isomer (XXI) whereas under conditions where the diene will quench the triplet of napthalene, the diene only disappears slowly and no monomeric products are formed[14].



(XIV) (XV) (XVI) (XVII)



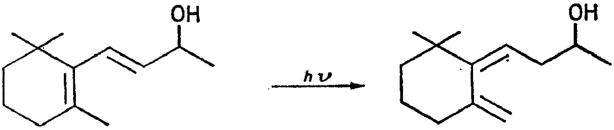
(XVIII) (XIX)



(XXI)

(XX)

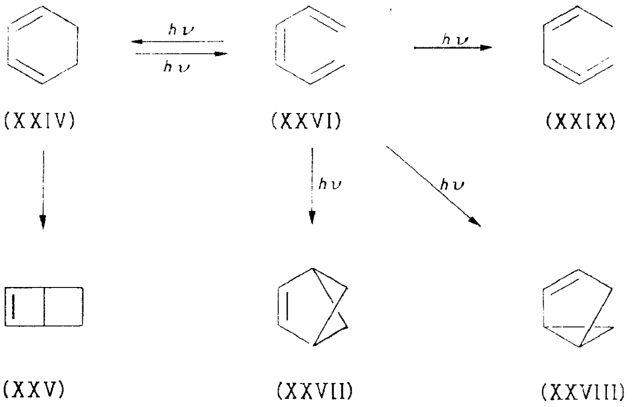
In all of the transformations so far discussed, only the π-electron system of the diene has been involved. In a recent study, it has been reported that when the diene system is part of a dienol, as in (XXII), a hydrogen migration occurs and an isomeric conjugated diene (XXIII) is formed[15]. The



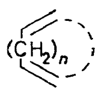
(XXII) (XXIII)

close relationship of this diene system to the others discussed suggests that the different reaction course taken most likely is due to the presence of the hydroxyl group or related oxygen functions.

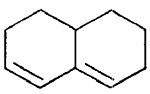
When the conjugated diene is incorporated into a six-membered ring, a major new reaction pathway is available for the excited diene. When 1,3-cyclohexadiene (XXIV) is irradiated, the formation of the valence isomeric bicyclo[2,2,0]hexene structure (XXV) occurs only in a few cases[16–20]. The usual route followed by the 1,3-cyclohexadienes is ring opening to a 1,3,5-hexatriene (XXVI)[21–37]. This is a reversible reaction and the triene can reform the starting diene. There are at least three other reaction pathways open to the triene and since the products formed normally contain a chromophore which is not efficiently activated by most light sources, the reactions can be viewed as being irreversible. As in the acyclic dienes, the bond crossing reaction of the two terminal bonds occurs and a bicyclo[2,1,1]hexene system (XXVII) is formed[31]. A second type of bond crossing reaction is also found to occur and a bicyclo[3,1,0]hexene (XXVIII) is formed[32, 33, 34, 36]. The factors which are important in determining whether a triene undergoes bond crossing to (XXVII) or (XXVIII) are not known. It is to be noted that in the transformation of the 1,3-cyclohexadienes to the valence isomeric structure (XXV), to the ring opened triene (XXVI) and subsequent bond crossing reactions of the triene, only the carbon–carbon bonds have been involved. The breaking of a carbon–hydrogen bond, however, can also occur and an allene (XXIX) can be formed[29, 31]. Thus, starting with a 1,3-cyclohexadiene there are at least five different end products which can be obtained and at present it is not possible to predict in advance which material will be the major product.



So far only those dienes which can exist in a *cisoid* conformation (XXX),



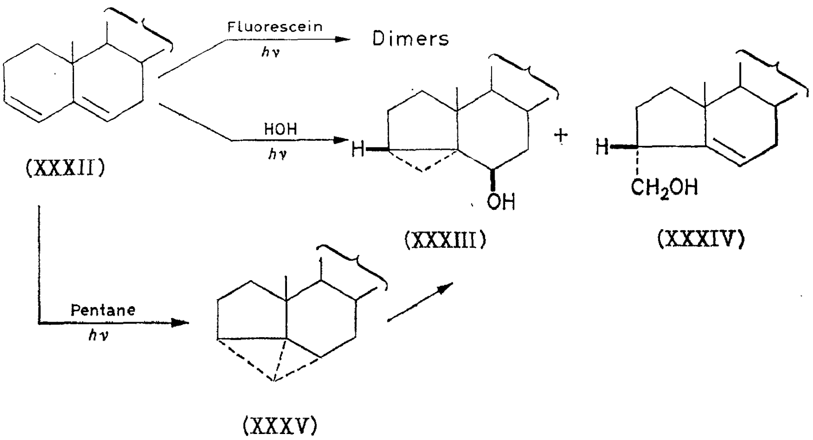
(XXX)



(XXXI)

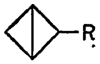
a conformation in which the terminal atoms are in a position to permit bonding and form a valence isomer, have been considered. If the diene system is placed into a rigid *transoid* conformation (XXXI) practically all of the previous reactions are prohibited. Therefore attention must now be directed towards other possible reaction pathways if a reaction is to occur.

The first *trans*-diene to be investigated was 3,5-cholestadiene (XXXII). This material upon irradiation in the presence of the sensitizer fluorescein

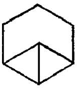


yields only dimeric materials[38, 39]. Direct irradiation in the presence of water, however, yields two monomeric materials, a cyclopropylcarbinol (XXXIII) in 60 per cent yield and a primary alcohol (XXXIV) in 15 per cent yield[40, 41]. When the irradiation is conducted under aprotic conditions in the complete absence of oxygen and water, a valence isomeric hydrocarbon (XXXV) is obtained. This material is extremely reactive and upon being allowed to stand in aqueous dioxan it is rapidly transformed into the two previously obtained alcohols (XXXIII) and (XXXIV)[41]. This new reactive hydrocarbon has been shown to have the bicyclobutane structure (XXXV). The formation of such a valence isomer is unexpected on the basis of simple molecular orbital theory since 1,3-bonding is forbidden in the excited state. If the valence isomerization does occur in the electronically excited state, the bonding must occur after a number of vibrations which permit the molecule to attain a geometrical configuration in which the original wave functions calculated for a Franck-Condon excited state are modified and permit bonding. Also, it must be considered that the reaction can occur in a vibrationally excited ground state.

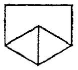
Before going into the mechanistic details of the reaction of the *trans*-diene system, it is of interest to look into the reactions and the properties of this bicyclobutane. In the past three years bicyclobutane and a variety of substituted derivatives have been prepared[42–50]. Of these materials, only the parent hydrocarbon (XXXVI) has been made by direct irradiation of a conjugated diene and in this case photolysis of 1,3-butadiene yields both the cyclobutene and the bicyclobutane[44]. However, in no case does the ring system appear to be as reactive as the one contained in the steroidal system. This reactivity speaks for the highly strained nature of the photochemical intermediate (XXXV). The greatly increased reactivity, however, is surprising when consideration is given to the hybridization of the bonds in the ring system. By the usual ^{13}C-satellite coupling method the percent *s*-character of the C—H bond of the diagonal bond has been determined and for the parent bicyclobutane[43], it is 34 per cent *s*-character, showing the



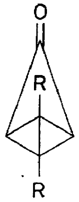
(XXXVI)



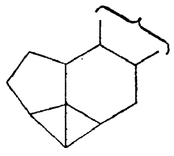
(XXXVII)



(XXXVIII)



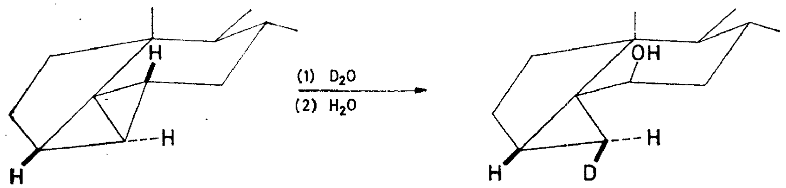
(XXXIX)



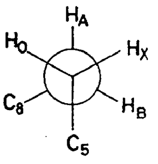
(XL)

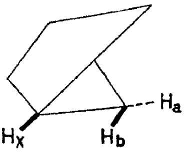
expected increased *p*-character of the C—C bond. In the trimethylene bridged analogue (XXXVII) this C—H bond possesses 40 per cent *s*-character[51], showing that the bridge has significantly deformed the bicyclobutane ring. In the steroidal case (XXXV) the *s*-character is only 38 per cent. This finding is surprising since it would have been expected to have the reactivity follow the *s*-character of the external bond.

The stereochemistry of the ring-opening reaction to yield the cyclopropylcarbinol (XXXIII) was determined by allowing the bicyclobutane to



(XXXV) (XXXIII)



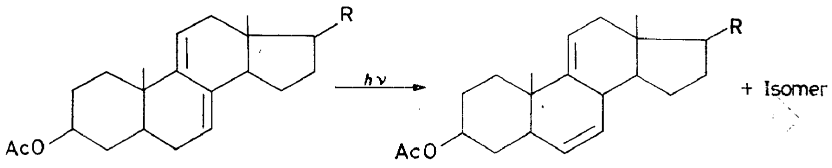


H_a: $\tau = 9 \cdot 69$, $J_{ax} = 4 \cdot 2$ c/s

H_b: $\tau = 10 \cdot 18$, $J_{bx} = 7 \cdot 3$ c/s

$J_{AX} \simeq J_{BX} \simeq 3$ c/s

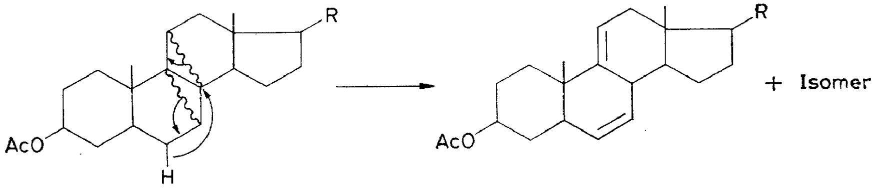
react with deuterium oxide. The solvent adds in a stereospecific manner to yield the single monodeuterated (XXXIII) (after washing with water). The 6β-configuration of the hydroxyl group is assigned on the basis of the n.m.r. spectrum as well as solvolytic rate studies. In the n.m.r. the C_6-α proton is found to possess the typical coupling pattern of an equatorial proton, that is, $J_{AX} \sim J_{BX} \sim 3$ c/s[52]. The stereochemical assignment of the C_4-deuterium also is β but in this case the assignment is still open to question. In a typical bicyclo[3,1,0]hexene the *endo* proton, H_a, absorbs at higher field than the *exo* proton, H_b, and its coupling constant J_{ax} is smaller than J_{bx} since *trans* coupling in cyclopropanes is always smaller than *cis* coupling[53]. In our case, it is seen that there is no such consistent relationship. The cyclopropyl proton which absorbs at higher field also has the larger coupling constant. We prefer to use the coupling constant for the stereochemical assignment since this value appears to be more directly related to the steric relationship between two adjacent centres. Using these stereochemical assignments, it is seen that the C_6 is inverted in the opening of the bicyclobutane.



(XL) (XLI)

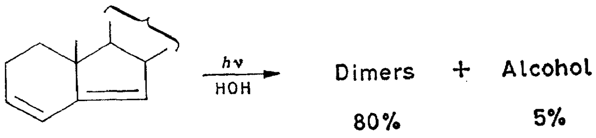
In order to evaluate the effect of strain on the photo-reaction of the *trans* dienes, two other systems which should yield highly strained bicyclobutanes have been studied. When 7,8:9,11-ergostadiene (XL) is irradiated it is found that the reaction is independent of the solvent employed, a finding quite different from that seen with 3,5-cholestadiene (XXXII)[54]. Photolysis in protic or aprotic solvents gives the same products and these materials have been shown to be isomeric non-conjugated dienes possessing the original ergostane skeleton. One of the products has been shown to be the 6,7:9,11-ergostadiene (XLI).

If it is assumed that all the reactions of a *trans*-diene go *via* a bicyclobutane intermediate, the rearrangement obtained with the ergostane diene (XL) is not surprising when the strain in the possible bicyclobutane is considered. Such a structure would be formed in a high vibrationally excited state (XLII) and rearrangement could be the preferred path rather than loss of vibrational energy to a stable ground state entity. The rearrangement with 1,3-hydride shift from (XLII) could account for the result. If such a high vibrationally excited state is involved, be it in the electronically excited or ground state, it is not meaningful to ascribe to such a state any one of many possible valence structures prior to the loss of considerable vibrational energy.



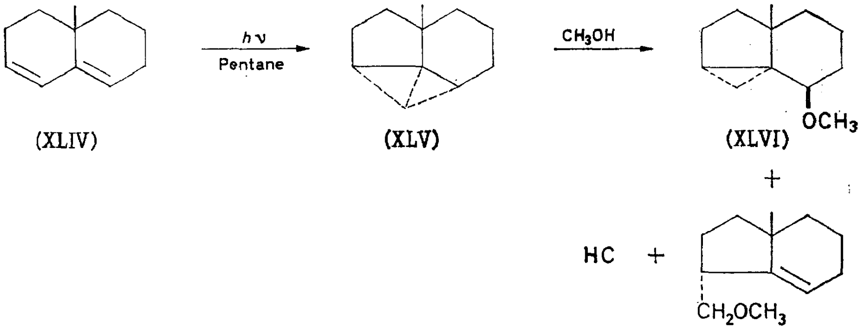
(XLII) (XLI)

next, a diene of intermediate strain has been investigated. It has been found that B-norcholestadiene (XLIII) reacts in a manner entirely different from the other two cases[55]. Again the reaction was practically solvent-independent but in this case the major product to the extent of 80 per cent was a dimer. That the dimer is not formed in the ergostadiene case (XL) can be attributed to steric factors and both the unimolecular reaction in that series and the bimolecular reaction in the B-nor series could stem from a common type of intermediate state. Another possibility is that in the B-nor diene, efficient intersystem crossing from singlet to triplet occurs. The formation of the dimer is quite surprising, however, since when the reaction is run in very dilute solution, 10^{-4}M, the dimer still is the major product. Thus, clearly, changes in the strain in the potential bicyclobutane system have an effect on the course of the reaction.



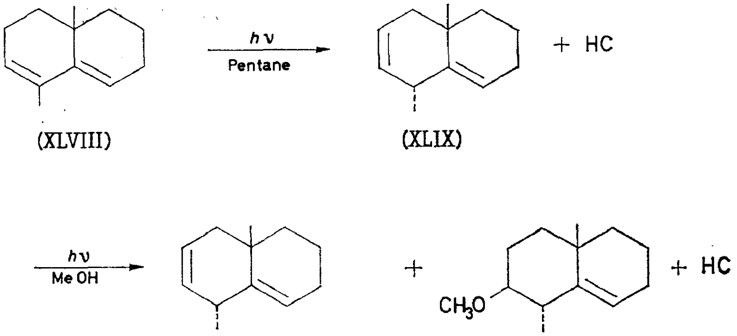
(XLIII)

In the steroid cases, only about 75–80 per cent of the products formed could be identified and in order to see if the above variation in results is merely a change in degree rather than in kind of reaction, the simple substituted hexalins have been studied. In direct analogy to the steroids, 10-methyl-$\Delta^{3,5}$-hexalin (XLIV) upon irradiation in pentane is transformed into a bicyclobutane (XLV). This material, although very reactive, is quite stable and it can be distilled under reduced pressure. Upon reaction with methanol, the bicyclobutane yields 80 per cent of the cyclopropyl ether (XLVI), 10–15 per cent of the A-nor ether (XLVII), and only 5–10 per cent of hydrocarbons. Thus, in this simple case the major reactions of the bicyclobutane are again the formation of two ethers.



(XLIV) (XLV) (XLVI) (XLVII)

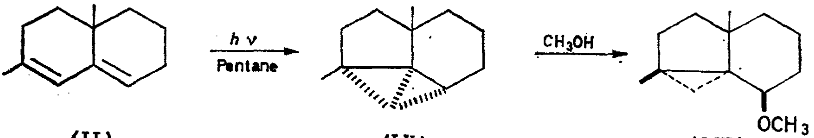
When 4,10-dimethyl-$\Delta^{3,5}$-hexalin (XLVIII), a compound equivalent to the ergostadiene (XL) in substitution, is irradiated in pentane no bicyclobutane could be detected and a 60 per cent yield of the isomerized non-conjugated diene (XLIX) is isolated. Irradiation of (XLVIII) in methanol yields 35 per cent of the diene (XLIX), 16 per cent of the ether (L), and the remainder of the material is other hydrocarbons. Thus, in this case where the strain should be similar to the lesser substituted hexalin (XLIV), no bicyclobutane can be obtained. The similarity of the reactions of (XLVIII) to those of ergostadiene (XL) in the predominant formation of unconjugated diene hydrocarbons indicates that the degree of substitution of the conjugated diene system is probably the most important reason for the divergence of the reaction of ergostadiene (XL) from that shown by cholestadiene (XXXII). The increased strain discussed earlier must be playing a lesser but still significant rôle in that in the reaction in methanol some protic solvent addition product was formed in the lesser strained hexalin.



(XLVIII) (XLIX)

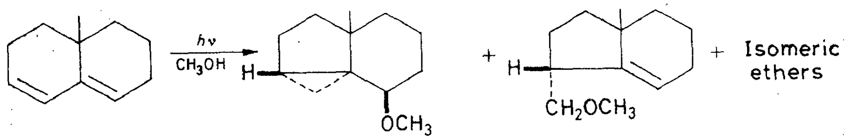
(XLIX) (L)

To further evaluate the rôle of a substituent on the reaction of the diene system as well as the reaction of the derived bicyclobutane, 3,10-dimethyl-$\Delta^{3,5}$-hexalin (LI) has been photolysed in pentane. In this case again the bicyclobutane (LII) is formed but when the product is allowed to react with methanol, only the cyclopropyl ether (LIII) is formed and no A-nor material is obtained.

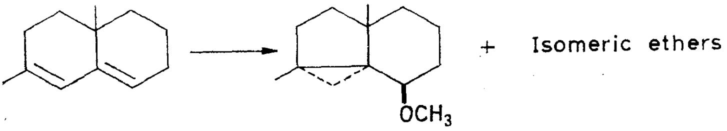


(LI) (LII) (LIII)

When the irradiations of (XXXII) and (LI) are conducted in methanol, quite different results are obtained. It is to be recalled that when the bicyclobutane is preformed, the cyclopropyl ethers are the main, if not the sole, product of the reaction. The finding of 31–79 per cent of other ethers in the reaction product of protic solvent irradiations clearly demonstrates that the solvent reacts with some excited intermediate, that is, there is a competitive reaction between the solvent reaction and the formation of a bicyclobutane. Furthermore, in the 10-methyl-$\Delta^{3,5}$-hexalin case, the formation of the bicyclobutane is still the main reaction while in the 3,10-dimethyl-$\Delta^{3,5}$-hexalin example, the protic solvent reaction with excited species becomes the predominant reaction.



(XXXII) 51% 18% 31%



(LI) 8% 79%

Further insight into the various competitive reactions in the photolysis of *trans*-dienes has been obtained by a more detailed study of the photolysis of 3,10-dimethyl-$\Delta^{3,5}$-hexalin. In this reaction it has been found that five ethers are formed, the cyclopropyl ether (LIII) arising from the bicyclobutane and the ethers (LIV–LVII) arising from other intermediates. The amounts of these various products formed depend upon the concentration of methanol present during the irradiation. The results which have been obtained are summarized in *Table 1*. It is seen that the amount of ether (LIV), the first ether formed by a pathway not involving the bicyclobutane,

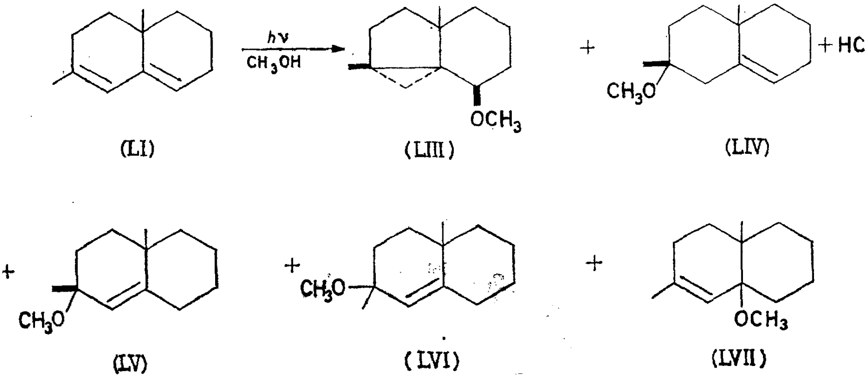


Table 1. Irradiation of 3,10-dimethyl-$\Delta^{3,5}$-hexalin in pentane containing methanol

Conc. CH_3OH	% (LIII)	% (LIV)	% (LV)	% (LVI)	% (LVII)	% HC
10^{-2}M	7	0	0	0	0	93
1M	12	26	0	0	0	62
10M	15	24	3	18	17	23
17M	12	18	4	20	24	22
25M	8	16	6	25	32	13

goes down as the concentration of methanol increases but its decrease is not as large as the decrease of hydrocarbon compounds. The hydrocarbons are most likely derived from the bicyclobutane (LII) which has not reacted with the methanol; it has been found that the rate of reaction of methanol with the bicyclobutane is slow. Next, it is seen that the formation of the ethers (LV, LVI and LVII) occurs at the expense of the formation of both the bicyclobutane (LII) and the ether (LIV). The methanol reaction giving rise to (LV, LVI and LVII) must be intercepting some species which is in the series of reaction steps related to the formation of (LII and LIV).

The decrease in production of (LIV) while ethers (LV, LVI, and LVII) are increasing shows that ether (LIV) does not come from the same precursor as the latter three ethers. These data also suggest that these last three ethers do come from a common precursor since their percentage appearance roughly follows one another. Finally, for the production of (LV, LVI, and LVII) to overtake the production of (LIV) as the concentration of methanol increases, the molar dependency of methanol in the former reaction must be of a higher order. Approximate rate constants have been obtained for this series of competitive reactions using a computer programme and a best fit is obtained when it is assumed that two molecules of methanol are involved in the formation of (LV, LVI and LVII).

A further demand made upon any mechanistic concept is the finding that when the diene is excited in methanol using naphthalene as a sensitizer, only the ethers (LV, LVI and LVII) are formed and the product formation is independent of the methanol concentration. When the diene is sensitized in pure pentane under conditions which will quench the triplet of naphthalene, the diene is recovered unchanged. Thus ethers (LV, LVI and LVII) must be formed from a second intermediate whose concentration increases with methanol concentration.

Figure 3 illustrates one possible reaction scheme which will accommodate the results. In this figure no intermediate is used unless the data demands its presence even though it is likely other intermediates are involved.

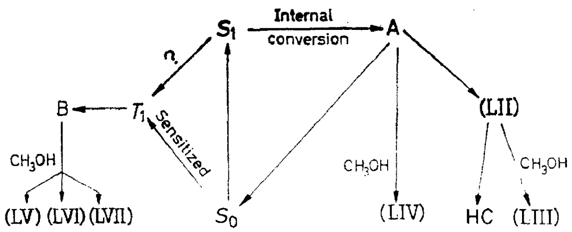


Figure 3

The initial excitation raises the diene molecule from the ground state S_0 to the electronically excited singlet state S_1. Consideration of the energetics of the various reactions found in the reaction sequence leads one to prefer that all reactions occur in going to the ground state or in the ground state. The singlet S_1 undergoes internal conversion to a vibrationally excited ground state A. This internal conversion occurs in the solvent cage and when no protic solvent is present, conversion to the bicyclobutane (LII) or return to a lower vibrational state S_0 occurs. The bicyclobutane can, in turn, react with methanol when it is present to yield the ether (LIII) or can isomerize to other hydrocarbons. If the protic solvent is a nearest neighbour in the solvent cage when the internal conversion occurs, the vibrationally excited ground state A during its downward cascade to lower vibrational levels can also react with the protic solvent to form the ether (LIV).

The formation of ethers (LV, LVI and LVII) must arise from an intermediate different than A. Since these ethers are formed in the sensitized irradiation, they could result from reaction of the protic solvent with the triplet T_1 or with the vibrationally excited ground state B formed by the intersystem crossing in the solvent cage. The vibrational energy of this ground state must be lower than that of A formed from the singlet S_1 since no ether (LIV) is formed. The critical part of this postulated sequence is that an intermediate different from A must be involved and the triplet is a reasonable intermediate. In view of the fact that the products from the reaction are ethers and not alcohols, it seems more likely that the protic solvent reaction occurs with the vibrationally excited ground state and the triplet simply functions as an intermediate which in turn can give use to the different vibrationally excited ground state B. It should be recalled, however, that the ethers (LV, LVI and LVII) are also formed by direct irradiation of the diene when methanol is present in high concentration. If the triplet is an essential intermediate in their formation, a rôle of the methanol in the reaction must be to facilitate the intersystem crossing from S_1 to T_1, a process normally strongly forbidden.

An alternative process to the involvement of a triplet is that of electron ejection[56]. In this process the equivalent of a carbonium ion and a solvated electron is formed and the high concentration of the protic solvent could aid such a process.

At this time the exact nature of this second intermediate cannot be given with certainty. It is clear, nevertheless, that the photochemical reaction of *transoid*-dienes is complex. In such a system of competitive reactions it is evident that small changes in the molecule may have detectable effect on the overall reaction, such as has been found.

The type of reaction of a diene shown in *Figure 4* is not limited only to

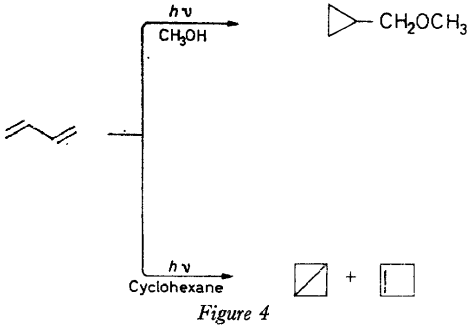


Figure 4

those systems[57] which have been frozen into a *trans* configuration. Butadiene, itself, when irradiated in methanol gives rise to cyclopropylcarbinyl methyl ether. Such a result can be compared to the formation of bicyclobutane and cyclobutene when butadiene is irradiated in cyclohexane[10]. Thus, the preparation of cyclopropylcarbinyl systems by photolysis of a conjugated diene appears to be a general synthetic organic reaction.

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