

PHOTOCHEMICAL REACTIONS WITH NON-CONJUGATED DIENES

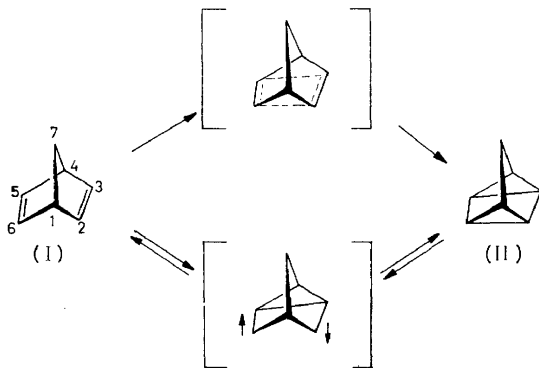
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INTRODUCTION

Electronic interactions between classically non-conjugated, by one or several sp^3 -hybridized carbon-atoms insulated centres, have been studied intensively. Today, homoallylic ions and homoaromatic compounds, to mention a few, are experimentally well documented and theoretically well understood¹. Far less settled is the state of affairs when we talk about interactions in the excited states. Such interactions of nominally unconjugated, supposedly simple chromophores have been observed in a number of chemically distinct systems, but physical interpretation of these observations turned out to be rather difficult, even for the simple case of two C=C double bonds². In this talk I would like to present some further examples where light-induced interactions within homodiene- and within homo-vinyl-cyclopropane systems have been used for the synthesis of some valuable, by other means hardly accessible, products.

In the first part we will start from a well known photoisomerization reaction. Following the original report by Cristol and Snell³ the intramolecular cycloaddition reaction norbornadiene–quadricyclane (I) \rightarrow (II)



has been studied in all details. There are three points of direct interest for our subsequent discussion:

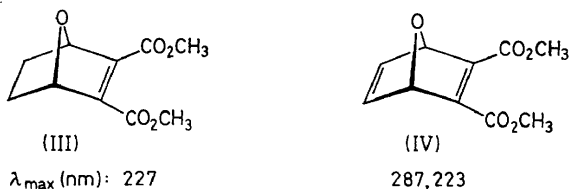
- (i) The conversion (I) \rightarrow (II) can be brought about either by direct or sensitized excitation, the process being reversible in the presence of certain sensitizers, the photostationary state concentration being determined by the triplet energies of the sensitizers (Hammond).

- (ii) The photoproducts (II) are thermally surprisingly stable [$t_{\frac{1}{2}}$ for (II) > 14 h at 140°], the $2\sigma \rightarrow 2\pi$ opening (II) \rightarrow (I) being "forbidden" by the Woodward-Hoffmann rules. [As it was shown very recently⁴, the rate of reaction (II) \rightarrow (I) is dramatically increased ($t_{\frac{1}{2}} = 45$ min at -26°) by coordination with metal complexes making the isomerization an "allowed" process].
- (iii) Structural distortions of the basic skeleton caused by substitution have practically no influence on the results of the photochemical reaction. Norbornadiene derivatives substituted by several voluminous groups are still very effectively converted to the tetracyclic systems (II)^{3,5}.

For reasons which will become obvious somewhat later we have intensively studied derivatives of (I) in which the sp^3 -hybridized C-7 carbon atom was replaced by hetero atoms (O,N,Si,P) or a sp^2 -hybridized carbon atom.

OXANORBORNADIENE-OXAQUADRICYCLANE

Replacement of a CH_2 -group by an oxygen atom in general does not alter very drastically the structural parameters of a molecule. In other words the consequences of the structurally imposed close proximity of the two ethylenic bonds in (I) and in the oxygen analogues should be comparable. In fact, the bathochromic shift of the long wavelength absorption on going from (III) to (IV) has already been attributed to the trans-annular electronic interaction in the excited state of (IV)⁶. Apparently, such a low



energy transition in the range 260–290 nm is common to the oxanorbornadiene derivatives (V) which we studied recently (*Figure 1*)⁷.

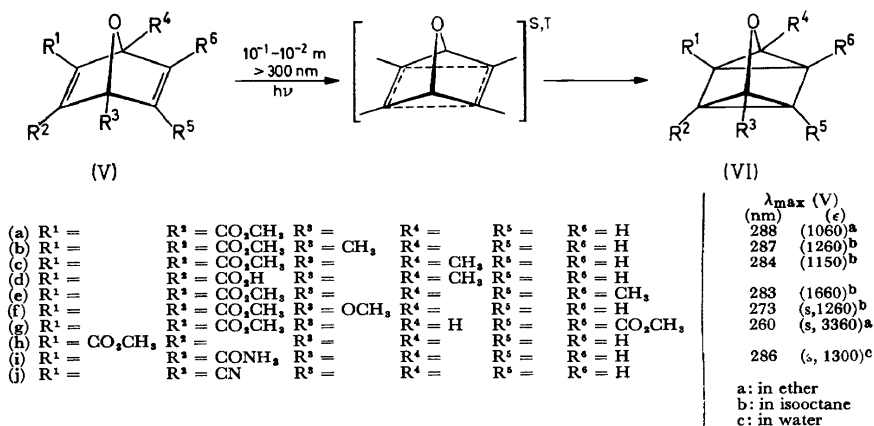
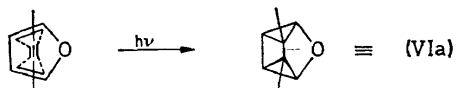


Figure 1. Transformation of oxanorbornadiene derivatives (V) to (VI); and u.v. absorption data of (V)

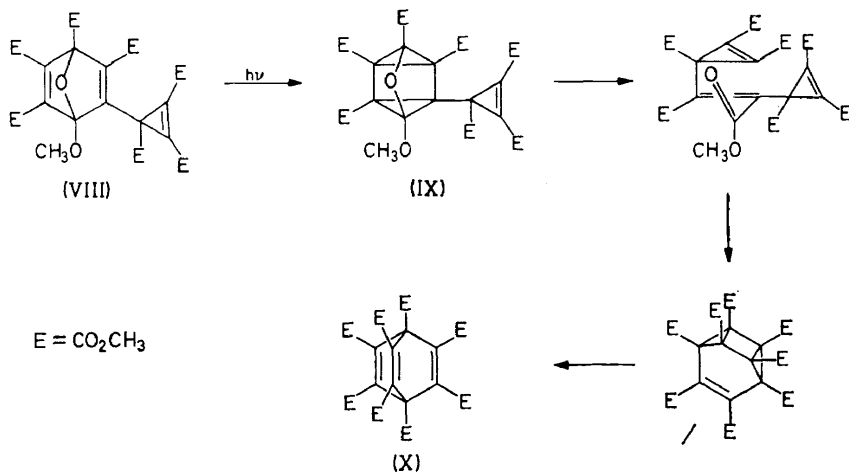
PHOTOCHEMICAL REACTIONS WITH NON-CONJUGATED DIENES

As it was proved for (IV), the transformations (V) \rightarrow (VI) can be photosensitized by acetone or benzophenone. However, in contrast to the findings with the hydrocarbons (II) the reactions seem not to be reversible under these conditions. Because of side reactions with the sensitizers the isolation of photoproducts becomes more complicated. It should be mentioned at this



point that (VIa) was isolated in a small yield independently by Schenck and Mannsfeld⁹ after photolysis of acetylene-dicarboxylate in furane. The question, however, is still open, whether (VIa) was formed by photoaddition of the type (2 + 2 + 2), observed in other cases^{3,10} or by way of the thermally produced Diels-Alder adduct (Va). After our original publication^{10a} the conversion (Va) \rightarrow (VIa) was described by Payo *et al.*¹¹ (*see Note 1 added in proof on p. 43*).

An oxanorbomadiene-oxaquadricyclane valence isomerization (VIII) \rightarrow (IX) was also postulated by LeGoff and LaCount¹² in order to explain the formation of what was assumed to be the barrelene derivative (X) on irradiating the tetrameric acetylene-dicarboxylate (VIII).



METHYLENE-NORBORNADIENE-METHYLENE-QUADRICYCLANE

Numerous derivatives of the so far unknown methylene-norbornadiene, easily available from fulvenes (XI) and acetylenic dienophiles, are described in the literature¹³. Our preliminary studies have primarily been concerned with (XII a-h); comparison of their u.v. spectra (*Figure 2*) with the ones of the identically substituted hydrocarbons (I) and oxygen analogues (V) (*Figure 1*) reveals an even more pronounced bathochromic displacement of the first absorption maxima as already noted on going from (I) to (V).

Judged by this criterion for trans-annular interaction the isomerization

(XII) \rightarrow (XIII) should pose no problems. And indeed, following the prescriptions worked out for the transformations (I) \rightarrow (II) and (V) \rightarrow (VI) the cyclization (XII) \rightarrow (XIII) has been achieved with pleasing results¹⁴. The long wavelength u.v. absorption maxima of the products (XIII)—while demonstrating nicely the favourable arrangement for electron delocalization in the vinyl-cyclopropane chromophore¹⁵—are sufficiently separated from the excited triene maxima in order to exclude further transformations.

Concerning the true nature of the excited states of (XII) responsible for the maxima given in *Figure 2* the same uncertainty already mentioned² refrains one from giving definite explanations. At least in the case of (XII b) it seems established beyond doubt that fluorenone can function as photosensitizer; (XIII b) again being stable towards such an indirect energy transfer¹⁶.

With the sequence (XI) \rightarrow (XII) \rightarrow (XIII) \rightarrow (XIV) we have worked

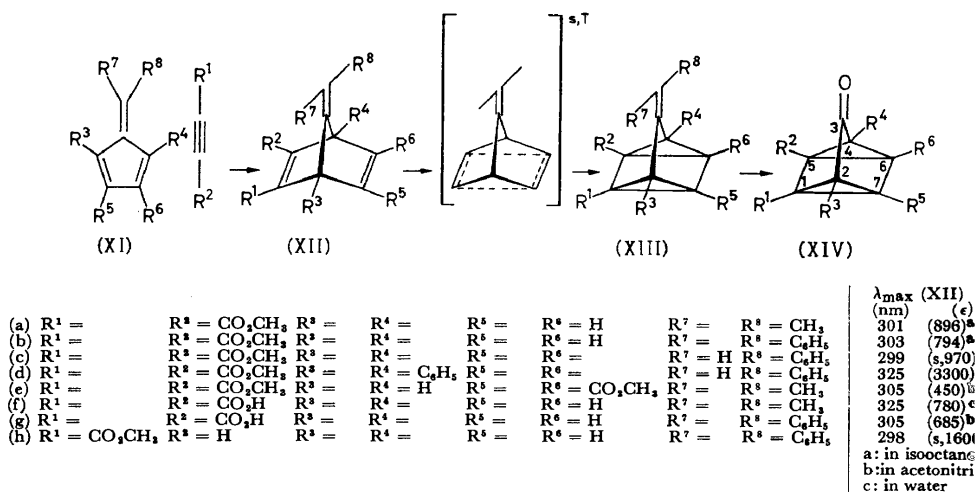
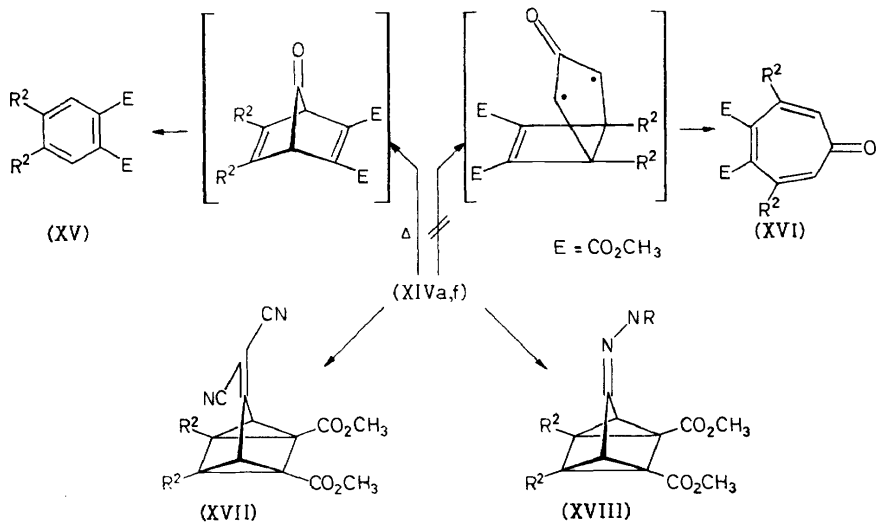


Figure 2. Conversion of methylene-norbornadienes (XII) into methylene-quadricyclanes (XIII) and "quadricyclanones" (XIV) [(XII) are obtained easily from fulvenes (XI)]; and the u.v. absorption data of (XII)

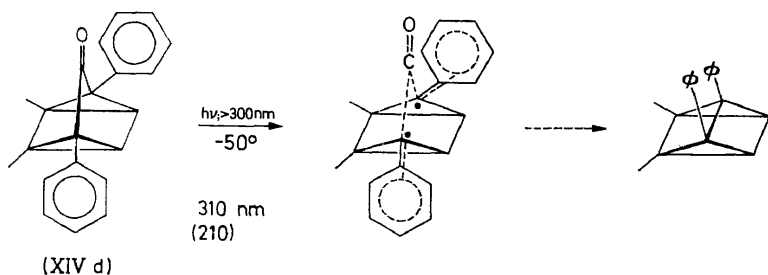
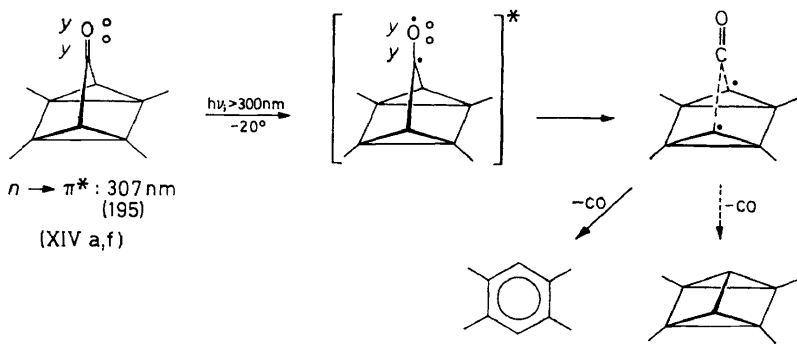
out a versatile high yield new entry into the 3-oxotetracyclo[3.2.0.0².7.0⁴.6] heptane ("Quadricyclanone")-system¹⁷. As already indicated, for the step (XI) \rightarrow (XII) many variations are known, the photoisomerization (XII) \rightarrow (XIII) so far proceeds very selectively and the oxidation (XIII) \rightarrow (XIV) under carefully controlled conditions is practically quantitative. Further work currently under way will have to define the applicability of this method to the synthesis of the unsubstituted quadricyclanone¹⁸ and its alkylated derivatives. The limiting factor will be the well known resistance of fulvenes to undergo Diels-Alder additions with non-activated C \equiv C triple bonds.

The ketones (XIV a,f) have a thermal stability comparable to the one of the equally substituted quadricyclanes (II) or methylene-quadricyclanes (XIII); beyond 120°C (XIV a,f) decompose with measurable rate to give CO and the benzenoid fragments (XV); scission of the C-1, C-2 and C-4, C-5 bonds leading to the tropones (XVI) cannot compete. Only the ketone

PHOTOCHEMICAL REACTIONS WITH NON-CONJUGATED DIENES



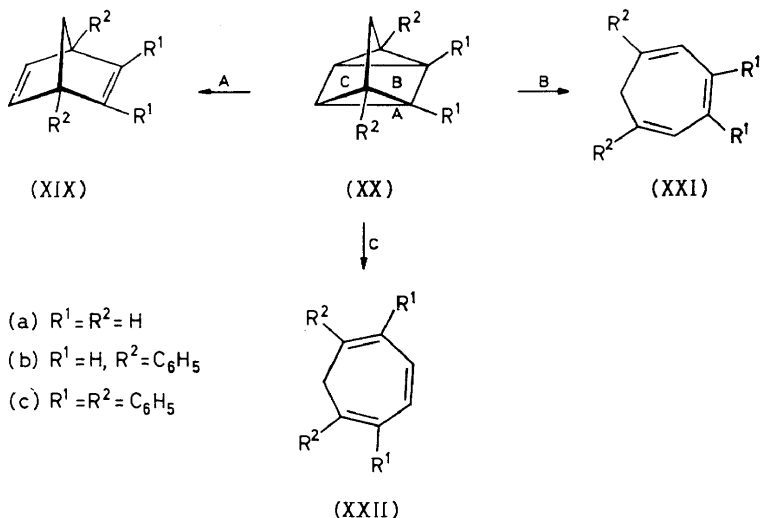
(XIV d) with the phenyl groups in the bridgehead positions is thermally so much labile that its isolation and characterization pose some difficulties¹⁹. Since the base-catalyzed condensation reactions, e.g. with malodinitrile (XVII) or dinitrophenylhydrazine (XVIII) can be achieved without rearrangements of the carbon skeleton²⁰ the ketones (XIV a, d, f) present themselves as valuable starting materials for the preparation of other



methylene-quadricyclanes not available directly from the appropriate fulvenes. Another attractive and in the view of Quinkert's work²¹ promising feature presently under investigation is the photodecarbonylation of the ketones (XIV), especially of (XIV d). To summarize, we have seen so far that a great many substituted oxa-quadricyclanes, methylene-quadricyclanes and oxa-quadricyclanes are now readily available.

At this point you will ask yourself, why a reasonably intelligent man spends so much time and effort to substantiate a known reaction by such a number of analogous cases. The answer is, that these photochemically produced tetracyclic, highly strained compounds constitute starting materials for some very useful applications. We will restrict the discussion to two aspects: thermal reorganization and cycloaddition to ethylenic- and acetylenic-dienophiles.

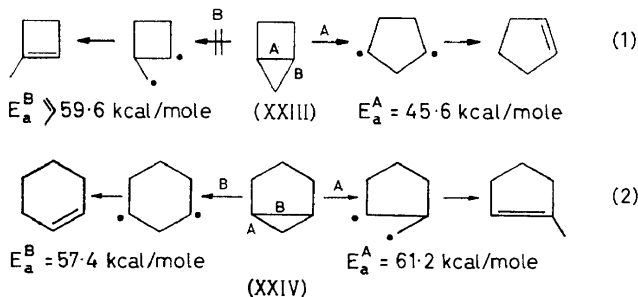
I have already drawn your attention to the fact that quadricyclane and its derivatives, in spite of their high degree of ring strain²², are thermally rather stable. In the temperature range of 120–200°C (XX a) reverts back exclusively to norbornadiene (XIX a), no scission of B or C bonds leading to cycloheptatriene takes place. Even with phenyl rings in the bridgehead positions [(XX b)] this course is maintained, the activation energies for the alternative paths being so much higher, that no (XXI b) or (XXII b) could be identified during pyrolysis of (XX b)¹⁹.



This preference of A-cleavage can be rationalized in a very qualitative manner on the basis of the activation energies reported for the sub-structures (XXIII)²³ and (XXIV)²⁴. Assuming that the influence of the second cyclopropane ring in (XX) favouring the A-cleavage compensates the roughly 4 kcal/mole advantage of the B-scission according to Eq. (2) we would expect for (XX) a selectivity comparable to Eq. (1).

The point of interest to us is our finding that the oxygen-bridge in the oxa-quadricyclanes (VI) provides enough stabilization in the transition

PHOTOCHEMICAL REACTIONS WITH NON-CONJUGATED DIENES



state (XXV)—nothing should be said with this formulation concerning the still open question as to the extent of concertion—to direct the thermal reorganization exclusively—5 per cent of (V)/(XXVII) could have been detected with certainty—on to the pathway (VI) → (XXV) → (XXVI). With up till now one exception—the oxa-quadracyclane (VIe) on pyrolysis yielded a complex mixture of at least three products, seemingly formed by the competition of A-, B- and C-cleavage. The combined effects of alkyl substitution and steric repulsion of the *cis* methyl groups might be responsible for the lacking specificity.

Since the oxepines/benzene oxides (XXVI) are prone to dimerizations†,

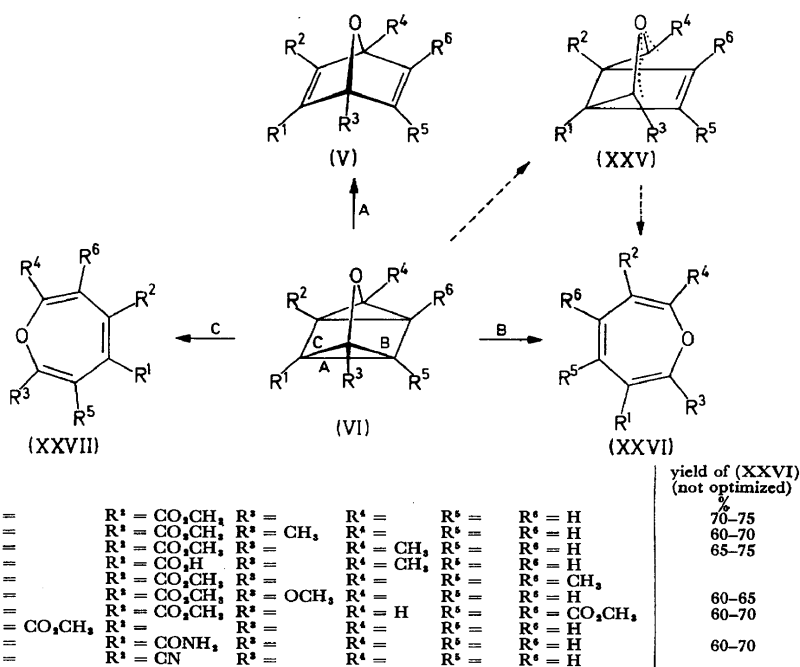
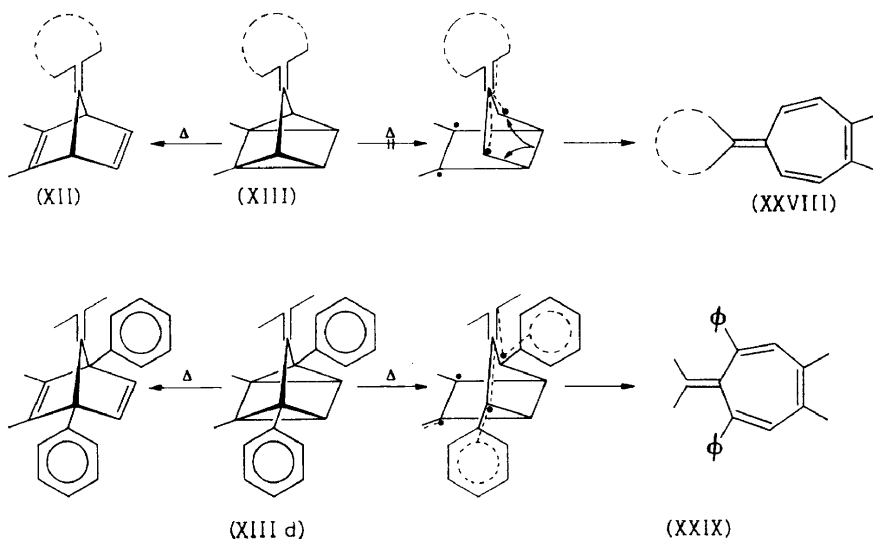


Figure 3. Synthesis of substituted oxepines (XXVI) starting from oxa-quadracyclanes (VI); the yields obtained are given

† In the case of (VI a)/(XXVI a), for instance, three dimeric substances were formed under conditions advantageous to dimerizations²⁶.

to cycloadditions with the oxa-quadracyclanes (VI), the yields of isolated oxepines depend decisively on the experimental conditions. As shown, however, in *Figure 3*, this method of synthesizing substituted oxepine compares favourably with the one developed by Vogel and colleagues²⁵. Some limitations of our procedure lie in the known difficulties of the Diels-Alder addition reaction with substituted furanes¹³ and in the possibility of more than one reorganization pattern exemplified by the behaviour of (VI e).

In view of the measured resonance energies for allylic bonds²⁷ one is not surprised to find that in contrast to the *O*-heterocycles (VI), the methylene-quadracyclanes (XIII) again are preferentially transformed to the starting trienes (XII). Apparently, the aforementioned energetic advantage of the A-cleavage cannot be sufficiently compensated for by the additional double bond, there is no indication in the cases (XIII) for the formation of the corresponding heptafulvenes (XXVIII). In this system, however, the

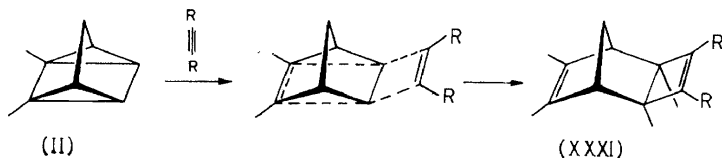
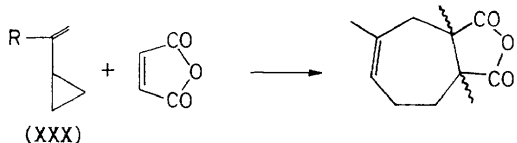


additional help of two phenyl groups in the bridgehead positions of (XIII d) induces the isomerization to (XXIX). In fact, in (XIII d) the B-bonds are weakened to such an extent that (XIII d) starts to decompose with measurable rate already at 20°¹⁹.

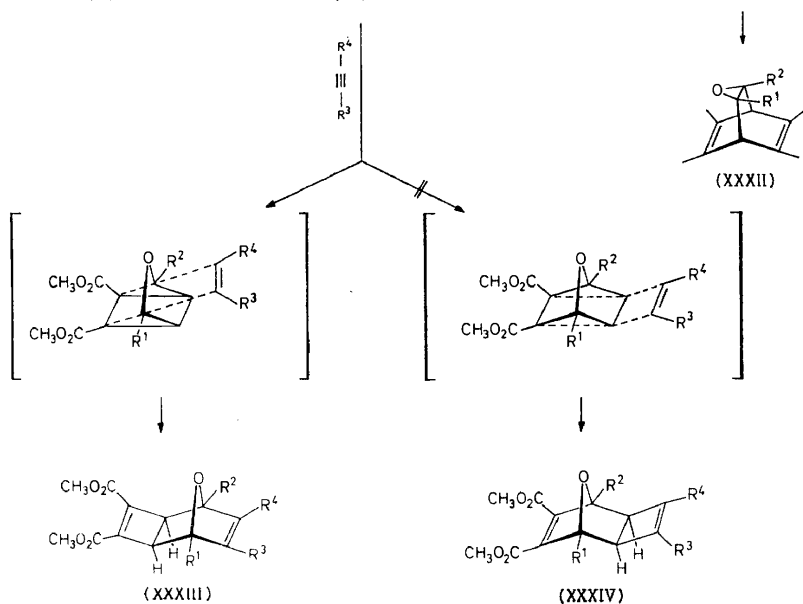
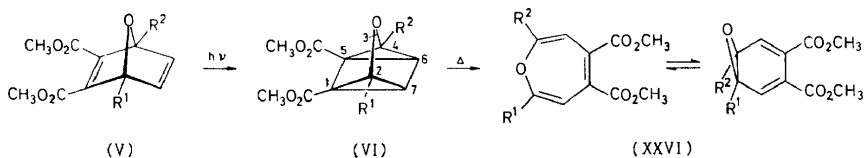
Let us turn now to cycloaddition reactions, the second aspect thought to emphasize the synthetic utility of our tetracyclic photoisomers. Already years ago it was demonstrated that a vinyl-cyclopropane system substituted in an appropriate fashion [e.g. (XXX)] may well behave as diene component towards reactive dienophiles²⁸. Very recently it was found by Smith²⁹ and in our group³⁰ that bishomodienes like the highly strained quadracyclanes add a variety of dienophiles, the reaction to (XXXI) showing a high degree of stereospecificity.

We have taken advantage of the ring strain in the ethers (VI) in order to

PHOTOCHEMICAL REACTIONS WITH NON-CONJUGATED DIENES



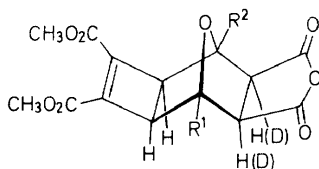
effect the same type of cycloadditions^{30a}. In a temperature range where the transformation (VI) \rightarrow (XXVI) does play if at all only a minor role—small amounts of (XXXII) can easily be separated—the saturated compounds (VI) undergo additions with several dienophiles. The present information allow a safe decision concerning the stereochemical details. As with the hydrocarbons (II) the attack is stereospecific from the exo-side, only that



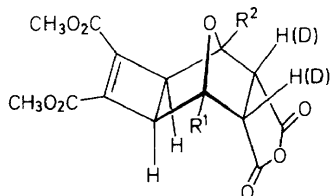
- | | | | |
|----------------------|----------------------------------|--------------------|--|
| (a) R ¹ = | R ² = H | R ³ = | R ⁴ = CO ₂ CH ₃ |
| (b) R ¹ = | R ² = H | R ³ = H | R ⁴ = CO ₂ CH ₃ |
| (c) R ¹ = | R ² = CH ₃ | R ³ = H | R ⁴ = CO ₂ CH ₃ |
| (d) R ¹ = | R ² = CH ₃ | R ³ = H | R ⁴ = CO ₂ CH ₃ |

the addition here takes place at the positions 2,4; in other words, whilst the hydrocarbons (II) behave like "bishomocyclobutadienes", the ethers (VI) undergo additions in the manner of "bishomofuranes". These conclusions are convincingly supported by the n.m.r. data of the adducts with acetylenemonocarboxylate (XXXIII b) and with maleic anhydride (XXXV a), (XXXVI a). The spectrum of (XXXIII b) clearly shows a vicinal coupling of the expected order of magnitude (2.0 cps) between the olefinic proton ($\tau = 2.78$) and the one in α -position to the bridge-oxygen ($\tau = 5.17$), thus eliminating the alternative structure (XXXIV b).

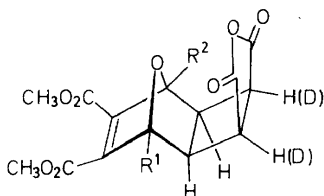
With maleic anhydride, (VI a) gives two 1:1 adducts in about equal amounts. *A priori* the structures (XXXV a), (XXXVI a) and (XXXVII a), (XXXVIII a) respectively were considered. In the spectrum of one of the two products (XXXV a) again vicinal coupling exists between the MA-protons ($\tau = 6.10$)-identified with MA-d₂- and the bridgehead protons ($\tau = 5.00$), inconsistent with (XXXVII a) or (XXXVIII a). In favour of the now more probable structure (XXXVI a) for the second adduct—and



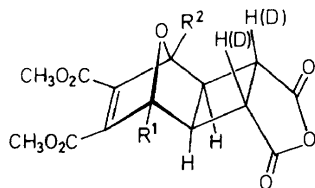
(XXXV)



(XXXVI)



(XXXVII)

(a) $R^1 = R^2 = H$ (b) $R^1 = R^2 = CH_3$ 

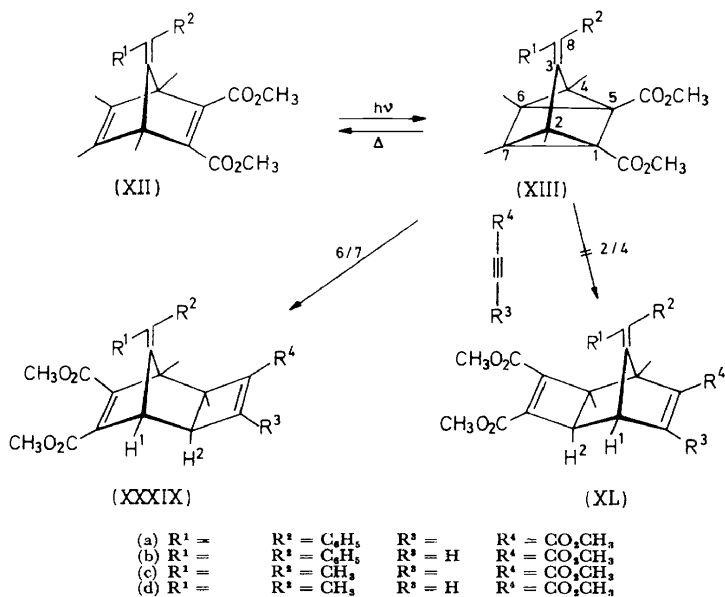
(XXXVIII)

against (XXXVII a), (XXXVIII a)—speaks the singlet peak of the two MA protons ($\tau = 6.72$). In the two recent reviews of proton-proton coupling constant data for saturated four membered rings³¹ no vicinal *cis* or *trans* coupling constants—as required by (XXVII), (XXVIII)—smaller than 2.0 cps are collected. By the same argument the exo arrangement of the anhydride rings is confirmed. We may add a further experimental observation in accord with these assignments: the signal of the two MA protons oriented *cis* in (XXXVI a) with respect to the oxygen bridge are paramagnetically shifted (0.62 ppm) compared with the ones in (XXXV a), an anisotropy effect of the oxygen well substantiated by the recent literature³².

Similarly, the methylene-quadracyclanes (XIII) react with acetylene-di- and mono-carboxylate (the sole reagents which we have used so far) under

PHOTOCHEMICAL REACTIONS WITH NON-CONJUGATED DIENES

conditions, which are sufficiently mild to avoid appreciable isomerization (XIII) \rightarrow (XII)³³. Depending on the nature of R¹/R² in (XIII) products of varying composition arise: with R¹=R²=phenyl we obtain the 1:1 adducts (XXXIX), with R¹=R²=CH₃ adducts with two equivalents of dienophile of as yet not rigorously proven structures. The structures (XXXIX) are based on the same argument as applied to (XXXIII). Because of J¹² \leq 0.5 cps for (XXXIX a) and J=1.2 cps for (XXXIX b) the four membered rings must be exo; a decision between the two mechanisms leading to (XXXIX) or (XL) was offered by the observation, that in (XXXIX b) the olefinic proton (R³) couples weakly but definitely with the allylic H² and not with the doublyallylic H¹; in agreement with (XXXIX b), explained by addition to C-6, C-7 and by rupture of the bonds 1-7 and 5-6, which are evidently the same disclosed to be the weakest on thermal isomerization.



There are still uncertainties concerning the structural details of the 1:2-adducts with (XIII c), the spectroscopic data allow no rigorous proof. For the ambitious reader the n.m.r. spectrum of the adduct between (XIII c) and two equivalents of acetylene-dicarbomethoxyate [λ_{max} (methanol) 330 nm, ϵ = 5800] is given (Figure 4). It is conceivable, that (XIII c) functions primarily as monohomodiene (C¹-C⁷-C²-C³-C⁸), all efforts to intercept³⁴ a 1:1 intermediate have up to now been unsuccessful.

The same diene-type reactivity has been established for the ketone (XIV a): with acetylene-di- and mono-carboxylate the COT derivatives (XLI) are produced in a rather uniform manner. As evidenced by the n.m.r. data and as was to be expected³⁵ the equilibria lie strongly on the side of the isomers (XLI b). By analogy to the above examples it is concluded, that

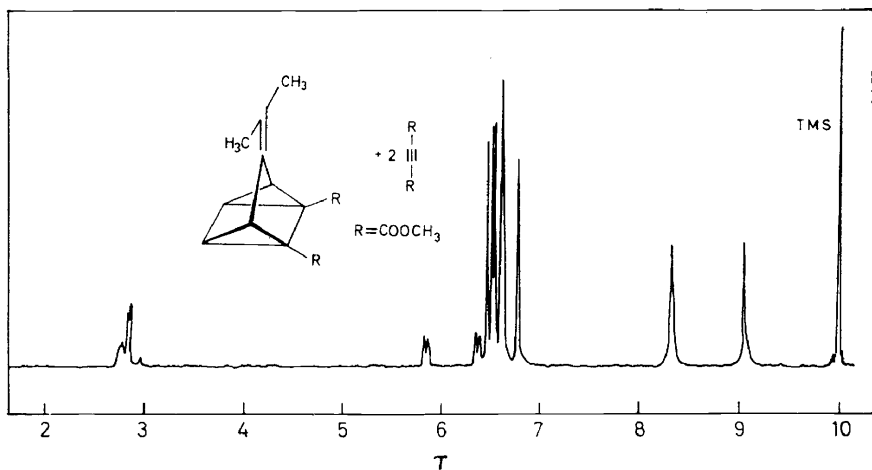
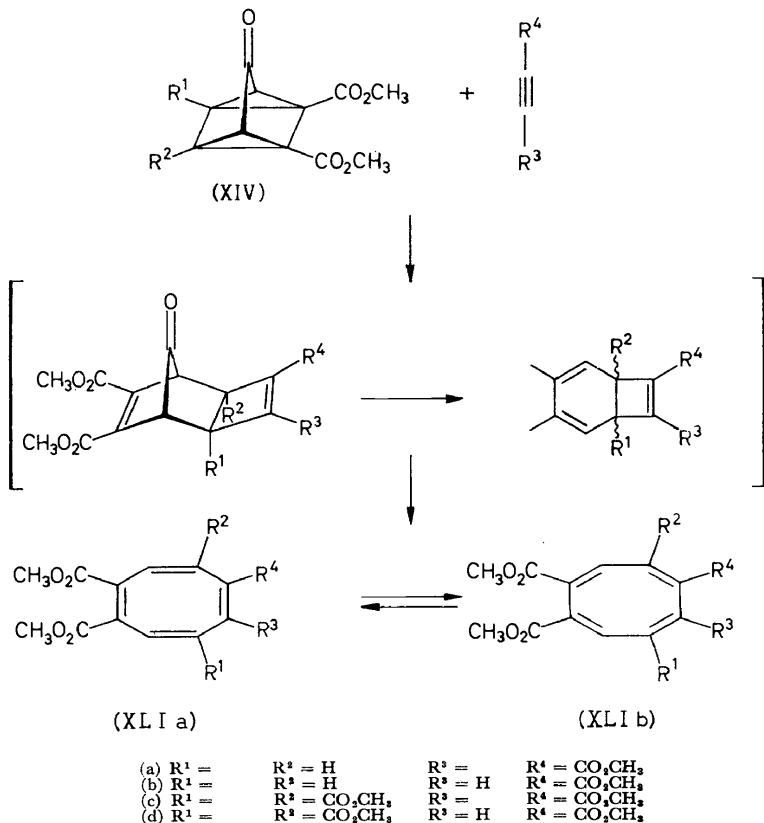


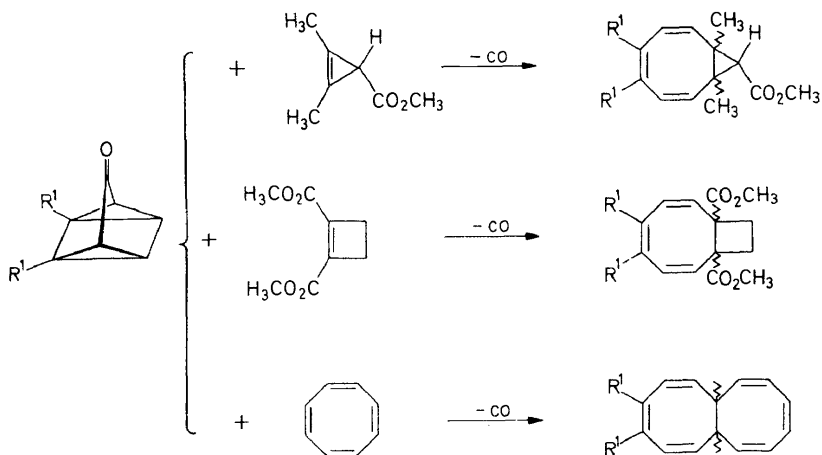
Figure 4. N.m.r. spectrum of the adduct between (XIII c) and two equivalents of acetylenedicarbomethoxyate



PHOTOCHEMICAL REACTIONS WITH NON-CONJUGATED DIENES

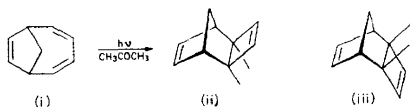
again carbon atoms 6 and 7 are the points of addition, what would nicely explain, why the ketone (XIV c) even under more drastic conditions is resistant towards the same dienophiles.

It was attractive to explore the capability of the "bishomocyclopentadienones" (XIV) to function as precursors of further COT derivatives remembering the many applications of cyclopentadienones for the synthesis of benzenoid compounds¹³. Our preliminary results with dienophiles like 1,2-dimethylcyclopropene-carbomethoxylate, cyclobutene-1,2-dicarbomethoxylate or COT were somewhat disappointing³⁶.

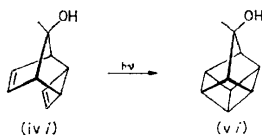


I might also mention in this connection that the now easy availability of the adducts (XXXIII a-d), (XXXIX a,b) and (XLII a-e) has prompted an intensive study of their photochemistry³⁷. The idea behind this effort was that light-induced $2\sigma \rightarrow 2\pi$ valence isomerization furnishes bridged cyclooctatrienes of the type (XLIII), for which rather interesting photochemical transformations can be envisaged[†]. Exemplary cases are (XLII a,b), the sensitized excitation (acetone) of which results in the formation of small amounts of one single dimer (XLIV?), besides two isomers, for which the spectroscopic data (u.v., i.r., n.m.r., m/e) suggest the barbaralane structures

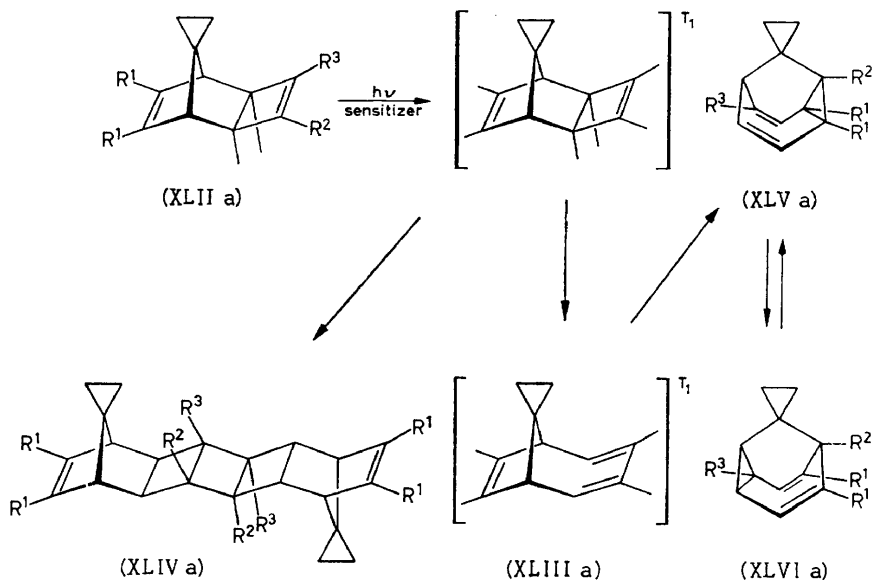
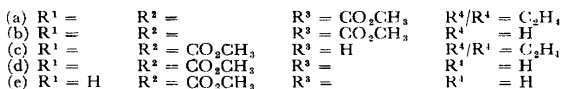
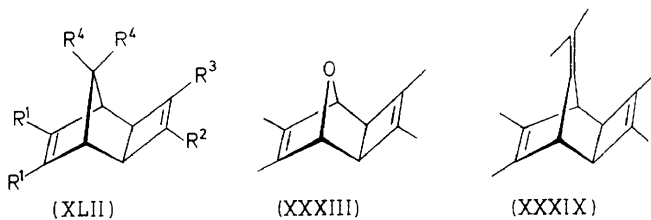
[†] The reverse process leads to two of the major products, (ii) and (iii), which are formed by photolyzing the triene (i) in acetone³⁸.



Irradiation of the alcohol (iv i) under unspecified conditions gave the homocubanol (v i)³⁹.



(XLV) and (XLVI) respectively⁴⁰. Whilst the change of the carbon skeleton (XLII) to (XLV)/(XLVI) finds a plausible explanation in the earlier work by Roth⁴¹ and Winstein⁴² on the cyclooctatriene-1,3,6 the specific substitution pattern in (XLV/XLVI), if correct (see Note 2 added in proof on p. 43), asks for complex pathways.



Similar investigations with the oxa and methylene analogues, (XXXIII) and (XXXIX), chemical degradation studies with (XLV a,b), and (XLVI a,b) presently under way are expected to allow unambiguous structure assignments and a more detailed description of the reaction course.

7-AZANORBORNADIENE-3-AZAQUADRICYCLANE

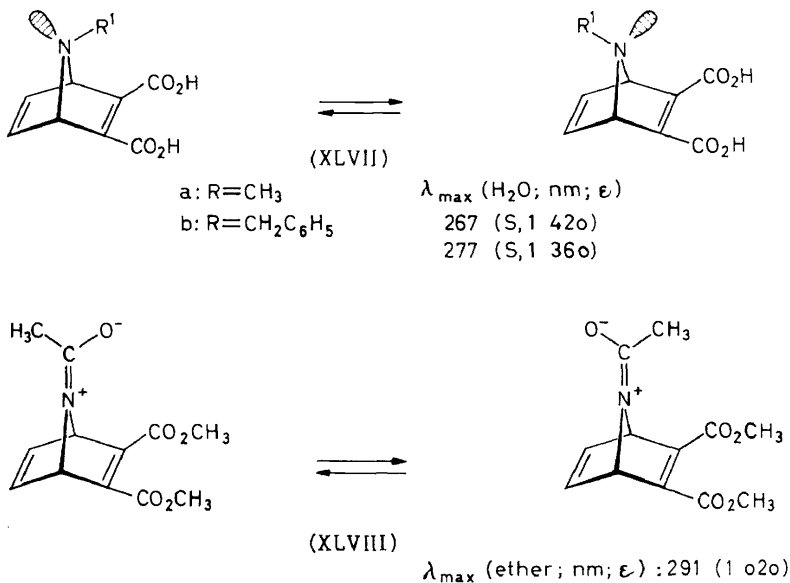
A priori experimental difficulties not encountered with the analogues (I), (V) and (XII) had to be expected in this system. In general, attempts to carry out Diels-Alder addition reactions between simple pyrrole and acetylene derivatives lead to substitution or to normal Diels-Alder products

PHOTOCHEMICAL REACTIONS WITH NON-CONJUGATED DIENES

followed rapidly by retrogression or further transformations⁴³. Aromatization, for instance, is especially facilitated by substitution in the 2- and 5-positions of the starting pyrrole⁴⁴.

In low yields we prepared the azanorbornadienes (XLVII a,b) following literature procedures⁴⁵ and synthesized additionally the *N*-acetyl derivative (XLVIII) in substantial quantities^{46†}. Again, and with the same reservation², the u.v. data, more specifically the low energy absorptions may be interpreted as indications of appreciable electronic interaction between the two insulated double bonds.

Let me restrict this discussion to the example (XLVIII). When the ethereal solution is irradiated under the conditions most favourable for the conversion (XII) → (XIII) (practically zero transmission below 290 nm) the 291 nm maximum rapidly disappears giving rise, however, to a new, red shifted maximum (*c.* 332 nm with shoulder at 350 nm), which again decreases on longer irradiation. Because of the much slower rate of the consecutive



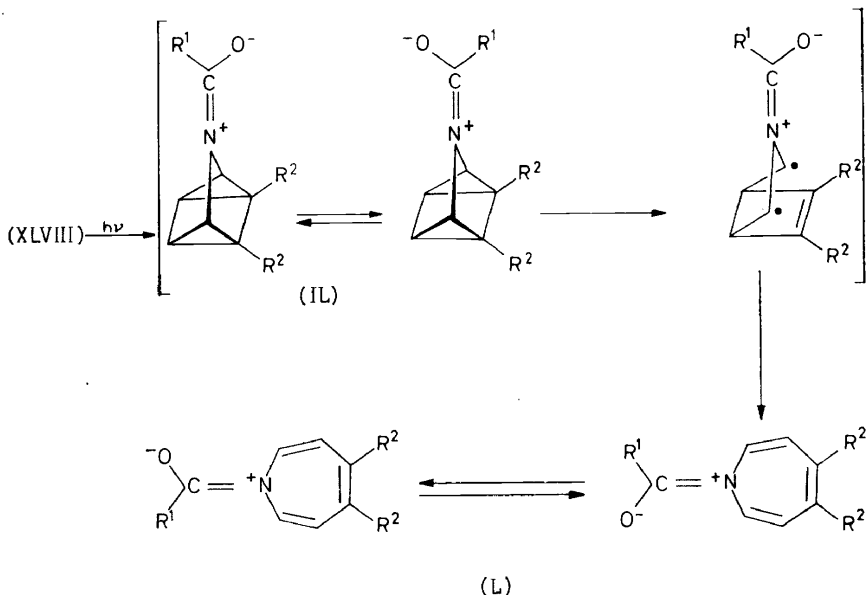
reaction the orange and principal product which belongs to the 330–350 nm absorption can be intercepted. Its n.m.r. spectra at varying temperatures and the other spectroscopic evidence ($\lambda_{\max} = 355, 226 \text{ nm}$)⁴⁷ are suggestive of the azepine structure (L).

Whilst we have little doubt as to the intermediacy of the azaquadricyclane (II) in the conversion (XLVIII) → (L) we are still not sure whether the step (II) → (L) is initiated thermally or photochemically. The rapid transformation of (II) in spite of its supposedly ineffective (<290 nm) chromophore makes us prefer the former possibility. Careful n.m.r. monitoring at low temperatures will provide more insight. In addition, the *N*-methyl compound

† The synthesis of some additional *N*-aryl- and *N*-acyl-aza-norbornadienes have been developed in the meantime^{46a}.

(XLVII a) certainly should be photochemically stable at the above conditions.

More experimental results which we expect in the near future will certainly teach us more about the thermal and photochemical properties of the azaquadracyclane system and about the scope of the isomerization (XLVIII) = (L) (see Note 3 added in proof on p. 44).

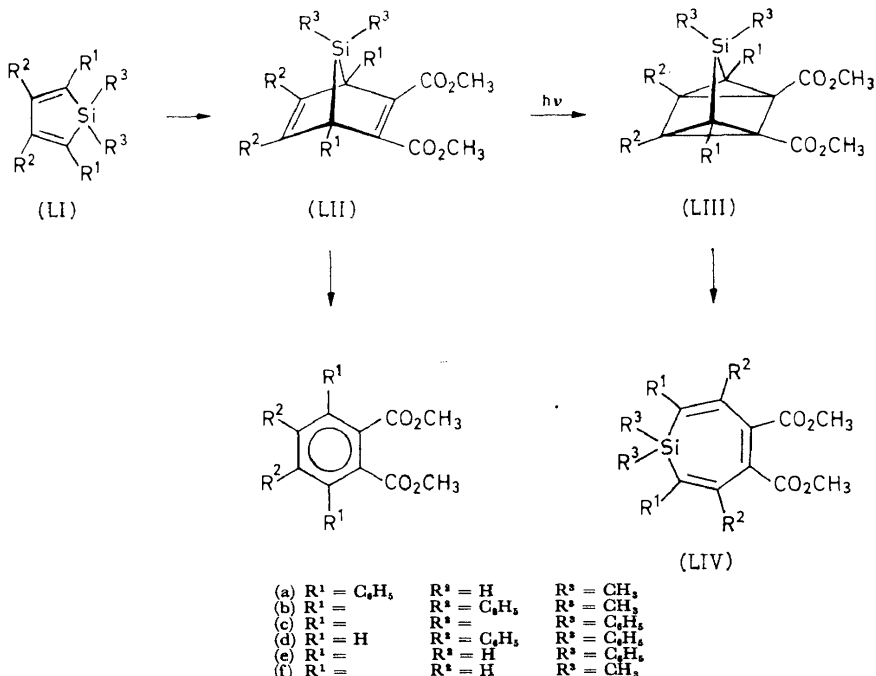


7-SILANORBORNADIENE-3-SILAQUADRICYCLANE

It was tempting to develop by a route similar to the one described above a conversion (LI) \rightarrow (LII) \rightarrow (LIII) \rightarrow (LIV); a preparation of the silepine system of which, to our knowledge, no member has definitely been established. Unfortunately, only a few siloles (LI) have so far been described and the ones which are easy to make have phenyl groups in the positions 2,5⁴⁸. The very same substituents in (LII), however, facilitate greatly the aromatization by elimination of R₂Si [compare the stability of the diphenylquadracyclanone (XIV d)]. In fact, Gilman and collaborators⁴⁹ reported the high thermal instability of the phenylsubstituted silanorbornadienes (LII a,b) and their unusual sensitivity towards ethanol. (LII a) in contact with ethanol loses rapidly R₂Si with formation of the diphenylphthalate.

We have just finished the first irradiation experiments with (LII a,b) and are confronted with the arduous task of differentiating between thermal and photochemical effects. Any statement would seem premature. We think the isomerization (LII) \rightarrow (LIII) has better chances with silanorbornadienes having no substituents in the 1,4 positions and having no oxygen containing substituents⁵⁰. We are struggling at the moment to make such substrates as (LII d,f) (the —CO₂R group being replaced by —CN).

PHOTOCHEMICAL REACTIONS WITH NON-CONJUGATED DIENES

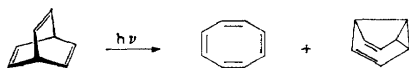


BICYCLO [2.2.2] OCTADIENE

Although no details have been published, efforts have been made by different research groups to duplicate the norbornadiene-quadracyclane ring closure in the related homodiene (LV); the failure seems to us to be worldwide. One obvious interpretation is the weaker interaction between the atomic *p*-orbitals because of the greater angle θ between the planes defined by the orbitals of one double bond and the axis S (*Figure 5*). As a consequence, competitive reactions become predominant.† We have tested very carefully the derivatives (LV a) and (LV b)^{7a,51} applying the conditions worked out in the systems (I) \rightarrow (II), and as we will see (LXVI) \rightarrow (LXVII), (LXIX) \rightarrow (LXX).

To make a long story short, in aprotic solvents (ether, pentane) irradiation of the diester (LV) using a Hanovia 450 watt high pressure Hg lamp (vycor filter) results in a very complex mixture of dimeric, hydrogenated and solvent addition products. In contrast, and this observation makes this example worth mentioning here, the same treatment in the case of the diacid (LV a) or the dianion (LV b) yields in a very fast, completely stereospecific and quantitative reaction the alcohol (LVI), by 1,5-addition of the

† In this context the formation of cyclooctatetraene (besides semibullvalene) on sensitized excitation of barrelene should be mentioned^{51a}.



elements of water to the homodiene system. In a control run the water was removed by dry freezing thus eliminating the objection that (LVI) might have been formed by a thermal addition of water to the photoisomer (LXI), an idea not unreasonable taking into consideration the rapid addition of water to the quadricyclane (II)⁵².

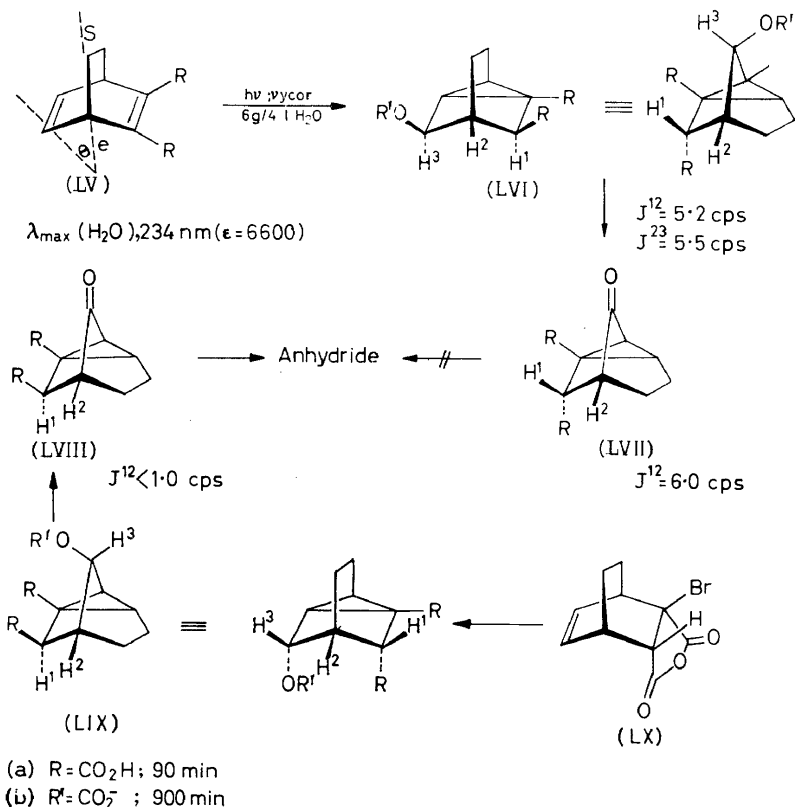
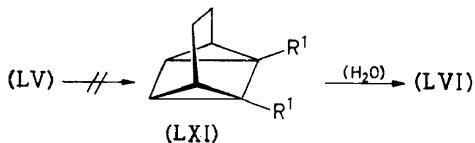


Figure 5. Attempted ring closure in the homodiene (LV). The stereochemical relationships for (LVI) and (LVII), derived from the n.m.r. data, and reassured by a comparison of the coupling situations in (LIX) and (LVIII).

The stereochemical relationships given in Figure 5 for (LVI) and the ketone (LVII) were derived from the n.m.r. data and were confirmed by the coupling situations in (LIX) and (LVIII) which were synthesized for comparison⁵³. The stereospecificity of the addition (LV) \rightarrow (LVI) contrasts the usually much more complex outcome in acid catalyzed addition reactions

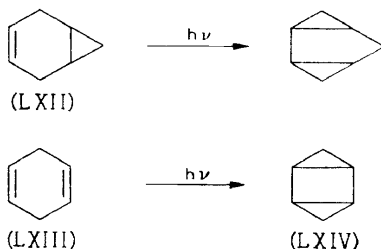


to bicyclooctadiene⁵⁴. For this and other reasons we do not believe, that (LVI) is the result of an ionic reaction of the ground state diene, although the endo attachment of the hydrogen is in agreement with the well established preference of electrophilic reagents for endo addition to bicyclooctadiene⁵⁵ (see p. 41).

BICYCLO [4.1.0] HEPTENE-3

In this last section we will be dealing with homovinylcyclopropane systems of the general type (LXII), derived from the homodienes (LXIII) by substituting one C=C double bond by a cyclopropane ring.

For the very same reasons which enhance the chances of the intramolecular ring closure (LXIII) → (LXIV) by going from the monocyclic (LXIII) to the bicyclic homodiene (I) we originally started with the tricyclo [3.2.1.0^{2,4}] octenes (LXVI) and (LXIX)⁵⁶. The u.v. absorption curves of (LXVI a-d) and (LXIX a-d) do not reveal any details which one might interpret as reliable indication of any electronic interaction between double bond and three membered ring⁵⁷, the first absorption maximum of the exo isomers,

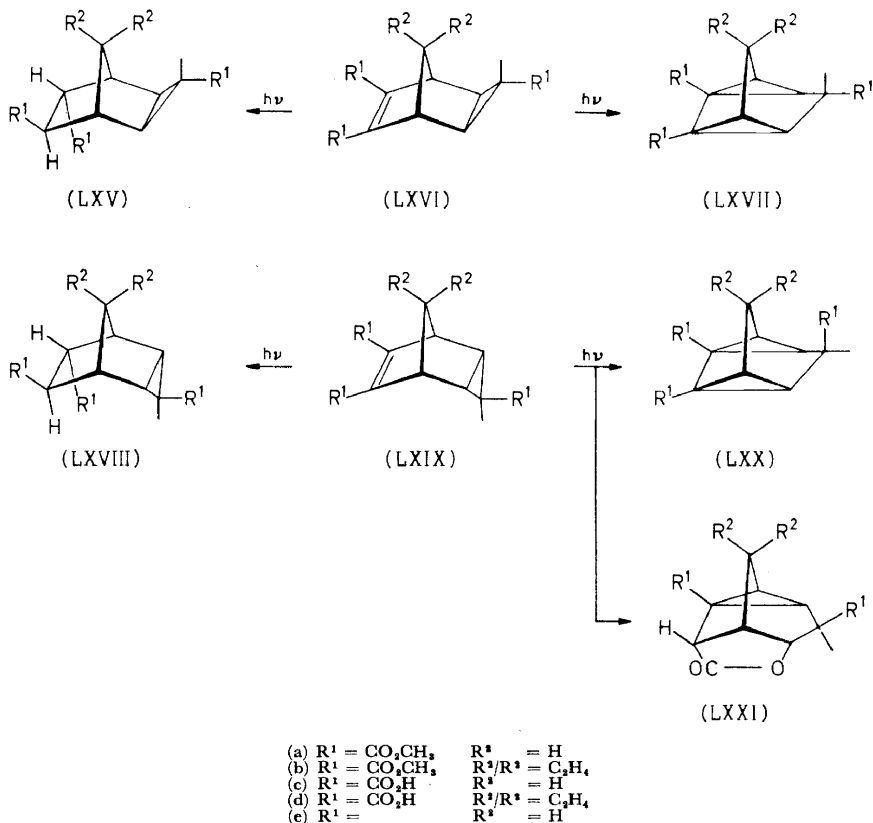


however, being consistently redshifted by about 10 nm compared with the endo absorptions (*Table 1*). Undoubtedly, the geometric requirements for overlap of the Δ orbitals of the cyclopropane ring with the π orbital of the C=C bond are better satisfied in (LXVI) than in (LXIX). For both, the exo as well the endo substrates (LXVI b,d) and (LXIX b,d) a systematic

Table 1. Ultraviolet absorption data vs. product distribution

	Solvent (200 mg/470 ml)	λ_{max} (nm)	(ϵ)	Time (min)	(LXVII) (%)	(LXV) (%)	
(LXVI b)	Ether	245	(5260)	30	4	40	
	Cyclohexane	243	(5300)	25	4	40	
	n-Hexane	243	(5650)	25	4	40	
(LXVI d)	Water	259	(6250)	70	87-93		
					(LXX) (%)	(LXVIII) (%)	(LXXI) (%)
(LXIX b)	Ether	236	(4350)	40	—	70	
	Cyclohexane	235	(4520)	35	—	70	
	n-Hexane	236	(4800)	35	—	70	
	Ether/THF (7/3)	237	(5060)	30	—	70	
(LXIX d)	Water	249	(5020)	240	26		18
	Ether/THF (7/3)	251	(5300)	75	20	10	

investigation of the solvent dependency was carried out (*Table 1*)⁵⁸. (Hanau Q81, 0–10°C, vycor filter; *c.* 10⁻² mol. solutions). Contrary to the clean valence isomerization of the similarly substituted bicycloheptadienes the triesters (LXVI b) and (LXIX b) in aprotic solvents are rapidly hydrogenated (preferentially by *trans* addition), the valence isomerization has only a small chance with (LXVI b), practically none with (LXIX b). Neither acetone nor benzophenone are able to sensitize the desired conversions.



For reasons which are not yet understood and for which one might advance only speculative explanations the intramolecular [$2\pi + 2\sigma$] cycloadditions become much more important when the triacids (LXVI c,d), (LXIX c,d) are irradiated in water, being almost quantitative for the *exo* isomers and competing favourably with the water addition and with hydrogenation for the *endo* isomers.

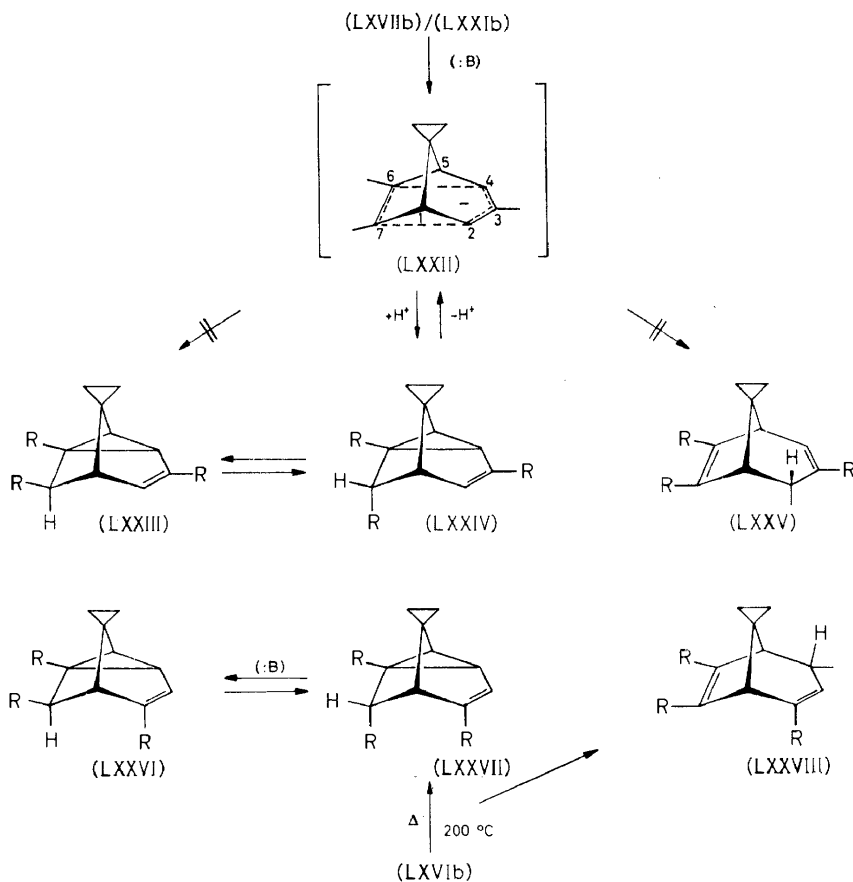
In a communication following our original report⁵⁶ Freeman and collaborators⁵⁹ announced the valence isomerizations in the basic hydrocarbons (LXVI e) and (LXIX e) in 29 and 15 per cent yields respectively, this 2:1 ratio being in the anticipated direction. Here, the stereochemical differences between (LXVI) and (LXIX) are not at all reflected in the u.v.

PHOTOCHEMICAL REACTIONS WITH NON-CONJUGATED DIENES

spectra (λ_{\max} 192 (3.95) and 192 (4.00) nm respectively), [quite similar to the one of norbornadiene (λ_{\max} 195 (3.73) nm)].

The "bishomocyclopentadienes" (LXVII a,b) and (LXX a,b) in strong bases are isomerized to the exo 6-H product (LXXIV a,b) which slowly equilibrates with (LXXIII a,b). No (LXXV a,b) was found. Our earlier suggestion⁵⁶, that the intermediate anion might best be represented as bishomocyclopentadienide ion (LXXII) has received support by the recent direct observations of this 6π -anion by Winstein and collaborators⁶⁰ and by Brown⁶¹. That our equilibration studies with (LXVII b) resulted in no measurable H/D exchange in the positions C-2, C-4⁶² could be rationalized in two ways: either the charge distribution in the anion is altered by the ester groups in such a way as to favour protonation at C-6, C-7, or deuterium addition and deuterium abstraction in the positions C-2, C-4 are both stereospecific.

The analytical problems brought about by those polycyclic systems were mainly elaborated by n.m.r. work, the conclusions being supported by the data collected from the structurally very similar (the position of R at the double bond makes all the difference) isomers (LXXVI), (LXXVII),



(LXXVIII) and (LXXXIII), (LXXXIV). The last four were readily obtained from solution pyrolysis of the thermally rather labile exo photo-substrates (LXVI). Every step, making up the sequence (*Figure 6*) proposed earlier for these thermal rearrangements⁶³ has now been realized for (LXVI a), the intermediates (LXXIX)[†], (LXXX), and (LXXXI) being stable enough to allow their isolation and characterization⁶⁴. The photo-

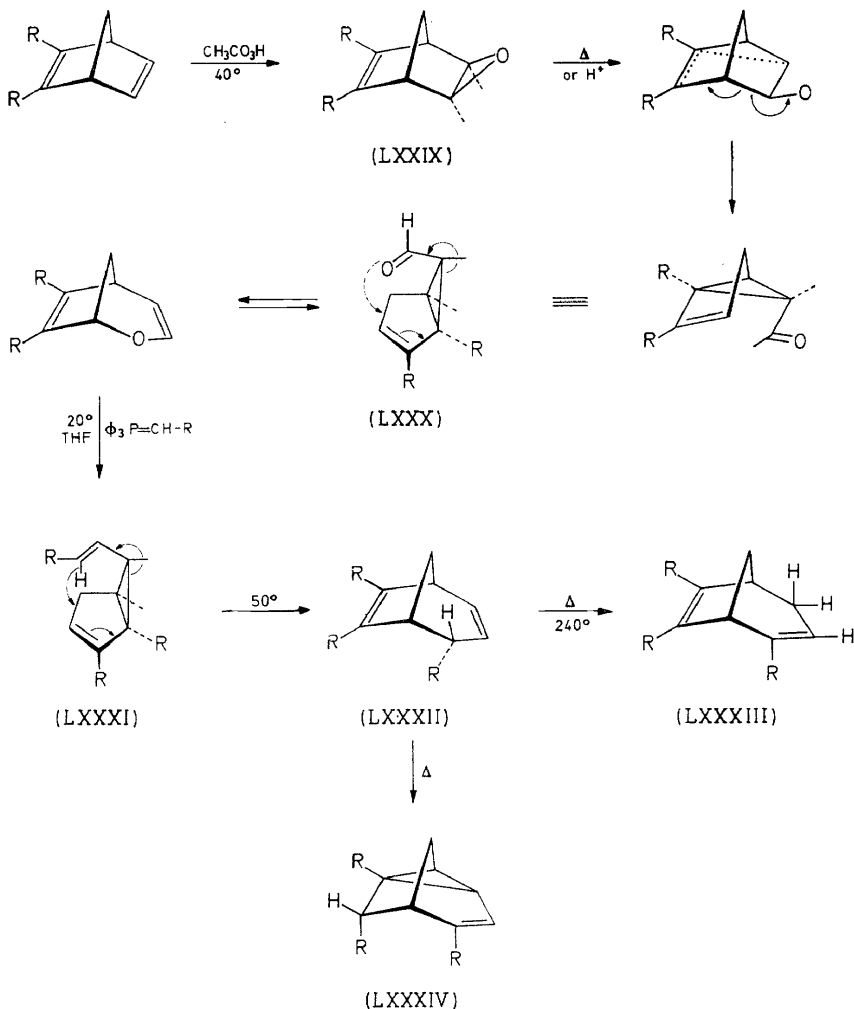


Figure 6. Intermediates in the pyrolysis of (LXVI a)

[†] The homovinylepoxy (LXXIX; R = CO₂H), when treated similarly to the exotriacid (LXVI c) is, according to very preliminary studies, not induced to an analogous rearrangement giving the "bishomofurane" (i)⁶⁴.

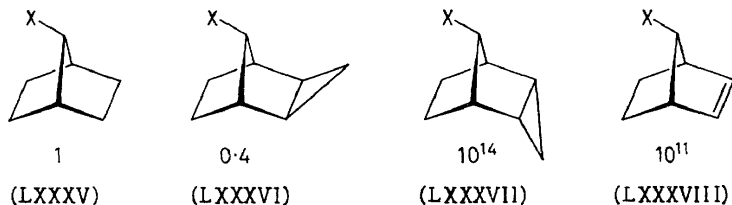


PHOTOCHEMICAL REACTIONS WITH NON-CONJUGATED DIENES

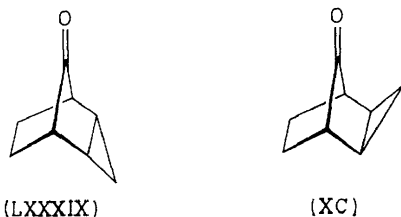
product (LXVII a) did not show up in the pyrolysis mixture, although it would have survived the conditions employed.

In recent papers^{65,66} further evidence can be found for the special geometric requirements of electron delocalization between cyclopropyl rings and unsaturated centres in the tricyclo [3.2.1.0^{2,4}] octene skeleton. The striking ratio of rates in acetolysis of the anti-tosylates (LXXXV)–(LXXXVIII) were taken as evidence for extensive backside participation by the cyclopropane C-2, C-4 bonding electrons which are ideally oriented in the endo configuration (LXXXVII)⁶⁵.

Similarly, the facile decarbonylation of the endo-octanone (LXXXIX) as compared with the exo-ketone (XC) indicates the better orbital overlap



between the developing new centres on going from (LXXXIX) to tropilidene⁶⁶.



This question of homovinyl-cyclopropane interaction in photochemical transformations was further pursued in the tetracyclo [4.3.0.0^{2,4}.0^{3,7}] nonene system (XCI)⁶⁷—formally built from (LXVI) by connecting C-3 and C-8 by a methylene bridge. As a consequence, the planes of the Δ -orbitals and the π -orbitals should become more parallel directed, the interaction, if existing at all, should get weakened.

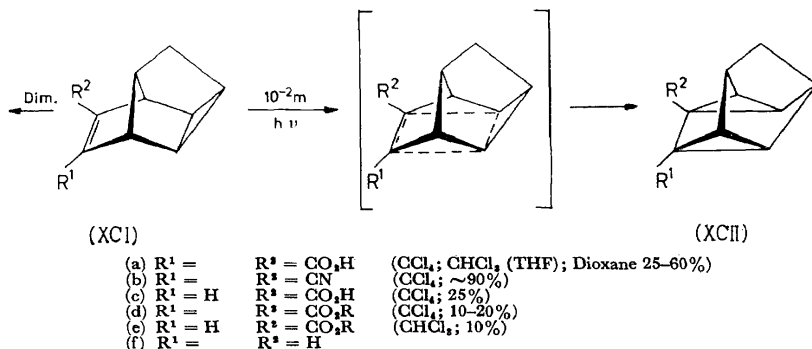
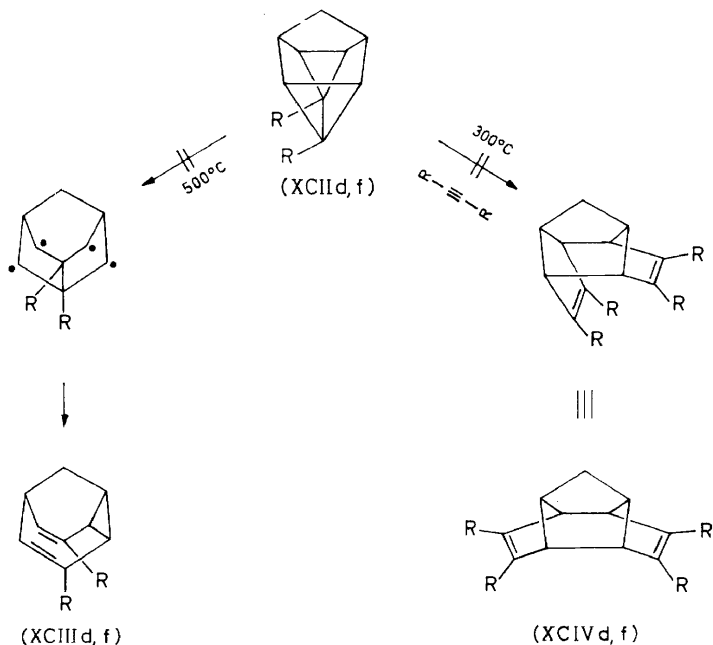


Figure 7. Photoisomerization of the derivatives of (XCI) to those of (XCII)

Once more we had to experience how unwise it is in photochemistry to expect similar behaviour in similar substrates. Under the very same set of conditions which permitted the very uniform photoisomerization (LXVI b) \rightarrow (LXVII b) the diacid (XCI a) furnished only a trace amount of (XCII a). By varying again (see *Figure 7*) the solvents—in a way dictated more by intuition and perseverance than by rational deduction—the yields given in *Figure 7* were realized⁶⁸.

In a very similar fashion the diacid (XCI a) was also prepared by Wenkert and collaborators⁶⁹. By heating in triisopropylbenzene the *t*-butyl-peroxyesters the di- and mono-carboxylic acids (XCI a) and (XCI c) were degraded to the new pentacyclo[4.3.0^{2,4}.0^{3,8}.0^{5,7}.7]nonane (XCII f)^{67,†}. Both (XCII f) and the diester (XCII d) are thermally extremely stable (500°). Our hopes, that thermal reorganization might open a new and versatile synthesis of substituted barbaralanes (XCIII) were not fulfilled. Such a thermal stability makes us understand, why (XCII d) and (XCII f) contrasting the diene-type reactivity of the iso- and heterocyclic quadricyclanes (II), (VI), (XIII) and (XIV) even at rather high temperatures (300°) do not add acetylene-dicarboxylate to give (XCIV)⁶⁸.

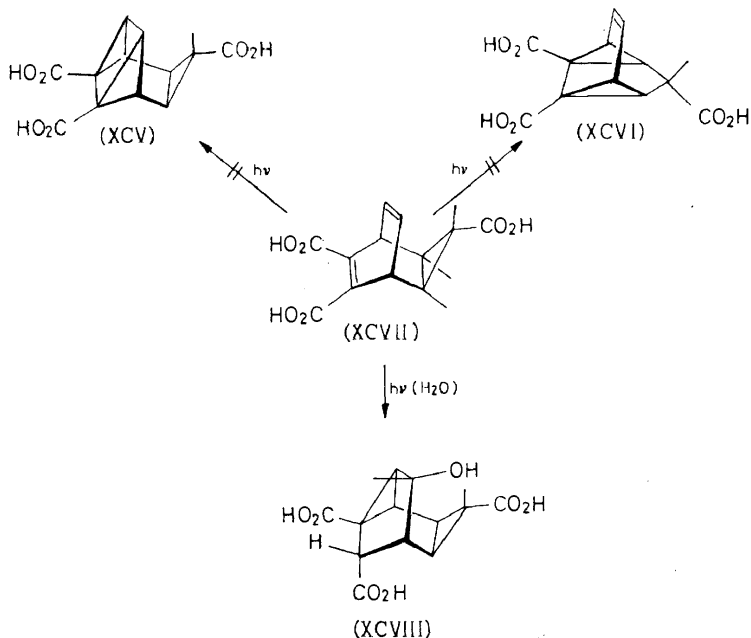


The rather narrow limits within which such light induced homovinyl-cyclopropane rearrangements are possible and a parallelism with the homo-

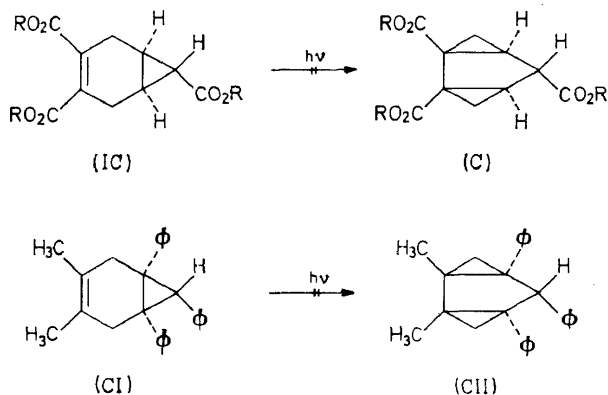
† The hydrocarbon (XCII f) has since been produced by two independent routes^{69a}. Under our conditions (irradiation in several solvents using the comparatively weak Hanau Q81 lamp) the unsubstituted substrate (XCI f) had furnished only a disappointingly low yield of (XCII f)⁶⁸.

PHOTOCHEMICAL REACTIONS WITH NON-CONJUGATED DIENES

diene system become obvious in the substrate (XCVII) (formally a homobarralene) which offers both a homodiene as well as a homovinylcyclopropane arrangement, the cyclopropyl ring having the favourable exo configuration⁷¹ with respect to the substituted (and excited) double bond. The irradiation experiments conducted as described for the bicyclooctadienes (LV) brought also the same results. No valency isomerization, either to (XCV) or to (XCVI), takes place, instead the elements of water are incorporated, completely stereospecifically, in a formal 1,5-addition to the two double bonds, the hydrogen again attacking the ester-bearing carbon atom from the endo-, the OH group from the side of the saturated bridge (XCVIII)⁵¹.

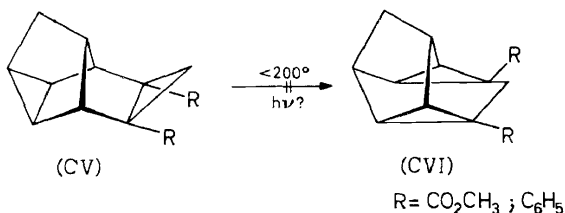
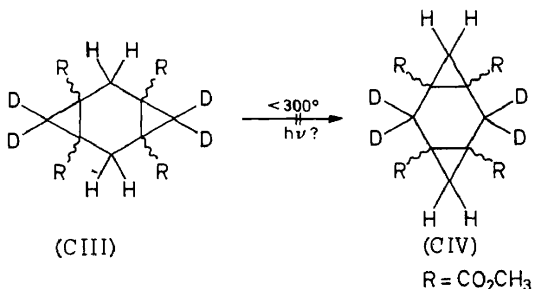


We are not surprised anymore, that the direct and indirect excitation in various media of the bicyclo [4.1.0] heptene derivatives (IC) and (CI) did



not cause any isomerization to (C) or (CII)⁷². These failures are in agreement with the results accumulated with the analogous homodienes (LXIII)⁷³ and are understandable in view of the disadvantageous spatial arrangement of C=C double bonds and cyclopropyl rings. †

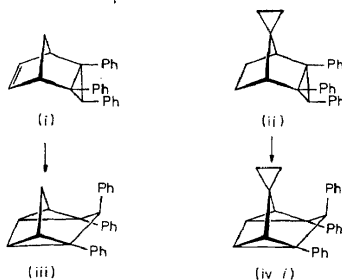
Finally, let me say that it was obviously worthwhile to extend these photochemical investigations with homodienes and homovinylcyclopropanes to saturated hydrocarbons of the type (CIII) and (CV) in which both C=C double bonds of the homodiene (LXIII) are replaced by cyclopropyl rings. As we have reported sometime ago^{7a}, (CIII) and (CV) are not changed on heating till 300°. According to preliminary indirect excitation experiments the chances are not much better to effect the transformations respectively to (CIV) and (CVI) photochemically⁷⁴.



ACKNOWLEDGEMENTS

I wish to express my sincere appreciation to my young colleagues, who deserve the major credit for the results described in this paper, namely Drs. E. Druckrey, W. Eberbach, H. Hagemann, R. Kitzing, G. v. Veh and

† According to more recent experiments^{73a} the bridged analogues of (CI) i and ii are amenable to a thermal $[2\pi + 2\sigma]$ cycloaddition reaction leading to the bishomocyclopentadiene derivatives iii and iv *i* respectively.



PHOTOCHEMICAL REACTIONS WITH NON-CONJUGATED DIENES

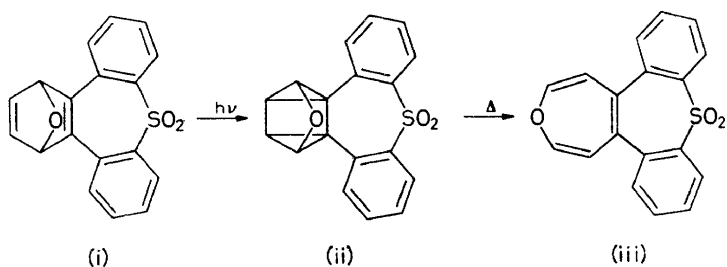
Dipl. Chem. W. Auge, D. Hunkler, M. Klaus, H.-D. Martin, M. Arguëlles, R. Fuchs, M. Joyeux, M. Thyès, J. Rivier, P. Vogel, and P. Wursch.

Generous support by the "Schweizerische Nationalfonds zur Förderung der wissenschaftlichen Forschung", the "Deutsche Forschungsgemeinschaft", and the "Fonds der Chemie" is gratefully acknowledged.

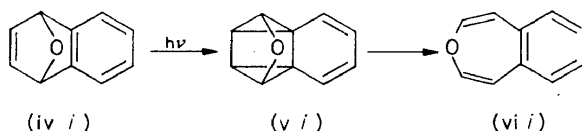
Notes added in proof

1. Refers to page 19

In the case of (i) and (ii) the u.v. absorption curves are sufficiently different to allow a selective excitation of the substrate, rendering (ii) photostable which, however, isomerizes thermally to (iii) at room temperature.

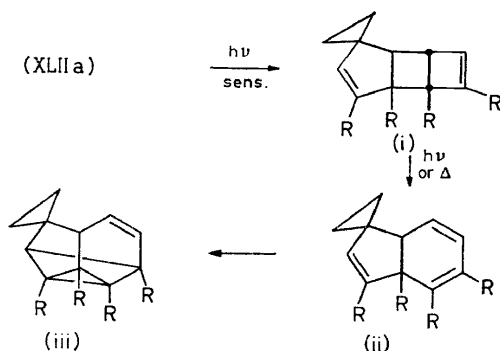


In contrast, on irradiating directly the benzoxanorbornadiene (iv i) the valence isomer (v i) cannot be seen. The first identified product is the benzoxepine (vi i). The mechanism proposed^{11a} in analogy to the conversion (V) → (VI) → (XXVI) has recently been proved by Ziegler and Hammond^{11b}.



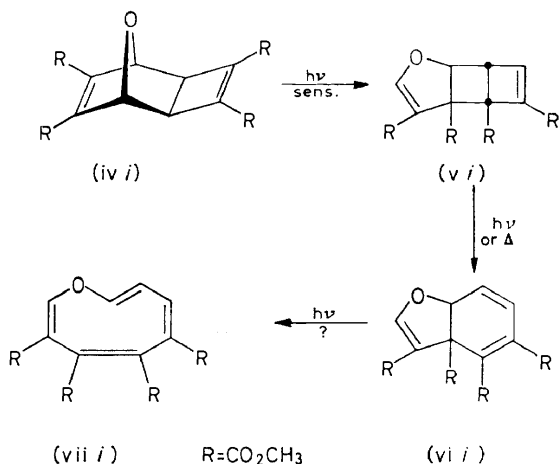
2. Refers to page 30

Our doubts concerning (XLV a) and (XLVI a) have turned out to be justified. As we have shown in the meantime^{42a}, the structures (i) and (ii)



respectively have to be assigned to the two isomeric photoproducts. In the latter by direct excitation the intramolecular ($2\pi + 2\pi$) addition yielding (iii) could be achieved.

The photochemical behaviour of the adduct (iv i) resembles that of (XLII a). (v i) and (vii) besides two more not yet fully characterized components are the products of the acetone sensitized energy transfer^{42b}. Because of the oxygen the electrocyclic opening—leading to the heterocyclic 10π system (vii i)—should be more favourable than in the case of (ii).



3. Refers to page 32

Indeed, when the irradiation experiments with (XLVIII) or with the *N*-tosyl-derivative are carried out at sufficiently low temperatures, the corresponding tetracyclic products (II) can be isolated and characterized. In solution they are even less stable than the oxaquadracyclanes and rearrange rather selectively on mild heating to the azepines (L)^{47a}. Nevertheless, in excess acetylene-mono- or di-carboxylate cycloadditions with the bis-homo-pyrrole systems in (IL) can be effected without much competition by the process (II) \rightarrow (I)^{47b}.

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HORST PRINZBACH

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