

THE PHOTOCHEMISTRY OF CYCLOHEPTADIENONES

HAROLD HART

*Department of Chemistry, Michigan State University,
East Lansing, Michigan 48823, USA*

ABSTRACT

In the first part of this paper the relationship between cyclohexadienone and cycloheptadienone photochemistry is examined. The photochemical behaviour of 2,5- and 2,6-cycloheptadienones parallels that of 2,4- and 2,5-cyclohexadienones, respectively. 2,4-Cycloheptadienones have no precise counterpart in cyclohexadienone chemistry. A unifying scheme is presented which accounts for the diverse photochemistry of these substances; it calls special attention to the importance of the excited state ($n\pi^*$ or $\pi\pi^*$) and substituents in determining product structure.

In the second part of this paper an unusual photodimerization of a 2,3-benzo-2,4-cycloheptadienone is described which calls attention once again to the relatively low level of the art with regard to predictability, and to the need for studies which involve wide structural variations in systems with a common chromophore.

INTRODUCTION

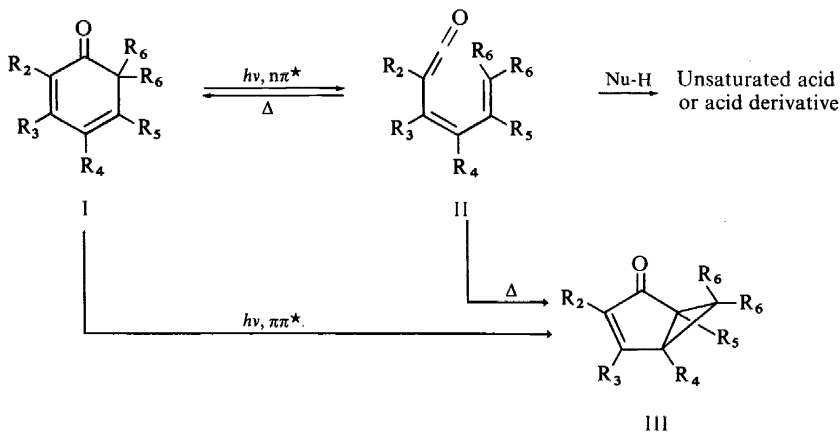
The mechanistic photochemistry of fully- and cross-conjugated cyclohexadienones has been studied in great detail and is now reasonably well understood¹. The same cannot be said for the cycloheptadienones. Although examples of all three types of conjugated cycloheptadienones (2,4-, 2,5- and 2,6-), as well as the non-conjugated 3,5-isomer, have been irradiated, the delineation of reaction mechanism with regard to which excited states do what, and how substituents affect product structure has barely begun.

It will be shown that 2,5- and 2,6-cycloheptadienones react photochemically in a manner very much like 2,4- and 2,5-cyclohexadienones, respectively. The diverse photoisomerizations of 2,4-cycloheptadienones, however, have no counterpart in those of their lower homologues; a general mechanistic scheme will be developed which rationalizes what is now known about them. Finally, a most unusual photodimerization which occurs when the α,β -double bond of a 2,4-cycloheptadienone is incorporated in a benzene ring will be described.

2,5-CYCLOHEPTADIENONES

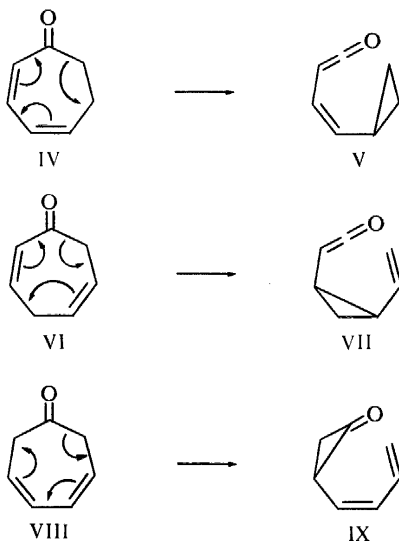
The most studied photoreaction of 2,4-cyclohexadienones (I) is their photoisomerization to dieneketenes (II) via an $n\pi^*$ singlet state². Depending

on the solvent and the substitution pattern, the ketene may recyclize to I, react with a nucleophile to give unsaturated acids or their derivatives, or in the case of highly substituted ketenes (for example $R_2-R_6=CH_3$), cyclize via a $[\pi 4a + \pi 2a]$ reaction³ to bicyclo[3.1.0]hexenones, III. The latter



compounds may also be produced directly from I in highly polar media via a $\pi\pi^*$ state⁴.

The counterpart of the photoisomerization $I \rightarrow II$ could conceivably be realized from 2,4-, 2,5- or 3,5-cycloheptadienones as shown. In fact, no

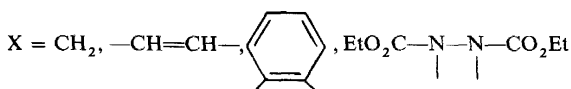
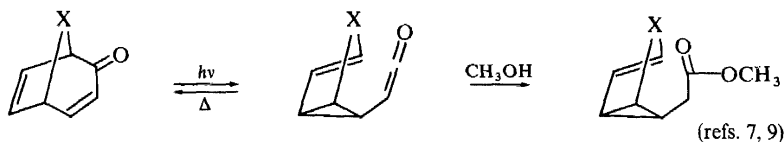
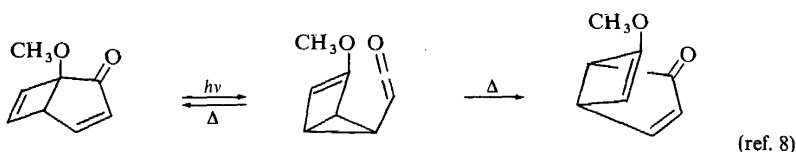


example of the reaction $IV \rightarrow V$ is known; what does happen when 2,4-cycloheptadienones are irradiated is discussed in some detail in a later

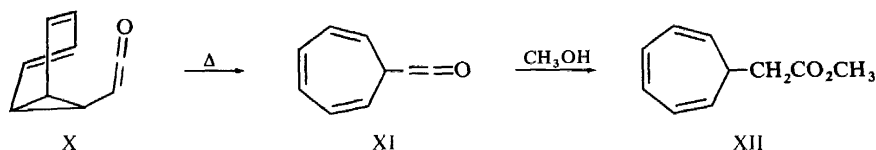
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section of this paper. 3,5-Cycloheptadienones (VIII) eliminate carbon monoxide and form trienes⁵ from an $n\pi^*$ singlet state⁶; this reaction is thought to be concerted, though a stepwise process involving a cyclopropanone intermediate such as IX has not been considered or rigorously excluded. Triplet sensitized irradiation of 3,5-cycloheptadienone gives the valence tautomer, bicyclo[3.2.0]hept-6-en-3-one⁶.

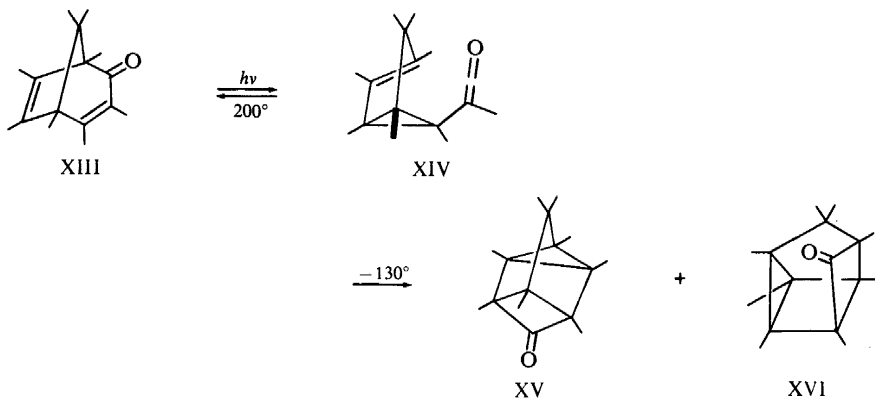
The generality of the photoconversion VI \rightarrow VII was first recognized by Chapman⁷. The following examples typify the reaction.



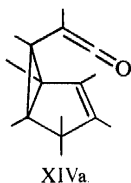
In the special case when $X = -\text{CH}=\text{CH}-$, first formed norcaradieneketene X rearranges to XI which is trapped as the cycloheptatrienyl ester, XII.



The analogy between the photochemical behaviour of 2,5-cycloheptadienones and 2,4-cyclohexadienones even carries over to the effect of heavy substitution on the subsequent thermal reactions of the resulting ketenes. For example we have observed¹⁰ that the octamethyldienone(XIII) produces a ketene(XIV) (observed in the infra-red, on low temperature irradiation) which cannot be trapped with methanol or dimethylamine, but which undergoes an allowed $[\pi 2s + \pi 2a]$ intramolecular cycloaddition reaction¹¹ to give the tetracyclic cyclobutanones XV (92 per cent) and XVI (8 per cent), even at -130° ! The ketene XIV may have a preferred conformation XIVA in which the ketene and cyclopentene carbon-carbon double bonds are nearly in the perfect geometric arrangement¹¹ for such a cycloaddition. The



reaction constitutes the counterpart of $\text{II} \rightarrow \text{III}$ observed with highly substituted cyclohexadienones. At high temperatures (200°), XV and XVI are

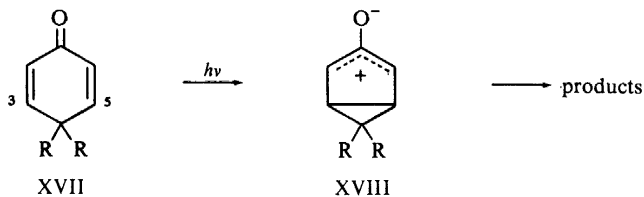


quantitatively reconverted to XIII, presumably via the ketene XIV. These reactions are under further study.

2,6-CYCLOHEPTADIENONES

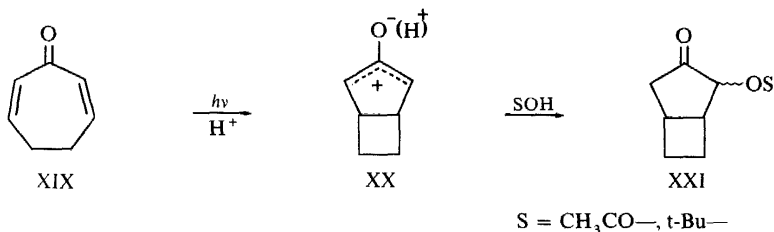
The 2,6-cycloheptadienones have not been studied with anywhere near the degree of thoroughness applied to the cross-conjugated cyclohexadienones. However, some parallels can be drawn between the two classes of compounds.

Many 2,5-cyclohexadienones (XVII) rearrange by the so-called Type A intermediate XVIII, in which a new bond is formed between C3 and C5¹².

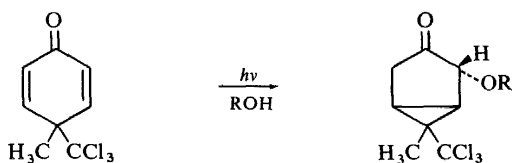


The counterpart of this reaction with cycloheptadienones was observed when 2,6-cycloheptadienone (XIX) was irradiated in acidic media¹³. The postulated intermediate XX is a cyclobutylcarbinyl cation which is trapped by the solvent,

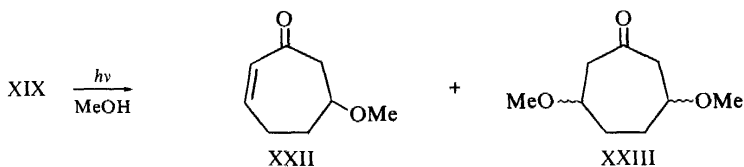
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and does not undergo any rearrangements of the type which are so characteristic of the cyclopropylcarbinyl cation XVIII. Intermediates of the type XVIII have been similarly captured by nucleophiles¹⁴.



When irradiated in non-polar solvents, XIX gave cyclobutane dimers, a reaction more characteristic of enones than dienones. In methanol, the



products were XXII and XXIII, presumably arising from dipolar intermediates which are captured by the nucleophile faster than they form a C₃—C₆ bond.

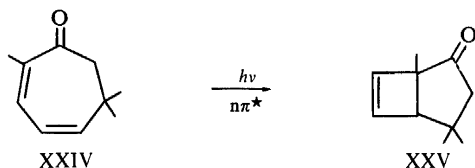
2,4-CYCLOHEPTADIENONES

2,4-Cycloheptadienones exhibit great variety in their photochemical behaviour, depending upon the presence and location of substituents, the solvent and the particular state from which the reaction occurs. Nevertheless, it will be shown here that all of the reactions can be accounted for in terms of two fundamental reaction paths.

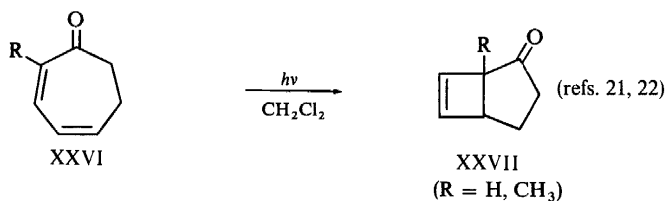
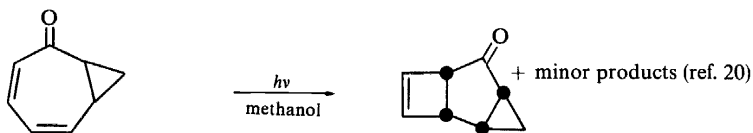
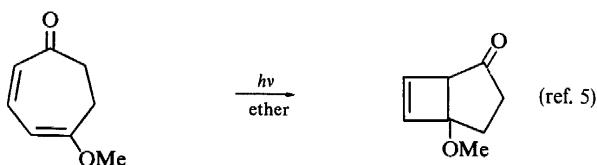
Eucarvone (2,6,6-trimethyl-2,4-cycloheptadienone, XXIV) was the first and most studied compound of this type, because of its accessibility from carvone¹⁵. Its u.v. spectrum in cyclohexane has a $\pi\pi^*$ maximum at 298 nm (ϵ 5500) and an $n\pi^*$ maximum at 350 nm (ϵ 40). In polar solvents the $\pi\pi^*$ band shifts to longer wavelengths as expected (303 nm in EtOH, 310 nm in CF₃CH₂OH, and 318 nm for eucarvone adsorbed on silica gel suspended in

cyclohexane)¹⁶. In sulphuric acid, where the ketone is fully protonated, this maximum is shifted to 400 nm¹⁷. It is not surprising, therefore, that the product structure depends upon the solvent polarity.

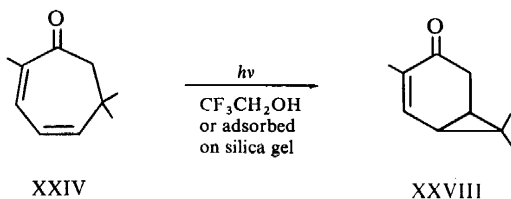
The photoisomerization of XXIV to a bicyclo[3.2.0]hept-6-en-2-one XXV¹⁸ is a relatively inefficient process ($\Phi_{\text{benzene}} = 0.0025$) which is thought to



occur from both singlet and triplet states ($n\pi^*$) of XXIV¹⁹. This type of photoisomerization has been observed for several 2,4-cycloheptadienones:



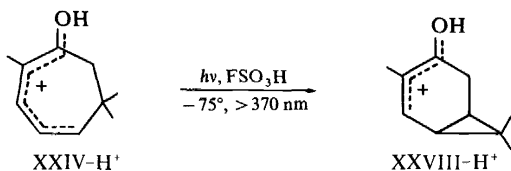
A second type of photoisomerization of eucarvone occurs in highly polar solvents, where a major primary product is the bicyclo[4.1.0]hept-2-en-4-one



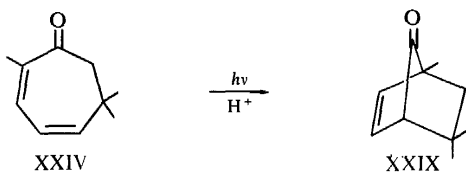
XXVIII¹⁶. In these solvents tailing of the $\pi\pi^*$ absorption masks the weak $n\pi^*$ band, and it now seems certain that XXVIII is formed from a $\pi\pi^*$ state

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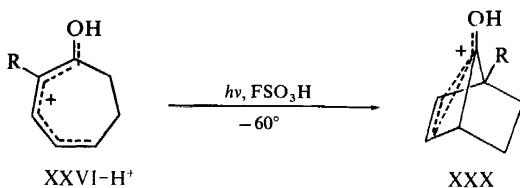
of XXIV†. The major product from protonated eucarvone (XXIV—H⁺), which can only react from a $\pi\pi^*$ state, is XXVIII—H⁺¹⁷.



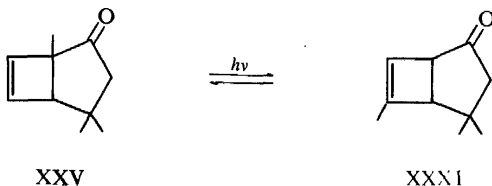
A third type of photoproduct, the trimethyl 7-norbornenone XXIX, was observed when eucarvone was irradiated in aqueous acetic acid²³ and in other acidic media^{16, 17, 24}. Although this type of product is formed in rela-



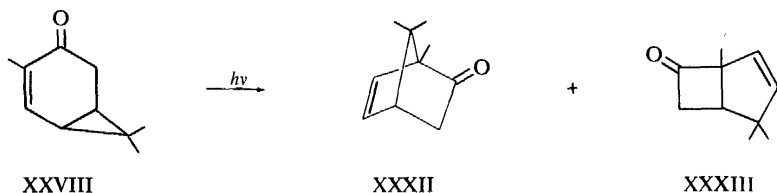
tively minor amounts from eucarvone, it is the *exclusive* photoproduct of protonated 2,4-cycloheptadienone or its 2-methyl derivative (XXVI—H⁺)²¹.



Several other photoproducts of eucarvone have been reported from time to time, but they arise from further isomerization of the primary photoproducts described above. Thus XXXI¹⁸ is a 1,3-acyl migration product of



† The multiplicity of the excited state is not known. The reaction in trifluoroethanol was not quenched by piperlyene or 1,3-cyclohexadiene, indicating that reaction probably occurs from a $\pi\pi^*$ singlet state.

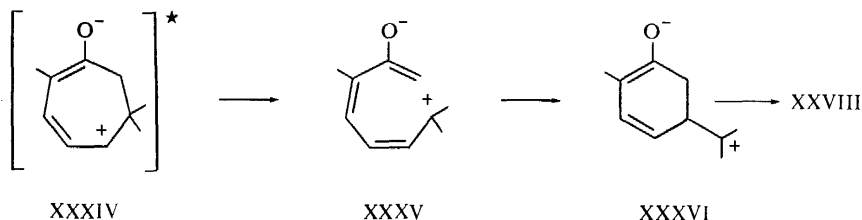


XXV^{16, 18, 25} and dehydrocamphor XXXII²⁴ arises together with the cyclobutanone XXXIII as a vinylcyclopropane-cyclopentene photoisomerization product of XXVIII¹⁶.

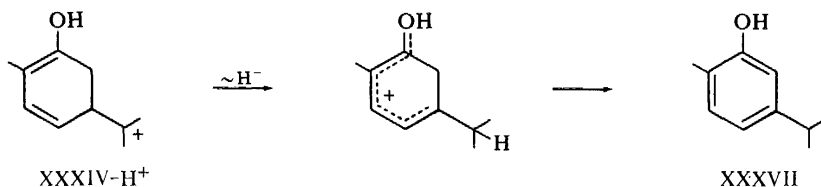
Mechanisms

Quenching and sensitization experiments^{19, 22} indicate that the formation of bicyclo[3.2.0]hex-6-en-2-ones such as XXV and XXVII from 2,4-cycloheptadienones in neutral solvents probably arises from the lowest $n\pi^*$ singlet and triplet states. Orbital symmetry-allowed disrotatory ring closures could account for the products.

The $\pi\pi^*$ process XXIV \rightarrow XXVIII (and its protonated analogue) is more interesting since it involves cleavage of a carbon-carbon bond β to the carbonyl group. Since this reaction path is favoured by polar solvents, it may best be represented by dipolar intermediates (or in the case of the protonated ketones, carbonium ions). This interpretation accounts for the observed substituent effects more satisfactorily than does the alternative view of the reaction as an allowed $[\sigma 2a + \pi 2a]$ concerted reaction²⁶. If the $\pi\pi^*$ state is represented as the dipolar structure XXXIV, then an electrolytic ring opening to XXXV can lead to the observed product either directly or through the intermediate XXXVI. Since Hine and Childs¹⁷, in their irradiation



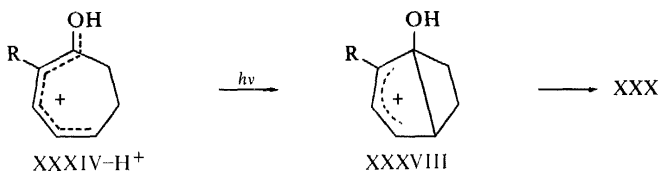
of XXIV—H⁺, found the phenol XXXVII amongst the products after quenching, the stepwise path via XXXVI seems the more likely²⁷. The ion



XXXVI—H⁺ partitions between the paths which lead to XXVIII and XXXVII.

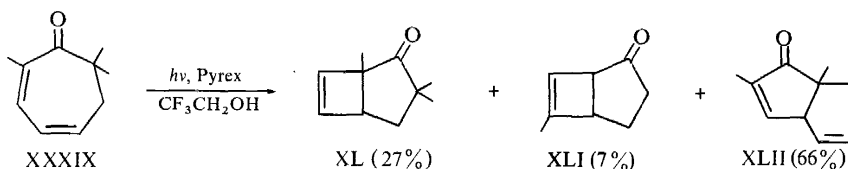
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The ring-opening reaction $\text{XXXIV} \rightarrow \text{XXXV}$ is aided by the gem-dimethyl substituents at C-6 of eucarvone. If these substituents are absent, as in the case of 2,4-cycloheptadienone itself, the reaction takes an alternative path. The protonated ketone, reacting from a $\pi\pi^*$ state, undergoes a photochemically allowed²⁸ ring closure of the pentadienyl cation $\text{XXXIV}-\text{H}^+$ to the allyl cation XXXVIII ; a thermal 1,2-alkyl shift leads to the observed protonated 7-norbornenone XXX . The formation of XXX is undoubtedly aided

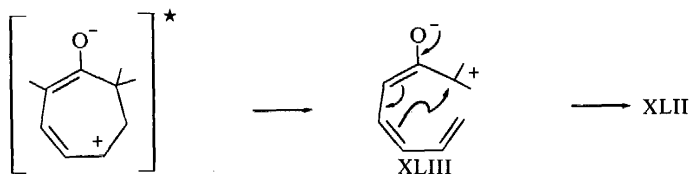


by stabilization from the C_2-C_3 double bond. In the case of eucarvone this path (which leads to XXIX) competes rather poorly with the ring opening (to XXXV).

The ring-opening reaction $\text{XXXIV} \rightarrow \text{XXXV}$ should occur equally well whether the gem-dimethyl group is at C-6 or C-7 in the original ketone; methyl groups can stabilize the positive charge by being located at either end of the heptatrienyl cation. However, since the conversion of XXXV to XXXVI should be strongly disfavoured if methyl groups are absent from C-6, the ion corresponding to XXXV but with methyls at the other end of the carbonium ion system might be expected to react in some different manner. To test this idea, we synthesized and irradiated XXXIX^{27} .

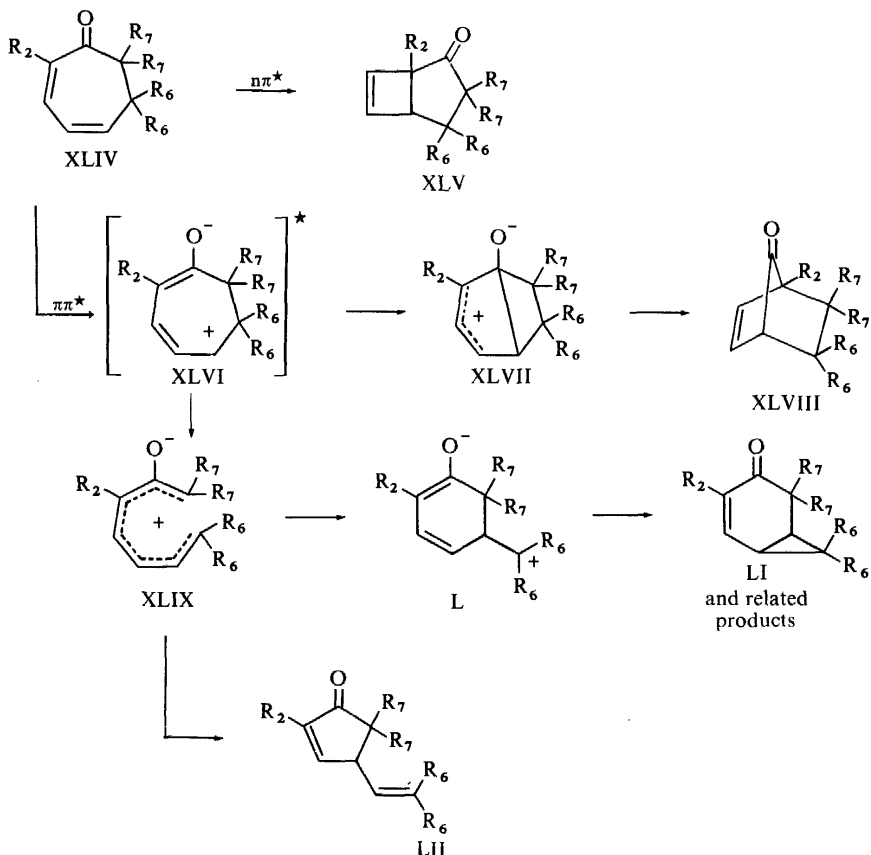


In addition to the $n\pi^*$ product XL and its 1,3-acyl shift isomer XLI , we obtained the vinyl cyclopentenone XLII as the major product. That this was a $\pi\pi^*$ product was clear from the observation that $\text{XXXIX}-\text{H}^+$ gave only $\text{XLII}-\text{H}^+$ as the primary photoproduct on irradiation in FSO_3H at -78° ($>330 \text{ nm}$). Thus the ring-opening of the $\pi\pi^*$ excited state of XXXIX proceeds as with eucarvone, but the ring-closure (of XLIII) takes a different



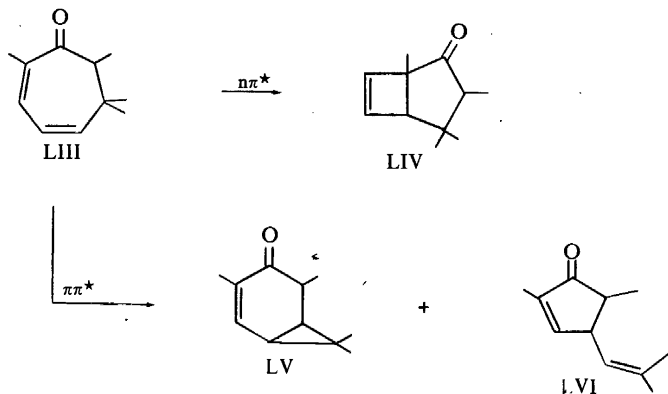
path, leading to XLII as shown. Thus the $n\pi^*$ and $\pi\pi^*$ reactions of XXXIX proceed in a manner completely analogous to those of eucarvone, though the products from the $\pi\pi^*$ states in the two cases have quite different structures. It is noteworthy that no α -cleavage occurs with XXXIX despite the fact that the α -carbon is tertiary and that one can envisage several plausible reaction products from such a reaction path.

To summarize, 2,4-cycloheptadienones react photochemically by two paths depending on whether an $n\pi^*$ or $\pi\pi^*$ state is produced (see the Summary Scheme). The $n\pi^*$ state leads to bicyclo[3.2.0]hex-6-en-2-ones XLV, possibly from both the lowest singlet and lowest triplet states. The $\pi\pi^*$ state XLVI (possibly singlet) undergoes one of two electrocyclic processes, depending on the substitution pattern. When neither R_6 nor R_7 are carbonium ion-



Summary of 2,4-cycloheptadienone photochemistry

stabilizing groups (for example, $R_6 = R_7 = H$), ring closure followed by an alkyl shift occurs, leading via XLVII to a 7-norbornenone XLVIII. Since such reactions have only been reported to occur in acidic media, protonation may be required. When either R_6 or R_7 can stabilize a positive charge, electrocyclic ring opening competes favourably with this path, to give XLIX,

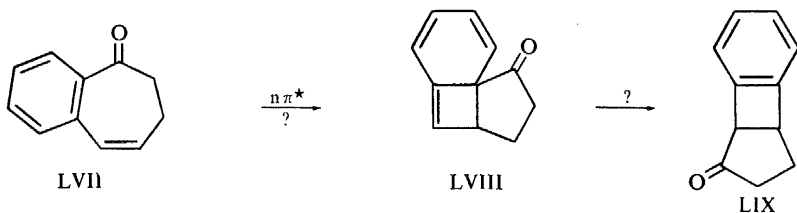


which cyclizes to L if the stabilizing substituents are at C-6, or to LII if they are at C-7. Indeed we have found that 7-methyleucarvone LIII, which has carbonium-ion stabilizing substituents at both positions gives both types of products (LV and LVI) from the $\pi\pi^*$ state (irradiation in trifluoroethanol at 300 nm)^{29†}. Irradiation of LIII in a non-polar solvent (cyclohexane) at longer wavelengths (350 nm) gave LIV as the exclusive photoproduct, presumably via an $n\pi^*$ excited state.

The summary scheme thus rationalizes the main features of all of the known photochemistry of 2,4-cycloheptadienones. The effect of substituents at other ring positions might be predicted from this scheme, but such predictions remain to be tested experimentally.

2,3-BENZO-2,4-CYCLOHEPTADIENONES³⁰

In the remainder of this paper, I will describe some of our recent results on the photochemistry of 2,3-benzo-2,4-cycloheptadienones. The work was undertaken with the following ideas in mind. Reaction from an $n\pi^*$ state to give a bicyclo[3.2.0]hexenone would lead to a rather strained structure and also destroy the aromaticity of the benzene ring; a product such as LVIII

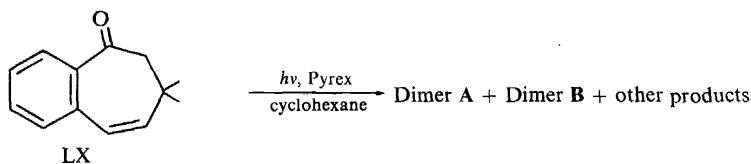


therefore seemed unlikely, though the possibility existed that it might form and re-aromatize, for example via a 1,3-acyl shift to produce LIX. Alternatively, the 2,3-benzo ring might 'flatten' the dienone chromophore and bring

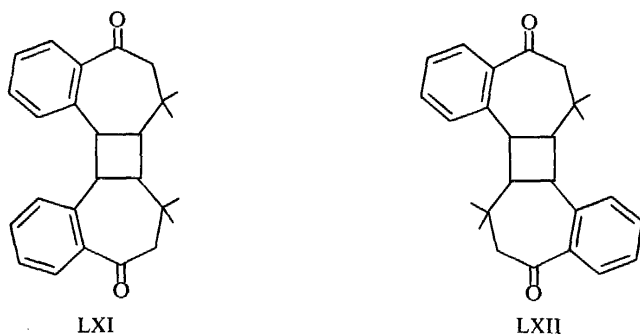
† However, irradiation of LIII—H⁺ (in FSO₃H) gave only LV—H⁺, and no product corresponding to LVI.

about reaction from a $\pi\pi^*$ state. If methyl substituents were present at C-6 or C-7 one could easily envisage the formation of the 2,3-benzo analogue of XXVIII or XLII respectively. It also seemed possible that the reaction might take a new course, not previously observed with 2,4-cycloheptadienones themselves. In the event, the unexpected occurred.

We began with 6,6-dimethyl-2,3-benzo-2,4-cycloheptadienone (LX), the benzo analogue of eucarvone \dagger . As expected, the $\pi\pi^*$ absorption band of LX appeared at longer wavelengths (315 nm in cyclohexane, 327 nm adsorbed on silica gel) and was less affected by polar solvents than that of eucarvone. LX was very rapidly converted to photoproducts on irradiation through Pyrex in cyclohexane (in marked contrast with eucarvone, which isomerizes very slowly in non-polar solvents). *No monomeric photoisomers of LX were formed!* The major products were two crystalline dimers, designated **A** (m.pt 208°–210°) and **B** (m.pt 199°–200°). It was immediately apparent



from the infra-red spectra of these dimers that they were *not* the head-to-head or head-to-tail cyclobutane dimers LXI or LXII, since each possessed one non-conjugated carbonyl group (1730 cm^{-1}), as well as a conjugated carbonyl



group (1661 cm^{-1} in **A**, 1673 cm^{-1} in **B**). In support of this conclusion, the mass spectral fragmentation patterns of **A** and **B** did not contain any major peak at half the parent mass. The presence of a non-conjugated carbonyl group required that at some stage during the reaction a phenyl-carbonyl bond must be broken. Since this type of cleavage is most unusual for aryl ketones, we were spurred on to determine the structures of the dimers \ddagger .

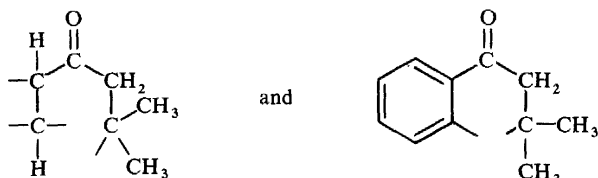
\dagger The synthesis of LX, and all the experimental details of this portion of the paper will be described in a full paper elsewhere. Only the principal results are presented here.

\ddagger One of the minor products was a cyclobutane dimer; evidence regarding its structure and formation will be presented in detail elsewhere.

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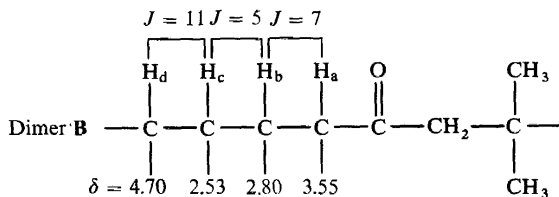
Many features of the n.m.r. spectra of **A** and **B** suggested that they had closely related overall structures, and were probably stereoisomers. For example, each dimer had two methylene groups adjacent to a carbonyl group, as in the starting material. One of these appeared as a fairly sharp singlet (at δ 2.30 in **A**, δ 2.26 in **B**), the other as a pair of geminally coupled doublets (at δ 2.80 and 3.25, $J = 13.0$ Hz in **A**, and at δ 2.57 and 3.14, $J = 16.0$ Hz in **B**). Since neither of the sets of methylene protons appeared to be further split, they were both presumably still adjacent to a carbon bearing a gem-dimethyl group, as in the starting material. The n.m.r. spectrum of each dimer contained four sharp singlets corresponding to the two gem-dimethyl groups (at δ 0.42, 0.96, 1.02 and 1.10 in **A**, and at δ 0.70, 0.84, 1.36 and 1.40 in **B**).

To confirm the presence of methylene groups adjacent to the carbonyls, each dimer was treated with NaOCH_3 in CH_3OD at room temperature. The dimers were recovered unchanged, but the n.m.r. peaks assigned to the methylene groups were absent. Also absent from the n.m.r. spectrum of each dimer recovered from this exchange was a one-proton doublet (at δ 3.45, $J = 10$ Hz in **A**, and at δ 3.55, $J = 7.0$ Hz in **B**). This proton must be adjacent to the non-conjugated carbonyl group, and must also be adjacent to another $-\text{C}-\text{H}$ group (because of the coupling pattern). The data thus far presented require that the partial structures



be present in each dimer.

The n.m.r. spectrum of dimer **B** contained a readily interpretable series of peaks for four protons, one on each of four adjacent carbon atoms, starting with the proton adjacent to the non-conjugated carbonyl group. Thus in dimer **B**, the partial structure is readily extended to

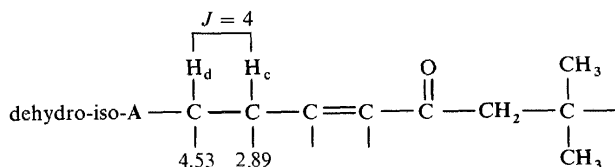


where H_a was a doublet, as described, coupled with H_b (7.0 Hz). H_d was also a doublet (δ 4.70, $J = 11$ Hz) coupled with H_c . H_b and H_c were doublets of doublets, at δ 2.80 ($J = 7.0$ Hz, 5.0 Hz) and δ 2.53 ($J = 5.0$ Hz, 11 Hz) respectively.

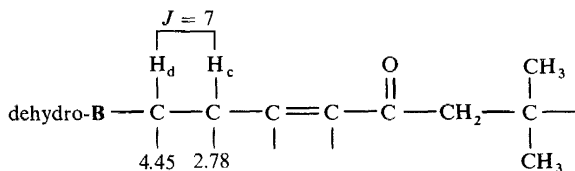
In dimer **A**, four protons, one each on separate carbon atoms, appeared at

Precedent exists for such oxidations³¹. Other data (mass spectrometric fragmentation pattern, deuterium exchange, etc.) support gross structure LXV for the ester.

Dimer **A** was not readily dehydrogenated, but iso-A gave a crystalline dehydro compound (m/e 370, m.pt 213°–214°) when refluxed with *o*-chloranil. The product was an α,β -unsaturated ketone [$\lambda_{\text{max}}^{\text{MeOH}}$ 288 nm (ϵ 7500), 236 (22800); $\nu_{\text{C=O}}$ 1698, 1670 cm^{-1}] in which only two of the methine protons remained:



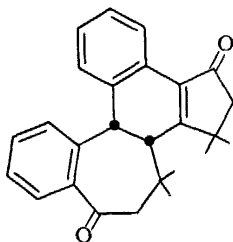
Similarly, dimer **B** gave a dehydro product [$\lambda_{\text{max}}^{\text{MeOH}}$ 292 nm (ϵ 8900), 245 (22800), 238 (24800); $\nu_{\text{C=O}}$ 1691, 1665 cm^{-1} ; m.pt 204°] isomeric with that obtained from iso-A, with the following methine pattern:



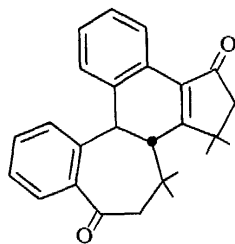
The structural and stereochemical link between dimers **A** and **B** was completed when it was found that dehydro-B was converted to dehydro-iso-A on treatment with sodium methoxide in methanol. Labelling experiments showed once again that the conversion was due to epimerization of H_d .

The structures of the dimers

Dehydro-B and dehydro-iso-A clearly differ only in the stereochemistry of the six–seven ring juncture. Consequently one of these compounds must have structure LXVI and the other structure LXVII, the particular assignments being left open for the moment.

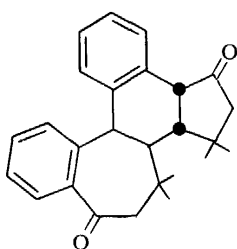


LXVI

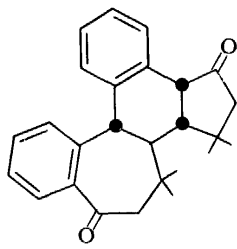


LXVII

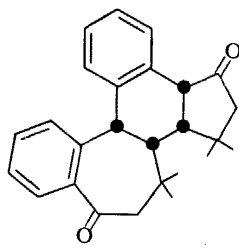
Since it was possible to exchange H_a in dimer **A**, dimer **B** and iso-**A** without causing any epimerization at that site, it seems likely that the five-six ring juncture in all cases is *cis*. To rationalize the facile dehydrogenation of iso-**A** and dimer **B**, but the difficult dehydrogenation of dimer **A**, we suggest that the latter has the stereochemistry shown in structure LXVIII. In this structure, access to the two hydrogens which must be removed (H_a and H_b) is sterically hindered by the seven-membered ring and its substituents.



LXVIII
(dimer **A**)



LXIX
(iso-**A**)



LXX
(dimer **B**)

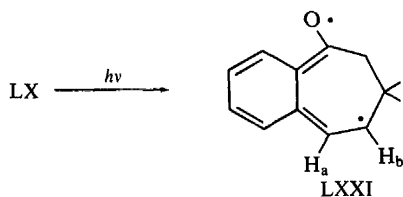
Since the isomerization of dimer **A** to iso-**A** involved epimerization of H_d (labelling results), iso-**A** is assigned structure LXIX. Dimer **B**, which affords a different dehydro product to that of iso-**A**, must have structure LXX. It follows that LXVI represents dehydro-**B**, and LXVII represents the structure of dehydro-iso-**A**. Consistent with this assignment, the small amount of dehydro product isolated from attempts to dehydrogenate dimer **A** were identical with dehydro-**B**.

Further arguments for the correctness of these stereochemical assignments will be presented in a full paper. Although the stereochemical assignments are not rigorously unequivocal, they are reasonably secure. The compounds are being subjected to x-ray crystallographic analysis.

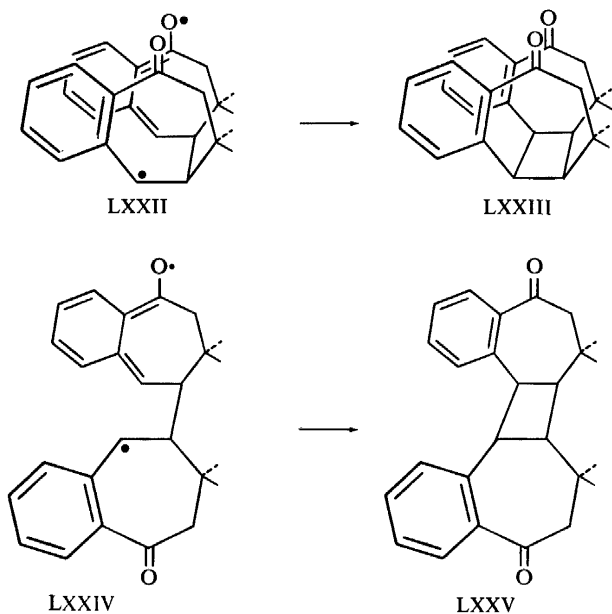
The mechanism for the formation of dimers **A** and **B**

Clearly the fact that only two of the eight possible stereoisomers are formed requires a dimerization mechanism with geometric constraints that limit the product to these structures.

The formation of dimers **A** and **B** from LX was readily quenched by 1,3-cyclohexadiene or piperylene. It seems certain, therefore, that the reaction occurs from a triplet state of LX, represented here by structure LXXI.

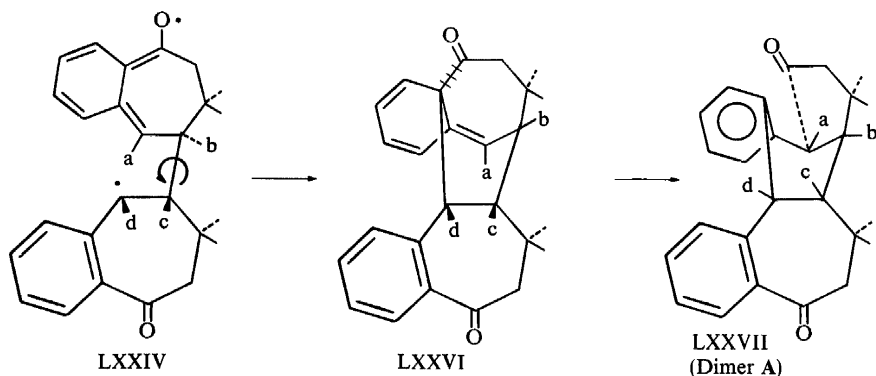


One would expect LXXI to add to a ground state molecule LX in such a manner as to produce a benzylic radical. Depending on the orientation of the two reacting moieties, one could readily form either the *cis-syn* or *trans-syn* cyclobutane dimers (LXXIII and LXXV).



The diradical represented by LXXII is severely strained, as would be the dimer LXXIII derived from it. Even in LXXIV some strain due to interaction between the gem-dimethyl groups might be expected. This strain can be relieved by rotation about the newly formed covalent bond, as shown in the scheme. Bonding at the aromatic ring carbon gives the triene LXXVI which

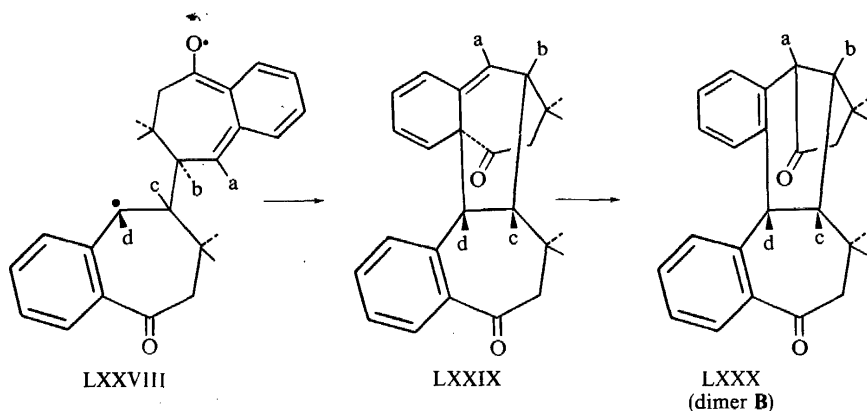
Scheme for Dimer A



can re-aromatize via a 1,3-acyl shift. If this occurs suprafacially, the product (LXXVII) will have the same geometry at the various ring junctures as shown in LXXVIII for dimer **A**.

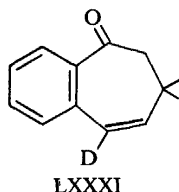
The transition state leading to LXXIV is of the DL-type. An alternative approach of the excited monomer (LXXI) to the ground state monomer would have the meso-type geometry shown in LXXVIII. The analogous sequence of steps leads directly to the all-*cis* dimer **B**. These reaction schemes explain

Scheme for Dimer **B**



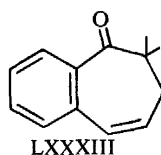
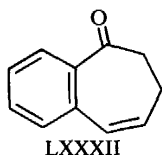
why only two of the eight racemates corresponding to structure LXIII are formed during the photolysis of LX.

To confirm the relative positions taken by the four methine protons in the dimers, we synthesized and irradiated the deuterated monomer LXXXI.



Consistent with the reaction scheme, the deuterium label appeared as H_a and H_d in the dimers (as determined by n.m.r. and by exchange experiments).

Experiments with the monomer lacking methyl substituents (LXXXII), and with the gem-dimethyl group located α to the carbonyl function



(LXXXIII) are at the time of writing less complete than those of LX, but in all cases the products are dimers even when the reaction is run in very dilute solution. The principal dimers from LXXXII and LXXXIII appear to have cyclobutane structures. Thus the methyl substituents at C-6 in LX probably constitute a major factor directing its dimerization along such an unusual course†.

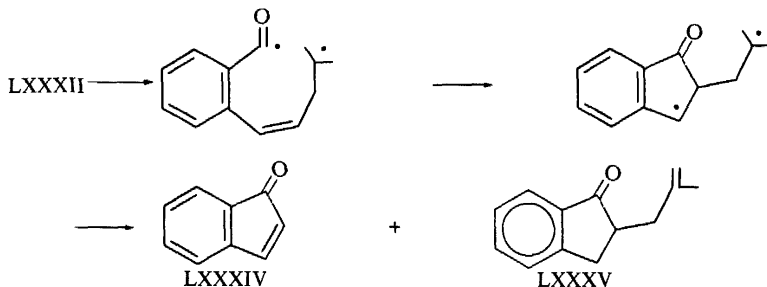
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† When LXXXII was widely dispersed on a silica gel surface and irradiated, two monomeric products LXXXIV and LXXXV were obtained²⁹. They probably arise as follows:



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