PHOTOCHEMISTRY OF POLYENES. CONTROL BY ORBITAL SYMMETRY AND GROUND STATE CONFORMATIONS ?

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Abstract – It is shown that ground state conformations of cyclohexadienes
and acyclic hexatrienes play an important role, in addition to orbital symmetry
factors, to govern the stereochemistry of the photoisomerization reactions of
these compounds.   Studying the influence of the wave-length of irradiation
allows to attribute to discrete conformations some specific photoreactions
(H shift, formation of bicyclo {3.1.0 }hexene).   New examples are given,
with kinetic data, showing a {4π a + 2π a } stereospecificity for the hexatriene
Photo-DIELS-ALDER reaction with a predominent orbital control.   The
concertedness of the reaction is discussed.   Kinetics of Z, E-photoisomerizations
around C-C double bonds of hexatrienes are shown, in relation with the ease
of terminal compared to central double bonds rotations.   Singlet and triplet
states have different behaviours in this respect, as well as different wave-lengths
of excitation.

The photochemical behaviour of conjugated polyenes is an important field of interest in chemistry,
and a good part of the efforts have been concentrated to the understanding of the properties of these
remarkable compounds (1).   This is probably due not only to the theoretical significance of that
class of π-electron systems but also to their practical importance (2).   A very stimulating
challenge was indeed initiated eleven years ago by the fruitful ideas of WOODWARD and HOFFMANN
(3) but a good deal of understanding is still left to be gained, as far as the excited state chemistry
is concerned (4), if it is true that the ground state behaviour is now very widely interpreted.   The
difficulty with the light initiated processes is indeed that: 1 -.   The exact nature of the excited
state is not always clearly known. 2-.   The reaction may occur after loss of the electronic
excitation.   3-.   There may be several consecutive fast photoreactions and the primary process is
sometimes difficult to individualize.   This is probably why several groups found it interesting to
synthesise some specific polyenes and to study their photoisomerization reactions, particularly in
relation with orbital symmetry conservation concepts.

An especially stimulating question raised about conjugated π-electron compounds is their
conformational mobility (2, 5) : a polyene in the ground state is generally described as being in
equilibrium between two or more conformations which unfortunately are not quantitatively determined
in most of cases, but which may be qualitatively estimated.   What happens to that equilibrium
distribution after excitation ?   Is it possible that the reaction act occurs before any conformational
reequilibration or is there a fast relaxation to a potential minimum before the reaction starts ?

We have been able to give partial answers to these questions : how does the conservation of orbital
symmetry work in the photochemical behaviour of conjugated polyenes and what is the importance
of the ground state conformational distribution in regard to their photochemistry ?   The results
we have obtained leave some questions unanswered, and I have the temptation to direct these towards
theoreticians, who indeed experience large difficulties to make precise calculations on these
mobile systems (4).

The first examples I would like to choose to illustrate my talk are the ones about the
cyclohexa-1, 3 dienes.   We had the opportunity to report a very specific case of stereo-specificity
by choosing two isomeric cis and trans-methyl-disubstituted-cyclohexadienes (6).   In each case we
could determine the configuration of the triene formed as a primary product, as the ring opening
reaction was more efficient than the further isomerization of the primary product : starting from the
E-5, 6-dimethyl-1, 4-diphenylcyclohexa-1, 3-diene 1, we obtained as the sole photoproduct the
E, Z, E-hexatriene 3, whereas the Z-cyclodiene yielded exclusively the Z, Z, E-hexatriene 4.   The
reaction is then specifically conrotatory as predicted by applying simple W-H considerations. But
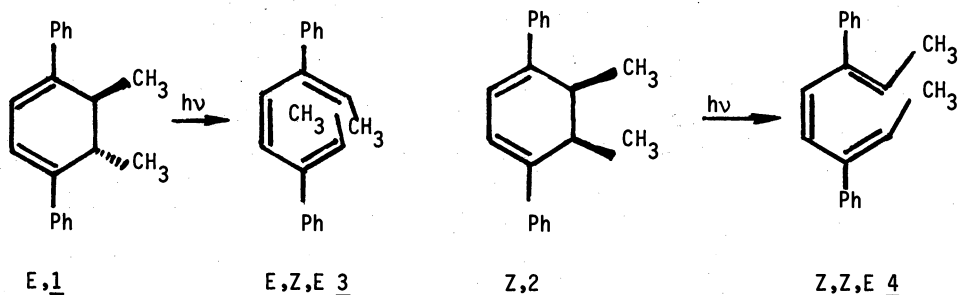
let us go further into these remarkable reactions and especially the ring opening of the E-cyclodiene 1. If the experiment confirms the predominance of orbital control on the photoprocess, a secondary effect is to be found since a Z, Z, Z-hexatriene could as well be formed from E- 1, again with a conrotatory mode of ring opening. We interpret this second degree control as a structural effect, as we are able to demonstrate that the E-triene 1 exists in the ground state as a unique pseudo-diaxial conformation : that result is inferred from the structure of the corresponding dialcohol which we synthesized as the precursor of the cyclodiene 1 (7). That dialcohol exists in a pseudo-diaxial conformation exclusively, as we were unable to detect any intramolecular hydrogen bond between the two OH groups (7), which should have a stabilizing effect on a pseudo-diequatorial conformation (and which we detected in the Z-dialcohol, which is pseudo-axial-pseudo-equatorial). It must be the case a fortiori for the methyl groups of the E-diene 1. The reason of this is probably the A strain reported for cyclohexene systems, which is relieved when the substituent is in a pseudo-axial situation.
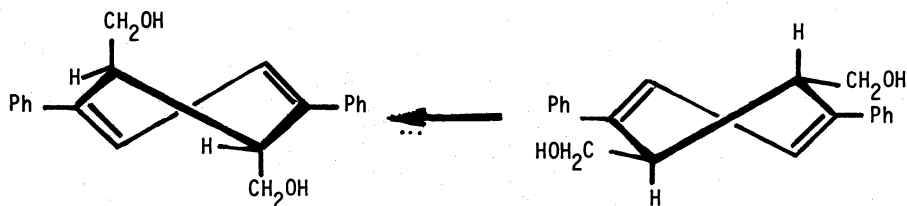
The same is true with the 1-phenyl 6-methyl cyclohexa-1,3-diene recently studied by us (8) : the only primary photo-triene is the Z, E-phenyl-methyl hexatriene explained with the same arguments.
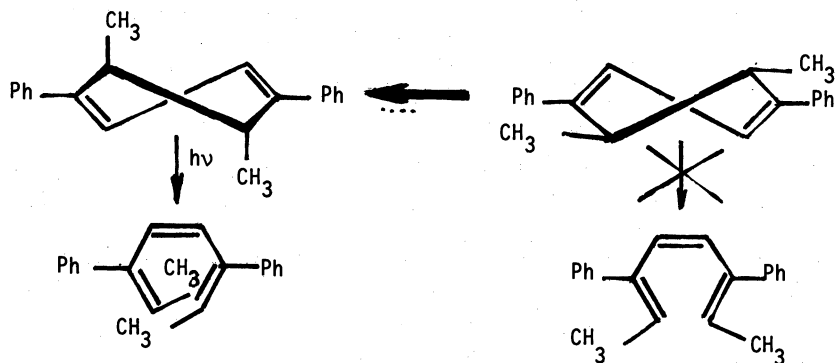
With another series of compounds (16), if a phenyl group is substituted on the saturated carbon of the ring, we observe again the same stereospecificity.
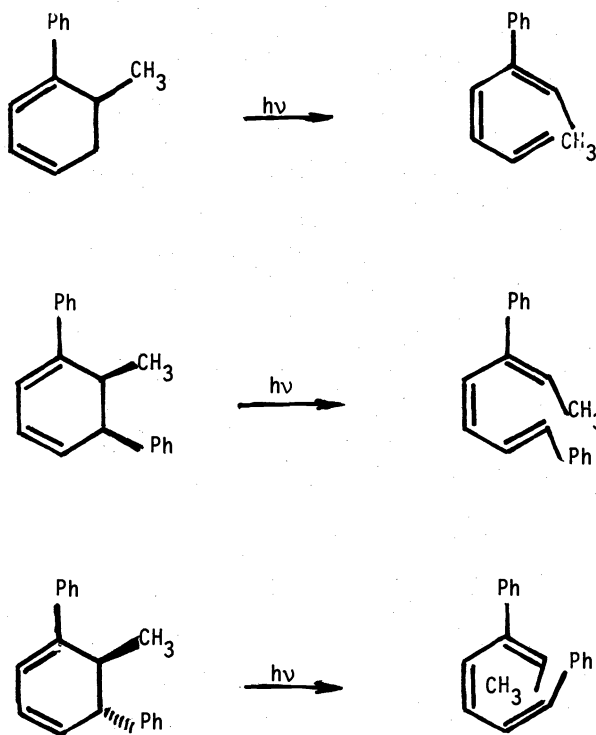

These stereospecific photoreactions may then be used to synthesize particular hexatrienes but one often has to prevent a reabsorption of quanta by the products which have maximum in the same wavelength region. The quantum efficiency of the ring opening should be larger than the one for rotation around a C-C double bond (9) and we have shown (6) that this quantum yield is increased by steric factors, for instance the stronger repulsion of methyl groups in the Z-cyclodiene 2. Useless to say that all of the hexatrienes obtained show either a thermal disrotatory reverse cyclization reaction, or a thermal suprafacial {1, 7 } H shift to yield the more stable isomeric hexatriene (6, 8).

Now I would like to stress a somewhat more complicated problem : in the case when two or more conformations of a polyene exist at the equilibrium in the ground state (2, 5) what correlation can we draw with the result of the photochemical act and is there a modification of the distribution of the conformers ? Though our results are not enough accurate to give a quantitative answer, I think we can bring a good deal of information to shed light into this intriguing area.

As preliminary reflexions, I would say that, in the excited state, the rotation around C-C single bonds of conjugated polyolefins is supposed to be slowed down (5, 10) compared to the ground state. On the other hand, if the reaction proceeds from the singlet state (which is the case for many of the photoisomerizations I shall deal with), the maximum time the molecule disposes to equilibrate is 10^{-8} s, which is very short for a molecular movement.   If the reaction goes from the triplet state, the limitation is much less important, as the range goes from the nanosecond to the second or more. But with most of the reactions of the acyclic polyenes we studied, we were able to make sure that reactions without sensitizers went through singlet states, as the intersystem crossing is very inefficient when there is no hetero or heavy atom in and around the molecule.

HAVINGA and his coworkers made some interesting observations in this respect by comparing the behaviour of 2-methyl-1, 3, 5 hexatriene 5 to unsubstituted 6 and to 2, 6-disubstituted hexatrienes 7 (10) : with the unsubstituted Z-hexatrienes 6, the only reaction observed in solution is an isomerization of the central double bond yielding a photostationary equilibrated mixture. With the 2-methyl-Z-triene 5, three modes of reactions are observed, which are supposed to derive from a c Z t preferred conformation ;   at last with the 2, 5-dimethyl-Z-triene 7 , the preferred

c Z c conformation would yield the cyclodiene.
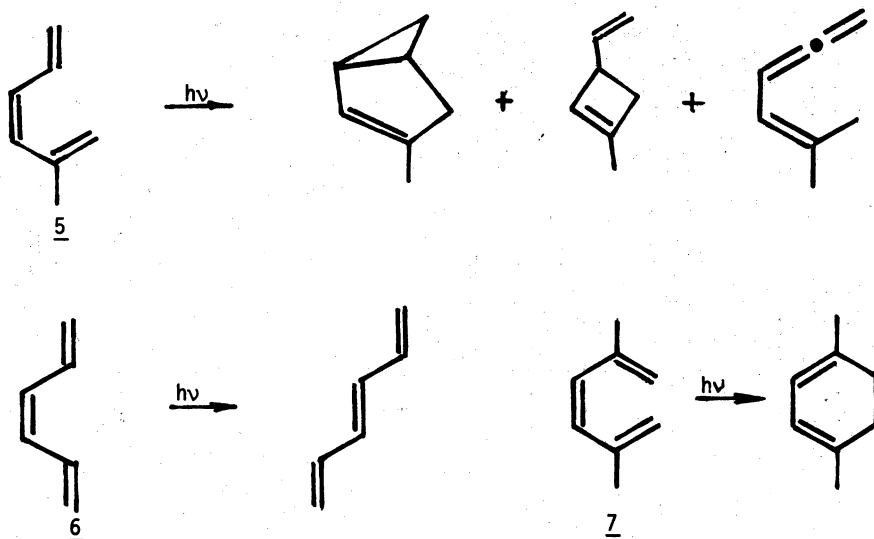
The same type of arguments have been used by DAUBEN and coworkers (11) who determined a decreasing of the yield of bicyclo{3.1.0}hexene 8 when the bulk of the R substituent was increased, which should favour the c Z c conformations over the c Z t.
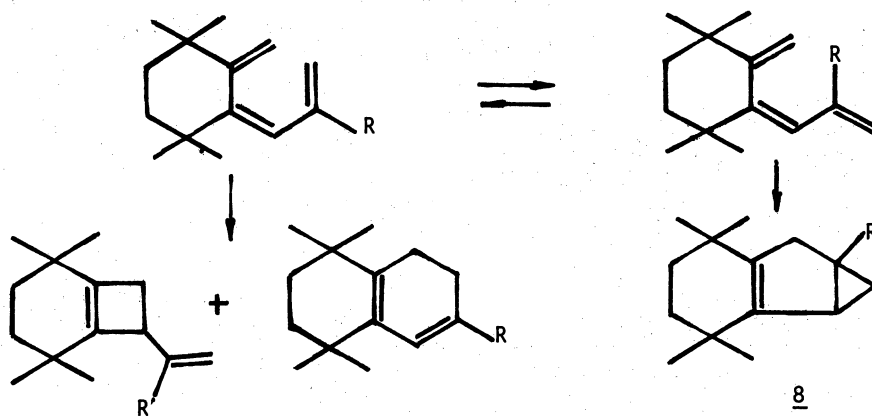

The idea of examining the possibility to excite one of the equilibrium conformers was challenging and we applied it (12) to a 1,1,5-trimethylhexatriene which turned to have a wavelenth dependent behaviour : the E, Z isomerization is the main photoreaction when irradiating with short wavelength whereas a photobicyclization results from a longer wavelength irradiation. From such experimental results we may infer that the c Z t conformation absorbs to the red compared to the t Z t conformation : this is corroborated by a theoretical study of the electronic absorptions of hexatrienes (4 f).
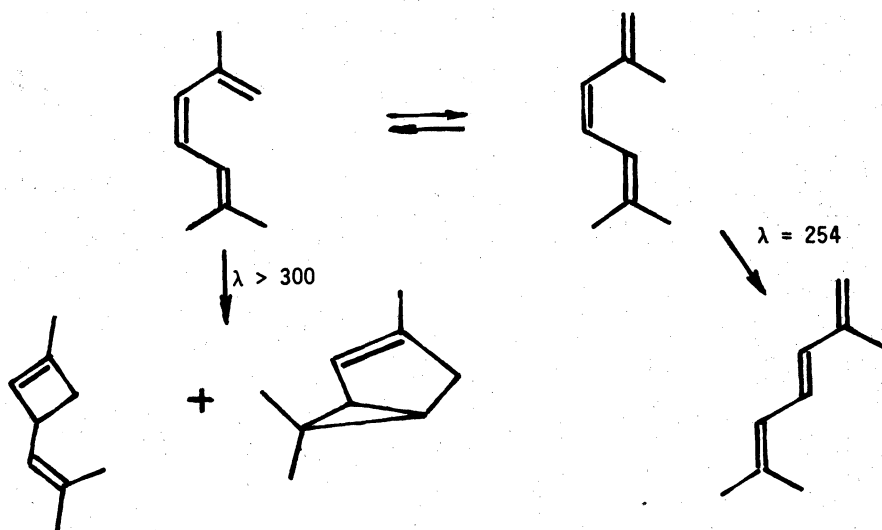
Let us turn now to that puzzling cyclization which has been called intramolecular Photo-DIELS-ALDER reaction (1,3,13). Since 1958 (13a) so many examples have been described but very few studies went into the detailed mechanism, because of absence of stereo-labeling. The questions raised about that reaction are as follows : 1 -. is a c Z t conformation necessary for the cyclization to take place ? 2-. Where does the observed regiospecificity come from ? 3-. Is there a stereo-specificity and which is it ? 4-. Is it reasonable to look at this reaction as a concerted one and if yes, what kind of orbital symmetry arguments are we supposed to use ?

To the first question, it has been answered yes, a c Z t conformation is necessary, but the evidence is difficult to bring because most demonstrations are indirect. I would rather say that there is no Photo-DIELS-ALDER reaction if there is no c Z t conformation for the triene.
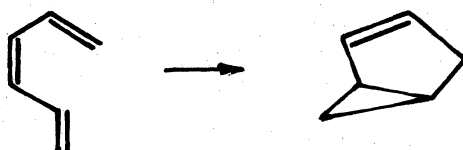
As far as the regiospecificity is concerned, there is a large agreement about the fact that when the hexatriene is dissymetric, the only bicyclo[3,1,0]hexene formed always originates from the more end-substituted terminal double bond, yielding the more substituted cyclo-propane.
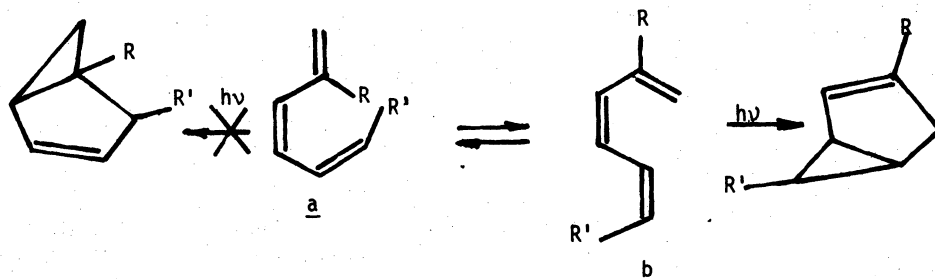
This may be purely due to the ground state equilibrium where a conformation such as a is probably less favoured than b. It is convenient to remember at this point that the CURTIN-HAMMETT principle may be applied to these systems : assuming that there is no redistribution of the conformers in the excited state, if there is a more efficient ring closure of b to the bicyclo [3,1,0]hexene shown, there is a rapid reformation of b in the ground state which makes all the reaction start from that favourable conformation.

On the other hand, a substituent in position 2 on the triene orients the cyclopropane to the other end
of the system : this may again be a purely conformational effect as the conformer c is less
favoured than d.   This is true even if the cyclopropane formed is now less substituted.
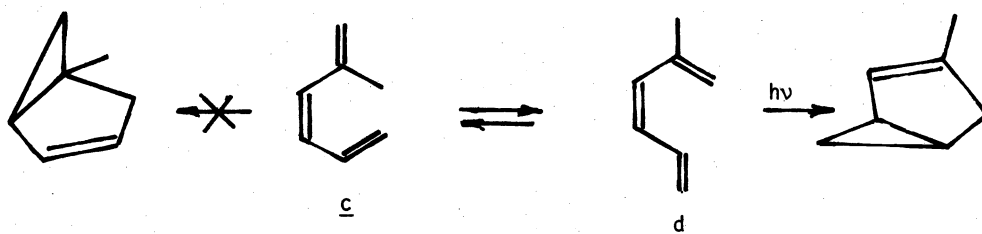
These last two examples may also reflect the difficulty to effect the closure of the 5-membered
ring as a, as well as c, show unfavourable 1, 5-interactions.

We have experimented (8) that the phenyl-methyl-hexatriene 10 does not give any bicyclo {3.1.0}
hexene, but only Z, E-isomerization.   This is probably explained by conformational and
1, 5-interaction factors.
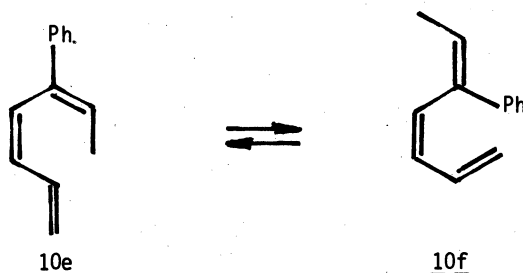
But these results are difficult to compare to those concerning the trienes 11, 12 and 13 where the
same steric factors seem to be operating, with only a phenyl group added at the end of the system (14).
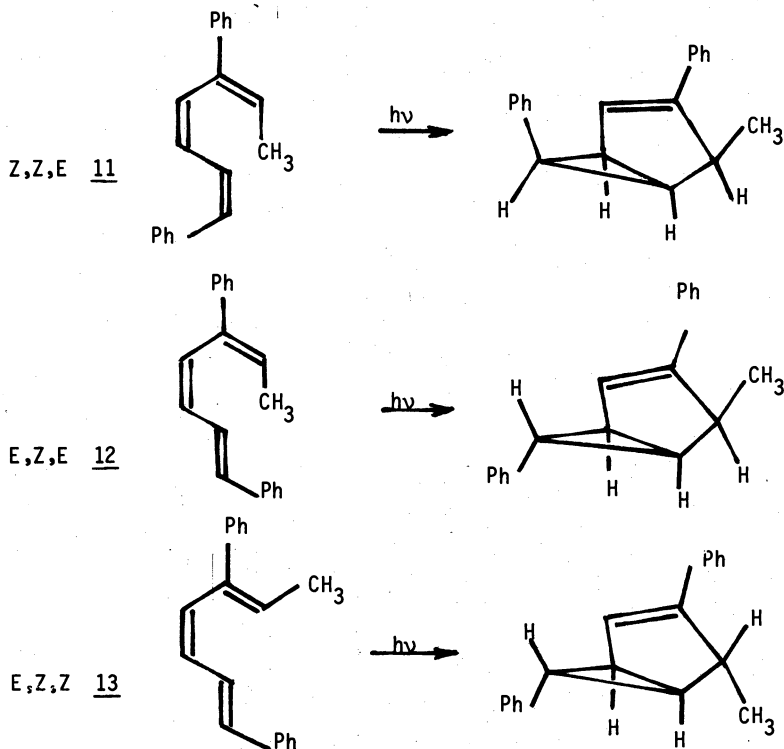
Now comes the problem of the stereospecificity of the bicyclization. I would like to retain for this discussion only cases where the configuration of the initial triene is established with maximum probability, the difficulty being that the triene has often a ring-opening origin and that there may be previous photoisomerizations. Moreover, the kinetics have not been measured in most cases.

Working with cyclic trienes, DAUBEN et al. (1b, 15) showed the following :

14 → no bicyclo{3.1.0}

15

16

endo, exo

endo, exo
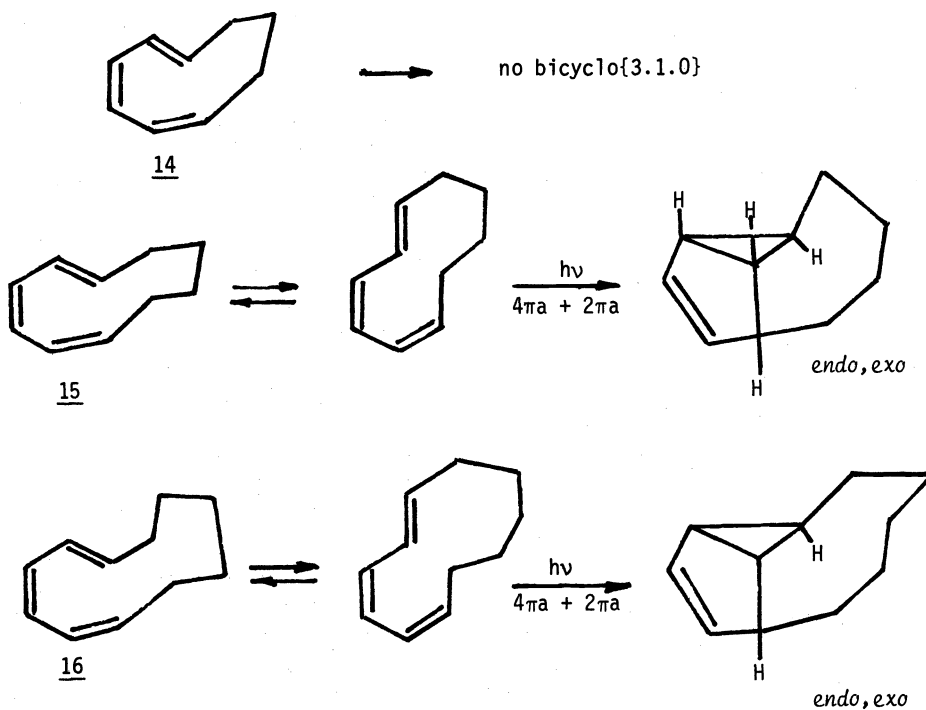
The authors concluded (1b) in the case of **16** that "the triene to bicyclo {3.1.0} hexene conversion does not occur via a concerted {4 π + 2π } cycloaddition route" and, in the case of **15,** that the situation might be different for cyclic trienes compared to acyclic series.

The only cases studied with some details in the acyclic series have been described by PADWA et al. (13 c) : starting from the Z, Z, E or Z, Z, Z trienes, the authors assume that the first step is a rapid photoisomerization around a terminal double bond and that the bicyclo-hexenes are indeed formed from the E, Z, E and E, Z, Z-hexatrienes.

Z,Z,E

E,Z,E

$4 \pi s + 2 \pi a$

exo, exo

Z,Z,Z

E,Z,Z

$4 \pi s + 2 \pi a$

exo, endo
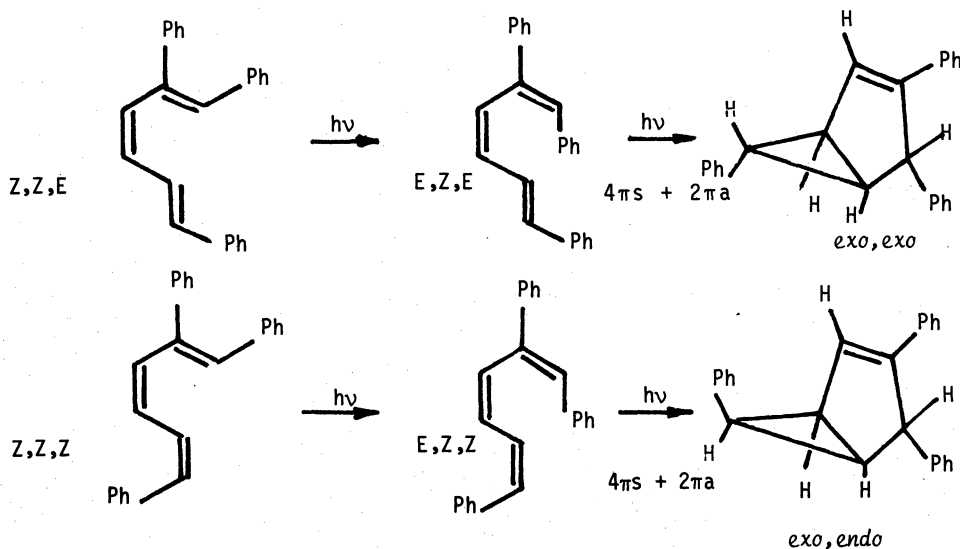
The stereochemistry, assumed as that of a concerted process, is concluded to be in accordance with prevision i.e. $\{4\pi s + 2\pi a\}$. But detailed kinetic data could not be effected, which would have given more information about the detailed stereochemistry.

We decided to synthesize (16) a series of acyclic trienes, with substituents allowing the determination of the stereochemistry by unequivocal means, and also permitting a kinetic investigation of the reacting species. We performed the chemical synthesis (16) of the eight stereoisomers of 1, 5-diphenylhepta-1, 3, 5 triene. Our structural assignments will not be detailed here to make short but the evidence is obtained by a number of stereo-correlations, in addition to spectroscopic arguments. We wanted to have in hands also the E-central trienes, to be able to monitor the photoreactions by NMR without ambiguity. Of the four Z-central trienes, three gave a bicyclo {3.1.0}hexene as major primary product, in addition to isomerizations around double bonds. A second bicyclic isomer appeared at later stages of the irradiation but it can be attributed without ambiguity to the formation of isomerized hexatrienes. The details of the kinetics are given now (16) in tables 1 to 4.
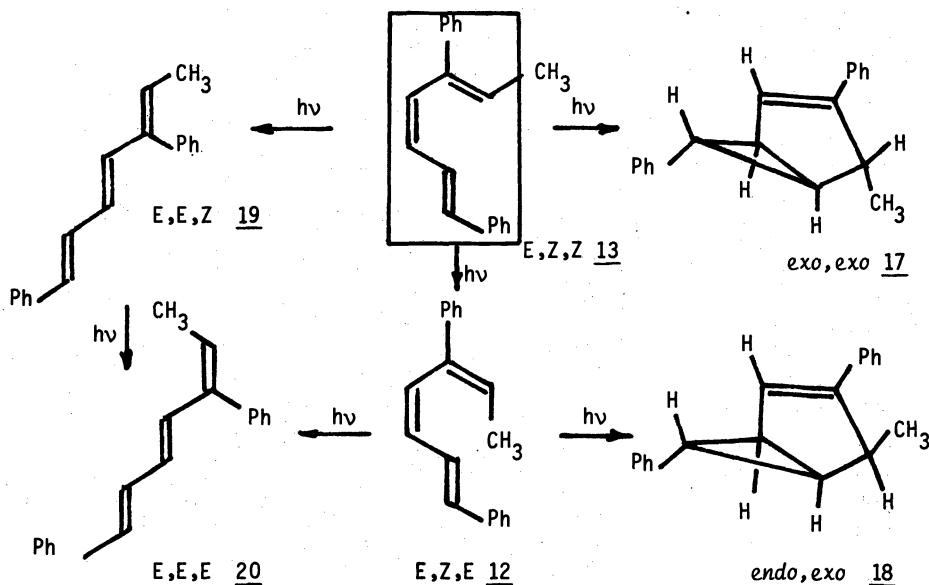

TABLE 1 - Irradiation of E, Z, Z-triene 13

time mn	% trienes				% bicyclo{3.1.0} hexenes	
	E, Z, Z 13	E, Z, E 12	E, E, Z 19	E, E, E 20	exo, exo 17	endo, exo 18
0	100	-	-	-	-	-
5	60	24	5	4	7	0
10	40	30	9	7	13	traces
15	36	28	10	9	14	3
20	25	24	15	12	17	7
30	16	11	25	18	20	10
40	4	4	27	23	28	14
50	0	0	29	26	29	16

Although the isomerization around the methylstyrene terminal double bond in the Ē, Z, Z-triene 13 is efficient, the appearance of the second bicyclic isomer 18 after only 15 mn of irradiation allows us to conclude that the exo, exo isomer 17 is the primary product formed from 13.

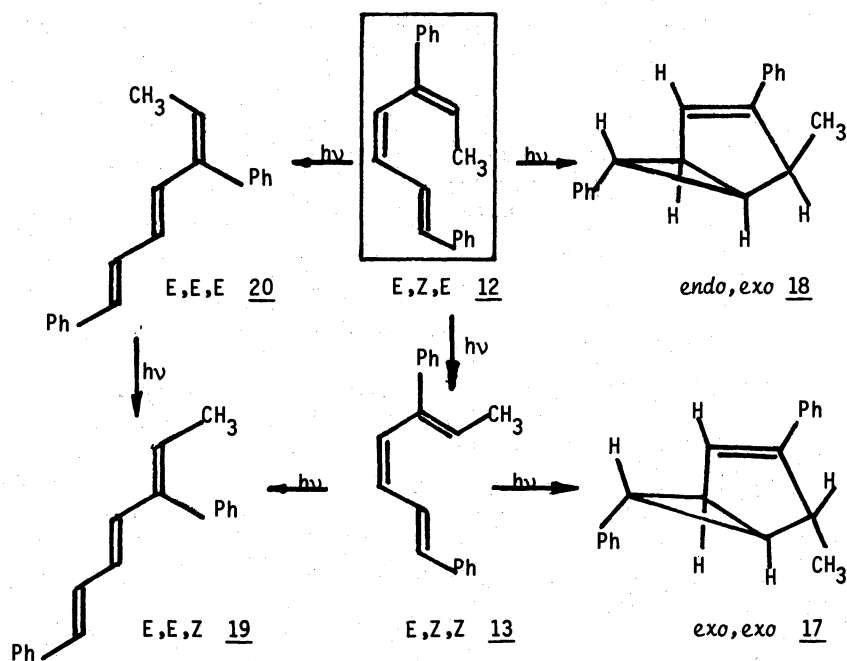Starting from the E, Z, E triene 12, the results are shown on table 2.

TABLE 2 - Irradiation of the E, Z, E triene 12

time mn	% trienes				% bicyclo{3.1.0}hexenes	
	E, Z, E 12	E, Z, Z 13	E, E, Z 19	E, E, E 20	endo, exo 18	exo, exo 17
0	100	-	-	-	-	-
5	92	8	-	-	-	-
10	80	18	-	-	2	-
15	57	28	3	6	5	-
20	33	30	12	13	8	2
25	23	29	17	16	10	5
35	14	10	28	18	15	15
55	-	5	27	23	21	21
75	-	-	30	24	22	22

Here also, the isomerization around the terminal methylstyrene double bond is more rapid than around the central double bond. But there is no doubt, looking at tables 1 and 2, that the endo, exo triene 18 is the primary product from the E, Z, E triene 12 whereas the exo, exo triene 19 is the one from the E, Z, Z triene 13.

With the Z, Z, E triene 11, the kinetics is more complicated, but having the preceding results in hands, we can make a clear decision.
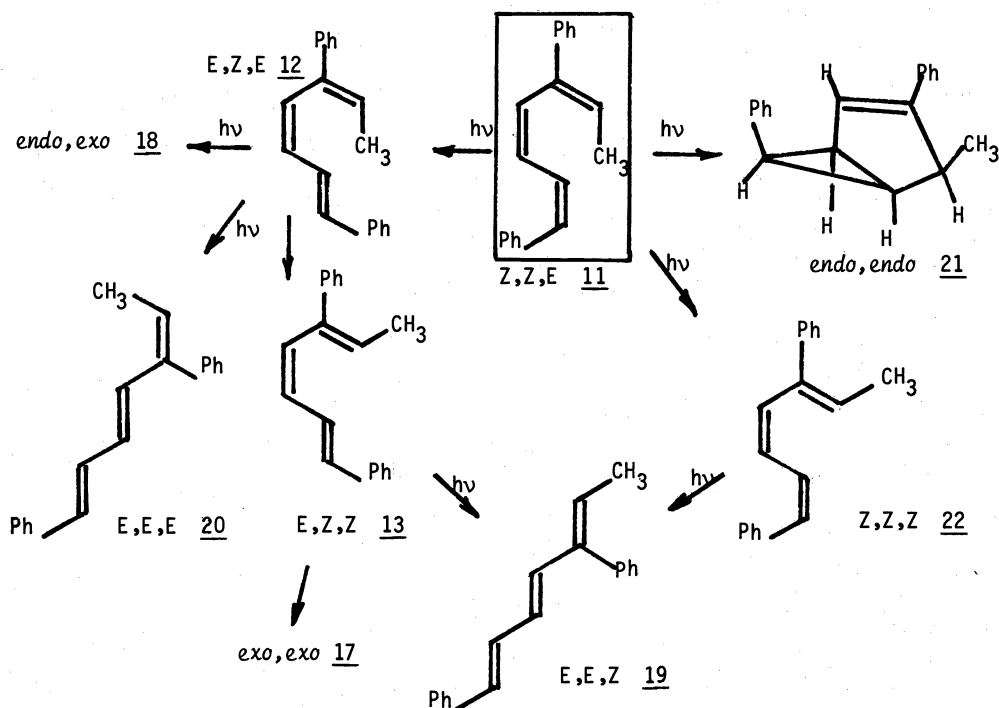
E,Z,E 12   Ph   CH₃

endo,exo 18   hν

hν   Ph   CH₃   Z,Z,E 11   hν   endo,endo 21

CH₃   Ph   Ph   CH₃   Ph   CH₃

Ph   E,E,E 20   E,Z,Z 13   Z,Z,Z 22

exo,exo 17   CH₃   Ph   E,E,Z 19   Ph

TABLE 3 - Irradiation of the Z, Z, E triene 11.

time mn	% trienes					% bicyclo{3.1.0}hexenes	
	Z, Z, E 11	Z, Z, Z 22	E, Z, Z 13	E, E, Z 19	E, E, E 20	17 + 18	endo, endo 21
0	100	-	-	-	-	-	-
10	75	4	4	3	4	6	4
15	56	10	4	6	8	10	8
25	33	14	4	9	11	13	13
35	10	19	7	15	13	18	18
50	-	16	4	20	20	20	20
prolonged	-	-	-	33	27	20	20

The bicyclization of the Z, Z, E triene 11 is probably slower than that of E, Z, E and E, Z, Z trienes since the two bicyclo hexenes 17 and 18 formed from these trienes appear after the first 10 mn of irradiation. But here also, we can state that the endo, endo isomer 21 originates from the triene 11, as it is formed only in this case and not in the two preceding irradiations.

With the Z, Z, Z hexatriene 22, there is a rapid isomerization around the central double bond, which probably is the reason why no bicyclic photoisomer is formed from that compound, but only minor quantities of the three bicyclohexenes already determined. The fourth possible bicyclic isomer (exo, endo) has not been detected in any of the irradiations.
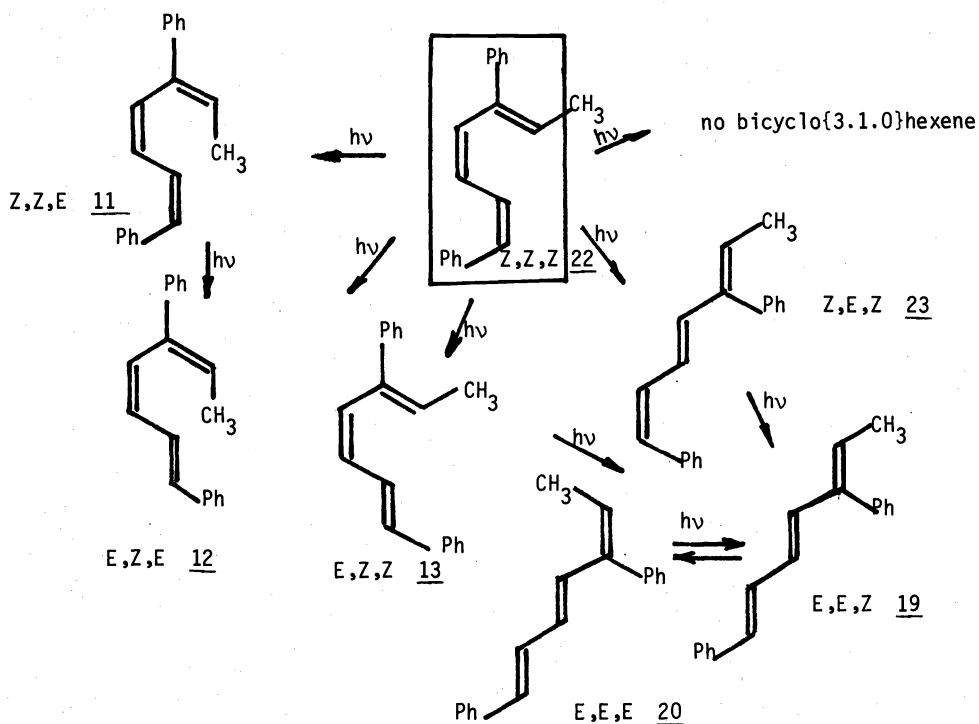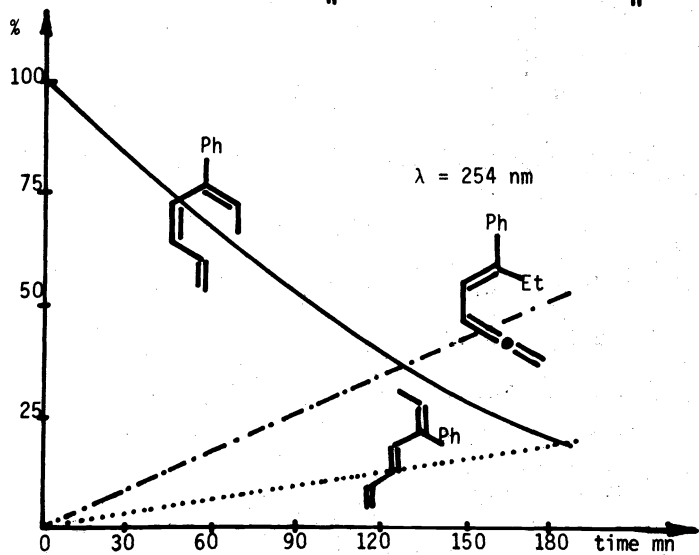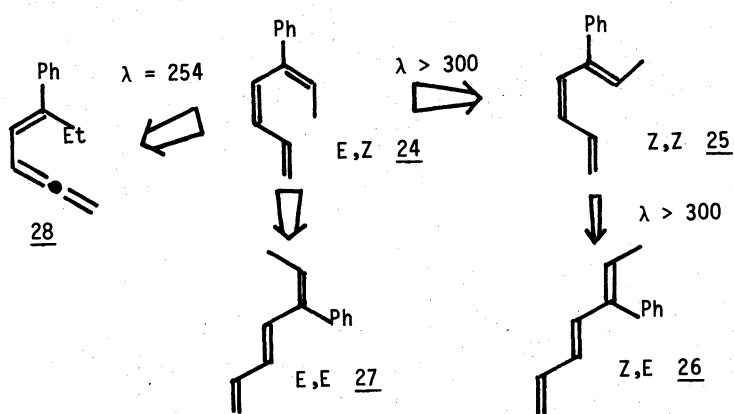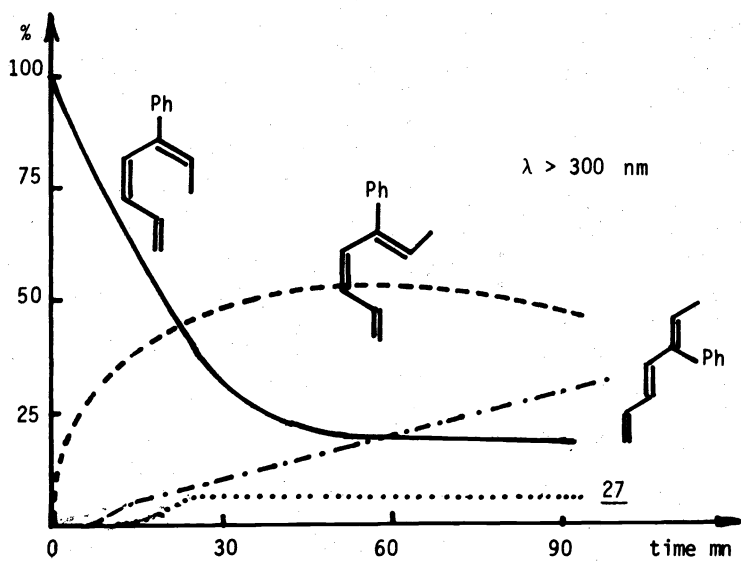

TABLE 4 - Irradiation of Z, Z, Z-triene 22

time mn	% trienes				
	Z, Z, Z 22	Z, Z, E 11 and/or E, Z, E 12	E, Z, Z 13 and/or Z, E, Z 23	E, E, Z 19	E, E, E 20
0	100	-	-	-	-
5	83	6	2	4	5
10	54	12	8	14	12
15	21	18	11	26	24
20	18	20	10	27	25
27	11	21	9	31	28
35	5	15	-	45	30
45	-	8	-	54	38
60	-	-	-	55	45

Fig. 1 - Irradiation at λ = 254 nm of the E,Z-triene 24

Fig. 2 - Irradiation at λ > 300 nm of the E,Z-triene 24
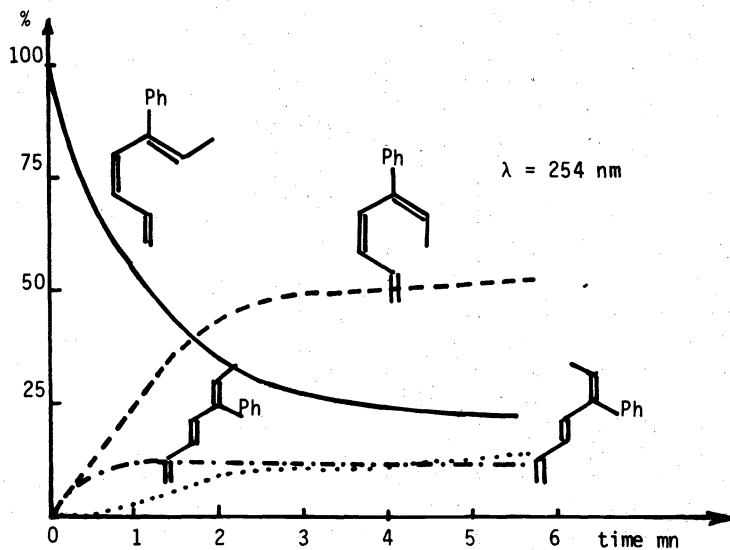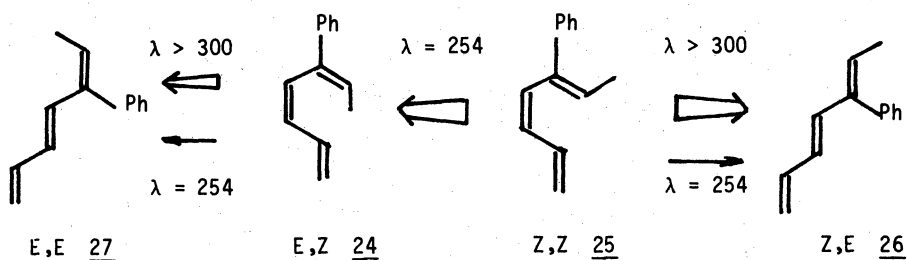
Fig. 3 - Irradiation at λ = 254 nm of the Z,Z-triene 25
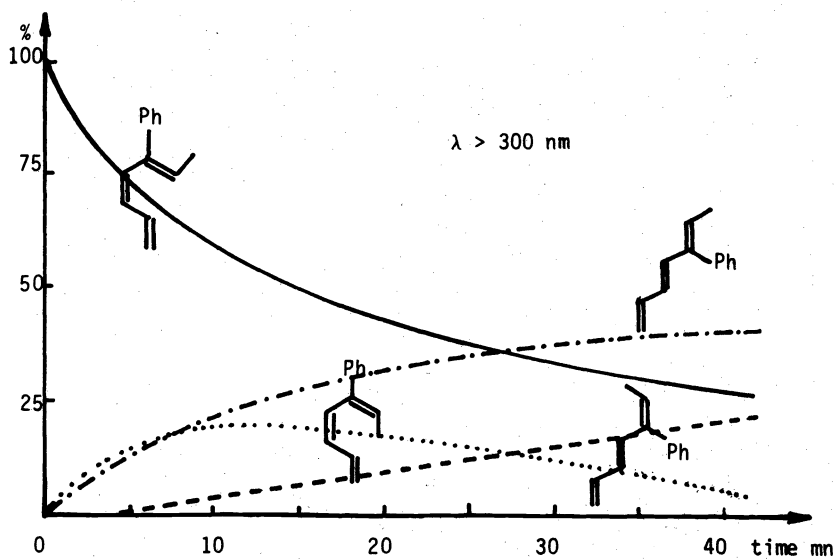
Fig. 4 - Irradiation at λ > 300 nm of the Z,Z-triene 25

It is now possible to assure that the intramolecular Photo-DIELS-ALDER reaction shows a strong stereospecificity of the {4πa + 2πa} type, as demonstrated with cyclic and acyclic hexatrienes. That supposes that the two rings formed are closed via conrotatory modes, whatever the overall steric interactions are. So this looks very strongly like a concerted mode, for which the simple orbital symmetry considerations would predict a {4πs + 2πa} or {4πa + 2πs} stereochemistry. If one should favour a priori the formation of one ring, I would think the 1 and 5 carbons are in good position in the ground state of the triene to initiate the cyclization process, followed by the cyclopropane formation. But it is clear that one can invoke only electronic and/or orbital factors, at the exclusion of steric ones, as the cyclization to an endo, endo -bicyclo{3.1.0}hexene is probably not favoured energetically. If concerted, these reactions should, I think, be interpreted in terms of frontier orbital theory, by interaction of the terminal double bond with the butadiene part of the triene. But I leave these experimental results to the appreciation of theoreticians (4e).

Now, I would like to discuss the problem dealing with the photoisomerizations around double bonds in a conjugated hexatriene. The results obtained in our laboratory (8, 14, 16) and others (17, 18) allow only a limited generalization : both terminal double bonds are isomerized at nearly the same rate, whatever the substitution is ; that rate is of the same order of magnitude as the one of the Z to E photoisomerization of the central double bond but it differs according to the nature and position of the substituents ; there is no reversibility with these compounds when the double bond is disubstituted (E → Z).

We tried to simplify the problem by studying a triene with only two photoisomerizable double bonds (8), and we looked for a possible wave-length effect (16). As already mentioned, there is no bicyclization with these 3-phenylhepta-2, 4, 6 trienes, but a {1,5} H shift yielding an enallenic isomer 28.

Starting from the E, Z triene 24, we can obtain the enallene 28 by irradiation at 254 nm (figure 1) while the most efficient process at λ > 300 nm (figure 2) is the isomerization around the terminal double bond, yielding the Z, Z triene 25. Sensitization by different triplet donors like benzophenone, Michler's ketone and fluorenone eliminates the H shift and makes izomerization around the central double bond more efficient (compare 17, 18).

Starting from the Z, Z triene 25, there is no H shift even through singlet state, but successive isomerizations (figures 3 and 4) : the terminal double bond is now more rapidly isomerized at 254 nm than at λ > 300 nm. The same sensitizers as preceding effect predominantly isomerization around the terminal bond, yielding the E, Z triene 24 as the major compound in the photostationary state. This permits for instance to obtain a 75% yield of E, Z triene 24 by irradiation in the presence of fluorenone, starting from the Z, Z hexatriene 25.

In conclusion, I think I can answer yes to the question about the role of the ground state conformation of the systems we studied : the specificity and the wavelength influence are strong arguments in favour of this. About the orbital symmetry control, I shall be more careful, although the new examples we reported are in favour of the occurrence of such factors in the formation of bicyclo{3.1.0}hexenes from hexatrienes.

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