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A Stereoselective Rule for the Cross-bicyclization in Linear Conjugated Polyenes

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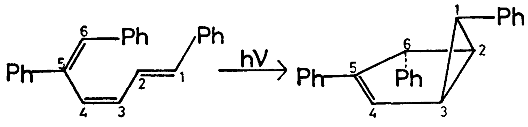
A concept of the cross-bicyclization complementary to that of the cycloaddition is defined for interpreting the mechanism of the simultaneous bicyclizations in linear conjugated polyenes based on the perturbation treatment in the frame of Hückel MO's. Stereoselective modes in thermal and photo-induced reactions are shown to depend on the sign of the bond-bond-polarizability, $\Pi_{rs,tu}$, of the concerned polyene, where r, s, t, and u refer to the atomic positions at which the bicyclization occurs. From the properties of $\Pi_{rs,tu}$ of linear conjugated polyenes, these modes are simply determined by the relationship among r, s, t, and u in thermal cases, but not in photo-induced ones. The predicted stereoselective modes are discussed in line with experimental observations. It is demonstrated that the "symmetry-disfavored" reactions inferred from the usual cycloaddition mechanism can be interpreted as the concerted cross-bicyclization reactions.

The stereoselective rules from the concept of the concerted cycloaddition reactions by Woodward and Hoffmann[1] or those from the orbital interaction approach, particularly among the highest occupied (HO)MO, the lowest unoccupied (LU)MO, and the singly occupied (SO)MO, by the present authors' group[2] have clearly interpreted steric control modes of both thermal and photo-induced (2+2) or (4+2) cycloadditions and so on. These rules have also been applied to most of the intramolecular cases without hesitation. Some of the recent experimental informations, however, have shown discrepancies with the predictions issued from the above rules with regard to the stereoselections in photo-induced (2+2) and (4+2) cycloadditions in the conjugated dienes and trienes, respectively. For instance, Padwa *et al.* have essentially provided (4_s+2_a) photoisomerizations of **1** and **2** in accordance with the rules of cycloadditions,[3] while, on the contrary, Courtot *et al.* have unambiguously observed disfavoured (4_a+2_a) modes in those of **3**, **4**, and **5** with monitoring by NMR.[4]



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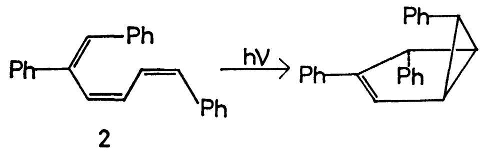

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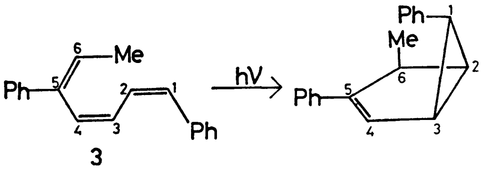

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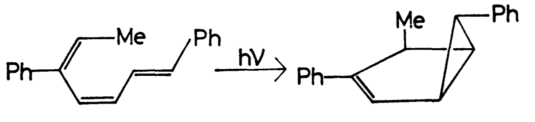

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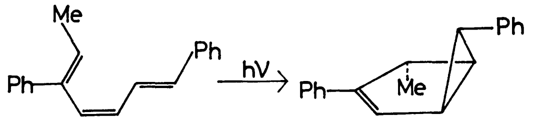

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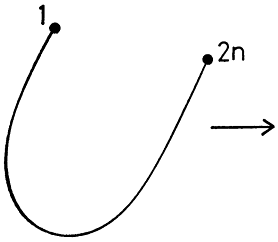
Other examples of disfavored modes in photoisomerizations of dienes or trienes have also been found out[5—8] as will be shown later. Almost all of these "troublesome" reactions within the category of the usual cycloadditions have been excluded out from the concerted reactions. But why concerted in **1** and **2**, and non-concerted in **3**, **4**, and **5**? Can we not interpret the concertedness and the stereoselective modes of these bicyclizations in conjugated polyenes? The answer is yes. At first it should be pointed out that the stereoselective rules of the cycloaddition mentioned above are suitable for merely cyclic additions between two separate conjugated polyene parts whichever they are in different molecules or in a molecule. Therefore, from the theoretical point of view, one had better distinguish the nature of the bicyclizations in a conjugated polyene from the usual cyclic additions. In this paper, we will present a new theoretical interpretation, which is complementary to the concept of the concerted cycloaddition reactions, so that one might comprehend the concertedness and the stereoselective rules of the above reactions with "disfavored" mode.

We define a simultaneous bicyclization between the r-th and the s-th and between the t-th and the u-th carbons (**6**→**7**) in a linear conjugated polyene containing $2n$ π electrons as a *[r,s/t,u] cross-bicyclization* under the condition that r and s are odd and t and u are even or *vice versa*, where the numbering of carbons is counted from the end of conjugated carbon chain and $r<t<s<u$ holds.



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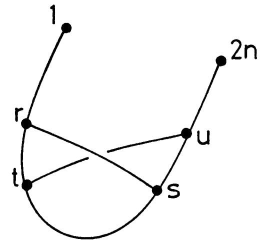

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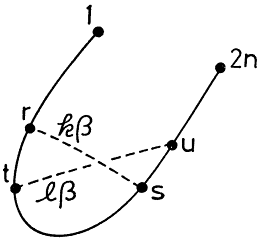
In the cross-bicyclization thus defined, the conjugation between the *s*-th and the *t*-th carbons generally exists throughout the process of reaction. This is the point of essential importance. If this conjugation does not exist, the reaction would turn out as a usual cycloaddition. In what follows, we try to establish a simple but reasonable method in such reactions employing the perturbation theory in the scheme of the Hückel MO approach.[9] Similar method has been used successfully to treat the stereospecific ring-closure of conjugated polyenes.[10] Then the predicted stereoselective rules will be applied to interpret the latest several experimental results.

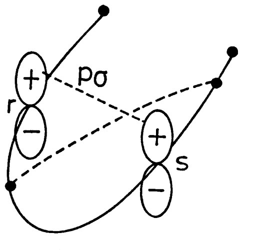
Formulation

Consider two simultaneous conjugations, $k\beta$ and $l\beta$, appearing as a perturbation as indicated in **6′**.

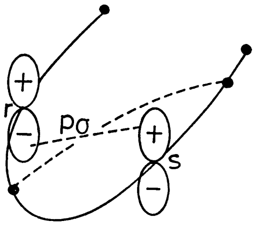


6′

The quantity β is the resonance integral between two adjacent 2pπ atomic orbitals (AO's). Hence, $k\beta$, for instance, is adopted to be the resonance integral between ϕ_r and ϕ_s when σ-like overlapping of these two AO's in the distorted π electron system occurs, where ϕ_r denotes 2pπ AO of the r-th carbon. The signs of $k\beta$ and $l\beta$ concern the mode of overlap stabilization as indicated below.

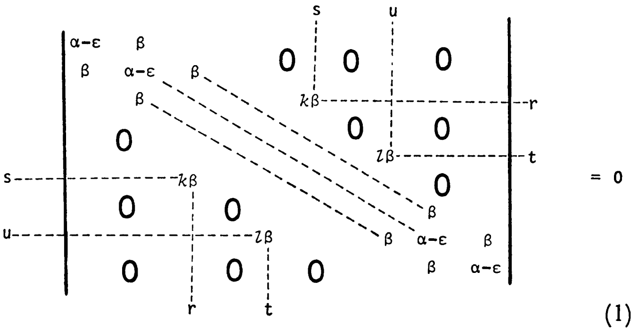


$k\beta<0(k>0)$; Disrotatory



$k\beta>0(k<0)$; Conrotatory

Letting α be the Coulomb integral of 2pπ AO, the perturbed secular determinant in the present case becomes as follows.



(1)

According to the procedure previously reported ("method of perturbed secular determinant"),[11] we get the following formula within the second-order perturbation treatment.

$$\frac{\Delta E}{\beta}=2kP_{rs}+2lP_{tu}+k^2\Pi_{rs,rs}+2kl\Pi_{rs,tu}+l^2\Pi_{tu,tu}. \tag{2}$$

Here ΔE represents the change in the π-electronic energy, and P_{rs} and $\Pi_{rs,tu}$ are the same quantities as the usual bond-order and bond-bond-polarizability, respectively, defined as

$$P_{rs}=\sum_{i}^{\text{all}} n_i C_r^i C_s^i, \tag{3}$$

$$\Pi_{rs,tu}=\frac{1}{2}\sum_{i}^{\text{all}}\sum_{j(\neq i)}^{\text{all}} \times n_i(2-n_j)\frac{(C_r^iC_s^j+C_r^jC_s^i)(C_t^iC_u^j+C_t^jC_u^i)}{x_i-x_j}$$

$$\left(x_i=\frac{\varepsilon_i-\alpha}{\beta}\right) \tag{4}$$

where n_i, ε_i, and C_r^i represent the occupation number, the orbital energy, and the coefficient of ϕ_r, respectively, of the i-th MO of the unperturbed system **6**. Since the sign of β is negative, the overlap stabilization is brought about in the system when the sign of the right hand side in Eq. 2 becomes positive. We have only to judge the sign of the next formula, because the required values of P_{rs} and P_{tu} vanish in the case of the present $2n$ conjugated polyene.

$$\frac{\Delta E}{\beta}=k^2\Pi_{rs,rs}+2kl\Pi_{rs,tu}+l^2\Pi_{tu,tu}. \tag{2'}$$

It is easily shown that this quadratic form is positive by the Cauchy-Schwartz' inequality. According to the sign of the $\Pi_{rs,tu}$ value, the mode of cross-bicyclization may be classified into the following four types of rotations in the direction of increasing value of $\Delta E/\beta$.

$\Pi_{rs,tu}$	k	l	Rotating mode
positive	positive	positive	A(disrotatory-disrotatory)
	negative	negative	B(conrotatory-conrotatory)
negative	positive	negative	C(disrotatory-conrotatory)
	negative	positive	D(conrotatory-disrotatory)

No distinction can be made of mode A from B, nor of mode C from D within the present second-order perturbation treatment. However, in some favorable cases, consideration of steric circumstances, which is important in such cases as the cross-bicyclization, may assist in predicting the more probable mode. It is not difficult to show that, in thermal case, the sign of $\Pi_{rs,tu}$ is positive or negative according as $(s-r)+(u-t)$ is equal to $4m+2$ or $4m$, respectively, from the integral representation for $\Pi_{rs,tu}$ obtained by Coulson and Longuet-Higgins.[9c)] On the contrary, in photo-induced case, there is no such a simple relationship between the sign of $\Pi_{rs,tu}$, which is calculated in regard to the first excited configuration, and r, s, t, and u. Hence one has to examine the numerical value of the concerned $\Pi_{rs,tu}$ in order to predict the mode of photo-induced cross-bicyclization.

Stereoselective Modes of Cross-bicyclization and Cycloaddition

For the cases of diene, triene, and tetraene, we show all kinds of rotating modes in thermal and photo-induced cross-bicyclizations in Table 1 along with the numerical values of $\Pi_{rs,tu}$. Interestingly, it is seen that the predicted stereoselective modes make no difference in both thermal and photo-induced reactions in each cross-bicyclization of diene, triene, and tetraene.[12)] These predictions are remarkably different from those issued from the concept of the cycloaddition by Woodward and Hoffmann or from the frontier orbital interaction approach. It should also be emphasized that modes A and B are favored when $(s-r)+(u-t)$ is equal to $4m+2$, while modes C and D are favoured when it is $4m$ in these polyenes. The cases of longer polyenes could also be treated by a simple extension of the present calculations, with which we will not further deal in this study.

Table 1. Rotating modes in cross-bicyclization

Polyene	$[r,s/t,u]$	Thermal ($\Pi_{rs,tu}$)	Photo-induced ($\Pi_{rs,tu}$)
Diene	[1,3/2,4][a)]	C,D(−0.3578)	C,D(−0.1789)
Triene	[1,3/2,6][b)]	A,B(0.2352)	A,B(0.0762)
	[1,3/2,4]	C,D(−0.2906)	C,D(−0.0694)
	[1,5/2,6]	C,D(−0.3597)	C,D(−0.1661)
	[3,5/2,4]	C,D(−0.0274)	C,D(−0.2072)
Tetraene	[1,3/2,4]	C,D(−0.2659)	C,D(−0.0410)
	[1,3/2,6]	A,B(0.2013)	A,B(0.0053)
	[1,3/2,8][c)]	C,D(−0.1809)	C,D(−0.0029)
	[1,5/2,6]	C,D(−0.2998)	C,D(−0.1269)
	[1,5/2,8]	A,B(0.2359)	A,B(0.0725)
	[1,5/4,6]	A,B(0.1863)	A,B(0.0830)
	[1,5/4,8][d)]	C,D(−0.1685)	C,D(−0.1135)
	[1,7/2,8]	C,D(−0.3548)	C,D(−0.1965)
	[3,5/4,6]	C,D(−0.2270)	C,D(−0.0878)
	[3,5/2,4]	C,D(−0.0311)	C,D(−0.1626)
	[3,7/2,6]	C,D(−0.0515)	C,D(−0.1649)
	[3,7/2,4]	A,B(0.0054)	A,B(0.0801)

a), b), c), and d) have been classified into (2+2), (4+2), (6+2), and (4+4) cycloaddition, respectively, up to now.

Let us treat here some of the usual cycloadditions with our formulation for the sake of comparison. In the case of the (4+2) cycloaddition, for instance, the triene is divided into a diene and an olefin and thus the conjugation between C_2 and C_3 is cut off as shown in Fig. 1(A). In this case, the amplitudes of the frontier orbitals on C_1, C_2, C_3, and C_6 are large and the orbital energy differences among them are small as a matter of fact, so $\Pi_{rs,tu}$ defined by Eq. 4 mainly depends on the expansion terms of $(i,j)=(2,4)$ and $(3,5)$ in the thermal process, while of $(i,j)=(2,3)$ and $(4,5)$ in the photo-induced process. In other words, the HOMO-LUMO interactions in the former process and the HOMO-SOMO and the SO'MO-LUMO interactions in the latter between a diene and an olefin shown in Figs. 1(B) and (C), respectively, are essentially important in order to predict the distinct stereoselective mode in

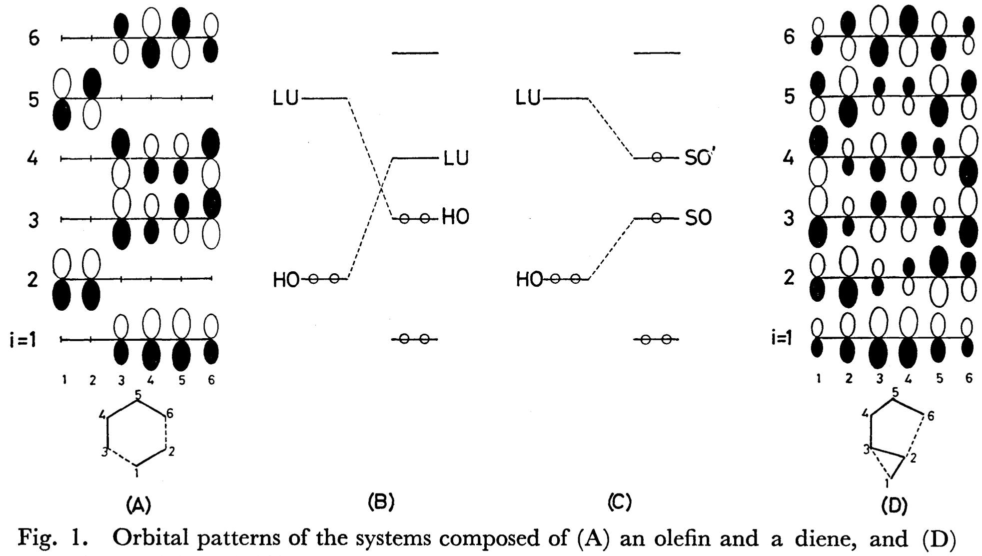


Fig. 1. Orbital patterns of the systems composed of (A) an olefin and a diene, and (D) a triene. (B) and (C) show the frontier orbital interactions in (A) in thermal and photo-induced processes, respectively. It should be noted that σ bond between C_2 and C_3 may remain in (A).

TABLE 2. STEREOSELECTIVE MODES IN CYCLOADDITION THROUGH THE TREATMENT OF THE PRESENT FORMULATION

Type of Cycloaddition	Thermal ($\Pi_{rs,tu}$; its main term[a)])		Photo-induced ($\Pi_{rs,tu}$; its main term[b)])	
2+2	C,D(−0.5000; −0.5000)	(2_s+2_a or 2_a+2_s)	A,B(+∞; +∞)	(2_s+2_s or 2_a+2_a)
4+2	A,B(0.3416; 0.4472)	(4_s+2_s or 4_a+2_a)	C,D(−0.8292; −0.9472)	(4_a+2_s or 4_s+2_a)
6+2	C,D(−0.2588; −0.3759)	(6_a+2_s or 6_s+2_a)	A,B(0.4185; 0.4893)	(6_s+2_s or 6_a+2_a)
4+4	C,D(−0.2683; −0.4236)	(4_s+4_a or 4_a+4_s)	A,B(+∞; +∞)	(4_s+4_s or 4_a+4_a)

a) Contribution to $\Pi_{rs,tu}$ from the HOMO-LUMO interactions between two separate polyene parts. b) Contribution to $\Pi_{rs,tu}$ from the HOMO-SOMO and the SO′MO-LUMO interactions between two separate polyene parts.

each process of the cycloaddition. On the contrary, in the case of the cross-bicyclization in a triene, the same criterion would no longer serve because of the alterations of the amplitudes in the MO's with $i=2$, 3, 4, and 5 on the concerned carbons as shown in Fig. 1(D). In this sense one can not always expect a conspicuous difference of the stereoselective mode between the thermal and photo-induced processes and has to sum up extending over all MO's such as in Eq. 4 in order to judge the signs of $\Pi_{rs,tu}$'s in the cross-bicyclization apart from the cycloaddition.

The values of $\Pi_{rs,tu}$ and the predicted stereoselective modes for cycloadditions in the cases of (2+2), (4+2), (6+2), and (4+4) are listed in Table 2 along with the main terms in $\Pi_{rs,tu}$ arising from the frontier orbital interactions. For cycloaddition reactions, the required $\Pi_{rs,tu}$'s are formally evaluated on the basis of the secular determinant in Eq. 1 with setting the resonance integral to be zero at the position where the conjugation is cut off. In photo-induced (2+2) and (4+4) cases, the degeneracies between the HOMO and the SOMO and between the SO′MO and the LUMO invalidate to evaluate the required $\Pi_{rs,tu}$. Actually, however, these degeneracies would be reduced by the energetical splittings between these MO's on account of the presence of the electron correlation as illustrated in Fig. 2.[13)] Therefore, we tentatively set here the values of ($x_{HO}-x_{SO}$) and ($x_{SO'}-x_{LU}$) in Eq. 4 to be infinitely small positive, from which the concerned $\Pi_{rs,tu}$'s are positive infinite. This means that photo-induced [1,3/2,4] cross-bicyclization of diene or [1,5/4,8] case of tetraene might rather favour the (2+2) or (4+4) cycloaddition, respectively, from the viewpoint of the energetical stabilization, as will be seen in the next section.

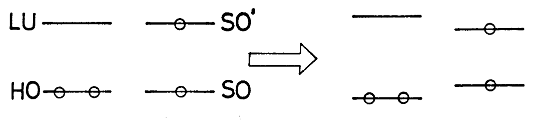
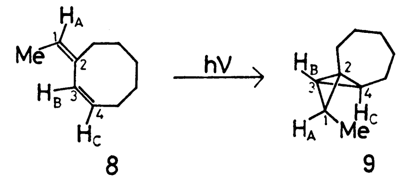


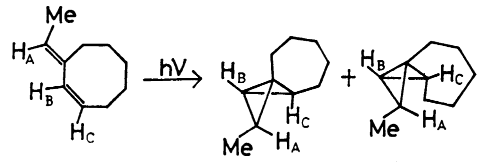
Fig. 2. The splittings of the levels between the HOMO and the SOMO and between the SO′MO and the LUMO.

Application

[1,3/2,4] Cross-bicyclization of Diene. Dauben and Ritscher have early obtained the photoproducts **9**, **11**, and **12** from ethylidenecyclooctenes **8** and **10**.[5)]



8 **9**



10 **11** 75% **12** 25%

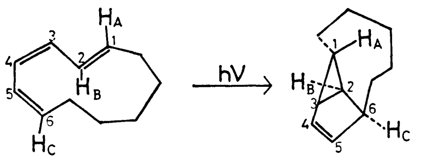
Both **9** and **11** are the results of mode B and compatible with the usual (2_a+2_a) cycloaddition. However, **12** is the result of the disfavoured mode C or D ((2_s+2_a) or (2_a+2_s)), so they have supposed an anomalous concerted reaction from a vibrationally relaxed singlet having an electronic configuration composed of an allyl anion and a methyl cation, while, from the standpoint of the cross-bicyclization, **12** is a reasonable product but **9** and **11** are not. The reason why these reactions rather favor these products can be explained by not a little energetical stabilizations in the photo-induced (2+2) cycloadditions as has been stated above. Furthermore, some steric hindrance in connection with the cyclooctene ring might play a role in separating the C_2–C_3 conjugation. Therefore, the photo-induced [1,5-/4,8] case of tetraene, which has not been reported, would also be of interest because of the possibility of the competition with (4+4) cycloaddition.

[1,3/2,6] Cross-bicyclization of Triene. In the photoinduced [1,3/2,6] case of triene, mode A or B is favored, which predicts exactly the products from **3**, **4**, and **5** provided by Courtot *et al.*[4)] The products from **1** and **2** by Padwa *et al.*,[3)] however, show the opposite mode of stereoselection in the sense of the cross-bicyclization. In order to examine these discrepancies, we have evaluated $\Pi_{13,26}$ values as functions of the resonance integrals between C_2 and C_3 (β_{23}) of **1** or **2**, and **3**, **4**, or

TABLE 3. THE VALUES OF $\Pi_{13,26}$ AS FUNCTIONS OF β_{23} IN **1** OR **2**, AND **3**, **4**, OR **5** IN THEIR FIRST EXCITED CONFIGURATIONS

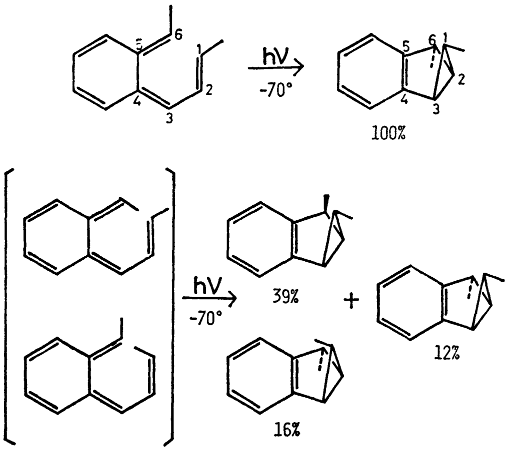
β_{23}	**1** or **2**	**3**, **4**, or **5**
β	0.0382	0.0859
0.7β	0.0042	0.0822
0.6β	−0.0219	0.0686
0.5β	−0.0599	0.0391

5 in their first excited configurations taking phenyl groups into considerations as listed in Table 3. It is evidently seen that the $\Pi_{13,26}$ of **3**, **4**, or **5** used by Courtot *et al.* is less sensitive to the weakening of β_{23}, while that of **1** or **2** by Padwa *et al.* is the smaller at $\beta_{23}=\beta$ and changes its sign at $\beta_{23}=0.6\beta$. That is, the stereoselective modes in photo-induced [1,3/2,6] cases of **1** and **2** will more easily change into that issued from the (4+2) cycloaddition than those of **3**, **4**, and **5**, according to the weakening of the conjugation between C_2 and C_3, if it takes place for some reason. We infer that these situations are reflected in the reactions of Padwa *et al.* to a certain extent, although more detailed calculation including σ electrons is requisite to provide a definite information on these species. An example as to the hexatriene free from the conjugated substituents has also been shown. Dauben and Kellogg have obtained the photoproduct *via* (4_a+2_a) cycloaddition from 1,3,5-cycloundecatriene,[6]

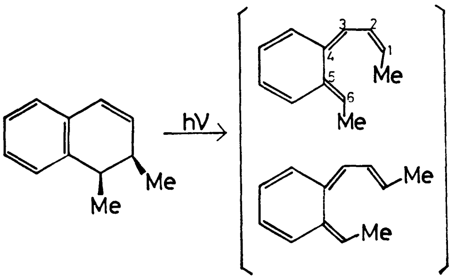


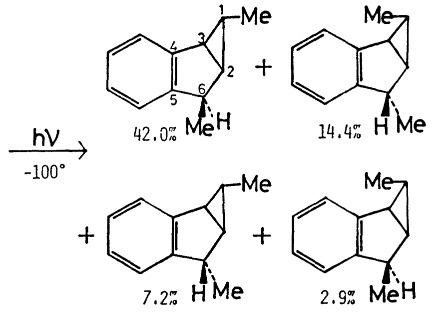
and supposed that the cyclization is initiated from the vibrationally relaxed first excited singlet state like the above case of ethylidenecyclooctene. But this stereoselective mode is easily explained by the cross-bicyclization of triene.

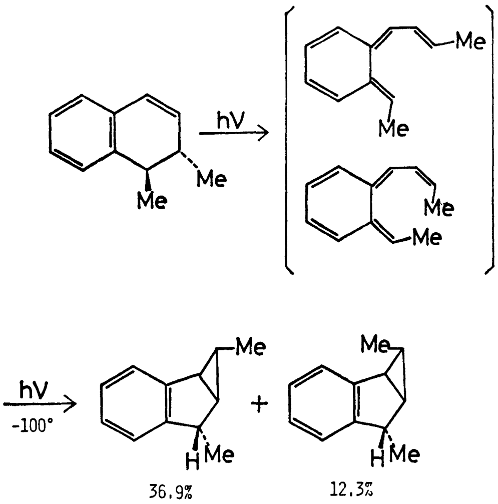
There have been other examples of the cross-bicyclizations that are found out in the photoisomerizations of benzohexatrienes reported by Seeley,[7]



and by Sieber *et al.*[8]







Since the major products of these reactions are not controlled by the stereoselective modes from the cycloaddition, these authors have ascribed these results to nonconcerted reactions. But we are now in a position to tell that these reactions are concerted as well with the aid of the concept of the cross-bicyclization.

Summary

We have defined the concept of the cross-bicyclization complementary to that of the cycloaddition and pointed out the essential difference between these two. The predicted stereoselective modes from the cross-bicyclization are in reasonable agreement on the whole with the experimental observations that have been discarded from the category of the concerted reactions because of the faith in the cycloaddition rules. However, one should pay attention to the application of the rules to photo-induced [1,3/2,4] case of diene or [1,5/4,8] case of tetraene as well as to the case of polyene with conjugated substituents. To the authors' knowledge, any stereospecific bicyclizations in a conjugated polyene treated by the concept of the cycloaddition up to the present have been probed in this study.

It is also an interesting conclusion, in diene, triene, and tetraene, that the thermal and photo-induced processes happen to yield quite identical results and that there occurs a distinct difference in the stereoselective mode according as $(s-r)+(u-t)$ is equal to $4m+2$ or $4m$. Further experimental observations are desirable in order to assess the utility of the present concept of the cross-bicyclization.

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12) The identity of the predicted stereoselective modes in thermal cases with those in photo-induced ones is quite accidental. For instance, $\Pi_{13,210}$ of pentaene is positive (0.1491) in thermal case, whereas it is negative (−0.0341) in photo-induced case. Therefore, thermal and photo-induced [1,3/2,10] cases of pentaene will show different stereoselective modes each other.

13) For example, see p. 48 of Ref. 2b and references therein.