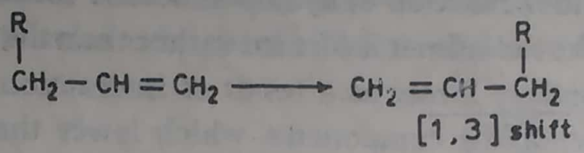
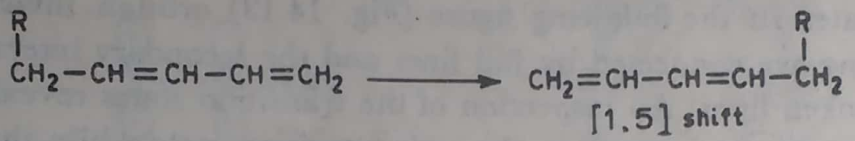
14.4. Sigmatropic Rearrangements: FMO Method

Many thermal (or photochemical) rearrangements involve the shifting of a σ bond, flanked by one or more π electron systems, to a new position [*i*,*j*] within the molecule in an uncatalyzed intramolecular process. Since it is rearrangement of a σ bond, these reactions are called *sigmatropic rearrangements* of order [*i*, *j*]. These reactions are often classified with two numbers *i* and *j*, set in brackets [*i*, *j*] and the system is numbered by starting with the atoms forming the migrating σ bond. These numbers [*i* and *j*] indicate the new positions of the σ bond whose termini are *i*—1 and *j*—1 atoms removed from the original bonded loci.



$$\overset{R}{\overset{|}{CH_2}}-CH=CH_2 \longrightarrow CH_2=CH-\overset{R}{\overset{|}{CH_2}}$$

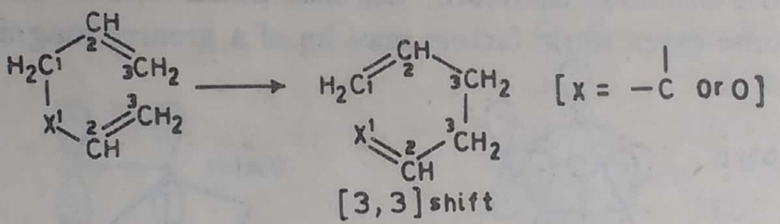
[1,3] shift



$$\overset{R}{\overset{|}{CH_2}}-CH=CH-CH=CH_2 \longrightarrow CH_2=CH-CH=CH-\overset{R}{\overset{|}{CH_2}}$$

[1,5] shift

Very often the migrating σ bond is situated in between two conjugated π bond systems as in Cope and Claisen rearrangements.

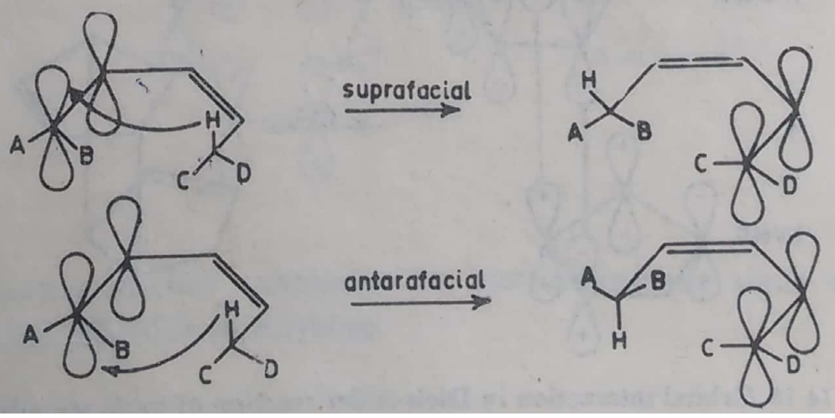


[3,3] shift

$[X = -\overset{|}{C}$ or O$]$

14.4.1 SUPRAFACIAL AND ANTARAFACIAL PROCESSES

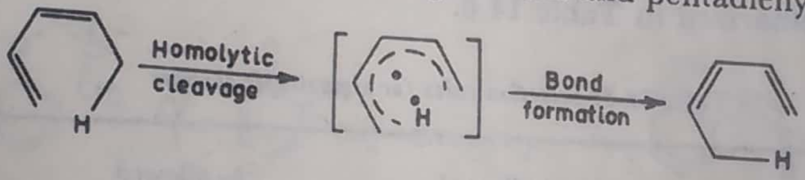
Since a sigmatropic reaction involves the migration of a σ bond across the π electron system, there are two different stereochemical courses by which the process may occur. When the migrating σ bond moves across the same face of the conjugated system, it is called a *suprafacial* process whereas in the *antarafacial* process the migrating σ bond is reformed on the opposite π electron face of the conjugated system. The following [1, 5] sigmatropic shift illustrates both these processes and their stereochemical consequences.



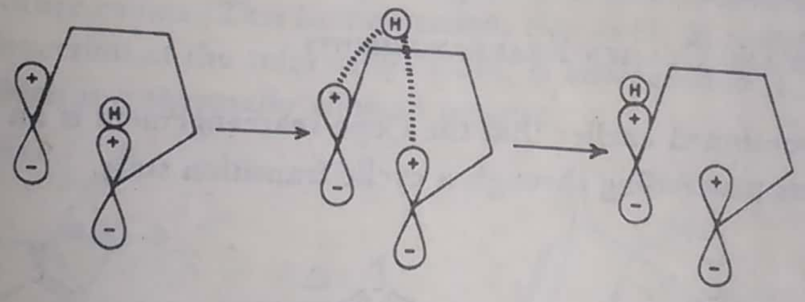
Due to steric reasons, suprafacial migrations are more common than antarafacial shifts. However, with the lengthening of the conjugated system, sometimes it is possible for a σ bond to migrate to the opposite π electron face.

14.4.2 ANALYSIS OF SIGMATROPIC REARRANGEMENTS

One of the ways to analyze sigmatropic rearrangements is to assume that the migrating bond undergoes homolytic cleavage resulting in the formation of a pair of radicals. As bonding characters are to be maintained throughout the course of the rearrangement, the most important bonding interaction will be between the HOMO's of the two species produced by this cleavage. This is to be expected as it is these orbitals that contain the unpaired electrons. We shall illustrate this analysis by examining a suprafacial [1, 5] sigmatropic shift of hydrogen in which the homolytic cleavage results in the production of a hydrogen atom and pentadienyl radical.



The ground state electronic configuration of pentadienyl radical is $\psi_1^2\psi_2^2\psi_3$. Since HOMO (ψ_3) of this radical has similar sign on the terminal lobes (plane symmetry), [1, 5] *suprafacial* migration will be a thermally allowed process.



The first excited state of the pentadienyl radical has the configuration $\psi_1^2\psi_2^2\psi_4$ (Fig 14.14) and the symmetry characteristics of HOMO (ψ_4) are thus reversed (C_2 symmetry).

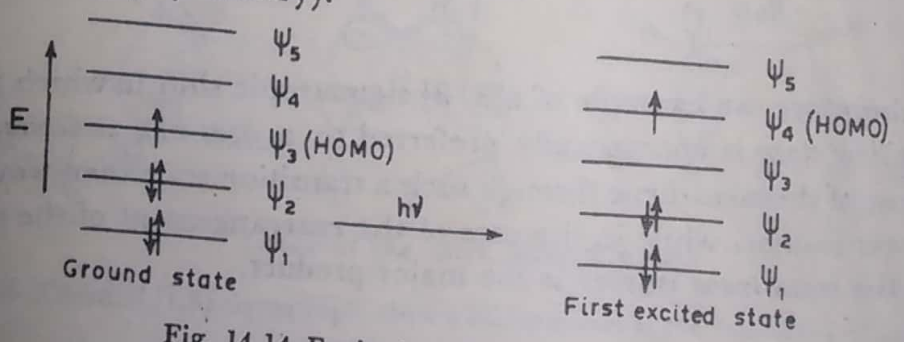
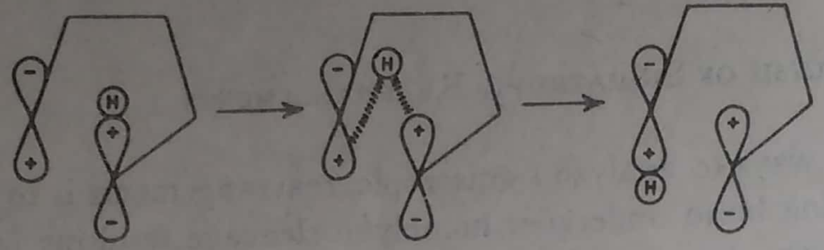


Fig. 14.14 Excitation of pentadienyl radical

[1, 5] *Suprafacial* migration is no longer possible and the shift has to be an *antarafacial* process.



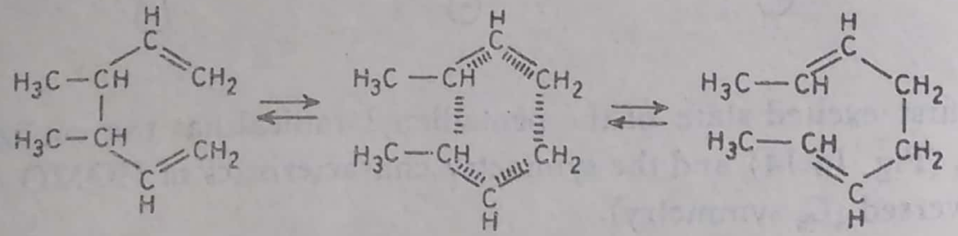
A similar analysis of such systems has led to the formulation of selection rules which state that if a sigmatropic reaction of the order $[i, j]$ (for hydrogen migration $i=1$) has $i+j=4q+2$, then thermal reaction is *suprafacial* and photochemical reaction will be *antarafacial*. However, for those cases in which $i+j=4q$ the rules are reversed and the thermal reactions are *antarafacial* while the photochemical reaction will be *suprafacial*. These rules are summarized in Table 14.6.

Table 14.6: Selection rules for sigmatropic changes

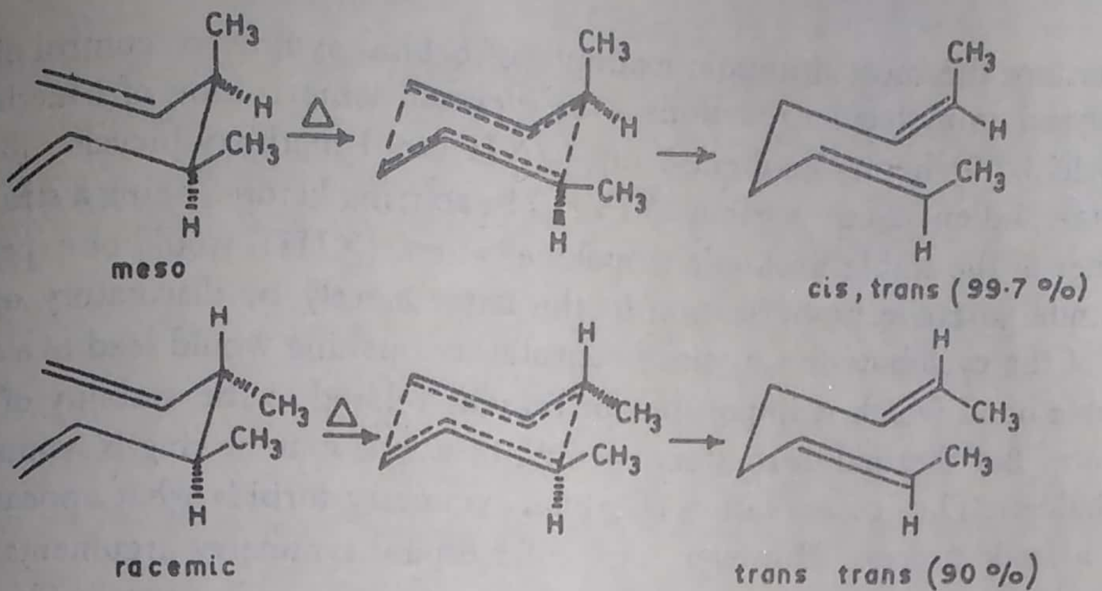
$[i+j]$	Δallowed $h\nu$ forbidden	$h\nu$ allowed Δforbidden
$4q$	*antara*	*supra*
$4q+2$	*supra*	*antara*

14.4.3 COPE AND CLAISEN REARRANGEMENTS

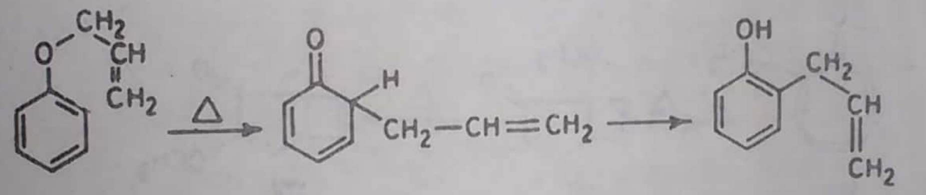
We have mentioned earlier that the Cope rearrangement is an intramolecular process proceeding through a cyclic transition state.



It is, therefore, an example of a[3, 3] sigmatropic shift in which a *chair-like transition state* is energetically preferred to a *boat-like structure*. Rearrangement of the *meso*-diene through such a transition state then would give the *cis-trans* isomer, while in the case of the rearrangement of the racemic mixture the *trans-trans* isomer is the major product.



The Claisen rearrangement is another example of a thermal reaction in which the fragments do not separate during the course of the rearrangement. Like the Cope rearrangement, the Claisen rearrangement is also a [3, 3] sigmatropic shift.



The following thermal isomerization, a [1,3] shift (Fig. 14.15), though apparently forbidden, proceeds with inversion at the carbon atom that moves. This may be regarded as a triumph of the orbital symmetry rules because the transition-state has severe non-bonded interactions and migration with retention of configuration at the migrating carbon atom would seem to be easier on all other counts. This isomerization, that is [1, 3] *suprafacial* migration with inversion at the migrating centre, is analogous to [1, 3] *antarafacial* shift which is a thermally allowed process.

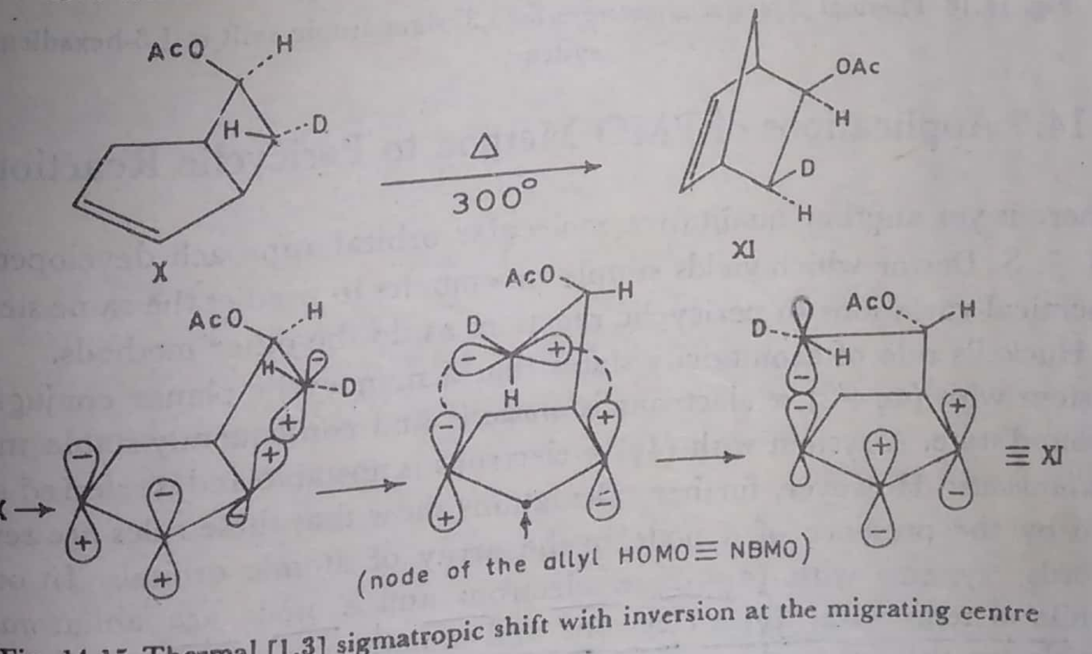


Fig. 14.15 Thermal [1,3] sigmatropic shift with inversion at the migrating centre

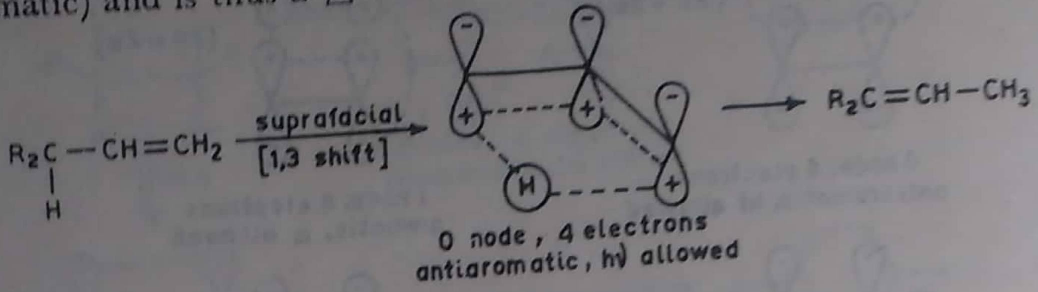
14.5 Applications of PMO Method to Pericyclic Reactions

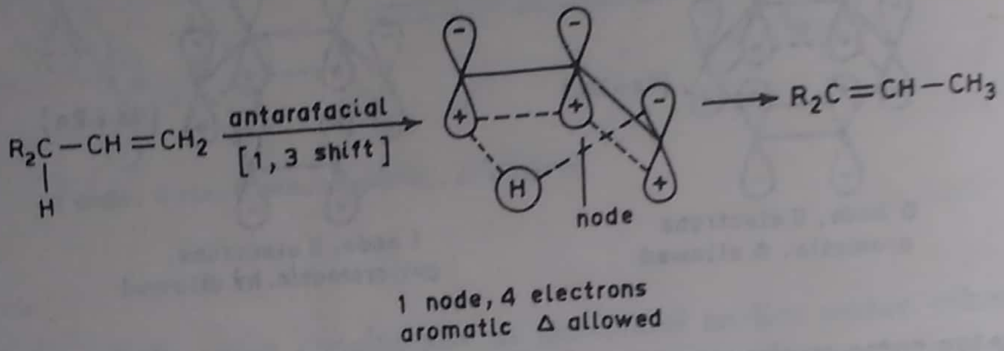
There is yet another qualitative molecular orbital approach developed by M. J. S. Dewar which yields simple mnemonics to predict the same stereochemical variations in pericyclic reactions as do the other methods.

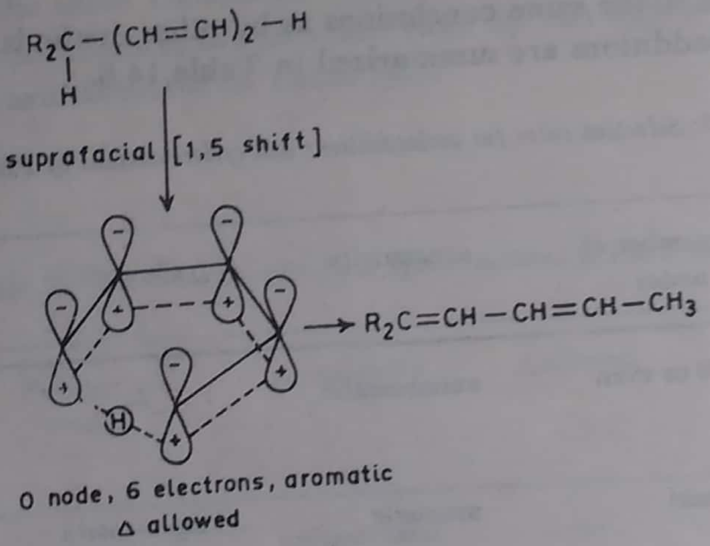
Huckel's rule of aromaticity states that a monocyclic planar conjugated system with $(4q+2)$ π electrons is *aromatic* and consequently stable in the ground state. A system with $(4q)$ π electrons is unstable and is referred to as *antiaromatic*. However, further calculations show that these rules are reversed by the presence of a node in the array of atomic orbitals. In other words, systems with $(4q+2)$ π electrons and a node are antiaromatic while systems with $(4q)$ π electrons and a node are aromatic and hence stable (in theory) in the ground state. Application of these rules to per-

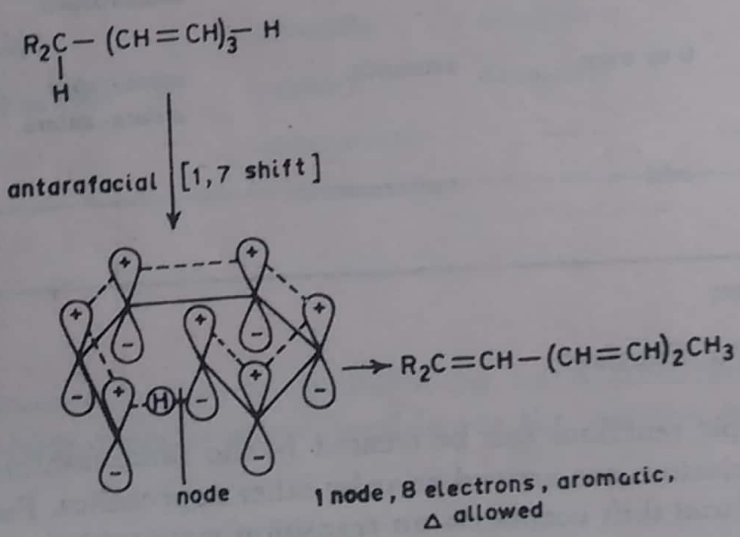
C. Sigmatropic Reactions

Sigmatropic reactions can be treated in the same fashion as above and similar conclusions are arrived at as by other approaches. For instance, the [1, 3] *suprafacial* shift occurs *via* an transition state with 0 node and 4 electrons (antiaromatic) and thus is an $h\nu$-allowed process, whereas the [1, 3] *antarafacial* shift can occur *via* a transition state with 1 node, 4 electrons (aromatic) and is thus a △allowed process.









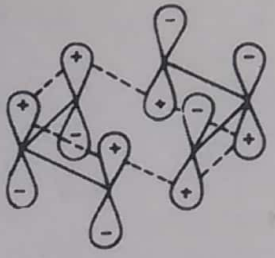
The selection rules for sigmatropic reactions of order $[1, j]$ by this method are summarized in Table 14.9

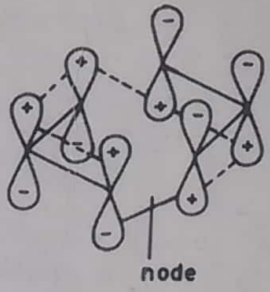
Table 14.9: Selection rules for sigmatropic change by PMO method

Number of electrons involved $[1+j]$	Number of nodes	Aromaticity	Shift mode
$4q$	0 or even	antiaromatic	*supra* ($h\nu$)
$4q$	odd	aromatic	*antara* (Δ)
$4q+2$	0 or even	aromatic	*supra* (Δ)
$4q+2$	odd	antiaromatic	*antara* ($h\nu$)

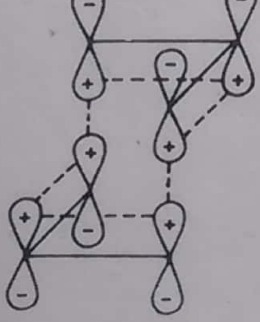
Concerted Cope and Claisen rearrangement reactions are all sigmatropic changes of order $[i, j]$ where i and j are both 3, and predictions of the stereochemical variations in these reactions following the selection rules in Table 14.8 (where $m+n=i+j$) conform to those made by other methods.

In the Cope rearrangement, for instance, there can be two stereochemical variations, *suprafacial-suprafacial*, (≡*antarafacial-antarafacial*) and *suprafacial-antarafacial* as shown in the following transition states.

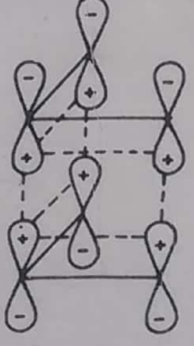




The chair shape transition-state for the *supra-supra* [3,3] sigmatropic shift is favoured over the boat shape transition state as shown below.



Chair shape transition state; isoconjugate with benzene, aromatic



Boat shape transition state; isoconjugate with bicyclohexatriene which is unstable

The two examples (Figs. 14.15 and 14.16) may also be explained with the help of the PMO method. In the first example, the transition state has 4 electrons and 1 node, and is therefore an aromatic system. The [1, 3] shift with inversion at the migrating carbon atom is thus thermally allowed. In the second example, there are six electrons and 2 nodes and therefore the transition-state is an aromatic system. The *antarafacial-antarafacial* sigmatropic change of order [3, 3] of the 1, 5-hexadiene system is thus thermally allowed.

In conclusion, it must be said that while the prediction rules under different methods have dramatic success for thermolytic reactions (symmetry-allowed reactions on heating), photolytic reactions are more complex. Photolysis is initiated by light absorption first to a high-energy excited state which may also collapse *via* other, not necessarily concerted, pathways.