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# UNIT 12 PERICYCLIC REACTIONS

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## 12.1 INTRODUCTION

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Most of the organic reactions you have studied so far proceed stepwise, exceptions being the  $S_N2$  and E2 type of reactions. A large number of reactions of conjugated polyenes, however, proceed by concerted mechanisms, i.e., the old bonds are broken and the new ones formed in a single concerted step. These reactions are called pericyclic reactions, they are characterised by a cyclic transition state involving sigma or pi-bonds. Pericyclic reactions are initiated by heat or light and are highly stereospecific. In this unit we will discuss these reactions.

### Objectives

After studying this unit you should be able to:

- define pericyclic reactions and describe their broad characteristics,
- classify pericyclic reactions into cyclo-addition reactions, electrocyclic reactions and sigmatropic rearrangements, and
- explain the mechanism of these reactions using the frontier orbital method.

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## 12.2 PERICYCLIC REACTIONS

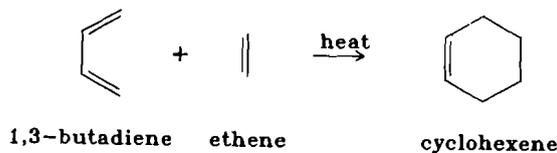
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Pericyclic reactions are concerted reactions. They are characterised by the making or breaking of bonds in a single concerted step through a cyclic transition state involving  $\pi$  or  $\sigma$  electrons. Energy of activation for pericyclic reactions is supplied by heat in a thermally induced reaction and by ultraviolet light in a photo-induced reaction. Pericyclic

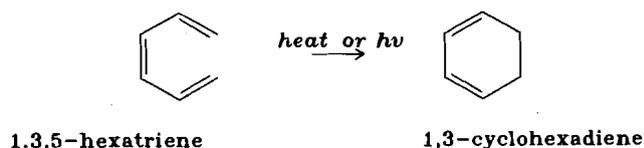
reactions are highly stereospecific, often the thermal and photochemical processes yield products with different but specific stereochemistry. Since pericyclic reactions do not involve ionic or free radical intermediates, solvents, and nucleophilic or electrophilic reagents have no effect on the course of these reactions.

There are three principal types of pericyclic reactions.

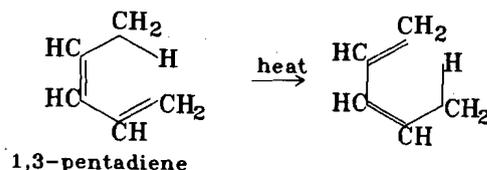
- 1) **Cycloaddition reactions:** in which two molecules combine to form a ring; two  $\pi$  bonds being converted to two sigma bonds in the process. The best known example of a cycloaddition reactions is the **Diels-Alder reaction** shown below.



- 2) **Electrocyclic reactions** are reversible reactions in which a compound with conjugated double bonds undergoes cyclisation. In this process two pi electrons are used to form a sigma bond.



- 3) **Sigmatropic rearrangements** are concerted intramolecular rearrangements in which an atom or a group of atoms shifts from one position to another.

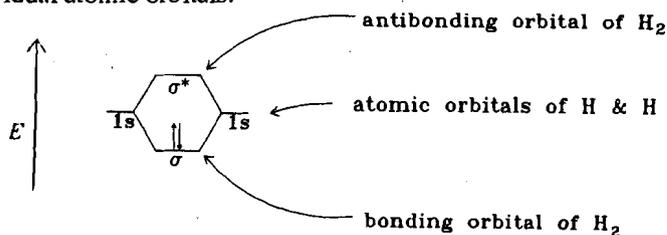


## 12.3 THEORETICAL BASIS OF PERICYCLIC REACTIONS

A theoretical understanding of pericyclic reactions had eluded chemists for many years. However, since 1960 several theories have been proposed to give a rational explanation of these reactions. Woodward and Hoffmann have proposed the principle of **conservation of orbital symmetry** as the theoretical basis for explaining these reactions. Fukui has used the **frontier orbital method**. We will use the latter here for studying pericyclic reactions. Before we discuss the mechanism of these reactions, it would be better to recapitulate salient features of the molecular orbital theory.

### 12.3.1 Molecular Orbital Theory

According to the molecular orbital theory, molecular orbitals are formed by linear combination of atomic orbitals (LCAO). For example when a molecule of hydrogen is formed from two atoms of hydrogen, the atomic orbitals are supposed to combine to give a bonding orbital which is lower in energy than the separate atomic orbitals. In addition, an antibonding orbital is also supposed to exist, which as its name implies does not contribute to the bond formation between the atoms.  $\sigma^*$  is higher in energy than  $\sigma$  orbital or the individual atomic orbitals.



R.B. Woodward of Harvard University got Nobel prize in 1965 for his work on the synthesis of complex organic compounds including chlorophyll.

R. Hoffman of Cornell University and K Fukui of Kyoto University shared the 1981 Nobel prize for their understanding of pericyclic reactions

The bonding molecular orbital is supposed to arise from reinforcement of in-phase s-atomic orbitals, whereas the antibonding molecular orbital arises from interference between the out-of-phase s-atomic orbitals. This is shown diagrammatically in Fig. 12.1.

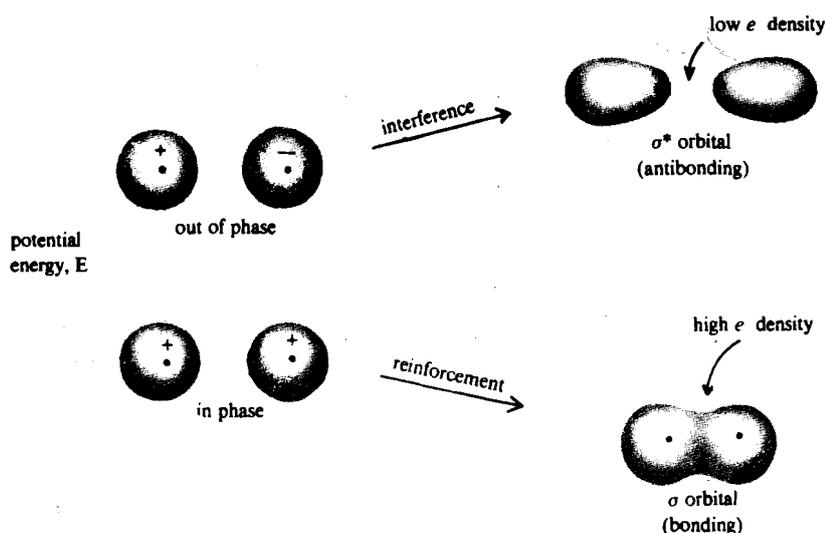


Fig. 12.1 : Bonding and antibonding orbitals of hydrogen molecular

As you know, in saturated hydrocarbons like methane or ethane carbon atoms are  $sp^3$  hybridised and there are sigma bonds between carbon atoms as well as between carbon and hydrogen atoms formed by the overlap of  $sp^3$ - $sp^3$  or  $sp^3$ -s atomic orbitals. Each of these sigma bonds will have a bonding orbital and the corresponding antibonding orbital.

However, hybridisation of carbon atoms becomes different in an alkene like ethene. Here the carbon atoms are supposed to be  $sp^2$  hybridised. The double bond between the two carbon atoms is supposed to comprise of a  $\sigma$  and a  $\pi$  bond. The carbon-carbon  $\sigma$  bond is formed by the overlap of two  $sp^2$  orbitals, resulting in a bonding orbital and an antibonding orbital. The  $\pi$  bond is formed by the sideways overlap of p-orbitals resulting in two  $\pi$ -molecular orbitals. One of these is the bonding  $\pi$  orbital formed by the overlap of in-phase p-orbitals, the other, antibonding  $\pi^*$  orbital, arises from the interference between two p-orbitals of opposite phases. These orbitals are also designated as  $\pi_1$  and  $\pi_2^*$  respectively.

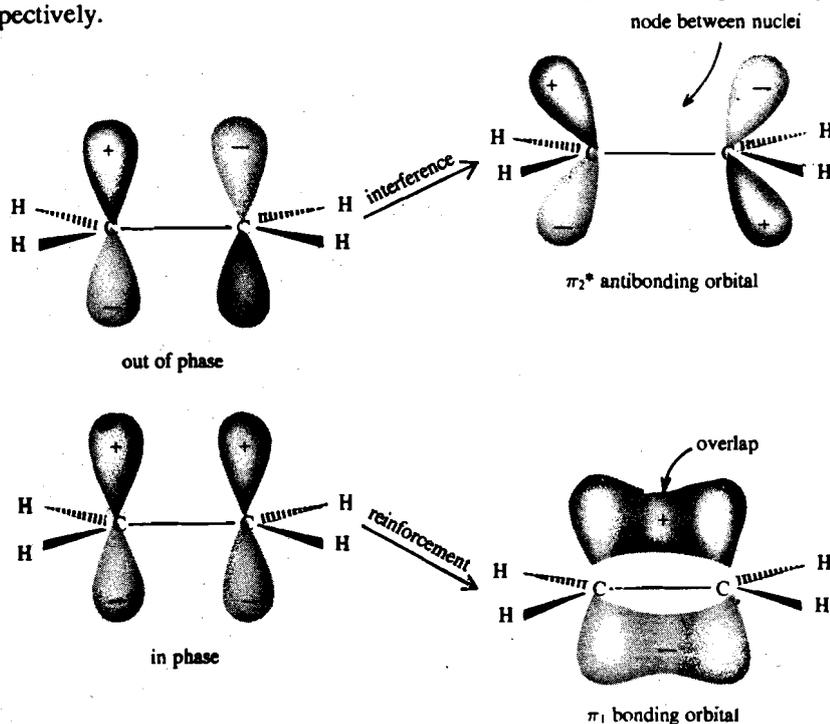
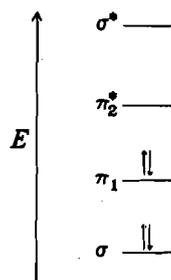


Fig. 12.2 :  $\pi_1$  and  $\pi_2^*$  orbitals of ethene

Fig. 12.2 shows the representation of  $\pi_1$  and  $\pi_2^*$  orbitals of ethene. Note that  $\pi_2^*$ , which is formed by interference between the out-of-phase  $p$ -orbitals has a node or a region of minimum electron density between the nuclei.  $\pi_2^*$  Orbital is of higher energy than  $\pi_1$ . The following diagram compares the energies of  $\sigma$ ,  $\sigma^*$ ,  $\pi_1$  and  $\pi_2^*$  orbitals. As expected the bonding electrons are in the two orbitals with lowest energies,  $\sigma$  and  $\pi_1$  in the ground state of ethene.



Ground state of C=C in ethene

As you can see  $\sigma^*$  orbital is of higher energy than  $\pi_2^*$ . The amount of energy required to promote an electron from  $\sigma$  to  $\sigma^*$  orbital is greater than that required to promote a  $\pi$  electron to  $\pi^*$  orbital. Because of the large amount of energy required to promote a sigma electron, electron transitions of this type are rare and therefore unimportant to the organic chemist. However,  $\pi \rightarrow \pi^*$  transitions, which require less energy, are important. In the reactions discussed in this unit, you will come across examples of such transitions.

### 12.3.2 Molecular Orbitals of Conjugated Polyenes

After this brief description of bonding and antibonding molecular orbitals, let us study some features of the molecular orbitals of conjugated polyenes. A conjugated polyene contains either  $4n$  or  $(4n+2)$  pi electrons in its conjugated system.  $n$  is an integer and the simplest  $4n$  system is represented by 1,3-butadiene where  $n=1$ . Any conjugated diene contains  $n$  molecular orbitals similar to those of 1,3-butadiene. We can, therefore, use 1,3-butadiene as a model for all conjugated dienes.

In 1,3-butadiene, four  $p$ -orbitals are used in the formation of the  $\pi$  molecular orbitals, thus four  $\pi$  molecular orbitals result. Of these  $\pi_1$  and  $\pi_2$  are bonding orbitals and  $\pi_3^*$  and  $\pi_4^*$  are antibonding orbitals. Fig. 12.3 depicts these orbitals in terms of increasing energy. As you can see higher energy orbitals are associated with greater number of nodes.

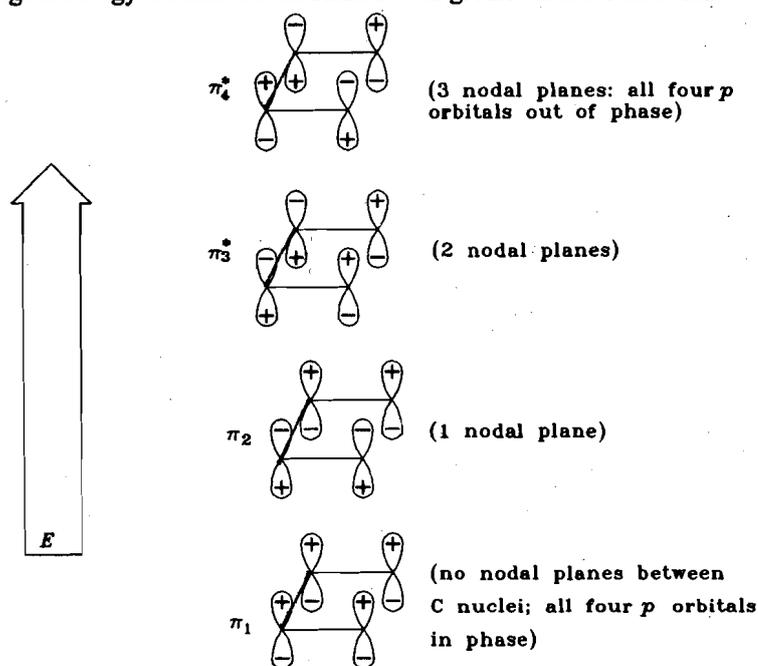
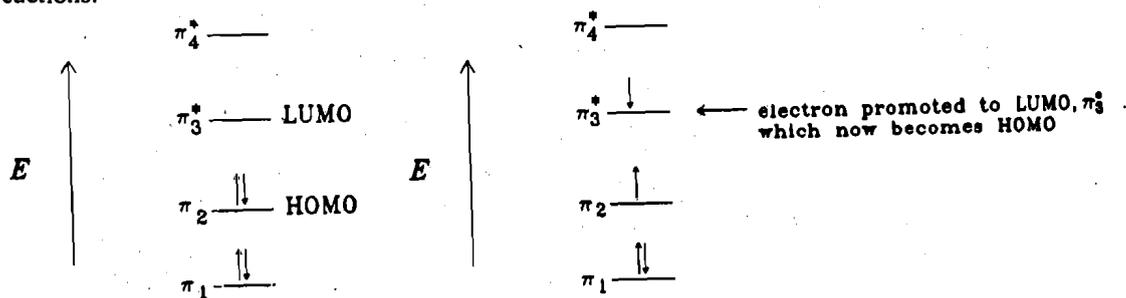


Figure 12.3 : The bonding and antibonding  $\pi$  molecular orbitals of 1,3-butadiene.

In the ground state of butadiene, the four  $\pi$  electrons are in the two orbitals of lowest energy  $\pi_1$  and  $\pi_2$ . In this case

$\pi_2$  is the Highest Occupied Molecular Orbital, HOMO and  $\pi_3^*$  is the Lowest Unoccupied Molecular Orbital, LUMO. HOMO and LUMO are referred to as frontier orbitals. These orbitals are used in the frontier orbital method of analysing pericyclic reactions.



When 1,3-butadiene absorbs a photon of the proper wavelength (in the uv range), an electron is promoted from  $\pi_2$  to  $\pi_3^*$  which then becomes the new HOMO.

Aside from ethene ( $n=0$ ), the simplest ( $4n+2$ ) system is represented by a conjugated triene ( $n=1$ ), such as 1,3,5-hexatriene. Because a triene contains a pi system formed from six  $p$ -orbitals, a total of six  $\pi$  molecular orbitals results. These are shown in fig. 12.4 with the  $\pi$  orbital diagram of the ground state. Of these  $\pi_1, \pi_2$  and  $\pi_3$  are bonding molecular orbitals and Fig. and  $\pi_4^*, \pi_5^*$  and  $\pi_6^*$  are antibonding.

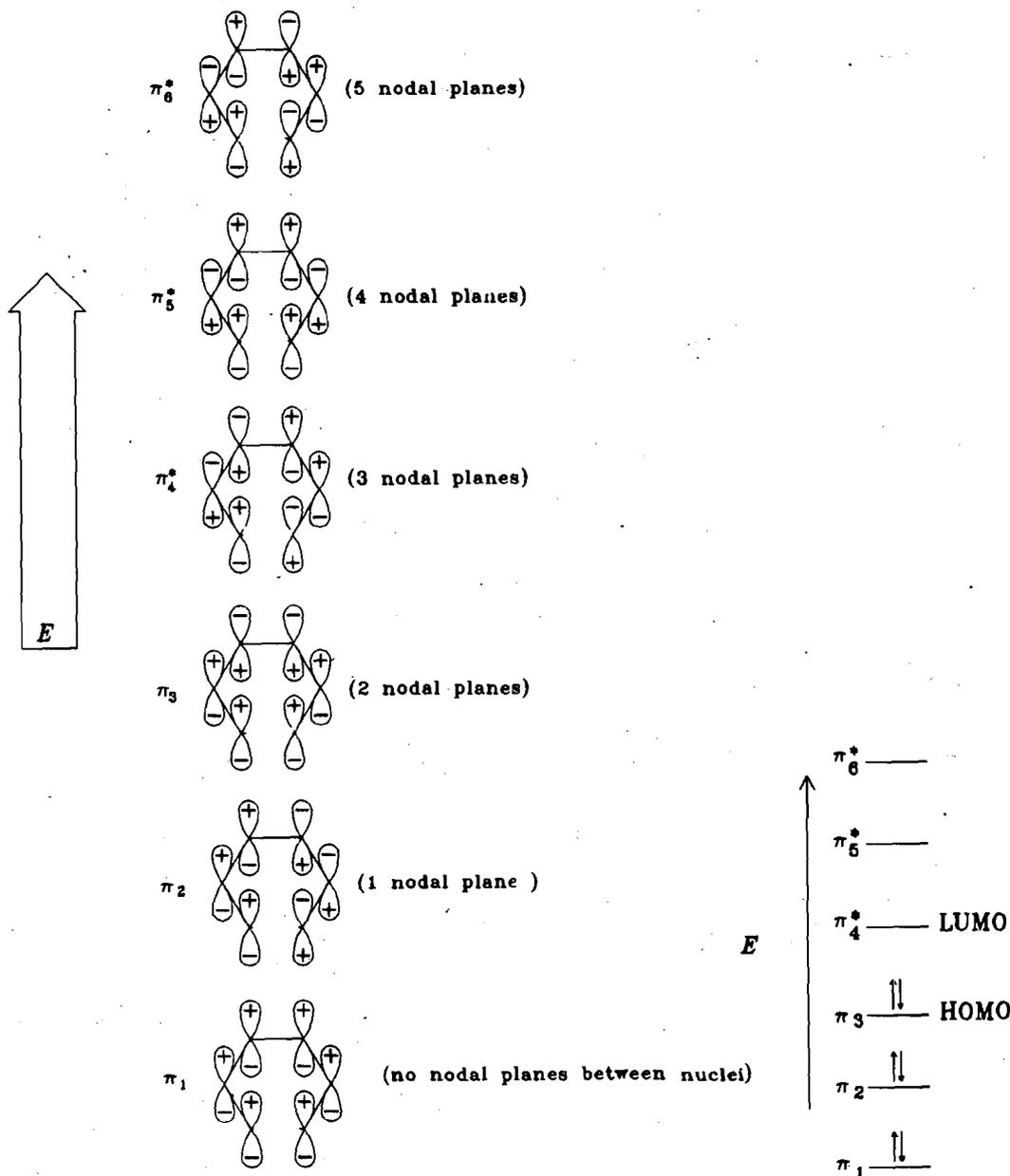


Fig. 12.4 : The bonding and antibonding  $\pi$  molecular orbitals of 1,3,5-hexatriene

We can now discuss the mechanism of pericyclic reactions, but before that try the following SAQ.

### SAQ 1

Draw the orbital diagram for the lowest energy excited state of 1,3,5-hexatriene.

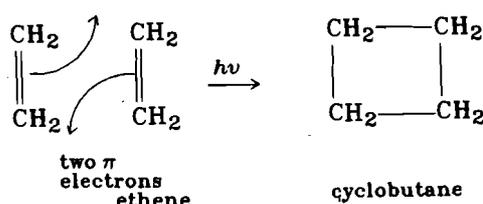
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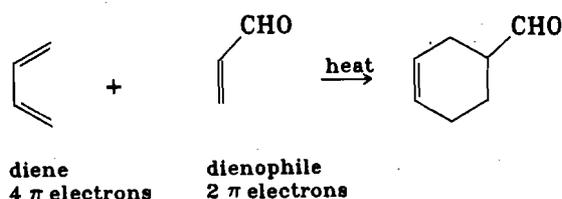
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## 12.4 CYCLOADDITION REACTIONS

As said earlier, in a cycloaddition reaction two unsaturated molecules undergo an addition reaction to yield a cyclic product. For example, cyclisation of ethene to cyclobutane on irradiation with light.



The cycloaddition of ethene or any two simple alkenes is called a **[2+2] cycloaddition** as two pi electrons + two pi electrons are involved. The Diels-Alder reaction shown below is an example of a **[4+2] cycloaddition**. The diene here contains four  $\pi$  electrons and the dienophile two. The carbonyl pi electrons which are not used in bond formation in the reaction are not included in the number classification of this cycloaddition.

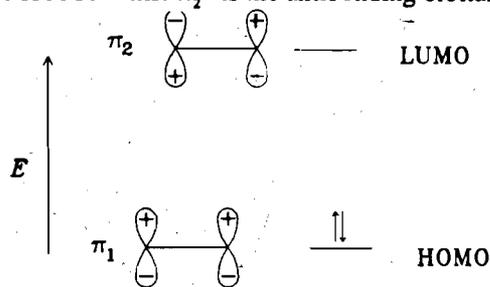


Cycloaddition reactions are concerted, stereospecific reactions. Any particular reaction is either thermal or photo-induced but not both. Let us try to analyse these reactions in terms of frontier orbital theory.

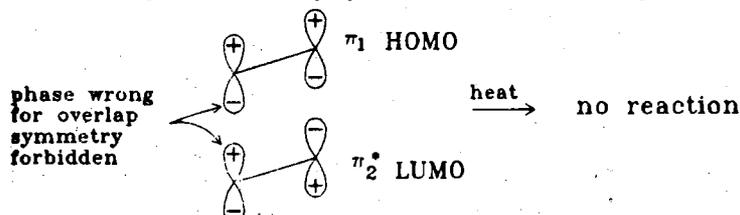
### 12.4.1 [2+2] Cycloadditions

[2+2] Cycloadditions proceed readily in the presence of light of proper wavelength but not when the mixture is heated. According to frontier orbital theory, this can be easily explained by assuming that the electrons "flow" from the HOMO of one molecule to LUMO of the other. For this the HOMO of one molecule must overlap with the LUMO of the second molecule. It cannot overlap with HOMO of the second molecule because this orbital is already occupied. Simultaneously with the merging of the  $\pi$  orbitals, these orbitals undergo rehybridisation to yield new  $sp^3$  sigma bonds.

Let us consider [2+2] cycloaddition of ethene to give cyclobutane. As discussed above ethene has two  $\pi$  molecular orbitals  $\pi_1$  and  $\pi_2^*$ . In the ground state  $\pi_1$  is the bonding orbital and the HOMO while  $\pi_2^*$  is the antibonding orbital and LUMO.

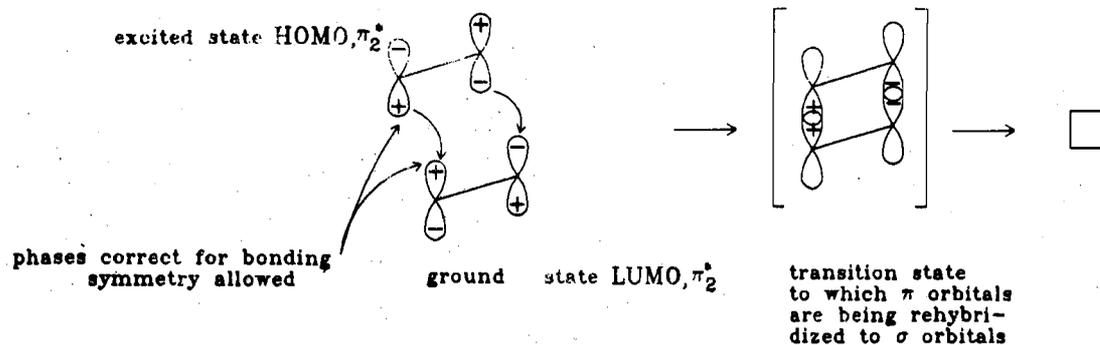


When ethene is heated,  $\pi$  electrons are not promoted but remain in the ground state. If you examine the phases of the ground state HOMO of ethene molecule and the LUMO of another ethene molecule, you can see why cyclisation does not occur by thermal induction.



For bonding to occur, the phases of the overlapping orbitals HOMO of one molecule and LUMO of the other molecule must be the same. This is not the case in the ground state HOMO and LUMO of two ethene or any [2+2] system. Because the phases of the orbitals are incorrect for bonding, a thermally induced [2+2] cycloaddition is said to be a **symmetry-forbidden reaction**.

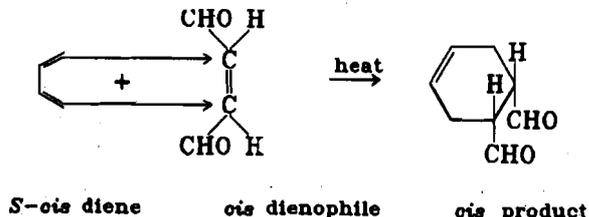
When ethene is irradiated with ultraviolet light, a  $\pi$  electron is promoted from  $\pi_1$  to  $\pi_2^*$  orbital in some, but not all molecules. This results in a mixture of the ground state and excited state ethene molecules. Now, if you examine the HOMO of an excited molecule and the LUMO of a ground state molecule you can see that the phases are correct for bonding. Such a reaction has a relatively low energy of activation and is said to be **symmetry-allowed**.



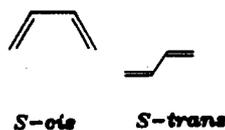
In general, thermally induced [2+2] cycloadditions are symmetry forbidden and photo-induced [2+2] cycloadditions are symmetry allowed. A symmetry forbidden reaction may take place under different conditions, but then the energy of activation is very high. This will not be a concerted reaction and may proceed stepwise through radical intermediate.

## 12.4.2 [4+2] Cycloadditions

The thermal [4+2] cycloaddition has been known for almost half a century as the Diels-Alder reaction. It has proved synthetically useful since it unites two carbon skeletons smoothly and stereospecifically. In Diels-Alder reaction, a six membered ring is formed by 1,4-addition of an olefinic unit to a conjugated diene. Diels Alder is a *cis* or *syn* addition, the diene must have *S-cis* conformation.

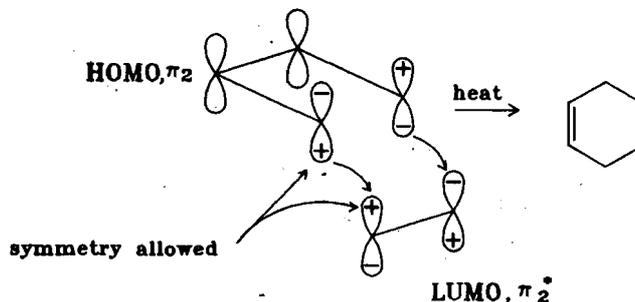


Here  $S$ -cis refers to the geometry around the single bond which determines the conformation. The two conformations of 1,3-butadiene are

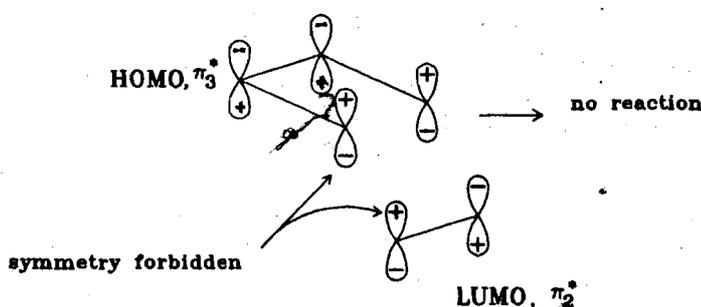


The dienes are activated by electron-donor substituents. For example, 1,3-butadiene is less reactive than its mono, di or trimethyl derivatives. However, in the case of tetramethylbutadienes, steric hindrance decreases activity. The dienophile is activated by electron-withdrawing substituents like  $-\text{COOH}$ ,  $-\text{COOR}$ ,  $-\text{CHO}$ ,  $-\text{COR}$ ,  $-\text{CN}$ ,  $-\text{NO}_2$ , etc. Some reactive dienes do not need activation as is illustrated by the dimerisation of cyclopentadiene.

You may like to know why experimental conditions for [2+2] cycloaddition are different from those for [4+2] cycloaddition, the former being a photo-induced process while the latter is induced thermally. To see why this is so, we would have to examine the HOMO-LUMO interactions of the  $p$ -orbitals that will form new sigma bonds in [4+2] cycloaddition. Let us first compare the HOMO-LUMO interactions for the ground state for a thermally induced reaction. We will use the simplest [4+2] system, the cycloaddition of 1,3-butadiene and ethene. In the thermally induced cycloaddition between these two reactants, we can visualise the pi electrons flowing from HOMO,  $\pi_2$  of the diene (Fig. 12.3) to the LUMO  $\pi_2^*$  of the dienophile. You can see that orbitals that lead to cycloaddition are in phase. The reaction therefore is symmetry allowed.



Now let us see how things are if we try to photo induce the reaction. When the diene is excited by light, its HOMO becomes the  $\pi_3^*$  orbital (Fig 12.3). This molecular orbital cannot overlap with the LUMO of the dienophile because the two are not in-phase. The photo induced [4+2] cyclisation, therefore, is symmetry-forbidden.



SAQ 2

- Explain why in [4+2] cycloaddition, diene is activated by electron donor substituents and dienophile by electron-withdrawing substituents.
- Predict whether a photo induced [4+2] cycloaddition would be possible if the dienophile instead of the diene were the excited reactant.

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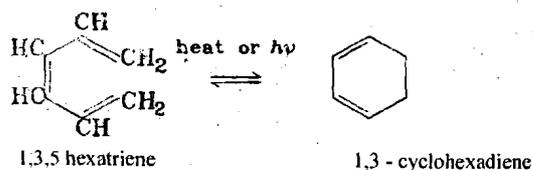
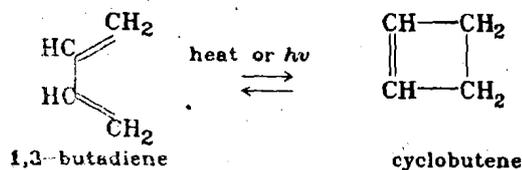
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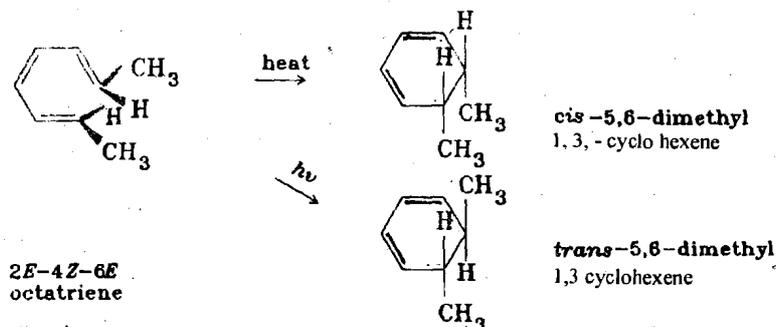
## 12.5 ELECTROCYCLIC REACTIONS

An electrocyclic reaction is the concerted inter-conversion of a conjugated polyene into a cycloalkene. Here we will discuss cyclisation. The reverse reaction, ring opening proceeds by the same mechanism, but in the reverse direction.

Electrocyclic reactions are induced either thermally or photochemically, for example.



However, the stereochemistry of the product depends on whether the reaction is thermally or photo-induced as the following example would show:

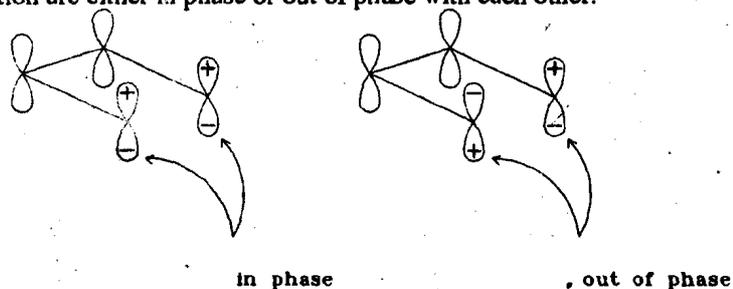


Let us study electrocyclic reactions of some systems.

### 12.5.1 Cyclisation of $4n$ systems

1,3-Butadiene is the simplest polyene with  $4n$  electrons. Interconversion of 1,3-butadiene and cyclobutene can be taken to illustrate the mechanism of such reactions. Since cyclobutenes are strained ring systems, the reverse reaction, ring opening is usually favoured. However, as said earlier, the mechanism for ring opening is just the reverse for ring closure.

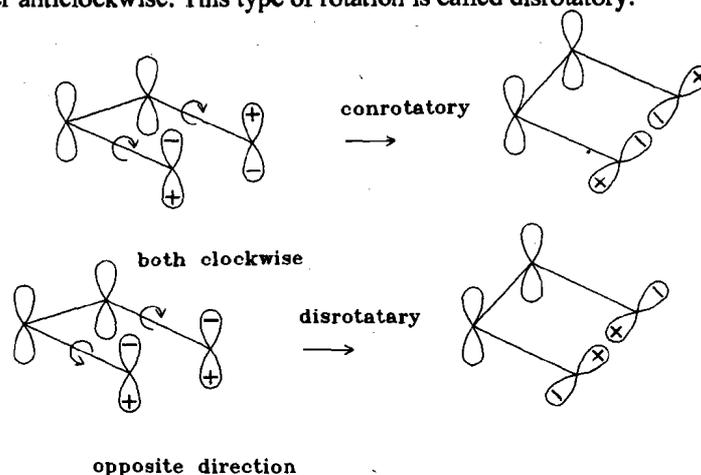
1,3-Butadiene, like any conjugated polyene, yields cyclobutene by the end-to-end overlap of its  $p$  orbitals and simultaneous rehybridisation of the carbon atoms involved in bond formation. Now the two lobes of each  $p$ -orbital that will form the new sigma bond in cyclisation are either in phase or out of phase with each other.



In order that a new sigma bond can be formed, the existing C—C sigma bonds must rotate so that the  $p$ -orbitals can undergo end-to-end overlap. The energy for the  $\pi$ -bond breakage and bond rotation is supplied by heat or ultraviolet radiation used to induce the reaction. The pair of overlapping lobes of  $p$  orbitals must be in phase after rotation. There are two

ways in which the existing C—C sigma bonds can rotate in order to bring the *p*-orbitals in phase for overlap.

- The two C—C sigma bonds can rotate in the same direction, either both clockwise or both counter-clockwise. This type of rotation is called conrotatory.
- The two C—C sigma bonds can rotate in the opposite directions, one clockwise and the other anticlockwise. This type of rotation is called disrotatory.



In the first of above examples, you can see that the phases of *p*-orbitals in the starting dienes are different. You may also note that when the *p*-orbitals are out of phase before rotation, conrotatory motion can bring them into phase for symmetry allowed overlap; and when the *p*-orbitals are in phase before rotation (second example) disrotatory motion is required. In other words, direction of rotation for symmetry allowed overlap depends on the phases of *p*-orbitals just prior to cyclisation. The phases of *p*-orbitals of the diene just prior to the reaction, in turn, depend on whether the molecule is in the ground state or in the excited state. Let us consider both these cases.

When 1,3-butadiene is heated, reaction takes place from the ground state. The electrons that are used for sigma bond formation are in the HOMO,  $\pi_2$ . If you refer to Fig. 12.3, you can see that the pertinent *p*-orbitals in this HOMO are out of phase with each other. So for the sigma bond to form, rotation must be conrotatory. Disrotatory motion would not bring lobes of *p*-orbitals in phase for overlap.

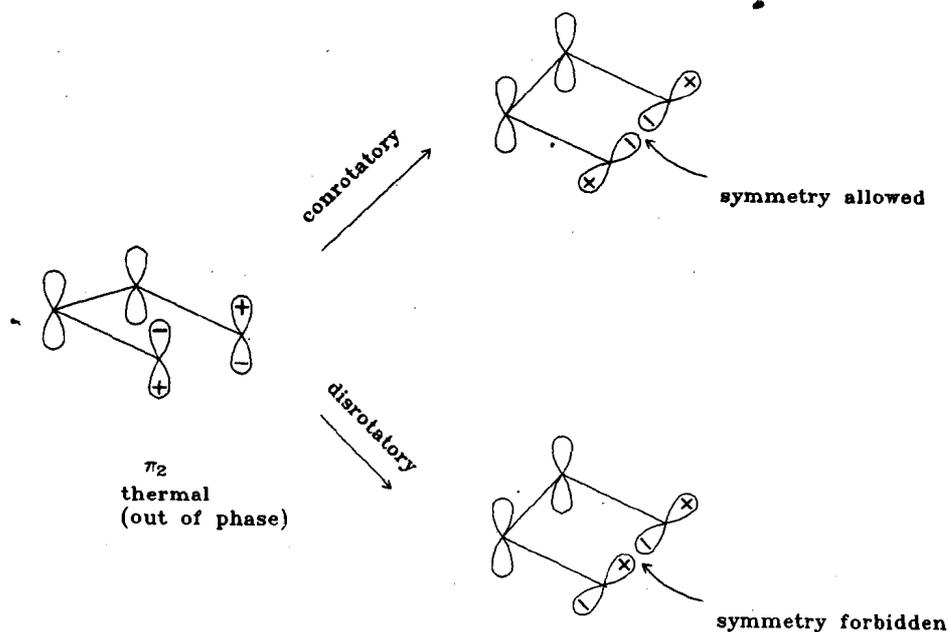
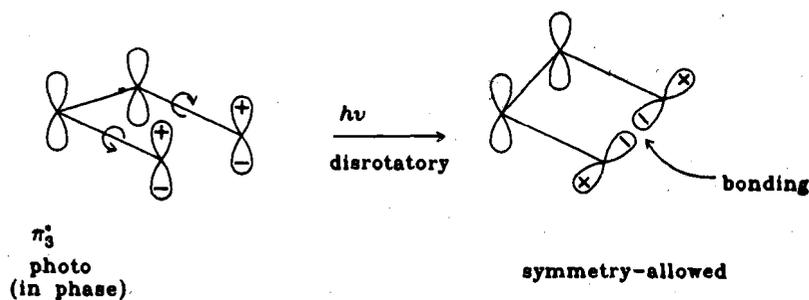


Photo induced cyclisation takes place in the excited state. Here HOMO is  $\pi_3^*$ , in which phases of *p*-orbitals are in phase. Therefore, the rotation of C—C sigma bonds has to be disrotatory for a symmetry allowed reaction to take place.

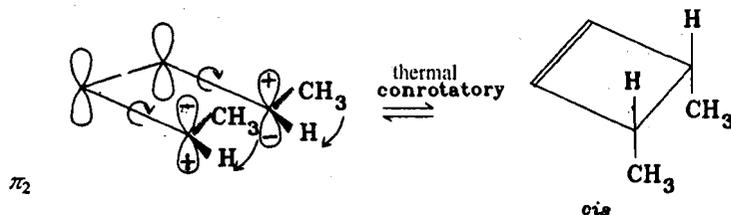


### Stereochemistry of a $4n$ cyclisation

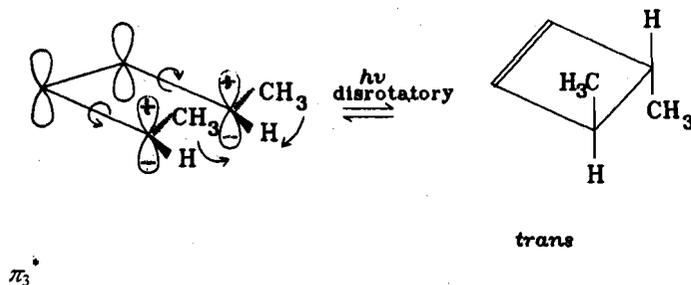
We have said above that the stereochemistry of the product in electrocyclic cyclisation depends on whether the reaction is thermally or photo induced.

Let us see why. In order to study the stereochemistry of electrocyclic cyclisation of  $4n$  systems we will take a substituted 1,3-butadiene. If (2*E*,4*Z*)-hexadiene is cyclised *cis*-dimethyl cyclobutene results from heating and the *trans* isomer from a photochemical reaction.

As you can deduce from the discussion above, in thermal cyclisation conrotatory motion is required for bond formation. So both methyl groups rotate in the same direction. As a result they are on the same side of the ring or *cis* in the product.

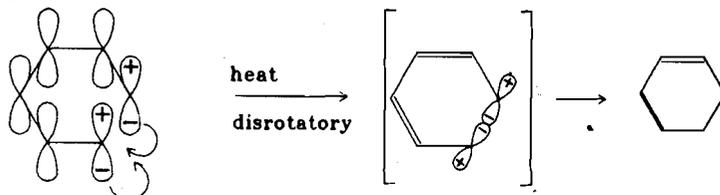


In photochemical cyclisation, on the other hand, disrotatory motion would be required for bond formation. The two methyl groups rotate in opposite directions, one rotates up, the other down; with the result that they are *trans* in the product.

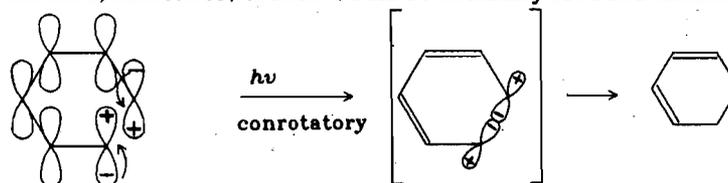


### 12.5.2 Cyclisation of $(4n+2)$ Systems

A typical example can be cyclisation of 1,3,5-hexatriene to 1,3-cyclohexadiene. As you can see in Fig.12.4, the HOMO in the ground state is  $\pi_3$ . In this molecular orbital, the *p*-orbitals that form sigma bond are in phase so thermal cyclisation would proceed by disrotatory motion.



When 1,3,5-hexatriene is irradiated by ultraviolet light, one electron is promoted to  $\pi^*$ , which now becomes the HOMO. In this molecular orbital the  $p$ -orbitals are out of phase. Therefore, conrotatory motion would be necessary for bond formation.



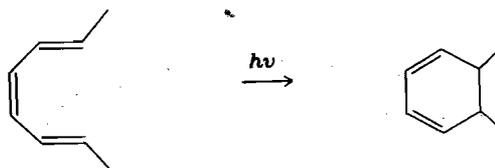
So you can see that the symmetry allowed reactions of  $(4n+2)$  systems are just opposite to those of  $4n$  systems. Table 12.1 gives a summary of types of motions expected in thermal and photo induced reactions in these two systems.

Table 12.1: Types of electrocyclic reactions

Number of Pi Electrons	Reaction	Motion
$4n$	thermal	conrotatory
$4n$	photochemical	disrotatory
$(4n + 2)$	thermal	disrotatory
$(4n + 2)$	photochemical	conrotatory

### SAQ 3

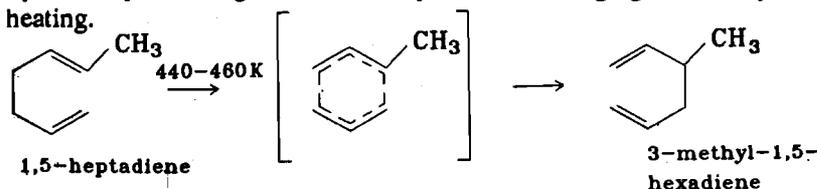
- (a) Would you expect  $(2E,4E)$ -hexadiene to yield *cis* or *trans* 3,4-dimethyl butene in a photo induced reactions.
- (b) Predict the stereochemistry of the product in the following reaction.



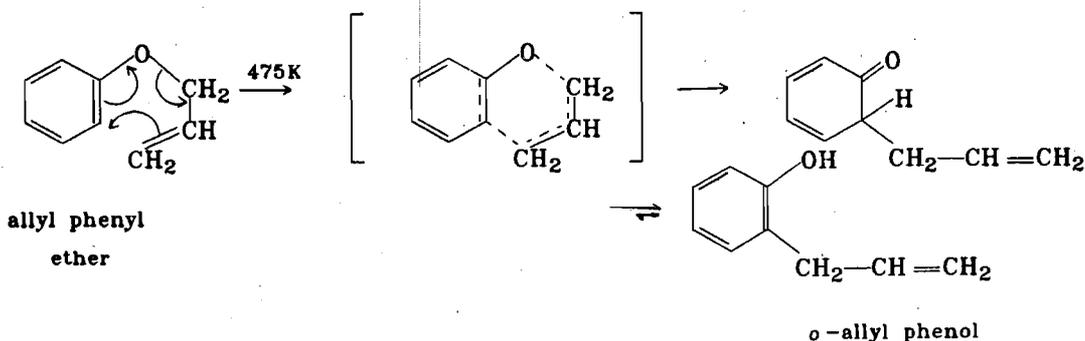
## 12.6 SIGMATROPIC REARRANGEMENTS

A sigmatropic rearrangement is a concerted intramolecular shift of an atom or a group of atoms. Cope and Claisen rearrangements are the two well known examples of sigmatropic rearrangements.

A typical example of Cope rearrangement is 1,5-heptadiene rearranging to 3-methyl-1,5-hexadiene on heating.



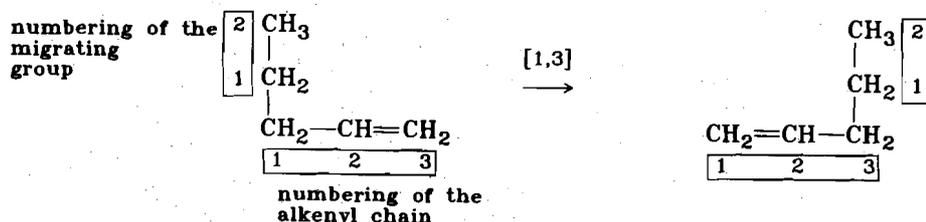
In Claisen rearrangement an allyl phenyl ether rearranges to *o*-allylphenol on heating.



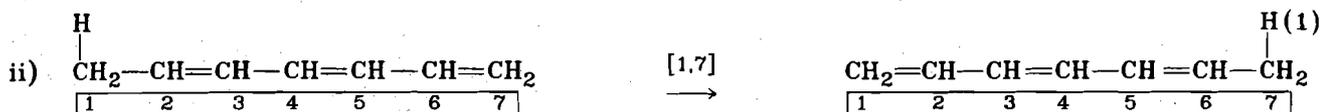
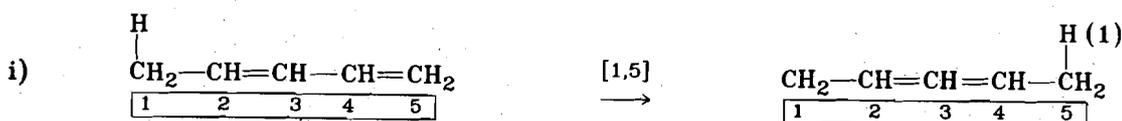
In Claisen rearrangement, the allyl group migrates to the *ortho* position. However, if both *ortho* positions are filled, *para* migration takes place, but never *meta*. There is no reaction when both *ortho* and the *para* positions are filled. Further, experiments with compounds labelled with  $^{14}\text{C}$  have shown that *ortho* migration is always accompanied by an allylic shift where as in *para* migration there is never an allylic shift.

### 12.6.1 Classification of Sigmatropic Rearrangements

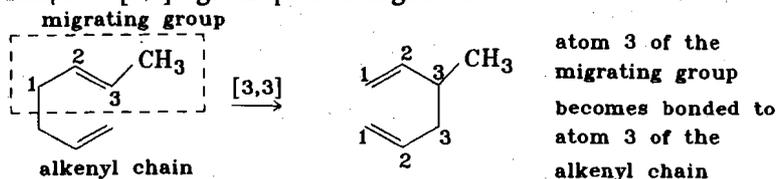
The method of classification of sigmatropic rearrangements differs from cycloadditions and electrocyclic reactions. Whereas in the latter two types of reactions, classification is based on the number of electrons involved in the cyclic transition state, the sigmatropic rearrangements are classified by a double numbering system that refers to the relative position of the atoms involved in the migration. This is best explained by taking a few examples.



As you can see both the alkenyl chain and the migrating group are numbered starting at the position of their original attachment. This may not be a carbon atom. Also these numbers are not related to nomenclature numbers. In the above example atom 1 of the migrating group ends up on atom 3 of the alkenyl chain, so this rearrangement is classified as [1,3] sigmatropic rearrangement. Examples of [1,5] and [1,7] sigmatropic rearrangements are given below. In both cases the migrating group is H.



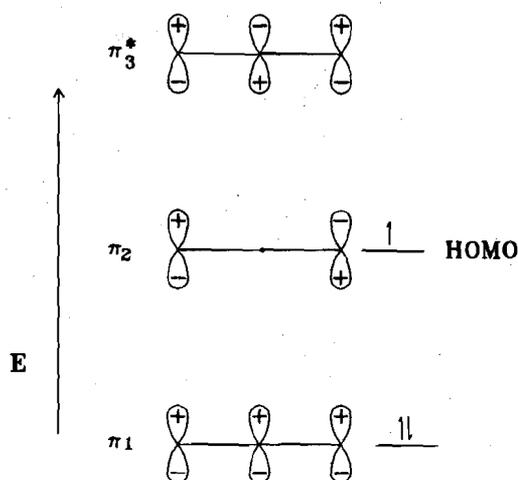
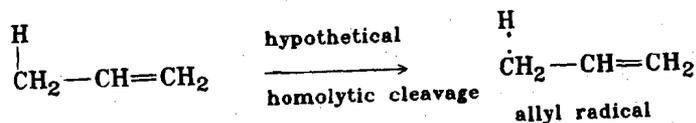
[1,3] sigmatropic rearrangements are relatively rare, while [1,5] sigmatropic rearrangements are fairly common. First atom of the migrating group may not always become bonded to the alkenyl chain. In the example of Cope rearrangement given above, atom 3 of the migrating group becomes bonded to atom 3 of the alkenyl chain. So this is an example of [3,3] sigmatropic rearrangement.



### 12.6.2 Mechanism of Sigmatropic Rearrangements

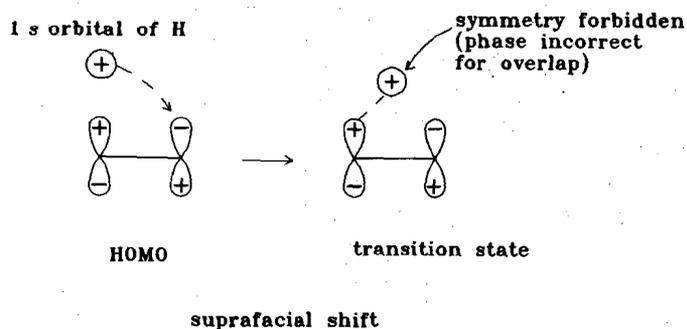
We can use frontier orbital method for analysing the mechanism of sigmatropic rearrangements also. For the purpose of analysing the orbitals, it is assumed that the sigma bond connecting the migrating group to its original position undergoes homolytic cleavage to yield two radicals. You must bear in mind that this is not how the reaction takes place. The reaction is concerted. The assumption is made to allow an easy analysis of the molecular orbitals.

Let us first take the case of a [1,3] sigmatropic rearrangement. The products of the hypothetical cleavage are a hydrogen atom and an allyl radical which contains three pi electrons and so three  $\pi$  molecular orbitals.

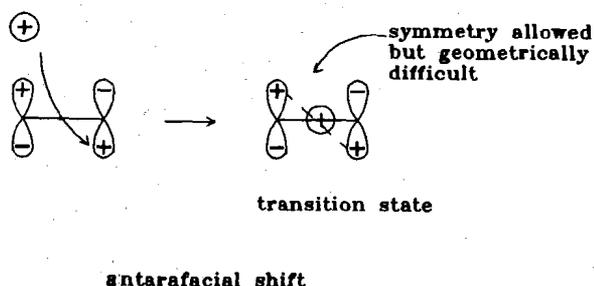


There are two modes in which H can shift. In one case the migrating group remains on the same side of the alkenyl chain, such a migrating is called **suprafacial**. In the other the migrating group migrates to the opposite face of the orbital system, this is known as **antarafacial**.

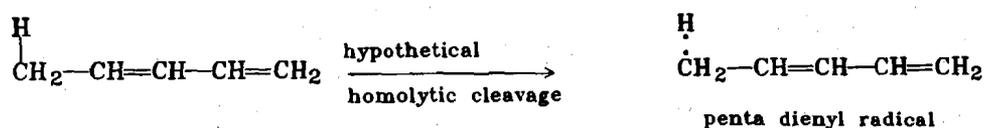
If you examine the HOMO of the allyl radical in a [1,3] sigmatropic shift, you can see that suprafacial migration is symmetry forbidden though it may be geometrically feasible.



Let us see what happens in the case of antarafacial shift. You can see that this is symmetry allowed but geometrically unfavourable. This leads to the conclusion that [1,3] sigmatropic rearrangements should not occur readily. As mentioned above, it has been found in practice that they are rare.



By contrast [1,5] sigmatropic shifts are quite common. If we assume a homolytic bond cleavage for the purpose of analysis, we have to consider  $\pi$  molecular orbitals of pentadienyl radical which has five  $\pi$  electrons and hence five molecular orbitals shown in Fig 12.5.



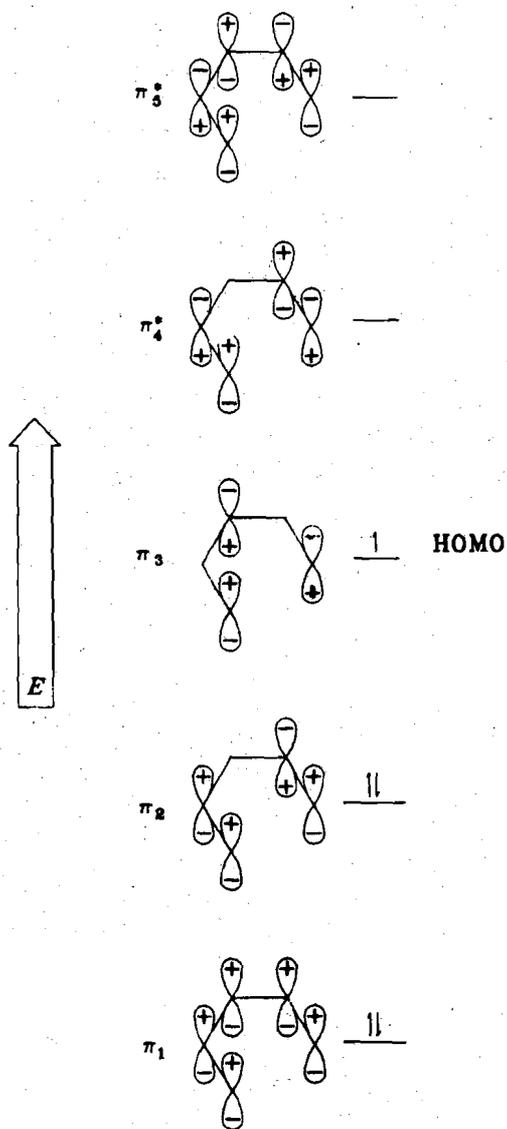
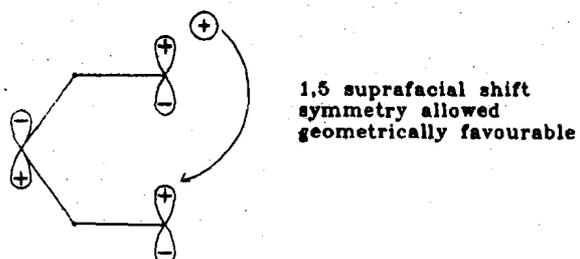


Fig 12.5 : The five  $\pi$  molecular orbitals of the pentadienyl radical

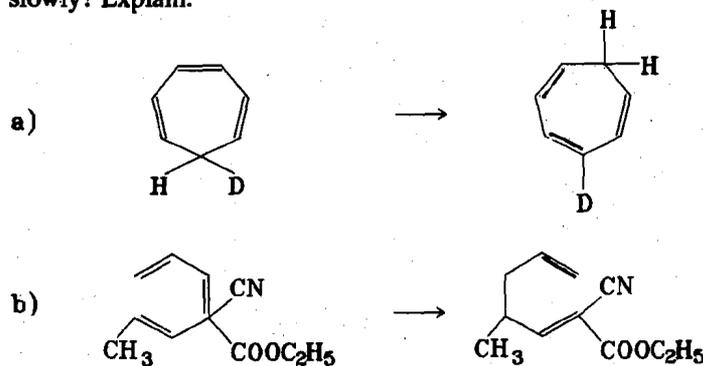
Considering  $\pi_3$ , the HOMO of this radical, we can see that suprafacial [1,5] shift is both symmetry allowed and geometrically favourable, which makes it facile.



rotate through 90°

SAQ 4

Which of the following sigmatropic rearrangements would proceed readily and which slowly? Explain.



## 12.7 SUMMARY

In this unit we have discussed pericyclic reactions. These reactions are thermal or photo induced concerted reactions with cyclic transition states. Pericyclic reactions have been classified into,

- Cycloaddition reactions
- Electrocyclic reactions
- Sigmatropic rearrangements

In this unit we have used the frontier orbital method for analysing the mechanism of these reactions, according to which the electrons are assumed to flow from the HOMO of one molecule to LUMO of the other. If these orbitals are in phase, the reaction is symmetry allowed. If the orbitals are not in phase the reaction is symmetry forbidden.

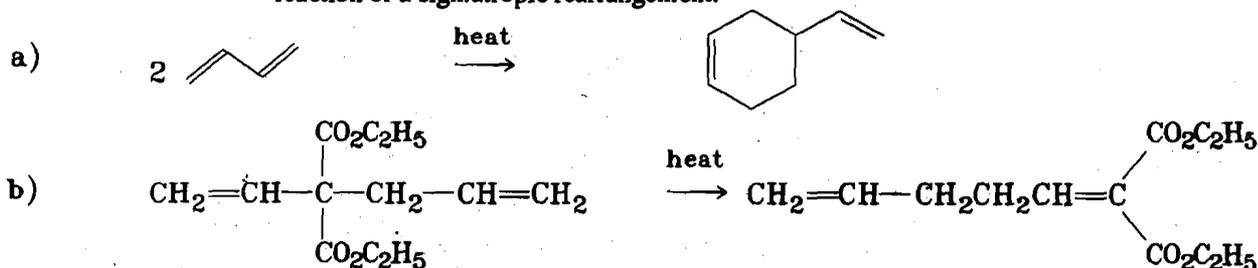
Cycloaddition reactions of  $4n$  and  $(4n+2)$  systems have been discussed. It has been shown by analysis of the frontier orbitals in the ground state and the excited state that cycloadditions of  $4n$  systems would be photo induced while those of  $(4n+2)$  thermally induced.

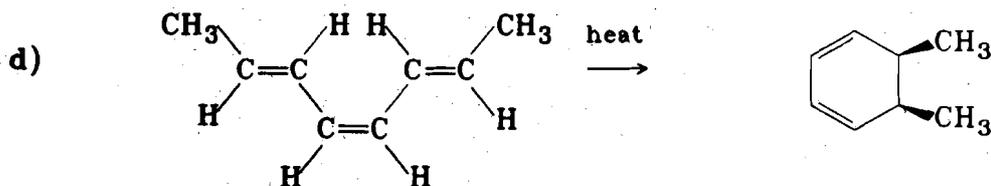
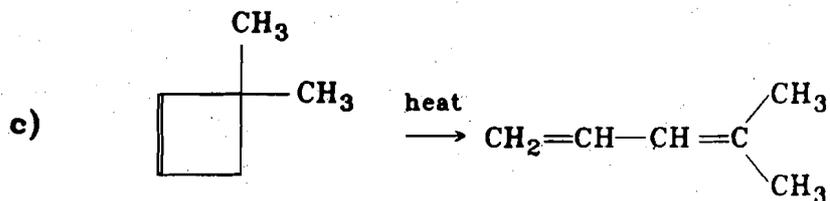
Electrocyclic reactions of  $4n$  and  $(4n+2)$  systems have been discussed next. Here  $p$ -orbital components of the HOMO undergo end-to-end overlap to form new sigma bonds. For this they must undergo conrotatory or disrotatory motion which in turn determines the stereochemistry of the product. Rationale for the stereochemistry of the products obtained in thermal and photochemical reactions has been established on this basis.

Sigmatropic rearrangements are concerted intramolecular rearrangements. These occur suprafacially or antarafacially depending on the phases of interacting orbitals in the HOMO of the hypothetical radical system. The facility of [1,3] and [1,5] sigmatropic shifts has been analysed in terms of orbital symmetry and geometry of the transition state.

## 12.8 TERMINAL QUESTIONS

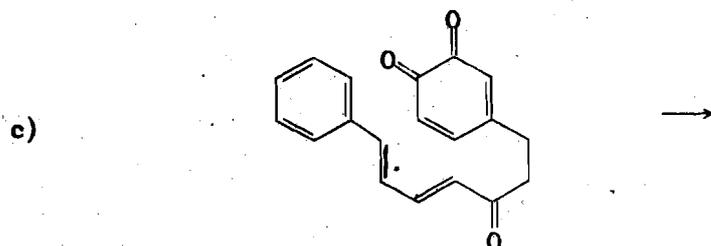
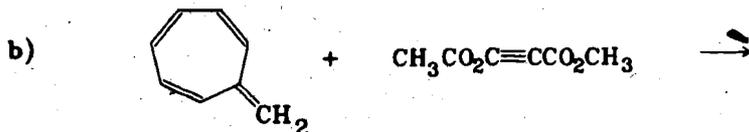
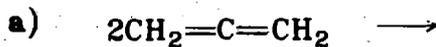
1) Identify each of the following reactions as a cycloaddition, an electrocycloaddition reaction or a sigmatropic rearrangement.



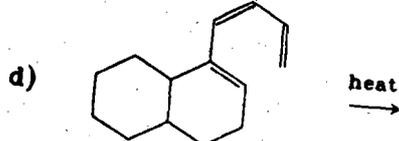
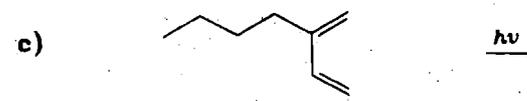
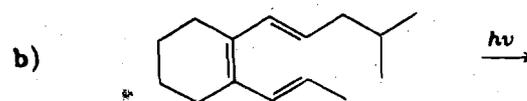
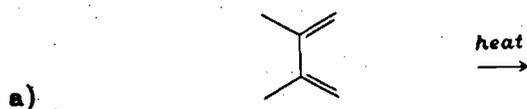


2) Draw the  $\pi$  orbital diagram for the lowest energy excited state of 1,3,5-hexatriene and indicate the HOMO.

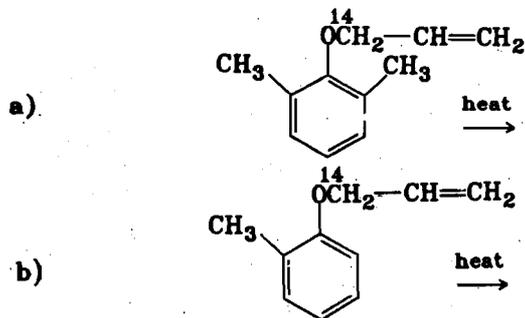
3) What would be the products in the following cyclo addition reactions. Classify each as [2+2] or [4+2] cyclo addition.



4) Specify which type of rotatory motion, conrotatory or disrotatory would each of the following undergo in an electrocycloaddition reaction. Also indicate the product formed.



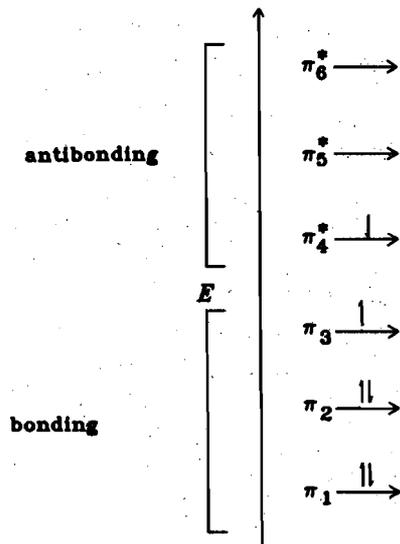
5) Predict the products in the following:



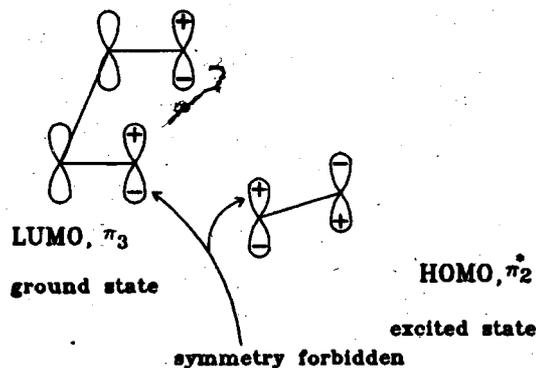
## 12.9 ANSWERS

### Self-assessment Questions

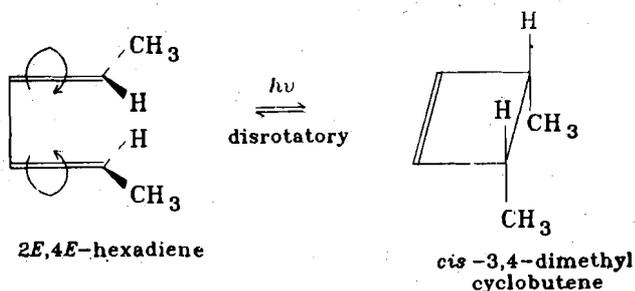
1)



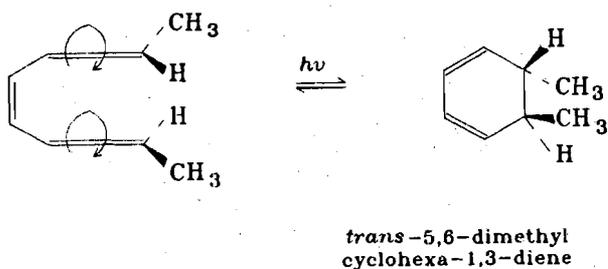
- 2) a) The reaction visualises  $\pi$  electrons flowing from HOMO,  $\pi_2$  of the diene to the LUMO  $\pi_3^*$  of the dienophile. Therefore, a high electron density in the former and a low electron density in the latter would favour the reaction.
- b) Photoinduced (4+2) cycloaddition is not possible in this case. Because LUMO  $\pi_3$  of the diene is not in phase with HOMO  $\pi_2^*$  of the dienophile reaction would be symmetry forbidden.



- 3) a) 2,4-Hexadiene is a  $4n$  polyene. Therefore, the photochemical electrocyclic reaction takes place by disrotatory motion. The product would be *cis*-3,4-dimethyl cyclobutene.



b) 1,3,5-Hexatriene is a  $(4\pi+2)$  polyene. Photochemical electrocyclic reaction would involve conrotatory motion to give the *trans* product.

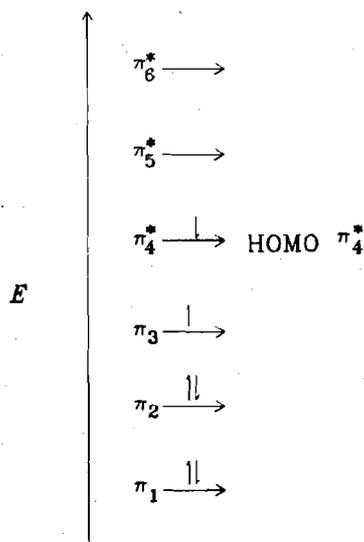


4) Both would proceed readily (a) by [1,5] sigmatropic shift and (b) by [3,3] sigmatropic shift.

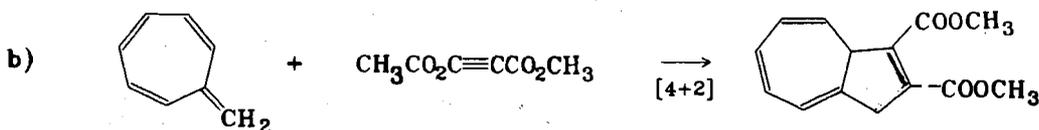
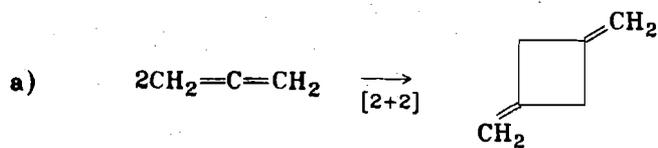
Terminal Questions

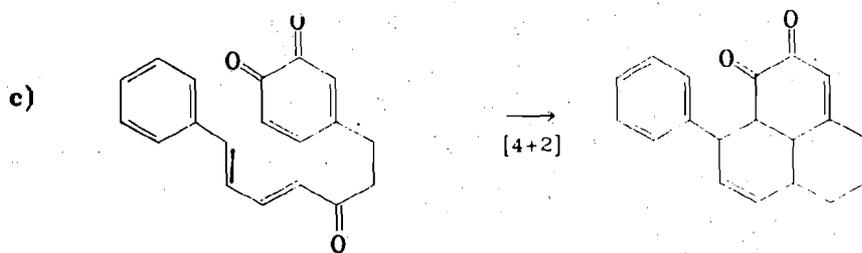
- 1) a) cyclo addition  
 b) sigmatropic rearrangement  
 c) electrocyclic reaction  
 d) electrocyclic reaction

2)

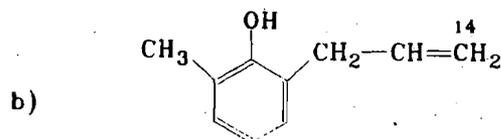
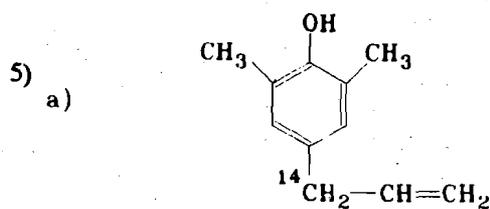


3)





- 4) a)  $[4n]$  thermal reaction would involve conrotatory motion.  
 b)  $[4n+2]$  photochemical reaction would involve conrotatory motion.  
 c)  $[4n]$  photochemical reaction would involve disrotatory motion.  
 d)  $[4n+2]$  thermal reaction would involve disrotatory motion.



#### Further Readings

- 1) *Organic Chemistry*, 6th edition; by R.T. Morrison and R.N. Boyd; Prentice-Hall of India Pvt. Ltd.
- 2) *A Text Book of Organic Chemistry*; by B.S. Bahal and Arun Bahal; S. Chand & Company Ltd.
- 3) *Organic Chemistry*, Vol.I and II; by S.M. Mukherji, S.P. Singh and R.P. Kapoor; Wiley Eastern Ltd.
- 4) *Text Book of Organic Chemistry*, 24th edition; by P.L. Soni and H.M. Chawla; Sultan Chand & Sons.
- 5) *Text Book of Organic Chemistry*, 2nd edition; by Lloyd N. Ferguson; Affiliated East West Press Pvt. Ltd.
- 6) *Reaction Mechanism and Reagent in Organic Chemistry*, 2nd edition, by Gurdeep K. Chatwal; Himalaya Publishing House.
- 7) *Reaction Mechanism in Organic Chemistry*, by S.M. Mukharji, S.P. Singh, The Macmillan Company of India Limited.
- 8) *Organic Chemistry*, by Pine, Hendickson, Cram, Hammond, Mc Graw-Hill Kogakusha, Ltd. (Fourth Edition).