

## 2.6 THE WOODWARD-HOFFMANN RULE FOR ELECTROCYCLIC REACTIONS

Fortunately, all the conclusions that can be drawn laboriously from correlation diagrams can be drawn more easily from a pair of rules, known as the *Woodward-Hoffmann rules*. Rules distil the essence of the idea into two statements governing all pericyclic reactions, one rule of thermal reactions and its opposite for photochemical reactions. Correlation diagrams explain why they work, but we no longer depend upon constructing such diagrams.

### 2.6.1 Woodward-Hoffmann rule for Electrocyclic Thermal Reactions

A thermal (ground state) electrocyclic reactions is symmetry allowed when the total number of  $(4q + 2)s$  and  $(4r)a$  components is odd.

### 2.6.2 For Photochemical Electrocyclic Reactions

An electrocyclic reaction in the first electronically excited state is symmetry allowed when the total number of  $(4q + 2) a$  and  $(4r)s$  is odd.

These rules need some explanation.

#### Component

A component is a bond or orbital taking part in a pericyclic reaction as a single unit. A double bond is a  $\pi^2$  component. The number *two* is the most important part of this designation and simply refers to the number of electrons. The prefix  $\pi$  tells us the type of electrons. A component may have any number of electrons, for examples 1, 3-butadiene is a  $\pi^4$  component. Component may not have mixtures of  $\pi$  and  $\sigma$  electrons. Component either contains only  $\sigma$  electrons or contains only  $\pi$  electrons. Designations  $(4q + 2)$  and  $(4r)$  simply refer to the number of electrons in the component where  $q$  and  $r$  are integers  $(0, 1, 2, 3, 4 \dots n)$ . An alkene is a  $\pi^2$  component and so it is of the  $(4q + 2)$  kind where  $q = 0$  while diene is a  $\pi^4$  component and so it is of the  $(4r)$  kind where  $r = 1$ .

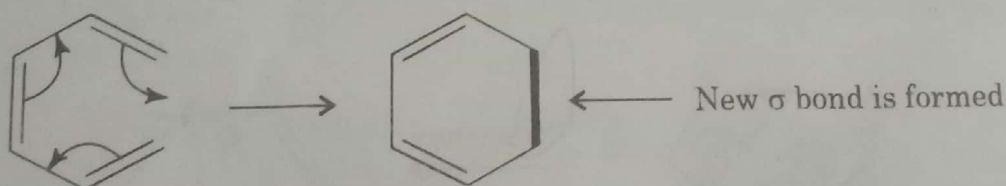
#### Suffix s and a

In electrocyclic reaction *s* means when upper (or lower) lobe of one frontier orbital overlaps with upper (or lower) lobe of other frontier orbital and *a* means when upper lobe of one orbital overlaps with lower lobe of other.

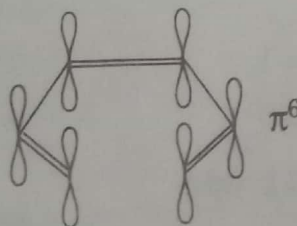
Let us start with hexatriene ring closer. As a preliminary, we would just note that hexatriene is, of course, a  $6\pi$  electrons ( $\pi^6$ ) conjugated system and, on forming cyclohexadiene, the end two orbitals have to form a  $\sigma$  bond.

So, now for the Woodward-Hoffmann treatment:

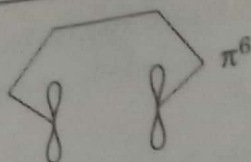
(1) Draw the mechanism for the reaction



(2) Choose the components. All the bonds taking part in the mechanism must be included and no others.



(3) Make the three dimensional drawing of the way the components come together for the reaction putting in orbitals at the ends of the components.



These orbitals are simple  $p$ -orbitals and do not make up HOMO's or LUMO's or any particular MO's. Do not attempt to mix frontier orbitals and Woodward-Hoffmann description of correlation of pericyclic reactions.

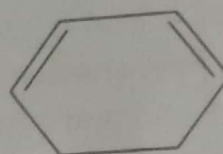
(4) Join up the component(s) where new bond(s) are to be formed. Make sure you join orbitals that are going to form new bonds.

In this case formation of new  $\sigma$  bond takes place by two possible ways:

**Case 1:** When component is  $s$ . In this case overlapping will be possible if motion is disrotatory.



Disrotatory  
motion



$\pi^6 s$

Notice that we call the component ' $s$ ' because the upper lobes of the two  $p$ -orbitals are joining together. If upper lobe of one orbital and lower lobe of another orbital is joined together then component will be ' $a$ '.

$$\text{Number of } (4q + 2) s \text{ Component} = 1$$

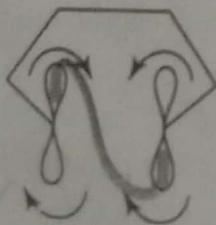
$$\text{Number of } (4r) a \text{ component} = 0$$

$$\text{Total} = 1, \text{ odd}$$

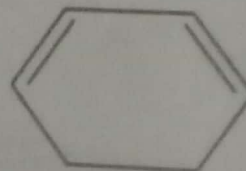
Thermal : Allowed

Photochemical : Forbidden

**Case II:** When component is ' $a$ '. In this case overlapping will be possible if motion is conrotatory.



Conrotatory



$\pi^6 a$

$$\text{Number of } (4q + 2) a = 1$$

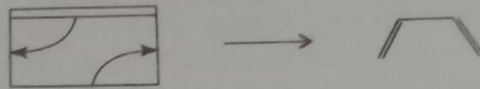
$$\text{Number of } (4r) s = 0$$

$$\text{Total} = 1, \text{ odd}$$

Thermal : Forbidden

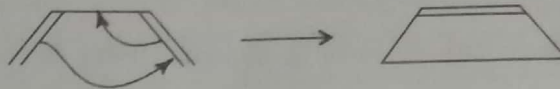
Photochemical : Allowed

Similarly take the example of conversion of cyclobutene to 1,3-butadiene.

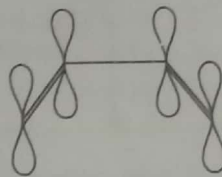


But for the use of Woodward-Hoffmann rule always considers the process in which open system converts into cyclic system.

(1) Draw the mechanism for the reaction

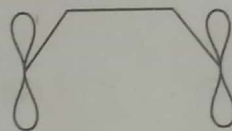


(2) Choose the components. All the bonds taking part in the mechanism must be included and no others.



$\pi^4$

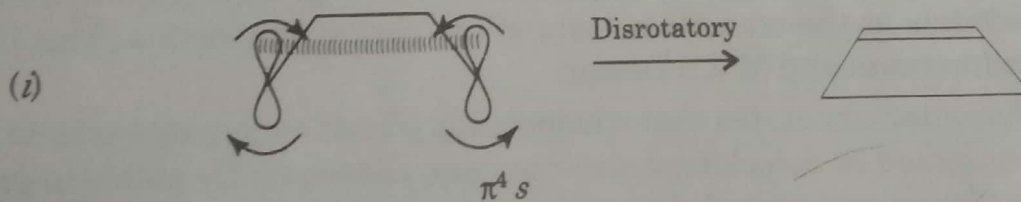
(3) Make the three dimensional drawing of the way in which the component comes together for the reaction, putting the orbitals at the ends of the component.



$\pi^4$

(4) Join up the component ( $s$ ) where now bond ( $s$ ) are to be formed.

(5) Show bond formation by conrotatory as well as disrotatory motion. Label each component  $s$  or  $a$ .



$$\text{Number of } (4q+2) s \text{ Component} = 0$$

$$\text{Number of } (4r) a \text{ component} = 0$$

$$\text{Total} = 0$$

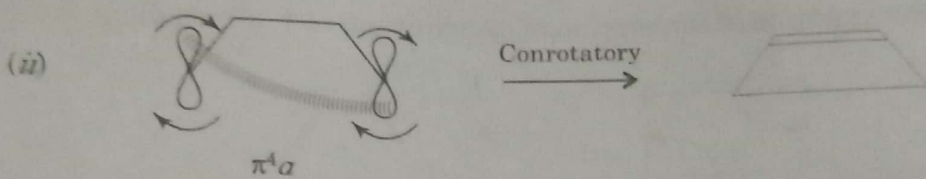
Thermally: Disallowed.

$$\text{Number of } (4q+2) a \text{ component} = 0$$

$$\text{Number of } (4r) s \text{ component} = 1$$

$$\text{Total} = 1, \text{ odd}$$

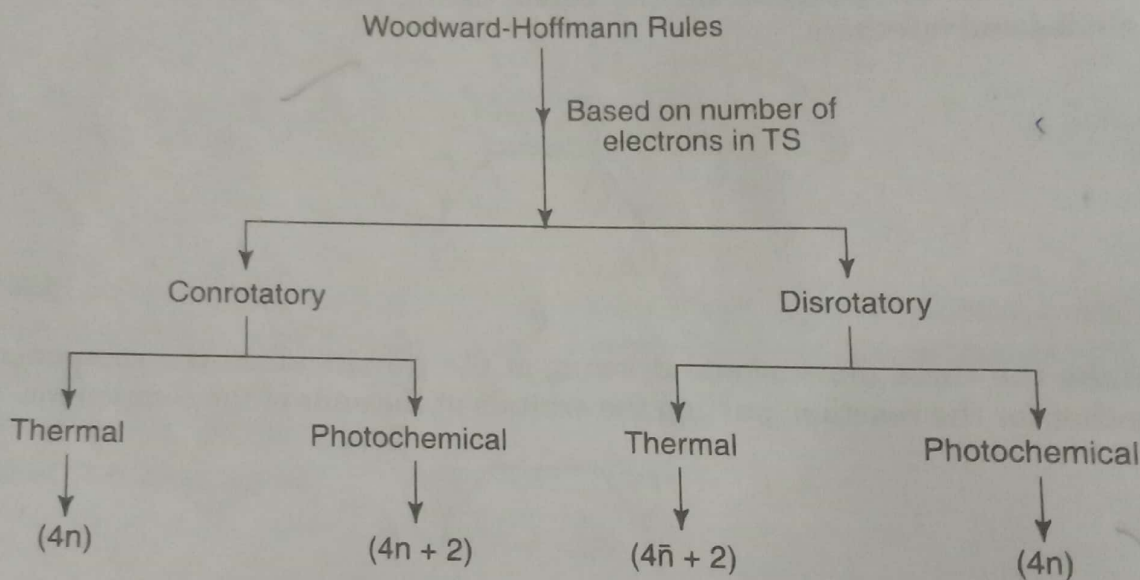
Photochemically: Allowed.



$$\begin{array}{r} \text{Number of } (4r)\sigma = 1 \\ \text{Number of } (4q + 2)s = 0 \\ \hline \text{Total} = 1, \text{ odd.} \end{array}$$

Thermally: Allowed.

Thus we can conclude the following results from Woodward-Hoffmann rule for electrocyclic reactions:



## 2.7 HÜCKEL-MOBIUS (H-M) METHOD OR PMO (PERTURBATION MOLECULAR ORBITAL) METHOD

Another method for quickly assessing whether a given pericyclic process is allowed is to examine the cyclic array of orbitals at the transition state of the pericyclic reaction. This method is popularised by H. Zimmerman and M.J.S Dewar.

Hückel rule of aromaticity states that a monocyclic planar conjugated system is aromatic if it has  $(4n + 2) \pi$  conjugated or delocalised electrons and consequently stable in ground state. Similarly monocyclic planar conjugated system is anti-aromatic if it has  $(4n) \pi$  conjugated delocalised electrons. This system is unstable in ground state. However further calculation shows that these rules are reversed by the presence of a node in the array of atomic orbitals. Thus system with  $(4n + 2) \pi$  electrons and a node is antiaromatic while system with  $(4n) \pi$  electrons and a node is aromatic.

Thus system has no nodes when:

$(4n + 2) \pi$  electrons Aromatic + Stable