

Pericyclic Reactions

↳ means 'around the cycle'

The term pericyclic reactions is suggested by Woodward and Hoffman which have the following characteristics:

I. **CONCERTED** i.e., the reactant bonds are broken and product bonds are formed simultaneously through a single transition state (T.S.)

II. **ELECTRON SHIFT** in a **CYCLIC** manner i.e., pericyclic rxns have no intermediates but have cyclic conjugated T.S.

Four kinds of pericyclic rxns.

a) **ELECTROCYCLIC** reactions

b) **CYCLOADDITION** reactions

c) **SIGMATROPIC** reactions

d) **CHELETROPIC** reactions.

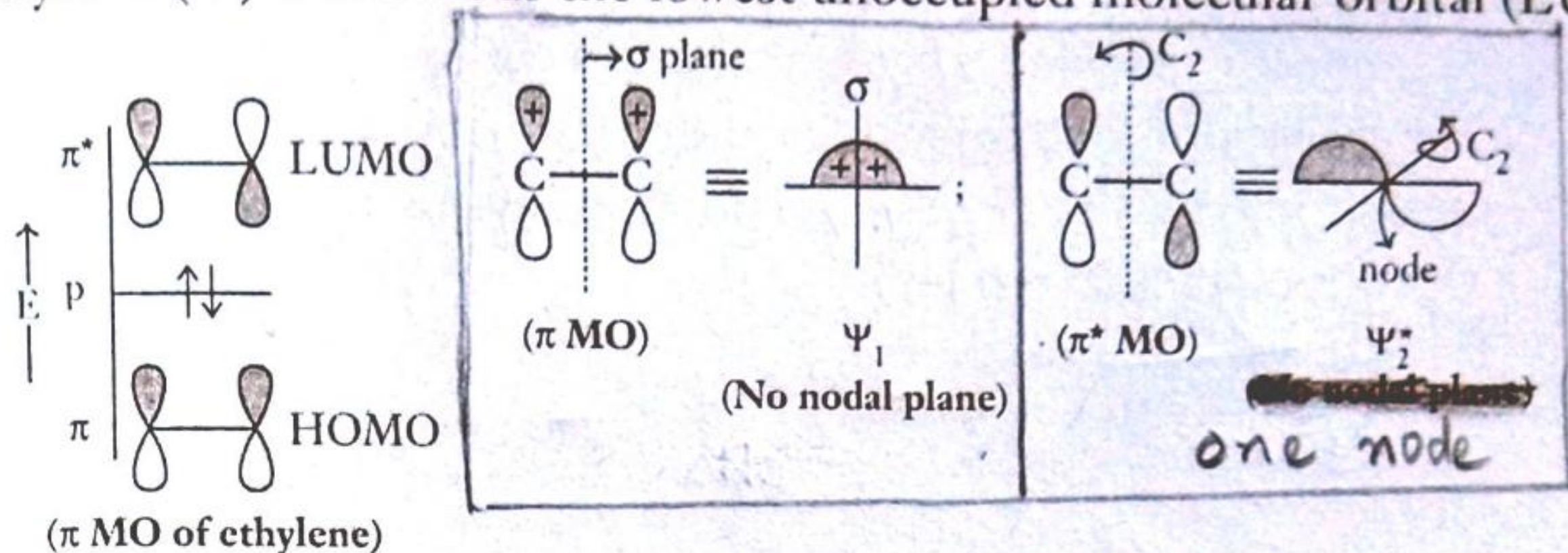
⊙ SALIENT FEATURES OF PERICYCLIC RXNS:

1. Pericyclic rxns do not take place by ionic or radical or carbene intermediate i.e., reactive intermediates are not formed.
2. They are insensitive to catalysts [some exceptions also for DA rxn where acid-catalysts influences the rxn]
3. Solvent effect is negligible.
4. To initiate a pericyclic reaction, thermal or photochemical energy is required.
5. Pericyclic rxns involve the formation or cleavage of  $\sigma$ -bonds and consumption or formation of  $\pi$ -bonds, so at least one of the reactants or products is an unsaturated molecule.
6. The reactions are reversible and the equilibrium depends on the thermodynamic stability of the reactants and products.
7. Pericyclic rxns occur with high degree of selectivity.
8. The stereochemical course depends on the number of e's involved in the process.

## Elementary ideas about Molecular Orbitals (MO)

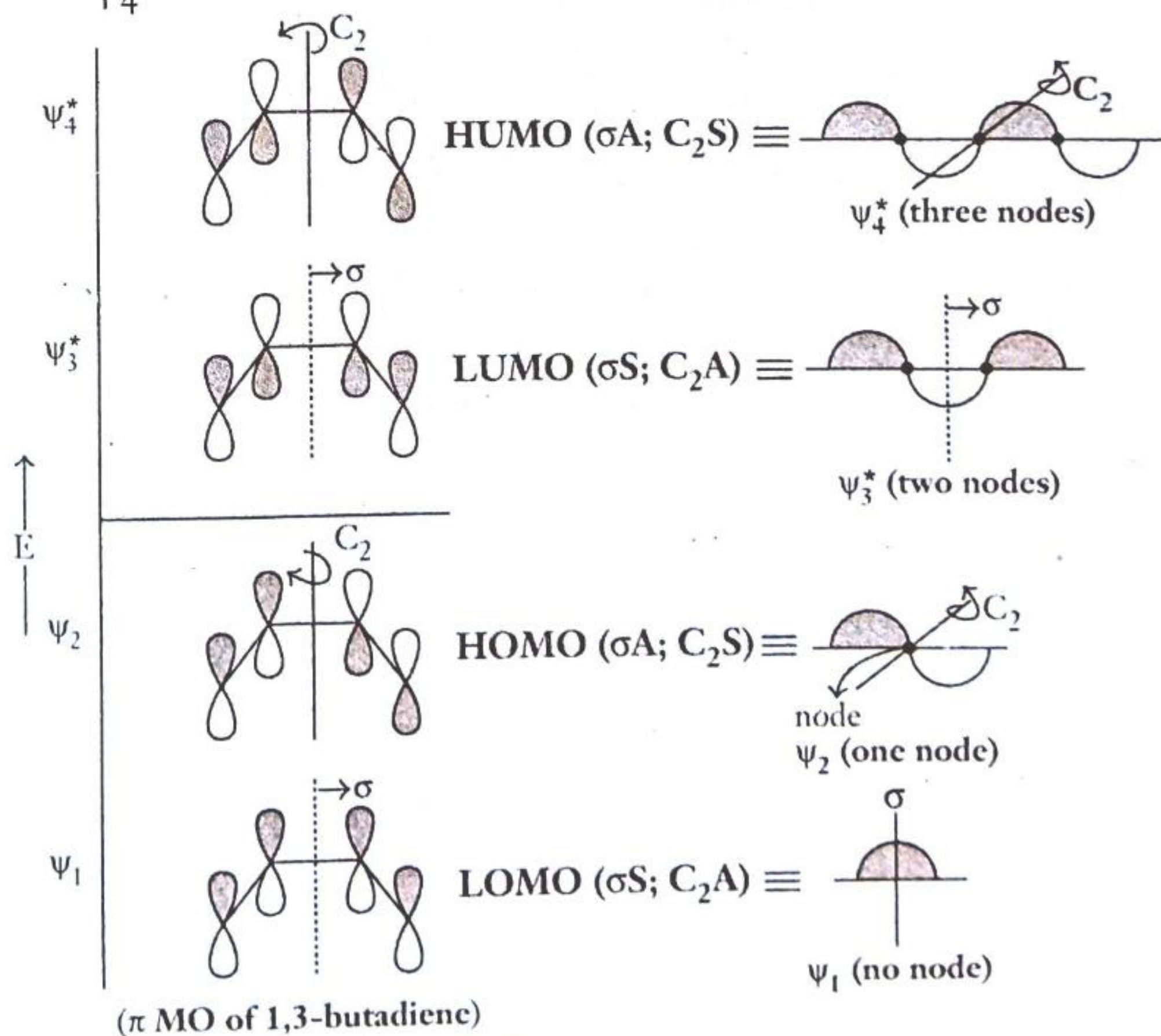
A bonding MO results when two orbitals of the same phase overlap. The bonding MO of ethylene is known as the highest occupied molecular orbital (HOMO). When two orbitals

of opposite phases overlap, an antibonding molecular orbital results. This antibonding  $\pi$  MO of ethylene ( $\pi^*$ ) is known as the lowest unoccupied molecular orbital (LUMO).



It is important to note that as the energy content of the  $\pi$  (bonding and antibonding) molecular orbitals increases, the number of nodes in the wave function increases. For example,  $\pi$  MO of ethylene has no node, as it is the first MO of ethylene and  $\pi^*$  orbital of ethylene has one node as it is the second molecular orbital. In fact, the  $n$ th  $\pi$  orbital, bonding or antibonding has  $(n - 1)$  nodes. The  $\pi$  MO of ethylene has a  $\sigma$  plane of symmetry and it is said to be  $\sigma$  symmetric (S) with respect to the  $\sigma$  plane. This  $\sigma$  plane bisects the molecule and is perpendicular to the plane of the molecule. It has no  $C_2$  axis, so  $\pi$  orbital of ethylene is antisymmetric (A) with respect to  $C_2$  axis which lies **on the plane** of the molecule. Similarly  $\pi^*$  MO of ethylene is symmetric (S) with respect to  $C_2$  axis and antisymmetric (A) with respect to  $\sigma$  plane.

However, a linear combination of four p atomic orbitals of 1,3-butadiene will give rise to four molecular orbitals two bonding and two antibonding. These are designated as  $\psi_1$ ,  $\psi_2$ ,  $\psi_3^*$  and  $\psi_4^*$ .



Similarly you practise for 1,3,5-hexatriene MOs