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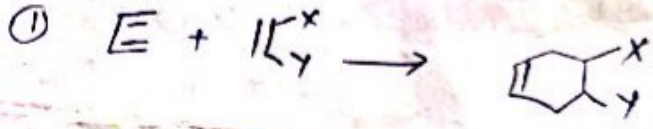
Pericyclic Reactions

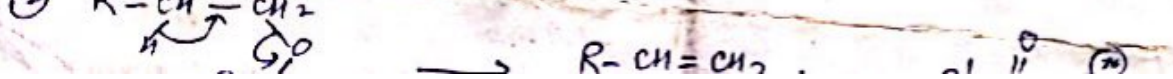
M.Sc. II Sem. (1)
M - 2008

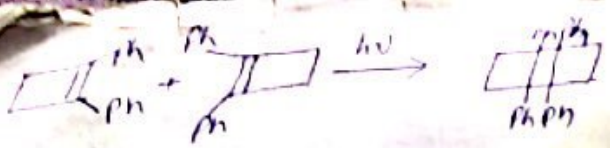
Dr. P.K. Sharma. ISL Lect. 9-4-20

Pericyclic Reaction
or
Electrocyclic Reaction
or
Symmetry Controlled Reactions (Morrison and Boyd, Jerry March, Peter Sykes)

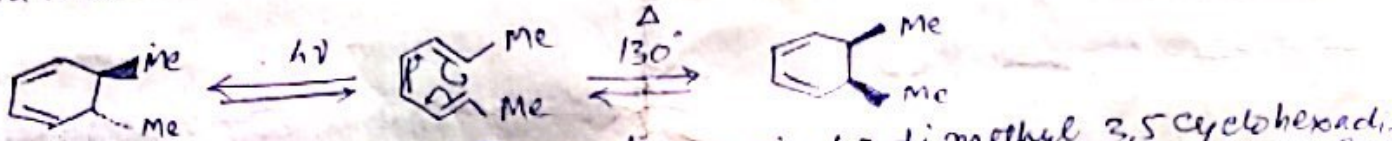
Most of organic reactions proceed via reaction intermediate, as revealed by their reaction mechanisms, yet there are a no. of reactions which proceed neither by polar nor by a radical pathway and are also uninfluenced by changes in solvent polarity, presence of radical initiators or inhibitors and other catalysts and so the attempts to isolate or detect reaction intermediates in such reactions have failed. Examples are - Diels - Alder reaction (1) and Pyrolytic elimination reactions of carboxylic esters (2) and xanthates (3) to yield alkenes.

(1) 

(2) 



Stereochemical effects can be seen clearly as, 2,4,6 trans- octa triene cyclise on heating to give cis-1,2 dimethyl 3,5 cyclohexadiene only. while on photochemical irradiation trans-1,2 dimethyl 3,5 cyclo hexadiene is obtained.



Trans-1,2 dimethyl 3.5 cyclo hexa diene

2,4,6 Trans-octa -triene

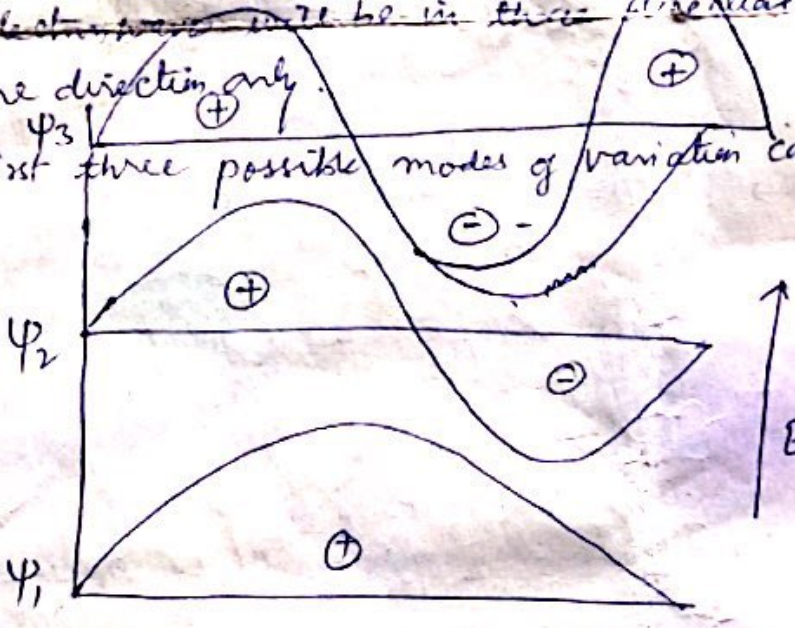
cis, 1,2 dimethyl 3,5 cyclohexadi- ene

The above reaction too is Electrocyclic reaction.

Phase and Symmetry of Orbitals

Individual electrons of an atom can be symbolised by wave function, as Ψ (Psi).

Analogy can be drawn between the behaviour of such a wave like electron and standing waves, that can be generated in a string fastened at both the ends, with the difference that vibration ~~of electron wave may be in three directions~~ while that of string is in one direction only.



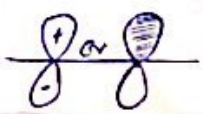
First three possible modes of variation can be shown as -

In Ψ_1 — Amplitude of wave increases from zero to max and then decreases to zero again

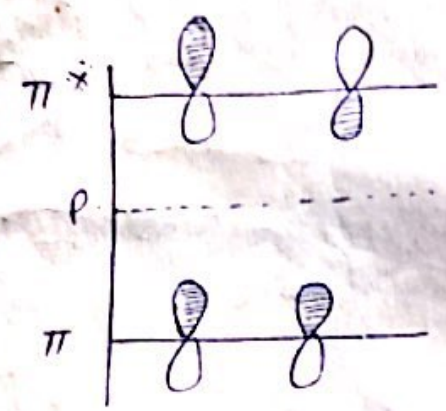
In Ψ_2 - Amplitude increases to maximum and then decreases through zero (Single node)

In Ψ_3 — Two such nodes are present

The lobes of a 2p. atomic orbital wherein has one nodal plane thus differ in phase, conventionally designated as + and - or shading or no shading.



Molecular orbitals are obtained by linear combination of atomic orbitals. We can represent the molecular orbitals π and π^* arising from $2p$ atomic orbitals in ethene.



Similarly four molecular orbitals arising from four 'p' orbitals in Buta diene in cis-oid conformation can be represented as.

A.O's M.O's Ground state Ist Excited state

Only orbitals of same phase will overlap resulting into BMO, while overlapping of orbitals of different phase will lead to repulsive anti-bonding situation. Essential feature of pericyclic reaction is simultaneous overlapping of bond orbitals of participating in the proces, so that they may pass smoothly into the bond orbitals of the products. This transmission passes through a transition state of merging orbitals, which will be of relatively very low energy, and the reaction is favoured so long as symmetry of orbitals is conserved or retained. When the symmetry of the reactant and product orbitals is the same, i.e. orbital symmetry is conserved in the reaction, it is said to be symmetry allowed or energetically favoured reaction.

- Symmetry allowed reactions proceed smoothly on heating.
Symmetry forbidden reactions proceed usually on photolysis. Three main families of Pericyclic reactions are - Electrocyclic reactions, cycloaddition reaction and Sigmatropic reactions. These reactions are very important because -

(1) They create new C-C σ bonds and hence are used for Carbon skeleton construction.

(2) Reactions are independent of external influences such as - effect of solvent, change of concentration, Catalysis and side reactions.

(3) Stereospecificity of these reactions is very high.

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(3) Orbital Symmetry or HOMO Theory or Frontal Orbital Approach.

Let us examine - Thermal Cyclization of 1,3 Butadiene.

The above electrocyclic reaction involving conversion of 2π bonds into 1σ and 1π bond. The reaction is completely stereospecific. Substituent on bond which breaks in cyclobutane must rotate to come into developing plane of butadiene molecule. There are two rotational ways in which this change can occur —

(1) Conrotatory motion - when bonds rotate in the same direction

(2) Disrotatory motion - when bonds rotate in opposite direction.