

Chemistry

B.Sc. Second Sem.

DIENES

By Prof. Ranjana Sharma

What are Dienes?

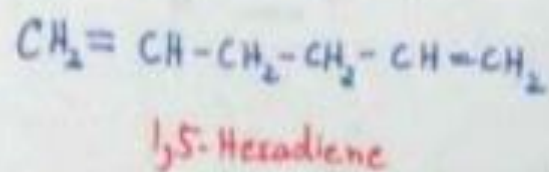
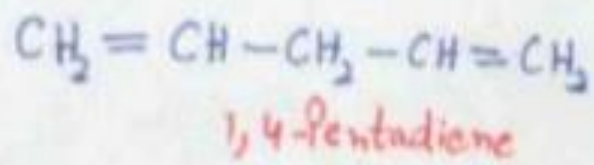
A Diene is an unsaturated hydrocarbon containing two double bonds between carbon atoms and the double bonds may or may not be adjacent to each other.

The arrangements of these double bonds can have varying affects on the compounds reactivity and stability.

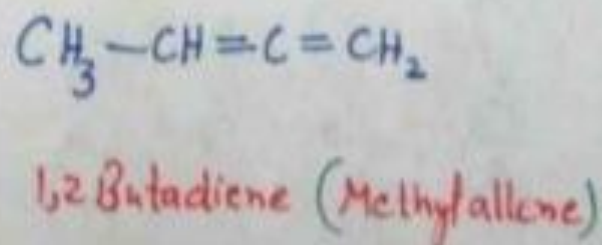
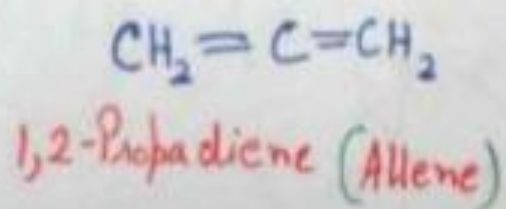
General formula of Diene - C_nH_{2n-2}

They are Isomeric With Alkynes but the behaviour is quite different from each other.

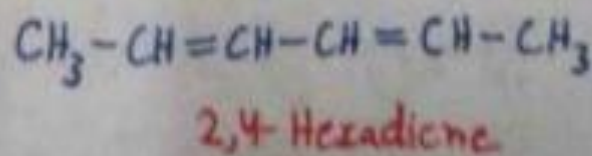
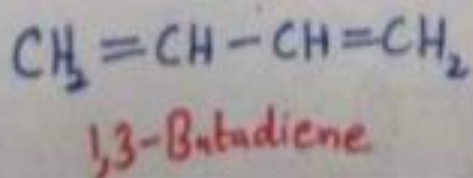
i) Isolated dienes → double bonds are separated by more than one single bond -



ii) Cumulated diene → two double bonds are present b/w successive carbon atoms



iii) Conjugated dienes → double bonds are separated by single bond



NOMENCLATURE

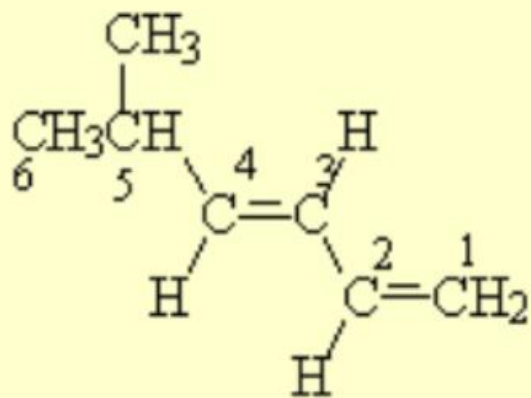
Look for the longest chain that contains the maximum possible number of double bonds.

The chain is numbered in such a way that the double bonds end up with the lowest possible numbers, exception made when there is another dominant function in which case the numbering starts by it.

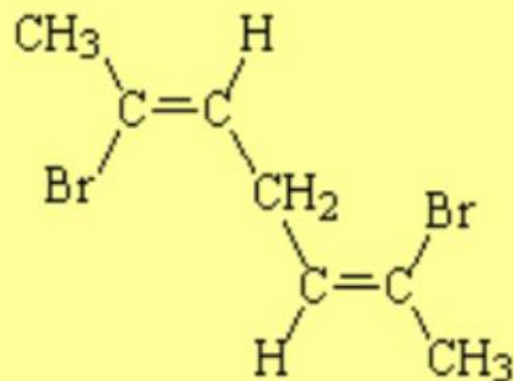
If there are substituents, they are assigned the corresponding numbering in the name.

In the case that two equivalent numberings are possible, one will take the one that assigns the lowest possible numbers to the substituents.

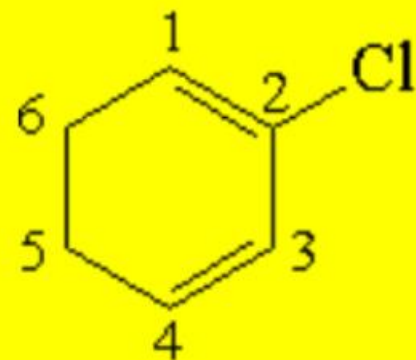
Examples



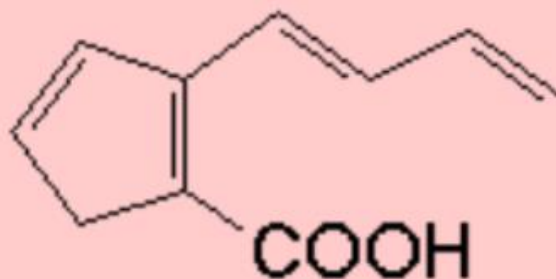
trans-5-methyl-1,3-hexadiene



(*Z,Z*)-2,6-dibromo-2,5-heptadiene



2-chloro-1,3-cyclohexadiene



2-[(1*E*)-buta-1,3-dien-1-yl]cyclopenta-1,3-diene-1-carboxylic acid

RELATIVE STABILITIES OF DIENES

Which is the most stable arrangement of double bonds in an alkadiene—isolated, conjugated, or cumulated?

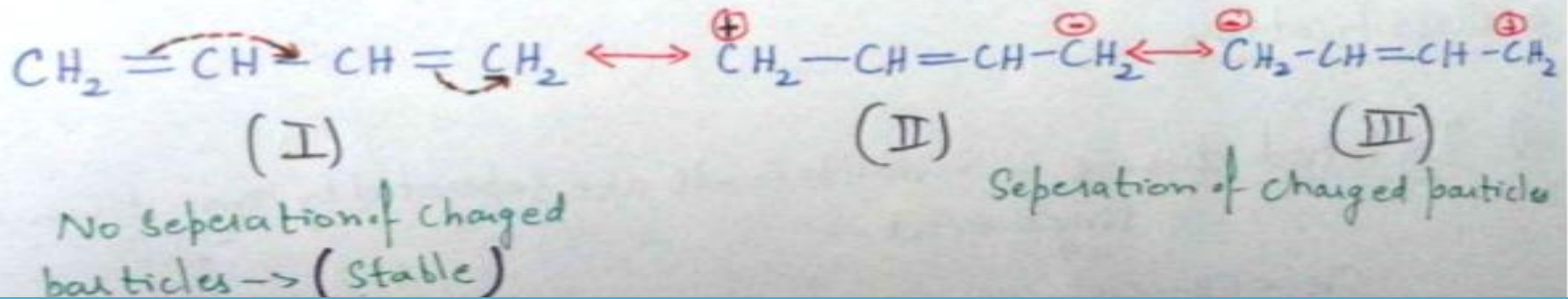
The stabilities of alkenes may be assessed by comparing their heats of hydrogenation.

The measured heat of hydrogenation of the two double bonds in 1,4-pentadiene is 252 kJ/mol (60.2 kcal/mol), exactly twice the heat of hydrogenation of 1-pentene. Furthermore, the heat evolved on hydrogenation of each double bond must be 126 kJ/mol (30.1 kcal/mol), since 1-pentene is an intermediate in the hydrogenation of 1,4-pentadiene to pentane.

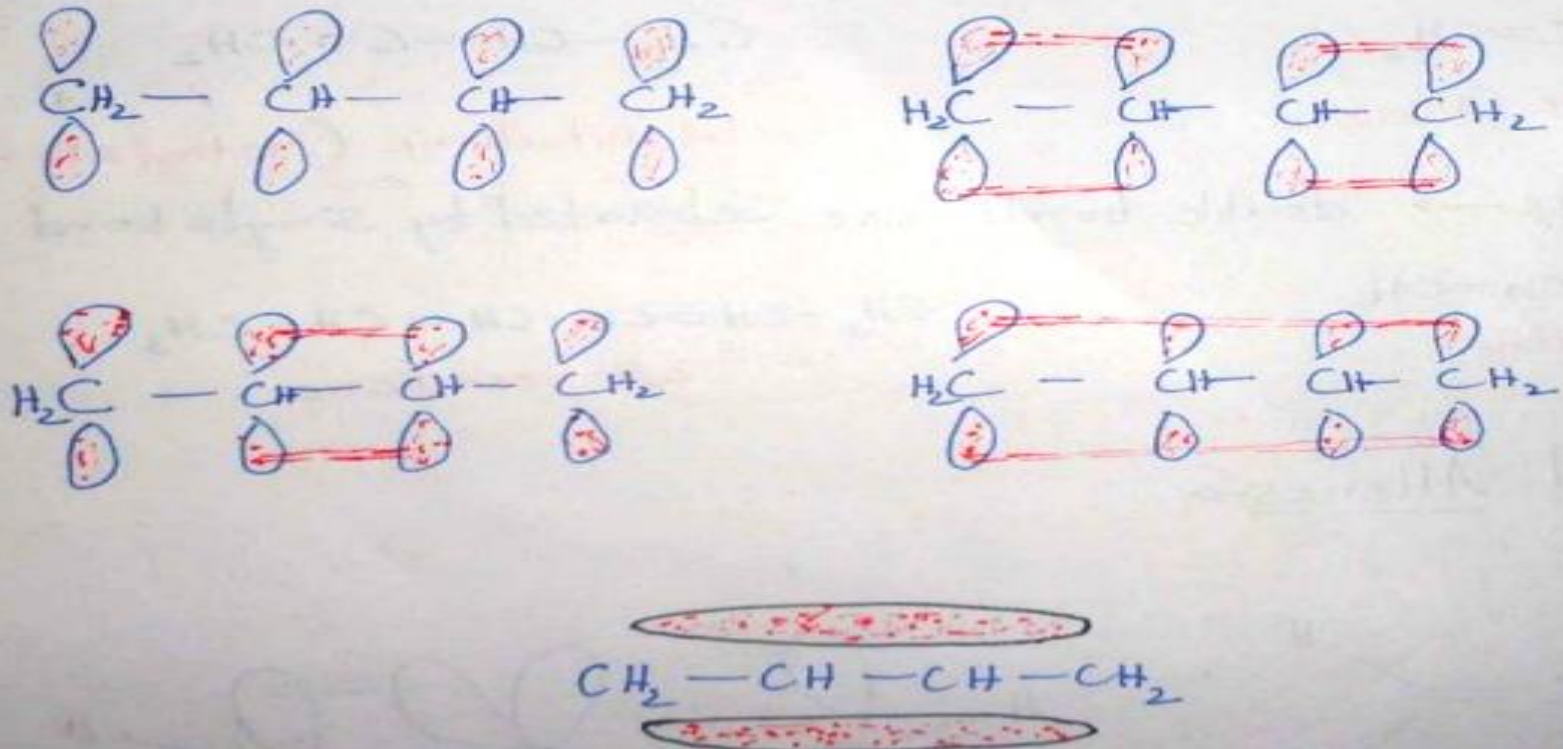
Hydrogenation of the terminal double bond in the conjugated diene evolves 15 kJ/mol (3.6 kcal/mol) less heat than hydrogenation of a terminal double bond in the diene with isolated double bonds. *A conjugated double bond is 15 kJ/mol (3.6 kcal/mol) more stable than a simple double bond.* We call this increased stability due to conjugation the **delocalization energy, resonance energy, or conjugation energy.**

Structure of 1,3-Butadiene

Resonance Structure →



Orbital structure



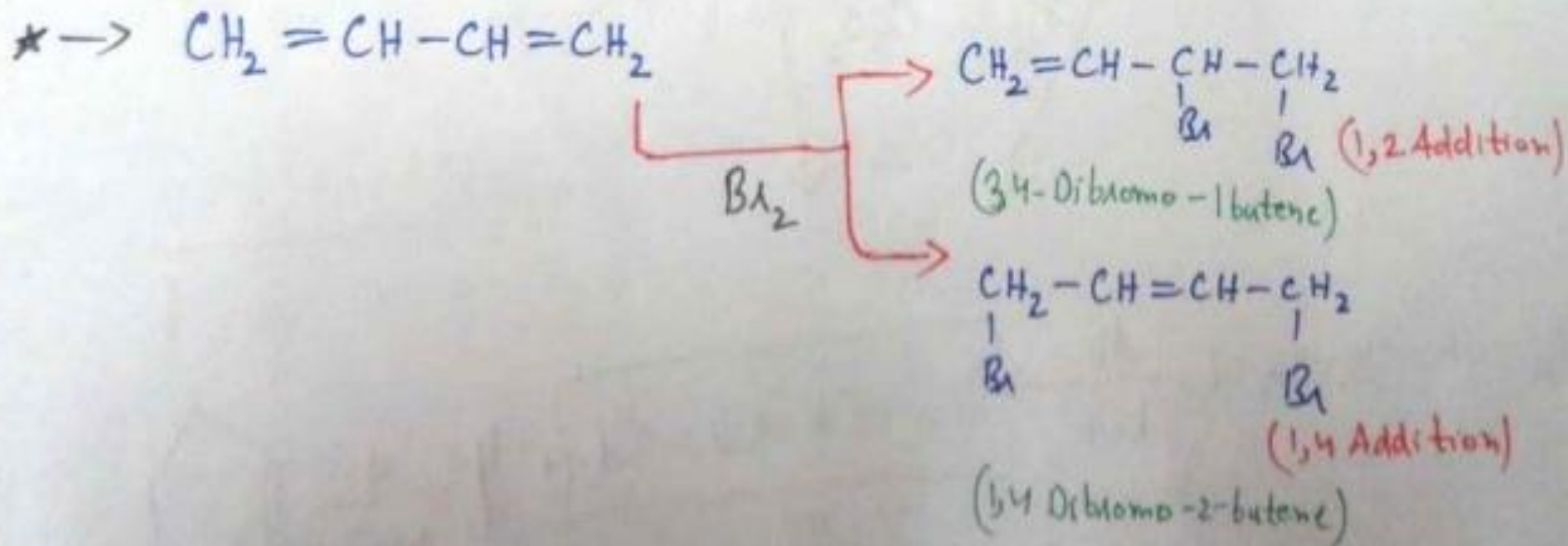
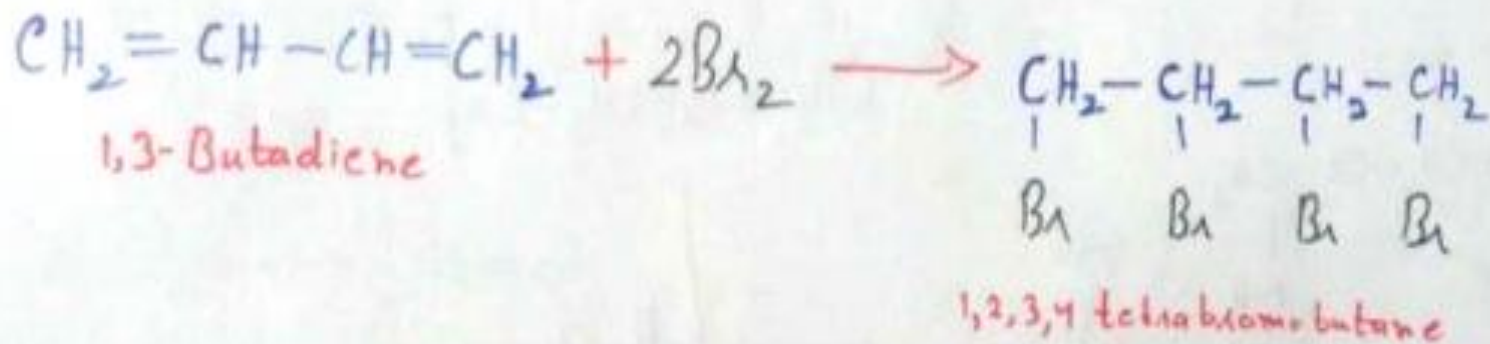
Chemical reactions of Dienes

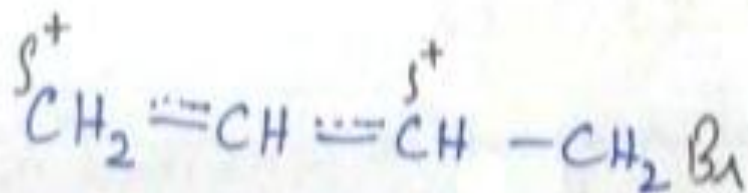
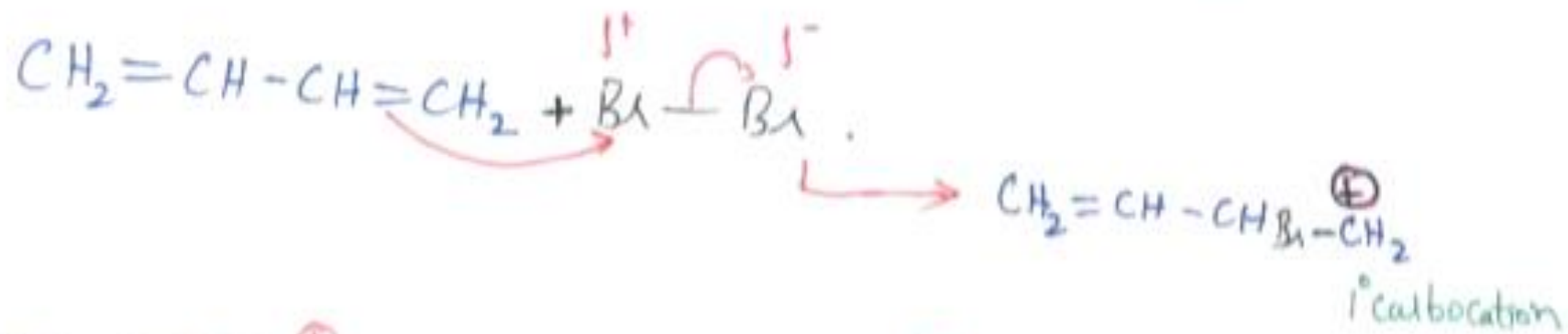
- **1,2 and 1,4 Additions**

Both isolated and conjugated dienes undergo electrophilic addition reactions. In the case of isolated dienes, the reaction proceeds in a manner identical to alkene electrophilic addition. The addition of hydrogen bromide to 1,4-pentadiene leads to two products. This reaction follows the standard carbocation mechanism for addition across a double bond. The addition of more hydrogen bromide results in addition across the second double bond in the molecule. In the case of conjugated dienes, a 1,4-addition product forms in addition to the Markovnikov and anti-Markovnikov products.

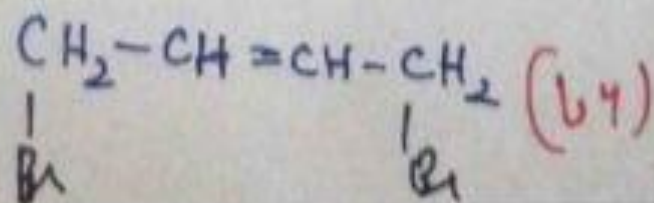
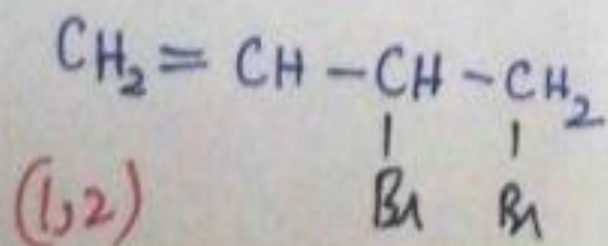
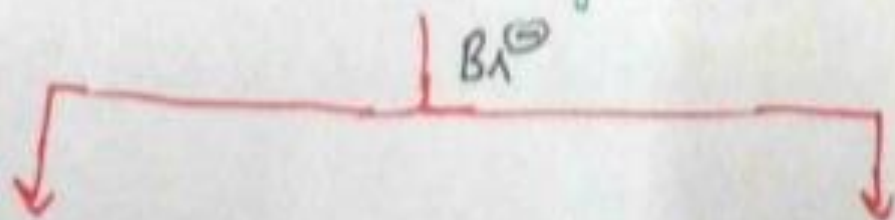
MECHANISM

i) Addition of Halogens →

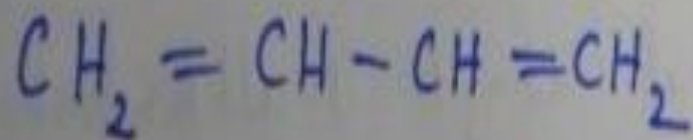




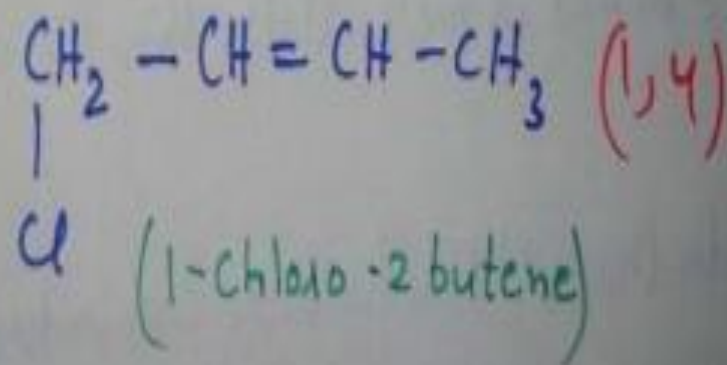
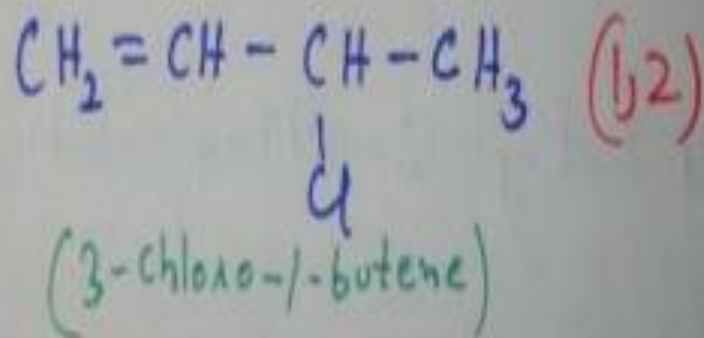
Resonance hybrid



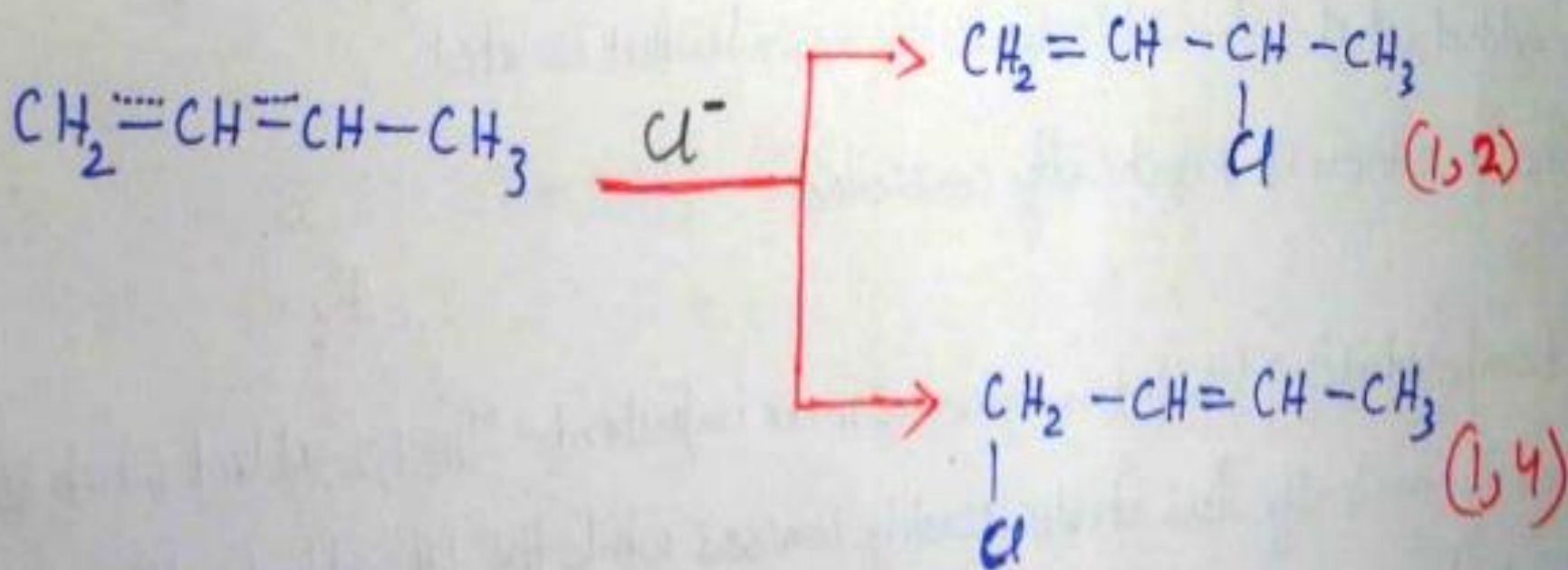
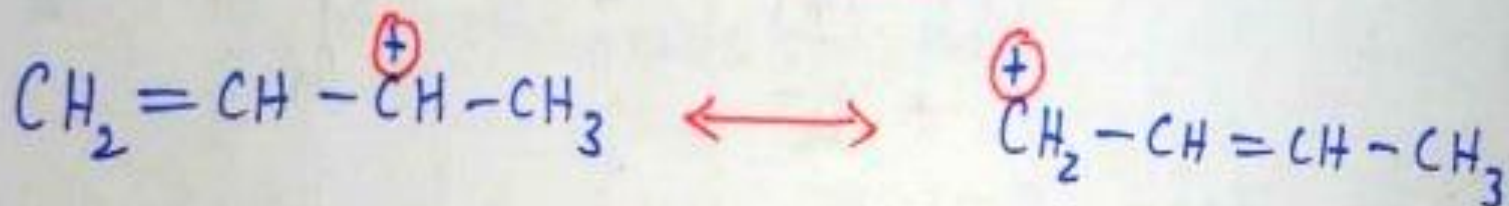
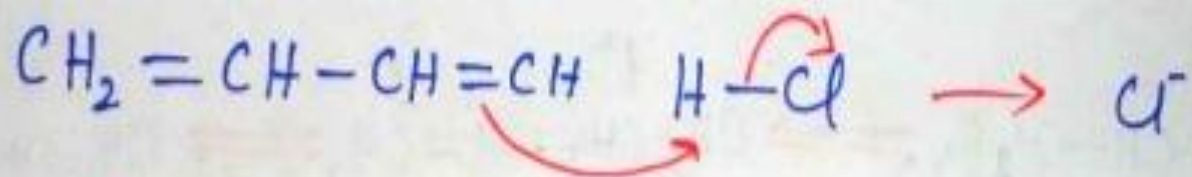
Addition of Halogen acids



HCl

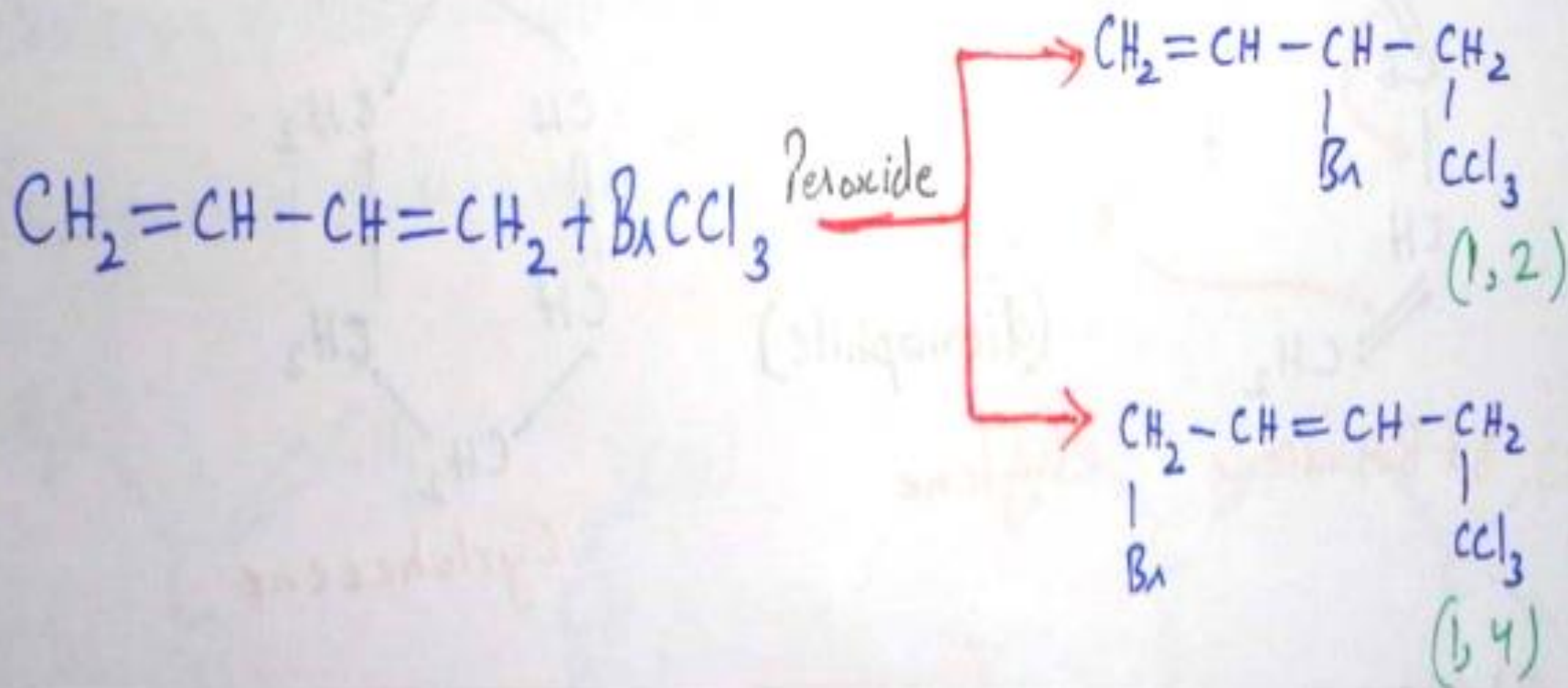


Mechanism →

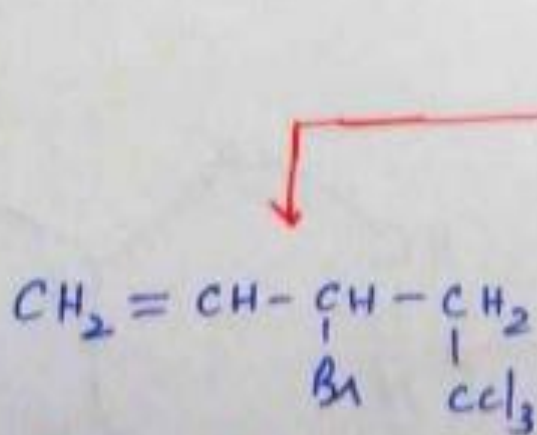
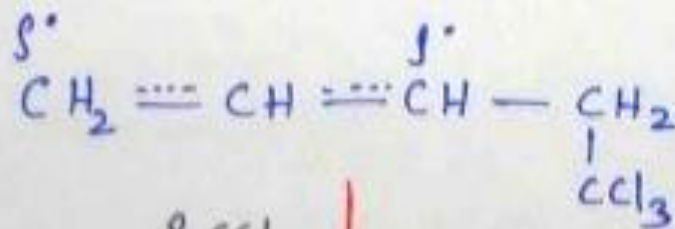
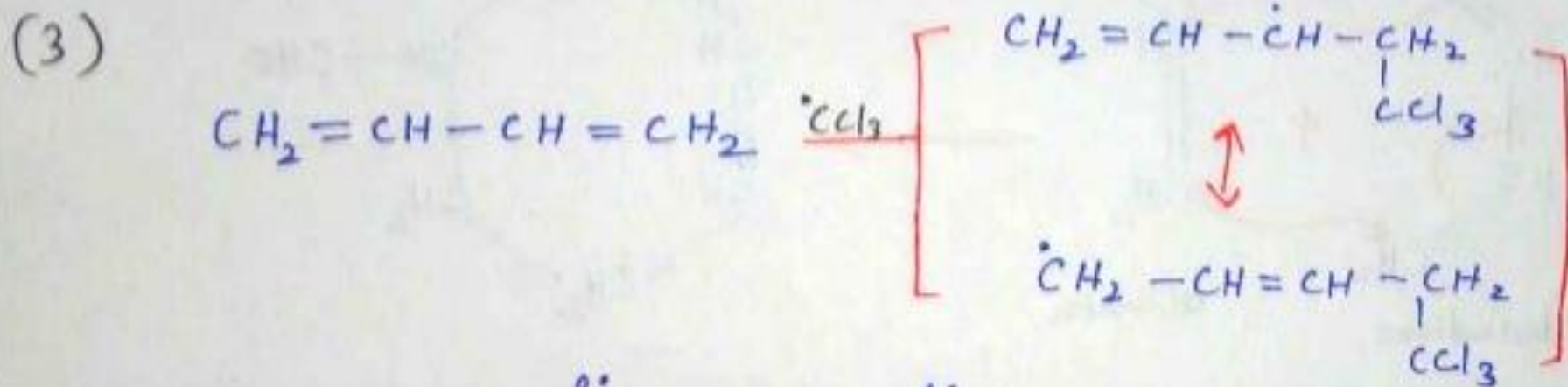


Free radical addition reactions

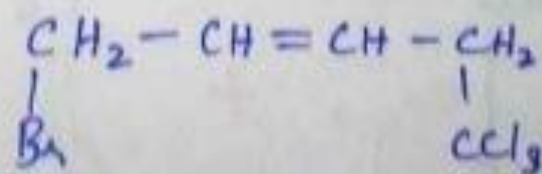
★ Free Radical Addition Rxn's →



Mechanism \rightarrow (1) Peroxide \rightarrow Rad \cdot



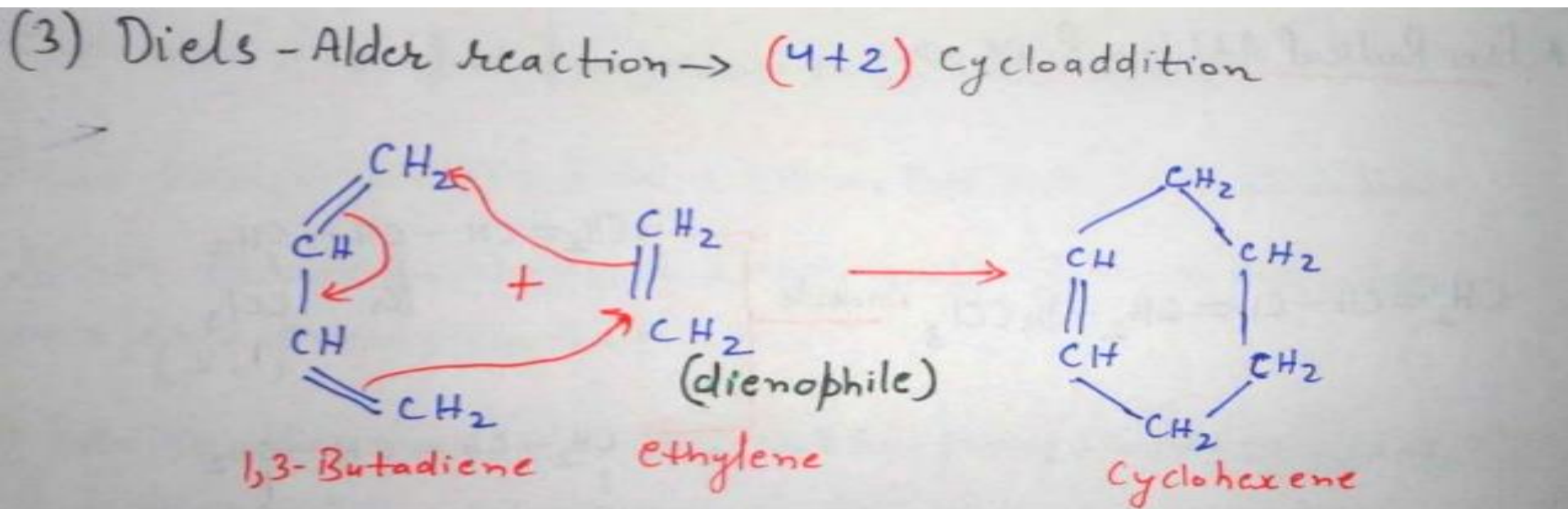
(1,2-Addition)



(1,4-Addition)

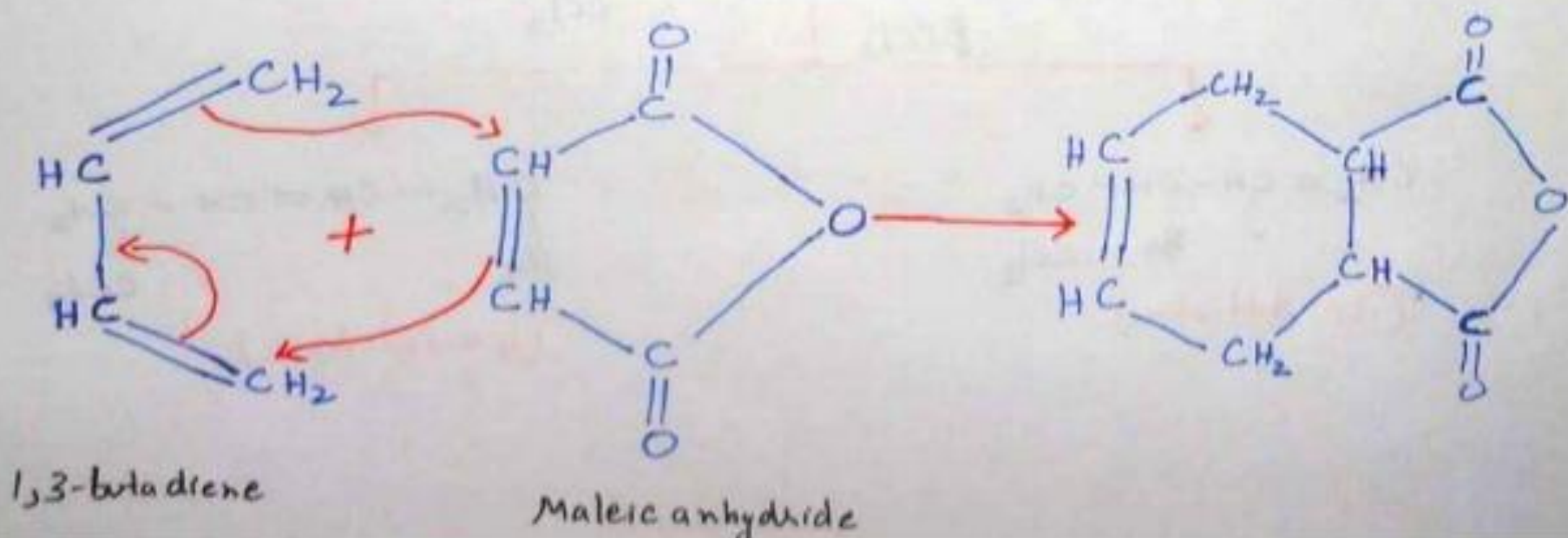
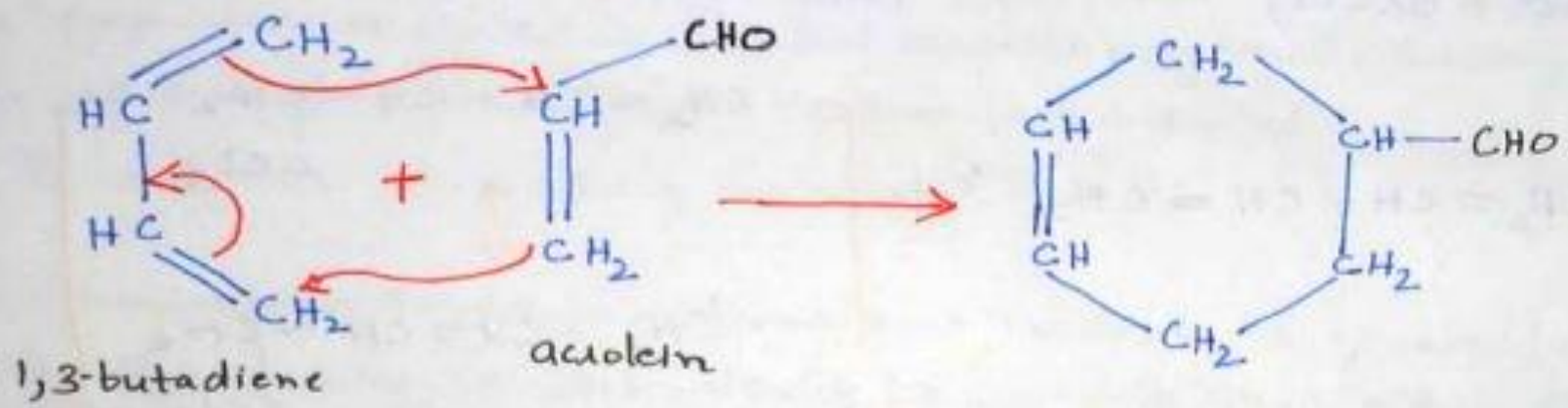
DIELS-ALDER REACTION

The **Diels-Alder reaction** is a cycloaddition reaction between a conjugated diene and an alkene. This reaction produces a 1,4-addition product. A typical example is the reaction of



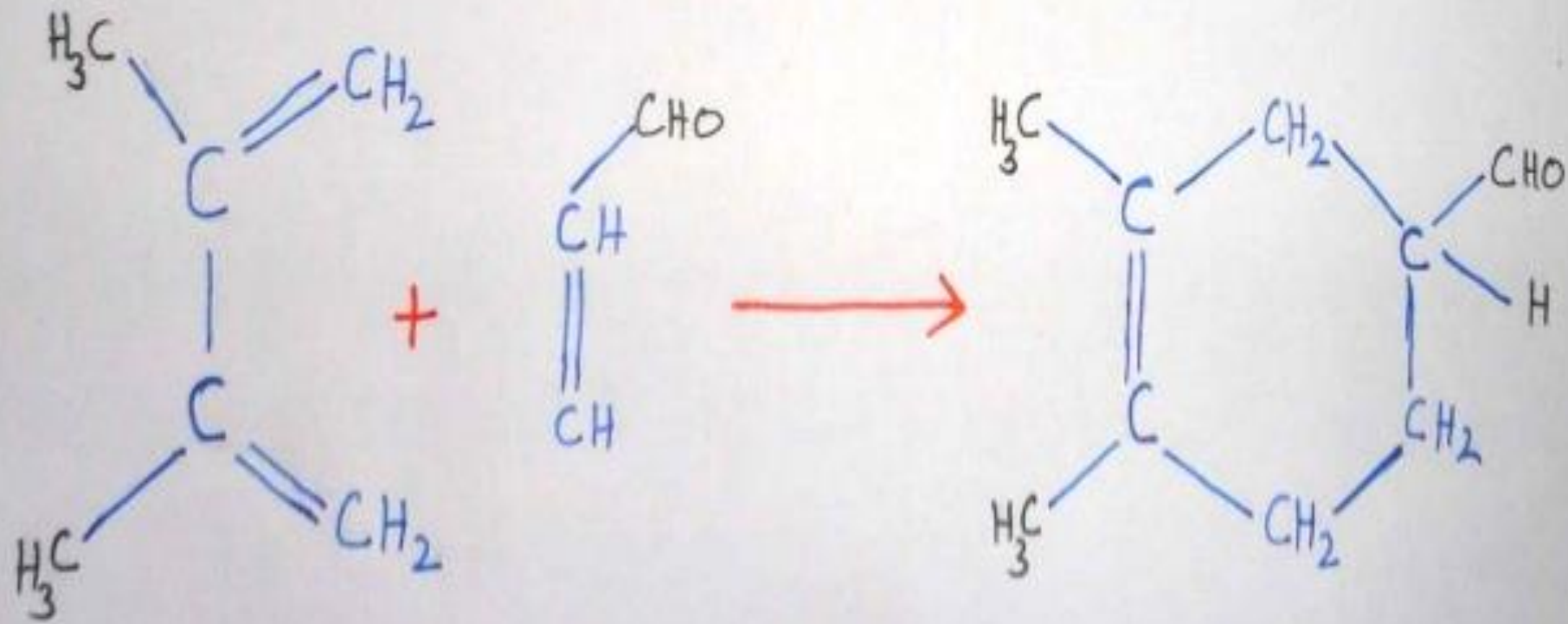
The Diels-Alder reaction is favored by the presence of electron-withdrawing groups on the diene and electron-releasing groups on the dienophile, which is a group or bond that is attracted to a diene.

DIELS-ALDER REACTION TAKES PLACE VERY READILY WHEN SUBSTITUTED ALKENES CONTAINING ELECTRON WITHDRAWING GROUPS ARE USED AS DIENOPHILE FOR example :- ACROLEIN and MALEIC ANHYDRIDE



Factor's which favour the reaction →

- i) Presence of electron withdrawing group in dienophile
- ii) Presence of electron releasing group in diene



End

Of

Lecture