B.Sc. I

Paper II Organic Chemistry

CONJUGATION AND HYPERCONJUGATION

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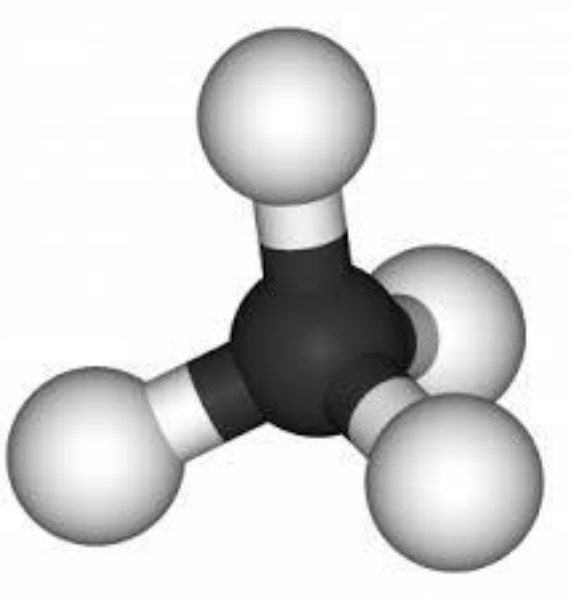
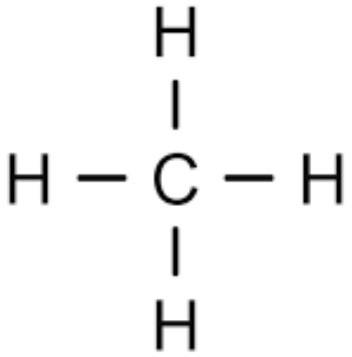
ALIGARH

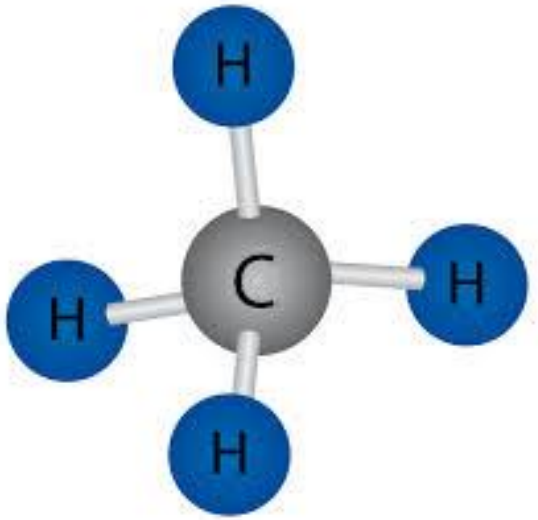
LOCALIZED BOND - SIGMA

A localized bond pair travels between two atoms. All bonds are localized bonds formed between two atoms.

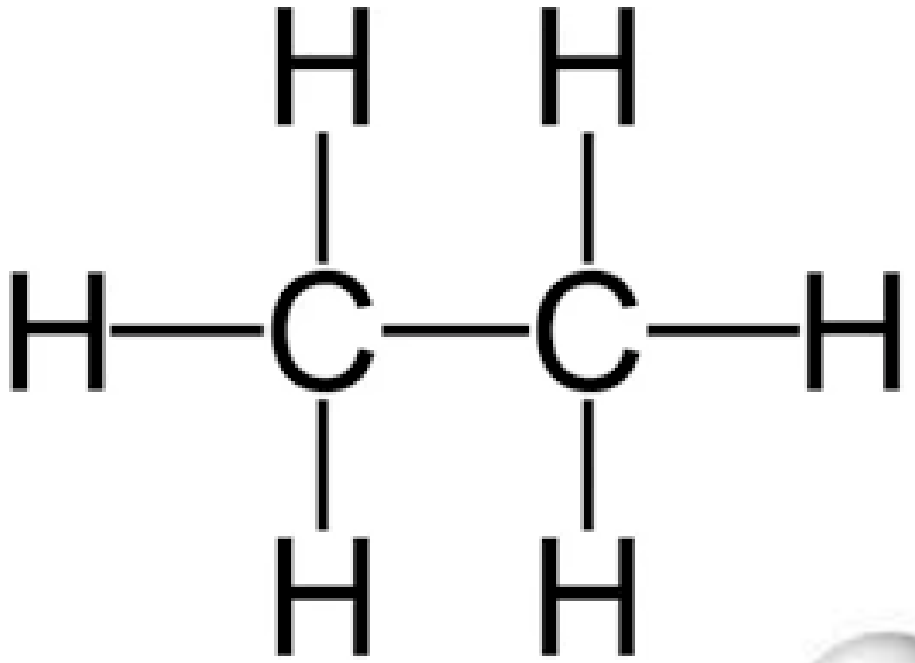


METHANE

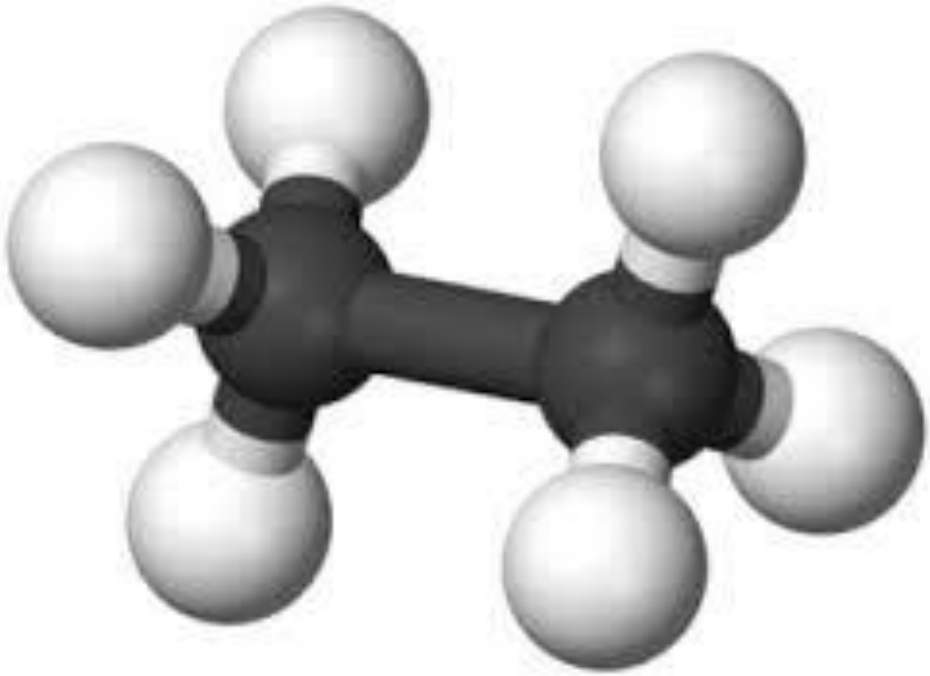




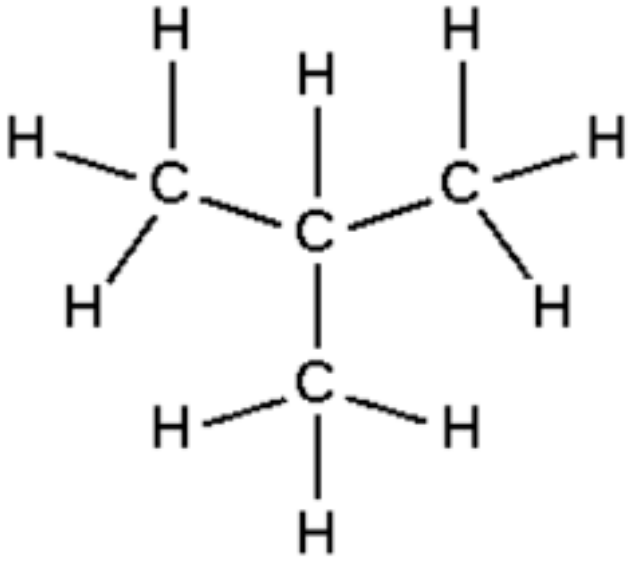
LOCALIZED BOND - SIGMA



ETHANE

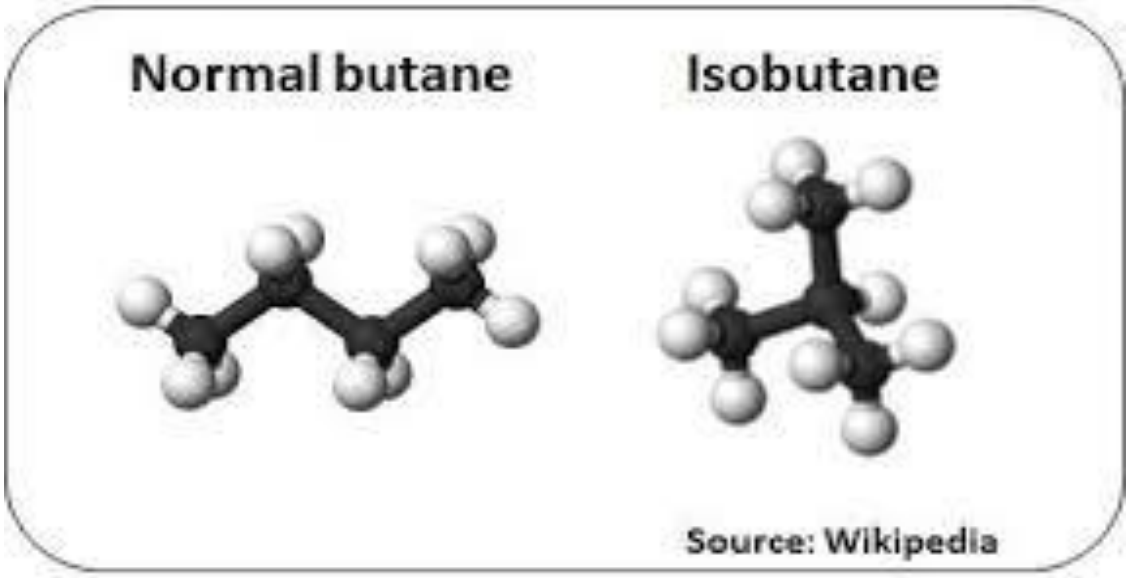


LOCALIZED BOND - SIGMA



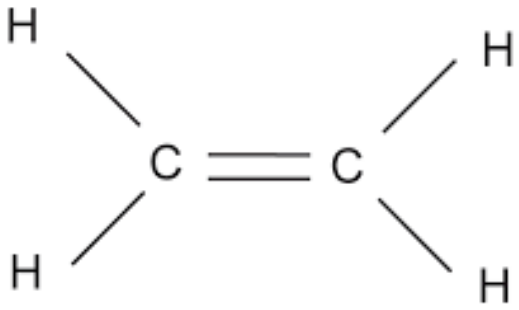
ISOBUTANE

Figure #1

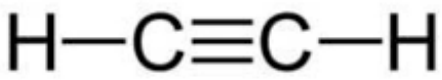


LOCALIZED BONDS – SIGMA, PI

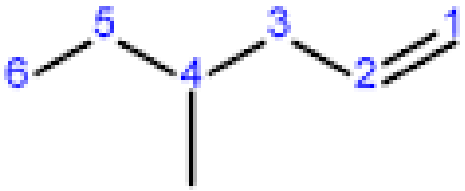
Ethylene



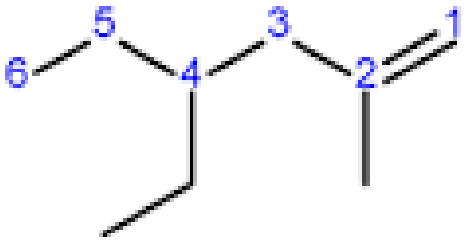
ACETYLENE



hex-1-ene

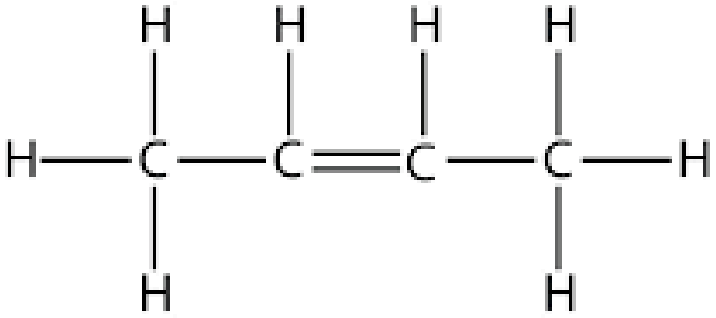


4-methylhex-1-ene

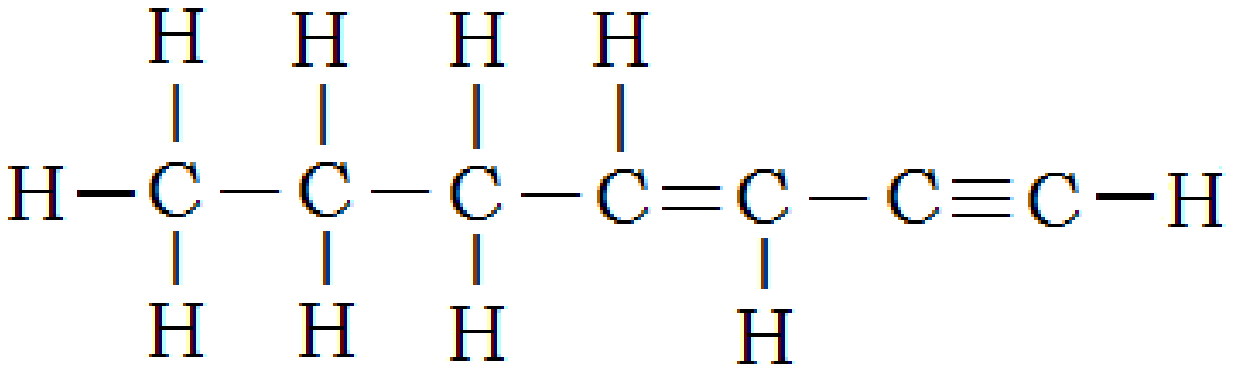


4-ethyl-2-methylhex-1-ene

LOCALIZED BONDS – SIGMA, PI



LOCALIZED

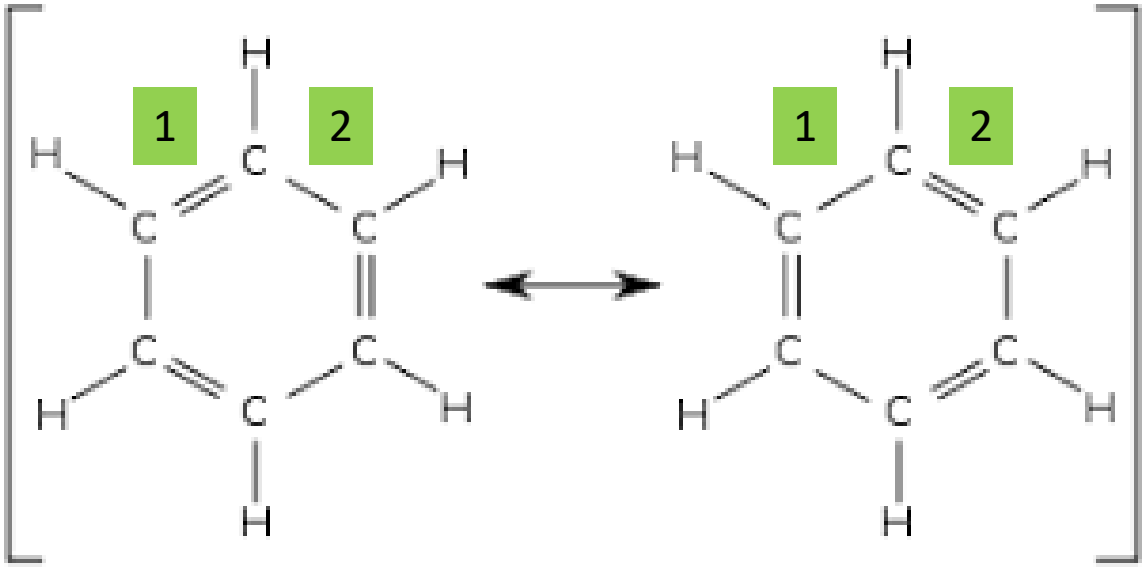


LOCALIZED

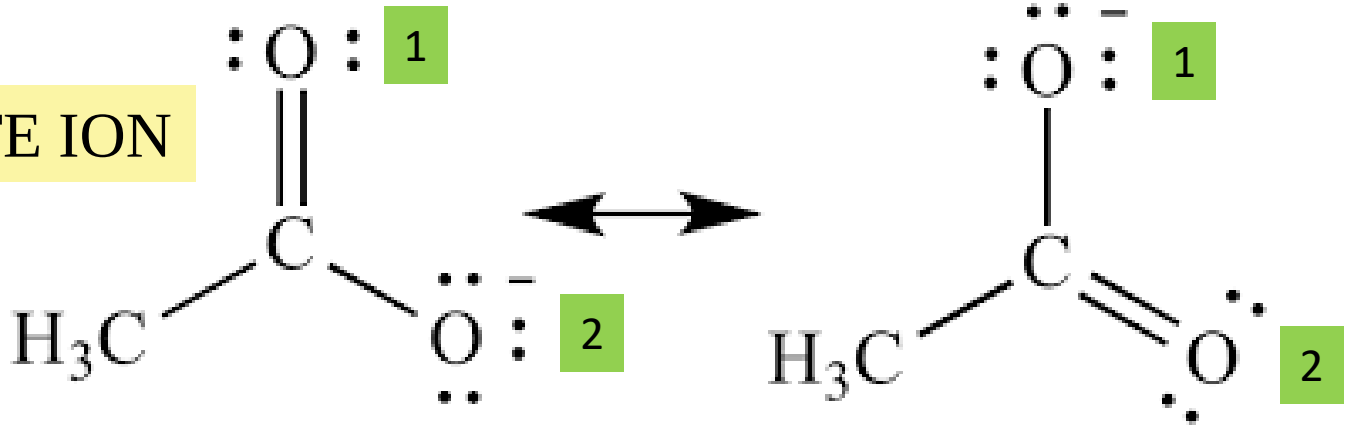
CONJUGATED

DELOCALIZED BONDS – PI and LONE PAIR

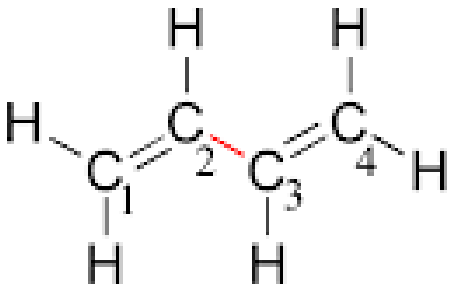
BENZENE

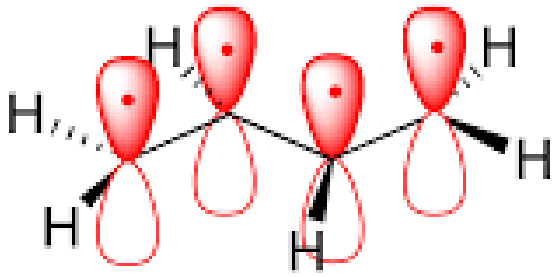


ACETATE ION

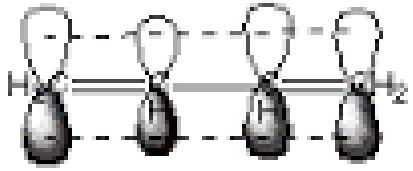


DELOCALIZED BONDS





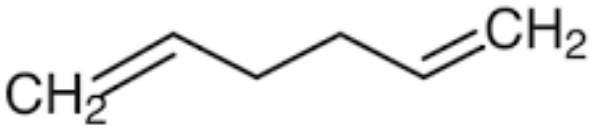
1,3-butadiene



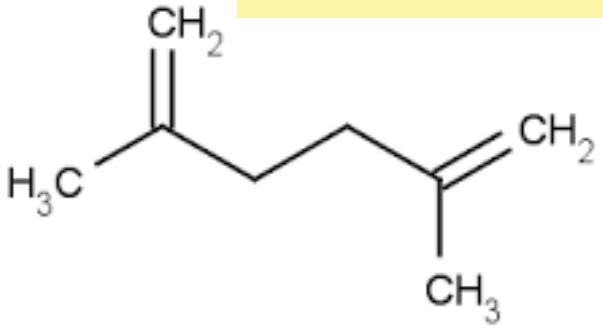
4 AO conjugated system of 1,3-butadiene

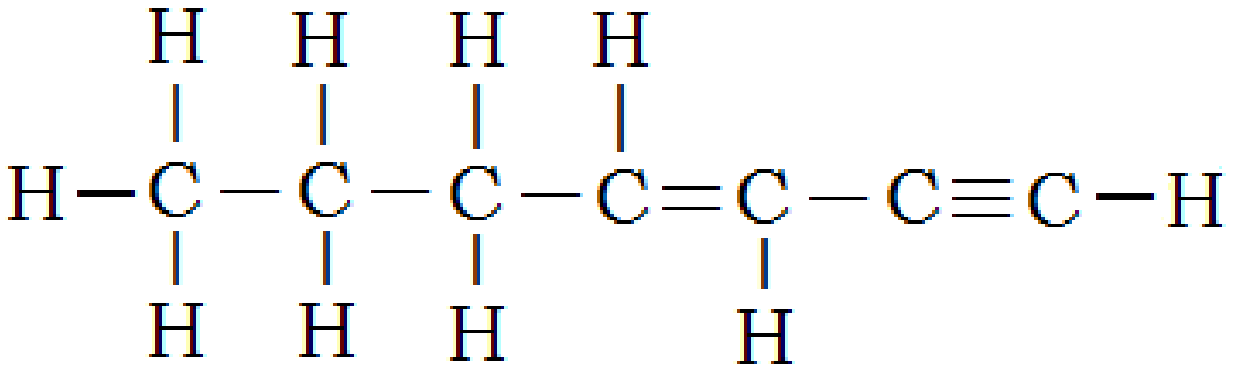
LOCALIZED AND DELOCALIZED BONDS

1. LOCALIZED



2. LOCALIZED





LOCALIZED

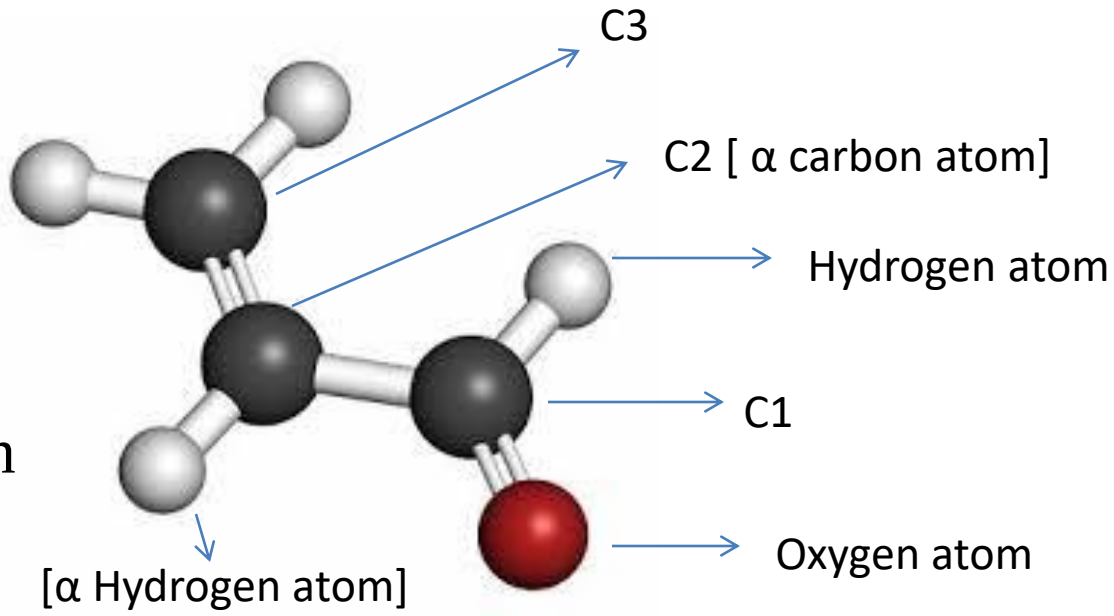
DELOCALIZED

TYPES OF CONJUGATION 1

1. ACROLEIN: [= – =]

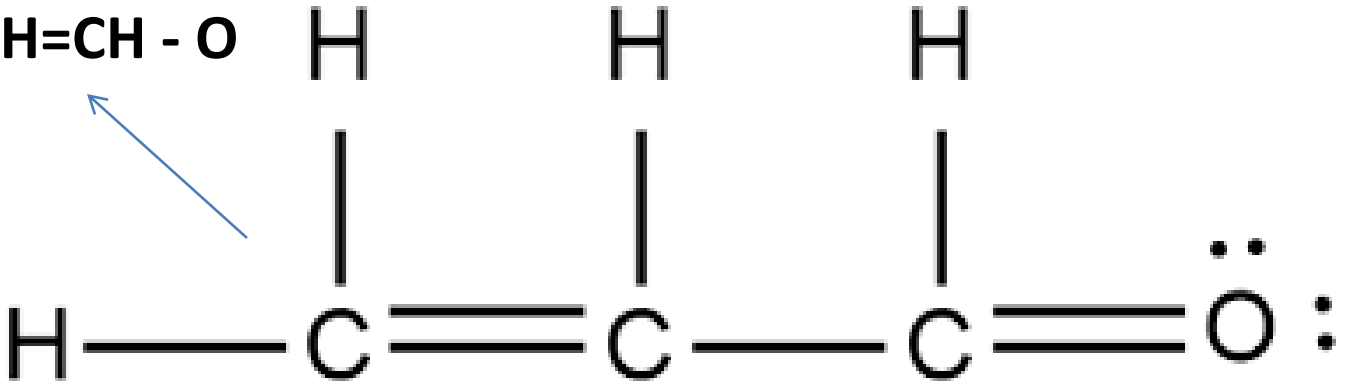
Refer to example 1
in book

Real shape of Acrolein



+ -

CH2 – CH=CH - O



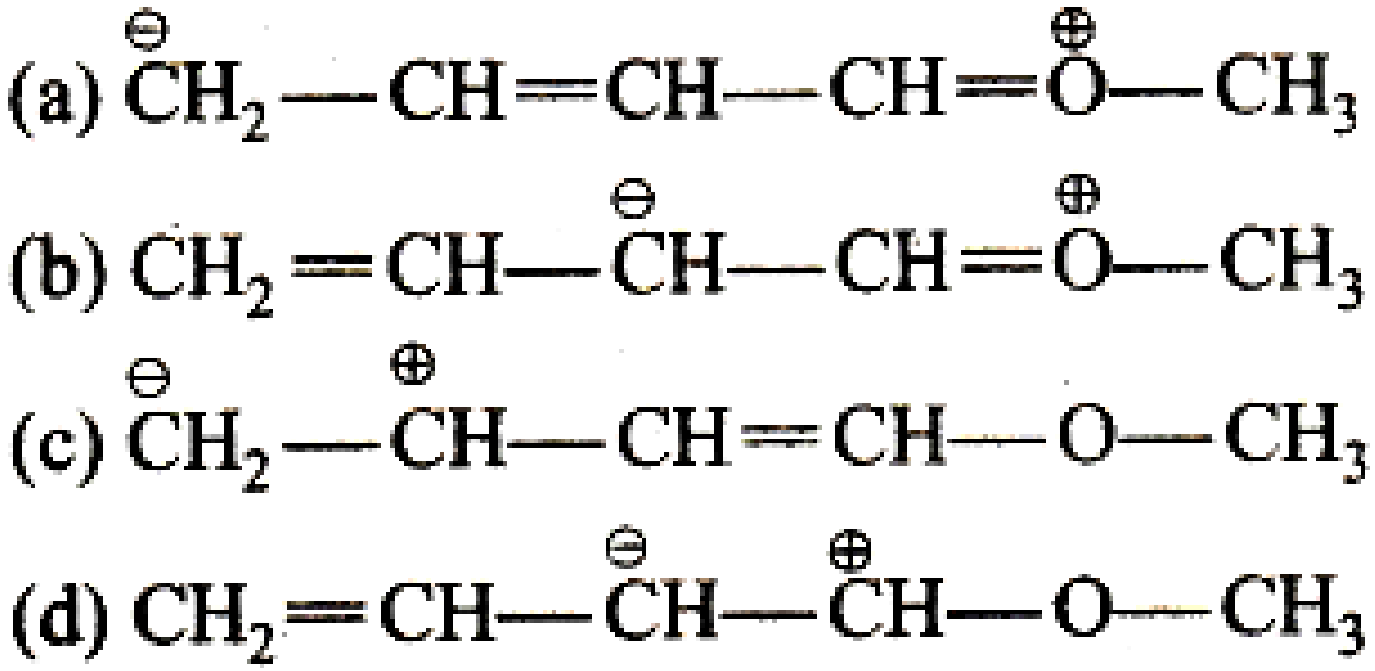
Structure as drawn on paper

TYPES OF CONJUGATION 1

2. [1-methoxy-1, 3-butadiene]

$CH_2=CH-CH=CH-OCH_3$

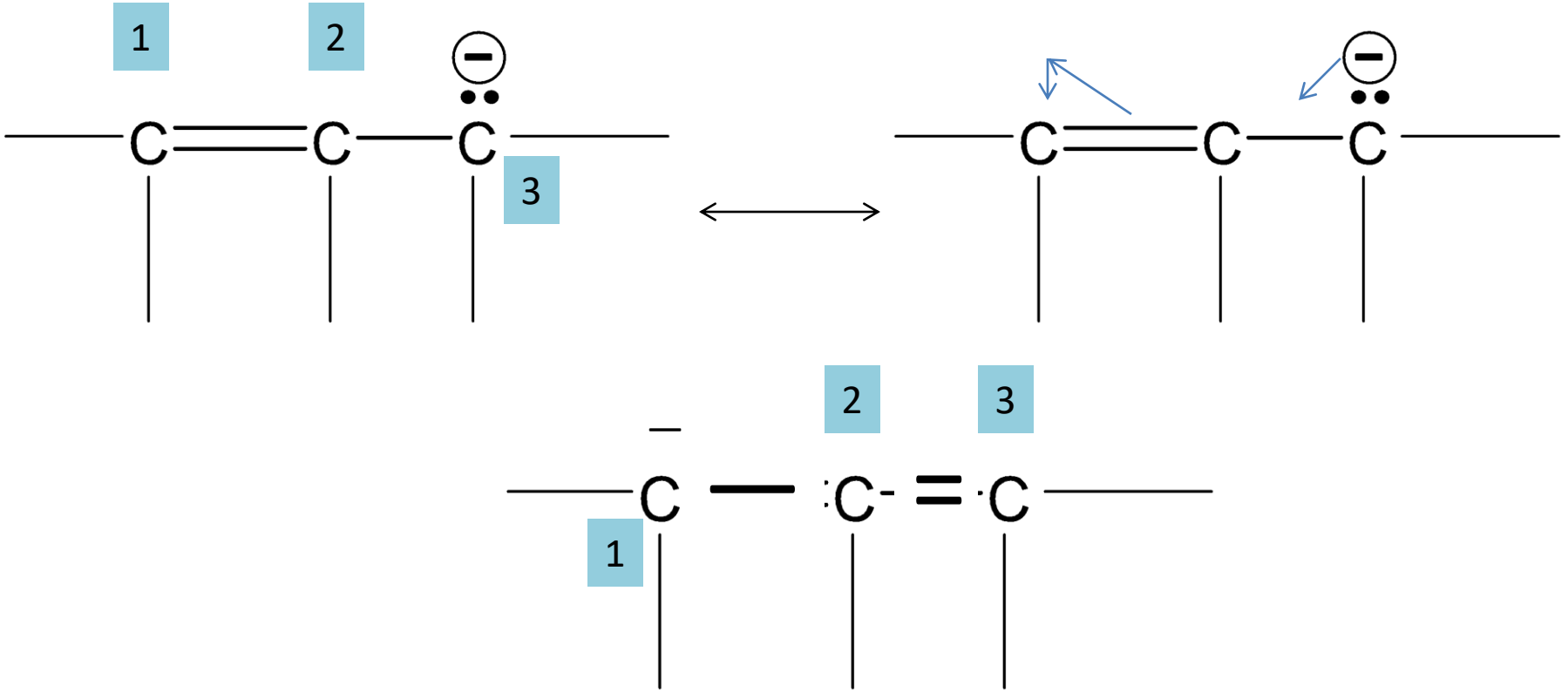
4 3 2 1



TYPES OF CONJUGATION 2

DOUBLE BOND – SINGLE BOND – LONE PAIR OF ELECTRONS

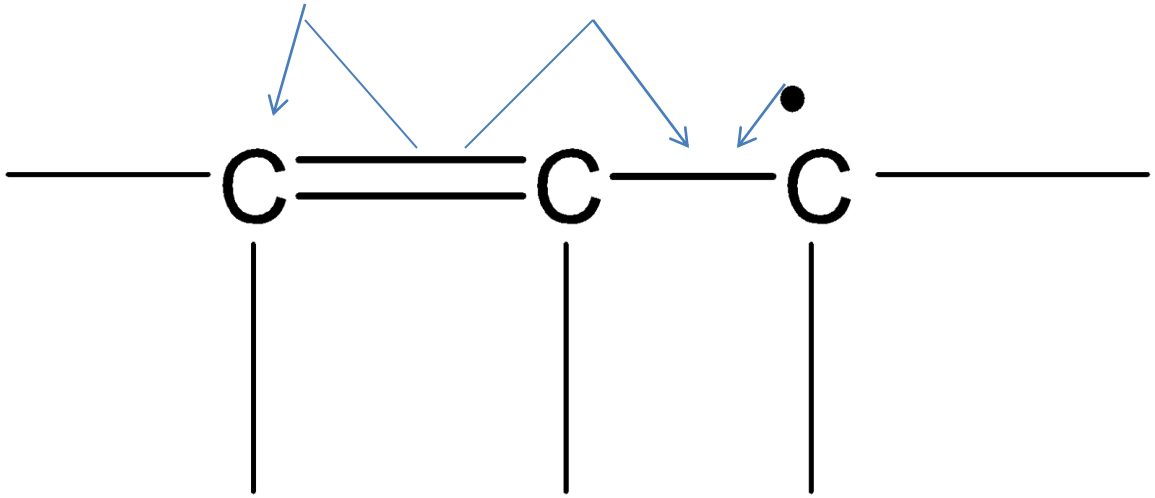
ALLYL ANION /VINYL CHLORIDE



TYPES OF CONJUGATION 3

DOUBLE BOND – SINGLE BOND – ONE ELECTRON/FREE RADICAL

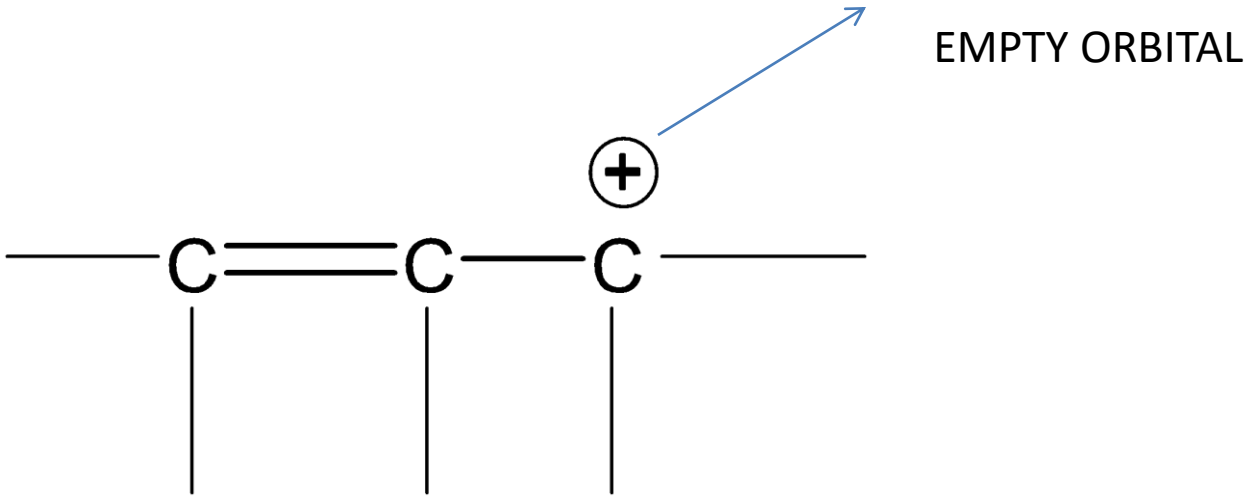
ALLYL FREE RADICAL



TYPES OF CONJUGATION 4

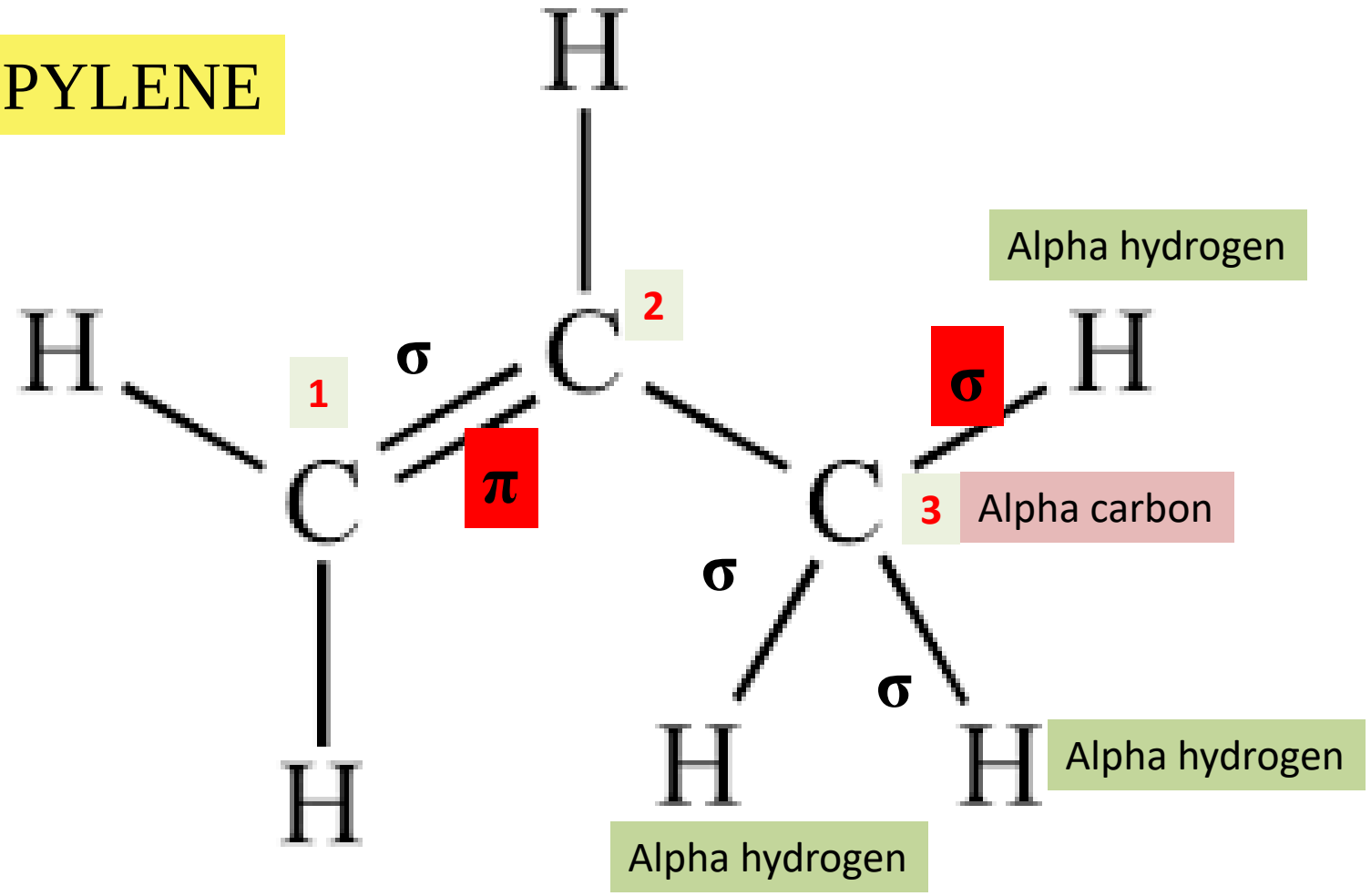
DOUBLE BOND – SINGLE BOND – EMPTY ORBITAL

ALLYL CATION



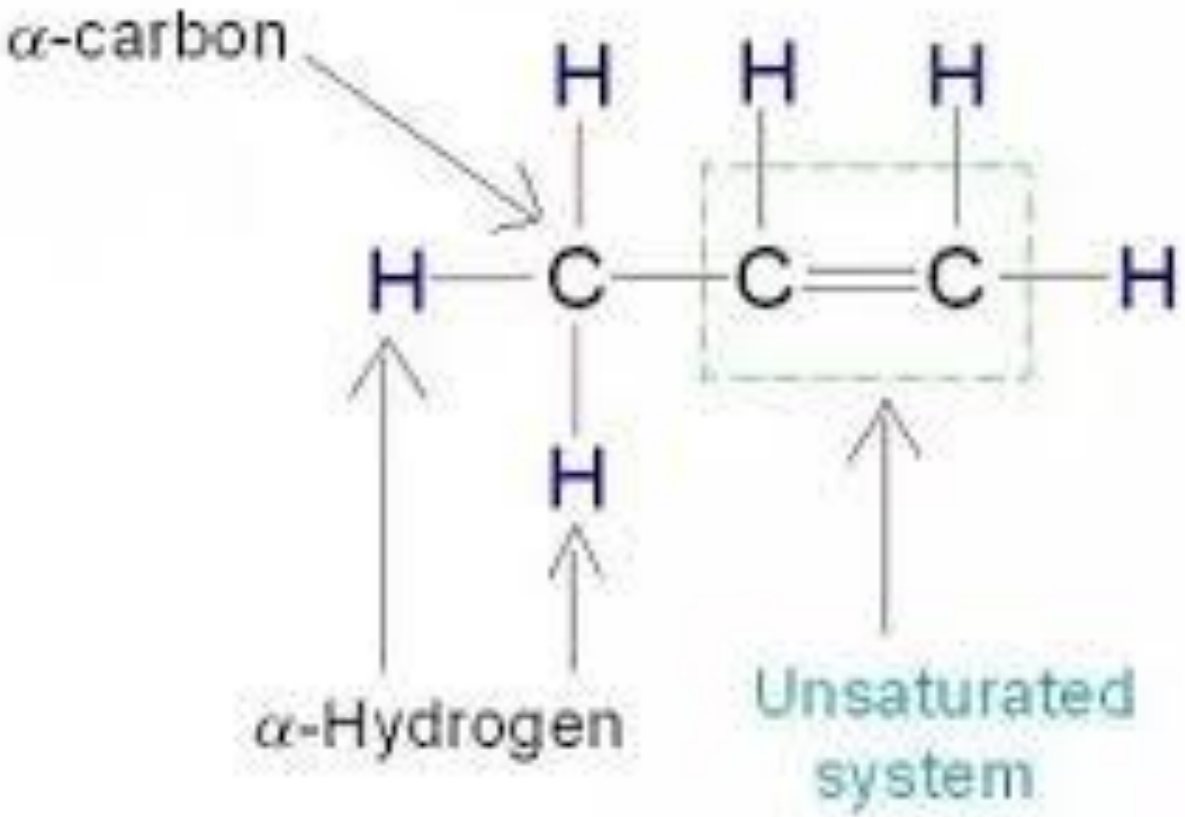
[σ – π] CONJUGATION

PROPYLENE



[σ – π] CONJUGATION

PROPYLENE



HYPERCONJUGATION 5

IMPORTANT POINTS TO REMEMBER:

Carbon atom with at least ONE hydrogen should be attached to a DOUBLE bond. [α Carbon atom]

'Sigma' electrons of C-H are in conjugation with 'Pi' electrons of double bond.

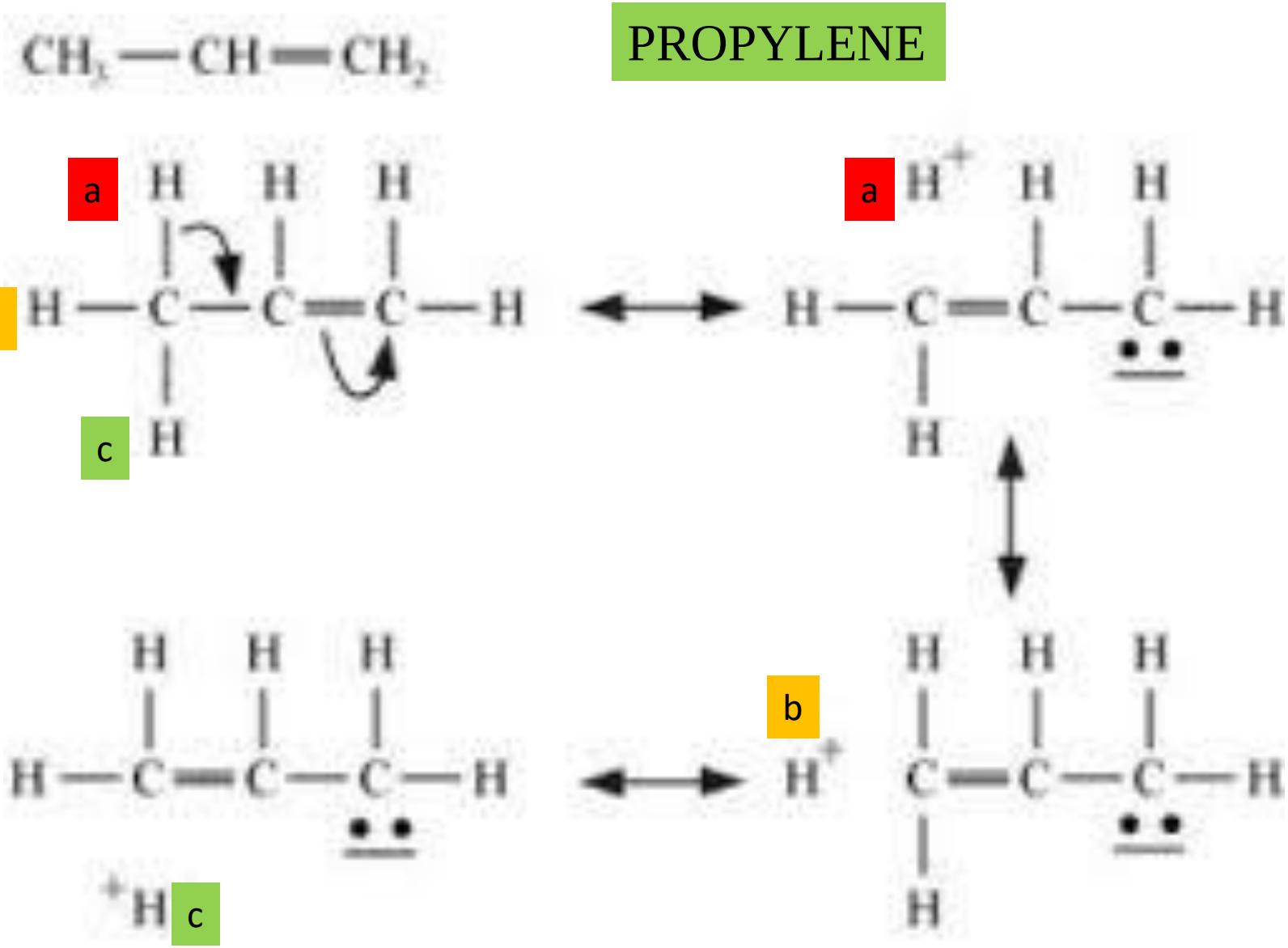
Hyper conjugation involves movement of 'sigma' electrons of C-H bond towards double bond.

The 'sigma' electrons are transferred from α Carbon towards unsaturated carbon.

Thus the double bond gets polarized.

STABILITY OF CARBOCATIONS

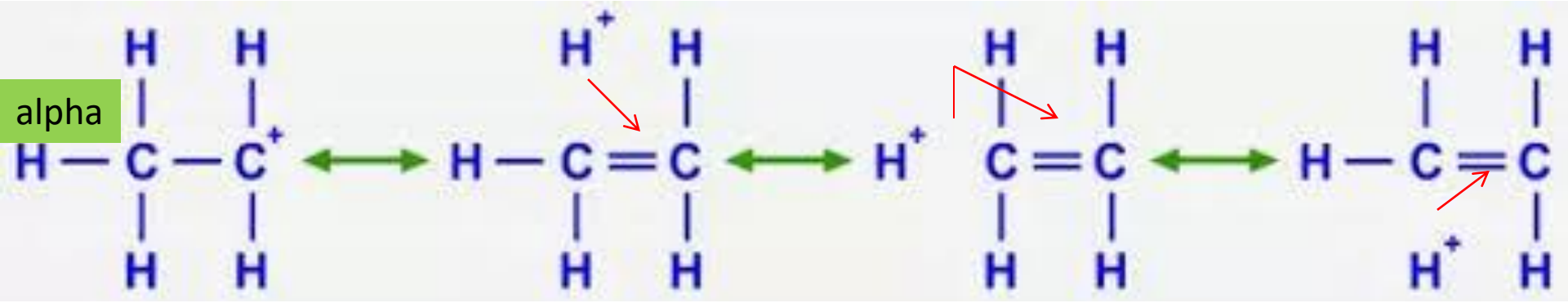
PROPYLENE

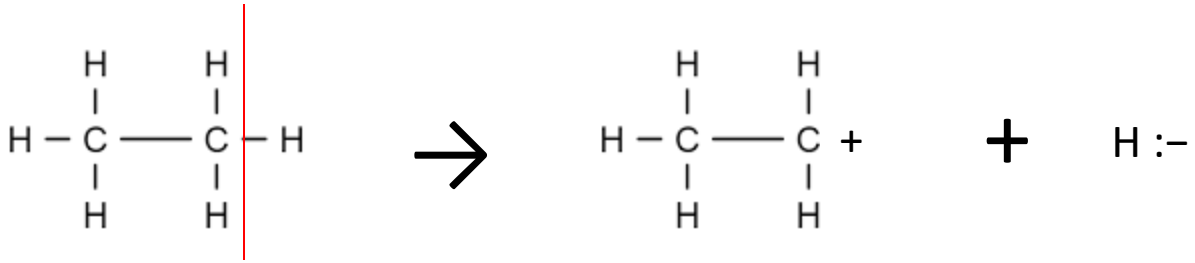


STABILITY OF CARBOCATIONS

ETHANE CATION

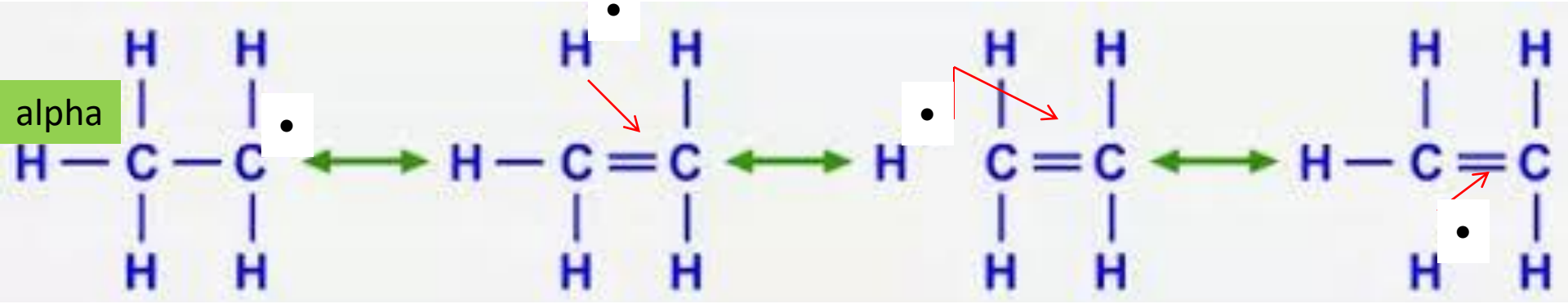
alpha

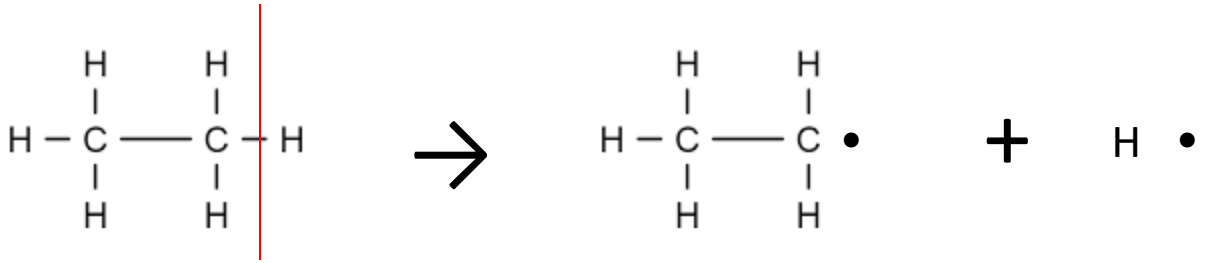




STABILITY OF FREE RADICALS

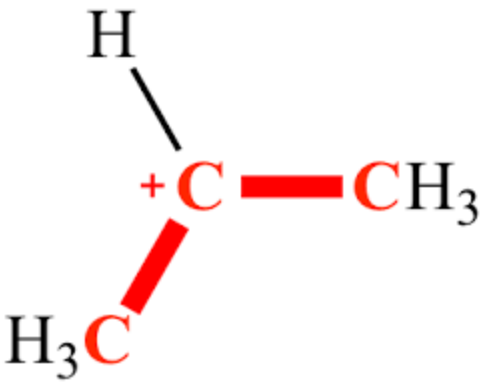
ETHANE FREE RADICAL

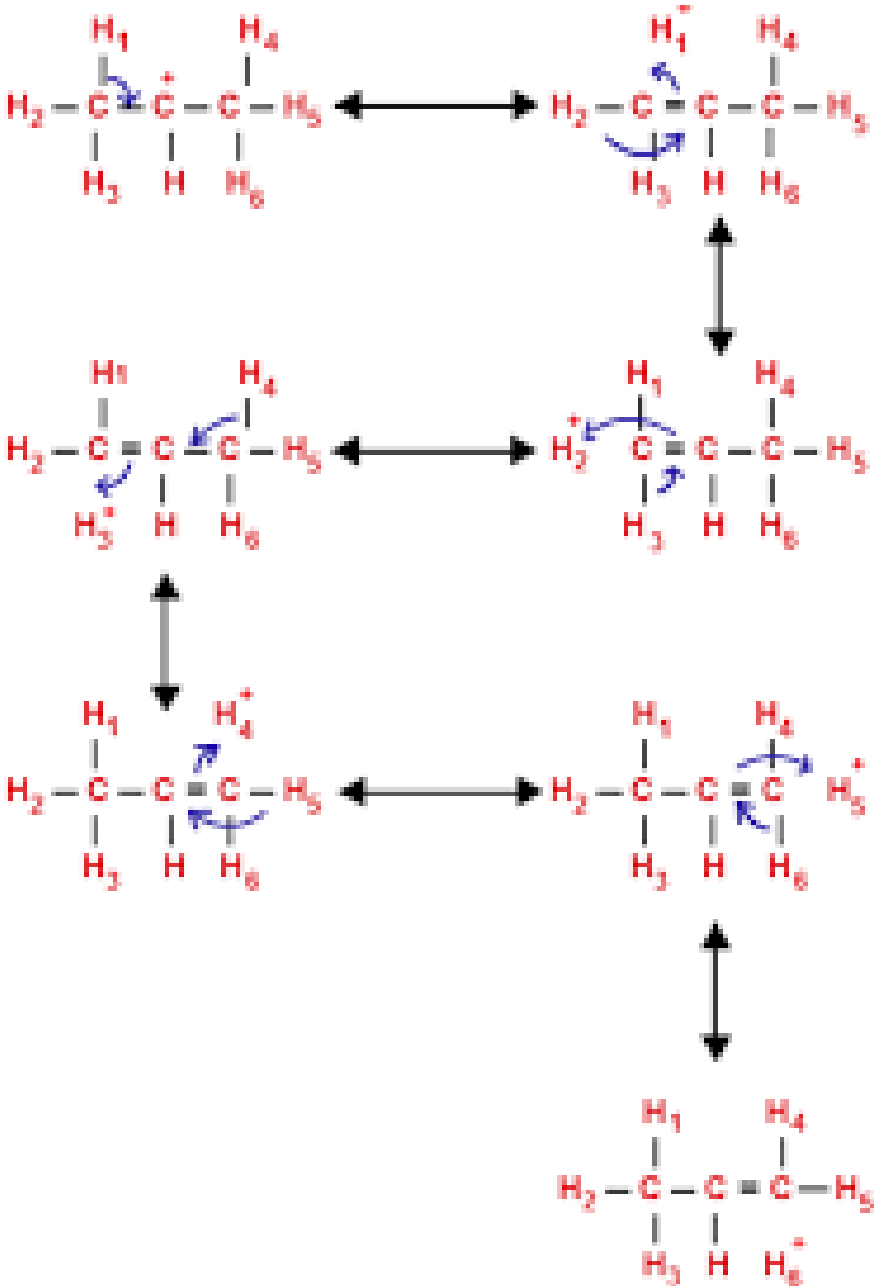




STABILITY OF CARBOCATIONS

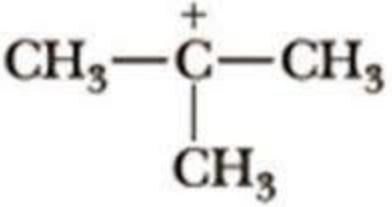
ISO PROPYL CATION



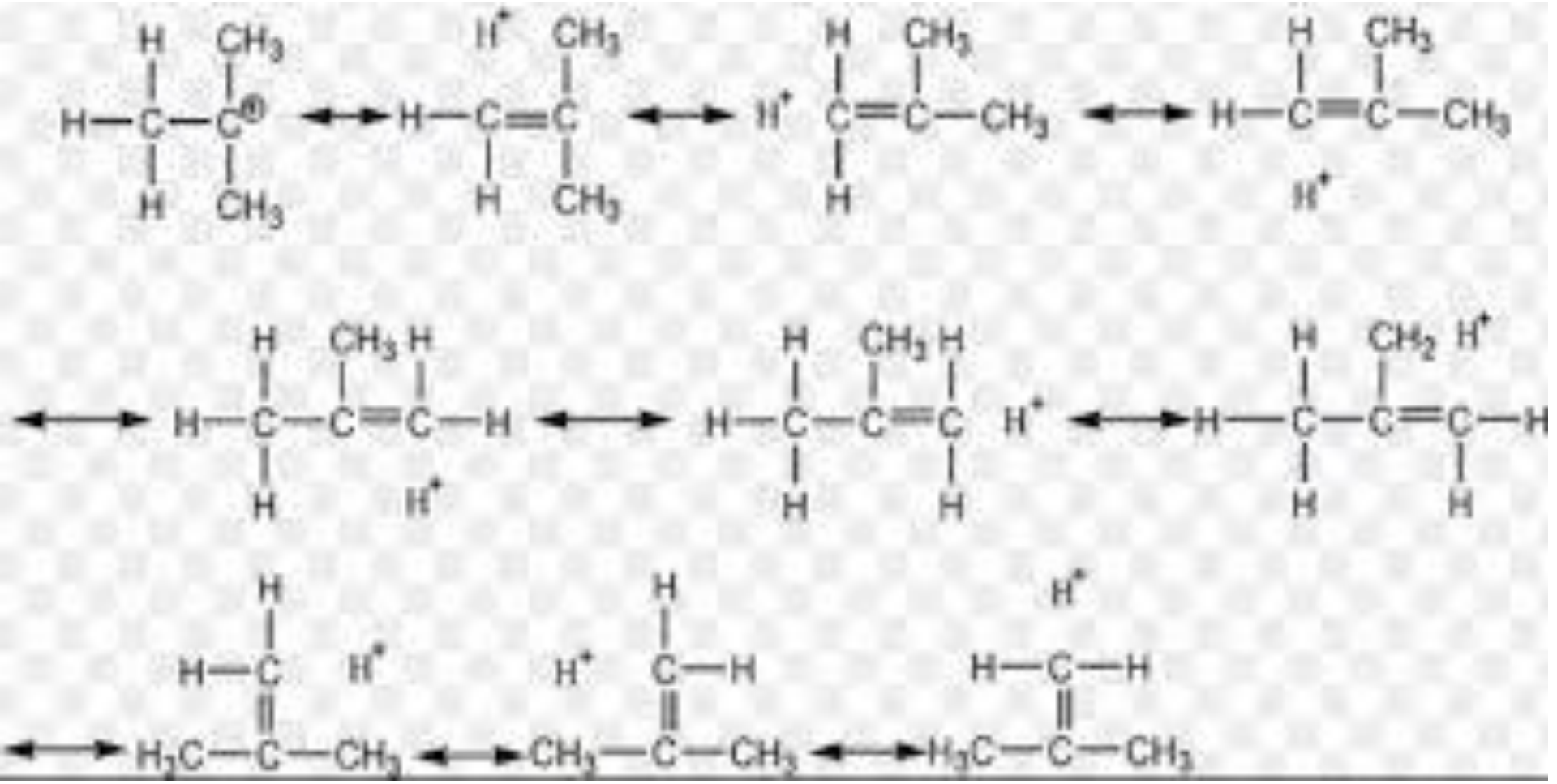


STABILITY OF CARBOCATIONS

TERTIARY BUTYL CATION



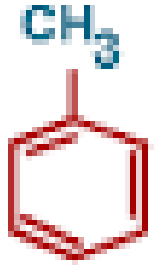
***tert*-Butyl cation**
(a carbocation)



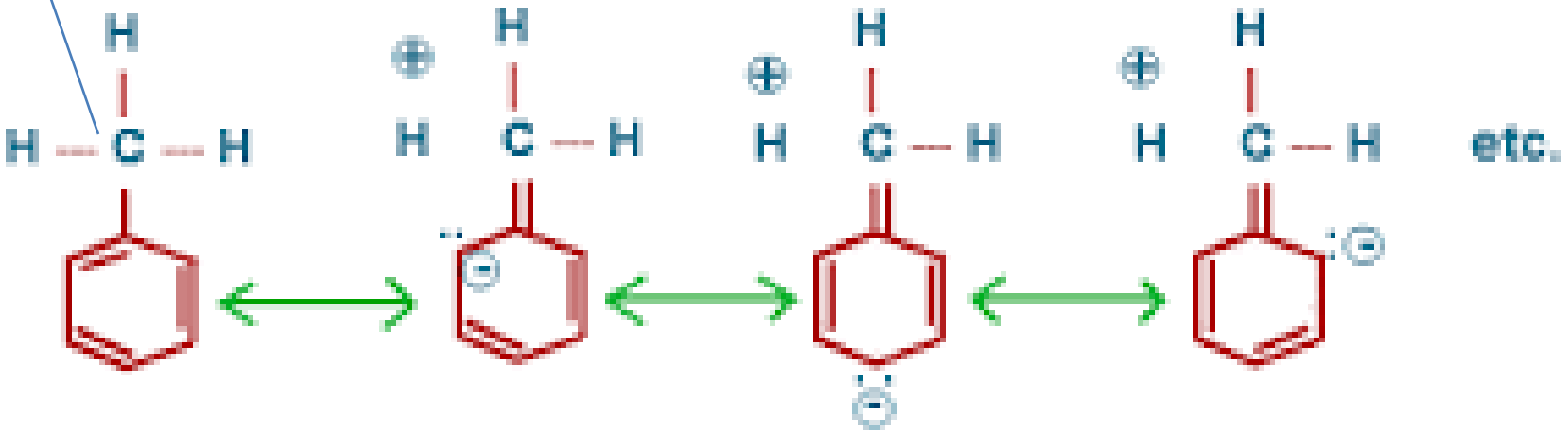
DIRECTIVE INFLUENCE OF ALKYL GROUP ATTACHED TO BENZENE RING

TOLUENE [+ I]

α - CARBON ATOM WITH THREE α - HYDROGENS



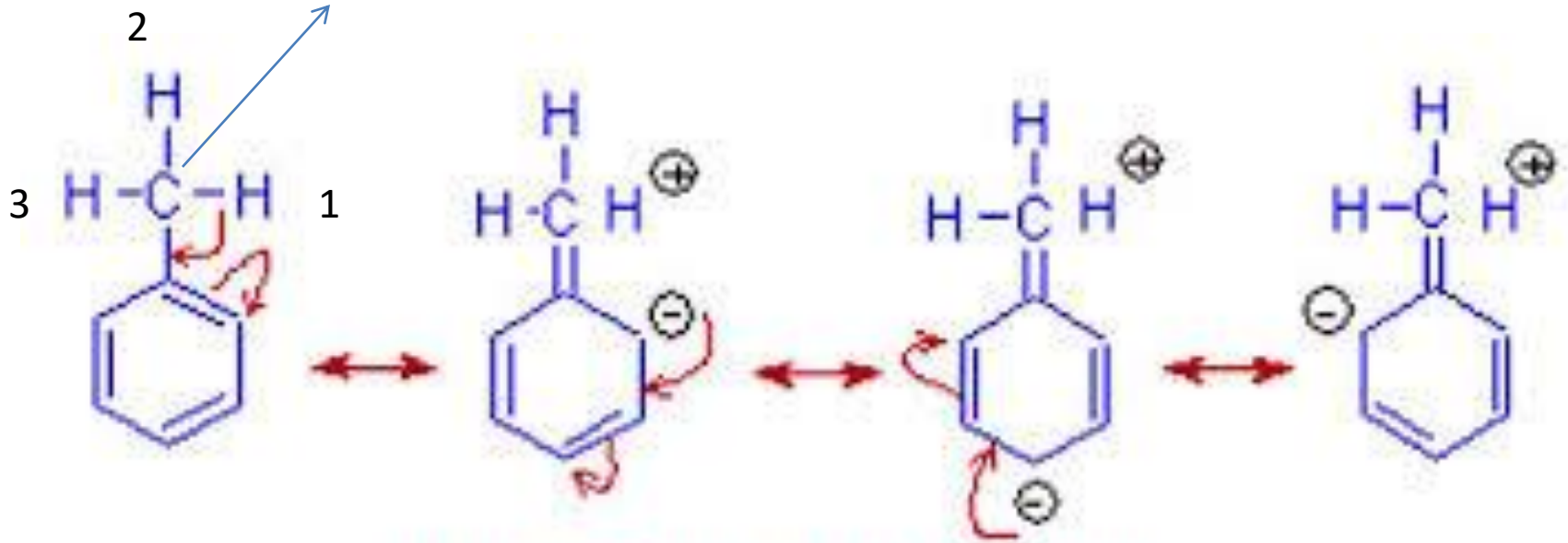
(orientation influence of the methyl group due to +I effect)



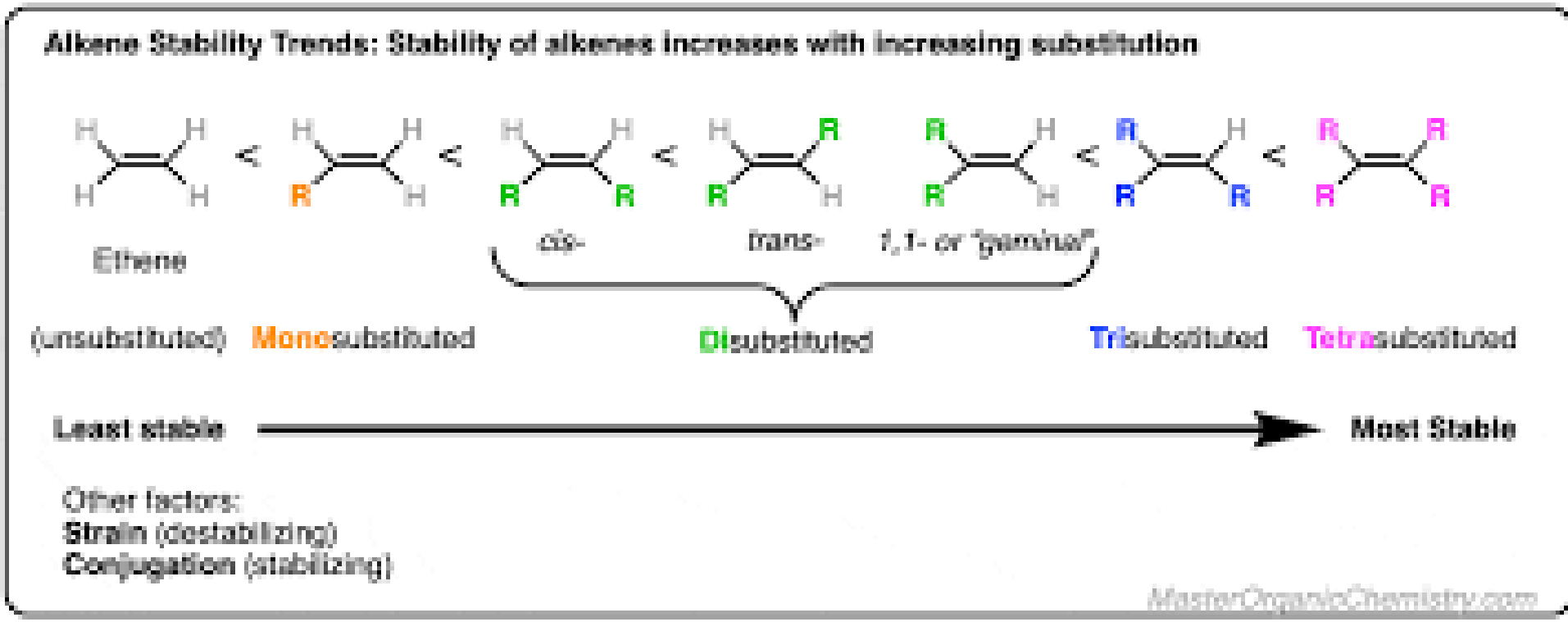
(orientation influence of the methyl group due to hyperconjugation)

DIRECTIVE INFLUENCE OF ALKYL GROUP ATTACHED TO BENZENE RING

α - CARBON ATOM WITH THREE α - HYDROGENS



RELATIVE STABILITY OF ALKENES DUE TO HYPERCONJUGATION

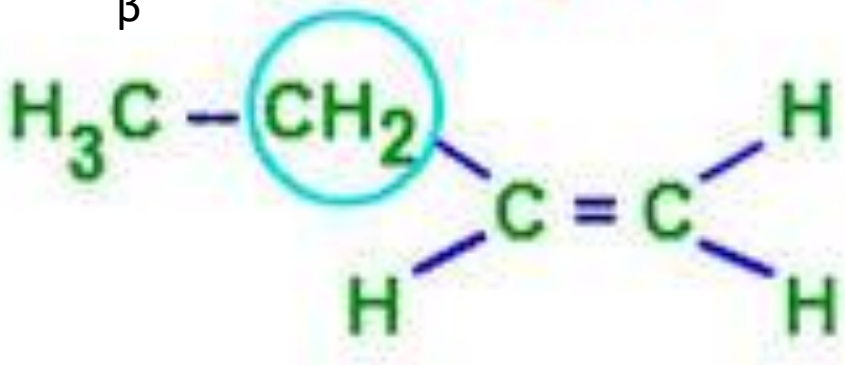


RELATIVE STABILITY OF ALKENES DUE TO HYPERCONJUGATION

α carbon with

2 hydrogen

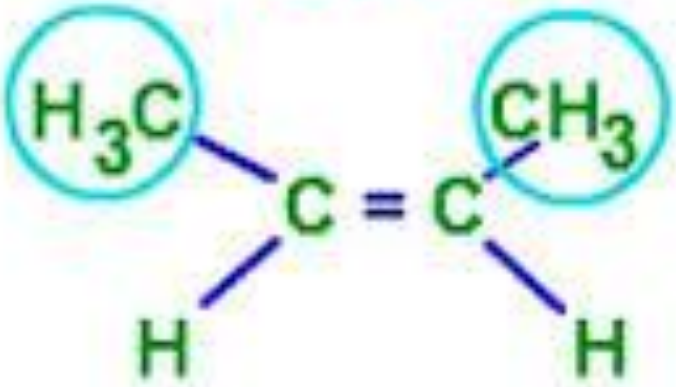
β



1 - butene

α carbon with

6 hydrogen



2 - butene

ADDITION OF HYDROGEN BROMIDE TO ALLYL BROMIDE

If Inductive effect takes place then 1, 3 Di bromo propane is formed

If Hyper conjugative effect takes place then **1,2 Di bromo propane** is formed.

HYPERCONJUGATIVE EFFECT IS STRONGER THAN INDUCTIVE EFFECT

ADDITION OF HYDROGEN BROMIDE TO ALLYL BROMIDE

HYPERCONJUGATIVE EFFECT

$$[1]HBr \rightarrow \overset{+}{H} + \overset{-}{Br}$$

[2] Hyper conjugation Effect

$$CH_2 = \underset{[\alpha]}{CH}-CH_2-Br \leftrightarrow CH_2 = CH-\overset{H}{\underset{|}{CH}}-Br \leftrightarrow \overset{-}{CH_2} - \overset{+}{CH}-CH-Br$$

$$\overset{-}{CH_2}- \overset{+}{CH}-CH-Br + \overset{+}{H} + \overset{-}{Br} \rightarrow CH_2 - \underset{H}{CH}-\underset{Br}{CH}-Br$$

$$\rightarrow CH_3- CHBr-CH_2Br$$

1, 2 Di Bromo Propane

ADDITION OF HYDROGEN BROMIDE TO ALLYL BROMIDE

INDUCTIVE EFFECT

$$[1]\ HBr \rightarrow \overset{+}{H} + \overset{-}{Br}$$

[2]

$$CH_2 = CH{-}CH_2{-}Br \leftrightarrow CH_2 = CH{-}CH_2{->}{-}Br \leftrightarrow \overset{+}{C}H_2 - CH{-}CH_2{-}\overset{-}{B}r$$

[3]

$$\overset{+}{C}H_2 - CH{-}CH_2{-}Br + \overset{+}{H} + \overset{-}{Br} \rightarrow \overset{Br}{CH2}{-}\overset{H}{CH}{-}\ CH_2{-}\ Br$$

$$\rightarrow CH2Br{-}CH2{-}CH2Br$$

1, 3 Di Bromo Propane

HYPERCONJUGATION

VERSUS

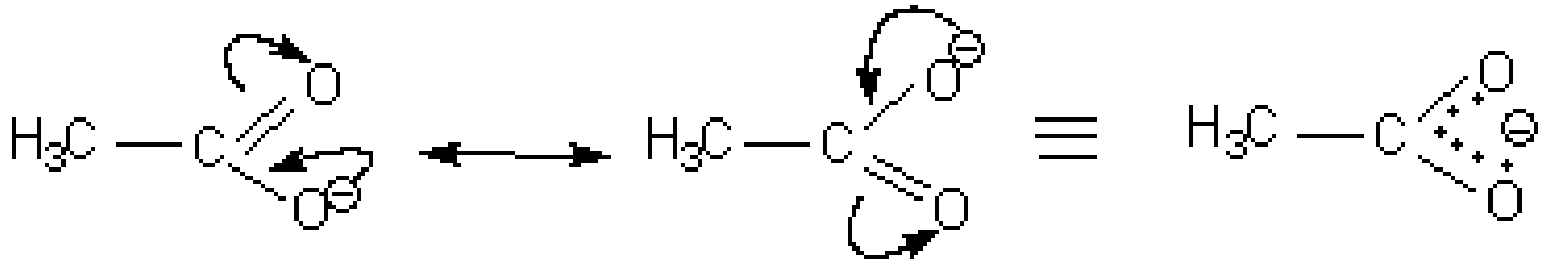
RESONANCE

HYPERCONJUGATION	RESONANCE
Hyperconjugation is the stabilization effect on a molecule due to the interaction between a sigma bond and a pi bond	Resonance is the stabilizing of a molecule through delocalization of bonding electrons in the pi orbital
Involves sigma bond orbitals and p orbitals or pi bond orbitals	Involves only pi bond orbitals
Causes the sigma bond length to be shortened	Has no effect on sigma bonds

RESONANCE VERSUS HYPERCONJUGATION

Resonance involves movement of ‘pi’ electrons or lone pair of electrons.

EXAMPLE 1 – ACETATE ION



EXAMPLE 2 – PHENOL