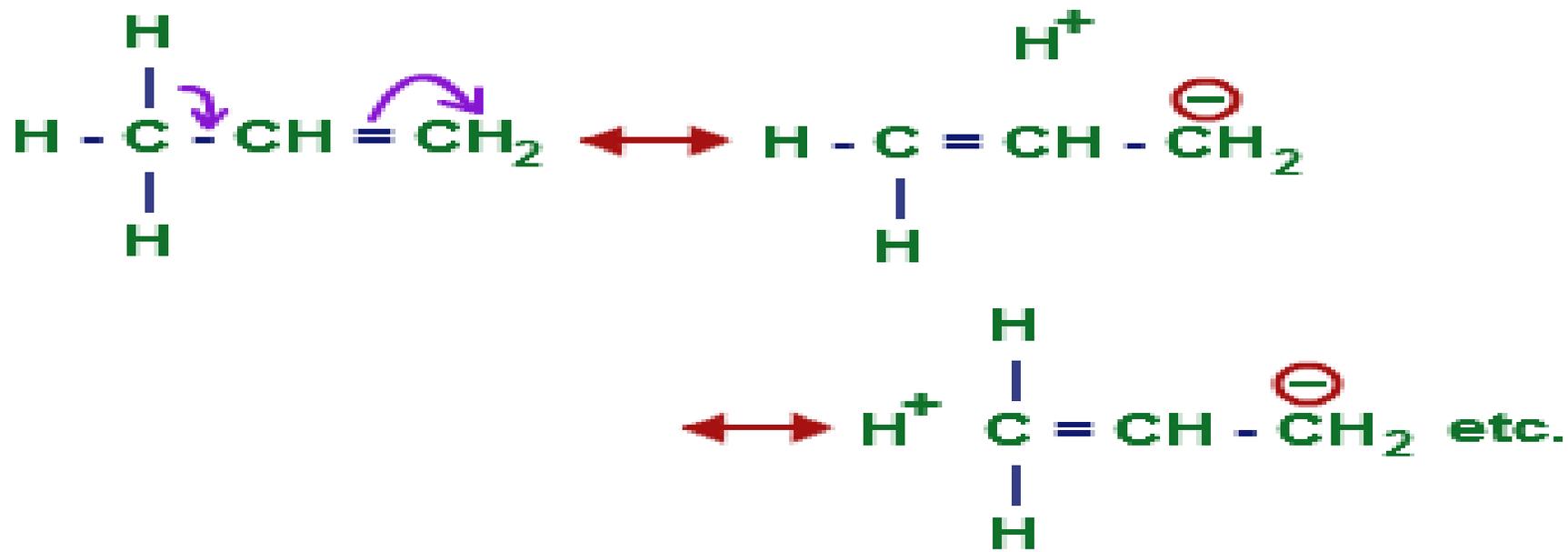


Hyperconjugation

- Devyani Joshi

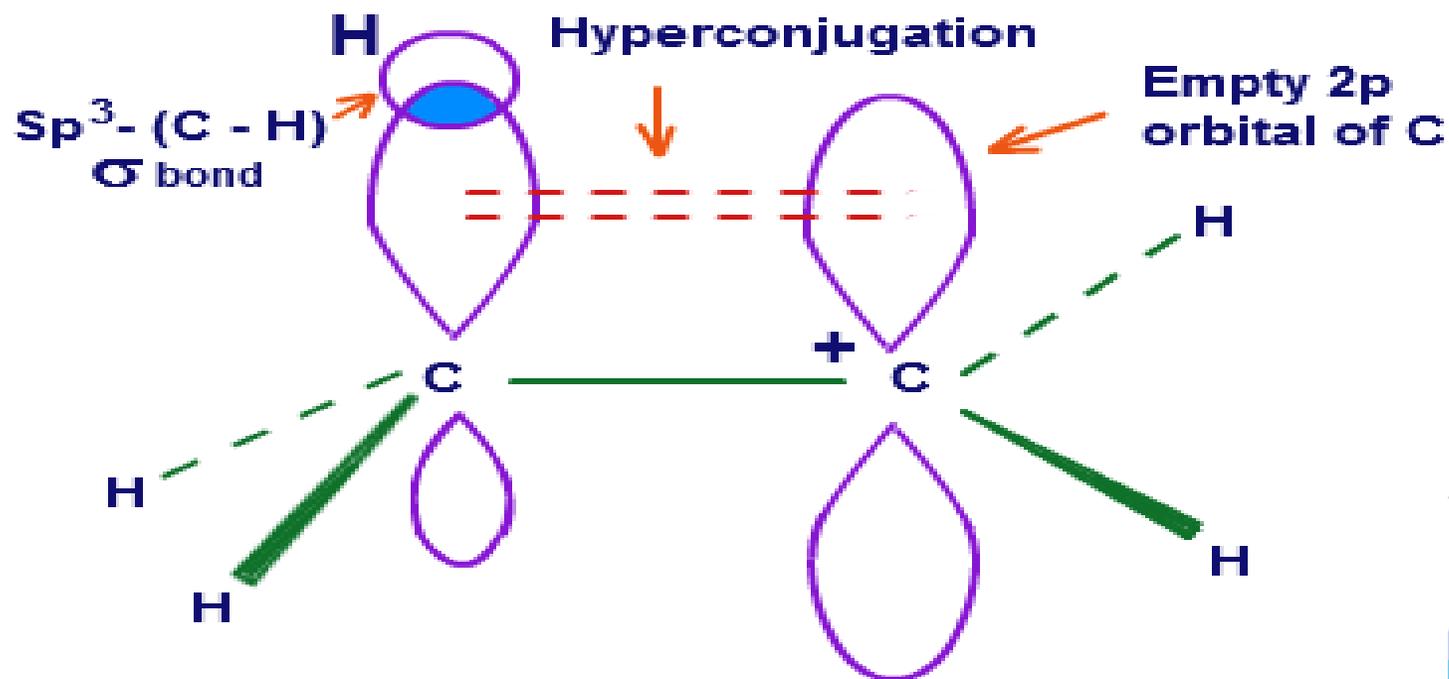
- ▶ Resonance involves delocalization of π electrons, leaving the σ bond untouched.
- ▶ However in some cases, a σ bond and an adjacent π bond may get involved in resonance.
- ▶ Such a delocalization is called as Hyperconjugation.



- Stabilizing effect of the molecule
- Interaction of sigma (σ) bond (eg. C – H, C – C) with a pi (π) network.

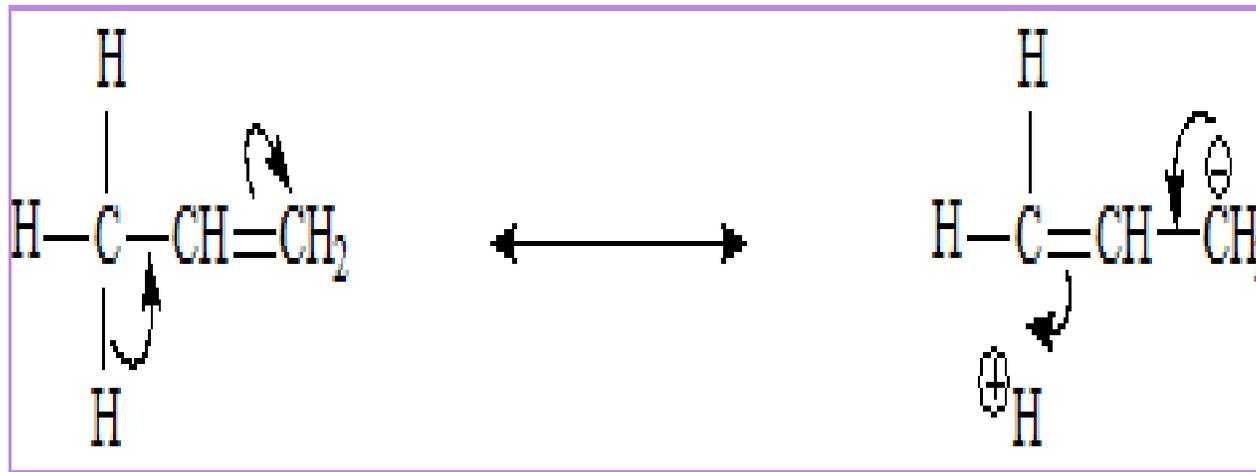
- ▶ When carbon possessing at least one Hydrogen is attached to another carbon bearing an unshared orbital or to an unsaturated carbon, there are more than one structure (canonical forms) possible for the molecule.
- ▶ These result from the overlap of the bonding electrons of C – H σ bond with 2p or π orbital of the adjacent carbon atom.
- ▶ As a result, the bond between carbon and hydrogen does not exist anymore.

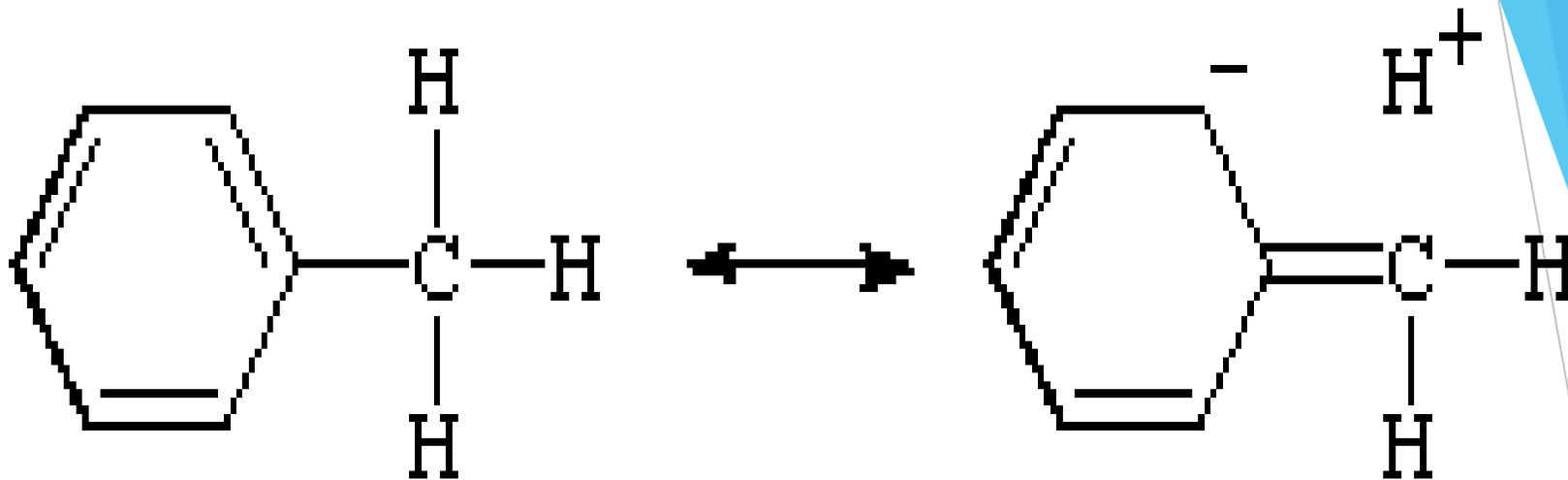
- ▶ The shared pair of electrons is now borne by carbon alone and hydrogen is in its close proximity as proton.
- ▶ The negative charge developed on the carbon gets delocalized by overlap with adjacent p orbital.



Hyperconjugation: No bond resonance

- ▶ The electrons of the sigma bond between C and H are involved in delocalization.
- ▶ In structure to the right: No bond between C and H due to migration of the sigma bond. Hence Hyperconjugation is also called as ‘NO BOND RESONANCE’.
- ▶ This does not indicate that hydrogen is completely detached from the structure, but some degree of ionic character in the C – H bond and some single bond character between carbon – carbon double bond.



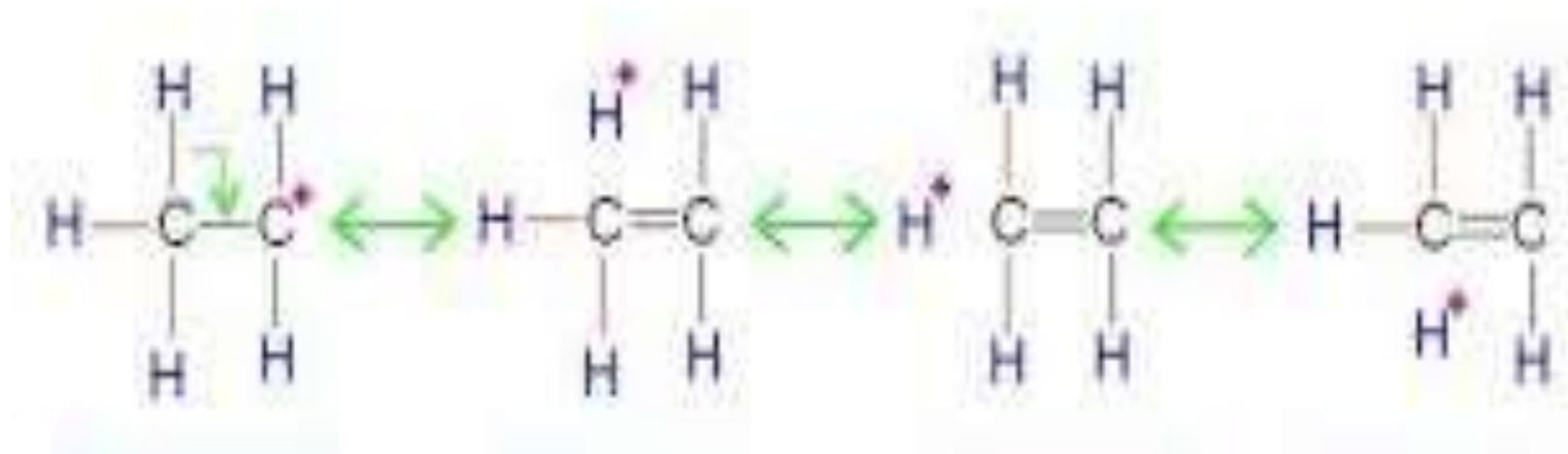


- ▶ Such an interaction is also referred to as ‘Heterovalent’ or ‘Sacrificial hyperconjugation’.
- ▶ This is so named because the contributing structure contains one two-electron bond less than the normal Lewis formula of the compound.
- ▶ At present, there is no evidence of sacrificial hyperconjugation with neutral hydrocarbons

Effect of
Hyperconjugation on
the chemical
properties:

Alkyl cations and their relative stability

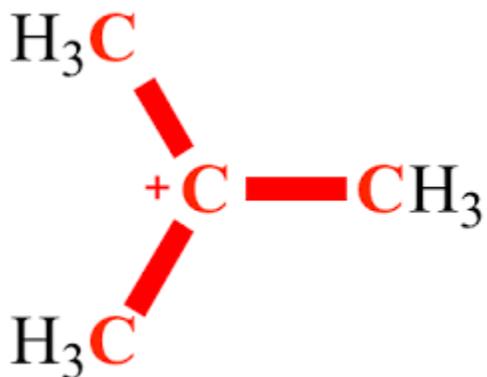
- ▶ Carbocations have an electron deficient (positively charged) carbon.
- ▶ The empty p orbital of this sp^2 carbon can overlap with σ orbital of C – H bond of adjacent alkyl group (α C – H bond).
- ▶ This overlap permits individual electrons to help bind together three nucleus: 2 carbon and 1 hydrogen.
- ▶ The positive charge thus gets dispersed over large volume of space and is stabilized.



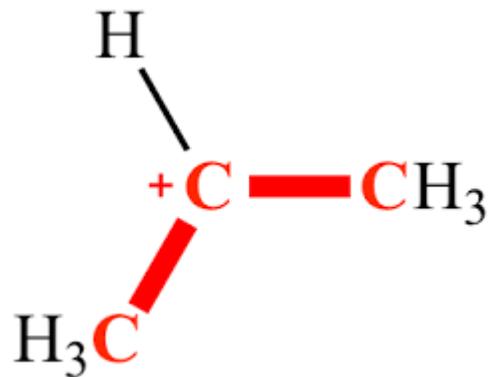
▶ The more the number of alkyl groups on the carbocation, more is the number of α C – H σ bonds and hence more are the possibilities for hyperconjugation which makes the carbocation more stable.

▶ The order of stability of the Carbocations is:

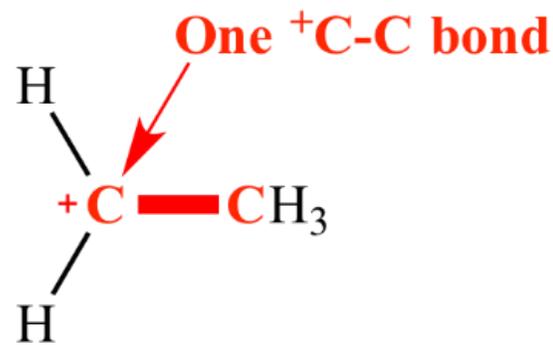
3^oalkyl carbocation > 2^oalkyl carbocation > 1^oalkyl carbocation > methyl carbocation



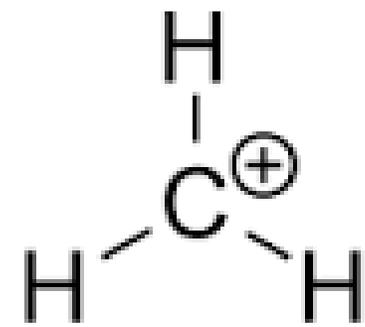
9
Hyperconjugable
H



6
Hyperconjugable
H



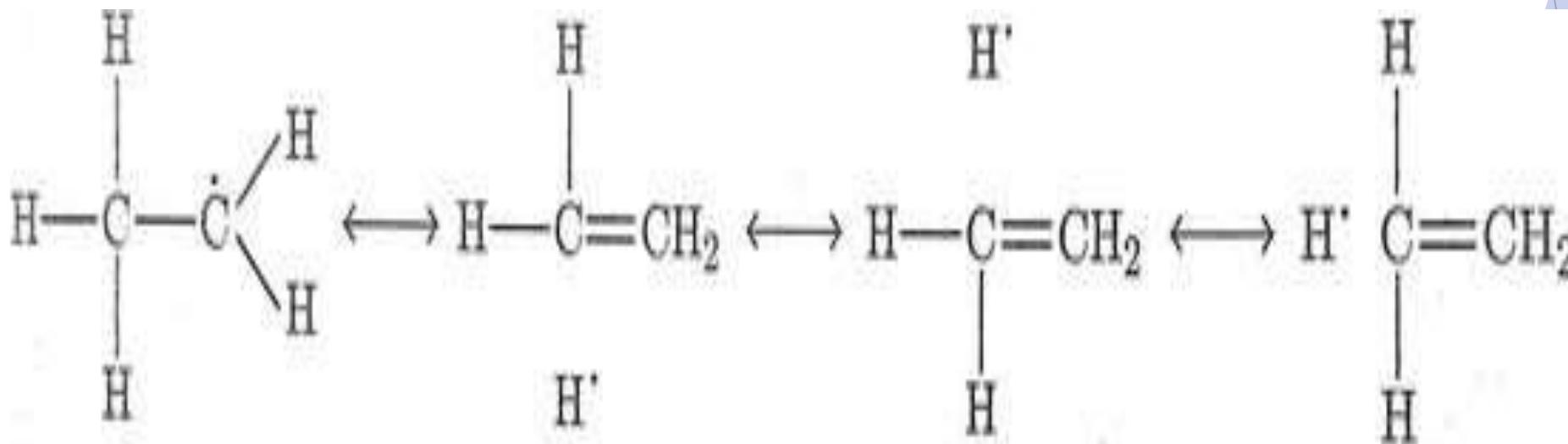
3
Hyperconjugable
H



No
Hyperconjugable
H

Alkyl radicals and their relative stability:

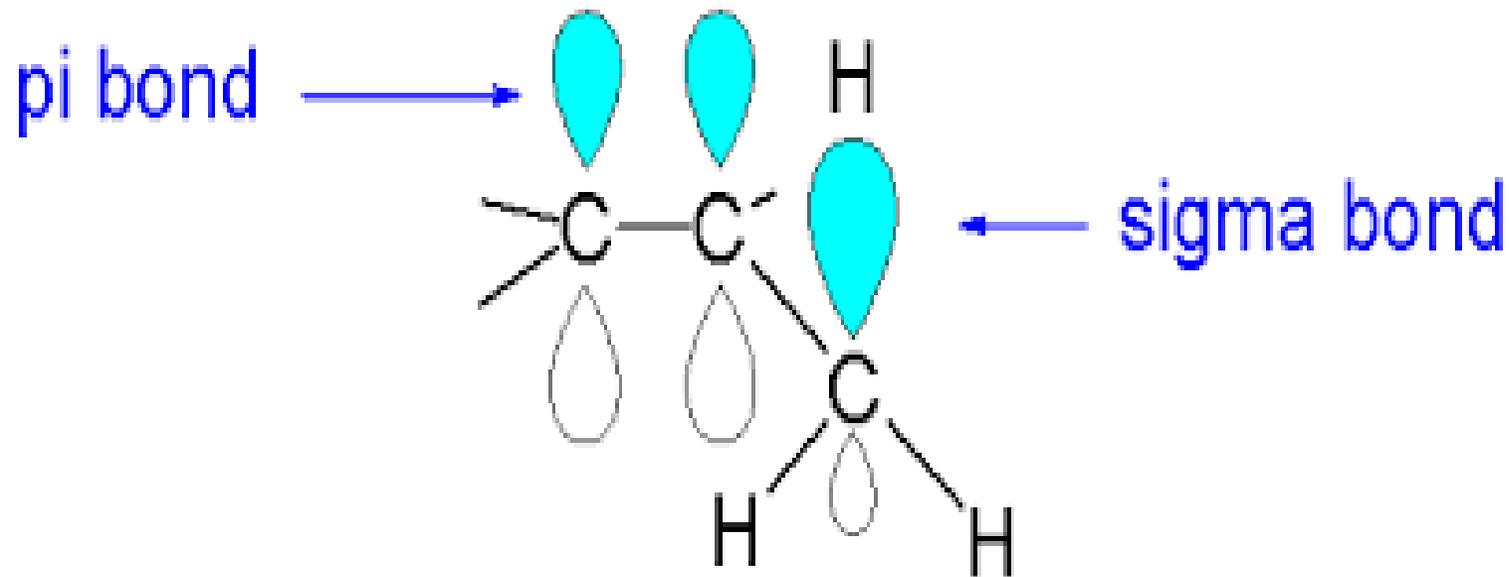
- ▶ Alkyl radicals have p-orbital of carbon occupied by an odd electron which gets delocalized over three nuclei (2 carbon and 1 hydrogen) by the overlap with the σ orbital of C – H bond of adjacent alkyl groups.
- ▶ The bond is formed between 2 carbons and odd electron is held by the hydrogen atom.



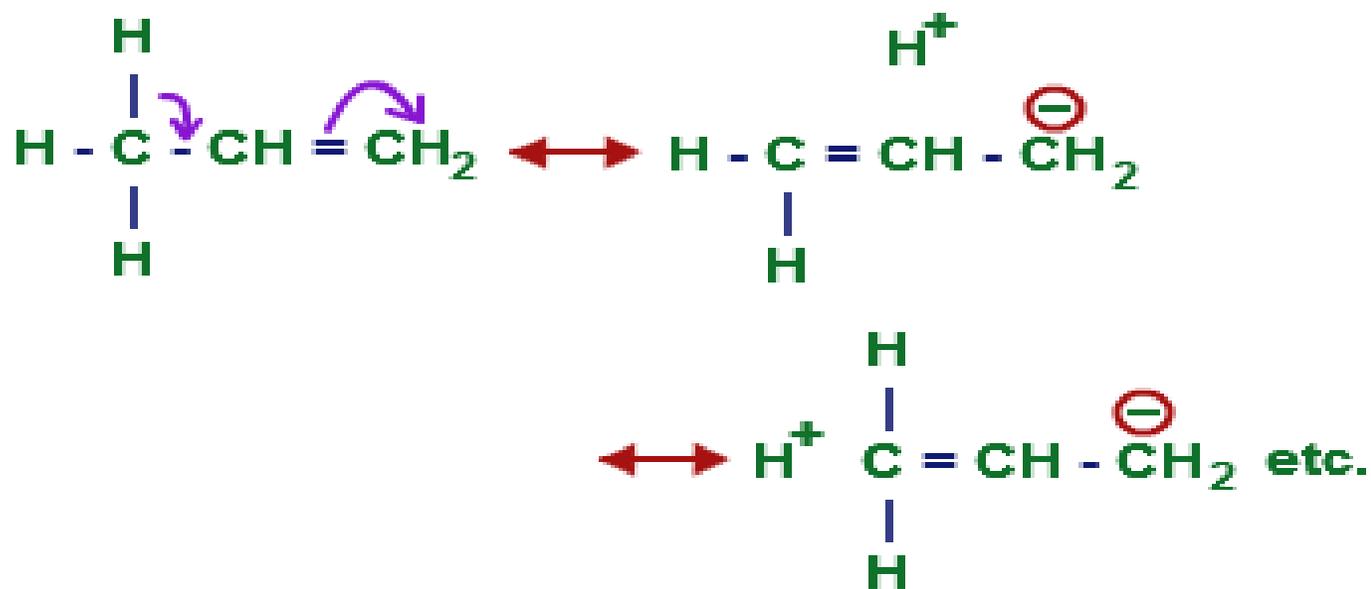
- ▶ The order of stability depends on the extent of delocalization. The greater the delocalization, the more is the stability.
- ▶ 3° alkyl radical > 2° alkyl radical > 1° alkyl radical > methyl radical

Alkenes and their stability

- ▶ Overlap of σ orbital of C – H bond with π orbital of adjacent C – C double bond gives rise to canonical structures.
- ▶ Delocalization of electrons occurs over three nuclei and thus stabilizes the alkene.



- ▶ α C – H possesses partial ionic character and its electrons get delocalized into the adjacent π system.
- ▶ More the substituent, more is the opportunity for hyperconjugation and more stable is the alkene.



- ▶ Stability of alkenes will increase with increase in number of Hydrogen α to unsaturated system.
- ▶ Increasing order of stability of alkenes because of Hyperconjugation:

Alkene	Number of Hyperconjugable Hydrogen (α to unsaturated function)
$\text{CH}_2=\text{CH}_2$	0
$(\text{CH}_3)\text{CH}=\text{CH}_2$	3
$(\text{CH}_3)_2\text{C}=\text{CH}_2 \approx (\text{CH}_3)\text{CH}=\text{CH}(\text{CH}_3)$	6
$(\text{CH}_3)_2\text{C}=\text{CH}(\text{CH}_3)$	9
$(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)_2$	12

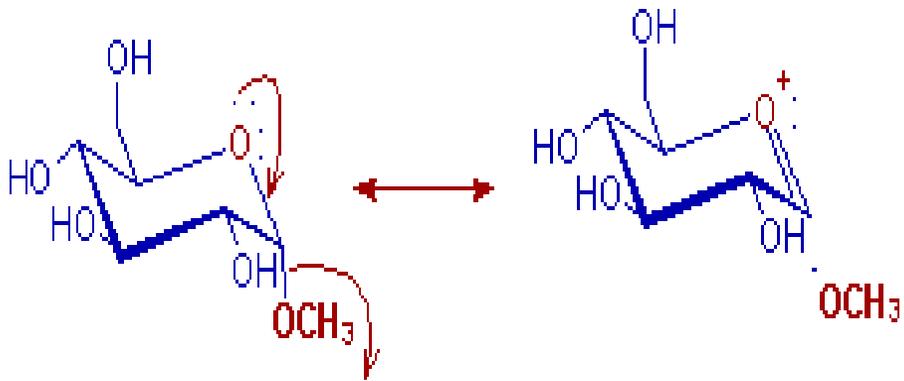
Bond length

- ▶ Hyperconjugation leads to shortening of sigma (σ) bond.
- ▶ Eg. C – C bond in 1,3-butadiene and methylacetylene is 1.46 \AA in length, much less as compared to 1.54 \AA found in saturated hydrocarbons.

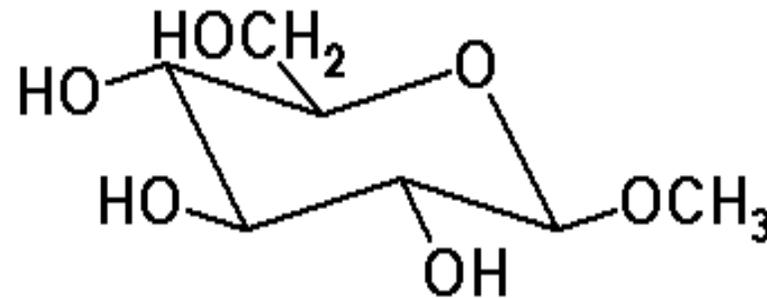
For butadiene, this can be explained by the normal conjugation of 2 alkenyl parts. But for methylacetylene, hyperconjugation between alkyl and alkynyl parts.

Anomeric effect

- ▶ The general tendency of anomeric substituents to prefer an axial orientation is called as anomeric effect.
- ▶ α -methyl glucoside is more stable than β -methyl glucoside due to hyperconjugation.
- ▶ In β -methyl glucoside the methoxy group is at equatorial position and cannot involve in hyperconjugation. Therefore β -methyl glucoside is less stable than the α -methyl glucoside.



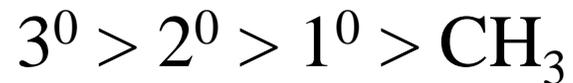
α -methyl glucoside



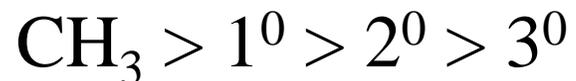
β -methyl glucoside

Baker – Nathan Effect

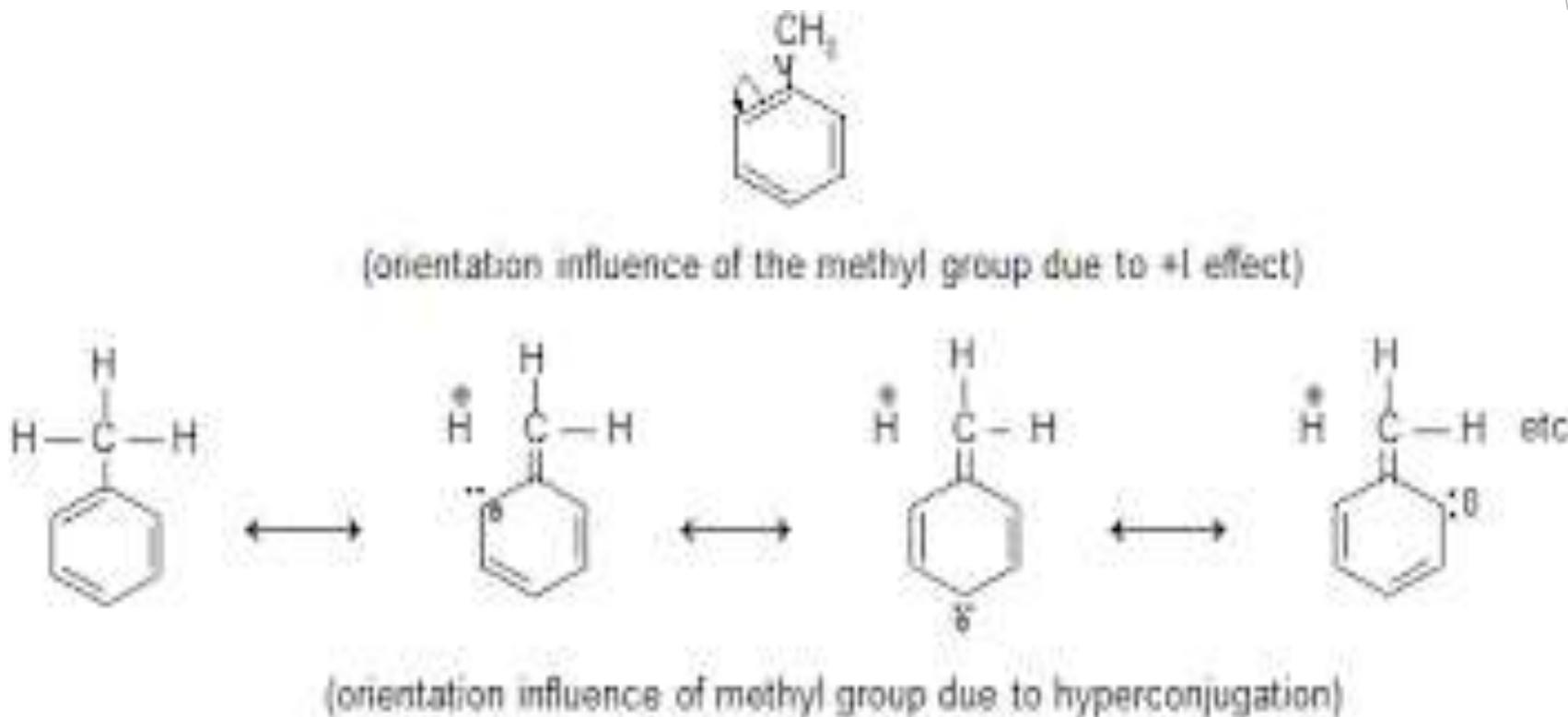
- ▶ Alkyl groups are electron donating. The relative magnitude of this inductive effect of alkyl groups is:



- ▶ This order is reversed when an alkyl group is directly attached to an unsaturated system, where the electron release is maximum for CH_3 & the order is:



- ▶ This is known as a Baker – Nathan effect and was explained by John W. Baker and W. S. Nathan on the basis of Hyperconjugation.



- ▶ In $-\text{CH}_3$ there are 3 hyperconjugable hydrogen atoms, thus more stabilization by hyperconjugation.
- ▶ In $-\text{CH}_2\text{CH}_3$ there are only 2
In $-\text{CHR}$ there is only 1.
- ▶ This explains the reversal of order where electron release is not by inductive effect but by Hyperconjugation.



THANK YOU