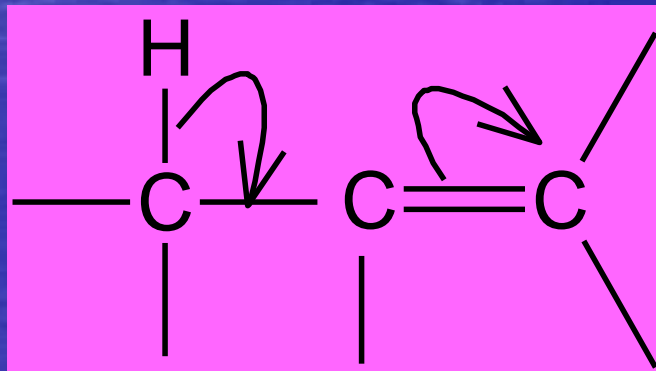
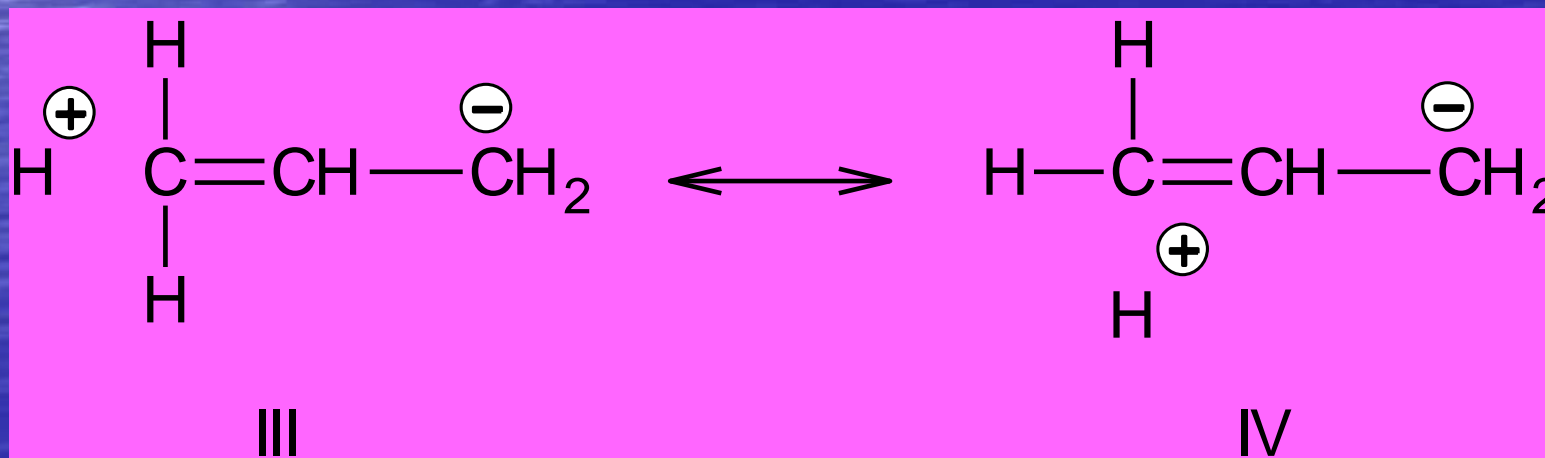
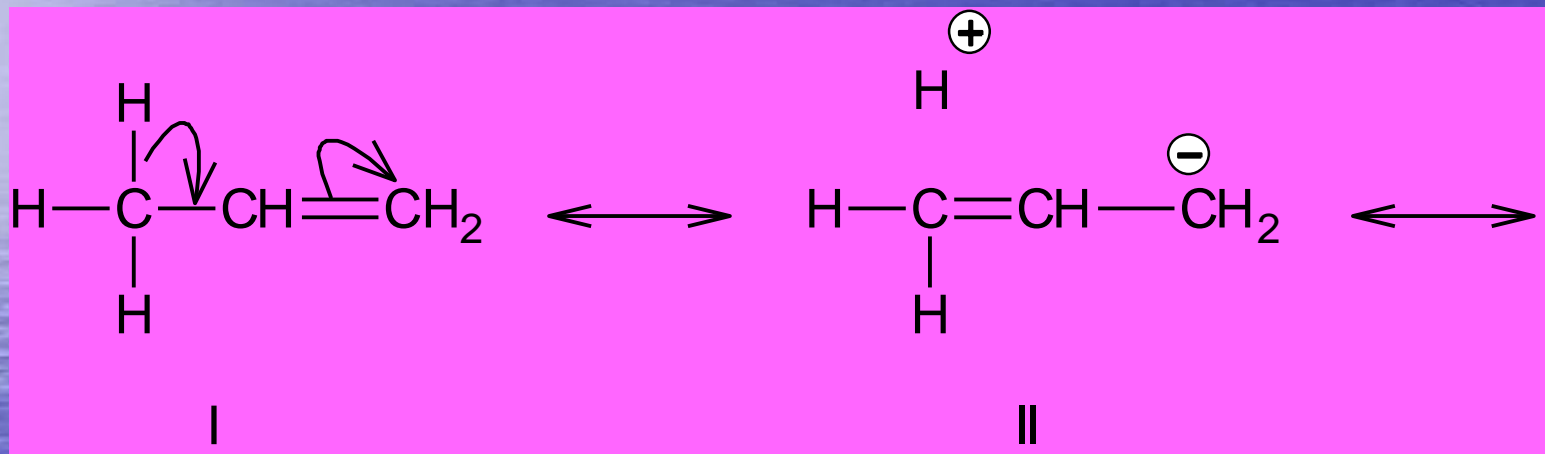


# Hyperconjugation

Baker and Nathan suggested that an alkyl group with at least one H-atom on the  $\alpha$ -carbon atom when attached to an unsaturated C-atom, is able to release electron by a mechanism similar to that of electromeric effect.

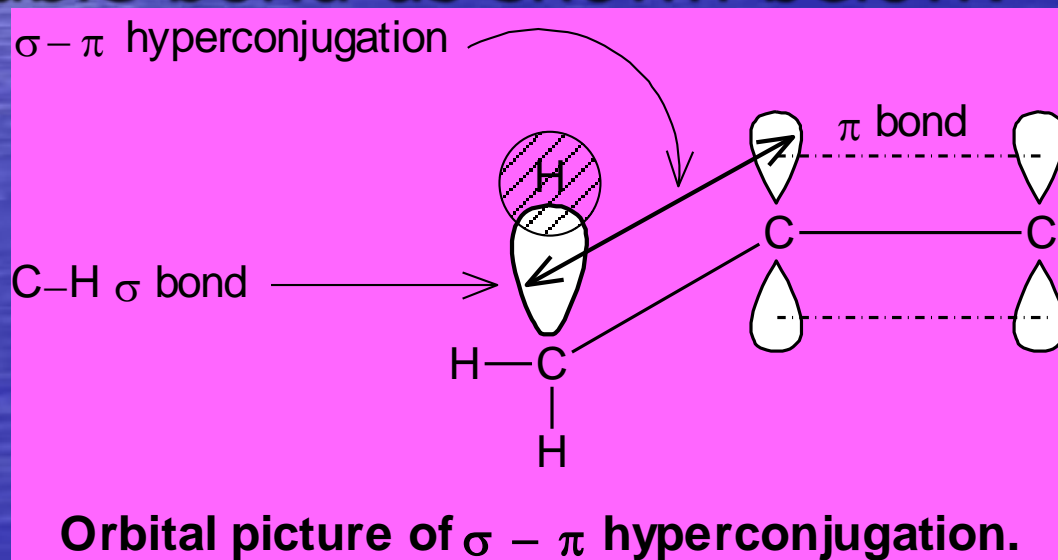


- This type of electron release due to presence of the system  $\text{H}-\text{C}-\text{C}=\text{C}$  is known as hyperconjugation. For example, Propylene may be regarded as the resonance hybrid of the following structures due to hyperconjugation.



- The various hyperconjugation forms of propylene are called contributing structures. In fact hyperconjugation effect is similar to resonance effect.
- Since structure II, III & IV have no definite bond between the  $\alpha$ -C – atom and one of the H–atom, hence hyperconjugation is also known as **no bond resonance**. It is also known as **second order resonance** or **Baker Nathan effect**.

- The orbital concept of hyperconjugation may be explained with the help of propylene. In this concept, the electron pair of C–H bond ( $\sigma$  bond) is involved in conjugation with the  $\pi$  electron pair of the double bond. Therefore, hyperconjugation involves delocalization of  $\sigma$  electrons of C–H bond through overlapping of p-orbital of double bond as shown below:

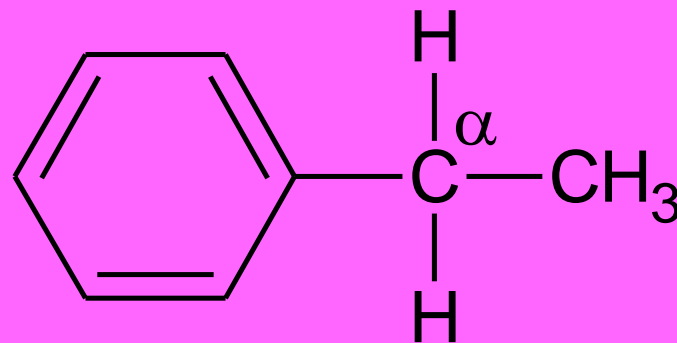
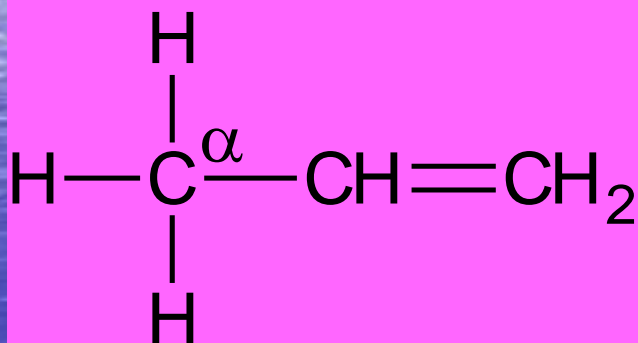


# Structural requirements of hyperconjugation:

- Any organic compound can show hyperconjugation if it will fulfill the following conditions:
  1. Compound should have  $sp^2$  hybrid carbon of alkene, arenes, carbocations and free radicals.
  2.  $\alpha$ -Carbon atom with respect to  $sp^2$  hybrid C-atom should have at least one hydrogen atom and  $\alpha$ -carbon atom should be  $sp^3$  hybridized.
- Thus, hyperconjugation is of following types:

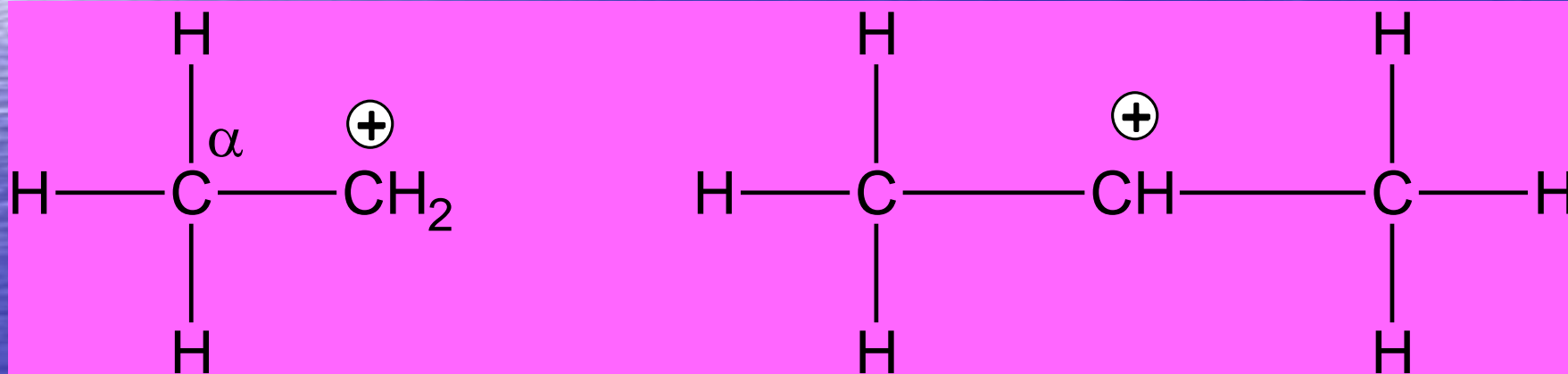
## (i) $\sigma$ (C-H), $\pi$ conjugation:

- This type of conjugation occurs in alkenes and alkyl substituted aromatic compounds.



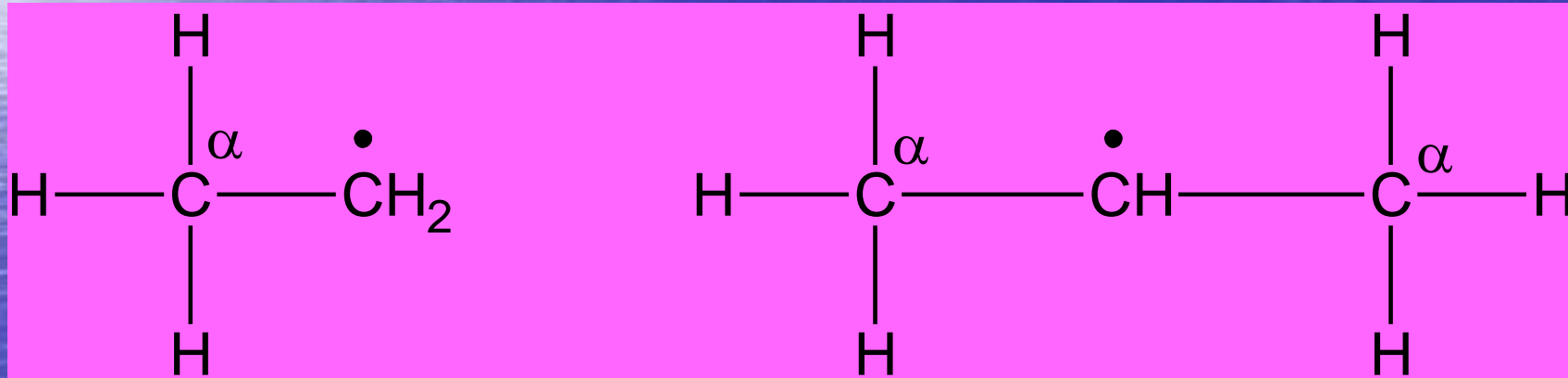
## (ii) $\sigma(\text{C-H})$ , positive charge (vacant p-orbital) conjugation:

- This type of conjugation occurs in alkyl carbocations.



### (iii) $\sigma(\text{C-H})$ , odd electron (incomplete p-orbital conjugation):

- This type of conjugation occurs in alkyl free radicals.





# Applications:

## 1. Stability of alkenes:

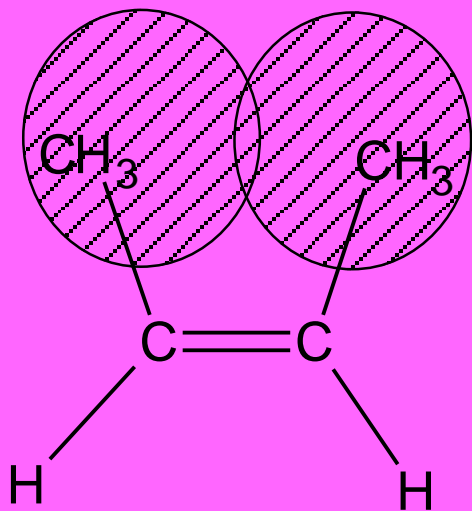
- Heat of hydrogenation shows that the greater the number of alkyl groups attached to the double bonded C – atom, greater is the stability of alkene (lower is the heat of hydrogenation). Thus on the basis of heat of hydrogenation, the order of stability of different alkenes have been found to be: Tetrasubstituted > Trisubstituted > Disubstituted > Monosubstituted > Ethylene.

- The above order of stability of substituted alkenes can also be explained on the basis of hyperconjugation.

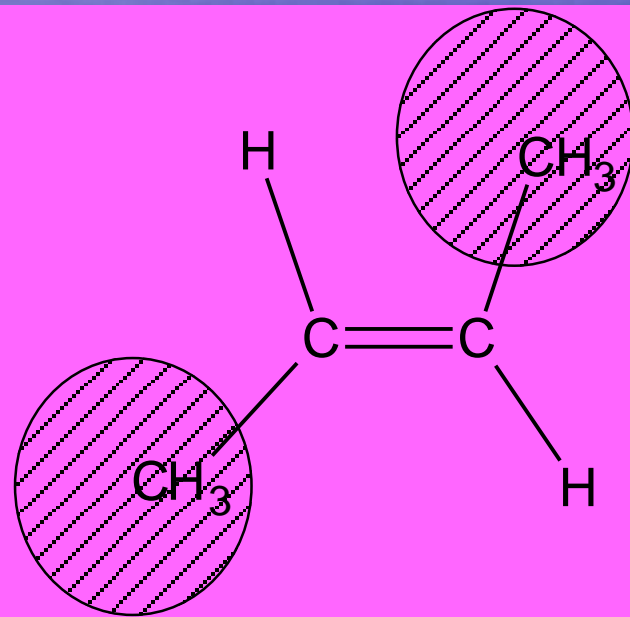
Alkenes				
No. of $\alpha$ - H atoms	12	9	6	3
No. of Resonating structures	13	10	7	4

The greater the number of resonating structures of a molecule, greater will be its stability.

- Trans-2-Butene is more stable than cis-2-butene, in which two methyl groups are close together and hence their electronic cloud (steric hindrance) repel each other.



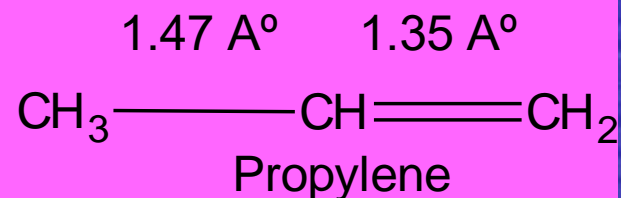
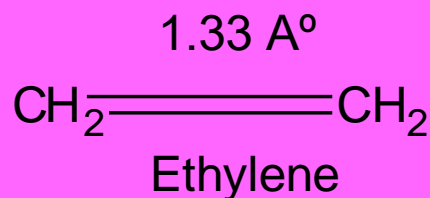
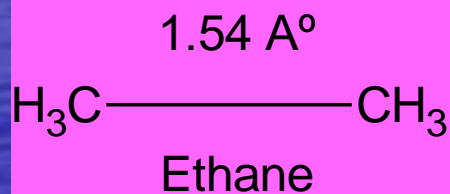
Steric hindrance  
in cis-2-butene



No Steric hindrance  
in trans-2-butene

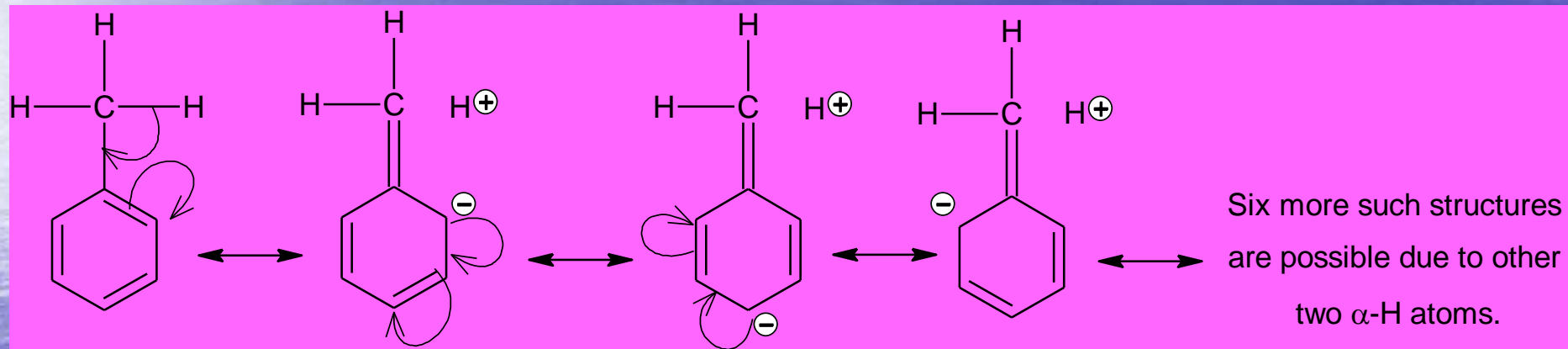
## 2. Abnormal bond lengths:

In hyperconjugation a single bond acquires a double bond character and vice versa, hence abnormality in bond lengths is observed in the compounds showing hyperconjugation. For example, Ethane and ethylene, C–C and C=C bonds show normal length  $1.54\text{\AA}$  and  $1.33\text{\AA}$ , respectively due to no hyperconjugation in the compounds but in propene, the bond lengths are  $1.47\text{\AA}$  and  $1.35\text{\AA}$  for C–C and C = C bonds, respectively. This change in bond lengths may be explained by hyperconjugation.



### 3. Directive influence of alkyl groups:

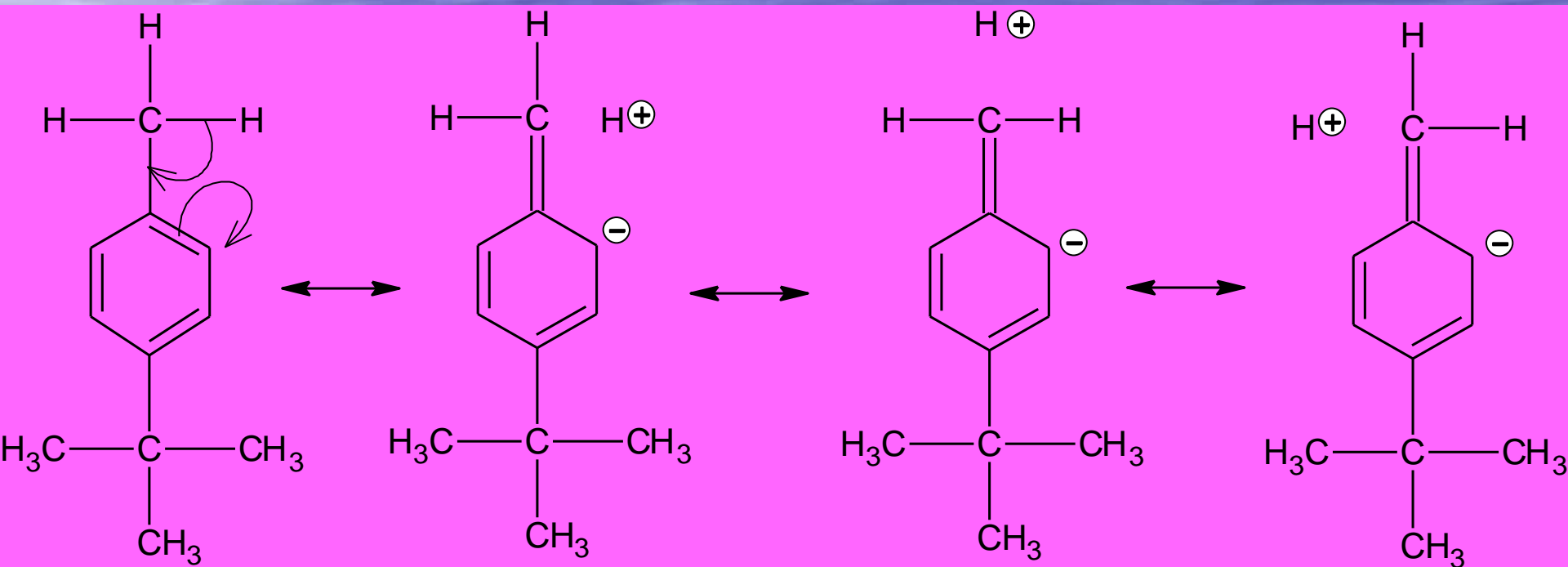
- The  $-CH_3$  and other alkyl groups are o- and p- directing which can be explained on the basis of hyperconjugation as follows:



As a result of hyperconjugation, electron density at o- and p- position (w.r.t. methyl group) increases and therefore electrophilic substitution in toluene takes place at o- and p- positions. Thus alkyl groups are o- and p- directing.

## 4. Orienting power of methyl group in p-substituted toluene:

- In p-t-butyl toluene, further substitution occurs at o- position with respect to methyl group even though the (+) inductive effect of t-butyl group is far greater than methyl group. This anomaly is due to greater hyperconjugative effect of methyl group (having  $3\alpha$  - H atoms) which increases the electron density at o- position w.r.t. methyl group than t-butyl groups which have no  $\alpha$  - H atoms and hence no hyperconjugation occurs. Here hyperconjugation over weight inductive effect.

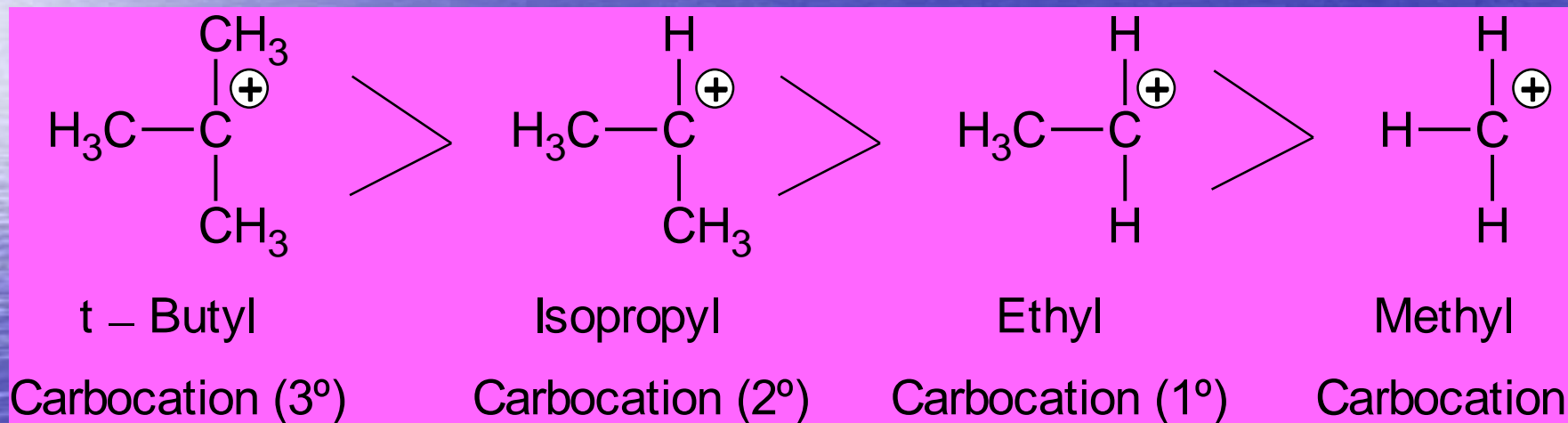


- Hyperconjugation in t-butyl toluene

## 5. Stability of free radicals and carbocations:

### 1. Stability of alkyl carbocations:

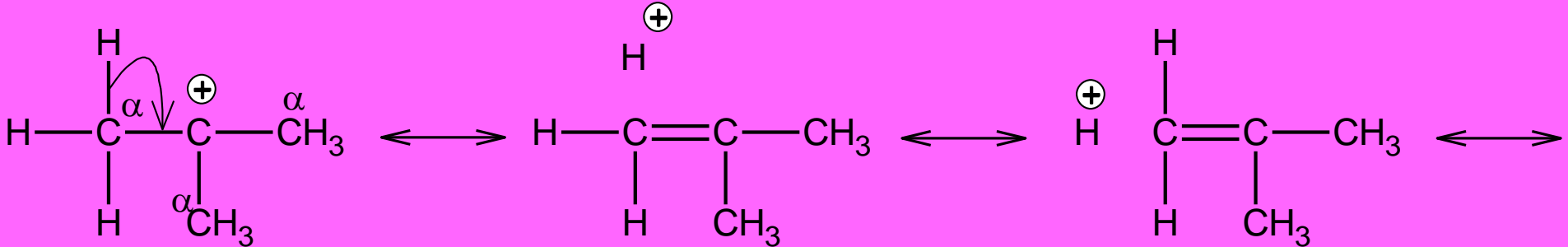
- The order of stability of different alkyl carbocations is:



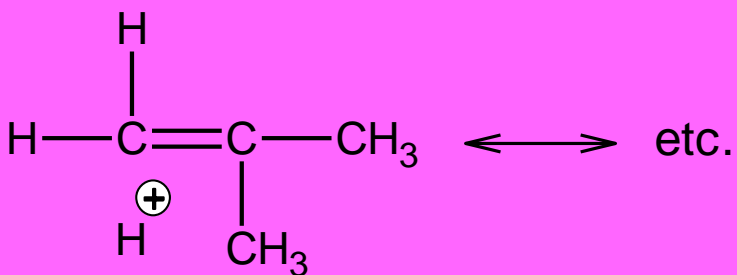
This order of stability of alkyl carbocations can be explained on the basis of inductive effect & hyperconjugation as follows:



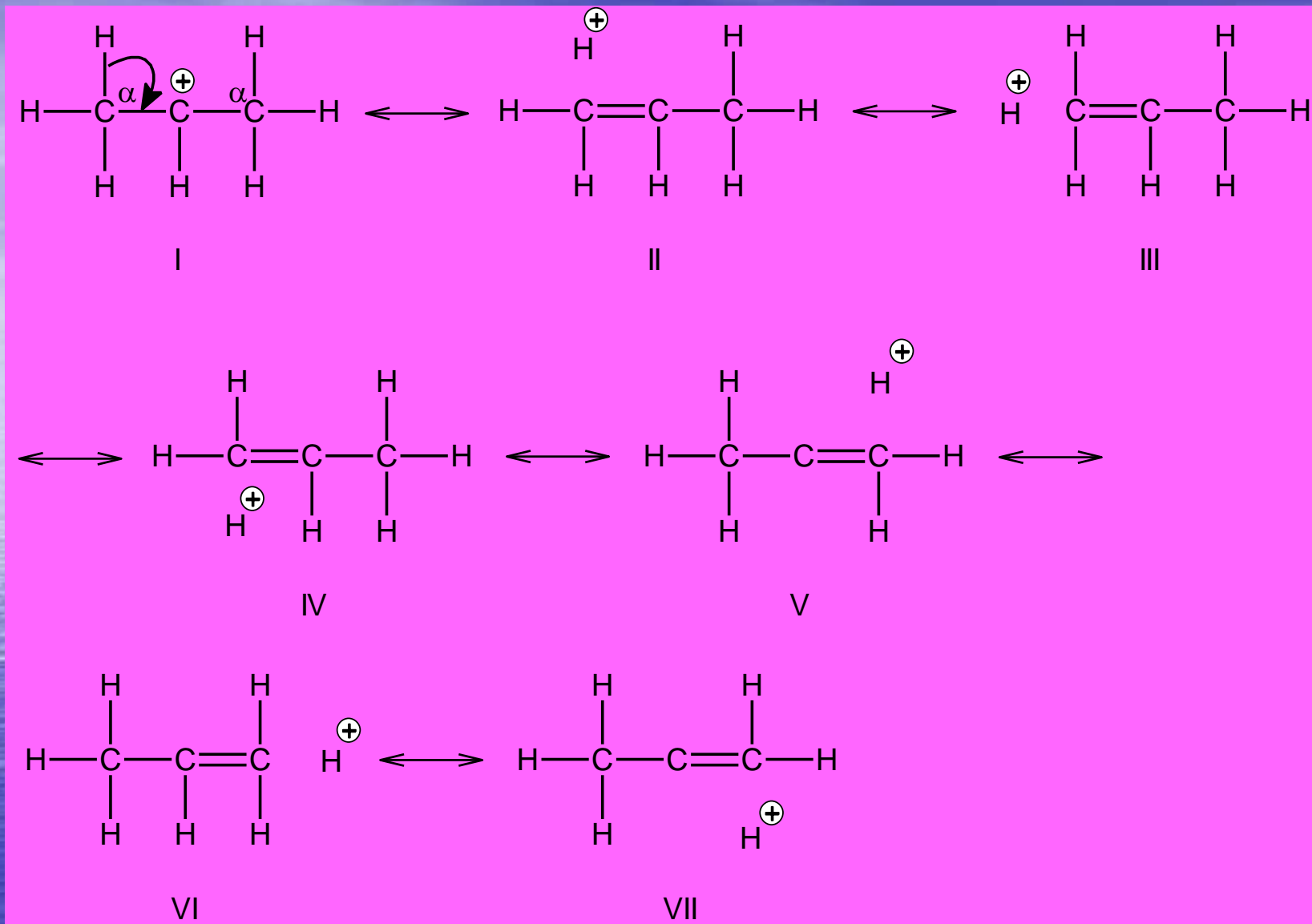
- hyperconjugation states that greater the number of  $\alpha$ -hydrogen atoms on a carbocation greater is the number of hyperconjugative structures (greater the dispersion of positive charge) and hence more is the stability of carbocation.
- Thus t-butyl carbocation ( $3^\circ$ ) with nine  $\alpha$ -hydrogen atoms has one usual and nine hyperconjugative structures is more stable than isopropyl carbocation ( $2^\circ$ ) with six  $\alpha$ -hydrogen atoms, having one usual and six hyperconjugative structures which, in turn, is more stable than ethyl carbocation ( $1^\circ$ ) with three  $\alpha$ -hydrogens, having one usual & three hyperconjugative structures, while methyl carbocation with no  $\alpha$ -hydrogen, has one usual and no hyperconjugative structure, is least stable.



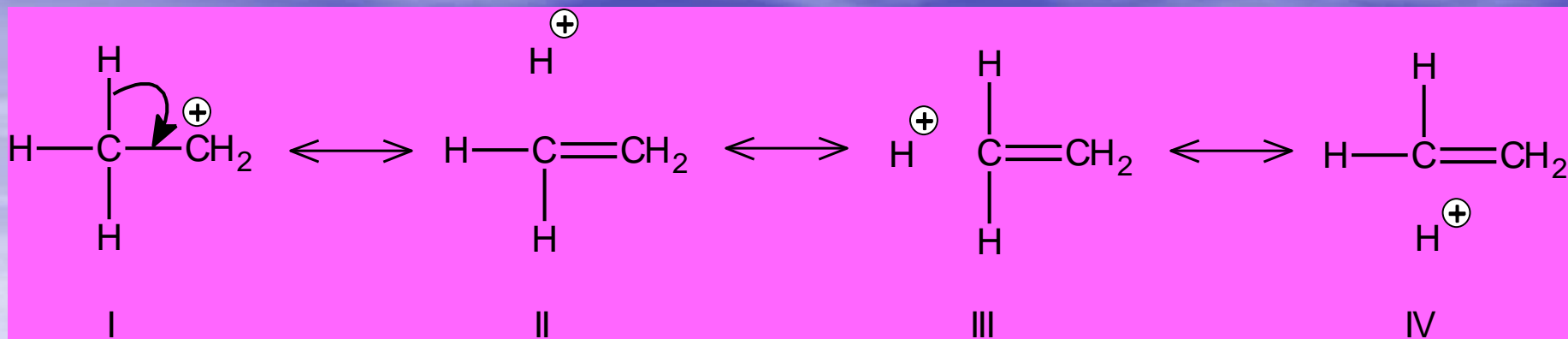
t - Butyl Carbocation



- One usual and nine hyperconjugative structures of t-butyl carbocation ( $3^\circ$ )



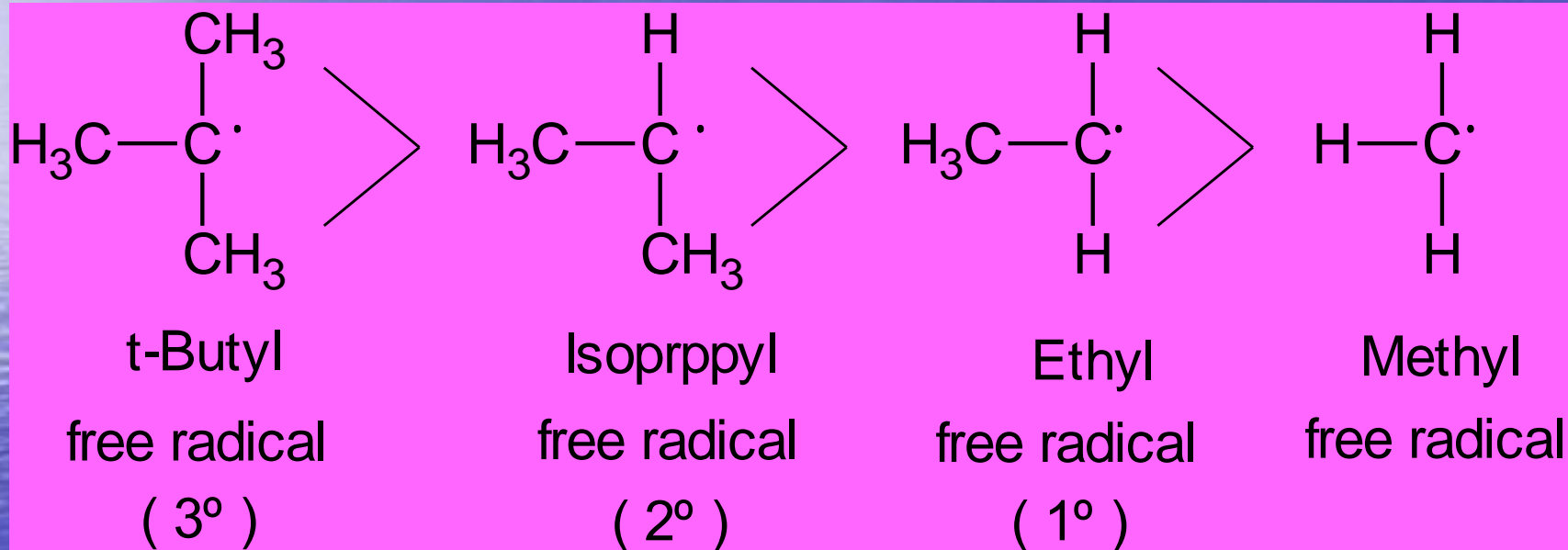
- One usual and six hyperconjugative structures of isopropyl carbocation ( $2^\circ$ )



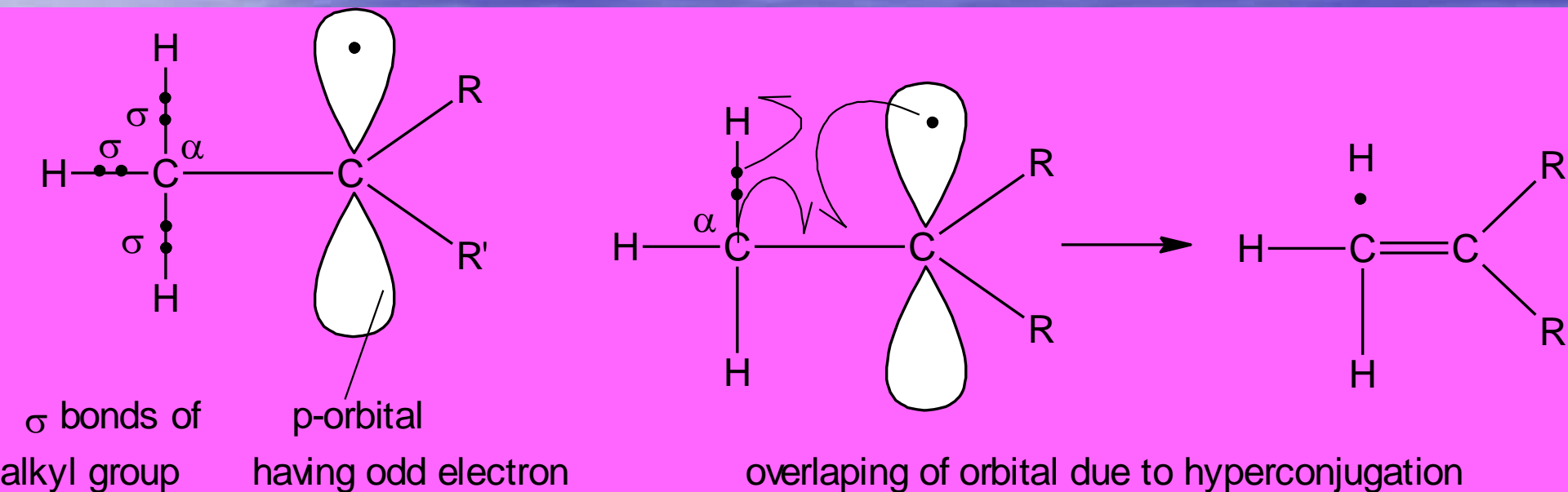
- One usual & three hyperconjugative structures of ethyl carbocation ( $1^\circ$ )

# Stability of alkyl free radicals:

- The order of stability of different alkyl free radicals is as follows:

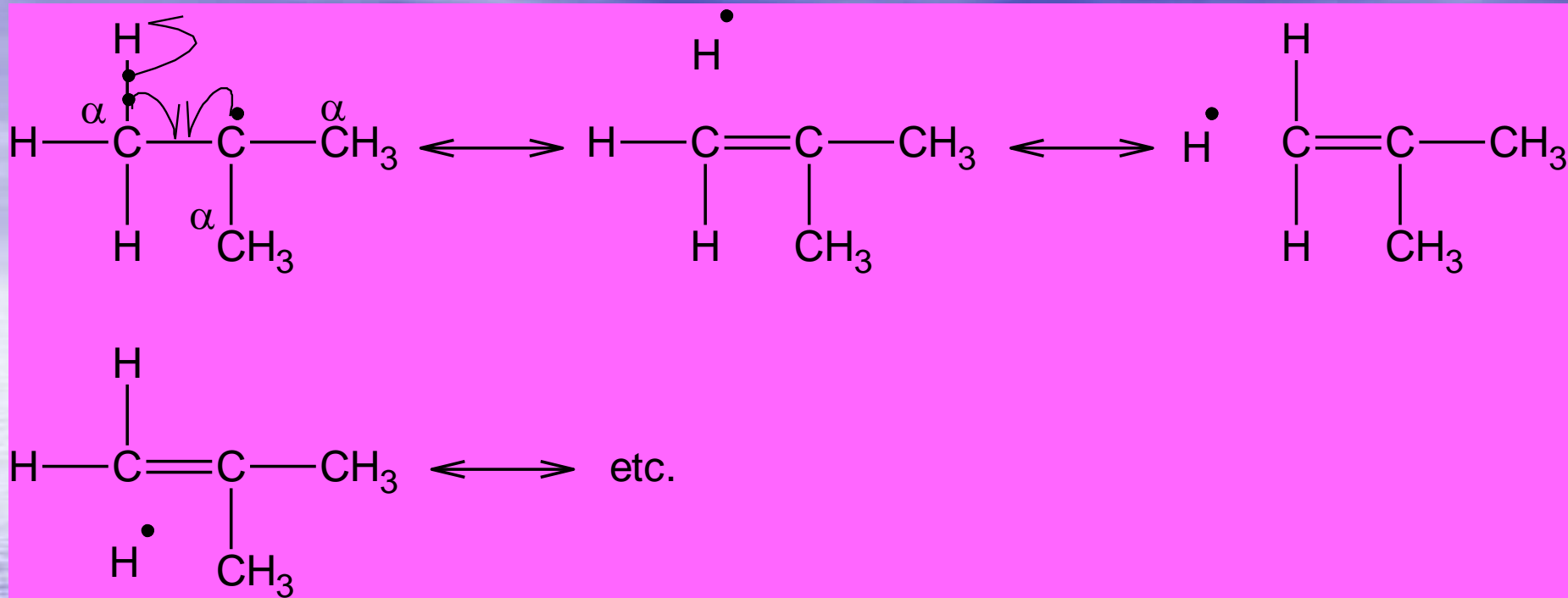


- The above order of stability can be explained on the basis of hyperconjugation.



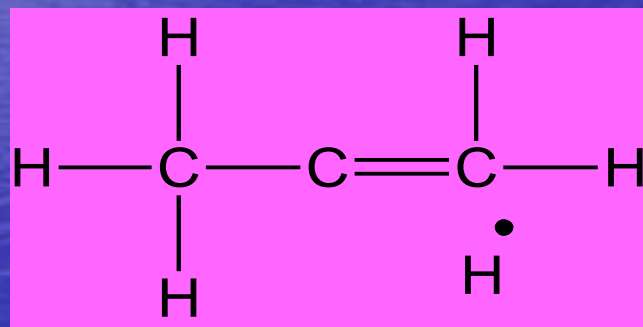
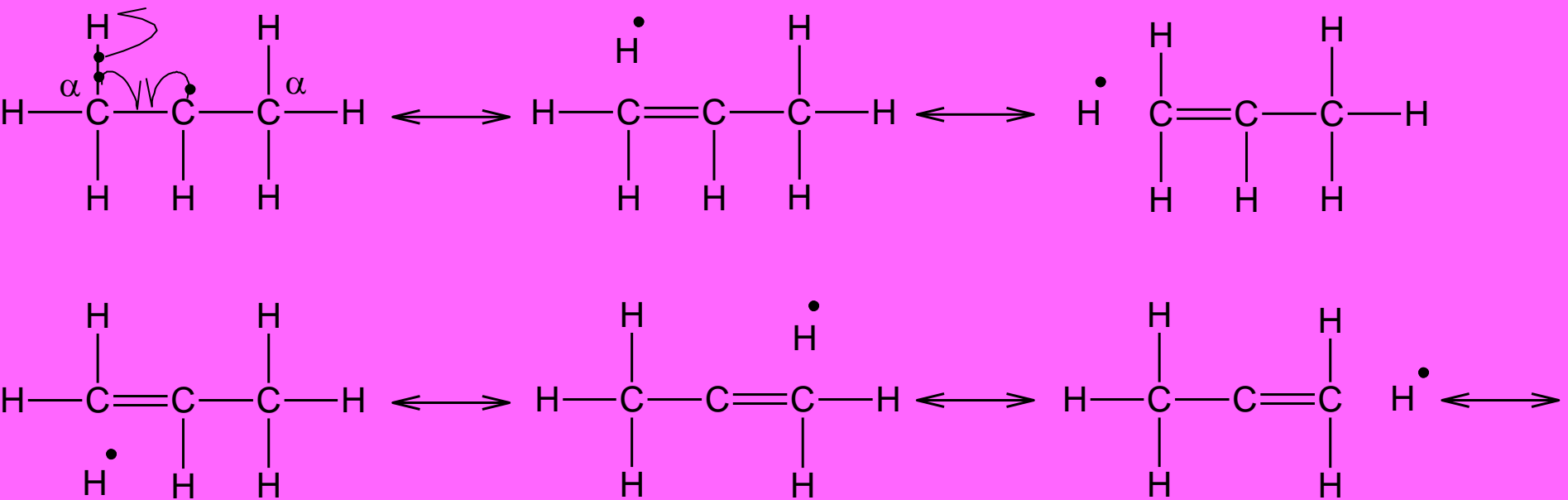
Structure of a radical  
having  $\alpha$ -H atoms

- In general, greater the number of  $\alpha$ -hydrogens, greater is the number of hyperconjugative structures and hence more stable is the free radical. Thus t-butyl free radicals ( $3^\circ$ ) with nine  $\alpha$ -hydrogens has one usual and nine hyperconjugative structures, is more stable than isopropyl free radical ( $2^\circ$ ) with six  $\alpha$ -hydrogens has one usual & six hyperconjugative structures which in turn, is more stable than ethyl free radical ( $1^\circ$ ) with three  $\alpha$ -hydrogens has one usual & three hyperconjugative structures while methyl free radical with no  $\alpha$ -hydrogens has one usual & no hyperconjugative structures is least stable.

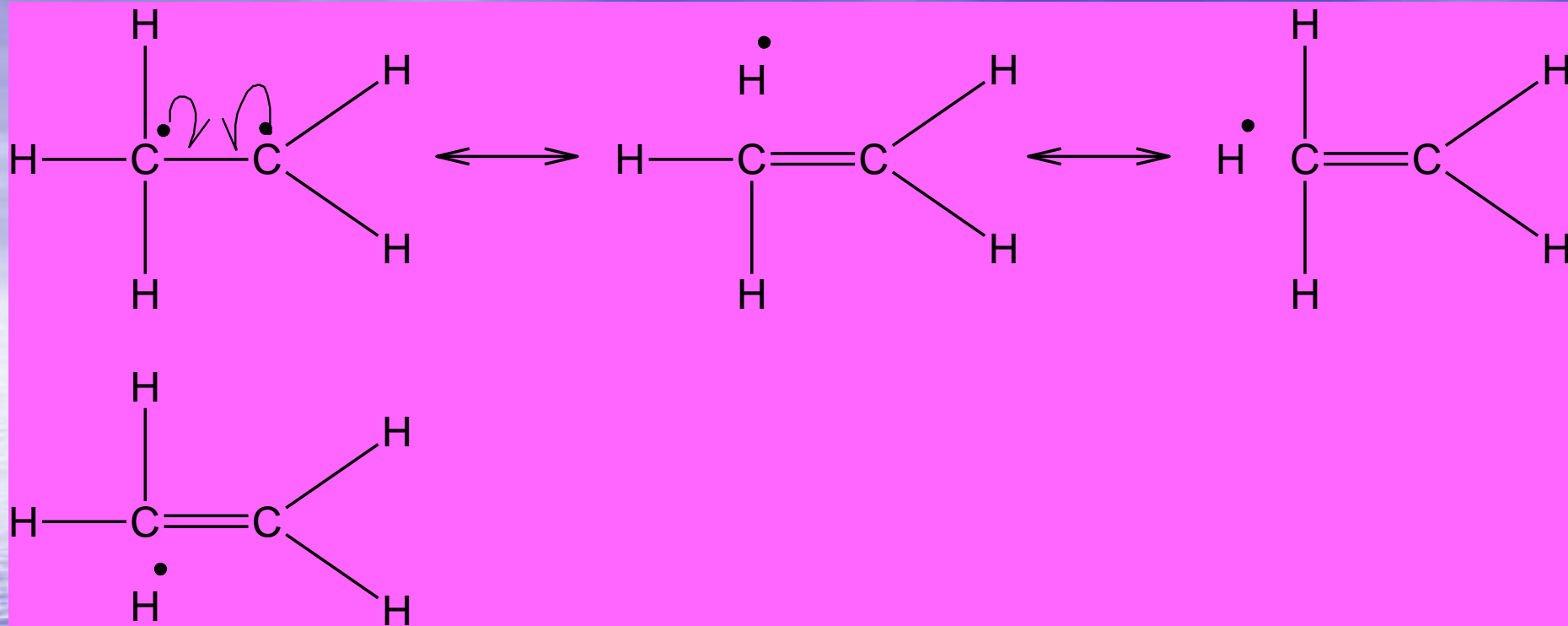


- One usual & nine hyperconjugative structures of t-butyl free radical ( $3^\circ$ )





- One usual and six hyperconjugative structures of isopropyl free radical ( $2^{\circ}$ )



- One usual and three hyperconjugative structures of ethyl free radical ( $1^\circ$ )