

B.Sc. Part III (Hons.)  
Organic chemistry.

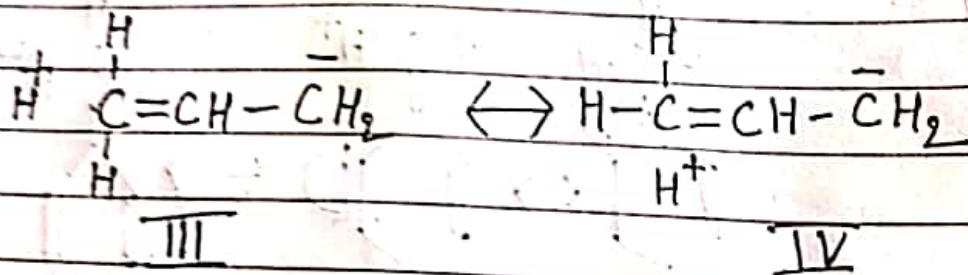
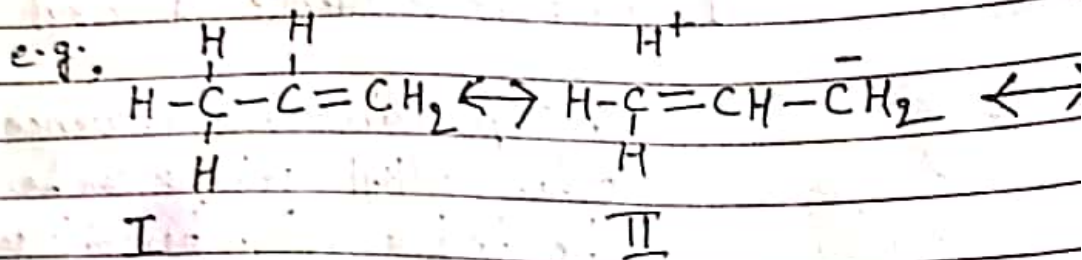
Paper: VII - by Manju Kumari

### General Principles:

Hyperconjugation: It is the delocalisation of sigma electron. Also known as sigma-pi conjugation or no bond resonance.

Occurrence: Alkene, Alkynes, free radicals (saturated types) carbonium ions.

Condition: Presence of  $\alpha$ -H with respect to double bond, triple bond carbon containing positive charge or unpaired electron (in free radicals).

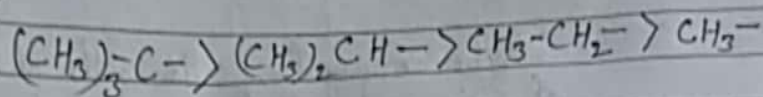


In above examples str. I, II, III and IV are hyperconjugative structures (H-structure)

Hyperconjugation is a permanent effect.

2.

Hyperconjugation effect:— The +I effect of the alkyl groups generally follows the sequence:

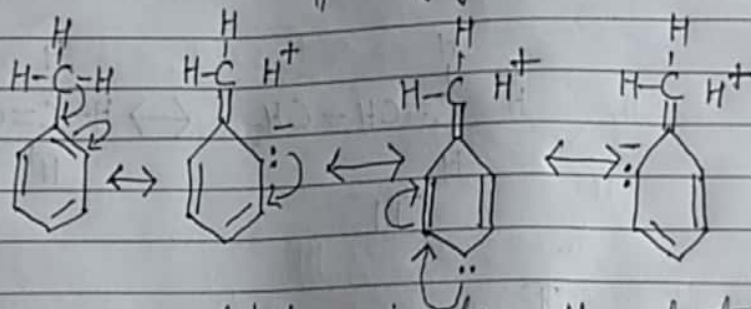


However when these alkyl groups are attached to an unsaturated system such as double bond or triple bond benzene ring, this order of +I-effect is actually reversed. This effect is called hyperconjugation effect or Baker-Nathan effect or no-bond resonance.

Significance of Hyperconjugation effect:

1. Directive influence of alkyl groups.

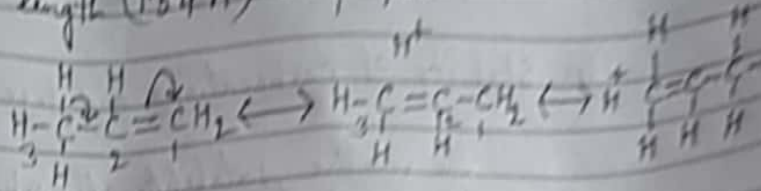
The o, p-directing influence of  $\text{CH}_3$  and other alkyl groups can be explained on the basis of hyperconjugation.



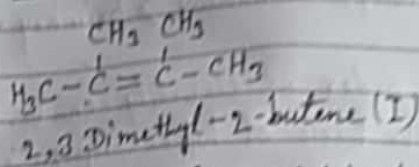
As a result of hyperconjugation, the electron density at o- and p- position w.r.t. the  $\text{CH}_3$  group increases and hence the electrophilic substitution reactions in toluene will occur at o- and p- position w.r.t. the  $-\text{CH}_3$ . Thus, Alkyl groups are o, p-directing.

2. Shortening of Carbon-Carbon single bonds adjacent to multiple bonds.

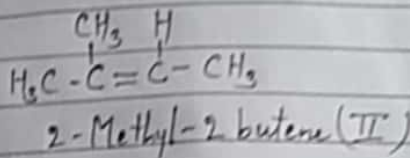
Because of hyperconjugation, C<sub>2</sub>-C<sub>3</sub> single bond in propene acquires some double bond character and hence its little shorter (1.49 Å) than the normal carbon-carbon single bond length (1.54 Å) in propane.



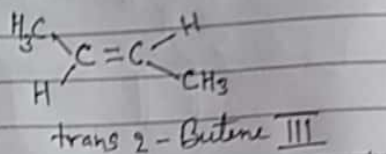
### 3. Relative stability of alkenes.



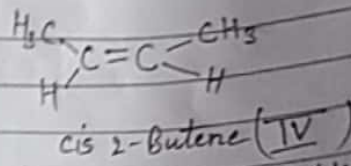
(Twelve  $\alpha$ -H;  $\Delta H_2 = 26.6 \text{ kcal mol}^{-1}$ )



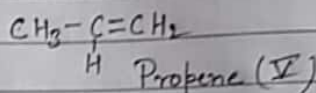
(Nine  $\alpha$ -H;  $\Delta H_2 = 26.9 \text{ kcal mol}^{-1}$ )



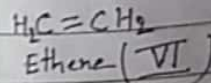
(Six  $\alpha$ -H;  $27.6 \text{ kcal mol}^{-1}$ )



(Six  $\alpha$ -H;  $\Delta H_2 = 28.6 \text{ kcal mol}^{-1}$ )



(Three  $\alpha$ -H;  $\Delta H_2 = 30.1 \text{ kcal mol}^{-1}$ )

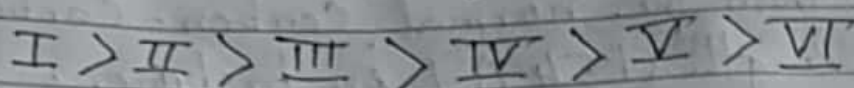


(No  $\alpha$ -H;  $\Delta H_2 = 32.8 \text{ kcal mol}^{-1}$ )

Alkenes I, II, III (or IV), V and VI have twelve, nine, six, three and none  $\alpha$ -hydrogen respectively and hence equal number of hyperconjugation sets. can be written for each one of them.

4.

Since greater the number of hyperconjugation structures, more stable is the alkene, therefore, the relative stability of these alkenes follows the sequence;



4. Stability of Carbocations and free radical

The relative stability of carbocations and free radicals follows the sequence;

tertiary > Secondary > primary.

This order of stability can be easily explained on the basis of hyperconjugation.

