

The delocalization further explains the low reactivity of vinyl chloride and chlorobenzene due to strengthening of carbon-chlorine bond. The +R effect in chlorobenzene and vinyl chloride results in the development of a double bond character between carbon and chlorine, which provides the extra stability to this bond (refer Sections 11.5.2 and 12.3.1).

Further in p - π overlap, the delocalization of π -electrons may occur through vacant or half filled p orbitals. This explains the stability of carbocations and free radicals through resonance effect and is discussed later in this chapter.

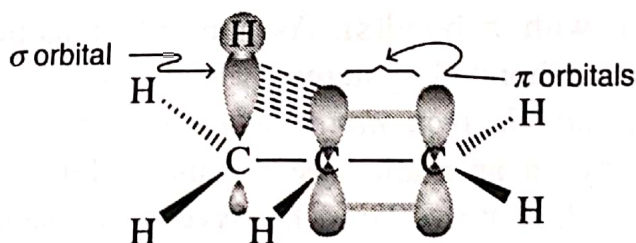
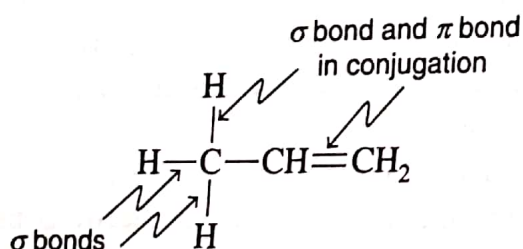
4.1.4 Hyperconjugation (No bond resonance)

[Delocalization involving σ electrons]

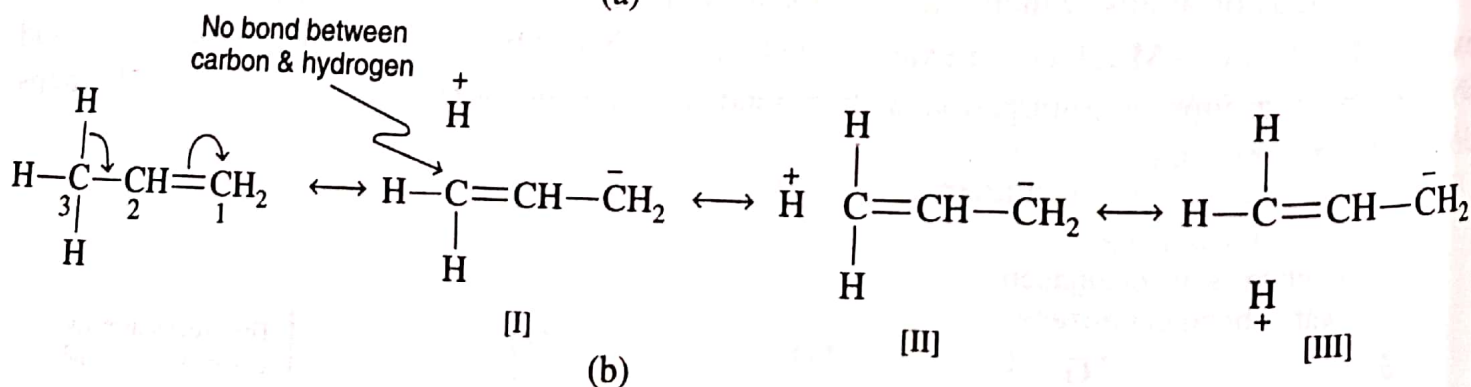
In resonance effect, the delocalization of electrons occurs through π - π and p - π overlap, that is, π electrons are involved in delocalization. Now, we discuss the delocalization of σ electrons through σ - π or σ - p overlap, known as hyperconjugation. The σ bond in conjugation with the π bond, or σ bond in conjugation with p orbital (vacant or filled) participates in delocalization and thus stabilizes the system. The process is similar to resonance but is extended to σ bonds and therefore named as hyperconjugation.

For example, in propene, the three C-H σ bonds of CH_3 group are in conjugation with π bond. The σ electrons are transferred in the process to adjacent carbon-carbon bond, in turn π electrons are shifted to terminal CH_2 carbon.

There are three C-H σ bonds so three contributing structures are possible for propene. Due to participation of σ electrons in delocalization, the bond between carbon and hydrogen does not exist in contributing structures and for this reason, hyperconjugation is also referred as No bond resonance.



Hyperconjugation in propene:
overlap between σ and π orbitals.

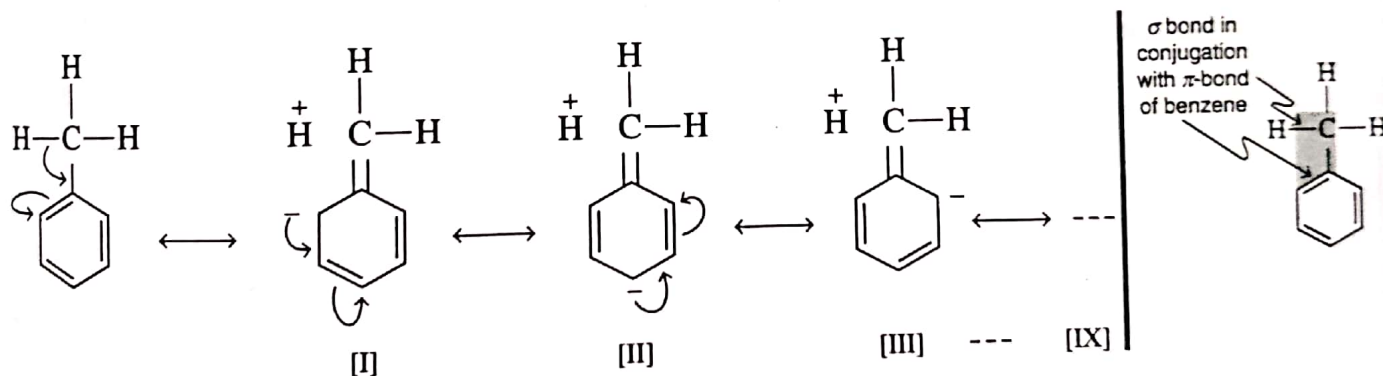


Hyperconjugation in propene (a) Overlap between σ & π orbitals (b) Contributing structures

Hyperconjugation explains the stability of substituted alkenes. A more substituted alkene is more stable due to availability of more number of conjugated C-H σ bonds which can participate in hyperconjugation. In ethene, hyperconjugation does not occur due to non-availability of conjugated C-H σ bonds.

- Hyperconjugation in propene explains its stability compared to ethene [Note that more the number of contributing structures, more stable is the system].
- The hyperconjugation also explains the shortening of σ bond between C2 and C3 in case of propene. As evident from the contributing structures, a double bond character develops between carbons at the 2nd and 3rd position which causes shortening of C2-C3 σ bond.

Similarly in case of toluene, the carbon-hydrogen σ bonds of methyl group participate in delocalization with π bonds of benzene ring. The presence of three C-H σ bonds in conjugation with π bonds of benzene ring results in formation of nine contributing structures.

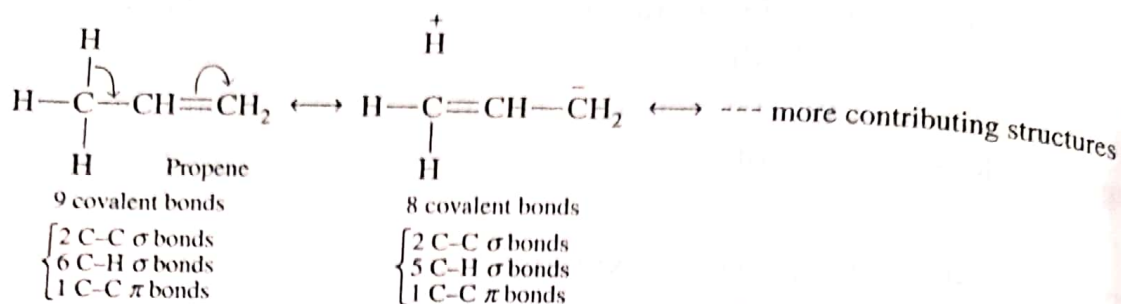


Hyperconjugation in toluene: Three C-H σ bonds. Therefore in all there are 9 contributing structures (3 for each σ bond).

In case the number of covalent bonds in the contributing structures during hyperconjugation is less than the number of covalent bonds in the original structure (as in case of propene and toluene), hyperconjugation is referred to as **sacrificial hyperconjugation**.

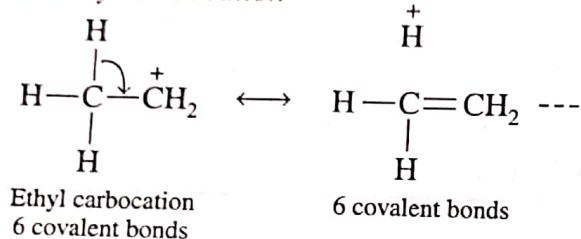
Another type of hyperconjugation that occurs in carbocations and free radicals is referred to as **isovalent hyperconjugation** since the number of covalent bonds in contributing structures is same as the number of covalent bonds in the structure of carbocation or free radical. This hyperconjugation occurs through delocalization involving p orbitals (vacant or half-filled) and a conjugated σ bond (σ - p overlap), and explains the stability of carbocations and free radicals. This is discussed in detail in the subsequent sections of this chapter (Sections 4.2.1 and 4.2.3).

Sacrificial hyperconjugation

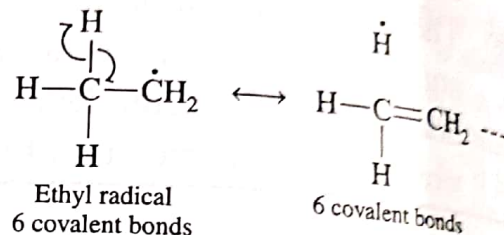


Isovalent hyperconjugation

In ethyl carbocation

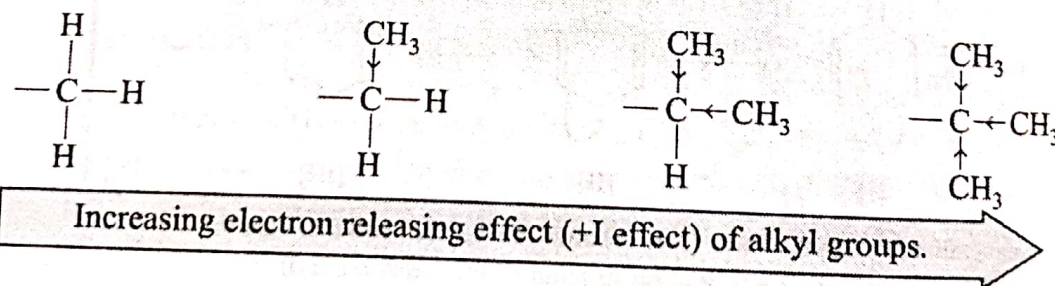


In ethyl radical

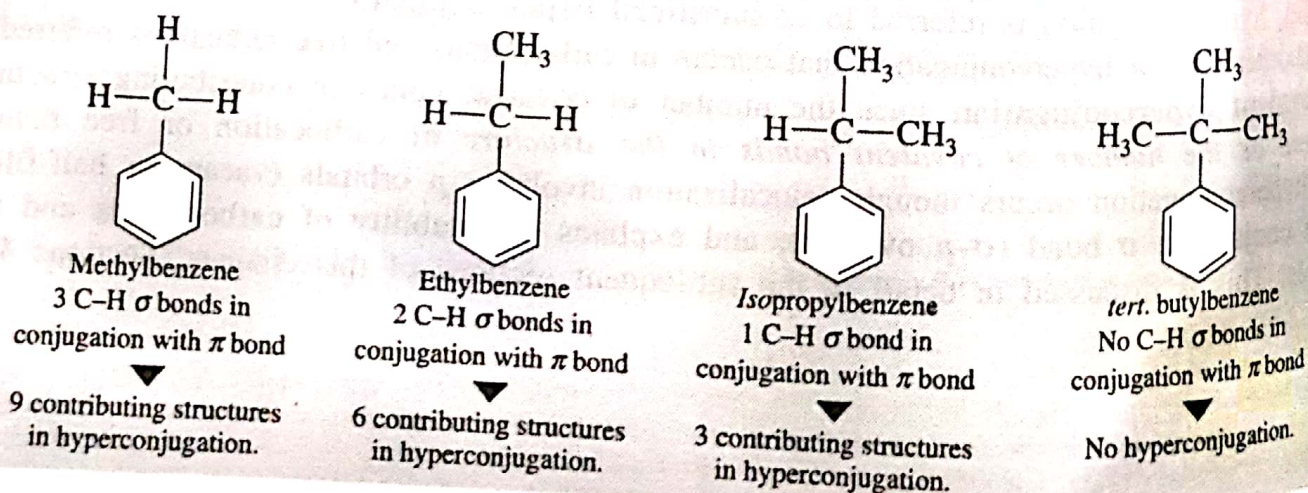


Alkyl groups behave differently when attached to benzene ring (i.e. alkylbenzenes): (Hyperconjugation explains this anomalous behaviour).

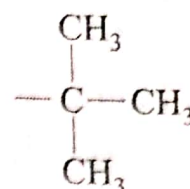
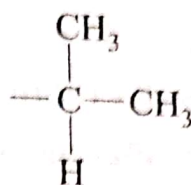
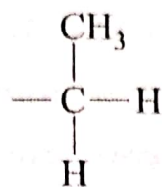
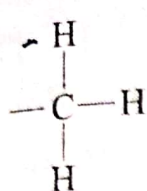
We have already discussed, in Section 4.1.1 that the electron releasing effect (+I effect) of different alkyl groups increases with an increase in the number of alkyl groups and follows the order



But when these groups are attached to benzene ring, the electron releasing effect of alkyl groups follows a reverse order. In alkyl benzenes, the electron release occurs through hyperconjugation. This is illustrated as follows:



Thus, the order of electron release now become



Increasing electron releasing effect of alkyl groups when attached directly to benzene ring.

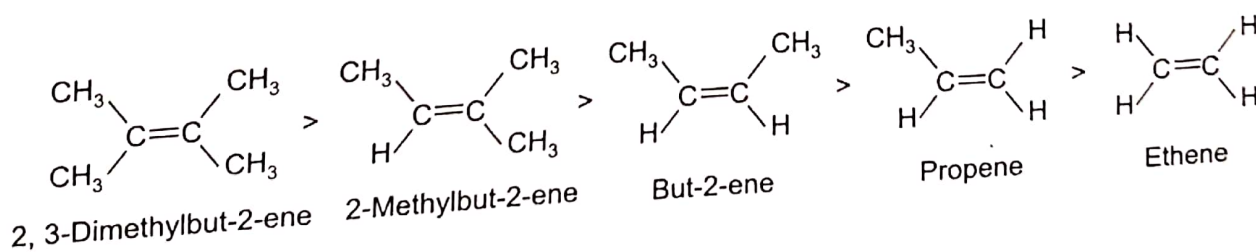
This can be explained on the basis of hyperconjugation. In methylbenzene, there are three C-H σ bonds in conjugation with π bonds of benzene ring. In ethylbenzene, *isopropylbenzene* and *tertiarybutylbenzene*, the number of conjugated C-H σ bonds is two, one, and zero respectively.

Each C-H σ bond participates in delocalization and increases the negative charge density in benzene ring. More the number of C-H σ bonds, more are the contributing structures and thus higher is the electron releasing effect of alkyl groups. The number of contributing structures in methylbenzene, ethylbenzene, *isopropylbenzene*, and *tertiarybutylbenzene* are nine, six, three, and zero respectively. Thus, the electron releasing effect of alkyl groups, in alkylbenzenes, is observed to be maximum for methyl and minimum for *tertiarybutyl* group.

20.5.1 Application of the Hyperconjugation Effect

Although hyperconjugation effect is a much weaker effect than resonance effect, yet it is quite useful in explaining some of the physical and chemical properties of the organic molecules. Some of these are as follows:

- 1 **Shortening of carbon-carbon bonds adjacent to multiple bonds:** The hyperconjugation imparts partial double bond character to the (C — C) adjacent to multiple bond, e.g. C₂ — C₃ bond in propene acquires some double bond character and hence is little shorter (1.49 Å) than the normal carbon-carbon single bond length (1.54 Å) in propane.
- 2 **Relative stability of alkenes:** Relative stabilities are related to the number of alkyl groups linked to the double-bonded carbon atoms. It may be noted that in alkenes, the relative stabilities are related to the number of the alkyl groups linked to the double-bonded carbon atoms. The order of the relative stabilities of a few alkenes is as follows:



The decrease in the relative stabilities of the alkenes listed above is because of the decrease in the number of the methyl groups attached to the double-bonded carbon atoms. As a result, the number of hyperconjugated structures decreases thereby decreasing the stability of the alkene. For example, in 2,3-dimethylbut-2-ene, there are four methyl groups and twelve α-hydrogen atoms, which means that there will be twelve contributing structures possible. But no α-hydrogen atom is present in ethane. Thus, the former is the most stable while the latter is the least stable. Thus, the order of the relative stabilities of the alkenes listed above can be justified.

Thus we can conclude that greater the number of alkyl groups attached to the double-bonded carbon atoms, greater will be hyperconjugative structures as shown above, and hence greater will be the delocalization of electrons. This is evident from the heats of hydrogenation (ΔH) of various alkenes as shown below:

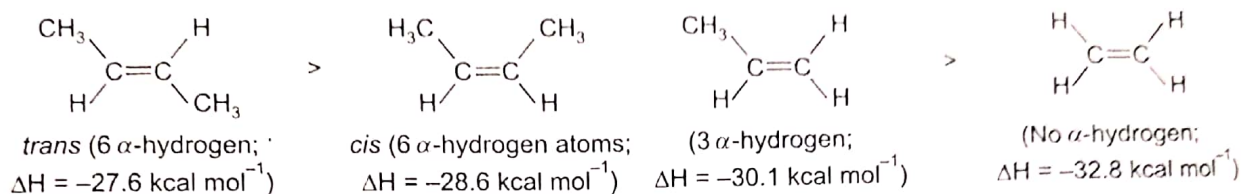
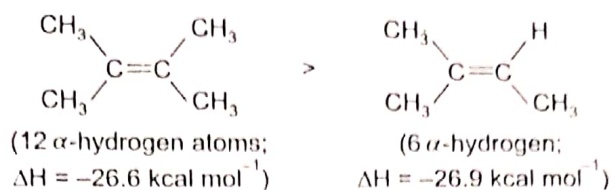
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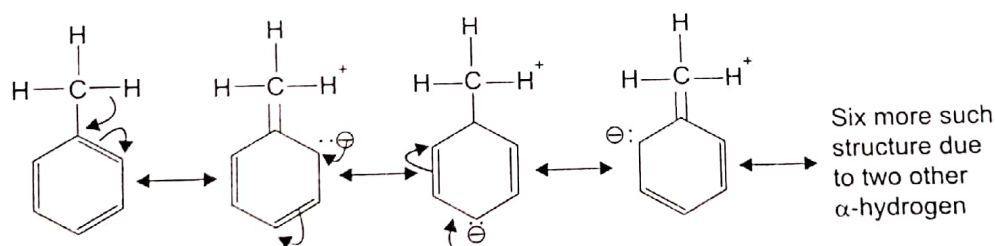


Note: *trans*-2-Butene is more stable than *cis*-2-butene because of steric strain as the two methyl groups in *cis*-isomer are close together.

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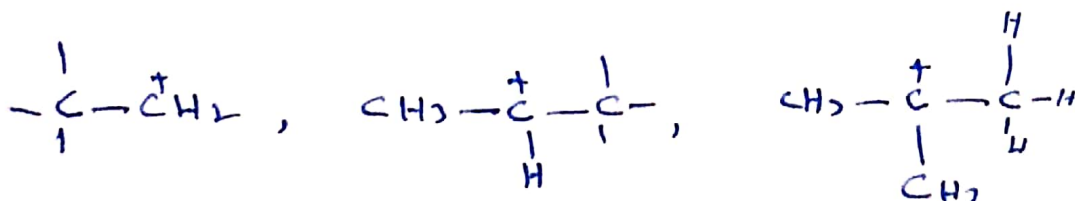
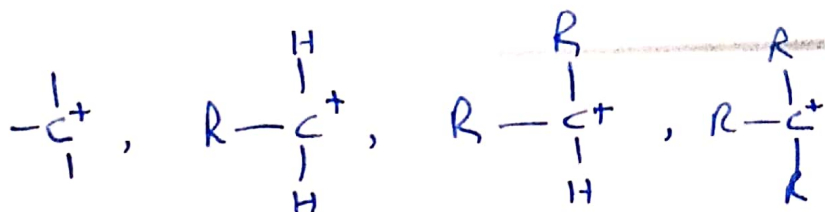
3. **Directive influence of alkyl groups in arenes:** The *o*- and *p*-directing influence of methyl or any other alkyl group can be explained on the basis of hyperconjugation.



In the above hyperconjugative structures, ortho and para positions in the ring get negatively charged or the electron density at *o*- and *p*-position with respect to the methyl group increases due to hyperconjugation. As the substitution reactions in the ring are electrophilic in nature, they take place mainly at the ortho and para positions.

Similarly other alkyl group will increase electron densities at *o*- and *p*-position. Therefore, alkyl groups are *o*- and *p*-directing groups.

4. **Relative stabilities of various types of carbonium ions and free radicals:** This is explained in detail in the coming section of reaction intermediates.



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