

Study material: For B.Sc. part-III

Subject: Organic Chemistry, paper VII

Topic: General Principles

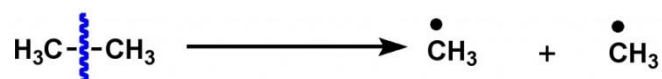
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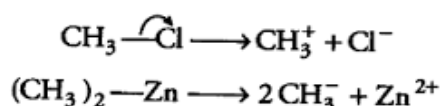
Mechanism of organic reaction: Organic reaction involve the breaking of the old and making the new covalent bond. Most reactions in organic chemistry do not proceed in a single step but take several to yield the desired product. In the course of these multi-step reactions, short-lived intermediates can be generated that quickly convert into other intermediates, reactants, products or side products.

Breaking of a covalent bond between two atoms can take place mainly in two ways viz. homolytic and heterolytic fissions depending on the relative electro-negativities of the two concerned atoms.

(1) Homolytic fission: Homolytic fission is chemical bond dissociation of a molecule by a process where each of the fragments retains one of the shared pair of electrons from the bond. Homolytic fission occurs when two bonded atoms are of similar electronegativity. The intermediates formed are known as free radicals.



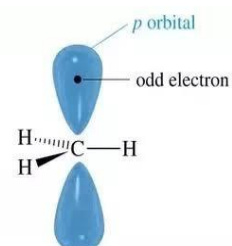
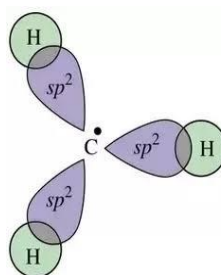
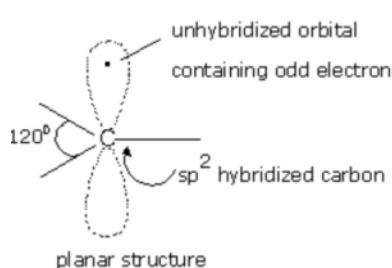
(2) Heterolytic fission: Heterolytic fission occurs when the covalent bond breaks unevenly, and one of the bonded atoms takes both of the electrons from the bond. The atom that takes both electrons becomes a negative ion (anion). The atom that does not take the electrons becomes a positive ion (cation). Heterolytic fission occurs when two bonded atoms are of different electronegativity.



The organic species containing a positive charge at its carbon centre is known as carbocation or carbonium ion (Symbolised as R^+) while the organic species containing a negative charge at its carbon centre is known as carbanion (Symbolised as R^-).

So, fission results in the formation of three important reaction intermediates i.e. Free radical, carbocation (Carbonium ion) and Carbanion.

Free radical: A free radical may be defined as a species that have odd or unpaired electrons. Free radicals are sp^2 hybridized, planar and neutral species with an odd electron in a perpendicular p orbital.

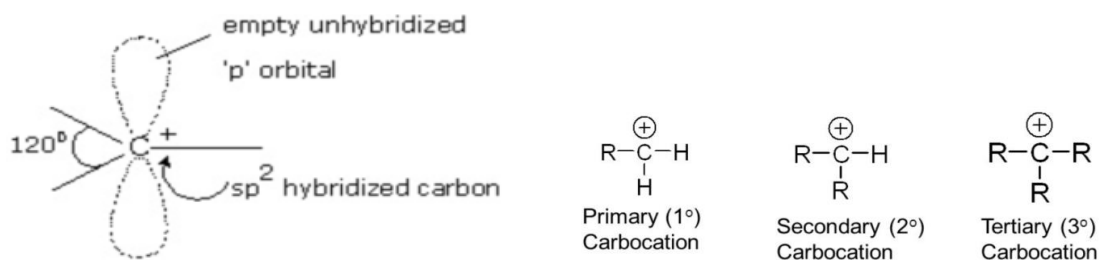


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- The more substituted radical is more stable.
- Radicals next to functional groups, such as carbonyl, nitrile, and ether are even more stable than tertiary alkyl radicals.
- The relative order of stability of the common free radicals:
Benzyl > Allyl > Tertiary > Secondary > Primary > Methyl > Vinyl

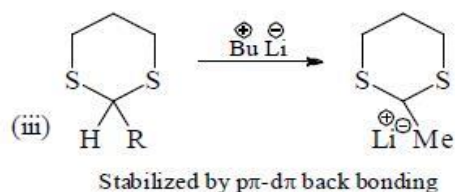
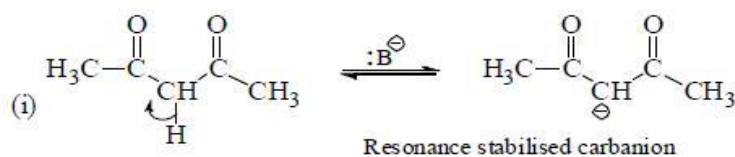
Carbocation (Carbonium ion, R⁺): A carbonium ion is an organic species in which a carbon atom has only three pairs of electrons (i.e. six electrons) and a positive charge.

The positively charged carbon atom in carbocations is sp² hybridized, and is planar. The three substituents of the carbocation lie in a plane leaving the unhybridized empty p orbital perpendicular to them.



Carbanion (R⁻): Some organic compounds when treated with strong Lewis bases lose a hydrogen atom, from a C-H bond, as a proton and form anionic species known as carbanion. The stability of the carbanion is directly related to the strength of the conjugate acid. The weaker is the acid, the greater is the base strength and the lower is the stability of the carbanion.

- The stability of Carbanions increase with an increase in the amount of s character at the carbanionic carbon.
- The presence of electron withdrawing groups such as -NO₂, -CN, -C=O stabilizes a carbanion and vice versa.
- The presence of double bond or aromatic ring in conjugation stabilizes a carbanion. For example:



Other types of reaction intermediates:

Carbene, Nitrene, and Benzyne: Discuss in next notes