

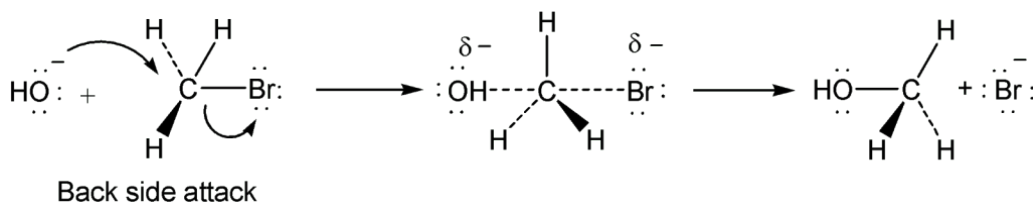
Types of Organic Reactions

Kumud Bala

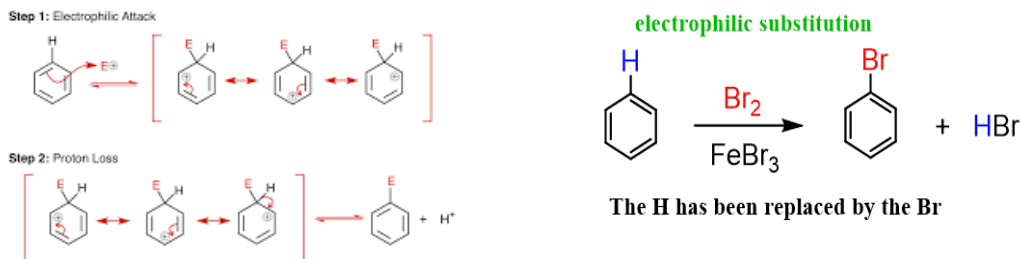
All the organic reactions can be broadly classified into following eight types:

(1) Substitution reactions: A substitution reaction is that which involves the direct replacement (displacement or substitution) of an atom or a group of atoms in an organic molecule by another atom or a group of atoms without any change in the remaining part of the molecule. The product obtained as a result of substitution is called the substitution product and the new atom or group of atoms which enters the molecule is called a substituent. Depending upon the nature of the attacking species (nucleophiles, electrophiles or a free radical) the substitution reactions are of the following three types:

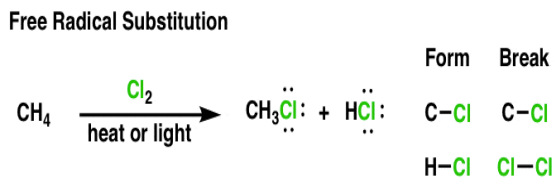
(i) Nucleophilic substitution reactions: Substitution reactions which are brought about by nucleophiles are called nucleophilic substitution reactions. In all these reactions stronger nucleophile usually displaces a weaker nucleophile. These reactions are typical of alkyl halides. For example, hydrolysis of an alkyl halide with an aqueous base:



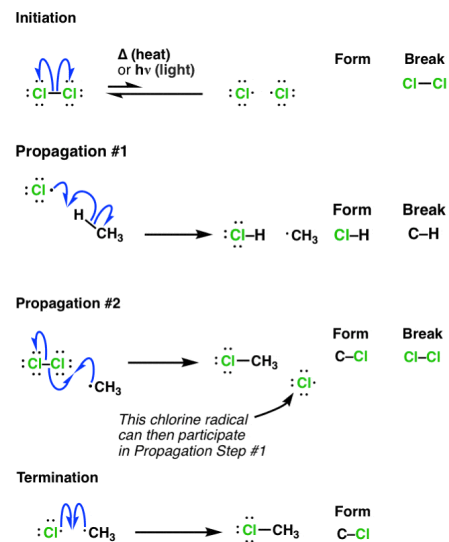
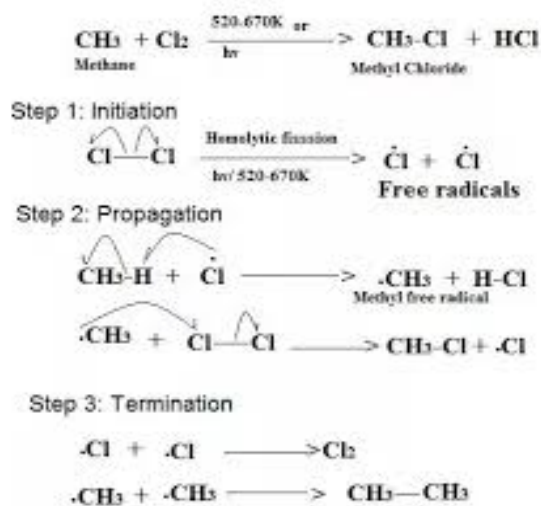
(ii) Electrophilic substitution reactions: Substitution reactions which are brought about by electrophiles are called electrophilic substitution reactions. These reactions are typical of arenes and other aromatic compounds. For example, halogenations, nitration, sulphonation and Friedel-Crafts reactions.



(iii) Free radical substitution reactions: Substitution reactions brought about by free radicals are called free radical substitution reactions. For example, chlorination of methane in presence of heat or diffused sunlight to give methyl chloride and hydrogen chloride.

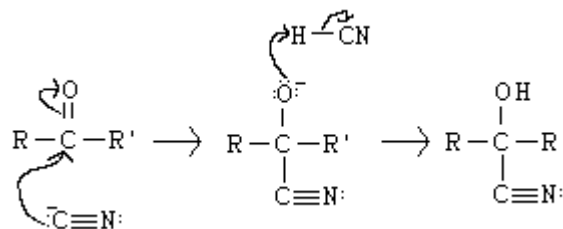


The reaction occurs by a free radical mechanism which involves the following three steps:

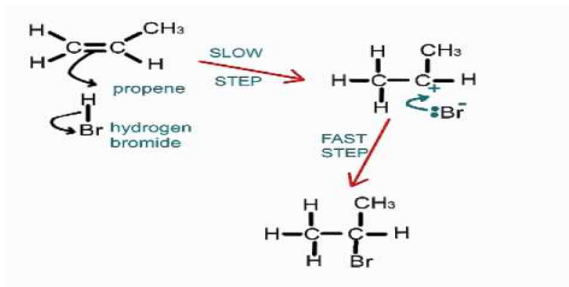


(2) **Addition reactions:** Reactions which involve combination of two reacting molecules to give a single molecule are called addition reactions. Such reactions are typical of compounds containing multiple (double and triple) bonds. Depending upon the nature of the attacking species (electrophiles, nucleophiles or free radicals), addition reactions are of following three types:

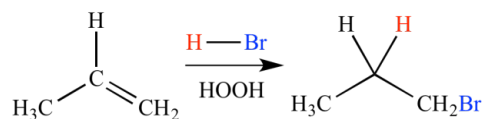
(i) **Nucleophilic addition reactions:** Addition reaction brought about by nucleophile are called nucleophilic addition reactions. These reactions are typical of aldehyde and ketones. For example, base-catalysed addition of hydrogen cyanide to aldehydes or ketones.



(ii) **Electrophilic addition reactions:** Addition reactions brought about by electrophiles are called electrophilic addition reactions. These reactions are typical of alkenes and alkynes. For example, addition of bromine or HBr to propylene:

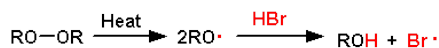


(iii) **Free radical addition reactions:** Addition reactions brought about by free radicals are called free radical addition reactions. For example, addition of HBr to alkene in the presence of peroxides:

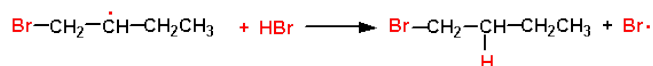
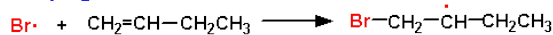


The reaction occurs by the following mechanism:

Initiation



Propagation

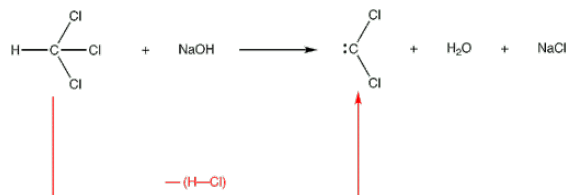


Termination



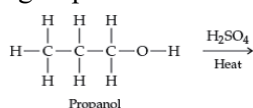
(3) **Elimination reactions:** An elimination reaction is one that involves the loss of two atoms or groups of atoms from the same or adjacent atoms of a substance leading to the formation of a multiple (double or triple) bond. Depending upon the relative position of the atoms or groups eliminated, these reactions are classified as (α) alpha, (β) beta and gamma (γ) elimination reactions.

(i) (α) alpha elimination reactions: In these reactions, the loss of two atoms or groups occurs from the same atom of the substrate molecule. For example, base-catalysed dehydrohalogenation of chloroform to form dichlorocarbene:

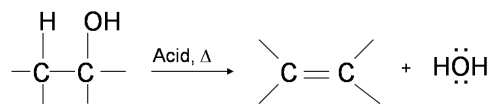


Dichlorocarbene is the reactive intermediate involved in carbylamine reaction and Reimer-Tiemann reaction.

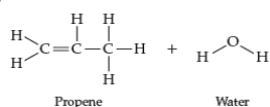
(ii) β -Elimination reaction: In these reactions, the loss of two atoms or groups occurs from the adjacent atoms of the substrate molecule.



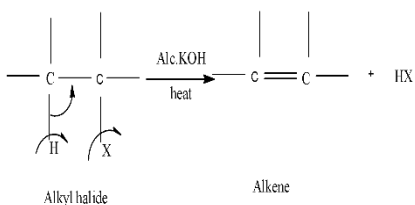
For example, acid-catalysed dehydration of alcohol and



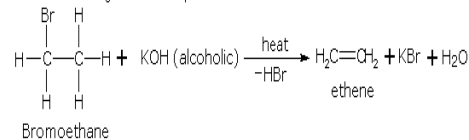
base-catalysed dehydrohalogenation of alkyl halides:



Base-catalysed dehydrohalogenation of alkyl halides:

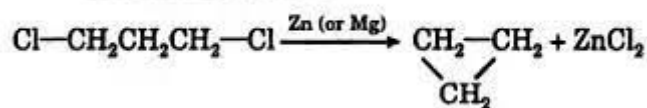


Bromoethane gives ethene,



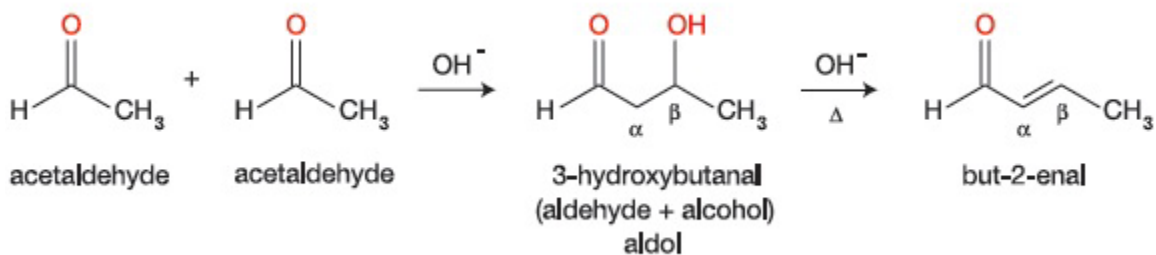
(iii) γ - Elimination: In these reactions loss of two atom or groups occurs from alpha and gamma position (i.e., three bonds away) of the molecule leading to the formation of three membered rings. For example,

Freund Reaction

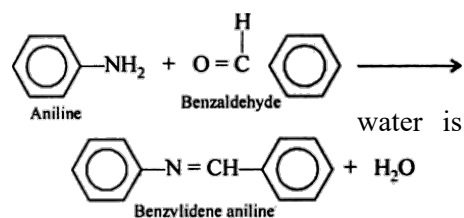


This reaction is called Freund reaction and is extensively used for the synthesis of three membered rings.

(4) **Condensation reactions:** In this reaction two or more molecules of the same or different reactants combine to form a product with or without the elimination of simple molecules such as H_2O , HCl , NH_3 , ROH etc. For example, two molecules of acetaldehyde condense in presence of dilute alkali to form 3-hydroxybutanal. Since β -hydroxyaldehydes or ketone are commonly known as aldols, therefore, this reaction is called aldol condensation.

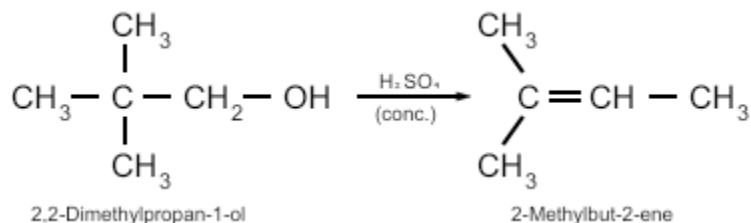


Aldols on heating with dilute mineral acid readily undergo dehydration to form alpha, beta unsaturated aldehydes or ketones. An example of condensation reaction which occurs with the elimination of a molecule of the reaction between benzaldehyde and aniline to form benzylideneaniline.



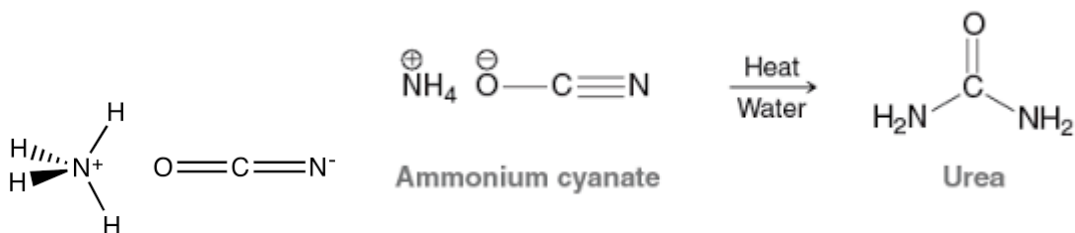
(5) **Rearrangement reactions:** Reaction involving the migration of an atom or a group from one atom to another within the same molecule are called rearrangement reactions. For example:

(i) dehydration of 2, 2- dimethyl propan-1-ol with concentrated sulphuric acid occurs through 1,2 migration of the methyl group to give the rearrangement product, i.e., 2- methylbut -2-ene.

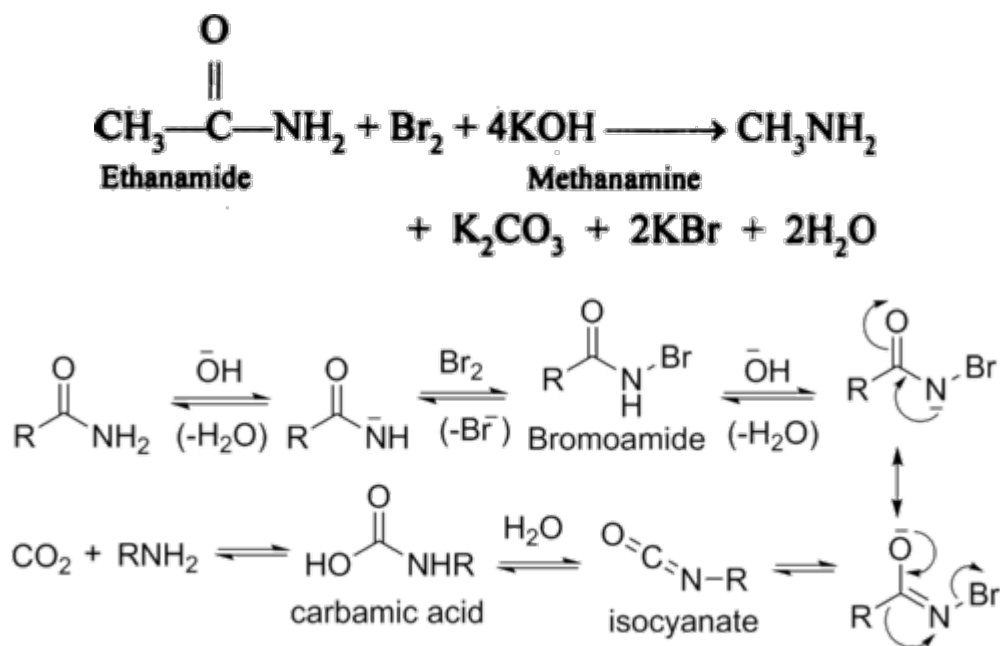


(ii) Wohler synthesis of urea from ammonium cyanate (formed by double decomposition of a mixture of ammonium chloride and sodium cyanate) is also an example of a rearrangement reaction.



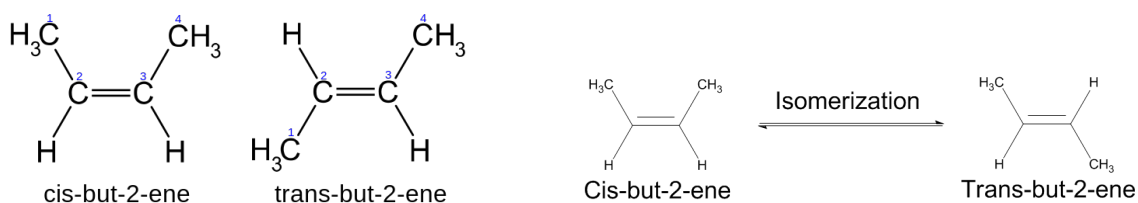


(iii) Hofmann bromamide reaction involving the conversion of 1° amides to 1° amines on treatment with Br₂ in presence of KOH.

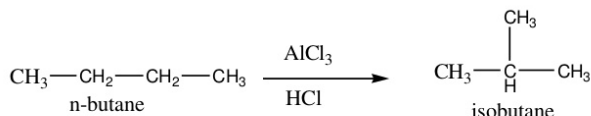


In this rearrangement reaction, group R migrates from carbon to nitrogen to first give an alkyl isocyanate which upon hydrolysis gives a primary amine with one carbon atom less than original amide.

(6) **Isomerisation reactions:** Reactions which involve interconversion of one isomer into another keeping the molecular formulae as well as the carbon skeletons of the reactants and products intact are called isomerization reactions. For example, interconversion of trans-but-2-ene to cis-but-2-ene and vice versa may be regarded as geometrical isomerism reaction.

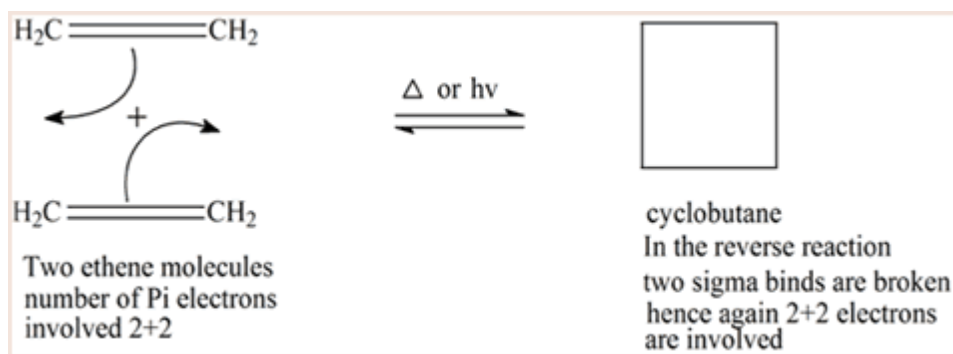


Similarly, n-butane isomerises to iso-butane in presence of anhydrous aluminium chloride and dry HCl



(7) **Pericyclic reactions:** There are large number of organic reactions which do not involve ionic or free radical intermediates. Instead these reactions occur in a single step via a cyclic transition state. In these reactions, bond making and bond breaking occur simultaneously. These reaction do not require any catalyst and are initiated either by heat or light. All such reactions are called pericyclic reactions. For example,

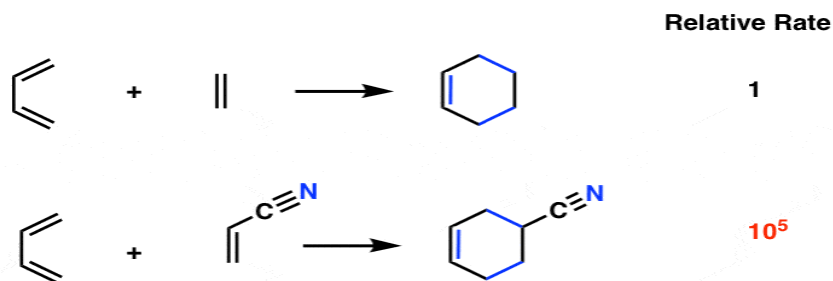
(i)



The addition of one ethene molecule (2π - electron system) to another ethene molecule (2π - electron system) is commonly called $2\pi + 2\pi$ or simply $(2 + 2)$ cycloaddition reaction.

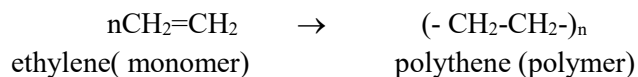
(ii)

Electron withdrawing groups on the dienophile increase the reaction rate



The addition of a diene (4π - electron system) to a dienophile (2π - electron system) to form a 6 membered ring is called $(4 + 2)$ cycloaddition reaction or Diels- alder reaction.

(8) **Polymerization reaction:** These reactions involve the union of a large number of small molecules called monomers to form a molecule with the high molecular weight called polymer. For example,



Assignment

- Which of the following carbocation has the least stability?
(A) methyl (B) ethyl (C) isopropyl (D) tert-butyl
- An electrophilic reagent is :
(A) electron deficient species (B) electron rich species
(C) negatively charged species (D) a Lewis base
- Which of the following carbocation will be the most stable?
(A) $(\text{CH}_3)_2\text{CH}^+$ (B) Ph_3C^+ (C) $\text{CH}_2=\text{CHCH}_2^+$ (D) CH_3CH_2^+
- The shape of carbocation is:
(A) planar (B) linear (C) pyramidal (D) tetrahedral
- Which of the following is not an electrophile?
(A) carbocation (B) SO_3 (C) carbene (D) thioalcohol
- Which of the following is an electrophile?
(A) CN^- (B) ROH (C) AlCl_3 (D) NH_3
- Which of the following is an example of elimination reaction?
(A) chlorination of methane (B) dehydration of alcohol
(C) nitration of benzene (D) hydroxylation of ethylene
- In which of the following are nucleophiles?
(A) H_2O , NO_2^+ , $(\text{CH}_3)_3\text{N}$ (B) HS^- , BF_3 , $\text{CH}_3\text{C}^+=\text{O}$
(C) SH^- , $\text{C}_2\text{H}_5\text{O}^-$, $(\text{CH}_3)_3\text{N}$ (D) NO_2^+ , BF_3 , Cl^+
- The arrangement of $(\text{CH}_3)_3\text{C}-$, $(\text{CH}_3)_2\text{CH}-$, CH_3CH_2- when attached to benzene or unsaturated group in increasing order of inductive effect is:
(A) $(\text{CH}_3)_3\text{C}- < (\text{CH}_3)_2\text{CH}- < \text{CH}_3\text{CH}_2-$ (B) $\text{CH}_3\text{CH}_2- < (\text{CH}_3)_2\text{CH}- < (\text{CH}_3)_3\text{C}-$
(C) $(\text{CH}_3)_2\text{CH}- < (\text{CH}_3)_3\text{C}- < \text{CH}_3\text{CH}_2-$ (D) $(\text{CH}_3)_3\text{C}- < \text{CH}_3\text{CH}_2- < (\text{CH}_3)_2\text{CH}-$
- The increasing order of stability of the following free radicals is:
(A) $(\text{C}_6\text{H}_5)_3\text{C}\cdot < (\text{C}_6\text{H}_5)_2\text{CH}\cdot < (\text{CH}_3)_3\text{C}\cdot < (\text{CH}_3)_2\text{CH}\cdot$
(B) $(\text{C}_6\text{H}_5)_2\text{C}\cdot\text{H} < (\text{C}_6\text{H}_5)_3\text{C}\cdot < (\text{CH}_3)_3\text{C}\cdot < (\text{CH}_3)_2\text{CH}\cdot$
(C) $(\text{CH}_3)_2\text{CH}\cdot < (\text{CH}_3)_3\text{C}\cdot < (\text{C}_6\text{H}_5)_3\text{C}\cdot < (\text{C}_6\text{H}_5)_2\text{C}\cdot\text{H}$
(D) $(\text{CH}_3)_2\text{CH}\cdot < (\text{CH}_3)_3\text{C}\cdot < (\text{C}_6\text{H}_5)_2\text{C}\cdot\text{H} < (\text{C}_6\text{H}_5)_3\text{C}\cdot$
- Hyperconjugation involves overlap of the following orbitals:
(A) $\sigma-\sigma$ (B) $\sigma-p$ (C) $p-p$ (D) $\pi-\pi$

12. Stability of iso-butylene can be best explained by:
 (A) inductive effect (B) mesomeric effect (C) hyperconjugation effect (D) steric effect
13. Hyperconjugation is most useful for stabilizing which of the following carbocation?
 (A) neo-pentyl (B) tert-butyl (C) iso-propyl (D) ethyl
14. Homolytic fission of a covalent bond leads to the formation of :
 (A) electrophile (B) nucleophile (C) free radical (D) carbocation
15. The stablest radical among the following is:
 (A) $C_6H_5CH_2\cdot$ (B) $CH_3CH_2\cdot$ (C) $C_6H_5\cdot$ (D) $CH_3\cdot$
16. Which one of the following characteristics belong to an electrophile?
 (A) it is any species having electron deficiency which reacts at an electron rich C-centre.
 (B) it is any species having electron enrichment, that reacts at an electron deficient C-centre.
 (C) it is cationic in nature.
 (D) it is anionic in nature.
17. Among the following carocations: (I) $Ph_2C^+CH_2Me$ (II) $PhCH_2CH_2CH^+Ph$ (III) Ph_2CHCH^+Me (IV) $Ph_2C(Me)CH_2^+$ the order of stability is:
 (A) $IV > II > I > III$ (B) $I > II > III > IV$ (C) $II > I > IV > III$ (D) $I > IV > III > II$
18. A nucleophile must have:
 (A) a negative charge (B) a positive charge
 (C) a lone pair of electron (D) an electron deficient centre
19. The least stable free radical is----
 (A) $CH_3C\cdot H_2$ (B) $CH_3CH_2C\cdot H_2$ (C) $(CH_3)_2C\cdot H$ (D) $\cdot CH_3$
20. Which one of the following is not true regarding electromeric effect?
 (A) it results in the appearance of partial charges on the carbon atoms
 (B) it is a temporary effect
 (C) it operates on multiple bonds
 (D) it requires an attacking reagent

11. (A) 1. (A) 2. (A) 3. (B) 4. (A) 5. (D) 6. (C) 7. (B) 8. (C) 9. (A) 10. (D) 20. (A)

ANSWERS