

MODEL QUESTIONS

I. SHORT ANSWER TYPE QUESTIONS

Prob.1 What do you mean by organic reaction?

Sol. An organic reaction is a change in structure or functional group leading to formation of a new substance. The compound undergoing a change in structure or functional group is called a reactant or substrate. The knowledge of organic reactions helps in the synthesis of useful chemical compounds such as polymers, dyes, drugs, perfumes, cosmetics, fertilizers, food preservatives.

Prob.2 What are the types of organic reactions?

Sol. The organic reactions can be generally classified as substitution, addition, elimination, rearrangement, oxidation and reduction reactions.

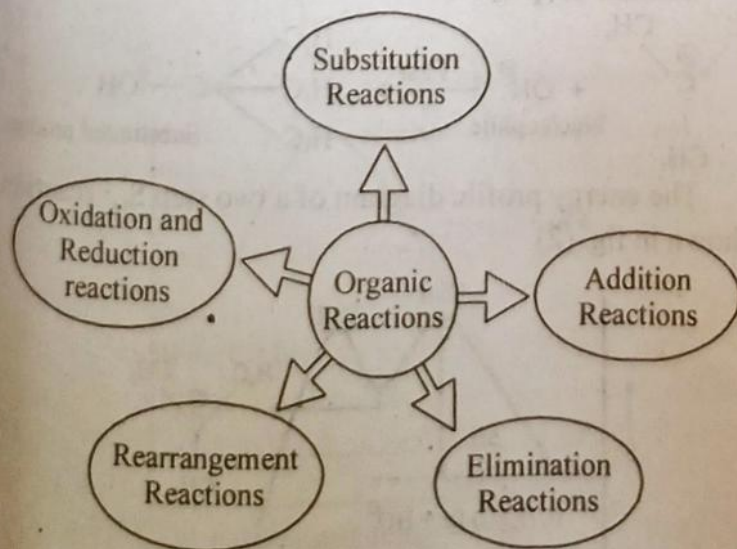
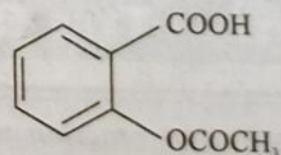


Fig. : Types of Organic Reactions

Sol. Drugs are a way of modifying the chemistry of the body. They can be used to treat diseases and infections, correct imbalances in electrolytes and fluids, or alter mental status (such as inducing amnesia or stopping hallucination). Drugs are used both for medical purposes and for recreation. In both cases, no drug is perfect. A perfect drug would be 100% effective while causing no side effects. Drugs offer many benefits, but there are always trade-offs and risks to consider.

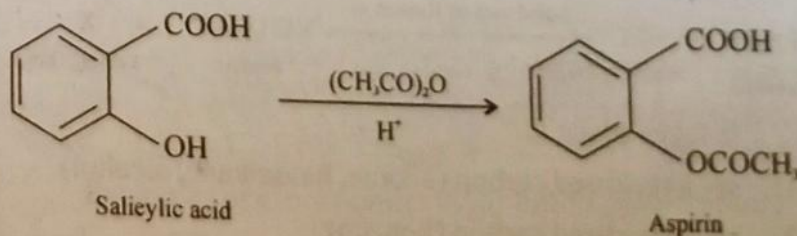
Prob.4 Write down the properties and uses of aspirin.

Sol.



2-Acetoxybenzoic acid (or) Acetyl anlicytain

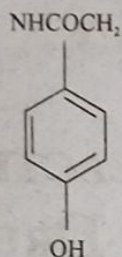
Synthesis



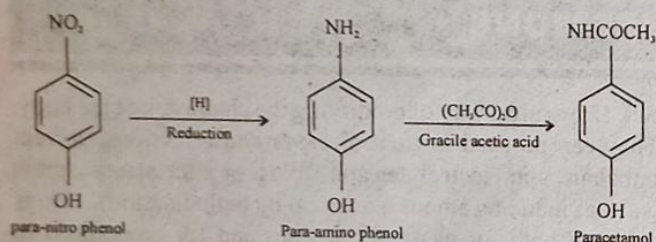
Properties and Uses : Aspirin is a white crystalline powder, slightly soluble in water and soluble in alcohol, indicated for the relief of minor aches and mild-to-moderate pain in the conditions such as arthritis and related arthritic condition. Also used in myocardial infarction prophylaxis.

Prob.5 Write down the properties and uses of paracetamol.

Prob.3 What do you mean by drugs?



Para-acetamino phenol

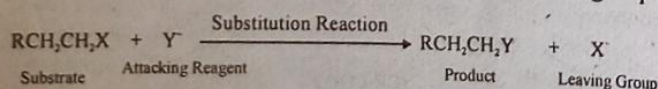
Synthesis

Properties and uses : Paracetamols exist as white crystalline powder, sparingly soluble in water, soluble in alcohol, and very slightly soluble in methylene chloride. Paracetamols produce antipyresis by acting on the death have been observed following over dosage; hepatic damage is likely in an adult who takes more than 10g in a single dose or if a 2-year old child takes more than 3g.

II. LONG ANSWER TYPE QUESTIONS

Prob.1 Explain substitution reaction with the help of example.

Sol. Substitution Reactions : These reactions involve the displacement of an atom or a group by another atom or group.



It takes place at

1. sp^3 hybridised carbon (alkane, haloalkane, alcohol)
2. sp^2 hybridised carbon (benzene)

A substitution reaction can be nucleophilic, electrophilic or free radical substitution reaction.

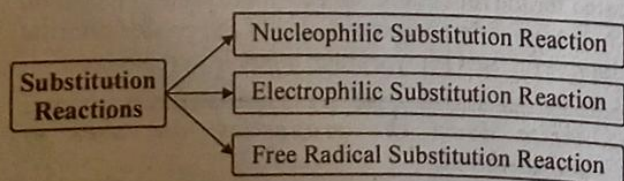
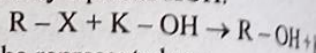


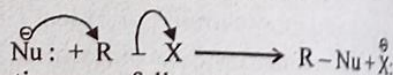
Fig. 1 : Types of Substitution Reaction

1. Nucleophilic Substitution (S_N) Reactions

These reactions involve the attack of a nucleophile and are more common in aliphatic compounds. For example, hydrolysis of alkyl halides by aqueous KOH.



In general it may be represented as :



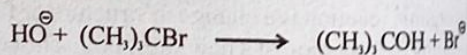
These reactions may follow two mechanisms :

(i) Unimolecular Mechanism ($\text{S}_\text{N}1$)

The rate of such reactions depends only on the concentration of alkyl halide (substrate) and is independent of nucleophile.

$$\text{Rate} \propto [\text{RX}]$$

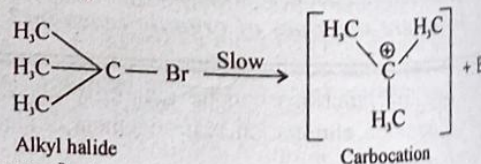
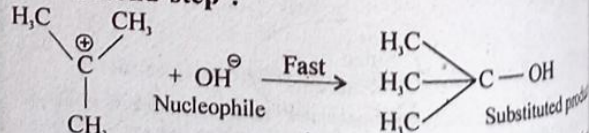
Such reactions are believed to be completed in two steps. The first step is the rate determining step (slow) in which the alkyl halide ionizes to give a carbocation. In the second step, the carbocation combines with the nucleophile to give the substituted product. This can be explained by the hydrolysis of *tert*-butyl bromide.



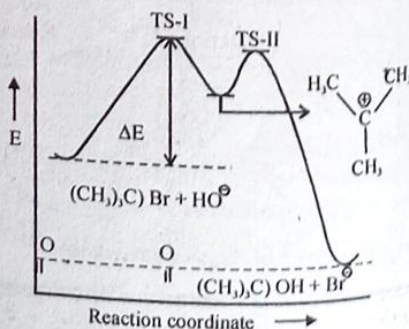
The rate of above reaction depends only on the concentration of *tert*-butyl bromide

$$\text{Rate} = k[(\text{CH}_3)_3\text{C-Br}]$$

Based on the kinetics, the reaction takes place in the following two steps:

First Step**Second step :**

The energy profile diagram of a two-step $\text{S}_\text{N}1$ reaction is shown in fig. (2)

Fig. 2 : Energy Profile for an $\text{S}_\text{N}1$ Reaction

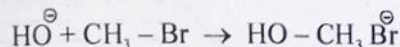
Solvents play very important role in S_N1 reactions as the ionization is facilitated by solvation of carbocation.

(ii) Bimolecular (S_N2) Mechanism

The rate of such reactions depends on the concentration of alkyl halide (substrate) as well as the base (nucleophile).

$$\text{Rate} \propto [\text{RX}] [\text{OH}^-] \quad \dots(3)$$

Such reactions are completed in one step. Consider the hydrolysis of methyl bromide by aqueous NaOH.

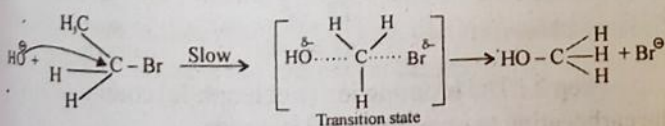


Kinetic studies of this reaction reveals that the rate of such a reaction depends upon the concentration of alkyl halide as well as the hydroxide ion.

$$\text{Rate} \propto [\text{CH}_3\text{Br}] [\text{OH}^-] \quad \dots(4)$$

If the concentration of any of them is doubled then the rate of reaction is also doubled and when the rate or reaction of any one of them is halved, the rate of reaction is also halved.

In such a process the hydroxide ion (nucleophile) attacks the carbon atom from the side opposite to that of the bromine (leaving group). This is because of the fact that both hydroxide ion and the bromine are electron rich. So, the bond breaking and bond making are simultaneous processes and such a reaction, therefore, involve a transition state in which the carbon atom appears to be pentavalent. In transition state, carbon atom is joined to three substituents by full covalent bonds and to the nucleophile and leaving group by partial bonds. The three substituents acquire a coplanar geometry.



(3). The energy profile of such a reaction is shown in Fig.

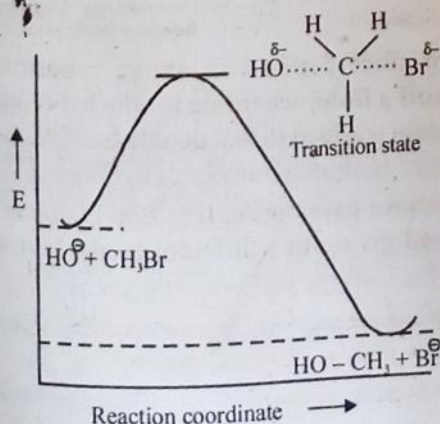


Fig. 3 : Energy Profile for an S_N2 Reaction

Sol.

S. No.	S_N1	S_N2
1.	These are first order reactions.	These are second order reactions.
2.	The nucleophile can attack from both back side as well as front side.	The nucleophile can attack only from the back side.
3.	Reaction rate is influenced by electronic factors.	Reactions is influenced by steric factors.
4.	The order of reactivities of alkyl halides is : Benzyl > allyl > 3° > 2° > 1° halides.	The order of reactivities is : Methyl > 1° > 2° > 3° halides.
5.	Favoured by low concentration of nucleophiles	Favoured by high concentration of nucleophiles.
6.	Favoured by polar solvents	Favoured by non-or low polar solvents

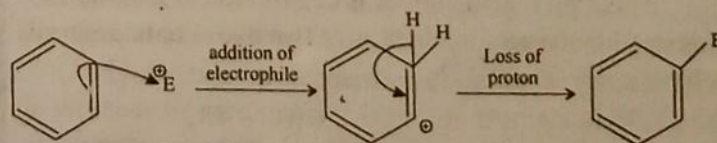
Prob.3 Write short notes on

(i) Electrophilic Substitution Reactions

(ii) Free Radical Substitution Reaction

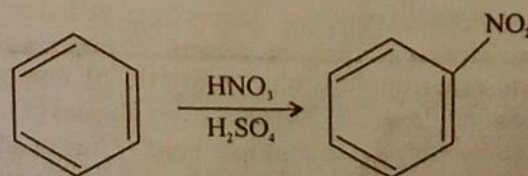
Sol.(i) Electrophilic Substitution Reactions

It involves substitution in the aromatic ring by an electrophile. In the first step the electrophile is attacked by the π -electrons of the aromatic ring leading to the formation of a new carbocation bond. It is followed by loss of a proton. In these reaction, electrophile first attack to give an intermediate with positive charge, known as arenium ion and in the second step leaving group departs. This is known as arenium ion mechanism.



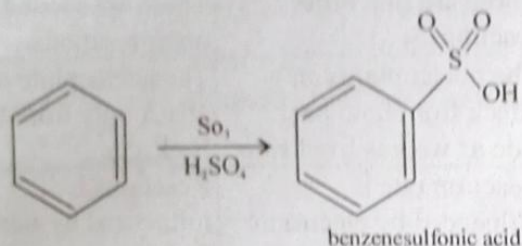
Examples of electrophilic substitution reactions are :

(a) Nitration : It involves a nitronium ion (NO_2^+) as an electrophile.



Prob.2 Give the difference between S_N1 and S_N2 reaction.

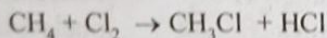
reactions are of four type namely electrophilic, nucleophilic, free radical and concerted. The first three are the ionic processes, with initial attack by electrophile, nucleophile or free radical. The second step consists of a combination of the resulting intermediate with a negative species, a positive species or a neutral entity. In addition, attack at the two atoms of the double or triple bond is simultaneous.



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graph LR
    A[Addition Reactions] --> B[Electrophilic Addition]
    A --> C[Nucleophilic Addition]
    A --> D[Free Radical Addition]
    A --> E[Concerted Addition]
  
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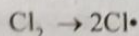
1. Electrophilic addition reaction



The first step is initiation i.e free radical formation by homolytic cleavage of bonds. Second step is chain propagation and finally chain termination step

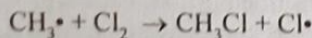
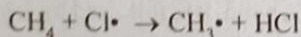
Initiation

Initiation step may happen spontaneously or may be induced by heat or light depending on the type of bond.



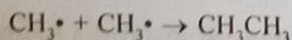
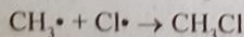
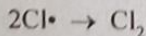
Chain Propagation

In this step, a molecule reacts with a free radical to generate a new radical.



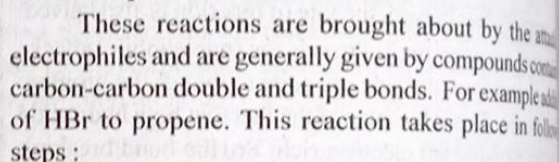
Chain Termination

This step is also known as destruction of free radicals. This step involves a combination of two like or unlike radicals to form a new bond.

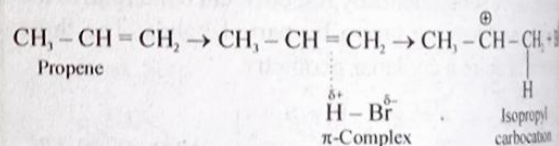


Prob.4 Explain addition reaction with the help of example.

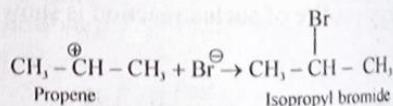
Sol. These reactions are characteristic of compounds containing multiple bonds. The alkene ($=$), alkynes (\equiv), $C=O$, $C\equiv N$ react by addition to multiple bond. Thus in addition reaction there is increase in the number of groups attached to the substrate and decrease in its unsaturation. Addition



Step 1 : H^+ from HBr is added to propene to form π -complex, which then forms isopropyl carbocation (2°-carbocation, which is more stable than 1°-carbocation).

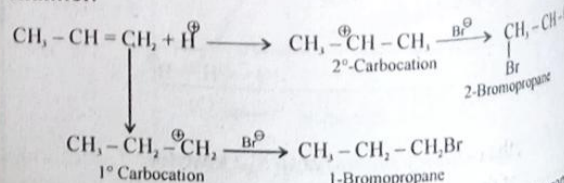


Step 2 : The bromide ion (nucleophile) combines the carbocation to give isopropyl bromide.



The product formed in above reaction follows Markownikoff's Rule, according to which the negative part of the addendum is added to that doubly bonded carbon atom which bears the minimum number of hydrogens.

In the above case during first step : two carbocation may be formed giving two different products in following manner.

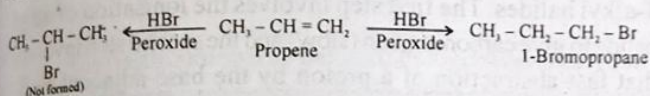


The major product of the reaction is 2-bromopropane as the secondary carbocation formed is more stable

primary carbocation forming 1-bromopropane. Thus, Markownikoff's rule is obeyed.

Anti-Markownikoff's Addition or Peroxide Effect :

According to this effect, the addition of HBr to propene in presence of peroxides gives 1-bromopropane as major product rather than 2-bromopropane.



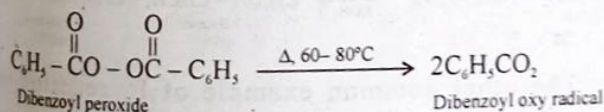
This is because in the presence of peroxides the addition involves free radical mechanism. This effect was put forth by Kharasch and Mayo, so it is also called Kharasch effect.

2. Radical Addition Reactions

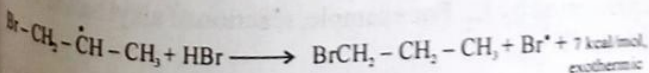
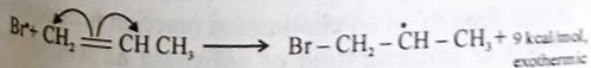
The addition reactions of alkenes catalyzed by small amount of peroxides or irradiated by ultraviolet light are nearly always free radical chain reactions and often lead to the formation of polymetric products. These reactions are illustrated by some examples.

Addition of HBr to Olefins : This is most famous 'abnormal' addition to alkenes and the entire mechanism consists of chain initiation, propagation and finally termination.

Chain Initiation : It starts with light or by thermal decomposition of initiators such as peroxides. The peroxides present in most olefin samples due to autoxidation, are sufficient to initiate the chain. In fact, olefins must be carefully purified to suppress the radical processes.



Chain Propagation : With propylene the chain propagating steps are as follows :

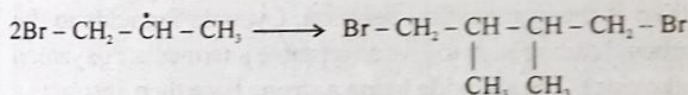
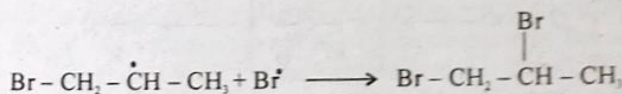


Thus, the overall result is 'anti-Markownikoff' addition, i.e. reverse of the normal addition to the olefin. The bromine adds to the less hindered end of the bond and forms a more stable radical. Therefore, we find that with the decomposition

of a single initiator molecule, a large number of molecules of the product are formed.

This abnormal addition of bromine is a good method of preparing primary bromides from terminal olefins.

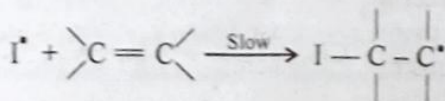
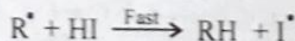
Chain Termination : Chain termination occurs by combination with bromine atoms, or with alkyl radicals or by coupling or disproportionation of alkyl radicals.



It is interesting to note that in presence of polar solvents or in presence of inhibitors like thiophenol or hydroquinone, the above addition becomes a heterolytic process. It is homolytic in conditions in which it is described. So we can say that homolytic addition is the result of peroxide effect and distinguishes it from ionic reactions.

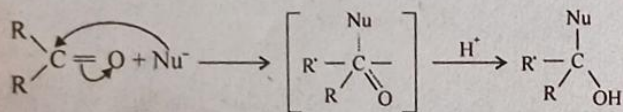
We can explain the analogy in orientation in the same manner as we explain orientation in heterolytic addition. In heterolytic addition, just as the secondary carbocation $\text{CH}_3-\text{CHR}^\oplus$ is more stable than primary $\text{CH}_2^\oplus-\text{CH}_2\text{R}$, so is the secondary radical $\text{CH}_2\text{Br}-\text{CR}^\cdot$ is assumed to be more stable than the primary radical $\text{CH}_2^\cdot-\text{CHR}-\text{Br}$. Therefore, the basic difference is not that in one, the process is heterolytic and in the other it is homolytic, but in one case the addition begins with the formation of a new C-H bond whereas in the other it is the C-Br bond, which is formed first. However, if somehow the reaction conditions could be so altered that the initial attack at the double bond were by a H radical, than Markownikoff's type of addition would be expected.

Having read the mechanism of addition of HBr to olefins in presence of peroxides, it is pertinent to ask if HCl or HI also combine by radical addition? In this connection it has to be noted that HCl or HI do not undergo abnormal addition to olefins under normal conditions. The reasons for failure are different for the two compounds. The H-Cl bond is too strong to be broken readily in the atom abstraction reaction. The hydrogen iodide bond breaks up easily to give atoms but these do not add rapidly to double bonds.

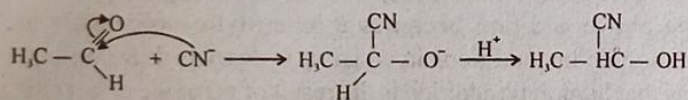


3. Nucleophilic Additions

The carbonyl group of aldehydes and ketones facilitates addition reactions by both nucleophilic as well as electrophilic pathways. The electron deficient carbonyl carbon atom can react with nucleophiles while the electron rich carbonyl oxygen can react with electrophiles. The typical reaction of aldehydes and ketones is nucleophilic addition involving a base can be represented in general as



One of the simplest addition reactions to the carbonyl group is the cyanohydrin reaction. Cyanide ion adds to the carbonyl carbon atom to give an unstable intermediate oxyanion (alkoxide). The alkoxide being a strong base then abstracts a proton from the solvent or another molecule of the weak acid HCN to form the cyanohydrin.

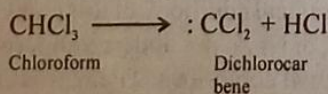


Other examples of nucleophilic additions include the addition of acids (HCl), alcohols to hemiacetals or hemiketals, addition of Grignard reagents, addition of organozinc compounds (Reformatsky reaction), etc. An interesting example is the aldol condensation.

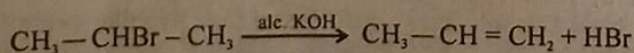
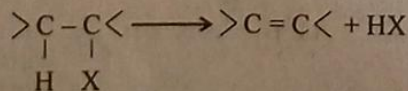
Prob.5 What is Elimination Reaction? Explain its reaction mechanism with an example.

Sol. These reactions are reverse of addition reaction and involve the loss of atoms or groups from the same molecule to form multiple linkage. On the basis of mechanism, elimination reactions may be of two types.

1. α -Elimination : This type of elimination is very rare and involves elimination of two groups or atoms from the same carbon atom. For example,



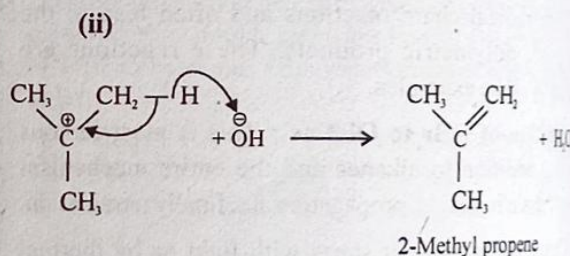
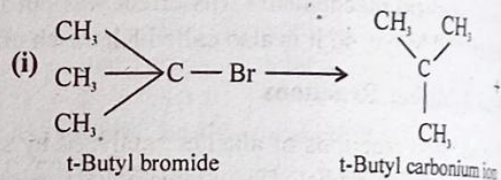
2. β -Elimination : It involves the removal of two groups or atoms from the two adjacent (α and β) carbon atoms of the molecule. For example,



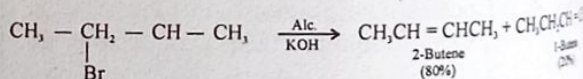
These reactions proceed via unimolecular (E_1) bimolecular (E_2) mechanism.

1. Unimolecular (E_1) mechanism

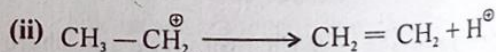
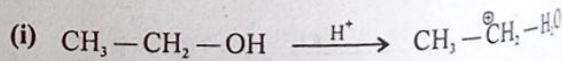
When the rate of an elimination reaction depends on the concentration of the substrate. Like S_N1 reactions also occur in two steps. For example, dehydrohalogenation of T -alkyl halides. The first step involves the ionisation of alkyl halide to give carbonium ion (slow) and the second step involves fast abstraction of a proton by the base adjacent to the carbon leading to the formation of alkene.



When there is a possibility of formation of two types of alkenes, then the main product is most highly substituted alkene as per Saytzeff rule. For example

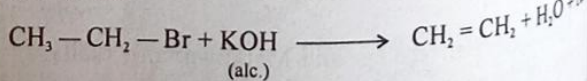


The other common example of E_1 reaction is dehydration of alcohols, which occurs as:



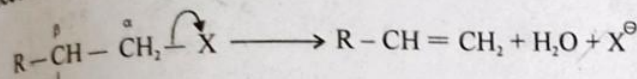
2. Bimolecular (E_2) Mechanism

When the rate of an elimination reaction is dependent both upon the concentration of substrate as well as the attacking reagent, the reaction is of second order and is represented by E_2 . For example, reaction of alkyl halide with alc. KOH.



$$\text{Rate} = k [\text{CH}_3\text{CH}_2\text{Br}] [\text{KOH}]$$

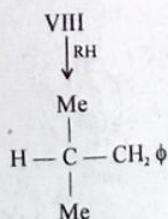
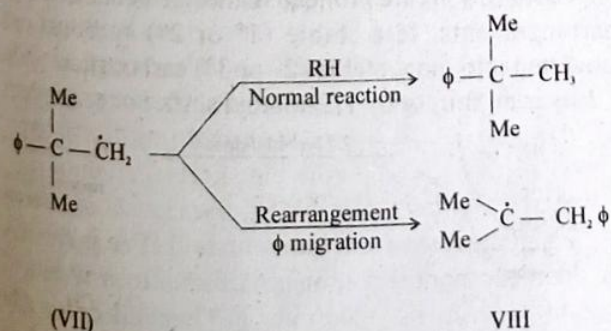
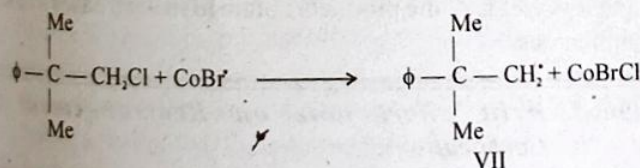
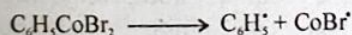
The mechanism is a one step process in which the abstraction of the proton from the β -carbon and the expulsion of the leaving group, i.e., halide ion from the α -carbon atom occur simultaneously.



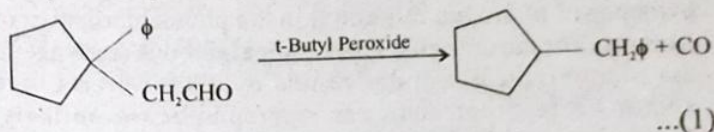
This is also known as dehydro halogenation reaction.

Prob.6 What is free radicals? How they are formed.

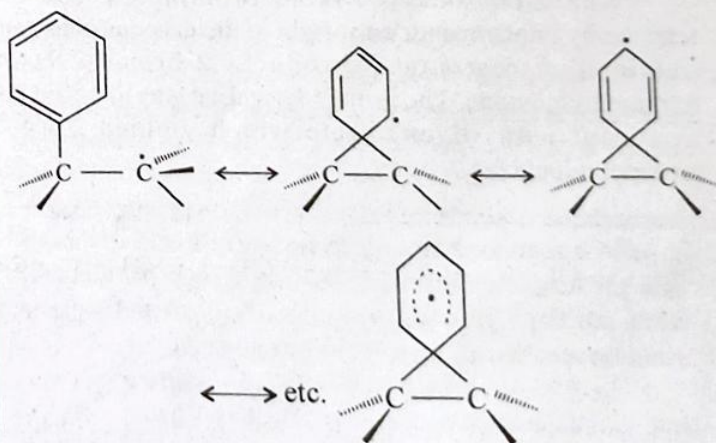
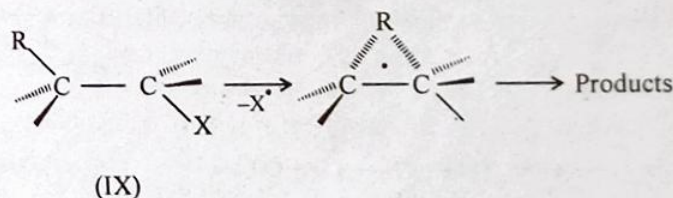
Sol. Free radicals, compared to many other electron deficient species, show less tendency to undergo rearrangements. The largest number of radical rearrangements known are those in which an aryl group migrates to an adjacent position. However, no example of a hydrogen or alkyl shift in a monoradical has been reported. The first case of a phenyl migration scheme was observed in 1944 by Urry and Kharasch. Treatment of 1-chloro-2-methyl-2-phenylpropane with phenylmagnesium bromide, in the presence of cabaltous bromide, afforded a mixture of products. The following radical mechanism was proposed to rationalize the products. The neopentyl radical (VII) may abstract a hydrogen atom to give the normal product:



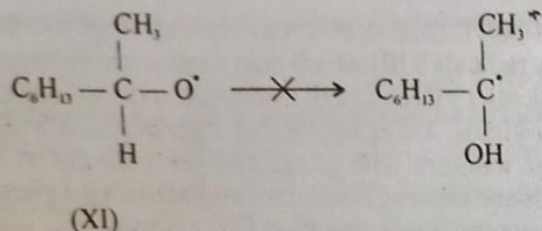
t-butylbenzene, or it may also rearrange to a more stable tertiary radical (VIII) which then forms isobutylbenzene. Both the radicals, (VII) and (VIII), dimerize and are disproportionate in their yields. This sequence of steps was confirmed by subsequent workers who generated the radicals by different methods and observed exclusive migration of the phenyl group. In cycle compounds, equation (1)



of the migration of a phenyl group was reported by Wild and Philip. The mechanism of radical rearrangements has not been investigated in detail but the intramolecular 1, 2-shift, in general, may be described. This assumes the formation of a triangular non-classical radical (IX) which presumably provides a path of lower activation energy compared to the dissociation and coupling processes. Moreover, for aryl migration additional resonance structures are available for the delocalization of the odd electron, as shown, and thus stabilization is possible as in (X).

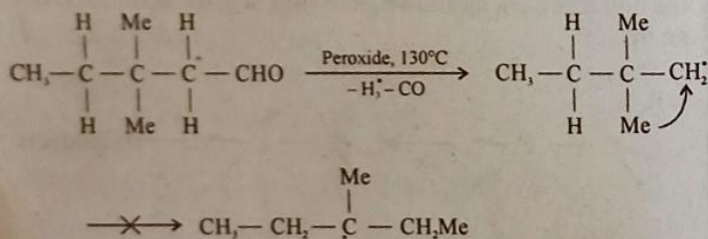


Based on the molecular orbital treatment of Huckelx, it has been argued that the transition state (IX) is less stable than either the initial or the rearranged product when R is hydrogen or an alkyl group. This implies that there is no reason to expect 1,2-alkyl or hydrogen shifts in radical reactions though they are well known in the corresponding carbocations. No unambiguous case of an alkyl or hydrogen migration is yet known in simple radicals. Kornblum and coworkers pyrolyzed optically active 2-octyl nitrite and obtained an optically active octanol. They concluded that the radical (XI) does not undergo a 1, 2 hydrogen shift to carbon to give XI (a) but, rather, abstracts a hydrogen atom from the solvent to yield actanol. Brown and Russel found similar negative

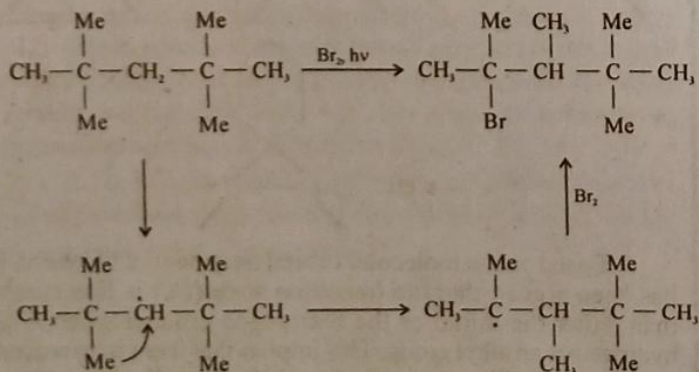


evidence of hydrogen migration in the photochlorination of isobutane because the isobutyl radical did not rearrange to the t-butyl radical. Similar results by other workers have demonstrated that such rearrangements are unlikely. Considerations of orbital symmetry do not apply to reactions proceeding through bridged intermediates. Thus intermediates of the above type are possible.

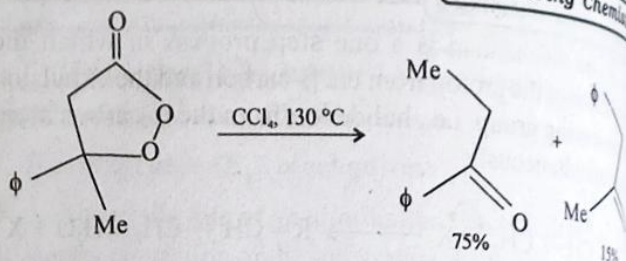
The migration of an alkyl group in carbocations is frequently observed, but the free radicals show no tendency to rearrange. Seubald observed no rearrangement of 2,2-dimethylpentanal to t-amyl radical on decarbonylation in the liquid phase.



Kharasch and coworkers brominated 2,2,4,4-tetramethylpentane under u.v. light in the gaseous phase and obtained a rearranged product, 2-bromo-2,3,4,4-tetramethylpentane. The bromo derivative was identified by treatment with silver nitrate which yielded 2,3,4,4-tetramethylpentane.

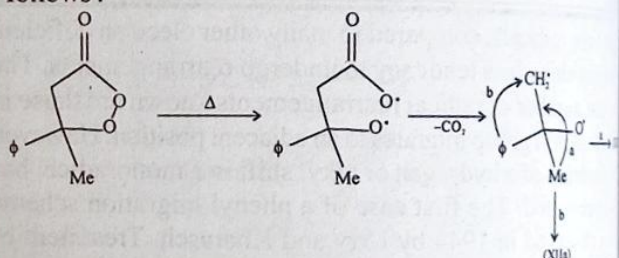


These authors postulated the formation of the original product as the result of the initially formed secondary to the rearranged tertiary radical by a 1, 2-shift. The validity of this interpretation was questioned later and it was suggested that the rearrangement actually took place on reaction of the rearranged bromide with silver nitrate. Nevertheless, recently, several reactions have been reported in which the alkyl group



(XII)

migration has been observed to be even faster than that of the phenyl group. Green and coworkers, for instance, among others, isolated two major products (XII) and (XIIa) in the decarbonylation of β -methyl- β -phenyl- β -peroxypropylacetate. A possible mechanism for this may be postulated as follows:



These products are derived from a diradical intermediate and the yield of (XII) via methyl migration (path a) is almost five times more than that obtained from phenyl migration (path b). The formation of these products can, however, be explained alternatively by a two-step rather than a one-step intramolecular rearrangement. According to the latter pathway the migrating group may fragment and then recombine in the cage to form the product. Though alkyl migrations have been suggested to take place at high temperatures, the complexity and low yields of the products obtained in such cases are rather ambiguous.

Prob.7 Write short note on Rearrangement of Carbocations.

Sol. Carbocations are prone to rearrangements. During these rearrangements, less stable (1° or 2°) carbocations are converted into more stable (2° or 3°) carbocations either by 1, 2-hydride shift or by 1, 2-methyl shift. For example:

