

CHAPTER 6

AKYL HALIDES & AMINES



“Organic compounds that contain at least one halogen atom (fluorine, chlorine, bromine or iodine) bonded to an alkyl group are called haloalkanes.”

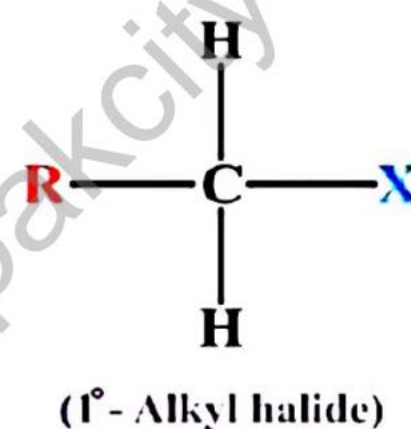
Types of Haloalkanes:

- ❖ **Monohaloalkanes** have only one halogen atom. (They are also called **alkyl halides**)
The general formula of alkyl halides is $R-X$, where R is alkyl group and X is halogen atom (functional group).
Another general formula is $C_nH_{2n+1}X$ where n represents the number of carbon atoms.
- ❖ **Dihaloalkanes** have only two halogen atoms.
- ❖ **Trihaloalkanes** have only three halogen atoms.

Classification of Alkyl Halides:

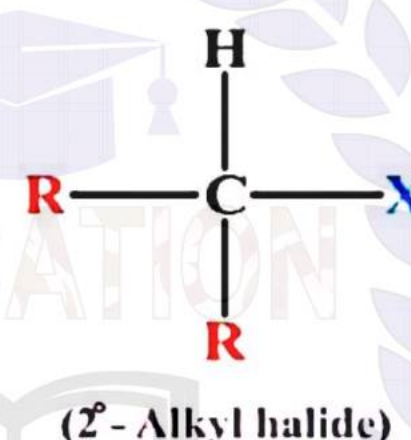


- ❖ **Primary alkyl halides or 1° alkyl halides:** Only one alkyl radical is bonded to α carbon.



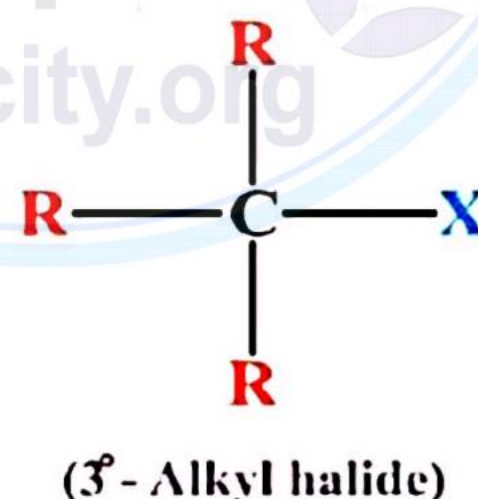
For example: 1-bromo propane ($\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$)

- ❖ **Secondary alkyl halides or 2° alkyl halides:** Two alkyl radical is bonded to α carbon.



For example: 2-bromo propane ($\text{CH}_3\text{CHBrCH}_3$)

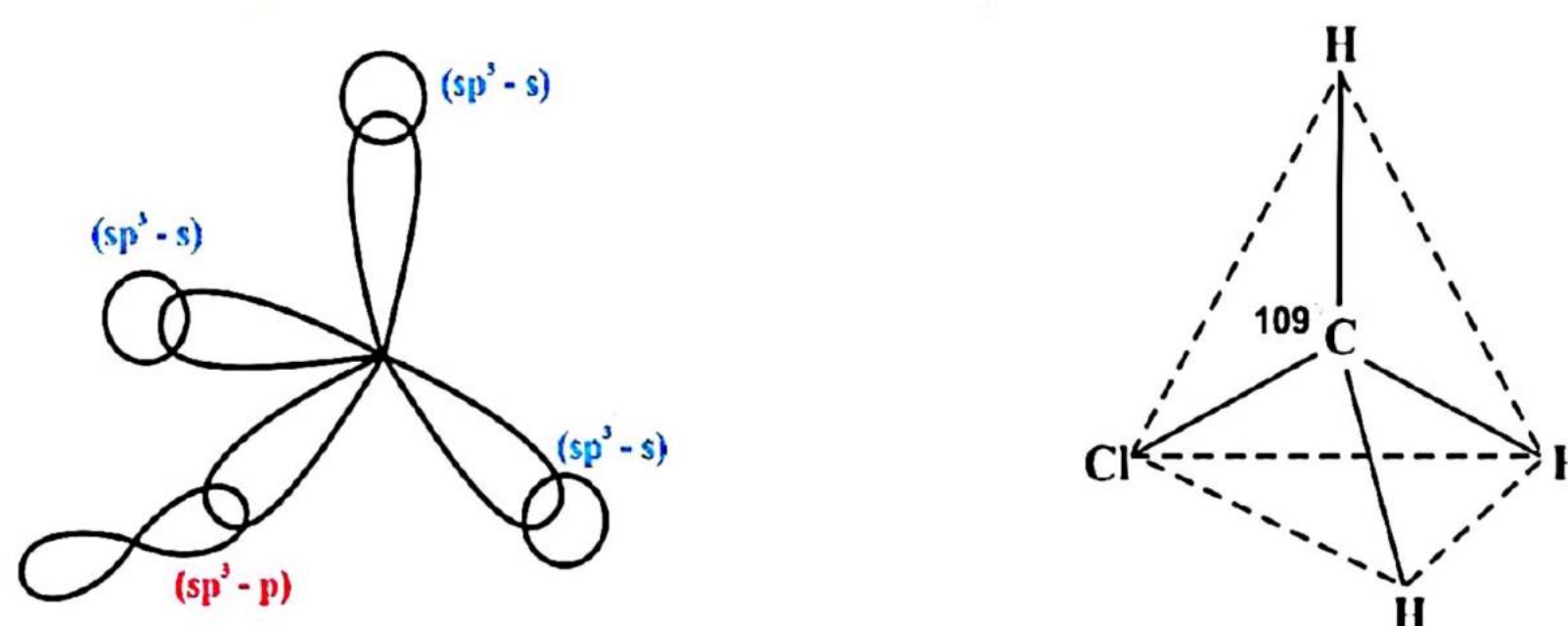
- ❖ **Tertiary alkyl halides or 3° alkyl halides:** Three alkyl radical is bonded to α carbon.



For example: 2-bromo-2-methylpropane $\text{CH}_3\text{C}(\text{CH}_3)_2\text{Br}$

Structure of Alkyl Halide

Let us consider methyl chloride ($\text{CH}_3\text{-Cl}$) as an alkyl halide. The geometry of molecule is explained by hybrid orbital theory. Carbon of methyl halide is bonded with four atoms which means carbon is utilizing its all four valence electrons to produce four sp^3 hybrid orbitals, which are oriented at an angle of 109° to give a tetrahedral geometry. These four sp^3 hybrid orbitals are shared with three s-orbitals of hydrogen atoms and one p-orbital of chlorine by head on overlapping to make four sigma bonds (Fig.6.1).



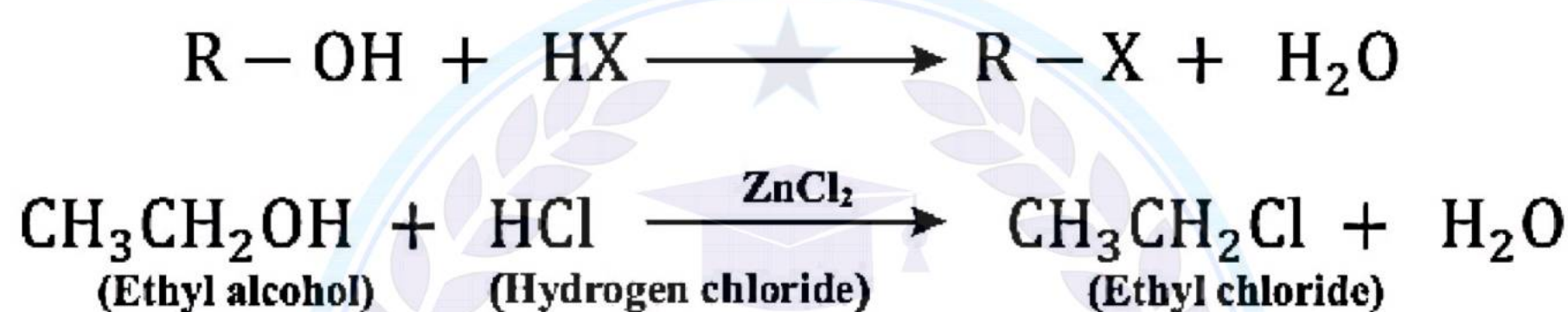
Physical Properties of Alkyl Halides

- They are mostly gases and liquids.
- Alkyl halides with more than 18 carbon atoms are colorless solids.
- They are soluble in organic solvents.
- They have higher melting and boiling point than alkanes.

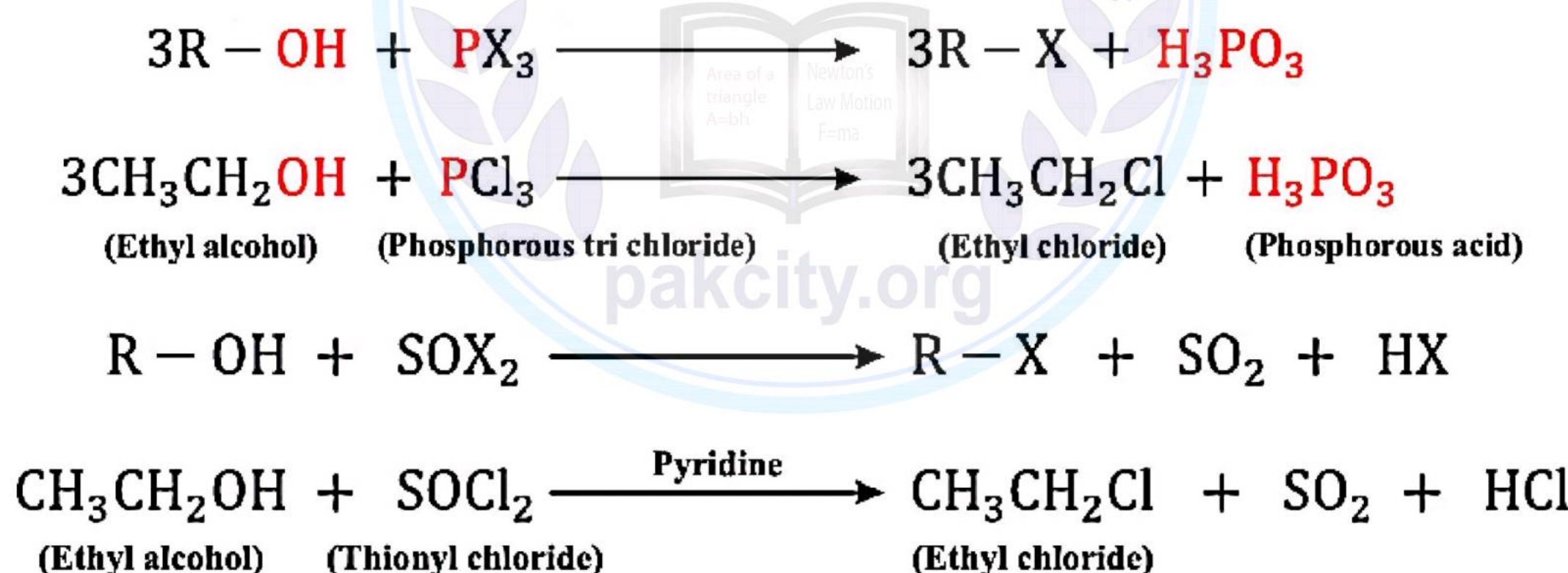


Preparation of Alkyl Halides

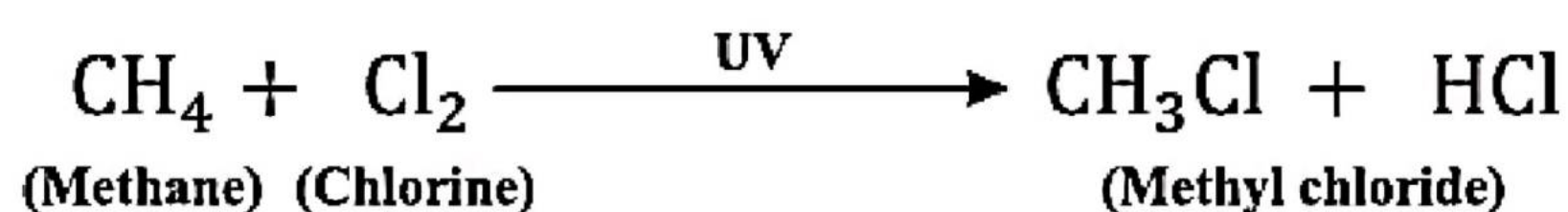
1. Reaction of Alcohol with Hydrogen Halides:



2. Reaction of Alcohol with halogenating agents:

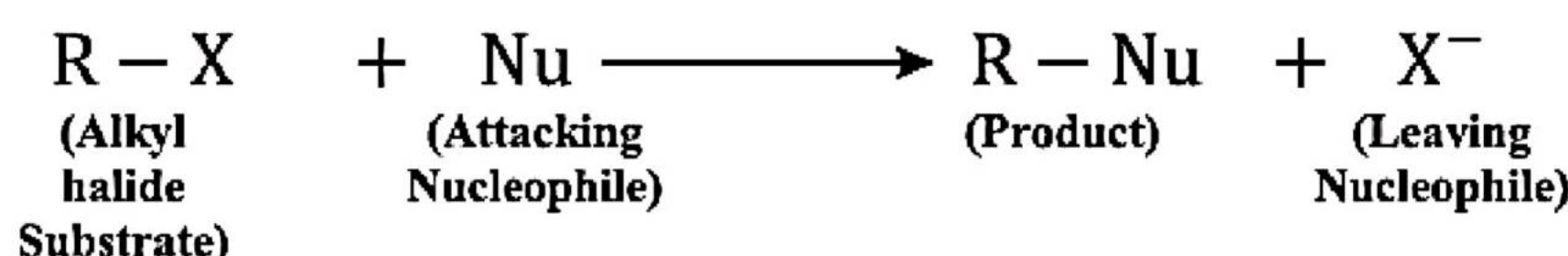


3. By the halogenation of alkane:



Nucleophilic Substitution Reactions

“A type of chemical reactions in which a strong nucleophile (electron efficient species) replaces the weak nucleophile of the substrate is termed as nucleophilic substitution reactions.”



Different strong nucleophilic can produce a variety of organic compounds when treated with an alkyl halide.

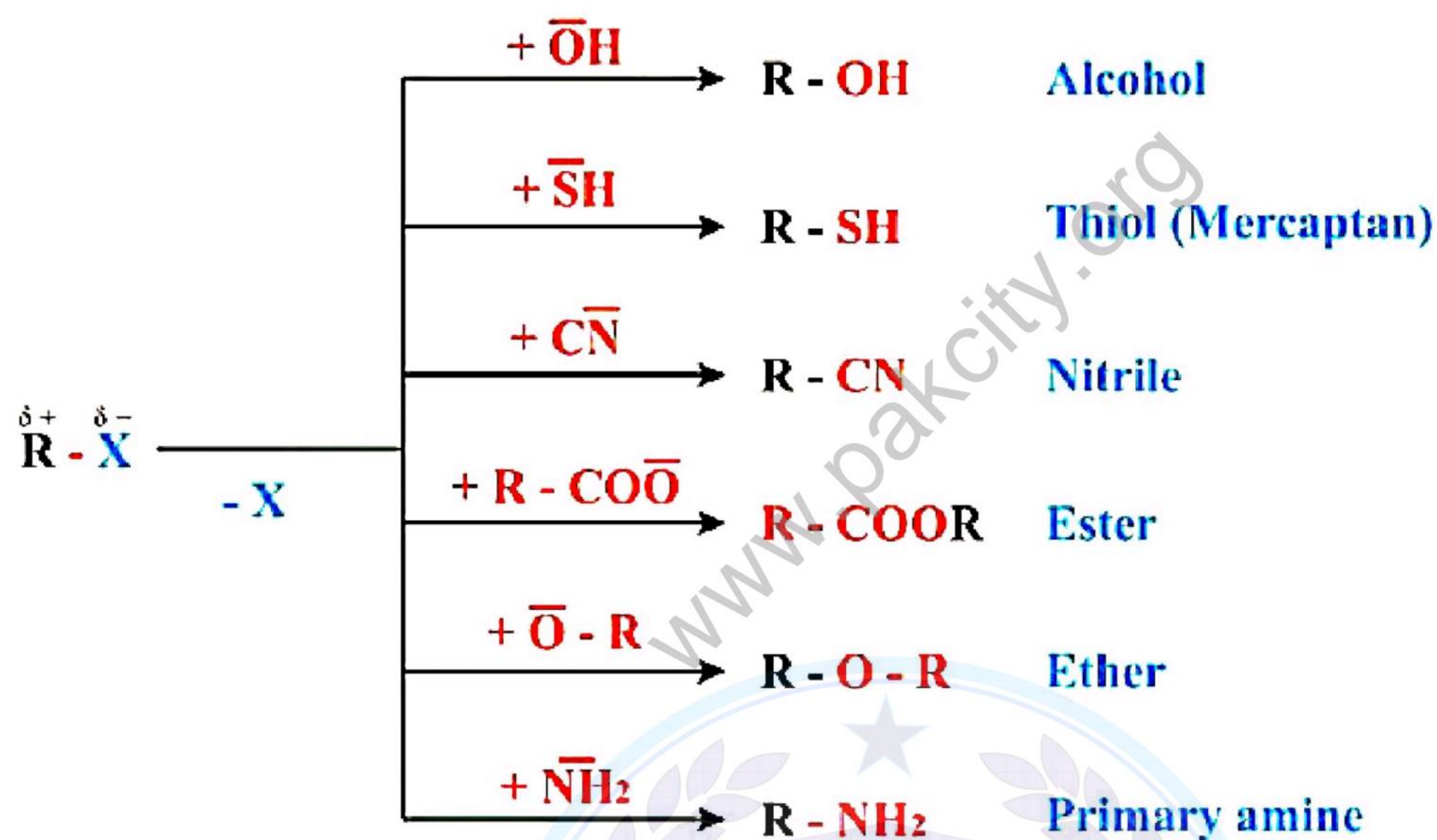


Table 6.1 Some common strong Nucleophiles along with their typical reagents.

Nucleophiles	Typical Reagent
$-\text{OH}^-$	NaOH, KOH
$-\text{SH}^-$	KSH
CN^-	NaCN
$\text{CH}_3\text{-COO}^-$	$\text{CH}_3\text{-COONa}$
$\text{CH}_3\text{-CH}_2\text{-O}^-$	$\text{CH}_3\text{-CH}_2\text{-ONa}$
NH_2^-	NaNH_2



Self-Assessment

Why alkyl halide undergoes nucleophilic substitution reaction? Which reagent is required to convert a methyl iodide into:

(i) Methanol (ii) Methyl cyanide (iii) Dimethyl ether (iv) Thiol

Ans. Alkyl halide undergoes nucleophilic substitution reaction because of the presence of polar covalent bond between carbon atom and halogen atom. Due to the high electronegativity of halogens, it carries a partial negative charge and carbon carries a partial positive charge.

Carbon with a positive charge is called carbonium ion or carbocation. Carbonium ion is a good place for the attack of nucleophile. Nucleophile makes bond with carbon and the halogen is removed.

(i) H_2O

(ii) KCN

(iii) CH_3ONa

(iv) KSH

Mechanism of nucleophilic substitution reactions

The mechanism of nucleophilic substitution reaction is divided into:

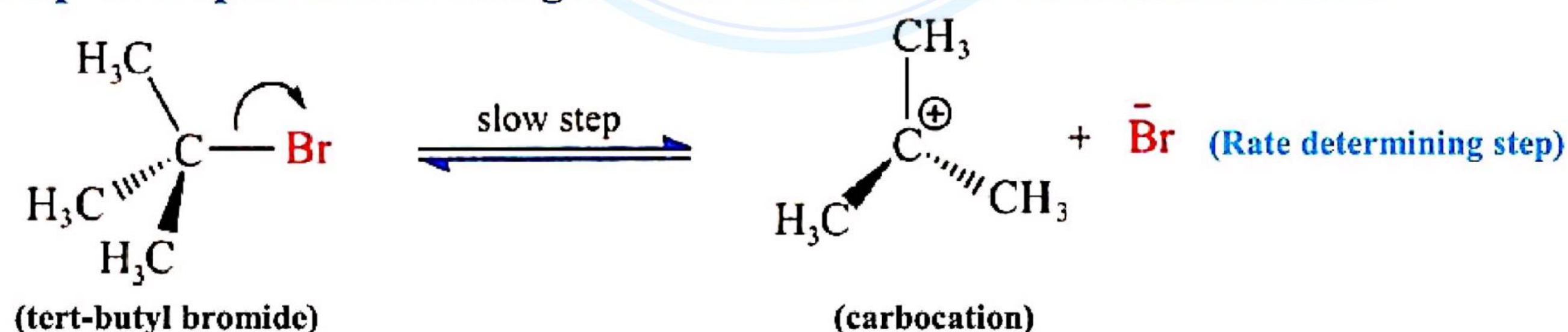
(i) S_N^1 Reactions

(ii) S_N^2 Reactions

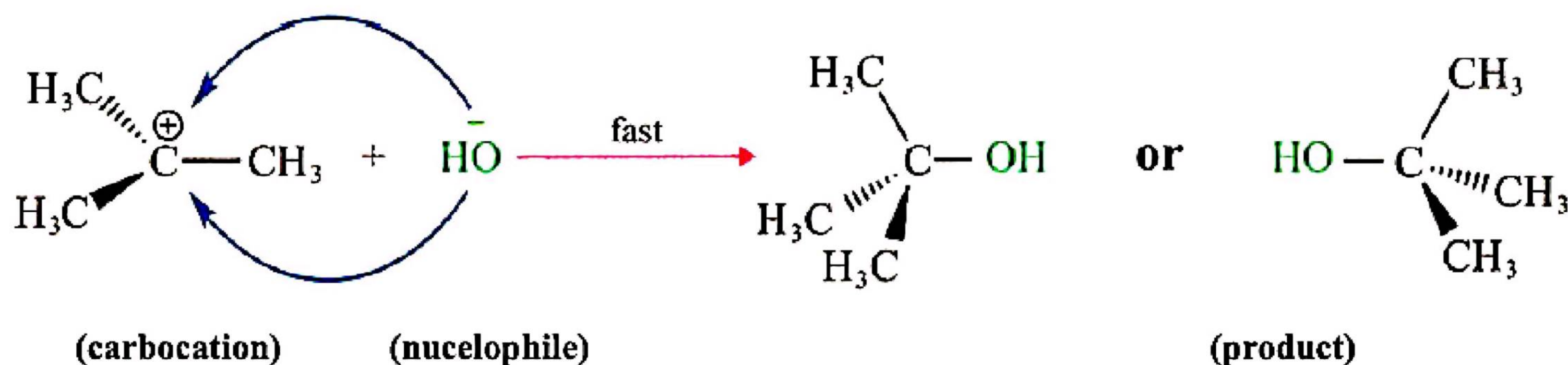
S_N^1 mechanism

It is unimolecular bi-step S_N reaction. "The $\text{S}_\text{N}1$ reaction mechanism proceeds in two distinct steps, with the first step involving the departure of the leaving group (the halogen atom) from the substrate molecule, leading to the formation of a carbocation intermediate, followed by nucleophilic attack in the second step".

Step-1: Departure of halogen from substrate to form carbocation



Step-2: Attack of strong nucleophile on carbocation to form product



Tertiary alkyl halides undergo SN^1 reactions more readily than primary or secondary alkyl halides due to the stabilizing effect of electron-donating alkyl groups, and favoring the formation of the carbocation intermediate, thus facilitating the SN^1 reaction.

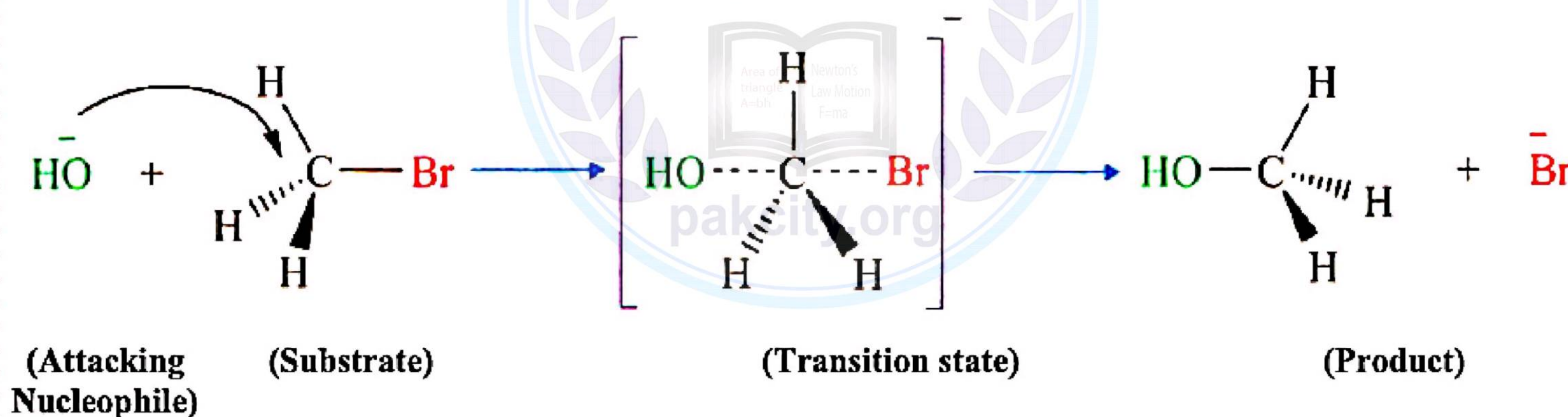
Chemical reactions that processed via the SN^1 mechanism exhibit first-order Kinetics, and the rate of the reaction is dependent on the concentration of the substrate, not on the nucleophile involved in the reaction.

$$R = K [\text{Substrate}]$$



SN^2 mechanism

It is bimolecular single step SN reaction **“In the SN^2 mechanism, bond formation and bond breaking occur simultaneously in a single step process”**. The nucleophile directly attacks the electrophilic carbon atom of the substrate, leading to the departure of the halogen atom attached to the electrophilic carbon. The nucleophile attacks from the back side because the front side is sterically hindered by the nucleophile of the substrate.



The SN^2 mechanism is typically observed in primary alkyl halides and methyl halides because primary carbocation and methyl carbocation are highly unstable due to the lack of electron donating alkyl groups.

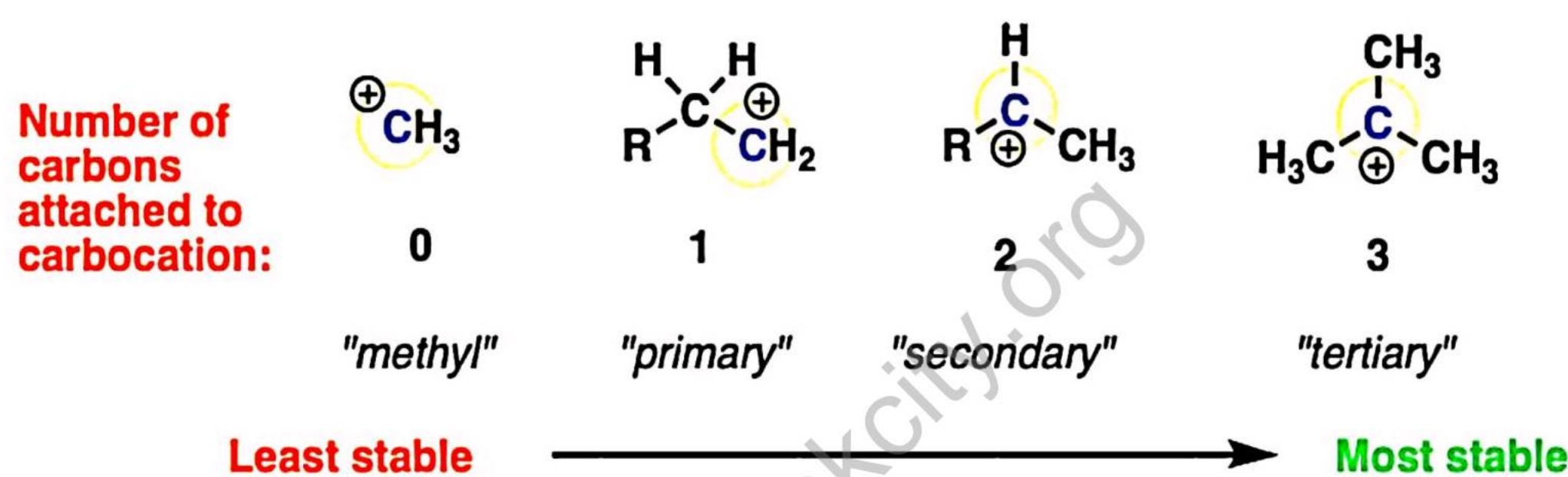
The SN^2 mechanism is followed by second order kinetics which means that the reaction rate is dependent upon the concentration of both substrate and attacking nucleophile.

$$R = K [\text{Substrate}] [\text{Nu}^-]$$

Carbocations and their stability



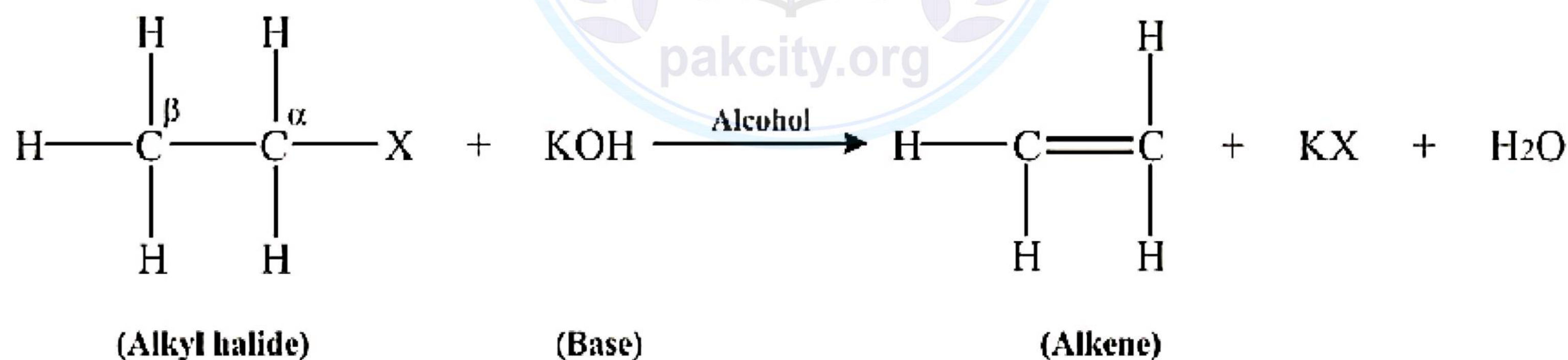
“Carbocations are organic ions that have a positively charged carbon atom. They are formed when a carbon atom loses a pair of electrons.”



Elimination Reactions

An elimination reaction refers to a type of organic reaction where the substituents are removed from the adjacent carbon atoms of substrate molecule.

“When an alkyl halide reacts with alcoholic potassium hydroxide, the removal of hydrogen and halogen atoms from two adjacent carbon atoms of substrate takes place, giving a multiple bond product”. It is referred as 1, 2-elimination or β -elimination reaction.



There are two common types of β -elimination reactions named as E_1 and E_2 .

(i) E_1 (Uni molecular elimination reactions)

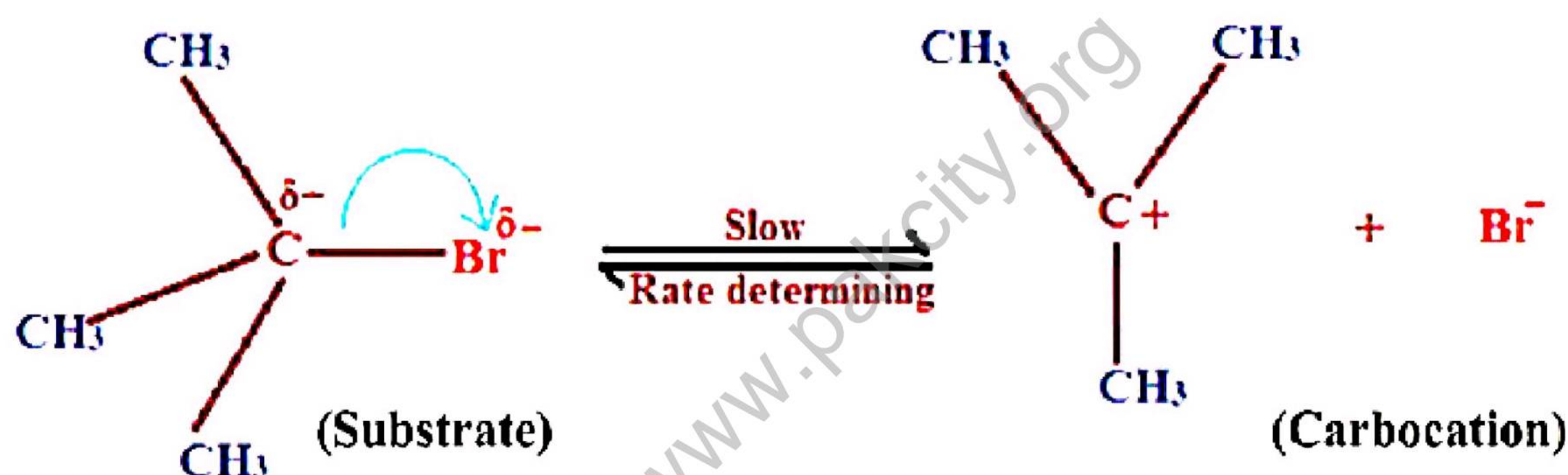
(ii) E_2 (Bi molecular elimination reactions)

Mechanism of E_1 Reaction

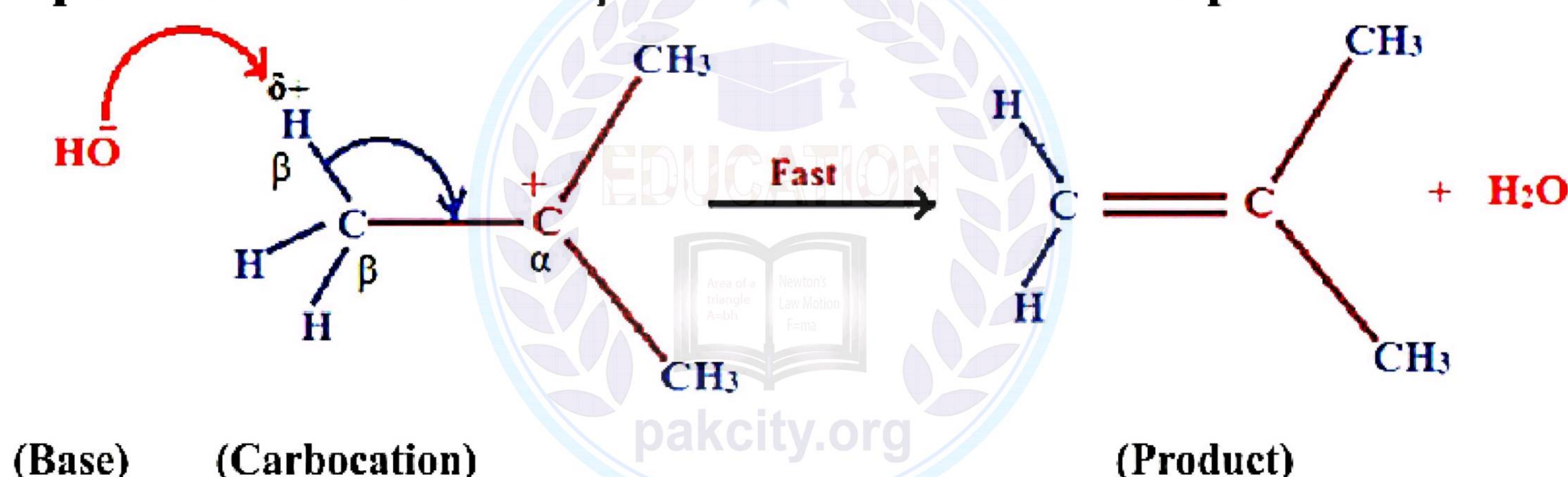


E_1 reactions, known as unimolecular elimination reactions, occur in two steps. In the first step, the halogen atom departs from the substrate, forming a carbocation intermediate, which is the slow and rate-determining step. In the second step, a base abstracts a proton from the carbon next to the halogenated carbon, leading to the formation of a double bond between the two adjacent carbon atoms.

Step-1: Formation of carbocation



Step-2: Attack of Base on β -H & formation of multiple bond

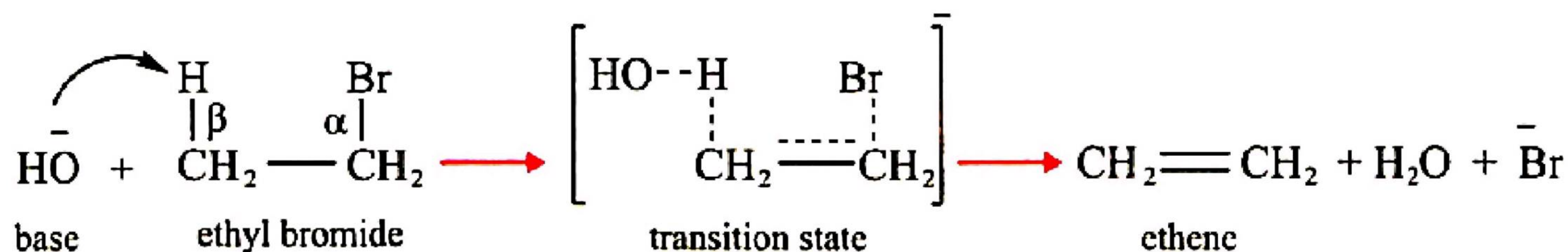


The rate determining step in E_1 mechanism involves the unimolecular ionization of the substrate molecule. Therefore, the rate of the reaction depends only on the concentration of reactant, and not on the concentration of base.

$$R = K [\text{Substrate}]$$

Mechanism of E₂ – reaction

E₂-reaction is referred as bimolecular elimination reaction. The mechanism completes in single step in which both substrate and attacking base are involved.



Mechanism of E₂ reaction is feasible in primary alkyl halides for example when ethyl bromide is allowed to react with hot alcoholic potassium hydroxide, it gives ethene followed by E₂-mechanism. Base first attacks on ethyl bromide and abstracts a proton from β-carbon. Simultaneous halide ion eliminates from α-carbon and the lone pair of electrons is shifted between α and β carbon to give an ethene.

Therefore, as far as kinetics of E₂ reaction is concerned, the rate of this reaction depends upon the concentration of both substrate and attacking base, the rate law may be written as

$$R = K [\text{Sub}] [\text{base}]$$



Self-Assessment

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Explain the following:

- Why β-elimination reactions are not possible in methyl halides?
- Why S_N² reaction is not favourable in tertiary alkyl halides?
- Why tertiary carbocation is more stable than secondary and primary carbocations?

(i) β-elimination reactions lead to the formation of alkene via elimination of β hydrogen. Since, methyl halides don't contain β hydrogen. That's why β-elimination reactions is not possible.

(ii) S_N² reaction is not favorable in tertiary alkyl halides because of high steric hindrance of alkyl radicals. It is also the reason for high stability of tertiary alkyl halides.

(iii) tertiary carbocation is more stable than secondary and primary carbocations because of high steric hindrance.

(ORGANOMETALLIC COMPOUNDS)

“Organic compounds that possess at least one bond between a carbon atom and a metal atom are called organometallic compounds.”

Some common examples of organometallic compounds are as follows:

(i) Grignard's Reagent (R-Mg-X)

(ii) Tetraethyl lead (C₂H₅)₄Pb → It is used as knock inhibitor in petroleum industry

GRIGNARD'S REAGENT:



“Grignard's reagent is an organometallic compound that contains a carbon-magnesium (C-Mg) bond.”

The name Grignard is derived from a French chemist Victor Grignard, who first synthesized this compound and was subsequently awarded the Nobel Prize in Chemistry in 1912.

Preparation of Grignard Reagent

Grignard reagents are prepared in the laboratory by the reaction of an alkyl halide with magnesium metal in the presence of anhydrous ether.



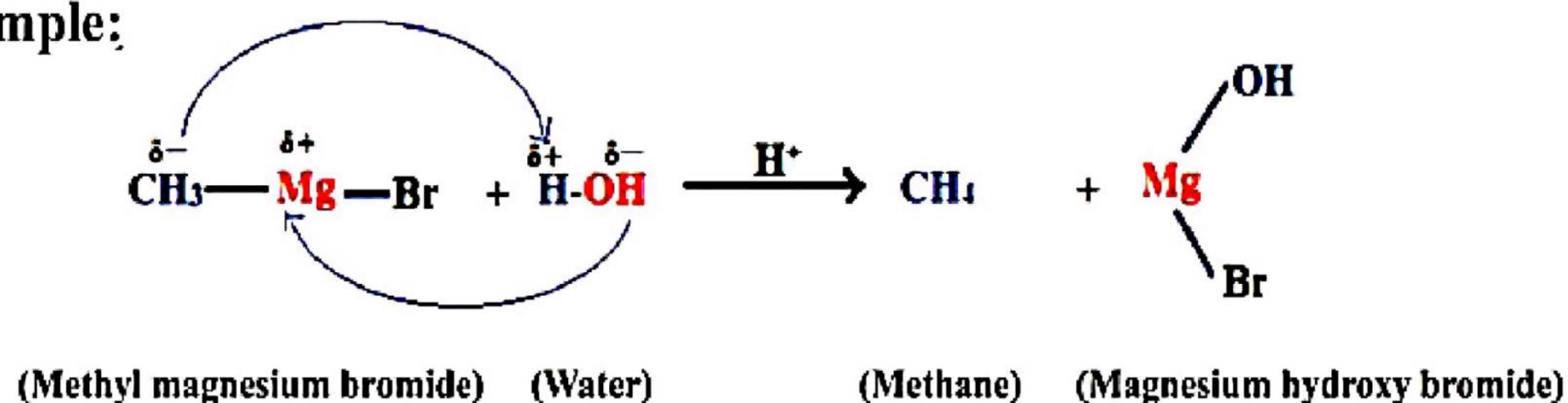
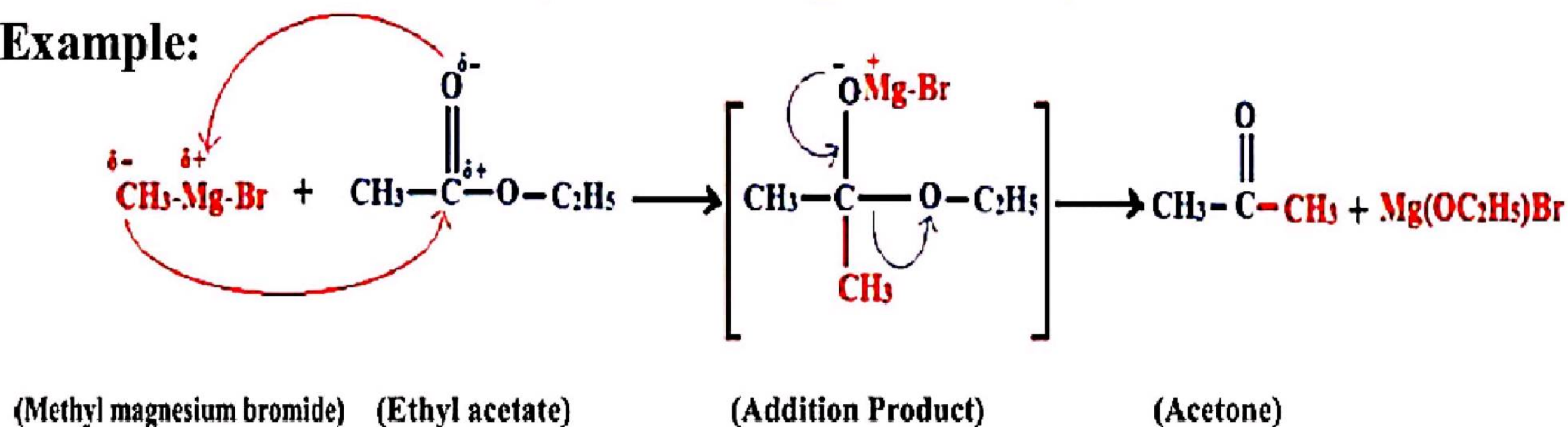
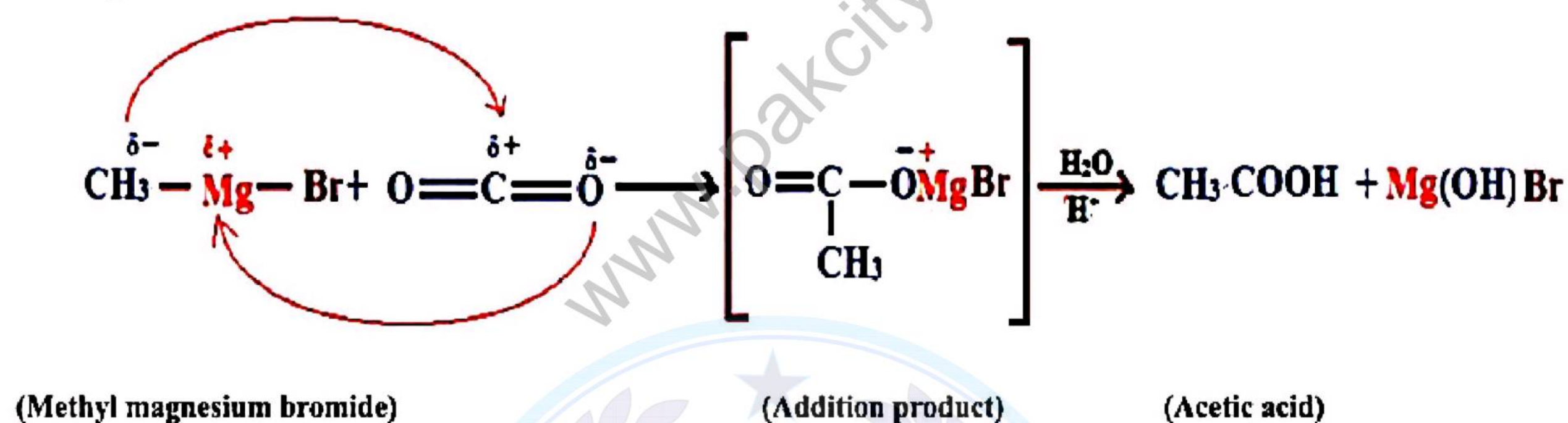
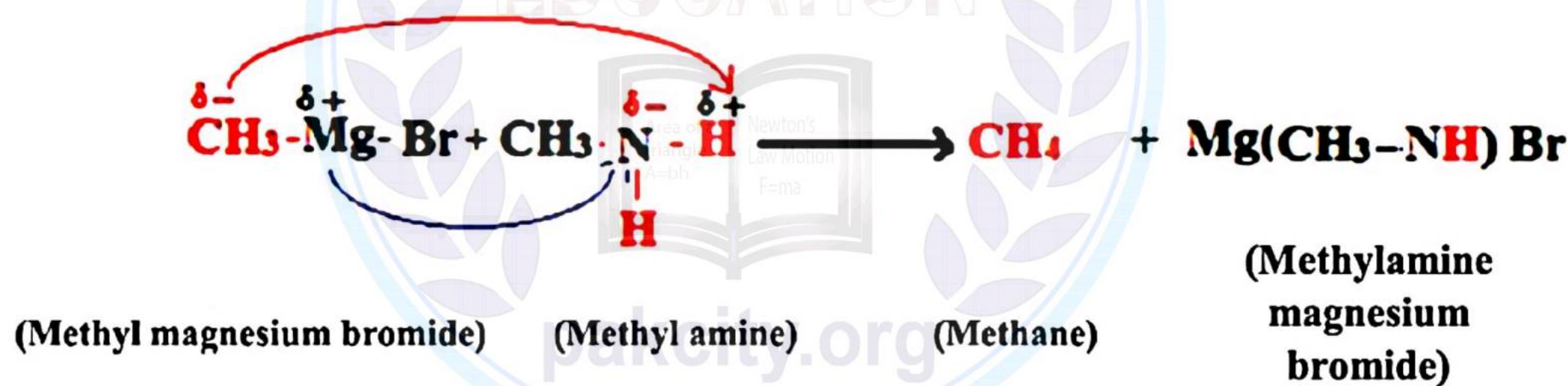
Where R = alkyl group, for example -CH₃, -C₂H₅ etc

X = halogen, for example -Cl, -Br, -I



Reactions of Grignard Reagent

(i) Reaction with water:

Example:**(ii) Reaction with Ester:****Example:****(iii) Reaction with CO₂:****Example:****(iv) Reaction with Primary Amine:****Example:****AMINES**

“Organic compounds that contain a nitrogen atom bonded to one or more alkyl or aryl group are known as amines.”

$\text{R}-\text{NH}_2$ \leftarrow NH_3 \rightarrow $\text{R}-\text{NH}-\text{R}$
 Primary amine Ammonia Secondary amine

\downarrow

$\text{R}-\text{N}-\text{R}$
 $|$
 R
 Tertiary amine

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- ## STRUCTURE OF AMINE:

Lone pair of electrons

sp^3 orbital

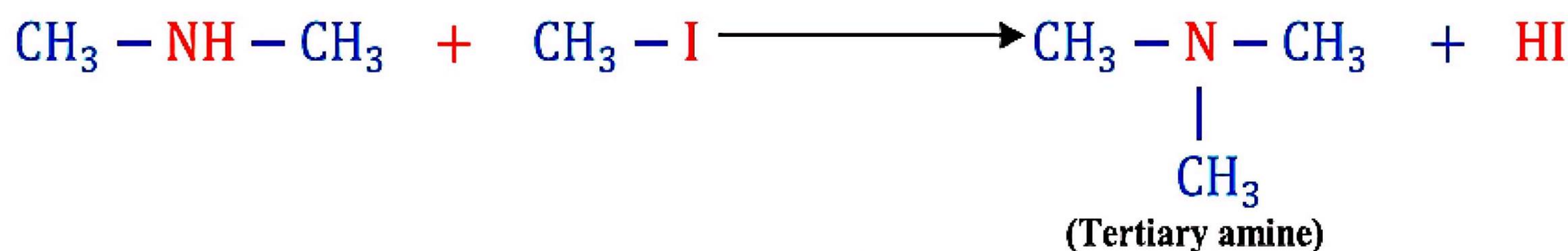
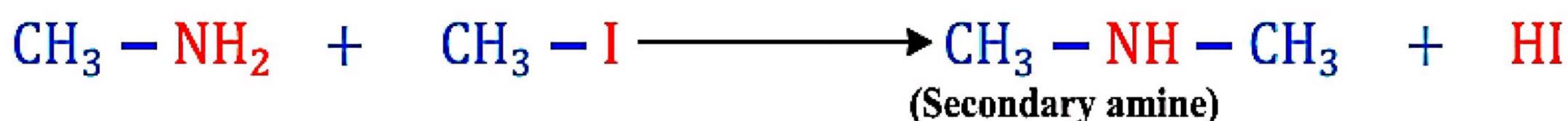
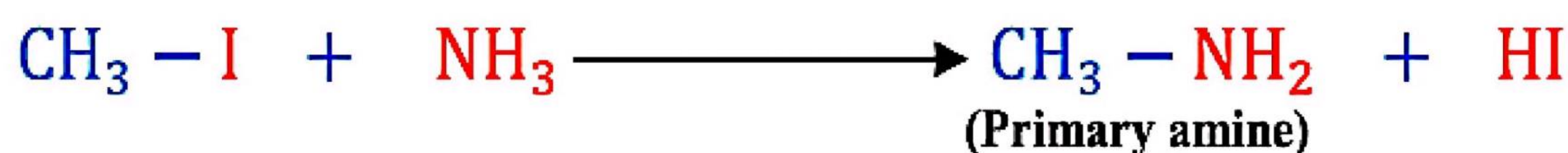
107°

Amines are basic in nature. The basicity of amines is explained by the presence of lone pair of electrons on nitrogen atom.

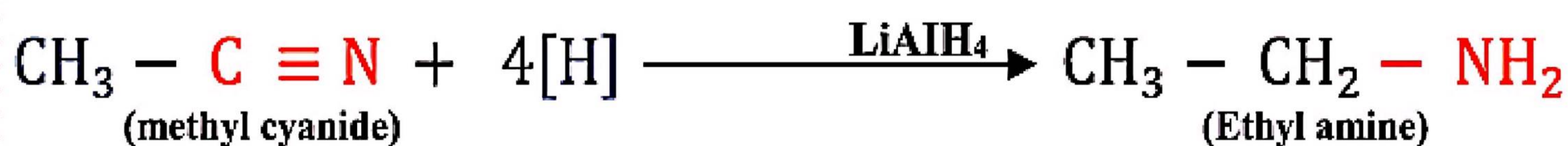


Preparation of Amines

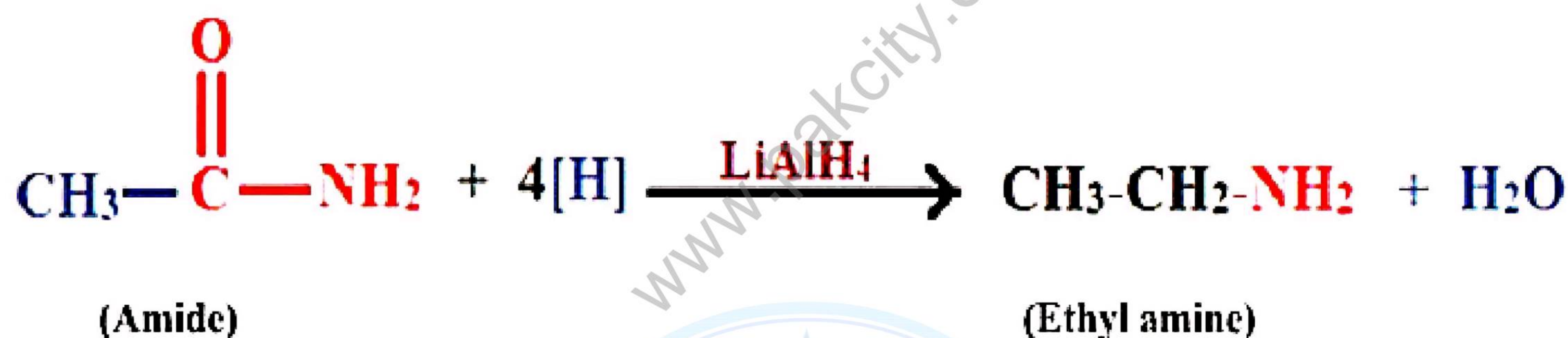
(i) Alkylation of Ammonia by Alkyl Halides



(ii) Reduction of Nitriles



(iii) Reduction of Amides



Reactions of Amines

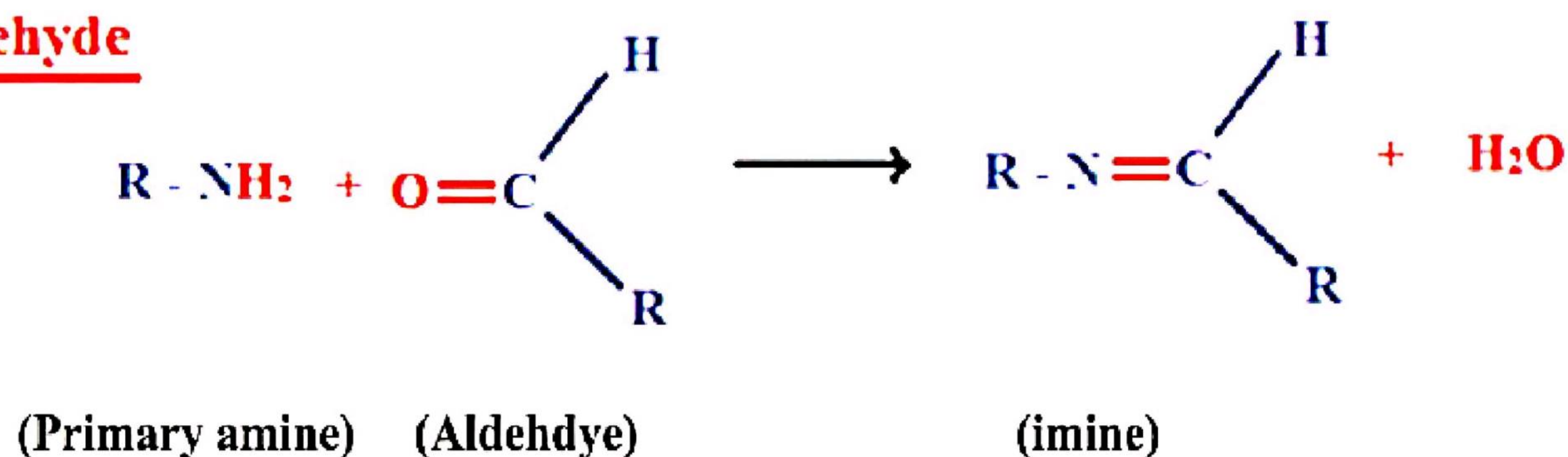
(i) Alkylation of Amines by Alkyl Amines



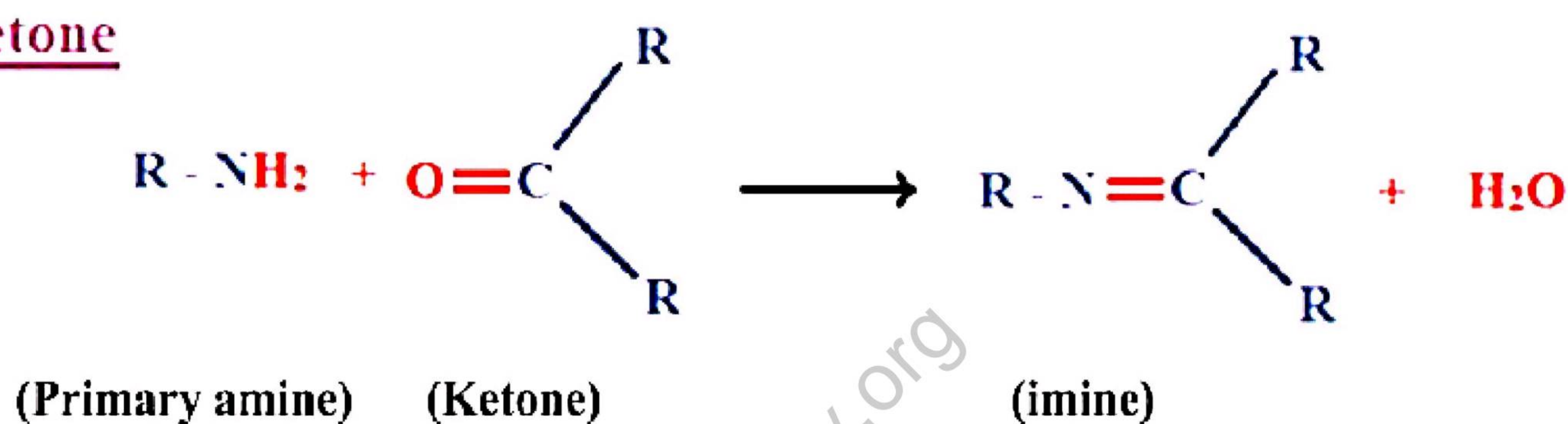
(ii) Reaction of Amine with aldehyde and ketone

Primary amines can react with aldehydes and ketones to produce “imines” which also referred as Schiff bases.

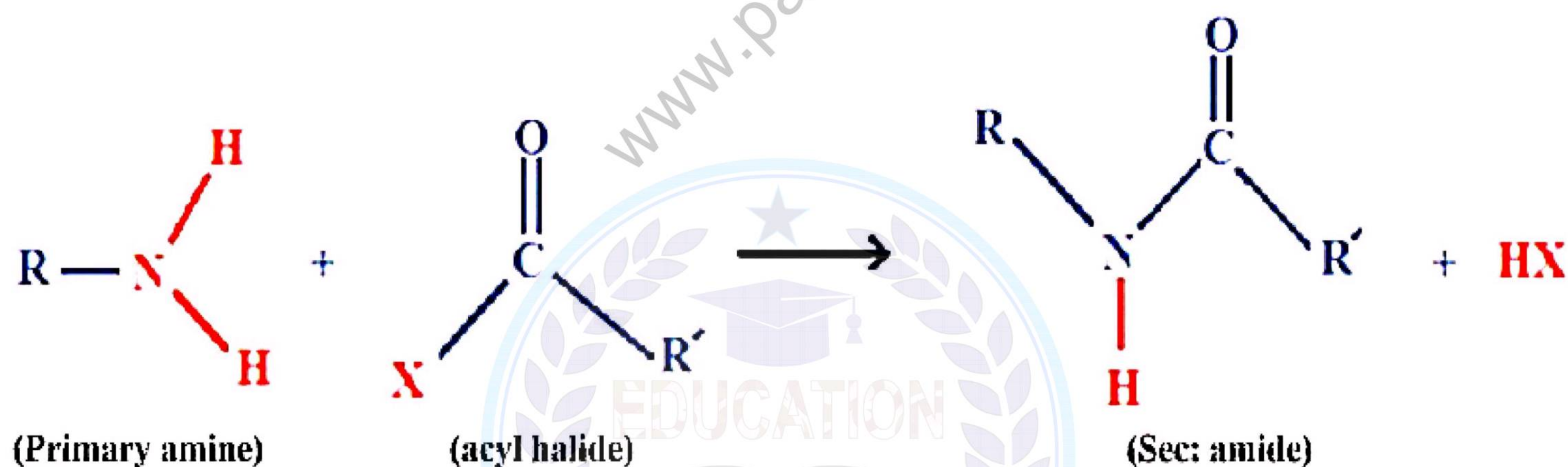
with Aldehyde



with ketone



(iii) Preparation of Amides



(iv) Preparation of Diazonium salts



Multiple Choice Questions

- (i) Which of the following composition justifies the secondary alkyl halide?
(a) R_3CX
(b) R_2CHX
(c) RCH_2X
(d) CH_3X
- (ii) Which of the following alkyl halide cannot produce an alkene while treated with alcoholic potassium hydroxide:
(a) Methyl bromide
(b) Ethyl bromide
(c) Propyl bromide
(d) Butyl bromide
- (iii) Ethyl magnesium bromide with carbon dioxide yields.
(a) Methanoic acid
(b) Ethanoic acid
(c) Propanoic acid
(d) Butanoic acid
- (iv) Grignard reagent with ester produces:
(a) Aldehyde
(b) Carboxylic acid
(c) Ketone
(d) Ether
- (v) Amines act as bases because:
(a) They accept OH^-
(b) They accept H^+
(c) They donate H^+
(d) They donate the OH^-
- (vi) The structure of Primary amine is:
(a) Planar trigonal
(b) Linear
(c) Tetrahedral pyramidal
(d) Regular tetrahedral

- (vii) Alkyl amine when reacts with nitrous acid in the presence of hydrochloric acid, yields:
 (a) Diazonium salt (b) Aldehyde
 (c) Ketone (d) Alcohol
- (viii) S_N2 reaction occurs most easily if the substrate molecule is:
 (a) A methyl iodide (b) An ethyl iodide
 (c) 2-iodo propane (d) 2-iodo butane
- (ix) Suitable reagent required for the synthesis of propane from methyl magnesium iodide is:
 (a) H_2O (b) NH_3
 (c) CH_3OH (d) CH_3NH_2
- (x) The rate of S_N1 mechanism depends upon:
 (a) Conc. of substrate only
 (b) Conc. of attacking nucleophile only
 (c) Conc. of both substrate and attacking nucleophile
 (d) Polar solvent

Short Questions

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1. How are alkyl halides prepared by the reaction of alcohol with
 (i) HX (ii) PX_3 (iii) $SOCl_2$. Give the equations.

ALREADY DISCUSSED ABOVE

2. How are amines prepared from nitriles, give the equations.

ALREADY DISCUSSED ABOVE

3. Why are secondary and tertiary amines more alkaline than primary amines?

WRONG QUESTION

The correct order of basicity is **Primary > Secondary > Tertiary**

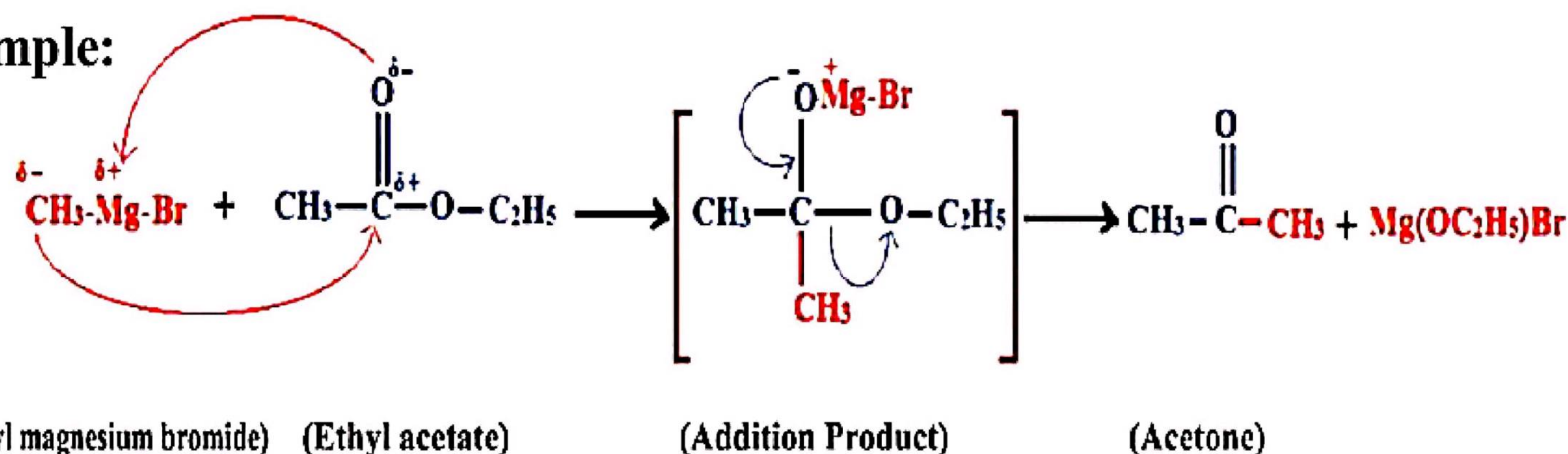
4. Why the alkyl part of Grignard reagent is nucleophilic in nature?

Ans. Alkyl part of Grignard's reagent is nucleophilic in nature due to high electro positivity of magnesium. Magnesium metal has the tendency to loss electron which creates a partial negative charge on alkyl radical. Hence, it behaves as a nucleophile.

5. Convert the followings:

(a) Methyl magnesium bromide into acetone

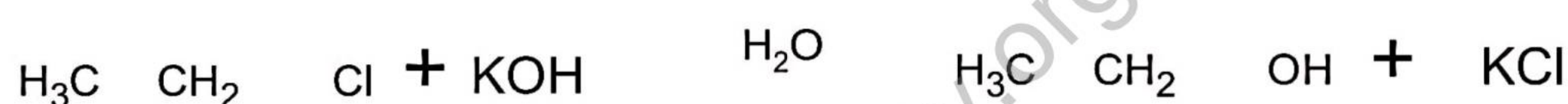
Example:



(b) Ethyl chloride into ethyl amine



(c) Ethyl chloride into ethyl alcohol



(d) Ethyl amine into imine



6. How is primary amine converted into secondary and tertiary amines, give the equations.

ALREADY DISCUSSED ABOVE

7. Give an account on the basicity of amines.

ALREADY DISCUSSED ABOVE

8. How can you justify the fact that alkyl halides are water insoluble?

Alkyl halides are soluble in organic solvents but are slightly soluble in water, this is due to the inability of alkyl halides to form hydrogen bonds with water.

9. How can you define a nucleophile? Write the names of four nucleophiles along with their typical reagents.

Ans. Nucleophile is a chemical species within a molecule that can donate a pair of electrons to form a covalent bond with another atom or molecule.

Nucleophile	Reagent
OH^-	KOH
CN^-	KCN
SH^-	KSH
OR^-	RONa

10. Why the mechanism of SN^2 reaction completes in one step?

Ans. Because of less steric hindrance the removal of halogen and formation of C-Nu bond takes place in the same time in primary alkyl halides. That's why SN^2 reaction completes in one step.

Descriptive Questions



1. How can you define nucleophilic substitution reactions? Describe the mechanisms of SN^1 and SN^2 reactions.

ALREADY DISCUSSED ABOVE

2. What is β -elimination? Discuss the mechanisms of E_1 and E_2 reactions.

ALREADY DISCUSSED ABOVE

3. What are organometallic compounds? How is Grignard reagent prepared? Write down the reactions of Grignard reagent with water, carbon dioxide, ester and amines.

ALREADY DISCUSSED ABOVE

4. What are alkyl halides? Define primary, secondary and tertiary alkyl halides.

ALREADY DISCUSSED ABOVE

5. Draw the orbital structure of methyl iodide and explain the type of hybridization in it.

The structure of methyl chloride has been discussed above. Just change chloride with iodide and the whole answer will remain same.

6. Give a comparative study between nucleophilic substitution reactions and elimination reactions of alkyl halides.

Nucleophilic Substitution Reaction	Elimination Reaction
It follows SN^1 and SN^2 mechanism	It follows E^1 and E^2 mechanism
It occurs in aqueous medium.	It occurs in alcoholic medium
No pi bond is formed in this reaction.	Pi bond is formed in this reaction.
It is favored by polar medium	It is favored by non-polar medium

