

Chapter#10
Alkyl Halides



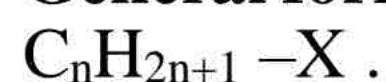
1. What are alkyl halides? Write their general formula and example of monohaloalkanes.

Ans: Alkyl halides:

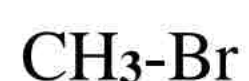
“Those hydrocarbons in which one or more hydrogen atoms of alkanes are replaced by one or more halogen atoms are called alkyl halides or haloalkanes.”

Alkyl halides are represented by R-X.

General formula of monohaloalkanes:



Example:



Methyl bromide

2. What are primary and tertiary alkyl halides? Give one example of each.

Ans: Primary alkyl halides:

The alkyl halides in which halogen atom is attached to a carbon atom which is further attached with one carbon atom or no carbon atom are called primary alkyl halides.

Tertiary alkyl halides:

The alkyl halides in which halogen atom is attached to a carbon atom which is further attached with three carbon atoms are called tertiary alkyl halides.

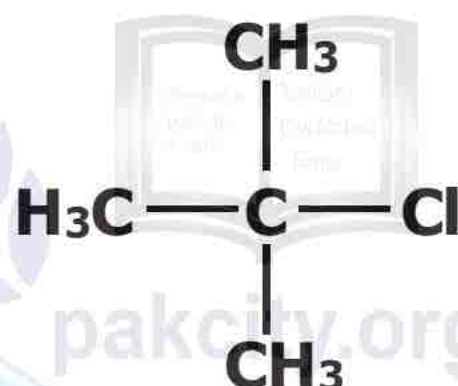
Examples:

Primary alkyl halide:



Methyl bromide

Tertiary alkyl halide:



2-Chloro-2-methylpropane

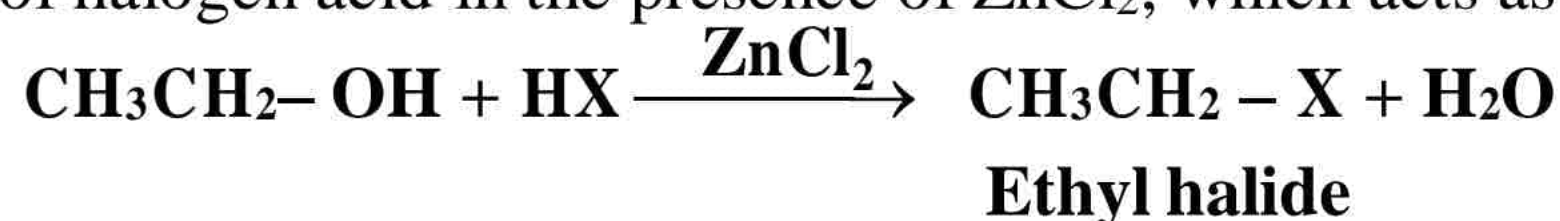
3. How alkyl halides can be prepared by alcohols? Give two examples.

Or

What are the necessary conditions to convert alcohols into alkyl halides using halogen acids and thionyl chloride?

Ans: (a) Reaction of alcohols with halogen acids:

Alcohols may be converted to the corresponding alkyl halides by the action of halogen acid in the presence of ZnCl_2 , which acts as a catalyst



(b) Reaction of alcohols with thionyl chloride:

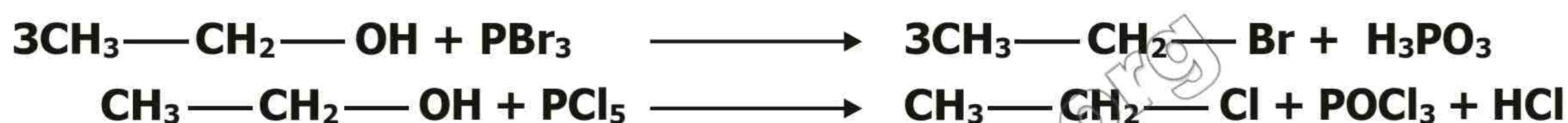
Alcohols react with thionyl chloride in pyridine as a solvent to give alkyl chlorides. This is the best method because HCl , and SO_2 gases escape leaving behind the pure product.



4. Write down reactions of ethanol with (i) PBr_3 (ii) PCl_5

Ans: Reactions of ethanol with phosphorus halides:

Phosphorus tribromide and Phosphorus pentachloride react with Ethanol to produce alkyl halides as follows.



5. Explain the order of reactivity of alkyl halides on the basis of bond polarity.

Ans: According to this factor, greater the electronegativity difference between carbon and halogen greater the bond polarity. Greater the polarity greater the reactivity. So with this rule the alkyl fluorides should be the most polar and the most reactive and alkyl iodides least polar and least reactive.

It means reactivity order must be like this;



6. What is the order of reactivity of HX with Ethene?

Ans: Ethene reacts with HX to form Ethyl halide.



The order of reactivity of HX is given below.



7. How the bond dissociation energy of carbon suggests that alkyl iodides should have maximum reactivity?

Ans: Bond energy directly depends on bond polarity. The bond dissociation energy of C-X bond is in the order:



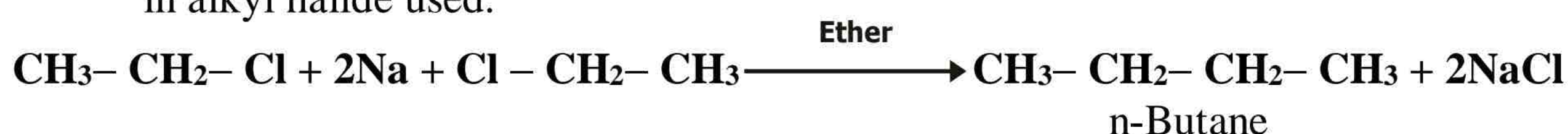
Greater the bond energy, stronger the bond and lesser the reactivity. With this rule the reactivity order must be like this;



Alkyl iodides should be most reactive due to least bond energy.

8. What is Wurtz's synthesis reaction?

Ans: Alkyl halides react with sodium in ether (solvent) to give alkanes. This is called Wurtz's synthesis. The reaction is particularly useful for preparation of symmetrical alkanes with double number of carbon atoms as compared with that in alkyl halide used.



9. What is the difference between molecularity and order of reaction?

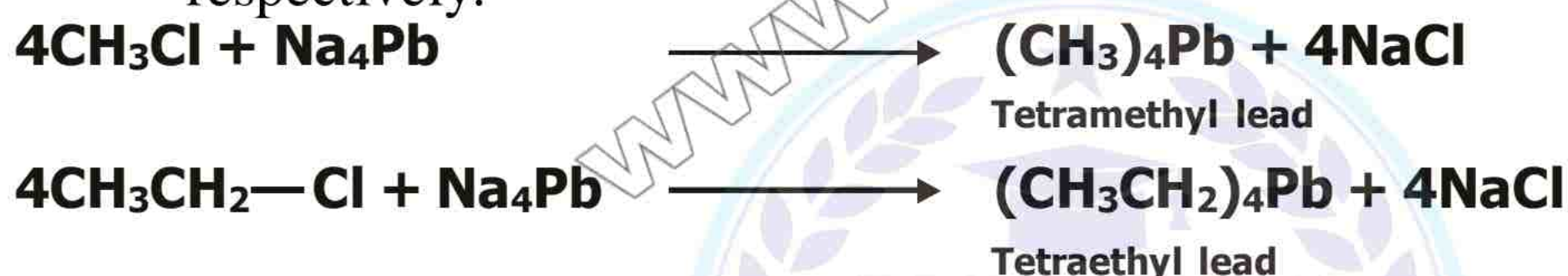
Ans:

Molecularity	Order of Reaction
Molecularity is defined as the number of molecules taking part in the rate determining step of reaction.	Sum of exponents of conc. terms in the rate expression of a chemical equation is called order of reaction.
It is calculated through balanced chemical equation	It is always experimentally determined.

10. How anti-knocking agents are prepared?

Ans: Preparation of anti-knocking agents:

Methyl chloride and Ethyl chloride can react with sodium lead alloy to produce anti-knocking agents, Tetramethyl lead (TML) and Tetraethyl lead (TEL), respectively.



11. In tertiary alkyl halides, S_N1 reaction takes place but not S_N2 reaction. Why?

Ans: In tertiary alkyl halides, attacking nucleophile cannot reach directly at the electrophilic center (carbon) due to steric hindrance. So attachment of attacking nucleophile and removal of leaving group can't occur simultaneously as occurs in S_N2 reactions. As a result, in tertiary alkyl halides nucleophilic substitution occurs in two steps i.e. S_N1 mechanism occurs. In first step halogen (leaving group) is removed to reduce steric hindrance and planar carbocation is formed. In second step attack of new nucleophile takes place.

12. What is the role of carbonium ion for determining S_N1 or S_N2 mechanism?

Ans: Greater the stability of the carbonium ion, greater the possibility for two step mechanism which is S_N1 . These alkyl halides which can provide unstable carbonium ion

give S_N2 mechanism, which is a single step reaction. Carbonium ion is stable if it is bonded to maximum number of alkyl groups.

13. What is meant by attacking nucleophile? Give examples.

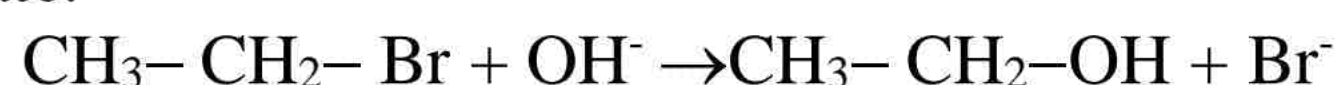
Ans: In S_N reactions, the nucleophile which attacks on the electrophilic carbon of alkyl halide from outside is called attacking nucleophile.

Examples:

$-\text{OH}^-$, $-\text{CN}^-$ etc.

14. Reaction of Ethyl bromide with OH^- nucleophile is S_N2 . Why?

Ans: Reaction of ethyl bromide with OH^- is S_N2 because it is a bimolecular reaction. The rate of reaction depends upon the concentration of nucleophile as well as substrate.



$$\text{Rate} = k [\text{CH}_3\text{CH}_2\text{Br}][\text{OH}^-]$$

$$\text{Order} = 2$$

15. What is difference between Electrophile and Nucleophile?

Ans:

Electrophile	Nucleophile
(i) It is an electron deficient species.	It is electron rich species.
(ii) It always acts as Lewis acid.	It always acts as Lewis base.
(iii) It may be neutral or positively charged.	It may be negatively charged or neutral with one or more lone pairs.
(iv) Examples: NO_2^+ , SO_3	Examples: Cl^- , NH_3

16. What are differences between S_N1 and S_N2 reactions?

Ans:

S_N1	S_N2
(i) It is a two step mechanism.	It is a single step mechanism.
(ii) First step is slow and second is fast.	It has only one step and that is slow.
(iii) It is unimolecular reaction.	It is a bimolecular reaction.
(iv) It is favored in polar solvents.	It is favored in non-polar solvents.

17. Why tertiary alkyl halides follow S_N1 mechanism and not S_N2 mechanism? OR During S_N1 reaction, what is the significance of first step?

Ans: S_N1 mechanism involves two steps. Due to steric (space) hindrance, the attack of nucleophile on the α -carbon of substrate is not directly possible. In order to create space for the attack, older nucleophile means halogen needs to be removed first.

This is the reason that reaction occurs in two steps. The first step is the reversible ionization of the alkyl halide. This step provides a carbocation as an intermediate. In the second step this carbocation is attacked by the nucleophile to give the substitution product.

In S_N2 reactions, there is no issue of steric hindrance as α -carbon of primary alkyl halide is surrounded by small groups e.g. Hydrogen atoms and attacking nucleophile finds space to attack on carbon.

18. What are leaving group and substrate?

Ans: Leaving Group:

Leaving group (L) is also a nucleophile. In S_N reactions of alkyl halides, the halogens are the leaving groups. It is called leaving group because it departs from alkyl halide.

Examples:



Substrate Molecule:

The alkyl halide molecule on which a nucleophile attacks is called a substrate molecule.

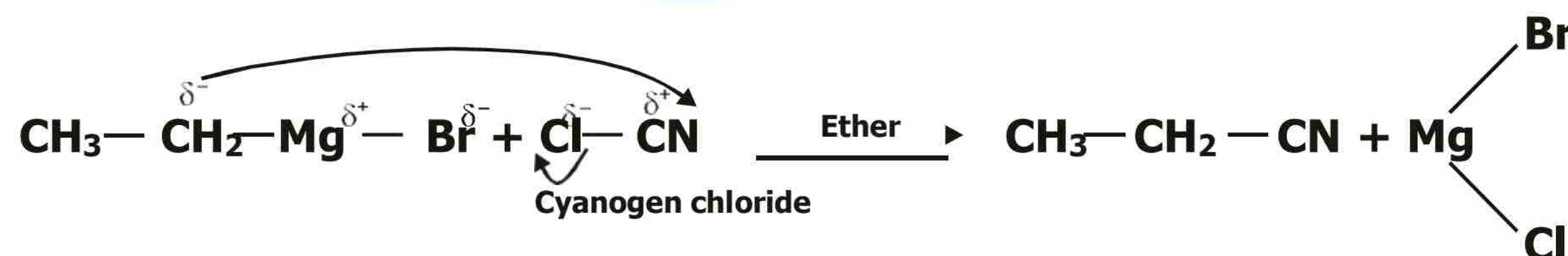
19. What is the difference between Elimination and substitution reactions?

Ans:

Elimination	substitution
Elimination of two atoms or groups from adjacent carbon atoms in the presence of a nucleophile or a base is called elimination reaction.	Substitution reaction involves the breakage of C-X bond and the formation of C-Nu bond.
The product of an elimination reaction is alkene usually.	Substitution reaction yields substitution product
Example: $\text{CH}_3\text{CH}_2\text{X} + \text{OH}^- \longrightarrow \text{H}_2\text{C}=\text{CH}_2 + \text{H}_2\text{O}$	Example: $\text{CH}_3\text{-X} + \text{OH}^- \rightarrow \text{CH}_3\text{-OH} + \text{X}^-$

20. How do we get alkyl nitriles from Grignard's reagent?

Ans: When Cl-CN is reacted with Grignard's reagent. The alkyl group of the Grignard's reagent combines with $-\text{CN}$ group to give Alkyl nitrile. See example below;



21. Explain the structure and reactivity of Grignard's reagent.

Ans: Grignard's reagent is much more reactive than most of the organic compounds. The reactivity is due to the nature of C-Mg bond which is highly polar.

Magnesium is more electropositive than carbon and C-Mg bond though covalent is highly polar, giving alkyl carbon the partial negative charge. The negative charge is an unusual character which makes the alkyl groups highly reactive towards electrophilic centers.

22. What is the nature of C-Mg bond in R-Mg-X?

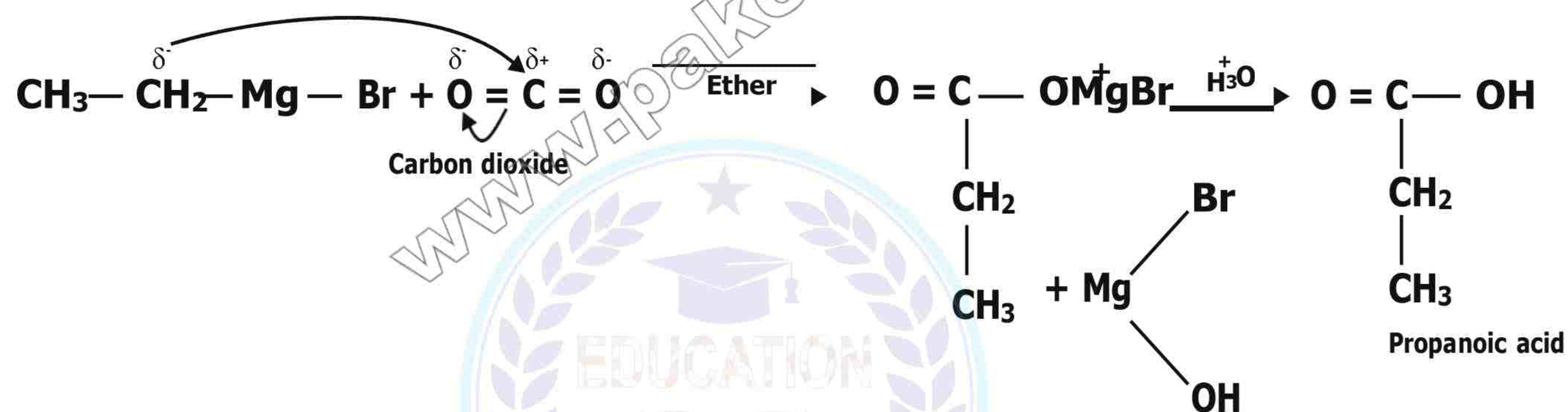
Ans: Grignard's reagents are very reactive organic compounds. Their reactivity is due to C-Mg bond which is highly polar.



Magnesium is less electronegative than carbon so partial positive charge appears on magnesium and partial negative on carbon attached to it. This negative charge on carbon is very unusual which makes alkyl group very reactive towards electrophiles.

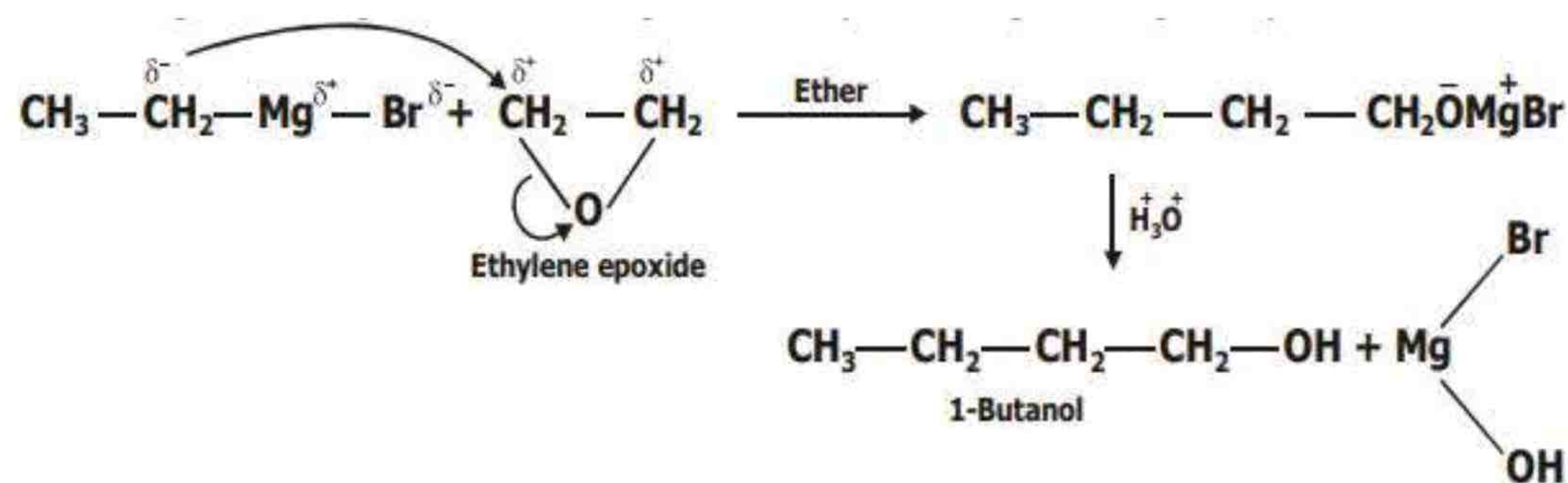
23. How is carboxylic acid prepared from Grignard's reagent?

Ans: When Grignard's reagent is reacted with carbon dioxide gas, we get carboxylic acids as follows;



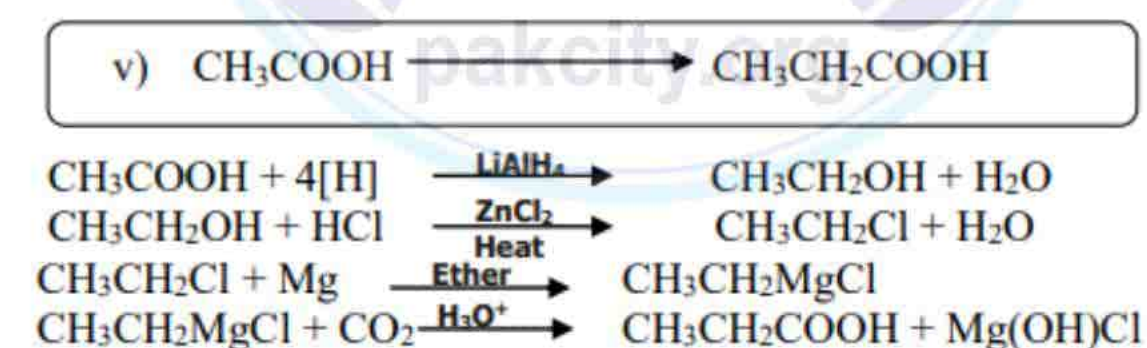
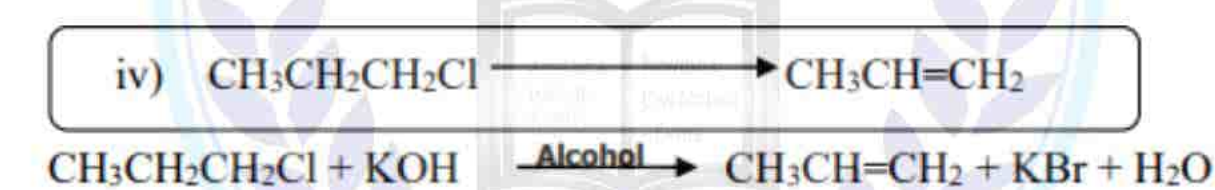
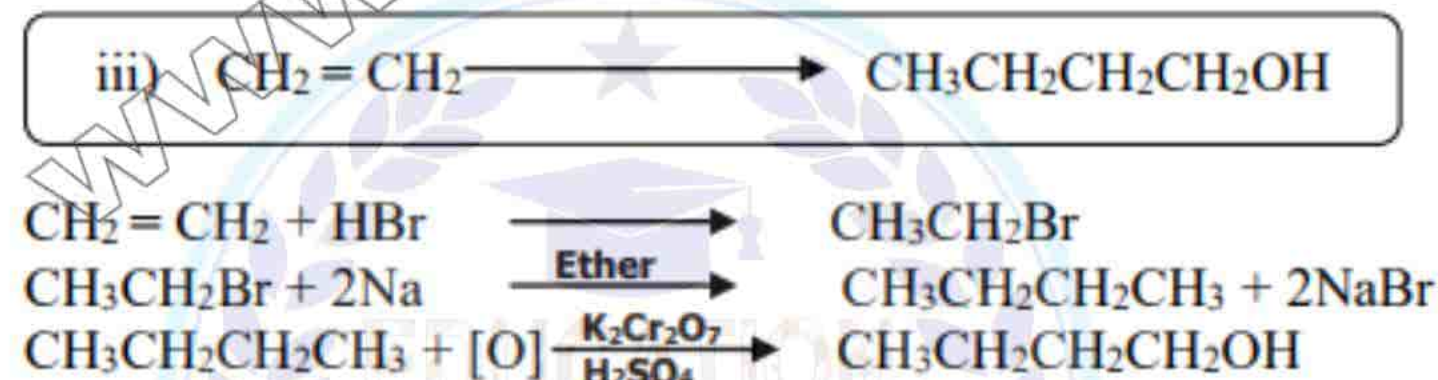
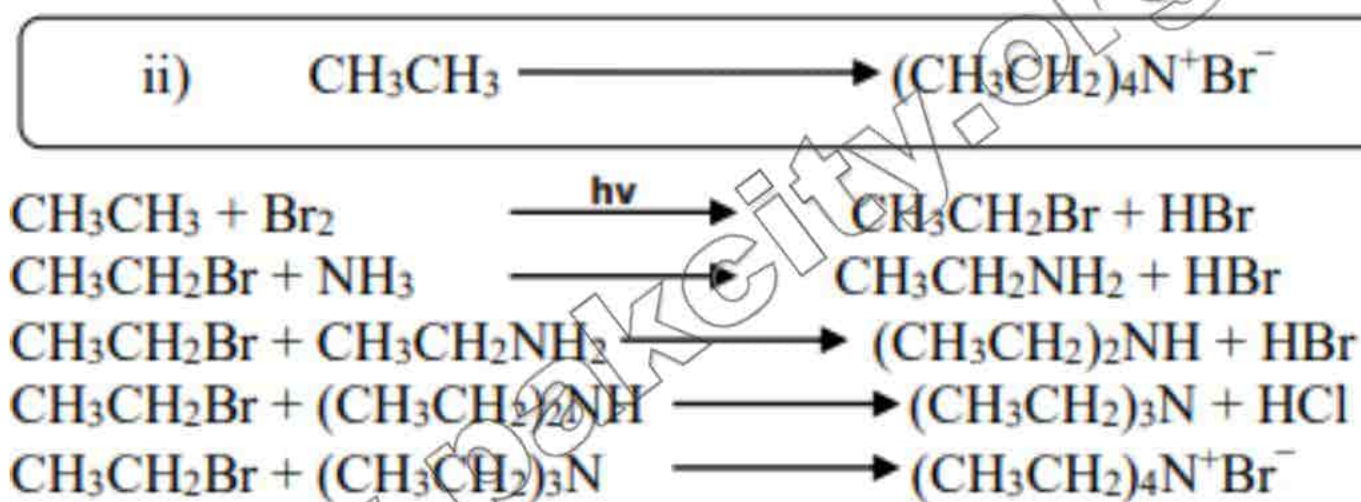
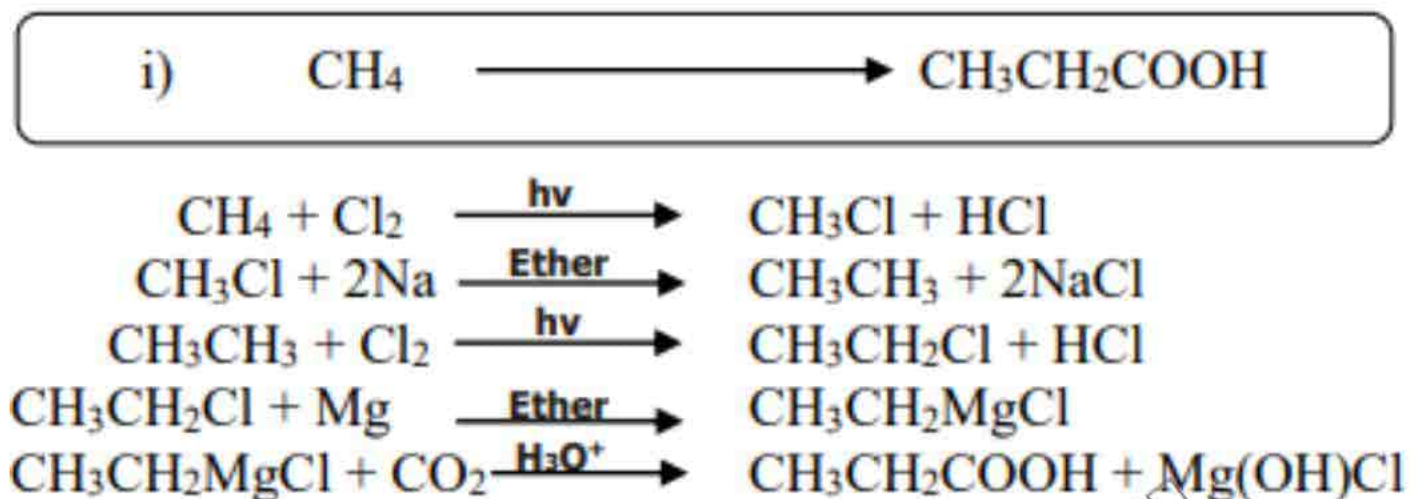
24. How Grignard reagent reacts with epoxides to form alcohol?

Ans: Grignard's reagent reacts with epoxide in dry ether to generate primary alcohols.



25. How will you carry out the following conversions:

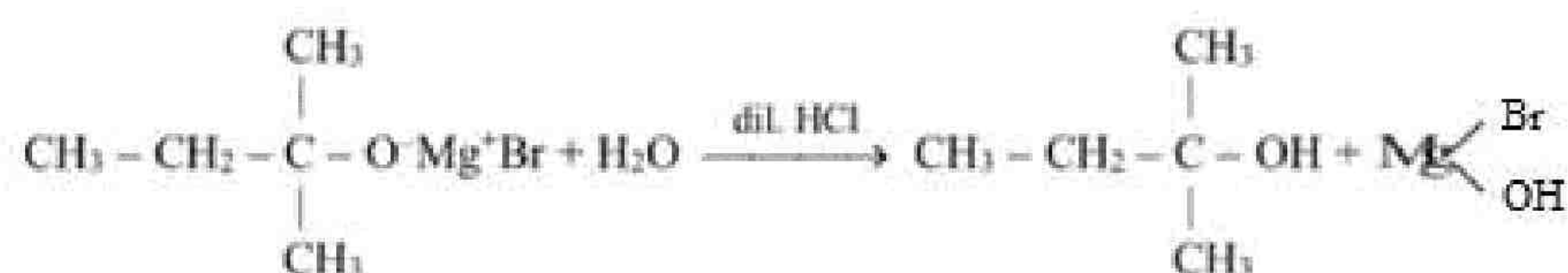
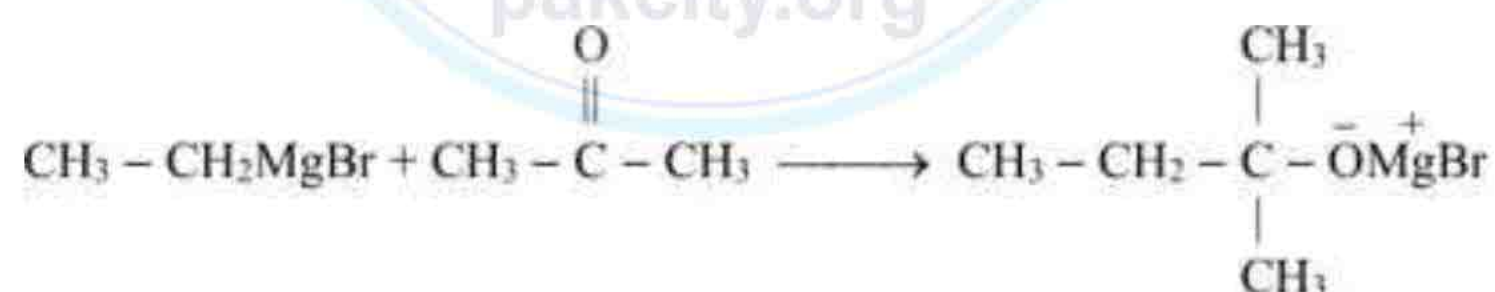
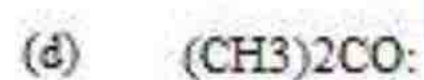
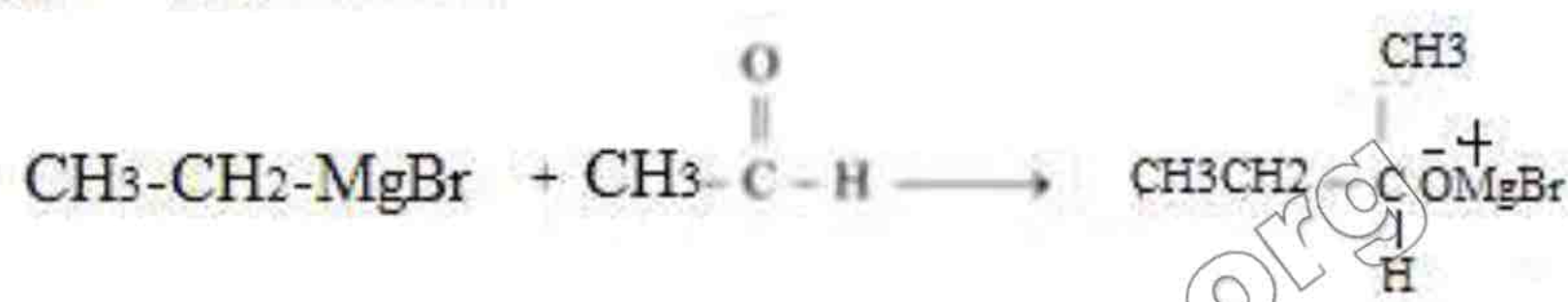
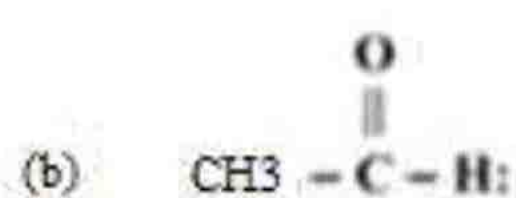
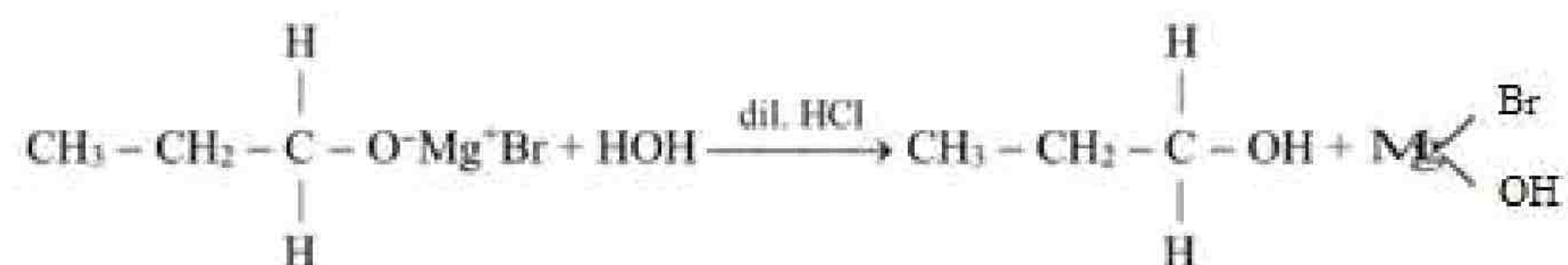
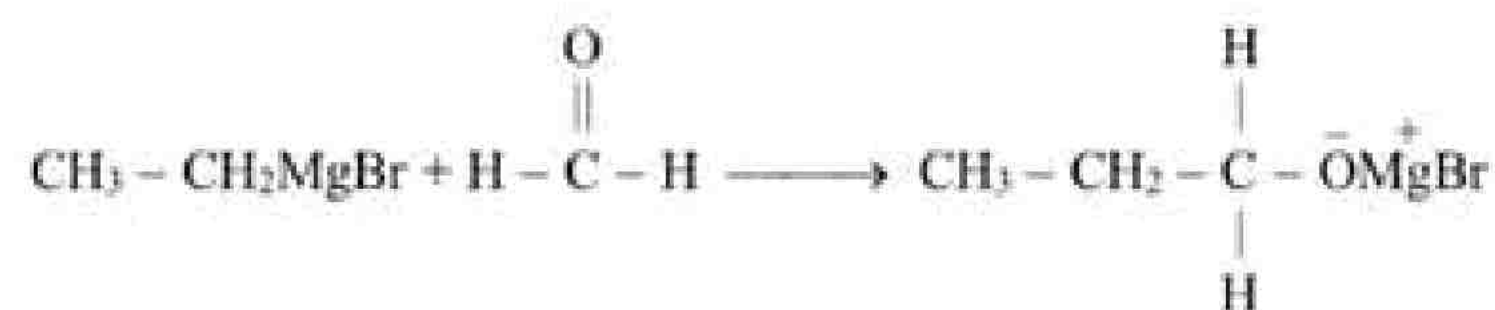
Ans:

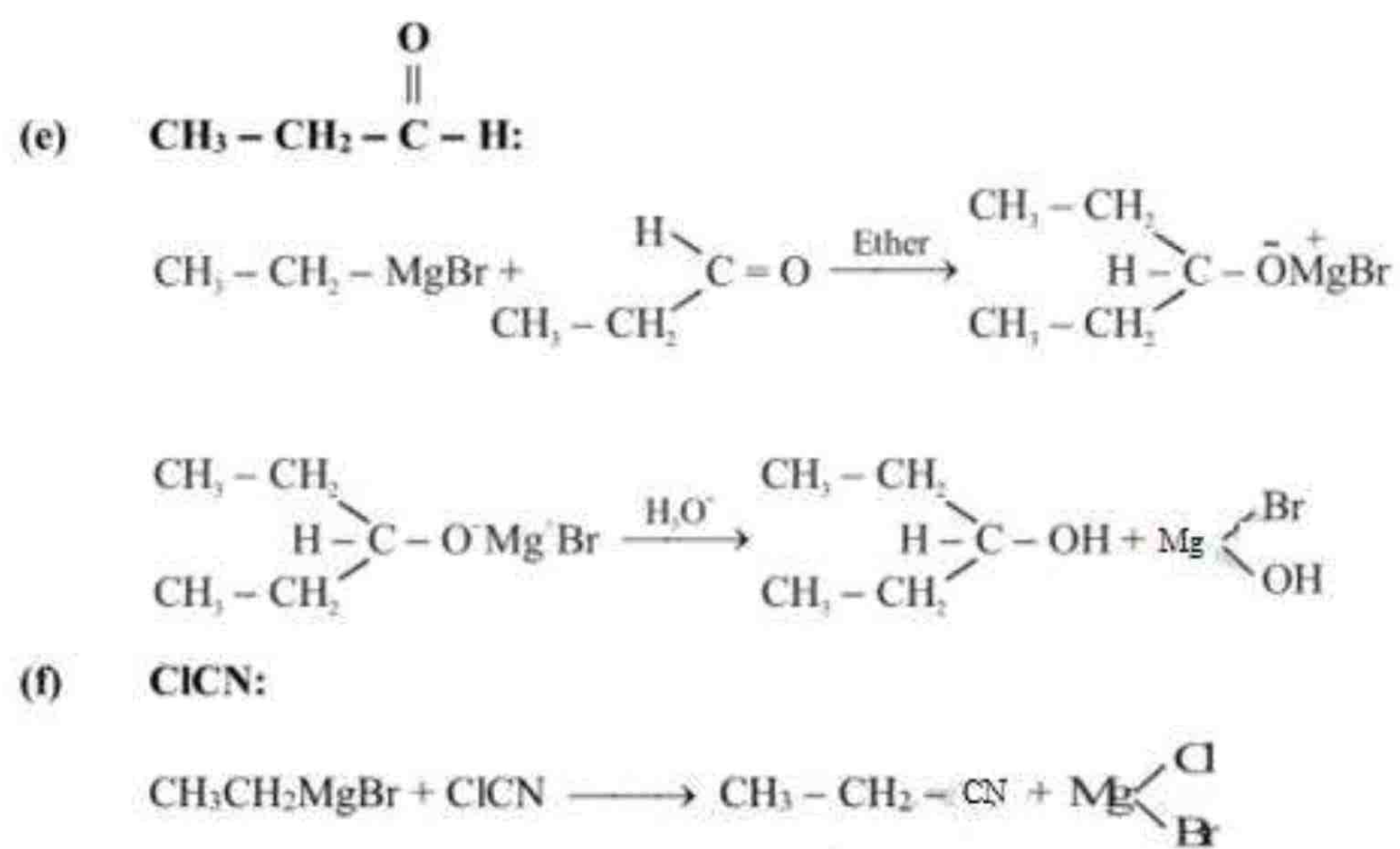


26. What products are formed when the following compounds are treated with ethyl-Mg-bromide followed by hydrolysis in the presence of an acid?

Ans:

(a) HCHO

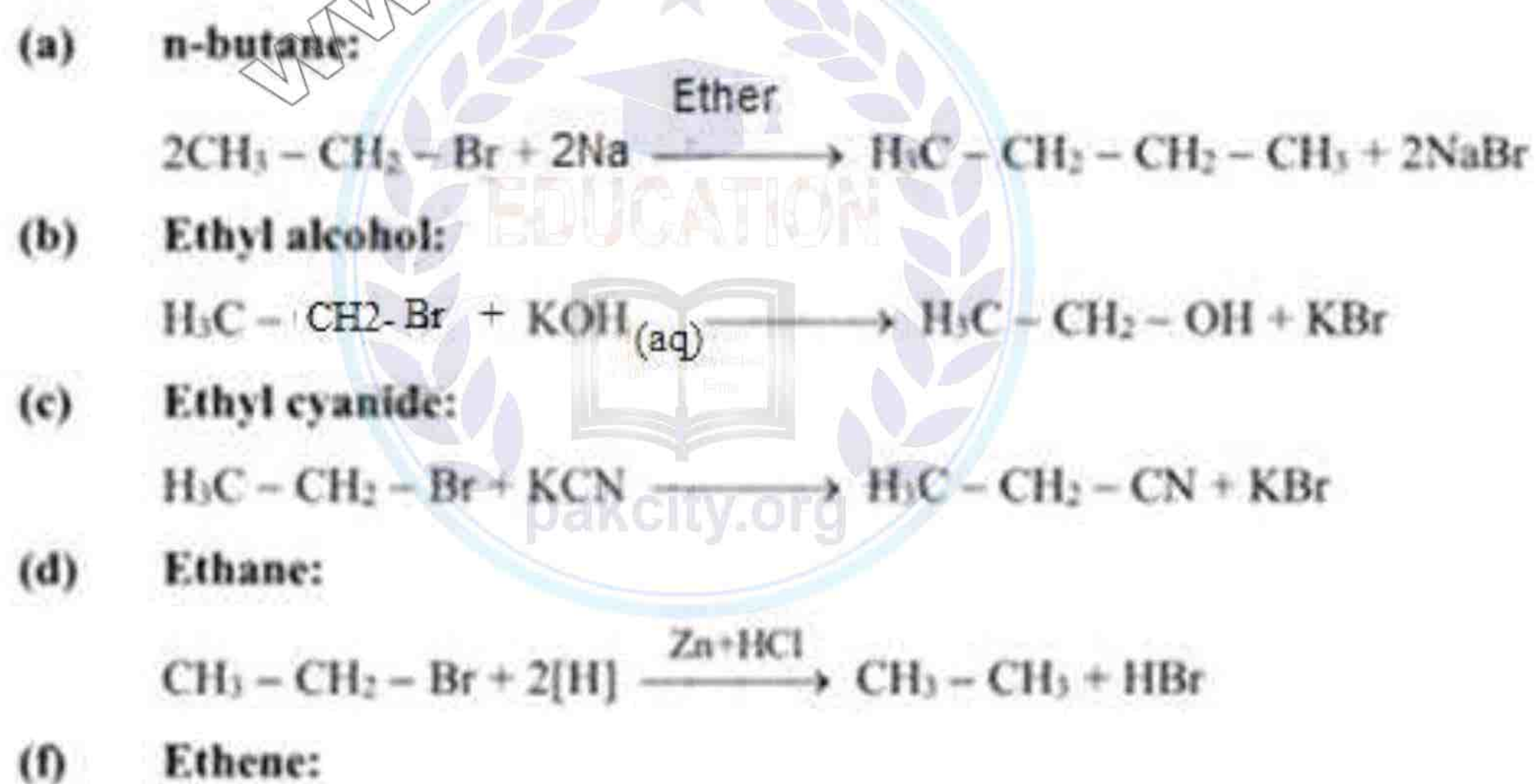


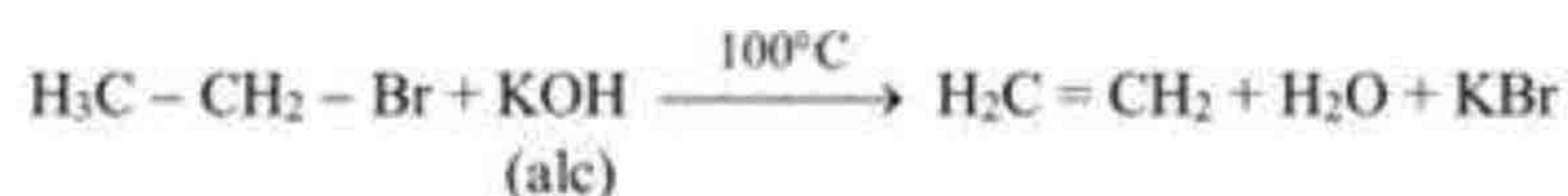


27. Using ethyl bromide as a starting material how would you prepare the following compounds.

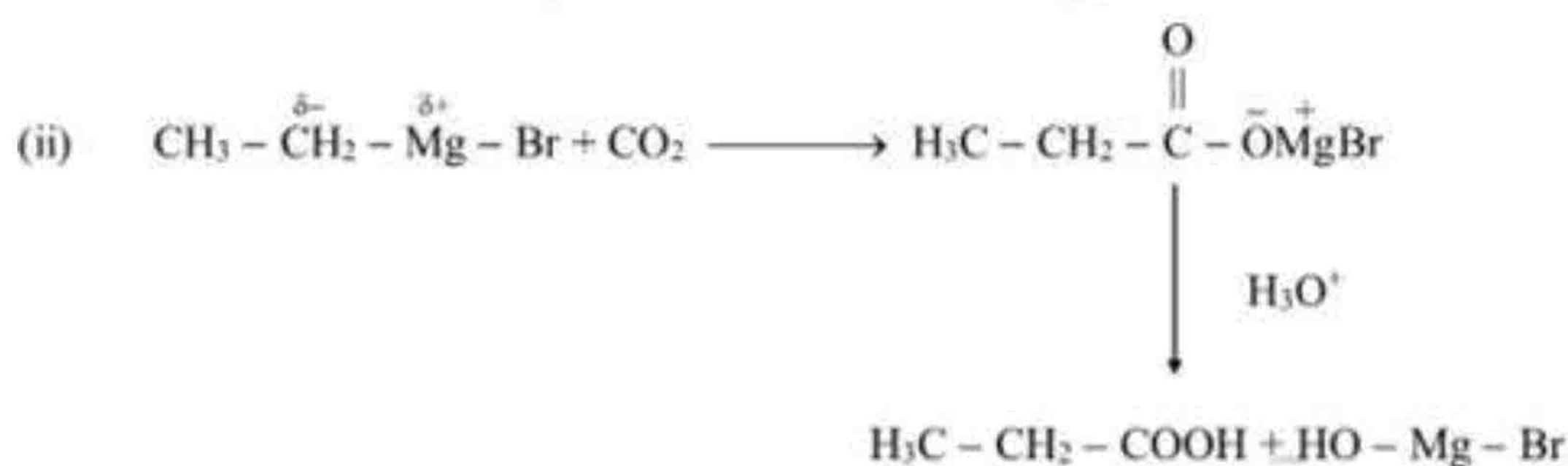
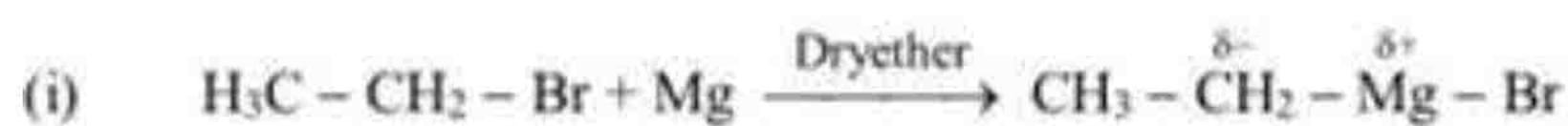
Also mention the inorganic reagents involved.

Ans:



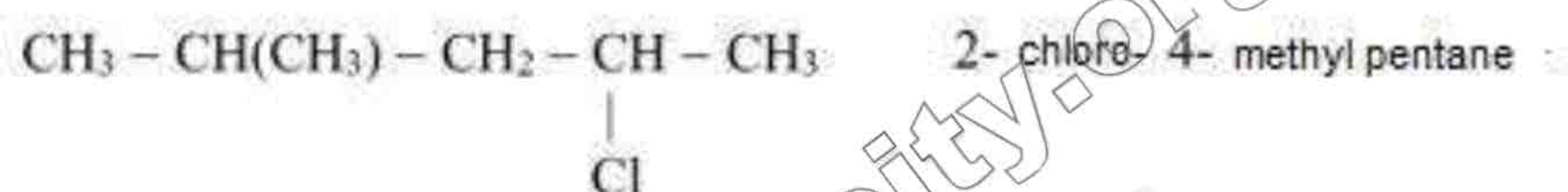


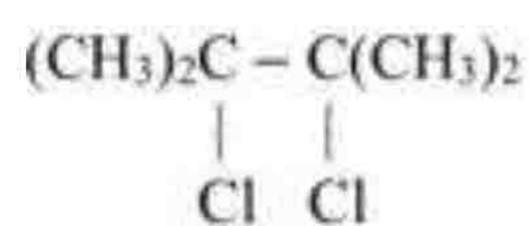
(g) **Propanoic acid:**



28. Give IUPAC names to the following compounds

Ans:





2, 3-dichloro-2, 3-dimethyl butane



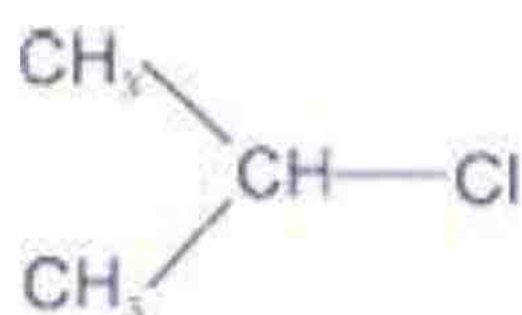
3-bromo-3-ethyl pentane

29. How are the alkyl halides classified?

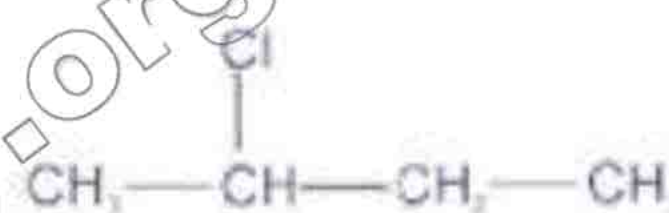
Ans: Mono haloalkanes or alkyl halides are further classified into primary, secondary and tertiary alkyl halides depending upon the type of carbon atom bearing the halogen atom. In a primary alkyl halide halogen atom is attached with a carbon which is further attached to one or no carbon atom e.g.,



Secondary alkyl halides are those in which halogen atom is attached with a carbon atom which is further attached to two other carbon atoms directly, e.g., secondary carbon atom.

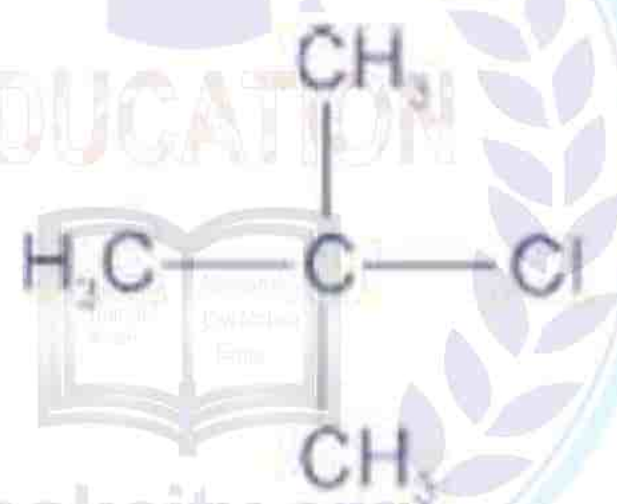


2-Chloropropane



2-Chlorobutane

In tertiary alkyl halides halogen atom is attached to a carbon which is further attached to three carbon atoms directly.



2-Chloro-2-methyl propane

30. Mention the factors responsible for reactivity of alkyl halides.

Ans: There are two main factors which govern the reactivity of R — X bond.

These are:

- i) C — X Bond energy
- ii) C — X Bond polarity

31. Explain the factor of bond energy.

Ans: The strength of the bonds show that iodo compound (with the weakest bonds) would be the most reactive one while fluoro compound will be the least reactive i.e., the order of reactivity of alkyl halides should be.

**32. Explain the factor of bond strength.**

Ans: Electronegativities of halogen, carbon and hydrogen atoms present in alkyl halides are shown in the table. The greatest electronegativity difference exists between carbon and fluorine atoms in alkyl fluorides.

If an electrophile is the attacking reagent then this difference suggests that alkyl fluorides would be the most reactive one. On the same lines, alkyl iodides should be the least reactive alkyl halides. In the light of the above discussion it is clear that the two factors mentioned above predict different types of behaviour about the reactivity of alkyl halides

Experiments have shown that the strength of carbon halogen bond is the main factor which decides the reactivity of alkyl halides



In fact the C-F bond is so strong that alkyl fluorides do not react under ordinary conditions.

33. Define nucleophile, electrophile, leaving group and substrate molecule.

Ans:

Nucleophile

Nucleophile means nucleus loving. It has an unshared electron pair available for bonding and in most cases it is basic in character. It may be negatively charged or neutral.

Examples of Nucleophiles

HO ⁻	Hydroxide ion	Cl ⁻	Chloride ion
C ₂ H ₅ O ⁻	Ethoxide ion	Br ⁻	Bromide ion
HS ⁻	Hydrogen sulphide ion	NH ₃	Ammonia
SCN ⁻	Thiocyanate ion	CN ⁻	Cyanide ion
H ₂ O:	Water	I ⁻	Iodide ion
NH ₂ ⁻	Amino group		

Electrophile

It is a species which attracts electrons (electron loving). The carbon atom of an alkyl group attached with the halogen atom and bearing a partial positive charge is called an electrophile or electrophilic center. An electrophile may be neutral or positively charged. Example, C⁺, Na⁺, K⁺, BF₃

Leaving Group

L is also a nucleophile. It is called leaving group because it departs with an unshared pair of electrons. If we wish an S_N reaction to proceed in the forward direction the incoming nucleophile must be stronger than the departing one. Cl⁻, Br⁻, I⁻, HSO₄⁻ are good leaving groups. Poor leaving groups are OH⁻, and NH₂⁻. Iodide ion is a good nucleophile as well as a good leaving group.

Substrate Molecule

The alkyl halide molecule on which a nucleophile attacks is called a substrate molecule.

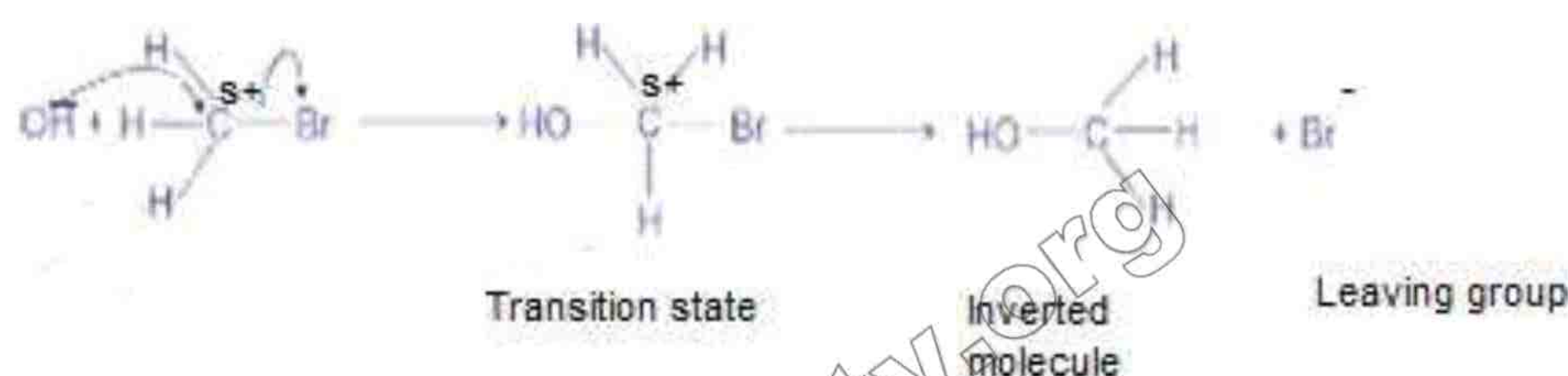
34. Mention types of nucleophilic substitution reactions.

Ans: Alkyl halides may undergo nucleophilic substitution reactions in two different ways:

1. Nucleophilic Substitution Bimolecular (SN_2)
2. Nucleophilic Substitution Unimolecular (SN_1)

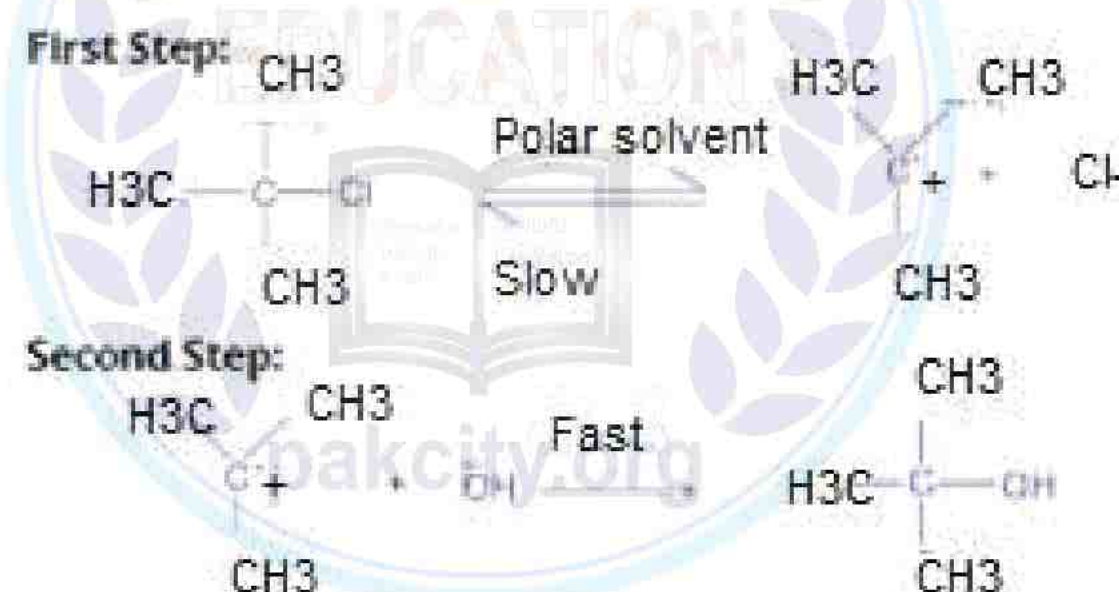
35. Define SN_2 reaction. Give mechanism.

Ans: Nucleophilic substitution reactions on alkyl halides involve two main processes, the breakage of C — X bond and the formation of C — Nu bond. The mechanism of the nucleophilic substitution reactions depends upon the timing of these two processes. If the two processes occur simultaneously the mechanism is called SN_2 .



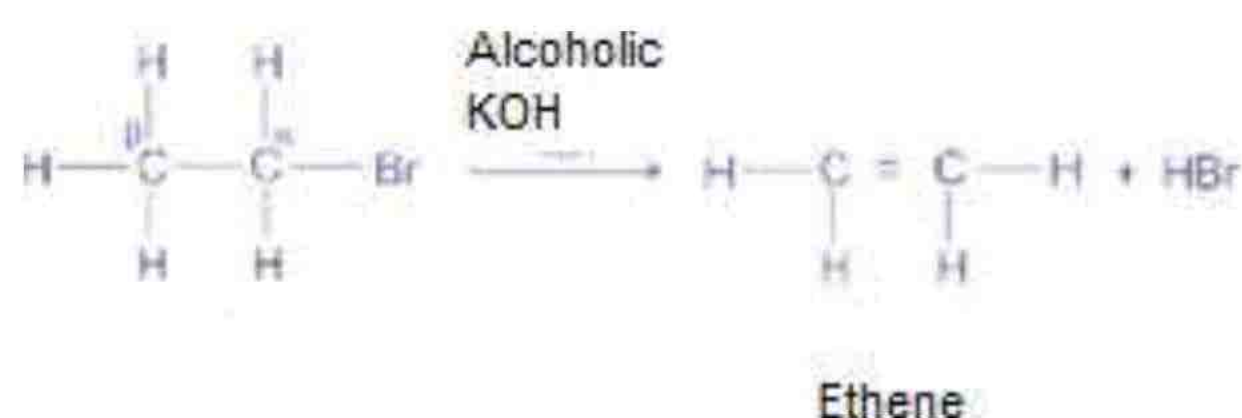
36. Define SN_1 reaction. Give mechanism.

Ans: Nucleophilic substitution reactions on alkyl halides involve two main processes, the breakage of C — X bond and the formation of C — Nu bond. The mechanism of the nucleophilic substitution reactions depends upon the timing of these two processes. If the bond breaks first followed by the formation of a new bond, the mechanism is called SN_1 .



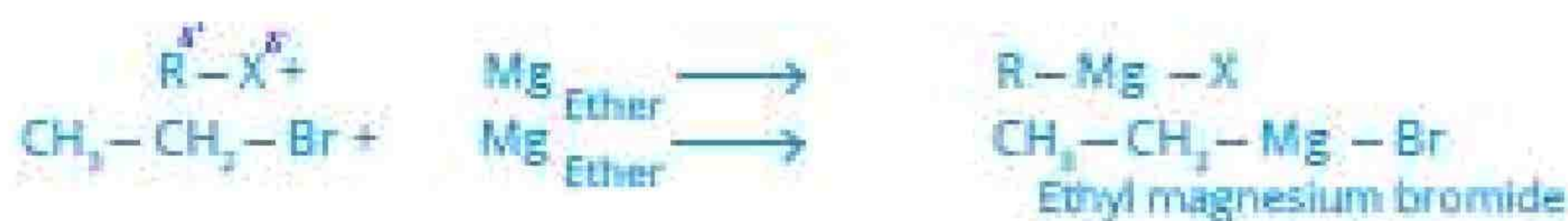
37. Define β -elimination reactions.

Ans: During nucleophilic substitution reactions, the attacking nucleophile attacks the electrophilic carbon atom of the alkyl halide. There is another site present in the alkyl halide molecule where the nucleophile can attack at the same time. Such a site is an electrophilic hydrogen atom attached to the β -carbon of the alkyl halide. When the attack takes place on hydrogen, we get an alkene instead of a substitution product. Such type of reactions is called elimination reactions. These reactions take place simultaneously with substitution reactions and often compete with them.



38. How Grignard reagent is prepared?

Ans: Grignard reagents are prepared by the reaction of magnesium metal with alkyl halides in the presence of dry ether (alcohol free, moisture free).



39. Explain structure and reactivity of Grignard reagent.

Ans: Grignard reagents are much more reactive than most of the organic compounds. The reactivity is due to the nature of C - Mg bond which is highly polar.



Magnesium is more electropositive than carbon and the C-Mg bond though covalent is highly polar, giving alkyl carbon the partial negative charge. This negative charge is an unusual character which makes the alkyl groups highly reactive towards electrophile centres. Mostly reactions shown by Grignard reagent are exothermic.