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## Chapter 4: Alkylhalides (R-X, X = Cl, Br, I)

These are compounds with atleast one halogen aaton attached to the parent chain.

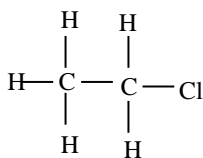
### Classification of mono substuted alkylhalide

As seen earlier, they are classified like alcohols.

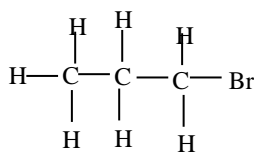
They are **three** classes of alkylhalide depending on the number of alkyl groups attached to a carbon atom that carry a halide.

(a) Primary alkylhalide have **one** alkyl group on the carbon atom that carries a halide.

Examples



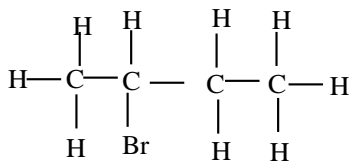
Chloroethane



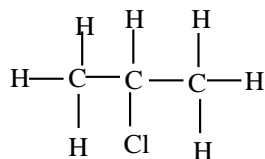
1-Bromopropane

(b) Secondary alkylhalide have **two** alkyl groups attached to a carbon atom that carry a halide

Examples



2-Bromobutane



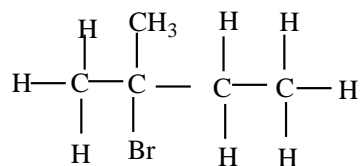
2-chloropropane

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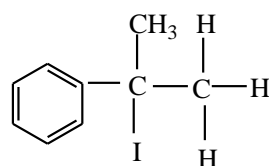
(c) Tertiary alkylhalide

Tertiary alkylhalide have **three** alkylgroups attached to the carbon atoms that carry OH group

Examples



2-bromo-2-methylbutane

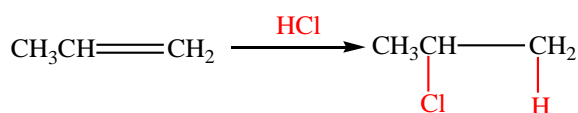


2-iodo-2-phenylpropane

Preparation of alkylhalide

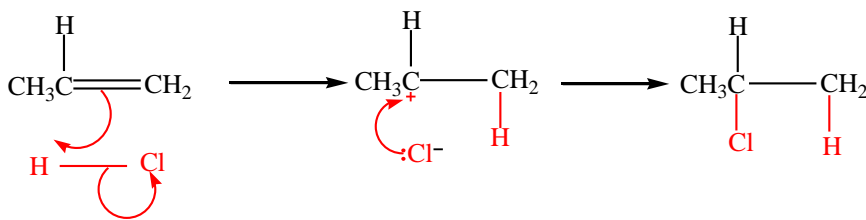
1. By reacting alkenes with halogenhalide

Example



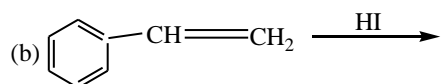
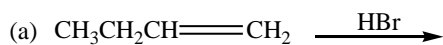
Mechanism

Remember: the reaction occurs at **the double bond** and hydrogen atom goes to a carbon that carries highest number of hydrogen atoms.



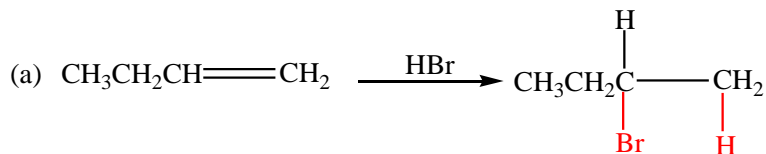
Exercise

Complete and write a mechanism for the following reactions (mark yourself after)

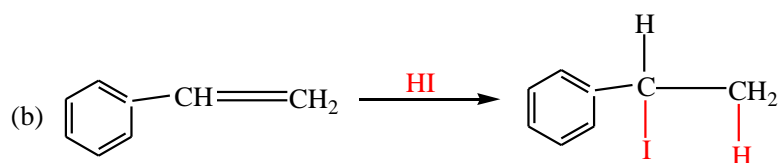
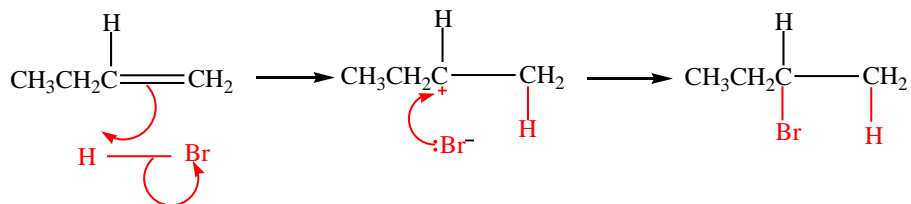


Mark yourself

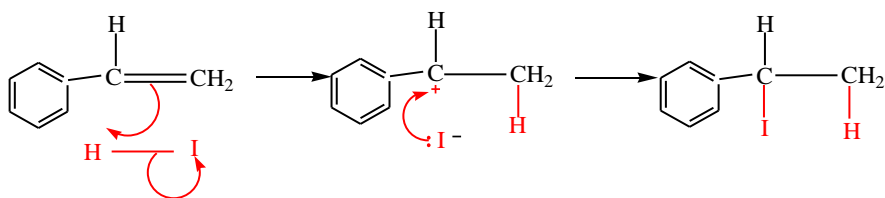
In these reactions, the double bond breaks and hydrogen halide adds itself across the carbon atoms that were forming the double bond. Hydrogen atom adds to a carbon atom that carries the highest number of hydrogen atoms of those that form a double bond. Make sure you account for the charges.



Mechanism

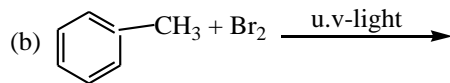
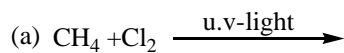


Mechanism



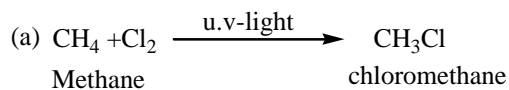
2. By reacting chlorine gas or bromine with alkanes. The reaction occurs in the presence of u.v light. This was dealt with when dealing with reactions of alkanes.

Complete the following equation and write a mechanism

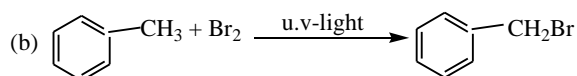
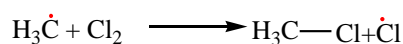
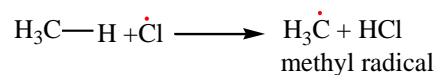
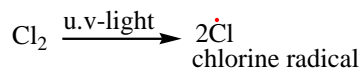


Mark yourself

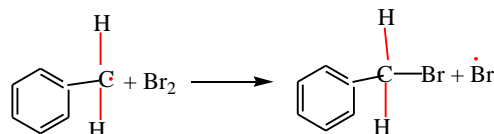
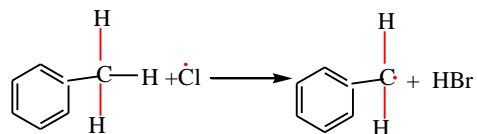
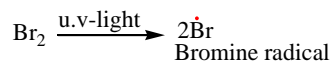
These reactions follow a free radical mechanism, be keen to observe the initiation and formation of free radicals as the reaction proceeds. Every dot (un paired electron) must be accounted for.



Mechanism



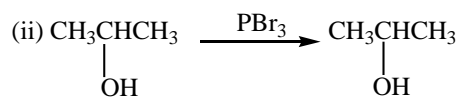
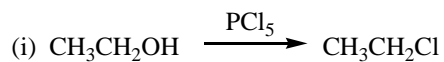
Mechanism



### 3. By reacting alcohols with

#### (a) Phosphorus halide

Examples



#### (b) With HX (X= Cl, Br, I)

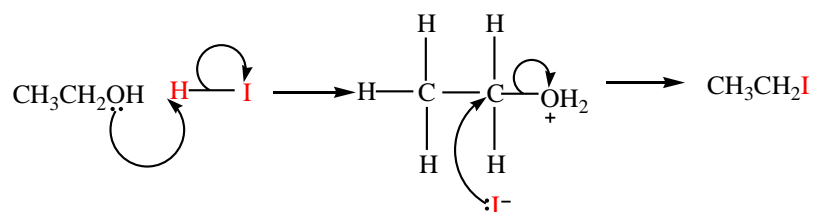
HI and HBr react readily with alcohols but the reaction of HCl is catalyzed with anhydrous zinc chloride. The mechanism of the reaction depends on the class of alcohol. Though secondary alcohols react like either primary or tertiary alcohols.

Examples

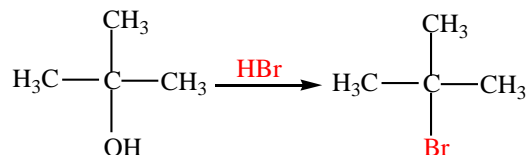
Primary alcohol



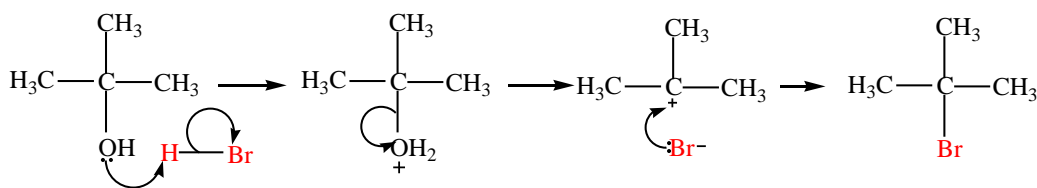
Mechanism



Tertiary alcohol

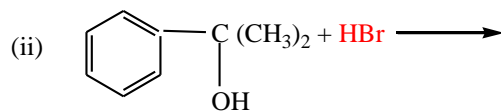
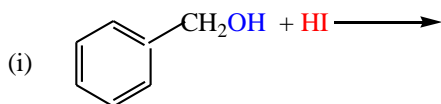


Mechanism

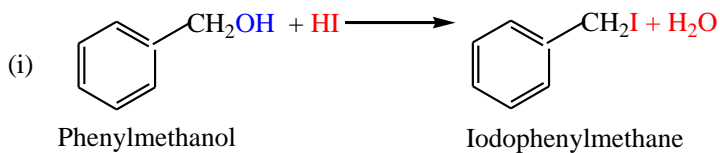


Exercise

Complete and write a mechanism, thereafter mark yourself

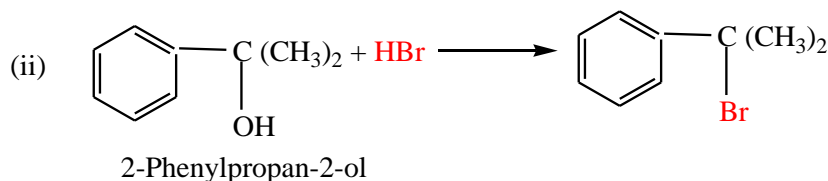
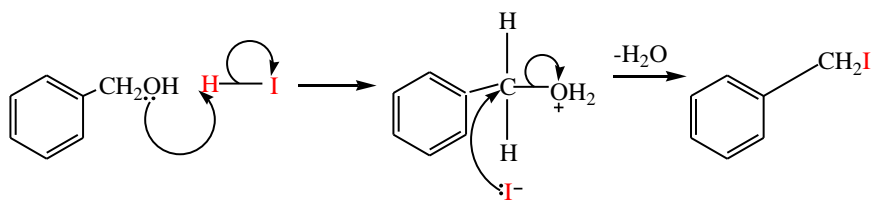


Mark yourself



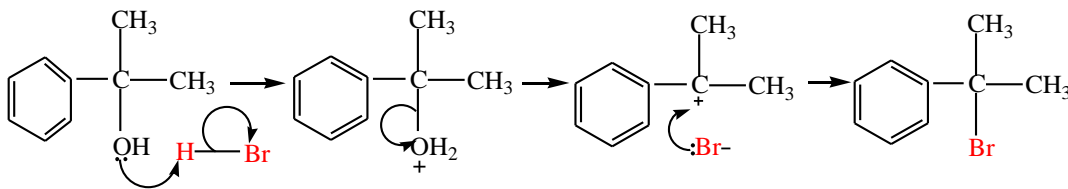
Mechanism

Note that phenylmethanol is a primary alcohol



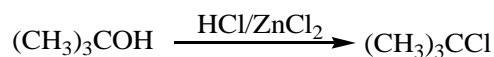
Mechanism

Please note that 2-phenylpropan-2-ol is a tertiary alcohol

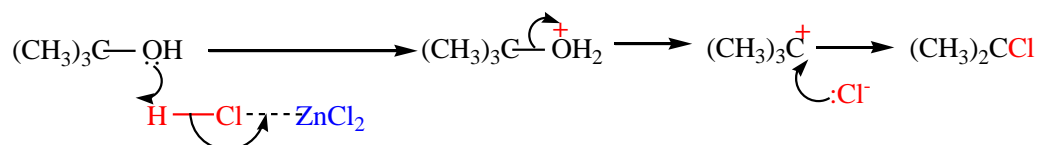


- (c) Reaction of HCl with alcohols is catalyzed by anhydrous zinc chloride because HCl bond is strong. Primary alcohol does not react, secondary alcohol reacts slowly, and tertiary alcohol reacts faster.

Example



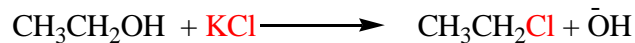
Mechanism



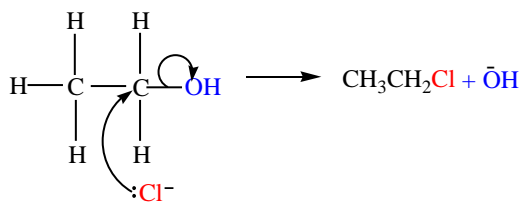
- (d) Reaction of alcohol with KX (X= Cl, Br, I)

The mechanisms depend on the class of alcohols. The mechanism of secondary alcohols

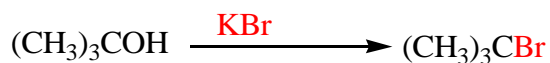
Primary alcohol



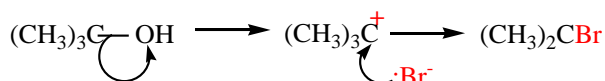
Mechanism



Tertiary alcohol



Mechanism

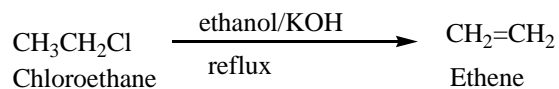


### CHEMICAL PROPERTIES

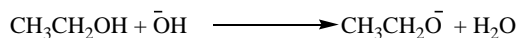
(a) Formation of alkenes

Alkylhalides react with hot alcoholic potassium hydroxide to form alkenes. The mechanism depends on the class of alkylhalide but the mechanism of reaction for secondary alkylhalide is similar to that of the primary or tertiary alkylhalide. These reactions were also considered when we dealt with preparation of alkene

(i) Example for primary alkylhalides,

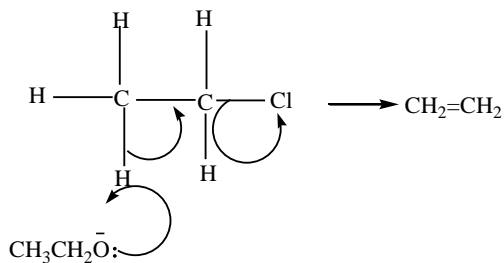


Mechanism

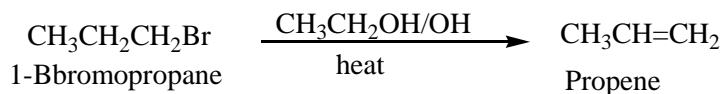


Ethanol

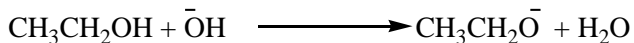
Then



Example II

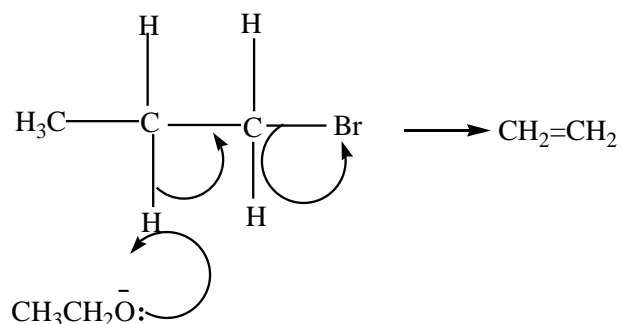


Mechanism



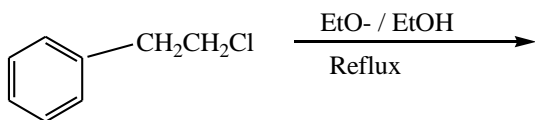
Ethanol

Then

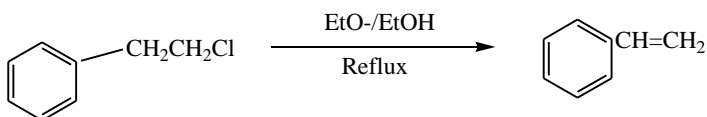


Exercise

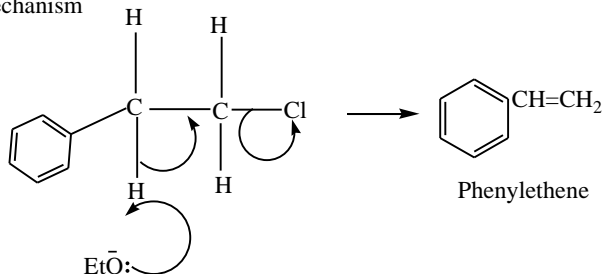
Complete and write a mechanism



Solution



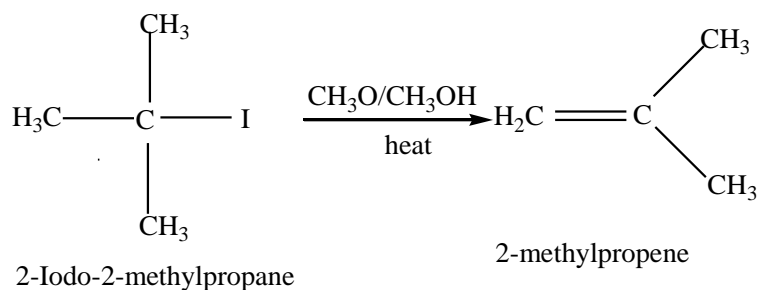
Mechanism



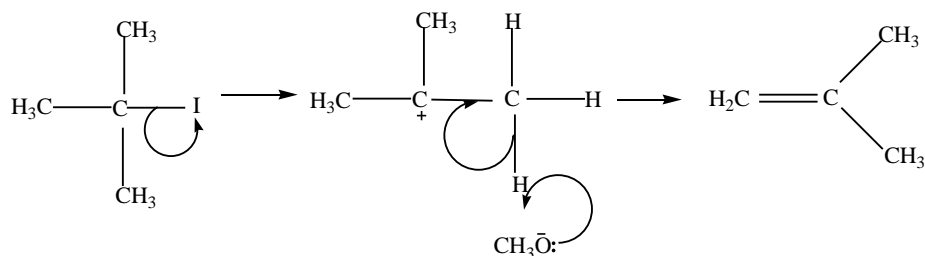
- (ii) Secondary alkyl halides undergo the same mechanism as primary alkyl halides or that of tertiary alkyl halides
- (iii) Tertiary alkyl halides undergo a mechanism called E1 or elimination unimolecular because a water molecule is eliminated and the slowest step involves one molecule only.



Example

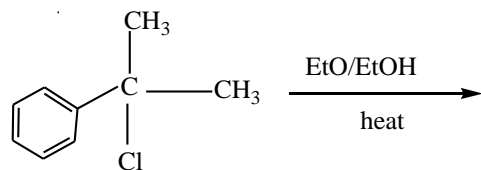


Mechanism

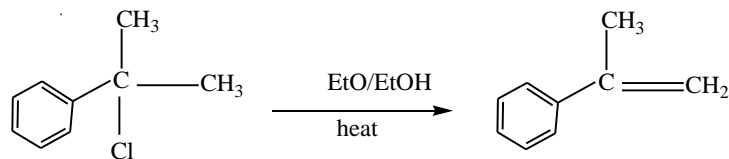


Exercise

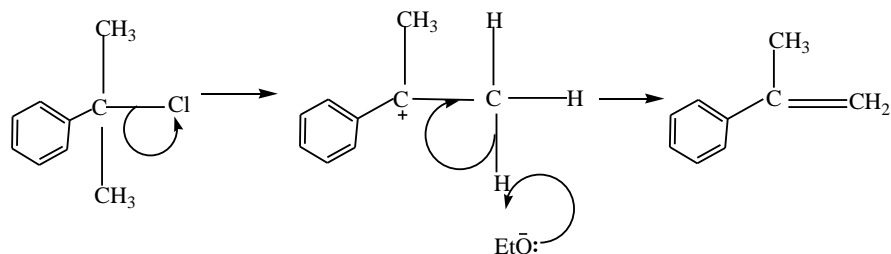
Complete and write a mechanism



Solution



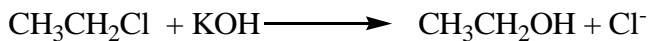
Mechanism



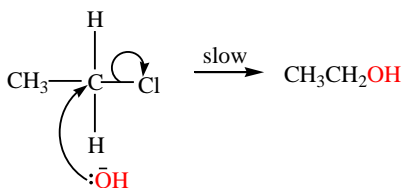
**(b) Reaction of alkyl halide with alkalis (NaOH or KOH)**

Alkyl halides react with hot alkalis to form alcohols. The secondary alkyl halides react by either mechanism of primary or tertiary alkyl halides.

Primary alkyl halide



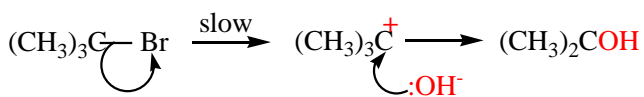
Mechanisms



The mechanism is described as  $\text{S}_{\text{N}}2$  (substitution nucleophilic bimolecular) because a nucleophile ( $-\text{OH}$ ) substitutes a halide atom and the slow step in the reaction involved two species i.e.  $-\text{OH}$  and alkylhalide.

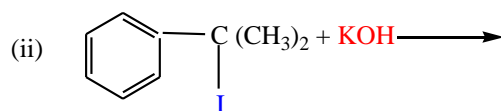
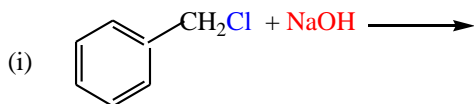


Mechanism

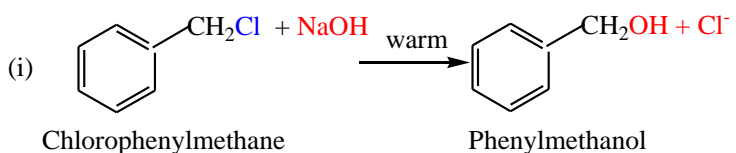


Exercise

Complete and write a mechanism, thereafter mark yourself

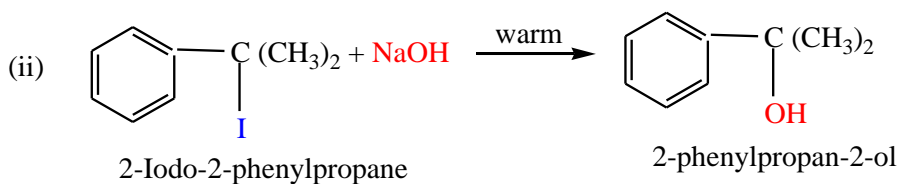
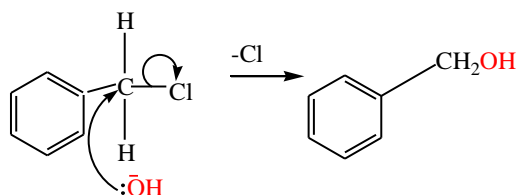


Mark yourself



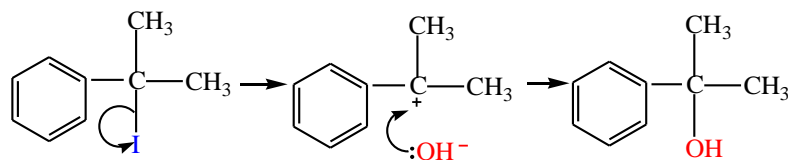
## Mechanism

Note that chlorophenylmethane is a primary alkyl halide



## Mechanism

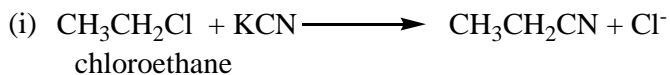
Note that 2-iodo-2-phenylpropane is a tertiary alkyl halide



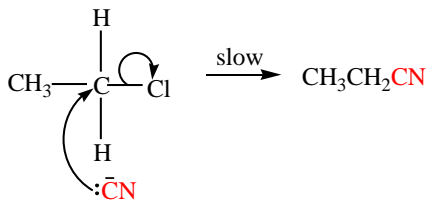
### (c) Reaction with potassium cyanide

Alkyl halides react with potassium cyanide to form nitrile. This reaction is important because it increases the carbon chain by one carbon atom. Primary alkyl halide undergo  $\text{S}_\text{N}2$  while tertiary alkyl halide undergo  $\text{S}_\text{N}1$  mechanism whereas secondary alkyl halides undergo either mechanism.

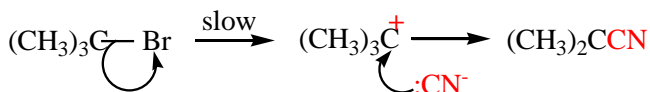
### Examples



Mechanism (note that chloroethane is a primary alkyl halide)

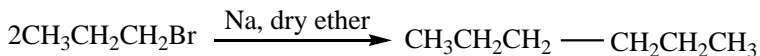
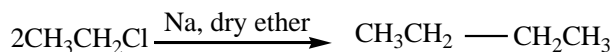


Mechanism (2-bromo-2-methylpropane is tertiary alkyl halide)



(d) Coupling reaction

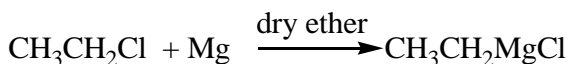
Two alkyl halides couple in presence of sodium and dry ether or zinc-copper couple to form alkane of twice the number of carbon atoms as the parent alkyl halide.



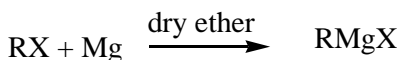
(e) Formation of Grignard's reagent

Alkyl halides react with magnesium in presence of dry ether to form compound called Grignard's reagent.

Example

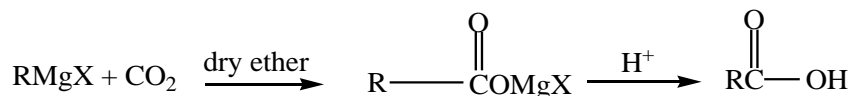


Generally

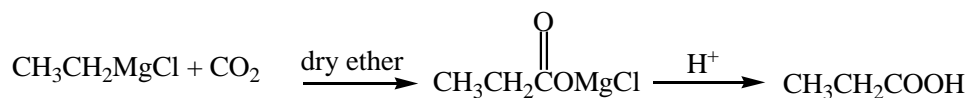


Grignard's reagents are important synthetic molecules that enable us to increase the parent carbon chain by unlimited number of carbon atoms in synthesis.

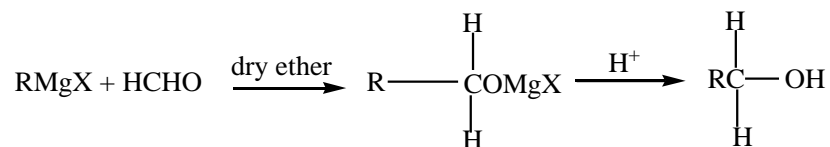
(i) Grignard's reagent reacts with carbon dioxide to produce carboxylic acid. The parent chain increase by one carbon atom.



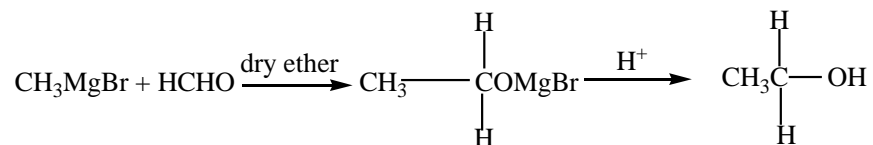
Example



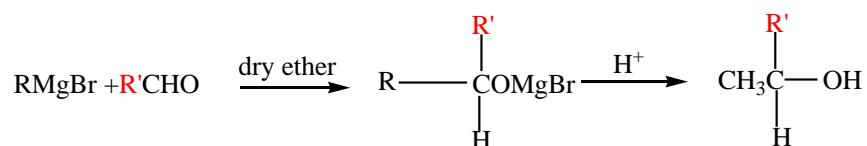
- (ii) Grignard's reagent reacts with methanal to produce primary alcohols. The parent chain increase by one carbon atom.



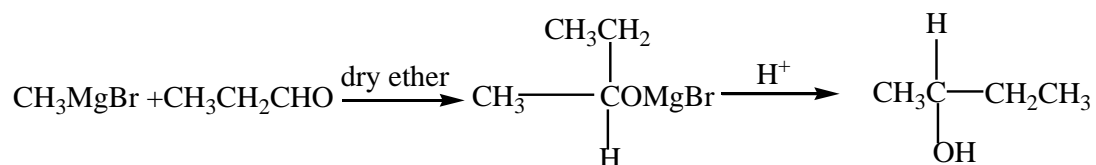
Example



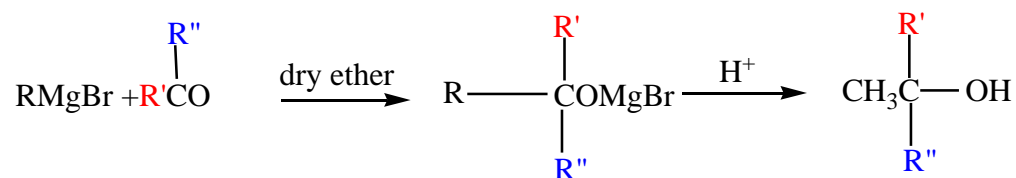
- (iii) Grignard's reagent reacts with aldehydes to produce secondary alcohols.



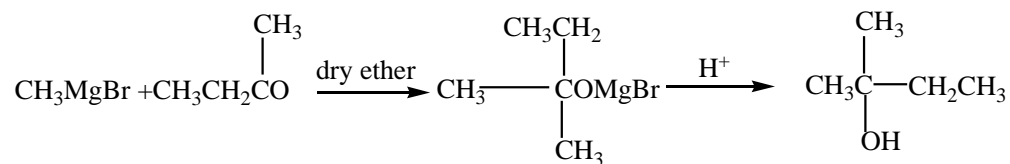
Example



- (iv) Grignard's reagent reacts with ketones to produce secondary alcohols.



Example



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