



CHAPTER 7

HALOALKANES (ALKYL HALIDES)



7.1

LEARNING OUTCOMES

INTRODUCTION TO HALOALKANES

Give the **name of haloalkanes** according to the IUPAC nomenclature. (C2)

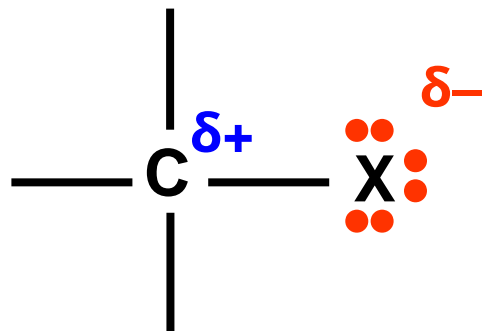
Give the **structural formulae** for haloalkanes (C2)

Classify haloalkanes into primary, secondary and tertiary haloalkanes (C2)

Describe haloalkanes as compounds that contain **polar bond** and the carbon bearing the halogen is **susceptible to nucleophilic attack**. (C2)

HALOALKANES

- Contain **halogen** atom **X** bonded to **sp^3** hybridized C atom



- General formula: $C_nH_{2n+1}X$ (acyclic)
 $C_nH_{2n-1}X$ (cyclic)
 $R-X$; $X = F, Cl, Br, I$
- Also known as **alkyl halides**

CLASSIFICATION

Depends on the classification of **C** that bonds to the **halogen**

CLASS	EXAMPLE
Primary (1°) Halogen is bonded to 1° C	$\begin{array}{c} \text{H} \\ \\ \text{CH}_3 - \text{C} - \text{Cl} \\ \\ \text{H} \end{array}$
Secondary (2°) Halogen is bonded to 2° C	$\begin{array}{c} \text{H} \\ \\ \text{CH}_3 - \text{C} - \text{CH}_3 \\ \\ \text{Br} \end{array}$
Tertiary (3°) Halogen is bonded to 3° C	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{C} - \text{CH}_3 \\ \\ \text{I} \end{array}$

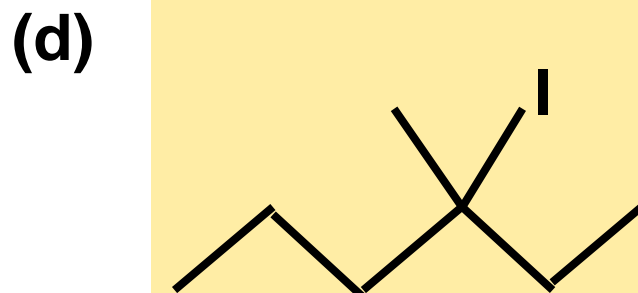
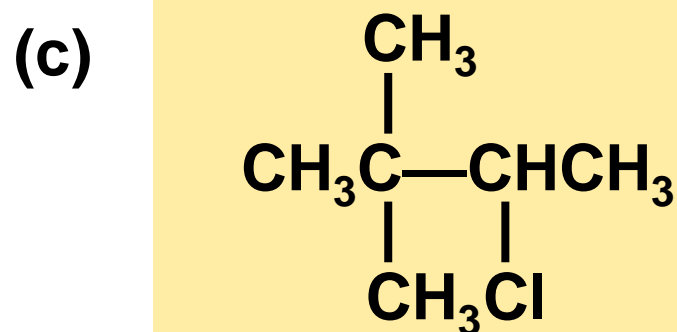
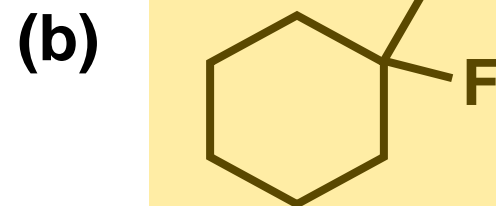
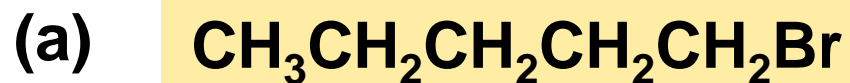
Note: $\text{CH}_3 - \text{Cl}$ is methyl haloalkane



EXERCISE 1

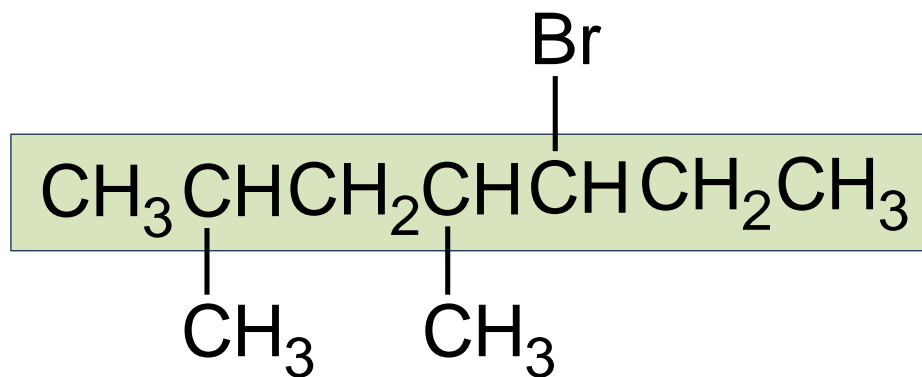


Classify each alkyl halide as 1°, 2° and 3°.



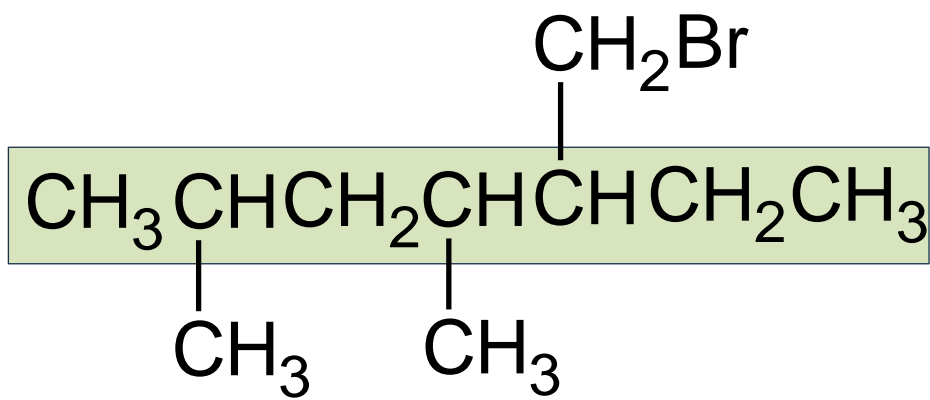
IUPAC NAMES

- Find **longest C** chain



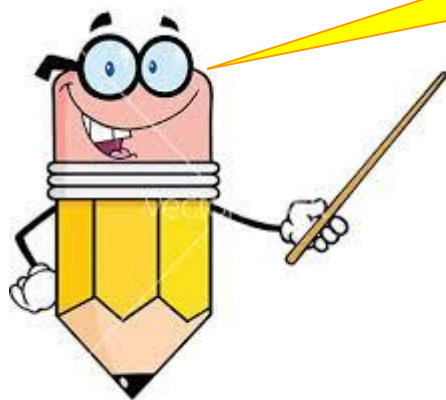
parent name = **heptane**





parent name = **heptane**

IUPAC nomenclature for **alkyl halides** follows the **basic rules** as described in **alkanes**



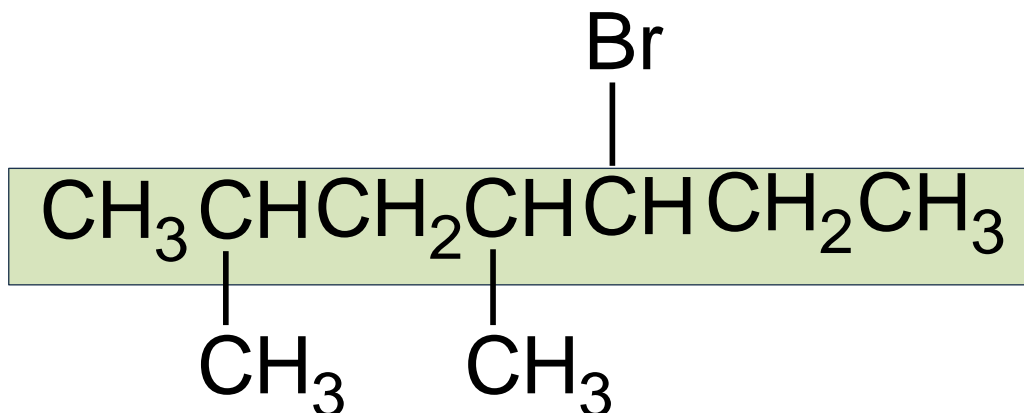
—F  fluoro

—Cl  chloro

—Br  bromo

—I  iodo

- ❑ Number parent chain beginning at the **end nearer** to the **first substituent**, **regardless** of whether it is **alkyl** or **halo**

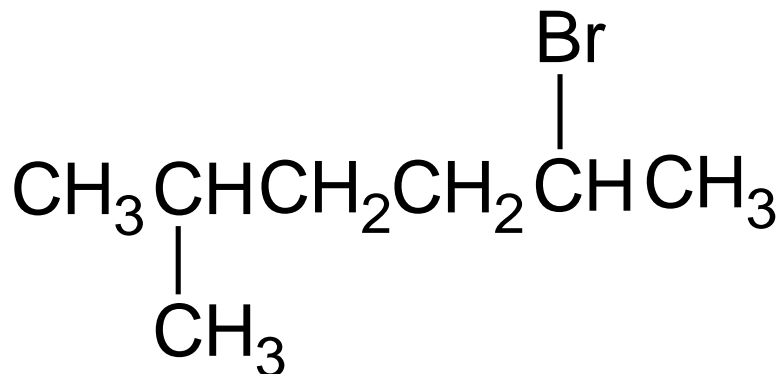


5-bromo-2,4-dimethylheptane

Substituent	5-bromo 2,4-dimethyl
Parent	heptane

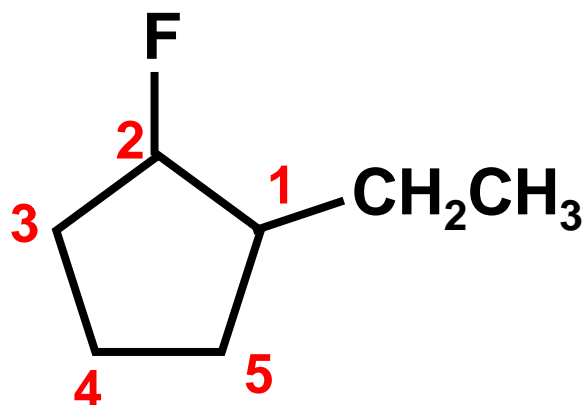
□ Treat **halogens** exactly like **alkyl** for **numbering** and **alphabetizing** purpose

(because the reactivity of halogen and alkyl group are almost similar)



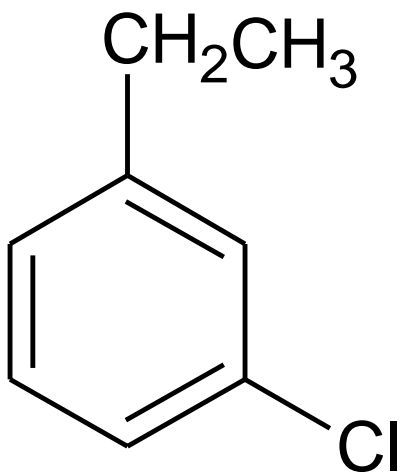
2-bromo-5-methylhexane

Substituent	2-bromo 5-methyl
Parent	hexane



1-ethyl-2-fluorocyclopentane

Substituent	1-ethyl 2-fluoro
Parent	cyclopentane



1-chloro-3-ethylbenzene

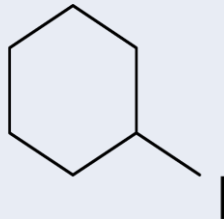
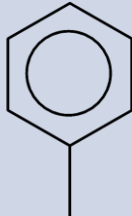
Substituent	1-chloro 3-ethyl
Parent	benzene



EXERCISE 2

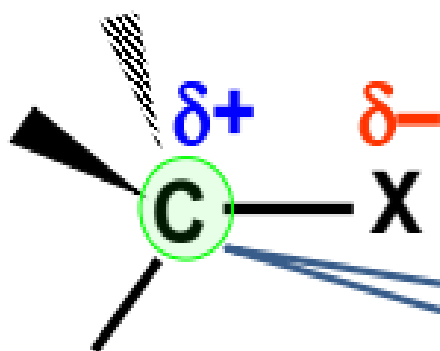


Give the IUPAC name for each compound.

No	Structure	No	Structure
1	$\begin{array}{ccccccc} & & & & \text{Br} & & \\ & & & & & & \\ \text{CH}_3 & \text{CH} & \text{CH}_2 & \text{CH} & \text{CH} & \text{CH}_2 & \text{CH}_3 \\ & & & & & & \\ & \text{CH}_3 & & \text{CH}_3 & & & \end{array}$ _____	4	$\begin{array}{ccccccc} \text{F} & \text{CH}_2 & \text{CH}_2 & \text{CH} & \text{CH}_3 \\ & & & & \\ & & & \text{CH}_3 & \end{array}$ _____
2	$\begin{array}{ccccccc} \text{Br} & \text{CH}_2 & \text{CH}_2 & \text{CH} & \text{CH} & \text{CH}_3 \\ & & & & & \\ & & & \text{Cl} & \text{CH}_3 & \end{array}$ _____	5	 _____
3	$\begin{array}{ccccccc} \text{CH}_3 & \text{CH} & \text{CH}_2 & \text{CH}_2 & \text{CH} & \text{CH}_3 \\ & & & & & \\ & \text{CH}_3 & & & \text{Br} & \end{array}$ _____	6	 _____

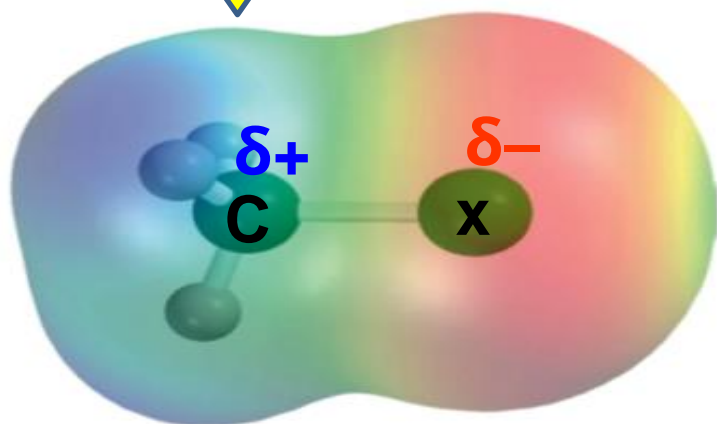
POLAR C–X BOND

- The **electronegative** halogen X creates a polar **C–X bond**, making C atom **electron deficient**

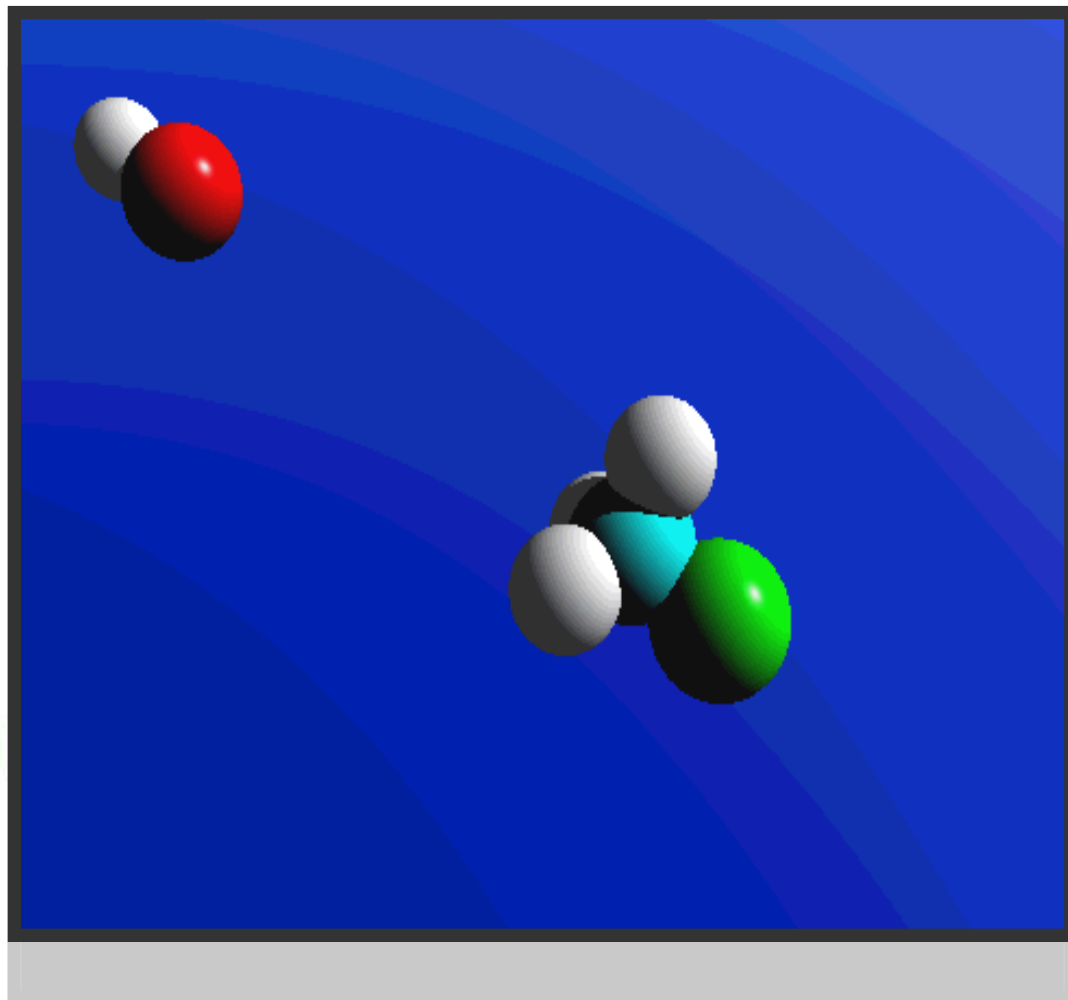


Electrophilic site

Attack!
(by nucleophile)



Chloromethane (CH_3Cl)



- ❑ The **electrophilic C** of alkyl halide is susceptible to **nucleophilic attack**

The background of the slide features a blurred image of laboratory glassware, including several Erlenmeyer flasks and test tubes, some containing liquids of different colors (yellow, red, blue, green).

HALOALKANES (ALKYL HALIDES)

Chemical Properties of Haloalkanes

An inset image showing a collection of small Erlenmeyer flasks, each containing a liquid of a different color: yellow, orange, red, purple, blue, and green. A glass dropper is also visible among the flasks.

7.2

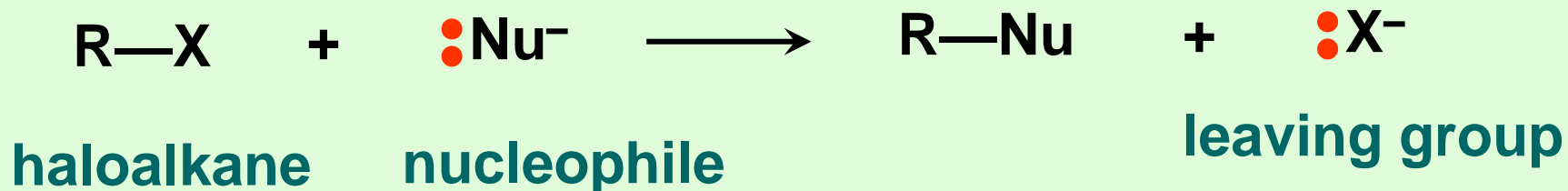
7.2 LEARNING OUTCOMES

Chemical Properties

- a) Explain **nucleophilic substitution** reaction of haloalkanes. **(C2)**
- b) **Explain S_N1 and S_N2 mechanisms** **(C2)**
- c) **Illustrate S_N1 and S_N2 mechanism** of a given haloalkanes. **(C3, C4)**
- d) Compare the **relative reactivities** of primary, secondary and tertiary haloalkanes towards hydrolysis or alcoholysis. **(C4)**
- e) Explain **elimination** reaction of haloalkanes. **(C3)**
- f) Explain the use of haloalkanes in the **synthesis of Grignard reagent**, $RMgX$ / $ArMgX$. **(C3,C4)**
- g) Deduce the structural formulas of **alcohols and carboxylic acids prepared** using Grignard reagents. **(C4)**

NUCLEOPHILIC SUBSTITUTION REACTION

□ Haloalkanes undergo **substitution** reactions with **nucleophiles**



A **nucleophile** replaces a **leaving group** on a **sp^3** hybridized carbon

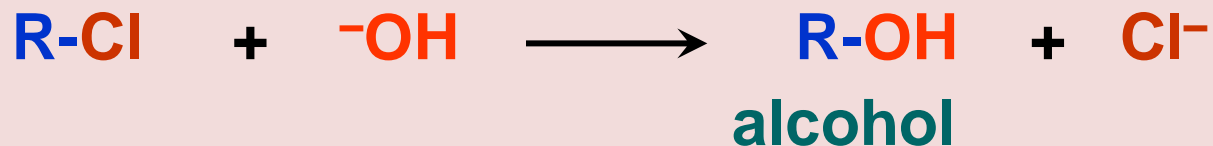


NUCLEOPHILES

Strong nucleophile	Weak nucleophile
HO^-	H_2O
^-OR ; e.g: CH_3O^-	ROH ; e.g: CH_3OH
^-CN	NH_3
	CH_3COO^-



1. Reaction with NaOH



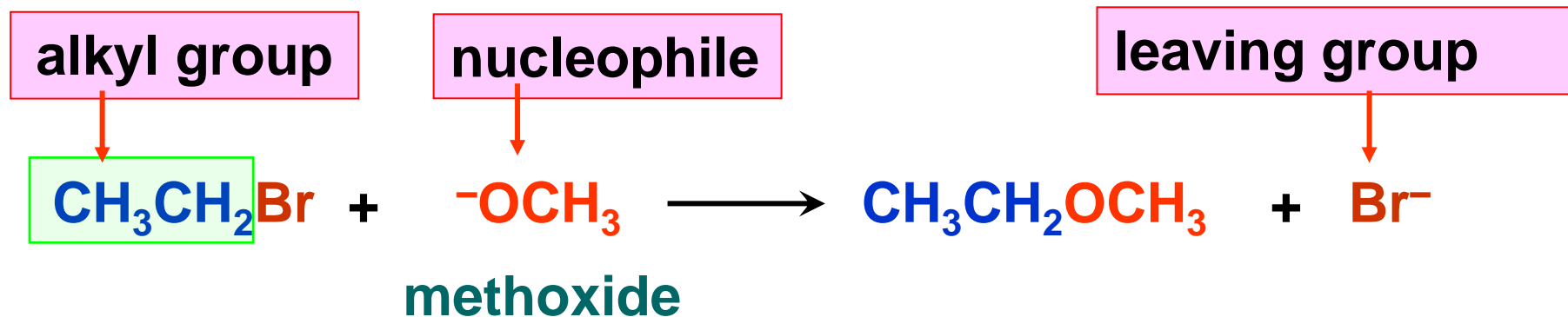
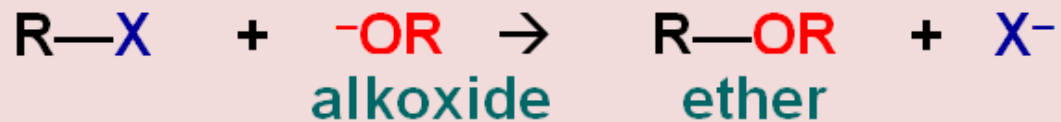
alkyl group

nucleophile

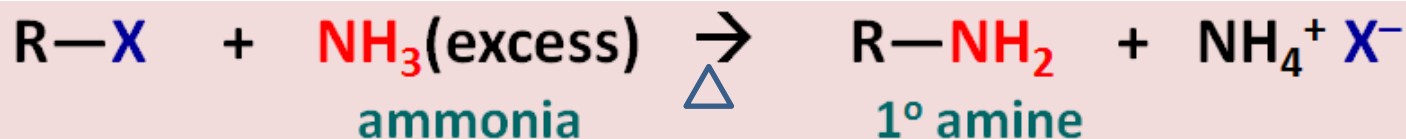
leaving group



2. Reaction with Alkoxide Ion, RO⁻



3. Reaction with excess Ammonia



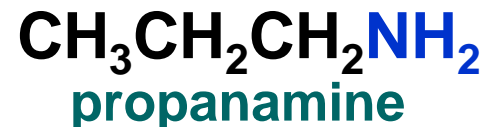
alkyl group

nucleophile

leaving group

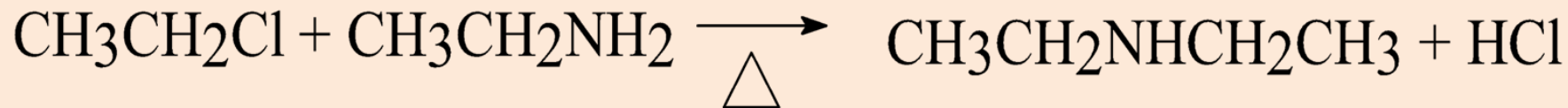


+



React with 1° amine to form 2° amine

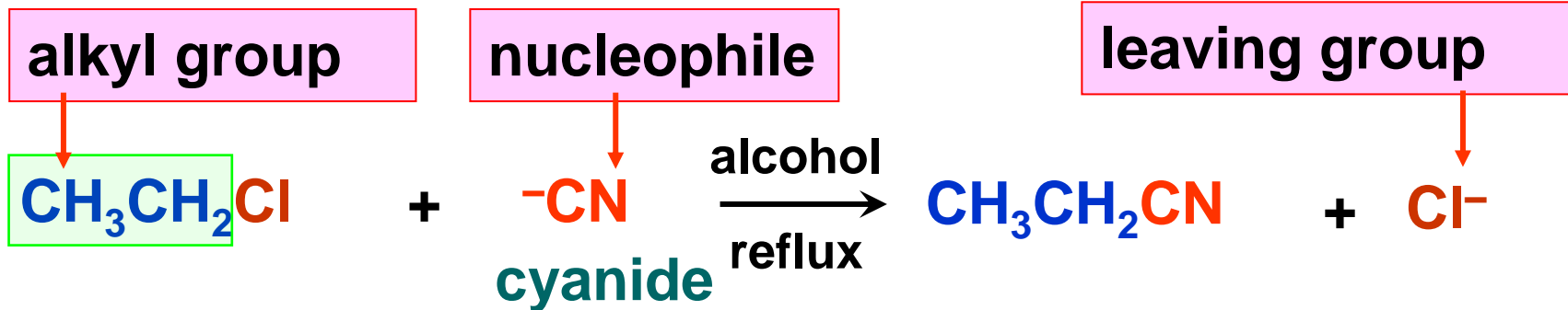
Example :



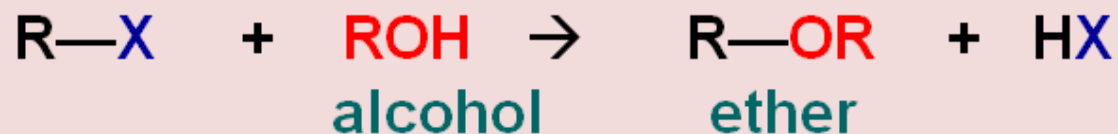
NOTE :

* Similar reaction can be used to produce tertiary amine.

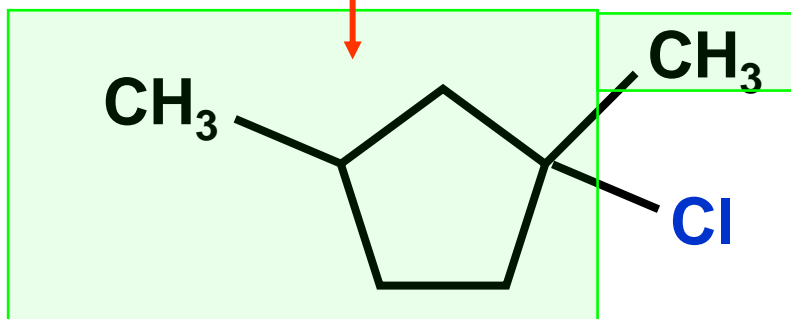
4. Reaction with KCN or NaCN or ^-CN



5. Reaction with Alcohol, **RO-**

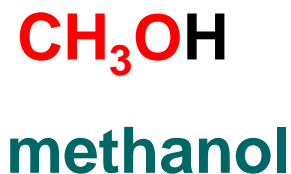


alkyl group



1-chloro-1,3-dimethylcyclopentane

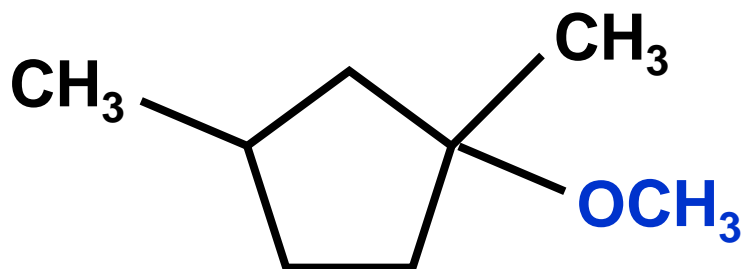
nucleophile



+



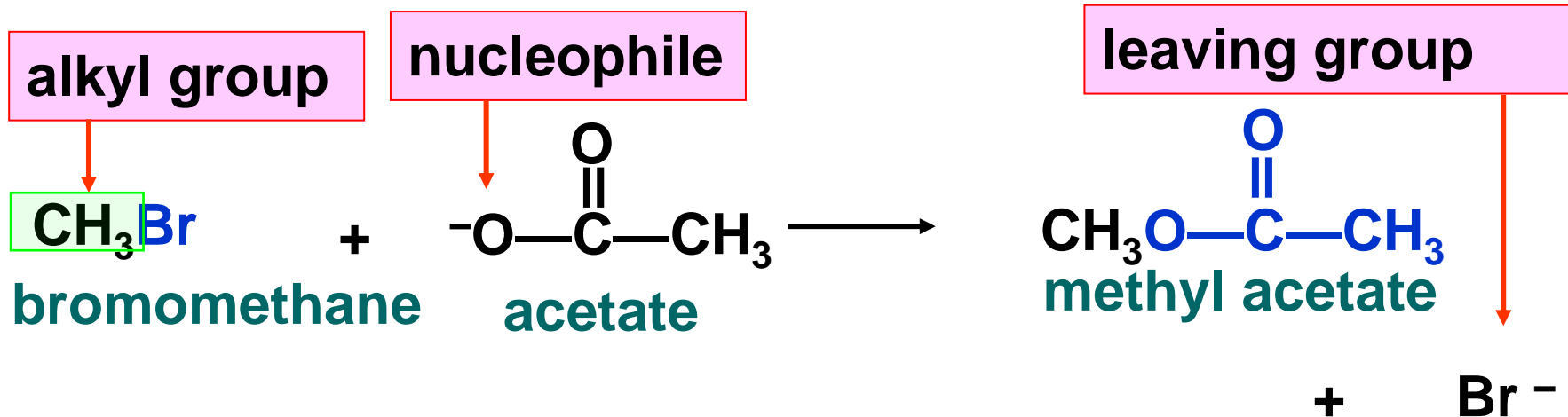
leaving group



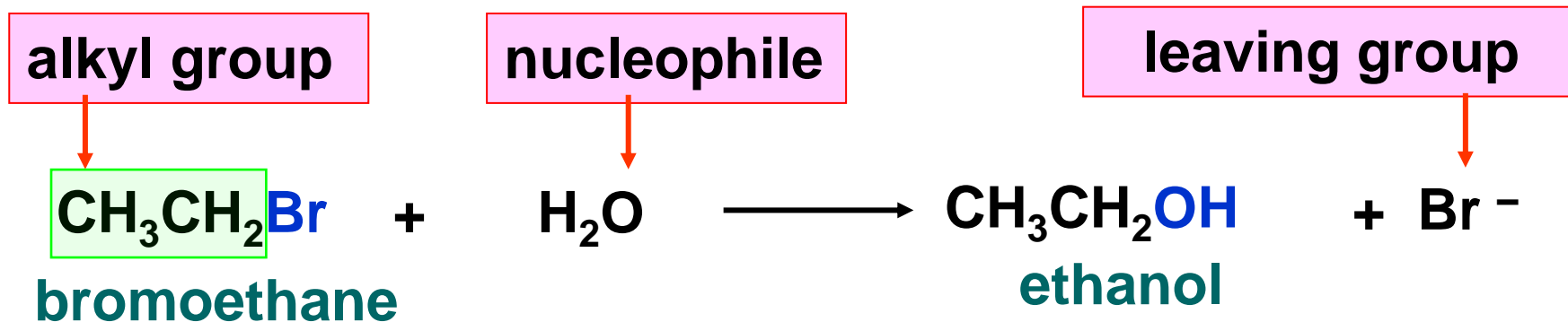
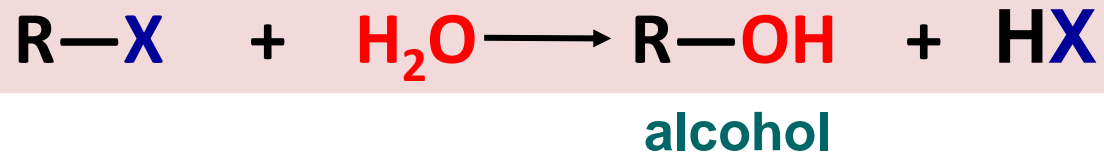
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6. Reaction with acetate ion



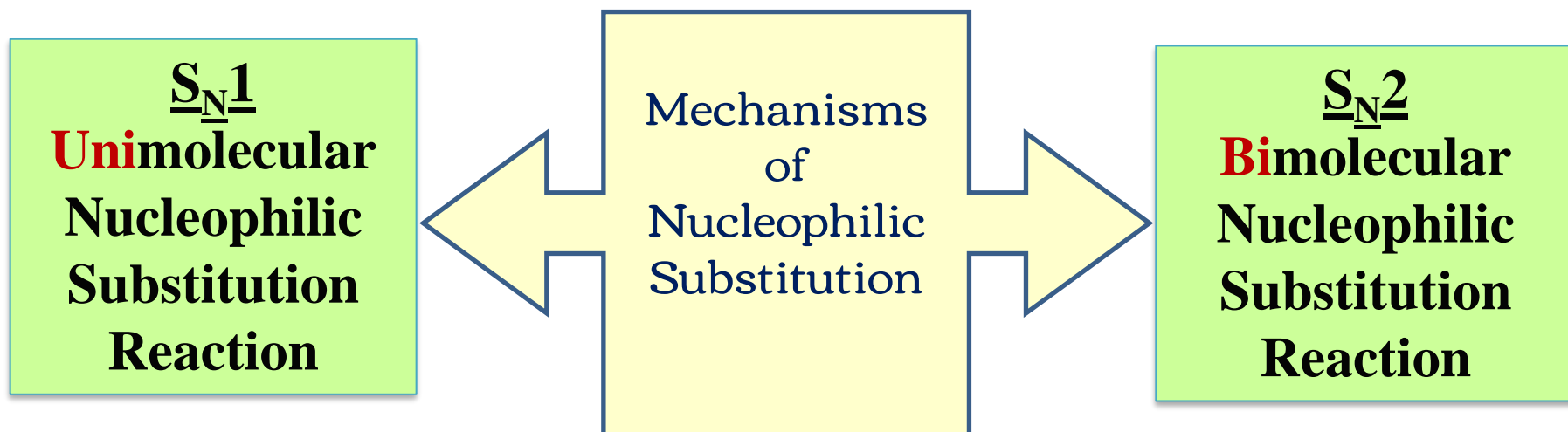
7. Reaction with water, H_2O



S_N1
Unimolecular
Nucleophilic
Substitution
Reaction

Mechanisms
of
Nucleophilic
Substitution

S_N2
Bimolecular
Nucleophilic
Substitution
Reaction



S_N2 MECHANISM

① Bimolecular Nucleophilic Substitution

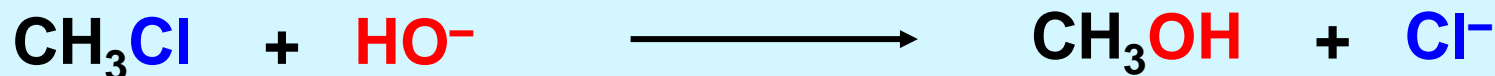
The reaction involve two molecule
(Haloalkane & Nucleophile)

S_N2 MECHANISM

2 Second-order reaction

$$\text{Rate} = k[\text{R—X}][\text{:Nu}^-]$$

EXAMPLE :

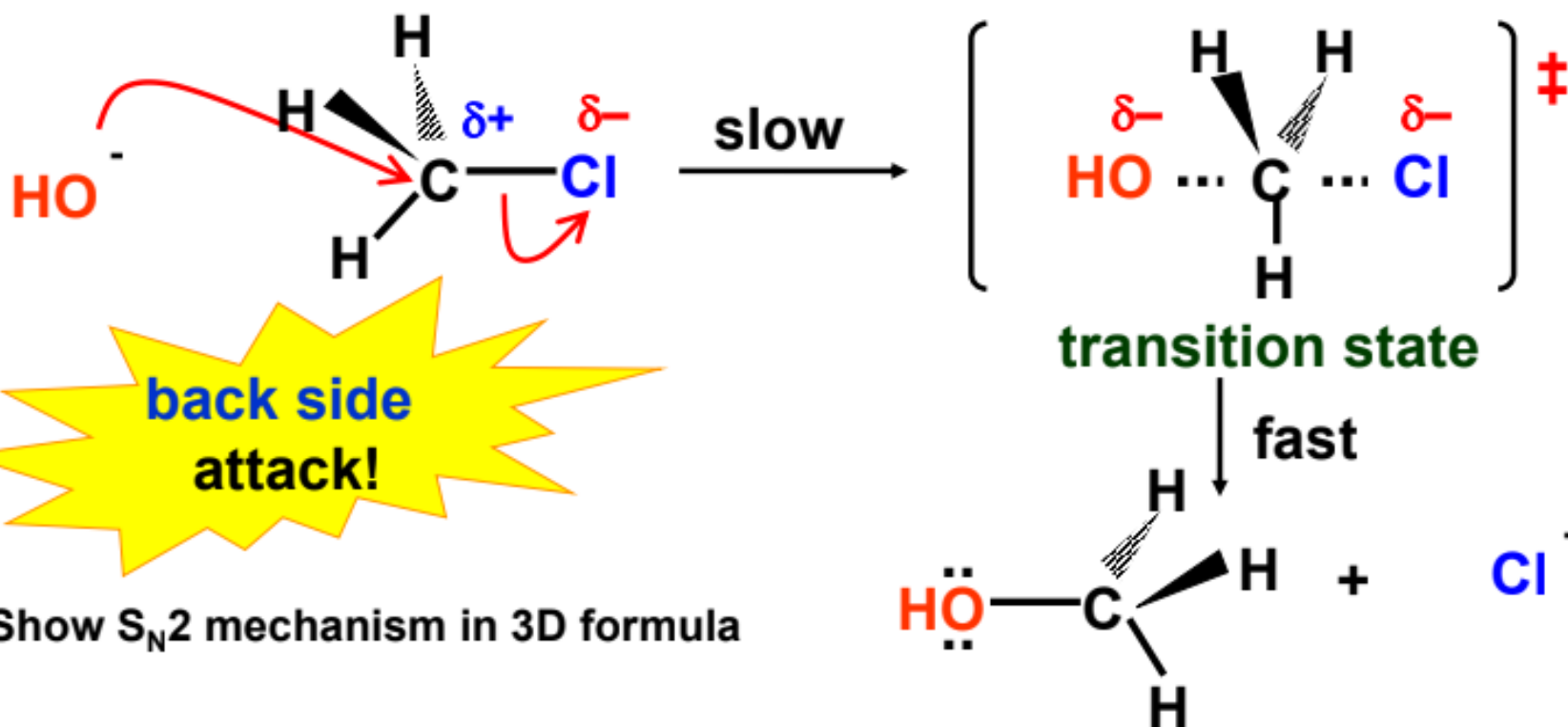


$$\text{Rate} = k[\text{CH}_3\text{Cl}][\text{HO}^-]$$

- ☐ depend on [CH₃Cl] and [HO⁻]
- ☐ second order overall

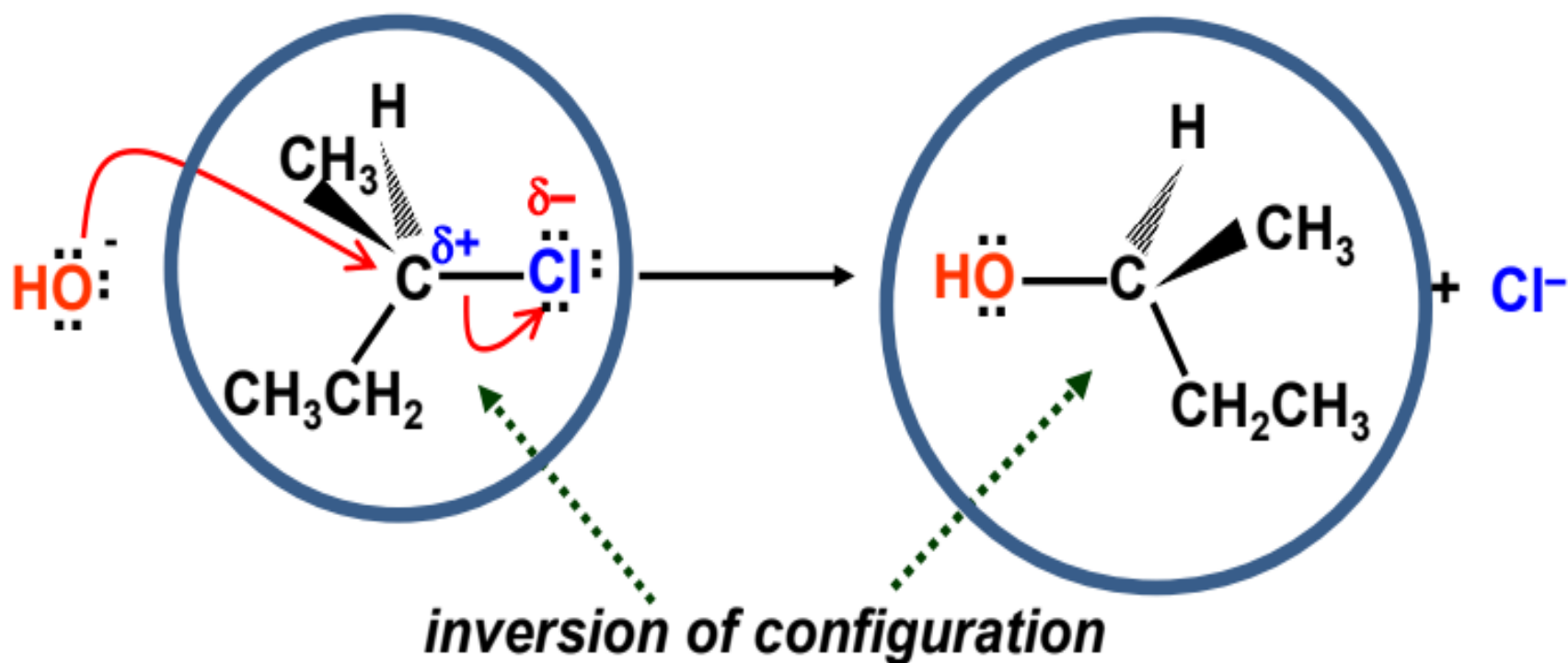
3 One-step mechanism

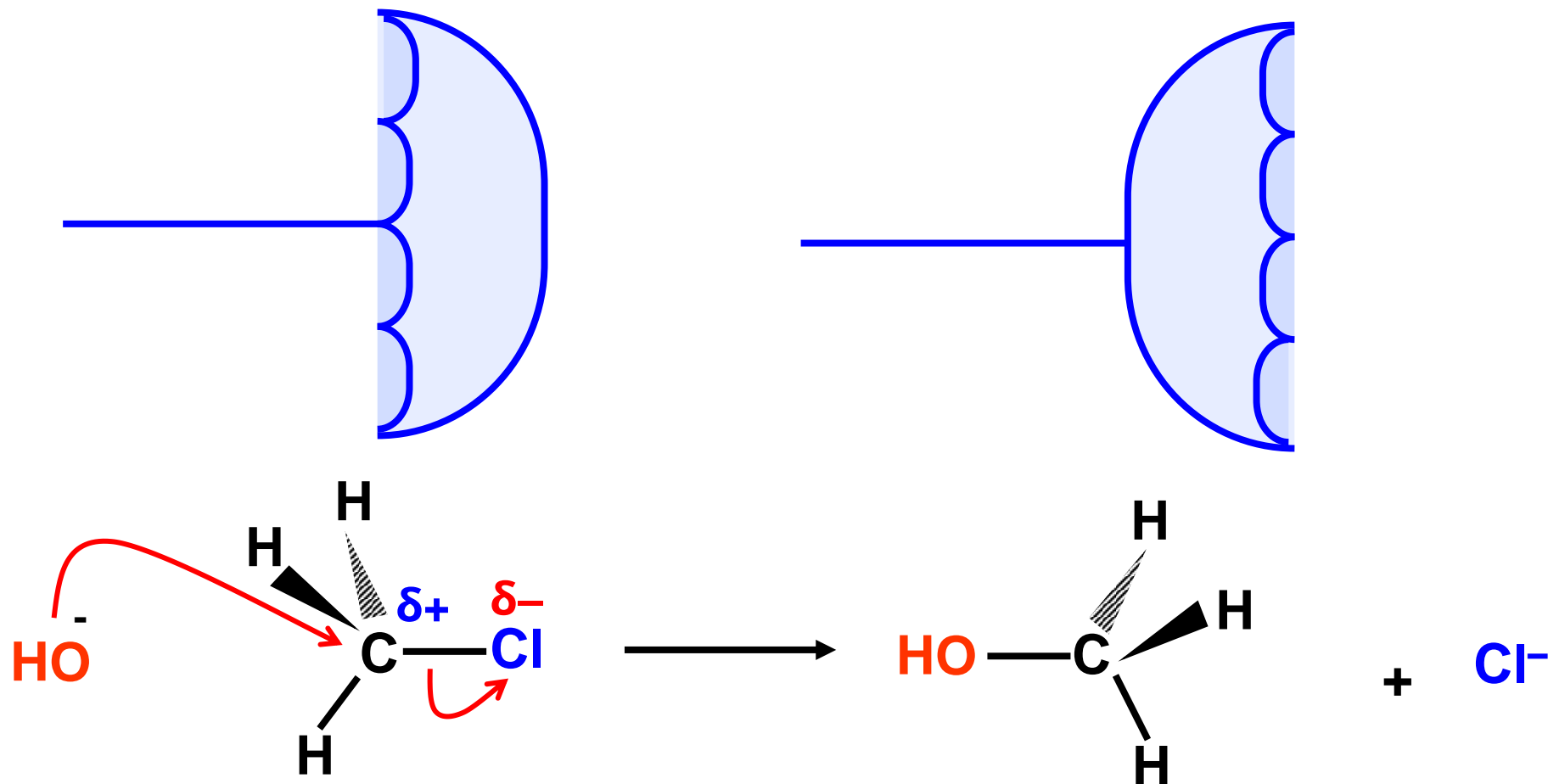
- ☐ Has a transition state
- ☐ ***No carbocation*** rearrangement



S_N2 MECHANISM

- All S_N2 reactions proceed with **backside attack**, resulting in **inversion** of **configuration** at a **stereogenic center**





Backside attack literally attack from the C atom inside out, like an umbrella caught by the wind

STERIC EFFECT

- S_N2 reactions are affected by **steric factors** (steric effect).

Steric effect :

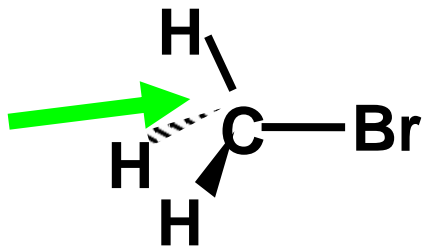
Is an effect on relative rates caused by the **space - filling properties** of parts of molecules attached at or near to the reacting site.



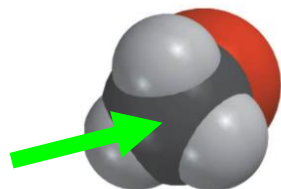
The **reactivity** on S_N2 reaction **depends on the size of atoms or groups** attached to the C – X.



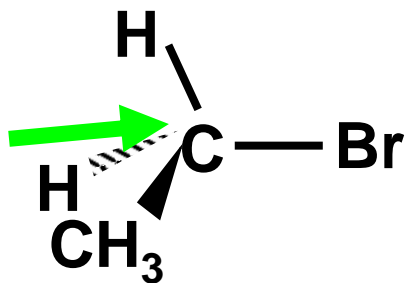
Larger no. of alkyl groups, shielded the carbon atom in the C-X from attack by the incoming nucleophile



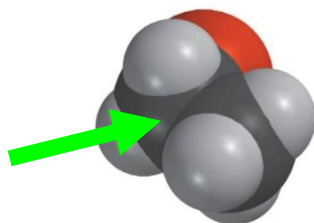
methyl bromide



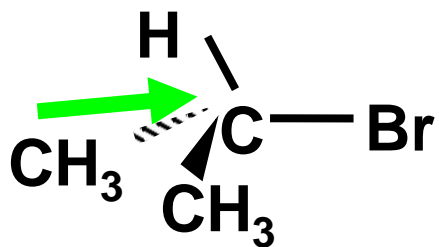
Attack is **very easy!**



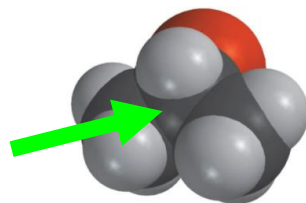
ethyl bromide
(1°)



Attack is **easy!**



isopropyl bromide
(2°)



Attack is **slightly difficult!**

ORDER OF REACTIVITY

Increasing rate of an S_N2 reaction



<



<



<



3°

2°

1°

methyl

more **crowded**
more **steric hindrance**
less **reactive**

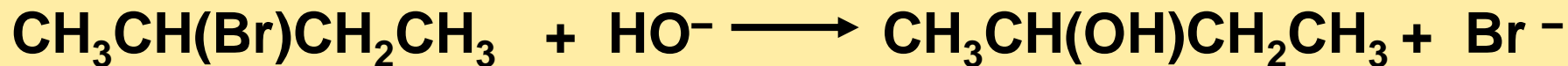
less **crowded**
less **steric hindrance**
more **reactive**



EXERCISE 3



Give the S_N2 mechanism for the formation of the product in the following reaction.



S_N1 MECHANISM

① Unimolecular Nucleophilic Substitution

First step involve only one molecule (haloalkane)

 The rate of S_N1 reaction **does not depend on the concentration of nucleophile.**

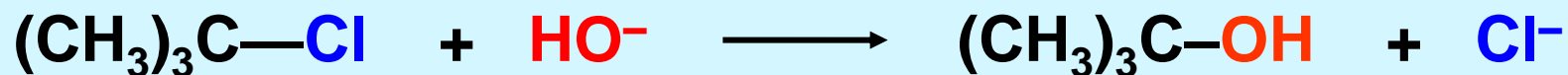
 The rate **depends only on the concentration of the substrate, alkyl halide.**

$$\text{Rate} = k [\text{R-X}]$$

* S_N1 is a first order reaction

S_N1 MECHANISM

2 First-order reaction



$$\text{Rate} = k[(\text{CH}_3)_3\text{CCl}]$$

- depend on $[(\text{CH}_3)_3\text{CCl}]$
- first order overall

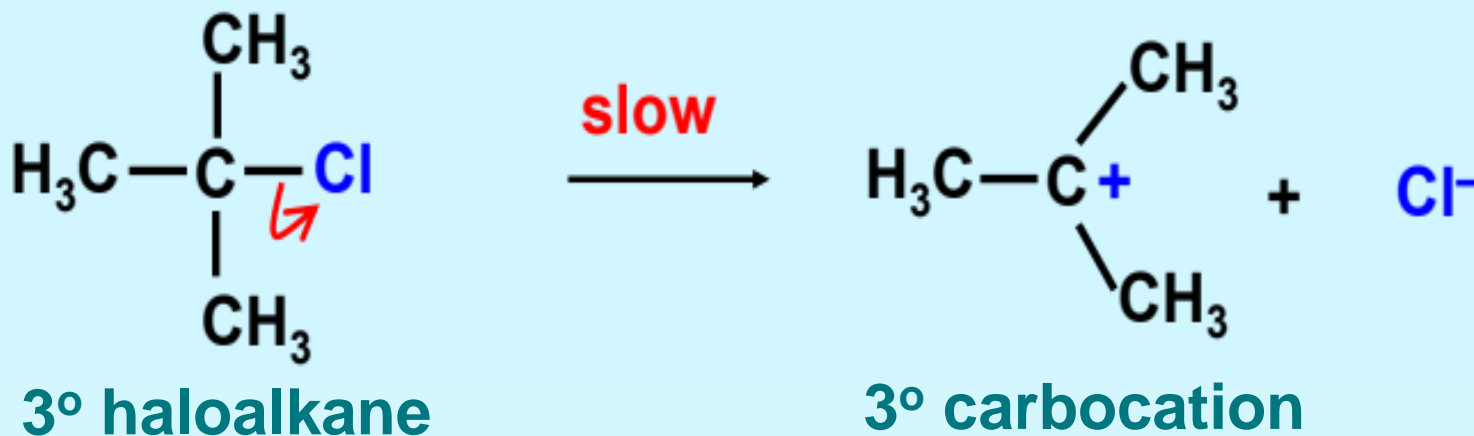
Only $(\text{CH}_3)_3\text{CCl}$ involved in the step that control reaction rate
☞ **unimolecular**



3 Two-step mechanism

- **Carbocation** is formed as a **reactive intermediate**

STEP 1 Formation of Carbocation



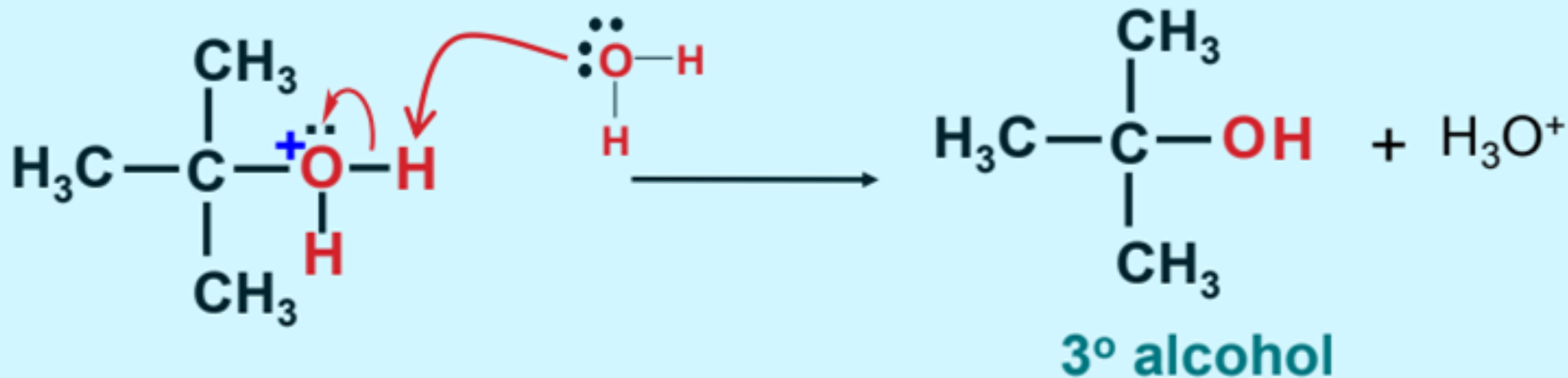
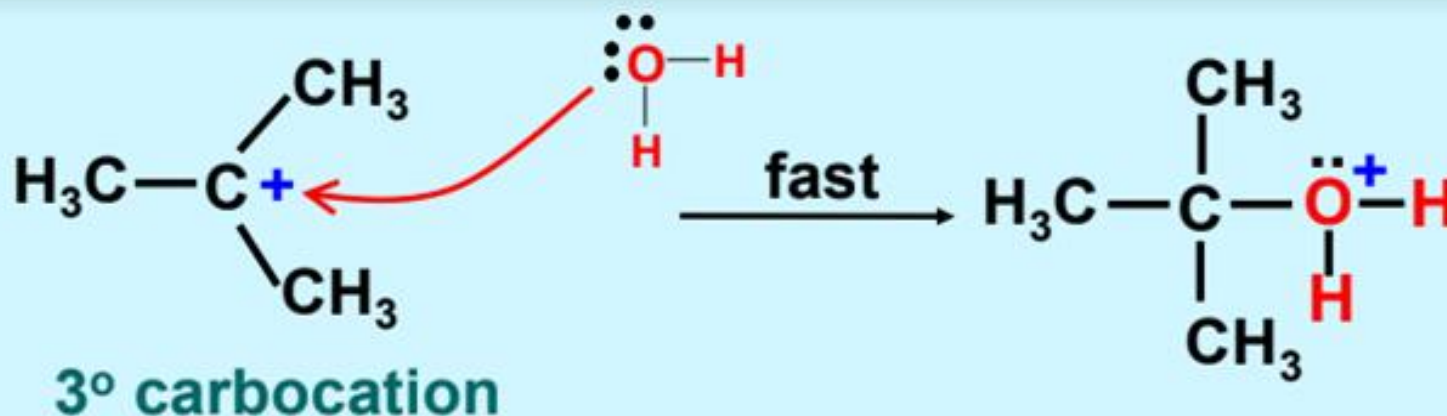
Step 1 (**slow**) the **rate-determining step** (*slowest step*)



3 Two-step mechanism

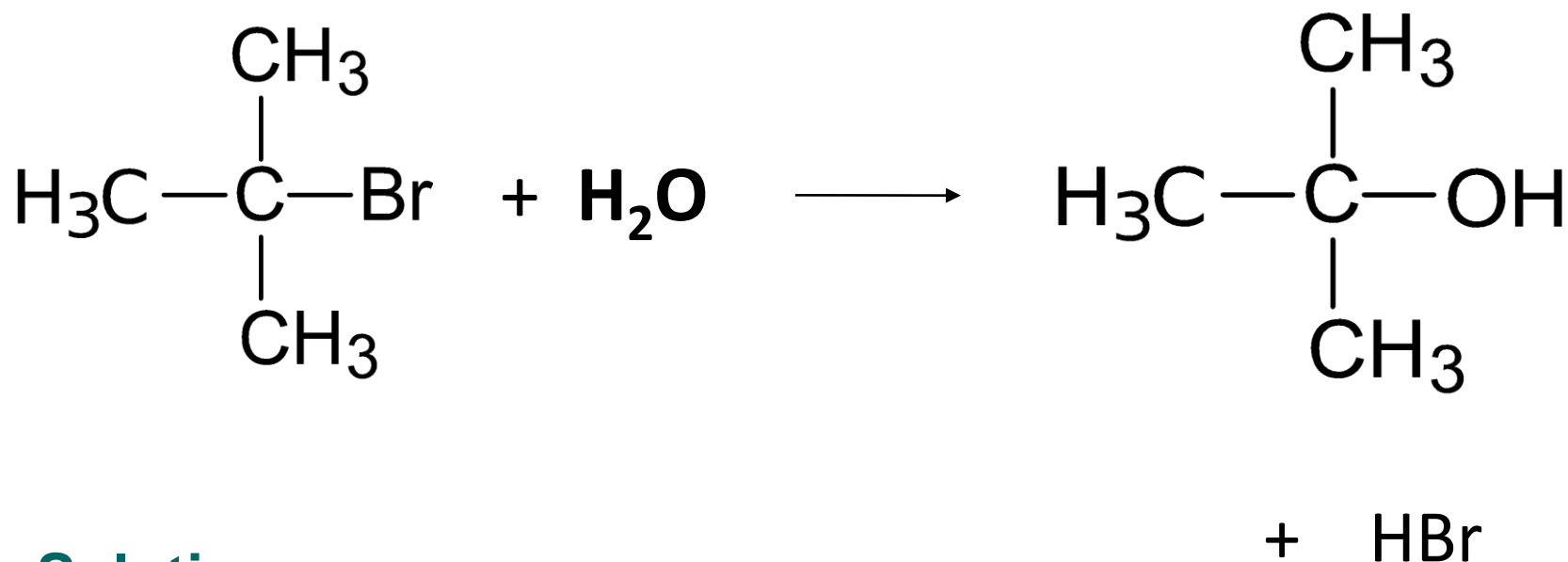
STEP 2

Nucleophilic attack on the Carbocation





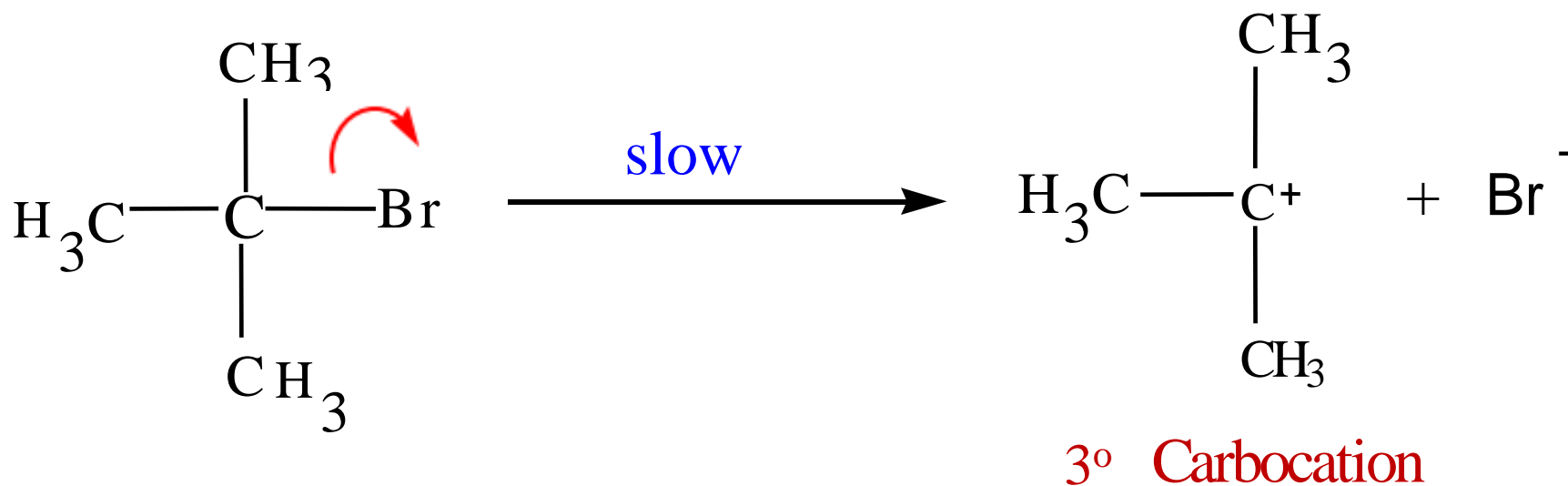
Write the mechanism for the following reaction



Solution

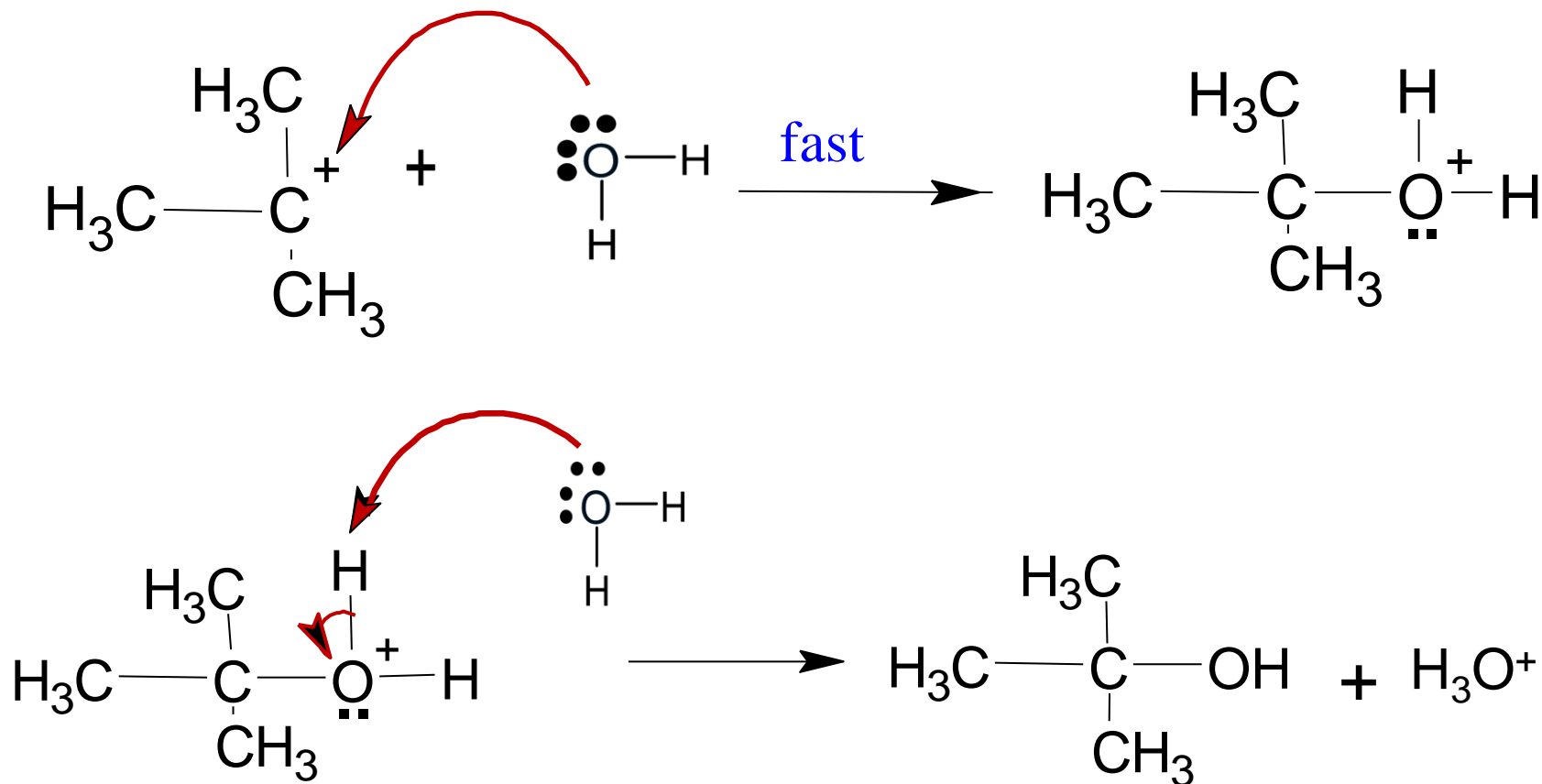
- > 3° haloalkane
- > weak nucleophile
- > 2 steps mechanism involve, $\text{S}_{\text{N}}1$

Step 1 : Formation of carbocation



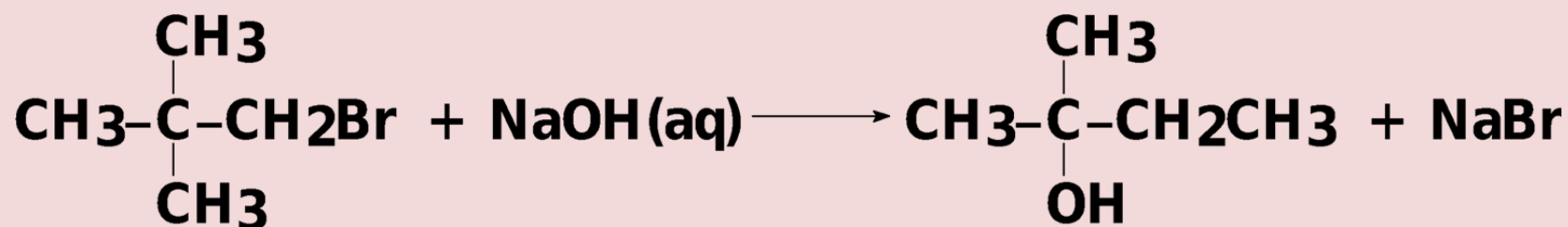
S_N1 MECHANISM

Step 2: Nucleophilic attack on the carbocation





Write the mechanism for the following reaction.



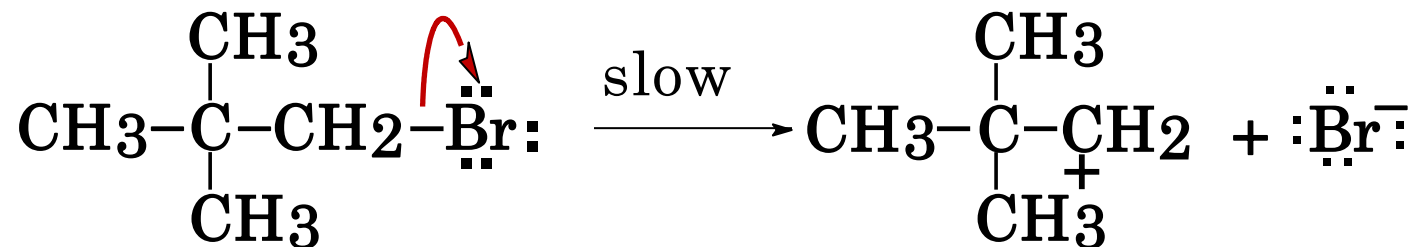
Solution

1^o haloalkane but more **steric effect**

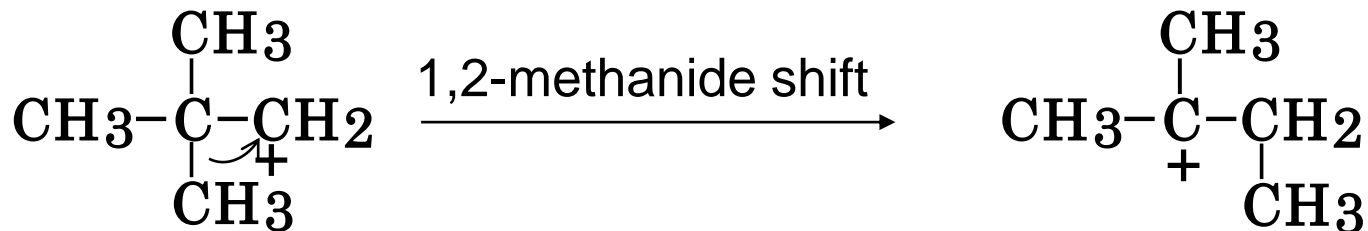
Has *rearrangement*

S_N1 MECHANISM

Step 1 : Formation of carbocation



Rearrangement :

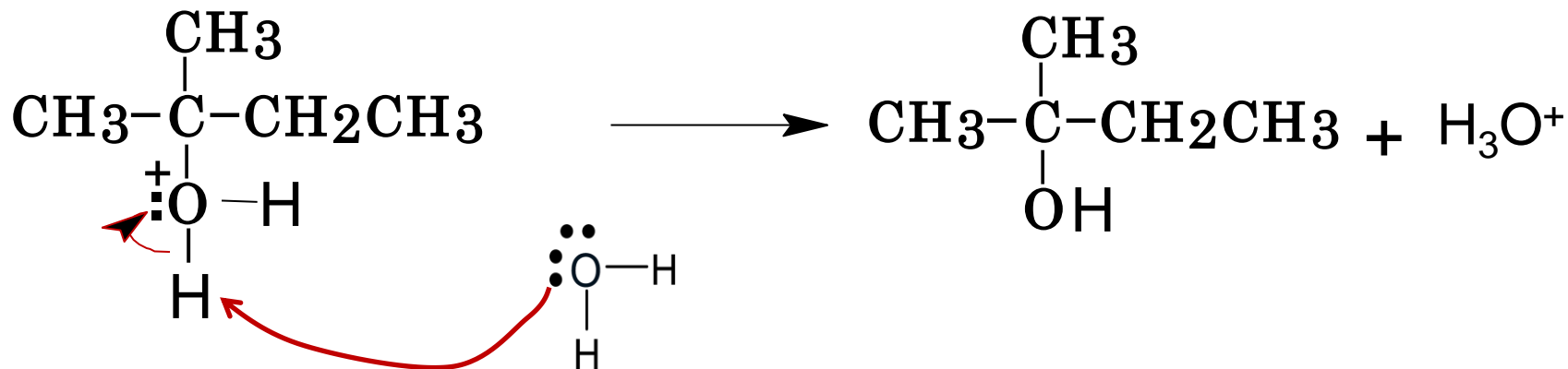
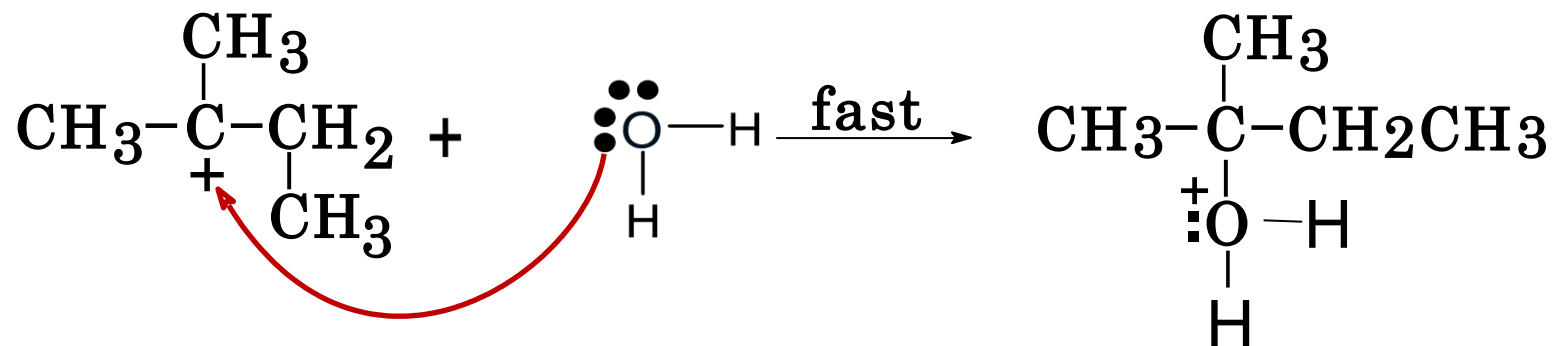


1° carbocation

3° carbocation

S_N1 MECHANISM

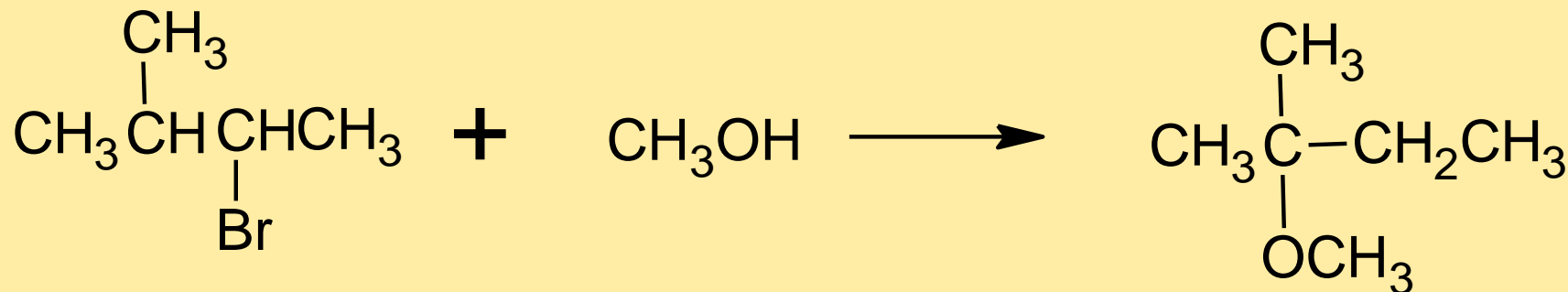
Step 2 : Nucleophilic attack on the carbocation





EXERCISE 4

Give the S_N1 mechanism for the formation of the product in the following reaction.



S_N1 MECHANISM

Step 1 : Formation of carbocation

Rearrangement :

S_N1 MECHANISM

Step 2 : Nucleophilic attack on the carbocation

ORDER OF REACTIVITY



Reactivity and reaction rate determined by the **stability of carbocation** formed

Increasing rate of an S_N1 reaction



<



<



<



methyl

1°

2°

3°

form least
stable **carbocation**

form most
stable **carbocation**

TYPES OF ALKYL HALIDES	NUCLEOPHILIC SUBSTITUTION MECHANISM
1° and CH ₃ X	S _N 2
2°	S _N 2 or S _N 1
3°	S _N 1

2° alkyl halide undergo both S_N1 and S_N2 reactions. Other factors determine the mechanism



EFFECT OF NUCLEOPHILE

S_N1

❑ Nucleophile **strength** is **unimportant**

- Favored by **weak** nucleophiles (usually **neutral**)

S_N2

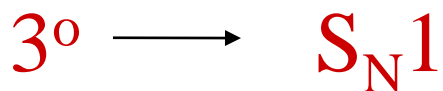
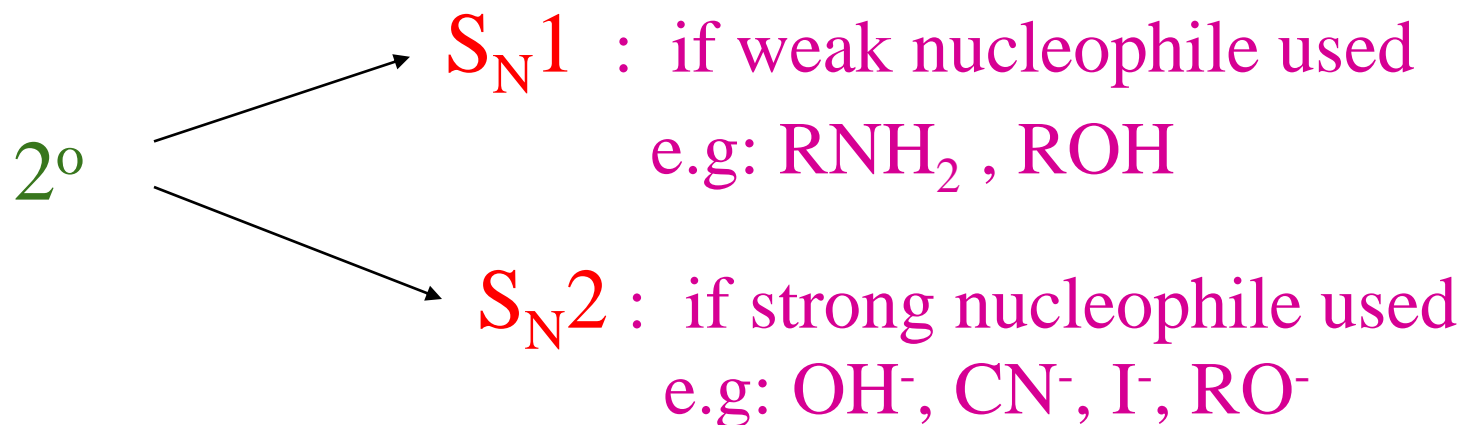
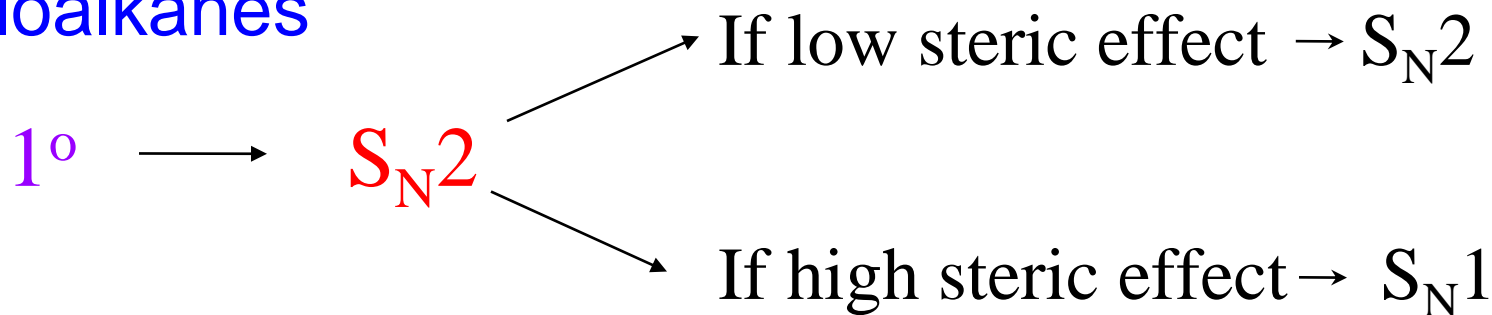
❑ **Strong nucleophiles** is required

- Favored by **strong** nucleophiles (usually a net **negative** charge)



S_N1 or S_N2 ???

Haloalkanes



S_N1 MECHANISM

Unimolecular Nucleophilic Substitution

- First step involve only one molecule (Haloalkane)

First Order reaction Rate = $k [RX]$

Carbocation as intermediate

Two steps mechanism

Order of reactivity :

Methyl halide < 1° < 2° < 3°

Weak nucleophiles (usually neutral species)

S_N2 MECHANISM

Bimolecular Nucleophilic Substitution

- The reaction involve two molecule (Haloalkane & Nucleophile)

Second Order Reaction

Rate = $k [RX][Nu^-]$

No carbocation, Has a **transition state**

One step mechanism

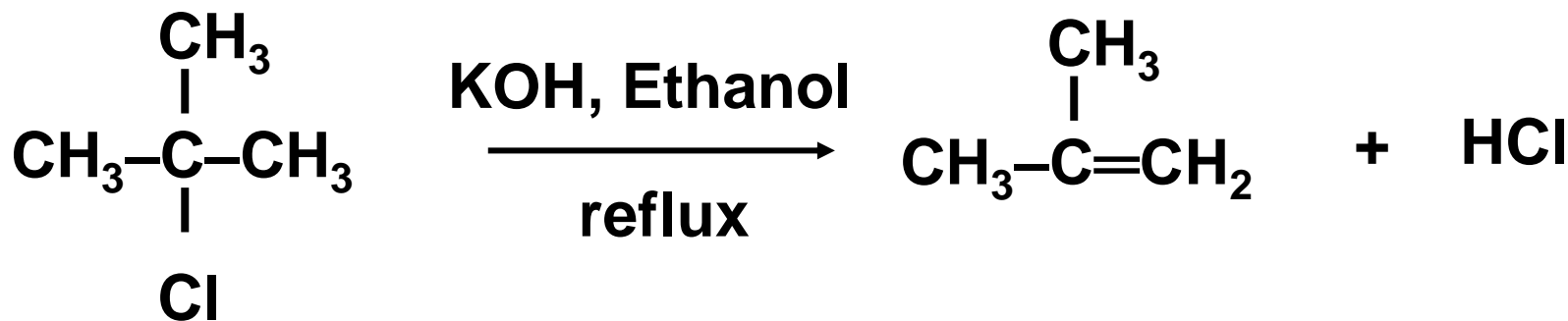
Order of reactivity :

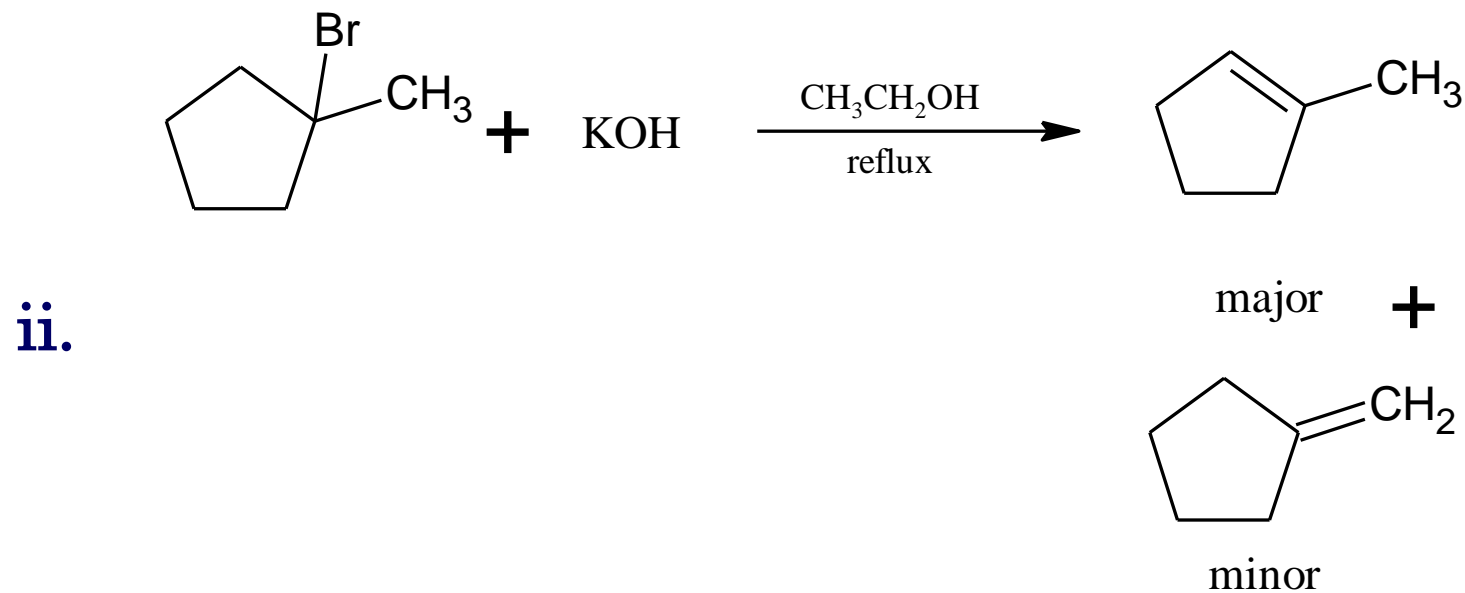
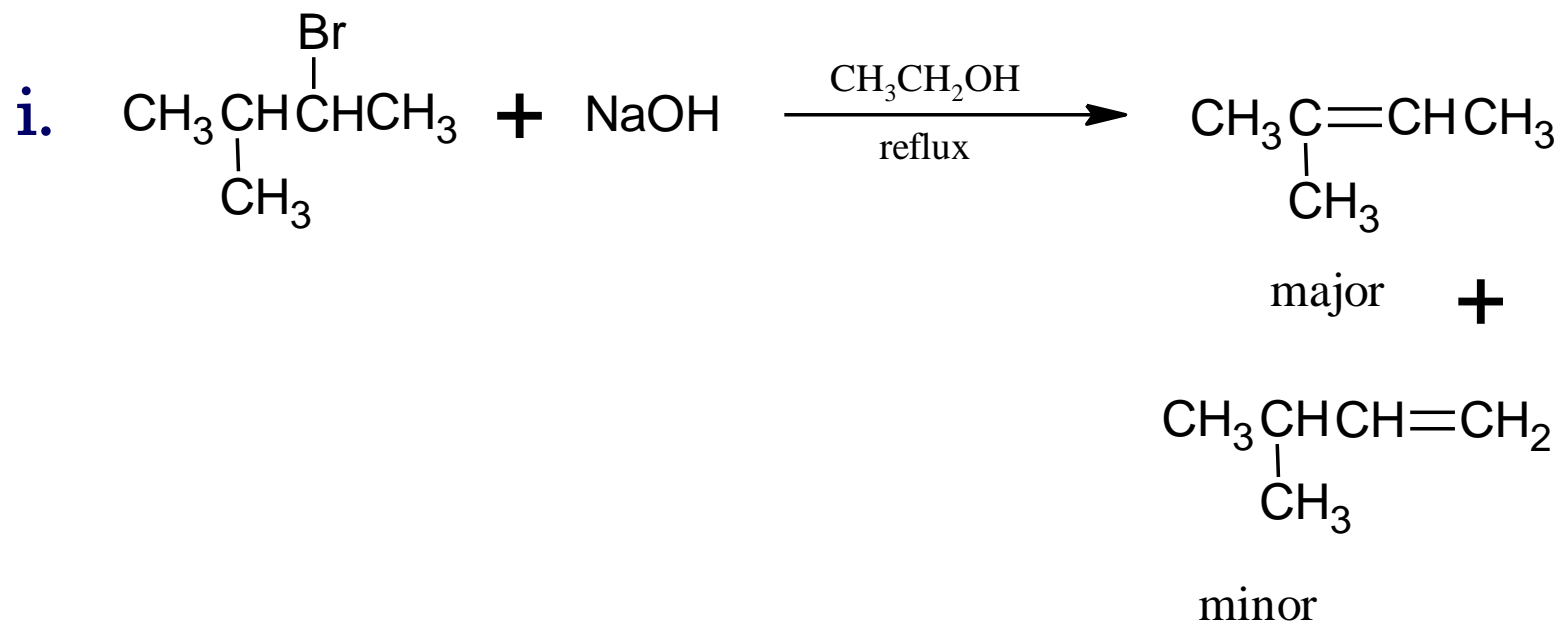
3° < 2° < 1° < Methyl halide

Strong nucleophile (usually -ve charge ion)

ELIMINATION REACTION OF HALOALKANES

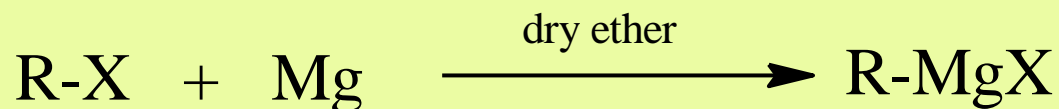
- Haloalkanes undergo **elimination** reactions with **bases** to form **alkene**.
- Name of reaction:
Dehydrohalogenation of haloalkanes



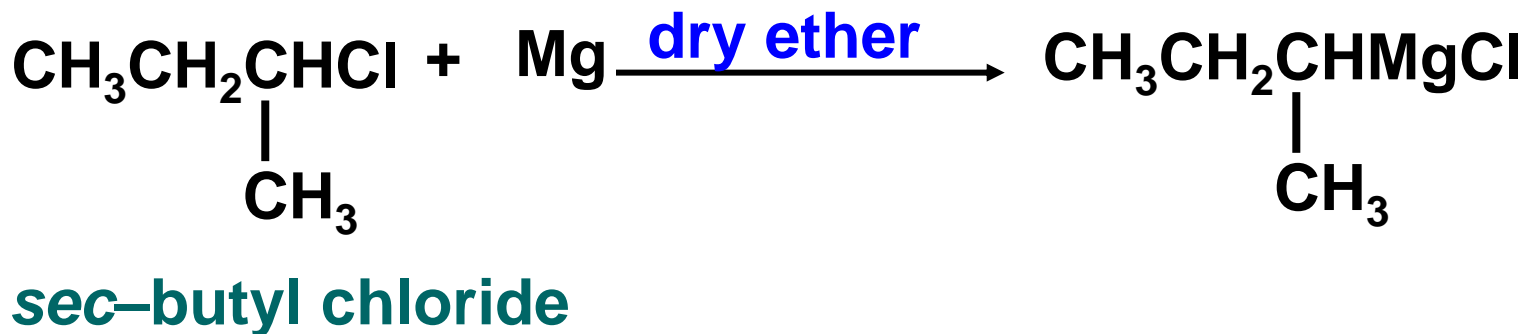
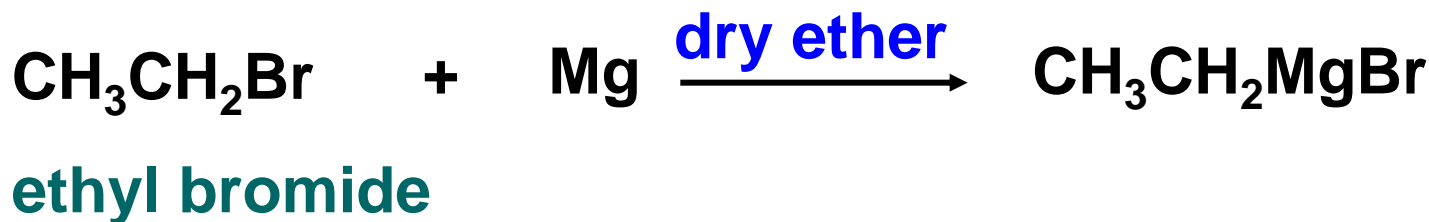
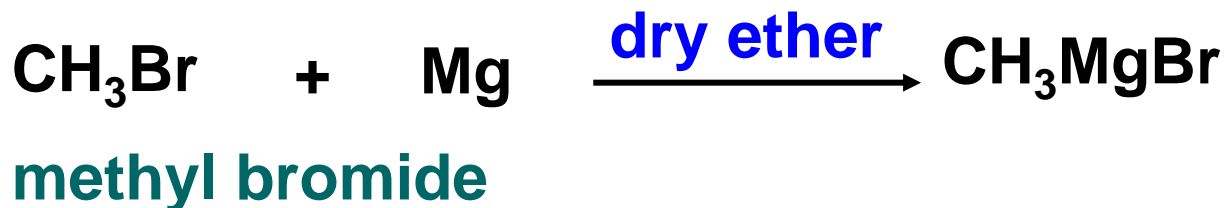


USE OF HALOALKANES IN THE SYNTHESIS OF GRIGNARD REAGENTS

- ❑ **Synthesis of Grignard Reagents (R- Mg-X)**
by the reaction of haloalkanes with
magnesium metal in anhydrous (dry) ether
as a solvent.



Grignard Reagent
(alkylmagnesium halide)



GRIGNARD REAGENTS (RMgX)

Haloalkanes (R-X) + Mg

dry ether

Grignard Reagents
(RMgX)

Uses of RMgX

$\text{H}_2\text{O}/\text{H}^+$

ALKANES

**[1] RCOR' , ether
[2] H_3O^+**

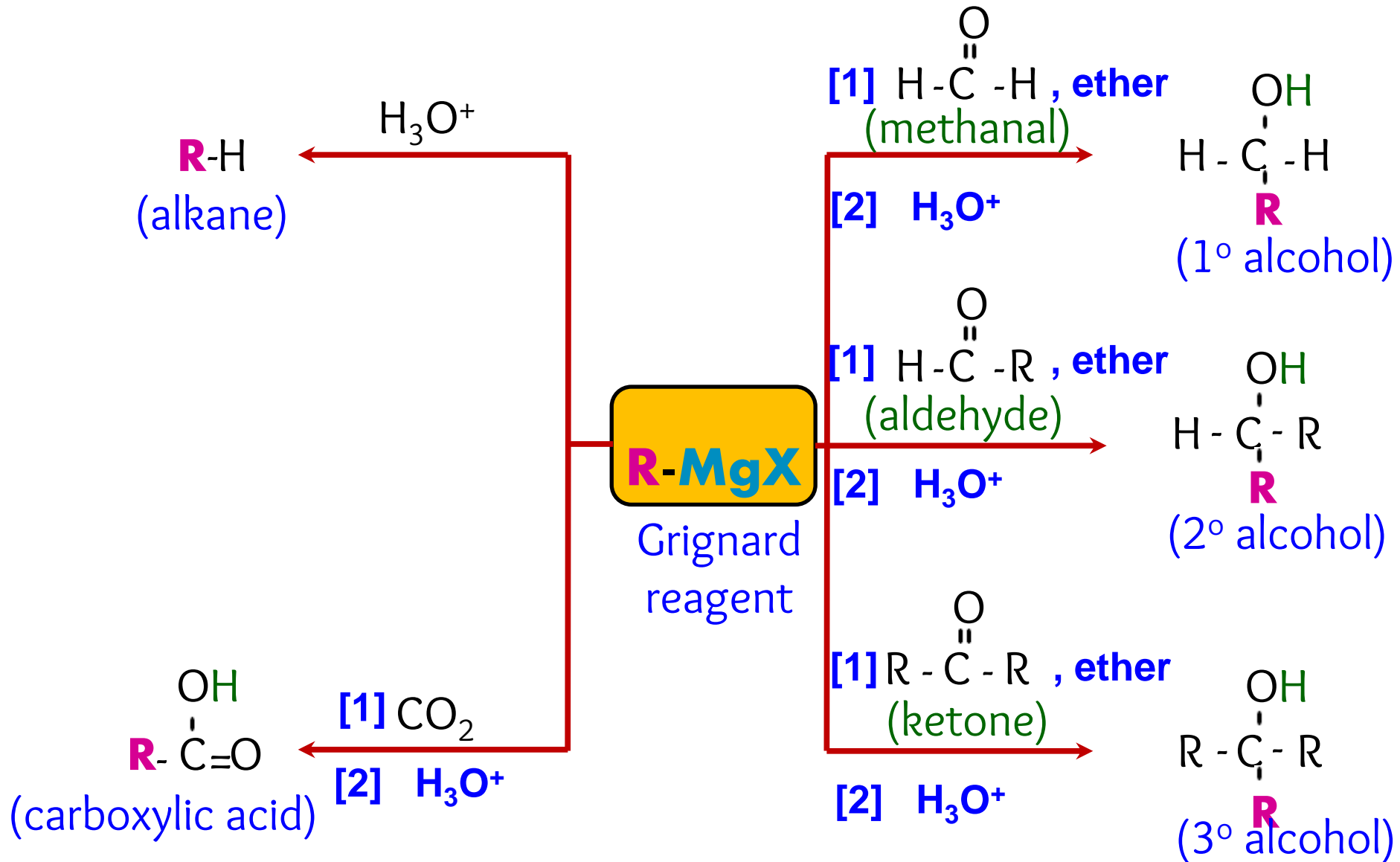
ALCOHOLS

**[1] CO_2
[2] H_3O^+**

CARBOXYLIC
ACIDS

$\text{R}' = \text{H}$ or alkyl

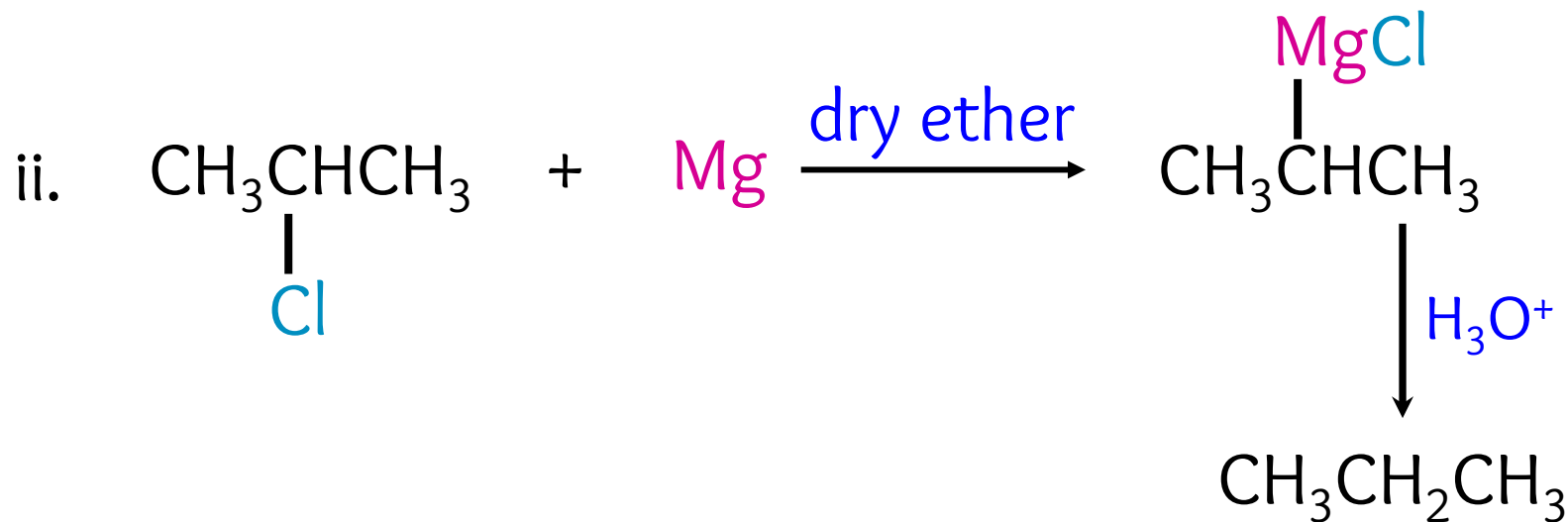
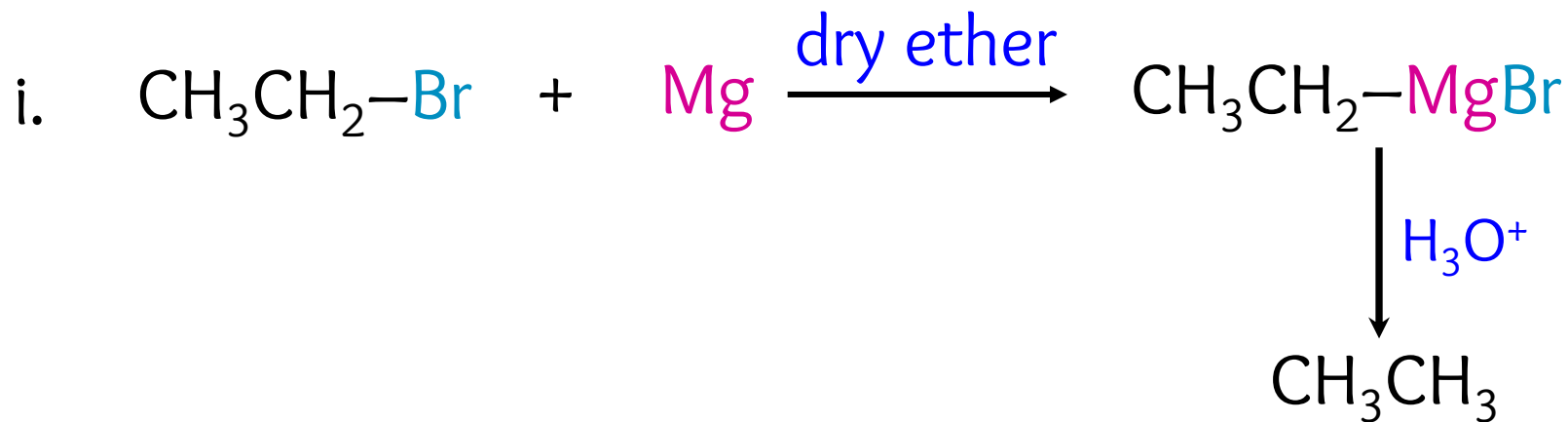
Uses of Grignard Reagent



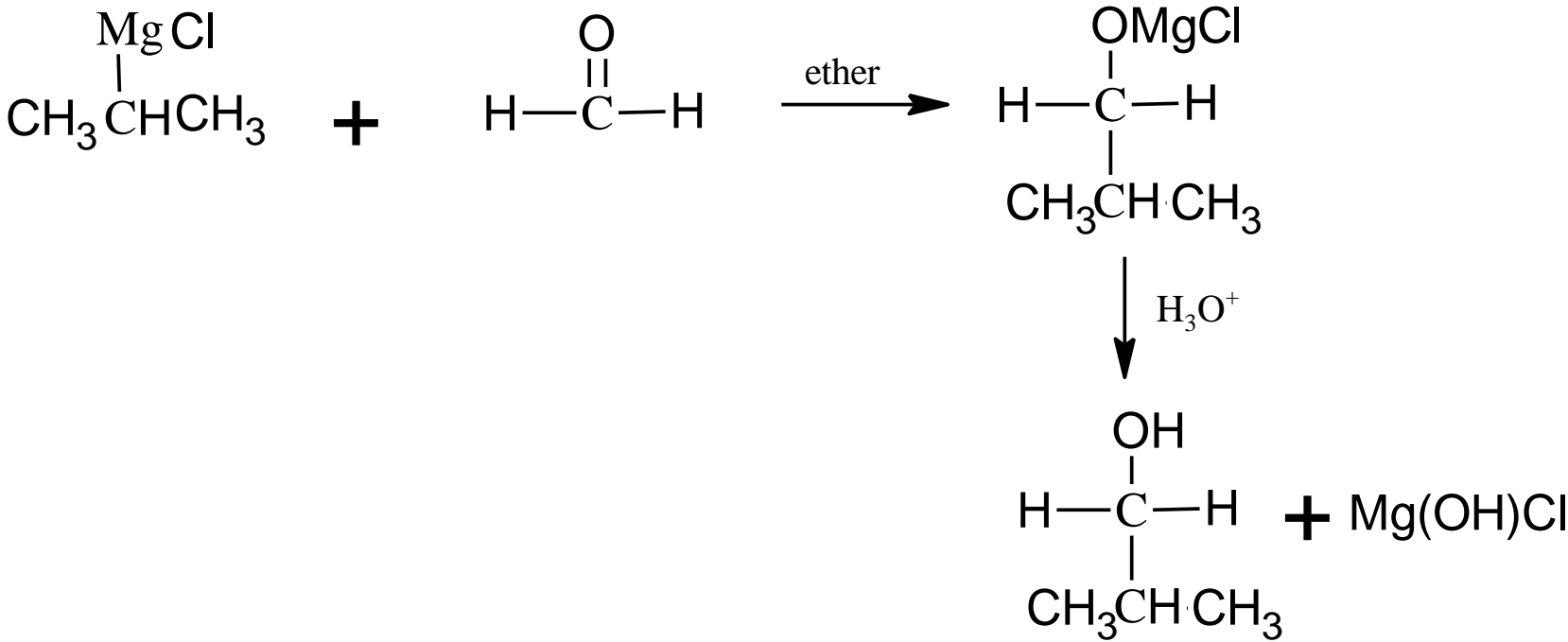
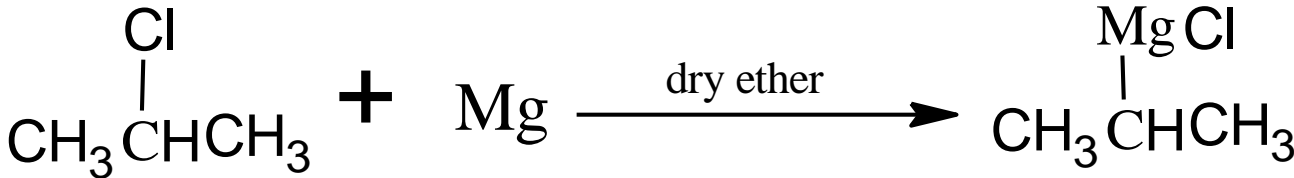
Uses of Grignard Reagent



Synthesis of Alkane



Synthesis of 1° Alcohol

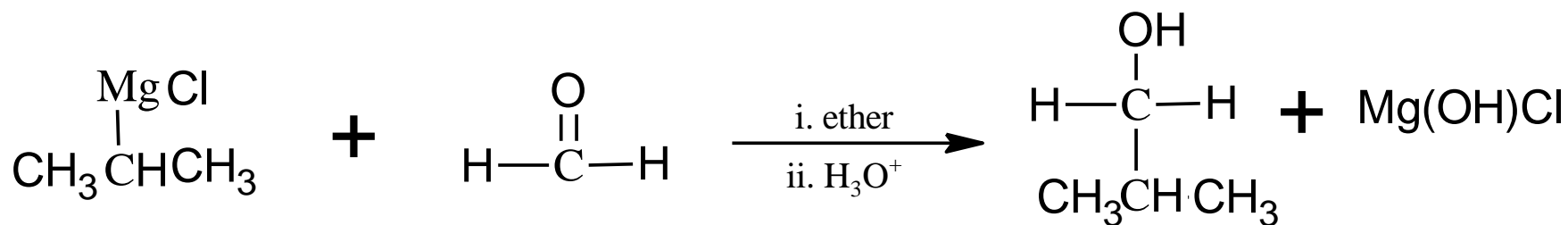


Uses of Grignard Reagent



Synthesis of 1° Alcohol

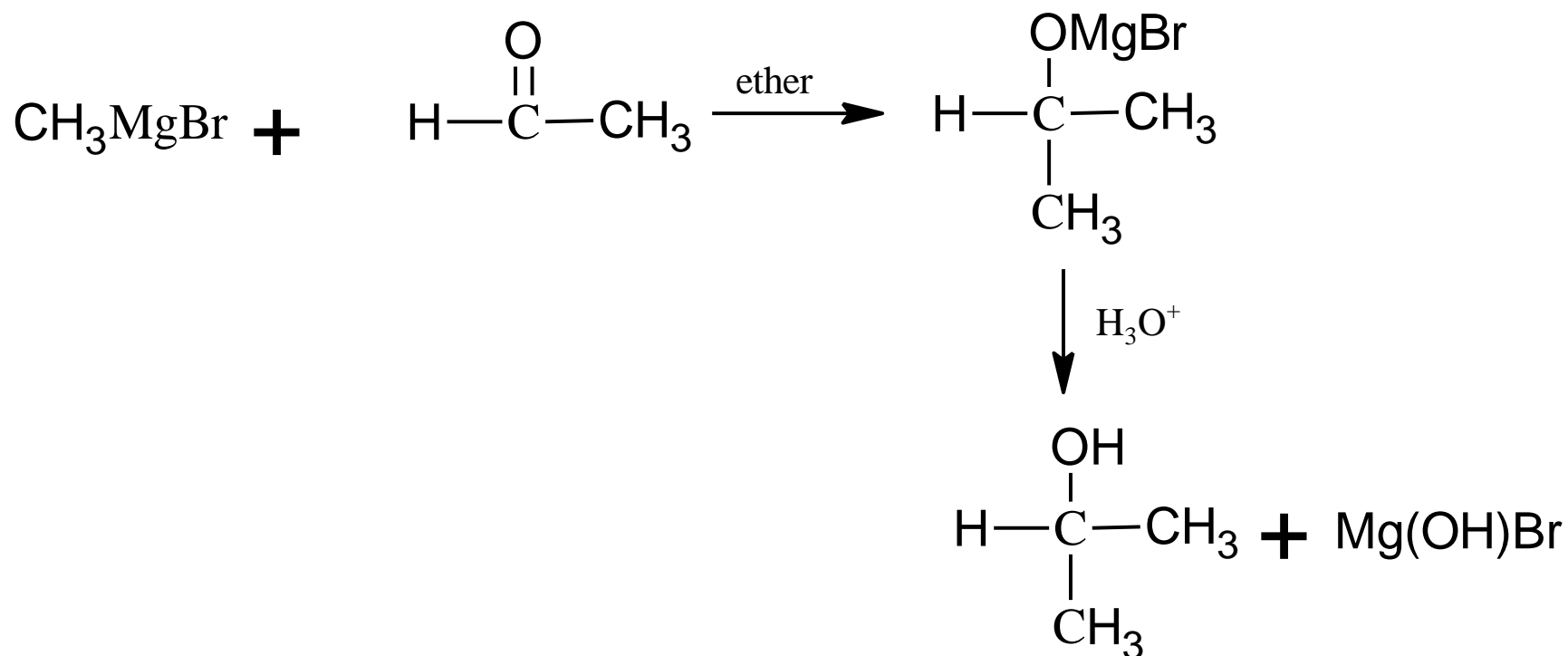
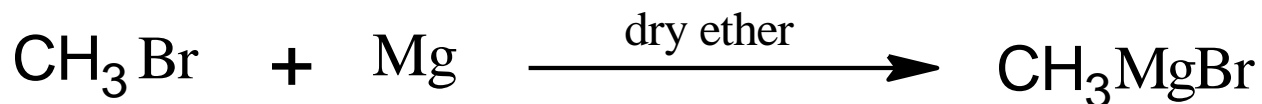
or



Uses of Grignard Reagent



Synthesis of 2° Alcohol

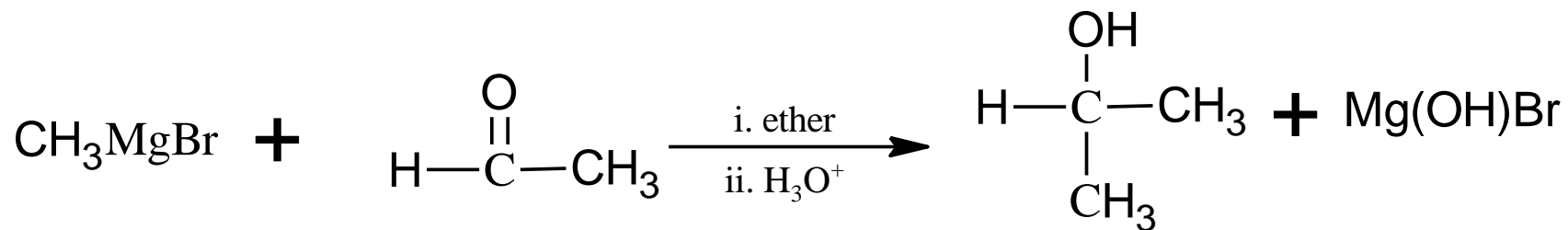


Uses of Grignard Reagent



Synthesis of 2° Alcohol

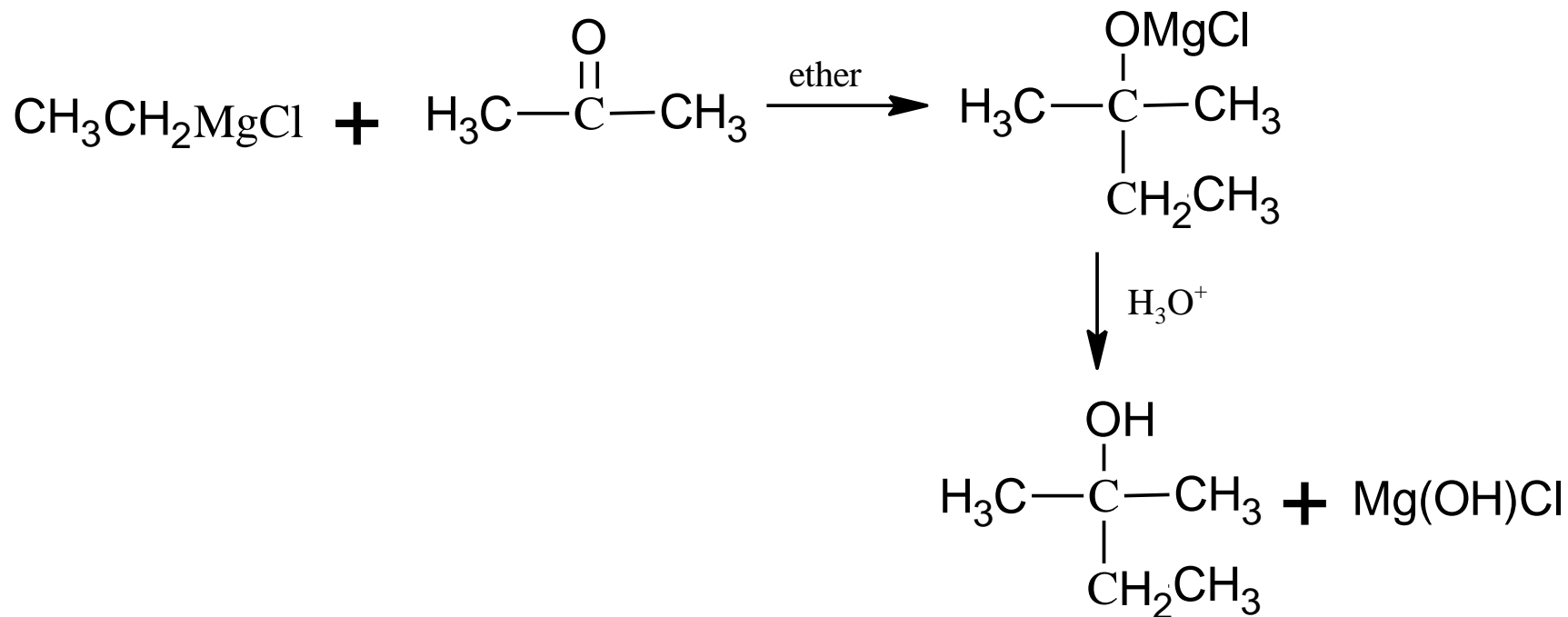
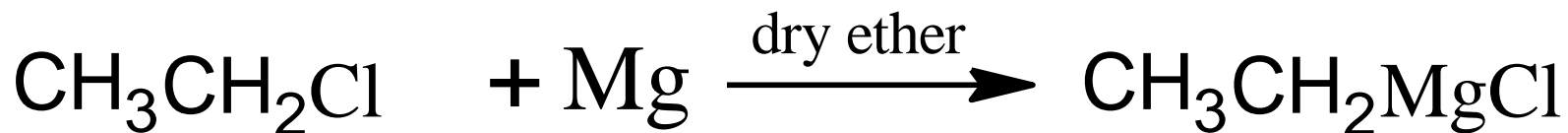
or



Uses of Grignard Reagent



Synthesis of 3° Alcohol

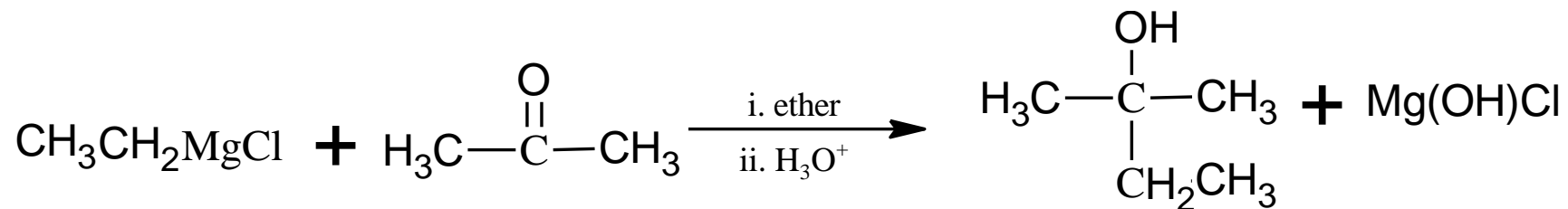


Uses of Grignard Reagent



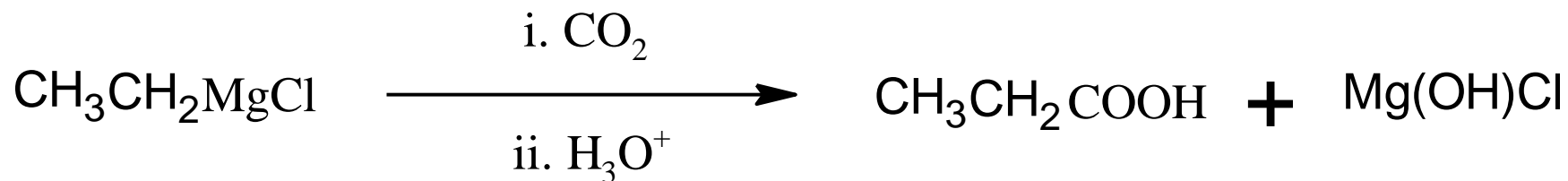
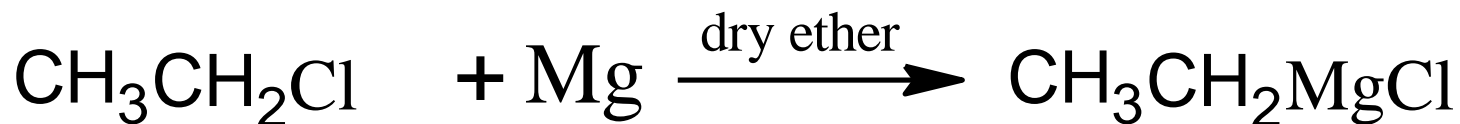
Synthesis of 3° Alcohol

or





Synthesis of Carboxylic Acid



GLOSSARY

1. **Haloalkanes** – organic compound contains halogen atom, (fluorine, chlorine, etc.) bonded to sp^3 hybridized C atom. Also known as alkyl halides.
2. **Electrophilic site** – electron-deficient site in the molecule and susceptible to nucleophilic attack.
3. **Leaving group** – an atom or group of atoms that detaches from the main or residual part of a substrate during a reaction or elementary step of a reaction.
4. **S_N1** – Unimolecular Nucleophilic Substitution Reaction – The first step involves only one molecule (haloalkane)

GLOSSARY

5. **S_N2** - Bimolecular Nucleophilic Substitution Reaction - The reaction involves two molecules (Haloalkane & Nucleophile)
6. **Transition state** – a configuration attended by reactants during complex formation along with the reaction coordinates where maximum potential energy is attained. It is often marked with the double dagger ‡ symbol.
7. **Steric hindrance** – the prevention or retardation of inter- or intramolecular interactions because of the spatial structure of a molecule.
8. **Steric effect** – is an effect on relative rates caused by the space-filling properties of parts of molecules attached at or near the reacting site.