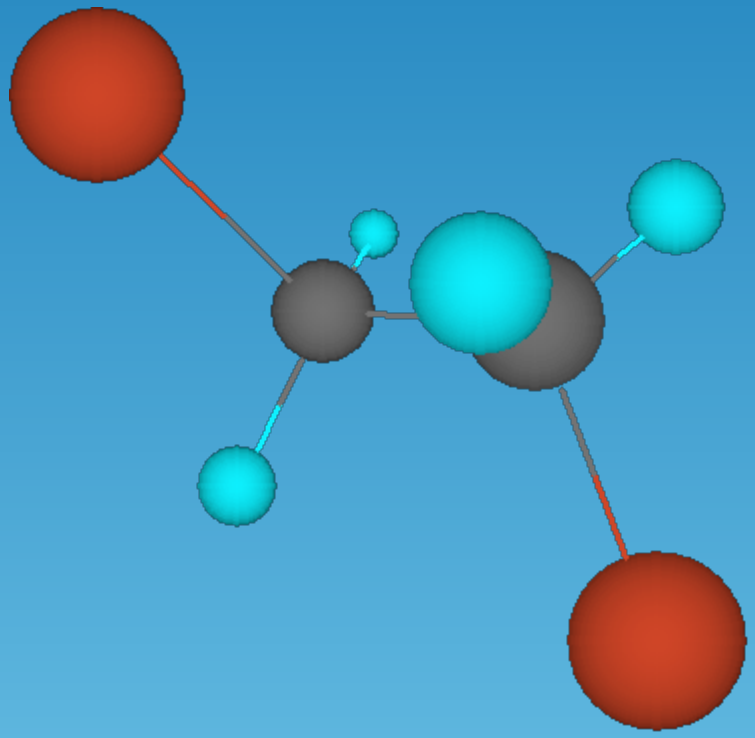
ALKYL HALIDES



ALKYL HALIDES (Organohalides)

- Alkyl halides are halogen-substituted organic compounds.
- An organic compound containing at least one carbon-halogen bond (C-X).
- X=(F, Cl, Br, I) replaces H.
- Can contain many C-X bonds.

Example: CH_3Cl (Chloromethane)

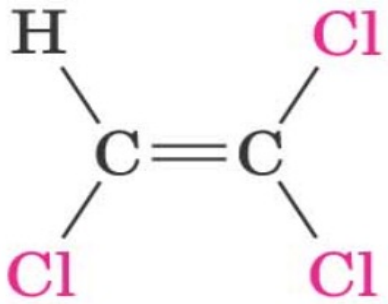
CCl_4 (Tetra chloromethane)

Organohalides are useful as,

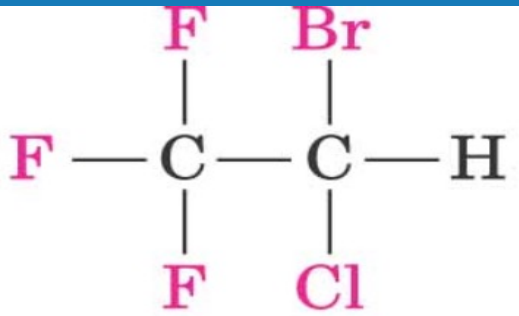
- Solvents.($CHCl=CCl_2$)
- Inhaled anesthetics. Eg. Haloethane ($CF_3CHBrCl$)
- Refrigerants.(CF_2CCl_2)
- Pesticides

The modern electronic industry relies on trichloroethylene for cleaning semiconductor chips.

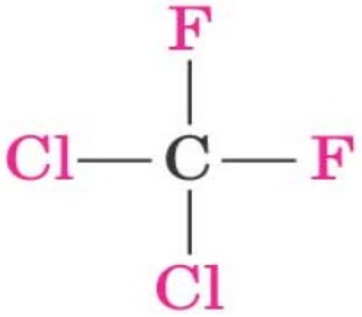
Examples of Alkyl Halides



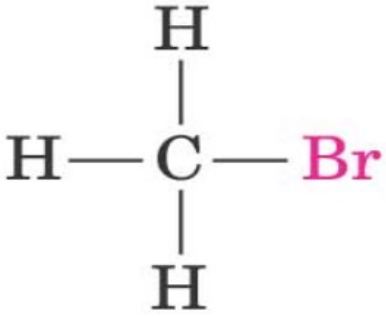
Trichloroethylene
(a solvent)



Halothane
(an inhaled anesthetic)



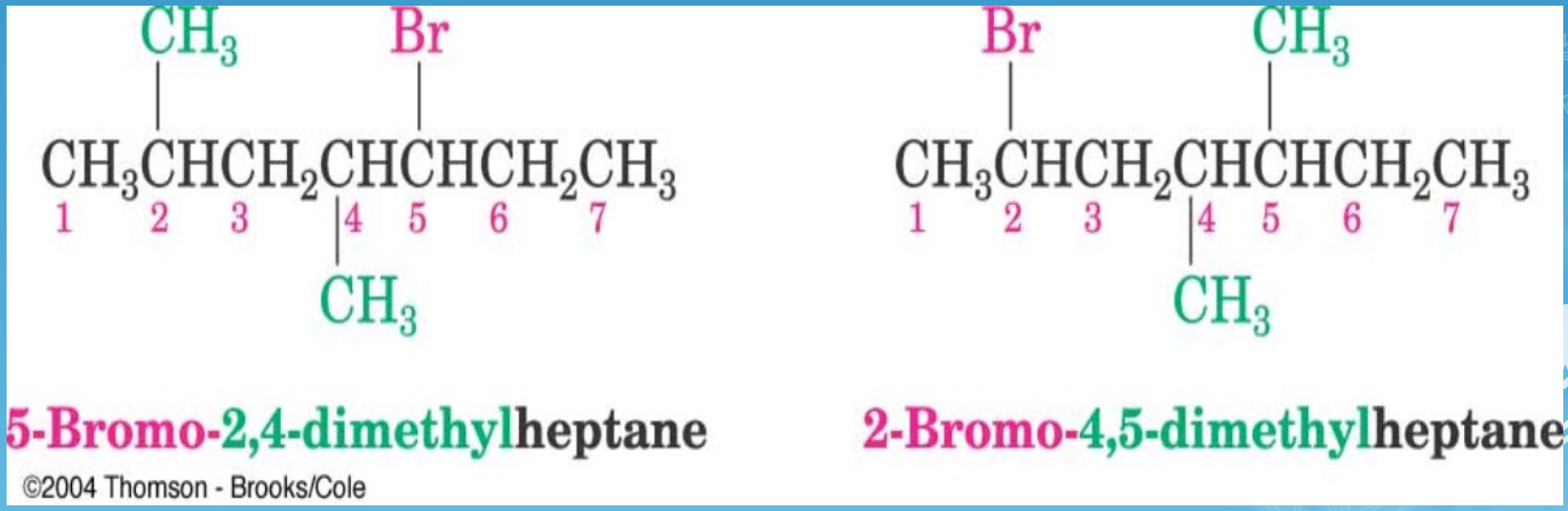
Dichlorodifluoromethane
(a refrigerant)



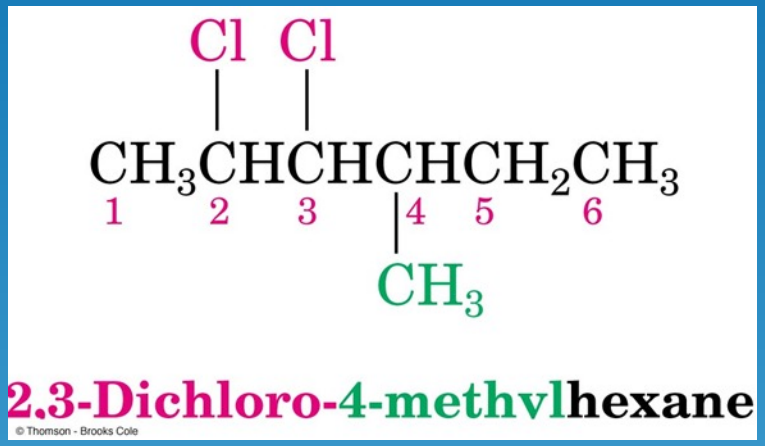
Bromomethane
(a fumigant)

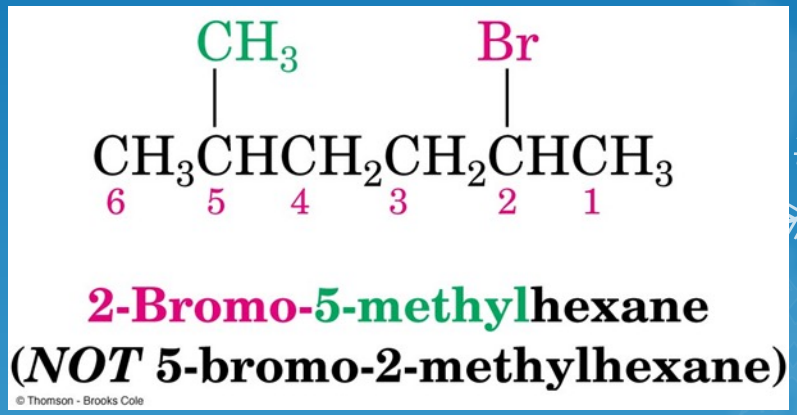
Nomenclature of Alkyl Halides

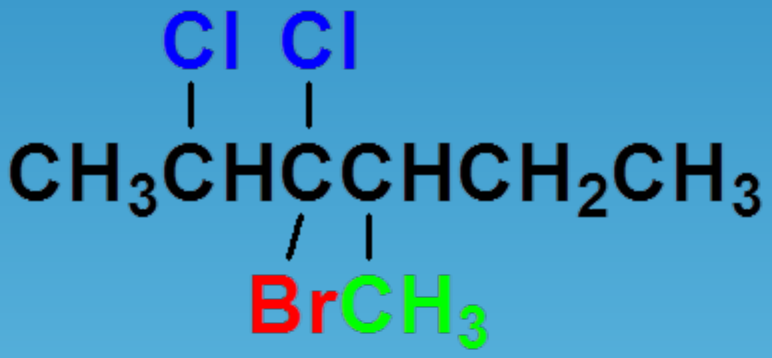
- Find the longest chain, and name the parent chain.
- Number the carbons of the parent chain beginning at the end nearer the first substituent, regardless of whether it is a alkyl or halo.
- List all the substituents in alphabetical order.
- If more than one of the same substituent is present, use the prefixes di, tri,tetra, etc.



Examples



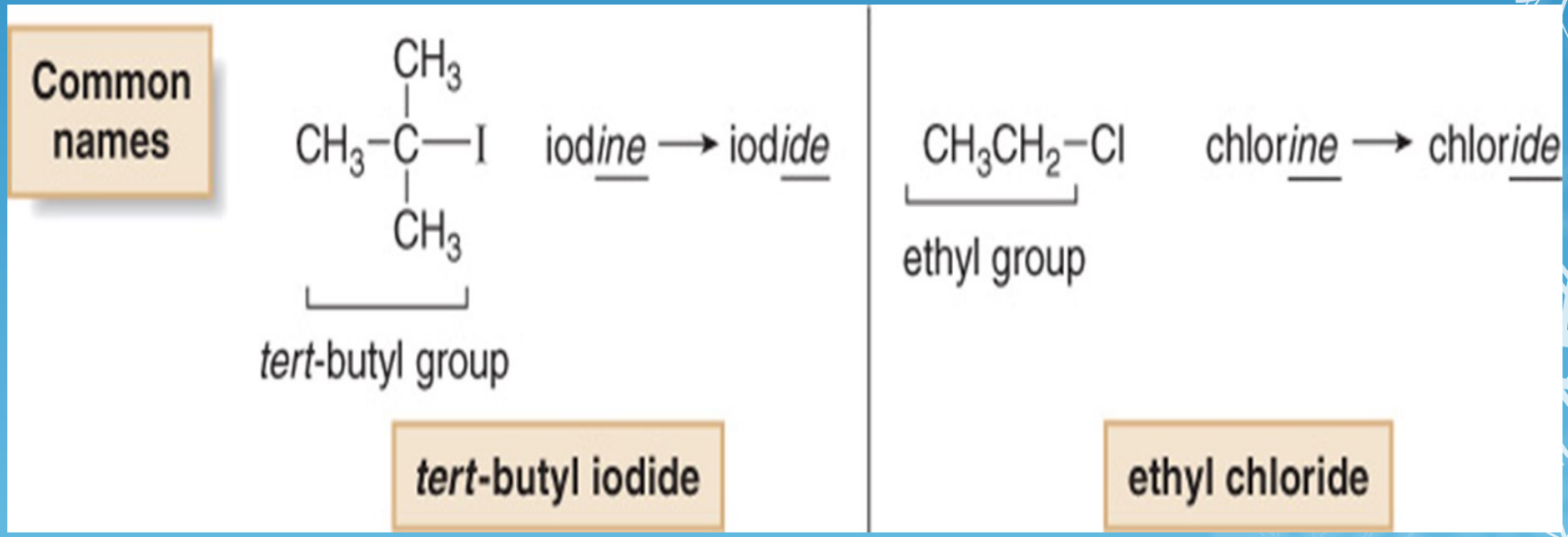




3-bromo-2,3-dichloro-4-methylhexane

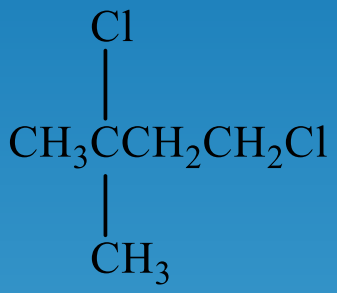
Common Names of Alkyl Halides

- Common names are often used for simple alkyl halides. To assign a common name:
- Name all the carbon atoms of the molecule as a single alkyl group.
- Name the halogen bonded to the alkyl group.
- Combine the names of the alkyl group and halide, separating the words with a space.

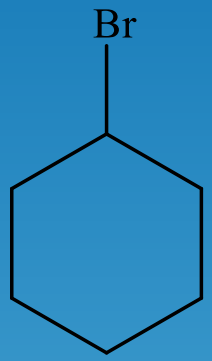


Practice Problems

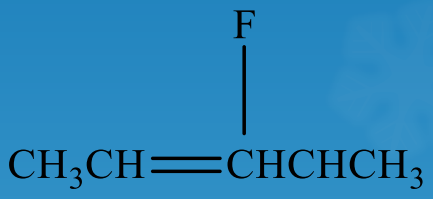
1. Write the Correct IUPAC name of the following organic compounds.



a



b



c

2. Draw the structures to the following IUPAC names.

a. 2,3-Dichloro-4-methylhexane.

b. 4-Bromo-4-ethyl-2-methylhexane.

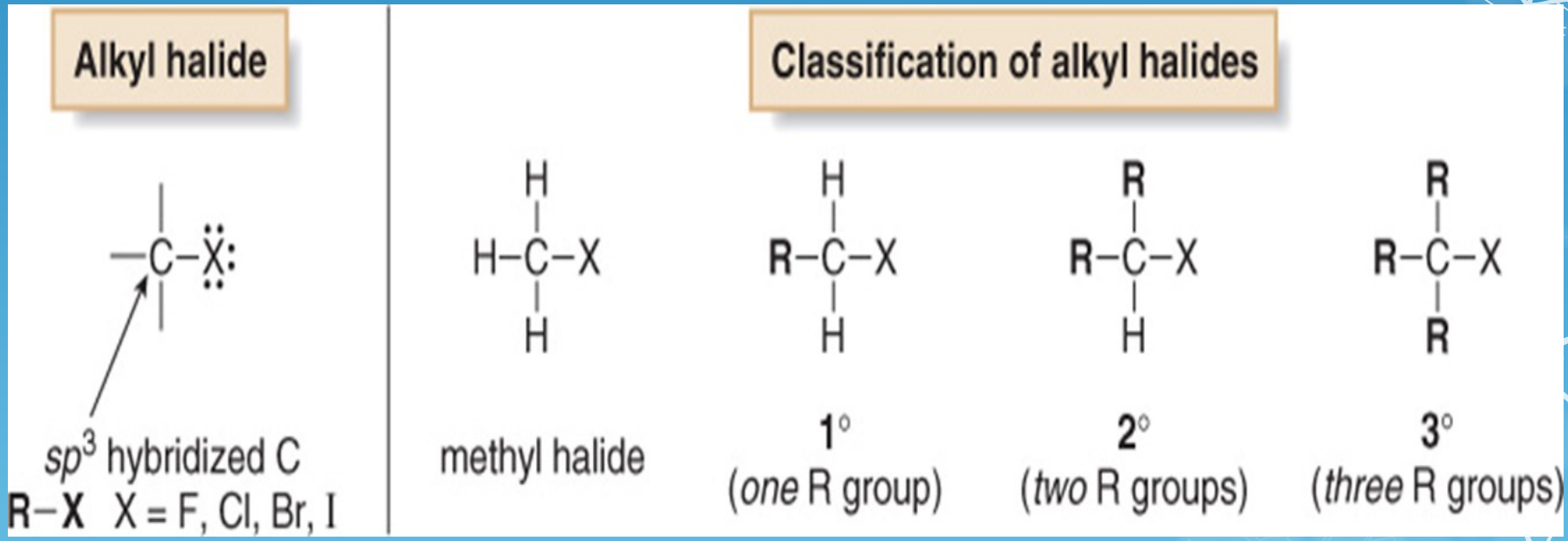
c. 3-Iodo-2,2,4,4-tetramethy;pentane.

d. Bromocyclohexane.

e. 1-Chloro-1-methylcyclopentane.

Alkyl Halides

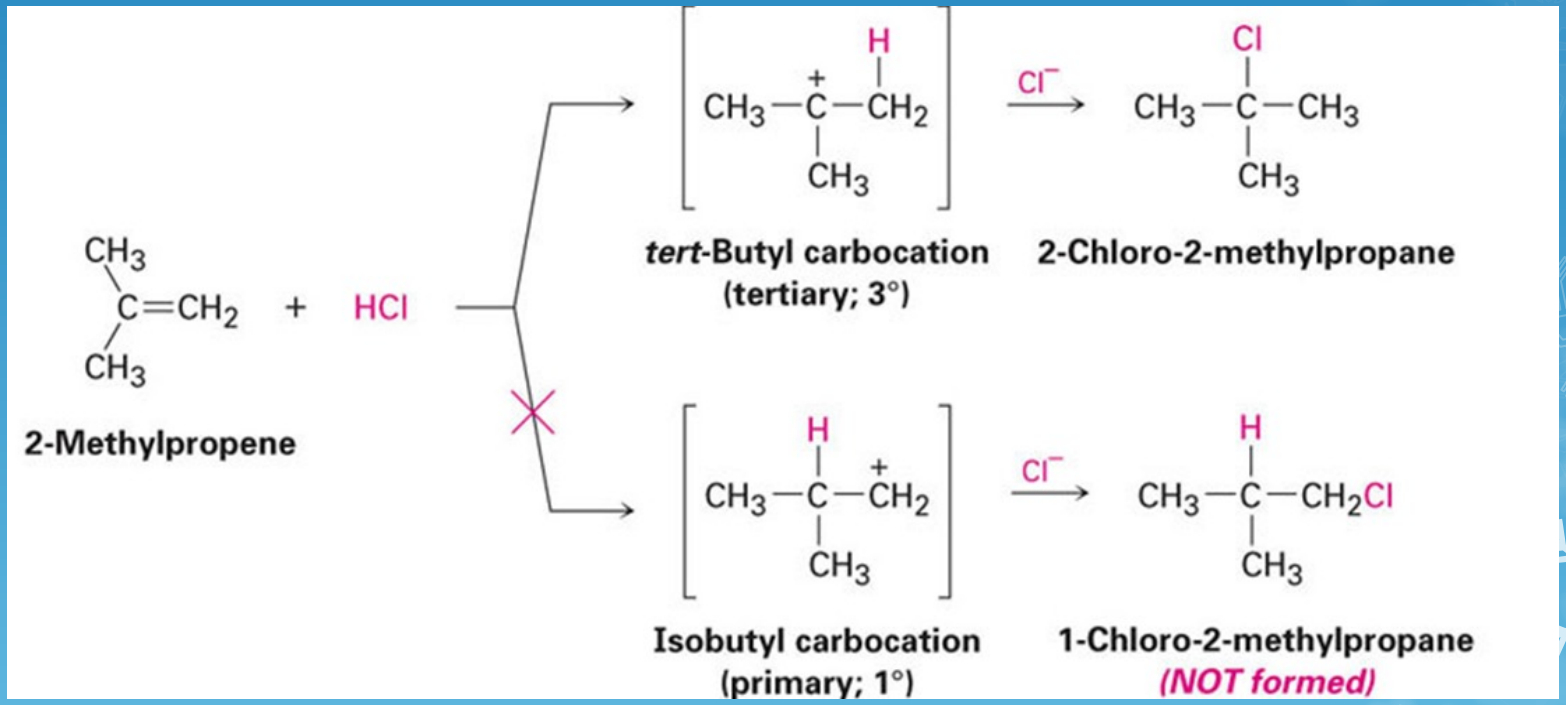
- Alkyl halides are organic molecules containing a halogen atom bonded to an sp^3 hybridized carbon atom.
- Alkyl halides are classified as primary (1°), secondary (2°), or tertiary (3°), depending on the number of carbons bonded to the carbon with the halogen atom.



Preparation of Alkyl Halides

Preparation of alkyl halides from Alkenes:

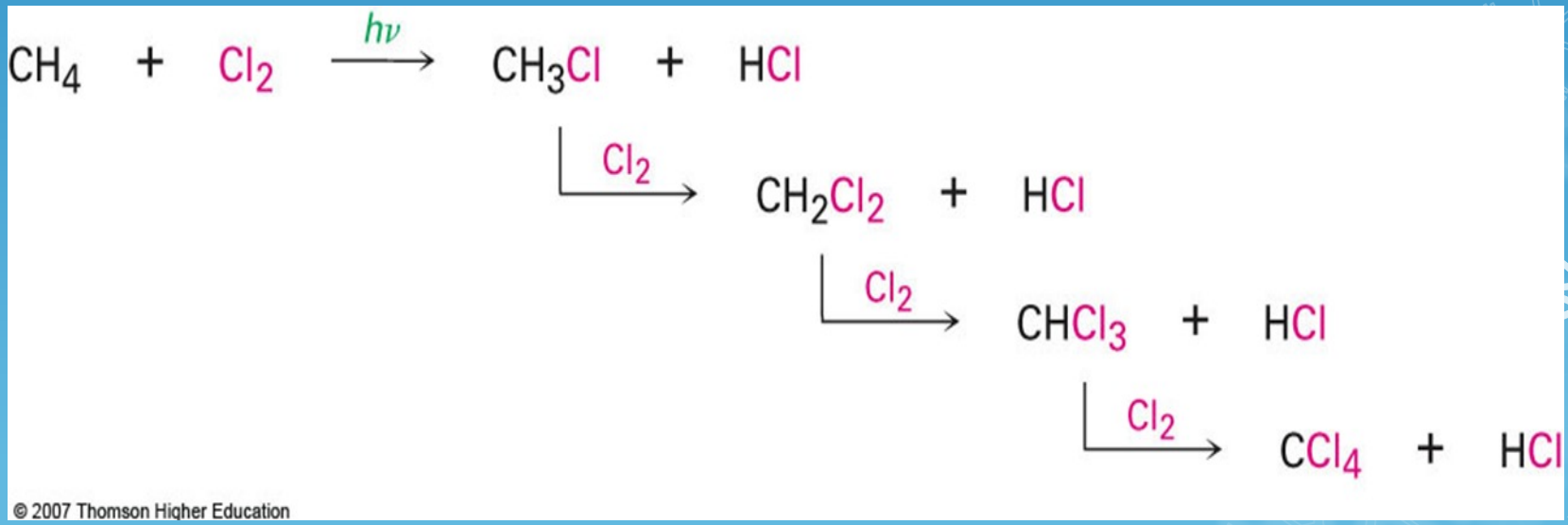
Alkyl halide from addition of HCl, HBr, HI to alkenes to give Markovnikov's product (see Alkenes chapter).



Preparation of Alkyl Halides

Preparation of alkyl halides from alkanes:

- Alkanes react with Cl_2 in presence of heat or light to form mixture of chlorinated products. [C-H replaces with C-X]
- Hard to control.
- Via free radical mechanism.
- It is usually not a good idea to plan a synthesis that uses this method [multiple products].

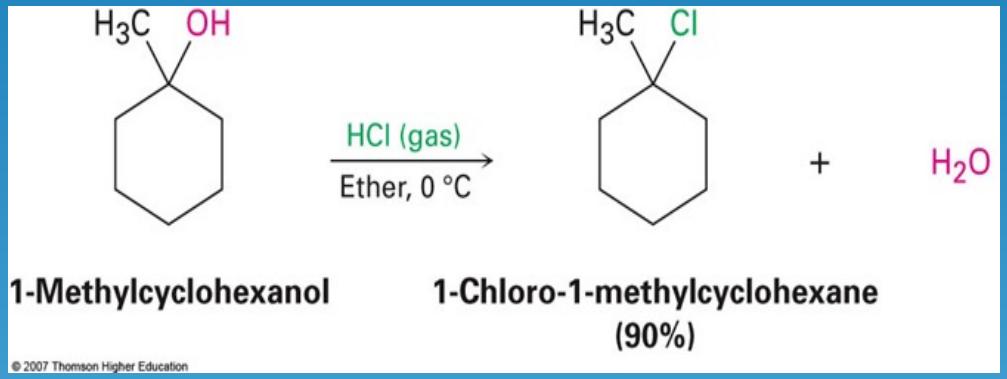


Preparation of Alkyl Halides

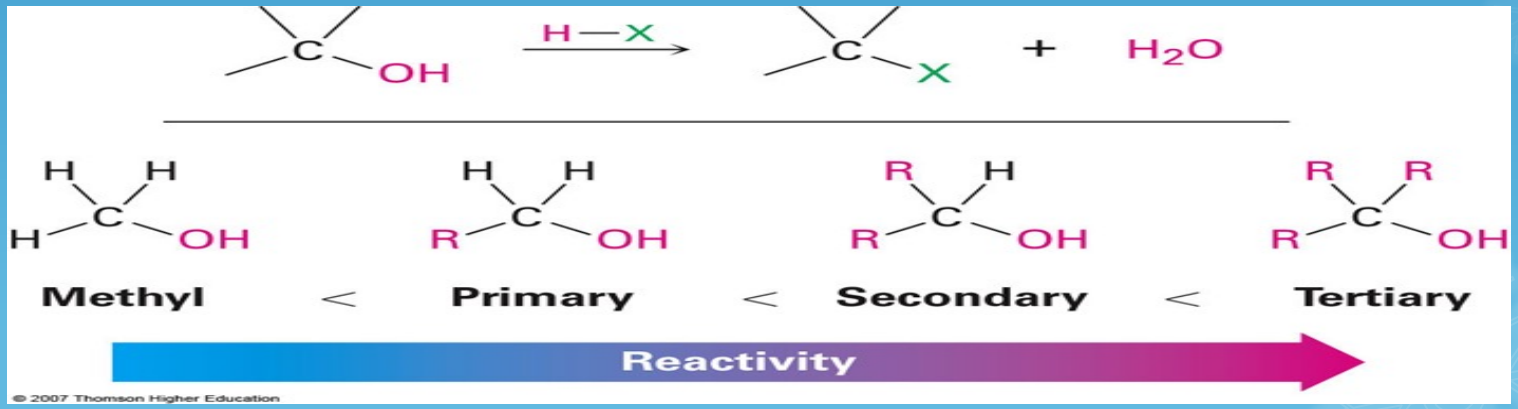
Preparation of alkyl halides from alcohols:

Alcohols react with hydrogen halides to form alkyl halides.

Example:

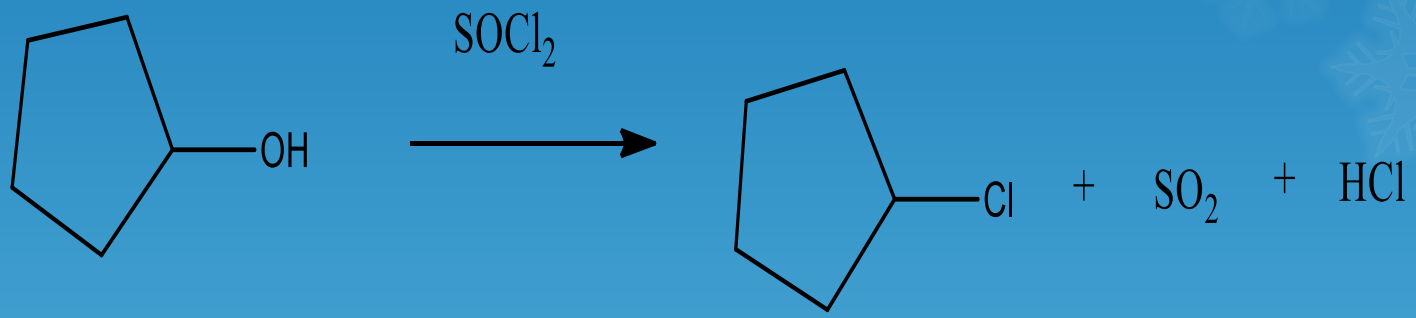


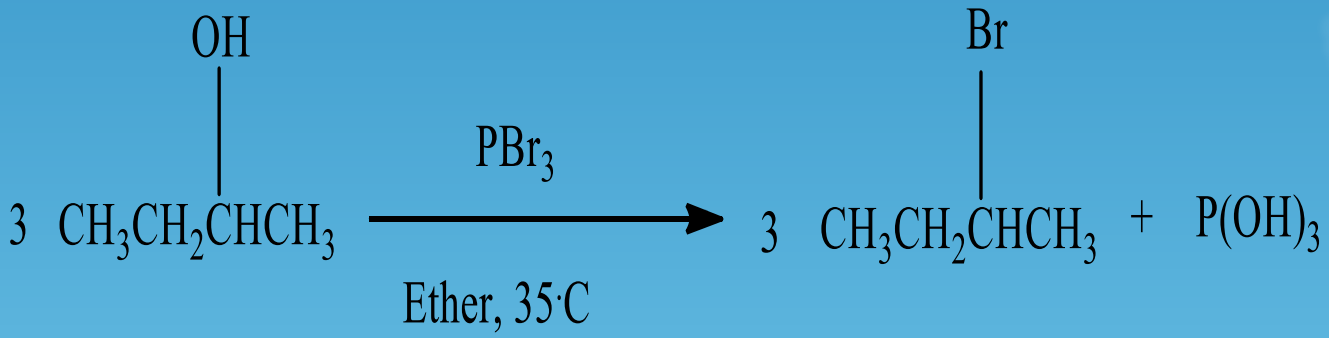
- But the reaction works better with tertiary alcohols.
- Primary and secondary alcohols react much more slowly.



Preparation of Alkyl Halides

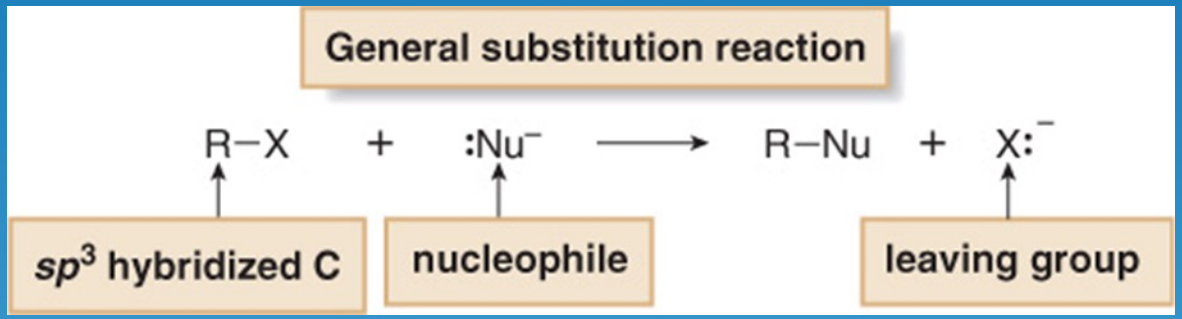
Primary and secondary alcohols react very slowly and often rearrange, so alternative methods are used: $SOCl_2$ or PBr_3 .

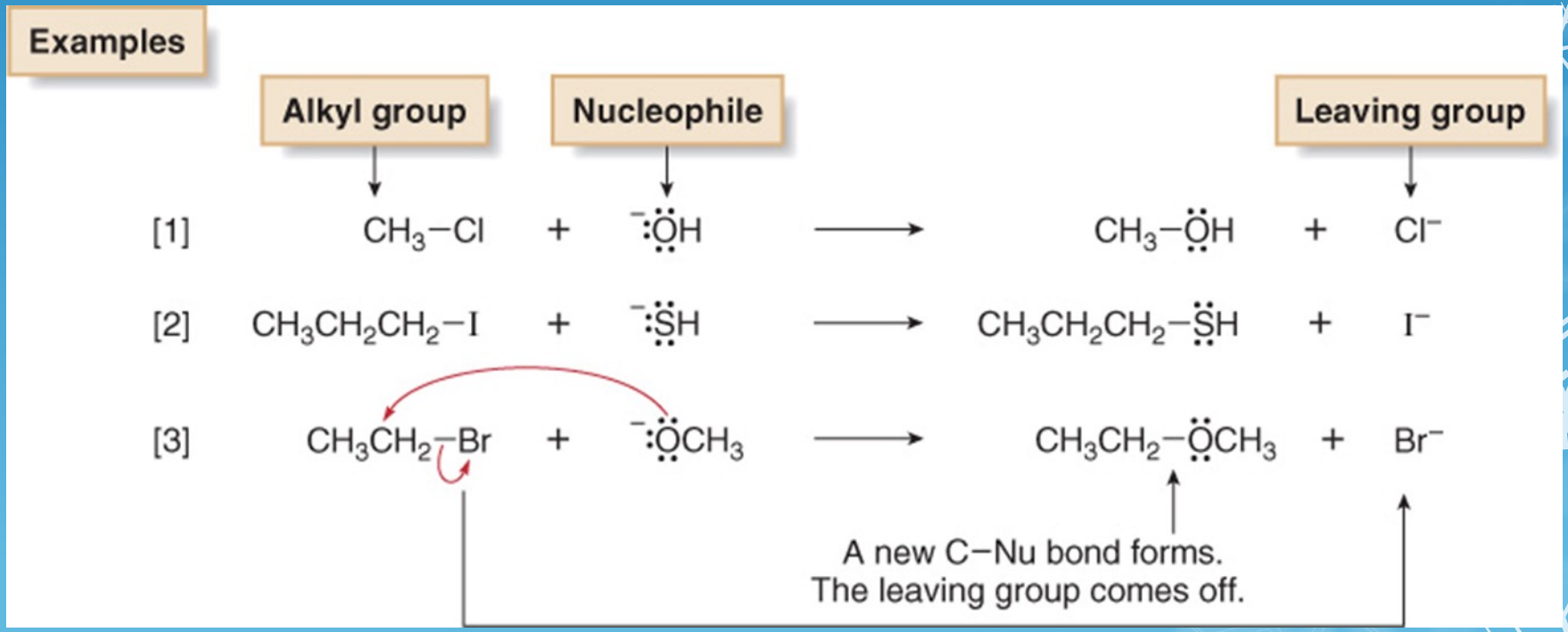




Nucleophilic Substitution Reactions

General Features of Nucleophilic Substitution.





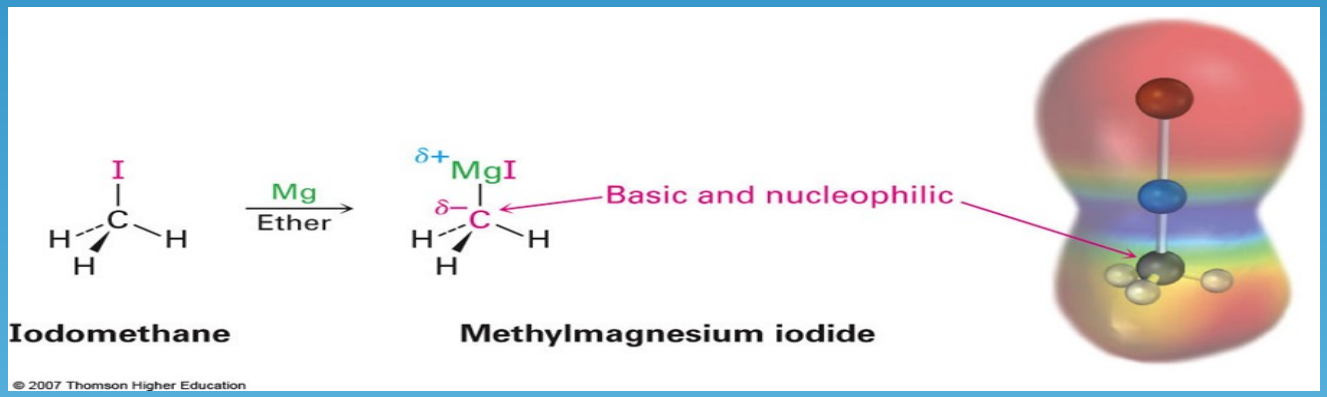
Reactions of Alkyl Halides

Alkyl Halides react with magnesium metal in ether solvent to yield organo-magnesium halides, called Grignard reagents.

$$R\text{-}X + Mg \longrightarrow R\text{-}Mg\text{-}X$$

where R= 1°,2°,3° alkyl, aryl or alkenyl.

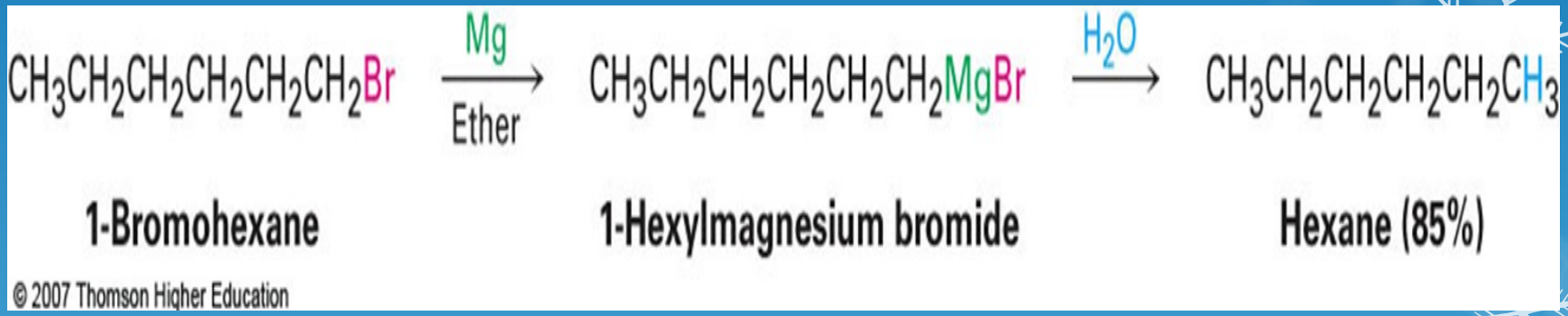
X=Cl, Br or I

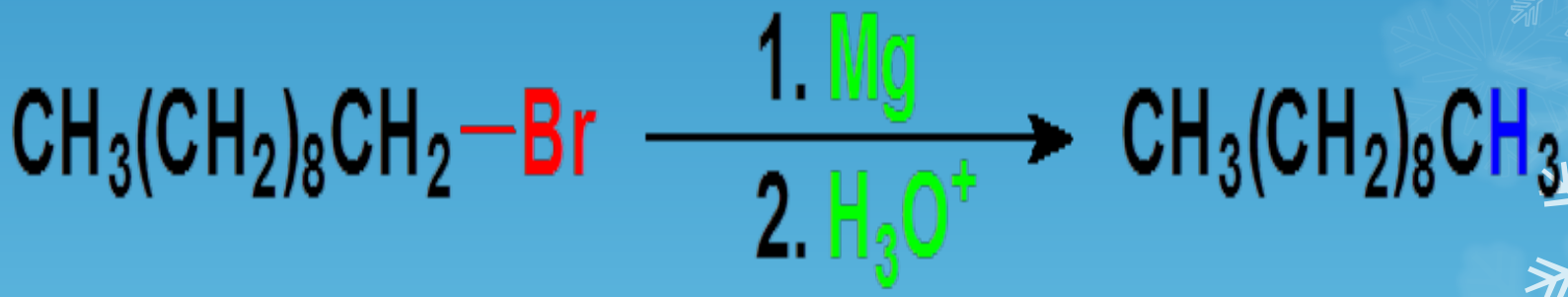


Because of the strongly polarized carbon-magnesium bond, organomagnesium halides react with acids or electrophiles to yield hydrocarbons.

Grignard Reagents

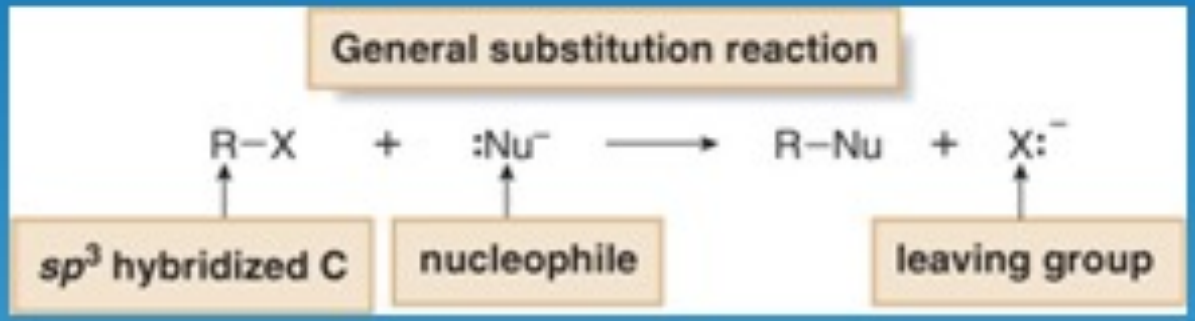
Conversion of organic halide to a hydrocarbon.

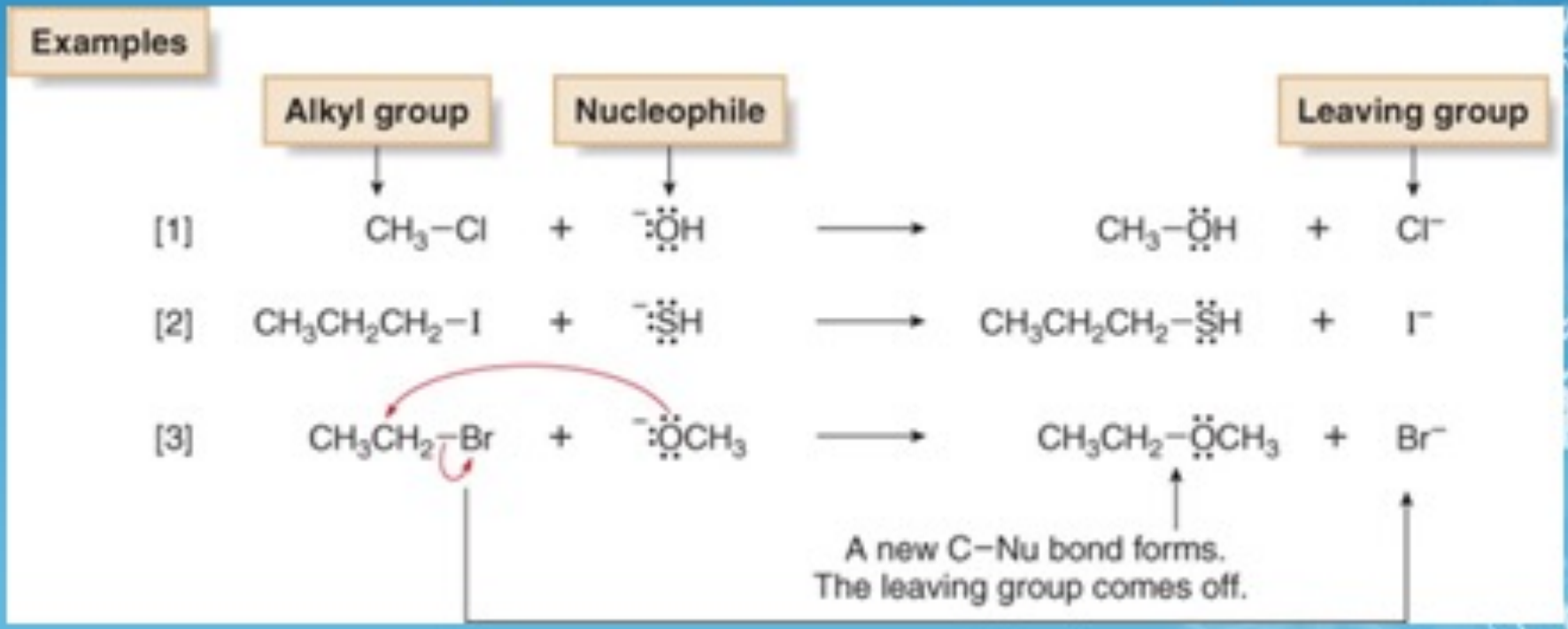




Nucleophilic Substitution Reactions

- General Features of Nucleophilic Substitution





S_N Reactions

There are 2 types of nucleophilic substitution reactions, S_N1 and S_N2 reactions.

S_N 2 reaction - 2nd Order Nucleophilic Substitution Reactions.

Bimolecular reaction: a reaction in which two reactants are involved in the rate-limiting step.

1. Bond breaking and bond forming occur simultaneously.

2. Departure of the leaving group is assisted by the incoming nucleophile.

3. Reaction is with inversion at reacting center.

The mechanism is designated S_N2 where;

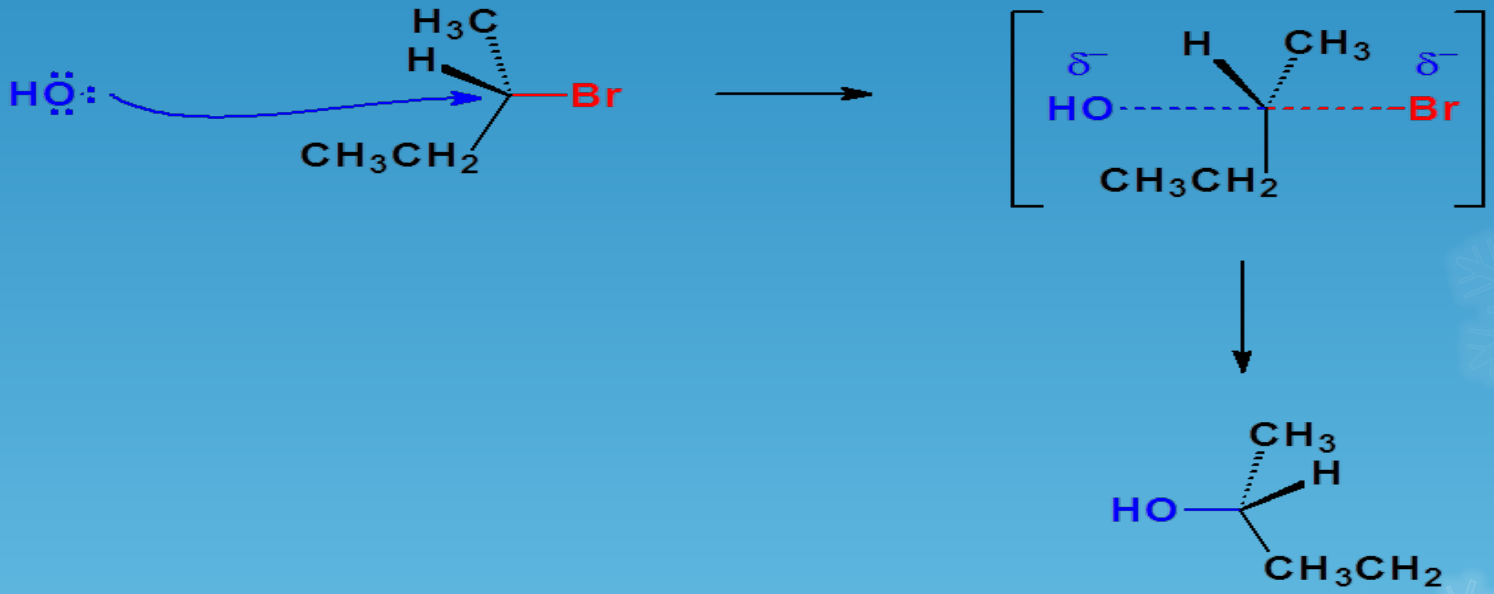
S = substitution.

N = nucleophilic.

2 = bimolecular.

S_N2 Mechanism

- Reaction takes place in one step.
- Incoming nucleophile attacks side opposite the leaving group.
- The product formed is with inversion.
- The order of reactivity tert-alkyl halides<sec-alkyl halides<primary alkyl halides<methyl halides, i.e. methyl halides (CH_3X) are more reactive).



S_N1 Reaction

- 1st Order Nucleophilic Substitution Reactions, i.e., S_N1 reactions.
- Bond breaking between carbon and the leaving group is entirely completed before bond forming with the nucleophile begins.
- Two distinct steps.

This mechanism is designated S_N1 where:

S = substitution.

N = nucleophilic.

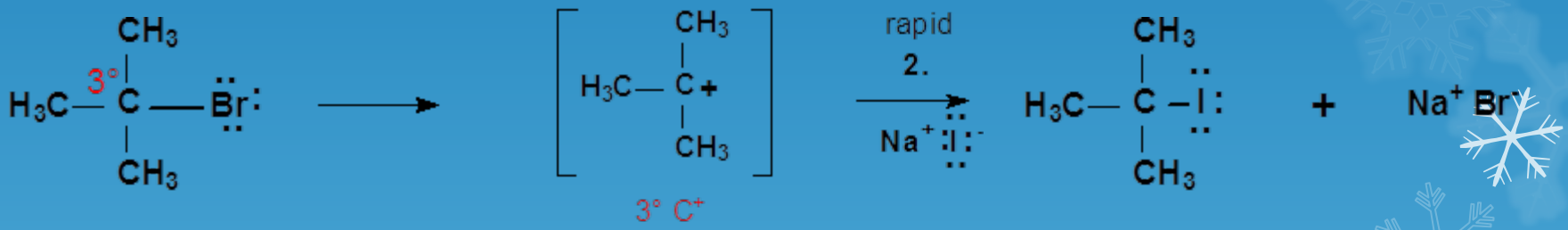
1 = unimolecular.

Unimolecular reaction: a reaction in which only one species is involved in the rate-limiting step.

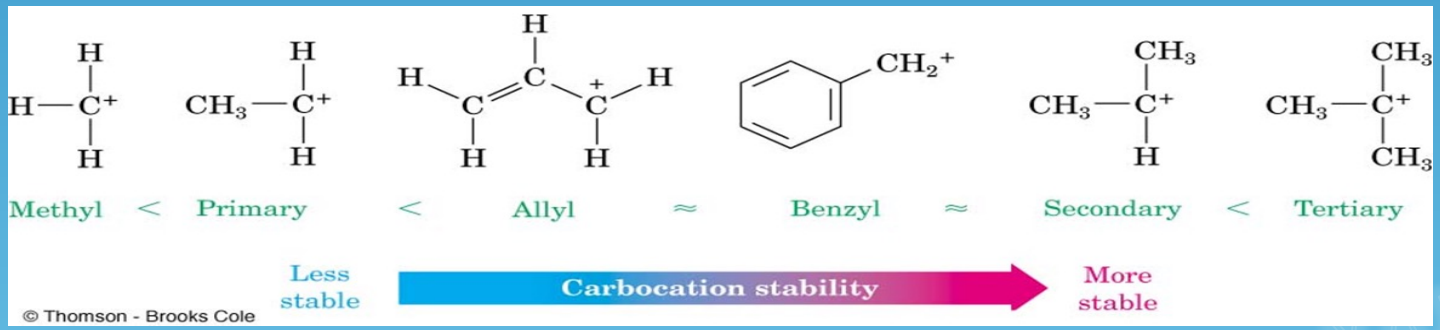
S_N1 Mechanism

Reaction Steps …

- the slower, rate-limiting dissociation of the alkyl halide forming a C+ intermediate.
- a rapid nucleophilic attack on the $(CH_3)_3C+$



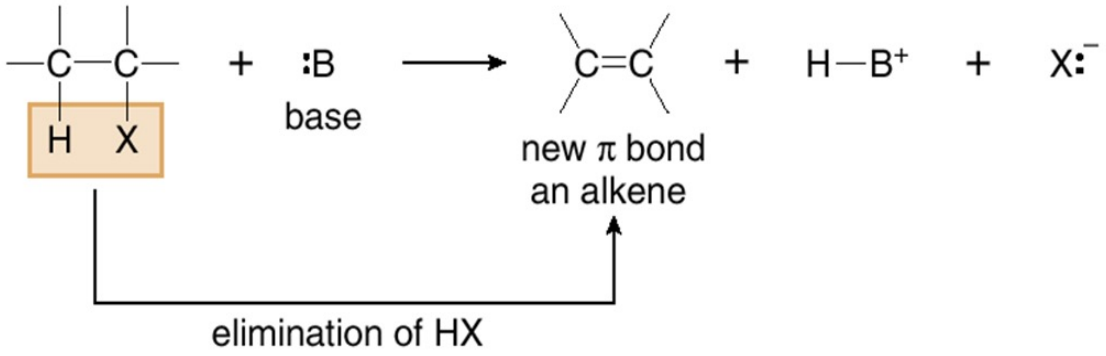
Tertiary alkyl halide is most reactive by this mechanism.



Elimination Reactions

- The 2 types of elimination reactions are E_1 reaction and E_2 reaction.
- Elimination reaction of alkyl halides results in the formation of alkenes.

- Alkyl halides undergo elimination reactions with Brønsted–Lowry bases.

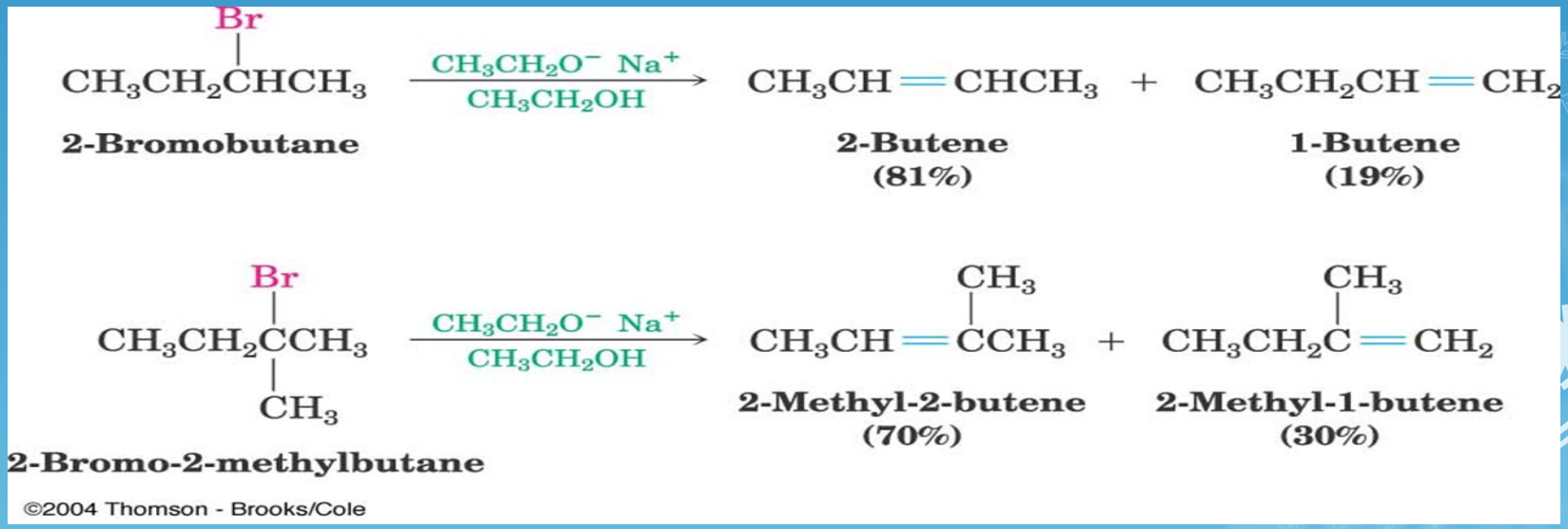


E_2 Reaction

- In the elimination of HX from an alkyl halide, the more highly substituted alkene product predominates .
- bond breaking and bond forming occur simultaneously.
- This mechanism is designated E_2 where;

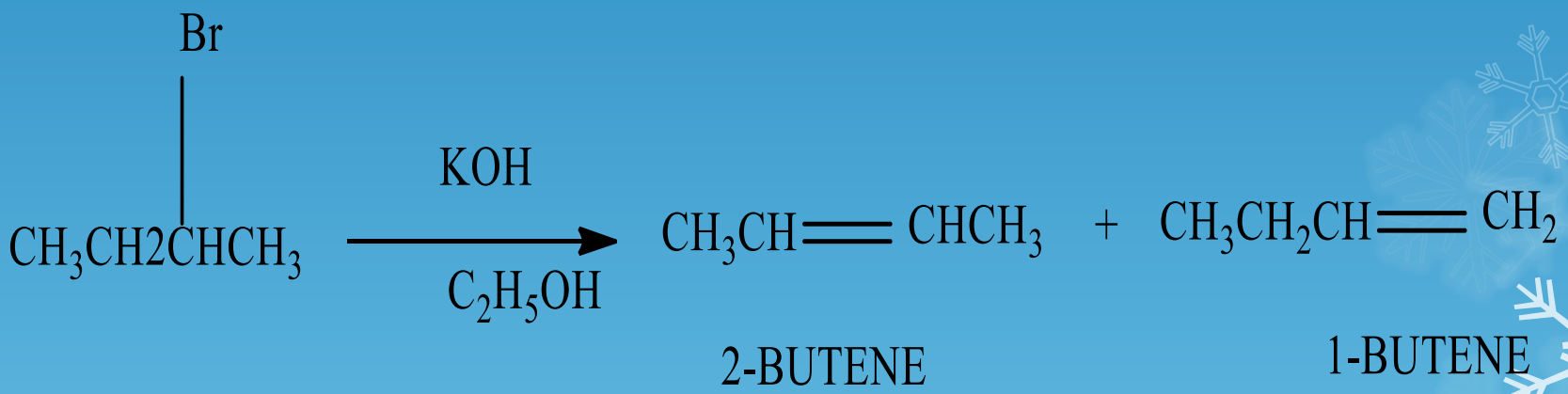
E = elimination.

2 = bimolecular.



E_2 Reaction

- The reaction of 2-bromobutane with KOH gives 2-butene rather than 1-butene.
- The elimination of HBr follows Zaitsev's rule.
- Zaitsev's rule states that elimination of HBr (HX) from an alkyl halide forms a more highly substituted product.
- 2-butene is disubstituted product whereas 1-butene is monosubstituted product.



E_1 REACTION

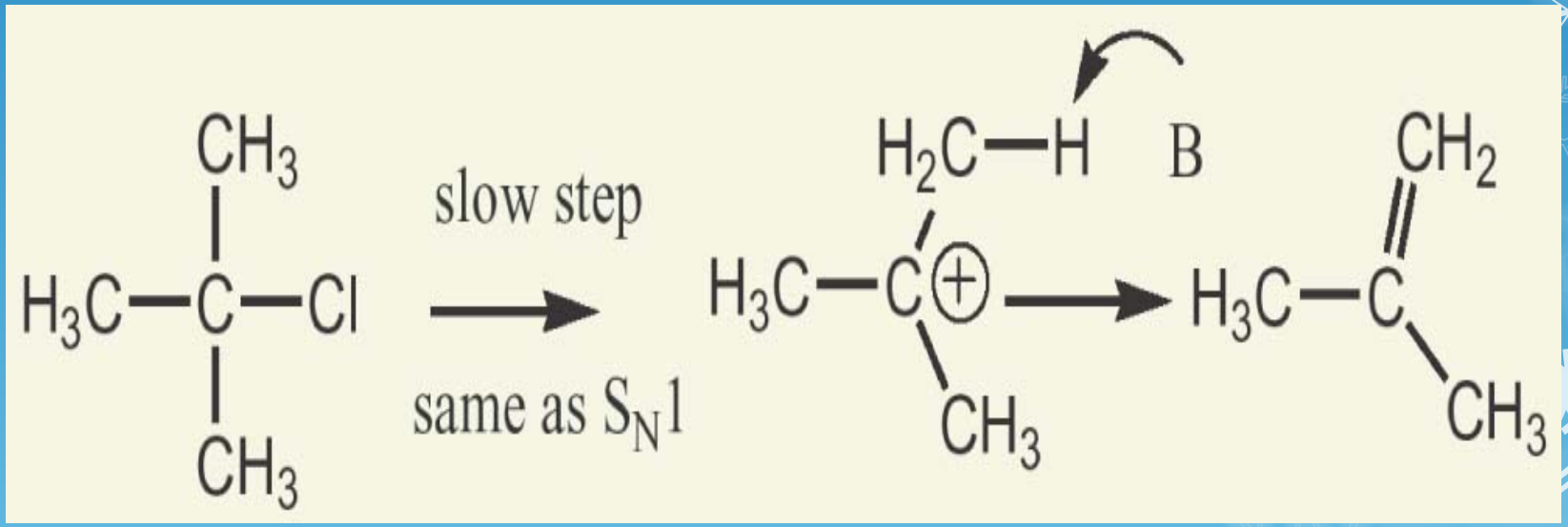
E_1 elimination reactions has a close analog with S_N1 reactions.

This mechanism is designated as E_1 ;

E = Elimination.

1 = Unimolecular

Example: Elimination of HCl from 2-chloro-2-methylpropane.

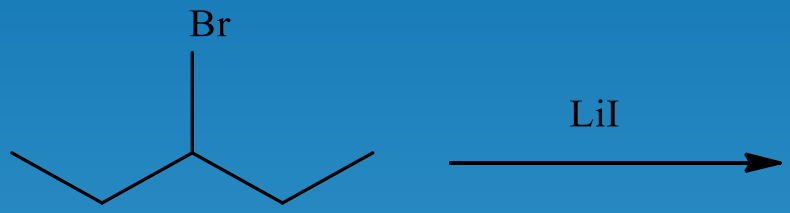


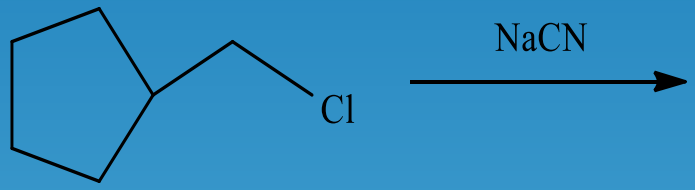
Summary Of Reactivity

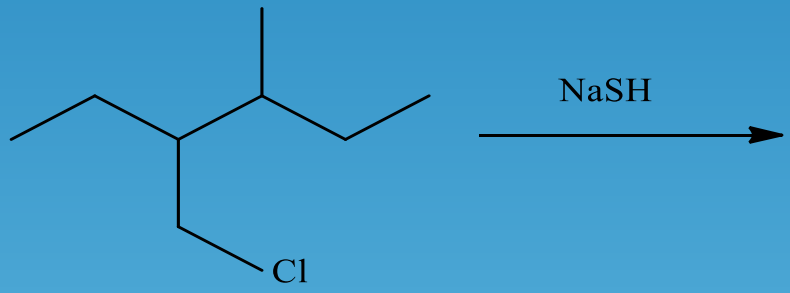
TABLE 11.4 A Summary of Substitution and Elimination Reactions

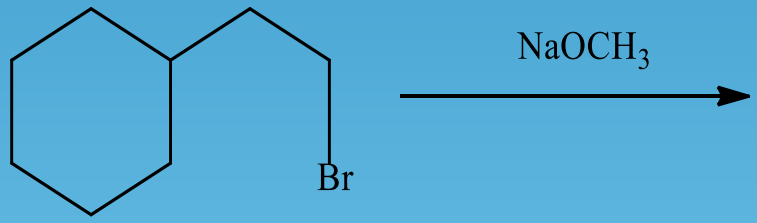
Halide type	S_N1	S_N2	E1	E2
RCH_2X (primary)	Does not occur	Highly favored	Does not occur	Occurs when strong bases are used
R_2CHX (secondary)	Can occur with benzylic and allylic halides	Occurs in competition with E2 reaction	Can occur with benzylic and allylic halides	Favored when strong bases are used
R_3CX (tertiary)	Favored in hydroxylic solvents	Does not occur	Occurs in competition with S_N1 reaction	Favored when bases are used

Practice Problems

1. 

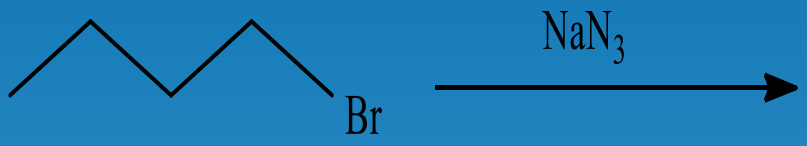
2. 

3. 

4. 

Practice problems

5.



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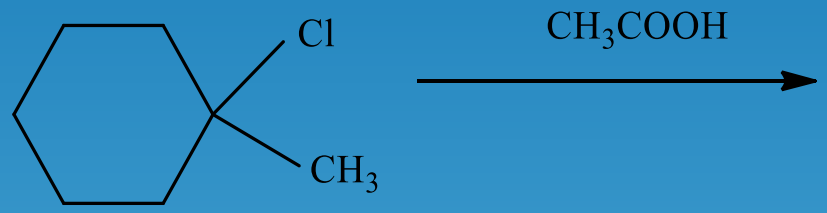

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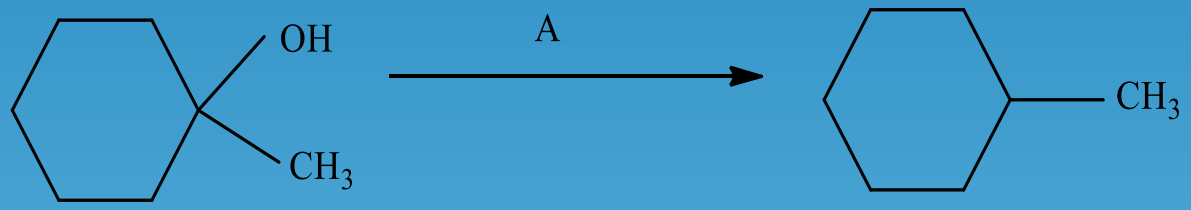

8. What is the product obtained when 1-chloro-1-methylcyclohexane reacts with KOH in ethanol?