Organic Chemistry

1st year students

Lecture No. 8

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Outline

- Nomenclature and structures of alkyl halides.
- Classification of alkyl halides.
- Physical properties of alkyl halides.
- Reaction of alkyl halides.
- 1-Nucleophilic substitution reaction:
- Example: formation of alcohol, Williamson ether synthesis, amine synthesis, nitrile synthesis
- 2-Elimination reaction (dehydrohalogenation of alkyl halides).
- Uses of alkyl halides.

Nomenclature and structures of alkyl halides.

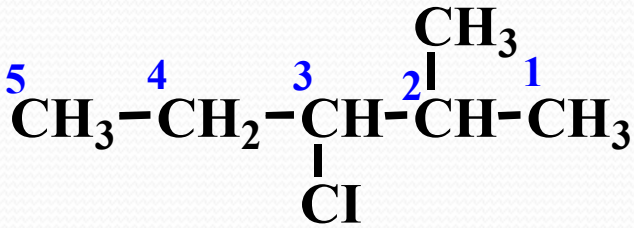
- **General formula: $C_nH_{2n+1}X$ where n = 1,2,… and X (halogen)**

- **Functional group: halogen, -X (X = F, Cl, Br, I)**

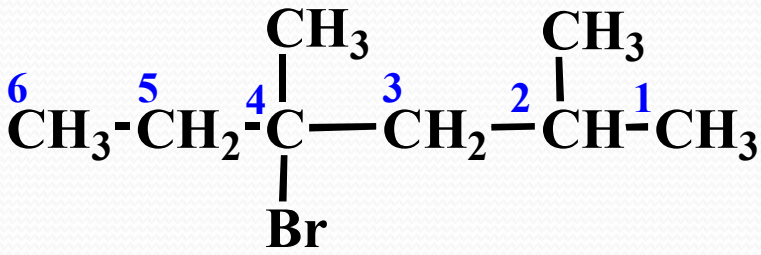
- **Naming alkyl halides:**

  - same as nomenclature of alkanes

iodomethane



3-chloro-2-methylpentane

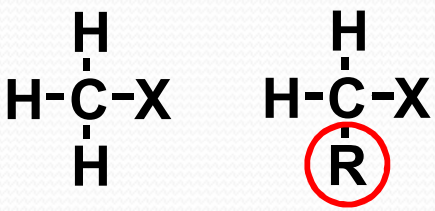


4-bromo-2,4-dimethylhexane

Classification of alkyl halides

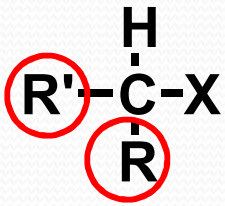
a) Primary (1°)

no. of alkyl groups: none or one



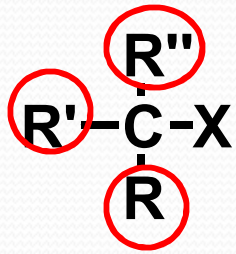
b) Secondary (2°)

no. of alkyl groups: 2



c) Tertiary (3°)

no. of alkyl groups: 3



PHYSICAL PROPERTIES

- **BOILING POINTS**

  - molecules with higher molecular weight have higher boiling points.

  - *reasons:* the molecule is heavier, slower moving, have greater surface area, have larger London attractions, resulting higher boiling points.

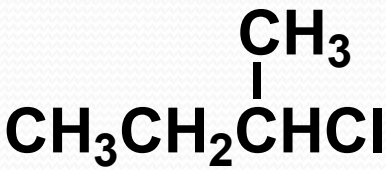
  - example:

	CH_3F	CH_3Cl	CH_3Br	CH_3I
RMM	34	50.5	95	142
bp (°C)	-78	-24	4	42

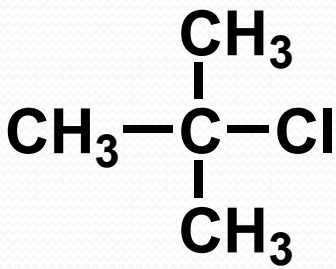
- compounds with branched have more spherical shapes, have smaller surface area, resulting lower boiling points.

$CH_3CH_2CH_2CH_2Cl$

bp 78 ^oC



bp 67 ^oC



bp 52 ^oC

- alkyl halides with more carbon atoms have higher boiling points.

CH_3Cl

bp -24^oC

CH_3CH_2Cl

bp 12^oC

$CH_3CH_2CH_2Cl$

bp 47^oC

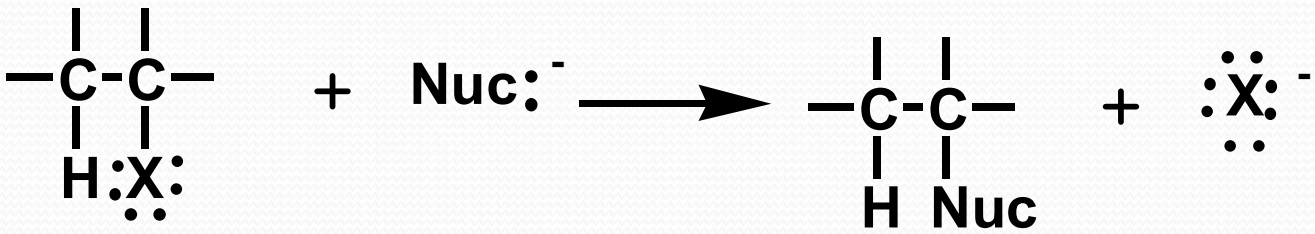
Reactions of alkyl halides

- Two types of reactions:

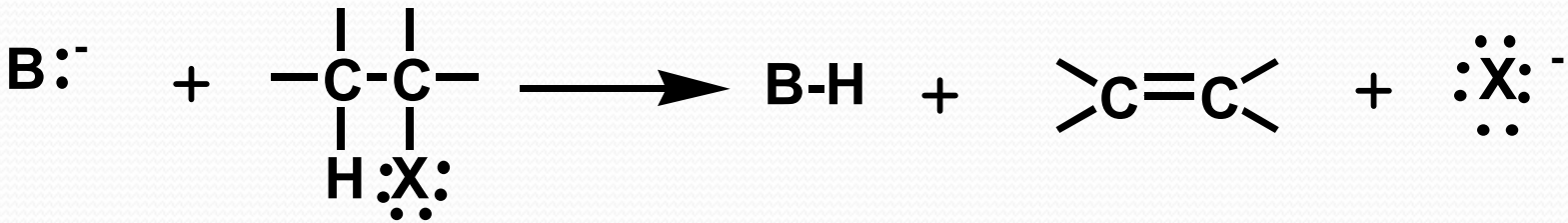
  i) substitution reactions

  ii) elimination reactions

a) nucleophilic substitution



b) elimination



NUCLEOPHILIC SUBSTITUTION REACTIONS

1) Formation of alcohol

$$R\text{-}X + {}^{-}\!:\!\ddot{O}H \longrightarrow R\text{-}OH + :\ddot{X}:^{-}$$

nucleophile

example

$$CH_3CH_2{-}Br + NaOH \longrightarrow CH_3CH_2{-}OH + NaBr$$

ethyl bromide — ethyl alcohol

2) Williamson ether synthesis

$$R\text{-}X + R'\ddot{O}:^{-} \longrightarrow R\text{-}\ddot{O}\text{-}R' + :\ddot{X}:^{-}$$

nucleophile

example

$$CH_3{-}I + CH_3CH_2{-}O^{-}\ Na^{+} \longrightarrow CH_3{-}O{-}CH_2CH_3 + Na^{+}\ I^{-}$$

methyl iodide — sodium ethoxide — ethyl methyl ether

$$CH_3CH_2{-}OH + Na \longrightarrow CH_3CH_2{-}O^{-}Na^{+}$$

sodium ethoxide

3) Amine synthesis

$$R\text{-}X + \underset{\text{nucleophile}}{:NH_3} \longrightarrow R\text{-}NH_2 + HX$$

example

$$CH_3CH_2{-}Br + H\text{-}NH_2 \longrightarrow CH_3CH_2{-}NH_2 + HBr$$

ethyl bromide

ethylamine (primary amine)

$$HBr(g) + NH_3\,(g) \longrightarrow NH_4Br\,(s)$$

amine are also act as nucleophile (more reactive than ammonia)

$$C_2H_5Br + H{-}\underset{\underset{H}{|}}{N}{-}C_2H_5 \longrightarrow (C_2H_5)_2NH + HBr$$

diethylamine
(secondary amine)

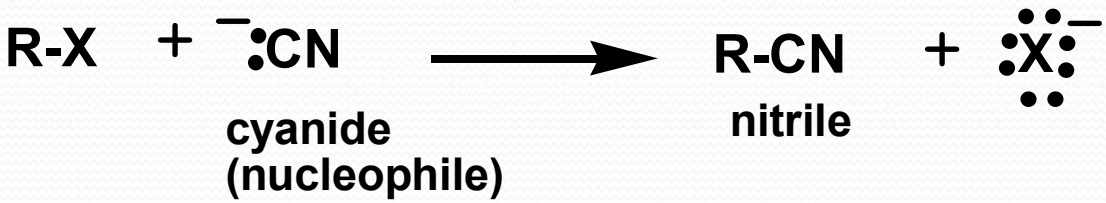
$$C_2H_5Br + (C_2H_5)_2NH \longrightarrow (C_2H_5)_3N + HBr$$

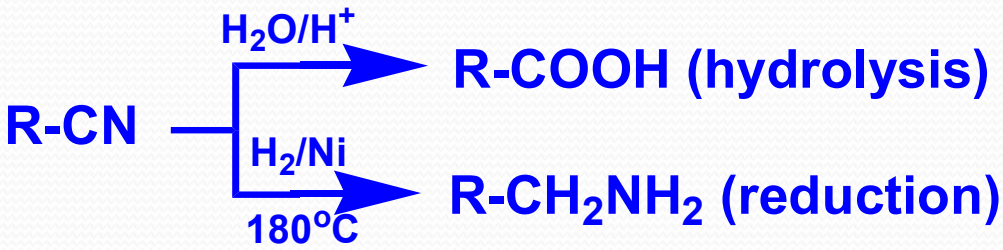
triethylamine
(tertiary amine)

$$C_2H_5Br + (C_2H_5)_3N \longrightarrow (C_2H_5)_4N^+\,Br^-$$

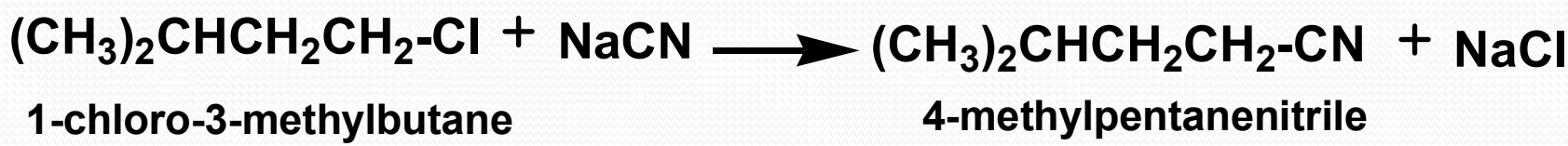
tetraethylammonium bromide

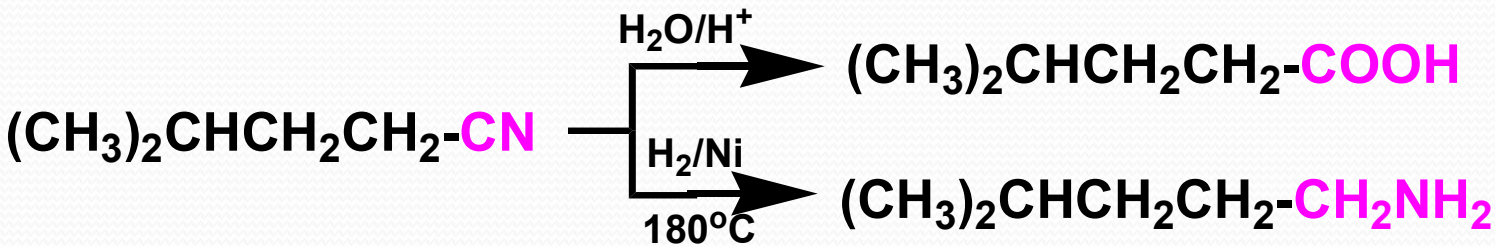
4) Nitrile synthesis



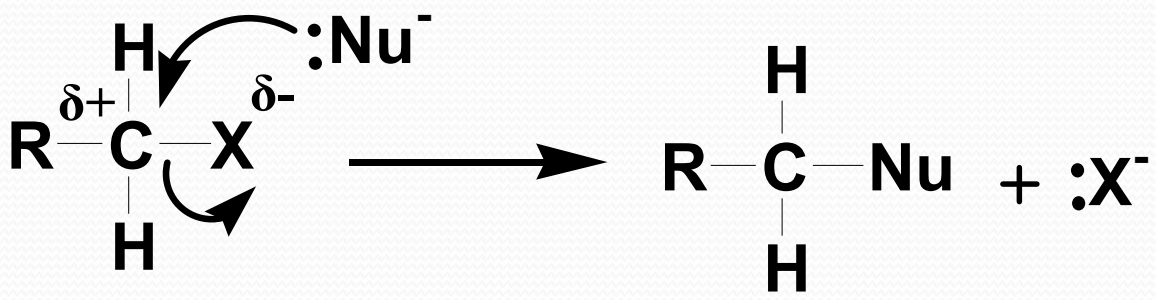


example

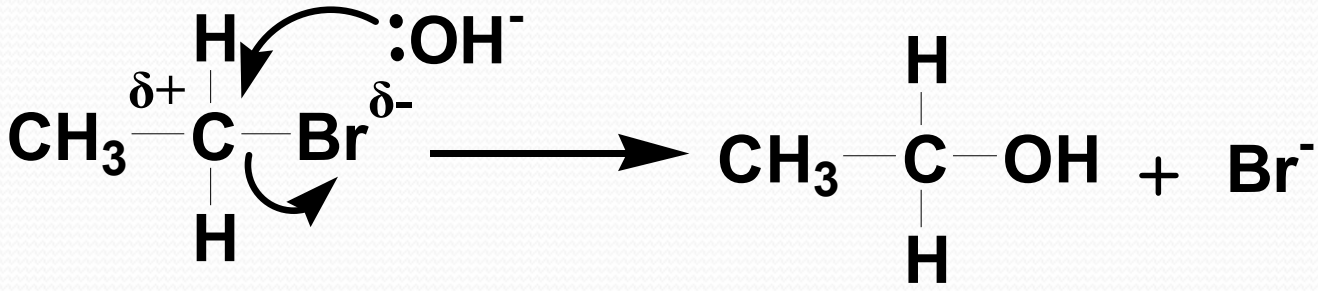




Mechanism of nucleophilic substitution reactions



EXAMPLE



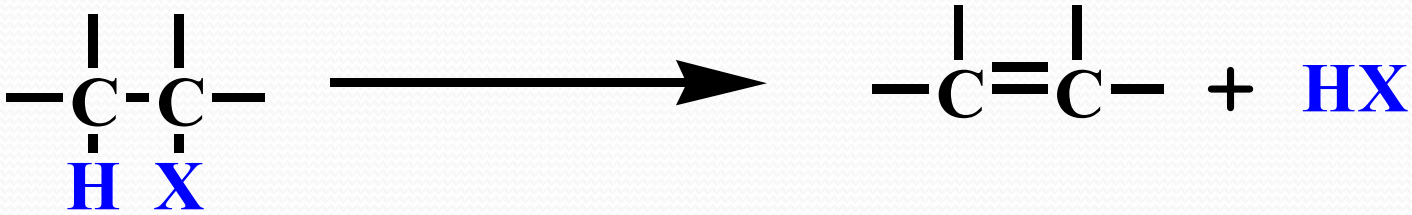
formation of alcohol

Type of nucleophilic substitution reactions: S_N1 and S_N2 reactions

- S = substitution
- N = nucleophilic
- 1 = a first order (unimolecular) reaction
- 2 = a second order (bimolecular) reaction

Elimination reactions- dehydrohalogenation of alkyl halides

- **Elimination: loss of two atoms or groups from the substrate to form a pi bonds.**
- **Dehydrohalogenation (removal of hydrogen and a halogen atom) of alkyl halide to form alkene.**



alkyl halide **alkene**

HX = HCl or HBr or HI

USES OF ALKYL HALIDES

- **Solvents**

  - industrial and household solvents.

  - carbon tetrachloride (CCl_4) used for dry cleaning, spot removing.

  - methylene chloride (CH_2Cl_2) is used to dissolve the caffeine from coffee beans to produce decaffeinated coffee.

- **Reagents**

  - as starting materials for making complex molecules.

  - for example, the conversion of alkyl halides to organometallic reagents (compounds containing carbon-metal bonds) is important tool for organic synthesis.

- **Anesthetics**

  - examples: chloroform ($CHCl_3$) and ethyl chloride.

- **Freons: Refrigerants and foaming agents**

  - Freons (called chlorofluorocarbons, or CFCs) is used as a refrigerant gas.

- **Pesticides**

  - example: DDT (Dichloro Diphenyl-Trichloroethane) is used as insecticides.