South valley University

Faculty of Education

Functional Groups in Organic Chemistry

1st year students

Chemistry Group

First term 2023/2024

Dr. Ibrahim Abdul-Motaleb Mousa

Contents

1- **Classification of organic compounds.**

2- **Functional groups in organic chemistry.**

3- **Alkyl halides and aryl halides.**

4- **Alcohols.**

5- **Phenols.**

6- **Ethers.**

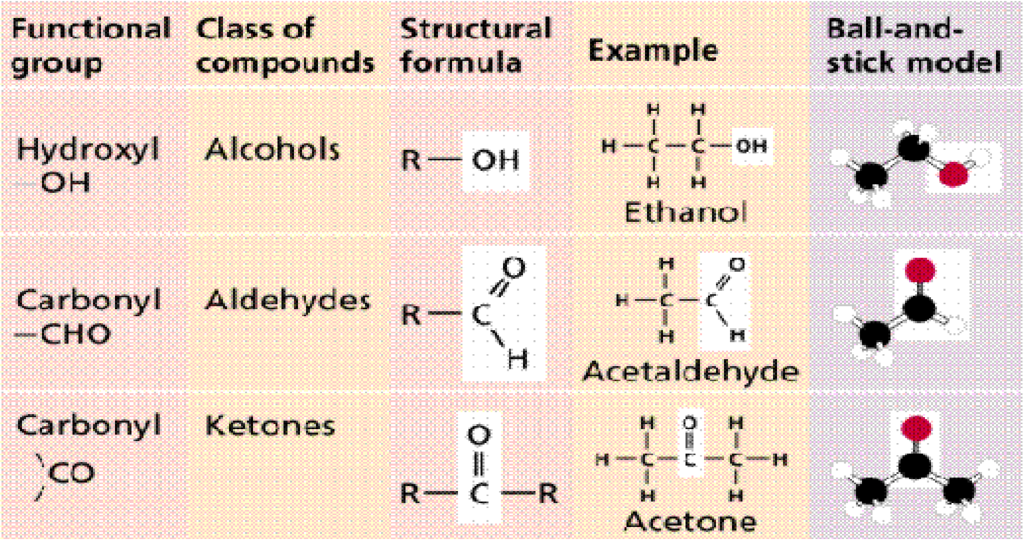
7- **Aldehydes and ketones.**

8- **Carboxylic acids.**

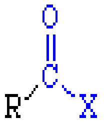
9- **Esters.**

Classification of organic compounds

Related compounds that have the same functional group (groups of atoms found within molecules that are involved in the chemical reactions characteristic of those molecules).



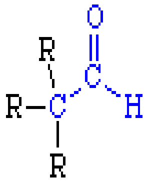
Functional group	Class of compounds	Structural formula	Example	Ball-and-stick model
Hydroxyl —OH	Alcohols	$R-OH$	Ethanol	
Carbonyl —CHO	Aldehydes	$R-C(=O)-H$	Acetaldehyde	
Carbonyl >CO	Ketones	$R-\overset{O}{\overset{\|}{C}}-R$	Acetone	



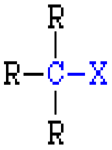
acyl halides
(X = F, Cl, Br, I)

$R-O-H$

alcohols



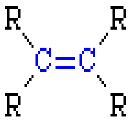
aldehydes



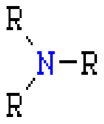
alkyl halides
(X = F, Cl, Br, I)

$R-C\equiv C-R$

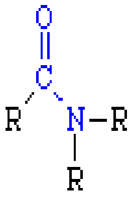
alkynes



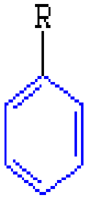
alkenes



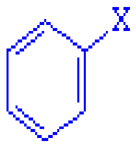
amines



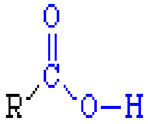
amides



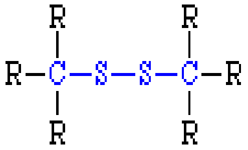
aromatic rings



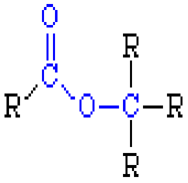
aryl halides
(X = F, Cl, Br, I)



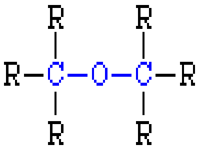
carboxylic acids



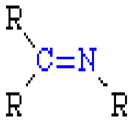
disulfides



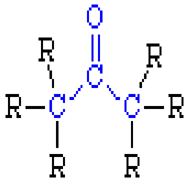
esters



ethers



imines



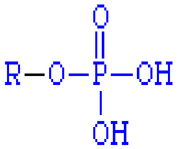
ketones

$R-C\equiv N$

nitriles

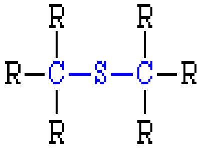
$R-NO_2$

nitro groups



$R-O-P(=O)(OH)-OH$

phosphate esters

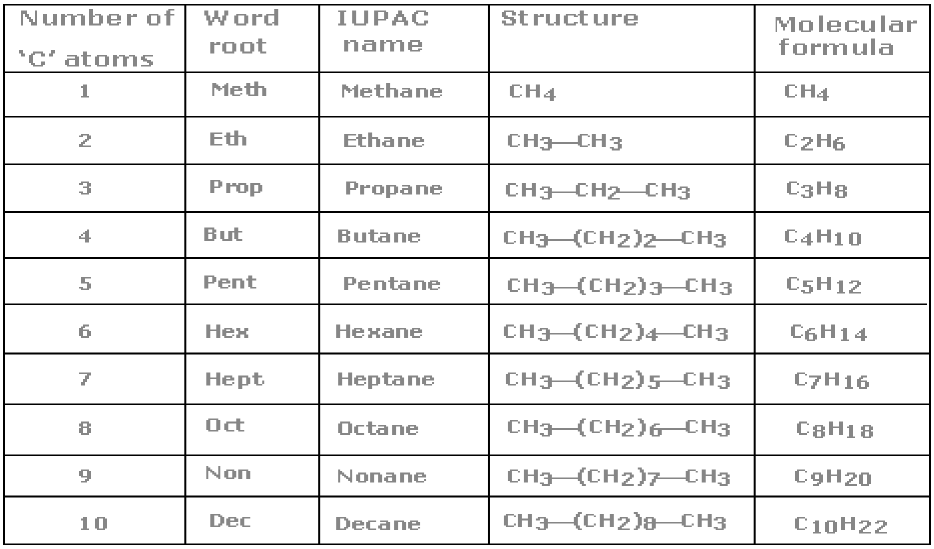


thioethers

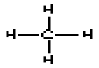
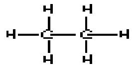
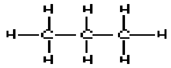
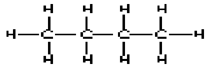
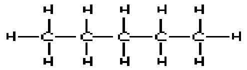
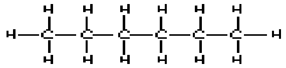
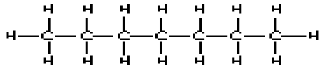
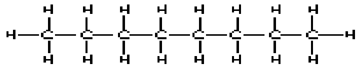
$R-S-H$

thiols

- **differ from each other by a CH_2 unit can be represented by a general formula**
    - **examples: C_nH_{2n+2} (alkanes) or C_nH_{2n} (alkenes) or…**



Number of 'C' atoms	Word root	IUPAC name	Structure	Molecular formula
1	Meth	Methane	CH_4	CH_4
2	Eth	Ethane	$CH_3—CH_3$	C_2H_6
3	Prop	Propane	$CH_3—CH_2—CH_3$	C_3H_8
4	But	Butane	$CH_3—(CH_2)_2—CH_3$	C_4H_{10}
5	Pent	Pentane	$CH_3—(CH_2)_3—CH_3$	C_5H_{12}
6	Hex	Hexane	$CH_3—(CH_2)_4—CH_3$	C_6H_{14}
7	Hept	Heptane	$CH_3—(CH_2)_5—CH_3$	C_7H_{16}
8	Oct	Octane	$CH_3—(CH_2)_6—CH_3$	C_8H_{18}
9	Non	Nonane	$CH_3—(CH_2)_7—CH_3$	C_9H_{20}
10	Dec	Decane	$CH_3—(CH_2)_8—CH_3$	$C_{10}H_{22}$

# Carbons	Name	Structure
1	methane	
2	ethane	
3	propane	
4	butane	
5	pentane	
6	hexane	
7	heptane	
8	octane	

Naming Organic Compounds

The name of any organic compound is comprised of three portions:

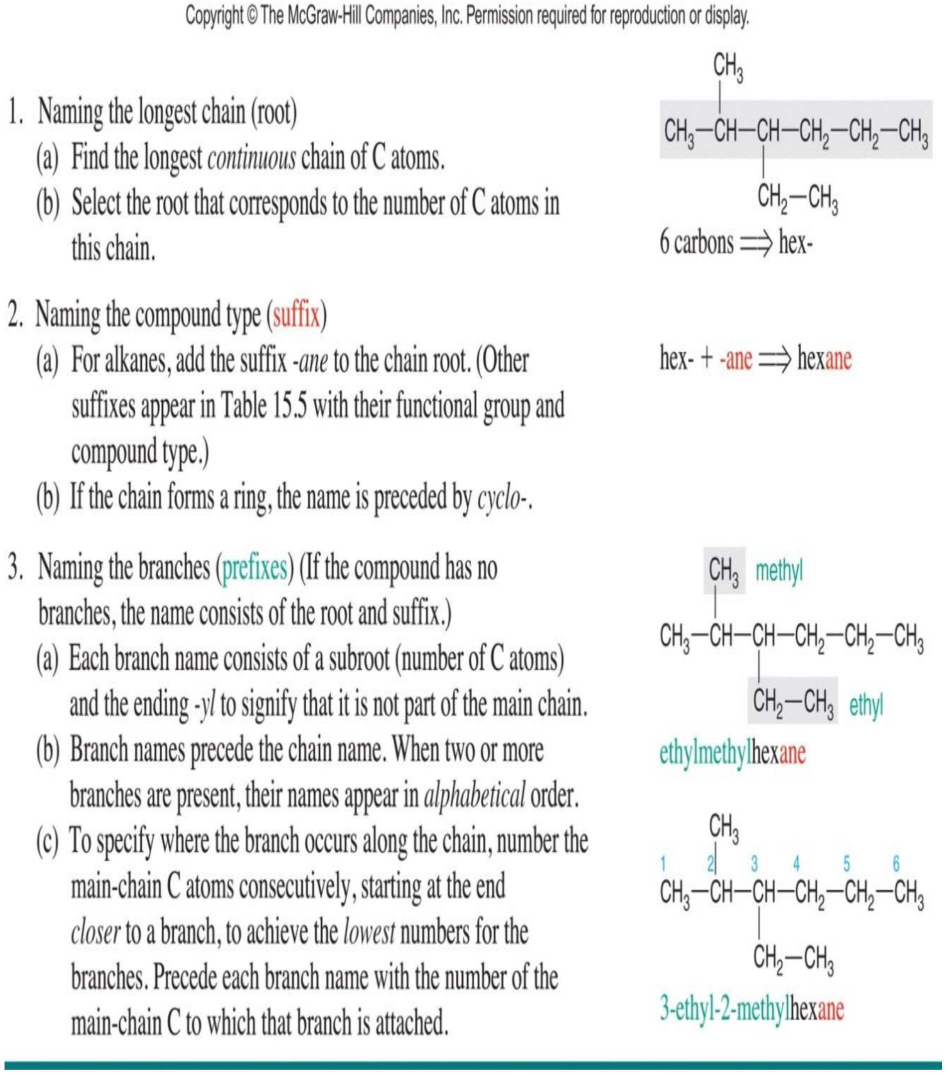
PREFIX + ROOT + SUFFIX

The *root* name of the compound is determined from the *number* of C atoms in the *longest continuous chain.* The *suffix* indicates the *type* of organic compound, and is placed after the root. The suffix for an alkane is –ane. The *prefix* identifies any groups attached to the main chain.

Numerical Roots for Carbon Chains and Branches

Roots	Number of C Atoms
meth-	1
eth-	2
prop-	3
but-	4
pent-	5
hex-	6
hept-	7
oct-	8
non-	9

Rules for Naming an Organic Compound



1. Naming the longest chain (root)
   (a) Find the longest *continuous* chain of C atoms.
   (b) Select the root that corresponds to the number of C atoms in this chain.

6 carbons ⟹ hex-

2. Naming the compound type (suffix)
   (a) For alkanes, add the suffix *-ane* to the chain root. (Other suffixes appear in Table 15.5 with their functional group and compound type.)
   (b) If the chain forms a ring, the name is preceded by *cyclo-*.

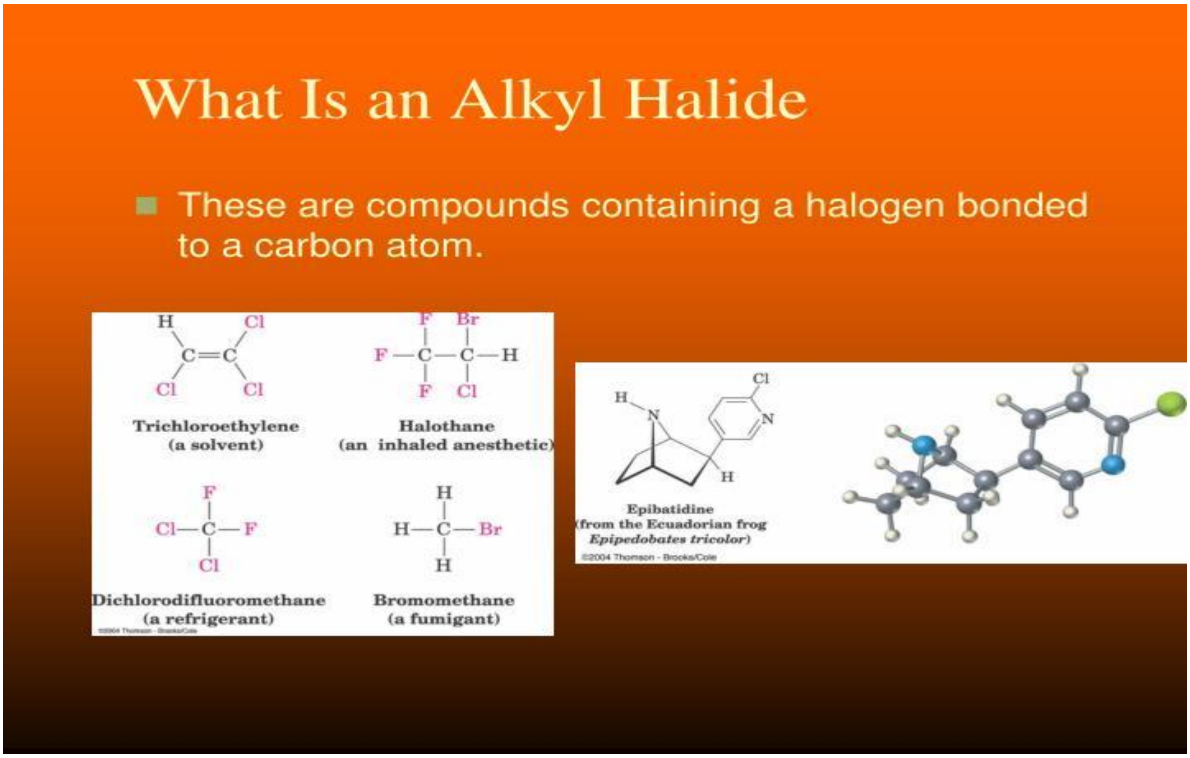
hex- + -ane ⟹ hexane

3. Naming the branches (prefixes) (If the compound has no branches, the name consists of the root and suffix.)
   (a) Each branch name consists of a subroot (number of C atoms) and the ending *-yl* to signify that it is not part of the main chain.
   (b) Branch names precede the chain name. When two or more branches are present, their names appear in *alphabetical* order.
   (c) To specify where the branch occurs along the chain, number the main-chain C atoms consecutively, starting at the end *closer* to a branch, to achieve the *lowest* numbers for the branches. Precede each branch name with the number of the main-chain C to which that branch is attached.

ethylmethylhexane

3-ethyl-2-methylhexane

Alkyl Halides



What Is an Alkyl Halide

- These are compounds containing a halogen bonded to a carbon atom.

Trichloroethylene
(a solvent)

Halothane
(an inhaled anesthetic)

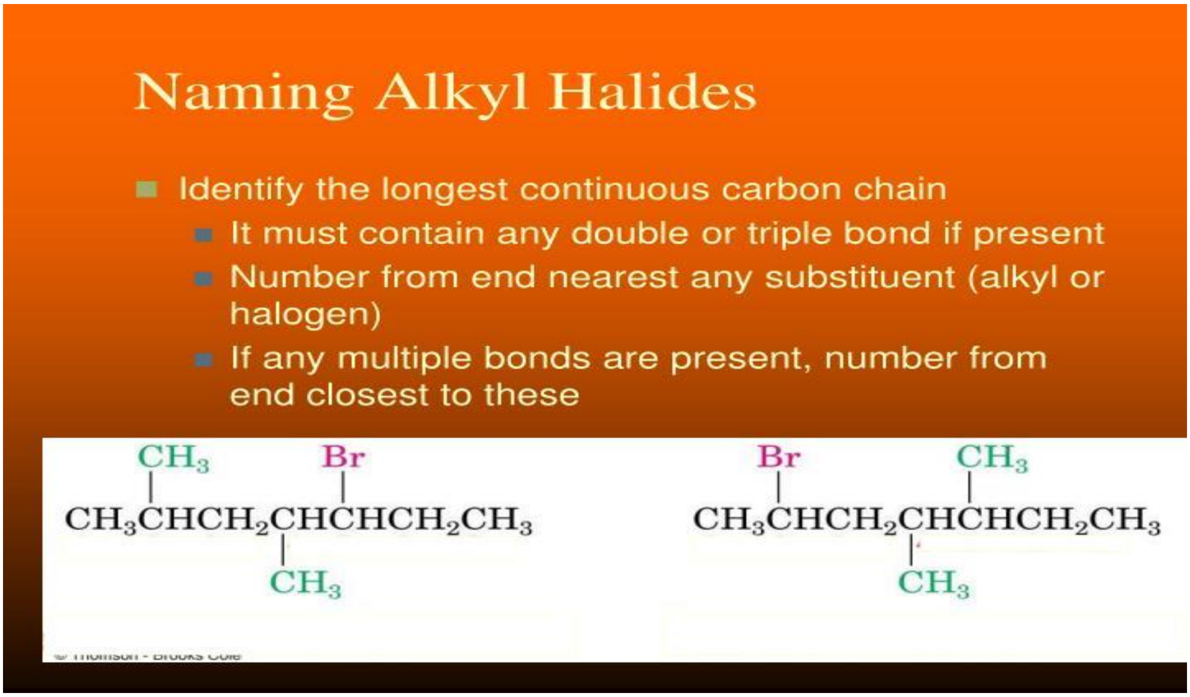
Dichlorodifluoromethane
(a refrigerant)

Bromomethane
(a fumigant)

©2004 Thomson - Brooks/Cole

Epibatidine
(from the Ecuadorian frog *Epipedobates tricolor*)

©2004 Thomson - Brooks/Cole



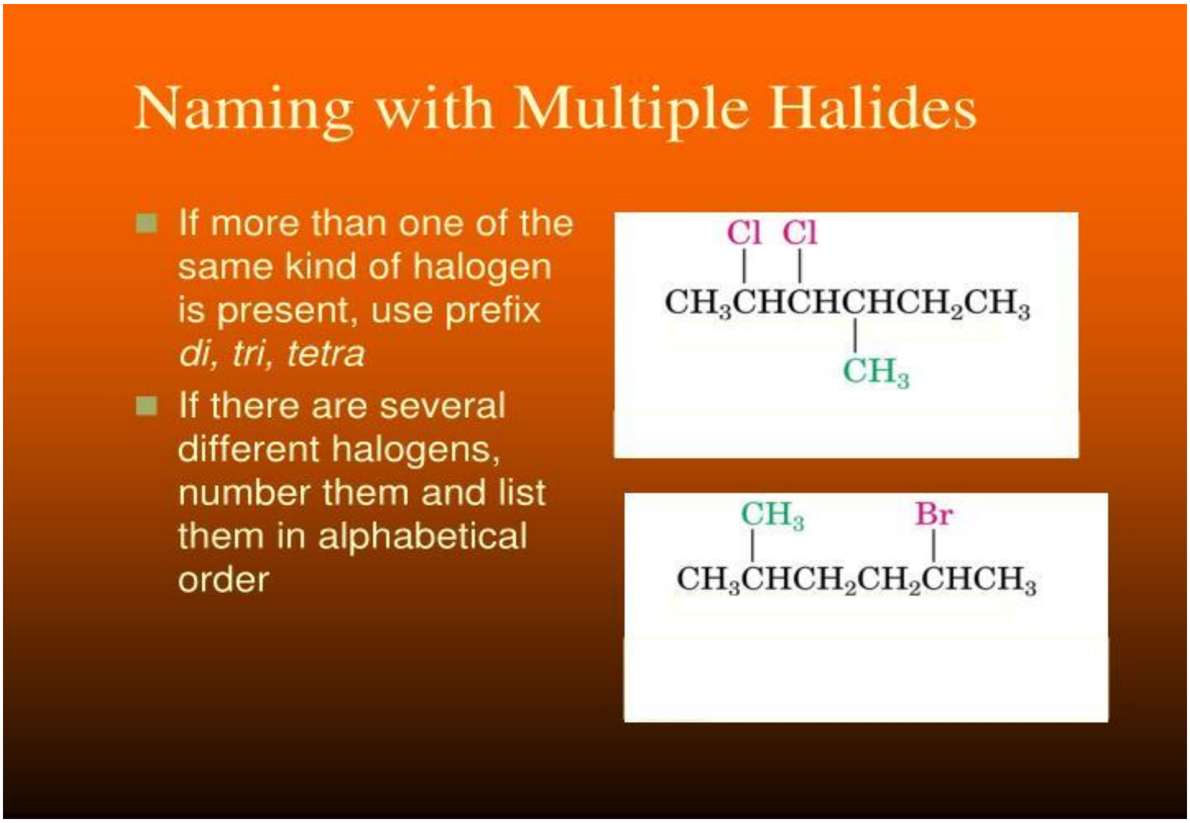
Naming Alkyl Halides

- Identify the longest continuous carbon chain
  - It must contain any double or triple bond if present
  - Number from end nearest any substituent (alkyl or halogen)
  - If any multiple bonds are present, number from end closest to these

$CH_3\overset{CH_3}{C}HCH_2\underset{CH_3}{C}H\overset{Br}{C}HCH_2CH_3$

$CH_3\overset{Br}{C}HCH_2\underset{CH_3}{C}H\overset{CH_3}{C}HCH_2CH_3$

© Thomson - Brooks Cole

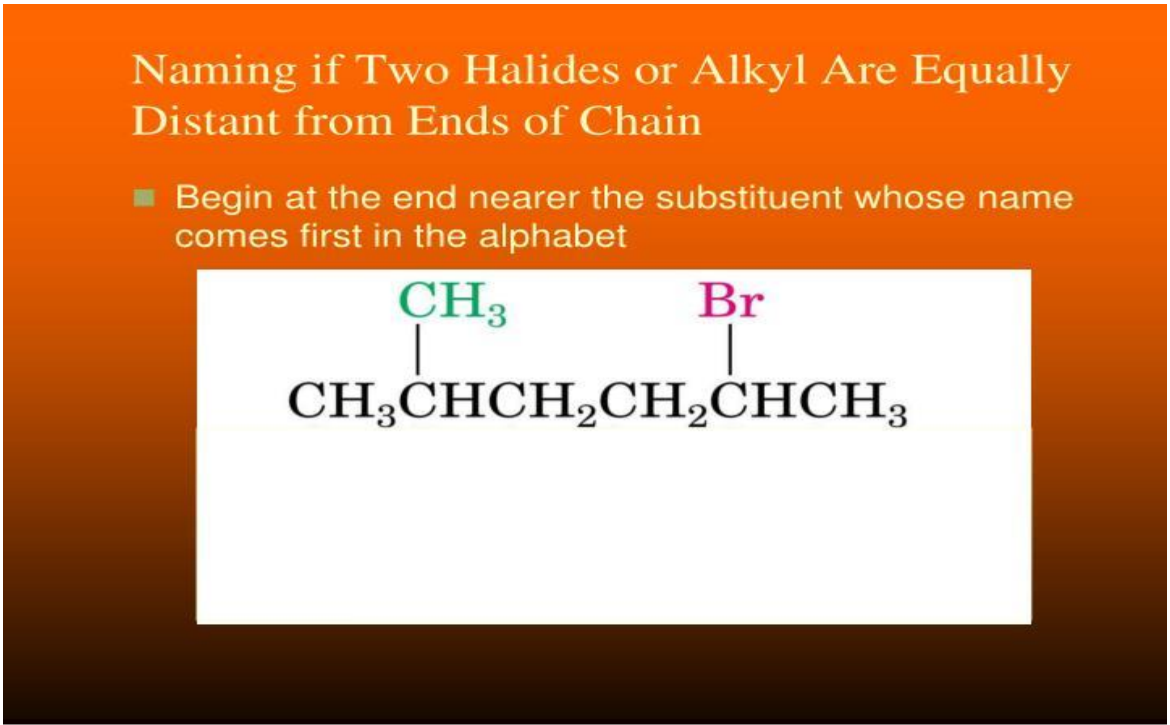


Naming with Multiple Halides

- If more than one of the same kind of halogen is present, use prefix *di, tri, tetra*
- If there are several different halogens, number them and list them in alphabetical order

$$CH_3\overset{Cl}{C}H\overset{Cl}{C}H\underset{CH_3}{C}HCH_2CH_3$$

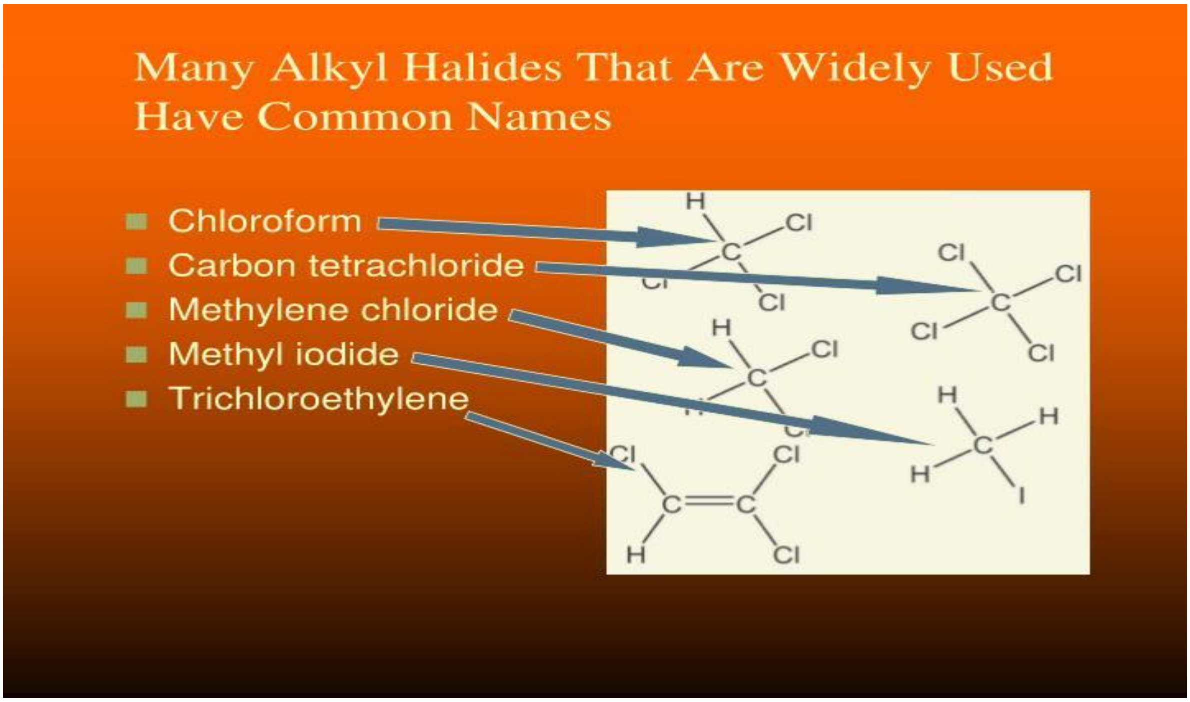
$$CH_3\overset{CH_3}{C}HCH_2CH_2\overset{Br}{C}HCH_3$$



Naming if Two Halides or Alkyl Are Equally Distant from Ends of Chain

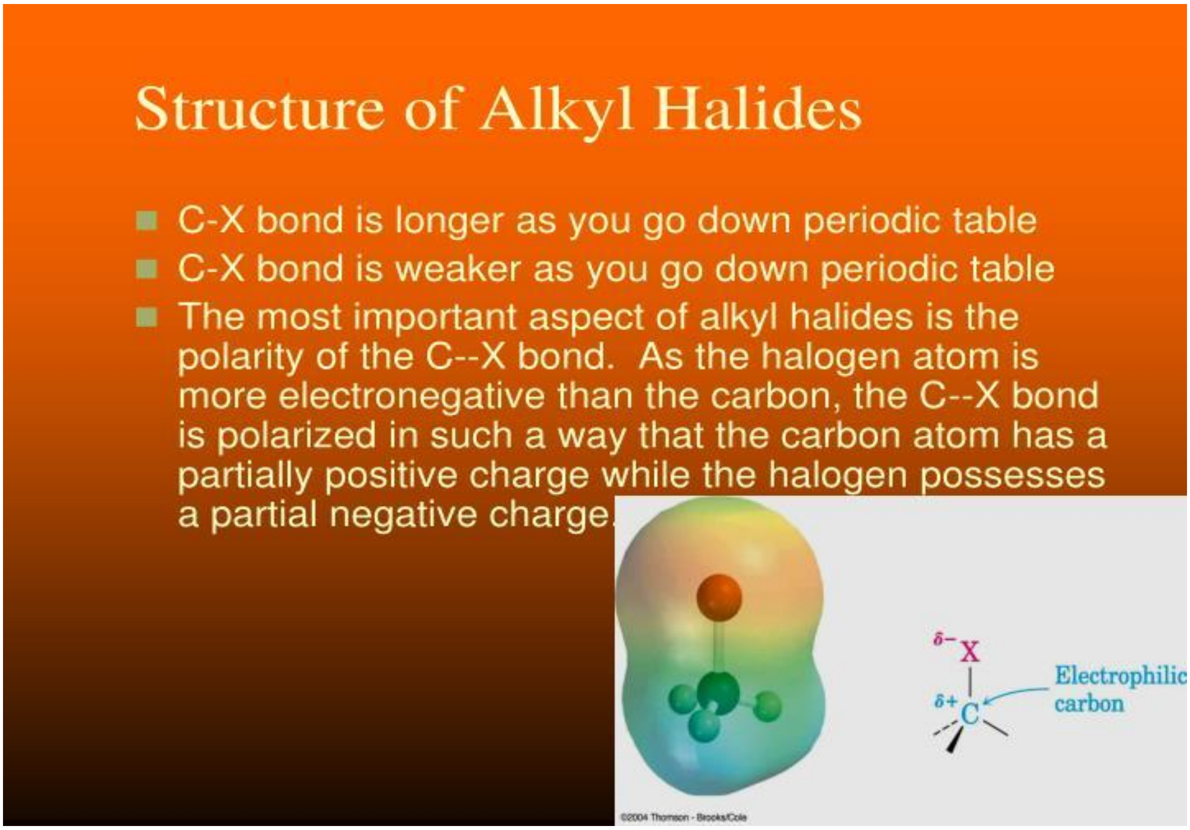
- Begin at the end nearer the substituent whose name comes first in the alphabet

$$CH_3\overset{CH_3}{C}HCH_2CH_2\overset{Br}{C}HCH_3$$



Many Alkyl Halides That Are Widely Used Have Common Names

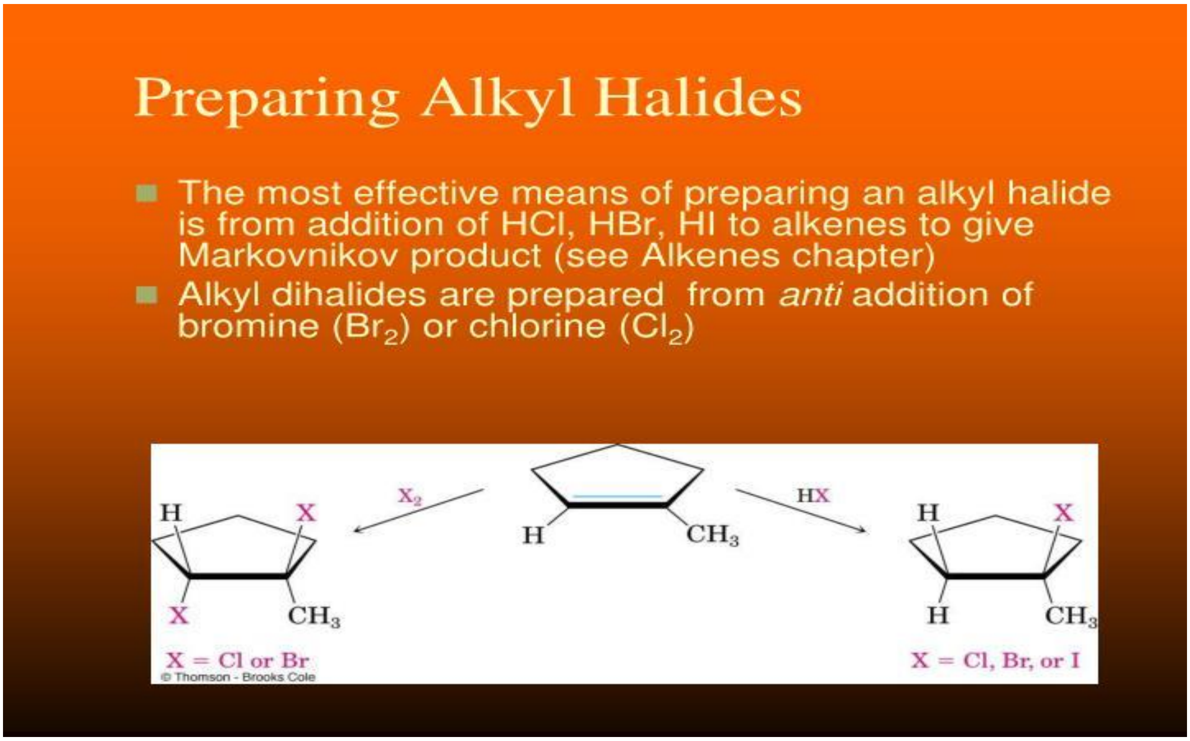
- Chloroform
- Carbon tetrachloride
- Methylene chloride
- Methyl iodide
- Trichloroethylene



Structure of Alkyl Halides

- C-X bond is longer as you go down periodic table
- C-X bond is weaker as you go down periodic table
- The most important aspect of alkyl halides is the polarity of the C--X bond. As the halogen atom is more electronegative than the carbon, the C--X bond is polarized in such a way that the carbon atom has a partially positive charge while the halogen possesses a partial negative charge.

©2004 Thomson - Brooks/Cole



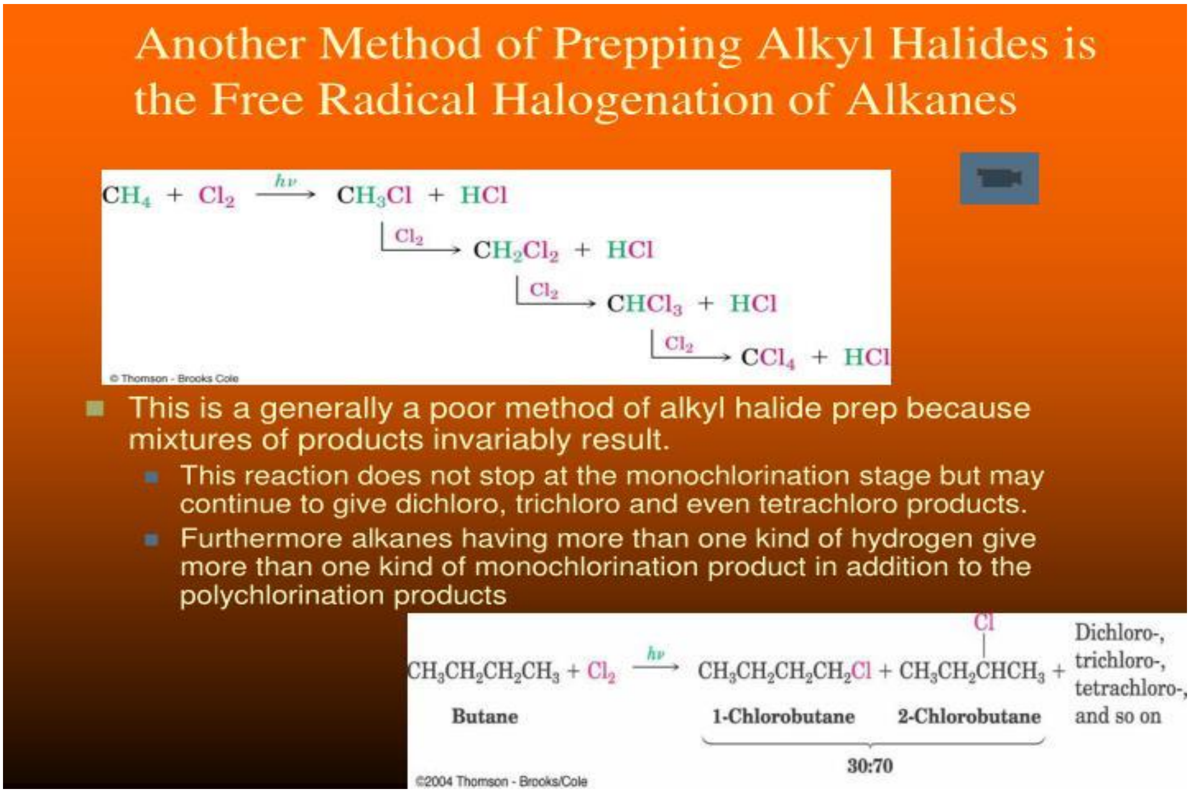
Preparing Alkyl Halides

- The most effective means of preparing an alkyl halide is from addition of HCl, HBr, HI to alkenes to give Markovnikov product (see Alkenes chapter)
- Alkyl dihalides are prepared from *anti* addition of bromine (Br_2) or chlorine (Cl_2)

X = Cl or Br

X = Cl, Br, or I

© Thomson - Brooks Cole



Another Method of Prepping Alkyl Halides is the Free Radical Halogenation of Alkanes

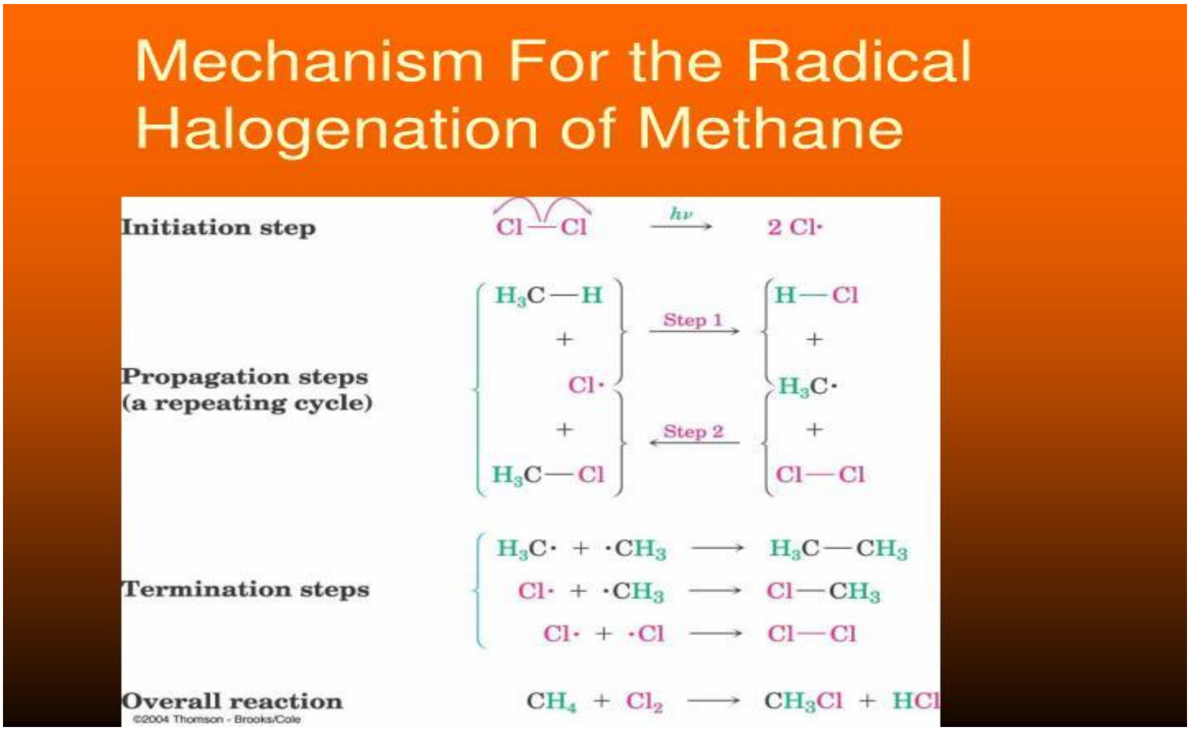
$$CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl + HCl$$
$$\xrightarrow{Cl_2} CH_2Cl_2 + HCl$$
$$\xrightarrow{Cl_2} CHCl_3 + HCl$$
$$\xrightarrow{Cl_2} CCl_4 + HCl$$

© Thomson - Brooks Cole

- This is a generally a poor method of alkyl halide prep because mixtures of products invariably result.
  - This reaction does not stop at the monochlorination stage but may continue to give dichloro, trichloro and even tetrachloro products.
  - Furthermore alkanes having more than one kind of hydrogen give more than one kind of monochlorination product in addition to the polychlorination products

$$\underset{\text{Butane}}{CH_3CH_2CH_2CH_3} + Cl_2 \xrightarrow{h\nu} \underbrace{\underset{\text{1-Chlorobutane}}{CH_3CH_2CH_2CH_2Cl} + \underset{\text{2-Chlorobutane}}{CH_3CH_2\overset{Cl}{C}HCH_3}}_{30:70} + \text{Dichloro-, trichloro-, tetrachloro-, and so on}$$

©2004 Thomson - Brooks/Cole



Mechanism For the Radical Halogenation of Methane

Initiation step

$$Cl-Cl \xrightarrow{h\nu} 2\,Cl\cdot$$

Propagation steps (a repeating cycle)

$$H_3C-H + Cl\cdot \xrightarrow{\text{Step 1}} H-Cl + H_3C\cdot$$

$$Cl\cdot + H_3C-Cl \xleftarrow{\text{Step 2}} H_3C\cdot + Cl-Cl$$

Termination steps

$$H_3C\cdot + \cdot CH_3 \longrightarrow H_3C-CH_3$$

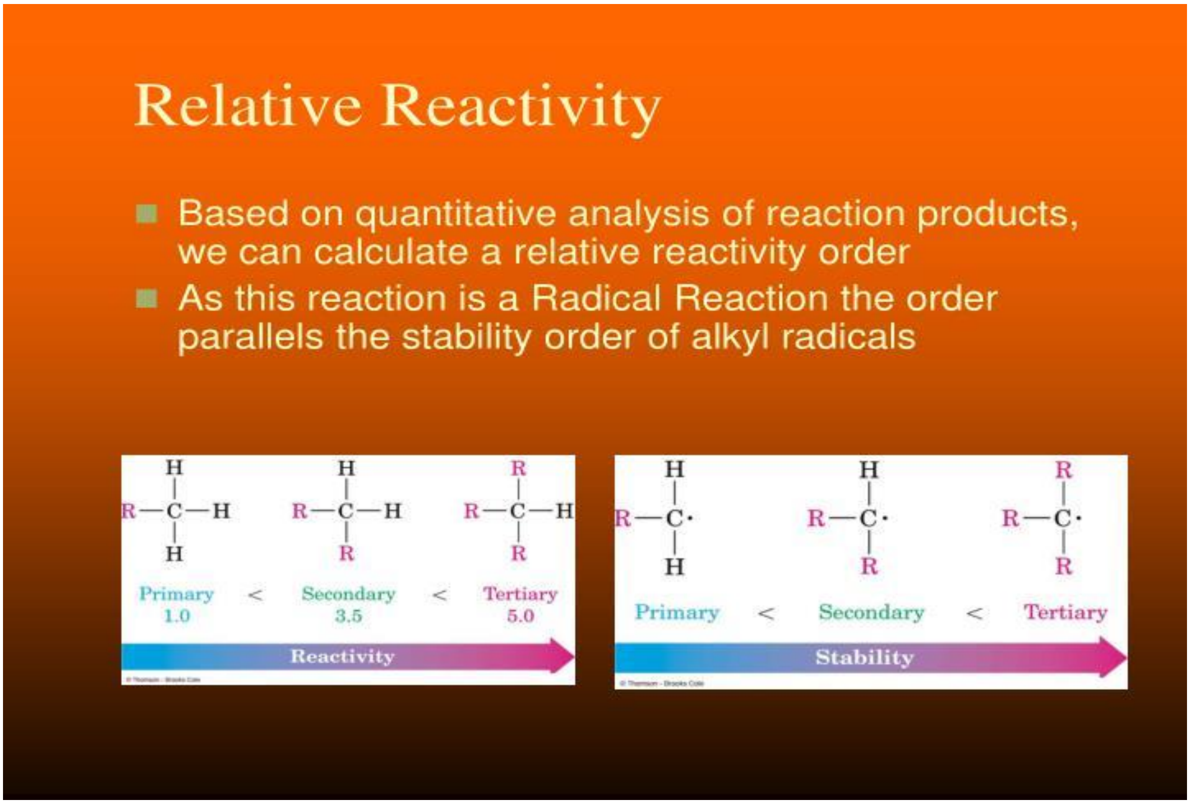
$$Cl\cdot + \cdot CH_3 \longrightarrow Cl-CH_3$$

$$Cl\cdot + \cdot Cl \longrightarrow Cl-Cl$$

Overall reaction

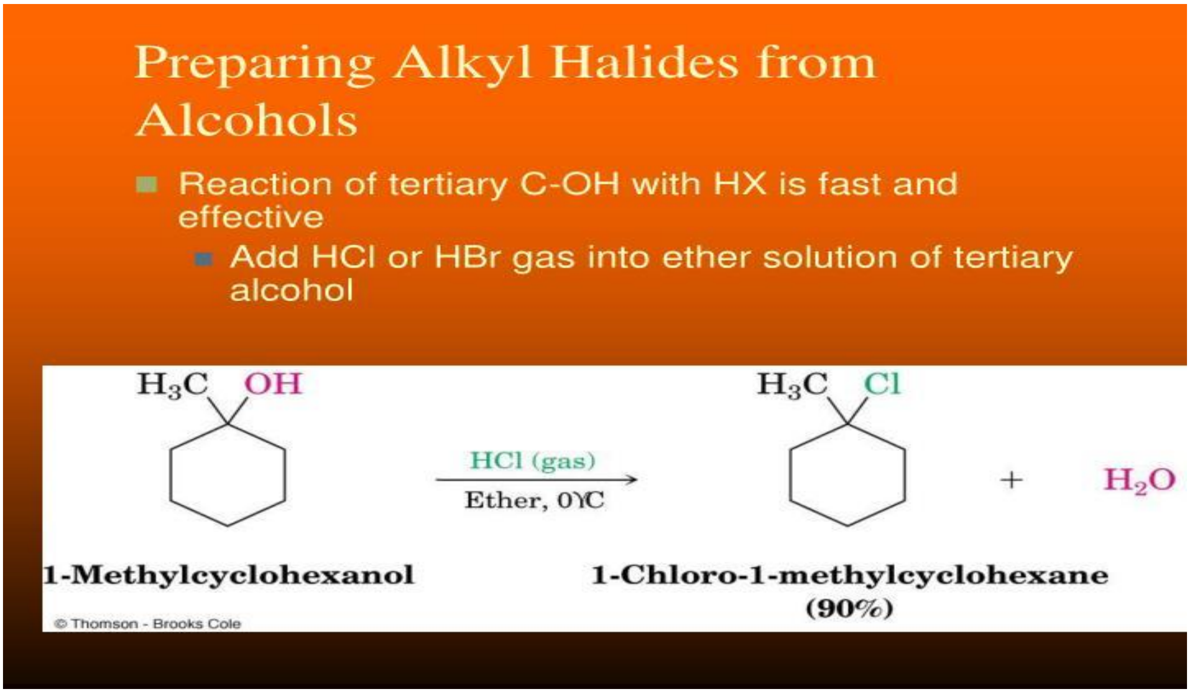
$$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$$

©2004 Thomson - Brooks/Cole



Relative Reactivity

- Based on quantitative analysis of reaction products, we can calculate a relative reactivity order
- As this reaction is a Radical Reaction the order parallels the stability order of alkyl radicals



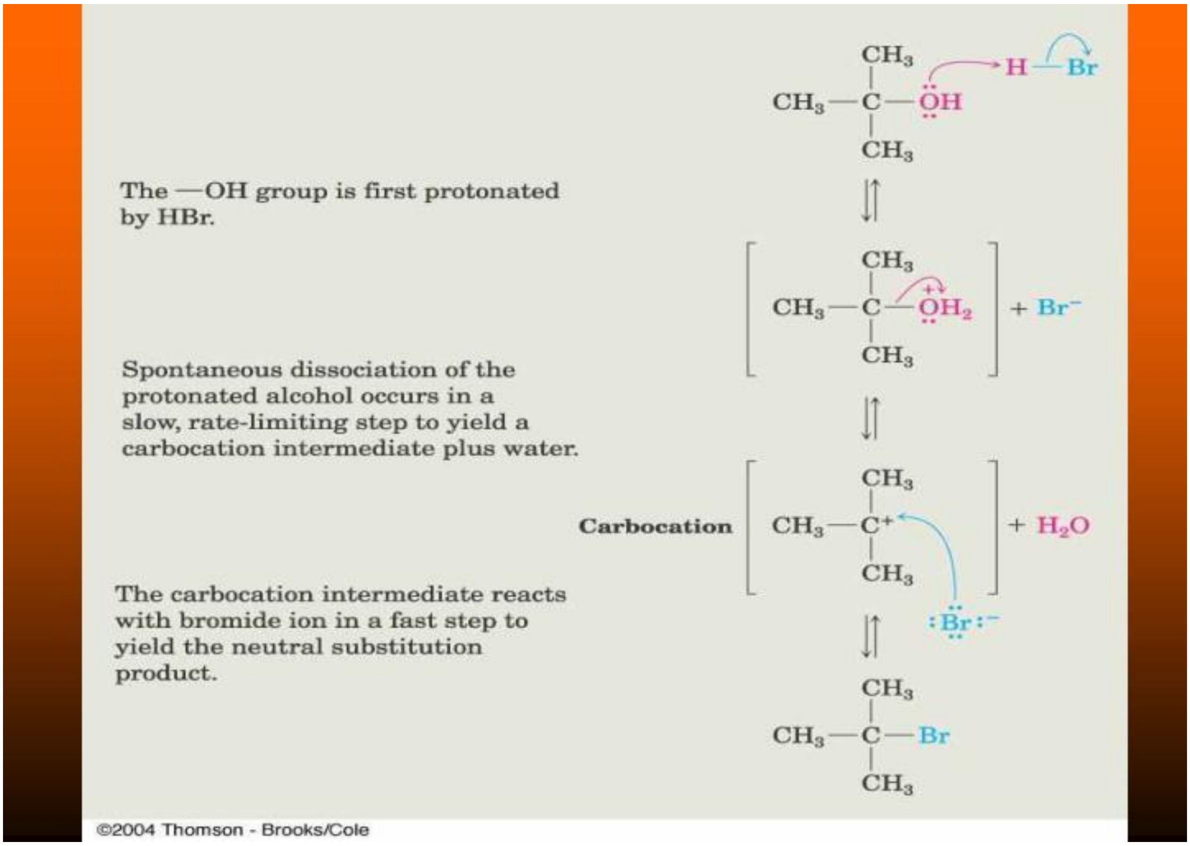
Preparing Alkyl Halides from Alcohols

- Reaction of tertiary C-OH with HX is fast and effective
  - Add HCl or HBr gas into ether solution of tertiary alcohol

1-Methylcyclohexanol

1-Chloro-1-methylcyclohexane (90%)

© Thomson - Brooks Cole



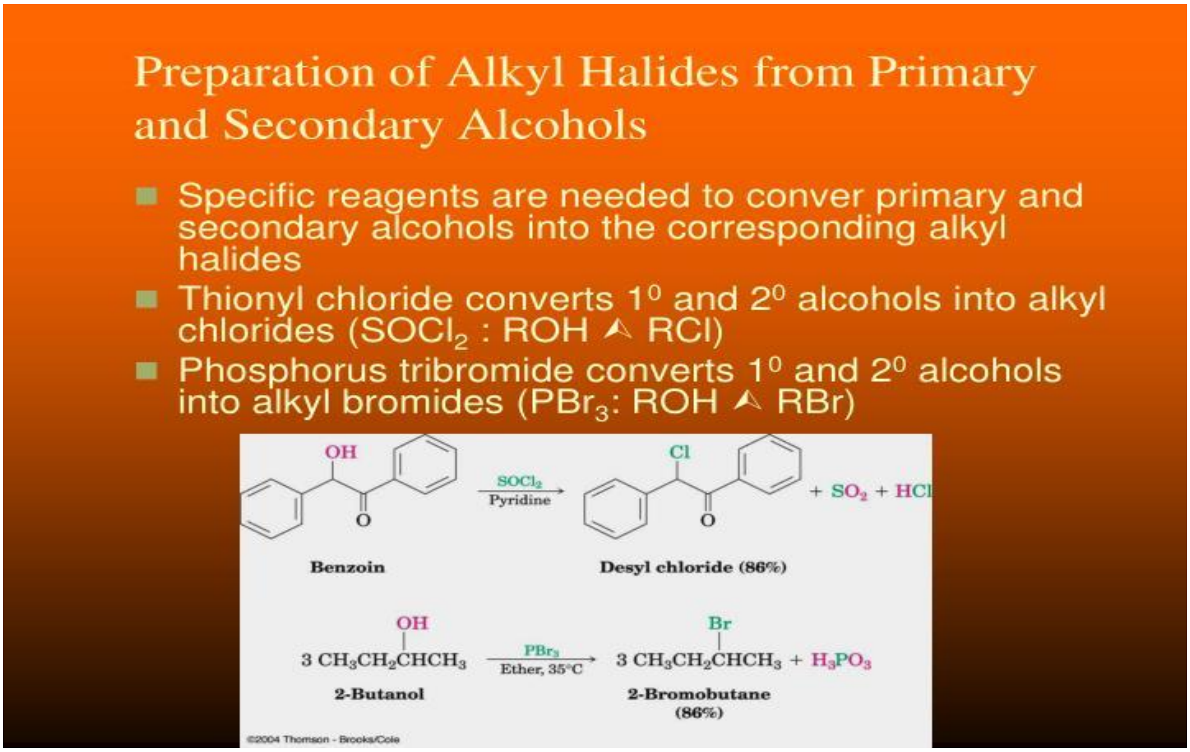
The —OH group is first protonated by HBr.

Spontaneous dissociation of the protonated alcohol occurs in a slow, rate-limiting step to yield a carbocation intermediate plus water.

Carbocation

The carbocation intermediate reacts with bromide ion in a fast step to yield the neutral substitution product.

©2004 Thomson - Brooks/Cole



Preparation of Alkyl Halides from Primary and Secondary Alcohols

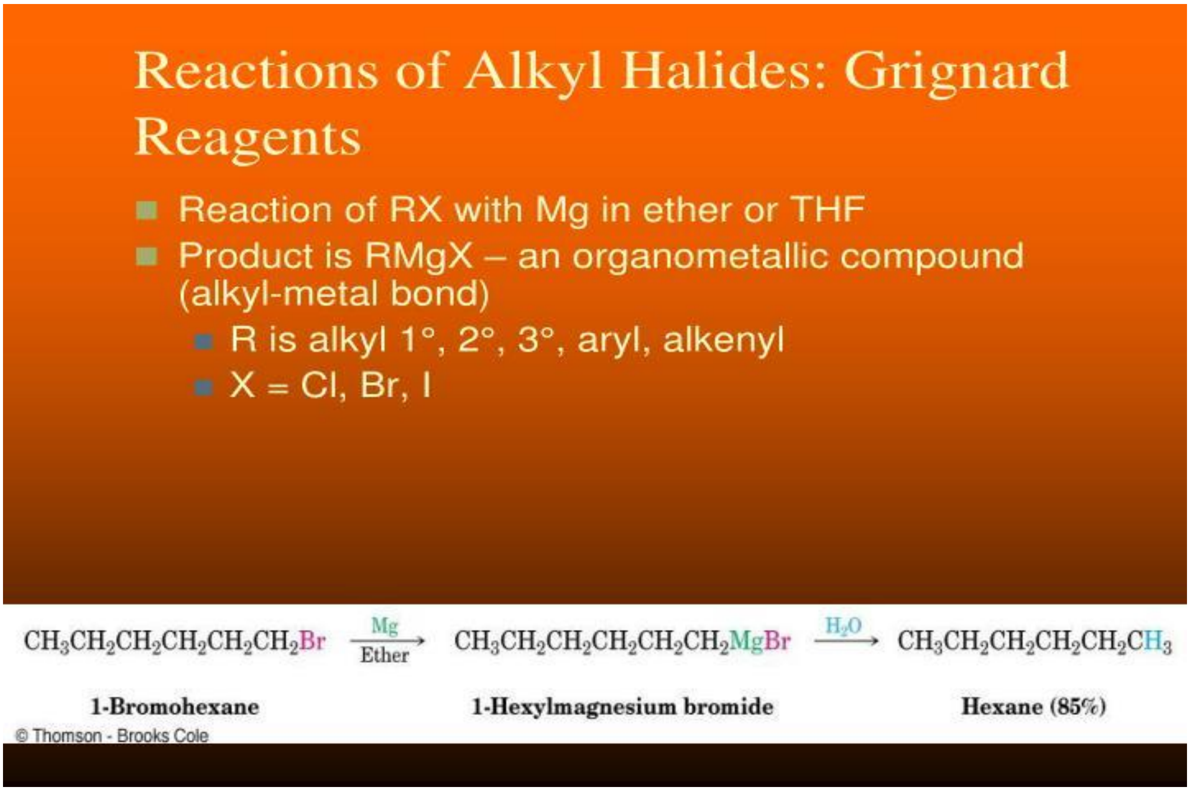
- Specific reagents are needed to conver primary and secondary alcohols into the corresponding alkyl halides
- Thionyl chloride converts 1^0 and 2^0 alcohols into alkyl chlorides ($SOCl_2$: ROH → RCl)
- Phosphorus tribromide converts 1^0 and 2^0 alcohols into alkyl bromides (PBr_3: ROH → RBr)

Benzoin **Desyl chloride (86%)**

$$3\ CH_3CH_2\overset{OH}{\overset{|}{C}}HCH_3 \xrightarrow[\text{Ether, 35°C}]{PBr_3} 3\ CH_3CH_2\overset{Br}{\overset{|}{C}}HCH_3 + H_3PO_3$$

2-Butanol **2-Bromobutane (86%)**

©2004 Thomson - Brooks/Cole



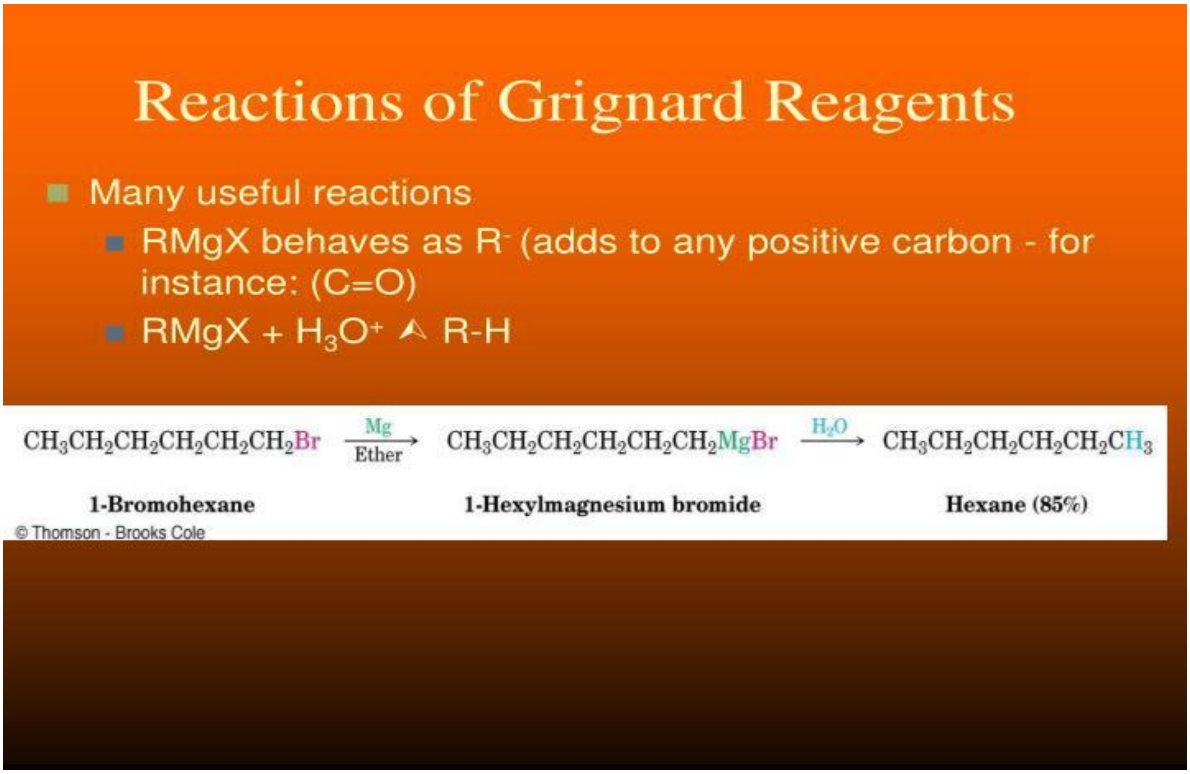
Reactions of Alkyl Halides: Grignard Reagents

- Reaction of RX with Mg in ether or THF
- Product is RMgX – an organometallic compound (alkyl-metal bond)
  - R is alkyl 1°, 2°, 3°, aryl, alkenyl
  - X = Cl, Br, I

$$CH_3CH_2CH_2CH_2CH_2CH_2Br \xrightarrow[\text{Ether}]{Mg} CH_3CH_2CH_2CH_2CH_2CH_2MgBr \xrightarrow{H_2O} CH_3CH_2CH_2CH_2CH_2CH_3$$

1-Bromohexane **1-Hexylmagnesium bromide** **Hexane (85%)**

© Thomson - Brooks Cole



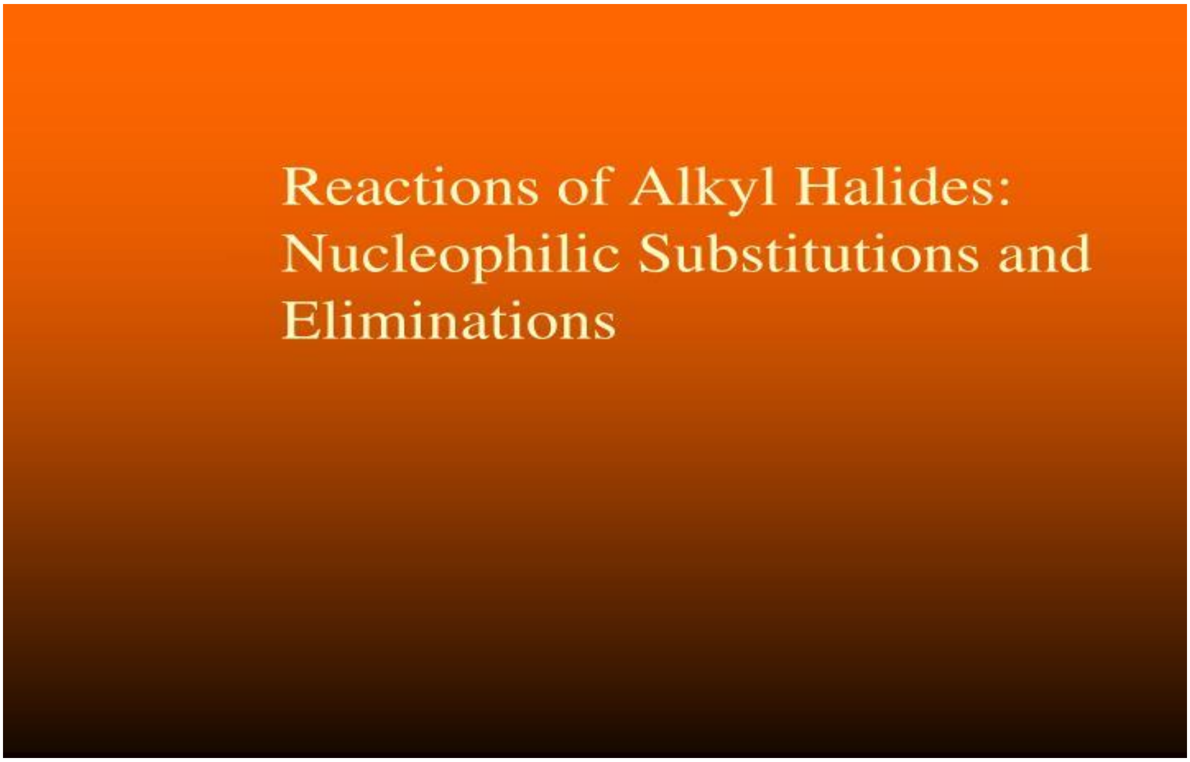
Reactions of Grignard Reagents

- Many useful reactions
  - RMgX behaves as R^- (adds to any positive carbon - for instance: (C=O)
  - $RMgX + H_3O^+$ ⮝ R-H

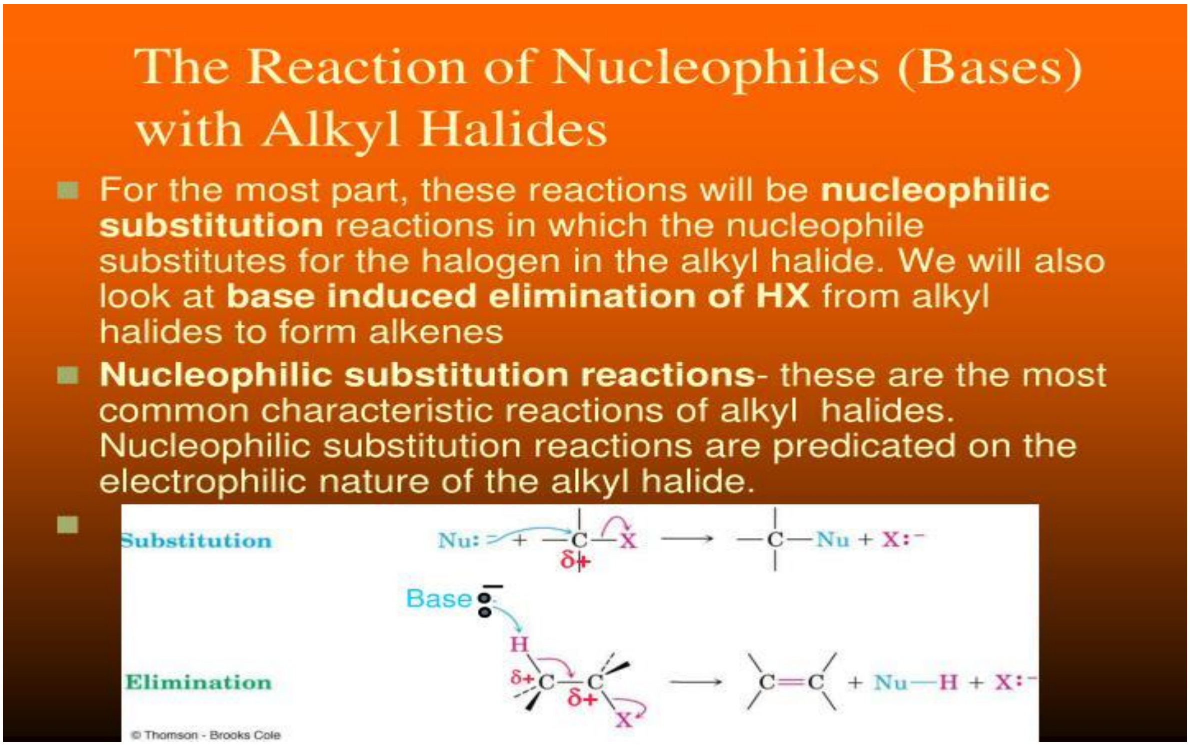
$$CH_3CH_2CH_2CH_2CH_2CH_2Br \xrightarrow[Ether]{Mg} CH_3CH_2CH_2CH_2CH_2CH_2MgBr \xrightarrow{H_2O} CH_3CH_2CH_2CH_2CH_2CH_3$$

1-Bromohexane **1-Hexylmagnesium bromide** **Hexane (85%)**

© Thomson - Brooks Cole



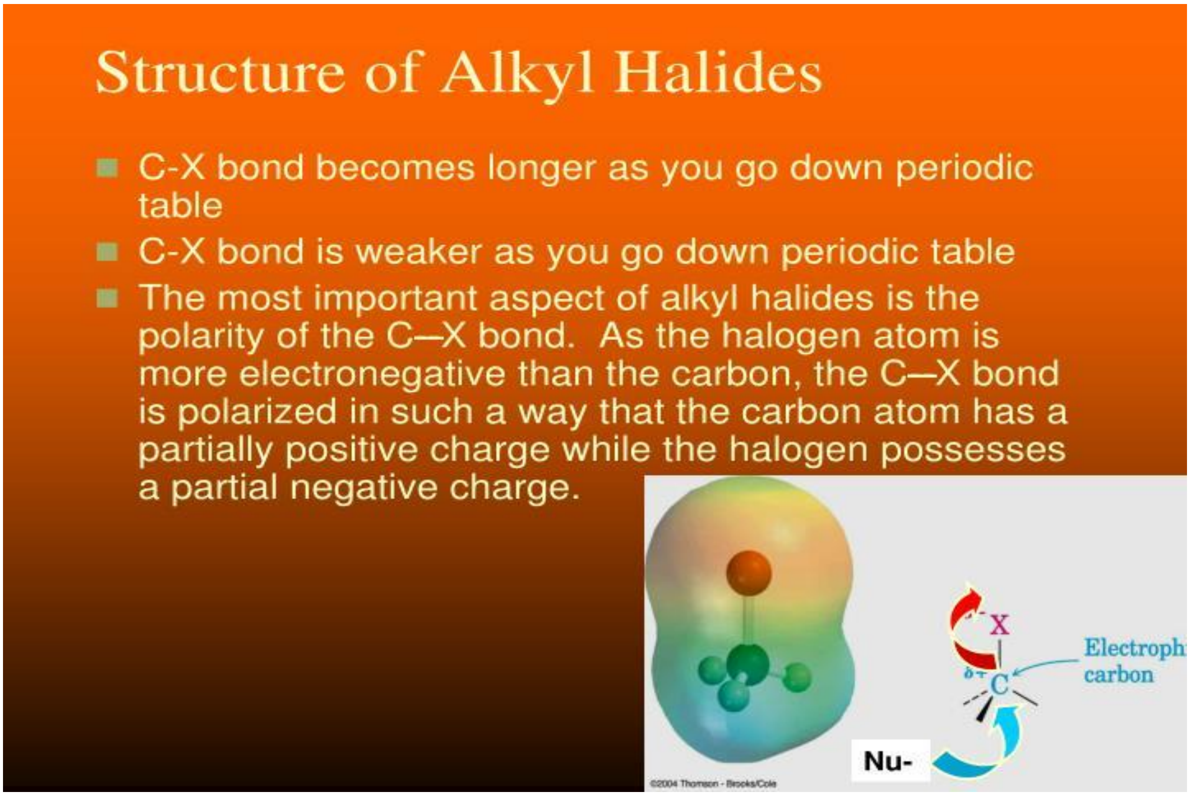
Reactions of Alkyl Halides: Nucleophilic Substitutions and Eliminations



The Reaction of Nucleophiles (Bases) with Alkyl Halides

- For the most part, these reactions will be **nucleophilic substitution** reactions in which the nucleophile substitutes for the halogen in the alkyl halide. We will also look at **base induced elimination of HX** from alkyl halides to form alkenes
- **Nucleophilic substitution reactions**- these are the most common characteristic reactions of alkyl halides. Nucleophilic substitution reactions are predicated on the electrophilic nature of the alkyl halide.
-

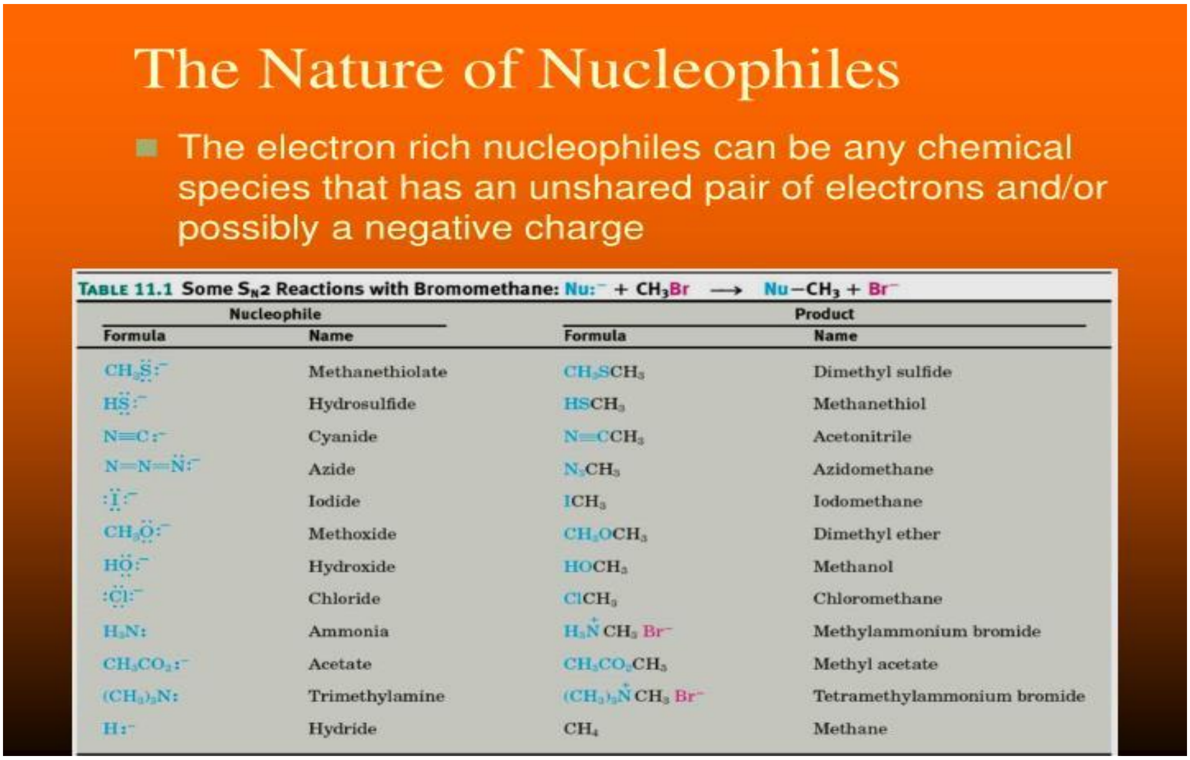
© Thomson - Brooks Cole



Structure of Alkyl Halides

- C-X bond becomes longer as you go down periodic table
- C-X bond is weaker as you go down periodic table
- The most important aspect of alkyl halides is the polarity of the C—X bond. As the halogen atom is more electronegative than the carbon, the C—X bond is polarized in such a way that the carbon atom has a partially positive charge while the halogen possesses a partial negative charge.

©2004 Thomson - Brooks/Cole

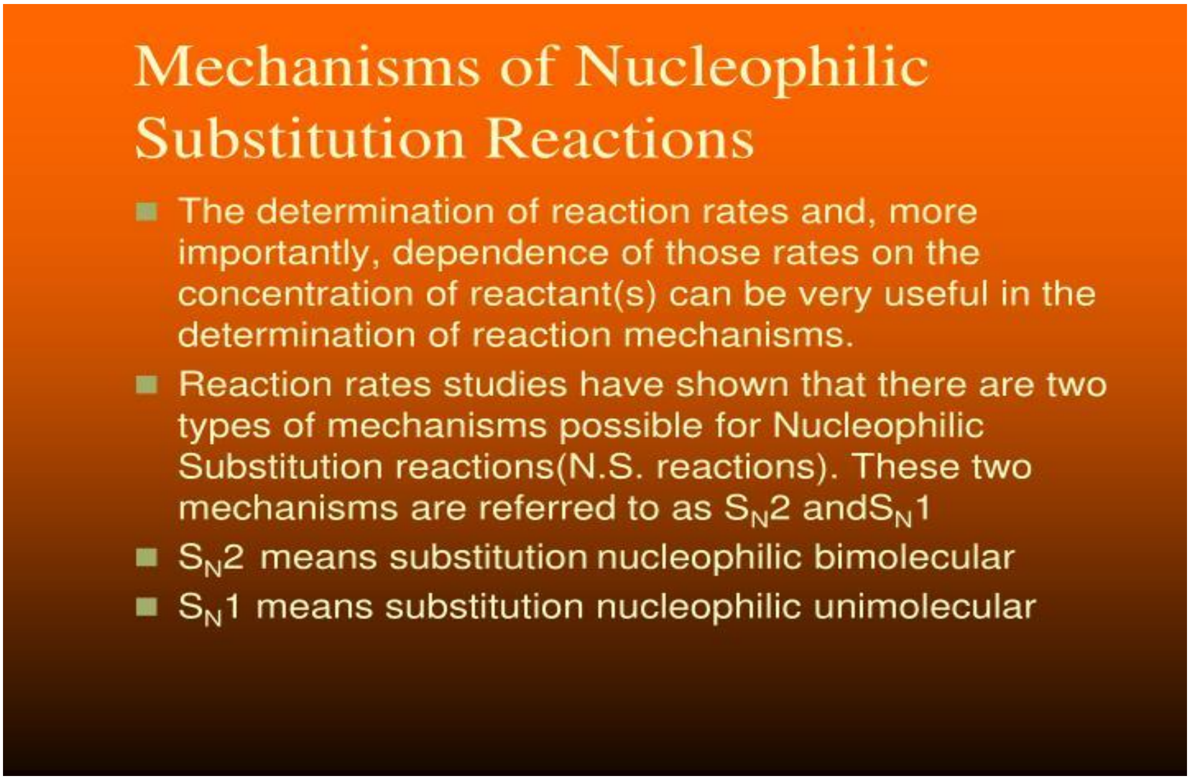


The Nature of Nucleophiles

- The electron rich nucleophiles can be any chemical species that has an unshared pair of electrons and/or possibly a negative charge

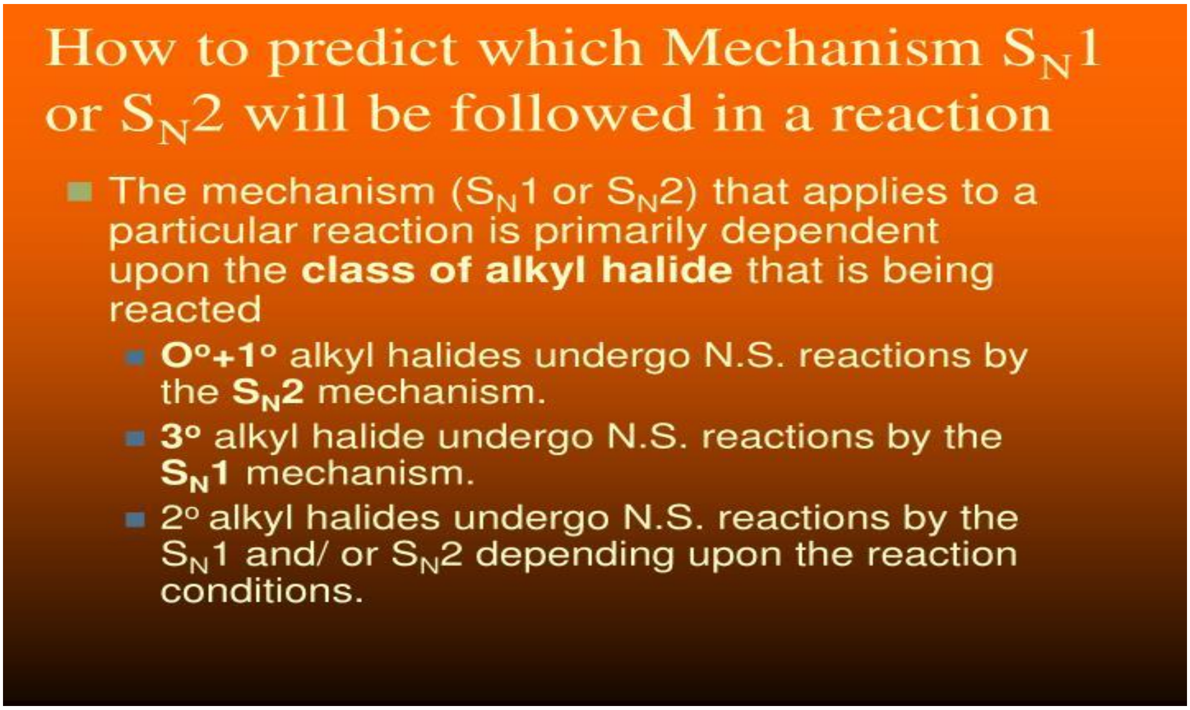
TABLE 11.1 Some S_N2 Reactions with Bromomethane: $Nu:^- + CH_3Br \longrightarrow Nu{-}CH_3 + Br^-$

Nucleophile		Product	
Formula	**Name**	**Formula**	**Name**
$CH_3\ddot{S}:^-$	Methanethiolate	CH_3SCH_3	Dimethyl sulfide
$H\ddot{S}:^-$	Hydrosulfide	$HSCH_3$	Methanethiol
$N{\equiv}C:^-$	Cyanide	$N{\equiv}CCH_3$	Acetonitrile
$N{=}N{=}\ddot{N}:^-$	Azide	N_3CH_3	Azidomethane
$:\ddot{I}:^-$	Iodide	ICH_3	Iodomethane
$CH_3\ddot{O}:^-$	Methoxide	CH_3OCH_3	Dimethyl ether
$H\ddot{O}:^-$	Hydroxide	$HOCH_3$	Methanol
$:\ddot{Cl}:^-$	Chloride	$ClCH_3$	Chloromethane
$H_3N:$	Ammonia	$H_3\overset{+}{N}CH_3\ Br^-$	Methylammonium bromide
$CH_3CO_2:^-$	Acetate	$CH_3CO_2CH_3$	Methyl acetate
$(CH_3)_3N:$	Trimethylamine	$(CH_3)_3\overset{+}{N}CH_3\ Br^-$	Tetramethylammonium bromide
$H:^-$	Hydride	CH_4	Methane



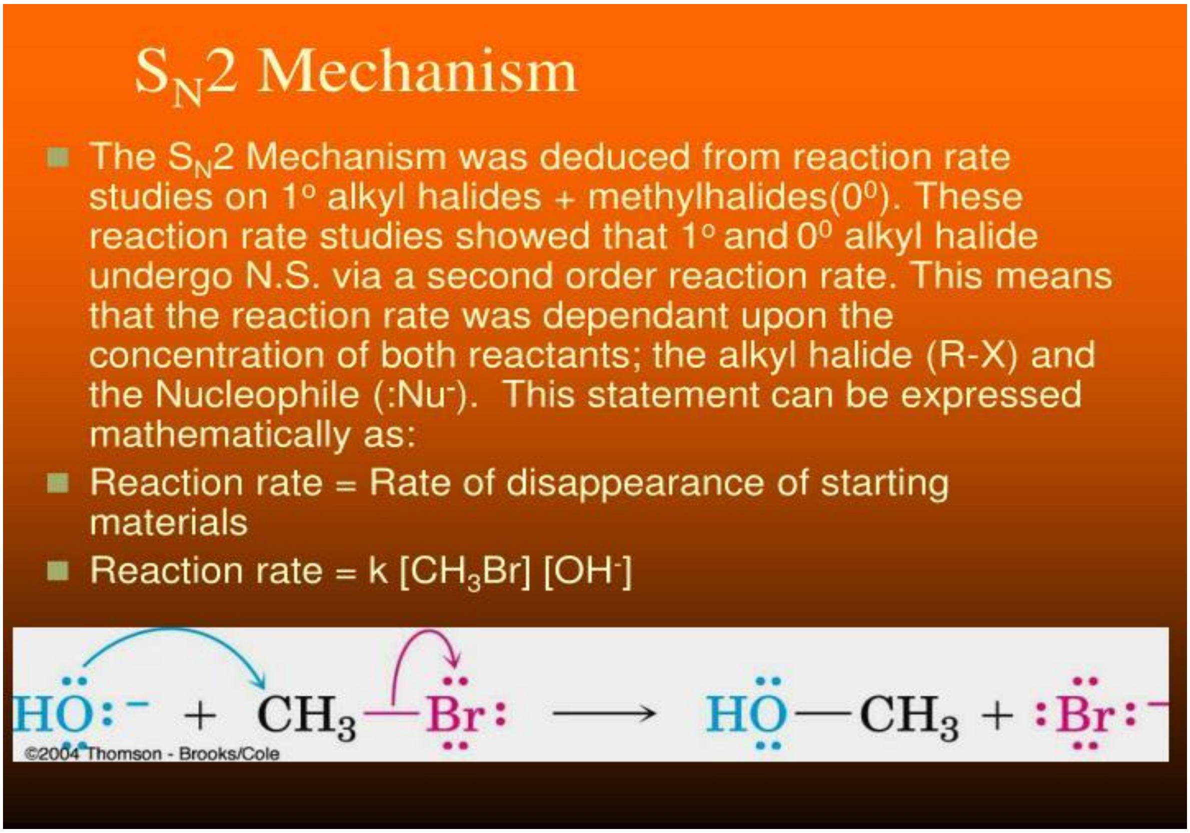
Mechanisms of Nucleophilic Substitution Reactions

- The determination of reaction rates and, more importantly, dependence of those rates on the concentration of reactant(s) can be very useful in the determination of reaction mechanisms.
- Reaction rates studies have shown that there are two types of mechanisms possible for Nucleophilic Substitution reactions(N.S. reactions). These two mechanisms are referred to as S_N2 andS_N1
- S_N2 means substitution nucleophilic bimolecular
- S_N1 means substitution nucleophilic unimolecular



How to predict which Mechanism S_N1 or S_N2 will be followed in a reaction

- The mechanism (S_N1 or S_N2) that applies to a particular reaction is primarily dependent upon the **class of alkyl halide** that is being reacted
  - **O°+1°** alkyl halides undergo N.S. reactions by the **S_N2** mechanism.
  - **3°** alkyl halide undergo N.S. reactions by the **S_N1** mechanism.
  - 2° alkyl halides undergo N.S. reactions by the S_N1 and/ or S_N2 depending upon the reaction conditions.



S_N2 Mechanism

- The S_N2 Mechanism was deduced from reaction rate studies on 1° alkyl halides + methylhalides(0°). These reaction rate studies showed that 1° and 0° alkyl halide undergo N.S. via a second order reaction rate. This means that the reaction rate was dependant upon the concentration of both reactants; the alkyl halide (R-X) and the Nucleophile ($:Nu^-$). This statement can be expressed mathematically as:
- Reaction rate = Rate of disappearance of starting materials
- Reaction rate = k $[CH_3Br]$ $[OH^-]$

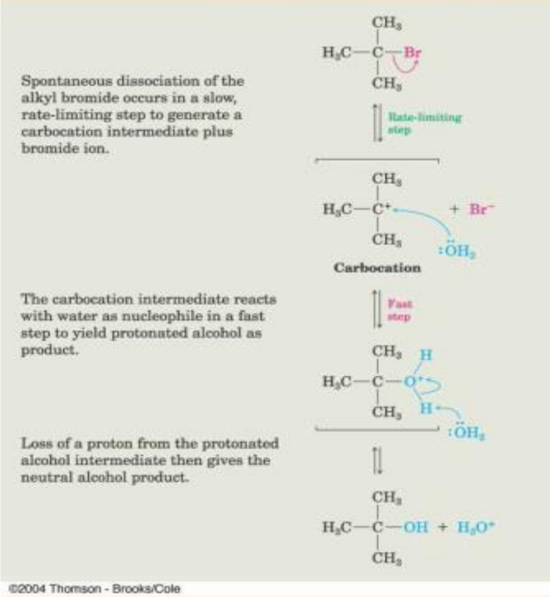
$$HO:^- + CH_3-Br: \longrightarrow HO-CH_3 + :Br:^-$$

©2004 Thomson - Brooks/Cole

The S_N1 Rxn. Mechanism

- Reaction rate studies on the nucleophilic substitution of 3° alkyl halides in **protic solvents** revealed interesting facts. The reaction rate for these reactions was a **first order process**. That is to say the reaction rate was only dependent on the concentration of **alkyl halide**. Rxn Rate = k [RX]
- **The concentration of the nucleophile does not appear in the rate expression!**
- If the concentration of alkyl halide is doubled, halfed or quadrupled the reaction rate will double, half or quadruple. If, on the other hand, the concentration of nucleophile is changed the reaction rate will be unaffected
- If the rate of this reaction does not depend upon the concentration of the Nucleophile this can only mean that:
  - 1) the reaction mechanism involves more than one step
  - 2) the slow step of the mechanism (rate determining step) does not involve the nucleophile
- These observations and assumptions indicate that the alkyl halide is involved in a unimolecular rate determining step. In other words the alkyl halide must undergo some sort of spontaneous unimolecular reaction without assistance from the nucleophilic. The mechanism shown on the following slide accounts for these kinetic observations

The S_N1 Rxn. Mechanism

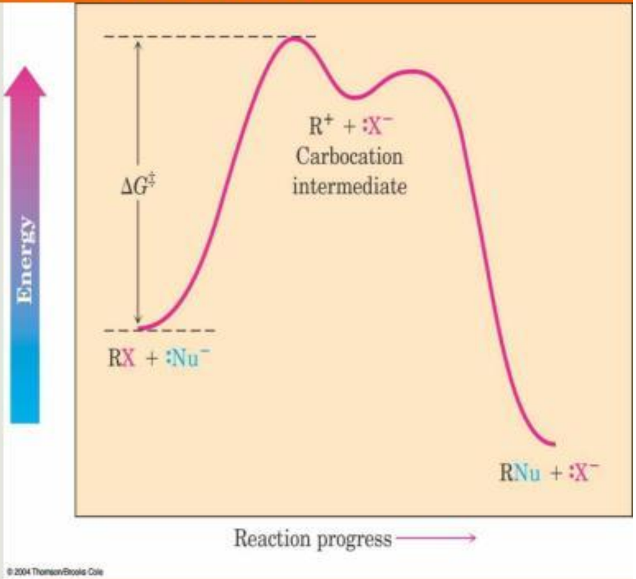


Spontaneous dissociation of the alkyl bromide occurs in a slow, rate-limiting step to generate a carbocation intermediate plus bromide ion.

The carbocation intermediate reacts with water as nucleophile in a fast step to yield protonated alcohol as product.

Loss of a proton from the protonated alcohol intermediate then gives the neutral alcohol product.

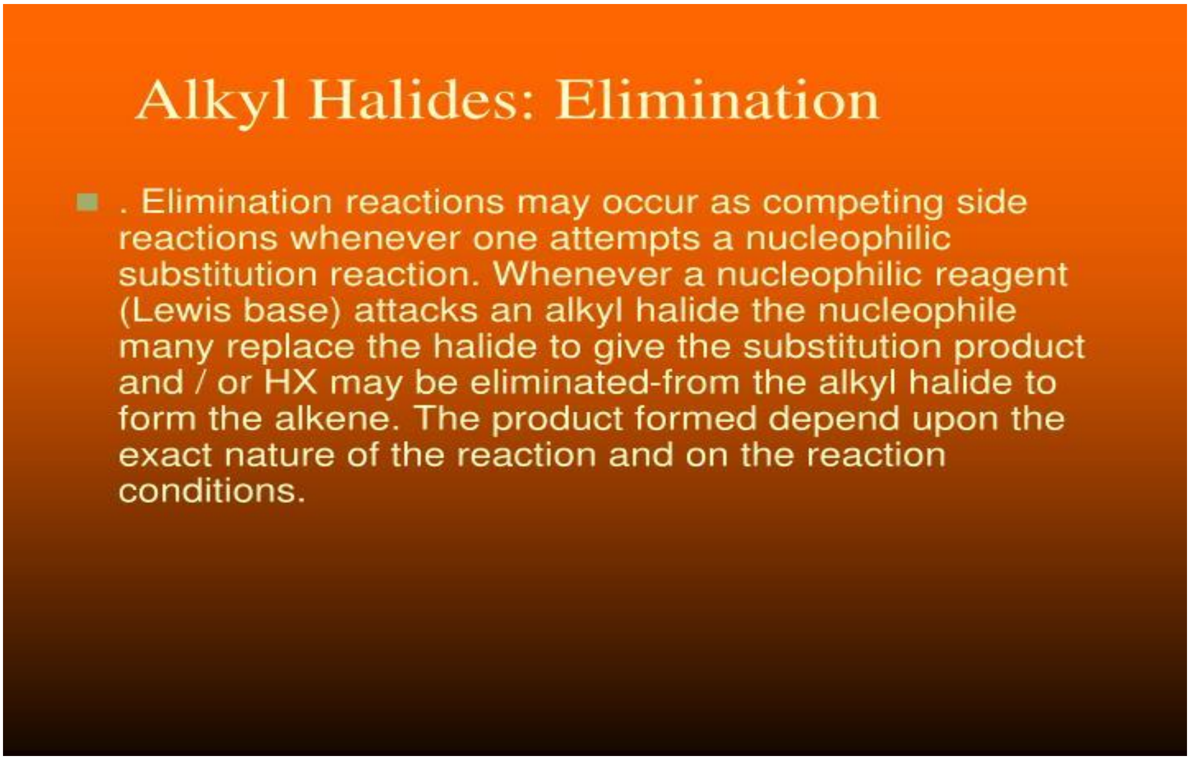
©2004 Thomson - Brooks/Cole



© 2004 Thomson/Brooks Cole

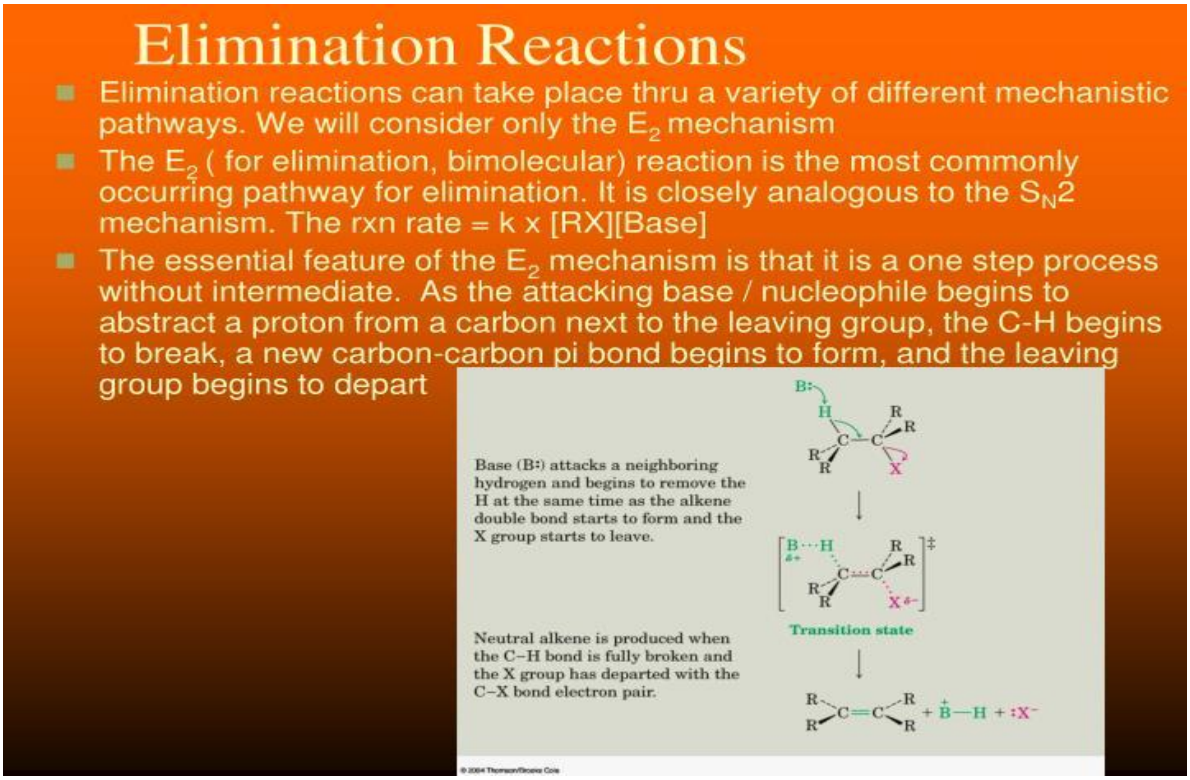
. This mechanism is referred to as " Substitution Nucleophic Unimolecular or S_N1".

The term unimolecule relates to the fact that the slow step (rate determining step) involves only one molecule, the alkyl halide.



Alkyl Halides: Elimination

- . Elimination reactions may occur as competing side reactions whenever one attempts a nucleophilic substitution reaction. Whenever a nucleophilic reagent (Lewis base) attacks an alkyl halide the nucleophile many replace the halide to give the substitution product and / or HX may be eliminated-from the alkyl halide to form the alkene. The product formed depend upon the exact nature of the reaction and on the reaction conditions.



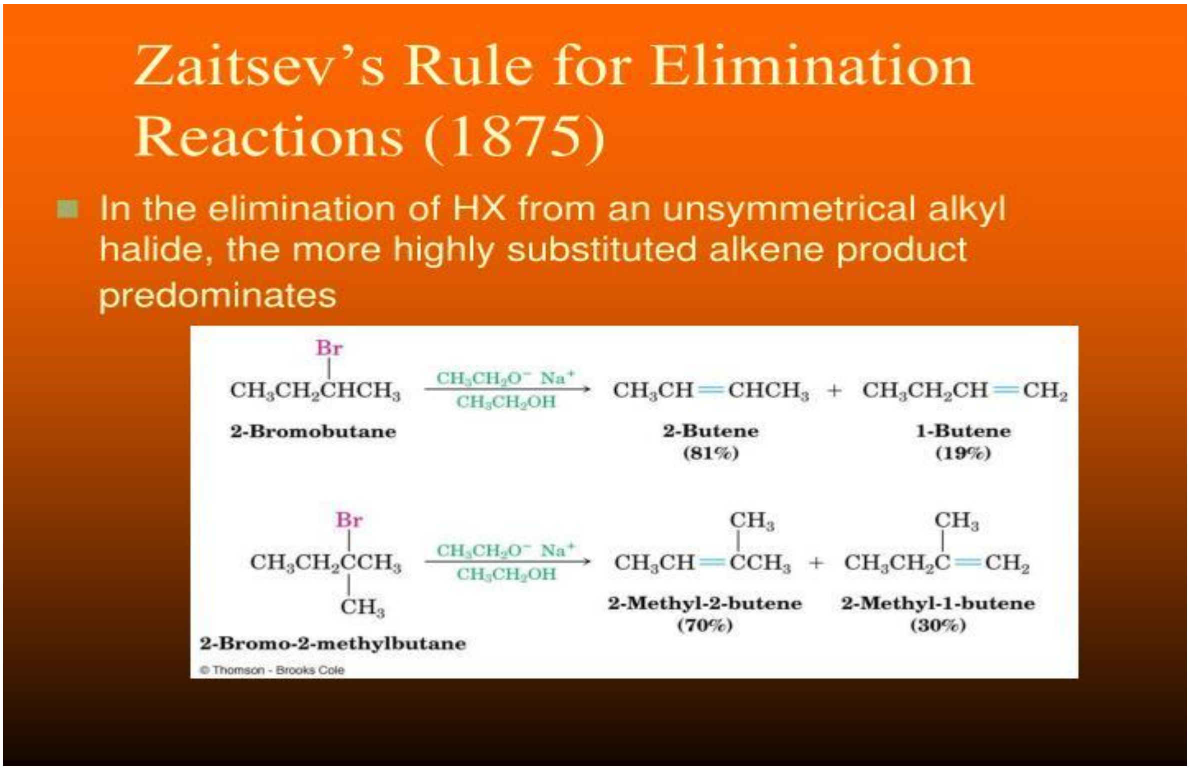
Elimination Reactions

- Elimination reactions can take place thru a variety of different mechanistic pathways. We will consider only the E_2 mechanism
- The E_2 (for elimination, bimolecular) reaction is the most commonly occurring pathway for elimination. It is closely analogous to the S_N2 mechanism. The rxn rate = k x [RX][Base]
- The essential feature of the E_2 mechanism is that it is a one step process without intermediate. As the attacking base / nucleophile begins to abstract a proton from a carbon next to the leaving group, the C-H begins to break, a new carbon-carbon pi bond begins to form, and the leaving group begins to depart

Base (B:) attacks a neighboring hydrogen and begins to remove the H at the same time as the alkene double bond starts to form and the X group starts to leave.

Neutral alkene is produced when the C–H bond is fully broken and the X group has departed with the C–X bond electron pair.

© 2004 Thomson/Brooks Cole



Zaitsev's Rule for Elimination Reactions (1875)

- In the elimination of HX from an unsymmetrical alkyl halide, the more highly substituted alkene product predominates

$$CH_3CH_2\overset{Br}{C}HCH_3 \xrightarrow[CH_3CH_2OH]{CH_3CH_2O^-\ Na^+} CH_3CH{=}CHCH_3 + CH_3CH_2CH{=}CH_2$$

2-Bromobutane **2-Butene** **(81%)** **1-Butene** **(19%)**

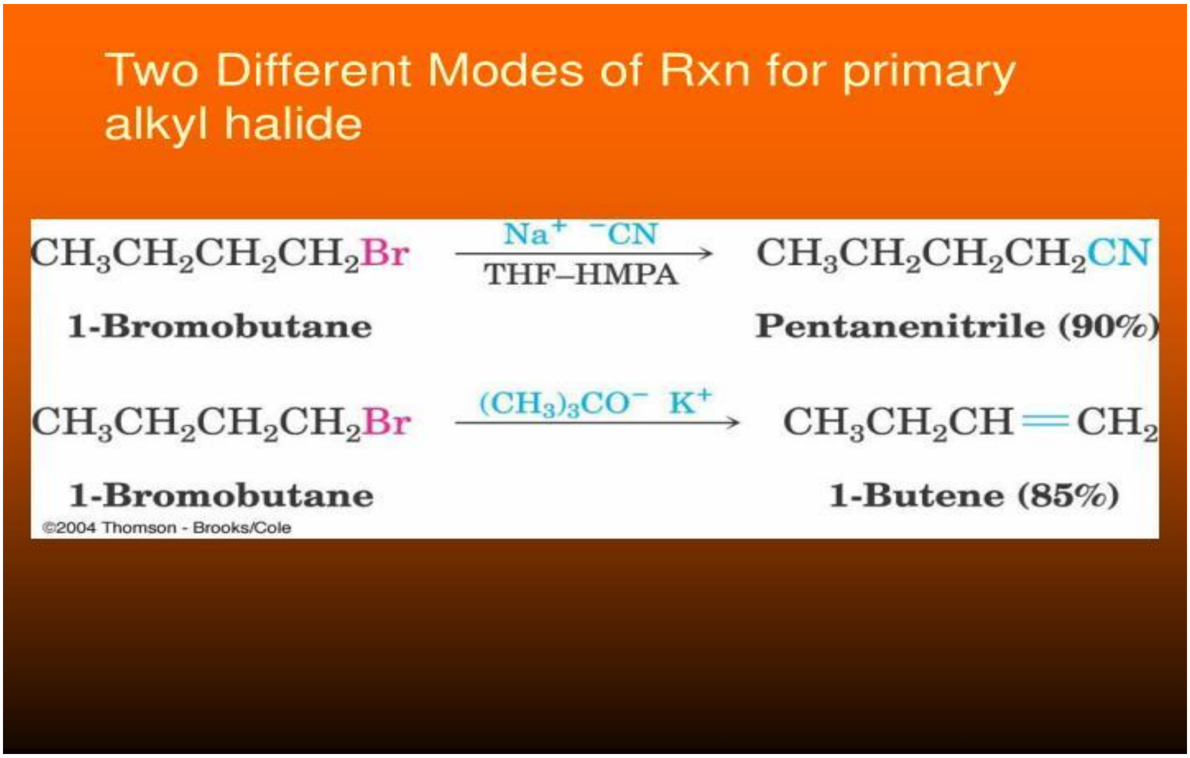
$$CH_3CH_2\underset{CH_3}{\overset{Br}{C}}CH_3 \xrightarrow[CH_3CH_2OH]{CH_3CH_2O^-\ Na^+} CH_3CH{=}\overset{CH_3}{C}CH_3 + CH_3CH_2\overset{CH_3}{C}{=}CH_2$$

2-Bromo-2-methylbutane **2-Methyl-2-butene** **(70%)** **2-Methyl-1-butene** **(30%)**

© Thomson - Brooks Cole

Summary of Reactivity SN^1,SN^2, E$_2$

- We have examined three possible modes of reactions between an alkyl halide and a base / nucleophile, and you may well wonder how to predict what will happen in any given case. While it is difficult to provide definite answers there are some valuable generalization about what to expect
  - 1. Primary alkyl halides react by either S$_N$2 or E$_2$ mechanisms. The S$_N$2 mechanism is highly favored under most conditions. The E$_2$ mechanism is favored only when the nucleophile is a strong bulky base such as t-butoxide. T-butoxide is a strong base because it readily reacts with a proton to form t-butanol but it is too bulky to act as an SN^2 nucleophile In such cases nucleophilic substitution (S$_N$2) discouraged as bulk of the nucleophile prohibits an effective back side attack. Potassium t-butoxide is $(CH_3)_3CO^- K^+$
  - See next slide for example rxn



Two Different Modes of Rxn for primary alkyl halide

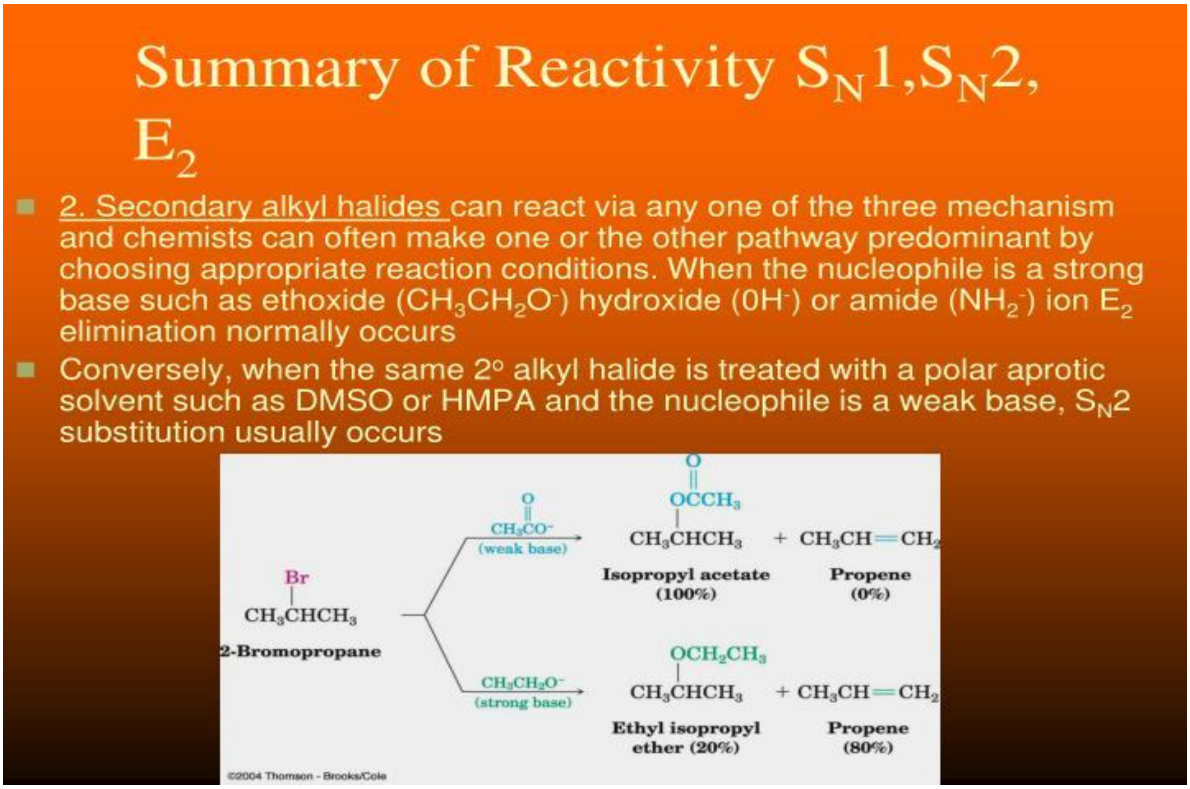
$$CH_3CH_2CH_2CH_2Br \xrightarrow[\text{THF–HMPA}]{Na^+ \ {}^-CN} CH_3CH_2CH_2CH_2CN$$

1-Bromobutane **Pentanenitrile (90%)**

$$CH_3CH_2CH_2CH_2Br \xrightarrow{(CH_3)_3CO^- \ K^+} CH_3CH_2CH{=}CH_2$$

1-Bromobutane **1-Butene (85%)**

©2004 Thomson - Brooks/Cole



Summary of Reactivity S_N1, S_N2, E_2

- 2. Secondary alkyl halides can react via any one of the three mechanism and chemists can often make one or the other pathway predominant by choosing appropriate reaction conditions. When the nucleophile is a strong base such as ethoxide ($CH_3CH_2O^-$) hydroxide ($0H^-$) or amide (NH_2^-) ion E_2 elimination normally occurs
- Conversely, when the same 2° alkyl halide is treated with a polar aprotic solvent such as DMSO or HMPA and the nucleophile is a weak base, S_N2 substitution usually occurs

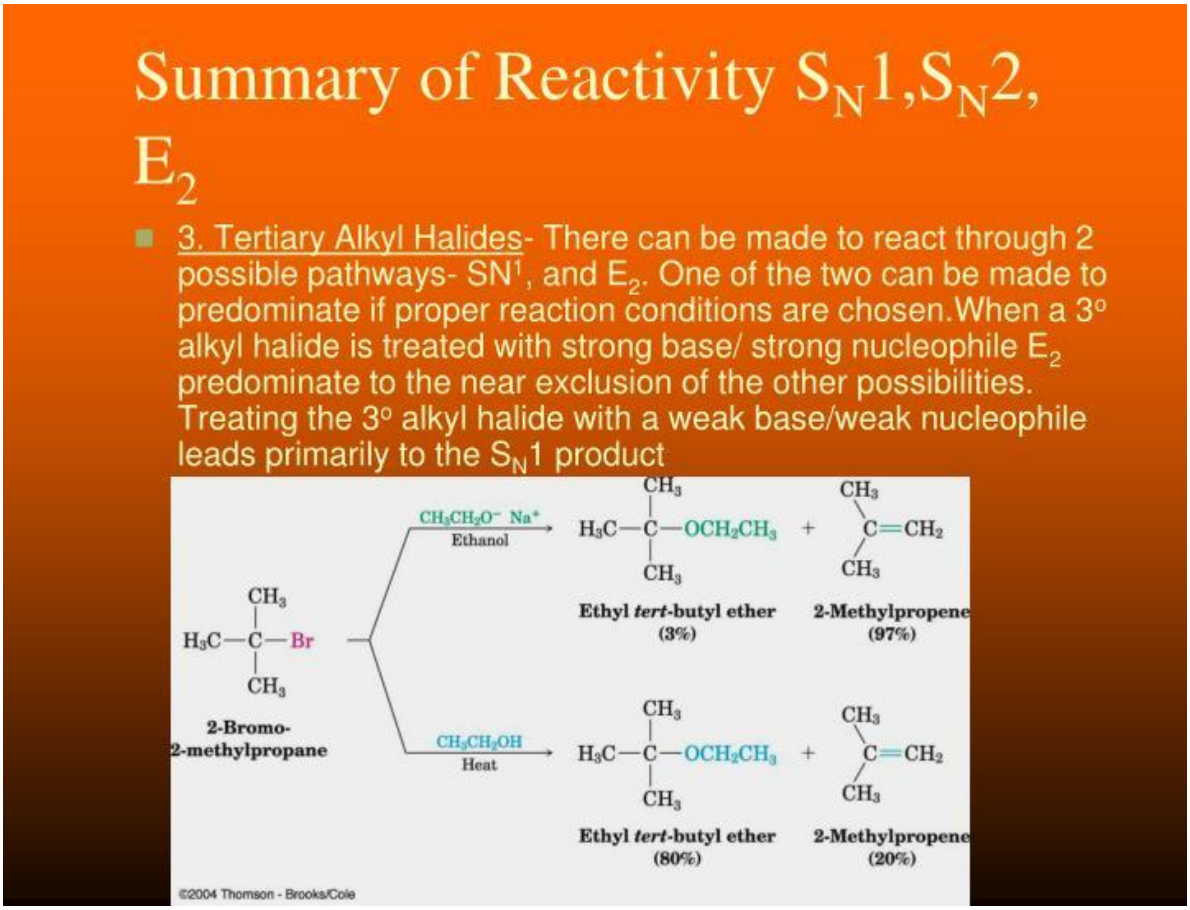
$$\overset{Br}{\overset{|}{CH_3CHCH_3}} \xrightarrow[\text{(weak base)}]{CH_3\overset{O}{\overset{\|}{C}}O^-} \overset{O\overset{O}{\overset{\|}{C}}CH_3}{\overset{|}{CH_3CHCH_3}} + CH_3CH{=}CH_2$$

2-Bromopropane **Isopropyl acetate (100%)** **Propene (0%)**

$$\overset{Br}{\overset{|}{CH_3CHCH_3}} \xrightarrow[\text{(strong base)}]{CH_3CH_2O^-} \overset{OCH_2CH_3}{\overset{|}{CH_3CHCH_3}} + CH_3CH{=}CH_2$$

Ethyl isopropyl ether (20%) **Propene (80%)**

©2004 Thomson - Brooks/Cole



Summary of Reactivity S_N1, S_N2, E_2

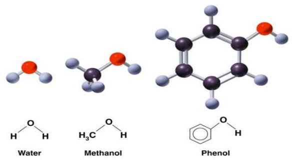
- <u>3. Tertiary Alkyl Halides</u>- There can be made to react through 2 possible pathways- SN^1, and E_2. One of the two can be made to predominate if proper reaction conditions are chosen.When a 3° alkyl halide is treated with strong base/ strong nucleophile E_2 predominate to the near exclusion of the other possibilities. Treating the 3° alkyl halide with a weak base/weak nucleophile leads primarily to the S_N1 product

©2004 Thomson - Brooks/Cole

Alcohols, Phenols and Ethers

- **Alcohols, phenols and ethers** may be viewed as organic *derivatives of water*.
- **Alcohols and phenols** have a common functional group, *the hydroxyl group, -OH*.

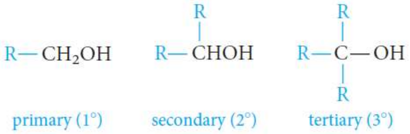
H-O-H	**R-O-H**	**Ar-O-H**	**R-O-R**	**R-O-Ar**	**Ar-O-Ar**
Water	**Alcohol**	**Phenol**		**Ether**	



- **Alcohols** are compounds whose molecules have a hydroxyl group attached to a *saturated* carbon atom.
- **Phenols** are compounds that have a hydroxyl group attached directly to a ***benzene ring .***
- **Ethers** are compounds whose molecules have an oxygen atom bonded to two carbon atom.

Classification of Alcohols and Ethers

- **Alcohols** are classified as primary (1°), secondary (2°), or tertiary (3°), depending on whether one, two, or three organic groups are connected to the hydroxyl-bearing carbon atom.



$R-CH_2OH$ primary (1°)

R_2CHOH secondary (2°)

R_3C-OH tertiary (3°)

  - ***Methyl alcohol****, which is not strictly covered by this classification, is usually grouped with the primary alcohols.*

- **Ethers are classified as**
  - **Symmetrical ethers;**

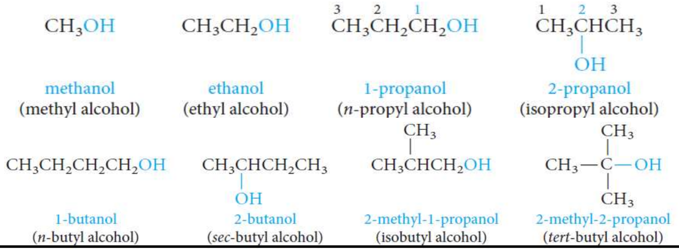
    When the organic groups attached to the oxygen are identical.
  - **Unsymmetrical ethers** (*mixed ethers*)**;**

    When the organic groups attached to the oxygen are different.

Nomenclature of Alcohols

- The **common names** for the simplest alcohols consist of alkyl group attached to the hydroxyl function followed by the word alcohol: Alkyl *alcohol* .
- In the **IUPAC system**, alcohols are named according to the following rules.
  1. Select the longest continuous carbon chain that *contains the* -OH *group*.

     Drop the –e ending of the parent alkane and replace it by the suffix *-ol*: *Alkanol*
  2. When isomers are possible, the chain is numbered so as to give the functional group (-OH) the *lowest possible number*.



CH_3OH methanol (methyl alcohol)

CH_3CH_2OH ethanol (ethyl alcohol)

$CH_3CH_2CH_2OH$ 1-propanol (*n*-propyl alcohol)

$CH_3CH(OH)CH_3$ 2-propanol (isopropyl alcohol)

$CH_3CH_2CH_2CH_2OH$ 1-butanol (*n*-butyl alcohol)

$CH_3CH(OH)CH_2CH_3$ 2-butanol (*sec*-butyl alcohol)

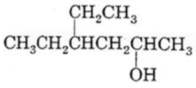
$CH_3CH(CH_3)CH_2OH$ 2-methyl-1-propanol (isobutyl alcohol)

$(CH_3)_3C-OH$ 2-methyl-2-propanol (*tert*-butyl alcohol)

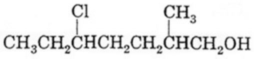
Nomenclature of Alcohols

3. When alkyl side chains or other groups are present; they are named alphabetically and their positions are indicated by a number.

The position of the functional group (-OH) is always given the lowest possible number at the end of the name.

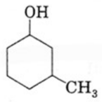

$CH_3CH_2\overset{CH_2CH_3}{\overset{|}{C}}HCH_2\underset{OH}{\underset{|}{C}}HCH_3$

4-Ethyl-2-hexanol
(*not* 3-Ethyl-5-hexanol)

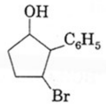

$CH_3CH_2\overset{Cl}{\overset{|}{C}}HCH_2CH_2\overset{CH_3}{\overset{|}{C}}HCH_2OH$

5-Chloro-2-methyl-1-heptanol
(*not* 3-Chloro-6-methyl-7-heptanol)

For cyclic alcohols, numbering always starts from the carbon bearing the -OH group.



3-Methylcyclohexanol
(*not* 1-Methyl-3-cyclohexanol)



3-Bromo-2-phenylcyclopentanol
(*not* 1-Bromo-2-phenyl-3-cyclopentanol)

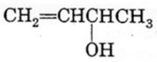
Nomenclature of Alcohols

4. With Unsaturated Alcohols; If a molecule contains both an -OH group and a C=C or C-C triple bond, the -OH group takes preference before the double or triple bonds in getting the lower number.

The name should include (if possible) both the hydroxyl and the unsaturated groups, even if this does not make the longest chain the parent hydrocarbon.

$CH_2{=}CHCH_2OH$

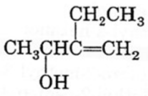
2-propen-1-ol
(allyl alcohol)


$CH_2{=}CH\underset{OH}{\underset{|}{C}}HCH_3$

3-Buten-2-ol
(*not* 1-Buten-3-ol)

$HC{\equiv}CCH_2CH_2OH$

3-Butyn-1-ol
(*not* 1-Butyn-4-ol)

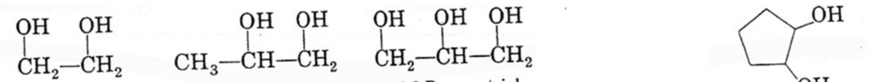

$CH_3\underset{OH}{\underset{|}{C}}H\overset{CH_2CH_3}{\overset{|}{C}}{=}CH_2$

3-Ethyl-3-buten-2-ol
(longest chain including C=C)

Nomenclature of Alcohols

○ Alcohols with More Than One Hydroxyl Group

- ➢ Compounds with two adjacent alcohol groups are called *glycols*.
  The most important example is ethylene glycol.
- ➢ Compounds with more than two hydroxyl groups are also known, and several, such as glycerol and sorbitol, are important commercial chemicals.



$\overset{OH}{CH_2}-\overset{OH}{CH_2}$ $\quad CH_3-\overset{OH}{CH}-\overset{OH}{CH_2}$ $\quad \overset{OH}{CH_2}-\overset{OH}{CH}-\overset{OH}{CH_2}$

IUPAC name:	1,2-Ethanediol	1,2-Propanediol	1,2,3-Propanetriol	IUPAC name:	1,2-Cyclopentanediol
Common name:	Ethylene glycol	Propylene glycol	Glycerol or Glycerin		

- *Ethylene glycol is used as the "permanent" antifreeze in automobile radiators and as a raw material in the manufacture of Dacron.*
- *Ethylene glycol is completely miscible with water.*
- *Glycerol is a syrupy, colorless, water-soluble, high-boiling liquid with a distinctly sweet taste. Its soothing qualities make it useful in shaving and toilet soaps and in cough drops and syrups.*

Physical Properties of Alcohols and Ethers

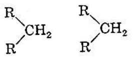
Physical State

- *The simplest alcohol, methanol, is a liquid at room temperature.*
  In contrast, alkanes from methane to butane are gases.
- Phenol is a colorless, crystalline, and low-melting solid and other phenols also are solids, .
- Ethers are colorless compounds with characteristic, relatively pleasant odors.

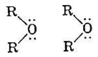
Boiling Points

- *Ethers have lower boiling points (bp's) than alcohols with an equal number of carbon atoms.*
- Ether has nearly the same b.p. as the corresponding hydrocarbon in which a -CH_2- group replaces the ether's oxygen.

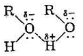
Because of their structures (no O-H bonds), ether molecules cannot form hydrogen bonds with one another.



Alkanes: No hydrogen bonding between molecules; low boiling points



Ethers: No hydrogen bonding between molecules; low boiling points



Alcohols: Hydrogen bonding between molecules; high boiling points

Compound	Formula	bp	mol wt	Water solubility (g/100 mL, 20°C)
1-butanol	$CH_3CH_2CH_2CH_2OH$	118°C	74	7.9
diethyl ether	$CH_3CH_2—O—CH_2CH_3$	35°C	74	7.5
pentane	$CH_3CH_2—CH_2—CH_2CH_3$	36°C	72	0.03

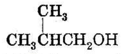
Physical Properties of Alcohols and Ethers

Boiling Points

- *Series of normal alcohols; The boiling points increase with increasing molecular weights.*
- *A comparison of boiling points among isomeric alcohols; The boiling points decrease as the number of alkyl branches from the carbinol group increases.*

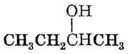
$CH_3CH_2CH_2CH_2OH$

1-Butanol
(mol wt = 74; bp = 118°C)



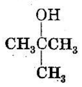
$CH_3\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_2OH$

2-Methyl-1-propanol
(mol wt = 74; bp = 108°C)



$CH_3CH_2\overset{\overset{\displaystyle OH}{|}}{C}HCH_3$

2-Butanol
(mol wt = 74; bp = 99.5°C)



$CH_3\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}CH_3$

2-Methyl-2-propanol
(mol wt = 74; bp = 83°C)

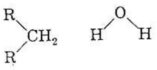
- Phenol and most other phenols have high boiling points.

Physical Properties of Alcohols and Ethers

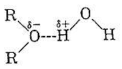
Solubility

- *The lower alcohols are completely miscible with water.*
- *As the number of carbons in the alcohol increases, the solubility in water decreases.*
- Low-molecular-weight ethers, such as dimethyl ether, are quite soluble in water.

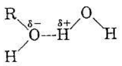
Ether molecules can form hydrogen bonds to water.



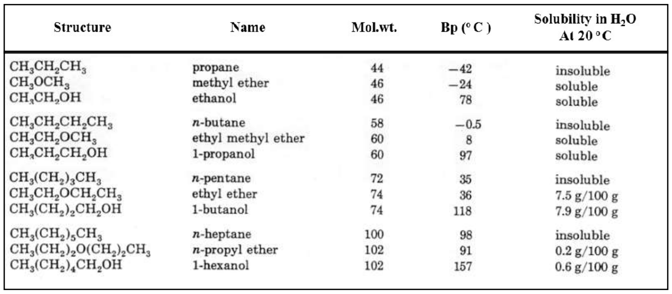
Alkanes: No hydrogen bonding with water; insoluble



Ethers: Hydrogen bonding with water; soluble



Alcohols: Hydrogen bonding with water; soluble



Structure	Name	Mol.wt.	Bp (° C)	Solubility in H_2O At 20 °C
$CH_3CH_2CH_3$	propane	44	−42	insoluble
CH_3OCH_3	methyl ether	46	−24	soluble
CH_3CH_2OH	ethanol	46	78	soluble
$CH_3CH_2CH_2CH_3$	*n*-butane	58	−0.5	insoluble
$CH_3CH_2OCH_3$	ethyl methyl ether	60	8	soluble
$CH_3CH_2CH_2OH$	1-propanol	60	97	soluble
$CH_3(CH_2)_3CH_3$	*n*-pentane	72	35	insoluble
$CH_3CH_2OCH_2CH_3$	ethyl ether	74	36	7.5 g/100 g
$CH_3(CH_2)_2CH_2OH$	1-butanol	74	118	7.9 g/100 g
$CH_3(CH_2)_5CH_3$	*n*-heptane	100	98	insoluble
$CH_3(CH_2)_2O(CH_2)_2CH_3$	*n*-propyl ether	102	91	0.2 g/100 g
$CH_3(CH_2)_4CH_2OH$	1-hexanol	102	157	0.6 g/100 g

- Phenol and most other phenols are slightly soluble in water .

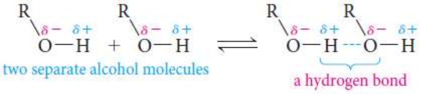
Hydrogen Bonding in Alcohols and Ethers

- The **boiling points** (bp's) of alcohols are much higher than those of ethers or hydrocarbons with similar molecular weights.

	CH_3CH_2OH	CH_3OCH_3	$CH_3CH_2CH_3$
mol wt	46	46	44
bp	+78.5°C	−24°C	−42°C

Why? Because alcohols form *hydrogen bonds* with one another.

The O-H bond is polarized by the high electronegativity of the oxygen atom and places a partial positive charge on the hydrogen atom and a partial negative charge on the oxygen atom.

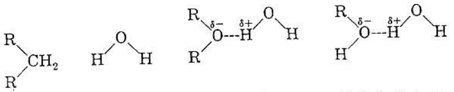


Two or more alcohol molecules thus become loosely bonded to one another through hydrogen bonds.

- Consequently, alcohols have relatively high boiling points because they must supply enough heat to break the hydrogen bonds before each molecule.
- Hydrogen bonds are weaker than ordinary covalent bonds.

Hydrogen Bonding in Alcohols and Ethers

- The lower molecular-weight alcohols and ethers can form H-bond with water molecules.
- This accounts for the complete miscibility of the lower alcohols and ethers with water.



Alkanes: No hydrogen bonding with water; insoluble

Ethers: Hydrogen bonding with water; soluble

Alcohols: Hydrogen bonding with water; soluble

- However, as the organic chain lengthens and the alcohol becomes relatively more hydrocarbon like, its water solubility decreases.

Table 7.1 Boiling Point and Water Solubility of Some Alcohols

Name	Formula	bp, °C	Solubility in H_2O g/100 g at 20°C
methanol	CH_3OH	65	completely miscible
ethanol	CH_3CH_2OH	78.5	completely miscible
1-propanol	$CH_3CH_2CH_2OH$	97	completely miscible
1-butanol	$CH_3CH_2CH_2CH_2OH$	117.7	7.9
1-pentanol	$CH_3CH_2CH_2CH_2CH_2OH$	137.9	2.7
1-hexanol	$CH_3CH_2CH_2CH_2CH_2CH_2OH$	155.8	0.59

The Acidity of Alcohols and Phenols

- **Like water, alcohols and phenols are weak acids.**

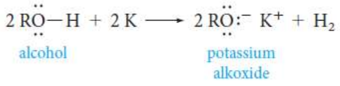
  The hydroxyl group can act as a proton donor, and dissociation occurs in a manner similar to that for water

$$\underset{\substack{\text{Alcohol}\\\text{as acid}}}{\mathrm{RO{-}\mathbf{H}}} + \mathrm{Base} \longrightarrow \underset{\substack{\text{Alkoxide ion}\\\text{(conjugate base}\\\text{of alcohol)}}}{\mathrm{RO}{:}^{-}} + \mathrm{Base{-}\mathbf{H}}$$

$$\underset{\substack{\text{Phenol}\\\text{as acid}}}{\mathrm{ArO{-}\mathbf{H}}} + \mathrm{Base} \longrightarrow \underset{\substack{\text{Phenoxide ion}\\\text{(conjugate base}\\\text{of phenol)}}}{\mathrm{ArO}{:}^{-}} + \mathrm{Base{-}\mathbf{H}}$$

The Acidity of Alcohols and Phenols

- **Alkoxides**, the conjugate bases of alcohols, can be prepared by the reaction of an alcohol with sodium or potassium metal.



$$2\,R\ddot{\underset{..}{O}}{-}H + 2\,K \longrightarrow 2\,R\ddot{\underset{..}{O}}{:}^{-}\;K^{+} + H_2$$

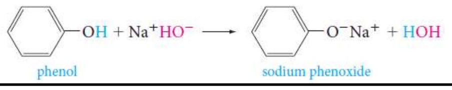
alcohol — potassium alkoxide

- Treatment of alcohols with sodium hydroxide does not convert them to their alkoxides.

This is because alkoxides are stronger bases than hydroxide ion, so the reaction goes in the reverse direction. Since alcohols are weaker acids than water, it is not possible to form the salt of an alcohol in aqueous alkaline solutions.

- Treatment of phenols with sodium hydroxide converts them to phenoxide ions.

$$ROH + Na^{+}HO^{-} \not\rightleftharpoons RO^{-}Na^{+} + H_2O$$

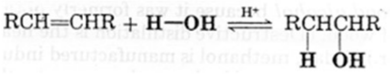


phenol — sodium phenoxide

Preparation of Alcohols

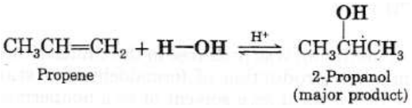
1. Hydration of Alkenes

a. Addition of water to a double bond in the presence of an *acid catalyst, H^+*.



$$RCH{=}CHR + H{-}OH \overset{H^+}{\rightleftharpoons} \underset{H}{RCH}\underset{OH}{CHR}$$

b. The addition follows *Markovnikov's rule*.



$$CH_3CH{=}CH_2 + H{-}OH \overset{H^+}{\rightleftharpoons} CH_3\overset{OH}{C}HCH_3$$

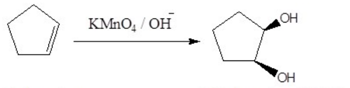
Propene

2-Propanol (major product)

c. *It is not possible to prepare primary alcohols* except Ethanol.

2. Oxidation of Cycloalkenes

Alkenes react with alkaline potassium permanganate to form glycols.

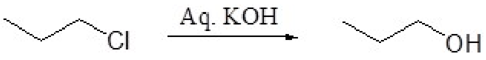


Cyclopentene

cis-Cyclopentane-1,2-diol

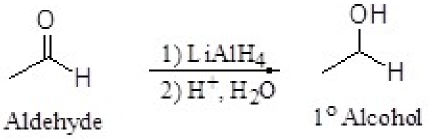
Preparation of Alcohols

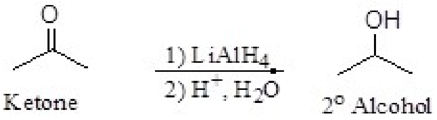
- ***Nucleophilic Substitution of Alkyl Halide***



- ***Reduction of Ketones, and Aldehydes***

Aldehydes and ketones are easily reduced to primary and secondary alcohols, respectively.

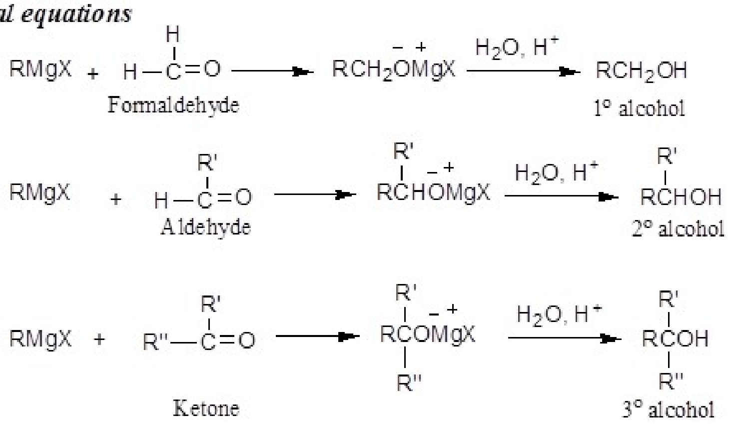




Preparation of Alcohols

- *Addition of Grignard's Reagent to Aldehydes and Ketones*

General equations



$$RMgX + \underset{\text{Formaldehyde}}{H-\overset{H}{\overset{|}{C}}=O} \longrightarrow RCH_2\overset{-}{O}\overset{+}{Mg}X \xrightarrow{H_2O,\ H^+} \underset{1^\circ\ \text{alcohol}}{RCH_2OH}$$

$$RMgX + \underset{\text{Aldehyde}}{H-\overset{R'}{\overset{|}{C}}=O} \longrightarrow R\overset{R'}{\overset{|}{C}}H\overset{-}{O}\overset{+}{Mg}X \xrightarrow{H_2O,\ H^+} \underset{2^\circ\ \text{alcohol}}{R\overset{R'}{\overset{|}{C}}HOH}$$

$$RMgX + \underset{\text{Ketone}}{R''-\overset{R'}{\overset{|}{C}}=O} \longrightarrow R\underset{R''}{\underset{|}{\overset{R'}{\overset{|}{C}}}}\overset{-}{O}\overset{+}{Mg}X \xrightarrow{H_2O,\ H^+} \underset{3^\circ\ \text{alcohol}}{R\underset{R''}{\underset{|}{\overset{R'}{\overset{|}{C}}}}OH}$$

Reactions of Alcohols, Phenols and Ethers

- **Alcohols** undergo two kinds of reactions:
  - Those that involve the breaking of the oxygen-hydrogen bond (CO-H).
  - Those that involve the rupture of the carbon-oxygen bond (C-OH).
- **Phenols** do not participate in reactions where the C-OH bond is broken.
- **Ethers** are quite stable compounds.
  - The ether linkage does not react with bases, reducing agents, oxidizing agents, or active metals.
  - *Ethers react only under strongly acidic conditions.*

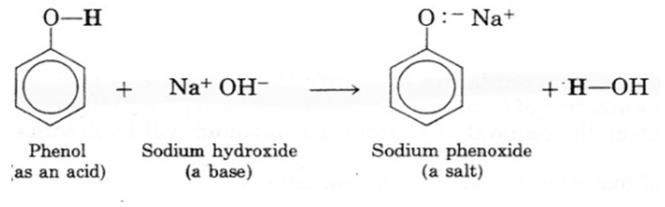
Reactions of Alcohols

A) Those that involve the breaking of the oxygen-hydrogen bond (CO-H).

1) Reactions of Alcohols and Phenols as Acids: Salt Formation.

$$\text{R—OH} + \text{Na}^+\,\text{OH}^- \longrightarrow \text{No reaction}$$

$$\underset{\text{Methanol}}{2\,\text{CH}_3\text{O—}\mathbf{H}} + 2\,\text{Na} \longrightarrow \underset{\text{Sodium methoxide}}{2\,\text{CH}_3\text{O:}^-\,\text{Na}^+} + \mathbf{H_2}\uparrow$$



Reactions of Alcohols

A) Those that involve the rupture of the carbon-oxygen bond (C-OH).

1) Nucleophilic Substitution Reaction; The Reaction of Alcohols with Hydrogen Halides: Alkyl Halides

Alcohols react with hydrogen halides (HCl, HBr and HI) to give alkyl halides.

$$\underset{\text{alcohol}}{R{-}OH} + H{-}X \longrightarrow \underset{\text{alkyl halide}}{R{-}X} + H{-}OH$$

2) Dehydration of Alcohols: Formation of Alkenes

Alcohols can be dehydrated by heating them with strong acid.

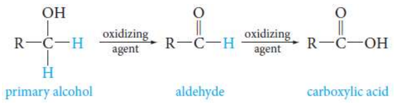
$$\underset{\text{ethanol}}{H{-}CH_2CH_2{-}OH} \xrightarrow{H^+,\ 180^\circ C} \underset{\text{ethylene}}{CH_2{=}CH_2} + H{-}OH$$

Reactions of Alcohols

B) Oxidation Reactions

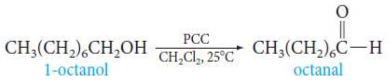
Alcohols with at least one hydrogen attached to the hydroxyl-bearing carbon can be oxidized to carbonyl compounds.

- **Primary alcohols** give aldehydes, which may be further oxidized to carboxylic acids.

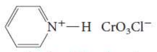


$$\underset{\text{primary alcohol}}{R{-}\overset{OH}{\underset{H}{C}}{-}H} \xrightarrow[\text{agent}]{\text{oxidizing}} \underset{\text{aldehyde}}{R{-}\overset{O}{\overset{\|}{C}}{-}H} \xrightarrow[\text{agent}]{\text{oxidizing}} \underset{\text{carboxylic acid}}{R{-}\overset{O}{\overset{\|}{C}}{-}OH}$$

  - **Primary alcohols**, oxidation can be stopped at aldehyde stage by special reagents, such as "pyridinium chlorochromate (PCC)".



$$\underset{\text{1-octanol}}{CH_3(CH_2)_6CH_2OH} \xrightarrow[CH_2Cl_2,\ 25^\circ C]{PCC} \underset{\text{octanal}}{CH_3(CH_2)_6\overset{O}{\overset{\|}{C}}{-}H}$$

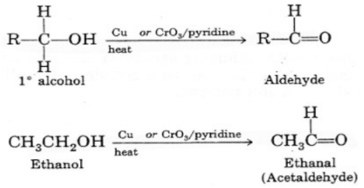


pyridinium chlorochromate (PCC)

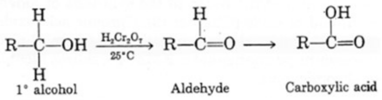
Reactions of Alcohols

B) Oxidation Reactions

- **Primary alcohols** yield aldehydes when treated with *mild oxidizing agents* such as hot metallic copper or CrO_3 in pyridine.



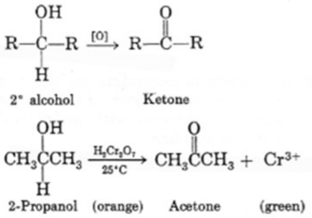
- **Primary alcohols;** when treated with *stronger oxidizing agents*, such as chromic acid, $H_2Cr_2O_7$, or neutral potassium permanganate, $KMnO_4$, the intermediate aldehydes formed initially are oxidized further to carboxylic acids.



Reactions of Alcohols

B) Oxidation Reactions

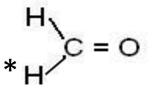
- **Secondary alcohols**, when treated with any of the oxidizing agents mentioned previously, yield ketones.



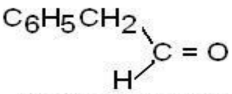
- **Tertiary alcohols**, having no hydrogen atom on hydroxyl-bearing carbon, *do not undergo oxidation*.

ALDEHYDES AND KETONES

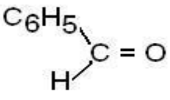
- In aldehydes, the carbonyl group is linked to either two hydrogen atom or one hydrogen atom and one carbon containing group such as alkyl, aryl or aralkyl group Examples



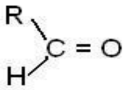
formaldehyde



phenyl acetaldehyde

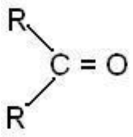


benzaldehyde

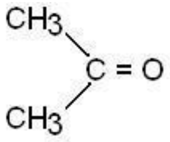


aldehyde

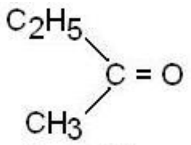
- In ketones, the carbonyl group is linked to two carbon containing groups which may be same or different alkyl, aryl group. If two R and R’ groups are same, the ketone is called simple or symmetrical ketone and if R and R’ are different, then ketone is known as mixed or an unsymmetrical ketone.



ketone



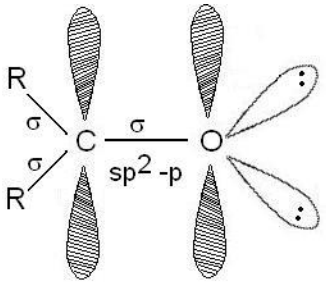
dimethyl ketone
(simple ketone)

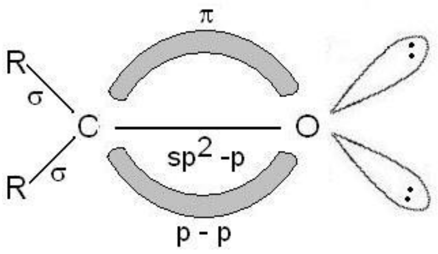


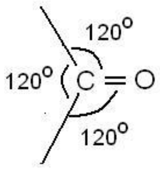
ethyl methyl ketone
(mixed ketone)

STRUCTURE

- Carbonyl carbon of both aldehyde and ketones is sp^2 – hybridised, One of the three sp^2 hybridised orbital get involved in σ- bond formation with half –filled p-orbital of oxygen atom whereas rest of the two are consumed in σ-bond formation with hydrogen and carbon depending on the structure of aldehyde or ketone.
- Unhybridised p-orbital of carbonyl carbon form π-bond with another half-filled p-orbital of oxygen atom by sideways overlapping.





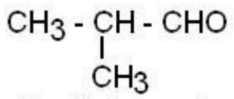


ISOMERISM IN ALDEHYDES AND KETONES

(a) Chain isomerism: Aldehydes (with 4 or more carbon atoms) and ketone (with 5 or more carbon atoms) show chain isomerism. Example

i) C_4H_8O

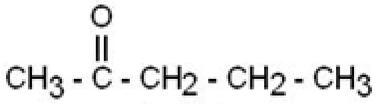
CH_3-CH_2-CH_2-CHO (butanal)



$CH_3-\underset{CH_3}{\underset{|}{CH}}-CHO$

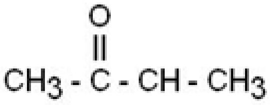
2-methylpropanal

ii) $C_5H_{10}O$



$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_3$

pentan-2-one

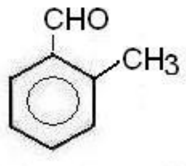


$CH_3-\overset{O}{\overset{\|}{C}}-CH-CH_3$

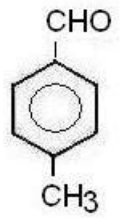
3-methylbutan-2-one

(b) Position isomerism: aliphatic aldehydes do not show position isomerism, because –CHO group is always present at the end of carbon chain.
Aromatic aldehyde show position isomerism. Example

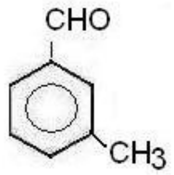
(c) Metamerism: Higher ketones show metamerism due to presence of different alkyl groups attached to the same functional group
$C_5H_{10}O$



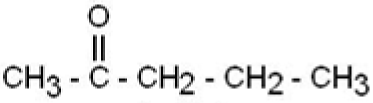
2-methylbenzaldehyde or
o - tolualdehyde



4-methylbenzaldehyde
or p-tolualdehyde

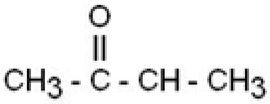


3-methylbenzaldehyde
or m-tolualdehyde



$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_3$

pentan-2-one



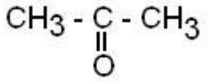
$CH_3-\overset{O}{\overset{\|}{C}}-CH-CH_3$

3-methylbutan-2-one

(d) Functional isomerism : Aldehydes and ketones show functional isomerism in them. In addition, they are also related to alcohols, ethers and other cyclic compounds. Example
C_3H_6O

ALDEHYDES AND KETONE

CH_3CH_2CHO propanal



$CH_3-\underset{\underset{O}{\|}}{C}-CH_3$ propanone

$CH_2{=}CH-CH_2-OH$ Prop-2-en-1-ol

$CH_2 = CH-OCH_3$ methoxy ethene

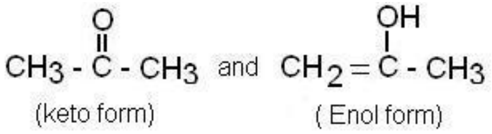
(e) Tautomerism : Aldehydes and ketones also show tautomerism

(I) C_2H_4O

$CH_3-\overset{\overset{O}{\|}}{C}-H$ and $CH_2=\overset{\overset{OH}{|}}{CH}$

acetaldehyde vinyl alcohol

(II) C_3H_6O



$CH_3-\overset{\overset{O}{\|}}{C}-CH_3$ and $CH_2=\overset{\overset{OH}{|}}{C}-CH_3$

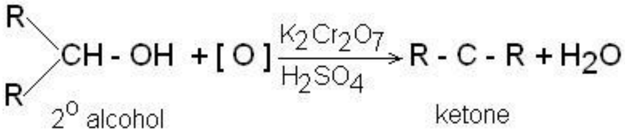
(keto form) (Enol form)

GENERAL METHODS OF PREPARATION OF ALDEHYDES AND KETONES

1. From alcohol

(i) Oxidation of alcohol

$$R-CH_2-OH+[O]\xrightarrow[H_2SO_4]{K_2Cr_2O_7}R\text{-}CHO+H_2O$$



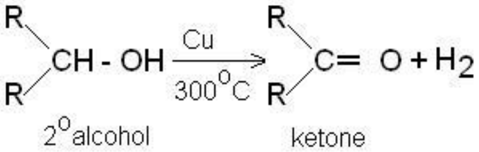
$$\underset{2^o\ \text{alcohol}}{R_2CH-OH}+[O]\xrightarrow[H_2SO_4]{K_2Cr_2O_7}\underset{\text{ketone}}{R-C-R}+H_2O$$

- Since the oxidizing agent used in the above reactions is a strong oxidizing agent, it oxidizes aldehydes and ketone further to carboxylic acids
- To prevent further oxidation, a mild oxidizing agent such as pyridinium chlorochromate (pcc), $CrO_3.C_5H_5N\cdot HCl$ or $CrO_3NH^+CrO_3Cl^-$ are used Collin's reagent [$(C_5H_5N)_2\cdot CrO_3$] can also used.

$$\underset{1^o\ \text{alcohol}}{R-CH_2OH}\xrightarrow[\text{collin's reagent}]{\text{pcc,}}\underset{\text{aldehyde}}{RCHO}$$

(ii) Catalytic dehydrogenation of alcohols

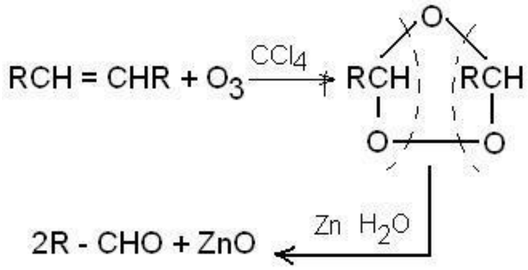
$$\underset{1^o\ \text{alcohol}}{RCH_2OH}\xrightarrow[300^oC]{Cu}\underset{\text{Aldehyde}}{RCHO}+H_2$$



$$R_2CH-OH \xrightarrow[300^oC]{Cu} R_2C=O + H_2$$

2°alcohol ketone

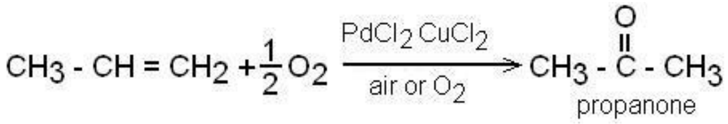
2. From alkenes
   (i) Reductive ozonolysis of alkenes.



$$RCH=CHR + O_3 \xrightarrow{CCl_4} \text{ozonide} \xrightarrow{Zn\ H_2O} 2R-CHO + ZnO$$

   (ii) Wacker process.

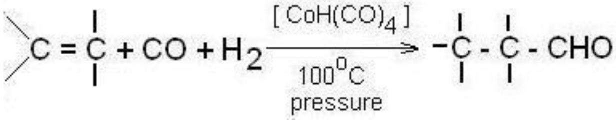
$$CH_2=CH_2 + \frac{1}{2}O_2 \xrightarrow[\text{air or } O_2]{PdCl_2\ CuCl_2} CH_3-CHO$$



$$CH_3-CH=CH_2 + \frac{1}{2}O_2 \xrightarrow[\text{air or } O_2]{PdCl_2\ CuCl_2} CH_3-\overset{\overset{O}{\|}}{C}-CH_3$$

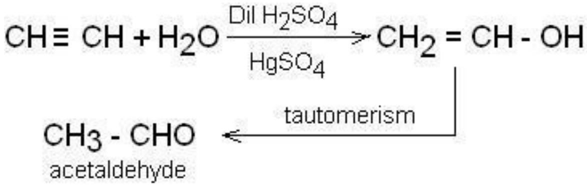
propanone

   (iii) OXO process [Carbonylation / Hydroformylation]



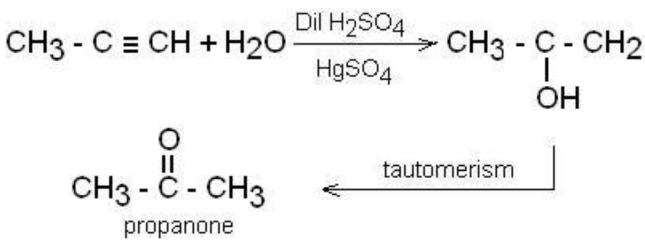
$$>C=\overset{|}{\underset{|}{C}} + CO + H_2 \xrightarrow[\substack{100^oC\\ \text{pressure}}]{[CoH(CO)_4]} -\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-CHO$$

3. From alkynes



$$CH\equiv CH + H_2O \xrightarrow[HgSO_4]{Dil\ H_2SO_4} CH_2=CH-OH \xrightarrow{\text{tautomerism}} CH_3-CHO$$

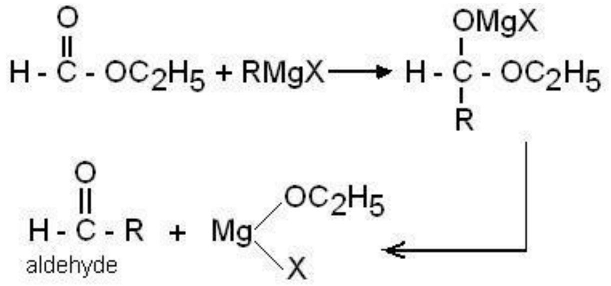
acetaldehyde



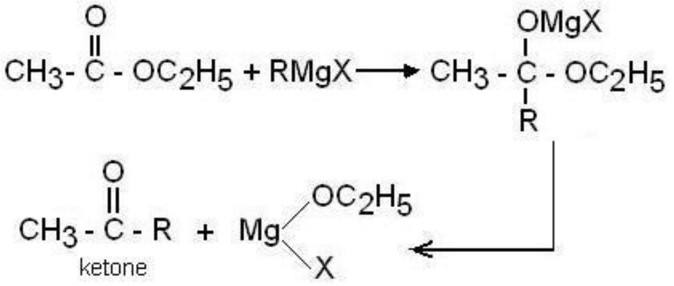
$$CH_3-C\equiv CH + H_2O \xrightarrow[HgSO_4]{Dil\ H_2SO_4} CH_3-\underset{\underset{OH}{|}}{C}-CH_2 \xrightarrow{\text{tautomerism}} CH_3-\overset{\overset{O}{\|}}{C}-CH_3$$

propanone

4. From Grignard reagent
   (1) By addition to ester

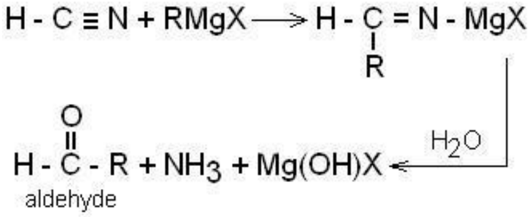


$$H-\overset{O}{\overset{\|}{C}}-OC_2H_5 + RMgX \longrightarrow H-\underset{R}{\overset{OMgX}{C}}-OC_2H_5 \longrightarrow \underset{\text{aldehyde}}{H-\overset{O}{\overset{\|}{C}}-R} + Mg\begin{matrix}OC_2H_5\\X\end{matrix}$$

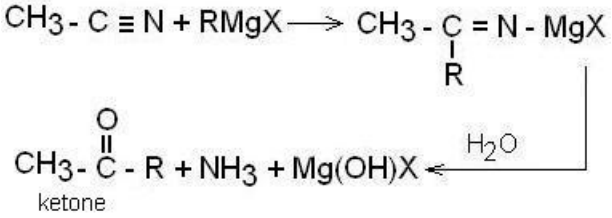


$$CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5 + RMgX \longrightarrow CH_3-\underset{R}{\overset{OMgX}{C}}-OC_2H_5 \longrightarrow \underset{\text{ketone}}{CH_3-\overset{O}{\overset{\|}{C}}-R} + Mg\begin{matrix}OC_2H_5\\X\end{matrix}$$

(iii) By addition to nitriles



$$H-C\equiv N + RMgX \longrightarrow H-\underset{R}{C}=N-MgX \xrightarrow{H_2O} \underset{\text{aldehyde}}{H-\overset{O}{\overset{\|}{C}}-R} + NH_3 + Mg(OH)X$$

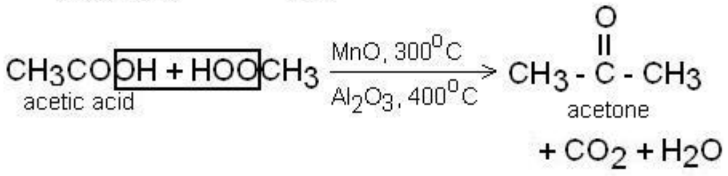


$$CH_3-C\equiv N + RMgX \longrightarrow CH_3-\underset{R}{C}=N-MgX \xrightarrow{H_2O} \underset{\text{ketone}}{CH_3-\overset{O}{\overset{\|}{C}}-R} + NH_3 + Mg(OH)X$$

5. From carboxylic acids

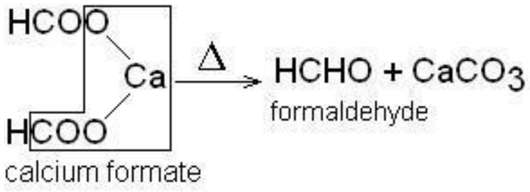
(i) Catalytic decomposition of carboxylic acid.

$$\underset{\text{formic acid}}{HCO\boxed{OH + HCOO}H} \xrightarrow[Al_2O_3,\ 400^0C]{MnO,\ 300^0C} HCHO + CO_2 + H_2O$$

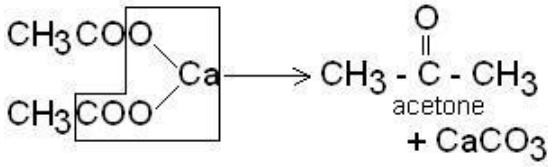


$$\underset{\text{acetic acid}}{CH_3CO\boxed{OH + HOO}CH_3} \xrightarrow[Al_2O_3,\ 400^0C]{MnO,\ 300^0C} \underset{\text{acetone}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_3} + CO_2 + H_2O$$

(ii) From calcium salt of carboxylic acids



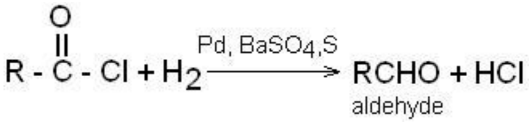
$$\underset{\text{calcium formate}}{(HCOO)_2Ca} \xrightarrow{\Delta} \underset{\text{formaldehyde}}{HCHO} + CaCO_3$$



$$(CH_3COO)_2Ca \longrightarrow \underset{\text{acetone}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_3} + CaCO_3$$

6. From derivatives of carboxylic acids

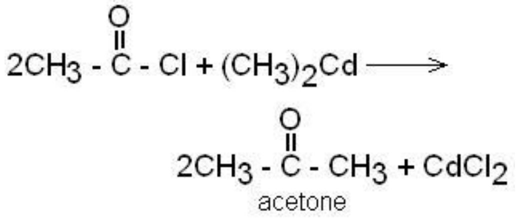
(i) Reduction of acid chlorides (Rosenmund's reaction)



$$R-\overset{O}{\overset{\|}{C}}-Cl + H_2 \xrightarrow{Pd,\ BaSO_4, S} \underset{\text{aldehyde}}{RCHO} + HCl$$

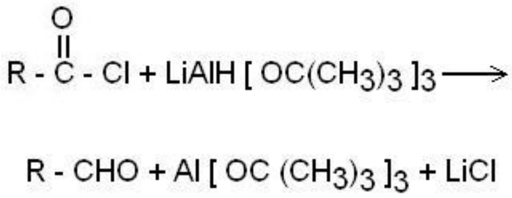
- Above reaction is known as Rosenmund's reduction and is applicable for preparation of aldehydes
- $BaSO_4$, sulphur act as poison for Pd catalyst and prevents reduction of RCHO into RCH_2OH

(ii) Reduction of acid chloride with dialkyl cadmium.



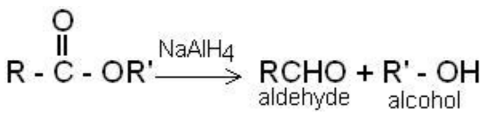
$$2CH_3-\overset{O}{\overset{\|}{C}}-Cl + (CH_3)_2Cd \longrightarrow \underset{\text{acetone}}{2CH_3-\overset{O}{\overset{\|}{C}}-CH_3} + CdCl_2$$

Reduction of acid chloride into ester can also be carried out by lithium tri--butoxy aluminium hydride, $LiAlH[OC(CH_3)_3]$



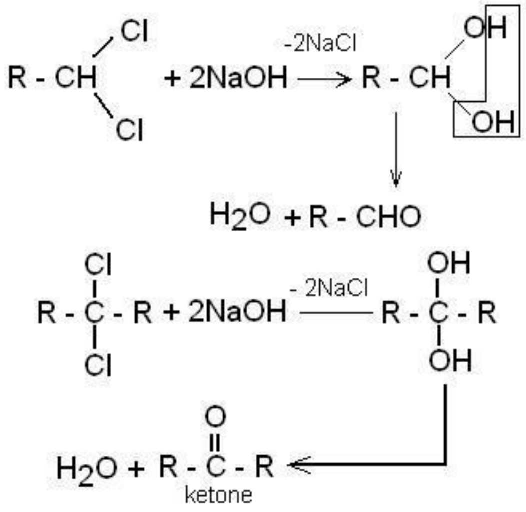
$$R-\overset{O}{\overset{\|}{C}}-Cl + LiAlH[OC(CH_3)_3]_3 \longrightarrow R-CHO + Al[OC(CH_3)_3]_3 + LiCl$$

(iii) Reduction of esters

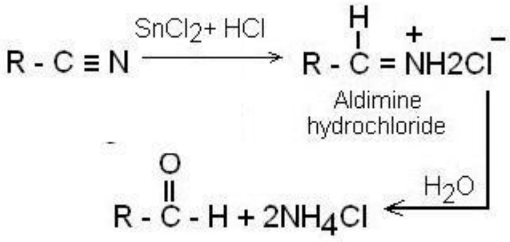


$$R-\overset{O}{\overset{\|}{C}}-OR' \xrightarrow{NaAlH_4} \underset{\text{aldehyde}}{RCHO} + \underset{\text{alcohol}}{R'-OH}$$

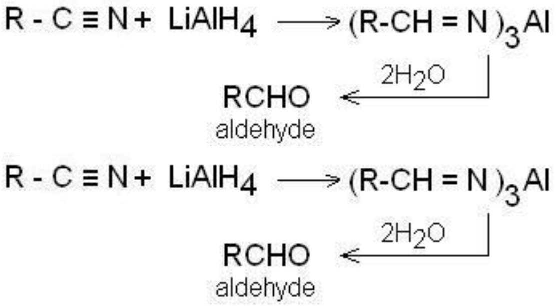
7. From gem-dihalides by hydrolysis



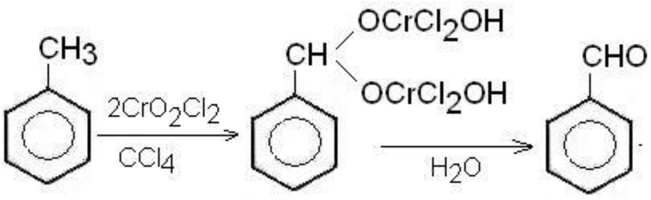
8. From nitriles by reduction
   (i) Stephen’s reduction.



   (ii) Reduction with $LiAlH_4$

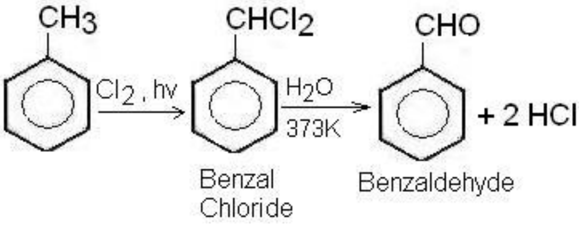


9. Preparation of aromatic carbonyl compounds.
   (i)

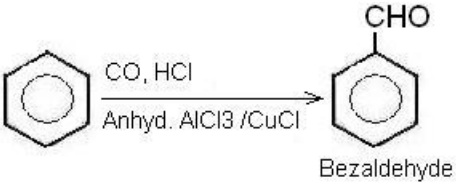


This is known as Etard reaction

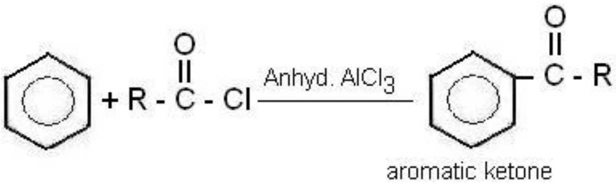
(ii) By side chain chlorination followed by hydrolysis

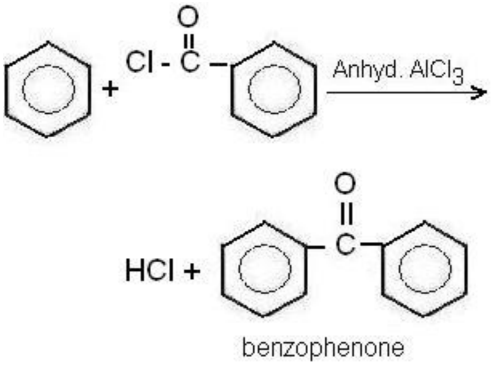


(iii) Gatterman – Koch reaction

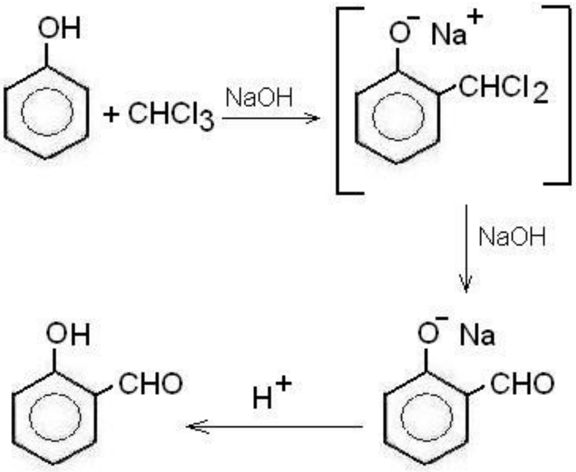


(iv) Friedel Craft Acylation





(v) Reimer – Tiemann reaction



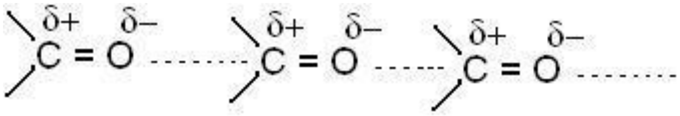
PHYSICAL PROPERTIES OF ALDEHYDES AND KETONE

1. Physical state

- Lower members of aldehydes and ketones (upto C_{10}) are colourless volatile liquids except formaldehyde which is gas at ordinary temperature
- Higher members of aldehyde and ketones are solids with fruity odour
- Lower aldehydes have unplesent odour but ketones posses pleasant smell

2. Boiling point

- Boiling point of aldehyde and ketones is slightly lower than corresponding alcohol due to lack of hydrogen bonding. However their boiling point is slightly higher than that of corresponding non-polar hydrocarbon or weakly polar ether. This may attributed to reason that aldehydes and ketones are polar compounds and thus possess intermolecular dipole-dipole interaction



- Among isomeric aldehydes and ketones, boiling point of ketones is slightly higher than that of aldehydes due to the presence of two electron donating alkyl groups making them more polar.

3. Solubility

- Lower members of aldehydes and ketones (upto C_4) are soluble in water due to H-bonding between polar carbonyl group and water.
- However, solubility decreases with increase in molecular weight
- Aromatic aldehydes and ketones are much less soluble than corresponding aliphatic aldehydes and ketones due to large benzene ring. However all carbonyl compounds are fairly soluble in organic solvents.

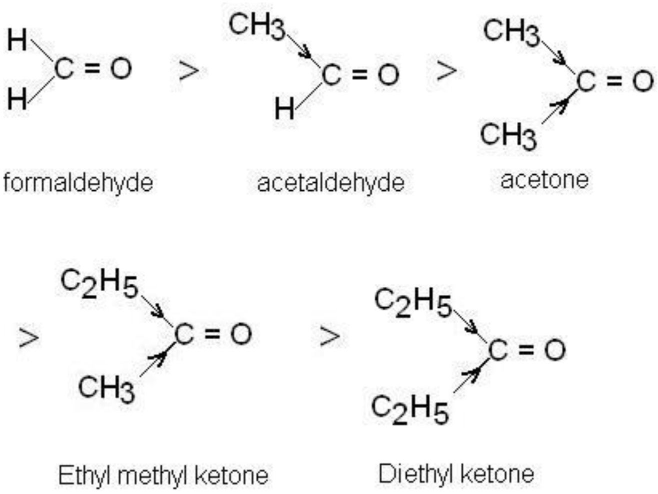
RELATIVE REACTIVITY OF ALDEHYDES AND KETONES

Aldehydes are more reactive than ketones on account of the following facts:

(a) Aliphatic aldehydes and ketones

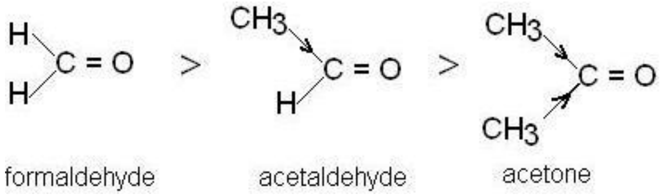
(i) Inductive effect:

The reactivity of the carbonyl group towards the addition reaction depends upon the magnitude of the positive charge on the carbonyl carbon atom. Hence, any substituent that increases the positive charge on the carbonyl carbon must increase its reactivity towards addition reactions. The introduction of negative group (-I effect) increases the reactivity, while introduction of alkyl group (+I effect) decreases the reactivity, therefore, greater the number of alkyl groups attached to the carbonyl group and hence, lower is its reactivity towards nucleophilic addition reactions. Thus, the following decreasing order of reactivity is observed



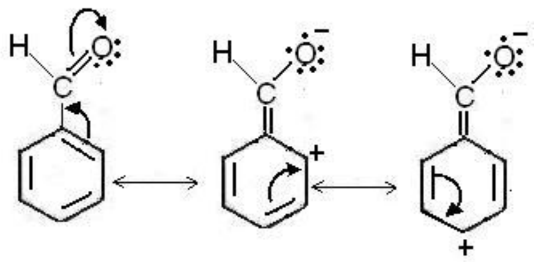
(ii) Steric effect

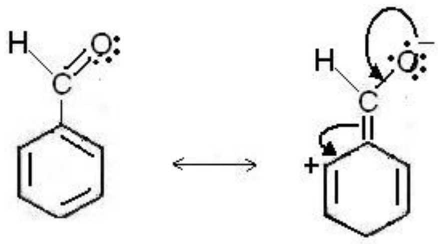
- In formaldehyde there is no alkyl group while in all other aldehyde there is one alkyl group so here the nucleophile attack is relatively more easy but in ketones there are two alkyl groups attached to carbonyl group and these causes hinderance, to the attacking group. This factor is called steric hinderance (crowding). In other words the hindrance increases, the reactivity decreases accordingly. Thus order of reactivity is



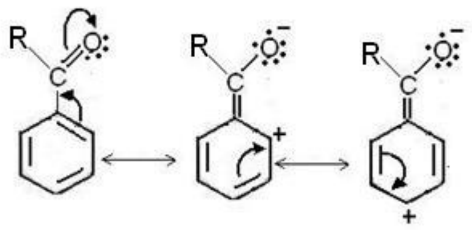
(b) Aromatic aldehydes and ketones

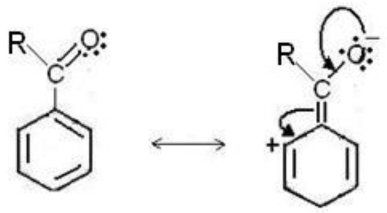
- In general, aromatic aldehydes and ketones are less reactive than the corresponding aliphatic aldehydes and ketones. It is due electron releasing resonance effect of bezene ring





- Due to electron withdrawing resonance effect (-R effect) of benzene ring, the magnitude of positive charge on carbonyl group decreases and consequently it becomes less susceptible to nucleophilic attack.





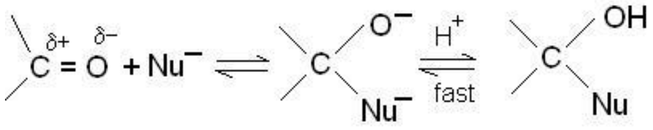
The order of reactivity of aromatic aldehydes and ketones is

$C_6H_5CH_2CHO$ > C_6H_5CHO > $C_6H_5COCH_3$
phenyl acetaldehyde, benzaldehyde, acetophenone

> $C_6H_5COC_6H_5$
benzophenone

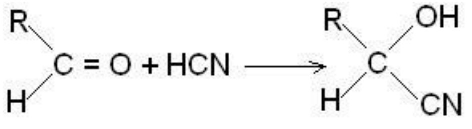
CHEMICAL PROPERTIES OF ALDEHYDES AND KETONES

Nucleophilic addition reaction

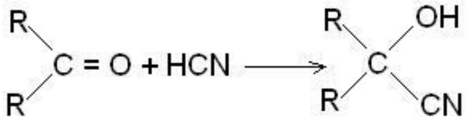


In this reaction carbon atom of carbonyl group changes from sp^2 to sp^3 hybridised

(i) Addition of hydrogen cyanide (HCN)



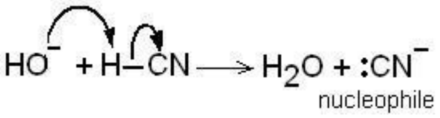
cyanohydrien



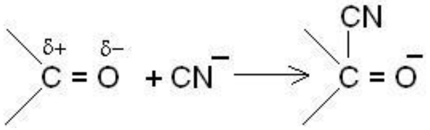
cyanohyrin

Mechanism

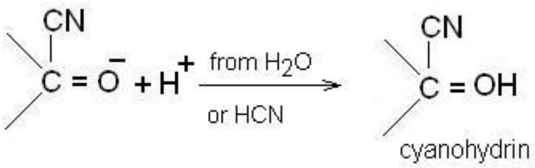
Step I : The hydrogen cyanide interacts with the base to form nucleophile



Step II : The nucleophile attacks the carbonyl carbon to form an anion

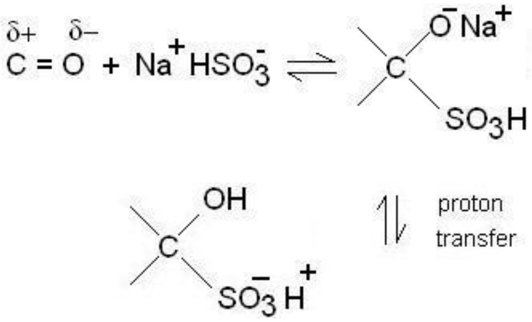


StepIII: The proton from the solvent (usually water) combines with the anion to form cyanohydrin.

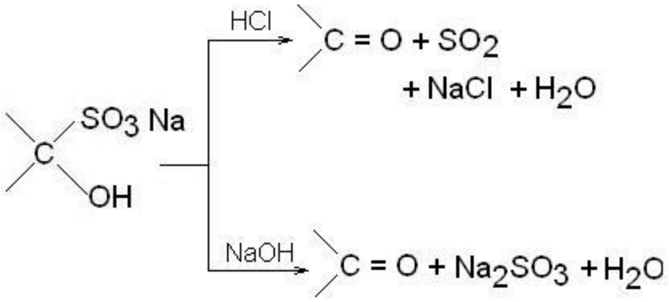


Cyanohydrins are formed by all aldehydes but in ketones, only acetone, butanone, 3-pethenone and pinacolone form cyanohydrins.

(ii) Addition of sodium bisulphate ($NaHSO_4$)

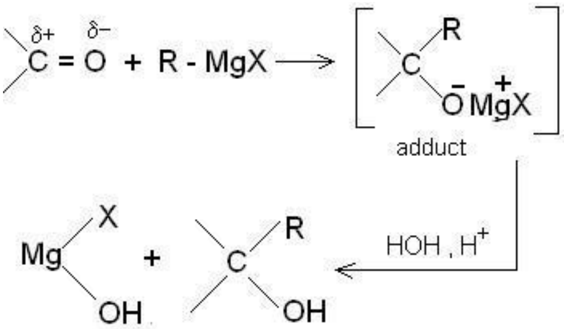


- All ketones do not undergo this reaction only methyl ketone form addition product with sodium bisulphate
- On reacting the crystalline solid bisulphate derivative with dilute HCl or alkali, these adducts decompose to regenerate the original aldehyde or ketones. Hence, this reaction is used in the separation and purification of aldehydes and ketones from non-carbonyl compounds.

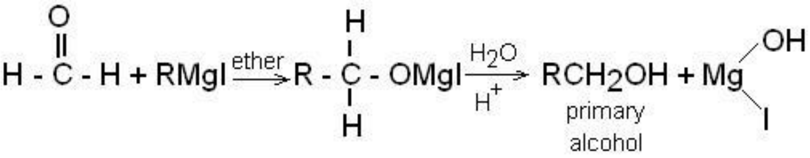


(iii) Addition of Grignard reagent

ALDEHYDES AND KETONE

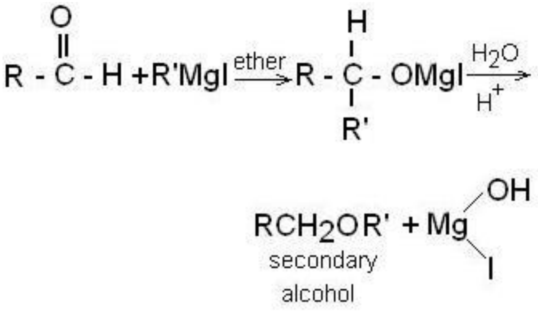


Formaldehyde form a primary alcohol



$$H-\overset{O}{\overset{\|}{C}}-H + RMgI \xrightarrow{ether} R-\underset{H}{\overset{H}{C}}-OMgI \xrightarrow[H^+]{H_2O} \underset{\text{primary alcohol}}{RCH_2OH} + Mg\langle{}^{OH}_{I}$$

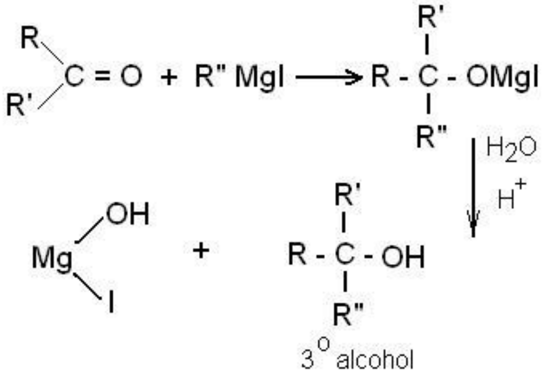
- Higher aldehydes give secondary alcohol



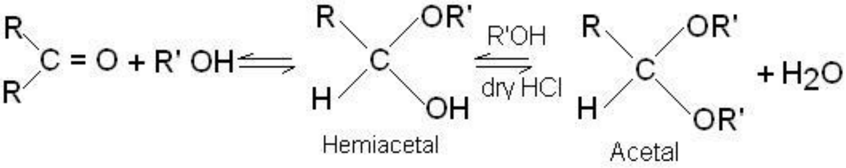
$$R-\overset{O}{\overset{\|}{C}}-H + R'MgI \xrightarrow{ether} R-\underset{R'}{\overset{H}{C}}-OMgI \xrightarrow[H^+]{H_2O}$$

$$\underset{\text{secondary alcohol}}{RCH_2OR'} + Mg\langle{}^{OH}_{I}$$

- Ketone give tertiary alcohols

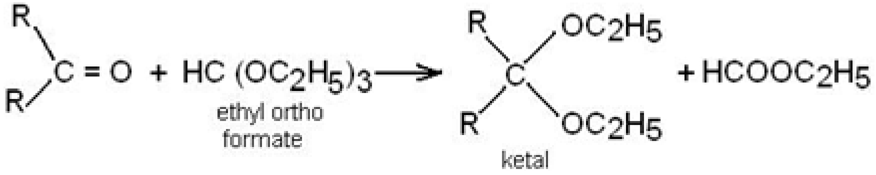


(iv) Addition of alcohols

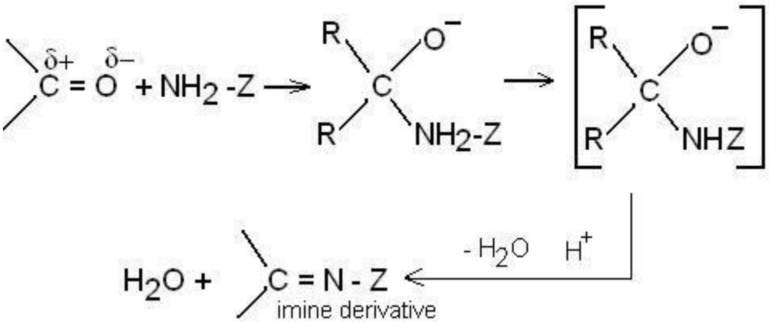


Dry HCl protonates the oxygen atom of the carbonyl compounds and therefore, increases the electrophilicity of the carbonyl carbon and hence facilitating the nucleophilic attack by the alcohol molecule. Dry HCl gas also absorbs the water produced in these reactions and thereby shifting equilibrium in forward direction.

Ketals can be prepared by treating the ketone with ethyl ortho formate



(v) Addition of ammonia derivative

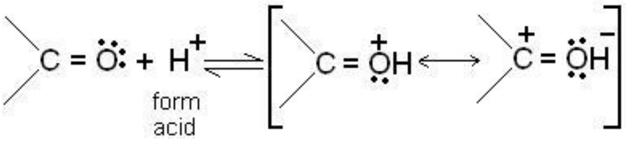


Z = OH, NH_2 , NHC_6H_5 , $NHCOCH_2$ etc.

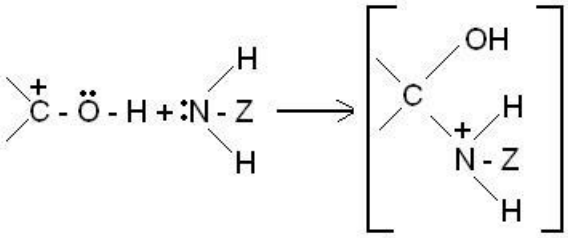
The reaction of ammonia derivatives to aldehydes and ketones is called by acids

Mechanism

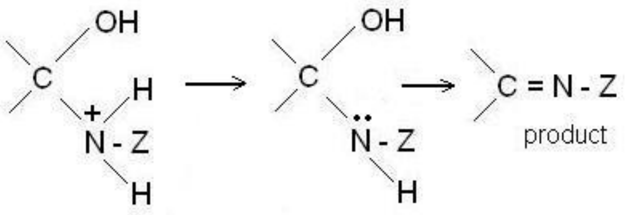
Step I: In acidic medium, the carbonyl oxygen gets protonated.



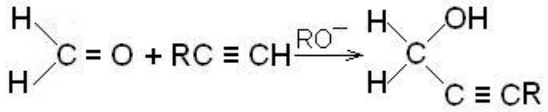
Step II : In ammonia derivatives, the nitrogen atom has a lone pair of electrons, which attack the positively charged carbonyl carbon and results in positive charge on nitrogen atom



Step III : The unstable intermediate loses a proton, H^+ and water molecule to form stable product (imines)



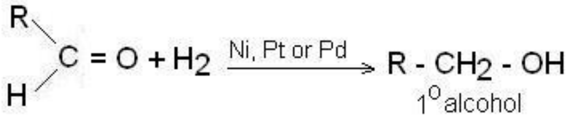
(vi) Addition of alkynes

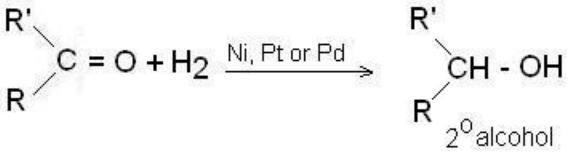


This reaction is also known as ethinylation

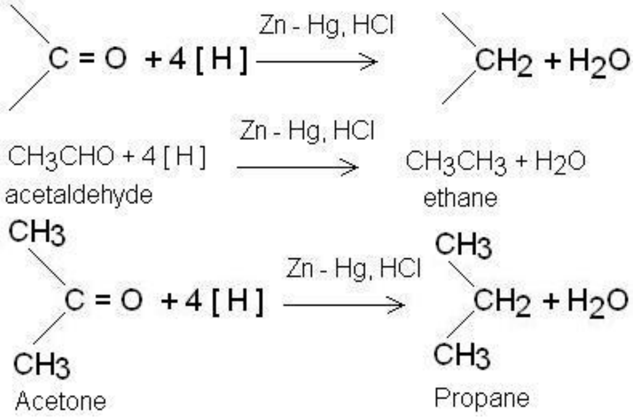
2. Reduction reactions

I. Catalytic reduction to alcohol

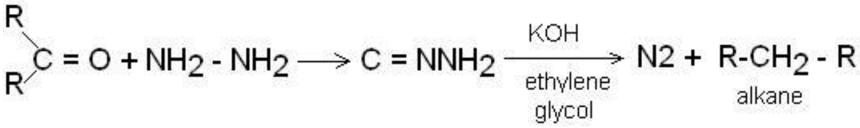


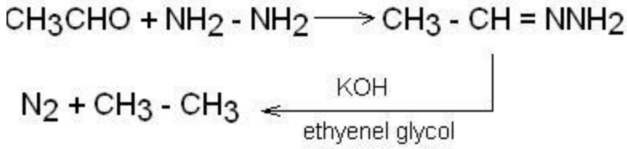


II. Clemmensen reduction



III. Wolf-Kishner reduction





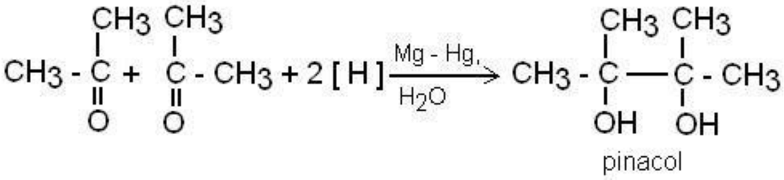
$$CH_3COCH_3 \xrightarrow[\text{ethylene glycol}]{NH_2\text{-}NH_2 + KOH} CH_3 - CH_2 - CH_3 + H_2O$$

IV. Reduction with HI + P (red)

$$CH_3 - CHO + 4HI \xrightarrow[150^0C]{\text{red P}} CH_3\text{-}CH_3 + H_2O + 2I_2$$

$$CH_3COCH_3 + 4HI \xrightarrow[150^0C]{\text{red P}} CH_3 - CH_2 - CH_3 + H_2O + 2I_2$$

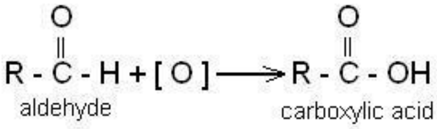
V. Reduction to pinacols



$$CH_3 - \underset{\underset{O}{\|}}{\overset{\overset{CH_3}{|}}{C}} + \underset{\underset{O}{\|}}{\overset{\overset{CH_3}{|}}{C}} - CH_3 + 2\,[\,H\,] \xrightarrow[H_2O]{Mg - Hg,} \underset{\text{pinacol}}{CH_3 - \underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}} — \underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH_3}$$

3. Oxidation reactions

i. Oxidation with mild oxidizing agents



$$\underset{\text{aldehyde}}{R - \overset{\overset{O}{\|}}{C} - H} + [\,O\,] \longrightarrow \underset{\text{carboxylic acid}}{R - \overset{\overset{O}{\|}}{C} - OH}$$

Ketones are not oxidized by mild oxidizing agents

(a) Aldehydes reduces Tollen's reagent to metallic silver which appears as a silver mirror on wall of test tube. Thus the reaction is also known as silver mirror test.

$$RCHO + 2\,[\,Ag\,(NH_3)_2]^+ + 3OH^- \longrightarrow$$

$$RCOO^- + \underset{\text{silver mirror}}{2Ag\downarrow} + 4NH_3 + 2H_2O$$

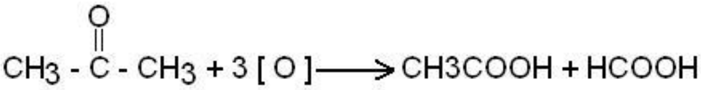
(b) Reduction of Fehling's solution
Fehling's solution is an alkaline solution of $CuSO_4$ mixed with Rochelle slat i.e. sodium potassium tartarate. Aldehydes reduces cupric ion (Cu^{2+}) of Fehling's solution to cuprous ions (Cu^+) to form red precipitate of cuprous oxide

$$RCHO + 2Cu_2^+ + 5\,OH^- \longrightarrow RCOO^- + Cu_2O + 3H_2O$$

Fehling's solution is reduced by aliphatic aldehydes only. Aromatic aldehydes and ketones so not give this reaction.

ii. Oxidation with strong oxidizing agent

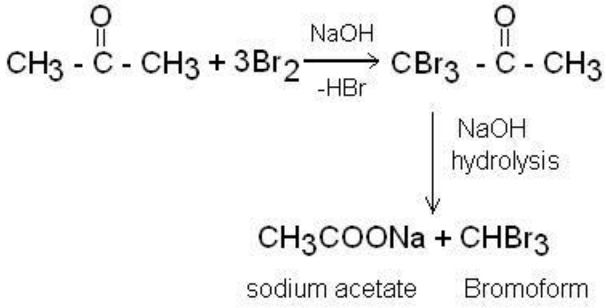
$$\underset{\text{aldehyde}}{RCHO} + [\,O\,] \xrightarrow{NHO_3\,(\text{conc.})} \underset{\text{carboxylic acid}}{RCOOH}$$



$$CH_3 - \overset{\overset{O}{\|}}{C} - CH_3 + 3\,[\,O\,] \longrightarrow CH3COOH + HCOOH$$

iii. Haloform reaction

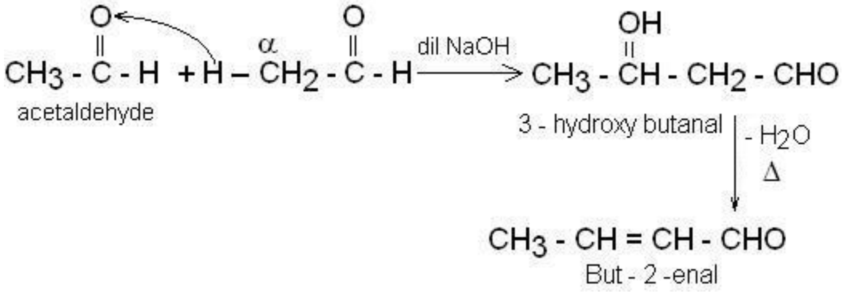
$$CH_3-CHO + 3Cl_2 \xrightarrow[-3HCl]{NaOH} CCl_3CHO \longrightarrow \underset{\text{sodium formate}}{HCOONa} + \underset{\text{chloroform}}{CHCl_3}$$



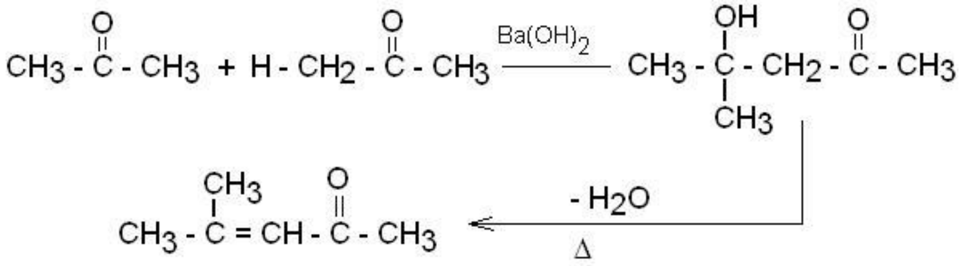
$$CH_3-\overset{O}{\overset{\parallel}{C}}-CH_3 + 3Br_2 \xrightarrow[-HBr]{NaOH} CBr_3-\overset{O}{\overset{\parallel}{C}}-CH_3 \xrightarrow[\text{hydrolysis}]{NaOH} \underset{\text{sodium acetate}}{CH_3COONa} + \underset{\text{Bromoform}}{CHBr_3}$$

4. Condensation reactions

   (1) Aldol condensation

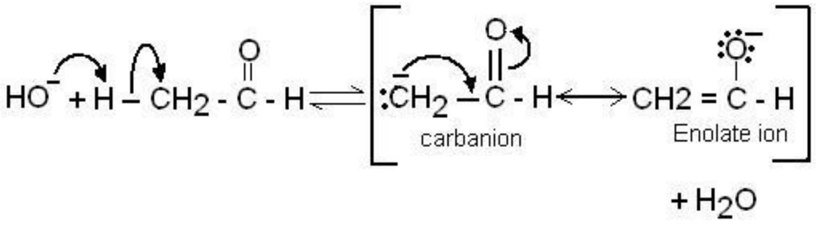


$$\underset{\text{acetaldehyde}}{CH_3-\overset{O}{\overset{\parallel}{C}}-H} + H-\overset{\alpha}{CH_2}-\overset{O}{\overset{\parallel}{C}}-H \xrightarrow{\text{dil NaOH}} \underset{\text{3 - hydroxy butanal}}{CH_3-\overset{OH}{CH}-CH_2-CHO} \xrightarrow[\Delta]{-H_2O} \underset{\text{But - 2 -enal}}{CH_3-CH=CH-CHO}$$

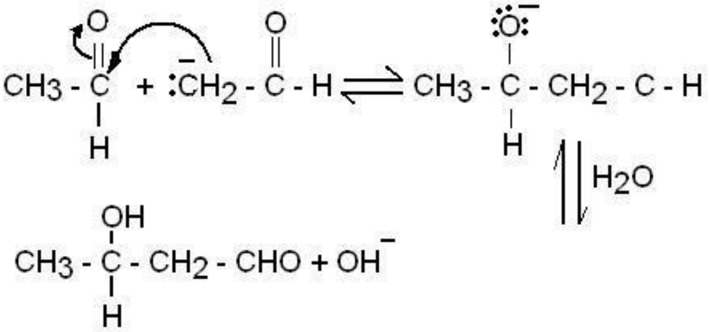


$$CH_3-\overset{O}{\overset{\parallel}{C}}-CH_3 + H-CH_2-\overset{O}{\overset{\parallel}{C}}-CH_3 \xrightarrow{Ba(OH)_2} CH_3-\underset{CH_3}{\overset{OH}{C}}-CH_2-\overset{O}{\overset{\parallel}{C}}-CH_3 \xrightarrow[\Delta]{-H_2O} CH_3-\overset{CH_3}{C}=CH-\overset{O}{\overset{\parallel}{C}}-CH_3$$

Mechanism



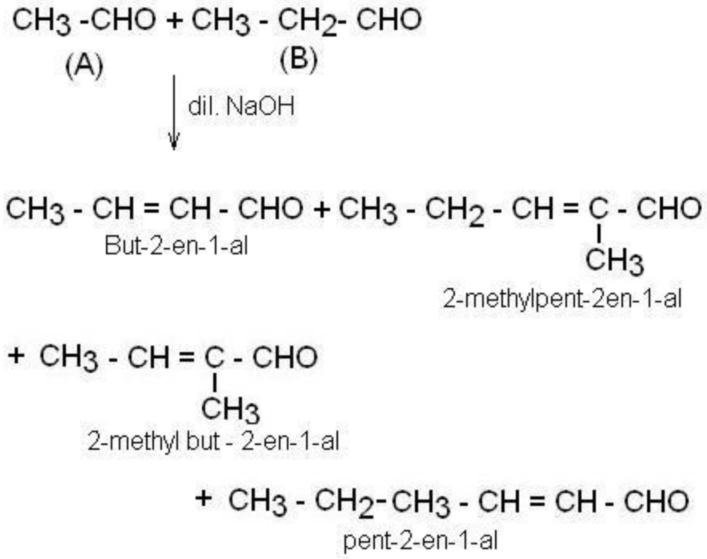
$$HO^- + H-CH_2-\overset{O}{\overset{\parallel}{C}}-H \rightleftharpoons \left[\underset{\text{carbanion}}{:\overset{-}{C}H_2-\overset{O}{\overset{\parallel}{C}}-H} \longleftrightarrow \underset{\text{Enolate ion}}{CH2=\overset{:\ddot{O}:^-}{C}-H}\right] + H_2O$$



$$CH_3-\underset{H}{\overset{O}{\overset{\parallel}{C}}} + :\overset{-}{C}H_2-\overset{O}{\overset{\parallel}{C}}-H \rightleftharpoons CH_3-\underset{H}{\overset{:\ddot{O}:^-}{C}}-CH_2-C-H \underset{}{\overset{H_2O}{\rightleftharpoons}} CH_3-\underset{H}{\overset{OH}{C}}-CH_2-CHO + OH^-$$

Aldehyde or ketones which do not contain α-hydrogen atom like formaldehyde (HCHO), benzaldehyde (C_6H_5CHO) and benzophenone ($C_6H_5COC_6H_5$) do not undergo aldol condensation.

(2) Cross aldol condensation



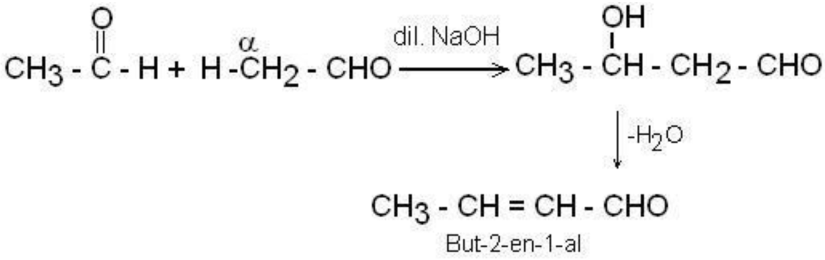
$$\underset{(A)}{CH_3-CHO} + \underset{(B)}{CH_3-CH_2-CHO} \xrightarrow{\text{dil. NaOH}}$$

$$\underset{\text{But-2-en-1-al}}{CH_3-CH=CH-CHO} + \underset{\text{2-methylpent-2en-1-al}}{CH_3-CH_2-CH=\underset{CH_3}{\underset{|}{C}}-CHO}$$

$$+ \underset{\text{2-methyl but - 2-en-1-al}}{CH_3-CH=\underset{CH_3}{\underset{|}{C}}-CHO}$$

$$+ \underset{\text{pent-2-en-1-al}}{CH_3-CH_2-CH_3-CH=CH-CHO}$$

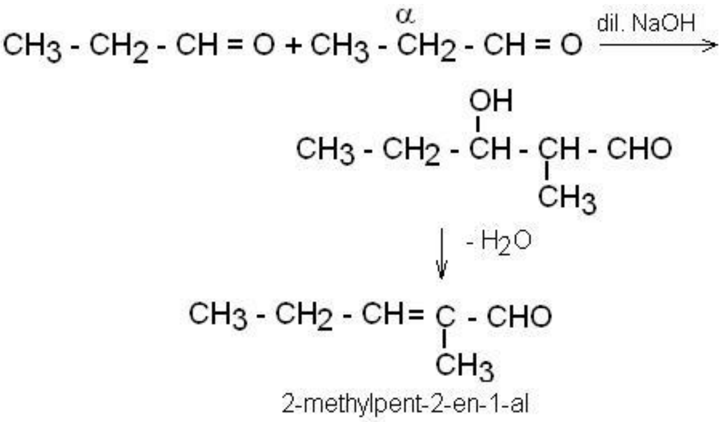
A- A Condensation



$$CH_3-\overset{\overset{O}{||}}{C}-H + H-\overset{\alpha}{C}H_2-CHO \xrightarrow{\text{dil. NaOH}} CH_3-\overset{\overset{OH}{|}}{C}H-CH_2-CHO$$

$$\xrightarrow{-H_2O} \underset{\text{But-2-en-1-al}}{CH_3-CH=CH-CHO}$$

B-B Condensation

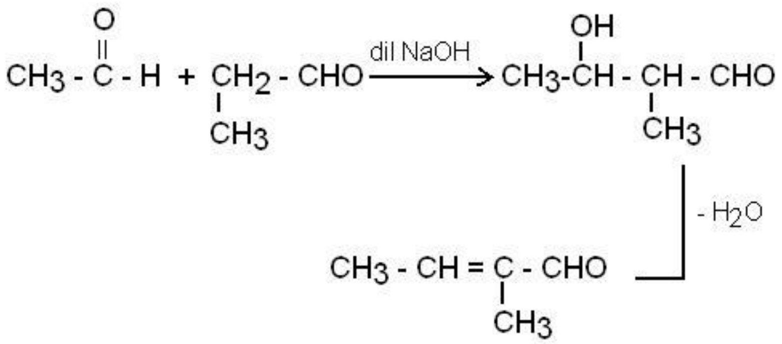


$$CH_3-CH_2-CH=O + CH_3-\overset{\alpha}{C}H_2-CH=O \xrightarrow{\text{dil. NaOH}}$$

$$CH_3-CH_2-\overset{\overset{OH}{|}}{C}H-\underset{CH_3}{\underset{|}{C}H}-CHO$$

$$\xrightarrow{-H_2O} \underset{\text{2-methylpent-2-en-1-al}}{CH_3-CH_2-CH=\underset{CH_3}{\underset{|}{C}}-CHO}$$

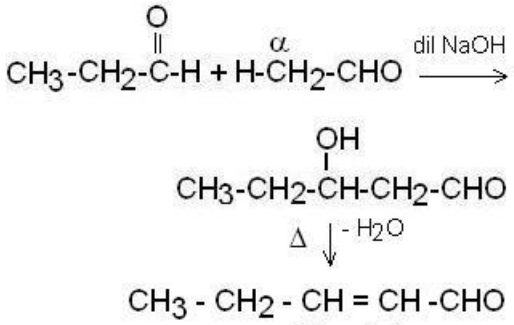
A-B Condensation



$$CH_3-\overset{\overset{O}{\|}}{C}-H + \underset{CH_3}{\underset{|}{CH_2}}-CHO \xrightarrow{dil\ NaOH} CH_3-\overset{OH}{\overset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-CHO \xrightarrow{-H_2O} CH_3-CH=\underset{CH_3}{\underset{|}{C}}-CHO$$

2-methyl but - 2-en-1-al

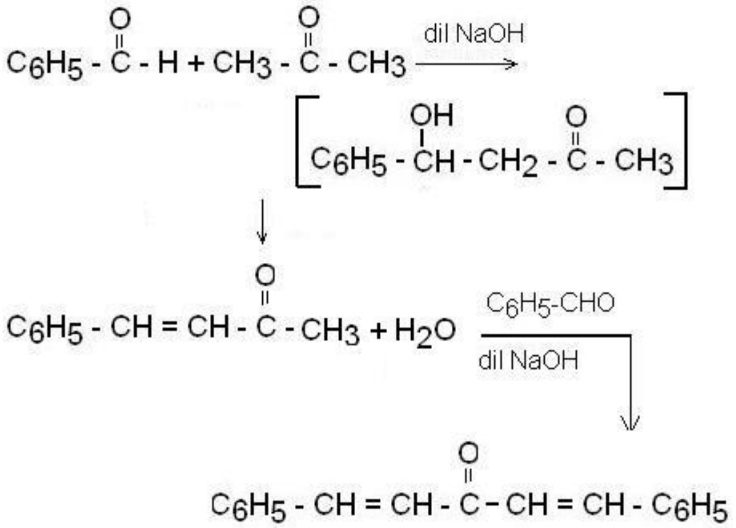
B-A Condensation



$$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-H + H-\overset{\alpha}{CH_2}-CHO \xrightarrow{dil\ NaOH} CH_3-CH_2-\overset{OH}{\overset{|}{CH}}-CH_2-CHO \xrightarrow[\Delta]{-H_2O} CH_3-CH_2-CH=CH-CHO$$

pent-2-en-1-al

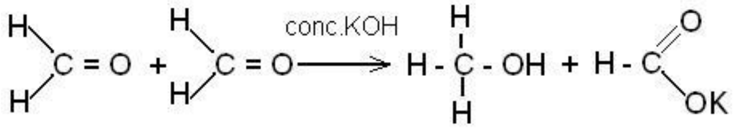
(3) Claisen – Schmidt condensation



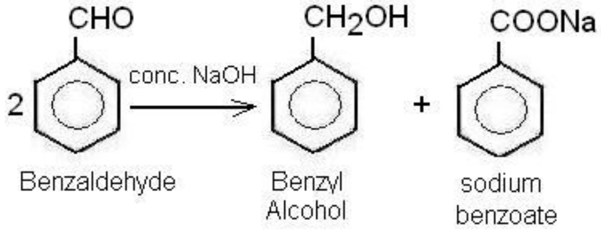
$$C_6H_5-\overset{\overset{O}{\|}}{C}-H + CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{dil\ NaOH} \left[C_6H_5-\overset{OH}{\overset{|}{CH}}-CH_2-\overset{\overset{O}{\|}}{C}-CH_3\right] \rightarrow C_6H_5-CH=CH-\overset{\overset{O}{\|}}{C}-CH_3 + H_2O \xrightarrow[dil\ NaOH]{C_6H_5-CHO} C_6H_5-CH=CH-\overset{\overset{O}{\|}}{C}-CH=CH-C_6H_5$$

Dibenzal acetone

5. Cannizzaro reaction

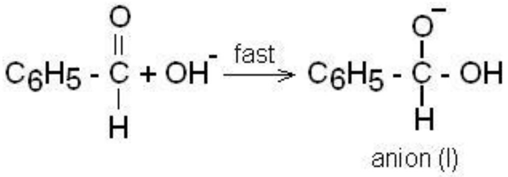


$$H_2C=O + H_2C=O \xrightarrow{conc.KOH} H-\underset{H}{\overset{H}{C}}-OH + H-C(=O)OK$$



Mechanism

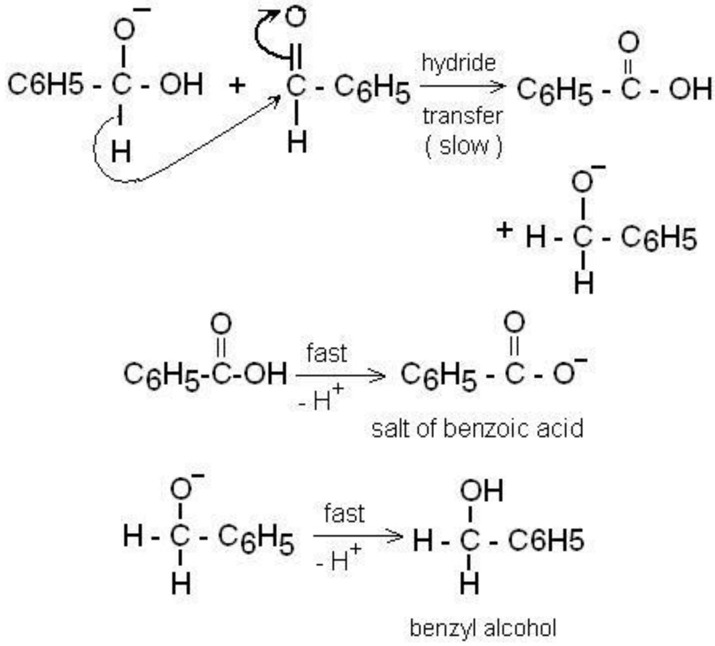
Step I : The OH^- ion attacks the carbonyl carbon to form hydroxyl alkoxide



$$C_6H_5-\overset{\overset{O}{\|}}{\underset{\underset{H}{|}}{C}} + OH^- \xrightarrow{fast} C_6H_5-\overset{\overset{O^-}{|}}{\underset{\underset{H}{|}}{C}}-OH$$

anion (I)

Step II : Anion (I) acts as hybride ion donor to the second molecule of aldehyde. In the final step of the reaction, the acid and the alkoxide ion transfer H^+ to acquire stability.

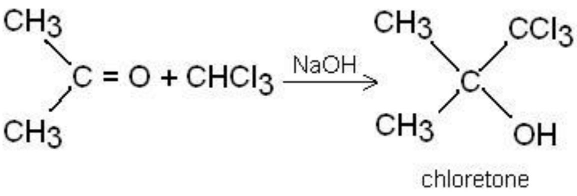


$$C6H5-\overset{\overset{O^-}{|}}{\underset{\underset{H}{|}}{C}}-OH + \overset{\overset{O}{\|}}{\underset{\underset{H}{|}}{C}}-C_6H_5 \xrightarrow[\text{transfer (slow)}]{\text{hydride}} C_6H_5-\overset{\overset{O}{\|}}{C}-OH + H-\overset{\overset{O^-}{|}}{\underset{\underset{H}{|}}{C}}-C6H5$$

$$C_6H_5-\overset{\overset{O}{\|}}{C}-OH \xrightarrow[-H^+]{fast} C_6H_5-\overset{\overset{O}{\|}}{C}-O^-$$

$$H-\overset{\overset{O^-}{|}}{\underset{\underset{H}{|}}{C}}-C_6H_5 \xrightarrow[-H^+]{fast} H-\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}}-C6H5$$

6. Reaction with chloroform

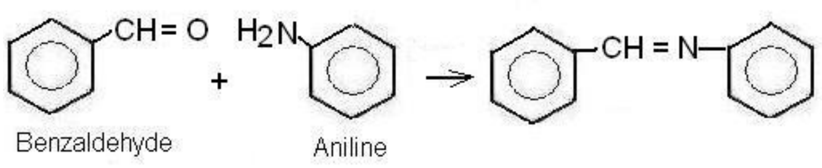


Chloretone is used as hypnotic.

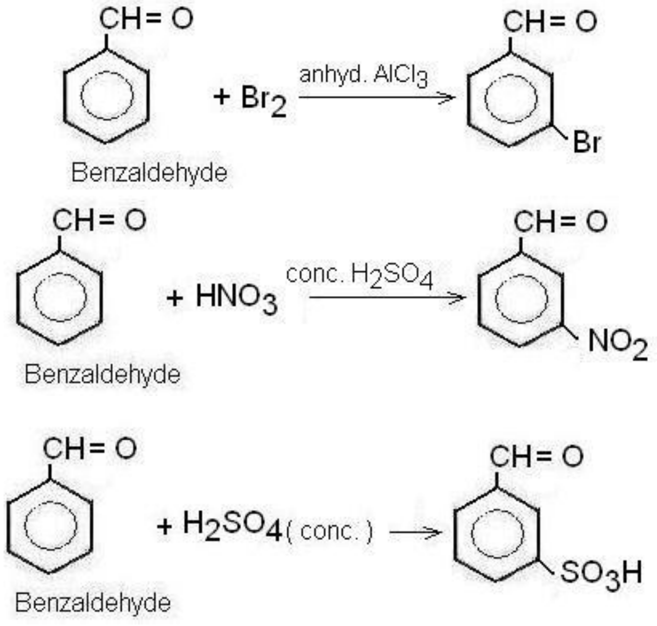
7. Reaction with primary amine

$$RCH\boxed{O + H_2}NR' \xrightarrow[\Delta]{H^+} R\,CH = NR' + H_2O$$

schiff's base



8. Electrophilic substitution reaction of aromatic carbonyl compounds



USES OF ALDEHYDES AND KETONES

(a) Uses of formaldehyde
   - i. The 40% solution of formaldehyde in water (formaline) is used as disinfectant, germicide and antiseptic. It is used for the preservation of biological specimens
   - ii. It is used for silvering of mirrors
   - iii. It is used for making synthetic plastics, like Bakelite, urea- formaldehyde resin etc

(b) Uses of acetaldehyde
   - i. It is used in preparation of acetic acid, dyes, drugs, etc
   - ii. As an antiseptic inhalant in nose troubles

(c) Uses of benzaldehyde
   - i. As flavouring agent in perfume industry
   - ii. In manufacture of dyes.

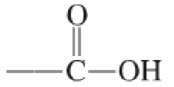
(d) Uses of acetone
   - i. As a solvent for cellulose acetate, resin etc.
   - ii. As a nailpolish remover
   - iii. In the preparation of an artificial scent and synthetic rubber

Chapter 16: Carboxylic Acids, Esters, and Other Acid Derivatives

In Chapter 15, we discussed the carbonyl group and two families of compounds -aldehydes and ketones—that contain C=O group. In this chapter, we discuss four more families of compounds in which the carbonyl group is present: a) carboxylic acid, b) esters, c) amides, d) acid chlorides, and e) acid anhydrides and f) carboxylic acid salts.

16.1 Structure of Carboxylic Acids and Their Derivatives

A carboxylic acid is an organic compound whose functional group is the carboxyl group. What is a carboxyl group? A carboxyl group is a carbonyl group (C=O) with a hydroxyl group (—OH) bonded to the carboxyl carbon atom. A general structural representation fit a carboxyl group is

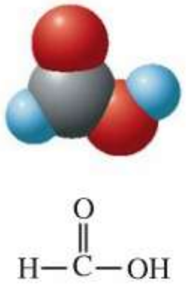


$$-\overset{\overset{O}{\|}}{C}-OH$$

Abbreviated linear designations for the carboxyl group are

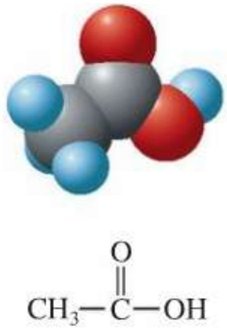
$-COOH$ and $-CO_2H$

Although we see within a carboxyl group both a carbonyl group (C=O) and hydroxyl group (—OH).



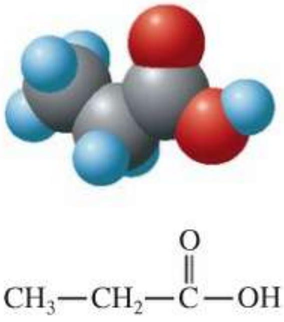
$$H-\overset{\overset{O}{\|}}{C}-OH$$

Methanoic acid



$$CH_3-\overset{\overset{O}{\|}}{C}-OH$$

Ethanoic acid



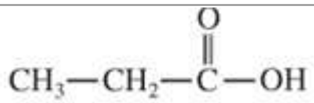
$$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-OH$$

Propanoic acid

16.2 IUPAC Nomenclature for Carboxylic Acids

The naming of carboxylic acids is fairly simple. You simply find the longest carbon chain which includes the carboxylic group. Use that as the stem for the name, cross off the **-e** on the ending of the alkane name and replace it with **-oic acid**.

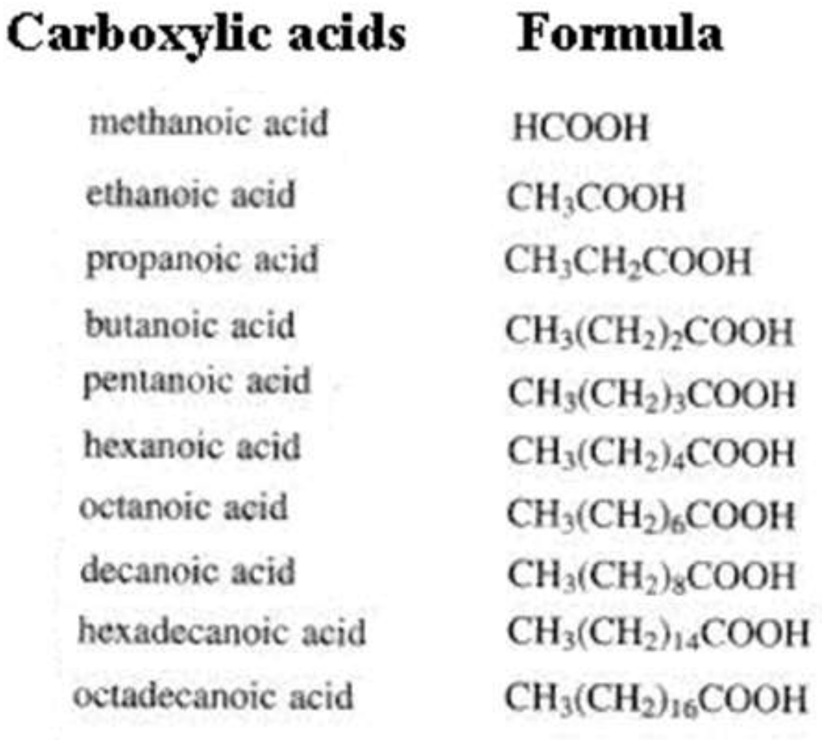
I think you can see how that works, if you look at this example (which is also shown in Example 1-a in your workbook). It gives you, in this case (with a three-carbon-atom chain), the name **propanoic acid**.



$$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-OH$$

propanoic acid
(from **propan** + **oic acid**)

As with aldehydes, it is **not necessary to indicate where** the acid functional group is because it has to be at the end of the molecule, on the #1 carbon. There is no way that this functional group can be anywhere else. Therefore, if there is any numbering to be done, it will be to show where additional alkyl groups or other groups are attached to the carbon chain. The numbering starts from the carboxylic group.

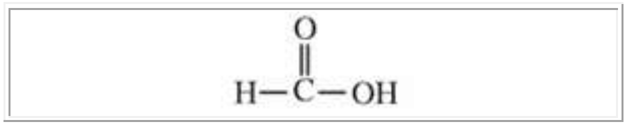


Carboxylic acids	Formula
methanoic acid	$HCOOH$
ethanoic acid	CH_3COOH
propanoic acid	CH_3CH_2COOH
butanoic acid	$CH_3(CH_2)_2COOH$
pentanoic acid	$CH_3(CH_2)_3COOH$
hexanoic acid	$CH_3(CH_2)_4COOH$
octanoic acid	$CH_3(CH_2)_6COOH$
decanoic acid	$CH_3(CH_2)_8COOH$
hexadecanoic acid	$CH_3(CH_2)_{14}COOH$
octadecanoic acid	$CH_3(CH_2)_{16}COOH$

16.3 Common Names for Carboxylic Acids

Carboxylic acids are another example of a situation where the compounds were known and named long before anyone thought of the IUPAC method of naming compounds. Consequently, many carboxylic acids have their own common name which is distinct from the IUPAC name. The two most important of these (and the only two you will be held responsible for in this course) are shown below. They are **formic acid** and **acetic acid**. (These are also shown in Examples 1b and c in your workbook.)

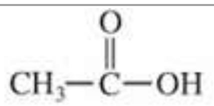
Here is the structural formula for **formic acid**. Its IUPAC name is methanoic acid, using the **meth-** stem because it has **one** carbon atom.



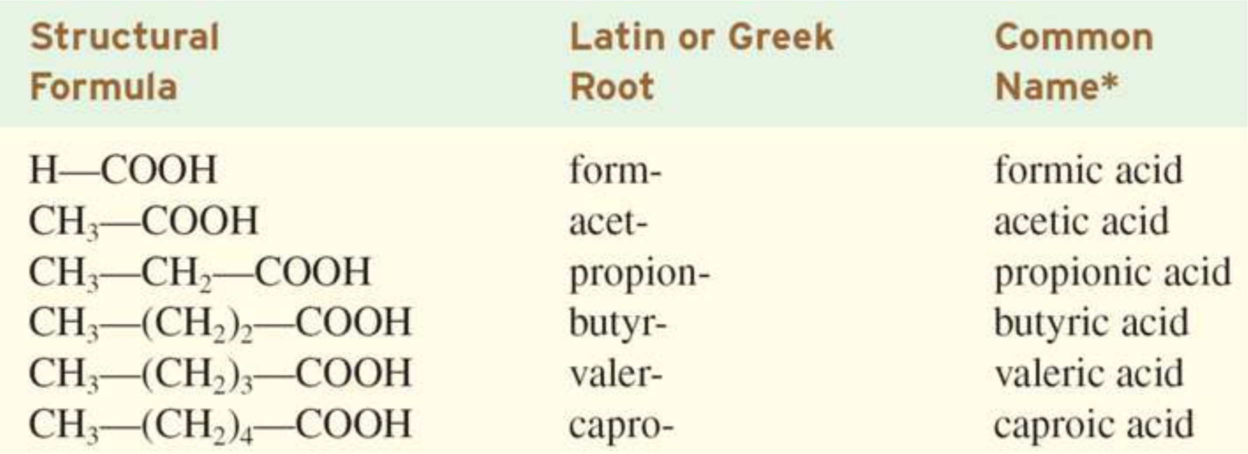
$$H-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

formic acid
methanoic acid

Acetic acid has two carbon atoms. Therefore it can also be called ethanoic acid.


$CH_3-\overset{\overset{O}{\|}}{C}-OH$

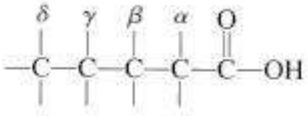
acetic acid
ethanoic acid



Structural Formula	Latin or Greek Root	Common Name*
$H—COOH$	form-	formic acid
$CH_3—COOH$	acet-	acetic acid
$CH_3—CH_2—COOH$	propion-	propionic acid
$CH_3—(CH_2)_2—COOH$	butyr-	butyric acid
$CH_3—(CH_2)_3—COOH$	valer-	valeric acid
$CH_3—(CH_2)_4—COOH$	capro-	caproic acid

Naming using Greek letters ε δ γ β α

There are two ways to identify substituent carbons in carboxylic acid: numbers or Greek letters.
Using numbers, the carboxyl group carbon is given the number one.

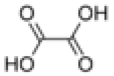
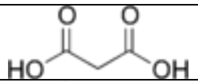
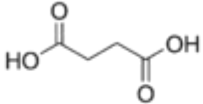
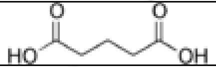
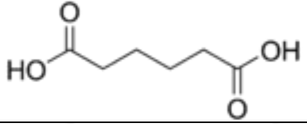
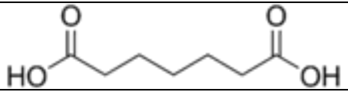


6 5 4 3 2 1
C-C-C-C-C-COOH
ε δ γ β α

When Greek letters are used, Greek letters are used to designate the position of substituent relative to the carbon of the carboxyl group. The carbon of the carboxyl group is **NOT** given a Greek letter.
6) A special group of carboxylic acids are those that also have a keto group. They are called alpha-keto carboxylic acids

16.4 Polyfunctional Carboxylic Acids

Dicarboxylic acids are organic compounds that are substituted with two carboxylic acid functional groups.They are important metabolic products of fatty acids when they undergo oxidation.

Common Name	**IUPAC Name**	**Condensed Formula**	**Structural Fromula**
Oxalic acid	**ethanedioic acid**	$HOOC-COOH$	
Malonic acid	**propanedioic acid**	$HOOC-(CH_2)-COOH$	
Succinic acid	**butanedioic acid**	$HOOC-(CH_2)_2-COOH$	
Glutaric acid	**pentanedioic acid**	$HOOC-(CH_2)_3-COOH$	
Adipic acid	**hexanedioic acid**	$HOOC-(CH_2)_4-COOH$	
Pimelic acid	**heptanedioic acid**	$HOOC-(CH_2)_5-COOH$	

16.5 "Metabolic" Acids

Metabolism is the set of chemical reactions that occur in a cell, which enable it to keep living, growing and dividing. There many acids involved in metabolic processes and a basic understanding of their structures and properties are necessary to understand the biochemistry.

Metabolic acids are polyfunctional acids formed as intermediates of metabolic reactions in the human body. There are eight such acids that will appear repeatedly in the biochemical pathways.

Metabolic acids are derived from:

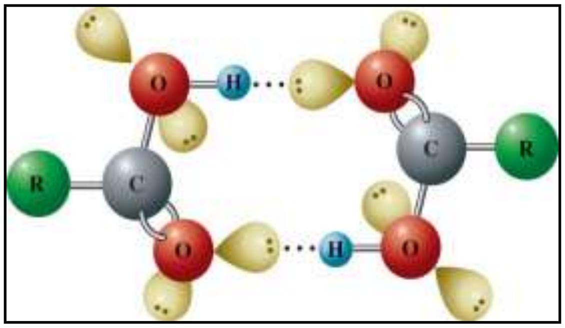
Propionic acid, (C3 mono acids):
lactic, glyceric, and
pyruvic acids

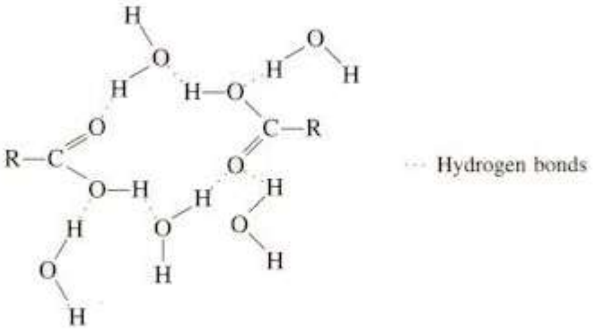
Succinic acid (C4 diacid): fumaric, oxaloacetic, and malic acids
Glutaric acid (C5 diacid): α-ketoglutaric and citric acids

16.6 Physical Properties of Carboxylic Acids

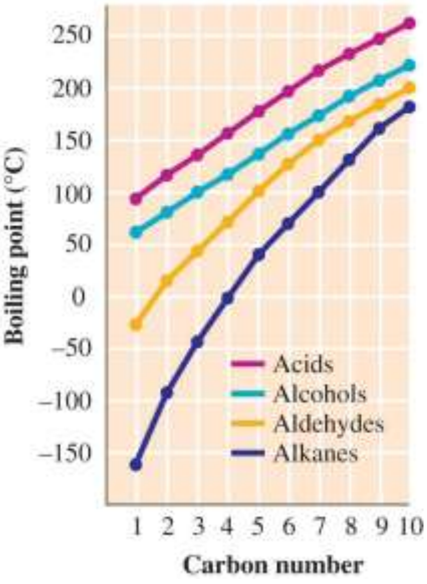
Carboxyl groups exhibit very strong hydrogen bonding. A given carboxylic acid molecule form two hydrogen bonds to another carboxylic acid molecule, producing a “dimer”, a complex with a mass twice that of a single molecule.

Compounds with carboxyl groups have higher boiling points than alcohols. This is because the carboxyl groups hydrogen bond more strongly than alcohols.





Carboxyl groups make molecules very soluble in water because the group can strongly hydrogen bond with water.



Physical Properties of carboxylic acids derivatives

Depending upon the substituent replacing -OH of the caboxylic functional group the physical properties could change.

However, they have lower boiling and melting points than parent acid.

16.7 Preparation of Carboxylic Acids

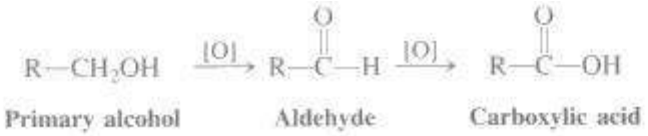
Carboxylic acids are easily by oxidation of primary alcohols and aldehydes. When the oxidation process begins with an alcohol it is difficult to stop at the aldehyde stage of oxidation.

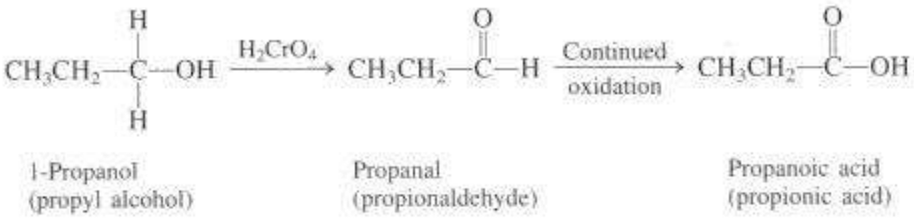
Oxidation of primary alcohol to carboxylic acid.

Chemical equations

$CH_3CH_2CH_2OH$ ---> CH_3CH_2CHO ---> CH_3CH_2COOH
primary alcohol aldehyde acid

$Ar-CH_2-OH$ ---> $ArCHO$ ---> $Ar-COOH$





Oxidation using basic $Ag(NH_3)_2^+$

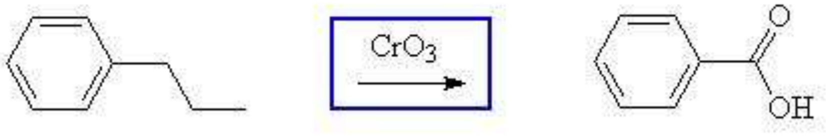
A basic $Ag(NH_3)_2^+$ in aqueous ammonia reduces to metallic silver (mirror) with aldehyde oxidized to carboxylic acid.

$$R-\overset{O}{\overset{\|}{C}}-H + Ag(NH_3)_2^+ \longrightarrow R-\overset{O}{\overset{\|}{C}}-OH + Ag^0(s)$$

The commercial manufacture of silver mirrors uses a similar process.

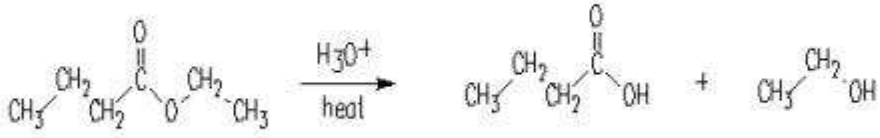
Oxidation of alkyl side chain substituted on a benzene ring to an acid functional group.

$Ar- CH_2 -CH_3$ ---> $Ar- COOH$



hydrolysis of esters.

acid-catalyzed hydrolysis is the exact reverse of Fisher esterification (same mechanism)



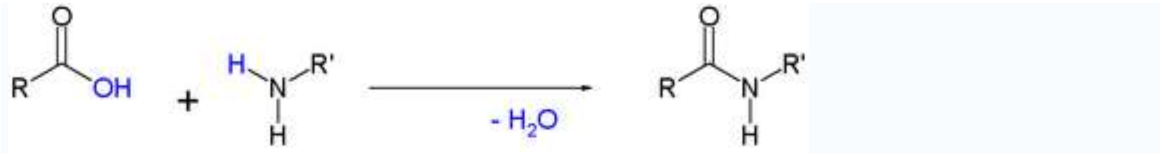
Reactions of Carboxylic Acid

Reaction with strong bases to form acid salts (described below in preparation of acid salts)

Reaction with strong alcohols to form esters (described below in preparation of esters-esterification)

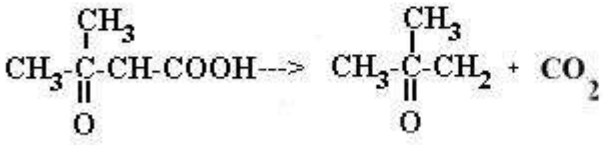
Reaction with halogen compounds to form acid chlorides(described below in preparation of acid chloride preparations)

Reaction with ammonia and amine compounds to form amides (described below in preparation of amides chapter 18)



Reactions of β-keto acids.

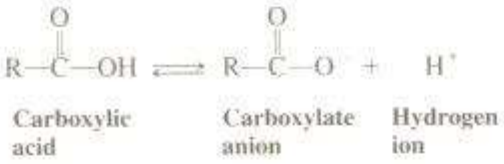
β-keto acids are readily decarboxylated.



$$CH_3\text{-}\underset{\underset{O}{\parallel}}{\overset{\overset{CH_3}{|}}{C}}\text{-}CH\text{-}COOH \text{--->} CH_3\text{-}\underset{\underset{O}{\parallel}}{\overset{\overset{CH_3}{|}}{C}}\text{-}CH_2 + CO_2$$

16.8 Acidity of Carboxylic Acids

Carboxylic acids are weak acids.

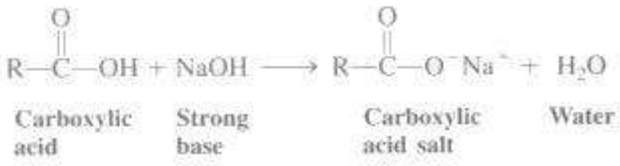


$$R\text{—}\overset{\overset{O}{\parallel}}{C}\text{—}OH \rightleftharpoons R\text{—}\overset{\overset{O}{\parallel}}{C}\text{—}O^- + H^+$$

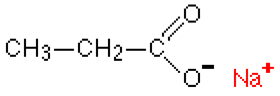
$HCl + H_2O \text{--->} H^+ + Cl^-$ (100%)

$CH_3\text{-}COOH$ (95%) $\overset{\text{-->}}{\text{<---}}$ $CH_3\text{-}COO^-$ (5%) + H^+

Acid base reactions:

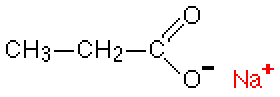


16.9 Carboxylic Acid Salts



Naming carboxylic acid follows certain pattern for example the structural formula for the compound. Since this sodium salt of propanoic acid - so start from propanoic acid is a three carbon acid with no carbon-carbon double bonds and this negative ion without the H$^+$ atom is called propanoate. There this salt is named: **sodium propanoate**

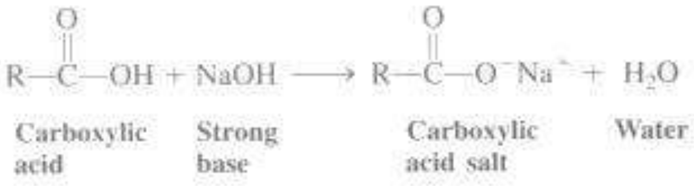
When the carboxylic acids form salts, the hydrogen in the -COOH group is replaced by a metal. Sodium alkan**oate (propan-oate)** is therefore:



sodium propanoate

Preparation of acid salts

Acid salts are prepared by the reaction of acid with a base such as sodium hydroxide.



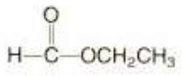
16.11 Preparation of Esters

Naming Esters:

1. Identify the alkyl group that is attached to the oxygen atom
2. Number according to the end closest to the -CO- group regardless of where alkyl substituents are.
3. Determine the alkane that links the carbon atoms together. If there is a separation of a continuous link of carbon atoms due to the oxygen atom, individually name the two alkanes before and after the oxygen atom. The longer structural alkane is the one that should contain the carbonyl atom.

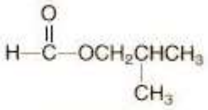
4. The format is as follows: (alkane further from carbonyl) (alkane closest to carbony)(parent chain)
5. Change the parent chain -e ending and replace it with an -oate.
   Example:
   $CH_3COOC_7H_{14}CH_3$
   octyl ethanoate

Common Esters


$H-\overset{O}{\overset{\|}{C}}-OCH_2CH_3$

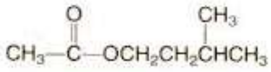
Rum

Ethyl methanoate
(ethyl formate)


$H-\overset{O}{\overset{\|}{C}}-OCH_2\underset{CH_3}{\underset{|}{C}}HCH_3$

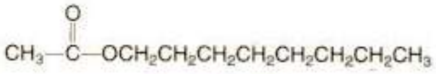
Raspberries

Isobutyl methanoate
(isobutyl formate)


$CH_3-\overset{O}{\overset{\|}{C}}-OCH_2CH_2\overset{CH_3}{\overset{|}{C}}HCH_3$

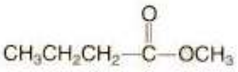
Bananas

3-Methylbutyl ethanoate
(isoamyl acetate)


$CH_3-\overset{O}{\overset{\|}{C}}-OCH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$

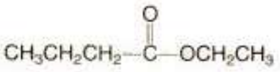
Oranges

Octyl ethanoate
(octyl acetate)


$CH_3CH_2CH_2-\overset{O}{\overset{\|}{C}}-OCH_3$

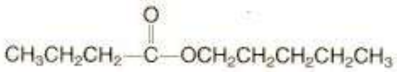
Apples

Methyl butanoate
(methyl butyrate)


$CH_3CH_2CH_2-\overset{O}{\overset{\|}{C}}-OCH_2CH_3$

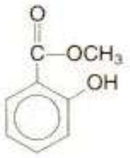
Pineapples

Ethyl butanoate
(ethyl butyrate)

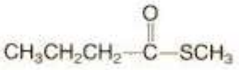

$CH_3CH_2CH_2-\overset{O}{\overset{\|}{C}}-OCH_2CH_2CH_2CH_2CH_3$

Apricots

Pentyl butanoate
(pentyl butyrate)


Oil of wintergreen

Methyl salicylate

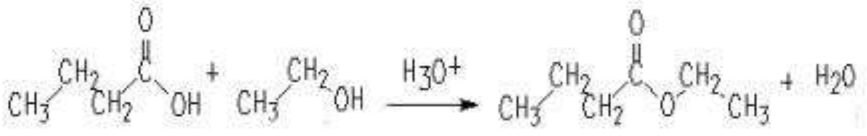

$CH_3CH_2CH_2-\overset{O}{\overset{\|}{C}}-SCH_3$

Strawberries

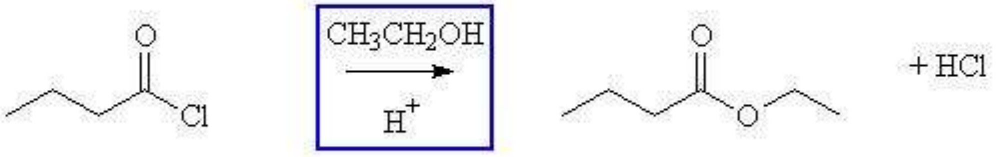
Methyl thiobutanoate
(methyl thiobutyrate)

Esterification form acid and alcohol

acid + alcohol ----> ester + H_2O



Esterification from acid chlorides and alcohol



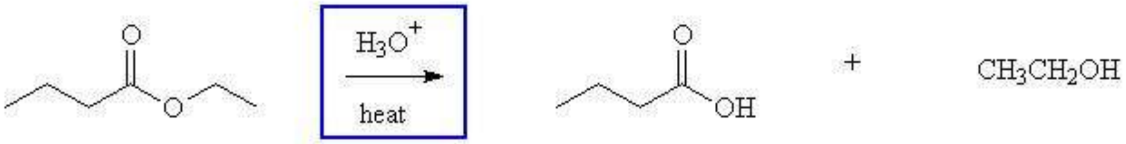
Note: the acid loses an -OH units and the alcohol loses a -H in this reaction.

16.14 Isomerism for Carboxylic Acids and Esters

16.16 Chemical Reactions of Esters

Hydrolysis

1) **acid-catalyzed hydrolysis** is the exact reverse of Fisher esterification (same mechanism)

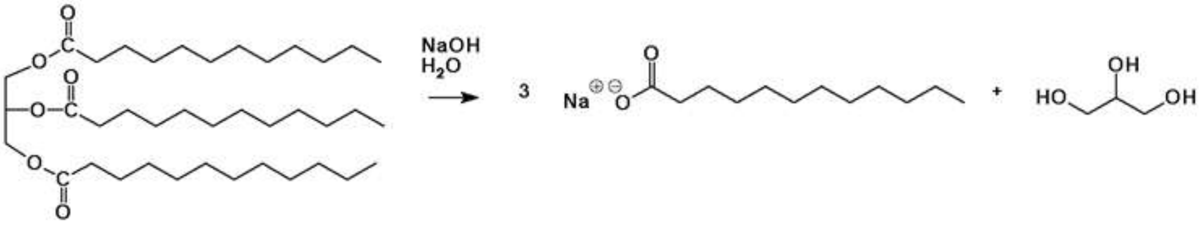


2) **base-catalyzed hydrolysis** is often called **saponification** (soap-making) saponification is irreversible because a carboxylate salt is formed.

Saponification of triglycerides and action of soap in the emulsification of grease and oils.

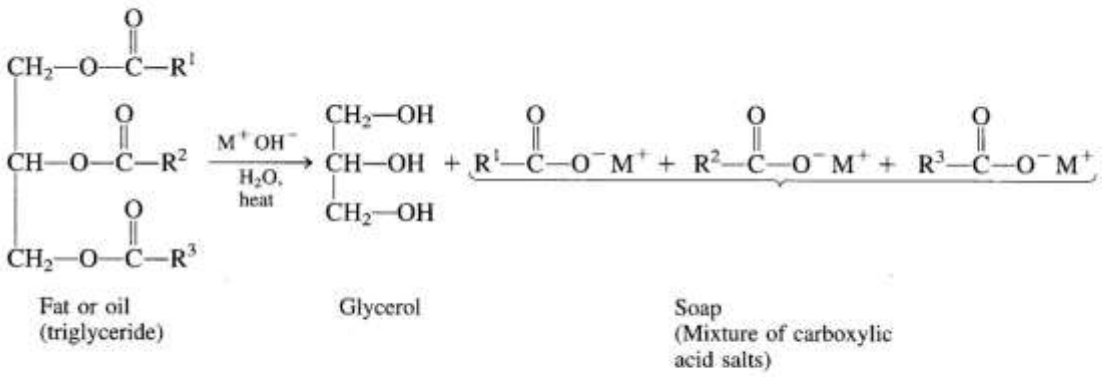
Soap has been around for hundreds of years. In it's simplest form, soap is made by heating fat in boiling water that also has sodium hydroxide (NaOH)or potsssium hydroxide (KOH) ions in it. Each fat molecue breaks down into three molecules of fatty acids. The molecules of fatty acids then react with the sodium or potassium ions to form soap molecules and glycerin.

triglyceride



glycerol

If the triglyceride had three different fatty acids following products with three fatty acids are formed.



where $M^+ = Na^+$ or K^+

Soaps are water-soluble sodium or potassium salts of long-chain (fatty) acids (C8-C20). Fats are the esters of fatty acids and glycerol (1,2,3-propanetriol). Base-catalyzed hydrolysis is often called saponification (soap-making) saponification is irreversible because a carboxylate salt is formed.

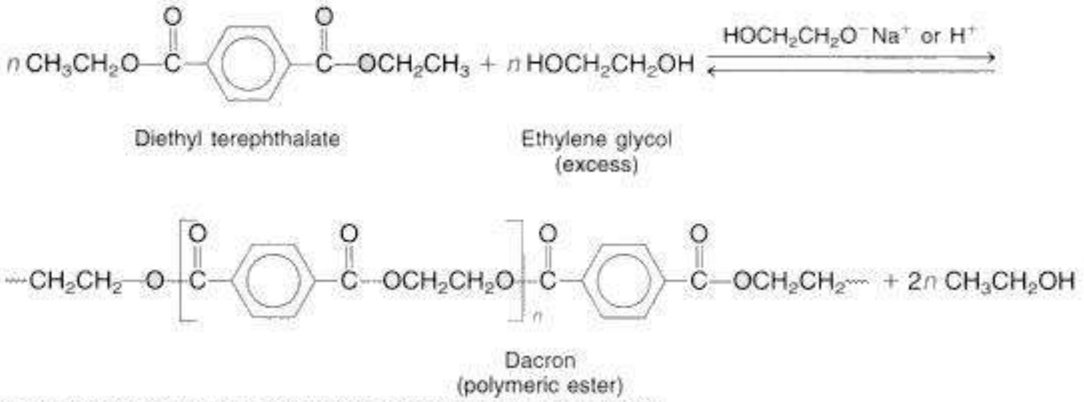
How does soap work?

In the cleaning process, surface tension must be reduced so water can spread and wet surfaces. Chemicals that are able to do this effectively are called surface active agents, or surfactants. They are said to make water "wetter." Soap perform other important functions in cleaning, such as loosening, emulsifying (dispersing in water) and holding soil in suspension until it can be rinsed away. Soap can also provide alkalinity, which is useful in removing acidic soils.

16.18 Polyesters

Polyesters are formed by condensation polymers are any kind of polymers formed through a condensation reaction, releasing small molecules as by-products such as water or methanol, as opposed to addition polymers which involve the reaction of unsaturated monomers. Types of condensation polymers also include polyamides, polyacetals.

Condensation polymerization

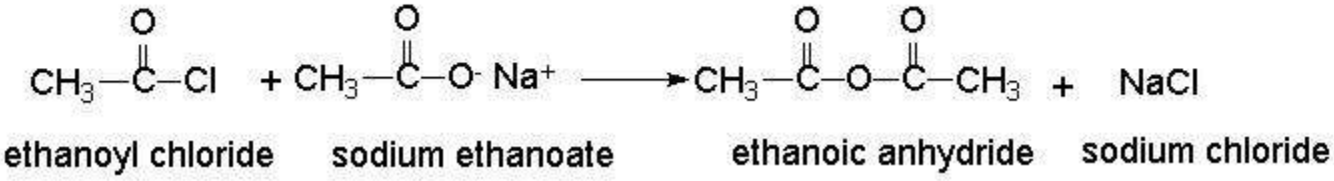


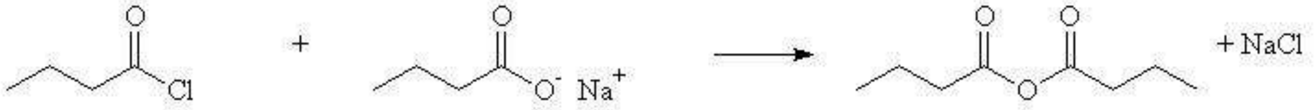
The polymerization process for difunctional compounds (shown for Dacron).

16.19 Acid Chlorides and Acid Anhydrides

Preparation of acid anhydrides

Acid chlorides are prepared by the rection of acid with PCl_3, PCl_5 or $SOCl_2$.. Acid anhydrides are prepared by the rection of acid chlorides with its sodium salt.

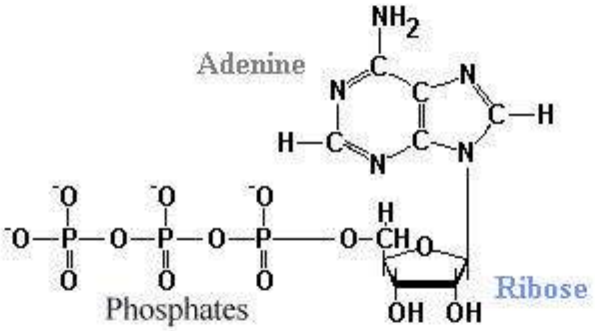

$$CH_3-\overset{\overset{O}{\|}}{C}-Cl + CH_3-\overset{\overset{O}{\|}}{C}-O^- Na^+ \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH_3 + NaCl$$



Butanoyl chloride **sodium butanoate** **butanoic anhydride**

16.20 Esters and Anhydrides of Inorganic Acids

Adenosine triphosphate (ATP) consists of the nitrogenous base adenine bonded to the sugar ribose, which is connected to a chain of 3 phosphate groups.

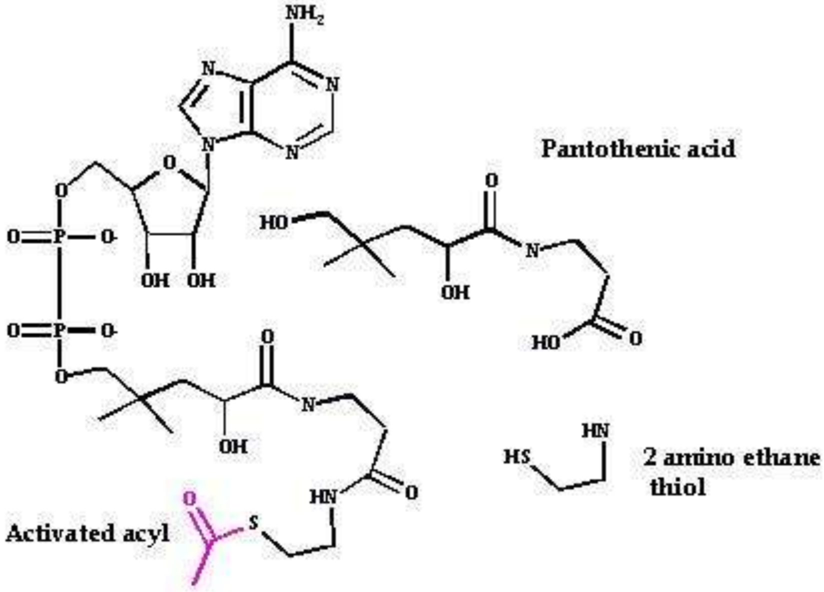


ATP hydrolysis releases energy

Phosphate groups are negatively charged, and repel in ATP.   Release of phosphate gives a large positive entropy change. We synthesize an amount of ATP equal to our body weight every day.
The first step in glycolysis is the formation of glucose-6 phosphate from glucose. The direct reaction of inorganic phosphate (Pi) with glucose is unfavorable. However, the hydrolysis of ATP is extremely favorable. In a cell the enzyme hexokinase catalyzes the coupled reaction of ATP with glucose favoring the formation of glucose-6-phosphate.

Thioesters : Acetyl CoA

Thioesters are more susceptible toward nucleophilic attack than are esters and acids. Thioesters are intermediate in reactivity between acid chlorides and esters making them perfect functional groups for biological systems.



References

1- **Principles of organic chemistry by Robert J. Ouellette, 2015.**

2- **Organic chemistry, Robert J. Ouellette, J. David Rawn, 2018.**

3- **Organic chemistry, Jonathan Clayden, Nick Greeves, and Stuart Warren, 2012.**

4- **Advanced organic chemistry, Francias A. Carey, Richard J. Sundberg, 2010.**

5- **Fundamentals of organic chemistry, John McMurry, 2013.**

6- **The organic chemistry lab. Survival manual, James W. Zubrick, 2016.**

7- **Fundamentals of reaction mechanism in organic chemistry, R. P. Narain, 2011.**