

Chapter 14 Organic Reactions

Types of Bond Breaking

Homolytic fission

Covalent bond breaks by splitting the shared pair of electrons between two products.

- Two free radical produced

Heterolytic fission

Covalent bond breaks while both electrons go for the same product.

- Two oppositely charged ions

Types of Reactions

Addition

Two reactants combine to form a single product.

Elimination

Removal of a small molecule (usually H_2O or HX) from a large one.

Substitution

One atom or group of atoms in a compound is replaced by a different atom or group.

Condensation

Two reactants join together while a small molecule (Usually H_2O , HCl or NH_3)

- Occurs between two functional groups

Hydrolysis

Breakdown of an organic molecule by water to form two other organic molecules.

- Often accelerated by alkali or acid

Oxidation

Involve the addition of oxygen atoms or the removal of hydrogen atoms.

Reduction

Involve the addition of hydrogen atoms or the removal of oxygen atoms.

Free Radical Substitution

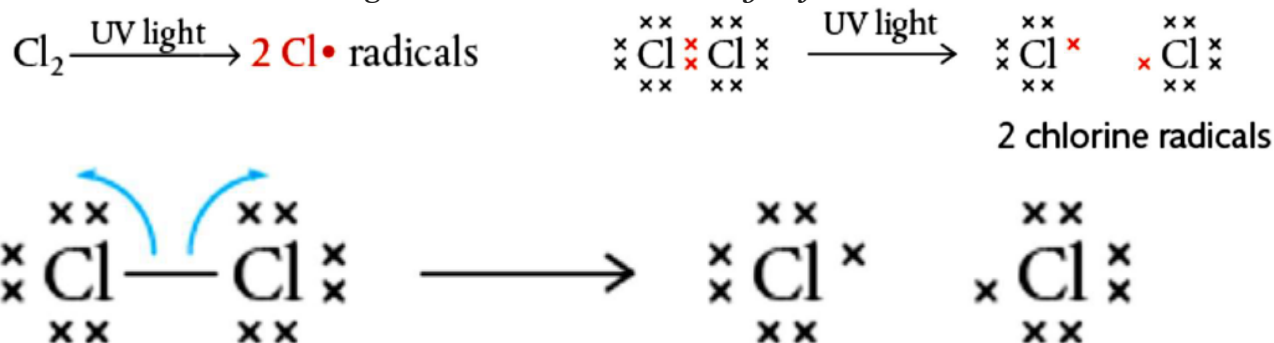
Reactant: Halogen, Alkane

Product: Halogenalkane, Hydrogen Halide

Condition: UV light

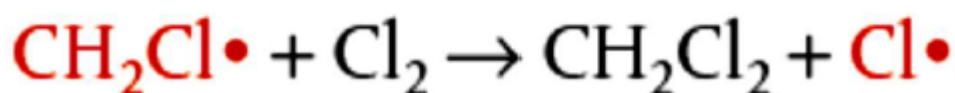
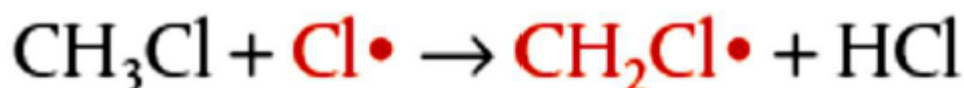
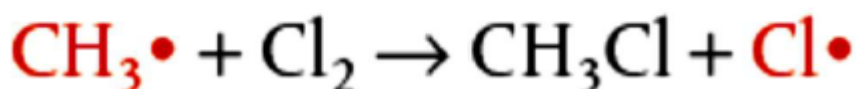
Reaction Mechanism (Take Chlorine and Methane as an example)

1. **Initiation** Chlorine undergoes *Photochemical homolytic fission*.



2. **Propagation** Both use and produce free radicals.

- Many possible propagation step triggers a *chain reaction*.



3. **Termination** Remove free radicals from the mixture, result in paired up electrons.

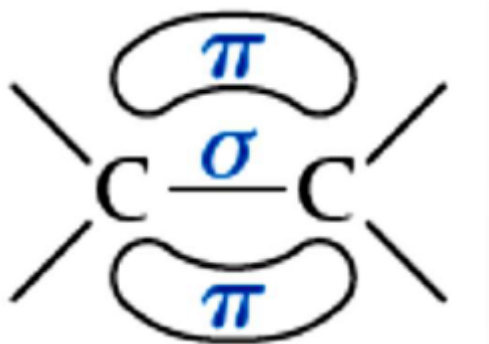
- Many termination steps are possible.



Electrophilic Addition

Property of Alkenes

- Unsaturated hydrocarbon, which contains a carbon-carbon double bond.
 - Double bonds has one σ bond and one π bond, the carbon atoms are sp^2 hybridized. The π bond is above and below the plane of bond axis.

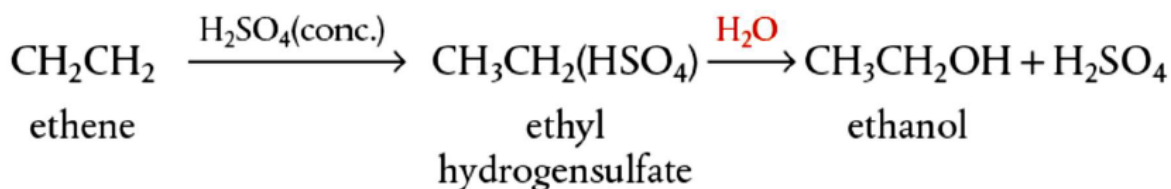
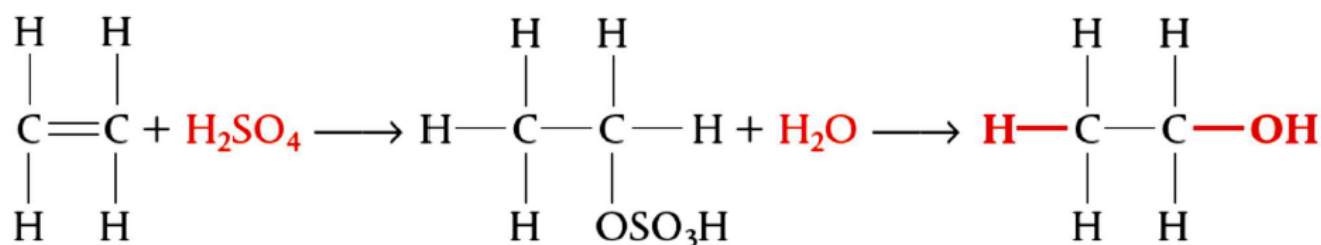


- The shape is called *Planar Triangular*.
- The π bond can break easily, creating two new bonding positions.
- Electron density of $C = C$ bond is higher than $C - C$ bond, attracting electrophile.

Reaction Process

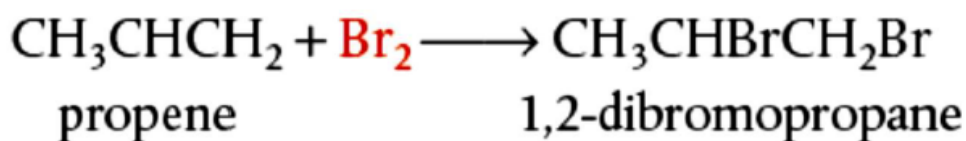
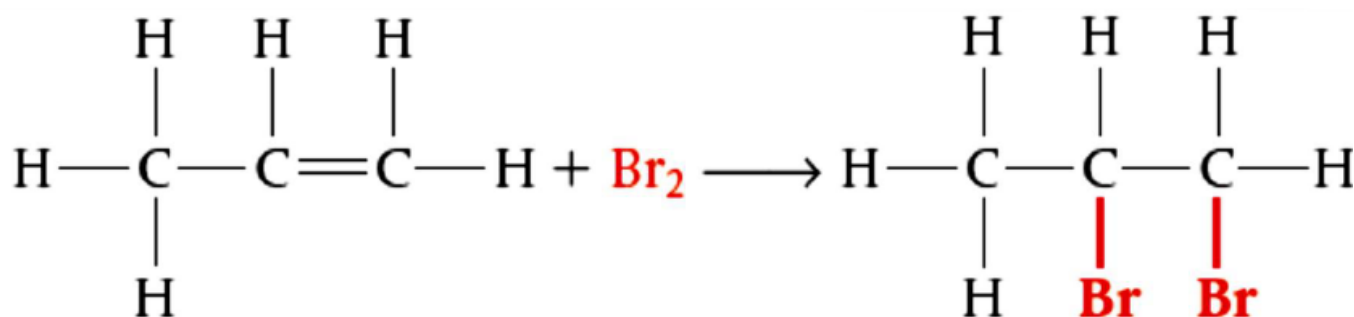
Addition of Water (Hydration)

- **Reactants:** Alkene, $H_2O_{(g)}$
- **Product:** Alcohol
- **Catalyst:** *conc.* H_2SO_4
- **Condition:** Heat



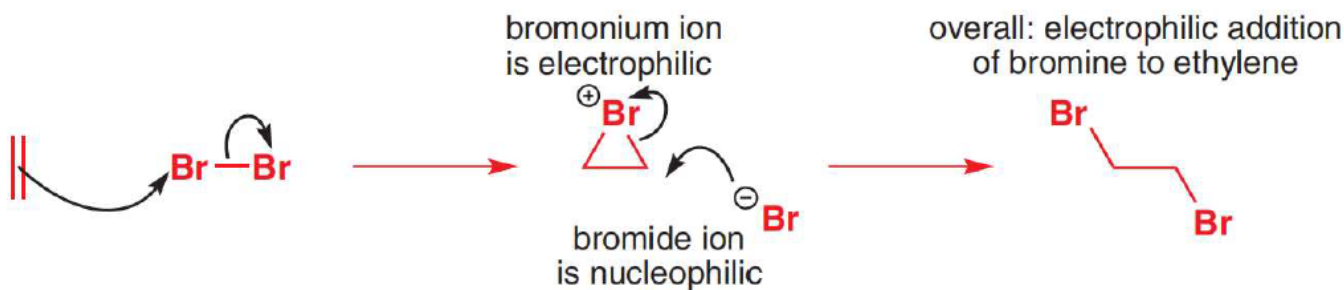
Addition of Halogens

- **Reactants:** Alkene, Halogen
- **Product:** Dihalogenoalkane
- **Catalyst:** /
- **Condition:** /



Mechanism:

1. Bromine approaches π bond to become polarized
2. Bromine atom near the double bond gain a $\delta+$.
3. Bromine molecule splits heterolytically. The positive ion breaks the π bond. SLOW STEP
4. Carbocation is formed. The positive charge is on Br^+ ion.
5. Br^- is introduced to form the final product to attach on C .



The Bromine Test

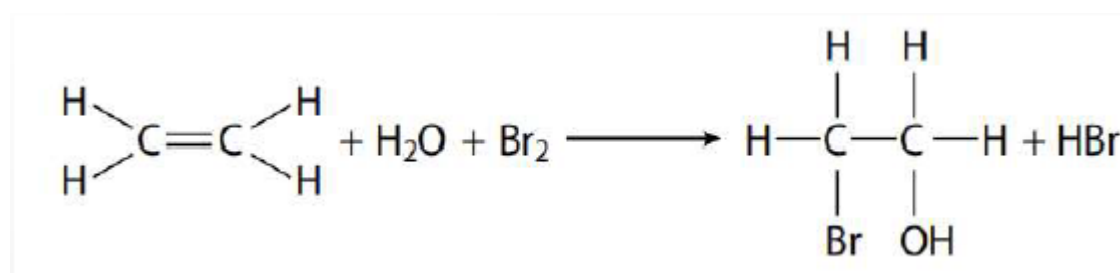
Distinguish between alkanes and alkenes

- Reactants: Alkane / Alkene (Colorless), Bromine water (Brown), Water

Phenomenon

The solution will appear in two layers

- Alkene
 - Upper level: *HBr* solution (light brown)
 - Lower level: Bromoalcohol (colorless)
- Alkane / Benzene
 - Upper level: Benzene / Alkane (Colorless)
 - Lower level: Bromine water (Brown)



Addition of Hydrogen Halides

Reactants: Alkenes, hydrogen halides (*HCl*, *HBr*)

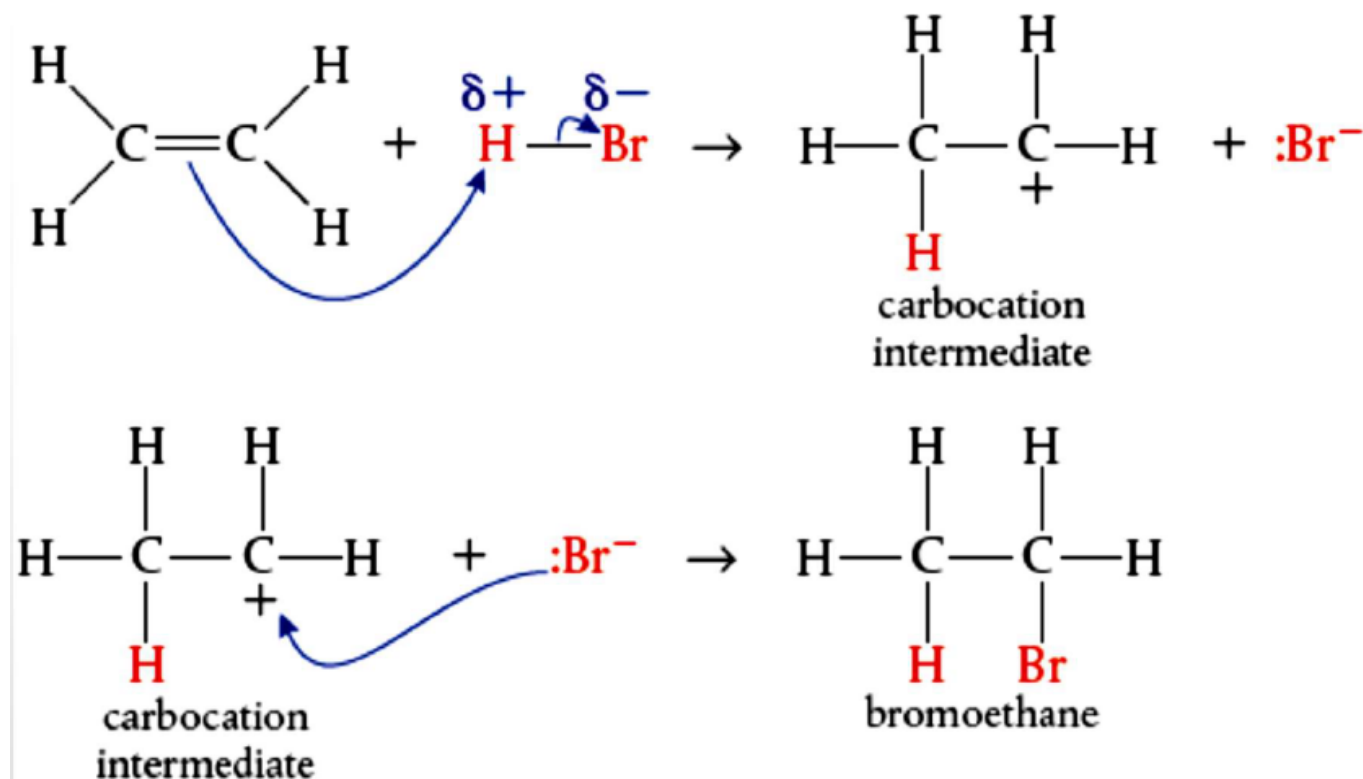
Products: Halogenalkane

Catalyst: /

Condition: /

Mechanism

1. HBr undergoes heterolytic fission as the $\delta+$ part of it (H^+) approaches the π bond.
2. Carbocation intermediate is formed ($C_2H_5^+$) (*Slow step*)
3. The intermediate bonds with the Br^- quickly to form final product (CH_3CH_2Br)



Reactivity

- $HI > HBr > HCl$ due to decreasing strength of bond.
- *Polar solvents* are favored (Help the production of ions in *heterolytic fission* step)

Asymmetric Addition

Two forms of *Positional Isomers* could be produced for *Asymmetric Alkenes*.

The formation will follow **Markovnikov's Rule**

The hydrogen will attach to the carbon that is already bonded with greater number of carbons.

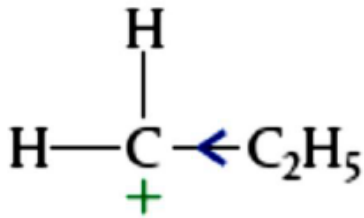
The mechanism that proceeds via the most stable carbocation will be favored.

$\delta+$ \rightarrow less carbon attached carbon atom / $\delta-$ \rightarrow more carbon attached carbon atom

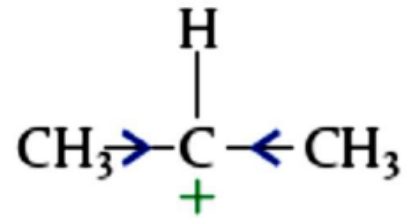
Explanation

- Alkyl groups stabilize the carbocation with *Positive Inductive Effects*.

- Secondary carbocation forms two effects while primary has only one.



primary carbocation
one positive inductive effect



secondary carbocation
two positive inductive effects:
more stable

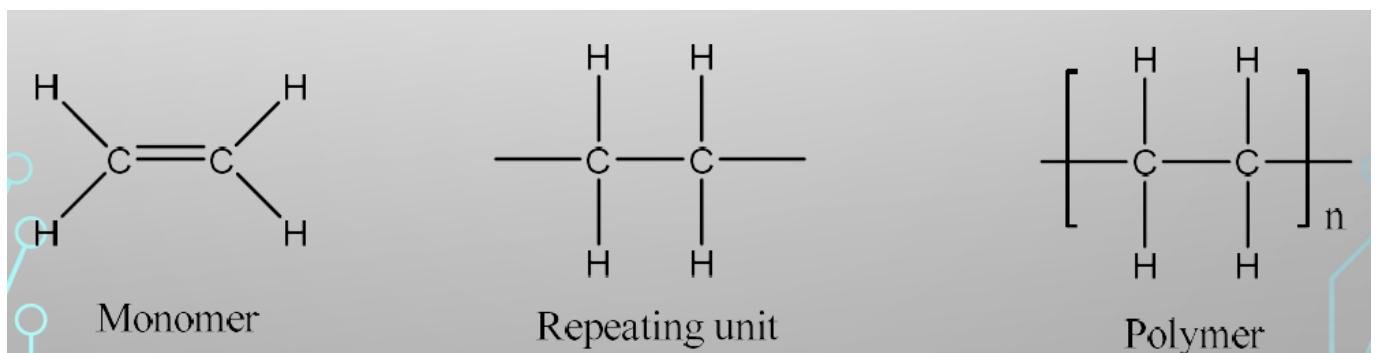
Addition Polymerization

Reactants: Monomers (usually alkene)

Products: Polymers (usually polyalkene)

Polymers:

- Low thermal and electrical conductivity
- Low density to other materials
- Macromolecules
- Synthetic polymers / Natural polymers
- High melting points and boiling points
 - More intermolecular force due to the length
 - Wind around each other and require energy to disentangle



Types of Plastic

- Polyphenylethene (polystyrene)

- Non-polar
- Melt down when heated, reshape easily.
- Brittle due to bulky phenyl groups
- Polyisoprene
 - Natural rubber
- Polyethene
 - Packaging

Why non-biodegradable?

- Strong covalent bonds
- Chemically inert and durable
- Crosslinking makes degrading even harder

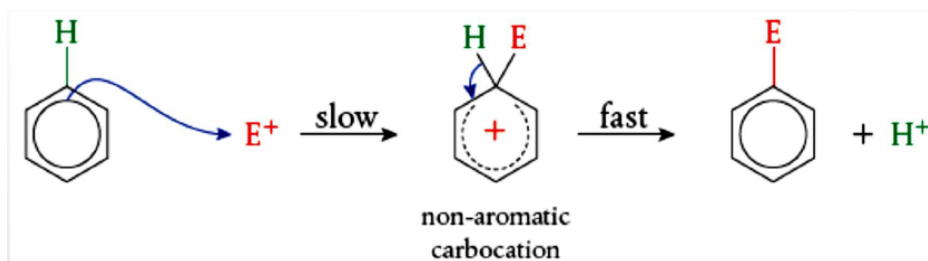
Electrophilic Substitution

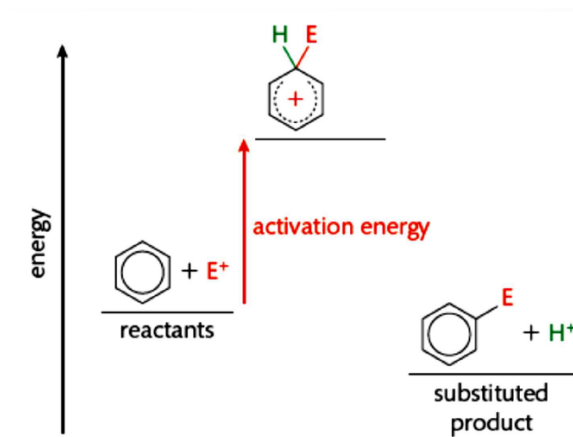
Reactants: Benzene, Electrophile

Products: Substituted benzene, H^+

Mechanism

1. Benzene is attractive to electrophiles for ring has high electron density.
2. Cloud of π electrons seek for electrophiles to form a new bond. Result in a carbocation intermediate having *both* entering group and leaving hydrogen. (Slow step require high activation energy)
3. A H^+ is lost after the process. (Fast step)





Chlorination of Benzene

Reactants:

- Benzene
- Electrophile: Cl^+ (Using aluminum chloride to obtain)

Products: Chlorobenzene, H^+

Production of Cl^+

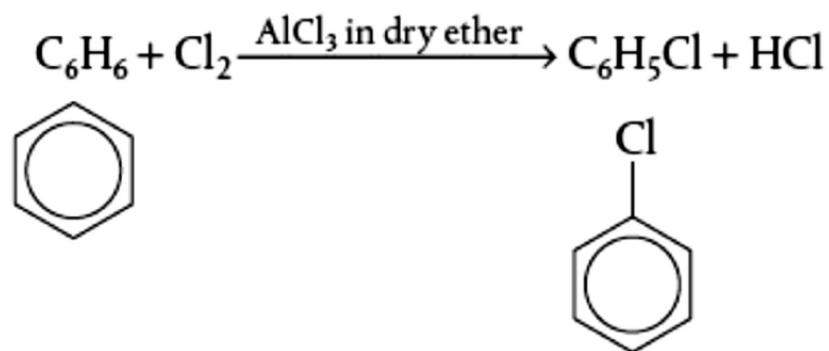
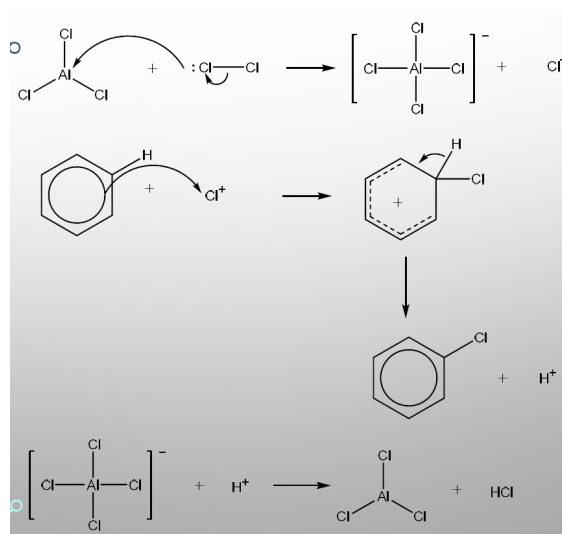
1. React Cl_2 with $AlCl_3$ at $55 - 60^\circ C$. $AlCl_3$ is dissolved in dry ether, to avoid ionization of itself in water.
2. Cl_2 splitted, forming $[AlCl_4]^-$ and Cl^+ .

Mechanism of Main Reaction

3. Cl^+ attack the π bond cloud in benzene
4. Carbocation intermediate is formed.
5. H^+ detached from the carbocation intermediate.

Follow-up Reaction

6. $[AlCl_4]^-$ react with detached H^+ to form $AlCl_3$ and HCl .



Nitration of Benzene

Reactants:

- Benzene
- Electrophile: NO_2^+ (using nitrating mixture to generate)

Products:

- Nitrobenzene (Appears as yellow oil)

Production of NO_2^+

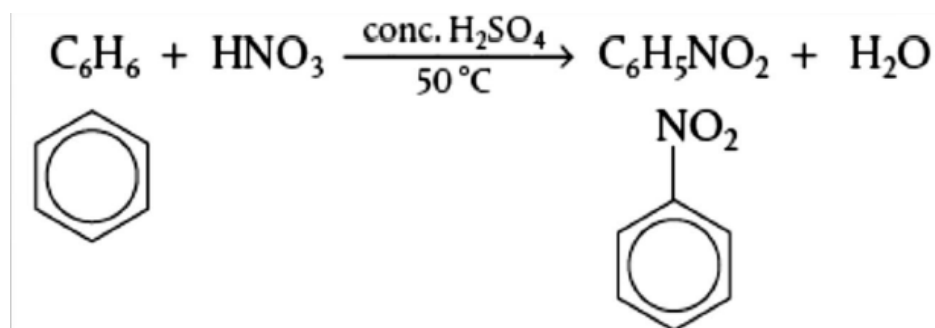
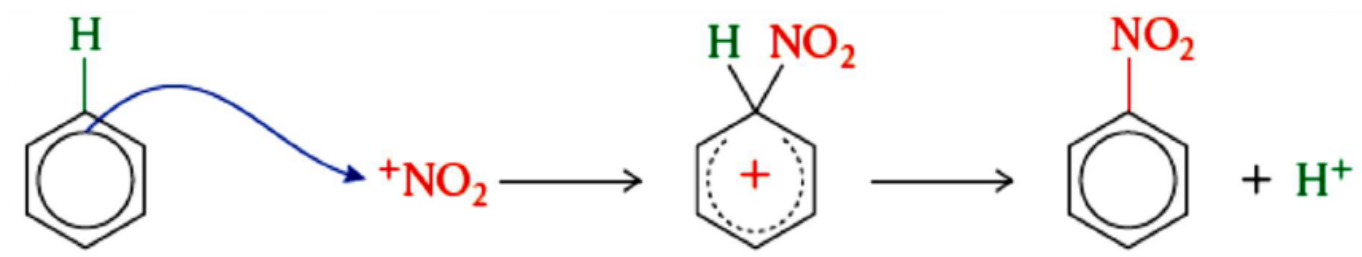
1. React Nitric Acid (*conc.* HNO_3) and Sulfuric Acid (*conc.* H_2SO_4) at 50°C .
2. A H^+ on Sulfuric acid is detached. It is captured by O with two lone-pair electrons.
3. The bond $\text{N} - \text{O}$ break, releasing a H_2O from the structure.
4. The nitronium ion NO_2^+ is formed.

Mechanism of Main Reaction

5. NO_2^+ attack the π bond cloud in benzene
6. Carbocation intermediate is formed.
7. H^+ detached from the carbocation intermediate.

Follow-up Reaction

8. The detached H^+ bond with $[\text{HSO}_4]^-$ to form sulfuric acid.



Nucleophilic Substitution (S_N)

Reactants: Halogenalkanes, Nucleophile (OH^- , H_2O , CN^- , NH_3)

Products: Depends on the property of nucleophile.

Why halogenalkanes?

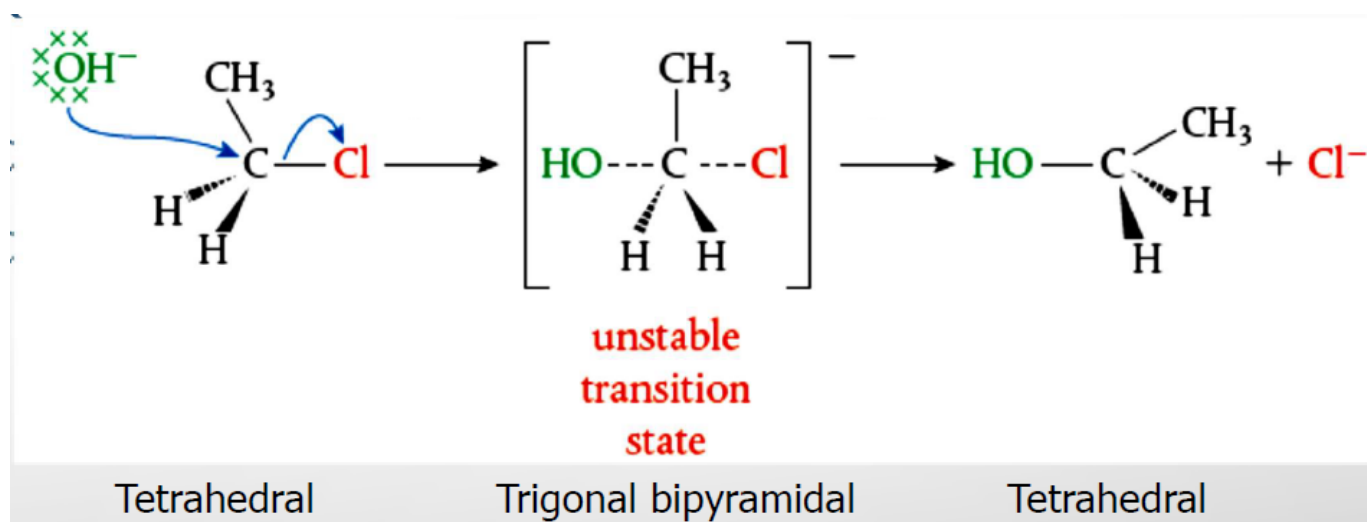
- Possess a polar bond makes them more reactive.

Number represents for the order of reaction (Number of molecule in the rate-determine step).

Mechanism of S_N2

- $\text{Rate} = k[\text{RX}][\text{OH}^-]$
- For Primary Halogenalkanes and Secondary Halogenalkanes (Because H atoms are small enough for nucleophile to attack directly to the carbon)
- Transition state: Carbon bonded with both halogen and nucleophile

- Arrangement around carbon atom is inverted
 - Optical molecules change its arrangement.
 - Stereospecific: 3D arrangement of reactants determines the final configuration.
1. Attacking nucleophile approaches the halogenalkane (tetrahedral) from the direction opposite from the leaving group.
 2. The nucleophile and the leaving group is both attached to the central carbon, forming unstable transition state (Trigonal Bipyramidal)
 3. The leaving group detaches. (tetrahedral)



Conditions:

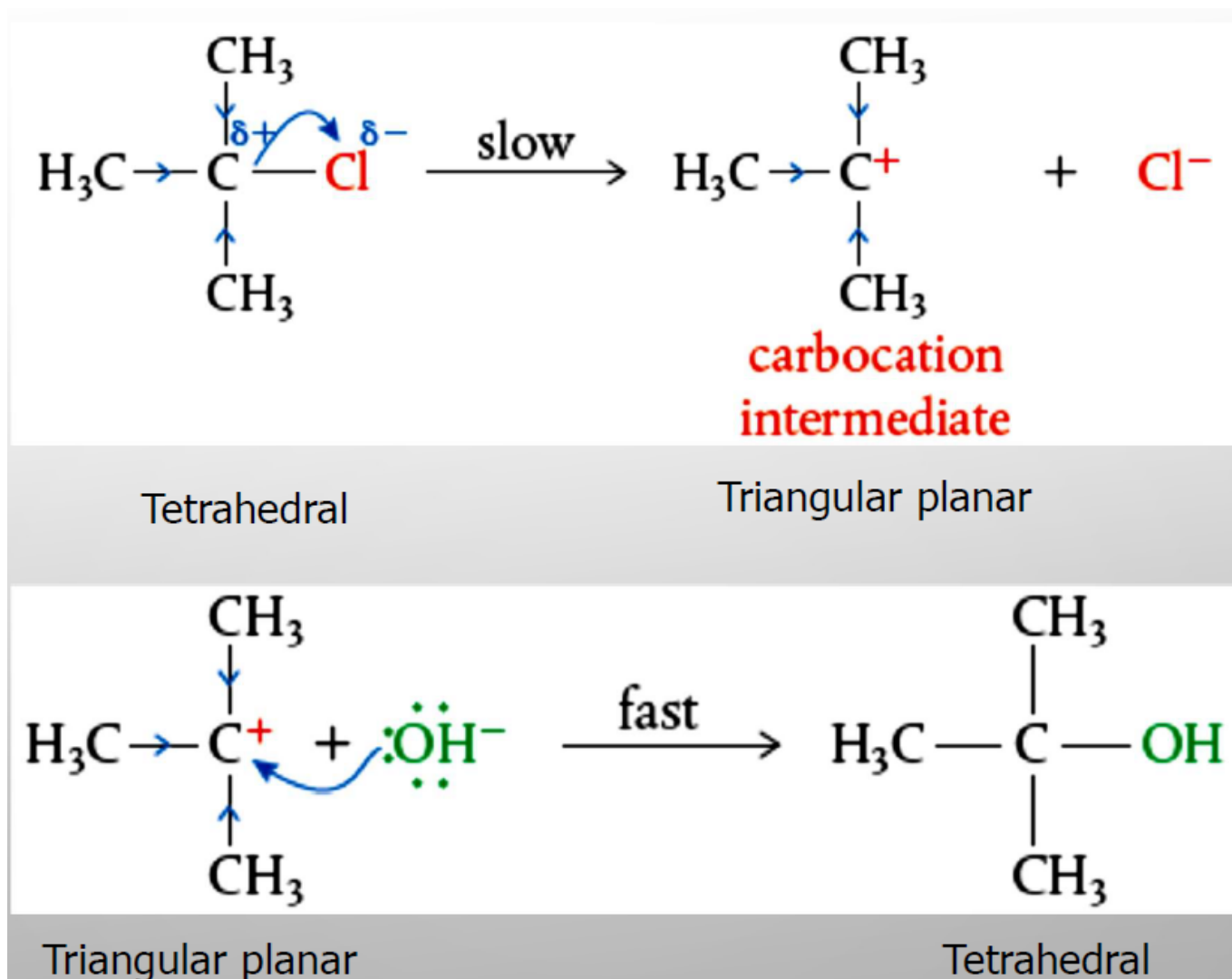
- Favoured by Polar, Aprotic solvents. (Aprotic: Do not form hydrogen bond (No $-OH$ or $-NH$ bonds))
 - The cation part can dissolve in such solvent
 - Nucleophile is rather less solvate, which is less stable and increase reaction rate.
 - Suitable include: Propanone and ethanenitrile.

Mechanism of S_N1

- $Rate = k[RX]$
- For Tertiary Halogenalkanes and Secondary Halogenalkanes (Alkyl groups around are called *Steric Hindrance*, difficult for an incoming group to attack this carbon atom)
- The detachment of leaving group and attachment of nucleophile are two separate steps.
- NOT Stereospecific (intermediate undergoes sp^2 hybridation, can be attack by both sides)

◦ The resultant product would be a racemic mixture.

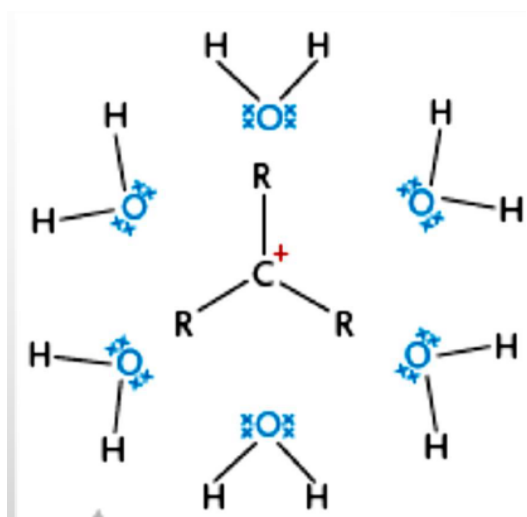
1. Bond between Carbon and the Leaving Group break, forming a carbocation intermediate under *Positive Induction Effect*. (Tetrahedral \rightarrow Triangular Planar) (slow step)
2. The nucleophile approaches the carbon and attach to it. (Triangular Planar \rightarrow Tetrahedral) (fast step)



Conditions:

Anything that stabilizes the intermediate favor the reaction

- Favored by Polar, Protic solvents.
 - Effective in stabilizing the positively charged intermediate through ion-dipole interactions.
 - The lone-pair electrons can attach to the positive part on the carbocation
- Suitable include: Water, alcohols, carboxylic acids



How could the Rate of S_N Reactions be altered?

Mechanism, Leaving group, Choice of Solvent

Mechanism

S_N1 mechanism is faster than S_N2 mechanism.

Therefore *Tertiary* > *Secondary* > *Primary*

Leaving Group

Polarity

- Electronegativity decreases down the group.
- Less electron deficient, less vulnerable to nucleophilic attack.

Fluoro- > *Chloro-* > *Bromo-* > *Iodo-*

Strength of Bond

- Bond strength decrease down the group

Iodo > *Bromo* > *Chloro* > *Fluoro*

In summary

Iodo > *Bromo* > *Chloro* > *Fluoro*

Choice of Solvent

- S_N1 favor polar, protic solvents

- S_N2 favor polar, aprotic solvents

Condensation

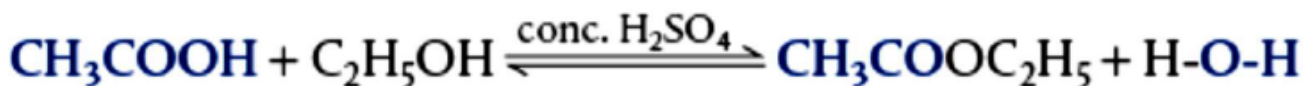
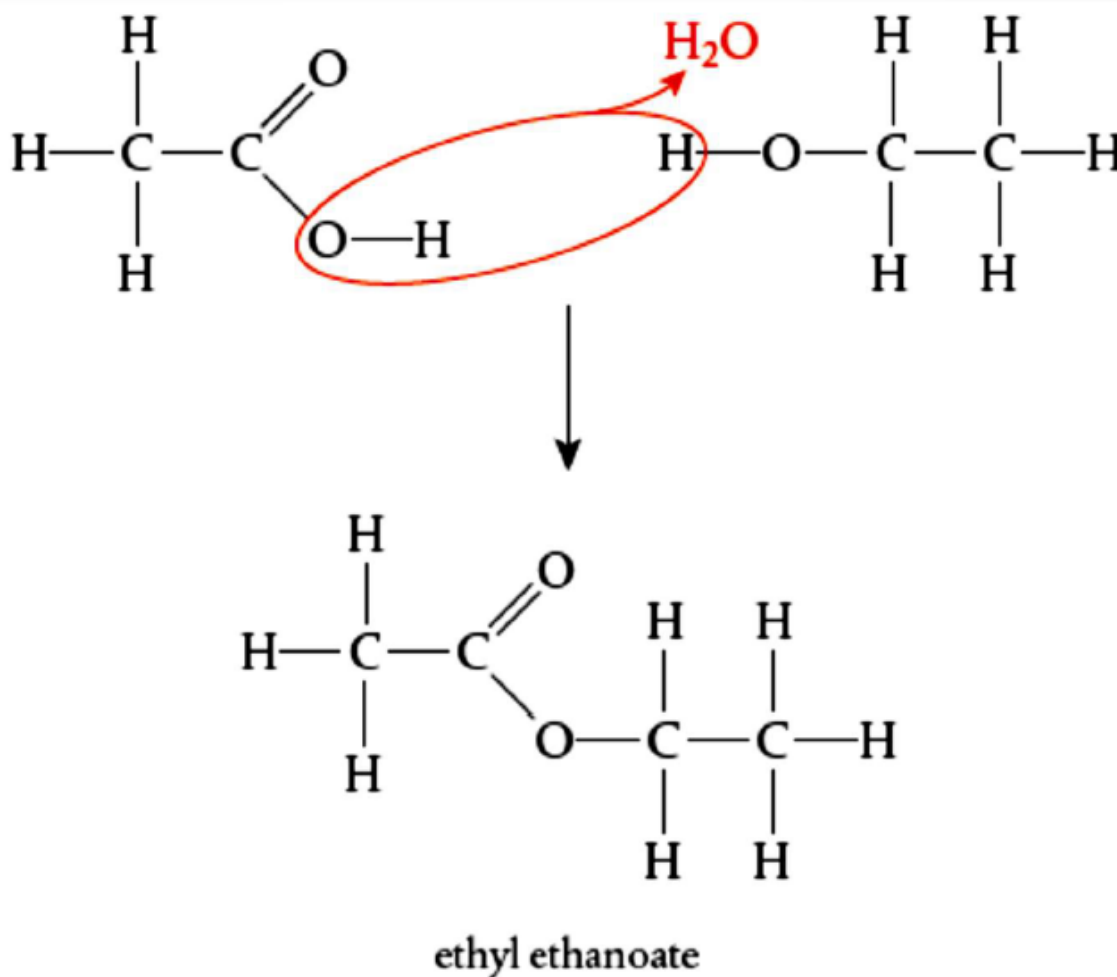
Esterification Reaction

Reactants: Alcohol, Carboxylic Acids

Products: Ester, water

Catalyst: *conc.* H_2SO_4

- Esters can be separated by distillation due to low boiling point.
- Insoluble in water due to no free $-OH$ groups



Condensation Polymers

Produced in a reaction between monomers that have reactive functional groups on either end.

Each bond formed between the monomers would release a small molecule.

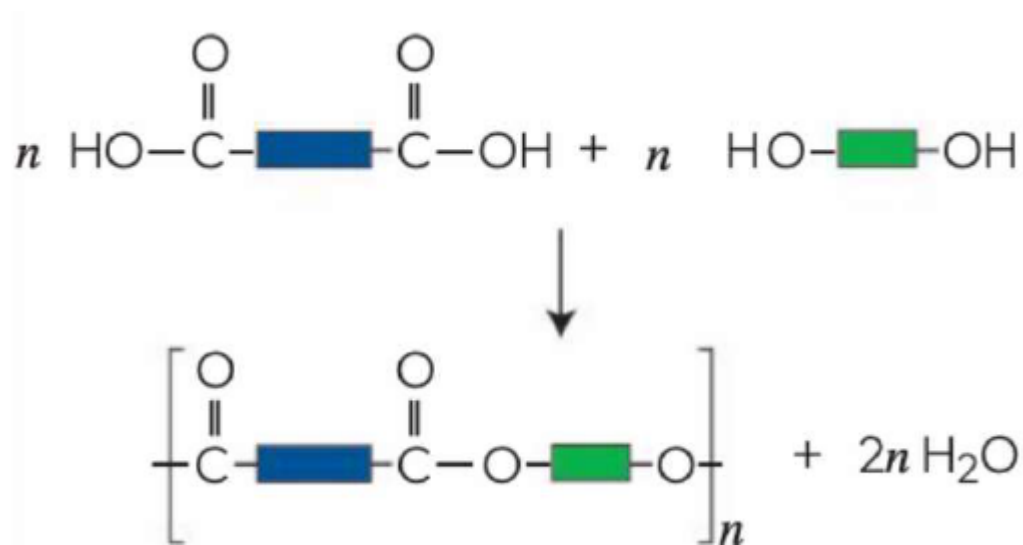
Condensation between Two Different Monomers

- Monomer with same functional group at either end.
- Monomer structure form ABABABABABAB

Ester Linkage

Between Dicarboxylic acid and Diol monomer.

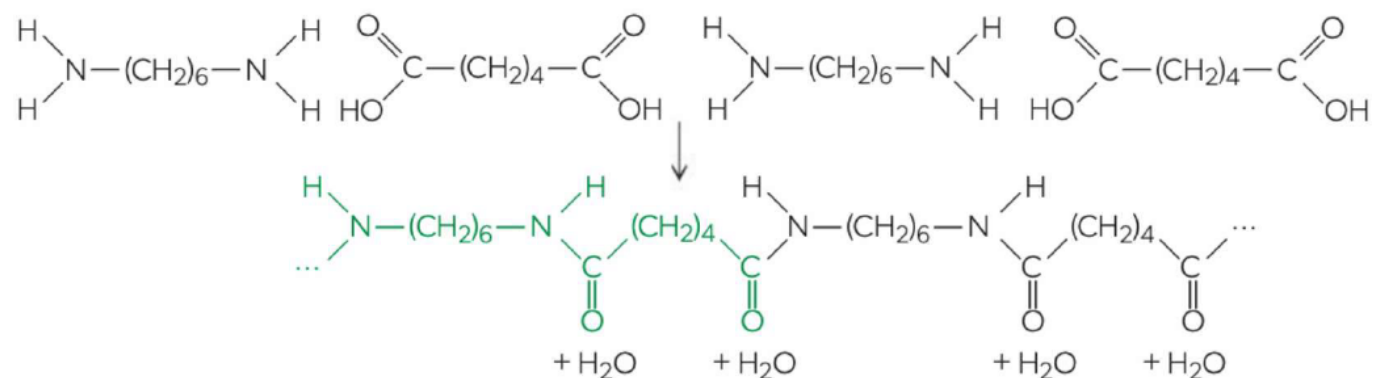
Result is called polyester.



Amide Linkage

Between Dicarboxylic acid and Amine.

Result is called polyamide



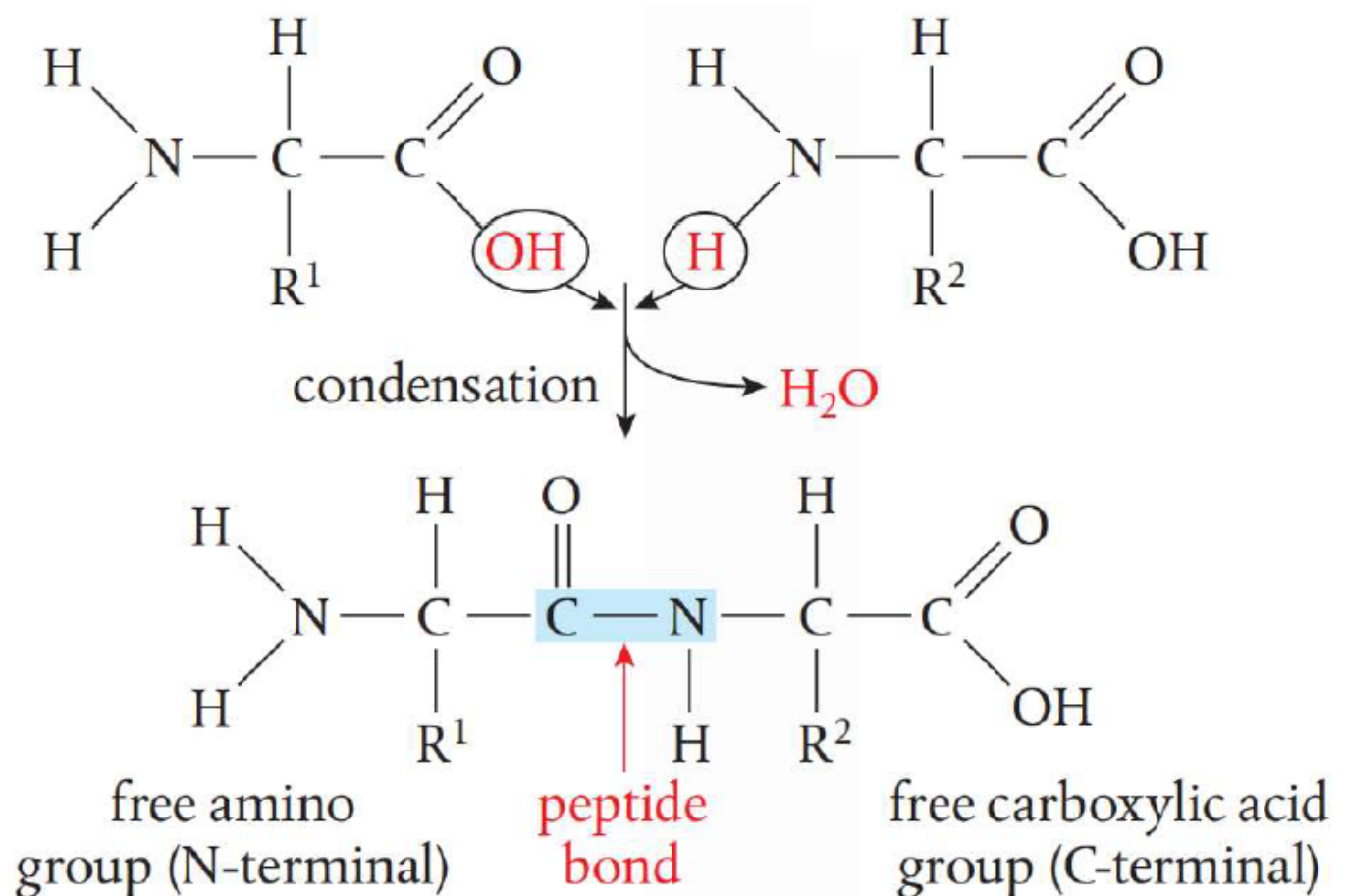
▲ Figure 31 The formation of nylon-6,6. The repeating unit is shown in green

Condensation of the Same Monomer

- Different functional group on each end of a monomer.
- Polymerize with itself.

Polypeptide (Peptide bond)

Monomer contain amino ($-NH_2$) and carboxylic acid ($-COOH$) group.



Oxidation

Reactant: Alcohol

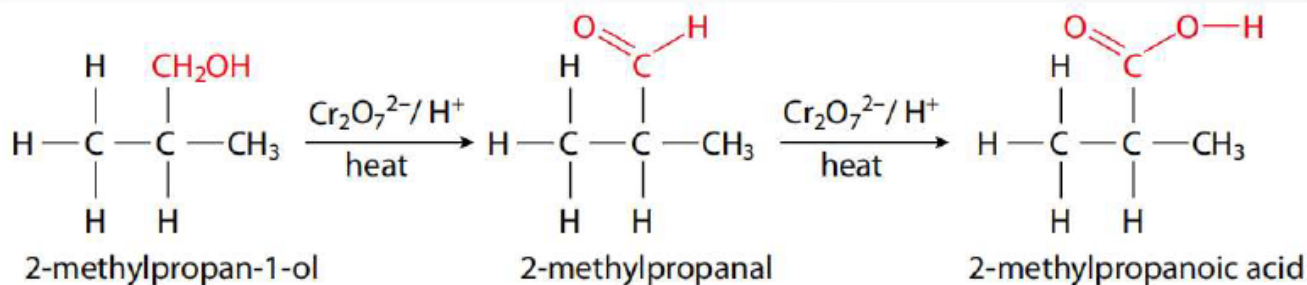
Product: Aldehyde / Carboxylic Acid

Catalyst: Acidified Potassium Dichromate ($K_2Cr_2O_{7(aq)}$) / Acidified potassium permanganate ($KMnO_{4(aq)}$)

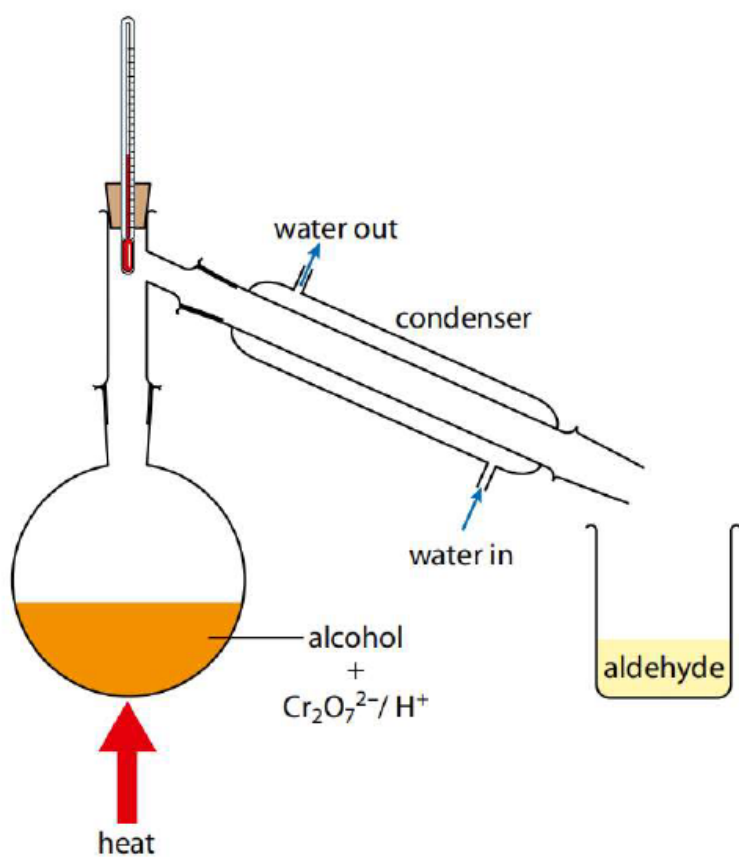
Condition: Heat

Primary Alcohols

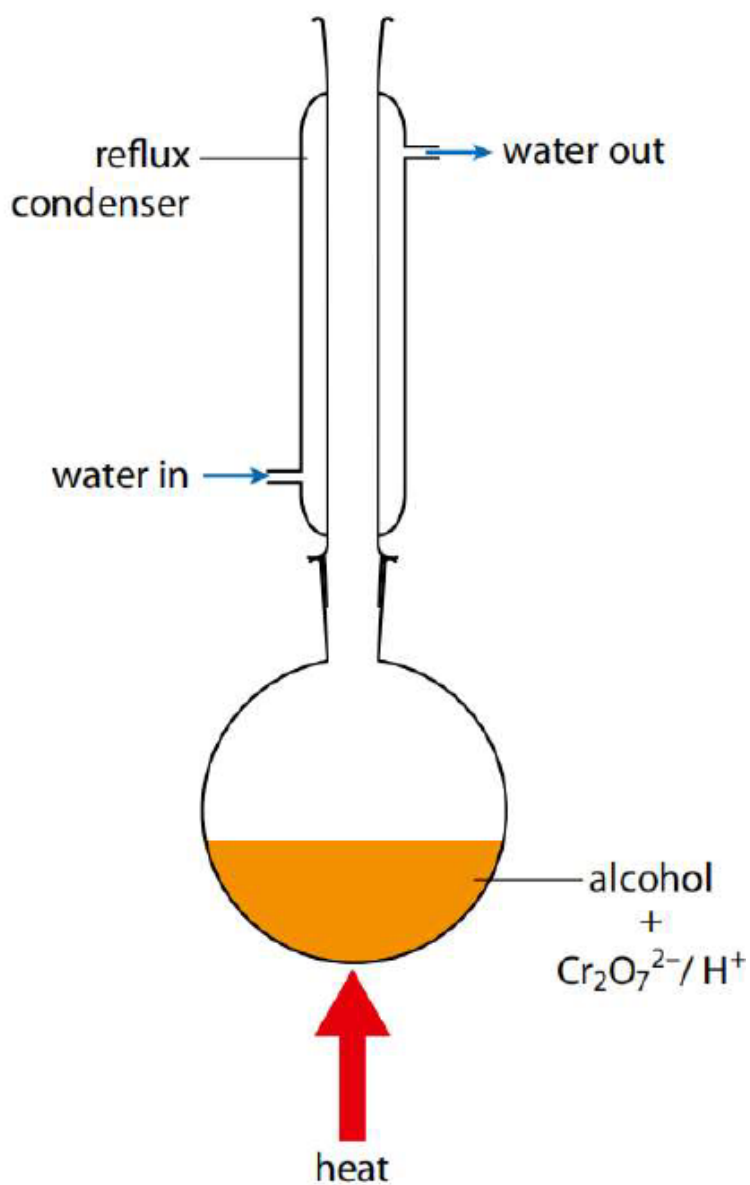
- Oxidized in Two steps: *Alcohol* \rightarrow *Aldehyde* \rightarrow *Carboxylic Acid*



- Can be stopped at first step using *distillation*.
 - Aldehyde has lowest boiling point (No hydrogen bond)
 - Excess alcohol in presence



- Can obtain *pure* carboxylic acid through *reflux* setup.
 - Prevent the produced aldehyde from escaping, forcing to be further oxidized.
 - Alcohol should be limiting, oxidizing agent should be in excess to obtain pure carboxylic acid.



Secondary Alcohols

- Oxidized in one step: *Alcohol* \rightarrow *Ketone*

Tertiary Alcohols

- Will not be oxidized under current condition.
- Required breaking the carbon skeleton.

Reactant	Oxidation Product	Color change with $K_2Cr_2O_7(aq)$	Color change with $KMnO_4(aq)$
Primary Alcohol	<i>Aldehyde</i> → <i>Ketone</i>	<i>Orange</i> → <i>Green</i>	<i>Purple</i> → <i>Colorless</i>
Secondary Alcohol	<i>Ketone</i>	<i>Orange</i> → <i>Green</i>	<i>Purple</i> → <i>Colorless</i>
Tertiary Alcohol	Not oxidized	No color change	No color change

Reduction

Carbonyl Compounds

Reactants: Carbonyl compounds

Products: Alcohol / Aldehyde

Catalysts: Sodium Borohydride ($NaBH_4$, in aqueous or alcoholic solution) / Lithium Aluminium Hydride ($LiAlH_4$, in anhydrous conditions (dry ether) followed by aqueous acid)

Carboxylic Acid → *Aldehyde* → *Primary Alcohol*

Condition: Heat with $LiAlH_4$ in dry ether, CANNOT be stopped at aldehyde.

Aldehyde → *Primary Alcohol* **and** *Ketone* → *Secondary Alcohol*

Condition: Heat with $LiAlH_4$ in dry ether **OR** Heat with $NaBH_4$ in aqueous or alcoholic solution.

Alkene & Alkyne (Hydrogenation)

Reactants: Alkene / Alkyne

Products: Alkane

Catalysts: Palladium $Pd_{(s)}$ / Nickel $Ni_{(s)}$ / Platinum $Pt_{(s)}$

- Decrease the degree of Unsaturation of compounds.

Alkyne → *Alkene*

- Using Palladium $Pd_{(s)}$

