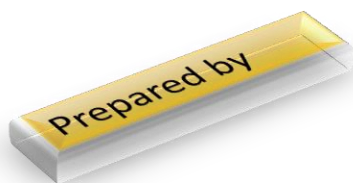


Industrial Polymers Synthesis Properties & Applications



Dr. Amrendra K Singh
Ph.D
Assistant Professor

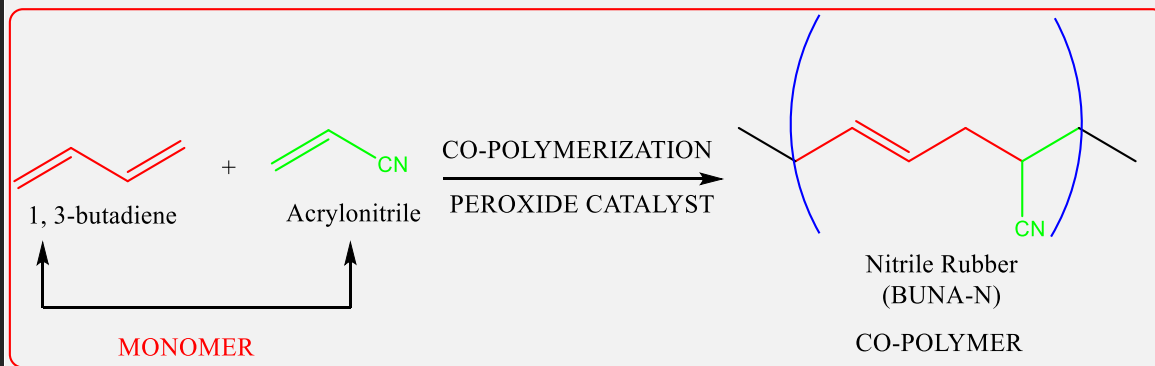
DEPARTMENT OF CHEMISTRY

Faculty of Engineering & Technology
VBS Purvanchal University Jaunpur-22003

CONTENTS:

- 1. BUNA-S**
- 2. BUNA-N**
- 3. NEOPRENE**
- 4. NYLON-6**
- 5. NYLON-66**
- 6. Terylene**

PREPARATION OF BUNA -N NITRILE BUTADIENE RUBBER (NBR)



—

This is a synthetic rubber co-polymer of acrylonitrile (ACN) and butadiene and produced by the polymerization of butadiene with acrylonitrile, invented in the mid-1930s in Germany and available in the United States just prior to the outbreak of World War II.

PROPERTISE OF BUNA-N

- ☐ **Buna-N is resistant to oil, fuel and aliphatic Hydrocarbons.**
- ☐ **It can be attacked by ozone, ketones, esters and aldehydes**
- ☐ **It have poor resistance to ozone, sunlight and weathering as the double bond present in the polybutadiene segment of the chemical backbone**
- ☐ **It is easily attacked by aromatic hydrocarbons**
- ☐ **The general properties of Buna-N are not altered by minor structural or compositional differences.**

APPLICATION OF BUNA-N

- ☐ **Buna-N is used in the automotive and aeronautical industry to make fuel and oil handling hoses, seals and grommets**
- ☐ **It is used to make protective gloves in the nuclear industry**
- ☐ **It is ideal material for aeronautical application as Buna-N can withstand a range of temperature from -40 to 108 °C**
- ☐ **Buna-N latex is used in the preparation of adhesives and as a pigment binder**
- ☐ **XNBR (carboxylated Butadiene Rubber), an improved version of Buna-N, is used for hoses, rubber belts, sealing parts etc.**

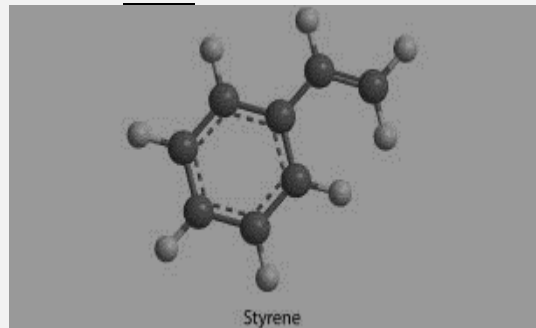
BUNA-S

Styrene Butadiene

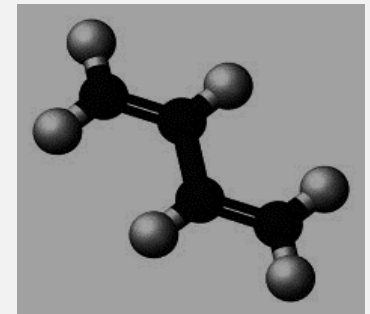
[SBR]

Styrene-Butadiene rubber (SBR or Styrene-butadiene) is a **synthetic rubber** comprising of **styrene** and **butadiene** monomers. The random copolymer has characteristics like natural rubber and contains:

- ❖ **Styrene content in the range of 10-25%** contributing to good wearing and bonding characteristics
- ❖ **While the butadiene unit is composed approximately 60 to 70% trans-1,4; 15 to 20% cis-1,4; and 15 to 20% 1,2 configurations for the polymer at 50°C.**

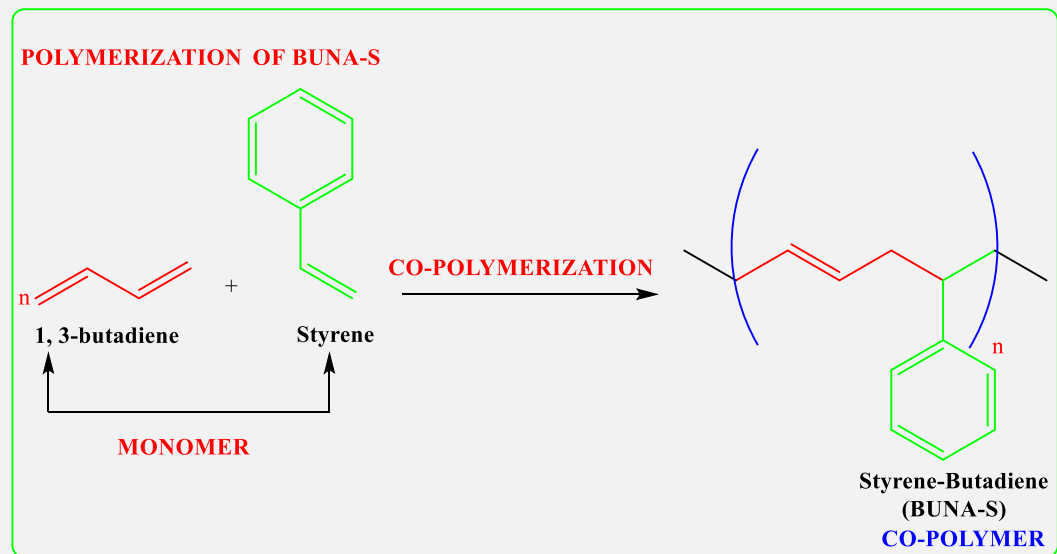


**3-D Structure of
Styrene**



**3-D Structure of
Butadiene**

PREPARATION OF BUNA-S Styrene Butadiene [SBR]



It is a **random co-polymer** formed by the **emulsion polymerization** of a mixture of **1:3 butadiene** and **styrene** in the presence of peroxide catalyst at 5 degree Celsius and therefore the product is called as cold rubber. The rubber obtained is also called Styrene butadiene rubber (SBR)

or

It is derived from two monomers, styrene and butadiene. The mixture of these two monomers is polymerized by two basically different processes: from **solution (S-SBR)** or as an **emulsion (E-SBR)**

PROPERTISE OF BUNA-S Styrene Butadiene [SBR]

KEY FEATURES OF BUNA-S:

- ❖ **Abrasion resistance**
- ❖ **Perfect impact strength**
- ❖ **Good resilience**
- ❖ **High tensile strength**
- ❖ **It is the most used synthetic rubber**

Also, when compared with polybutadiene rubber alone, styrene-butadiene rubber has improved strength, abrasion resistance, and blend compatibility. These properties are further enhanced with the use of additives.

It is vulcanized with sulfur. The rubber is slightly inferior to natural rubber in its physical properties.

APPLICATION OF BUNA-S Styrene Butadiene [SBR]

- ❖ It is used for the manufacture of passenger car tyres and treads, motorcycle and scooter tyres, cycle tyres and tubes.
- ❖ They are also used for the manufacture of conveyor belts, foot-wares, shoe soles, hoses and electrical insulation

—

NEOPRENE

[POLYCHLOROPRENE]

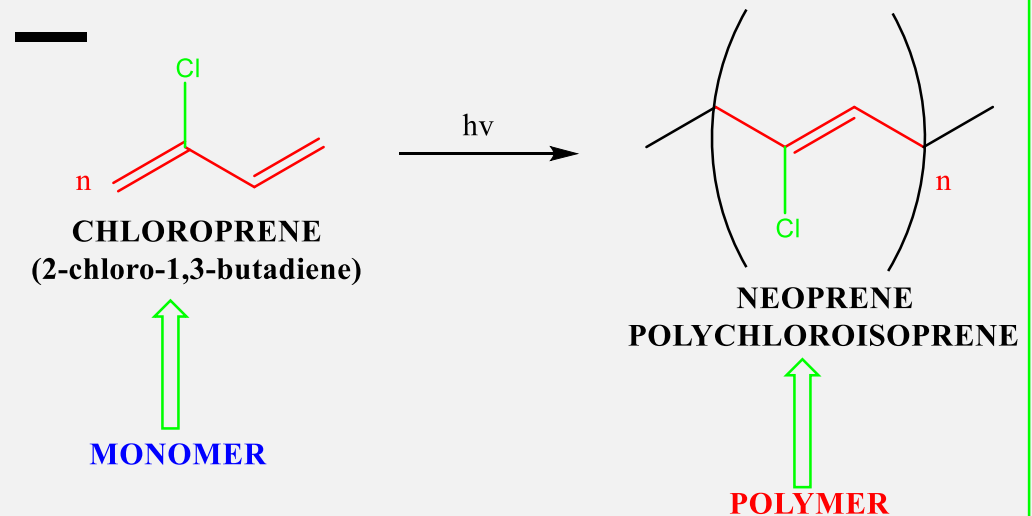
- ❖ Neoprene or polychloroprene is a family of synthetic rubbers produced by polymerization of the **CHLOPRENE (MONOMER of NEOPRENE)**
- ❖ Neoprene exhibit good chemical stability and retain flexibility over a wide range of temperatures.
- ❖ It is used in wide variety of commercial applications, such as laptops sleeves, orthopedic braces, electrical insulation and automotive fans belt.

NEOPRENE [POLYCHLOROPRENE]

PRODUCTION :

- ❖ Neoprene is produced by **FREE RADICAL** polymerization of chloroprene (**2-chloro-1,3-butadiene**)
- ❖ In commercial production this polymer is produced by **free radical emulsion polymerization** (FREP)
- ❖ Polymerization is initiated by using peroxide catalysts (i.e. Benzoylperoxide, potassium persulphate)

Synthesis of Neoprene:



NEOPRENE

[POLYCHLOROPRENE]

PROPERTISE :

- ❖ **It's a very heat resistant synthetic rubber**
 - ❖ **Neoprene is also cold resistant.**
 - ❖ **Elongation ranges from 350% to 400%.**
 - ❖ **Tensile strength ranges from 900 to 1,000 PSI**
 - ❖ **Stretch and cushioning properties**
-

NEOPRENE

[POLYCHLOROPRENE]

APPLICATIONS:

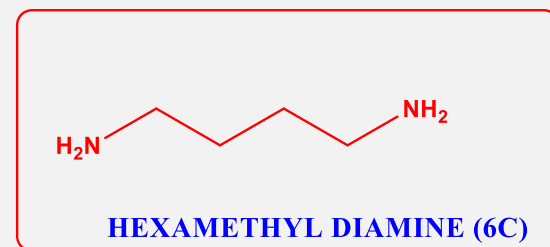
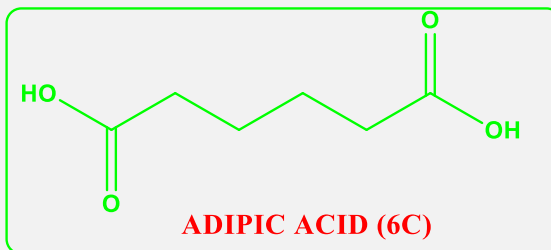
- ❖ Neoprene is used in sealing gaskets, especially in relation to electricity, due to its heat and static resistance.
- ❖ it is commonly used in power transformers, light bulbs, wires, and other electrical applications as an insulator
- ❖ It used in making bridge bearing pads.
- ❖ Use in making high tensile bands for athletic stretch.
- ❖ Use in making high-pressure gaskets.

NYLON-66

[Hexane-1,6-diamine]

INTRODUCTION:

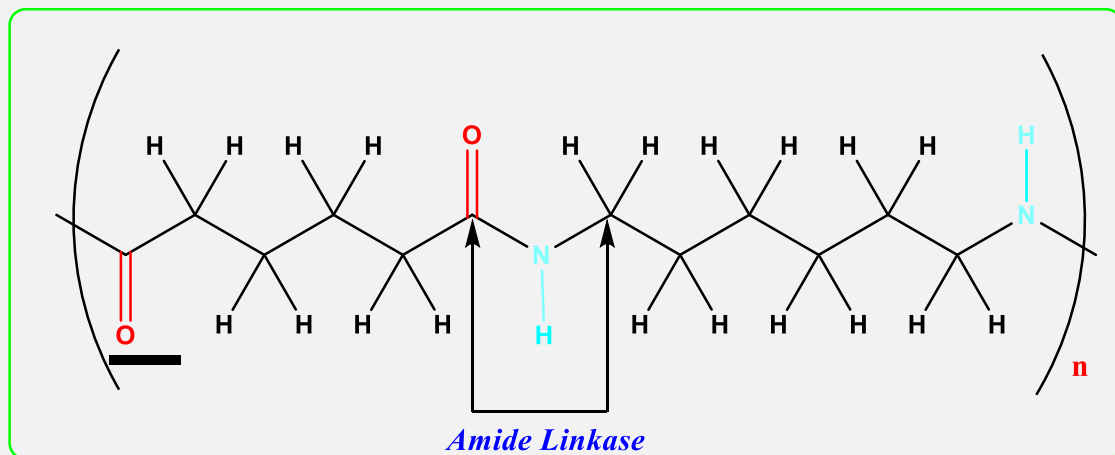
- ❖ Nylon comes from a family of synthetic polymers known as polyamide.
- ❖ It was first introduced by Wallace Carothers on 28th February 1935.
- ❖ Nylon 6,6 is a polyamide made by the step-growth condensation-polymerization of the **Adipic acid** & **Hexamethylenediamine** and contains a total of 12 carbon atoms in each repeating unit.
- ❖ The structure of its monomeric unit is as below.



NYLON-66

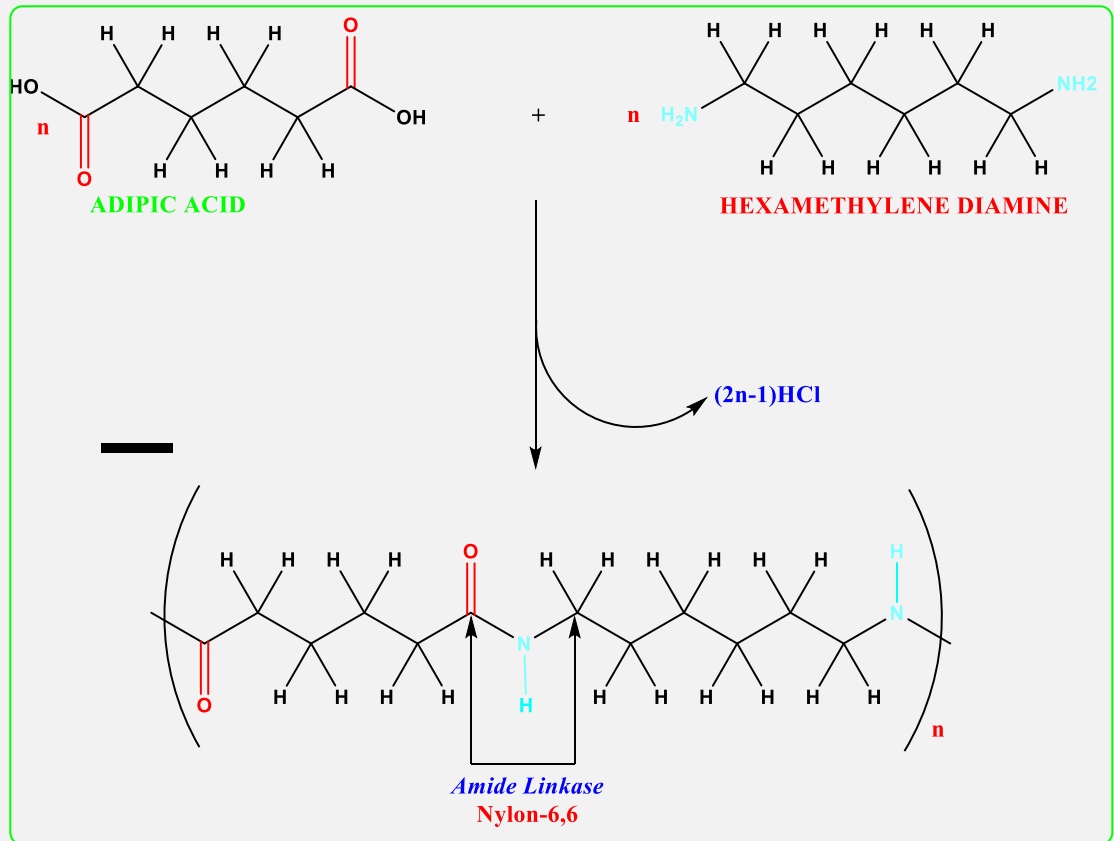
[Hexane-1,6-diamine]

Structure of Nylon-6,6



NYLON-66 [Hexane-1,6-diamine]

SYNTHESIS OF NYLON-6,6



NYLON-66

[Hexane-1,6-diamine]

PROPERTISE OF NYLON-6,6

- ❖ **Nylon has a M.P 268 °C**
- ❖ **Nylon 6,6 has high tensile strength and exhibits only half of shrinkage in steam.**
- ❖ **It also provides a very good resistance to photo degradation.**
- ❖ **Nylon 6,6 is very stable in nature.**
- ❖ **Nylon 6,6 has long molecular chains resulting in more hydrogen bonds , creating chemical springs and making it very resilient.**
- ❖ **Nylon 6,6 is an amorphous solid, so it has a large elastic property and is slightly soluble in boiling water.**
- ❖ **Its chemical properties does not allow it to be affected by solvents such as water , alcohol etc.**

APPLICATION OF NYLON-6,6

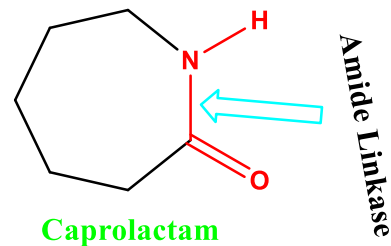
NYLON-66 **[Hexane-1,6-diamine]**

- ❖ Because Nylon is a light material , it is used in parachutes.
- ❖ Nylon 6,6 is waterproof in nature, so it is also used to make swimwear.
- ❖ Nylon 6,6 having a high melting point make it more resistant to heat and friction, so it is suitable to be used in in airports , offices and other places which are more liable to wear and tear.
- ❖ Nylon 6,6 being waterproof in nature is used to make machine parts. It is also used in the following like airbags , carpets , ropes . hoses etc. .

NYLON-6

[poly-(heano-6-lactum)]

Nylon-6 is formed by Ring Opening Polymerization (ROP) of CAPROLACTAM (7-membered cyclic amide) in aqueous solution at high temperature. It also known as POLYCAPROLACTAM.



NYLON-6

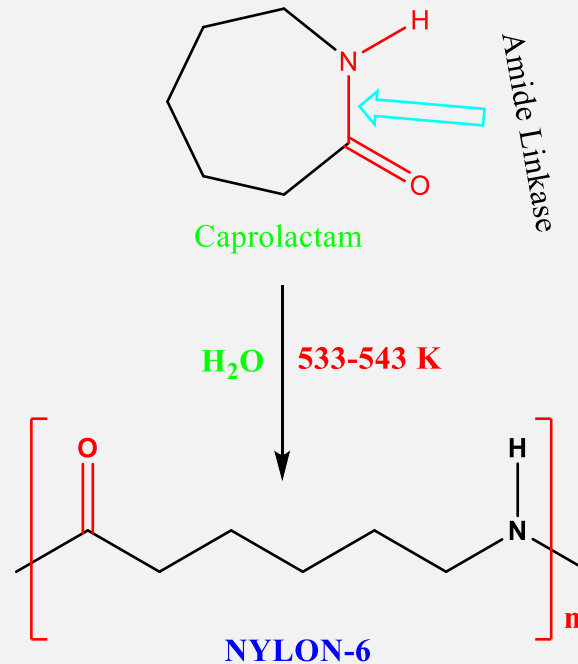
[poly-(heano-6-lactum)]

PREPARATION OF NYLON-6

Under aqueous condition the ring breaks and undergoes polymerization, the molten mass pass through spinnerets to form Nylon-6.

—

REACTION :



NYLON-6

[poly-(heano-6-lactum)]

PROPERTISE:

- ❖ It has high tensile strength.
- ❖ They are tough.
- ❖ Has well elasticity & luster.
- ❖ Resistant to abrasion and chemicals such as Acid & Alkalis.
- ❖ Tg value 47 °C (Tg: Glass Transition Temperature, “*the temperature range where the polymer substrate changes from a rigid glassy material to a soft material*”

NYLON-6

[poly-(heano-6-lactum)]

APPLICATIONS:

- ❖ **Used as a thread in bristles, for toothbrushes.**
- ❖ **As gears, fittings & bearings, automotive industries.**
- ❖ **Threads, ropes, filaments and nets.**
- ❖ **Surgical sutras, strings for surgical instruments.**
- ❖ **In hosiery and knitted garments.**

TERYLENE

[Dacron]
poly(ethylene
terephthalate)

- ❖ Terylene was the first wholly synthetic fiber invented in Britain. It was created by the Chemist JR Whinfield and J.T Dickson Accrington in 1941.
- ❖ It is formed by the condensation polymerization/step-growth polymerization of TEREPHTHALIC ACID & ETHYLENE GLYCOL.
- ❖ Terylene is class of polyester compounds which is a categories of polymer having ester functionality.
- ❖ Polyesters are specific material most commonly refers the PET (Polyethylene Terephthalate).

STRUCTURE OF MONOMER:



Terephthalic Acid
[Benzene-1,4-dicarboxylic Acid]

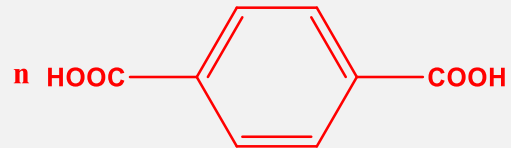


Ethylene Glycol
[Ethane-1,2-diol]

TERYLENE
[Dacron]
poly(ethylene
terephthalate

PREPARATION OF TERYLENE

CHEMICAL REACTION OF TERYLENE SYNTHESIS



Terephthallic Acid
[Benzene-1,4-dicarboxylic Acid]

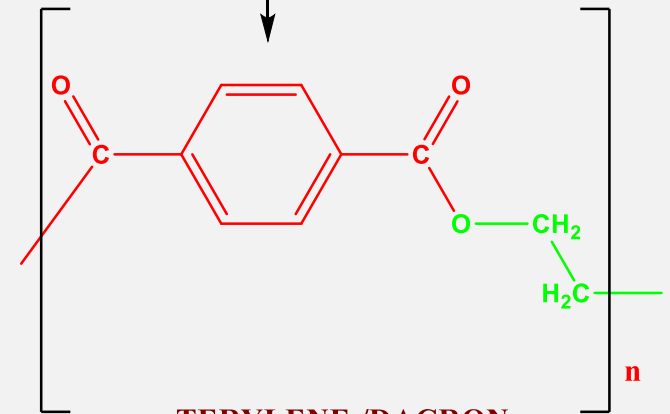
+



Ethylene Glycol
[Ethane-1,2-diol]

Condensation Polymerization

—



TERYLENE /DACRON

TERYLENE
[Dacron]
poly(ethylene terephthalate)

PROPERTISE OF TERYLENE

- ❖ PET in its natural state is a colorless, semi-crystalline resin.
- ❖ PET is hygroscopic, meaning that it absorbs water from its surroundings
- ❖ PET has intrinsic viscosity.
- ❖ PET becomes white when exposed to chloroform and certain other chemicals such as toluene.
- ❖ It is elastic in nature and possesses the property of ~~resist~~ resisting creasing.
- ❖ Its properties include high tensile strength, high resistance to stretching, both wet and dry, and good resistance to degradation by chemical bleaches and to abrasion.

TERYLENE
[Dacron]
poly(ethylene
terephthalate

APPLICATION OF TERYLENE

- ❖ Terylene is mainly used in making plastic bottles and clothing.
- ❖ Terylene fiber is used as polyester tericot knit as a fashion garments fabric.
- ❖ Terylene is also extensively used in textile industry to make hard wear clothes like sarees , taoestry and dress material

What is Polymer ?

What is a Polymer ?

Polymers are large molecules made of chain of **Monomer** (small molecule's that linked together)

Polymerization is the formation of Polymers from these small unit.

Polymer can occur **naturally** (proteins, Carbohydrate) and can be **synthesized** (Nylon, Teflon & Polyethylene)

They play an integral part in the function of life system and have **revolutionized** the way society function. (*for detailed classification click on the hypelink below and take the note appropriately*)

<https://youtu.be/YduOEGbtNfo>

What is Biodegradable Polymer ?

For Biodegradable Polymer click the hyper link below. Listen the Video and pause while taking the notes

[Biodegradable Polymer](#)

—

Biodegradable Polymer

Thank you

—

ORGANOMETALLIC'S SYNTHESIS & APPLICATION

Module 1
B.Tech. I
Year
Students



Department Of Chemistry
Faculty of Engineering & Technology
VBS Purvanchal University
Jaunpur-22003



Course Contents:

- ☐ Introduction
- ☐ Classification of Organometallics
- ☐ Synthesis's of Organometallic's reagent
- ☐ Synthetic Application of Organometallic's reagents



What is Organometallic's ?

Compounds that contain a metal-carbon bond, **R-M (alkali metal or transition metals)** are known as "**organometallic**" compounds. Organometallic compounds of **Li, Mg (Grignard reagents)** are amongst some of the most important organic reagents. Organometallic compounds provide a source of **nucleophilic carbon atoms** which can react with electrophilic carbon to form a new carbon-carbon bond. This is a very important for the synthesis of complex molecules from simple starting materials.

Organometallics compounds are name as:

- ❖ **Alkyl metal (Me.Li, MethylLithium)**
- ❖ **Alkyl metal halide (CH₃MgBr, Methylmagnesium bromide)**
- ❖ Organometallic are usually kept in solution in organic solvents due to their very high reactivity (**especially with H₂O, O₂ etc.**)
- ❖ Organolithiums and organomagnesiums have a σ bond between a C atom and the metal: C-M
- ❖ These are very **polar, covalent bonds** due to the **electropositive character of the metals**.



Classification of Organometallic Compounds.

There are several basic set to classify the Organometallics compound. The most important organometallic compounds considered here are those containing M-C bond, excluding Metal carbonyls (M-CO), Metal Cyanide (M-CN) and Metal Carbide (M-C). A useful classification is based on M-C type of bonds.

- ❖ Ionic Organometallic's (Group 1 elements)
- ❖ Covalent Organometallic's (Group 12,13, 14 & 15 elements)
- ❖ Electron Deficient Organometallic's (Li, Be, B, Mg etc.)

There is no such thing as electron deficient compounds, only theory deficient chemists.



ORGANOMAGNESIUM REAGENTS / GRIGNARD REAGENTS

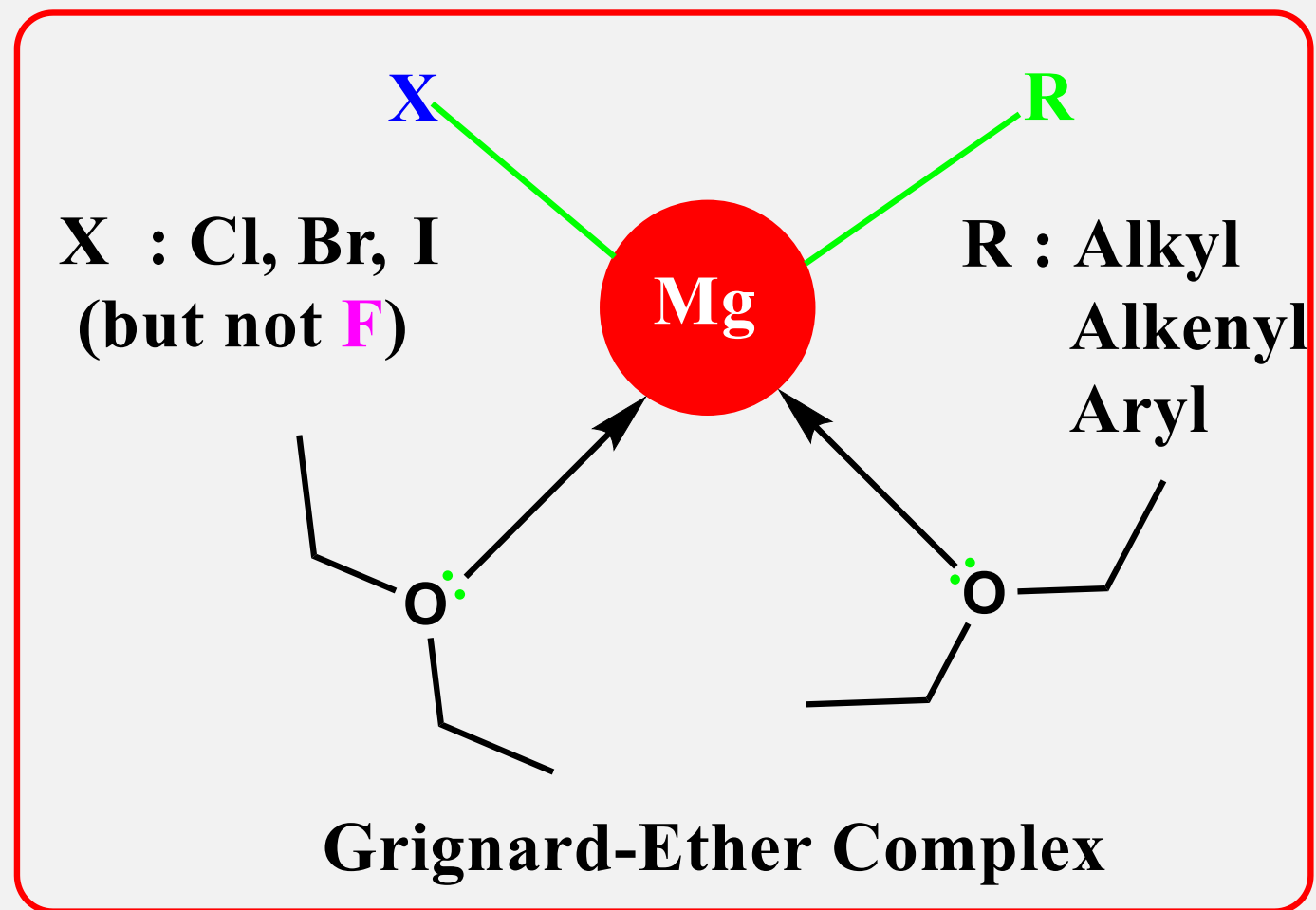
During the past 108 years the Grignard reagents probably have been the most widely used organometallic reagents. Most of them are easily prepared in ethereal solution (usually diethyl ether or, since the early 1950s, THF) by the reaction of an organic halide with metallic magnesium.



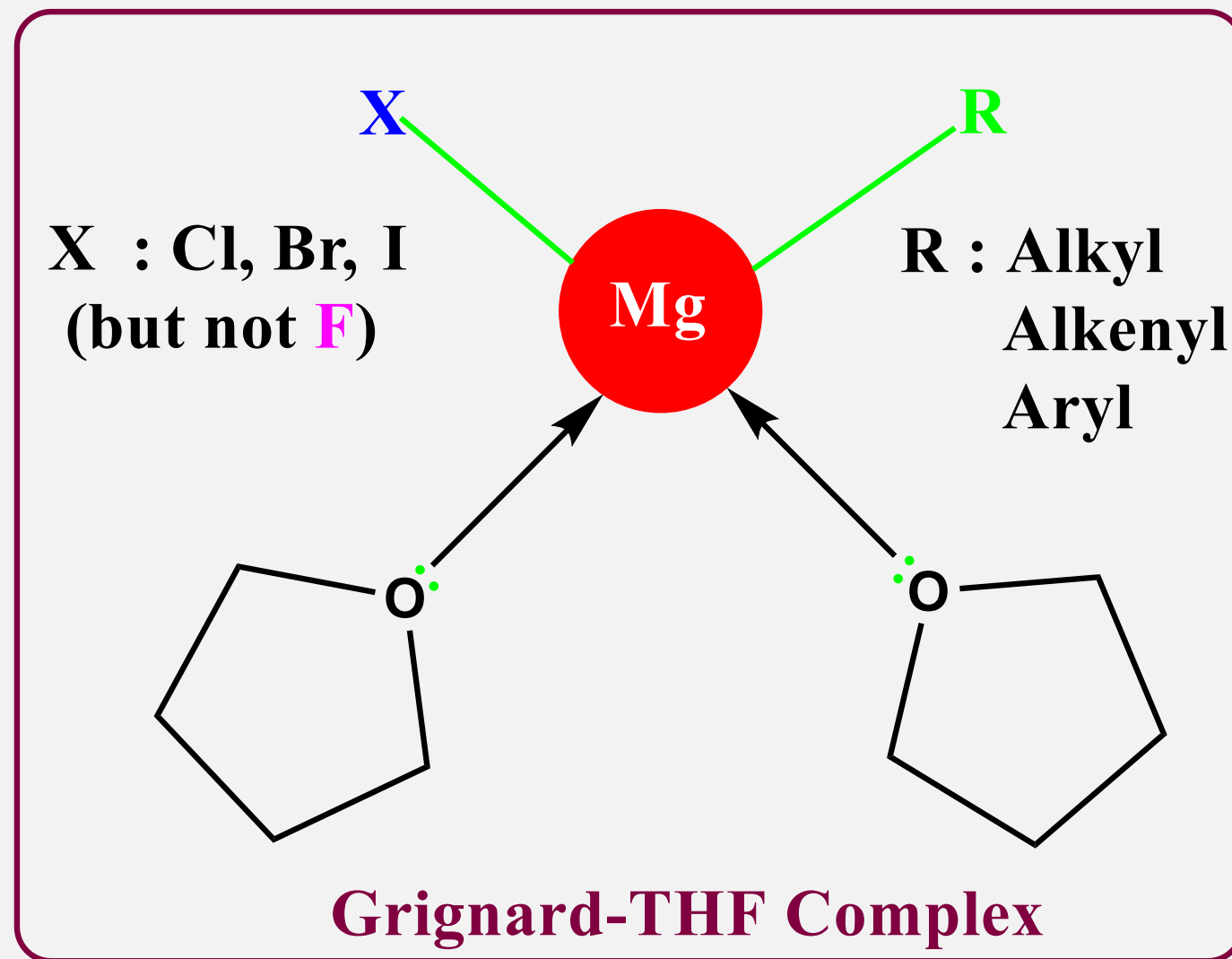
The importance of this contribution to synthetic chemistry was recognized very early, and for his discovery Grignard was awarded a Nobel Prize in Chemistry in 1912.



STRUCTURE OF GRIGNARD REAGENT



STRUCTURE OF GRIGNARD REAGENT



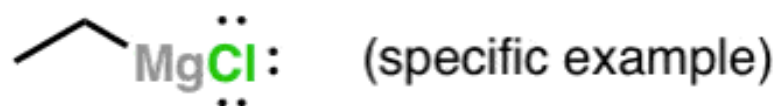
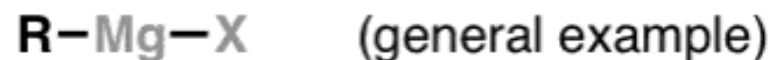
STRUCTURE OF GRIGNARD REAGENT

- ❖ The Grignard reagent is a highly reactive Organomagnesium compound formed by reacting a haloalkane with magnesium in an ether/THF (tetrahydrofuran)solvent.
- ❖ Pure Grignard reagents are extremely reactive solids. They are normally handled as solutions in solvents such as diethyl ether or tetrahydrofuran; which are relatively stable as long as water is excluded. In such a medium, a Grignard reagent is invariably present as a complex (look previous two slides) with the magnesium atom connected to the two ether oxygens by coordination bonds.



What is Grignard Reagent ?

A Grignard reagent or Grignard compound is a chemical compound with the generic formula R-Mg-X , where X is a **halogen** and R is an organic group, normally an **alkyl or aryl**. Two typical examples are methylmagnesium chloride Cl-Mg-CH_3 and phenylmagnesium bromide $(\text{C}_6\text{H}_5)\text{-Mg-Br}$. They are a subclass of the Organomagnesium compounds.



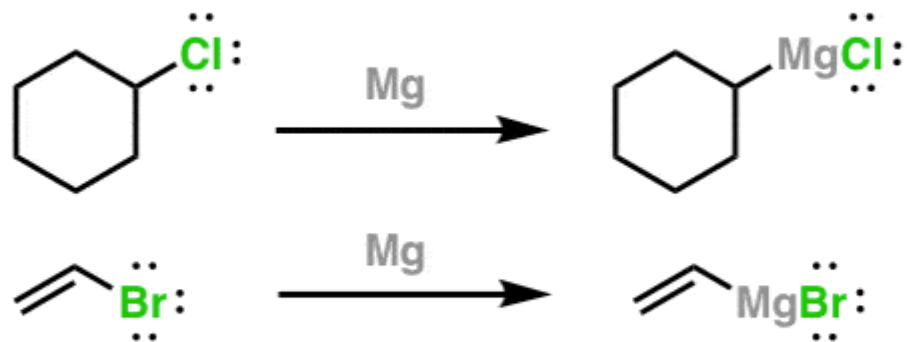
Grignard Reagents



PREPARATION OF GRIGNARD REAGENTS

Grignard reagents are made through the addition of magnesium metal to alkyl or alkenyl halides using anhydrous ether or THF as solvent. The halide can be **Cl**, **Br**, or **I** (**not F**).

Example 1: Formation of Grignard reagents



Grignards can be formed from alkyl or alkenyl chlorides, bromides or iodides (never fluorides)

PREPARATION OF GRIGNARD REAGENTS

Point to Remember:

- ❖ Organomagnesiums are formed by the reaction of alkyl halides with magnesium metal.
- ❖ Typical solvents are normally anhydrous diethyl ether or tetrahydrofuran.
- ❖ The alkyl group can be primary, secondary or tertiary.
- ❖ Halide reactivity : $I > Br > Cl$
- ❖ R can be alkyl, vinyl or aryl.



Synthetic Application of Grignard Reagent

A: Synthesis of Alcohols

Example 2: Reaction with aldehydes to form secondary alcohols



Acid is added in the second step to protonate the negatively charged oxygen

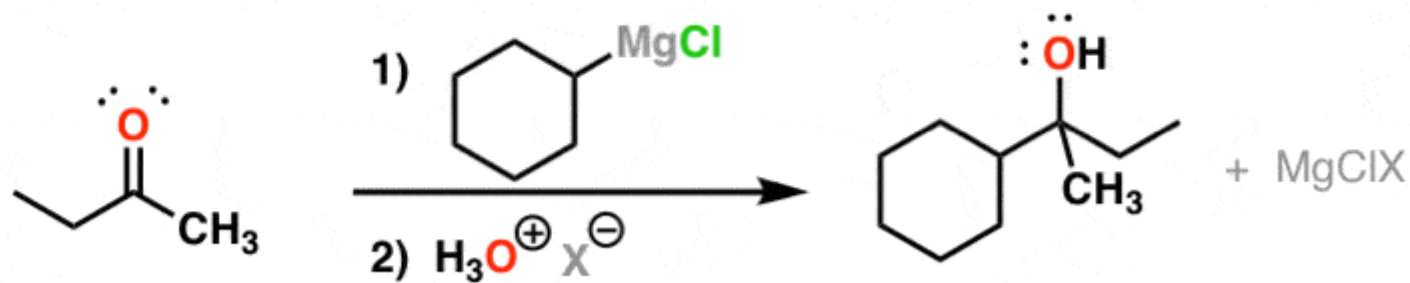
Upon addition of Grignard reagent to aldehyde it furnish **SECONDARY ALCOHOLS** (2° alcohol).

Formaldehyde only the aldehyde which gave PRIMARY ALCOHOLS (1° alcohols).

Synthetic Application of Grignard Reagent

B: Synthesis of 3^oAlcohols

Example 3: Reaction with ketones to form tertiary alcohols



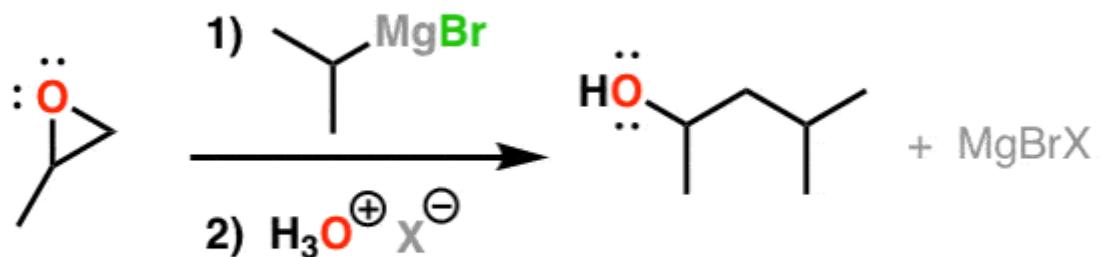
Upon addition of Grignard reagent to KETONE it furnish TERTIARY ALCOHOLS (3^o alcohol).

NB: Kindly to be noted that I used Cyclohexyl chloride to represent the reaction. You can use any alkyl/aryl group to depict the reaction. It invariable doesn't alter the course of reaction. It depends upon how you prepared the Grignard reagent (selection of halides with R groups)

Synthetic Application of Grignard Reagent

C: Synthesis of 3°Alcohols

Example 6: Reaction with epoxides



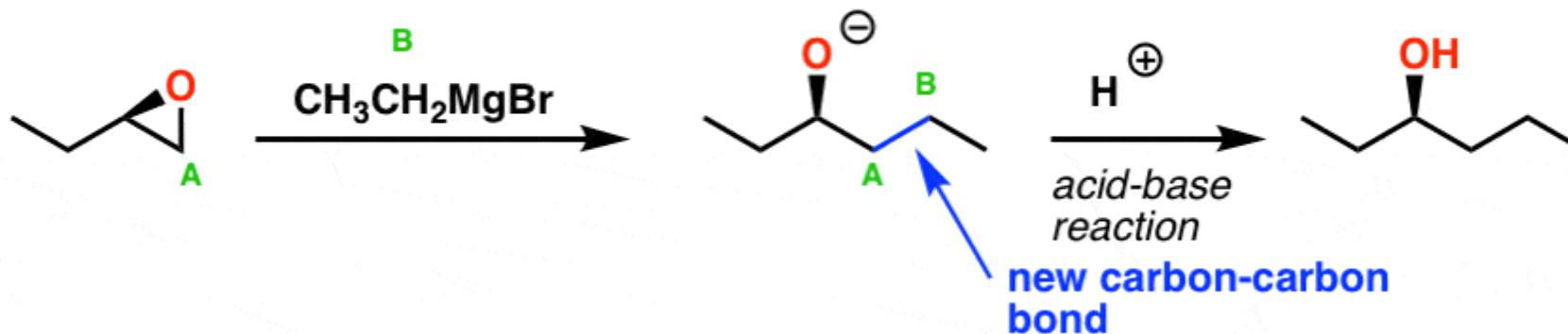
Grignard reagents add to the less substituted end of epoxides

Upon addition of Grignard reagent to EPOXIDE it furnish **SECONDARY ALCOHOLS** (2° alcohol) after acidic trituration of the complex.

Synthetic Application of Grignard Reagent

C: Synthesis of 3°Alcohols

Addition of Grignards to Epoxides



One can easily visualize how the Grignard reagent attack in ring opening of epoxides.

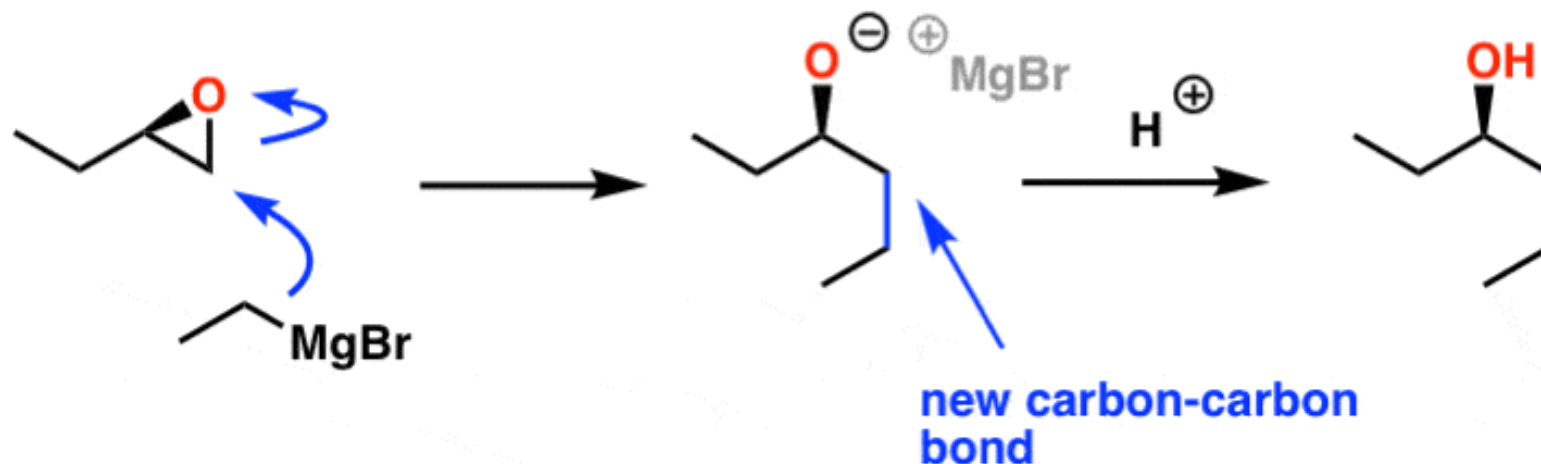
Synthetic Application of Grignard Reagent

How it works:

The pair of electrons in the C–Mg bond (nucleophile) attack the least hindered carbon of the epoxide (electrophile) forming a new C–C bond and breaking C–O. A proton source (i.e. acid) is then added, forming O–H

Step 1: Addition of Nucleophile to Epoxide

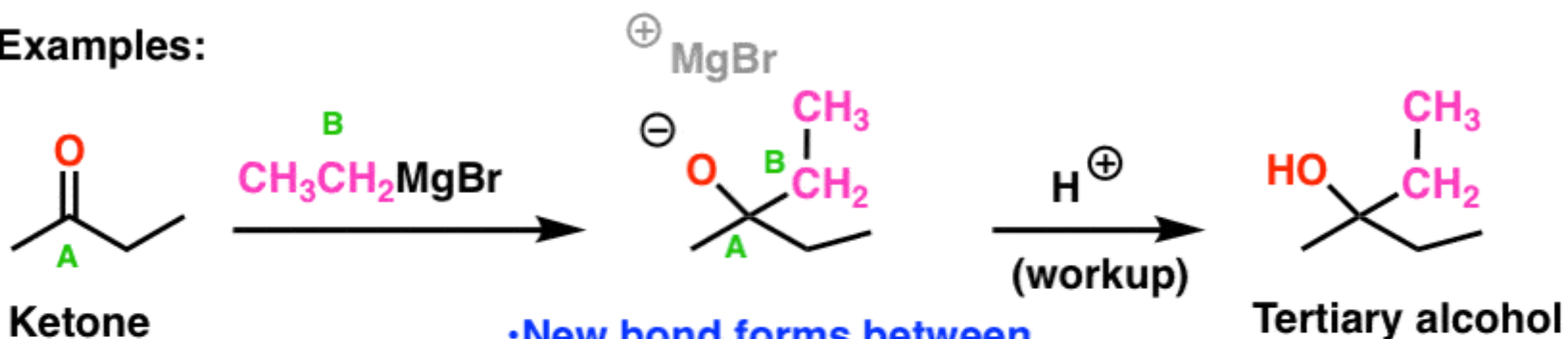
Step 2: Workup (Protonation)



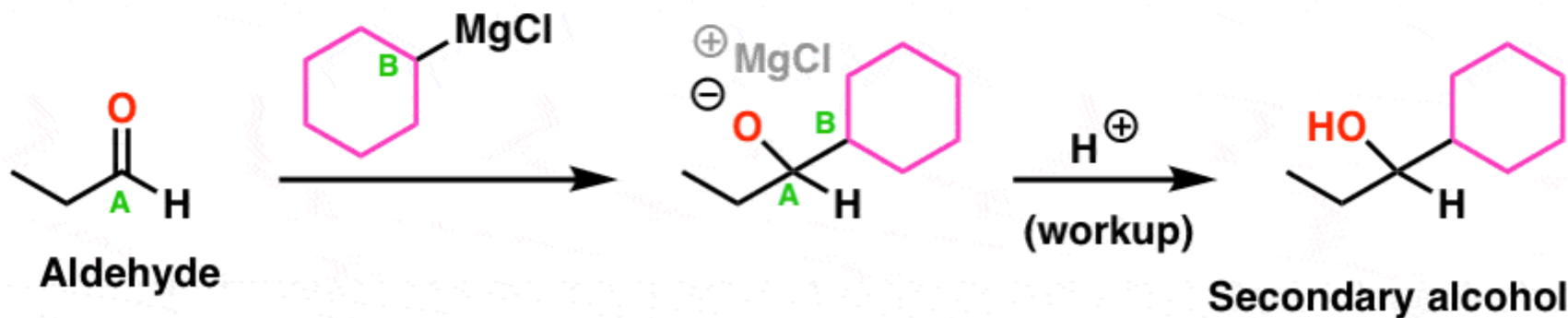
Synthetic Application of Grignard Reagent

REPERSENTATIVE EXAMPLE:

Examples:



- New bond forms between Carbon A and Carbon B
- Carbon A to Oxygen π bond breaks

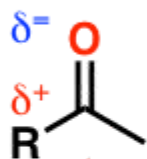


Synthetic Application of Grignard Reagent

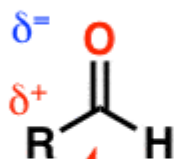
REPERSENTATIVE EXAMPLE:

Addition of Grignards (and organolithium reagents) to Aldehydes & Ketones

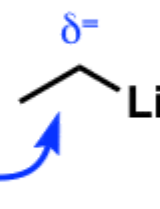
Ketone



Aldehyde



Electrophilic
"Carbonyl" Carbon



Nucleophilic
"Organometallic" Carbon

Synthetic Application of Grignard Reagent

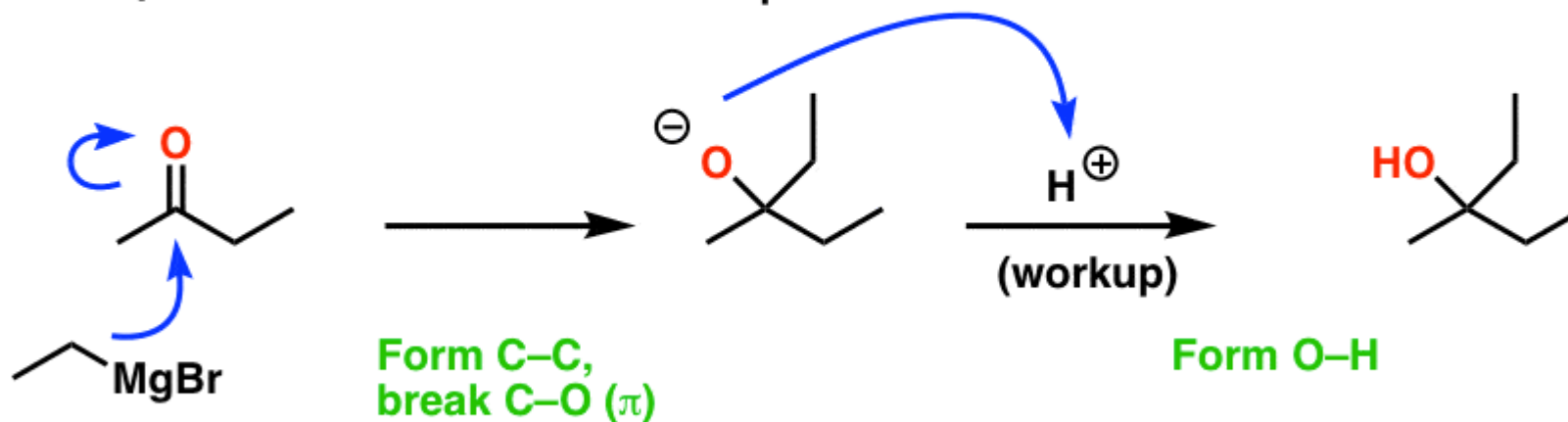
REPERSENTATIVE EXAMPLE:

Grignard Addition To Aldehydes and Ketones: How It Works

The nucleophilic pair of electrons in the C–Mg bond attack the carbonyl carbon, breaking the C–O (π) bond. In the second step, a proton source is added in workup.

Step 1: Addition

Step 2: Protonation



Note: "Addition" is **THE** most important mechanism for carbonyls. Carbonyl carbons are electrophiles, and will react with many different nucleophiles!

Synthetic Application of Grignard Reagent

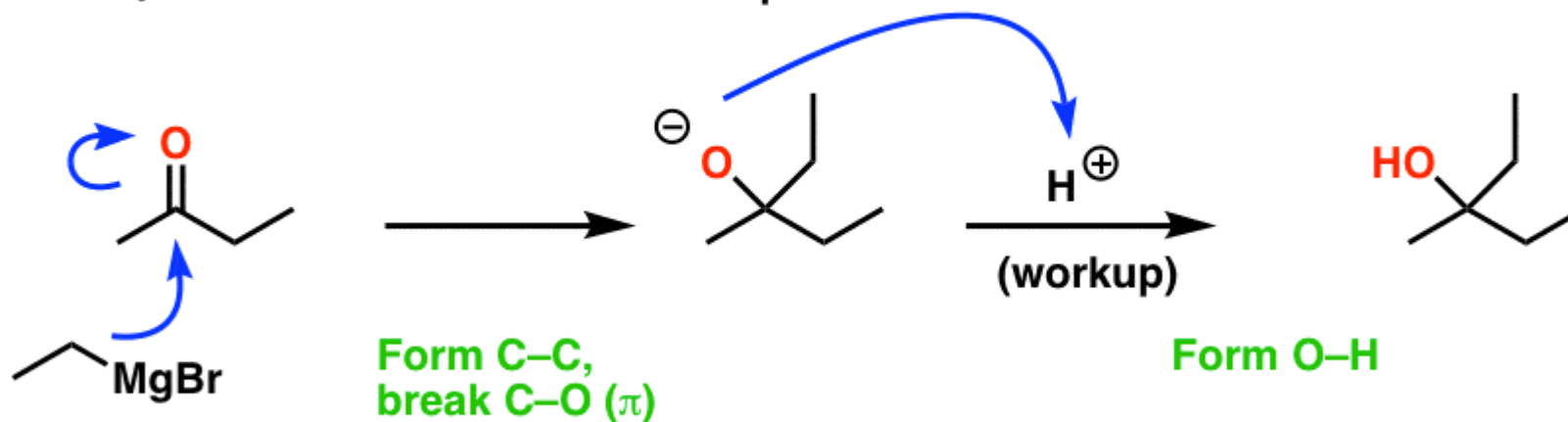
REPERSENTATIVE EXAMPLE:

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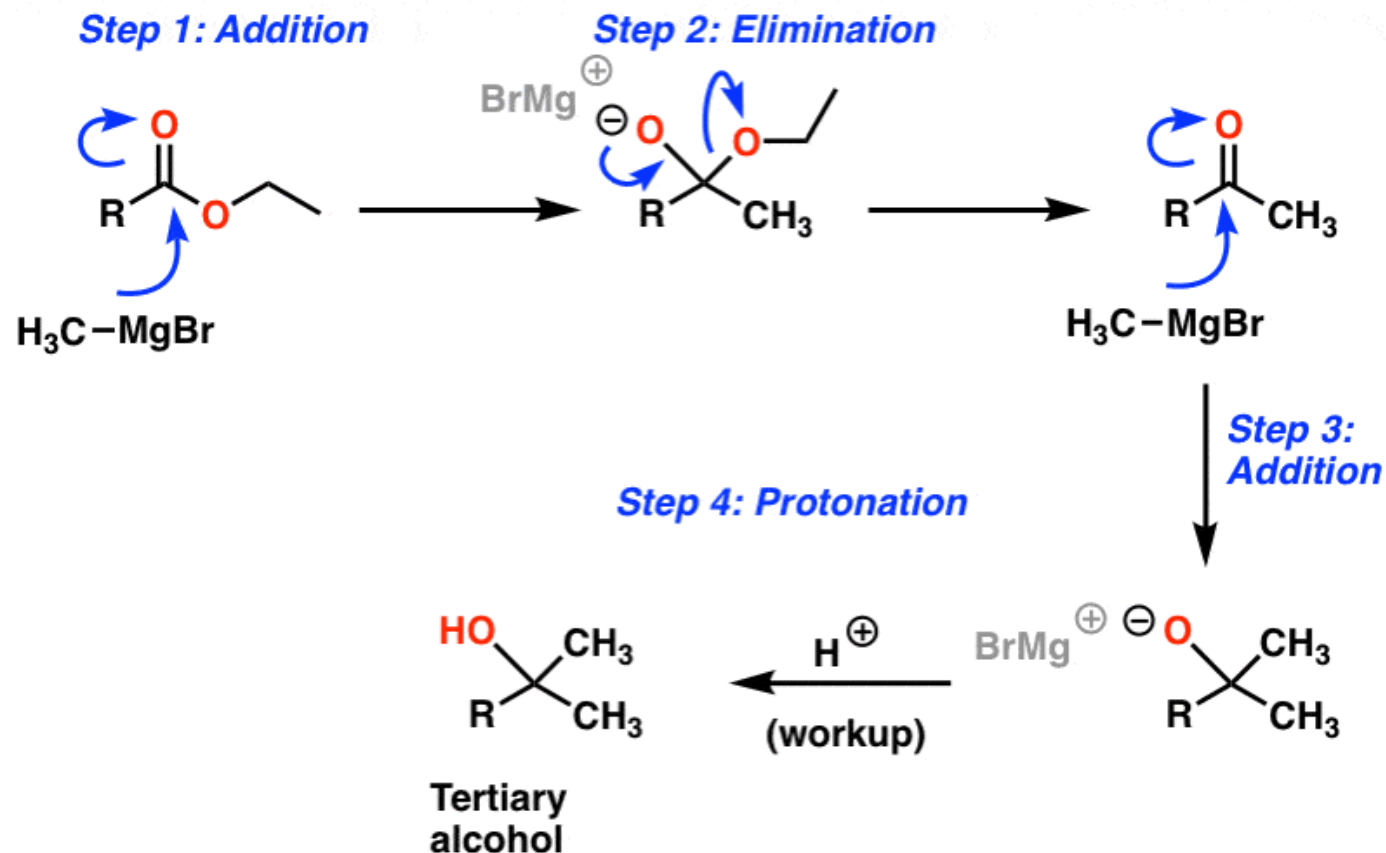
Step 2: Protonation



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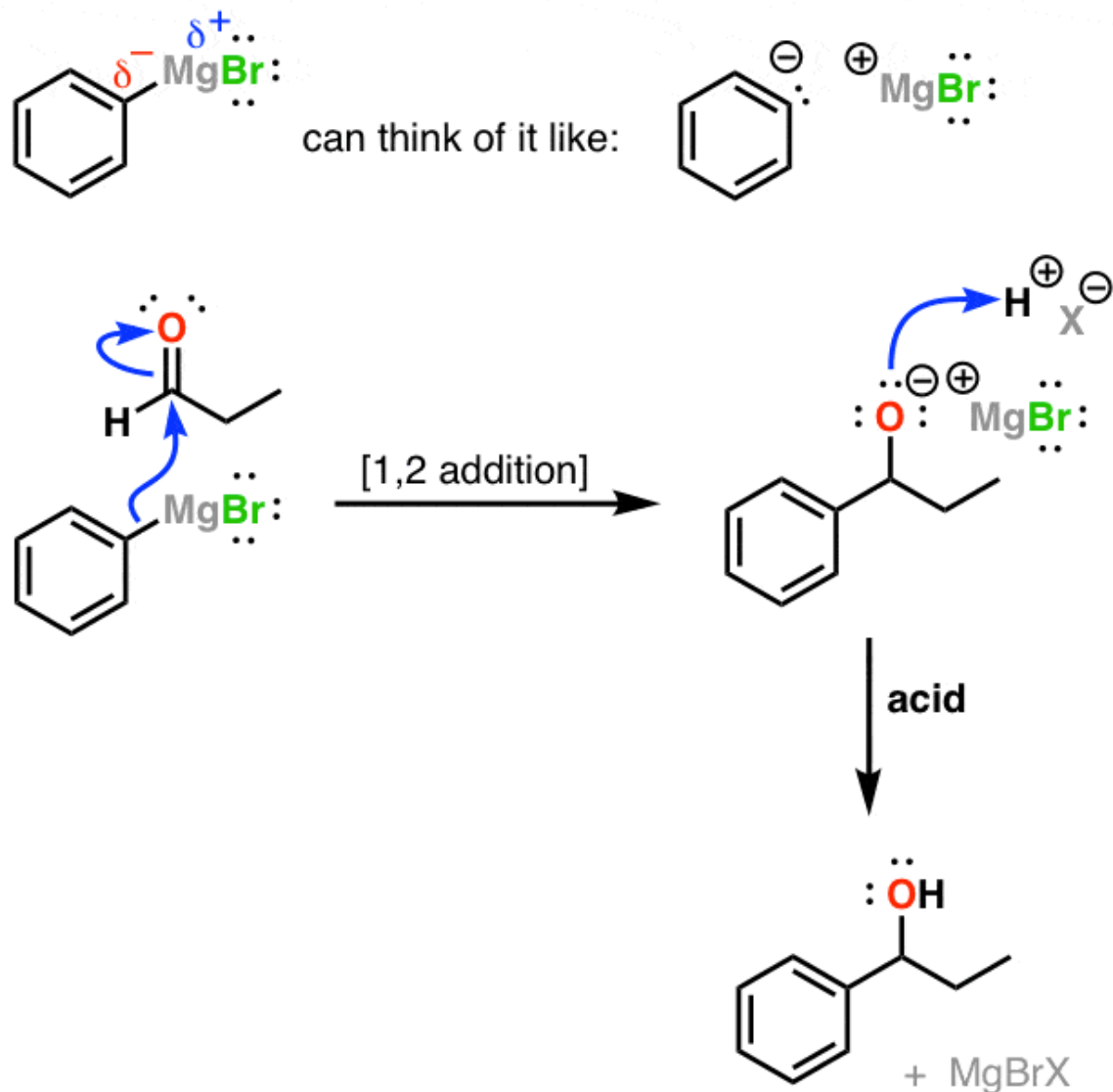
Addition of Grignard Reagents To Esters: How It Works

- In the first step, the nucleophile (Grignard) attacks the carbonyl carbon in an addition reaction (essentially the same step as for ketones/aldehydes).
- THEN, the C–O π bond re-forms, displacing a leaving group (alkoxide, RO⁻). This is a ketone!
- The ketone is then attacked by a second equivalent of nucleophile, leading to formation of a new alkoxide. Workup (addition of water or acid) completes the reaction.



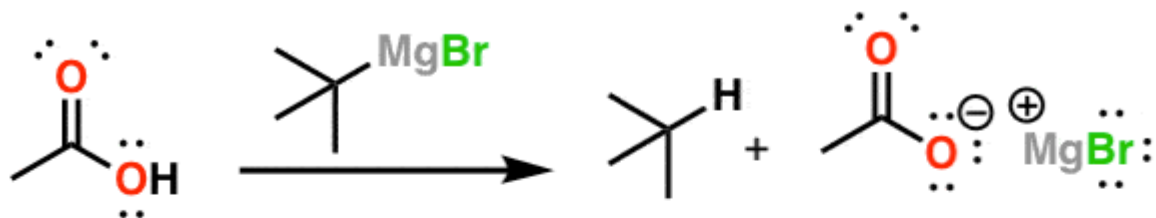
How it works: *Addition to aldehydes/ketones*

Grignard reagents are extremely strong nucleophiles - the electrons in the C-Mg bond are heavily polarized toward carbon.



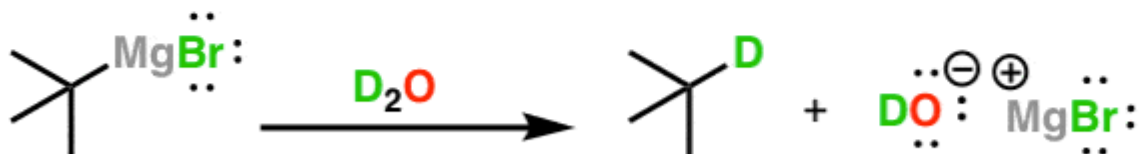
Mechanism of phenyl Grignard addition to propanal likewise you may visualize the mechanism of other aldehyde with GR

Example 8: Reaction with acidic hydrogens



Grignard reagents are strong bases and will not add to carboxylic acids - they will instead be protonated

This can be used to introduce deuterium:



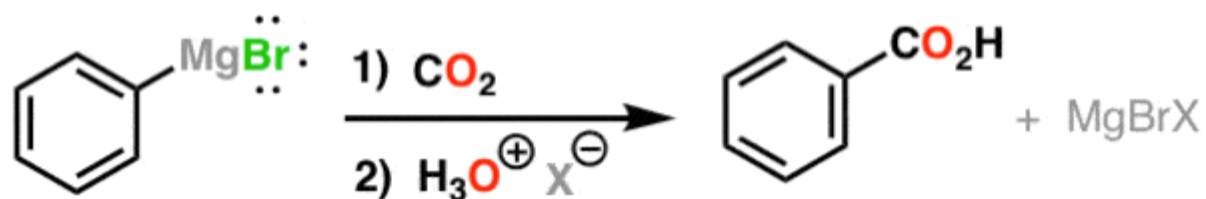
Deuterium (D) is the heavy isotope of hydrogen

Acid can not react to Grignard reagents like carbonyls due very strong basic character of GR and to be protonated rather addition.

SYNTHESIS OF ACID:

Reaction with Carbon Dioxide

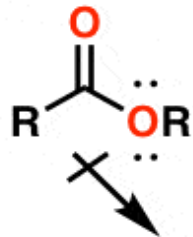
Example 7: Reaction with carbon dioxide to make carboxylic acids



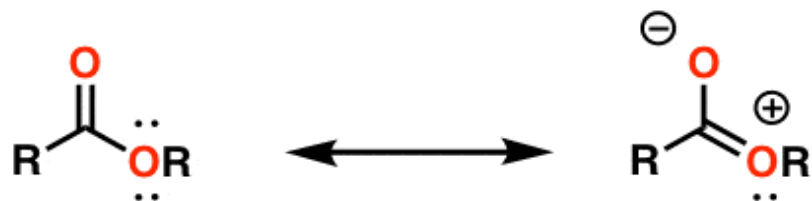
Like Phenyl magnesium bromide other GR corresponding to alkyl group gave respective acid with carbon dioxide.

What's More Reactive, Ester vs. Ketone vs. Aldehyde?

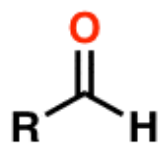
You might imagine that the ester is more reactive, since the highly negative oxygen makes the carbonyl carbon more electrophilic...



BUT... actually, the ester carbonyl carbon is **less** electrophilic, since the oxygen **donates** a pair of electrons to the carbonyl carbon. ("pi-donation")
One way to visualize this is through resonance:

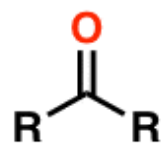


Bottom line is that **esters are actually less reactive towards nucleophiles than ketones and aldehydes.**

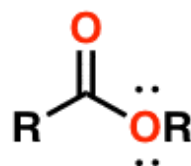


Aldehyde
(most reactive)

<

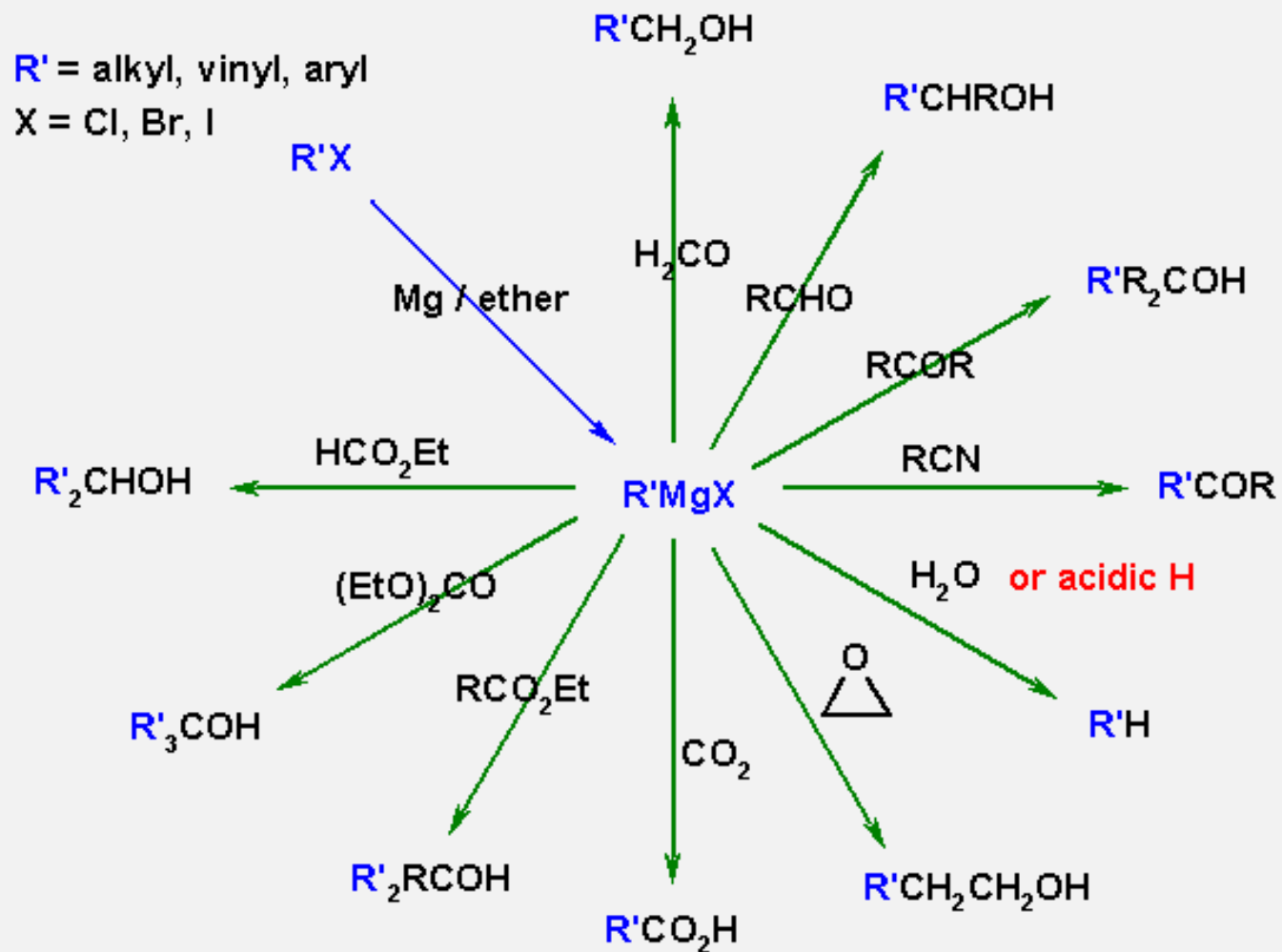


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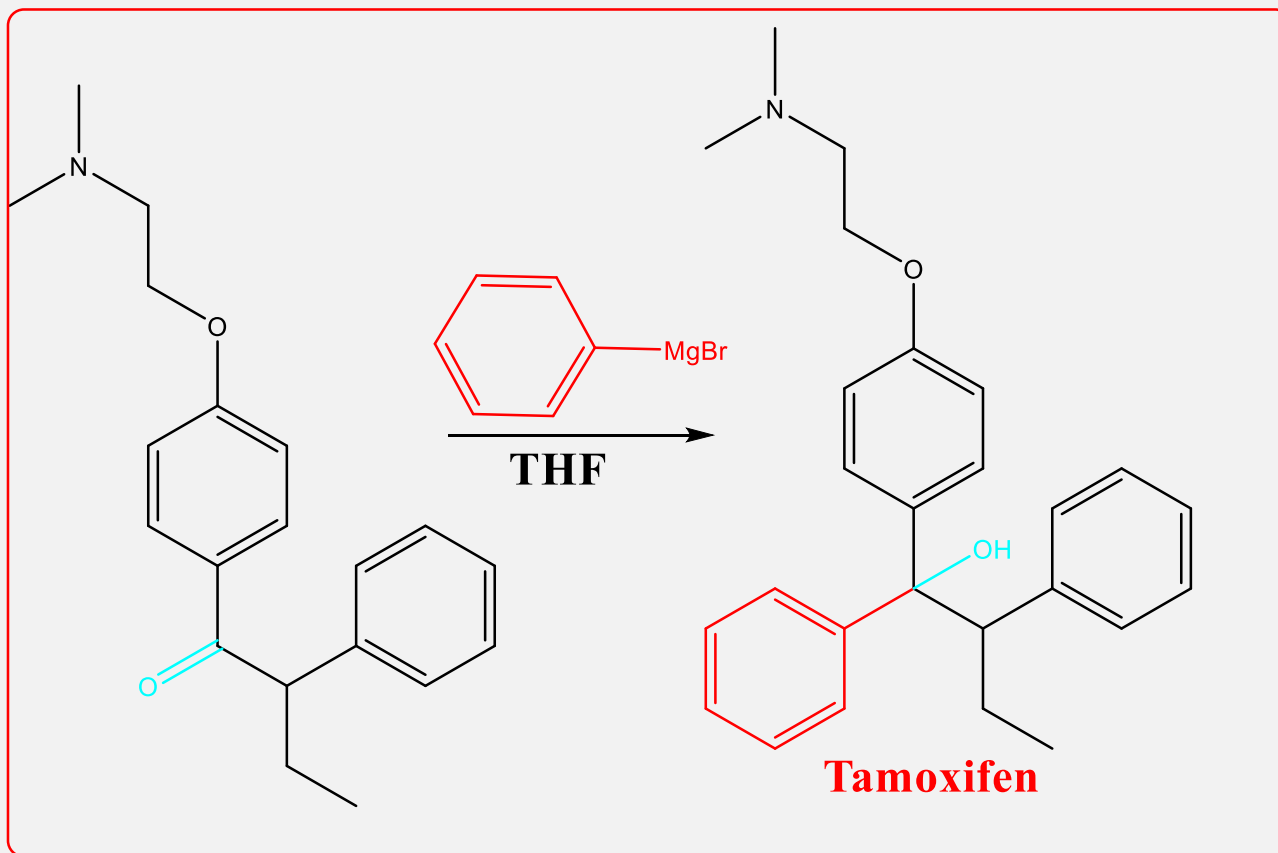
Ester
(least reactive)

OVERVIEW OF GRIGNARD REAGENT



Typical work-up for these reactions:
 1. Dilute aqueous acid or
 2. Aqueous ammonium chloride

INDUSRIAL APPLICATION OF GRIGNARD REAGENT



The most important applications of the Grignard reaction is the synthesis of the anti-cancer drug (Z)-tamoxifen.

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THANK YOU