



# PURIFICATION OF ORGANIC CHEMISTRY

## PURIFICATION METHODS DISTILLATION TECHNIQUES

Type :

**(A) SIMPLE DISTILLATION**

**Conditions**

- (i) When liquid sample has non volatile impurities
- (ii) When boiling point difference is 80 K or more.

**Examples**

- (i) Mixture of chloroform (BP = 334K) and Aniline (BP = 457K)
- (ii) Mixture of Ether (b.p. = 308K) & Toluene (b.p. = 384K)
- (iii) Hexane (342K) and Toluene(384K)

**(B) FRACTIONAL DISTILLATION**

When b.p. difference is 10K

**Examples**

- (i) Crude oil in petroleum industry
- (ii) Acetone (329 K) and Methyl alcohol (338K)

**(C) DISTILLATION UNDER REDUCED PRESSURE**

**(Vacuum distillation)**

When liquid boils at higher temperature and it may decompose before b.p. is attained.

- Example**
- (i) Concentration of sugar juice
  - (ii) Recovery of glycerol from spent lye.
  - (iii) Glycerol

**(D) STEAM DISTILLATION**

When the substance is immiscible with water and steam volatile.

**Example :**

- (i) Aniline is separated from water
- (ii) Turpentine oil
- (iv) Bromo Benzene
- (vi) o-Nitrophenol
- (iii) Nitro Benzene
- (v) Naphthalene

$$P = P_1 + P_2$$

Vapour pressure of Organic liquid	Vapour pressure of water
$P_1$	$P_2$

## LASSAIGNE'S METHOD (detection of elements)

Element	Sodium extract	Confirmed test
Nitrogen	$\text{Na} + \text{C} + \text{N}$ $\Delta \downarrow$ NaCN	$(\text{NaCN} + \text{FeSO}_4 + \text{NaOH})$ boil and cool $+ \text{FeCl}_3 + \text{conc. HCl} \rightarrow \text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ Prussian blue colour
Sulphur	$2\text{Na} + \text{S}$ $\Delta \downarrow$ Na <sub>2</sub> S	(i) $\text{Na}_2\text{S} + \text{Na}_4[\text{Fe}(\text{CN})_5\text{NO}]$ sodium nitrosoprasuide $\rightarrow \text{Na}_4[\text{Fe}(\text{CN})_5\text{NOS}]$ a deep violet colour  (ii) $\text{Na}_2\text{S} + \text{CH}_3\text{COOH} + (\text{CH}_3\text{COO})_2\text{Pb} \xrightarrow{\Delta}$ PbS↓ ← Black ppt.
Halogen	$\text{Na} + \text{X}$ $\Delta \downarrow$ NaX	$\text{NaX} + \text{HNO}_3 + \text{AgNO}_3$ (i) White ppt. soluble in aq. NH <sub>3</sub> confirms Cl. (ii) Yellow ppt. partially soluble in aq. NH <sub>3</sub> confirms Br. (iii) Yellow ppt. insoluble in aq. NH <sub>3</sub> confirms I.
Nitrogen and sulphur together	$\text{Na} + \text{C} + \text{N} + \text{S}$ $\Delta \downarrow$ NaCNS Sodium thiocyanate (Blood red colour)	As in test for nitrogen; instead of green or blue colour, blood red colouration confirms presence of N and S both

## QUANTITATIVE ANALYSIS OF ORGANIC COMPOUNDS

**Estimation of carbon and hydrogen**

**- Leebig's method**

**Note :** This method is suitable for estimation if organic compound contains C and H only. In case if other elements e.g., N, S, halogens are also present the organic compound will also give their oxides which is being absorbed in KOH and will increase the percentage of carbon and therefore following modification should be made.

**ESTIMATION OF NITROGEN**

**Duma's method :**

The nitrogen containing organic compound yields nitrogen gas on heating it with copper (II) oxide in the presence of CO<sub>2</sub> gas. The mixture of gases is collected over potassium hydroxide solution in which CO<sub>2</sub> is absorbed and volume of nitrogen gas is determined.

**Note :** This method can be used to estimate nitrogen in all types of organic compounds

**Kjeldahl's method :**

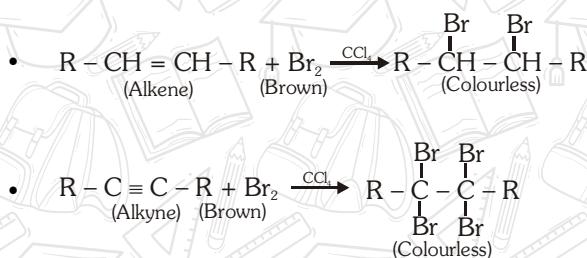
In this method nitrogen containing compound is heated with conc. H<sub>2</sub>SO<sub>4</sub> in presence of copper sulphate to convert nitrogen into ammonium sulphate which is decomposed with excess of alkali to liberate ammonia.

**Note :** This method is simpler and more convenient and is mainly used for finding out the percentage of nitrogen in food stuffs, soil, fertilizers and various agricultural products. This method cannot be used for compound having nitro groups, azo group (-N=N-) and nitrogen in the ring (pyridine, quinole etc.) Since nitrogen in these compounds is not quantitatively converted in to ammonium sulphate.

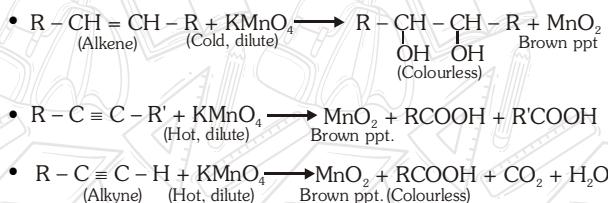
# PRACTICAL ORGANIC CHEMISTRY

## UNSATURATION TEST

- (a) Double/Triple bonded Compounds ( $C = C$ )/( $C \equiv C$ ) +  $Br_2$  in  $CCl_4$  (Brown colour) → Colourless compound



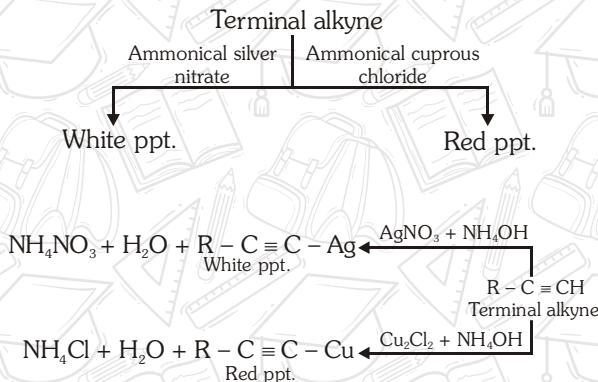
- (b) Double/Triple bonded Compounds + Baeyer's reagent (Pink colour) → Brown precipitate



Baeyer's reagent is cold, dilute  $KMnO_4$  solution having pink colour.

**Note :** The above test are not given by Benzene. Although it has unsaturation.

## TEST FOR TERMINAL ALKyne

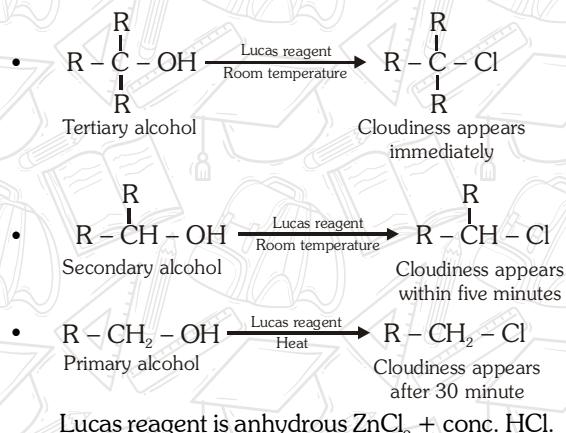


## NATURE OF X-GROUP IN C-X BOND

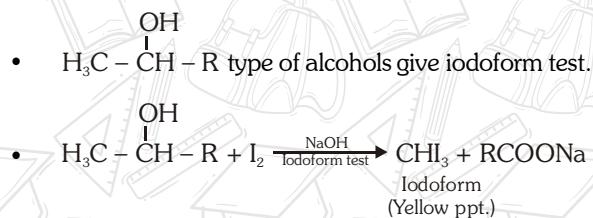


If X is Cl, precipitate will be white and for Br yellow precipitate will be obtained.

## DISTINCTION BETWEEN 1°, 2° & 3° ALCOHOLS



## HALOFORM REACTION IN ALCOHOL



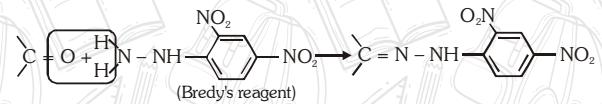
## PHENOL

Phenol + ferric chloride → Violet colouration  
(neutral)

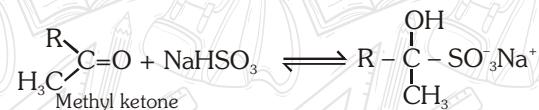
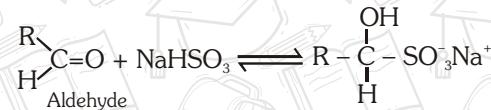


## CARBONYL GROUP

- Carbonyl compound + 2, 4-DNP → Yellow/orange crystal



- All aldehydes and only aliphatic methyl ketones +  $NaHSO_3$  → White crystalline bisulphite (Water soluble).



### **Ethanal and methanal (Iodoform test)**



#### **Acetophenone and benzophenone (Iodoform test)**

- $\text{C}_6\text{H}_5\text{COCH}_3 + \text{I}_2 + \text{NaOH} \xrightarrow{\text{Iodoform test}}$   
 $\text{CHI}_3 + (\text{Yellow ppt.})$   
 $\text{C}_6\text{H}_5\text{COOCNa}$

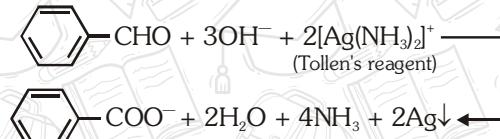
$\text{C}_6\text{H}_5\text{COCH}_3 + \text{I}_2 + \text{NaOH} \xrightarrow{\text{Iodoform test}}$  No ppt.  
 $\text{C}_6\text{H}_5\text{COCH}_3$  (Benzophenone)

## **Benzoic acid and ethylbenzoate**

- $\text{C}_6\text{H}_5\text{COOH} + \text{NaHCO}_3 \rightarrow \text{C}_6\text{H}_5\text{COONa} + \text{CO}_2 \uparrow + \text{H}_2\text{O}$   
effervescence
  - Ethyl benzoate + Sodium bicarbonate  
→ No effervescence

## **Benzaldehyde and acetophenone (Tollen's test)**

- Benzaldehyde + Tollen's reagent → Silver mirror

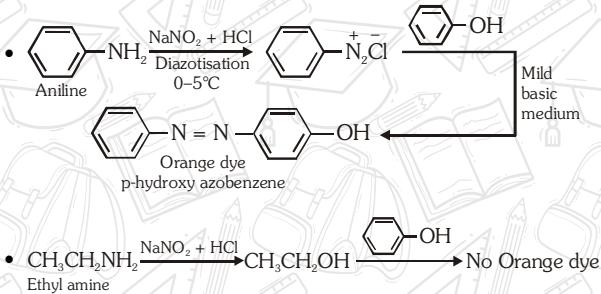


- Acetophenone + Tollen's reagent → No silver mirror

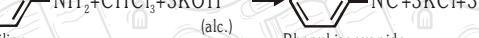
## **Methyl amine and dimethyl amine (Isocyanide test)**



## Aniline and ethyl amine (Diazotisation)



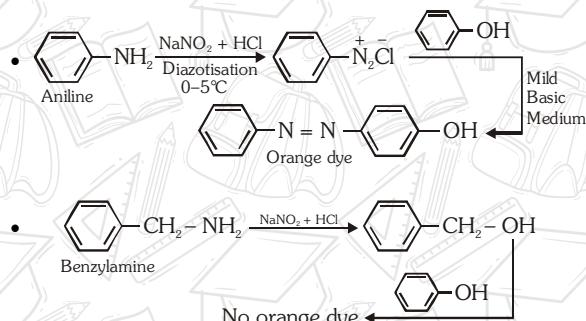
## Aniline and N-methylaniline (Isocyanide test)

- 

$$\text{Aniline} + \text{CHCl}_3 + 3\text{KOH} \xrightarrow{\text{(alc.)}} \text{Phenyl isocyanide} + 3\text{KCl} + 3\text{H}_2\text{O}$$
  - 

$$\text{N-Methylaniline} + \text{CHCl}_3 + 3\text{KOH} \xrightarrow{\text{(alc.)}} \text{N-Methylphenyl isocyanide} + 3\text{KCl}$$

## Aniline and Benzylamine (Diazotisation + phenol)



### **Glucose and fructose**

- Glucose +  $\text{Br}_2$  +  $\text{H}_2\text{O} \rightarrow$  Gluconic acid + 2HBr  
(brown) (colorless)
  - Fructose +  $\text{Br}_2$  +  $\text{H}_2\text{O} \rightarrow$  No change in color  
(brown)

## **Glucose and sucrose**

- Glucose + Tollen's reagent  $\longrightarrow$  Silver mirror
  - Sucrose + Tollen's reagent  $\longrightarrow$  No silver mirror

## *Glucose and starch*

- Glucose + Fehling's solution  $\longrightarrow$  Red ppt.
  - Starch + Fehling's solution  $\longrightarrow$  No red ppt.

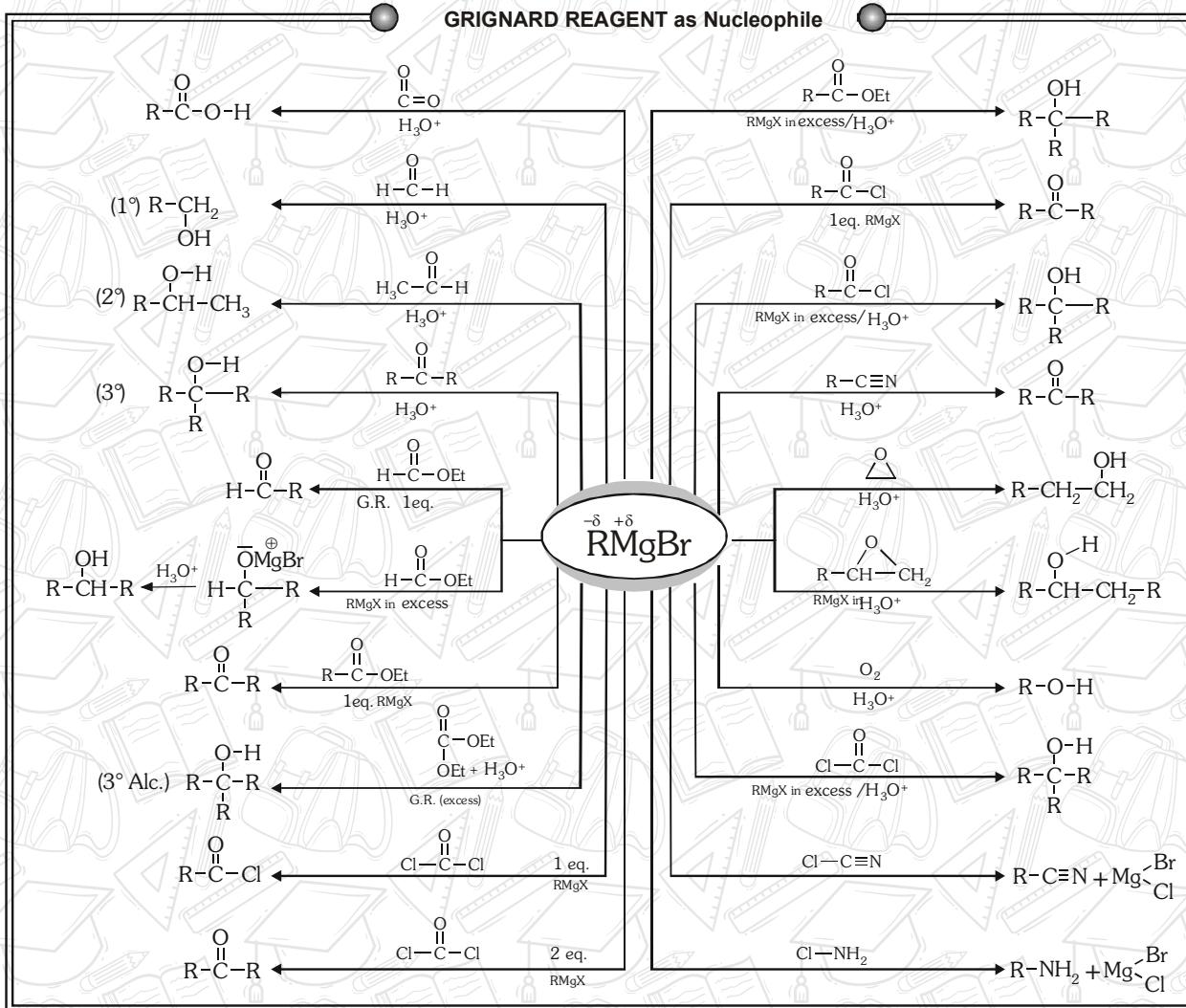
OR

- Glucose + I<sub>2</sub> solution → No blue colour
  - Starch + I<sub>2</sub> solution → Blue colour

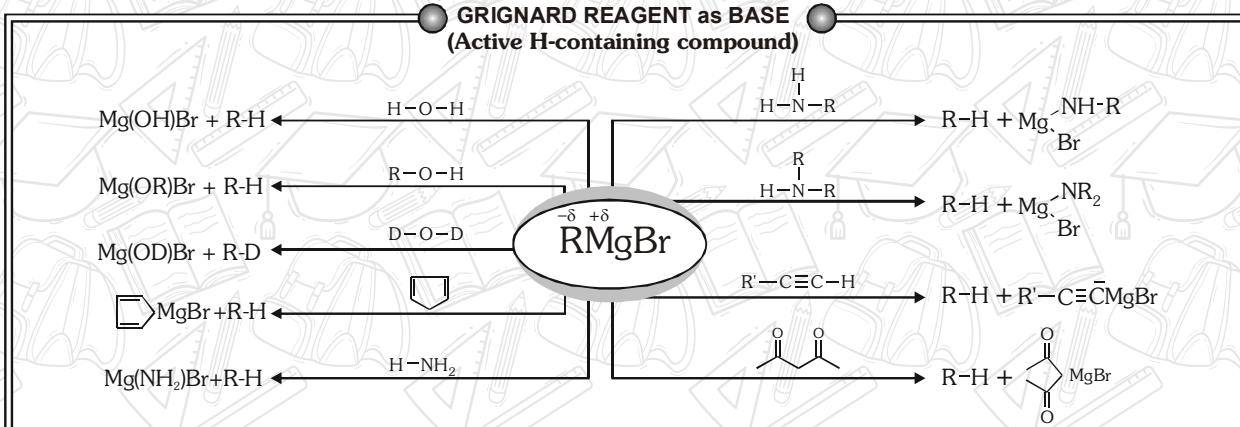
# GRIGNARD REAGENT

## REACTION

### GRIGNARD REAGENT as Nucleophile



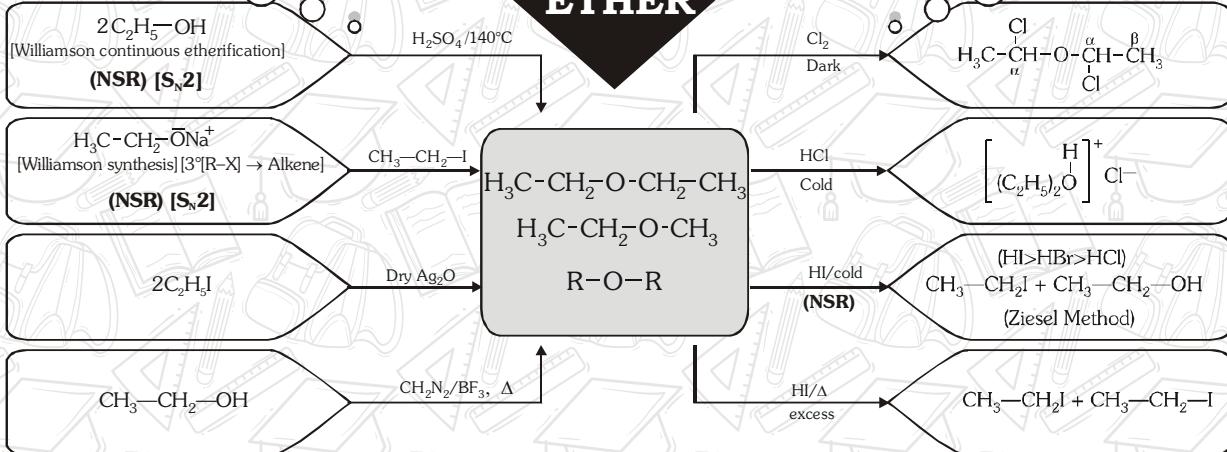
### GRIGNARD REAGENT as BASE (Active H-containing compound)



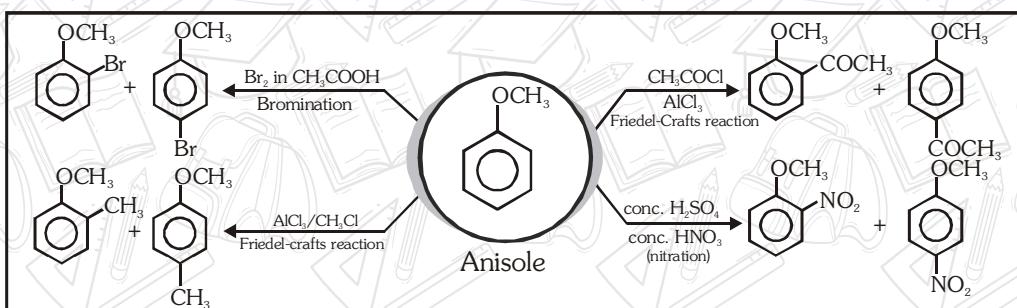
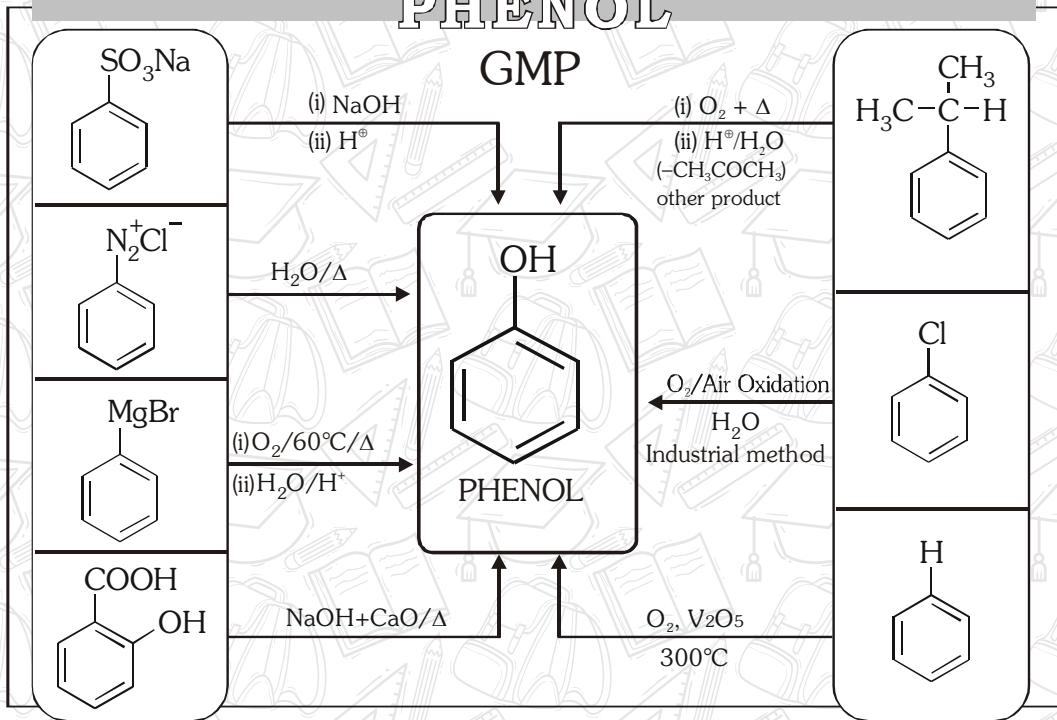
GMP

ETHER

Reactions



## PHENOL GMP



## Comparision of $S_N1$ and $S_N2$

REACTIONS		$S_N1$	$S_N2$
A	Kinetics	1 <sup>st</sup> order	2 <sup>nd</sup> order
B	Rate	$k[RX]$	$k[RX][Nu^{\ominus}]$
C	Stereochemistry	Racemisation	Inversion
D	Substrate (reactivity)	$3^\circ > 2^\circ > 1^\circ > MeX$	$MeX > 1^\circ > 2^\circ > 3^\circ$
E	Nucleophile	Rate Independent	Needs Strong Nu
F	Solvent	Good in protic	Faster in aprotic
G	Leaving Group	Needs Good LG	Needs Good LG
H	Rearrangement	Possible	Not Possible

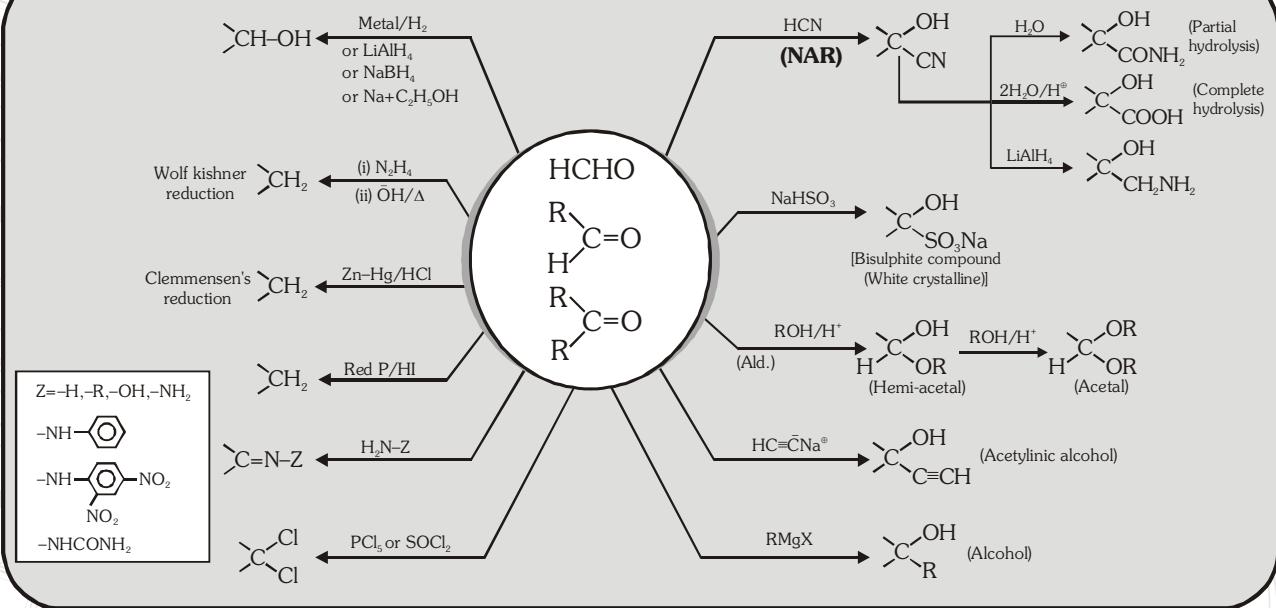
## Comparision of $E_1$ and $E_2$

REACTIONS		$E_1$	$E_2$
A	Kinetics	1 <sup>st</sup> order	2 <sup>nd</sup> order
B	Rate	$k[RX]$	$k[RX][B^{\ominus}]$
C	Stereochemistry	No special geometry	Anti-periplanar
D	Substrate	$3^\circ > 2^\circ > > 1^\circ$	$3^\circ > 2^\circ > 1^\circ$
E	Base Strength	Rate Independent	Needs Strong bases
F	Solvent	Good ionizing	Polarity not import
G	Leaving Group	Needs Good LG	Needs Good LG
H	Rearrangement	Possible	Not Possible

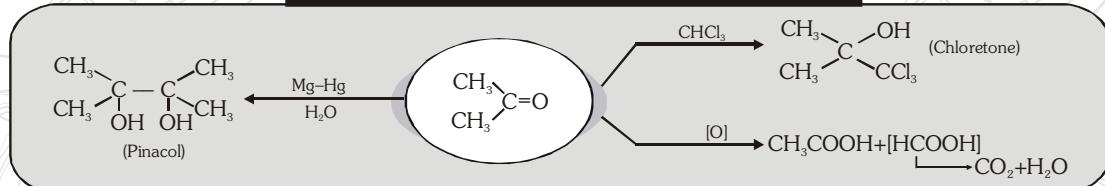
## Summary of $S_N1$ , $S_N2$ , $E_1$ and $E_2$ Reactions

$RX$	Mechanism	$Nu^{\ominus}/B^{\ominus}$	Solvent	Temp.
$1^\circ$	$S_N2$	Better $Nu^{\ominus}$ Aq. KOH, OR <sup>⊖</sup>	Polar aprotic	Low
	$E2$	Strong & bulky base Alc. KOH, $(CH_3)_3CO^{\ominus}$		High
$2^\circ$	$S_N2$	Aq. KOH	Polar aprotic	Low
	$E2$	$OR^{\ominus}, (CH_3)_3CO^{\ominus}$		High
	$(S_N1)$	Solvent	Polar protic	(Low)
	$(E1)$	Solvent		(High)
$3^\circ$	$S_N1$	Solvent	Protic	Low
	$E1$	Solvent	Protic	High
	$E2$	$Nu^{\ominus}/Base$	—	High
		Primary ( $1^\circ$ )	Secondary ( $2^\circ$ )	Tertiary ( $3^\circ$ )
Strong nucleophile		$S_N2 >> E2$	$S_N2 + E_2$ (if weak base, $S_N2$ favored)	$E2$
Weak nucleophile weak base		Mostly $S_N2$	Mostly $S_N2/S_N1$	Mostly $S_N1$ at low T mostly $E1$ at high T
Weak nucleophile strong base		Mostly E2	Mostly E2	E2

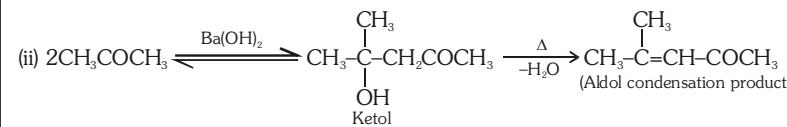
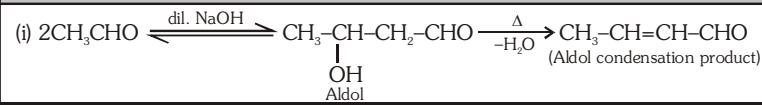
## Reaction of Aldehyde & Ketone



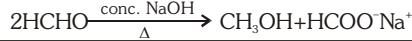
## Reaction of only Ketone



### Aldol Reaction (Aldehyde or ketone with αH)

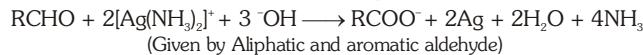


### Cannizzaro reaction (Aldehyde with no α H)

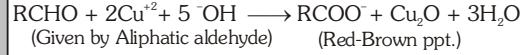


TESTS

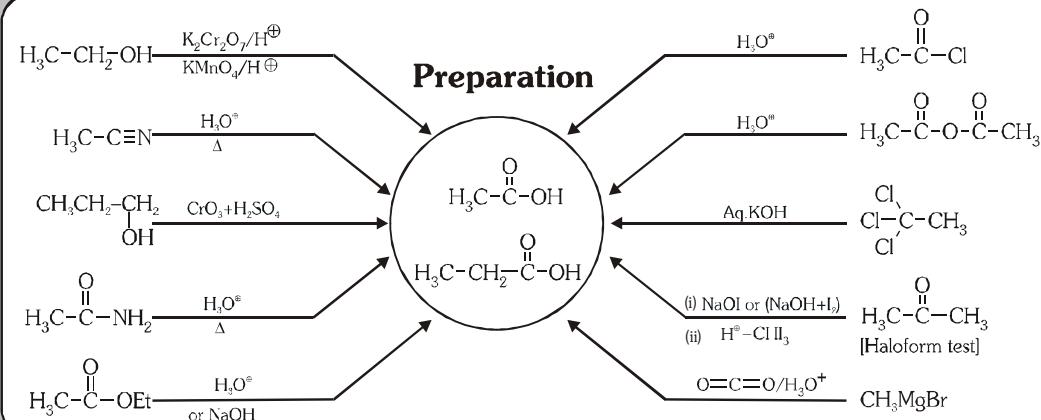
#### Tollen's test :-



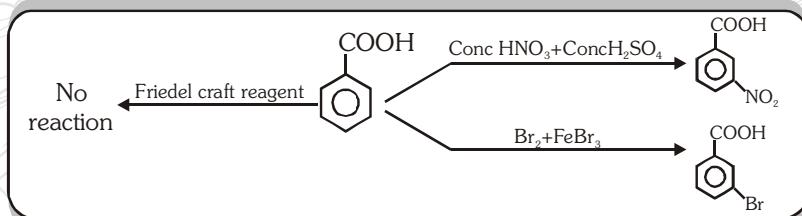
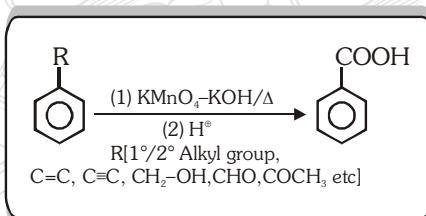
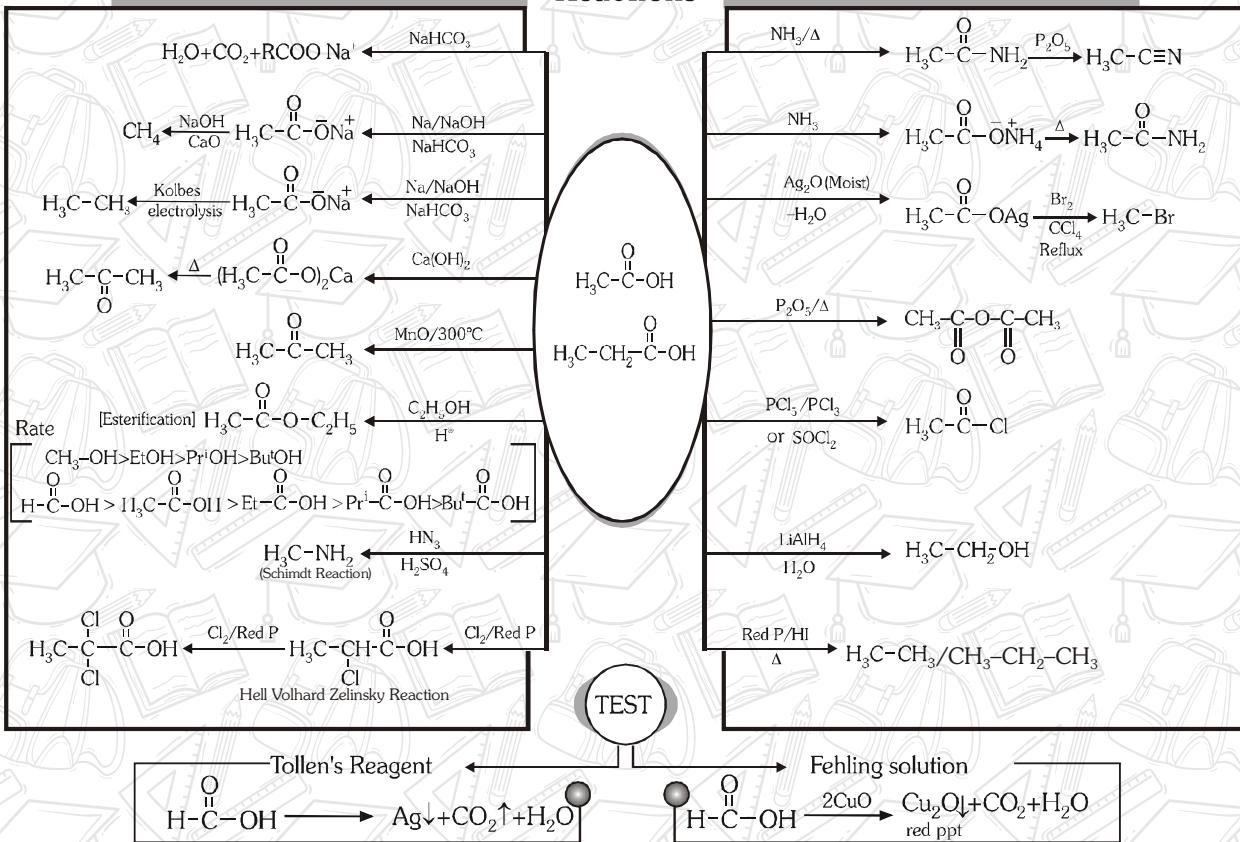
#### Fehling's test



# CARBOXYLIC ACID

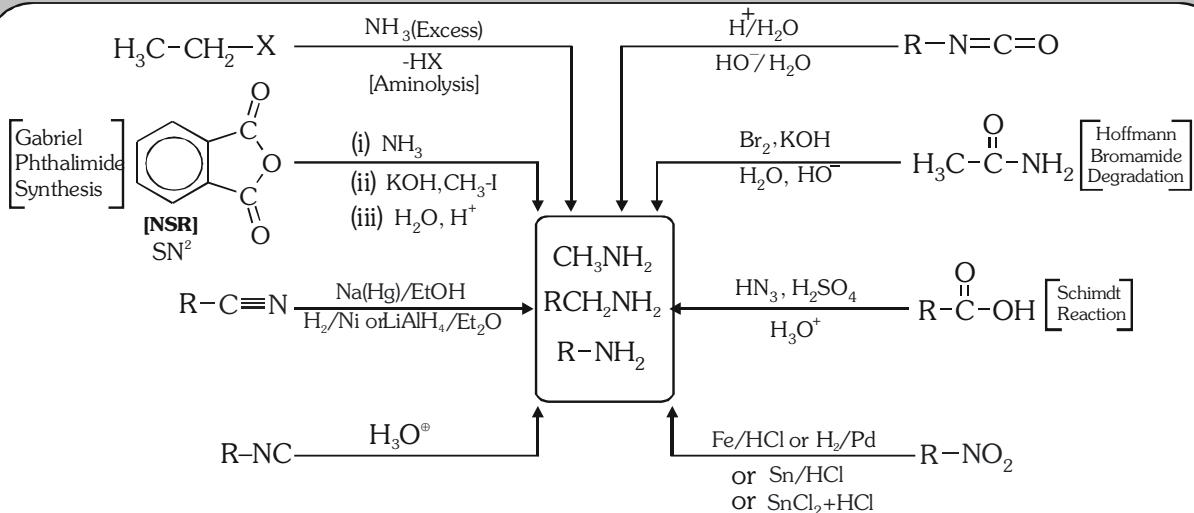


## Reactions

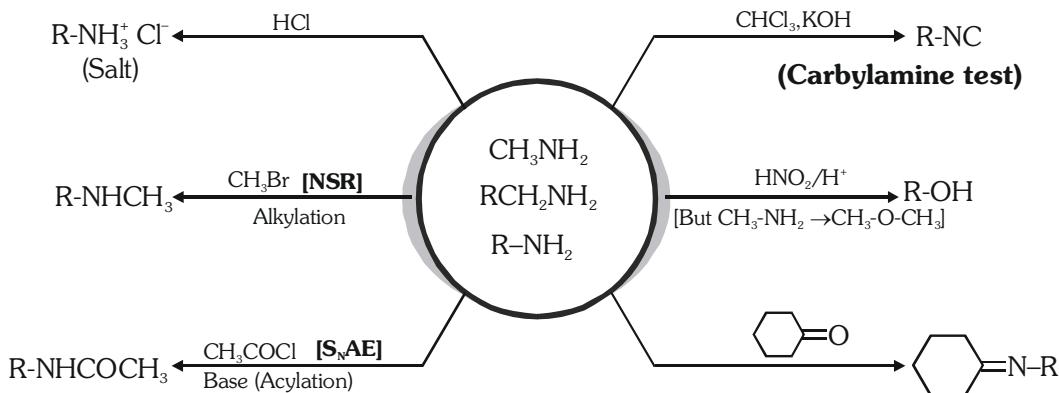


# AMINES

## PREPARATION



## REACTION

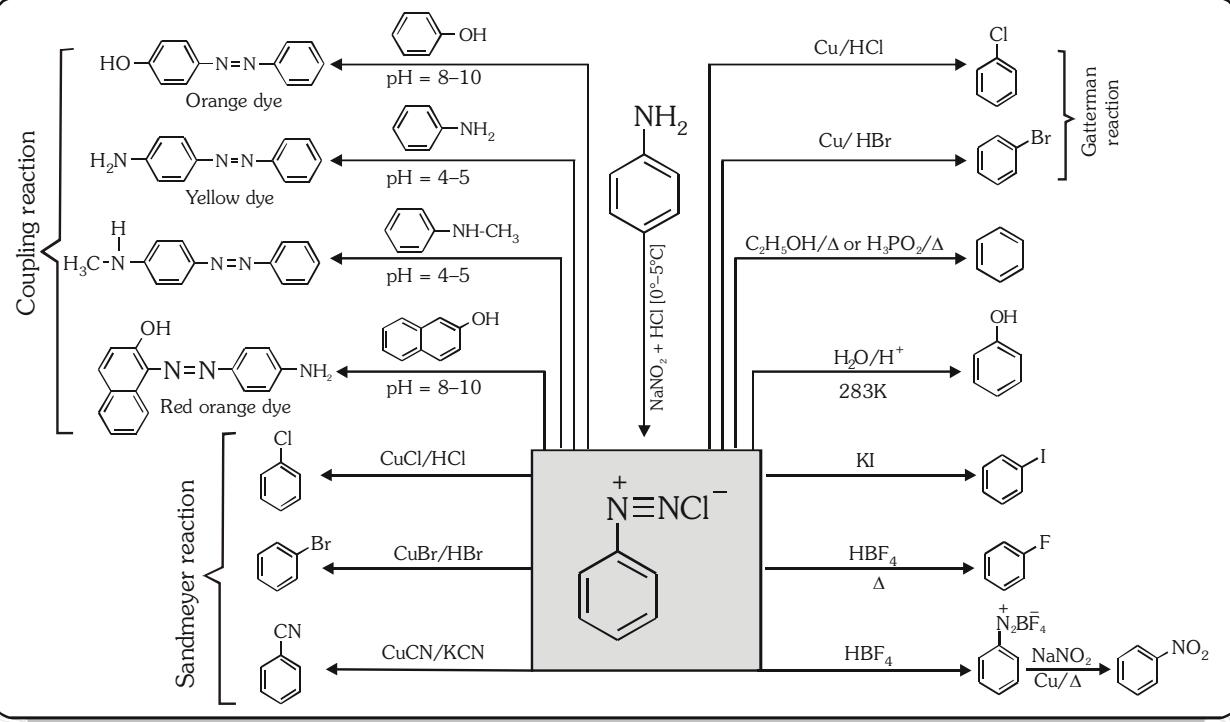


## TEST

Reagent	R-NH2(1°)	R2NH(2°)	R3N(3°)	
Ph-SO2Cl (Hinsberg reagent)	R-N(SO2Ph) <sub>2</sub> soluble NaOH ↓ [R-N(SO2Ph)2] <sup>+</sup> Na <sup>+</sup> soluble	R <sub>2</sub> N(SO2Ph) <sub>2</sub> ↓ NaOH Insoluble	No reaction	
S=C=S Δ/HgCl <sub>2</sub> Mustard oil test	R-NH-C(=S)-SH HgCl <sub>2</sub> Δ R-N=C=S+HgS	R <sub>2</sub> N-C(=S)-SH HgCl <sub>2</sub> Δ No reaction	No reaction	

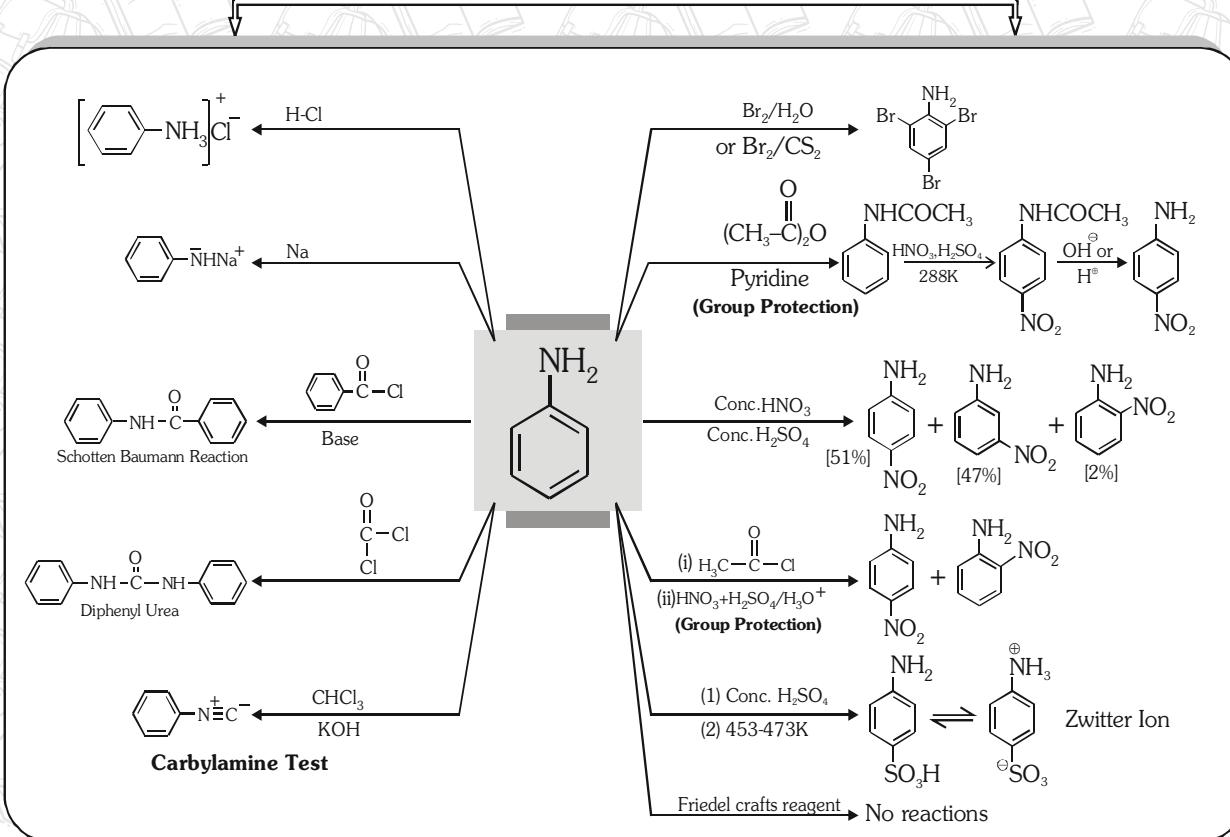
## BENZENE DIAZONIUM CHLORIDE

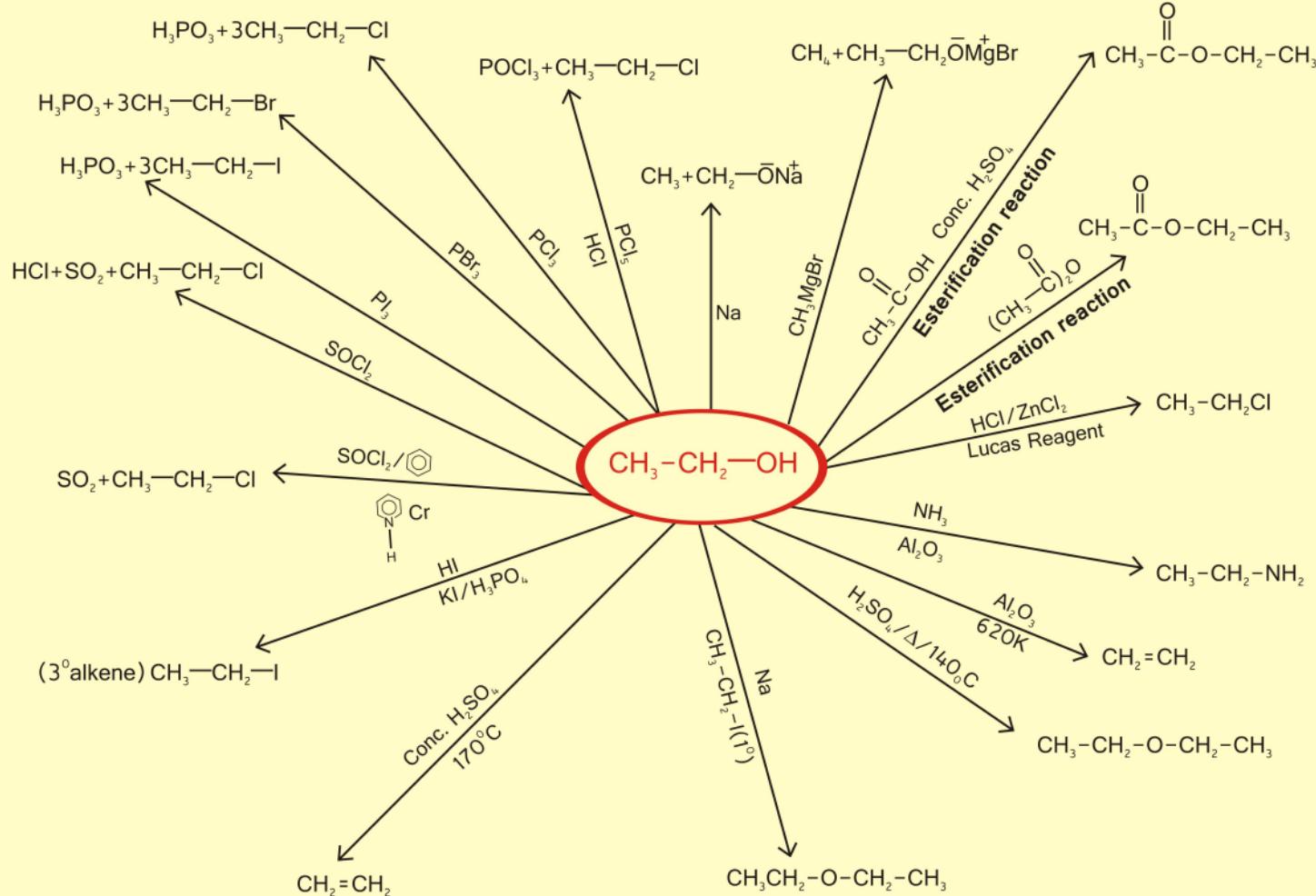
### REACTION



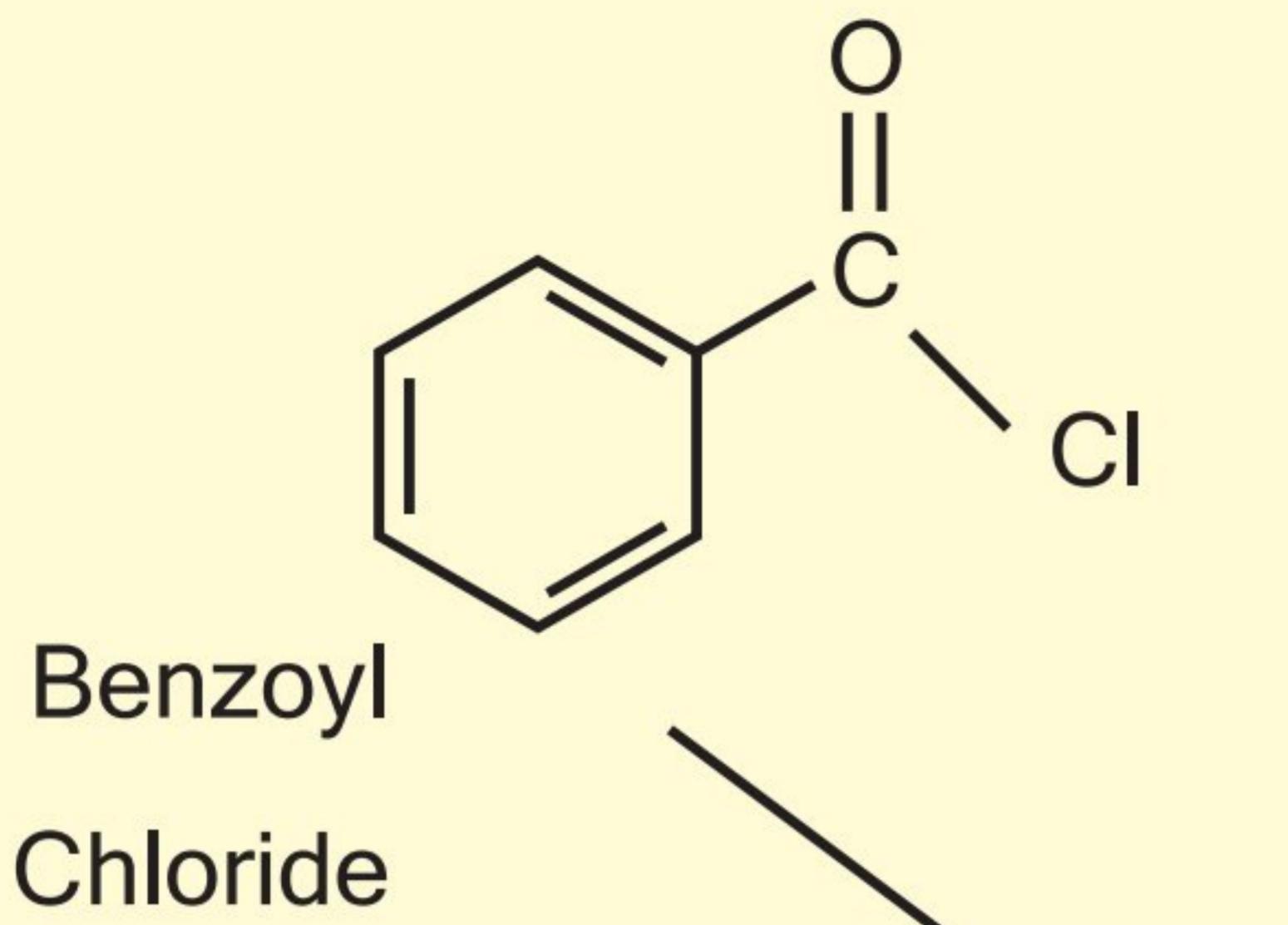
## ANILINE

### REACTION

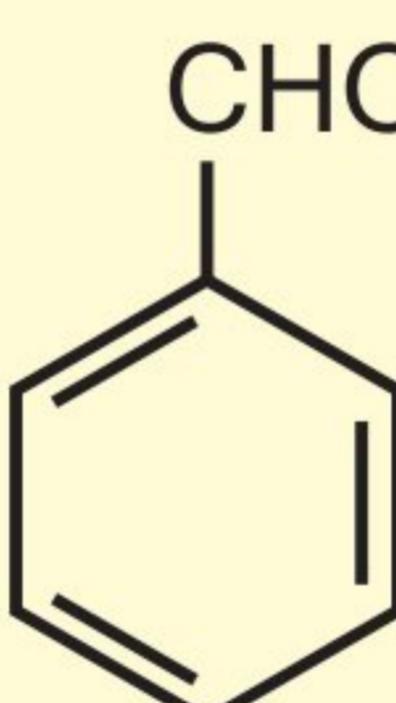




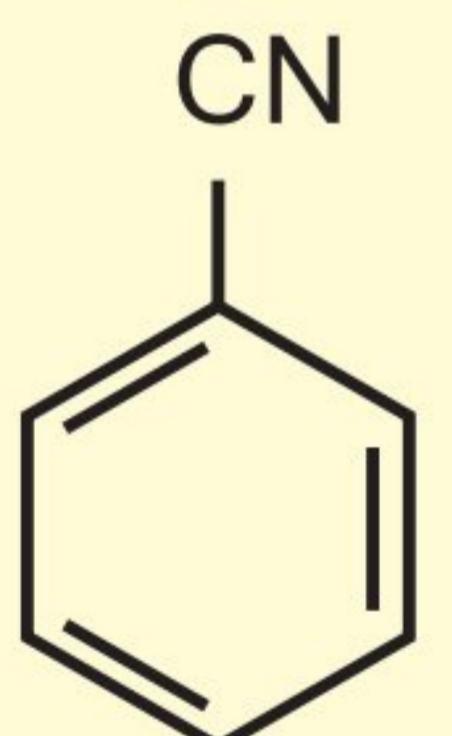
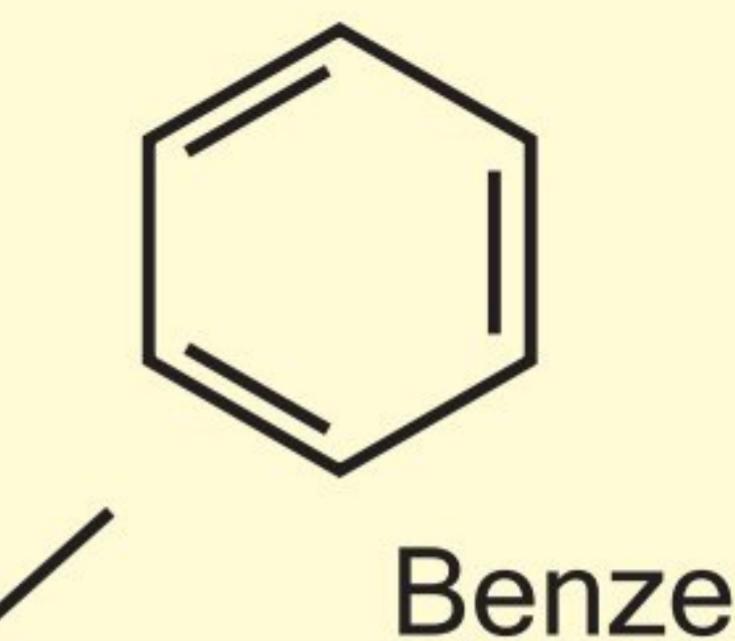
Reagent	$\text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OH}$ 1° Alcohol	$\begin{matrix} \text{OH} \\   \\ \text{H}_3\text{C}-\text{CH}_2-\text{CH}-\text{CH}_3 \end{matrix}$ 2° Alcohol	$\begin{matrix} \text{CH}_3 \\   \\ \text{H}_3\text{C}-\text{C}-\text{OH} \\   \\ \text{CH}_3 \end{matrix}$ 3° Alcohol
PCC/CH <sub>2</sub> Cl <sub>2</sub> H <sub>2</sub> CrO <sub>4</sub> /Acetone (Jones Reagent)	$\begin{matrix} \text{O} \\    \\ \text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{C}-\text{H} \end{matrix}$	$\begin{matrix} \text{O} \\    \\ \text{H}_3\text{C}-\text{CH}_2-\text{C}-\text{OH} \end{matrix}$	No Reaction
K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> /H <sup>+</sup> or KMnO <sub>4</sub> /H <sup>+</sup>	$\begin{matrix} \text{O} \\    \\ \text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{C}-\text{OH} \end{matrix}$	$\begin{matrix} \text{O} \\    \\ \text{H}_3\text{C}-\text{CH}_2-\text{C}-\text{CH}_3 \end{matrix}$	No Reaction
Cu/500°C	$\begin{matrix} \text{O} \\    \\ \text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{C}-\text{H} \end{matrix}$	$\begin{matrix} \text{O} \\    \\ \text{CH}_3-\text{CH}_2-\text{C}-\text{CH}_3 \end{matrix}$	$\begin{matrix} \text{CH}_3 \\   \\ \text{H}_3\text{C}-\text{C}=\text{CH}_2 \end{matrix}$
$\xrightarrow{\text{Al(OBu')}_3}$ Acetone or Cyclohexanone	$\begin{matrix} \text{O} \\    \\ \text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{C}-\text{H} \end{matrix}$	$\begin{matrix} \text{O} \\    \\ \text{H}_3\text{C}-\text{CH}_2-\text{C}-\text{CH}_3 \end{matrix}$	
Lucas Reagent HCl/ZnCl <sub>2</sub>	Cloudiness appear upon heating after 30 mins at normal temp. no reaction	within five mins	Immediately
Victor Mayer's Test			
P/I <sub>2</sub>	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{I}$	$\begin{matrix} \text{CH}_3 \\   \\ \text{H}_3\text{C}-\text{CH}_2-\text{CH}-\text{I} \end{matrix}$	$\begin{matrix} \text{CH}_3 \\   \\ \text{H}_3\text{C}-\text{C}-\text{I} \\   \\ \text{CH}_3 \end{matrix}$
AgNO <sub>3</sub>	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{NO}_2$	$\begin{matrix} \text{CH}_3 \\   \\ \text{H}_3\text{C}-\text{CH}_2-\text{CH}-\text{NO}_2 \end{matrix}$	$(\text{CH}_3)_3-\text{NO}_2$
HNO <sub>2</sub> NaOH	$\begin{matrix} \text{H}_3\text{C}-\text{CH}_2-\text{C}-\text{NO}_2 \\    \\ \text{N}-\text{OH} \end{matrix}$	$\begin{matrix} \text{CH}_3 \\   \\ \text{H}_3\text{C}-\text{CH}_2-\text{CH}-\text{NO}_2 \\   \\ \text{N}=\text{O} \end{matrix}$	No Reaction 



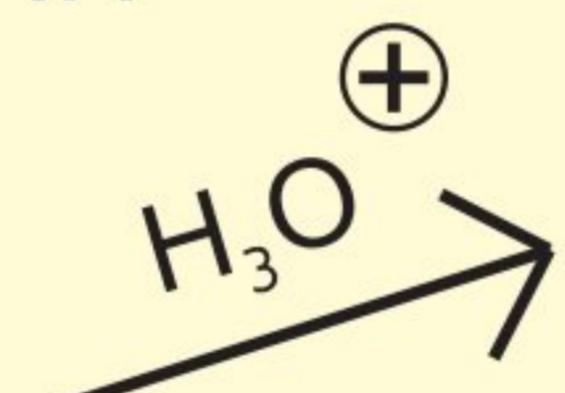
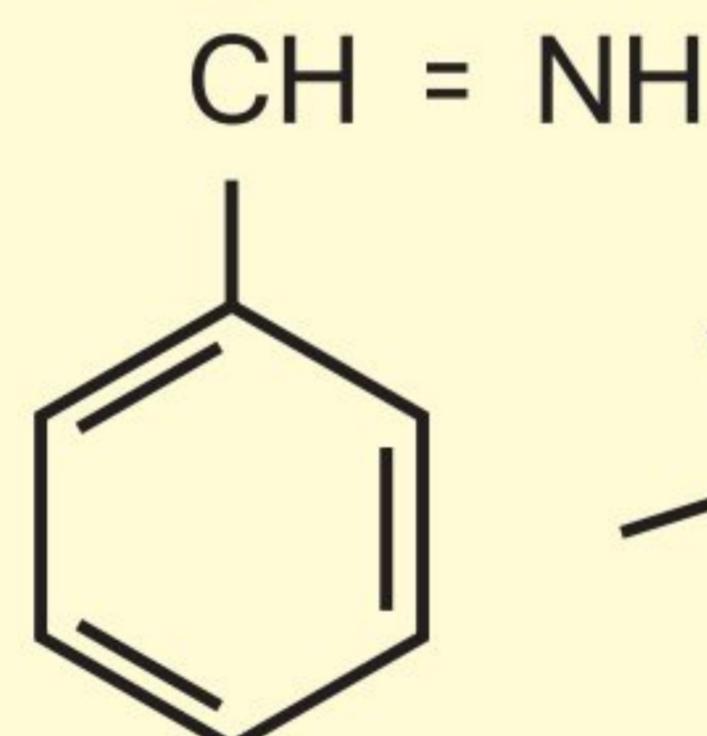
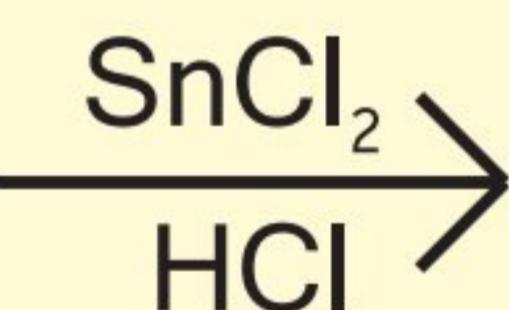
Pd - H<sub>2</sub>  
"Rosenmund Reduction"



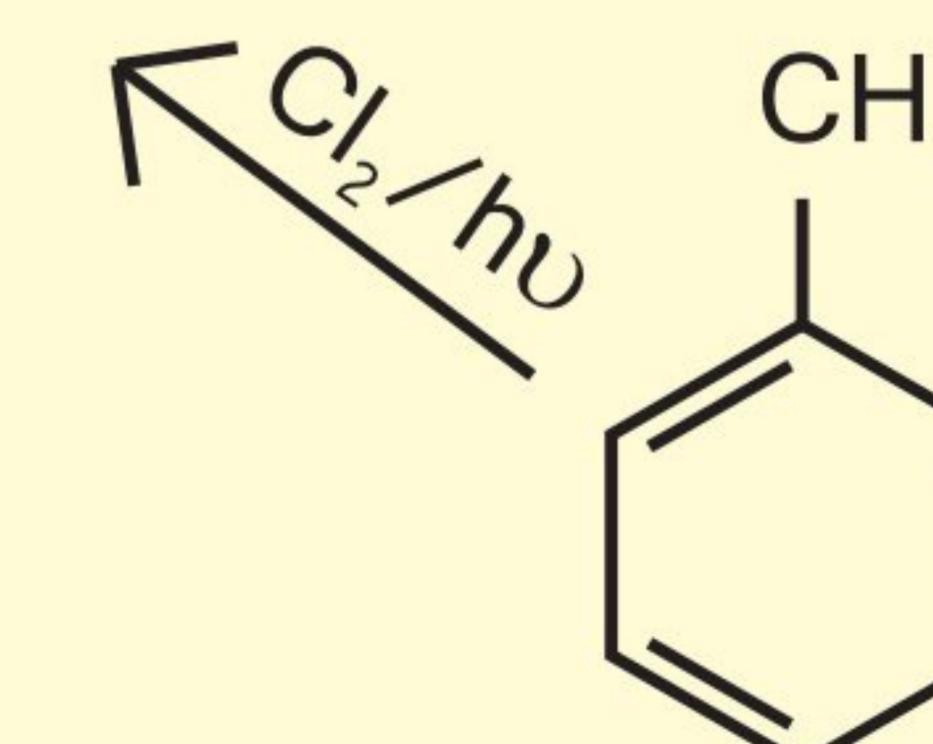
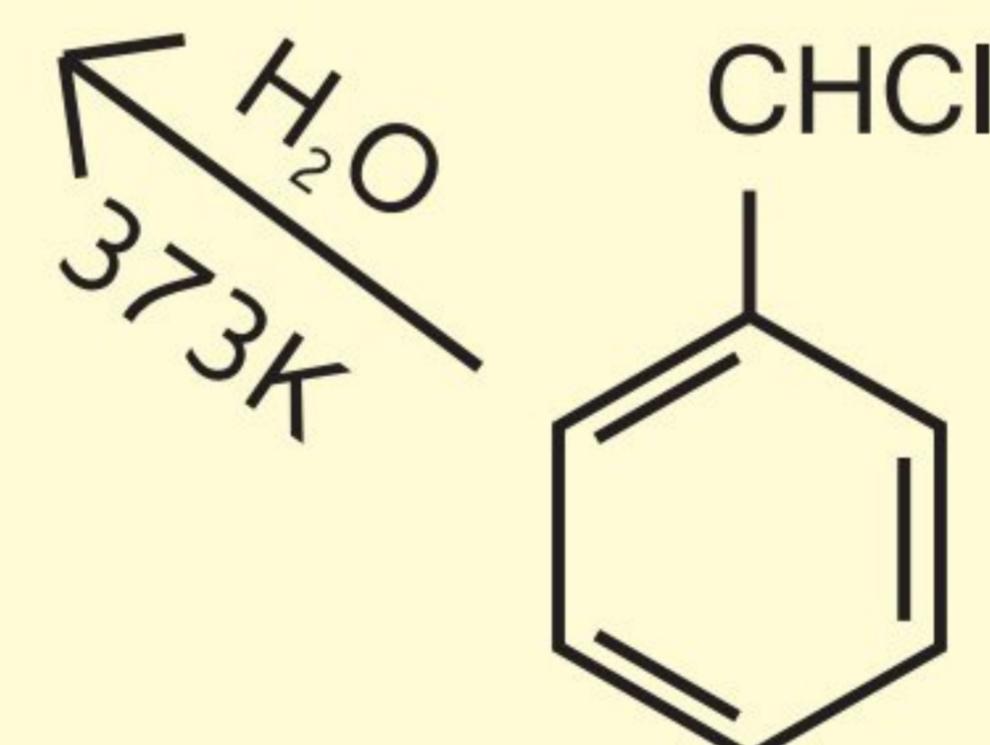
Anhy. AlCl<sub>3</sub> / CuCl  
"Gatterman Koch Reaction"



"Stephen Reduction"

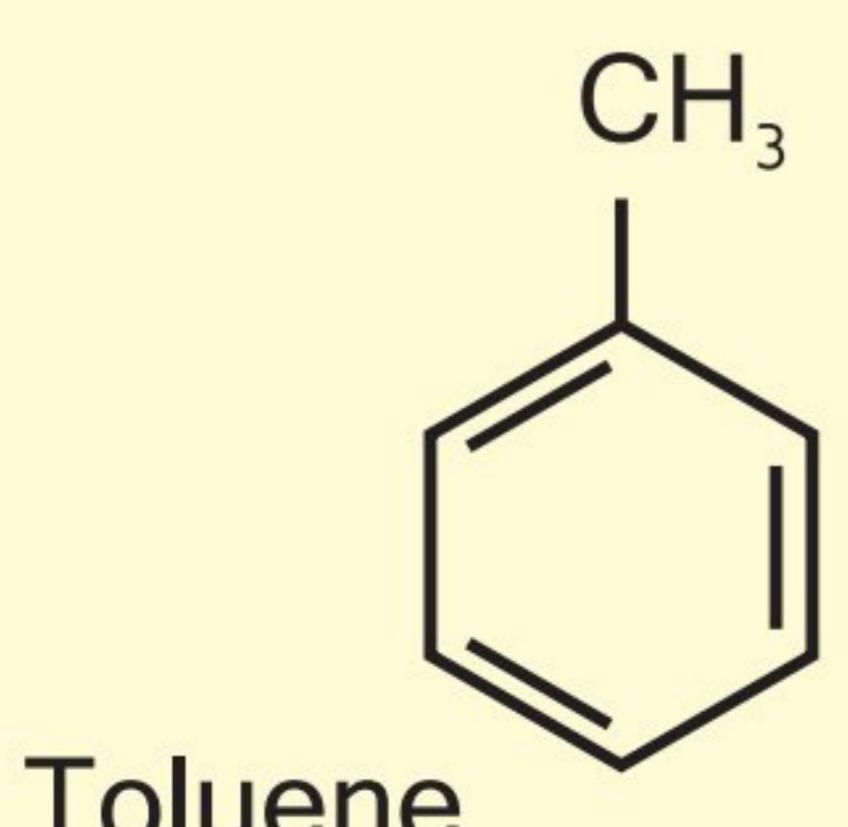


CrO<sub>2</sub>Cl<sub>2</sub> / CS<sub>2</sub>  
H<sub>3</sub>O<sup>⊕</sup>



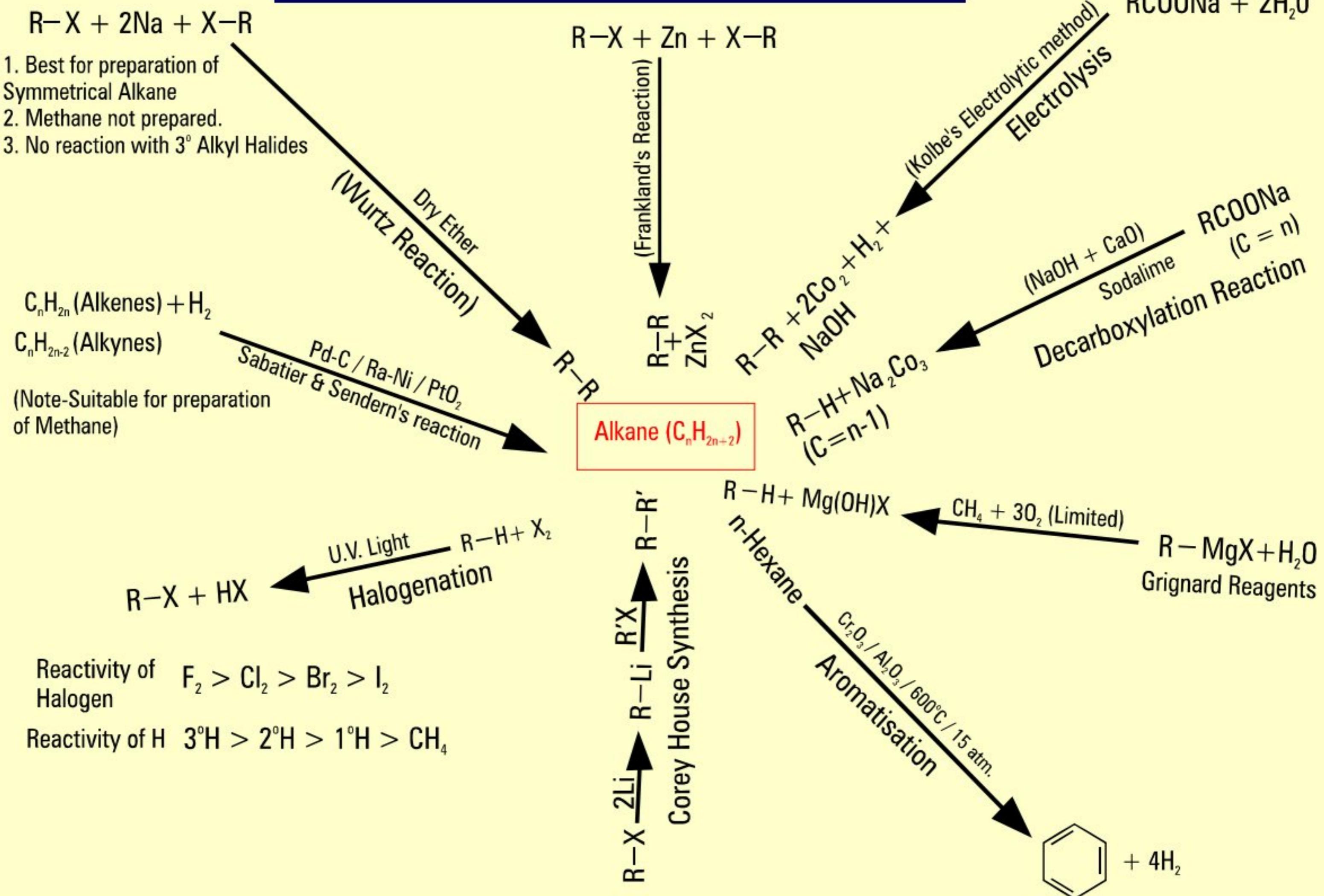
Toluene

"Etard Reaction"

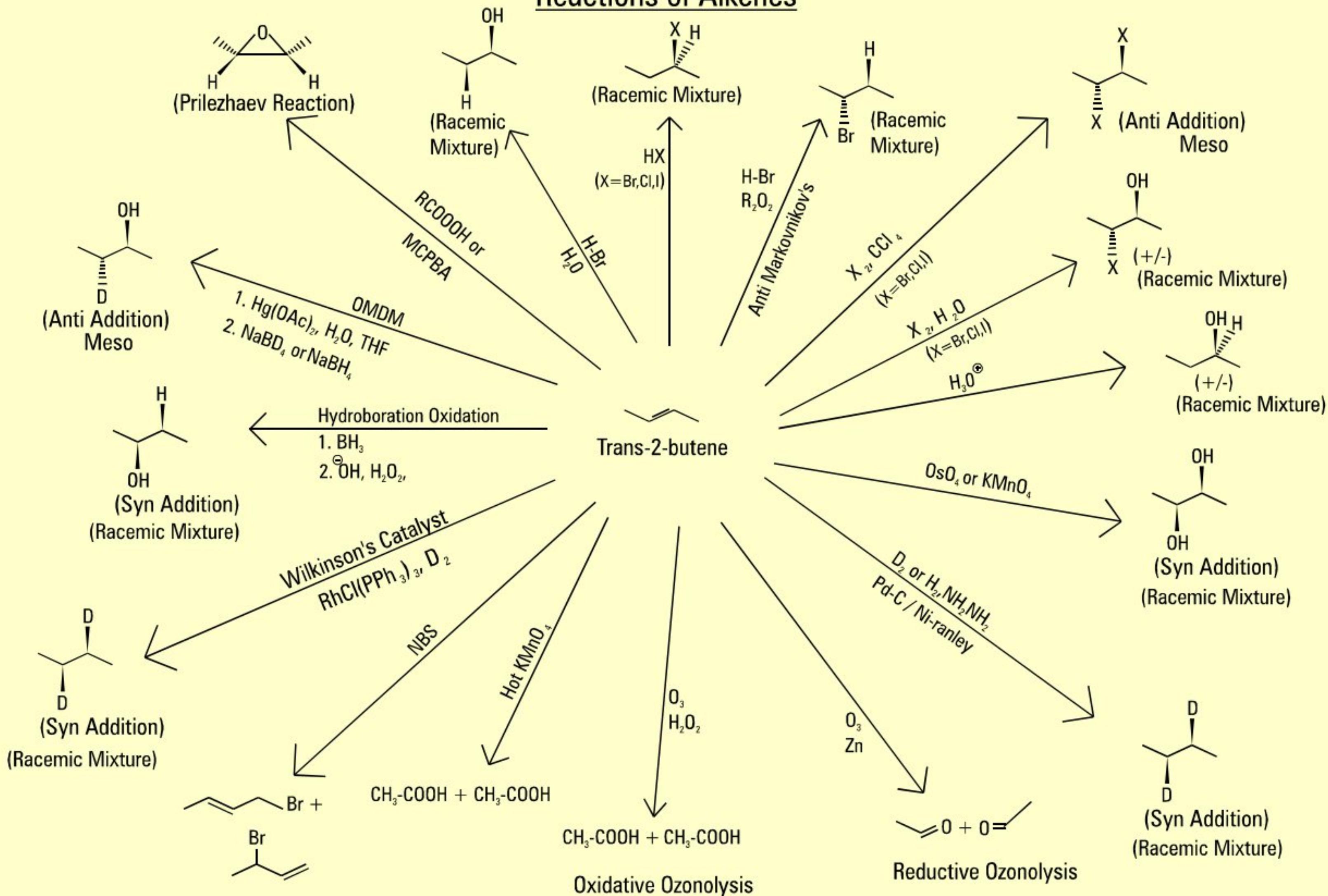


"Commercial method  
of Preparation"

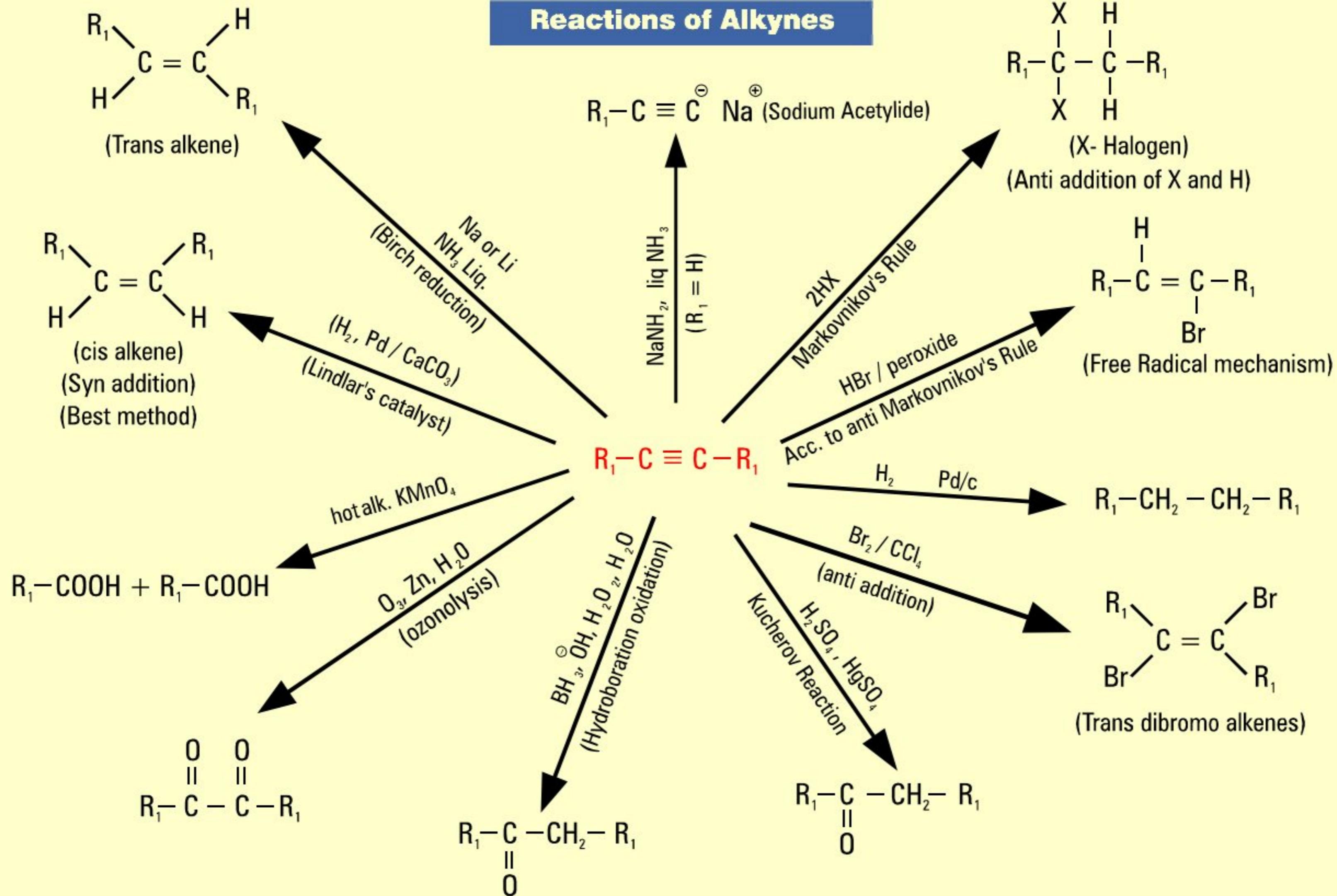
## Preparation & Chemical Reactions of Alkanes



## Reactions of Alkenes



## Reactions of Alkynes



# Flash card

## Preparation of Benzene

