

BRUSH UP for NEET/JEE

Brush up your concepts to get high rank in NEET/JEE (Main and Advanced) by reading this column. This specially designed column is updated year after year by a panel of highly qualified teaching experts well-tuned to the requirements of these Entrance Tests.

2020

Unit
5

Haloalkanes and Haloarenes | Alcohols, Phenols and Ethers

Haloalkanes and Haloarenes

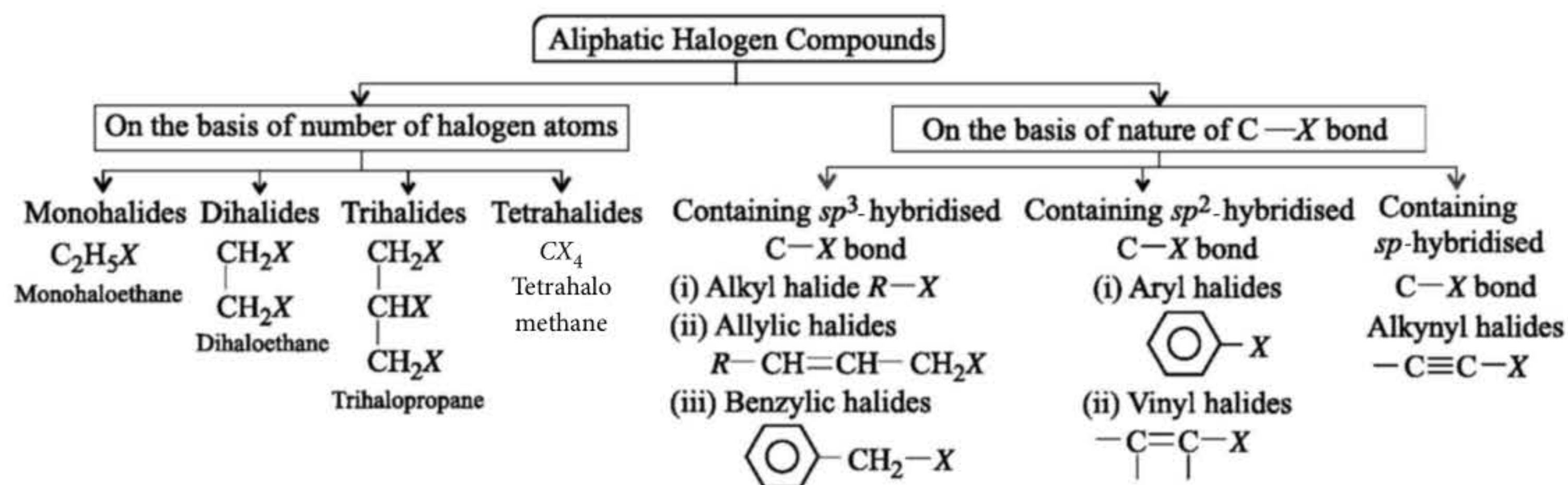
HALOALKANES

- Compounds obtained from alkanes by the replacement of one or more hydrogens by corresponding number of halogen atoms (-F, -Cl, -Br, -I) are termed as *haloalkanes*. e.g., RX .

HALOARENES

- When hydrogen atom of the benzene nucleus is substituted by a halogen atom, then haloarenes are formed with general formula C_6H_5X .
- When hydrogen atom of the side chain attached to benzene is substituted by a halogen atom, then aralkyl halide are formed, e.g., benzyl halide ($C_6H_5CH_2X$).

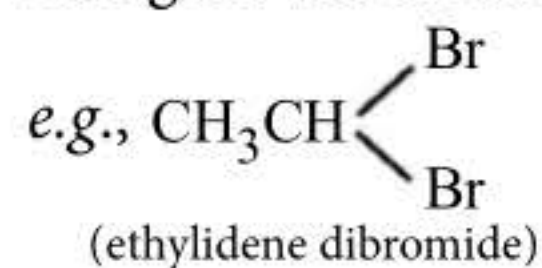
CLASSIFICATION



- General formula and nomenclature of alkyl/aryl halides :**

- Monohalogen derivatives - $C_nH_{2n+1}X$ (alkyl halides)
- Dihalogen derivatives - $C_nH_{2n}X_2$

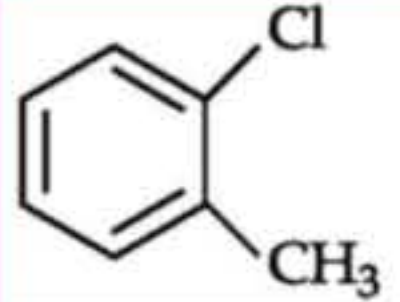
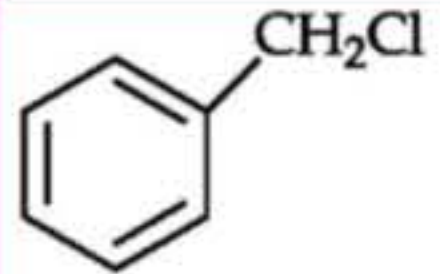
- Geminal dihalides* are formed when both halogens are on the same C-atom.



- *Vicinal dihalides* are formed when both halogens are attached to adjacent carbon atoms, e.g., $\text{ClH}_2\text{C} - \text{CH}_2\text{Cl}$ (ethylene dichloride)
- *Terminal dihalides* are formed when halogens

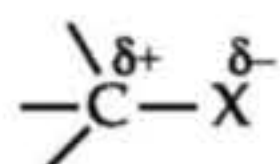
are attached to terminal C-atoms of a compound. e.g., $\text{ClH}_2\text{C} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2\text{Cl}$ (tetramethylene dichloride)

- General formula of aryl halides is ArX where Ar = aryl group

Structure	Common name	IUPAC name
$\text{CH}_3\text{CH}_2\text{CH}(\text{Cl})\text{CH}_3$	<i>sec</i> -Butyl chloride	2-Chlorobutane
$(\text{CH}_3)_3\text{CCH}_2\text{Br}$	<i>neo</i> -Pentyl bromide	1-Bromo-2,2-dimethylpropane
	<i>o</i> -Chlorotoluene	1-Chloro-2-methylbenzene or 2-Chlorotoluene
	Benzyl chloride	Chlorophenylmethane

NATURE OF C—X BOND

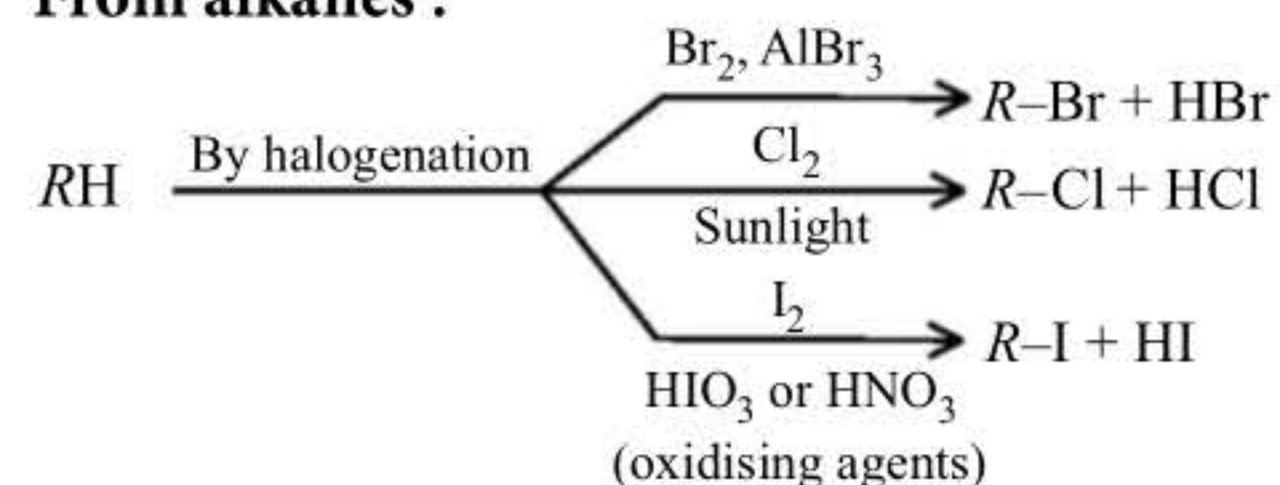
- Since halogen atoms are more electronegative than carbon, the C—X bond of an alkyl halide is polarised; the carbon atom bears a partial positive charge whereas the halogen atom bears a partial negative charge.



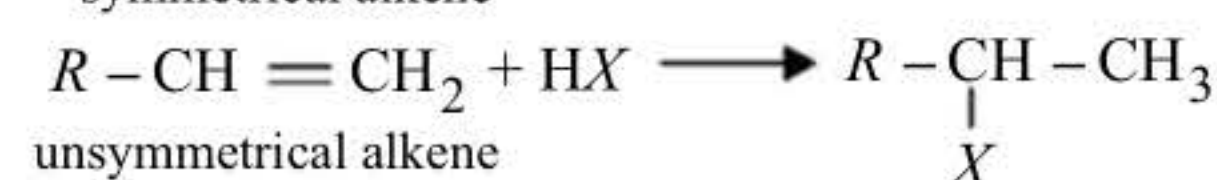
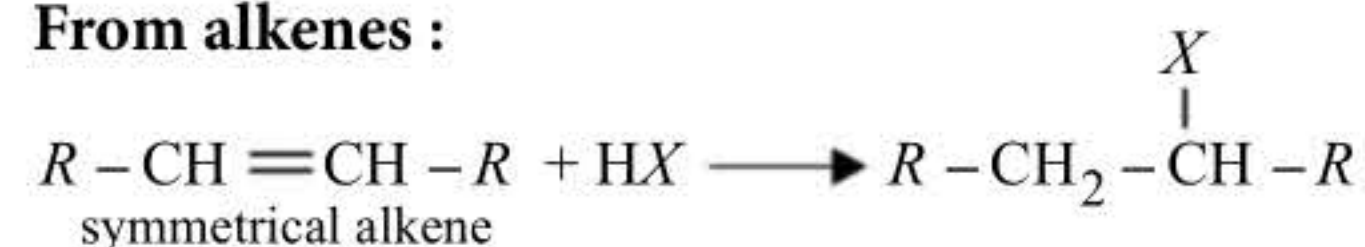
Since the size of halogen atom increases as we go down the group in the periodic table, fluorine atom is the smallest and iodine atom, the largest. Consequently, the carbon-halogen bond length also increases from C—F to C—I and bond enthalpy decreases from C—F to C—I.

GENERAL METHODS OF PREPARATION OF ALKYL HALIDES

- **From alkanes :**



- **From alkenes :**

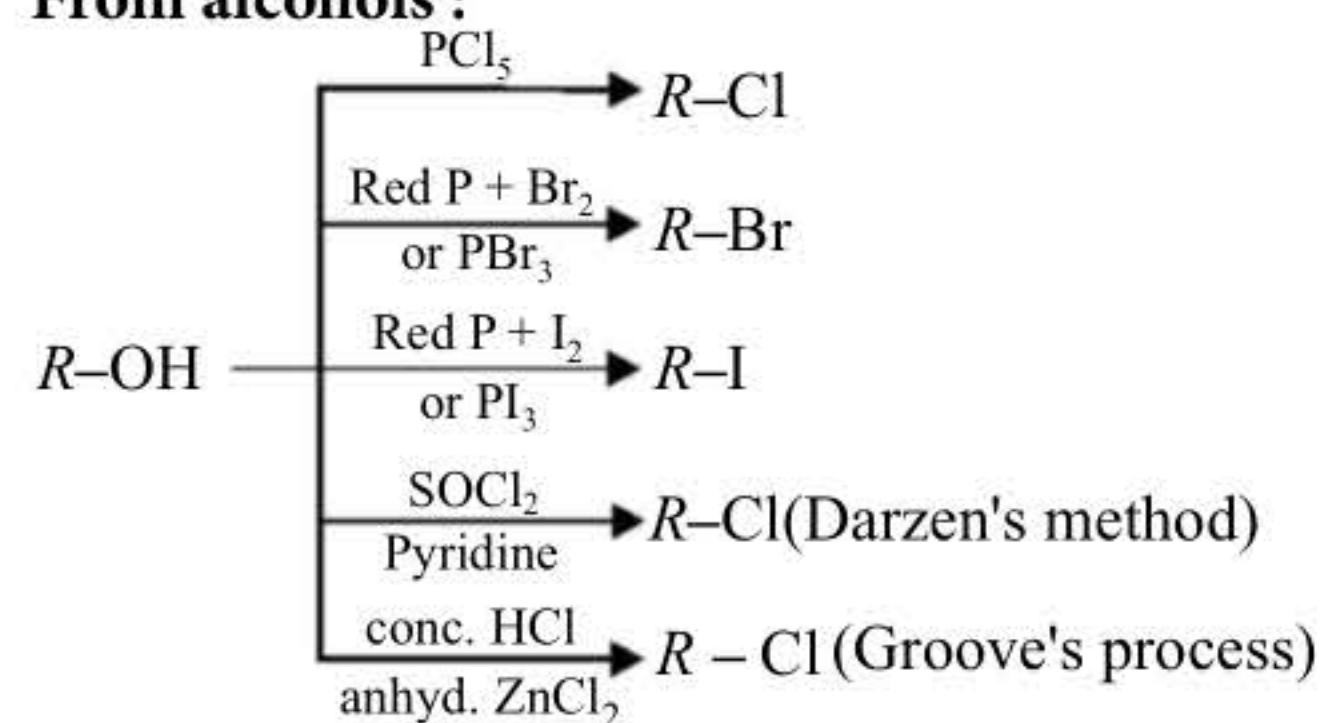


- In the addition of halogen acids to an unsymmetrical alkenes, generally the Markownikoff's rule is followed and the

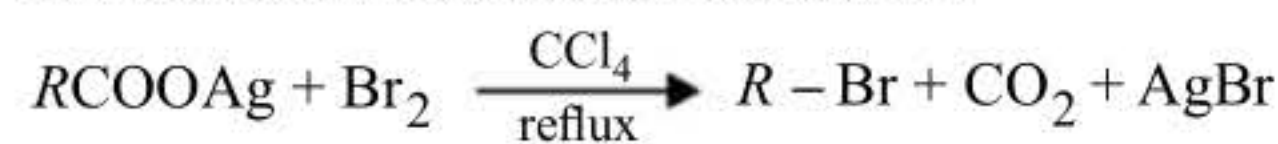
addition occurs through an electrophilic attack. However, in case of reaction with HBr in presence of peroxide, anti-Markownikoff's rule is followed, known as peroxide effect or Kharasch effect.

- The order of reactivity of halogen acids with alkenes is $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$.

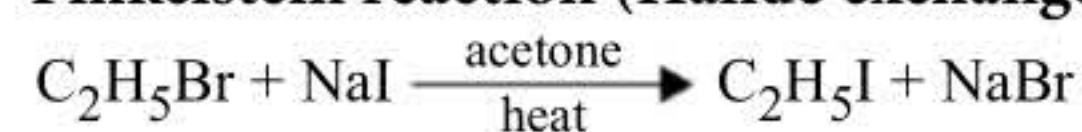
- **From alcohols :**



- **Borodine-Hunsdiecker reaction :**

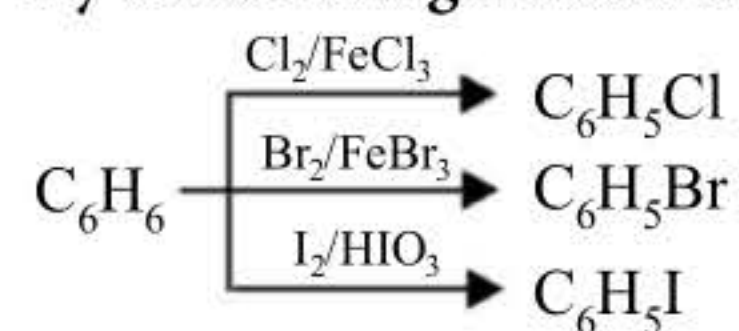


- **Finkelstein reaction (Halide exchange) :**



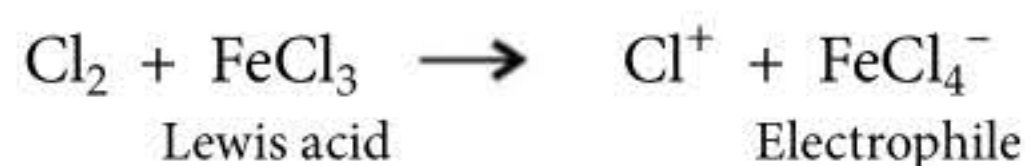
GENERAL METHODS OF PREPARATION OF ARYL HALIDES

- **By direct halogenation of benzene :**

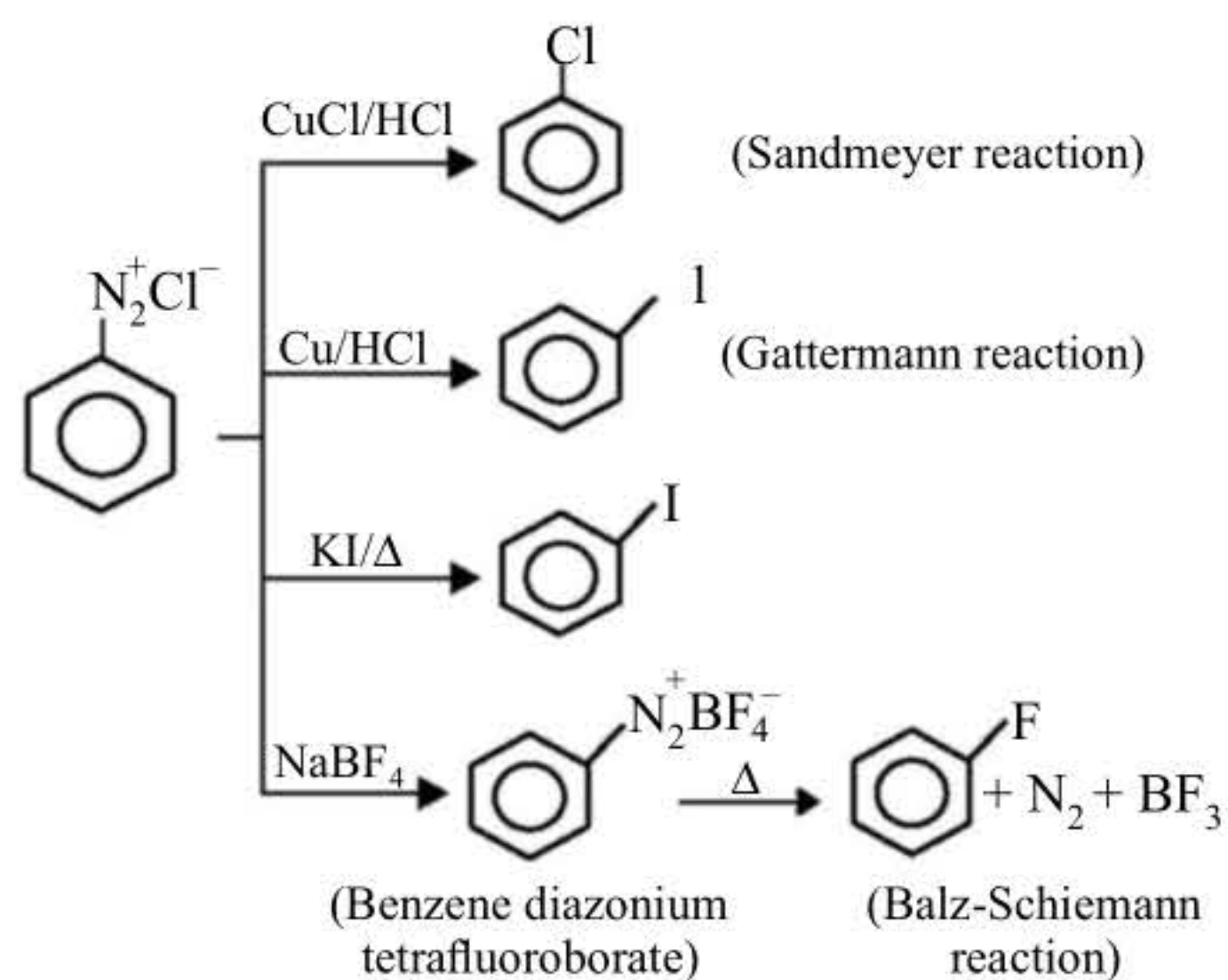


These are electrophilic substitution reaction.

Low temperature and the presence of a halogen carrier favours nuclear substitution. The function of the halogen carrier is to generate the electrophile for the attack.



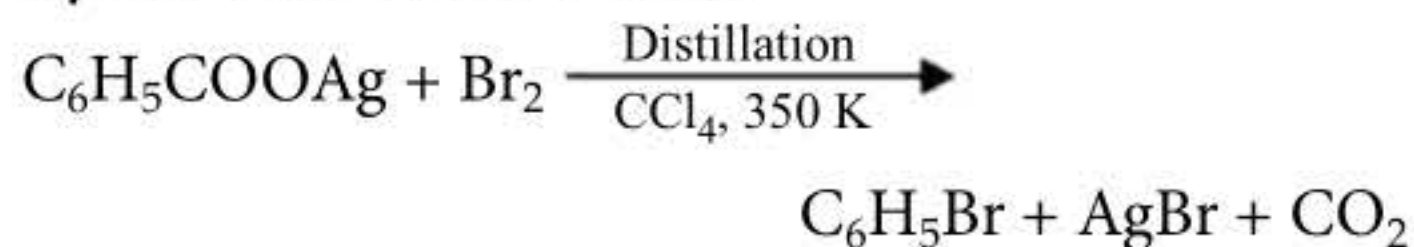
• From benzenediazonium salt :



• By Raschig process :



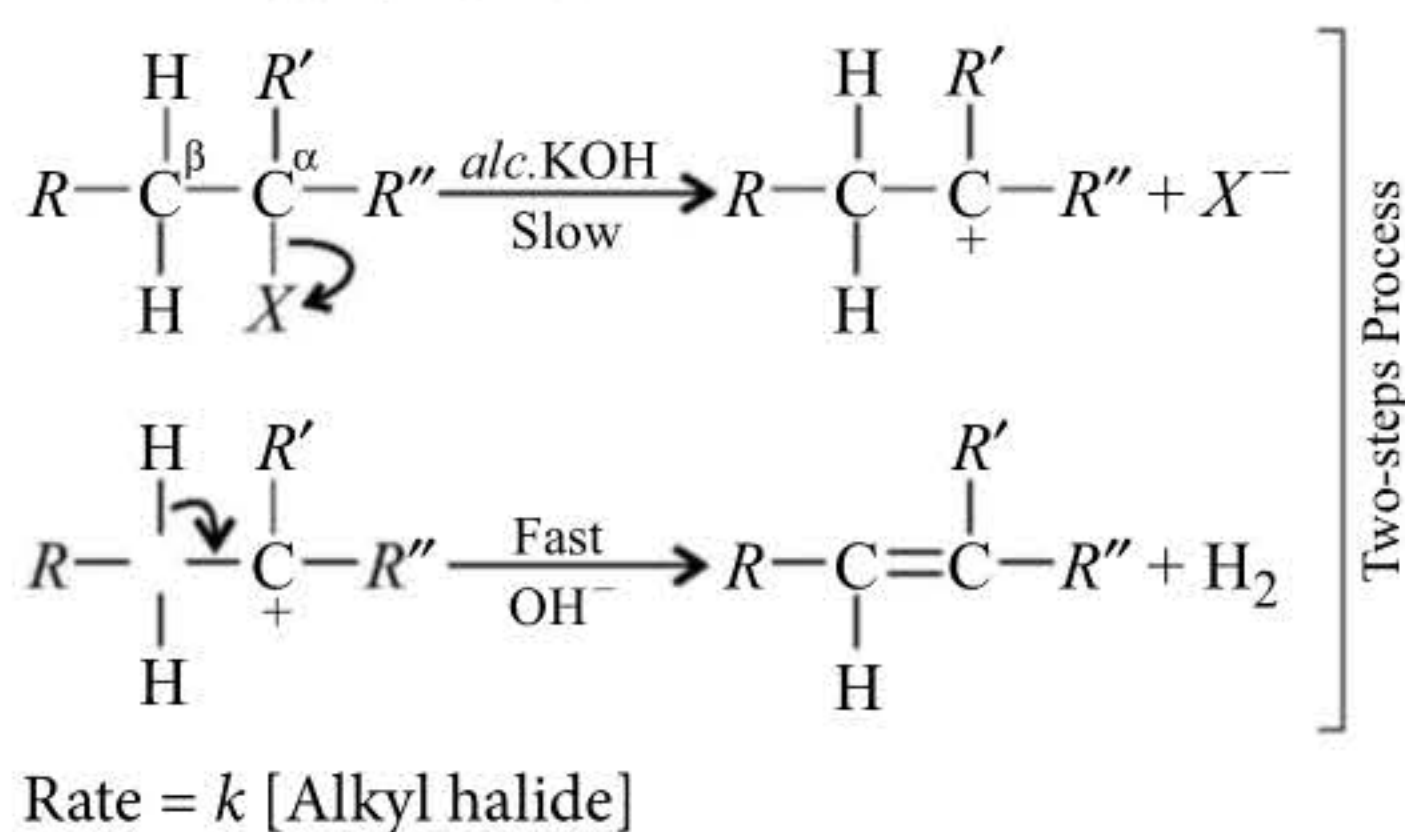
• By Hunsdiecker reaction :



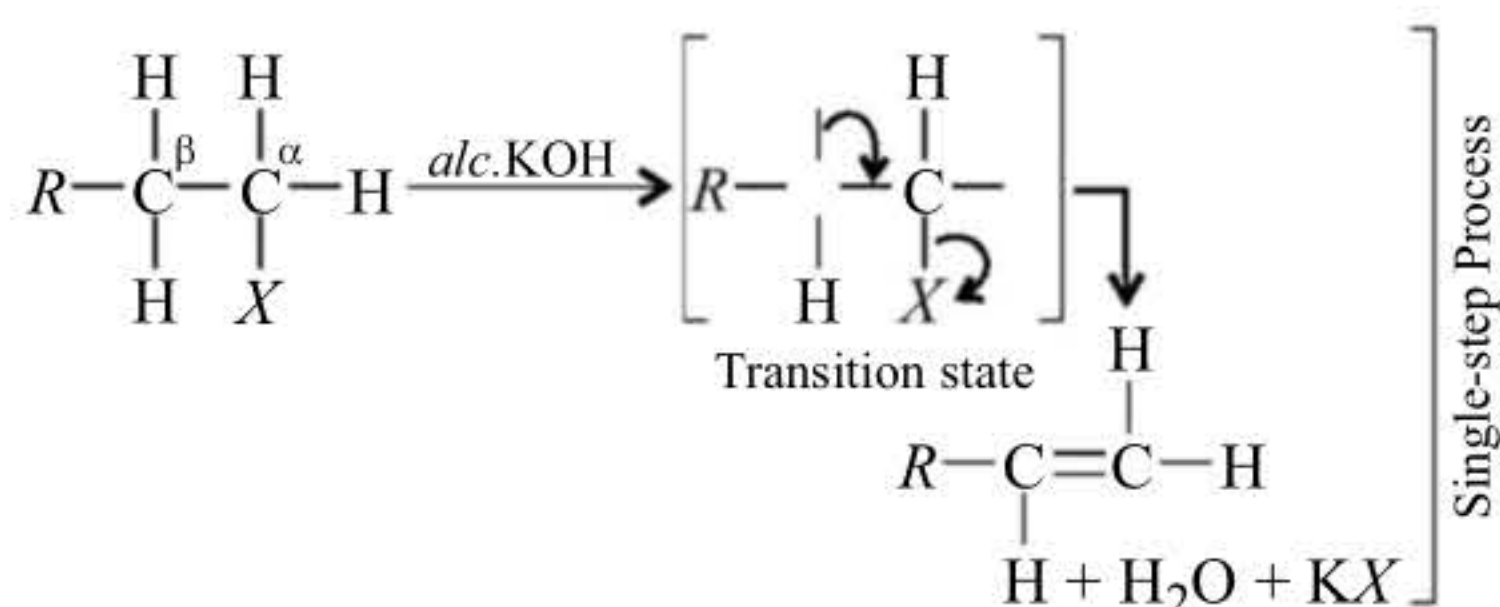
CHEMICAL PROPERTIES OF ALKYL HALIDES

- **Elimination reactions :** Alkyl halides undergo β -elimination reaction in the presence of potassium hydroxide in ethanol (high temperature) to yield alkene by E1 or E2 mechanism according to the structure of alkyl halides.

– **E1 mechanism :**



– **E2 mechanism :**



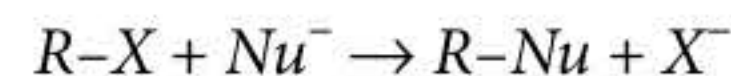
Rate = k [Alkyl halide] [base]

In E2, both departing groups H and X must be situated at anti position on adjacent carbon atoms.

NUCLEOPHILIC SUBSTITUTION REACTION

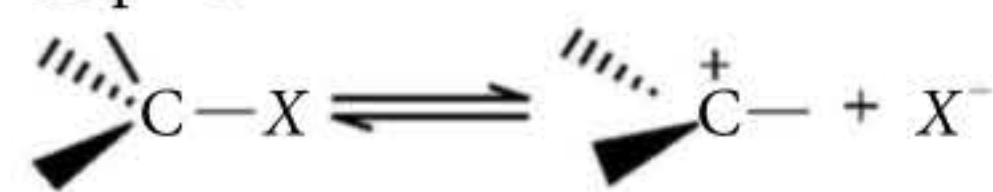
• **S_N1 Reaction**

- Substitution nucleophilic unimolecular reactions are abbreviated as S_N1. Consider a general reaction :



- The reaction follows first order kinetics. The rate of reaction is independent of the concentration of nucleophile.
- The S_N1 mechanism is a two step process, first one being the slow and the rate determining step.

Step - 1



Step - 2

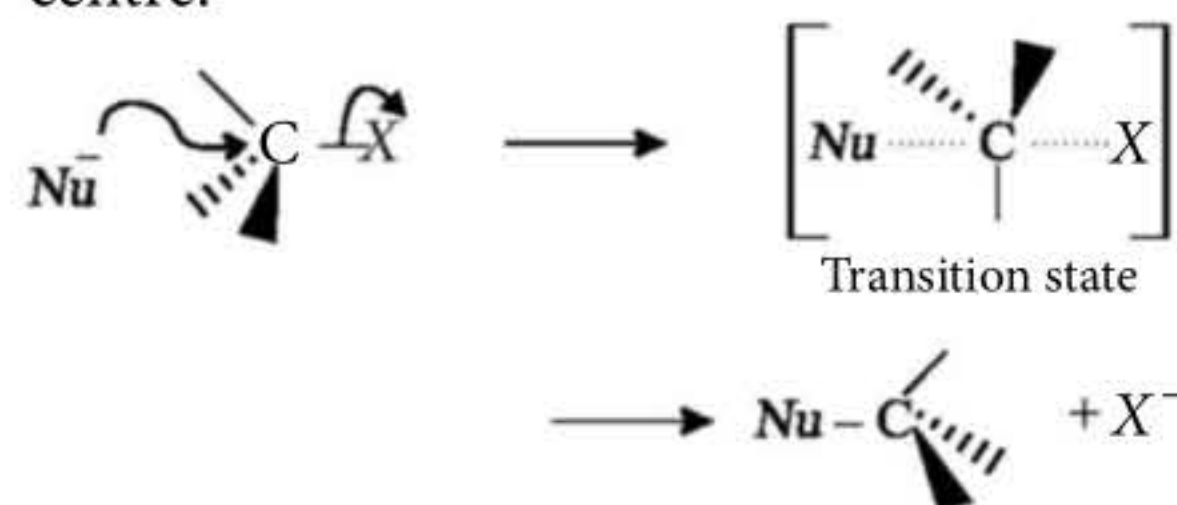


• **S_N2 Reaction**

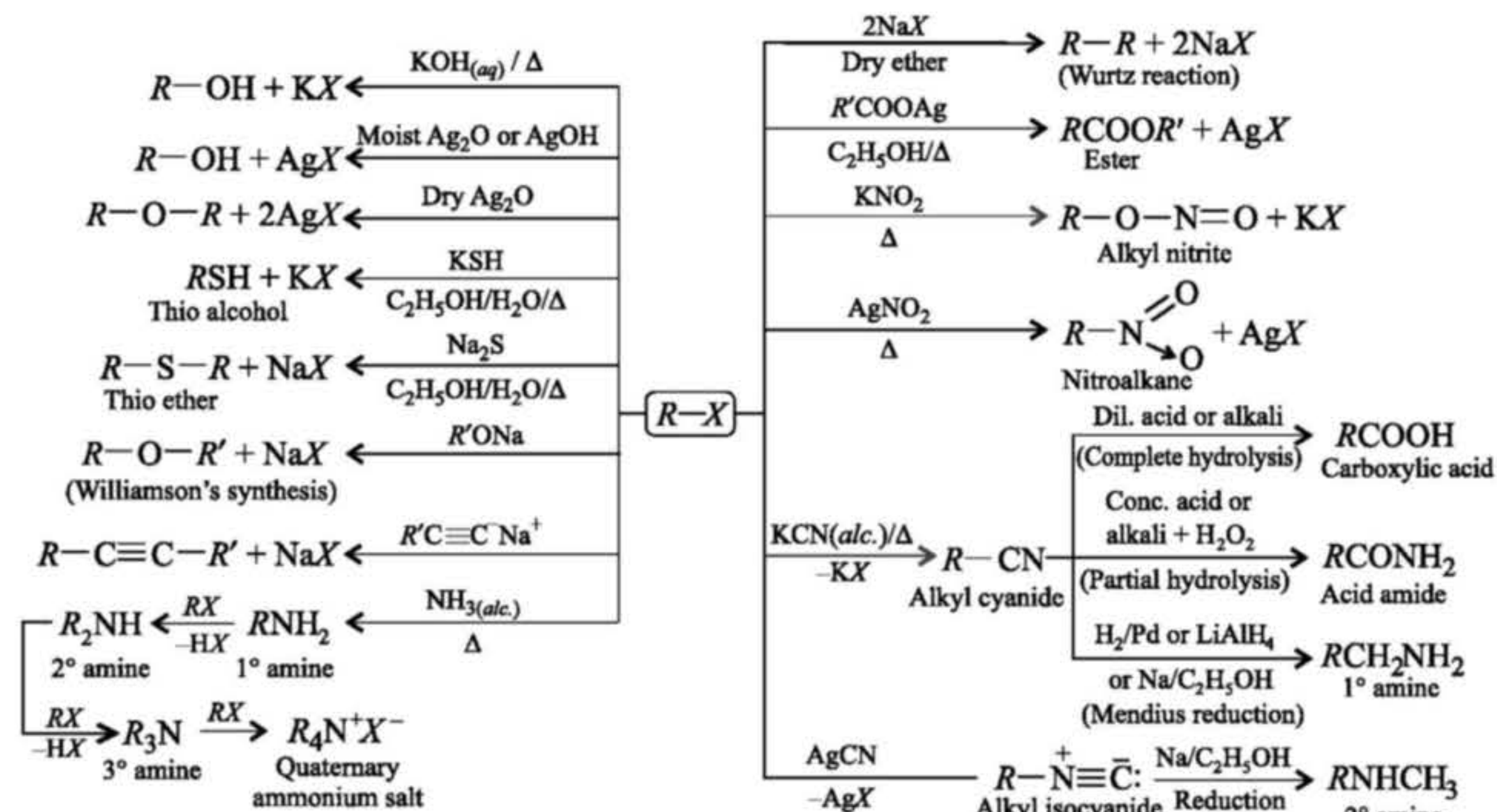
- S_N2 mechanism stands for substitution nucleophilic bimolecular. Consider a general reaction :



- The S_N2 mechanism is a single step process with no intermediate. Bond making and breaking take place simultaneously with the reaction centre.

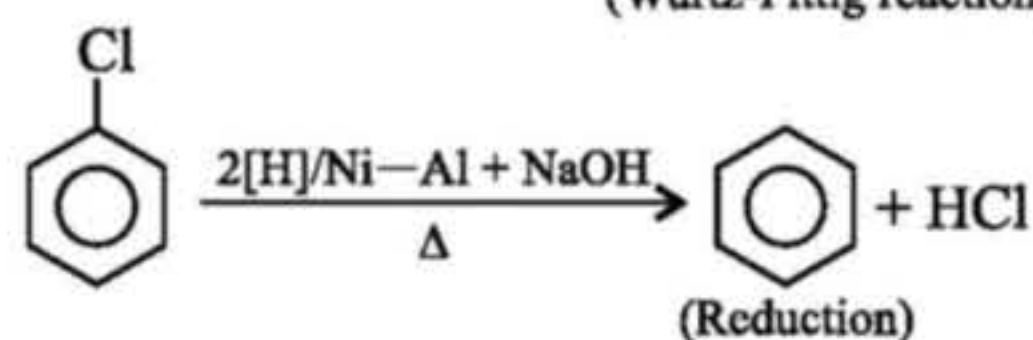
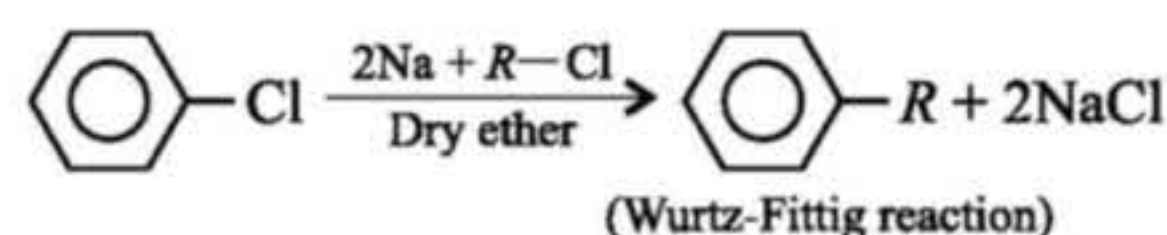
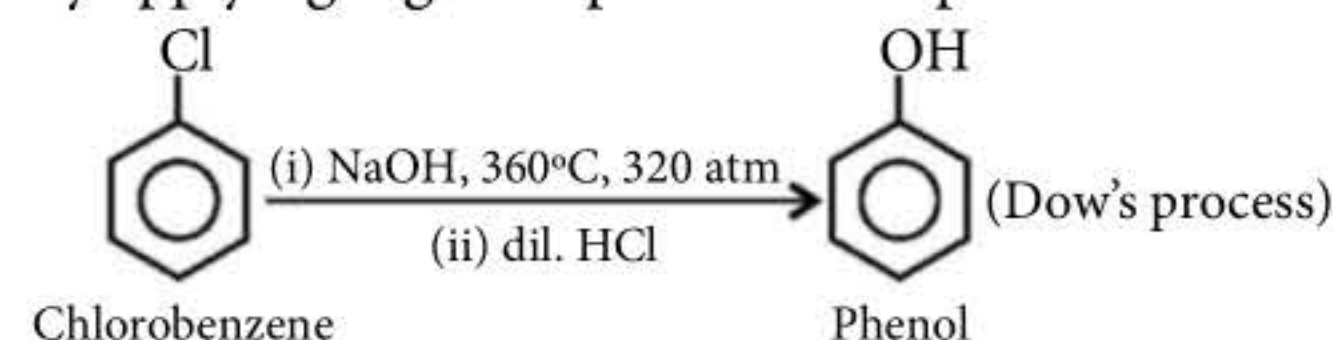


SOME IMPORTANT NUCLEOPHILIC SUBSTITUTION REACTIONS

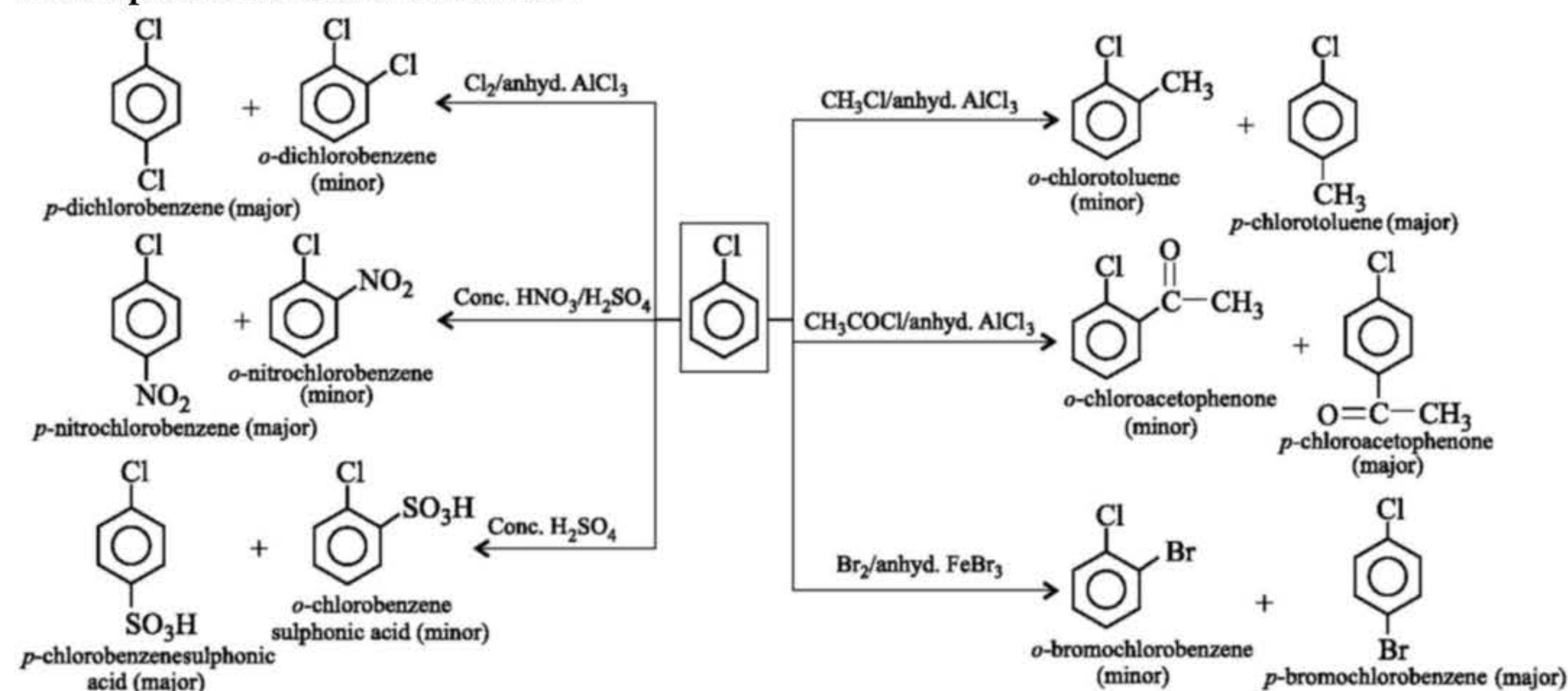


Chemical Properties of Aryl halides

- Nucleophilic substitution reactions :** Due to resonance effect, haloarenes acquire some double bond character between C-X bond, making them inert towards nucleophile but Cl-atom of chlorobenzene can be replaced by a nucleophile either (i) by placing electron withdrawing group at *ortho* and *para* positions or (ii) by using drastic conditions *i.e.*, by applying high temperature and pressure.



- Electrophilic substitution reactions :**



Alcohols, Phenols and Ethers

- The compounds obtained by replacing one hydrogen atom from aliphatic hydrocarbons by $-OH$ group are called alcohols whereas those obtained by replacing hydrogen of aromatic hydrocarbons by $-OH$ group are known as phenols. Compounds containing an oxygen atom bonded to two

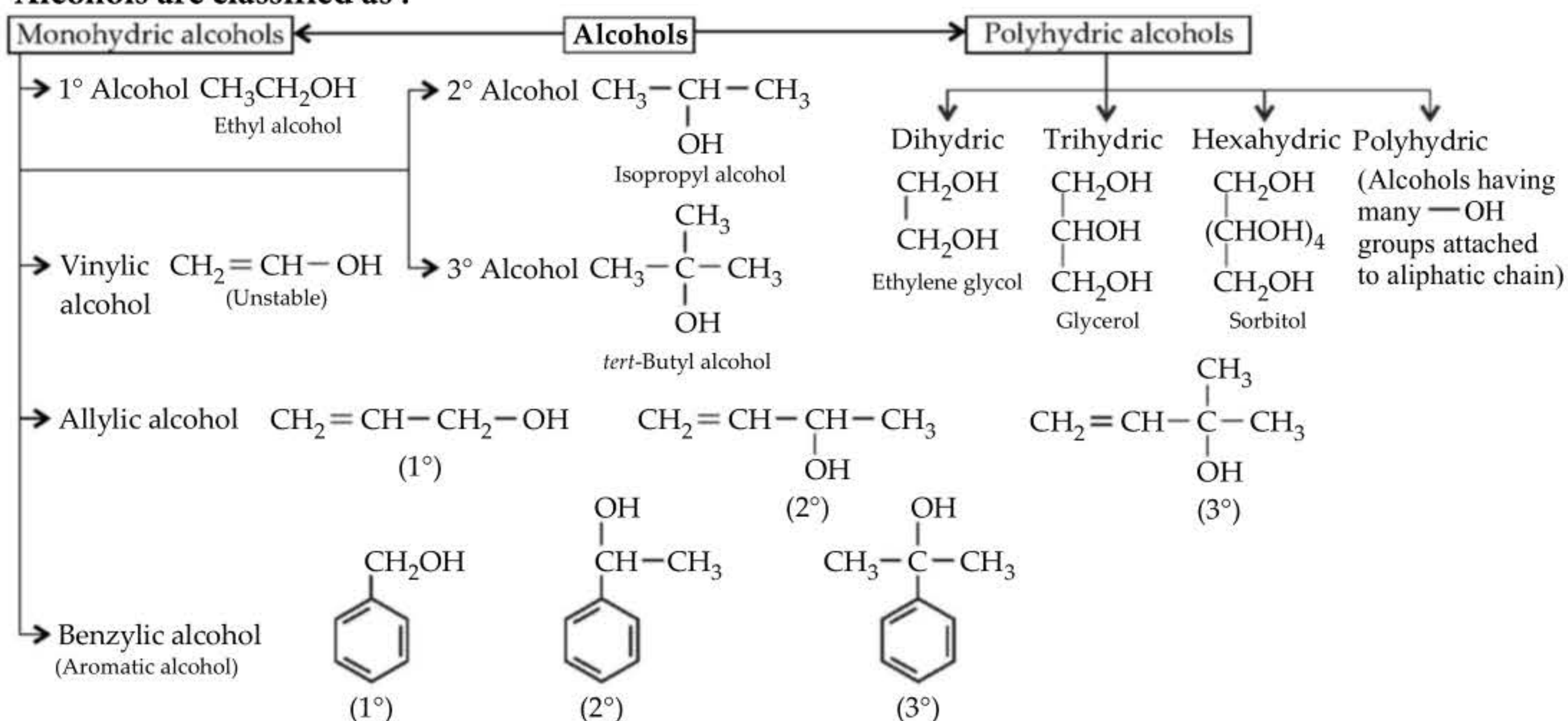
(same/different) alkyl/aryl groups are known as ethers.

General formula

- Alcohol : $C_nH_{2n+1}OH$ ($R-OH$)
- Phenol : C_6H_5OH ($Ar-OH$)
- Ethers : $C_nH_{2n+2}O$ ($R-O-R$ or $R-O-R'$); $n > 1$

CLASSIFICATION

- Alcohols are classified as :



- Ethers are classified as :

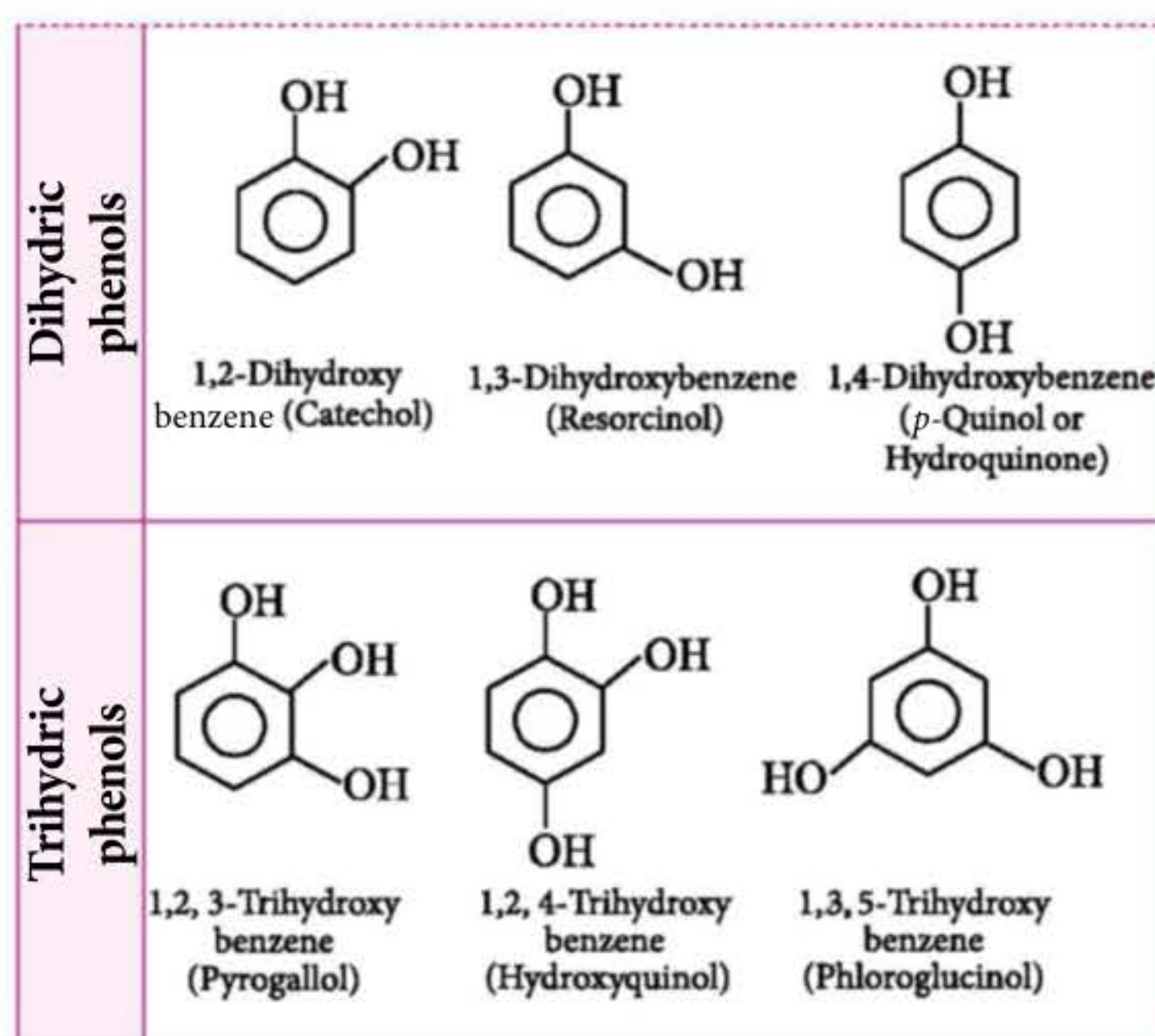
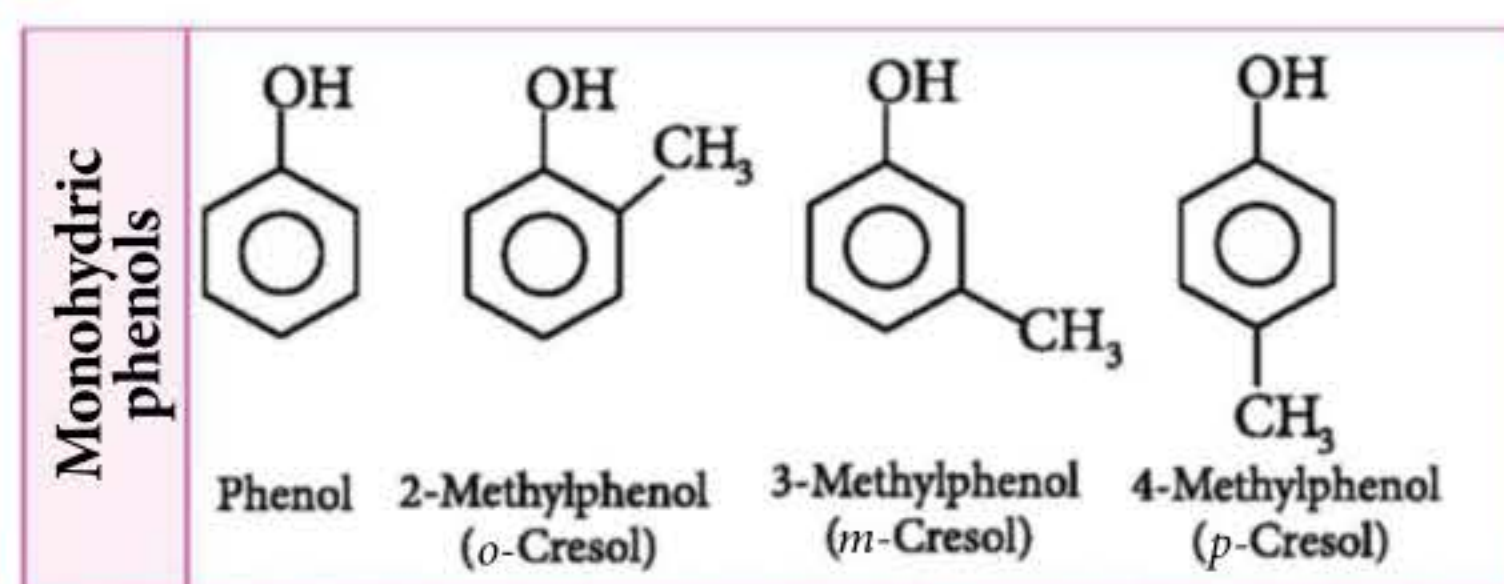
Aliphatic ethers :

e.g., CH_3-O-CH_3 , $CH_3-O-CH_2CH_3$
Dimethyl ether Ethyl methyl ether
(Symmetrical) (Unsymmetrical)

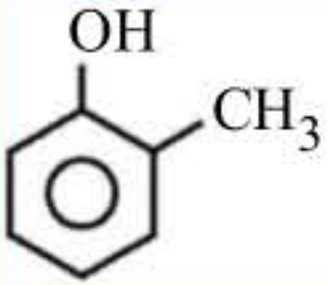
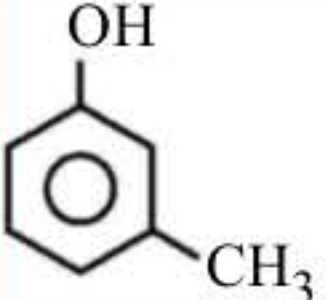
Aromatic ethers :

e.g., $C_6H_5-O-CH_3$, $C_6H_5-O-C_6H_5$
Methyl phenyl ether Diphenyl ether
(alkyl aryl ether) (diaryl ether)

- Phenols are classified as :

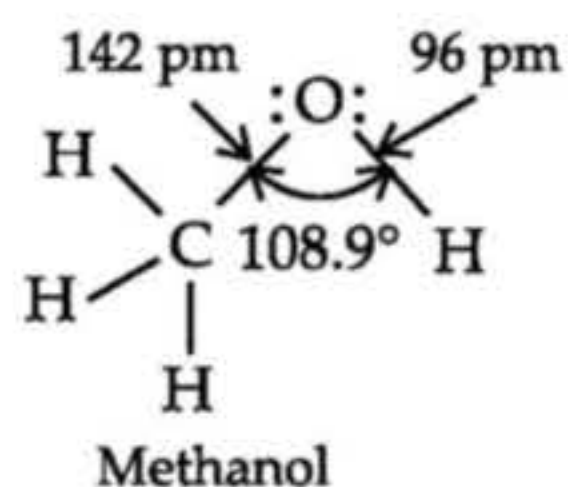


NOMENCLATURE

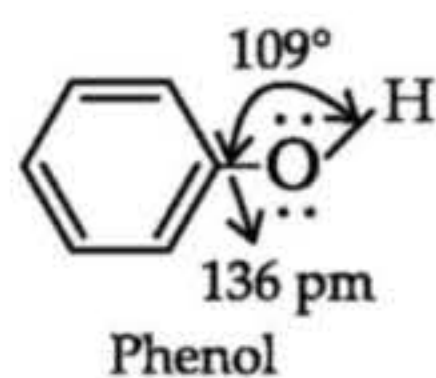
Class of compounds	Formula	General Name	IUPAC Name
Alcohols	CH ₃ CH ₂ CH ₂ OH	<i>n</i> -Propyl alcohol	Propan-1-ol
	CH ₃ CH(OH)CH ₃	<i>iso</i> -Propyl alcohol	Propan-2-ol
Phenols		<i>o</i> -Cresol	<i>o</i> -Methylphenol
		<i>m</i> -Cresol	<i>m</i> -Methylphenol
Ethers	CH ₃ OC ₂ H ₅	Ethylmethyl ether	Methoxyethane
	C ₆ H ₅ OCH ₃	Anisole	Methoxybenzene

STRUCTURES

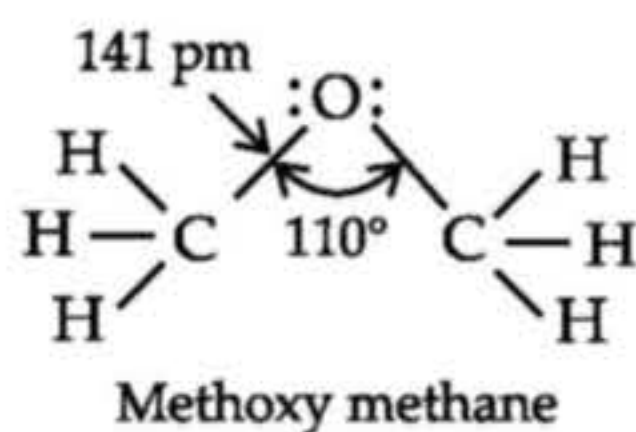
- In alcohols, the oxygen of the -OH group is attached to carbon by a sigma (σ) bond which is formed by the overlap of a sp^3 -hybridised orbital of carbon with a sp^3 -hybridised orbital of oxygen.



- In phenols, the -OH group is attached to sp^2 hybridised carbon of an aromatic ring.



- Ethers have a bent structure and are dipolar in nature. The oxygen atom in ethers is sp^3 -hybridized.



- The C-O-H bond angle in alcohols is slightly less than tetrahedral angle $109^\circ 28'$ due to greater repulsion between lone pair of electrons of oxygen.

ALCOHOLS

Methods of Preparation

Hydration of alkenes	$RCH=CH_2 \xrightarrow[\text{(Hydration)}]{H_2O/H^+}$	A
Hydroboration oxidation	$RCH=CH_2 \xrightarrow{B_2H_6/H_2O_2, OH^-}$	L
Oxymercuration reduction	$RCH=CH_2 \xrightarrow[\text{(ii) NaBH}_4]{\text{(i) Hg(OAc)}_2, H_2O}$	C
From Grignard reagent	$>C=O \xrightarrow[\text{(ii) H}^+/H_2O]{\text{(i) RMgX}}$	O
From aliphatic primary amines	$RNH_2 + HONO \rightarrow$	H
From haloalkanes	$R-X + KOH_{(aq)} \rightarrow$	O
From carbonyl compounds	$RCHO \xrightarrow[\text{or LiAlH}_4]{H_2/Ni}$	
	$R_2C=O \xrightarrow{H_2/Ni}$	L
	$RCOOH \xrightarrow{LiAlH_4}$	
	$RCOOR' \xrightarrow{LiAlH_4}$	
	$RCOOR' \xrightarrow{Na/C_2H_5OH}$	S

Chemical Properties

A	$\xrightarrow{\text{Na}} \text{RONa} + \text{H}_2$
	$\xrightarrow{\text{R}'\text{COOH}} \text{R}'\text{COOR} + \text{H}_2\text{O}$
L	$\xrightarrow{\text{RCOCl}} \text{RCOOR} + \text{HCl}$
	$\xrightarrow{(\text{RCO})_2\text{O}} \text{RCOOR} + \text{RCOOH}$
C	$\xrightarrow{\text{R}'\text{MgX}} \text{R}'\text{H} + \text{Mg}(\text{OR})\text{X}$
	$\xrightarrow{\text{HX}} \text{RX} + \text{H}_2\text{O}$
O	$\xrightarrow{\text{PX}_3} \text{RX} + \text{H}_2\text{O}$
	$\xrightarrow{\text{PCl}_5} \text{RCl} + \text{POCl}_3 + \text{HCl}$
H	$\xrightarrow{\text{SOCl}_2} \text{RCl} + \text{SO}_2 + \text{HCl}$
	$\xrightarrow[\text{443 K}]{\text{Conc. H}_2\text{SO}_4} \text{RCH}=\text{CH}_2 + \text{H}_2\text{O}$
O	$\xrightarrow[\text{413 K}]{\text{Conc. H}_2\text{SO}_4} \text{ROR} + \text{H}_2\text{O}$
	$\xrightarrow[\text{or KMnO}_4/\text{OH}^-]{\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+} \text{R}-\text{COOH}$
L	$\xrightarrow[\text{-H}_2]{\text{Cu}/\text{573 K}} \text{RCHO or RCOR or alkene}$ (from 1° alcohol) (from 2° alcohol) (from 3° alcohol)
S	$\xrightarrow[\text{or CrO}_3 \cdot \text{C}_5\text{H}_5\text{N} \cdot \text{HCl}]{\text{PCC}} \text{RCHO}$

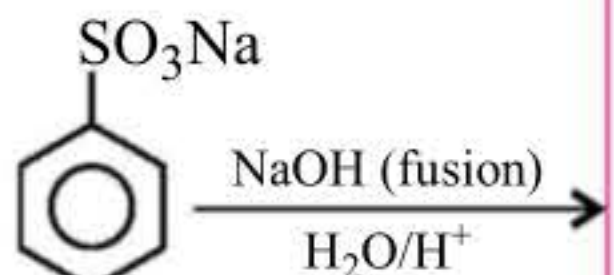

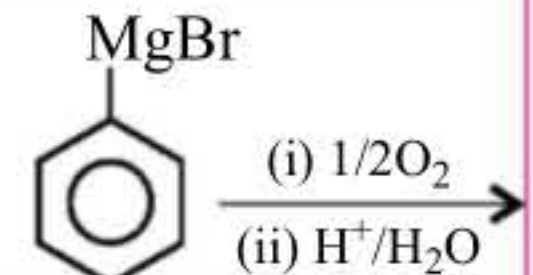
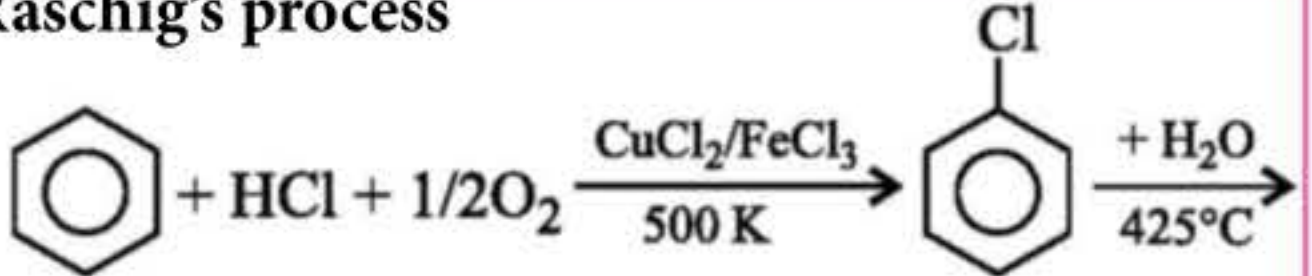
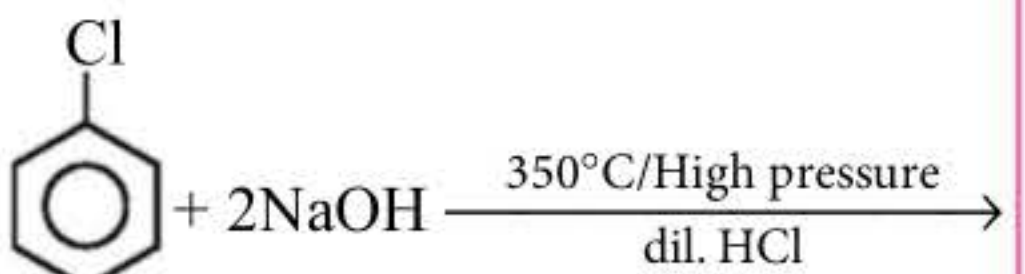
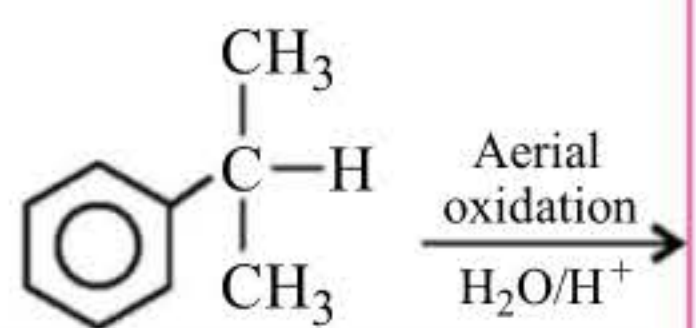
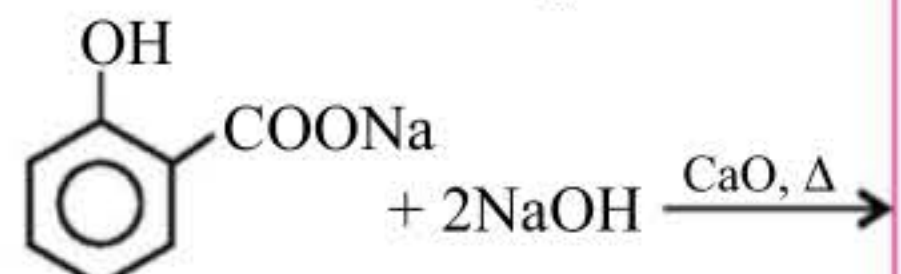
PEEP INTO PREVIOUS YEARS

7. When vapours of a secondary alcohol is passed over heated copper at 573 K, the product formed is
(a) a carboxylic acid (b) an aldehyde
(c) a ketone (d) an alkene.
(Odisha NEET 2019)
8. The number of alkene(s) which can produce 2-butanol by the successive treatment of (i) B_2H_6 in tetrahydrofuran solvent and (ii) alkaline H_2O_2 solution is
(a) 1 (b) 2
(c) 3 (d) 4 (WB JEE 2018)
9. Which of the following reaction(s) can be used for the preparation of alkyl halides?
(I) $\text{CH}_3\text{CH}_2\text{OH} + \text{HCl} \xrightarrow{\text{anh. ZnCl}_2}$
(II) $\text{CH}_3\text{CH}_2\text{OH} + \text{HCl} \longrightarrow$
(III) $(\text{CH}_3)_3\text{COH} + \text{HCl} \longrightarrow$
(IV) $(\text{CH}_3)_2\text{CHOH} + \text{HCl} \xrightarrow{\text{anh. ZnCl}_2}$

- (a) (I) and (II) only (b) (IV) only
(c) (III) and (IV) only
(d) (I), (III) and (IV) only (AIPMT 2017)

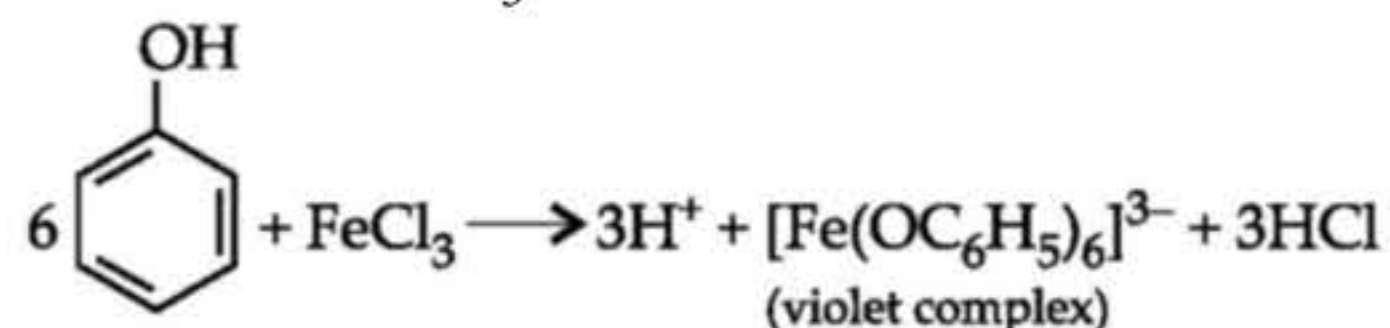
PHENOLS

Methods of Preparation

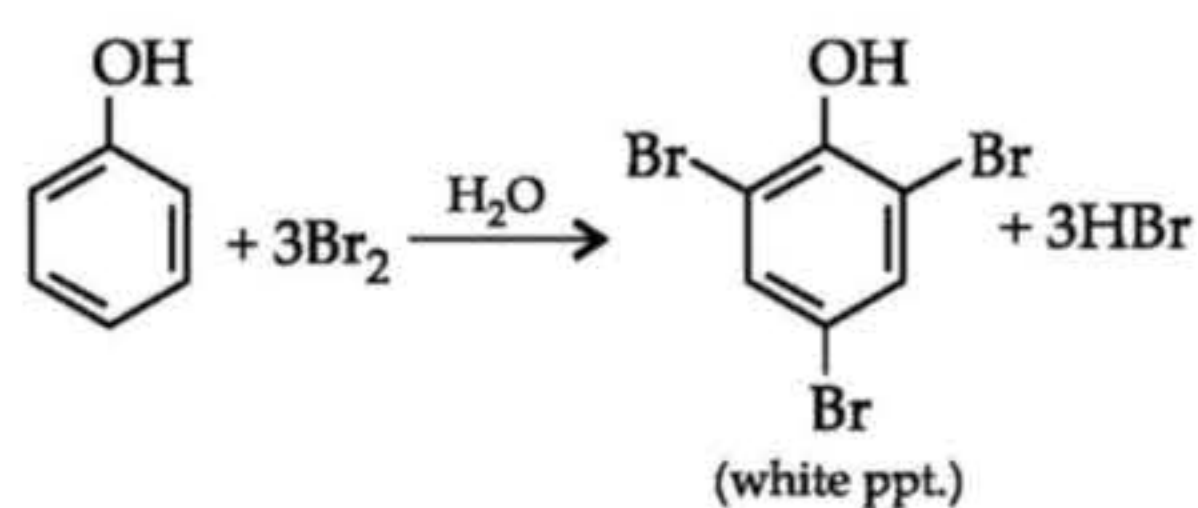
From benzene sulphonic acid		P
From diazonium salts		H
From Grignard reagent		E
Raschig's process		N
Dow's process		O
From cumene		L
By decarboxylation of sodium salicylate		S

Test for Phenols

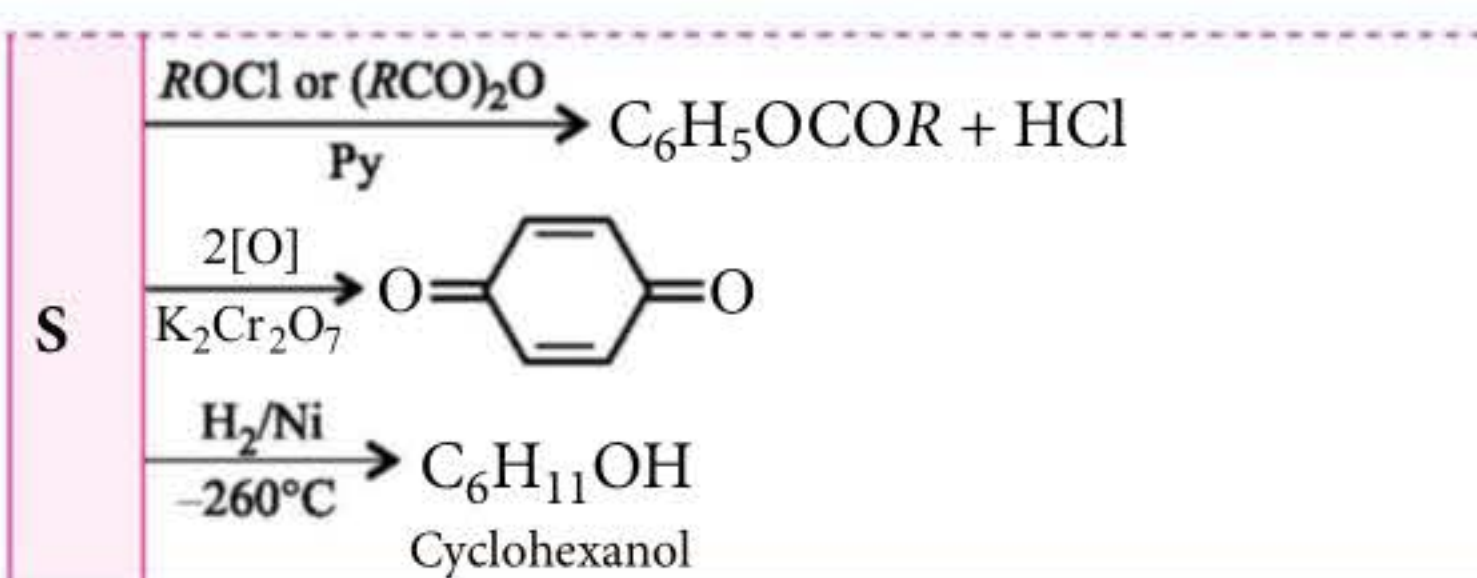
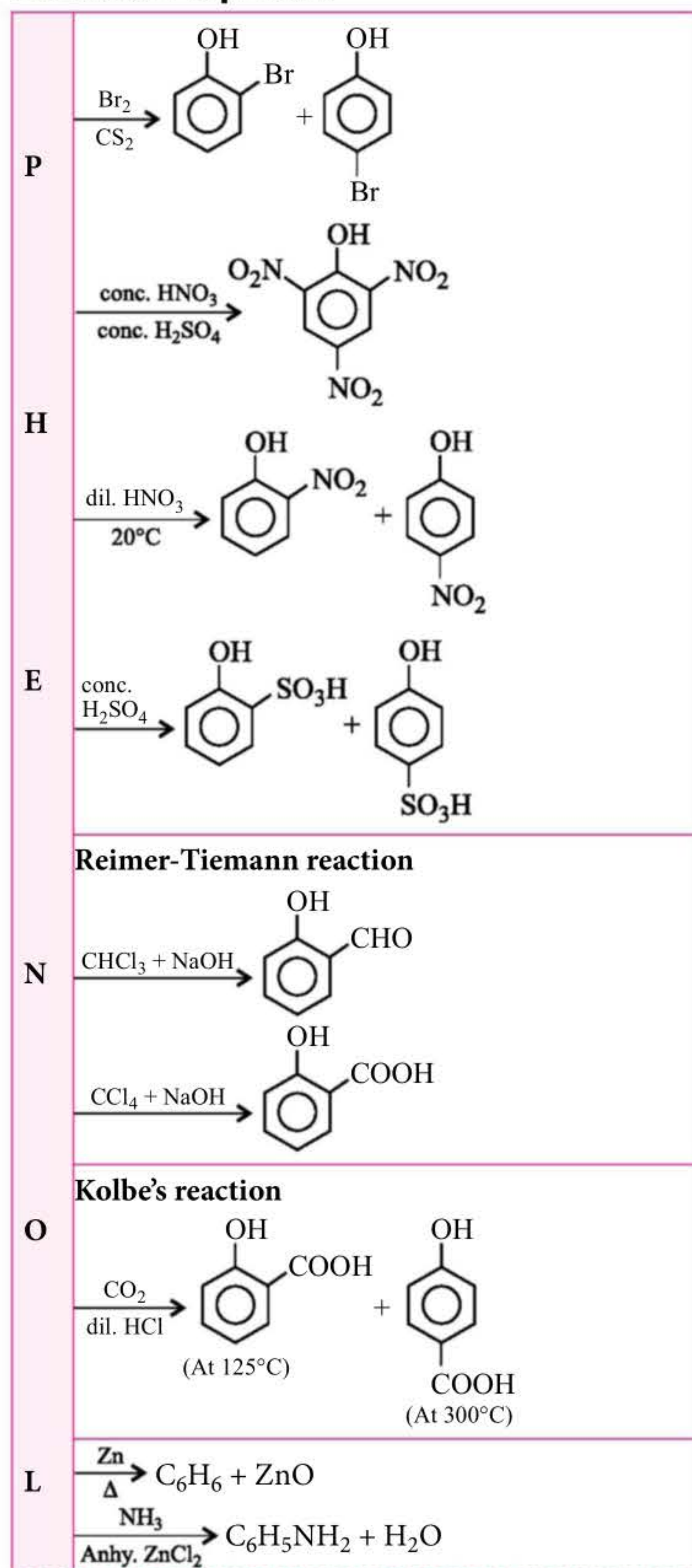
- Ferric chloride test** : Phenol gives violet colour with neutral FeCl_3 solution.



- Bromine water test** : Phenol gives white ppt. with Br_2 -water due to the formation of 2, 4, 6-tribromophenol.

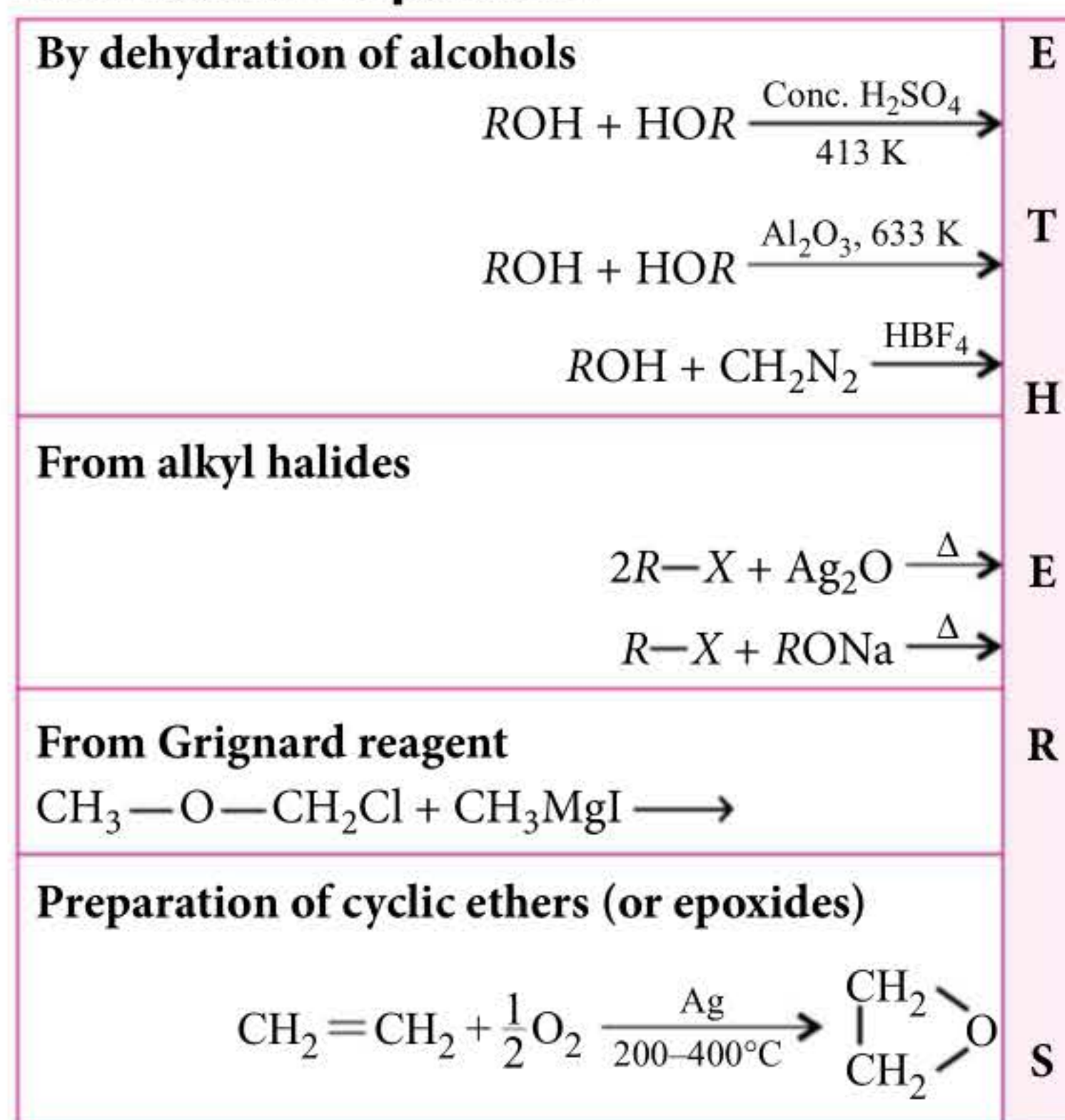


Chemical Properties

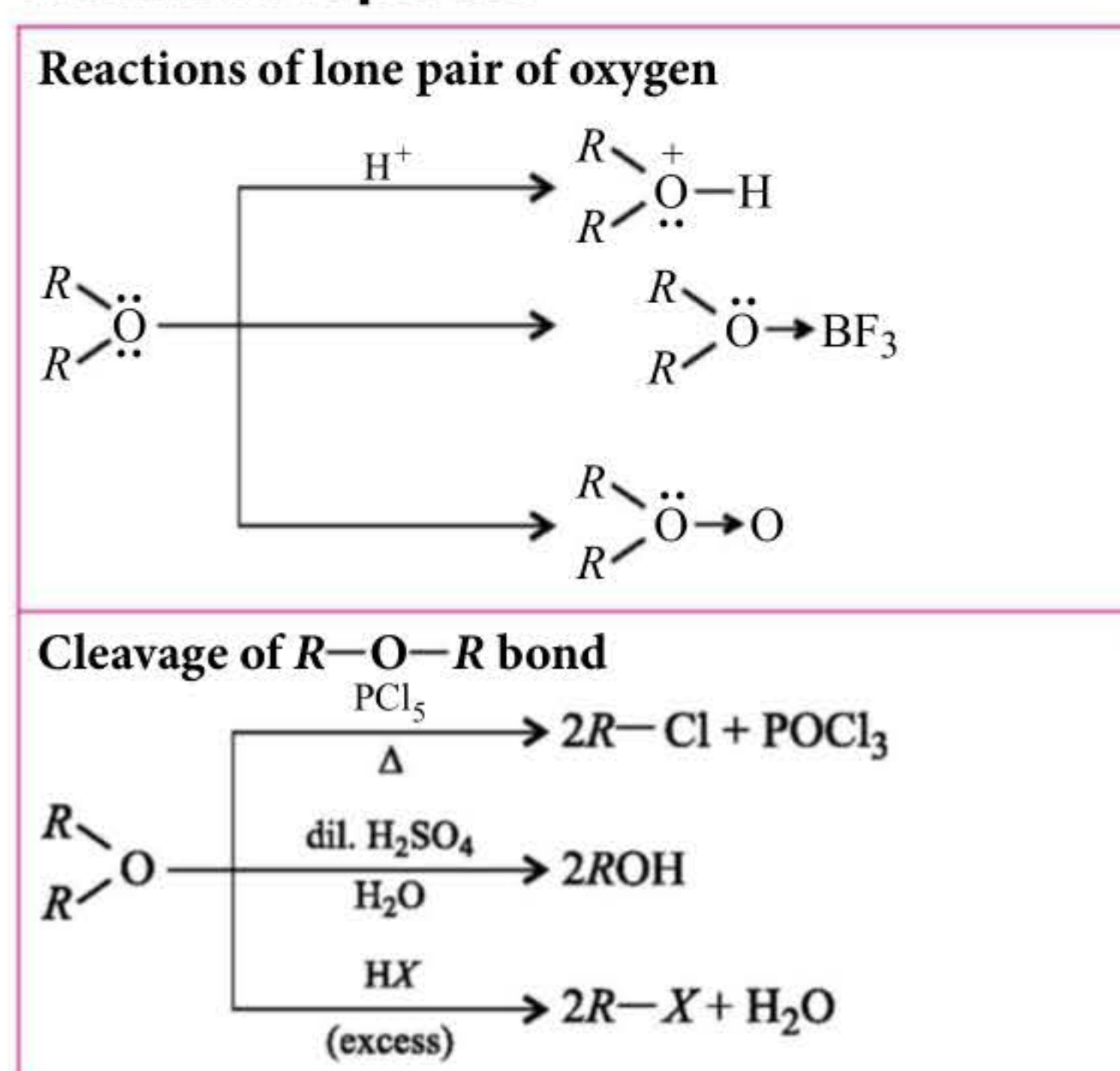


ETHERS

Methods of Preparation

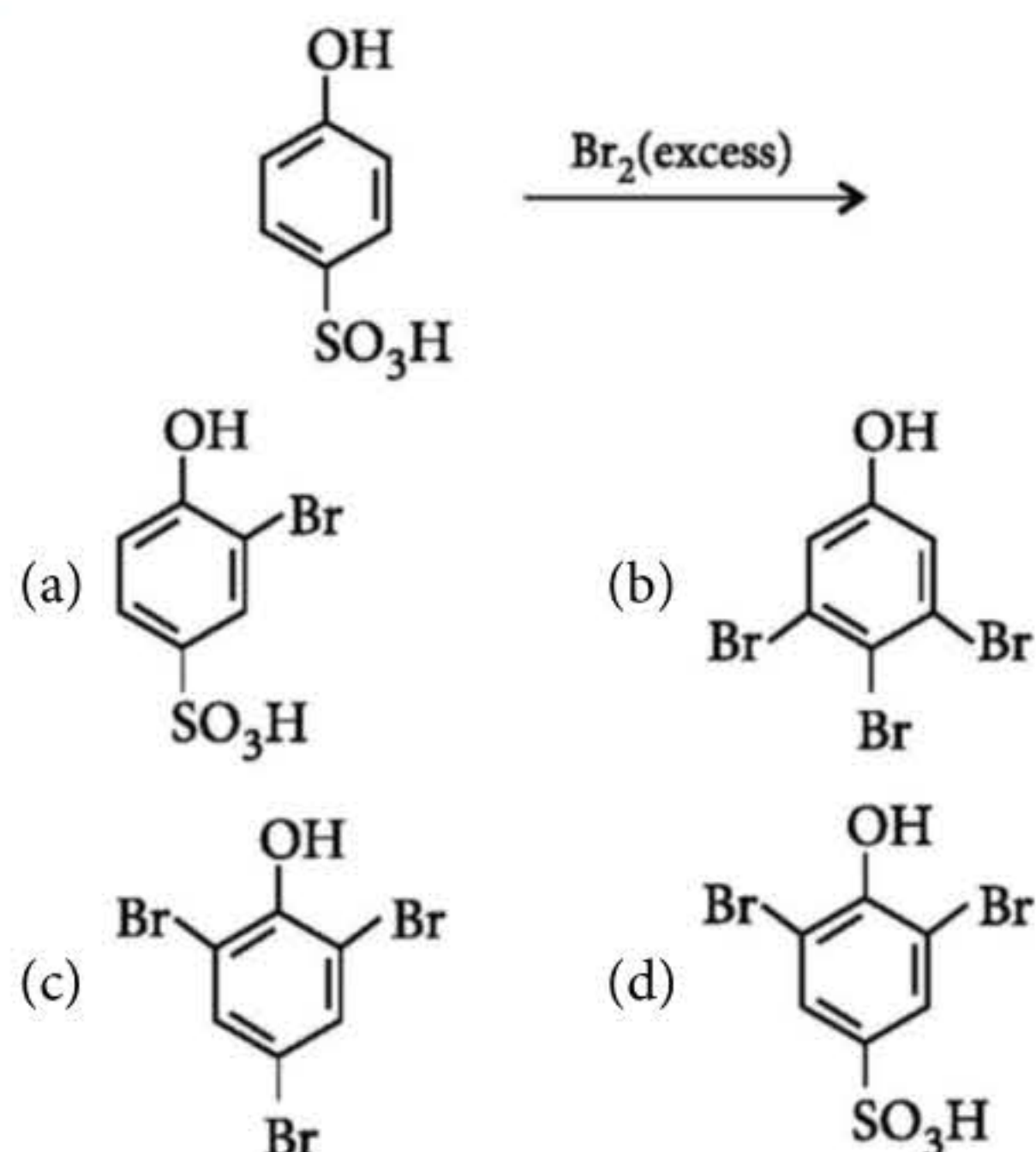


Chemical Properties



✓ **PEEP INTO PREVIOUS YEARS**

10. The major product of the following reaction is



(JEE Main 2019)

11. The heating of phenyl methyl ether with HI produces

- iodobenzene
- phenol
- benzene
- ethyl chloride.

(NEET 2017)

POINTS FOR EXTRA SCORING

Distinction test for 1°, 2° and 3° Alcohols

- **Lucas test :** Alcohol is treated with an equimolar mixture of concentrated hydrochloric acid and anhydrous ZnCl_2 (Lucas reagent).
 - If cloudiness appears immediately, the alcohol is tertiary.
 - If cloudiness appears within five minutes, the alcohol is secondary.
 - If cloudiness appears only upon heating, the alcohol is primary.

- **Victor Meyer's test :** Alcohol $\xrightarrow{\text{Red P} + \text{I}_2}$ RI $\xrightarrow{\text{AgNO}_2}$ Nitroalkane $\xrightarrow{\text{NaNO}_2 + \text{dil. H}_2\text{SO}_4}$ Solution made alkaline.
 - If blood red colour appears, alcohol is primary.
 - If blue colour appears, alcohol is secondary.
 - If colourless, alcohol is tertiary.

Distinction between Alcohols and Phenols

Test	Alcohol	Phenol
Litmus test	No effect	Turns blue litmus red
Reaction with FeCl_3	No reaction	Blue, violet or green colouration
Coupling reaction	No reaction	Forms yellow or orange coloured azo dyes.
Bromine water test	No reaction	A white ppt. of 2,4,6-tribromo phenol.

- Order of ease of cleavage of O—H bond and thus order of reactivity of alcohols is as follows : $\text{CH}_3\text{OH} > \text{Primary} > \text{Secondary} > \text{Tertiary}$
- Order of reactivity of different alcohols towards Fisher – Speier esterification is : $\text{CH}_3\text{OH} > \text{RCH}_2\text{OH} > \text{R}_2\text{CHOH} > \text{R}_3\text{COH}$
- Relative acidities of H_2O , ROH , $\text{CH}\equiv\text{CH}$, NH_3 and RH will be in order : $\text{H}_2\text{O} > \text{ROH} > \text{CH}\equiv\text{CH} > \text{NH}_3 > \text{RH}$
- Phenols are stronger acids than water and alcohols but weaker than carboxylic acids.
- Ethers (as Lewis bases) can form coordination complexes known as etherates with Lewis acids like BF_3 , AlCl_3 , RMgX . That is why Grignard reagents are usually prepared in ethers.
- In presence of atmospheric oxygen, ethers oxidise slowly to produce hydroperoxides and dialkylperoxides, both of which are explosives (auto-oxidation). Formation of peroxide can be prevented by adding small amount of Cu_2O to ether.

Answer Key For Peep Into Previous Years

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|----|-----|----|-----|----|-----|-----|-----|-----|-----|----|-------|
| 1. | (a) | 2. | (a) | 3. | (b) | 4. | (a) | 5. | (b) | 6. | (b,d) |
| 7. | (c) | 8. | (b) | 9. | (d) | 10. | (c) | 11. | (b) | | |