

B.Sc. Physical Sciences (Chemistry) I Year

Chemistry- Chemical Energetics, Equilibria and Functional Organic Chemistry

Section B Organic chemistry

Date: 23/04/2020

Unit 6

Alcohols, Phenols, Ether, aldehydes and Ketones

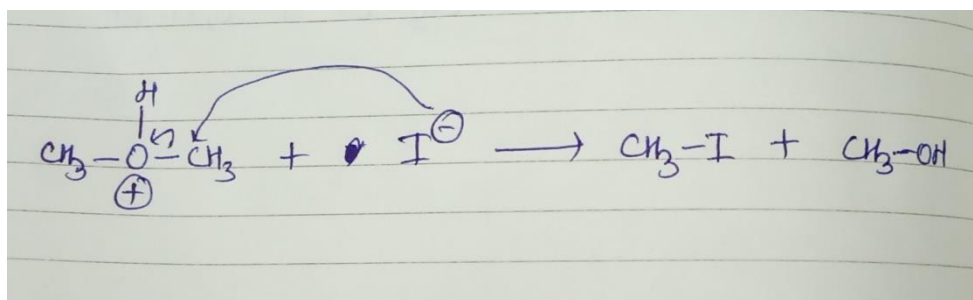
Phenols

Electrophilic substitution reactions of Phenols:

4) Reimer-Tiemann reaction: When phenol is treated with chloroform and aqueous NaOH followed by acidification then formylation occurs that is an aldehyde group ortho to -OH group in the phenol molecule is introduced.

This is called Reimer-Tiemann reaction.

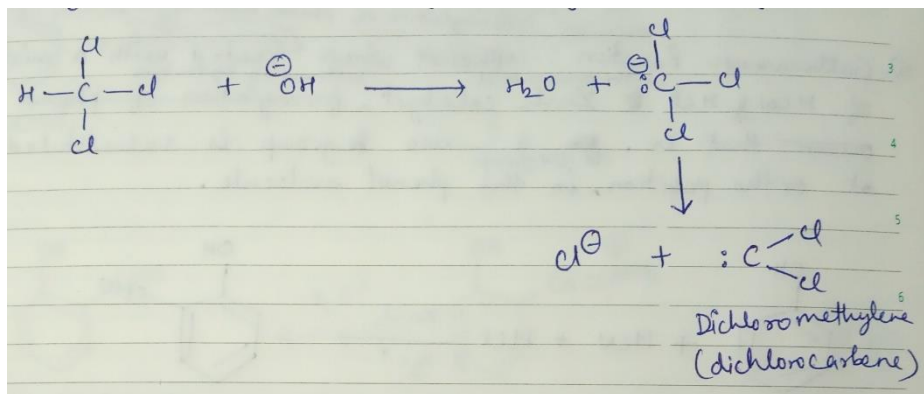
For example:



Mechanism:

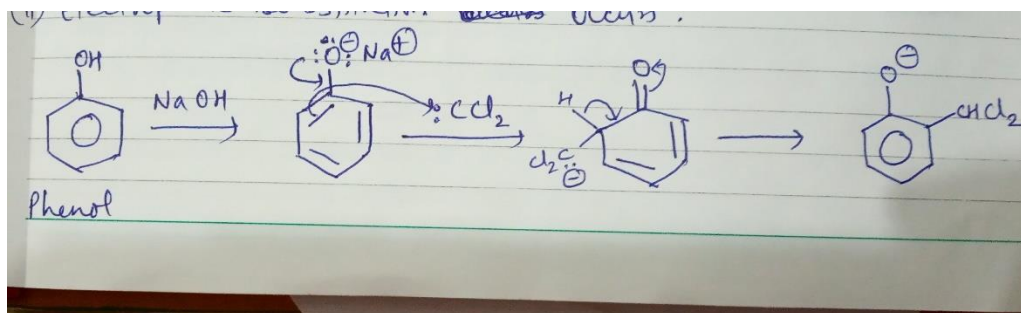
It takes place in the following steps:

(i) Firstly, dichlorocarbene is formed.

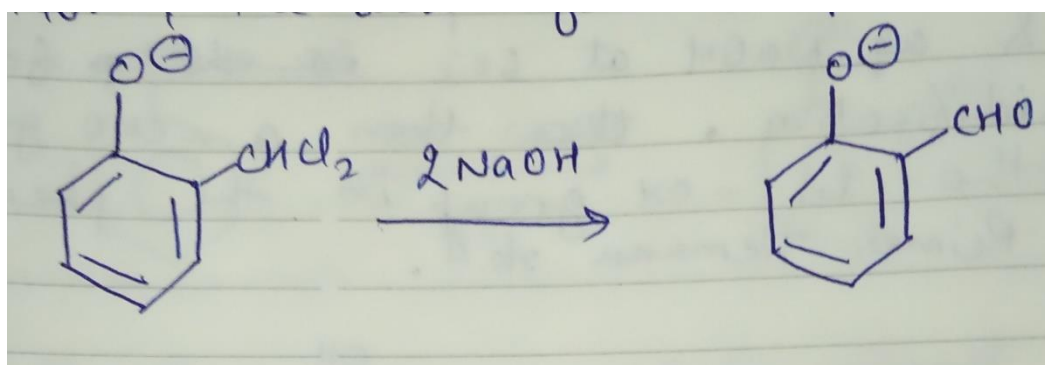


(ii) Then electrophilic substitution takes place.

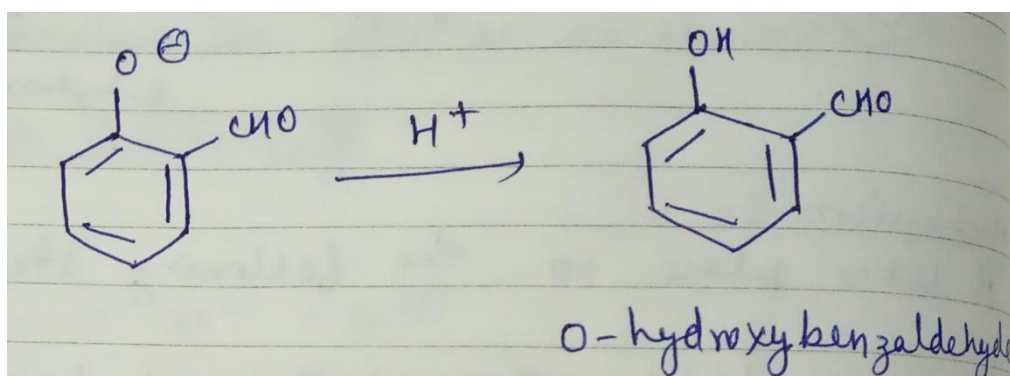
References: Organic Chemistry, R.T. Morrison, R.N. Boyd and S.K. Bhattacharjee, Pearson, 7th Edition and advance Organic Chemistry, Bahl and Bahl, S.Chand & Company Ltd.



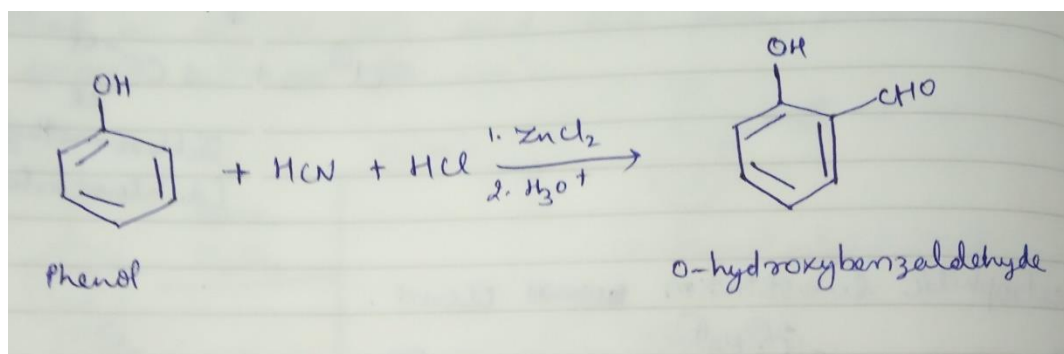
(iii) Now, the above formed compound is hydrolysed by NaOH.



(iv) Acidification gives the final product.

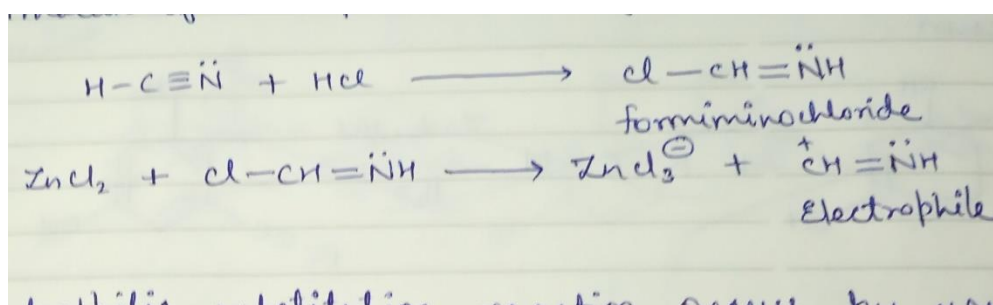


5) Gattermann reaction: In this reaction formylation of phenol occurs by treating it with a mixture of HCN and HCl in the presence of $ZnCl_2$ catalyst followed by hydrolysis. The -CHO group is substituted ortho to the -OH group in the phenol molecule.

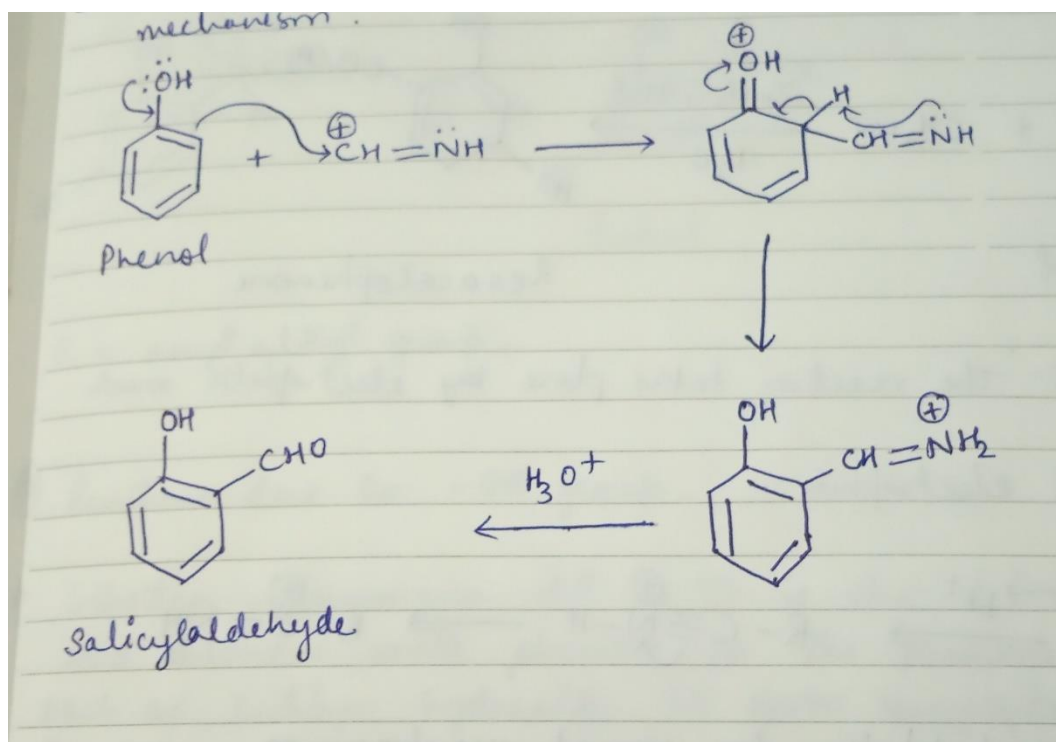


Mechanism:

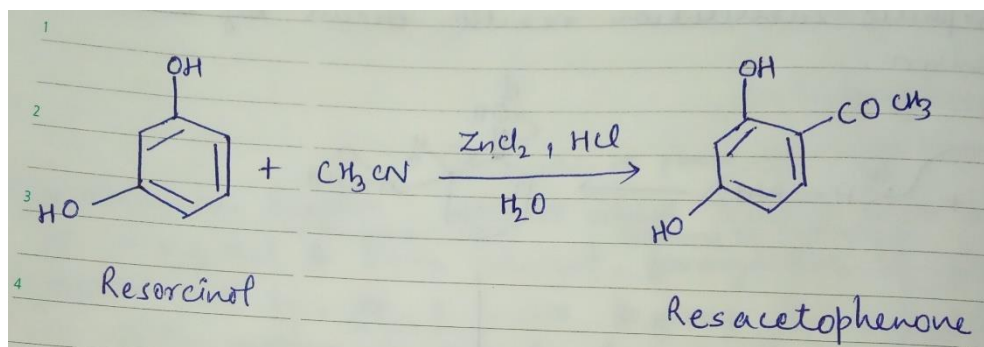
Step 1: Formation of electrophile.



Step 2: Electrophilic substitution reaction occurs by usual mechanism.

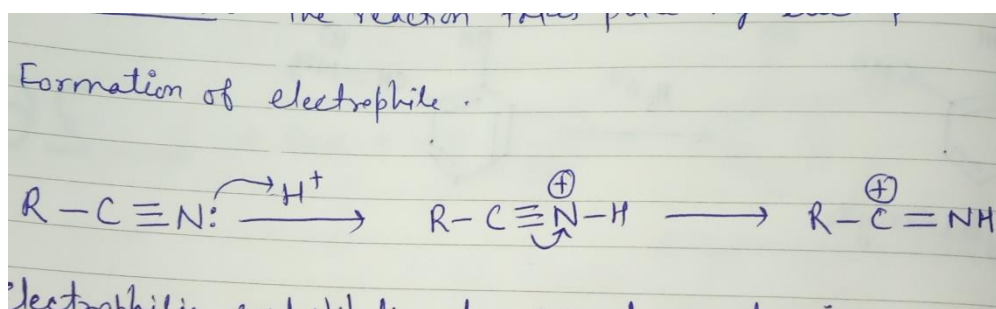


6) Houben – Hoesch reaction: When meta dihydric phenols are treated with alkyl cyanide in the presence of $ZnCl_2$ catalyst and HCl , then acylation occurs.

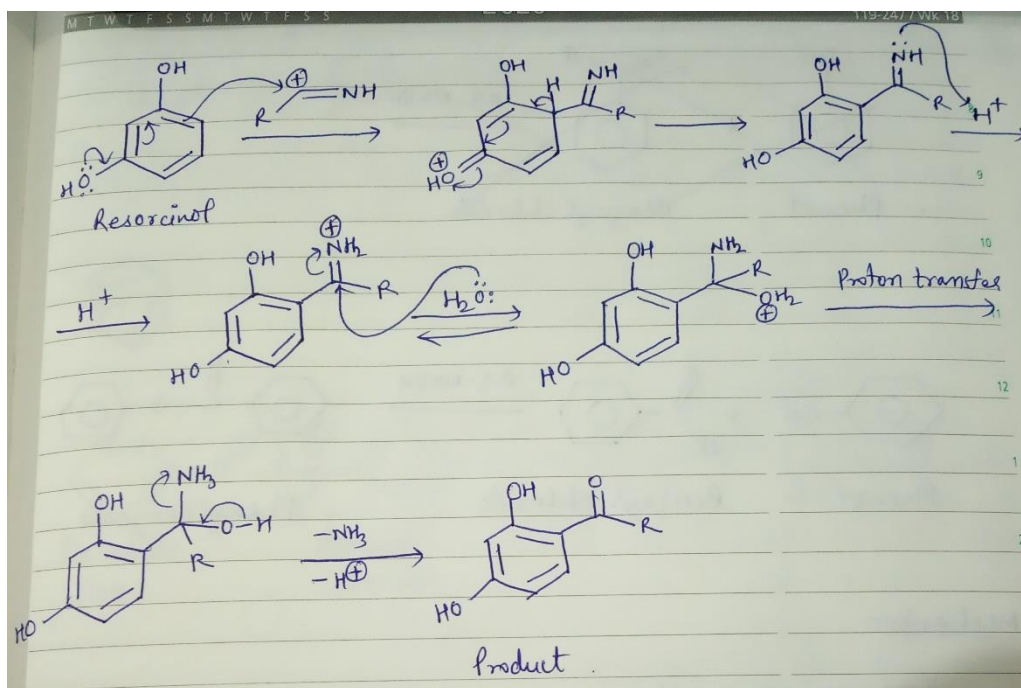


Mechanism:

(i) Formation of electrophile.



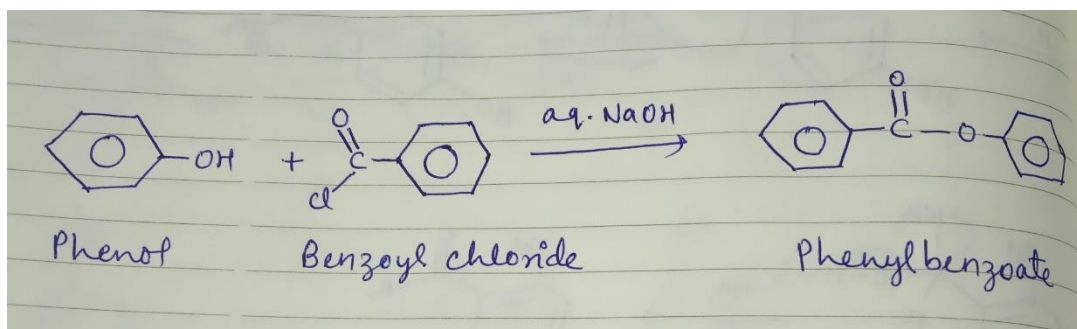
(ii) Electrophilic substitution by usual mechanism.



R = any alkyl group

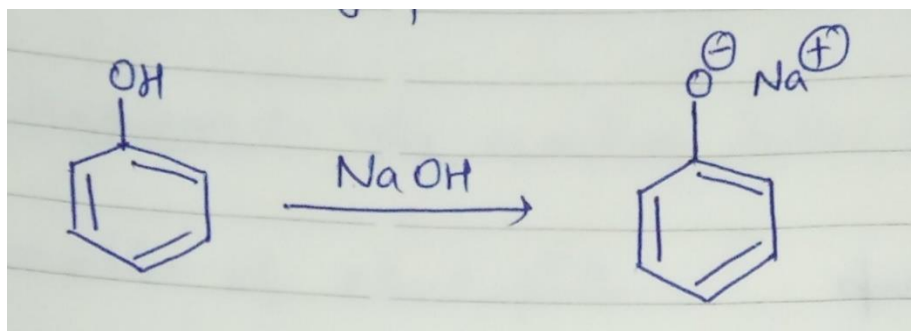
Reaction due to –OH group

Schotten – Baumann reaction: In this reaction an aromatic acid chloride reacts with phenols in the presence of a base such as NaOH to form phenyl benzoate.

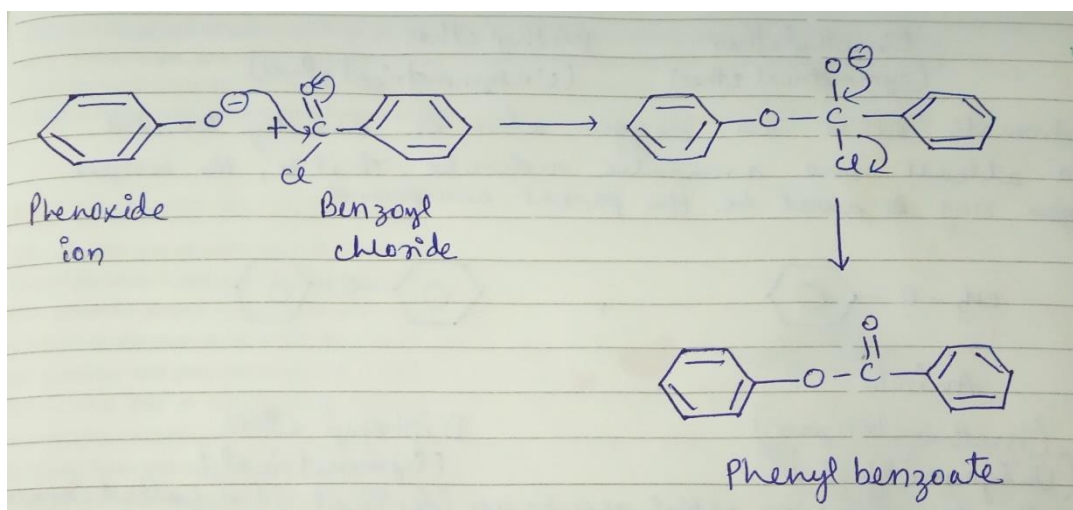


Mechanism:

(i) Formation of phenoxide anion.



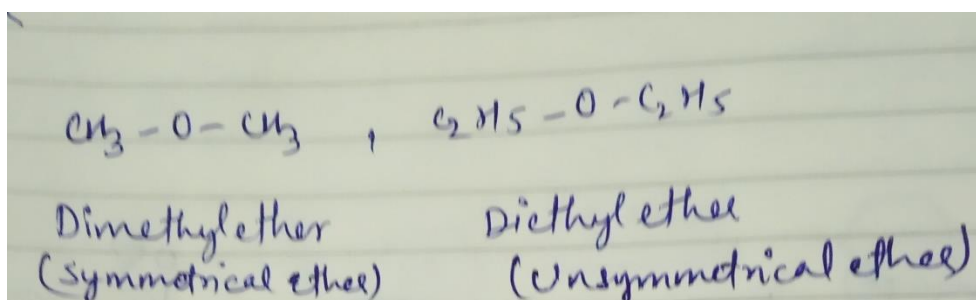
(ii) Attack of phenoxide anion on benzoyl chloride to give the product.



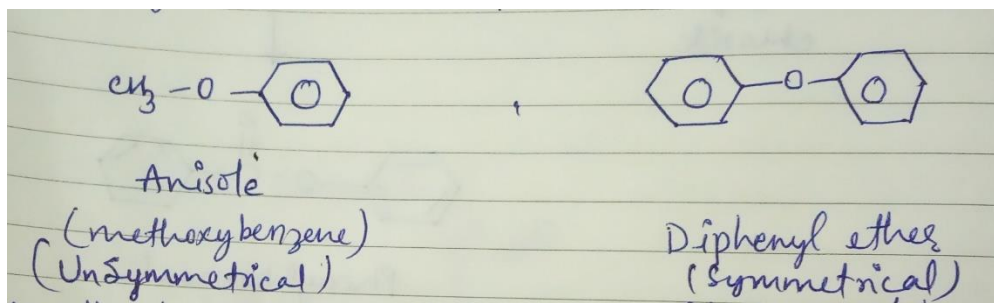
(D) Ethers

Ethers are compounds having general formula, $R-O-R$, $R-O-Ar$ or $Ar-O-Ar$, where, R is an alkyl group and Ar is an Aryl group. If the two groups are identical it is called symmetrical ether and if they are different then it is called unsymmetrical ether.

Aliphatic ethers are represented by $R-O-R$. Examples:

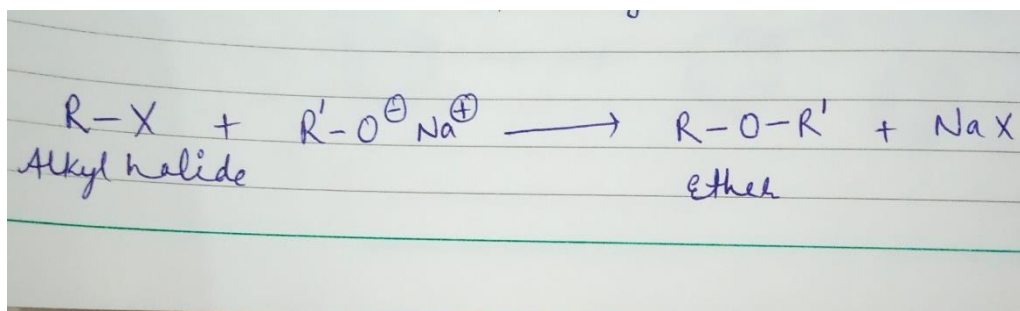


In Aromatic ether an oxygen group is directly bonded to atleast one aromatic compound. That is, the aromatic compound should be the parent compound. Examples:

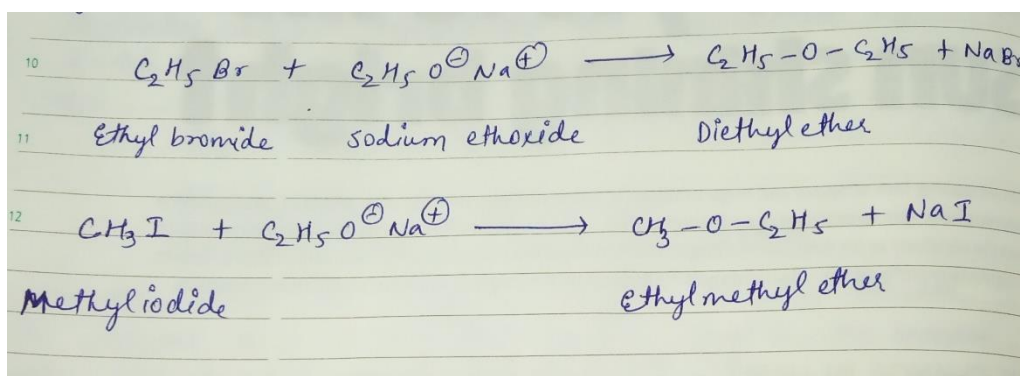


Williamson,s ether synthesis

Ethers can be synthesized by treating an alkyl halide with sodium alkoxide. This reaction is called Williamson,s ether synthesis.



This reaction is very useful because of its versatility as it can be used to prepare both types of ether that is, symmetrical and unsymmetrical ethers.



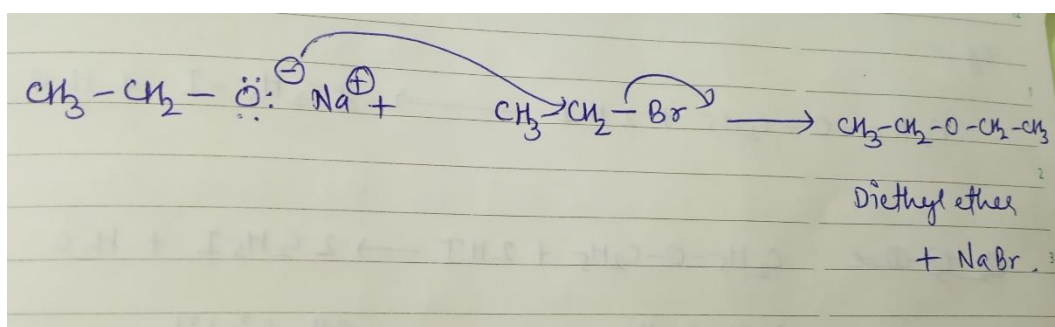
Note:

Tertiary alkyl halides cannot be used to form ethers because the alkoxide ions are good nucleophiles as well as good bases and can lead to dehydrohalogenation of tertiary alkyl halide to form alkenes as major product. Since, the reactivity order of alkyl halides for elimination reaction is $3^\circ > 2^\circ > 1^\circ$.

Therefore, in Williamson's ether synthesis primary alkyl halides are used and the reaction occurs through S_N2 mechanism. The reactivity order of alkyl halides for S_N2 reaction is $1^\circ > 2^\circ > 3^\circ$.

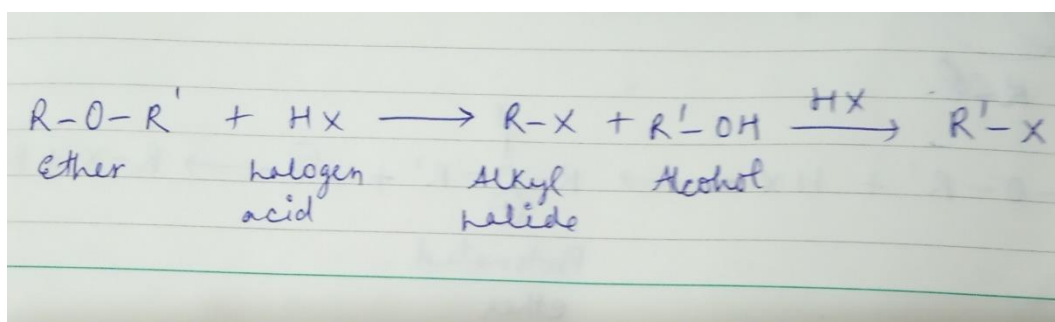
Mechanism:

Williamson's ether synthesis takes place through S_N2 mechanism shown as follows:



Cleavage of Ethers by HI

Ethers are quite stable and generally the ether linkage is not cleaved by bases, oxidising or reducing agents. But ethers are cleaved by halogen acids like HI or HBr.

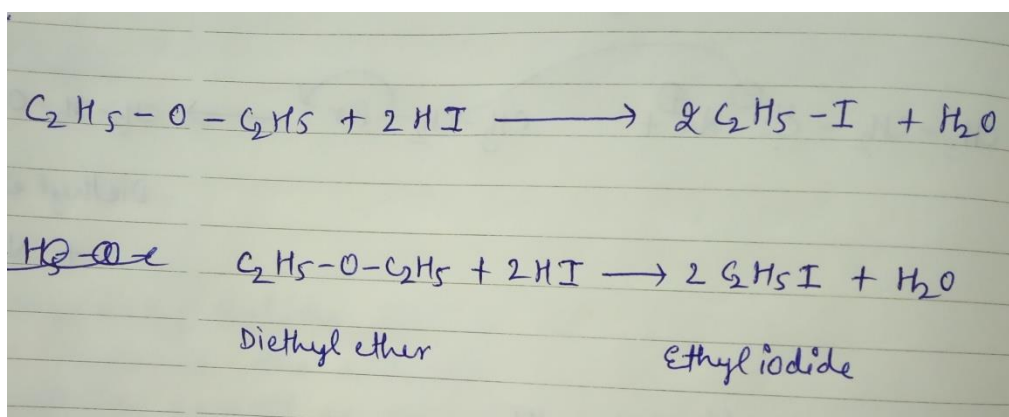


The reactivity order of halogen acids is $\text{HI} > \text{HBr} > \text{HCl}$.

The cleavage of ether occurs by concentrated HI or HBr at high temperatures.

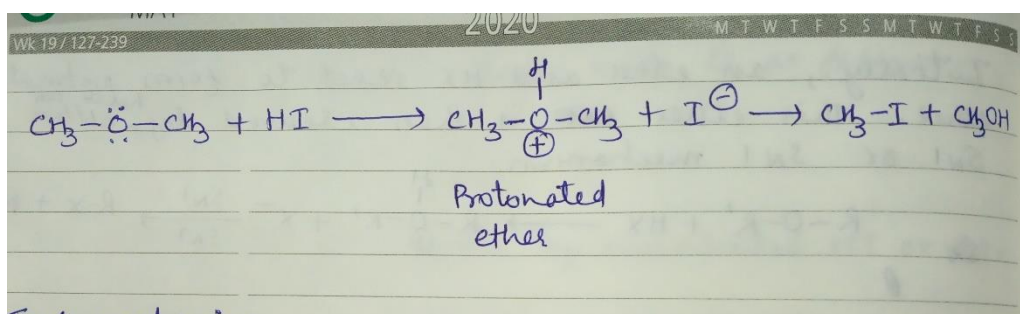
Dialkyl ethers react with HI to give first an alkyl halide and alcohol, this alcohol can further react with HI to form second molecule of alkyl halide.

References: Organic Chemistry, R.T. Morrison, R.N. Boyd and S.K. Bhattacharjee, Pearson, 7th Edition and advance Organic Chemistry, Bahl and Bahl, S.Chand & Company Ltd.



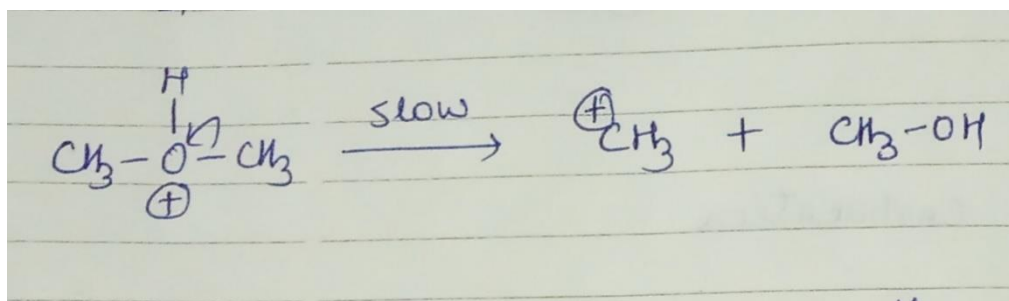
Mechanism:

Initially, an ether and HI react to form protonated ether. This ether is then cleaved by halide ion either by $\text{S}_{\text{N}}1$ or $\text{S}_{\text{N}}2$ mechanism.



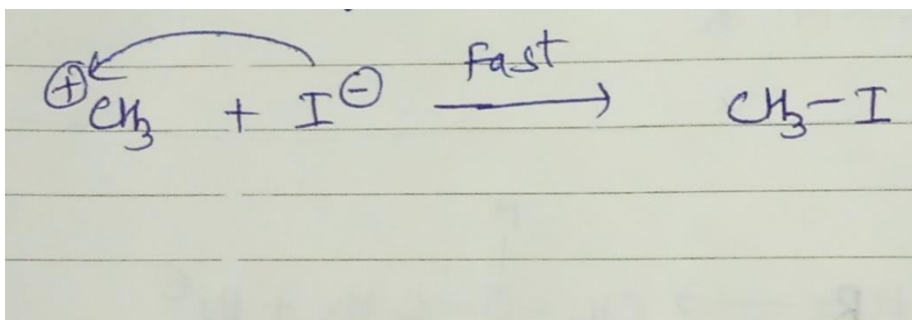
$\text{S}_{\text{N}}1$ mechanism:

Step 1: Formation of carbocation by the protonated ether.



Step 2: Attack of halide ion on the carbocation.

References: Organic Chemistry, R.T. Morrison, R.N. Boyd and S.K. Bhattacharjee, Pearson, 7th Edition and advance Organic Chemistry, Bahl and Bahl, S.Chand & Company Ltd.



$\text{S}_{\text{N}}2$ mechanism:

Attack of halide ion and departure of leaving group takes place in a single step.

