

Unit 11: Ether

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Unit 11: Ether

Syllabus

11.1 Aliphatic Ethers:

- ☐ Introduction, nomenclature classification, isomerism in ether
- ☐ Preparation of ethers from i. alcohol ii. Williamson's etherification process
- ☐ Laboratory preparation of ethoxy ethane from ethanol
- ☐ Physical properties of ether
- ☐ Chemical properties of ethoxyethane
 - action with HI, PCl_5 , conc. HCl, Conc. H_2SO_4 air and Cl_2
 - Uses of ethoxy ethane

11.2 Aromatic Ether:

- Preparation of methoxy benzene (anisole)
- Halogenation, nitration and sulphonation reactions

Some important terms, concepts and formulae

1. Diethyl ether or simply ether is prepared by dehydrating ethanol with conc. H_2SO_4 at 140°C .
2. Assymmetrical ether can be prepared by Williamson's etherification method.
3. Sodium phenoxide reacts with chloromethane in the presence of dilute acid to give anisole.
4. Ethers have lower boiling point than alcohols.
5. Ethers can be cleaved by halogen acids.
6. Aromatic ether gives phenol and haloalkane on cleavage.
7. Old samples of ether are dangerous to boil because it may explode.
8. Ethers are relatively inert and hence are used as solvents in many reactions.

Read the above mentioned various definitions, explanations and formulae carefully. Then go through the following solved examples. After doing the solved examples, try to solve the other similar questions independently.

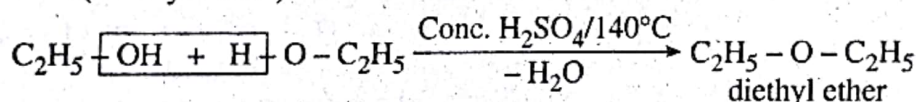
Subject Matter

11.1 Aliphatic ether

Very Short Questions-Answers

Q.1. Convert ethanol into diethyl ether.

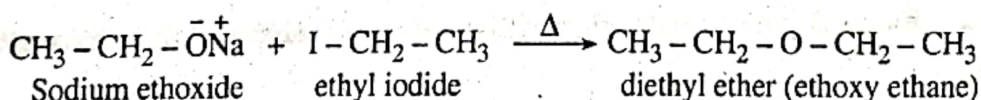
Ans: when excess of ethanol is heated with Conc. H_2SO_4 at about 140°C , two molecules of ethanol undergo condensation to give one molecule of diethyl ether (ethoxy ethane).



[Note: Only symmetrical (or simple) ether can be prepared by this method.]

Q.2. What is williamson's etherification?

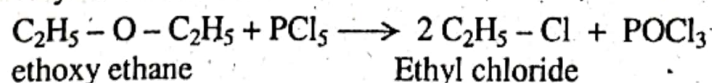
Ans: Williamson's etherification, a nucleophilic substitution reaction, is a convenient method to prepare simple as well as compound ether. In this method an alkyl halide (generally primary) is reacted with sodium or potassium alkoxide to get desired ether. For example, we can prepare ethoxy ethane by reacting sodium ethoxide with ethyl iodide. The reaction takes place as:



Q.3. What is the action of ethoxy ethane on:

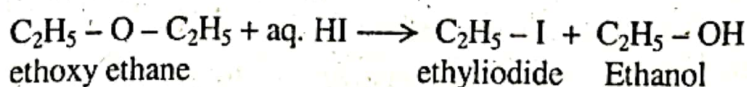
(i) PCl_5 (ii) aq. KI (Cold) ?

Ans: (i) With PCl_5 : Ethoxy ethane reacts with PCl_5 to give two molecules of ethyl chlorides as:

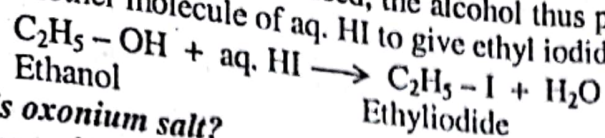


[Note: The C - O bond in ether is cleaved by PCl_5 .]

(ii) With aq. HI : when ethoxyethane reacts with aq. HI , the cleavage of C - O bond again takes place to give one molecule of ethyl iodide and one molecule of alcohol.



If excess of aq. HI is used, the alcohol thus produced again react with another molecule of aq. HI to give ethyl iodide and water

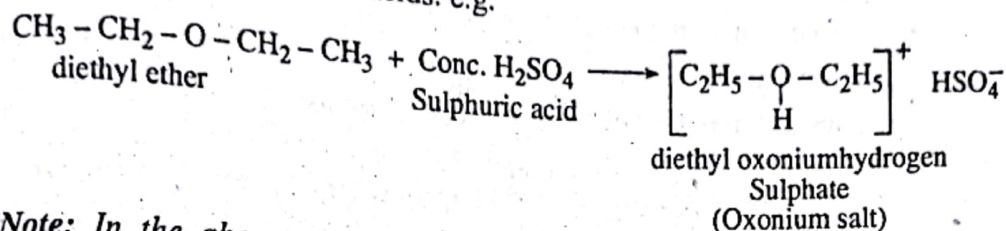


Q.4.

Ans:

What is oxonium salt?

Oxonium salts are organic salts produced by the reaction between ethers and cold concentrated inorganic acids. e.g.



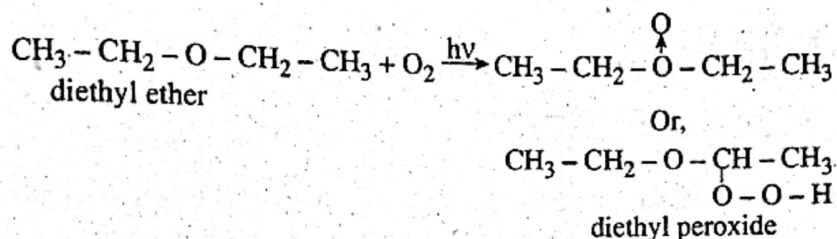
[Note: In the above reaction, ether behaves as a weak base due to the presence of lone pair of electrons on oxygen atom of it.]

Q.5.

Ans:

What happens when diethyl ether is exposed to air and light for a long time?

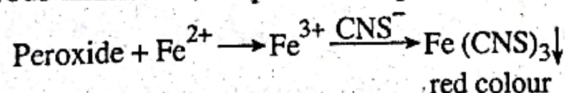
When diethyl ether is exposed to air and light for a long time, it changes into highly explosive diethyl peroxide.



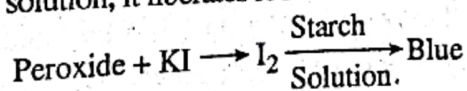
Q.6. Give a chemical test to detect the presence of peroxide in old samples of ether.

Ans: Presence of peroxide in the old samples of ether can be detected as follows:

(a) An impure ether having peroxide linkage will give red colour if shaken with ferrous ammonium sulphate and potassium thiocyanate.



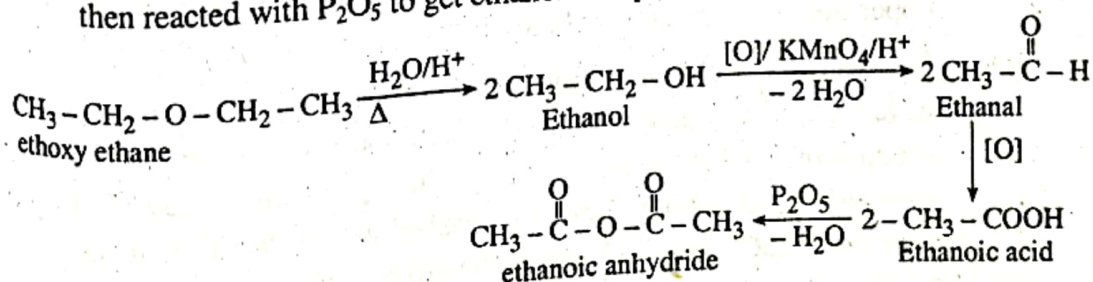
(b) Similarly, when ethers containing peroxides linkage is mixed with potassium iodide solution, it liberates iodine which turns starch solution blue.



Here, I^- reduces peroxides back to ether.

Q.7. How will you convert ethoxy ethane into ethanoic anhydride?

Ans: Ethanoic anhydride can be synthesized from ethoxyethane as follows: The ethoxyethane is first hydrolyzed in acidic medium to get ethanol. The ethanol is then oxidized to acetic acid (Ethanoic acid) by a strong oxidizing agent such as acidified KMnO_4 , or acidified $\text{K}_2\text{Cr}_2\text{O}_7$. Finally, the ethanoic acid is then reacted with P_2O_5 to get ethanoic anhydride. The reaction takes place as:



Ans: Laboratory preparation of ethoxyethane (diethyl ether) involves the followings:

$$\text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{SO}_4 \xrightarrow{100^\circ\text{C}} \text{C}_2\text{H}_5\text{HSO}_4 + \text{H}_2\text{O}$$

ethanol Ethylhydrogen Sulphate

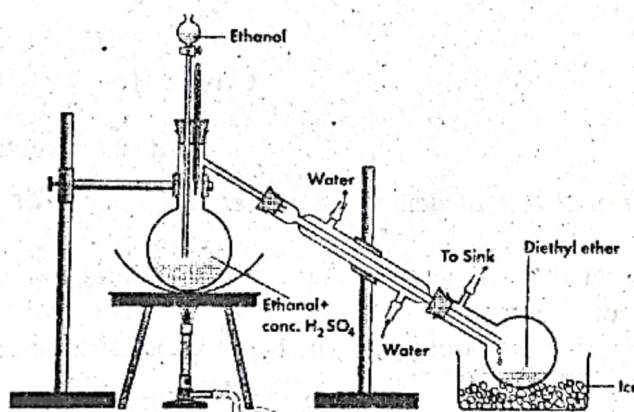
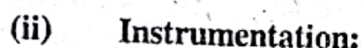


Fig: Laboratory preparation of diethylether

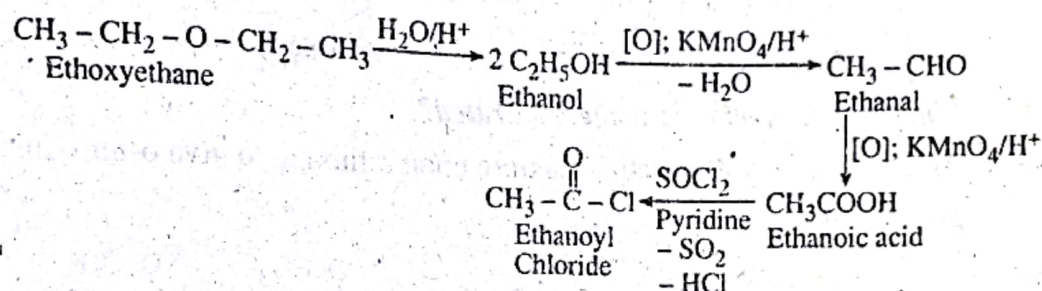
(iv) **Purification:** The impure distillate of ether is washed with dil. NaOH which removes sulphurous acid. The solution is then stirred with 50% solution of CaCl_2 to remove alcohol. The upper organic layer is then separated by separating funnel and washed with water. Then it is dried over fused CaCl_2 and finally redistilled to get pure ether.

Q.9. Convert the following organic compounds:

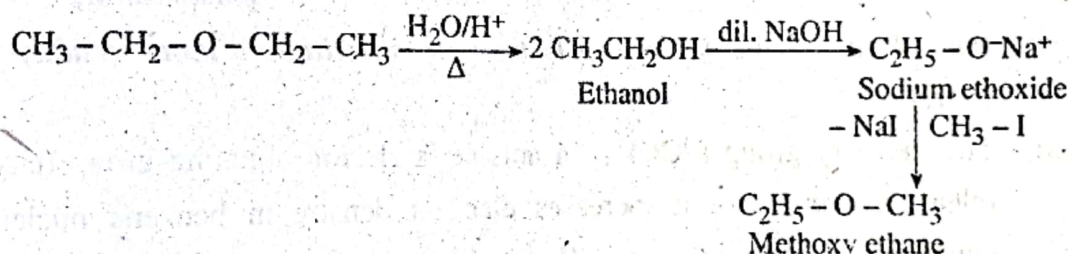
(i) Ethoxy ethane into ethanoyl chloride

(ii) Ethoxy ethane into methoxy ethane

Ans: (i) Ethoxy ethane into ethanoyl chloride: Ethoxy ethane can be converted into ethanoyl chloride by first hydrolysing the ethoxy ethane into ethanol in the presence of dilute mineral acid. The ethanol is then oxidized to ethanoic acid via ethanal by using oxidizing agents like acidified KMnO_4 . The ethanoic acid is then reacted with thionyl chloride in the presences of pyridine to get ethanoyl chloride. The reaction proceeds as follows:



(ii) Ethoxy ethane into methoxy ethane: Ethoxy ethane can be converted into methoxy ethane as follows:

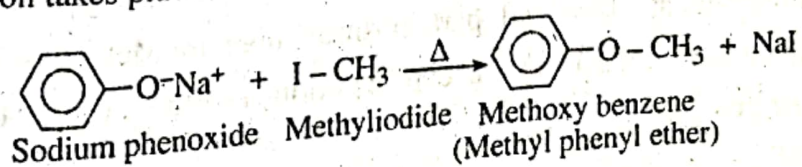


11.2 Aromatic ether

Very Short Questions-Answers

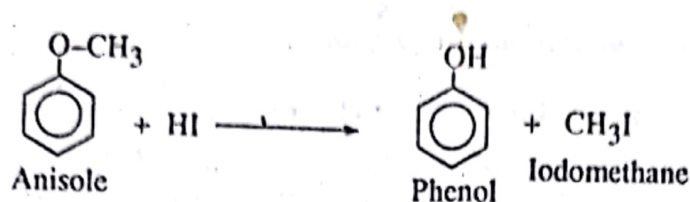
Q.1. How would you prepare methyl phenyl ether by the help of willamson's synthesis?

Ans: By using Williamson's synthesis method, we can prepare methoxybenzene (methyl phenyl ether) by reacting methyl iodide with sodium phenoxide. The reaction takes place as:



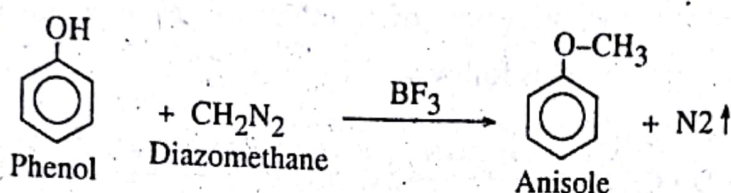
Q.2. Give the products obtained when Anisole is heated with HI.

Ans: When anisole is heated with HI, phenol and Iodomethane is obtained as major product.



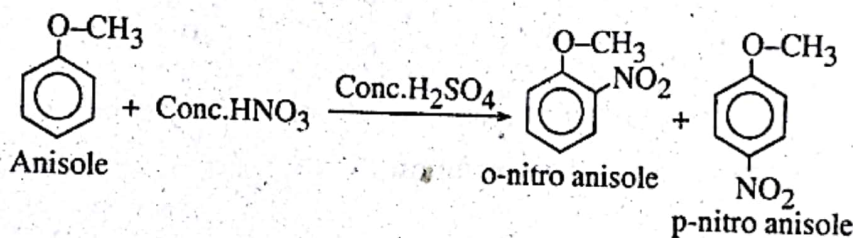
Q.3. How does phenol react with diazomethane?

Ans: Phenol reacts with diazomethane in presence of a lewis acid like BF_3 to give Anisole.



Q.4. What happens when anisole is nitrated?

Ans: Anisole reacts with nitrating mixture upon refluxing to give o-nitroanisole and p-nitro anisole.



Q.5. Why does anisole undergo electrophilic substitution more readily than benzene?

Ans: The methoxy group ($-\text{OCH}_3$) in anisole is electron donating group (electron releasing group) so, it increases electron density in benzene nucleus as compared to benzene alone. This is clear by the resonating structures of anisole given below:

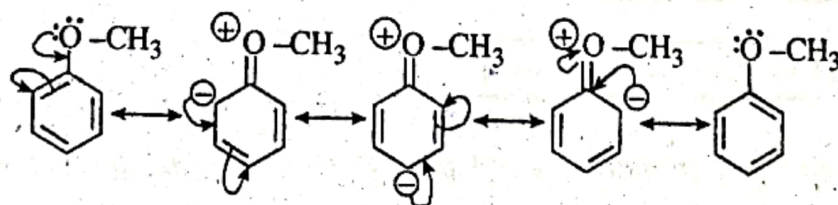


Fig: resonating structure of anisole

Due to more electron density in the benzene nucleus, anisole is more susceptible for electrophilic attack than benzene. Hence, Electrophilic substitution in anisole is faster than in benzene. Also, the negative charges are more condensed at ortho and para position than in Meta position so the electrophiles are directed to o- and p- position. In other word, $-\text{OCH}_3$ is o, p-directing group.