



11.21. Name the reagents used in the following reactions:

- (i) Oxidation of a primary alcohol to carboxylic acid.
- (ii) Oxidation of a primary alcohol to aldehyde.
- (iii) Bromination of phenol to 2,4,6-tribromophenol
- (iv) Benzyl alcohol to benzoic acid.
- (v) Dehydration of propan-2-ol to propene.
- (vi) Butan-2-one to butan-2-ol.

Ans: (i) Acidified potassium dichromate or neutral/acidic/alkaline potassium permanganate.

(ii) Pyridinium chlorochromate (PCC), $(C_5H_5NH)^+ ClCrO_3^-$ in CH_2Cl_2 or Pyridinium dichromate (PDC), $[(C_5H_5NH)_2]^{2+} Cr_2O_7^{2-}$ in CH_2Cl_2

(iii) Aqueous bromine, i.e., Br_2/H_2O .

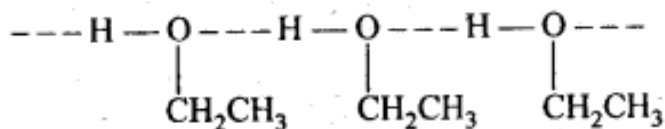
(iv) Acidified or alkaline potassium permanganate.

(v) 85% H_2SO_4 at 440 K.

(vi) Ni/H_2 or $NaBH_4$ or $LiAlH_4$.

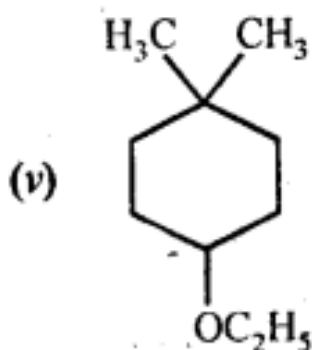
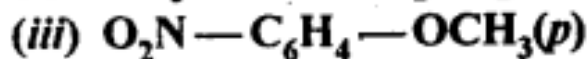
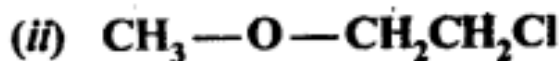
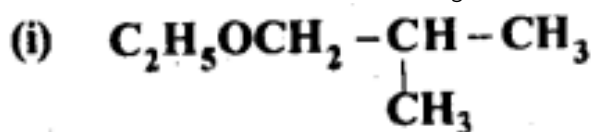
11.22. Give reason for the higher boiling point of ethanol in comparison to methoxymethane.

Ans: Ethanol undergoes intermolecular H-bonding due to the presence of a hydrogen atom attached to the electronegative oxygen atom. As a result, ethanol exists as associated molecules.

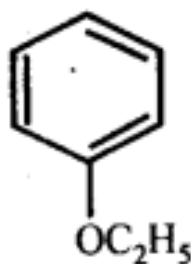


Consequently, a large amount of energy is required to break these hydrogen bonds. Therefore, the boiling point of ethanol is higher than that of methoxymethane which does not form H-bonds.

11.23. Give IUPAC names of the following ethers.



(vi)



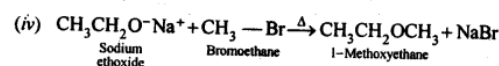
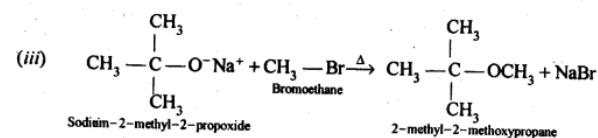
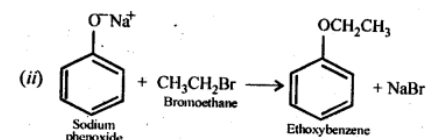
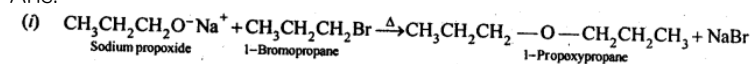
Ans:

- (i) 1-Ethoxy-2-methylpropane
- (ii) 2-Chloro-1-methoxyethane
- (iii) 4-Nitroanisole
- (iv) 1-Methoxypropane
- (v) 1-Ethoxy-4,4-dimethylcyclohexane
- (vi) Ethoxybenzene

11.24. Write the names of reagents and equations for the preparation of the following ethers by Williamson's synthesis:

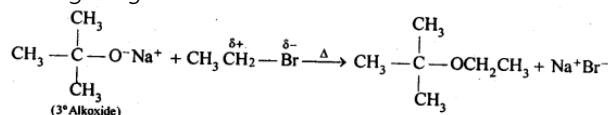
- (i) 1-Propoxypropane
- (ii) Ethoxybenzene
- (iii) 2-Methoxy-2-methylpropane
- (iv) 1-Methoxyethane

Ans:

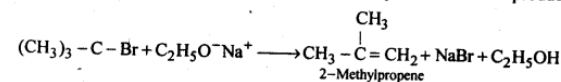


11.25. Illustrate with examples the limitations of Williamson synthesis for the preparation of certain types of ethers.

Ans: Williamson's synthesis is a versatile method for the synthesis of both symmetrical and unsymmetrical ethers. However, for the synthesis of unsymmetrical ethers, a proper choice of reactants is necessary. Since Williamson's synthesis occurs by $\text{S}_\text{N}2$ mechanism and primary alkyl halides are most reactive in $\text{S}_\text{N}2$ reaction, therefore, best yields of unsymmetrical ethers are obtained when the alkyl halides are primary and the alkoxide may be primary, secondary or tertiary. For example, tert-butylethyl ether is prepared by treating ethyl bromide with sodium tert-butoxide.



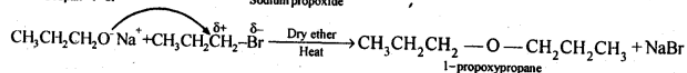
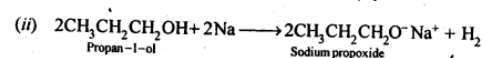
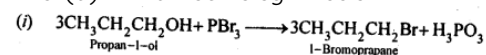
The above ether cannot be prepared by treating sodium ethoxide with tert-butyl chloride or bromide since under these condition an alkene, i.e., isobutylene is the main product.



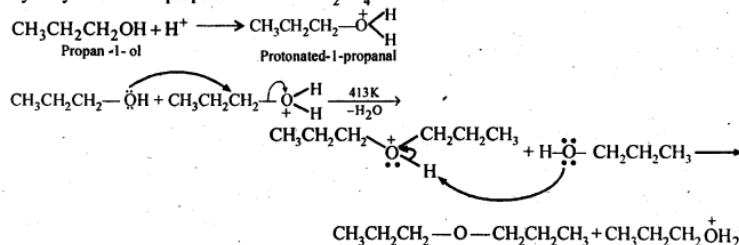
Aryl and vinyl halides cannot be used as substrates because they are less reactive in nucleophilic substitution.

11.26. How is 1-propoxypropane synthesised from propan-1-ol? Write the mechanism of this reaction.

Ans: (a) Williamson's synthesis

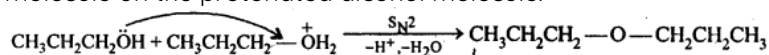


(b) By dehydration of 1-propanol with conc. H_2SO_4 at 413 K.

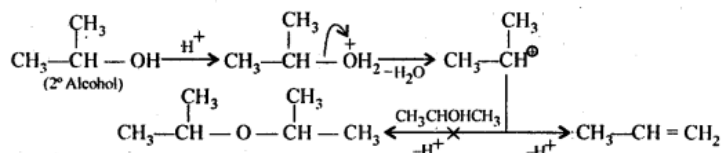


11.27. Preparation of ethers by acid dehydration of secondary or tertiary alcohols is not a suitable method. Give reason.

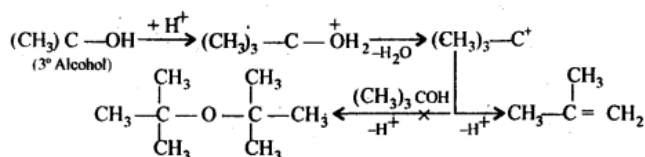
Ans: Acid catalysed dehydration of primary alcohols to ethers occurs by $\text{S}_\text{N}2$ reaction involving nucleophilic attack by the alcohol molecule on the protonated alcohol molecule.



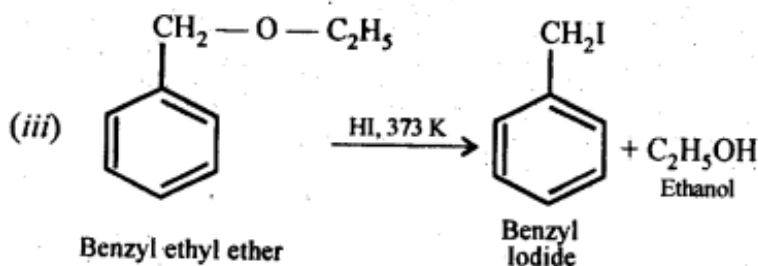
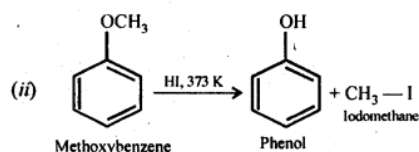
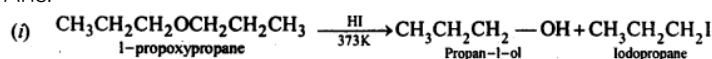
Under these conditions, 2° and 3° alcohols, however, give alkenes rather than ethers. The reason being that due to steric hindrance, nucleophilic attack by the alcohol molecule on the protonated alcohol molecule does not occur. Instead protonated 2° and 3° alcohols lose a molecule of water to form stable 2° and 3° carbocation. These carbocations prefer to lose a proton to form alkenes rather than undergoing nucleophilic attack by alcohol molecules to form ethers.



Similarly, 3° alcohols give alkenes rather than ethers.

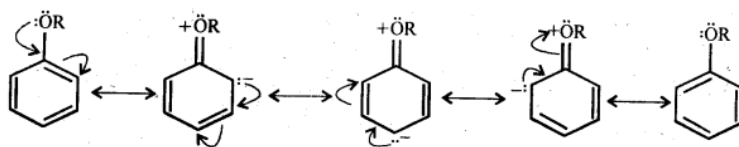


11.28. Write the equation of the reaction of hydrogen iodide with (i) 1-propoxypropane (ii) methoxybenzene, and (iii) benzyl ethyl ether
Ans:



11.29. Explain the fact that in aryl alkyl ethers (i) the alkoxy group activates the benzene ring towards electrophilic substitution and (ii) it directs the incoming substituents to ortho and para positions in benzene ring.

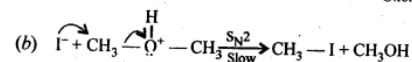
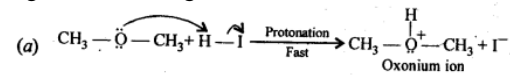
Ans: In aryl alkyl ethers, the +R-effect of the alkoxy (OR) group increases the electron density in the benzene ring, thereby activating the benzene ring towards electrophilic substitution reaction.



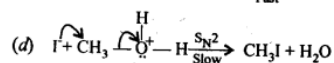
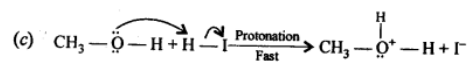
Since the electron density increases more at the two ortho and one para position as compared to meta position therefore, electrophilic substitution reactions mainly occur at o-and -positions.

11.30. Write the mechanism of the reaction of HI with methoxymethane.

Ans: When equimolar amounts of HI and methoxy methane are reacted, a mixture of methyl alcohol and methyl iodide is formed by the following mechanism:



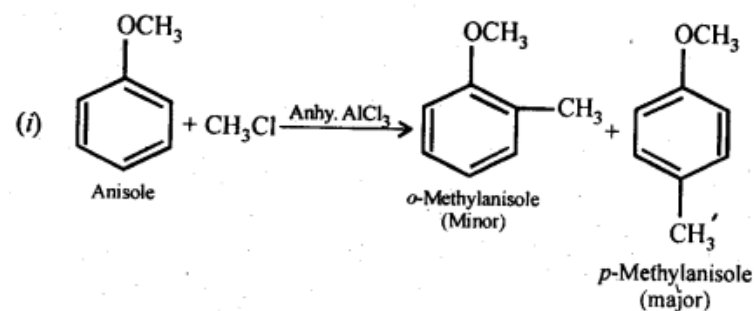
If however, excess of HI is used, methyl alcohol formed in step (b) is also converted into methyl iodide by following mechanism:

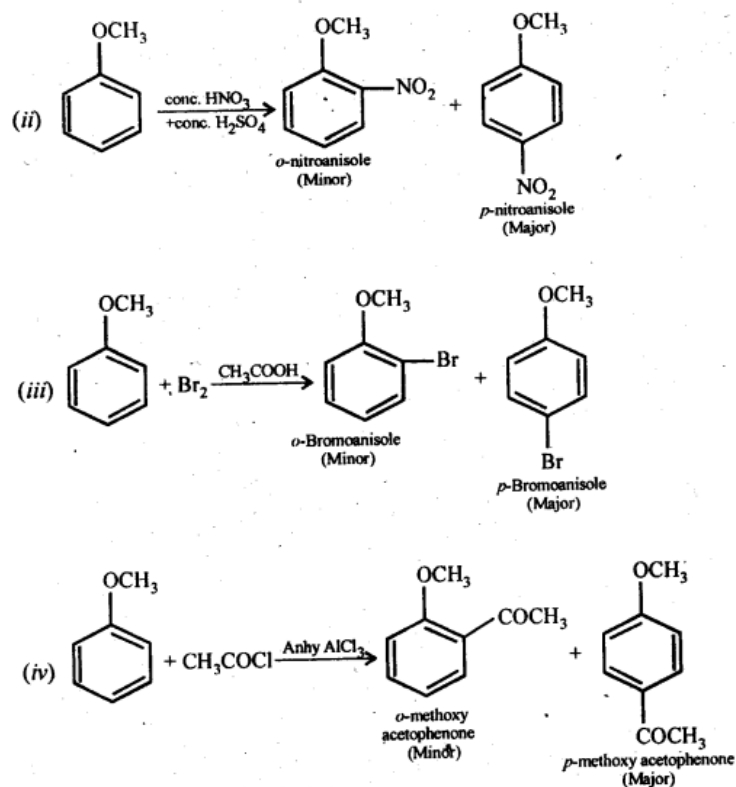


11.31. Write equations of the following reactions:

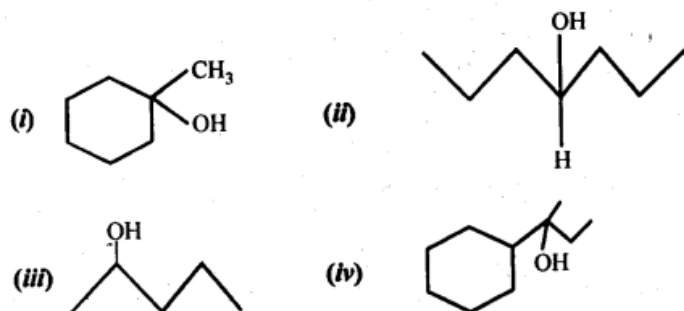
- Friedel-Crafts reaction -alkylation of anisole
- Nitration of anisole.
- Bromination of anisole in ethanoic acid medium
- Friedel-Craft's acetylation of anisole.

Ans:

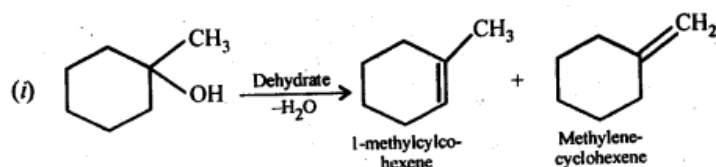




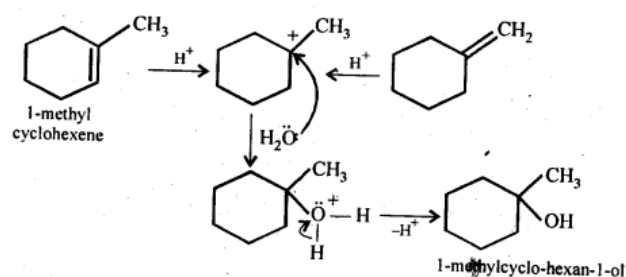
11.32. Show how would you synthesise the following alcohols from appropriate alkanes?

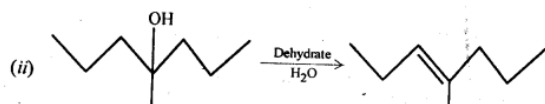


Ans:

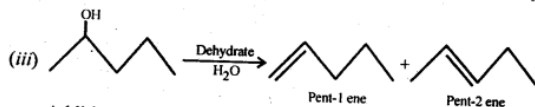
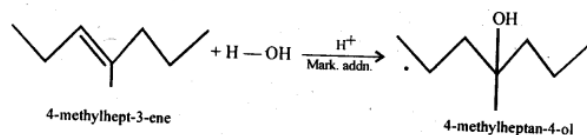


Addition of H_2O to both these alkenes gives the desired alcohol.

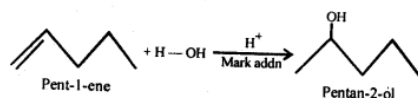




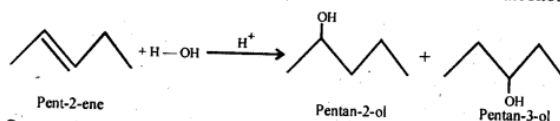
Addition of H_2O to 4-methylhept-3-ene in presence of an acid gives the desired alcohol.



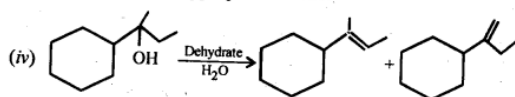
Addition of H_2O to pent-1-ene gives the desired alcohol.



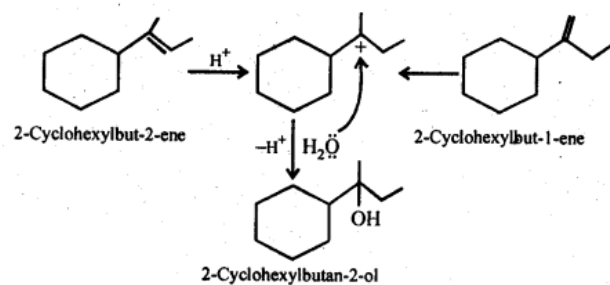
However, addition of H_2O to pent-2-ene gives a mixture of two alcohols.



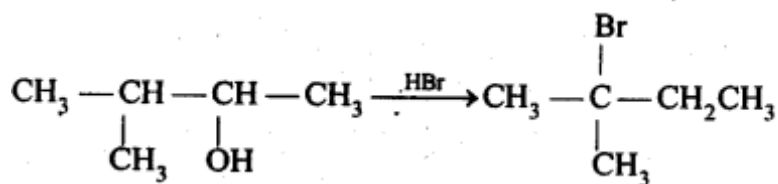
So pent-1-ene is appropriate alkene.



Now addition of H_2O to both in the presence of an acid gives the desired alcohol.



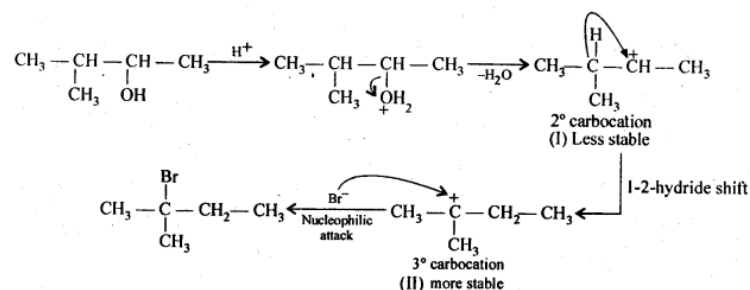
11.33. When 3-methylbutan-2-ol is treated with HBr , the following reaction takes place:



Give a mechanism for this reaction.

(Hint: The secondary carbocation formed in step II rearranges to a more stable tertiary carbocation by a hydride ion shift from 3rd carbon atom.)

Ans:



Protonation of the given alcohol followed by loss of water gives a 2° carbocation (I), which being unstable rearranges by 1,2-hydride shift to form the more stable 3° carbocation (II). Nucleophilic attack by Br^- ion on this carbocation (II) gives the final product.

*****END*****