

16 HYDROXY COMPOUNDS

➤ <https://subarnam.com.np/>

🌀 Learning outcomes

After completion of the chapter, Students should be able to:

- recall the reactions (reagents and conditions) by which alcohols can be produced:
 - electrophilic addition of steam to an alkene, $\text{H}_2\text{O}(\text{g})$ and H_3PO_4 catalyst
 - reaction of alkenes with cold, dilute, acidified potassium manganate(VII) to form a diol
 - substitution of a halogenoalkane using $\text{NaOH}(\text{aq})$ and heat
 - reduction of an aldehyde or ketone using NaBH_4 or LiAlH_4
 - reduction of a carboxylic acid using LiAlH_4
 - hydrolysis of an ester using dilute acid or dilute alkali and heat
- describe:
 - the reaction with oxygen (combustion)
 - substitution to halogenoalkanes, e.g. by reaction with HX or KBr with H_2SO_4 or H_3PO_4 ; or with PCl_3 and heat; or with PCl_5 ; or with SOCl_2
 - the reaction with $\text{Na}(\text{s})$
 - oxidation with acidified $\text{K}_2\text{Cr}_2\text{O}_7$ or acidified KMnO_4 to:
 - carbonyl compounds by distillation
 - carboxylic acids by refluxing(primary alcohols give aldehydes which can be further oxidised to carboxylic acids, secondary alcohols give ketones, tertiary alcohols cannot be oxidised)
 - dehydration to an alkene, by using a heated catalyst, e.g. Al_2O_3 or a concentrated acid
 - formation of esters by reaction with carboxylic acids and concentrated H_2SO_4 or H_3PO_4 as catalyst as exemplified by ethanol
- classify alcohols as primary, secondary and tertiary alcohols, to include examples with more than 1 -OH group
 - state characteristic distinguishing reactions, e.g. mild oxidation with acidified $\text{K}_2\text{Cr}_2\text{O}_7$, colour change from orange to green
- deduce the presence of a $\text{CH}_3\text{CH}(\text{OH})-$ group in an alcohol, $\text{CH}_3\text{CH}(\text{OH})-\text{R}$, from its reaction with alkaline $\text{I}_2(\text{aq})$ to form a yellow precipitate of tri-iodomethane and an ion, RCO_2^-
- Explain the acidity of alcohols compared with water

Initial assessment

- Which statement below describes what happens to an organic compound when it is reduced and then oxidised?
Discuss with a partner how to:
A It loses hydrogen, then loses oxygen
B It gains hydrogen, then gains oxygen
C It gains hydrogen, then loses oxygen
D It loses hydrogen, then gains oxygen
- complete these general equations
 - acid + base $\rightarrow$
 - acid + metal $\rightarrow$
 - acid + carbonate $\rightarrow$
- Give the skeletal formula for:
 - propan-2-ol
 - butanone

Introduction

Preparation

Addition of steam to alkenes (studied in alkenes)

Alkenes with cold dilute acidified potassium manganate(VII) (studied in alkenes)

Substitution of a halogenoalkanes (studied in halogenoalkanes)

Reduction of an aldehyde or ketone with NaBH_4 or LiAlH_4

There are three common methods of reducing carbonyl compounds.

» By hydrogen on a nickel catalyst:

» By sodium tetrahydridoborate(III) (sodium borohydride) in alkaline methanol:

» By lithium tetrahydridoaluminate(III) (lithium aluminium hydride) in dry ether:

Lithium tetrahydridoaluminate(III) is a dangerous reagent, producing heat and hydrogen gas (which usually catches fire) with any water, and ether is a hazardous solvent, being very volatile and flammable. Hence, this method is usually avoided.

Because these reagents (LiAlH_4 and NaBH_4) are nucleophilic, needing a δ^+ carbon to react with, they do not reduce $\text{C}=\text{C}$ double bonds, in contrast to catalytic hydrogenation.

Reduction of a carboxylic acid (using LiAlH₄)

Hydrolysis of an ester

a. **Acid hydrolysis**

b. **Basic hydrolysis**

Properties

Reaction with oxygen

Substitution (studied in halogenoalkanes)

to halogenoalkanes, e.g. by reaction with HX or KBr with H₂SO₄ or H₃PO₄; or with PCl₃ and heat; or with PCl₅; or with SOCl₂

Reaction with Na

Oxidation

Dehydration (studied in the preparation of alkenes)

Formation of ester (esterification)

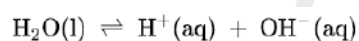
Iodoform test

Comparing the acidity of alcohols and water

Once dissolved in water, ethanol molecules do not dissociate (split up) to any great extent, although there is a very small **degree of dissociation**:



The position of equilibrium lies well over to the left, favouring the undissociated C₂H₅OH molecules. Even compared to the dissociation of water molecules:



the concentration of H⁺(aq) ions is much lower. So, we can say that ethanol is a weaker acid than water: its molecules are less likely to dissociate and form H⁺ ions. This is because of the electron-donating alkyl (ethyl) group bonded to the negatively charged oxygen atom in the ethoxide ion. The positive inductive effect of the ethyl group has the effect of concentrating more negative charge on this oxygen atom. So, the ethoxide ion more readily accepts an H ion than the hydroxide ion, OH⁻, from the dissociation of water. The hydroxide ion only has a hydrogen atom bonded to its negatively charged oxygen, and no alkyl groups.

.....

<https://subarnam.com.np/>