Assignment

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1. Discuss the two major classification of Alkanols. Give two examples each for each class.
2. In the Grignard Synthesis of Alkanols, react a named Grignard reagent with $CH_3CH_2CH_2CH_2C=OCH_2CH_2CH_3$. Show the rxn steps.
3. Discuss the industrial manufacture of ethanol showing all reaction equations and necessary enzymes and temperature of rxn.
4. Determine the products obtained in the reduction of Alkanone and Alkanal. Use a specific example for each and show the equation of rxn.

Answers:

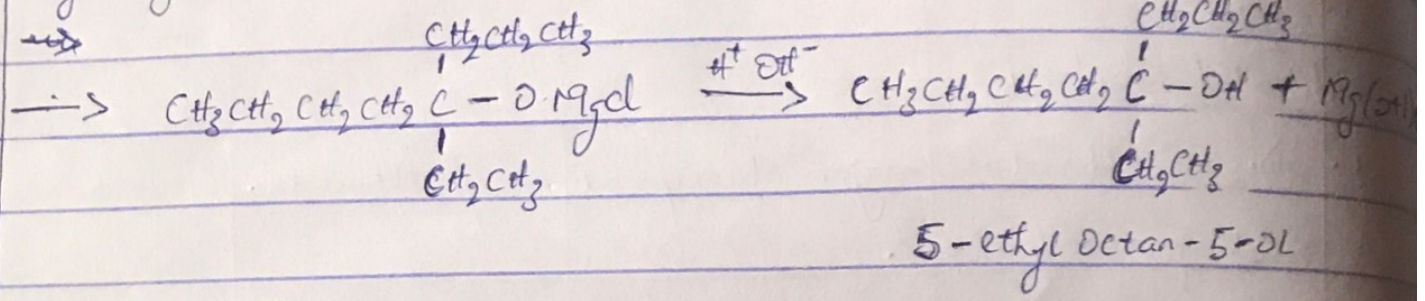
1. Two major classification of alkanols are;

a. Classification of alcohols based on the number of hydrogen atoms attached to the carbon atom containing the hydroxyl group; If the number of hydrogen atoms attached to the carbon atom containing the hydroxyl group is two/three, it is called a primary alcohol (1°), If it has only one hydrogen atom, it is called secondary alcohol (2°) and if no hydrogen atom is attached, it is called a tertiary alcohol (3°). Eg CH_3CH_2OH, $(CH_3)_3C-OH$

b. Classification based on the number of hydroxyl groups they possess. Monohydric alcohols have one hydroxyl group present in the alcohol structure. Dihydric alcohols have two hydroxyl group present in the alcohol structure. Polyhydric alcohols have more than three hydroxyl groups. Eg CH_3OH, $OHCH_2CH_2OH$

2- CH_3CH_2MgCl + $CH_3CH_2CH_2CH_2C(=O)CH_2CH_2CH_3$

Ethyl Magnesium Chloride Octan-4-One



5-ethyl Octan-5-ol

3- Carbohydrates such as starch are major group of natural compounds that can be made to yield ethanol by the biological process of fermentation.

⇒ The starch containing material is warmed with malt to 60°c for a specific period of time and converted into maltose by the enzyme diastase contained in the malt

$$2(C_6H_{10}O_5)_n + nH_2O \xrightarrow[\Delta]{60^\circ C/\text{diastase}} nC_{12}H_{22}O_{11}$$

Carbohydrate maltose

⇒ The maltose is broken down into glucose on addition of yeast which contains the enzyme maltase and at a temperature of 15°C.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{15^\circ C/\text{maltase}} 2C_6H_{12}O_6$$

Maltose Glucose

⇒ The glucose at constant temperature of 15°C is then converted into alcohol by the enzyme Zymase contained also in yeast.

$$C_6H_{12}O_6 \xrightarrow{15^\circ C/\text{Zymase}} 2CH_3CH_2OH + 2CO_2\uparrow$$

Glucose Ethanol

4. In the reduction of alkanal, primary alcohol is produced.

$$RCHO \xrightarrow[LiAlH_4/(C_2H_5)_2O]{} RCH_2OH$$

Alkanal Primary alcohol

while the reduction of alkanone, produces secondary alcohol

$$RR'C{=}O \xrightarrow{LiAlH_4 / (C_2H_5)_2O} RR'CHOH$$

Alkanone — Secondary alcohol

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Assignment on Carboxylic acids.

1. Give the IUPAC names of the following compounds.

a. $HCOOH$ b. $HOOCCH_2CH_2CH_2COOH$ c. $CH_3CH_2CH_2COOH$

d. HO_2C-CO_2H e. $CH_3(CH_2)_4COOH$ f. $CH_3CH=CHCH_2CH_2COOH$

2. Discuss briefly the physical properties of carboxylic acids under the following headings. i. Physical appearance ii. Boiling point iii. Solubility

3. Write 2 industrial preparations of carboxylic acids.

4. With equations and brief explanation discuss the synthetic preparation of carboxylic acid.

5. With chemical equation only, outline the reduction, decarboxylation, esterification of carboxylic acid.

Answers:

1a. $HCOOH$ ⇒ Methanoic acid b. $HOOCCH_2CH_2CH_2COOH$ ⇒ Pentan-1,5-dioic acid. c. $CH_3CH_2CH_2COOH$ ⇒ Butanoic acid d. HO_2C-CO_2H - Ethanedioic acid e. $CH_3(CH_2)_4COOH$ ⇒ Hexanoic acid

f. $CH_3CH=CHCH_2CH_2COOH$ ⇒ Hex-4-enoic acid

2i. Physical appearance: All simple aliphatic carboxylic acids up to C_{10} are liquids at room temperature. Most other carboxylic acids are solids at room temperature.

ii. Boiling point: Boiling point increases with increasing relative molecular mass.

iii. Solubility: Lower molecular mass carboxylic acids with up to four carbon atoms in their molecules are soluble in water. All carboxylic acids are soluble in organic solvents.

3a. From petroleum: Liquid phase air oxidation of C_5-C_7 alkanes, obtainable from petroleum at high temperature and pressure will give C_5-C_7 carboxylic acids with methanoic, propanoic and butanedioic acids as by-products.

$$C_5-C_7 \xrightarrow{O_2/\text{High temperature and pressure}} C_5-C_7 \text{ carboxylic acids.}$$

b. From ethanol: Ethanoic acid is obtained commercially by the liquid phase air-oxidation of 5% solution of ethanol to ethanoic acid using manganese(II) ethanoate catalyst. Ethanal itself is obtained from ethyne.

$$HC\equiv CH \xrightarrow{\text{dil. } H_2SO_4/HgSO_4} CH_3CHO \xrightarrow{O_2/(CH_3COO)_2Mn} CH_3COOH$$

4a. Oxidation of primary alcohols & aldehydes: It can be used to prepare carboxylic acids using the usual oxidizing agents (i.e $K_2Cr_2O_7$ or $KMnO_4$) in acidic solution.

$$RCH_2OH \xrightarrow[[O]]{\text{excess acid/KMnO}_4} RCHO \xrightarrow[[O]]{} RCOOH$$

b. Carbonation of Grignard Reagent: Aliphatic carboxylic acids are obtained by bubbling carbon(IV) oxide into the Grignard reagent and then hydrolyzed with dilute acid.

$$RMgBr + CO_2 \xrightarrow{(C_2H_5)_2O} RCOOMgBr \xrightarrow{H_2O/\text{dil. acid}} RCOOH + MgBrOH$$

c. Hydrolysis of nitriles (cyanides) or esters:

$$RCN + 2H_2O \xrightarrow{H^+} RCOOH + NH_4^+$$

5a. Reduction:

$$4RCOOH + 3LiAlH_4 \xrightarrow{(C_2H_5)_2O} (RCH_2O)_4AlLi + 2LiAlO_2 + 4H_2$$

$$\downarrow 4H_2O$$

$$4RCH_2OH + Al(OH)_3 + LiOH$$

$$CH_3CH_2CH_2COOH \xrightarrow{LiAlH_4} CH_3CH_2CH_2CH_2OH$$

Butanoic acid — Butanol

c. Decarboxylation:

$$CH_3CH_2CH_2COONa + NaOH \xrightarrow{\text{fuse}} CH_3CH_2CH_3 + Na_2CO_3$$

Kolbe Synthesis

$$2CH_3CH_2COONa + 2H_2O \xrightarrow{\text{electrolysis/aq. ethanol}} CH_3(CH_2)_2CH_3 + CO_2\,(\text{anode}) + 2NaOH + H_2\,(\text{cathode})$$

c. Esterification:

$CH_3CH_2CH_2COOH + CH_3CH_2CH_2OH \xrightleftharpoons{H^+} CH_3CH_2CH_2COOCH_2CH_2CH_3 + H_2O$.