CARBONYL COMPOUNDS

- Contain C=O group
- Examples include
  - ✓ Alkanals/Aldehyde RHC=O
  - ✓ Alkanones/ Ketones $RR_1C=O$
  - ✓ Alkanoic acids/ Carboxylic acids RCOOH
  - ✓ Alkanoates/ Esters $RCOOR_1$
  - ✓ Alkanoyl halide/Acyl halide RCOOX (where X can be F, Cl, Br, I)
  - ✓ Amides $RCONH_2$
- But carbonyl compounds centres majorly on alkanals and alkanones because their functional group is only carbonyl group and nothing else

POLARIZATION OF CARBONYL COMPOUNDS

- The double bond in C=O contains one sigma bond and one pi bond as in alkenes
- The sigma bond is formed from overlap of an SP^2 hybrid orbital of the carbonyl carbon and SP^2 hybrid orbital of the carbonyl oxygen
- The pi bond is formed from overlap of an p orbital of the carbonyl carbon and p orbital of the carbonyl oxygen
- The carbonyl oxygen is highly electronegative and it attracts electron to itself from carbonyl carbon
- This results to polarisation making oxygen atom bears a small negative charge and carbon atom bears a small positive charge
- The polarity of carbonyl bond is as a result of mesomeric effect $^{\delta+}C = O^{\delta-}$

STRUCTURES AND NOMECLATURE OF ALKANALS AND ALKANONES

- Alkanals have general formula RCHO where R can be alkyl group or hydrogen (for methanal)
- Alkanones have general formula RR_1CO where R and R_1 are strictly alkyl group and not hydrogen atom.
- The IUPAC naming system for alkanals is by replacing the 'e' of corresponding alkane with the suffix '-al' e.g. methanal HCHO, ethanal CH_3CHO, butanal CH_3CH_2 CH_2CHO etc.
- The common names are derived by replacing the ending '-ic' of the corresponding carboxylic acid with the suffix '-aldehyde' e.g. formaldehyde HCHO, acetaldehyde CH_3CHO, butyraldehyde CH_3CH_2 CH_2CHO from formalic acid, acetic acid and butyric acid respectively.
- The simplest of aromatic aldehyde is benzaldehyde C_6H_5CHO (phenylmethanal) from benzoic acid.
- The IUPAC naming system for alkanones is by replacing the 'e' of corresponding alkane with the suffix '-one' e.g. propanone $(CH_3)_2CO$, butanone CH_3CH_2 CH_2CO etc.
- The position of the carbonyl group is specified by including the carbonyl carbon in the numbering of the straight chain e.g. propanone, pentan-2-one, hexan-3-one
- Ketones in which the carbonyl carbon group is attached directly to benzene ring are called phenones (phenylketones) e.g. acetophenone, benzophenone
- The common name for alkanone is obtained by naming the groups attached to the carbonyl carbon separately followed by the word ketones e.g. dimethylketone (acetone/propanone), methylethylketone (butan-2-one)
- Class work: Draw all the structures of all the compounds in the note text above

PREPARATION OF ALKANALS AND ALKANONES

- Oxidation of Alcohol
- Ozonolyis of Alkenes
- Reduction of Carboxylic acid
- Addition of water to Alkynes (Catalytic hydration of Alkynes)
- Alkanones are also be prepared by (i) decarboxylation of calcium salts (calcium alkanoate) (ii) decarboxylation of carboxylic acid (iii) reaction between alkanals and Grignard reagent

PHYSICAL PROPERTIES OF ALKANALS AND ALKANONES

- Simple aliphatic alkanals and alkanones with exception of methanol are all colourless liquids at 20 ^{0}C
- Lower molecular weight alkanals have sharp unpleasant sweet odours
- Alkanals and Alkanones with less than five carbon atoms are soluble in water due to hydrogen bonding between water molecules and the carbonyl oxygen. Although solubility decreases with increasing molecular mass.
- They have high boiling points than alkanes and other non polar compounds of comparative molecular weight due to their intermolecular attractions between both series of polar carbonyl compounds .
- They are considerably less volatile than the corresponding alkanals and alkanoic acid because their molecules are unable to form hydrogen bond with one another.

CHEMICAL PROPERTIES OF ALKANALS AND ALKANONES

- 1. Addition Reaction : (a) with Grignard reagents (b) with hydrogen cyanide
  (c) with sodium hydrogen sulphite (d) with ammonia
  (e) with alcohol
- 2. Condensation Reaction (addition-elimination reaction): (a) with methylamine
  (b) with hydrazine (c) with hydroxylamine (d) with phenylhydrazine
- 3. Aldol Condensation: Only carbonyl compounds with alpha hydrogen react to form dimers called aldol in the presence of alkali.
- 4. Oxidation Reaction: This is used to distinguished between alkanals and alkanones using oxidizing agents such as acidified KCr_2O_7 or $KMnO_4$, Nitric acid
  Alkanals are easily oxidized while alkanones are easily oxidized
- 5(a). Reduction Reaction: Alkanals and alkanones are easily reduced to primary and secondary alcohols respectively using reducing agents such as hydrogen, sodium borohydride and lithium aluminium hydride
- 5(b).Clemenson Reduction Reaction: In this case all carbonyl compounds are reduced to appropriate hydrocarbon using zinc amalgam and concentrated HCl
- 6. Canizarro Reaction: Only alkanals that lack alpha hydrogen undergo this reaction e.g. methanal and phenylmethanal. This reaction is a self oxidation-reduction reaction (disproportionation reaction) in the presence of aqueous solution (40-60%) of alkali at room temperature to produce appropriate salt of the carboxylic acid and an alcohol.

TAUTOMERISM

- This is a term used to describe the phenomenon whereby two species that are structural isomers co-exist in rapid equilibrium
- Such structural isomers are called tautomers
- Carbonyl compounds exhibit keto-enol tautomerism

TEST FOR ALKANALS AND ALKANONES

- Reducing tendency of alkanals make them distinguishable from alkanones
- Common tests/reagents used to differentiate them are:
  (a) Fehling test (b) Tollen test (Silver Mirror test) (c) Haloform reaction
- Fehling Test: A deep blue colouration of Fehling reagent turns reddish brown precipitate with aliphatic alkanals but ketones and aromatic alkanals give no positive reaction
- Tollen Test (Silver Mirror Test): Both aliphatic and aromatic alkanals reduce silver (I) ion to silver metal which is precipitate and form silver mirror effect in the bottom part of the test tube. But alkanones give no reaction with Tollen reagent
- Haloform Reaction: Ethanal, methylalkanone and alkanals having the structure $CH_3CH(OH)R$ are oxidized by halogen in alkaline solution to give haloform (CHX_3)- chloroform, bromoform or iodoform. But methanol and phenylmethanal cannot undergo haloform reaction

ALKANOIC ACID/CARBOXYLIC ACID

- Contains carboxyl functional group –COOH
- Two functional groups are contained in carboxyl- carbonyl (C=O)and hydroxyl (-OH)
- Saturated aliphatic alkanoic acids have general formula RCOOH (where R can be hydrogen or alkyl)
- Higher members of alkanoic acids that occur in natural fat(ester) or oil are called fatty acids e.g. palmitic acid, stearic acid, lauric acid etc
- Alkanoic acids that contain two carboxyl group in its molecule are called Alkanedioic acid or dicarboxylic acid e.g. ethanedioic acid (oxalic acid), propane-1,3-dioic acid (malonic acid)

NOMECLATURE OF ALKANOIC ACID

- IUPAC naming system takes after the names of the appropriate alkane
- Replace the ending '-e' in alkane with '-oic acid'
- Positions of the substitution are denoted by numbering the longest unbranched chain containg the carboxyl group e.g. 2-methylpropanoic acid $(CH_3)_2CHCOOH$, 2-phenylethanoic acid $C_6H_5CH_2COOH$
- Names of aromatic acids are related to the appropriate hydrocarbon e.g. benzoic acid C_6H_5COOH, toluic acid $C_6H_4(CH_3)COOH$

PHYSICAL PROPERTIES OF ALKANOIC ACIDS

- Lower members are liquids which completely miscible with water due to hydrogen bonding
- The higher members are waxy solids with decreasing water solubility
- The aromatic acids are crystalline solids sparing soluble in water but have higher melting points than their aliphatic counterparts of comparable molecular weight
- They have higher boiling point and increased water solubility than alkanals because its hydrogen bonding occurs with the hydroxyl group and the carbonyl group
- Boiling points of alkanoic acid increases as their molecular weight increases

Class discussion: EXPLAIN THE RESONANCE EFFECT IN ALKANOIC ACID (ACIDITY)

- PREPARATION OF ALKANOIC ACIDS

(A) Oxidation of alkanals and alkanals (B) Hydrolysis of Cyanides/Nitrile

(C) Reaction of Grignard reagent with carbondioxide

CHEMICAL PROPERTIES OF ALKANOIC ACID

- (I). Esterification (II). Reduction with $NaBH_4$ or $LiAlH_4$ (iii). Decarboxylation (iv)Kolbe Electrolysis

DERIVATIVES OF ALKANOIC ACIDS

- Derivatives of alkanoic acid are formed by replacing the hydroxyl group (-OH) with X giving a general formular RCOX where

X = OR for Alkanoates (Esters)

$X = NH_2$ for Amides

X= halogen for Acyl halides

X= -OOCR for anhydride

METHODS OF PREPARATION OFALKANOIC ACID DERIVATIVES

- Acyl halides and esters are prepared directly from alkanoic acid but others are prepared preferably from acyl halides by attacked of a nucleophile

(i) Acyl halides: prepared by reacting alkanoic acid with phosphorous halides (PX_5, PX_3, POX_3) and thionyl halide (SOX_2) $RCOOH \xrightarrow{PX_5} RCOX + POX_3 + HX$

(ii) Amides: prepared by reacting ammonia or amines with acyl halides. At times substituted amides are also produced $RCOX + NH_3 \rightarrow RCONH_2 + HX$

(III) Anhydrides: prepared by reacting two molecules of alkanoic acids with elimination of water molecule $RCOOH + HOOCR \rightarrow RCOOOCR + H_2O$ (Theoretically)

or $RCOONa + RCOX \rightarrow RCOOOCR + NaX$ (Practically)

(IV) Alkanoates: prepared by reacting alkanoic acid with alkanals in the presence of concentrated mineral acids $RCOOH + R_1OH \xrightarrow{HCl} RCOOR_1 + H_2O$

ALKANOATES / ESTERS

- Produce by esterification reaction.
- Name by replacing the '-ic' from alkanoic acid by '-ate' preceeding this the name of the alkyl or aryl group of the appropriate alkanol or phenol
- Examples of natural ester are fats and oils
- Simple esters are colourless liquids possessing pleasant fruity odour and used in scenting perfumes and flavouring food
- Ester of aliphatic carboxylic acids are soluble but their solubility decreases as molecular weight increases
- Esters of aromatic carboxylic acids are insoluble.

PREPARATION OF ALKANOATES

- Fischer-Speier Esterification $RCOOH + R_1OH \xrightarrow{H^+} RCOOR_1 + H_2O$
- From Acid chloride or acid anhydride $RCOCl + R_1OH \longrightarrow RCOOR_1 + HCl$

$(RCO)_2O + R_1OH \longrightarrow RCOOR_1 + RCOOH$

CHEMICAL PROPERTIES OF ALKANOATES

(I) Hydrolysis

(II) Reduction using $LiAlH_4$ and ether

(III) Ammonolysis (Amide formation)

(IV) Reduction with Grignard Reagent

ORGANIC CHEMISTRY
TEST 30minutes

- 1.(a) Draw the structure of the following compounds:
- (i) β-hydroxybutyraldehyde (ii) 4- hydroxyl-4-methylpentan-2-one (iii) phthalic acid (iv) diphenylketone (v) acetophenone
- (b) Explain why alkanoic acids, alkanoates, amides and acylhalides are not strictly considered as carbonyl compounds while alkanals and alkanones are considered as carbonyl compounds.
- 2. (a) Starting with a named alkene, explain how a mixture of acetone and
- formaldehyde can be synthesized together in a reaction.
- (b) Explain tautomerism and use acetone to illustrate keto-enol tautomerism
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