Chapter 8: Aldehydes, Ketones and Carboxylic Acids

Exercises — Exercises

Q1 What is meant by the following terms? Give an example of the reaction in each case.
(i) Cyanohydrin
(ii) Acetal
(iii) Semicarbazone
(iv) Aldol
(v) Hemiacetal
(vi) Oxime
(vii) Ketal
(viii) Imine
(ix) 2,4-DNP-derivative
(x) Schiff's base

SOLUTION

(i) Cyanohydrin:
A cyanohydrin is a compound having both -OH and -CN groups on the same carbon, formed by the addition of HCN to the carbonyl carbon of an aldehyde or ketone.
Example: $CH_3CHO + HCN \rightarrow CH_3CH(OH)CN$ (acetaldehyde cyanohydrin / 2-hydroxypropanenitrile)

(ii) Acetal:
An acetal is a compound in which the carbonyl carbon of an aldehyde is bonded to two -OR groups (from two alcohol molecules), formed by reaction with excess alcohol in the presence of an acid catalyst.
Example: $CH_3CHO + 2\ CH_3OH \xrightarrow{(H^+)} CH_3CH(OCH_3)_2 + H_2O$ (dimethyl acetal of ethanal / 1,1-dimethoxyethane)

(iii) Semicarbazone:
A semicarbazone is formed by the condensation reaction of a carbonyl compound (aldehyde or ketone) with semicarbazide ($H_2N\text{-}NH\text{-}CO\text{-}NH_2$). The product contains a $-C{=}N\text{-}NH\text{-}CO\text{-}NH_2$ linkage.
Example: $CH_3CHO + H_2N\text{-}NH\text{-}CO\text{-}NH_2 \rightarrow CH_3CH{=}N\text{-}NH\text{-}CO\text{-}NH_2 + H_2O$ (ethanal semicarbazone)

(iv) Aldol:

An aldol (from aldehyde + alcohol) is the product of an aldol addition reaction. It is a beta-hydroxy carbonyl compound formed when an enolate (or enol) of one carbonyl compound attacks the carbonyl carbon of another.
Example: 2 CH_3CHO --(dil. NaOH)--> $CH_3CH(OH)CH_2CHO$ (3-hydroxybutanal / acetaldol)

(v) Hemiacetal:
A hemiacetal is formed when one molecule of alcohol adds to the carbonyl group of an aldehyde. The product has both -OH and -OR groups on the same carbon.
Example: $CH_3CHO + CH_3OH \rightarrow CH_3CH(OH)(OCH_3)$ (methyl hemiacetal of ethanal)

(vi) Oxime:
An oxime is formed by the condensation of an aldehyde or ketone with hydroxylamine (H_2NOH). The product contains a -C=N-OH (imine/N-oxide) linkage.
Example: $CH_3COCH_3 + H_2NOH \rightarrow CH_3C(=NOH)CH_3 + H_2O$ (acetone oxime / propan-2-one oxime)

(vii) Ketal:
A ketal is formed when a ketone reacts with excess alcohol (or a diol) under acid catalysis to give a compound in which the carbonyl carbon is bonded to two -OR groups.
Example: $CH_3COCH_3 + 2\ C_2H_5OH$ --(H^+)--> $CH_3C(OC_2H_5)_2CH_3 + H_2O$ (diethyl ketal of acetone / 2,2-diethoxypropane)

(viii) Imine:
An imine (Schiff's base in a broader sense) is formed by the condensation of a primary amine with an aldehyde or ketone. The product has a C=N-R linkage (an azomethine).
Example: $CH_3CHO + C_6H_5NH_2 \rightarrow CH_3CH{=}N{-}C_6H_5 + H_2O$ (N-ethylideneaniline / N-benzylideneaniline for benzaldehyde)

(ix) 2,4-DNP derivative (2,4-Dinitrophenylhydrazone):
A 2,4-DNP derivative is formed by the condensation of an aldehyde or ketone with 2,4-dinitrophenylhydrazine. The yellow-to-orange precipitate of the hydrazone is used to characterise carbonyl compounds.
Example: $CH_3CHO + 2,4\text{-}(O_2N)_2C_6H_3NHNH_2 \rightarrow CH_3CH{=}N{-}NH{-}C_6H_3(NO_2)_2 + H_2O$

(x) Schiff's base:
A Schiff's base is an imine formed by the condensation of a primary amine

(especially an arylamine) with an aldehyde (or sometimes a ketone). The product has the general formula R-CH=N-R'.
Example: $C_6H_5CHO + H_2N\text{-}C_6H_5 \rightarrow C_6H_5CH=N\text{-}C_6H_5 + H_2O$ (N-benzylideneaniline)

Answer: (i) Cyanohydrin: -OH and -CN on same C; e.g., $CH_3CHO + HCN \rightarrow CH_3CH(OH)CN$. (ii) Acetal: two -OR on same C from aldehyde + 2 ROH; e.g., $CH_3CH(OCH_3)_2$. (iii) Semicarbazone: C=N-NHCONH$_2$; e.g., $CH_3CH=N\text{-}NHCONH_2$. (iv) Aldol: beta-hydroxy carbonyl compound; e.g., $CH_3CH(OH)CH_2CHO$. (v) Hemiacetal: -OH and -OR on same C; e.g., $CH_3CH(OH)(OCH_3)$. (vi) Oxime: C=N-OH; e.g., $(CH_3)_2C=NOH$. (vii) Ketal: two -OR on ketone carbon; e.g., $(CH_3)_2C(OC_2H_5)_2$. (viii) Imine: C=N-R; e.g., $CH_3CH=NC_6H_5$. (ix) 2,4-DNP: yellow/orange hydrazone precipitate. (x) Schiff's base: aryl imine; e.g., $C_6H_5CH=NC_6H_5$.

Q2 Name the following compounds according to IUPAC system of nomenclature:
(i) $CH_3CH(CH_3)CH_2CH_2CHO$
(ii) $CH_3CH_2COCH(C_2H_5)CH_2CH_2Cl$
(iii) $CH_3CH=CHCHO$
(iv) $CH_3COCH_2COCH_3$
(v) $CH_3CH(CH_3)CH_2C(CH_3)_2COCH_3$
(vi) $(CH_3)_3CCH_2COOH$
(vii) OHC-C_6H_4-CHO (para)

SOLUTION

(i) $CH_3CH(CH_3)CH_2CH_2CHO$:
Parent chain = pentanal (5 carbons ending in -CHO, numbering CHO as C-1).
Methyl substituent at C-4.
IUPAC name: 4-Methylpentanal

(ii) $CH_3CH_2CO\text{-}CH(C_2H_5)CH_2CH_2Cl$:
Structure: $CH_3\text{-}CH_2\text{-}CO\text{-}CH(C_2H_5)\text{-}CH_2\text{-}CH_2Cl$ (8 carbons total: the ethyl is a branch).
Longest chain through C=O: $Cl\text{-}CH_2\text{-}CH_2\text{-}CH(-)\text{-}CO\text{-}CH_2\text{-}CH_3$ = 6 carbons (hexanone); the ethyl on the alpha carbon is a substituent.
Number to give C=O the lowest locant: from the CH_3CH_2 end — $C_1=CH_3$, $C_2=CH_2$, $C_3=CO$, $C_4=CH$, $C_5=CH_2$, $C_6=CH_2Cl$.
Ketone at C-3, ethyl at C-4, chloro at C-6.

IUPAC name: 6-Chloro-4-ethylhexan-3-one

(iii) $CH_3CH=CHCHO$:
Parent chain = but-2-enal (4 carbons, double bond starting at C-2, aldehyde at C-1).
IUPAC name: But-2-enal

(iv) $CH_3CO\text{-}CH_2\text{-}CO\text{-}CH_3$:
Parent chain = pentane-2,4-dione (5 carbons, ketone groups at C-2 and C-4).
IUPAC name: Pentane-2,4-dione

(v) $CH_3CH(CH_3)CH_2C(CH_3)_2COCH_3$:
Structure: $CH_3\text{-}CO\text{-}C(CH_3)_2\text{-}CH_2\text{-}CH(CH_3)\text{-}CH_3$
Parent chain: number from the end giving $-CO^-$ lowest locant.
Chain: $CH_3(1)\text{-}CO(2)\text{-}C(CH_3)_2(3)\text{-}CH_2(4)\text{-}CH(CH_3)(5)\text{-}CH_3(6)$ = hexan-2-one
Substituents: two CH_3 at C-3 (3,3-dimethyl), one CH_3 at C-5 (5-methyl).
IUPAC name: 3,3,5-Trimethylhexan-2-one

(vi) $(CH_3)_3CCH_2COOH$:
Parent chain = propanoic acid? No. Chain: $COOH\text{-}CH_2\text{-}C(CH_3)_3$.
Longest chain: $C_1=COOH$, $C_2=CH_2$, $C_3=C(CH_3)_3$ => but with three methyls the longest single chain:
Actually longest chain through the neopentyl group: $HOOC\text{-}CH_2\text{-}C(CH_3)_3$.
$C_1=COOH$, $C_2=CH_2$, $C_3=C$, $C_4=CH_3$ = 4 carbons + 3 Me branches at C_3.
Or: longest chain including one methyl: $C_1=COOH$, $C_2=CH_2$, $C_3=C(CH_3)_2$, $C_4=CH_3$ = butanoic acid with 3,3-dimethyl
But longest carbon chain: $HOOC\text{-}CH_2\text{-}C(CH_3)_3$. C_3 has three methyls; longest single path = 4 C giving butanoic acid.
3,3-Dimethylbutanoic acid is the IUPAC name.
IUPAC name: 3,3-Dimethylbutanoic acid

(vii) $OHC\text{-}C_6H_4\text{-}CHO$ (para):
Benzene ring with two -CHO groups at para positions.
Parent: benzene-1,4-dicarbaldehyde (or terephthalaldehyde).
IUPAC name: Benzene-1,4-dicarbaldehyde

Answer: (i) 4-Methylpentanal (ii) 6-Chloro-4-ethylhexan-3-one (iii) But-2-enal (iv) Pentane-2,4-dione (v) 3,3,5-Trimethylhexan-2-one (vi) 3,3-Dimethylbutanoic acid (vii) Benzene-1,4-dicarbaldehyde

Q3 Draw the structures of the following compounds.

(i) 3-Methylbutanal

(ii) p-Nitropropiophenone

(iii) p-Methylbenzaldehyde

(iv) 4-Methylpent-3-en-2-one

(v) 4-Chloropentan-2-one

(vi) 3-Bromo-4-phenylpentanoic acid

(vii) p,p'-Dihydroxybenzophenone

(viii) Hex-2-en-4-ynoic acid

SOLUTION

(i) 3-Methylbutanal:

$(CH_3)_2CH\text{-}CH_2\text{-}CHO$

Parent chain 4 carbons (butanal); methyl at C-3.

(ii) p-Nitropropiophenone:

Propiophenone = $C_6H_5\text{-}CO\text{-}CH_2CH_3$; para-nitro substituent on the ring.

Structure: $O_2N\text{-}C_6H_4\text{-}CO\text{-}CH_2CH_3$ (NO_2 at position 4)

(iii) p-Methylbenzaldehyde:

Benzaldehyde with $-CH_3$ at para position.

Structure: $CH_3\text{-}C_6H_4\text{-}CHO$ (CH_3 at position 4)

(iv) 4-Methylpent-3-en-2-one:

Pent-3-en-2-one = $CH_3\text{-}CO\text{-}CH{=}CH\text{-}CH_3$; methyl at C-4.

Structure: $CH_3\text{-}CO\text{-}CH{=}C(CH_3)\text{-}CH_3$ (double bond between C-3 and C-4; C-4 carries CH_3)

(v) 4-Chloropentan-2-one:

Pentan-2-one = $CH_3\text{-}CO\text{-}CH_2\text{-}CH_2\text{-}CH_3$; Cl at C-4.

Structure: $CH_3\text{-}CO\text{-}CH_2\text{-}CHCl\text{-}CH_3$

(vi) 3-Bromo-4-phenylpentanoic acid:

Pentanoic acid chain; Br at C-3, phenyl at C-4.

Structure: $CH_3\text{-}CH(C_6H_5)\text{-}CHBr\text{-}CH_2\text{-}COOH$

(vii) p,p'-Dihydroxybenzophenone:

Benzophenone = $C_6H_5\text{-}CO\text{-}C_6H_5$; OH at para position of each ring.

Structure: $HO\text{-}C_6H_4\text{-}CO\text{-}C_6H_4\text{-}OH$ (4,4'-dihydroxybenzophenone)

(viii) Hex-2-en-4-ynoic acid:

Hexanoic acid with double bond at C_2-C_3 and triple bond at C_4-C_5.

Structure: HOOC-CH=CH-C≡C-CH_3

Answer: (i) $(CH_3)_2CH\text{-}CH_2\text{-}CHO$ (ii) $O_2N\text{-}C_6H_4\text{-}CO\text{-}CH_2CH_3$ (NO_2 para) (iii) $CH_3\text{-}C_6H_4\text{-}CHO$ (CH_3 para) (iv) $CH_3\text{-}CO\text{-}CH=C(CH_3)\text{-}CH_3$ (v) $CH_3\text{-}CO\text{-}CH_2\text{-}CHCl\text{-}CH_3$ (vi) $CH_3\text{-}CH(C_6H_5)\text{-}CHBr\text{-}CH_2\text{-}COOH$ (vii) $HO\text{-}C_6H_4\text{-}CO\text{-}C_6H_4\text{-}OH$ (OH para on both rings) (viii) HOOC-CH=CH-C≡C-CH_3

Q4 Write the IUPAC names of the following ketones and aldehydes. Wherever possible, give also common names.
(i) $CH_3CO(CH_2)_4CH_3$
(ii) $CH_3CH_2CHBrCH_2CH(CH_3)CHO$
(iii) $CH_3(CH_2)_5CHO$
(iv) Ph-CH=CH-CHO
(v) Cyclohexanecarbaldehyde
(vi) PhCOPh

SOLUTION

(i) $CH_3CO(CH_2)_4CH_3$:
Chain: $CH_3\text{-}CO\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$ = 7 carbons (heptan-2-one).
IUPAC: Heptan-2-one
Common name: Methyl n-amyl ketone (or methyl pentyl ketone)

(ii) $CH_3CH_2CHBrCH_2CH(CH_3)CHO$:
Longest chain with CHO: $CHO\text{-}CH(CH_3)\text{-}CH_2\text{-}CHBr\text{-}CH_2\text{-}CH_3$ = 6 carbons (hexanal).
Number from CHO (C-1): C_1=CHO, C_2=$CH(CH_3)$, C_3=CH_2, C_4=CHBr, C_5=CH_2, C_6=CH_3.
Substituents: 4-bromo, 2-methyl.
IUPAC: 4-Bromo-2-methylhexanal

(iii) $CH_3(CH_2)_5CHO$:
Chain: $CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CHO$ = 7 carbons (heptanal).
IUPAC: Heptanal
Common name: Heptaldehyde (or oenanthaldehyde)

(iv) Ph-CH=CH-CHO:
C_6H_5-CH=CH-CHO; parent chain = 3 carbons (prop-2-enal, CHO = C_1), phenyl at C_3.
IUPAC: 3-Phenylprop-2-enal

Common name: Cinnamaldehyde (or beta-phenylacrolein)

(v) Cyclohexanecarbaldehyde:
A cyclohexane ring bearing a -CHO group directly (as substituent).
The CHO is C-1 of the chain: this is a cycloalkane carbaldehyde.
IUPAC: Cyclohexanecarbaldehyde (the name is already IUPAC; ring = cyclohexane, suffix = carbaldehyde)
Structure: C_6H_{11}-CHO (cyclohexyl group with -CHO appended)

(vi) PhCOPh:
C_6H_5-CO-C_6H_5 = diphenyl ketone.
IUPAC: Diphenylmethanone (or diphenyl ketone)
Common name: Benzophenone

Answer: (i) Heptan-2-one (methyl n-amyl ketone) (ii) 4-Bromo-2-methylhexanal (iii) Heptanal (heptaldehyde) (iv) 3-Phenylprop-2-enal (cinnamaldehyde) (v) Cyclohexanecarbaldehyde (vi) Diphenylmethanone (benzophenone)

Q5 Draw structures of the following derivatives.
(i) The 2,4-dinitrophenylhydrazone of benzaldehyde
(ii) Cyclopropanone oxime
(iii) Acetaldehyde dimethyl acetal
(iv) The semicarbazone of cyclobutanone
(v) The ethylene ketal of hexan-3-one
(vi) The methyl hemiacetal of formaldehyde

SOLUTION

(i) 2,4-Dinitrophenylhydrazone of benzaldehyde:
Benzaldehyde (C_6H_5CHO) + 2,4-$(NO_2)_2C_6H_3NHNH_2$ -> C_6H_5CH=N-NH-$C_6H_3(NO_2)_2$ + H_2O
Structure: C_6H_5-CH=N-NH-C_6H_3(2,4-$(NO_2)_2$)

(ii) Cyclopropanone oxime:
Cyclopropanone (three-membered ring ketone, cyclo-C_2H_4CO) + H_2NOH -> cyclo-C_2H_4C(=NOH) + H_2O
Structure: cyclopropylidene-hydroxylamine; the ring C=O becomes C=N-OH.
Written as: C_3H_4=N-OH where C_3H_4 = cyclopropane ring carbon losing =O

(iii) Acetaldehyde dimethyl acetal:
$CH_3CHO + 2\ CH_3OH \xrightarrow{(H^+)} CH_3CH(OCH_3)_2 + H_2O$

Structure: CH_3-CH(OCH_3)$_2$ (1,1-dimethoxyethane)

(iv) Semicarbazone of cyclobutanone:
Cyclobutanone (4-membered ring C=O) + $H_2NNHCONH_2$ -> cyclobutylidene semicarbazone + H_2O
Structure: [cyclobutane ring]-C=N-NH-CO-NH_2 (the ring C=O becomes C=N-$NHCONH_2$)

(v) Ethylene ketal of hexan-3-one:
Hexan-3-one: CH_3CH_2-CO-$CH_2CH_2CH_3$; reaction with ethylene glycol ($HOCH_2CH_2OH$) under acid.
The C=O is replaced by a cyclic 1,3-dioxolane ring.
Structure: CH_3CH_2-C(OCH_2CH_2O)-$CH_2CH_2CH_3$ [2-ethyl-2-propyl-1,3-dioxolane]

(vi) Methyl hemiacetal of formaldehyde:
HCHO + CH_3OH -> HO-CH_2-OCH_3
Structure: HO-CH_2-OCH_3 (methoxymethanol)

Answer: (i) C_6H_5-CH=N-NH-C_6H_3(2,4-diNO_2) (ii) Cyclopropane ring C=N-OH (iii) $CH_3CH(OCH_3)_2$ (iv) Cyclobutane ring C=N-NH-CO-NH_2 (v) CH_3CH_2-C(OCH_2CH_2O)-$CH_2CH_2CH_3$ (cyclic 1,3-dioxolane) (vi) HO-CH_2-OCH_3

Q6 Predict the products formed when cyclohexanecarbaldehyde reacts with the following reagents.
(i) PhMgBr and then H_3O^+
(ii) Tollens' reagent
(iii) Semicarbazide and weak acid
(iv) Excess ethanol and acid
(v) Zinc amalgam and dilute hydrochloric acid

SOLUTION

Cyclohexanecarbaldehyde = C_6H_{11}-CHO (cyclohexane ring bearing -CHO).

(i) PhMgBr, then H_3O^+ (Grignard addition):
PhMgBr acts as a nucleophile; its Ph^(-) attacks the electrophilic carbonyl carbon.
Step 1: C_6H_{11}-CHO + PhMgBr -> C_6H_{11}-CH(OMgBr)-Ph (magnesium alkoxide)
Step 2: + H_3O^+ -> C_6H_{11}-CH(OH)-Ph + Mg(OH)Br
Product: Cyclohexyl(phenyl)methanol [a secondary alcohol]
C_6H_{11}-CH(OH)-C_6H_5

(ii) Tollens' reagent (ammoniacal $AgNO_3$):

Aldehydes are oxidised to carboxylate ions; Ag^+ is reduced to Ag (silver mirror).
$C_6H_{11}\text{-}CHO + 2[Ag(NH_3)_2]^+ + 2OH^- \rightarrow C_6H_{11}\text{-}COO^- + 2Ag(s) + 4NH_3 + H_2O$
Product: Cyclohexanecarboxylate ion (and silver mirror).
Organic product = Cyclohexanecarboxylic acid (after acidification).

(iii) Semicarbazide, weak acid:
Condensation with $H_2N\text{-}NH\text{-}CO\text{-}NH_2$ in weakly acidic medium.
$C_6H_{11}\text{-}CHO + H_2N\text{-}NH\text{-}CO\text{-}NH_2 \rightarrow C_6H_{11}\text{-}CH{=}N\text{-}NH\text{-}CO\text{-}NH_2 + H_2O$
Product: Cyclohexanecarbaldehyde semicarbazone

(iv) Excess ethanol, acid (acetal formation):
Aldehyde + 2 C_2H_5OH --(H^+)--> acetal + H_2O
$C_6H_{11}\text{-}CHO + 2\ C_2H_5OH \xrightarrow{(H^+)} C_6H_{11}\text{-}CH(OC_2H_5)_2 + H_2O$
Product: Cyclohexanecarbaldehyde diethyl acetal $[C_6H_{11}\text{-}CH(OC_2H_5)_2]$

(v) Zinc amalgam + dil. HCl (Clemmensen reduction):
The -CHO group is reduced to $-CH_3$ (or $-CH_2^-$ if on a chain).
$C_6H_{11}\text{-}CHO + 4[H] \xrightarrow{(Zn\text{-}Hg/HCl)} C_6H_{11}\text{-}CH_3 + H_2O$
Product: Methylcyclohexane

Answer: (i) $C_6H_{11}\text{-}CH(OH)\text{-}C_6H_5$ (secondary alcohol) (ii) Cyclohexanecarboxylic acid + Ag mirror (iii) $C_6H_{11}\text{-}CH{=}N\text{-}NHCONH_2$ (semicarbazone) (iv) $C_6H_{11}\text{-}CH(OC_2H_5)_2$ (diethyl acetal) (v) Methylcyclohexane (Clemmensen reduction)

Q7 Which of the following compounds would undergo aldol condensation, which the Cannizzaro reaction and which neither? Write the structures of the expected products of aldol condensation and Cannizzaro reaction.
(i) Methanal
(ii) 2-Methylpentanal
(iii) Benzaldehyde
(iv) Benzophenone
(v) Cyclohexanone
(vi) 1-Phenylpropanone
(vii) Phenylacetaldehyde
(viii) Butan-1-ol
(ix) 2,2-Dimethylbutanal

SOLUTION

Aldol condensation requires at least one alpha-H (H on carbon adjacent to C=O).

Cannizzaro reaction is shown by aldehydes WITHOUT alpha-H (disproportionation in conc. NaOH).
Ketones without alpha-H and alcohols do neither.

(i) Methanal (HCHO):
No alpha-carbon -> no alpha-H. Has C=O aldehyde. -> Cannizzaro reaction.
2 HCHO + NaOH -> CH_3OH + HCOONa (methanol + sodium formate)

(ii) 2-Methylpentanal ($CH_3CH_2CH_2CH(CH_3)CHO$):
Has alpha-H (on C-2, the CH carbon adjacent to CHO). -> Aldol condensation.
Product: 2-Methylpentanal aldol beta-hydroxy aldehyde.
Self-aldol: $CH_3CH_2CH_2CH(CH_3)CHO$ + base -> enolate attacks another molecule's CHO.
Product: 2,4-dimethyl-3-hydroxyheptanal (after cross addition; exact structure from two 2-methylpentanal units:
$CH_3CH_2CH_2CH(CH_3)CH(OH)$-$C(CH_3)(CH_2CH_2CH_3)$-CHO

(iii) Benzaldehyde (C_6H_5CHO):
No alpha-H (alpha carbon is the ring carbon, no H). -> Cannizzaro reaction.
2 C_6H_5CHO + NaOH -> $C_6H_5CH_2OH$ + C_6H_5COONa (benzyl alcohol + sodium benzoate)

(iv) Benzophenone (C_6H_5-CO-C_6H_5):
Ketone with no alpha-H (both alpha carbons are aromatic ring carbons, no H).
Does neither aldol condensation nor Cannizzaro reaction. -> Neither

(v) Cyclohexanone:
Has alpha-H (CH_2 groups adjacent to C=O on the ring). -> Aldol condensation.
Self-aldol product: 2-(1-hydroxycyclohexyl)cyclohexan-1-one (beta-hydroxy ketone).
Condensation product (after dehydration): 2-cyclohexylidenecyclohexan-1-one

(vi) 1-Phenylpropanone (C_6H_5-CO-CH_2CH_3):
Has alpha-H (on the -CH_2^- adjacent to C=O). -> Aldol condensation.
Self-aldol product: C_6H_5-CO-$CH(CH_3)$-$C(OH)(CH_3)$-CO-C_6H_5 (beta-hydroxy diketone type),
or more precisely, enolate of the CH_2 attacks the C=O of another molecule.
Product: C_6H_5CO-$CH(CH_3)$-$CH(OH)$-CO-C_6H_5 (a beta-hydroxy diketone) on dehydration -> C_6H_5CO-$C(CH_3)$=C-CO-C_6H_5

(vii) Phenylacetaldehyde (C_6H_5-CH_2-CHO):

Has alpha-H (on -CH_2^- adjacent to CHO). -> Aldol condensation.
Self-aldol: two molecules condensing; enolate (C_6H_5-CH^(-)-CHO) attacks $C_6H_5CH_2CHO$.
Product (aldol): $C_6H_5CH_2CH(OH)CH(C_6H_5)CHO$
Dehydration product: $C_6H_5CH_2$-CH=C(C_6H_5)-CHO (conjugated)

(viii) Butan-1-ol ($CH_3CH_2CH_2CH_2OH$):
An alcohol, not a carbonyl compound. -> Neither aldol condensation nor Cannizzaro reaction.

(ix) 2,2-Dimethylbutanal ($CH_3CH_2C(CH_3)_2CHO$):
Alpha-carbon is $C(CH_3)_2$ with NO alpha-H (fully substituted). -> Cannizzaro reaction.
2 $(CH_3)_2(C_2H_5)$C-CHO + NaOH -> $(CH_3)_2(C_2H_5)$C-CH_2OH + $(CH_3)_2(C_2H_5)$C-COONa

Answer: Aldol condensation: (ii) 2-Methylpentanal, (v) Cyclohexanone, (vi) 1-Phenylpropanone, (vii) Phenylacetaldehyde. Cannizzaro reaction: (i) Methanal, (iii) Benzaldehyde, (ix) 2,2-Dimethylbutanal. Neither: (iv) Benzophenone (no alpha-H ketone), (viii) Butan-1-ol (alcohol).

Q8 How will you convert ethanal into the following compounds?
(i) Butane-1,3-diol
(ii) But-2-enal
(iii) But-2-enoic acid

SOLUTION

Starting material: CH_3CHO (ethanal).

(i) Butane-1,3-diol:
Step 1: Aldol condensation of 2 mol ethanal under dil. NaOH -> 3-Hydroxybutanal (aldol product).
2 CH_3CHO --(dil. NaOH)--> $CH_3CH(OH)CH_2CHO$
Step 2: Reduction of 3-hydroxybutanal with $NaBH_4$ (or $LiAlH_4$) reduces CHO to CH_2OH.
$CH_3CH(OH)CH_2CHO$ + 2[H] --($NaBH_4$)--> $CH_3CH(OH)CH_2CH_2OH$
Product: Butane-1,3-diol ($CH_3CH(OH)CH_2CH_2OH$).

(ii) But-2-enal:
Aldol condensation of 2 mol ethanal, then dehydration of the aldol product.
Step 1: 2 CH_3CHO --(dil. NaOH)--> $CH_3CH(OH)CH_2CHO$ (3-hydroxybutanal)

Step 2: Dehydration by heat or dilute acid -> $CH_3CH=CHCHO + H_2O$
Product: But-2-enal (crotonaldehyde).

(iii) But-2-enoic acid:
Step 1 & 2: As in (ii), form but-2-enal: $CH_3CH=CHCHO$.
Step 3: Oxidation of but-2-enal with $KMnO_4$ or Ag_2O -> $CH_3CH=CHCOOH$
Product: But-2-enoic acid (crotonic acid).
Alternatively from (ii): oxidise but-2-enal with Tollens' reagent or alkaline $KMnO_4$ -> but-2-enoic acid.

Answer: (i) Ethanal --aldol--> 3-hydroxybutanal --$NaBH_4$--> butane-1,3-diol. (ii) Ethanal --aldol--> 3-hydroxybutanal --heat/acid--> but-2-enal ($CH_3CH=CHCHO$). (iii) Ethanal --aldol/dehydration--> but-2-enal --[O]--> but-2-enoic acid ($CH_3CH=CHCOOH$).

Q9 Write structural formulas and names of four possible aldol condensation products from propanal and butanal. In each case, indicate which aldehyde acts as nucleophile and which as electrophile.

SOLUTION

Cross aldol condensation between propanal (CH_3CH_2CHO) and butanal ($CH_3CH_2CH_2CHO$).
The enolate (nucleophile) from one aldehyde attacks the carbonyl (electrophile) of the other.

Enolate from propanal: $CH_3CH^(-)CHO$ (alpha-C of propanal)
Enolate from butanal: $CH_3CH_2CH^(-)CHO$ (alpha-C of butanal)

Product 1: Propanal as nucleophile + Propanal as electrophile (self-aldol of propanal):
$CH_3CH^(-)-CHO + CH_3CH_2CHO \rightarrow CH_3CH_2CH(OH)-CH(CH_3)-CHO$
Name: 2-Methyl-3-hydroxypentanal
(Nucleophile: propanal; Electrophile: propanal)

Product 2: Butanal as nucleophile + Butanal as electrophile (self-aldol of butanal):
$CH_3CH_2CH^(-)-CHO + CH_3CH_2CH_2CHO \rightarrow CH_3CH_2CH_2CH(OH)-CH(CH_2CH_3)-CHO$
Name: 2-Ethyl-3-hydroxyhexanal
(Nucleophile: butanal; Electrophile: butanal)

Product 3: Propanal as nucleophile + Butanal as electrophile (cross aldol):

$CH_3CH^{(-)}-CHO + CH_3CH_2CH_2CHO \rightarrow CH_3CH_2CH_2CH(OH)-CH(CH_3)-CHO$
Name: 2-Methyl-3-hydroxyhexanal
(Nucleophile: propanal; Electrophile: butanal)

Product 4: Butanal as nucleophile + Propanal as electrophile (cross aldol):
$CH_3CH_2CH^{(-)}-CHO + CH_3CH_2CHO \rightarrow CH_3CH_2CH(OH)-CH(CH_2CH_3)-CHO$
Name: 2-Ethyl-3-hydroxypentanal
(Nucleophile: butanal; Electrophile: propanal)

Answer: Four aldol products: (1) 2-Methyl-3-hydroxypentanal (propanal + propanal, self-aldol), (2) 2-Ethyl-3-hydroxyhexanal (butanal + butanal, self-aldol), (3) 2-Methyl-3-hydroxyhexanal (propanal nucleophile + butanal electrophile), (4) 2-Ethyl-3-hydroxypentanal (butanal nucleophile + propanal electrophile).

Q10 An organic compound with the molecular formula $C_9H_{10}O$ forms 2,4-DNP derivative, reduces Tollens' reagent and undergoes Cannizzaro reaction. On vigorous oxidation, it gives 1,2-benzenedicarboxylic acid. Identify the compound.

SOLUTION

Given data:
- Molecular formula: $C_9H_{10}O$
- Forms 2,4-DNP derivative -> contains C=O group
- Reduces Tollens' reagent -> is an aldehyde
- Cannizzaro reaction -> no alpha-H (no H on C adjacent to CHO)
- Vigorous oxidation gives 1,2-benzenedicarboxylic acid (phthalic acid) -> ortho-disubstituted benzene ring

Analysis:
Phthalic acid ($1,2\text{-}C_6H_4(COOH)_2$) arises from oxidation of both substituents on an ortho-benzene ring.
The compound has: benzene ring (6C) + CHO (1C, 1O) + remaining = 2C with 10H.
The extra 2 carbons must be on the ring as an ethyl ($-C_2H_5$) substituent at the ortho position.

Proposed structure: 2-Ethylbenzaldehyde (o-ethylbenzaldehyde)
Structure: CHO and C_2H_5 both attached to benzene ring at ortho (1,2) positions.
Formula check: $C_6H_4 + CHO + C_2H_5 = C_9H_{10}O$ ✓

Verification:

- Aldehyde (CHO) -> 2,4-DNP derivative ✓, Tollens' positive ✓
- No alpha-H on carbon adjacent to CHO (the adjacent C is a ring carbon with no H) -> Cannizzaro ✓
- Vigorous oxidation: CHO -> COOH and C_2H_5 -> COOH (side-chain oxidation) Gives 1,2-benzenedicarboxylic acid (phthalic acid) ✓

Answer: The compound is 2-Ethylbenzaldehyde (o-ethylbenzaldehyde). Structure: ortho-C_2H_5-C_6H_4-CHO. Formula $C_9H_{10}O$; aldehyde (Tollens'+, 2,4-DNP$^+$); no alpha-H to CHO (Cannizzaro); vigorous oxidation gives phthalic acid.

Q11 An organic compound (A) (molecular formula $C_8H_{16}O_2$) was hydrolysed with dilute sulphuric acid to give a carboxylic acid (B) and an alcohol (C). Oxidation of (C) with chromic acid produced (B). (C) on dehydration gives but-1-ene. Write equations for the reactions involved.

SOLUTION

Step 1: Identify alcohol C.
(C) on dehydration gives but-1-ene (CH_2=CH-CH_2-CH_3).
Dehydration gives but-1-ene => C is butan-1-ol: $CH_3CH_2CH_2CH_2OH$.
(Butan-1-ol dehydrates preferentially to but-1-ene via Zaitsev/Hofmann; primary alcohols give terminal alkene.)

Step 2: Identify acid B.
Oxidation of C (butan-1-ol) with CrO_3/H_2SO_4 (chromic acid) gives B.
$CH_3CH_2CH_2CH_2OH$ + [O] -> $CH_3CH_2CH_2COOH$ (butanoic acid)
So B = butanoic acid ($CH_3CH_2CH_2COOH$).

Step 3: Identify ester A.
A ($C_8H_{16}O_2$) hydrolyses to B (butanoic acid, $C_4H_8O_2$) + C (butan-1-ol, $C_4H_{10}O$).
Ester A = n-butyl butanoate: $CH_3CH_2CH_2COO$-$CH_2CH_2CH_2CH_3$.
Formula check: C_4H_7O (butanoyl) + OC_4H_9 (n-butoxy) = $C_8H_{16}O_2$ ✓

Equations:
1. Hydrolysis of A:
$CH_3CH_2CH_2COOCH_2CH_2CH_2CH_3 + H_2O$ --(dil. H_2SO_4)--> $CH_3CH_2CH_2COOH + CH_3CH_2CH_2CH_2OH$

2. Oxidation of C to B:
$CH_3CH_2CH_2CH_2OH$ + [O] --(CrO_3/H_2SO_4)--> $CH_3CH_2CH_2COOH + H_2O$

3. Dehydration of C:

$CH_3CH_2CH_2CH_2OH$ --(conc. H_2SO_4, 170°C)--> $CH_2=CHCH_2CH_3$ + H_2O

Answer: A = n-Butyl butanoate ($CH_3CH_2CH_2COOCH_2CH_2CH_2CH_3$), B = Butanoic acid ($CH_3CH_2CH_2COOH$), C = Butan-1-ol ($CH_3CH_2CH_2CH_2OH$). Reactions: (1) A + H_2O/H_2SO_4 -> B + C; (2) C + [O]/CrO_3 -> B + H_2O; (3) C/H_2SO_4, heat -> but-1-ene + H_2O.

Q12 Arrange the following compounds in increasing order of their property as indicated:
(i) Acetaldehyde, Acetone, Di-tert-butyl ketone, Methyl tert-butyl ketone (reactivity towards HCN)
(ii) $CH_3CH_2CH(Br)COOH$, $CH_3CH(Br)CH_2COOH$, $(CH_3)_2CHCOOH$, $CH_3CH_2CH_2COOH$ (acid strength)
(iii) Benzoic acid, 4-Nitrobenzoic acid, 3,4-Dinitrobenzoic acid, 4-Methoxybenzoic acid (acid strength)

SOLUTION

(i) Reactivity towards HCN (nucleophilic addition):
Factors: (a) electrophilicity of carbonyl C (electron-withdrawing groups increase, electron-donating decrease); (b) steric hindrance (bulkier groups decrease reactivity).
- Acetaldehyde (CH_3CHO): one small methyl group, aldehyde (more electrophilic than ketone) -> most reactive.
- Acetone (CH_3COCH_3): two methyl groups (electron-donating), ketone -> less reactive than aldehyde.
- Methyl tert-butyl ketone ($CH_3CO-C(CH_3)_3$): one methyl + one bulky tert-butyl -> steric hindrance high.
- Di-tert-butyl ketone ($(CH_3)_3C-CO-C(CH_3)_3$): two bulky tert-butyl groups -> most hindered, least reactive.
Increasing order:
Di-tert-butyl ketone < Methyl tert-butyl ketone < Acetone < Acetaldehyde

(ii) Acid strength of alpha-bromobutyric acids:
Br is an electron-withdrawing group (inductive effect). Closer to -COOH = stronger effect = more acidic.
- $CH_3CH_2CH(Br)COOH$: Br at alpha (C-2), closest to COOH -> strongest acid.
- $CH_3CH(Br)CH_2COOH$: Br at beta (C-3), further from COOH -> intermediate.
- $CH_3CH_2CH_2COOH$: no Br (n-butanoic acid) -> weakest of the two bromine-free.

- $(CH_3)_2CHCOOH$: isobutyric acid; alpha-methyl groups are slightly electron-donating -> weakest acid.

Increasing order:

$(CH_3)_2CHCOOH$ < $CH_3CH_2CH_2COOH$ < $CH_3CH(Br)CH_2COOH$ < $CH_3CH_2CH(Br)COOH$

(iii) Acid strength of substituted benzoic acids:

Electron-withdrawing groups (EWG) stabilise the carboxylate anion -> stronger acid.

Electron-donating groups (EDG) destabilise the anion -> weaker acid.

- 4-Methoxybenzoic acid: $-OCH_3$ is EDG (resonance donor) -> weakest acid.
- Benzoic acid: no substituent -> reference.
- 4-Nitrobenzoic acid: $-NO_2$ at para is EWG -> stronger than benzoic acid.
- 3,4-Dinitrobenzoic acid: two $-NO_2$ groups -> strongest acid.

Increasing order:

4-Methoxybenzoic acid < Benzoic acid < 4-Nitrobenzoic acid < 3,4-Dinitrobenzoic acid

Answer: (i) Di-tert-butyl ketone < Methyl tert-butyl ketone < Acetone < Acetaldehyde (ii) $(CH_3)_2CHCOOH$ < $CH_3CH_2CH_2COOH$ < $CH_3CH(Br)CH_2COOH$ < $CH_3CH_2CH(Br)COOH$ (iii) 4-Methoxybenzoic acid < Benzoic acid < 4-Nitrobenzoic acid < 3,4-Dinitrobenzoic acid

---

Q13 Give simple chemical tests to distinguish between the following pairs of compounds.

(i) Propanal and Propanone

(ii) Acetophenone and Benzophenone

(iii) Phenol and Benzoic acid

(iv) Benzoic acid and Ethyl benzoate

(v) Pentan-2-one and Pentan-3-one

(vi) Benzaldehyde and Acetophenone

(vii) Ethanal and Propanal

SOLUTION

(i) Propanal (CH_3CH_2CHO) vs Propanone (CH_3COCH_3):

Test: Tollens' reagent (ammoniacal $AgNO_3$) or Fehling's solution.

Propanal (aldehyde): gives silver mirror (Tollens') or brick-red precipitate (Fehling's).

Propanone (ketone): no reaction with Tollens' or Fehling's.

(ii) Acetophenone ($C_6H_5COCH_3$) vs Benzophenone ($C_6H_5COC_6H_5$):
Test: Iodoform test (I_2/NaOH).
Acetophenone has a -$COCH_3$ (methyl ketone) group -> gives yellow iodoform precipitate (CHI_3).
Benzophenone has no alpha-H / no -$COCH_3$ -> no iodoform.

(iii) Phenol (C_6H_5OH) vs Benzoic acid (C_6H_5COOH):
Test: Add $NaHCO_3$ solution.
Benzoic acid: reacts with $NaHCO_3$ to give CO_2 gas (effervescence).
$C_6H_5COOH + NaHCO_3 \rightarrow C_6H_5COONa + H_2O + CO_2\uparrow$
Phenol: does NOT react with $NaHCO_3$ (too weak an acid; pKa ~10 vs CO_3^{2-} pKa ~6.3).

(iv) Benzoic acid (C_6H_5COOH) vs Ethyl benzoate ($C_6H_5COOC_2H_5$):
Test: Add $NaHCO_3$ or Na_2CO_3 solution.
Benzoic acid: dissolves with effervescence (CO_2) and gives a clear solution.
Ethyl benzoate (ester): does not dissolve in $NaHCO_3$; no effervescence.
(Alternative: Litmus — benzoic acid turns blue litmus red; ester does not.)

(v) Pentan-2-one ($CH_3COCH_2CH_2CH_3$) vs Pentan-3-one ($CH_3CH_2COCH_2CH_3$):
Test: Iodoform test (I_2/NaOH).
Pentan-2-one: has -$COCH_3$ (methyl ketone) -> positive iodoform test (yellow CHI_3 precipitate).
Pentan-3-one: no -$COCH_3$ group -> negative iodoform test.

(vi) Benzaldehyde (C_6H_5CHO) vs Acetophenone ($C_6H_5COCH_3$):
Test: Tollens' reagent (ammoniacal $AgNO_3$).
Benzaldehyde (aldehyde): gives silver mirror.
Acetophenone (ketone): no reaction with Tollens' reagent.
(Also: Schiff's test — benzaldehyde restores the pink colour of Schiff's reagent; acetophenone does not.)

(vii) Ethanal (CH_3CHO) vs Propanal (CH_3CH_2CHO):
Test: Iodoform test (I_2/NaOH).
Ethanal (CH_3CHO): has -$COCH_3$ group -> gives yellow iodoform precipitate (CHI_3).
Propanal (CH_3CH_2CHO): no -$COCH_3$ -> no iodoform precipitate.
(Both are aldehydes and give Tollens'/Fehling's positive, so that test does NOT distinguish them.)

Answer: (i) Tollens' reagent: propanal gives Ag mirror, propanone does not. (ii) Iodoform test: acetophenone (CH_3CO^-) gives CHI_3, benzophenone does not. (iii) $NaHCO_3$: benzoic acid gives CO_2, phenol does not. (iv) $NaHCO_3$: benzoic acid dissolves with CO_2, ethyl benzoate does not. (v) Iodoform: pentan-2-one (CH_3CO^-) positive, pentan-3-one negative. (vi) Tollens': benzaldehyde gives Ag mirror, acetophenone does not. (vii) Iodoform: ethanal positive, propanal negative.

Q14 How will you prepare the following compounds from benzene? You may use any inorganic reagent and any organic reagent having not more than one carbon atom.
(i) Methyl benzoate
(ii) m-Nitrobenzoic acid
(iii) p-Nitrobenzoic acid
(iv) Phenylacetic acid
(v) p-Nitrobenzaldehyde

SOLUTION

(i) Methyl benzoate ($C_6H_5COOCH_3$):
Step 1: Benzene + CH_3Cl + $AlCl_3$ (Friedel-Crafts alkylation) -> Toluene ($C_6H_5CH_3$).
Step 2: Toluene + $KMnO_4$ (alk.) -> Benzoic acid (C_6H_5COOH) [oxidation of $-CH_3$ to -COOH].
Step 3: Benzoic acid + CH_3OH (methanol) + conc. H_2SO_4 (Fischer esterification) -> Methyl benzoate ($C_6H_5COOCH_3$) + H_2O.

(ii) m-Nitrobenzoic acid:
Strategy: introduce -COOH first (directing to meta for $-NO_2$), then nitrate.
Step 1: Benzene + CH_3Cl + $AlCl_3$ -> Toluene.
Step 2: Toluene + $KMnO_4/OH^(-)$ -> Benzoic acid.
Step 3: Benzoic acid + HNO_3 + conc. H_2SO_4 (nitration) -> m-Nitrobenzoic acid.
(-COOH is meta-director; nitration gives predominantly meta-nitro product.)

(iii) p-Nitrobenzoic acid:
Strategy: introduce $-CH_3$ (ortho/para director) first, then nitrate to get p-nitrotoluene, then oxidise.
Step 1: Benzene + CH_3Cl + $AlCl_3$ -> Toluene.
Step 2: Toluene + HNO_3 + H_2SO_4 -> p-Nitrotoluene (major para product).
Step 3: p-Nitrotoluene + $KMnO_4$ (alk.) -> p-Nitrobenzoic acid.

(iv) Phenylacetic acid ($C_6H_5CH_2COOH$):

Strategy: need to add -CH_2COOH side chain.
Step 1: Benzene + CH_3Cl + $AlCl_3$ -> Toluene.
Step 2: Toluene + Cl_2 (hv, radical halogenation) -> Benzyl chloride ($C_6H_5CH_2Cl$).
Step 3: Benzyl chloride + NaCN -> Benzyl cyanide ($C_6H_5CH_2CN$).
Step 4: Benzyl cyanide + H_2O + H^+ (acid hydrolysis) -> Phenylacetic acid ($C_6H_5CH_2COOH$).
(Organic reagents used: CH_3Cl (one carbon), NaCN (one carbon, as -CN) — both ≤ 1 carbon.)

(v) p-Nitrobenzaldehyde:
Strategy: introduce -CHO at para to $-NO_2$ on the ring.
Step 1: Benzene + CH_3Cl + $AlCl_3$ -> Toluene.
Step 2: Toluene + HNO_3 + H_2SO_4 -> p-Nitrotoluene (major para product).
Step 3: p-Nitrotoluene + $CrO_3/(CH_3CO)_2O$ -> p-nitrobenzylidene diacetate, then hydrolysis (H_3O^+) -> p-Nitrobenzaldehyde. (The acetic anhydride protects the aldehyde as the diacetate, preventing over-oxidation to the acid; chromyl chloride CrO_2Cl_2 in the Étard reaction is an equivalent selective route.)

Answer: (i) Benzene -> toluene ($CH_3Cl/AlCl_3$) -> benzoic acid ($KMnO_4$) -> methyl benzoate (CH_3OH/H_2SO_4). (ii) Benzene -> toluene -> benzoic acid -> m-nitrobenzoic acid (HNO_3/H_2SO_4; -COOH is m-director). (iii) Benzene -> toluene -> p-nitrotoluene (HNO_3/H_2SO_4) -> p-nitrobenzoic acid ($KMnO_4$). (iv) Benzene -> toluene -> benzyl chloride (Cl_2/hv) -> benzyl cyanide (NaCN) -> phenylacetic acid (H_3O^+). (v) Benzene -> toluene -> p-nitrotoluene -> p-nitrobenzaldehyde (oxidation, e.g. CrO_3/Ac_2O).

Q15 How will you bring about the following conversions in not more than two steps?
(i) Propanone to Propene
(ii) Benzoic acid to Benzaldehyde
(iii) Ethanol to 3-Hydroxybutanal
(iv) Benzene to m-Nitroacetophenone
(v) Benzaldehyde to Benzophenone
(vi) Bromobenzene to 1-Phenylethanol
(vii) Benzaldehyde to 3-Phenylpropan-1-ol
(viii) Benzaldehyde to alpha-Hydroxyphenylacetic acid
(ix) Benzoic acid to m-Nitrobenzyl alcohol

SOLUTION

(i) Propanone to Propene:
Step 1: CH_3COCH_3 + $NaBH_4$ (reduction of C=O) -> $CH_3CH(OH)CH_3$ (propan-2-ol)
Step 2: $CH_3CH(OH)CH_3$ + conc. H_2SO_4, 170°C (dehydration) -> $CH_3CH=CH_2$ + H_2O (propene)

(ii) Benzoic acid to Benzaldehyde:
Step 1: Benzoic acid + $SOCl_2$ -> Benzoyl chloride (C_6H_5COCl) + SO_2 + HCl
Step 2: Benzoyl chloride + H_2 / Pd-$BaSO_4$ (Rosenmund reduction) -> Benzaldehyde (C_6H_5CHO) + HCl

(iii) Ethanol to 3-Hydroxybutanal:
Step 1: Ethanol + [O] (PCC or CrO_3/pyridine, or $K_2Cr_2O_7/H_2SO_4$ in mild conditions) -> Ethanal (CH_3CHO)
Step 2: 2 CH_3CHO + dil. NaOH (aldol condensation) -> $CH_3CH(OH)CH_2CHO$ (3-Hydroxybutanal)

(iv) Benzene to m-Nitroacetophenone:
Step 1: Benzene + CH_3COCl + $AlCl_3$ (Friedel-Crafts acylation) -> Acetophenone ($C_6H_5COCH_3$)
Step 2: Acetophenone + HNO_3 + H_2SO_4 (nitration) -> m-Nitroacetophenone
(-$COCH_3$ is meta-director; nitration gives meta product predominantly.)

(v) Benzaldehyde to Benzophenone:
Step 1: Benzaldehyde + PhMgBr (Grignard) -> Ph-CH(OH)-Ph (benzhydrol / diphenylmethanol)
Step 2: Ph-CH(OH)-Ph + [O] ($KMnO_4$ or CrO_3) -> Ph-CO-Ph (benzophenone)

(vi) Bromobenzene to 1-Phenylethanol:
Step 1: Bromobenzene + Mg / dry ether -> Phenylmagnesium bromide (PhMgBr, Grignard reagent)
Step 2: PhMgBr + CH_3CHO (ethanal) -> [hydrolysis with H_3O^+] -> $C_6H_5CH(OH)CH_3$ (1-Phenylethanol)

(vii) Benzaldehyde to 3-Phenylpropan-1-ol:
Step 1: C_6H_5CHO + CH_3CHO (dil. NaOH, cross aldol) -> $C_6H_5CH=CHCHO$ (Cinnamaldehyde, 3-phenylprop-2-enal)
Step 2: Cinnamaldehyde + 2 H_2 (H_2/Ni, catalytic hydrogenation) -> $C_6H_5CH_2CH_2CH_2OH$ (3-Phenylpropan-1-ol). (Catalytic hydrogenation reduces both the C=C and the C=O; $LiAlH_4$ would reduce only the C=O and leave the

double bond.)

(viii) Benzaldehyde to alpha-Hydroxyphenylacetic acid (mandelic acid):
Step 1: $C_6H_5CHO + HCN \rightarrow C_6H_5CH(OH)CN$ (cyanohydrin of benzaldehyde)
Step 2: $C_6H_5CH(OH)CN + H_2O + H^+$ (acid hydrolysis of nitrile) -> $C_6H_5CH(OH)COOH$ (mandelic acid)

(ix) Benzoic acid to m-Nitrobenzyl alcohol:
Step 1: Benzoic acid + $HNO_3 + H_2SO_4$ -> m-Nitrobenzoic acid (-COOH is m-director)
Step 2: m-Nitrobenzoic acid + $LiAlH_4$ (reduction of -COOH to $-CH_2OH$, in dry ether) -> m-Nitrobenzyl alcohol ($O_2N-C_6H_4-CH_2OH$)

Answer: (i) $CH_3COCH_3 + NaBH_4$ -> propan-2-ol; propan-2-ol + H_2SO_4/heat -> propene. (ii) $C_6H_5COOH + SOCl_2$ -> C_6H_5COCl; + H_2/Pd-$BaSO_4$ -> C_6H_5CHO. (iii) Ethanol + [O] -> ethanal; 2 CH_3CHO + NaOH -> 3-hydroxybutanal. (iv) Benzene + $CH_3COCl/AlCl_3$ -> acetophenone; + HNO_3/H_2SO_4 -> m-nitroacetophenone. (v) C_6H_5CHO + PhMgBr -> benzhydrol; + [O] -> benzophenone. (vi) C_6H_5Br + Mg -> PhMgBr; + CH_3CHO -> $C_6H_5CH(OH)CH_3$. (vii) $C_6H_5CHO + CH_3CHO$/NaOH -> cinnamaldehyde; + H_2/Ni -> 3-phenylpropan-1-ol. (viii) C_6H_5CHO + HCN -> cyanohydrin; + H_3O^+ -> mandelic acid. (ix) $C_6H_5COOH + HNO_3/H_2SO_4$ -> m-nitrobenzoic acid; + $LiAlH_4$ -> m-nitrobenzyl alcohol.

Q16 Describe the following:
(i) Acetylation
(ii) Cannizzaro reaction
(iii) Cross aldol condensation
(iv) Decarboxylation

SOLUTION

(i) Acetylation:
Acetylation is the introduction of an acetyl group ($-COCH_3$) into an organic molecule, typically replacing an active hydrogen (on -OH, $-NH_2$, or -SH) with $-COCH_3$.
Reagents used: acetic anhydride $(CH_3CO)_2O$ or acetyl chloride (CH_3COCl), often with a base.
Example: $C_6H_5OH + (CH_3CO)_2O$ -> $C_6H_5OOCCH_3 + CH_3COOH$ (phenol -> phenyl acetate)
Another example: R-OH + CH_3COCl -> $R-OOCCH_3$ + HCl (esterification /

acetylation of alcohol)

(ii) Cannizzaro reaction:
The Cannizzaro reaction is the disproportionation of an aldehyde lacking alpha-hydrogen atoms when treated with concentrated sodium hydroxide. One molecule is oxidised to the carboxylic acid (or its salt) and another is reduced to the alcohol.
Condition: no alpha-H; conc. NaOH.
Mechanism: OH^- adds to C=O of one molecule forming a tetrahedral intermediate; hydride transfer from this to another aldehyde molecule.
Example: 2 HCHO + NaOH -> CH_3OH + HCOONa (formaldehyde -> methanol + sodium formate)
Example: 2 C_6H_5CHO + NaOH -> $C_6H_5CH_2OH$ + C_6H_5COONa (Cannizzaro of benzaldehyde)

(iii) Cross aldol condensation:
Cross aldol condensation occurs between two different carbonyl compounds (aldehydes/ketones), each possessing alpha-hydrogen atoms. The enolate of one carbonyl compound (nucleophile) attacks the carbonyl carbon of the other (electrophile).
This generally gives a mixture of four products (each compound can act as either nucleophile or electrophile), but a mixed/crossed product can be the only product when one reactant has no alpha-H.
Example: CH_3CHO + HCHO --(NaOH)--> $HOCH_2CHO$ and $HOCH_2CH_2CHO$ etc.
Useful case: C_6H_5CHO (no alpha-H) + CH_3COCH_3 --(NaOH)--> $C_6H_5CH=CHCOCH_3$ (benzalacetone) + H_2O

(iv) Decarboxylation:
Decarboxylation is the loss of a carbon dioxide molecule (CO_2) from a carboxylic acid, typically from the alpha-carbon bearing a -COOH group. It requires heating, especially for beta-keto acids or carboxylate salts.
Example: CH_3COOH + NaOH -> CH_3COONa + CO_2 (if soda lime used, Na salt -> CH_4).
Better: Decarboxylation of carboxylate with soda lime (NaOH + CaO):
RCOONa + NaOH --(CaO, heat)--> R-H + Na_2CO_3
Beta-keto acid example: CH_3COCH_2COOH --(heat)--> CH_3COCH_3 + CO_2 (ethylacetoacetate type)
Kolbe electrolysis also causes decarboxylation: 2 $RCOO^-$ -> R-R + 2 CO_2 + 2e^-

Answer: (i) Acetylation: introduction of -$COCH_3$ replacing active H; e.g., ROH + $(CH_3CO)_2O$ -> $ROOOCCH_3$. (ii) Cannizzaro: disproportionation of alpha-H-free aldehyde with conc. NaOH; one oxidised to acid salt, one reduced to alcohol; e.g., 2 C_6H_5CHO + NaOH -> $C_6H_5CH_2OH$ + C_6H_5COONa. (iii) Cross aldol: enolate of one carbonyl attacks C=O of another (different) carbonyl; e.g., C_6H_5CHO + CH_3COCH_3 -> $C_6H_5CH=CHCOCH_3$. (iv) Decarboxylation: loss of CO_2 from carboxylate; e.g., RCOONa + NaOH/CaO -> R-H + Na_2CO_3.

Q17 Complete each synthesis by giving missing starting material, reagent or products:
(i) Ethylbenzene --($KMnO_4$, KOH, heat)--> ?
(ii) Benzene-1,2-dicarboxylic acid --($SOCl_2$, heat)--> ?
(iii) C_6H_5CHO + $H_2NCONHNH_2$ --> ?
(iv) Benzene --(?)--> Biphenyl
(v) 4-Oxocyclohexane-1-carbaldehyde + $[Ag(NH_3)_2]^+$ --> ?
(vi) 2-Formylbenzoic acid --(NaCN/HCl)--> ?
(vii) C_6H_5CHO + CH_3CH_2CHO --(dil. NaOH, heat)--> ?
(viii) $CH_3COCH_2COOC_2H_5$ --(i) $NaBH_4$ (ii) H^+--> ?
(ix) Cyclohexanol --(CrO_3)--> ?
(x) Methylenecyclohexane --(?)--> Cyclohexanecarbaldehyde
(xi) ? --(i) O_3 (ii) Zn-H_2O--> 2 Cyclohexanone

SOLUTION

The textbook figure shows the following schemes; the missing product / starting material / reagent for each is:

(i) Ethylbenzene (C_6H_5-CH_2CH_3) --($KMnO_4$, KOH, heat)--> [product]:
Oxidation of the alkyl side chain converts -CH_2CH_3 to -COOH.
Product: Benzoic acid (C_6H_5COOH).

(ii) Benzene-1,2-dicarboxylic acid (phthalic acid, o-$C_6H_4(COOH)_2$) --($SOCl_2$, heat)--> [product]:
$SOCl_2$ converts each -COOH to -COCl.
Product: Phthaloyl chloride (o-$C_6H_4(COCl)_2$).

(iii) C_6H_5CHO + $H_2NCONHNH_2$ (semicarbazide) --> [product]:
Condensation of the free -NH_2 of semicarbazide with the aldehyde C=O.
Product: Benzaldehyde semicarbazone, $C_6H_5CH=N-NH-CO-NH_2$.

(iv) Benzene --[reagent]--> Biphenyl (C_6H_5-C_6H_5):

Two benzene rings are joined by a C-C bond.
Missing reagent: Oxidative coupling — e.g. heat with a catalyst (or via the Wurtz-Fittig / diazonium coupling route from chlorobenzene/aniline). The intended answer is the coupling reagent that dimerises benzene to biphenyl.

(v) 4-Oxocyclohexane-1-carbaldehyde (a cyclohexane ring bearing a ketone C=O and a -CHO) + $[Ag(NH_3)_2]^+$ (Tollens') --> [product]:
Tollens' oxidises the aldehyde -CHO to -COOH; the ketone is unaffected.
Product: 4-Oxocyclohexane-1-carboxylic acid.

(vi) 2-Formylbenzoic acid (o-$C_6H_4(CHO)(COOH)$) + NaCN / HCl --> [product]:
HCN adds across the aldehyde C=O to give a cyanohydrin (-CH(OH)CN); the -COOH is unchanged.
Product: 2-(Hydroxy(cyano)methyl)benzoic acid, o-$C_6H_4(CH(OH)CN)(COOH)$ (the aldehyde cyanohydrin).

(vii) $C_6H_5CHO + CH_3CH_2CHO$ --(dil. NaOH, heat)--> [product]:
Cross aldol condensation: benzaldehyde has no alpha-H so it is the electrophile; the alpha-C of propanal is the nucleophile; the aldol then dehydrates.
Product: 2-Methyl-3-phenylprop-2-enal (alpha-methylcinnamaldehyde), C_6H_5-CH=C(CH_3)-CHO.

(viii) Ethyl acetoacetate $CH_3COCH_2COOC_2H_5$ --(i) $NaBH_4$ (ii) H^+--> [product]:
$NaBH_4$ selectively reduces the ketone C=O to -$CH(OH)^-$ (the ester is not reduced by $NaBH_4$).
Product: Ethyl 3-hydroxybutanoate, $CH_3CH(OH)CH_2COOC_2H_5$.

(ix) Cyclohexanol + CrO_3 --> [product]:
Oxidation of the secondary alcohol to the ketone.
Product: Cyclohexanone.

(x) Methylenecyclohexane (C_6H_{10}=CH_2) --[reagent]--> Cyclohexanecarbaldehyde (C_6H_{11}-CHO):
The exocyclic =CH_2 becomes -CHO.
Missing reagent: (i) B_2H_6 (hydroboration) then (ii) oxidation — i.e. anti-Markovnikov conversion of the terminal alkene to -CH_2OH followed by oxidation (PCC) to -CHO; equivalently a hydroformylation (oxo) route.

(xi) [starting material] --(i) O_3 (ii) Zn-H_2O--> 2 Cyclohexanone:
Reductive ozonolysis that yields two molecules of cyclohexanone means the C=C cleaved joined two cyclohexane rings.

Missing starting material: Cyclohexylidenecyclohexane (bicyclohexylidene), the alkene with a C=C between two cyclohexane rings.

Answer: (i) Benzoic acid (side-chain oxidation of ethylbenzene). (ii) Phthaloyl chloride, o-$C_6H_4(COCl)_2$. (iii) Benzaldehyde semicarbazone, $C_6H_5CH=N-NHCONH_2$. (iv) Biphenyl (missing = oxidative-coupling reagent joining two benzene rings). (v) 4-Oxocyclohexane-1-carboxylic acid (Tollens' oxidises the CHO, not the ketone). (vi) Aldehyde cyanohydrin o-$C_6H_4(CH(OH)CN)(COOH)$. (vii) 2-Methyl-3-phenylprop-2-enal (alpha-methylcinnamaldehyde), $C_6H_5CH=C(CH_3)CHO$. (viii) Ethyl 3-hydroxybutanoate, $CH_3CH(OH)CH_2COOC_2H_5$ ($NaBH_4$ reduces only the ketone). (ix) Cyclohexanone. (x) Cyclohexanecarbaldehyde (missing reagent = hydroboration then oxidation, $=CH_2$ -> -CHO). (xi) Cyclohexylidenecyclohexane (bicyclohexylidene).

Q18 Give plausible explanation for each of the following:
(i) Cyclohexanone forms cyanohydrin in good yield but 2,2,6-trimethylcyclohexanone does not.
(ii) There are two $-NH_2$ groups in semicarbazide. However, only one is involved in the formation of semicarbazones.
(iii) During the preparation of esters from a carboxylic acid and an alcohol in the presence of an acid catalyst, the water or the ester should be removed as soon as it is formed.

SOLUTION

(i) Steric hindrance in 2,2,6-trimethylcyclohexanone:

Nucleophilic addition of HCN to a carbonyl compound requires the nucleophile (CN^-) to approach the electrophilic carbonyl carbon from above or below the plane.

In cyclohexanone, the carbonyl carbon is relatively accessible -> HCN adds readily -> good yield of cyanohydrin.

In 2,2,6-trimethylcyclohexanone, the two methyl groups at C-2 and the methyl group at C-6 create severe steric hindrance around the carbonyl carbon on both faces.

The CN^- nucleophile cannot approach the crowded carbonyl carbon -> addition does not occur in good yield.

Conclusion: Steric hindrance by the three methyl groups (two at alpha and one at alpha') prevents nucleophilic addition of CN^-.

(ii) Only one -NH_2 of semicarbazide reacts:

Semicarbazide: H_2N-NH-CO-NH_2. The two -NH_2 groups have different reactivity.

The -NH_2 directly attached to the N-N linkage (N_1, next to -N=) is more nucleophilic because the lone pair is not directly conjugated with the carbonyl of -CO-NH_2.

The other -NH_2 (attached to C=O, at N_3) has its lone pair delocalized into the C=O through resonance (-CO-NH_2 ⇌ -C(OH)=NH), making it less nucleophilic (amide-type NH_2).

Therefore, only the free -NH_2 group (N_1) reacts with the aldehyde/ketone C=O to form the semicarbazone C=N-NH-CO-NH_2.

(iii) Removal of water or ester to drive equilibrium:

Esterification is a reversible reaction: RCOOH + R'OH ⇌ RCOOR' + H_2O

The reaction reaches an equilibrium state and does not go to completion on its own.

By removing water (e.g., using a drying agent, molecular sieves, or by distillation) or the ester product (by distillation) as soon as it forms, the equilibrium is shifted to the right (Le Chatelier's principle).

This drives the reaction forward and increases the yield of the ester.

If water accumulates, the reverse reaction (hydrolysis of ester) is favoured.

Answer: (i) 2,2,6-Trimethylcyclohexanone has three methyl groups creating steric congestion around the C=O; CN^- cannot approach -> no cyanohydrin. Cyclohexanone has accessible C=O -> good yield. (ii) In semicarbazide H_2N-NH-CO-NH_2, the -NH_2 on N_3 (amide type) is deactivated by resonance with C=O and is less nucleophilic; only the -NH_2 on N_1 (free) reacts. (iii) Esterification is reversible; removing H_2O or ester shifts equilibrium right (Le Chatelier's principle), increasing ester yield.

Q19 An organic compound contains 69.77% carbon, 11.63% hydrogen and rest oxygen. The molecular mass of the compound is 86. It does not reduce Tollens' reagent but forms an addition compound with sodium hydrogensulphite and gives positive iodoform test. On vigorous oxidation it gives ethanoic and propanoic acid. Write the possible structure of the compound.

SOLUTION

Step 1: Find molecular formula.
C% = 69.77%, H% = 11.63%, O% = 100 - 69.77 - 11.63 = 18.60%
Mole ratios: C = 69.77/12 = 5.814; H = 11.63/1 = 11.63; O = 18.60/16 = 1.163
Divide by smallest (1.163): C = 5.00, H = 10.00, O = 1.00
Empirical formula: $C_5H_{10}O$; empirical mass = 5(12) + 10(1) + 16 = 86.
n = 86/86 = 1. Molecular formula: $C_5H_{10}O$ ✓

Step 2: Apply the clues.
- Does NOT reduce Tollens' -> not an aldehyde; must be a ketone.
- Forms addition compound with $NaHSO_3$ -> accessible ketone (methyl ketone or non-hindered ketone reacts with $NaHSO_3$).
- Positive iodoform test -> contains CH_3CO^- (methyl ketone) group, or CH_3CHOH^- oxidisable to CH_3CO^-; since it is a ketone, it has CH_3CO^- directly.
- Vigorous oxidation gives ethanoic acid (CH_3COOH, 2C) and propanoic acid (CH_3CH_2COOH, 3C).
Oxidative cleavage of a ketone R-CO-R' gives R-COOH + R'-COOH.
CH_3COOH (from CH_3CO^-) and CH_3CH_2COOH (from $-COCH_2CH_3$), so R = CH_3 and R' = CH_2CH_3.

Step 3: Identify compound.
R-CO-R' where R = CH_3, R' = C_2H_5: CH_3-CO-CH_2CH_3 = Pentan-2-one.
CH_3-CO-CH_2-CH_2-CH_3 = Pentan-2-one, formula $C_5H_{10}O$, MW = 86 ✓

Verification:
- Ketone -> not Tollens' positive ✓
- Methyl ketone (CH_3CO^-) -> $NaHSO_3$ addition ✓
- CH_3CO^- -> positive iodoform test ✓
- Vigorous oxidation of CH_3-CO-$CH_2CH_2CH_3$ cleaves the C-C bonds on either side of the C=O:
the CH_3CO^- side gives CH_3COOH (ethanoic acid) and the $-CH_2CH_2CH_3$ side gives CH_3CH_2COOH (propanoic acid). ✓

Structure of compound: CH_3-CO-CH_2-CH_2-CH_3 (Pentan-2-one)

Answer: Molecular formula $C_5H_{10}O$ (MW 86). The compound is Pentan-2-one: CH_3-CO-$CH_2CH_2CH_3$. It is a ketone (no Tollens'), has CH_3CO^- ($NaHSO_3$ addition + iodoform positive), and vigorous oxidation cleaves the C=O to give CH_3COOH + CH_3CH_2COOH.

Q20 Although phenoxide ion has more number of resonating structures than carboxylate ion, carboxylic acid is a stronger acid than phenol. Why?

SOLUTION

The acid strength depends on the stability of the conjugate base (anion) formed after loss of a proton.

Phenol (C_6H_5OH) dissociates to phenoxide ion ($C_6H_5O^-$).
Phenoxide has resonating structures where the negative charge is delocalised onto the ring carbons (ortho and para).
However, the negative charge in phenoxide is delocalised over carbon atoms (which are less electronegative than oxygen).
Structures: $C_6H_5O^-$ ⇌ $^-C_6H_4$-OH (charge on ring carbons at ortho/para).
The charge is never concentrated on the more electronegative oxygen in the resonance forms with C-charge; moreover, the carbon atoms are not well suited to bear negative charge.

Carboxylic acid (RCOOH) dissociates to carboxylate ion ($RCOO^-$).
Carboxylate has only two main resonating structures, but the negative charge is distributed over TWO oxygen atoms (both more electronegative than carbon):
$RCOO^-$ ⇌ $[RC(=O)O^-]$ ⇌ $[RC(-O^-)=O]$ (charge shared equally between two oxygens).
The negative charge resides entirely on oxygen atoms in both resonating structures.

Comparison:
Even though phenoxide has more resonating structures (and hence greater extent of delocalisation in principle), the charge in carboxylate is stabilised more effectively because:
(a) The negative charge is on two equivalent, electronegative oxygen atoms.
(b) Both resonating structures of carboxylate are equivalent (equal energy) -> maximum stabilisation.
(c) In phenoxide, the charge on ring carbons (less electronegative) contributes less stability.

Result: Carboxylate ion is more stable than phenoxide ion. Therefore carboxylic acid (pKa ~5) is a stronger acid than phenol (pKa ~10).

Answer: Although phenoxide has more resonating structures, the negative charge in phenoxide is delocalised onto less electronegative ring carbon atoms. In carboxylate ($RCOO^-$), the charge is equally shared between two electronegative oxygen atoms (two equivalent resonating structures), providing greater stabilisation. Hence carboxylate is more stable than phenoxide, and carboxylic acid is a stronger acid than phenol.