Organic Synthesis

- Organic analysis
- Synthesis
- Outlining mechanisms

Write on both sides of the paper | Question _____ | Do not write in this margin

Synthesis

* Always use the shortest route possible.
* Have basic mean equation with correct conditions
* Count the number of carbon atoms of the initial compound and the final compound.
* Write correctly the symbols of the reagents especially the inorganic reagents eg $LiAlH_4$, $NaBH_4$, $FeCl_3$ etc.
* Take note of the correct arrangement of reagents eg:
  Acidified potassium permanganate MnO_4^-/H^+ not H^+/MnO_4^-
  Acidified water H^+/H_2O; not H_2O/H^+ etc.
* Note that a wrong step above the sequence costs you all the marks for the correct part down stream.

(1) Increasing the carbon chain.

(a) Reaction of alkynes with sodium in liquid ammonia.

$RC\equiv CH \xrightarrow{Na/\text{Liquid } NH_3} RC\equiv CNa$ ← usually charged $RC\equiv\bar{C}\,Na^+$

or $RC\equiv CH \xrightarrow[\text{dry ether}]{NaNH_2} RC\equiv CNa$ but leave that.

To this add an alkyl halide of the number to add up the number of carbon atoms you want, forming a higher alkyne.

$RC\equiv CNa \xrightarrow{R'X/\text{dry ether}} RC\equiv CR'$

To use this method;

- You must have a terminal alkyne i.e. first make it
- Adv: you can add all the number of carbon atoms you want.

(b) Cyanide formation or nitrile formation.

$RX + \text{Alcoholic KCN} \xrightarrow[\text{reflux}]{} RCN$

- You must have an alkyl halide
- Adds for you one carbon atom
- From here you can proceed to an amide, carboxylic acid, amine.

(c) $RCN \xrightarrow[\text{Heat}]{H^+/H_2O} RCONH_2$ (amide) $\xrightarrow[\text{Heat}]{H^+/H_2O} RCOOH$

or

$RCN \xrightarrow{\text{Excess } H^+/H_2O} RCOOH$

$RCN \xrightarrow[\text{dry ether}]{LiAlH_4} RCH_2NH_2$

Na/ethanol.

(c) Kolbe reaction

- This doubles the chain, you must have an alkyl halide first, it forms an alkane.

$2RX \xrightarrow{Na \text{ dry ether}} R-R$

(d) Using Grignard reagent

can add for you as many carbon atoms as you want depending.

(i) Prepare the reagent by reacting alkyl halide with magnesium in dry ether

$RX + Mg \xrightarrow{\text{dry ether}} RMgX$.

(ii) Preparation of 1° alcohol -- use only methanal. (dilute acid / dilute HCl)

$RMgX + H\overset{O}{\overset{\|}{C}}H \longrightarrow RCH_2OMgX \xrightarrow{H^+/H_2O} RCH_2OH$

or

$H\overset{O}{\overset{\|}{C}}H \xrightarrow[\text{② } H^+/H_2O]{\text{① } RMgX/\text{dry ether}} RCH_2OH$

(iii) Preparation of secondary alcohols - use other aldehydes

$RMgX + R'CHO \longrightarrow R\underset{\underset{OMgX}{|}}{C}HR' \xrightarrow{H^+/H_2O} R\underset{\underset{OH}{|}}{C}HR'$

or

$R'\overset{O}{\overset{\|}{C}}H \xrightarrow[\text{② } H^+/H_2O \text{ or dilute HCl}]{\text{① } RMgX} R\underset{\underset{OH}{|}}{C}HR'$.

(iii) Like ketones - tertiary alcohols are formed, hydrolysis is done in presence of ammonium chloride, because presence of an acid causes dehydration of the tertiary alcohol.

$$RMgX + R'\overset{O}{\overset{\|}{C}}R'' \longrightarrow R\overset{R'}{\underset{OMgX}{\overset{|}{C}}}-R'' \xrightarrow[NH_4Cl_{(aq)}]{H_2O} R-\overset{R'}{\underset{OH}{\overset{|}{C}}}-R''$$

or

$$R'\overset{O}{\overset{\|}{C}}R'' \xrightarrow[\text{② } H_2O/NH_4Cl]{\text{① } RMgX} R\overset{R'}{\underset{OH}{\overset{|}{C}}}-R''$$

(iv) Formation of ketones.

$$RMgX + R'CN \xrightarrow{\text{dry ether}} R\overset{R'}{\underset{NMgX}{\overset{|}{C}}} \xrightarrow[\text{dilute HCl}]{H_2O} R\overset{R'}{\underset{O}{\overset{\|}{C}}}$$

- The reaction of for the formation of aldehydes may not be good in synthetic pathways.

(v) Preparation of carboxylic acids

$$RMgX + CO_2 \longrightarrow RCOOMgX \xrightarrow{\text{dilute acid}} RCOOH.$$

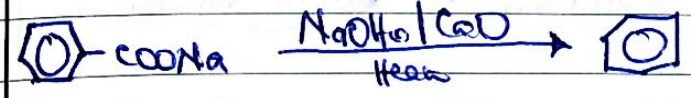
(2) Reducing the carbon chain

(a) Decarboxylation of carboxylic salts - Reduces 1 carbon atom.

(i) Sodium salts

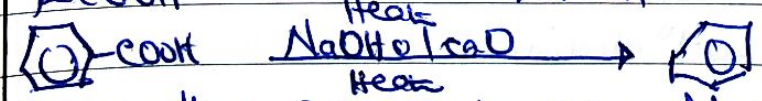
- Yield alkanes or benzene.

$$RCOONa \xrightarrow[\text{Heat}]{NaOH_{(s)}/CaO} R-H \qquad RCOOH \xrightarrow[\text{Heat}]{\text{Sodalime}} RH$$



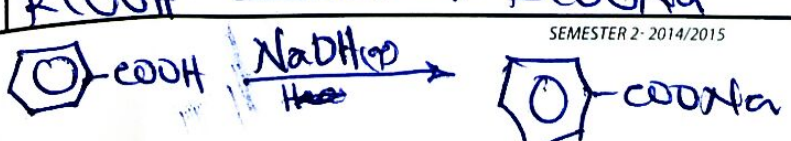
To reduces the number of sequences or steps, one is allowed to

$$RCOOH \xrightarrow[\text{Heat}]{NaOH_{(s)}/CaO} R-H$$



However these salts can be prepared by first reacting a carboxylic acid with aqueous sodium hydroxide.

$$RCOOH \xrightarrow{NaOH_{(aq)}} RCOONa$$



(ii) Calcium salts.

- You yield a ketone

$$(RCOO)_2Ca \xrightarrow{Heat} R\overset{O}{\overset{\|}{C}}R$$

These salts are prepared by reacting a carboxylic acid with $CaCO_3$ or Ca

$$RCOOH + CaCO_3 \longrightarrow (RCOO)_2Ca.$$

(b) Hoffman's degradation of amides

- Reduces one carbon atom.

$$RCONH_2 \xrightarrow[Heat]{Br_2 / NaOH} RNH_2 \quad RNH_2$$

The amide is prepared by heating an ammonia with a carboxylic acid

$$RCOOH \xrightarrow[Heat]{NH_3} RCONH_2$$

(c) Ozonolysis

- Reaction of ozone with an alkene and then subsequent hydrolysis to yield carbonyl compounds.

$$RCH=CHR' \xrightarrow[Zn \,/\, Ethanoic\ acid]{O_3 / CCl_4;\ <20^\circ C} R\overset{O}{\overset{\|}{C}}H + R'\overset{O}{\overset{\|}{C}}H$$

This is good to be used when the alkene is symmetrical otherwise always try to avoid passing this way.

(3) Reducing agents.

These reverse the process of oxidation by adding hydrogen onto compounds eg

(i) aldehydes back to 1° alcohols

(ii) ketones back to 2° alcohols

(iii) carboxylic acids back to 1° alcohols

(iv) nitrocompounds to amines

(v) amides to amines.

etc.

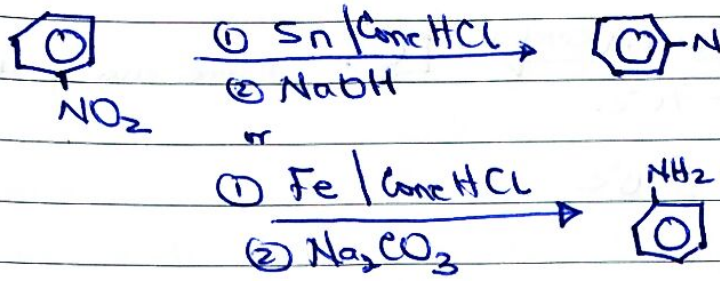
$LiAlH_4$ / dry ether - No heating required.

$NaBH_4$ / H_2O & cannot be used to reduce carboxylic acids.

H_2 / Ni ; Heat

Na / CH_3CH_2OH

Sn / Conc HCl - for aromatic nitro compounds to amines, eg



$NaBH_4$ / CH_3OH (only methanol) or alcoholic $NaBH_4$.

④ Oxidising agent.

- These reverse reduction process, by removing hydrogen or adding oxygen eg

(i) 1° alcohols to aldehydes or carboxylic acids

(ii) 2° alcohols to ketones (iv) methyl benzene to benzaldehyde.

(iii) alkenes to diols.

(v) amines to nitro compounds.

etc.

MnO_4^- / H^+ & Strong oxidising agent ie 1° alcohol → carboxylic acid

$Cr_2O_7^{2-}$ / H^+.
MnO_2 / H^+
Cr_2O_3 / H^+
} Mild oxidising agent. ∴ Used in excess if 1° → Prod

All these require heating for reaction to proceed.

Cu or ZnO ; 350-360°C

Question

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(5) Temperature condition.

There are reactions that have specific temperature values which must always be quoted. eg:

(a) $RC{\equiv}CH \xrightarrow[HgSO_4;\ 60^\circ C]{H_2O/H_2SO_4} R\overset{O}{\overset{\|}{C}}CH_3$ hydrolysis of alkyne

(b) $HC{\equiv}CH \xrightarrow[60-70^\circ C]{\text{Organo-nickel catalyst}}$  Polymerisation of ethene

$Cu;\ 300^\circ C$

(c) Nitration of benzene $55-60^\circ C$

 $\xrightarrow[55^\circ C - 60^\circ C]{Conc\ HNO_3/Conc\ H_2SO_4}$

(d) Sulphonation

 $\longrightarrow$ 

Conc H_2SO_4; heat/reflux at $180^\circ C$

Fuming H_2SO_4; $40^\circ C$ ($35^\circ C - 50^\circ C$)

Fuming H_2SO_4; Warm

Cold fuming Sulphuric acid

Fuming H_2SO_4; Room temperature.

(e) Dehydration of alcohols.

(i) Use $180^\circ C$ always while using Concentrated H_2SO_4.

although $180^\circ C$ is for 1° alcohols

$120^\circ C$ is for 2° alcohols

$80^\circ C$ is for 3° alcohols

(ii) Al_2O_3 / $300^\circ C - 350^\circ C$

(iii) Conc H_3PO_4 / $360^\circ C$

(f) Hydrogen Hydrogenation using Ni

Ni / $150 - 250^\circ C$.

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(c) Nitration of benzene $55-60^\circ C$

 $\xrightarrow[55^\circ C - 60^\circ C]{\text{Conc } HNO_3/\text{Conc } H_2SO_4}$

(d) Sulphonation

 $\longrightarrow$  SO_3H

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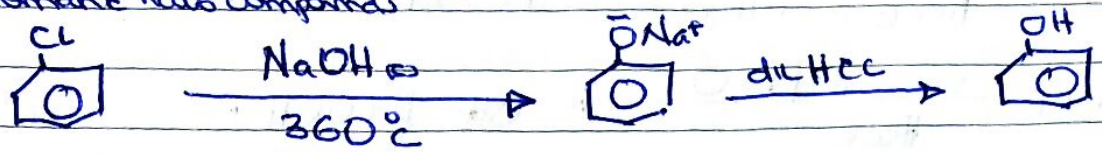
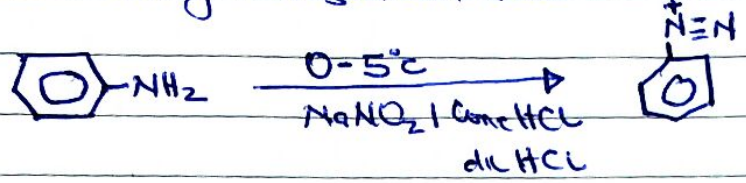
Ni / $150 - 250^\circ C$.

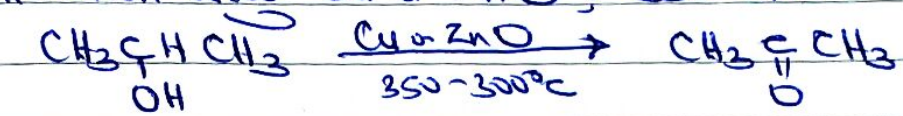
(a) Aromatic halo compounds



(b) Formation of a diazonium salt.

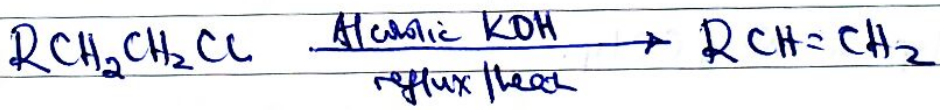


(c) (i) Oxidation using Cu or ZnO ; 350-380°C

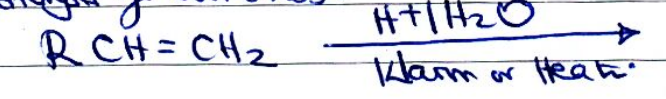


Some reactions have general mandatory temperature statements which are specific eg.

(a) Alcoholic KOH / reflux (heat) warming not required.



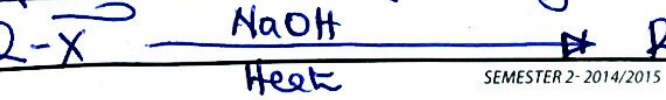
(b) Hydrolysis of alkenes.



(c) While using oxidising agents - Heating only required, reject warm or reflux.

(d) While dehydrating alcohols using Conc H_2SO_4, heating can be allowed.

(e) Preparing an alcohol from alkyl halides



(f) $R-X \xrightarrow[\text{Heat or reflux.}]{\text{Alcoholic KCN}} R-CN$

(g) $RCN \xrightarrow[\text{Heat}]{\text{excess } H^+/H_2O} RCOOH$.

There

† Including heat heads to loss of marks

There are other reactions that don't need heating condition and thus don't use acids. and for reactions are the majority es.

(a) While using $LiAlH_4$/ dry ether as a reducing agent.

(b) $R-OH \xrightarrow{PCl_5} RCl$

(c) $RCH=CH_2 \xrightarrow{HX} RCH(X)CH_3$

(d) Br_2/CCl_4. or X_2/CCl_4.

(e) Grignard synthesis and subsequents reactions

(f)  $\xrightarrow{Br_2/Fe}$

Examples

Write equations to show how the following conversions can be effected

(a) CH_3CH_2Br to CH_3COCH_3

(b)  to

(3) $CH_3\underset{\underset{O}{\|}}{C}CH_3$ to $HC\equiv CH$

(4) CH_3CH_2CHO to $CH_3CHBrCH_2Br$

(5) $CH_3CH=CH_2$ to $C_6H_5NH-N=C(CH_3)_2$.

(6) $CH_3CH_2CH_2Br$ to CH_3COCH_3.

(7) $C_6H_5COCH_3$ to $\{CH-CH_2\}_n$. 

(8) $CH_3CH=CH_2$ to $CH_3\underset{\underset{O}{\|}}{C}CH_3$.

(9)  to 

10 Propan-2-ol to $(CH_3)_2C=NNH_2$

(11) Benzene to 

12 Calcium carbonate to ethanol

13 Ethanol to Propane 1,2 diol

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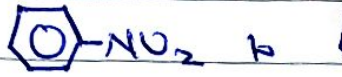
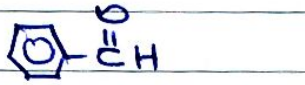
Question

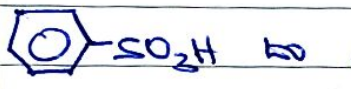
14 CH_3Cl to $CH_3COOCH_2CH_3$.

15  to 

16 CH_3Cl to $CH_3CH_2\overset{Cl}{\underset{Cl}{C}}CH_3$

17 CH_3CH_2OH to $CH_3\overset{O}{\overset{\|}{C}}CH_3$

18 $HC\equiv CH$ to 

19  to 

20 $CH_3\overset{O}{\overset{\|}{C}}-OCH_2CH_3$ to $CH_3CH=CH_2$

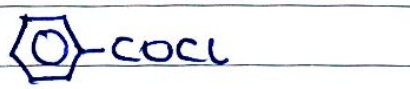
21  to 

22 C_2H_4 to $C_4H_{10}O$

23 $CH_3CH_2=CH_2$ to $CH_3C\equiv CH$

24 CH_3CH_2Cl to $CH_3CH_2OCH_2CH_3$

25 CH_3CHO to $CH_3COOCH_2CH_3$

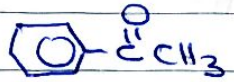
26  to 

27 CH_3CH_2Cl to $CH_3CH_2CH_2C\equiv CH$

28 ethene to $CH_3\overset{O}{\overset{\|}{C}}Cl$

29  from to

30 Propan-1-ol to $CH_3CH_2CH_2CO_2H$

31 ethene to 

32 CH_3CH_2OH to $CH_3CH_2CH_2OH$

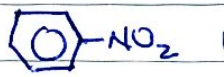
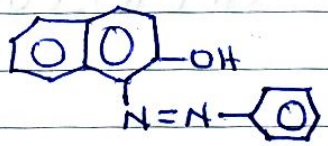
33 $CH_3CH_2CH_2Cl$ to $CH_3\underset{\underset{OH}{|}}{CH}CH_3$.

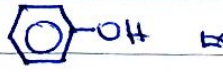
34 Ethanol + benzene

35 1,2 dibromoethene to ethanol

36 Phenyl propane to phenol.

37  to

38  to 

39  to  .

40 CH_3OH to $CH_3\underset{\underset{O}{\|}}{C}CH_3$

41 But-2-yne from butan-2-ol

42 Ethylamine from ethanal

43 Propanone from propene

44 Polystyrene from phenylethanone.

45 Cyclohexene from cyclohexanone

46 Butanone from Butanol

47 Bromobenzene from Phenyl chloromethane

48 $CH_3CH_2CH_2Cl$ to $CH_3CH_2CH_2CH_2NH_2$

49 $CH_3CH_2CH_2OH$ to $CH_3CH_2CH_2COOH$.

50 CH_3CH_2COOH to $CH_3CH_2NH_2$.

51 $CH_3CH=CH$ to $CH_3CH_2CH_2CH_2CH_2Br$

52 Propene to $CH_3C\equiv CH$

53 $CH_3CH=CHCH_3$ to $CH_3CH_2COCH_3$

54 Compound B was synthesised according to the reaction scheme below

$CH_3(CH_2)_3I \xrightarrow{\text{Step X}} CH_3(CH_2)_3OH \xrightarrow[\text{Heat}]{\text{Acidified Sodium dichromate}} A$

$A \xrightarrow{\text{Step Y}} CH_3(CH_2)_2COCl$

$CH_3(CH_2)_2COCl \xrightarrow{\text{ethanol}} B$

(a) Identify the reagents in

(i) Step X

(ii) Step Y.

(b) State the conditions for reaction in

Step X

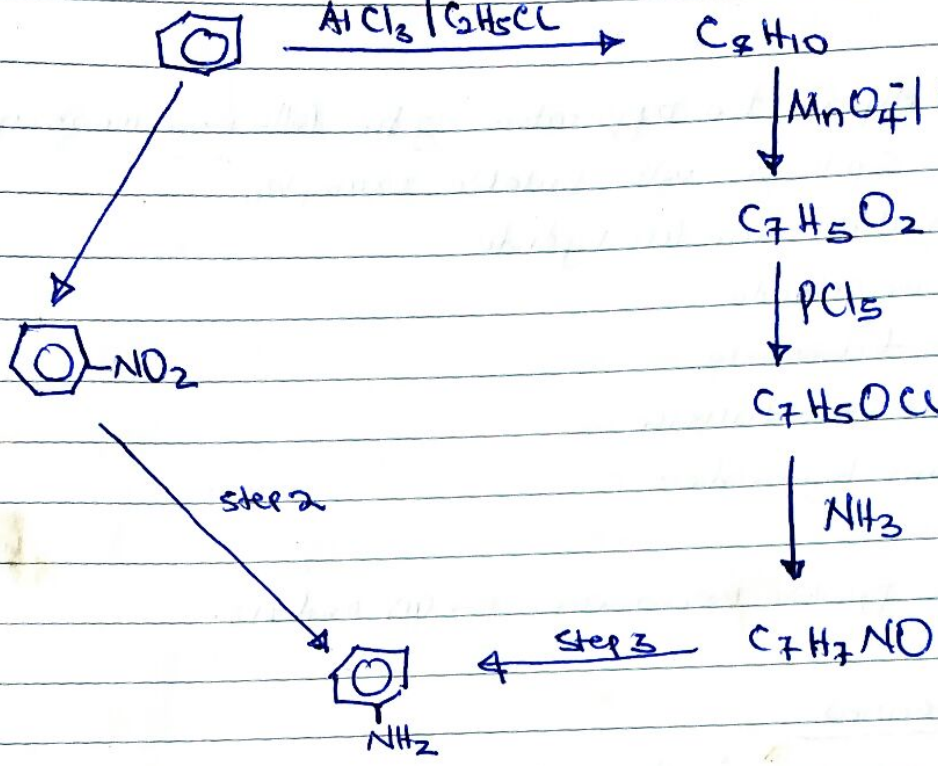
Step Y.

(c) Write the name and structural formulae of compound

(i) A

(ii) B.

55 Phenylamine $C_6H_5NH_2$ can be made in several ways from benzene. The following flow chart shows two of the outline.



a (i) Give the reagent and conditions needed for step 1

(ii) Write the mechanism for this reaction

(iii) Give the reagent for and condition for step 2

b (i) In the alternative pathway, identify compounds A to D

(ii) State the reagents and conditions needed for step 3.

(c) ~~Expl~~ Explain which pathway is commercially preferable for the manufacture of phenylamine.

5b(a) $(CH_3)_2C{=}NOH$ from ethanol

(b)  from nitrobenzene

(c) $CH_3COOCH_2CH_3$ from chloroethane.

(d) $CH_3\overset{\overset{O}{\|}}{C}CH_3$ from methanol.

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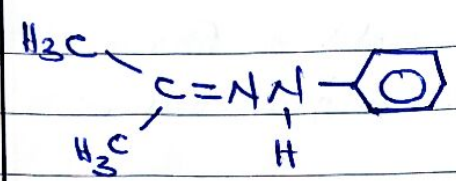
Question


from propene

57 Briefly explain the application of the following reagents in organic synthesis with suitable examples

(i) Lithium aluminium tetrahydride

(ii) Aluminium chloride

(iii) Potassium dichromate

(iv) Sodium hydrogen sulphite

(v) Potassium hydroxide.

(b) Suggest possible mechanisms for (ii) and (v).

Mechanism

- Having arrows is always make the arrows touch the bonds, pair of electrons or charge.
- Usually question require completion before the mechanism, don't both the completion, wrong completion can lead to loss of marks
- Follow basic rules and mechanism for the different homologous series eg Markovnikov's rule.
- Intermediates should always clearly be written
- Electron flow should be consistent

Examples of common mechanisms:

1. Write equation and mechanism for the reaction between

1 Phenylacetone and 2,4-dinitrophenylhydrazine

2 But-2-ene and hydrogen chloride gas

3 2-bromo-2-methyl propene and water

4 

5 $CH_3CHO + NaHSO_3$ (aq)

6 

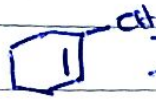
(7) 

(8) $CH_3CH=CH_2 \xrightarrow[\text{warm.}]{H^+/H_2O}$

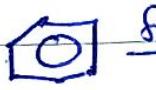
9 $CH_3\underset{OH}{\underset{|}{C}}HCH_3 \xrightarrow[\text{Heat}]{\text{Conc } H_3PO_4}$

10 $CH_3CH_2CH=CH_2 \xrightarrow[H_2O]{\text{Conc } H_2SO_4}$

11 $(CH_3)_2NH + CH_3\overset{O}{\overset{\|}{C}}-Br$

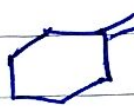
12  $+ HBr$

13  $\xrightarrow[\text{Heat}]{NaOH(aq)}$

14  $\xrightarrow{\text{fuming } H_2SO_4}$

15  $+ HNO_3 \xrightarrow[\text{Heat}]{\text{Conc } H_2SO_4}$

16  $-CH_2CH_2OH \xrightarrow[\text{Heat}]{\text{Conc } H_2SO_4}$

17  $+ H_2NNH_2 \xrightarrow[\text{warm}]{H^+(aq)}$

18  $+ (CH_3)_2C=CH_2 \xrightarrow{H_2SO_4(aq)}$

19 $CH_3CH_2Cl + HC\equiv\bar{C}Na^+ \xrightarrow[\text{dry ether}]{\text{Liquid } NH_3}$

20 $CH_3\underset{Br}{\underset{|}{C}}H\underset{Br}{\underset{|}{C}}HCH_3 \xrightarrow[\text{Heat}]{CH_3CH_2\bar{O}/CH_3CH_2OH}$

21 $(CH_3)_2\underset{Cl}{\underset{|}{C}}CH_2CH_3 \xrightarrow{NaOH(aq)}$

22  $+ CH_3COBr \xrightarrow{FeCl_3}$

23 $CH_3\overset{O}{\overset{\|}{C}}CH_3 + H_2N-NH-CONH_2 \xrightarrow{H^+}$

24 $CH_3CH_2CHO + HSO_3^-Na^+ \longrightarrow$

25 $(CH_3)_3CBr \xrightarrow[CH_3CH_2OH \text{ heat}]{CH_3CH_2\bar{O}Na^+}$

- Some reagents are prepared in situ and need to be known e.g.

 $+ Br_2 \xrightarrow{Fe}$

$2Fe + 3Br_2 \longrightarrow 2FeBr_3$

-  $\xrightarrow[\text{Heat}]{\text{Conc } HNO_3 / \text{Conc } H_2SO_4}$

$H_2SO_4 + HNO_3 \longrightarrow H_2O + \overset{+}{N}O_2 + \bar{O}SO_3H$

-  $\xrightarrow[\text{reflux}]{\text{Conc } H_2SO_4}$

$2H_2SO_4 \longrightarrow SO_3 + H_3O^+ + \bar{O}SO_3H$

* Electron flow should be correct.
* Intermediates should be correctly presented.
* Some may require naming the organic product formed.

Question

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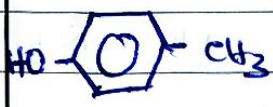
26 $CH_3CH_2OH \xrightarrow[140^\circ C]{Conc\ H_2SO_4}$

27  $\xrightarrow[Heat]{NaOH}$

28  $\xrightarrow[Heat]{NaOH\ (aq)}$

29 $CH_3\overset{O}{\overset{\|}{C}}CH_2CH_3 \xrightarrow{NaHSO_3\ (aq)}$

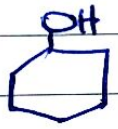
30 $(CH_3)_3C-I \xrightarrow[Heat]{EtO^-/EtOH}$

31 $CH_3CH=CHCH_2 \xrightarrow{Br_2/H_2O}$

32  $+ CH_3I \xrightarrow{AlCl_3}$

33 $RCHO + H_2N-OH \xrightarrow{H^+}$

34 $CH_3CHBr-CH_2Br \xrightarrow[Heat]{CH_3CH_2O^-Na^+}$

36  $\xrightarrow[Heat]{Conc.\ H_2SO_4}$

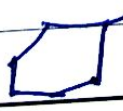
37  $+ CH_3\overset{CH_2}{\overset{|}{C}}=CH_2 \xrightarrow{H^+}$

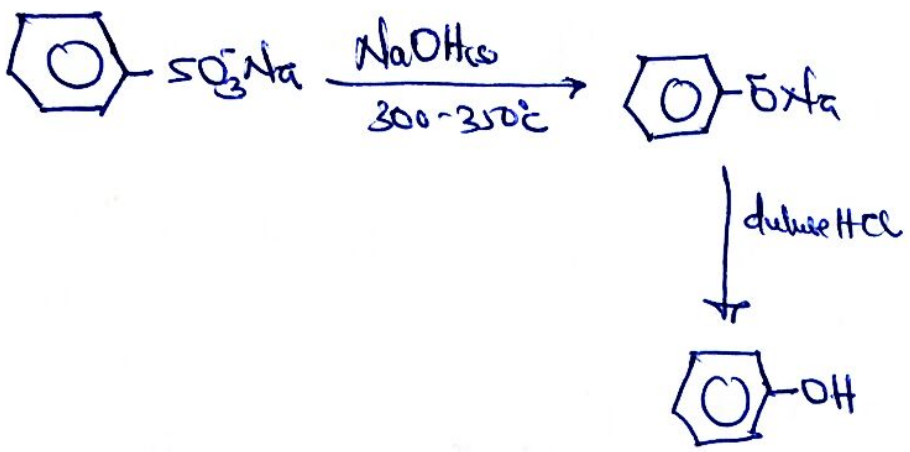
38  $\xrightarrow{HBr}$

39  $+ CH_3CH_2O^-Na^+ \xrightarrow[Heat]{CH_3CH_2OH}$

40 $CH_3\overset{Cl}{\overset{|}{C}}HCH_2CH_3$ (with CH_3 below) $\xrightarrow[Heat]{EtO^-/EtOH}$

41 $(CH_3)_2C=O +$  $\xrightarrow{H^+}$

42  $\xrightarrow[Heat]{OH^-\ (aq)}$


SO_3^-Na
NaOH(s)
300-350°C
ONa
dilute HCl
OH

43  $\xrightarrow{Cl_2/U.V}$

44  $+ CH_3CH=CH_2 \xrightarrow{H^+}$

45 $CH_3CH=CHCH_3 \xrightarrow{Conc\ H_2SO_4/H_2O}$

46 $(CH_3)_3CBr \xrightarrow[Heat]{C_2H_5\bar{O}K^+ / C_2H_5OH}$

47 $CH_3CH_2OH \xrightarrow[140^\circ C]{Conc.\ H_2SO_4}$

48 $CH_3CH=CHCH_3 \xrightarrow{Cl_2/H_2O}$

49  $+ CH_3\overset{O}{\overset{\|}{C}}Cl \xrightarrow{AlCl_3}$

50 $CH_3CH_2CHO + NH_2NH_2 \xrightarrow{H^+}$

51 $(CH_3)_2C=CH_2 + I_2 \xrightarrow{CCl_4}$

52 $HCOH + Na_2SO_3 \xrightarrow{H^+}$

53 $CH_3\overset{O}{\overset{\|}{C}}Cl +$  $\longrightarrow$

54 $CH_3CHO + CH_3CH_2NH_2 \longrightarrow$

55 $CH_3CH=CH_2 \xrightarrow{HBr/ROOR}$

56 $CH_3CH_2Cl + HC\equiv\bar{C}Na^+ \xrightarrow[Dry\ ether]{Liquid\ NH_3}$

Some reactions just need completion, without examiner requiring their mechanism eg:

* Esterification:

$CH_3CH_2CH_2COOH + CH_3CH_2OH \xrightarrow[Heat]{Conc\ H_2SO_4}$

* diol formation from alkenes

$CH_3CH=\underset{CH_3}{\underset{|}{C}}-CH_2 \xrightarrow{MnO_4^-/\bar{O}H}$

$HC\equiv C + 2Cu(NH_3)_2^+ \rightarrow CuC\equiv CCu + 2NH_4^+$

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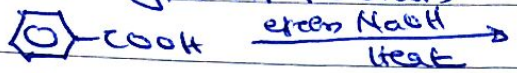
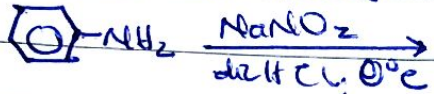
Question

* Decarboxylation reaction



* $CH_3CH_2CO_2H + PCl_5 \xrightarrow{Heat}$

* 

* $n\,CH_3CH=CH_2 \xrightarrow[Heat]{Catalyst}$

* $CH_3CH_2Br \xrightarrow[ethanol]{Zn-Cu\ Couple} CH_3CH_3$

$CH_3CH_2Br \xrightarrow{Zn/H^+} CH_3CH_2$

* Oxidation reaction

* Kling's reaction

* Aldol condensation

$2\,CH_3CH(=O) \xrightarrow{NaOH} CH_3CH(OH)CH_2CHO$

$2\,CH_3C(=O)CH_3 \xrightarrow{NaOH} CH_3C(OH)(CH_2)-CH_2C(=O)CH_3$

* Cannizzaro's reaction. (methanal and benzaldehyde)

$2\,HCHO \xrightarrow{NaOH} HCOONa + CH_3OH$

* Hydrolysis of alkynes to form ketones

* Reduction reactions - Hydrogen

etc.

Increasingly examiners are requiring to write reactions for the following.

* Tollen's reagent

* Aldehydes $RCHO + 2Ag(NH_3)_2^+ + H_2O \rightarrow 2Ag + RCOOH + 4NH_3^+ + H^+$

✓ $R-CH(=O) + 2Ag(NH_3)_{2(aq)}^+ + H_2O_{(l)} \rightarrow RCOOH + 2Ag + 2NH_4^+$

* Methanoic acid

* $2Ag(NH_3)_{2(aq)}^+ + HCOOH_{(aq)} + 2\bar{O}H \rightarrow 2Ag_{(s)} + 2H_2O_{(l)} + CO_{2(g)} + 2NH_3$

* $HCOOH + 2Ag^+ + 3\bar{O}H \rightarrow 2Ag + HCO_3^- + 2H_2O$

Ammoniacal copper (I) chloride
Terminal alkynes → Reddish brown / brown precipitate.

$HC\equiv CH + Cu_2Cl_2 + NH_4OH \longrightarrow CuC\equiv CCu + 2NH_4Cl + 2H_2O$

$HC\equiv CH + 2CuCl_2 + 2NH_3 \longrightarrow CuC\equiv CCu + 2NH_4Cl$

* Terminal alkynes.

$HC\equiv CH + 2AgNO_3 + 2NH_4OH \longrightarrow AgC\equiv CAg + 2NH_4NO_3 + 2H_2O$

$RC\equiv CH + AgNO_2 + NH_4OH \longrightarrow RC\equiv CAg + NH_4NO_3 + H_2O$

Organic analysis ← empirical formular
laboratory work (Reagents).

Distinguishing reagents

(1) Ammoniacal silver nitrate / silver nitrate and ammonia solution → Tollen's reagent

(a) Terminal alkynes Vs Internal alkynes

b/wite precipitate - Terminal alkyne eg

$CH_3CH_2C\equiv CH$ - White precipitate

$CH_3C\equiv CCH_3$ - No obtenable change.

(b) Methanoic acid Vs other carboxylic acids

Silver mirror

CH_3COOH - No obtenable change.

$HCOOH \rightarrow$ Silver mirror

(b) Aldehydes Vs Ketones.

Aldehydes - Silver mirror

Ketones - No obtenable change.

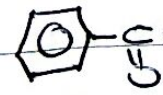
(2) Iodine solution and sodium hydroxide solution (Iodoform)

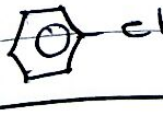
(a) Test for carbonyl compounds with to form $CH_3\underset{\underset{O}{\|}}{C}-$

- Methyl Ketones $CH_3CH_2\underset{\underset{O}{\|}}{C}-CH_3$.
- Distinguish ethanal from other aldehydes eg

$CH_3\underset{\underset{O}{\|}}{C}H$ from $CH_3CH_2\underset{\underset{O}{\|}}{C}-H$.

Observation - Yellow precipitate.

eg  - yellow precipitate

 - No obtenable

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Question

(b) Alcohols of the form $CH_3\overset{H}{\underset{OH}{C}}-$ give a positive test

- Distinguish ethanol from other primary alcohols

*Note- that tertiary alcohols doesn't give a positive test.

- carboxylic acids don't give a positive test (ethanoic acid)

(3) Neutral iron(III) chloride

(a) confirms phenol and distinguishes it from other alcohols

Observation: Violet solution.

Note: Gives a positive test for $C_6H_5COO^-$ or CH_3COO^- ⇒ a brown precipitate.

(4) Anhydrous zinc chloride and concentrated hydrochloric acid (Lucas reagent).

* Distinguishes between classes of alcohols

* Distinguish between primary, secondary and tertiary alcohols

Observation

1° alcohol - No observation at room temperature

2° alcohol - cloudiness 5-10 minutes

3° alcohol - Immediate cloudiness.

(5) sodium nitrate and concentrated hydrochloric acid

Distinguish between classes of amines.

Distinguish between 1°, 2° and 3° amines.

Temperature barrel if testing for aniline (Amino benzene) 0-5°C for

Observation.

1° Aliphatic amines - Bubbles of a colourless gas

aniline (amino benzene) - No observable change only at 0°C but at temperatures beyond 10°C - Bubbles of a colourless gas

2° amine - Yellow oil

3° amine - No observable change.

(6) Bromine water

(a) Alkenes and alkanes.

Alkenes - Reddish brown solution turns colourless

Alkanes - No observable change.

(b) Phenol - White precipitate.

(7) 2,4 dinitrophenylhydrazine (Brady's reagent)

Confirms presence of carbonyl compound.

→ Known as $-\overset{\overset{O}{\|}}{C}-X$

→ Yellow precipitate.

(8) Aqueous sodium carbonate / solid $NaHCO_3$

- Confirms carboxylic acid

Observation: Bubbles of a colourless gas.

(9) Phosphorus (V) chloride

- Organic compounds with a hydroxyl group $-\overset{|}{C}-OH$, i.e. alcohols & carboxylic acid $\overset{O}{\overset{\|}{C}}-OH$

Observation: Dense white fumes.

(10) Acidified oxidising agents {$KMnO_4$ solution.}

(a) Alkenes → Purple colour turns colourless

Alkane → No observable change.

(b) 1°, 2° alcohols from 3° alcohols. → Heat

1°, 2° → +ve test

3° - No observable change.

(c) Aldehydes from Ketones.

Aldehydes → +ve test

Ketone → -ve test (No observable change)

d) Methanoic acid and other carboxylic acid
Methanoic acid – +ve test
Other carboxylic – No observable change.

e) Oxalates from carboxylic acid

($KMnO_4$ only & Heats)
Purple solution turns colorless
No observable change.

** $Cr_2O_7^{2-}$ Orange solution turns to green solution.

(11) Hot sodium hydroxide solution and silver nitrate solution
– organic compound – halogen directly attached on benzene ring from that organic compound with halogen not directly attached to benzene ring.

White precipitate
Br^- – Pale yellow ppt
I^- – Yellow ppt.

(12) Copper (II) sulphate and sodium hydroxide solution distinguish aldehydes from ketones
Aldehydes – Red ppt
Ketones – No observable change.

Nature of question
(1) Given compound and asked reagent.
(2) Given the reagents and then told to
– identify what key test for
– Name example of cpds may test
– Name functional group tested for

(3) Analytical question