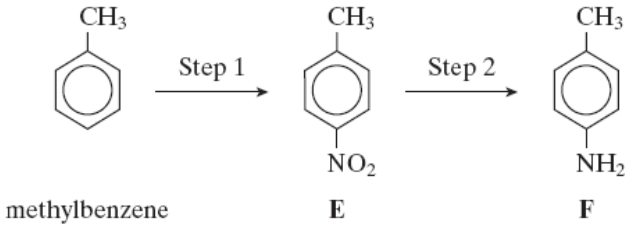
Topic 9 – Synthesis, Analysis and Chromatography
Revision Notes

1) Synthesis

- A synthesis is a series of reactions giving a desired chemical product
- Answering questions on synthesis requires a good knowledge of the reactions in CHEM4 (and CHEM2) i.e. reaction type, reagents and conditions
- A few favourite sequences include:
    - Nitration of benzene followed by reduction using Sn/HCl
    - Substitution of a halogen by CN^- to lengthen a carbon chain
    - Acylation of a benzene ring followed by reduction using $LiAlH_4$ to give an alcohol

a) Example question 1

Consider the following reaction sequence.



1) For Step 1, name the mechanism and give the reagents involved.

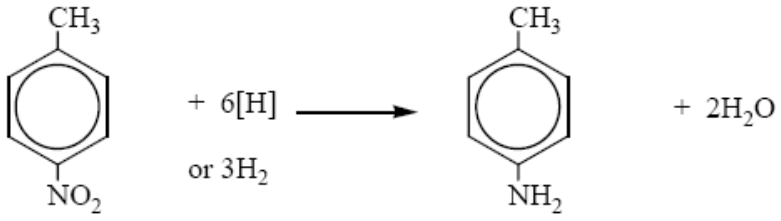
Answer:

Mechanism - electrophilic substitution
Reagents - concentrated HNO_3 and concentrated H_2SO_4

2) For Step 2, give a reagent or combination of reagents. Write an equation for this reaction using [H] to represent the reductant.

Answer:

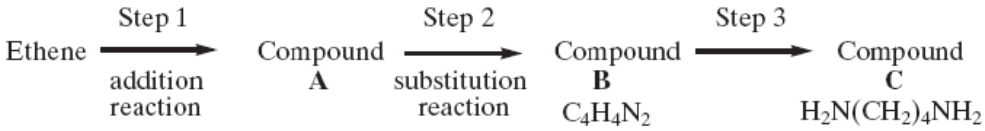
Reagents – Sn/HCl
Equation -



Source: AQA paper June 2005

b) Example question 2

Compound C, $H_2N(CH_2)_4NH_2$, can be synthesised from ethene in three steps as shown
below.



1) Name compound C and draw a structure for each of compounds A and B.

Answer:

Compound C – 1,4-diaminobutane
Compound A – $BrCH_2CH_2Br$ or $ClCH_2CH_2Cl$
Compound B – $NCCH_2CH_2CN$

2) State the reagent(s) required for each step and name the type of reaction involved in the conversion of B into C.

Answer:

Step 1 – Br_2 or Cl_2
Step 2 – KCN
Step 3 – $LiAlH_4$
Type of reaction - reduction

Source: AQA paper June 2002

2) <u>Chromatography</u>

- Chromatography is a technique for separating mixtures
- It separates the components of the mixture between a mobile phase and a stationary phase
- Separation depends on the balance between solubility in the mobile phase and retention in the stationary phase

a) <u>Gas-liquid Chromatography</u>

- Used to separate mixtures of volatile liquids (liquids with low boiling points)
- Mobile phase is a carrier gas e.g. nitrogen (which is inert)
- Sample mixture is injected into machine
- The retention time is the characteristic time it takes for a particular substance to pass through the system under set conditions
- The output is a graph of detector response (y-axis) against retention time (x-axis). This provides a spectrum of peaks for a sample representing the compounds present in a sample eluting from the column at different times
- Components of the mixture are identified by their retention times

b) <u>Column Chromatography</u>

- Stationary phase is a solid such as alumina or silica
- Mobile phase is a solvent
- Amino acids can be separated by column chromatography

3) Chemical Tests

- Chemical tests can be used to distinguish between compounds
- Answering questions on analysis requires a good knowledge of characteristic tests

Functional group	Test and result
Alkene	Decolourises bromine water
Carboxylic acid	Effervesces with Na_2CO_3(aq) or $NaHCO_3$(aq)
Aldehyde	Silver mirror with Tollens' reagent
Haloalkane	Add NaOH(aq) then acidified $AgNO_3$(aq) White ppt of AgCl(s)/cream ppt of AgBr(s)/ yellow ppt of AgI(s) Note: without NaOH, no ppt for chloroalkane
Acyl chloride	With $AgNO_3$(aq), white ppt of AgCl(s) & misty fumes of HCl
Primary and secondary alcohols	Add acidified potassium dichromate. Orange to green
Alcohols	Warm with CH_3COOH and a little conc H_2SO_4 Sweet smell of ester

4) Nucleophilic addition and optical isomerism

- Nucleophilic addition to aldehydes and ketones can produce racemic mixtures of optical isomers (racemates) e.g.

$$\mathbf{CH_3CHO + HCN \rightarrow CH_3CH(OH)CN}$$
$$\mathbf{CH_3COCH_2CH_3 + 2[H] \rightarrow CH_3CH(OH)CH_2CH_3}$$

- This happens because the carbonyl group is planar >C=O
- Attack by the nucleophile is equally likely from each side
- Equal amounts of the two optical isomers will be formed