Topic 4.10

ORGANIC SYNTHESIS AND ANALYSIS

Organic analysis
Organic synthesis

DISTINGUISHING BETWEEN DIFFERENT ORGANIC COMPOUNDS

Many of the organic compounds prepared in AS Unit 2 and in A2 Unit 4 can be distinguished by means of simple chemical tests. A number of these distinguishing tests will be discussed in this chapter.

a) **test for alkenes**

Alkenes decolorize bromine water because they undergo an electrophilic addition reaction with bromine:

Add a few drops of bromine water to the sample and shake. If the bromine decolorizes, an alkene is present. If not, no alkene is present.

b) **test for haloalkanes**

When haloalkanes are heated with dilute sodium hydroxide, a nucleophilic substitution reaction occurs and halide ions are produced. The halide ions can be identified using the tests described in AS Unit 2:

Add aqueous sodium hydroxide to the sample and heat. Then allow to cool, add dilute nitric acid and then aqueous silver nitrate. A white precipitate soluble in dilute ammonia indicates that a chloroalkane was present, a cream precipitate soluble in concentrated ammonia indicates that a bromoalkane was present, and a yellow precipitate insoluble in ammonia indicates that an iodoalkane was present.

c) **test for aldehydes**

Aldehydes can be oxidized by mild oxidizing agents such as Fehling’s solution or Tollen’s reagent.

Add Tollen’s reagent to the sample and heat. A silver mirror indicates the presence of an aldehyde.

Or

Add Fehling’s solution to the sample and heat. A brick-red precipitate indicates the presence of an aldehyde.

d) **test for carboxylic acids**

Carboxylic acids are acids and can liberate carbon dioxide from carbonates:

Add sodium carbonate solution to the sample. If effervescence is seen, and the gas produced turns limewater milky, a carboxylic acid is present.

e) **test for acyl chlorides**

Acyl chlorides release chloride ions very readily to give hydrogen chloride gas.

Add water to the sample slowly. If white misty fumes are given off, an acyl chloride is present.

f) **test for amines**

Amines are basic.

Add universal indicator to the sample. If it turns blue/purple an amine is present. It will also have a fishy smell.

g) **test for alcohols**

Alcohols react with carboxylic acids in the presence of sulphuric acid to make esters.

Add ethanoic acid to the sample, followed by sulphuric acid and heat. If a the mixture starts smelling sweet and fruity an alcohol was present.

h) **distinguishing tests for primary, secondary and tertiary alcohols**

Primary alcohols can be oxidized to form aldehydes. Secondary alcohols are oxidized to form ketones. Tertiary alcohols cannot be oxidized.

Add potassium dichromate and dilute sulphuric acid to the mixture and warm gently.
If the mixture goes green a primary or secondary alcohol is present. If it does not go green a tertiary alcohol is present. If the mixture does go green, add Fehling's solution to the mixture and heat. If a brick-red precipitate if formed then a primary alcohol was present. If no brick-red precipitate is formed then a secondary alcohol was present.

ORGANIC SYNTHESIS

It is possible to make a large number of organic products from a few starting compounds and the necessary reagents. The following organic pathways are required for Unit 4:

1. **alkane → chloroalkane**

reagents: chlorine
conditions: UV light
equation: $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$ (example)

NB This reaction introduces a new functional group onto the molecule

2. **chloroalkane → alcohol**

reagents: aqueous NaOH
conditions: warm, reflux
equation: $R\text{-}Cl + NaOH \rightarrow R\text{-}OH + NaCl$

3. **chloroalkane → alkene**

reagents: alcoholic KOH
conditions: heat, distillation
equation: $CH_3CH_2Cl + KOH \rightarrow CH_2{=}CH_2 + KCl + H_2O$ (example)

4. **chloroalkane → nitrile**

reagents: aqueous KCN
conditions: heat, reflux
equation: $R\text{-}Cl + KCN \rightarrow R\text{-}CN + KCl$

NB This reaction introduces an extra carbon atom onto the molecule

5. **chloroalkane → primary amine**

reagents: excess ammonia
conditions: heat
equation: $R\text{-}Cl + 2NH_3 \rightarrow R\text{-}NH_2 + NH_4Cl$

6. **primary amine → secondary amine**

reagents: chloroalkane
conditions: warm
equation: $R_1\text{-}NH_2 + R_2\text{-}Cl \rightarrow R_1R_2NH + HCl$

7. **secondary amine → tertiary amine**

reagents: chloroalkane
conditions: warm
equation: $R_1R_2NH + R_3\text{-}Cl \rightarrow R_1R_2R_3N + HCl$

8. **tertiary amine → quartenary ammonium salt**

reagents: chloroalkane
conditions: warm
equation: $R_1R_2R_3N + R_4\text{-}Cl \rightarrow R_1R_2R_3R_4N^+Cl^-$

9. **alkene → alkane**

reagents: hydrogen, Ni catalyst
conditions: 150 ^oC, 2 atm
equation: $CH_2{=}CH_2 + H_2 \rightarrow CH_3CH_3$ (example)

10. **alkene → dibromoalkane**

reagents: bromine
conditions: room temperature
equation: $CH_2{=}CH_2 + Br_2 \rightarrow CH_2BrCH_2Br$ (example)

NB This reaction introduces a new functional group onto the molecule

11. **alkene → bromoalkane**

reagents: hydrogen bromide
conditions: room temperature
equation: $CH_2{=}CH_2 + HBr \rightarrow CH_3CH_2Br$ (example)

12. **alkene → alkylhydrogensulphate**

reagents: concentrated sulphuric acid
conditions: cold
equation: $CH_2{=}CH_2 + H_2SO_4 \rightarrow CH_3CH_2OSO_3H$ (example)

13. **alkylhydrogensulphate → alcohol**

reagents: water
conditions: warm
equation: $CH_3CH_2OSO_3H + H_2O \rightarrow CH_3CH_2OH + H_2SO_4$ (example)

14. **alkene → alcohol**

reagents: steam
conditions: 300 ^{o}C, 600 kPa, phosphoric acid catalyst
equation: $CH_2=CH_2 + H_2O \rightarrow CH_3CH_2OH$

15. **nitrile → primary amine**

reagents: $LiAlH_4$
conditions: dry ether
equation: $R\text{-}CN + 4[H] \rightarrow R\text{-}CH_2NH_2$ (example)

16. **nitrile → carboxylic acid (**not examinable)

reagents: dilute HCl
conditions: heat under reflux
equation: $R\text{-}CN + 2H_2O + HCl \rightarrow R\text{-}COOH + NH_4Cl$

17. **alcohol → alkene**

reagents: concentrated sulphuric acid
conditions: heat, reflux
equation: $CH_3CH_2OH \rightarrow CH_2=CH_2 + H_2O$ (example)

18. **primary or secondary alcohol → carbonyl**

reagents: potassium dichromate and dilute sulphuric acid
conditions: warm, distillation
equation: $R_1R_2CHOH + [O] \rightarrow R_1\text{-}COR_2 + H_2O$

19. **primary alcohol → carboxylic acid**

reagents: potassium dichromate and dilute sulphuric acid
conditions: heat, reflux
equation: $R\text{-}CH_2OH + 2[O] \rightarrow R\text{-}COOH + H_2O$

20. **aldehyde → carboxylic acid**

reagents: potassium dichromate and dilute sulphuric acid
conditions: heat, reflux
equation: $R\text{-}CHO + [O] \rightarrow R\text{-}COOH$

21. **carbonyl → alcohol**

reagents: $NaBH_4(aq)$
conditions: room temperature
equation: $R_1\text{-}COR_2 + 2[H] \rightarrow R_1R_2CHOH$

22. **carboxylic acid → carboxylate salt**

reagents: NaOH
conditions: room temperature
equation: $R\text{-}COOH + NaOH \rightarrow R\text{-}COONa + HO$

23. **amine → alkylammonium salt**

reagents: HCl(aq)
conditions: room temperature
equation: $R_1R_2R_3N + HCl \rightarrow R_1R_2R_3NHCl$

24. **carbonyl → hydroxynitrile**

reagents: HCN
conditions: room temperature
equation: $R_1COR_2 + HCN \rightarrow R_1R_2COHCN$

NB This reaction adds an extra carbon atom and introduces an extra functional group onto the molecule

25. **acyl chloride → carboxylic acid**

reagents: water
conditions: room temperature
equation: $R\text{-}COCl + H_2O \rightarrow R\text{-}COOH$

26. **acyl chloride → amide**

reagents: ammonia
conditions: room temperature
equation: $R\text{-}COCl + NH_3 \rightarrow R\text{-}CONH_2$

27. **acid anhydride → carboxylic acid**

reagents: water
conditions: warm
equation: $(RCO)_2O + H_2O \rightarrow 2R\text{-}COOH$

28. **acid anhydride → amide**

reagents: ammonia
conditions: warm
equation: $(RCO)_2O + NH_3 \rightarrow R\text{-}CONH_2 + RCOOH$

29. **carboxylic acid + alcohol → ester**

reagents: concentrated sulphuric acid
conditions: heat, reflux
equation: $R_1COOH + R_2OH \rightarrow R_1COOR_2 + H_2O$

30. **acyl chloride + alcohol → ester**

conditions: room temperature
equation: $R_1COCl + R_2OH \rightarrow R_1COOR_2 + HCl$

31. **acid anhydride + alcohol → ester**

conditions: warm
equation: $(R_1CO)_2O + R_2OH \rightarrow R_1COOR_2 + R_1COOH$

32. **ester → carboxylic acid + alcohol**

reagents: concentrated sulphuric acid
conditions: heat under reflux
equation: $R_1COOR_2 + H_2O \rightarrow R_1COOH + R_2OH$

33. **ester → carboxylate salt + alcohol**

reagents: NaOH(aq)
conditions: heat under reflux
equation: $R_1COOR_2 + NaOH \rightarrow R_1COONa + R_2OH$

34. **acyl chloride + primary amine → N-substituted amide**

conditions: room temperature
equation: $R_1\text{-}COCl + 2R_2\text{-}NH_2 \rightarrow R_1\text{-}CONHR_2 + R_2\text{-}NH_3Cl$

35. **acid anhydride + primary amine → N-substituted amide**

conditions: warm
equation: $(R_1CO)_2O + R_2\text{-}NH_2 \rightarrow R_1\text{-}CONHR_2 + R_1\text{-}COOH$

36. **benzene → nitrobenzene**

reagents: concentrated sulphuric and nitric acids
conditions: warm, reflux
equation: $C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 + H_2O$

37. **benzene → alkylbenzene**

reagents: chloroalkane, $AlCl_3$
conditions: warm, reflux
equation: $C_6H_6 + RCl \rightarrow C_6H_5R + HCl$

38. **benzene → phenylalkanone**

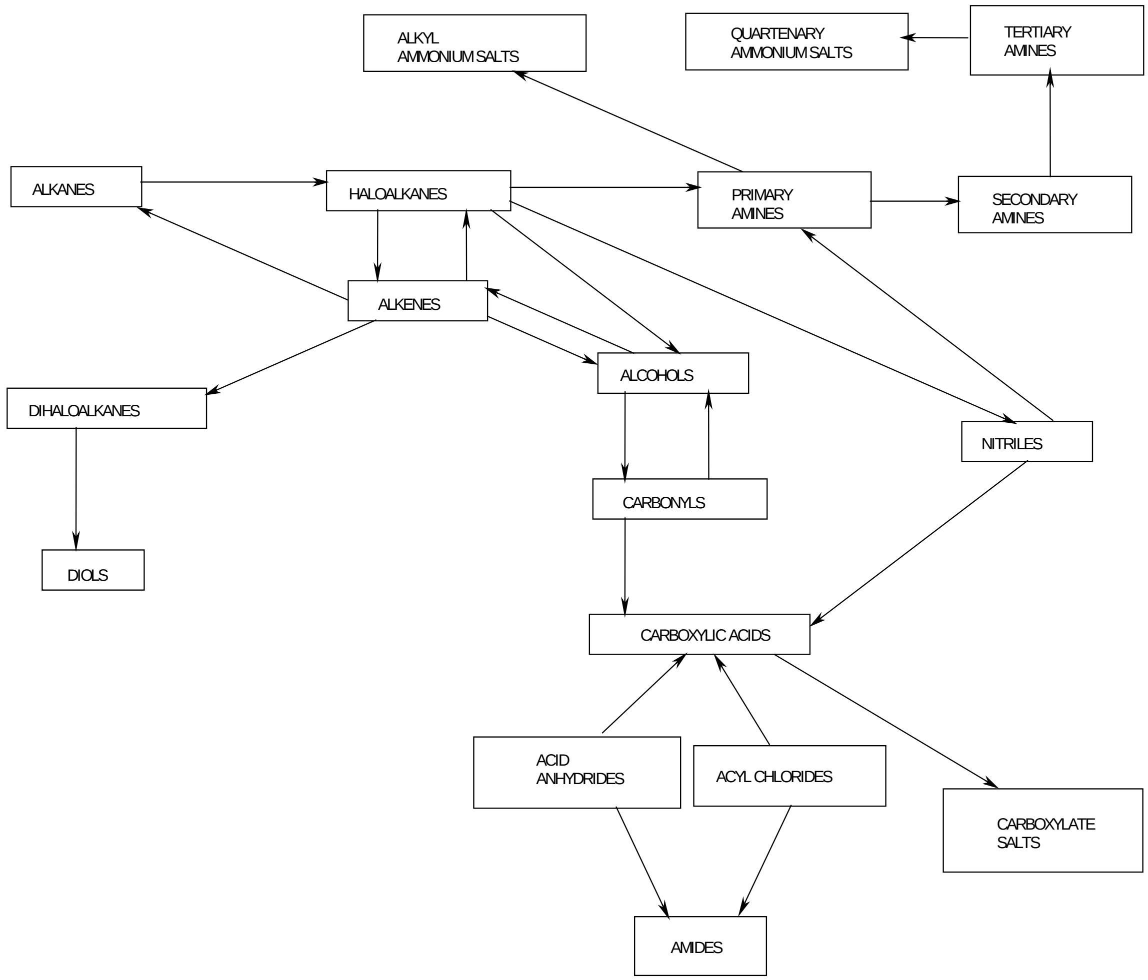
reagents: acyl chloride, $AlCl_3$
conditions: room temperature
equation: $C_6H_6 + RCOCl \rightarrow C_6H_5COR + HCl$

39. **nitrobenzene → phenylamine**

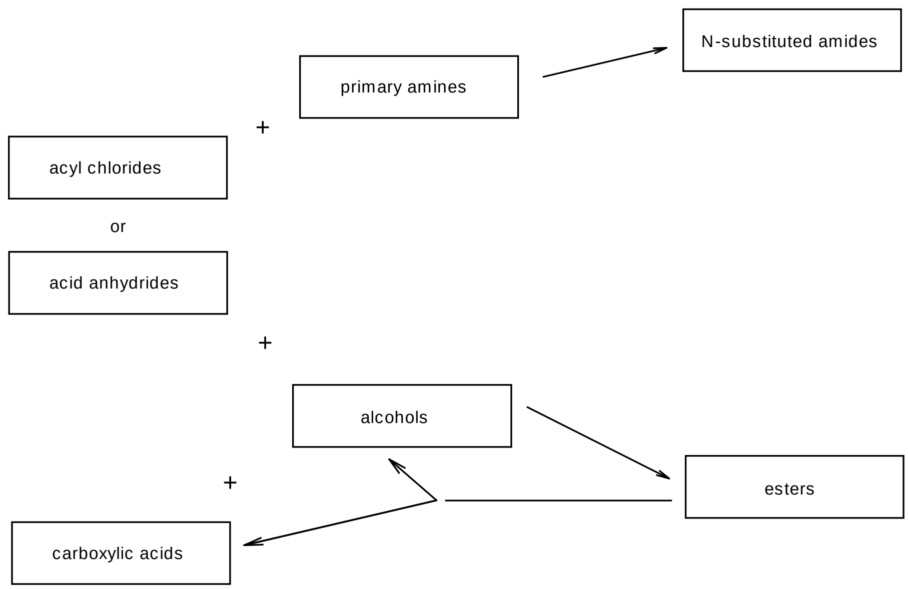
reagents: tin, concentrated HCl
conditions: room temperature
equation: $C_6H_6 + 6[H] \rightarrow C_6H_5NH_2 + 2H_2O$

The interconversion of these compounds can be summarised in the following synthesis maps:

a) **aliphatic synthesis map – simple conversions**



b) **condensation reactions**



c) **aromatic conversions**