

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 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 is 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: $\text{CH}_4 + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{HCl}$ (example)

NB This reaction introduces a new functional group onto the molecule

2. **chloroalkane → alcohol**

reagents: aqueous NaOH

conditions: warm, reflux

equation: $\text{R-Cl} + \text{NaOH} \rightarrow \text{R-OH} + \text{NaCl}$

3. **chloroalkane → alkene**

reagents: alcoholic KOH

conditions: heat, distillation

equation: $\text{CH}_3\text{CH}_2\text{Cl} + \text{KOH} \rightarrow \text{CH}_2=\text{CH}_2 + \text{KCl} + \text{H}_2\text{O}$ (example)

4. **chloroalkane → nitrile**

reagents: aqueous KCN

conditions: heat, reflux

equation: $\text{R-Cl} + \text{KCN} \rightarrow \text{R-CN} + \text{KCl}$

NB This reaction introduces an extra carbon atom onto the molecule

5. **chloroalkane → primary amine**

reagents: excess ammonia

conditions: heat

equation: $\text{R-Cl} + 2\text{NH}_3 \rightarrow \text{R-NH}_2 + \text{NH}_4\text{Cl}$

6. **primary amine → secondary amine**

reagents: chloroalkane

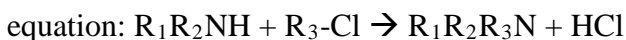
conditions: warm

equation: $\text{R}_1\text{-NH}_2 + \text{R}_2\text{-Cl} \rightarrow \text{R}_1\text{R}_2\text{NH} + \text{HCl}$

7. **secondary amine → tertiary amine**

reagents: chloroalkane

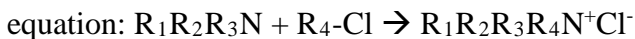
conditions: warm



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

reagents: chloroalkane

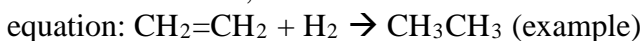
conditions: warm



9. **alkene → alkane**

reagents: hydrogen, Ni catalyst

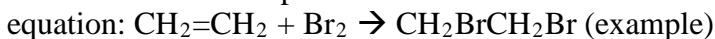
conditions: 150 °C, 2 atm



10. **alkene → dibromoalkane**

reagents: bromine

conditions: room temperature

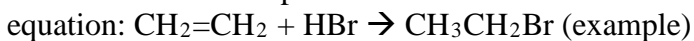


NB This reaction introduces a new functional group onto the molecule

11. **alkene → bromoalkane**

reagents: hydrogen bromide

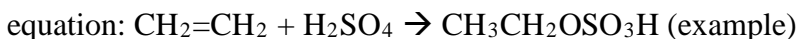
conditions: room temperature



12. **alkene → alkylhydrogensulphate**

reagents: concentrated sulphuric acid

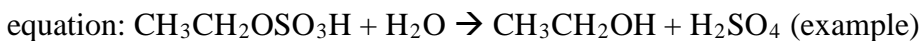
conditions: cold



13. **alkylhydrogensulphate → alcohol**

reagents: water

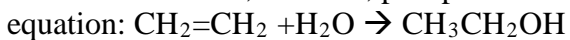
conditions: warm



14. **alkene → alcohol**

reagents: steam

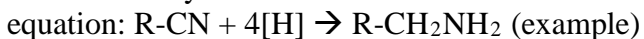
conditions: 300 °C, 600 kPa, phosphoric acid catalyst



15. **nitrile → primary amine**

reagents: LiAlH_4

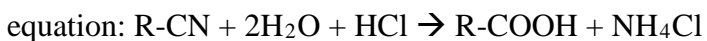
conditions: dry ether



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

reagents: dilute HCl

conditions: heat under reflux



17. **alcohol → alkene**

reagents: concentrated sulphuric acid

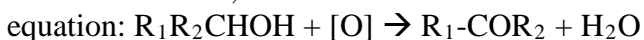
conditions: heat, reflux



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

reagents: potassium dichromate and dilute sulphuric acid

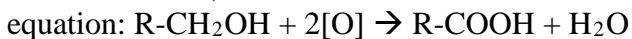
conditions: warm, distillation



19. **primary alcohol → carboxylic acid**

reagents: potassium dichromate and dilute sulphuric acid

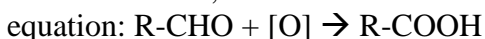
conditions: heat, reflux



20. **aldehyde → carboxylic acid**

reagents: potassium dichromate and dilute sulphuric acid

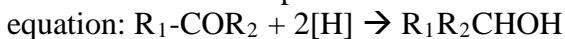
conditions: heat, reflux



21. **carbonyl → alcohol**

reagents: $\text{NaBH}_4(\text{aq})$

conditions: room temperature



22. **carboxylic acid → carboxylate salt**

reagents: NaOH

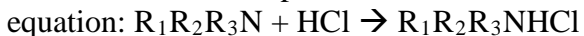
conditions: room temperature



23. **amine → alkylammonium salt**

reagents: $\text{HCl}(\text{aq})$

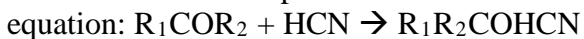
conditions: room temperature



24. **carbonyl → hydroxynitrile**

reagents: HCN

conditions: room temperature

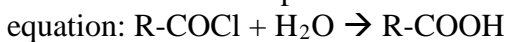


NB This reaction adds an extra carbon atom and introduces an extra functional group onto the molecule

25. **acyl chloride → carboxylic acid**

reagents: water

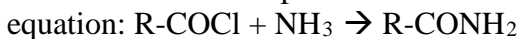
conditions: room temperature



26. **acyl chloride → amide**

reagents: ammonia

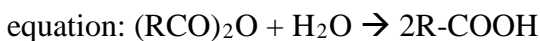
conditions: room temperature



27. **acid anhydride → carboxylic acid**

reagents: water

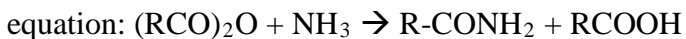
conditions: warm



28. **acid anhydride → amide**

reagents: ammonia

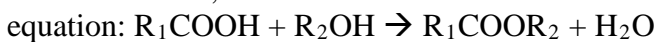
conditions: warm



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

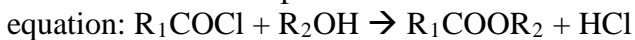
reagents: concentrated sulphuric acid

conditions: heat, reflux



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

conditions: room temperature



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

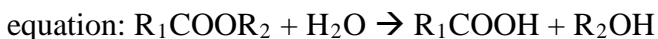
conditions: warm



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

reagents: concentrated sulphuric acid

conditions: heat under reflux



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

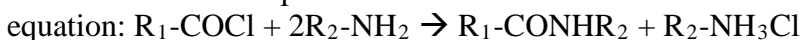
reagents: NaOH(aq)

conditions: heat under reflux



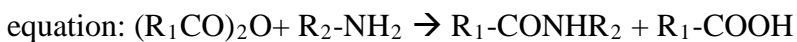
34. **acyl chloride + primary amine → N-substituted amide**

conditions: room temperature



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

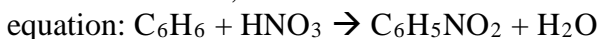
conditions: warm



36. **benzene → nitrobenzene**

reagents: concentrated sulphuric and nitric acids

conditions: warm, reflux



37. **benzene → alkylbenzene**

reagents: chloroalkane, AlCl₃

conditions: warm, reflux



38. **benzene → phenylalkanone**

reagents: acyl chloride, AlCl₃

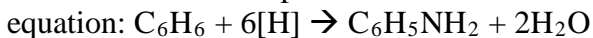
conditions: room temperature



39. **nitrobenzene → phenylamine**

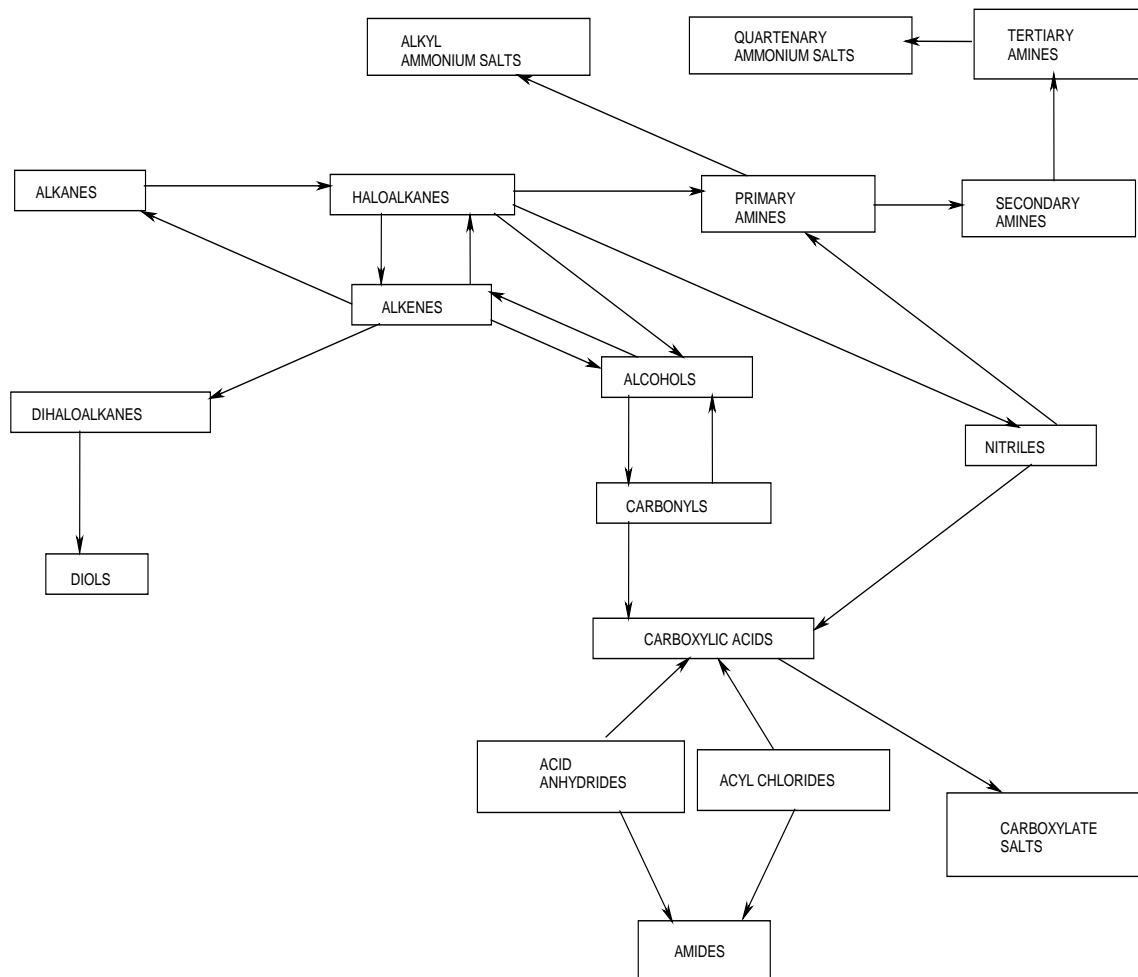
reagents: tin, concentrated HCl

conditions: room temperature

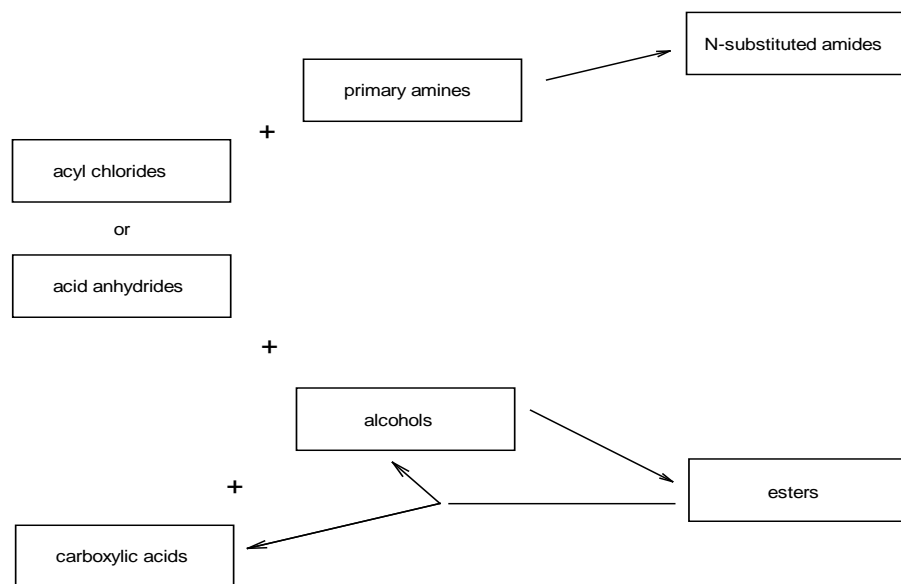


The interconversion of these compounds can be summarised in the following synthesis maps:

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



b) **condensation reactions**



c) **aromatic conversions**

