6.2.5 Synthesis

poly(alkene) → alkene
→ alcohol
→ aldehyde
→ ketone
→ hydroxynitrile
→ carboxylic acid

Br₂, Cl₂, room temp → alkene
→ alkane
→ haloalkane
→ amine
→ nitrile

H₂, Nickel Catalyst, addition/reduction → alkane
→ haloalkane
→ amine
→ nitrile

HBr, HCl, room temp → electrophilic addition
→ haloalkane
→ amine
→ nitrile

KOH aqueous → Nucleophilic substitution
→ haloalkane
→ amine
→ nitrile

Na₂Cr₂O₇/H⁺, heat under reflux, substitution → amine
→ nitrile

NaBH₄, Reduction → alcohol
→ aldehyde
→ ketone
→ hydroxynitrile
→ carboxylic acid

H₂O (g), Catalyst: Conc. H₃PO₄ → eliminination, dehydration → alcohol
→ aldehyde
→ ketone
→ hydroxynitrile
→ carboxylic acid

H₂O room temp → carboxylic acid

Acyl chloride

Acyl chloride, room temp → ester

Esters and amides can be hydrolysed by NaOH and acids

Acid hydrolysis

NH₃ room temp → Primary amide

1° amine, room temp → amide

Secondary amide

2° amine, 3° amine → Reduction

CN⁻ and ethanol, nucleophilic substitution

Acyl chloride, room temp → amide

Amide

Alcohol + H₂SO₄, heat → ester

Esterification

Alcohol + H₂SO₄, heat → ester

Esterification

Alcohol + H₂SO₄, heat → ester

Esterification

Alcohol, room temp → carboxylic acid

H₂O room temp → carboxylic acid

SOCl₂ → Acyl chloride

Acyl chloride, room temp → ester

Esterification

Acyl chloride, room temp → ester

Esterification

Acyl chloride, room temp → ester

Esterification
Aromatic synthetic routes

1. Hydrogen Nickel catalyst
2. Electrophilic substitution with \( \text{Br}_2 \) and \( \text{FeBr}_3 \)
3. Concentrated nitric acid + concentrated sulfuric acid
4. Electrophilic substitution
5. Acyl chloride in the presence of anhydrous aluminum chloride catalyst
6. Reduction with \( \text{Sn} \) and \( \text{HCl} \)
7. Nu Add with \( \text{CH}_3\text{Cl} \)
8. Red Nu Add
9. CH\(_3\)COCl
10. HCl/heat

\[ \text{CH}_3\text{CO}_2\text{H} + \text{H}_2\text{SO}_4 \]

\[ \text{Estherification} \]
Organic techniques

Distillation
In general used as separation technique to separate an organic product from its reacting mixture. Need to collect the distillate of the approximate boiling point range of the desired liquid.

Classic AS reaction using distillation
Reaction: primary alcohol $\rightarrow$ aldehyde
Reagent: potassium dichromate (VI) solution and dilute sulfuric acid.
Conditions: use a limited amount of dichromate and warm gently and distil out the aldehyde as it forms [This prevents further oxidation to the carboxylic acid]

$$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + [\text{O}] \rightarrow \text{CH}_3\text{CH}_2\text{CHO} + \text{H}_2\text{O}$$

Observation
Orange dichromate solution changes to green colour of $\text{Cr}^{3+}$ ions

Reflux
Reflux is used when heating organic reaction mixtures for long periods. The condenser prevents organic vapours from escaping by condensing them back to liquids.

Never seal the end of the condenser as the build up of gas pressure could cause the apparatus to explode. This is true of any apparatus where volatile liquids are heated

Classic AS reaction using reflux
Reaction: primary alcohol $\rightarrow$ carboxylic acid
Reagent: potassium dichromate(VI) solution and dilute sulfuric acid
Conditions: use an excess of dichromate, and heat under reflux: (distill off product after the reaction has finished using distillation set up)

$$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + 2[\text{O}] \rightarrow \text{CH}_3\text{CH}_2\text{CO}_2\text{H} + \text{H}_2\text{O}$$

Observation
Orange dichromate solution changes to green colour of $\text{Cr}^{3+}$ ions

Anti-bumping granules are added to the flask in both distillation and reflux to prevent vigorous, uneven boiling by making small bubbles form instead of large bubbles

It's important to be able to draw and label this apparatus accurately.
• Don’t draw lines between flask and condenser.
• Don’t have top of condenser sealed
• Condenser must have outer tube for water that is sealed at top and bottom
• Condenser must have two openings for water in and out that are open
Purifying an organic solid: Recrystallisation

<table>
<thead>
<tr>
<th>Step</th>
<th>Reason</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Dissolve the impure compound in a <strong>minimum volume of hot</strong> (near boiling) <strong>solvent.</strong></td>
<td>An appropriate solvent is one which will dissolve both compound and impurities when hot <strong>and</strong> one in which the compound itself does not dissolve well when cold. The minimum volume is used to obtain saturated solution <strong>and</strong> to enable crystallisation <strong>on cooling.</strong></td>
</tr>
<tr>
<td>2. <strong>Hot filter</strong> solution through (fluted) filter paper quickly.</td>
<td>This step will remove any insoluble impurities and heat will prevent crystals reforming during filtration.</td>
</tr>
<tr>
<td>3. <strong>Cool</strong> the filtered solution by inserting beaker in ice</td>
<td>Crystals will reform but soluble impurities will remain in solution form because they are present in small quantities so solution is not saturated. Ice will increase the yield of crystals.</td>
</tr>
<tr>
<td>4. <strong>Suction filtrate</strong> with a buchner flask to separate out crystals</td>
<td>The water pump connected to the Buchner flask reduces the pressure and speeds up the filtration.</td>
</tr>
<tr>
<td>5 Wash the crystals with distilled water</td>
<td>To remove soluble impurities</td>
</tr>
<tr>
<td>6. Dry the crystals between absorbent paper</td>
<td></td>
</tr>
</tbody>
</table>

**Loss of yield in this process**
- Crystals lost when filtering or washing
- Some product stays in solution after recrystallisation
- Other side reactions occurring

---

**Purifying an organic liquid**

**General method**
- Put the distillate of impure product into a separating funnel
- Wash product by adding either
  - sodium hydrogen carbonate solution, shaking and releasing the pressure from CO₂ produced.
  - Saturated sodium chloride solution
- Allow the layers to separate in the funnel, and then run and discard the aqueous layer.
- Run the organic layer into a clean, dry conical flask and add three spatula loads of drying agent (e.g., anhydrous sodium sulfate, calcium chloride) to dry the organic liquid. When dry the organic liquid should appear clear.
- Carefully decant the liquid into the distillation flask
- Distill to collect pure product

Sodium hydrogen carbonate will neutralise any remaining reactant acid.
Sodium chloride will help separate the organic layer from the aqueous layer.
The layer with lower density will be the upper layer. This is usually the organic layer.

The drying agent should
* be insoluble in the organic liquid
* not react with the organic liquid

Decant means carefully pour off organic liquid leaving the drying agent in the conical flask.
Measuring melting point

One way of testing for the degree of purity is to determine the melting "point", or melting range, of the sample.

If the sample is very pure then the melting point will be a sharp one, at the same value as quoted in data books.

If impurities are present (and this can include solvent from the recrystallisation process) the melting point will be lowered and the sample will melt over a range of several degrees Celsius.

Melting point can be measured in an electronic melting point machine or by using a practical set up where the capillary tube is strapped to a thermometer immersed in some heating oil.

In both cases a small amount of the sample is put into a capillary tube. The tube is heated up and is heated slowly near the melting point.

Comparing an experimentally determined melting point value with one quoted in a data source will verify the degree of purity.

Sometimes an error may occur if the temperature on the thermometer is not the same as the temperature in the actual sample tube.

Measuring boiling point

Purity of liquid can be determined by measuring a boiling point. This can be done in a distillation set up or by simply boiling a tube of the sample in an heating oil bath.

Pressure should be noted as changing pressure can change the boiling point of a liquid.

Measuring boiling point is not the most accurate method of identifying a substance as several substances may have the same boiling point.

To get a correct measure of boiling point the thermometer should be above the level of the surface of the boiling liquid and be measuring the temperature of the saturated vapour.