Grignard Reactions

Grignard Reagent is used to increase the length of the carbon chain in a molecule

Preparing Grignard Reagent

A halogenoalkane is dissolved in dry ether and reacted with magnesium to produce the reactive Grignard Reagent

\[
\text{CH}_3\text{CH}_2\text{I} + \text{Mg} \rightarrow \text{CH}_3\text{CH}_2\text{MgI}
\]

Ethyl magnesium iodide

Grignard Reagent

This Grignard reagent is highly reactive and the alkyl group can be considered to have a negative charge. The \( \text{R}^-[\text{MgI}] \) and so contains a nucleophilic carbon atom

Reactions of Grignard Reagent

Reactions with carboxyls

With methanal will produce a primary alcohol

\[
\text{H}_2\text{O}
\]

\[
\text{CH}_3\text{CH}_2\text{MgI} + \text{HCHO} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{Mg(OH)}\text{I}
\]

\[
\text{RMgI} + \text{HCHO} \rightarrow \text{RCH}_2\text{OH} + \text{Mg(OH)}\text{I}
\]

With other aldehydes will produce secondary alcohols

\[
\text{H}_2\text{O}
\]

\[
\text{CH}_3\text{CH}_2\text{MgI} + \text{CH}_3\text{CHO} \rightarrow \text{H}_3\text{C} - \text{CH}_2 - \text{OH} + \text{Mg(OH)}\text{I}
\]

\[
\text{RGmI} + \text{R'}\text{CHO} \rightarrow \text{RCH(OH)}\text{R'} + \text{Mg(OH)}\text{I}
\]

With ketones will produce tertiary alcohols

\[
\text{H}_2\text{O}
\]

\[
\text{CH}_3\text{CH}_2\text{MgI} + \text{H}_3\text{C}-\text{C} - \text{CH}_3 \rightarrow \text{H}_3\text{C} - \text{CH}_2 - \text{C} - \text{OH} + \text{Mg(OH)}\text{I}
\]

\[
\text{RMgI} + \text{R'}\text{COR}^- \rightarrow \text{R'R}^\prime\text{C(OH)}\text{R'} + \text{Mg(OH)}\text{I}
\]

Reaction with carbon dioxide

With \( \text{CO}_2 \) will produce a carboxylic acid

\[
\text{H}_2\text{O}
\]

\[
\text{CH}_3\text{CH}_2\text{MgI} + \text{CO}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CO}_2\text{H} + \text{Mg(OH)}\text{I}
\]

The carbon chain can also be increased by the introduction of a nitrile group into a compound by either reacting a halogenoalkane with \( \text{KCN} \) (see chapter 6D) or producing hydroxynitriles from carboxyls (see chapter 17B)
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 sulphuric 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]

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

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

Reflex

Reflex 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 sulphuric acid

**Conditions**: use an excess of dichromate, and **heat under reflux**: (distill off product after the reaction has finished using distillation set up)

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

**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 and one in which the compound itself does not dissolve well when cold. The minimum volume is used to obtain saturated solution and to enable crystallisation on cooling (If excess (solvent) is used, crystals might not form on cooling)</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 <strong>ice</strong></td>
<td>Crystals will reform but soluble impurities will remain in solution form because they are present in small quantities so the solution is not saturated with the impurities. 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

If the crystals are not dried properly the mass will be larger than expected which can lead to a percentage yield >100%
Steam distillation

In steam distillation steam is passed into the mixture and the product vapour is distilled off with the water and condensed.

Advantage of steam distillation:
The product distils at a lower temperature which can prevent decomposition of the product if it has a high boiling point.

Solvent extraction

Mix organic solvent and oil-water mixture in a separating funnel then separate the oil layer. Distil to separate oil from organic solvent. Add anhydrous CaCl$_2$ to clove oil to dry oil. Decant to remove CaCl$_2$.

Safety and hazards

A hazard is a substance or procedure that can have the potential to do harm. Typical hazards are toxic/flammable/harmful/irritant/corrosive/oxidizing/carcinogenic.

**RISK:** This is the probability or chance that harm will result from the use of a hazardous substance or a procedure.

Hazardous substances in low concentrations or amounts will not pose the same risks as the pure substance.

- Irritant - dilute acid and alkalis - wear googles
- Corrosive - stronger acids and alkalis wear goggles
- Flammable - keep away from naked flames
- Toxic - wear gloves, avoid skin contact, wash hands after use
- Oxidising - keep away from flammable / easily oxidised materials
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 salt is put into a capillary tube.

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.
Combustion Analysis

0.328 g of a compound containing C, H and O was burnt completely in excess oxygen, producing 0.880 g of carbon dioxide and 0.216 g of water. Use these data to calculate the empirical formula of the compound.

Work out moles of CO₂ = \( \frac{\text{Mass of CO}_2}{\text{Mr of CO}_2} \)

\[= \frac{0.88}{44} = 0.02 \text{ mol}\]

Moles of C in compound = moles of CO₂ = 0.02 mol

Mass of C in compound = mol of C x 12

\[= 0.02 \times 12 = 0.24 \text{ g}\]

Work out moles of H₂O = \( \frac{\text{Mass of H}_2\text{O}}{\text{Mr of H}_2\text{O}} \)

\[= \frac{0.216}{18} = 0.012 \text{ mol}\]

Moles of H in compound = 2 x moles of H₂O = 0.024 mol

Mass of H in compound = mol of H x 1

\[= 0.024 \times 1 = 0.024 \text{ g}\]

Work out mass of O in compound = mass of compound – mass of C – mass of H

\[= 0.328 - 0.24 - 0.024 = 0.064 \text{ g}\]

Work out moles of O in compound = \( \frac{\text{Mass of O}}{\text{Ar of O}} \)

\[= \frac{0.064}{16} = \text{mol 0.004}\]

Work out molar ratio of 3 elements (divide by smallest moles)

\[C = \frac{0.02}{0.004} = 5\]

\[H = \frac{0.024}{0.004} = 6\]

\[O = \frac{0.004}{0.004} = 1\]

empirical formula = C₅H₆O

See notes in chapter 10 and 15E on spectroscopy for mass spec, IR, and NMR
Bringing it all together

1. Work out empirical formula
Elemental analysis C 66.63% H 11.18% O 22.19%

\[
\begin{align*}
C & = \frac{66.63}{12} = 5.5525 \\
H & = \frac{11.18}{1} = 11.18 \\
O & = \frac{22.19}{16} = 1.386875
\end{align*}
\]

1. Using molecular ion peak m/z value from mass spectrum calculate Molecular formula

molecular ion peak m/z value = 144

Mr empirical formula C_8H_16O_2 = 72

If Mr molecular formula 144 then compound is C_8H_16O_2

2. Using IR spectra or functional group chemical tests to identify main bonds/functional group

C_8H_16O_2 could be an ester, carboxylic acid or combination of alcohol and carbonyl. Look for IR spectra for C=O and O-H bonds

There is a C=O but no O-H absorptions, so must be an ester.

3. Use IR spectra or functional group chemical tests to identify main bonds/functional group

4. Use NMR spectra to give details of carbon chain

4 peaks – only 4 different environments.

Peak at δ 4 shows H-C-O
Area 2 suggests CH_2
Quartet means next to a CH_3

Peak at δ 2.2 shows H-C=O
Area 2 suggests CH_3
Singlet means adjacent to C with no hydrogens

Peak at δ 1.2 shows R-CH_3
Area 3 means CH_3
Triplet means next to a CH_2

Put all together to give final structure

\[
\begin{align*}
H_3C-C-\overset{\text{CH_3}}{\text{CH_2}}-C-O-\overset{\text{CH_3}}{\text{CH_2}}-CH_3
\end{align*}
\]
### Testing for Organic Functional Groups

<table>
<thead>
<tr>
<th>Functional group</th>
<th>Reagent</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkene</td>
<td>Bromine water</td>
<td>Orange colour decolourises</td>
</tr>
<tr>
<td>Alcohols + carboxylic acids</td>
<td>PCl$_5$</td>
<td>Misty fumes of HCl produced</td>
</tr>
<tr>
<td>Alcohols, phenols, carboxylic acids</td>
<td>Sodium metal</td>
<td>Effervescence due to H$_2$ gas</td>
</tr>
<tr>
<td>Carbonyls</td>
<td>2,4-DNP</td>
<td>Orange/red crystals produced</td>
</tr>
<tr>
<td>Aldehyde</td>
<td>Fehling's solution</td>
<td>Blue solution to red precipitate</td>
</tr>
<tr>
<td>Aldehyde</td>
<td>Tollens Reagent</td>
<td>Silver mirror formed</td>
</tr>
<tr>
<td>Carboxylic acid</td>
<td>Sodium carbonate</td>
<td>Effervescence of CO$_2$ evolved</td>
</tr>
<tr>
<td>1° 2° alcohol and aldehyde</td>
<td>Sodium dichromate and sulphuric acid</td>
<td>Orange to green colour change</td>
</tr>
<tr>
<td>chloroalkane</td>
<td>Warm with silver nitrate</td>
<td>Slow formation of white precipitate of AgCl</td>
</tr>
<tr>
<td>Acyl chloride</td>
<td>Silver nitrate</td>
<td>Vigorous reaction- steamy fumes of HCl- rapid white precipitate of AgCl</td>
</tr>
</tbody>
</table>

### Tollens Reagent

**Reagent**: Tollens’s Reagent formed by mixing aqueous ammonia and silver nitrate. The active substance is the complex ion of [Ag(NH$_3$)$_2$]$_2^+$.  
**Conditions**: heat gently  
**Reaction**: aldehydes only are oxidised by Tollens’s reagent into a carboxylic acid and the silver(I) ions are reduced to silver atoms  
**Observation**: with aldehydes, a silver mirror forms coating the inside of the test tube. Ketones result in no change.

$$\text{CH}_3\text{CHO} + 2\text{Ag}^+ + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + 2\text{Ag} + 2\text{H}^+$$

### Fehling’s solution

**Reagent**: Fehling’s Solution containing blue Cu$^{2+}$ ions.  
**Conditions**: heat gently  
**Reaction**: aldehydes only are oxidised by Fehling’s Solution into a carboxylic acid and the copper ions are reduced to copper(I) oxide.  
**Observation**: Aldehydes: Blue Cu$^{2+}$ ions in solution change to a red precipitate of Cu$_2$O. Ketones do not react.

$$\text{CH}_3\text{CHO} + 2\text{Cu}^{2+} + 2\text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + \text{Cu}_2\text{O} + 4\text{H}^+$$

The presence of a carboxylic acid can be tested by addition of sodium carbonate. It will fizz and produce carbon dioxide.

$$2\text{CH}_3\text{CO}_2\text{H} + \text{Na}_2\text{CO}_3 \rightarrow 2\text{CH}_3\text{CO}_2\text{Na}^+ + \text{H}_2\text{O} + \text{CO}_2$$

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