CAIE Chemistry A-level

36: Organic Synthesis

(A-level only)

Notes

Synthetic Routes

Synthetic routes are the routes which can be used to produce a **certain product from a starting organic compound**. It is important that you understand the different methods and **conditions** required to convert compounds to other products.

Below is a table showing the typical reactions of different functional groups and how they can be identified. This table contains both reactions from AS and the A2 course.

Homologous series	Typical reactions	Identification
Alkanes **C-C**	*Combustion* *Electrophilic substitution/ free radical substitution* with Br_2 or Cl_2 (forms haloalkanes) *Cracking* (forms short chain alkenes and alkanes)	
Alkenes **C=C**	*Electrophilic addition:* - Steam (forms alcohols) - Hydrogen halides (forms haloalkanes) - Halogens (forms dihaloalkanes) - Hydrogen (forms alkanes) *Oxidation* with H^+/MnO_4^- (forms diols) *Addition polymerisation* (forms polymers) *Combustion*	**React with bromine water:** Decolorises in the presence of C=C.
Halogenoalkanes **C-F/ C-Cl/ C-Br/ C-I**	*Nucleophilic substitution:* - Hydrolysis (forms alcohols) - Reaction with ethanolic cyanide (forms nitriles) - Reaction with ammonia (forms primary amines) *Elimination* of hydrogen halide using ethanolic hydroxide ions (forms alkenes)	**React with $AgNO_3$(aq), test precipitate with NH_3(aq):** AgCl - white ppt soluble in dilute NH_3(aq) AgBr - cream ppt soluble in concentrated NH_3(aq) AgI - yellow ppt insoluble in NH_3(aq)
Alcohols **-OH**	*Combustion* *Substitution* with hydrogen halides, sulfur dichloride oxide or phosphorus(III) halides (forms haloalkanes) Ethanol and sodium (forms sodium ethoxide and hydrogen gas) *Oxidation* with $H^+/Cr_2O_7^{2-}$ (forms carbonyls and carboxylic acids) *Dehydration* using an acid catalyst (forms alkenes) *Esterification* with carboxylic acids or acyl chlorides	**React with $H^+/Cr_2O_7^{2-}$:** Colour change from **orange** to **green** in the presence of primary and secondary alcohols (no change for tertiary alcohols)

Aldehydes **-CHO**	*Oxidation* with $H^+/Cr_2O_7^{2-}$ (forms carboxylic acids) *Reduction* using $NaBH_4$ or $LiAlH_4$ (forms primary alcohols) *Nucleophilic addition* with HCN (forms hydroxynitriles)	**React with 2,4-DNPH**: A yellow-orange precipitate is formed in the presence of a carbonyl group. **React with Tollens' reagent:** A silver mirror is produced if an aldehyde is present. **React with Fehling's reagent:** The blue solution forms a brick red precipitate in the presence of an aldehyde **React with acidified potassium dichromate(VI):** Orange solution turns green .
Ketones **RCOR'**	*Reduction* using $NaBH_4$ or $LiAlH_4$ (forms secondary alcohols) *Nucleophilic addition* with HCN (forms hydroxynitriles)	**React with 2,4-DNPH**: A yellow-orange precipitate is formed in the presence of a carbonyl group.
Carboxylic acids **-COOH**	Reaction with metals, alkalis or carbonates (forms a salt and inorganic products) *Esterification* with alcohols *Reduction* with $LiAlH_4$ (forms alcohols) Reaction with $SOCl_2$ (forms acyl chlorides, sulfur dioxide and hydrochloric acid) Reaction with phosphorus(V) chloride or phosphorus(III) chloride (forms acyl chlorides) *Oxidation* of methanoic acid using Fehling's or Tollens' (forms carbon dioxide and water) *Oxidation* of ethanedioic acid using acidified potassium manganate(VII) (forms water and carbon dioxide)	**Test pH:** pH less than 7 when measured using a pH probe **React with a carbonate**: effervescence as CO_2 is formed
Esters **RCOOR'**	*Acid hydrolysis* (forms a carboxylic acid and an alcohol) *Alkali hydrolysis* (forms a carboxylate salt and an alcohol)	
Amines **-NH_2**	Reaction with acids (forms a salt)	
Nitriles **C≡N**	*Acid hydrolysis* (forms a carboxylic acid and a salt) *Alkali hydrolysis* (forms a carboxylate salt and ammonia)	

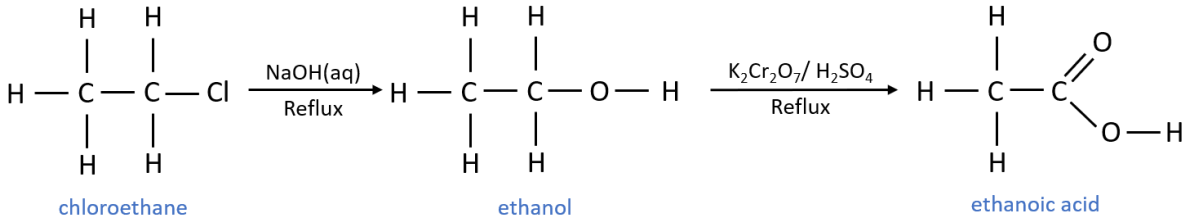
Arenes **-C_6H_5**	*Electrophilic substitution:* - Halogen (forms chlorobenzene with Cl_2 and bromobenzene with Br_2) - Nitration (forms nitrobenzene) Friedel-Crafts *acylation* and *alkylation* *Oxidation* of a side chain (forms benzoic acid) *Hydrogenation* (forms cyclohexane)	
Phenol **C_6H_5OH**	Reactions with strong bases (not acidic enough to react with carbonates) Reaction with sodium (forms sodium phenoxide and hydrogen gas) Reaction with diazonium salts (forms azo compounds) *Electrophilic substitution:* - Nitration using HNO_3 (forms nitrophenol) - Bromination using Br_2 (forms bromophenol)	
Acyl chlorides **-COCl**	*Hydrolysis* with water (forms carboxylic acids and HCl) *Hydrolysis* with sodium hydroxide (forms a carboxylate salt and water) *Esterification* with alcohols or phenol Reaction with ammonia (forms an amide and HCl) Reactions with primary amines (forms an N-substituted amide)	
Amides **-$CONH_2$**	*Acid hydrolysis* (forms a carboxylic acid and ammonium ions) *Alkali hydrolysis* (forms a carboxylate salt and ammonia or an amine) *Reduction* using $LiAlH_4$ (forms a primary amine)	

Multi-Stage Synthesis

Some organic molecules can be prepared using a **multi-stage synthesis**. Typically, this involves two stages: reactant → intermediate → product. It can cover more stages.

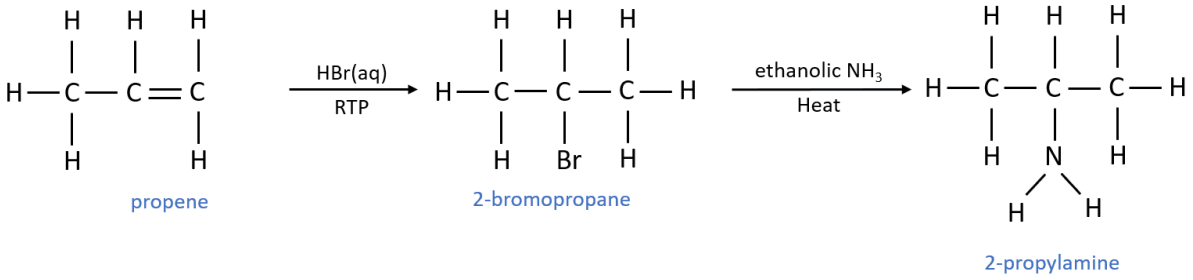
Example 1

Below is a diagram showing how ethanoic acid can be formed from chloroethane:



Example 2

2-propylamine can be formed from propene:



Analysing Synthetic Routes

When **synthesising** an organic compound, several factors are considered before deciding which synthetic route to use:

- **Type of reaction** - addition reactions are more sustainable than substitution or elimination reactions as there are no waste products.
- **Reagents** - renewable reagents with few safety concerns are preferred.
- **By-products** - less harmful by-products are favoured as there would be fewer safety and environmental concerns. If the by-products can be used in another industry, the process is more sustainable.
- **Conditions** - choose the reaction with the most energy efficient and safe conditions.