CAIE Chemistry A-level

21: Organic Synthesis

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.

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)

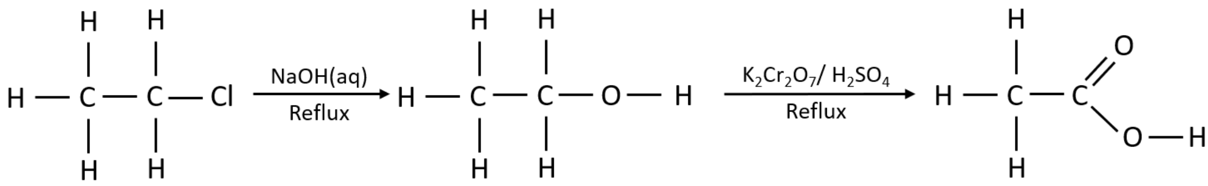
Aldehydes **-CHO**	*Oxidation* with $H^+/Cr_2O_7^{2-}$ (forms carboxylic acids) *Reduction* using $NaBH_4$ or $LiAlH_4$ (forms primary alcohols) *Nucleophilic addition* with HCN (forms hydroxynitriles)	**React with 2,4-DNPH**: A yellow-orange precipitate is formed in the presence of a carbonyl group. **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)	

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

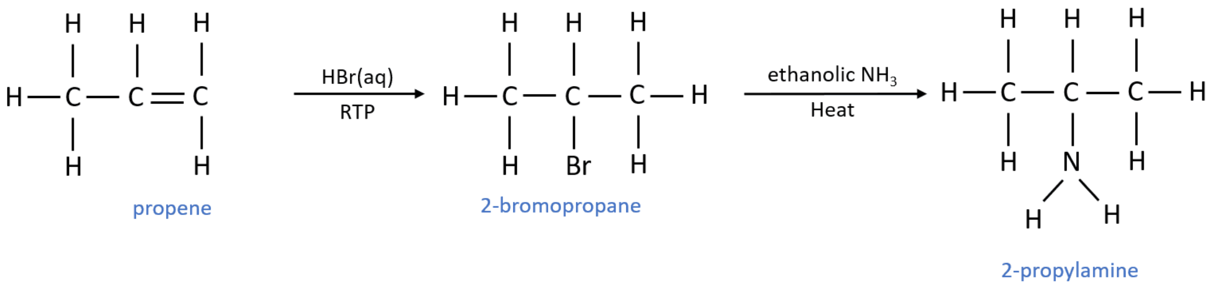
Below is a diagram showing how ethanoic acid can be formed from chloroethane:



chloroethane ethanol ethanoic acid

Example 2

2-propylamine can be formed from propene as follows:



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.

For an organic molecule containing several functional groups: (a) identify organic functional groups using the reactions in the syllabus (b) predict properties and reactions 2 devise multi-step synthetic routes for preparing organic molecules using the reactions in the syllabus 3 analyse a given synthetic route in terms of type of reaction and reagents used for each step of it, and possible by-products.