Alcohols and organic techniques

Naming and classifying alcohols, their reactions, oxidation of primary and secondary alcohols, and the techniques for preparing and purifying liquids (reflux, distillation, separating funnel, drying).

Alcohols

Alcohols contain the $-OH$ group, with the general formula $C_nH_{2n+1}OH$. They are named with the suffix **-ol** and a locant: propan-1-ol, propan-2-ol, 2-methylpropan-2-ol.

- **Primary**: the carbon bonded to $-OH$ is attached to one other carbon (CH_3CH_2OH).
- **Secondary**: attached to two other carbons ($CH_3CH(OH)CH_3$).
- **Tertiary**: attached to three other carbons ($(CH_3)_3COH$).

Reactions of alcohols

Combustion

$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$$

Halogenation

Reagent	Product	Notes
PCl_5 (solid, room temperature)	Chloroalkane, $POCl_3$ and **steamy fumes of HCl**	Also a **test for the –OH group**
Sodium or potassium bromide with 50% concentrated sulfuric acid	Bromoalkane	HBr forms in the flask, heated under reflux
Red phosphorus and iodine	Iodoalkane	PI_3 forms in the flask

$$C_2H_5OH + PCl_5 \rightarrow C_2H_5Cl + POCl_3 + HCl$$

Dehydration

Heating with concentrated **phosphoric acid** (or concentrated sulfuric acid, or passing vapour over hot aluminium oxide) removes water and forms an **alkene** by **elimination**: $C_2H_5OH \rightarrow C_2H_4 + H_2O$.

NOTE

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Descriptions of the mechanisms of these reactions are not needed.

Oxidation

Acidified **potassium dichromate(VI)** (orange) is an oxidising agent that turns green as Cr^{3+} forms. In equations the oxidising agent can be written $[O]$.

Alcohol	Conditions	Product
Primary	**Distil off** the product as it forms	**Aldehyde**
Primary	**Heat under reflux** with excess oxidising agent	**Carboxylic acid**
Secondary	Reflux or distil	**Ketone**
Tertiary	—	**No reaction** (the colour stays orange)

$$CH_3CH_2CH_2OH + [O] \rightarrow CH_3CH_2CHO + H_2O \; CH_3CH_2CHO + [O] \rightarrow CH_3CH_2COOH$$

Tests on the products

- **Aldehydes** give a **brick-red** precipitate with Benedict's or Fehling's solution (on warming), and a silver mirror with Tollens' reagent. Ketones do not.
- **Carboxylic acids** give effervescence with sodium carbonate or sodium hydrogencarbonate, giving off carbon dioxide.

The aldehyde is more easily oxidised than the alcohol. To stop at the aldehyde, remove it by distillation as soon as it forms. Its boiling temperature is lower than the alcohol's because it has no hydrogen bonding.

Techniques for preparing a liquid

Heating under reflux

The mixture is heated in a flask fitted with a **vertical condenser**. Vapours condense and return to the flask, so the reaction can be heated for a long time without loss. Add anti-bumping granules, and use an electric heater or a water bath rather than a flame for flammable liquids. The water flows into the condenser at the **bottom** and out at the top, so the jacket stays full.

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Distillation

The mixture is heated in a flask with a still head, thermometer and **downward** condenser. The component with the **lowest boiling temperature** distils over first. The thermometer bulb is level with the side arm so that it measures the temperature of the vapour. Distillation is used to separate a product from the reaction mixture and to purify it, and the temperature range at which the product comes over is a check on its purity (**boiling temperature determination**).

Solvent extraction

Shake the mixture with a second, immiscible solvent in a **separating funnel**. Release the pressure by opening the tap with the funnel inverted. Let the layers separate. The organic layer lies above water if its density is lower, and below if the density is higher. Run off the lower layer through the tap.

Drying

Add an **anhydrous salt** such as anhydrous magnesium sulfate, sodium sulfate or calcium chloride to the organic liquid and swirl. It takes up water. Add more until the solid no longer clumps and the liquid is clear. Filter or decant the dried liquid.

> **TRY IT**
>
> Order these steps for preparing 1-bromobutane from butan-1-ol: wash, dry, reflux, distil.

Reflux (reaction); distil to separate the crude product; wash the distillate with sodium hydrogencarbonate in a separating funnel; dry with an anhydrous salt; then do a final distillation and collect the fraction at the boiling temperature of 1-bromobutane (102 °C).

Core Practical 7: oxidation of propan-1-ol

Two products are made in two experiments from propan-1-ol with acidified potassium dichromate(VI):

1. **Propanal** by **distillation**: add the alcohol dropwise to the heated oxidising mixture and distil off the propanal as it forms, so that it is not oxidised further.
2. **Propanoic acid** by **reflux**: heat the mixture for a longer time under reflux, then distil to collect the acid.

Tests: the aldehyde gives a positive Benedict's test and the acid gives carbon dioxide with sodium carbonate.

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