

Aldehydes, Ketones and Carboxylic Acids

the $C=O$ carbon is electrophilic, so a nucleophile always attacks there first, no matter what happens after

Aldehyde vs ketone *

Aldehyde

- carbonyl carbon bonded to at least one H, e.g. CH_3CHO
- carbonyl carbon less hindered, so more electrophilic
- easily oxidised to a carboxylic acid; gives a positive Tollens' and Fehling's test

Ketone

- carbonyl carbon bonded to two carbon groups, e.g. CH_3COCH_3
- more hindered and less electrophilic than an aldehyde's carbonyl carbon
- resists mild oxidation; negative Tollens' and Fehling's test

the difference in oxidisability is the fastest way to tell them apart on paper: only an aldehyde has an H directly on the carbonyl carbon to be oxidised away

Nomenclature and structure

- IUPAC: aldehyde suffix -al, ketone suffix -one; aldehyde's carbonyl carbon is always C1, no locant
- carbonyl carbon is sp^2 hybridised, planar, $C=O$ at roughly 120° to its other two bonds
- polarity: O is more electronegative, so carbonyl carbon is partial positive, O is partial negative

Preparation from other functional groups

from a 1° alcohol, mild oxidation (PCC), stops at the aldehyde $R-CH_2OH \rightarrow R-CHO$

from a 2° alcohol, oxidation gives a ketone $R_2CH-OH \rightarrow R_2C=O$

from an acid chloride, Rosenmund reduction $R-COCl + H_2 \rightarrow R-CHO + HCl$

$Pd-BaSO_4$, poisoned



Rosenmund reduction: an acid chloride is reduced back only as far as the aldehyde, the poisoned catalyst stops it going further to the alcohol

PCC (pyridinium chlorochromate) is a MILD oxidiser that stops cleanly at the aldehyde; a strong oxidiser like acidic $KMnO_4$ or $K_2Cr_2O_7$ pushes straight through to the carboxylic acid