Optical isomerism and carbonyl compounds

Chirality and optical activity, racemic mixtures, evidence for SN1 and SN2, aldehydes and ketones, their reactions and tests, and nucleophilic addition of hydrogen cyanide.

Optical isomerism

A carbon atom bonded to **four different groups** is a **chiral centre** (asymmetric carbon). A molecule with one chiral centre has two **optical isomers (enantiomers)**: they are **non-superimposable mirror images**. Draw them in three dimensions with wedges and dashes, as mirror images of each other.

Optical activity: a single enantiomer **rotates the plane of plane-polarised monochromatic light**. One enantiomer rotates it clockwise, the other by the same amount anticlockwise. In other respects (melting temperature, chemical reactions with achiral reagents) they are the same.

A **racemic mixture** (racemate) contains **equal amounts** of both enantiomers. The rotations cancel, so it is **optically inactive**.

NOTE

2-hydroxypropanoic acid (lactic acid), $CH_3CH(OH)COOH$, has a chiral centre at the second carbon, which has H, OH, CH_3 and COOH attached.

Evidence for mechanisms

Optical activity can show how a reaction proceeds.

- **SN2** (one step, the nucleophile attacks from the side opposite to the leaving group): a single enantiomer of the halogenoalkane gives a **single enantiomer of the product**, with inverted configuration. Optical activity is kept.
- **SN1** (carbocation intermediate): the carbocation is **planar**, so the nucleophile can attack from either face with equal probability. The product is a **racemic mixture**, with no optical activity.

The same reasoning applies to **nucleophilic addition to carbonyl compounds**, where the carbonyl carbon is planar.

Aldehydes and ketones

Both contain the **carbonyl group**, $C=O$.

- **Aldehydes** have the C=O at the end of a chain, $-CHO$. Named with the suffix **-al**: ethanal, propanal.

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- **Ketones** have it within the chain, $R-CO-R'$. Named with **-one** and a locant if needed: propanone, pentan-3-one.

Physical properties

Carbonyl compounds cannot form hydrogen bonds with each other (no H on the oxygen), so they have **lower boiling temperatures** than alcohols of similar M_r, but higher than alkanes because of **permanent dipole interactions**. Small aldehydes and ketones are **soluble in water**, because the oxygen lone pair can form hydrogen bonds with water molecules. Solubility decreases as the carbon chain gets longer.

Reactions of carbonyl compounds

Oxidation

Aldehydes are easily oxidised to carboxylic acids; **ketones are not**, which allows them to be distinguished.

Reagent	Aldehyde	Ketone
Benedict's or Fehling's solution, warmed	Blue to **brick-red** precipitate (Cu_2O)	No change
Tollens' reagent (ammoniacal silver nitrate), warmed	**Silver mirror**	No change
Acidified dichromate(VI), warmed	Orange to green	No change

$$RCHO + [O] \rightarrow RCOOH$$

Reduction

Lithium tetrahydridoaluminate(III) ($LiAlH_4$, lithium aluminium hydride) in **dry ether** reduces carbonyls. In equations the reducing agent can be shown as $[H]$.

$RCHO + 2[H] \rightarrow RCH_2OH$ (primary alcohol) $RCOR' + 2[H] \rightarrow RCH(OH)R'$ (secondary alcohol)

$LiAlH_4$ reacts violently with water, hence the dry ether.

Nucleophilic addition of HCN

The reaction with **HCN with KCN (as a catalyst, giving CN^-)** forms a **hydroxynitrile**. It lengthens the carbon chain.

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Mechanism (for ethanal):

1. The nucleophile CN^- attacks the $\delta+$ carbon of the carbonyl group using its lone pair (curly arrow from the lone pair on carbon to the carbonyl carbon). The C=O π bond breaks, with the electrons moving to oxygen (curly arrow from the bond to O), giving an alkoxide ion intermediate.
2. The negative oxygen picks up H^+ from HCN (or from water), giving 2-hydroxypropanenitrile, $CH_3CH(OH)CN$, and regenerating CN^-.

The carbonyl carbon is planar, so CN^- attacks from either side with equal chance and, for an aldehyde or an unsymmetrical ketone, the product has a new chiral centre and forms as a **racemic mixture**. This is **evidence** for the planar C=O.

> **Learn the mechanism fully: show the dipole $C^{\delta+}=O^{\delta-}$, the lone pair on the nucleophile and the curly arrows from lone pair to carbon, from the double bond to oxygen, and from the O^- to H in HCN.**

2,4-Dinitrophenylhydrazine (2,4-DNPH)

2,4-DNPH is a **qualitative test for the carbonyl group**: both aldehydes and ketones give an **orange-yellow precipitate** (a condensation reaction, with a hydrazone formed). The precipitate is filtered, **recrystallised** and its **melting temperature** measured. Comparing it with a data table identifies the original aldehyde or ketone.

Iodoform test

Warm the compound with **iodine and sodium hydroxide**. A **pale yellow precipitate** of triiodomethane (CHI_3, iodoform), with a distinctive antiseptic smell, shows a methyl ketone, CH_3CO- (or an alcohol with $CH_3CH(OH)-$, which is oxidised first to a methyl ketone, as in ethanol).

> **TRY IT**
>
> An unknown compound C_4H_8O gives an orange precipitate with 2,4-DNPH, no reaction with Fehling's solution and a yellow precipitate with iodine and alkali. Identify it.

The orange precipitate shows a carbonyl group. No reaction with Fehling's solution means a ketone. The iodoform test shows CH_3CO-. Butanone, $CH_3COCH_2CH_3$, fits.

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