

## 4.5.2 Carbonyl tests, reduction and cyanide addition

Name: \_\_\_\_\_ Class: \_\_\_\_\_ Date: \_\_\_\_\_

Total: 20 marks

**KEY WORDS** nucleophilic addition

### Objective

Combine test results and reaction conditions to identify and transform carbonyls. Questions and marking guidance are original.

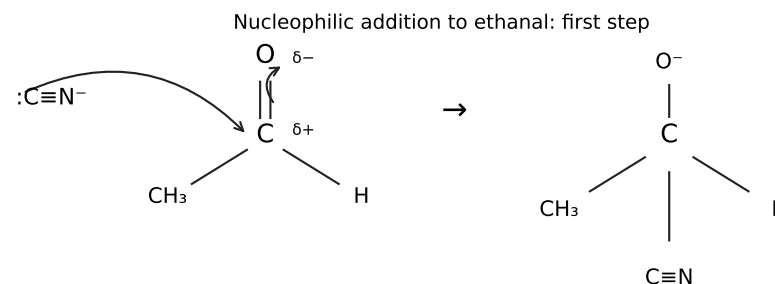
### 1 Key knowledge and worked examples

Aldehydes have terminal  $\text{-CHO}$ ; ketones have carbon groups on both sides of  $\text{C=O}$ . Both give a 2,4-DNPH precipitate. Warm Tollens' gives silver with an aldehyde; warm Fehling's/Benedict's gives brick-red  $\text{Cu}_2\text{O}$ . Ordinary ketones do not give these reducing tests. An isolated positive 2,4-DNPH result does not distinguish them.

#### ■ Worked identification

$\text{C}_3\text{H}_6\text{O}$  with  $\text{C=O}$ , positive Tollens' and three carbon-13 environments fits propanal,  $\text{CH}_3\text{CH}_2\text{CHO}$ . Propanone fits the formula but fails the other two observations.  $\text{LiAlH}_4$  in dry ether reduces propanal to propan-1-ol after suitable work-up.

$\text{HCN}$  with  $\text{CN}^-$  catalyst adds across  $\text{C=O}$ : a carbon lone pair of  $\text{CN}^-$  attacks carbonyl carbon and the  $\pi$  pair moves to O. The  $\text{O}^-$  intermediate gains  $\text{H}^+$  from  $\text{HCN}$ . Propanal gives  $\text{CH}_3\text{CH}_2\text{CH(OH)CN}$ , a racemate in achiral conditions because either face of the planar carbonyl is available. Propanone's product has identical methyl groups and is achiral. Cyanide/Tollens' chemistry requires approved controlled handling.



Then  $\text{O}^-$  takes  $\text{H}^+$  from  $\text{HCN}$ :  $\text{CH}_3\text{CH(OH)CN} + \text{CN}^-$ .  
Arrows start at an electron pair;  $\text{CN}^-$  attacks through carbon.

### 2 Practice

**2.1** Give one test that distinguishes propanal from propanone and both observations. [3]

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**2.2** Give product and reagent conditions for reduction of propanone. [2]

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**2.3** State the observation with 2,4-DNPH and explain its identification limit. [2]

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### 3 Exam-style questions

**3.1** An unknown  $\text{C}_3\text{H}_6\text{O}$  gives 2,4-DNPH and iodoform precipitates, no Tollens' silver and two carbon-13 signals. Identify it, explain all evidence, and predict whether its HCN product is chiral. [5]

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**3.2** Describe the electron-pair movements for  $\text{CN}^-$  addition to ethanal and the following proton transfer. State why a racemate results under achiral conditions. [4]

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**3.3** Draw the first-step electron-pair arrows for  $\text{CN}^-$  addition to ethanal and the charged intermediate. [4]

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## Solutions

Original marking guidance: M1 method, A1 accuracy, B1 explanation.

**2.1** Warm Tollens' reagent: propanal gives a silver mirror/grey silver, propanone gives no such change. Accept correct Fehling's/Benedict's alternative.

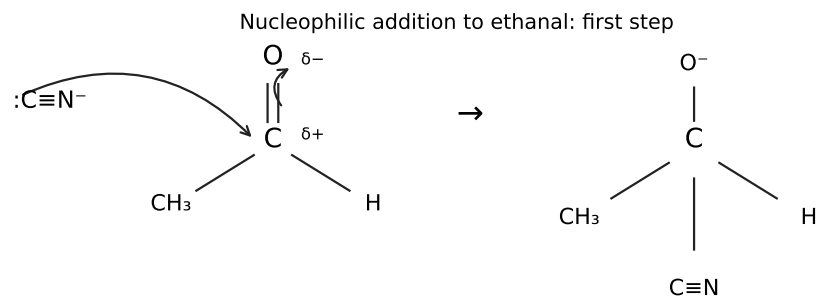
**2.2** Propan-2-ol;  $\text{LiAlH}_4$  in dry ether then appropriate work-up.

**2.3** Yellow/orange precipitate; both aldehydes and ketones respond, so it is not a distinction between them.

**3.1** Propanone  $\text{CH}_3\text{COCH}_3$ . Carbonyl gives DNPH;  $\text{CH}_3\text{CO}-$  gives iodoform and ketone gives no Tollens' silver. Two equivalent methyl carbons and one carbonyl environment give two signals. HCN product  $(\text{CH}_3)_2\text{C}(\text{OH})\text{CN}$  has identical methyl groups, so is achiral.

**3.2**  $\text{CN}^-$  carbon lone pair  $\rightarrow$  carbonyl C;  $\text{C}=\text{O}$   $\pi$  pair  $\rightarrow$  O.  $\text{O}^-$  gains  $\text{H}^+$  from HCN, regenerating  $\text{CN}^-$ . Either face of planar carbonyl is attacked equally in the ideal achiral model, giving equal enantiomers of  $\text{CH}_3\text{CH}(\text{OH})\text{CN}$ .

**3.3**



B1 lone pair on CN carbon to carbonyl carbon; B1  $\text{C}=\text{O}$   $\pi$  pair to oxygen; B1 correct intermediate connectivity; B1 negative oxygen.