

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.

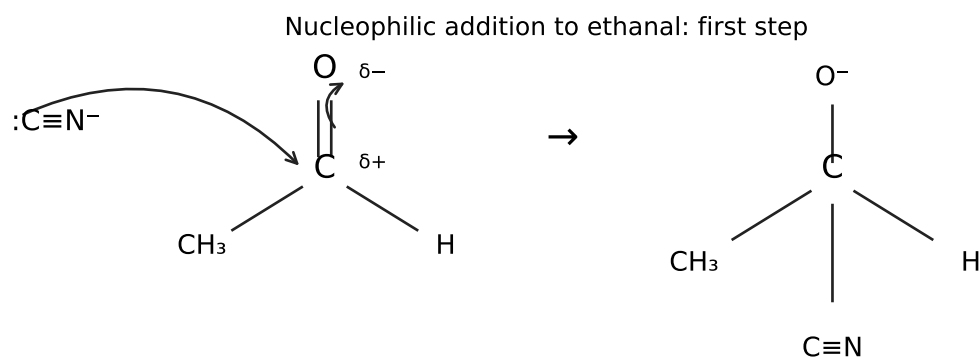
1 Key knowledge and worked examples

Aldehydes have terminal -CHO ; ketones have carbon groups on both sides of C=O . Both give a 2,4-DNPH precipitate. Warm Tollens' gives silver with an aldehyde; warm Fehling's/Benedict's gives brick-red Cu_2O . 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 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. LiAlH_4 in dry ether reduces propanal to propan-1-ol after suitable work-up.

HCN with CN^- catalyst adds across C=O : a carbon lone pair of CN^- attacks carbonyl carbon and the π pair moves to O. The O^- intermediate gains H^+ from HCN . Propanal gives $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CN}$, 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 O^- takes H^+ from HCN : $\text{CH}_3\text{CH}(\text{OH})\text{CN} + \text{CN}^-$.
 Arrows start at an electron pair; CN^- attacks through carbon.

2 Practice

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

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

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

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]

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

3.3 Draw the first-step electron-pair arrows for CN^- addition to ethanal and the charged intermediate. [4]

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.

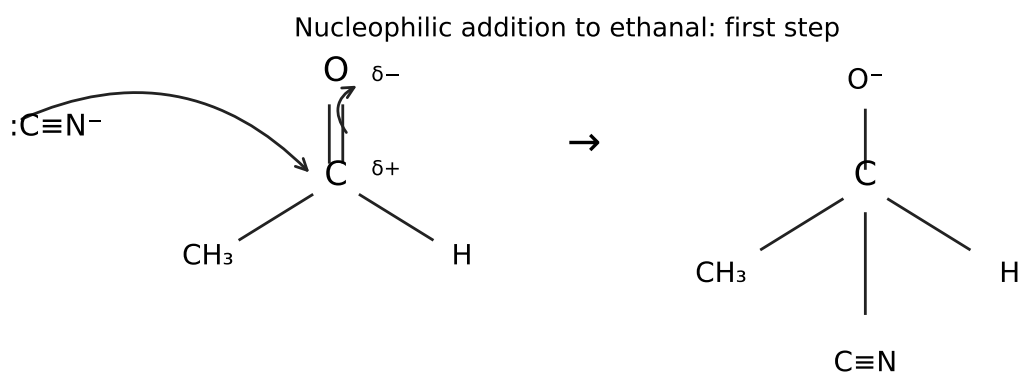
2.2 Propan-2-ol; LiAlH_4 in dry ether then appropriate work-up.

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

3.1 Propanone CH_3COCH_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 CN^- carbon lone pair $\rightarrow$ carbonyl C; $\text{C}=\text{O}$ π pair $\rightarrow$ O. O^- gains H^+ from HCN, regenerating 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 $\text{C}=\text{O}$ π pair to oxygen; B1 correct intermediate connectivity; B1 negative oxygen.