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.

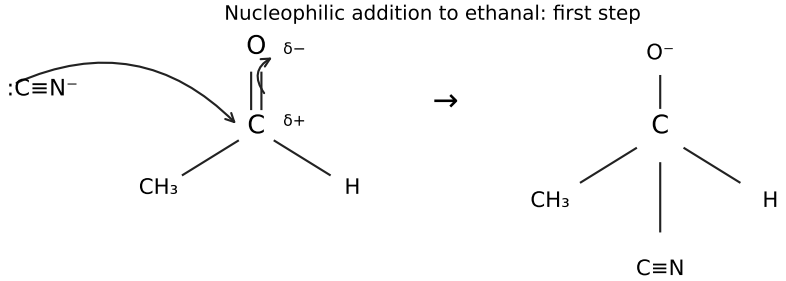
1 Key knowledge and worked examples

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

C_3H_6O with C=O, positive Tollens' and three carbon-13 environments fits propanal, CH_3CH_2CHO. 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 $CH_3CH_2CH(OH)CN$, 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.



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 C_3H_6O 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]