Victoria Junior College
JC2 H2 Chemistry
Tutorial: Carbonyl Compounds

Complete the following tables.

1. Preparation of aldehydes and ketones

starting compound	reagents and conditions	product
		$(CH_3)_2CHCH_2CHO$
$(CH_3)_2CHCH(OH)CH_3$	$K_2Cr_2O_7$(aq), H_2SO_4(aq), heat	

2. Reactions of aldehydes and ketones

reaction type	reagents & conditions	organic product(s) [if any] for	
		$(CH_3)_2CHCH_2CHO$	**$(CH_3)_2CHCOCH_3$**
	HCN(aq), NaCN		
reduction			
@condensation			
	$K_2Cr_2O_7$(aq), H_2SO_4(aq), heat or $KMnO_4$(aq), H_2SO_4(aq) heat		

	#Tollens' reagebt or Fehling's solution, heat		
	*I_2, NaOH(aq), heat		

Remarks:

@ 2,4-DNPH is used to identify the carbonyl C=O functional group in aldehyde and ketone

Tollens' reagent and Fehling's solution is used to identify aldehyde and aliphatic aldehyde respectively

* Alkaline aqueous I_2 is used to identify $CH_3CH(OH)–$ or $CH_3CO–$ structural unit in organic compounds

Reduction of Aldehydes and Ketones

1 A fresh salad may contain the following compounds.

X $CH_3CH_2CH_2CH=CHCHO$, an aroma of tomatoes

Y $CH_3CH_2CH_2CH_2CH=CHCOCH_3$, a flavour of mushrooms

Z $CH_3CH_2CH_2CH_2CH=CHCH=CHCHO$, an aroma of cucumbers

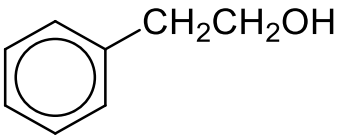
If these compounds are all present in the ratio *X* : *Y* : *Z* = 2 : 2 : 1, and all are reduced by a solution of an excess of $NaBH_4$, how many hydrogen atoms would be incorporated on average per molecule?

A 2.0 **B** 2.4 **C** 3.6 **D** 4.4

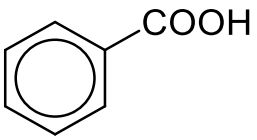
N10/I/2

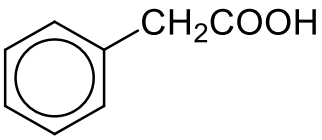
Organic Synthesis

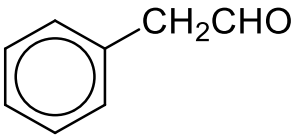
2 Suggest how the following transformation can be achieved from the following starting compound:

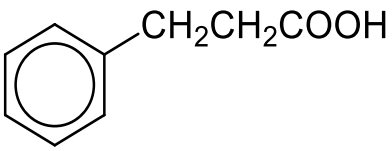


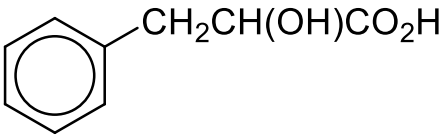
Indicate reagents and conditions you would use for each step. [7]

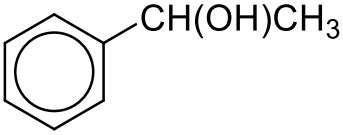
(a) 

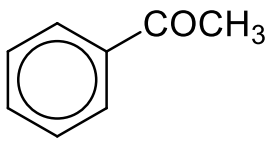
(b) 

(c) 

(d) 

(e) 

(f) 

(g) 

Nucleophilic Addition Mechanism

3 The simplest amide, methanamide, $HCONH_2$, can be dehydrated to hydrogen cyanide, HCN.

$$HCONH_2 \rightarrow HCN + H_2O$$

(a) Draw the mechanism of the reaction between hydrogen cyanide and ethanal, CH_3CHO, to form 2-hydroxypropanenitrile, $CH_3CH(OH)CN$. [2]

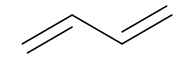
(b) In some circumstances, double bonds will undergo a nucleophilic addition reaction.

By applying your understanding of the following concepts:

(i) electronegativity;
(ii) electronic and steric effects;
(iii) delocalisation of electrons,

suggest reasons to explain why the following reactions occur or do not occur. [3]

Reaction scheme 1

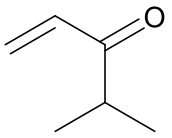


buta-1,3-diene

+ HCN

no addition reaction

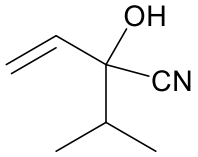
Reaction scheme 2



4-methylpent-1-en-3-one

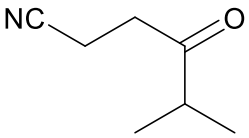
+ HCN

does not react to give



A

alkene reacts to give



B

N18/III/1(e) [modified]

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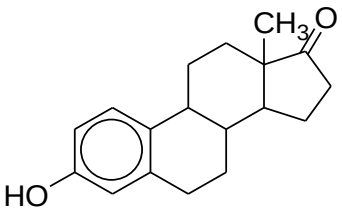
20

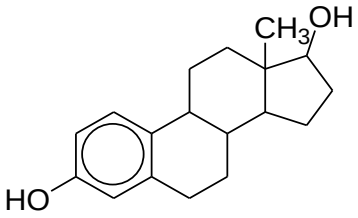
Distinguishing tests

Use of 2,4-dinitrophenylhydrazine (2,4-DNPH) to detect carbonyl functional group

4 Two female sex hormones are oestrone and oestradiol.



oestrone



oestradiol

Which of the following reagents could be used to distinguish between the two hormones?

A $Br_2(aq)$ at room temperature

B 2,4-dinitrophenylhydrazine

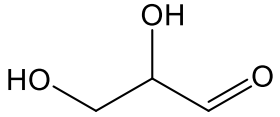
C Fehling's or Tollen's reagent

D I_2 in NaOH(*aq*)

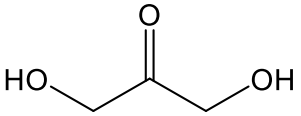
J00/III/24

Use of Tollens' and Fehling's reagents to detect aldehydes

5 Which statement is correct for **both** 2,3-dihydroxypropanal **and** 1,3-dihydroxypropanone?



2,3-dihydroxypropanal



1,3-dihydroxypropanone

A They are chiral.

B They give a silver mirror with Tollens' reagent.

C They give a yellow precipitate with alkaline aqueous iodine.

D They have the same empirical formula.

N14/I/23

6(a) Three compounds **E**, **F** and **G** all have the molecular formula C_3H_6O. **E** is an alcohol, **F** is a ketone, and **G** is an aldehyde.

(i) Draw possible structural formulae for **E**, **F** and **G**. [3]

E	**F**	**G**

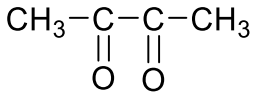
(ii) Describe tests (reagents, conditions and observations with each compound) that would allow you to show that:

1. E is an alcohol, whereas F and G are not.
2. F and G are carbonyl compounds, whereas E is not.
3. G is an aldehyde, whereas E and F are not.

Write balanced equations for all reactions that occur. [3]

Use of alkaline aqueous iodine to detect presence of a $CH_3CO–$ group

(b) One of the compounds responsible for the flavour of butter is butane-2,3-dione:



Give the structural formula of the organic products formed when butane-2,3-dione reacts completely with J97/I/7

(i) H_2, Ni catalyst, heat [1]	**(ii)** I_2, NaOH(aq) [1]

Structural Elucidation

7 Citral, a constituent of lemon-grass oil, gives a silver mirror with Tollens' reagent.

When 0.100 g of citral is catalytically hydrogenated at 0°C and 1 bar, 44.2 cm^3 of hydrogen react to give $(CH_3)_2CH(CH_2)_3CH(CH_3)CH_2CH_2OH$.

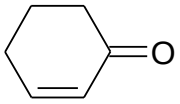
Oxidation of citral with hot acidified potassium manganate(VII) gives initially three compounds, **D**, $C_2H_2O_4$, **E**, C_3H_6O and **F**, $C_5H_8O_3$.

Suggest structural formulae for citral, **D**, **E** and **F** from the information given above. Explain your reasoning. [8]

[Remark: Explanation should include reaction type, functional group type and stoichiometric calculation.]

Victoria Junior College
JC2 Chemistry
Supplementary Questions: Carbonyl Compounds

1 How many σ and π bonds are there in the following molecule?



	σ	**π**
A	5	4
B	7	2
C	8	1
D	15	2

2 Propanone, $(CH_3)_2CO$, may be used as the starting point for synthesising methacrylic acid, $H_2C=C(CO_2H)CH_3$.

Which sequence would be most suitable?

A $(CH_3)_2CO \rightarrow (CH_3)_2C(OH)_2 \rightarrow (CH_3)_2C(OH)CN \rightarrow H_2C=C(CO_2H)CH_3$

B $(CH_3)_2CO \rightarrow (CH_3)_2CH(OH) \rightarrow (CH_3)_2CH(CN) \rightarrow H_2C=C(CO_2H)CH_3$

C $(CH_3)_2CO \rightarrow (CH_3)_2C(OH)CN \rightarrow H_2C=C(CN)CH_3 \rightarrow H_2C=C(CO_2H)CH_3$

D $(CH_3)_2CO \rightarrow H_2C=C(OH)CH_3 \rightarrow H_2C=C(CN)CH_3 \rightarrow H_2C=C(CO_2H)CH_3$

3 The compound C_3H_7Br undergoes a sequence of reactions as follows:

$$C_3H_7Br \xrightarrow{OH^-(aq)} \mathbf{X} \xrightarrow[K_2Cr_2O_7]{\text{acidified}} \mathbf{Y} \xrightarrow{\text{Tollens' reagent}} \mathbf{Z} + \text{silver mirror}$$

What could be the formulae for **X**, **Y** and **Z**?

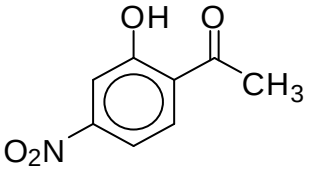
	X	**Y**	**Z**
A	$CH_3CH_2CH_2OH$	$CH_3CH_2CO_2H$	CH_3CH_2CHO
B	$CH_3CH_2CH_2OH$	$CH_3CH(OH)CH_2OH$	CH_3CO_2H
C	$CH_3CH_2CH_2OH$	CH_3CH_2CHO	$CH_3CH_2CO_2H$
D	$CH_3CH(OH)CH_3$	CH_3COCH_3	CH_3CO_2H

4 Compound **X**

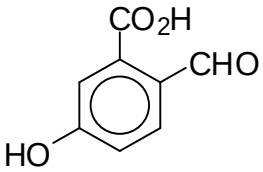
- gives a violet colouration with neutral iron(III) chloride.
- does not give any visible reaction with Fehling's solution.
- gives a silver mirror with ammonical silver(I) nitrate.
- does not give any visible reaction with sodium carbonate.

What could **X** be?

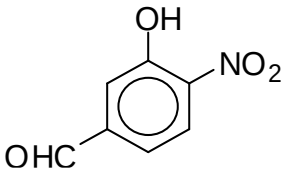
A



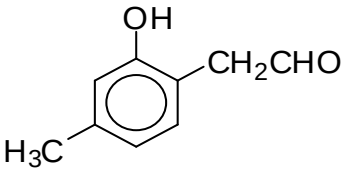
B



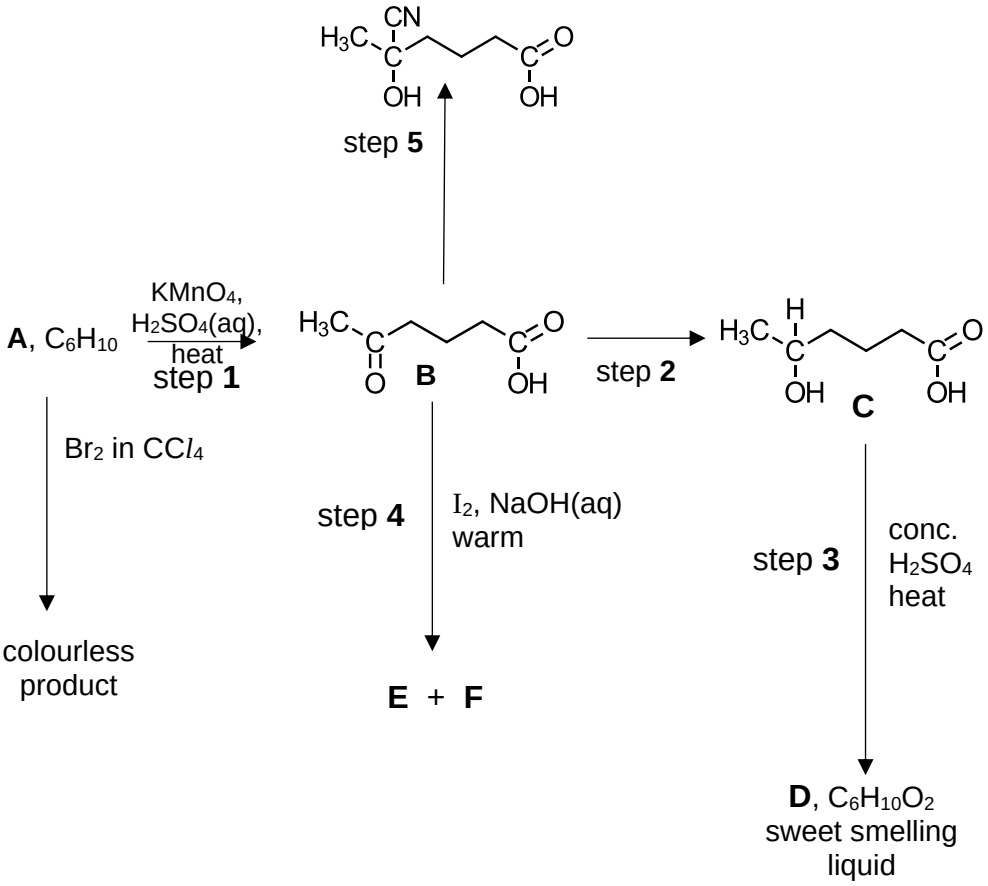
C



D



5 **(a)** Compound **A**, C_6H_{10}, is used commercially to slow down the ripening of fruits and to help maintain the freshness of cut flowers. The following is a series of reactions involving Compound **A** and its intermediates.



(i) State the reagents and conditions for steps **2** and **5**.

(ii) Draw the structures of the organic products **A**, **D**, **E** and **F**.

(iii) Describe a simple chemical test to distinguish between compounds **B** and **C**.

(b) Propose a 2-step synthesis for the following conversion. Draw the structure of the intermediate in the box below and state clearly the reagents and conditions used for both steps.

Step **I**:

Step **II**:

6 The reaction between hydrocyanic acid, HCN, and carbonyl compounds is of unusual interest in that it is almost certainly the first organic reaction to have its mechanistic pathway established in 1903 by Lapworth.

The reaction usually requires a *trace* amount of a base to be added.

(a) Give the name of the type of reaction between HCN and carbonyl compounds.

(b) Describe the mechanism for the reaction between HCN and propanal, detailing the role of the trace amount of base.
In your answer show any relevant charges, dipoles or lone pairs of electrons you consider to be important in this mechanism.

(c) The product in **(*b*)** contains a chiral centre. Is the resulting product optically active? Explain your answer.

Reactions of Alcohols and Ketones