HYDROXY COMPOUNDS



Structured / Free Response Questions

[JJC 2011/III/3(c)(f)&(iii)]

Pharmaceutical companies produce and market the drugs, salbutamol hydrochloride and ephedrine hydrochloride, for the treatment of asthmatic attacks. The active ingredients are saibutamol and ephedrine respectively.

salbutamoi

ephedrine

- (i) Suggest a simple chemical test to distinguish between salbutamol and ephedrine.
- (ii) An isomer of salbutamol, compound G, has the structure shown,

o punoduo

Predict, with reasoning, whether salbutamol or compound G has a lower melting point.

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2 [DHS 2011////3(b)]

Alkynes are also found in many naturally occurring organic molecules, such as the hormone molecules shown below.

Complete the following sequence of chemical tests by stating suitable reagents, conditions and observations at each step, to identify the stated hormone molecules.

14 Hydroxy Compounds

step	reagents, conditions and observations	molecule
	reagent and conditions;	
-	observation;	9
r	reagent and conditions.	The state of the s
1	observation;	I.
Ç.	reagent and conditions;	
,	observation:	L
৸	reagent and conditions;	
	observation;	ม
		[9]

[MJC 2011/III/5(a) & (c)]

The compound chloroxylenol and Triclosan are two chlorinated phenol compounds which has been featured for its anti-microbial action, and used in soaps and detergents. While these compounds are relatively safe for humans to handle, they may have a tendency to persist in the environment for a long period of time, where in turn, they can be converted to other more toxic compounds, causing environmental problems.

chloroxylenol

Triclosan

- By considering their solubility and reaction with water, suggest two reasons why such compounds are likely to persist in the environment.
- (II) Triclosan can be synthesised from 2,4-dichlorophenol.

Compare the acidity of 2,4-dichlorophenol with chloroxylenol.

Give the structural formulae of the organic products formed when compound A reacts with the following reagents. [Modified HCI 2011/III/3(d)]
(a) Give the structural for

hot alkaline KMnO₄

=

- dilute HNO₃ €
- hot acidified K2Cr2O; \equiv
- aqueous bromine ()
- PC/5 (1)
- CH3CO2H and a small amount of concentrated H2SO4, heat Ξ

 Ξ Explain why compound A is more soluble in aqueous sodium hydroxide than in water. <u>a</u>

[Modified PJC 2011/III/7(a)] 157

plastic materials. The reaction scheme shown below outlines how compound D can be Compound D is an amine-containing monomer which is used in polymerisation to form textiles. ă commonly found in polymers used in plastics formed from 2-chloroethylhexane. Amines are

14 Hydroxy Compounds

- Suggest the structural formulae for the compounds A, B and C. =
- Name the type of reactions in steps I to V. (11)
- Suggest suitable reagents and conditions in steps I, II, IV and V. (11)

Z

The following table lists the boiling points of some unbranched alkanes and alcohols. [YJC 2011/III/2(c)(III) & (IV) & RI 2011/III/4(c)(II) & RI 2009/III/1(c)] φ

boiling points / °C	88-	-42	0	, 5 9	82	26	118	133
formula	S.E.	i i i	£4H ₁₀	CH3OH	С2Н5ОН	HOH!S	C.H.O.H	CSH.OH

Explain why the boiling points of the alcohols are much higher than those of the alkanes. = (B)

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- (ii) A mixture containing two of the alcohols listed in the table above, is to be separated using fractional distillation. The mixture is placed in the distillation apparatus at room temperature and then gently heated. The first fraction is collected at 97.2 °C.
- Identify one alcohol from the table above that could not be present in the
- By specifically referring to this experiment, explain why the alcohol identified in (I) could not be present.
- III Give a reason why the distillation flask should not be heated using a bunsen burner.
- (b) Dehydration occurs when alcohols are heated over Al₂O₃
- Compound N is obtained when propan-2-of is heated over A₂O₃, identify compound N,
- (ii) Suggest reagents and conditions to convert N into 2-hydroxypropanoic acid (commonly known as lactic acid) in no more than 3 steps,
- (c) When lactic acid is refluxed with a catalytic amount of concentrated sulfuric acid, compound Z with the molecular formula of C₈H₈O₄ is formed. It does not react with sodium. Deduce the structural formula of Z, giving reasons for your answer.

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[SRJC 2011/III/5(c)]

Organometallic compounds, usually a metal attached to an R group, can be used to convert carbonyl compounds to alcohols. An example is shown below:

R-CH#O + R'-LI ---- R-CH(OH)-R' + LIOH

2-bromobutane can be converted to 2-methylbutan-2-of in **3 steps**. Write the reagents and conditions required for the conversion, including intermediate compounds. $^{\varepsilon}$

3 [CJC 2011/III/4(c)]

A hydrocarbon A has the molecular formula of C₁₀H₁₄. When A is treated with hot aqueous acidified KMnO₄, benzolo acid is formed.

When reacted with bromine in the presence of ultraviolet light, A produced four isomeric monobromo compounds with the formula $C_{10}H_{13}Br$.

14 Hydroxy Compounds

Upon heating with alcoholic NaOH, two of the monobromo compounds B and C gave the same compound which can exist as a pair of geometric isomers, D and E.

Heating **B** with aqueous NaOH produces compound **F** which does not react with acidified potassium dichromate(VI),

Suggest the structures of A-F, explaining your reasoning.

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9 [PJC 2011/III/2(c)]

A recently discovered organic compound L possesses a pleasant floral scent and is therefore being used as a component of many essential oils and perfumes. A molecule of L has the molecular formula, C₁₀H₁₈O.

A sample of L has the ability to rotate plane-polarised light.

No reaction occurs between L and 2,4-dinitrophenylhydrazine. However, L produces M, $G_{\rm to}H_{\rm 2}O$, with hydrogen with nickel catalyst.

No change is observed when L is heated with acidified potassium dichromate(VI).

Heating L with aluminium oxide produces a mixture of two products. N, with molecular formula C₀H₁s, is present as the major product.

N reacts with hot concentrated acidified potassium manganate(VII) to produce propanone and P, C₈H₈O₈. A colouriess gas, which forms a white precipitate in limewater, is liberated.

P can also be produced by the reaction of the following compound with hot concentrated acidified potassium manganate(VII).

Deduce the structures of compounds L, M, N, and P. Explain the chemistry of the reactions described.

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[IJC 2011/III/5(d)]

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a Terpineol, C16H1sO, has a pleasant smell similar to illac and is a common ingredient in perfumes, cosmetics, and flavours. a-Terpineol contains a cyclohexene ring and an alcohol group which is not readily oxidised.

Heating a-Terpineol with concentrated acidified KIMnO4 gives H, C10H18O4, which gives a yellow precipitate on warming with alkaline aqueous iodine. On hydrogenation in the presence of palladium catalyst, a-Terpineol gives J, CtoH20O.

CreHis. K is exidised by warm acidified KMnO4 to give M, CsHisO along with the evolution of J reacts readily in the presence of a few drops of concentrated sulfaric acid to give K,

Deduce the structural formulae for H, J, K and α-Terpineol: Explain your reasoning.

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[NYJC 2015/III/1(a)] -

Functional groups in a molecule must be protected in order to react in a desired way with reagents used in a synthesis. For instance, alcohols undergo oxidation or nucleophilic substitution reactions readily. To avoid these reactions, the alcohol can be protected by

OCH₃ using converting it to an unreactive methoxymethyl ether (MOM), RO methylchloromethyl ether (MOMC/), Cl'

Protection Process

14 Hydroxy Compounds

Deprotection Process

RO OCH₃
$$\xrightarrow{H^*(aq)}$$
 ROH + $\xrightarrow{\alpha}$ + $\xrightarrow{h_2O}$ H $\xrightarrow{H_2O}$ + CH₃OH H \xrightarrow{MOM} Intermediate A

intermediate A

- Suggest why ROH is converted to RO- in Step I. 0 <u>(9</u>
- Brønsted-Lowry bases are usually used in Step I of the protection process. Bulky organic bases such as N.N-dlisopropylethylamine (DIPEA) is one \equiv

DIPEA

Bulky organic bases such as DIPEA are preferred over

- less bulky organic bases such as primary amine and
 - alkalis such as sodium hydroxide.

Explain why primary amine is unsuitable to be used as a base in step I of the protection process.

- Explain why Step I does not occur if the base was changed to sodium hydroxide (111)
- Describe the mechanism of **Step II** for the protection process using MOMC/ (Recall the content learnt in RX) (EV)
- State the oxidation state of carbon labelled a in intermediate A Ξ
- Compound F can be made from compound B in four steps, where the first step involves the protection of alcohol using MOMCI. (<u>X</u>)

(vii) State the types of reaction for Steps IV, V and VII.

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[CJC 2016/II/5(a)]
The compound p-cresol is used in the production of antioxidants. It is also used in the fragrance and dye industries.

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p-cresol

Draw the displayed formula of a functional group isomer of p-cresol, and describe a laboratory test that will distinguish these two compounds. You should state the reagents used and the observations expected.

(a) Draw the displayed formula of a functional group isomer of p-cresol, and describe a laboratory test that will distinguish these two compounds. You should state the reagents used and the observations expected.

13 [DHS 2016/II/5]

The male slik moth secretes 'juvenile hormone', Clethao, which contains are unknown number of epoxide rings. Epoxide rings are readily hydrolysed by cold aqueous acid.

The reactions that 'juvenile hormone' and the resulting derivatives undergo are shown in the table below.

Reactant	Reagent	Result
	hydrogen in the presence of a palladium catalyst	S, C ₁₆ H ₂₈ O4, formed.
'Suvenile hormone'	cold dilute hydrochloric acid	cold dilute hydrochloric alcoholic groups and three acid chiral centres is formed.
1-	warmed with aqueous sodium hydroxide and then acidified	Methanol and U, CrsH ₂₈ O ₆ are formed.
כ	Mild oxidation	V, C ₁₈ H ₂₄ O ₆ , which has two alcoholic groups, is formed.

14 Hydroxy Compounds

A	hot concentrated acidified KMnO ₄	hot concentrated acidified Two moles of carbon dioxide RMnO ₄ and one mole of W , C ₁₃ H ₂₂ O ₅ are formed.
×	2,4 dintrophenylhydrazine reagent	orange pracipitate formed.
	alkaline aqueous iodine	yellow precipitate formed.

In addition, it is known that 'juvenife hormone' has a continuous 12-carbon long backbone. There are three methyl substituents on the skeletal backbone of 'juvenile hormone' and that each methyl substituent is five carbon atoms apart from the next methyl substituent.

- (a) Give the products that will be formed when methylethyl either, CH₃OCH₂CH₃
 undergoes hydrolysis with aqueous acid.
- (b) State and explain the number of epoxide ring(s) in 'juverile hormone'.
- (c) State the type of reaction that T has undergone and the functional group that it contains other than the four alcoholic groups.
- (d) Classify the two alcoholic groups in V into either primary, secondary and tertiary alcohols. State the number of each alcohol and explain how you arrive at your conclusion.
- (e) V produced an intermediate upon reacting with hot concentrated addiffied KMnO₄ which eventually produced carbon dioxide. Draw the displayed formula of this intermediate.
- (f) State the type of reaction between W and 2,4 dinitrophenylhydrazine reagent. State the deduction about W from the result of W reacting with aqueous alkaline iodine.
- (g) Suggest the structures for compounds S to W and for 'juvenile hormone'.

14 [HCl 2016/II/3(b)]

- (b) Under certain conditions, but-2-ene gives alcohol A, C₄H₁₀O, which exists as a liquid at room temperature.
- (i) State the reagents and conditions required in this reaction. Draw the displayed formula of alcohol A formed in this reaction.
- (II) Explain, in terms of structure and bonding, the difference in the physical state of but-2-ene and alcohol A at room temperature. Draw a diagram to illustrate your answer for alcohol A.

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[IJC 2016/III/4(e)] ç

Compound P, C₉H₁₂O₂, shows optical activity and does not react with aqueous potassium carbonate. However, it is soluble in aqueous potassium hydroxide. When P reacts with not acidified potassium dichromate(VI), the solution turns from orange to green. P also decolourises aqueous bromine to form a white precipitate, Q, (e)

Upon heating with concentrated sulfuric acid, P gives only compound R, C₉H₁₀O, which displays geometric isomerism. R gives compound S and ethanoic acid on reacting with hot acidified potassium manganate(VII) solution. Suggest the structures of P, Q, R and S, explaining the reactions (gyolved.

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[NJC 2016/III/4(b)(i)] ě

Capsaidn is a slightly addic compound responsible for the burning sensation of chilli peppers, its molecular structure can be deduced by the following reaction scheme. Assume that -OCH₃ group is inert.] **a**

When N is heated with concentrated acidified potassium manganate(VII), P, C₆H₁₆O₄, and Q, C₄H₈O, are formed. =

P is formed from the reaction of Br(CH₂),Br with hot ethanolic KCN followed by hydrolysis. Q can be reduced to an alcohol, R, which is optically active.

Deduce the structures of N, P, Q, R and capsaicin

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[NYJC 2016/III/2(e)(i)-(ii)]

Alcohols react with concentrated sulfuric acid at high temperatures to form alkanes. A common side reaction that can happen is the formation of ethers, which is also catalysed by concentrated suffuric acid. (e)

14 Hydroxy Compounds

The mechanism occurs via 3 steps:

An acid base reaction in which H* from H2SO4 protonates the oxygen atom in alcohol. This step is very fast and reversible.

Step 2;

'H intermediate. creates an oxonium ion R'

Another acid base reaction in which the proton in the oxonium ion is removed by a suitable base (in this case a water molecule) to give the ether product. This step is very fast and reversible.

Draw the ether formed when cyclopentanol undergoes the above reaction.

cyclopentanol

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Draw out the full mechanism for the reaction between two cyclopentanol molecules to form an ether. In your answer, show any relevant charges, lone Ξ pairs of electrons and movement of electrons.

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[SRJC 2016/III/2(a)(i)-(ii)]

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Thiophenol is an organosulfur compound with the formula C_6H_8SH . The chemical structure of thiophenol is analogous to phenol, except that the oxygen atom in the hydroxyl group bonded to the aromatic ring is replaced by a sulfur atom. (a)

Thiophenol

- o E Suggest if the C-S-H bond angle in thiophenol will be larger than the C-O-H =
- Explain why thiophenol has a lower pKa value than phenol. 0

E

[TPJC 2016/III/2(a)([v)] d)

 CH_3CH_4CI can be prepared by reacting ethanol with $SOCI_2$. Write an equation for this reaction and suggest an advantage of using $SOCI_2$ as a reagent for halogenation, <u>(</u> (8)

[VJC 2016/III/2(a)(i)] 0

Styrene (phénylethene) is a useful organic intermediate used for the synthesis of many products. For instance, styrene is able to undergo the reaction shown below: 3

State the reagents and conditions required for reactions I, II and III.

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[VJC 2016/III/5(c)] 22

Draw a labelled diagram to show how benzaldehyde can be synthesised from phenylmethanol in a laboratory. ō

benzaldehyde

phenylmethanol

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[MI 2016/II/4(b)(i)-(ii)]

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2-propanol reacts with hot excess concentrated sulfuric acid to form propene. The reaction follows a 3-step mechanism as described below: **(p**)

<u></u>

14 Hydroxy Compounds

Step 2	The C-O bond in intermediate A breaks, forming a carbocation 8
	and water. This step is endothermic and is the rate determining
	Step.
Step 3	The carbocation is then deprotonated in an exothermic reaction,
	forming propene, H ₂ SO ₄ is regenerated.

- State the type of reaction undergone when 2-propand reacts with hot excess concentrated sulfuric acid, =
- the reaction between 2-propanol and concentrated sulfurle acid, indicating the movement of electrons using curly arrows and showing clearly the lone pair of electrons involved in the mechanism. You are advised to use structural formulae for all species, so that it is clear which bonds are broken and which Use the information given in the table above to draw out the full mechanism for are formed. €

[NYJC 2016/II/5] 23

K₂Cl₂O₂, 1 mole of A reacts with 1 mole of PCl₃ to form B. A reacts with cold dilute KMnO₄ to form C (C₁₂H₁₃O₄). Upon heating with acidified KMnO₄, A gives D (C₃H₁₀O₄) and E. D produces effervescence when aqueous Na₂CO₃ is added. 1 mole of D reacts with 3 moles Compound A (C₁₂H₁₈O₂) exhibits optical isomerism. It does not react with hot acidified of aqueous bromine. E gives F, a yellow precipitate with warm alkaline aqueous lodine.

Draw the structures of A, B, C, D, E and F.

9

[SAJC 2016/11/7(b)] 겫

On heating with dilute acid, chlorogenic acid produces two compounds, X and Y. 9

Compound X

Compound Y

When compound Y reacts with hot excess concentrated sulfuric acid, a product with a molecular formula of CrHsO₃ is formed. A student claims that the product formed has the following structural formula but the teacher disagrees.

Draw the correct structure of the product and explain what is wrong with the student's 2

[VJC 2016/II/6(b)(i)-(ii)] ņ

Allyl alcohol, CH2#CHCH2OH, is a colourless liquid which is soluble in water, (a)

ŝ Crotyl alcohol, CH₃CH≈CHCH₂OH, is a colourless liquid which is used

- Describe how you would distinguish between allyl alcohol and crotyl alcohol. The compounds may be distinguished by a preliminary chemical reaction followed by a subsequent testing of the reaction products, include clearly the reagents, conditions and observations for each compound. =
- Allyl alcohol may be converted into propanal by using a ruthenium(IV) catalyst in water. €

State the type of reaction and explain your answer.

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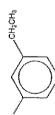
Multiple Choice Questions (Section A)

[CJC 2011///24] Which of the following reagents may be used to distinguish between 1-bromobutane and 2brompbutane?

- alkaline aqueous iodine
- sodium hydroxide ⋖
- acidified potassium manganate(VII)
- aqueous silver nitrate OO

[SAJC 2011///24] e,

Which of the following reagent should not be used to distinguish the following two compounds?



and CH, CH=C(CH,)CH, OH

- Hot acidified KMnO,
- Br₂ (aq)
- Ě
- NaOH (aq)

14 Hydroxy Compounds

[MJC 2011/1/17] Which of the following alcohols yield only a single product upon hearing with concentrated £.)

- CH3CH(CH3)CH2OH ⋖
- CH,CH,CH(OH)CH, m
- CH3CH2CH2CH(OH)CH3 O
- CHICHICH(OH)CHICH ۵

[AJC 2011///22] 4

Cafestol and Kahweol are fat-soluble compounds known as diterpenes, which are present in the oil derived from coffee beans. Both compounds have liver-protecting properties of caffeine. The structures of Cafestol and Kahweol are given below.

Cafestoi

Kahweol

In the following reactions, -CH2OR remains unaffered,

Which of the following statements is true?

- Both compounds do not react with acidified K2Cr2O1.
- I mol of Cafestol reacts with excess Na to produce 1 mol of Ha.
- 1 mol of Kahweol reacts with Brz to give a product with 11 chiral centres.
- When treated with an excess of hot concentrated acidified KMnO₄, Cafestol will produce a compound with 4 carbonyl groups.

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INYJC 2011/I/24] Compound E, CsHsOlO_{2, gives} compound F, CsHrOlO_{2, on} mild oxidation. F gives a yellow precipitate on warming with alkaline lodine and reacts with 2 moles of aquecus bromine.

Which one of the following is the correct structure for E?

[CJC 2011///20] ø

* Binapacryl is used as a fungicide and can be synthesized from phenol via the following synthetic route. Which of the following describes Steps I and II correctly?

Electrophile in Step I

Reagents and Conditions for Step III

concentrated HNOs, concentrated HzSOs, 30°C

dilute HNO3

1

14 Hydroxy Compounds

(TPJC 2011///29) A compound has the following structure:

All of the following reagents will react with the above compound, except

- B phosphorous pentachloride

A aqueous bromine

- C hydrogen chloride
- D potassium cyanide

[RI 2011/1/20]

Taxol is a drug isolated from the Pacific yew tree and is used in the treatment of lung and ovarian cancers. The tricyclic core of Taxol has the following structure.

In the reactions given below, the ____ ring remains unaltered.

The tricyclic core was first reacted with H1 and Pt catalyst, followed by hot acidified

How many chiral centres are present in the product of reaction?

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14 Hydroxy Compounds

(HCI 2011/I/19] Consider the following reaction scheme.

Which of the following statements about the aboye reaction scheme is **incorrect?**

Compound P is a planar molecule.

∢

- Step I is an electrophilic substitution. Ø
- Compound Q can exhibit cis-trans isomerism. O
- Step III can be carried out by heating compound N over AtoDa.

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[HCI 2011/I/26] The dehydration of propan-2-ol to form propene is thought to involve the following steps:

Which of the following statements is false?

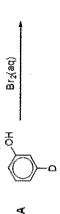
- Propan-2-of acts as a base in Step 1.
- H₂SO₄ is a catalyst in this reaction.

m

- A possible side product of the reaction is CH1CH(OSO3H)CH3.
- It is more likely for primary alcohols to proceed via this mechanism than tertiary 0 0

14 Hydroxy Compounds

 $^{\circ}$ 11 [RI 2011//26] Which of the following reactions yields an organic compound which has no deuterium incorporated? (Deuterium, D = 2H)



[SRJC 2011///21] 7. C4

In which of the following reactions is the reactive carbon sp² hybridised in the reactant and sp2 hybridised in the product?

Br in CCA.
in the dark
CH3CHCHCH3.

LIAMA in dry

**2

[Ri 2009/I/27]
One industrial preparation of ethanoic acid is the direct carbonylation of methanol, using a rhodium catalyst.

↓ CH3CO2H thadium catalyst CH3OH + CO - Which compound could be expected to produce HQ2CCH(CH2CO2H)2 by this method?

HOCH2CH(OH)CO2H

⋖(

HOCHICH(CHICOIH)

m

- HOSCH(OH)CHSCOSH
- HOCHICH(OH)CHICOIH a

14 [Modified RI 2009/I/28] Which of the following shows the given ions arranged in the order of increasing p K_a values?

- 2-chloroethoxide ion, ethoxide ion, 4-nitrophenoxide ion, phenoxide ion
- ethoxide ion, 2--chloroethoxide ion, phenoxide ion, 4-nitrophenoxide ion < @ ∪ o
- phenoxide ion, 4-nitrophenoxide ion, ethoxide ion, 2-chloroethoxide ion 4-nitrophenoxide ion, phenoxide ion, 2-chloroethoxide ion, ethoxide ion

14 Hydroxy Compounds

15 The pinacol rearrangement involves the reaction of a diol in acidic conditions to form a carbonyl compound as shown below.

2, 3-d methylbutane-2,3-diol

3, 3-dimethylbutan-2-one

Which of the following structural formulae is **not** a product of the pinacol rearrangement of 2,3-diphenylpentane-2,3-diol with the structure as shown below?

2,3-diphenyipentane-2,3-diol

O

[NYJC 2011///39]

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Which of the following reagents will have different reactions with the two alcohols, (CH3) $_3$ CCH2 $_5$ CH and (CH3) $_4$ CHCH2 $_5$ CH2 $_5$ CH3

- concentrated sulfuric acid
- phosphorus pentachloride
- acidified aqueous potassium manganate(VII)
- 1, 2 and 3 only
- 2 and 3 only
- t and 2 only 1 only m

[SAJC 2011///38]

P~

Which of the following pairs will give the same organic product when treated with hot acidified KMnO.2

- (COOH), and CH2=CH2
- CHICH OHOH and CHICH OH
- CeHsCH2CH2OH and CeHsCH=CH2
- 1, 2 and 3 only
- 2 and 3 only
- and 2 only **@** O

NJC 2011///36]

8

Geraniol is one of several compounds produced by the scent glands of honey bees to help them mark nectar-bearing flowers and locate the entrances to their hives.

geranioi

Which statements are true for geraniol?

- The molecule reacts with hot alkaline KMnOx to give 3 organic fragments.
 - The molecule has 4 sp2 carbons and 6 sp2 parbons,
- There are 2 pi bands and 10 sigma bands in each molecule of geranial.
- 1, 2 and 3 only
- 1 and 2 only œ
- 2 and 3 only
- 1 only

3

14 Hydroxy Compounds

Which of the following statements are correct about compound H shown below? (PJC 2011///39) ø

- 1 mol of H reacts with 4 mgl of hydrogen in presence of platinum catalyst.
 - 2 1 mol of H reacts with 1 mol of sodium to form 1 mol of hydrogen gas.
- 1 mol of H reacts with 1 mol of sodium hydroxide.
- 1, 2 and 3 only

S

1 and 2 only

1 only

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- 2 and 3 only
- Pentaerythritol is an intermediate in the manufacture of paint, PJC 2011///381

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Which of the following statements about pentaerythritol are correct?

- It reacts with sodium.
- It is dehydrated by concentrated sulfuric acid to an alkene.
- its empirical formula is CH₃O.
 - 1, 2 and 3 only
- 1 and 2 only
 - 2 and 3 only
 - , ∫only

[DHS 2011/1/38]

in the presence of concentrated acids, alcohols can act as a base. Which of the following ions can be found in a mixture of ethanol and excess concentrated sulfuric acid? ž

- CH3CH3O
- CH2CH2OH2
- 1, 2 and 3 only

- - 2 and 3 only

1 only

- m
- 1 and 2 only

LSO'.

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22

[ACJC 2016/I/24] The main reason that phenol is a better Brønsted acid than cyclohexanol is

- that it is a better proton donor. < □
- the cyclohexyl group is an electron donating group by induction, which destabilises the anion formed during the dissociation.
 - O
- the phenyl group is an electron withdrawing group by induction, which stabilises phenol is able to stabilise the anion formed during the dissociation by resonance, where the electrons are delocalised in the phenyl ring. Ω
- [HCI 2016/1/21] 5

the anion formed during the dissociation.

\$-naphthol is a crystalline solid that is widely used in the production of dyes.

Which of the following is likely to be a property of β-naphthol?

- Its pKa is lower than that of phenol. It gives white fumes with SOCI2.
- It reacts with carboxylic acid to form ester.
- It undergoes nucleaphilic substitution in the reaction below. < B O D

[JJC 2016/I/26] 4

Which of the following reagents is able to convert compound Q to compound R?

PBB ⋖

[MI 2016/I/23]

EV)

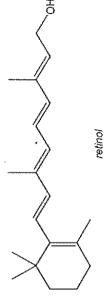
What is the major organic product formed when excess aqueous bromine is added to the following compound?

14 Hydroxy Compounds

IMJC 2016/1/291

26

The rod cells at the back of the eye contain a primary alcohol called retinol which is responsible for their sensitivity to light. Retinol is oxidised by an enzyme-catalysed reaction that keeps the double bonds intact, to retinal, an aldehyde.



Which of the following is correct?

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SOB₁₂

O

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- The number of stereoisomers in retinol is 32.
- There are six o bonds formed by $2sp^2-2sp^3$ overlap in a molecule of retinol. ω
- In laboratory preparations, retinal can be formed from heating retinol under reflux with hot potassium dichromate(VI).

One mole of retinol reacts with 4 moles of hydrogen gas in the presence of palladium catalyst. Δ

5

[NJC 2016/I/25] Compound Y can be prepared from compound X in the following reaction sequence. (CH₂),CH₃

Compound X

Step 2

O(CH2)/CO2H

ફું

Compound Y

Which reagents can be used to prepare compound Y?

	Step	Step II
⋖	Na	CH2(OH)(CH2)2CO2H
മാ	NaOH	CH2O/CH2CO2H
ပ	NaOH	CH2C/CH2CH2CO2H
Ω	Na ₂ CO ₃	CH2(OH)CH2CO2H

[NYJC 2016/I/24] 28

Compound X is used to synthesize DEET, a common active ingredient in mosquito repellent. A brick-red precipitate is observed when it reacts with Fehling's reagent. 1 mol of X undergoes the following reactions.

$$V \stackrel{K_2Cr_2O_7/H^*}{\longleftarrow} X \stackrel{KMnO_4/H^*}{\longrightarrow} Y$$

14 Hydroxy Compounds

Y reacts with HNO₃ under suitable conditions to produce only 1 possible organic product. V reacts with Na₂CO₃ to produce only 1 mol of CO₂(g).

What could X be?

Q)

[SAJC 2016//28] Bolandiol is a banned synthetic anabolic steroid.

Which of the following statements is not true?

- Bolandiol has 27 stereoisomers when reacted with liquid bromine. ⋖
- Passing hot aluminium oxide over bolandiol produces a compound with three double bonds.

- Orange potassium dichromate (VI) turns green when Bolandiol is heated with O
- Bolandiol produces one mole of hydrogen gas when reacted with sodium metal. ۵
- [TJC 2016///22] 30

The compound hex-3-en-1-of has a strong 'leafy' smell of newly cut grass and is used in perfumery.

CH3CH=CHCH2CH2OH hex-3-en-1-ol What are the organic products when hex-3-en-1-of is treated with hot acidic K2Cr2O7, followed by hydrogen gas in the presence of platinum?

- CH3CH2CH2CH2CH2OH ⋖
- CH₃CH₂CO₂H and HO₂CCH₂CO₂H

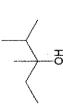
ω O

- CHICHICHIOH and HOCHICHICHIOH
- CH3CH2CH2CH2CO2H
- TJC 2016///23] Ö

Which of the follow reaction produces an organic species that contains deuterium atom?

- NaOD(aq) heat CHO TEB ⋖
- MnO47, NaOD(aq) heat CHICHION m
- conc D₂SO₄ heat CHICHIOH O
- CONC D2SO4 heat CHICOIH + CHICH 0
- [YJC 2016/I/20] 32

The structure of compound Z is as seen below:



14 Hydroxy Compounds

Compound 2

It is completely reacted with hot concentrated H_2SO_4 to form compound Y. What is the total number of isomers of Y?

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HYDROXY COMPOUNDS SUGGESTED SOLUTIONS 5

Multiple Choice Questions (Section A)

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Structured/Free Response Questions

Test: Add Br₂(aq) to both samples separately.

Salbutamol: Brown Br₂ decolourises. Observations:

Ephedrine: Brown Br₂ remains.

Test: Add neutral FeC/s(aq) to both samples separately.

Observations:

Salbutamol: Violet colouration observed.* Ephedrine: No violet colouration. Salbutamol has a lower melting point than compound G. (1) Both compounds have simple molecular structures with hydrogen bonds between their respective molecules.

However, for Salbutamol, it is possible to form intramolecular hydrogen bonds between the phenal group and the primary alcohol group.

Thus, less energy is required to overcome the less extensive intermolecular hydrogen bonds between salbutamol molecules as compared to that in G.

Step	reagents, conditions and observations	molecule
	Reagent and conditions: K2Cr2Or(aq), H2SO2(aq), Heat under reflux	Ø
	Observation: Orange solution turns green	
2	Reagent and conditions: 2.4-dinitrophenylhydrazine, warm Observation: Orange ppt formed	
ಬ	Reagent and conditions: PC/s Observation: White fumes produced.	E.
4	Reagent and conditions: Aqueous bromine / bromine in CCL in the dark / Neutral FeCts	
	Observation: Decolourisation of brown aqueous bromine and white ppt formed / Decolourisation of brown bromine in CC4 and	ш

 The presence of the bulky hydrophobic benzene ring interferes with the formation of hydrogen bonding between the compounds and water. Hence the compounds are likely to be insoluble in water.

=

m

The p orbital of chlorine atom overlaps with the π electron cloud of the benzene ring, giving rise to the partial double bond character of the C--C/ bond. This makes halogenoarenes less susceptible to nucleophilic substitutions. Hence the compounds cannot be easily hydrolysed by water.

As such they are difficult to remove by natural processes in the environment.

(ii) There are more electron-withdrawing "Cl groups attached to the benzene ring in 2,4-dichlorophenol.

This disperses the negative charge on the oxygen atom of the phenoxide ion more, thus, further stabilising the phenoxide ion from 2,4-dichlorophenol with respect to that from chloroxylenol.

Therefore, 2,4-dichlorophenol is a stronger acid than chloroxylenol.

14 Hydroxy Compounds

Ä

(b) The presence of the bulky hydrophobic group in compound A prevents it from dissolving well in water despite being able to form some hydrogen bonds with mater. (Note: Energy evolved from formation of solute – solvent interactions is insufficient to compensate for the energy required to overcome the solute – solute interactions and solvent – solvent interactions.)

In the presence of sodium hydroxide, compound A reacts to form a sodium salt which dissociates completely. Strong ion-dipole interactions between water molecules and the oppositely charged ions allow compound A to dissolve in sodium hydroxide.

(ii) Step I Step II Step III Step IV Nucleophilic Oxidation Nucleophilic Elimination Addition

Step V Reduction

(iii) Step I NaOH(aq), Heat under reflux

Step II K2Cr2O7(aq), H2SO4(aq), Heat under reflux

Step IV Excess concentrated H₂SO₄, 170°C

Step V LIA/H, in dry ether

14 Hydroxy Compounds

 (a) The intermolecular hydrogen bonding between alcohol molecules is stronger than the instantaneous-dipole induced-dipole forces of attraction between alkane molecules.

Hence greater amount of energy is required to overcome the hydrogen bonds in alcohols.

(ii) I methanol or ethanol

II if methanol (ethanol) had been present in the mixture it would have condensed as the first fraction at 65 °C (78 °C);

The boiling temperature of methanol (ethanol) is below 97 °C. Hence the methanol (ethanol) could have boiled off before the first fraction is collected,

III Flammability of alcohol vapours or risk of fire or explosion

(b) (i) OH A/2O₃ heat Compound N

Compound N NaOH(aq)

Compound N K₂CC₁₂O₇

H2SO₄(aq)

€

OH NaBH₄ HO

2-hydroxypropanoic acid

LIAIH4 not accepted for last step as it will reduce -COOH too.

9

Compound **D** is

D does not contain -OH nor -COOH since it does not react with sodium,

It is a diester formed when -OH and -COOH groups of one lactic acid molecule reacts with the -COOH and -OH groups respectively of another latetic acid

CH3CH2C(CH3)(OH)CH3 7 59 KMnOu/HySOt, Heat under reflux ► CH3CH2COCH3 CH3CH2CH(OH)CH3 CH3CH(Br)CH3 NaOH(aq), Heat under reflux

2nd step: H₂SO₄(aq), KMnO₄(aq), Heat under reflux 3nd step: <u>CH₃-</u>Li (and H₂O) 1step: NaOH(aq), Heat under reflux

Eree radical substitution occurred on the alkyl side-chain in A A has only 1 alkyl side-chain on the Nucleophilic substitution occurred. F is an alcohol. Side-chain oxidation occurred. F does not undergo oxidation. F is a tertian alcohol. Deduction Elimination occurred.

D and E contain C≈C benzene ring. A reacts with bromine in the presence of uv Upon heating with alcoholic NaOH, both B and C gave the same products, D and E. Heating B with NaOH(aq) gives F which does not react with acidified K2CrO3. When A is treated with hot aqueous acidited KMnO₄, benzolc acid is formed. light, producing 4 isomeric monobromo compounds. which are geometric isomers. Evidence

14 Hydroxy Compounds

COH3H H BY COH3	F. CH ₃ CH ₂ CH ₃ OH
B: CH ₃ CH	9 HO D H
A: CH3 C—C—CH2CH3	D and E H ₃ C C=C CH ₃

Evidence	Deduction
L rotates plane-polarised light.	L exhibits optical isomerism and contains at least 1 chiral carbon
No reaction occurs between L and 2,4—dinitrophenylhydrazine.	No condensation reaction occurred. No aldehyde or ketone functional group in L.
L produces M, Cı _s H ₂₂ O	Reduction occurred. L is unsaturated, Addition of 4 H atoms indicate presence of 2 C=C bonds.
No change is observed when L is heated with acidified potassium dichromate(VI).	L does not undergo oxidation.
Heating L with aluminium oxide forms N as major product,	L contains alcohol that undergoes elimination. N contains an additional C=C bond upon elimination.
N reacts with hot concentrated acidified KMnO ₄ to produce propanone, P and a gas which gives a white precipitate with limewater.	Oxidative cleavage of all three C=C occurred. Gas evolved is CO ₂ . The white ppt formed is CaCO ₃ . Presence of <u>2 terminal C=C bond</u> due to 2 moles of CO ₂ produced during oxidative cleavage. (loss of 2 C from N to propanone & P).
P can also be produced by <u>oxidation</u> of the given compound with concentrated acidified KMnO₄ and heating.	P Is HO CH2-CH2-C-C

CH ₃	
HO-0-HO	
CH5==CH-CH2-CH2-CH2-CH2-Or CH2=CH-C-CH2-CH2-CH=CH2	
(Note: The 2 structures below are not accepted as they will not lead to formation of the correct structure for N)	0
CH ₃ CH ₃ CH ₃ CH ₂ CH=CH ₂ CH ₂ CH=CH ₂ CH=CH ₂ CH ₂ CH=CH ₂ CH ₂ CH=CH ₂ CH=CH=CH ₂ CH=CH=CH=CH ₂ CH=CH=CH=CH ₂ CH=CH=CH=CH=CH=CH=CH=CH=CH=CH=CH=CH=CH=C	······································
OH3 OH3 OH3 OH3 OH3 OH3 OH3 OH3 OH3 OH3	
CH ₃ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₃ or CH ₃ -CH ₂ -CH ₂ -CH ₂ -CH ₃ -CH ₃ -CH ₂ -CH ₂ -CH ₃ -CH ₃ -CH ₃ -CH ₂ -CH ₃ -CH	***************************************
CH ₃ CH ₃	
N: CH2=CH-CH-CH2CH2CH2CH2	

Evidence	Deduction
d-Terpineol has an alcohol group which is not readily oxidised.	α-Terpineol has a <u>tertiary alcohol.</u>
Heating a-Terpineol with concentrated acidified KMnO ₄ gives H.	Oxidative cleavage occurred. C=C is broken.
H gives yellow ppt when warmed with alkaline I₂(aq)	H contains <u>-CH₃CO.</u> H undergoes mild <u>oxidation</u> with alkaline aqueous lodine to give <u>CHI</u> 3, a yellow ppt.
On hydrogenation, α-Terpineol gives J	Reduction occurred. a-Terpineol is unsaturated. Additional of 2 H atoms indicate presence of 1 C=C bonds. (recall: a-Terpineol has a cyclohexene ring)

0

14 Hydroxy Compounds

Li tu	m.				
J contains <u>alcohol</u> that undergoes <u>elimination</u> . K contains an additional <u>C=C bond</u> upon elimination. Oxidative cleavage occurred. <u>C=C</u> is broken.	Presence of terminal C=C bond due to one mole of CO ₂ produced during oxidative cleavage, (loss of 1 C from K to M).	CH ₂	CH3 K[1]	OH OH3	CH ₃ a-Terpineol [1]
J reacts with a few drops of conc H ₂ SO ₄ to give K.	110	H3C CH3 H3C	DE 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1.	H ₃ C CH ₃ H ₃ C	H ₃ C O _H

11 [NYJC 2015/III/1(a)]

(a) The base added will <u>deprotonate the alcohol to form the alkoxide ion</u> which is a <u>stronger nucleophile</u>. [1] The negatively charged alkoxide ion can better attack the electron-deficient carbon in MOMCI, substituting the halogen atom to form

- Less bulky organic bases are not preferred as they may act as nucleophilies and attack MOMC/Instead. [1] The lone pair of electrons on primary amines are more accessible as it contains less bulky alkyl groups hence they are stronger nucleophiles. €
- Alkalis are not preferred as <u>alighatic alcohols</u> are not acidic enough to <u>be deprotonated by alkalis</u>. [1] The electron donating alkyl group of ROH will increase the electron density on the O atom of its conjugate base, making it more negative, therefore destabilising it. Hence, ROH is weakly acidic.

 Type of reaction: Nucleophilic Substitution (S_N2) [1] (III)
 - (M)

HC/(sq) or H₂SO₄(sq) Heat under reflux

Step Vil

3

14 Hydroxy Compounds

Step IV: Electrophilic addition [1] Step V: Nucleophilic substitution [1] Step VI: Acidic hydrolysis [1]

12 [CJC 2016/II/5(a)]

To separate test tube containing each sample, add neutral FeCls. Violet colouration will be formed with p-cresol whereas no violet colouration for its isomer. OR To separate test tube containing each sample, add aqueous Br. Orange bromine solution decolourise and a white precipitate is formed with p-cresol whereas no decolourisation of orange bromine solution with its isomer. [3]

NOT ACCEPTED: PC/s

Note: Oxidation using KMnO_x/H₂SO₄ is not accepted for p-cresol and phenylmethanol since both can undergo side-chain oxidation.

are not accepted because these are positional isomers of p-cresol. Positional isomers have the same carbon chain, but different positions of functional groups. Functional groups.

[DHS 2016/II/5] <u>e3</u>

- CH3OH and CH3CH2OH. (e)
- Two epoxide rings. <u>(p</u>

Two alcoholic groups are produced for every epoxide ring that will be hydrolysed. Since there are four alcoholic groups formed after 'juvenile hormone' undergoes hydrolysis, this implies that there are two epoxide rings in 'juvenile hormone'.

- Tundergoes basic hydrolysis to give methanol and U. T is likely to contain an ester. 3
- Two tertiary alcohol groups. Đ

T has four alcohol groups which were retained in U even after basic hydrolysis. Since V has only two alcohol groups left after mild oxidation, this implies that the two alcohol group must be tertiary in order to resist oxidation.

(e)

€

Condensation, W contains either

14 Hydroxy Compounds

Juvenile hormone

(V)

 \supset

14 [HCI 2016/II/3(b)]

Steam, 300°C, 70 atm (or 60 atm), (conc) H₂PO₄ [1] OR conc H₂SO₄ followed by warming with water. ⊜ ρ

(ii) Both but-2-ene and alcohol are simple covalent compounds /simple, discrete molecules /have simple molecular structure, [1/2]

For but.2-ene, there are weak dispersion forces between its molecules. For alcohol A (butan-2-oi) with polar O-H bond, there are strong intermolecular hydrogen bonding between its molecules. [1/2]

More energy is required to overcome the stronger intermolecular hydrogen bonding in alcohol A than the weak dispersion forces in but-2-ene which is therefore in gasecus state. [1/2]

the energy provided by room temperature is insufficient to overcome the strong hydrogen bonds between alcohol A moleculies,

hydrogen borius between accord A motecules,
Hence alcohol A exists as a liquid at room temperature and but-2-ene exists as
gas. [1/2]

Diagram [1]
o showing correct hydrogen
bond (must be oxygen atom
and the H atom from the OH
group)
o labelling hydrogen bond

labelling hydrogen bond showing lone pair of electrons on oxygen

or oxygen labelling 5+ and 5- for the O-H group forming H bond.

Fach mistake minus 1/2 mark

15 [IJC 2018/III/4(e)]

(e)

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14 Hydroxy Compounds

Q 0

Q F

1m for each structure

► snows optical activity	P has chiral carbon[v]
P does not react with aqueous potassium carbonate.	No -COOH

However, it its soluble in aqueous potassium hydroxide.	Undergoes <u>acid-base reaction.</u> Contains phenol [√]
P reacts with hot acidified potassium	P undergoes oxidation, [V]
orange to green	Contains <u>primary or secondary</u> <u>alcohol</u> [√]
P also decolourises aqueous bromine to form a white precipitate, Q, CeHtoO2Br2.	P undergoes <u>electrophilic</u> substitution[√]
	P contain phenol group[√]
\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \	Br atoms added to 2 or 4 positions on ring
Upon heating with concentrated sulfurio	P undergoes elimination of H.O(v)
acid, r gives only compound n, CeHroO, which displays geometric isomerism	R is an <u>alkens</u> / contains C=C[v]
R gives compound S and ethanoic acid on reacting with hot acidified potassium manganate(VII) solution.	R undergoes <u>oxidative cleavage</u> [√]

6-8 [√]- 2m 3-5 [√]- 1m 0-2 [√]- 0m

16 [NJC 2016/III/4(b)(I)]

P, HOOCCH₂CH₂CH₂CO₂H CH₃CH(OH)CH₂CH₃ (a)

o:

Q: CH3COCH2CH3

(1) each

14 Hydroxy Compounds

17 [NYJC 2016/III/2(e)(I)-(II)]

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[1] for each step (with arrows, lone pairs) total [3]

[SRJC 2016/III/2(a)(i)-(ii)] (2)

Thiophenol is an organosufur compound with the formula $C_{\rm e}H_{\rm s}SH$. The chemical structure of thiophenol is analogous to phenol, except that the oxygen atom in the hydroxyl group bonded to the aromatic ring is replaced by a sulfur atom.

Thiophenoi

- (i) Oxygen is more electronegative than sulfur thus the electron density around O atom will be greater. The bond-pair electrons will be nearer to the nucleus resulting in more regulsion. Thus the bond angle of C-O-H in phenol will be larger.
- (ii) Thiophenol has a lower pKe.

The sulfur atom is less electronegative and the lone pair of electrons on the conjugate base is able to delocalise into the benzene ring more readily as compared to phenol, thus stabilising its conjugate base more than the phenoxide ion.

19 [TPJC 2016/III/2(a)(Iv)]

(a) (IV) CH₃CH₂OH + SOC₁ -- CH₃CH₂C/ + SO₂ + HC/

This method has the advantage of forming only gaseous side-products which are easily removed from the system.

20 [VJC 2016/III/2(a)(i)]

(a) (i) I: Hi(g), room temperature (ignore state symbol unless it's given as aqueous state)
II: NaOH(aq), heat
III: KzCrzO₂(aq), HzSO₄(aq), heat

21 [VJC 2018/III/5(c)]

K2Cr2O₇, H2SO₄, water out water in heating granules mantle benzaldehyde

14 Hydroxy Compounds

22 [MI 2016/II/4(b)(i)-(ii)]

(b) (i) Elimination.

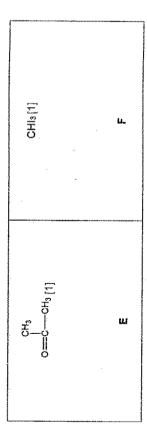
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23 [NYJC 2016/II/5]

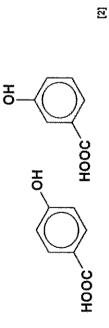
CH ₃ H CH ₃ Cl—C—C—CH ₃ OH [1]	HO-C-C=0 OH-[1]
HO————————————————————————————————————	HO—C—C—CH ₃ H CH ₃ OH OH OH CH ₃ OH OH CH ₃

7



24 [SAJC 2016/II/7(b)]

(b) The product formed is unstable as there is ring strain, Or sp hybridized C should have linear shape but this is not possible in a ring structure and hence it is unstable.



25 [VJC 2016/II/6(b)(I)-(II)]

- (b) (i) Step I: KMnO₄, NaOH(aq), cold Step II: I₂, NaOH(aq), warm Crotyf alcohol gives yellow ppt. Allyl alcohol does not give yellow ppt
- (II) It is a <u>disproportionation</u> reaction where the C≈C bond is reduced and the primary alcohol is exidised.