PROSPERITY ACADEMY

AS CHEMISTRY 9701

Crash Course

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ALCOHOLS

COMPLETE NOTES

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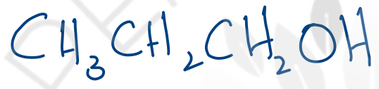
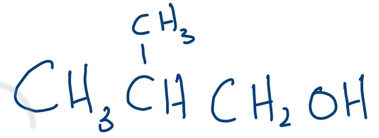
Alcohols:- Organic compounds in which one or more hydrogens are replaced by an OH-group.

Primary Alcohols:- The carbon carrying the OH group is attached to only 1 alkyl group (has 2H)

ethanol

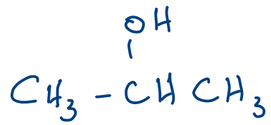


propan-1-ol

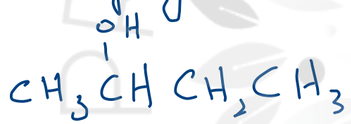


2-methyl propan-1-ol

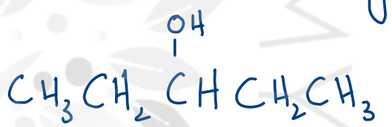
Secondary Alcohols:- The carbon carrying the OH group is attached to 2 alkyl groups (has 1H)



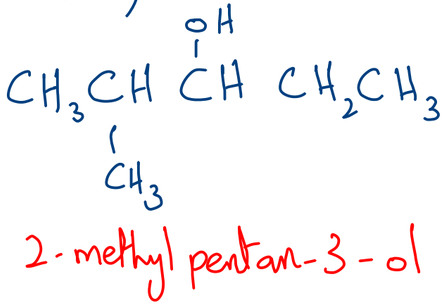
propan-2-ol



butan-2-ol

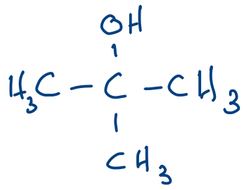


pentan-3-ol

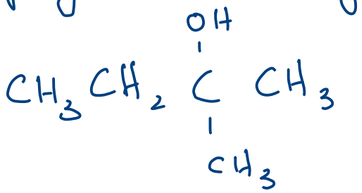


2-methyl pentan-3-ol

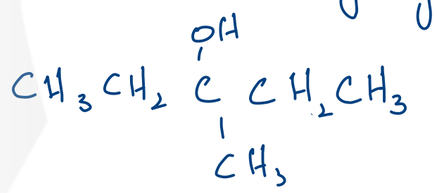
Tertiary Alcohol:- The carbon carrying the OH group is attached to 3 alkyl groups (has 0H)



2-methyl propan-2-ol

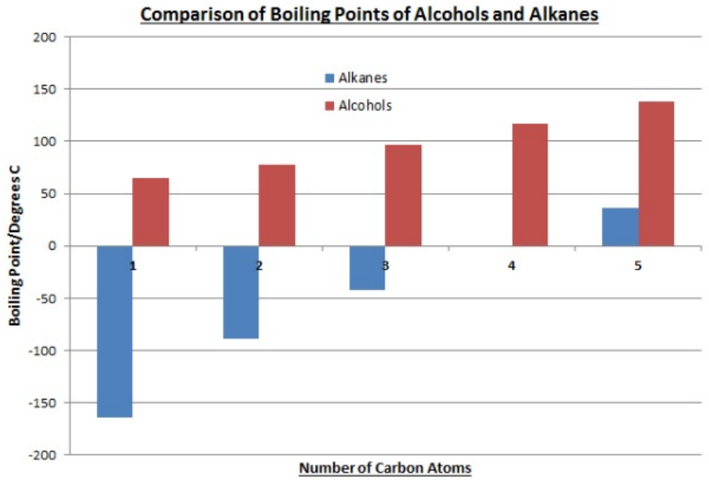


2-methyl butan-2-ol



3-methyl pentan-3-ol

Physical properties :-

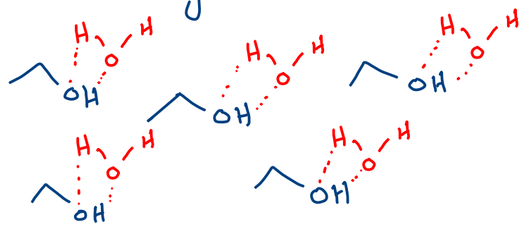


- Alcohols have much higher boiling points than alkanes :-
  1) Alcohols have hydrogen bonding
  2) Alcohols have permanent dipoles
  3) Alcohols have more electrons than some carbon chain alkanes.

- Boiling point increases as carbon chain length increases
  - no. of electrons ↑ ⟶ Stronger temporary dipole forces

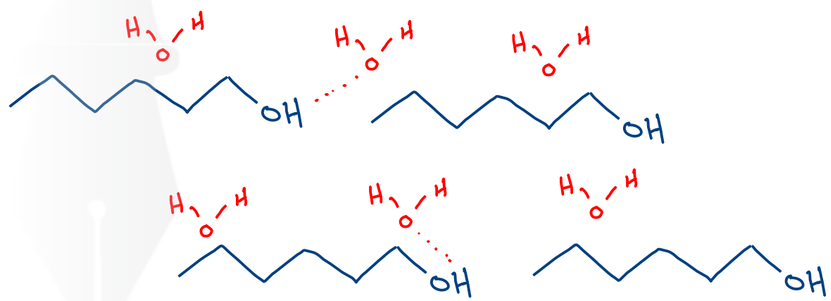
- Alcohols are polar and can form hydrogen bonds with water ⟶ hence soluble in water
  However, still only small alcohols are soluble and solubility decreases with increasing carbon chain length

ethanol dissolving in water :-



small carbon chain so hydrogen bonding is efficient

Hexan-1-ol dissolving in water



large carbon chain so hydrogen bonding inefficient

* Revisit bonding pdf to see how hydrogen bonding is shown if asked by the examiner

Chemical properties:- Alcohols give the following reactions:-

1) Reaction with Sodium metal:-

$CH_3CH_2OH_{(aq)} + Na_{(s)} \longrightarrow CH_3CH_2ONa_{(aq)} + H_{2(g)}$

ethanol — sodium ethoxide

$CH_3CH_2CH_2OH_{(aq)} + Na_{(s)} \longrightarrow CH_3CH_2CH_2ONa_{(aq)} + H_{2(g)}$

propan-1-ol — name not needed to know (sodium propoxide)

$CH_3CH_2O^-$ (ethoxide ion)

2) Oxidation of Alcohols:- $K_2Cr_2O_7$ + dil H_2SO_4 (acidified potassium dichromate)

Observation:- Colour changes from green to orange

Oxidation of primary alcohol

To aldehyde
- Keep alcohol in excess
- distill aldehyde as soon as it forms

$CH_3CH_2OH + [O] \longrightarrow CH_3CHO + H_2O$

ethanol — ethanal

$CH_3CH_2CH_2OH + [O] \longrightarrow CH_3CH_2CHO + H_2O$

propan-1-ol — propanal

To carboxylic acid
- Keep oxidising agent in excess
- heat under reflux until complete oxidation

$CH_3CH_2OH + 2[O] \longrightarrow CH_3COOH + H_2O$

ethanol — ethanoic acid

$CH_3CH_2CH_2OH + 2[O] \longrightarrow CH_3CH_2COOH + H_2O$

propan-1-ol — propanoic acid

Oxidation of secondary alcohol:- To Ketone (heat under reflux)

$CH_3CH(OH)CH_3 + [O] \longrightarrow CH_3COCH_3 + H_2O$

propan-2-ol

$CH_3CH(CH_3)CH(OH)CH_3 + [O] \longrightarrow CH_3CH(CH_3)COCH_3 + H_2O$

3-methyl butan-2-ol — 3-methyl butan-2-one

Oxidation of tertiary alcohols:- Donot oxidise (C carrying OH has no hydrogens to lose)

3) Substitution reactions:- Substitution of a halogen via Nucleophillic substitution

Substituting Cl

Using HCl

- HCl produced in situ by reaction conc. H_2SO_4 with NaCl
- heat with alcohol

$CH_3CH_2OH + HCl \longrightarrow CH_3CH_2Cl + H_2O$

$CH_3CH_2CH_2CH_2OH + HCl \rightarrow CH_3CH_2CH_2CH_2Cl + H_2O$

Using PCl_5

- PCl_5 is used to test OH group
- No conditions

$CH_3CH_2OH + PCl_5 \longrightarrow CH_3CH_2Cl + HCl + POCl_3$

$CH_3CH_2CH_2OH + PCl_5 \longrightarrow CH_3CH_2CH_2Cl + HCl + POCl_3$

steamy fumes of HCl: observation

will react with H_2O, carboxylic acids, alkalis

Using $SOCl_2$

- no conditions

$CH_3CH_2OH + SOCl_2 \longrightarrow CH_3CH_2Cl + HCl + SO_2$

$CH_3CH_2CH_2OH + SOCl_2 \longrightarrow CH_3CH_2Cl + HCl + SO_2$

steamy fumes: observation

Using PCl_3

- heat under reflux

$3CH_3CH_2OH + PCl_3 \longrightarrow 3CH_3CH_2Cl + H_3PO_3$ (phosphorous acid)

$3CH_3CH_2CH_2CH_2OH + PCl_3 \rightarrow 3CH_3CH_2CH_2CH_2Cl + H_3PO_3$

Substituting Br

Using HBr

- HBr produced in situ by reacting conc. H_2SO_4 with NaBr
- heat with alcohol
- not used usually as other products also made like SO_2

$$CH_3CH_2OH + HBr \longrightarrow CH_3CH_2Br + H_2O$$

Using PBr_3

- PBr_3 is produced in situ by reacting phosphorus with bromine gas and heating under reflux

$$P_4 + 6Br_2 \longrightarrow 4PBr_3$$

- Alcohol present in the mixture

$$3CH_3CH_2OH + PBr_3 \longrightarrow 3CH_3CH_2Br + H_3PO_3$$

Substituting I

- We donot use HI as producing it is messy, reacting NaI with conc. H_2SO_4 gives other products like SO_2, S, H_2S
- PI_3 is produced in situ by reacting phosphorus with bromine gas and heating under reflux:-

$$P_4 + 6I_2 \longrightarrow 4PI_3$$

- Alcohol present in the mixture

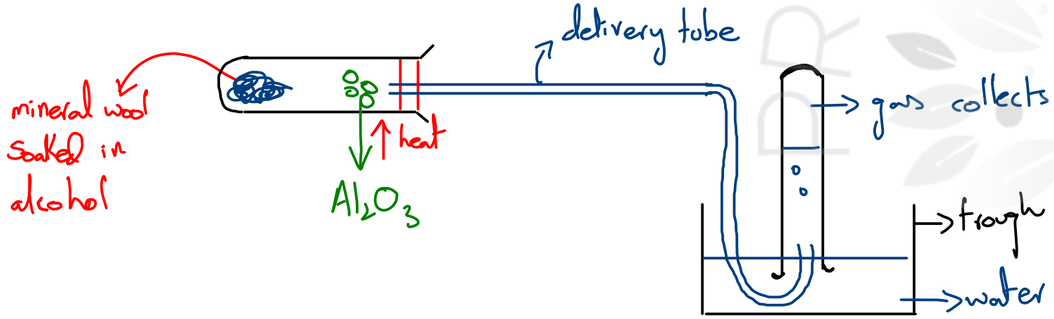
$$3CH_3CH_2OH + PI_3 \longrightarrow 3CH_3CH_2I + H_3PO_3$$

4) Dehydration of Alcohol (Alkene formed)

Using Al_2O_3 as catalyst

- heating required
- OH group and H from neighbouring C removed

$$CH_3CH_2OH \xrightarrow{Al_2O_3} CH_2=CH_2$$



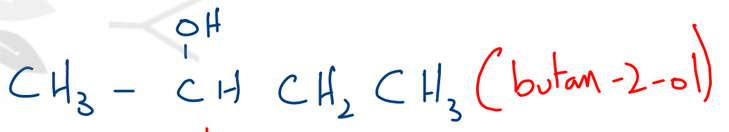
(When dismantling the setup, remove the delivery tube first before stopping the heating, otherwise water will rush back from the delivery tube very fast and explode, this is known as 'suckback')

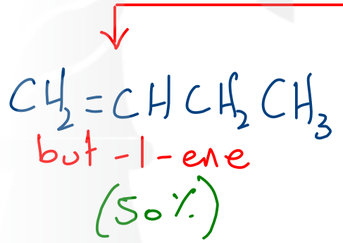
Using concentrated H_2SO_4

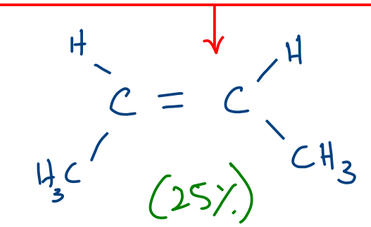
- heating required
- OH group and H from neighbouring C removed

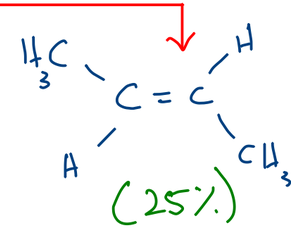
$$CH_3CH_2OH \xrightarrow{H_2SO_4} CH_2=CH_2$$

Dehydrating Complex Alcohols:-









5) Esterification :- Alcohols react with carboxylic acids to produce esters + conc. H_2SO_4 + heat
- heating required

Esters :- Esters constitute of the functional group $(R)-\overset{O}{\overset{\|}{C}}-O-(R')$

CH_3CH_2OH + CH_3CO_2H $\rightleftharpoons^{H_2SO_4}$ $CH_3CO_2CH_2CH_3$ + H_2O
ethanol ethanoic acid ethyl ethanoate

CH_3CH_2-OH + $CH_3-\overset{O}{\overset{\|}{C}}-OH$ $\rightleftharpoons$ $CH_3-\overset{O}{\overset{\|}{C}}-O-CH_2CH_3$
ethanoate ethyl

Name the following esters and identify the alcohol and carboxylic acid used to make the ester :-

$CH_3CH_2\overset{O}{\overset{\|}{C}}-O-CH_2CH_3$
propanoate ethyl
ethyl propanoate
- ethanol
- propanoic acid

$CH_3-\overset{O}{\overset{\|}{C}}-O-CH_2CH_2CH_3$
ethanoate propyl
propyl methanoate
- propanol
- ethanoic acid

$CH_3-O-\overset{O}{\overset{\|}{C}}-CH_2CH_3$
methyl propanoate
methyl propanoate
- methanol
- propanoic acid

- To separate the ester, add water, alcohol and carboxylic acid will dissolve and ester will not dissolve
(alcohol and carboxylic acid: hydrogen bonding; ester: temporary dipoles)

- esters are used to make perfumes, glue etc.

2 An organic compound will decolorise dilute acidified aqueous potassium manganate(VII) on warming, but will not decolorise bromine water.

What could the organic compound be?

A butane

B ethanol

C ethene

D ethanoic acid

4 Compound **X** undergoes the following reactions.

$$\underset{\mathbf{X}}{C_4H_9Br} \xrightarrow{NaOH(aq)\ /\ heat} C_4H_{10}O \xrightarrow{Cr_2O_7^{2-},\ H^+(aq)\ /\ heat} C_4H_8O \text{ only}$$

What is **X**?

A 1-bromobutane

B 2-bromobutane

C 1-bromo-2-methylpropane

D 2-bromo-2-methylpropane

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

$CH_3CH_2CH{=}CHCH_2CH_2OH$

P

What is produced when **P** is treated with an excess of hot concentrated acidic $KMnO_4$?

A $CH_3CH_2CH(OH)CH(OH)CH_2CH_2OH$

B $CH_3CH_2CH{=}CHCH_2CO_2H$

C CH_3CH_2CHO and $OCHCH_2CH_2OH$

D $CH_3CH_2CO_2H$ and $HO_2CCH_2CO_2H$

8 Which alcohol gives only **one** oxidation product when warmed with dilute acidified potassium dichromate(VI)?

A butan-1-ol

B butan-2-ol

C 2-methylpropan-1-ol

D 2-methylpropan-2-ol

10 Compound **X**

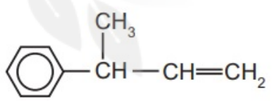
- has the molecular formula $C_{10}H_{14}O$;
- is unreactive towards mild oxidising agents.

What is the structure of the compound formed by dehydration of **X**?

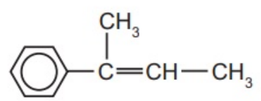
A

B

C



D



13 Which compound reacts with its own oxidation product (an oxidation which involves no loss of carbon) to give a sweet-smelling liquid?

A propanal

B propanoic acid

C propanone

D propan–1–ol

22 Compound **X**, $C_6H_{12}O$, is oxidised by acidified sodium dichromate(VI) to compound **Y**.

Compound **Y** reacts with ethanol in the presence of a little concentrated sulphuric acid to give liquid **Z**.

What is the formula of **Z**?

A $CH_3(CH_2)_2CH{=}CHCO_2H$ ✗

B $CH_3(CH_2)_4CH_2COCH_2CH_3$ ✗

C $CH_3(CH_2)_4CO_2CH_2CH_3$ ✓ (ethyl)

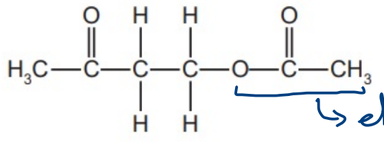
D $CH_3CH_2CO_2(CH_2)_4CH_3$ ✗

21 The functional group in a primary alcohol is $-CH_2OH$.

Which reagent reacts with a primary alcohol, under suitable conditions, to give an organic product with the same number of oxygen atoms as the alcohol?

A Al_2O_3 **B** CH_3CO_2H **C** HBr **D** Na

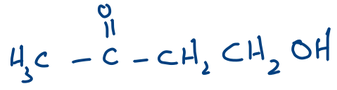
25 Compound X reacts with ethanoic acid in the presence of an H^+ catalyst to produce the compound below.



↳ ethanoate from ethanoic acid

What is the molecular formula of compound X?

A $C_2H_6O_2$ **B** $C_2H_6O_3$ **C** C_4H_8O **D** $C_4H_8O_2$



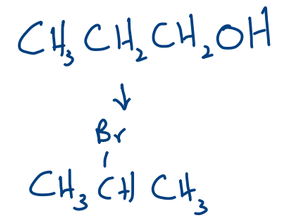
27 Which sequence of reagents may be used in the laboratory to convert propan-1-ol into 2-bromopropane?

A concentrated sulfuric acid, followed by bromine

B concentrated sulfuric acid, followed by hydrogen bromide ✓

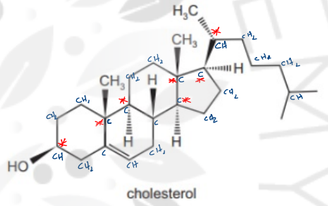
C ethanolic sodium hydroxide, followed by bromine ✗

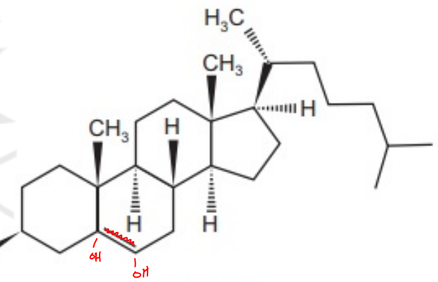
D ethanolic sodium hydroxide, followed by hydrogen bromide ✗



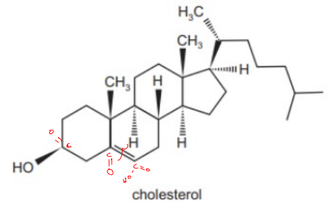
31 This question should be answered by considering the reactions of $KMnO_4$ with different functional groups under the stated conditions.

The diagram shows the structure of the naturally-occurring molecule cholesterol.





cholesterol



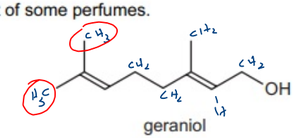
Cholesterol is separately treated with

- cold, dilute acidified $KMnO_4$,
- hot, concentrated acidified $KMnO_4$.

What is the change in the **number** of chiral carbon atoms in the molecule during each reaction?

	cold, dilute acidified $KMnO_4$	hot, concentrated acidified $KMnO_4$
A	+1	0
B	+1	−1
C	+2	0
D	+2 ✓	−1 ✓

32 Geraniol is a constituent of some perfumes.



geraniol

Which statement about geraniol is **not** correct?

A Geraniol causes hot acidified potassium dichromate(VI) to change colour from orange to green.

B Geraniol decolourises bromine water.

C There are three methyl groups and three methylene (CH_2) groups in geraniol.

D There are two pairs of *cis-trans* isomers of geraniol. ✗

38 An organic compound X

- is unaffected by hot acidified potassium manganate(VII),
- reacts with ethanoic acid in the presence of concentrated sulfuric acid.

What is compound X?

A $CH_3CO_2C_2H_5$

B $CH_3CH_2COCH_3$

C $(CH_3)_3COH$

D $CH_3CH_2CHOHCH_3$

50 Which alcohol has a chiral centre **and** can be oxidised to a ketone?

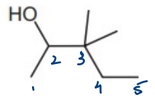
A pentan-2-ol ✓

B pentan-3-ol

C 3-methylhexan-1-ol

D 3-methylhexan-3-ol

67 What is the correct name of the molecule with the skeletal formula shown?



A 1,2,2-trimethylbutan-3-ol

B 2-ethyl-2-methylbutan-2-ol

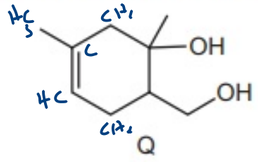
C 3,3-dimethylpentan-2-ol

D 4-hydroxy-3,3-dimethylpentane

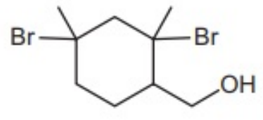
55 Considering **only** structural isomers, what is the number of alcohols of each type with the formula $C_5H_{12}O$?

	primary	secondary	tertiary
A	3	3	2
B	4	2	2
C	4	3	1
D	5	2	1

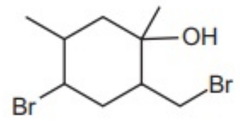
59 What is the major product formed when compound Q is warmed with excess HBr?



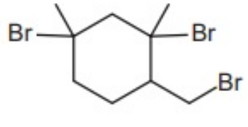
A



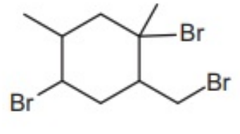
B ✗



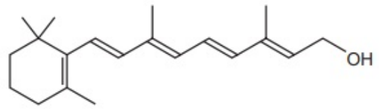
C



D ✗



68 Vitamin A contains retinol.



retinol

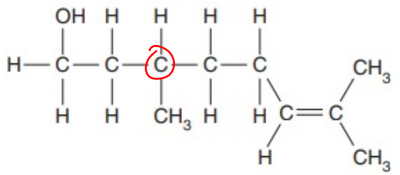
Under appropriate conditions, acidified $KMnO_4(aq)$ can be used to break apart C=C bonds.

After these bonds have been broken, further oxidation of the fragments may occur.

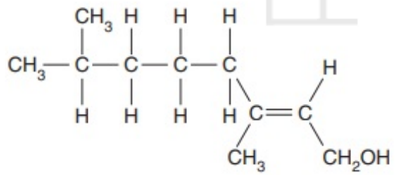
Under which conditions is the acidified $KMnO_4(aq)$ used and what do the final oxidation products include?

	conditions	final oxidation products
A	cold, dilute	aldehydes and carboxylic acids
B	cold, dilute	ketones and carboxylic acids
C	hot, concentrated ✓	aldehydes and carboxylic acids
D	hot, concentrated ✓	ketones and carboxylic acids ✓

2 Some perfumes and scents of flowers and fruit contain compounds which are structural isomers. Two such examples are citronellol and geraniol.



citronellol



geraniol

(a) Confirm that citronellol and geraniol are isomers by calculating their molecular formula and their relative molecular mass, M_r.

(i) Molecular formula $C_{10}H_{20}O$

(ii) M_r 156 [2]

(b) Name two functional groups present in **both** molecules.

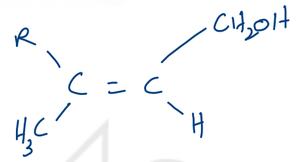
(i) alkene

(ii) primary alcohol [3]

Citronellol and geraniol also show stereo isomerism.

(c) On the diagram of the structure of citronellol above, draw a circle around a chiral carbon atom. [1]

(d) **(i)** Draw the other *cis-trans* isomer of geraniol. [In parts **(d)** and **(f)** use R – to represent a part of the molecule.]



(ii) Explain why geraniol has no optical isomers.

It does not have a chiral carbon atom

[2]

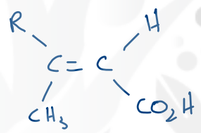
(e) State what you would expect to see if citronellol was reacted with aqueous bromine.

solution turns from brown to colourless

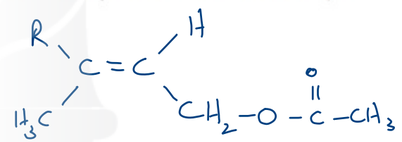
[1]

(f) Draw structures of the organic products when geraniol reacts with each of the following reagents.

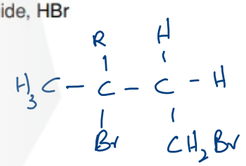
(i) an excess of $H^+/Cr_2O_7^{2-}$ under reflux



(ii) ethanoic acid in the presence of an acidic catalyst



(iii) hydrogen bromide, HBr



[4]

5 Compounds containing the allyl group, $CH_2=CHCH_2-$, have pungent smells and are found in onions and garlic.
Allyl alcohol, $CH_2=CHCH_2OH$, is a colourless liquid which is soluble in water.

(a) Allyl alcohol behaves as an alkene and as a primary alcohol.

Give the structural formula of the organic compound formed when allyl alcohol is

(i) reacted with Br_2,

$CH_2Br-CHBrCH_2OH$

(ii) heated under reflux with an acidified solution of $Cr_2O_7^{2-}$ ions.

$CH_2=CHCO_2H$

[2]

(b) When allyl alcohol is reacted with MnO_2 at room temperature, propenal, $CH_2=CHCHO$ is formed.

What type of reaction is this?

redox [1]

(c) Allyl alcohol may be converted into propanal, CH_3CH_2CHO, by using a ruthenium(IV) catalyst in water.

$$CH_2=CHCH_2OH \xrightarrow{\text{ruthenium(IV) catalyst}} CH_3CH_2CHO$$

The reactant and the product are isomers.
What form of isomerism do they display?

functional group (structural) isomerism [1]

(d) Allyl alcohol can be converted into propanal in two steps **without** the use of a ruthenium(IV) catalyst.

$$CH_2=CHCH_2OH \xrightarrow{\text{step I}} CH_3CH_2CH_2OH \xrightarrow{\text{step II}} CH_3CH_2CHO$$

What reagents and conditions would be used for **each** step?

step I

reagent(s) H_2 + Ni catalyst

condition(s) 180°C temperature

step II

reagent(s) Acidified $K_2Cr_2O_7$

condition(s) heat + distill off the aldehyde immediately [4]

(e) By considering your answers to **(b)** and **(d)**, suggest what is unusual about the single-step reaction in **(c)**.

the organic product was both reduced and oxidised

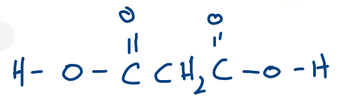
[1]

(f) Suggest the structural formula of the organic compound formed when allyl alcohol is

(i) reacted with cold, dilute MnO_4^- ions,

$CH_2(OH)-CH(OH)CH_2OH$

(ii) heated under reflux with acidified MnO_4^- ions.



[3]

6 Lactic acid, 2-hydroxypropanoic acid, $CH_3CH(OH)CO_2H$, occurs in sour milk.

Glycollic acid, 2-hydroxyethanoic acid, $HOCH_2CO_2H$, occurs in sugar cane.

(a) Lactic acid may be synthesised from propene by the following sequence.

$$CH_3CH{=}CH_2 \xrightarrow{\text{step I}} CH_3CH(OH)CH_2OH \xrightarrow{\text{step II}} CH_3CH(OH)CO_2H$$

(i) What reagent(s) and condition(s) are used for step I?

reagent(s) $KMnO_4$ (aq) (acidified)

condition(s) cold, dilute

(ii) What type of reaction is step II?

redox

[3]

(b) Glycollic acid may be synthesised from ethanoic acid by the following sequence.

$$CH_3CO_2H \xrightarrow{\text{step III}} ClCH_2CO_2H \xrightarrow{\text{step IV}} HOCH_2CO_2H$$

(i) Suggest the reagent(s) and condition(s) that are used for step III.

reagent(s) Cl_2 gas

condition(s) U.V light

(ii) What reagents and conditions are used in step IV?

reagent(s) NaOH (aq) dissolved in water

condition(s) heat under reflux

[4]

(c) Lactic acid and glycollic acid react differently when heated under reflux with acidified dichromate(VI) ions.

Draw the structural formula of the organic product in **each** case.

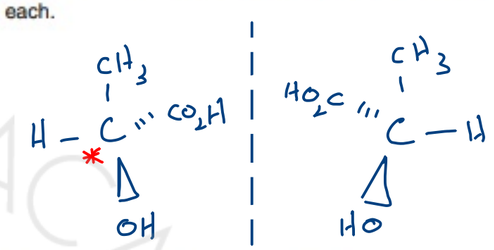
product from lactic acid

CH_3COCO_2H

product from glycollic acid

HO_2C-CO_2H

(d) Lactic acid is chiral. Draw displayed formulae of the two optical isomers of lactic acid clearly showing their three-dimensional structures. Indicate with an asterisk (*) the chiral carbon atom in each.

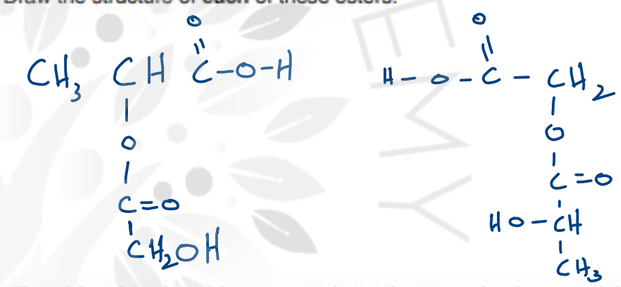


[2]

Glycollic acid and lactic acid each give the reactions of an alcohol group and of a carboxylic acid group. Each compound will react with the other to give an ester.

(e) When one molecule of glycollic acid reacts with one molecule of lactic acid, it is possible to form two different esters.

Draw the structure of **each** of these esters.



[2]

Glycollic acid and lactic acid are reacted together to make the material for 'soluble stitches' (also known as 'soluble sutures') which are used in surgery.

In this material, many molecules of each acid have been reacted to form a long chain 'polyester' molecule which contains many ester groups.

This polyester is used in surgery to sew up wounds inside the body.

Over a period of time, the polyester undergoes a chemical reaction and breaks up to re-form the two individual hydroxy-acids.

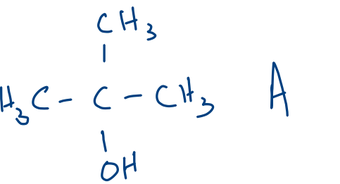
(f) **(i)** This reaction occurs where the pH of the body is about pH5 to pH6. Suggest what type of chemical reaction causes the polyester material to break up.

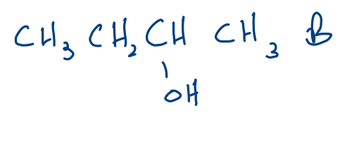
hydrolysis

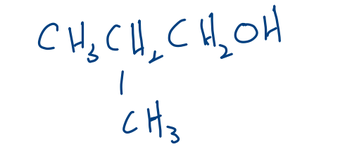
(ii) Suggest why the products of this reaction are soluble in water.

the products can form hydrogen bonds with water

[2]







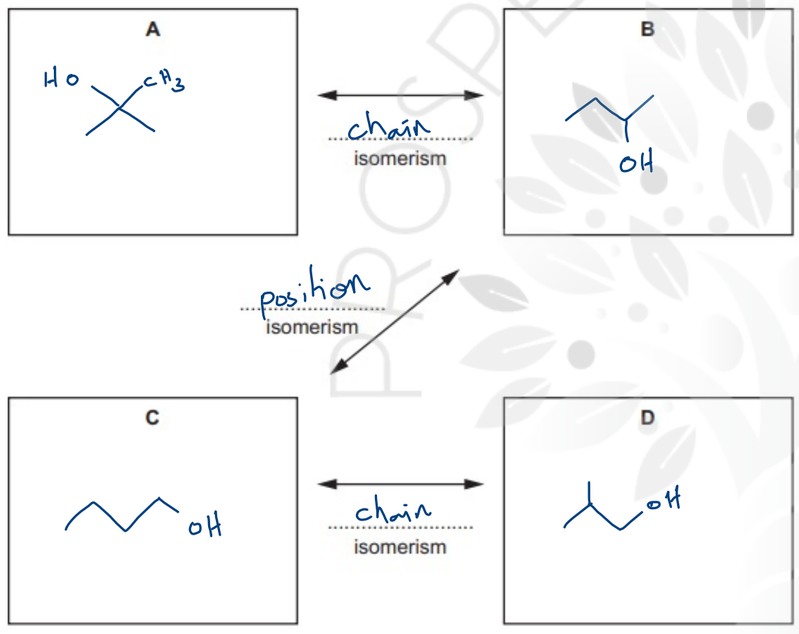
15 There are four alcohols, **A**, **B**, **C** and **D**, which are structural isomers with the molecular formula $C_4H_{10}O$.

tertiary

Alcohol **A** does not react with acidified potassium dichromate(VI) solution but **B**, **C** and **D** do.

All four alcohols react with hot, concentrated sulfuric acid to form products with the molecular formula C_4H_8. **A**, **C** and **D** each give a single product in this reaction. **B** gives a mixture of two structural isomers, one of which shows stereoisomerism.

(a) Give the **skeletal** formula for each of the four alcohols and complete the diagram with the names of the types of structural isomerism shown by each linked pair of compounds.



[7]

(b) **(i)** Give the names of the two structural isomers produced by the reaction of **B** with hot, concentrated sulfuric acid

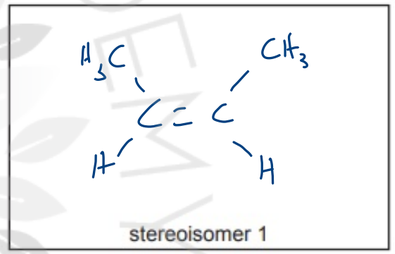
but-1-ene ..... but-2-ene ..... [2]

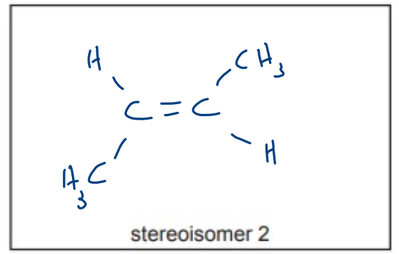
(ii) State which of these two isomers shows stereoisomerism. Explain why this molecule is capable of showing stereoisomerism.

but-2-ene shows geometric isomerism as its carbons involved in the C=C carry 2 different groups which give rise to isomers as π bond restricts rotation

..... [2]

(iii) Draw **displayed** formulae to show the two stereoisomers.


stereoisomer 1


stereoisomer 2

[2]