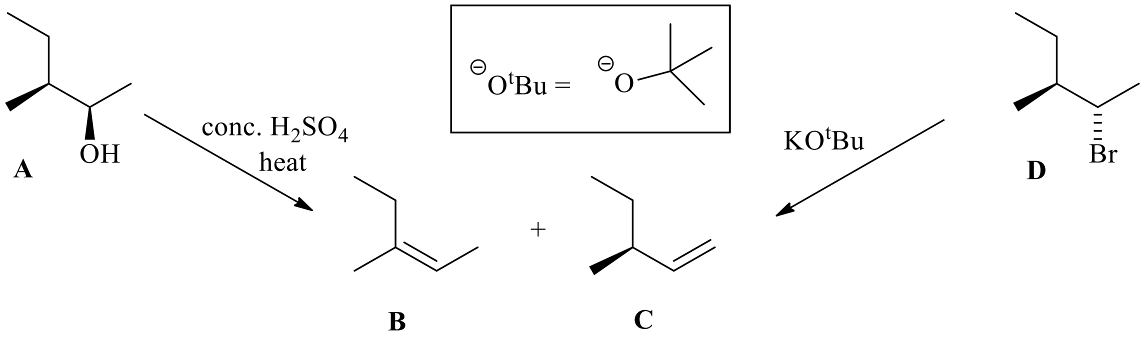
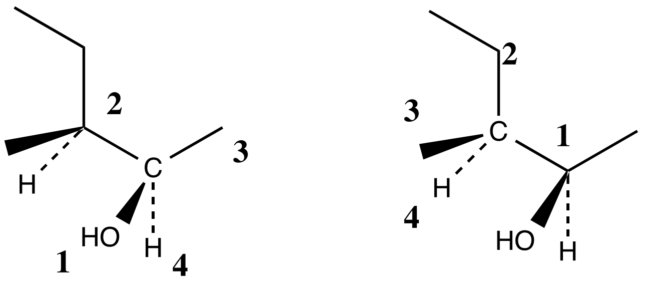
**Marks**
**7**

- The elimination of $H_2O$ from alcohol **A** can form the isomeric alkenes **B** and **C**. Elimination of HBr from the alkyl halide **D** can generate the same two alkenes.



Assign the absolute configuration of alcohol **A**. Show your working.



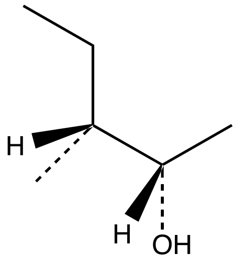
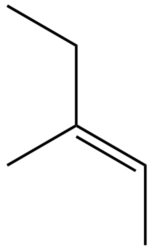
(*R*) (*S*)

**There are 2 chiral centres. On the diagram on the left, the priorities are as shown and are in an (*R*) configuration. On the diagram on the right, the priorities are in an (*S*) arrangement.**

Name compound **B** fully.

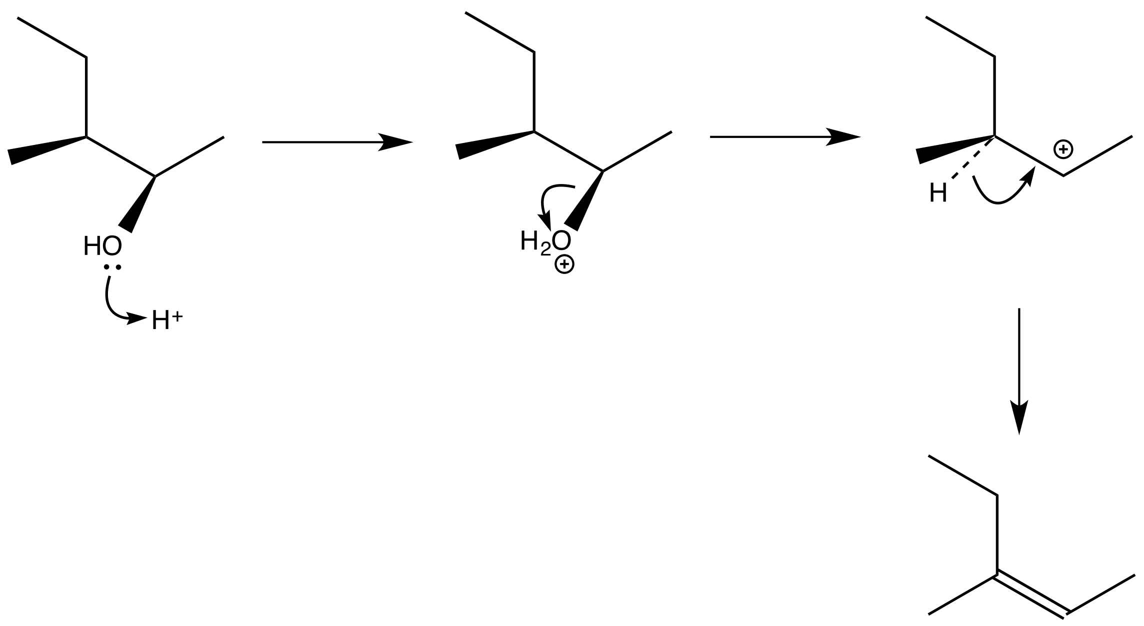
**(Z)-3-methylpent-2-ene**

A diastereoisomer of **B** is also formed in these reactions. Draw the enantiomer of **A** and the diastereoisomer of **B**.

| enantiomer of **A** | diastereoisomer of **B** |
|---|---|
|  |  |

**ANSWERS CONTINUES ON THE NEXT PAGE**

Propose a mechanism for the formation of **B** from **A** under the conditions shown. Use curly arrows and draw the structures of any intermediates.



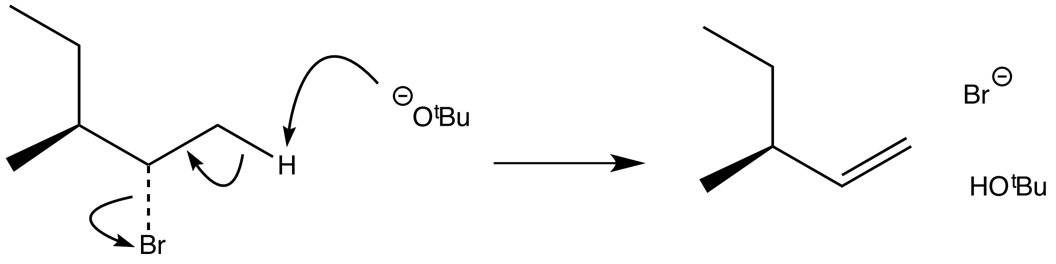
**THIS QUESTION CONTINUES ON THE NEXT PAGE.**

**Marks**
**4**

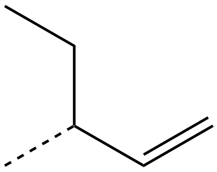
Explain why compound **C** is the minor product of this reaction.

**C has the new C=C bond with fewer substituents. This is an example of Zeitsev's rule: the more substituted alkene is more thermodynamically stable.**

Propose a mechanism for the formation of **C** from **D** under the conditions shown. Use curly arrows and draw the structures of any intermediates.



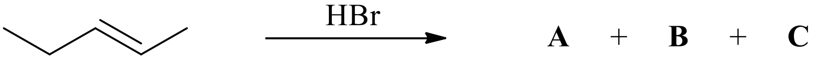
Compound **C** is the major product formed from **D** under these conditions. What would be the major product if the enantiomer of **D** were exposed to the same reaction conditions?



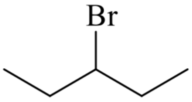
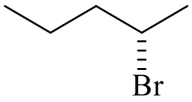
**THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.**

**Marks**
**8**

- Addition of HBr to the isomer of 2-pentene shown below gives 3 isomeric products, **A**, **B** and **C**, in an approximate ratio of 50:25:25 respectively.



Draw the three products **A**, **B** and **C**.

| **A** | **B** | **C** |
|---|---|---|
| <br>**A** | <br>**B** | <br>**C** |

Explain the ratio of products observed.

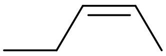
**The double bond is equally substituted, so attack of the electrophile $H^+$ is equally likely at C2 or C3. The carbocations at C3 and C2 should therefore be formed in equal amounts. Subsequent attack of the trigonal planar carbocation by $Br^-$ is equally likely from above or below the molecule. Attack at C3 produces only one compound. Attack at C2 produces either the (*R*)- or (*S*)- enantiomer in equal amounts.**

| | |
|---|---|
| What is the isomeric relationship between **A** and **B**? | **Constitutional isomers** |
| What is the isomeric relationship between **B** and **C**? | **Enantiomers** |

Assign the stereochemistry of the starting material isomer. Show your working.

**The higher priority groups are methyl (at C2) and ethyl (at C3). These are on opposite sides of the double bond and hence the molecule has (*E*) stereochemistry.**

Draw the other configurational isomer of 2-pentene and assign its stereochemistry.



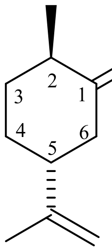
**(*Z*)- isomer**

What product(s) would you expect from the addition of HBr to this stereoisomer, and in what ratio?

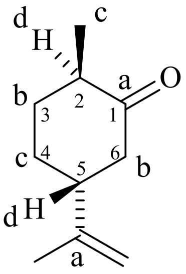
**Same ratio as for the (*E*) isomer, *i.e.* 50% A, 25% B, 25% C.**

**Marks**
**7**

- Consider the structure of dihydrocarvone shown below.



Assign the absolute configuration of dihydrocarvone. Explain your reasoning.



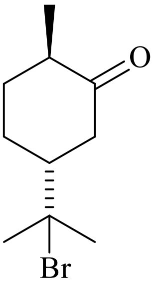
**C$_2$: (*R*)**
**Around C$_2$, the order of priorities is:**
**a: C$_1$(O,O,C) > b: C$_3$(C,H,H) > c: C$_{\text{methyl}}$(H,H,H) > d: H**

**Looking down C$_2$–H bond, a →b→c is clockwise**

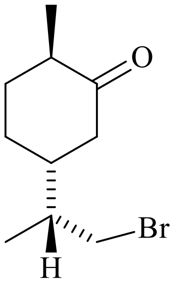
**C$_5$: (*R*)**
**Around C$_5$, the order of priorities is:**
**a: C(C,C,C) > b: C$_6$(C,H,H) > c: C$_4$(C,H,H) > d: H**

**As C$_4$ and C$_6$ are equivalent, C$_1$ > C$_3$ is used to prioritise them. Looking down C$_5$–H bond (*i.e.* out of paper), a →b→c is clockwise**

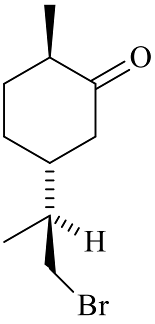
Draw all of the products that can result from the electrophilic addition of HBr to dihydrocarvone and explain the isomeric relationship between each pair.



A



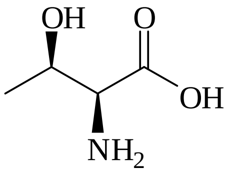
B



C

**A and B are constitutional isomers. A and C are constitutional isomers. B and C are diastereoisomers.**

- The systematic name of threonine is 2-amino-3-hydroxybutanoic acid. Assign the absolute configuration of L-threonine. Show your working.

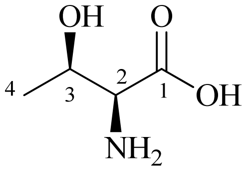


L-threonine

**About C2: $NH_2$ > COOH > $CH(OH)CH_3$ > H - anticlockwise**

**About C3: OH > $CH(NH_2)COOH$ > $CH_3$ > H - clockwise**

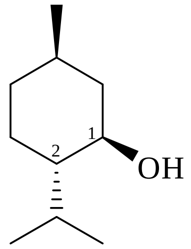
**Therefore (2*S*, 3*R*)-2-amino-3-hydroxybutanoic acid**



**Marks**
**10**

- The following questions pertain to the terpene natural product menthol (**J**), whose structure is shown. Carbons 1 and 2 are numbered to help you construct your answer.

**J**



Ignoring the stereochemistry, what is the systematic name for menthol?

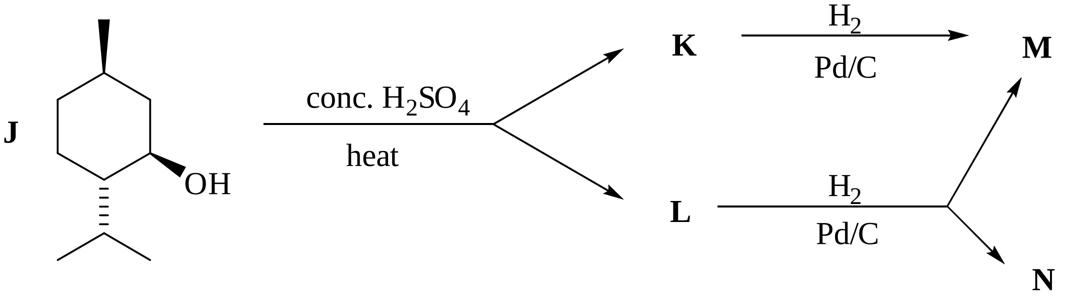
**2-isopropyl-5-methylcyclohexanol**

**2-(1-methylethyl)-5-methylcyclohexanol is also acceptable.**

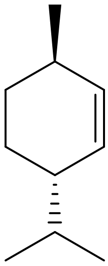
Assign the absolute configuration at C1 and at C2. Explain your reasoning.

| | |
|---|---|
| C1 **is (*R*)**<br>**Priorities: OH > C2 C(C,C,H) > C6 C(C,H,H) > H**<br>**With H at back, the order of –OH → –C2 → –C6 goes clockwise** | C2 **is (*S*)**<br>**Priorities: C1 C(O,C,H) > isopropyl C(C,C,H) > C3 C(C,H,H) > H**<br>**Remember the H is pointing in front of the paper.**<br>**With H at back, the order of –C1 → –CH(CH$_3$)$_2$ → –C3 goes anticlockwise** |

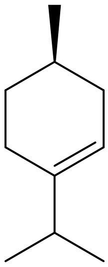
When menthol (**J**) is heated with concentrated sulfuric acid, two isomeric products **K** and **L** are formed. When **K** and **L** are treated with excess $H_2$ in the presence of a Pd/C catalyst, two products **M** and **N** are observed: **K** gives only **M**, while **L** gives a mixture of **M** and **N**. Propose structures for **K**, **L**, **M** and **N**.



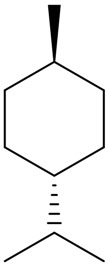
**K**



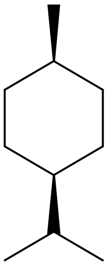
**L**



**M**



**N**

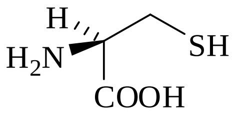


**ANSWER CONTINUES ON THE NEXT PAGE**

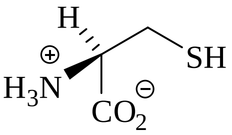
| | |
|---|---|
| What is the isomeric relationship between **K** and **L**? | **constitutional isomers** |
| What is the isomeric relationship between **M** and **N**? | **diastereoisomers** |
| Which (if any) of the compounds **J**, **K**, **L**, **M** and **N** are optically active? | **J, K and L** |

**Marks**
**5**

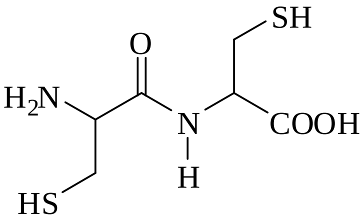
- Consider the amino acid L-cysteine shown below.



Draw the zwitterionic form of L-cysteine.



Draw the dipeptide L-cysteinyl-L-cysteine.

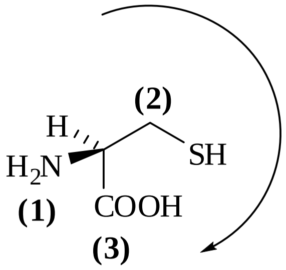


Assign the absolute configuration (*R* or *S*) of L-cysteine. Show your working.

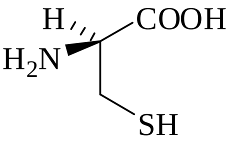
**Absolute configuration is (*R*)-**

**Priorities: $-NH_2 > -CH_2SH > -COOH > -H$**

**With H at back, the order of $-NH_2 \rightarrow -CH_2SH \rightarrow -COOH$ goes clockwise**

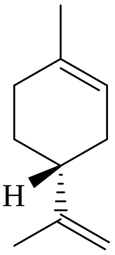


Draw the enantiomer of L-cysteine.

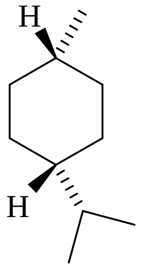


**Marks**
**9**

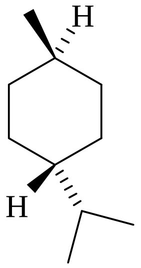
- Consider the isomer of limonene shown below.



Show the major organic products formed when limonene is treated with excess $H_2$ in the presence of a Pd/C catalyst. Pay particular attention to any relevant stereochemistry. Identify which would be the major product and explain why it forms preferentially.



A



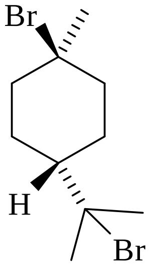
B

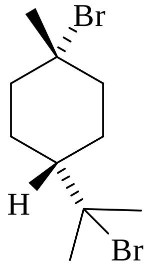
**Isomer A would be the major product.**

**The reaction takes place on the surface of the catalyst. The isopropyl group provides steric hindrance to the side of the ring that is *cis* to this group.**

**Both H's therefore are delivered to the other side of the molecule.**

Use Markovnikov's rule to predict the two major products of the reaction between limonene and excess HBr. Draw these isomers and identify the isomeric relationship between them. Specify the optical activity (active or inactive) of each isomer.





**They are diastereoisomers. Both isomers are optically inactive.**

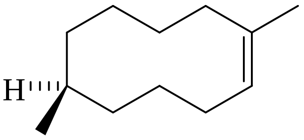
At what *m*/*z* would the molecular ion of one of these isomers appear in its mass spectrum? Explain your answer.

**Br exists as two isotopes $^{79}$Br and $^{81}$Br, which occur in approximately equal amounts.**

**There would be 3 molecular ion peaks at *m*/*z* 296, 298 and 300 due to the ions containing 2 $^{79}$Br atoms, 1 $^{79}$Br and 1 $^{81}$Br atom and 2 $^{81}$Br atoms, respectively.**

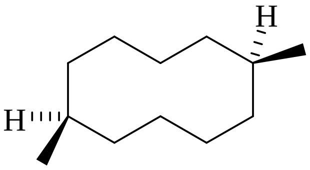
**Marks**
**6**

- Compound **X** undergoes an addition reaction on treatment with hydrogen gas in the presence of a palladium on carbon catalyst to form a mixture of cyclic alkanes.

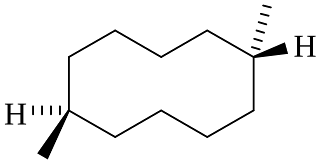


**X**

Clearly draw all possible products that can form from this reaction, taking care to represent the stereochemistry of the products clearly.



**achiral**



**achiral**

Clearly label each isomer drawn above as either chiral or achiral (not chiral).

Circle one of the isomers and provide a full systematic name for this compound below. Make sure you include all relevant stereochemical descriptors.

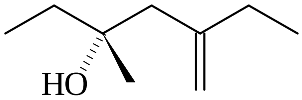
***cis*-1,6-dimethylcyclodecane** ***trans*-1,6-dimethylcyclodecane**

**THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.**

**Marks**
**7**

- Compound **X** undergoes an addition reaction on treatment with dilute aqueous sulfuric acid to form a mixture of diol compounds.

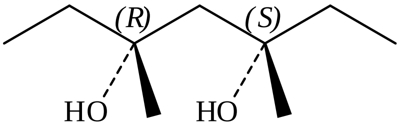
**X**



Draw all possible products (major and minor) that can form from this reaction. Take care to represent clearly the stereochemistry of all the products.

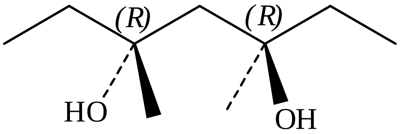
**Major (from Markovnikov's rule)**

**achiral**



**(3*R*,5*S*)-3,5-dimethylheptane-3,5-diol**

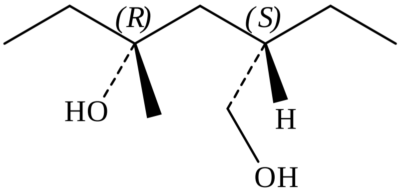
**chiral**



**(3*R*,5*R*)-3,5-dimethylheptane-3,5-diol**

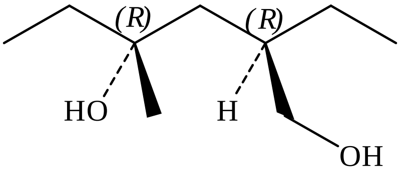
**Minor (anti-Markovnikov)**

**chiral**



**(2*S*,4*R*)-2-ethyl-4-methylhexane-1,4-diol**

**chiral**



**(2*R*,4*R*)-2-ethyl-4-methylhexane-1,4-diol**

Clearly label each isomer drawn above as either chiral or achiral (not chiral).

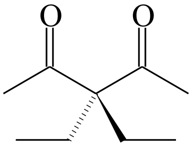
Circle one of the isomers that you expect to be a major product of the reaction and provide a full systematic name for this compound below. Make sure you include all relevant stereochemical descriptors.

**See above**

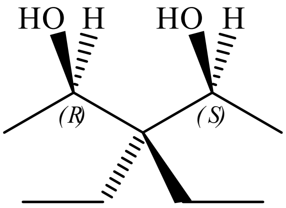
**Marks**
**6**

- Compound **X** can be reduced by treatment with sodium borohydride followed by dilute hydrochloric acid to form a mixture of diol compounds.

**X**

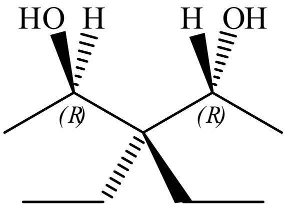


Clearly draw all possible product stereoisomers that can form from this reduction, taking care to represent clearly the stereochemistry of the products.

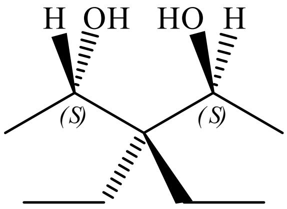


achiral

meso



chiral



chiral

enantiomers

Clearly label each isomer drawn above as either chiral or achiral (not chiral).

Circle one of the product isomers you have drawn above and provide a full systematic name for this compound below. Make sure you include all relevant stereochemical descriptors.

(2*R*,4*R*)-3,3-diethylpentane-2,4-diol

(2*R*,4*S*)-3,3-diethylpentane-2,4-diol

(2*S*,4*S*)-3,3-diethylpentane-2,4-diol