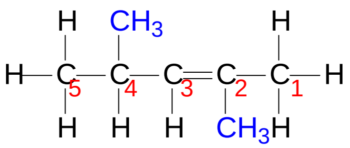
4 Alkenes Tutorial

Structure and naming

1 Give the IUPAC names of the following compounds.

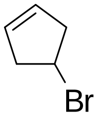
(a)

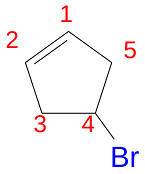


$(CH_3)_2CHCH=C(CH_3)_2$

2,4-dimethylpent-2-ene

(c)

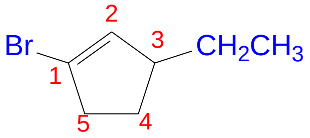




4-bromocyclopentene

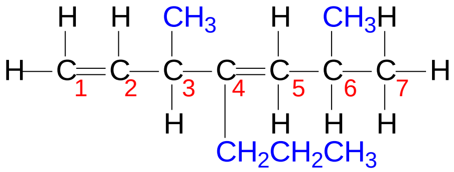
2 Draw the structural formula for each of the following compounds.

(a)



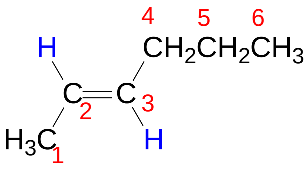
1-bromo-3-ethylcyclopentene

(b)



3,6-dimethyl-4-propylhepta-1,4-diene

(c)



trans-hex-2-ene

Electrophilic addition

3 (2021/P1/16) Which statement about propene explains how it reacts with bromine?

A Electrons in the carbon−carbon π bond are donated to an electrophile.

B Electrons in the carbon−carbon σ are donated to an electrophile.

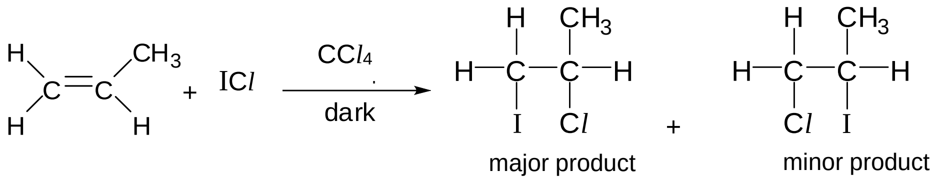
C The sp^2 hybridised carbon is an electrophile and accepts a pair of electrons.

D The σ bond between the sp^2 hybridised carbon atoms is weak and readily broken.

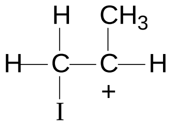
4. For each of the following reactions,

(i) give the structures of the product(s) formed in each of the following reactions.
(ii) identify with explanation the major product where applicable.
(iii) state the observation during reaction where applicable.

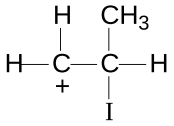
(a)



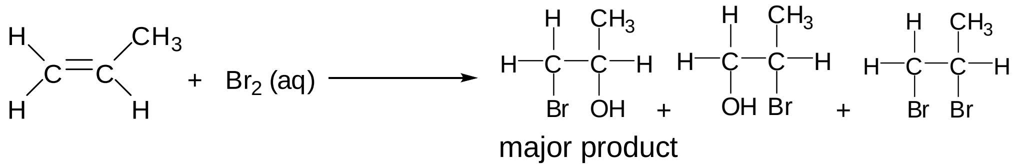
I is less electronegative than C*l*, hence $^{\delta+}$I is the electrophile and the more stable carbocation with greater number of electron-donating alkyl groups attached to the electron deficient carbocation to reduce its electron deficiency. This more stable carbocation is formed more abundantly in the rate-determining step, leading to a higher yield of the product.



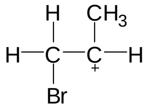
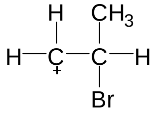
(more stable carbocation)

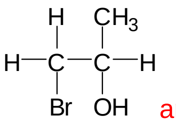


4 (b)



The halohydrin(-Br & -OH) products are formed as major products due to the presence of huge amount of H_2O (since it is a solvent). It is more likely for H_2O to carry out the nucleophilic attack in step 2, rather than Br^- due to greater amount of H_2O in the reaction system as compared to Br^-.

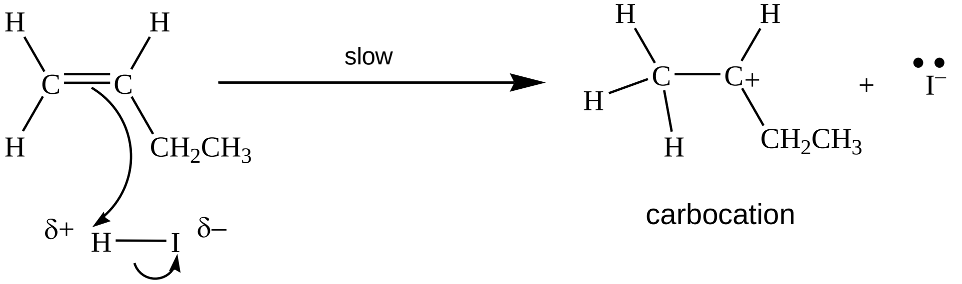
 is more stable than  as the former has more electron-donating alkyl group bonded to the carbocation to reduce its electron deficiency.
This more stable carbocation is formed more abundantly in the rate-determining step, leading to a higher yield of the product.
Observations: ***Orange* aqueous bromine is decolourised**.

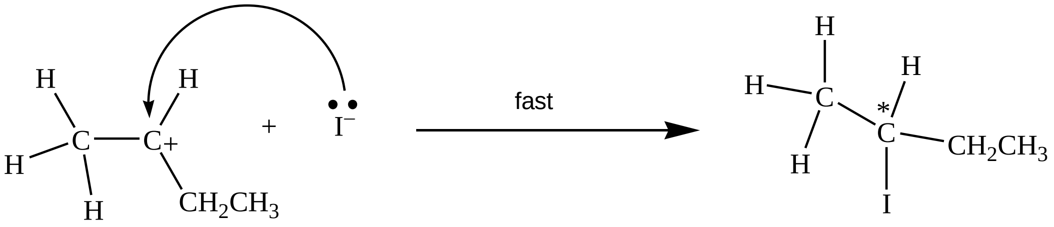
Common mistake for question 4b:
When asked to draw mechanism for such question, many students drew the OH^- attacking the carbocation in the 2nd step, instead of H_2O. This is incorrect. Pls check the notes that H_2O is the nucleophile instead. There is a further attack by Br^- on the H atom to obtain the final product  and HBr.

5 Explain each of the following observations, as fully as you can, by making reference to the reaction mechanism of alkenes:

a) Addition of pure hydrogen iodide to but-1-ene gives a mixture of two optical isomers in equal molar proportions.

Electrophilic addition



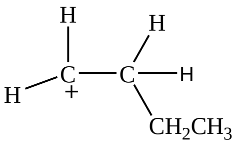
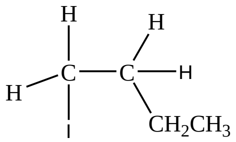


In the second step, I^- has equal likelihood to attack the trigonal planar carbocation from above or below the plane, and there are four different groups attached to C in the product. Hence there are two optical isomers of equal proportion.

Learning points/ question 4a.

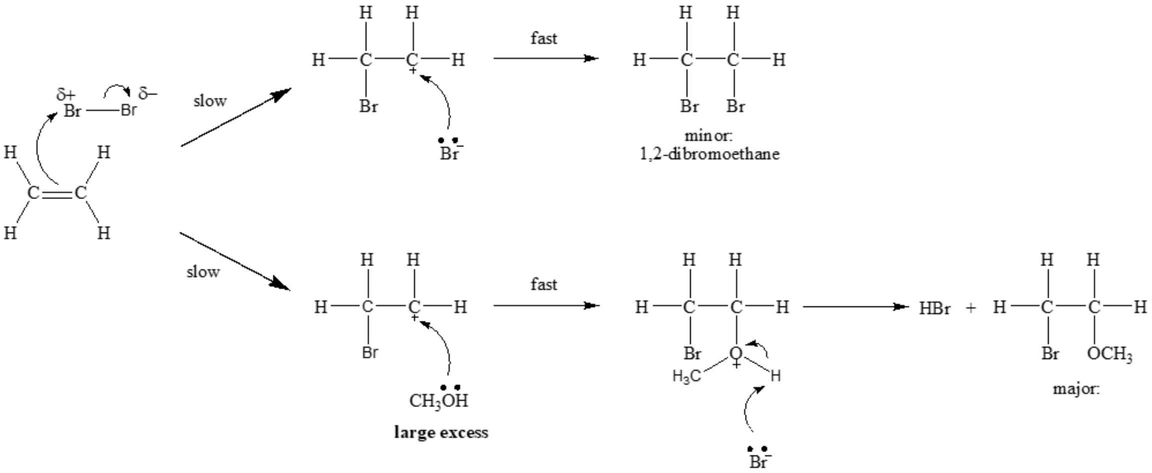
Laboratory synthesis with alkene as the reactant (in electrophilic addition) always end up with producing an optically inactive mixture, even with a chiral carbon present, since a racemic mixture will always be formed.

Note:

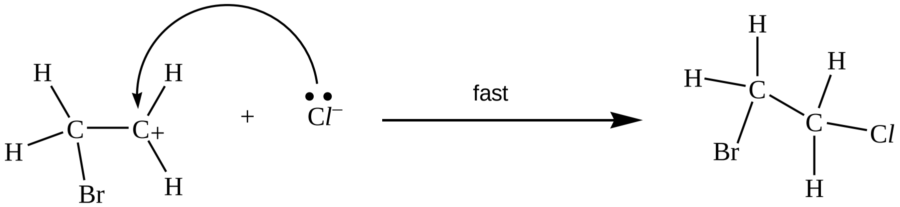
 is formed as well but the resulting product  does not have a chiral carbon.

5 b) Addition of liquid bromine to a solution of ethene in methanol gives a mixture of 1,2-dibromoethane and $CH_2BrCH_2OCH_3$. However, when ethene is shaken with an aqueous solution containing both bromine and sodium chloride, 1-bromo-2-chloroethane is also formed, but not 1,2-dichloroethane.

Electrophilic addition



In aqueous solution of Br_2 and NaC*l*, the same carbocation is formed.



1,2-dichloroethane cannot be formed as Cl^- is an nucleophile and it does not react with ethene to formed carbocation in the first step.

Thinking process to solve such question

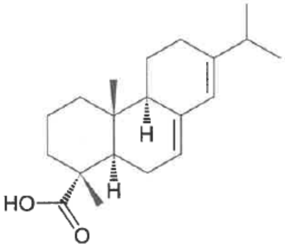
Step 1: write out all reactants present (in this question, NaC*l*, Br_2, H_2O)

Step 2: Have a table as such:

E^+(attacked in step 1)	Nu− (attack carbocation in step 2)	Product
δ+ Br in Br_2	Br^-	CH_2BrCH_2Br
	Cl^-	CH_2BrCH_2Cl
	H_2O	CH_2BrCH_2OH

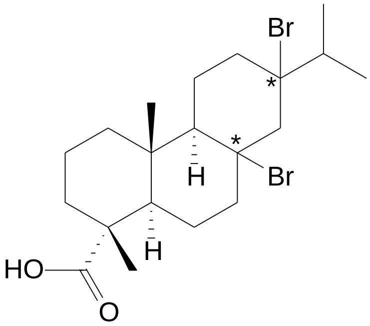
- Na^+ cannot be E+ since it only forms ionic bond.
- Cl^- cannot be E+ since it is electron rich, not electron deficient.
- H_2O cannot be E+ since O–H bond in H_2O is strong and does not break readily.

6 (2018 P3 Q4d) Abietic acid is a major component of many resins and has the following structure.



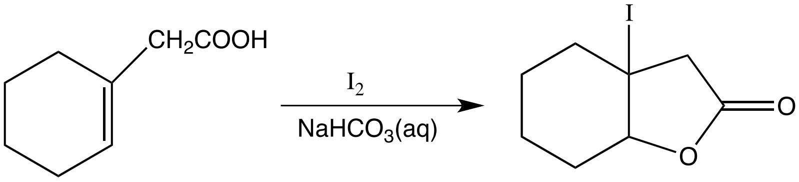
abietic acid, $C_{20}H_{30}O_2$

Draw the structure of the major product when abietic acid is reacted with an excess of HBr. State how many extra chiral centres are formed.



2 additional chiral centres are formed.

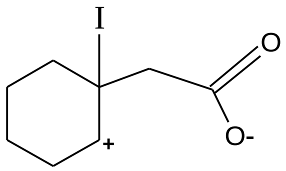
7. When compound **R** is reacted with iodine in the presence of aqueous sodium hydrogencarbonate, iodine does **not** add across the carbon–carbon double bond of compound **R** as might be expected. Instead, a compound **S**, which has a molecular formula, $C_8H_{11}O_2I$, is formed as shown:



R **S**

$NaHCO_3$ function as a base during this reaction. Suggest an explanation for the observation.

R undergoes electrophilic addition with iodine followed by acid-base reaction in alkaline medium(HCO_3^-) to form



The -COO$^-$ attack the carbocation to form compound **S**.

Learning points/ Thinking process for question 5 (and similar application question you see in future)

- Product is given, you are supposed to deduce a logical sequence of steps to get this product.
- There is a double bond in R, I_2 is present and no more double bond in S. Electrophilic addition (otherwise what else?) must have occur.
- If you are wondering which carbon does I add across in step 1 of electrophilic addition, look at the product. I is added to the top carbon, hence the carbocation should be on the bottom carbon.
- Looking at the product, the bottom carbocation is likely to be attacked by O$^-$ in step 2 of electrophilic addition.
- $NaHCO_3$ can react with CH_2CO_2H to give $CH_2CO_2^-$, which happens to be the nucleophile to react with the carbocation in step 2.

More advanced way of looking at it: When a product has 1 additional ring than a reactant, an intramolecular reaction must have taken place. This will hint towards a nucleophile being in the same molecule as R.

Oxidation

8 For each of the following, identify the alkene which forms the products upon vigorous oxidation by hot acidified $KMnO_4$, giving its structure and IUPAC name.
Draw the cis-trans isomers of the alkene (if any).

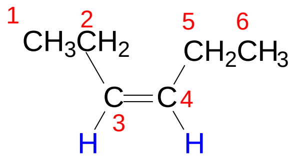
Thinking process/comments for question 6:

Working backwards from the product of vigorous oxidation to derive the 4 groups attached to the C=C of an alkene.

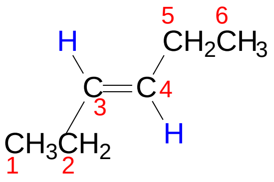
- Refer to pg 15 of Alkene notes if unsure

(i) $CH_3CH_2CO_2H$ only

$CH_3CH_2CO_2H$ is formed from $CH_3CH_2CH=$ fragment



cis-hex-3-ene

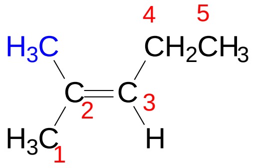


trans-hex-3-ene

(ii) $(CH_3)_2CO$ and CH_3CH_2COOH

$(CH_3)_2CO$ is formed from $(CH_3)_2C=$ fragment

$CH_3CH_2CO_2H$ is formed from $CH_3CH_2CH=$ fragment

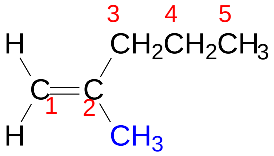


2-methylpent-2-ene

(iii) CO_2 and $CH_3COCH_2CH_2CH_3$

CO_2 is formed from $CH_2=$ fragment

$CH_3COCH_2CH_2CH_3$ is formed from $(CH_3)(CH_3CH_2CH_2)C=$ fragment



2-methylpent-1-ene

Distinguishing Test

9 Describe one simple chemical test to distinguish each set of compounds, stating clearly the observation for each compound in each chemical test. Support your answers with appropriate balanced equations.

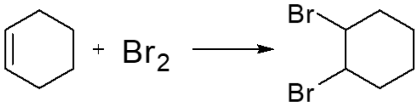
Requirement for all distinguishing test questions:

1. Reagent/conditions
2. ALL observations (Do not write no observation/no reaction/no change observed etc. Instead give negative observation like purple solution remains, no brown ppt observed etc)
3. Equations (only if question asks for it)

(a) cyclohexane and cyclohexene

Test: Br_2 in hexane/CCl_4 or aqueous Br_2

With cyclohexene, orange red bromine (in hexane/CCl_4) is decolourised.



Thinking process: reactions of different functional groups

With cyclohexane, orange red bromine (in hexane/CCl_4) remains.

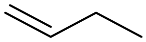
Note: if Br_2(aq) is used, the orange Br_2(aq) is decolourised.

Alternatively, use cold $KMnO_4$ with NaOH(aq). Cyclohexene decolourises purple $KMnO_4$ and brown precipitate of MnO_2 is observed.

Or use $KMnO_4$, dilute H_2SO_4, heat. Cyclohexene decolourises purple $KMnO_4$.

For both tests with cyclohexane, purple $KMnO_4$ solution remains.

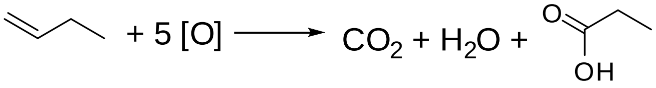
(b)



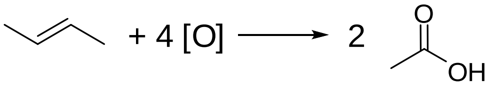
Test: $KMnO_4$, dilute H_2SO_4; heat

Thinking process: same functional group, difference in the structure of alkene

Balanced equations:



Observations: purple solution is decolourised and effervescence is observed.



Observations: purple solution is decolourised.

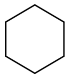
Application question

10 Suggest, with reasons, a possible structural formula for each of the compounds, **A** – **F**, all of which have the molecular formula C_6H_{12}. Note that no two structures should be the same.

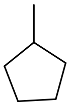
(a) **A** does not decolourises aqueous bromine solution.

A is not an alkene. Isomer of alkene with general formula of C_nH_{2n} is cycloalkane.

A:

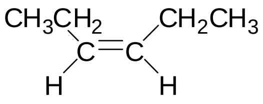


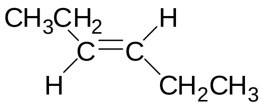
or



(b) **B** decolourises liquid bromine dissolved in tetrachloromethane and exists as a pair of cis-trans isomers.

B:



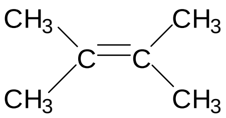


The two groups on each C=C are not the same, hence it exhibits cis-trans isomerism.

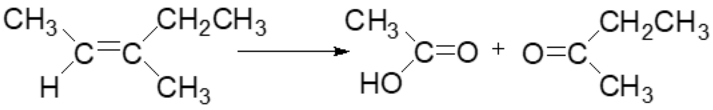
Accept any other cis-trans isomers of C_6H_{12}.

(c) **C** reacts with hot acidified potassium manganate(VII) to give only **one** product, C_3H_6O.

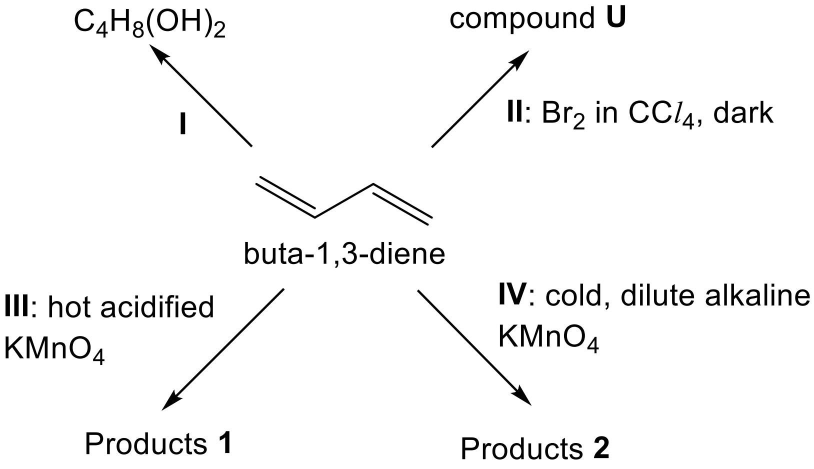
C_3H_6O is a ketone. It cannot be an aldehyde as aldehyde should have been further oxidised to carboxylic acid. There is only one oxidation product ⇒ two identical fragments are produced, hence the alkene must be symmetrical.

C:


(d) **D** undergoes reaction with $KMnO_4(aq)$ in dilute acid when heated to give CH_3CO_2H and $CH_3CH_2COCH_3$.

D:


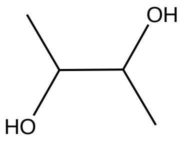
11 Buta-1,3-diene undergoes the reactions shown in the scheme below



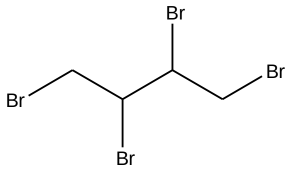
(a) **(i)** Suggest the reagents and conditions for reaction **I**. [1]

Step 1: Conc. H_2SO_4, room temp, Step 2: H_2O, warm
Or
$H_2O(g)$, conc H_3PO_4, heat and high pressure

(ii) Give the structural formulae of the major product formed in reaction **I**.[1]



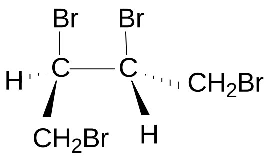
(b) **(i)** Name the reaction mechansim of reaction **II** and deduce the structure of compound **U**. [2]

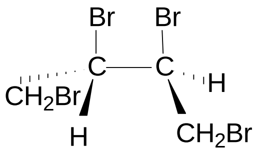


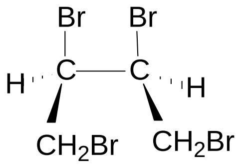
Electrophilic addition

(ii) **U** has 2 chiral centers but only 3 stereoisomers. Explain.

There are 2 chiral centres in **U** which is supposed to give 4 stereoisomers. However, 2 of them are the same compound (meso compound), hence resulting in 3 stereoisomers.

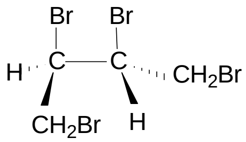


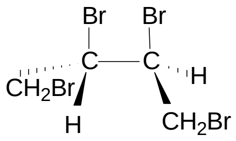




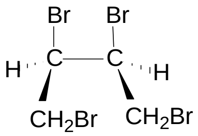
(iii) Give 2 reasons why the product mixture from reaction **II** does not exhibit optical activity.

The product mixture contains a racemic mixture as the following 2 optical isomers are formed in equal proportion due to a trigonal planar carbocation intermediate that allows the nucleophile Br^- to attack from both the top and bottom of the plane with equal probability. The effect on rotation of plane polarised light by each enantiomer cancels out completely.

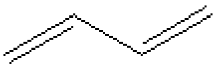




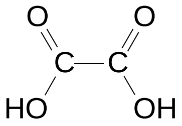
The meso compound is optically inactive as the effect on rotation of plane polarised light by each chiral carbon in the molecule cancels out completely (the 2 chiral carbon are mirror images of each other).



(c) Write balanced equations for reactions **III** and **IV**

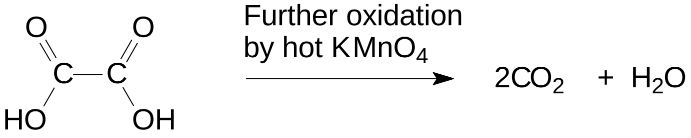
Reaction III:  + 11 [O] → $4CO_2 + 3H_2O$

The immediate vigorous oxidation products are

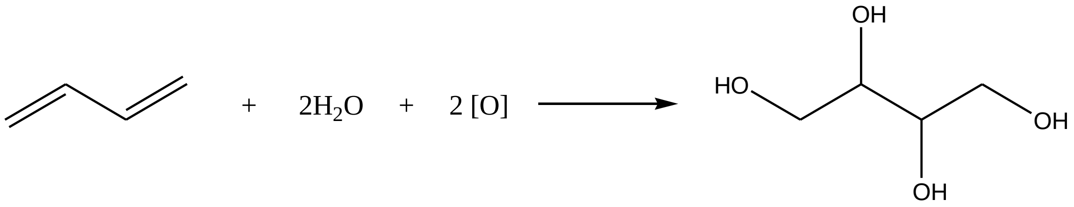
$2\ CO_2 + 2\ H_2O$ + 

(from oxidation of $=CH_2$)

Further oxidation happened



Reaction IV



Integrated Questions

12 A hydrocarbon, **A**, contains 87.8% carbon and 12.2% hydrogen by mass and has a M_r of 82. **A** decolourises bromine water. In the presence of nickel catalyst, it reacts with hydrogen to form **B**. 0.1 g of **A** was found to absorb 27.7 cm^3 of hydrogen (measured at s.t.p). **B** does not decolourise bromine water.

(a) Calculate the empirical formula of **A** and hence determine its molecular formula.

	C	H
Mass in 100 g /g	87.8	12.2
Amt /mol	87.8/12 = 7.32	12.2/1 = 12.2
Mole ratio	7.32/7.32 = 1	12.2 /7.32 = 1.67
Simplest ratio	3	5

Common mistakes:

- Students round up 1.67 to 2. Pls take note that 1.67 = 5/3 and hence it should be not rounded up to 2.
- Similarly, if ratio is 1.33, it is 4/3 and not rounded down to 1.

Empirical formula of **A** is C_3H_5.

Let molecular formula of A be $(C_3H_5)_n$

n(36+5) = 82

n = 2

Molecular formula of **A** is C_6H_{10}.

(b) Determine the number of moles of hydrogen reacted with 1 mole of **A**. Hence, determine the number of double bonds in a molecule of **A**.

Amount of A = 0.1/82.0 = 1.2195×10^{-3} mol
Amount of H_2 = 27.7/ 22700 = 1.220×10^{-3} mol

1 mol of H_2 reacted with 1 mol of **A**.

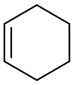
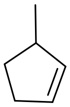
Therefore, **A** only has 1 C=C bond.

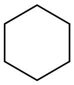
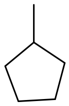
(c) Suggest the structural formulae of **A** and **B**.

A has 1 C=C bond but the formula is C_6H_{10} instead of C_6H_{12}. This implies that **A** has one ring.

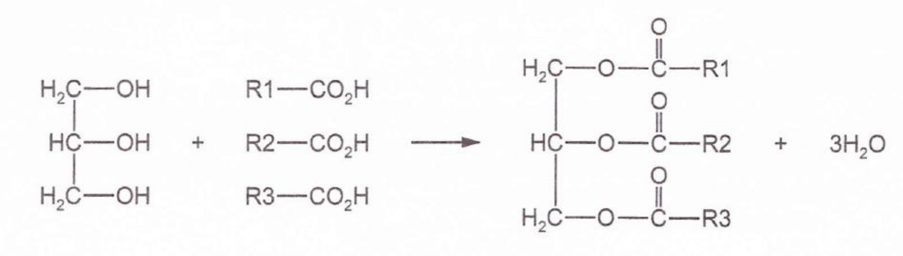
Thinking process/comments for question 10c:

- From the molecular formula, C_6H_{10}. However, there is only 1 C=C double bond based on analysis in part (b).
- This suggests structure will have 1 ring (reduce number of H by 2).
- 5 or 6 membered ring is preferred as any smaller ring contains high angle strain resulting in lower stability.

A:  or  and other positional isomers

B:  or 

13 (Modified from 2016/P2/2) Olive oil contains a mixture of triester formed from glycerol (propane-1,2,3-triol) and three long chain carboxylic acids (fatty acids), as shown by the general equation.



The groups R1, R2 and R3 represent hydrocarbon chains each containing either 15 or 17 carbon atoms. A given oil molecule (triester) can be formed from any combination of the following fatty acids.

name	formula and systematic name	M_r	melting point /°C
palmitic acid	$CH_3(CH_2)_{14}CO_2H$ hexadecanoic acid	256	63
stearic acid	$CH_3(CH_2)_{16}CO_2H$ octadecanoic acid	284	69
oleic acid	$CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2H$ *cis*-9-octadecenoic acid	282	13
linoleic acid	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7CO_2H$ *cis*,*cis*-9,12-octadecadienoic acid	280	–5
linolenic acid	$CH_3CH_2(CH{=}CHCH_2)_3(CH_2)_6CO_2H$ *cis*,*cis*,*cis*-9,12,15-octadecatrienoic acid	278	–11

(a) A particular triester found in olive oils melts at 15°C.

(i) Explain why this triester melts at a lower temperature than any of the individual fatty acids.

The fatty acids and triester are covalent compounds with simple molecular structures. More energy is required to overcome the hydrogen bonding and instantaneous dipole − induced dipole attraction (id−id) between fatty acids molecules than the permanent dipole – permanent dipole and id−id forces between triester molecules, resulting in its lower melting point as compared to the fatty acids.

(ii) Trans-9-octadecenoic acid melts at 44°C. Explain the difference in its melting point with cis-9-octadecenoic acid.

Trans-9-octadecenoic acid **pack better** into a crystal lattice, leading to more intermolecular forces per unit volume compared to cis-9-octadecenoic acid. Hence more energy is required to overcome the stronger intermolecular forces, resulting in higher melting point.

(iii) State how the presence of C=C bonds affects the melting point of the fatty acids.

Based on the data provided, increasing the number of C=C bonds will lower the melting point of the fatty acids

(b) The average number of C=C bonds per molecule in different oils can be compared experimentally by determining the mass of iodine that reacts with 100g of the oil.
In one experiment, 0.256g of olive oil was found to react with 0.237g of iodine.

(i) State the name of the mechanism for the reaction occurring between iodine and the C=C bonds in the olive oil.

Electrophilic addition

(ii) Calculate the mass of iodine that would react with the 100g of olive oil.

Mass of iodine required to react with 100 g of olive oil = $0.237 \times \frac{100}{0.256} = 92.58 \approx$ **92.6 g**

(iii) Use your answer from b(ii) to calculate the average number of C=C bonds in each oil molecule in olive oil. The average Mr of an olive oil molecule is 782. Give your answer to three significant figures.

Amount of olive oil in 100 g = $\frac{100}{782}$= 0.1279 mol

Amount of iodine required to react with 100 g of olive oil = $\frac{92.6}{126.9\times2}$ = 0.3649 mol
Since 1 mol of C=C reacts with 1 mol of I_2 during electrophilic addition,
average number of C=C bonds in each olive oil molecule = $\frac{0.3649}{0.1279}$ = 2.85

(iv) The triesters in olive oil are formed mainly from oleic acid.

Use this information and the data in the table on page 22 to explain the significance of your answer to b(iii) with respect to the composition of olive oil.

If the triester is formed purely from oleic acid, there will be 3 C=C bonds in each olive oil molecule. As the average number of C=C bonds is 2.85, the triester in olive oil is likely to be formed from oleic acid (majority), palmitic acid and stearic acid.
Note: Unlikely to contain linoleic acid and linolenic acid as these fatty acids will cause an increase in the average number of C=C bonds in each olive oil molecule.

(c) Olive oil can be used to make margarine. Part of the manufacturing process involves decreasing the number of C=C bonds in the oil.

(i) State suitable reagents and conditions to carry out this process.

H_2(g), Pt(s) at room conditions OR H2(g), Ni(s), high temperature and pressure

(ii) The conditions in c(i) can also result in isomerization of the C=C bonds, to form trans fatty acids.
Draw a skeletal formula to show the trans isomer of oleic acid, $CH_3(CH_2)_7CH=CH(CH_2)_7CO_2H$.