Chem Factsheet

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The Application of Organic Reactions To Unfamiliar Molecules (AS)

(1) The objective of this Factsheet is to test your understanding of AS level organic chemistry by applying your knowledge of familiar reactions to unusual molecules and unfamiliar situations. ***This type of exercise is an excellent way of revising organic chemistry.***

(2) You should learn the basic chemical reactions of each of the functional groups and make sure you understand concepts such as isomerism and spectroscopy.

(3) The main point to remember is that, although the problems may appear to be daunting, as far as the examination is concerned, ***the functional groups, provided they are not too close to each other, behave chemically independently of each other***.

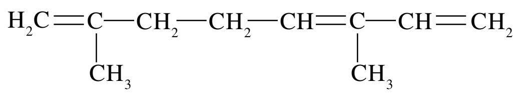
(4) In problems of the type 'A reacts and gives B' etc., it is best to draw a flow chart. On many exam papers the problem is presented in a flow chart anyway.

Exam Hint: *Examiners may set questions on molecules that you have not studied! But if they do this will be because molecules which behave in a similar way are on your specification and they expect you to be able to apply your knowledge to these unfamiliar situations.*

Note *: Some parts of the problems that follow may not apply to your particular specification. If you know your stuff thoroughly, you will recognise these parts! You can also reinterpret the question e.g. when asked for a skeletal formula it may be more appropriate to you to give a full structural formula.*

Problems

1. Ocimene is an unsaturated hydrocarbon that belongs to a group of compounds called terpenes. Ocimene is found naturally in some well known cooking herbs and has the structure shown below.

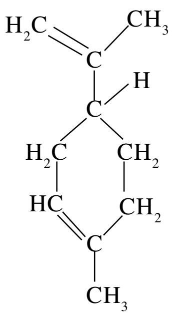


(a) What is the molecular formula of ocimene?
(b) How many moles of hydrogen would be needed to fully hydrogenate one mole of ocimene?
(c) Draw the skeletal structure, and give the systematic name of the compound formed when ocimene is fully hydrogenated.
(d) Ocimene exists as a pair of geometric isomers. Specifically, what is the feature that causes geometric isomerism in this molecule? Draw the full structural formula of **one** of the two geometric isomers.
(e) The systematic name for ocimene is 3,7-dimethylocta-1,3,7-triene. Explain the formation of this name.
(f) Explain whether this ocimene would have a higher or lower boiling point than 2,6-dimethyloctan-1-ol.
(g) Draw a skeletal structural formula for ocimene.

2. When propane reacts with chlorine in the presence of ultra violet light, two isomers containing one chlorine atom per molecule, four isomers containing two chorine atoms per molecule and five isomers containing three chlorine atoms per molecule are formed.
(a) Draw abbreviated structural formula (i.e. CH_3CH_2- etc) for all eleven compounds and systematically name all of them.
(b) When the chlorinated compounds above are reacted with aqueous sodium hydroxide, the chlorine atom in the molecule is replaced by a hydroxy group forming an alcohol.
  (i) Which of the chlorinated compounds in (a) would give propane-1,3- diol in this reaction.
  (ii) If the chlorine atom in 1-chloropropane was replaced by an iodine atom, would the iodo compound be more or less reactive? (Bond energies C-Cl = 338 and C-I = 238 ($kJmol^{-1}$))
(c) What type of reaction is occurring between propane and chlorine in the presence of ultra-violet light?
(d) Give the initiation step for this type of reaction.
(e) Pentane (Bpt. = 36°C), 1-choropropane (Bpt. = 47°C), and butan-1-ol (Bpt. = 117°C) all have similar molecular masses. Explain the trend in boiling points for these three compounds.
(f) Why are there no chain isomers for any of the compounds in (a)?
(g) Why does the mass spectrum of 1,3-dichloropropane give three peaks at 112, 114 and 116? What might be the formula of the peak at m/z = 49?

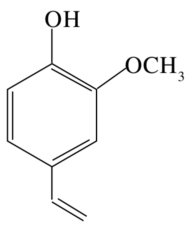
3. There are five **alkanes** with the formula C_6H_{14}.
(a) Systematically name all five.
(b) Name the isomers with the lowest and highest boiling points. Explain your reasons.
(c) Give the name of the isomer that gives only two isomeric compounds containing only one chlorine atom per molecule.
(d) Hexane can be cracked to give propene and propane. Give an equation showing this reaction.
(e) What type of mechanism is undergone by alkenes when they react?
(f) What type of mechanism is undergone by alkanes when they react?
(g) Give an equation showing the complete combustion of hexane in air.
(h) Explain how, when hexane reacts with chlorine in the presence of ultra violet light, there are traces of $C_{12}H_{26}$ in the reaction mixture.

4. There are five **alkenes** with the molecular formula C_5H_{10}.
(a) Draw abbreviated structural formulae for each of the five compounds.
(b) Identify which of the five structures, if any, will exist as a pair of geometric isomers.
(c) When all five compounds are reacted in the presence of a nickel catalyst, only two products are formed. Name these compounds.
(d) Explain why 2,2-dimethylpropane cannot be a product of the reaction between hydrogen and any of the five compounds with the formula C_5H_{10}.
(e) What process is used in industry to produce alkenes from alkanes?



5. This is the structure of limonene, a compound found in lemons.
(a) What is the molecular formula of limonene?
(b) What is the empirical formula of limonene?
(c) Draw the skeletal structure of limonene.
(d) Draw the skeletal structure of the compound formed when limonene reacts with bromine. What would you observe?
(e) Draw the skeletal structure of the compound formed when limonene reacts with hydrogen in the presence of a catalyst.
(f) When the compound formed in (d) is treated with sodium hydroxide, all the bromine atoms in the molecule are replaced by hydroxy groups. Draw the structure of this compound and label each hydroxy group as primary, secondary, or tertiary.

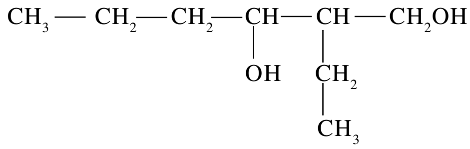
6. The compound below, eugenol, is found in clove oil and has, in the past, been used to relieve toothache.



(a) What is the molecular formula of eugenol?
(b) Draw the skeletal structure of the compound formed when eugenol is completely hydrogenated.
(c) Can eugenol exist as a pair of geometric isomers?
(d) What type of alcohol is the compound formed in b)

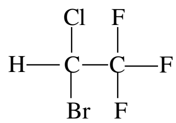
7. The elemental composition of substance X is; 64.9%C; 13.5%H; 21.6%O.
(a) Calculate the empirical formula of X.
(b) The mass spectrum of X shows a molecular ion peak at m/z = 74. What is the molecular formula of X?
(c) There are four alcohols with this molecular formula. Draw and name all four.
(d) Alcohols can be dehydrated to give alkenes. X is the only alcohol that can be dehydrated to give a mixture of two alkenes, Y and Z. Y can exist as a pair of geometric isomers whilst Z does not exhibit geometric isomerism. Deduce the structures of X, Y, and Z.

8. The compound below has been used as an insect repellent.



(a) What is the systematic name for this compound?
(b) The boiling point of the above compound is 245°C while that of decane (which has a similar molecular mass) is only 174°C. Why is the boiling point of decane so much lower?
(c) When the compound is oxidised, two compounds are formed depending on the conditions. Draw abbreviated structures for both compounds. Name a suitable oxidising agent.

9. Halothane, a well known general anaesthetic, has the structural formula shown below.



(a) What is the systematic name of halothane?
(b) Draw the structural for its isomer 1-bromo-2-chloro-1,1,2- trifluoroethane.
(c) A related compound, bromochlorodifluoromethane is sold under the name Halon which is used in automatic fire extinguisher systems. Draw the structural isomer for Halon.
(d) State, with an explanation whether halon, or halothane, has the highest boiling point.
(e) Considering the uses that both these compounds are put to, do you think that these compounds are very reactive?
(f) Both these compounds are related to 'CFC's. Why might it not be a good idea to release large quantities of these compounds into the upper atmosphere?

10. Compound A has the following composition; 60%C; 13.3%H; 26.7%O. The empirical and molecular formulas of A are the same. When A is oxidised, two products (B) and (C) are possible depending on the conditions of the reaction. Compound B will release carbon dioxide from sodium carbonate solution but compound C will not do this. Compound C also has a much lower boiling point than B. A is capable of being dehydrated to an alkene (D). When D is reacted with hydrogen bromide, E is produced as a major product (95%) whilst F, the minor product is only produced in small amounts (5%). When E is refluxed with sodium hydroxide solution G is formed. G is an isomer of A.

(a) Calculate the empirical formula of A.
(b) What are the two possible structures of A that are alcohols.
(c) Deduce the identities of compounds A to G.
(d) Why does B have a much higher boiling point than C?
(e) What type of mechanism occurs when D reacts with HBr?
(f) What does 'reflux' mean?
(g) Draw the repeat unit for the polymer formed from D.

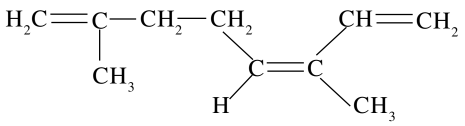
Answers

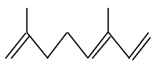
1. (a) $C_{10}H_{16}$
(b) 3
(c)

or $CH_3CH(CH_3)CH_2CH_2CH_2CH(CH_3)CH_2CH_3$

2,6-dimethyloctante

(d) The non-rotating double bond between carbon atoms 3 and 4 gives rise to geometric isomerism.

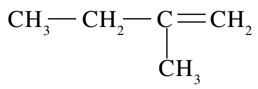


(e) The double bonds take precedence in the numbering system. They are labelled with the lowest carbon atom they are attached to hence '1,3,7 triene'. This makes the carbon atoms that the methyl groups are attached to numbers 3 and 7.
(f) 2,6-dimethyloctan-1-ol would exhibit hydrogen bonding whereas ocimene being a hydrocarbon would not. Hence the alcohol would have the higher boiling point.
(g)

or $CH_2{=}CH(CH_3)CH_2CH_2CH{=}CH(CH_3)CH{=}CH_2$

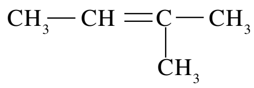
2. (a) 1-chloropropane $CH_3CH_2CH_2Cl$
2-chloropropane $CH_3CHClCH_3$
1,1-dichloropropane $CH_3CH_2CHCl_2$
1,2-dichloropropane $CH_3CHClCH_2Cl$
2,2-dichlropropane $CH_3CHCl_2CH_3$
1,3-dichlropropane $CH_2ClCH_2CH_2Cl$
1,1,1-trichloropropane $CH_3CH_2CHCl_3$
1,1,2-trichloropropane $CH_3CHClCHCl_2$
1,2,3-trichloropropane $CH_2ClCHClCH_2Cl$
1,2,2-trichloropropane $CH_3CHCl_2CH_2Cl$
1,1,3-trichloropropane $CH_2ClCH_2CH_2Cl$
(b) (i) 1,3 –dichloropropane
(ii) The iodo compound would be more reactive because the C-I bond is easier to break (lower energy needed).
(c) Free radical substitution.
(d) Homolytic fission : $Cl_2 \rightarrow 2Cl^{\cdot}$
(e) Pentane is essentially a non-polar molecule hence intermolecular attractions are minimised and only temporary van der Waals forces act between the molecules.
1-chloropropane has a permanent dipole so attractions are greater and thus the boiling point is higher. Butan-1-ol like all alcohols exhibits hydrogen bonding and since this is the strongest force between molecules the boiling point is higher than the other two compounds.
(f) It is impossible to make another chain out of just three carbon atoms.
(g) Chlorine exists as two isotopes ^{35}Cl and ^{37}Cl. This gives three possible masses for the dichloropropanes (ignoring the presence of small amounts of any isotopes of carbon and hydrogen) $CH^{35}ClCH_2CH^{35}Cl$ (112); $CH^{35}ClCH_2CH^{37}Cl$ (114) and $CH^{37}ClCH_2CH^{37}Cl$ (116).
$[CH_2{}^{35}Cl]^+$

3. (a) hexane, 2-methylpentane, 3-methylpentane, 2,3-dimethylbutane and 2,2-dimethylbutane
(b) Hexane (highest); 2,2-dimethylbutane (lowest) Surface area is maximised in the linear hexane molecule and so intermolecular forces are also maximised.
(c) 2,3-dimethylbutane (d) $C_6H_{14} \rightarrow C_3H_6 + C_3H_8$
(e) Electrophilic addition(f) Free radical substitution
(g) $2C_6H_{14} + 19O_2 \rightarrow 12CO_2 + 14H_2O$
(h) During the propagation steps in the reaction mechanism, the $C_6H_{13}^{\cdot}$;radical is formed. Two of these can combine in the termination step to form $C_{12}H_{26}$.

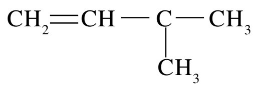
4. (a) $CH_3{-}CH_2{-}CH_2{-}CH{=}CH_2$ (pent-1-ene)
$CH_3{-}CH_2{-}CH{=}CH{-}CH_3$ (pent-2-ene)



2-methylbut-1-ene

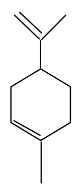
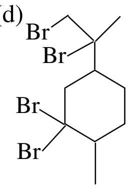


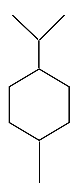
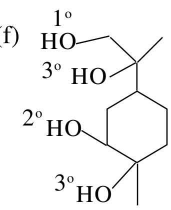
2-methylbut-2-ene



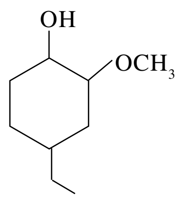
3-methylbut-1-ene

(b) Only pent-2-ene would exist as geometric isomers.
(c) Pentane and methylbutane.
(d) It is impossible to produce 2,2-dimethylbutane because the central carbon atom in the alkene molecule would then have five covalent bonds.
(e) Cracking

5. (a) $C_{10}H_{16}$
(b) C_5H_8
(c)

(d)


(e)

(f)


Obs: Decolourisation

6. (a) $C_9H_{10}O_2$
(b)


(c) No, none of the double bonds within the ring system can give rise to geometric isomerism since they are delocalised and the terminal double bond at the bottom of the structure has two hydrogen atoms attached to one of the carbon atoms that make up the double bond.
(d) Tertiary.

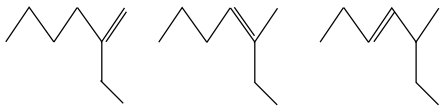
7. (a) $C_4H_{10}O$

(b) Mr = Er so molecular formula is $C_4H_{10}O$.

(c) $CH_3CH_2CH_2CH_2OH$ (Butan-1-ol)
$CH_3CH_2CH_2(OH)CH_3$ (Butan-2-ol)
$CH_3CH(CH_3)CH_2OH$ (methylpropan-1-ol)
$CH_3C(CH_3)(OH)CH_3$ (methylpropan-2-ol)

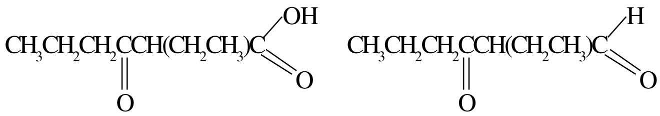
(d) Only butan-2-ol can be dehydrated to give two alkenes; but-1-ene and but-2-ene so X is butan-2-ol.
Only but-2-ene exists as two geometric isomers and so this is Y.
Thus Z is but-1-ene.

8. (a) 2-ethylhexan-1,3-diol



(b) Hydrogen bonding is present in the compound but absent in decane.

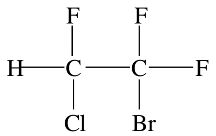
(c)



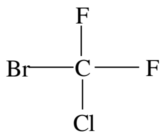
acidified dichromate

9. (a) 2-bromo-2-chloro-1,1,1-trifluoroethane

(b)



(c)



(d) Halothane is a larger molecule with a greater molecular mass than halon hence the van der Waals forces will be greater and the boiling point will be higher. Dipole-dipole forces also exist but will be similar.

(e) As an anaesthetic halothane must have a low toxicity and to extinguish fires, halon must not degrade easily to give toxic gases so the reactivity of both these compounds must be very low.

(f) CFC's degrade in the upper atmosphere to deplete ozone. This depletion allows more uv light t reach the Earth's surface and cause a higher incidence of skin cancer.

10. (a) C_3H_8O

(b) $CH_3CH_2CH_2OH$ (propan-1-ol) and $CH_3CH(OH)CH_3$ (propan-2-ol)

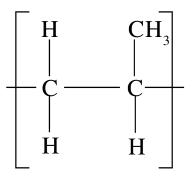
(c) A = Propan-1-ol ; B = Propanoic acid ; C = Propanal ; D = Propene ;
E = 2-bromopropane ; F = 1-bromopropane ; G = Propan-2-ol

(d) Hydrogen bonding exists in carboxylic acids but not in aldehydes

(e) Electrophilic addition

(f) Condenser is vertically above reaction flask so that vapours run back into the reaction flask for prolonged reaction.

(g)



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