Chem Factsheet

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The Application of Organic Reactions To Unfamiliar Molecules (A2)

(1) The objective of this Factsheet is to test your understanding of A2 level organic chemistry by applying your knowledge of reactions you have studied in the course 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 (including those from your AS course!) and make sure you understand concepts such 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**.

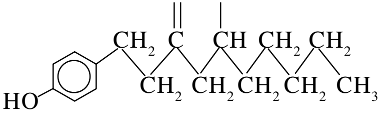
(4) In problems of the type 'A reacts and gives B' etc., it is best to draw a flow chart. On many exam papers the problem is presented in a flow chart anyway.

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.*

Problem 1.

Look at the molecule below.

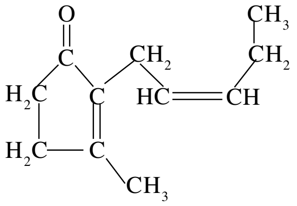


This molecule is called gingerol, a compound found in ginger, an ingredient often used in cooking.

(a) Explain why the gingerol exists as two optical isomers.
(b) Explain why gingerol does not exist as a pair of geometric isomers.
(c) What is the molecular formula of gingerol?
(d) Draw a dotted circle around the phenolic group in gingerol.
(e) Describe what you would **see** if gingerol was added to 2,4-dinitrophenylhydrazine reagent. What functional group present in the molecule is reacting?
(f) Describe what you would see, if anything, when gingerol is added to Tollen's reagent and warmed. Explain your reasoning.
(g) Explain why gingerol does not give a positive test with the tri-iodomethane (iodoform) reaction.

Problem 2.

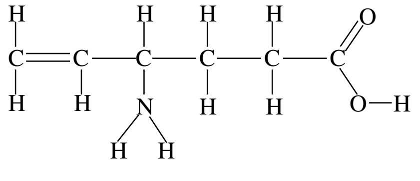
Look at the molecule below.



This is the chemical structure of jasmone. It is secreted by plants and attracts some insects and repels others. It is an important chemical in the perfumery industry

(a) What is the molecular formula and molecular mass of jasmone?
(b) Jasmone can exist as a pair of geometric isomers. What molecular feature of the molecule allows jasmone to exhibit this type of stereoisomerism?
(c) Draw the trans isomer of jasmone.
(d) What would you observe if some bromine water was added to jasmone?
(e) Draw the structure of the compound formed when jasmone reacts with bromine.
(f) How many moles of bromine would react with 1.64g of jasmone?
(g) There are four chiral centres in the structure you have drawn for (e). Mark with an asterisk all four chiral centres.

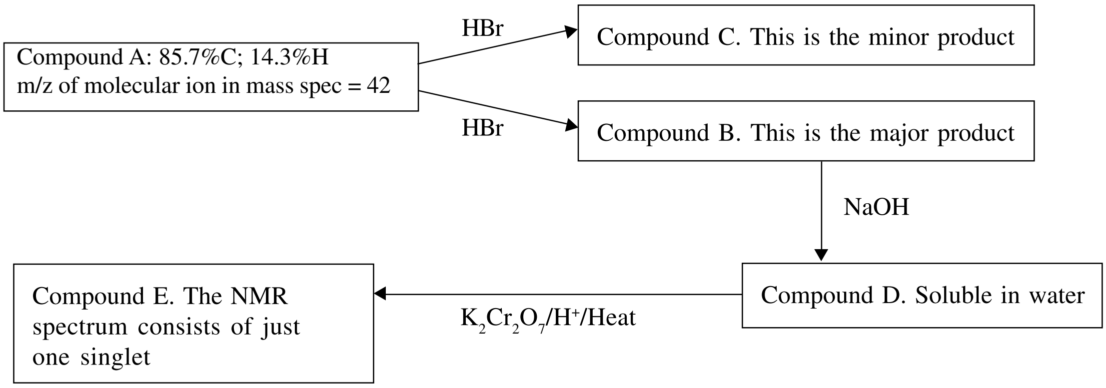
Problem 3



Vigabatrin is used in the treatment of epilepsy.

(a) Identify the chiral centre in this structure.
(b) Double bonds in compounds often give rise to geometric isomerism. Explain why this is so and explain why, although vigabatrin contains a double bond, it does not exist as geometric isomers.
(c) What would you observe when vigabatrin was treated was treated with
   (i) A cold solution of nitrous (nitric (III)) acid.
   (ii) A solution of bromine
   (iii) A solution of sodium hydrogen carbonate.
(d) Give the structure of the compound formed when vigabatrin reacts with ethanol in the presence of sulphuric acid as a catalyst.

Problem 4



(a) Calculate the empirical and molecular formulas of A.

(b) Deduce the structures of compounds A to E

(c) Explain why there are 'major' and 'minor' products in the first reaction.

(d) Explain why compound E has only one singlet in its NMR spectrum.

Problem 5

Substance A has the molecular formula $C_4H_{10}O$. There are four possible alcohols with this formula of which only A is optically active.

When A is treated with concentrated sulphuric acid, two compounds are formed, B and C. B shows geometric isomerism whilst C does not.

When B is treated with hydrogen bromide, only one product, D is formed but, when C is treated with the same reagent, D is formed as the major product **and** E is formed as a minor product.

Treatment of D with aqueous sodium hydroxide under the appropriate conditions gives A while similar treatment of E gives F, an isomer of A.

When F is gently heated with a solution of potassium dichromate(VI) in sulphuric acid, G is formed. G gives a silver mirror when treated with ammoniacal silver nitrate solution.

(a) Draw full graphical formulae for all the possible alcohols with the molecular formula $C_4H_{10}O$. Give the systematic names for each one.

(b) Which one the four compounds is optically active and hence is the structure of A?

(c) Which one of the structures gives only two singlets in its NMR spectrum?

(d) Deduce the structures of compounds B to G.

(e) Explain why B is capable of geometric isomerism whilst C is not.

(f) Give a chemical test that would distinguish between A and F

(g) Name another reagent that would confirm the identity of the functional group in G

(h) Name a third reagent that would react with G but would not distinguish it from a second different functional group.

Problem 6

A substance M has the following composition; 38.9%C; 5.4%H; 17.3%O; 38.4%Cl. Its molecular and empirical formulae are the same. M has a vigorous reaction with water and steamy white fumes are seen evolving. Compound N is formed in this reaction.

When N is heated with soda lime, O is formed – a compound that contains only carbon and hydrogen. When O is reacted with chlorine gas in the presence of UV light, P is formed which contains one chlorine atom per molecule and can react with aqueous sodium hydroxide to form Q, a compound that can itself undergo dehydration to give R, a compound that will decolourise bromine water. R undergoes an industrially important reaction reacting as a monomer to give S and reacts with hydrogen chloride to reform P. P reacts with potassium cyanide to give T which is hydrolysed when heated with a concentrated strong acid to reform N. T can also react with a suitable reducing agent to give U. Finally, M and U can react together to form V a compound that has a linkage found in many biological molecules.

(a) Deduce the molecular formula of M and hence deduce the identities of molecules N-V.

(b) What are the 'white steamy fumes' observed in the reaction between M and water?

(c) What is the type of reaction between N and soda lime called?

(d) What is the type of mechanism occurring when O reacts with chlorine in the presence of UV light?

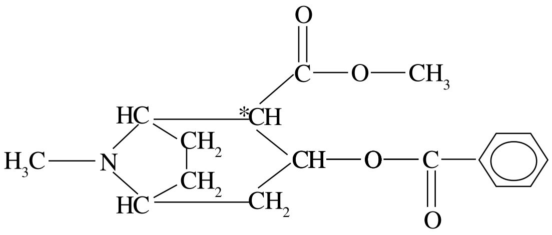
(e) What type of compound is S? Give an advantage and disadvantage of is presence in modern society.

(f) What type of reaction is undergone when R reacts with bromine water?

(g) What type of reaction occurs when P reacts with potassium cyanide?

(h) What is the name of the molecular linkage found in V? What type of biological molecule is this linkage found in? What type of synthetic fibre is this type of linkage also found in?

Problem 7



The above is the structural formula of cocaine, a class A restricted drug.

(a) What is the molecular formula of cocaine?

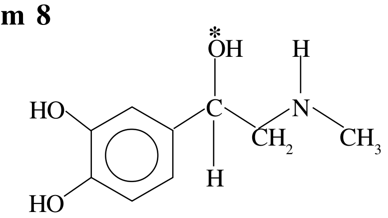
(b) Put a ring around the tertiary amine group in cocaine.

(c) The carbon atoms marked with an asterisk (*) can be described as chiral. What does this mean and what affect does the presence of a chiral carbon have in a molecule?

(d) How would you detect the presence of the chiral carbon atom?

(e) Draw the structures of the 3 organic molecules formed when cocaine is treated with sodium hydroxide and then acidified.

Problem 8



The above structure is of adrenaline – the so-called 'fight or flight' hormone

(a) Draw the structure of the compound formed (A) when adrenaline is reacted with an oxidising agent such as acidified potassium dichromate (VI)

(b) What would you observe when molecule A is treated with 2,4-dinitrophenylhydrazine?

(c) What type of amine is adrenaline?

(d) How many phenolic groups are there in adrenaline?

(e) If adrenaline is capable of reacting as a phenol, what would you observe when adrenaline was added to iron (III) chloride solution?

(f) Would compound A give a positive tri-iodoform test. Explain your answer.

(g) If the alcohol group marked with an asterisk is dehydrated compound B is formed and exists as two geometric isomers. Draw both of these stereo isomers.

Answers

Problem 1

(a) The carbon atom attached to the hydroxyl group has four different atoms groups attached to it. This is a chiral carbon atom and makes the molecule optically active.

(b) Gingerol does not contain a double bond.

(c) $C_{16}H_{24}O_3$

(d) Dotted circle around the hydroxyl group attached to the benzene ring.

(e) The carbonyl group (C=O) reacts to form an orange crystalline precipitate.

(f) There would be no reaction with Tollen's reagent because there is no aldehyde group in gingerol.

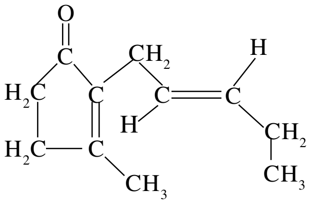
(g) The tri-iodoform tests for either a $CH_3C=O$ group or a CH_3CHOH- group. Both of these are absent in gingerol.

Problem 2

(a) Molecular formula = $C_{11}H_{16}O$; Mr. = (164)

(b) All organic compounds that exist as geometric isomers (as far as A level courses go) contain double bonds which restricts internal rotation about them. It is the double bond that is part of the chain that causes geometric isomerism.

(c)

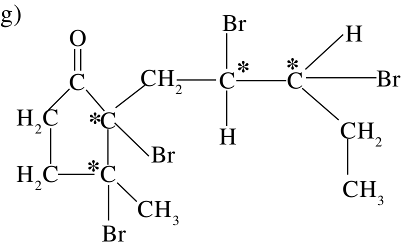


Trans isomer of jasmone

(d) The bromine water would change from orange/red to colourless

(f) 1.64g of jasmone = 1.64/164 = 0.01moles. There are two C=C bonds in one molecule of jasmone. Hence 0.02 moles of bromine would react.

(e/g)



Problem 3

(a) The carbon atom bonded to the nitrogen atom is chiral.

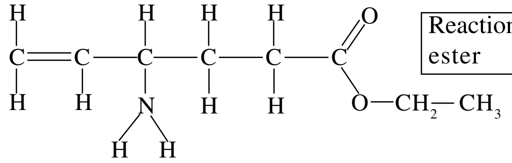
(b) Double bonds restrict internal rotation. Vigabatrin does not form geometric isomers because there are two identical groups attached to one of the carbon atoms forming the double bond.

(c) (i) Effervescence (N_2 evolved)

(ii) Bromine is decolourised.

(iii) Effervescence (CO_2 evolved)

(d)



Reaction forms an ester

Acknowledgements: *This Factsheet was researched and written by Jeff Cole.* ***Curriculum Press, Bank House, 105 King Street, Wellington, Shropshire, TF1 1NU. ChemistryFactsheets*** *may be copied free of charge by teaching staff or students, provided that their school is a registered subscriber. No part of these Factsheets may be reproduced, stored in a retrieval system, or transmitted, in any other form or by any other means, without the prior permission of the publisher.* ***ISSN 1351-5136***

Problem 4

(a) C = 85.7/12 = 7.15; H = 14.3/1 = 14.3 ; Empirical formula = CH_2. Empirical mass = 12+2 = 14; 42/14 = 3 Molecular formula = C_3H_6.

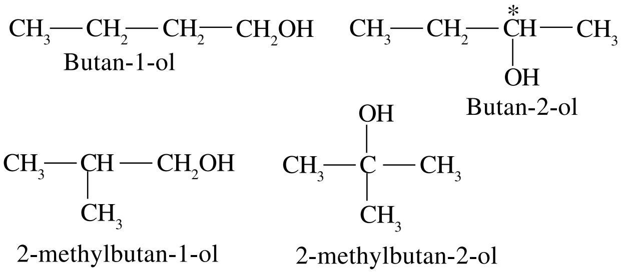
(b) A is propene. Addition of hydrogen bromide to this molecule will give 2-bromopropane ($CH_3CHBrCH_3$) as the major product, (B) and 1-bromopropane ($CH_3CH_2CH_2Br$) as the minor product, (C). D is propan-2-ol. This reaction is hydrolysis. Oxidation of D gives propanone (E).

(c) The mechanism for the reaction is one of electrophilic addition. There are two carbocations possible; $CH_3CH^+CH_3$ and $CH_3CH_2CH_2^+$. The former is a secondary carbocation and is stabilised by two alkyl groups. The latter is a primary carbocation and is stabilised by only one alkyl group. Primary carbocations, being less stable, are formed only in small amounts leading to only small amounts of 1-bromopropane. Conversely, secondary carbocations, being more stable, are formed in large amounts leading to 2-bromopropane being the major product.

(d) Compound E is propanone CH_3COCH_3. All 6 hydrogen atoms have the same molecular environment and so will give a singlet nmr absorption.

Problem 5

(a)



Butan-1-ol

Butan-2-ol

2-methylbutan-1-ol

2-methylbutan-2-ol

(b) Only butan-2-ol has a chiral carbon atom (marked with a *) and so this compound is A.

(c) 2-methylbutan-2-ol. All the methyl hydrogen atoms are equivalent and will give one peak. The hydroxy hydrogen atom will give the second peak. There is no coupling (no H on adjacent carbon atoms) between these two sets of hydrogen atoms. Hence the peaks are singlets.

(d) When A is dehydrated, but-1-ene ($CH_3CH_2CH{=}CH_2$) and but-2-ene ($CH_3CH{=}CHCH_3$) are formed. Only but-2-ene is capable of geometric isomerism so B is but-2-ene and C is but-1-ene. When both of these compounds are reacted with hydrogen bromide, but-2-ene being a symmetrical alkene gives only one product, 2-bromobutane ($CH_3CH_2CHBrCH_3$) (D). However, but-1-ene will give D as the major product and 1-bromobutane ($CH_3CH_2CH_2CH_2Br$) (E) as the minor product. Reaction of 2-bromobutane with sodium hydroxide solution will reform A (butan-2-ol) while the reaction of 1-bromobutane with sodium hydroxide will give butan-1-ol, ($CH_2CH_2CH_2CH_2OH$) (F), which is isomeric with A. When F is gently oxidised the product is butanal, ($CH_3CH_2CH_2CHO$) (G).

(e) B, but-2-ene, has two different groups bonded to the carbon atoms that form the double bond while C but-1-ene has two hydrogen atoms attached to one of these carbon atoms.

(f) Butan-2-ol (A) will give a positive tri-iodomethane test while butan-1-ol (F) will not.

(g) Fehling's solution will also give a positive reaction for an aldehyde group.

(h) 2,4-dintrophenylhydrazine would give an orange crystalline precipitate with butanal but would also give a similar reaction with a ketone.

Problem 6

(a) Molecular formula = empirical formula = C_3H_5OCl. M (from its vigorous reaction with water) is propanoyl chloride; CH_3CH_2COCl. N is thus propanoic acid; CH_3CH_2COOH. When this compound is reacted with soda lime the carboxyl group is cleaved off forming ethane, C_2H_6 (O) and carbon dioxide. Reacting ethane with chlorine gives chloroethane, CH_3CH_2Cl (P). Chloroethane reacts with sodium hydroxide to give ethanol, CH_3CH_2OH (Q). This compound can be dehydrated to give ethene, $CH_2{=}CH_2$ (R). Ethene can undergo polymerisation to poly(ethene), (S). When chloroethene (P) reacts with potassium cyanide a nitrile is formed, in this case propanonitrile, CH_3CH_2CN (T). Nitriles hydrolyse when heated with strong acids to yield carboxylic acids. Hence N, propanoic acid, is reformed. Nitriles are reduced to primary amines, so (U) is 1-aminopropane, $CH_3CH_2CH_2NH_2$. U and M react to give a substituted amide (V), $CH_3CH_2CH_2NHCOCH_2CH_3$.

(b) Hydrogen chloride

(c) Decarboxylation.

(d) Free radical substitution

(e) S is a polymer (forms material is non-corrodible but is also non-biodegradable)

(f) Electrophilic addition

(g) Nucleophilic substitution

(h) Linkage is amide (found in proteins and polyamides like nylon)

Problem 7

(a) $C_{17}H_{21}NO_4$

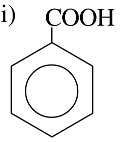
(b) Ring goes around the N atom.

(c) The chiral carbon atom destroys any symmetry in the molecule. Essentially it is a carbon atom that has four different groups attached to it. It renders the molecule optically active.

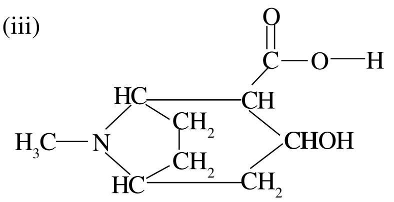
(d) A single enantiomer will rotate the plane of plane-polarised light in a polarimeter. This will not work if both enantiomers are present in equimolar amounts because of the cancelling effect. These mixtures are called racemic mixtures.

(e) The three structures are shown below.

(i) CH_3OH (ii)

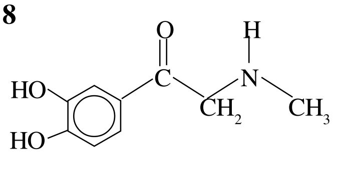


(iii)



Problem 8

(a)



(b) An orange crystalline precipitate of the hydrazone would be formed.

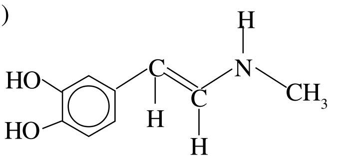
(c) Secondary

(d) 2

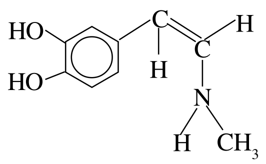
(e) Violet colouration produced.

(f) No. The molecule does not contain the CH_3CO- or CH_3CHOH- groups.

(g)



Cis isomer



Trans isomer