UNIVERSITY OF NAIROBI

UNIVERSITY EXAMINATIONS 2016/2017

SCH 202: CHEMISTRY OF ALKYL HALIDES, ALCOHOLS, ETHERS ALKENES, ALKYNES AND AROMATIC COMPOUNDS

DATE: **TIME:**

ANSWER ***ALL*** QUESTIONS

Q1 a) (i) What is the order of stability between methyl, 1°, 2° 3° carbocations? Name and explaineach of the two factors that determine the stability of carbocations. **[4 marks]**

Ans

The stability increases from methyl, 1°, 2° 3° carbocation **(*1 mark*)**

The stability is determined by two factors, hyperconjugation and inductive effect **(*1 mark*)**

Hyperconjugation: A weak interaction that results from the overlap of a vacant p-orbital on one atom with neighbouring σ bond. It results in stabilization of the carbocation **(*1 mark*)**

Inductive effect: The electron donating or electron withdrawing effect that is transmitted through the σ bond **(*1 mark*)**

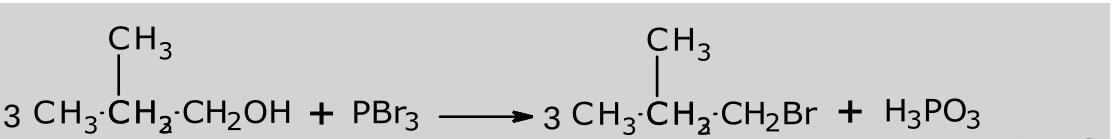
(ii) How does one detect the presence of a halogen in an organic compound using the Beilstein test? **[1 mark]**

Ans.

In the Beilstein test, the organic compound is coated on a clean copper wire and burnt on the Bunsen flame. A green colouration indicates the presence of a halogen. (1 mark)

(iii) In an experiment, 54.20 grams of phosphorus tribromide (PBr_3) was reacted with an excess of 2-methylpropanol ($CH_3CH(CH_3)CH_2OH$). The reaction yielded 57.96 grams of 1-Bromo-2-methylpropane ($CH_3CH(CH_3)CH_2Br$) and phosphoric acid (H_3PO_3), Write a blanced equation and calculate the percentage yield for the alkyl bromide. [H = 1, C = 12, P = 31, Br = 80] **[4 marks]**

Ans.



(1 mark)

Since alcohol is in excess, PBr_3 is the limiting reagent.

RFM of PBr_3 = 31 + 240 = 271 g. **(½ mark)**

54.2 g will thus be 54.2/271 = 0.2 mols **(½ mark)**

Mols of product = 0.2 X 3 = 0.6 **(½ mark)**

RFM of alkyl bromide = [(4 X12) + (1 X 10) + 80] = 138 **(½ mark)**

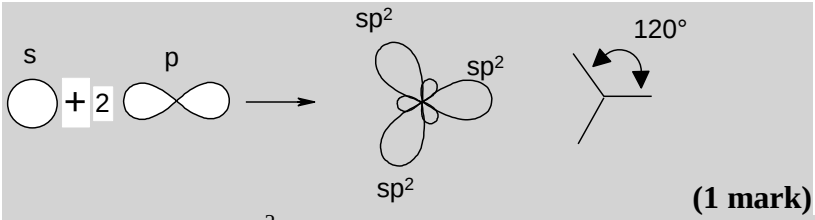
Expected yield = 0.6 X 138 = 82.8 g **(½ mark)**

Percentage yield = (57.96/82.8) X 100 = **70% (½ mark)**

b) Describe the bonding in the simplest alkene (ethene $H_2C{=}CH_2$) using sketches where applicable. **[8 marks]**

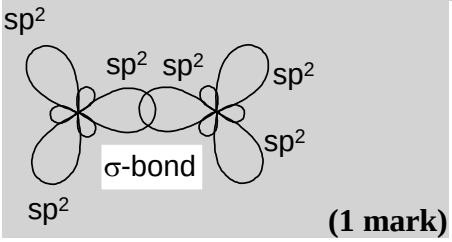
Ans

In ethene, each of the two carbon atoms is sp^2 hybridized. (1 mark)



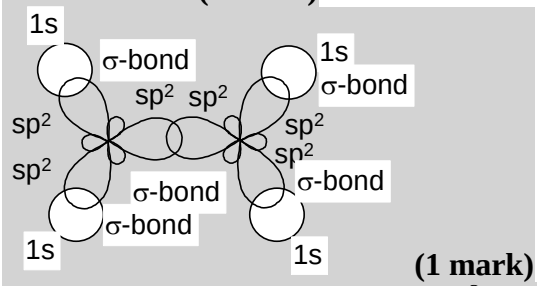
(1 mark)

The overlap of an sp^2 hybrid orbital in one carbon atom with a similar one in the other carbon atom results in C-C σ-covalent bond**. (1 mark)**



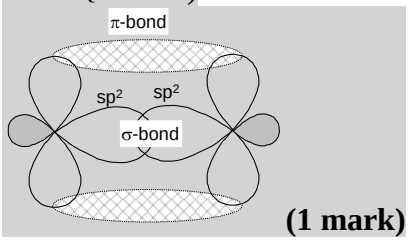
(1 mark)

Each of the remaining hybrid orbitals overlaps with a 1s orbital of hydrogen to form a C-H σ-covalent bond. **(1 mark)**



(1 mark)

The unhybridized p-orbitals (⊥ to sp^2 plane) overlap sideways to form a C-C π-covalent bond. {1 mark)



(1 mark)

c) (i) Why do alcohols have much higher boiling points than hydrocarbons of comparable molecular weight. **[1 mark]**

Ans

Boiling involves breaking of intermolecular forces. As opposed to hydrocarbons, alcohols have hydrogen bonds which must be broken besides the other intermolecular forces, hence higher boiling points (**1 mark**)

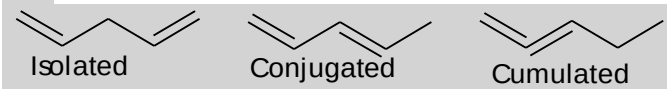
(ii) Explain the contrast of water miscibility of alcohols with increase in the carbon chain. **[3 marks]**

Ans.

The water miscibility of low molecular weight alcohols is in contrast with hydrocarbons of comparable molecular weight **(1 mark)**. The contrast decreases with increase in carbon chain **(1 mark)**. This is because increase in the proportion of the non-polar component in the molecule decreases the effect of the functional group in the physical properties of the compound **(1 mark)**.

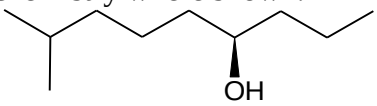
(iii) Draw the line structural formula for each of the three forms of pentadiene (isolated, conjugated, cumulated) **[3 marks]**

Ans



Q2 a) Write the IUPAC name for each of the following structures. Indicate the stereochemistry where shown.

(i)

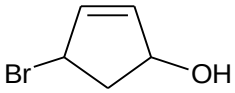


[2 Marks]

Ans

(*S*)-8-Methyl-4-nonanol

(ii)

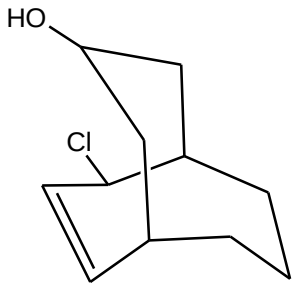


[2 marks]

Ans

4-Bromocyclopent-2-en-1-ol

(iii)

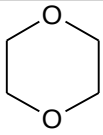


[2 marks]

Ans.

8-Chlorobicyclo[3.3.3]undec-6-en-3-ol

(iv)

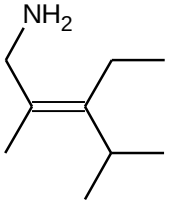


[2 marks]

Ans

1,4-Dioxacyclohexane (1,4-dioxane)

(v)



[2 marks]

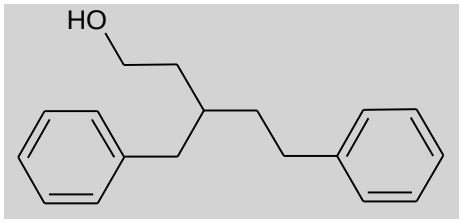
Ans

(E)-1-Amino-3-ethyl-2,4-dimethyl-2-pentene

b) Give the structural formula for each of the following compounds

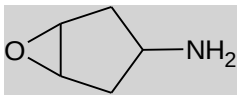
(i) 3-Benzyl-5-phenylpentanol [2 marks]

Ans

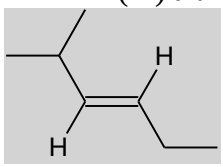


(ii) 4-amino-1,2-epoxycyclopentane [2 marks]

Ans

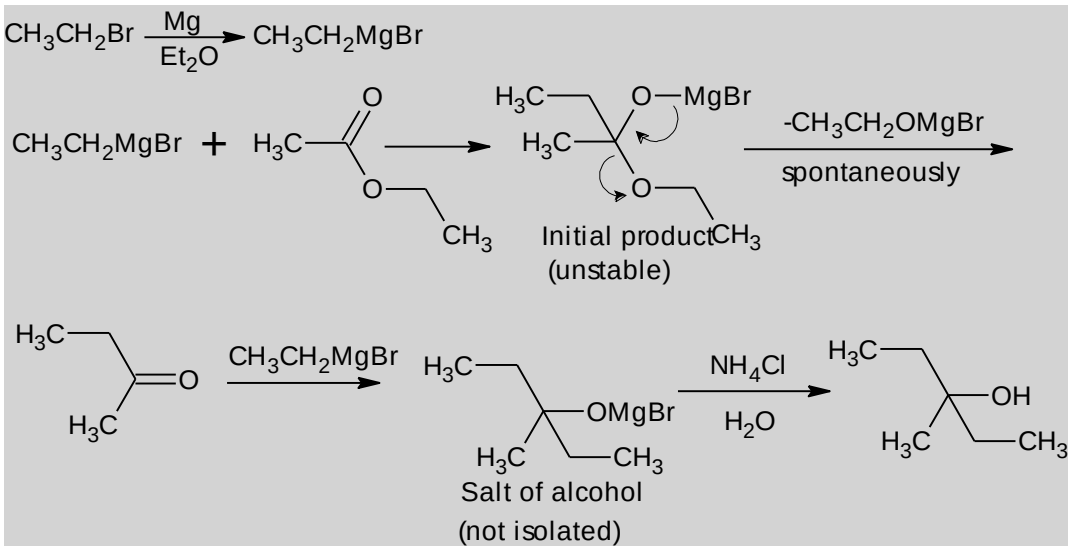


(iii) *trans*-2-Methyl-3-hexene [2 marks]

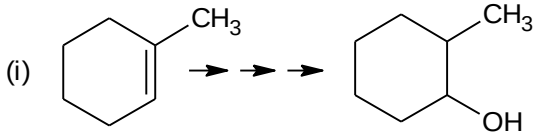


c) Given the reagents 1-bromoethane, magnesium, diethylether and ethyl acetate, show the steps in the synthesis of 3-methyl-3-pentanol [5 marks]

Ans

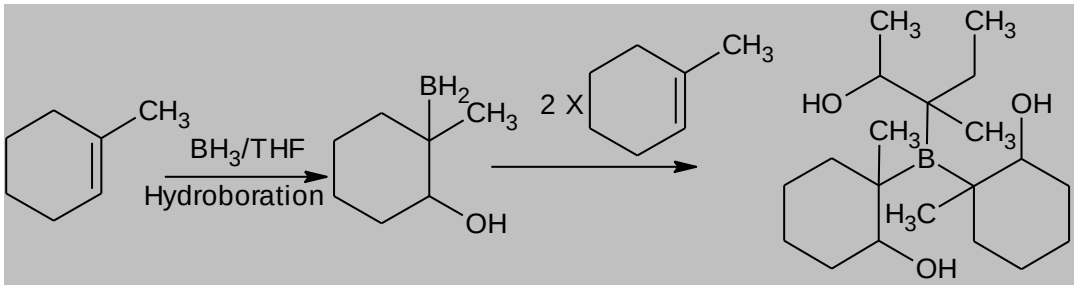


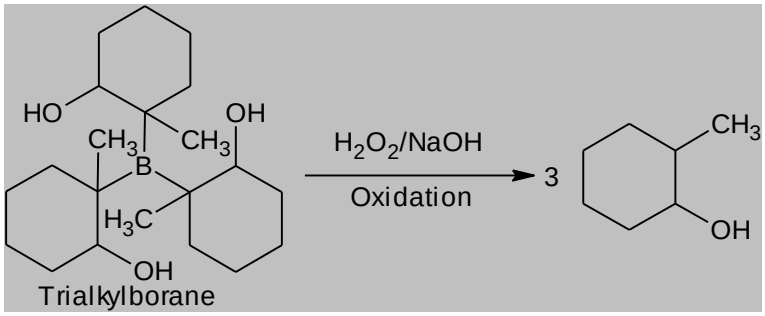
Q3 a) Starting with the compound on the left, outline the synthesis of the compound on the right. Show the structures of all reagents/intermediates in each synthesis

(i) 

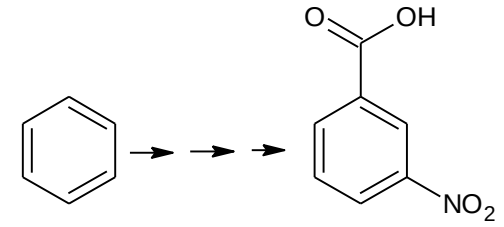
[5 marks]

Ans.





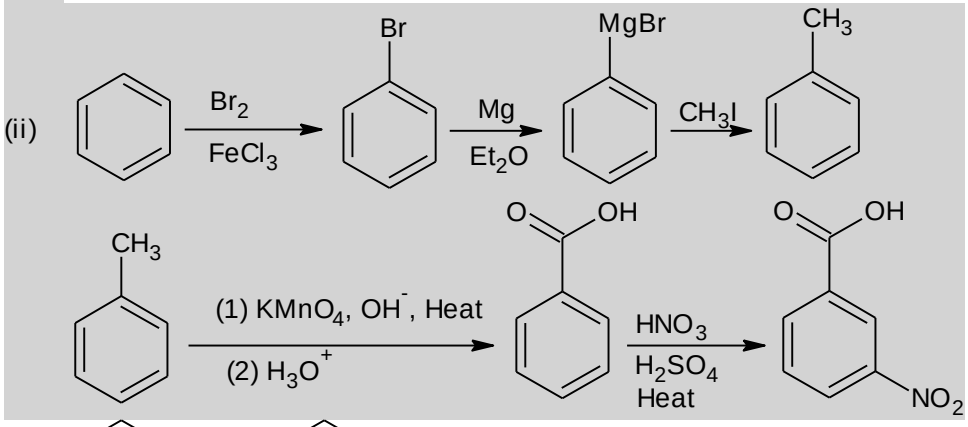
(ii)



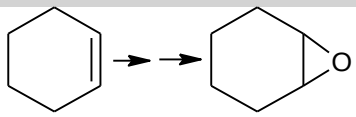
[5 marks]

Ans.

(ii)

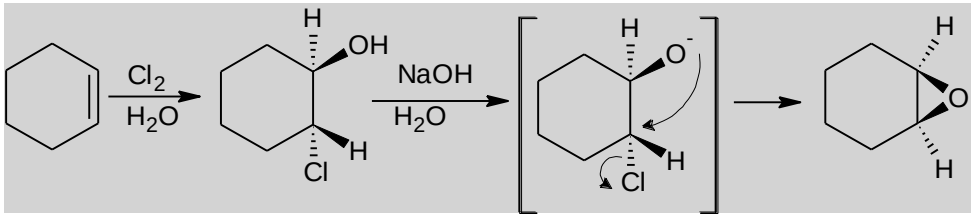


(iii)

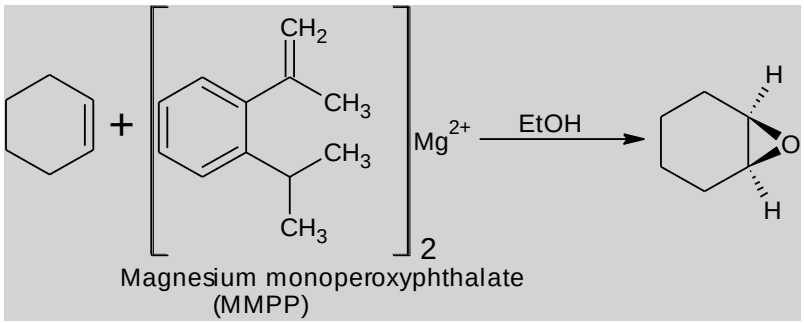


[3 marks]

Ans

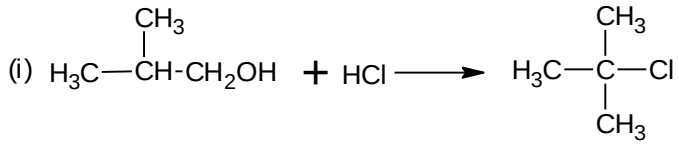


Or



Magnesium monoperoxyphthalate
(MMPP)

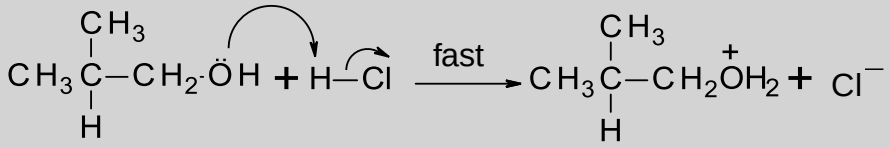
b) Give the complete mechanism for each of the following reaction. Use curly arrows to show movement of electrons.

(i) 

[4 marks]

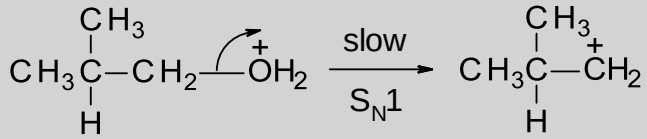
Ans

Alcohol abstracts a proton from the acid



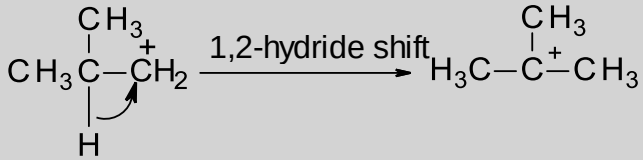
1 marks

The protonated alcohol spontaneously looses water to form a carbocation.



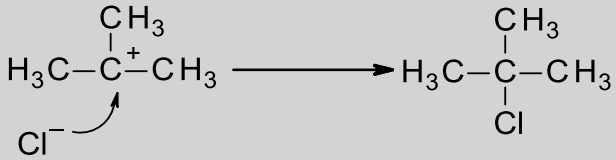
1 marks

The 1° carbocation rearranges to the more stable one

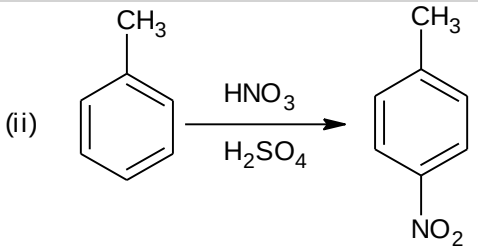


1 marks

Capture of tertially cation by chloride ion



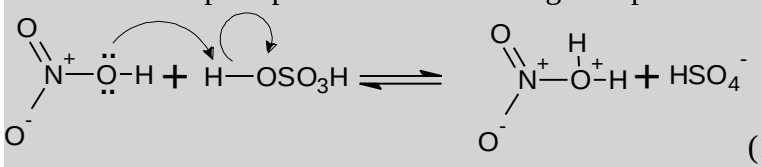
1 marks

(ii) 

[5 marks]

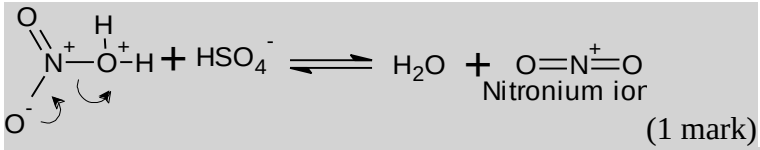
Ans

Nitric acid accepts a proton from the stronger sulphuric acid



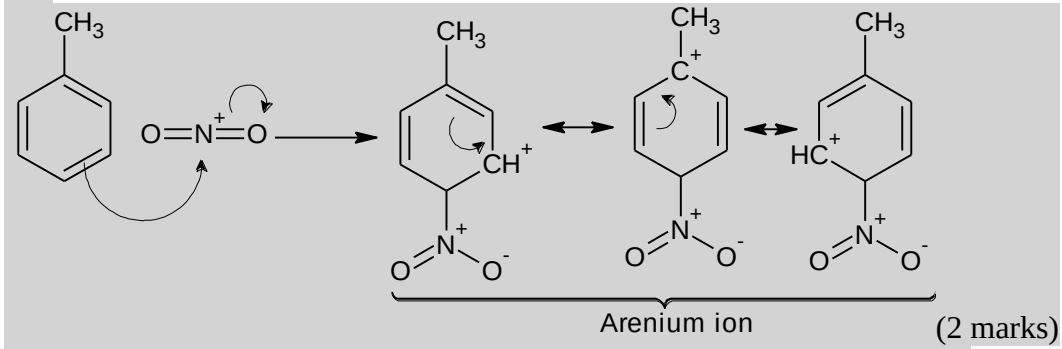
(1 mark)

The protonated nitric acid dissociates to form the nitronium ion (the actual electrophile in the nitration).



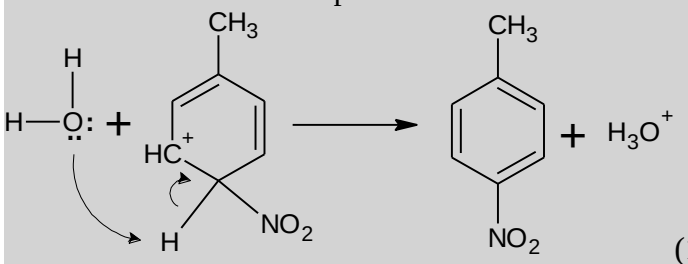
(1 mark)

The nitronium ion reacts with benzene (or derivative) to form a resonance stabilized arenium ion.



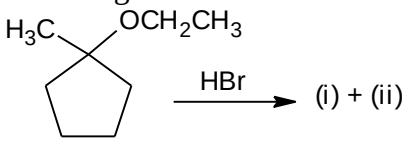
(2 marks)

The arenium ion looses a proton to a Lewis base and becomes nitrobenzene



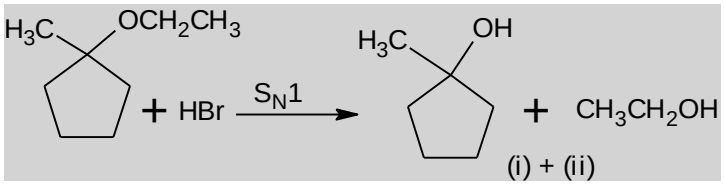
(1 mark)

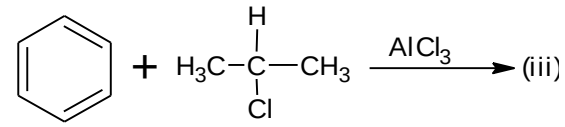
c) Write the structural formula of the organic product (indicated as i, ii, iii etc) in the following reactions.



[2 marks]

Ans





[1 mark]

Ans