UNIVERSITY OF SWAZILAND
RE-SIT EXAMINATION 2017/2018

TITLE OF PAPER	:	Organic Reactions & Synthesis
COURSE NUMBER	:	CHE 332
TIME	:	Three Hours
INSTRUCTIONS	:	Answer any **Four Questions**

This Paper contains four (**4**) pages.

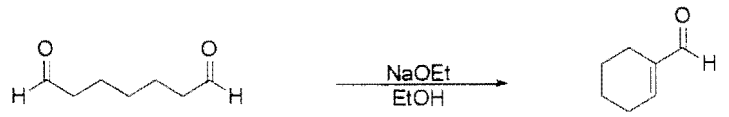
You must not open this paper until the Chief Invigilator has granted permission to do so.

Question 1

(a) Draw an energy diagram for each of the following;

(i) A one-step reaction that is fast and highly exergonic. [6]
(ii) The overall reaction of ethylene with HBr. [6]

(b) Consider the reaction below and answer the following question;

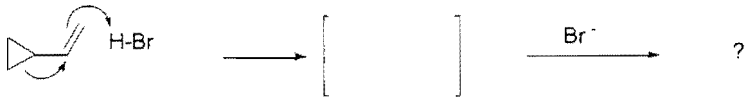


Write a complete stepwise mechanism for the reaction above. Show all intermediate structures and all electron flow with arrows.

[6]

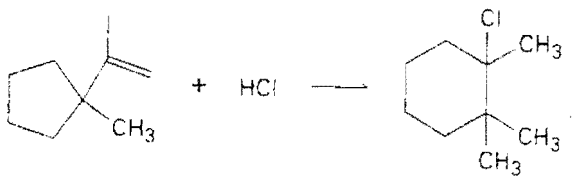
(c) Vinyl cyclopropane reacts with HBr to yield a re-arranged alkyl bromide. Follow the flow of electrons as represented by the curved arrows , Show the structure of the carbocation in brackets and show the structure of the final product.

[7]



Question 2

(a) (i) Addition of HCl to 1-isopropenyl-1-methylcyclopentane yields 1-chloro-1,2,2-trimethylcyclohexane. Suggest a mechanism, showing the structures of the intermediate and using curved arrows to indicate electron flow. [6]



(ii) Draw an energy diagram for the reaction, labeling all points of interest and making sure that the relative energy levels on the diagram are consistent with the information given. [6]

(b) (i) The reaction of hydroxide ion with chloromethane to yield methanol and chloride ion is an example of a general reaction type called nucleophilic substitution reaction:

$$HO^- + CH_3Cl \longrightarrow CH_3OH + Cl^-$$

The value of ΔH° for the reaction is -75 kJ/mol, and the value of ΔS° is +54 J/(K.mol). What is the value of ΔG° (in kJ/mol) at 298 K? Is the reaction exothermic or endothermic? Is it exergonic or endergonic?

[6]

(ii) The addition of water to ethylene to yield ethanol has the following thermodynamic parameters:

$$H_2C = CH_2 + H_2O \longrightarrow CH_3CH_2OH$$

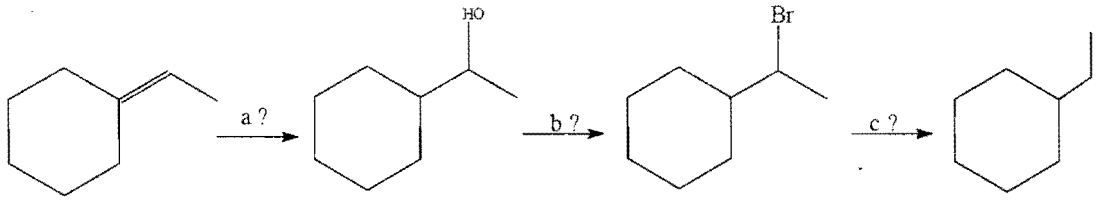
ΔH° = -44 kJ/mol
S° = -0.12 kJ/(K.mol)
K_{eq} = 24

(a) Is the reaction exothermic or endothermic?
(b) Is the reaction favorable (spontaneous) or unfavorable (nonspontaneous) at room temperature (298 K)?

[7]

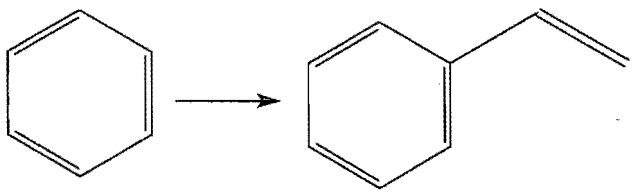
Question 3

(a) Identify reagents a – c in the following scheme. [12]



(b) Outline a sequence of reactions to carry out the following conversion.

[13]



Question 4

(a) Give an illustrated description of an orbital structure of the carbonyl group.

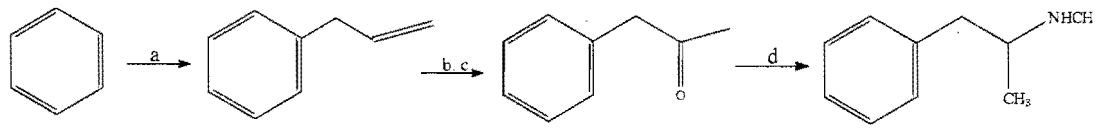
[10]

(b) How is the structure of the carbonyl group related to properties and reactivity of the carbonyl compounds. Explain with examples.

[15]

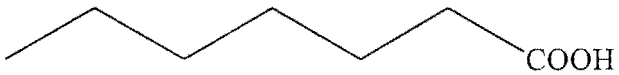
Question 5

(a) Fill in the reagents a – d in the following synthesis of racemic methamphetamine from benzene. **[12]**

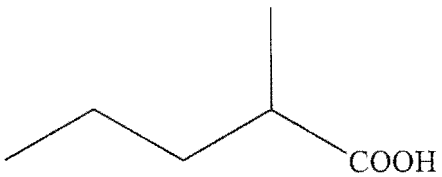


(R,S)-methampetamina

(b) Using a malonic ester synthesis method, write a sequence of reactions for the synthesis of the following carboxylic acids

(i) 

[6]

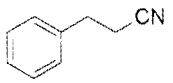
(ii) 

[7]

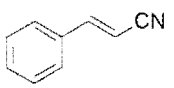
Question 6

(a) Electrophilic substitution on 3-phenylpropanenitrile occurs at the *ortho* and *para* positions, but reaction with phenylpropenenitrile occurs at the meta positions. Explain the differences using resonance structures of the intermediates.

[15]

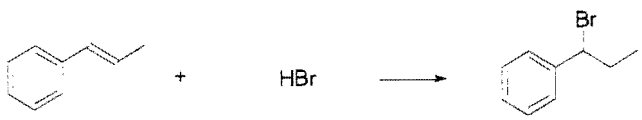


3-Phenylpropanenitrile



3-Phenylpropenenitrile

(b) Addition of HBr to 1-phenylpropene yields only (1-bromopropyl) benzene. Propose a mechanism for the reaction, and explain why none of the other regioisomer is produced.



[10]