First Semester Examination
Academic Session 2020/2021

February 2021

KOT222 – ORGANIC CHEMISTRY II

Duration: 3 hours

Please check that this examination paper consists of **TWELVE (12)** pages of printed material before you begin the examination.

Section A: Answer **ALL THREE (3)** questions.

Section B: Answer any **TWO (2)** questions.

You may answer the question either in Bahasa Malaysia or in English.

If a candidate answers more than five questions, only the answers to the first five questions in the answer sheet will be graded.

SPECTROSCOPIC TABLES

^{1}H NMR

	δ (ppm)
RC**H**$_3$	0.9
R$_2$C**H**$_2$	1.3
R$_3$C**H**	1.5
C=C-**H**	4.6 – 5.9
C≡C-**H**	2.0 – 3.0
Ar-**H**	6.0 – 8.5
Ar-C-**H**	2.2 – 3.0
C=C-C**H**$_3$	1.7
H-C-F	4.0 – 4.5
H-C-Cl	3.0 – 4.0
H-C-Br	2.5 – 4.0
H-C-I	2.0 – 4.0
H-C-OH	3.4 – 4.0
H-C-OR	3.3 – 4.0
H-C-O-CO-R	3.7 – 4.1
H-C-COOR	2.0 – 2.2
H-C-COOH	2.0 – 2.6
H-C-C=O	2.0 – 2.7
R-C**H**O	9.0 – 10.0
R-O**H**	1.0 – 5.5
Ar-O**H**	4.0 – 12.0
C=C-O**H**	15 - 17
R-COO**H**	10.5 – 12.0
R-N**H**$_2$	1.0 – 5.0

^{13}C NMR

	δ (ppm)
C-I	0 – 40
C-Br	25 – 65
C-Cl	35 – 80
-CH$_3$	8 – 30
-CH$_2$-	15 – 55
-CH-	20 – 60
≡C	65 – 85
=C	100 – 150
C-O	40 – 80
C=O	170 – 210
C(Ar)	110 – 160
C-N	30 – 65
C=N	110 – 125

Atomic Weight

H	1.0
C	12.0
N	14.0
O	16.0
F	19.0
Cl	35.45
Br	79.9
I	126.9
Si	28.0
P	31.0
S	32.0

IR

	cm^{-1}
=C-H	3020 – 3080
=C-H	675 – 1000
C=C	1640 – 1680
≡C-H	3300
≡C-H	600 – 700
C≡C	2100 – 2260
Ar-H	3000 – 3100
Ar-H	675 – 870
C=C	1500 – 1600
O-H	3610 – 3640
O-H	3200 – 3600 (broad)
C-O	1080 – 1300
C=O	1690 – 1760 (s)
O-H (acid)	2500 – 3000 (broad)
C-O	1080 – 1300
C=O	1690 – 1760
N-H	3300 – 3600
C-N	1180 – 1360
-NO$_2$	1515 – 1560 1345 – 1385

SECTION A: Answer **ALL THREE (3)** questions. **[TIME: 3 HOURS]**

1. (a) The oxidative cleavage of 3,4-dimethyl-3-hexene via ozonolysis forms compound **A**.

(i) Propose the structure of compound **A**.

(ii) Determine the *m/z* value of the molecular ion peak of **A**.

(iii) Fragmentation of **A** gives a cation. Draw the possible structure of this cation at *m/z* 57 and its resonance structure.

(4 marks)

(b) Based on the following spectral data, propose a structure for compound **B** by providing a detail explanation.

IR (ν, cm^{-1}) data: 2950, 2890, 1680, 1620, 1520.
Molecular ion peak = *m/z* 162

^{1}H NMR data:

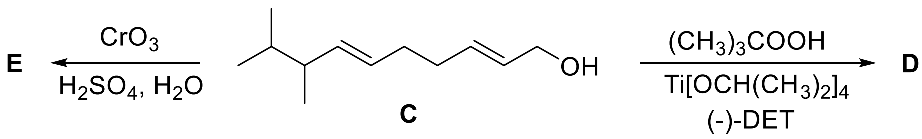
Chemical shift (δ, ppm)	1.20	2.50	5.10	7.22	7.43
Multiplicity	d	s	m	d	d
Number of protons	6H	3H	1H	2H	2H

^{13}C NMR data:

Chemical shift (δ, ppm)	23.8	26.6	35.2	126.0	128.5	133.9	152.8	197.0
Types of carbon	CH_3	CH_3	CH	CH	CH	C	C	CH

(5 marks)

(c) Compound **C** undergoes Sharpless epoxidation to form compound **D** and oxidation reaction to form compound **E**.



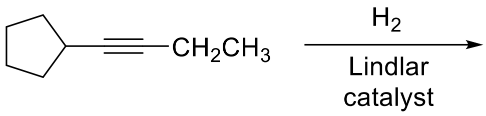
(i) Draw the structures of compounds **D** and **E**.

(ii) Explain why only one of the C=C of compound **C** is epoxidised with the Sharpless reagent.

(3 marks)

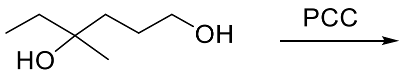
(d) Determine the structures of **F** to **I** in the following reactions.

(i)



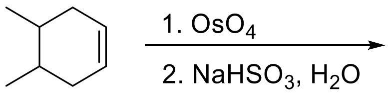
F

(ii)



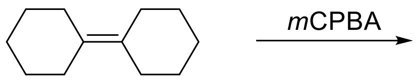
G

(iii)



H

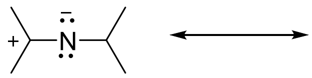
(iv)



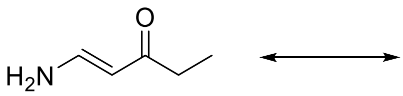
I

(4 marks)

(e) For the following compounds,



J



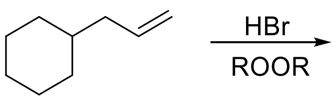
K

(i) Draw the second resonance structures of **J** and **K**.

(ii) With explanation, identify the more stable resonance structure for each pairs.

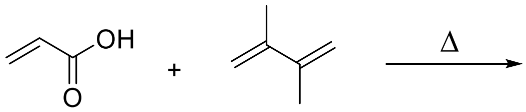
(4 marks)

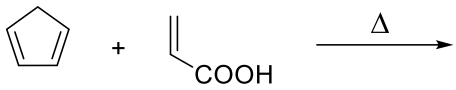
2. (a) In the mechanism of the radical addition of HBr to the alkene shown below, propose the initiation and propagation steps.

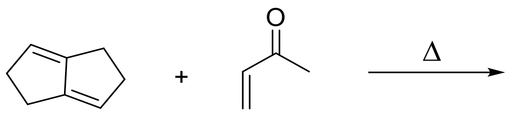


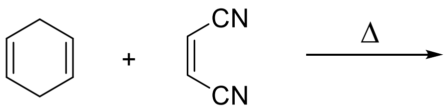
(4 marks)

(b) In the following Diels-Alder reactions, propose one possible product that could be formed. If there is no reaction, please explain in brief.

(i) 

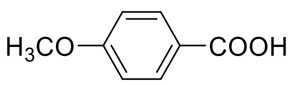
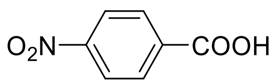
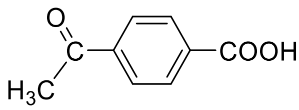
(ii) 

(iii) 

(iv) 

(6 marks)

(c) Show the arrangement of the following compounds in order of increasing pK_a with explanation.

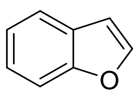
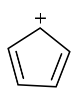
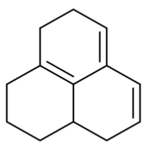
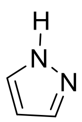
  

(4 marks)

(d) Octanoic acid and 1-octene can be separated using an aqueous extraction method. Explain how this separation can be carried out.

(6 marks)

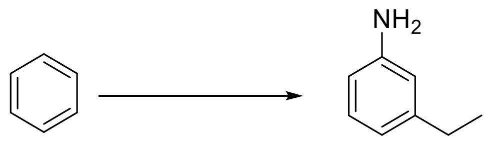
3. (a) Identify the following structures as aromatic, antiaromatic, or nonaromatic.

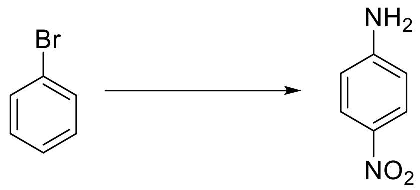
(4 marks)

(b) Propose the reagents for each of the reactions below.

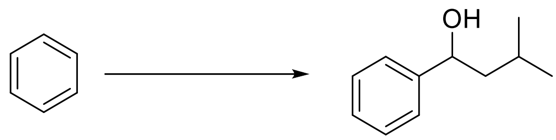
(i)



(ii)

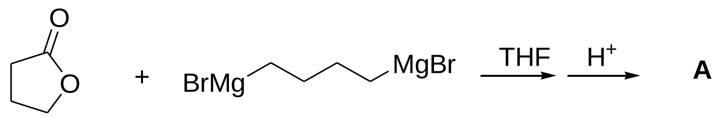


(iii)



(6 marks)

(c) Propose the product **A** and mechanism for the following reaction.



(6 marks)

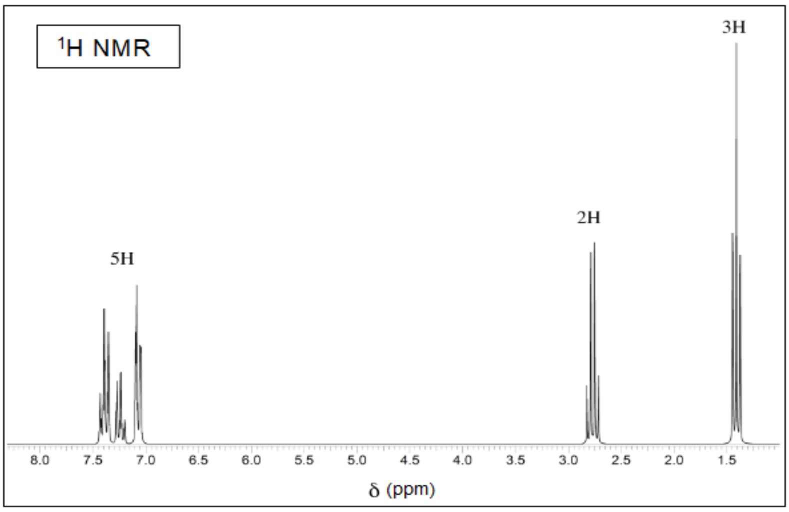
(d) Explain why Grignard reagent should be prepared under anhydrous condition.

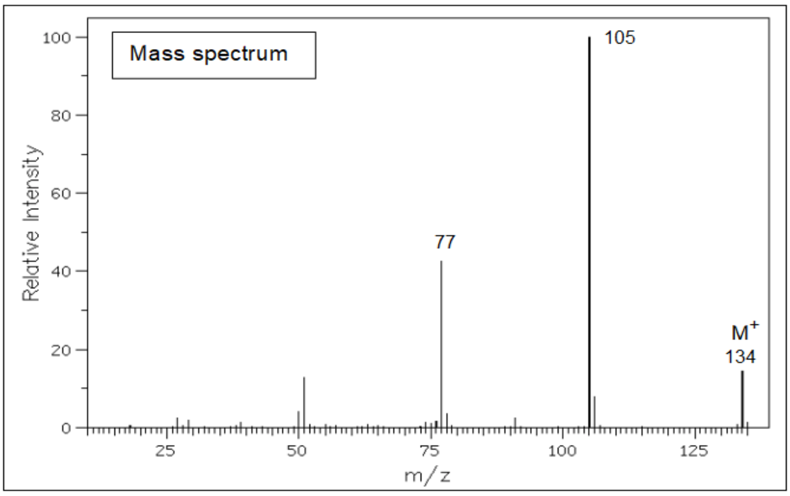
(4 marks)

SECTION B: Answer only **TWO (2)** questions.

4. (a) The IR, ^{1}H NMR and mass spectra of compound **A** are given below.

IR (ν, cm^{-1}): 3010, 2950, 2890, 1680 and 1600.



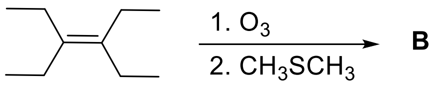


(i) Deduce the structure of compound **A** using these spectral data by providing a detailed explanation.

(ii) Propose the fragment ion at *m/z* 105 with its resonance structure.

(7 marks)

(b) For the following reaction.

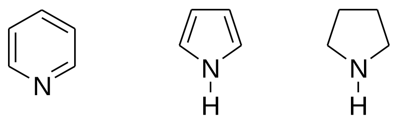


(i) Give the structure of **B**.

(ii) Explain how the IR spectroscopy can be used to determine whether the reaction is completed.

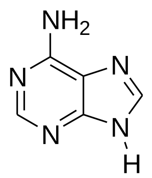
(3 marks)

(c) Show the arrangement of the following compounds in order of decreasing basicity with explanation.



(7 marks)

(d) The following molecule is adenine with a purine core. Explain why adenine is considered an aromatic compound.



(3 marks)

5. (a) Compound **A** (2,4-heptadiene) reacts with one equivalent of HBr to form two possible products which are compounds **B** (1,2-addition) and **C** (1,4-addition).

(i) Draw all possible carbocations and products formed in this reaction.

(ii) Identify the kinetic product.

(5 marks)

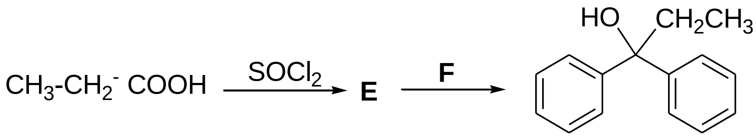
(b) Compound **D** ($C_{11}H_{16}$) displays significant absorption bands at 3012, 2910, 2870 and 1600 cm^{-1} in the IR spectrum. The peaks in ^1H NMR spectrum are observed at δ (ppm): 7.10-7.25 (m, 5H), 2.30 (s, 2H) and 1.22 (s, 9H).

(i) Deduce the structure of compound **D** using the given spectral data by providing a detailed explanation.

(ii) The mass spectrum of this compound shows a molecular ion peak at *m/z* 148 and a base peak at *m/z* 71. Propose a reasonable structure for the fragment ion at *m/z* 71.

(5 marks)

(c) Alcohol **G** can be prepared from propanoic acid as shown below.



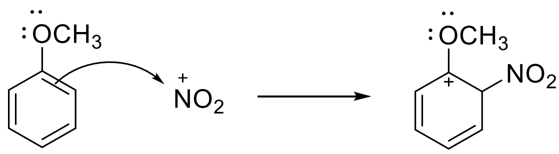
G

(i) Give the intermediate **E** and reagent **F**.

(ii) Propose the mechanism for the conversion of propanoic acid to alcohol **G**.

(5 marks)

(d) Nitration of anisole, **H** gives the resonance structure, **I** as shown below.



H **I**

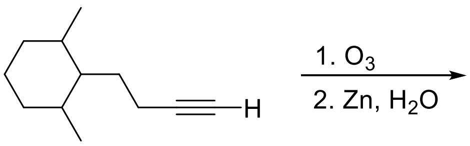
(i) Show all possible resonance structures of **I**.

(ii) Identify the most stable resonance structure with a brief explanation.

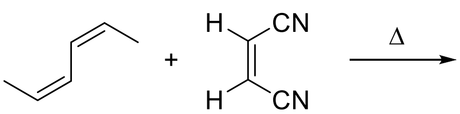
(5 marks)

6. (a) Determine the structures of **A** and **B** in the following reactions.

(i)

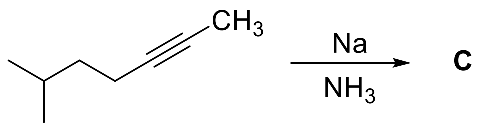


(ii)



(2 marks)

(b) Reaction of 6-methyl-2-heptyne shown below forms compound **C**.



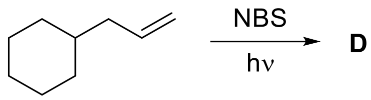
6-methyl-2-heptyne

(i) Propose the structure of **C**.

(ii) Explain using the IR spectroscopy whether the reaction is completed.

(3 marks)

(c) Allylcyclohexane undergoes reaction with NBS to form compound **D**.



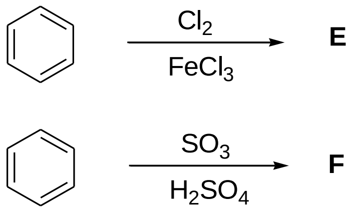
(i) Propose the structure of compound **D**.

(ii) In the mass spectrum of **D**, two molecular ion peaks are observed. Identify the *m/z* values of these peaks with a brief explanation.

(iii) Determine the intensity of these peaks.

(5 marks)

(d) The electrophilic aromatic substitution reactions below give products **E** and **F**, respectively.



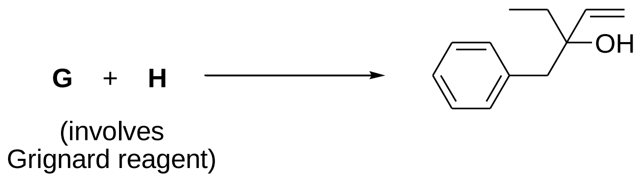
(i) Draw the products **E** and **F**.

(ii) Propose the mechanism for the electrophile generation for each of the reactions.

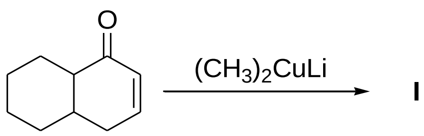
(5 marks)

(e) Give the starting material, reagent(s) or major product of each of the reactions below.

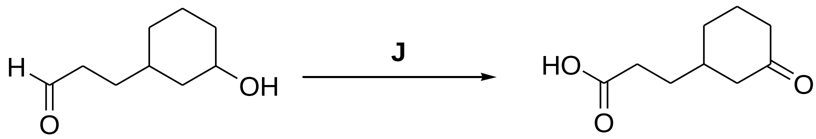
(i)



(ii)



(iii)



(5 marks)

7. (a) Compound **A** has a molecular formula of C_8H_7OCl. The spectral data of **A** is provided below.

IR (cm^{-1}): 3010, 2980, 2850, 1690, 1600.
^1H NMR (δ, ppm): 7.12 (d), 7.68 (d) and 1.24 (s).

(i) Based on the degree of unsaturation and the spectral data, propose the structure of **A**.

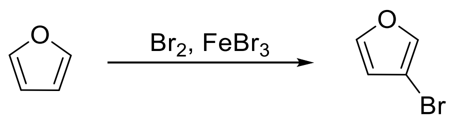
(ii) In the mass spectrum of **A**, two molecular ion peaks are observed. Identify the *m/z* values of both peaks with a brief explanation.

(iii) Explain the difference in the intensity of these two molecular ion peaks.

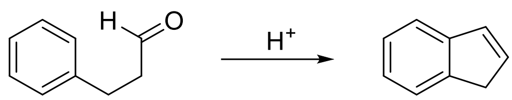
(10 marks)

(b) Propose a complete mechanism for the following reactions.

(i)



(ii)



(10 marks)

-oooOooo-