IMPORTANT INFORMATION

A table of Bond Dissociation Energies for Some Common Bonds is attached at the end of this paper

Section A Question 1 COMPULSORY (30 marks)

a. Define using structural example each of the following terms: (5 marks)

   i. Radical anions

   ii. Carbenes

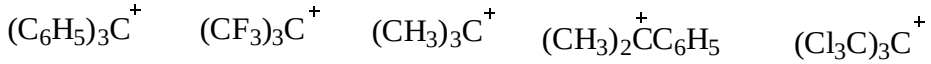
   iii. Carbocation

   iv. Heterolysis

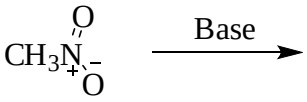
   v. Homolysis

b. What is the relationship between cis-1-chloro-2-fluorocyclohexane and trans-1-chloro-2-fluorocyclohexane? (2 marks)

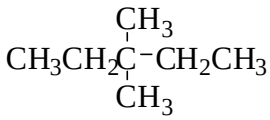
c. With a brief explanation arrange the following cations in the order of increasing stability: (5 marks)



d. In organic synthesis nitromethane is employed as a one carbon building block. Its acidity allows it to undergo deprotonation. Write the resonance structures of the resulting carbanion in the presence of a strong base. (3 marks)

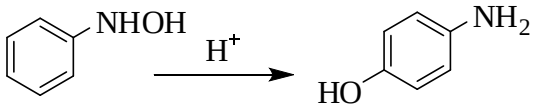


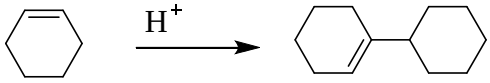
e. 3,3-dimethylpentane is likely to form two radicals in the presence of a suitable reagent. Indicate which radical would be more stable. (3 marks)



f. Define the Huckel's Rule and its application in predicting whether a compound is aromatic or not. (5 marks)

g. Suggest a plausible mechanism for each of the following reactions: (5 marks)

i 

ii 

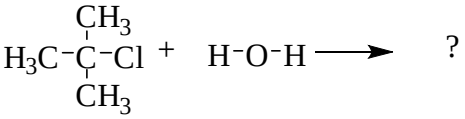
h. Would you expect m-dinitrobenzene to undergo bromination with a halogen carrier rapidly or slowly? Explain briefly. (2 marks)

Section B: This section contains FOUR questions. Answer ONLY TWO questions.

QUESTION 2 (20 marks)

a. Complete the reaction and state the type of reaction outlined below then using the table provided give the end product and determine the $\Delta H°$ for the following reaction:

(4 marks)

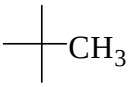


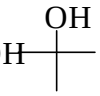
b. Draw the favoured conformation (gauche, anti or eclipsed) for the following molecules:

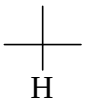
(6 marks)

a. 1,2-dichloroethane
b. 1,2-ethanediol
c. Propanaldehyde

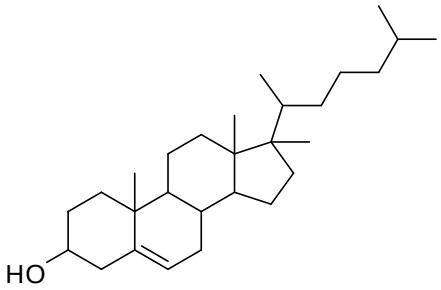
c. Complete each of the following structures by placing the missing substituents in the correct position. (6 marks)

i S-Alenine: CH_3CHNH_2COOH 

ii S-Glyceric aci: $HOCH_2CHOHCOOH$ 

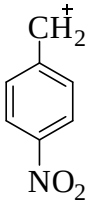
iii R-2-Chlorobutane 

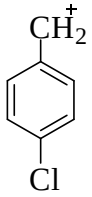
d. Circle all the chiral carbon atoms in cholesterol (below) and state its possible number of optical isomer. (4 marks)

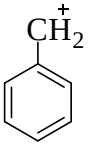


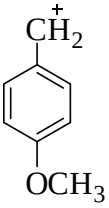
QUESTION 3 (20 marks)

a. Which of the following carbocation is the most stable and why? (4 marks)

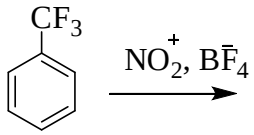
i 

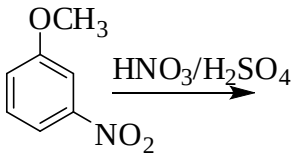
ii 

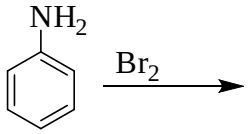
iii 

iv 

b. Predict the product of monosubstitution in the following reactions: (6 marks)

i 

ii 

iii 

c. Describe the necessary conditions and reagents required to convert benzene into the following: (8 marks)
   a. Nitrobenzene
   b. Ethylbenzene
   c. Cyclohexane
   d. *t*-Butylbenzene

d. What is Relative Configuration as used in stereochemistry? (2 marks)

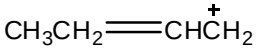
QUESTION 4 (20 marks)

a. Many radical reactions occur via a multistep process known as a chain reaction. Name and describe the three basic steps in the radical chain reaction. (6 marks)

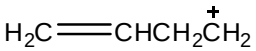
b. With a brief explanation write the order of the C-H bond weakness of the following alkanes: (4 marks)

   i. R_3CH ii. $R2CH_2$ iii. RCH_3 iv. HCH_3

c. Account for the following: Species A is more stable than B. (2 marks)



A



B

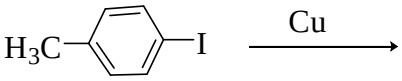
d. Explain briefly "when we say a carbocation is stable"? (2 marks)

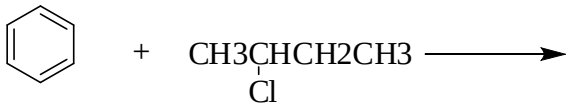
e. Discuss the influence of orientation of each of the following groups on substitution in aromatic compounds by electrophilic reagents: $-NH_2$, $-NO_2$, -Cl. (6 marks)

QUESTION 5 (20 marks)

a. Write a mechanism for the chlorination of benzene in the presence of $AlCl_3$ catalyst. (6 marks)

b. Complete the following reactions: (3 marks)

i 

ii 

iii 

c. Nitration of toluene is easier than that of benzene. Explain. (3 marks)

d. Discuss briefly electrophilic substitution in the benzene ring? (4 marks)

e. Cyclopentadiene anion (below) is aromatic. Explain briefly (4 marks)

-END-

TABLE 6.2 Bond Dissociation Energies for Some Common Bonds [A–B → A· + ·B]

Bond	$\Delta H°$ kcal/mol	(kJ/mol)
H–Z bonds		
H–F	136	(569)
H–Cl	103	(431)
H–Br	88	(368)
H–I	71	(297)
H–OH	119	(498)
Z–Z bonds		
H–H	104	(435)
F–F	38	(159)
Cl–Cl	58	(242)
Br–Br	46	(192)
I–I	36	(151)
HO–OH	51	(213)
R–H bonds		
CH_3–H	104	(435)
CH_3CH_2–H	98	(410)
$CH_3CH_2CH_2$–H	98	(410)
$(CH_3)_2CH$–H	95	(397)
$(CH_3)_3C$–H	91	(381)
CH_2=CH–H	104	(435)
HC≡C–H	125	(523)
CH_2=$CHCH_2$–H	87	(364)
C_6H_5–H	110	(460)
$C_6H_5CH_2$–H	85	(356)
R–R bonds		
CH_3–CH_3	88	(368)
CH_3–CH_2CH_3	85	(356)
CH_3–CH=CH_2	92	(385)
CH_3–C≡CH	117	(489)

Bond	$\Delta H°$ kcal/mol	(kJ/mol)
R–X bonds		
CH_3–F	109	(456)
CH_3–Cl	84	(351)
CH_3–Br	70	(293)
CH_3–I	56	(234)
CH_3CH_2–F	107	(448)
CH_3CH_2–Cl	81	(339)
CH_3CH_2–Br	68	(285)
CH_3CH_2–I	53	(222)
$(CH_3)_2CH$–F	106	(444)
$(CH_3)_2CH$–Cl	80	(335)
$(CH_3)_2CH$–Br	68	(285)
$(CH_3)_2CH$–I	53	(222)
$(CH_3)_3C$–F	106	(444)
$(CH_3)_3C$–Cl	79	(331)
$(CH_3)_3C$–Br	65	(272)
$(CH_3)_3C$–I	50	(209)
R–OH bonds		
CH_3–OH	91	(381)
CH_3CH_2–OH	91	(381)
$CH_3CH_2CH_2$–OH	91	(381)
$(CH_3)_2CH$–OH	91	(381)
$(CH_3)_3C$–OH	91	(381)