INDEX NO: | | | | | | |

THE OPEN UNIVRVERSITY OF SRI LANKA

B. Sc. DEGREE PROGRAMME / STAND ALONE COURSE 2009 / 2010

LEVEL 4 - FINAL EXAMINATION

CHU 2221 / CHE 4221 - ORGANIC CHEMISTRY - PAPER I

DURATION: $2^1/_2$ HOURS

Monday 19th July 2010 — 9.30 a.m.-12.00 noon.

Attempt as many questions as possible.

Maximum marks allocated to this paper are 120. However a candidate who scores 100 marks or above will be awarded 100% and those scoring less will be awarded the score they make.

Write your answers in the space provided at each question.

1. Answer both parts.

(a) State whether each of the following compounds show a dipole moment or not. (Yes /No)

(i) CO_2 (ii) CH_2Cl_2 (iii) CH_3CHO (iv) CBr_4

....

(2 Marks)

(b) What is the main type of intermolecular force present in each of the following compounds?

i. *Ortho*-nitrophenol .....

ii. Ethanol .....

iii. Acetone .....

iv. 2-methylbutane .....

(2 Marks)

2. Explain why CH_3CN is less basic than $CH_3CH_2NH_2$.

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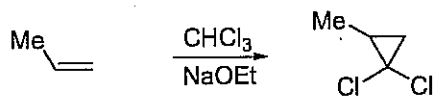
(2 Marks)

INDEX NO: | | | | | |

3. Classify the following reactions using a suitable term selecting from: *Nucleophilic substitution*; *Nucleophilic addition*; *Electrophilic substitution*; *Electrophilic addition*; *Elimination* or *Other type*.

i. 

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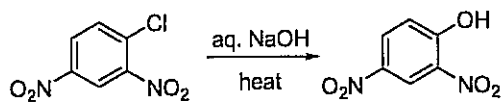
ii. 

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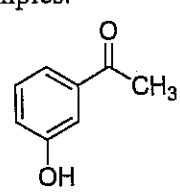
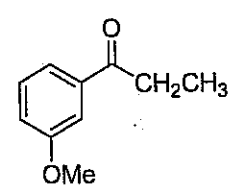
iii. $CH_3CHO \xrightarrow{LiAlH_4} CH_3CH_2OH$ .....

iv $CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_2CHO \xrightarrow{H^+/\text{ heat}} CH_3CH{=}CHCHO$ .....

(2 Marks)

4. Give a chemical test to distinguish between the compounds in each of the following pairs of examples.

(a) 

and 

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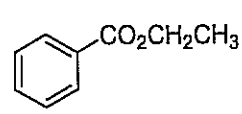
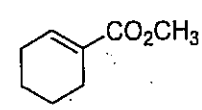
(b) 

and 

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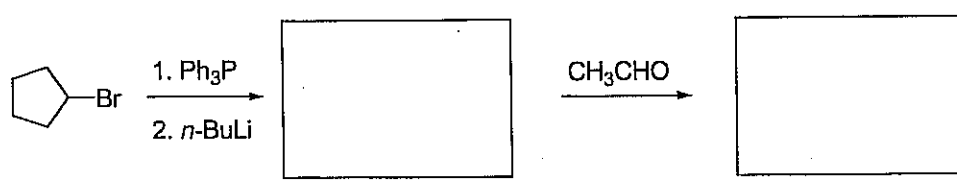
(4 Marks)

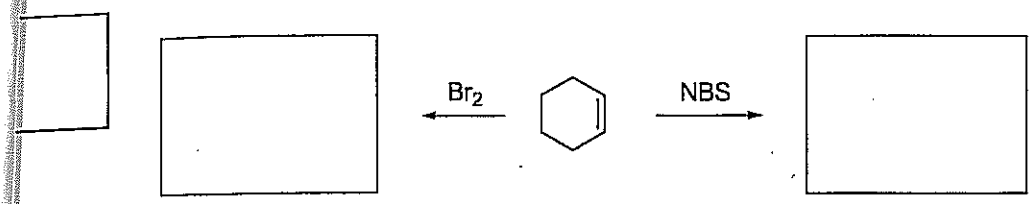
5. Complete the following reaction scheme by giving the structures of the missing compounds in the boxes.



(4 Marks)

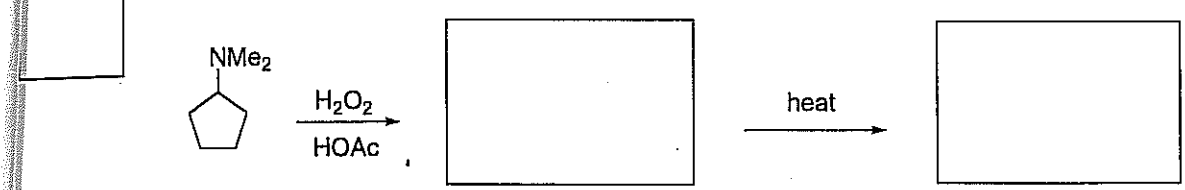
INDEX NO: | | | | | | |

6. Give the products with the stereochemistry (*where necessary*) of the following reactions.



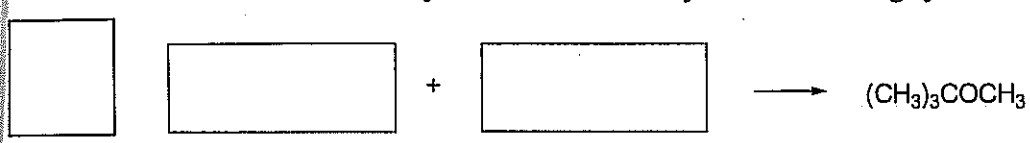
(4 Marks)

7. Complete the following reaction scheme by giving structures of the missing compounds in the boxes.



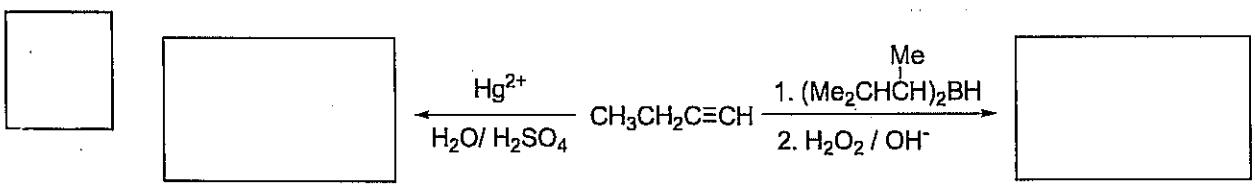
(4 Marks)

8. What are the reactants you would use to carryout the following synthesis?



(4 Marks)

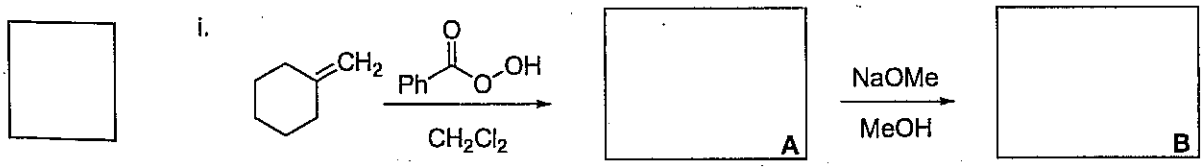
9. Give the structures of the products of the following reactions



(4 Marks)

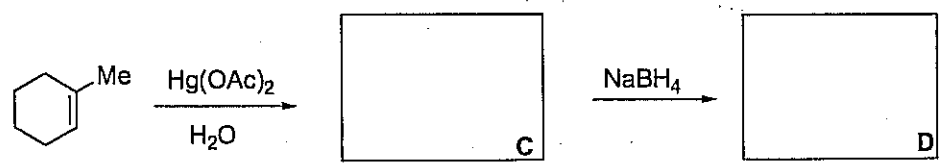
10. Give the structures of the products **A**, **B**, **C** and **D** of the following reactions.

i.



(4 Marks)

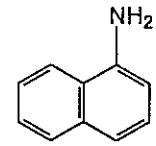
ii.



(4 Marks)

INDEX NO:					

11. α-naphthylamine shows UV λ_{max} at 320nm, which disappears on addition of HCl. Explain.



α-naphthylamine

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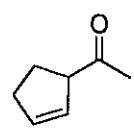
(3 marks)

12. Which of the following pair of compounds will absorb at a lower carbonyl stretching frequency in IR? Explain.



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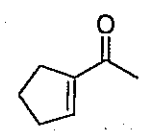
and



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(5 marks)

13. Draw the structure of the compound of molecular formula $C_5H_{10}Br_2$ with the following ^{1}H-NMR spectra, δ 1.0 (triplet, 6H); δ 2.4 (quartet, 4H)

(4 marks)

14. The base peak in the mass spectrum of 2,2,4,4-tetramethylpentane appears at m/z 57. Draw the structure of the fragment ion responsible for this peak.

(3 marks)

INDEX NO: | | | | | |

15. Explain why acetylinic protons are more shielded than olefinic protons.

(5 marks)

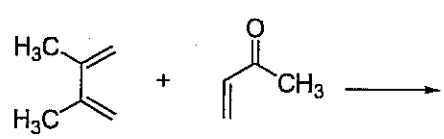
16. Draw the molecular orbital energy level diagrams for cyclobutadiene and cyclooctatetraene and show the electron distribution.

energy level diagrams for cyclobutadiene

energy level diagrams for cyclooctatetraene

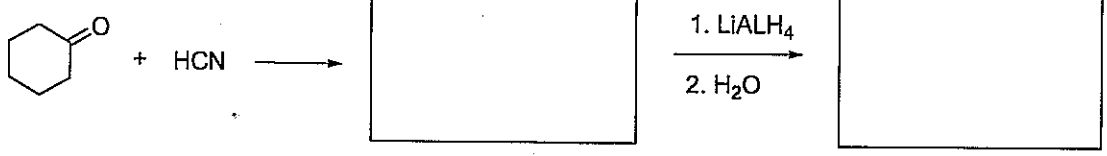
(5 marks)

17. What is the structure of the product of the following reaction?



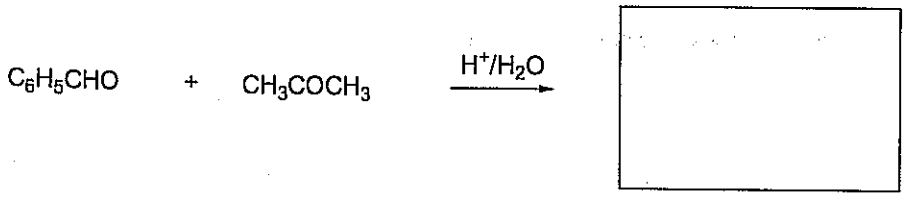
(3 marks)

18. Give the structures of the products of the following reaction.



(6 marks)

19. What is the structure of the product of the following reaction?



(3 Marks)

INDEX NO: | | | | | |

20. Arrange the following acid derivatives in the order of increasing reactivity toward nucleophilic acyl substitution.

RCOCl, (A) RCOOCOR, (B) $RCOOR^1$, (C) $RCONH_2$ (D)

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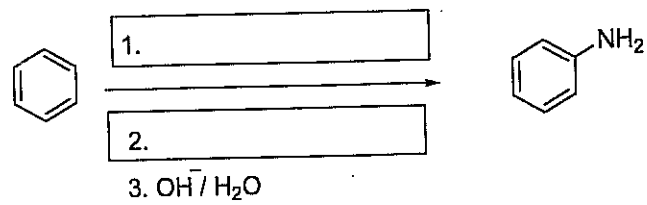
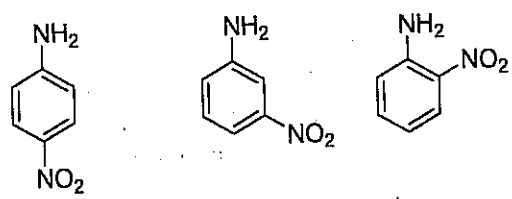
(3 Marks)

21. Give suitable reagents and conditions for the following reaction.



(4 marks)

22. Arrange the following amines in the increasing order of basicity.



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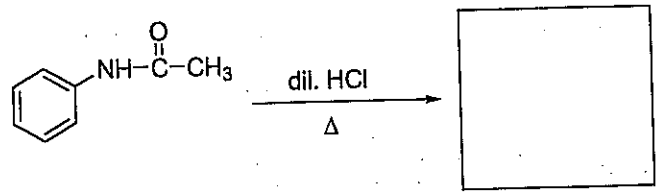
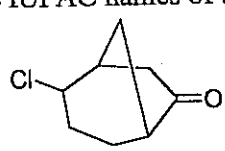
(3 marks)

23. Give the products of the following hydrolysis.



(4 marks)

24. Give IUPAC names of the following.

i. 

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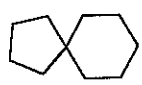
ii. 

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(6 marks)

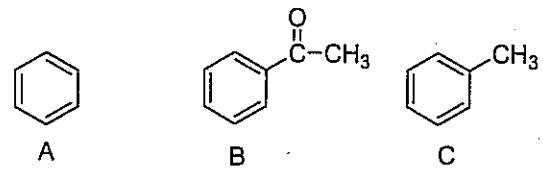
25. Write the inference of the test given below performed on an amine.

Test	Observation	Inference
Heated with $CHCl_3$ and ethanolic KOH	Characteristic smell of carbyl amine is not given.	

(3 marks)

INDEX NO:					

26. Arrange the following three compounds in the increasing order of reactivity towards $Br_2/FeBr_3$.

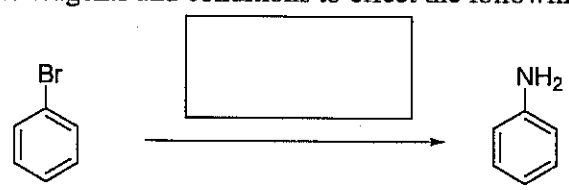


A B C

……<……<……

(4 marks)

27. Give the reagents and conditions to effect the following reaction.



(4 marks)

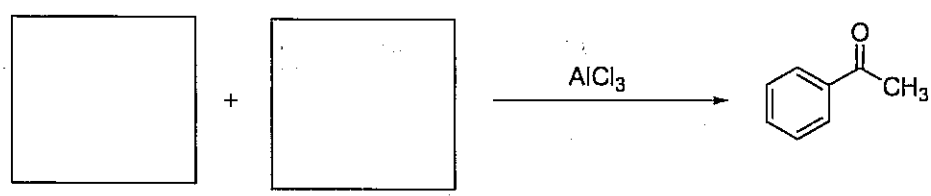
28. i. Give the reagents used for Birch reduction.

……

ii Give the structure of the product when benzene undergoes Birch reduction.

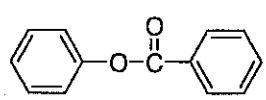
(5 marks)

29. Suggest the starting materials for the following reaction.



(4 marks)

30. Phenyl benzoate has two aromatic rings.



A ring B ring

i. Which ring undergoes electrophilic substitution readily? ……

ii Give the reason for your answer……

……

(3 marks)

THE OPEN UNIVERSITY OF SRI LANKA

B. Sc DEGREE PROGRAMME / STAND ALONE COURSE 2009/2010

LEVEL 4 - FINAL EXAMINATION

CHU 2221 / CHE 4221 - ORGANIC CHEMISTRY - PAPER II

DURATION: 2 1/2 HOURS

405

Monday, 19th July 2010 1.00 p.m. - 3.30 p.m.

Answer any FOUR (04) questions. ***Only the first four answers will be marked.***

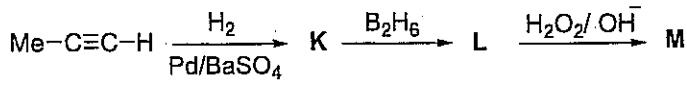
1. (a) Alcohol **A** ($C_6H_{14}O$) shows optical isomerism. On oxidation with acidic $K_2Cr_2O_7$ it gave **B** ($C_6H_{12}O_2$) and on heating with conc. H_2SO_4 it gave **C** (C_6H_{12}). Both **B** and **C** also exhibit optical isomerism. **C** when reacted with cold conc. H_2SO_4 followed by hydrolysis gave **D** ($C_6H_{14}O$) which does not show optical isomerism. **C** when reacted with H_2O in the presence of $Hg(OAc)_2$ followed by reaction with $NaBH_4$ gave **E** which also shows optical isomerism. **A, D** and **E** are structural isomers. **D** reacted with conc. H_2SO_4 to give a product mixture containing **F** and **G** which are stereoisomers of each other. **E** also gave **F** and **G** as the major products when reacted with conc. H_2SO_4. Both **F** and **G** underwent ozonolysis in the presence of Zn/H_2O to give **H** (C_2H_4O) and **J** (C_4H_8O). **J** did not give silver mirror with Tollen's reagent

   i. Deduce the structures of **A, B, C, D, E, F, G, H** and **J.**

   ii. Give the mechanisms for the formation of **D** and **E** from **C.**

(76 Marks)

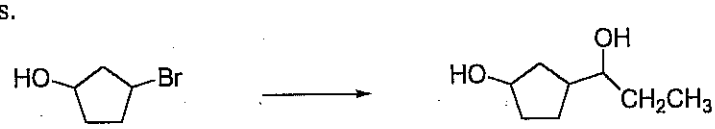
(b) Give the structures of products **K, L** and **M** of the following reaction scheme.



(24 Marks)

2. (a) Giving necessary reagents and conditions show how you would perform the following conversions.

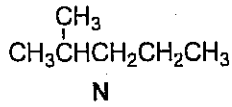
i.



ii.

(30 Marks)

(b) How would you synthesize the compound (**N**) given below using only the reactants and reagents given in the list provided.



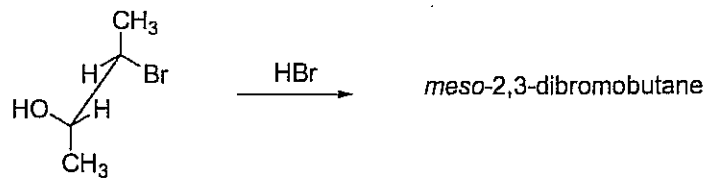
N

List of reactants and reagents:
$CH_3CH_2CH_2Br$,
alc. KOH, Li, HBr, CuI

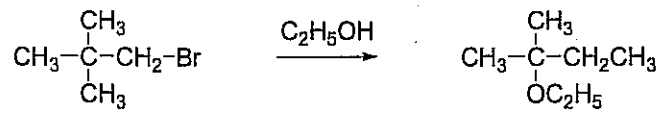
(15 Marks)

(c) Give the mechanisms of the following reactions.

(i)



(ii)

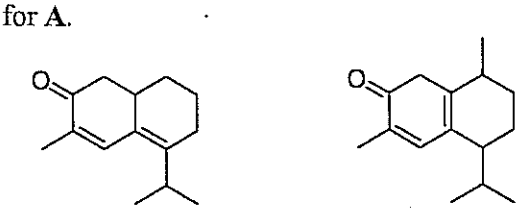


(40 Marks)

(d) Explain why, 2-chloro-2-methylpropane undergoes hydrolysis in water slowly while chloroethane is unreactive under the same conditions.

(15 Marks)

3. (a) A naturally occurring ketone **A**, showed a λ_{max} 312 nm, in its UV spectrum. Two possible structures of **A** are given below. [(I) and (II)].Using Woodward-Fieser rules calculate the expected λ_{max} for the two structures and suggest which of them could be correct structure for **A**.



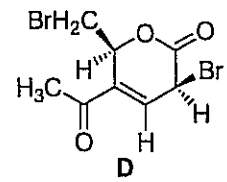
Basic value for α, β-unsaturated ketone = 215 nm, Increments; Homoannular diene component +39 nm, Extended conjugation +30 nm, Exocyclic double bond +5 nm, Alkyl substitution or ring residues; α-position +10 nm, β-position +12 nm, γ-position or higher position +18 nm)

(30 marks)

(b) The compound **B**, $CH_3CHBrCOCH_2CH_3$ showed a strong absorption at ν_{max}=1710 cm^{-1}, in IR. What is the absorption due to? Treatment of **B** with alcoholic KOH gave **C**, C_5H_8O in which this absorption is shifted. Give the structure of **C** and predict ν_{max} value at which this absorption would occur in **C**. Explain your answer.

(20 marks)

(c) Sketch the ^{1}H-NMR spectrum of **D** showing the relative distance from TMS, relative areas and multiplicities of the signals. (Assign the signals to the H atoms in **D** by labeling them as a, b, c…etc.)



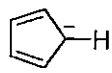
D

(25 marks)

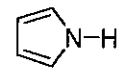
(d) Give the structures of the fragment ions responsible for the peaks at m/z 57, 44 and 29 in the mass spectrum of 3-methylbutanal. How would you distinguish 2-methylbutanal from 3-methylbutanal using mass spectroscopy?

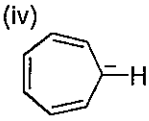
(25 marks)

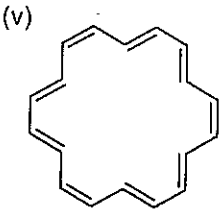
4. (a) Which of the following species will be expected to be aromatic? Account for your answer.

(i) 

(ii) 

(iii) 

(iv) 

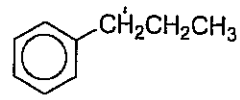
(v) 

(40 marks)

(b) Write the structures of products **P-R** from following reactions.

(i) $H_3C-C\equiv C-CH_3 \xrightarrow[HgSO_4]{H_2O/H_2SO_4}$ **P**

(ii) $C_6H_5COCl \xrightarrow[2.\ H^+/H_2O]{1.\ H\text{-}Al(O^tBu)_3}$ **Q**

(iii)  $\xrightarrow[2.\ H_3O^+]{1.\ KMnO_4 / \bar{O}H / heat}$ **R**

(30 marks)

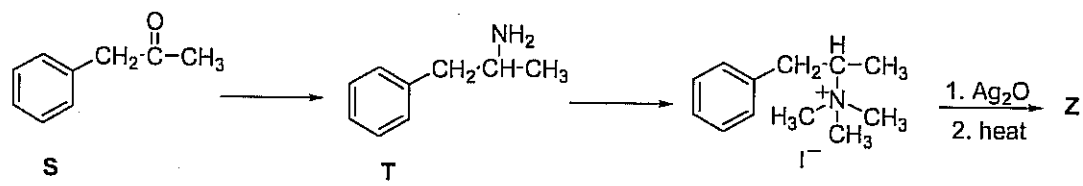
(c) Give the essential conditions and reagents necessary to carry out the following conversions. Give the mechanism of the reactions.

(i) $C_6H_5CHO \longrightarrow C_6H_5CH(OC_2H_5)_2$

(ii) $C_6H_5COCH_2CH_3 \longrightarrow C_6H_5COCHBrCH_3$

(30 marks)

5. (a) Consider the following reaction scheme to produce the alkene **Z**.



(i) Give the structure of the alkene **Z** showing the mechanism for its formation.
(ii) Provide the missing reagents and conditions necessary to carry out the synthesis.
(iii) Outline a mechanism for the conversion of **S** to **T**.

(40 marks)

(b) Explain the following.

(i) Hydrolysis of substituted carboxylic acid amides is much faster than the hydrolysis of substituted sulfonamides.

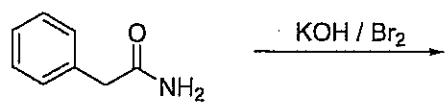
(ii) Cyclopropane is more reactive than propane towards many types of reagents.

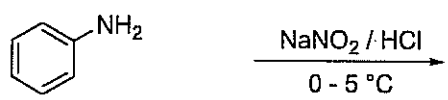
(40 marks)

(c) Predict the products of the following reactions.

(i). 

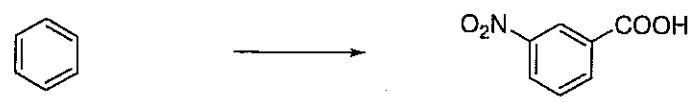
(ii). 

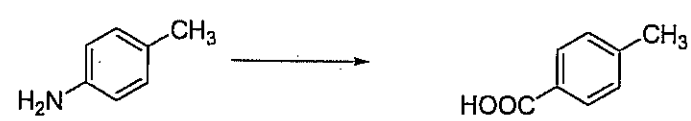
(iii). 

(iv). 

(20 marks)

6. (a) Giving necessary reagents and conditions show how any **two (2)** of the following transformations would be affected

(i). 

(ii). 

(iii). 

(60 Marks)

(b) Explain the statements given below briefly.

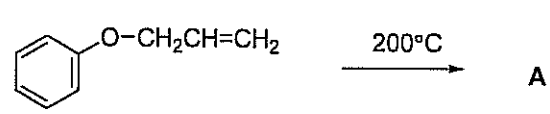
(i) Phenol is about 10^8 times as acidic as cyclohexanol.

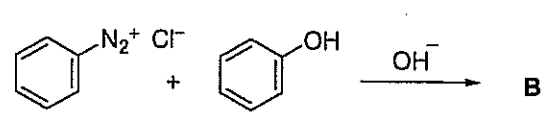
(ii) C-Br bond in bromobenzene is shorter than that of bromomethane.

(iii) Benzyne is a very reactive intermediate.

(30 marks)

(c) Predict the product of the following reactions.

(i) 

(ii) 

(10 marks)