



OBAFEMI AWOLowo UNIVERSITY, ILE-IFE, NIGERIA

DEPARTMENT OF CHEMISTRY

B.Sc. Degree (Chemistry) Examination (Part III)

CHM 306: Aromatic and Heterocyclic Chemistry

2017/2018 Rain Semester Examination

Date: January 19, 2019

Time Allowed: 2 1/2 Hours

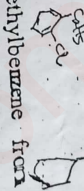
Instructions:

- (i) ANSWER QUESTION 1 (SECTION A)
(ii) ANSWER ANY THREE QUESTIONS IN SECTION B.

SECTION A

QUESTION 1

(a) Write balanced equations to show the conversion of the following compounds to phenyl bromide



(i) Phenol (ii) 4-bromobenzoic acid.

(iii) What are the reaction conditions necessary to obtain β -chloroethylbenzene from ethylbenzene? (5 marks)

(b) The reaction of 2,4-dicarbonyl compounds with ammonia or a primary amine describes the Paal-Knorr synthesis of pyrroles. Outline the synthesis of 1,2-diethyl-5-methylpyrrole by this method and show the appropriate mechanism. (6 marks)

SECTION B

QUESTION 2

(a) Outline the synthesis of benzyl alcohol from toluene.

(b) Explain by chemical equation(s) the synthesis of phenyl benzoate from chlorobenzene.

(c) Describe by chemical equation(s) the preparation of catechol from isopropylbenzene. (20 marks)

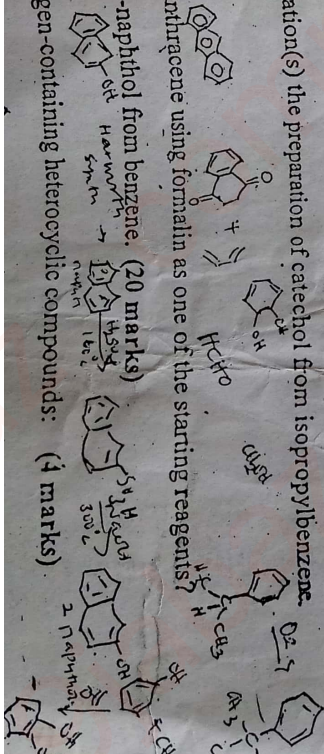
QUESTION 3

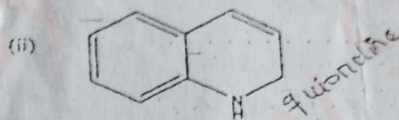
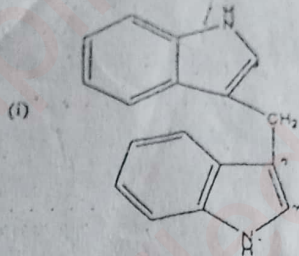
(a) How would you prepare anthracene using formalin as one of the starting reagents?

(b) Outline the synthesis of 2-naphthol from benzene. (20 marks)

QUESTION 4

(a) Name the following nitrogen-containing heterocyclic compounds: (4 marks)



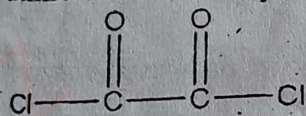


(b) Give appropriate equation(s) and name the organic product(s) formed for each of the following reactions of pyridine with:

(i) A named alkyl halide (4 marks) (ii) excess n-butyl Lithium. (6 marks)

(c) Give the structure and name of the product formed when isatin reacts with sodium hydroxide. (2 marks)

(d) Outline the reaction path for the conversion of indole to tryptamine using oxalyl chloride.



(4 marks)

QUESTION 4

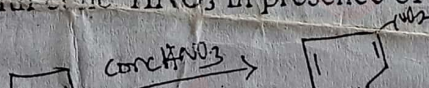
(a) Illustrate the reaction path for the formation of indophenine from isatin. (8 marks)

(b) Given glycerol and aniline, illustrate the process for the synthesis of quinolone. (8 marks)

(c) Give the structure and name of the product formed when:

(i) 2,3-dimethylindole is brominated in aqueous medium. (2 marks)

(ii) Pyrazole is reacted with conc. HNO_3 in presence of conc. H_2SO_4 . (2 marks)



Obafemi Awolowo University, Ile-Ife, Nigeria
Department of Chemistry

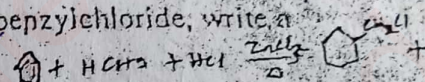
B.Sc. (Chemistry) Degree First Semester Examination 2011/2012 Academic Session
CHEM 306: Aromatic and Heterocyclic Chemistry

Date: January 2013.

Time Allowed: 2 hours

Instruction: Attempt ALL questions

1. Write the mechanism for Friedel-Craft alkylation for the synthesis of a typical alkylbenzene.
2. Diagrammatically explain why the C-X bond in an arylhalide is stronger than that of an alkylhalide.
3. Provide the structures of the following compounds; (i) 1,4-dimethyl-2-vinylbenzene (ii) dichlorodiphenyltrichloroethane (iii) adrenalin.
4. (i) Heating benzene with formalin and hydrochloric acid will yield benzylchloride, write a balanced equation with appropriate conditions for the reaction.

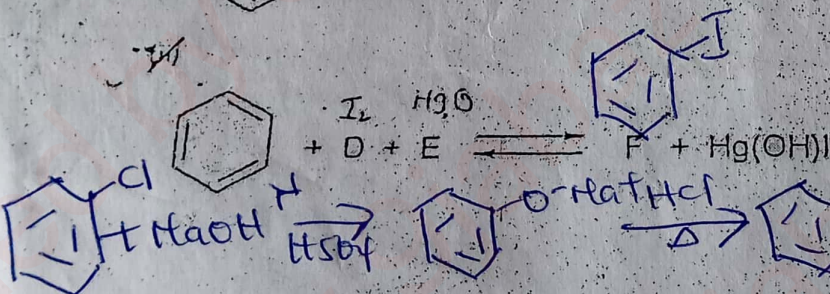
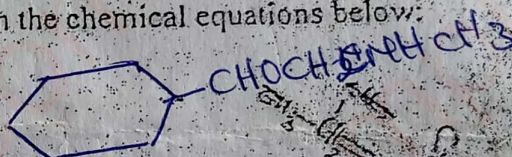
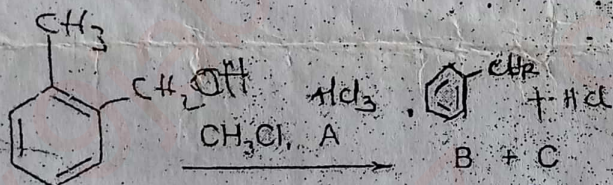


- (ii) What is Wurtz reaction? Give an example of this reaction.



5. Provide the lettered compounds/reagents (A - E) in the chemical equations below:

(i)



- 2a. (i) What is Dow process? Give a typical reaction of Dow process.

- (ii) Outline the synthesis of phenylbenzoate from phenol.

- b. (i) How would you produce 2-methyl-4-hydroxyacetophenone from m-cresol?

- (ii) Write a balanced equation for the production of aspirin.

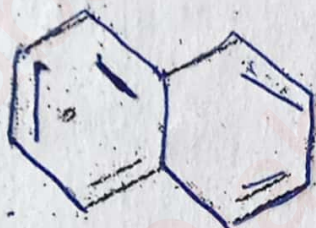
- c. (i) Write the mechanism for the synthesis of 5,8,9,10-tetrahydro-1,4-naphthoquinone from p-benzoquinone.

- (ii) Provide the products of the following reactions

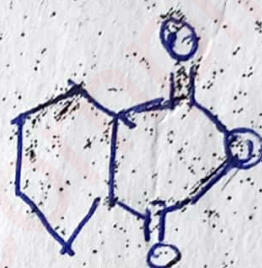




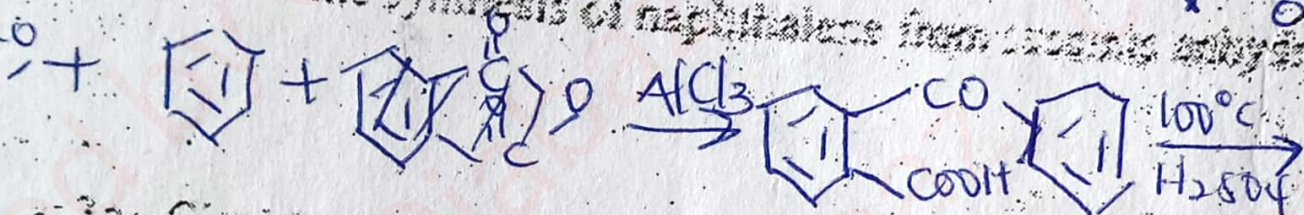
Cr_2O_3 at 25°C



$\text{O}_2, \text{V}_2\text{O}_5$ at $450 - 480^\circ\text{C}$



d. Outline the synthesis of naphthalene from acetylene and benzene



3a. Give the product of the reaction of heptan-3,5-dione with hydrazine and mechanism of the reaction.

b. If you are required to prepare 2-ethylindole starting with tryptan-2-one by indole method, what other reagent(s) would you need? Illustrate the mechanism.



c. Give simple equations to show how...



ORAFEMI AWOLowo UNIVERSITY, ILORIN, NIGERIA

BSc Degree First Semester Examination, 2001/2002

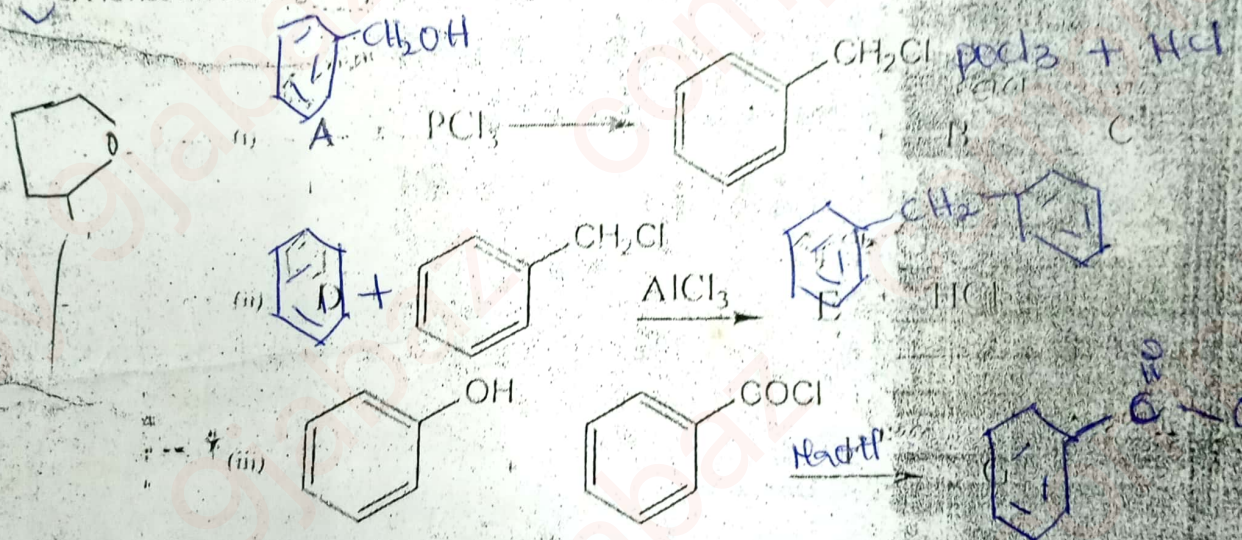
CHM 306: AROMATIC AND HETEROCYCLIC CHEMISTRY

TIME ALLOWED: 2 hours

DATE: April, 2015

INSTRUCTION: Answer ALL Questions

1. a. Write the mechanism of Friedel-Craft alkylation for the synthesis of alkylbenzene.
- b. What are the conditions that can make aryl chloride and aryl bromide to undergo Wurtz-Fittig reaction? Give an example.
- c. What are the products that will be obtained, when ethylbenzene is chlorinated in the presence of light at room temperature and when it is chlorinated in presence of light at boiling point?
- d. Provide the missing compounds or reagents indicated by letters in the following reaction:



2. a. Using chemical equation(s) only, outline the synthesis of phenanthrene from tetralene

b. State by chemical equation how you will produce phthalic acid from succinic anhydride

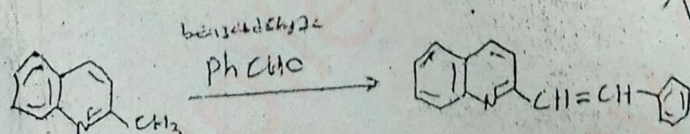
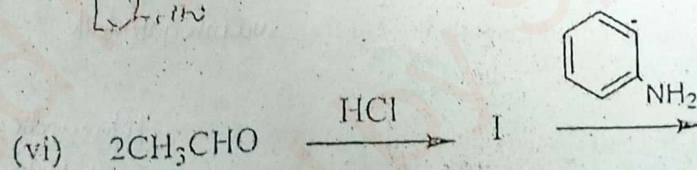
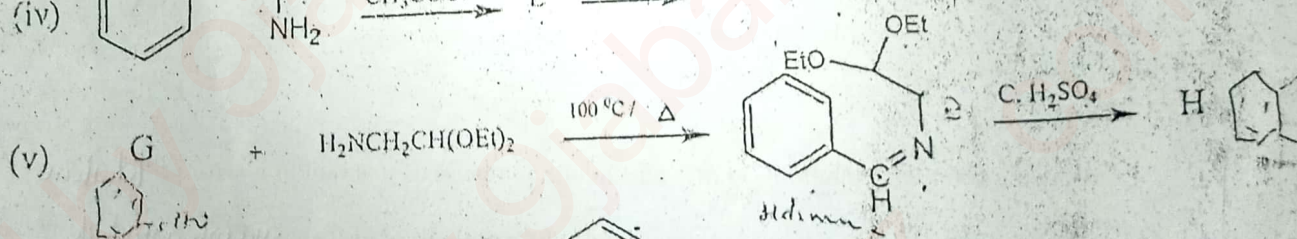
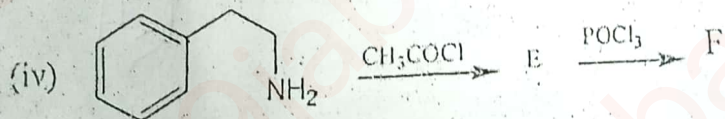
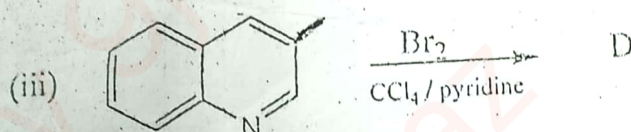
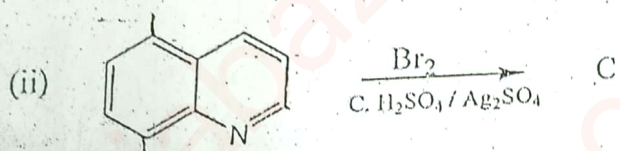
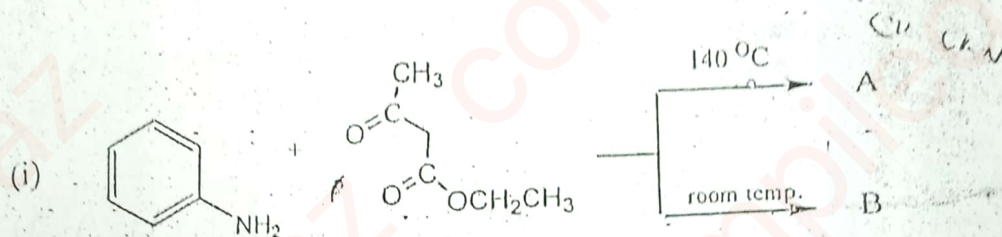
3. (a). Name and give the structure, in each case, of a naturally occurring nitrogen heterocyclic compound containing the basic skeleton of (i) pyrrole (ii) pyrazole (iii) imidazole (iv) pyridine and (v) quinoline

(b). Using appropriate equation(s) only, substantiate each of the following chemical information:

- quinoline can readily condense with benzaldehyde
- 2-methylindole can be obtained by cyclic dehydration of acyl ortho toluilide in presence of a strong base such as sodamide.

(c). Illustrate the mechanistic path for the synthesis of 2, 3-dimethylindole from butan-2-one and phenylhydrazine, using Fischer Indole synthesis

(d). Complete the following equations by writing the structures of the lettered compounds:



Obafemi Awolowo University, Ile-Ife, Nigeria
Department of Chemistry

B.Sc. (Chemistry) Degree Mid-Semester Examination 2011/2012 Academic Session
CHM 306: Aromatic, Heterocyclic and Bifunctional Chemistry

Date: 26th November 2012

Time Allowed: 40 minutes

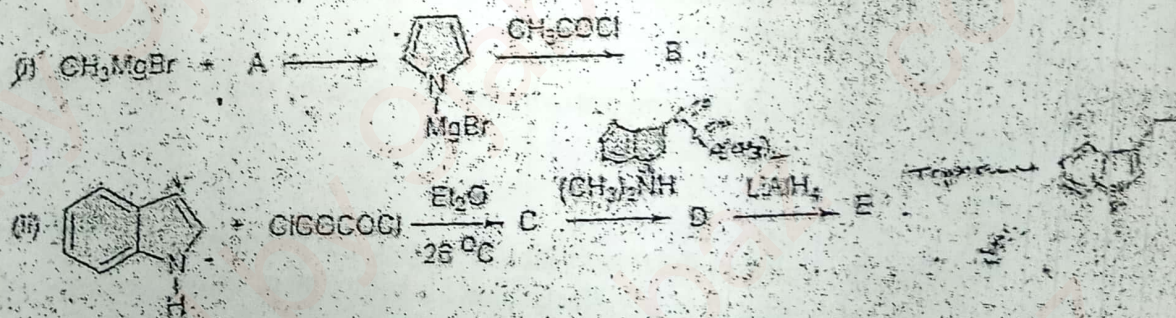
Instruction: Attempt ALL questions

1. a. Explain by chemical equation the synthesis of aniline from 4-chlorobenzoic acid.
- b. (i) What is Ullman reaction?
(ii) Outline the synthesis of biphenyl from benzene following Ullman synthetic route.
- c. Diagrammatically explain why the C-X bonds (where X = Br, Cl, F, I) in arylhalides are stronger than those in the alkylhalides.

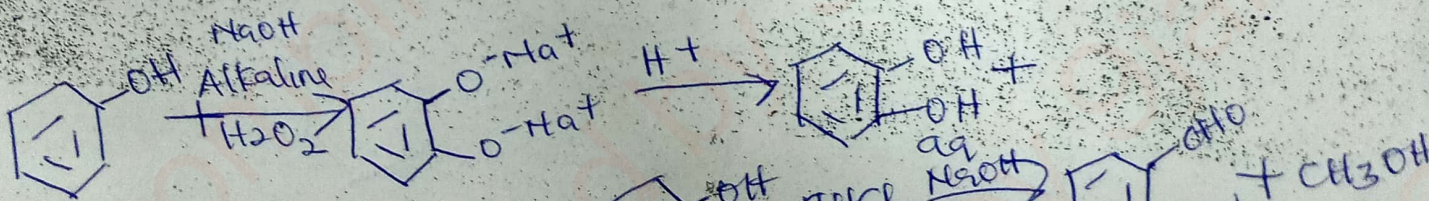
2. a. Justify the following chemical observations:

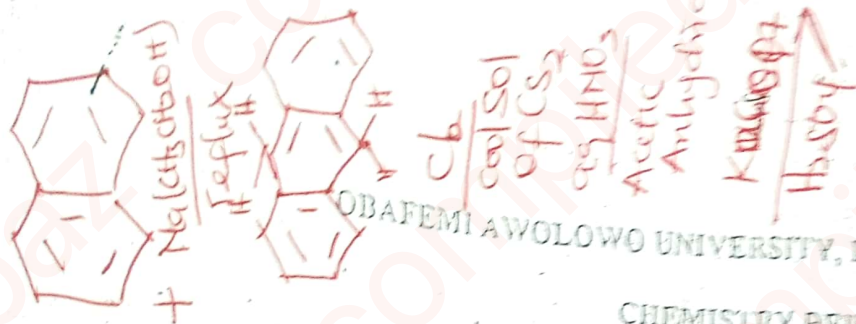
- (i) Electrophilic substitution takes place mainly at the α -position than at β -position in unsubstituted pyrrole
- (ii) Pyridine is very difficult to nitrate, but 2,6-dimethylpyridine is easily nitrated.

b. Complete the following chemical equations by writing the structures of lettered compounds:



- c. Give the structure of the product formed and the mechanism of the reaction between:
2-Chloroethanal, ammonia and methanamide.





Dr. MONDA

OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE, FACULTY OF SCIENCE

CHEMISTRY DEPARTMENT

B.Sc. Degree Examination, 2010/11 Rain Semester

CHM 306- AROMATIC AND HETEROCYCLIC CHEMISTRY

INSTRUCTION: Attempt ALL Questions.

Time: 45 mins

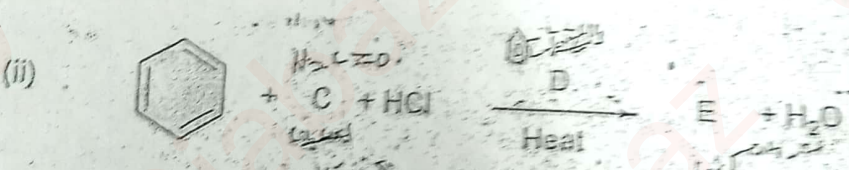
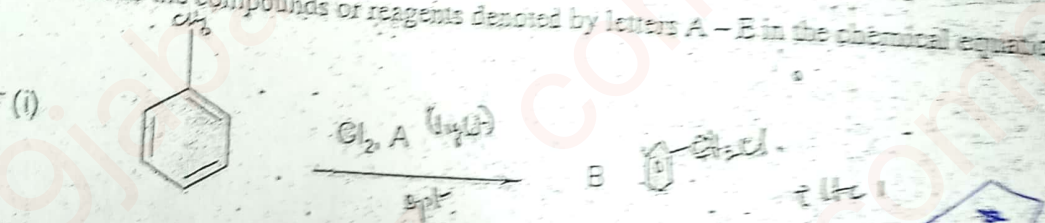
$\frac{1605}{4602-4802}$
 $\frac{O_2}{4602-4802}$

$\frac{C_2O_3}{250}$
 Acetic acid

a. Outline the mechanism of Friedel-Craft alkylation reaction for the synthesis of arylhalides.

b. State by chemical equation only, how you will prepare phthalic acid from naphthalene?

c. Provide the compounds or reagents denoted by letters A - E in the chemical equations below.



2a. Give the structure of the following compounds: (i) 2-phenylazopyrrole (ii) Tryptophan and (iii) prazoline

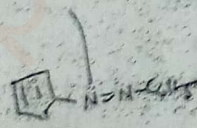
b. Given butan-2-one and phenylhydrazine, describe step by step the mechanism for the synthesis of 2-ethylindole.

c. Briefly compare the reactivities of pyrrole and pyridine under the following headings: (i) Reaction as a base (ii) Electrophilic substitution reaction

Pyrrole < pyridine
 0.2 5.0

pyrrole > pyridine

Pyrrole takes place at 2 position and 5 position
 Pyridine takes place at 2 position and 4 position
 same self with HCl



UNIVERSITY OF CALicut, KERALA
DEPARTMENT OF CHEMISTRY, FACULTY OF SCIENCE
2010/2011 SEMESTER TEST
CHEM 100 AROMATIC AND HETEROCYCLIC CHEMISTRY

NOVEMBER 2011

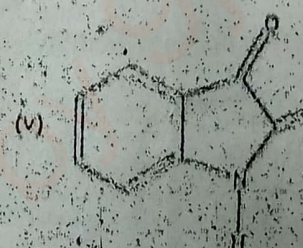
TIME: 2 HOUR

Instruction: Attempt all Questions. Answer the two sections in separate booklets.

1a. Draw the structure and give an appropriate name for the major product formed in each of the following reactions:

- (i) quinoline with Br_2 in CCl_4 (ii) Isoquinoline with Br_2 in CCl_4
(iii) 2,3 dimethylindole with Br_2 in aqueous medium

b. Complete the following equations by writing the structures of lettered compounds:



2a. Give the mechanism for the reaction between aniline (an aryl amine) and 2,4-pentanedione (a 1,3-diketone) and give the name of the final product.

b. Self condensation of ethanal forms 2-butanone, which undergoes Michael addition with aniline to form a quinolone derivative. Give equations to illustrate the reaction steps described above.

c. Compare the reactivities of pyridine and 2,6-dimethylpyridine towards nitration using $\text{HNO}_3/\text{H}_2\text{SO}_4$ as reagent, under appropriate reaction conditions.

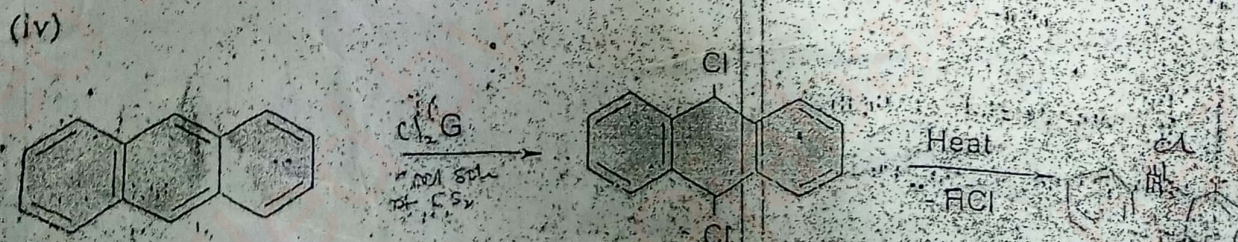
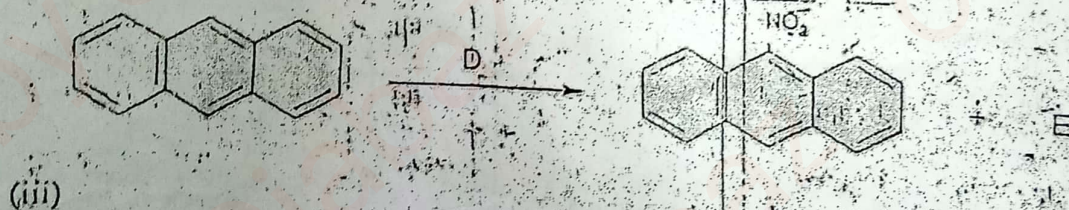
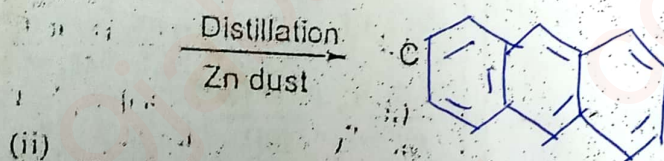
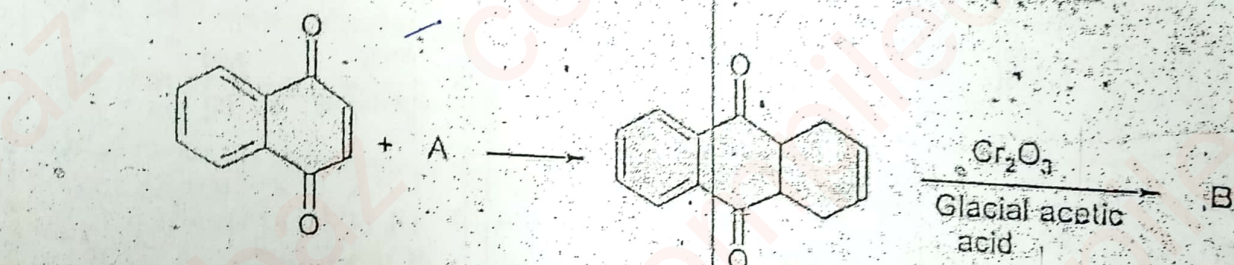
a. (i) What is Fittman reaction? (ii) Give a typical chemical equation of this reaction.

b. (i) What is Dow process? (ii) Explain by chemical equation how this process can be used to produce phenol on an industrial scale.

c. Outline the production of phenol from isopropylbenzene.

d. a. Explain how you would prepare naphthalene from succinic anhydride.

b. Provide the compounds denoted by letters A – H in the following chemical equations:



ORAFEMI AWOLOWO UNIVERSITY, ILORIN, NIGERIA
B.Sc. (CHEMISTRY) DEGREE EXAMINATION
ORGANIC, AROMATIC AND HETEROCYCLIC CHEMISTRY
MID-RAIN SEMESTER EXAMINATION 2005/2006 SESSION

AUGUST, 2006

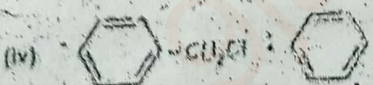
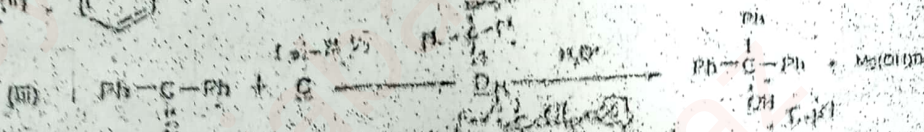
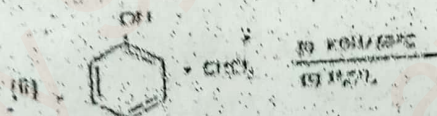
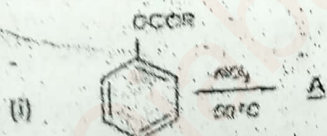
TIME ALLOWED: 1 H

INSTRUCTION: ANSWER ALL QUESTIONS.

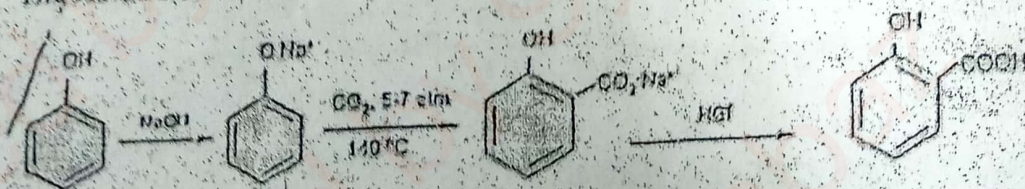
1 (a) Write the structure of each of the following compounds.

- (i) Acetylsalicylic acid (ii) Catechol (iii) Benzoinol
(iv) 1,4-Benzoquinone (v) Benzophenone (vi) trans-stilbene
(vii) Tolan (viii) Tritol (ix) β -Naphthol (x) Tetralin

Complete the following chemical equations by writing the structures of the lettered compounds.



The Kolbe-Schmitt reaction scheme for preparing salicylic acid is represented as:



Write a generally accepted mechanism for this reaction scheme.

2a. Write 2 chemical equations for the preparation of each of the following compounds:
(a) Indole (b) Thiophene (c) Furan (d) Pyrrole.

2b. State one example of their occurrence and one use in each case.

OBAFEMI AWOLOWO UNIVERSITY, ILE IFE, NIGERIA
 DEPARTMENT OF CHEMISTRY, FACULTY OF SCIENCE
 B.Sc. DEGREE (CHEMISTRY) EXAMINATIONS
 FIRST SEMESTER EXAMINATION, 2005/2006 SESSION

CHEM 306 - AROMATIC AND HETEROCYCLIC CHEMISTRY

SEPTEMBER, 2006

TIME ALLOWED: 2 HOURS

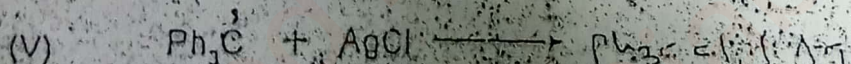
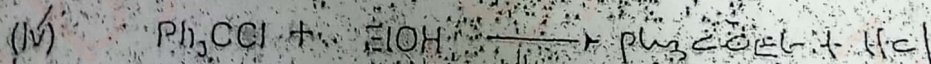
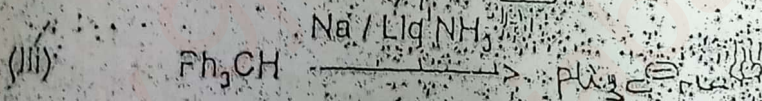
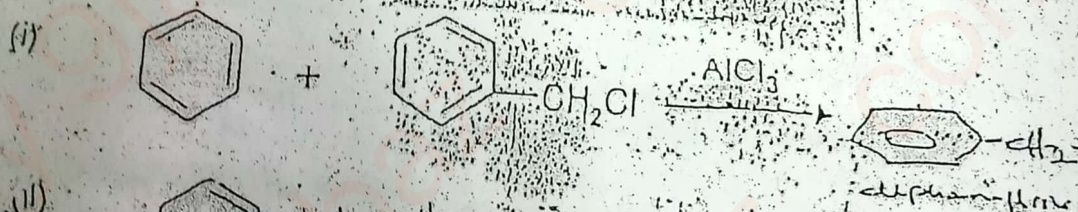
INSTRUCTION: Answer ALL questions.

1. (a) With the aid of structures and equations, explain why phenols are more acidic than alcohols.

(b) By means of equation(s) only, give the reaction of phenol with each of the following reagents:

- ✓ (i) Sodium hydroxide solution followed by iodomethane
- ✓ (ii) aqueous solution of bromine
- ✓ (iii) concentrated H_2SO_4 at $20^\circ C$
- ✓ (iv) Alkaline solution of formaldehyde in ratio 1:1 (Phenol: Formaldehyde)
- ✓ (v) t-butyl chloride in the presence of $AlCl_3$

(c) Draw the structures of the major product(s) of each of the following reactions:



2. (a) Outline, giving all reagents and experimental conditions, a procedure for the synthesis of 1-ethylphenanthrene, starting from naphthalene.

(b) For each of naphthalene, anthracene and phenanthrene, discuss the following:

ORAFEMI AWOLOWO UNIVERSITY, ILE IFE, NIGERIA
 DEPARTMENT OF CHEMISTRY, FACULTY OF SCIENCE
 B.SC. DEGREE (CHEMISTRY) EXAMINATIONS
 RAIN SEMESTER EXAMINATION, 2005/2006 SESSION

CHM 306 – AROMATIC AND HETEROCYCLIC CHEMISTRY

SEPTEMBER, 2006

TIME ALLOWED: 2 HRS

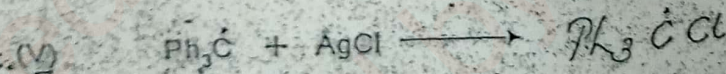
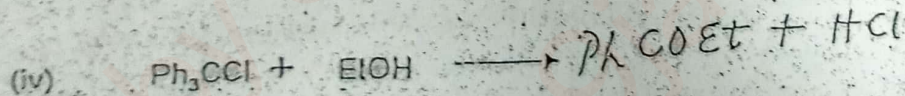
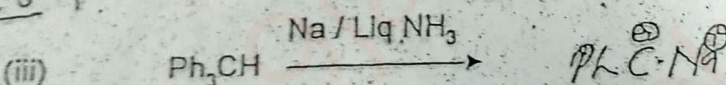
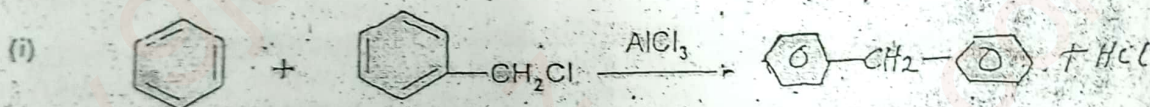
INSTRUCTION: Answer ALL questions

1. (a) With the aid of structures and equations, explain why phenols are more acidic than alcohols.

(b) By means of equation(s) only, give the reaction of phenol with each of the following reagents:

- Sodium hydroxide solution followed by iodomethane
- aqueous solution of bromine
- concentrated H_2SO_4 at 20°C
- Alkaline solution of formaldehyde in ratio 1:1 (Phenol: Formaldehyde)
- t-butyl chloride in the presence of AlCl_3

(c) Draw the structures of the major product(s) of each of the following reactions



2. (a) Outline, giving all reagents and experimental conditions, a procedure for the Haworth synthesis of 1-ethylphenanthrene, starting from naphthalene.

(b) For each of naphthalene, anthracene and phenanthrene, discuss the following reactions:

OBAFEMI AWOLowo UNIVERSITY, ILE-IFE
B.Sc (Chemistry) Degree Examination (Part III)
Rain Semester, 2006/2007 Session

December 2007

Time Allowed: 2 hours

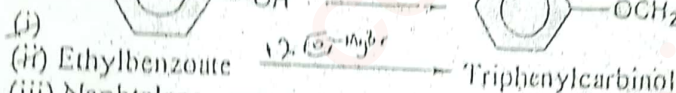
Instruction (i): (i) Answer ALL questions.

(ii) Each Section must be answered in separate answer booklet.

CHM 306: Aromatic Heterocyclic Chemistry

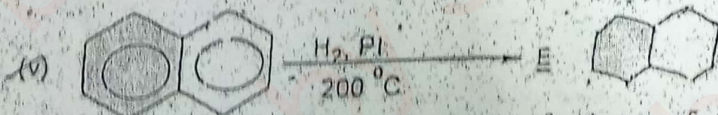
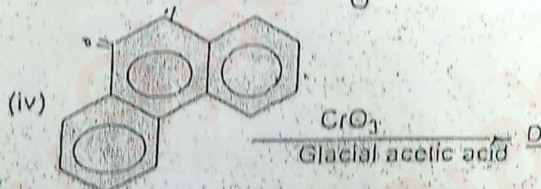
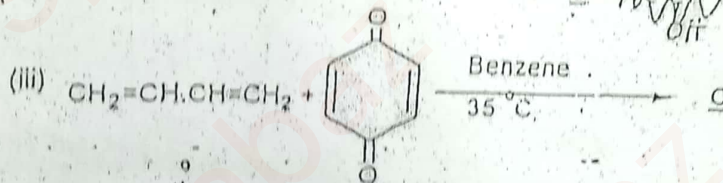
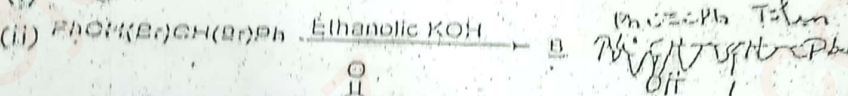
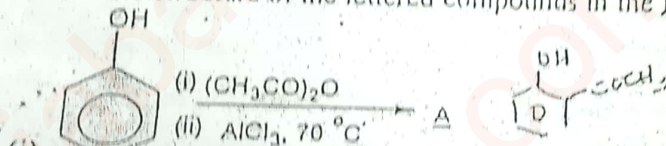
SECTION A

1. (a) Using Chemical equation only, show how you would effect each of the following conversion.

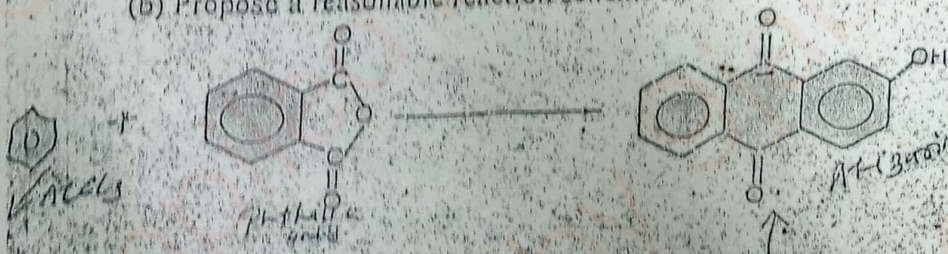


(b) Explain briefly why phenol is more acidic than cyclohexanol

2. (a) Draw the structure of the lettered compounds in the following reactions.



(b) Propose a reasonable reaction scheme for the transformation.



(a) Draw the structure of the following compounds.

(i) Acetylsalicylic acid (aspirin)

(ii) p-Benzoquinone

(iii) Fluorene

(iv) Trans-stilbene

(v) Endoanthracenemaleic anhydride

SECTION B

(a) What are alkaloids?

(b) Give two examples of named heterocyclic containing alkaloid compounds.

(c) Using chemical equations ONLY discuss the chemistry of quinoline with respect to the following:

(i) Synthesis

(ii) Oxidation

(iii) reduction

(iv) Ozonolysis

(v) substitutions

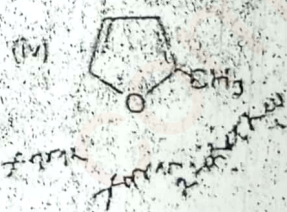
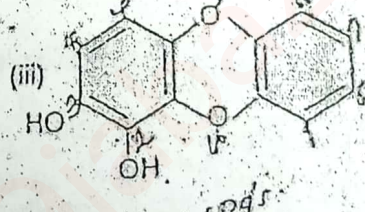
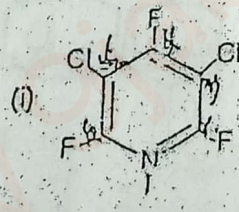
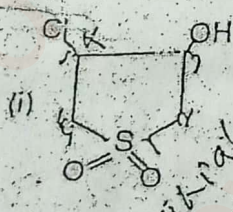
(vi) action with sodamide

Note: Credit is given to correct reaction conditions and products; (20 marks).

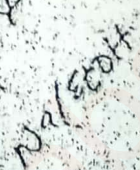
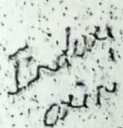
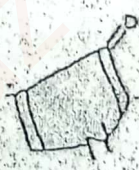
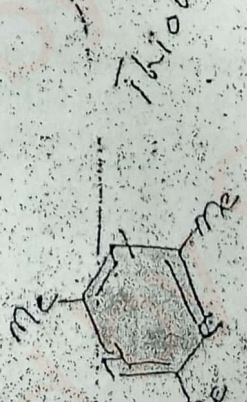
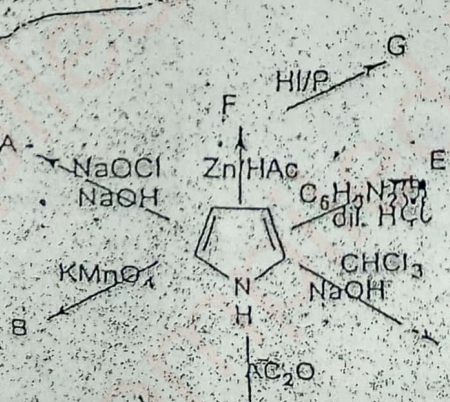
(i) Give two methods of synthesis of indole.

(ii) Using ONE chemical equation only, justify this statement "pyrrole shows a number of resemblances to phenols and aromatic amines."

(b) Supply the IUPAC names of these heterocyclic compounds.



(c) Give the structure(s) of the product(s) of the lettered following reactions of pyrrole.



Instruction(s): (i) Answer ALL questions.

(ii) Each Section must be answered in separate answer booklet.

CHM 306: Aromatic Heterocyclic Chemistry

SECTION A

1. (a) Using Chemical equation only, show how you would effect each of the following conversion.



(i)

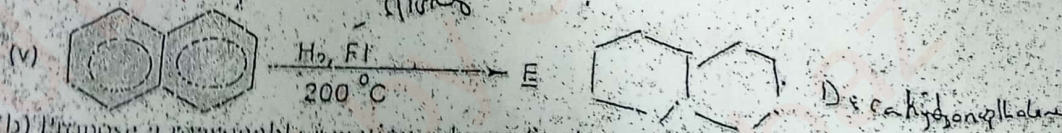
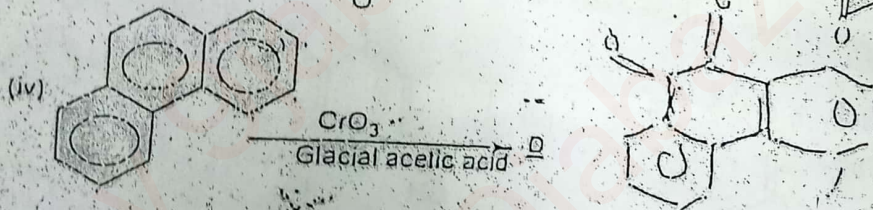
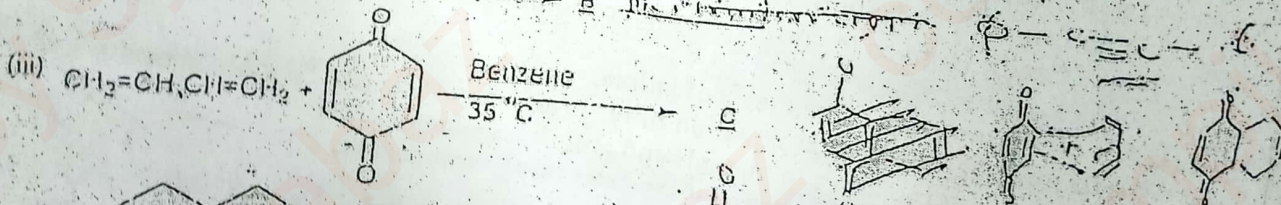
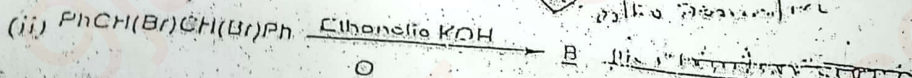
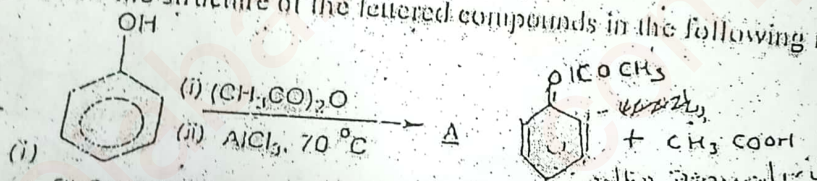
(ii) Ethylbenzoate

(iii) Naphthalene

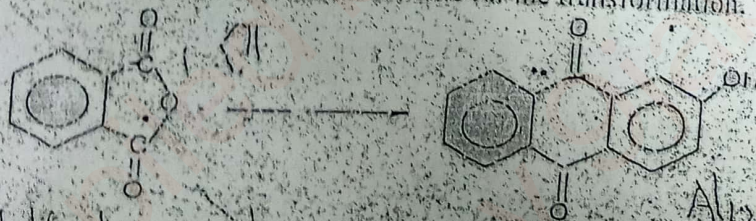
(ii) Ethylbenzoate $\xrightarrow{\text{LiAlH}_4}$ Triphenylcarbinol
(iii) Naphthalene $\xrightarrow{\text{LiAlH}_4}$ 3-ethylphenanthrene
(b) Explain-briefly why phenol is more acidic than ethanol.

(b) Explain-briefly why phenol is more acidic than cyclohexanol

2. Draw the structure of the lettered compounds in the following reactions.



(b) Propose a reasonable reaction scheme for the transformation.



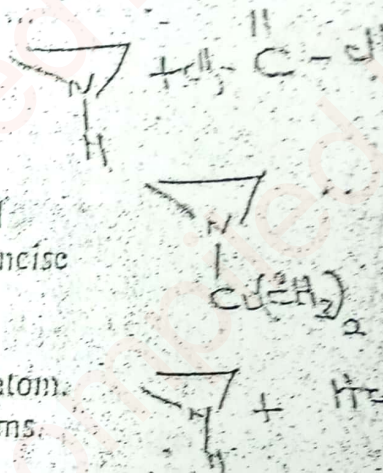
UNIVERSITY OF ILORIN, ILORIN, NIGERIA
 DEPARTMENT OF CHEMISTRY, FACULTY OF SCIENCE
 2007/2008 EXAM MID-SEMESTER TEST
 CHEM 306 - AROMATIC AND HETEROCYCLIC CHEMISTRY

NOVEMBER 2008

Attempt all Questions

TIME: 1 HOUR

1. Give the structures of the products formed when aziridine reacts with (i) ethyl acetate and (ii) hydrogen chloride (HCl)

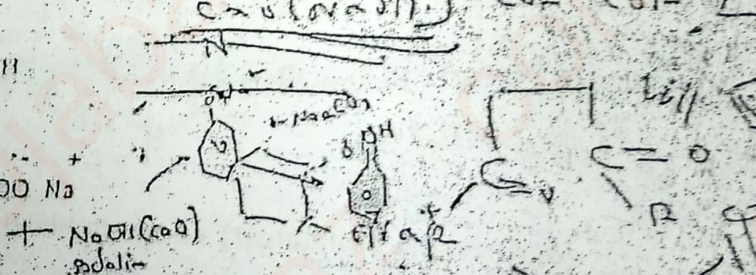
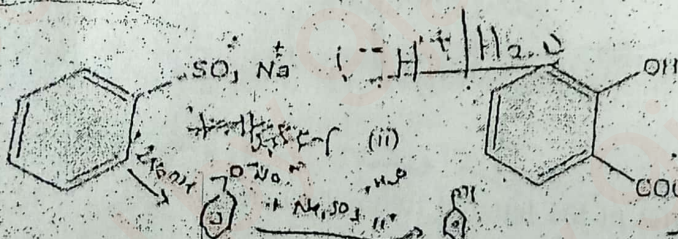


2. Knorr synthesis of furan involves the cyclization of 1,4-dicarbonyl with loss of water upon heating with dehydrating agents. Give a concise mechanism involved in this reaction.

3. Give the names of the five-membered ring heterocycles with one heteroatom. Electrophilic attack preferentially takes place on their α -carbon atoms.

4. Compare the basicities of pyrrole and pyridine, hence their reactions with HCl.

Handwritten notes: Pyrrole is more basic than pyridine. It uses 2 p-electrons in the ring system, hence it is more stable. Pyridine uses 2 s-orbitals in the ring system, hence it is less stable.
 Mechanism for pyrrole + HCl:
c1cc[nH]1 + HCl -> [c1cc[nH+]1].[Cl-]

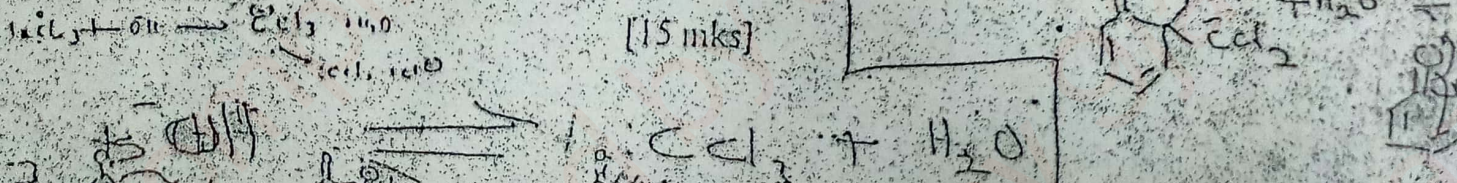


5. Give the structures of the following compounds:

(i) Salicylic acid (ii) o-Benzoquinone (iii) Tritol (iv) Trans-stilbene



6. Give the generally accepted mechanism for the formylation of phenol using an aqueous solution of chloroform at 60 °C, followed by acidification with sulphuric acid (Reimer-Tiemann Reaction).



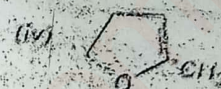
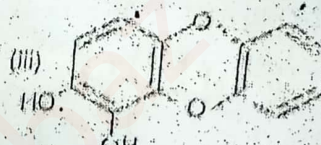
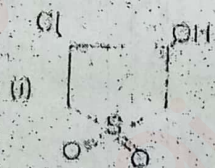
- (c) Draw the structure of the following compounds:
- Acetylsalicylic acid (aspirin)
 - o-Benzquinone
 - Eluorene
 - Trans-stilbene
 - Endomethanoneanilic anhydride

SECTION II

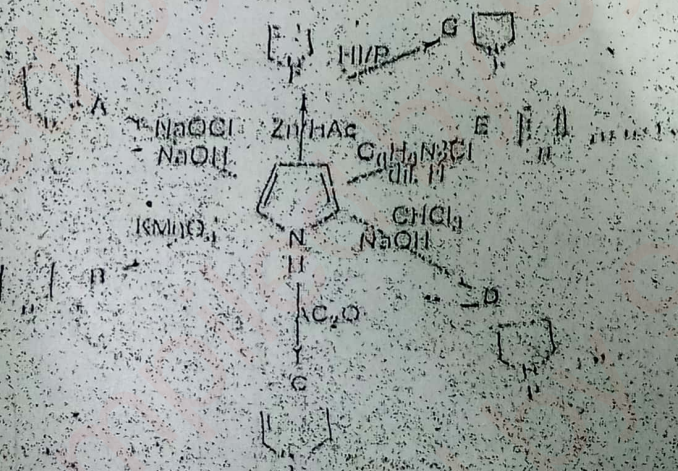
- What are alkaloids?
- Give two examples of named heterocyclic containing alkaloid compounds.
- Using chemical equations ONLY discuss the chemistry of quinoline with respect to the following:
 - Synthesis
 - Oxidation
 - reduction
 - Ozonolysis
 - substitutions
 - action with acidamide

Notes: Credit is given to correct reaction conditions and products; (20 marks)

- Give two methods of synthesis of indole.
 - Using ONE chemical equation only, justify this statement "pyrrole shows a number of resemblances to phenols and aromatic amines."
 - Supply the IUPAC names of these heterocyclic compounds.



- Give the structure(s) of the product(s) of the lettered following reactions of pyrrole.

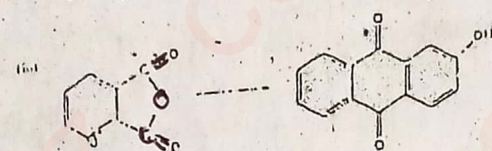
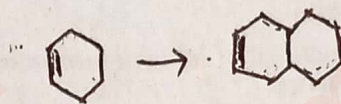


Section B

Draw the structure of each of the following compounds.

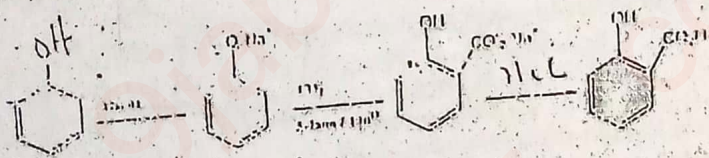
- (i) Bibenzyl, (ii) Entane, (iii) p-Benzoquinone, (iv) 9,10-anthraquinone and (v) Enchianthracene maleic anhydride

Write a reasonable reaction scheme for each of the following conversions:



Give all reagents and experiment conditions in each case.

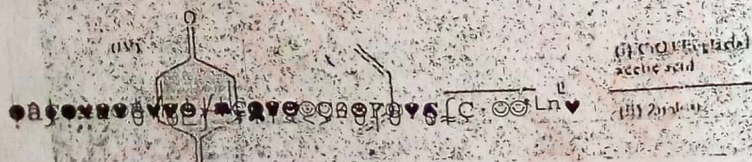
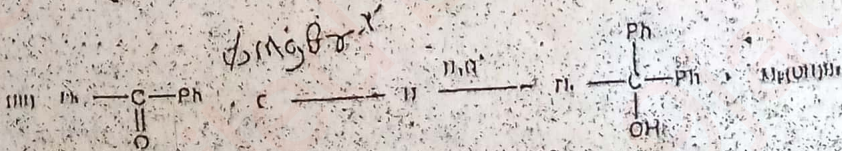
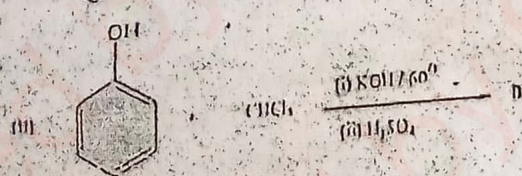
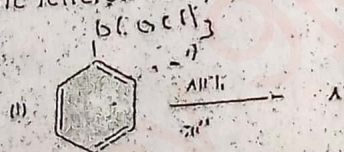
a. The Kolbe schidmit reaction scheme for the synthesis of salicylic acid [a precursor to aspirin] is represented as:



Write a generally accepted mechanism for this reaction scheme.

Write a chemical equation to show how salicylic acid is converted to aspirin.

Complete the following chemical equations by writing the structure of the lettered compounds.



PROFESSOR RAIN SEMESTER TEST
CHM 306: AROMATIC AND HETEROCYCLIC CHEMISTRY

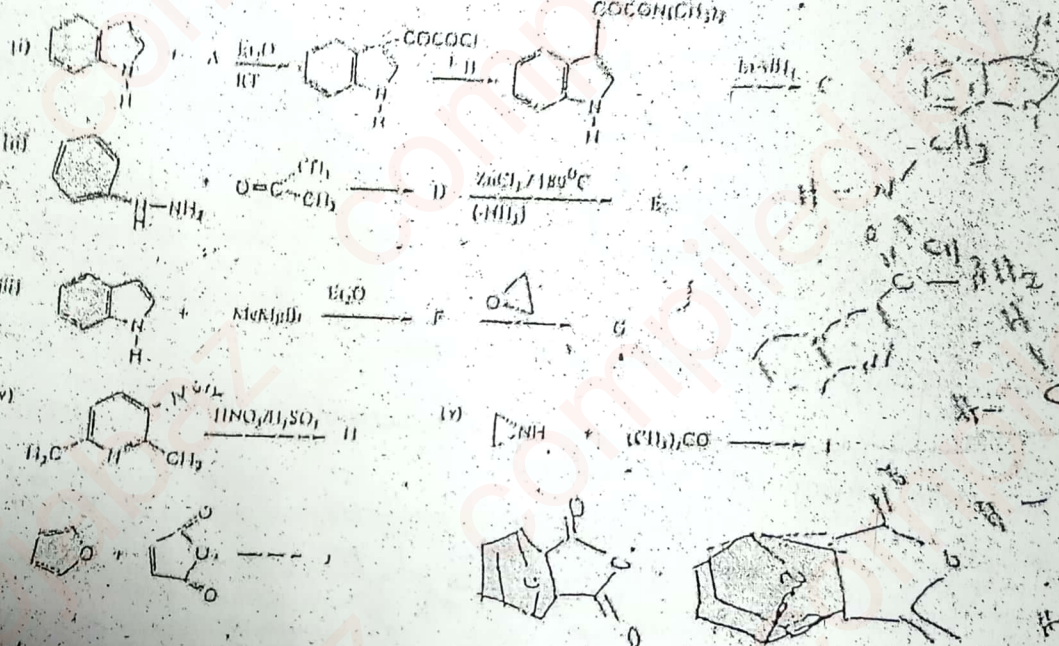
OCTOBER 2008

TIME: 2 HOUR

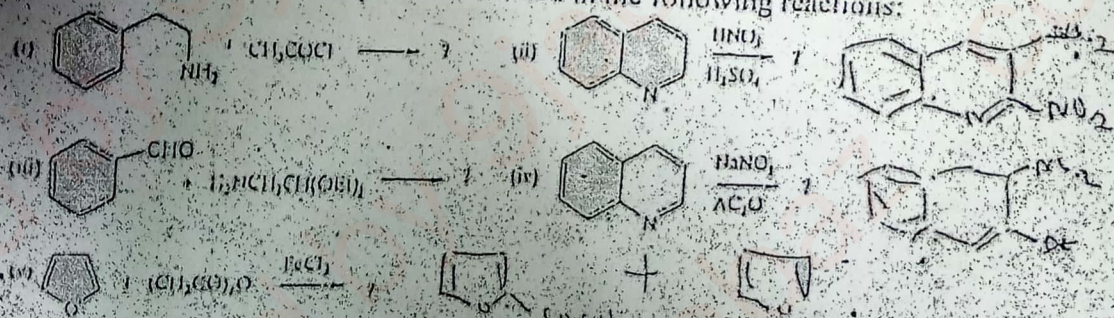
Instruction: Attempt all Questions. Answer the two sections in separate bindlets

Section A

- 1a. Outline the mechanism for Skraup synthesis of quinoline
b. Complete the following equations by writing the structures of lettered compounds:



- 2a. Give the equation of the reaction by which you would obtain indole starting with aniline and 3-hydroxybutan-2-one. Outline the mechanism of this reaction
b. Briefly describe appropriate reactions to justify the following statements:
(i) 2-hydroxyindole exists mainly as the amide while 3-hydroxyindole exists as enol tautomer with appreciable enol content.
(ii) The methyl protons of 2-methyl quinoline are acidic.
c. Give the structures of the products formed in the following reactions:



- d. Give the structure of the following compounds:
(i) Chloroquinoline; (ii) Nicotinic acid; (iii) Skatole; (iv) α -Picoline and
(v) 5-methyl-1,3-oxazole

INSTRUCTION: ANSWER ALL QUESTIONS

1. State two methods of synthesising in each case, for the following:

- (i) Furan (ii) Thiophene
(iii) Pyrrole (iv) Indole

b. Give the following reactions of each of them: (a) Halogenation
(b) Sulphonation
(c) Nitration

c. Discuss the physical properties of each of them.

d. Give five examples of the occurrence of indole

2a. Write short notes on the following:

(i) Effect of a ring substituent on the acid strength of phenols

(ii) Reactivity of the Hydroxy group in phenol

(iii) Reactions of: (a) Chloroform
(b) Carbon dioxide

(c) Formaldehyde with phenol giving their respective reaction mechanisms.

(d) Quinones

b. Outline, giving all reagents and experimental conditions, a procedure for the synthesis of a pure sample of triptophan using Gabriel's synthesis and starting from benzophenone and butadiene.

3a. State two methods of preparing, in each case of the following compounds:

(i) Triphenylmethylchloride both from benzene

(ii) Trans-stilbene, both from benzaldehyde

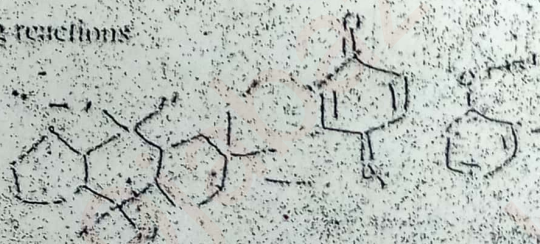
(iii) Triphenylethanol, both from benzaldehyde

b. Discuss, in each case, the following reactions

- (a) Nitration
(b) Sulphonation
(c) Halogenation and
(d) Reduction
(e) Oxidation

of the following

(i) Naphthalene



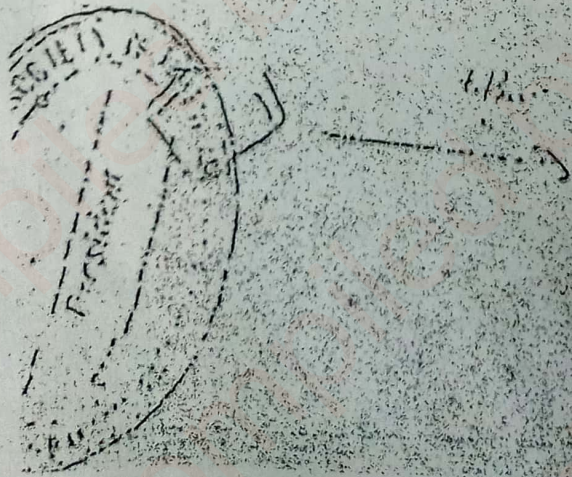
- (ii) Anthracene
- (iii) Phenanthrene

c. Outline, in each case, the method of synthesizing of the following compound

- (i) 3,8-dimethylnaphthalene
- (ii) 2-Methyl-9-phenylanthracene
- (iii) 3-methyl-9-phenyl-10-Carboxylic acid

phenanthrene

Anthracene
3-methylanthracene
10-carboxylic acid



OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE, FACULTY OF SCIENCE

CHEMISTRY DEPARTMENT

B.Sc. Degree Examination, 2008/09 Rain Semester

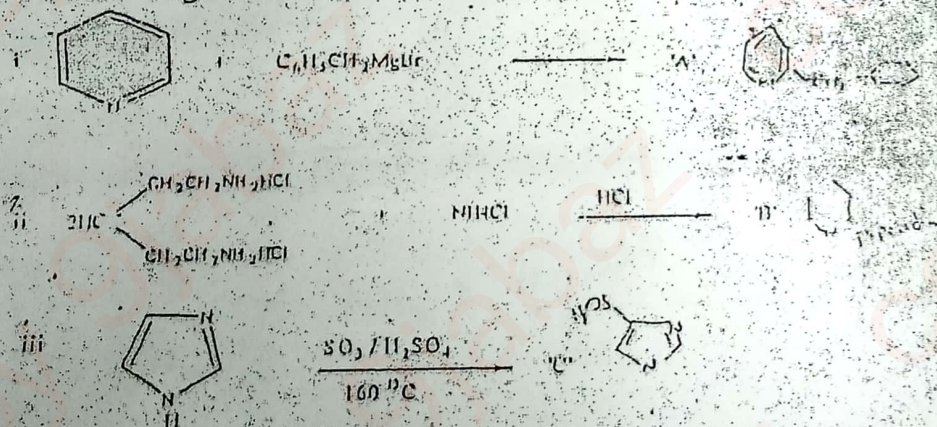
CHM 306- HETEROCYCLIC NITROGEN COMPOUNDS

INSTRUCTION: Attempt ALL Questions.

Time: 1 Hr

1. Give the various charged canonical (resonance) structures for pyrrole and pyridine.
(b) From the above structures, briefly compare the reactivity of pyrrole and pyridine towards electrophilic substitution reaction.
2. Arrange the following heterocyclic nitrogen compounds in order of increasing basicity, with reasons: Pyridine; pyrrole; pyrazole and imidazole.
3. Imidazole can be prepared from α -halocarbonyl compound in the presence of ammonia and formamide.
(a). Give equation for the above reaction.
(b). Illustrate mechanism for the above reaction.

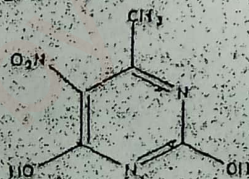
4(a). Complete the following reaction equations:



(b) Give the name of the following compounds:



2-phenylpyridine



2,4,6-trihydroxy-5-methylpyrimidine
+ Guanine (Cytosine)



1-methyl-2-(pyridin-2-yl)pyrrole

OBAFEMI AWOLOWO UNIVERSITY, AILE-IKE, NIGERIA
DEPARTMENT OF CHEMISTRY, FACULTY OF SCIENCE
2012/2013 RAIN MID-SEMESTER TEST

CHEM 306 - AROMATIC AND HETEROCYCLIC CHEMISTRY

MARCH 26, 2014

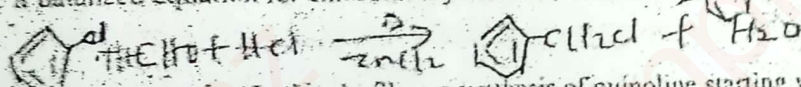
TIME: 1 HOUR 45 MIN

Instruction: Attempt all Questions. Answer the two sections in separate booklets

a. Write the mechanism for the synthesis of allylbenzene by Friedel-Crafts alkylation.

b. (i) What is Ellmann reaction? (ii) Give an example: *is a pyrimidinyl nucleoside*

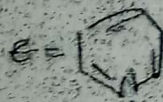
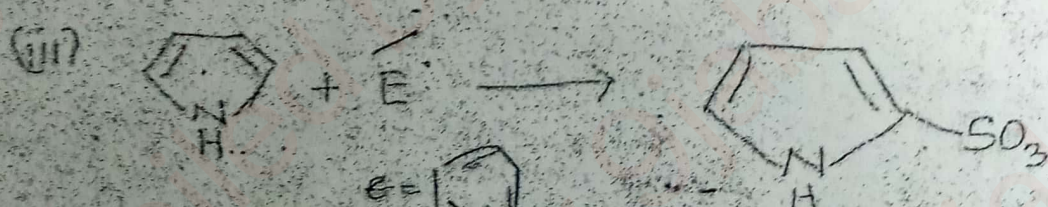
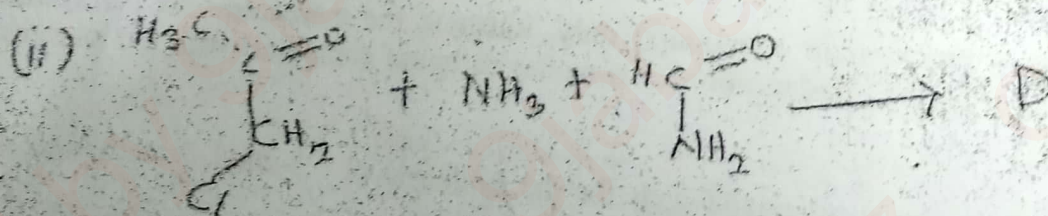
c. Write a balanced equation for chloromethylation of benzene.



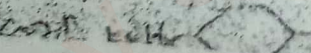
2a. Outline the steps involved in the Skraup synthesis of quinoline starting with glycerol on appropriate arylamine, showing the mechanism of each reaction step

b. Give equations to illustrate the conversion of isatin to (i) Sodium isatinate (ii) Anthranilic acid and (iii) Indophenine

c. Complete the following equations by writing the structures of lettered compounds:



Pyridinium Sulphonate



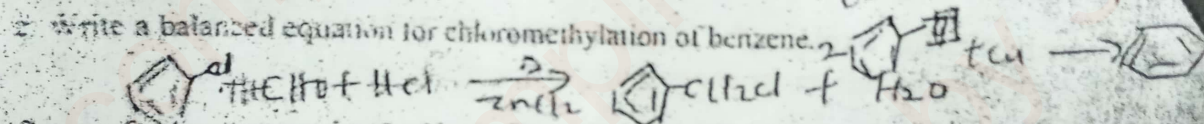
DEPARTMENT OF CHEMISTRY, FACULTY OF SCIENCE
2012-2013 RAIN MID-SEMESTER TEST
CHEM 306 - AROMATIC AND HETEROCYCLIC CHEMISTRY

MARCH 26, 2014

TIME: HOUR 4:50

Instruction: Attempt all Questions. Answer the two sections in separate booklets

1. (i) Write the mechanism for the synthesis of alkylbenzene by Friedel-Craft alkylation.
(ii) What is Hellmann reaction? (iii) Give an example. *is a rearrangement reaction*



2 a. Outline the steps involved in the Skraup synthesis of quinoline starting with glycerol and appropriate arylamine, showing the mechanism of each reaction step

b. Give equations to illustrate the conversion of isatin to (i) Sodium isatinate (ii) Anthranilic acid and (iii) Indophenine

c. Complete the following equations by writing the structures of lettered compounds:



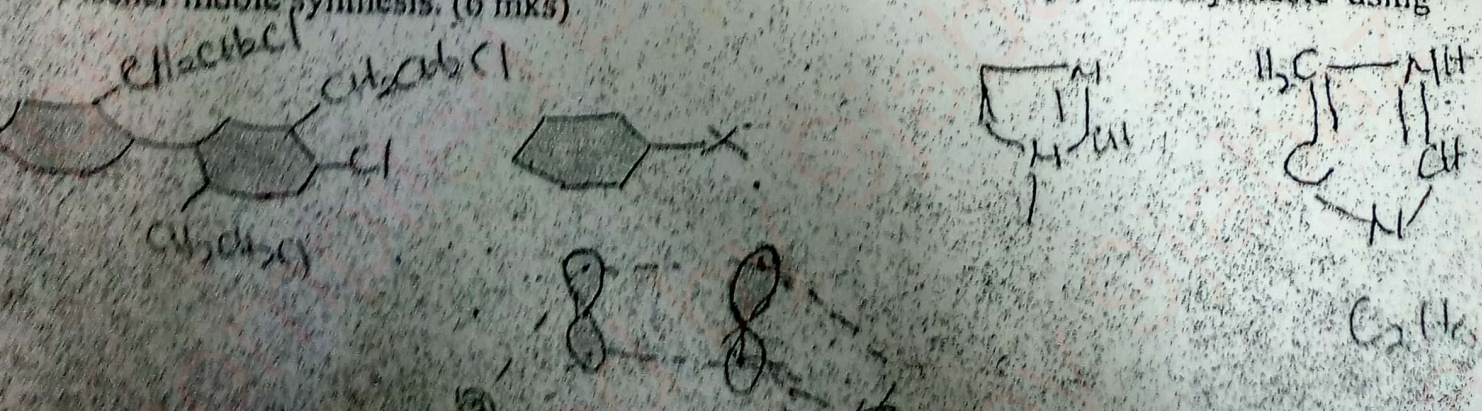
DEPARTMENT OF CHEMISTRY
OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE, NIGERIA.

2014/2015 RAIN MID-SEMESTER EXAMINATION
CIIM 306: AROMATIC AND HETEROCYCLIC CHEMISTRY

INSTRUCTION: Attempt ALL questions
Date: 8th February 2016

Time Allowed: 60 minutes

- What is the mechanism for the synthesis of alkyl benzene by Friedel-Craft alkylation? (6 mks)
 - Diagrammatically explain the double bond character of carbon-halogen bond in arylhalides. (3 mks)
 - Write the structures of the following compounds (i) Dichlorodiphenyltrichloroethane (ii) adrenalin. (2 mks)
 - Write a balanced equation for the action of phosphorus pentachloride on benzyl alcohol. (2 mks)
 - What are the reagents and product (s) of direct oxidation of o-xylene? (2 mks)
- Name and give the structure of any two naturally occurring nitrogen heterocyclic compounds containing the basic skeleton of (i) pyrrole and (ii) imidazole. (4 mks)
 - Using appropriate equation(s) only, illustrate the mechanism for the synthesis of imidazole by the condensation of α -amino carbonyl compound with a thiocyanate ion. (6 mks)
 - Illustrate the mechanistic path for the synthesis of 3-ethyl, 2-methylindole using Fischer Indole synthesis. (6 mks)



DEPARTMENT OF CHEMISTRY
OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE, NIGERIA.

2014/2015 RAIN SEMESTER EXAMINATION

CHEM 306: AROMATIC AND HETEROCYCLIC CHEMISTRY

INSTRUCTIONS:

(i) Question 1 is compulsory

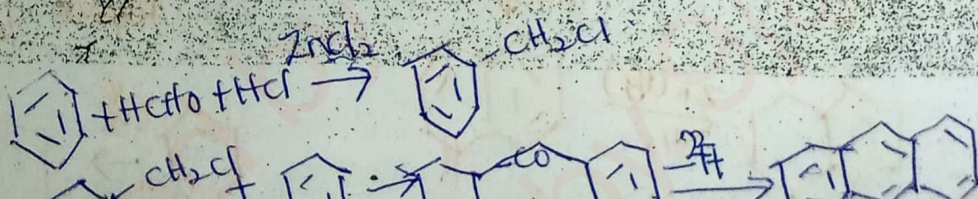
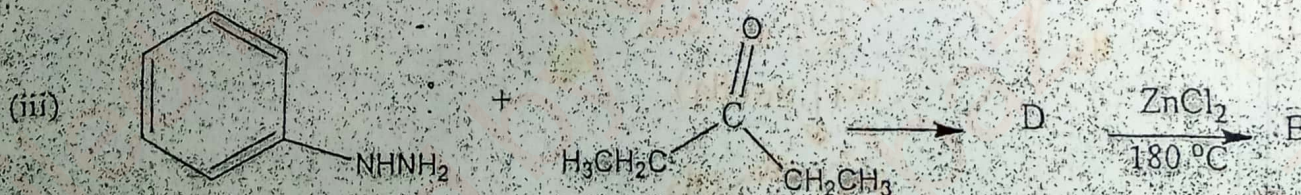
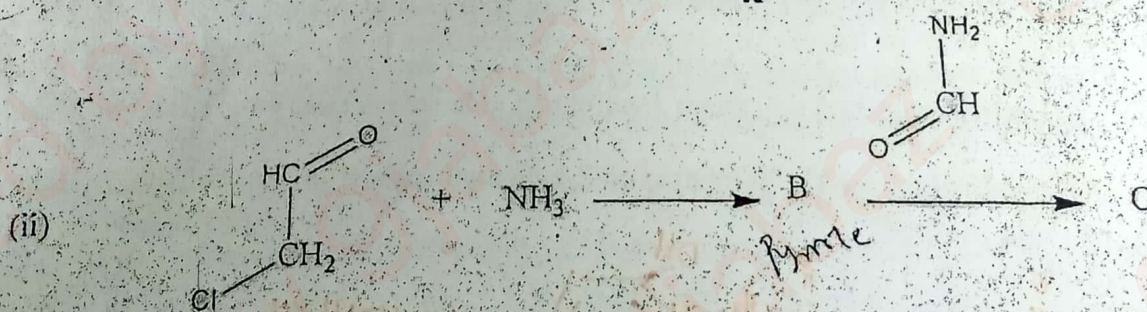
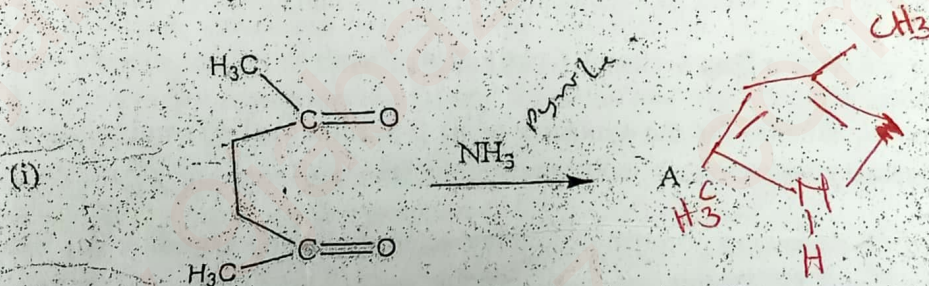
(ii) Answer any three questions from questions 2 to 5

(ii) Answer questions 1, 2 and 3 in one booklet and questions 4 and 5 in another booklet.

Time Allowed: 1 hr 20 minutes

1.a. Outline the synthesis of 9,10-dihydroanthracene using methanal as one of the starting materials. (5 mks)

b. Complete the following equations by writing the structures of the lettered compounds: (5 mks)





Handwritten notes and symbols at the top of the page, including some chemical symbols and mathematical notations.

2. a. Write the structures of the following compounds; dichlorodiphenyltrichloroethane, adrenalin, triphenyl methane, triphenyl carbinol and gamma-phenyl butanoic acid. (5 mks)

b. (i) Write a balanced equation for the decarboxylation of *p*-bromobenzoic acid (2 mks).

(ii) What is/are the product(s) of chlorination of ethylbenzene at room temperature and at boiling? (2 mks)

c. Outline the synthesis of 1-bromobenzene from isopropylbenzene (6 mks)

d. Explain by chemical equation how you would prepare anthracene from benzyl alcohol. (6 mks)

3. a. Illustrate by equations the synthesis of 2-naphthol from succinic anhydride. (15 mks)

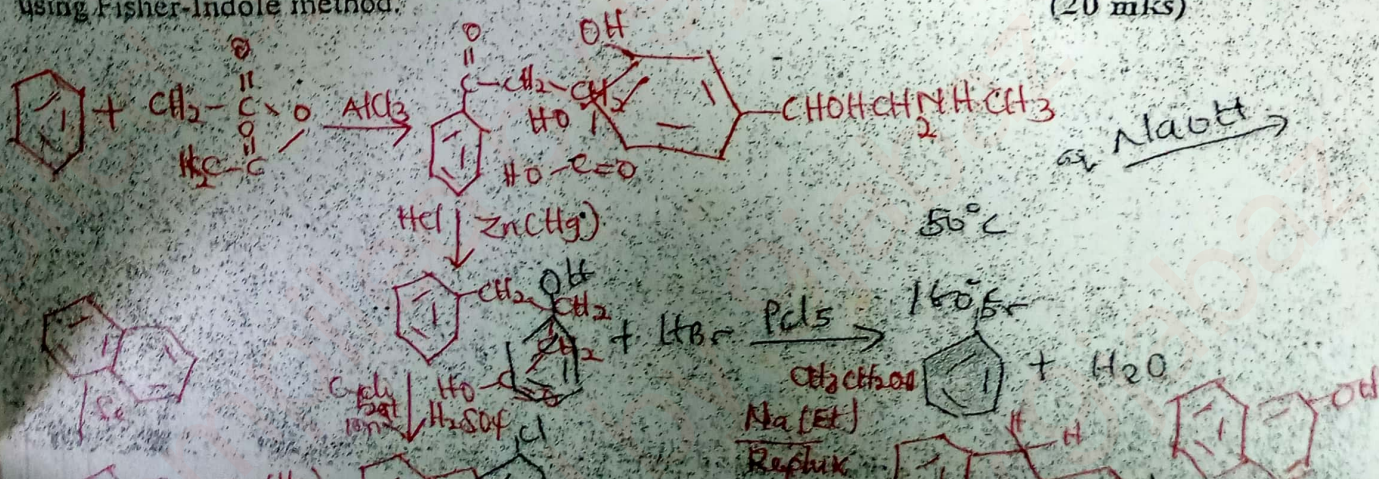
b. How would you prepare tetralin from 4-phenyl-1-butene? (5 mks)

4. a. Give the reaction equation(s) for the synthesis of (i) β -picoline and (ii) quinoline from acrolein, indicating necessary reagent(s) and reaction condition(s)

b. Give the structure of the following nitrogen-containing heterocycles: (i) Lepidine (ii) Skatole (iii) Chloroquine (iv) Isatin and (v) Antipyrine. (20 mks)

5. a. Illustrate the reaction-pathway for the synthesis of 4-methyl-2-quinolone from a β -keto ester. Freely use other reagent(s) you deem needful and indicate necessary reaction condition(s)

b. Outline the mechanism for the synthesis of 2,3-diethylindole starting with phenylhydrazine using Fisher-Indole method. (20 mks)



CHM 306: AROMATIC AND HETEROCYCLIC CHEMISTRY

TIME ALLOWED: 2 hours

DATE: March, 2013

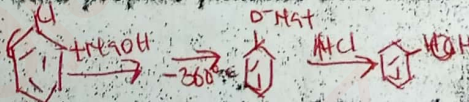
INSTRUCTION: (i) Answer two questions in each section.

(ii) Answer each section in separate booklets.

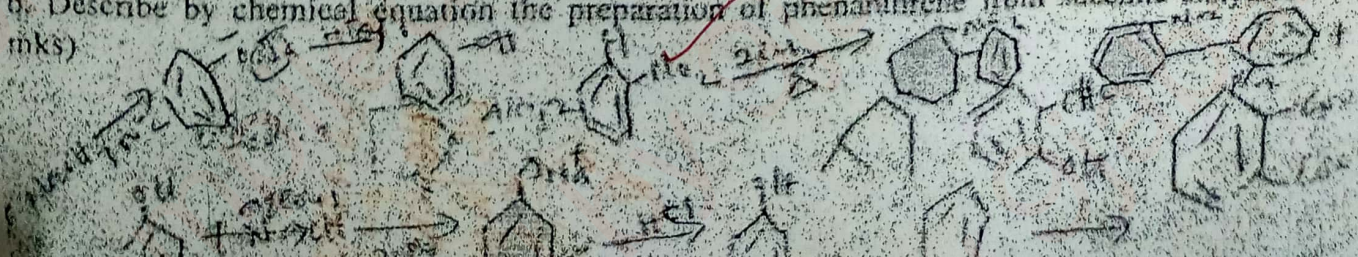
SECTION A

1. a. (i) Write the structures of the following compounds: ethynyl benzene, diphenylmethane, 1,1-dimethyl-2-vinylbenzene. (3 mks)
- (ii) Write a balanced equation for the synthesis of benzoic acid from styrene. (5 mks)
- b. (i) Diagrammatically explain the double bond character of carbon-halogen (C-X) bond in arylhalides. (3 mks)
- (ii) What are the conditions for the arylhalides to undergo nucleophilic substitution reaction? (2 mks)
- (iii) Which condition would make nucleophilic substitution reaction of the arylhalides be comparable to that of the alkylhalides? (1 mks)
- c. Under what condition would aryl bromide and aryl chloride undergo Ullmann reaction? Give an example. (3 mks)
- d. What is the product obtained when benzyl chloride is treated with sodium metal? Write a balanced equation for the reaction. (3 mks)

2. a (i) What is Dow Process? (1 mks)
 (ii) Explain using chemical equation the preparation of phenol using Dow process. (4 mks)
 b. Outline the synthesis of salicylaldehyde from isopropyl benzene. (6 mks)
 c. Explain by chemical equation how you would prepare phthalic acid from 4-phenyl-3-butenol acid. (9 mks)



3. a. (i) Sulphonation of naphthalene yields two products, which of the products is more stable and why? (2 mks)
- (ii) If the two products in (i) are treated with NaOH at high temperature, what are the products? (1 mks)
- b. Describe by chemical equation the preparation of phenanthrene from succinic anhydride. (1 mks)



SECTION B

5. a. Illustrate the mechanistic path for the synthesis of 3-ethyl-2-methylindole using Fischer Indole synthesis. 12 mks

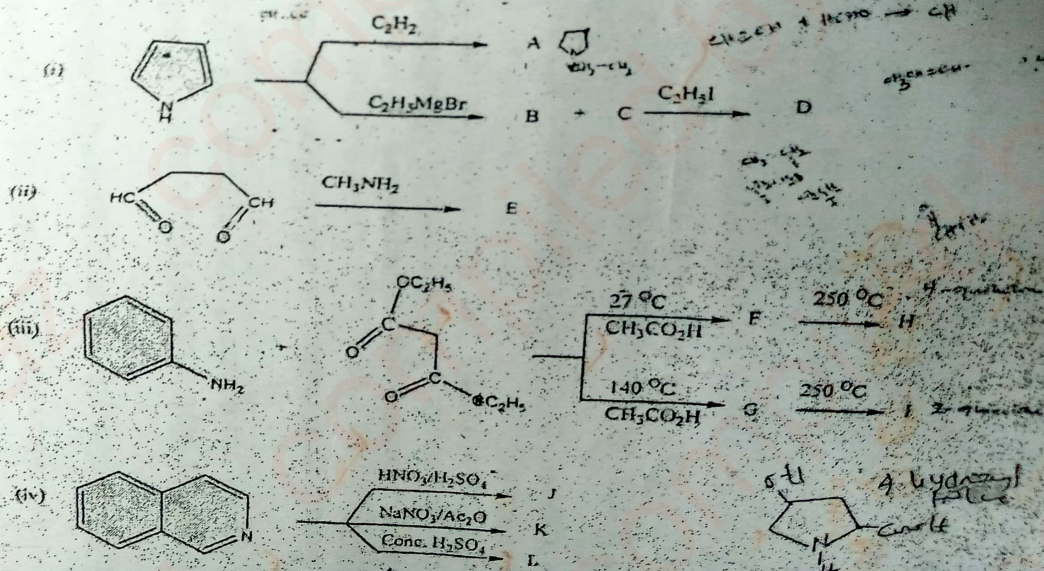
b. Using (i) the resonance (canonical) structures and (ii) nitration reaction, justify the chemical information that pyrazole is less susceptible to electrophilic substitution reaction than pyrrole. 10 mks

5. a. Give the equation for the reaction of methanal and ethyne to form pyrrole. Indicate necessary reaction condition(s). 6 mks

b. Outline the Skraup synthesis of quinoline using glycerol as source of $\alpha - \beta$ unsaturated carbonyl compound (acrolein). 16 mks

6. a. Arrange the following heterocyclic nitrogen compounds in order of increasing basicity: pyrrole, imidazole and pyrazole. 2 mks

b. Complete the following chemical equations by writing the structures of lettered compounds:



DEPARTMENT OF CHEMISTRY
OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE, NIGERIA.

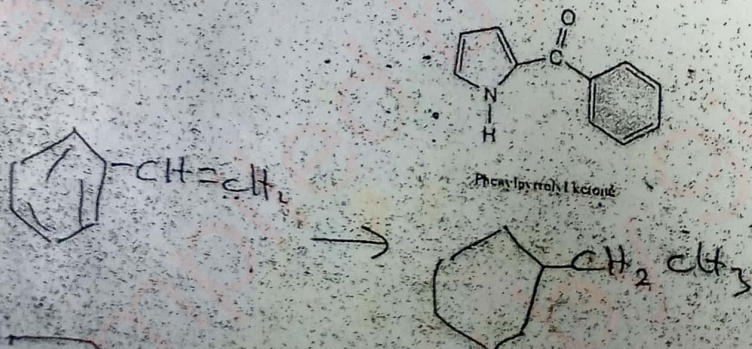
2015/2016 RAIN MID-SEMESTER EXAMINATION
CHM 306: AROMATIC AND HETEROCYCLIC CHEMISTRY

INSTRUCTION: Attempt ALL questions

Time Allowed: 50 minutes

Date: 15th February 2017

1. (a) How would you prepare ethylcyclohexane from ethenylbenzene? (5 mks)
(b) What is/are the product(s) of chlorination of ethylbenzene at room temperature and a boiling? (2 mks)
(c) Write a balanced equation for chloromethylation of benzene. (3 mks)
(d) Outline the synthesis of salicylaldehyde from isopropyl benzene. (6 mks)
2. (a) Give the resonance canonical structures for (i) pyrrole and (ii) pyrazole. Compare the ease of electrophilic substitution in the above nitrogen heterocycles.
(b) Pyridine is less susceptible to electrophilic substitution reaction than imidazole. Justify the above chemical information. *Pyrrrole, Pyridazole, Imidazole*
(c) Arrange the following nitrogen heterocycles in increasing order of basicity. Briefly explain your arrangement.
(d) Give a simple reaction scheme for the synthesis of phenyl pyrrolyl ketone from pyrrole through nucleophilic substitution pathway with ethane as the main organic side-product. You may freely use other possible chemical reagent(s) you consider needful.





OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE, NIGERIA
DEPARTMENT OF CHEMISTRY

B.Sc. Degree (Chemistry) Examination Part III
CHM 306: AROMATIC AND HETEROCYCLIC CHEMISTRY
Rain Semester Examination 2018/2019 Session

Time Allowed: 2½ Hours

Date: 18th December, 2019

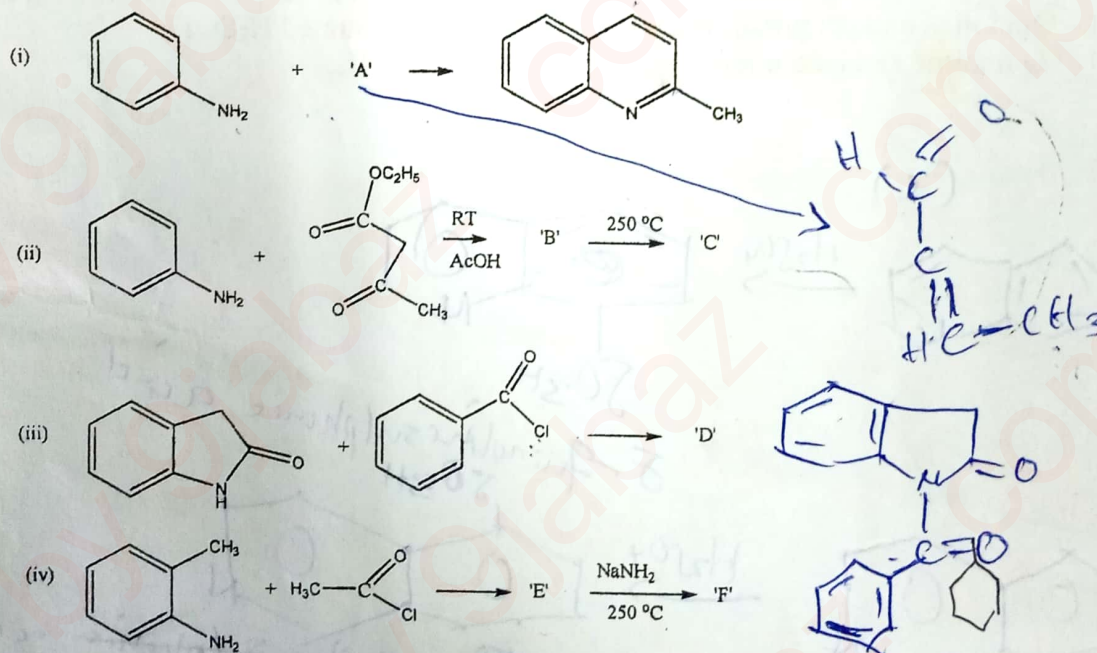
Instructions:

- (i) Question 1 is compulsory.
(ii) Answer any three questions from questions 2 to 5.

SECTION A

1. a. (i) Mention the coal oxidative product from which aromatic compounds can be obtained,
(ii) Outline a typical Bardhan-Sengupta synthesis of phenanthrene.

b. Complete the following reaction equations by writing the structures of lettered compounds:



SECTION B

2. a. How can you distinguish benzyl chloride from chlorotoluenes using chemical method. Write balanced equations for the reactions involved.
b. (i) Which is more stable between 1-naphthalenesulphonic acid and 2-naphthalenesulphonic acid? (ii) State the reason for your answer in b(i).
(iii) Describe by chemical equation(s) the preparation of 1-naphthalenesulphonic acid from 4-phenyl-3-butenic acid.
(iv) Write a balanced equation for the conversion of 2-naphthalenesulphonic acid to 2-naphthol.

3. a. Describe by chemical equation(s) the preparation of diphenylmethane using methanal as one of the starting materials

b. Explain by chemical equation(s) the synthesis of phthalic acid from β -benzoyl propanoic acid.

4. a. Give the name and structure of the compound that would be formed from allowing 2,5-hexadione to react with methyl amine according to Paal-Knorr synthesis.

b. Outline the mechanism for the reaction in 4a above.

c. Nitrogen heterocyclic compounds consist of different classes. Give the names and structures of any:

(i) Two members of fused heterocyclic compounds

(ii) Two members of azole class

(iii) One member of azine class

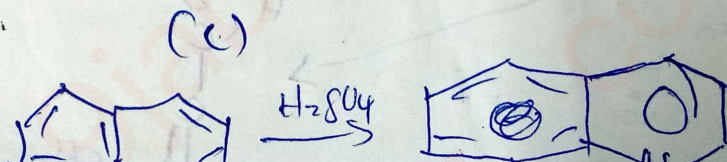
5. a. Give the name and structure of the final product that would be formed if phenylhydrazine first react with 3-pentanone and the resulting intermediate is heated with zinc chloride at about 180°C .

b. Outline the mechanism of the reaction in 5a above.

c. Give the names and structures of the products formed in each of the following reactions:

(i) Quinoline and isoquinoline each treated with concentrated H_2SO_4 .

(ii) Quinoline and isoquinoline each treated with KMnO_4 .



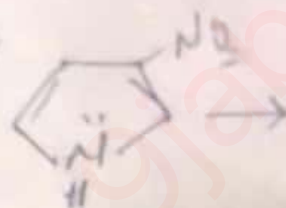
DEPARTMENT OF CHEMISTRY
OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE, NIGERIA.

2018/2019 RAIN MID-SEMESTER EXAMINATION
CHM 306: AROMATIC AND HETEROCYCLIC CHEMISTRY

INSTRUCTION: Attempt ALL questions

Time Allowed: 40 minutes

Date: 18th October 2017



1. a. Outline the synthesis of benzoic acid using benzene as one of the starting materials.
 - b. Diagrammatically explain why the C-X bond in aryl halides is stronger than C-X in alkyl halides.
 - c. Explain by chemical equation(s) how you would produce 1-bromo benzene from isopropyl benzene.
 - d. Write the structure of adrenalin.
2. a. If the product of the reaction of phenylhydrazine and propanaldehyde were heated at about 180°C in acidic medium of ZnCl_2 , give the name and structure of likely final product(s).
 - b. (i) Give all possible resonance canonical structures for pyrrole and pyrazole.
 - (ii) With reference to the resonance structures above, briefly discuss the chemistry of electrophilic substitution in pyrrole and pyrazole using only nitration reaction as example.

(40)

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B.Sc. (CHEMISTRY) DEGREE EXAMINATION

2019/2020 Rain Semester

CHM 306: AROMATIC AND HETEROCYCLIC CHEMISTRY

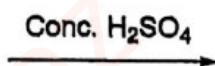
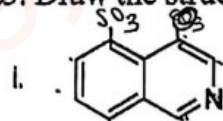
TIME ALLOWED: 2 hours

DATE: October 04, 2021

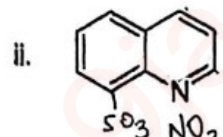
Instructions: Write your Name and Registration Number. Also append your signature on your answer scripts.

ATTEMPT ALL QUESTIONS

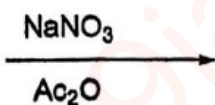
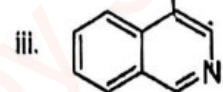
1. (a) Outline the synthesis of benzoic acid from the following compounds
(i) acetophenone (ii) styrene.
(b) Explain by chemical equation(s) the production of bromobenzene from isopropyl benzene.
(c) Compare and contrast Wurtz-Fittig reaction and Ullmann reaction. Give an example of each reaction.
2. (a) Describe how biphenyl can be prepared from phenol.
(b) Outline the synthesis of phenanthrene from 4-phenyl-3-butenic acid.
3. Draw the structures of the following lettered organic compounds:



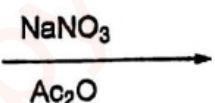
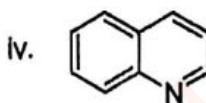
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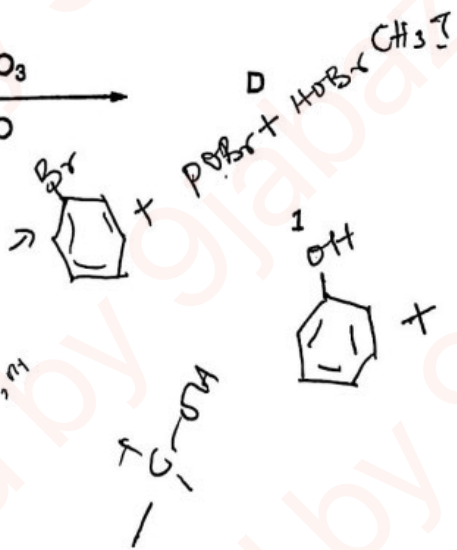
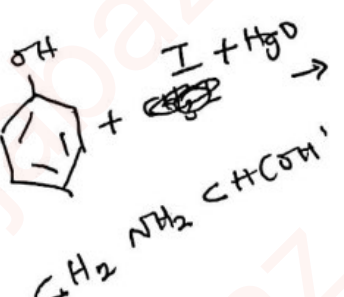
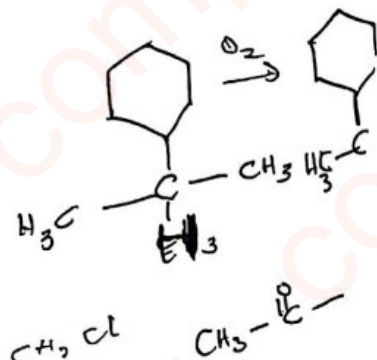
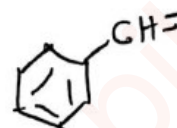
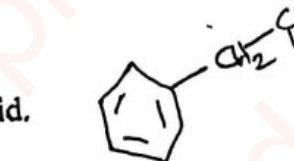
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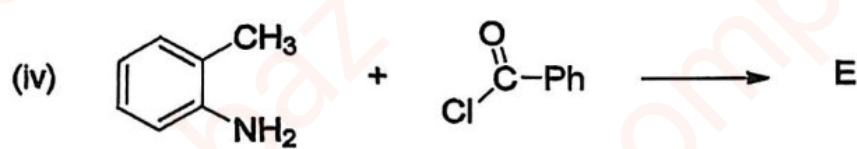
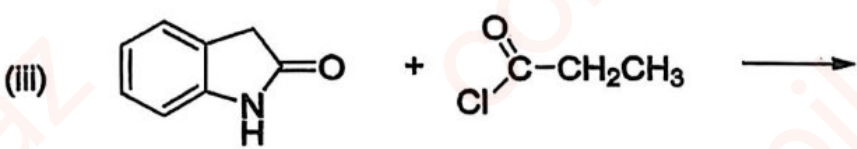
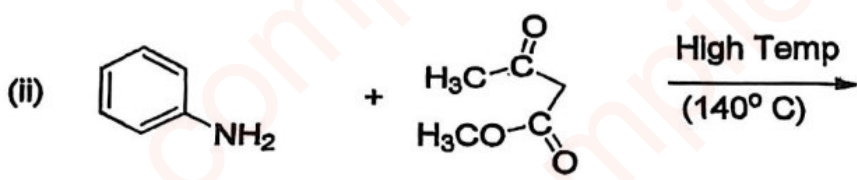


C



D





Quinone

B $\xrightarrow{250^\circ\text{C}}$ C

2-Phenyl-1,2-diphenyl



Strong base

F 2-Phenyl-1,2-diphenyl

- 4 a. Pyrrole, imidazole and pyrazole are azole alkaloids (organic bases). Arrange them in increasing order of basicity. Give reasons for your arrangement.
- b. (i) Give all possible resonance (canonical) structures for pyrrole.
- (ii) Give the equation for the reaction of pyrrole with phenylmagnesium bromide.
- (iii) Give the equation for the reaction of benzoyl chloride with the product of 2b (ii) above.



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B.Sc. (CHEMISTRY) DEGREE EXAMINATION

2019/2020 Rain Semester

CHM 306: AROMATIC AND HETEROCYCLIC CHEMISTRY

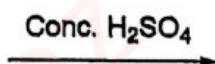
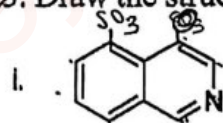
TIME ALLOWED: 2 hours

DATE: October 04, 2021

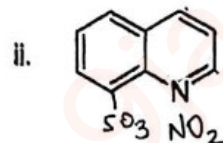
Instructions: Write your Name and Registration Number. Also append your signature on your answer scripts.

ATTEMPT ALL QUESTIONS

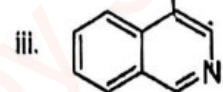
1. (a) Outline the synthesis of benzoic acid from the following compounds
(i) acetophenone (ii) styrene.
(b) Explain by chemical equation(s) the production of bromobenzene from isopropyl benzene.
(c) Compare and contrast Wurtz-Fittig reaction and Ullmann reaction. Give an example of each reaction.
2. (a) Describe how biphenyl can be prepared from phenol.
(b) Outline the synthesis of phenanthrene from 4-phenyl-3-butenic acid.
3. Draw the structures of the following lettered organic compounds:



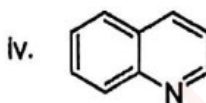
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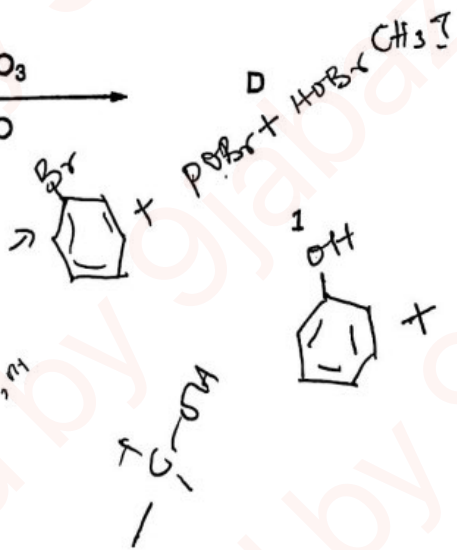
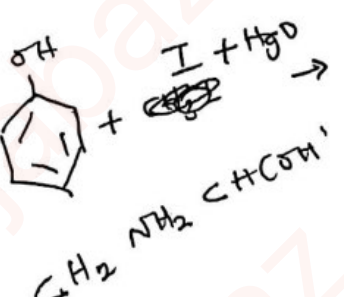
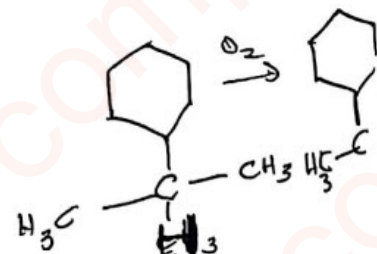
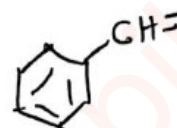
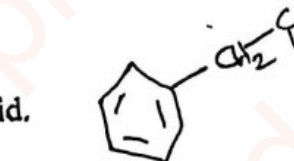
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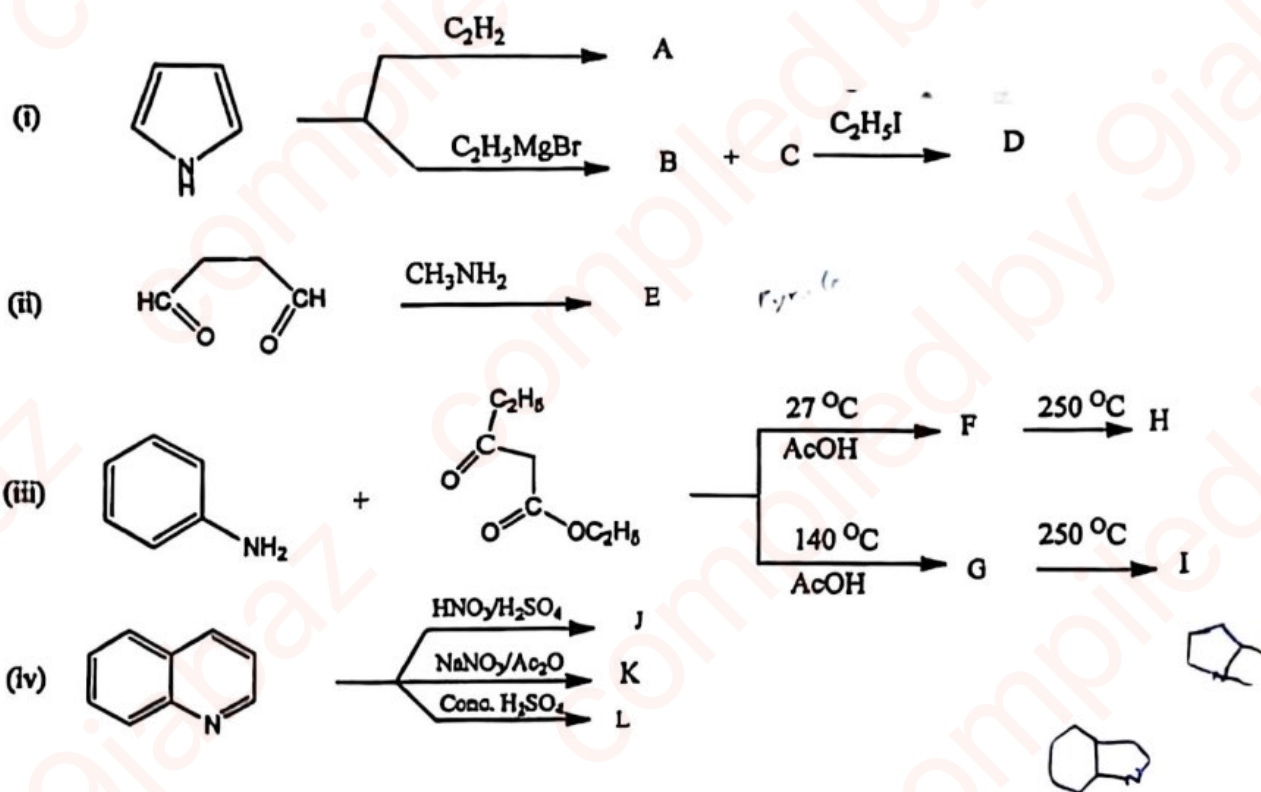


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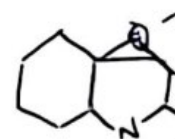




4. (a.) Using appropriate equations show how 2-phenylindole can be obtained by the reaction of ortho-toluidine (2-amino toluene) with appropriate acyl halide, indicate reaction condition.

(b.) Arrange the following heterocyclic nitrogen compounds in order of increasing basicity: pyrrole; imidazole and pyrazole.

(c.) Give the structures of lettered compounds in the following chemical equations:



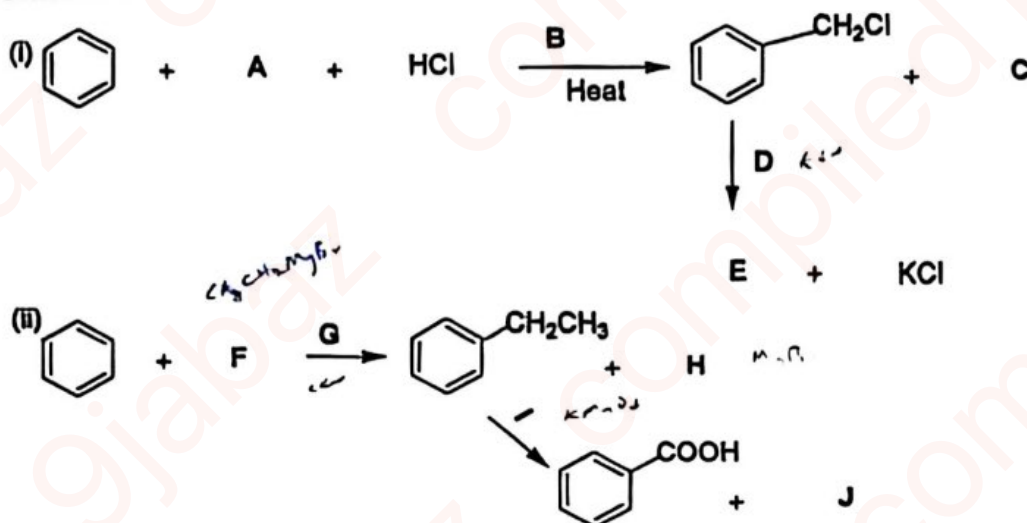
Department of Chemistry
OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE
 Part III B.Sc. Chemistry Degree Examination
RAIN SEMESTER EXAMINATION, 2022/2023 SESSION
CHM 306: AROMATIC AND HETEROCYCLIC CHEMISTRY

Time Allowed: 2 hours

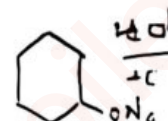
INSTRUCTION: Provide answers to new questions on a fresh page. Do not muddle up your answers.

SECTION A (Answer all questions in this section)

- 1 (a.) Provide the missing compounds or reagents indicated by letters in the following reactions.



- (b.) (i) Outline the synthesis of ethyl cyclohexane from ethenyl benzene.
 (ii) How would you prepare chloro benzene from sodium phenoxide?

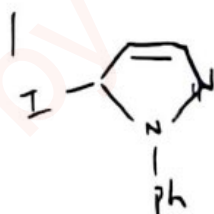


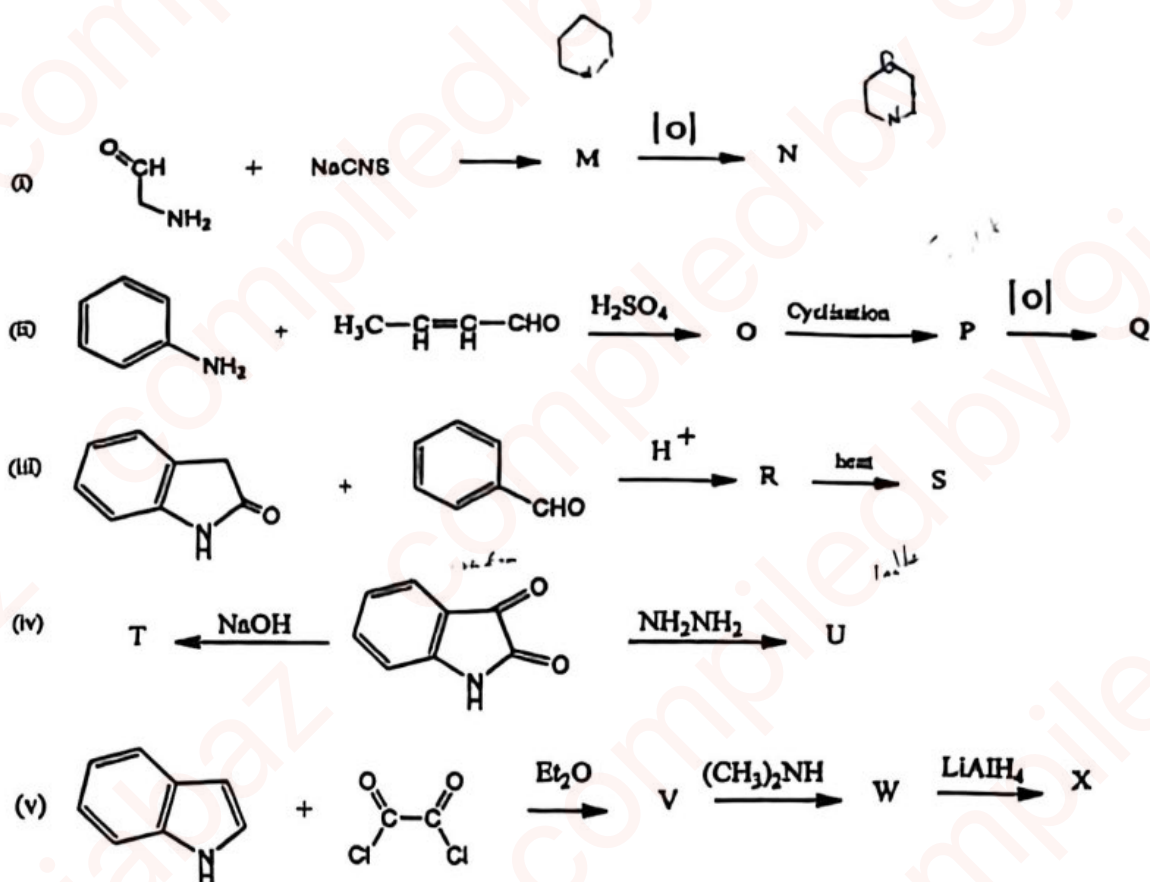
- 2 (a.) Describe the synthesis of trans-stilbene from benzylbromide.
 (b.) Explain by equations how 2-naphthol can be obtained from succinic anhydride.

SECTION B (Answer ANY two questions from this section)

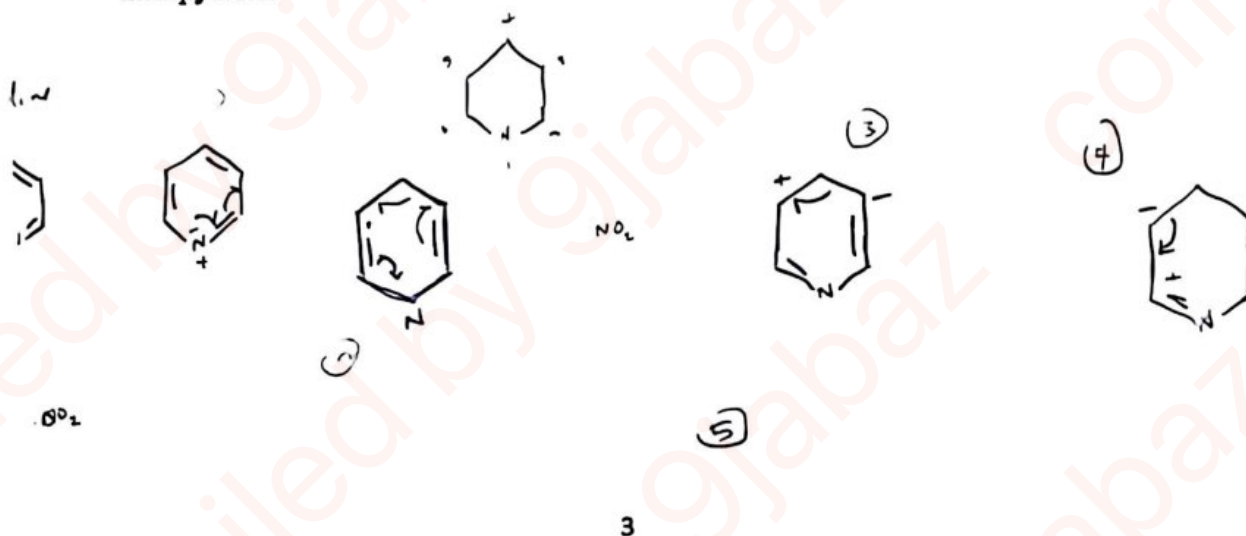
- 3 (a.) Name and give the structure of a naturally occurring nitrogen heterocyclic compound containing the basic skeleton of (i) pyrazole (ii) imidazole and (iii) indole
- (b.) Complete the following chemical equations by writing the structures of the lettered compounds

1





- 5 (a.) Illustrate the mechanistic path for the synthesis of a substituted indole from pentan-2-one and phenylhydrazine, using Fischer Indole method. Give the name the product formed.
- (b.) Using (i) the resonance (canonical) structures and (ii) nitration reaction, justify the chemical information that pyridine is less susceptible to electrophilic substitution reaction than pyrrole.



OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE, NIGERIA
DEPARTMENT OF CHEMISTRY
B.Sc (Chemistry) RAIN SEMESTER EXAMINATION 2023/2024 SESSION

CHM 306: AROMATIC AND HETEROCYCLIC CHEMISTRY

Date: 25th April 2025

TIME ALLOWED: 30 Minutes

INSTRUCTIONS: Attempt ALL questions.

1. a. Write the structures of the following compounds (i) 1,4-dimethyl-3-ethenyl benzene
(ii) ethynyl benzene (iii) dichlorodiphenyltrichloroethane
 - b. (i) Which of the oxidative products of coal can yield aromatic hydrocarbons?
(ii) Outline by chemical equations only, the synthesis of benzoic acid from acetophenone.
 - c. Explain by chemical equations, how to obtain bromobenzene from isopropyl benzene?
-



OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE, NIGERIA
DEPARTMENT OF CHEMISTRY

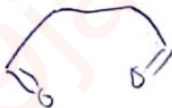
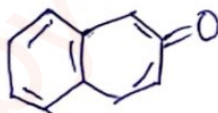
BSc, Degree (Chemistry) Examination Part III

CHM 306: Nitrogen Heterocyclic Compounds

Mid Rain Semester Examination 2023/2024 Session Time: 30 mins. Tuesday 13th May 2025

INSTRUCTION: Attempt all questions.

1. Give the structure of the following nitrogen heterocyclic compounds
(i). Imidazole; (ii). 3-methylindole (skatole); (iii). Pyridine-3-carboxylic acid (nicotinic acid); (iv). 2-aminoquinoline and (v). isoquinoline
2. Write equation for the following reactions and give expected product(s) of the reactions in the equation:
(i). Ethylmagnesium bromide reacts with pyrrole at its N-atom to form an intermediate, which was later treated with ethylbromide.
(ii). 3-methylpyrrole treated with potassium permanganate
(iii). Two moles of acrolein (2-propenal) react with one mole of ammonia
(iv). Ethanal was made to react with phenylhydrazine, the product formed reacted with ZnCl_2 (a Lewis acid) at about 180°C to give one main compound



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OBAFEMI AWOLOWO UNIVERSITY, ILE-IFE, NIGERIA
DEPARTMENT OF CHEMISTRY

B.Sc. (CHEMISTRY) DEGREE EXAMINATION
RAIN SEMESTER, 2023/2024 SESSION

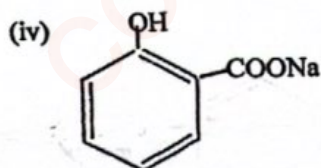
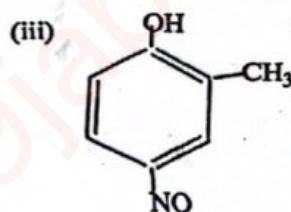
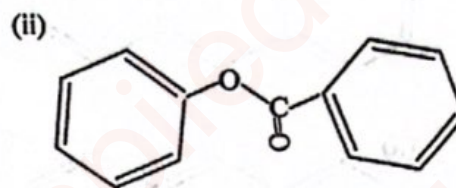
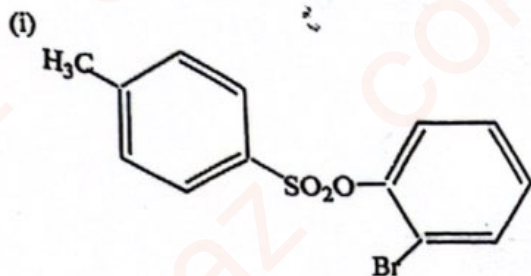
CHM 306: AROMATIC AND HETEROCYCLIC CHEMISTRY

TIME ALLOWED: 2 hours

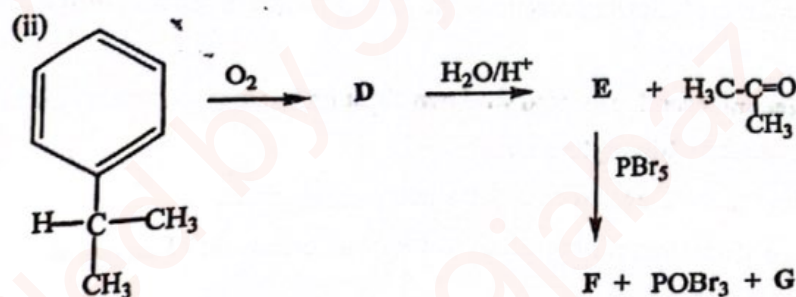
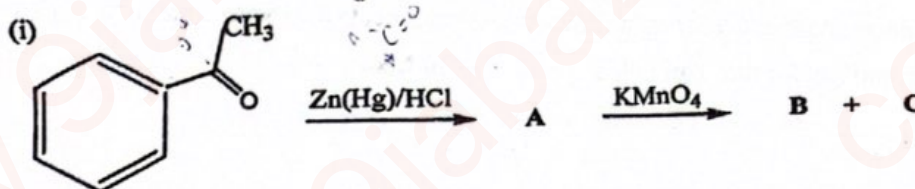
DATE: Saturday, 26th July 2025

INSTRUCTIONS: Attempt ALL questions

1(a) What are the names of the following compounds



(b) Provide the missing compounds indicated by letters in the following reactions.



CH₃ CH₃

CH₃ - CH₃

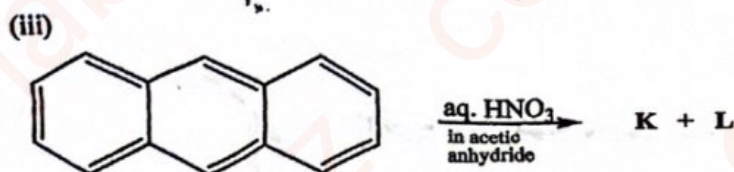
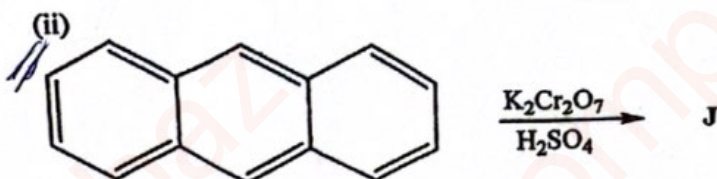
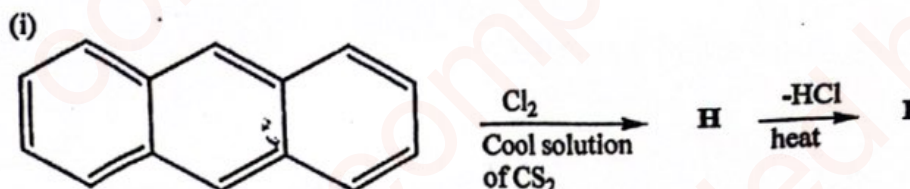
(c) (i) Diagrammatically explain why the C-X bond in aryl halides has double character and C-X bond in alkyl halides does not?

(ii) How would you prepare benzaldehyde from benzene?

2(a) Outline the synthesis of trans-stilbene from benzyl chloride.

(b) Explain by chemical equations the synthesis of anthracene from benzyl alcohol.

(c) Supply the missing compounds indicated by letters in the reactions below.



3. Give the structure of the following nitrogen heterocyclic compounds

- (i). Imidazole; (ii). 3-methylindole (skatole); (iii). Pyridine-3-carboxylic acid (nicotinic acid); (iv). 2-aminoquinoline; (v). isoquinoline; (vi). Histamine; (vii). Pyrazolone; (viii). Tryptamine; (ix). Isatin and (x). 8-bromoquinoline

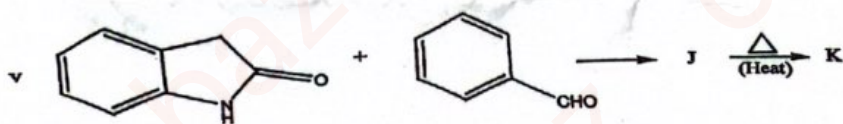
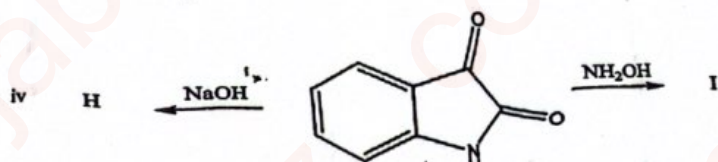
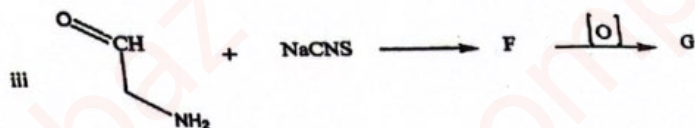
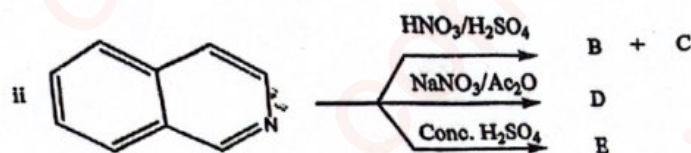
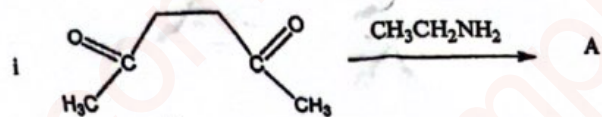
10 Mks

4(a) Write equation for the following reactions and give expected product(s) of the reactions in the equation:

- (i) Ethylmagnesium bromide reacted with pyrrole at its N-atom to form an intermediate, which was later treated with ethylbromide.
- (ii) 3-methylpyrrole was treated with potassium permanganate
- (iii) Two moles of acroleine (2-propenal) reacted with one mole of ammonia

(iv) Ethanal was made to react with phenylhydrazine, the product formed was treated with ZnCl_2 (a lewis acid) at about 180°C to give one main compound

(b) Give the structure of each of the lettered compounds below:

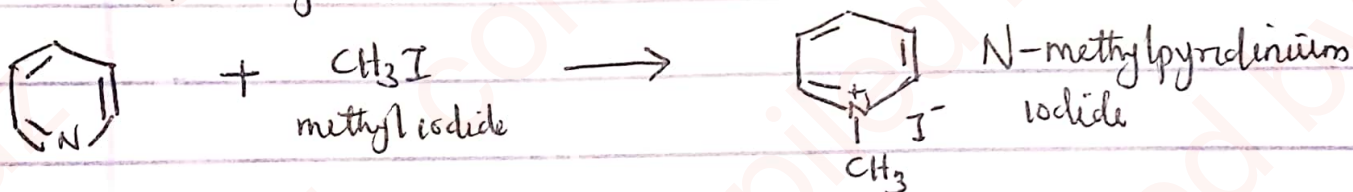


HETEROCYCLIC COMPOUNDS

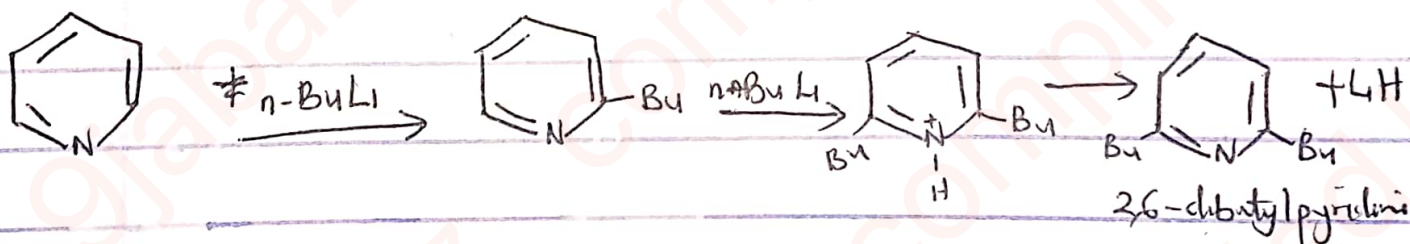
PQ

1. Give appropriate equations and name the organic product(s) formed for each of the following reactions of pyridine

(i) A named alkyl halide



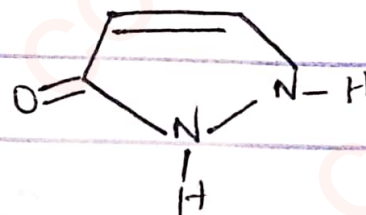
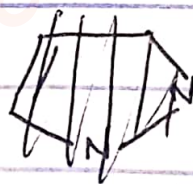
(ii) excess n-Butyl Lithium



2. Name and give the structure of a naturally occurring nitrogen heterocyclic compound containing the basic skeleton of

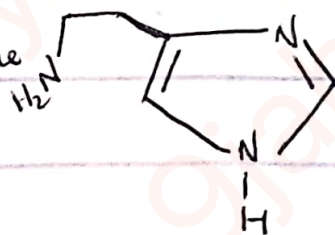
(i) pyrazole (ii) imidazole

Pyrazole — pyrazolone



Imidazole

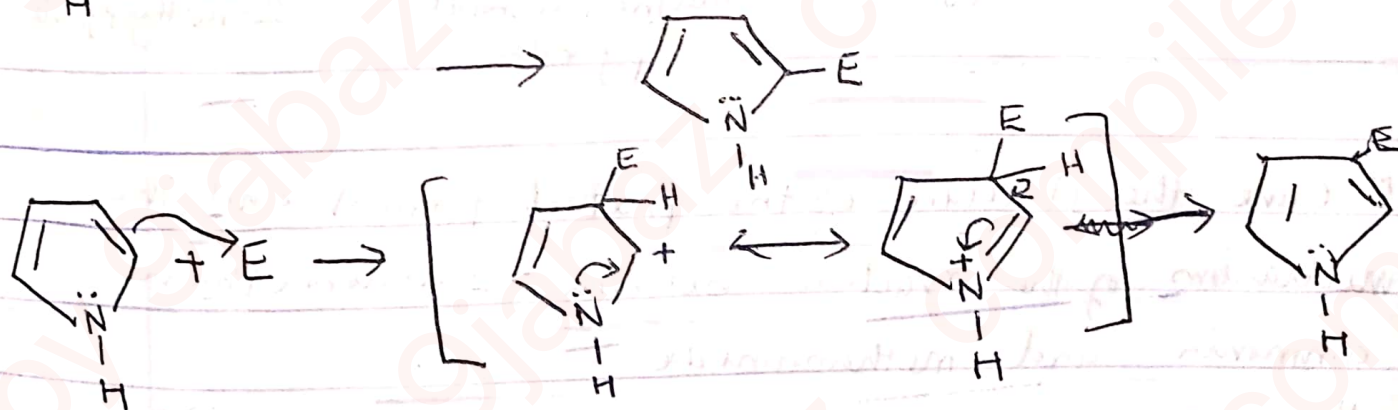
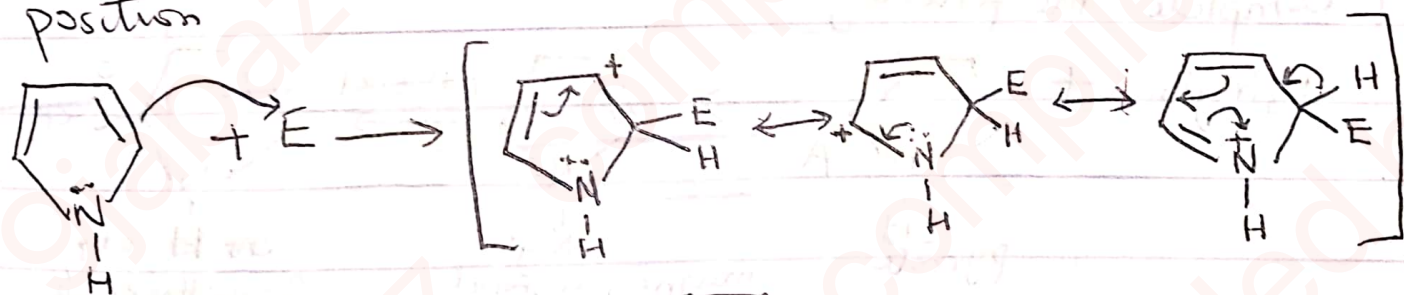
— Histamine



3. Justify the following chemical observations

1. Electrophilic substitution takes place mainly at the α position than the β position for unsubstituted pyrrole.

This is due to the fact that e^- s are more enhanced to move towards the π -rich nitrogen atom for the α position and the intermediate formed by α -position has more canonical structure which makes it more stable than the β position

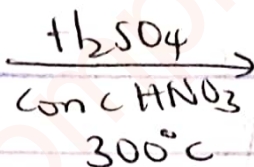


(ii) Pyridine is very difficult to nitrate but 2,6-dimethylpyridine is easy to nitrate

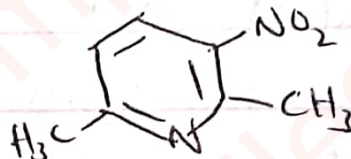
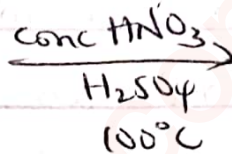
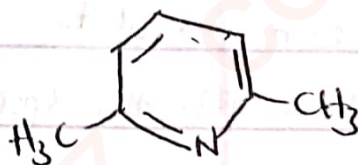
Unsubstituted pyridine is difficult to nitrate because none of its carbon atom is electron rich but upon alkylation, alkyl

Substituent
Substitution

activates the ring towards electrophilic substitution

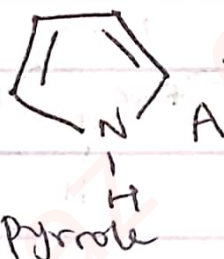
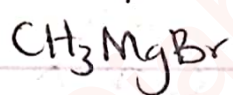


6% yield



67% yield

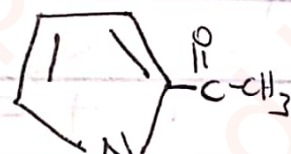
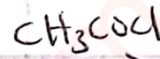
4 Complete the following.



pyrrole

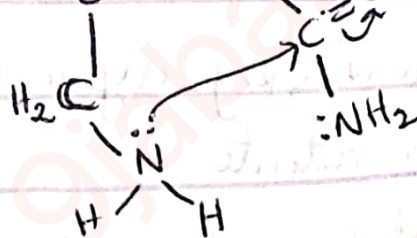
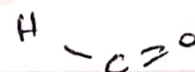
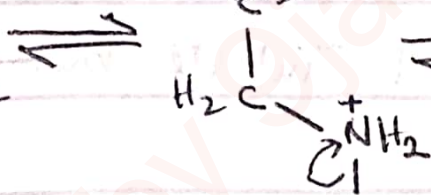
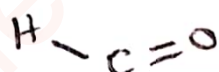


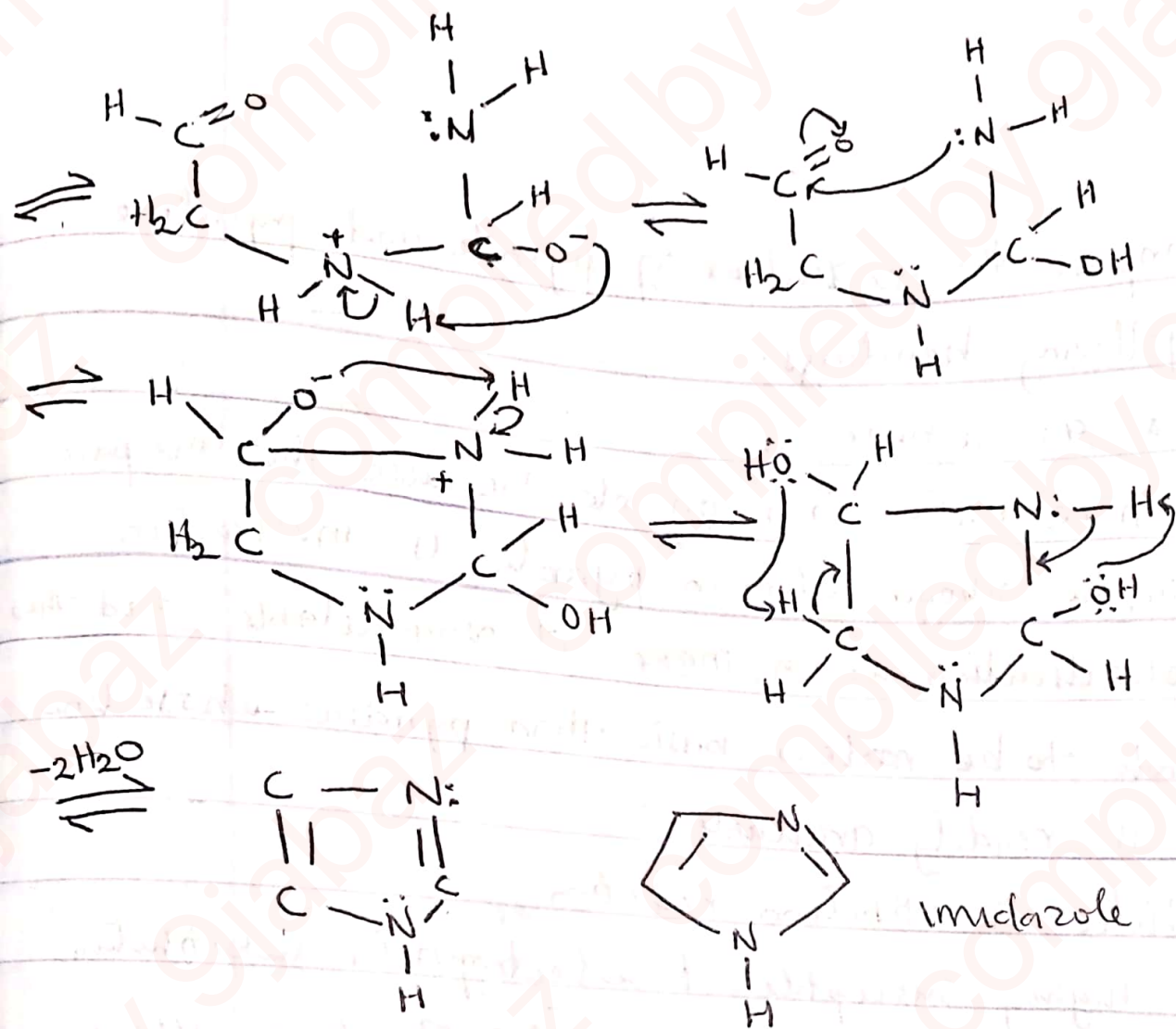
magnesium bromide
pyrrole



2-methylpyrrole

5 Draw the structure of the product formed and the mechanism of the reaction between 2-chloroethanal ammonia and methanamide

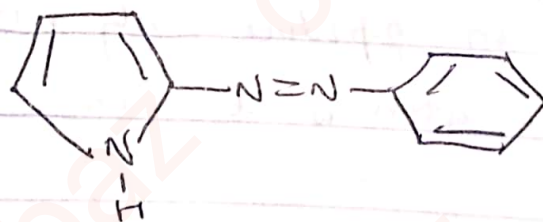
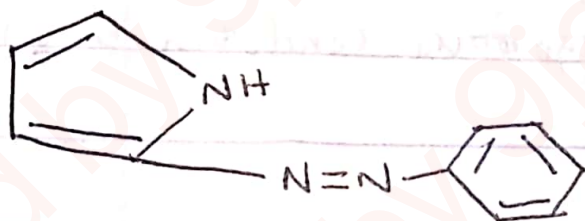




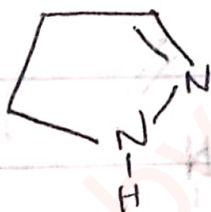
6. Give the structure of the following compounds

1) ~~2-phenyl azopyrrole~~

2-phenyl azopyrrole



2) Pyrazoline



7. Briefly compare the reactivities of pyrrole and pyridine

1. Under the following headings.

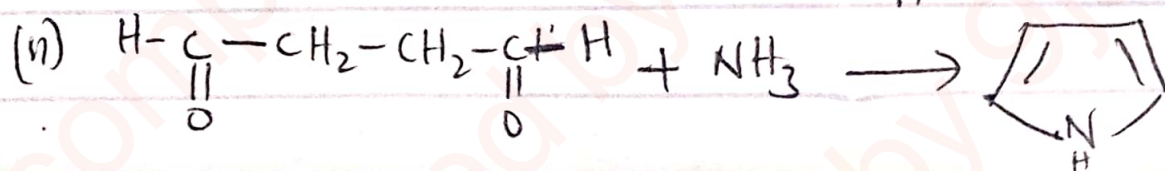
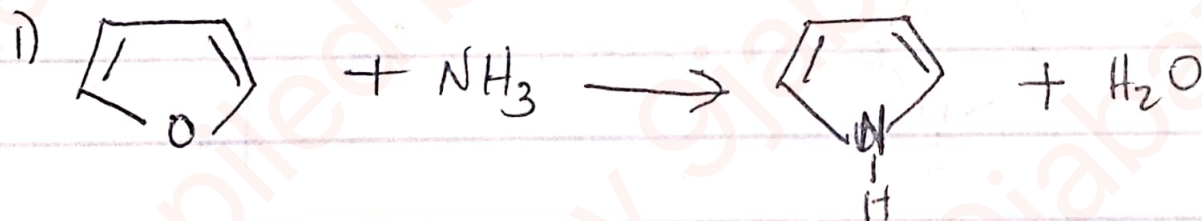
(i) Reactions as a base.

(i) Pyridine is more basic than pyrrole because the lone pair of electron on the nitrogen atom in pyrrole is involved in aromatic delocalization which makes it unavailable and this causes pyrrole to be less basic than pyridine whose lone pair of e^- is readily available.

(ii) Electrophilic substitution reaction

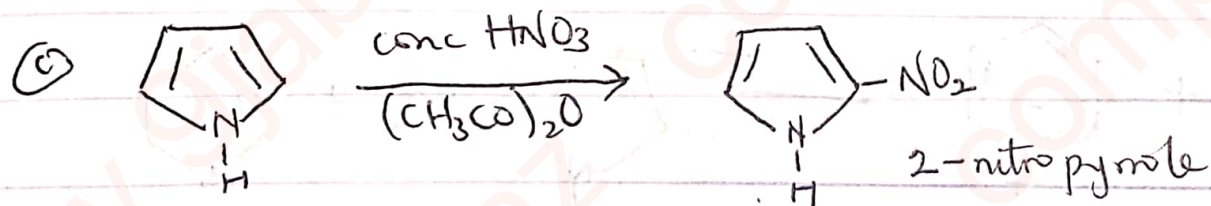
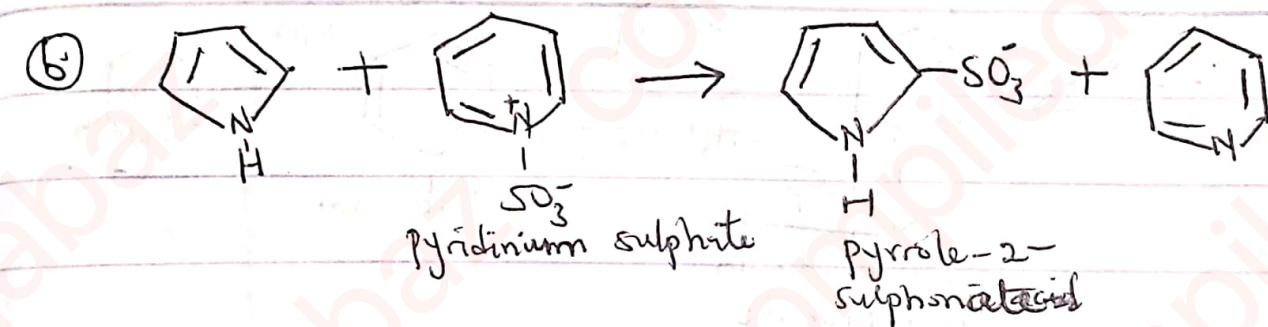
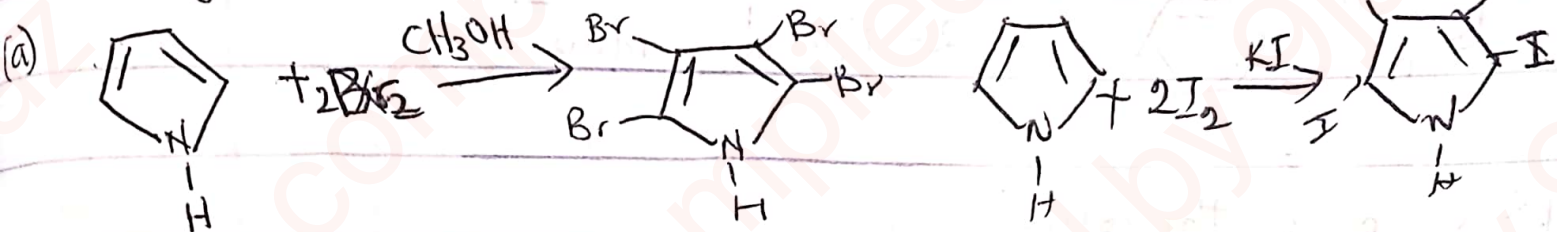
Pyrrole is highly susceptible to electrophilic substitution reaction because from the canonical structure all the carbon atoms are electron rich due to having higher electron density but this is not so in pyridine, electrophilic SR will occur in pyridine only with rigorous conditions but none of the C-atoms is e^- rich.

iv. 8a. Write 2 chemical equations for the preparation of Pyrrole



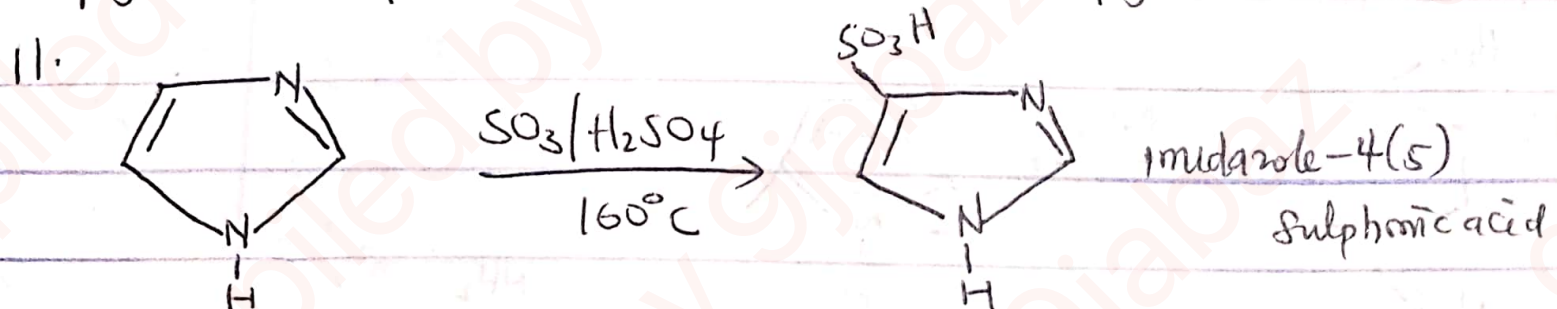
9. Give the following reactions of Pyrrole.

(a) Halogenation (b) Sulphonation (c) Nitration

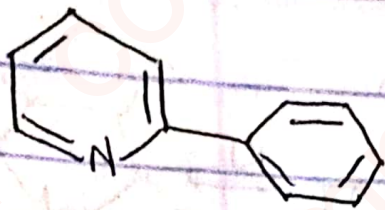


10. Arrange the following heterocyclic compounds in order of increasing basicity with reasons: pyridine, pyrrole, pyrazole and Imidazole:

pyrrole < pyrazole < imidazole < pyridine

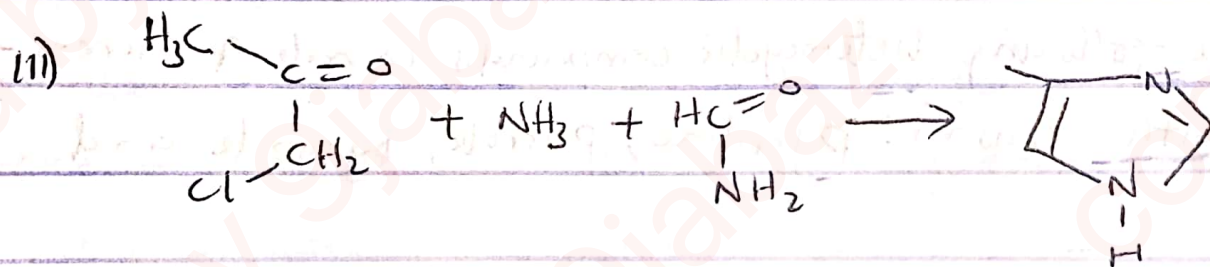
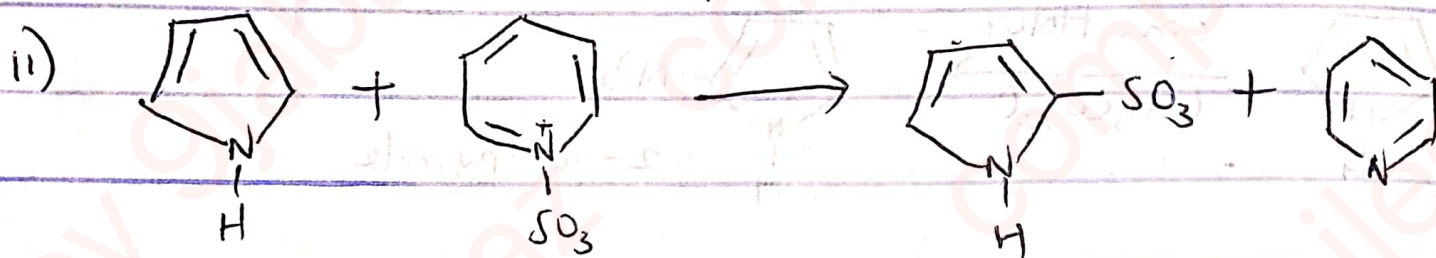
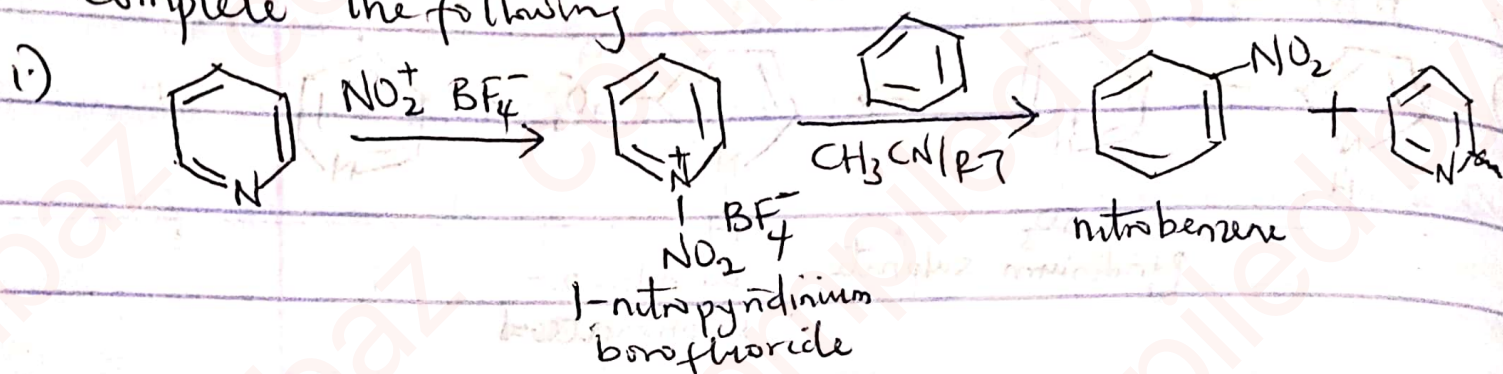


12. Give the name of the following compound

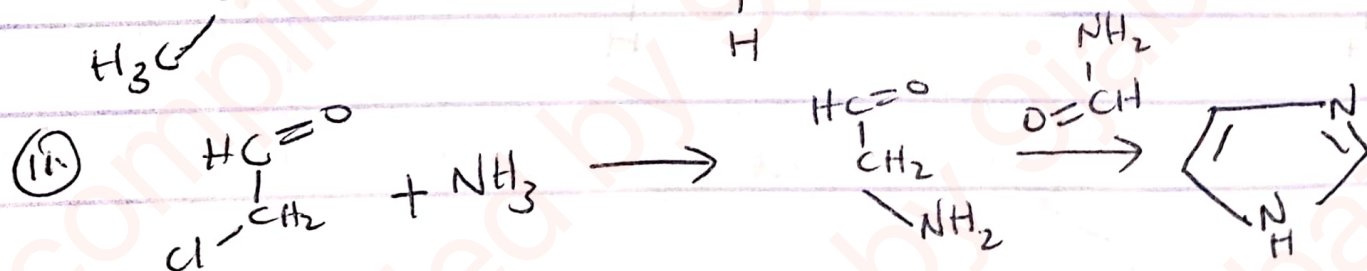
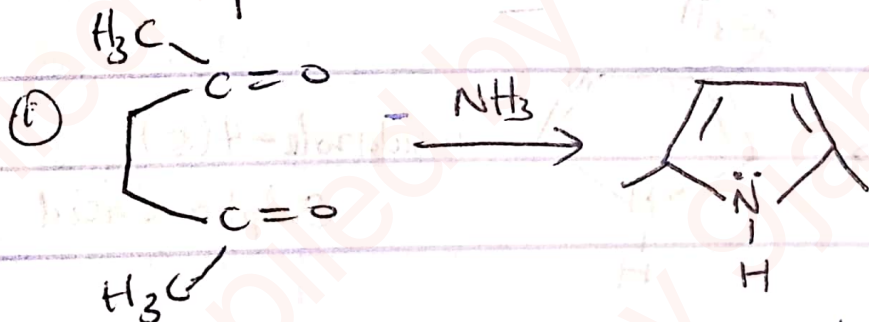


2-Phenylpyridine

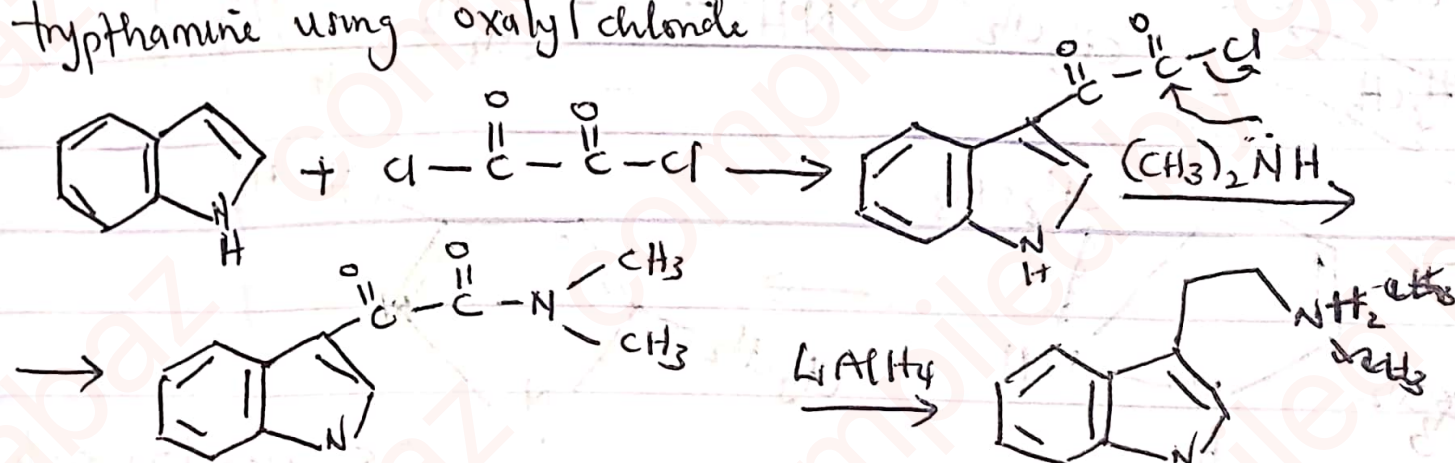
13. Complete the following



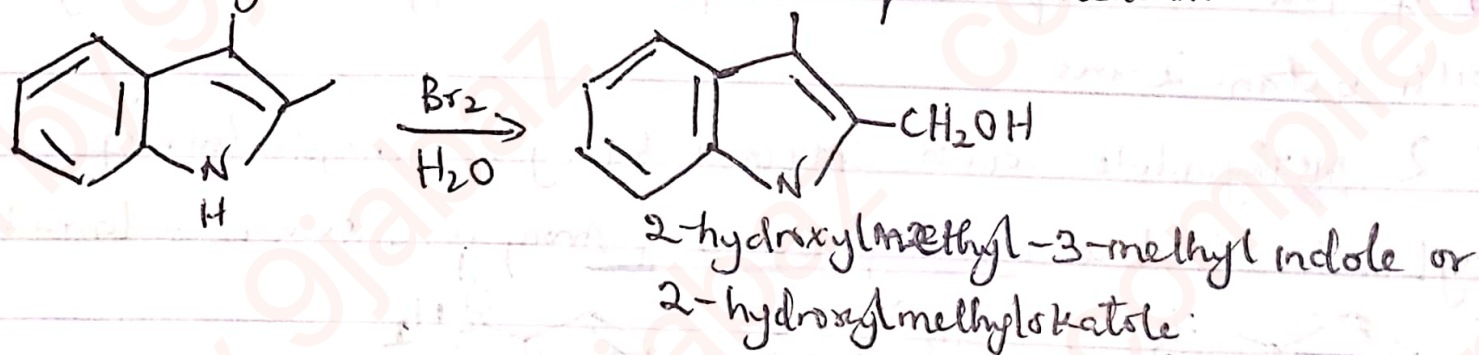
14. Complete the following



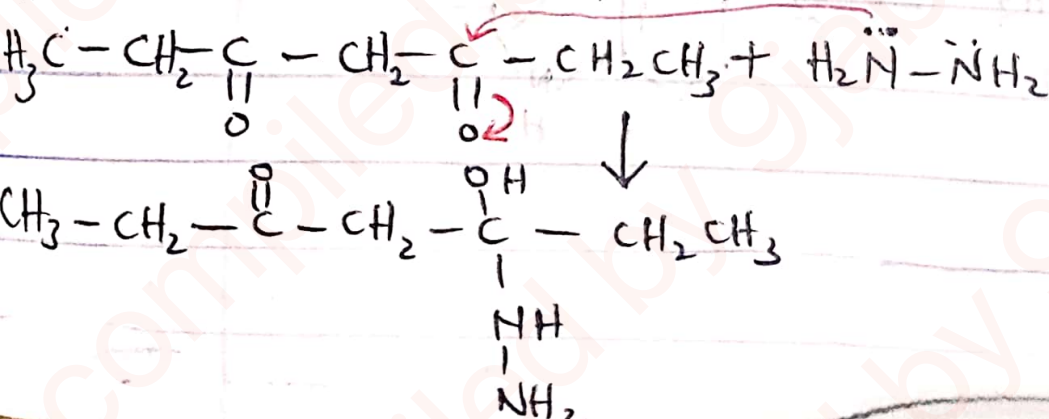
15 Outline the reaction path for the conversion of indole to tryptamine using oxalyl chloride



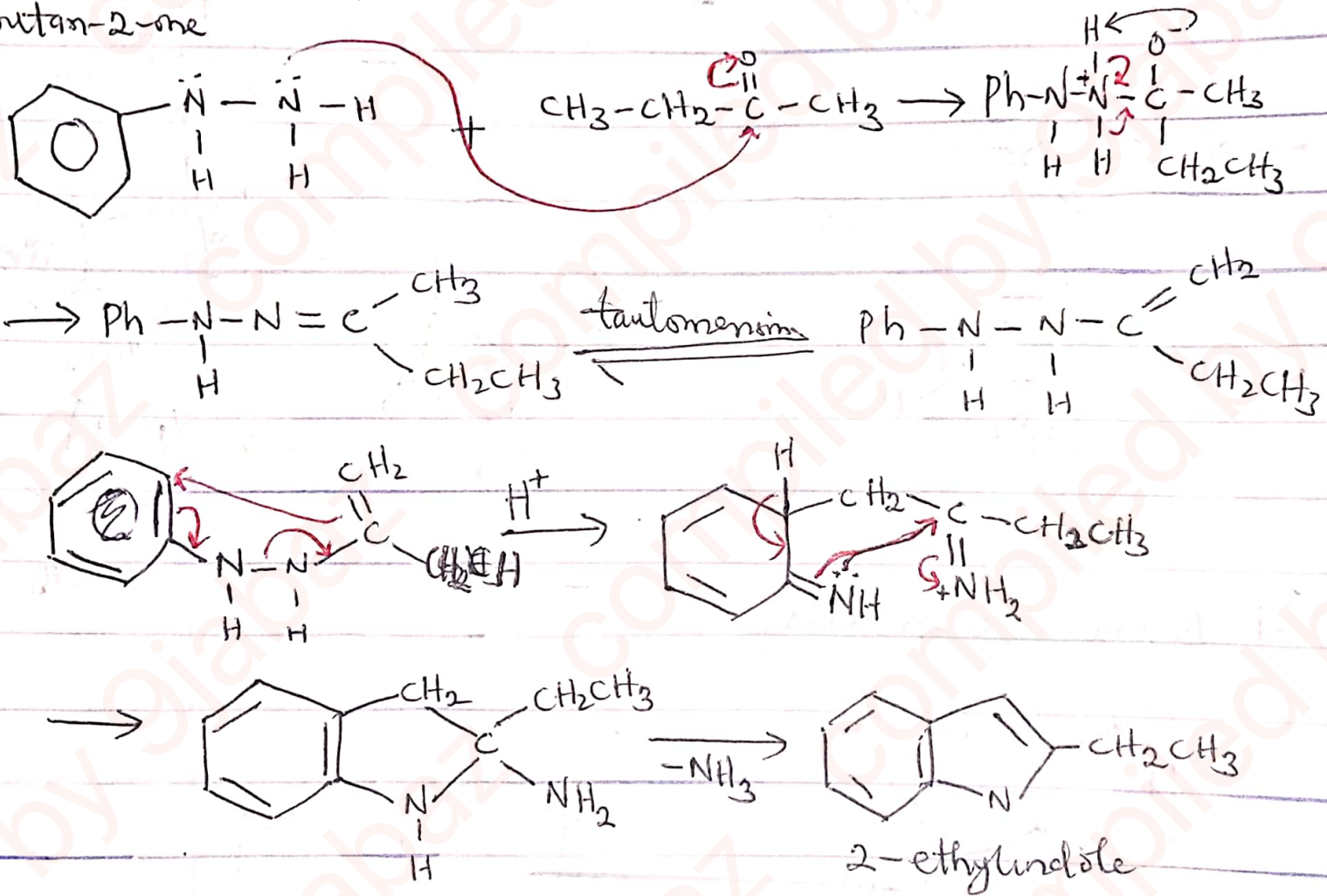
16 Give the structure and name of the product formed when 2,3-dimethylindole is brominated in aqueous medium



17 Give the product of the reaction of heptan-3,5-dione with hydrazine mechanism of the reaction.

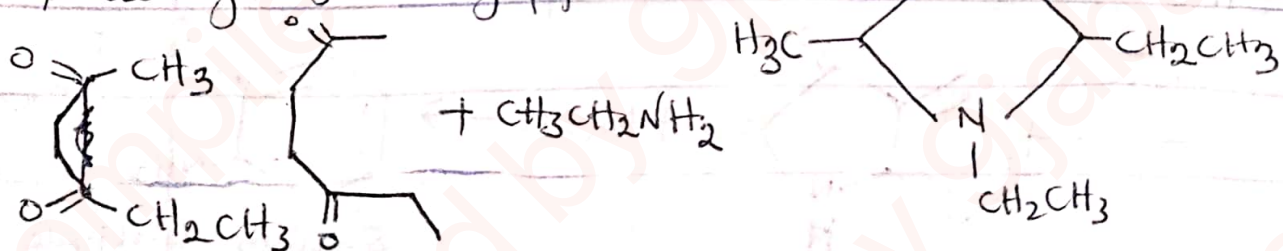


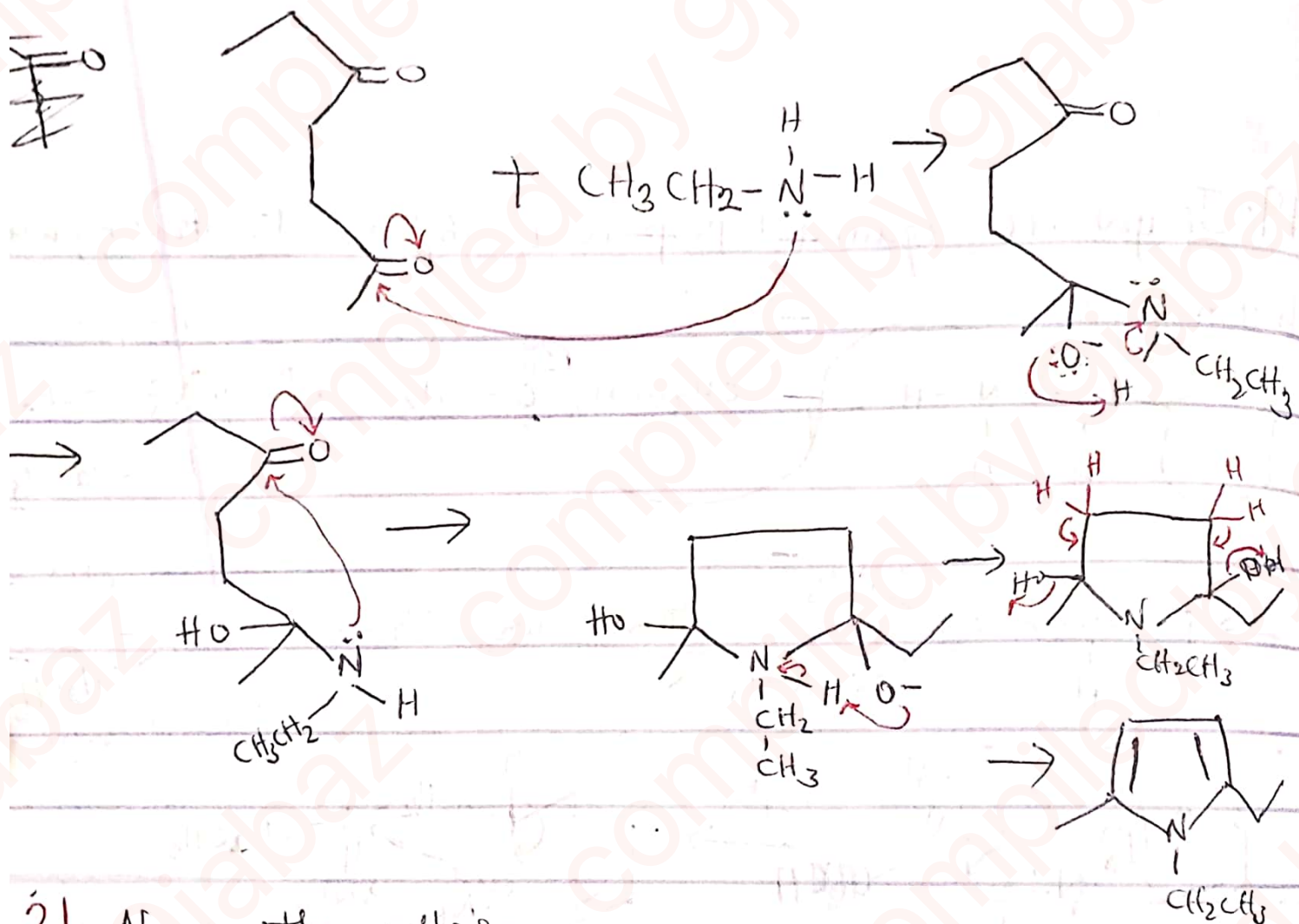
19. If you are required to prepare 2-ethyl indole starting with butan-2-one



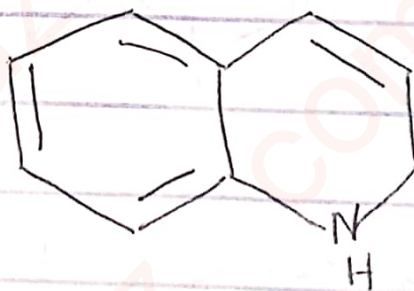
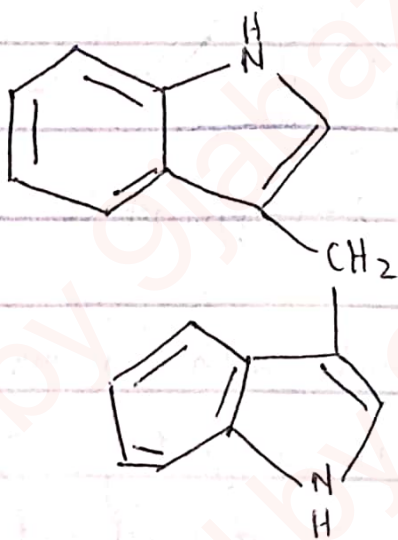
20 The reaction of 1,4-dicarbonyl compounds with ammonia or a primary amine describes Pictet-Knorr synthesis of pyrazoles. Outline the synthesis of 1,2-diethyl-5-methylpyrazole by the method and show the appropriate mechanism.

1,2-diethyl-5-methylpyrazole





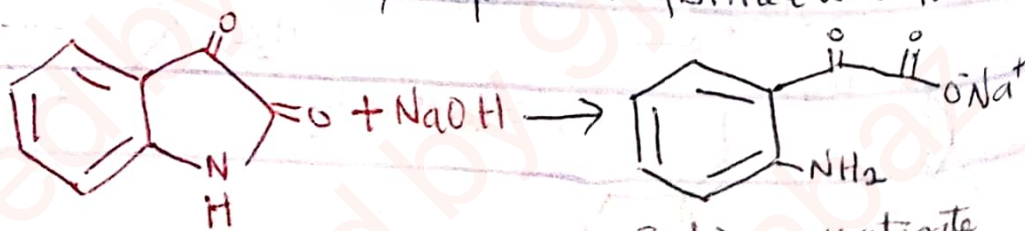
21 Name the following



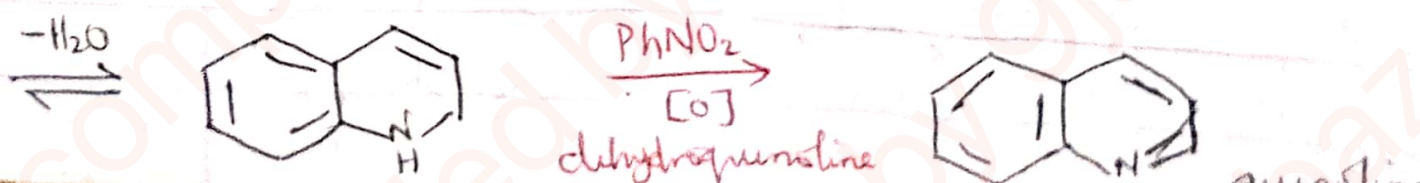
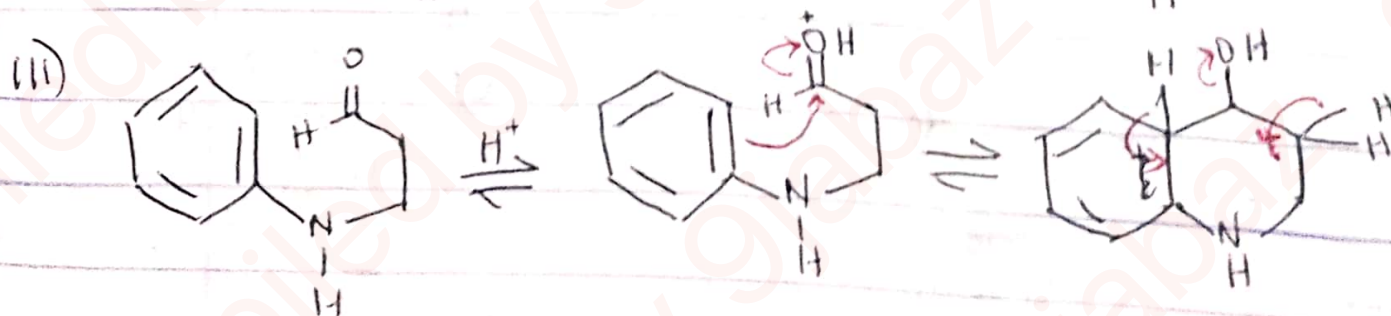
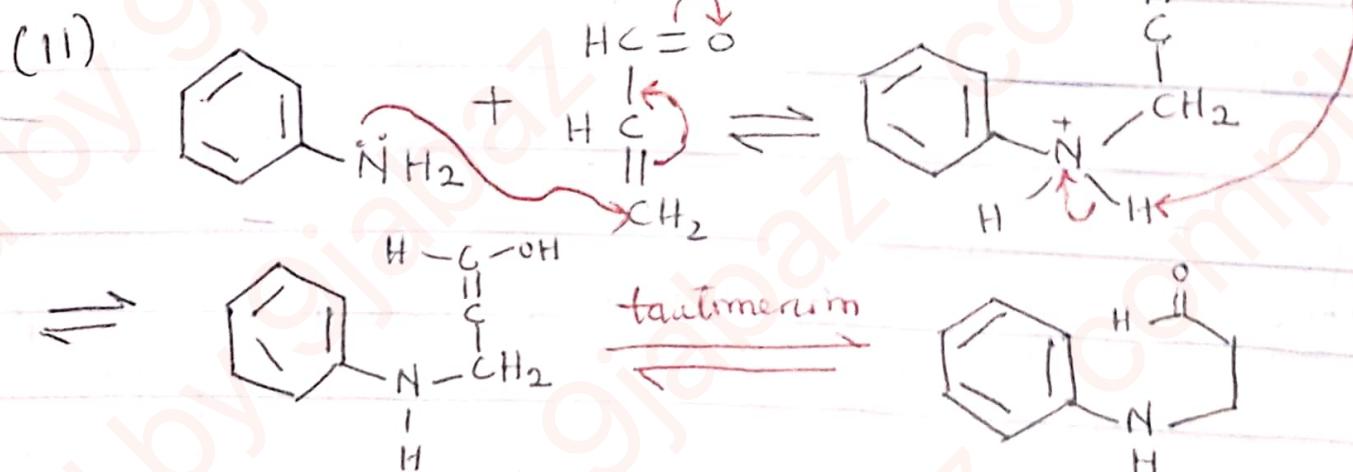
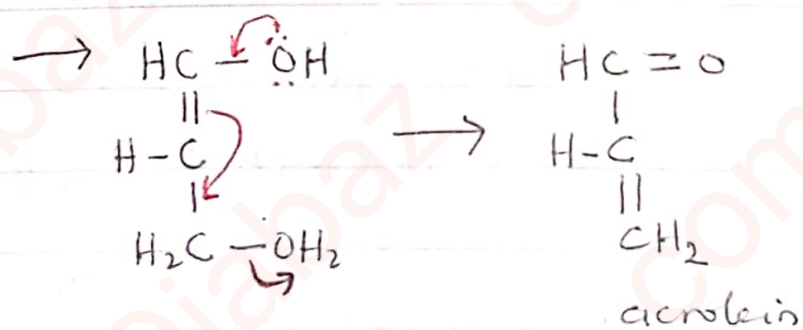
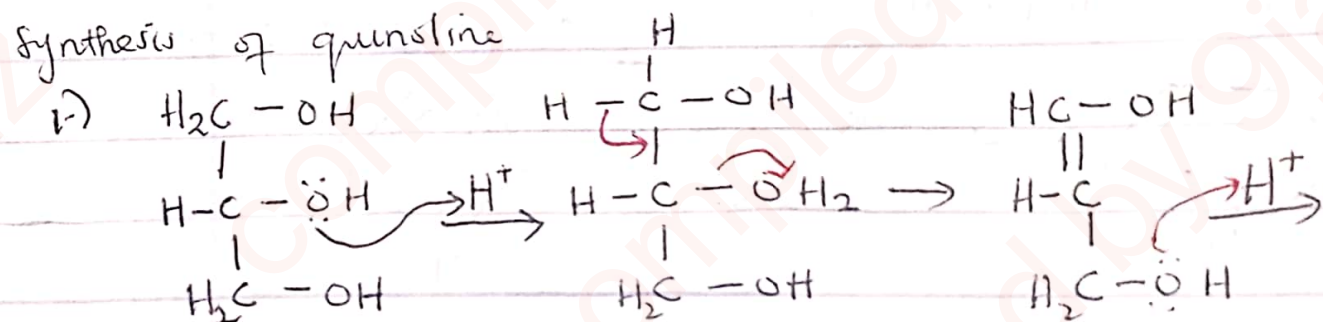
dehydroquinoline

b1 -indolyl methane

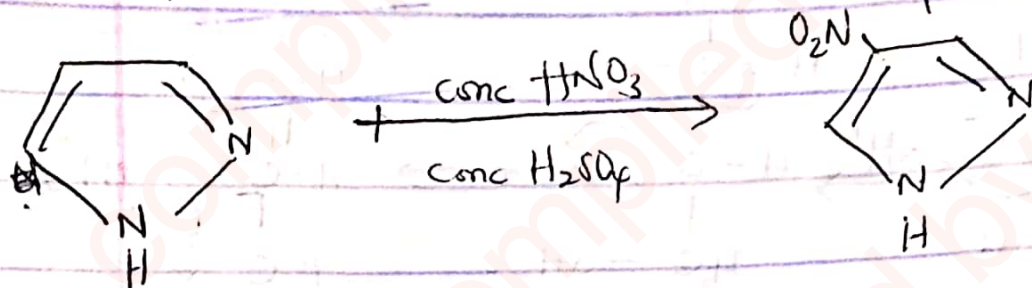
22 Give the structure and names of the product formed when water reacts with NaOH



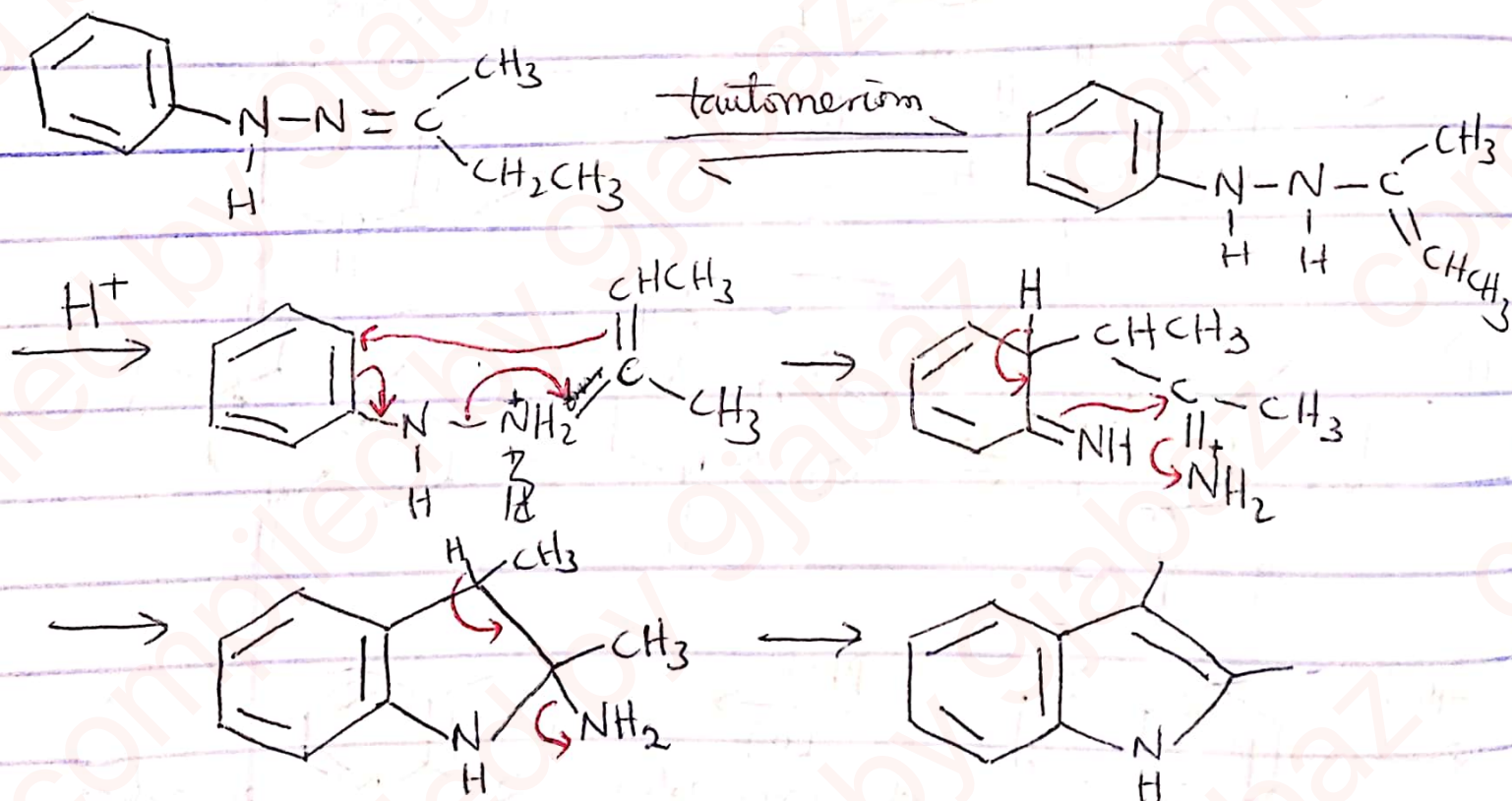
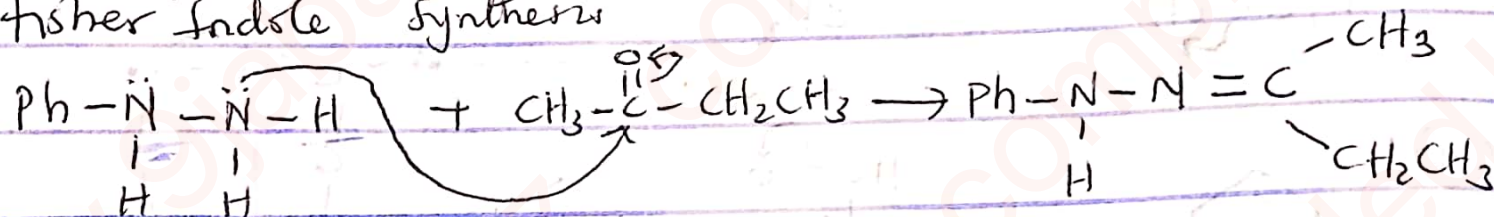
23- Given glycerol and aniline, illustrate the process for the synthesis of quinoline



24 Give the structure and name of the product formed when pyrazole is reacted with conc HNO_3 in the presence of conc H_2SO_4

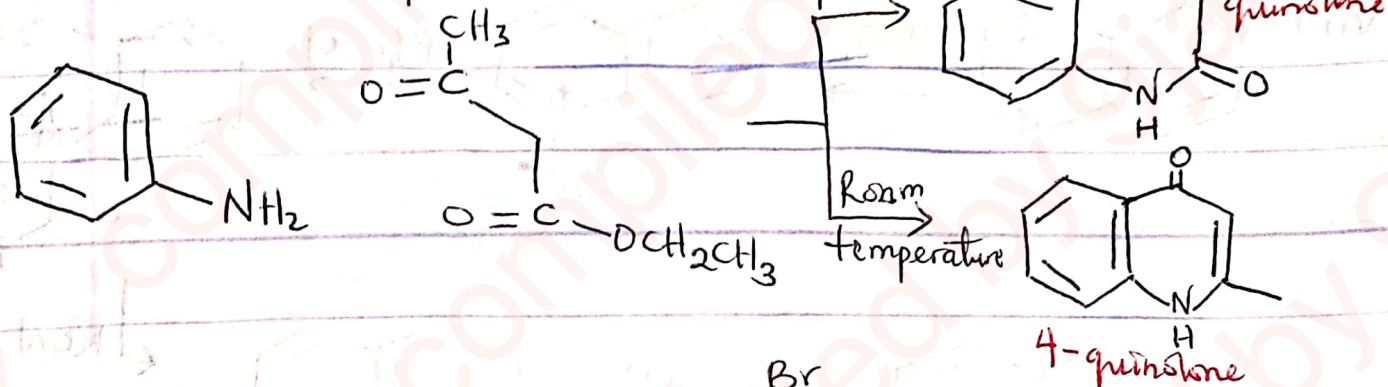


25 Illustrate the mechanistic path for the synthesis of 2,3-dimethylindole from butan-2-one and phenylhydrazine using Fisher Indole Synthesis

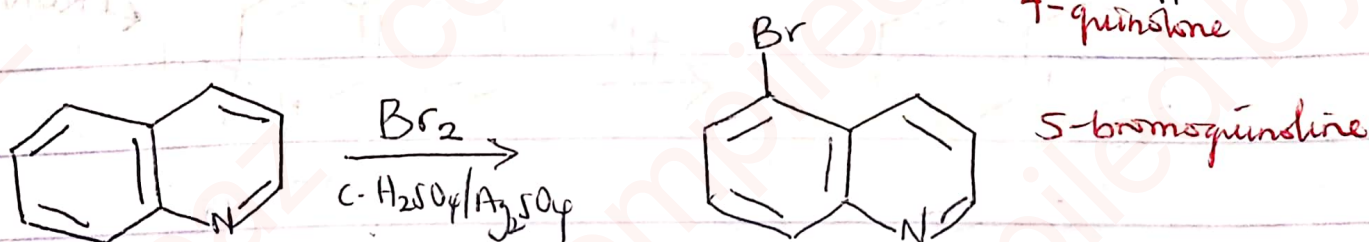


26 Complete the following equations by writing structures of the lettered compounds.

(i)



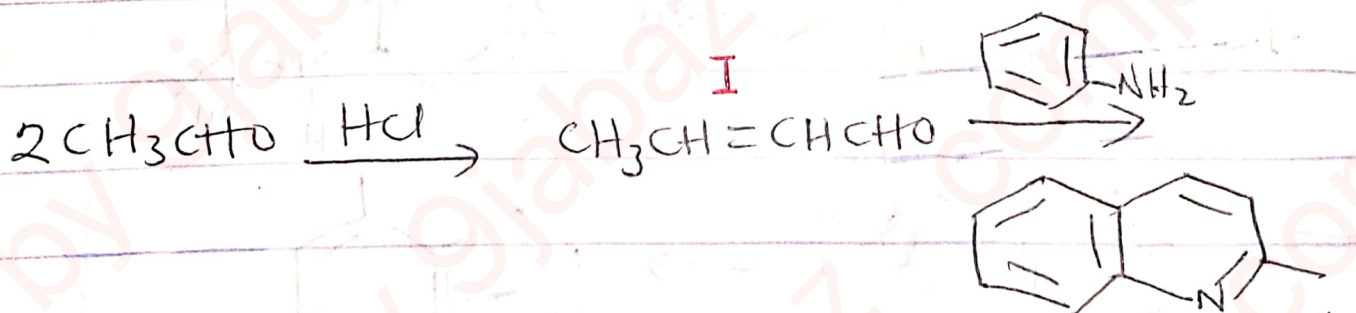
(ii)



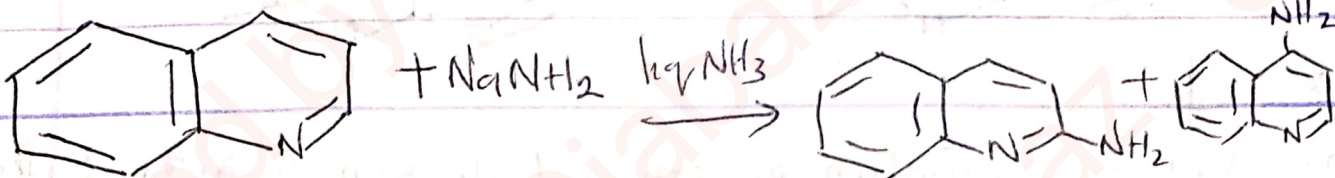
(iii)



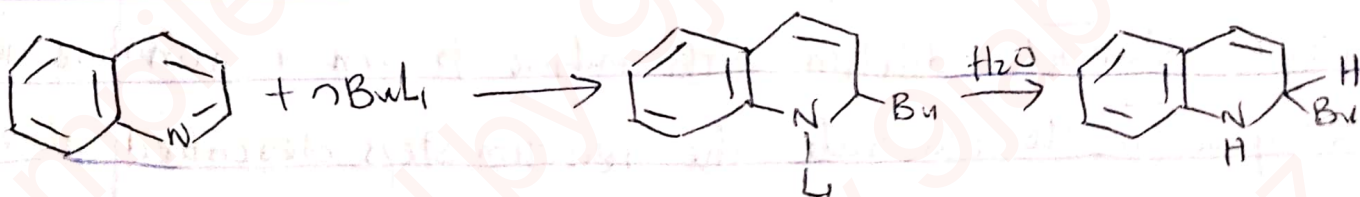
iv)

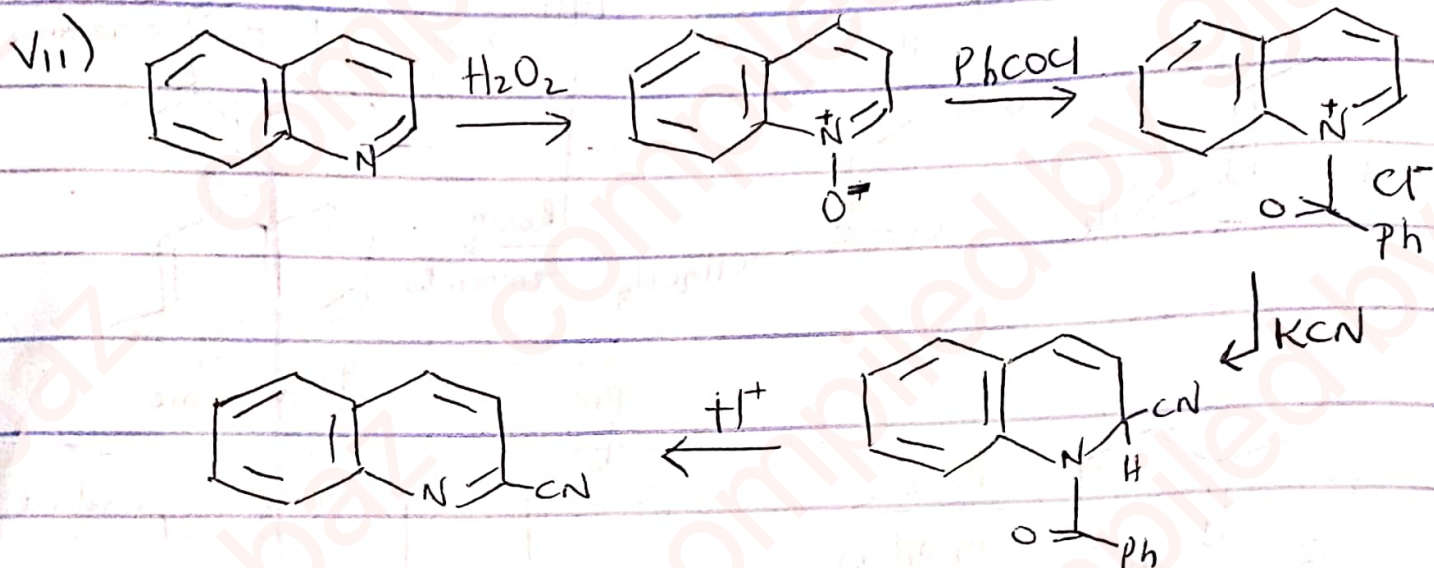
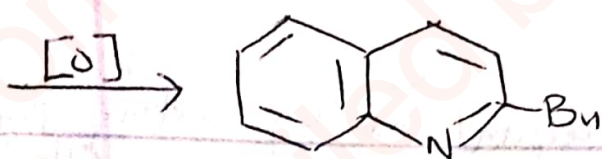


v)

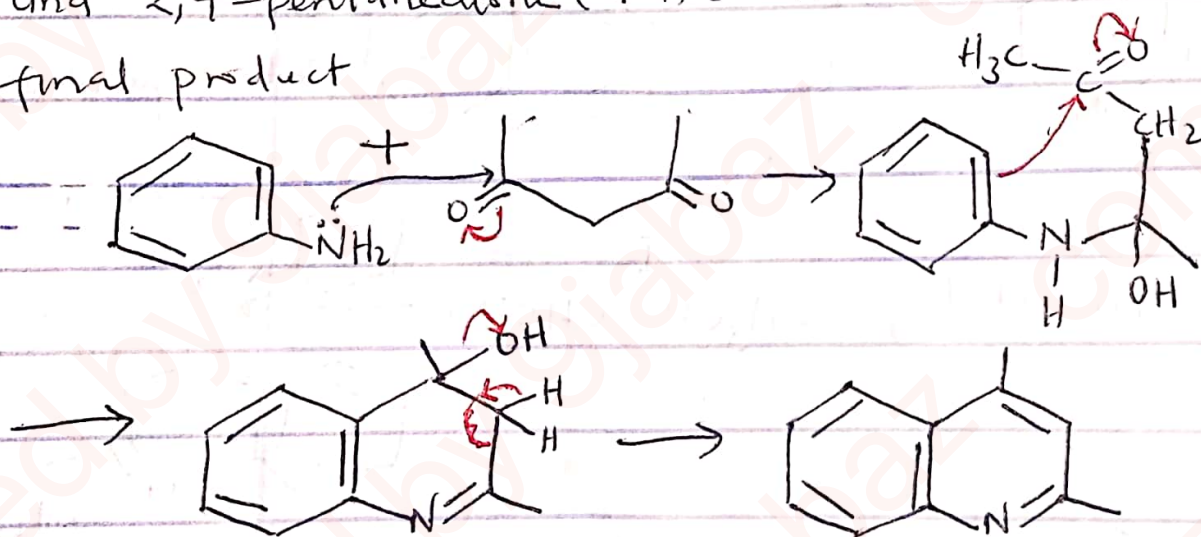


vi)



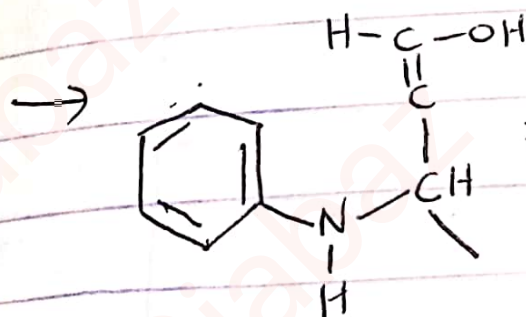
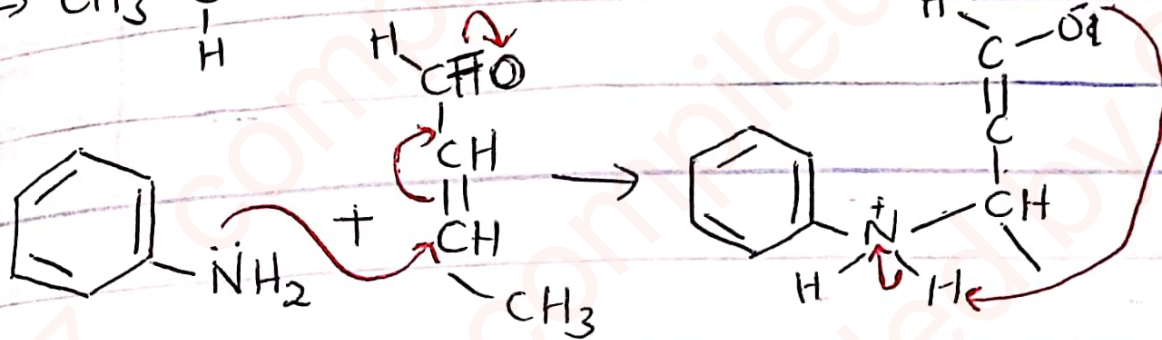
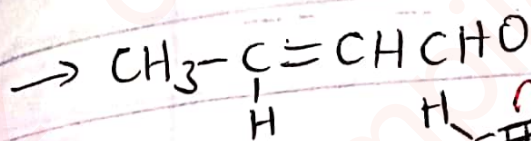
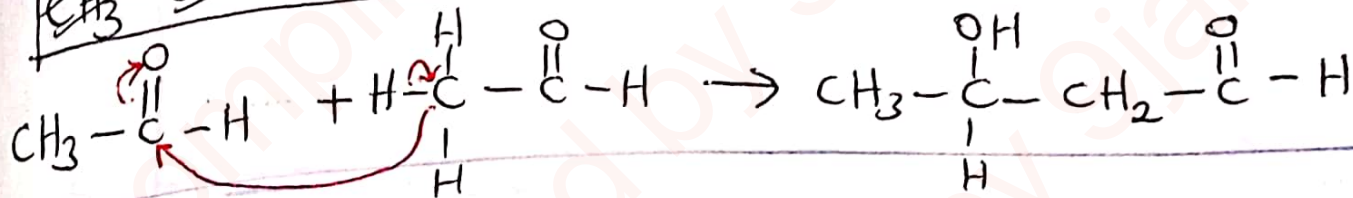
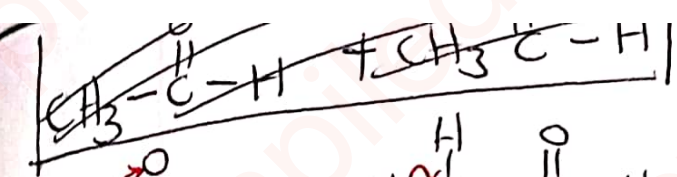


27: Give the mechanism for the reaction between aniline and 2,4-pentanedione (a 1,3-diketone) and the name of the final product



28. Self

28- Self condensation of ethanal to form 2-butenal which undergoes Michael addition with aniline to form a quinoline derivative. Give equations to illustrate the reaction steps described above



Keto-enol
tautomerism

