20-3-17

DOON UNIVERSITY, DEHRADUN

Mid Sem Examination, Even Semester, 2016–2017
School of Physical Sciences (SoPS)
4th Semester, Integrated M.Sc. 5 Years (Chemistry)

Dated: 20 Mar 2017 (Monday)

Course: *Org. Chem. III: Heterocyclic Chemistry* **Course Code:** *CYC–252*

Time Allowed: 2Hours ***Maximum Marks: 30***

Note: Attempt All Questions from Sections A,B,C.

SECTION: A ***(Marks: 6)***

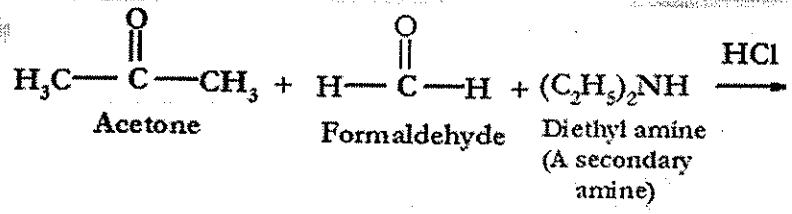
[1] Write a short note on Chichibabin Reaction: [1]

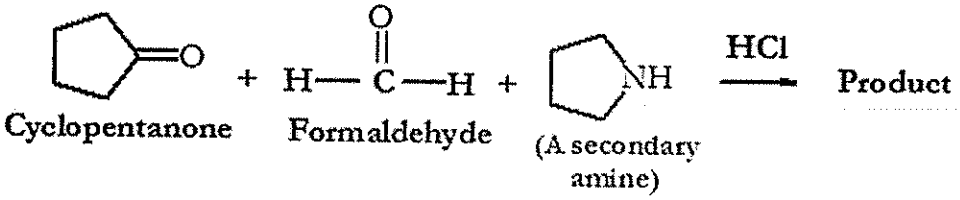
[2] Why is pyridine much less reactive towards electrophiles than pyrrole and benzene? [1]

[3] What is the structural formula of Hinsberg reagent [1]

[4] How can the presence of a primary amine be ensured in a mixture of Primary, Secondary and tertiary amines. [1]

[5] Draw the structural formulae for the major product in following two reactions: [1/2 + 1/2]





[6] (a) Methylamine dissociate partially into ions in the following manner: [1/2]

$$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$$

Express the value of base dissociation constant (K_b).

(b) What is the correlation between the value of base dissociation constant and basicity of a compound? [1/2]

SECTION: B *(Marks: 12)*

[7] What is the reason behind: [½ + ½ + ½ + ½]

(a) Arenediazonium salts are highly reactive compounds.

(b) High stability of benzenediazonium salts.

(c) Importance of benzenediazonium salts in synthesis.

(d) Predominance of the *less* highly substituted alkene in the mixture of the products in the Hofmann elimination

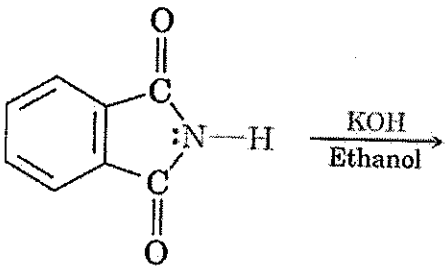
[8] Fill in the blanks: [2]

(a) An amine with three different substituents on nitrogen is chiral (in ..... but not in .....).

(b) Most amines that have 3 different substituents on N are not ..... because the molecules ..... by ..... inversion.

[9] Fill in the blanks: [2]

(a)



Phthalimide

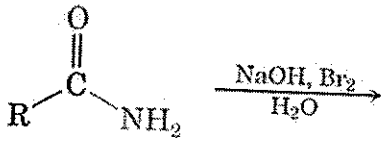
$\xrightarrow[\text{Ethanol}]{KOH}$

$\xrightarrow[DMF]{RX}$

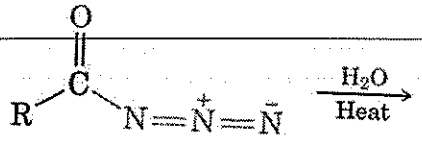
$\downarrow {}^-OH/H_2O$

+

(b)

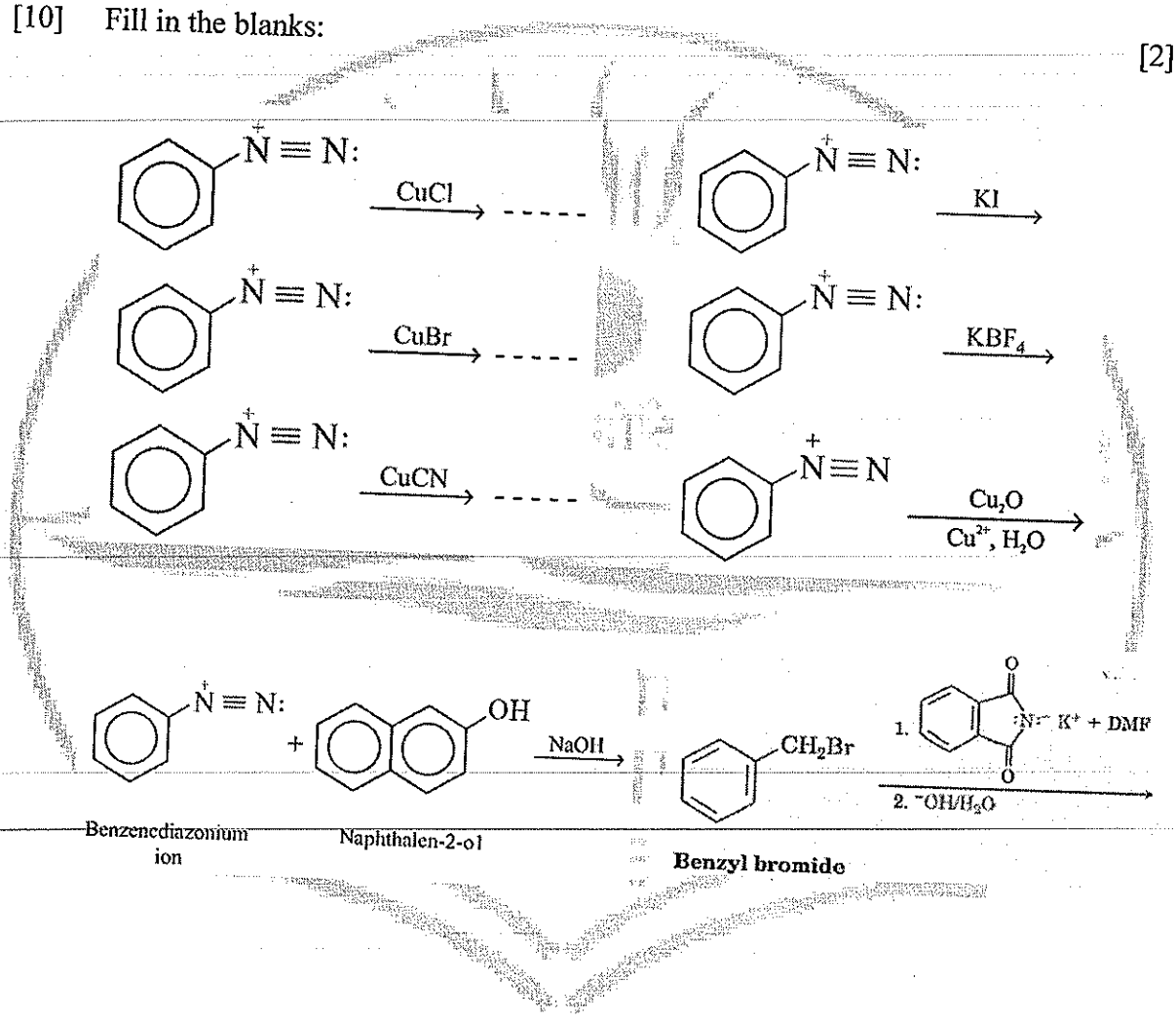


An amide



An acyl azide

[10] Fill in the blanks: [2]



Benzenediazonium ion

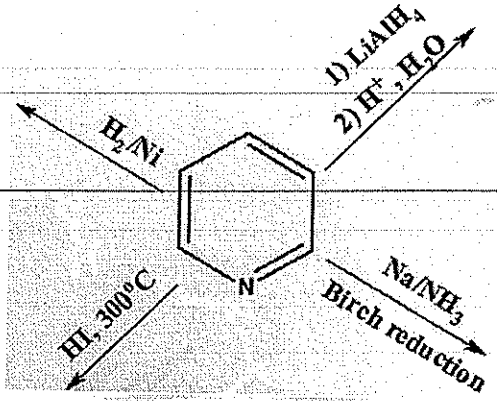
Naphthalen-2-ol

Benzyl bromide

[11] (a) Which one is more basic between pyridine and pyrrole? Also explain the reason. [1]

(b) Match the boiling points 65°C, –6°C and –88°C with the compounds CH_3CH_3, CH_3NH_2 and CH_3OH. Explain your answer briefly. [1]

[12] Write the products of the following reactions: [2]



SECTION: C

(Marks: 12)

[13] (a) Describe the two main factors which influence the basicity. [1]

(b) Arrange primary, secondary and tertiary amines and ammonia in decreasing order of overall basicity determined experimentally. [½]

(c) Among pyridine and piperidine, which one is more basic and why? [½]

(d) How does hybridization affect the basicity? [½]

(e) Why is ammonia a stronger base than aromatic amines? [½]

(f) Why is there a difference between basicity of aniline and methyl amine? [½]

(g) Why are *p*-toluidine and *p*-aminophenol two compounds stronger base than aniline? [½]

(h) Why is nitroanilinle a weaker base than aniline? [½]

(i) Why is acetamide less basic than aniline? [½]

(j) Compare the basic strength of $(CH_3CH_2)_2NH$ and $CH_3CH_2NHCOCH_3$ with reason. [½]

(k) Arrange aliphatic amines, ammonia, aromatic amines and amides in decreasing order of basicity. [½]

[14] Write short notes including chemical reaction on following: [6]

(a) Manniich Reaction

(b) Hoffman Exhaustive Methylation

(c) Hantzsch Synthesis

(d) Fischer Indole Synthesis