

M. Sc. CHEMISTRY
FIRST SEMESTER
ORGANIC CHEMISTRY - I
MSC - 102

Duration: 3 Hrs.

Marks: 70

Part : A (Objective) = 20
Part : B (Descriptive) = 50

[PART-B : Descriptive]

Duration: 2 Hrs. 40 Mins.

Marks: 50

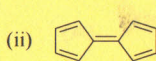
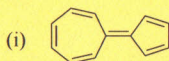
[Answer question no. One (1) & any four (4) from the rest]

1. Answer the following:

2×

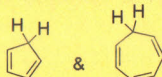
(a) Which one of the following compounds will have dipole-moment? Explain.

5=

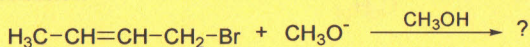


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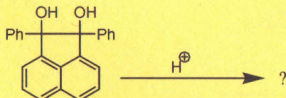
(b) Which one of the following compounds will have lower pka value? Explain.



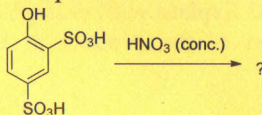
(c) write down the product of the following reaction under SN1 condition



(d) Predict the products in the following reaction with suitable mechanisms.

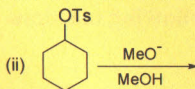
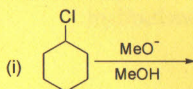


(e) Write down the product of the following reaction with explanation.



2. (a) Explain why an SN² reaction is favoured by polar aprotic solvent? 3

(b) Which of the following will show a faster rate and why? 2

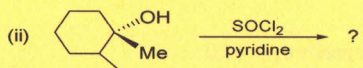
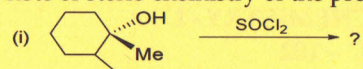


(c) What are S_N^i reactions?

2

(d) Write down the products in the following reactions with mechanism. Take note of stereo chemistry of the products formed.

3

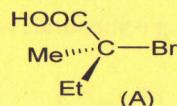


3. (a) What do you mean by neighbouring group participation (NGP) in nucleophilic substitution reactions?

2

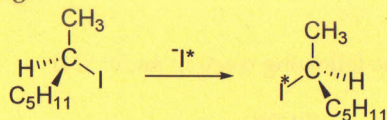
(b) The following substrate (A) give the product with retention of configuration with higher rate when treated with dilute solution of NaOH but give invert product with conc. NaOH having lower rate of reaction than the former. Write down the products with mechanism of the reactions to justify.

3



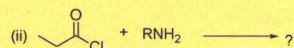
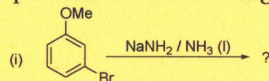
(c) Explain why in the reaction of radioactive iodine with 2-iodooctane, the rate of racemisation is exactly twice the rate of isotopic iodide exchange.

2



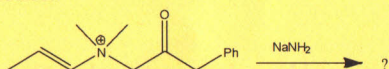
(d) Give the product of the following reactions with mechanism.

3



4. (a) What is Stevens rearrangement? Explain with examples. Write with suitable mechanism the formation of the product in the following reaction.

3



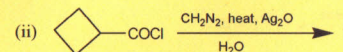
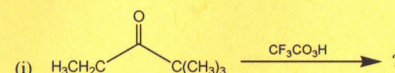
(b) What is Favorskii rearrangement? Explain with examples with proper mechanism.

3

(c) Give the product of the following reactions with mechanism.

2+

2=

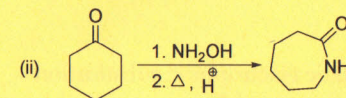
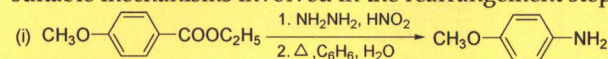


5. (a) Explain the formation of the products for the following reactions with suitable mechanisms involved in the rearrangement step.

3+

3=

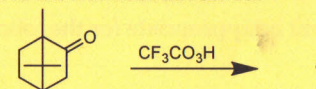
6



(b) Why 2-bromobutanone undergo semibenzilic rearrangement instead of Favorskii rearrangement in presence of a strong base? Explain.

(c) What will be the major product formed in the following reaction? Write the suitable mechanism involved.

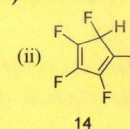
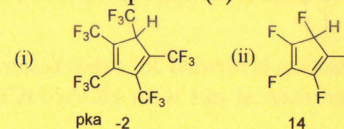
2



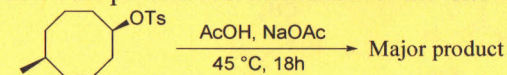
2

6. (a) Why the pKa value of the compound (i) is very low (-2) while the pKa value of the compound (ii) is moderate (14)? Explain

3

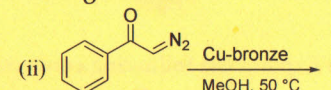
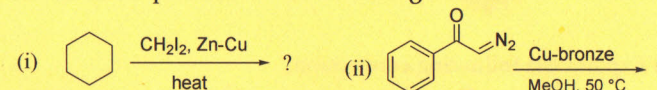


(b) Write down the product and mechanism of the following reaction.



(c) Write down the products of the following reaction.

3



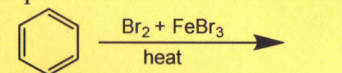
2+

2=

4

7. (a) Write down the product with suitable mechanism.

2



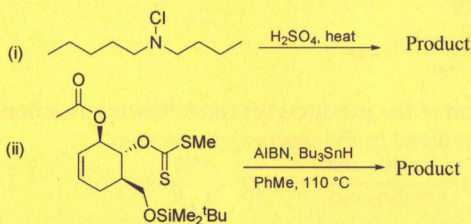
(b) What is ipso attack? Explain with example.

3

(c) Write down the products with mechanism of the following reactions.

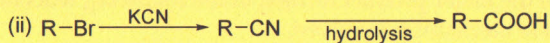
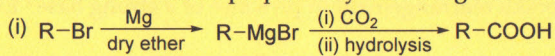
2+

3=

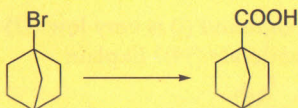


8. (a) Describe in short different types of aliphatic electrophilic substitution reactions. What are their stereo chemical consequences? 3

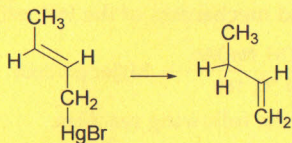
(b) Carboxylic acids can be prepared by following methods 2.5



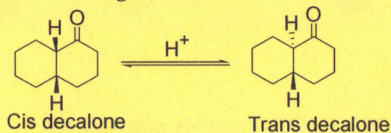
Which of the above methods will be appropriate for the following conversion? Give reason.



(c) The product in the following reaction is formed 10^7 times faster in presence of HCl as compared to when carried out with HOAc-HClO₄ mixture. Explain. 2.5



(d) Explain the following conversion. 2



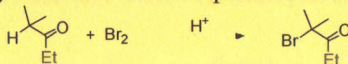
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[PART-A : Objective]

Choose the correct answer from the following :

1×20=20

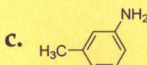
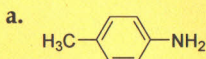
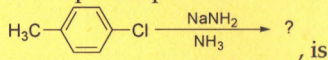
1. The following reaction is an example of -

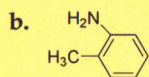


- Nucleophilic substitution
 - Addition reaction
 - Electrophilic substitution
 - Rearrangement reaction
2. Which is not a correct statement for an $\text{S}_\text{N}2$ reaction?
- Proceed with inversion of configuration
 - Weak nucleophile will favour the reaction.
 - Proceed without formation any intermediate.
 - All these statements are correct.
3. Non-occurrence of the following reaction



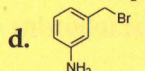
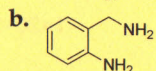
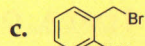
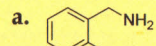
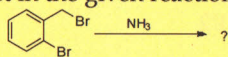
- Attacking nucleophile is a stronger one
 - Leaving group is a strong base
 - Alcohols are not reactive
 - Hydroxide bases are weak bases
4. Substitution of the following substitution reaction
- $$\text{(2R,3S)-2-bromo-3-methylpentane} \xrightarrow[\text{DMF}]{\text{conc. CH}_3\text{O}^-} ? \quad , \text{ will produce}$$
- (2R,3R)-2-methoxy-3-methylpentane
 - (2R,3S)-2-methoxy-3-methylpentane
 - (2S,3S)-2-methoxy-3-methylpentane
 - (2S,3R)-2-methoxy-3-methylpentane
5. The expected product in the following reaction





d. Both 'a' and 'c'

6. The major product in the given reaction



7. Nucleophilic nature of the following nucleophiles (1) $C_6H_5O^-$, (2) $C_2H_5O^-$, (3) $C_2H_5S^-$ in methanol will follow the order

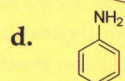
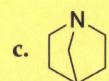
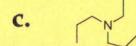
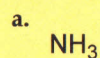
a. 3>1>2

c. 1>2>3

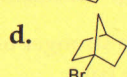
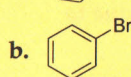
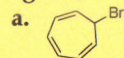
b. 2>1>3

d. 3>2>1

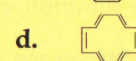
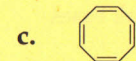
8. Which one is the strongest base among the followings?



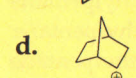
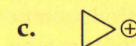
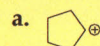
9. Which one of the followings will give rapid precipitation of $AgBr$ in the presence of $AgNO_3$



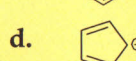
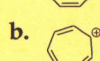
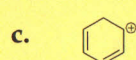
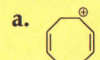
10. Which one of the followings is nonaromatic



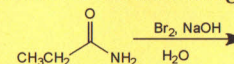
11. The example of a non-classical carbocation is



12. Which one of the followings is homoaromatic



13. Which is the main product in the following reaction of an amide?



a. $CH_3CH_2CH_2NH_2$

c. CH_3CH_2COOH

b. $CH_3CH_2NH_2$

d. $CH_3COCH_2NH_2$

14. The transformation of an allylic ether into a homoallylic alcohol in presence of a base at low temperature is a

a. [1,2] Wittig rearrangement

b. Steven rearrangement

c. [2,3] Wittig rearrangement

d. Sommelet-Hauser rearrangement

15. The migratory aptitude of aryl groups in Baeyer-Villiger rearrangement is

a. p-anisyl > p-tolyl > phenyl > p-chlorophenyl > p-nitrophenyl

b. p-anisyl > p-tolyl > phenyl > p-nitrophenyl > p-chlorophenyl

c. p-anisyl < p-tolyl < phenyl < p-chlorophenyl < p-nitrophenyl

d. p-tolyl < p-anisyl < phenyl < p-chlorophenyl < p-nitrophenyl

16. The intermediate formed in Neber rearrangement is

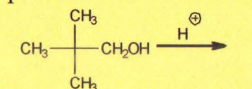
a. Isocyanate

b. Carbanion

c. carbocation

d. Azirine

17. What will be the product formed in the following reaction



a. $(CH_3)_2C=CHCH_3$

c. $CH_2=C(CH_3)CH_2CH_3$

b. $(CH_3)_3CCH_3$

d. None of the above

18. In aromatic electrophilic substitution reaction aniline act as

a. ortho/para directing and activating

b. ortho/para directing and deactivating

c. meta directing and activating

d. meta directing and deactivating

19. Hammett equation is not applicable for aromatic compound which has

a. functional group at para position

b. functional group at ortho position

c. functional group at meta position

d. no functional group

20. For the linear free energy relationship in aromatic substitution reaction, Taft equation considers

a. only polar effect

b. only steric effect

c. both polar and steric effects

d. none of them

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