

G 18001607



18001607

Reg. No.....

Name.....

M.Sc. DEGREE (C.S.S.) EXAMINATION, JUNE 2018

Second Semester

Faculty of Science

Branch : Chemistry

AN2C06/AP2C06/CH2C06/PH2C06/POH2C06—ORGANIC REACTION MECHANISMS

(2012 Admission onwards)

[Common to all Branches of Chemistry]

Time : Three Hours

Maximum Weight : 30

Section A

*Answer any **ten** questions, each question carries weight 1.*

1. What is Markovnikov's rule ? Explain using a suitable example. Compare this rule with Kharasch effect ?
2. Arrange the following groups in the increasing order of leaving ability in nucleophilic substitution reactions at SP^3 carbon :
Tosyl, Nosyl, Brosyl, Sulphonate, Sulphate, Acetate, Bromide, Iodide.
3. What are enamines ? How they are formed ? What is the benefit of enamine alkylation compared to enolate alkylation ?
4. Vinyl and aryl halides have very low reactivity in nucleophilic substitution reactions. Explain
5. What are non-classical carbocations ? Give an example. State a chemical reaction which undergoes via a non-classical carbocations as intermediate.
6. Arrange the following carbenes in the increasing order of stability :
: CH_2 : CCl_2 : $C(CH_3)_2$: CBr_2 : CF_2 : $C(NCH_3)$.
7. Give one example each for the insertion reaction and addition reaction of carbenes.
8. Name two common radical initiators (one peroxide and another azo) used in free radical reactions. Explain how these initiates a radical reaction.
9. What is Clemmenson reduction ? What are the reagents used for the reduction ? What is the mechanism of the reaction ?

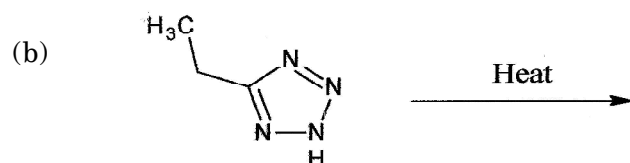
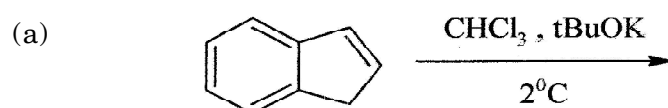
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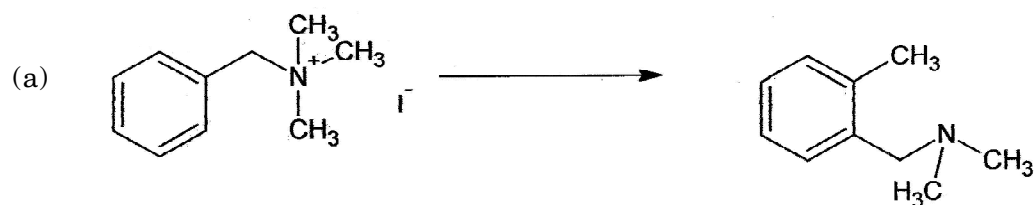


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10. Give the mechanism of Stork enamine reaction. State one of its important application in synthesis.
11. Give the sequence of reactions in which phenol is converted to caprolactam.
12. Complete the following reactions :



13. How are the following conversions are effected ?



(10 × 1 = 10)





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Section B

Answer any **five** questions by attempting not more than **three** questions from each bunch.

Each question carries weight 2.

BUNCH 1

14. Give the important synthetic applications of Grignard reagents.
15. Draw the correlation diagram for (4 + 2) cyclo addition reaction and explain whether the reaction is thermally or photo chemically feasible.
16. Discuss briefly the use of Baldwin rules in cyclisation reactions taking appropriate examples.
17. Give the mechanism of Cope reaction with special emphasis to stereochemistry.

BUNCH 2

18. What is Noyori annulations reaction ? What is its synthetic application ?
19. Write briefly on Farvorski rearrangement.
20. Write a note on Barton deoxygenation reaction.
21. Give the mechanism of Curtius rearrangements.

(5 × 2 = 10)

Section C

Answer any **two** questions.

Each question carries weight 5.

22. Give the mechanism of the following reactions :—
 - (a) McMurry couplings.
 - (a) Robinson annulations.
 - (c) Beckmann rearrangements.
23. Give a brief account of the synthetic applications of the following reactions :
 - (a) Diels-Alder reaction.
 - (b) Mannich reaction.
 - (c) Dieckmann condensation.
24. Write briefly on the β -eliminations involving cyclic transition states with special reference to N-oxides, Acetates and Xanthates, using suitable examples.

Turn over





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25. Write notes on :

- (a) Woodward-Hoffmann rules for concerted reactions.
- (b) Amination of haloarenes.
- (c) Carbenes.

(2 × 5 = 10)

