

This question paper contains 4+2 printed pages]

AG—80—2018

FACULTY OF SCIENCE

M.Sc. (Chemistry) (First Year) (First Semester) EXAMINATION

OCTOBER/NOVEMBER, 2018

(CBCS Pattern)

CHEMISTRY

Paper—I (CH-412)

(Organic Chemistry)

(Wednesday, 28-11-2018)

Time : 10.00 a.m. to 1.00 p.m.

Time—3 Hours

Maximum Marks—75

N.B. :— (i) Attempt All questions.

(ii) Figures to the right indicate full marks.

(iii) Use of logarithmic table and calculator is allowed.

(iv) Multiple Choice Questions (MCQ) should be attempted only once on page No. 3 of answer-book with complete answer.

1. Attempt any *three* of the following : 15

(a) Explain arenium ion mechanism with suitable examples.

(b) Derive the Hammett equation and calculate the substituent constant of the following ethyl benzoate.

(Given data : pK_a values of substituted ethyl benzoate at M-Me = 4.26, P-H = 4.20, M-NO₂ = 3.49, P-OMe = 4.47, M-Br = 3.80 and pK_{aH} = 4.20)

Calculate :

$$\sigma_{M-Me} = ?$$

$$\sigma_{P-H} = ?$$

$$\sigma_{M-NO_2} = ?$$

$$\sigma_{P-OMe} = ?$$

$$\sigma_{M-Br} = ?$$

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- (c) Explain the effect of substrate, attacking nucleophile and leaving group in aliphatic nucleophilic substitution reaction.
- (d) What is photofries reaction ? Explain the photofries reaction of anilides with suitable example.
- (e) What is Jablonski diagram ? Explain in detail with suitable examples.

2. Attempt any *three* of the following : 15

- (a) Explain the generation and stability of Carbocation and Nitrene.
- (b) Explain the primary and secondary kinetic isotopic effect with examples.
- (c) Explain the term Anchimeric assistance and SN^i mechanism with examples.
- (d) What is Photochemistry ? Explain the Norrish Type-I and II reactions with example.
- (e) Discuss the photochemistry of cis-trans isomerisation of stilbenes in the presence of photosensitiser.

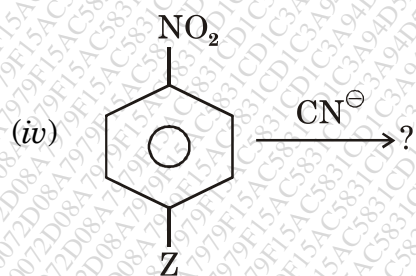
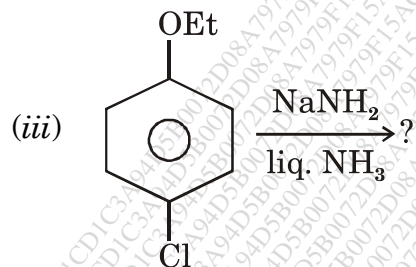
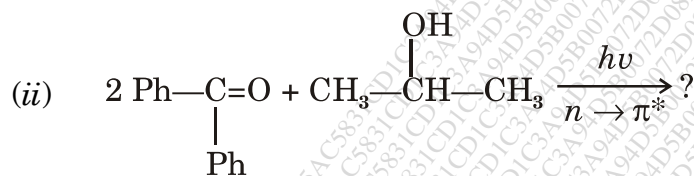
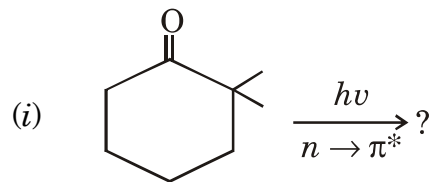
3. (a) Comment on the following : 7

- (i) Hammond postulate
- (ii) Alternate and non-alternate hydrocarbon.

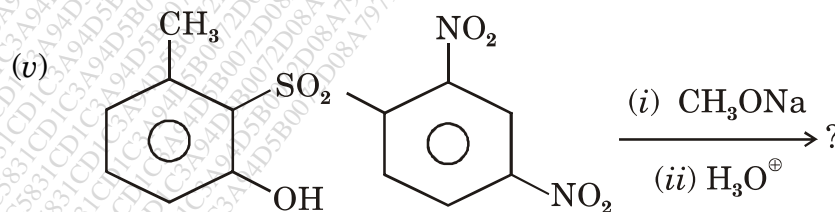
Or

What is photoreduction ? Explain the photoreduction of benzophenone with mechanism.

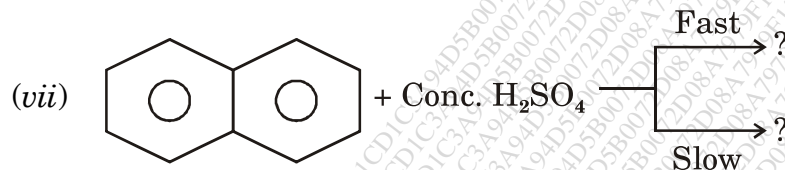
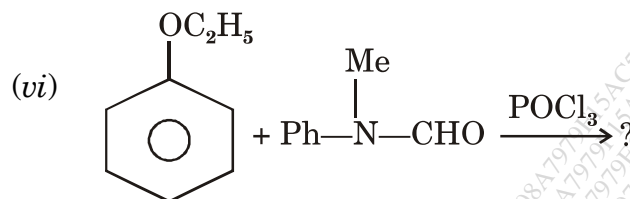
(b) Predict the products with mechanism of the following (any four) : 8



(Z = Electron withdrawing group)



P.T.O.



4. (a) Explain the Paterno-Buchi reaction and photochemistry of α , β -unsaturated ketones with examples. 7

Or

Discuss the following :

- (i) SN^i mechanism
(ii) Benzyne intermediate reaction.

- (b) Explain the following : 8

- (i) Ortho-para ratio
(ii) Diazonium coupling reaction.

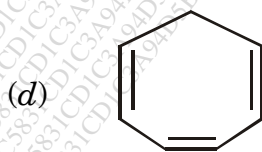
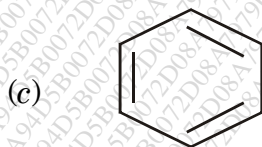
Or

- (i) What are annulenes ? Explain the aromaticity of [10] annulenes.
(ii) Substituent constant and reaction constant.

5. (A) Select the *correct* answer from the given options for each of the following : 5

- (i) The conversion of singlet to triplet state takes place via :
(a) Internal conversion
(b) Intersystem crossing
(c) Fluorescence
(d) Phosphorescence

- (ii) σ_x in Hammett equation indicates
- (a) Reaction constant
 - (b) Equilibrium constant
 - (c) Rate constant
 - (d) Substituent constant
- (iii) By the absorption of correct energy $h\nu$, the electronic excitation from ground state to excited state with spin inversion gives
- (a) Singlet state
 - (b) Triplet state
 - (c) Transition state
 - (d) None of the above
- (iv) Which of the following compounds is non-aromatic ?



P.T.O.

- (v) A phenomenon of hyperconjugation is not shown by :
- (a) Methyl carbocation
 - (b) Ethyl carbocation
 - (c) Isopropyl carbocation
 - (d) Tert. butyl carbocation
- (B) Write short notes on any *two* of the following : 10
- (i) Photodegradation of polymer
 - (ii) NGP
 - (iii) Taft equation.