

Name: ID No.

Course No: CHEM F212

Course Title: ORGANIC CHEMISTRY I

PART I (CLOSED BOOK)

Max. Marks: 30

Time: 60 minutes

Date: 09th December 2017

Note: Write your name and ID no. on the question paper. All questions are compulsory.

Part I contains 14 questions in all. Indicate the most appropriate answer by entering A, B, C or D in boxes provided in front of the questions (Q. No. 1-12). Use a blue or a black point pen. Each question (Q. 1-12) carries 2 mark. Q. 13-14 are to be solved in the space provided. Part II may be collected after submitting Part I.

Q.No.1. The correct order of decreasing acid strength of trichloroacetic acid (P), trifluoroacetic acid (Q), acetic acid (R) and formic acid (S) is

- (A) P > Q > R > S (B) P > R > Q > S (C) Q > P > S > R (D) Q > S > R > P

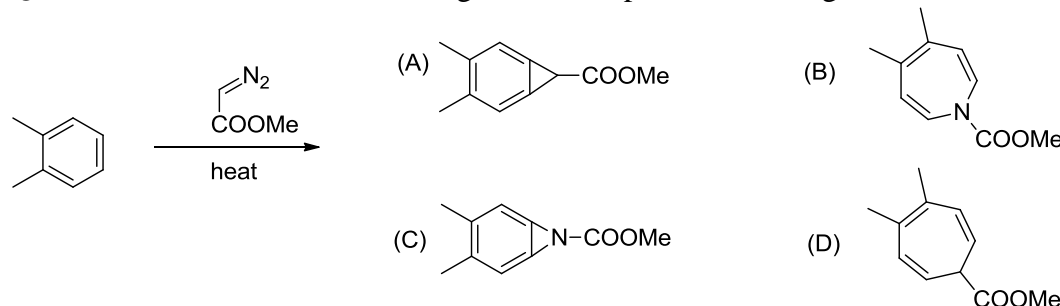
Q.No.2. Which one of the following reactions will not result in the formation of carbon-carbon bond?

- (A) Reimer-Tieman reaction (B) Friedel Crafts acylation
 (C) Aldol condensation (D) Cannizzaro reaction

Q.No.3. The correct sequence of steps involved in the mechanism of Cannizzaro's reaction is

- (A) nucleophilic attack by OH⁻, transfer of H⁻ and transfer of H⁺
 (B) electrophilic attack by OH⁻, transfer of H⁺ and transfer of H⁻
 (C) transfer of H⁻, transfer of H⁺ and nucleophilic attack
 (D) transfer of H⁺, nucleophilic attack and transfer of H⁻

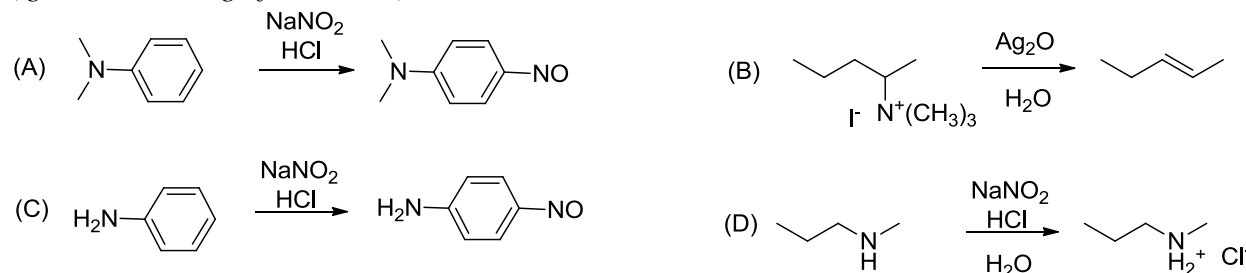
Q.No.4. Which one of the following is the final product for the given chemical transformation?



Q.No.5. When 1,3-butadiene reacts with HCl, two products, 3-chloro-1-butene and 1-chloro-2-butene are formed. At low temperatures (-78°C), which of the following statements is correct?

- (A) Thermodynamic control favors formation of 3-chloro-1-butene
 (B) Kinetic control favors formation of 3-chloro-1-butene
 (C) Thermodynamic control favors formation of 1-chloro-2-butene
 (D) Kinetic control favors formation of 1-chloro-2-butene

Q.No.6. Which one of the following chemical equations correctly represents the formation of the major product? (ignore balancing of reactions)



Q.No.7. A Michael reaction is an example of a conjugate addition. What is a conjugate addition?

- (A) It is a synchronous addition of an electrophile and nucleophile to a double bond
 (B) It is a nucleophilic addition to a triple bond followed by protonation
 (C) It converts an α,β -unsaturated ketone into a substituted saturated ketone
 (D) It is a nucleophilic addition to an aromatic ring followed by expulsion of a leaving group

Q.No.8. Which one of the following is the most appropriate reducing agent for carrying direct reductive amination of ketones (without isolating imines)?

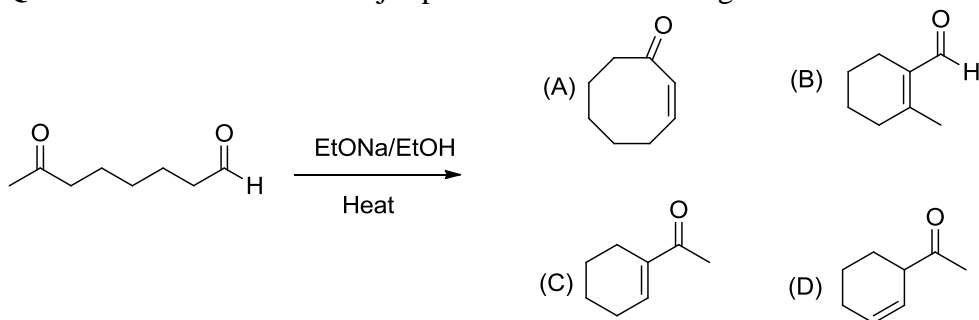
(A) NaBH_4

(B) LiAlH_4

(C) $\text{NaBH}(\text{CN})_3$

(D) H_2/Ni

Q.No.9. Which one is the major product of the following reaction?



Q.No.10. The order **not correct** for basic strength of amines is

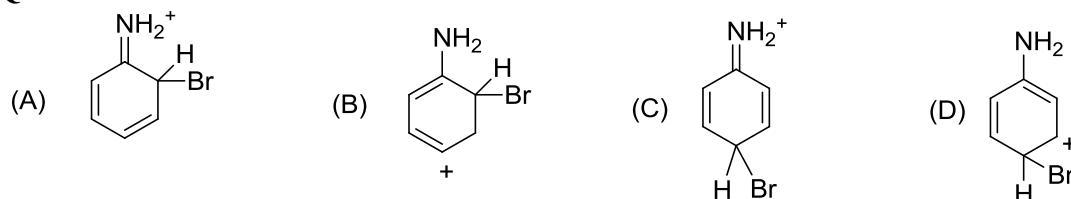
(A) Dimethyl amine > methyl amine > trimethyl amine in aqueous solution

(B) Trimethyl amine > dimethyl amine > methyl amine in gas phase

(C) methyl amine > aniline

(D) aniline > pyridine

Q.No.11. Which one of the arenium ions is **not** involved in the bromination of aniline?



Q.No. 12. Which one of the following compounds will react most rapidly with water?

(A) acetone

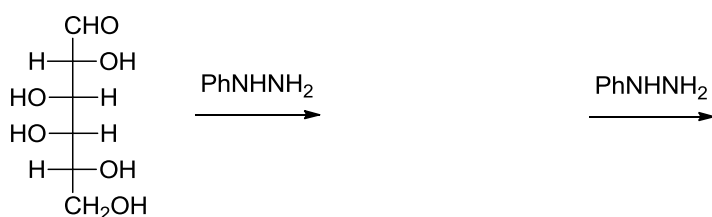
(B) acetyl chloride

(C) acetic anhydride

(D) ethyl acetate

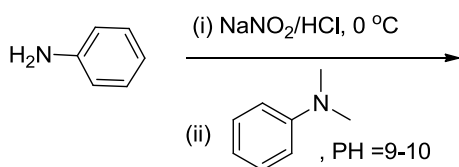
Q.No. 13. Draw the missing structures in the following reaction sequence.

[2]



Q.No. 14. Identify the product & Propose a detailed mechanism for the following chemical transformation.

[4]



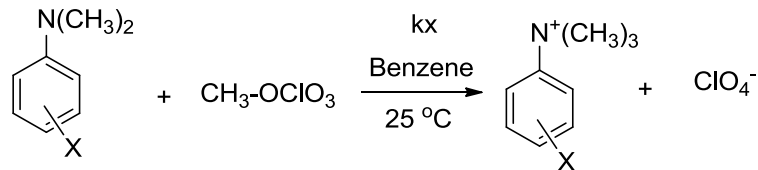
Course No: CHEM F212
Max. Marks: 60

Course Title: ORGANIC CHEMISTRY I
Time: 120 minutes

PART II (OPEN BOOK)
Date: 09th December 2017

Note: Write your name and ID no on the question paper and answer sheet. All questions are compulsory.

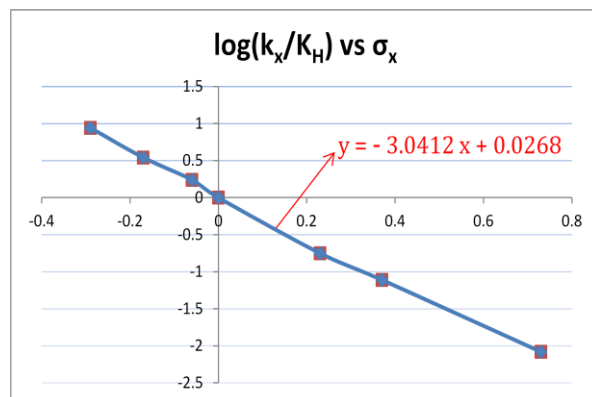
Q. No. 1. (i) Consider the following reaction, and the plot of its $\log(k_x/K_H)$ versus σ_x for different substituents (X) present on phenyl ring.



(a) Determine the reaction constant for this reaction, and propose a mechanism showing the transition state involved. [1+2]

(b) Comment on the effect of positive and negative values of σ_x on the stability of transition state and k_x . [2]

(c) Predict the rate constant (k_x) for substitution reaction of *N,N*-dimethyl *para*-nitroaniline, if $k_H = 3.44 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ and σ_x (*p*-NO₂) = 0.78. [1]



(ii) A competitive experiment was performed for the borohydride reductions of benzaldehyde and deuterated benzaldehyde separately (Reactions 1 & 2, Figure 1). The respective rate constants k_1 and k_2 for the reactions 1 & 2 are $0.14 \text{ M}^{-1} \text{ s}^{-1}$ and $0.20 \text{ M}^{-1} \text{ s}^{-1}$ respectively.

(a) Determine the type of isotope effect & Justify. [1]

(b) Identify the structure of product(s) in each case, and comment on their optical activity. [3]

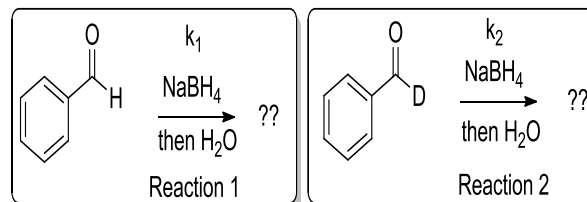
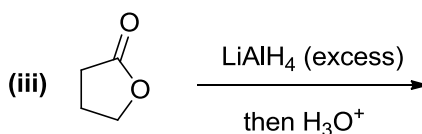
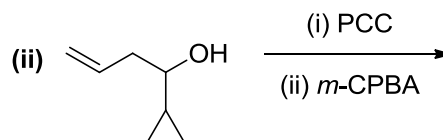
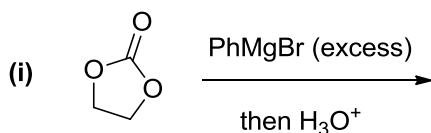


Figure 1

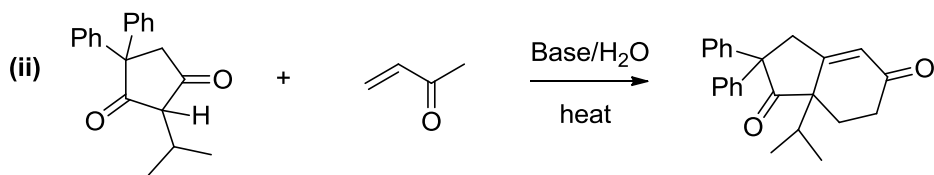
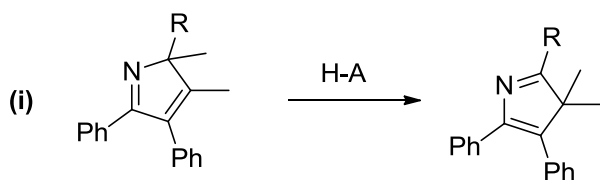
Q. No. 2. (i) Compare the reaction of *p*-chlorotoluene with KNH₂ followed by addition of water with the reaction of *m*-chlorotoluene under same conditions. Identify the structures of possible products in both cases with justification. [5]

(ii) You are provided with four compounds (**P** = 2-Bromobenzaldehyde; **Q** = 3-Bromobenzaldehyde; **R** = 4-Bromotoluene; **S** = 4-Bromoanisole). Which one of these (**P-S**) is most likely to undergo ammonolysis fastest *via* addition-elimination pathway? Explain. Draw a detailed energy profile diagram for the above reaction showing the structures of intermediate(s) and labeling slow/fast steps. [2+3]

Q. No. 3. Predict the structure of the product(s) and propose a detailed mechanism for the following chemical transformations. [3+4+3=10]

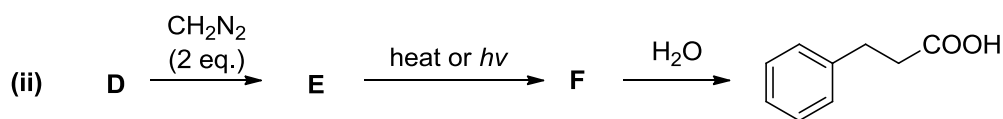
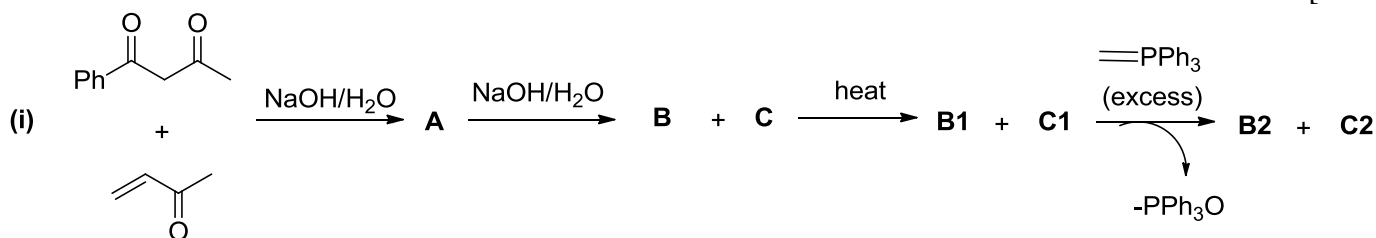


Q. No. 4. Propose a detailed mechanism for the following chemical transformations. [2x5=10]

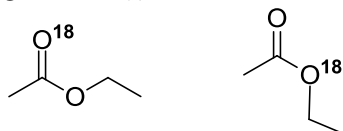


Q. No. 5. (i) Identify the structures of **A-F** in the following series of reactions. (*No mechanism required*)

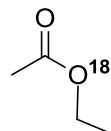
[10x1=10]



Q. No. 6. (i) Consider the hydrolysis of labeled ethyl ethanoates, **1** or **2**, in normal water.



Compound **1**



Compound **2**

Which of the two compounds (**1** or **2**) upon hydrolysis will retain ^{18}O isotope either in the main product or in side product respectively. Justify using an appropriate detailed mechanism. [4]

(ii) Carry out the following conversion using appropriate reagents/solvents/catalyst. [6]

