

# CHAROTARUNIVERSITY OF SCIENCE & TECHNOLOGY

## 2<sup>nd</sup> Semester of B. Pharm. Examination

University Theory Examination April-May 2018

### PH119/PH127 Pharmaceutical Chemistry-II

Date: 15.05.18, Tuesday Time: 10:00 a.m. to 01:00 p.m. Maximum Marks: 80

#### Instructions:

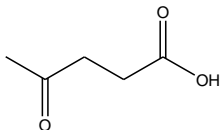
1. There are three sections in this question paper.
2. SECTION – I comprises of Question 1. Total marks for Section 1 are 20. There are 20 sub-questions (MCQ type). Answers to SECTION – I are to be given in Answer Sheet for MCQ type questions provided to you. Maximum time allotted for SECTION – I is 30 minutes. Answers to SECTION – I must be written during the first 30 minutes of the examination.
3. Answers to SECTION – II and SECTION – III are to be provided in separate Main Answer Books provided to you.
4. Figures to right indicate marks.
5. Draw neat sketches wherever necessary.

### Solution

#### Section – I

**Q 1 Attempt all questions. Each question is of one mark. 20**

1. The following statements are correct for carbocation; Except One.  
[A] Stability order of carbocation is  $3^{\circ} > 2^{\circ} > 1^{\circ}$   
[B] Amine group increase the stability of carbocation  
[C] Carbocation can act as an electrophile  
**[D] Chlorine group increase the stability of carbocation**
2. Orientation of Elimination reaction follows...  
[A] Markovnikov's rule  
**[B] Saytzeff's rule**  
[C] Micheal addition  
[D] Hoffmann rule
3. Alkyl halides undergo a type of reaction  
P. Nucleophilic substitution  
Q. Nucleophilic addition  
R. Elimination  
S. Electrophilic aromatic substitution  
[A] P and Q are correct  
**[B] P and R are correct**  
[C] P, Q, R and S are correct  
[D] Q and R are correct
4. Addition of water to alkene will give \_\_\_\_\_ .  
[A] Aldehyde  
[B] Ketone  
**[C] Alcohol**  
[D] Carboxylic acid

5. In which of the following molecule Intramolecular H- Bonding is exist.
- [A] **2 - hydroxy Benzoic acid**  
 [B] 3 - hydroxy Benzoic acid  
 [C] 4 - hydroxy Benzoic acid  
 [D] 3,5 - dihydroxy Benzoic acid
6. 2 methyl-2 propanol is an example of
- [A] Primary alcohol  
 [B] Secondary alcohol  
 [C] **Tertiary alcohol**  
 [D] Quaternary alcohol
7. Which of the following compounds contain all the carbon atoms in the same hybridization state?
- [A]  $\text{H}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{H}$   
 [B]  $\text{CH}_3-\text{C}\equiv\text{C}-\text{CH}_3$   
 [C]  **$\text{CH}_2 = \text{C} = \text{CH}_2$**   
 [D]  $\text{CH}_2 = \text{CH}-\text{CH} = \text{CH}_2$
8. Identify the correct steps involved in Free radical reaction.
- [A] Step 1. Initiation Step 2. Termination Step 3. Propagation  
 [B] Step 1. Termination Step 2. Initiation Step 3. Propagation  
 [C] Step 1. Propagation Step 2. Initiation Step 3. Termination  
 [D] **Step 1. Initiation Step 2. Propagation Step 3. Termination**
9. Which of the following has more electronegativity?
- [A] O  
 [B] N  
 [C] S  
 [D] **F**
10. The bond angle in  $\text{SP}^2$  hybridized carbon is \_\_\_\_\_.
- [A] 109.5  
 [B] **120**  
 [C] 90  
 [D] 180
11. The IUPAC name for
- 
- [A] 1-hydroxypentane-1,4-dione  
 [B] 1,4-dioxopentanol  
 [C] 1-carboxybutan-3-one  
 [D] **4-oxopentanoic acid**
12. Which of the following is most basic?
- [A] Ammonia  
 [B] Ethyl amine  
 [C] Aniline  
 [D] **Triethyl amine**
13. Which of the following alkene is more stable?
- [A] 1-Propene  
 [B] Ethene  
 [C] 2-Butene  
 [D] **2-methyl-2-butene**

14. Which of the following metals is used as a catalyst in the catalytic hydrogenation of both alkenes and alkynes?

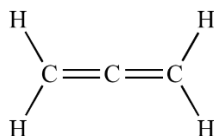
[A] **Palladium**

[B] Iron

[C] Magnesium

[D] Copper

15. Identify the following type's dienes.



[A] Conjugated Diene

[B] Isolated Diene

[C] **Cumulated Diene**

[D] None of above

16. All are the example of Heterogeneous Catalyst. Except One.

[A] Pd

[B] Ni

[C] Pt

[D] **Wilkinson's**

17. All statement is correct for  $S_N2$  reaction. Except one

[A] Follow Second order kinetic

[B] **Rearrangement is possible**

[C] Inversion of configuration takes place

[D] Single step reaction

18. Which of the following reactive intermediate is act as a Nucleophile?

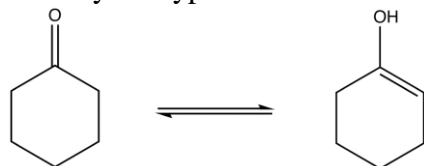
[A] Carbocation

[B] Nitrene

[C] Carbene

[D] **Carbanion**

19. Identify the types of tautomerism observed in following figure.



[A] Amine Imine

[B] **Keto Enol**

[C] Lactam Lactim

[D] Amide Imidic

20. Which of the following is a polar aprotic solvent?

[A] **DMF**

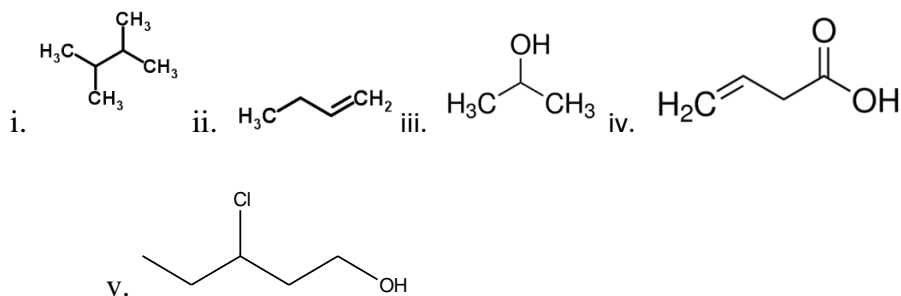
[B] Ethanol

[C] Water

[D] Butanol

## SECTION – II

- Q 2** Attempt any **TWO** of the following; **05**
- A** Define Hybridization – 02 Marks **05**  
Explanation about  $SP^3$  hybridization with examples ( $SP^3$  hybridization in C, N and O) with its Bond angle and Shape, S-Character and electronic configuration
- B** Definition Resonance effect – 01 Marks **05**  
Electron donation resonance effect with resonating structures – 02 Marks  
Electron withdrawing resonance effect with resonating structures – 02 Marks
- C** Define following terms; - Each correct definition will get 01 Marks **05**
- Conjugation
  - Polar and non-polar bonds
  - Hyper-conjugation
  - Tautomerism
  - H- bonding
- Q 3** Attempt any **TWO** of the following; **05**
- A** Classify different reactive intermediates of carbon – 02 Marks **05**  
Carbocation, Carbanion, Carbene, Nitrene, Free Radicals, Nitronium ion  
Any three stability aspects of Carbanion – 03 Marks  
Stability in Allylic, Benzylic, Field effect
- B** Compare  $SN_1$  and  $SN_2$  reaction. **05**  
Any Five points about  $SN_1$  and  $SN_2$  – 05 Marks
- Reaction
  - Kinetic
  - Reactivity
  - Steps involved
  - Stereochemistry
  - Rearrangement
- C** Construct the structure from the following IUPAC names **05**

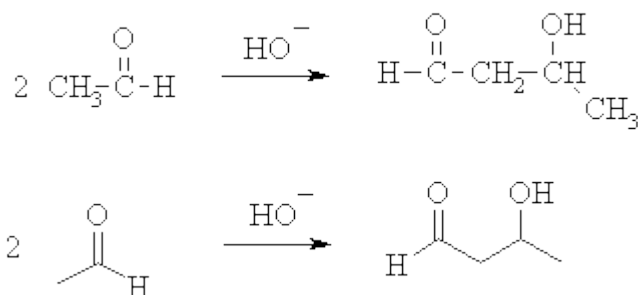


### SECTION – III

**Q 4** Attempt any **FOUR** of the following;

**A** Write reaction – 02 Marks and mechanism- 03 Marks of Aldol Condensation. **05**

- Reagents: commonly a base such as NaOH or KOH is added to the aldehyde.
- The reaction involves an aldehyde enolate reacting with another molecule of the aldehyde.
- Remember enolates are good nucleophiles and carbonyl C are good electrophiles.
- Since the  $pK_a$  of an aldehyde is close to that of NaOH, both enolate and aldehyde are present simultaneously.
- The products of these reactions are  $\beta$ -hydroxyaldehydes or aldehyde-alcohols = aldols.
- Examples:



#### MECHANISM OF THE ALDOL CONDENSATION

##### 1. MECHANISM OF THE ALDOL REACTION

**Step 1:**

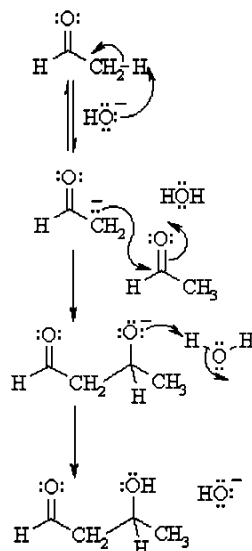
First, an acid-base reaction. Hydroxide functions as a base and removes the acidic  $\alpha$ -hydrogen giving the reactive enolate.

**Step 2:**

The nucleophilic enolate attacks the aldehyde at the electrophilic carbonyl C in a nucleophilic addition type process giving an intermediate alkoxide.

**Step 3:**

An acid-base reaction. The alkoxide deprotonates a water molecule creating hydroxide and the  $\beta$ -hydroxyaldehydes or **aldol** product.



**B**

- Write reaction and mechanism – 02 Marks
- Reactivity and kinetic – 01 Marks
- Stereochemistry of  $S_N2$  mechanism with examples – 02 Marks

**05**

C Give any three preparation and reactions of Alkenes

05

**Preparation of alkene – 2.5 Marks**

1. Dehydrohalogenation of alkyl halide
2. Dehydration of alcohol
3. Dehalogenation of vicinal dihalides
4. Reduction to alkynes
5. Conversion of aldehyde and ketone to alkene

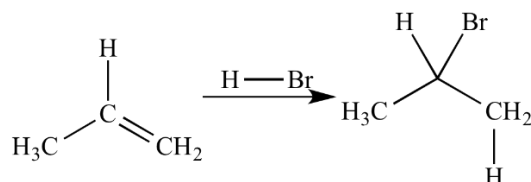
**Reaction of alkene – 2.5 Marks**

1. Catalytic Hydrogenation
2. Addition of Halogens
3. Addition of HX
4. Addition of H<sub>2</sub>SO<sub>4</sub>
5. Addition of Water
6. Halohydrin Formation
7. Dimerization
8. Alkylation
9. Oxymercuration- Demercuration

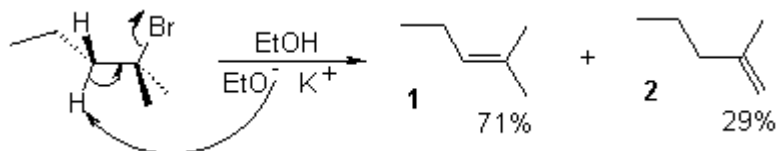
D Write Markovnikov's – 2.5 Marks and Saytzeff's rules – 2.5 Marks with suitable examples.

05

**1. Markovnikov's rule:** In an addition reaction of a protic acid HX (hydrogen chloride, hydrogen bromide, or hydrogen iodide) to an alkene or alkyne, the hydrogen atom of HX becomes bonded to the carbon atom that had the greatest number of hydrogen atoms in the starting alkene or alkyne.



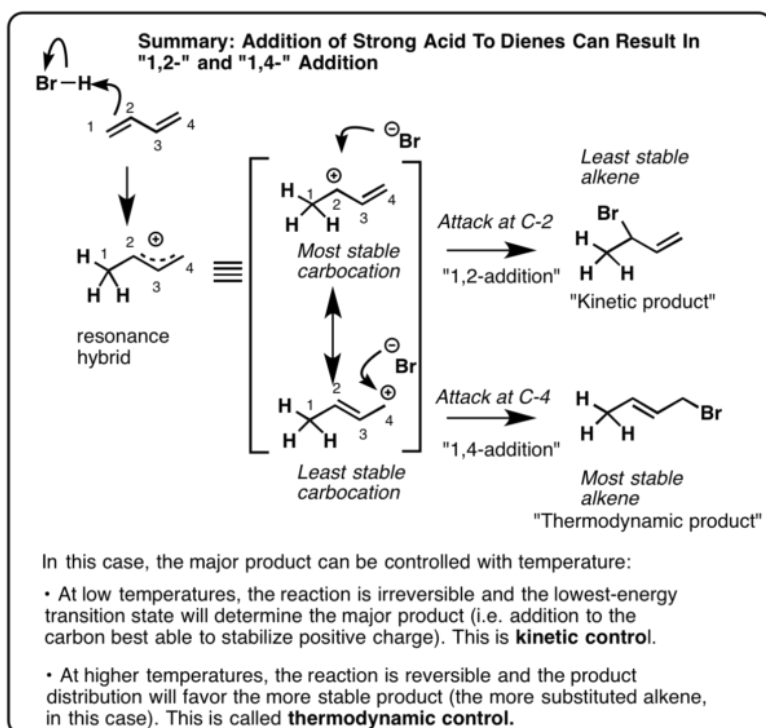
**2. Saytzeff's rules:** A double bond is formed due to loss of water molecule. It is an elimination reaction. According to Saytzeff's rule (also Zaitsev's rule), during dehydration, more substituted alkene (olefin) is formed as a major product, since greater the substitution of double bond greater is the stability of alkene.



E Explain 1, 4 addition Vs. 1, 2 addition in dienes.

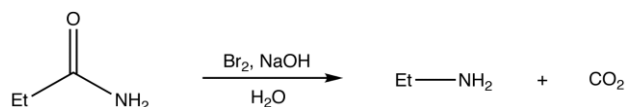
05

1,2 and 1,4 Addition of Acid to Diene with reaction – 05 Marks

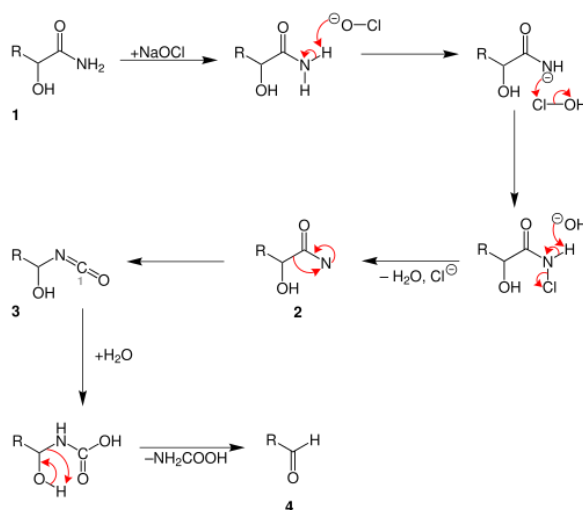


**F** Write reaction – 02 Marks and mechanism – 03 Marks for Hoffmann degradation of amide. **05**

Hofmann rearrangement, also known as Hofmann degradation and not to be confused with Hofmann elimination, is the reaction of a primary amide with a halogen (chlorine or bromine) in strongly basic (sodium or potassium hydroxide) aqueous medium, which converts the amide to a primary amine.



**Suitable Mechanism – 03 Marks**



**Q 5** Attempt any **FOUR** of the following;  
**A** Write reaction and mechanism – 02 Marks  
 Orientation – 02 Marks

**05**

- Reactivity and Kinetic of E<sub>2</sub> mechanism – 01 Marks
- B** Explain various factor affecting SN<sub>1</sub> and SN<sub>2</sub> reaction. **05**
- Write various factors affecting rate of SN<sub>2</sub> reaction. **(03 Marks)**
- Effect of Leaving group
  - Effect of Nucleophile
  - Effect of Solvent
  - Effect of Substrate
- Write various factors affecting rate of SN<sub>1</sub> reaction. **(02 Marks)**
- Effect of Leaving group
  - Effect of Solvent
  - Effect of Substrate
- C** Write any three preparation and reaction of Amine. **05**
- Preparation of amine – 2.5 Marks**
1. Reduction of Nitro
  2. Reaction of Halide with Ammonia/Amine
  3. Reductive Amination
  4. Reduction of Nitrile
  5. Reduction of amide
  6. Hofmann degradation of amide
- Reaction of amine – 2.5 Marks**
1. Basicity; Salt formation
  2. Alkylation
  3. Conversion into amide
  4. Ring substitution in aromatic amines
  5. Hofmann elimination / cope elimination
  6. Reaction with nitrous acid
- D** Give any three preparation and reactions of Alkyl halide. **05**
- Preparation of alkyl halide – 2.5 Marks**
1. From Alcohol
  2. Halogenation of hydrocarbon
  3. Addition of HX to alkene
  4. Addition of X<sub>2</sub> to alkene/alkyne
  5. Halide Exchange
- Reaction of alkyl halide – 2.5 Marks**
1. Nucleophilic Substitution
  2. Dehydrohalogenation
  3. Preparation of Grignard Reagent
  4. Reduction
- E** Give any three preparation and reactions of Alkane. **05**
- Preparation of alkane – 2.5 Marks**
1. Hydrogenation of Alkenes
  2. Reduction to Alkyl halide
  3. Coupling reaction
- Reaction of alkane – 2.5 Marks**
1. Halogenation



2. Combustion
3. Pyrolysis

**F** Write in detail about the preparation and reaction of Alcohol.

**05**

**Preparation: (Any Three – 2.5 Marks)**

1. Oxymercuration- demercuration
2. Hydroboration – oxidation
3. Hydrolysis of alkyl halides
4. Aldol Condensation
5. Reduction of Carbonyl compounds
6. Reduction to Acids and ester

**Reaction: (Any Three – 2.5 Marks)**

1. Reaction with HX
  2. Reaction with  $PX_3$
  3. Dehydration
  4. Reaction as acids: reaction with active metals
  5. Ester Formation
  6. Oxidation
-