

B.Pharmacy, 2nd Semester
Sub: Pharmaceutical Organic Chemistry-I
Unit-I and II

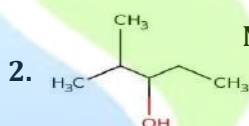
MODEL QUESTIONS FOR UNIT-I
PART-A

I. Multiple choice Questions (MCQs)

(1mark)

1. What is a prefix used for carboxylic acid?

- a) -carboxyl
- b) -oic acid
- c) -oxo
- d) -ate



Nomenclature of this compound is?

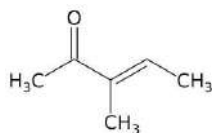
- 1.2-methylpentan-3-ol
- 2.3-methylpentan-2-ol
- 3.2-methylpentan-2-ol
- 4.3-hydroxy-2-methyl pentane

3. n-pentane and neopentane shows which type of isomerism ?

- a) chain isomerism
- b) position isomerism
- c) metamerism
- d) functional isomerism

4. Cyclic compound which contain only carbon atoms called _____

- a) Heterocyclic
- b) Alicyclic
- c) Aromatic
- d) Aliphatic



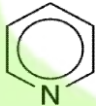
Nomenclature of this compound is?

- a) 3-methyl-3-penten-2-one
- b) 3-methyl-3-penten-3-one
- c) 2-methyl-2-penten-2-one
- d) 2-methyl-2-penten-3-one

6. which of the following shows metamerism ?

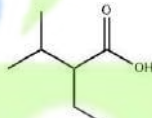
- a) n-butane & isobutene
- b) 1-chlorobutane & 2-chlorobutane
- c) diethyl ether & methyl propyl ether
- d) keto & enol form

7. which type of compound this is?



- a. Alicyclic
- b. Heterocyclic
- c. Saturated
- d. Aliphatic

8. What Nomenclature of this compound is ?

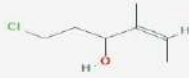


- a) 2-ethyl-3-methyl butanoic acid
 - b) 2-ethyl-1-methyl butanoic acid
 - c) 3-ethyl-2-methyl butanoic acid
 - d) 2-ethyl-3-methyl propanoic acid
9. what is the common name of ethanoic acid?

- a. Formic acid
- b. Valeric acid
- c. Acetic acid
- d. Butyric acid

10. Which of the following is not a heterocyclic compound?

- a) Pyrrole
- b) Pyridine
- c) Naphthalene
- d) Oxirane



11. Nomenclature of this compound is?

- a) 1-chloro-4-methylhex-5-en-3-ol
- b) 1-chloro-4-methylhex-4-en-3-ol
- c) 6-chloro-3-methylhex-2-en-4-ol
- d) 1-chloro-4,5-dimethylpent-4-en-3-ol

PART-B

II. Short-answered type questions

(5 MARK)

What are the types of structural isomerism? Give one example of each

PART-C

III. Long answer type question

(10MARK)

How will distinguish pri, sec, ter? alcohol? Briefly discuss types of structural isomerism with examples.

ANSWERS TO MODEL QUESTIONS FOR UNIT-I

PART-A

1. a

1. a

2. a

3. b

4. a

5. c

6. b

7. a

8. c

9. c

10. a

PART-B

1. There are 5 types of structural isomerism

- ❖ Chain isomerism - n-butane & isobutene
- ❖ Position isomerism - 1-chlorobutane & 2-chlorobutane
- ❖ Functional isomerism - ethyl alcohol & dimethyl ether
- ❖ Metamerism - diethyl ether & propyl ether
- ❖ Tautomerism - keto & enol form

PART-C

1. Primary alcohol: -

- These are the alcohols where the carbon to which the hydroxide group is linked is 1^o carbon, as it has an alkyl group attached to it.
- Example: Ethanol

Secondary alcohol: -

- These are the alcohols where the carbon to which the hydroxide group is linked is 2^o carbon, as it 2 alkyl groups attached to it
- Example: Propna-2-ol

Tertiary alcohol: -

- These are the alcohols where the carbon to which the hydroxide group is linked is 3° carbon, as it has 3 alkyl groups attached to it.
- Example: 2-methylpropan-2-ol

Types of structural isomerism:

- ❖ **Chain isomerism:** same molecular formula but differ in order in which the C-atoms are bonded to each other. e.g- n-butane & isobutene
- ❖ **Position isomerism:** same molecular formula but differ in position of functional group . e.g- 1-chlorobutane & 2-chlorobutane
- ❖ **Functional isomerism :** same molecular formula but different functional group . e.g- ethyl alcohol & dimethyl ether
- ❖ **Metamerism :** unequal distribution of C-atoms on either side of functional group. e.g - diethyl ether & propyl ether
- ❖ **Tautomerism:** type of functional isomerism in which isomers are in dynamic equilibrium. e.g - keto & enol form

MODEL QUESTIONS FOR UNIT-II

PART-A

1. chloroform (CHCl_3) react with Cl_2 to give

- a) Methyl chloride
- b) Tetrachloromethane
- c) Dichloromethane
- d) Methylene chloride

2. E1 reaction favoured which type of halide?

- a) Pri halide
- b) Sec halide
- c) Ter halide
- d) Both b&c

3. propene react with Br_2 in presence of CCl_4 to give _____

- a) 1-bromopropane
- b) 1,1-dibromopropane
- c) 1,2-dibromopropane
- d) 2-bromopropane

4. In the addition of HX , H_2O , ROH to alkene, Hydrogen adds to the carbon of the double bond having greater no. of hydrogens is which rule ?

- a) Markovnikov's rule
- b) Anti- Markovnikov's rule
- c) Saytzeff rule
- d) All of the above

5. what is the common name of ethanamide ?

- a) Acetyl chloride
- b) Formamide

- c) Acetamide
- d) Caproic acid

6. E2 reaction is _____ order kinetics.

- a) 1st
- b) 2nd
- c) 3rd
- d) Both a & b

7. Ethene undergo ozonolysis to form _____

- a) Acetaldehyde
- b) Formaldehyde
- c) Both a & b
- d) Butanaldehyde

8. E1 reaction favoured by _____

- a) Strong base
- b) Weak base
- c) Both a & b
- d) Strong acid

9. what is the relative reactivity of alkyl halide in E2 & E1 reaction ?

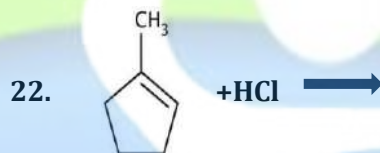
- a) $RI > RBr > RCl > RF$
- b) $RF > RBr > RCl > RI$
- c) $RI > RF > RBr > RCl$
- d) $RF > RCl > RBr > RI$

10. major product of elimination reaction is the more substituted alkene given by which rule ?

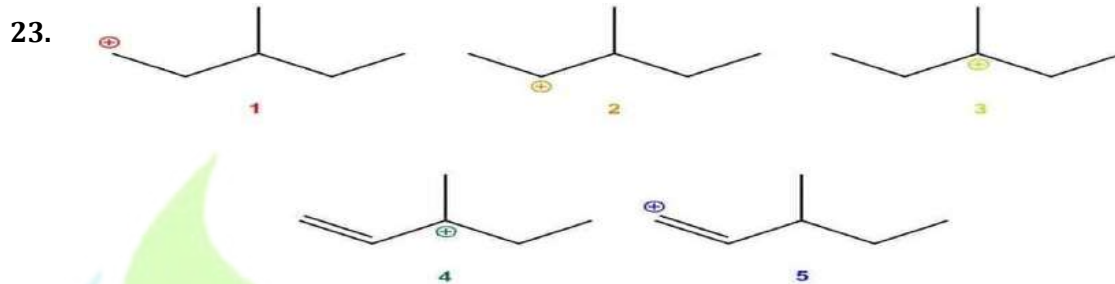
- a) Markownikoff's rule
- b) Anti- Markownikoff's rule
- c) Saytzeff rule
- d) Both a & b

11. In Diels-Alder reaction how many new sigma bonds formed?
- 1
 - 2
 - 3
 - No sigma bond formed
12. $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2 + \text{CH}_2=\text{CH}_2$
- Cyclohexene
 - Hexane
 - Cyclohexane
 - Both a& c
13. 1,4-addition is favoured.
- Kinetically
 - Thermodynamically
 - Both
 - None
14. halogenations of alkanes take place by
- electrophilic substitution
 - cyclic addition
 - E1 elimination
 - Free radical chain reaction
15. alkyl halide undergoes β - elimination reaction to give
- Alkane
 - Alkene
 - Alkyne
 - Alkyl halide
16. Addition of HBr in presence of peroxide follows
- Markovnikov addition
 - Anti-Markovnikov addition
 - Both a and b
 - None
17. I. The most rapidly formed product is kinetic product.
II. most stable product is the thermodynamic product. Which statement/s is correct?
- Only I
 - Only II
 - Both I & II
 - None

18. 1,2-addition product is favoured.
- Thermodynamically
 - Kinetically
 - Both
 - None
19. Reactivity of dienophile increased with
- Electron-withdrawing group
 - Electron-donating group
 - Both
 - None
20. propane reacts with bromine in the presence of light to give (major product: 92%)
- 1-bromopropane
 - 2-bromopropane
 - 1,2-dibromo propane
 - HBr
21. Relative reactivity of alkyl halides in E2 reaction?
- Pri > sec > tert
 - Tert > sec > pri
 - Tert > pri > sec
 - Sec > tert > pri



- 1-chloro-1-methylcyclopentane
- 1-chloro-2-methylcyclopentane
- 2-chloro-1-methylcyclopentane
- 1-chloro-2-methylcyclopentene

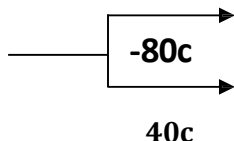


What is the order of carbocation stability?

- a) 1>2>3>4>5
 b) 4>3>2>1>5
 c) 3>4>2>1>5
 d) 4>3>2>5>1
24. 2-methylpropene react with HBr in presence of peroxide give
 a) 1-bromo-1-methylpropane
 b) 1-bromo-2-methylpropane
 c) 2-bromo-2-methylpropane
 d) 2-bromo-1-methylpropane
25. Diels-alder reaction is .
 a) [2+2] cycloaddition
 b) [4+2] cycloaddition
 c) Both
 d) Not a cycloaddition reaction
24. 2-methylpropene react with HBr in presence of peroxide give
 a) 1-bromo-1-methylpropane
 b) 1-bromo-2-methylpropane
 c) 2-bromo-2-methylpropane
 d) 2-bromo-1-methylpropane
25. Diels-alder reaction is .
 a) [2+2] cycloaddition
 b) [4+2] cycloaddition
 c) Both
 d) Not a cycloaddition reaction

PART-B

1. Explain different type of hybridization with example.
2. Differentiate between E1 & E2 elimination.
3. What is the Reactivity of alkyl halides towards elimination reaction ?
4. What are the uses of alkane ? How to prepare haloalkane from alkane?
5. What is mechanism of E1cb reaction ?
6. What is ozonolysis? What product formed when But-2-ene react with O₃ in presence of Zn/H₂O ?
7. $\text{CH}_2=\text{CHCH}=\text{CH}_2 + \text{HBr}$

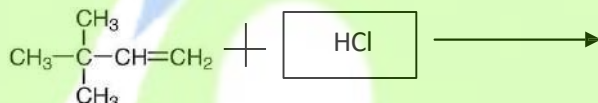


Write the major product formed from above reaction.

8. What is Markovnikov rule ? explain with suitable example.
9. Write down the mechanism for the diels-alder reaction.

PART-C

1. What is rearrangement & 1,2-shift?



what is the product formed & mechanism of this reaction?

2. What is anti-markovnikov rule? What is the product formed ? Give a mechanism to this reaction.



- 3.



Write down 1,2-addition & 1,4-addition product formed. Also show mechanism for reaction .

4. Differentiate Markovnikov and anti-Markovnikov rule with suitable example.
5. What is cycloaddition reaction & what are the types? Give example of each . Write down mechanism for Diels-Alder reaction.

Prepared by: Biswajit Biswal

ANSWERS TO MODEL QUESTIONS FOR UNIT-II

PART-A

1. b
2. c
3. c
4. a
5. c
6. b
7. b
8. b
9. a
- 10.c
- 11.b
- 12.a
- 13.b
- 14.d
- 15.b
- 16.b
- 17.c
- 18.b
- 19.a
- 20.b
- 21.b
- 22.a
- 23.b
- 24.b
- 25.b

PART-B

1.

sp Hybridization:

- **Formation:** One 2s orbital and one 2p orbital combine to form two sp hybrid orbitals.
- **Geometry:** Linear.
- **Example:** BeCl₂ (Beryllium chloride)

□ sp² Hybridization:

- **Formation:** One 2s orbital and two 2p orbitals combine to form three sp^2 hybrid orbitals.
- **Geometry:** Trigonal planar.
- **Example:** BF_3 (Boron trifluoride)

□ sp^3 Hybridization:

- **Formation:** One 2s orbital and three 2p orbitals combine to form four sp^3 hybrid orbitals.
- **Geometry:** Tetrahedral.
- **Example:** CH_4 (Methane)

2.

E1 Elimination

- **Mechanism:** A two-step process.
 - Ionization:** The leaving group leaves, forming a carbocation intermediate.
 - Deprotonation:** A base removes a hydrogen atom from the beta- carbon (adjacent to the carbocation) to form the double bond.
 - **Reaction Conditions:**
 - Weak bases (e.g., water, alcohols)
 - Favorable for tertiary and secondary substrates
- Rate Law:** First-order rate law (rate depends only on the concentration of the substrate)

E2 Elimination

- **Mechanism:** A one-step process.
 - **Concerted:** The leaving group and the hydrogen atom are removed simultaneously, forming the double bond in a single step.
- **Reaction Conditions:**
 - Strong bases (e.g., hydroxide, alkoxide ions)
 - Favorable for primary and secondary substrates
- **Rate Law:** Second-order rate law (rate depends on the concentration of both the substrate and the base).

3. Reactivity of alkyl halides in E1 reaction:

1°- E2 only 2°- E1 & E2

3°-E1 & E2

Relative reactivity of alkyl halides in E1 reaction :

Tert > sec > pri

Relative reactivity of alkyl halides in E1 reaction :

3°benzylic = 3°allylic > 2°benzylic = 2°allylic = 3° > 1°benzylic = 1°allylic

= 2° > 1°

4.

uses of alkane :

- ☐ Methane used for heating purposes.
- ☐ Ethane used as heating fuel.
- ☐ Propane used in petrochemistry.
- ☐ Butane used in petrochemical industry.

Preparation of haloalkane:

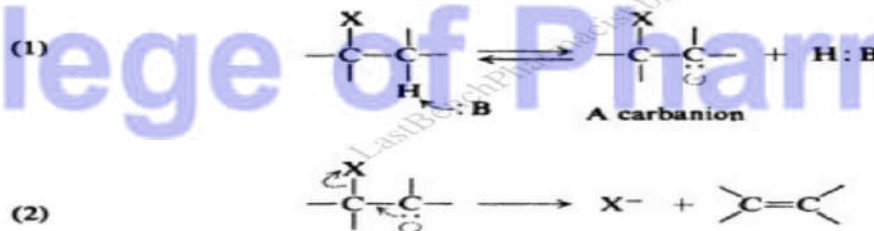
- ☐ Halogenations of alkanes $\text{CH}_4 + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl}$
- ☐ Addition of X_2 to alkenes

5.

Formation of the Conjugate Base: The base abstracts a proton from the beta- carbon, forming a carbanion intermediate.

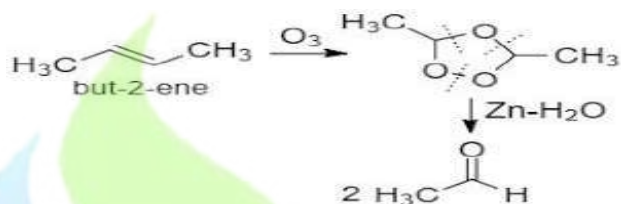
Elimination of the Leaving Group: The leaving group departs from the alpha- carbon, forming the double bond.

– E1cB mechanism



6. Ozonolysis: The unsaturated bonds of alkenes and alkynes are cleaved with ozone. Multiple carbon-carbon bonds are replaced by a carbonyl group.

The reaction of but-2-ene with ozone results in the formation of ethanol.



7. When temp. is -80°C , major product is 3-bromobut-1-ene, as in -80°C reaction kinetically favoured to form 1,2-addition product

When temp. is 40°C , major product is 4-bromobut-2-ene, as in 40°C reaction thermodynamically favoured to form 1,4-addition product.

8. Markovnikov's rule : . In the addition of HX, H_2O , ROH to alkene, Hydrogen adds to the carbon of the double bond having greater no. of hydrogens. In simpler terms, the hydrogen atom will prefer to add to the less substituted carbon.

Example: Addition of HBr to Propene

When hydrogen bromide (HBr) is added to propene, the major product formed is 2-bromopropane, and the minor product is 1-bromopropane. This follows Markovnikov's

Rule:

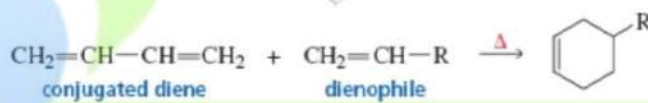


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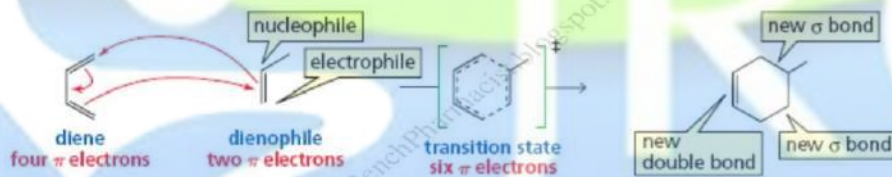
Diels Alder Reaction

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- [4+2] cycloaddition
 - Diels - Alder reaction
 - 1,4 - addition reaction
 - Conjugated diene and dienophile
- Example



- Mechanism



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PART-C

1.

- **Rearrangement**

- A change in connectivity of the atoms in a product compared with the connectivity of the same atoms in the starting material

- **1,2-Shift**

- A type of rearrangement in which an atom or group of atoms moves with its bonding electrons from one atom to an adjacent electron deficient atom

- Step-1: Proton transfer to alkene gives 2^o carbocation



- Step-2: Migration of methyl group with bonding electrons gives a more stable 3^o carbocation

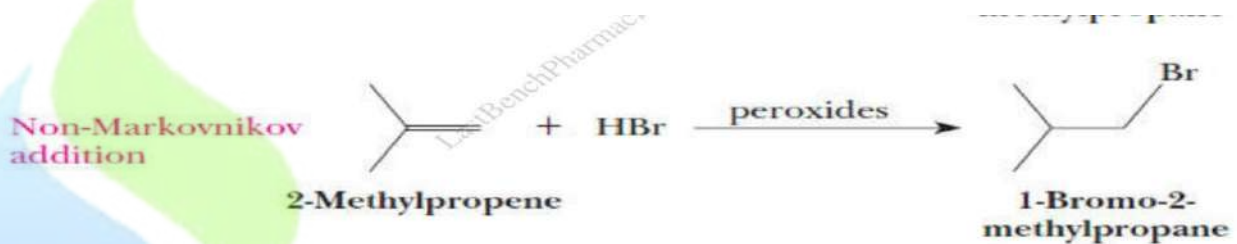


- Step-3: Reaction of 3^o carbocation with chloride ion



2.

Anti-Markovnikov addition occurs in the presence of a peroxide or a free radical initiator. The reaction proceeds through a radical mechanism, where the hydrogen atom adds to the carbon atom with the greater number of alkyl groups attached to form the more stable radical.



- Chain Initiation: Homolytic cleavage of a dialkyl peroxide is induced by light or heat to give two alkoxy radicals

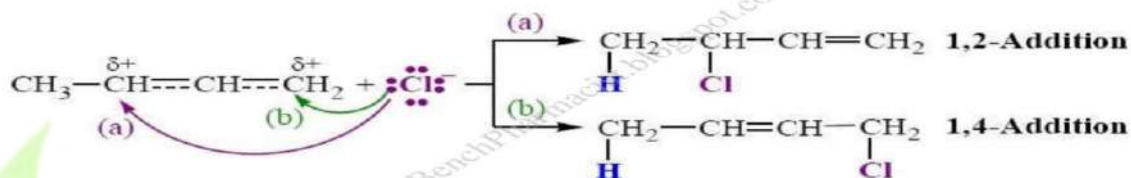


- An alkoxy radical then reacts with HBr by hydrogen abstraction to give an alcohol and a bromine radical



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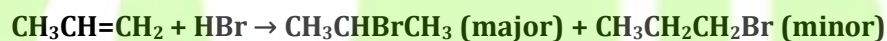
- Step 2



4.

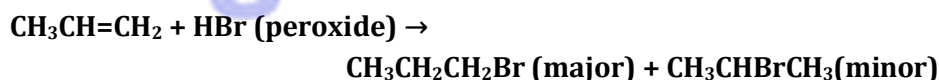
Markovnikov's Rule

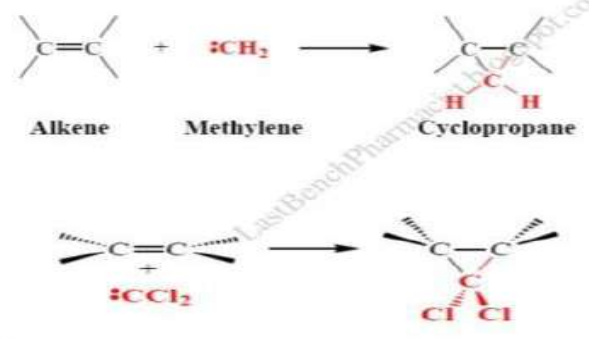
- **Statement:** The hydrogen atom of the acid will add to the carbon atom of the alkene with the greater number of hydrogen atoms already attached.
- **Explanation:** The intermediate formed during the addition reaction is a carbocation. Carbocations with more alkyl groups attached are more stable due to hyperconjugation. Therefore, the hydrogen atom will prefer to add to the less substituted carbon to form the more stable carbocation.
- **Example:** Addition of HBr to propene:



Anti-Markovnikov's Rule

- **Statement:** The hydrogen atom of the acid will add to the carbon atom of the alkene with the fewer number of hydrogen atoms already attached.
- **Explanation:** Anti-Markovnikov addition occurs in the presence of a peroxide or a free radical initiator. The reaction proceeds through a radical mechanism, where the hydrogen atom adds to the carbon atom with the greater number of alkyl groups attached to form the more stable radical.
- **Example:** Addition of HBr to propene in the presence of peroxides:





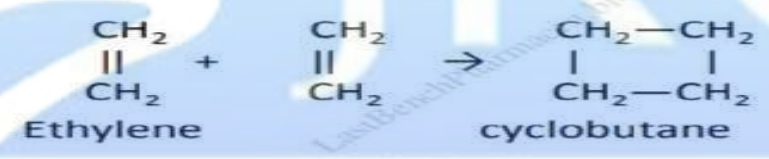
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Cycloaddition Reaction Contd...

Types of cycloaddition reactions

- > [2+2] cycloaddition
- > [4+2] cycloaddition
- [2+2] cycloaddition
- Example



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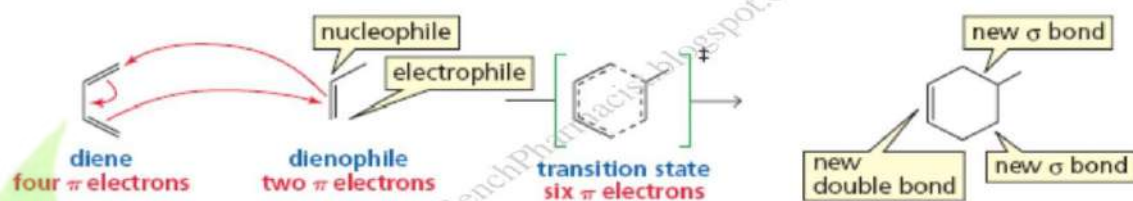
Diels Alder Reaction

- [4+2] cycloaddition
 - Diels - Alder reaction
 - 1,4 - addition reaction
 - Conjugated diene and dienophile
- Example



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Mechanism



Thank You

B.Pharmacy, 2nd Semester
Sub: Pharmaceutical Organic Chemistry-I
Unit-III

MODEL QUESTIONS FOR UNIT-III

PART-A

I. Multiple choice Questions (MCQs)

(1mark)

1. What is the leaving ability among halogens?
 - a. I->Br->Cl->F-
 - b. F->Cl->Br->I-
 - c. I->Cl->Br->F-
 - d. I->Br->F->Cl-
2. SN₂ reaction which order kinetics?
 - a. 1st
 - b. 2nd
 - c. 3rd
 - d. None
3. Rate of SN₂ reaction depend upon_
 - a. Substrate
 - b. Nucleophile
 - c. Both
 - d. Leaving group
4. What is the reactivity order of alkyl halide towards SN₂?
 - a. 1alkyl halide> 2alkyl halide>3alkyl halide
 - b. 3alkyl halide> 2alkyl halide>1alkyl halide
 - c. 2alkyl halide> 1alkyl halide>3alkyl halide
 - d. 1alkyl halide=2alkyl halide=3alkyl halide
5. For better SN₂ reaction, leaving group should be
 - a) good leaving gr
 - b) Halide ion
 - c) Weak base
 - d) All of these
6. Which solvent favors SN₂ reaction?
 - a) Non polar
 - b) Polar protic
 - c) Polar aprotic
 - d) Both b&c
7. Which reaction involves complete inversion of configuration?
 - a) SN₁
 - b) SN₂
 - c) Both
 - d) E₁
8. The reaction of (+)-2-Bromooctane with NaOH gives_
 - a) (-)-2-Octanol
 - b) (+)-2-Octanol
 - c) Both
 - d) (-)-3-Octanol



9. Rate of SN2 reaction depend upon_
 - a) Substrate
 - b) Nucleophile
 - c) Both
 - d) Leaving group
10. Rate determining step in SN1 reaction is_
 - a) Fast
 - b) Slow
 - c) May fast & slow
 - d) None
11. What is the reactivity order of alkyl halide towards SN1?
 - a) 1alkyl halide> 2alkyl halide>3alkyl halide
 - b) 3alkyl halide> 2alkyl halide>1alkyl halide
 - c) 2alkyl halide> 1alkyl halide>3alkyl halide
 - d) 1alkyl halide=2alkyl halide=3alkyl halide
12. Which solvent favors SN1 reaction?
 - a) Non polar
 - b) Polar protic
 - c) Polar aprotic
 - d) Both b&c
13. SN1 reaction is favoured by_
 - a) Poor nucleophile
 - b) Low conc. Of nucleophile
 - c) Strong nucleophile
 - d) Both a & b
14. Tertiary alkyl halides prefer_
 - a) Unimolecular substitution reaction
 - b) Bimolecular substitution reaction
 - c) Both
 - d) None
15. Carbanion stabilize by_
 - a) EN atom adjacent to charge
 - b) Conjugation of anion
 - c) Resonance effect
 - d) All
16. Which species have complete octet around carbon?
 - a) Free radical
 - b) Carbocation
 - c) Carbanion
 - d) Carbene

17. Species which is having odd or unpaired electron called _
a) Free radical
b) Carbocation
c) Carbanion
d) Carbene
18. Relative stability of free radical _
a) Benzyl >allyl >tert > sec > pri
b) Benzyl >tert > sec > pri > allyl
c) allyl >Benzyl> tert > sec > pri
d) tert > sec > pri >benzyl >allyl
19. Thermal cleavage or photochemical cleavage of covalent bonds leads to form_
a) Free radical
b) Carbocation
c) Carbanion
d) Carbene
20. Methylene(:CH₂) reacts with methane to give_
a) Methane
b) Ethane
c) Propane
d) B & C
21. Nitrenes are _
a) Electron deficient species
b) Electron rich species
c) Neutral
d) None
22. Photolytic or thermal decomposition of azides give_
a) Free radical
b) Nitrene
c) Carbanion
d) Carbene
23. Permanent displacement of electrons through sigma bond called_
a) Inductive effect
b) Resonance effect
c) Electrometric Effect
d) Hyperconjugation
24. Which of the following is correct for the -I effect?
a) -NO₂>-F>-COOH>-Cl>-Br>-I
b) -F>-NO₂>-COOH>-Cl>-Br>-I
c) -NO₂>-COOH>-F>-Cl>-Br>-I
d) -COOH>-NO₂>-F>-Cl>-Br>-I

25. Which of the following shows +M effect?
a) Halogens and hydroxyl group
b) Cyano group
c) Aldehyde group
d) Ketone group
26. Substrate reactivity order for SN1 reaction based on_
a) Carbanion stability
b) Free radical stability
c) Carbocation stability
d) None
27. Which of the following is Lucas's reagent?
a) chromic acid in sulfuric acid
b) Zinc chloride in HCl
c) Zinc chloride in HNO₃
d) chromic acid in HCl
28. Which of the following is not uses of tetrachloromethane?
a) Fire extinguisher
b) Precursor to refrigerants
c) cleaning agent
d) Anesthetic

PART-B

I. Short-answered type questions (5 MARK)

1. What is SN2 reaction? Write down mechanism.
2. Discuss Stereochemistry of SN2 Mechanism.
3. Explain kinetics and mechanism involved in SN1 reaction.
4. Give a Comparison between SN1 & SN2. (No mechanism)
5. Differentiate between carbene & nitrene. And give a method of preparation for each.
6. Explain inductive & mesomeric effect with examples.
7. Discuss Jones Oxidation for Pri, Sec, ter alcohol.
8. How to distinguish between Pri, Sec, ter alcohol using lucas test ?
9. What are the uses of chloroform & tetrachloromethane?
10. Write the structure & uses of cetosteryl alcohol ad glycerol.
11. Explain rearrangement of carbocation through 1,2-shift.

PART-C

III. Long answer type question (10MARK)

1. What is SN2 reaction? List out & explain Factors affecting rate of reaction.
2. Differentiate SN1 & SN2 by its kinetics and mechanisms.
3. How to distinguish between Pri, Sec, ter alcohol by Qualitative tests for alcohols.

ANSERS TO MODEL QUESTIONS FOR UNIT-III

PART-A

1. A
2. B
3. C
4. A
5. D
6. C
7. B
8. A
9. A
10. B
11. B
12. B
13. D
14. A
15. D
16. C
17. A
18. A
19. A
20. D
21. A
22. B
23. A
24. A
25. A
26. C
27. B
28. D



Prepared by: Biswajit Biswal

PART-B

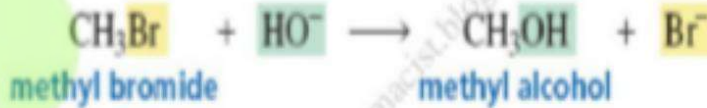
1.

S_N2 Reaction

- Definition

- Bimolecular nucleophilic substitution

- Example

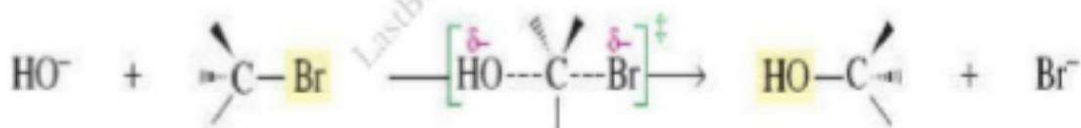


- Kinetics

- 2nd order kinetics
 - Rate \propto [substrate] [nucleophile]

- Mechanism

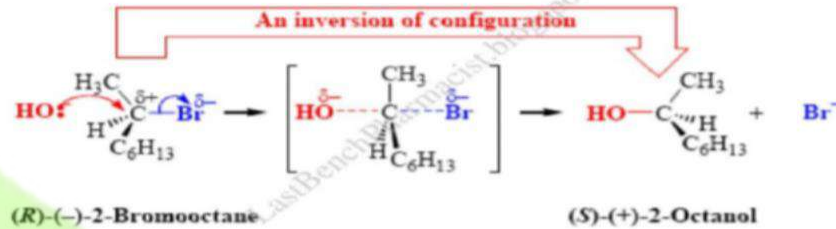
- Backside attack



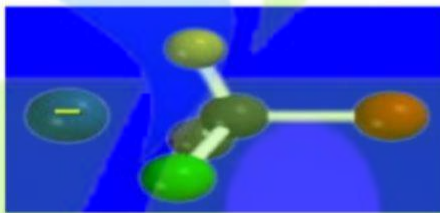
2.

Stereochemistry of SN2 mechanism

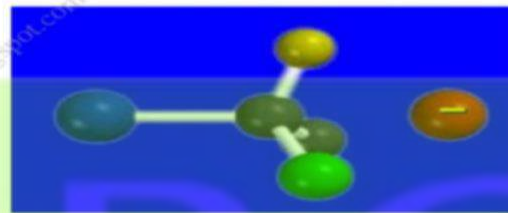
- Walden inversion



Inversion of Configuration



nucleophile attacks carbon from side opposite bond to the leaving group



three-dimensional arrangement of bonds in product is opposite to

3.

S_N1 Reaction

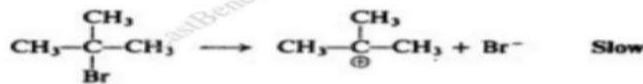
- Definition
 - Unimolecular nucleophilic substitution
- Example: Hydrolysis of 3° butyl bromide to 3° butyl alcohol



- Kinetics
 - 1st order kinetics
 - Rate \propto [substrate]
 - Rate = k [RBr]

Mechanism

- Step 1
 - Slow ionisation to give carbonium ion
 - C-Br bond breaks heterolytically
 - Nucleophile is not involved
 - Rate determining step



- Step 2
 - Fast attack of nucleophile on carbonium ion



4.

Comparison between S_N1 and S_N2

S _N 2	S _N 1
A one-step mechanism	A stepwise mechanism that forms a carbocation intermediate
A bimolecular rate-determining step	A unimolecular rate-determining step
No carbocation rearrangements	Carbocation rearrangements
Product has inverted configuration relative to the reactant	Products have both retained and inverted configurations relative to the reactant
Reactivity order: methyl > 1° > 2° > 3°	Reactivity order: 3° > 2° > 1° > methyl

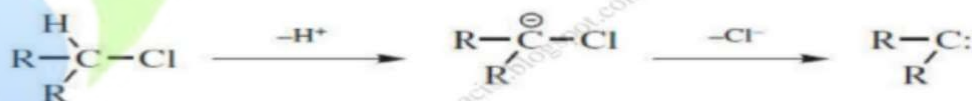
5.

Carbenes

- Carbenes are neutral species
- Carbon atom with two bonds and two electrons

Generation of carbenes

- In an elimination, a carbon loses a group without its electron pair, usually a proton, and then a group with its pair, usually a halide ion



- Formation of dichlorocarbene by treatment of chloroform with base
- Photolysis of ketene

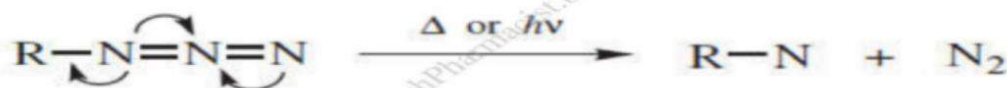


Nitrenes

- Nitrogen analogue of carbene
- Electron deficient species
- Nitrogen has six electrons
- $\text{RN}:$

Generation of nitrenes

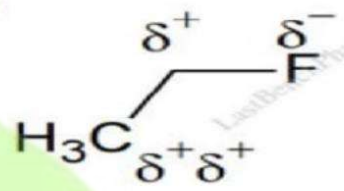
- Breakdown of certain double bond compounds
- Photolytic or thermal decomposition of azides



6.

Inductive effect

- Permanent displacement of electrons through sigma bonds
- -I effect
- +I effect



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Inductive effect Contd...

- -I effect
-NO₂ > -F > -COOH > -Cl > -Br > -I
- +I effect
tert-butyl > isopropyl > ethyl > methyl

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Resonance Effect / Mesomeric Effect

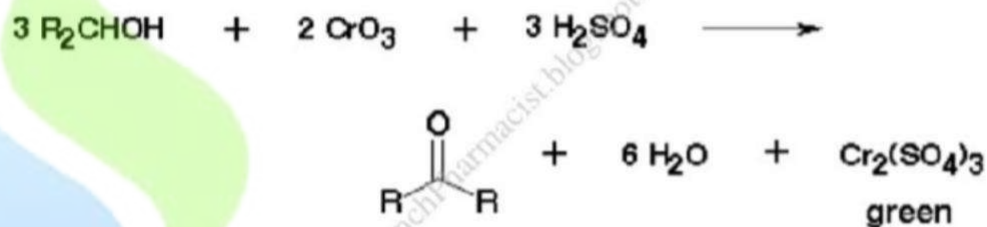
- Movement of pi electrons gives rise to different canonical structure
- Conjugative system
- +M effect
- Halogens and hydroxyl group
- -M effect
- Cyano group ,carbonyl group
- Comparison between I and M effect

College of Pharmacy

7.

Jones Oxidation for Primary and Secondary Alcohols

- Jones reagent (chromic acid in sulfuric acid)



- Formation of green color within 15 sec- primary or secondary alcohol
- Tertiary alcohols- remain orange in color

8.

- Lucas reagent- Zinc chloride in HCl

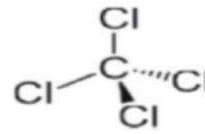


- Formation of alkyl chloride as insoluble layer or emulsion
- 3° alcohols: immediate to 2-3 minutes
- 2° alcohols: 5 -10 minutes
- 1° alcohols: no reaction

9.

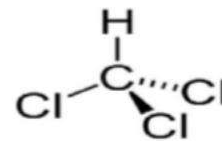
Tetrachloromethane

- Structure
- Also as carbon tetrachloride
- Colorless liquid with sweet smell
- Uses
- Good solvent in chemistry



Chloroform

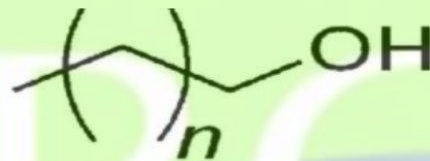
- Structure
- Also as trichloromethane
- Uses
- Precursor to refrigerants
- Good solvent in chemistry



10.

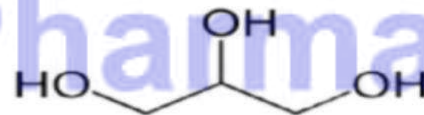
Cetosteryl alcohol

- Structure
- Where n is ~14-16
- Also called as **Cetostearyl alcohol**, **cetearyl alcohol** or **cetylstearyl alcohol**, **mixture of fatty alcohols**
- predominantly of cetyl (C16) and stearyl alcohols (C18)
- Uses
- emulsion stabilizer, opacifying agent, and foam boosting surfactant,



Glycerol

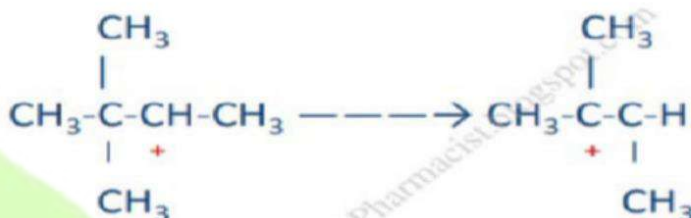
- Structure
- Simple polyol compound- glycerine
- Uses
- Food industry- sweetener
- Pharmaceutical- humectant, to improve smoothness, lubricant



11.

Rearrangement of Carbocations

- 2° carbonium ion rearrange to 3° carbonium ion



- Rearrangement takes place by 1,2-shift
- Migration of hydrogen - hydride shift
- Migration of alkyl group - alkyl shift

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Rearrangement of Carbocations

- 1,2 – hydride shift



- 1,2 – methyl shift



PART-C

1.

S_N2 Reaction

- Definition
 - Bimolecular nucleophilic substitution

- Example

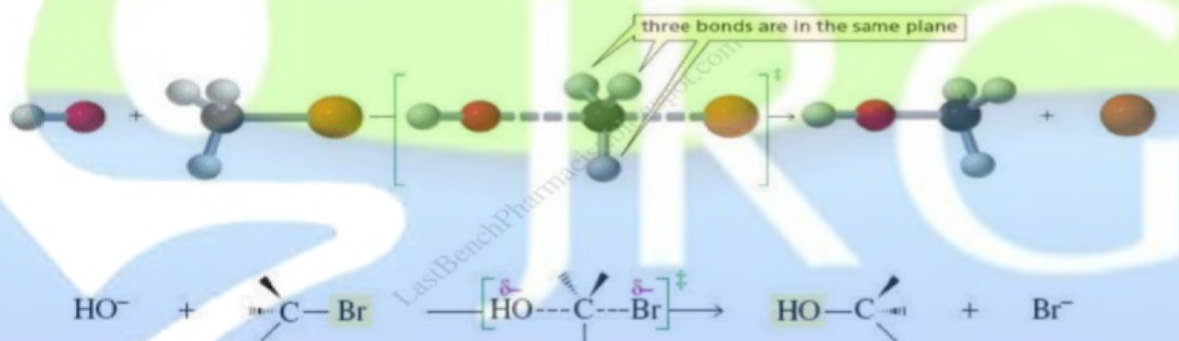


- Kinetics

- 2nd order kinetics
- Rate \propto [substrate] [nucleophile]

- Mechanism

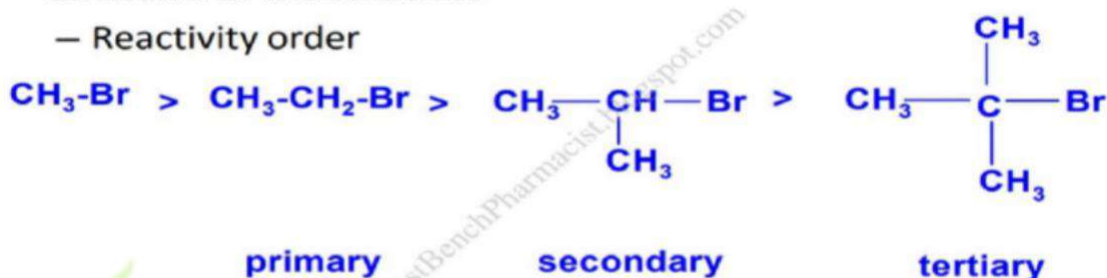
- Backside attack



Factors affecting the rates of S_N2 reaction

- Structure of the substrate
- Concentration and reactivity of the nucleophile
- Effect of the solvent
- Nature of the leaving group

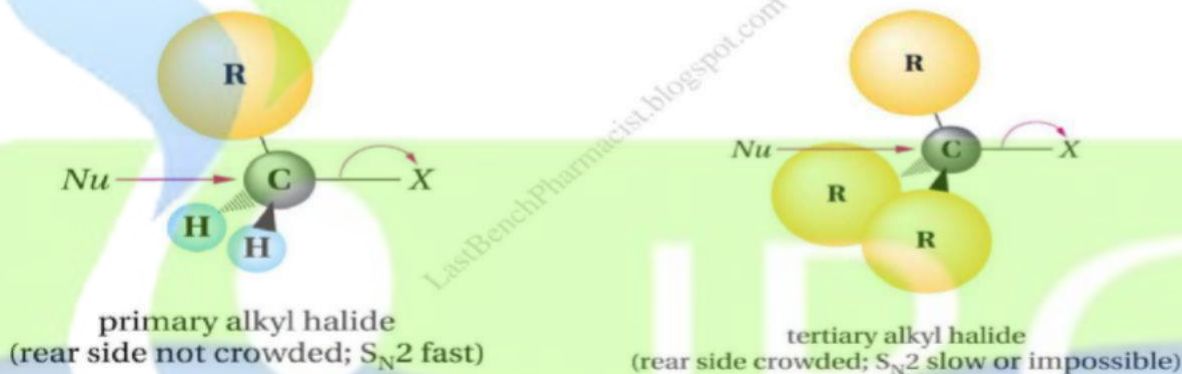
- Structure of the substrate
 - Reactivity order



most reactive \leftarrow methyl halide $>$ 1° alkyl halide $>$ 2° alkyl halide $>$ 3° alkyl halide \rightarrow least reactive

- Reason

- Steric hindrance



- Concentration & strength of nucleophile
 - Strong & high concentration of nucleophile
- Solvents
 - Polar aprotic solvents
- Leaving group
 - Good leaving groups
 - Weak bases
 - Halide ions

best leaving group \leftarrow I⁻ $>$ Br⁻ $>$ Cl⁻ $>$ F⁻ \rightarrow worst leaving group

Role of solvents

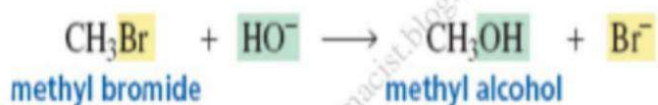
- Polar protic solvents
 - Decreases the rate of S_N2 reaction
 - E_{act} is high
- Polar aprotic solvents
 - Increases the rate of S_N2 reaction
 - Solvate cations very well
 - No hydrogen bonding
 - Anions reactive as nucleophiles
- Rate of S_N2 reaction depends on steric hindrance
- Bulkier the groups at the backside of the carbon slower the reaction
- Methyl halides and primary alkyl halides readily undergo S_N2 reaction
- Rate of S_N2 reaction is favoured by strong & high concentration of nucleophile in polar aprotic solvents

2.

S_N2 Reaction

- Definition
 - Bimolecular nucleophilic substitution

- Example

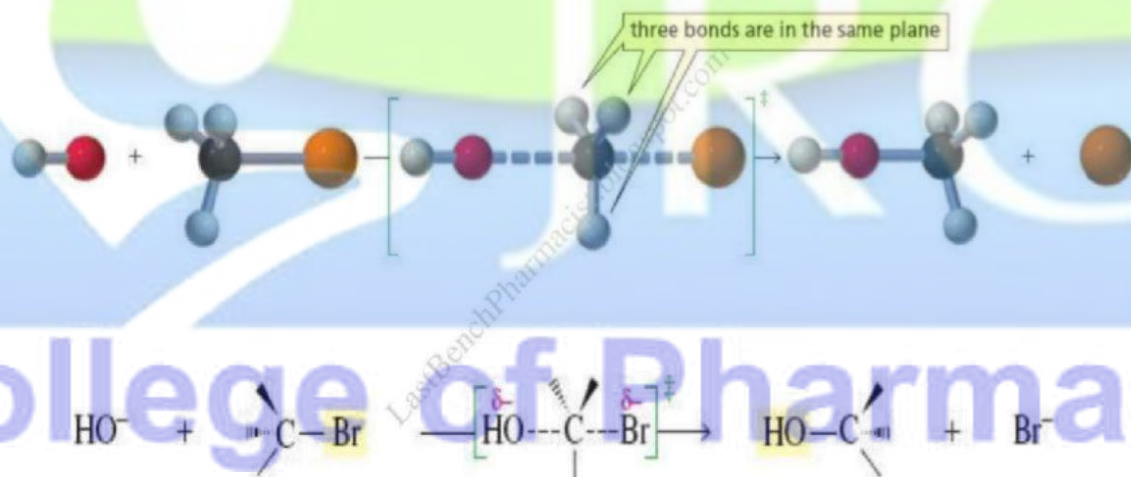


- Kinetics

- 2nd order kinetics
- Rate \propto [substrate] [nucleophile]

- Mechanism

- Backside attack



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S_N1 Reaction

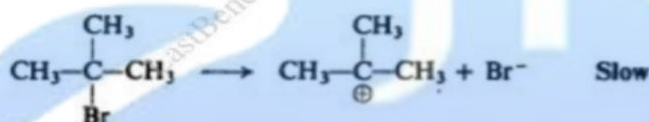
- Definition
 - Unimolecular nucleophilic substitution
- Example: Hydrolysis of 3°butyl bromide to 3°butyl alcohol



- Kinetics
 - 1st order kinetics
 - Rate \propto [substrate]
 - Rate = k [RBr]

Mechanism

- Step 1
 - Slow ionisation to give carbonium ion
 - C-Br bond breaks heterolytically
 - Nucleophile is not involved
 - Rate determining step

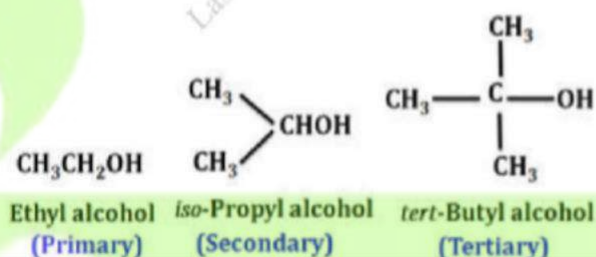


- Step 2
 - Fast attack of nucleophile on carbonium ion



3.

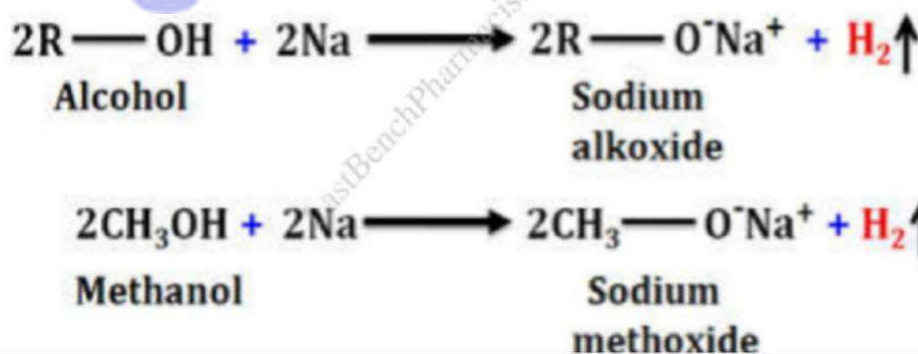
- Alcohols are compounds in which the hydroxyl group (-OH) is linked to aliphatic carbon chain or in the side chain of an organic compound
- Further classified as primary (1°), secondary (2°) and tertiary (3°) according to the -OH group is attached to the primary, secondary and tertiary carbon atoms respectively



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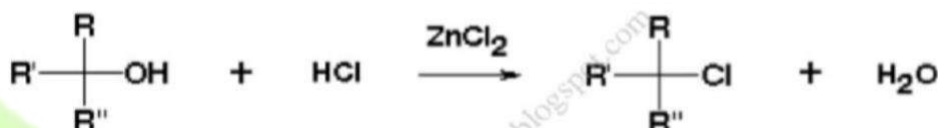
Qualitative tests for Alcohols

- Sodium metal test
- Alcohols react with active metals like sodium and liberate hydrogen gas that can be observed in the form of effervescence



Lucas test for secondary and tertiary alcohol

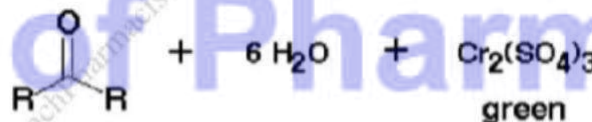
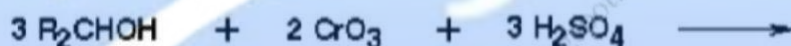
- Lucas reagent- Zinc chloride in HCl



- Formation of alkyl chloride as insoluble layer or emulsion
- 3° alcohols: immediate to 2-3 minutes
- 2° alcohols: 5 -10 minutes
- 1° alcohols: no reaction

Jones Oxidation for Primary and Secondary Alcohols

- Jones reagent (chromic acid in sulfuric acid)



- Formation of green color within 15 sec- primary or secondary alcohol
- Tertiary alcohols- remain orange in color

B.Pharmacy, 2nd Semester
Sub: Pharmaceutical Organic Chemistry-I
Unit-IV

MODEL QUESTIONS FOR UNIT-IV

PART-A

I. Multiple choice Questions (MCQs)

(1mark)

1. What is the reactivity order towards nucleophilic addition?

- a. $\text{HCHO} = \text{RCHO} = \text{RCOR}'$
- b. $\text{HCHO} > \text{RCHO} > \text{RCOR}'$
- c. $\text{HCHO} < \text{RCHO} < \text{RCOR}'$
- d. $\text{RCHO} > \text{HCHO} > \text{RCOR}'$

2. Carbonyl compounds include _____

- a. Aldehyde
- b. Ketone
- c. Alcohol
- d. Both a & b

3. Carbonyl compounds are _____ compound.

- a. Trigonal planar
- b. Planer
- c. Tetrahedral
- d. Trigonal bipyramidal

4. The mechanism involved in aldol reaction is _____

- a. Nucleophilic substitution
- b. Nucleophilic addition
- c. Addition elimination
- d. Electrophilic substitution

5. The product formed in the aldol reaction is
 - a. α -hydroxy aldehyde
 - b. β -hydroxy aldehyde
 - c. β -hydroxy ketone
 - d. B or C

6. Cross Aldol condensation is the reaction between
 - a. Two Same carbonyl compound
 - b. Two Different Carbonyl compound
 - c. One carbonyl compound & base
 - d. One carbonyl compound & alcohol

7. What is the aldol product when acetophenone reacts with acetaldehyde?
 - a. Benzaldehyde
 - b. Diphenyl ketone
 - c. 1-phenyl but-2-en-1-one
 - d. 4-phenyl but-2-en-4-one

8. The reaction in which aldehyde with no α -H undergoes self-oxd and red in the presence of conc alkali, called
 - a. Cannizzaro reaction
 - b. Aldol condensation reaction
 - c. Cross aldol condensation reaction
 - d. E1cb elimination

9. Product/s formed in Cannizzaro reaction
 - a. Alcohol
 - b. Salt of carboxylic acid
 - c. Both
 - d. Carbonyl compound

10. Formaldehyde undergoes Cannizzaro reaction to give
 - a. Phenol
 - b. Methanol
 - c. Sodium formate
 - d. Both b & c

11. The mechanism involved in the crossed Cannizzaro reaction is
 - a. Nucleophilic aromatic addition
 - b. Nucleophilic substitution
 - c. Addition elimination
 - d. Electrophilic substitution

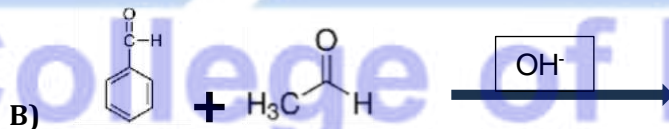
12. Self-condensation of aromatic aldehyde in the presence of CN, called
 - a. Cannizzaro reaction
 - b. Aldol condensation reaction
 - c. Cross aldol condensation reaction
 - d. Benzoin condensation

13. The product formed in Benzoin condensation is
- α -hydroxy ketone
 - β -hydroxy aldehyde
 - β -hydroxy ketone
 - B or C
14. Condensation reaction between aromatic aldehyde and aliphatic anhydride, called
- Aldol condensation reaction
 - Cross aldol condensation reaction
 - Benzoin condensation
 - Perkin condensation
15. A positive result for 2,4- DNP test indicated by the formation of
- 2,4- dinitrophenyl hydrazone
 - 2,4- dinitrophenyl hydrazine
 - 2,4- dinitrophenol hydrazone
 - 2,4- dinitrophenyl
16. _____ give pink or magenta color with Schiff's base
- Ketone
 - Aldehyde
 - Both
 - Alcohol
17. Ammoniacal silver nitrate is _____ reagent.
- Tollen's
 - Benedict's
 - Fehling's
 - None
18. Which of the following is the simplest aldehyde?
- Acetaldehyde
 - Ethanal
 - Benzaldehyde
 - Formaldehyde
19. Hexamethylenetetramine also called
- Hexamine
 - Methenamine
 - Both
 - Vanillin
20. Which of the following is the simplest aromatic aldehyde?
- Acetaldehyde
 - Ethanal
 - Benzaldehyde
 - Formaldehyde

21. Which of the following is used as primary content for bitter almond oil ?
- Acetaldehyde
 - Acetone
 - Benzaldehyde
 - Formaldehyde
22. In structure of vanillin include functional groups-
- Aldehyde
 - Hydroxyl
 - Ether
 - All of the following
23. Which of the following is used in essential oil of cinnamon ?
- Acetaldehyde
 - Cinnamaldehyde
 - Benzaldehyde
 - Formaldehyde

PART-B

- II. Short-answered type questions (5 MARK)
- Write the mechanism of aldol reaction under basic conditions.
 - Write the mechanism for Cannizzaro reaction.
 - Explain mechanism for benzoin condensation reaction.
 - Write structure & uses of paraldehyde and acetone.
 - Write structure & uses of cinnamaldehyde and vanillin.



PART-C

- II. Long answer type question (10MARK)

- Briefly explain qualitative tests for carbonyl compounds.
- Write the mechanism of aldol reaction under both acidic & basic conditions.
- Differentiate between Cannizzaro reaction and crossed Cannizzaro reaction with mechanism.

ANSWERS TO MODEL QUESTIONS FOR UNIT-IV

PART-A

1. B

2. D

3. A

4. B

5. D

6. B

7. C

8. A

9. C

10. D

11. A

12. D

13. A

14. D

15. A

16. B

17. A

18. D

19. C

20. C

21. C

22. D

23. B

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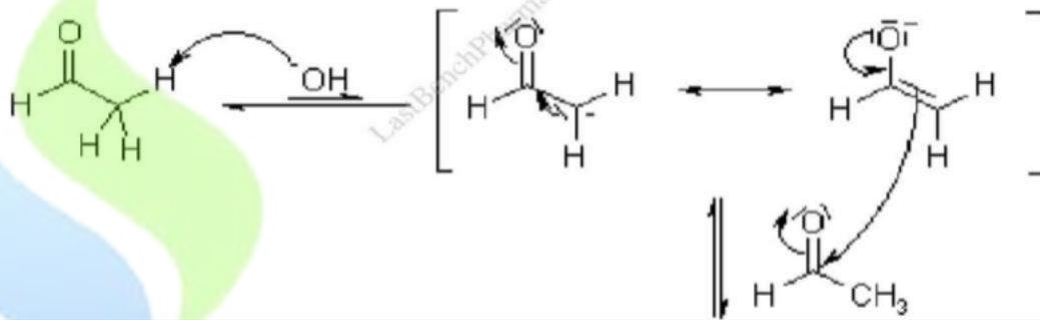


PART-B

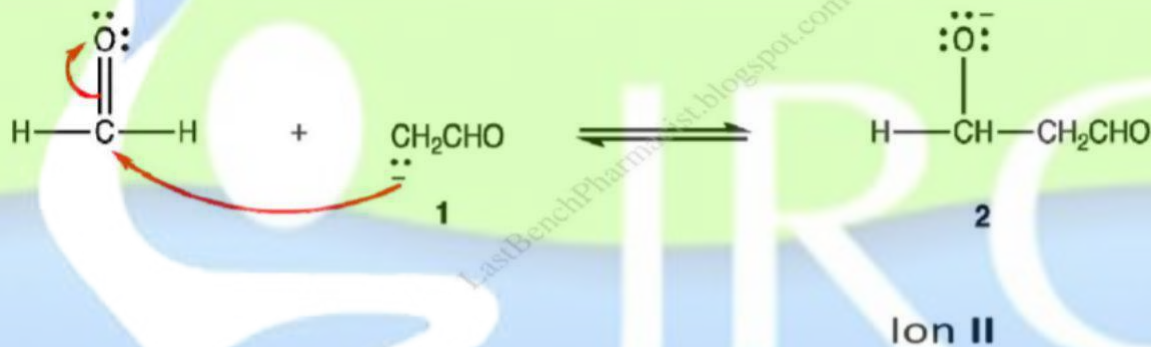
1.

- Step 1

Hydroxide ion abstracts hydrogen ion from α carbon of aldehyde to form carbanion I

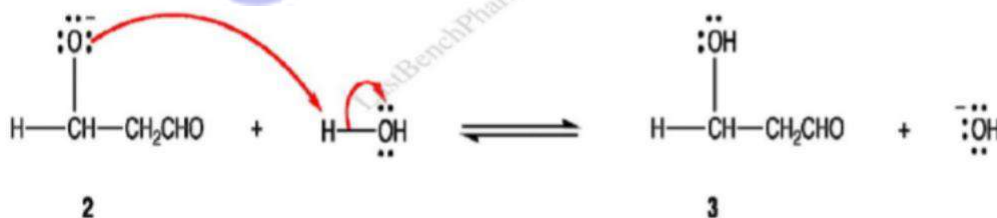


- Step 2 Carbanion I attacks carbonyl carbon to form ion II



- Step 3

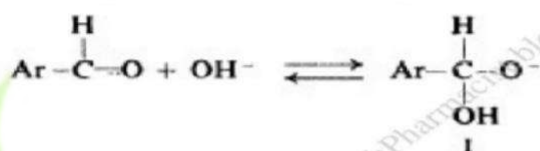
Ion II abstracts hydrogen ion from water to form β hydroxy aldehyde /aldol



2.

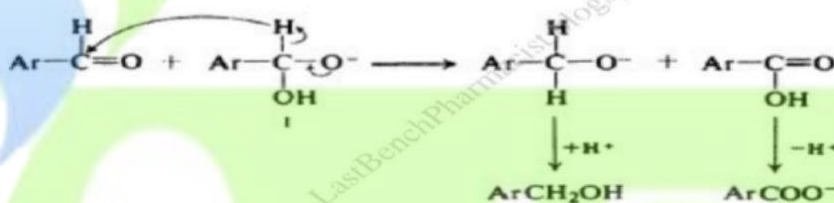
- Step 1

Addition of hydroxide ion to give intermediate ion



- Step 2

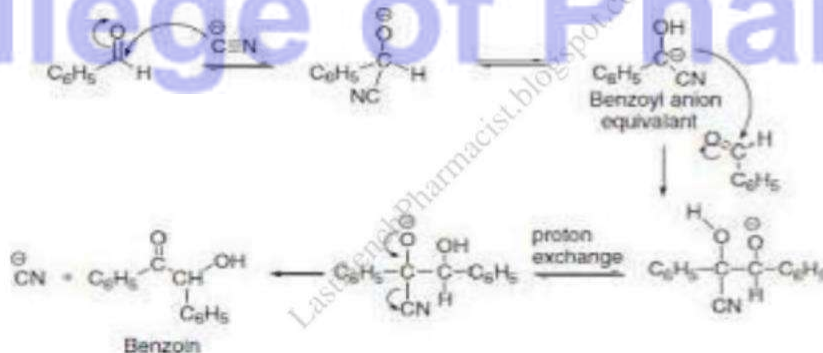
Transfer of hydride ion to the carbonyl carbon of aldehyde



3.

Benzoin Condensation Contd...

- Mechanism



4.

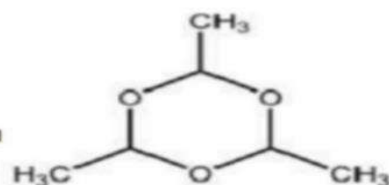
Acetone

- Structure
- Named propanone
- Uses
- Good solvent in chemistry
- Also as solvent for plastics and synthetic fibres
- Cleaning tools, paints and varnishes, degreasing



Paraldehyde

- Structure
- Trimer of acetaldehyde molecules
- Slowly oxidizes in air with an odor of acetic a
- Quickly reacts with plastic and rubber

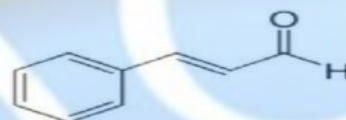


- Uses
 - Hypnotic
 - Sedative

5.

Cinnamaldedhye

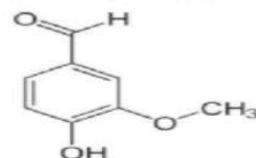
- Structure
- Gives cinnamon- its flavor and odor
- Essential oil of cinnamon



- Uses
- As flavor in chewing gums, ice cream, candy, beverages, perfumes
- Fungicide- agrochemical
- Antimicrobial

Vanillin

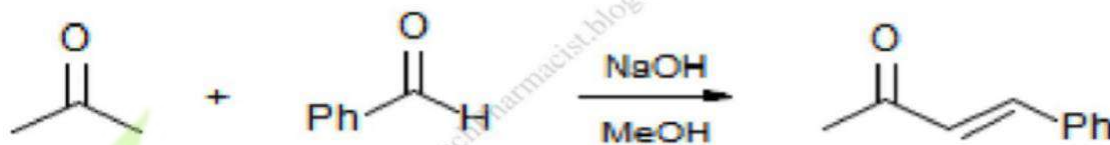
- Structure
- Functional groups- aldehyde, hydroxyl and ether
- Primary component of vanilla bean



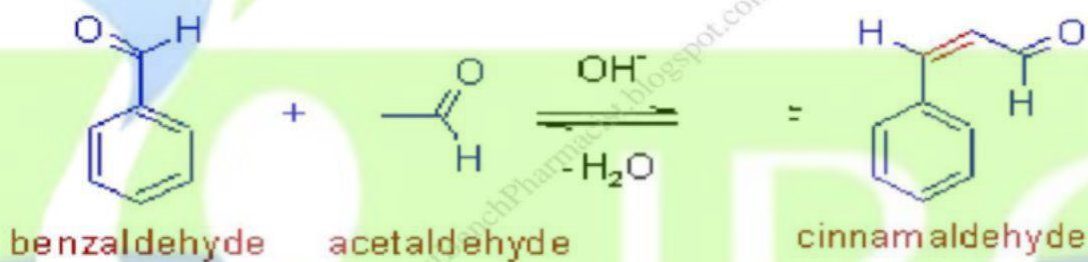
- Use
 - Pharmaceutical aid as flavouring agent in food, beverages and pharmaceuticals
 - Used in ice creams, confections, baked goods, perfumes

6.

A)



B)



Prepared By: Biswajit Biswal

PART-C

1.

Test for aldehydes and ketones

- **2,4-dinitrophenyl hydrazine test (2,4-DNP test)**
- 2,4-dinitrophenyl hydrazine can be used to qualitatively detect the carbonyl group of an aldehyde or ketone
- A positive result is indicated by the formation of a yellow or orange-red precipitate of 2,4-dinitrophenyl hydrazone

Differentiating tests for aldehydes

- Aldehyde is readily oxidised to carboxylic acid whereas ketone cannot be oxidised easily
- Schiff's test- Aldehydes give pink or magenta colour with Schiff reagent
- Tollen's test- Tollen's reagent is ammoniacal silver nitrate. Aldehydes react with Tollen's reagent to form elemental silver

Differentiating tests for Ketones

Following tests are given by ketones but not by aldehydes:

m-dinitrobenzene Test

Ketones react with m-dinitrobenzene to give a violet colouration.

Sodium nitroprusside Test

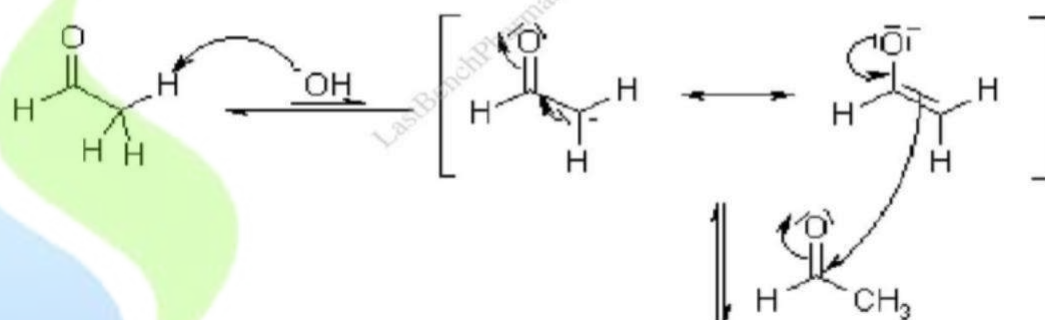
The anion of ketone formed by an alkali reacts with nitroprusside ion to form a red coloured complex.

2.

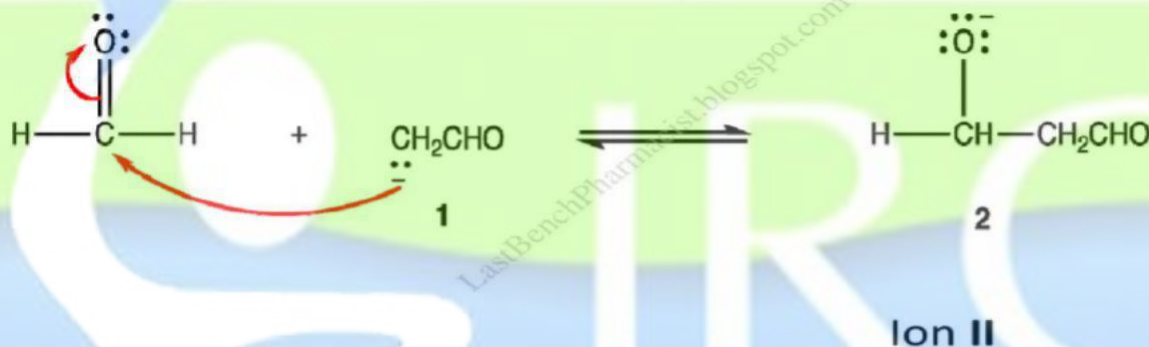
In basic condition

• Step 1

Hydroxide ion abstracts hydrogen ion from α carbon of aldehyde to form carbanion I

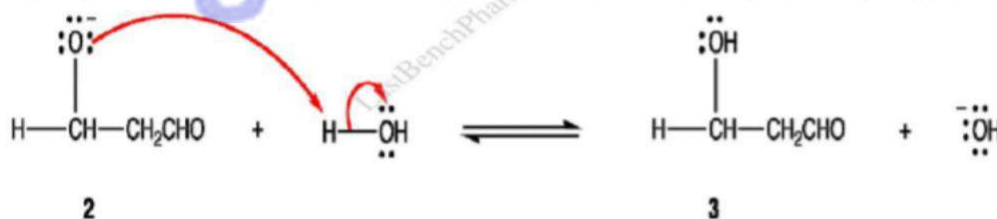


• Step 2 Carbanion I attacks carbonyl carbon to form ion II

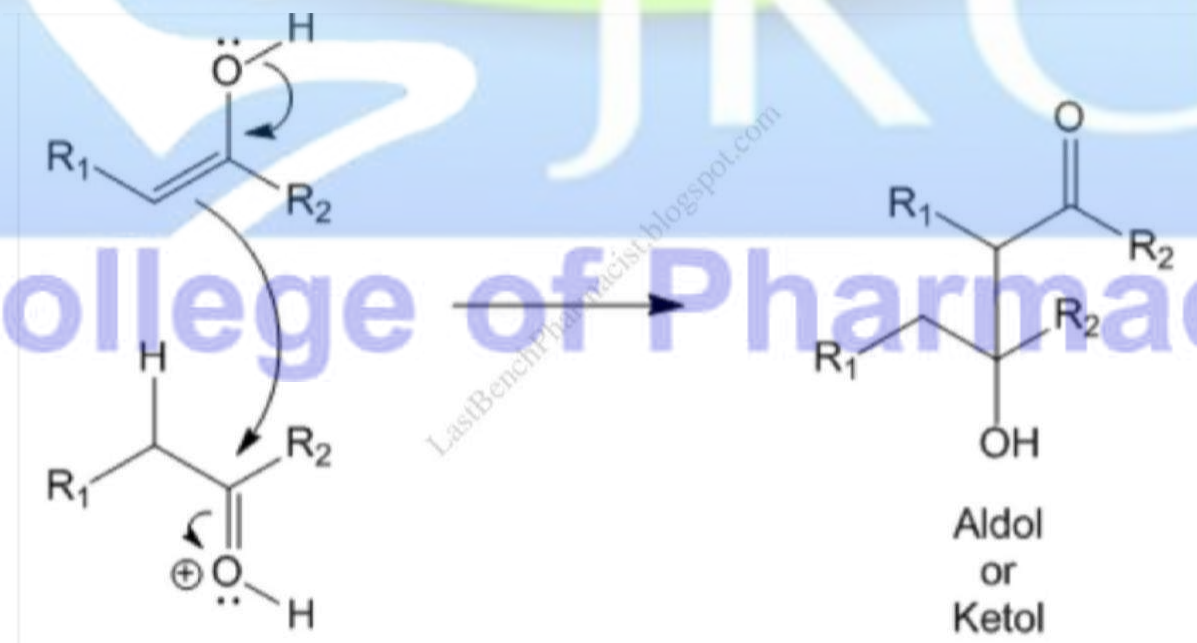
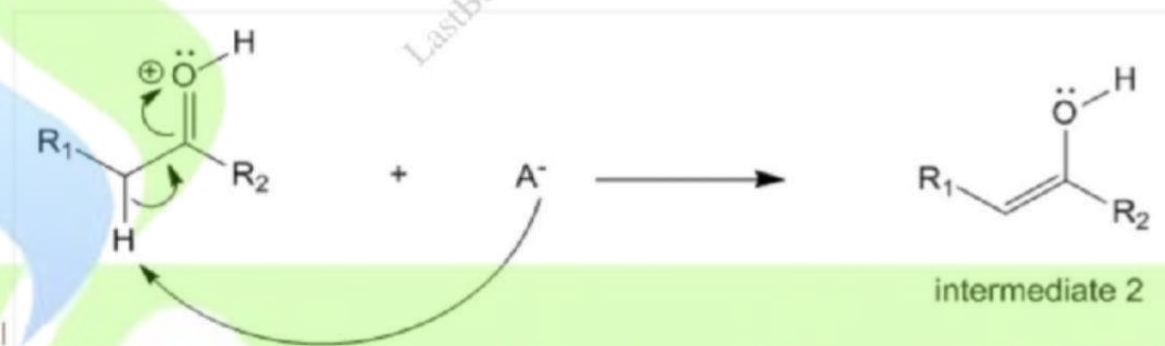
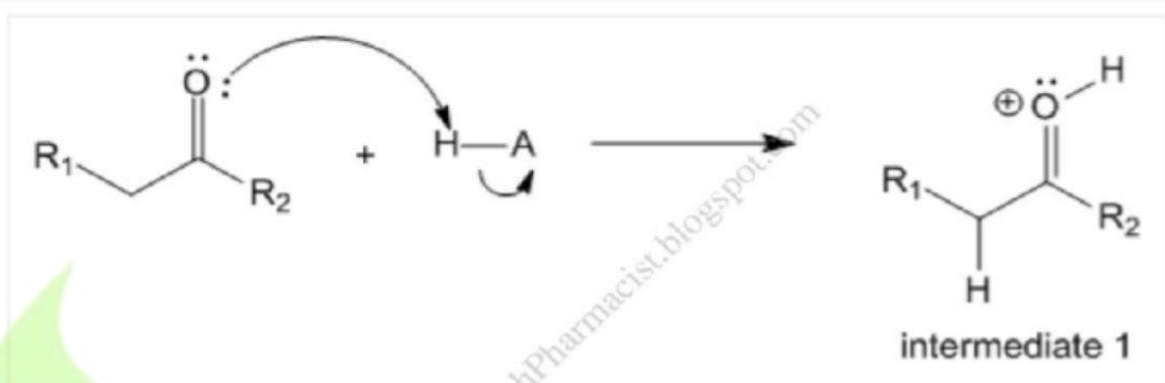


• Step 3

Ion II abstracts hydrogen ion from water to form β hydroxy aldehyde /aldol



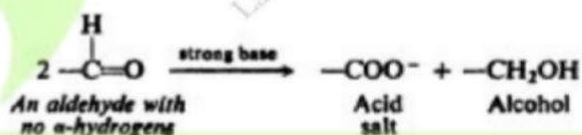
In acidic condition



3.

Cannizzaro Reaction

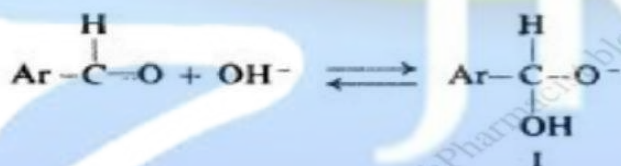
- Aldehydes containing no α -hydrogens undergo self-oxidation and reduction
- In the presence of concentrated alkali
- Products - mixture of alcohol and salt of carboxylic acid



Mechanism:

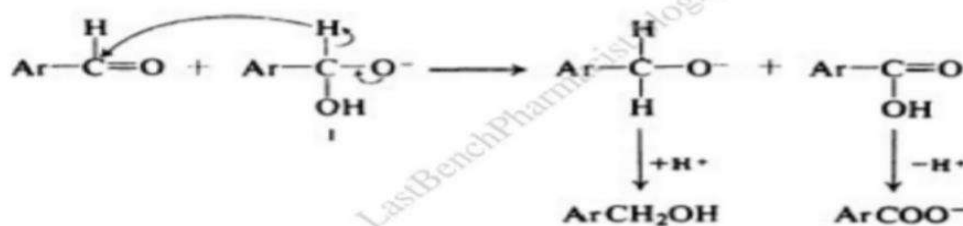
- Step 1

Addition of hydroxide ion to give intermediate ion



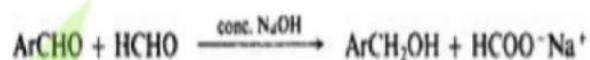
- Step 2

Transfer of hydride ion to the carbonyl carbon of aldehyde



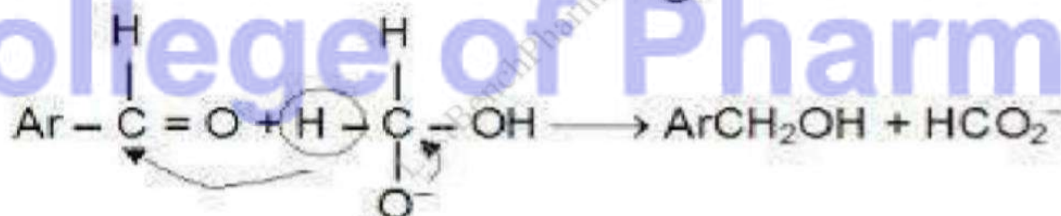
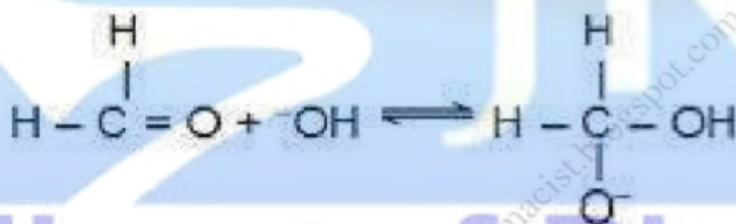
Crossed Cannizzaro Reaction Contd...

- Cannizzaro reaction between 2 different aldehydes



- If one of the aldehyde is formaldehyde, products - sodium formate and alcohol from other aldehyde

- Mechanism



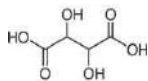
B.Pharmacy, 2nd Semester
Sub: Pharmaceutical Organic Chemistry-I
Unit-V

MODEL QUESTIONS FOR UNIT-V
PART-A

I. Multiple choice Questions (MCQs) (1mark)

- Which of the following is not a functional derivative of carboxylic acid?
 - Acid halide
 - Amide
 - Ester
 - Alcohol
- Which are the correct relative acidities?
 - $\text{RCOOH} > \text{HOH} > \text{ROH}$
 - $\text{RCOOH} > \text{ROH} > \text{HOH}$
 - $\text{RCOOH} > \text{NH}_3 > \text{ROH}$
 - $\text{ROH} > \text{HOH} > \text{RCOOH}$
- Which of the following has the greatest K_a ?
 - ROH
 - RCOOH
 - NH_3
 - RH
- The acidity of a carboxylic acid is due to _____.
 - Powerful resonance stabilization of its anion
 - Powerful resonance stabilization of its cation
 - Increase energy for ionization
 - None
- Which of the following is the simplest carboxylic acid?
 - Formic acid
 - Acetic acid
 - Ethanoic acid
 - Citric acid
- Which of the following substituents decrease acidity?
 - halide gr
 - alkyl gr
 - carbonyl gr
 - cyanide gr
- Which are the correct relative acidities?
 - $\text{FCH}_2\text{COOH} > \text{ClCH}_2\text{COOH} > \text{ICH}_2\text{COOH}$
 - $\text{FCH}_2\text{COOH} > \text{BrCH}_2\text{COOH} > \text{ClCH}_2\text{COOH}$
 - $\text{ICH}_2\text{COOH} > \text{ClCH}_2\text{COOH} > \text{FCH}_2\text{COOH}$
 - $\text{FCH}_2\text{COOH} > \text{CH}_3\text{COOH} > \text{ClCH}_2\text{COOH}$

8. Which of the following has the highest acidity?
- Cl_3CCOOH
 - Cl_2CHCOOH
 - ClCH_2COOH
 - CH_3COOH
9. Which of the following statements about carboxylic acid is incorrect?
- Electron withdrawing substituents increase acidity
 - Electron-releasing substituents decrease acidity
 - Acid strength increases with increasing distance from the carboxylic group
 - Larger the $k_a \rightarrow$ greater the ionization \rightarrow stronger the acid
10. Carboxylic acids react with sodium hydrogen carbonate to produce gas.
- H_2
 - CO_2
 - O_2
 - N_2
11. Carboxylic acid reacts with alcohol in the presence of conc. sulphuric to form
- Ester
 - Ether
 - Amide
 - Acid anhydride
12. Amides are decomposed by NaOH to evolve gas.
- H_2
 - CO_2
 - N_2
 - NH_3
13. Alkaline hydrolysis of aromatic amide gives
- Aromatic alcohol
 - Aromatic aldehyde
 - Aromatic acid
 - No product
14. Esters react with hydroxylamines to yield_
- hydroxamic acids
 - Carboxylic acid
 - Benzoic acid
 - None
15. Which of the following is used as a good solvent, in vinegar, in titration?
- Citric acid
 - Acetic acid
 - Succinic acid
 - Tartaric acid



16. Name this carboxylic acid.
- Citric acid
 - Acetic acid
 - Succinic acid
 - Tartaric acid
17. Which of the following is the simplest dicarboxylic acid?
- Succinic acid
 - Tartaric acid
 - Oxalic acid
 - Salicylic acid
18. Which of the following is the simplest aromatic carboxylic acid?
- Benzoic acid
 - Benzyl Benzoate
 - Acetyl Salicylic acid
 - Salicylic acid
19. Which of the following is used for analgesic and antipyretic?
- Benzyl Benzoate
 - Acetyl Salicylic acid
 - Salicylic acid
 - Dimethyl Phthalate
20. Which of the following statements is incorrect?
- Basicity of amines $\rightarrow K_b \rightarrow$ basicity constant
 - Aliphatic amines are more basic than ammonia.
 - Ammonia is more basic than aliphatic amines
 - Aromatic amines are weaker than ammonia.
21. Which of the following statements is incorrect about amine?
- Aliphatic amine is more basic than ammonia.
 - Electron-releasing group disperses positive charge of substituted ammonium ion.
 - The alkyl group pushes electrons toward nitrogen.
 - Amines are basic in nature & turn blue litmus red.
22. Which of the following has both primary amine and primary alcohol?
- Ethanolamine
 - Ethylenediamine
 - methylphenethylamine
 - Amphetamine
23. Which of the following is used as a Precursor to chelation agents, drugs, and polymers?
- Ethanolamine
 - Ethylenediamine
 - methylphenethylamine
 - Amphetamine

24. Which of the following statements is incorrect?

- Nitrous acid test with tertiary amines there is no reaction.
- Nitrous acid test with secondary amines, an N-nitroso compound.
- Hinsberg reaction with tertiary amines- if amine is soluble in water, it remains soluble.
- Hinsberg reaction with secondary amines product is soluble in water also in acidic solution.

PART-B

II. Short-answered type questions (5 MARK)

- Explain why Carboxylic acids are more acidic than corresponding alcohol.
- What is the difference between the Hydroxamic acid test of ester and amide?
- Write any two Qualitative tests for carboxylic acids.
- Write the structure and uses of acetic acid & benzoic acid.
- Explain the basicity of amines & Comparison of the basicity of ammonia with aliphatic and aromatic amines.
- Write the structure and uses of ethanolamine & Ethylenediamine.

PART-C

III. Long answer type question (10MARK)

- Differentiate between pri, sec, tert aliphatic amines. And Explain Hinsberg test & nitrous acid test for pri, sec, tert aliphatic amines.
- Explain acidity of Carboxylic Acids with resonance & inductive effect. Also effect of Substituents on acidity of carboxylic acid.



ANSWERS TO MODEL QUESTIONS FOR UNIT-V

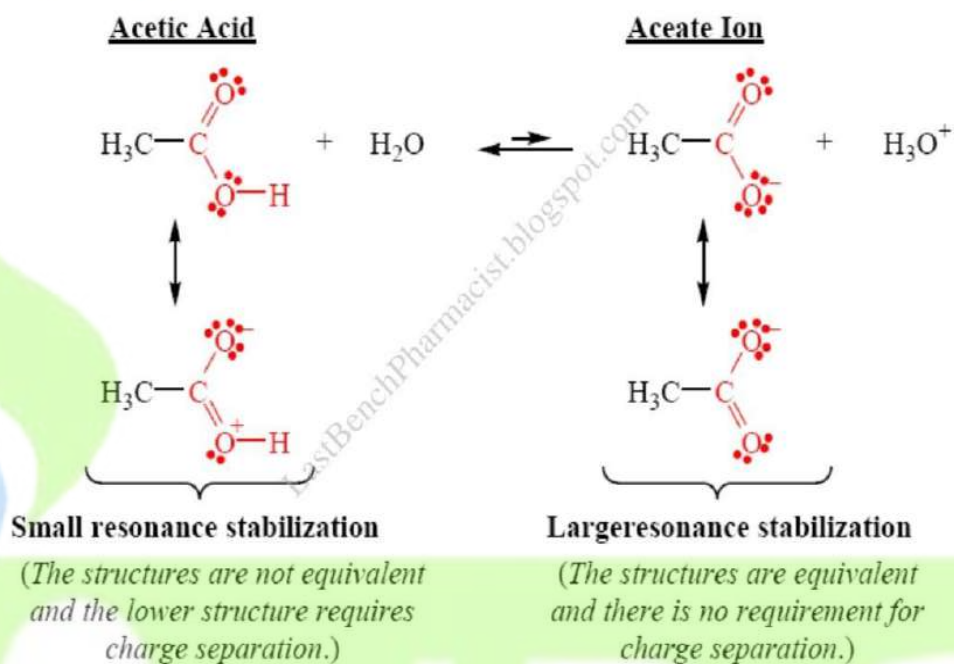
PART-A

1. d
 2. a
 3. b
 4. a
 5. a
 6. b
 7. a
 8. a
 9. c
 10. b
 11. a
 12. d
 13. c
 14. a
 15. b
 16. d
 17. c
 18. a
 19. b
 20. c
 21. d
 22. a
 23. b
 24. d
- 

PART-B

1.

• Resonance effect



Resonance stabilised acetate ion

- Equivalent resonance structures for acetate ion
- Greater resonance stabilization
- Reduces energy for ionisation

No resonance stabilization for alcohol and alkoxide ion

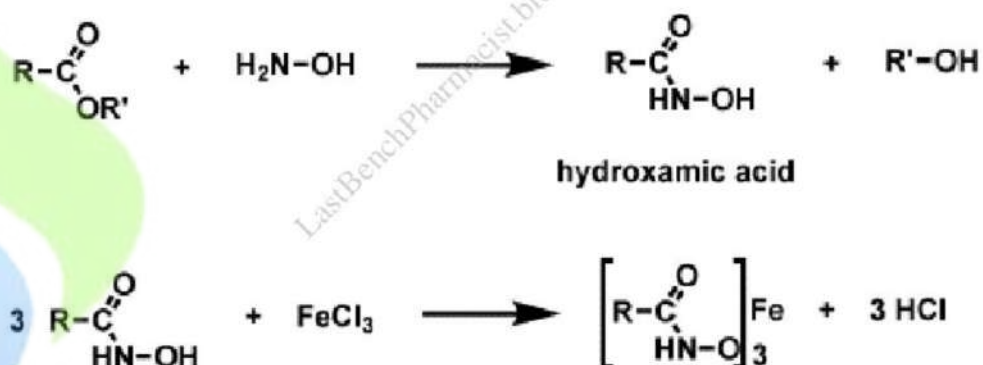
- Carboxylic acid yields resonance-stabilized anion, stronger acid than alcohol



2.

Qualitative tests for esters

- Hydroxamic acid test
- Esters react with hydroxylamines to yield hydroxamic acids which in their turn form a wine red ferric hydroxamate with ferric ions



Qualitative tests for amides

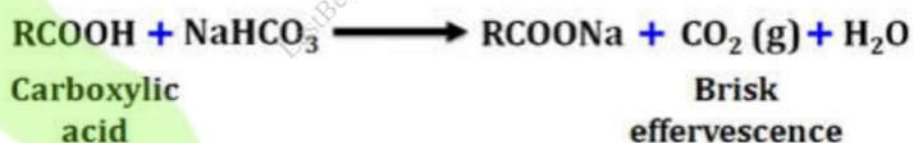
- Hydroxamic acid test for aromatic primary amides:**
- Hydrogen peroxide reacts with aromatic primary amides to form the hydroxamic acid, which then reacts with ferric chloride to form ferric hydroxamate complex having a violet colour.



3.

- **Sodium Hydrogen Carbonate Test**

- Carboxylic acids reacts with sodium hydrogen carbonate to produce carbon dioxide gas which can be seen in the form of a brisk effervescence



- **Ester Test**

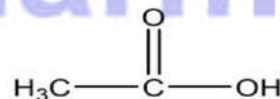
- Carboxylic acid reacts with alcohol in presence of conc. sulphuric acid to form ester that is identified by the presence of a fruity smell.



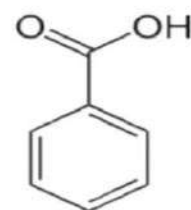
4.

Acetic acid

- Structure
- Systematically ethanoic acid
- Undiluted- glacial acetic acid
- Vinegar- roughly 3-9% acetic acid
- Uses
- Chemical reagent
- Good solvent, recrystallization solvent



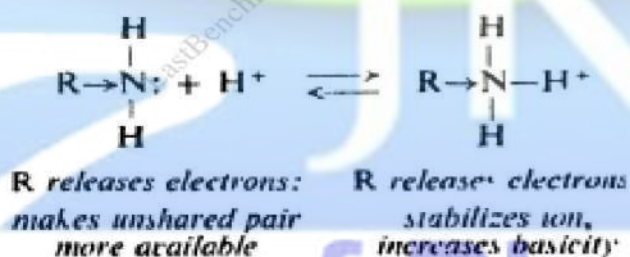
Benzoic acid



- Structure
- Simple aromatic carboxylic acid
- Uses
- Production of phenols by oxidative decarboxylation at 300-400 °C
- Precursor to plasticizers, sodium benzoate and other preservatives
- Constituent of Whitefield's ointment- fungal skin diseases

5.

- Aliphatic amine more basic than ammonia
 - Electron releasing group **disperses positive charge** of substituted ammonium ion
 - Alkyl group **pushes electrons** towards nitrogen



College of Pharmacy

6.

Ethanolamine

Structure



2-aminoethanol or monoethanolamine

Has both primary amine and primary alcohol

Uses

As gas stream scrubbing

As buffer, pH regulator in cosmetics

Injectable sclerosant

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Ethylenediamine

Structure



Strongly basic amine

Uses

Precursor to chelation agents, drugs, and agrochemicals, polymers

Ingredient in the common bronchodilator drug aminophylline

PART-C

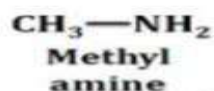
1.

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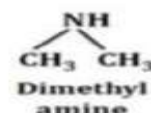
Qualitative tests for aliphatic amines

Litmus test- Amines are basic in nature and turns red litmus blue

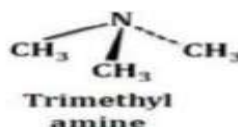
Primary amines



Secondary amines



Tertiary amines



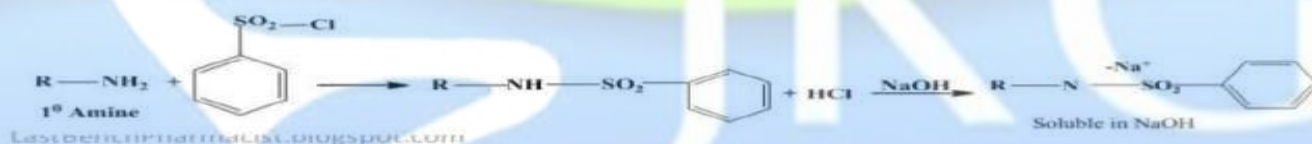
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Qualitative tests for aliphatic amines

- **Hinsberg reaction:** Hinsberg reagent is called benzenesulfonyl chloride
- Primary aliphatic amines on reaction with benzenesulfonyl chloride & NaOH gives N-alkylsulphonamide which contains an acidic hydrogen and hence dissolve in NaOH solution to form the soluble sodium salt. Solution thus obtained on acidification gives a precipitate of free sulfonamide



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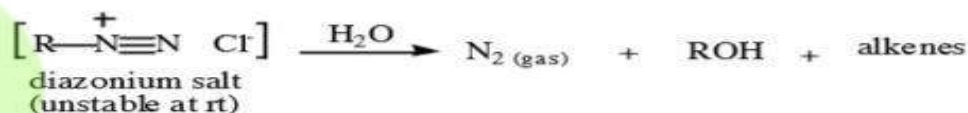
Qualitative tests for aliphatic amines

- **Hinsberg reaction:**
- With secondary amines- product is not soluble in water
- Also not soluble in acidic solution
- With tertiary amines- if amine is soluble in water, it remains soluble
- If not, it will form an organic layer on the top of water
- This layer will dissolve in 5% HCl

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Qualitative tests for aliphatic amines

- **Nitrous acid test**
- Treatment of the primary aliphatic amine with sodium nitrite in the presence of hydrochloric acid generates the very reactive and electron deficient nitroso ion which reacts rapidly with the nucleophilic amine to give a nitrosoammonium adduct which then loses water to give the diazonium salt.
- This is unstable and immediately loses N₂ gas which bubbles out of the solution



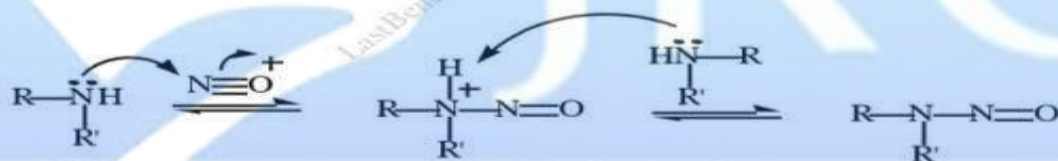
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Qualitative tests for aliphatic amines

- **Nitrous acid test**
- With secondary amines, an N-nitroso compound is formed when the amine attacks the nitroso ion
- This is relatively stable and separates from the aqueous solution as a yellow or orange liquid. No N₂ gas is evolved



N-nitroso compound
(stable at rt)

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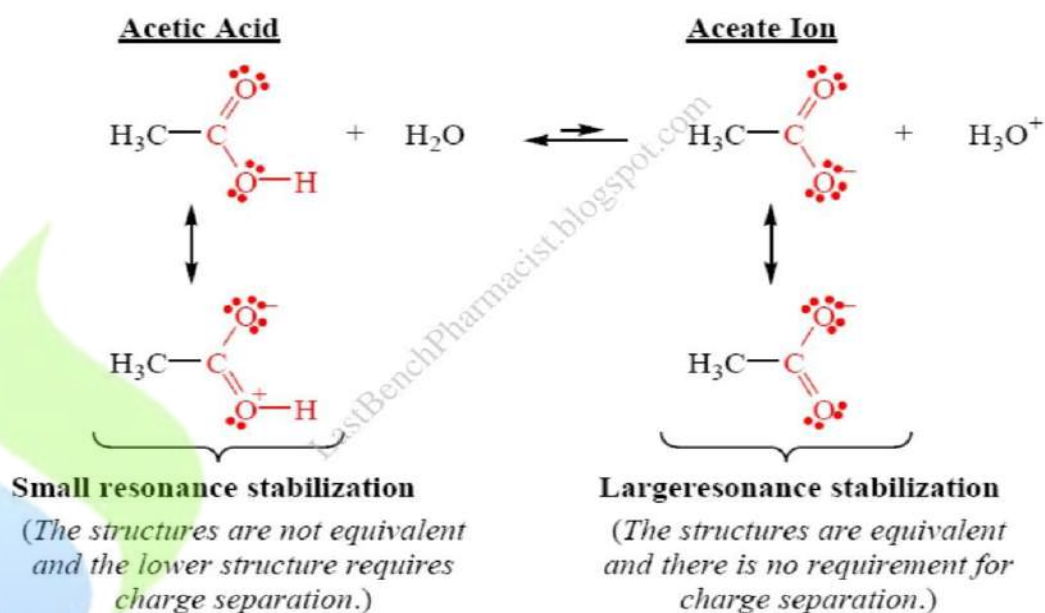
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Qualitative tests for aliphatic amines

- **Nitrous acid test**
- With tertiary amines there is no reaction

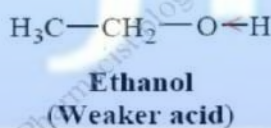
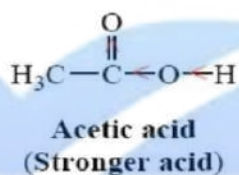
2.

• **Resonance effect**



Inductive effect

- Inductive effect of carbonyl group – responsible for acidity of carboxylic acids



- In both compounds - O—H bond - highly polarized by greater electronegativity of the oxygen atom
- Carbonyl group – more powerful electron attracting inductive effect than CH₂ group

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- Electronegativity and electron withdrawing power of the halogen substituent and strength of the acid decreases in the order



- Number of electron withdrawing chloro group and acid strength decreases in the order



- Inductive effect & acid strength decreases rapidly with increasing distance from the carboxylic group

