STUDY MATERIAL

Dumkal College
Basantapur Dumkal

Topic: General Treatment of Reaction Mechanism II : Tautomerism

Course Code: CHEMHT-4

Semester: II (Hons)

Name of the Teacher: Md Muttakin Sarkar

Name of the Department: Chemistry

Tautomerism

Tautomerism:- It is one type of structural isomerism where two forms of a molecule can be present in equilibrium. One structure or one form of the molecule may be converted into another by means of transfer of the mobile atom from one possition to another. This phenomena is known as tautomerism. Individual form of the molecule is called tautomer.

Tautomerism is also called dyanamic isomerism or desmotropism.

- Different between resonance and tautomerism:-

(1) Tautomerism is a real concept and individual form or tautomer has real existance. On the other hand resonance is a hypothetical concept and resonating structures have no real existance.

(2) Tautomerism is the presence of two forms of the same compound that are capable of interconversion. Resonance is the presence of several forms which determine the actual structure of the compound.

(3) Tautomers exist equilibrium with each other. Resonance structures do not exist in equilibrium.

(4) Tautomerism has no effect on stability of the molecule where as resonance has a profound effect on the stability of the molecule.

(5) Taumers can be obtained by relocation of proton. One the other hand resonance structures can be obtained by relocation of π-bond electrons and lone pair electrons.

(6) Tautomerism has no effect on bond length where as resonance affects the bond length (single bond is shortened and double bond becomes longer)

Prototropy :- It is a type of tautomerism that occurs due to the acid-base behaviour of the compound. Here two forms differ only in the position of proton. The structure will have the same emperical formular and the number of charges.

(i) **Keto-enol system :-**

Keto form enol form.

(ii) **Nitro-aci-nitro system :-**

Nitro form Aci-nitro form.

(iii) **Amido-imidol tautomerism :-**

Amido form Imidol form

(iv) **Nitroso-oximino tautomerism :-**

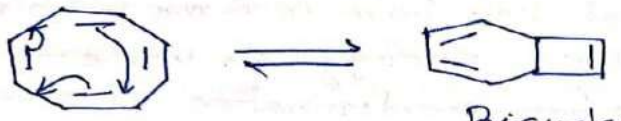
(v) **Imine-enamine tautomerism :-**

Imine form Enamine form.

(vi) **Diazo-amino tautomerism :-**

Valence tautomerism:- Tautomerism in which change in interatomic distances through the formation of new bonds by redistribution of valence electrons within a molecule without migration of any atom is termed as valence tautomerism.

(i)



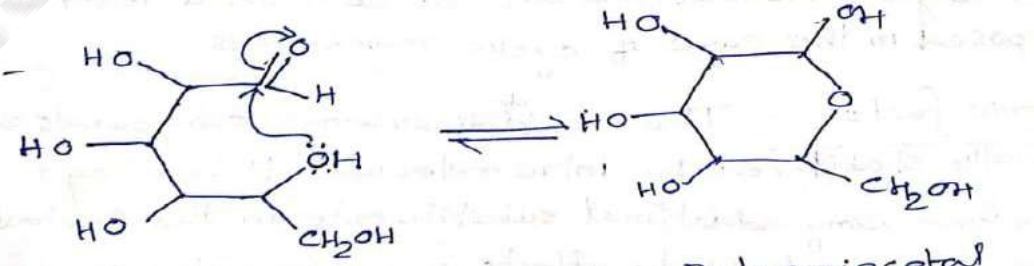
Cyclooctatetraene ⇌ Bicyclooctatriene

(ii)

Oxepin ⇌ Benzene oxide

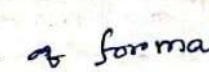
- **Ring-chain tautomerism:-** The type of tautomerism in which one tautomer is acyclic and the other is cyclic is denoted as ring-chain tautomerism. This tautomerism takes place when one functional group of a bifunctional acyclic molecule reacts with other and form a cyclic system. Sugars like D-glucose, D-mannose etc. exhibit ring-chain tautomerism.

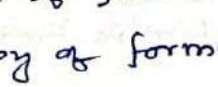
Eg :-



An aldohexose (chain form) ⇌ A hemiacetal (ring form)

Possition of equilibrium in keto-enol tautomerism :-

Enthalpy of formation of  = -1870 kJ/mole

Enthalpy of formation of  = -1820 kJ/mole

Difference = 50 kJ/mole

There it is found that keto form is more stable than enol form by 50 kJ/mol energy. So under ordinary condition keto form predominates.

If the enol form could be stabilised by some factors by an amount more than 50 kJ/mol energy, the enol form predominates. This stabilisation may occurs through the following factors —

(1) Resonance :- If the extent of resonance increases in the enol form, then amount of enol content in the equilibrium increases.

(2) Entropy factor.

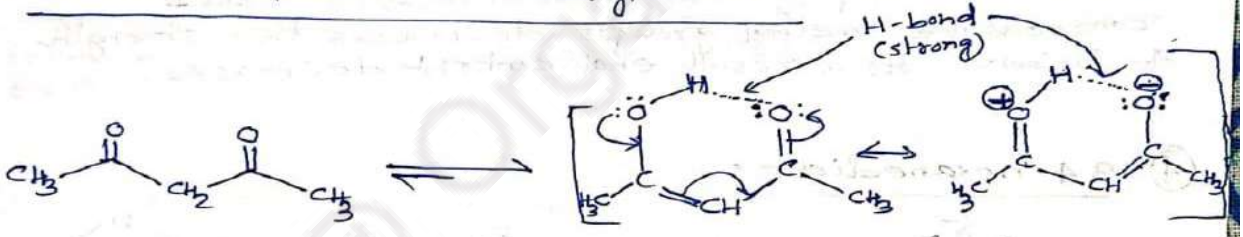
Cyclic mono ketone enolise appreciably than acyclic monoketone because introduction of a C=C bond in enolization decreases the conformational freedom of the acyclic monoketone but no such extra restriction is imposed in the case of cyclic monoketones.

(3) Steric factor :- The enols of dicarbonyl compounds are generally stabisized by intramolecular H-bonding. Therefore, any additional substituents on the C-atoms in the ring adversely affects ring formation by H-bonding due to steric strain. As a result enol content decreases.

④ Nature of solvent :- In the end form of dicarbonyl compounds, the intramolecular H-bond is quite strong and it is not considerably affected by solvents like water and ethanol. But the keto form is well stabilised by these solvents due to H-bonding. Therefore, such protic solvents tend to reduce the enol content. However nonpolar solvents like hexane, benzene etc which are unable to form H-bond, tend to increase the enol content.

Let us considered the following examples —

① Pentane-2,4-dione or acetylacetone :-



Keto form (24%) Enol form (76%)

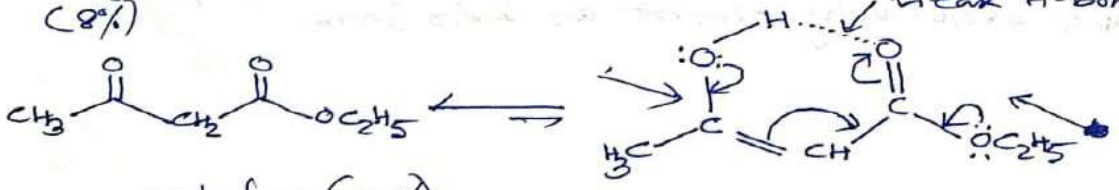
Here amount of enol form in equilibrium is 76% which is due to —

ⓐ- because of extended conjugation, the enol form of pentane-2,4-dione is stabilized by resonance.

ⓑ H-bonding (intramolecular)

ⓒ Ring structure.

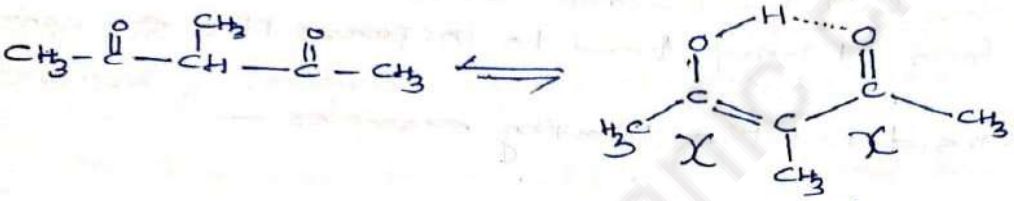
② Ethyl acetoacetate :- The enol content of ethyl acetoacetate (EAA) at equilibrium is very small (8%)



Keto form (92%) Enol form (8%)

The enol form of the following molecule is stabilized by H-bond and ring structure but there is cross conjugation with the ester group which destabilized the enol form.

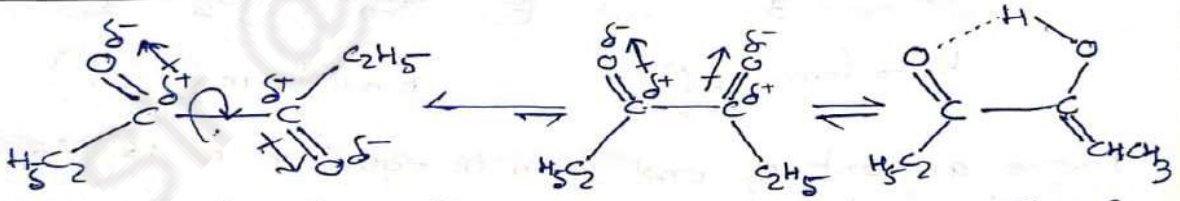
③ α-methyl acetyl acetone :-



~43%

Here steric repulsion between the three consecutive methyl groups decreases the strength of H-bond. As a result enol content decreases.

④ 3,4-hexanedione :-



Keto form (≈ 100%)

Anti-conformation more stable or s-trans form.

Keto form (Syn-conformation less stable) or s-cis form

Enol form

In the above compound, there is dipolar repulsive interaction between two carbonyl group in s-cis form. So in order to reduce this interaction the molecule converted to s-trans form. So this compound almost exclusively present as keto form.

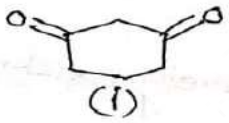
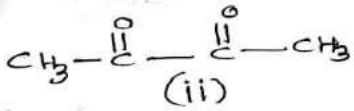
(5) 1,2-cyclohexadione :-

1,2-cyclohexadione exists almost exclusively in the enol form.

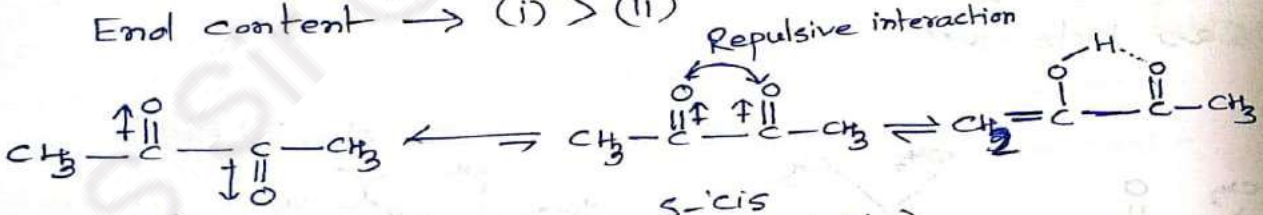
Keto form Enol form (≈100%)

In this diketone, the two carbonyl groups are in s-cis orientation. Here s-trans orientation is not possible because this is ring system (rigid).

In order to avoid this repulsion keto form converted into enol form and at equilibrium almost 100% enol form exists.

(6)  (i) and  (ii)

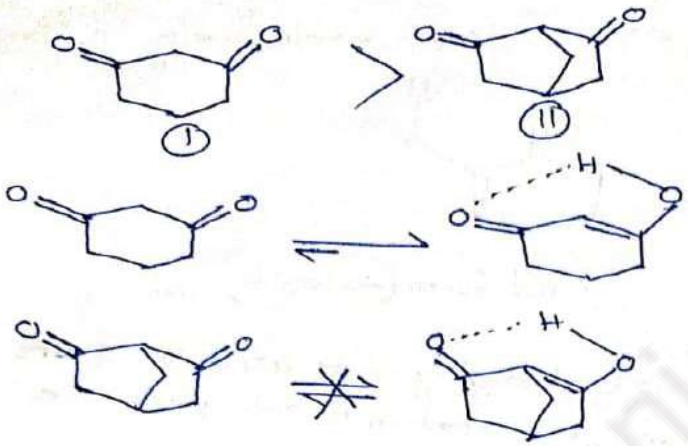
Enol content → (i) > (ii)



s-trans
more stable

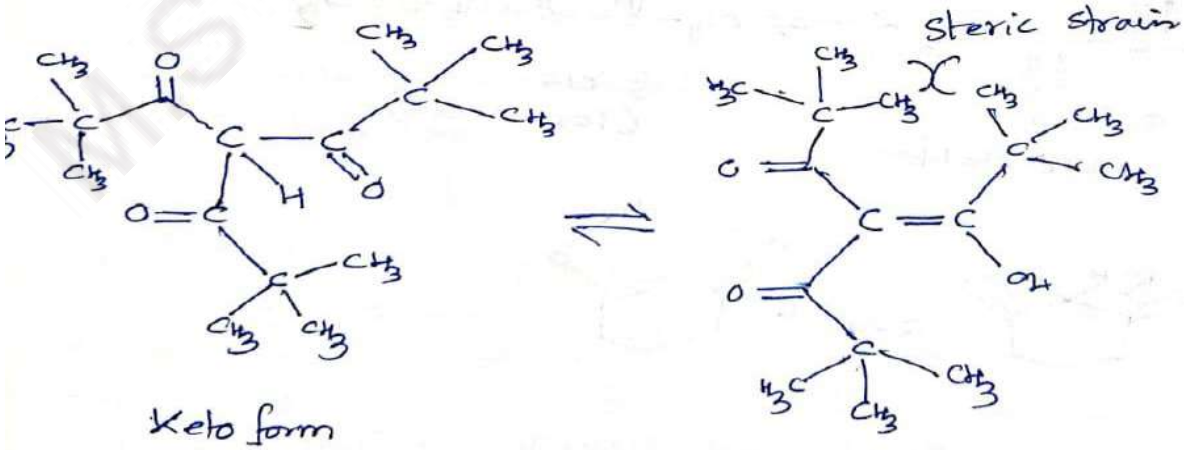
s-cis
(less stable)

⑦ End content of

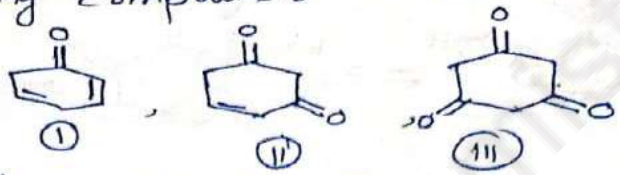


According to Bredt's rule a double bond will not go to the bridgehead carbon atom in the bicyclic system. So compound (ii) will not undergo enolisation and its enol content will be lower.

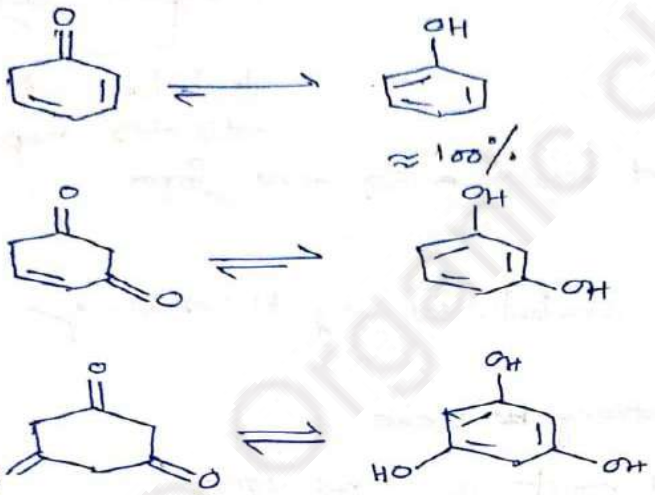
⑧ $(Me_3CO)_3CH$ compound almost exclusively exist as keto form.



Q. Arrange the following compounds inorder to their enol content —

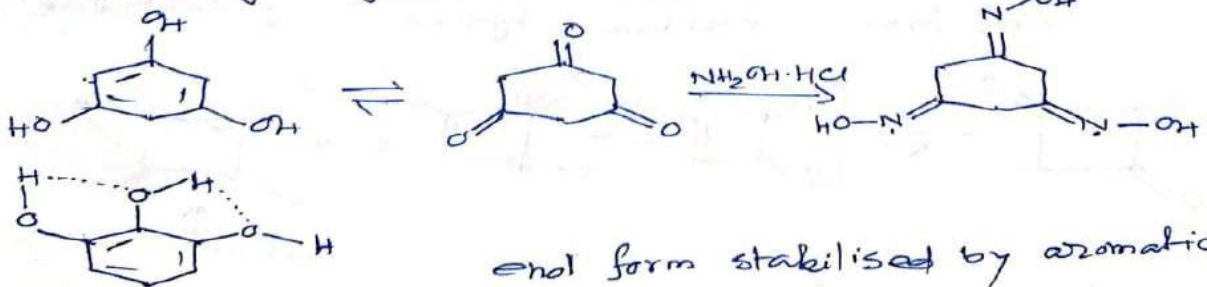


Order of enol content ① > ② > ③



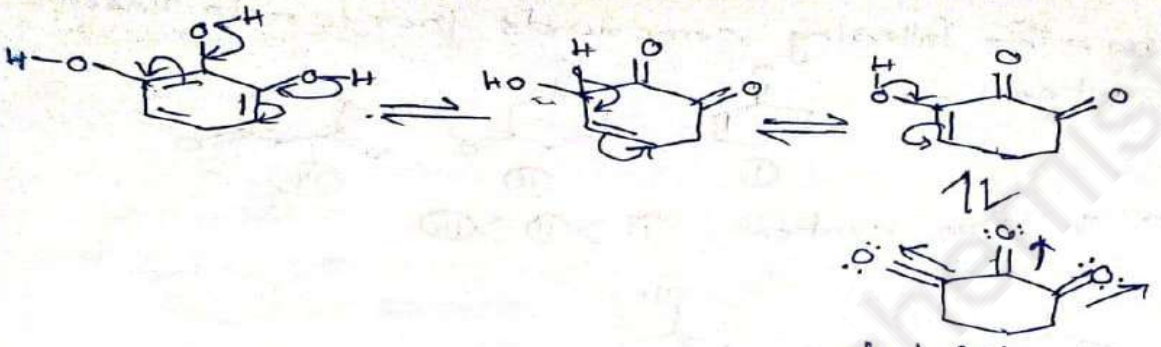
As no. of keto groups in the ring increases, the difference in stability between the enol form and keto form progressively decreases because aromatic stability becomes progressively less able to make the enol form very stable. As a result of this enol content decreases from ① → ② → ③.

- 1,3,5-trihydroxy benzene $\xrightarrow[NH_2OH \cdot HCl]{\text{excess}}$ trioxione derivative



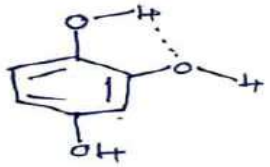
1,2,3-trihydroxy benzene

enol form stabilised by aromaticity and H-bonding.



destabilised by dipolar repulsion.

So this compound exists as enol form.

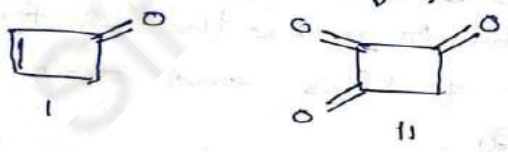


stabilized by H-bonding

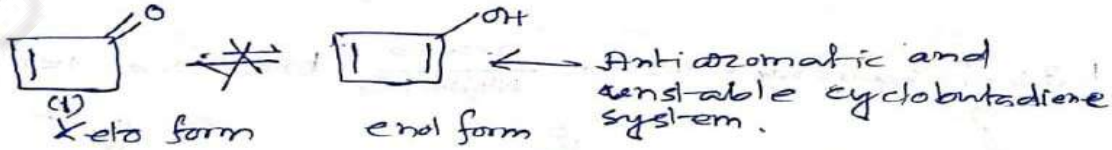
1,2,4-trihydroxy benzene.

This compound exists as enol form.

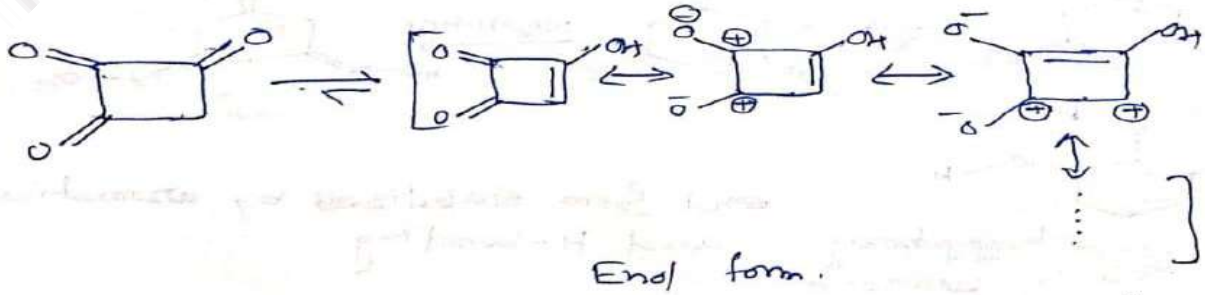
- Which one of the following two carbonyl compounds will enolize and why?



I II



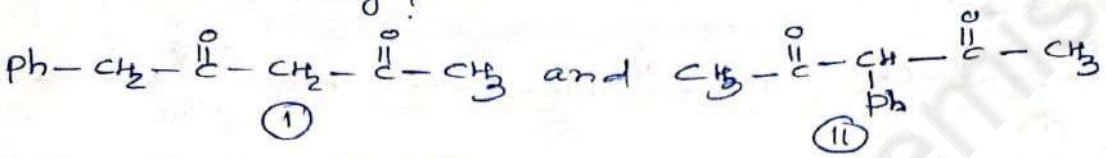
(I) Keto form — enol form — Antiaromatic and unstable cyclobutadiene system.



Enol form.

Aromatic and cyclobutadienyl di-cation system.

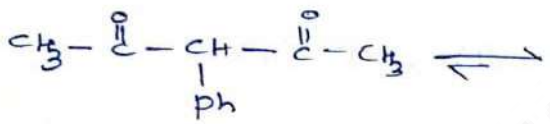
Q. Of the following compounds, which one has higher enol content and why?

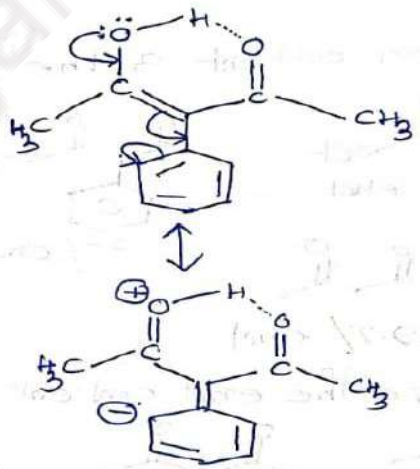


(I) and (II)

Enol content — (II) > (I)

Stability due to H-bonding, ring structure, resonance



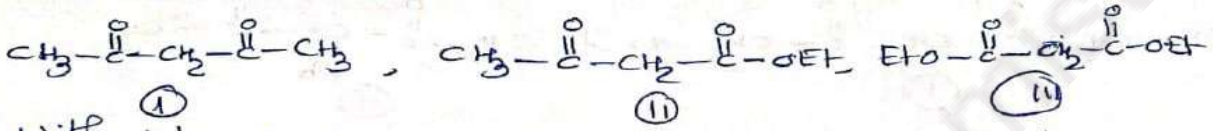


Extra stability of enol form is due to extended conjugation.

Q. Arrange the following compounds in the increasing order of enol contents and justify.

$CH_3COCH_2COCH_3$, $CH_3COCH_2CH_2COCH_3$, $[(CH_3)_3C\,CO]_3CH$

Q. Arrang the following compounds in order to their enol contents —



(I) , (II) , (III)

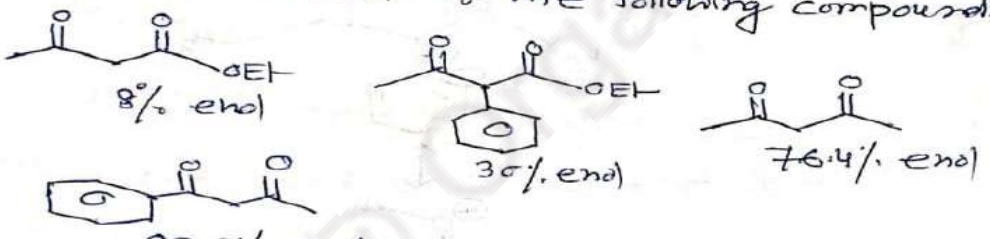
With introduction of ester group enol content decreases because —

(1) Ester is less electrophilic than Keto group.

(2) Cross conjugation

So the correct order is (I) > (II) > (III)

- The enol content of the following compounds —



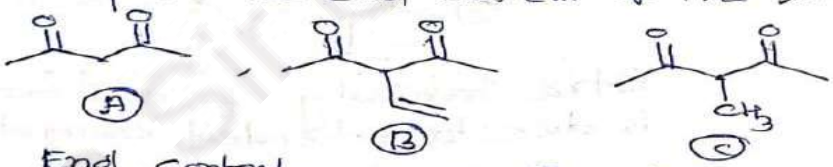
8% enol

30% enol

76.4% enol

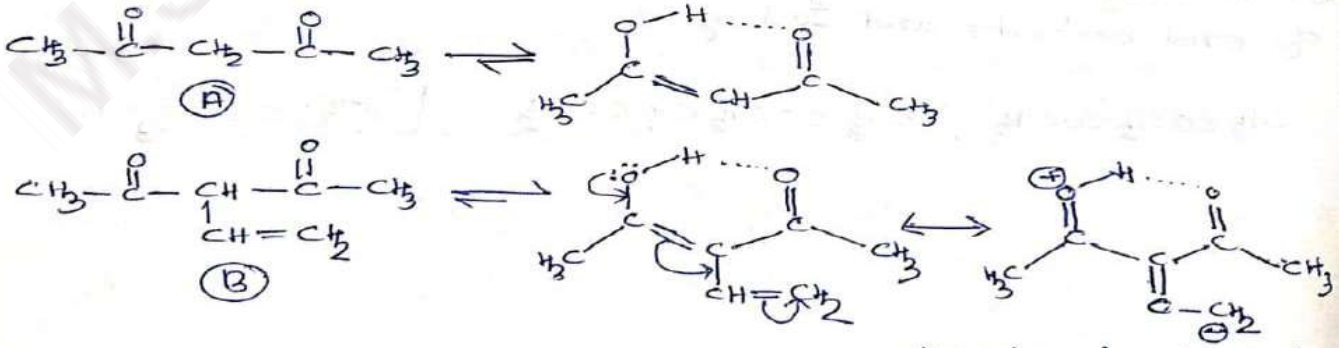
89.2% enol

Q. Compare the enol content of the following :—

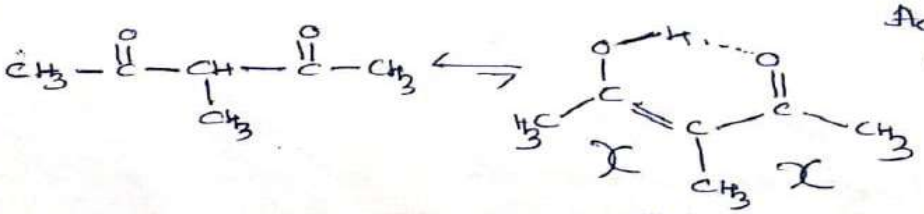


(A) , (B) , (C)

Enol content ⇒ (B) > (A) > (C)



Additional extended conjugation



Steric repulsion

- Mechanism of tautomerism :-

  (A) Step-wise mechanism

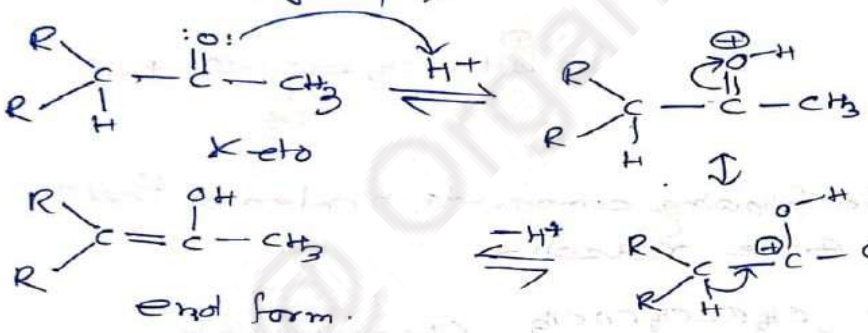
  (B) Concerted mechanism.

(A) Step-wise mechanism :-

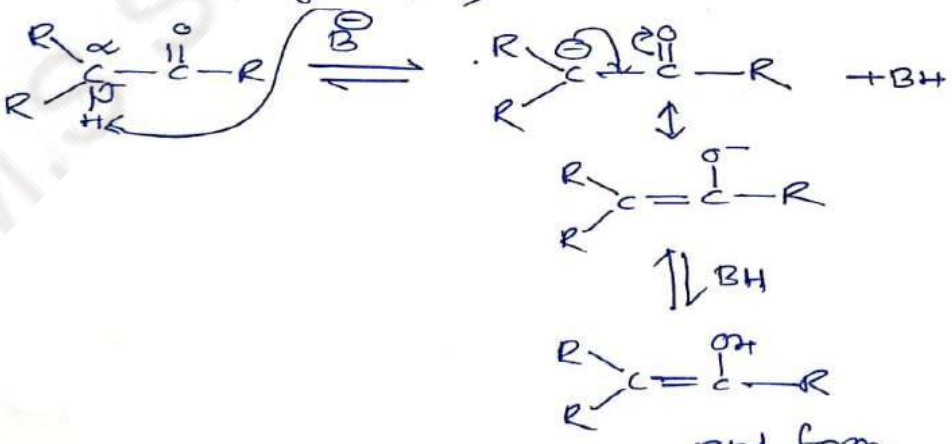
(i) Acid catalysed

(ii) Base catalysed

(i) Acid catalysed ⇒

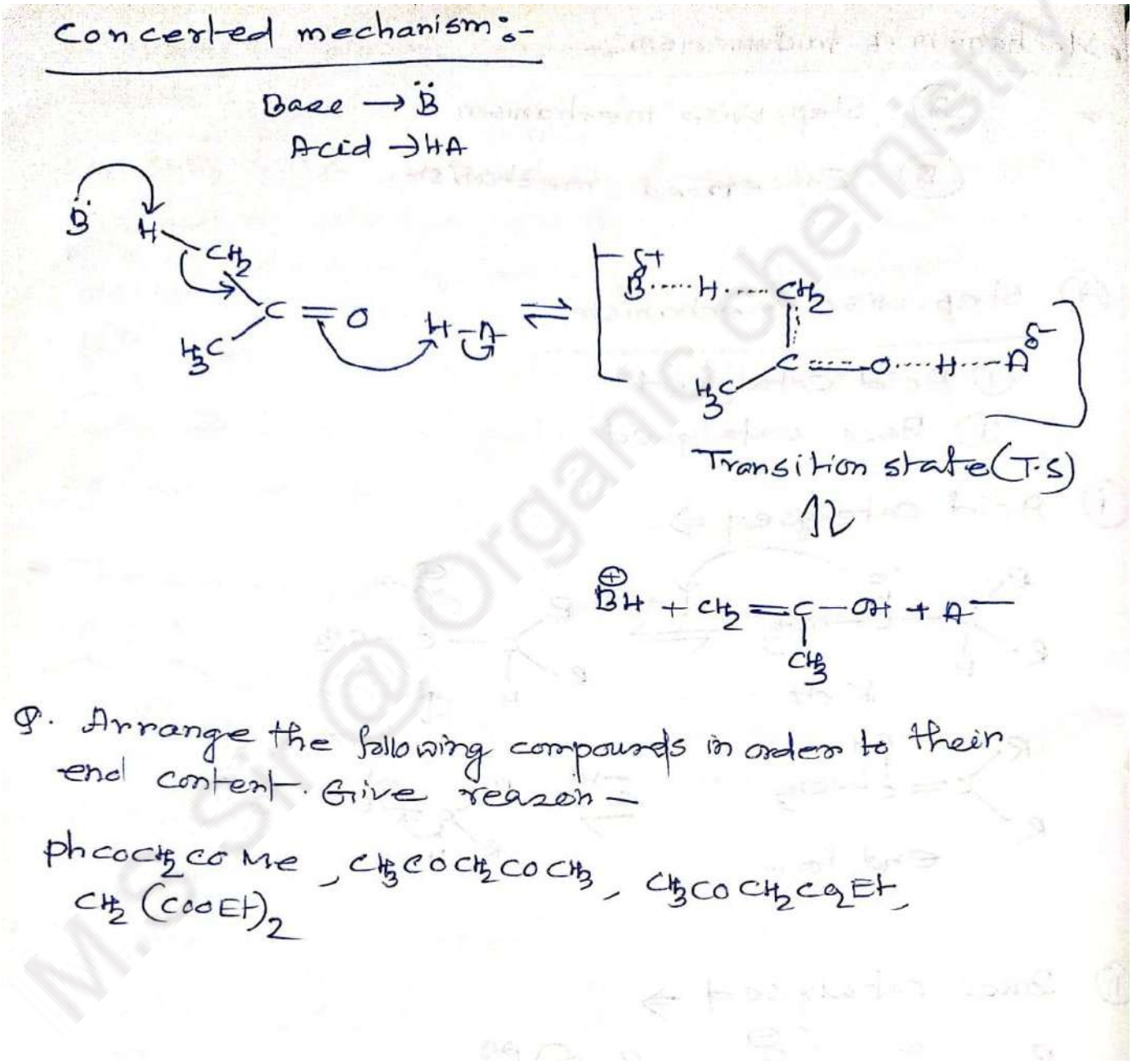


(ii) Base catalysed ⇒



Alkyl substitution on α-carbon decreases base catalysed endisation because resulting carbanion will be less stable for +I effect of alkyl group.

But alkyl substituent on α-carbon will prefer acid catalysed tautomerism for higher stability of double bond.



Q. Arrange the following compounds in order to their end content. Give reason —

$PhCOCH_2COMe$, $CH_3COCH_2COCH_3$, $CH_3COCH_2CO_2Et$, $CH_2(COOEt)_2$

Reference Books

1. Smith, J. G. Organic Chemistry, Tata McGraw-Hill Publishing Company Limited.
2. Eames, J., Peach, J. M. Stereochemistry at a Glance, Blackwell Publishing, 2003.
3. Robinson, M. J. T. Stereochemistry, Oxford Chemistry Primer, Oxford University Press, 2005.