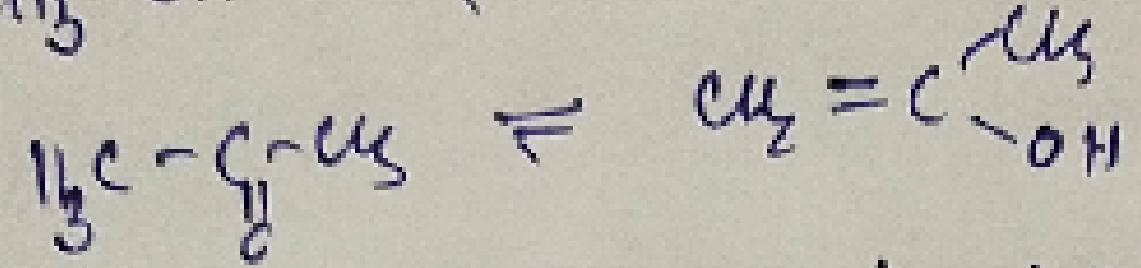
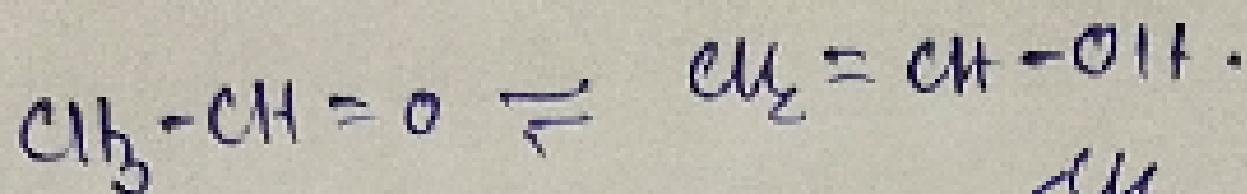


## Tautomers:

1

When functional isomers are in dynamic equilibrium, then they are called tautomers.



In both examples, the pair of functional isomers are in dynamic equilibrium, hence they are called tautomers.

: Reactions:  $\Rightarrow$  It takes place in liquid phase

$\Rightarrow$  It is catalysed by acid or base.

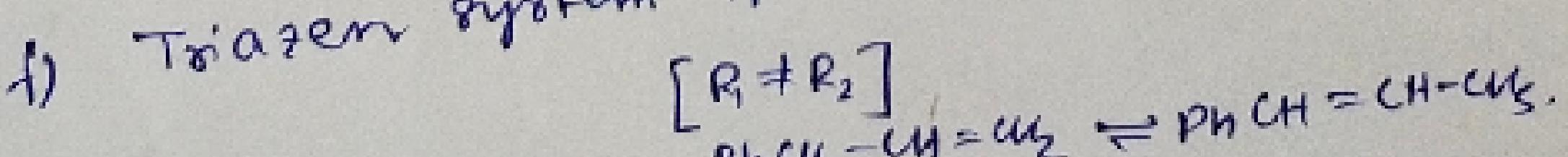
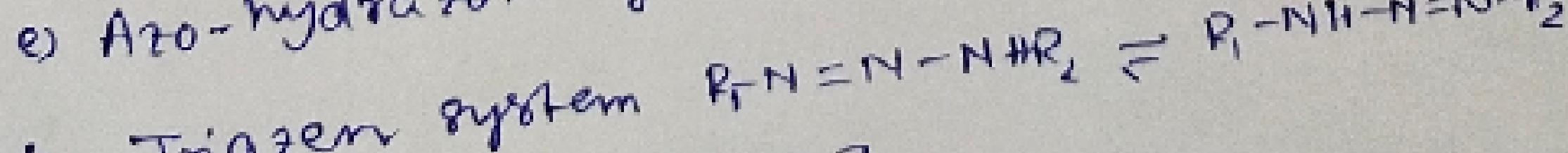
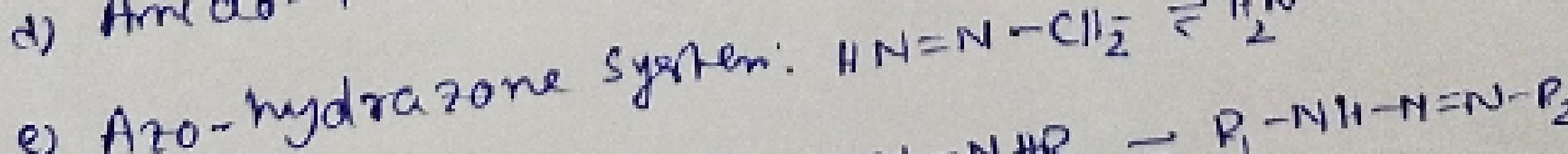
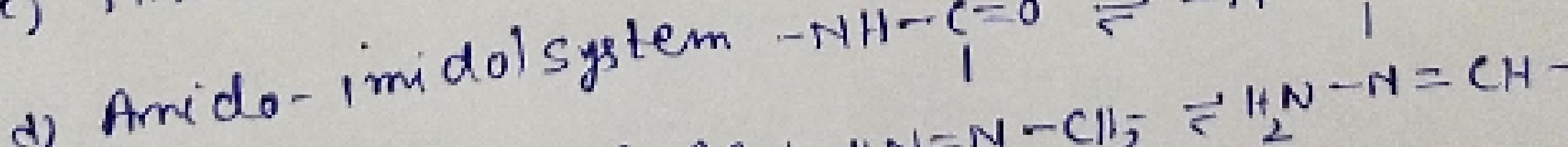
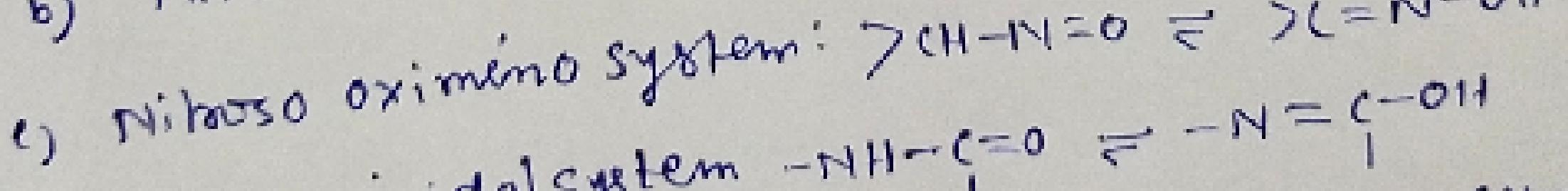
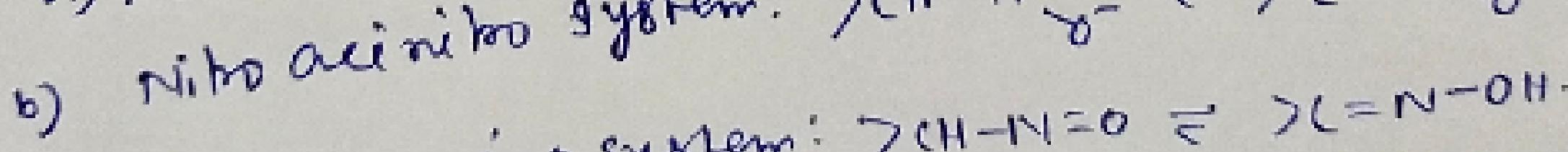
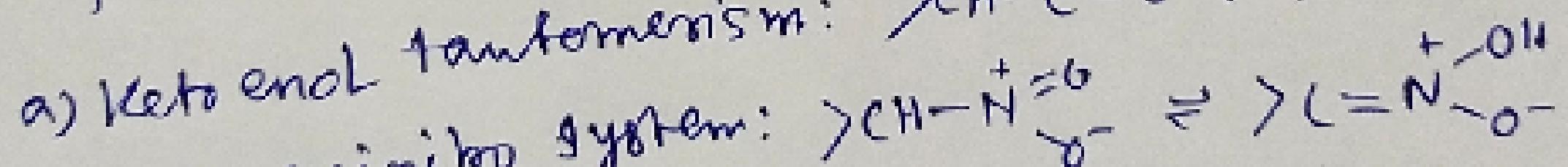
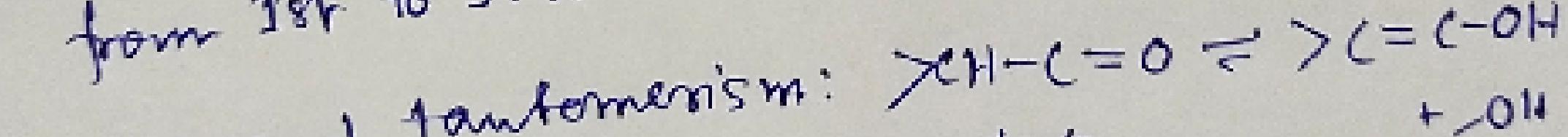
$\Rightarrow$  Atom migration takes place in tautomers where as in R.S.,  $\delta$  migration takes place.

$\Rightarrow$  Number of  $\sigma$ ,  $\pi$  & lone pair of electrons in both tautomers are always the same.

Different types of tautomeric systems:

a) Triad-system: When H atom migrates

b) Triad-system: when H atom migrates from 1st to 3rd atom.



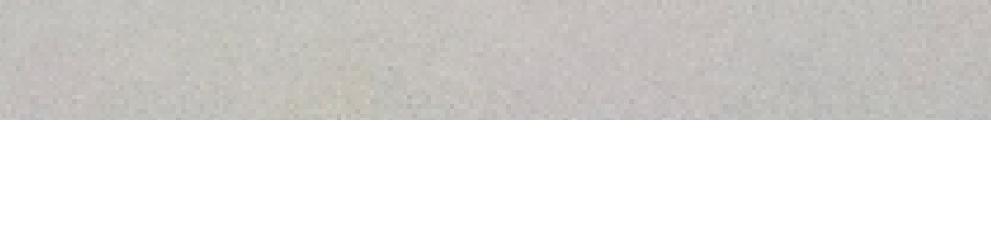
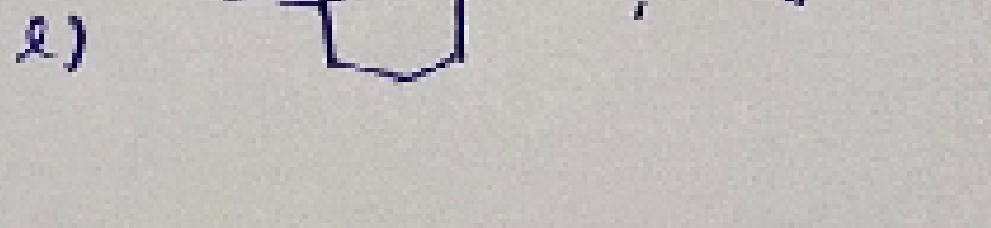
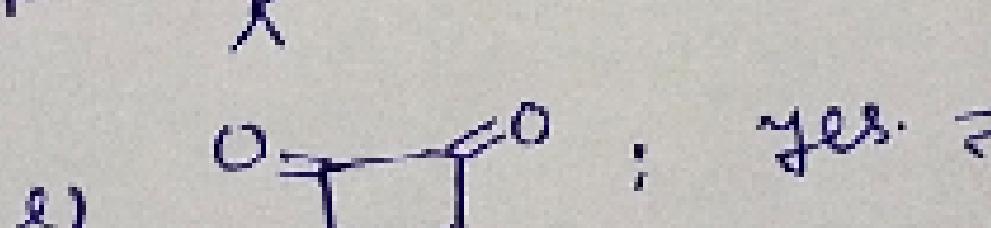
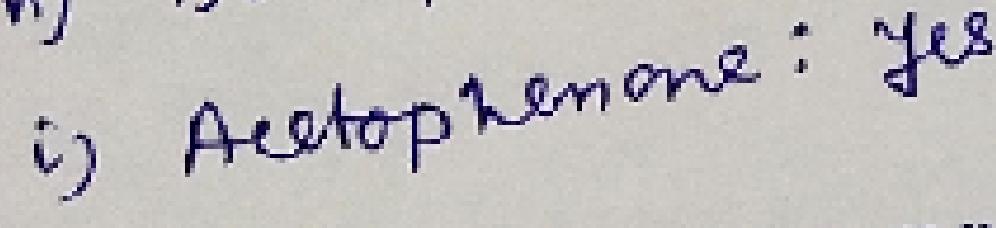
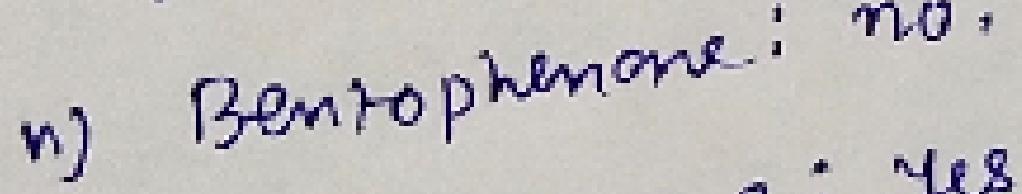
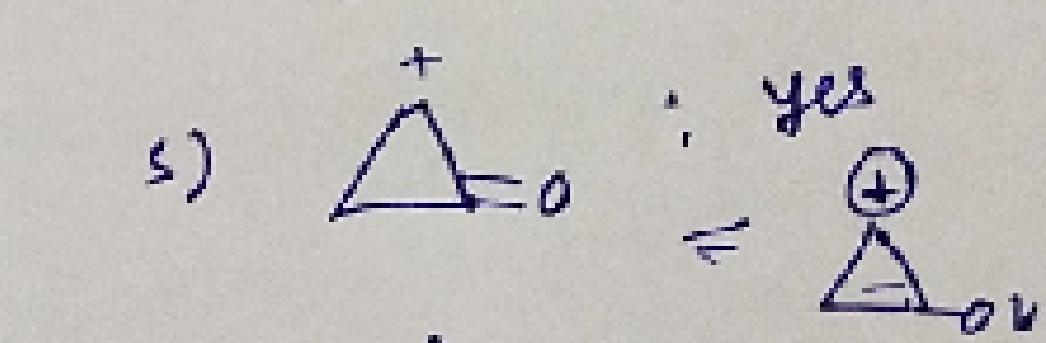
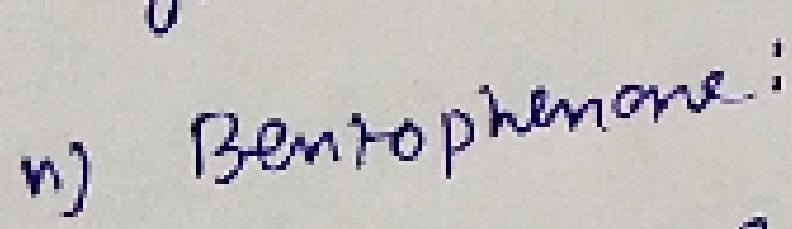
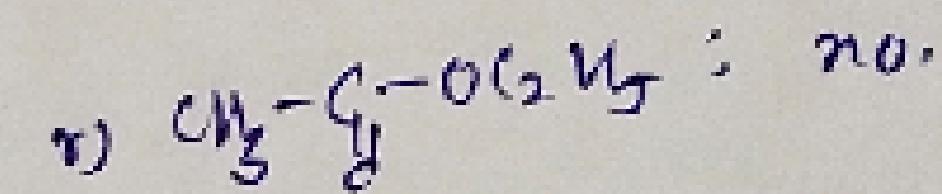
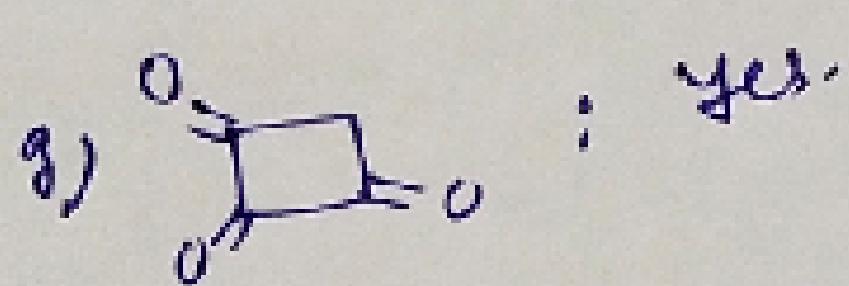
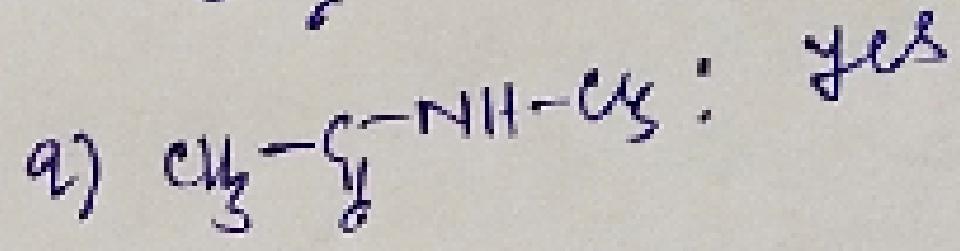
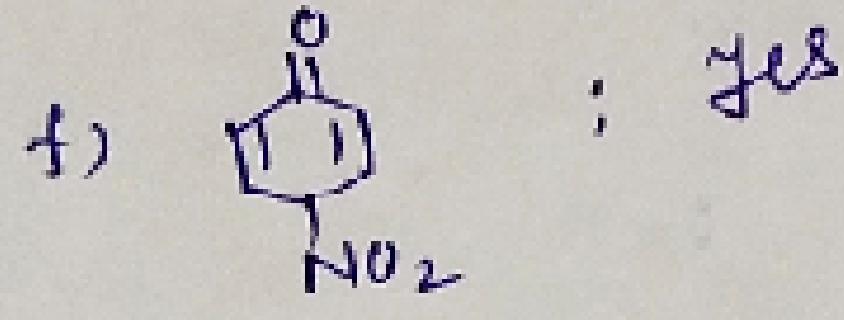
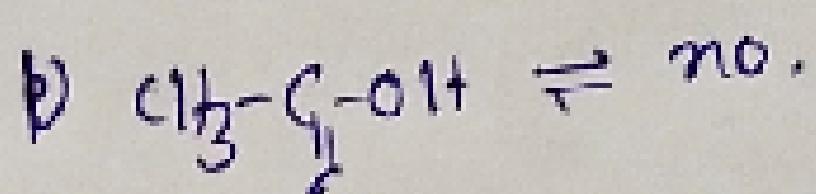
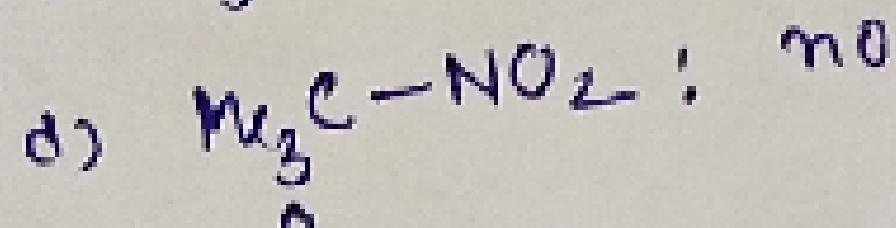
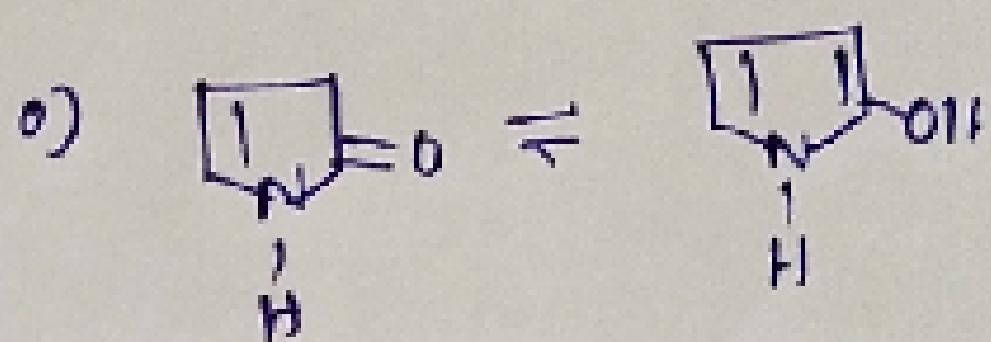
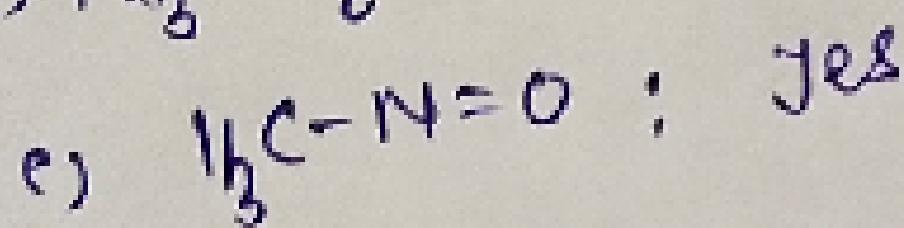
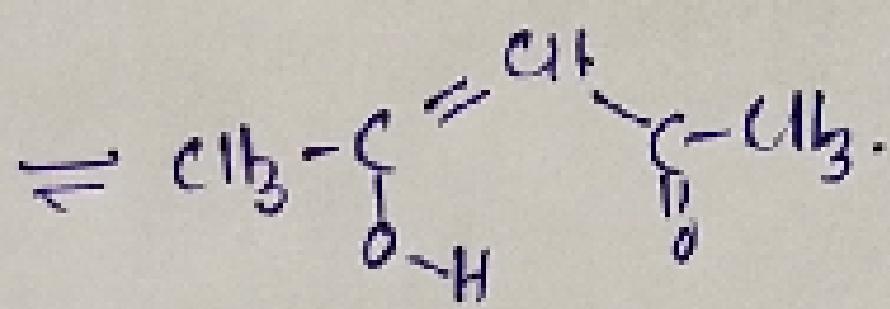
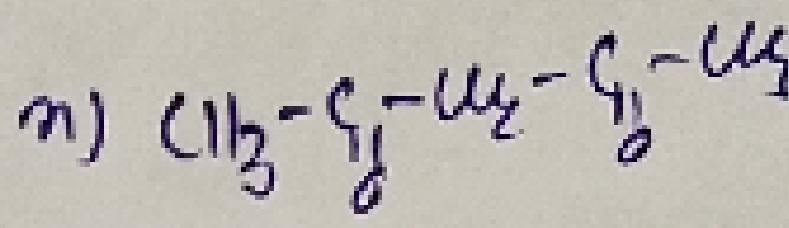
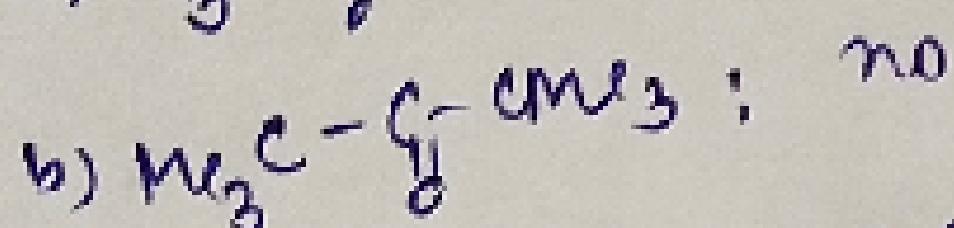
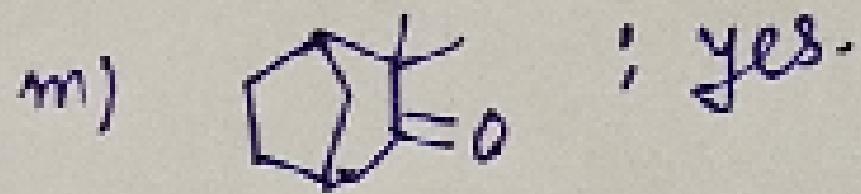
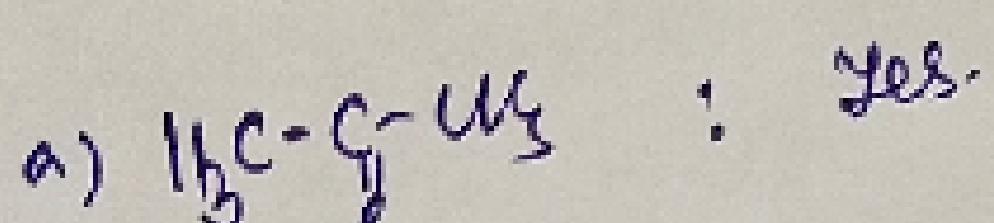
g) 3-Carbon system

2

(condition for tautomerism  
(keto-enol system))

In keto form / aldehyde form, w.r.t. (=O, next carbon(s))  
should be  $sp^3$  & it must have at least 1  $\alpha$ H.  
then it can show tautomerism. for other system (f.g.)

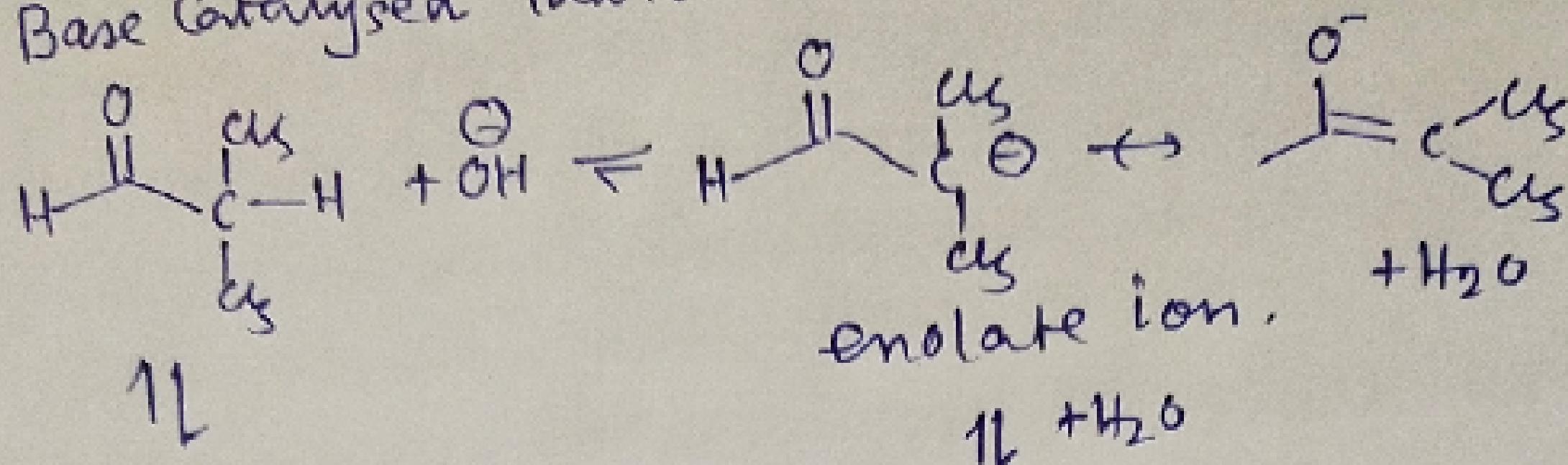
same concept is applicable.  
i) which of the following can show tautomerism



Mechanism for tautomerism:

3

Base Catalysed tautomerism:



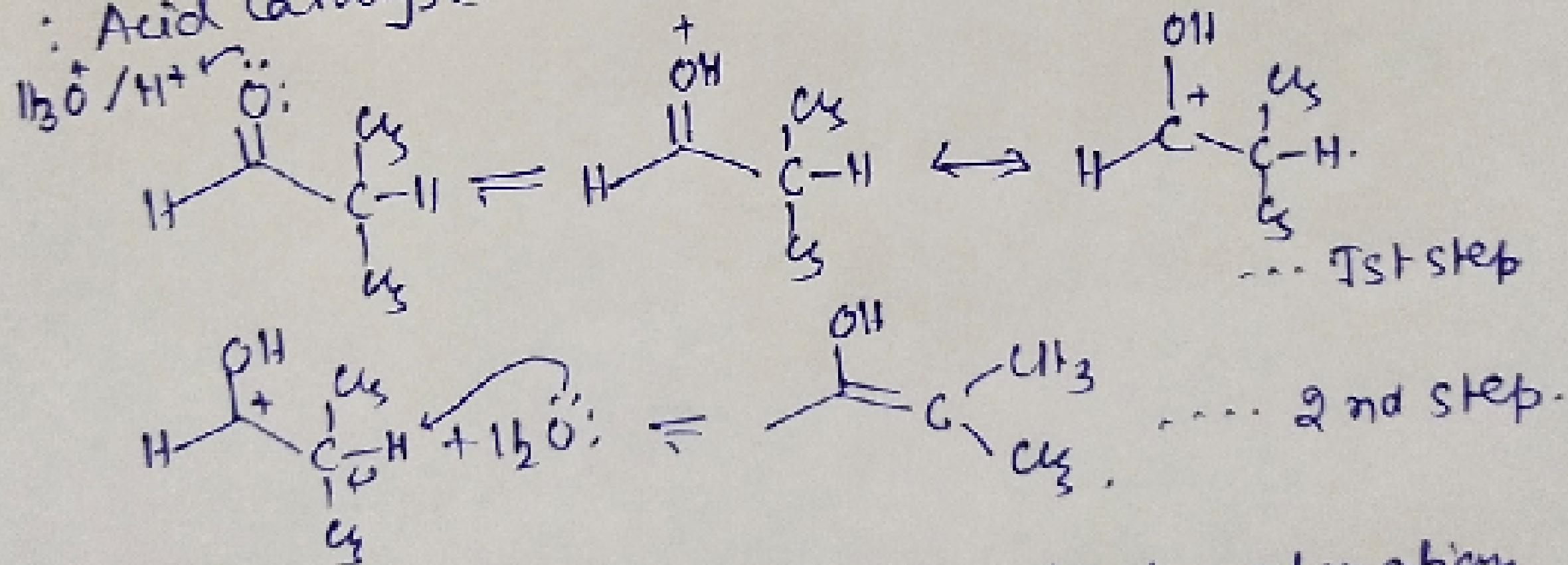
$\Rightarrow$  2 step process. (Both steps are acid base reaction)

$\Rightarrow$  carbocation is formed as intermediate in R.O.S

$\Rightarrow$  more stable carbocation leads to higher

% yield of enol.

: Acid Catalysed tautomerism:



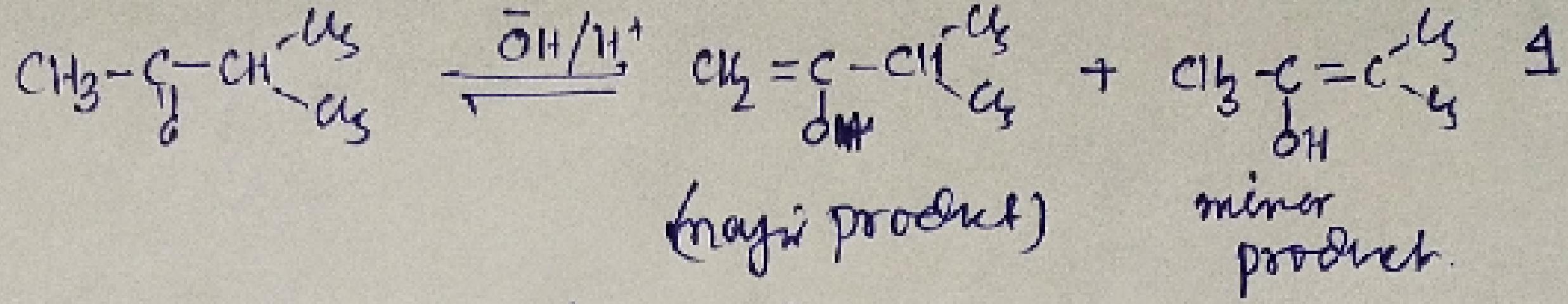
$\Rightarrow$  2 step process; 1st step is called protonation

2nd step is called deprotonation.

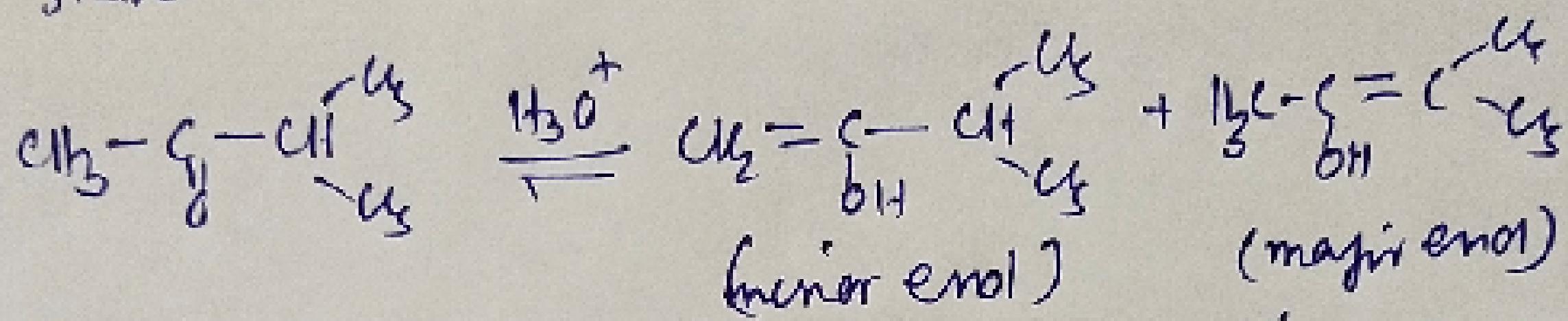
$\Rightarrow$  carbocation is formed as intermediate.

$\Rightarrow$  If more than one enol is formed, that enol will

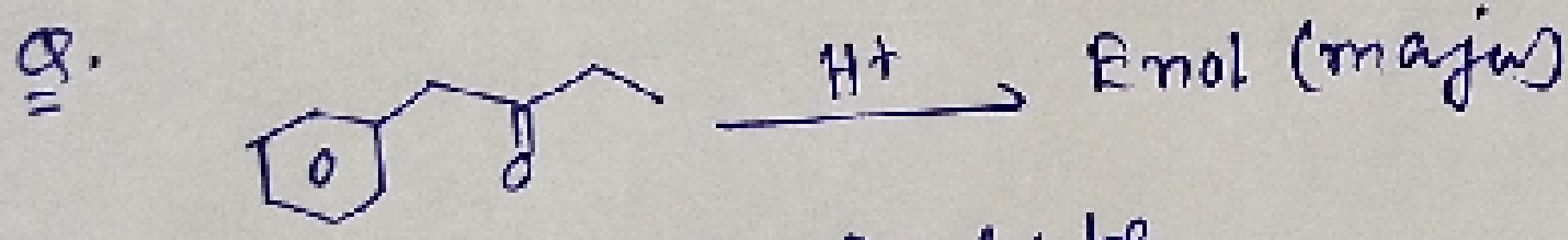
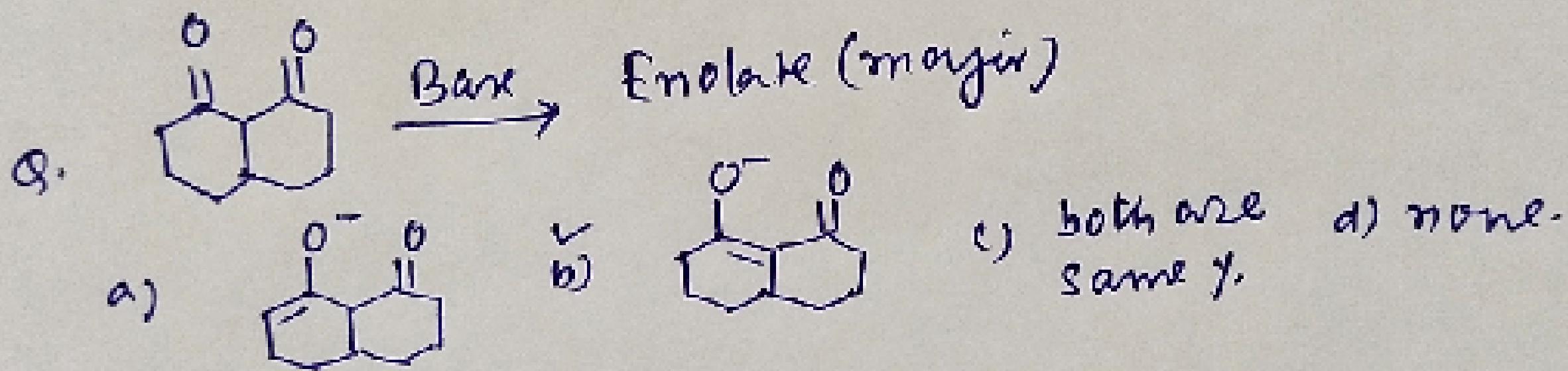
be major product which is thermodynamically more stable.



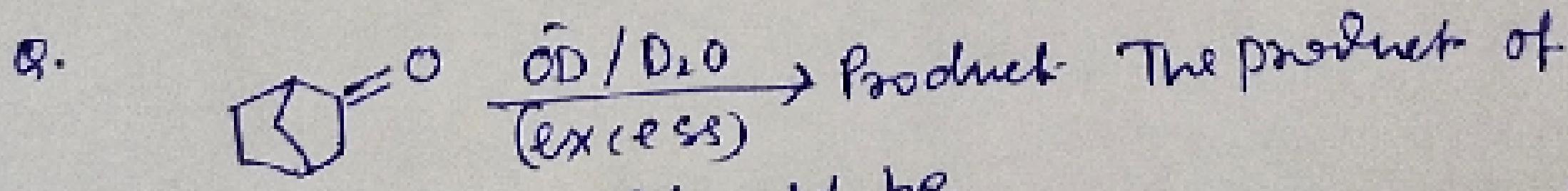
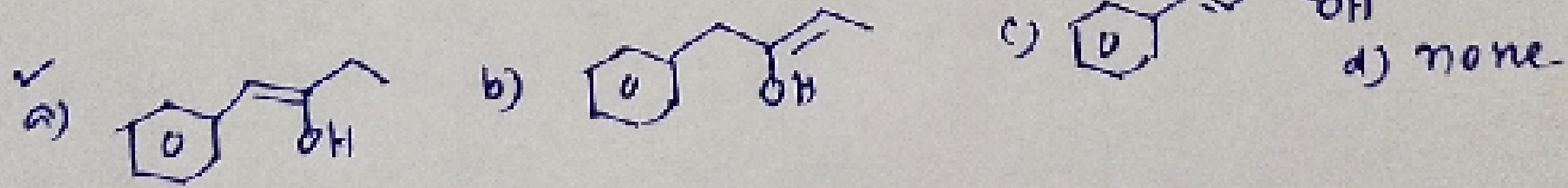
Here major enol is formed through more stable carbocation/enolate ion.



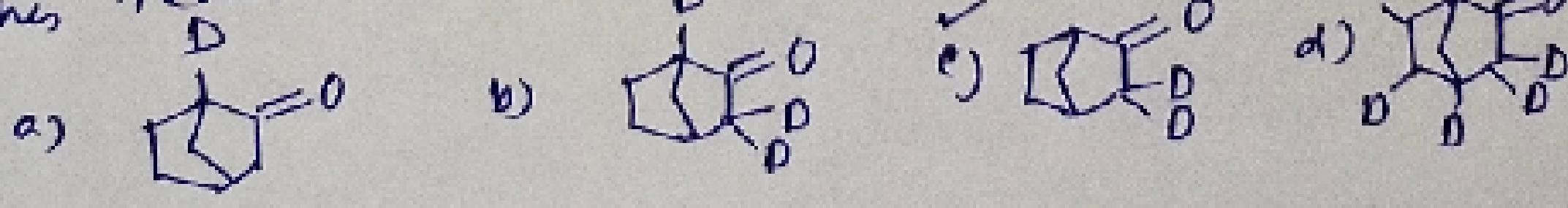
Here major enol will be that enol which is thermodynamically more stable.



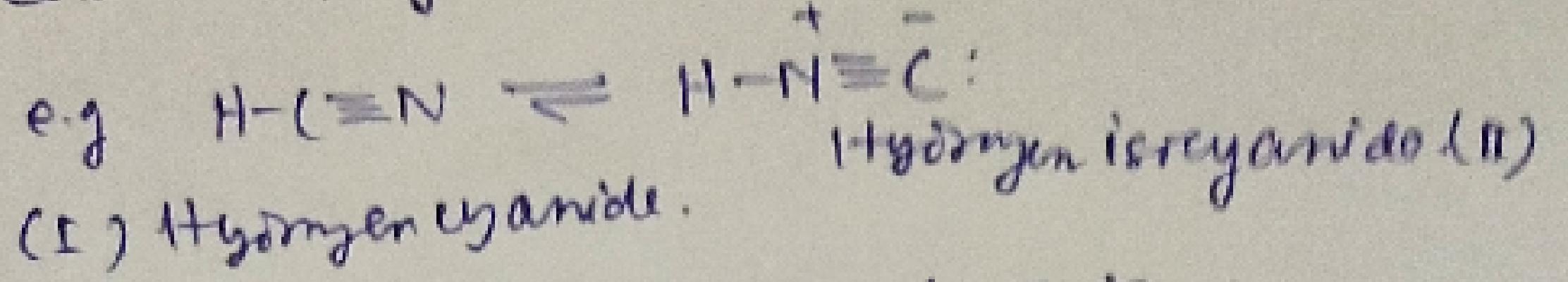
The major enol should be



this reaction should be



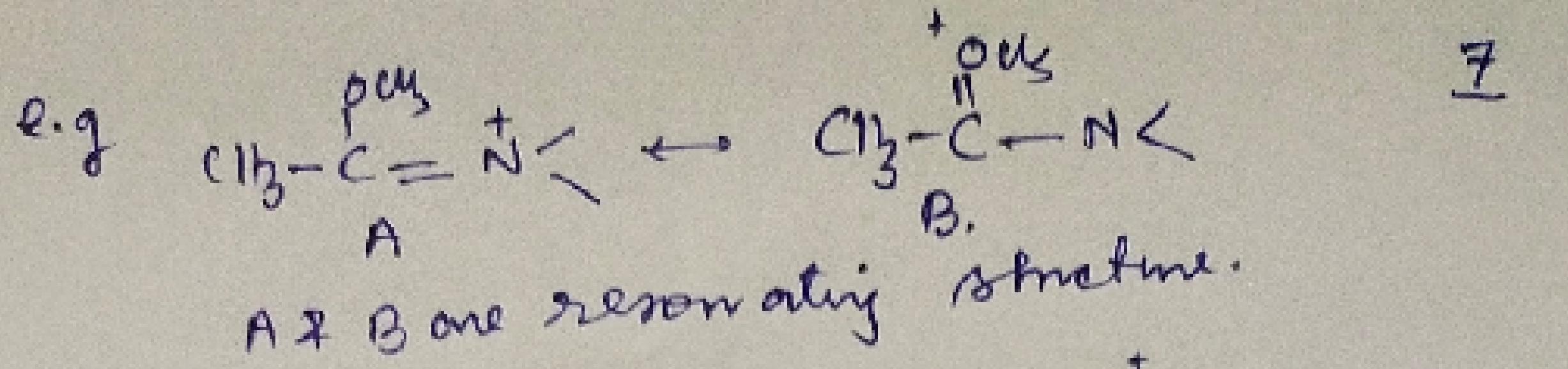
⇒ Dyad system: It involves the migration of H atom between two polyvalent atoms 5



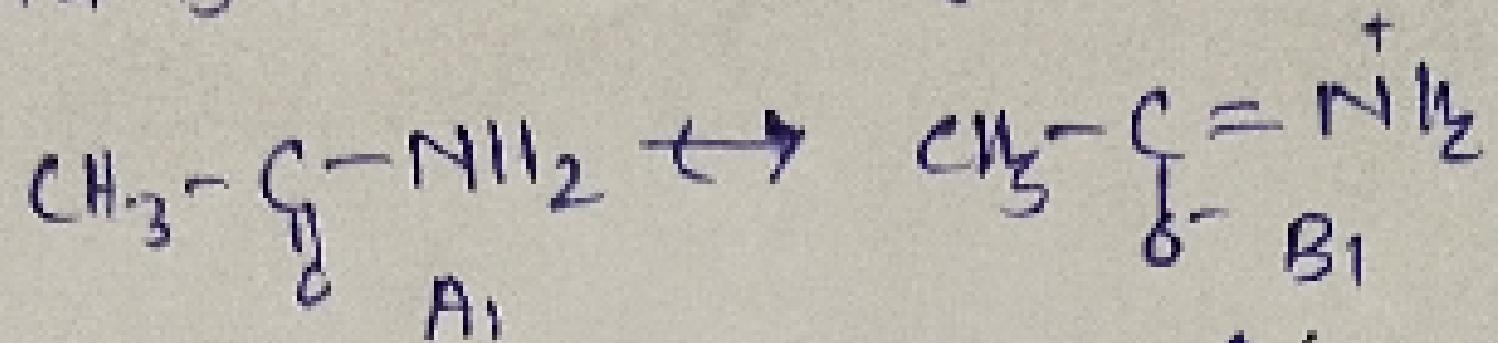
⇒ Points to be noted during tautomerism:

- ⇒ i) Generally one H is removed but sometimes 2 more than 2 H's can be removed in enolisation provided enol has aromatic character.
- ii) In between methyl & active methylene H, it is always active methylene H (more acidic) will be removed to get major enol.
- iii) Generally keto form is more stable than enol form but sometimes enol form can be more stable due to a) H bonding b) Aromaticity in enol form c) extended conjugation.
- iv)  $\text{CH}_2=\text{CH}-\text{CH}=\text{O}$  (for this compound) shows tautomerism where 2d H can be removed. Otherwise during enolisation 1d H is removed because bridgehead H cannot be removed because it can not change its hybridisation state from  $\text{sp}^3 \rightarrow \text{sp}^2$ .
- v) Phenol can not show p-tautomerism (according to IIT) because its keto form can not be isolated as it is very unstable.

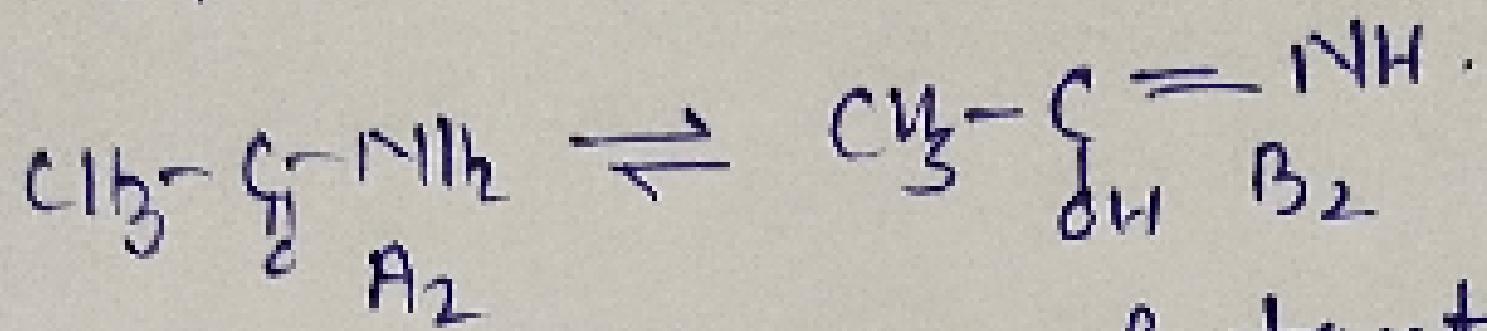
- vii) Nitrobenzene & Phenol can not show tautomerism but nitrosophenol can show tautomerism.
- viii) In Resonating strs, electron migration takes place & resonating structures are hypothetical but in tautomers atom migration takes place & tautomers are real.
- ix) The compounds whose enol form is stable e.g.  $\text{[CH}_2-\text{C}_6\text{H}_4-\text{C}_6\text{H}_5] \rightleftharpoons \text{CH}_2-\text{C}_6\text{H}_4-\text{C}_6\text{H}_5$  can decolorise  $\text{Br}_2/\text{water}$  but compounds like  $\text{C}_6\text{H}_5\text{CO}$  whose enol form is unstable can not decolorise  $\text{Br}_2/\text{water}$  test.
- x)  $\begin{array}{ccc} -\text{CH}_2-\text{C}=\text{O} & \rightleftharpoons & -\text{CH}=\text{C}-\text{OH} \\ \text{keto form} & & \text{(enol form)} \end{array}$
- $(\text{Total b.d.e}) = 2(\text{C-H}) + (\text{C-C}) + (\text{C=O})$   
 $\text{keto form} = 1870 \text{ KJ mole}^{-1}$ .
- $(\text{Total b.d.e})_{\text{enol form}} = (\text{C-H}) + (\text{C=O}) + (\text{C-O}) + (\text{O-H})$   
 $\text{enol form} = 1820 \text{ KJ mole}^{-1}$ .
- As  $\text{Total b.d.e}_{\text{keto form}} > \text{Total b.d.e}_{\text{enol form}}$ .  
So keto form is more stable than enol form.
- iii) P.E |   
P.E | reaction  
keto form end form
- P.E |   
reaction  
(R,S)II  $\text{CH}_2-\text{C}_6\text{H}_4-\text{C}_6\text{H}_5$  (R,S)I  
(R,S)I  $\text{CH}_2-\text{C}_6\text{H}_4-\text{C}_6\text{H}_5$  (R,S)I  
R.H.
- The energy diagram for tautomers  $\text{C}_6\text{H}_5\text{CO}$  of  $\text{C}_6\text{H}_5\text{OH}$ .



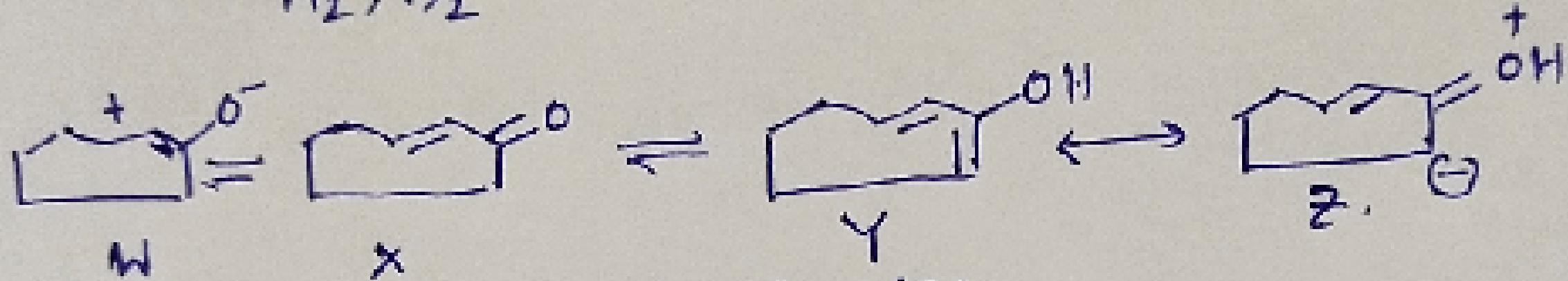
A & B are resonating structures.



$\text{A}_1$  &  $\text{B}_1$  are resonating structures



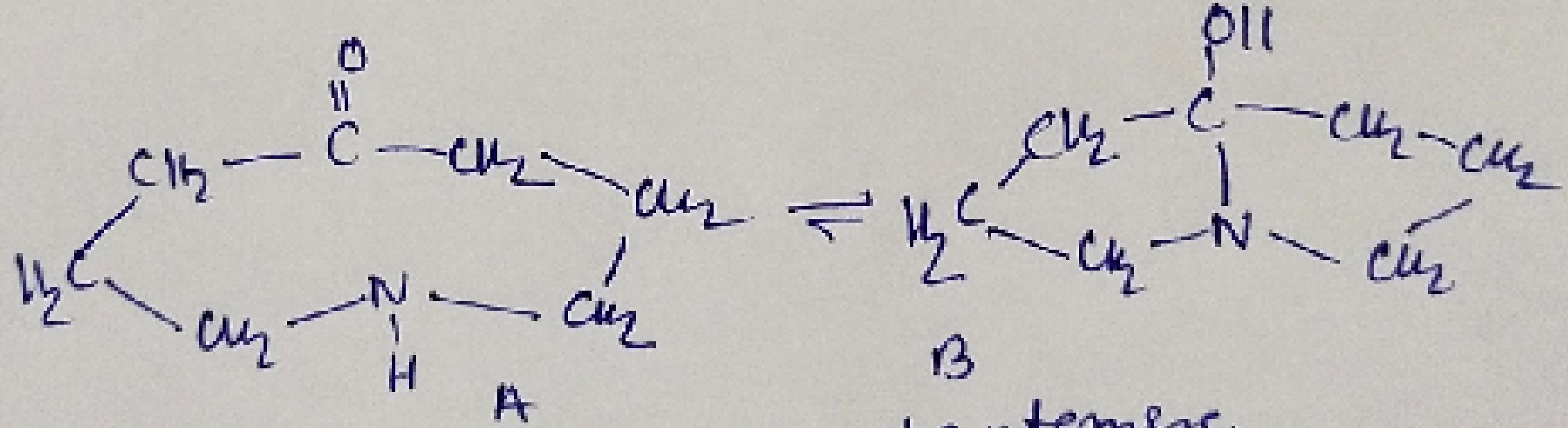
$\text{A}_2, \text{B}_2$  are examples of tautomers.



$\text{W}$  &  $\text{Y}$  are tautomers.

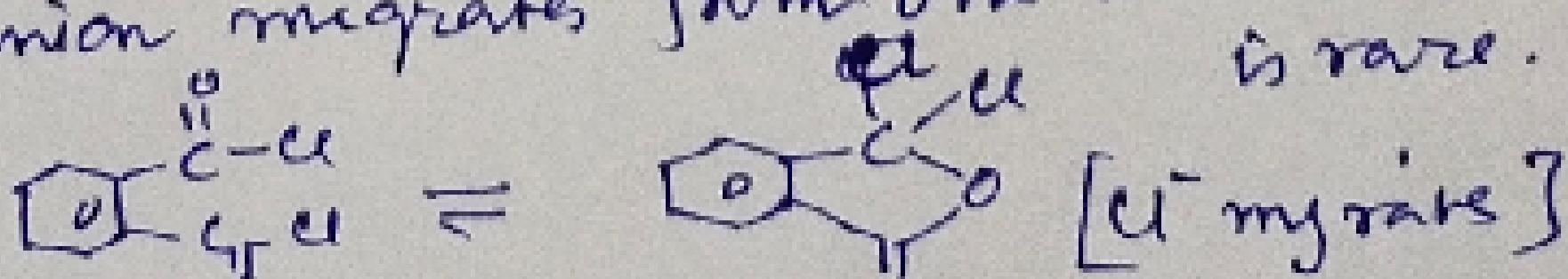
$\text{Y}$  &  $\text{Z}$  are resonating structures

$\text{W}$  &  $\text{X}$  are resonating structures



$\text{A}$  &  $\text{B}$  are examples of tautomers.

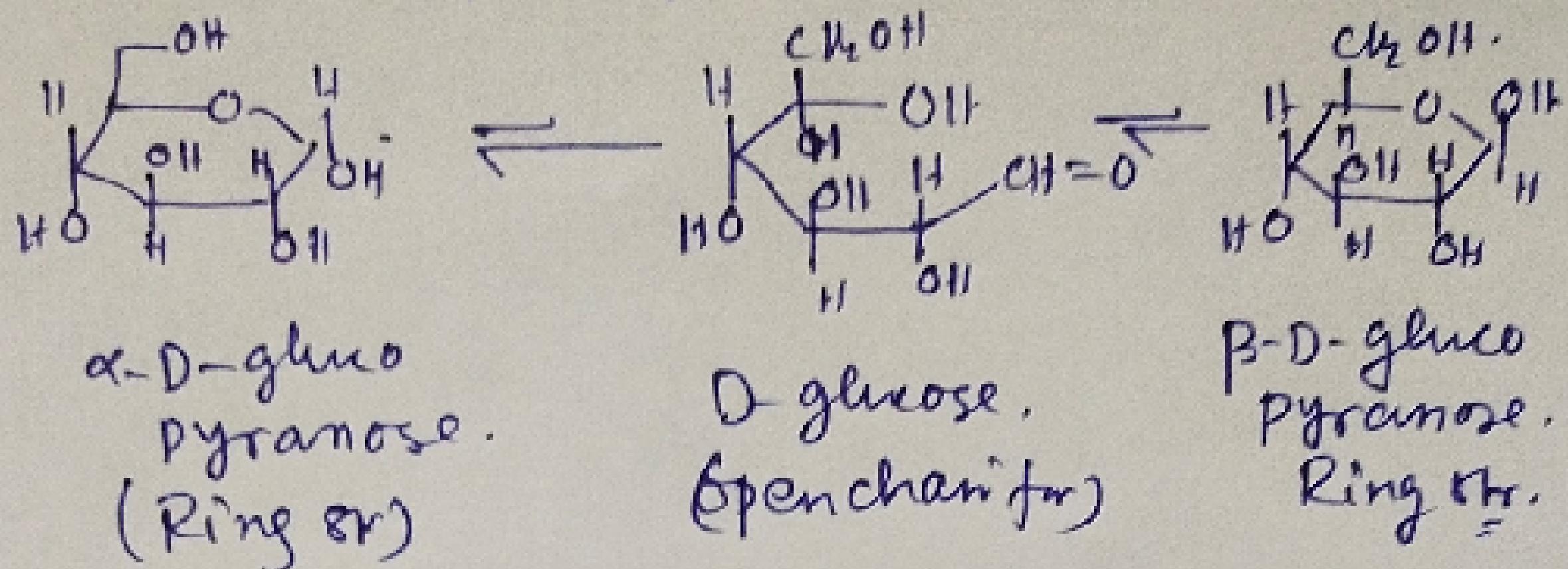
In all tautomerism,  $\text{H}^+$  migrates from one atom to another. It is also called cationotropy or prototropy. Example of anionotropy where anion migrates from one atom to another.  $\text{Cl}^-$  migration is rare.



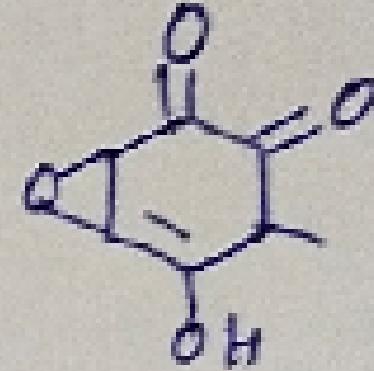
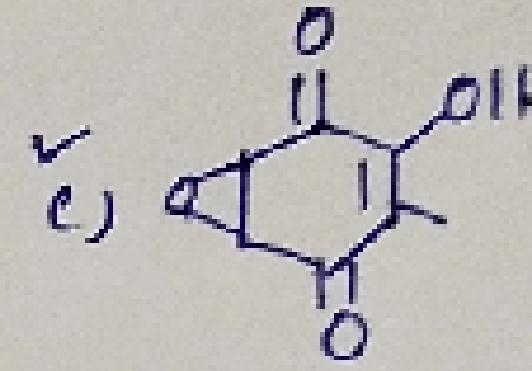
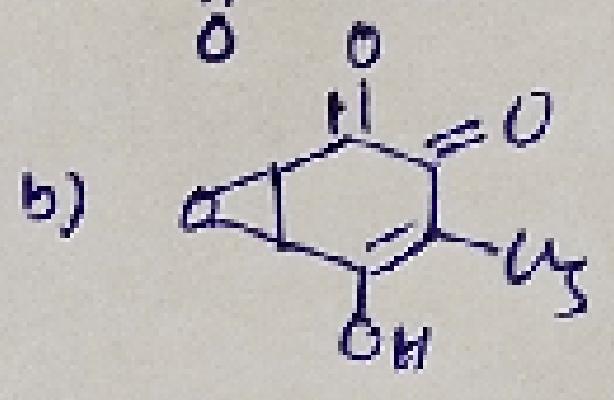
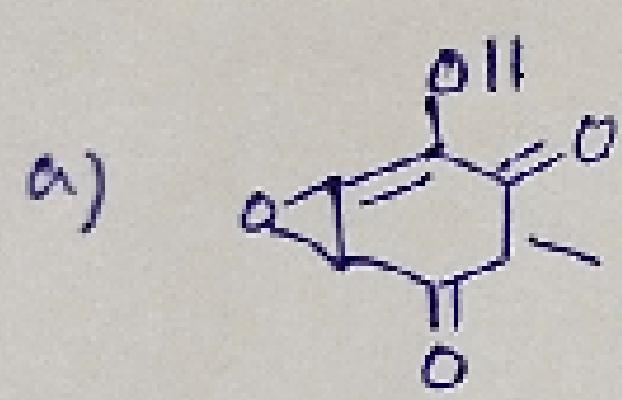
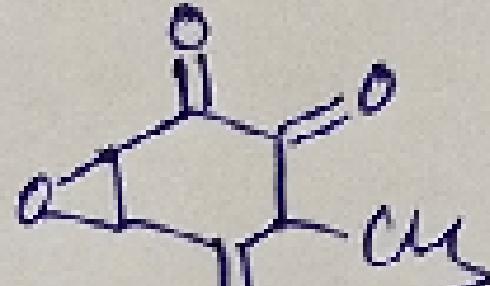
This is also called ring chain tautomerism.

Other example of Ring chain tautomerism:

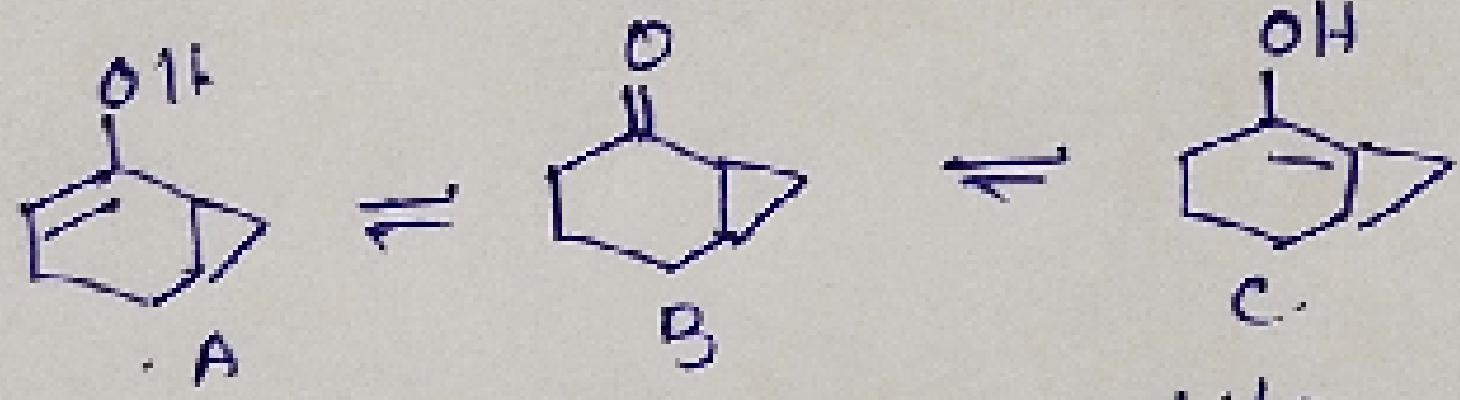
8



Q. Identify the most stable enol form of triciclic acid.



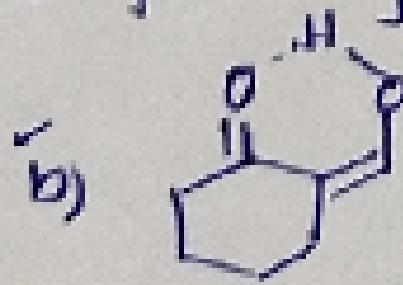
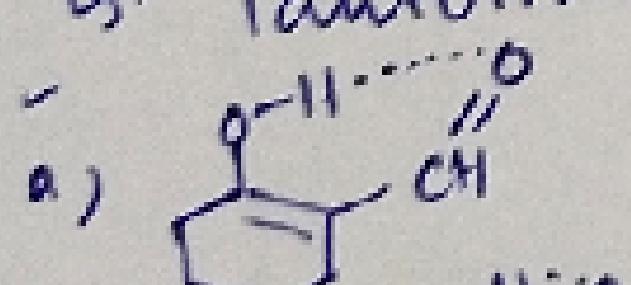
Q.



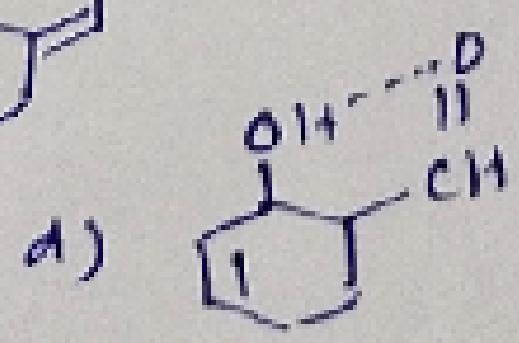
The correct order of stability:

- a) A > B > C    b) B > A > C    c) B > C > A    d) A > C > B.

Q. Tautomeric form for the compound can be

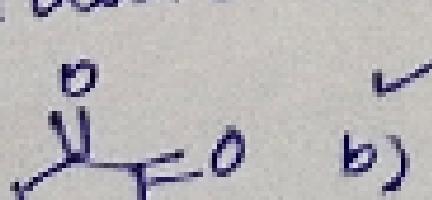


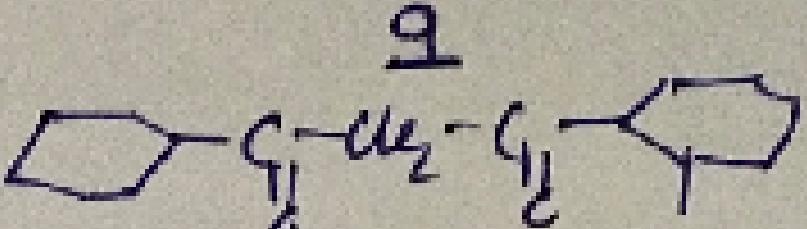
c)

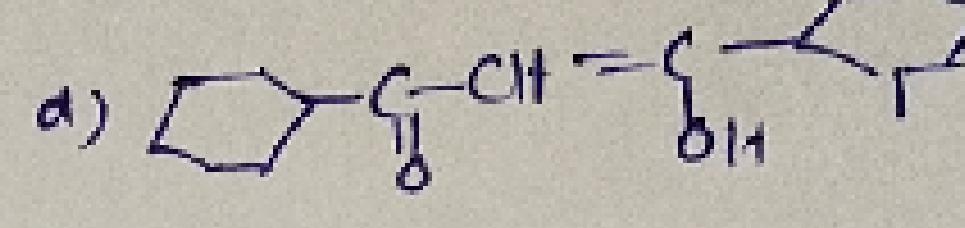
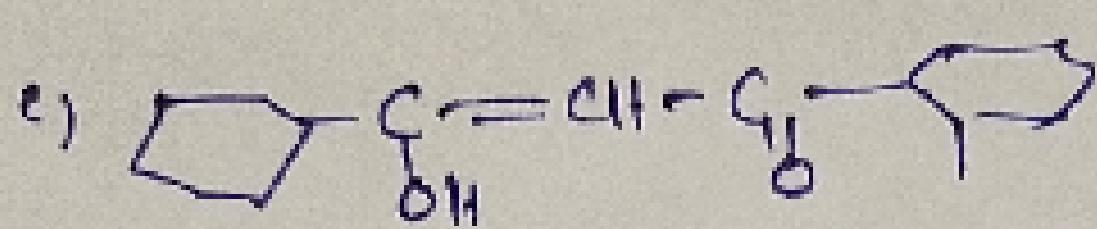
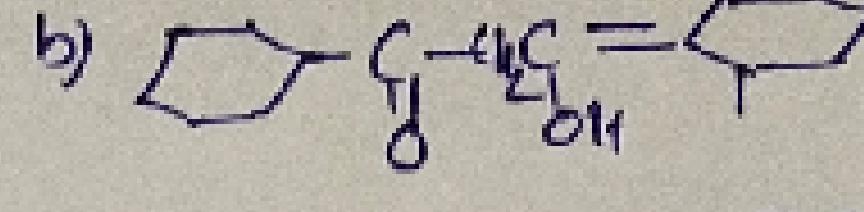
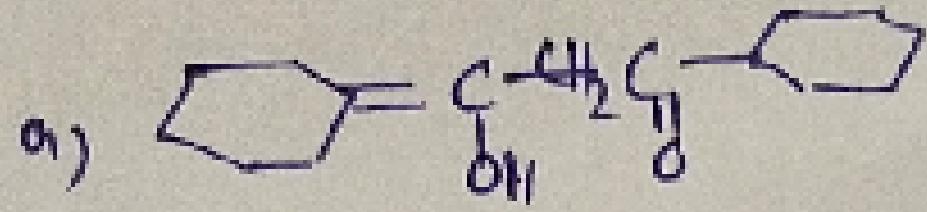


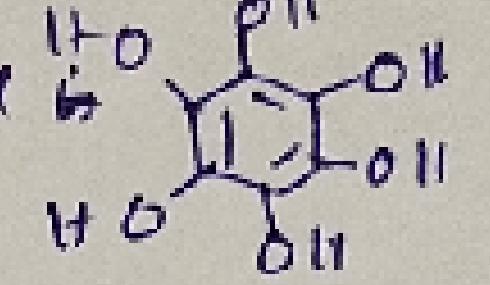
Q. Tautomeric form for the compound

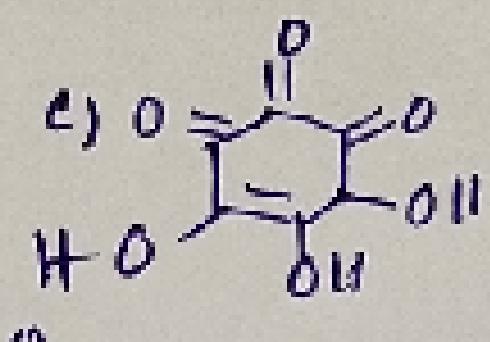
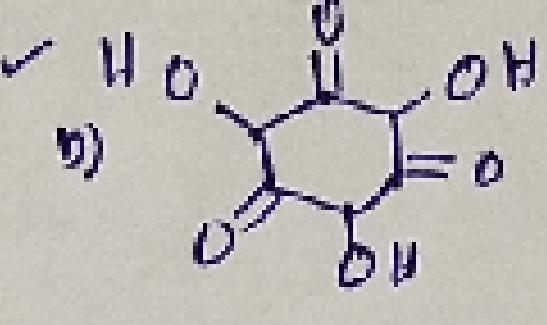
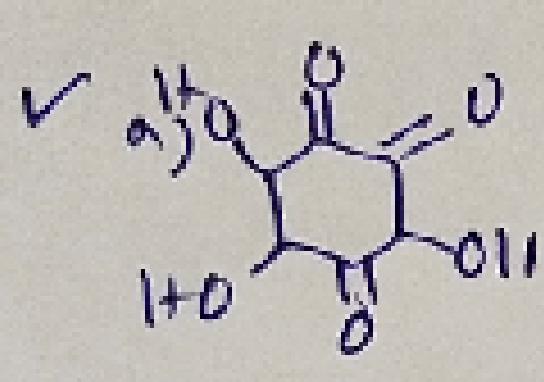
Can be a)



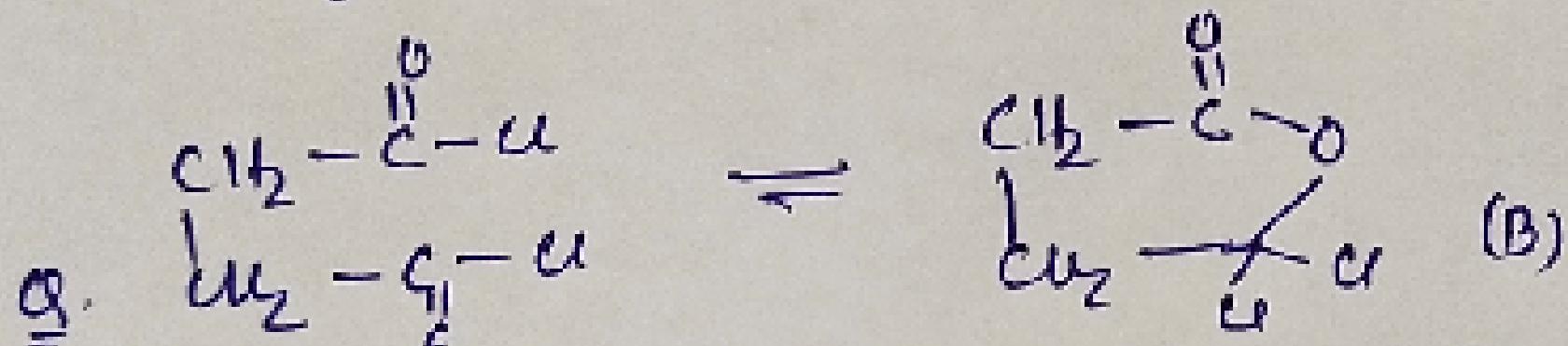
Q. Tautomeric form of the compound.  9



Q. Tautomer of this compound  can be



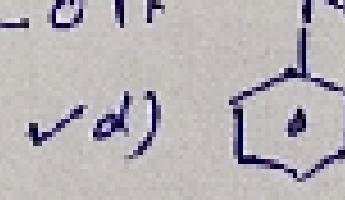
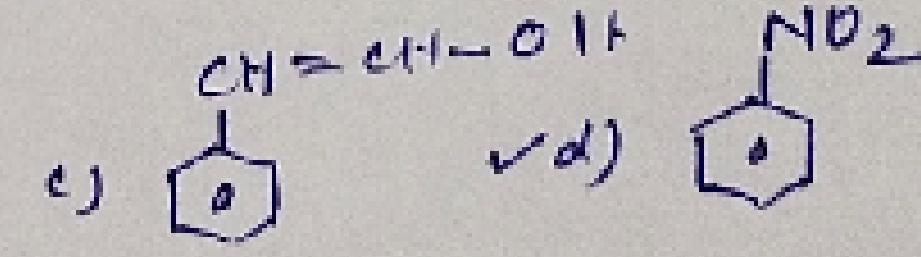
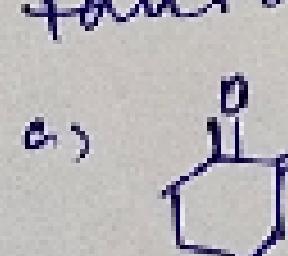
d)  all the above.



which of the following statements are correct?

- a) A, B are tautomer (ring chain)
- b) Anion migration takes place which is example of anisotropy
- c) A & B exists in dynamic equilibrium.
- d) A, B are example of Resonating structures.

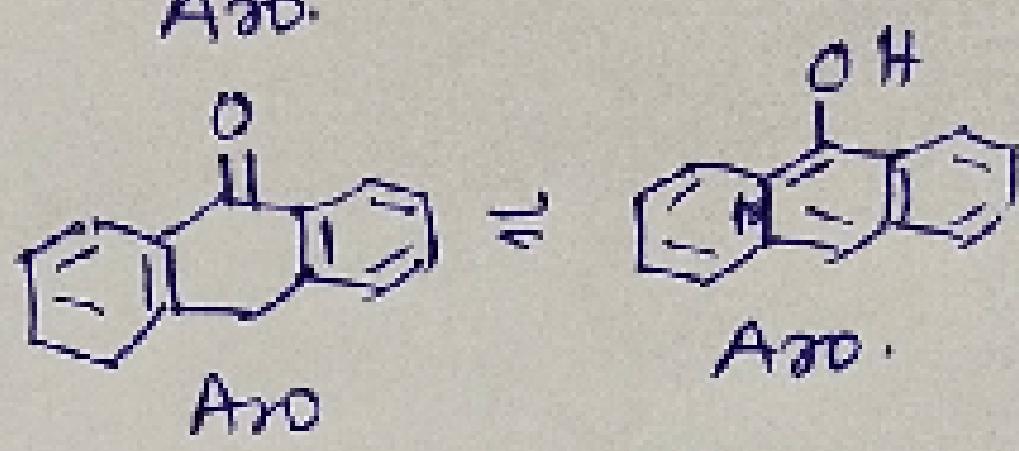
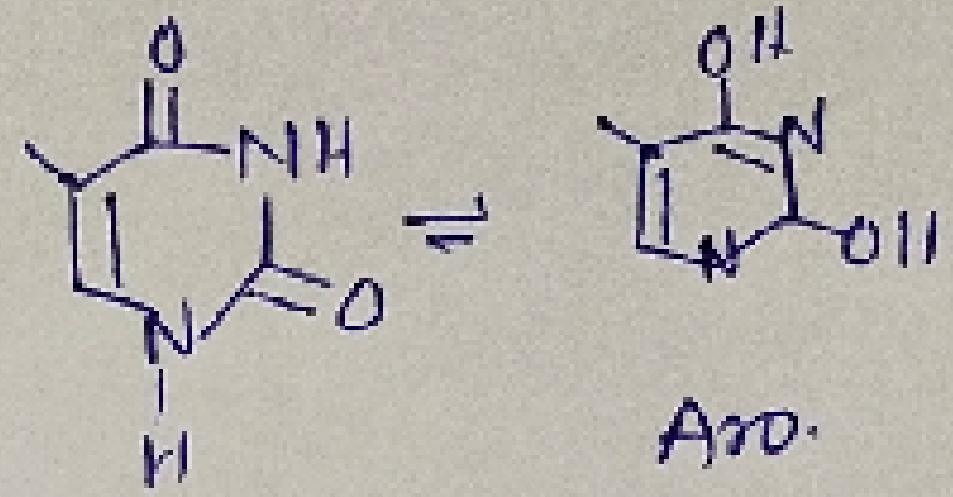
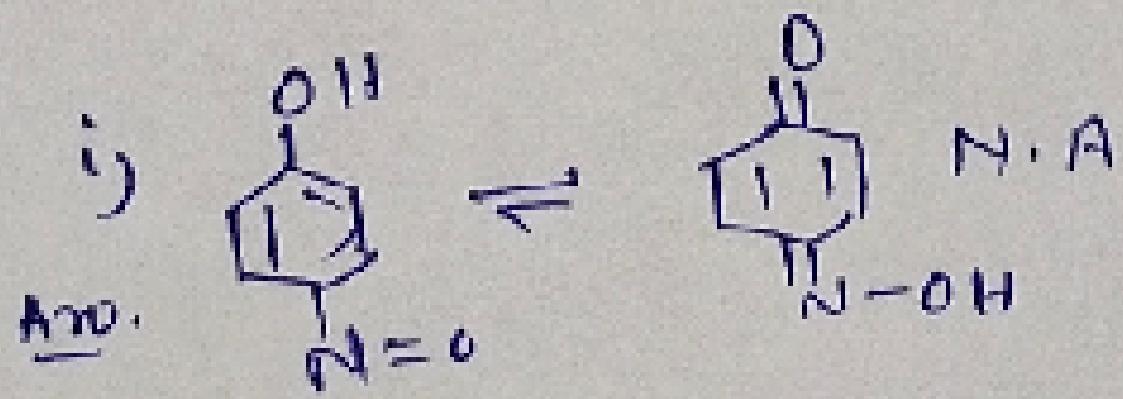
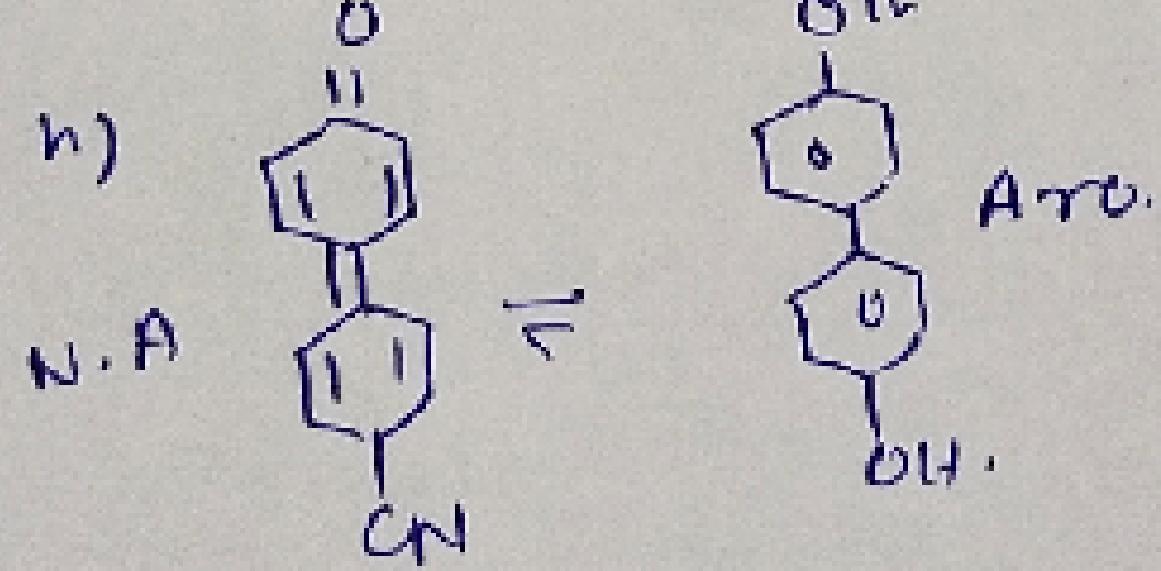
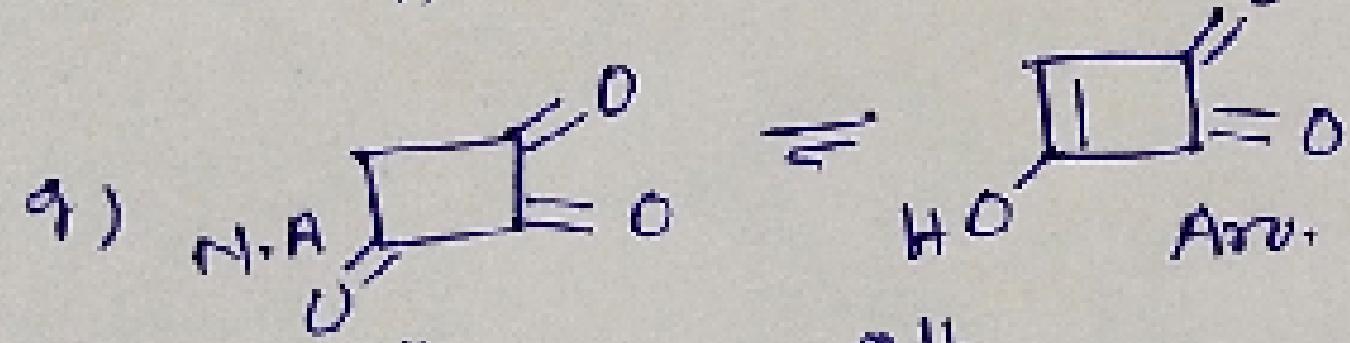
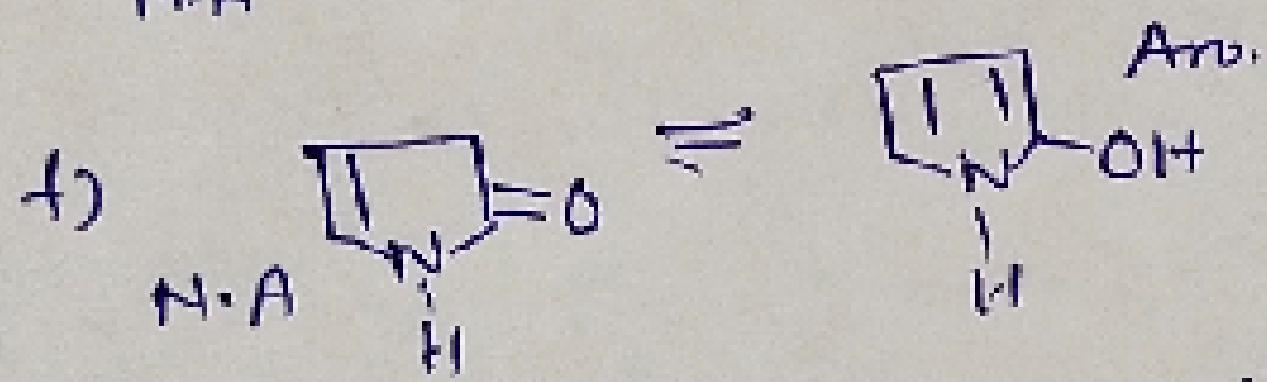
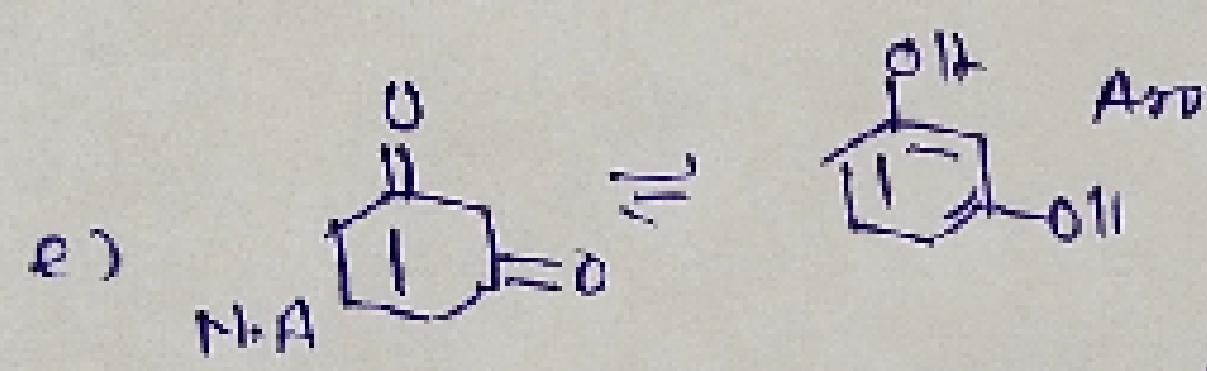
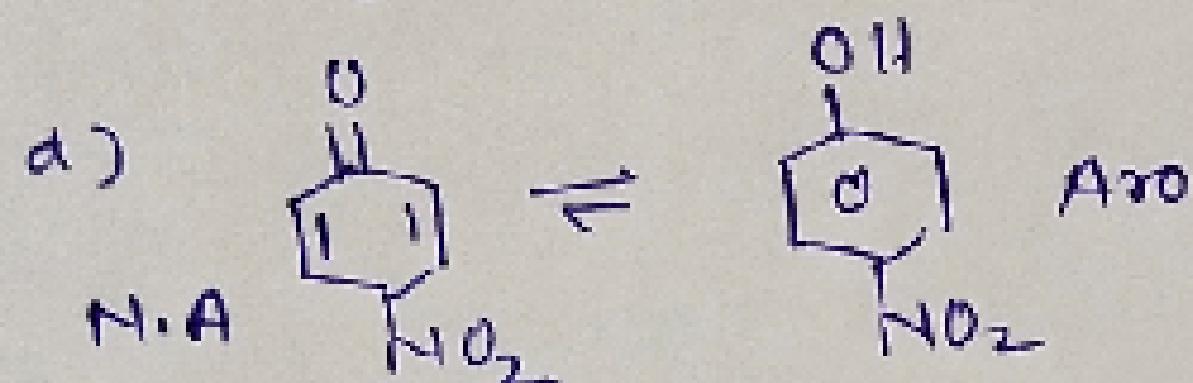
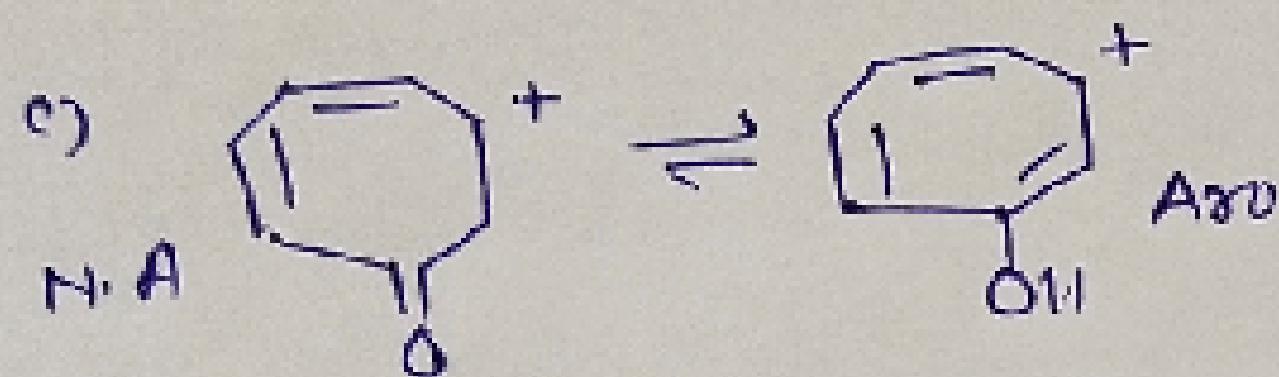
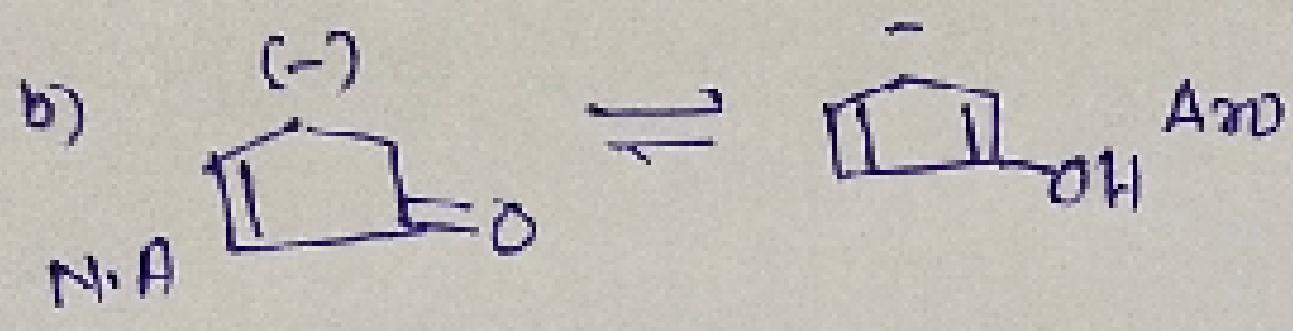
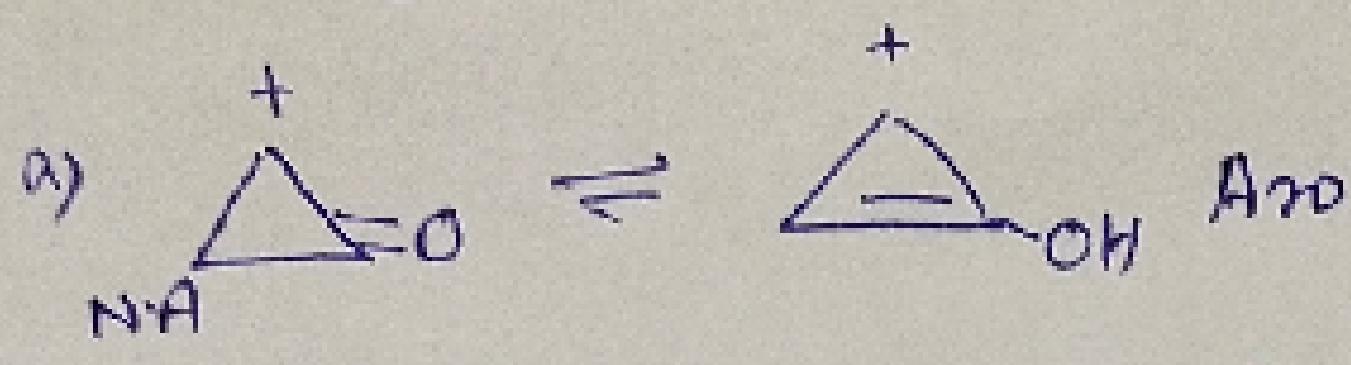
Q. Which of the following is incapable of exhibiting tautomerism?



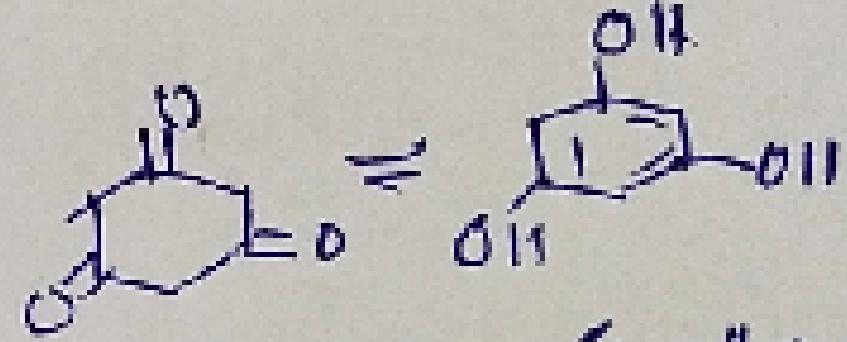
Q. No. of  $\sigma$  &  $\pi$  bonds present in enol form of acetone. Ans: 9  $\sigma$  bond & 1  $\pi$  bond.

10

Examples where enol form is more stable than keto form because of aromaticity:



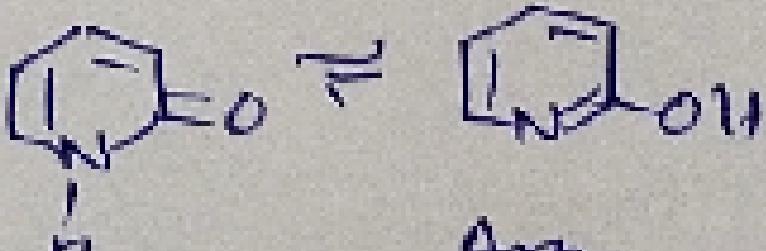
As both keto & enol form both are aro, so keto form is more stable than enol form.



enol form < keto form  
(stability order)

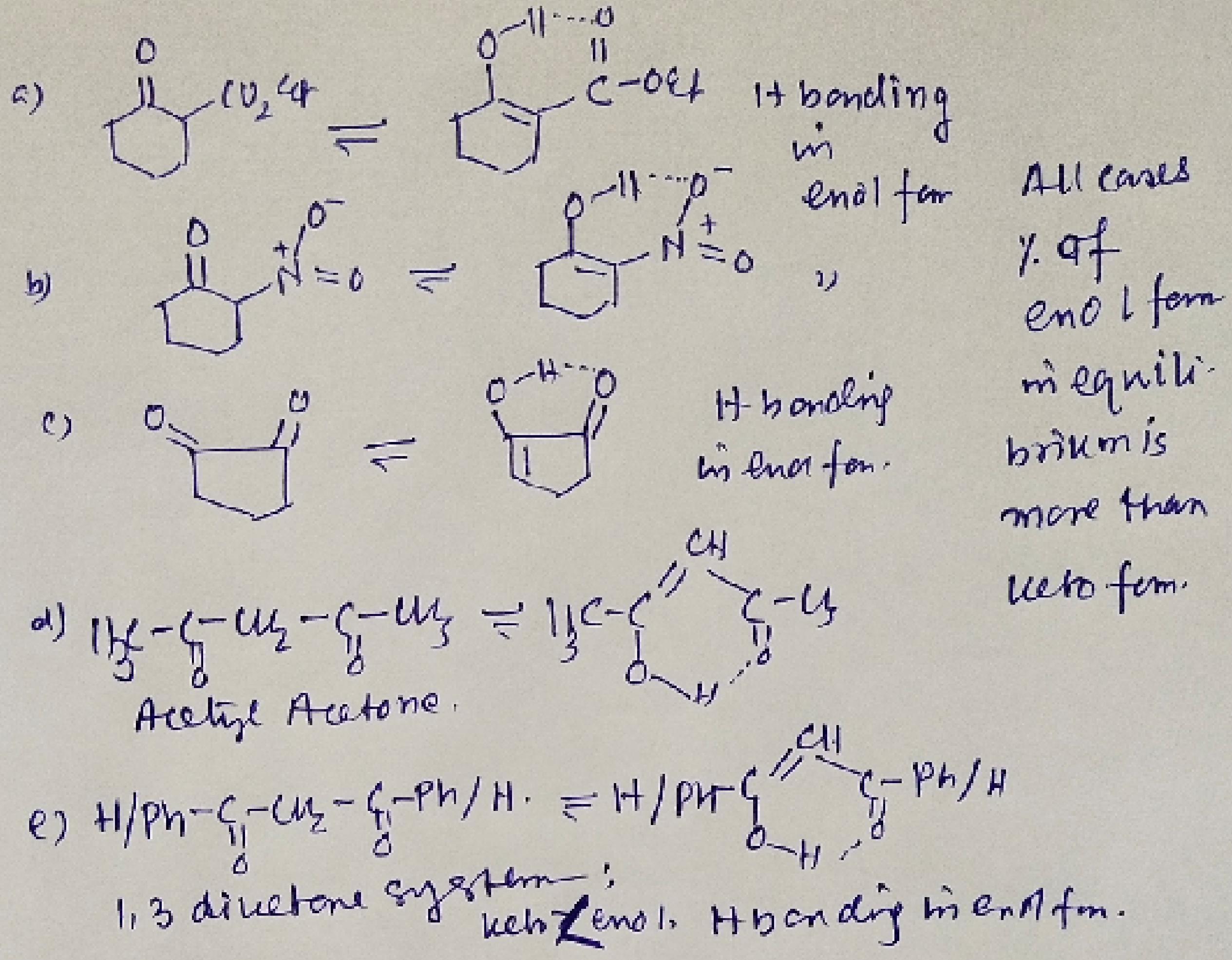
Because aromaticity

in enol form cannot compensate the loss of 3 keto group.

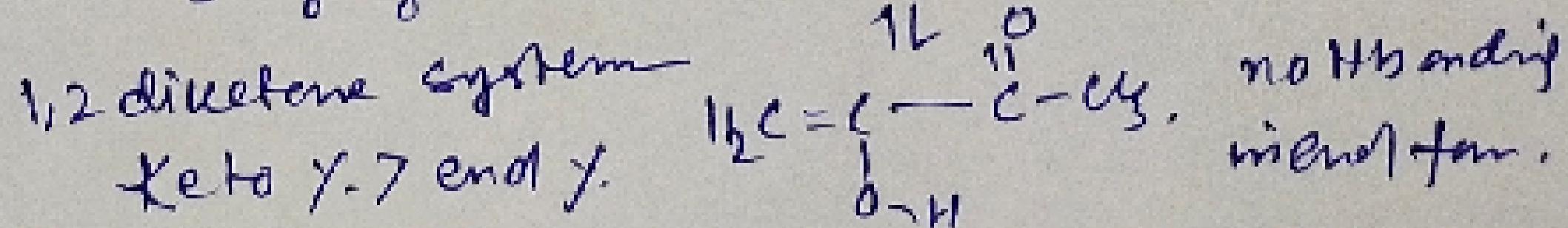
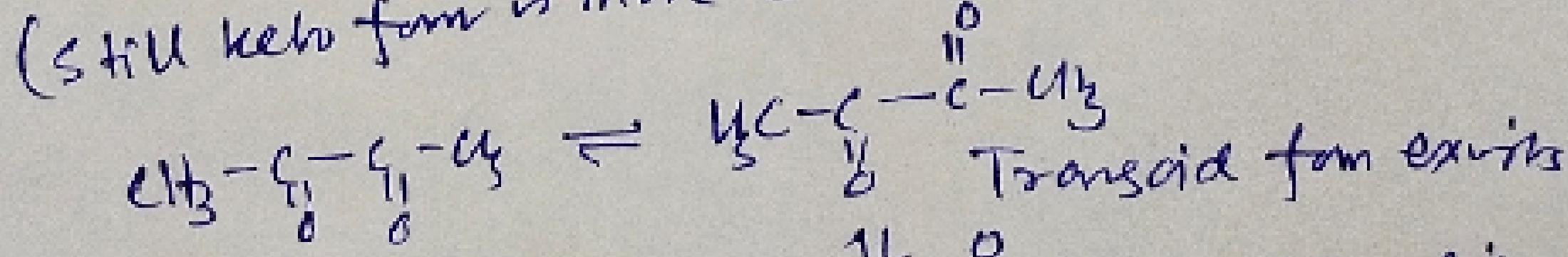
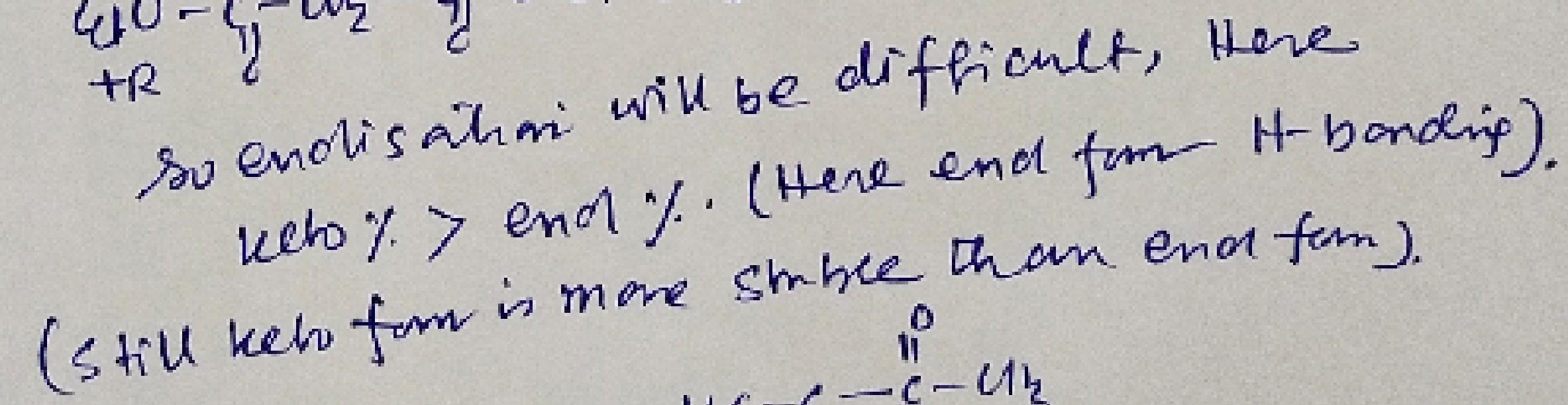
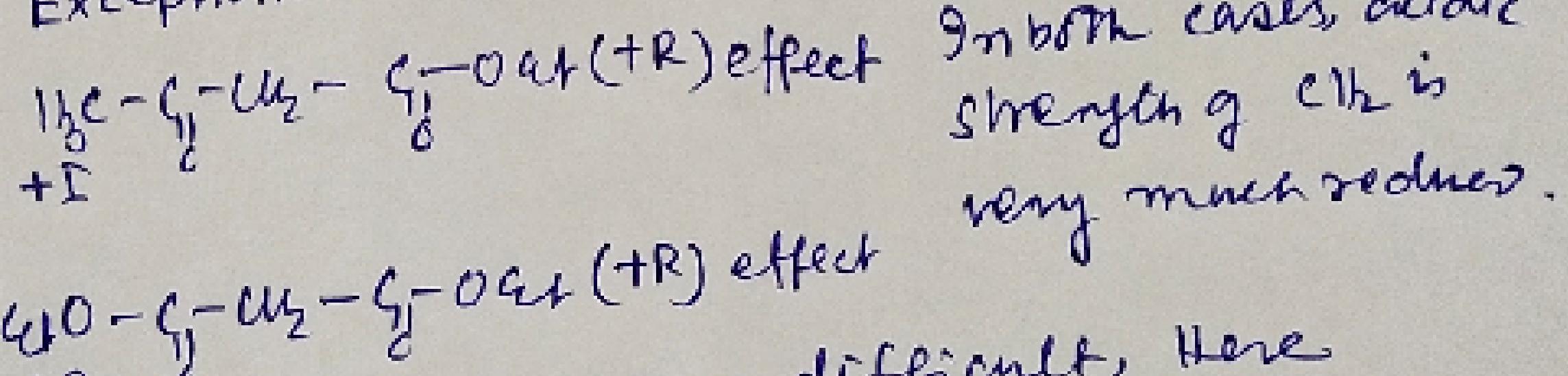


Aro. I > II.

Examples of systems where enol form is more stable than keto form due to hydrogen bonding

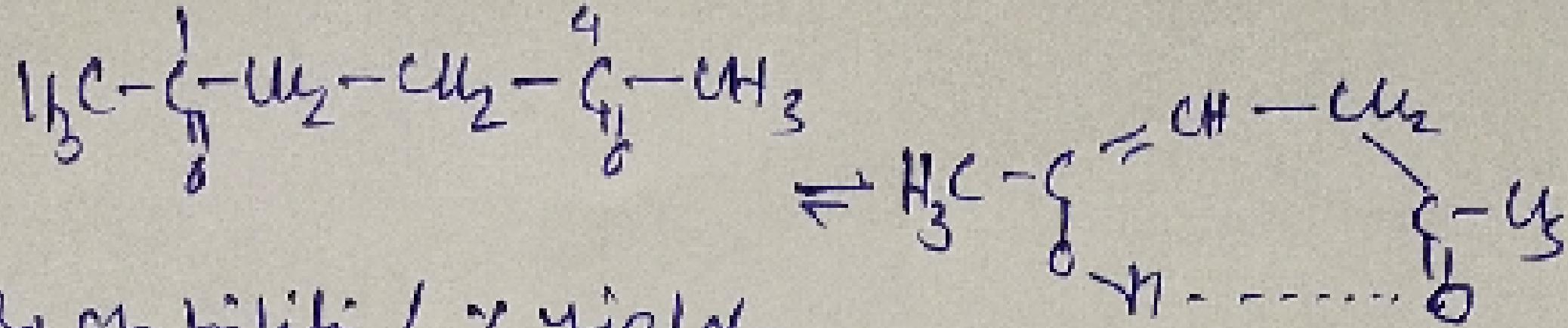


: Exception:



$\Rightarrow$  For 1, n diatomic system

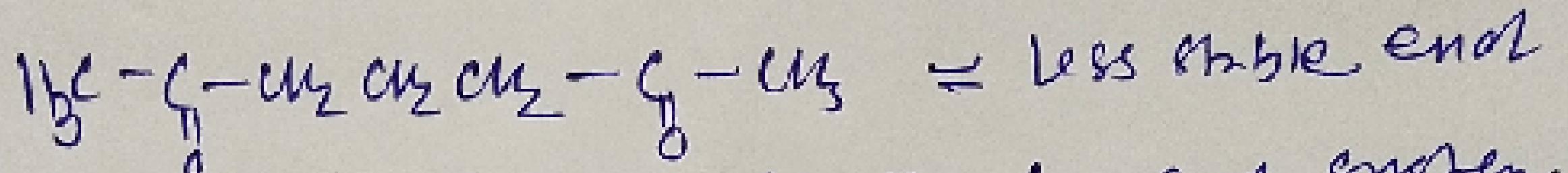
12



So stability / y. yield

Strong H. bond  
reduces enthalpy.

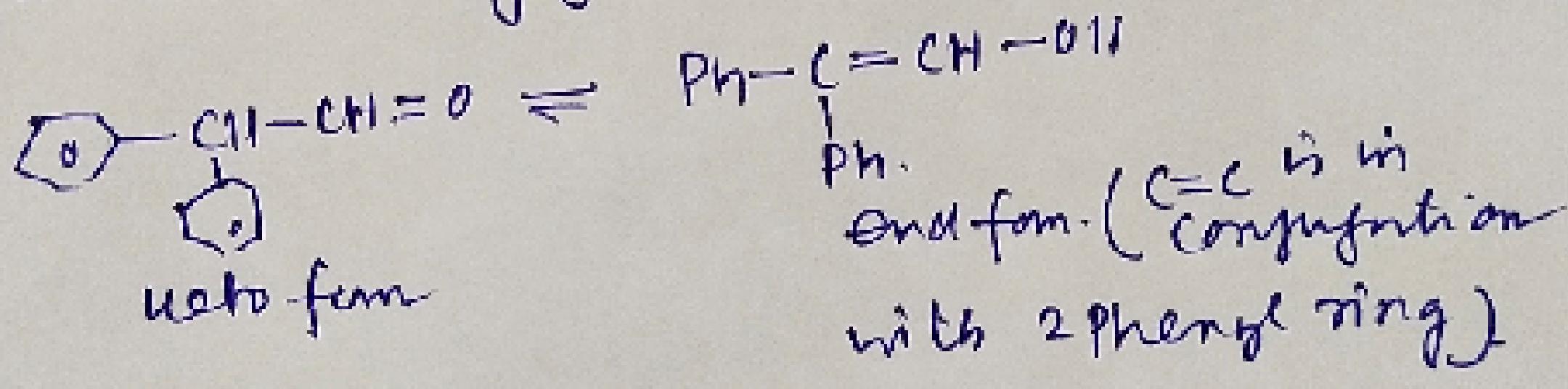
$\Rightarrow$  For 1,5 dinetone system.



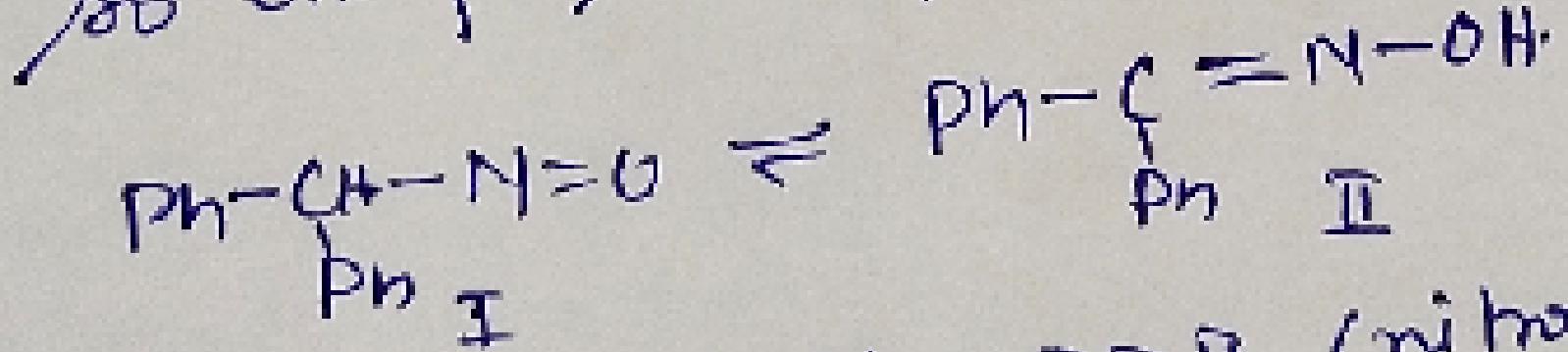
Also H bonding not effective for end system.

Gov. keto-form > enol form

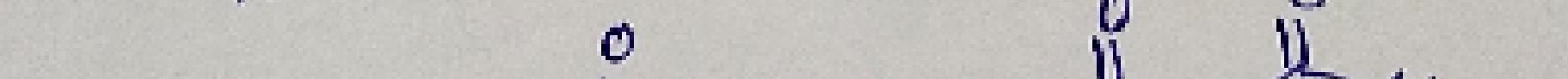
: Extender congnisi:



so end for > neto form.



Pr I Here stability  $I > O$  (nitroso) oxime system.

- Q. 

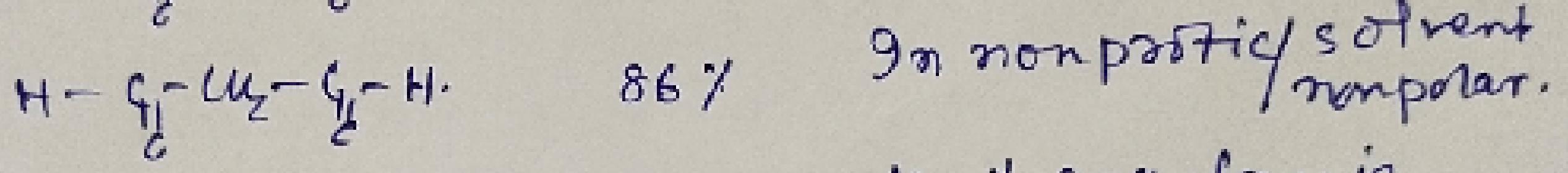
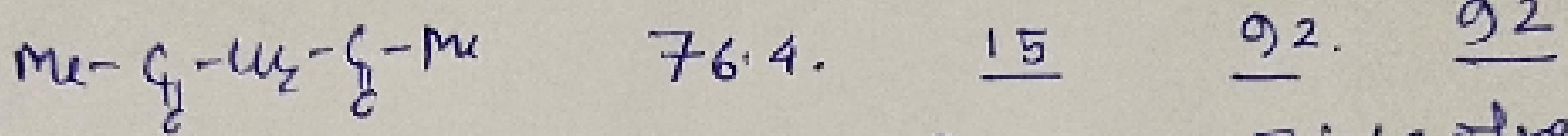
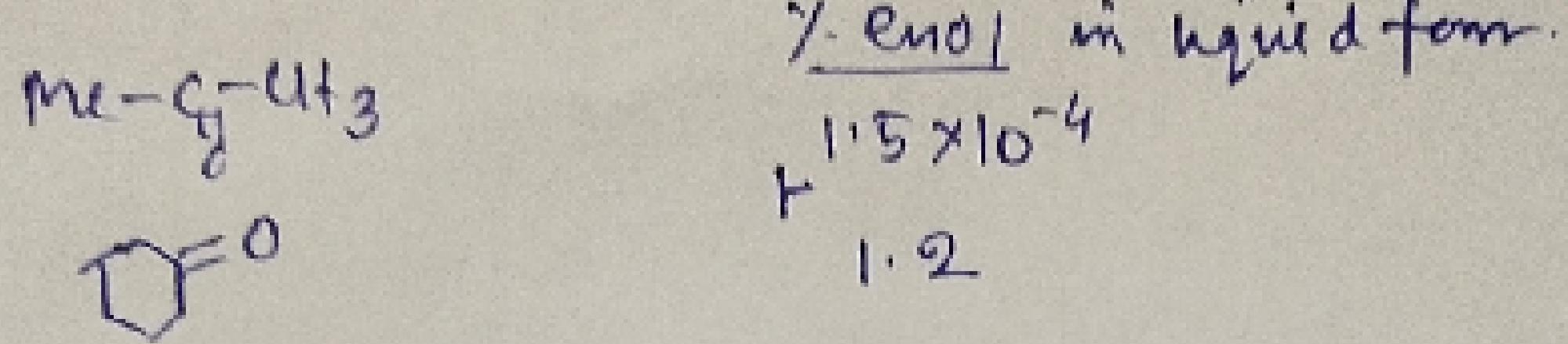
Q.  $\text{O}_2 \rightleftharpoons \text{N}=\text{H}$  (I) is more stable than its end form (II)  
As I is aromatic  $I > II$  (stability)

What is the % of enol content in following cyclo. 13

- a) [More is the acidic strength, more is the % of enol content]
- b) [In the enolisation, more is the % of enol content]
- c) [In basic medium.]
- d) [In basic medium.]
- e)
- f)
- g)
- h)
- i)
- j) [In basic medium.]
- enol is aromatic.
- 4dH in enol.
- 3dH in enol.

## Solvent Effect on keto enol tautomerism: 14

In simple carbonyl compound e.g. Me-C<sub>2</sub>-Me, the proportion of enol at eqm<sup>m</sup> is very small.



Ph-C<sub>2</sub>-CH<sub>2</sub>-C<sub>2</sub>-Ph.      96%.      the % enol form is  
same as that of gas phase. In highly protic

solvent % enol drops & % of keto form increases.

Because enol form as already forms intra-

lecular H-bonding, so it can not be further

stabilised by H-bonding with H<sub>2</sub>O. But keto

form forms extensive intermolecular H-bonding

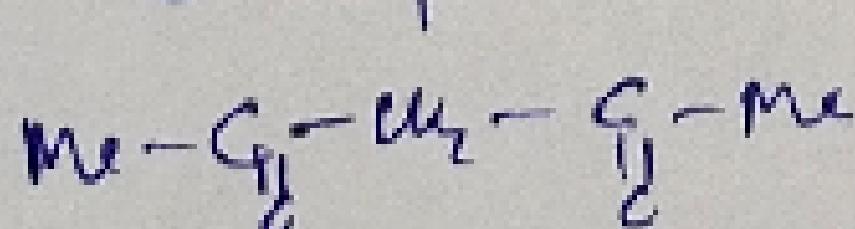
with H<sub>2</sub>O & solvated enough so that its %

% enol form & % of keto form  $\uparrow$

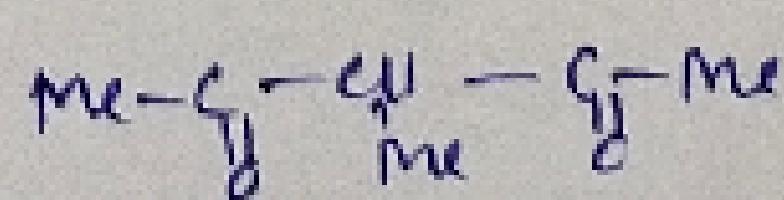
[It is applicable for those systems where

keto form can not form intra H-bonding but

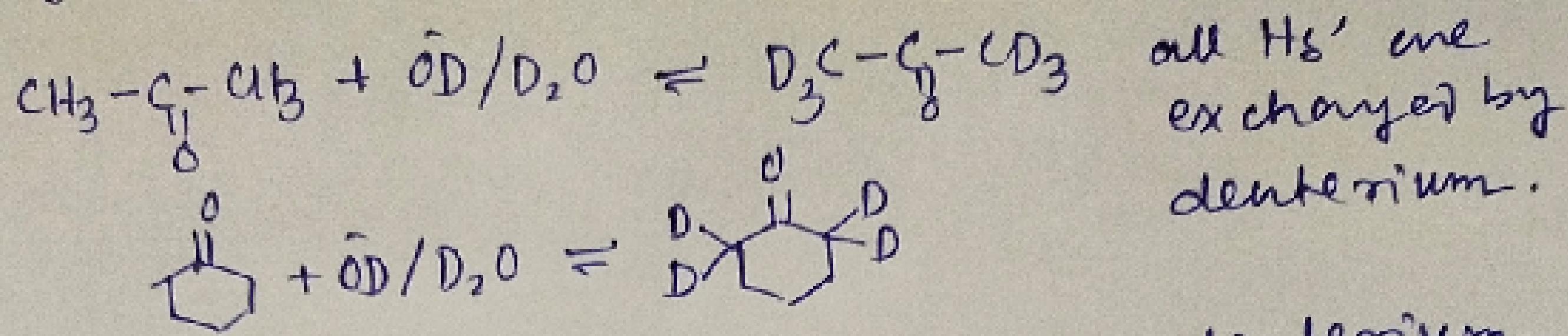
enol form can form intra H-bonding].



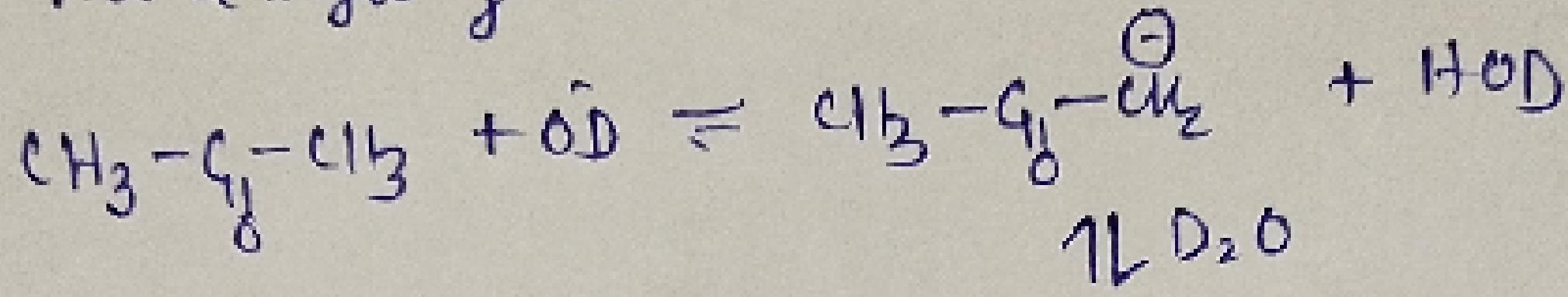
92% (gasphase) (gasphase) 41-43%



"Hydrogen exchange by Deuterium"

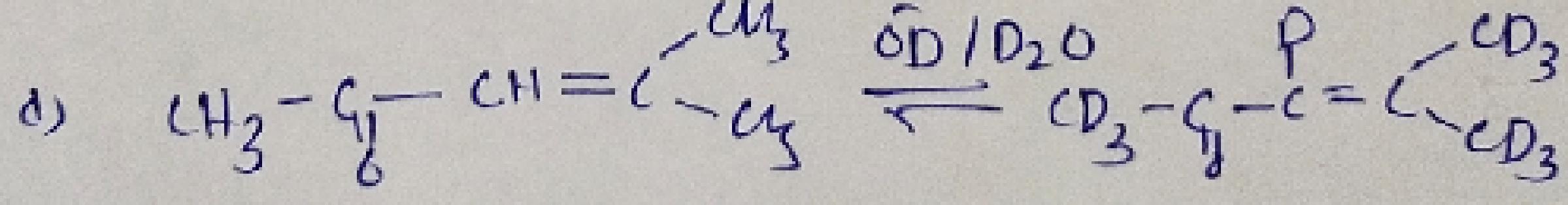
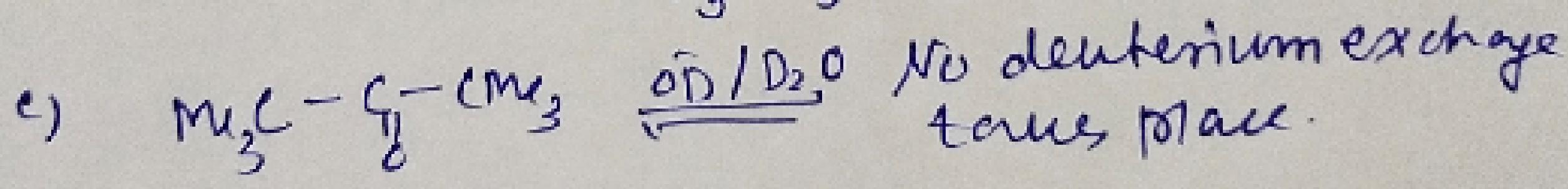
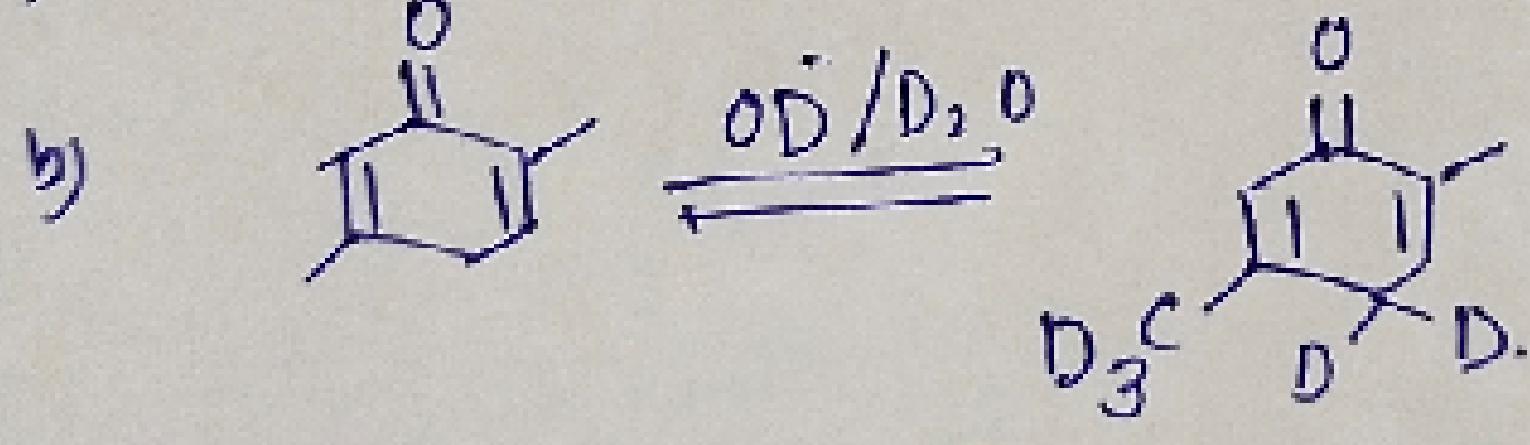
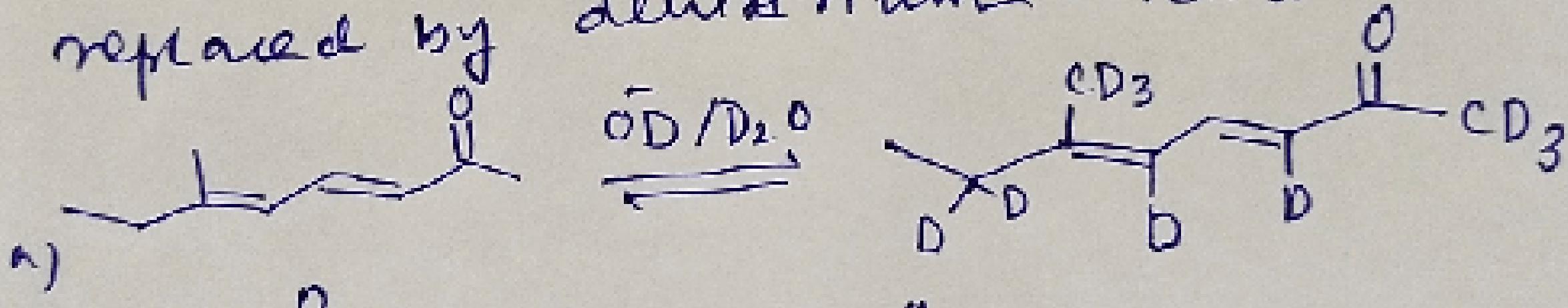


All  $\alpha$  Hydrogens are exchanged by deuterium.



All Hs from carbon on where carb anion is formed [ $\beta$  undergoes

reso with  $-\text{C}_\beta^-$ ] are replaced by deuterium atoms.



Total 10 hydrogens are replaced by D.

