Tautomerism

The phenomenon in which two structural isomers undergoes rapid interconversion and exist in dynamic equillibrium in a liquid state or in a solution state under laboratory condition is known as tautomerism.

And two structural isomers are known as tautomer.

Keto - enol Tautomerism.

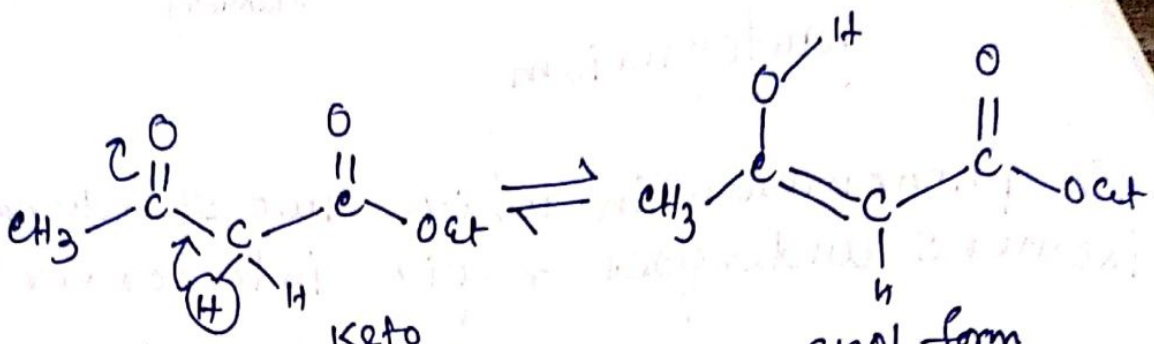
Keto form

enol form.

(In simple case ~~keto form~~ equillibrium lies well to the left).

Keto form (bond energy)		Enol form (bond energy).	
C–H	99 Kcal/mole	C=C	145 Kcal/mole
C–C	83 "	C–O	80 "
C=O	166 Kcal/mole	O–H	111 "
	348 Kcal/mole		336 Kcal/mole

∴ keto form is thermodynamically more stable than enol form by (348 – 336) = 12 Kcal/mole

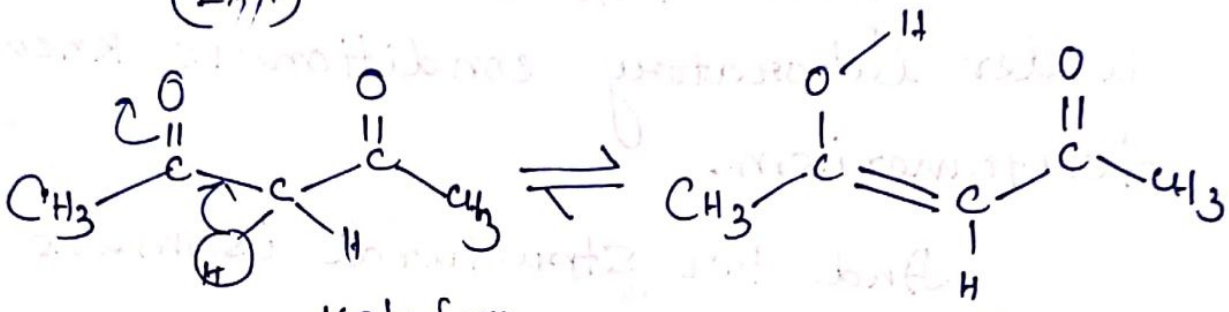


Keto

enol form.

Ethylacetoacetate

(EAA)



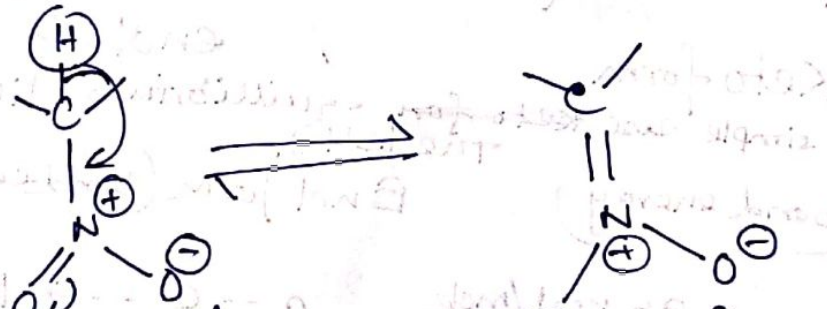
Keto form

enol form.

Acetylacetone

(acac)

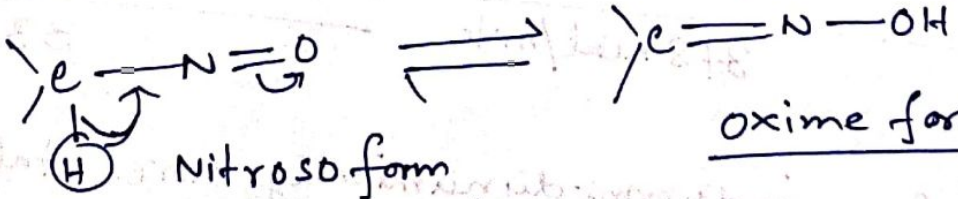
Nitro - Aci Tautomerism.



nitro form

aci-form.

Nitroso - oxime Tautomerism.

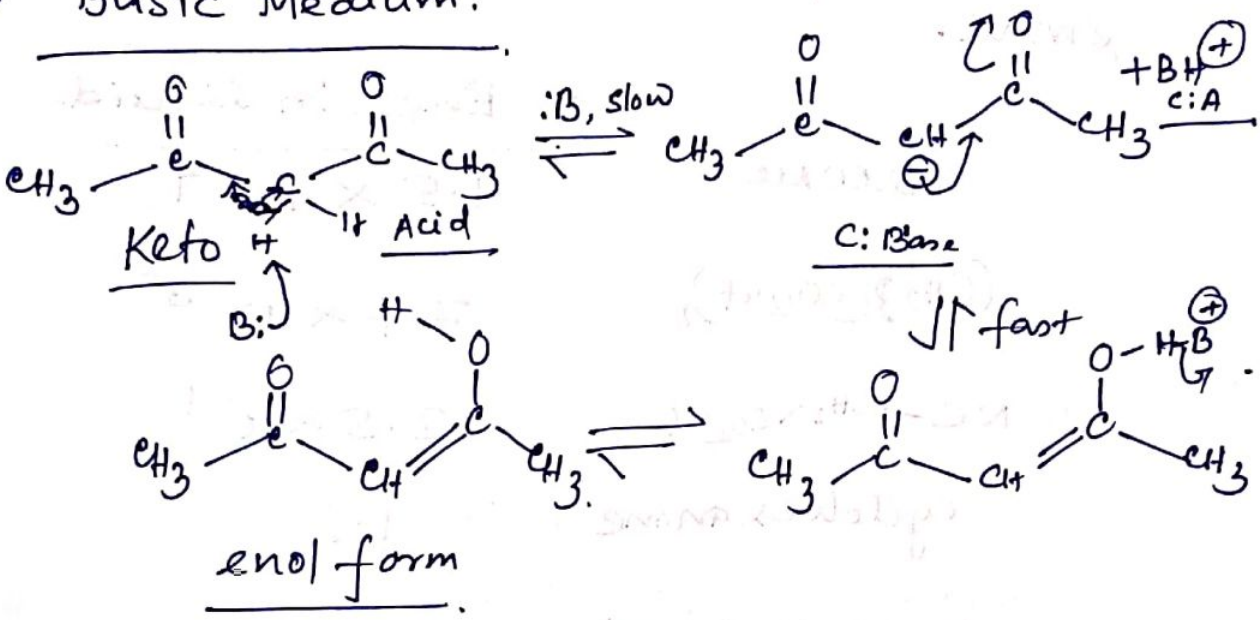


Nitroso form

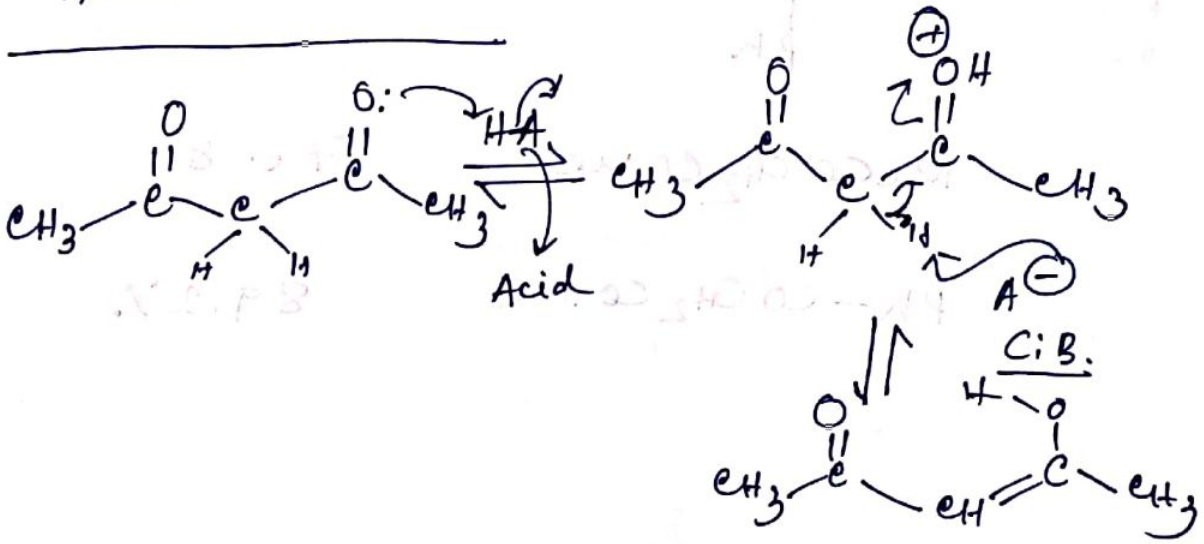
oxime form.

Mechanism of Tautomerism.

(i) Basic Medium.



(ii) Acid Medium

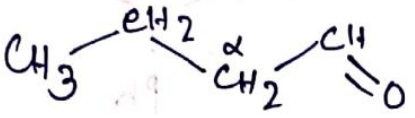


In simple carbonyl compounds e.g. MeCOMe, the proportion of enol at equillibrium is extremely small.

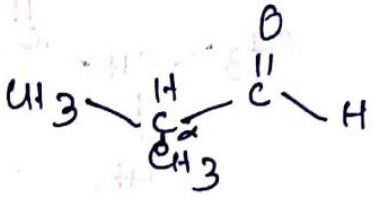
	% Enol in liquid
MeCOMe	1.5×10^{-4}
$(CH_2)(CO_2Et)_2$	7.7×10^{-3}
$NC-CH_2-CO_2Et$	2.5×10^{-1}
Cyclohexanone	1.2
$MeCOCH_2CO_2Et$	8.0
$MeCOCH(Ph)-CO_2Et$	30
$MeCOCH_2COMe$	76.8
$Ph-COCH_2COMe$	89.2%

Factors shift the equilibrium towards enol form

① Substitution

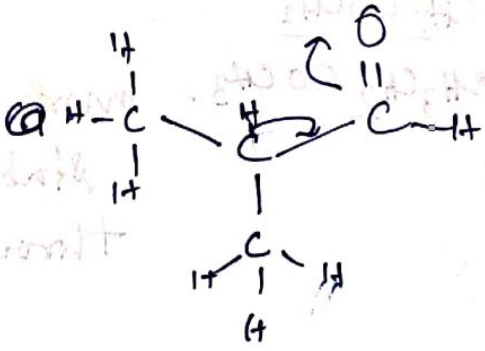


enol → 5.5×10^{-4} %.

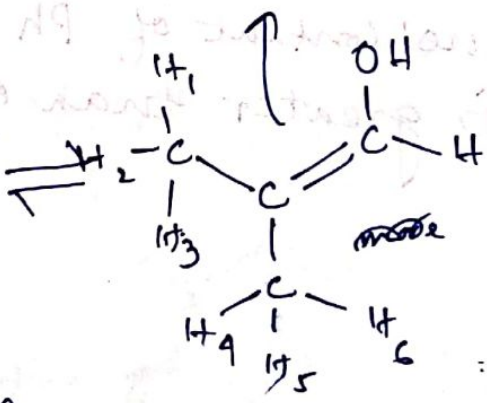


enol content 1.4×10^{-2} %.

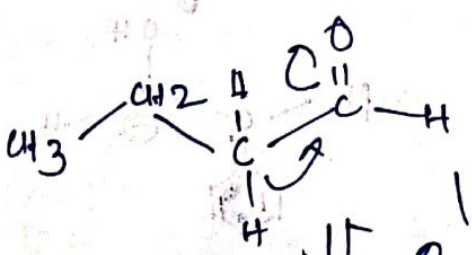
alkyl gr. at α-position of C=O gr. increases enol content due to hyperconjugative stabilization of the C=C bond in enol form.



more substituted double bond



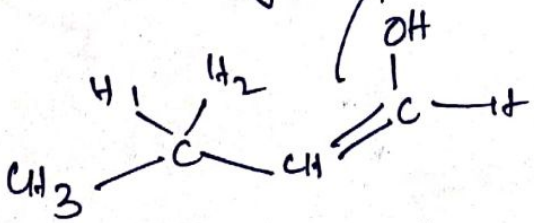
But



less substituted d.b.

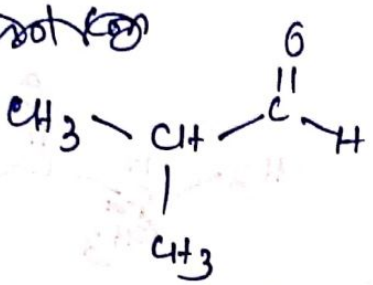
6α Hydrogen for hyperconjugation

so 6-hyperconjugative str.

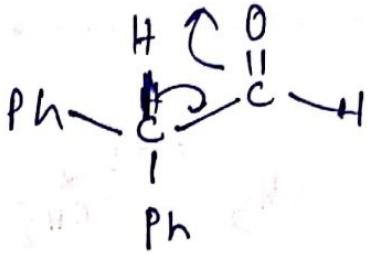


2-αH, so 2 hyperconjugative str.

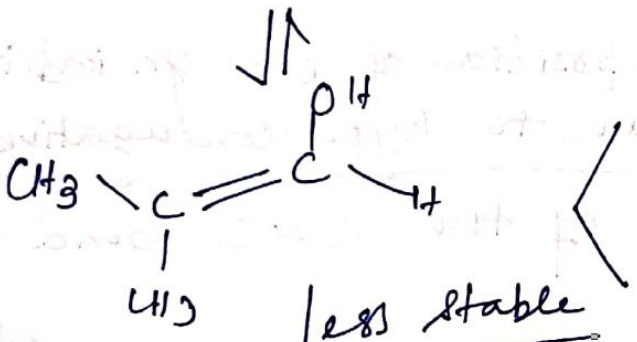
② Aryl group at α-carbon. → increases the enol content.



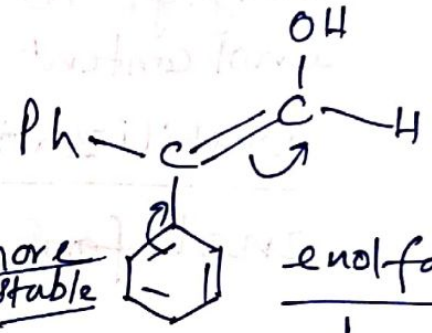
enol content $1.4 \times 10^{-2}\%$



enol content 9.1%



less stable

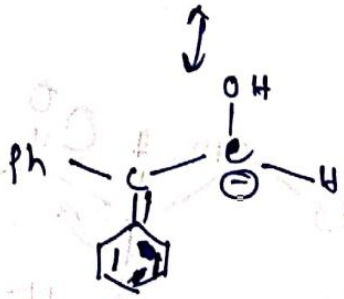


more stable

enol form

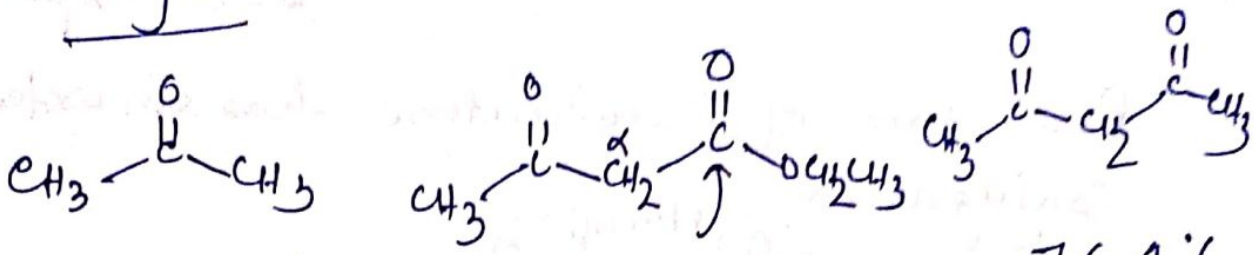
∴ enol content of $PhCH_2COCH_3$ is greater than $CH_3CH_2COCH_3$.

more resonance stabilization through conjugation.



③ Carbonyl group on α-Carbon of Carbonyl

Compd :



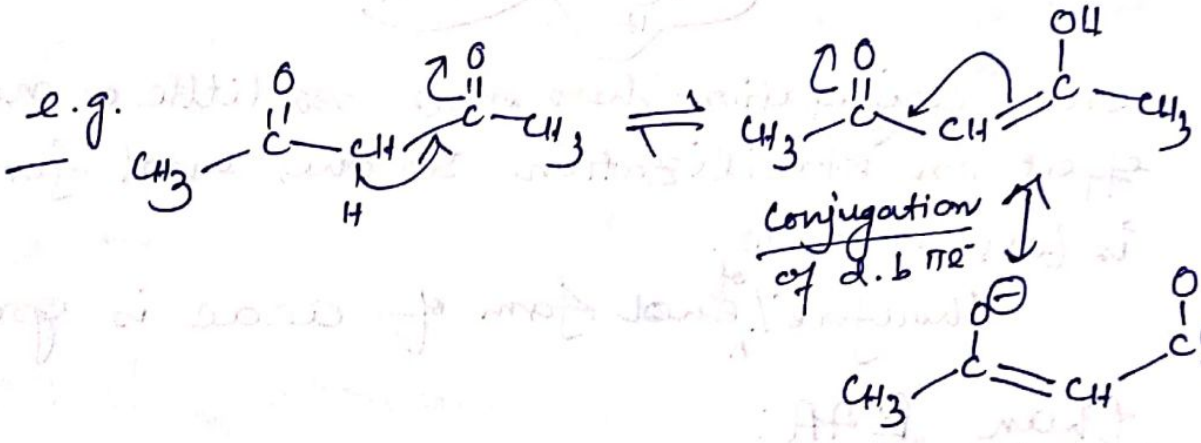
enol → 1.5×10^{-4} %. 8%. 76.4 %

c=o gr. at α-Carbon of Keto Compd.

Enol content increases. because.

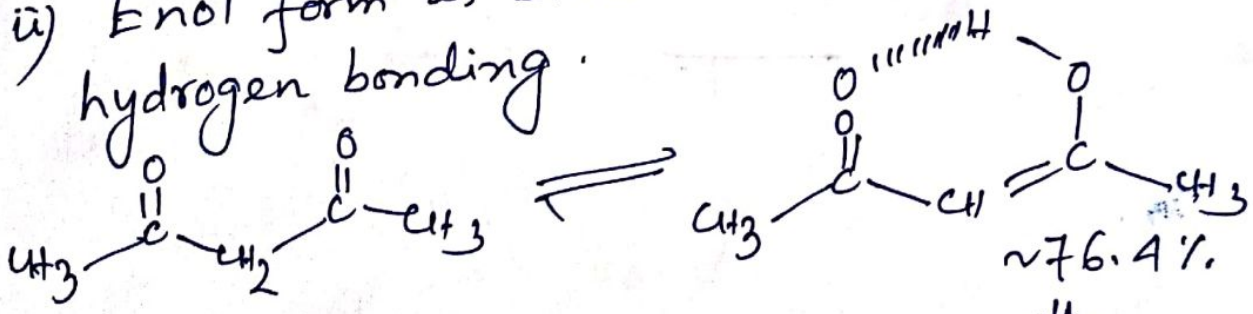
(i) Enol form is stabilised through conjugation with c=o gr., so resonance energy increases.

e.g.

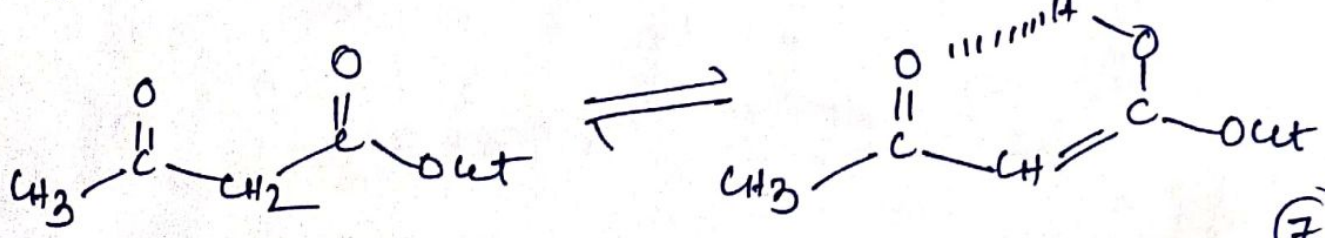


Conjugation of 2 lone pair

(ii) Enol form is stabilized through intramolecular hydrogen bonding.

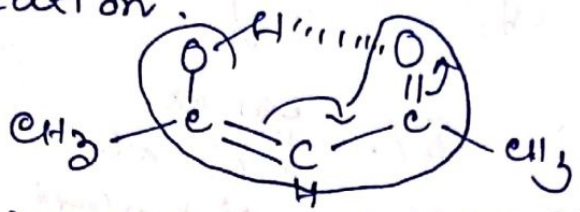


~76.4 %.

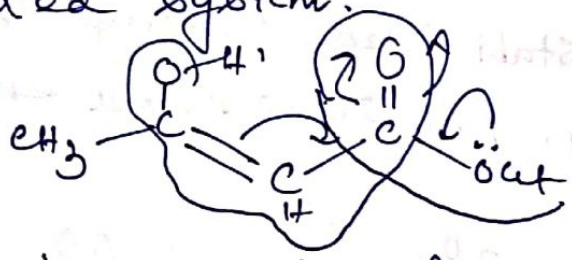


Q Enol Content of EAA is less than acac.
—— Explain.

Enol form of Acetylacetone has an extended conjugation.



So resonanance stabilization is high, which increases the enol content.
whereas enol form of EAA is a cross-conjugated system.



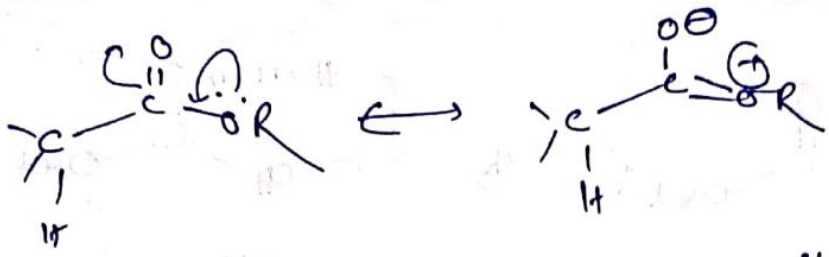
cross conjugation has little or no effect on stabilization. So this enol form is less stable.

Therefore % of enol form of acac is greater than EAA.

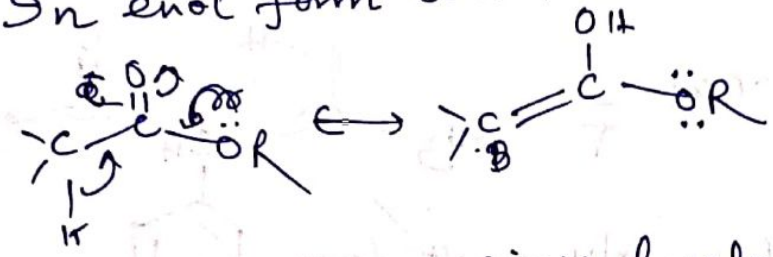
———

) Enol content of ester is less than ketone.

Because ester groups are itself resonance stabilised.

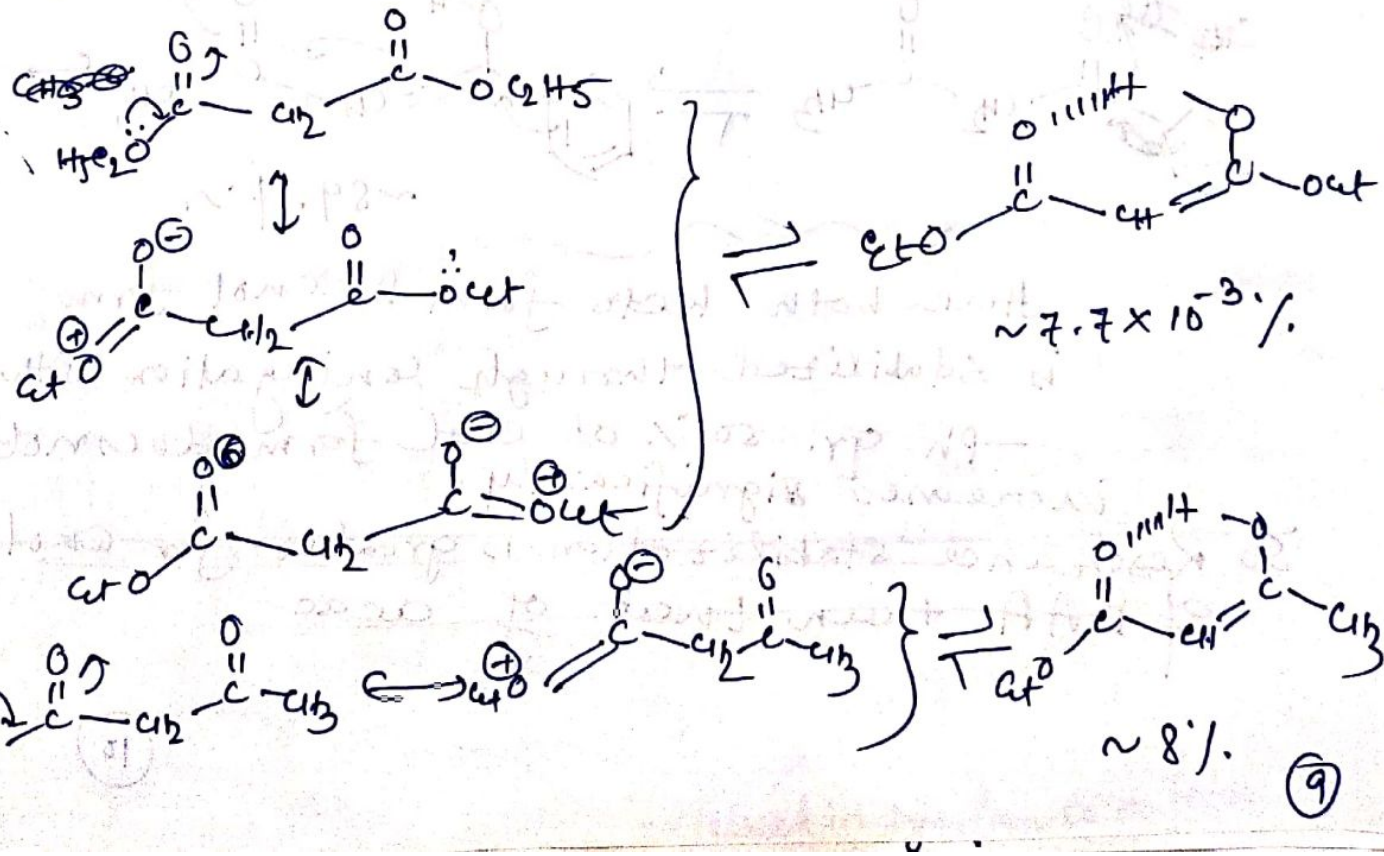


In enol form this resonance stabilization is hampered.

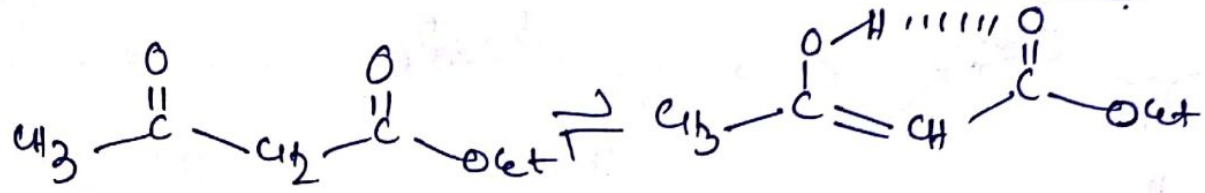


The enol content of diethylmalonate is less than EAA (DEM).

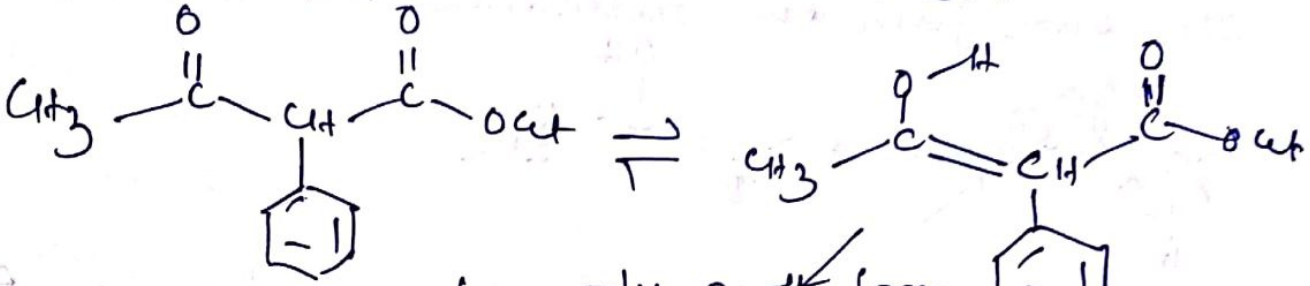
Because DEM is more resonance stabilized than EAA and this stabilization is hampered due to enol formation. So % of keto form of DEM is greater than that of EAA.



⑥ Aryl gr. at C_2 position of 1,3-dicarbonyl comp. increases the ~~keto~~ enol content to greater extent than Aryl gr. at C_1 position.

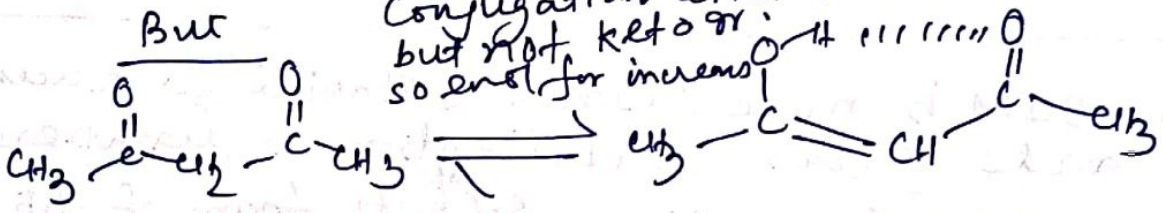


~8%.

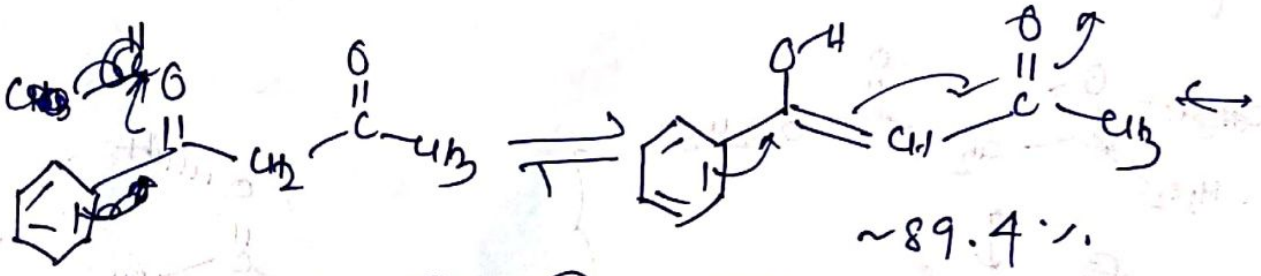


here only enol form get stability through conjugation with -Ph gr. ~30%.

But



Here on ↓ ~76.4%.



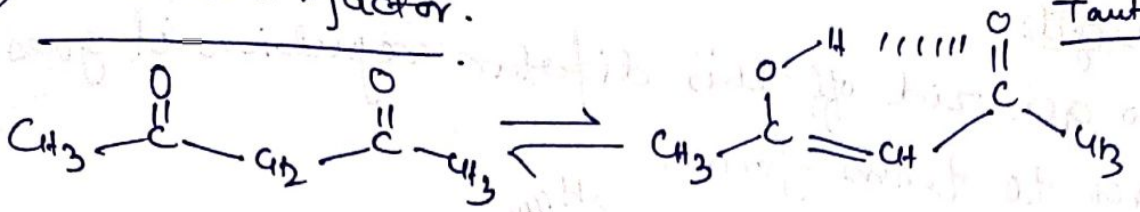
~89.4%.

Here both keto form & enol form is stabilized through conjugation with -Ph gr. so % of enol form does not increases significantly.

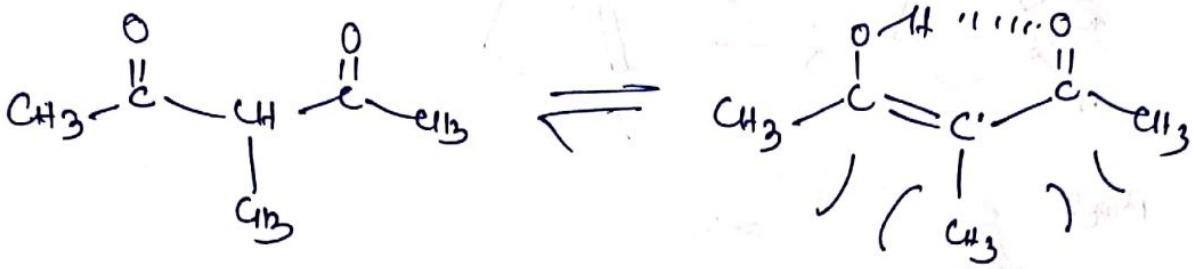
~~So Resonance stabilization is greater for enol form of EAA than that of acac~~

(2) Steric factor.

Tautomerism:



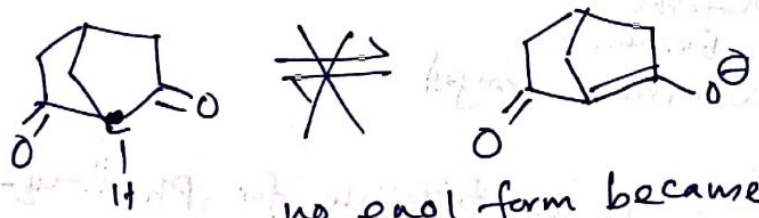
91–93% in gas phase



~43.5–44.5%.

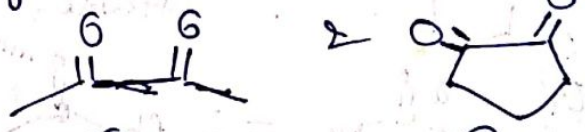
greater steric repulsion

(3) (*)



no enol form because ~~bred~~ introduction of double bond in bridge head position is against Bredt's rule.

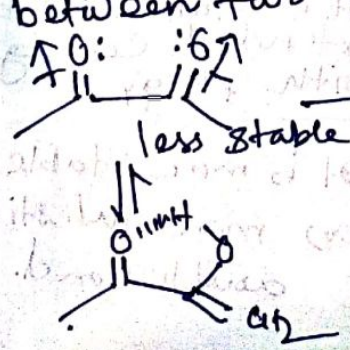
(4) (*) Enol content of



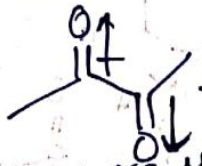
(A) (B)

Ans: Enol content of (B) is greater than (A)

(A) almost exist in the anti-orientation. Because in syn-orientation there exist dipolar repulsion between two vicinal carbonyl groups. so cannot give ~~keto~~ enol form.



less stable



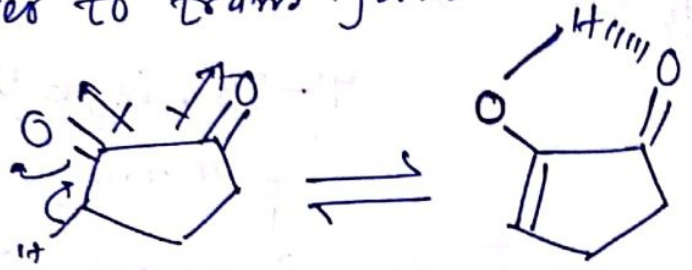
→ no dipolar repulsion.

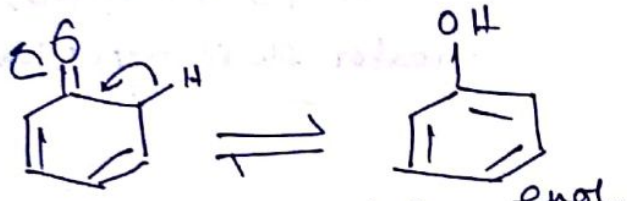
more stable.

so dipolar repulsion is high.

→ locked in syn-form so ~~dipolar~~

To get rid off this difolar repulsion it goes over to trans form.

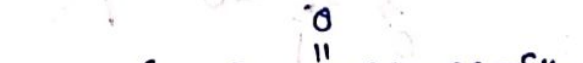


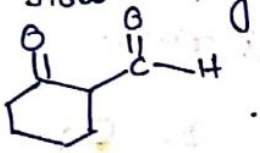
(5) 

[Phenol-Keto tautomerism]

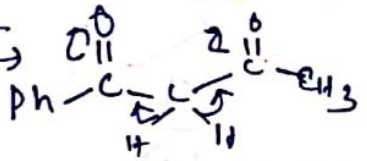
Keto — Here enol form is stable because this is aromatic compd.

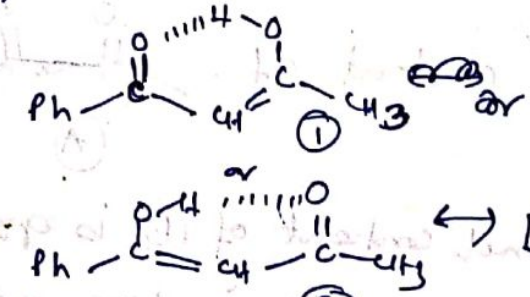
(6) 

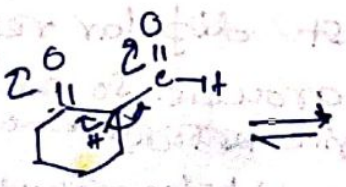
How many enols are possible for 

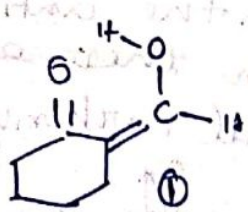
& 

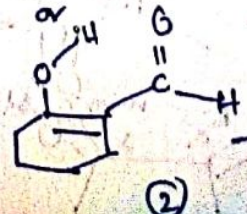
which enol is expected to be more stable.

For 









(2) is more stable than (1) because it is stabilised by extended conjugation with Ph gr.

It is more stable enol as more substituted double bond.