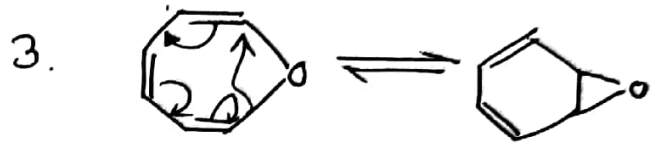
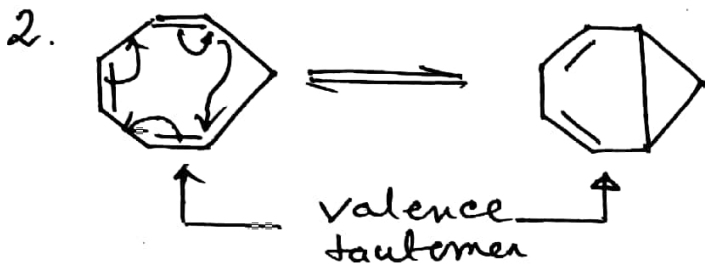
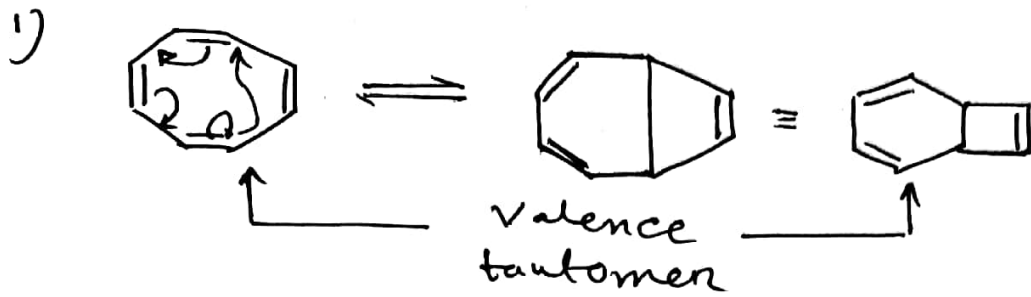
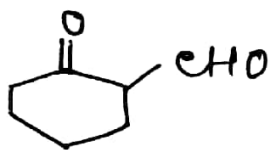


Tautomerism class-2 ①

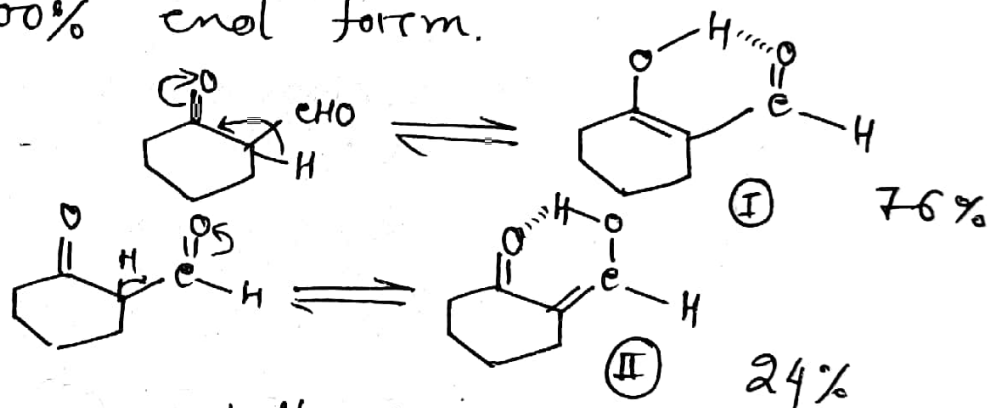
More example of valence tautomerism.



* Explain why the following ketone exist in 100% enol form.

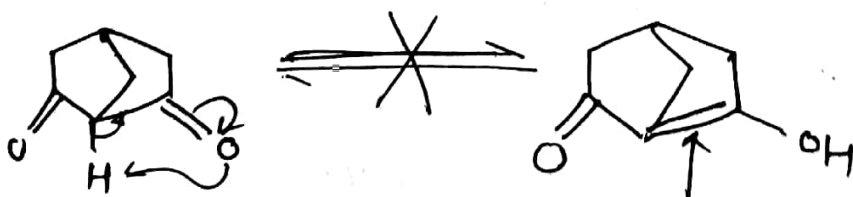


again



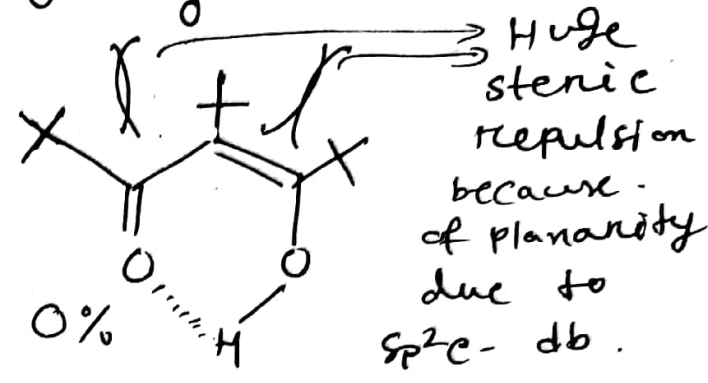
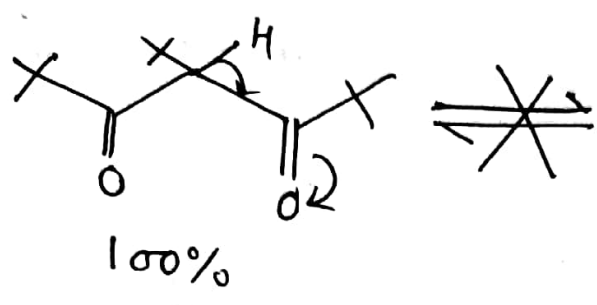
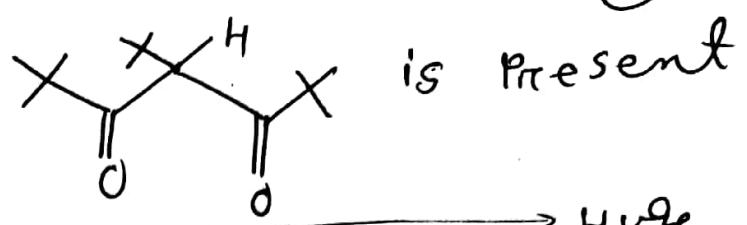
Str. I is more stable than Str-II, since the db in str. (I) has more hyperconjugative str's.

* The following ketone doesnot enolise. Explain



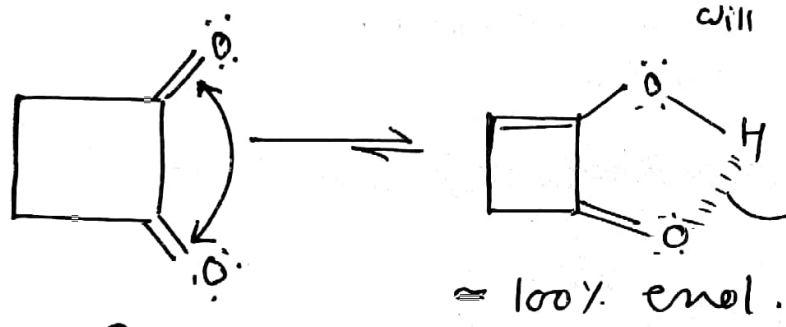
db is not formed at bridgehead carbon because of its rigidity, db can't attain planar geometry or 120° bond angle.

* The Ketone in 100% Keto form.



H.W → Under neat condition EAA → 8% enol but acetylacetone → 76% enol Explain

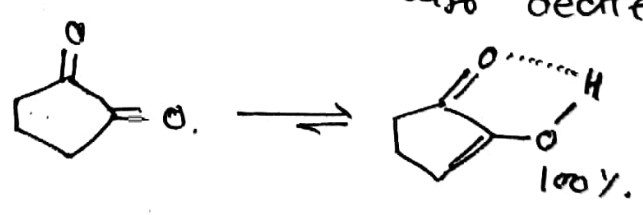
so it can't be enolise at all.
(t-Bu/t-Bu- steric repulsion → one pair) will destabilise the molecule.



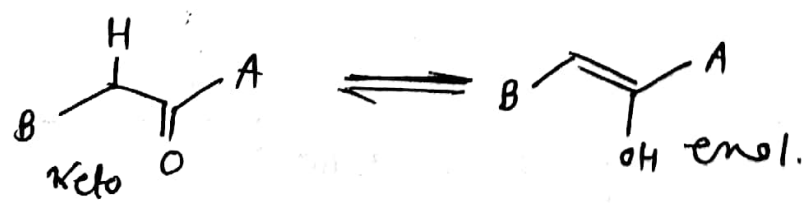
Strong dipole-dipole interaction destabilise the diketo form

intramolecular H-bond (5-memb) stabilises the enol form to much extent, again dipole interaction also decreased.

similar case →



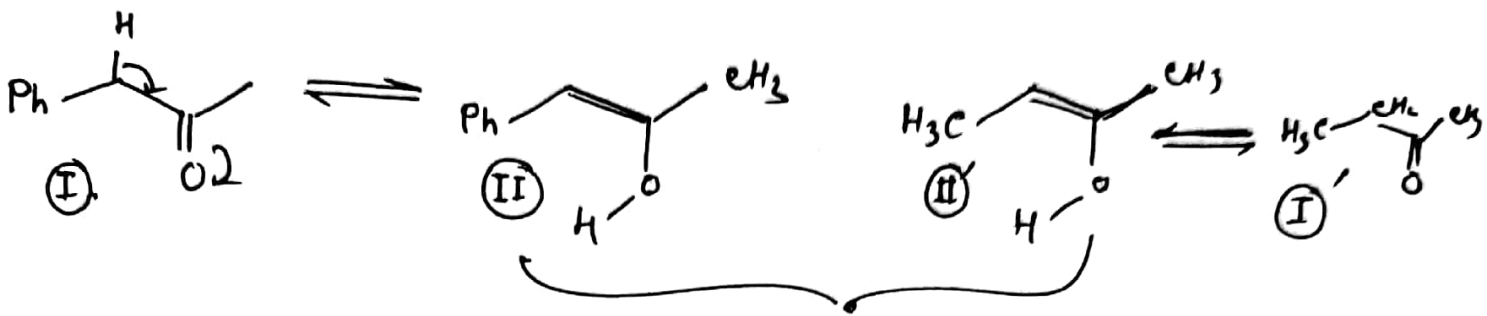
Consider KET for Ketone



The ratio of Keto-enol forms depend on the nature of A and B

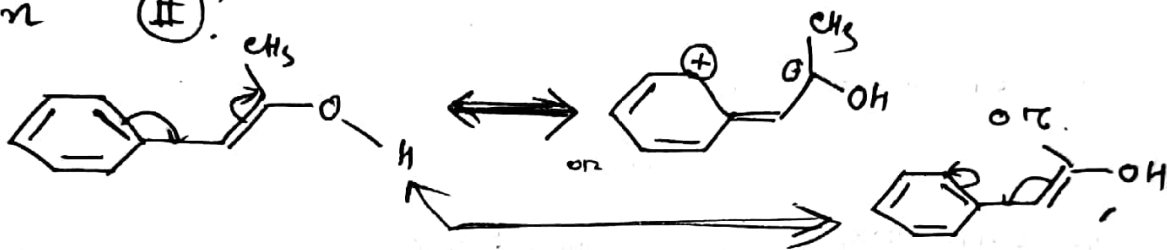
For e.g. If B is aryl gr. or unsaturated gr. the enol conformer gets resonance stabilisation. and the enol content of that comp. will be more

\therefore $\text{PhCH}_2\text{COCH}_3$ is more enol contained. (3)
 than $\text{H}_3\text{CCH}_2\text{COCH}_3$.



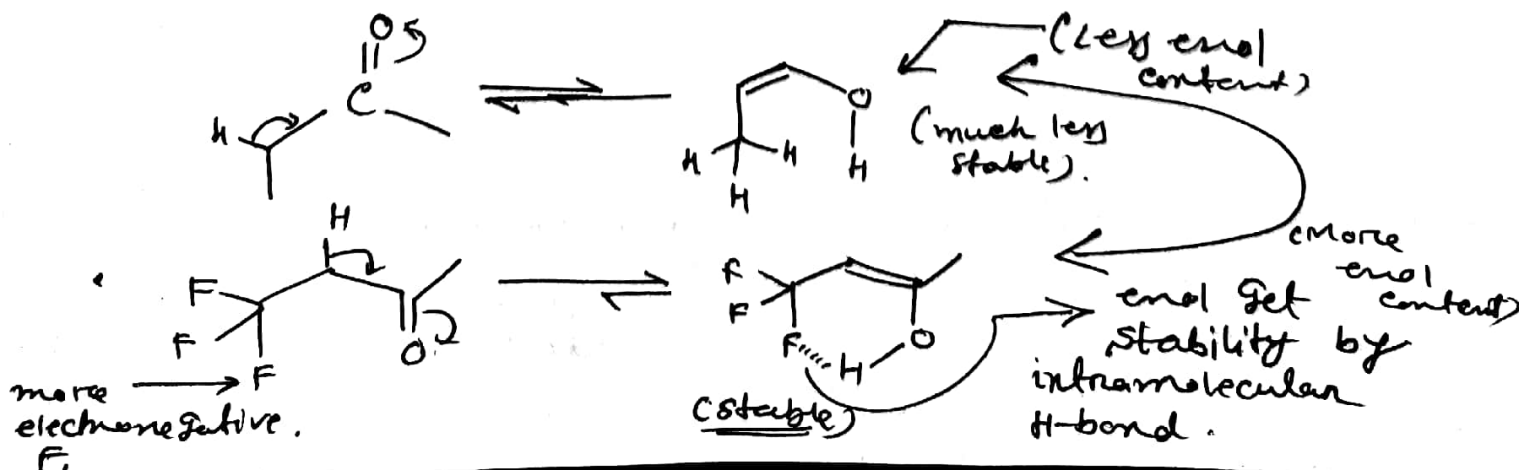
Show here db.
 is more stabilised by conjugation with ring.

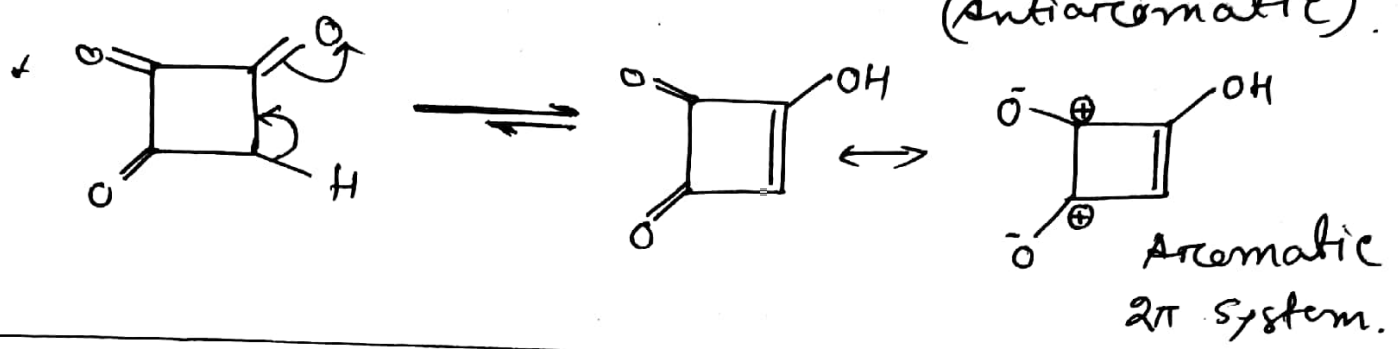
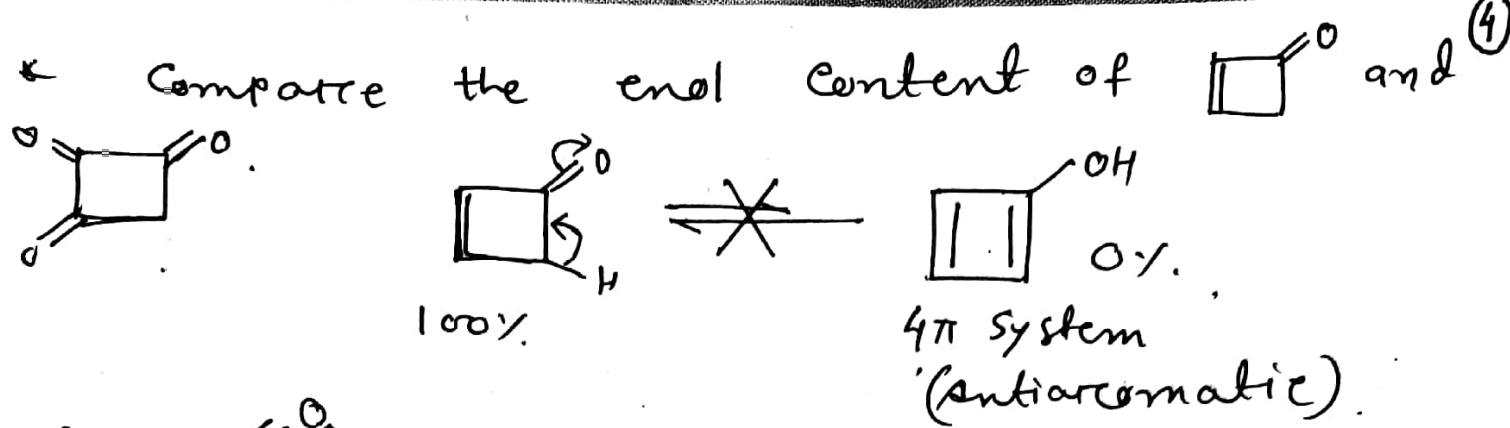
So enol content of (II) is much greater than (I').



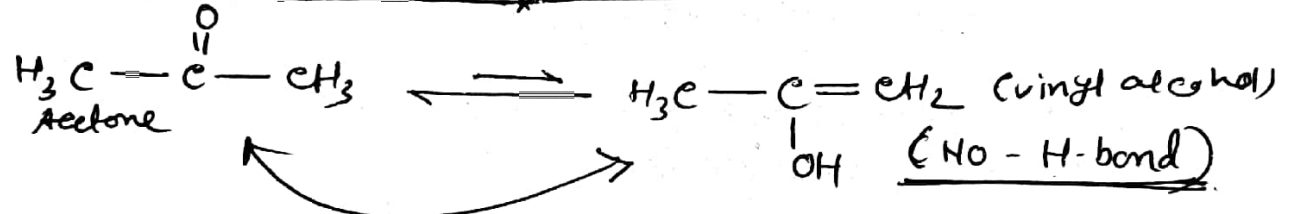
* If B contains a more electronegative atom than A then enol gets stabilisation by intramolecular H-bond, but this factor is less important in the Polar solvent where solvent play the role of H-bond.

e.g. Consider relative enol content of 2-butanone and $\text{F}_3\text{C}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$.





Thermodynamic consideration



Here this eqm is non spontaneous.

It can be explained by following bond energies.

$C-H = 99, C-C = 83, C=O = 179,$
 $C=C = 146, O-H = 111, C-O = 86.$ (all are in $Kcal\ mol^{-1}$)

In acetone (LHS) total bond energy

$\Delta H_1 = 6 \times (C-H) + 2 \times (C-C) + 1(C=O)$
 $= (6 \times 99 + 2 \times 83 + 179) K\ mol^{-1}$
 $= 939$

In vinyl alcohol (RHS)

$\Delta H_2 = 5(C-H) + 1(C-C) + 1(C=C) + 1(C-O) + 1(O-H)$
 $= (5 \times 99 + 83 + 146 + 86 + 111) = 921$

$\Delta H_{Keto \rightarrow enol} = \Delta H_1 - \Delta H_2 = (939 - 921) = +18$

$\Delta G_{Keto \rightarrow enol} = \Delta H_{Keto \rightarrow enol} - T\Delta S$ (So Keto \rightarrow enol can't occur) (ΔS = 0) - no. of moles same
 $= +18\ Kcal - T \times 0$
 $= +18$ (+ve, non spontaneous) \rightarrow not favourable