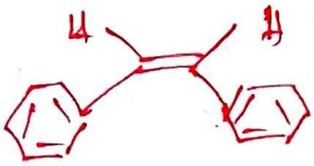
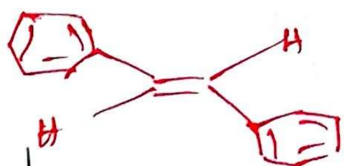
Cis & Trans Stilbene



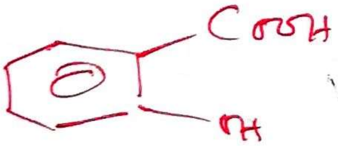
vs



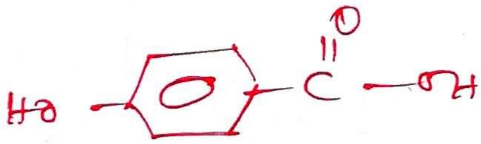
C=C stretching near 1640-1600 cm^{-1}	No such band as C=C stretch does not change the dipole moment

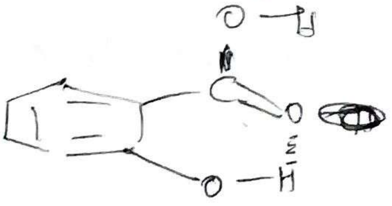
$CH_3-C\equiv C-H$ & $CH_3-C\equiv N$

a) $\equiv C-H$ stretching at 3300 cm^{-1} (strong band and sharp) b) $\equiv C-H$ out of plane bending at 680-610 cm^{-1} (strong but broad)	No such bands.

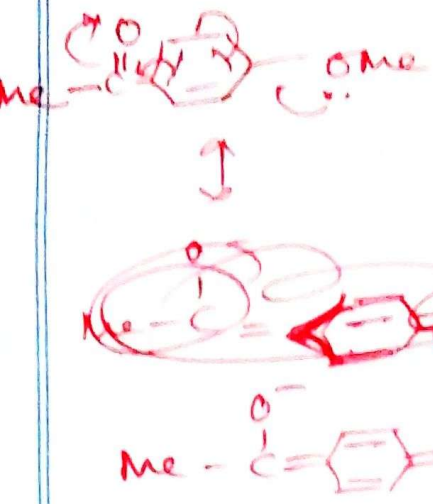


vs





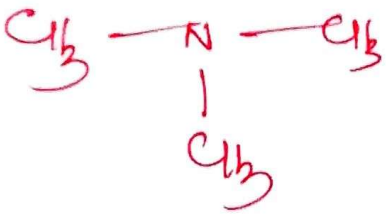
Intra mol H bonding. OH stretch at - - - does not change on dilution with CCl_4	Intermol H bonding. The O-H stretching frequency is shifted to lower values on dilution with CCl_4 - Extent of H bond decreases with dilution.



vs

C=O stretching freqny is lowered due to conjugation with OMe gr.

$-NH_2$ gr prevents such conjugation so C=O stretching freqny is somewhat higher.



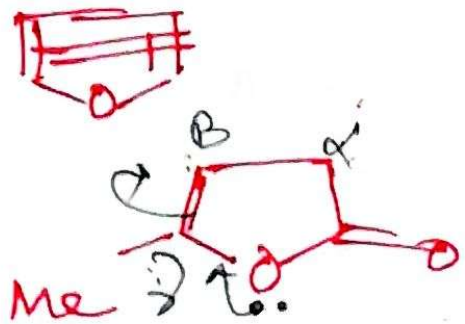
vs

No $-N-H$ band observed

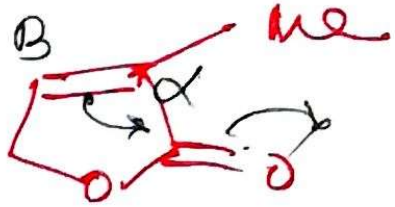
Two N-H stretching vibrations at 3400-3300 cm^{-1} (asymmetric) and one symmetric stretching at 3330-3250 cm^{-1}

$\bar{\nu}_{C=O}$ 1750 cm^{-1}

1715 cm^{-1}



vs

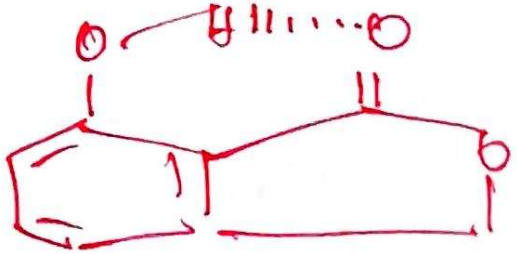


β,γ unsaturated lactone

α-β unsaturated lactone

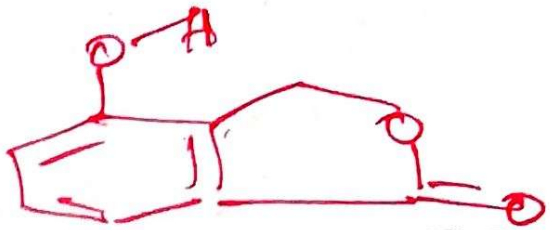
The C=O gr is not conjugated with the C=C. Moreover the l.p on oxygen is mostly engaged in conjugation with the C=C bond. Hence the C=O bond strength is much higher than the α-β unsaturated lactone

conjugation decreases the double bond character of the carbonyl gr and hence decreases the $\bar{\nu}_{C=O}$.



(A)

vs



(B)

Intramol H bond

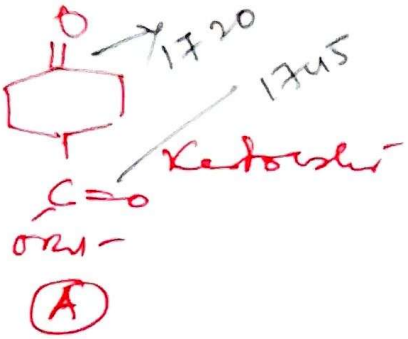
Intramol H bond.

$\bar{\nu}_{C=O}$ is less than free normal C=O stretching. On dilution with $CHCl_3$ $\bar{\nu}_{C=O}$ remains almost unaltered.

Intramol H bonding decreases with increasing dilution with $CHCl_3$. So $\bar{\nu}_{C=O}$ increases

Thus $\bar{\nu}^{CHCl_3}_{C=O}$ < $\bar{\nu}^{CHCl_3}_{C=O}$

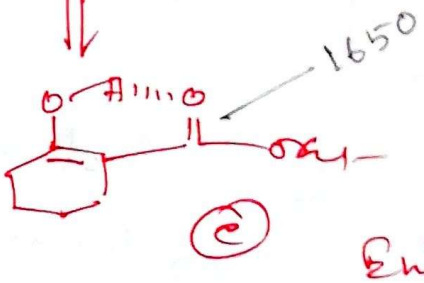
(A) (B)



(A)

Keto ester

(B)



(C)

Enol ester

A exists mainly as Ketoester. But B exists as an equilibrious mixture of - B and C (enolester)

So for A there is likely to be two bands:

$\bar{\nu}_{C=O}$ for Keto, ~ 1720 cm^{-1}

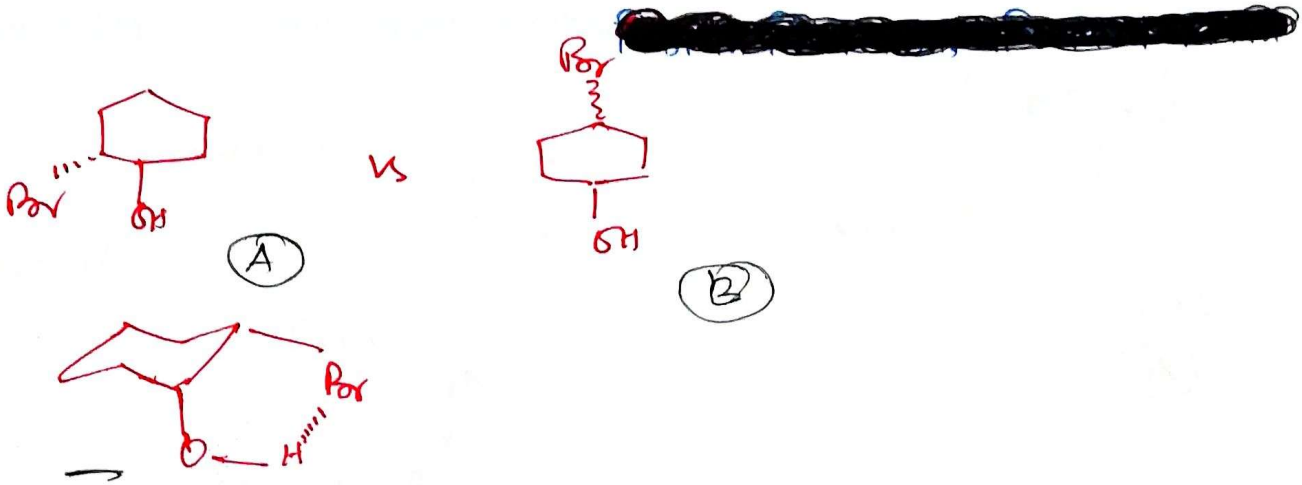
$\bar{\nu}_{C=O}$ for ester, ~ 1745 cm^{-1}

But for the second molecule B, there would be three $\bar{\nu}_{C=O}$ bands

$\bar{\nu}_{C=O}$ for Keto ~ 1720
for ester ~ 1745 } for B also where it is merely keto form

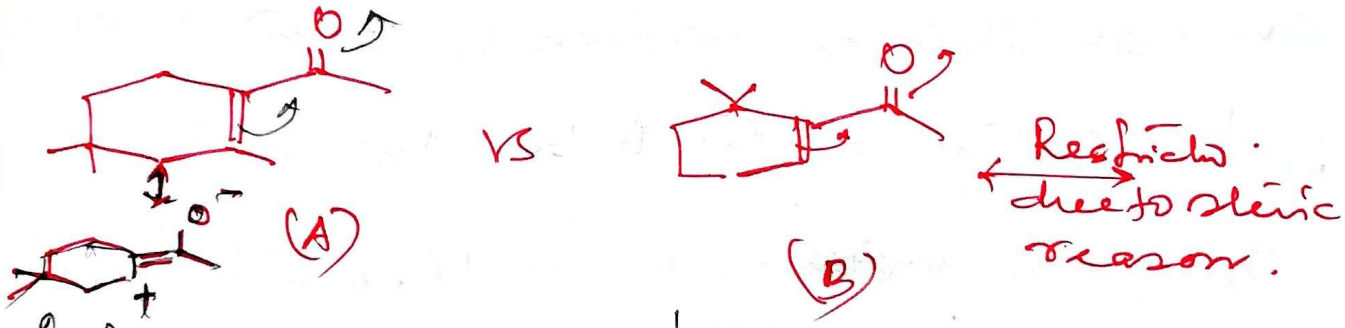
and

$\bar{\nu}_{C=O}$ for ester (H bonded) ~ 1650 cm^{-1} } for C



$\bar{\nu}_{O-H}$ of A decrease due to H bonding.
and $\bar{\nu}_{C-O}$ increases

Thus $\bar{\nu}_{OH_A} < \bar{\nu}_{O-H_B}$ But $\bar{\nu}_{C-H_A} > \bar{\nu}_{C-H_B}$

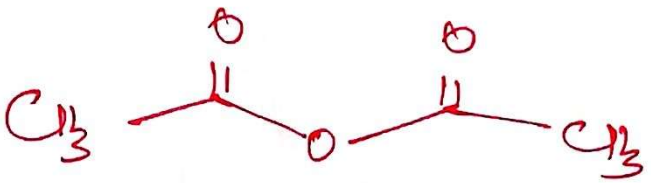


Restricted due to steric reason.

Delocalisation decreases the $\bar{\nu}_{C=O}$ Stretching frequency

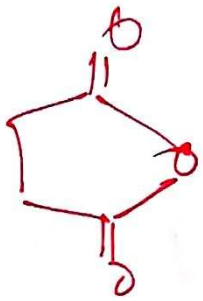
The Conjugation between C=O and C=C is somewhat restricted due to interaction with large methyl groups.

$\therefore \bar{\nu}_{CO_A} < \bar{\nu}_{C=O_B}$



Acetic anhydride

vs



Succinic anhydride

Acyclic anhydride show two $\bar{\nu}_{C=O}$,

$\bar{\nu}_{C=O} \sim \underline{1}818$ (asymmetric)

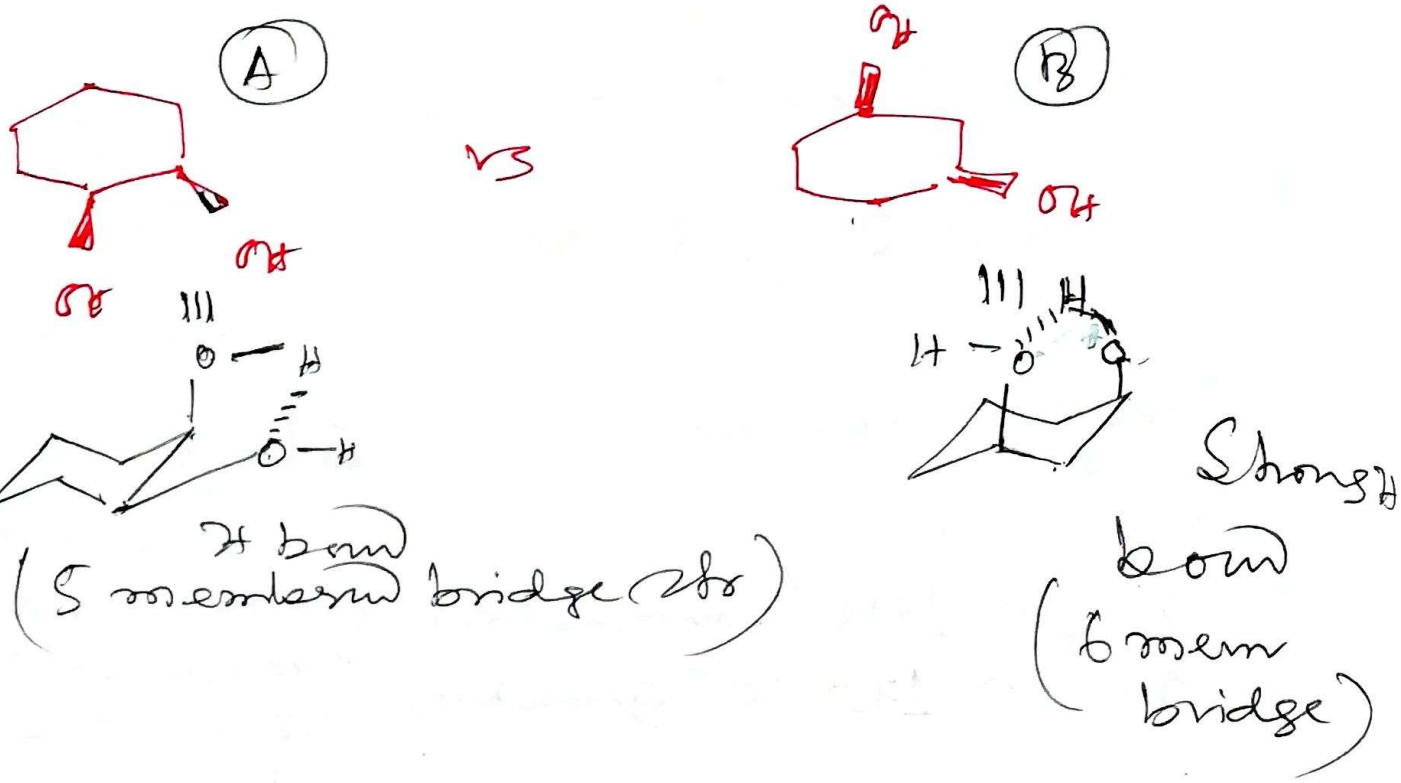
$\bar{\nu}_{C=O} \sim \underline{1}750$ cm^{-1} (symmetric)

Shows two C=O bond at higher frequency (lower angle compare greater S-character on the C=O carbon, hence strong C=O bond strength)

*Ring strain [1865 cm^{-1}, 1782 "

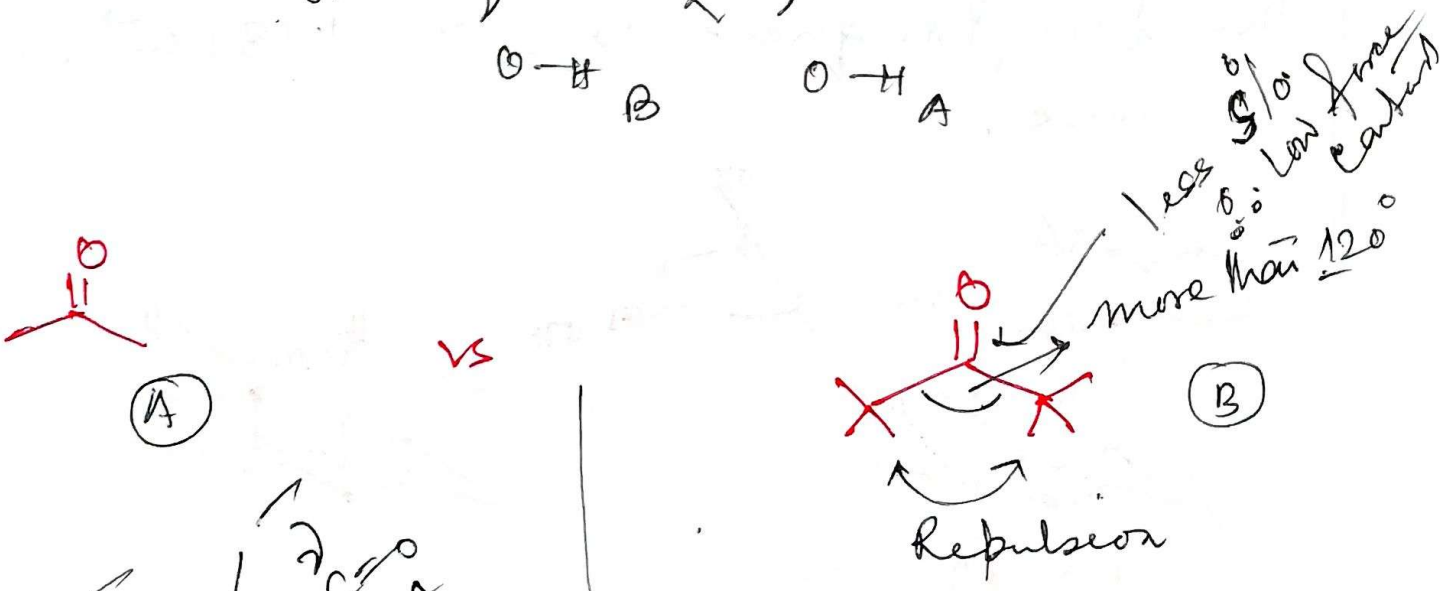
Note

But in acetic anhydride the higher frequency $\bar{\nu}_{C=O} \sim 1818$ cm^{-1} is more intense whereas for succinic anhydrides (or cyclic anhydride) the low frequency $\bar{\nu}_{C=O} \sim 1782$ cm^{-1} is more intense.



So a broad band of H bonded $\bar{\nu}_{O-H}$ can appear at low frequency for B than A.

or $\bar{\nu}_{O-H_B} < \bar{\nu}_{O-H_A}$

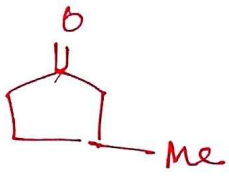


$\bar{\nu}_{C=O_A} > \bar{\nu}_{C=O_B}$

Larger ∠ or repulsion increases the bond angle than normal. So the carbonyl carbon gets more p-character. So $\bar{\nu}_{C=O}$ is low.

(A)

vs



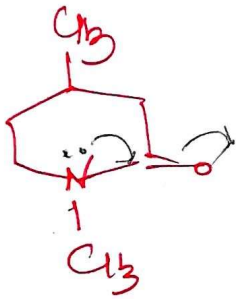
(B)

Smaller ring size increases $\bar{\nu}_{C=O}$ value.

$\bar{\nu}_{C=O}$ < $\bar{\nu}_{C=O}$

A B.

Q 15.



(A)

1670 cm^{-1}

vs

(B)

1720 cm^{-1}

Conjugation in A decreases the $\bar{\nu}_{C=O}$, and lone pair on N is no longer available for abstraction of proton from 5th position (neutral)

But in B the bridge restricts the conjugation between the L.P on N with the carbonyl gr (as that would require formation of double bond at bridgehead). So $\bar{\nu}_{C=O}$ is higher than A.

Q-16 → Same as question no - 13