

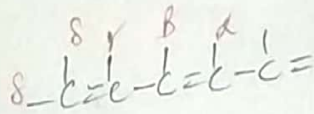
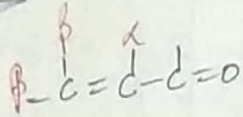
Woodward's rule for Enones:

⇒ Conjugation of γ $\text{C}=\text{O}$ & α bond gave intense absorption
 ($\epsilon = 8,000$ to $20,000$) for $\pi \rightarrow \pi^*$ transition of $\text{C}=\text{O}$ grp.
 $\Delta \lambda_{\text{max}} = 220 - 250 \text{ nm}$ in simple enones

→ then $n \rightarrow \pi^*$ is less intense ($\epsilon = 50 - 100$) & $\lambda_{\text{max}} = 310 - 330 \text{ nm}$.

Note By structure modification the $n \rightarrow \pi^*$ is not affected while
 $\pi \rightarrow \pi^*$ get affected by the addition of chromophore.

Rules are:-



Base value

- 6 membered ring / acyclic
- 5 membered ring
- Acyclic dienone

215 nm -

202 nm

245 nm

Increment for

- Double bond extended conjugation
- alkyl grp / ring residue

30

$\alpha = 10$

$\beta = 12$

ring hybrid = 18

Other grp

-OH

$\alpha = 35$

$\beta = 30$

$\gamma = 50$

-OOCCH₃

$\alpha, \beta, \gamma = 6$

-OCH₃

$\alpha = 35$

$\beta = 30$

$\gamma = 17$

$\delta = 31$

-Cl

$\alpha = 15, \beta = 12$

-Br

$\alpha = 25, \beta = 30$

-NR₂

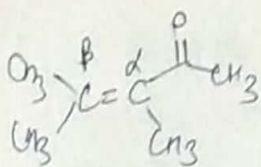
$\beta = 95$

Contd.

Exocyclic double bond.
Homocyclic diene component

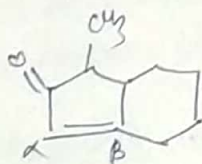
5
39

few examples:



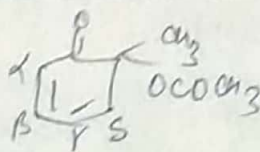
Bicyclic enone = 215 nm
 α CH₃ 10
 β CH₃ (2+12) 24

 249
 observed 249 nm



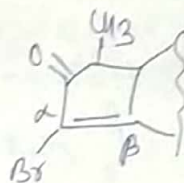
5 membered enone = 202 nm
 β -ring residue 202 = 24
 Exocyclic double bond = 5

 231
 observed 226 nm



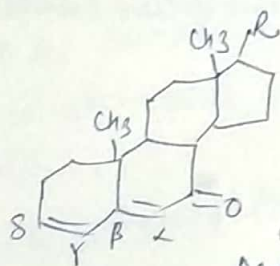
6 membered enone 215
 = bond extended conjugation 30
 Homocyclic diene 39
 β ring residue 18

 302
 observed = 300 nm



5 membered enone 202
 α -B 25
 β ring residue (2x12) 24
 Exocyclic double bond 5

 256
 observed = 251 nm



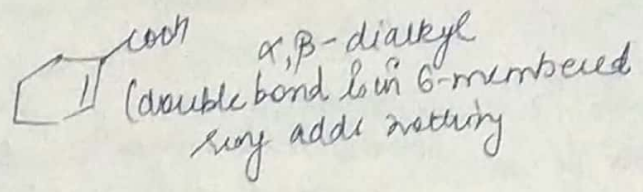
6 membered enone 215
 Double bond extension conjugation 30
 β -ring residue 12
 γ -ring residue 18
 Exocyclic double bond 5

 280 nm

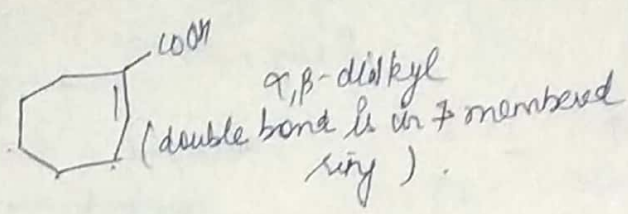
observed 280 nm

⇒ for α, β unsaturated aldehydes, acids and ~~esters~~ esters

⇒ follows the same rules as for enones
 ⇒ generally their absorptions are displaced by 5-8 nm towards shorter wavelength.



217 cal.



217 obs.

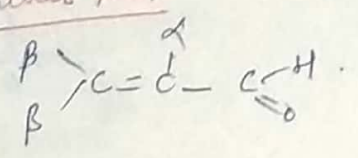
217

+ 5

222 Cal

observed = 222 nm

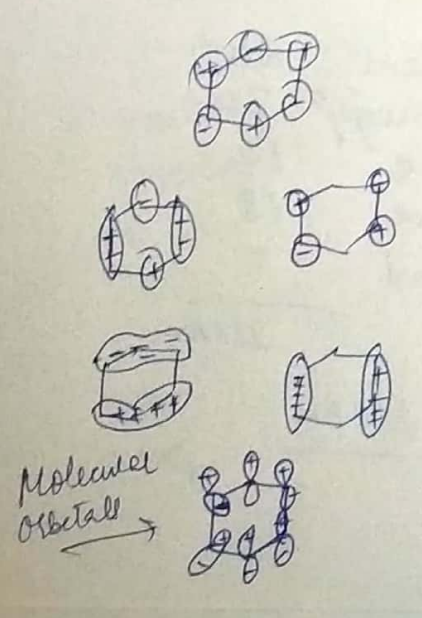
Empirical rules are:



Parent	208 nm
With α or β alkyls	220
With α, β or β, β alkyls	230
With α, β, β alkyls	242

Aromatic Compounds

Absorption from benzene gave 3 absorption bands - basically of $\pi \rightarrow \pi^*$ transition.



π_6^*

π_4^* π_5^*

π_2 π_3

π_1

E_{1u}

B_{1u} B_{2u}

200 (forbidden)

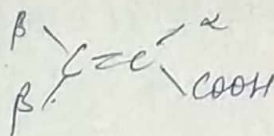
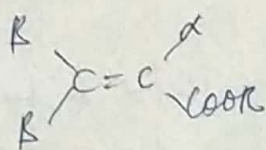
180 nm (allowed)

200 (forbidden)

A_{1g}

Energy states

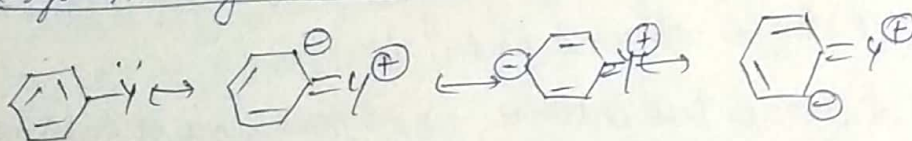
Empirical rules for unsaturated acids and esters



- With α or β alkyl group 208
- With α, β or β, β alkyl group 217
- With α, β, β alkyl group 225
- For an exocyclic α, β double bond Add 5nm -
- For an endocyclic α, β double bond in a 5 or 7 membered ring Add 5nm -

Substituents with unshared electrons

→ Substituents that can carry nonbonding e^- (n -electrons) can cause shifts in primary and secondary absorption bands. The nonbonding e^- can res the benzene of π -system through resonance.



→ Availability of these $n e^-$ as res the greater the shift will be. e.g. with $-OH, -NH_2, -OCH_3$ groups.

→ Interaction of this type b/w n & πe^- usually cause shift in primary & secondary benzene absorption bands - to longer wavelength (extended conjugation)

→ If $n e^-$ is present then there will be a possibility of $n \rightarrow \pi^*$ transition.

→ If $n \rightarrow \pi^*$ transition occur, then the atom from which it was removed becomes e^- deficient while the π -system of the aromatic ring acquires an extra e^- .

