Woodward - Fieser Rule for dienes :

Value of λ_{max} depends on:-

a) No. of alkyl substituents or ring residues on = bond.

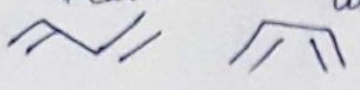
b) No. of = bonds, which extend conjugation

c) +nce of polar gps (-Cl, -Br, -OR etc)

~~Basic value~~/group	Homoannular	Heteroannular
Basic value	253 nm	214 nm
Groups Ting λ_{max}		
i) = bond	+30 nm	+30 nm
ii) alkyl sub. or ring residue	+5 nm	+5 nm
iii) exocyclic = bond	+5 nm	+5 nm
iv) $-OCOCH_3$	0	0
v) $-OR$	+6 nm	+6 nm
vi) $-SR$	+30 nm	+30 nm
vii) $-Cl, Br$	+5 nm	+5 nm
viii) $-NR_2$	+60 nm	+60 nm

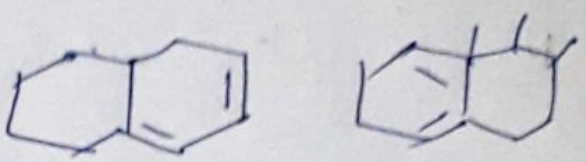
Conjugated dienes

a) trans cis

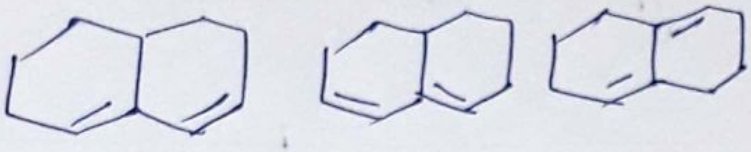


alicyclic

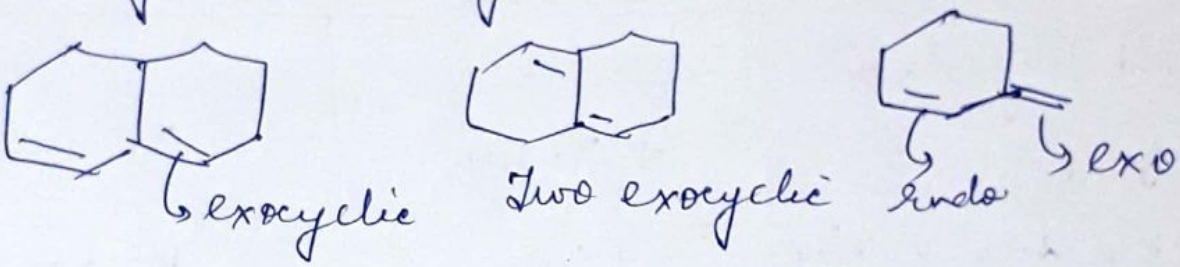
b) Homoannular



c) Heteroannular



d) Exocyclic / Endocyclic



Examples:-

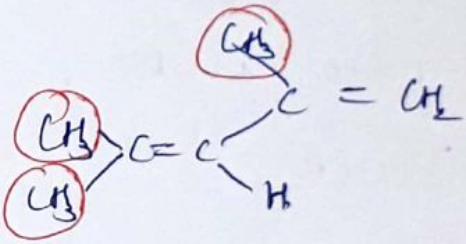
(1) $CH_2 = CH - CH = CH_2$

1,3 butadiene

Calculated λ_{max} = 214nm

Observed λ_{max} = 217nm

(2)



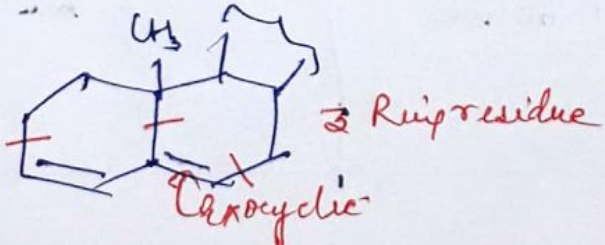
Basic value = 214 nm

3 alkyl gps = 15 nm

Calculated = 229 nm

Observed = 228 nm

(3)



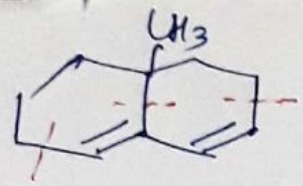
Basic value = 214 nm

Three ring residue = 15 nm

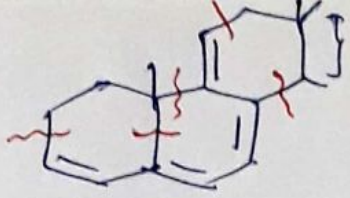
One exocyclic = 5 nm

234 nm

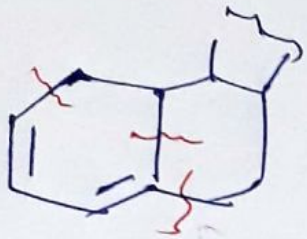
Observed λ_{max} = 235 nm



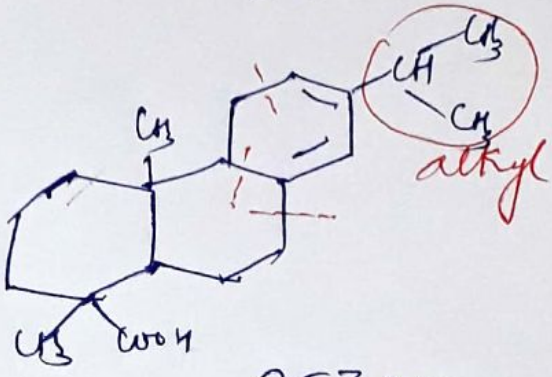
214 nm
+15 nm
+5
234 nm



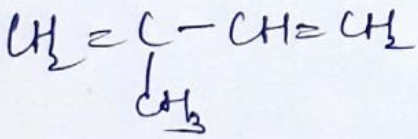
253 nm (Homoannular)
5 x 5 = 25 nm
2 = bond = 60 nm
3 exocyclic = 15 nm
= 353 nm



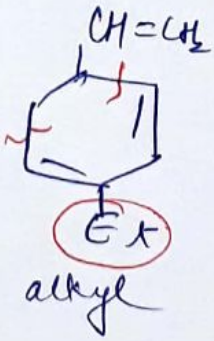
Homoannular 253 nm
3 ring residue +15 nm
exocyclic 5 nm
λ_{max} = 273 nm



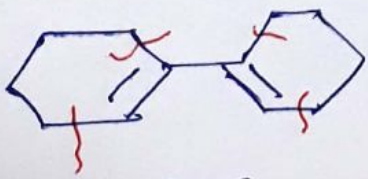
253 nm
3 ring residue 15 nm
1 alkyl 5 nm
exocyclic 5 nm
278 nm.



217 nm
+5
222 nm.



253 nm
+10 nm
+5 nm
268 nm.



215 nm
20 nm
235 nm

217 nm
10 nm
10 nm.
Strain correction 15 nm
252 nm.

α, β - Unsaturated Ketones or Enones

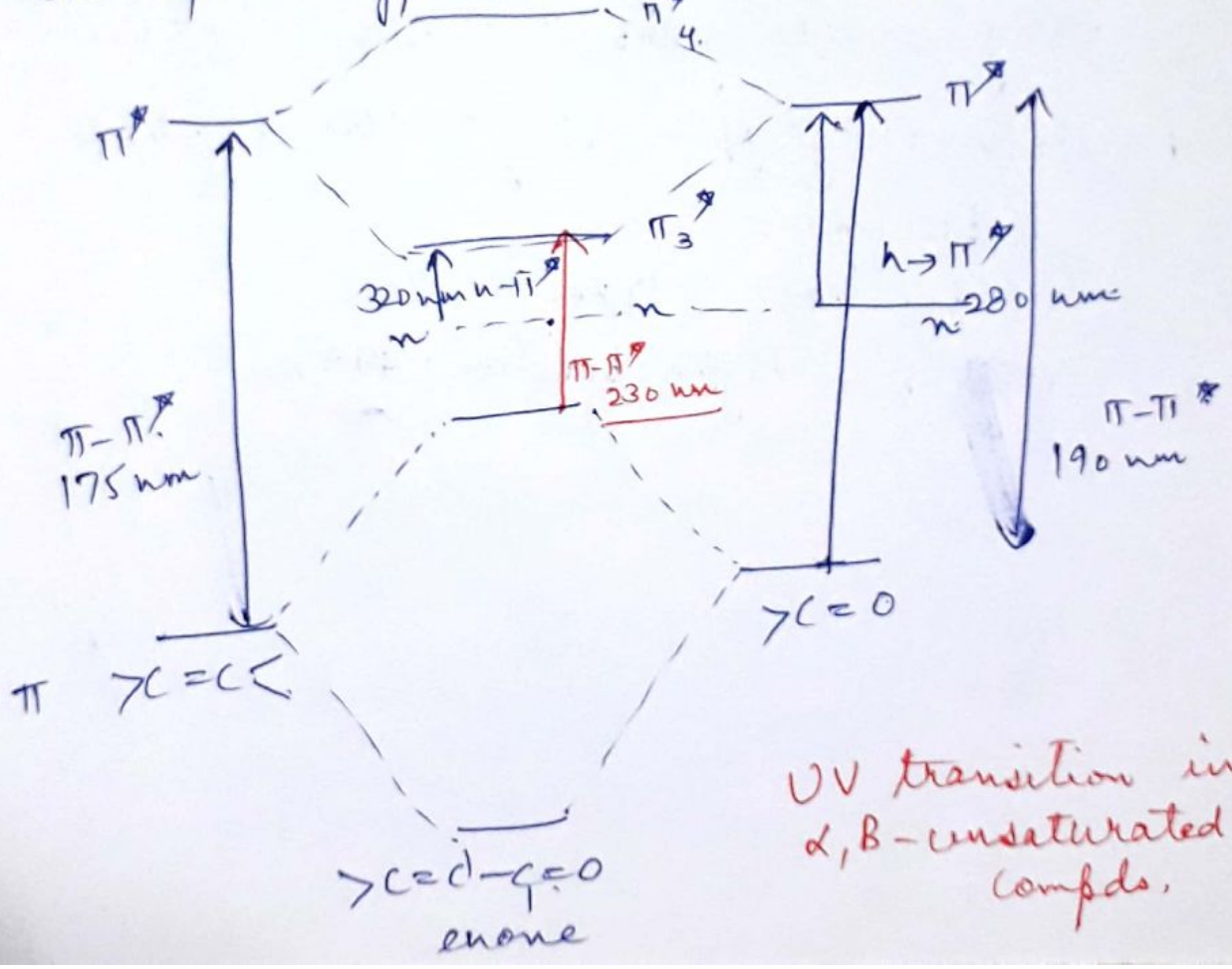
→ In α, β - unsaturated carbonyl compounds, = bond & >C=O gp are in conjugation & are k/n as enones.

→ They have

i) intense absorption band (K-band) in 215-250 nm region due to $\pi \rightarrow \pi^*$ transition ($\epsilon_{max} = 10^4 - 20^4$)

ii) Weak absorption band (R-band) in 310-330 nm ($\epsilon_{max} = 100$) due to $n \rightarrow \pi^*$ transition as compared to $\pi \rightarrow \pi^*$ transition at 165 nm in alkene & $n \rightarrow \pi^*$ transition at 280 nm in >C=O (sat. Ketone)

→ In enones, energy diff. b/n Ground state & excited state is ↓ed due to conjugation of two chromophoric gps (>C=C< & >C=O)



UV transition in α, β - unsaturated >C=O compds.

Woodward Fieser Rule :

1) Basic value of α,β-unsaturated Ketone (acyclic/six membered) = 215 nm.

2) If = bond & >C=O in five membered ring (cyclopentenone), then Basic value = 202 nm.

3) Acyclic dienones, Basic value = 245 nm.

4) Structural addition:

a) For each = bond extending conjugation = +30 nm

b) For homoannular conjugated diene = +39 nm component

c) For each exocyclic = bond = +5 nm

d) For each = bond endocyclic in 5 or 7 membered ring except cyclopent-2-enone = +5 nm

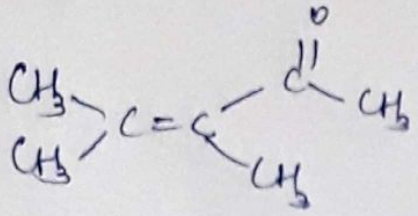
e) For each alkyl gp or ring residue at the

α position = +10 nm

β position = +12 nm

γ or δ or higher position = +18 nm

1)



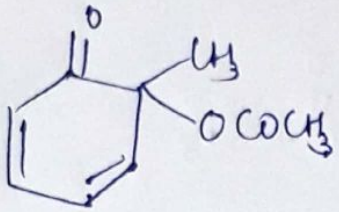
Acyclic enone basic value = 215 nm

One α-CH_3 gp = +10 nm

Two β-CH_3 gp 2×12 = +24 nm

Calculated λ_{max} = 249 nm

2)



Six membered enone basic value = 215 nm

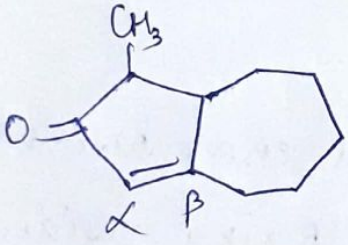
One =bond extending conjugation = +30 nm

Homocyclic diene = +39 nm

3 ring residue = +18 nm

Calculated λ_{max} = 302 nm

3)



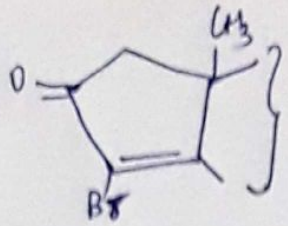
Five membered enone basic value = 202 nm

Two β ring residue = 24 nm

One exocyclic = 5 nm

Calculated λ_{max} = 231 nm

4)



Five membered enone basic value = 202 nm

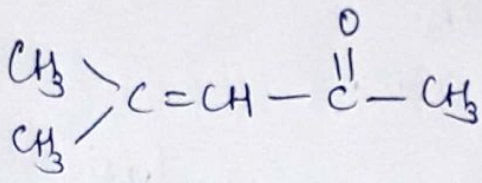
One auxochrome (-Br) at α position = +25 nm

Two β-ring residue 2×12 = +24 nm

One exocyclic = bond = +5 nm

Calculated λ_{max} = 256 nm

5)

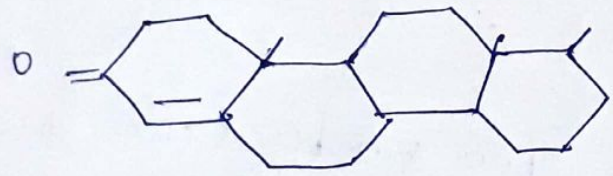


acyclic ketone basic value = 215 nm

Two β-alkyl ring residue = 24 nm

Calculated λ_{max} = 239 nm

6)



Six membered enone basic value = 215 nm

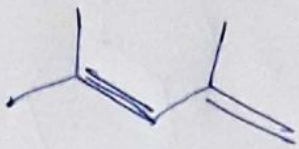
Two β ring residues = 24 nm

One exocyclic bond = +5 nm

λ_{max} = 244 nm

Problems

1)



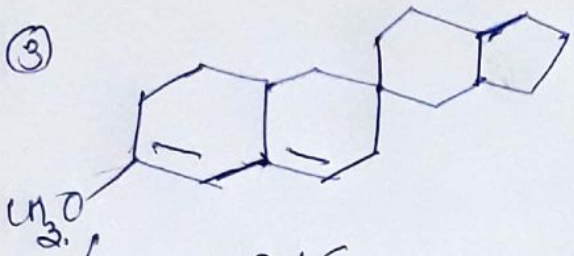
Core = 215 nm
3 alkyl gps = +15 nm
Other = 0
230 nm

Observed = 234 nm

2)

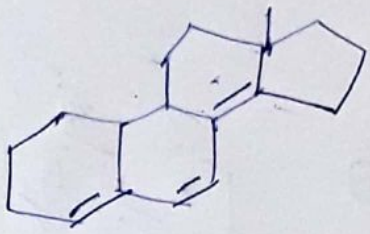
Core = 253 nm
1 alkyl gp = 5 nm
2 ring residue = 10 nm
268 nm

3)



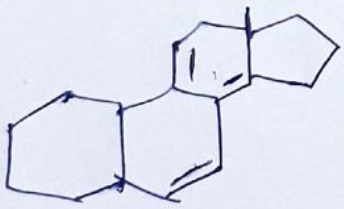
Core = 215 nm
3 ring residues = 15 nm
1 alkoxy gp = 6 nm
Exocyclic = bond = 5 nm
241 nm

4)



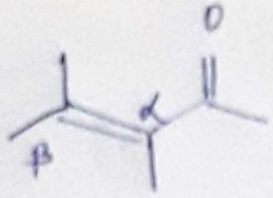
Core = 215 nm
5 ring residues = 25 nm
1 = bond extending conjugation = 30 nm
3 exocyclic bond = +15 nm
285 nm

5)



253 nm
25 nm
exo 15 nm
= bond 30 nm
323 nm

(6)



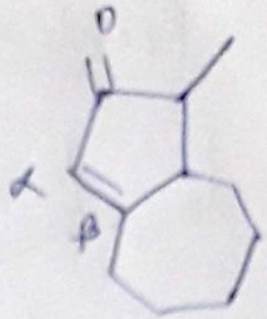
+ 215 nm

1 gp α position 10 nm

2 gp β position 2×12 = 24 nm

249 nm

(7)



Cyclopentenone = 202 nm

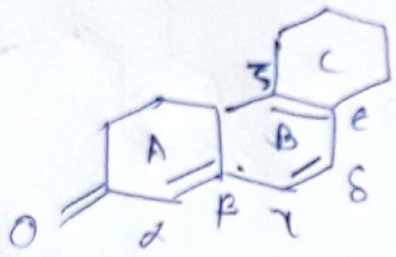
α = –

2 gp β = 24 nm

1 exocyclic = 5 nm

231 nm

(8)



Cyclohexenone 215 nm

α position –

β position 12 nm

γ " –

δ " –

ε position 18 nm

2 gp δ " 60 nm

Homoannular diene system ring B 35 nm

1 exocyclic +5 nm

351 nm

(9)