Spectroscopy

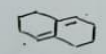
U.V (Lect.2)

Woodward and Fiesers empirical rule

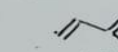
Theortical_Calculation of λ_{max}

* The Calculated value is (±5) actual value applied on (diene) and (enone) systems

diene

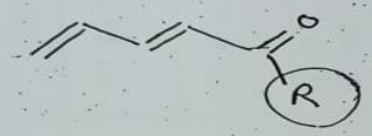
* Base value of diene	217 nm
* Base value of heteroannular diene (trans) 	217 nm
* Base value of Homo annular (cis) 	217+36 nm (253)
* extended conjugation	30
* exocyclic 	5
* alkyl substitution (Ring residue)	5
* OH ∩ OR	6
* Cl ∩ Br	5
* NR_2 / NH_2 / NHR	60
* OCO R	—

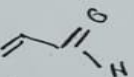
enone

* α,β-unsaturated ketone 	215
* six-membered enone 	215
* Five-membered enone 	205
* extended conjugation	30
* Homo annular	39
* exocyclic double bond	5
* Substitution (depends on position)	

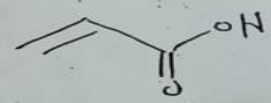
	α	β	γ	δ and higher
alkyl gr.	10	12	18	18
OH, OR	35	35	—	—
NH_2, Cl	20	20	—	—

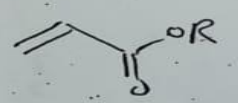
In Case of enones



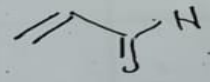
when R = I (unsaturated aldehyde )

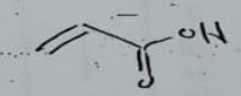
نطرح Substrat 6 nm

when R = OH (acid) 

او R = OR (ester) 

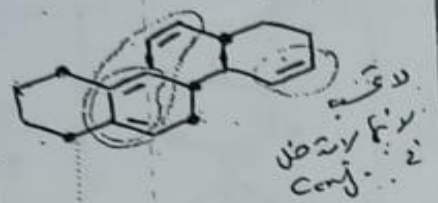
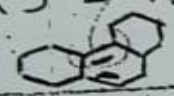
نطرح Substract 20nm

نطرح 6nm  aldehyde حالة *

نطرح 20nm {  acid او ester حالة *

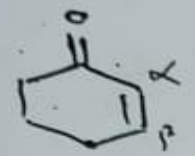
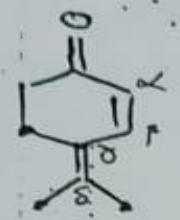
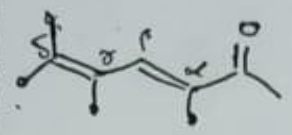
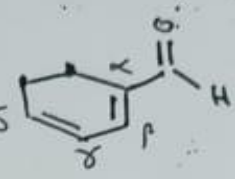
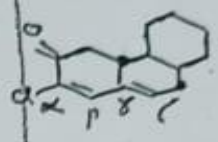
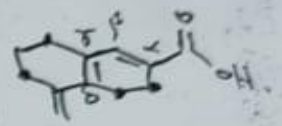
λ_{max}

Examples

Woodward Fieser rule					
Parent diene	217 + 36 = 253	217 + 36 = 253	217	217 + 36 = 253	217 + 36 = 253
extended Conjugation	—	1 X 30 = 30	1 X 30 = 30	1 X 30 = 30	1 X 30 = 30
Exocyclic double bond	2 X 5 = 10	3 X 5 = 15 	2 X 5 = 10	1 X 5 = 5	2 X 5 = 10
Ring residue	4 X 5 = 20	5 X 5 = 25	4 X 5 = 20	3 X 5 = 15	① Cl 5 ① OR 6 ④ alkyl 4 X 5 = 20
λ_{max} Calculated	283 nm	323 nm	277 nm	303 nm	324 nm

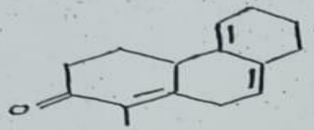
Woodward rule

Examples

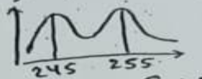
						
Base value	215 nm	215 nm	215 nm	215 nm	215 nm	215 nm
extended Conjugation	—	1X30 = 30 nm	1X30 = 30 nm	1X30 = 30	1X30 = 30	2X30 = 60
Homo annular	—	—	—	1X39 = 39	—	1X39 = 39
Exocyclic	—	1X5 = 5 nm	—	—	1X5 = 5	1X5 = 5
Ring residue	α β γ — 1 — 1X12 = 12 nm	α β γ and higher — — 3 3X18 = 54	α β γ and higher 1 3 1X10 = 10 3X18 = 54	α β γ 1 — 1 1X16 = 16 1X18 = 18	α β γ ① Cl — 2 1X20 = 20 2X18 = 36	α β γ 1 — 3 1X16 = 6 3X18 = 54
λmax	227 nm	304 nm	309 nm	aldehyde — 6 λmax = 312 - 6 =	306 nm	acid — 20 λmax = 383 - 20 = 363

(17)

ex



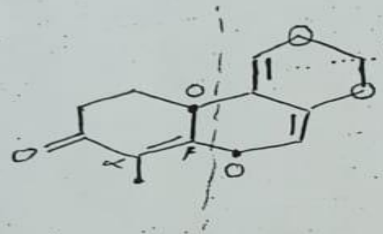
This molecule gives 2 peaks why ??



* Because it has enones and diene systems

* اذا كان Conjugation غير متصل نحسب كل واحد على حده.

* اذا كان Conj. متصل نحسب enones



enone Calculation

* parent value = 215
* extended Conjugation —
* Homo annular —
* exocyclic 1x5 = 5
* Ring residue

α	β	γ
1	2	—

1x10 = 10
2x12 = 24

λmax = 254 nm

diene Calculation

* parent value = 217
* extended Conj. = —
* exocyclic 2x5 = 10
* Ring residue 4x5 = 20

λmax 247 nm