

Spectroscopy

U.V (Lect.2)



Woodward and Fieser empirical rule

Theoretical Calculation of λ_{max}

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

diene

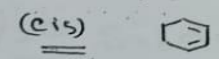


* Base value of diene 217 nm

* Base Value of heteroannular diene 217 nm



* Base value of Homo annular (cis) 217+36 nm (253)



* extended conjugation 30

* exocyclic C1=CC=C1C=C 5

* alkyl substitution (Ring residue) 5

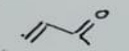
* OH or OR 6

* Cl or Br 5

* NR₂, NH₂, NHR 60

* OCO R -

enone



* α,β -unsaturated ketone 215

* six-membered enone C1=CC(=O)C=CC1 215

* Five-membered enone C1=CC(=O)C=C1 205

* extended conjugation 30

* Homo annular 39

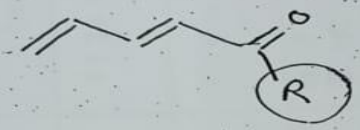
* exocyclic double bond 5

* Substitution (depends on position)

	α	β	γ	δ and higher
alkyl or	10	12	18	18
OH, OR	35	35	-	-
NH ₂ , Cl	20	20	-	-



In Case of Enones



When R = H (unsaturated aldehyde) C=C=C(H)C(=O)H
2^o Substrat 6 nm

when R = OH (acid) C=C=C(OH)C(=O)OH

or R = OR (ester) C=C=C(OR)C(=O)OR

2^o Substrat 2 nm

6 nm 2^o C=C=C(H)C(=O)H aldehyde 2^o X

2 nm 2^o C=C=C(OH)C(=O)OH acid 2^o X

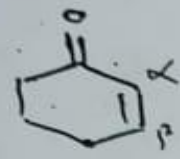
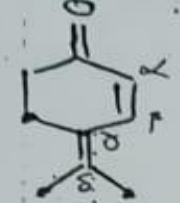
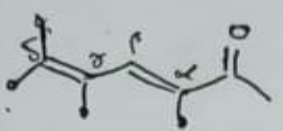
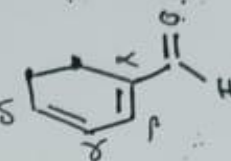
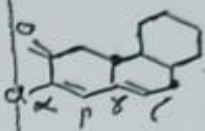
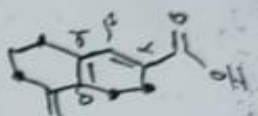
2 nm 2^o C=C=C(OR)C(=O)OR ester 2^o X



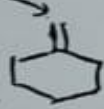
Examples

Woodward Fieser rule					
Parent diene	$217 + 36 = 253$	$217 + 36 = 253$	217	$217 + 36 = 253$	$217 + 36 = 253$
extended conjugation	—	$1 \times 30 = 30$	$1 \times 30 = 30$	$1 \times 30 = 30$	$1 \times 30 = 30$
Exocyclic double bond	$2 \times 5 = 10$	$3 \times 5 = 15$ 	$2 \times 5 = 10$	$1 \times 5 = 5$	$2 \times 5 = 10$
Ring residue	$4 \times 5 = 20$	$5 \times 5 = 25$	$4 \times 5 = 20$	$3 \times 5 = 15$	<ul style="list-style-type: none"> ⓐ Cl 5 ⓑ OR 6 ⓒ alkyl 4 $\times 5 = 20$
λ_{max} calculated	283 nm	323 nm	277 nm	303 nm	324 nm



Woodward rule						
<u>rule</u>						
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
Homoannular	—	—	—	1X39 = 39	—	1X39 = 39
<u>Exocyclic</u>	—	1X5 = 5 nm	—	—	1X5 = 5	1X5 = 5
Ring residue	α — β 1 γ — $1 \times 12 = 12$ nm	α — β — γ and high 3 $3 \times 18 = 54$	α 1 β — γ 3 $1 \times 10 = 10$ $3 \times 18 = 54$	α 1 β — γ 1 $1 \times 6 = 6$ $1 \times 18 = 18$	α ① — β 2 γ — $1 \times 20 = 20$ $2 \times 18 = 36$	α 1 β — γ 3 $1 \times 6 = 6$ $3 \times 18 = 54$
λ_{max}	227 nm	304 nm	309 nm	aldehyde -6 312 - 6 = 306 nm	306 nm	acid -20 $\lambda_{max} = 383 - 20 = 363$

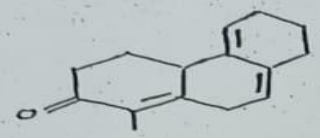
Exocyclic



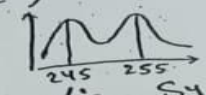
Examples



67

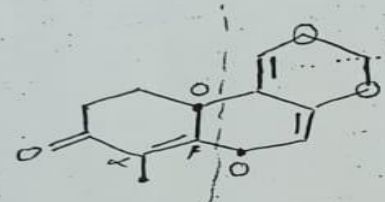


This molecule gives 2 peaks why??



* Because it has enones and diene systems

Conjugation ~ 131 *
 cis trans is
 one for each
 trans Conj. ~ 131 *
 enones ~ 131



Enone Calculation

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

	α	β	γ
	1	2	—
	1x10 = 10		
	2x12 = 24		

$\lambda_{max} = 254 \text{ nm}$

diene Calculation

- * parent value = 217
 - * extended Conj. = —
 - * exocyclic 2x5 = 10
 - * Ring residue 4x5 = 20
- $\lambda_{max} = 247 \text{ nm}$

