

Spectroscopy

U.V (Lect.2)



Woodward and Fieser empirical rule

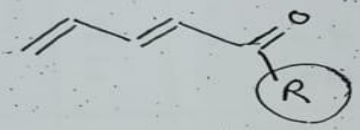
Theoretical Calculation of λ_{max}

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

<u>diene</u>	<u>enone</u>																				
* Base value of diene <chem>C=CC=C</chem> 217 nm	* α, β -unsaturated ketone <chem>C=CC(=O)C</chem> 215																				
* Base value of heteroannular diene <chem>C1=CC=CC=C1</chem> 217 nm	* Six-membered enone <chem>C1=CC(=O)CCC1</chem> 215																				
* <u>(trans)</u> Base value of Homoannular diene <chem>C1=CC=CC=C1</chem> 217 + 36 nm (253)	* Five-membered enone <chem>C1=CC(=O)CC1</chem> 205																				
* <u>(cis)</u> Base value of Homoannular diene <chem>C1=CC=CC=C1</chem> 217 + 36 nm (253)	* extended conjugation 30																				
* extended conjugation 30	* Homoannular 39																				
* exocyclic <chem>C1=CC(=O)C1</chem> 5	* exocyclic double bond 5																				
* alkyl substitution (Ring residue) 5	* Substitution <u>depends on position</u>																				
* OH or OR 6	<table border="1"> <thead> <tr> <th></th> <th>α</th> <th>β</th> <th>γ</th> <th>δ and higher</th> </tr> </thead> <tbody> <tr> <td>alkyl or</td> <td>10</td> <td>12</td> <td>18</td> <td>18</td> </tr> <tr> <td>OH, OR</td> <td>35</td> <td>35</td> <td>-</td> <td>-</td> </tr> <tr> <td>NH₂, Cl</td> <td>20</td> <td>20</td> <td>-</td> <td>-</td> </tr> </tbody> </table>		α	β	γ	δ and higher	alkyl or	10	12	18	18	OH, OR	35	35	-	-	NH ₂ , Cl	20	20	-	-
	α	β	γ	δ and higher																	
alkyl or	10	12	18	18																	
OH, OR	35	35	-	-																	
NH ₂ , Cl	20	20	-	-																	
* Cl or Br 5																					
* NR ₂ , NH ₂ , NHR 60																					
* OCO R -																					



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 1^o 2^o X

2 nm 2^o C=C=C(OH)C(=O)OH acid 1^o 2^o X

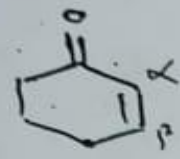
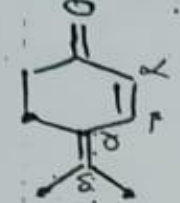
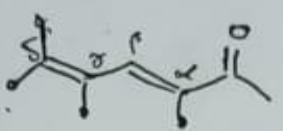
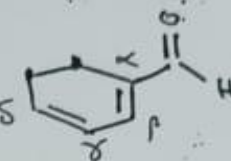
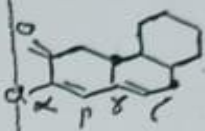
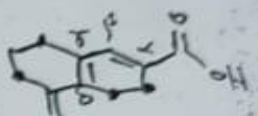
2 nm 2^o C=C=C(OR)C(=O)OR ester 1^o 2^o X

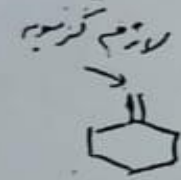


Examples

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



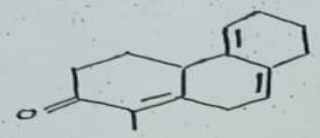
Woodward rule						
<u>rule</u>						
Base value	215 nm	215 nm	215 nm	215 nm	215 nm	215 nm
extended conjugation	—	1x30 = 30 nm	1x30 = 30 nm	1x30 = 30	1x30 = 30	2x30 = 60
Homoannular	—	—	—	1x39 = 39	—	1x39 = 39
<u>Exocyclic</u>	—	1x5 = 5 nm	—	—	1x5 = 5	1x5 = 5
Ring residue	α — β 1 γ — $1 \times 12 = 12$ nm	α — β — γ and δ high 3 $3 \times 18 = 54$	α 1 β — γ and δ high 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 — γ 2 $1 \times 20 = 20$ $2 \times 18 = 36$	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 $\lambda_{max} = 383 - 20 = 363$



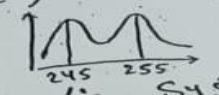
Examples



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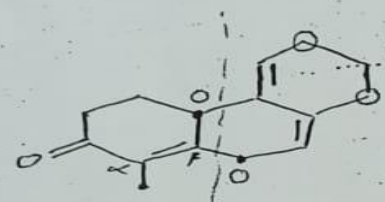


This molecule gives 2 peaks why??



* Because it has enones and diene systems

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



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
- $\lambda_{max} = 247 \text{ nm}$

