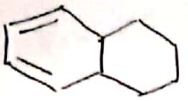
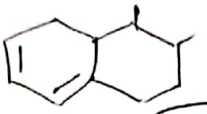
Woodward-Fieser Rules for Conjugated Dienes

(1) **Alicyclic dienes** – Dienes contained in an open chain system. Butadiene is the basic unit.

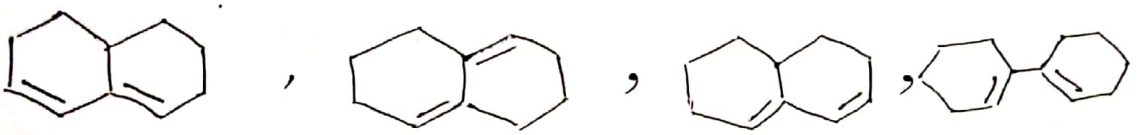
λ_{max} = 217 nm

(2) **Homoannular diene** – It is a cyclic diene in which double bonds are in conjugation within the same ring.

eg  or 

Basic value of λ_{max} = 253 nm

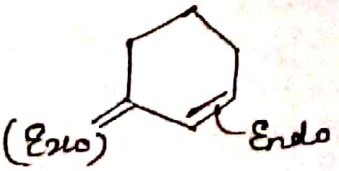
(3) **Heteroannular dienes** – Double bonds are in conjugation and in different ring

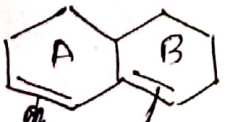


λ_{max} = 214 nm.

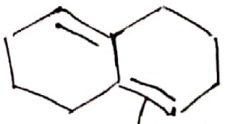
(4) **Exocyclic and Endocyclic double bond** –

Exocyclic double bond refers to a double bond in which a doubly bonded atom is the part of a ring system.





(Exocyclic double bond to ring A)



C contains 2 exocyclic double bo

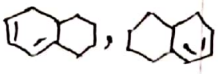
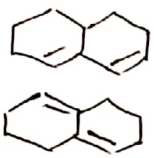
Parent Values

(i) Butadiene = 217 nm
(ii) Cyclic Conjugated diene = 217 nm
(iii) Acyclic triene = 245 nm
(iv) Homoannular Conj. diene = 253 nm
(v) Heteroannular diene = 215 nm

Increment for each Substituent

(i) Alkyl substituent or ring residue = 5nm
(ii) Exocyclic double bond = 5nm
(iii) Double bond extending conjugation = 30nm

Woodward Fieser Rules for Diene & Triene

	Base Value
Acyclic Diene >C=C–C=C<	217 nm
Acyclic Triene	245 nm
Homoannular diene 	253 nm
Heteroannular diene 	214 nm

Addition for each Substituent

–R alkyl or ring residue	5nm
–OR (alkoxy)	6 nm
Exocyclic double bond to one ring 	5 nm
Exocyclic double bond (to 2 rings)	10 nm
Double bond extending Conjugation	30nm

Auxochrome

–OR	6nm
–SR	30 nm
–Cl, –Br	5 nm
$-NR_2$	60 nm
$-OCOCH_3$	0nm

Auxochrome

(i)	$-OR$	+6 nm
(ii)	$-SR$	+30 nm
(iii)	$-Cl$, $-Br$	+5 nm
(iv)	$-NR_2$	+60 nm
(v)	$-OCOCH_3$	0 nm.

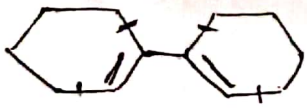
Calculation of λ_{max} using Woodward Fieser Rule -

① $CH_3+CH=CH-CH=CH+CH_3$

Basic Value = 217

(2) alkyl substituents (2×5) = 10

Calculated λ_{max} = 227 nm

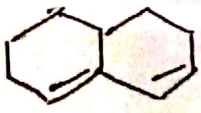
②  heteroannular diene

Basic value for heteroannular diene = 215

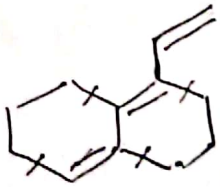
ring residue (4×5) = 20

Calculated value λ_{max} = 235 nm

Observed value λ_{max} = 236 nm

③  or 

λ_{max} = 235 nm



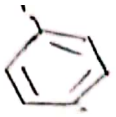
B.V = 215

double bond extending conjugation = 30

ring residue = 20

exocyclic double bond =

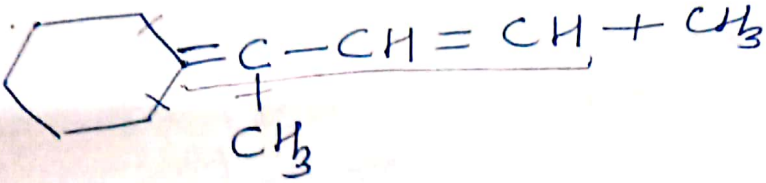
λ_{max} = 275 nm

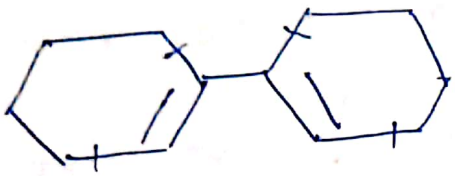


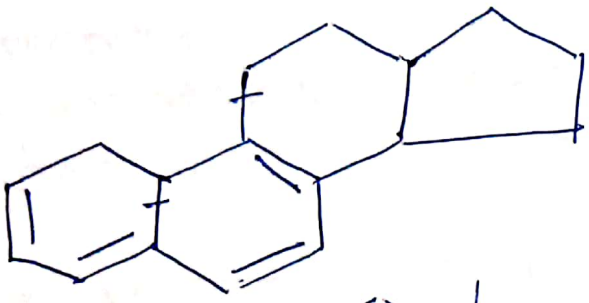
line

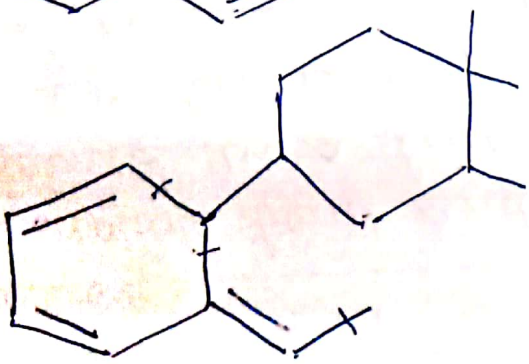
Questions on Woodward's Fiesers Rule

1. $CH_3 + CH = CH - CH = CH + CH_3$ 227

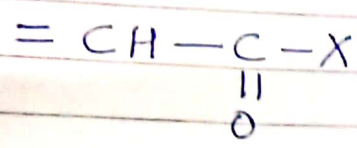
2.  24

3.  2

4.  34

5. 

Woodward Fieser Rule for α-β unsaturated Carbonyl Compounds



If X = alkyl group (Ketone); base value = 215 nm
X = H (aldehyde) ; " " = 207 nm
X = OH (Carboxylic acid); " " = 193 nm

If the double bond and the carbonyl group are contained in a five membered ring (cyclopentanone), then for such α,β unsaturated ketone base value becomes 202 nm.

⇒ The structural increments for estimating λmax for a given α,β unsaturated Carbonyl comp. are as follows —

(i) For each exocyclic double bond +5 nm

(ii) For each alkyl substituent or ring residues at

α-position	+10 nm
β-position	+12 nm
γ or β-position	+18 nm

(iii) For each double bond extending conjugation = +30

(iv) For a homoannular conjugated diene = +39

Teacher's Signature : _____

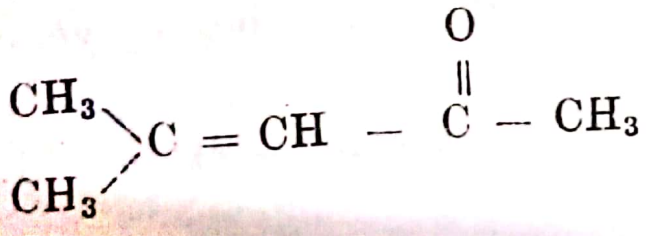
etc. positions

Table T_2—9

Chromophore	Increment in nm (or $m\mu$) for position w. r. t. the carbonyl group			
	α-	β-	γ-	δ- or higher
—OH	+35	+30	—	+50
—OAc	+6	+6	+6	+6
—Cl	+15	+12	—	—
—Br	+25	+35	—	—
—OR	+35	+30	17	31
—SR	—	+85	—	—
—NR_2	—	+95	—	—

Making use of the above rules, the absorption maximum for the various α, β-unsaturated compounds can be estimated.

Example 1. Calculate λ_{max} (Ethanol) for the given structure :

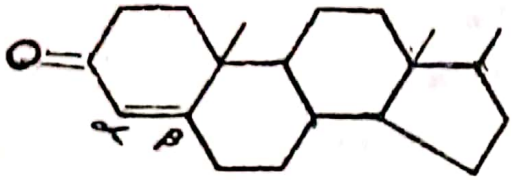


The basic value for a cyclic α. β-unsaturated ketone is 215 $m\mu$. In this structure, we see two β—alkyl substituents. The value of absorption maximum is thus calculated as :

Basic value	$= 215\ m\mu$
2β-alkyl substituents (2×12)	$= 24\ m\mu$
Calculated value	$= 239\ m\mu$.

The observed value is found to be 237$m\mu$ $\in_{max}$ 12,500.

Example 2. Calculate λ_{max} for the structure.

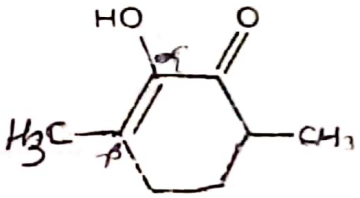


Basic value	$= 215 m\mu$
2β-ring residues (2×12)	$= 24 m\mu$
1 exocyclic double bond	$= 5 m\mu$
Calculated value	$= 244 m\mu$

The observed value is found to be 241 $m\mu$.

Example 3. Calculate λ_{max} for the structure.

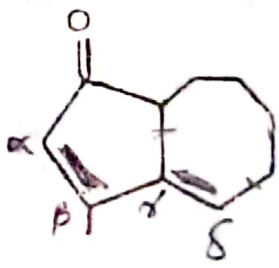
Basic value	$= 215\ m\mu$
OH substitution at α-position	$= 35\ m\mu$
2β-substituents (one alky and one ring residue)	$= 24\ m\mu$
Calculated value	$= 274\ m\mu$
Observed value	$= 275\ m\mu$



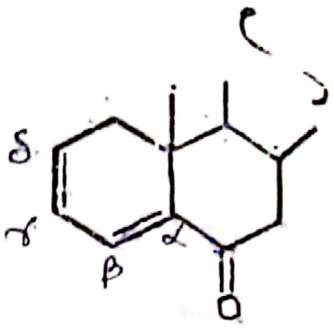
Example 4. Calculate λ_{max} for the structure.

It is an α β-unsaturated cyclopentenone system.

Basic value	$= 202\ m\mu$
1 β-alkyl substitution	$= 12\ m\mu$
1 exocyclic double bond	$= 5\ m\mu$
1 double bond extending conjugation	$= 30\ m\mu$
1 γ-ring residue	$= 18\ m\mu$
1 δ-ring residue	$= 18\ m\mu$
Calculated value	$= 285\ m\mu$
Observed value	$= 287\ m\mu$

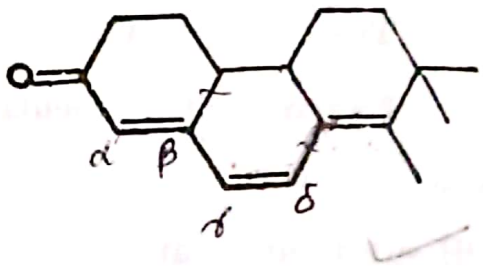


Example 5. Calculate λ_{max} for the structure



Basic value	= 215 $m\mu$
α-ring residue	= 10 $m\mu$
δ-ring residue	= 18 $m\mu$
1 exocyclic double bond	= 5 $m\mu$
Homoannular conjugated diene	= 39 $m\mu$
1 double bond extending conjugation	= 30 $m\mu$
Calculated value	= **317** $m\mu$
Observed value	= 319 $m\mu$

Example 6. Calculate λ_{max} for the structure



Basic value	= 215 $m\mu$
1 β-ring residue	= 12 $m\mu$
1 (δ+2) ring residue	= 18 $m\mu$
2 (δ+2) ring residues (2×18)	= 36 $m\mu$
2 double bonds extending conjugation (2×30)	= 60 $m\mu$
2 exocyclic double bonds (2×5)	= 10 $m\mu$
Calculated value	= **351** $m\mu$
Observed value	= 354 $m\mu$

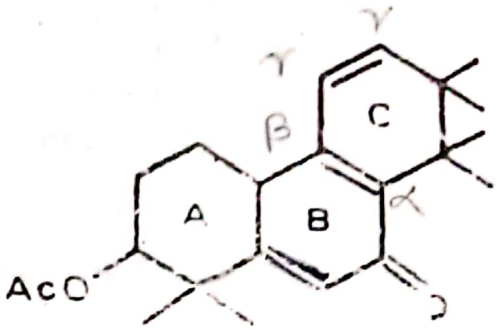
It may be noted that the value of absorption maximum is shifted due to the change in the polarity of the solvent, *i.e.*, absorption maximum is solvent dependant. More polar solvents will experience hydrogen bonding with the carbonyl group and $n \rightarrow \pi^*$ transition will experience blue shift. Solvent corrections may be noted as follows :

Hexane	= +11 $m\mu$
Dioxane	= + 7 $m\mu$
Methanol	= 0 $m\mu$
Water	= − 8 $m\mu$
Chlotoform	= − 1 $m\mu$

After making the necessary solvent corrections the value of absorption maximum is obtained in ethanol.

In case there is a cross conjugation in a compound, *i.e.*, the carbonyl group has α, β-unsaturation on either side; then the value of absorption maximum is estimated by considering the most highly substituted conjugated system. Consider the following example.

In ring B, the carbonyl group is conjugated on either side but conjugated system is highly substituted towards ring C. Thus, the value of absorption maximum is calculated as follows :



Basic value	=	215 $m\mu$
1 α-ring residue	=	10 $m\mu$
1 β-ring residue	=	12 $m\mu$
1 δ-ring residue	=	18 $m\mu$
1 double bond extending conjugation	=	30 $m\mu$
Homoannular conjugation diene	=	39 $m\mu$
Calculated value	=	**324 $m\mu$**
Observed value	=	**327 $m\mu$**

For such compounds, the value of the extinction coefficient is usually high.

$\pi \rightarrow \pi^*$ transitions are respon-