1.14.1. WOODWARD–FIESER RULES FOR CALCULATION OF λ_{max} FOR π–π^* (TRANSITION) ABSORPTION BAND OF α, β-UNSATURATED CARBONYL COMPOUNDS : ENONES

We have discussed above that when a double bond is conjugated with a carbonyl group, it gives two absorption bands—an intense ($\in = 8{,}000 - 20{,}000$) absorption band in the region 220–250 nm due to π-π^* transition and a weak ($\in = 50\text{-}100$) absorption in the region 310-330 nm due to n-π^* transition. While the π-π^* transition is affected in a predictable manner by structural modification of the chromophore, n-π^* transition does not show this predictable behaviour.

Woodward and Fieser examined the UV spectra of a number of α, β-unsaturated compounds in ethanol and formulated a set of empirical rules which help us to predict the λ_{max} of π-π^* transition in an unknown compound. These rules are summarised in Table 1.6.

Solvent correction. Since π-π^* absorption band is strongly affected by polarity of the solvent, therefore, to convert λ_{max} values obtained in other solvents to standard ethanol solvent, the following solvent corrections have been proposed.

Solvent	Correction	Solvent	Correction
Methanol	0	Cyclohexane	+ 11
Chloroform	+ 1	Dioxan	+ 5
Ether	+ 7	Water	− 8
Hexane	+ 11		

TABLE 1.6. Rules for calculating the λ_{max} of $\pi–\pi^*$ (transition) absorption band of α, β-unsaturated carbonyl compounds (solvent ethanol).
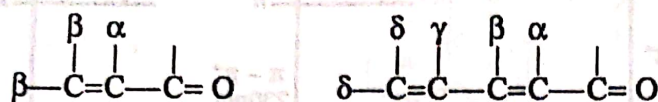
Base values :

(i) α, β-unsaturated acyclic or six-membered ring ketone	215 nm
(ii) α, β-unsaturated five-membered ring ketone	202 nm
(iii) α, β-unsaturated aldehydes	207 nm
(iv) α, β-unsaturated acids or esters	197 nm

Increments :

(i) Each alkyl group or ring residue

α	10 nm
β	12 nm
γ and higher	18 nm
(ii) Each double bond extending conjugation	30 nm
(iii) Each exocyclic double bond	5 nm
(iv) Homoannular diene component	39 nm

(*i.e.* two double bonds which are conjugated with C = O group lie in the same ring)

(v) Auxochromes :

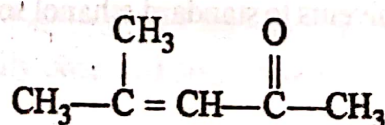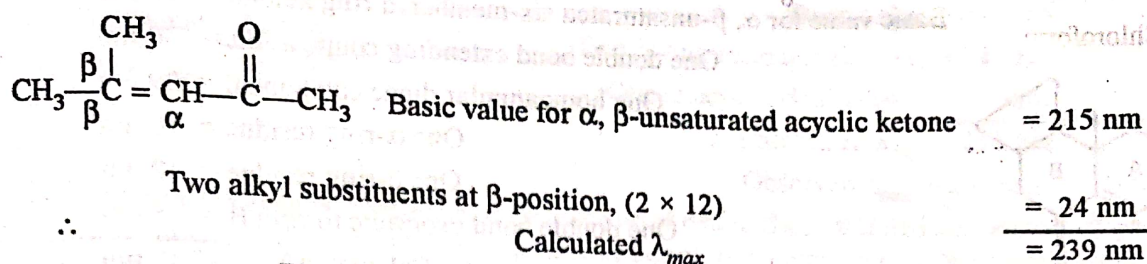|	Position			
	α	β	γ	δ
—OH, Hydroxy	35 nm	30 nm	30 nm	50 nm
—OR, Alkoxy	35 nm	30 nm	17 nm	31 nm
—OCOCH₃, Acetoxy	α = β = γ = δ = 6 nm			
—Cl	15 nm	12 nm	—	—
—Br	25 nm	30 nm	—	—
—NH₂	—	95 nm	—	—

(vi) solvent correction | | | | variable

$$\lambda_{max}^{EtOH} \text{ (calc.) = Total}$$

These rules are illustrated by the following examples.

**Example 5.** *Calculate λ_{max} for the following compound*

$$CH_3-\underset{\underset{CH_3}{|}}{C} = CH - \underset{\overset{||}{O}}{C} - CH_3$$

Solution. The given compound is an α, β-unsaturated ketone having two alkyl subtituents (*i.e.* methyl) at β-position.

$$CH_3-\underset{\beta}{\overset{\overset{\displaystyle CH_3}{\overset{\displaystyle |}{\underset{\beta}{C}}}}{C}}=\underset{\alpha}{CH}-\overset{\overset{\displaystyle O}{\parallel}}{C}-CH_3$$

Basic value for α, β-unsaturated acyclic ketone = 215 nm

$\therefore$ Two alkyl substituents at β-position, (2×12) = 24 nm

Calculated λ_{max} = 239 nm

The observed value is 237 nm ($\in_{max}$ = 12,500)

Example 6. *Calculate the λ_{max} for the following compounds*

I II III IV V
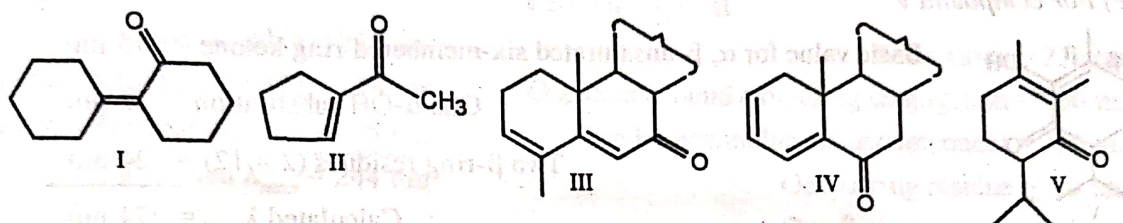
Solution. (*a*) *For compound I*

I
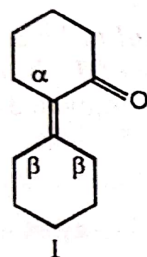
Basic value = 215 nm

One α-ring residue (1×10) = 10 nm

Two β-ring residues (2×12) = 24 nm

One double bond exocyclic to two rings (2×5) = 10 nm

$\therefore$ Calculated λ_{max} = 259 nm

Observed λ_{max} = 256 nm

(*b*) *For compound II*

II
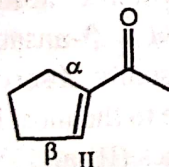
Basic value for α, β-unsaturated acyclic ketone = 215 nm

One α-ring residue = 10 nm

One β-ring residue = 12 nm

$\therefore$ Calculated λ_{max} = 237 nm

(*c*) *For compound III*
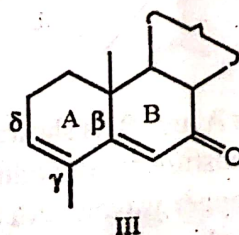
III

Basic value for α, β-unsaturated six-membered ring ketone = 215 nm

One double bond extending conjugation = 30 nm
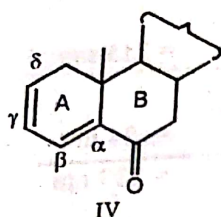
One double bond exocyclic to ring A = 5 nm

One β-ring residue = 12 nm

One γ-ring residue = 18 nm

One δ-ring residue = 18 nm

$\therefore$ Calculated λ_{max} = 298 nm

(d) For compound IV

Basic value for α, β-unsaturated six-membered ring ketone = 215 nm

One double bond extending conjugation = 30 nm

One homoannular diene component = 39 nm
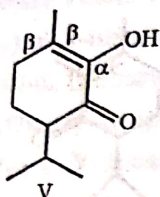
One α-ring residue = 10 nm

One δ-ring residue = 18 nm

One double bond exocyclic to ring B = 5 nm

$\therefore$ Calculated λ_{max} = 317 nm

Observed λ_{max} = 319 nm

(e) For compound V

Basic value for α, β-unsaturated six-membered ring ketone = 215 nm

One α-OH substitution = 35 nm

Two β-ring residues (2 × 12) = 24 nm

$\therefore$ Calculated λ_{max} = 274 nm

1.14.2. LINEARLY AND CROSS-CONJUGATED ENONES

If the two or more double bonds lie only on one side of the keto group, it is said to be a linearly conjugated enone and if, on the other hand, one or more double bonds lie on either side of the keto group, it is said to be a cross-conjugated enone. For example, structure (I) represents a linearly conjugated dienone while structure (II) represents a cross-conjugated dienone.
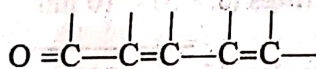
I

Linearly conjugated dienone
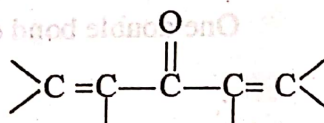
II

Cross-conjugated dienone

Thus, a cross-conjugated dienone contains a branched chromophore. Such systems contain two overlapping α, β-unsaturated ketonic chromophores, each one of which will give its own π-π^* absorption band with a high extinction coefficient. But due to band nature of the spectra, only that α, β-unsaturated ketonic chromophore which absorbs at longer wavelength with higher intensity is usually observed. In other words, in cross-conjugated systems, the longest wavelength absorption band is due to the most highly substituted simple conjugated system present. For example, consider the steroidal enones (III and IV)
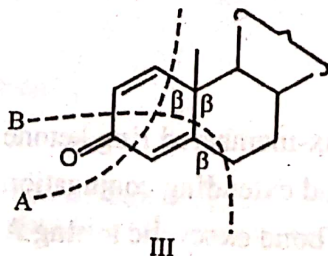
III
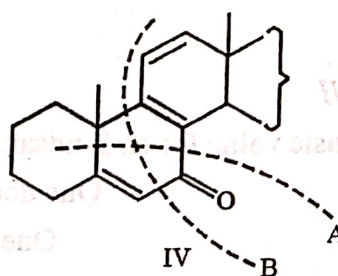
IV

Dienone (III) may be regarded to consist of two α, β-unsaturated chromophores A and B as shown by dotted lines. Whereas dienone A has only one β-substituent, dienone B has two β-substituents in addition to an exocyclic double bond. Therefore, chromophore B is expected to absorb at a longer wavelength and hence, for the purpose of calculating the λ_{max}, we consider the most highly conjugated system B.

Chromophore A

Basic value = 215 nm

One β-ring residue = 12 nm

∴ Calculated λ_{max} = 227 nm

Chromophore B

Basic value = 215 nm

Two β-ring residues, (2 × 12) = 24 nm

One exocyclic double bond = 5 nm

∴ Calculated λ_{max} = 244 nm

Observed λ_{max} = 246 nm (ε 15000)

Similarly trienone (IV) can be considered to be made up of two α, β-unsaturated ketonic chromophores A and B. Since chromophore B has two conjugated double bonds, one homoannular diene component, one α, one β and one δ-ring residue, it is expected to absorb at a longer wavelength than chromophore A as calculated below :

Chromophore A

Basic value = 215 nm

Two β-ring residues, (2 × 12) = 24 nm

One exocyclic double bond = 5 nm

∴ Calculated λ_{max} = 244 nm

Chromophore B

Basic value = 215 nm

One double bond extending conjugation = 30 nm

One homoannular diene component = 39 nm

One α-ring residue = 10 nm

One β-ring residue = 12 nm

One δ-ring residue = 18 nm

Calculated λ_{max} = 324 nm

PROBLEMS FOR PRACTICE

1. On the basis of Woodward–Fieser rules, calculate λ_{max} for the following compounds :
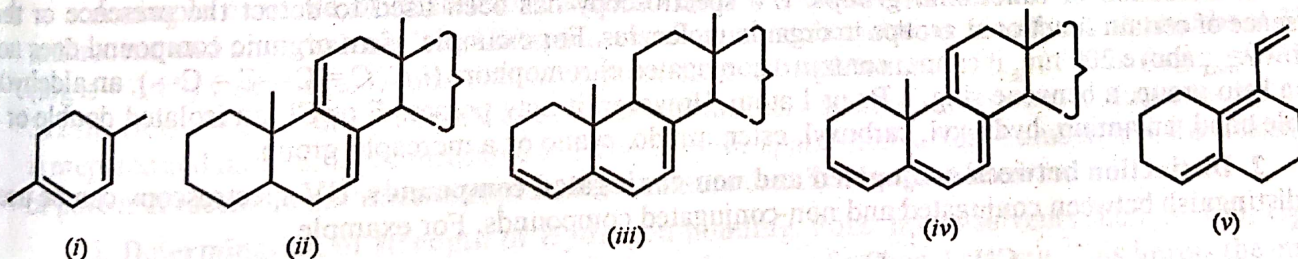
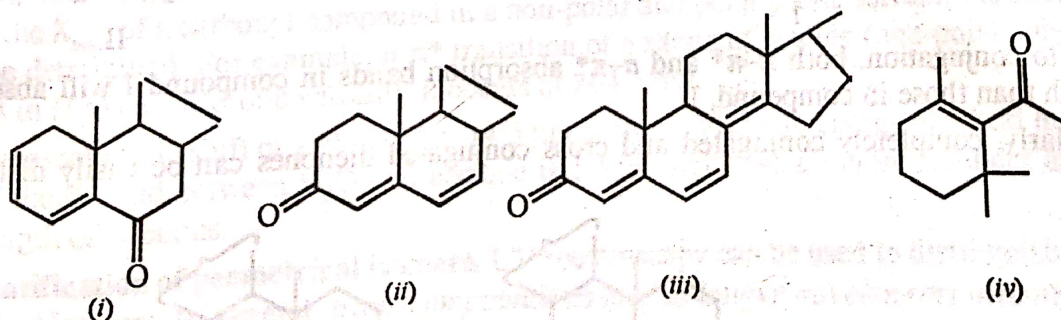   (i) Methyl vinyl ketone

   (ii) 2-Cyclopentenone

   (iii) 2-Methyl-1-acetylcyclopentene

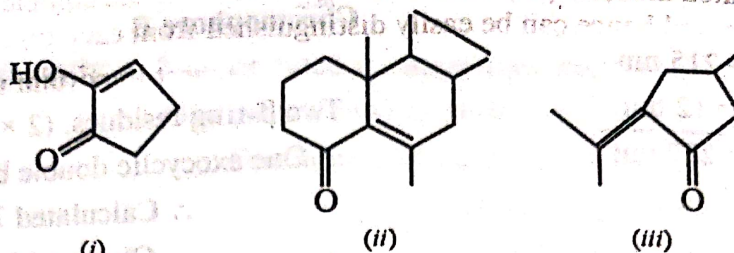   (iv) 3, 4-Dimethylpent-3-en-2-one

2. Calculate the λ_{max} for the most intense band for the following dienes and polyenes.


(i)   (ii)   (iii)   (iv)   (v)

3. The following enones have λ_{max} at 284 nm (ε = 28000), 315 nm (ε = 7000) and 348 nm (ε = 26500), 249 nm (ε = 13000) in ethanol. Which is which ?

(i)   (ii)   (iii)   (iv)

4. The following α, β-unsaturated ketones have λ_{max} 241 nm (ε = 4700) 249 nm (ε = 9500) and 259 nm (ε = 10790) in ethanol. Which is which ?

(i)   (ii)   (iii)

5. α-Cyperone is expected to have either structure I or II. Its UV spectrum shows λ_{max} at 252 nm. Predict its actual structure.

I   II
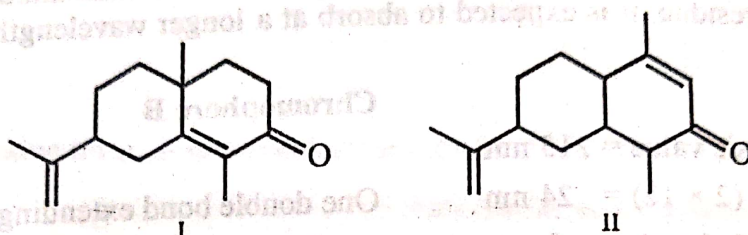
ANSWERS

1. (i) 215 nm (ii) 214 nm (iii) 249 nm (iv) 249 nm

2. (i) 273 nm (ii) 244 nm (iii) 313 nm (iv) 353 nm (v) 274 nm

3. (i) 315 nm (ii) 284 nm (iii) 348 nm (iv) 249 nm

4. (i) 249 nm (ii) 254 nm and (iii) 241 nm.

5. Actual structure is I since II will absorb at 239 nm.