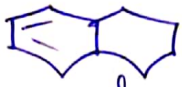
Cyclic dienes

Cyclic dienes are of two types :—

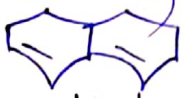
1) Homoannular dienes 2) Heteroannular dienes

1 Homoannular dienes — Conjugated dienes in which the two double bonds are present in the same ring are called homoannular dienes. (Cisoid orientation)

2 Heteromuclear dienes — Conjugated dienes in which the two double bonds are present in diffrant rings are called heteroannular dienes - (transoid orientation)



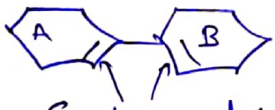
Homoannular diene
λ_{max} - 263nm



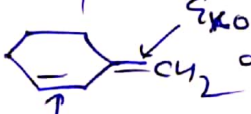
Heteroannular diene
λ_{max} - 234nm

Effect of endocyclic & exocyclic double bonds on the absorption maxima of dienes

A double bond is said to be exocyclic if it lies within a particular ring and exocyclic if it lies outside a particular ring.



Endocyclic double bonds



Endocyclic double bond

Note :— In general, each exocyclic double bond increases the ~~double~~ wavelength of absorption of a given cyclic conjugated diene by 5nm.

WOODWARD — FIESER Rules for Calculation of λ_{max} of Simple Conjugated dienes

Woodward formulated certain empirical rules for calculating λ_{max} for the long wavelength $\pi - \pi^*$ transition for dienes & polyenes. These rules further modified by Fieser in 1959. According to these rules, each diene has a certain fixed basic value and the value of λ_{max} depends upon the following points

1) The no. of alkyl substituents or ring residues present on the diene system
2) The no. of double bonds extending conjugation beyond the diene system

3. The presence of polar groups or auxochromes (2)
Such as $-X$ (Cl, Br etc) or ($-OR$, NH_2) etc

Rules for calculating λ_{max} of the $\pi-\pi^*$ absorption band of dienes

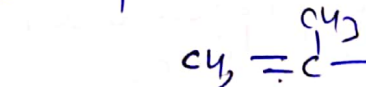
Parent heteroannular or open chain diene	214 nm
Parent homoannular diene	253 nm
for each double bond extending conjugation	add 30 nm
for each alkyl substituent or ring residue	add 5nm
for each exocyclic double bond	add 5nm

Auxochromes

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

Q1 Calculate the λ_{max} for the most intense band in UV spectrum of
1) 2,3-dimethyl-1,3-butadiene
2) 1,4-dimethylcyclohexa-1,3-diene

1 2,3-dimethyl-1,3-butadiene

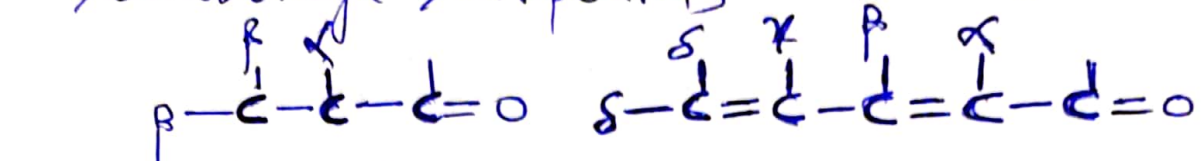


It has two methyl substituents ➔
Parent Value of acyclic diene = 214nm
Two alkyl substituent = 2x5 = 10nm
Calculated → λ_{max} = 214
10
224 nm

2

It is a homoannular diene with the two methyl substituents marked as (a & c) and the two ring residues marked as (b & d)

Woodward-Fiesers rules for calculation of λ_{max} (3)
for $\pi-\pi^*$ absorption band of α,β-unsaturated carbonyl compounds



Base values :-

1) α,β-unsaturated acyclic or six membered ring ketone – 215nm
2) α,β-unsaturated five membered ring ketone – 202nm
3) α,β-unsaturated aldehydes – 207nm
4) α,β-unsaturated acids or esters – 197nm

Increments :

1) Each alkyl group or ring residue
   α – 10nm
   β – 12nm
   γ and higher – 18nm
2) Each double bond extending conjugation – 30nm
3) Each exocyclic double bond – 5nm
4) Homoannular diene component – 39nm

Auxochromes	Positions α	β	γ	δ
–OH	35nm	30nm	50nm	
–OR	35nm	30nm	17nm	31nm
–OCOCH$_3$	6nm	6nm	6nm	6nm
–Cl	15nm	12nm	—	—
–Br	25nm	30nm	—	—
–NH$_2$		95nm		

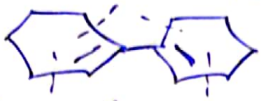
Parent Value of homoannular diene = 253 nm

Two methyl substituents (2×5) = 10nm

Two ring residues (2×5) = 10nm

λ_{max} = 273 nm

Q3 Calculate λ_{max} for diene



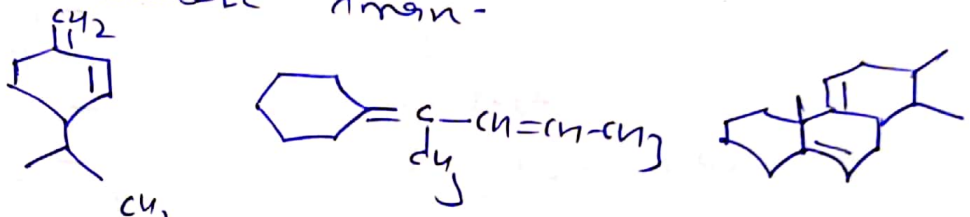
Soln The given compound is heteroannular diene with four ring residues

Parent value of heteroannular diene = 214 nm

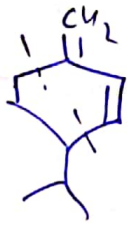
four ring residues (4×5) = 20nm

234 nm

Q4 Calculate λ_{max}.



Soln

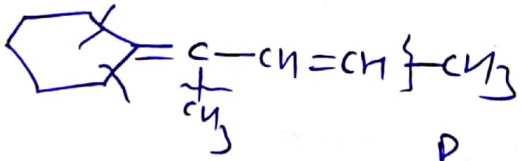


Parent Value of cyclic conjugated diene = 214nm

Two ring residues = (2×5)nm

One exocyclic double bond = 5nm

229 nm



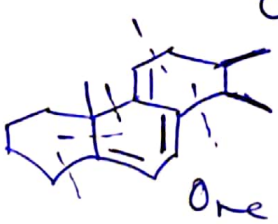
Parent Value = 214nm

Two methyl substituent = 10nm

Two ring residue = 10nm

One exocyclic double bond = 5nm

239 nm



Parent Value = 253 nm

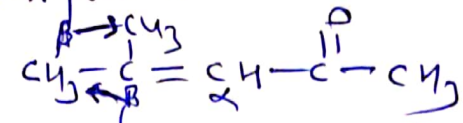
One double bond Extending conjugation = 30nm

five ring residue (5×5) = 25nm

Three exocyclic double bond = 15nm

λ = 323 nm

Q1 Calculate λ_{max} for the following compounds (5)



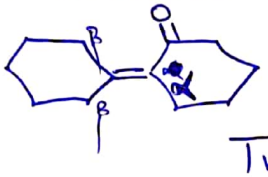
Soln The given compound is α,β-unsaturated ketone having two alkyl substituents at β-positions

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

Two alkyl substituents at β position (2×12) = 24 nm

calculated λ_{max} 239 nm

Q2 Calculate the λ_{max} Value.

1) 

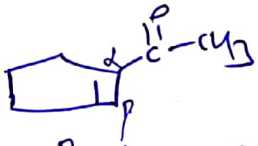
Basic value = 215 nm

One α-ring residue (1×10) = 10nm

Two β-ring residues (2×12) = 24 nm

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

259 nm

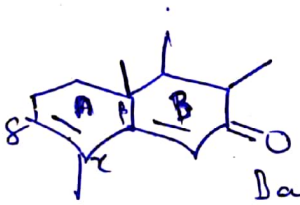
2) 

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

One α-ring residue = 10nm

One β ring residue = 12nm

237 nm

3) 

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

One double bond Extending conjugation = 30nm

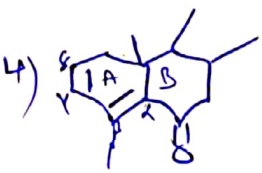
One double bond Exocyclic to ring A = 5nm

One β-ring residue = 12nm

One γ ring residue = 18nm

One δ ring residue = 18nm

296 nm

4) 

Basic = 215nm

One double bond Extending Conjugation = 30nm

One homo annular diene component = 39nm

One α-ring residue = 10nm

One δ ring residue = 18nm

One double bond exocyclic to B = 5nm

Total 317nm