Quadrant II – Transcript and Related Materials

Programme: Bachelor of Science (Second Year)

Subject: Chemistry

Course Code: CHC103

Course Title: Physical and Organic Chemistry (Section B)

Unit: UV-Visible Spectroscopy in Organic Chemistry

Module Name: Woodward - Fieser Calculations of λ_{max} : α,β-unsaturated carbonyls

Name of the Presenter: Dr. Mira V. Parmekar

Notes

Introduction

- In 1945 Robert Burns Woodward gave certain rules for correlating λ_{max} with molecular structure which in 1959, were modified by Louis Frederick Fieser with the help of more experimental data.
- These modified rules are known as **Woodward-Fieser Rules**.
- It is used to calculate the position and λ_{max} for a given structure by relating the position and degree of substitution of chromophore.

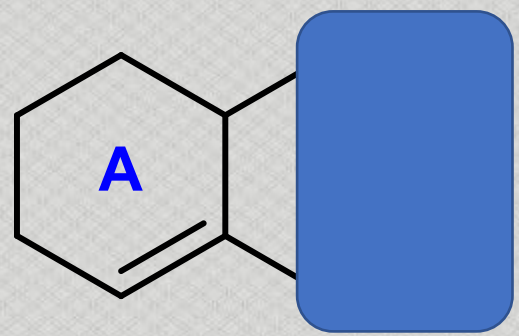
Woodward – Fieser Rules

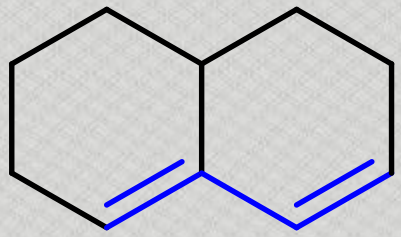
Each α,β-unsaturated carbonyl system has a certain fixed value at which absorption takes place; this constitutes the Base value or Parent value. The contribution made by various alkyl substituents or ring residue, double bond extending conjugation and polar groups such as –Cl, -Br etc are added to this basic value to obtain λ_{max} for a particular compound.

Terminology

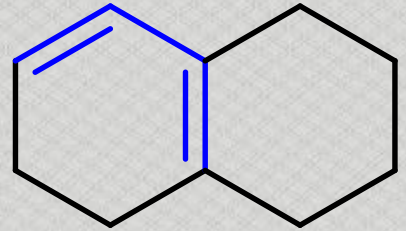
S-trans

S-cis





Heterodiene component



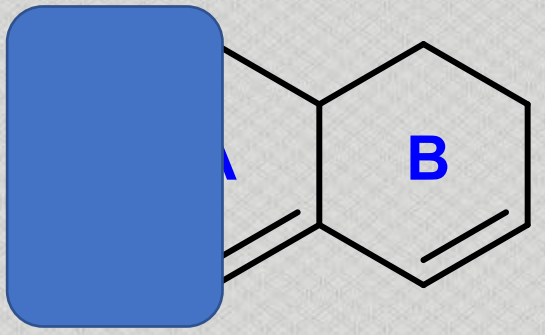
Homodiene component

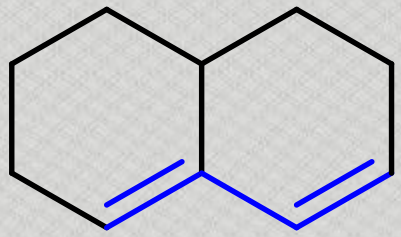
Endocyclic double bond

Terminology

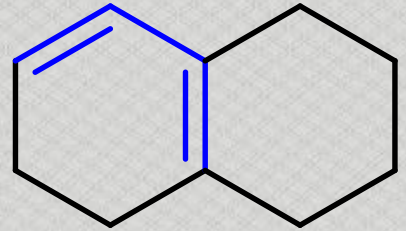
S-trans

S-cis



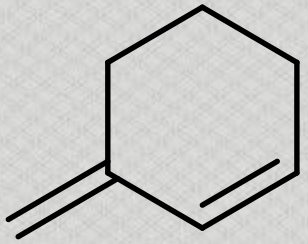


Heterodiene component



Homodiene component

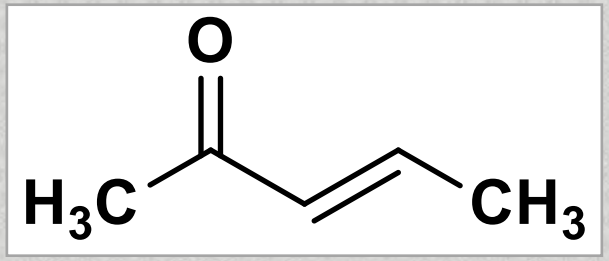
Endocyclic double bond



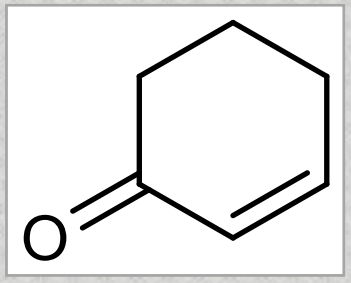
Exocyclic double bond

1. Base Values → Chromophores

a) Acyclic α, β unsaturated ketones = 214 nm

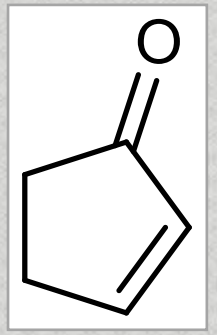


b) 6 membered cyclic α, β unsaturated ketones = 215 nm



c) 5 membered cyclic α, β unsaturated ketones = 202 nm

d) α, β unsaturated aldehydes = 210 nm



e) α, β unsaturated carboxylic acids & esters = 195 nm

2. Increments → Auxochromes

2. Alkyl substituent or Ring residue in α position = 10 nm

3. Alkyl substituent or Ring residue in β position = 12 nm

4. Alkyl substituent or Ring residue in γ and higher positions = 18 nm

5. Double bond extending conjugation = 30 nm

6. Exocyclic double bonds = 5 nm

7. Homodiene compound = 39 nm

2. Increments → Auxochromes

8. Polar groups:

a) –OH in α position = 35 nm

–OH in β position = 30 nm

–OH in δ position = 50 nm

b) –OAc in α, β, γ, δ positions = 6 nm

c) –OMe in α position = 35 nm

–OMe in β position = 30 nm

–OMe in γ position = 17 nm

–OMe in δ position = 31 nm

d) –Cl in α position = 15 nm

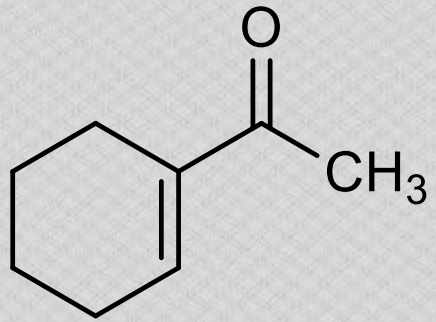
–Cl in β position = 12 nm

e) –Br in α position = 25 nm

–Br in β position = 30 nm

f) –NR2 in β position = 95 nm

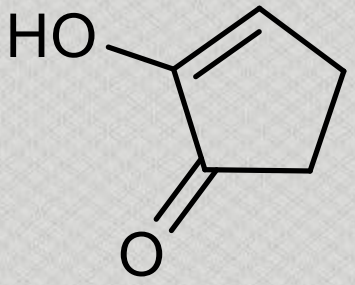
Example 1



Base value	→	**+ 215 nm**
Ring residue α-position	→	**+ 10 nm**
Ring residue β-position	→	**+ 12 nm**
Exocyclic double bond	→	**+ 0 nm**
Extended conjugation	→	**+ 0 nm**

$$\lambda_{max} = 237 \text{ nm}$$

Example 2



Base value	→	+ 202 nm
Ring residue at β-position	→	+ 12 nm
Exocyclic double bond	→	+ 0 nm
Extended conjugation	→	+ 0 nm
-OH substituent at α-position	→	+ 35 nm

$$\lambda_{max} = \underline{\overline{249\ nm}}$$

Summary

- **Robert Burns Woodward and Louis Frederick Fieser gave certain rules for correlating λ_{max} with molecular structure known as Woodward-Fieser Rules, used to calculate the position and λ_{max} for a given structure by relating the position and degree of substitution.**
- **Each conjugated enone system has a certain fixed value at which absorption takes place. The contribution made by various substituents or ring residue, etc. are added to this basic value to obtain λ_{max} for a particular α,β-unsaturated carbonyl compound.**
- **Extended conjugation always results in Bathochromic shifts.**