

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SARGODHA, SARGODHA.

FIESER RULES.

Ques.1: Calculation of lambda max of Organic compounds using Fieser Rules and explain objectives with example?

Introduction:

In 1945 Robert Woodward gave certain standards of relating most extreme frequency with sub-atomic structure.

In 1959 Luis Federico Fieser changed these guidelines with increasingly exploratory information and modified rules known as Woodward Fieser Rules.

Woodward Fieser Rules.

- Woodward Rules function admirably for dienes and polyenes with upto 4-twofold bonds or less.
- Fieser Rules must be applied for certain plant color, for example, carotenoids have significantly more than 4 conjugated twofold bonds and stretched out principles to conjugated aldehydes and ketones.

Objectives:

- To familiarize the Woodward Fieser Rules.
- To compute the most extreme frequency of organic compound theoretically.

Advantage:

- It is utilized to compute the position and most extreme wavelength of a given structure by relating the position and level of substitution of chromophore.

Woodward Fieser Rules:

- It means each kind of diene or triene framework is having a specific fixed quality at which assimilation occurs; this constitutes the base worth or parent esteem.
- The commitment made by different alkyl substituents

On the other hand ring buildup, twofold bond broadening conjugation and polar gatherings, for example, - Cl, - Br, ...and so on are added to the base to get most extreme frequency of a specific compound.

Terminology

Conjugated Diene:

“Organic compounds containing two or more double bonds each separated from each other by a single bond.

Diene:

“It is also known as alkadiene, diolefin.

- It is one class of organic compound containing two ethylenic linkages (**carbon to carbon double bond**).

Basic Introduction

Acyclic Diene:

“Organic compound in which two alternative double and single bond present in linear or branched form not in cycle called acyclic diene” Cyclic diene:

REG “Organic compounds in which two or more double bonds are present each separated by a



single bond but in form of ring called cyclic dienes.” Types:

It has two types

1. **HOMOANNULAR:**

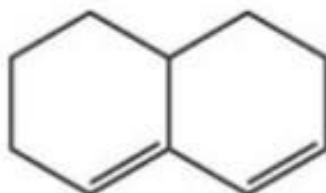
“Cyclic dienes having conjugated double bonds in same ring called homoannular “

2. **HETEROANNULAR:**

“Cyclic diene having conjugated double bonds in different rings is called heteroannular rings.”



**BASIC INFORMATION REGARDING CALCULATION OF
MAX. WAVELENGTH OF A COMPOUND:**



Endocyclic double bond

“ when double bond present within a ring it is called endocyclic double bond ” (A)

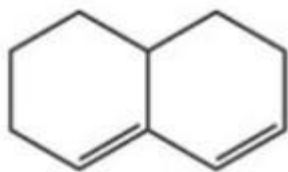


Exocyclic double bond :

“ double bond in which one of the doubly bonded atoms is a part of ring system”

OR

“ if double bond present laterally to the line joining two rings”



(B)

- Here the (B) ring has **one exocyclic bond and two endocyclic double bond.**
- ring (A) has **only one endocyclic double bond.**

PARENT VALUES AND INCREMENTS FOR Different substituents and groups for calculating max.wavelength:

Conjugated diene system

a. Base value for acyclic diene= 217nm b. Base

value for homoannular diene= 253nm C. Base

value for heteroannular diene= +214nm

d. Alkyl substitution (-R) to ring residue attached to parent diene= +5nm

Double bond extended conjugation=+ 30nm

Exocyclic double bonds=+ 5nm

(-OR) [OCH₃, OC₂H₅] = +6nm

Halogens (-Cl, -Br, F) = +5nm

Acyl group (OCOCH₃)= 0

NR₂ group = +60nm Thio

group (-SR) = +30nm

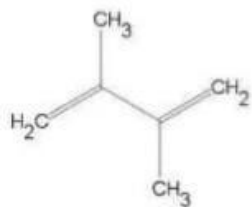
Note:

As a parent diene Homoannular would be prefer over Heteroannular diene.

Examples:

1.

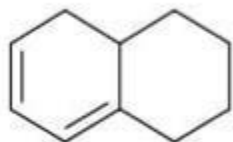
Acyclic Conjugated diene= 217nm



Two Alkyl substituents= +10nm

Max.wavelength = 227nm

Example 2



Parent= homoannular diene= 253nm

1 Endocyclic double bond= 5nm

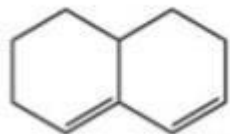
3 Alkyl substituents = +15nm

Total max.wavelength= 273nm

Example 3

Base value= 214nm = heteroannular diene

1 exocyclic double bond= 5nm

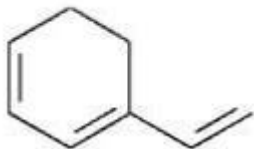


1 exocyclic double bond= 5nm

3 Alkyl substituents= 15nm

Total max.wavelength = 234nm

Example 4



Base value= 217nm

Extended diene= 30nm

2 alkyl substituents= 10nm

Total max.wavelength= 257nm

APPLICATION OF WOODWARD FIESER RULES FOR ALPHA,BETA UNSATURATED COMPOUNDS

- in this alpha, beta unsaturated compounds the compound may be a aldehydes or ketones.
- It may be acyclic or 6 membered or 5 membered ring system.

Substituents effect

- According to Woodward, in case of alpha and beta unsaturated carbonyl compounds the location of the substituent is significant in determining substituent is significant in determining the influence on the wavelength of maximum absorption.
- Substituents can be located on either alpha or beta position.
- If the conjugation is extended to gamma or sigma position the substituents at these position also play a vital role in determining the wavelength[1].

BASE VALUES FOR DIFFERENT FUNCTIONAL GROUPS:

KETONES

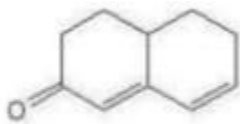
KETONES

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BASE VALUES FOR DIFFERENT FUNCTIONAL GROUPS:

KETONES

KETONES



Base value = 214nm

Beta substituents = $1 \times 12 = 12\text{nm}$

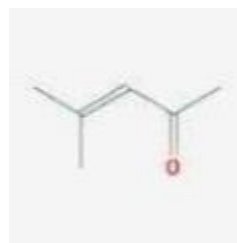
Sigma substituents = $1 \times 18 = 18\text{nm}$

Double bond extended conjugation = $1 \times 30 = 30\text{nm}$

Exocyclic double bond = 5nm

Total max.wavelength = 279nm

Example 2

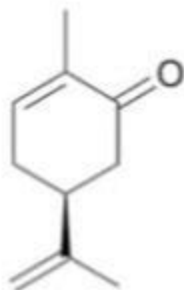


Parent conjugated enone in acyclic compound = 215nm

2 alkyl residue on alpha, beta position = $12 + 12 = 24\text{nm}$

Total wavelength = 239nm

Example 3



Parent conjugated enone in six membered ring = 215nm

Substituents of alkyl group at alpha position = +10nm

Total max. wavelength = 257nm

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- Substituents can be located on either alpha or beta position.
- If the conjugation is extended to gamma or sigma position the substituents at these position also play a vital role in determining the wavelength.[2]

BASE VALUES FOR DIFFERENT FUNCTIONAL GROUPS:

KETONES

- If it is acyclic compound = 215nm
- If it is 6-membered ring system = 215nm
- If 5-membered ring system = 202nm

ALDEHYDE

- If it is acyclic compound = 210nm
- If 6-membered ring system = 215nm
- If 5-membered ring system = 207nm

CARBOXYLIC AND ESTER

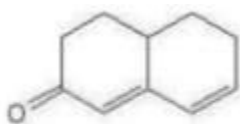
- If compound is carboxylic acid or ester = 197nm

Values for substituents

- Double bond extended conjugation = 30nm
- Exocyclic double bond = 5nm • homodiene compound = 39nm

Group	α	β	γ	δ
Alkyl R	10 nm	12 nm	18 nm	18 nm
Alkoxy OR	35 nm	30 nm	17 nm	31 nm
Hydroxyl OH	35 nm	30 nm	30 nm	50 nm
Chlorine -Cl	15 nm	12 nm	12 nm	12 nm
Bromine -Br	25 nm	30 nm	25 nm	25 nm

Example 1



Base value = 214nm

Beta substituents = $1 \times 12 = 12\text{nm}$

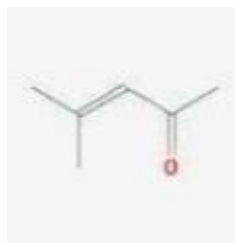
Sigma substituents = $1 \times 18 = 18\text{nm}$

Double bond extended conjugation = $1 \times 30 = 30\text{nm}$

Exocyclic double bond = 5nm

Total max.wavelength= 279nm

Example 2

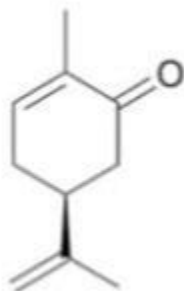


Parent conjugated enone in acyclic compound= 215nm

2 alkyl residue on alpha ,beta position= 12+ 12=24nm

Total wavelength = 239nm

Example 3



Parent conjugated enone in six membered ring= 215nm

Substituents of alkyl group at alpha position = 10nm

Substituents of alkyl group at beta position= 12nm Total
wavelength= 237nm.

APPLICATION OF WOODWARD FIESER RULES FOR AROMATIC COMPOUNDS:

1.BASE VALUES:-

- Ar COR = 246nm
- Ar CHO = 250nm
- Ar CO₂H = 230nm
- Ar CO₂R = 230nm
- alkyl groups on ortho and meta position = 3nm
- Alkyl groups in para position= 10nm

Values for substituents or groups

Groups	Ortho position nm	Meta position nm	Para position nm
-OH	7	7	25
-OCH ₃	7	7	25
-O	11	20	78
-Cl	0	0	10
-Br	2	2	15
-NH ₂	13	13	58

Example 1

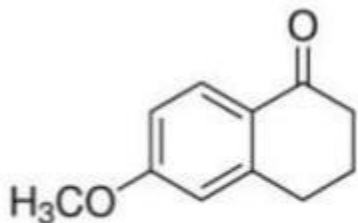
Base value= 246nm

Hydroxy group at meta position= 7nm

Hydroxy group at para position= 25nm

Total max wavelength= 278nm

Example 2



Base value = 246nm

Ring residue = 3nm

OCH₃ group at meta position = 7nm

Total max wavelength = 256nm

IMPORTANT POINTS

- in case for which both types of diene systems are present then the one with the longer wavelength is designated as a parent value.
- upto four conjugation Woodward Fieser rule is applied.
- > four conjugation we have to use Fieser-Kuhn rules.

APPLICATION/ OBJECTIVES:

● **Detection of conjugation**

It helps to show the relationship b/w the different groups particularly with respect to conjugation.

- Determination of geometrical isomers. Trans isomers exhibit max. wavelength at slightly longer wavelength.

● **Detection of functional group.**

It is possible to detect the functional group with the help of UV spectrum

- Determination of strength of hydrogen bonding.

Question 2

Woodward Fieser Rule its application and solvent use in uv its characteristics **Woodward**

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Woodward Fieser Rules:

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; this constitute the base worth or parent esteem.

- The commitment made by different alkyl substituents

Or on the other hand ring buildup , twofold bond broadening conjugation and polar gatherings, for example, - Cl , - Br, ...and so on are added to the base to get most extreme frequency of a specific compound

CONJUGATED CORRELATIONS DIENE R₂C=CR-CR=CR₂

Base:

(chose the highest appropriate base value) for acyclic 214, or for heteroannular 214, or for homoannular 253 Auxochrome Corrections: +60 for each dialkylamino +30 for each extending olefin +30 for each alkylthio +5 for each Cl, Br, or alkoxy +5 for each exocyclic olefin +5 for each alkyl (cyclic or acyclic)

ENONE CORRELATIONS $\beta \alpha$ R₂C=CR-CO-R Base: for acyclic or cyclohexenone 215, or for cyclopentenone 202 Auxochromes: +30 for each extending olefin +5 for each exocyclic olefin.[4]

α	Auxochrome	β	$\gamma, \delta, \text{etc.}$
+35	-OH or -OR	+30	
+25	-Br	+30	
+15	-Cl	+12	
+10	aliphatic	+12	+18
+6	-OCOR	+6	+6

The rules listed above apply only to diene, enone or benzoyl containing compounds. If a compound does not contain one of these three chromophores, you will not be able to predict or calculate a diagnostic λ_{max} value using these tables. Also, if a compound contains one of the listed chromophores, but it has an auxochrome that is not listed, then, the best that you will be able to do is to predict a minimum value for the diagnostic λ_{max} . In these cases, the diagnostic λ_{max} will be greater than the predicted λ_{max} using the tables. In the event that you have a compound that fits the rules, the calculated λ_{max} should be within (+/-) 3 nm of the λ_{max} observed in the UV-Vis spectrum. Work through each of the examples listed in the following application notes to see how the rules are applied. As you work through them double-check the identification of chromophores, auxochromes, and special corrections (homoannular, heteroannular, exocyclic, etc.) that are applied to each case. You should NOT memorize the data tables.[3]

Applications

Diene Example #1:

Calc. $\lambda_{\text{max}} = 214$ (acyclic base) + 5 (alkyl auxochrome at C3) + 5 (alkyl auxochrome at C4) = 224 nm

One way to identify an auxochrome is to draw a loop around the entire conjugated system (including extending olefins) and then add hash marks across all bonds attached to the loop. The hash marks define auxochrome attachments.

Diene Example 2

Calc. $\lambda_{\text{max}} = 214$ (heteroannular since two pi bonds are not in the same ring) + 20 (5 + 5 + 5 + 5 = 20, for each of the alkyl or ring auxochromes attached to C1, C2, C4, and C4) + 5 (pi bond of C1-C2 is exocyclic to ring B) = 239 nm

Diene Example #3:

Calc. $\lambda_{\max} = 253$ (choose diene with highest base value, pi bonds C1-2 and C3-4 are within same ring, so homoannular base should be selected) + 30 (C5-6 pi bond is conjugated to diene and is therefore an extending diene) + 5 (C5-6 is exocyclic to ring B) + 30 (5 + 5 + 5 + 5 + 5 + 5 = 30, for the alkyl or ring auxochromes at C1, C1, C2, C3, C5, and C6) = 318 nm

Enone Example #1:

Calc. $\lambda_{\max} = 215$ (cyclohexenone base) + 30 (extending conjugation) + 5 (α,β olefin is exocyclic to ring B) + 12 (β auxochrome) + 36 (2 δ auxochromes) = 298 nm

Benzoyl Example #1:

Calc. $\lambda_{\max} = 246$ (Benzoyl Base, where Z is the aliphatic methyl group) + 3 (o auxochrome) + 3 (m auxochrome) = 252 nm

Benzoyl Example # 2:

Calc. $\lambda_{\max} = 230$ (Benzoyl Base, where Z is O-R in this ester functionality) + ? (There is no value listed for a meta nitro group.) > 230 nm. The rules are not perfect. They do not allow you to make predictions for all compounds, not even all the simple ones. The best you can predict in this situation is that the observed λ_{\max} should be greater than 230 nm. After all, the nitro group contains a π bond that extends the length of the conjugated π system. And if nothing else, you know that greater conjugation means longer wavelength λ_{\max} .