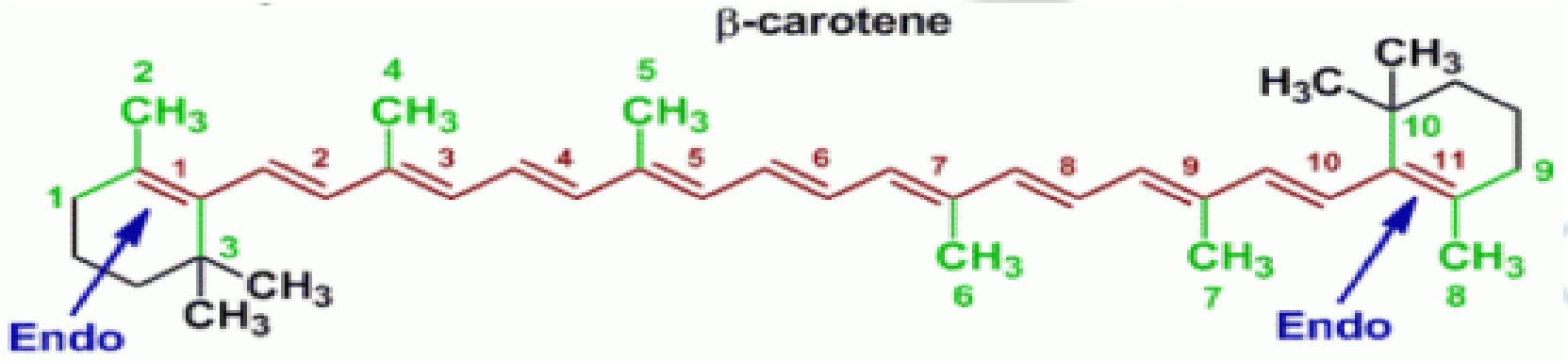
calculate λmax

- For polyenes with more than 4 conjugated double bonds, Fieser-Kuhn rule is used to calculate λmax Fieser-Kuhn derived the following equation to calculate the wavelength of maximum absorption λmax and also maximum absorptivity εmax

λmax = 114 + 5x + y (48.0 – 1.7 y) – 16.5 Rendo – 10 Rexo

calculate λmax

- Where:
- λmax is the wavelength of maximum absorption
- x is the number of alkyl substituents / ring residues in the conjugated system
- y is the number of conjugated double bonds
- R endo is the number of rings with endocyclic double bonds in the conjugated system
- R exo is the number of rings with exocyclic double bonds in the conjugated system



- x (number of alkyl substituents) = 10
- y (number of conjugated double bonds) = 11
- Rendo (number of endocyclic double bonds) = 2
- Rexo (number of exocyclic double bonds) = 0

$\lambda max = 114 + 5x + y\,(48.0 - 1.7\,y) - 16.5\,Rendo - 10\,Rexo = 114 + 5(10) + 11\,(48.0 - 1.7(11)) - 16.5\,(2) - 10\,(0) = 114 + 50 + 11\,(29.3) - 33 - 0 = 114 + 50 + 322.3 - 33 = 453.30$ nm

Woodward Fieser Rules

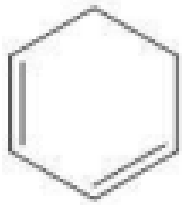
- In 1945 Robert Burns Woodward gave certain rules for correlating λmax with molecular structure.
- In 1959 Louis Frederick Fieser modified these rules with more experimental data, and the modified rule is known as Woodward-Fieser Rules.
- Each type of diene or triene system is having a certain fixed value at which absorption takes place; this constitutes the **Base value** or **Parent value.**

Woodward Fieser Rules

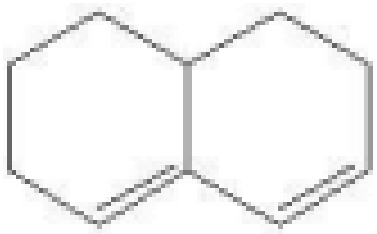
- The contribution made by various alkyl substituents or ring residue, double bond extending conjugation and polar groups such as –Cl, - Br etc are added to the basic value to obtain λmax for a particular compound.

CONJUGATED DIENE CORRELATIONS:

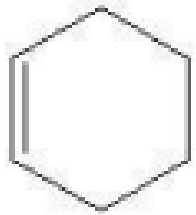
- **Homoannular Diene**:- Cyclic diene having conjugated double bonds in same ring



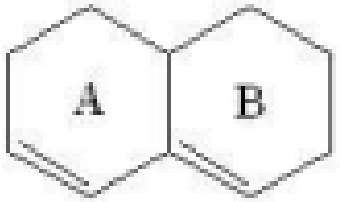
- **Heteroannular Diene**:-
- Cyclic diene having conjugated double bonds in different rings.



- Endocyclic double bond:- Double bond present in a ring.



- Exocyclic double bond: - Double bond in which one of the doubly bonded atoms is a part of a ring



- Here Ring A has one exocyclic and endocyclic double bond. Ring B has only one endocyclic double bond.

PARENT VALUES AND INCREMENTS FOR DIFFERENT SUBSTITUENTS/GROUPS:

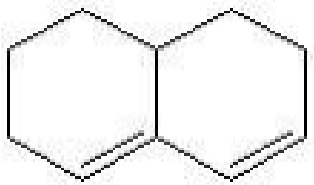
- i) Base value for an unsubstituted, conjugated, homoannular diene = 253 nm.
- ii) Base value for an unsubstituted, conjugated, acyclic or heteroannular diene = 214 nm.
- Each extra double bonds in conjugation + 30 nm.
- Exocyclic double bond (effect is twofold if the bond is exocyclic to two rings) + 5 nm

Substituent effect:

- -OCOR or –OCOAr + 0 nm
- Simple alkyl substituents or ring residue+5 nm
- Halogen (-Cl, -Br) + 5 nm
- OR (R=Alkyl) + 6 nm
- SR (R=Alkyl + 30 nm
- NR2 (R=Alkyl) + 60 nm

Eg:

1.

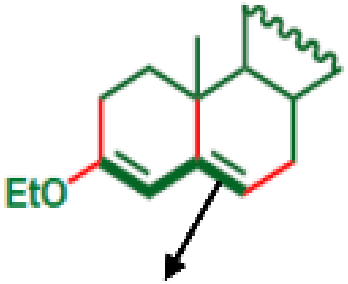


Base value = 214 nm
Ring residue = 3 x 5 = 15 nm

Exocyclic double bond = 1 x 5 = 5 nm

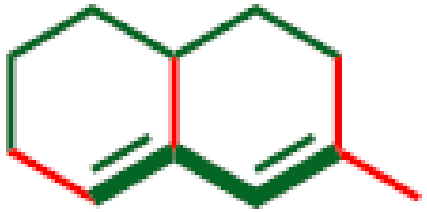
λ_{max} = 214 + 15 + 5 = 234 nm

base value : 214 nm
3 ring residues : +15
1 exocyclic C=C : + 5 .
Total λ_{max} : 234 nm
Observed : 235 nm

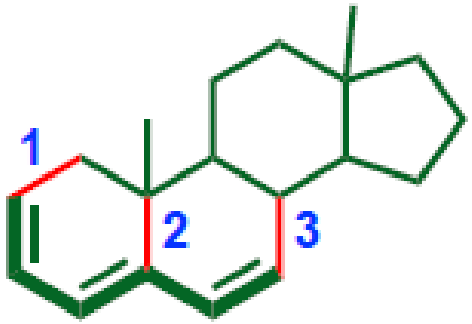


Exocyclic double

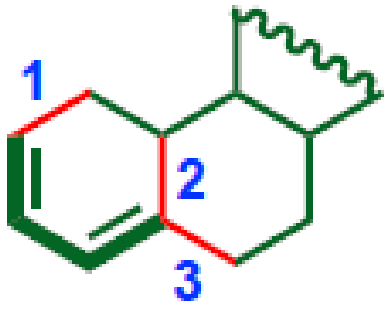
base value :214 nm
3 ring residues : +15
1 exocyclic C=C : + 5
-OR : + 6 .
Total λ_{max} : 240 nm
Observed : 241 nm



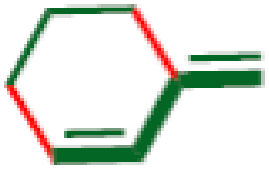
Base value : 214 nm
3 Ring residues : +15
1 Alkyl substituent: + 5
1 Exocyclic C=C : + 5.
Total λ_{max} : 239 nm



base Value: 253 nm
3 Ring residues: +15
1 Exocyclic C=C: + 5
Double-bond Extending Conjugation: +30 .
Total λ_{max} : 303 nm
Observed: 304 nm



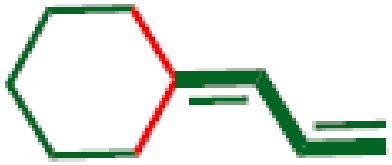
base value (Homoannular) : 253 nm
3 ring residues : +15
1 exocyclic C=C : + 5
Total λ_{max} : 273 nm (Observed : 235 nm)



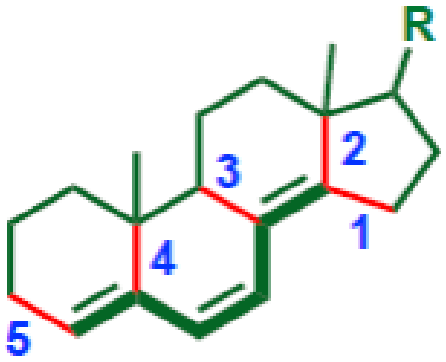
Base value: 214 nm

2 Ring residue +10
Exocyclic C=C: + 5
Total λ_{max}: 229 nm

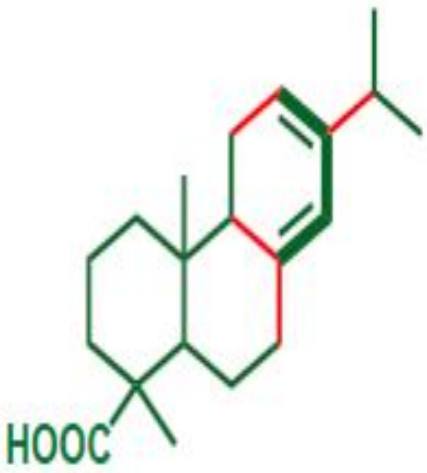
Observed: 230 nm



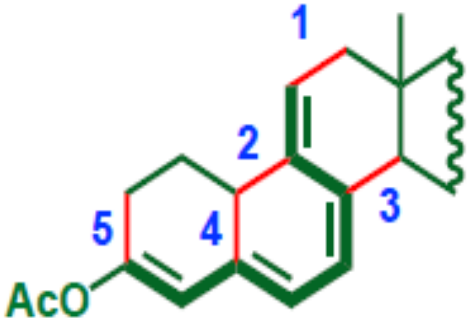
Base value: 214 nm
2 Ring residue: +10
Exocyclic C=C: + 5 .
Total λ_{max} 229 nm
Observed: 236 nm



Transoid (base): 214 nm
5 ring residues: +25
1 DEC: +30
3 exocyclic C=C +15 .
Total λ_{max}: 284 nm
Observed: 283 nm



Cisoid (base): 253 nm
3 ring residues: +15
1 Alkyl subs: +5
1 exocyclic C=C +5.
Total λ_{max}: 278 nm
Observed: 275 nm



Cisoid (base): 253 nm
5 ring residues: +25
2 DEC: +60
3 exocyclic C=C +15 .
Total λ_{max}: 353 nm
Observed: 355 nm

ENONE:

Rules of Enon & Dienone Absorption

Base values:

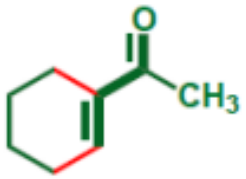
- Acyclic α,β-unsaturated ketones 215 nm
- **6-membered cyclic α,β-unsaturated ketones 215 nm**
- **5-membered cyclic α,β-unsaturated ketones 202 nm**
- α,β-unsaturated aldehydes 210 nm
- α,β-unsaturated carboxylic acid & esters 195 nm
- Increments for:
- Double bond extending conjugation (DEC): +30
- Exocyclic double bond: + 5
- Homodiene component: +39

Substituent effect:

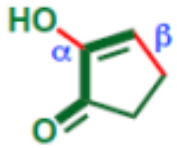
- Alkyl group/ring residue: α position +10, β position +12, γ & higher position +18

Polar. groups:

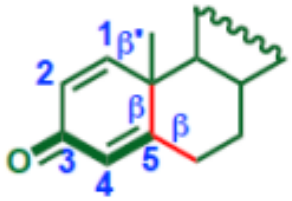
- -OH: α position +35, β position +30, δ position +50
- OAc: α, β, γ + 6
- OMe: α +35, β +30 γ +17 δ +31.
- SAlk: β +85 -Cl: α +15 β +12 -Br: α +25 β +30 -NR2: β +95



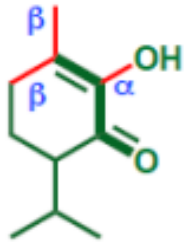
Base value:	215 nm
α substituent:	+10
β substituent:	+12
Total:	237 nm
Observed:	232 nm



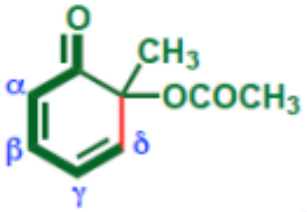
Base value:	202 nm
β substituent:	+12
α-OH:	+35
Total:	249 nm
Observed:	247 nm



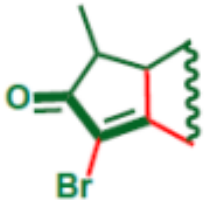
$\Delta^{4,5}$ system (base):	215 nm
2 β substituents:	+24
1 exocyclic C=C:	+ 5
Total:	244 nm
Observed:	245 nm



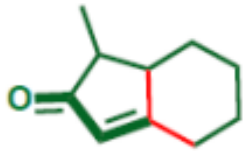
Base value:	215 nm
2 β substituents:	+24
α-OH:	+35
Total:	274 nm
Observed:	270 nm



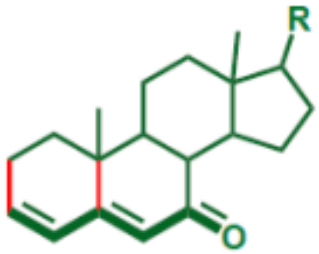
Base value:	215 nm
1 DEC:	+30
Homocyclic diene:	+39
δ ring residue:	+18
Total:	302 nm
Observed:	300 nm



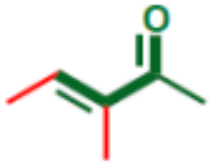
Base value:	202 nm
1 α-Br:	+25
2 β-ring residue:	+24
Exocyclic *C=C*:	+ 5
Total:	256 nm
Observed:	251 nm



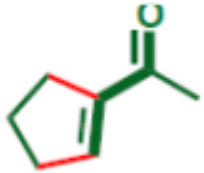
Base value:	202 nm
Exocyclic *C=C*:	+ 5
2 β-ring residues:	+24
Total:	231 nm
Observed:	226 nm



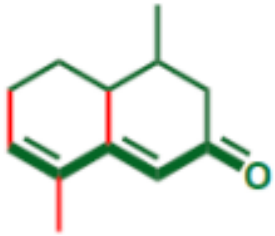
Base value:	215 nm
1 DEC:	+30
β-ring residue:	+12
δ ring residue:	+18
2 Exocyclic *C=C*:	+ 5
Total:	280 nm
Observed:	280 nm



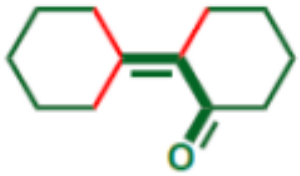
Base value:	215 nm
α alkyl substituent:	+10
β alkyl substituent:	+12
Total:	237 nm



Base value:	215 nm
α alkyl:	+10
β alkyl:	+12
Total:	237 nm



Base value:	215 nm
1 DEC:	+30
Exocyclic C=C:	+ 5
β-alkyl substituent:	+12
γ-alkyl substituent:	+18
δ-alkyl substituent:	+18
Total:	298 nm



Base value:	215 nm
1 α-alkyl:	+10
2 β-alkyl:	+24
2 Exocyclic C=C:	+10
Total:	259 nm