Woodward Fieser rule for UV spectroscopy

* It is used to calculate the position & λmax for a given str. by relating the position and degree of substitution of chromophore.
* 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.

*. 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 compd.

Rules for conjugated dienes - ① longer the conjugated diene system, greater the wavelength of absorption maximum.

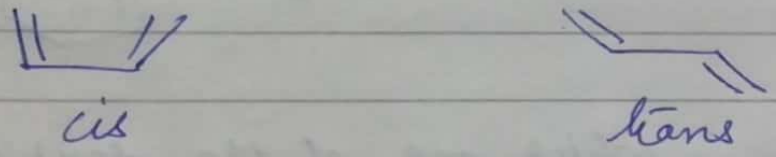
② According to woodward's rules the λmax of the molecule can be calculated using a formulae:

$$\lambda_{max} = \text{Base value} + \Sigma \text{ Substituent contributions} + \Sigma \text{ other contributions}$$

BASE VALUE - ① Each type of diene or liene system is having a certain fixed value at which absorption takes place; this constitutes the Base value or Parent value.

② The first step in predicting the λ of max. UV absorption for conjugated dienes is to determine whether it lies in an cis ~~trans~~ or formation or trans conformation.

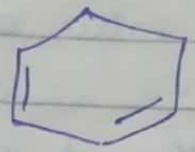
③ If it lies in the trans conformation, its base λ = 217 nm
If it lies in the cis conformation, its base λ = 253 nm.



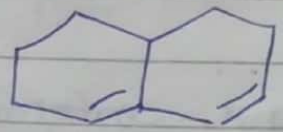
④ the base value depends upon whether the diene is a linear or hetero-annular or transoid diene or whether it is a cyclic or homo-annular diene.

⑤ The sum of all substituents contributions are added to the base value to obtain the λ of max absorption of the molecule.

1. Homoannular Dienes - Cyclic diene having conjugated double bonds in same ring.



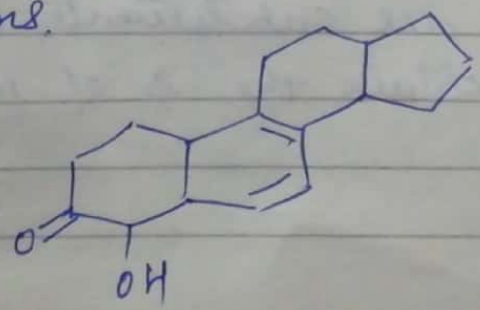
2. Heteroannular dienes - Cyclic diene having conjugated double bonds in different rings.



3. Endocyclic double bond - = bond present in the ring.

4. Exocyclic double bond - = bond in which one of the doubly bonded atoms is a part of ring system.

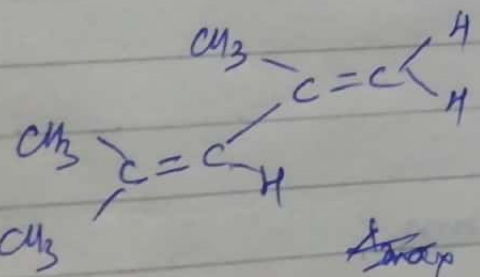
5. Double bond extending - when more double bonds are present other than conjugations.



Parent Values and Increments for diff Substituents or Gps.

Parent Value	
Acyclic conjugated dienes & heteroannular conjugated dienes	215nm
Homo annular conjugated dienes	253nm
Acyclic trienes	245nm
Increments	
Each alkyl substitute or ring residue	5nm
Exocyclic double bond	5nm
Double bond extending conjugation	30nm
Auxochromes	
$-OR$	6nm
$-SR$	30nm
$-Cl, -Br$	5nm
$-NR_2$	60nm
$-OCOCH_3$	0nm

eg.

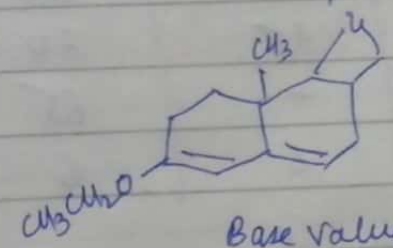
① 

~~Stereo~~

Base Value = 214nm

Substituents alkyl gps = 3 × 5 = 15nm

229nm

② 

Base value = 214nm

Ring residue = 3 × 5 = 15nm

Exocyclic double bond = 5nm

$-OCH_2CH_3$ = 6nm

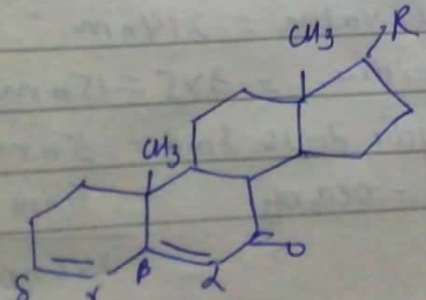
240nm

Parent Values & Increments for diff. Substituents or Grps

Parent Value	
α,β-unsaturated acyclic or 6-memb. ring ketone	215nm
α,β-unsaturated 5-memb. ring ketone	202nm
α,β-unsaturated aldehyde	207nm
Increments	
Alkyl substituents at α-position	10nm
β-position	12nm
γ-position	18nm
Each exocyclic bond	5nm
Double bond extending conjugation	30nm
Homo annular conjugated diene	39nm

Auxochromes	α	β	γ
-OH	35	30	50
-OR	35	30	17
-SR	-	85	-
-O CO CH_3	6	6	6

eg.



6-memb. ring = 215nm
β-residue = 12 nm
δ-residue = 18 nm
Exocyclic bond = 5 nm
bond extending conjugation = 30 nm

λ_{max} = 280 nm