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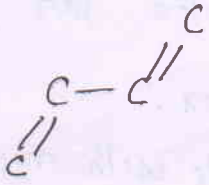
Compound containing carbon-carbon Multiple bonds

Types of conjugated alkenes:-

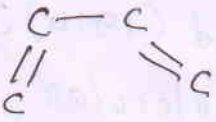
i) Acyclic diene or heteroannular diene

Most acyclic dienes have transoid conformation (I), i.e, trans disposition of double bonds about a single bond. The base absorption is 217 nm.



transoid (s-trans)

I



cisoid (s-cis)

IV

A heteroannular diene, however is conjugated system in which the two double bonds are confined to two different rings (II). However, these double bonds are exocyclic, one of them being exo-to ring A and other exo-to ring B. The base absorption of II is 214 nm.

II

III

ii) Homoannular diene

In the homoannular diene, the two conjugated double bonds are confined to a single ring (III), i.e, the cyclic dienes are forced into an s-cis (cisoid) conformation (IV). This types of diene has a base absorption at 253 nm.

iii) Semicycle diene :-

In the semicycle diene, one of the double bond forms part of a ring and the other is exocyclic or outside the ring as shown in structure V.

V

Empirical Approach To structure Determination

Woodward-Fieser Rule

Woodward (1914): gave certain rules for correlate with molecular structure with λmax.

Scott-Feiser (1959):- modified rule with more experimental data, the modified rule is known as woodward-Feiser rule.

It is used to correlated the λmax of for a given structure by relating position and degree of substitution of Chromophores.

Woodward-Fieser Rules for Conjugated acyclic dienes

Woodward had predicted an emperical rule for calculating λmax of conjugated acyclic and cyclic diene based on base value and contribution of different substituent.

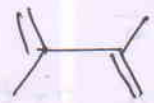
The equation is

$$\lambda max = \text{Base value} + \sum \text{substituents contribution} + \sum \text{other contribution.}$$

Empirical Rules for dienes

1) Parent acyclic diene	217 nm
2) Parent heteroannular diene	214 nm
3) Parent homoannular diene	253 nm
Increments for substituents	
i) alkyl group on ring residues	+5 nm
ii) Exocyclic double bond	+5 nm
iii) Double bond extending conjugation	+30 nm
iv) Halogen (-Cl, -Br)	+5 nm
v) O-(alkyl) (-OR)	+6 nm
vi) O-acyl (-O-COR)	+0 nm
S-alkyl (S-R)	+30 nm
N-(alkyl)$_2$ (-NRR)	+60 nm

Some important examples



Parent acyclic diene = 217 nm
Substituent 2x5 = 10 nm
Calc dmax = 227 nm

Parent acyclic diene = 217 nm
ring or substituent residue 2x5 = 10 nm
Exocyclic double bond 1x5 = 5 nm
Calc. dmax = 232 nm

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Parent acyclic dienen = 217 nm
ring residue 4x5 = 20 nm
Exocyclic double bond = 10 nm
Calcd dmax = 247 nm

Base value (heteroannular diene) = 214 nm
Substituent or ring residue = 15 nm
Exocyclic double bond 1x5 = 5 nm
Cal dmax = 234 nm

parent heteroannular diene = 214 nm
Double bond extending conjugation 1x30 = 30 nm
ring residue 4x5 = 20 nm
Exo cyclic double bond 2x5 = 10 nm
Calc dmax = 274 nm

Parent heteroannular diene = 214 nm
ring residue 3x5 = 15 nm
Exocyclic double bond 1x5 = 5 nm
Calc. dmax = 234 nm

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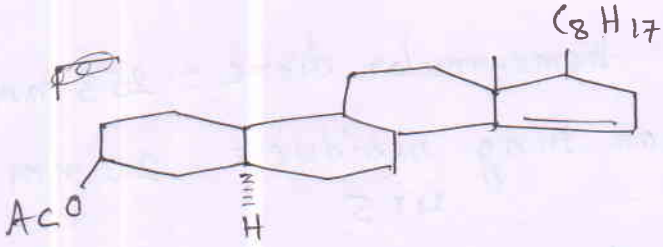
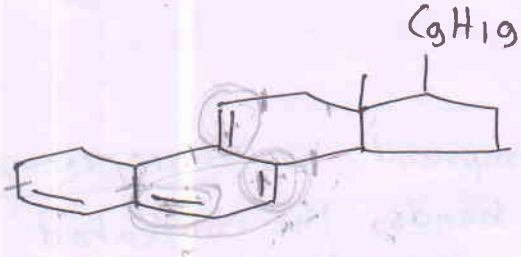


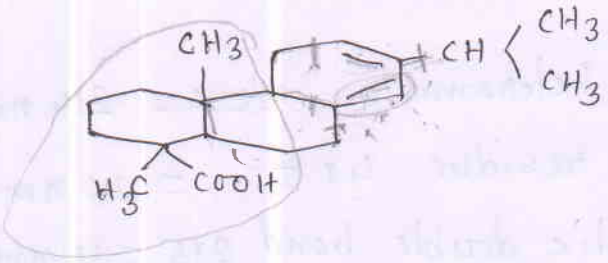
Parent heteroannular diene = 214 nm
Ring residue 4 x 5 = 20 nm
Exocyclic double bond 2 x 5 = 10 nm
Calc. dmax = 244 nm

Parent homoannular diene = 253 nm
Ring residue 4 x 5 = 20 nm
Calc. dmax = 273 nm

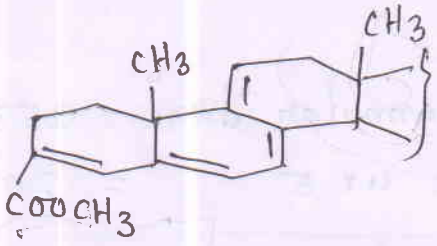
Parent homoannular diene = 253 nm
Ring residue 3 x 5 = 15 nm
Exocyclic double bond 1 x 5 = 5 nm
Calc. dmax = 273 nm



Parent homoannular diene = 253 nm
Double bond extending conjugation 2 x 30 = 60 nm
Ring residues 5 x 5 = 25 nm
Exocyclic double bond 3 x 5 = 15 nm
Calc. dmax = 353 nm



Parent homoannular diene	= 253 nm
alkyl or ring residue 4 x 5	= 20 nm
Exocyclic double bond	= 5 nm
Calc. dmax	= 278 nm



Parent homoannular diene	= 253 nm
Ring residues 5 x 5	= 25 nm
Double bond extended conjugation (2 x 30)	= 60 nm
Exocyclic double bond 3 x 5	= 15 nm
CH_3COO-	= 0
Calc. dmax	= 353 nm

(*) Three common errors :-

This compound has three exocyclic double bonds, the indicated bond is exocyclic to two rings.

This is not a heteroannular diene, you would use the base for an acyclic diene.

Likewise, this is not a homoannular diene, you would use the base value for acyclic diene