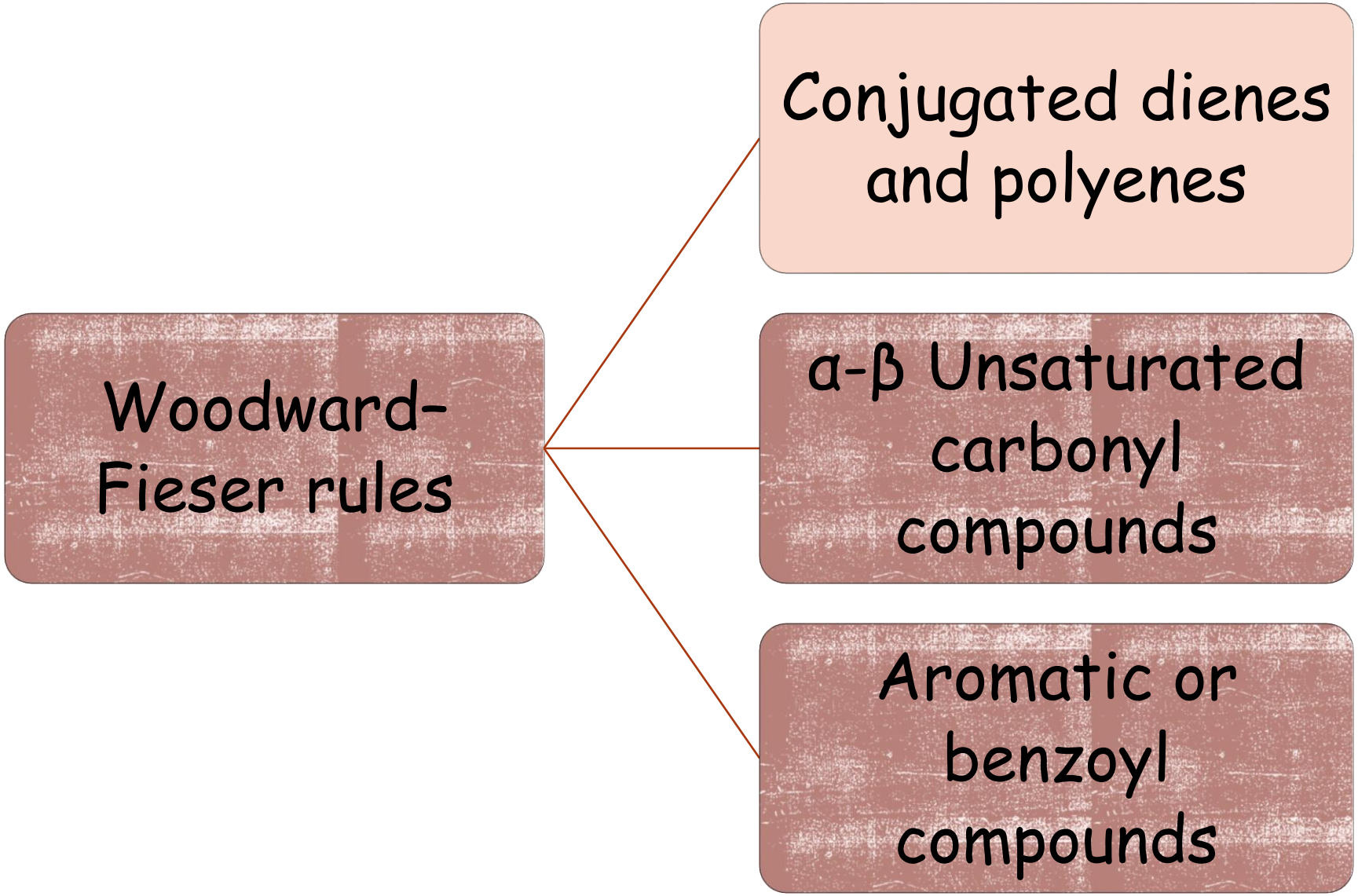
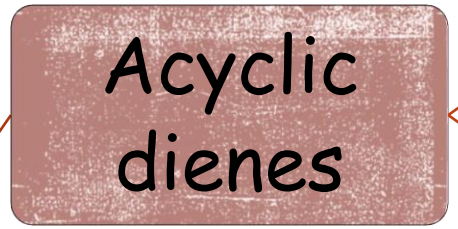
SPECTROCHEMICAL ANALYSIS

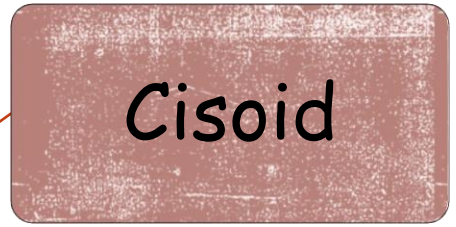
Calculation of λ_{max} : Woodward-Fieser rules

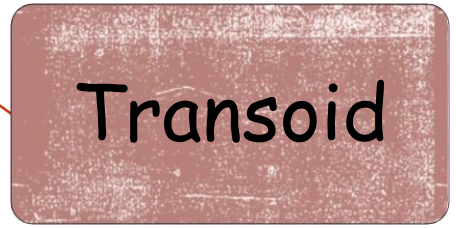
3

2021-2022

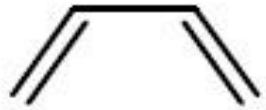

Woodward-Fieser rules
Conjugated dienes and polyenes
α-β Unsaturated carbonyl compounds
Aromatic or benzoyl compounds



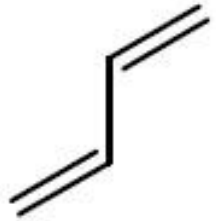




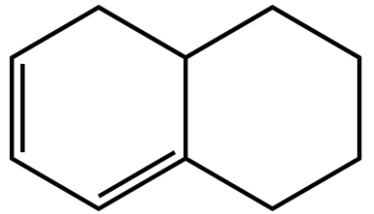
Basic values of λ_{max}



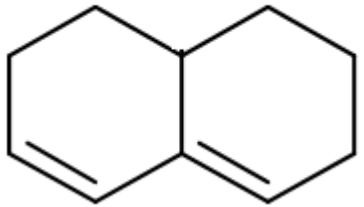
253 nm



217nm



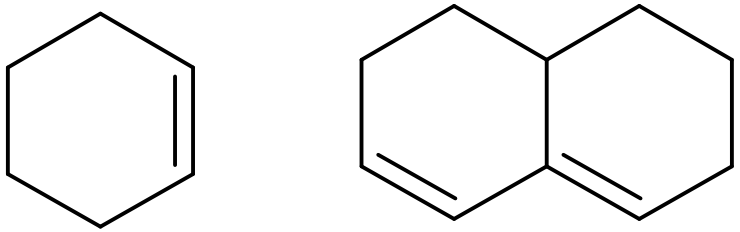
253 nm



214 nm

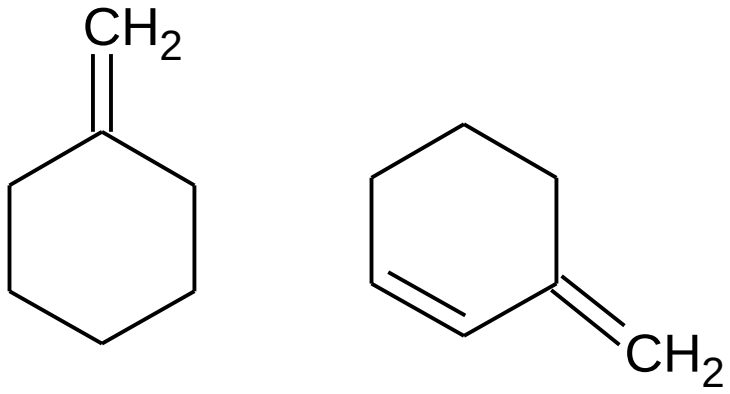
Endocyclic double bond

The double bond present in a ring only (inside).

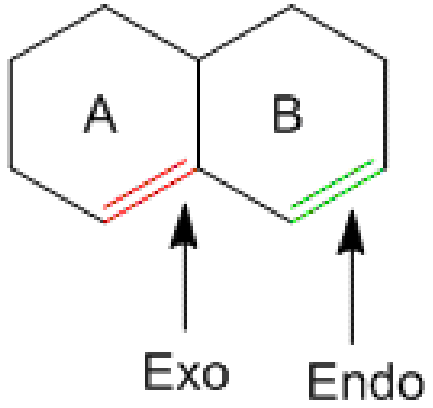


Exocyclic double bond

The double bond is a part of the ring (outside).



1]



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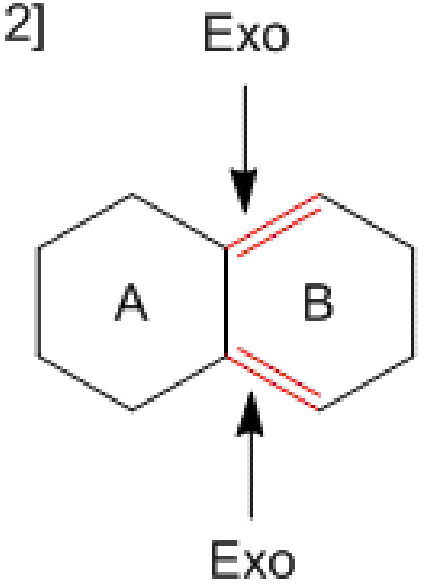

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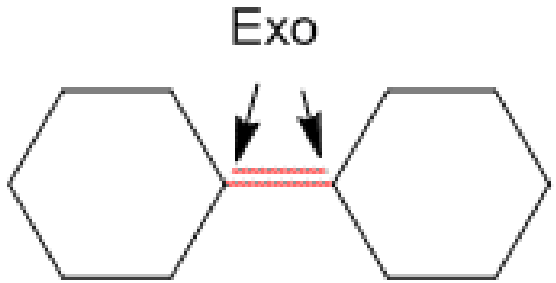
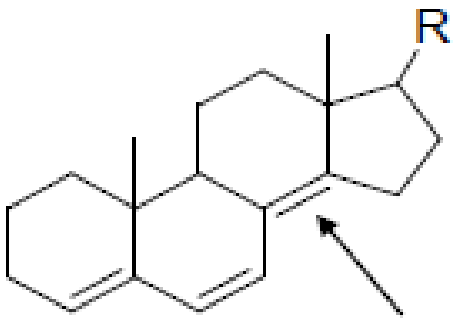
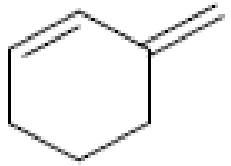


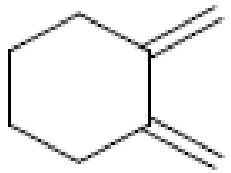
Increments:	values
For each additional conjugated double bond	+ 30 nm
For each exocyclic double bond	+ 5 nm
For each alkyl group	+ 5 nm
Auxochrome	
- OR	+ 6 nm
- O(C=O)R	0
- Cl	+ 5 nm
- Br	+ 5 nm
- SR	+ 30 nm
- NR_2	+ 60 nm
Phenyl ring	+ 60 nm



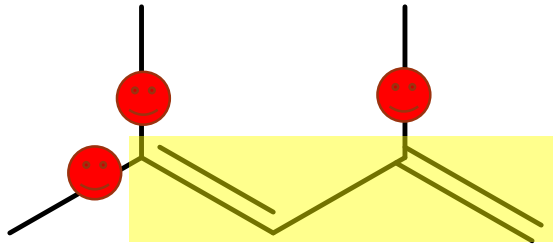
This compound has three exocyclic double bonds; the indicated bond is exocyclic to ***two*** rings



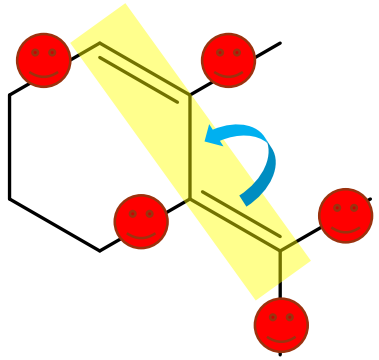
This is ***not*** a heteroannular diene; you would use the base value for an acyclic diene



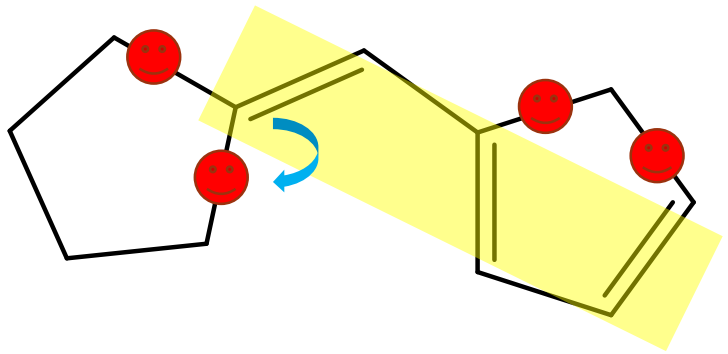
Likewise, this is ***not*** a homooannular diene; you would use the base value for an acyclic diene



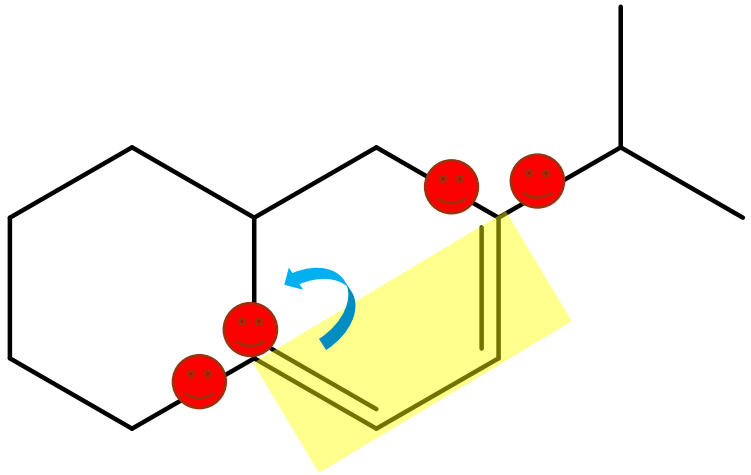
Acyclic diene	217
Alkyl subst.	3 x 5
Calculated value	232
Observed	234



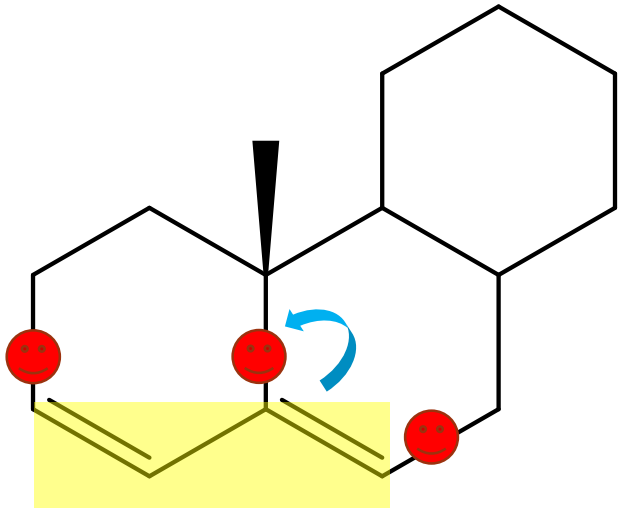
Acyclic diene	217 nm
Alkyl substitution	(5 x 5) nm
Exocyclic double bond	(1 x 5) nm
Calculated value	247 nm



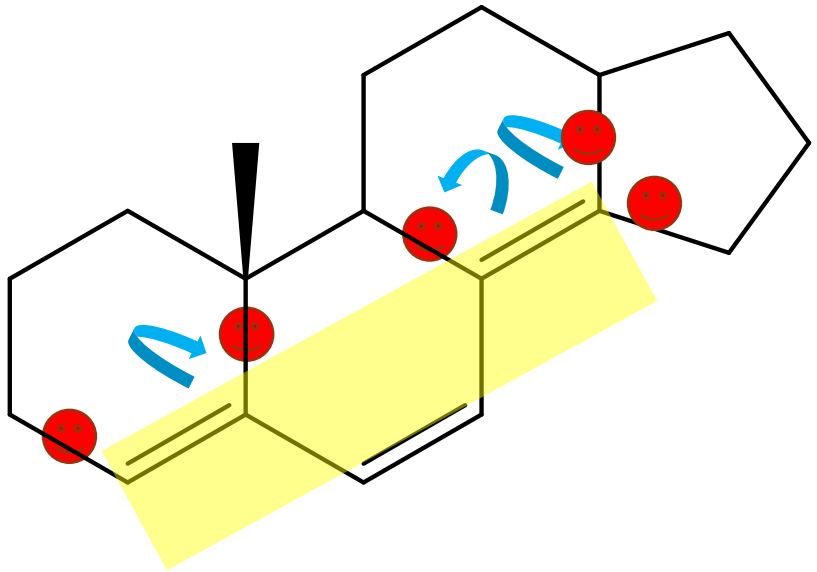
Homo-annular	253 nm
Alkyl substitution	(4 x 5) nm
Exocyclic double bond	(1 x 5) nm
Extra-conjugation	(1 x 30) nm
Calculated value	**308** nm



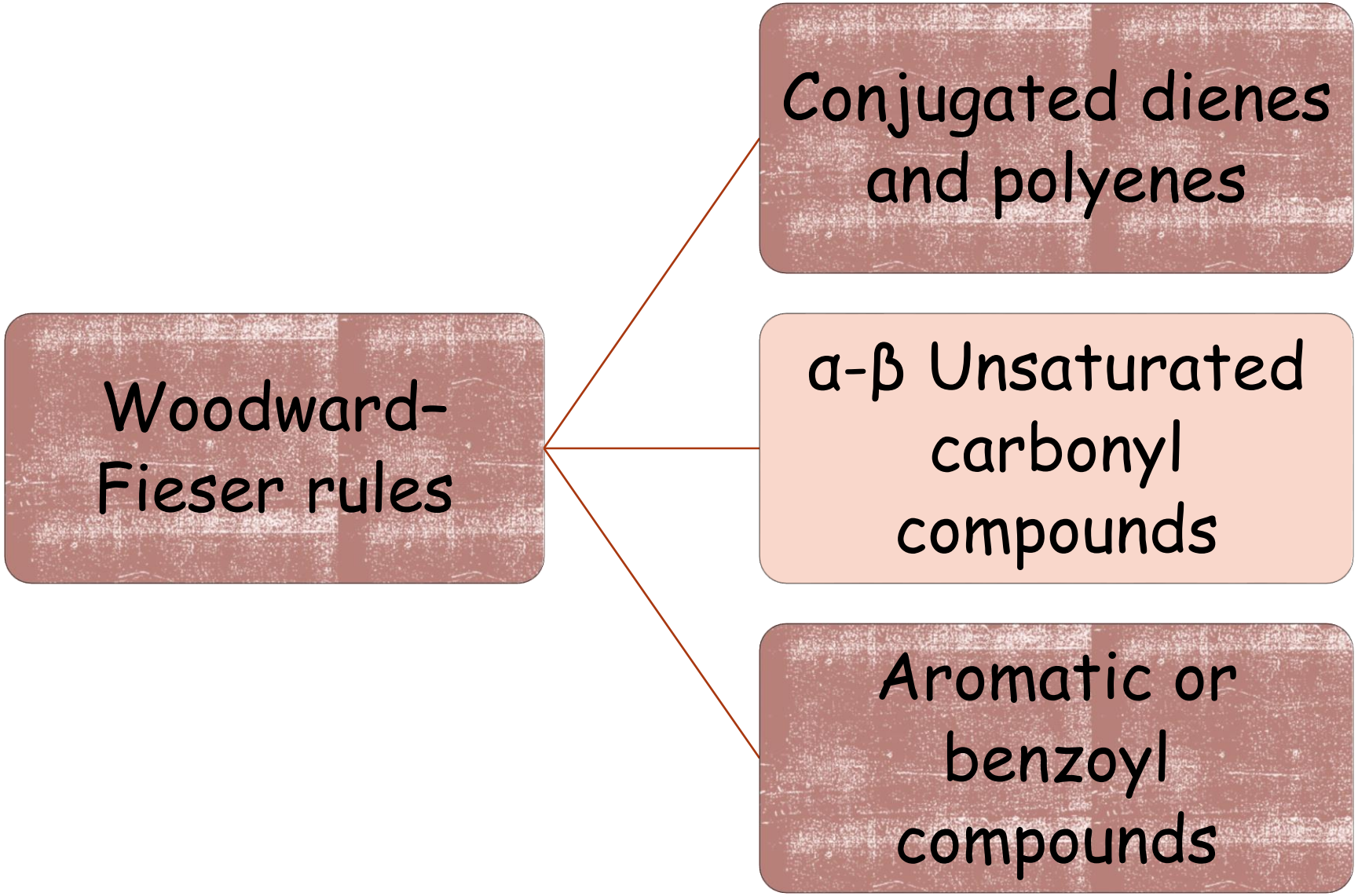
Homo-annular	253 nm
Alkyl substitution	(4 x 5) nm
Exocyclic double bond	(1 x 5) nm
Calculated value	**278** nm
Observed value	275 nm



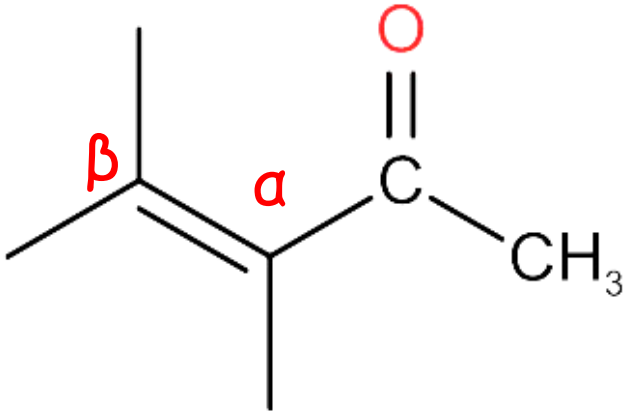
Hetero-annular	214 nm
Alkyl substitution	(3 x 5) nm
Exocyclic double bond	(1 x 5) nm
Calculated value	**234** nm
Observed value	235 nm



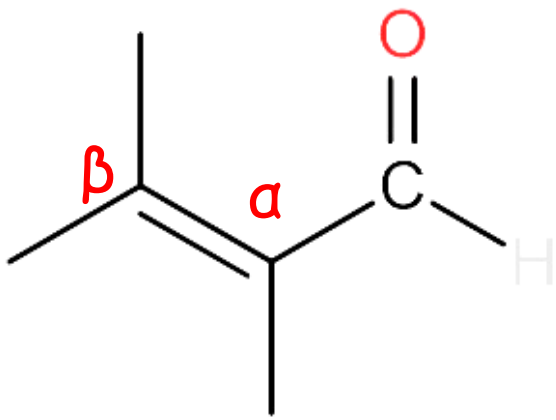
Hetero-annular	214 nm
Alkyl substitution	(5 x 5) nm
Exocyclic double bond	(3 x 5) nm
Extra conjugation	(1 x 30) nm
Calculated value	**284** nm


Woodward-Fieser rules
Conjugated dienes and polyenes
α-β Unsaturated carbonyl compounds
Aromatic or benzoyl compounds

α-β unsaturated carbonyl compounds



Enone

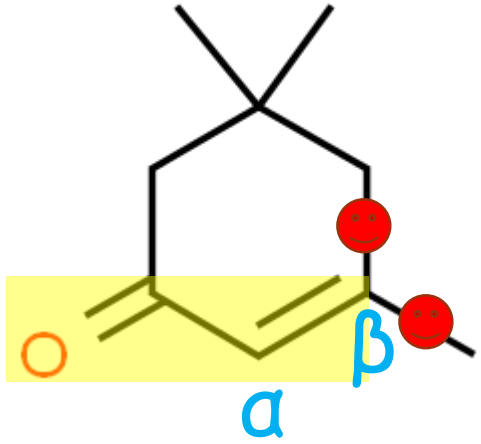


Enal

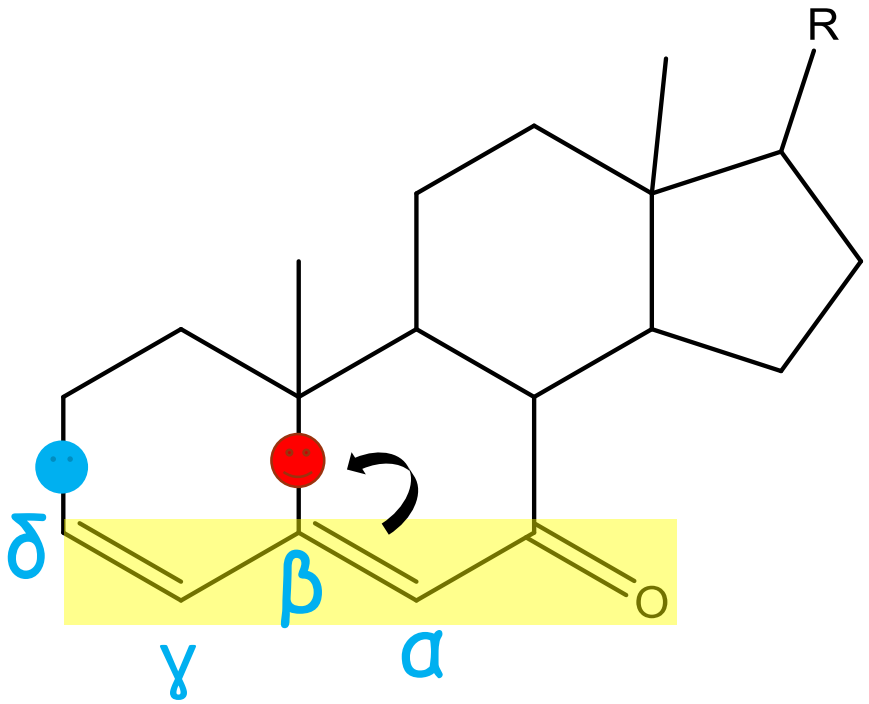
α-β unsaturated carbonyl compounds

Compounds	base values
α-β unsaturated aldehydes	210 nm
α-β unsaturated (carboxylic acids & esters)	195 nm
A cyclic α-β unsaturated ketones	215 nm
Cyclic α-β unsaturated ketones (six membered)	215 nm
Cyclic α-β unsaturated ketones (five membered)	202 nm
Increments:	**values**
For each additional conjugated double bond	+ 30 nm
For each exocyclic double bond	+ 5 nm
Homo-annular diene	+ 39 nm

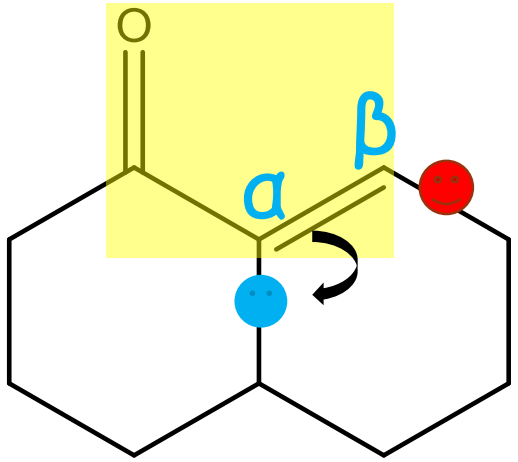
Substituent	α- position	β- position	ɣ- position	δ- position
Alkyl substituent or ring residue	10 nm	12 nm	18 nm	18 nm
- OH	35 nm	30 nm	50 nm	50 nm
-OAc	6 nm	6 nm	6 nm	6 nm
-OMe	35 nm	30 nm	17 nm	31 nm
-Cl	15 nm	12 nm	12 nm	12 nm
-Br	25 nm	30 nm	25 nm	25 nm
-SR	-	85 nm	-	-
$-NR_2$	-	95 nm	-	-



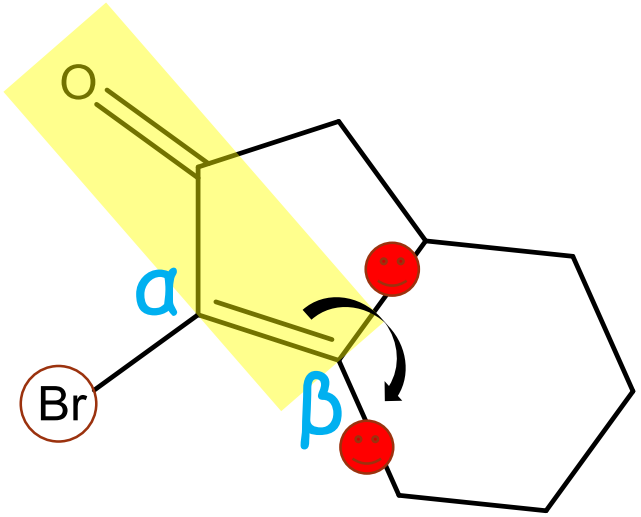
Six cyclic enone	215 nm
2 x β Alkyl substitution	(2 x 12) nm
Calculated value	239 nm
Experimental value	238 nm



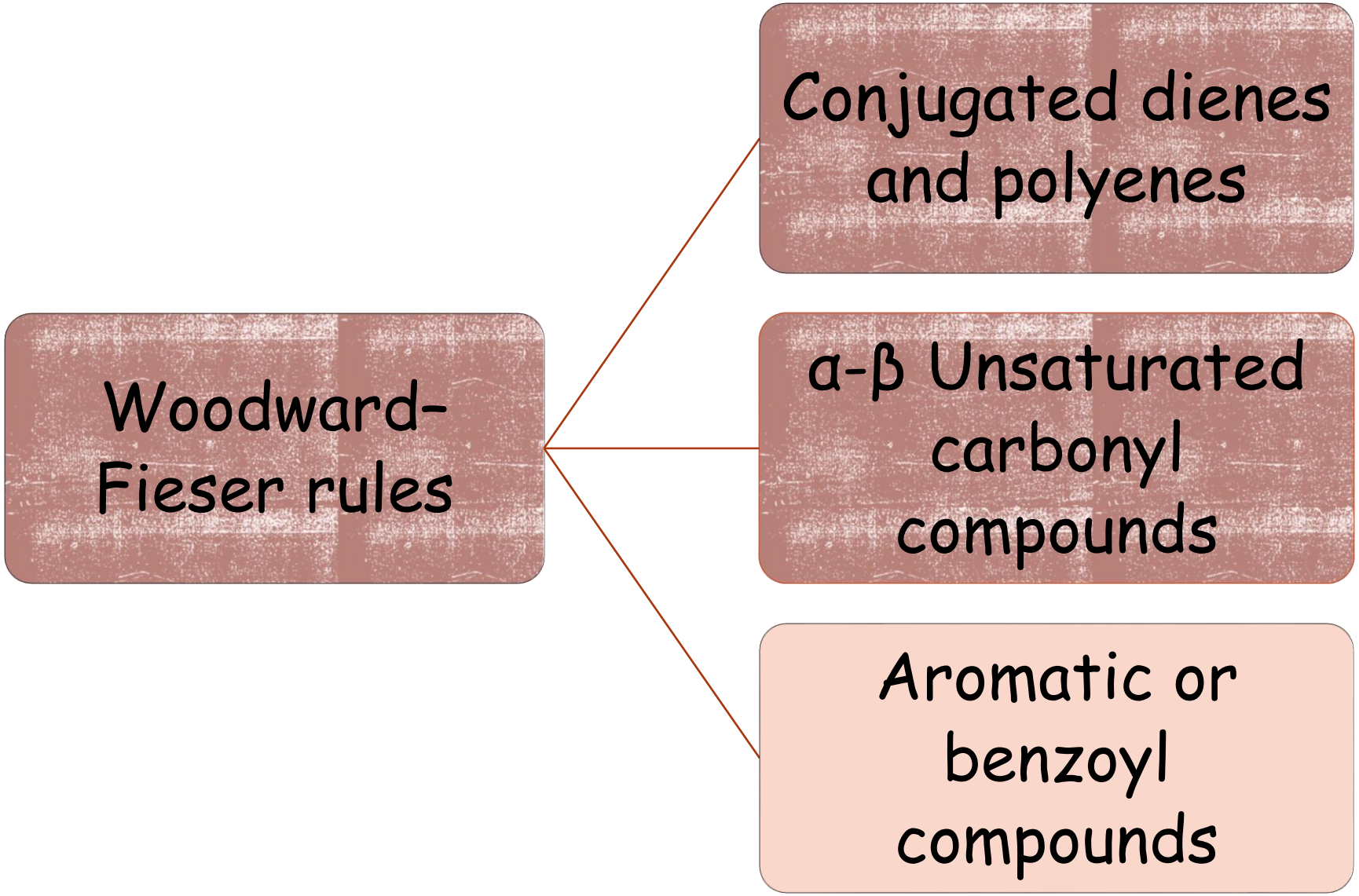
Six cyclic enone	215 nm
Extra-conjugation	(1 x 30) nm
1 x β Alkyl substitution	(1 x 12) nm
1 x δ Alkyl substitution	(1 x 18) nm
Exo-cyclic double bond	(1 x 5) nm
Calculated value	**280 nm**



Six cyclic enone	215 nm
1 x α Alkyl substitution	(1 x 10) nm
1 x β Alkyl substitution	(1 x 12) nm
Exo-cyclic double bond	(1 x 5) nm
Calculated value	**242 nm**
Experimental value	238 nm



Five cyclic enone	202 nm
1 x α (Br) substitution	(1 x 25) nm
2 x β Alkyl substitution	(2 x 12) nm
Exo-cyclic double bond	(1 x 5) nm
Calculated value	**256 nm**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α-β Unsaturated carbonyl compounds
Aromatic or benzoyl compounds

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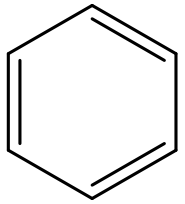
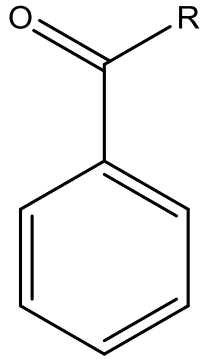
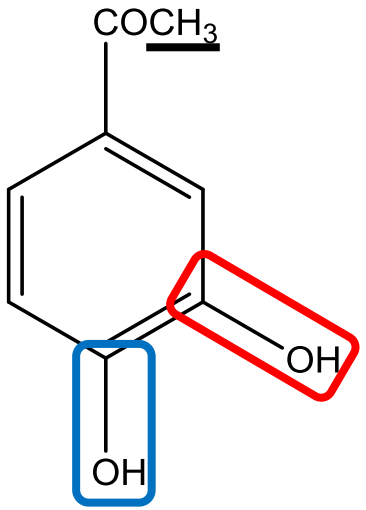


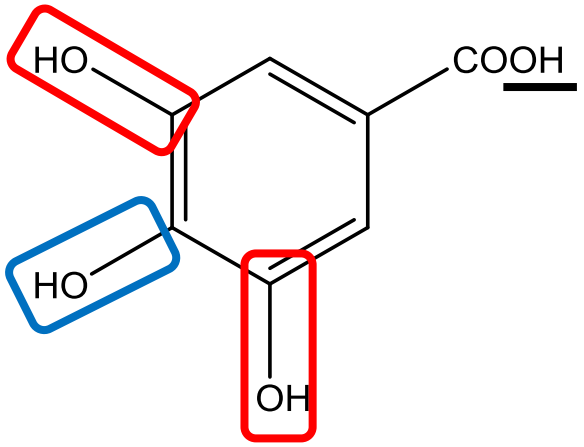


Parent chromophore	Basic value
R = alkyl or ring residue	246 nm
R = H	250 nm
R = OH or O-Alkyl	230 nm

Substituent	o- position	m- position	p- position
Alkyl or ring residue	3 nm	3 nm	10 nm
- OH, -OR, O-ring	7 nm	7 nm	25 nm
-Cl	0 nm	0 nm	10 nm
-Br	2 nm	2 nm	15 nm
$-NH_2$	13 nm	13 nm	58 nm
$-NH(CO)CH_3$	20 nm	20 nm	45 nm
$-NHCH_3$	-	-	73 nm
$-NR_2$	20 nm	20 nm	85 nm



Base value of aromatic ketone	246 nm
Hydroxy group at m-position	7 nm
Hydroxy group at p-position	25 nm
Experimental value	278 nm



Base value of Ar-COOH	230 nm
Hydroxy group at m-position	(2 x 7) nm
Hydroxy group at p-position	25 nm
Experimental value	269 nm