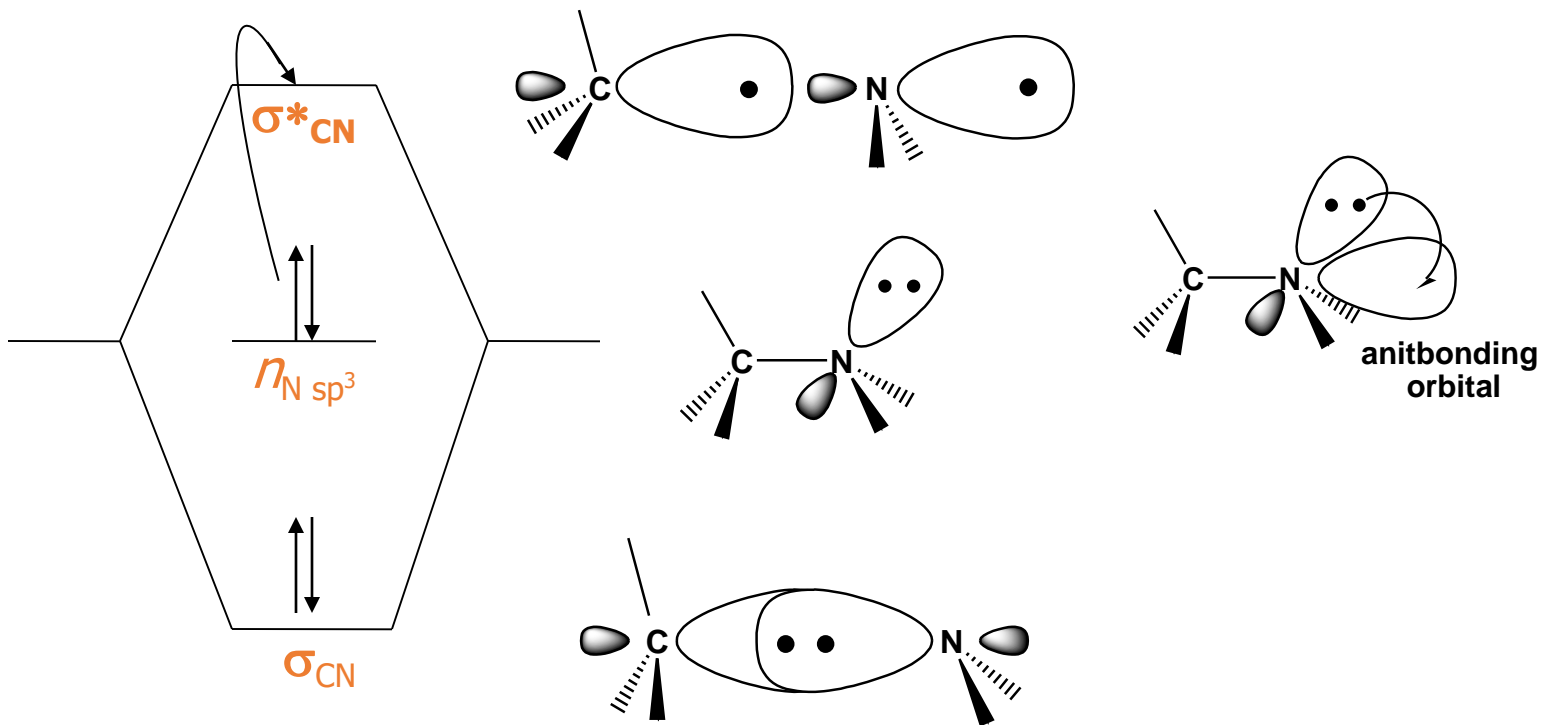


III. Chromophores

B. Organic Chromophores

2. Alcohols, ethers, amines and sulfur compounds – in the cases of simple, aliphatic examples of these compounds the $n \rightarrow \sigma^*$ is the most often observed transition; like the alkane $\sigma \rightarrow \sigma^*$ it is most often at shorter λ than 200 nm

Note how this transition occurs from the HOMO to the LUMO

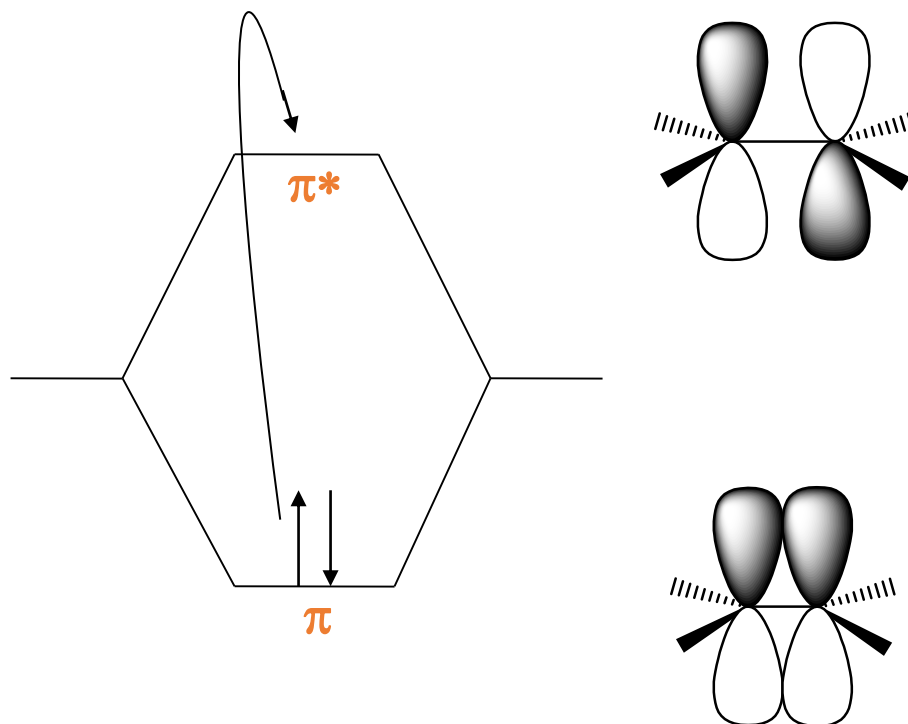


III. Chromophores

B. Organic Chromophores

3. **Alkenes and Alkynes** – in the case of isolated examples of these compounds the $\pi \rightarrow \pi^*$ is observed at 175 and 170 nm, respectively

Even though this transition is of lower energy than $\sigma \rightarrow \sigma^*$, it is still in the far UV – however, the transition energy is sensitive to substitution



III. Chromophores

B. Organic Chromophores

4. **Carbonyls** – unsaturated systems incorporating N or O can undergo $n \rightarrow \pi^*$ transitions (~ 285 nm) in addition to $\pi \rightarrow \pi^*$

Despite the fact this transition is forbidden by the selection rules ($\epsilon = 15$), it is the most often observed and studied transition for carbonyls

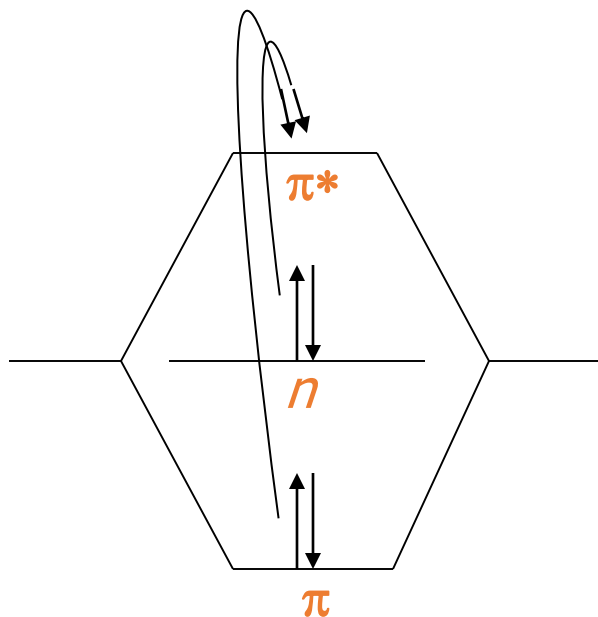
This transition is also sensitive to substituents on the carbonyl

Similar to alkenes and alkynes, non-substituted carbonyls undergo the $\pi \rightarrow \pi^*$ transition in the vacuum UV (188 nm, $\epsilon = 900$); sensitive to substitution effects

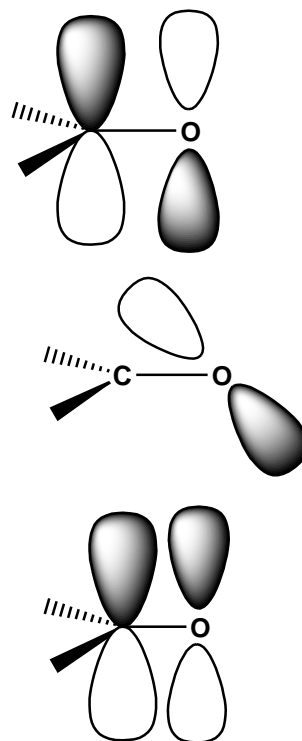
III. Chromophores

B. Organic Chromophores

4. **Carbonyls** – $n \rightarrow \pi^*$ transitions (~ 285 nm); $\pi \rightarrow \pi^*$ (188 nm)



σ_{CO} transitions omitted for clarity



It has been determined from spectral studies, that carbonyl oxygen more approximates sp rather than sp^2 !

III. Chromophores

C. Substituent Effects

General – from our brief study of these general chromophores, only the weak $n \rightarrow \pi^*$ transition occurs in the routinely observed UV

The attachment of substituent groups (other than H) can shift the energy of the transition

Substituents that increase the intensity and often wavelength of an absorption are called *auxochromes*

Common auxochromes include alkyl, hydroxyl, alkoxy and amino groups and the halogens

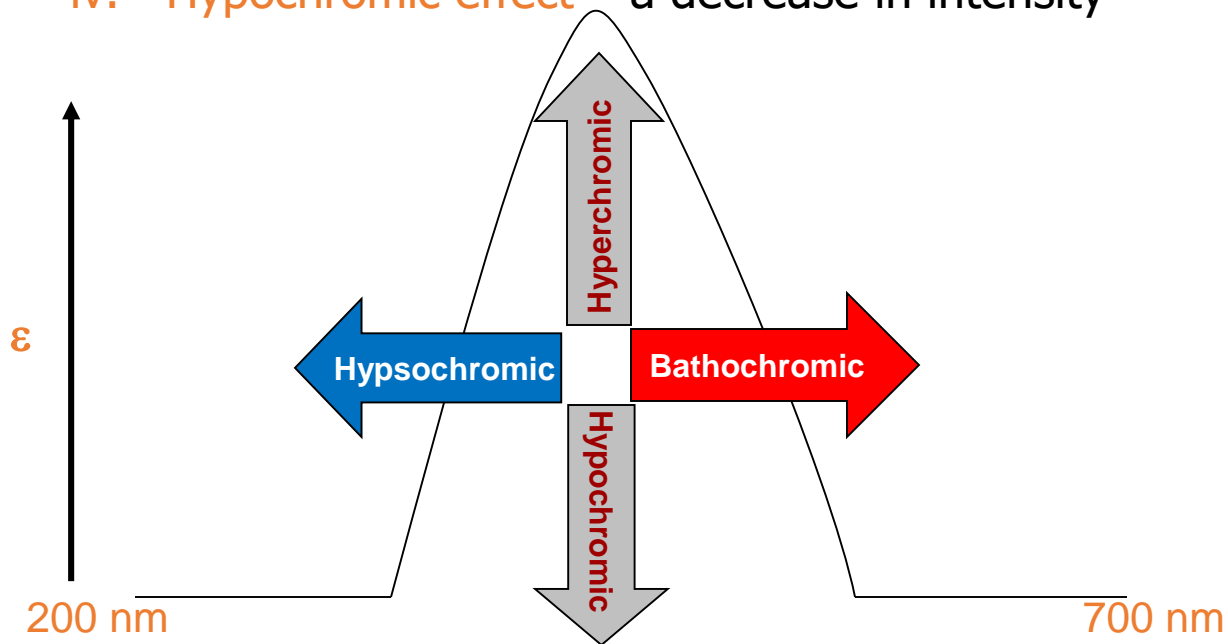
UV -VIS Spectroscopy

III. Chromophores

C. Substituent Effects

General – Substituents may have any of four effects on a chromophore

- i. **Bathochromic shift** (red shift) – a shift to longer λ ; lower energy
- ii. **Hypsochromic shift** (blue shift) – shift to shorter λ ; higher energy
- iii. **Hyperchromic effect** – an increase in intensity
- iv. **Hypochromic effect** – a decrease in intensity

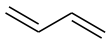
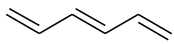
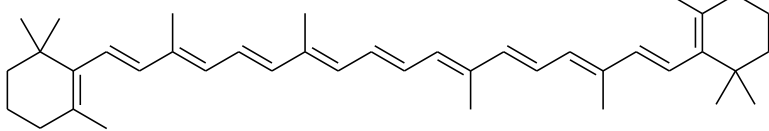
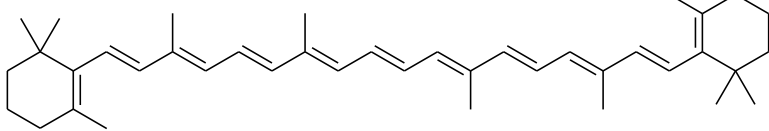

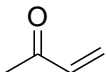


UV -VIS Spectroscopy

III. Chromophores

C. Substituent Effects

1. **Conjugation** – most efficient means of bringing about a bathochromic and hyperchromic shift of an unsaturated chromophore:

$\text{H}_2\text{C}=\text{CH}_2$	λ_{max} nm	ϵ	
	175	15,000	
	217	21,000	
	258	35,000	
 β -carotene	465	125,000	
	$n \rightarrow \pi^*$	280	12
	$\pi \rightarrow \pi^*$	189	900
	$n \rightarrow \pi^*$	280	27
	$\pi \rightarrow \pi^*$	213	7,100

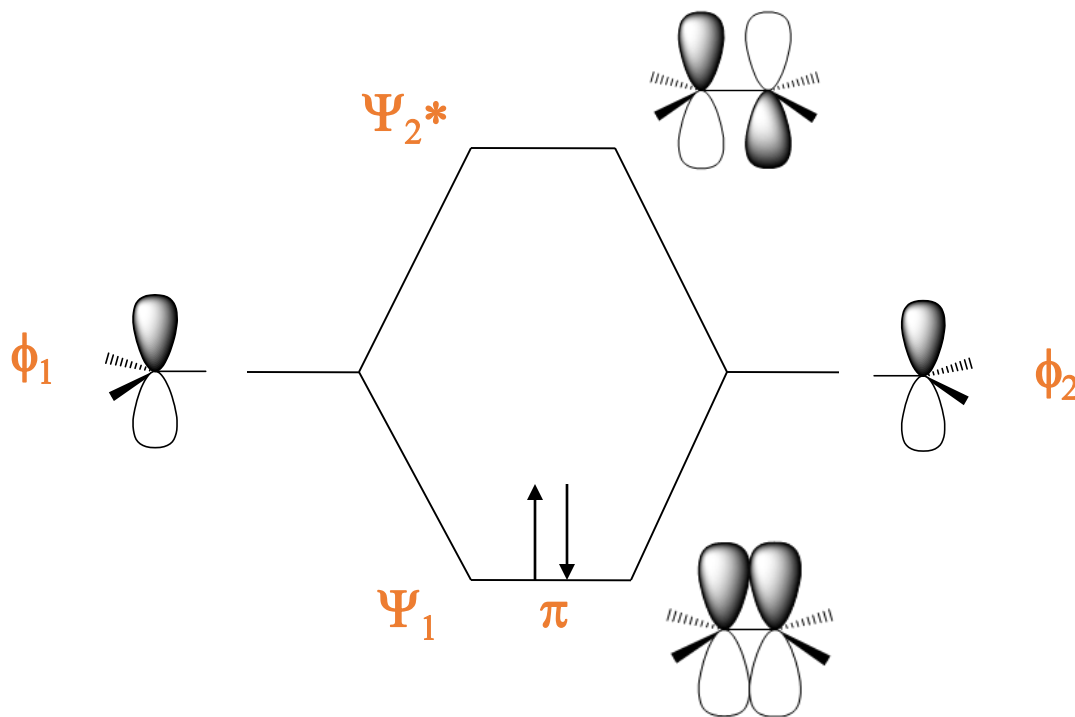
III. Chromophores

C. Substituent Effects

1. Conjugation – Alkenes

The observed shifts from conjugation imply that an increase in conjugation decreases the energy required for electronic excitation

From molecular orbital (MO) theory two atomic p orbitals, ϕ_1 and ϕ_2 from two sp^2 hybrid carbons combine to form two MOs Ψ_1 and Ψ_2^* in ethylene

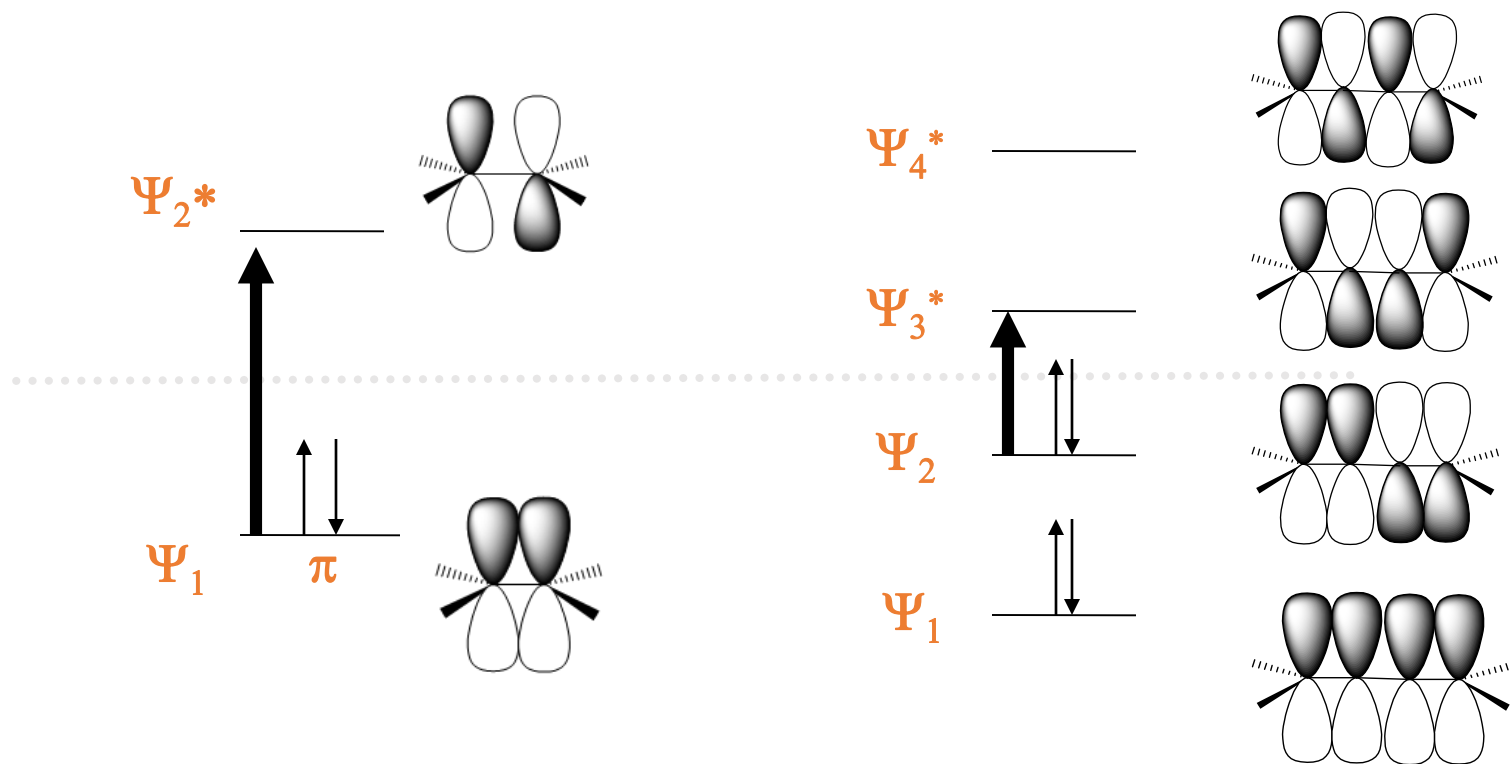


III. Chromophores

C. Substituent Effects

2. Conjugation – Alkenes

When we consider butadiene, we are now mixing 4 p orbitals giving 4 MOs of an energetically symmetrical distribution compared to ethylene



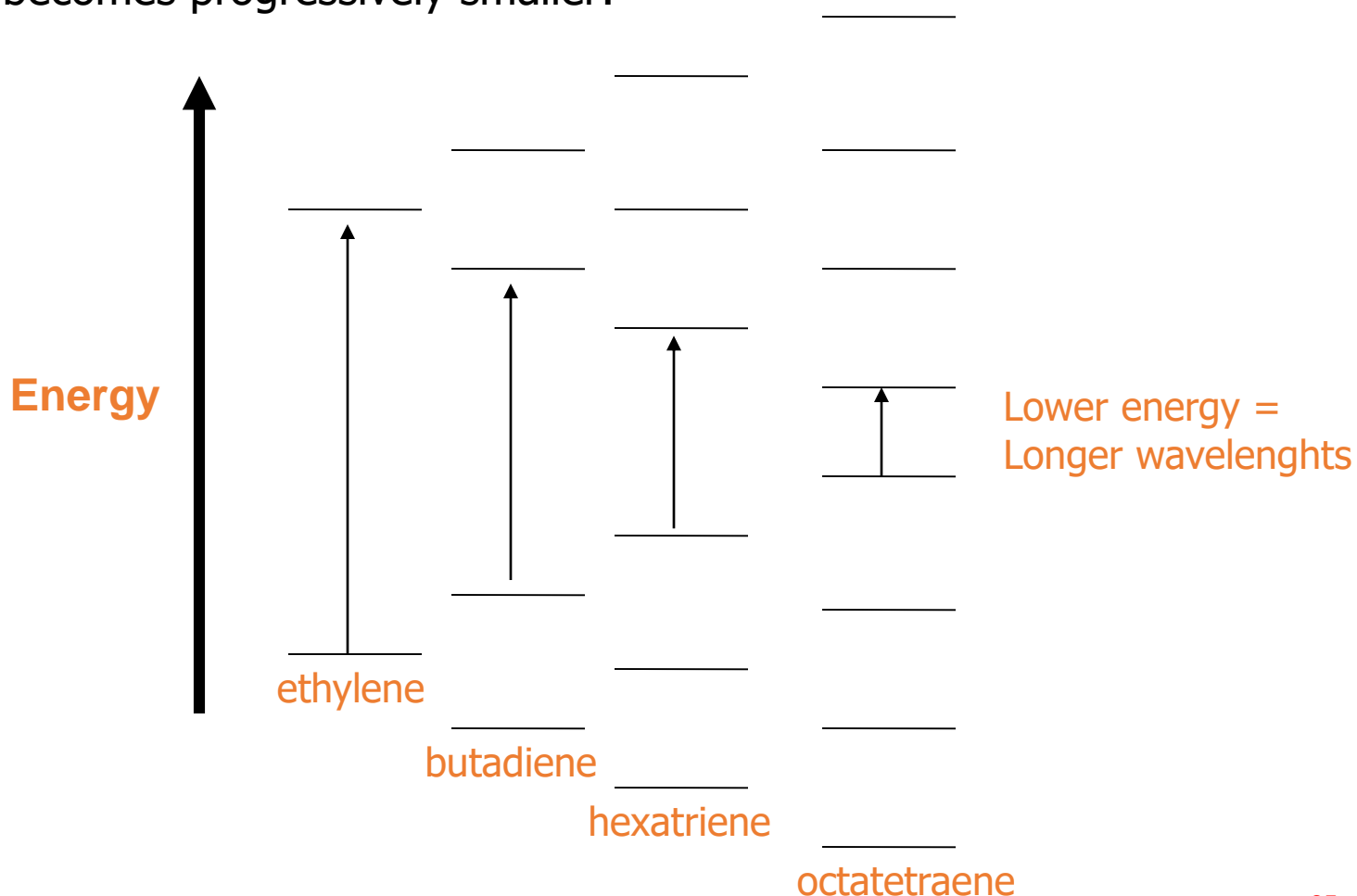
ΔE for the HOMO \rightarrow LUMO transition is **reduced**

III. Chromophores

C. Substituent Effects

2. Conjugation – Alkenes

Extending this effect out to longer conjugated systems the energy gap becomes progressively smaller:



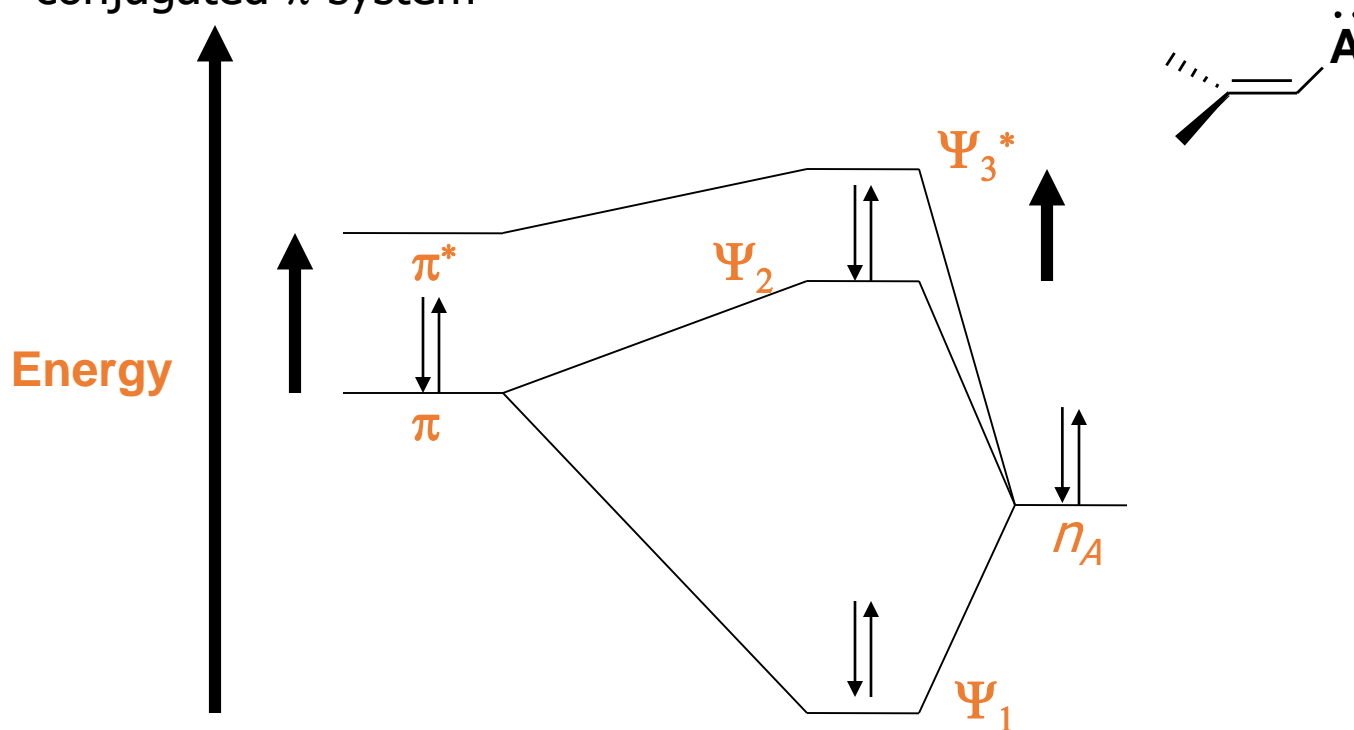
III. Chromophores

C. Substituent Effects

2. Conjugation – Alkenes

Similarly, the lone pairs of electrons on N, O, S, X can extend conjugated systems – auxochromes

Here we create 3 MOs – this interaction is not as strong as that of a conjugated π -system



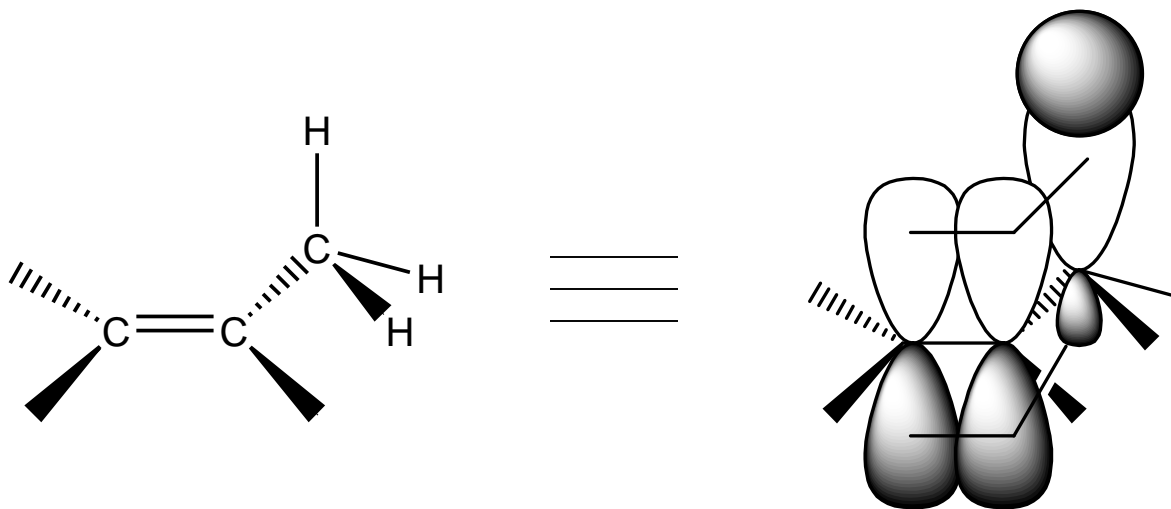
III. Chromophores

C. Substituent Effects

2. Conjugation – Alkenes

Methyl groups also cause a bathochromic shift, even though they are devoid of π - or n -electrons

This effect is thought to be through what is termed “hyperconjugation” or sigma bond resonance

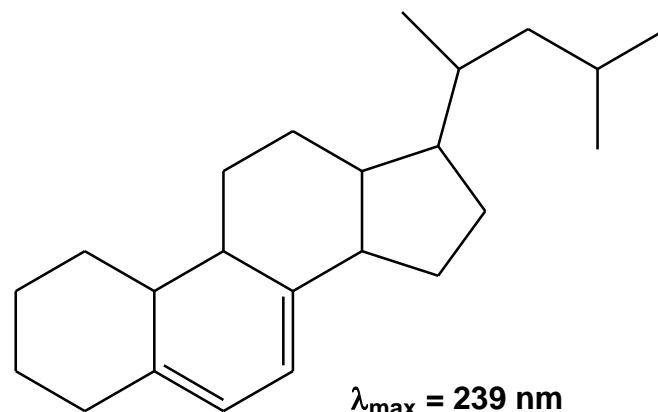


UV -VIS Spectroscopy

Next time – We will find that the effect of substituent groups can be reliably quantified from empirical observation of known conjugated structures and applied to new systems

This quantification is referred to as the Woodward-Fieser Rules which we will apply to three specific chromophores:

1. Conjugated dienes
2. Conjugated dienones
3. Aromatic systems

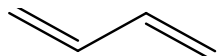


IV. Structure Determination

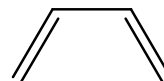
A. Dienes

1. General Features

For acyclic butadiene, two conformers are possible – *s-cis* and *s-trans*



s-trans



s-cis

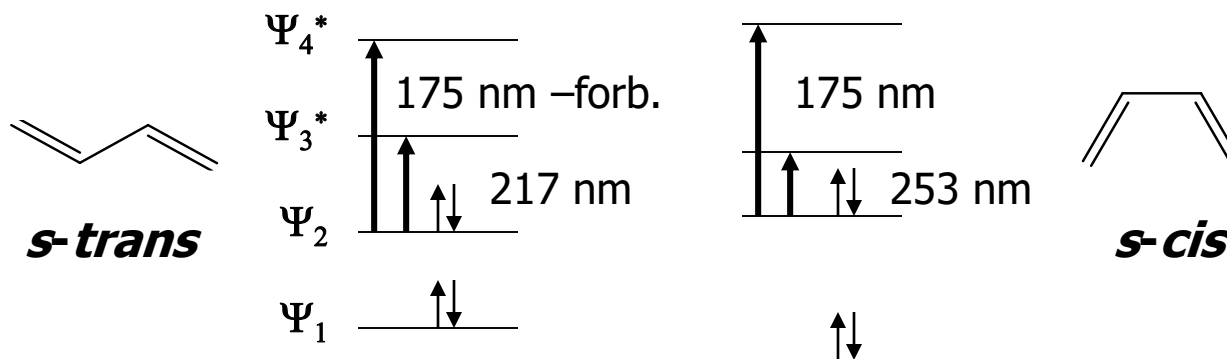
The *s-cis* conformer is at an overall higher potential energy than the *s-trans*; therefore the HOMO electrons of the conjugated system have less of a jump to the LUMO – lower energy, longer wavelength.

IV. Structure Determination

A. Dienes

1. General Features

Two possible $\pi \rightarrow \pi^*$ transitions can occur for butadiene $\Psi_2 \rightarrow \Psi_3^*$ and $\Psi_2 \rightarrow \Psi_4^*$



The $\Psi_2 \rightarrow \Psi_4^*$ transition is not typically observed:

- The energy of this transition places it outside the region typically observed – 175 nm
- For the more favorable *s-trans* conformation, this transition is forbidden

The $\Psi_2 \rightarrow \Psi_3^*$ transition is observed as an intense absorption

IV. Structure Determination

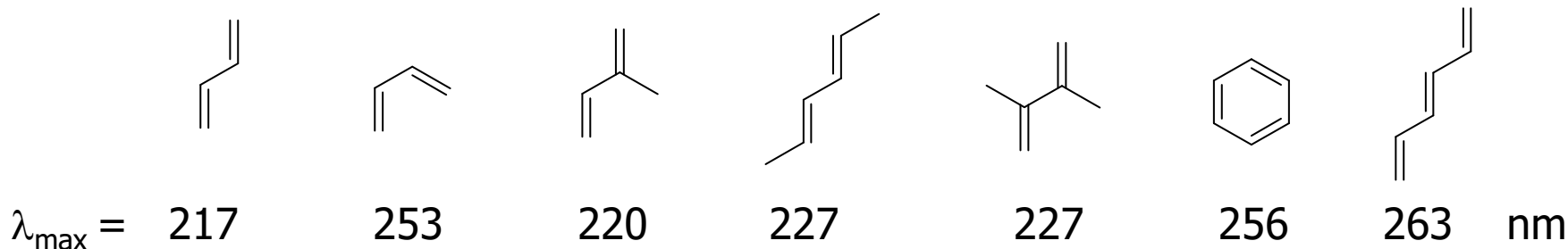
A. Dienes

1. General Features

The $\Psi_2 \rightarrow \Psi_3^*$ transition is observed as an intense absorption ($\epsilon = 20,000+$) based at 217 nm within the observed region of the UV

While this band is insensitive to solvent (as would be expected) it is subject to the bathochromic and hyperchromic effects of alkyl substituents as well as further conjugation.

Consider:



IV. Structure Determination

A. Dienes

2. Woodward-Fieser Rules - Dienes

The rules begin with a base value for λ_{\max} of the chromophore being observed:



acyclic butadiene = 217 nm

The incremental contribution of substituents is added to this base value from the group tables:

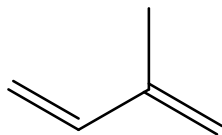
Group	Increment
Extended conjugation	+30
Each exo-cyclic C=C	+5
Alkyl	+5
-OCOCH ₃	+0
-OR	+6
-SR	+30
-Cl, -Br	+5
-NR ₂	+60

IV. Structure Determination

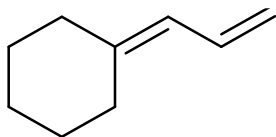
A. Dienes

2. Woodward-Fieser Rules – Dienes

For example:



Isoprene - acyclic butadiene =	217 nm
one alkyl subs.	+ 5 nm
	<u>222 nm</u>
Experimental value	220 nm



Allylidencyclohexane	
- acyclic butadiene =	217 nm
one exocyclic C=C	+ 5 nm
2 alkyl subs.	+10 nm
	<u>232 nm</u>
Experimental value	237 nm

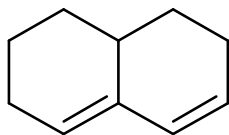
IV. Structure Determination

A. Dienes

3. Woodward-Fieser Rules – Cyclic Dienes

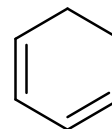
There are two major types of cyclic dienes, with two different base values

Heteroannular (transoid):



$$\varepsilon = 5,000 - 15,000$$
$$\text{base } \lambda_{\text{max}} = 214$$

Homoannular (cisoid):



$$\varepsilon = 12,000 - 28,000$$
$$\text{base } \lambda_{\text{max}} = 253$$

The increment table is the same as for acyclic butadienes with a couple additions:

Group	Increment
Additional homoannular	+39
Where both types of diene are present, the one with the longer λ becomes the base	

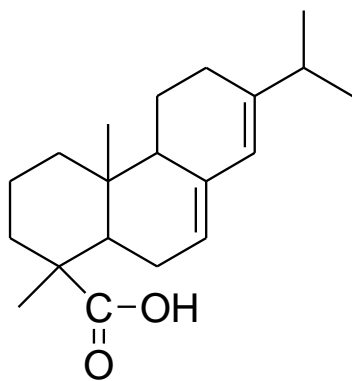
IV. Structure Determination

A. Dienes

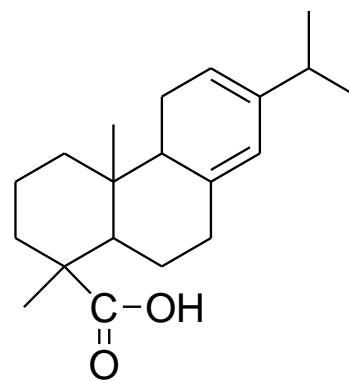
3. Woodward-Fieser Rules – Cyclic Dienes

In the pre-NMR era of organic spectral determination, the power of the method for discerning isomers is readily apparent

Consider abietic vs. levopimaric acid:



abietic acid



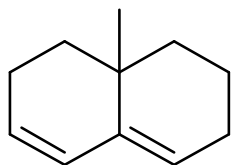
levopimaric acid

IV. Structure Determination

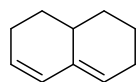
A. Dienes

3. Woodward-Fieser Rules – Cyclic Dienes

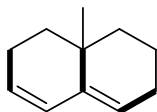
For example:



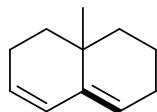
1,2,3,7,8,8a-hexahydro-8a-methylnaphthalene



heteroannular diene = 214 nm



3 alkyl subs. (3 x 5) +15 nm



1 exo C=C

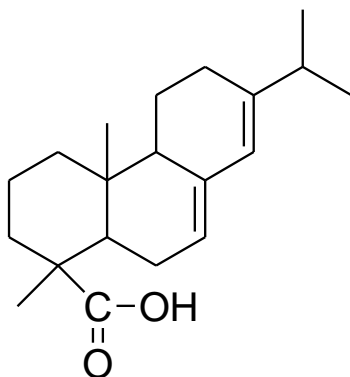
+ 5 nm
234 nm

Experimental value 235 nm

IV. Structure Determination

A. Dienes

3. Woodward-Fieser Rules – Cyclic Dienes

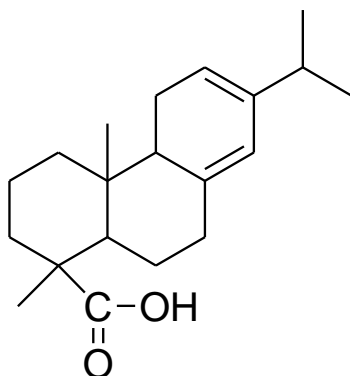


heteroannular diene = 214 nm

4 alkyl subs. (4 x 5) +20 nm

1 exo C=C + 5 nm

239 nm



homoannular diene = 253 nm

4 alkyl subs. (4 x 5) +20 nm

1 exo C=C + 5 nm

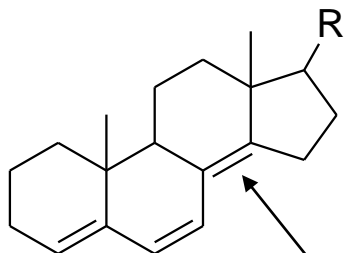
278 nm

IV. Structure Determination

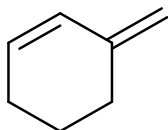
A. Dienes

3. Woodward-Fieser Rules – Cyclic Dienes

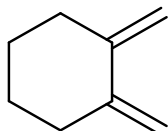
Be careful with your assignments – three common errors:



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 value for an acyclic diene



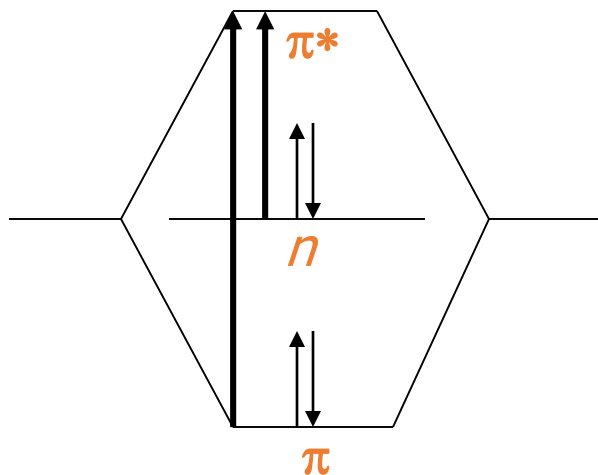
Likewise, this is *not* a homoannular diene; you would use the base value for an acyclic diene

IV. Structure Determination

B. Enones

1. General Features

Carbonyls, as we have discussed have two primary electronic transitions:



Remember, the $\pi \rightarrow \pi^*$ transition is allowed and gives a high ϵ , but lies outside the routine range of UV observation

The $n \rightarrow \pi^*$ transition is forbidden and gives a very low ϵ , but can routinely be observed

IV. Structure Determination

B. Enones

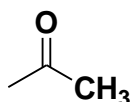
1. General Features

For auxochromic substitution on the carbonyl, pronounced hypsochromic shifts are observed for the $n \rightarrow \pi^*$ transition (λ_{\max}):

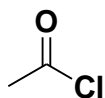


293 nm

This is explained by the inductive withdrawal of electrons by O, N or halogen from the carbonyl carbon – this causes the n -electrons on the carbonyl oxygen to be held more firmly

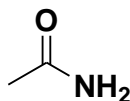


279

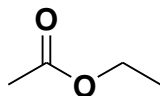


235

It is important to note this is different from the auxochromic effect on $\pi \rightarrow \pi^*$ which extends conjugation and causes a bathochromic shift

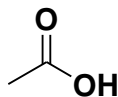


214



204

In most cases, this bathochromic shift is not enough to bring the $\pi \rightarrow \pi^*$ transition into the observed range



204

IV. Structure Determination

B. Enones

1. General Features

Conversely, if the C=O system is conjugated both the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ bands are bathochromically shifted

Here, several effects must be noted:

- i. the effect is more pronounced for $\pi \rightarrow \pi^*$
- ii. if the conjugated chain is long enough, the much higher intensity $\pi \rightarrow \pi^*$ band will overlap and drown out the $n \rightarrow \pi^*$ band
- iii. the shift of the $n \rightarrow \pi^*$ transition is not as predictable

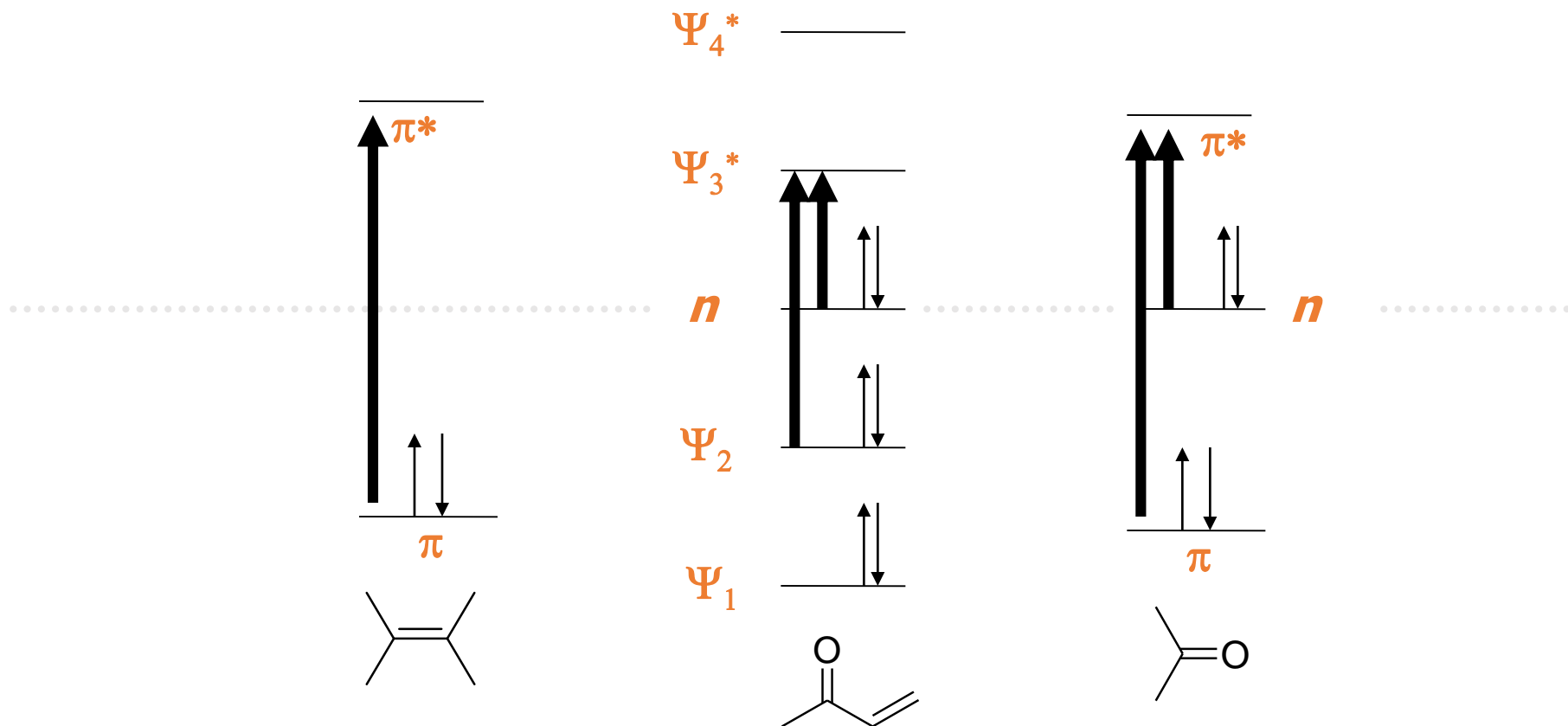
For these reasons, empirical Woodward-Fieser rules for conjugated enones are for the higher intensity, allowed $\pi \rightarrow \pi^*$ transition

IV. Structure Determination

B. Enones

1. General Features

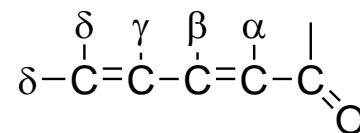
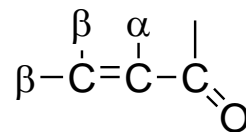
These effects are apparent from the MO diagram for a conjugated enone:



IV. Structure Determination

B. Enones

2. Woodward-Fieser Rules - Enones



Group		Increment
6-membered ring or acyclic enone		Base 215 nm
5-membered ring parent enone		Base 202 nm
Acyclic dienone		Base 245 nm
Double bond extending conjugation		30
Alkyl group or ring residue	α, β, γ and higher	10, 12, 18
-OH	α, β, γ and higher	35, 30, 18
-OR	$\alpha, \beta, \gamma, \delta$	35, 30, 17, 31
-O(C=O)R	α, β, δ	6
-Cl	α, β	15, 12
-Br	α, β	25, 30
-NR ₂	β	95
Exocyclic double bond		5
Homocyclic diene component		39

IV. Structure Determination

B. Enones

2. Woodward-Fieser Rules - Enones

Aldehydes, esters and carboxylic acids have different base values than ketones

Unsaturated system	Base Value
Aldehyde	208
With α or β alkyl groups	220
With α,β or β,β alkyl groups	230
With α,β,β alkyl groups	242
Acid or ester	
With α or β alkyl groups	208
With α,β or β,β alkyl groups	217
Group value – exocyclic α,β double bond	+5
Group value – endocyclic α,β bond in 5 or 7 membered ring	+5

IV. Structure Determination

B. Enones

2. Woodward-Fieser Rules - Enones

Unlike conjugated alkenes, solvent does have an effect on λ_{\max}

These effects are also described by the Woodward-Fieser rules

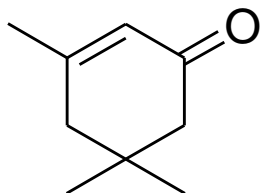
Solvent correction	Increment
Water	+8
Ethanol, methanol	0
Chloroform	-1
Dioxane	-5
Ether	-7
Hydrocarbon	-11

IV. Structure Determination

B. Enones

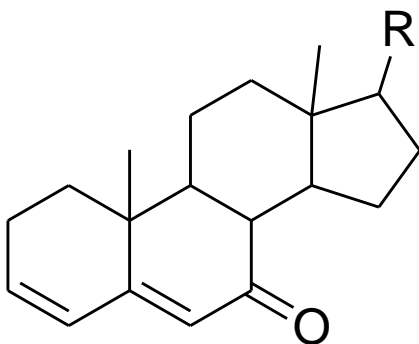
2. Woodward-Fieser Rules - Enones

Some examples – keep in mind these are more complex than dienes



cyclic enone =	215 nm
2 x β - alkyl subs. (2 x 12)	<u>+24 nm</u>
	239 nm

Experimental value 238 nm



cyclic enone =	215 nm
extended conj.	+30 nm
b-ring residue	+12 nm
d-ring residue	+18 nm
exocyclic double bond	<u>+ 5 nm</u>
	280 nm

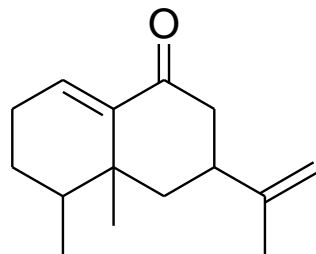
Experimental 280 nm

IV. Structure Determination

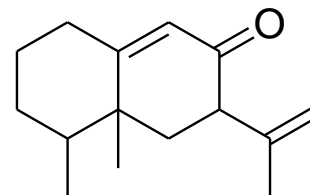
B. Enones

2. Woodward-Fieser Rules - Enones

Take home problem – can these two isomers be discerned by UV-spec.



Eremophilone



allo-Eremophilone

Comparison with Experiment

<u>• Substrates</u>	<u>Absorption Maxima (nm)</u>
• Simple alkenes	190-200
• Acyclic dienes	220-250
• Cyclic dienes	250-270
• Styrenes	270-300
• Saturated ketones	270-280
• α,β -unsaturated ketones	310-330
• Aromatic ketones and Aldehydes	280-300
• Aromatic compounds	250-280

REFERENCES

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- 3. <http://www.chem.ucla.edu/~webspectra/irintro.html>*
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- 4. <http://orgchem.colorado.edu/studylinks/studyds.html>*