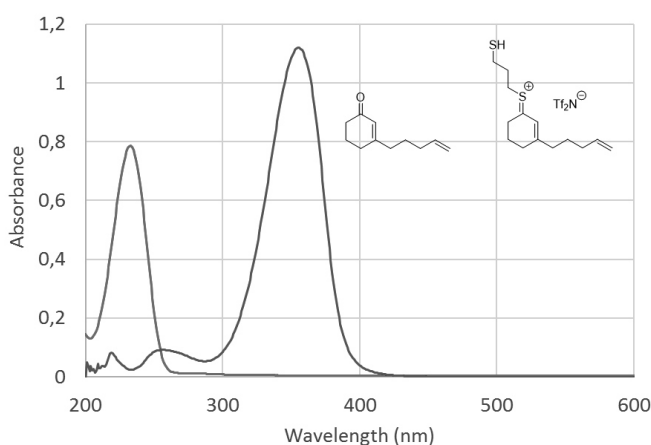


Exercise 1

UV/Vis spectra allow for the fast and easy calculations of extinction coefficients as well as the interpretation of different electronic transitions of the molecule.

- a) The UV/Vis spectra of the enone and sulfonium ion are shown below in red and blue, respectively. Assuming the spectra were recorded using a 1 mm quartz cuvette and 0.5 mM concentration for both samples, calculate the absorption coefficient for the enone at 235 nm and the sulfonium ion at 357 nm. The absorbance for the enone at 233 nm is 0.77 and the absorbance of the sulfonium ion at 357 nm is 1.11. To what transition do you assign the absorption?



Lambert-Beer Law: $A = c \cdot x \cdot \epsilon$

A = absorbance

c = concentration (M)

x = path length (cm)

ϵ (enone) = 15400 L·mol⁻¹·cm⁻¹

ϵ (sulfonium ion) = 22200 L·mol⁻¹·cm⁻¹

The absorption can be assigned to a (π, π^) transition.*

- b) The enone shown above shows phosphorescence at $\lambda = 410$ nm. Calculate the triplet energy of the enone.

$$E = (h \cdot c) / \lambda$$

h = Planck's constant = 6.626 x 10⁻³⁴ J·s

c = speed of light = 3 x 10⁸ m/sec

$\lambda = 410$ nm (given in the question above)

Therefore, $E_T = 292$ kJ/mol

- c) Using a Jablonski diagram, qualitatively explain why one observes fluorescence at lower wavelengths compared to phosphorescence (no mathematics required).

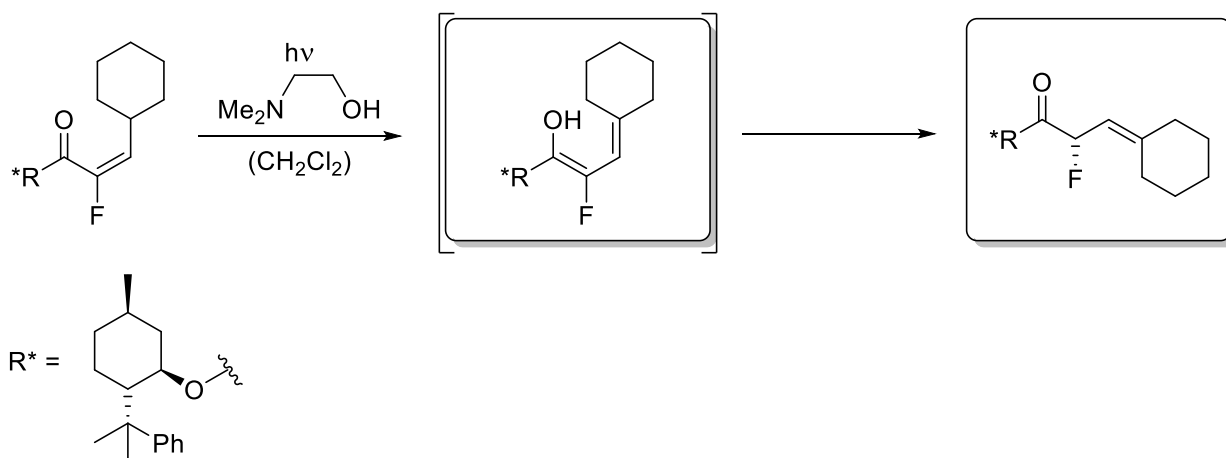
In the equation in part b above, energy is inversely proportional to wavelength. From the Jablonski diagram, one can see that T_1 is lower in energy compared to that of S_1 . Thus phosphorescence should occur at higher wavelength (lower energy) compared to fluorescence.

- d) The enone shown above is reported to undergo rapid intersystem crossing to the triplet state (T_1) when the $n\pi^*$ transition is excited at 320 nm. Explain what causes intersystem crossing for the above enone.

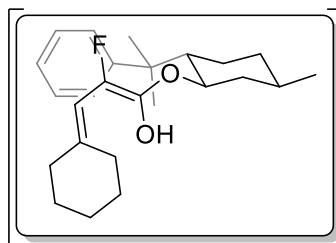
Spin Orbit Coupling (SOC). In essence, SOC states that when a spin flip occurs (a forbidden process), an orbital must also be changed. One can never have two electrons with the same spin in the same orbital, as this violates Hund's rule. Beside this, El-Sayed's rule states that the rate of ISC is relatively large if the transition involves a change of molecular orbital type, e.g. a (π,π^) singlet state could transition to a (n,π^*) triplet state, but not to a (π,π^*) triplet state and vice versa.*

Exercise 2

α,β -Unsaturated esters can be photochemically deconjugated and by use of chiral auxiliaries, such as 8-phenylmenthol, diastereoselectivity can be induced. Draw the intermediate and the product and give the configuration of the formed stereogenic center.

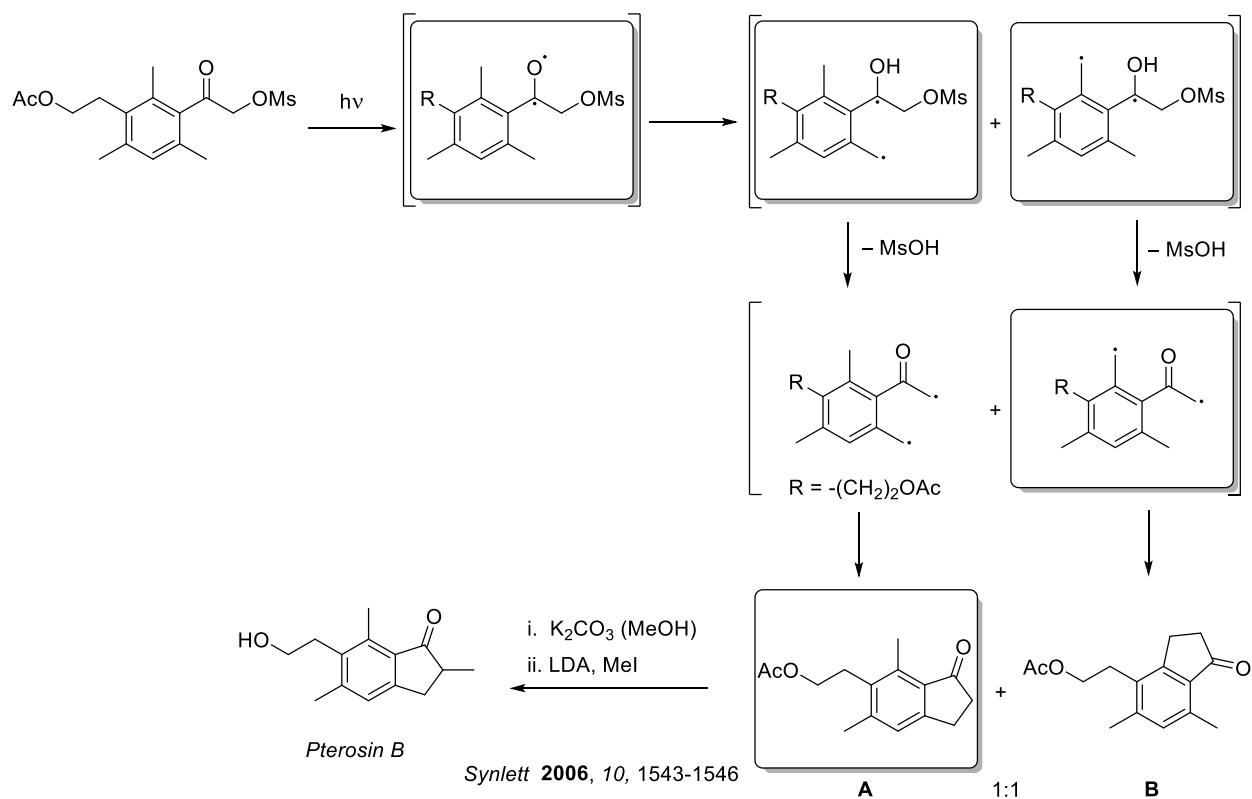


Draw the intermediate with the auxiliary in a chair conformation in the box below to help you visualize the selectivity for one diastereomer.



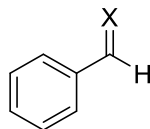
Exercise 3

In the total synthesis of *Pterosin B*, a photochemical step was implied in order to obtain an important precursor of the natural product. However, the photoreaction gave a 1:1 mixture of the desired product **A** and an unwanted regioisomer **B**. Explain the formation of both products by drawing all intermediates.



Exercise 1

Benzaldehyde and styrene have structural similarities. However, their energy gap between their singlet and triplet energies differ ($\Delta E_{(X=O)} = 21 \text{ kJ mol}^{-1}$, $\Delta E_{(X=CH_2)} = 157 \text{ kJ mol}^{-1}$).

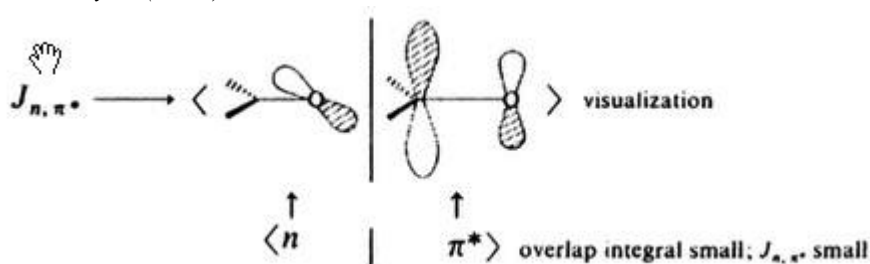


$$X = O \quad E(S_1) = 320 \text{ kJ mol}^{-1} \quad E(T_1) = 299 \text{ kJ mol}^{-1}$$

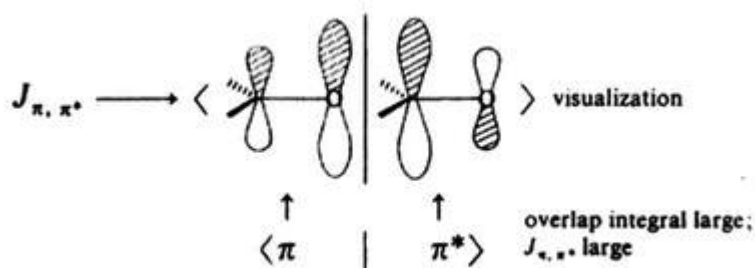
$$X = CH_2 \quad E(S_1) = 415 \text{ kJ mol}^{-1} \quad E(T_1) = 258 \text{ kJ mol}^{-1}$$

- Explain the occurrence of the energy gap between singlet and triplet states (singlet triplet splitting). *Hund's rule states that the configuration with the electron spins parallel is at a lower energy than the configuration with paired spins. According to the Pauli Principle, two electrons cannot be at the same place at the same time, therefore they need to correlate their motions in order to minimize electron-electron repulsions, in other words to avoid each other. In the triplet state, the same spin of the unpaired electrons lead to a better correlation of electron motions, i.e. a lower electronic energy of the triplet state compared to the singlet state.*
- Assign the configuration of the lowest singlet (S_1) and triplet state (T_1) in the case of benzaldehyde and in the case of styrene.
Benzaldehyde: $n\pi^$; Styrene $\pi\pi^*$*
- Why is the singlet triplet splitting significantly larger in the case of styrene compared to benzaldehyde? Draw the n -, π - and π^* - orbitals of the important ($C=O$, $C=C$) bond to help you explain your answer.

Benzaldehyde ($C=O$):



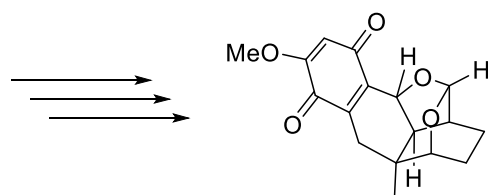
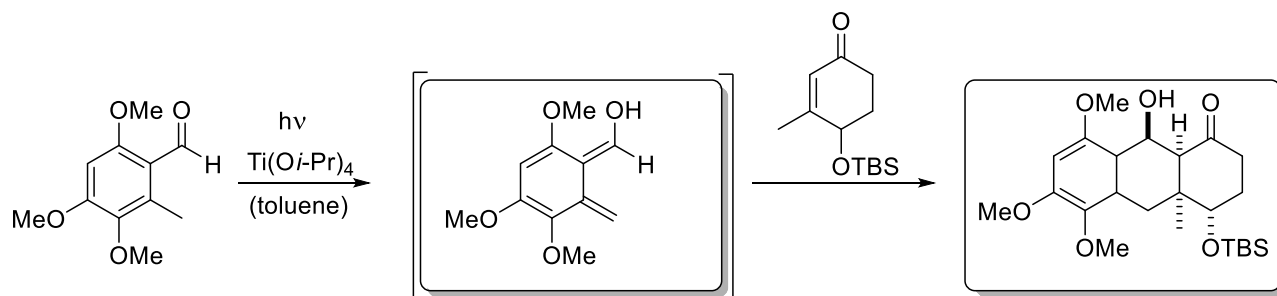
Styrene ($C=C$):



In benzaldehyde, the overlap between n - and π^ -orbital is small, therefore the unpaired electrons' repulsion is very small from the beginning, hence there is only little effect of the relative spin orientation of the unpaired electrons. In styrene the overlap between π - and π^* -orbital is significantly larger, hence the better correlation of electron motions in the triplet state has a larger effect and therefore leads to a higher energy gap between singlet and triplet state.*

Exercise 2

The total synthesis of Oncocalyxone B features a photochemical step, where the intermediate is trapped by a cyclohexanone derivative. Draw the intermediate and the final product. Assign the relative configuration of all stereogenic centers formed.

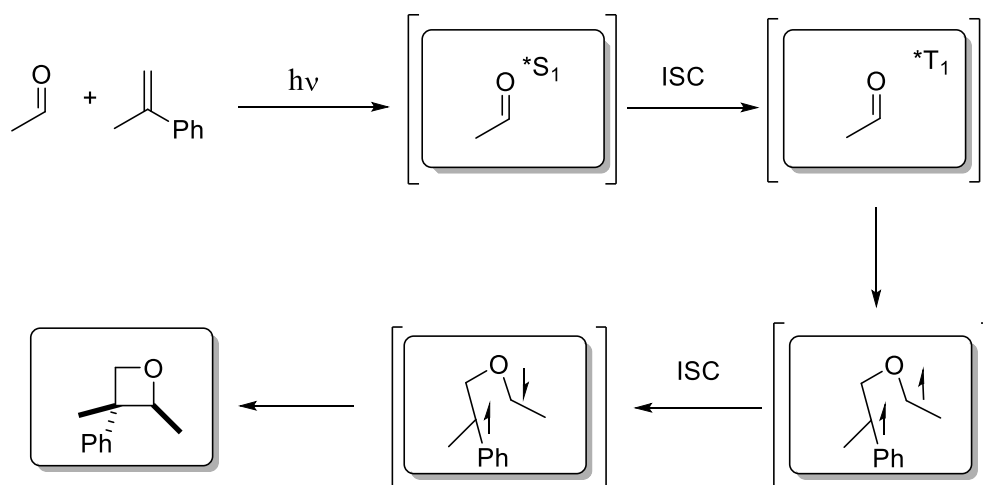


Nat. Commun. **2017**, *8*, 622

Oncocalyxone B

Exercise 3

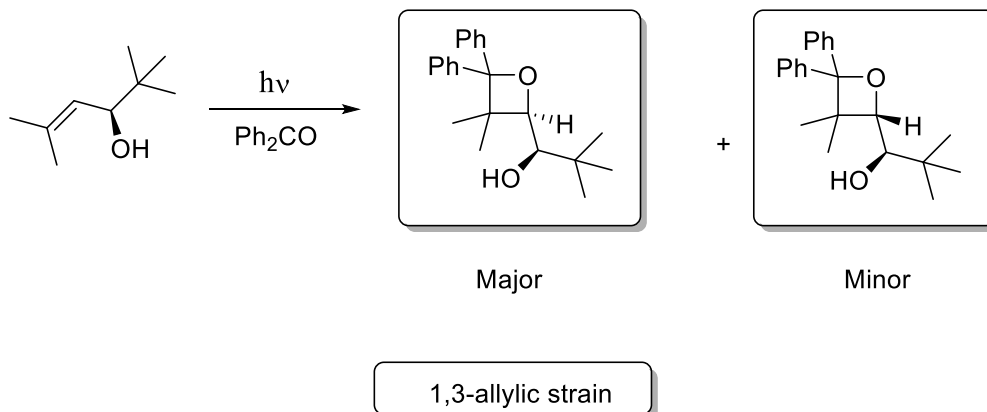
The Paternò-Büchi reaction is a very common method for the generation of highly substituted oxetanes that can be further functionalized using a variety of different reactions. Provide all intermediates and the final product from the Paternò-Büchi reaction shown below. Why do you observe one diastereomer in the final product?



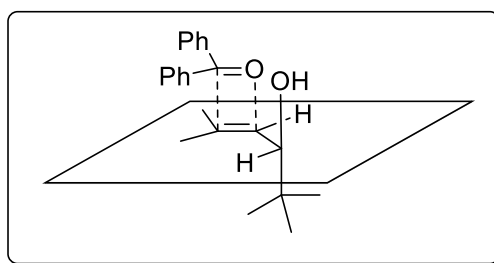
The two largest groups should be trans with respect to one another.

Exercise 4

The following Paternò-Büchi reaction provides one major diastereomer and one minor diastereomer. Draw the two products and rationalize the selectivity by drawing the transition state in the case of the major diastereomer. Which effect controls the stereoselectivity?



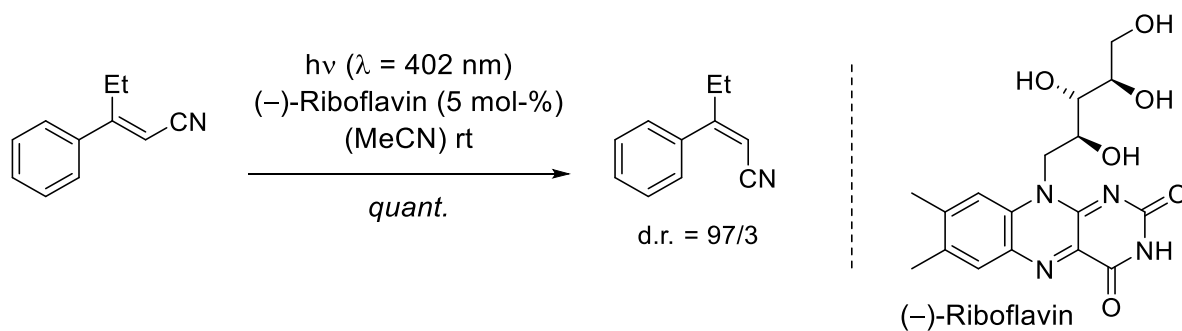
Intermediate to the major diastereomer:



Current Organic Chemistry, 2009, 13, 939-954

Exercise 5

Please explain the following photocatalytic $E \rightarrow Z$ isomerisation of cinnamitriles in the presence of (-)-Riboflavin.



See script: $E(T_1)[cis] > E(T_1)[Sens.] > E(T_1)[trans]$

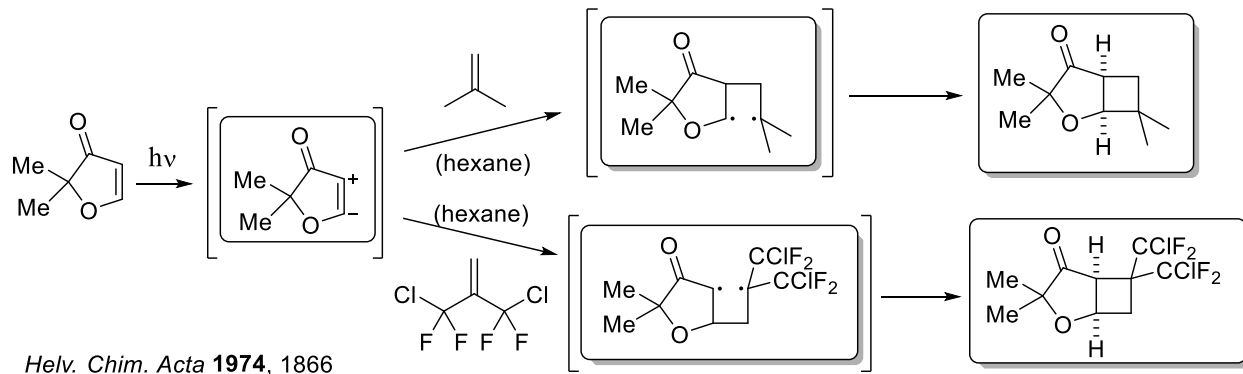
Organic Photochemistry – 3rd exercise 12.12.17 9.15 a.m.

Group I: room 27402

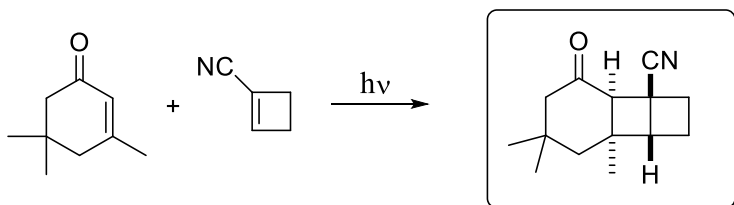
Group II: room 42306

Exercise 1

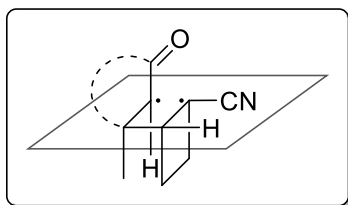
a) Explain the outcome of the irradiation of the following enone in presence of different olefins. Rationalize the regioselectivity by drawing the mechanism.



b) Draw the product of the [2+2] photocycloaddition reaction shown below and explain the regio- and diastereoselectivity.



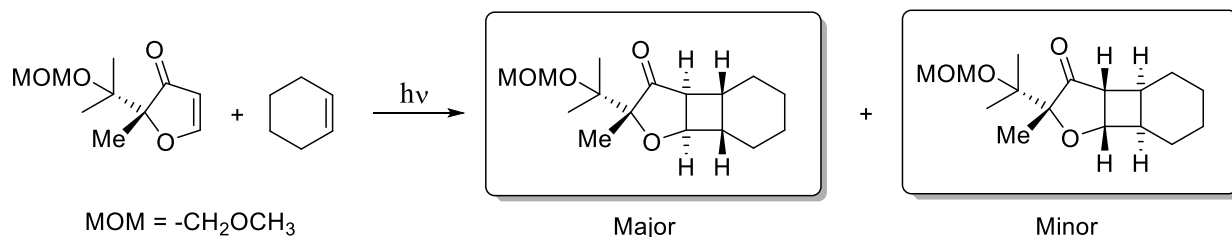
Intermediate:



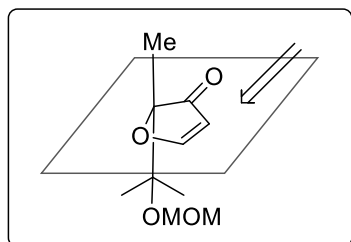
Org. React. **1993**, 44, 297

Exercise 2

Draw the two products for the photoreaction shown below and rationalize the diastereoselectivity of the major product by cyclic stereocontrol.



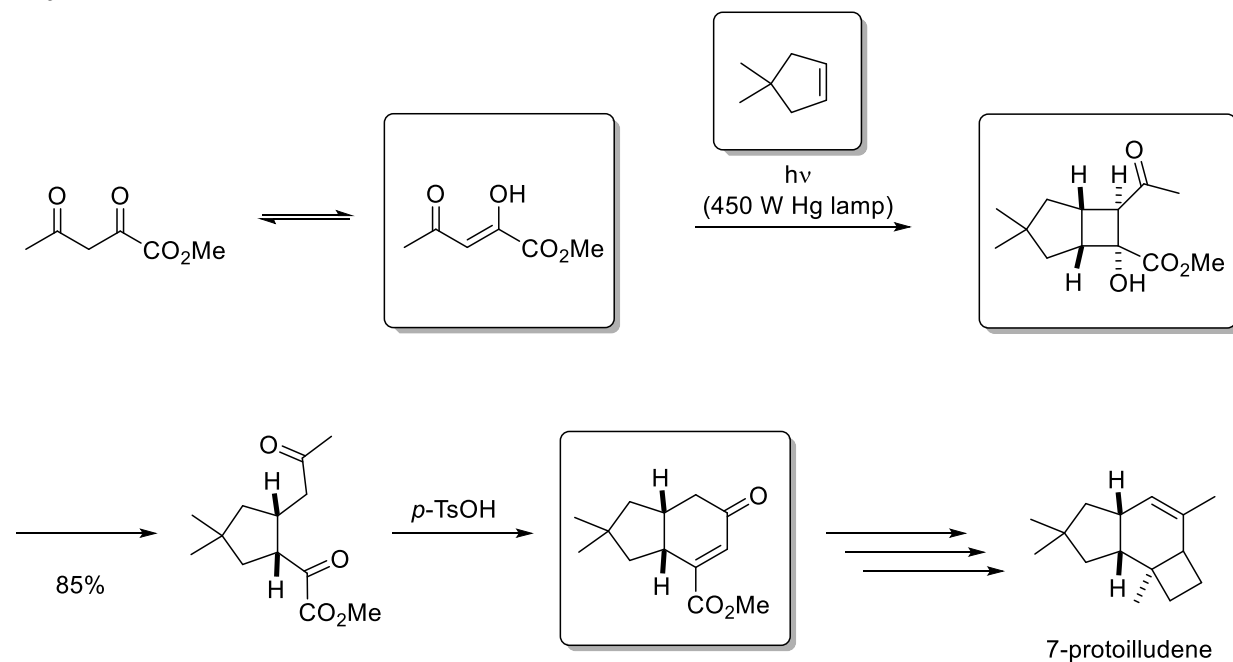
Diastereoface differentiation:



Org. React. **1993**, 44, 297

Exercise 3

The total synthesis of 7-protoilludene starts with a photoreaction of the diketoester shown below. Which form of the diketoester is capable of undergoing the shown photoreaction? Fill in the missing olefin. Draw the product of the photoreaction and state the name of the reaction sequence. What happens when the resulting compound is subjected to acidic conditions?

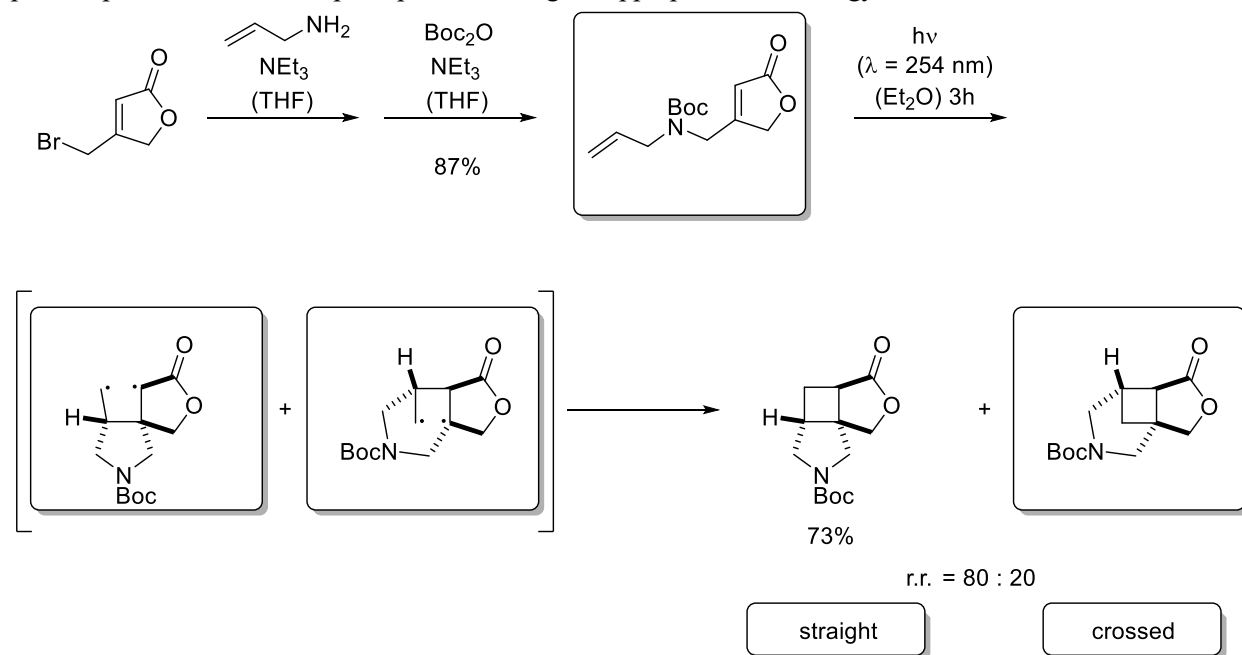


Chem. Lett. **1979**, 649
Eur. J. Org. Chem. **2011**, 7041

Reaction sequence: De Mayo reaction

Exercise 4

3-Azabicyclo[3.2.0]heptane scaffolds can be built up by using intramolecular [2+2] photocycloaddition reactions. Draw the irradiation precursor and the minor product that is formed in the photoreaction. In addition, draw possible intermediates that lead to the respective photocycloaddition products. Why is the formation of the given product preferred? Label the photoproducts using the appropriate terminology.



Chem. Commun. **2013**, 49, 2989

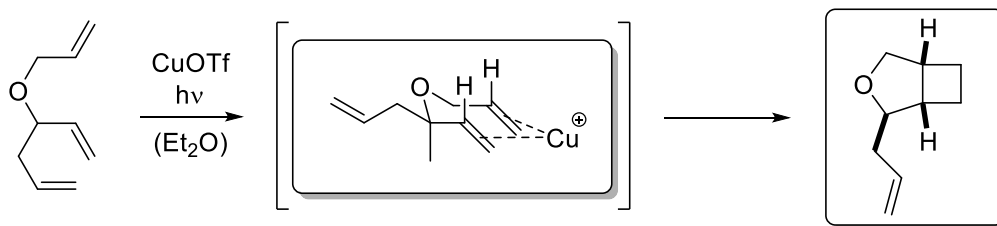
Organic Photochemistry – 4th exercise 11.01.2018 11.00 a.m.

Group I: room 22210

Group II: room 42306

Exercise 1

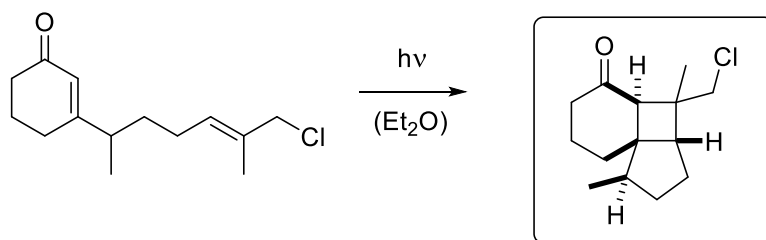
Draw the product of the following photocycloaddition and explain the regio- and stereoselectivity.



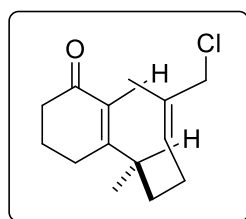
J. Org. Chem. **1987**, 52, 83

Exercise 2

Draw the product of the below [2+2] photocycloaddition and rationalize the stereochemical outcome. Which effect controls the stereoselectivity?



Stereoface differentiation:

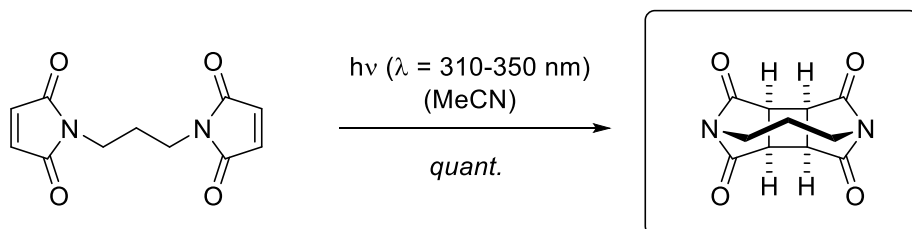


1,3-allylic strain

Org. React. **1993**, 44, 297

Exercise 3

Imides can react photochemically in a similar fashion as enones. In this case, irradiation of the shown dimaleimide gives a single product quantitatively. Draw the product with the relative configuration. Which type of photochemical reaction occurs.

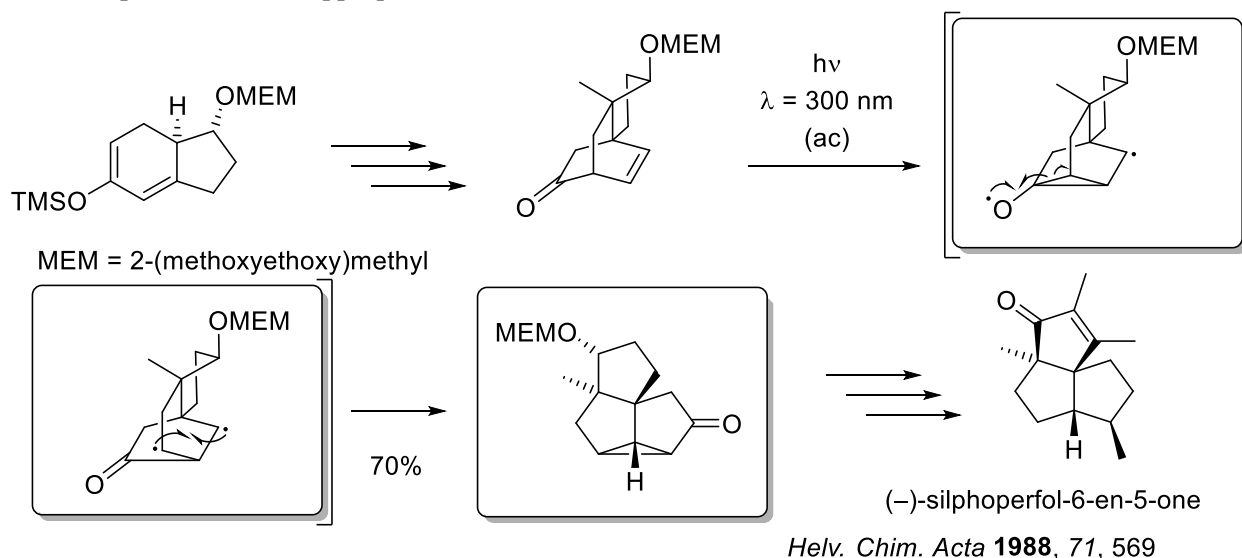


Type of reaction: photodimerisation

Angew. Chem. Int. Ed. **1969**, 8, 213

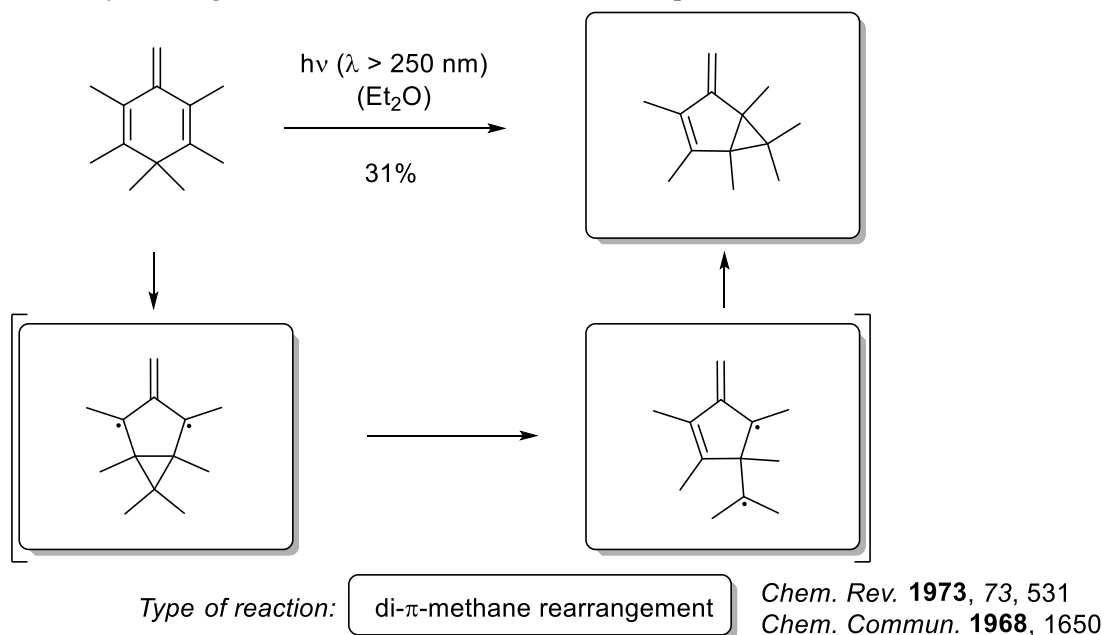
Exercise 4

(-)-Silphiperfol-6-en-5-one was synthetically accessible by using an oxadi- π -methane rearrangement. Draw the product and the appropriate intermediates.



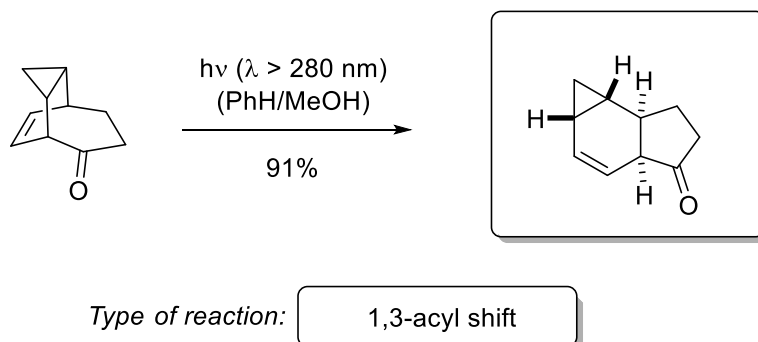
Exercise 5

Methylene-2,5-cyclohexadiene reacts when irradiated at short wavelength. Draw the product and explain its formation by drawing the intermediates. What reaction is depicted?



Exercise 6

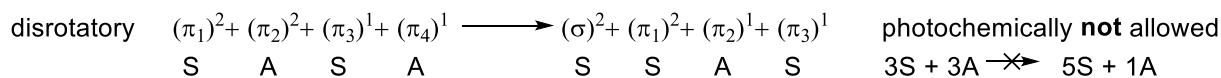
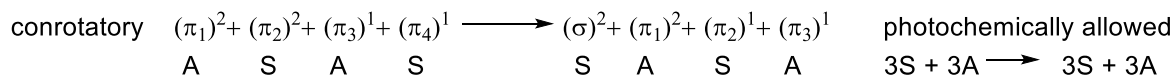
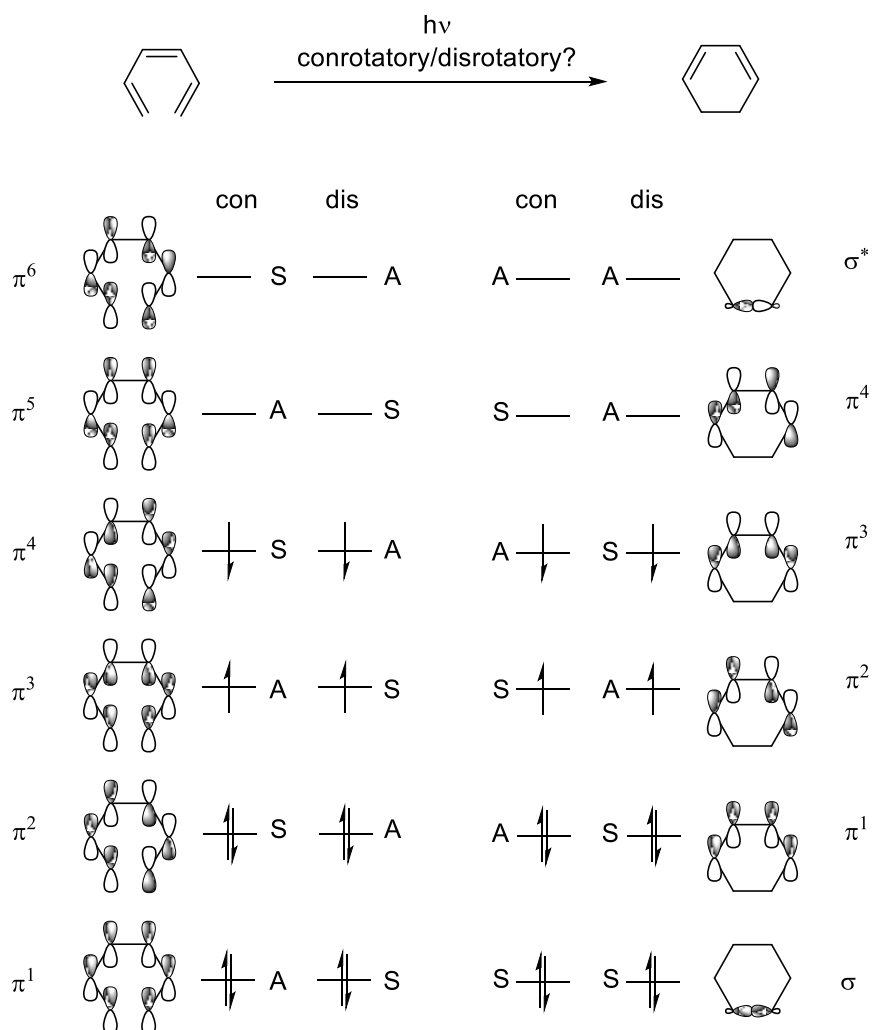
β,γ -unsaturated carbonyl compounds isomerize when irradiated under suitable conditions. Which reaction takes place? Draw the product including the relative configuration.



Tetrahedron Lett. **1978**, 6, 531

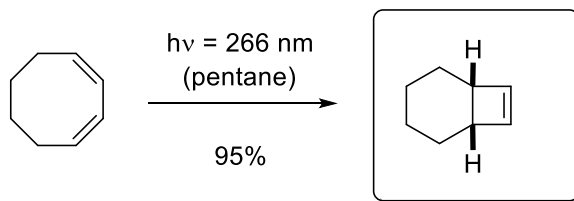
Exercise 1

Consider hexatriene as a model system for cyclisations. Does the photochemical [6 π] cyclisation occur conrotatory or disrotatory? Analyse the symmetry of the reaction using the Woodward-Hoffmann rules. Therefore draw the molecular orbitals of hexatriene and analyse their orbital symmetry for both cases, conrotatory and disrotatory. Which symmetry operation is important in the conrotatory, respectively disrotatory case?

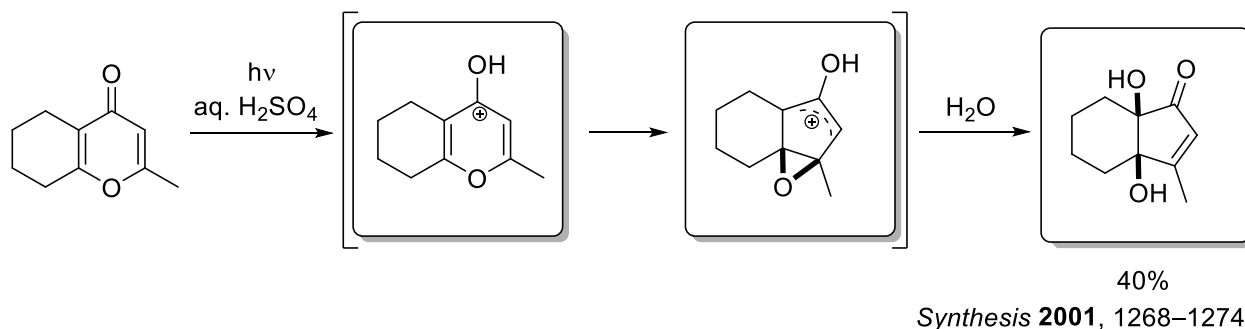


Exercise 2

Draw the expected product formed for each reaction.



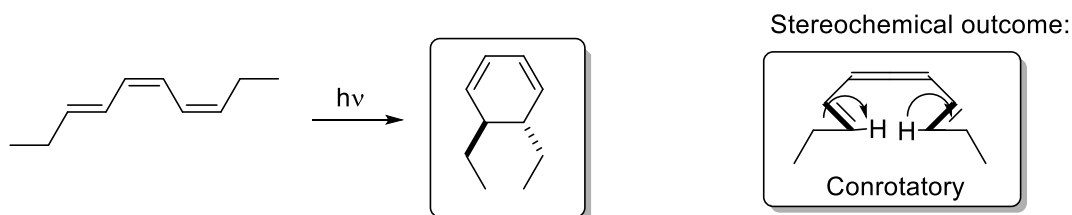
Photochem. Photobiol. Sci. **2017**, *16*, 146–150.



Exercise 3

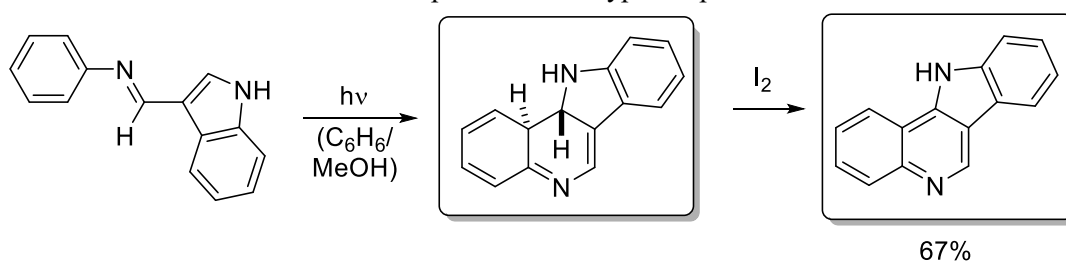
The triene shown below undergoes a $[6\pi]$ cyclisation. Draw the product and rationalize the stereochemical outcome.

Hint: Photoisomerisation is necessary



Exercise 4

Cryptosanguinolentine was synthesized from the indole shown below. Draw both the intermediate and the final product. Describe the reactive chromophore. Which types of photoreactions occur.



Reactive chromophore: 1,3,5-hexatriene

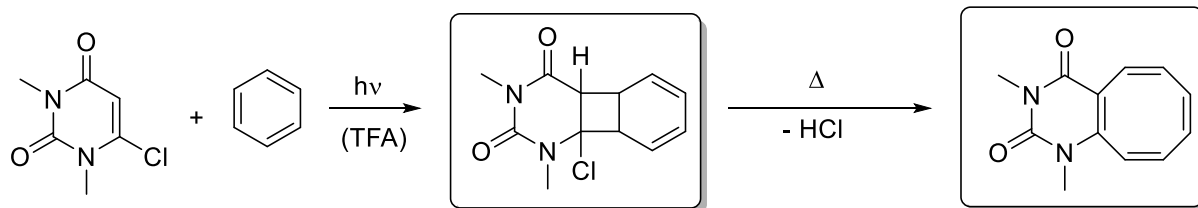
Type of photoreactions: 1. Initial photoisomerisation of *E* to *Z*-isomer
2. Conrotatory cyclisation to cyclohexadiene

Tetrahedron Lett. **2002**, *43*, 3327–2228

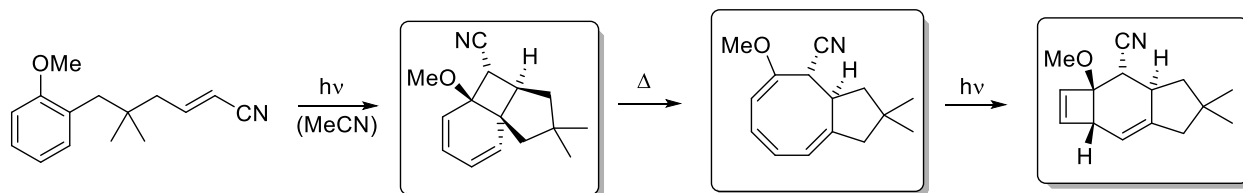
Exercise 5

In the ortho-photocycloaddition shown below, draw all intermediates and the final product. Rationalize, if necessary the stereochemical outcome of the product.

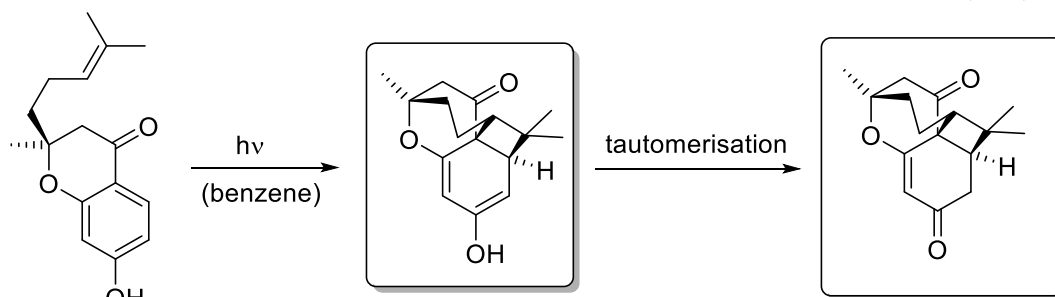
Hint: “ Δ ” indicates a thermally allowed pericyclic reaction.



Chem. Rev. **2016**, *116*, 9816–9849.



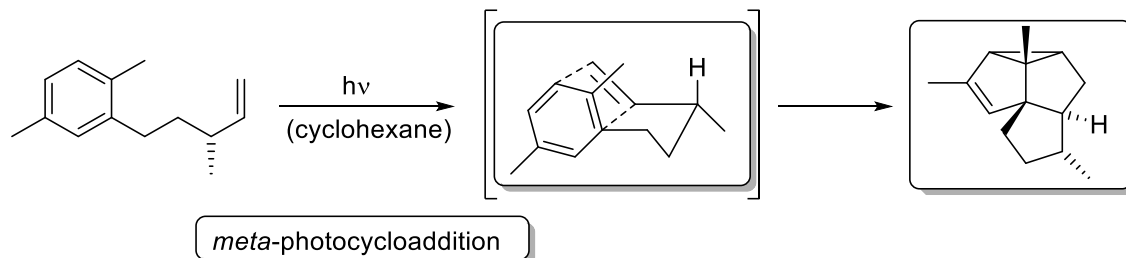
J. Am. Chem. Soc. **1995**, *117*, 6801–6802.



Beilstein J. Org. Chem. **2011**, *7*, 525–542.

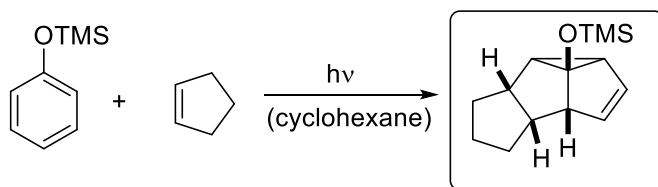
Exercise 1

a) The following photoreaction was used towards the total synthesis of retigeranic acid. Draw the product and name the type of reaction.



Tetrahedron Lett. **1990**, 31, 2517-2520.

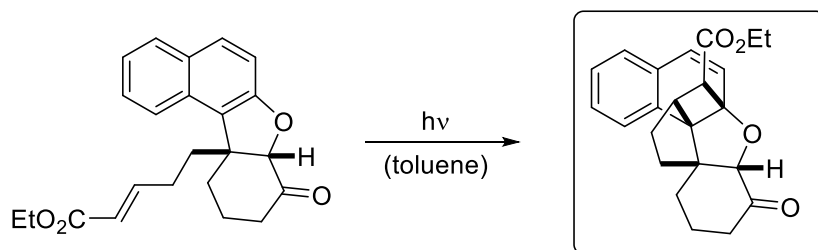
b) Draw the product of the following photoreaction and explain the endo or exo selectivity.



endo product favored due to dispersive interaction as the cyclopentene approaches the benzene ring.

Chem. Rev. **1993**, 93, 615-669.

c) Determine whether the following reaction would proceed via an *ortho*- or *meta*-photocycloaddition and draw the product.



Beilstein J. Org. Chem. **2011**, 7, 525-542.

The reaction proceeds via an *ortho*-photocycloaddition from the donor and acceptor partners.

Short Repetition:

Exercise 2

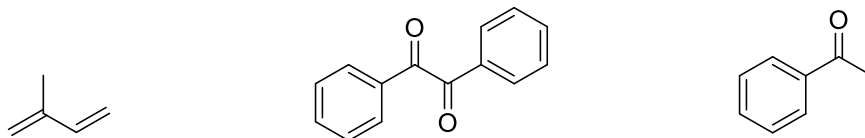
In general, one observes fluorescence emission at higher wavelengths compared to that of absorption. Using the Jablonski Diagram, explain why this is observed.

Answer: Absorbance will excite a molecule from the ground state (S_0) to the first excited singlet state (S_1).

The excitation to (S_1) will usually occur at higher vibrational levels within (S_1) and fluorescence is the emission of a photon from the lowest vibrational level within (S_1) back down to the ground state. In the following equation $E=(h\cdot c)/\lambda$, energy and wavelength is inversely proportional, and thus one would observe fluorescence at higher wavelength compared to absorption from vibrational loss.

Exercise 3

For the three molecules shown, indicate at which wavelength you would irradiate the molecule (220 nm, 310 nm, and/or 400 nm).

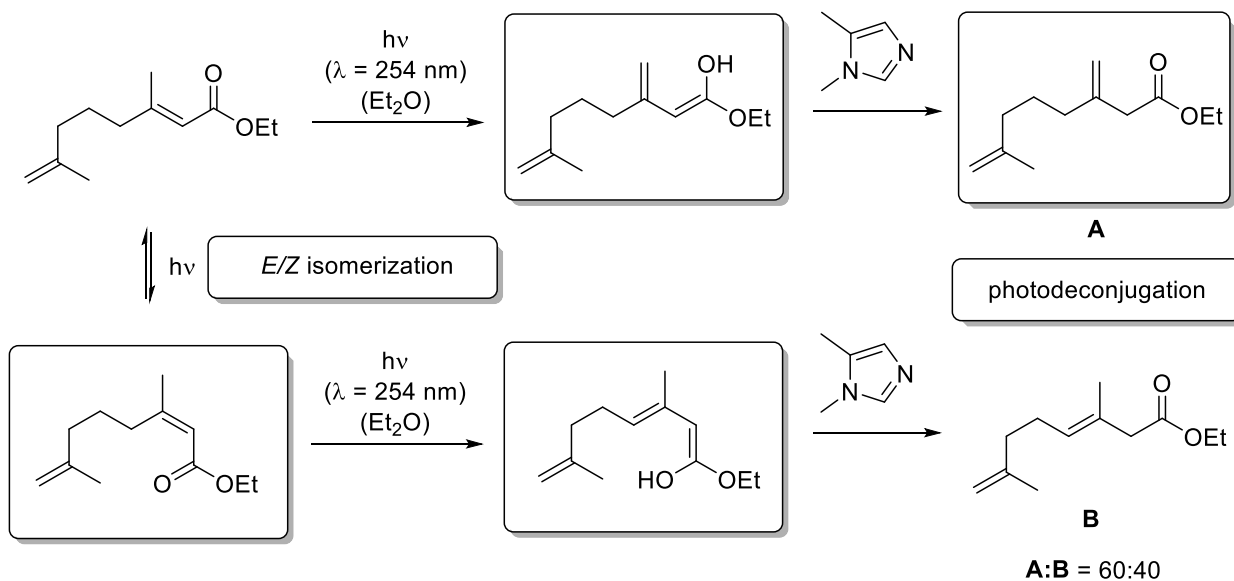


Butadiene- 220nm Acetophenone- 310nm Benzyl- 400nm

Exercise 4:

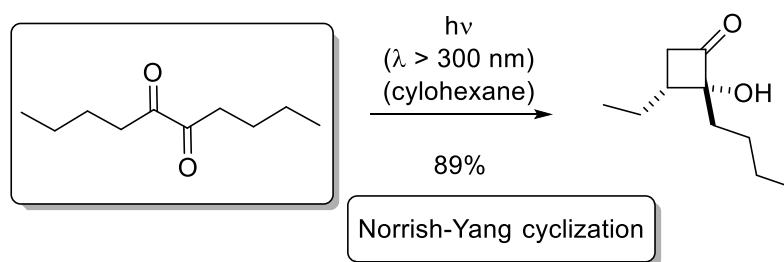
Draw the missing products and reactants and state the respective reaction names or specify the formed photoproducts.

a) Hint: 1,2-Dimethylimidazole acts equally as *N,N*-dimethylethanol



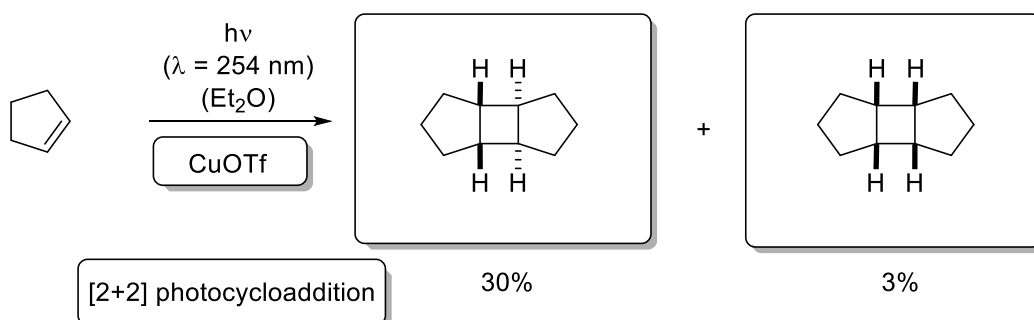
Tetrahedron Lett. **1986**, 27, 5555-5558.

b)



J. Am. Chem. Soc. **1962**, 84, 118-120.

c)



d)

