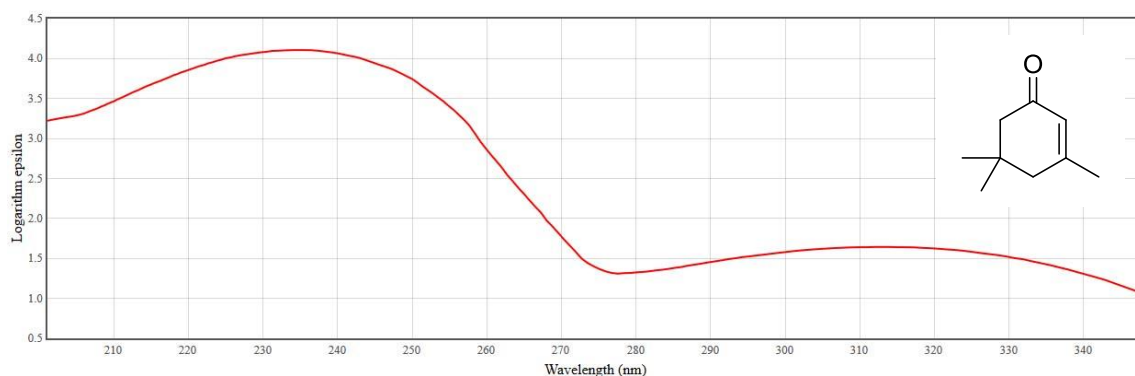


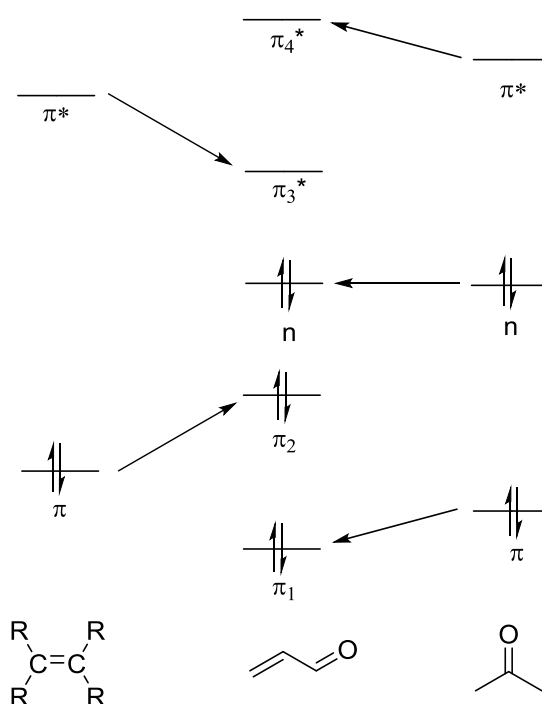
Exercise 1

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) Assign the absorption bands at 234 nm and 306 nm to $\pi\pi^*$ and $n\pi^*$ transition. Justify your decision using a molecular orbital scheme.



Lower ΔE of $n\pi^$ transition + lower molar extinction coefficient (quantum mechanically forbidden)*



- b) Why must the shown spectrum not be used for calculation of the molar extinction coefficient? In a second measurement an absorbance of 0.565 was measured. Calculate the extinction coefficient, if a 1 mm cuvette and a concentration of 0.5 mM was used.

Logarithmic scale: $\epsilon = A/(cx) = 0.565 / (0.5 \cdot 10^{-3} \text{ molL}^{-1} \cdot 0.1 \text{ cm}) = 11.300 \text{ L} \cdot (\text{mol} \cdot \text{cm})^{-1}$

- c) After laser flash excitation (266 nm or 306 nm) fluorescence at 345 nm was detected. Explain the lower energy of the emitted photon compared to the absorbed photon.

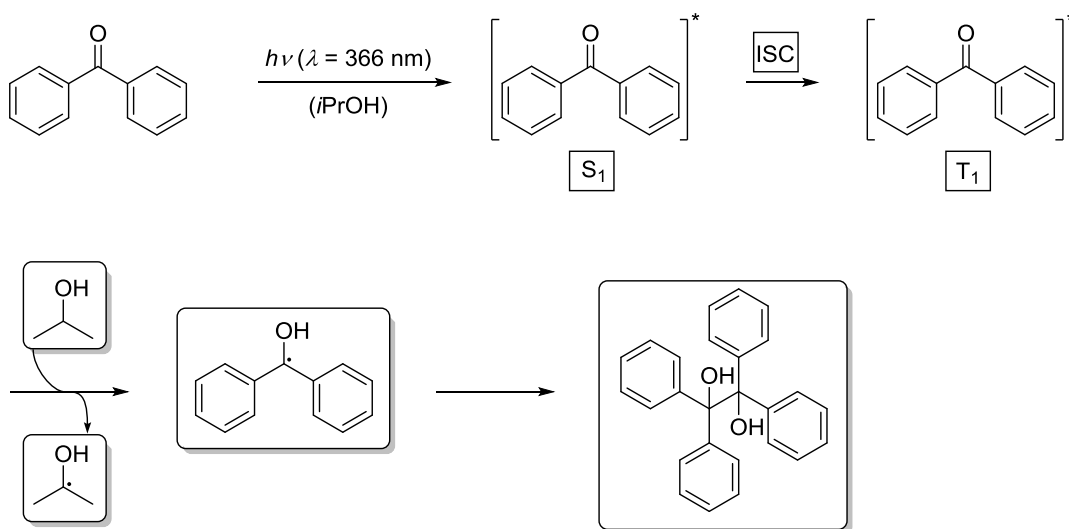
Stokes shift: relaxation of vibrational states

- d) α,β - unsaturated carbonyl compounds readily undergo an *intersystem crossing* into T_1 after excitation into its S_1 state. Do you expect longer or shorter wavelengths for relaxation into S_0 via phosphorescence compared to fluorescence?

longer wavelength. singulett- triplett gap

Exercise 2

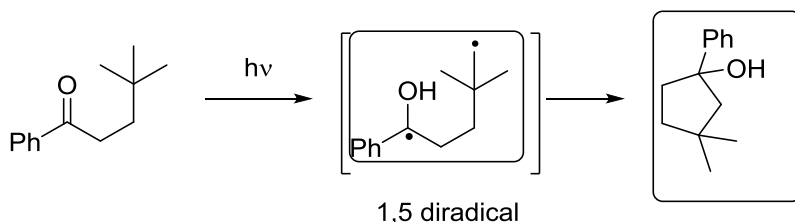
Irradiation of the shown benzophenone in isopropanol yields a homo-pinacol product. Please complete the mechanism below.



Tetrahedron **1996**, 52, 10399-10404.
see also: *Liebigs Ann. Chem.* **1888**, 249, 137-146.

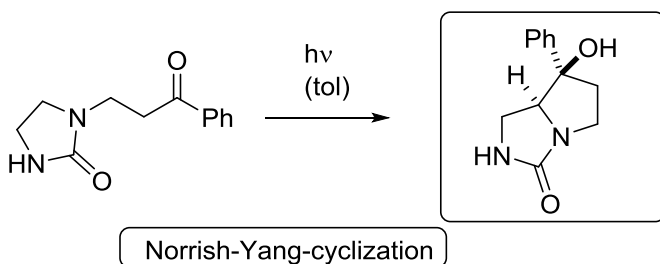
Exercise 1

- a) In case of a six-membered transition state, the abstraction is most rapid. But also seven-membered transition states are possible. Draw the 1,5-diradical as well as the expected product.



Nicholas J. Turro, Modern molecular Photochemistry.

- b) The shown substituted imidazolone will be irradiated at a certain wavelength. Draw the expected cyclization product. What is the name of the reaction? Explain also the simple diastereoselectivity!



Chem. Eur. J. **2002**, 8, 2464-2475.

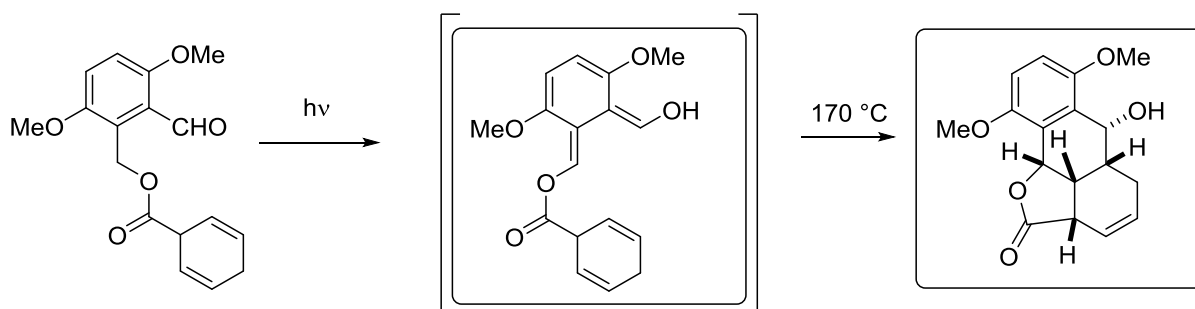
- c) What side reaction could occur?

In general, a Norrish type II cleavage could occur, if there is a γ -Hydrogen atom.

Exercise 2

Photoenolization can be useful in natural product synthesis. A pleurotin analogue was synthesized by a tandem photoenolization/Diels-Alder sequence.

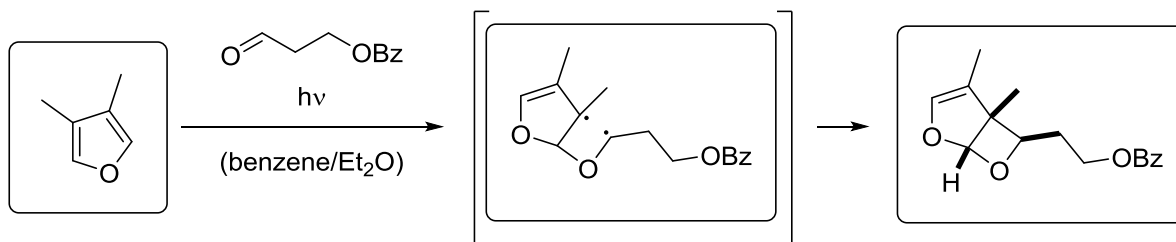
Hint: the *endo*-product is formed.



Synth. Commun. **1993**, 23, 2041-2049.

Exercise 3

Schreiber *et al.* published a total synthesis of asteltoxin in 1983. In their first step 3,4-dimethylfuran was irradiated in presence of an aldehyde. Fill in the missing molecules.

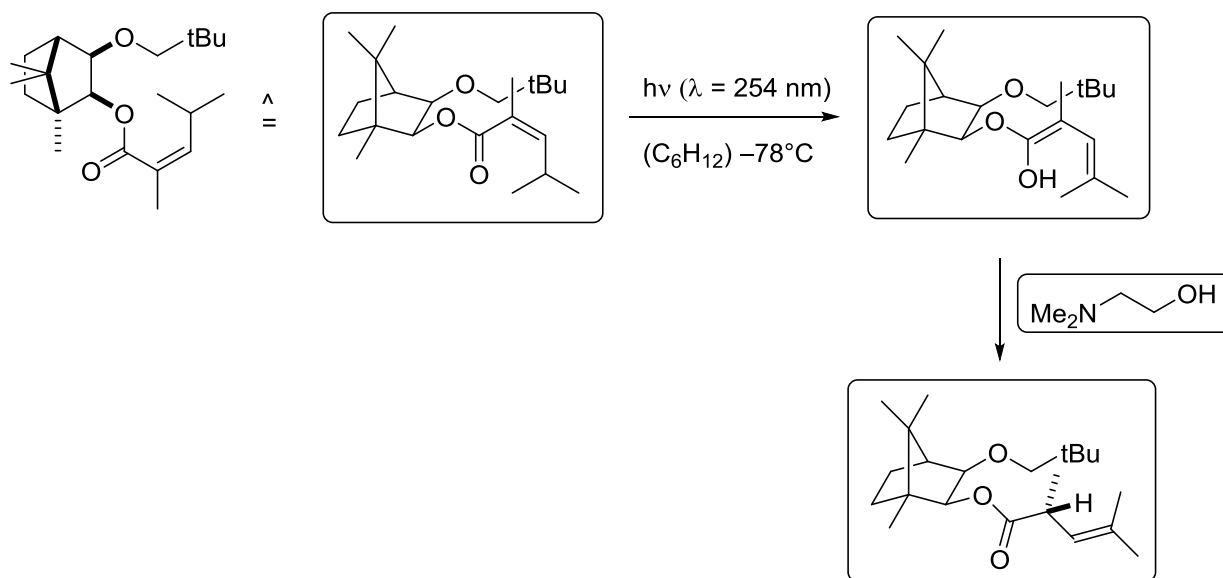


name reaction:

J. Am. Chem. Soc. **1984**, *106*, 4186-4188.

Exercise 4

Photodeconjugation of α,β -unsaturated esters were used in various total syntheses. Before its application enantioselective and diastereoselective methods had to be developed. One of the first diastereoselective examples is shown below. Draw the starting material in a three-dimensional way and fill in the missing structures and reagents.

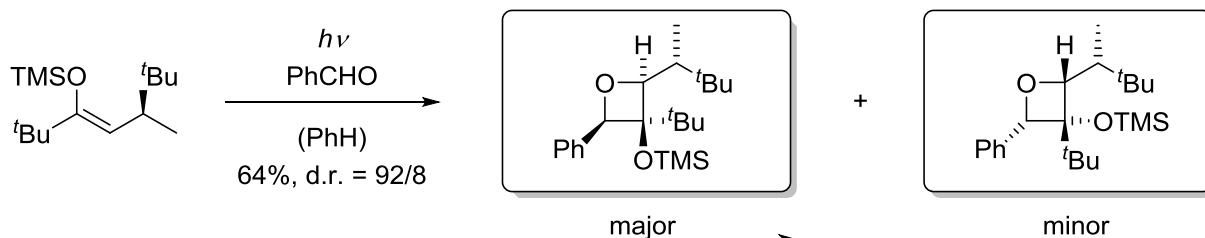


82%, 88% d.r.

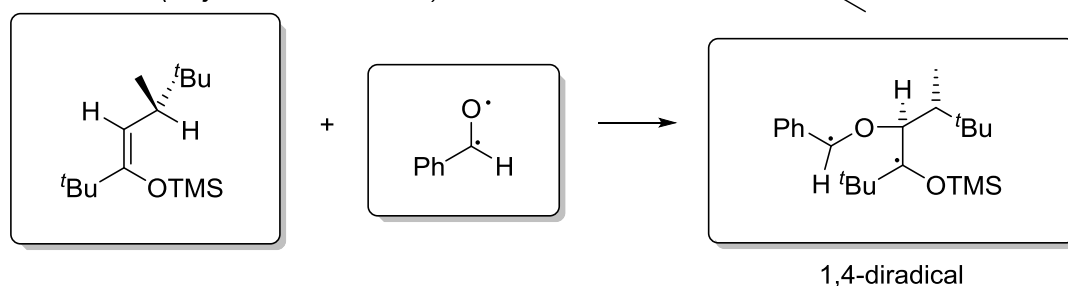
J. Am. Chem. Soc. **1988**, *110*, 4824-4826.

Exercise 1

Benzaldehyde is irradiated in the presence of a chiral alkene leading to a Paternò-Büchi reaction. Two stereoisomers are formed. Please describe the mechanism of the formation of the major diastereoisomer.



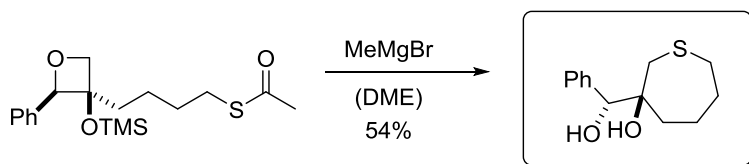
Mechanism (major diastereoisomer):



Angew. Chem. Int. Ed. **1995**, 34, 2271-2273.

Exercise 2

Oxetanes can be opened under various reaction conditions. In this example an intramolecular reaction takes place. Please give the product and type of the reaction.

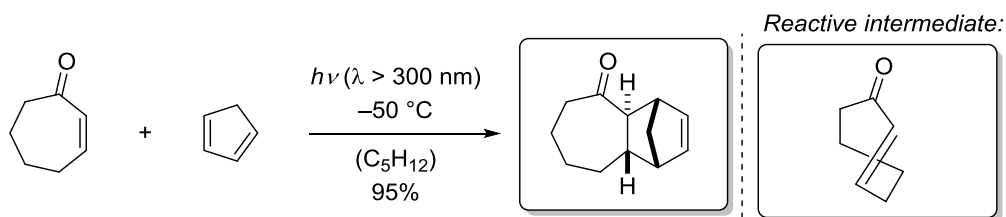


Type of reaction:

J. Org. Chem. **1998**, 63, 1910-1918.

Exercise 3

The depicted cyclic enone does not undergo a reaction without irradiation. Upon irradiation a reactive intermediate leads to a *Diels-Alder*-reaction. Explain this observation and please fill in the blanks.

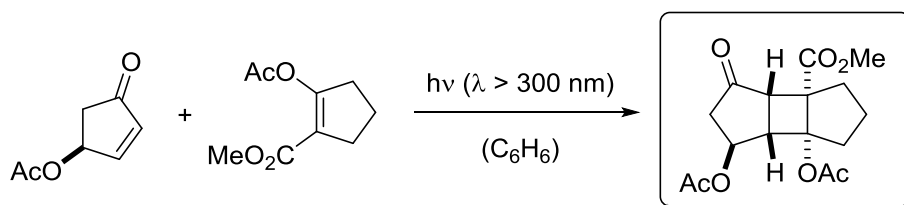


J. Am. Chem. Soc. **1965**, *87*, 2051-2052.

Exercise 4

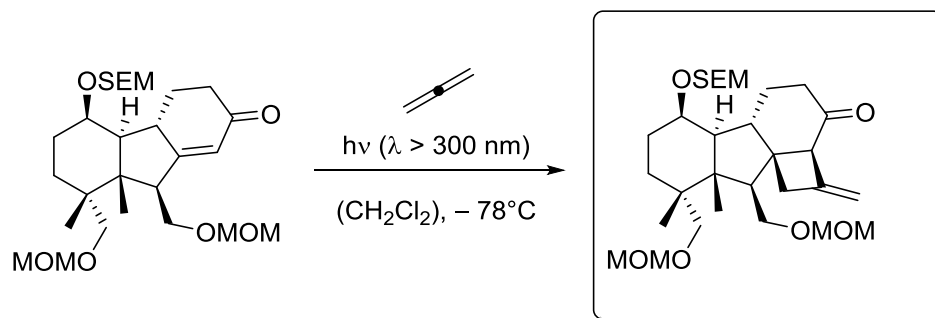
Intermolecular [2+2] photocycloaddition reactions are widely used for the synthesis of cyclobutanes. These strained rings are often key intermediates in total syntheses.

a)



Tetrahedron. Lett. **1977**, *18*, 3699-3702.

b) Hint: Allenes react similar to acceptor-substituted olefins.

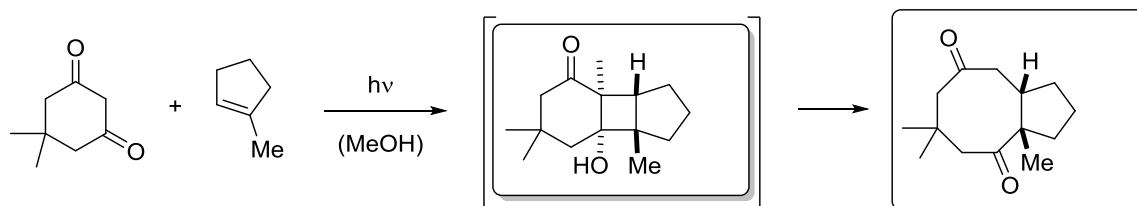


Tetrahedron. Lett. **1989**, *30*, 971-974.

Exercise 5

In some cases cyclobutanes are not stable and undergo ring opening reactions. Draw the intermediate and the final product. Name the ring opening reaction and the reaction sequence.

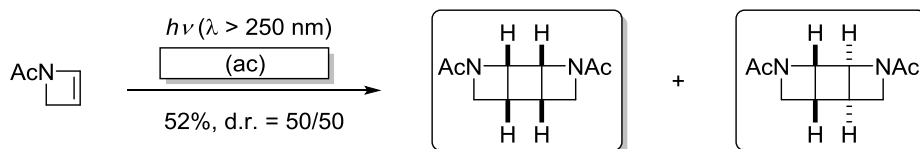
retro-aldol, de Mayo



J. Org. Chem. **1987**, *52*, 2905-2910.

Exercise 1

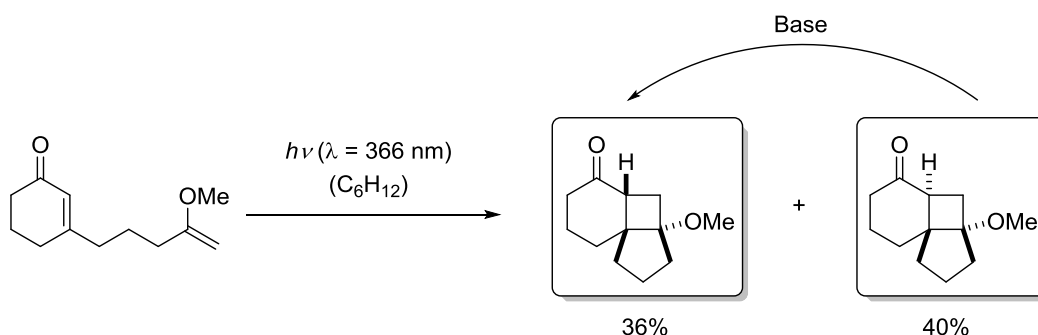
The *N*-acetyl azetine is irradiated under sensitized conditions. Please fill in the appropriate solvent and the two HH products.



Tetrahedron Lett. **1998**, 39, 5481-5484.

Exercise 2

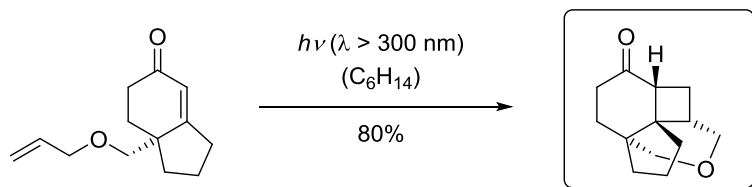
The given cyclohexanone derivative undergoes a [2+2]-photocycloaddition with simple diastereoselectivity. One of the diastereoisomers can be epimerized under basic conditions, please fill in the blanks accordingly.



Angew. Chem. **1989**, 101, 925-927.

Exercise 3

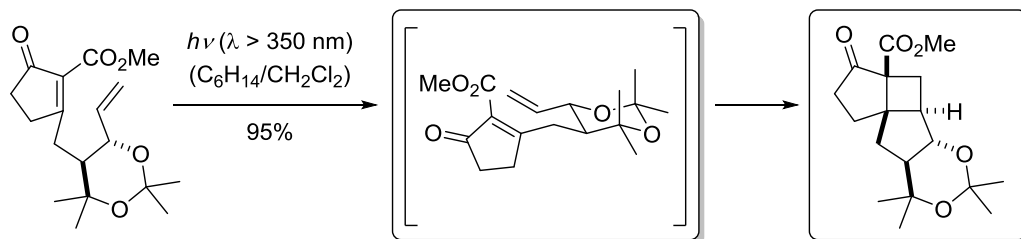
The following reaction yields a single product, please fill in the product with the right absolute configuration.



Eur. J. Org. Chem. **2006**, 351-370.

Exercise 4

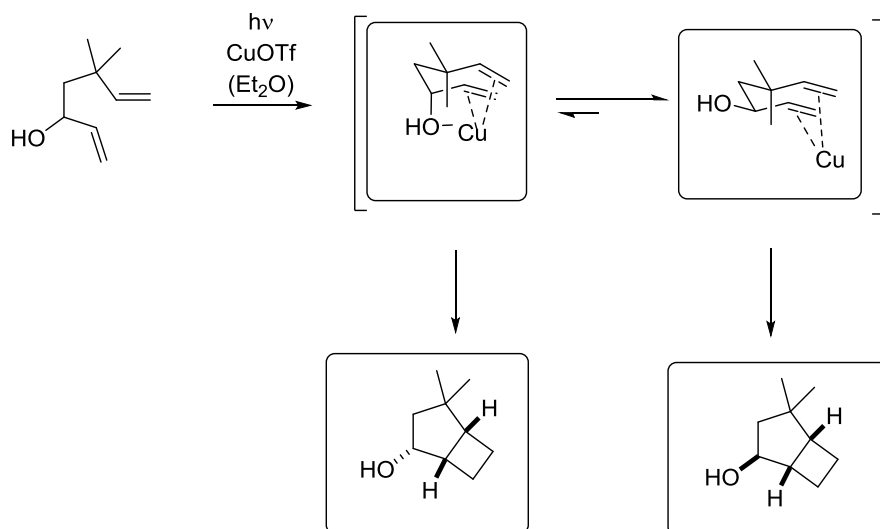
The given cyclopentenone derivative is a precursor for the synthesis of (\pm)-lubiminol. It reacts with high diastereoselectivity to give a single product, please fill in the correct transition state which leads to the product.



J. Am. Chem. Soc. **1998**, *120*, 1747-1756.

Exercise 5

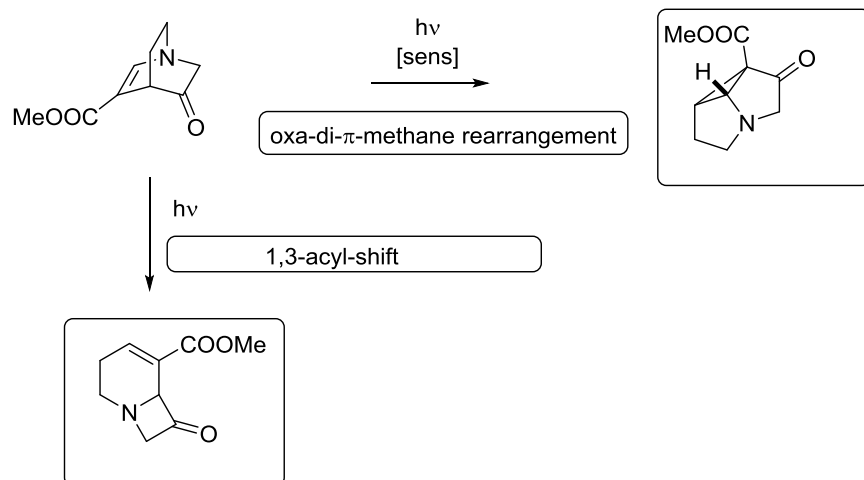
A tri-coordinated Cu(I) complex is usually formed in presence of an homoallylic hydroxy-group to yield the more favored *endo*-product. In the shown reaction sequence the *exo*-product is observed in a higher ratio (*exo*/*endo* = 4/3). Draw the two different Cu(I) complexes as well as the respective products and explain the outcome of the reaction.



J. Am. Chem. Soc. **1982**, *104*, 998-1007.

Exercise 6

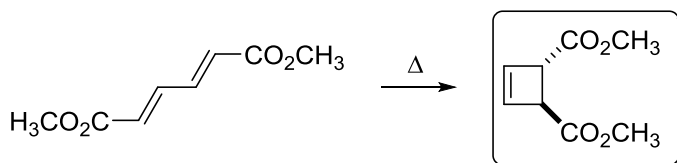
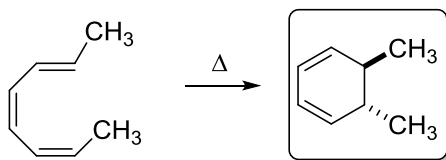
Two reaction pathways are possible in photochemical rearrangements of β,γ -unsaturated carbonyl compounds. Draw the expected products and name the reaction pathway.



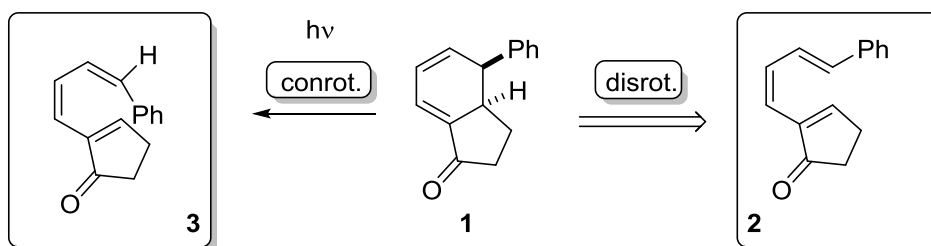
Org. Lett. **2003**, *5*, 3811-3813.

Exercise 1

- a) Fill in both products of the following reactions.



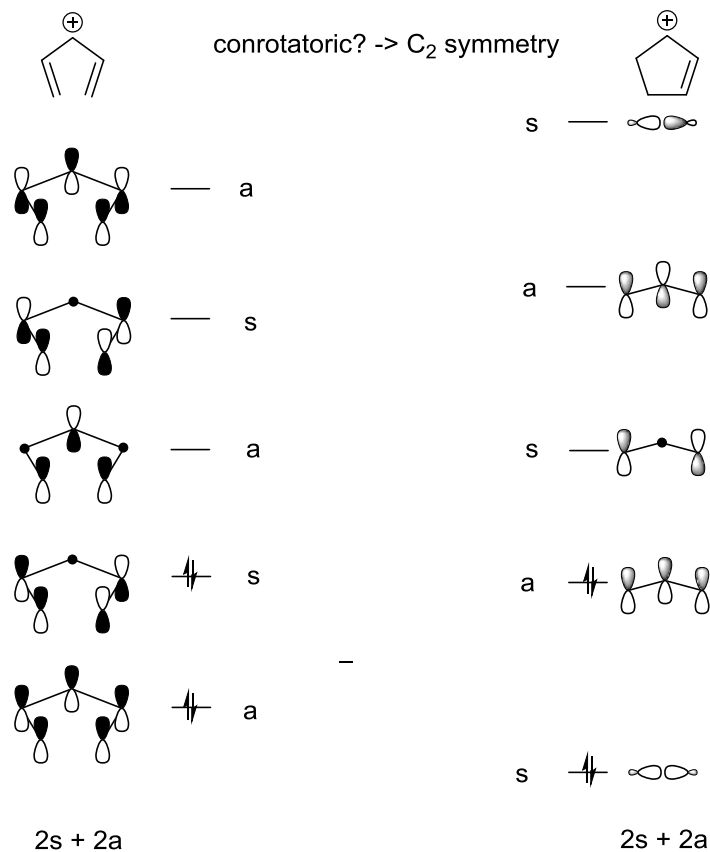
- b) Cyclohexadiene **1** was synthesized by a pericyclic reaction under thermal conditions. Which starting material **2** was used? After irradiation of **1** the cyclopentenone **3** was obtained. Explain its different configuration compared to **2**.



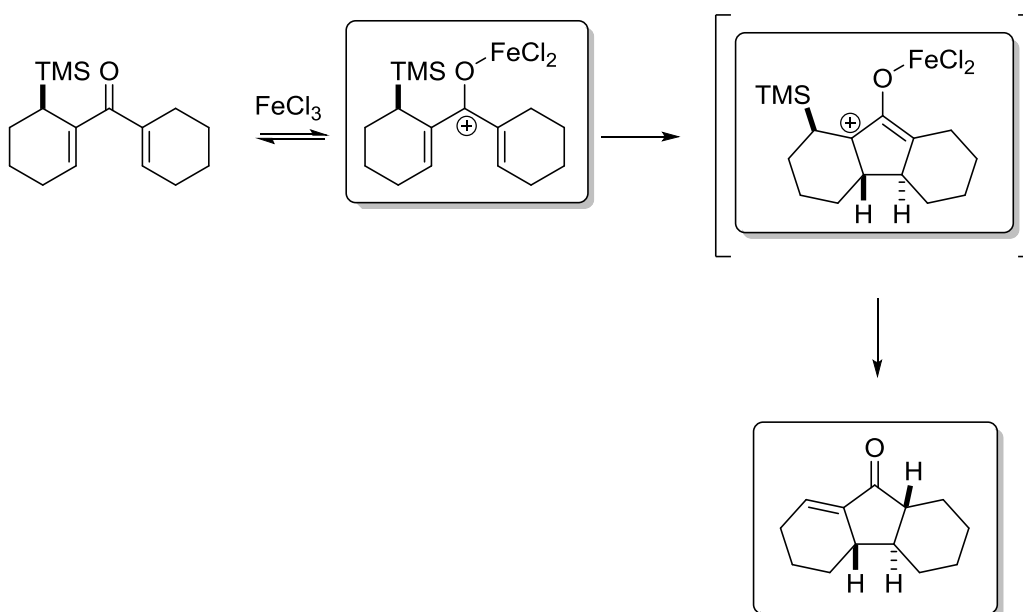
Synthesis **2010**, 2233–2244

Exercise 2

- a) The *Nazarov* cyclisation is a well established thermal reaction for the synthesis of cyclopentenones from divinyl ketones. Show that this conrotatory ring closure reaction is thermally allowed. Therefore draw the molecular orbitals of a 1,4-pentadiene cation and a cyclopentene cation and analyse their orbital symmetry.



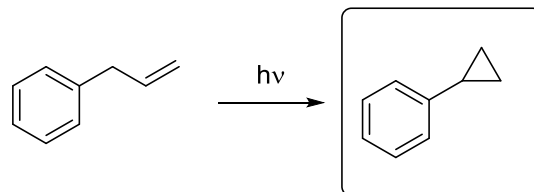
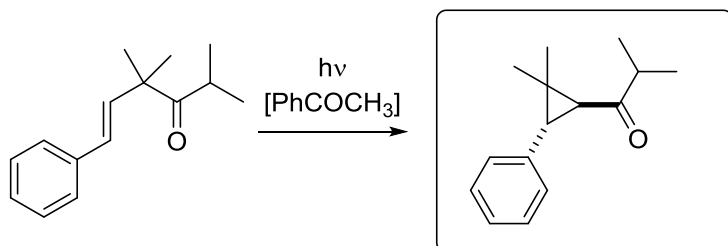
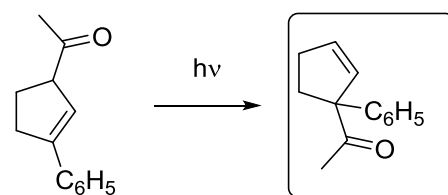
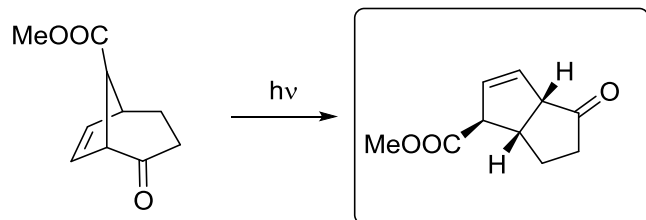
- b) In a *Nazarov* cyclisation usually divinyl ketones are activated by *Lewis*- or *Brønsted* acids. Fill in the missing intermediates and the final (stable) product.



J. Org. Chem. **1990**, *55*, 5543- 5445.

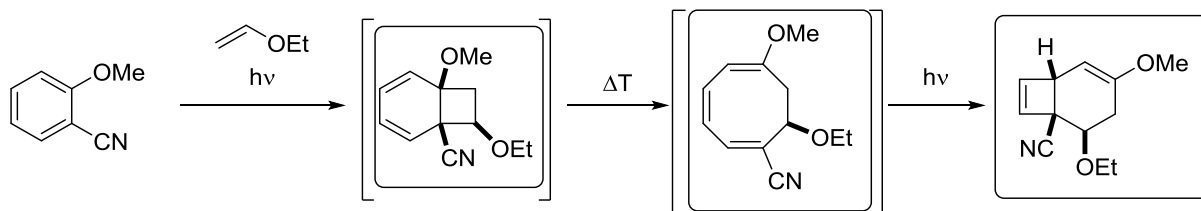
Exercise 3

Give the product of the occurring rearrangements with the correct stereochemistry if necessary.



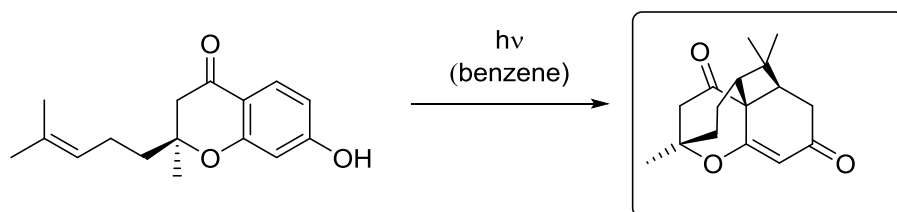
Exercise 1

Photocycloadditions of aromatic compounds lead to dearomatization of the aromatic system. Fill in the missing intermediates as well as the expected product.

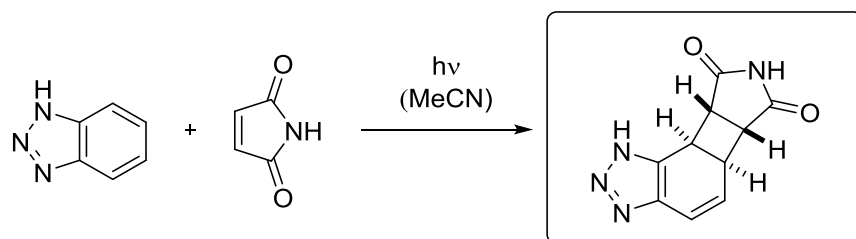


Hint: consecutive thermal ring opening

Tetrahedron Letters **1987**, 28, 5909-5912.



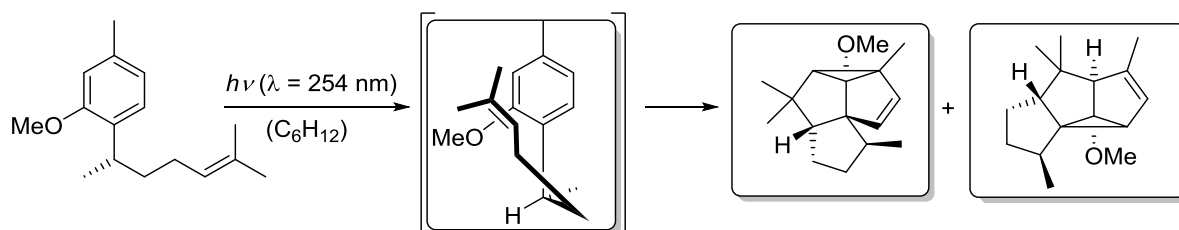
Tetrahedron Letters **1992**, 33, 7775-7778.



Org. Lett. **2002**, 4, 1487-1489.

Exercise 2

In the following intramolecular meta-photocycloaddition two regioisomers can be formed. Please consider draw the missing structures with the correct absolute configuration.



Intermolecular meta-photocycloadditions can yield exo- and endo-products. Please draw the main product.

