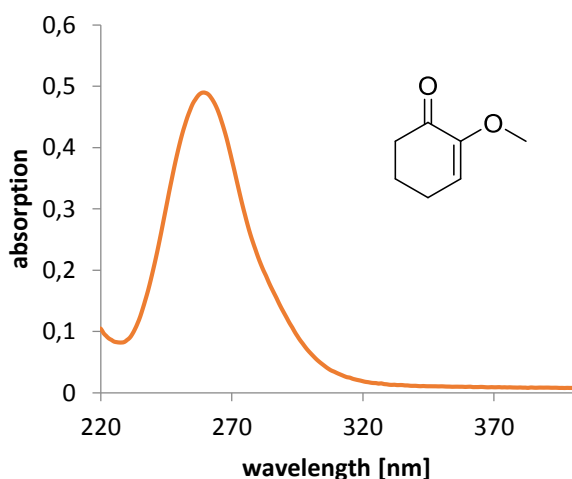


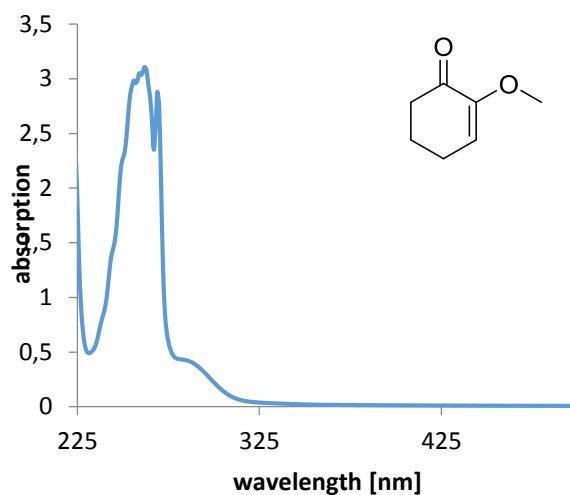
Exercise 1

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.

I) $c = 0.5 \text{ mmolL}^{-1}$



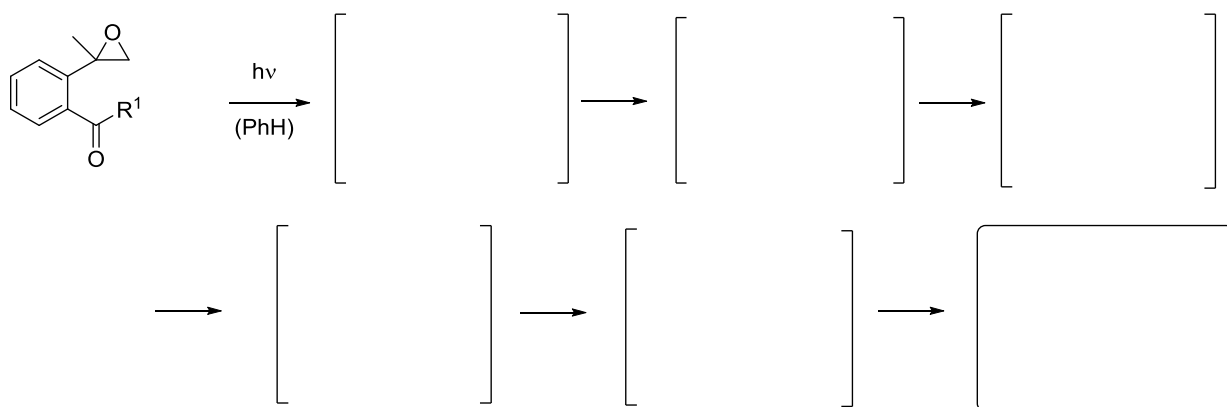
II) $c = 5.0 \text{ mmolL}^{-1}$



- Estimate λ_{max} in I) and assign the absorption band in I) and II) to $n\pi^*$ or $\pi\pi^*$ transitions. Justify your decision.
- Calculate the molar extinction coefficient at $\lambda = 300 \text{ nm}$ ($d = 1 \text{ mm}$).
- Calculate the energy of one mol of photon ($\lambda = 254 \text{ nm}$).

Exercise 2

Recent studies of epoxides and epoxy ketones have discovered that the type of photoinduced ring opening of epoxides is depending on the substitution of the substrate. Fill in the missing intermediates and the observed product.



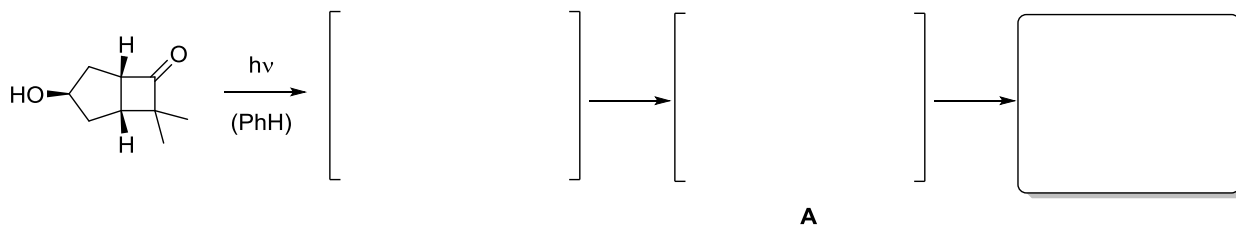
Exercise 3

The key step in the total synthesis of (\pm)-Herbertenolide is a stereoselective photochemical induced fragmentation reaction performed in the solid state. Draw the expected intermediate and the product of this transformation. What is the name of this reaction?



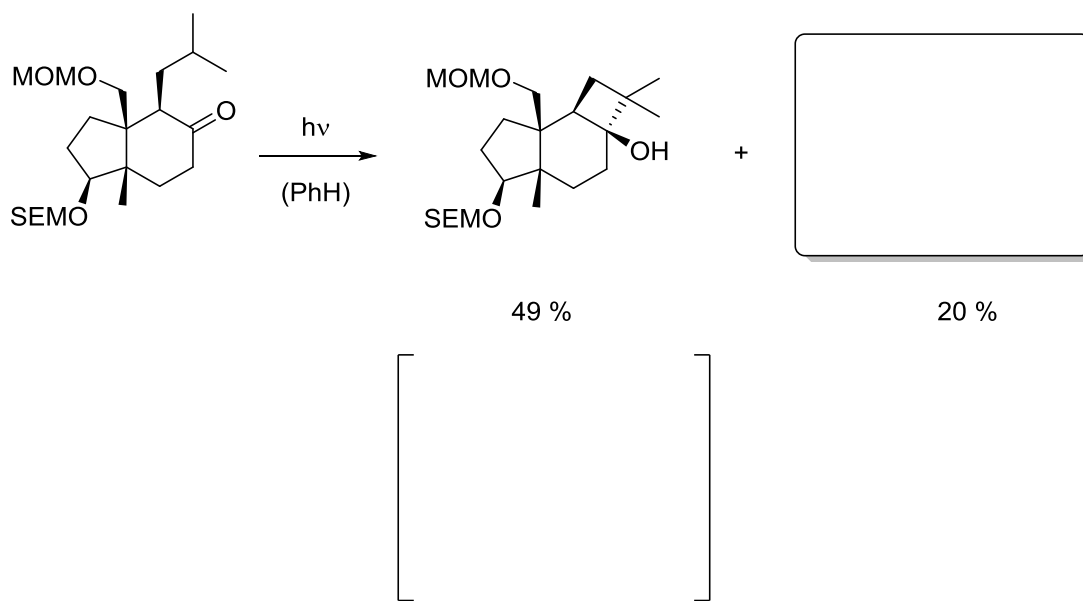
Exercise 4

Cyclobutane rings can be opened upon excitation with UV light and the reactive intermediate is normally trapped by polar-protic solvents. In non-polar solvents such as benzene, intermediate **A** is trapped intramolecularly. Complete the following reaction sequence by drawing all intermediates and the final product.



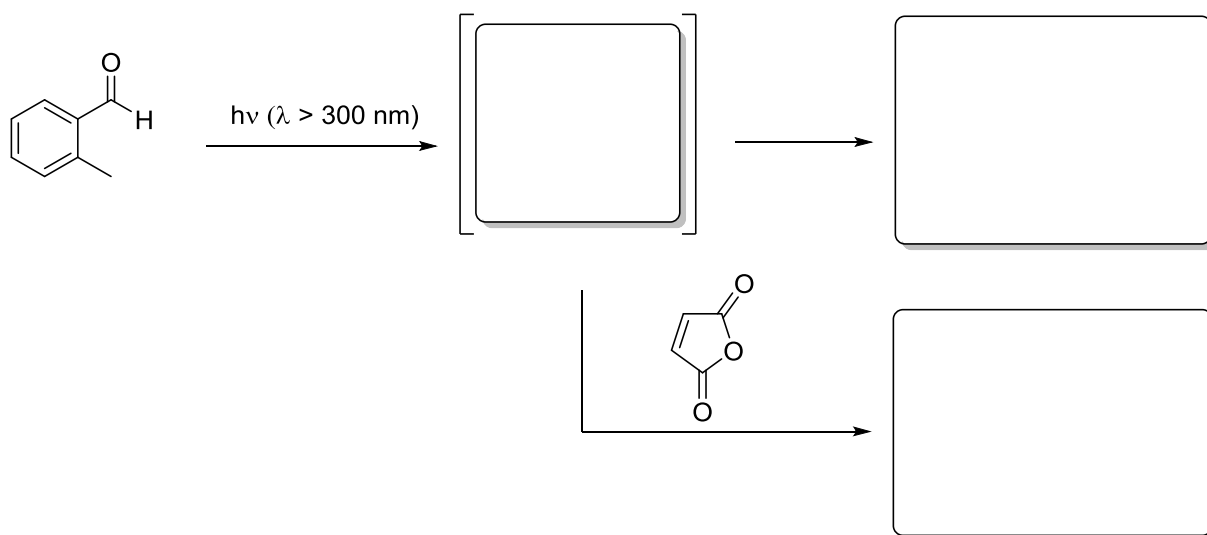
Exercise 5

Paquette and *Sugimura* successfully applied the *Norrish-Yang* cyclization in the total synthesis of (-)-Punctaporonin A, albeit in moderate yield. How does the side product of this reaction look like? Explain the formation by using an appropriate intermediate.

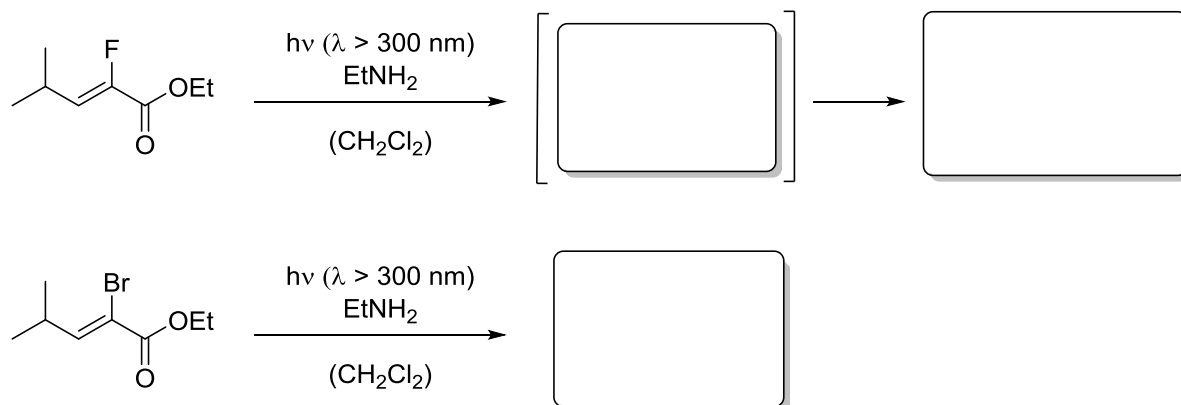


Exercise 1

o-Quinodimethanes are useful intermediates in organic synthesis and can be generated upon irradiation of aromatic ketones or aldehydes. Complete the given sequence and classify the reaction which traps the intermediate!

**Exercise 2**

Explain why the outcome of the irradiation of the following α,β -unsaturated esters strongly depend on the substituent in α -position. What is the driving force for the upper transformation?

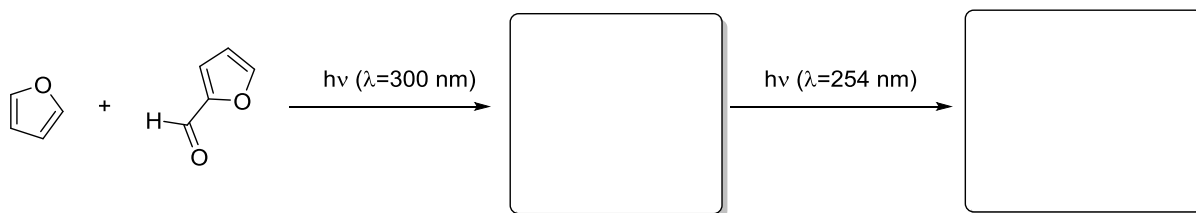
**Exercise 3**

To build up the carbon framework of the natural product 1,13-Herbertenediol, Boxall *et al.* made use of a photochemical induced cyclization/fragmentation sequence. Fill in the missing structures and explain the observed diastereoselectivity. *Hint*: LDBB (lithium di-*tert*-butyl-biphenylide) is a single electron donor!



Exercise 4

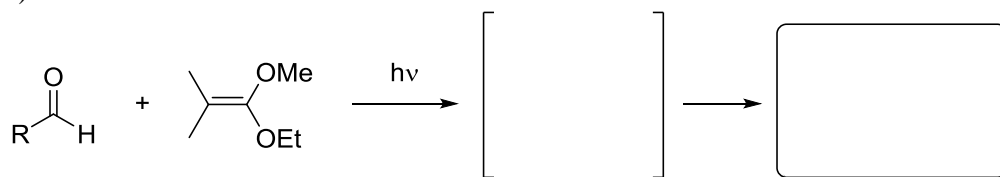
The shown furanes were subjected to direct irradiation at $\lambda = 300$ nm which resulted in the formation of a oxetane. Further irradiation at shorter wavelengths ($\lambda = 254$ nm) induces a opening of the four membered ring. Complete the synthesis to the final product.



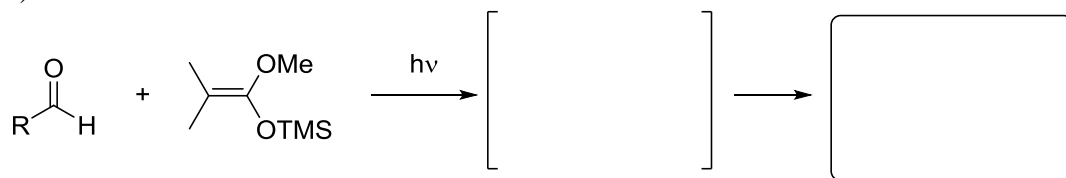
Exercise 5

Show the expected intermediates and products of the following Paternò-Büchi reactions.

a)

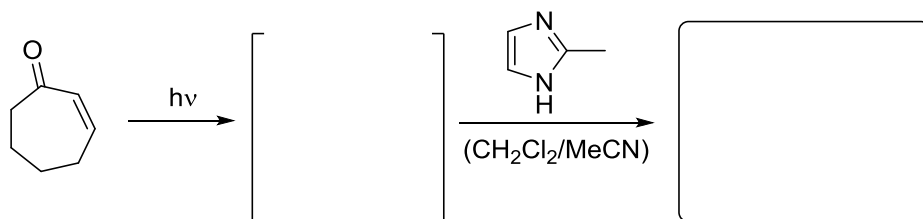


b)



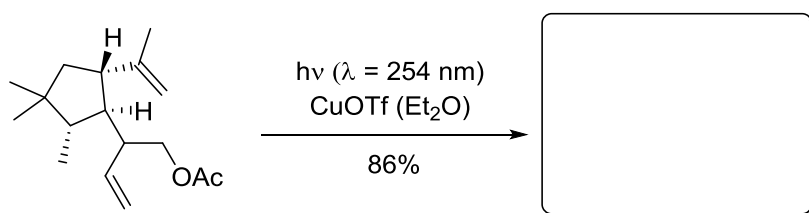
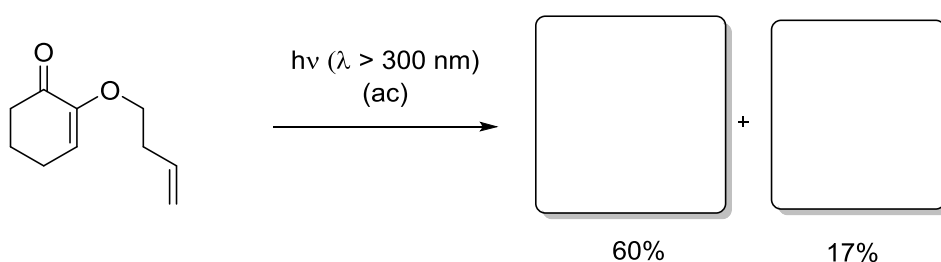
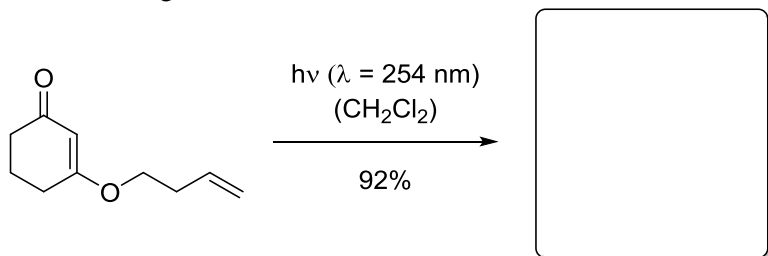
Exercise 6

UV irradiation of cyclic enones and nitrogen heterocycles lead to the formation of 1,4-adducts. Samples that were not exposed to UV radiation showed no conversion. Complete the following synthesis and propose a structure for the intermediate.



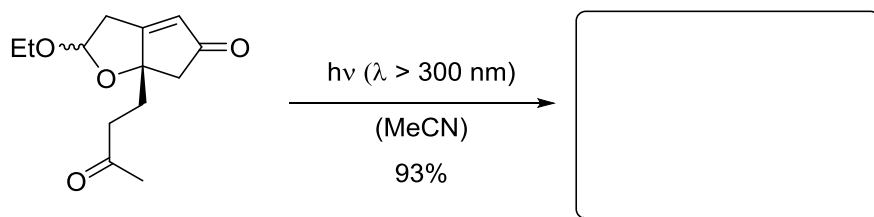
Exercise 1

Give the products of the following intramolecular [2+2]-photocycloaddition reactions with the correct relative configuration!

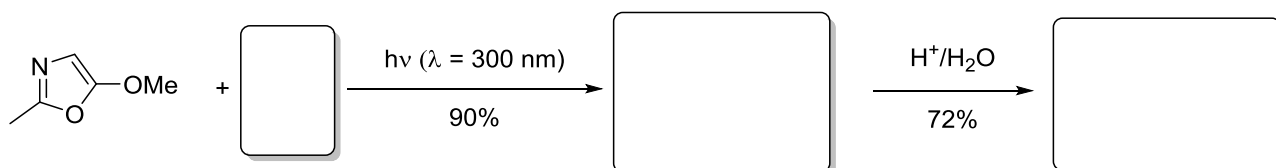


Exercise 2

a) In a [2+2] photocycloaddition a tetracyclic oxetane is formed. Draw the expected product.



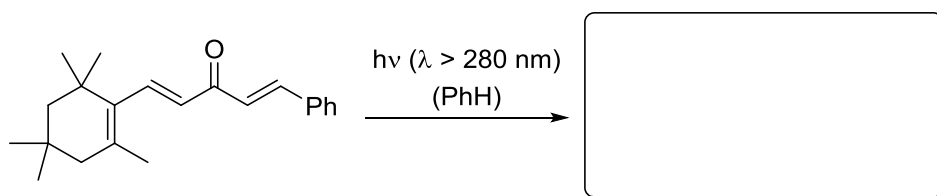
b) The shown alkoxyoxazole reacts with the ketone propionaldehyd. The formed product is further transformed into a α -amino- β -hydroxy acid derivative.



Exercise 3

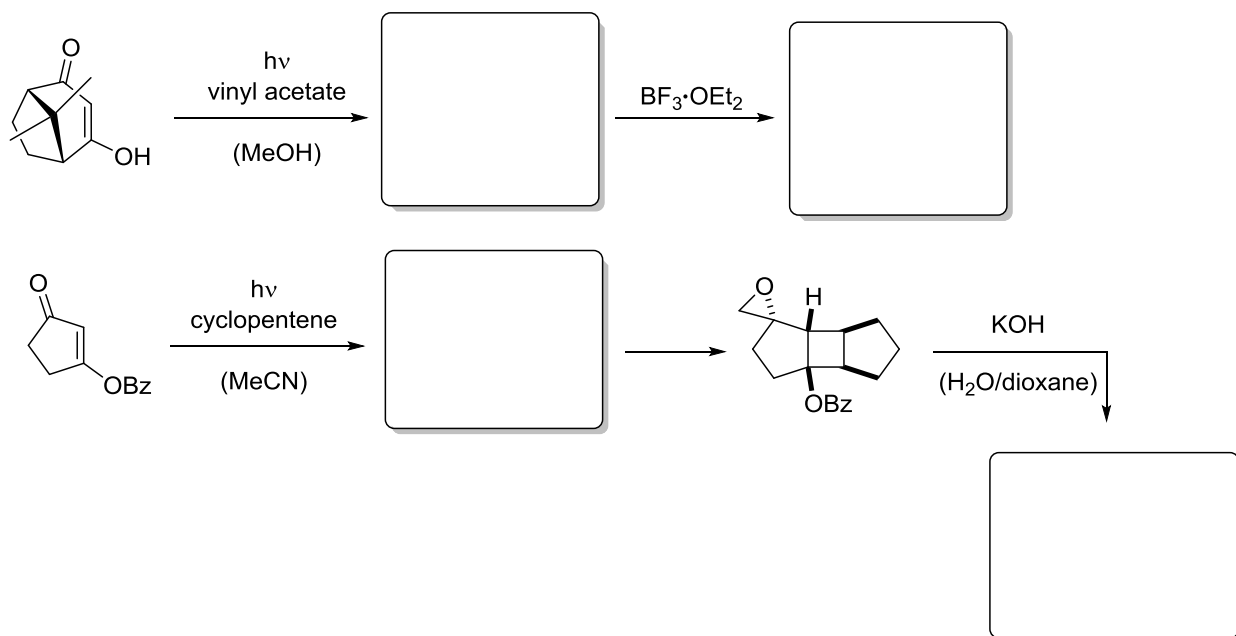
Irradiation of the here shown α,β -unsaturated ketone results in the formation of a bicyclic system. Give the structure of the photoproduct and make suggestions, which wavelength can be used to excite the ketone.

Hint: E/Z isomerization is crucial for the reaction to occur!



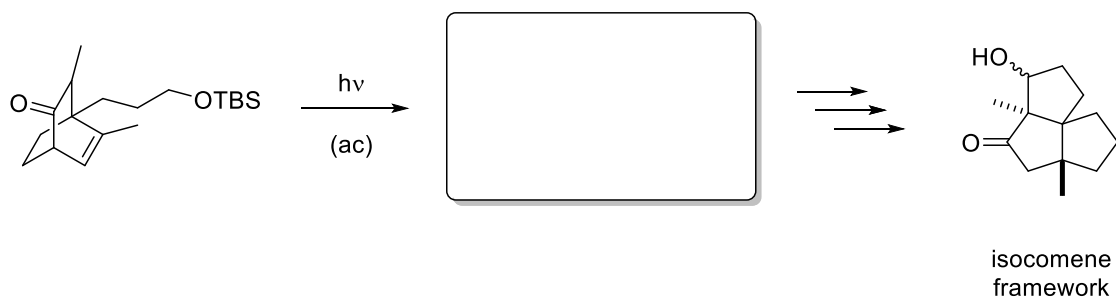
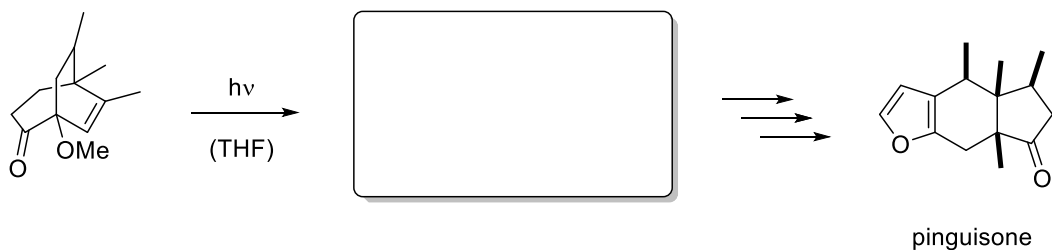
Exercise 4

Complete the given reaction sequences and consider, if necessary, the regio- and diastereoselectivity. What is the name of the second step in the first sequence?



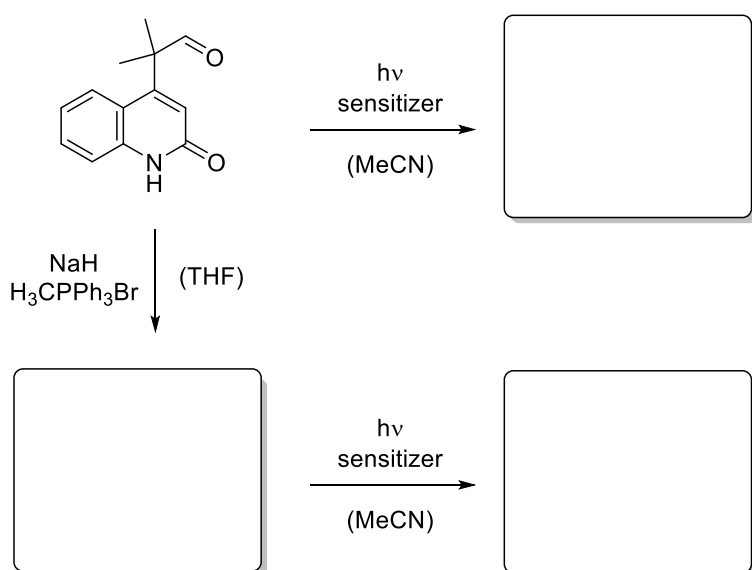
Exercise 1

Photochemical induced rearrangements allow the assembly of complex polycyclic frameworks and are therefore frequently used in natural product synthesis. Draw the structures of the intermediates in the below shown sequences!



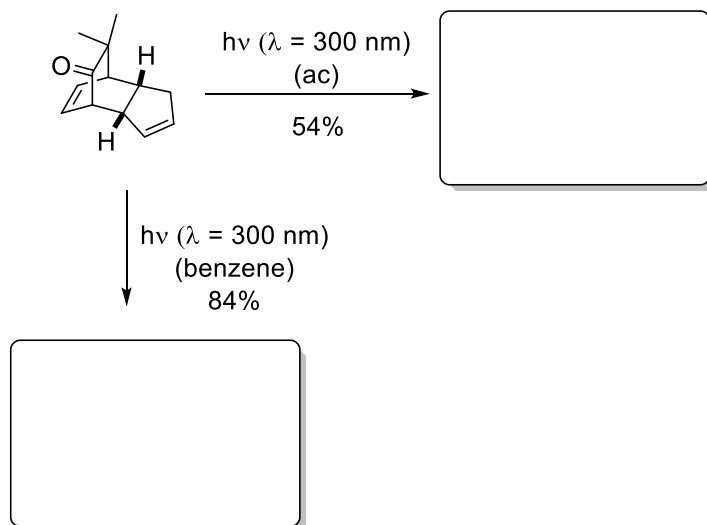
Exercise 2

The shown 4-substituted quinolones can rearrange under sensitization conditions. Give the photoproducts and name the occurring reactions!



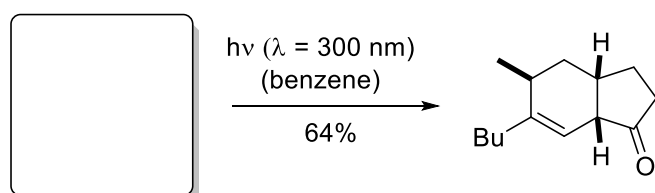
Exercise 3

Upon irradiation the tricyclic ketone generates two products dependent on the used solvent. Give the structure of the formed products and the name of the reaction types.



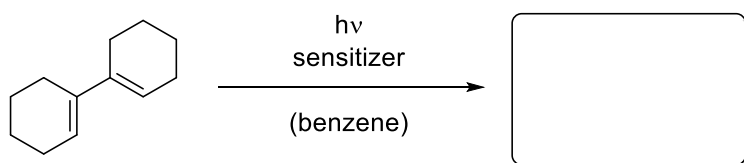
Exercise 4

A bicyclic product is formed after irradiation. Give the starting material of the reaction.



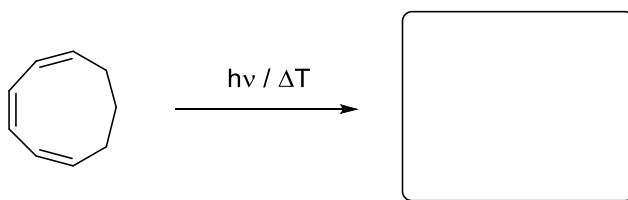
Exercise 5

The orbital symmetry must be conserved in pericyclic reactions according to the Woodward-Hofmann rules. Draw the expected product after a photochemical reaction.

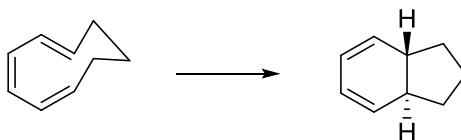


Exercise 1

- a) What product would be formed by the disrotatory cyclization of the given triene? Would this reaction occur under photochemical or thermal conditions?

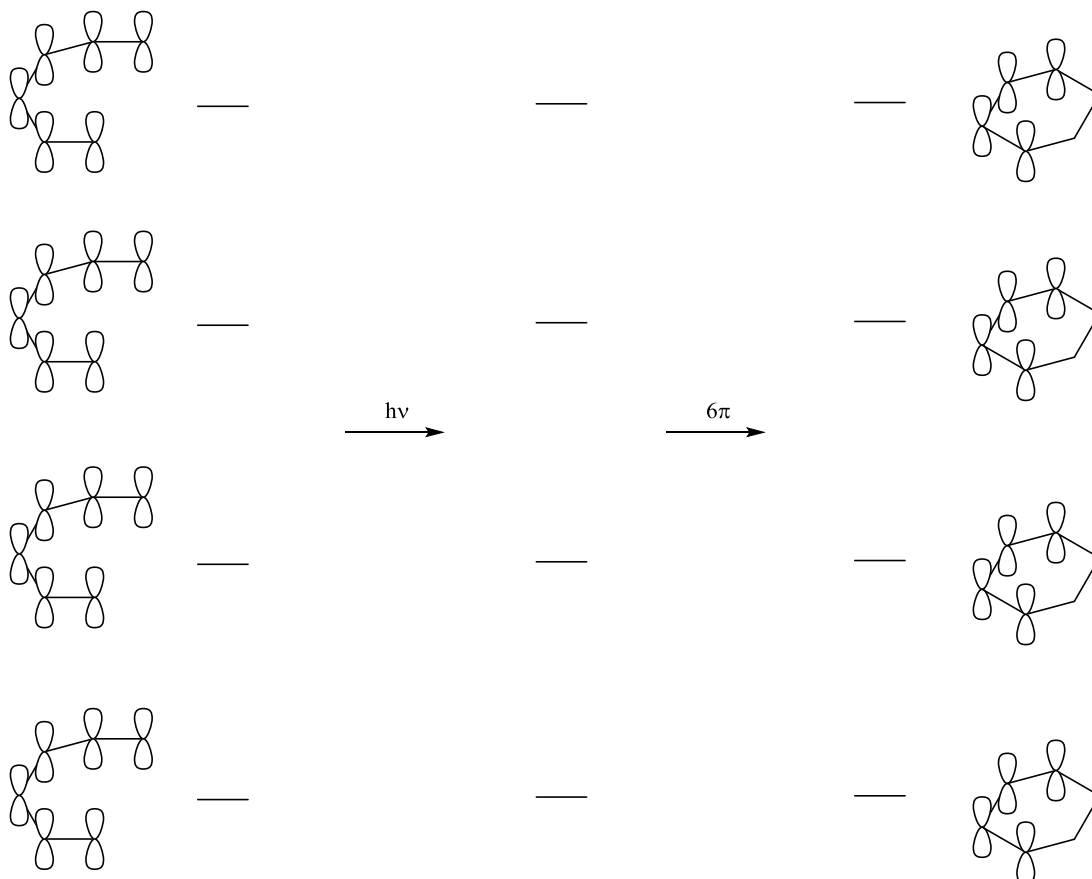


- b) Consider the following electrocyclic ring closure. Does the product form by a conrotatory or disrotatory process? Would this reaction occur under photochemical or thermal conditions?



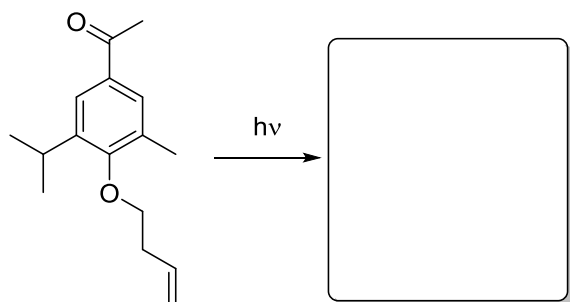
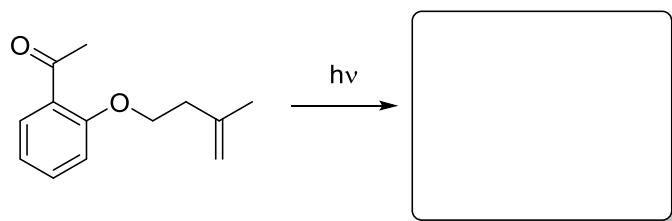
- c) Complete the given orbital diagram for a photochemical induced 6π -cyclization by adding electrons, the relevant orbital phases and the missing orbitals on the product side. Explain why the reaction occurs in a disrotatory fashion!

Note: For clarity reasons, only the important molecular orbitals are drawn!

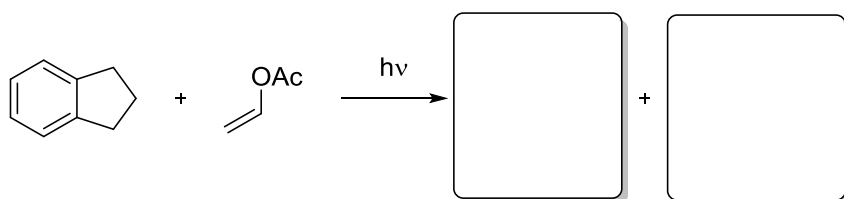
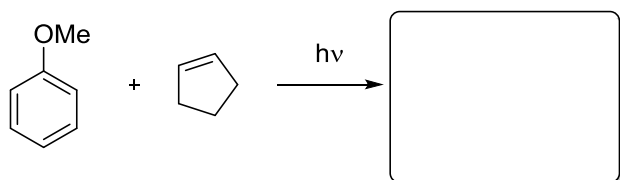
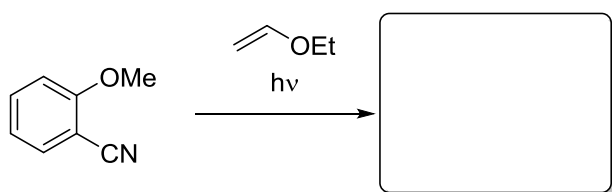


Exercise 2

Complete the following reaction sequences.



Hint: Regioselectivity is influenced by steric effects



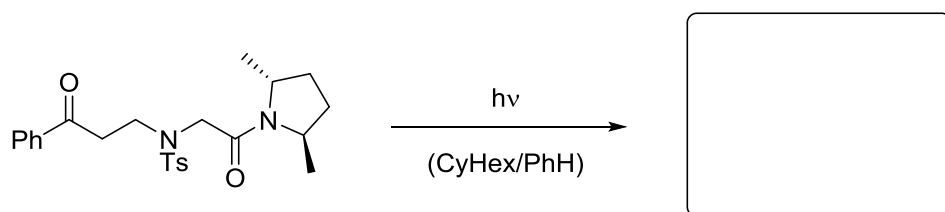
Organic Photochemistry – 6th exercise / questions

11.02.2016 11.15 a.m

Both groups in room 27402!

Exercise 1

Draw the product of the below shown irradiation experiment and explain the occurring enantioselectivity!



Helv. Chim. Acta **1994**, 77, 829-837.

Exercise 2

Give the product after irradiation with the correct relative stereochemistry if necessary.

