| **Organic Photochemistry – 1ˢᵗ exercise**	**21.10.2014 9.00 a.m.**
Group I: room xxx	**Group II: room xxx**

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) Calculate the molar extinction coefficient at 221 nm, 313 nm and 327 nm.

The spectrum was recorded in acetonitril at a concentration of 0.5 mM in a cell with a path length of 1 mm.

b) Assign the absorption bands at 221 nm, 313 nm and 327 nm to $n\pi^*$ and $\pi\pi^*$ transitions. Justify your decision.
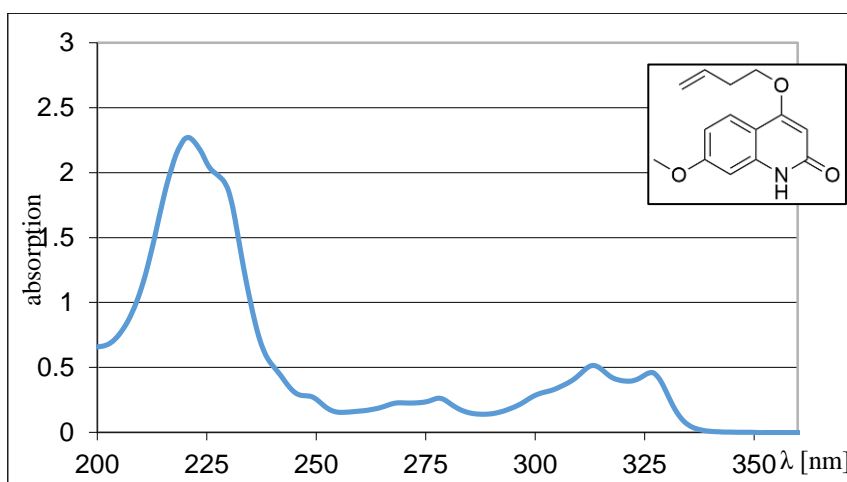
$A = \varepsilon \, c \, d$, $\varepsilon = A/(c \, d)$

A (221 nm) = 2.27, A (313 nm) = 0.51, A (327 nm) = 0.46

ε = (221 nm) 45400 L mol^{-1} cm^{-1}, ε = (313 nm) 10200 L mol^{-1} cm^{-1}, ε = (327 nm) 9200 L mol^{-1} cm^{-1},

c) The depicted molecule shows the same photochemical reactivity when irradiated at 245 nm or 300 nm. Give an explanation.
(Kasha's rule, reaction from lowest excited state)

Exercise 2

Irradiation of the shown Boc-protected amine provides a useful method to generate γ-lactams. Draw the expected intermediate and explain the mechanism of the lactam-formation!
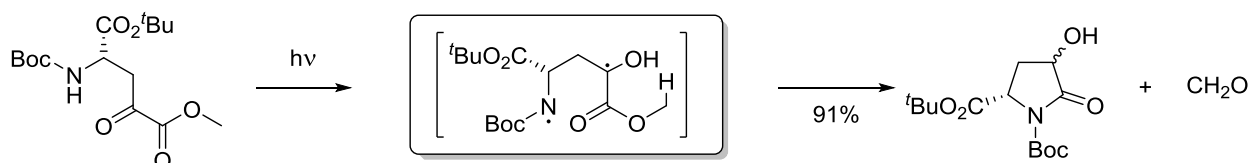

(γ-H abstraction, α-cleavage, radical recombination => lactam formation)

Exercise 3

In a similar way to the example above, hydrogen abstraction by an aromatic carbonyl function from the benzylic position of a side chain leads to a photoenol or, more precisely, a hydroxyquinodimethane derivative. Give the structure of the respec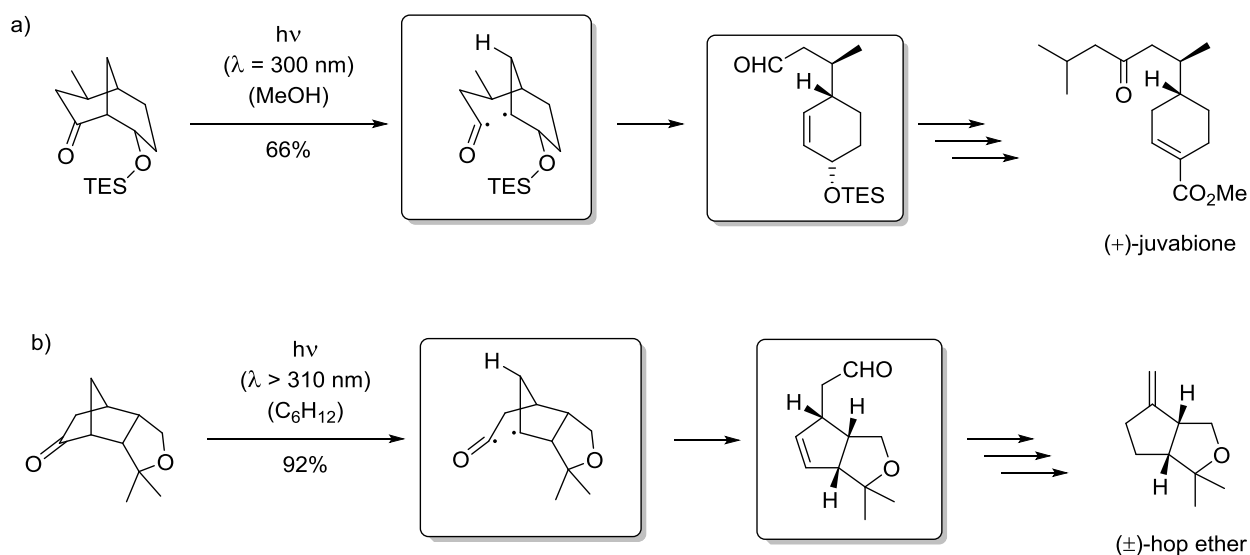tive starting materials and draw the expected intermediates. *Hint:* In order to form the product in b), a thermal reaction is used in the last step to form the tetracyclic product.

a)

b)

estrone
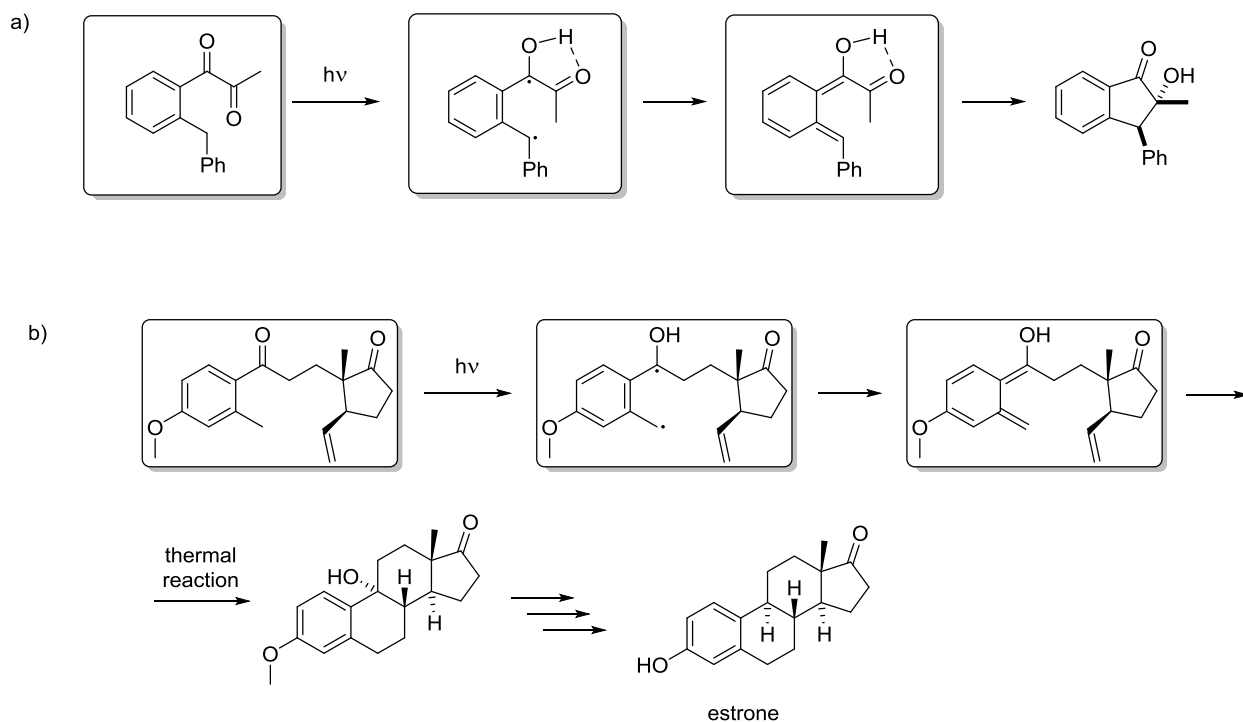
Exercise 4

The key steps in the total syntheses of (+)-juvabione and (±)-hop ether involve the irradiations of the compounds shown below. Draw the respective intermediates! What products do you expect to form? What is the name of this type of reaction?
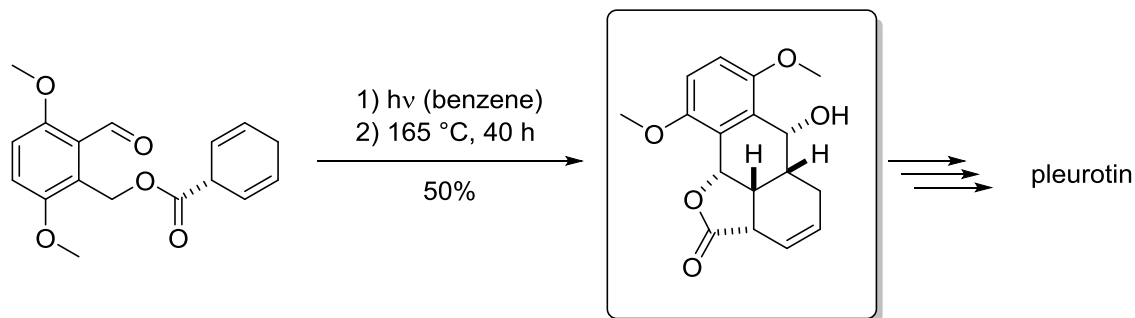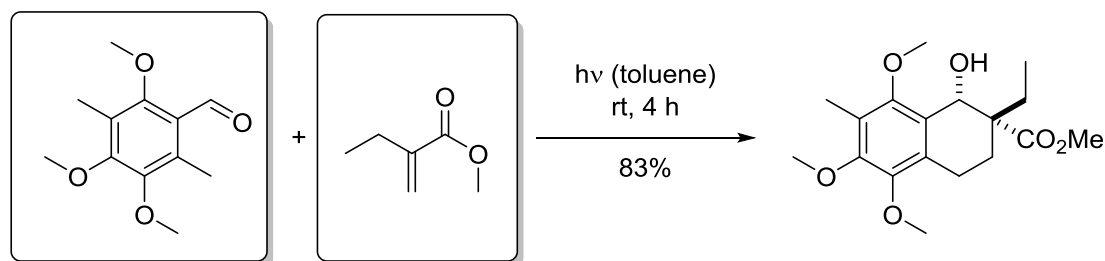
a)

(+)-juvabione

b)

(±)-hop ether

2

Exercise 1

Since we didn't have the chance to discuss exercises 3.a) and 3.b) from the last sheet: here's round 2! Give the structure of the respective starting materials and draw the expected intermediates.
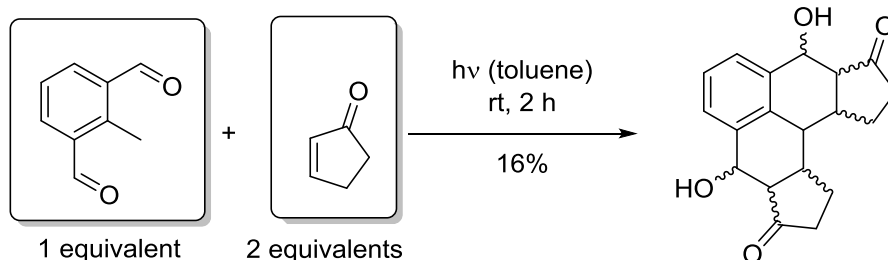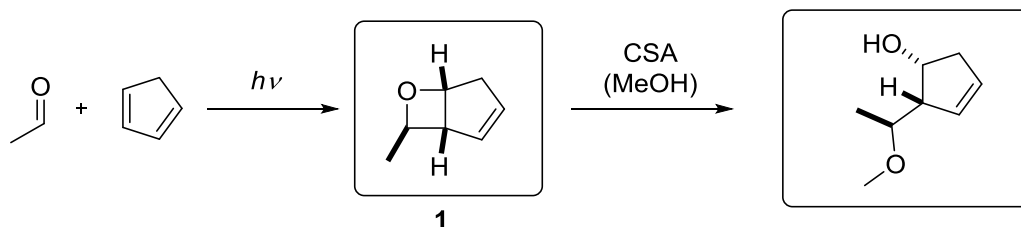
a)

b)


c)

1 equivalent   2 equivalents

Exercise 2

A short photochemical approach to (±)-sarracenine was reported by Hoye et al. Draw the expected photoproduct and the ring opened product, which was optained by treatment of 1 with camphorsulfonic acid. Explain the relative configuration of both products.

Answere: Paterno-Büchi, trans-configuration methyl/cyclopentene, inversion of stereogenic center SN2 type

Exercise 3

With the photocycloaddition of propion aldehyde and cyclohexa-1,3,-diene we enter the synthesis of the mediterrenean fruit fly pheromone. Give the photoproduct with its relative configuration. After hydrogenation of the remaining double bond the bicyclic product undergoes thermolysis upon heating. The resulting carbonyl compound is then reduced to the corresponding alcohol. Explain the configuration of the new formed double bond.
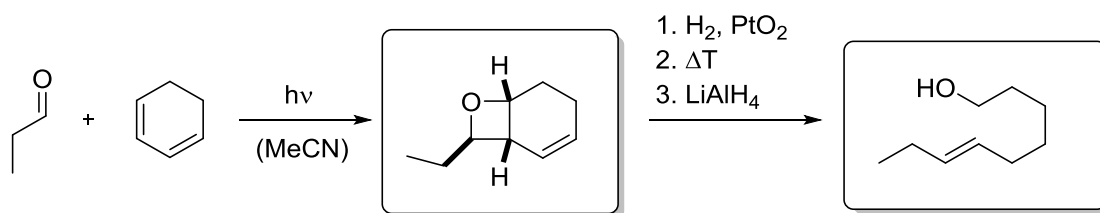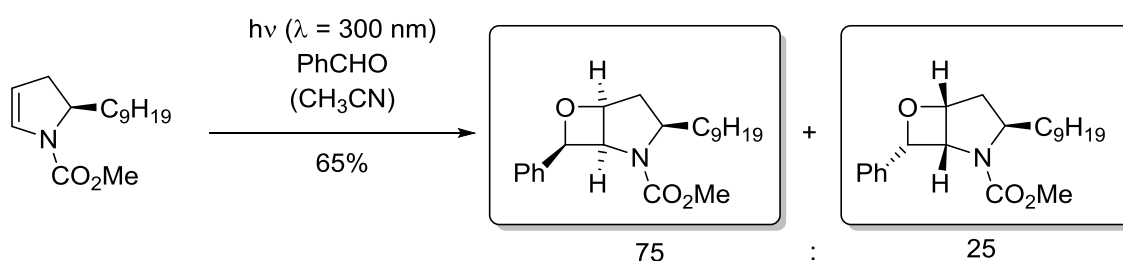

Answere: Paterno-Büchi, trans-configuration, retention of geometry during fragmentation, ergo (E)-config. Olefin
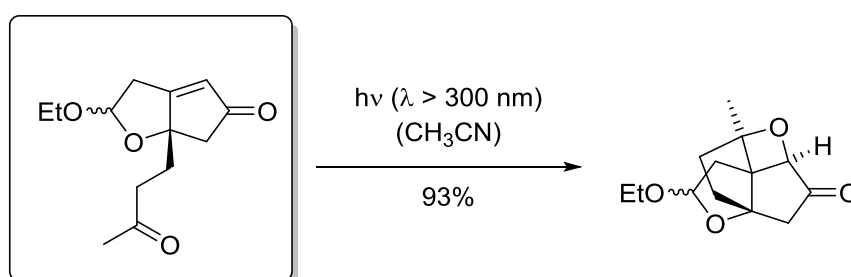
Exercise 4

Give the missing structures with the expected stereochemistry in the following photocycloadditons.
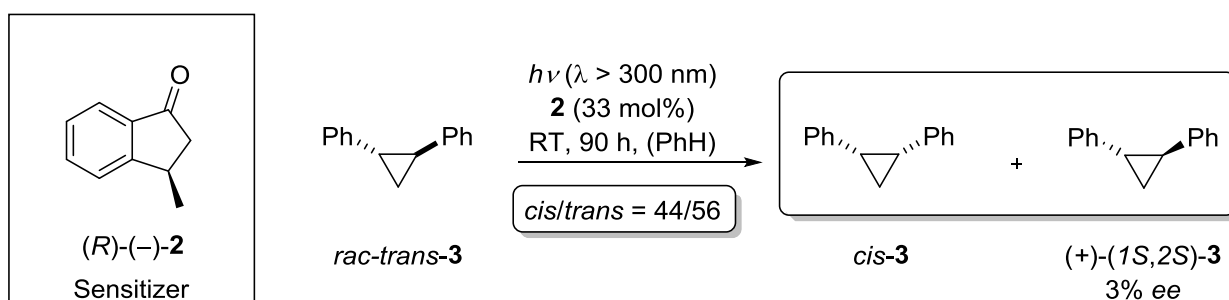
a)

b)

Exercise 5

The isomerization of **3** is sentized by chiral ketone **2**. Explain the driving force of this photochemical transformation. You can neglect the absolute configuration.

Answere: photostationary state is reached because ET (cis) > ET (trans).

Exercise 6

Stilbene favors one isomere upon irradtion (λ = 313 nm) with respect to the bridging double bond. Explain the photochemical process and give a reason for the selectivity.
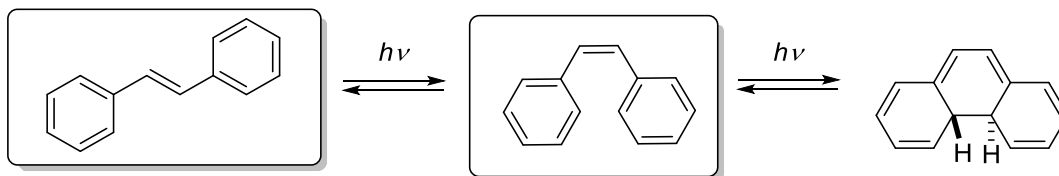

Answere: e (trans) = 19420 L/(mol*cm), e (cis) = 2510 L/(mol*cm) => 7/93 in PSS
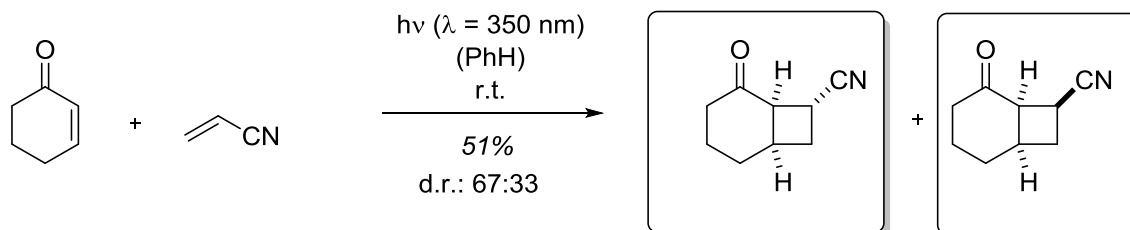
Exercise 1

In the following intermolecular [2+2] photocycloaddition reactions, give the expected product. Pay attention to the observed regiochemistry of addition and explain the underlying mechanism of the product formation using molecular orbital representations. Classify the products with appropriate terms.
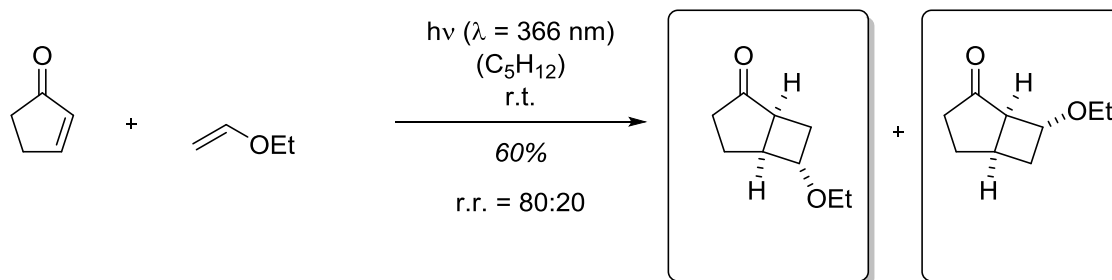
a)
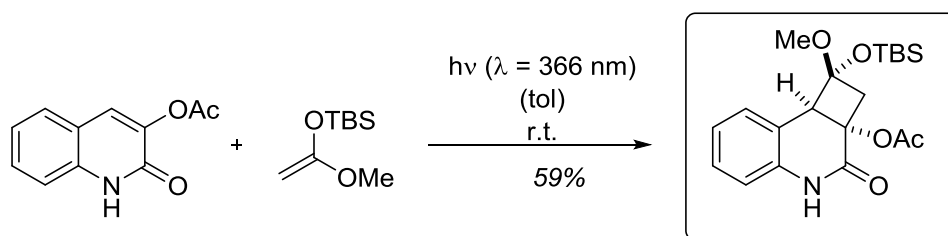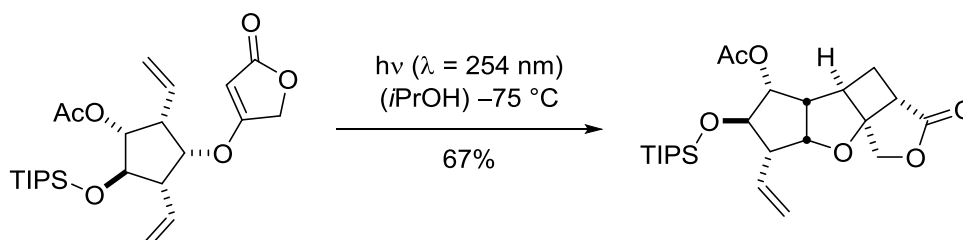

Head to tail

b)

head to head

c)

head to tail/head to head

Exercise 2

Below, you can see the intramolecular regio- and diastereoselective [2+2] photocycloaddition of a tetronate in the total synthesis of (±)-punctaporonin C. Give a reason for this high selectivity and draw the reactive conformation to discuss the problem. (TIPS = tri-iso-propylsilyl)
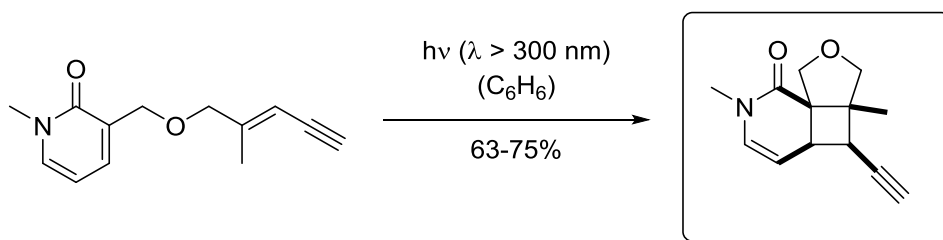
Exercise 3

Draw the respective products with the correct (absolute and) relative configuration. Give the transition states and thus the reason for the high selectivities.

a)
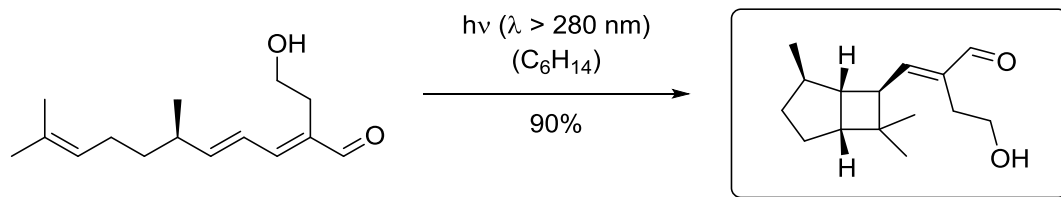
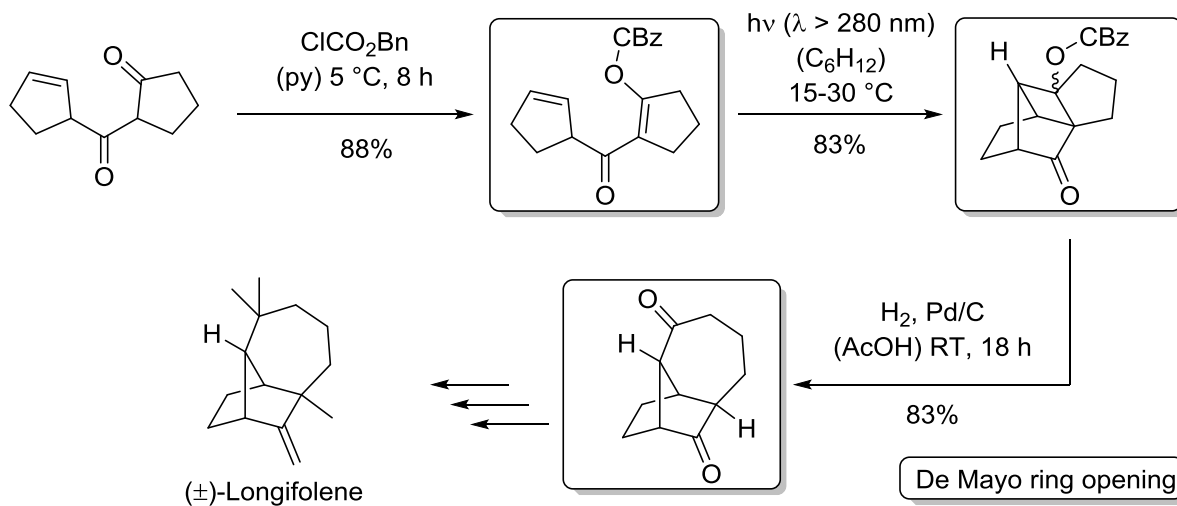*hint: the dienone chromophore represents a vinylogous enone, the γ,δ-double bond reacts.*
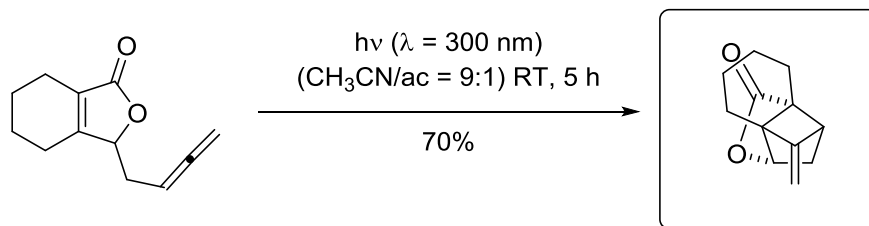
b)

Exercise 4

In the following sequences, give the respective intermediates and products. Also give the name of the first ring-opening-reaction. What other possibilities to open oxetane-rings do you know?

a)

b)

*hint: in this case, the inner double bond of the allene reacts.*

Organic Photochemistry – 4th exercise   16.12.2014   9.00 a.m.

Group I: room 42306   **Group II: room 27402**
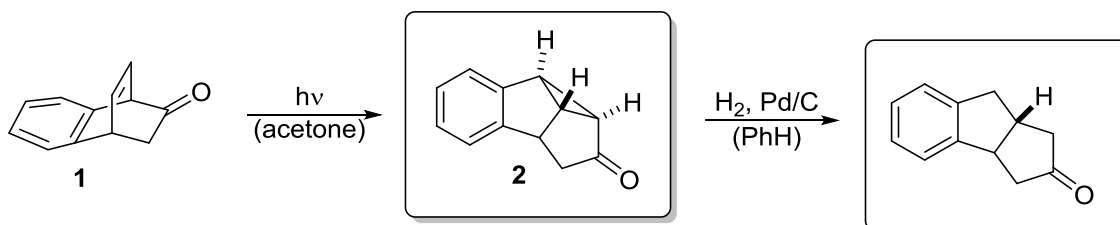
Exercise 1

The depicted, highly substituted bicyclic compound was irradiated in two different solvents. Draw the expected photoproducts and explain the difference of the observed photochemical processes, which obviously depend on the nature of the excited state of the chromophore.
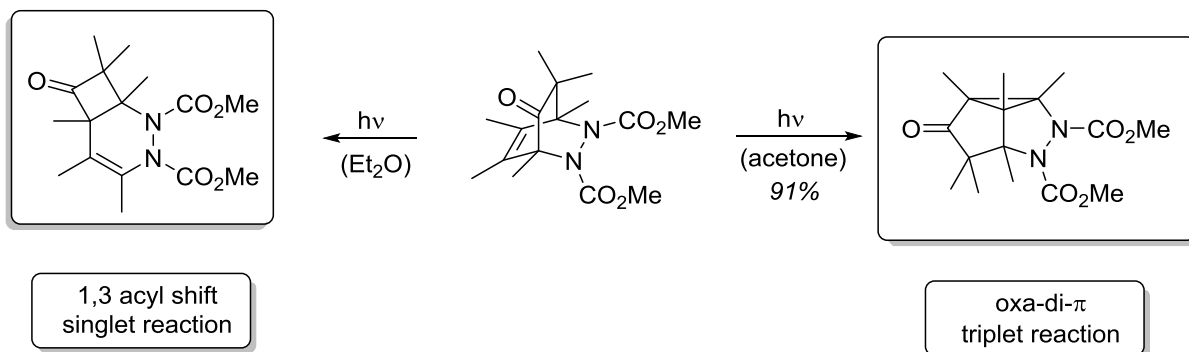
Exercise 2

Both compounds **1** and **3** undergo the same photochemical rearrangement.

a) The photoproduct **2** was then treated with palladium on charcoal, which leads to hydrogenolysis of the compound. Give the intermediate and the final product of the reaction and justify the selectivity of the hydrogenolysis.
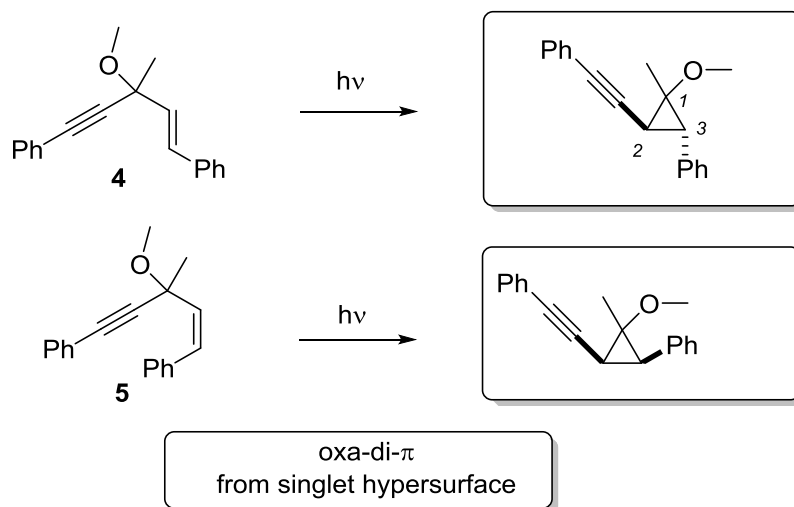

b) Explain the mechanism of this photochemical rearrangement by drawing the important radical intermediates.
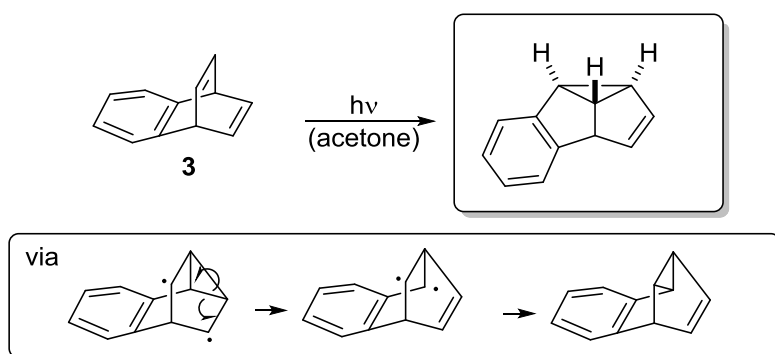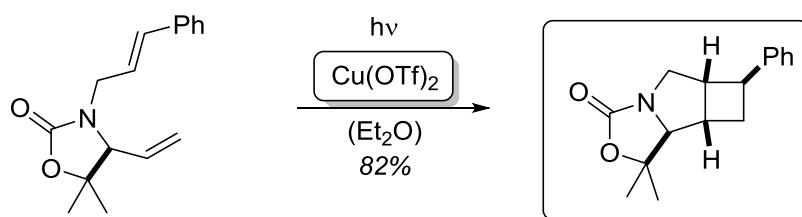
Exercise 3

The same photochemical process takes place upon irradiation of the isomers **4** and **5**.
Give the structure of the photoproducts. Neglect the configuration of the substituent. (Tricky question: Can you give an explanation for the configuration of the photoproducts of **4** and **5**, which only differ in the relative configuration of the substituents at C2 and C3?)

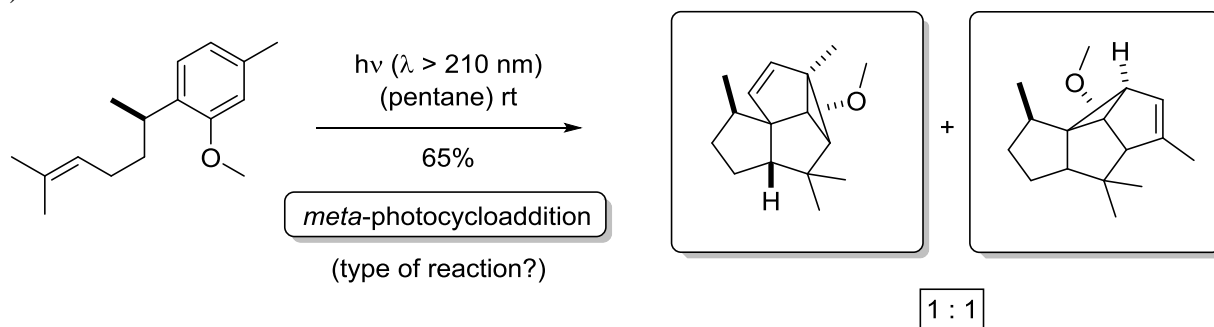oxa-di-π
from singlet hypersurface

Exercise 4

Give the photoproduct of this metal-mediated photochemical reaction. Which metal salt was used for this reaction? Explain the diastereoselectivity of the product and why the metal salt is necessary.
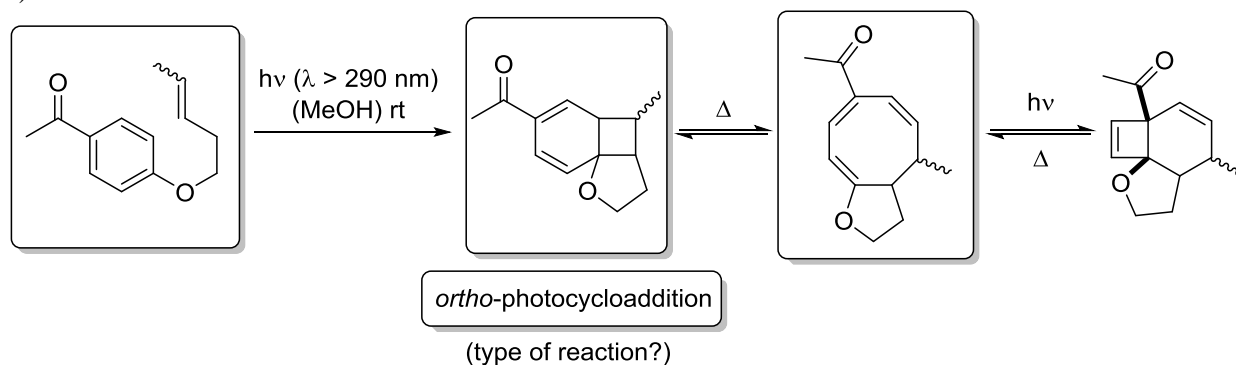
Exercise 1

Draw the missing structures for the following photochemical reactions. Don't forget to think about the respective mechanisms!

a)

hν (λ > 210 nm)
(pentane) rt

65%

meta-photocycloaddition

(type of reaction?)

1 : 1

b)

hν (λ > 290 nm)
(MeOH) rt

Δ

hν
Δ

*ortho*-photocycloaddition

(type of reaction?)

Exercise 2

Para-photocycloadditions giving access to bicyclo[2.2.2]octadiene systems by a formal *Diels–Alder* type reaction are very rare, and little is known about this mode. What are your thoughts about the shown intramolecular photochemical transformation of a cinnamoylamide and a benzamide moiety? Give a mechanistic explanation for the outcome of this reaction.

hν (λ > 250 nm)
benzil
(benzene) rt

93%
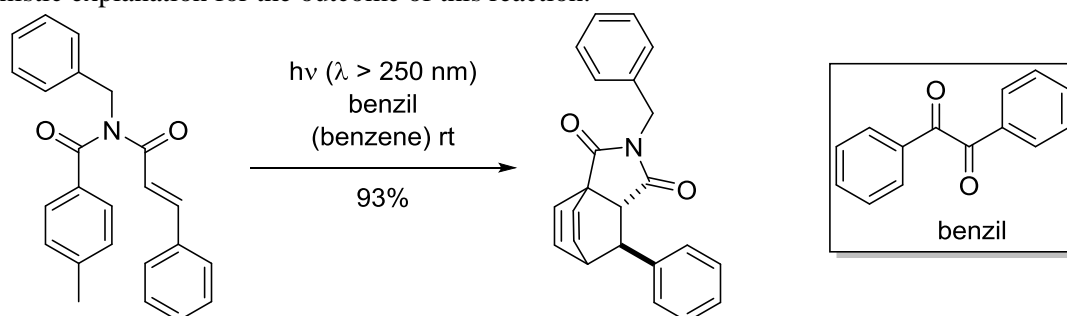
benzil

[In this example, the cinnamoylamide is sensitized by benzil to its triplet excited-state. The proposed mechanism involves the reaction of the olefin with the ipso position of the aromatic ring affording a spiro biradical intermediate. Recombination of these radicals proceeds further until formation of the final compound.]
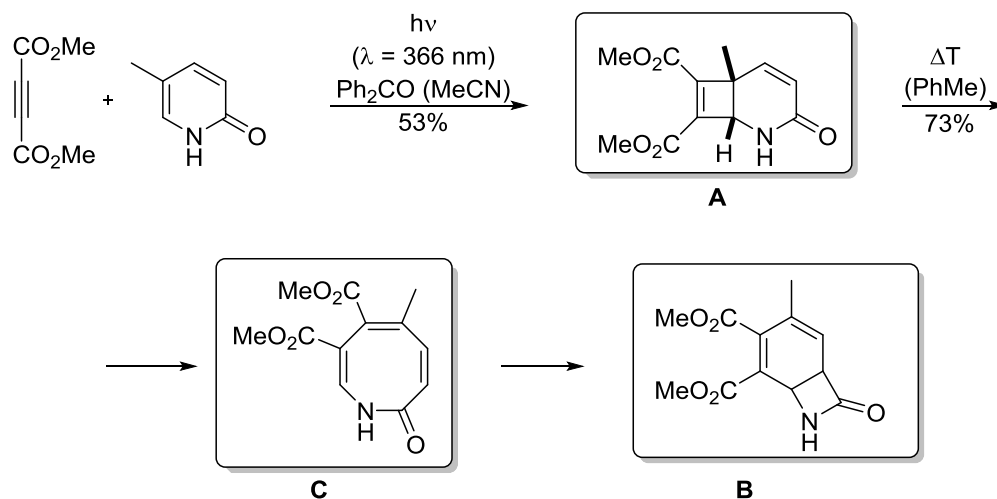
Exercise 3

According to the *Woodward-Hoffmann* rules, the Orbital Symmetry must be conserved in pericyclic reactions. Draw the corresponding orbitals for pentadiene carbocation and the cyclopentene carbocation. Assign the disrotatory and conrotatory cyclisation to the thermal and photochemical reaction.
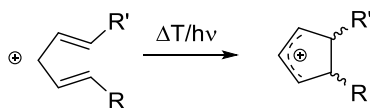
Answer: Thermal: Conrotatory, Photochemically: Disrotatory. 4π Electrons -> 4q with q = 1. (q must be 0, 1, 2 …).

Exercise 4

Irradiation of 5-methyl pyridine in presence of a triplet sensitizer and an electron deficient alkyne leads to the cyclobutene photoproduct **A** (annulation occurs at the 5,6-C-C double bond). Upon heating, **A** isomerizes to β-lactam **B**. Explain the reaction type of the thermal processes, and give the structure of **A**, **B** and **C**.

Exercise 5

The following photochemical reaction and subsequent auxiliary assisted stereoselective reduction with sodium borohydride lead to a precursor of (*S*)-pipecoline. Draw the intermediate and the final product. Which type of photochemical reaction has been used by the authors?