

Exercise 1

Fundamentals

Photochemistry quiz. Answer the following questions.

1. The fact that the fluorescence wavelength is often much longer than the irradiation wavelength (Stokes shift) is a consequence of which phenomenon?

- A low extinction coefficients (Lambert-Beer law)
- B vertical transitions (Kasha's rule)
- C high ISC rates (El Sayed rule)
- D low activation barriers (Hammond postulate)

2. 1 Es (\equiv 1 mol of photons) with a wavelength of $\lambda = 200$ nm corresponds (roughly) to which energy?

- A 800 kJ
- B 600 kJ
- C 400 kJ
- D 200 kJ

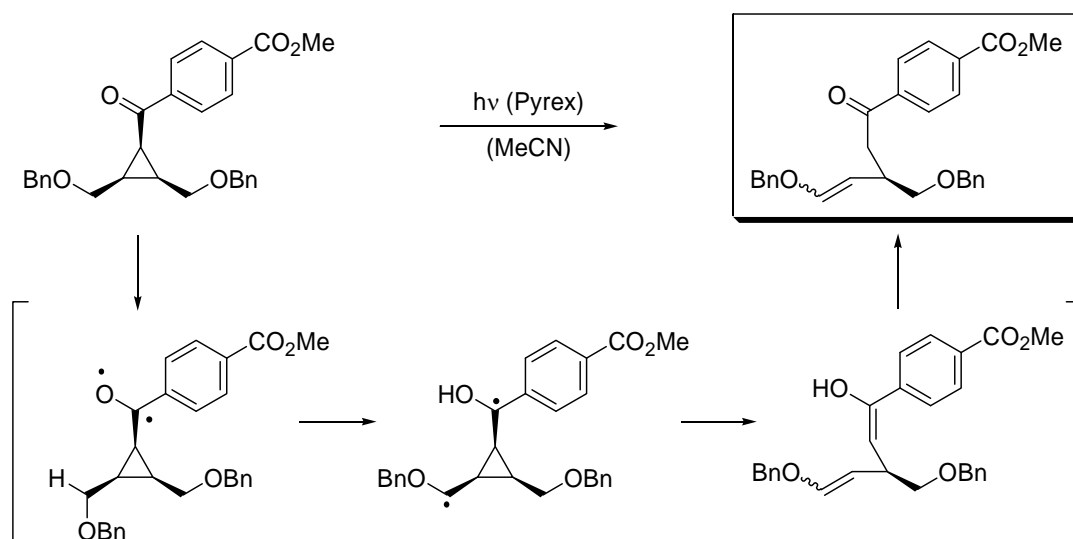
3. Which statement(s) is / are correct?

- A The total spin quantum number of the singlet state is 1.
- B Phosphorescence is spin-forbidden and occurs from S_1 .
- C An excitation with more energy than necessary is possible.
- D Most photochemical reactions occur out of T_1 .
- E Most photochemical reactions occur out of S_1 .

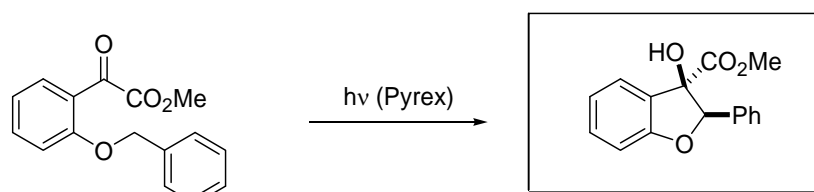
4. Describe the influence of the electronic excitation and the following processes on the respective nuclei.

H-Abstraction reactions

5. Explain the outcome of the following reaction.



6. Which is the main product of the following transformation?



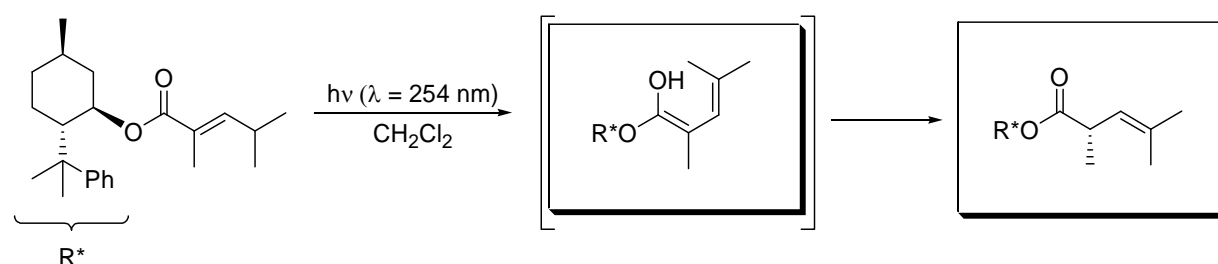
What conditions are best suited to achieve a high diastereoselectivity?

- 25 °C (*i*-PrOH)
- 30 °C (C_6H_6)
- 60 °C (heptane)

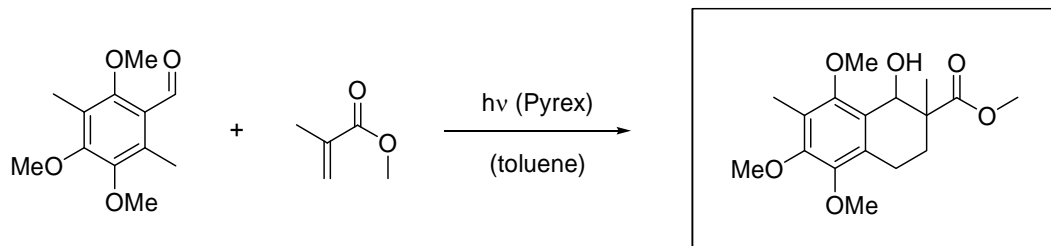
Formation of dienols

7. Give the expected products in the following reactions.

a)

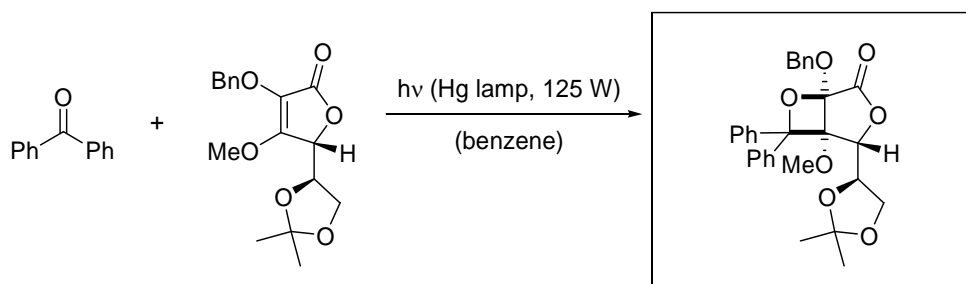


b)

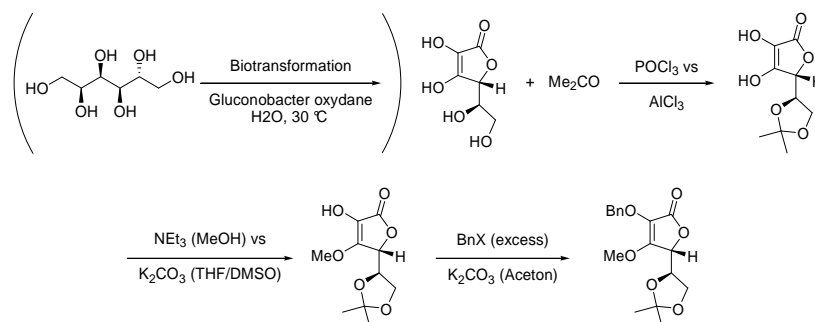


Paternò-Büchi reactions

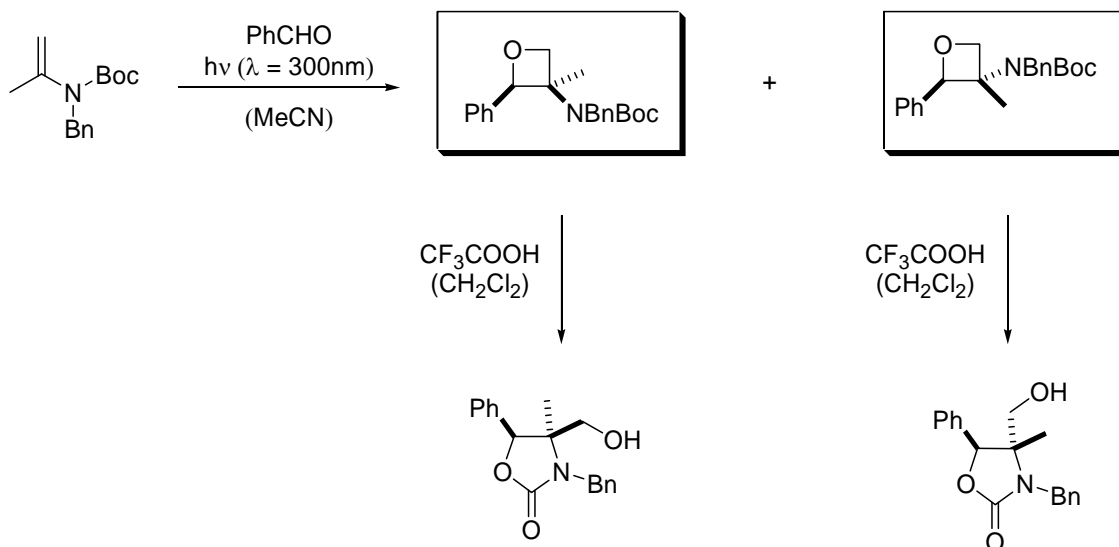
d)



How would you synthesize this substrate?

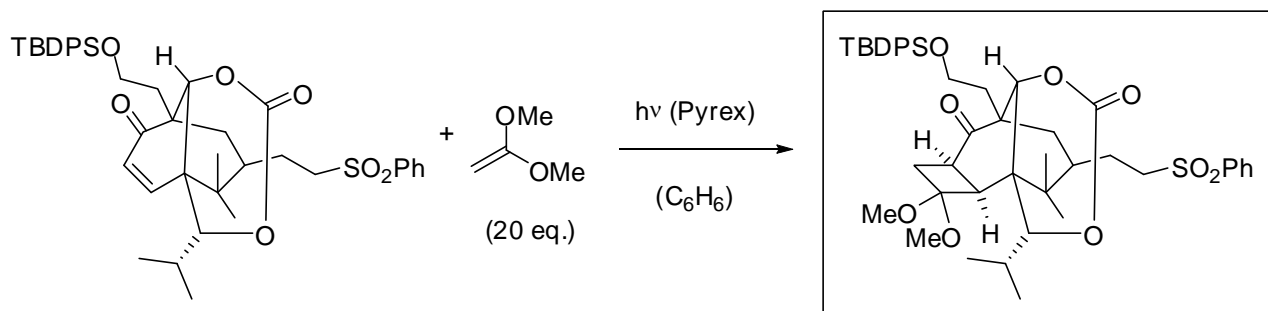


8. Give the reaction products with the expected stereochemistry in the following Paternò-Büchi reaction. The products undergo an interesting intramolecular substitution reaction to oxazolidinones when they are treated with trifluoroacetic acid. Describe the mechanism of this ring opening reaction.



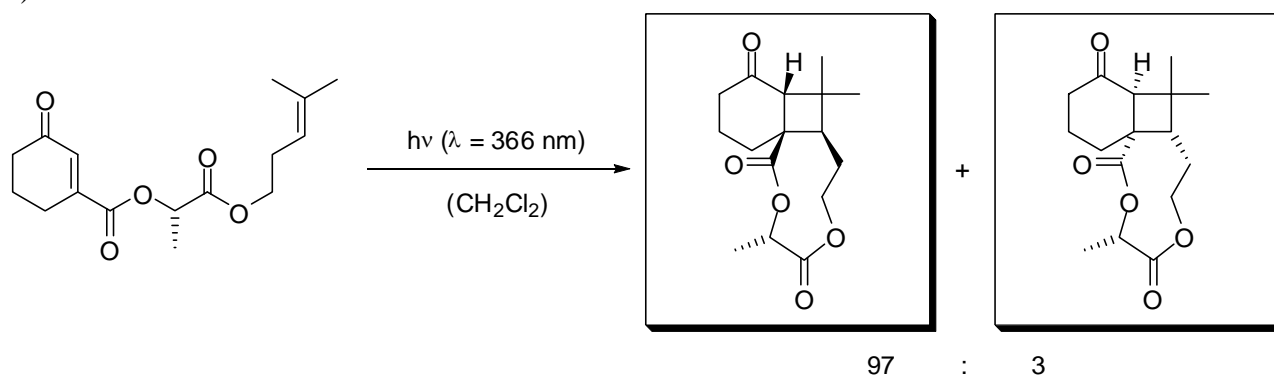
Exercise 2

1. The following reaction was described by Nicolaou et al. in the synthesis of the fully functionalized core of the natural product Garsubellin A. Which product did they obtain as a single regio- and diastereoisomer?

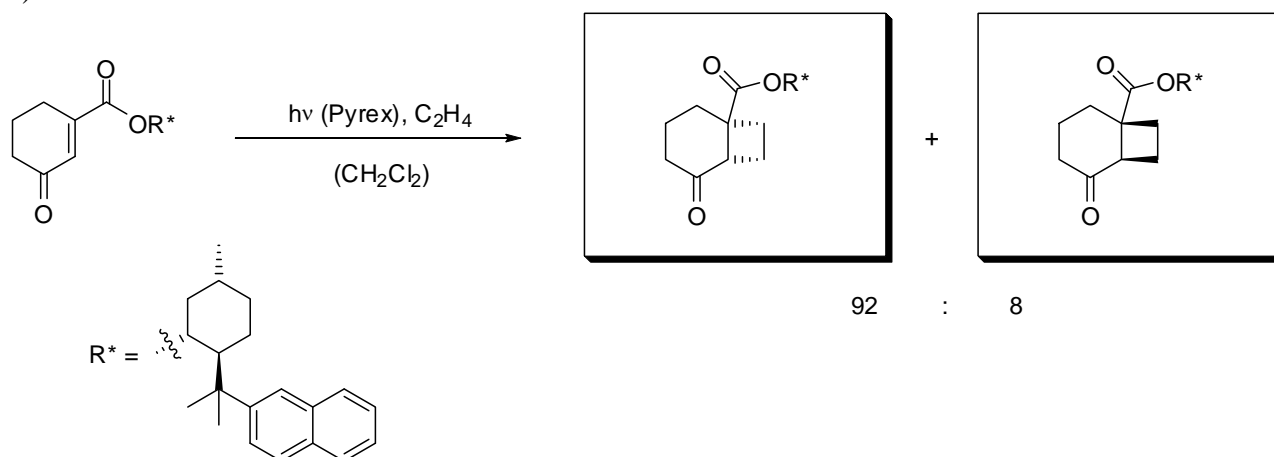


2. Give the reaction products with the expected stereochemistry in the following [2+2]-photocycloadditions.

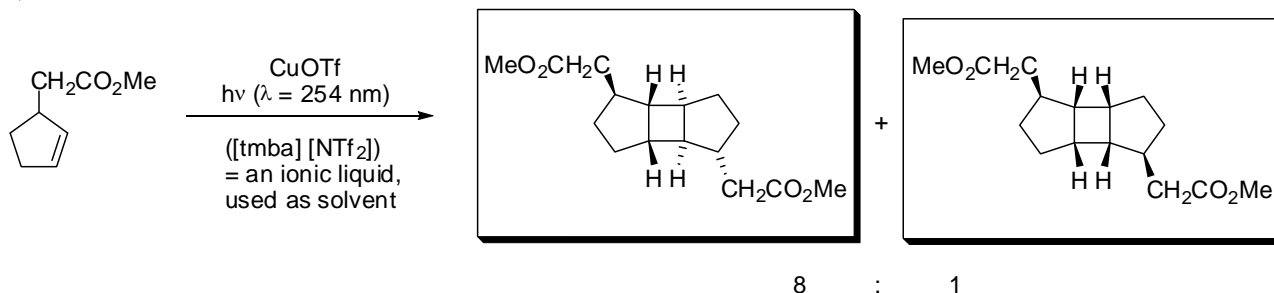
a)



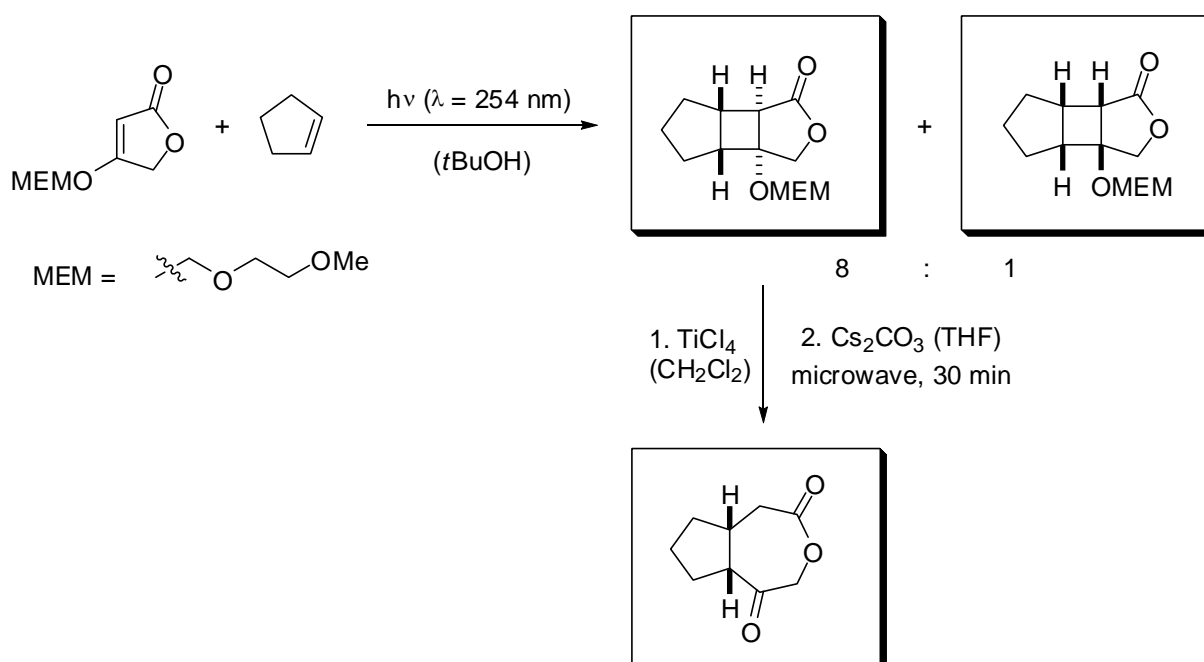
b)



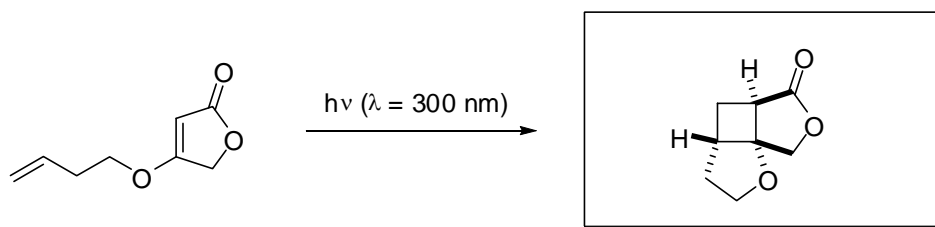
c)



5. The intermolecular photoreaction between MEM-protected tetronic acid and cyclopentene furnished an 8:1-mixture of two diastereomers. The main product was deprotected with TiCl_4 and subsequently treated with Cs_2CO_3 in a microwave oven.



6. The following compound with $\lambda_{\text{max}} = 220 \text{ nm}$ was irradiated in acetonitrile at $\lambda = 300 \text{ nm}$.



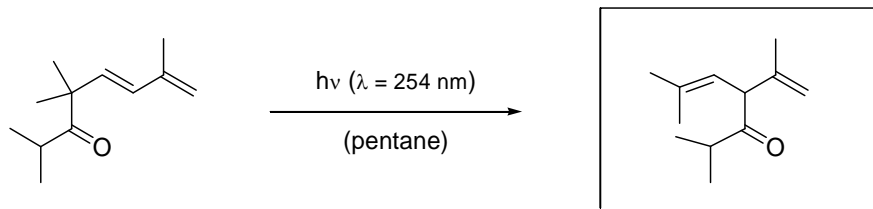
As expected, these conditions did not result in any product formation. Why? If 10% (v/v) acetone was added, the reaction led to the desired product. Explain this effect. Which product was obtained?

Analogous reactions were carried out in acetonitrile in the presence of acetophenone and benzophenone instead of acetone. In both reactions, no product formation could be observed. Which conclusions can be drawn from these observations?

Exercise 3

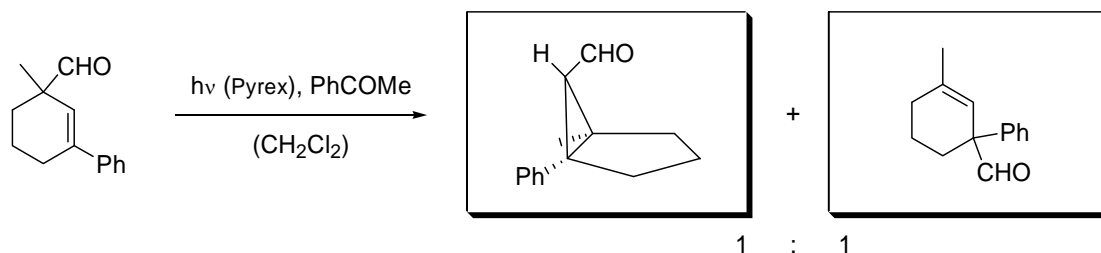
1. In the lecture you have learnt two different reaction types for β,γ -unsaturated ketones.

a) What product do you expect on the basis of the guidelines given in the lecture?



type: 1,3-acyl shift

b) However, these guidelines are less strict for aldehydes. In the following reaction a singlet and a triplet reactivity were observed.

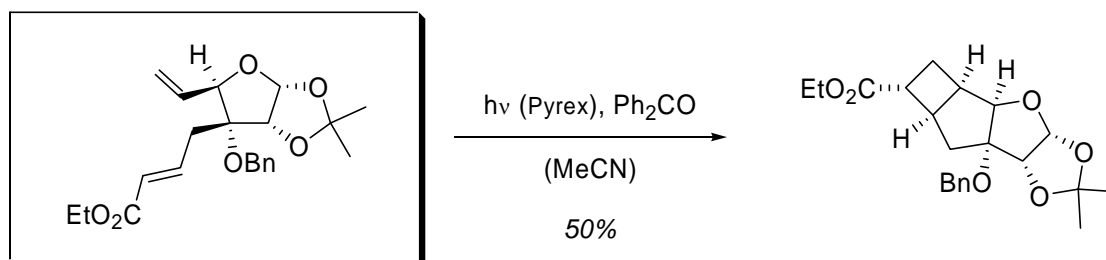


type: Oxadi- π -methan

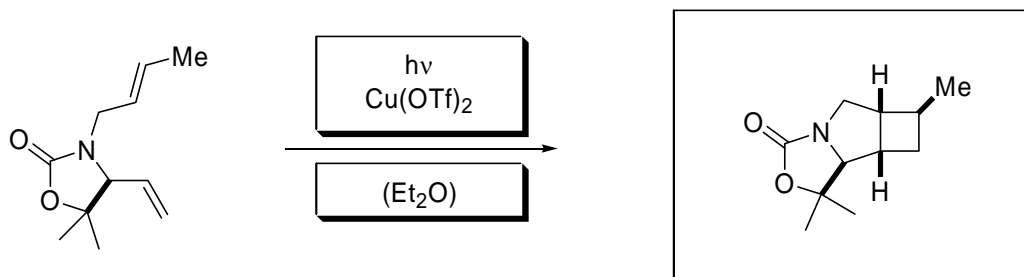
type: 1,3-acyl shift

2. Give the correct substrates or the products with the expected stereochemistry in the following [2+2]-photocycloadditions.

a)

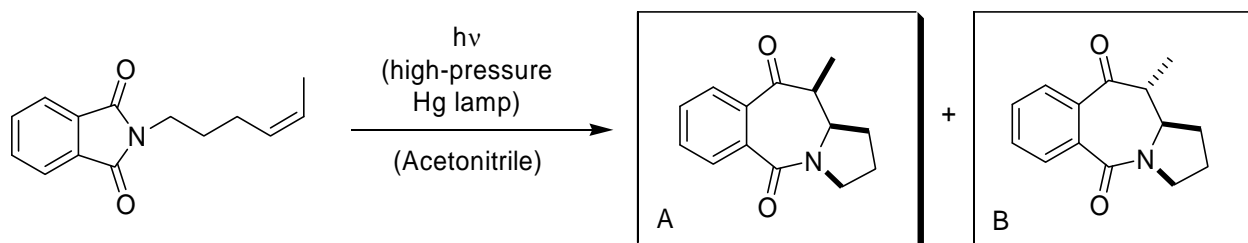


b)



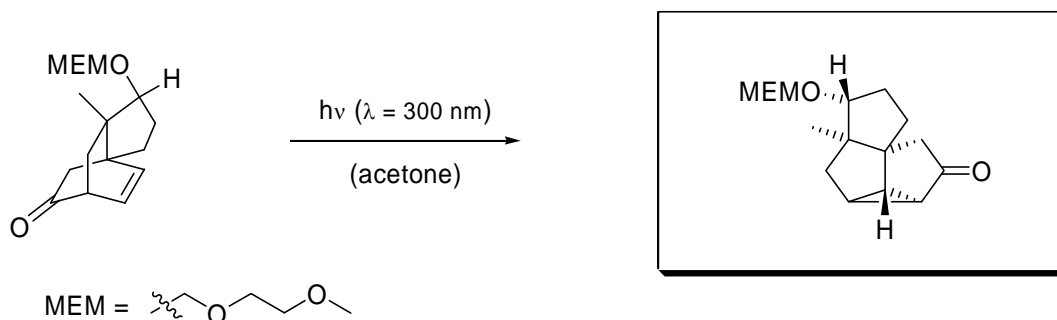
3. The following phthalimide was irradiated with a high-pressure Hg-lamp. At low conversion of the substrate, HPLC analysis indicated the almost exclusive formation of product A (plus large amounts of yet unreacted starting material), whereas after 8 days of irradiation a 40:60 ratio of product A and its diastereomer B was formed.

- Give the structures of A and B.
- What conclusion can be drawn from the fact, that only A is formed in the beginning of the reaction?
- Why does the ratio of A and B alter with prolonged reaction time?

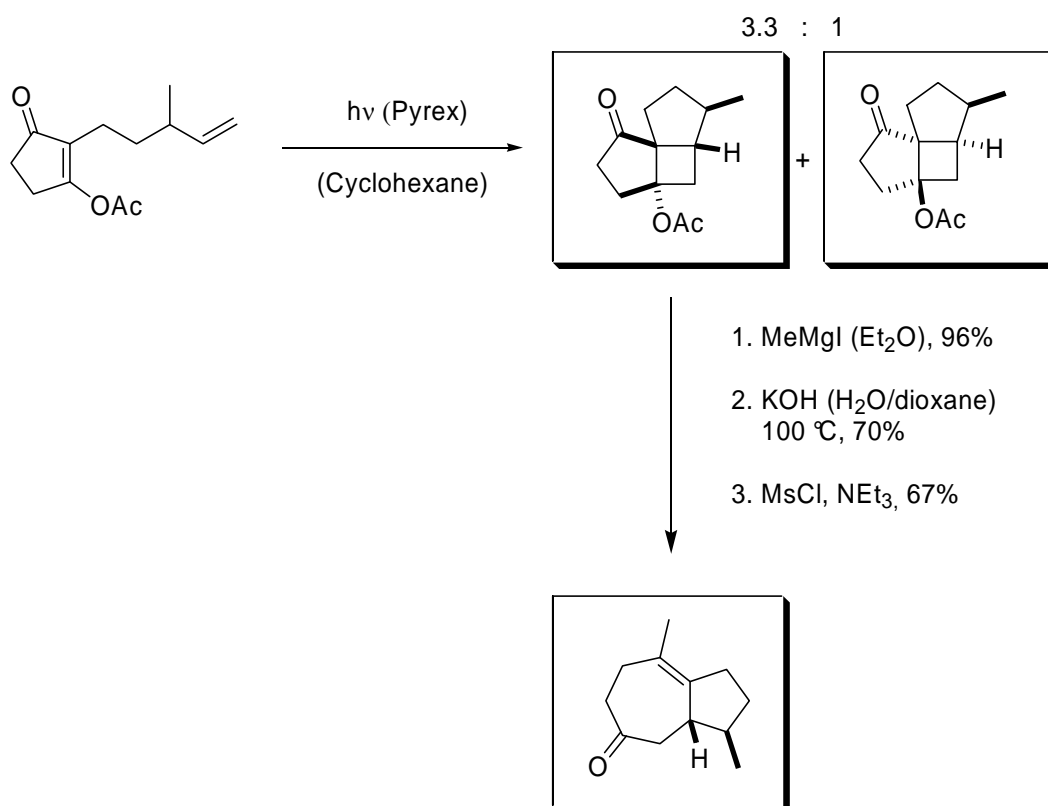


at low conversion:	97	:	3
after 8 d of irradiation:	40	:	60

4. The key step of this synthesis involves a highly efficient triplet-sensitized rearrangement of a structurally rather complex enone. Draw the main product of this rearrangement.

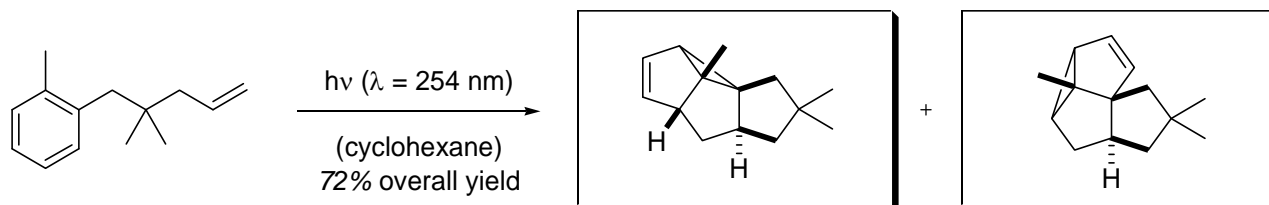


5. In a study related to the total synthesis of β -Bulnesene, the depicted cyclohexenone was irradiated. The main product was treated with 1.2 equiv. of MeMgI and saponified with KOH. Upon treatment with MsCl and NEt₃ a fragmentation reaction took place.



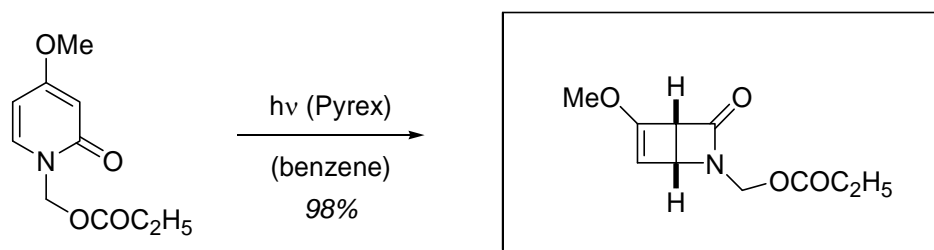
Exercise 4

1. This key step in a racemic total synthesis of ceratopicanol afforded two isomers.

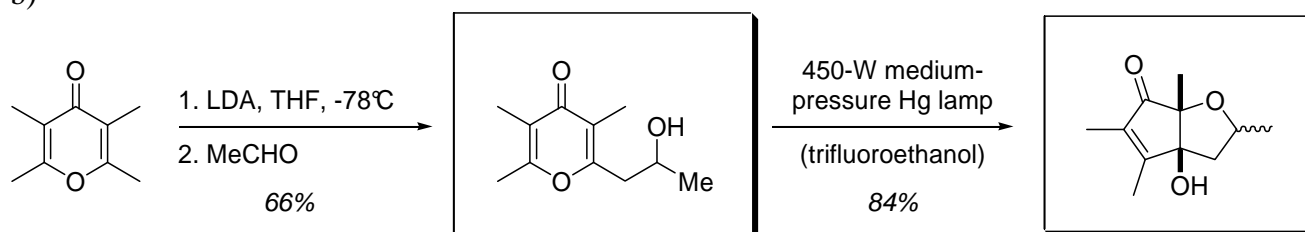


2. Give the correct products of the following photocycloadditions. Give a detailed explanation (Woodward-Hoffmann rules).

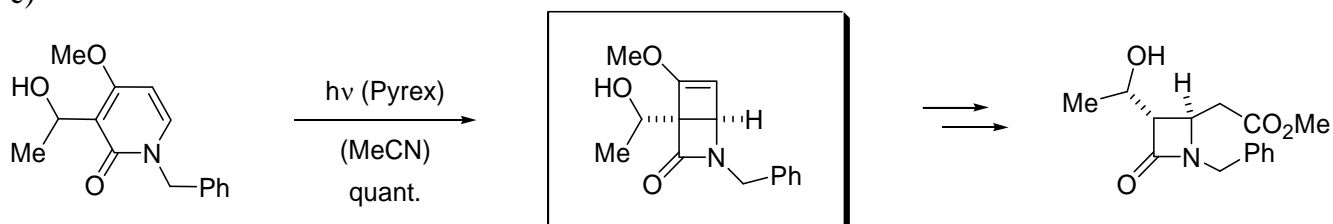
a)



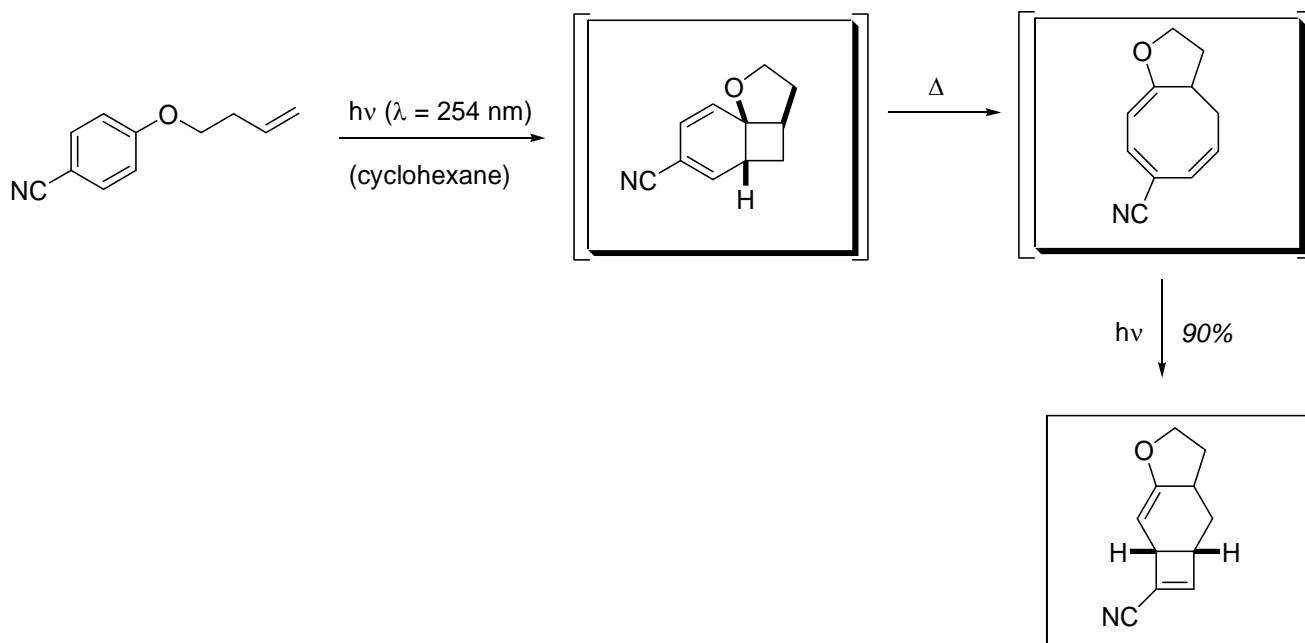
b)



c)

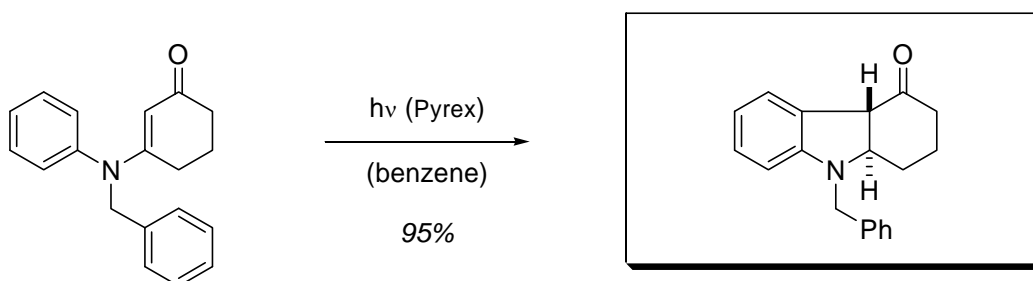


3. Irradiation of the following compound gave a tricyclic product in excellent yield.

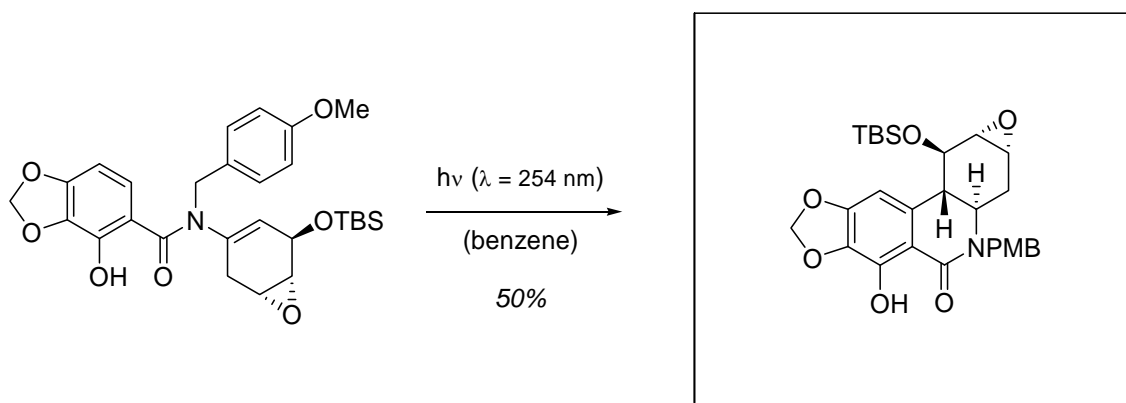


4. Give the correct products of the following photocycloadditions. Pay attention to potential isomeric forms. Give a detailed explanation (Woodward-Hoffmann rules).

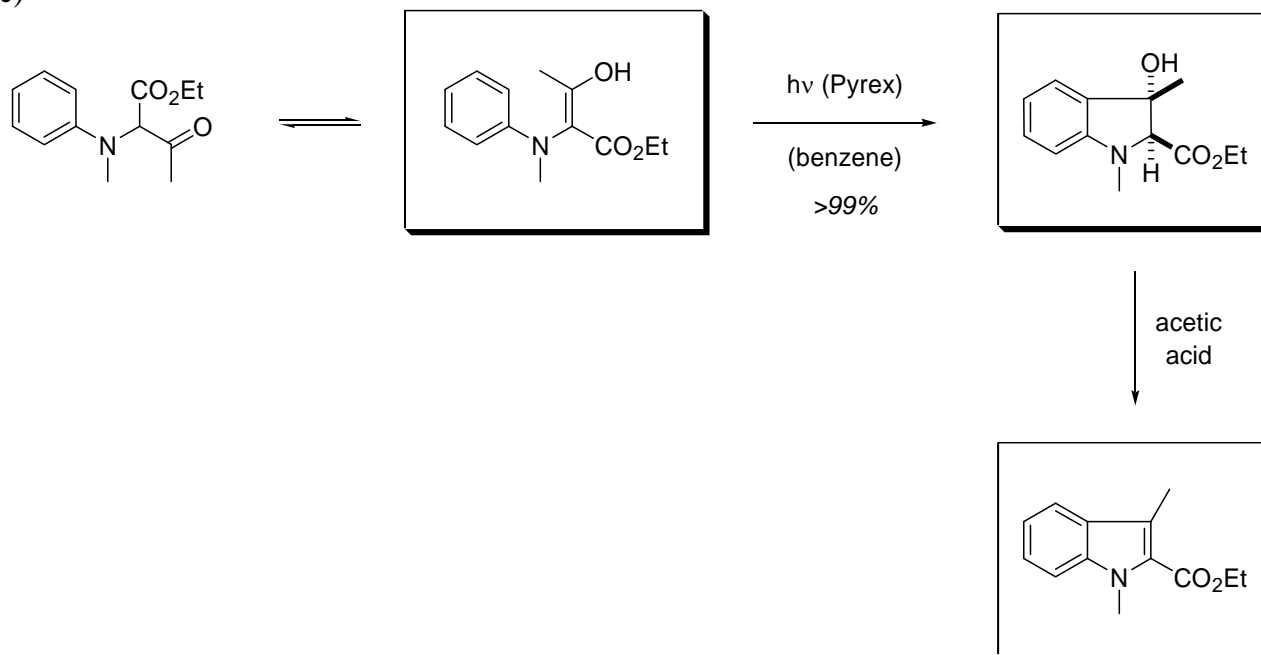
a)



b)



c)



5. What is the main product of the photocycloaddition of p-xylene und cyclopentene?

