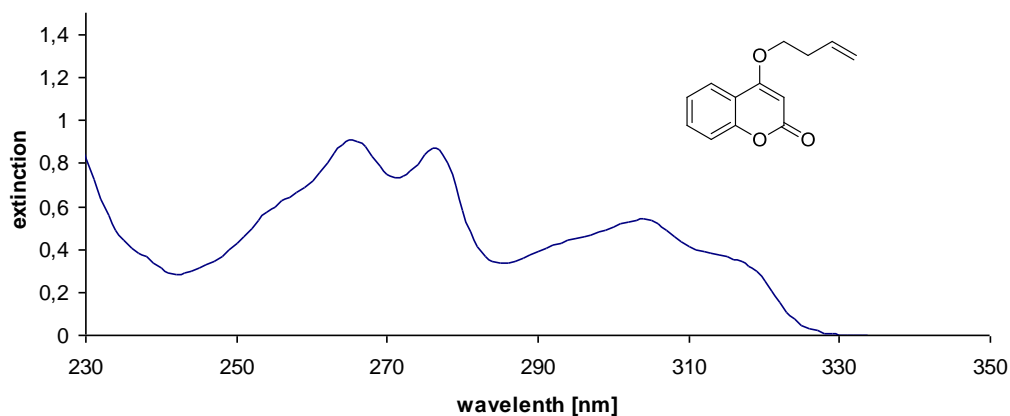


Exercise 1

a) Calculate the energy of one mole of photons ($\lambda = 400 \text{ nm}$)

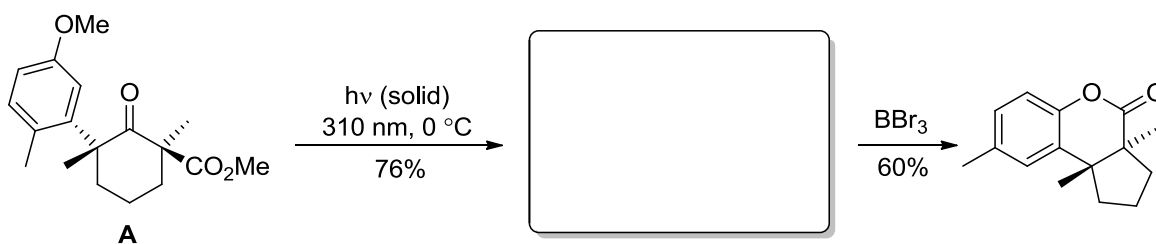
b) The UV-Vis spectrum of a coumarin derivative is shown below. The sample was prepared by dissolving 10.81 mg in 100 mL dichloromethane, and was analysed in a cell with a path length of 1 mm.



- Estimate the molar absorption coefficient for the absorption at approximately 305 nm
- Is this likely to be an allowed or a forbidden transition?

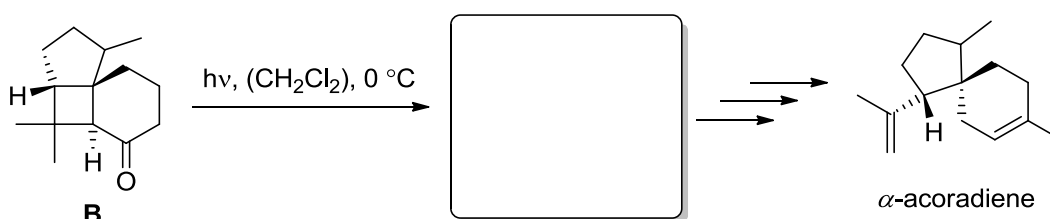
Exercise 2

A key step in the total synthesis of (\pm)-herbertenolide involves the irradiation of a finely powdered sample of cyclohexanone derivative **A** in the solid state. What product do you expect to form? What is the name of this type of reaction? *Hint*: BBr_3 deprotects methoxy groups with release of the free alcohol.



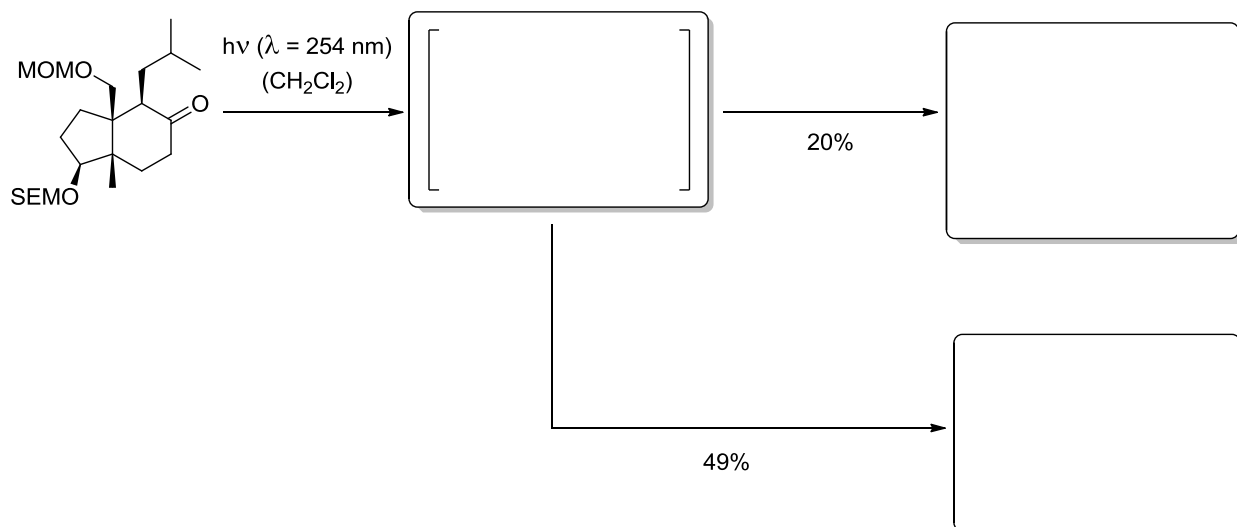
Exercise 3

Irradiation of tricycle **B** generates a useful intermediate for the total synthesis of the natural product α -acoradiene. What is the product and what type of reaction is this?



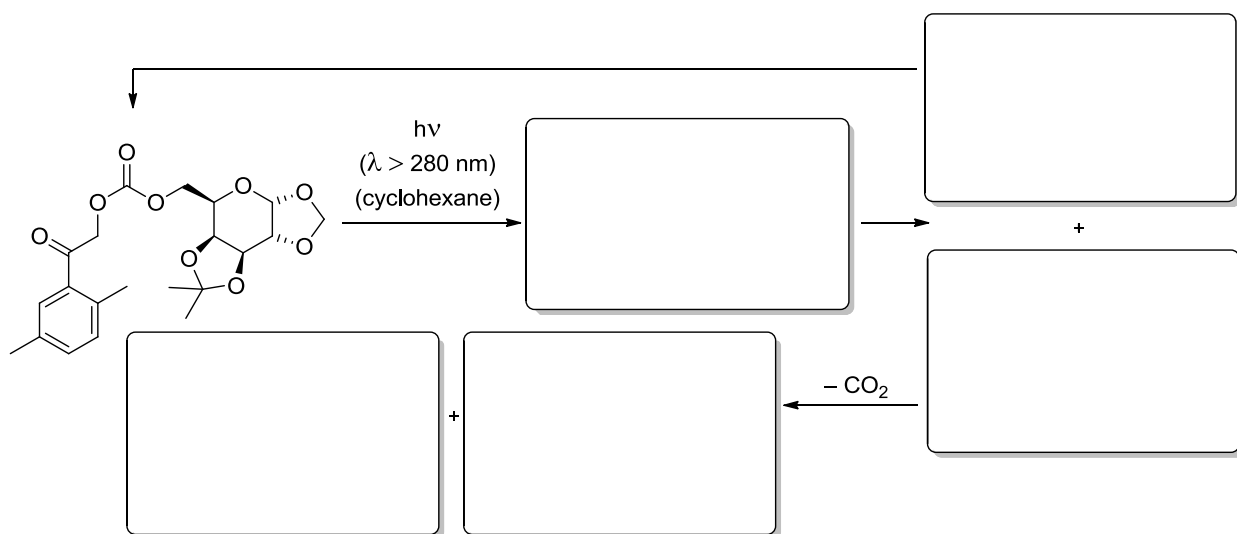
Exercise 4

Give the structure of the expected products for the reactions of the cyclohexanone shown upon irradiation and name the reaction types. Draw the intermediate and explain the stereochemical outcome of the reaction that forms the major product.



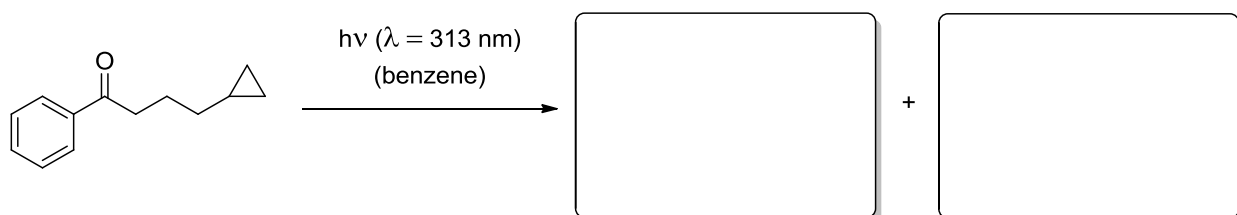
Exercise 5

Photoremoveable protecting groups have found numerous applications in many fields of chemistry and biochemistry. In this example, the 2,5-dimethylphenacyl (DMP) chromophore attached *via* a carbonate link is used to protect a primary alcohol. Draw the expected intermediates and the respective products.



Exercise 6

Which products are formed in the following reactions? Explain the mechanisms! *Hint*: cyclopropylcarbinyl radicals are highly reactive and therefore undergo very fast ring opening to homoallylic radicals.



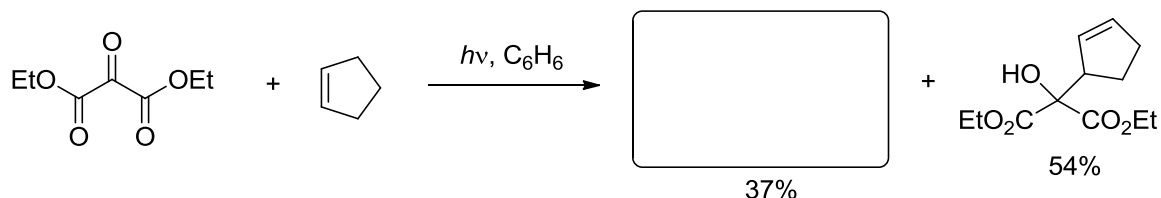
Organic Photochemistry – 2nd exercise 29.11.2012 11.05 a.m.

Group I: room 22210

Group II: room 42306

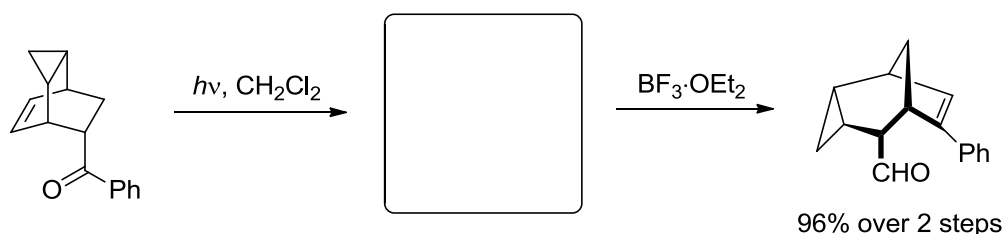
Exercise 1

Irradiation of the tricarbonyl compound below in a mixture of benzene and cyclopentene led to the desired product (37% yield) and the by-product shown (54% yield). Give the structure of the desired product and a mechanism for its formation, and suggest a mechanism to rationalise the formation of the by-product.



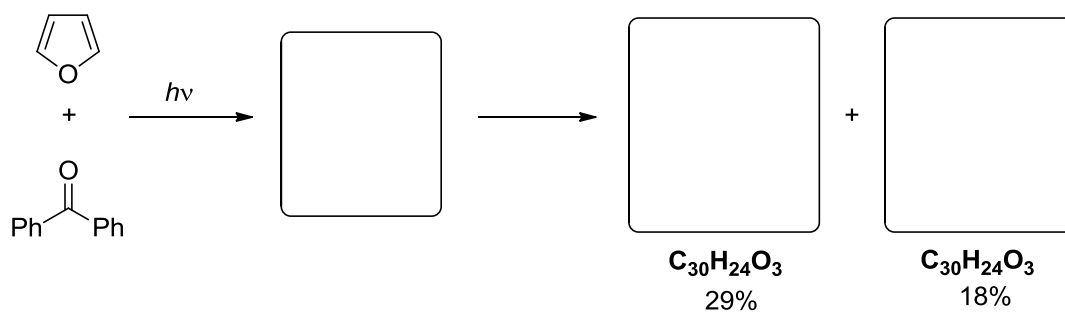
Exercise 2

Upon irradiation, the ketone below forms in a Paternó-Büchi-reaction a highly strained intermediate that can be converted into the aldehyde shown using $\text{BF}_3 \cdot \text{OEt}_2$. Provide the structure of the intermediate and a mechanism for its conversion into the aldehyde. *Hint*: cycloreversion in the second step.



Exercise 3

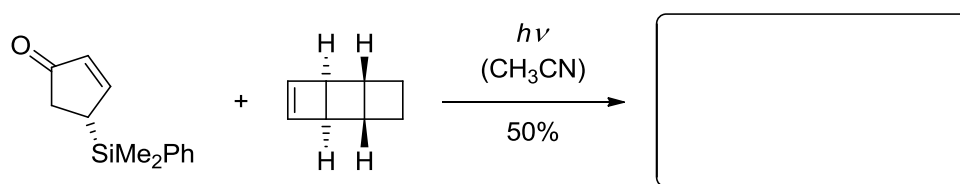
Irradiation of a mixture of furan and an excess of benzophenone initially generates an adduct that undergoes further reaction upon continued irradiation to give two further products. Identify the intermediate and the two final products.



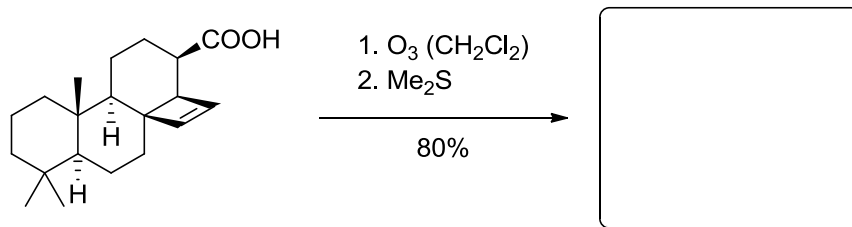
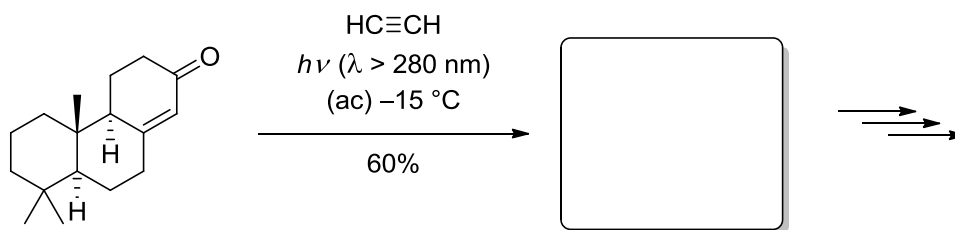
Exercise 4

Give the reaction products with expected stereochemistry in the following photocycloadditions!

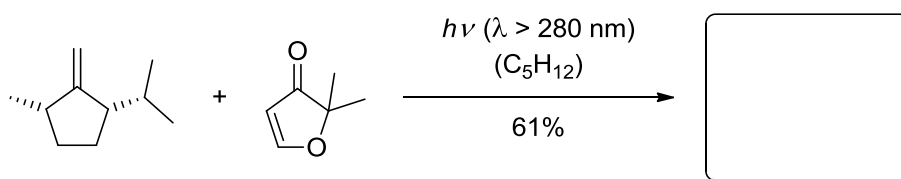
(a)



(b)

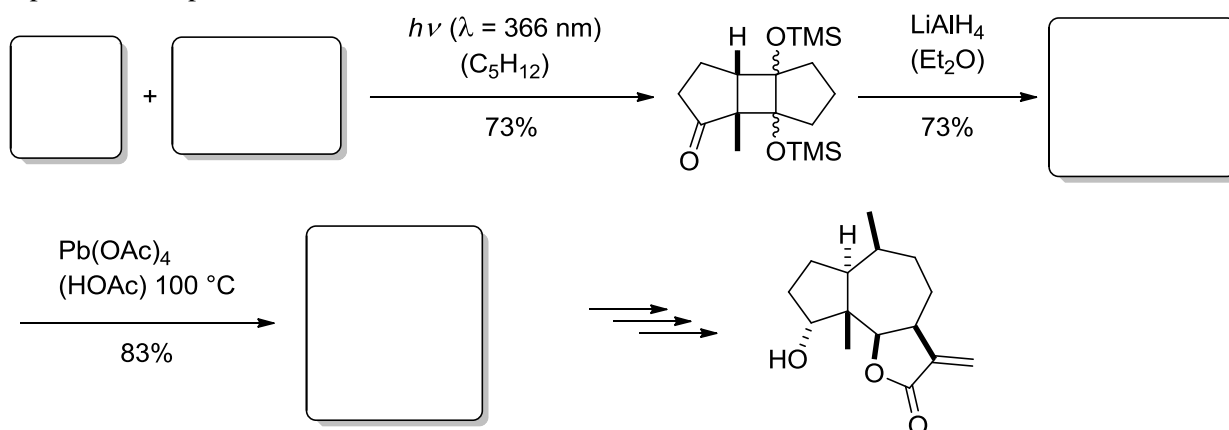


(c)



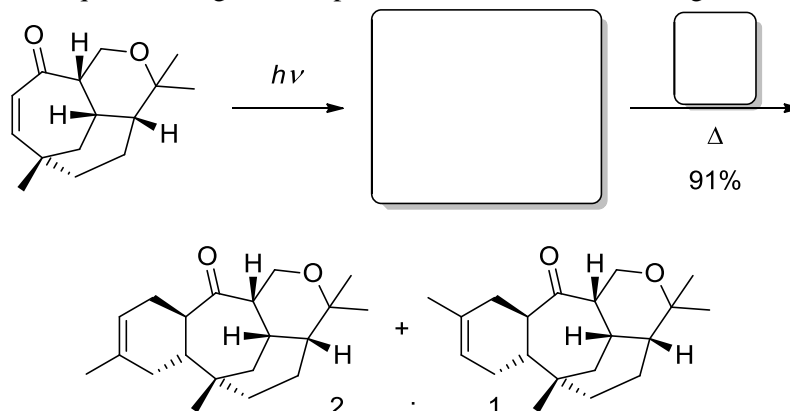
Exercise 5

Give the starting materials of the photoreaction and complete the reaction sequence! *Hint*: LAH is able to deprotect TMS-protected alcohols.



Exercise 6

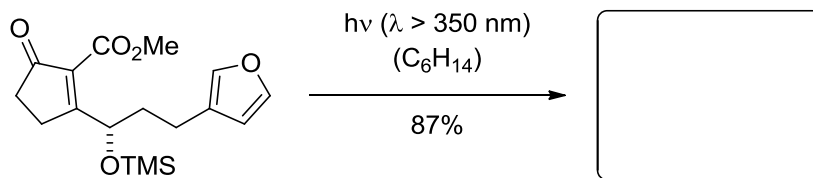
In the following example, an α,β -unsaturated ketone undergoes a photochemical reaction leading to an intermediate which is no longer electronically excited but highly strained. According to Woodward-Hoffmann rules, it may undergo a [4 + 2] suprafacial cycloaddition with a diene (Diels-Alder reaction). Complete the reaction sequence and give an explanation for the relative configuration of the products.



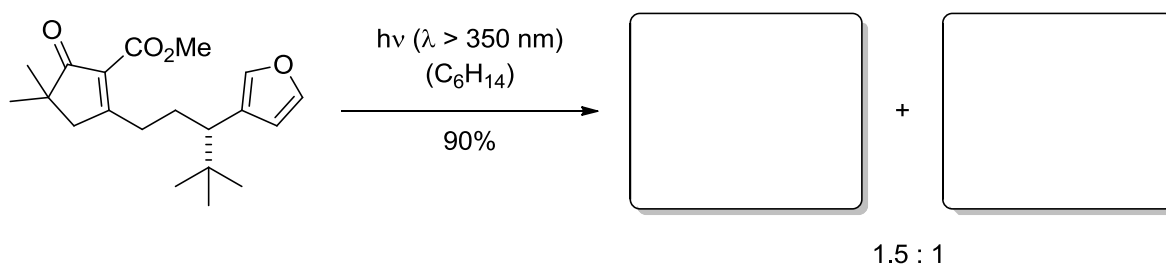
Exercise 1

During the investigation of diastereoselective enone-furan [2+2] photocycloadditions, two very similar substrates have been examined, to determine the influence of the individual substituents on the stereochemistry of this reaction. Provide the structures of the products (relative configuration!).

(a)



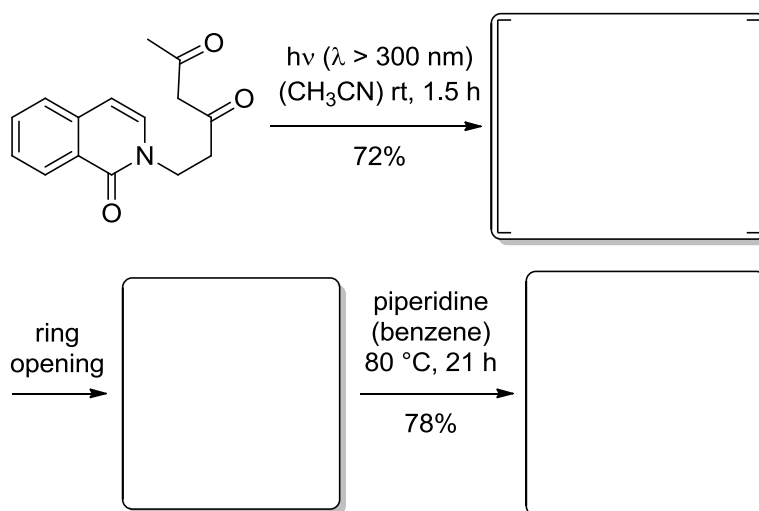
(b)



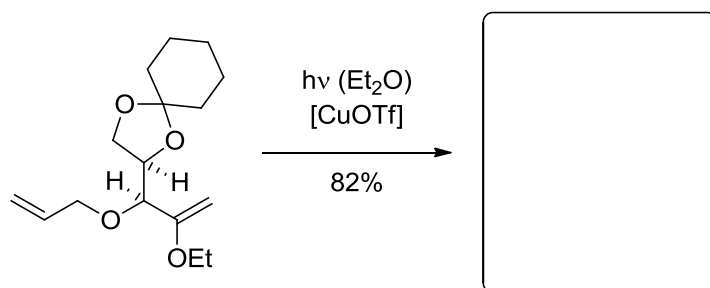
Exercise 2

Give the reaction products with expected stereochemistry in the following photocycloadditions!

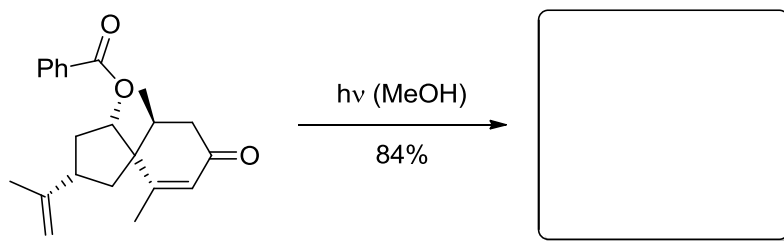
(a)



(b) *Hint: no coordination of heteroatoms.*

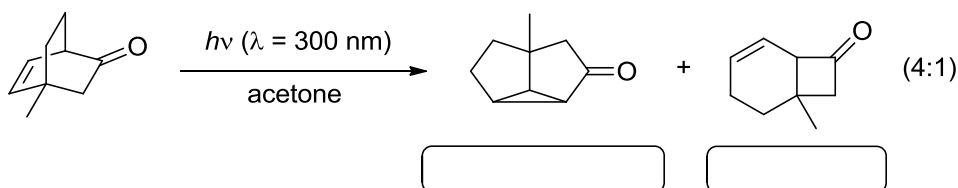


(c)

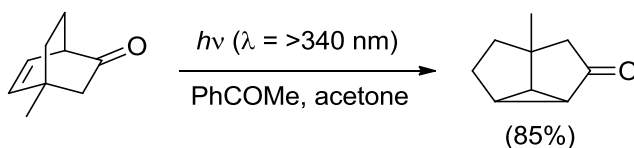


Exercise 3

(a) Upon irradiation at 300 nm in acetone, the bicyclic ketone below generates two products: a cyclopentanone and a cyclobutanone (4:1 ratio of products). Give a mechanism for the formation of each product and the names of the two reaction types.

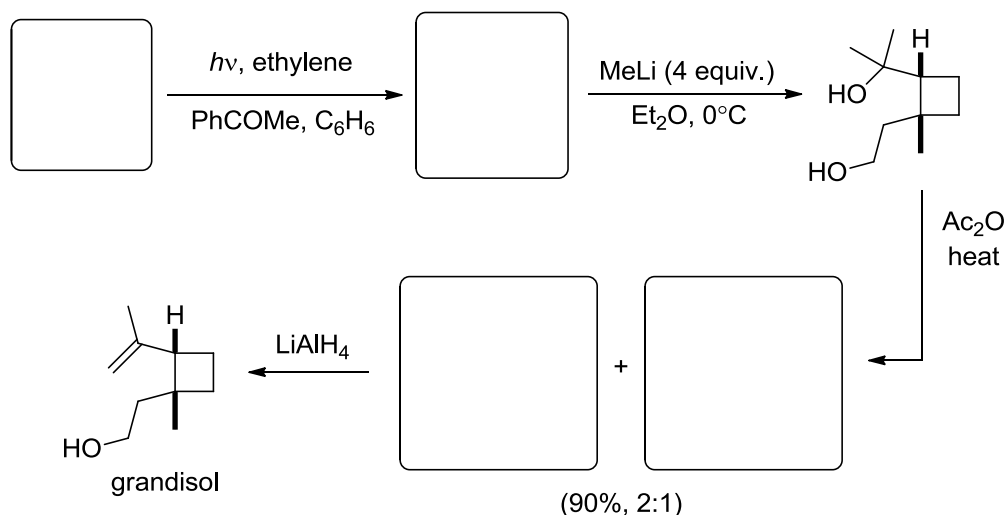


(b) Under the following slightly modified reaction conditions, the formation of the cyclobutanone can be completely suppressed. Why is this?



Exercise 4

A short synthesis of the natural product grandisol involved a sensitised [2+2] photocycloaddition involving ethylene as a key step.



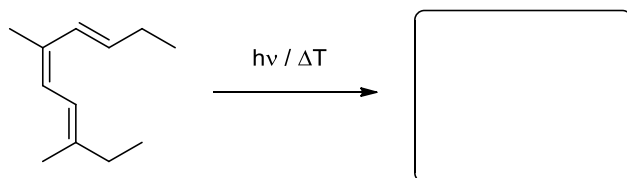
(a) Give the starting material and the product of the photocycloaddition. Why is the use of a sensitiser desirable for these types of substrates?

(b) If benzophenone is used instead of acetophenone, the reaction does not proceed. Why?

(c) Complete the remaining gaps in the synthesis.

Exercise 1

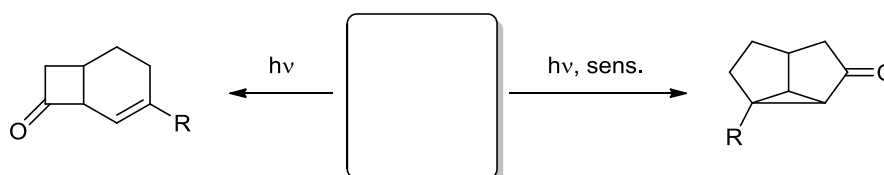
According to the Woodward-Hoffmann rules, the Orbital Symmetry must be conserved in pericyclic reactions. Draw the corresponding orbitals for the shown molecule and the products after conrotatory and disrotatory ring closure, respectively. Assign the disrotatory and conrotatory cyclization to the thermal and photochemical reaction.



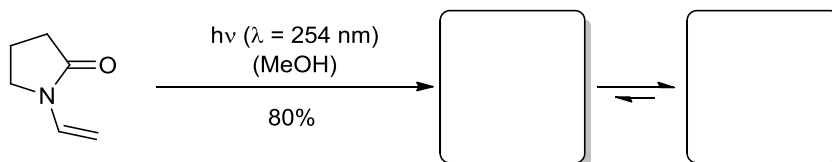
Exercise 2

Complete the following reactions!

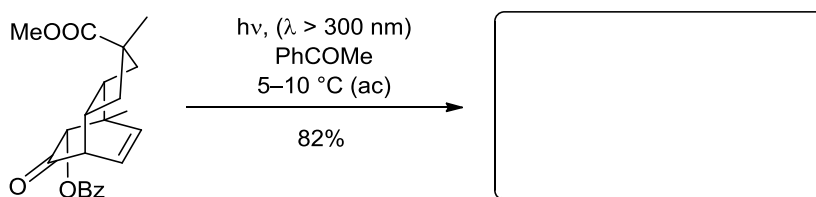
a)



b)



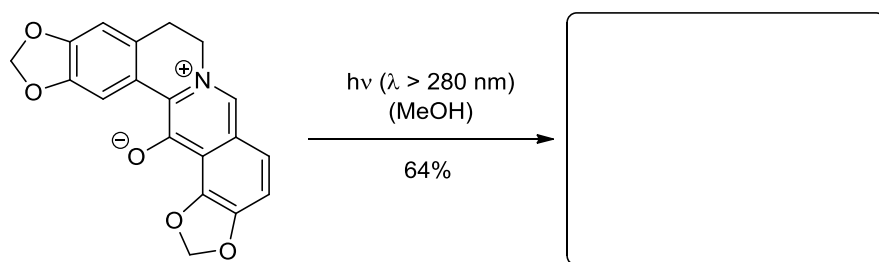
c)



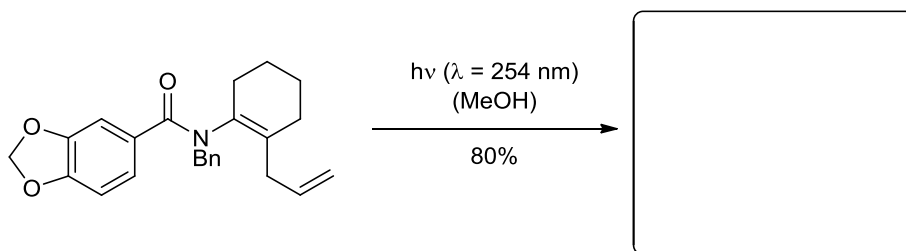
Exercise 3

Give the expected products in the following photocyclization reactions. Give a detailed explanation (Woodward-Hoffmann rules).

a)



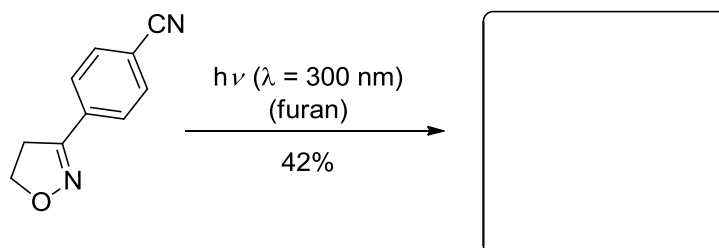
b)



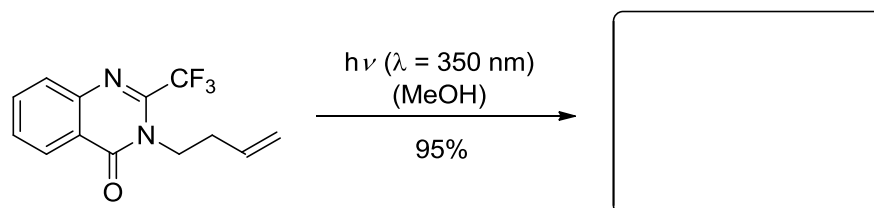
Exercise 4

Although the useful photochemistry of imines is limited, some efficient and selective reactions do occur. The following [2+2] photocycloadditions each generate a single product - give the structures (including relative configuration).

a)



b)



Exercise 5

The enantiopure 2,4-cyclohexadienone shown below undergoes an oxa-di- π -methane reaction upon irradiation, generating the two possible stereoisomers in a 1:1 ratio. Give the structures of the products.

