

Organic Photochemistry – 1st exercise 10.11.2011 11.05 a.m.

Family name starting with A-L: room 22210

Family name starting with M-Z: room 42306

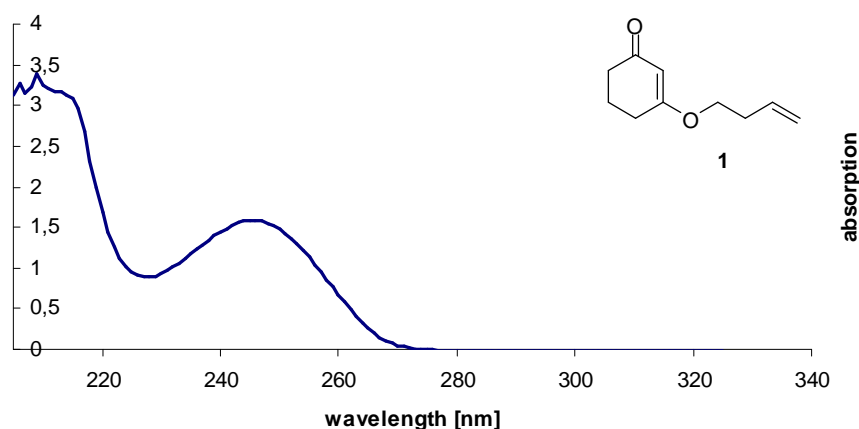
Exercise 1

Draw a Jablonsky diagram and explain the following concepts!

- Deactivation of excited states and Kasha's rule
- Intersystem crossing and El Sayed rules

Exercise 2

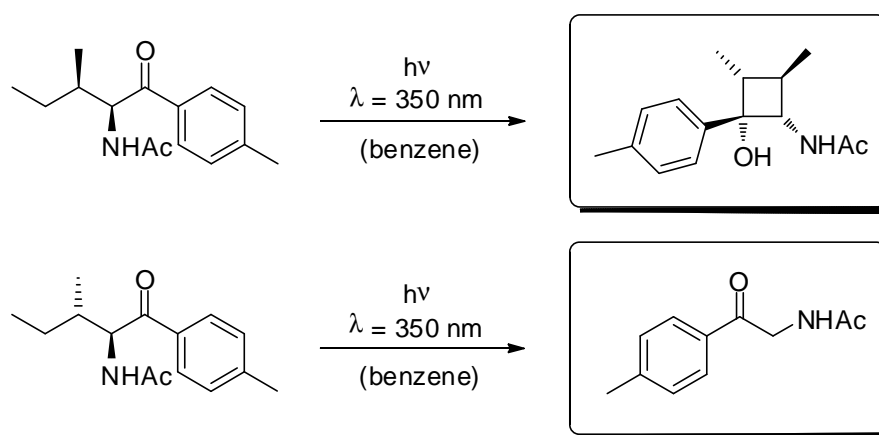
The UV-Vis spectrum of compound **1** is shown, which was prepared by dissolving 1.33 mg **1** in 10 mL dichloromethane and was analyzed in a cuvette with 1 mm layer thickness.



- Estimate the absorption maximum λ_{\max} and calculate the corresponding absorption coefficient by extracting the absorption from the spectrum.
- Using cyclohexane as solvent a forbidden transition can be detected at $\lambda = 309$ nm with an absorption coefficient of $40 \text{ l}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$. Calculate the expected absorption.
- Calculate the energy transferred from the photon to the molecule by inducing the allowed and the forbidden transition.

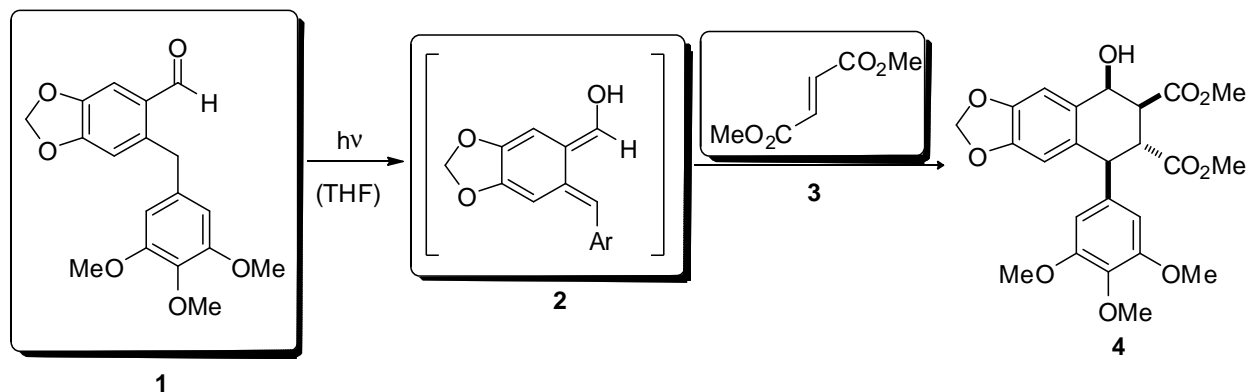
Exercise 3

The following two diastereoisomers are irradiated at 350 nm. Which product do you expect from each isomer? Explain the mechanism and the outcome of the reaction by the most stable conformation of the intermediates! For better clarity use the Newman-projection! *Hint*: the first step is the hydrogen abstraction at the ethyl substituent!



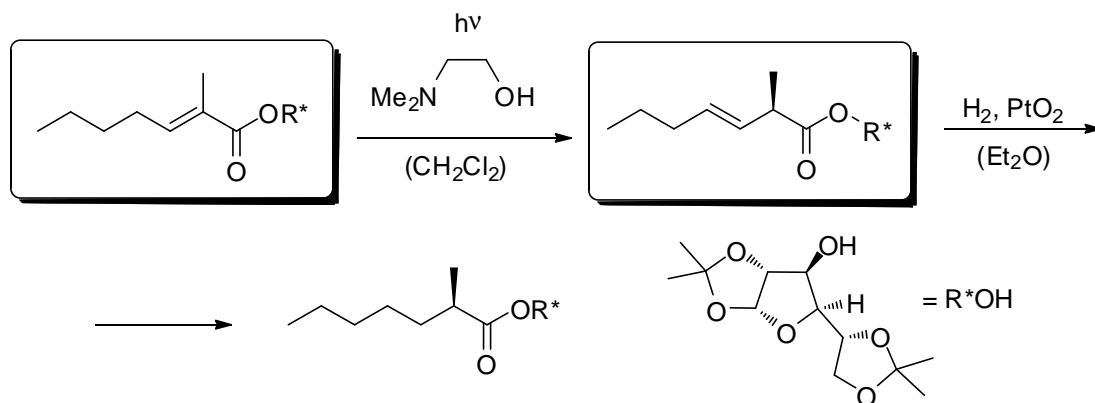
Exercise 4

Suggest the structure **1** of the starting material for the photochemical synthesis of compound **4**! Which most stable intermediate **2** is formed upon irradiation? Which reagent **3** is trapping intermediate **2**? Explain the relative configuration of the product!



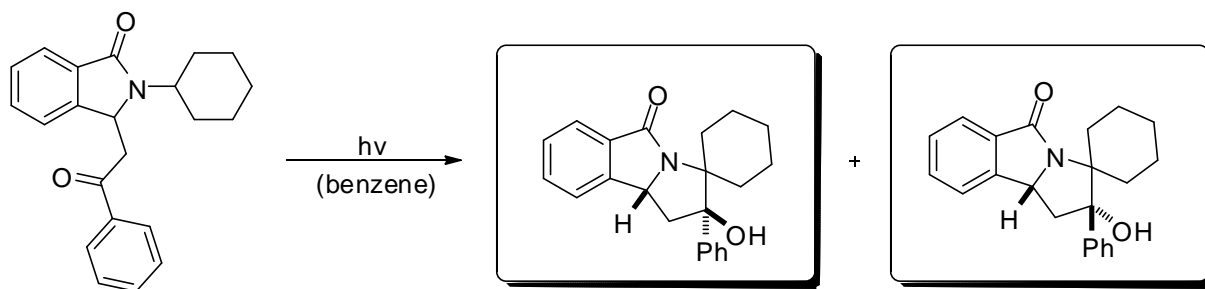
Exercise 5

Complete the following sequence!



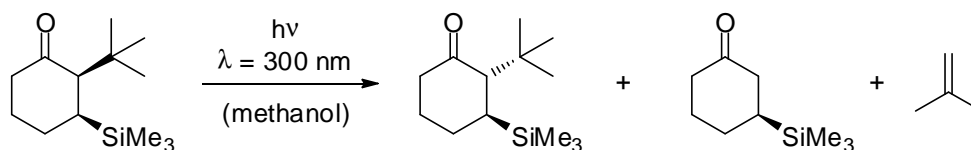
Exercise 6

Which diastereoisomers are formed in the following reaction? Explain the mechanism! What is the name of the reaction? *Hint*: consider the excitation energy of the two chromophoric systems!



Exercise 7

Irradiation of the following starting material leads to the given products. Suggest a mechanism!



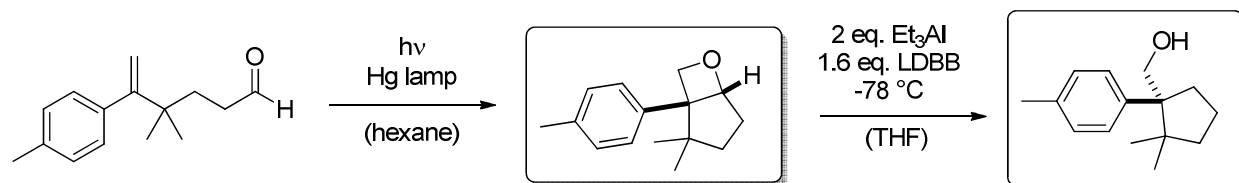
Organic Photochemistry – 2nd exercise 20.12.2011 9.05 a.m.

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Exercise 1

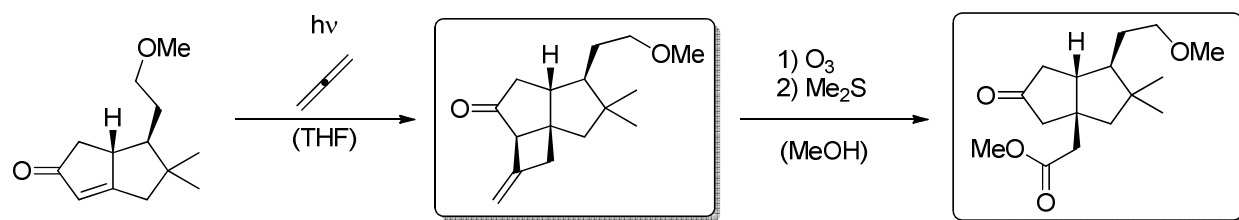
The following sequence was developed as a test system for the synthesis of the naturally occurring sesquiterpene 1,13-herbertenediol. Draw the expected products in the correct relative configuration! *Hint:* LDBB (lithium di-*tert*-butyl-biphenylide) is a single electron donor!



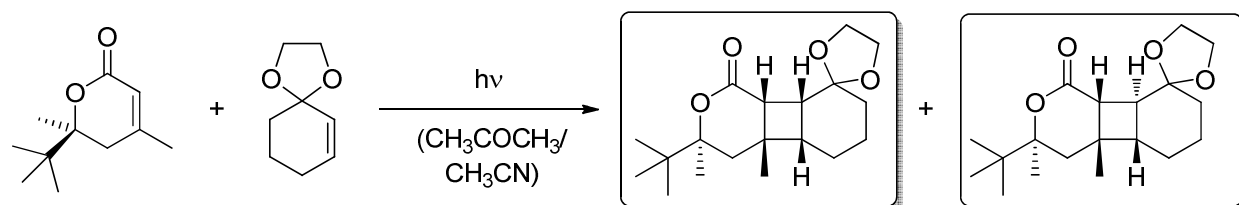
Exercise 2

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

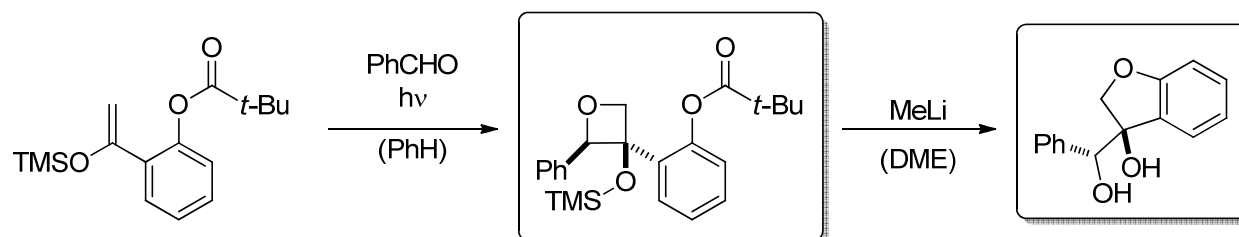
a)



b)



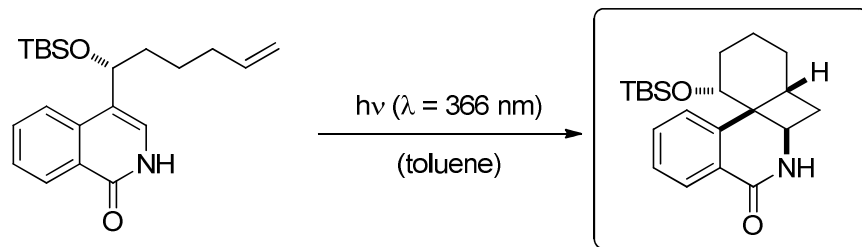
c)



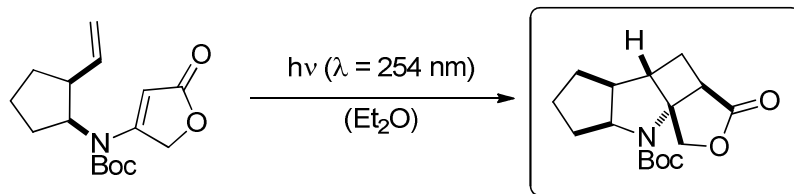
Exercise 3

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

a)

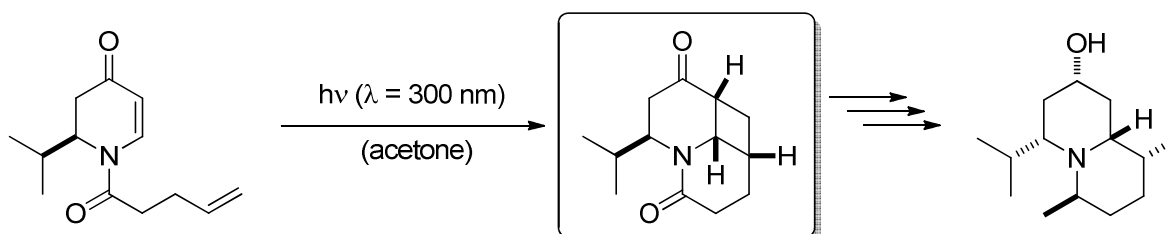


b)

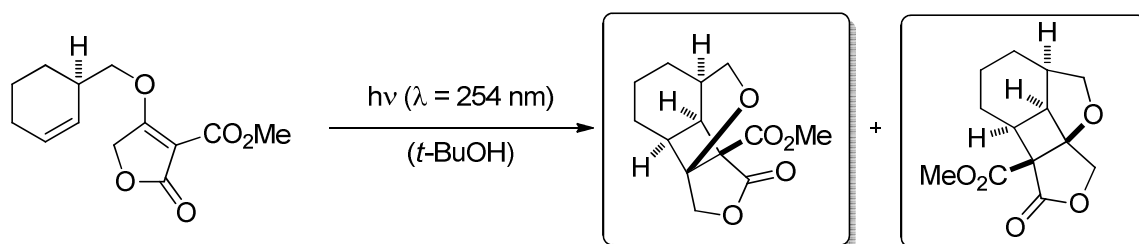


Draw the structure of the protected product! For the same substrate without protecting group a fragmentation product can be isolated as major product. Give the structure of this product and the mechanism of its formation!

c)



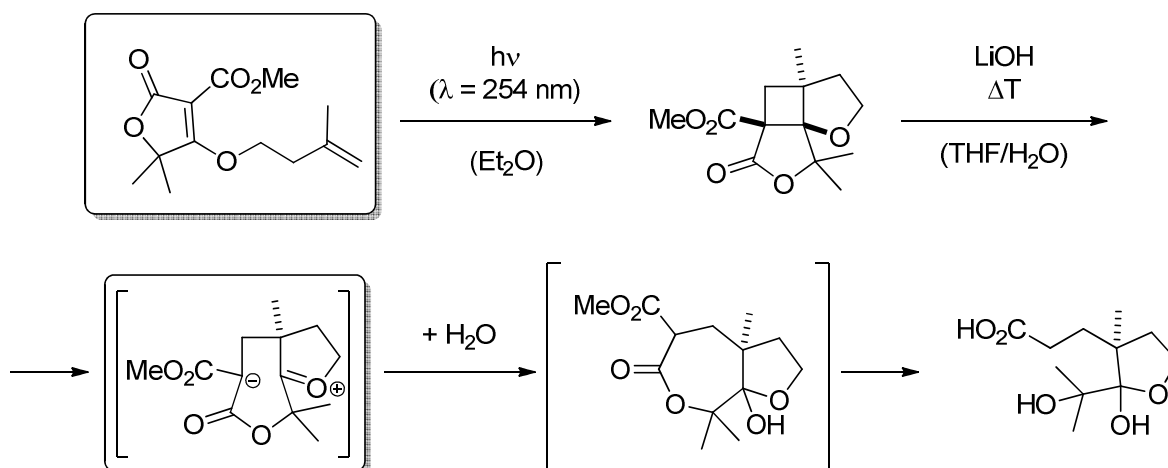
d)



Hint: in the following reaction the straight and crossed products are formed!

Exercise 4

Give the starting material of the photoreaction and suggest a mechanism for the fragmentation reaction of the product!



Organic Photochemistry – 3rd exercise 24.1.2012 11.05 a.m.

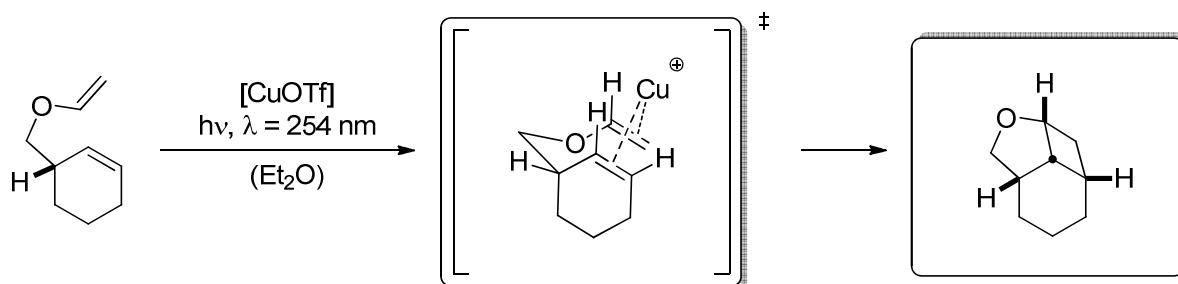
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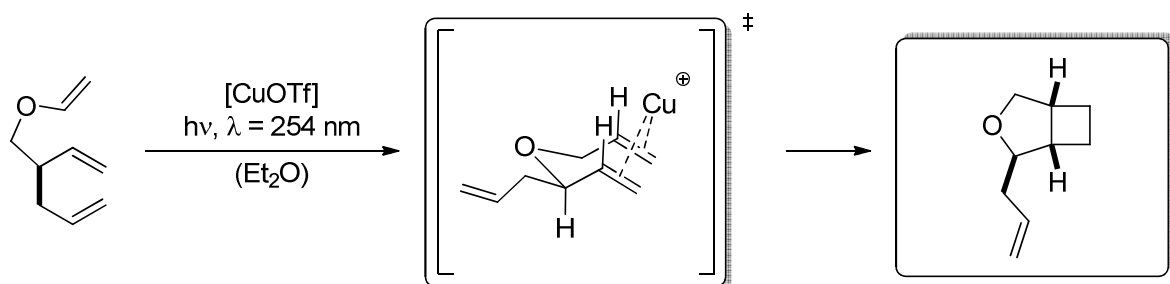
Exercise 1

Draw the products of the following Cu(I)-catalyzed [2+2]-photocycloaddition reactions and suggest the structure of the cyclic transition state to predict the relative configuration of the products! Explain the catalytic effect of Cu(I)-cations in [2+2]-photocycloadditions of olefins!

a)

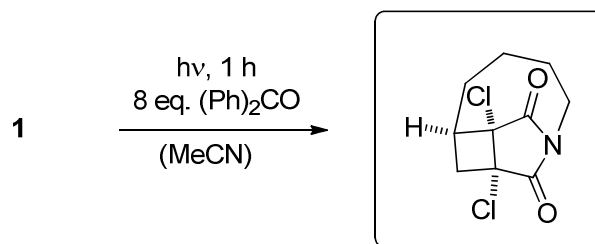
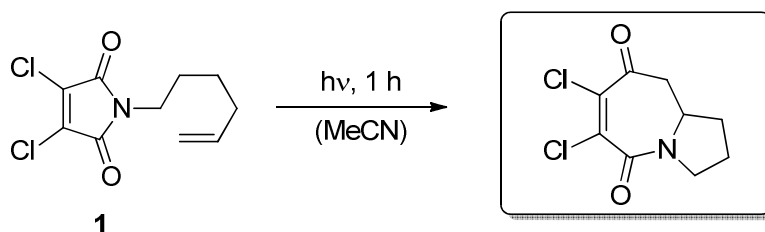


b)



Exercise 2

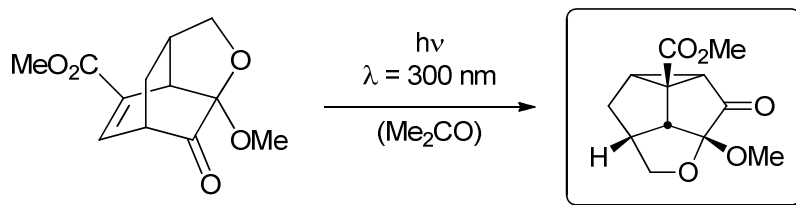
Irradiation of the *N*-substituted maleimide **1** using different reaction conditions leads to two different photoproducts. [2+5]-Photocycloaddition of **1** occurs by direct irradiation of the substrate to afford a bicyclic product. Irradiation in the presence of an excess of benzophenone leads to the corresponding [2+2]-photocycloaddition product. Give the structure of the products in the correct relative configuration! Explain the effect of benzophenone!



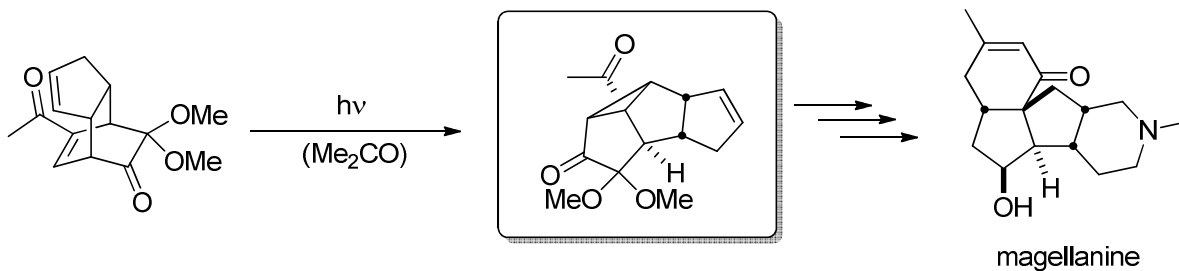
Exercise 3

Complete the following reaction sequences! Provide the correct configuration of the products!

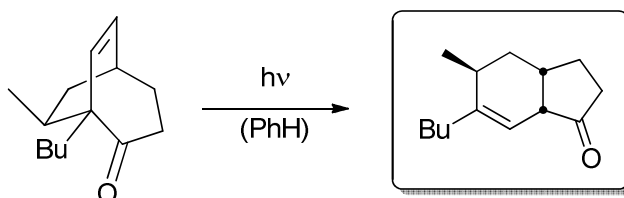
a)



b)

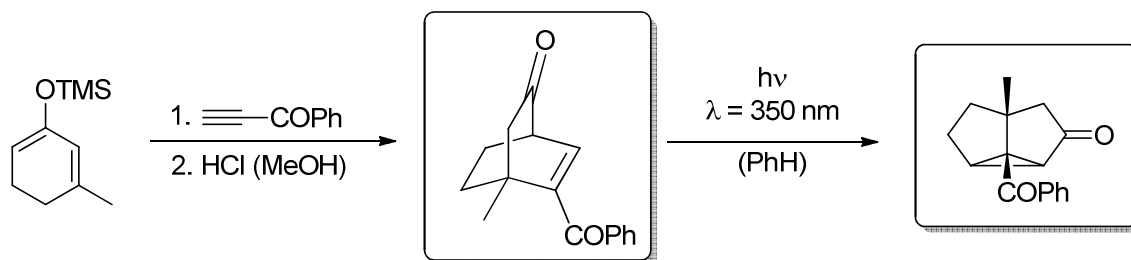


c)

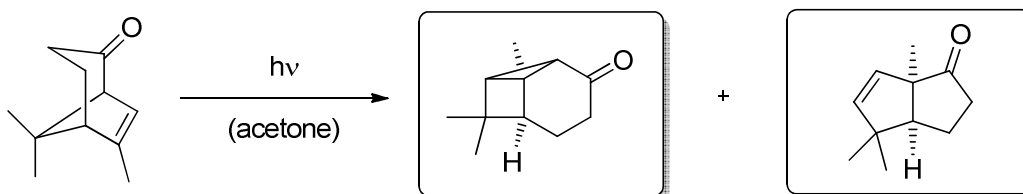


Exercise 4

a) In the following reaction the oxa-di- π -methane-rearrangement occurs without addition of a triplet sensitizer. Draw the isolated product! Which product would be expected if a 1,3-acyl shift was favoured?



b) In this reaction two products were isolated in the presence of acetone: the product of the oxa-di- π -methane-rearrangement and the product of the 1,3-acyl shift. Give the structure of both compounds!



name of the reaction: _____

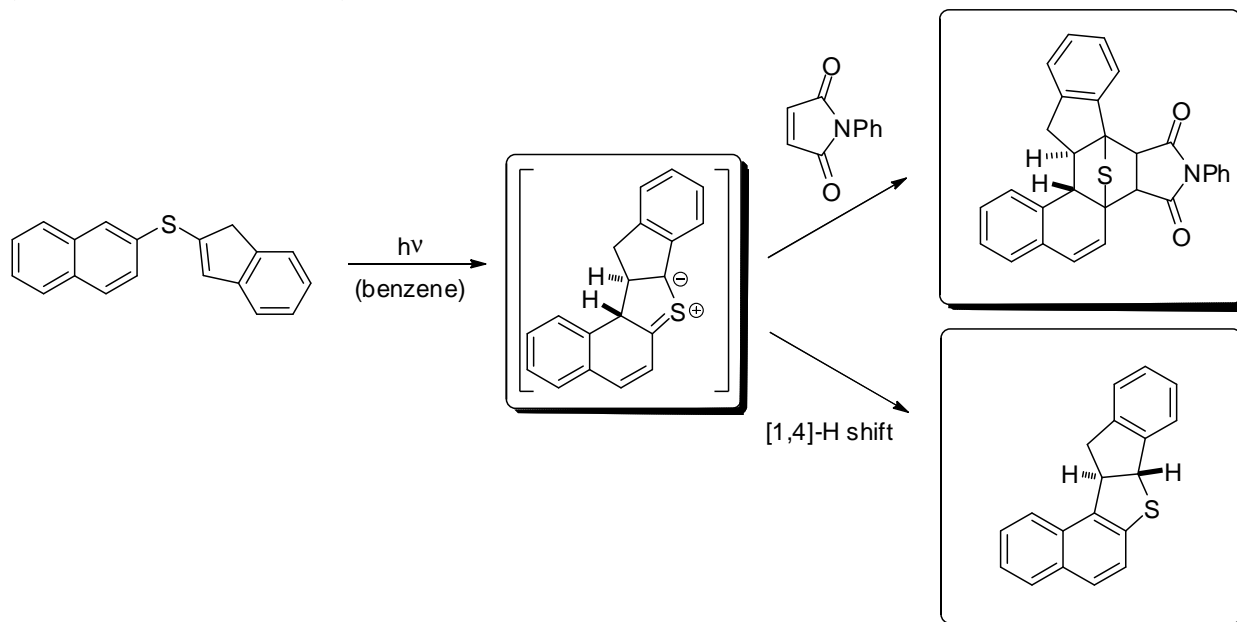
Organic Photochemistry – 4th exercise 9.2.2012 11.05 a.m.

Family name starting with A-L: room 22210

Family name starting with M-Z: room 42306

Exercise 1

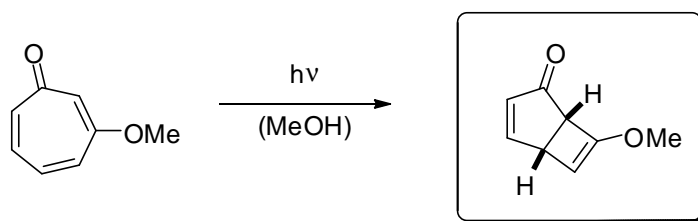
Which products would you expect after irradiation of the given sulfide? Draw the intermediate and products with the correct relative configuration and explain the diastereoselectivity of the first step (Woodward-Hoffmann rules)!



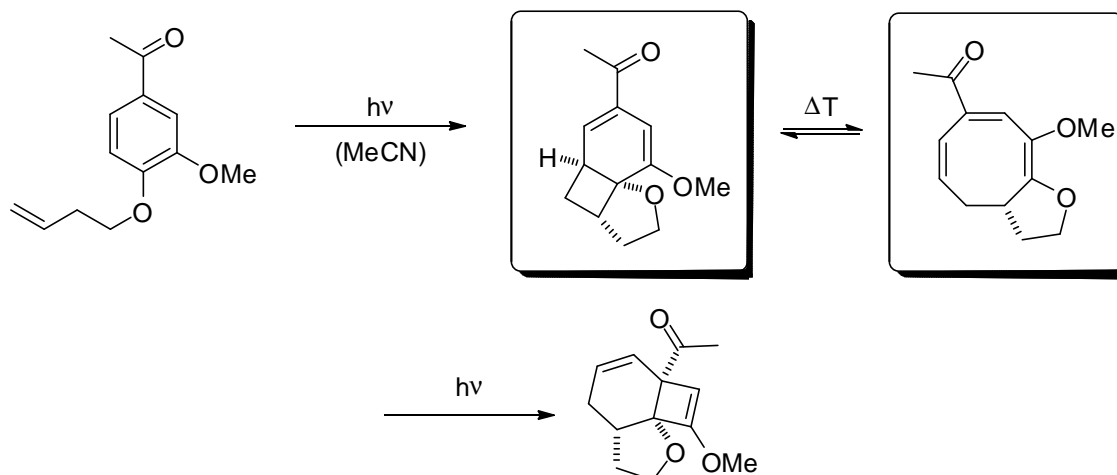
Exercise 2

Complete the following reaction sequences!

a)



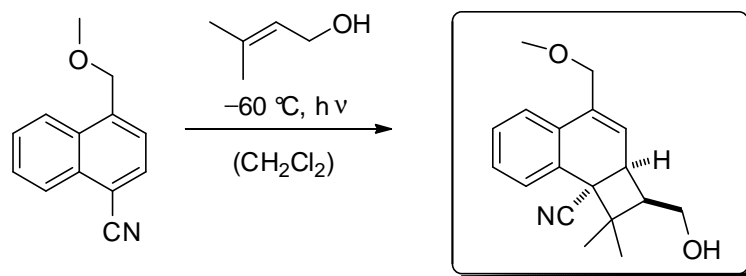
b)



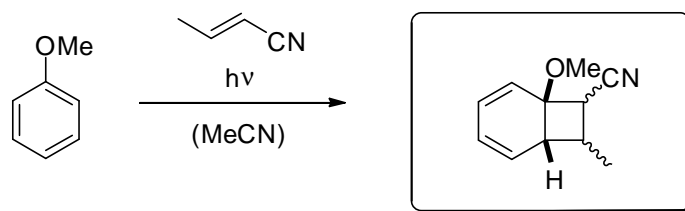
Exercise 3

Draw the products of the following photochemical reactions with the correct configuration!

a)

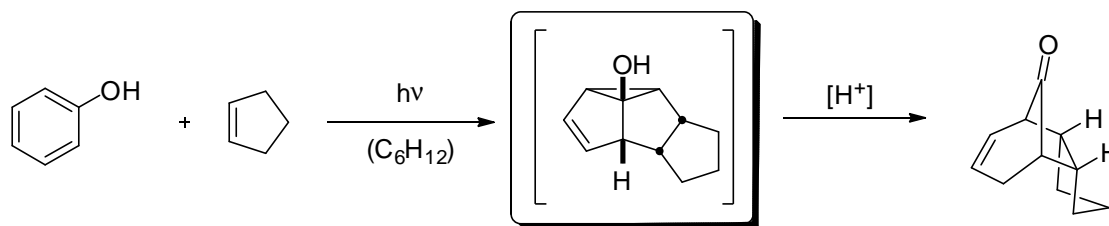


b)

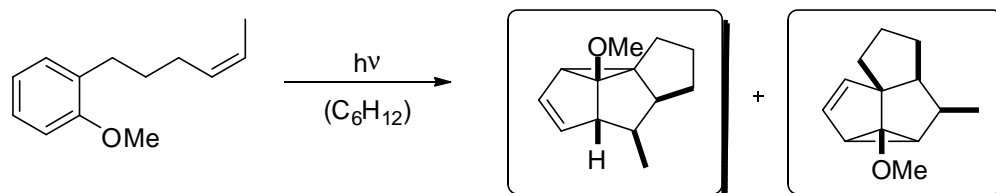


Exercise 4

a) In the following reaction the product of the *endo*-selective photocycloaddition reaction undergoes fragmentation under acidic conditions. Draw the product of the photochemical reaction and explain the mechanism of the fragmentation reaction!



b) Intramolecular photocycloaddition of 1,2-disubstituted olefins to the aromatic system occurs with retention of the configuration. Give the isolated products of the following reaction! Does the reaction occur via an excited singlet or triplet state?



c) Draw the products of the following diastereoselective photocycloaddition reaction!

