

# Organic Photochemistry – 1<sup>st</sup> exercise      05.11.2009    11.05 a.m.

Family name starting with A-L: room 22210

Family name starting with M-Z: room 42306

## Exercise 1

Why are many organic compounds yellow?

big molecules absorb light in the visible range (purple-blue)

bathochrom: shift to red (low-energy)

hypsochrom: shift to blue (energy-rich)

## Exercise 2

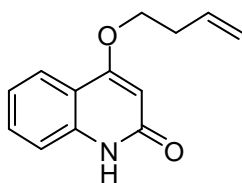
According to the Rule of *El Sayed* only two of the following four transitions are allowed. Tick the right answers.

	forbidden	allowed
${}^1n \pi^* \rightarrow {}^3\pi \pi^*$	<input type="checkbox"/>	<input checked="" type="checkbox"/>
${}^1\pi \pi^* \rightarrow {}^3\pi \pi^*$	<input checked="" type="checkbox"/>	<input type="checkbox"/>
${}^1n \pi^* \rightarrow {}^3n \pi^*$	<input checked="" type="checkbox"/>	<input type="checkbox"/>
${}^1\pi \pi^* \rightarrow {}^3n \pi^*$	<input type="checkbox"/>	<input checked="" type="checkbox"/>

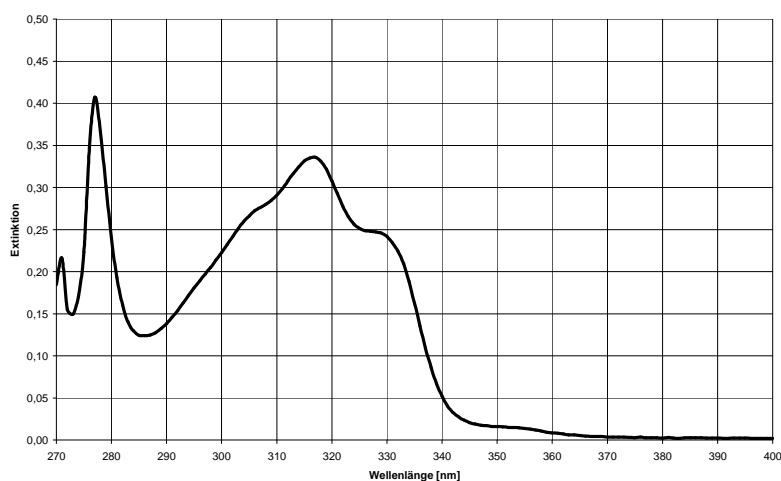
## Exercise 3

The following UV-VIS spectrum of quinolone **1** ( $M = 215.25 \text{ g mol}^{-1}$ ,  $E_T = 276 \text{ kJ mol}^{-1}$ ) was measured using 14.4 mg of the substance dissolved in 100 mL trifluorotoluene. The cuvette had a layer thickness of 1 mm.

- Determine the absorption maxima  $\lambda_{max}$  and calculate the molar absorption coefficient  $\epsilon$  for these transitions. Estimate from the respective values of  $\epsilon$  if these transitions are allowed.
- At which wavelength would you irradiate this compound? Why?



**1**



$$- c = 6.7 \cdot 10^{-4} \frac{\text{mol}}{\text{L}}$$

$$- \lambda_{max} = 277 \text{ nm}, \lambda_{max} = 317 \text{ nm}, \lambda_{max} = 328 \text{ nm}$$

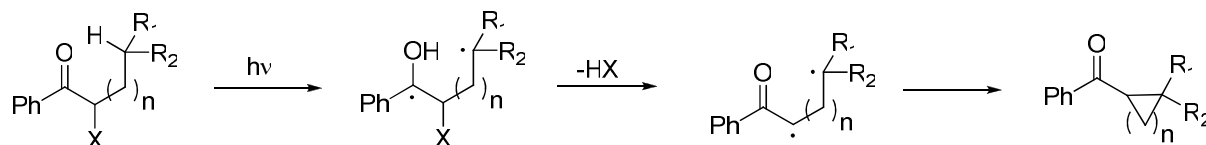
$$- \epsilon = \frac{E}{cx}$$

$$\Rightarrow \epsilon_{277} = \frac{0.407 \cdot 10^5}{6.7} = 6075, \epsilon_{317} = \frac{0.336 \cdot 10^5}{6.7} = 5015, \epsilon_{328} = \frac{0.247 \cdot 10^5}{6.7} = 3687$$

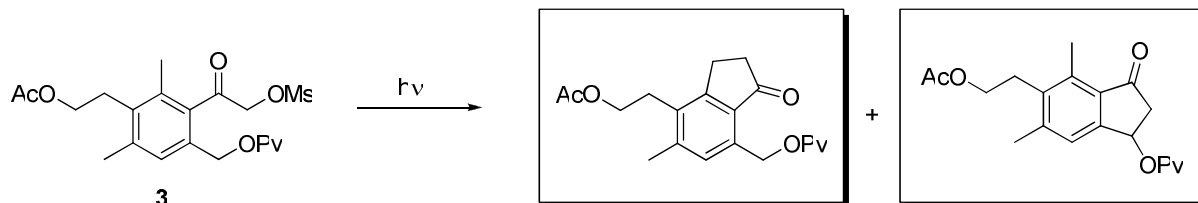
- All transitions are allowed ( $\geq 1000$ ).

### Exercise 4

In a modified version of the Norrish-Yang cyclisation the presence of a leaving group X adjacent to the carbonyl results in rapid elimination of HX from the excited biradical and a shift of one of the radical centres. Radical recombination then gives the cyclised product.

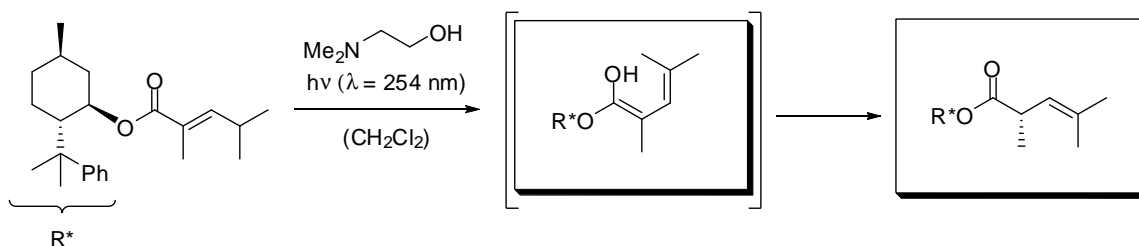


Use this information to draw the two regioisomeric products formed when compound **3** is irradiated.



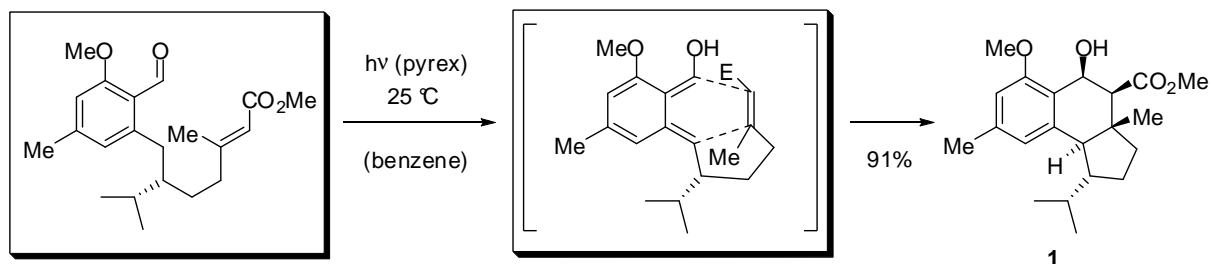
### Exercise 5

Draw the expected intermediate and product.

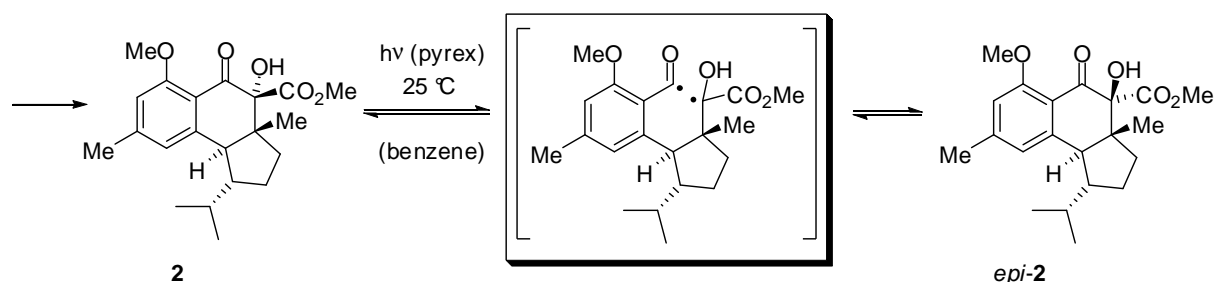


### Exercise 6

Give the structure of the monocyclic starting material for the synthesis of **1** and draw the transient species. Explain the stereochemical outcome of this reaction.

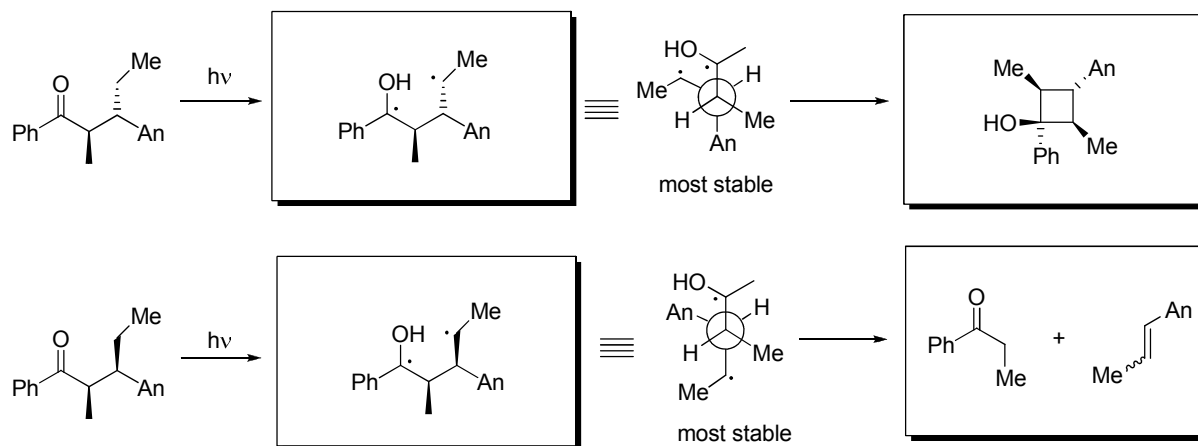


Compound **1** was further elaborated to ketone **2**. Upon irradiation of the latter, an epimerisation occurred to give a 3:1-mixture of *epi-2* and **2**. Draw the intermediate of this reaction. Which type of reaction took place here?



### Exercise 7

These two diastereomers give very different products when irradiated due to different conformational preferences. Draw the excited intermediates and complete the given *Newman*-projections. These were calculated to be the most stable conformations of the respective intermediates. Which products do you expect on the basis of these considerations?



# Organic Photochemistry – 2<sup>nd</sup> exercise 01.12.2009 9.05 a.m.

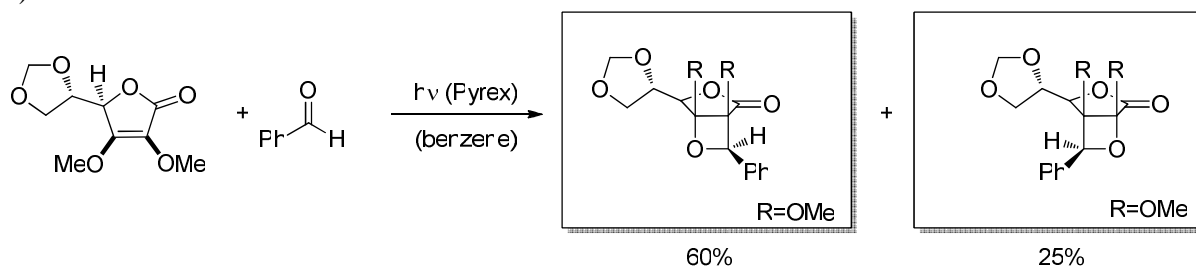
Family name starting with A-L: room 22210

Family name starting with M-Z: room 42306

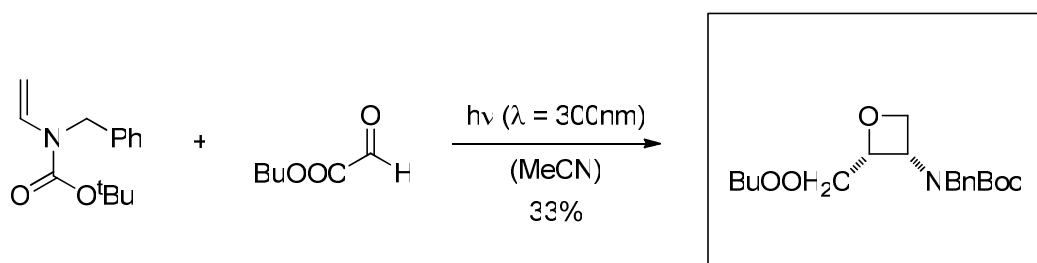
## Exercise 1

Give the reaction products (regioisomers) with the expected relative configuration in the following photocycloaddition reactions.

a)



b)

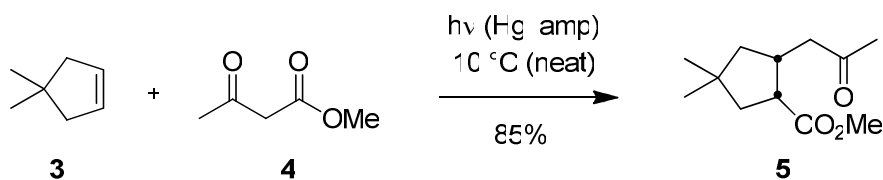


The low yield is due to decomposition of one of the starting materials. Which kind of photochemical side reaction is possible?

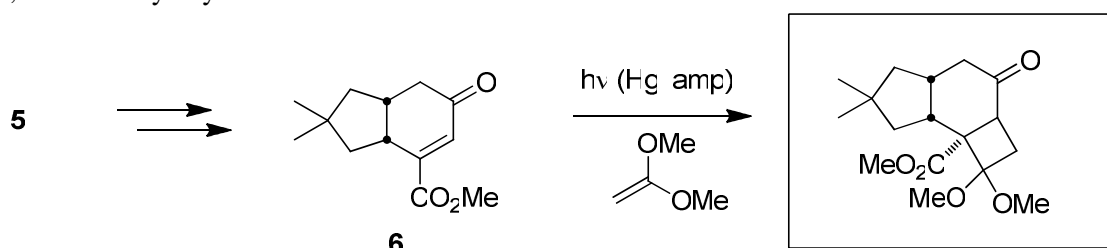
Norrish type I and II

## Exercise 2

The irradiation of **3** and **4** afforded the monocyclic product **5**. Give a mechanistic explanation.

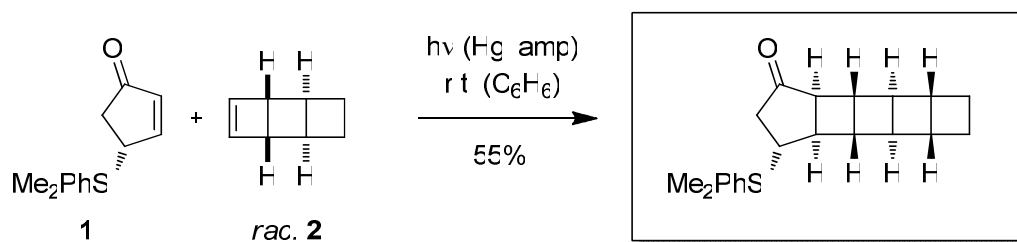


**5** was further elaborated to the enone **6**. Which product was obtained by irradiating **6** in the presence of 1,1-dimethoxyethylene?



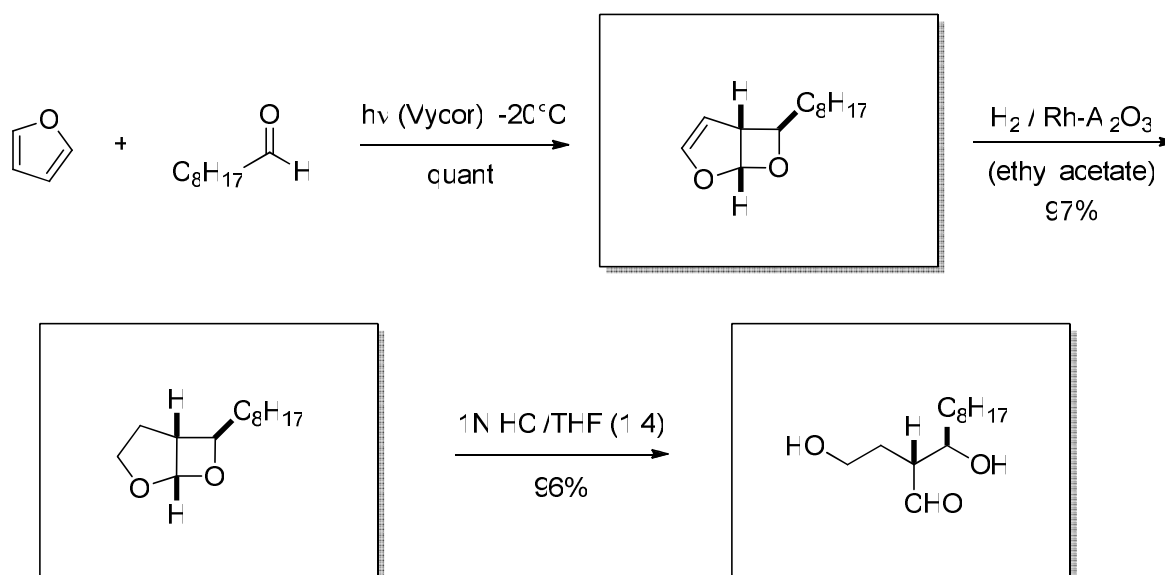
### Exercise 3

Which product was obtained as the main product of the [2+2]-photocycloaddition of the enantiomerically pure enone **1** and the achiral cyclobutene **2**?



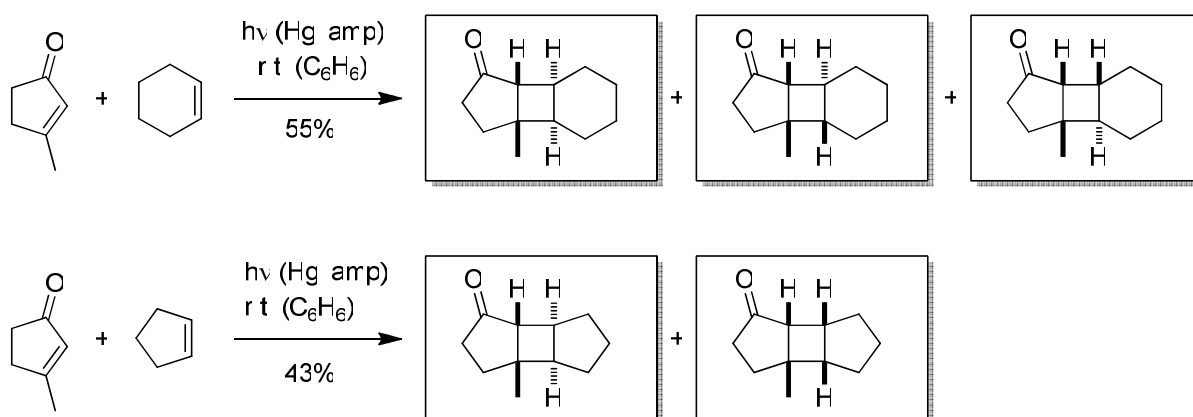
### Exercise 4

Which products do you expect from the following cyclisation/hydrogenation/ring opening sequence?



### Exercise 5

Give the reaction products with the expected relative configuration in the following [2+2]-photocycloaddition reactions! Which are the respective products? Avoid enantiomeric structures!



# Organic Photochemistry – 3<sup>rd</sup> exercise 07.01.2010 11.05 a.m.

Family name starting with A-L: room 22210

Family name starting with M-Z: room 42306

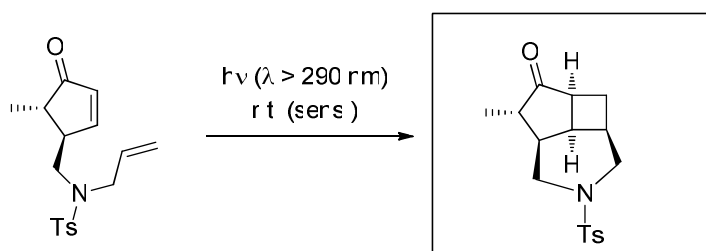
## Exercise 1

Give the products with the correct relative configuration in the following [2+2]-photocycloadditions.

Name at least three sensitizers that could be used in the first reaction.

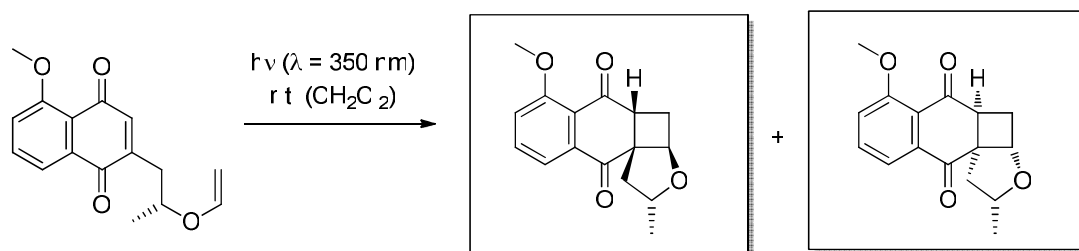
Explain the effect of a sensitizer on the basis of an energy diagram.

a)

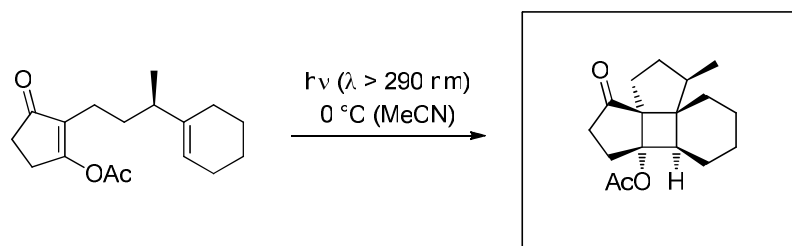


sens = acetone

b)

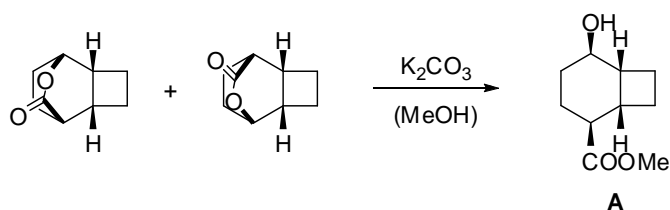
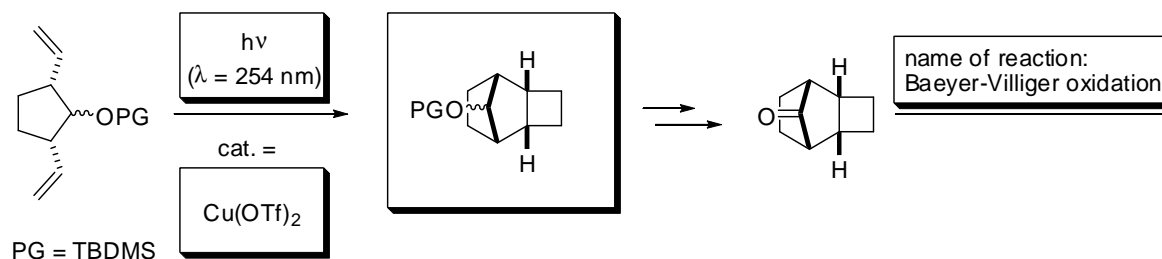


c)



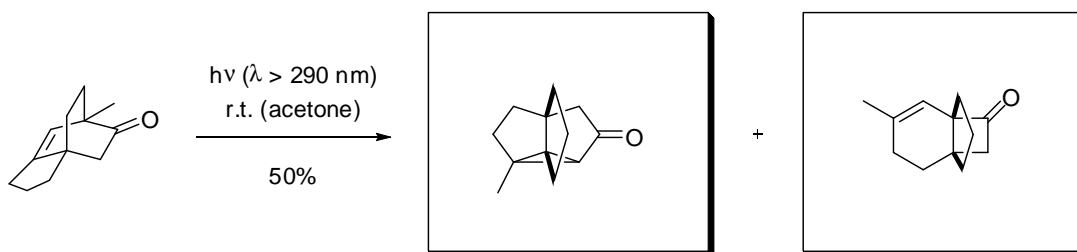
## Exercise 2

A smart way to synthesize bicyclo[4.2.0]octanes **A** is shown here. Complete the following scheme.



### Exercise 3

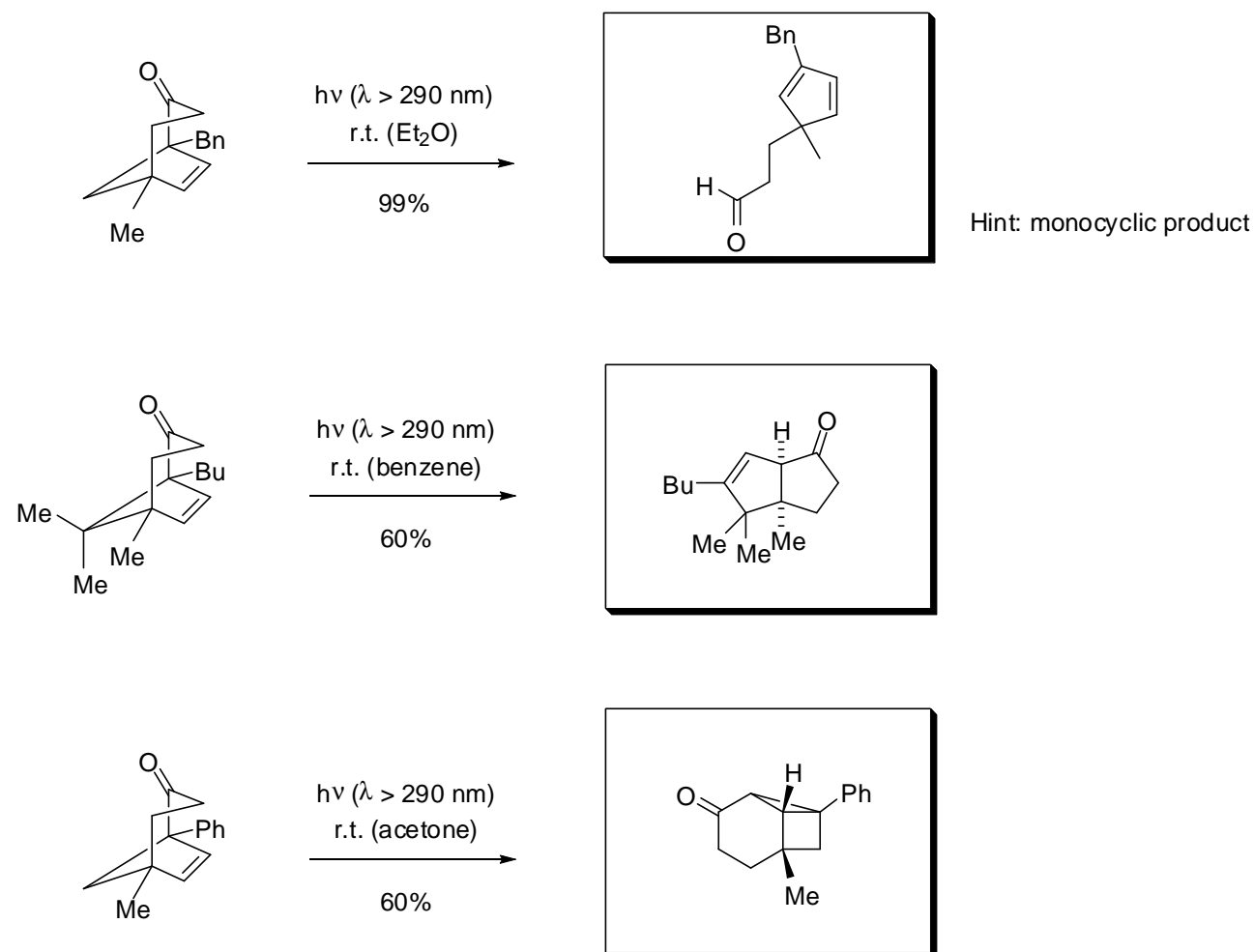
In the following reaction, the oxa-di- $\pi$ -methane-rearranged product and the product resulting from 1,3-acyl-shift were obtained. Draw the structures of these and the corresponding reaction mechanisms. Which product would you expect to be the main product under these reaction conditions? Why?



Resulting from which reaction? \_\_\_\_\_

### Exercise 4

The shown Bicyclo[3.2.1]oct-6-en-2-ones were irradiated with a high-pressure mercury lamp through Pyrex filters in different solvents. Which products do you expect?



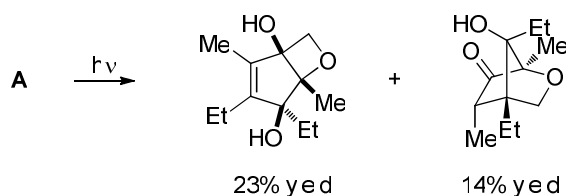
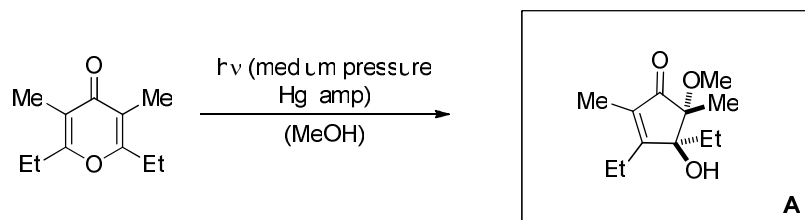
# Organic Photochemistry – 4<sup>th</sup> exercise 04.02.2010 11.05 a.m.

Family name starting with A-L: room 22210

Family name starting with M-Z: room 42306

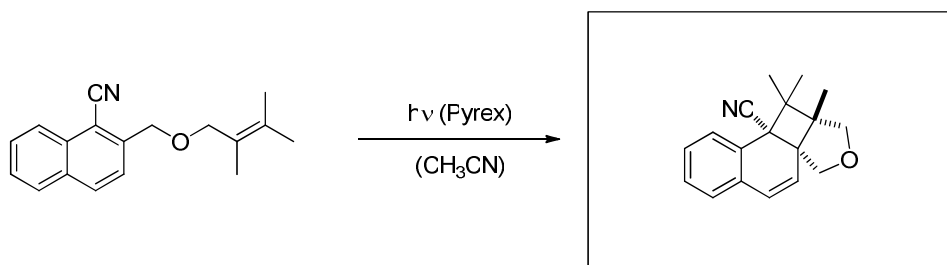
## Exercise 1

In the following pentadienylcation cyclisation, not only the expected product **A** but also two other products were isolated. Explain the formation of the unexpected products (resulting from irradiation of product **A**).



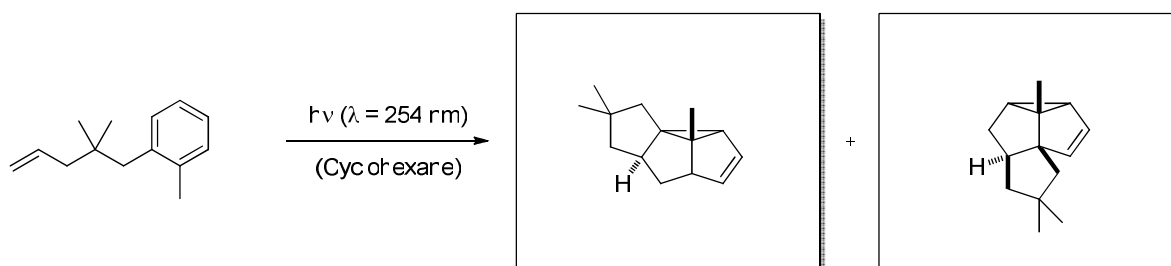
## Exercise 2

Which product would you expect upon irradiation of the depicted naphthalene?



## Exercise 3

Irradiation of the following phenylpentene gave a 2:1 mixture of two triquinanes. Draw the mechanism and give the structures of the products.

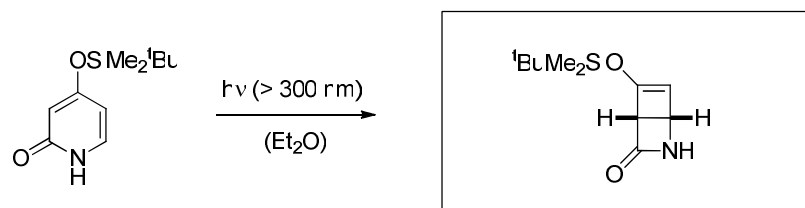




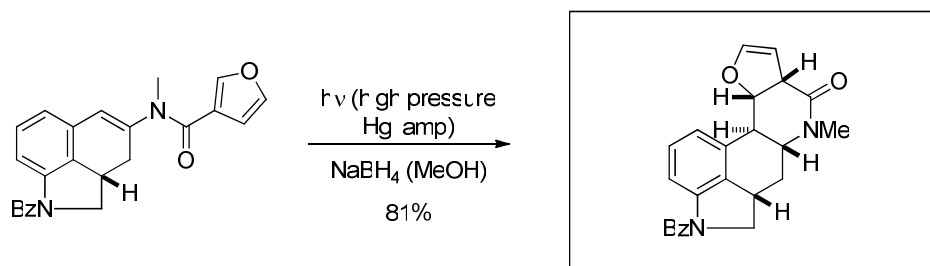
#### Exercise 4

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

a)



b)



#### Exercise 5

According to the Woodward-Hoffmann rules, the Orbital Symmetry must be conserved in pericyclic reactions. Draw the corresponding orbitals for hexatriene and 1,3-cyclohexadiene after conrotatory and disrotatory ring closure, respectively. Assign the disrotatory and conrotatory cyclisation to the thermal and photochemical reaction.

