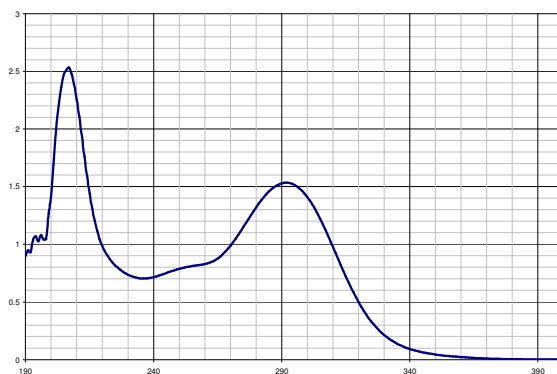


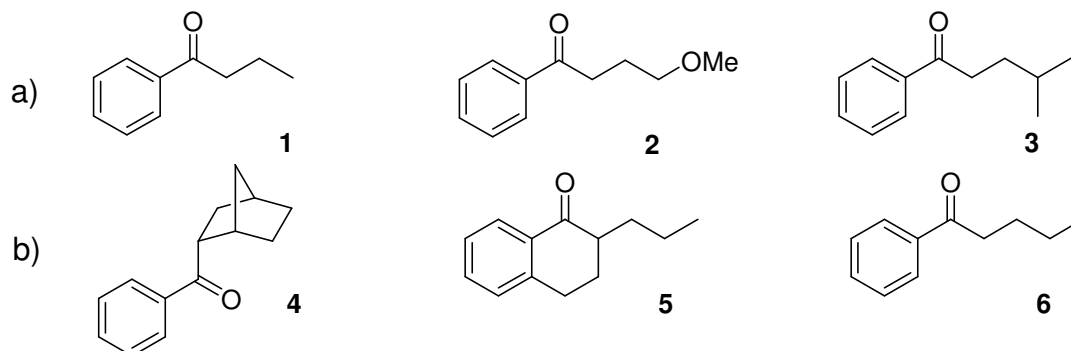
Exercise 1

Fundamentals

1. The following UV-VIS spectrum of a compound ($M = 309.09 \text{ g mol}^{-1}$) was measured in methanol. 170 mg of the substance was dissolved in 100 mL of methanol and the resulting solution was diluted 1:10. The cuvette used had a layer thickness of 10 mm. Calculate the molar absorption coefficient ϵ for both transitions at $\lambda = 207$ and 291 nm. Are the transitions allowed?

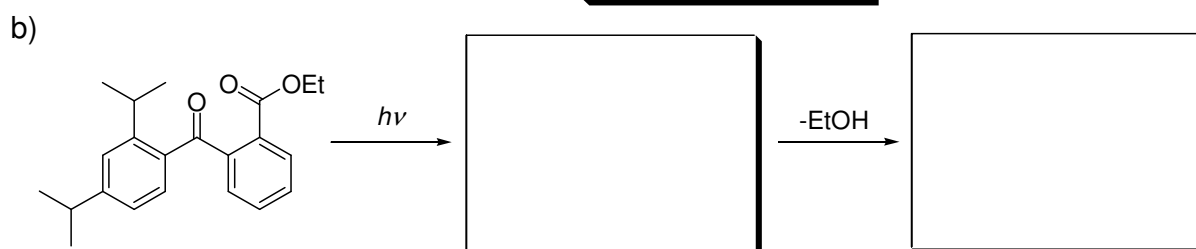
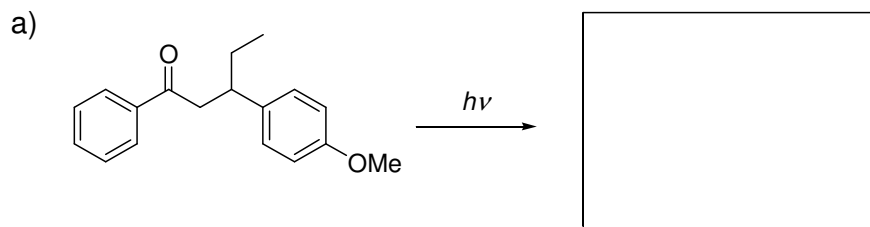


2. Order the compounds **1 – 3** and **4 – 6** according to their reactivity for the γ -H-Abstraction.

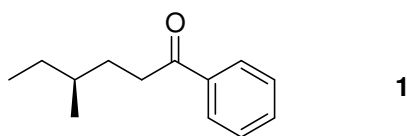


H-Abstraction reactions

3. Complete the following reaction schemes!



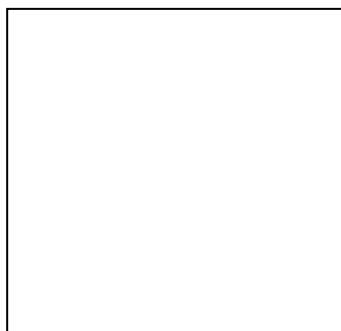
4. The following compound **1** racemises under irradiation with UV-light.



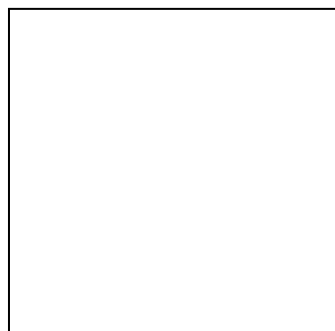
a) Give the mechanism of this racemisation!

b) In addition to the racemic substrate two other products are obtained by two different reaction pathways. Give the expected products! Which would you expect as the favored one?

Pathway I

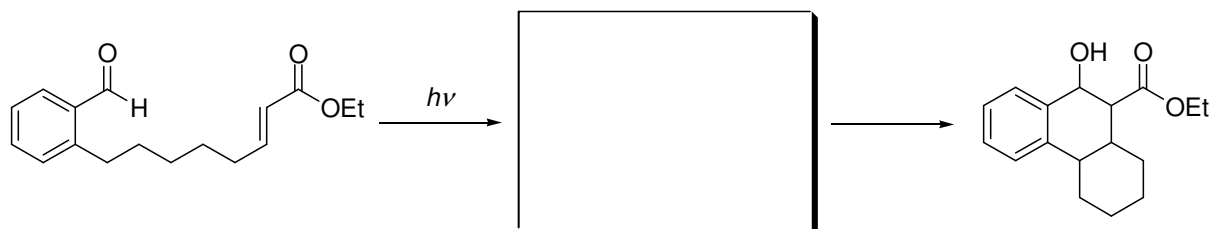


Pathway II (**two** products)

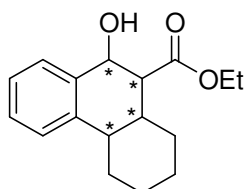


Formation of dienols

5. Complete the following reaction scheme and give the mechanism!



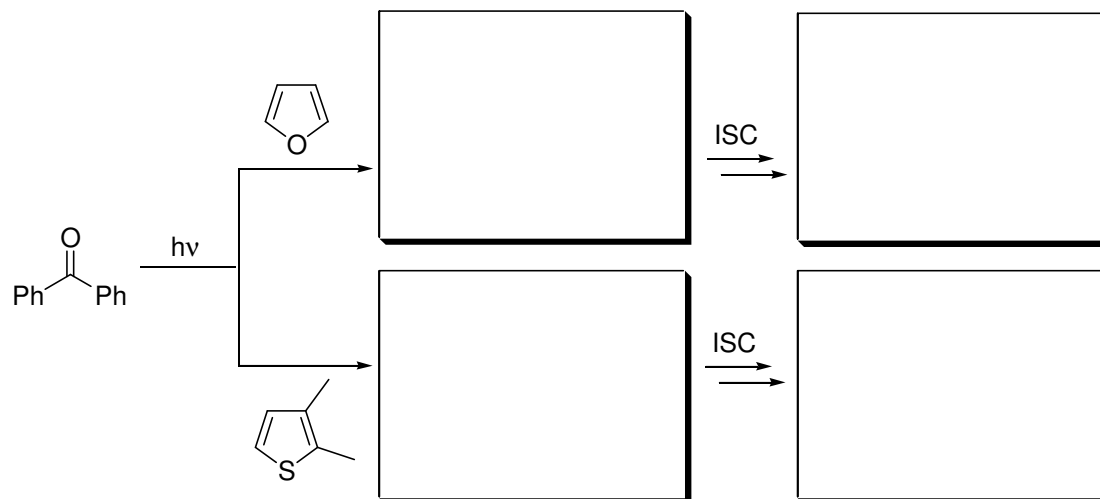
In this reaction 4 stereogenic centers are created, give the right stereochemistry!



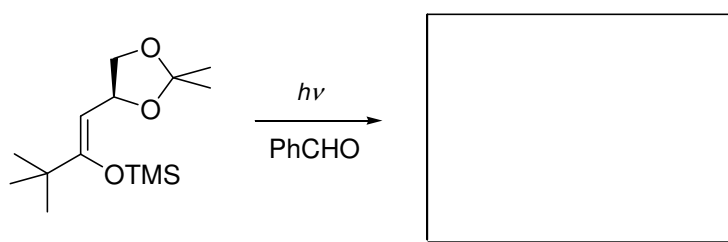
Paternò-Büchi reactions

6. Discuss the mechanism of the following Paternò-Büchi reactions briefly and explain the regio- and stereoselectivity!

a)



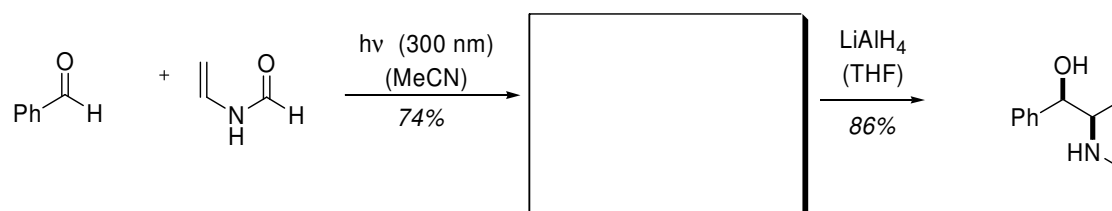
b)



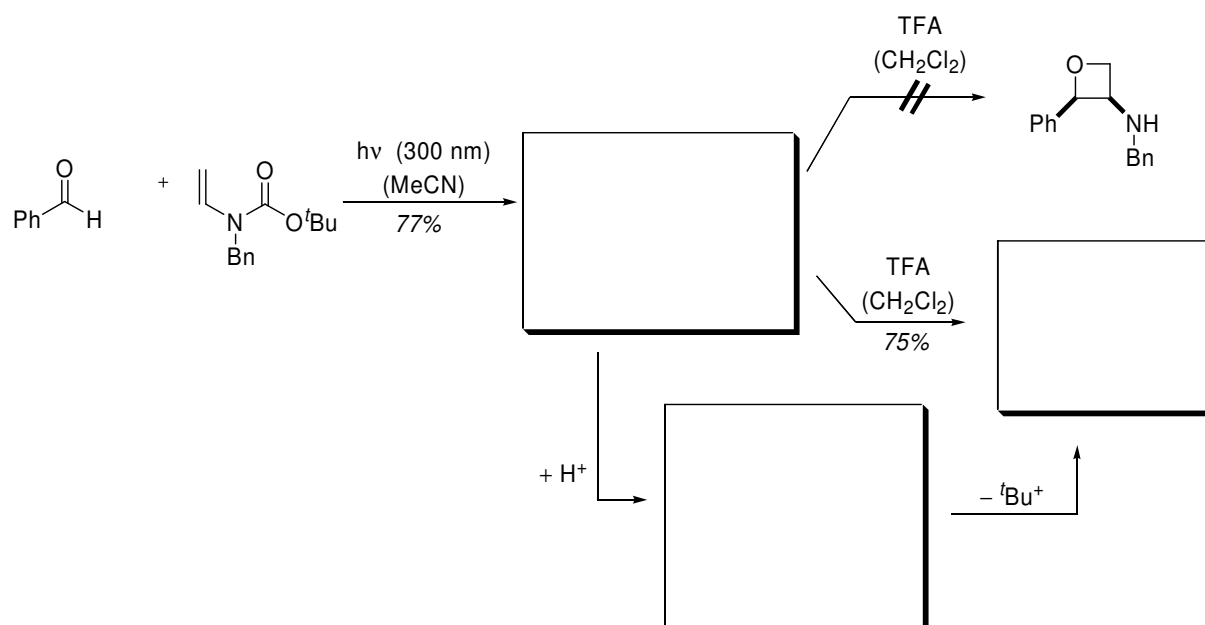
Exercise 2

Paternò-Büchi reaction

1. Complete the following reaction scheme! What is the product of the photochemical reaction. To find the right diastereoisomer note the given product of the oxetane ring opening reaction. Would you expect this oxetane configuration?



2. In a similar reaction, further transformation of the *N*-substituent did not give the expected *N*-deprotected product, but a 5-membered cyclic carbamate. Fill in the correct products and give a possible mechanism of the reaction.

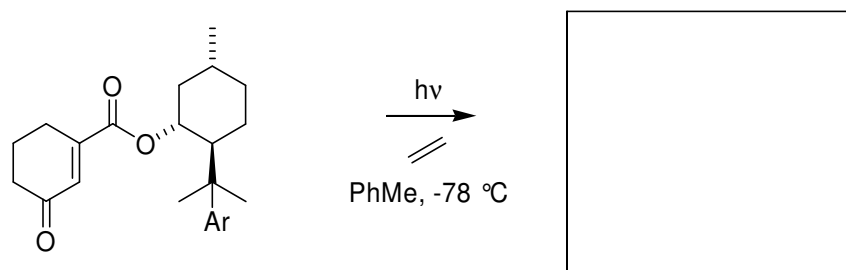


E/Z-isomerization and [2+2]-Photocycloadditions

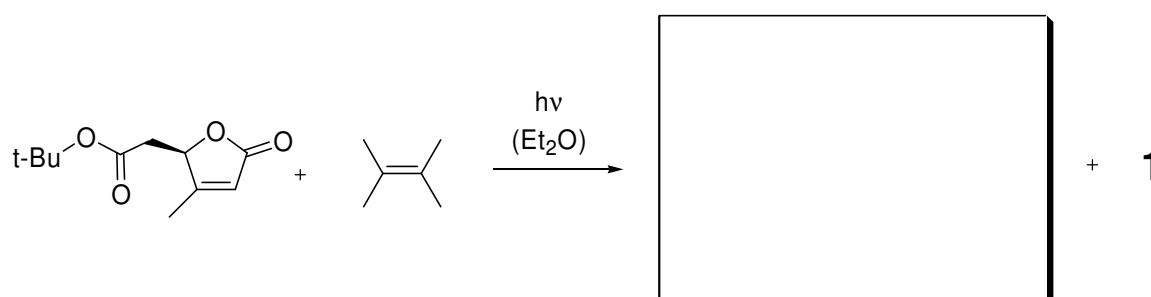
3. Complete the following reaction scheme!



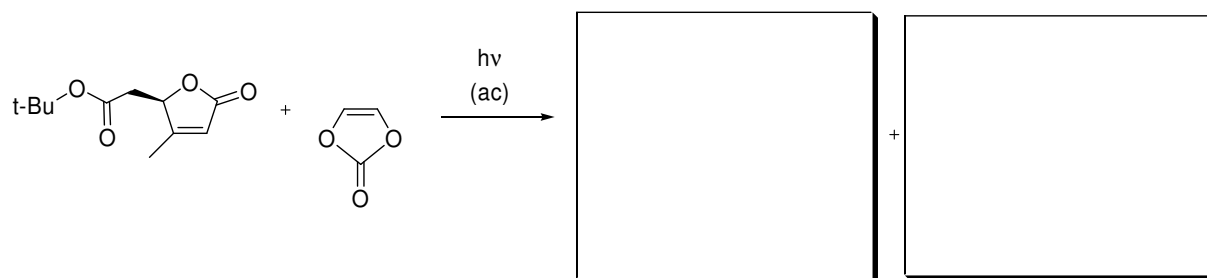
4. Give the major diastereoisomer in the following [2+2]-photocycloaddition!



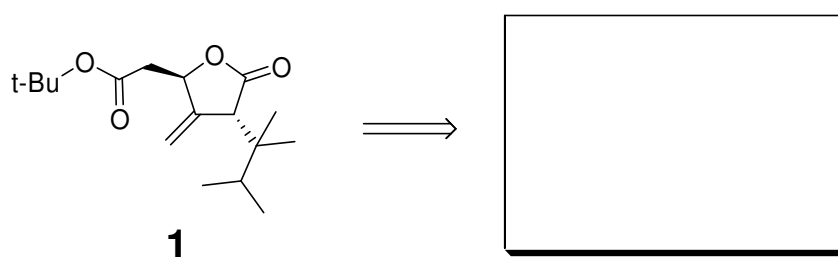
5a. What is the major diastereoisomer in the following [2+2]-photocycloaddition?



5b. Fill in *both* products of the following reaction! What is the major product formed? What other products could theoretically be formed and why are they not observed?



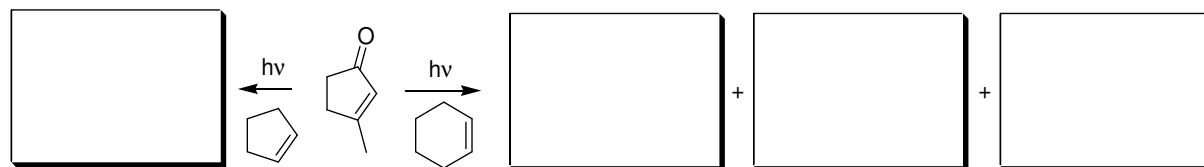
Bonus Question: In reaction **5a** considerable amounts of side product **1** are formed. Give a mechanistic explanation.



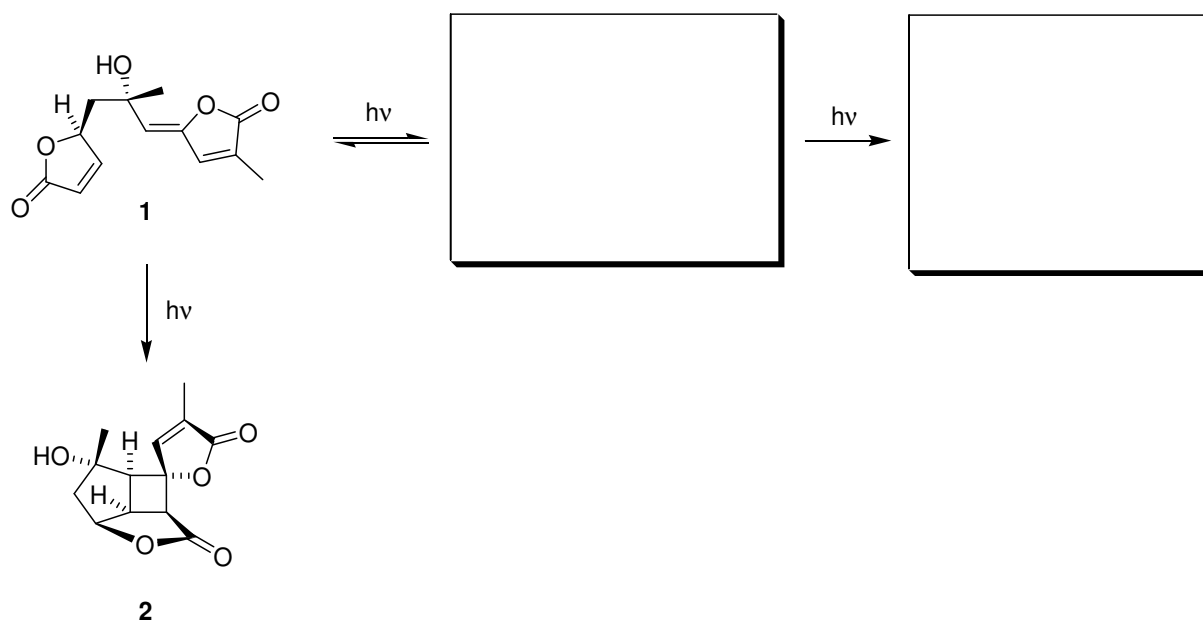
Exercise 3

[2+2]-Photocycloaddition

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

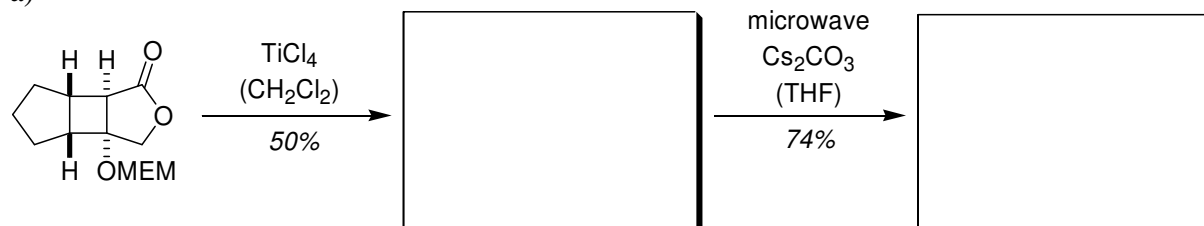


2. Bielschowskysin **2** has been prepared by an intramolecular [2+2]-photocycloaddition of 5-alkylidene-2(5*H*)-furanone **1**. Show the possible side-reaction (depict product in the 1. box) of the [2+2]-photocycloaddition and draw the structure of the diastereomer of **2**, which was also formed!

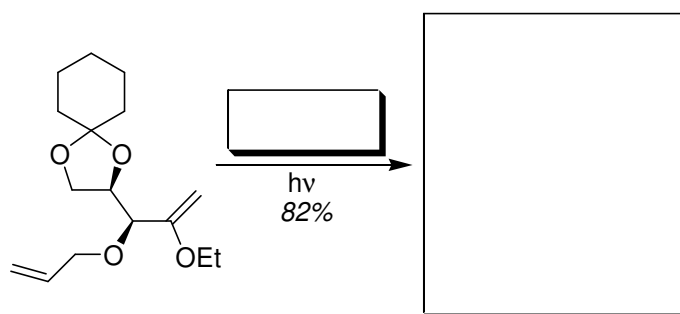


3. Complete the following reactions!

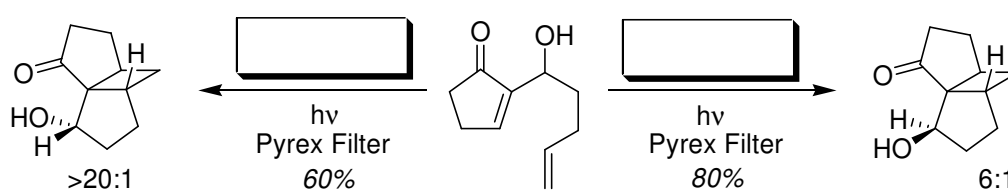
a)



b)



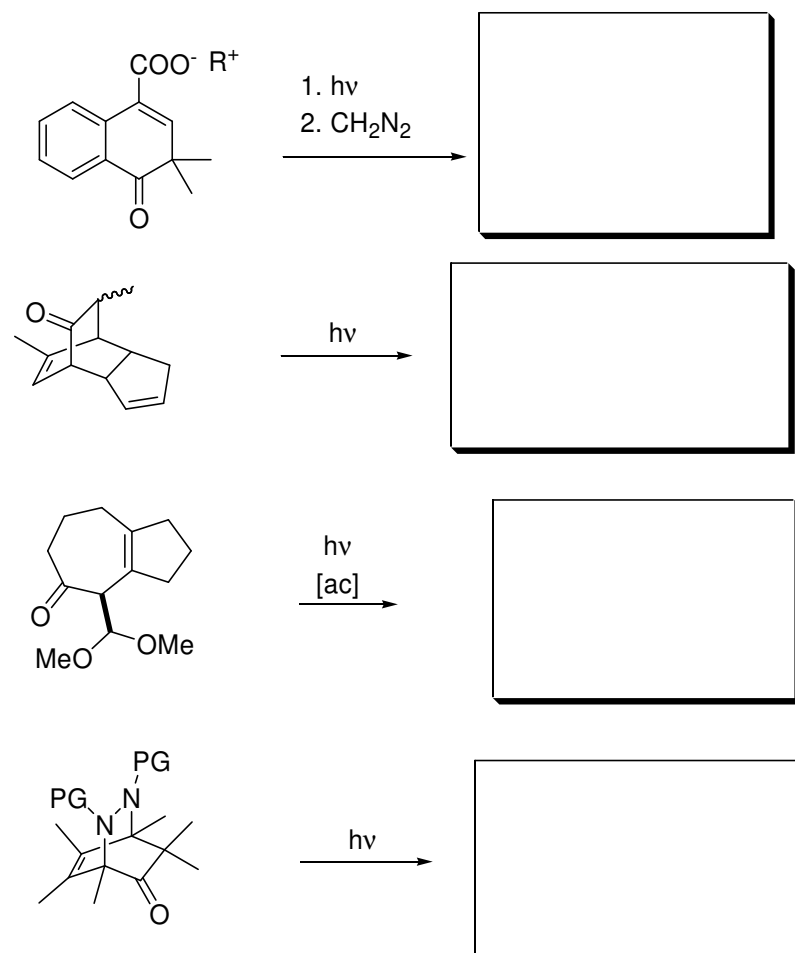
4. In the following reaction sequence both diastereoisomers can be obtained from the same compound by irradiation in different solvents. Give the right solvents and explain the mechanism!



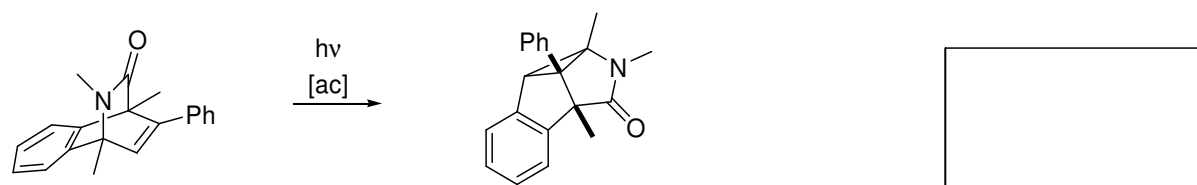
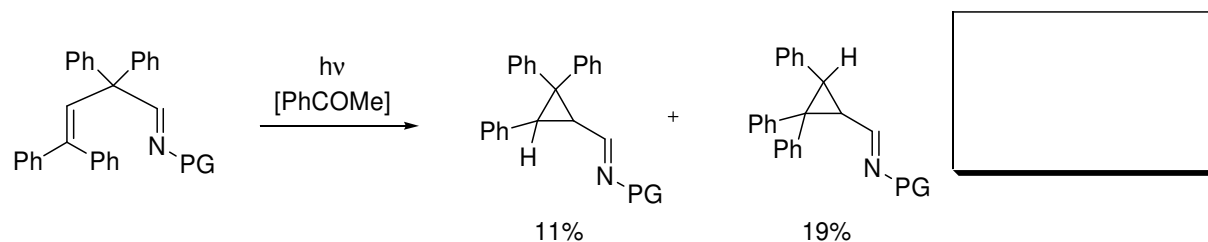
Photochemistry of β,γ -unsaturated carbonyl-compounds

a) Oxa-di- π -methane rearrangement (= 1,2-Acyl-shift)

5. Complete the following reactions!

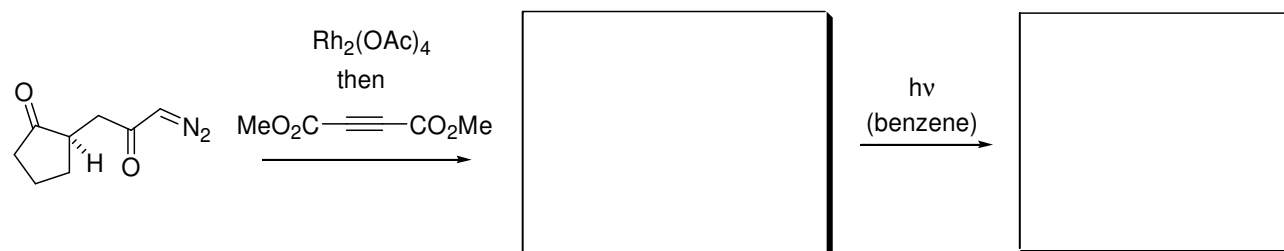
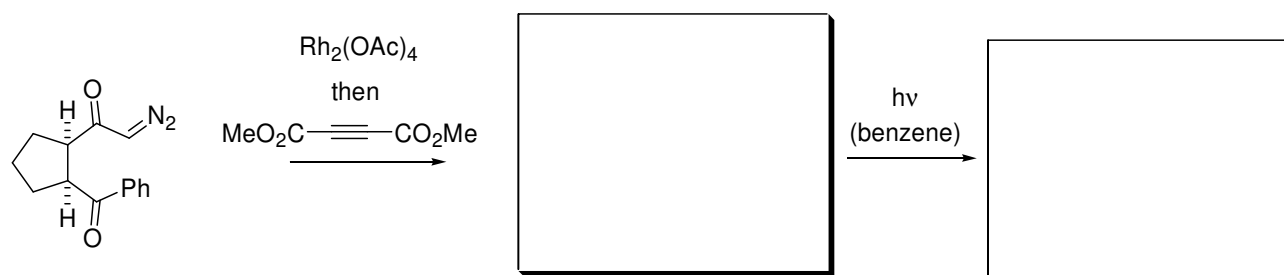


6. The last reaction constitutes a rare example of of an oxa-di- π -methane rearrangement in nitrogen-bearing compounds. How would you call the following, more common rearrangement reactions?



b) 1,3-Acyl-shift

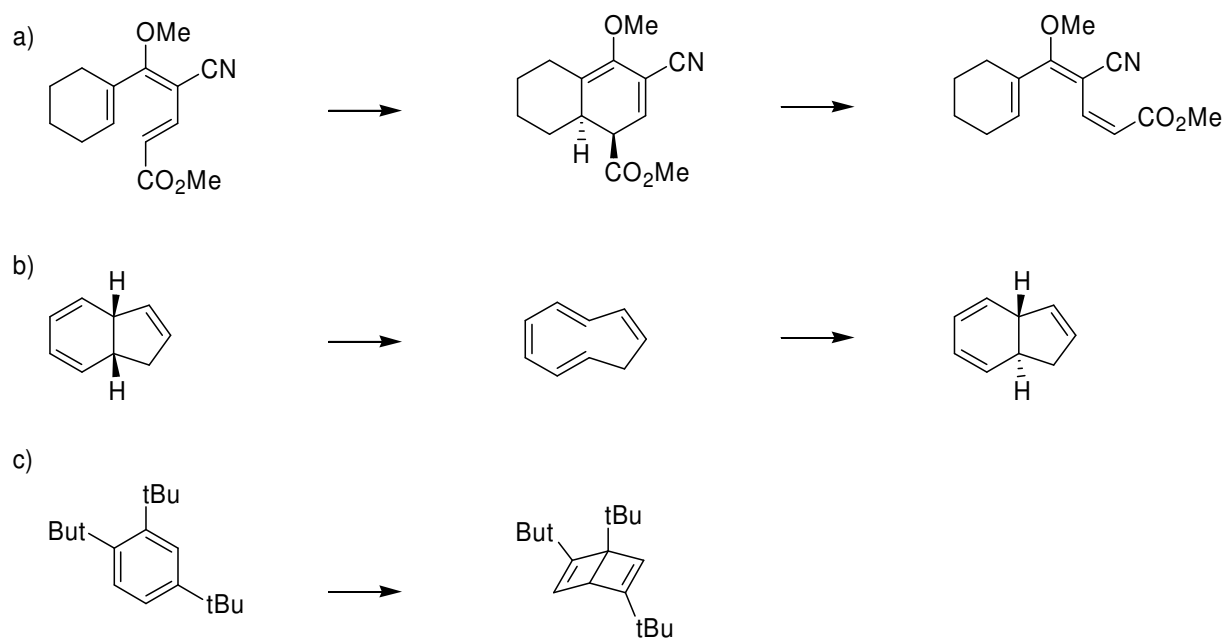
7. Complete the following reaction sequences!



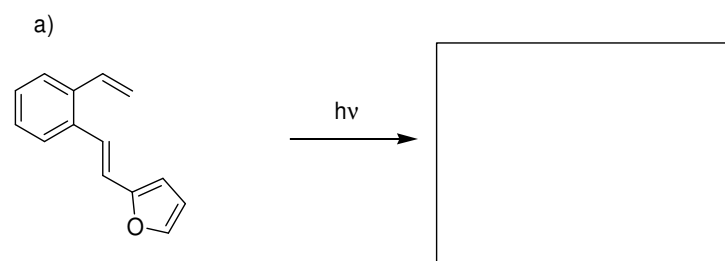
Exercise 4: Pericyclic reactions and Photoreactions of arenes

A. Pericyclic reactions

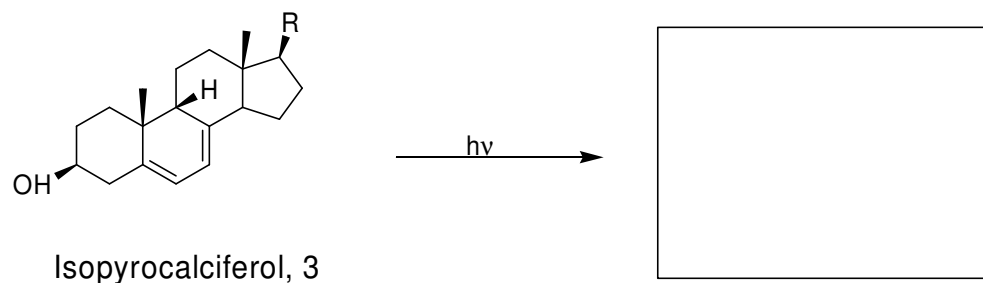
1. Explain the following reactions. Under which conditions do they take place?



2. Give the expected products in the following reactions



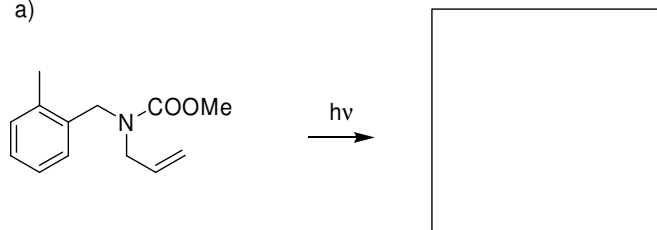
3. In the excursion, some of the photochemistry involved in Vitamin D production was examined. We will now look at this more in detail.
- The undesired tachysterol **1** can also be converted back to Previtamin D **2**, by a second, less high yielding pathway involving first irradiation at 254 nm, then heat treatment. Give the intermediate and explain the mechanisms involved. Will exactly the same isomer of previtamin D be obtained as in the pathway discussed in the excursion?
 - The epimeric compound of dehydrocholesterol, isopyrocalciferol **3**, cannot be photochemically converted to vitamin D. Explain why not. Which compound will be obtained instead? (hint: disrotatory process only).



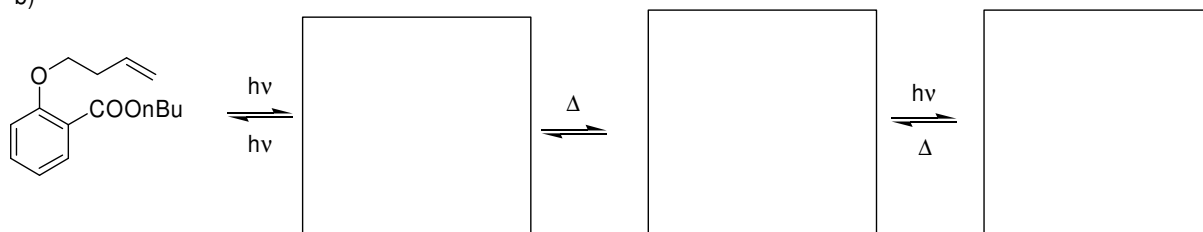
B. ortho- and meta- Photocycloadditions

- Complete the following reaction schemes! Give the correct relative configurations!

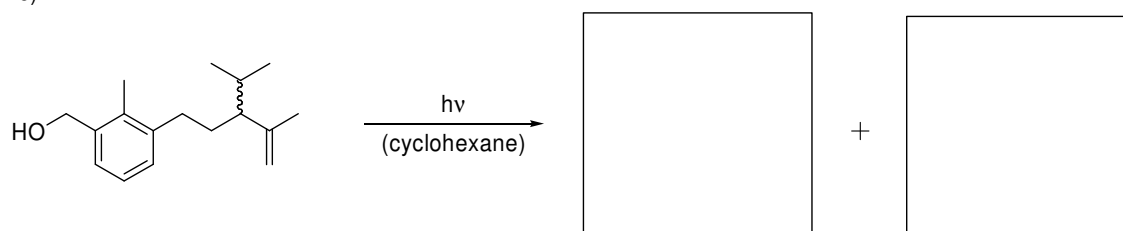
a)



b)



c)



2. The following pericyclic photocycloaddition yields two isomers. Give their structures and the intermediates which lead to the final product!. Which is the major isomer?

