

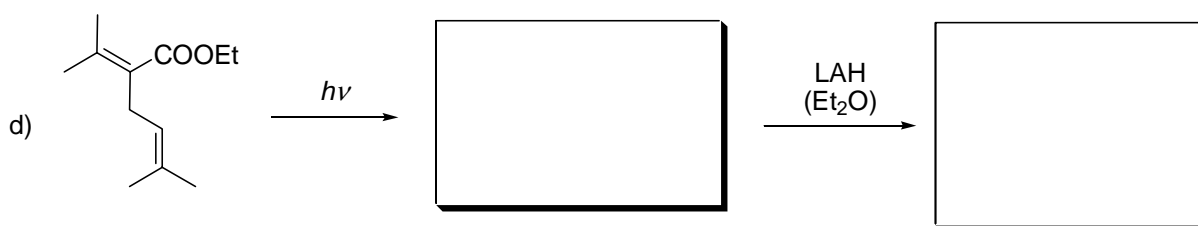
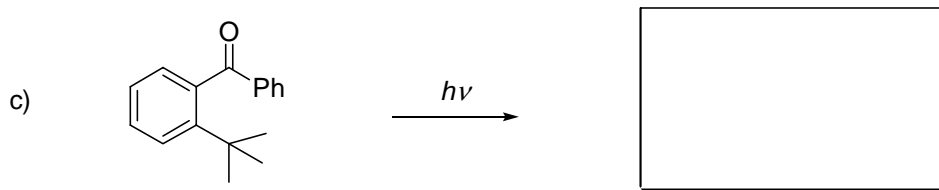
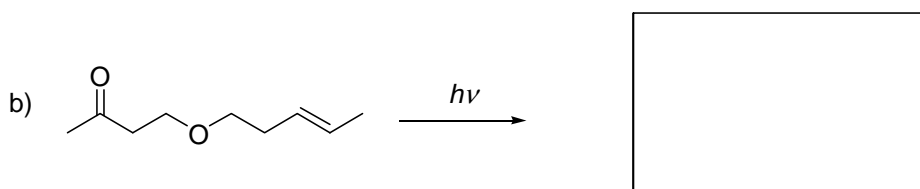
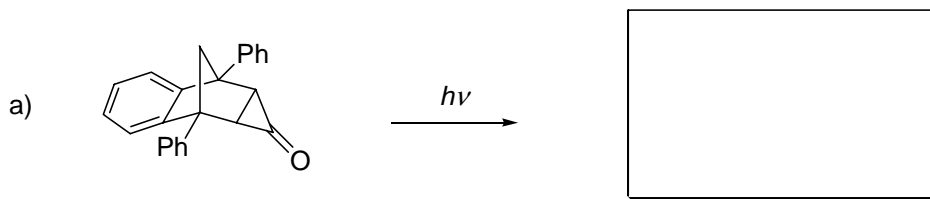
Exercise 1: Fundamentals, H-Abstraction reactions

1. Draw the energy potential curve of the ground state and the first two excited states of a carbonyl group.

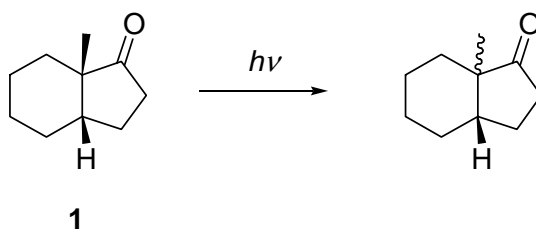
a) Plot all possible transitions and give a timescale for these transitions. What is the main difference between aliphatic and aromatic carbonyl compounds?

b) Explain the positions of the S_1 and T_1 potential curve relative each to the other and to the ground state S_0 .

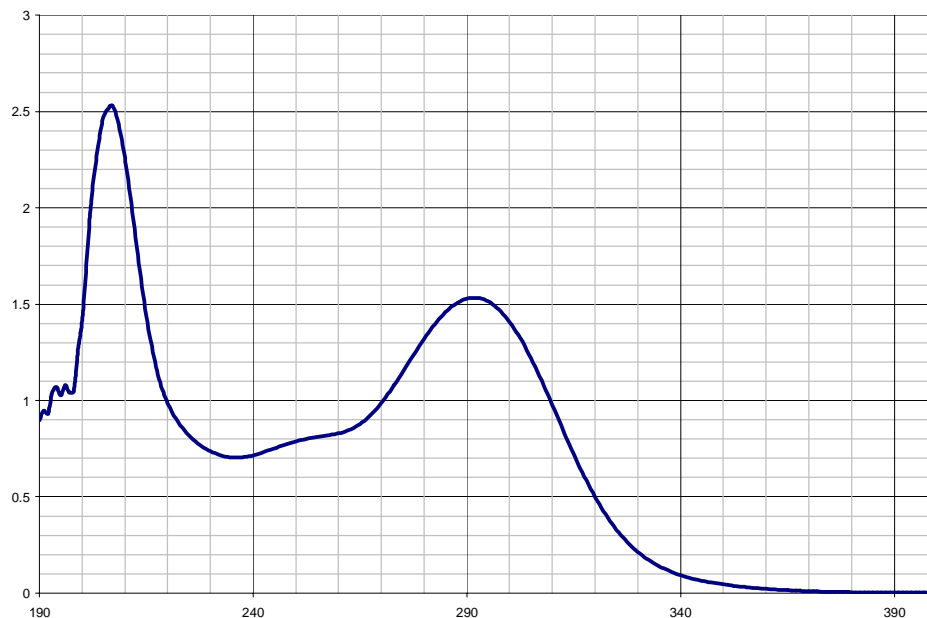
2. Complete the following reaction schemes!



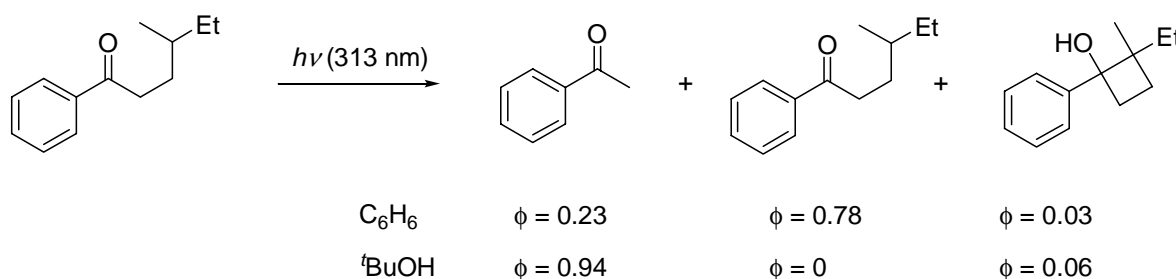
3. Upon irradiation of **1** the stereochemical information of the methyl group next to the carbonyl group is lost (epimerization). Explain this observation with a description of the mechanism.



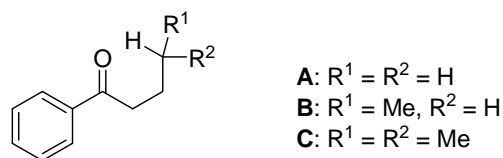
4. The following UV-VIS spectrum of a compound ($M = 309.09 \text{ g mol}^{-1}$) was measured in methanol. 170 mg of the substance was dissolved in 100 mL of methanol and the resulting solution was diluted 1:10. The cuvette used had a layer thickness of 10 mm. Calculate the molar absorption coefficient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



5. The following reaction has been performed in Benzene and in *tert*-Butanol. Explain the influence of the solvent with the detailed reaction mechanism.



6. Order the compounds **A** – **C** according to their reactivity for the γH -Abstraction.



7. We take a closer look at a carbonyl group.

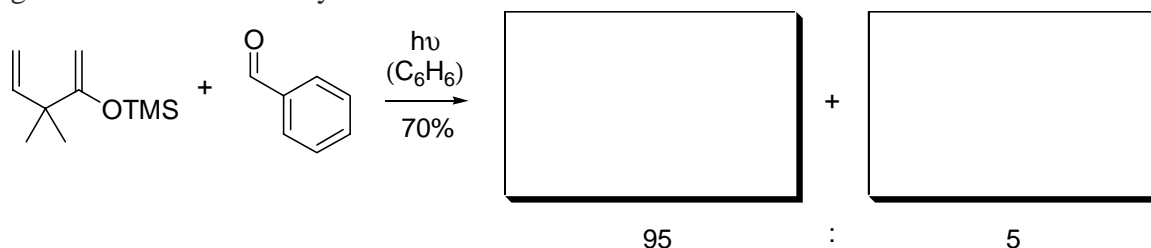
a) Draw the orbitals involved in a $\pi^* \leftarrow n$ transition. Which physical property of the group / molecule is influenced by this transition?

b) A good approximation for the nonbonding orbital is $\text{O}2p_y$ and for the anti-bonding π^* an approximate wavefunction would be $\psi_{\pi^*} = c' \phi(\text{C}2p_x) + c \phi(\text{O}2p_x)$.

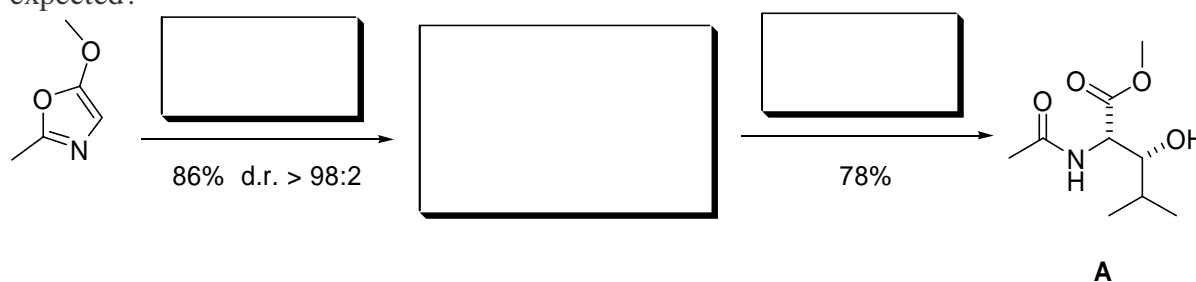
Construct the matrix element $\langle \pi^* | \mu | n \rangle$ for the transition dipole moment with these wavefunctions.

Exercise 2: Paternò-Büchi-reaction, E/Z-isomerization

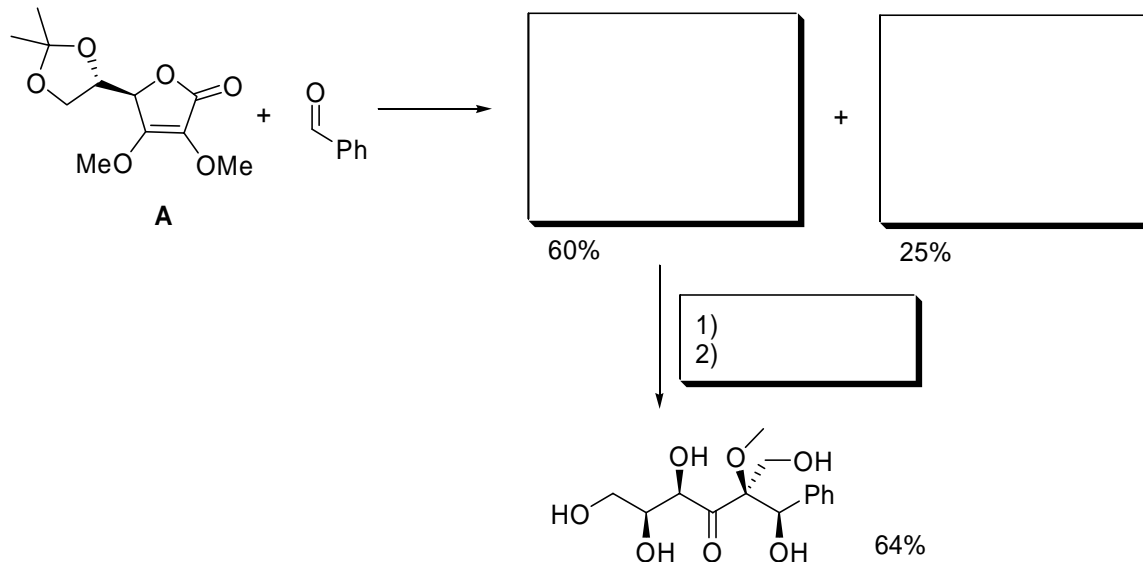
1. Discuss the mechanism of the following Paternò-Büchi-reaction briefly and explain the regio- and stereoselectivity!



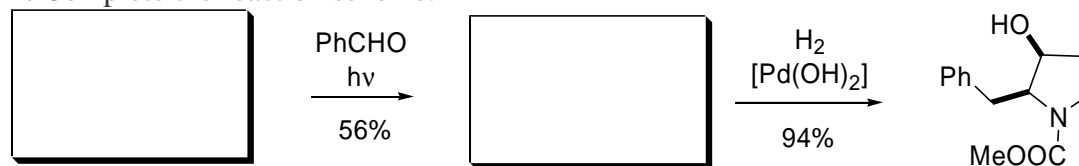
2. The relative stereochemistry of the β -hydroxy aminoacid ester **A** is established in a Paternò-Büchi-reaction. Complete the reaction sequence. Is the observed regioselectivity expected?



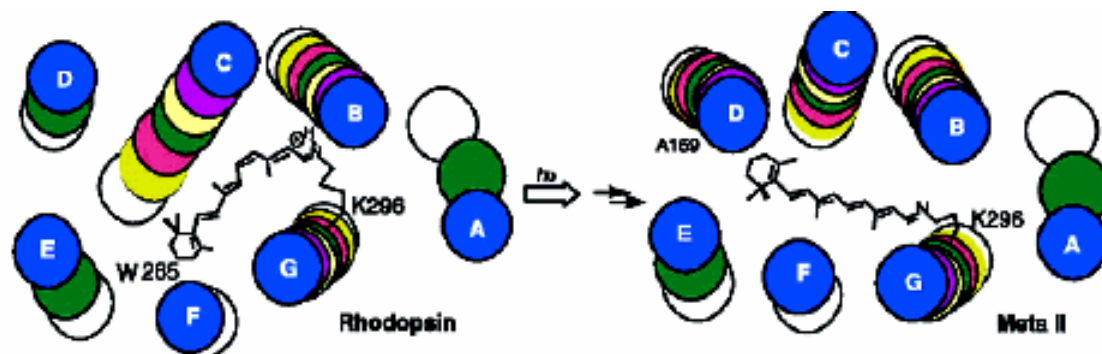
3. The vitamin C derivative **A** undergoes Paternò-Büchi-reactions in moderate regioselectivity. Formulate the products and give reagents for the subsequent ring opening reaction.



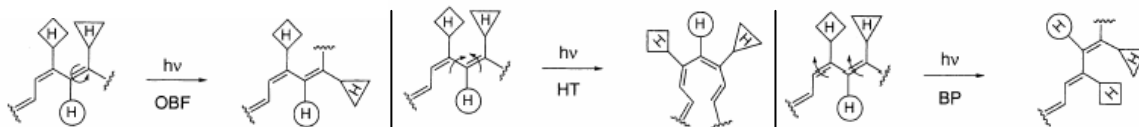
4. Complete the reaction scheme.



5. The following scheme shows a schematic representation of the active site of rhodopsin. Try to work out which bonds of the prosthetic group are involved in the conformational change upon irradiation.



There are three possible ways of *E/Z*-photoisomerization of a polyene which differ strongly in their spatial requirement: OBF (One-Bond Flip), HT (Hula Twist) and BP (Bicyclic Pedal) mechanisms. Which mechanism is performed by the retinal in rhodopsin?



6. Anthrylethylene derivatives undergo *E/Z*-isomerization upon irradiation. An excitation wavelength of $\lambda \geq 400$ nm applied to a solution in hexane yield a photostationary ratio of *E/Z* = 6:94.

Explain this selectivity considering the following UV-Vis spectra.

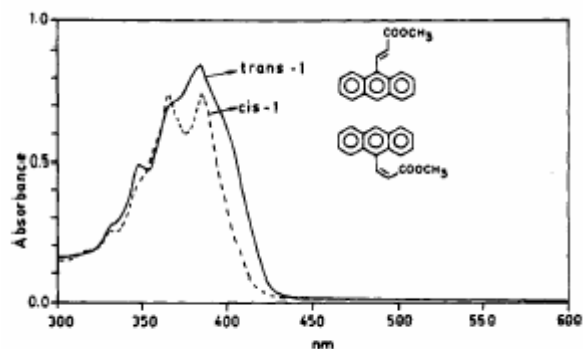


Figure 2. UV-vis absorption spectra of *trans*-1 (solid line) and *cis*-1 (broken line) in hexane solvent.

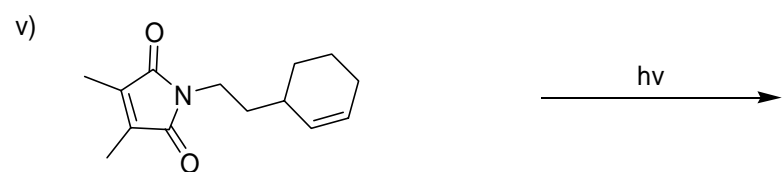
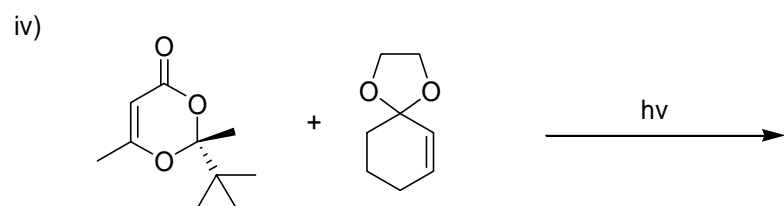
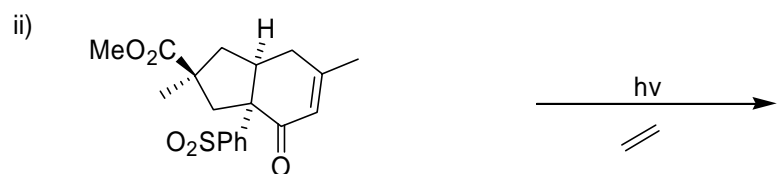
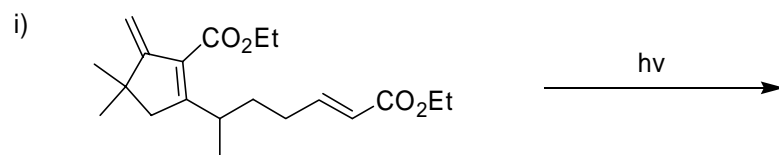
With a sensitizer the selectivity of the reaction is completely inverted (See table!). What does a sensitizer do? Explain this phenomena by drawing a rough scheme of the possible energy distribution of the electronic states involved in the reaction.

Triplet-Sensitized Photostationary Compositions

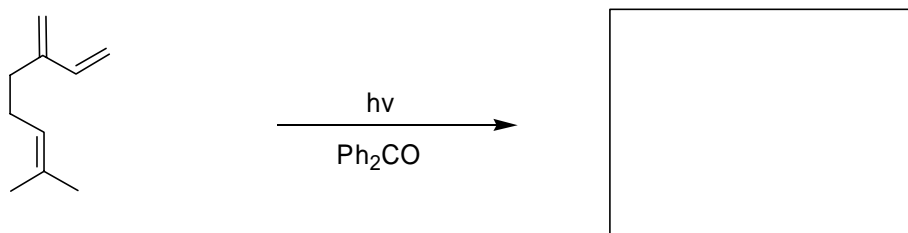
Sensitizer	Absorption [nm]	sens. energy (kcal/mol)	Z (%)	E (%)
erythrocine	515	42	2	98
rose bengal	550	39	2	98
methyl violet	585	37	no reaction	
methylene blue	660	32	no reaction	

Exercise 3: [2+2] Photocycloadditions

1. Give the expected products of the following reactions, with any relevant stereochemical information.



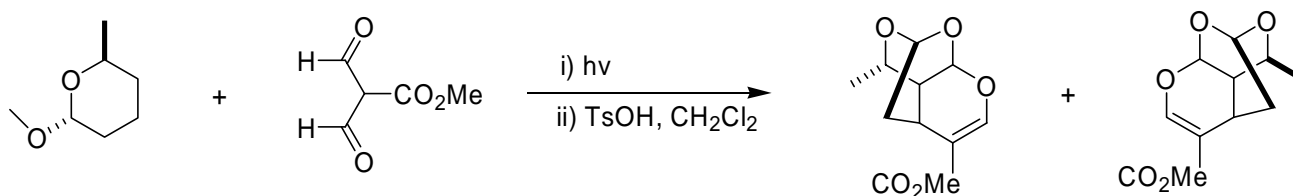
2. The following reaction gives only one product. Explain why.



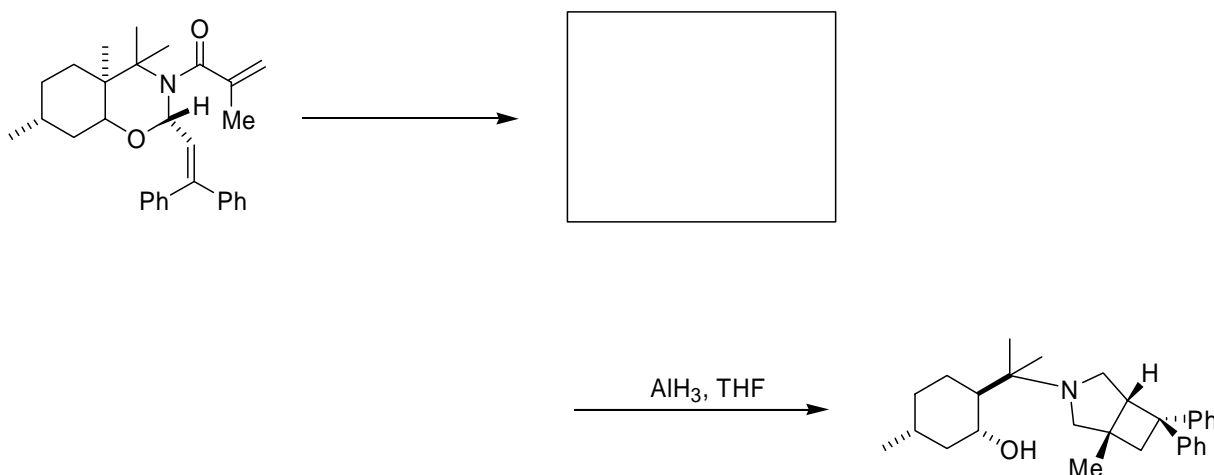
3. Give the intermediate in the following reaction sequence.



4. In the following DeMayo sequence, the major isomer obtained was not that expected. Explain the stereochemical outcome of the reaction. Which isomer was the main product of the reaction?

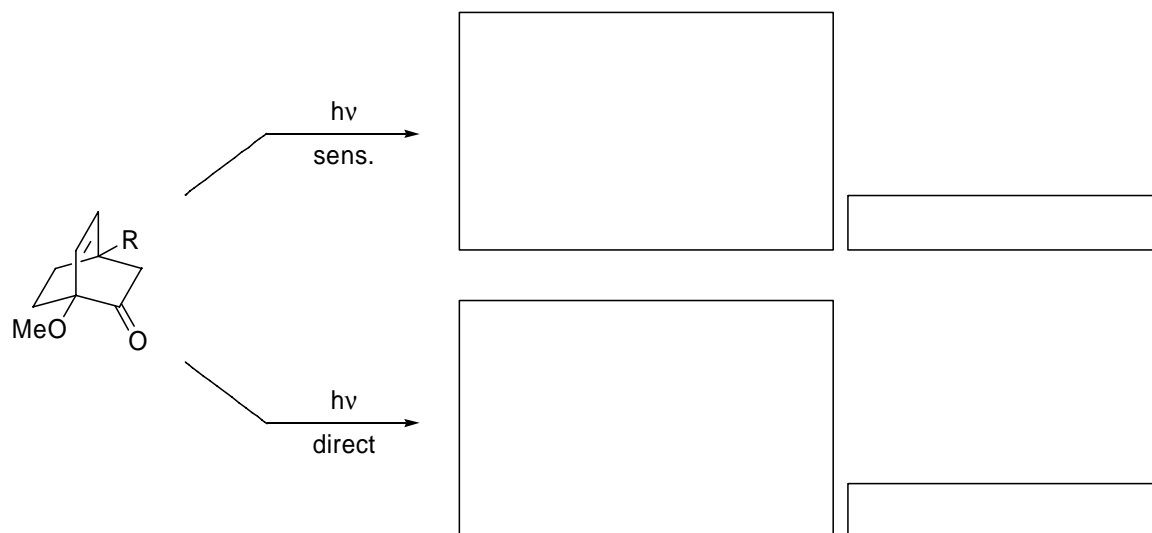


5. Give the photocycloaddition product in the following sequence, and explain the stereochemistry observed. (hint : consider the ground state configuration)

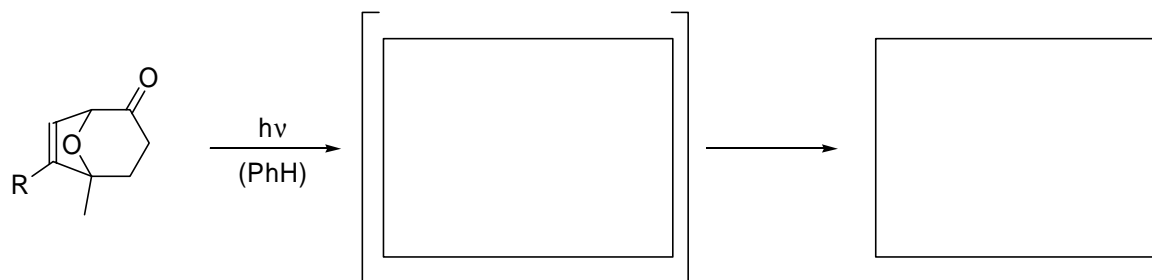
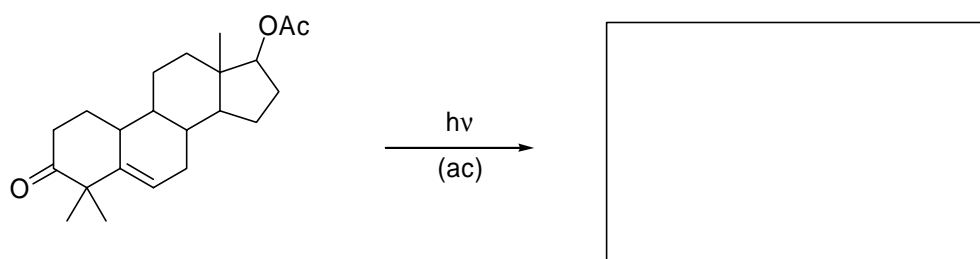


Exercise 4 - Part 1: Rearrangement of β,γ -unsaturated Carbonyl Compounds
- Part 2: Pericyclic Photochemical Reactions

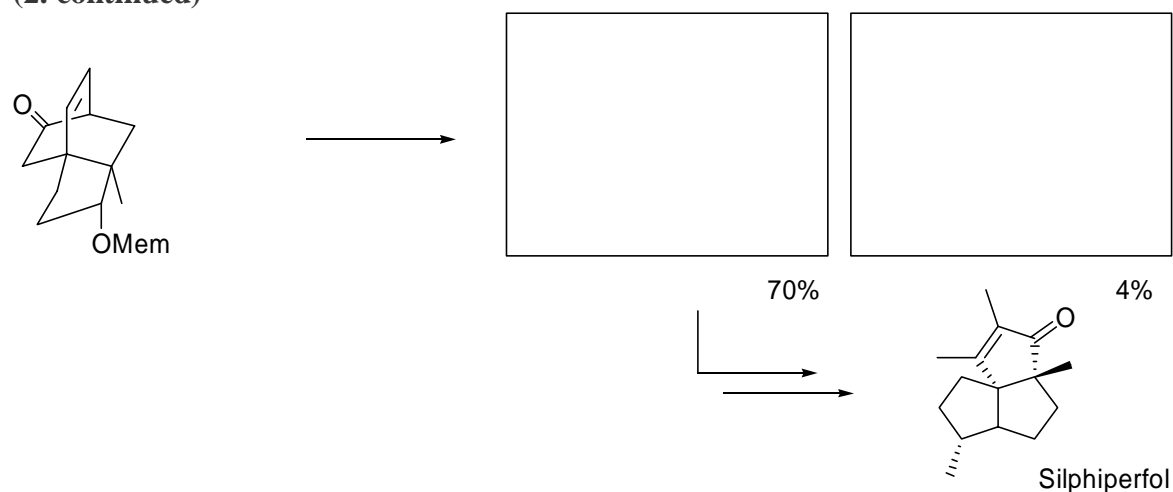
1. There are two reaction pathways for β,γ -unsaturated carbonyl compounds in photochemical rearrangements depending on the excitation conditions. Give the expected products and name the reactions.



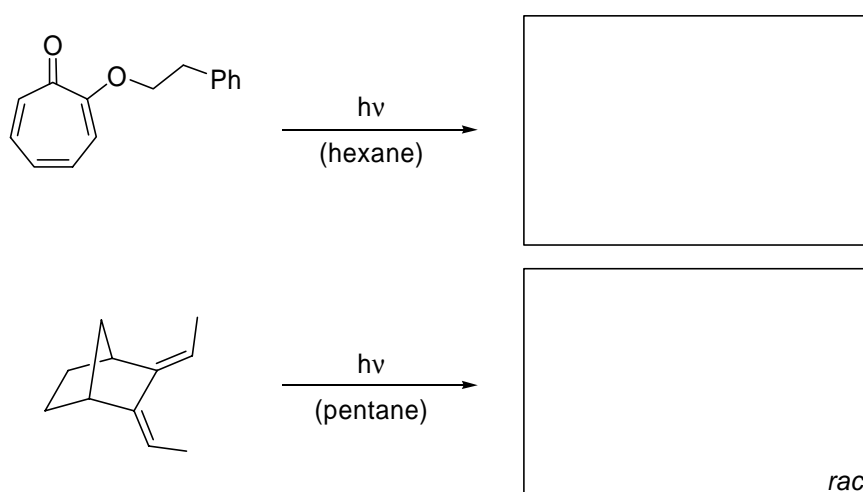
2. Give the expected products under the given reaction conditions.



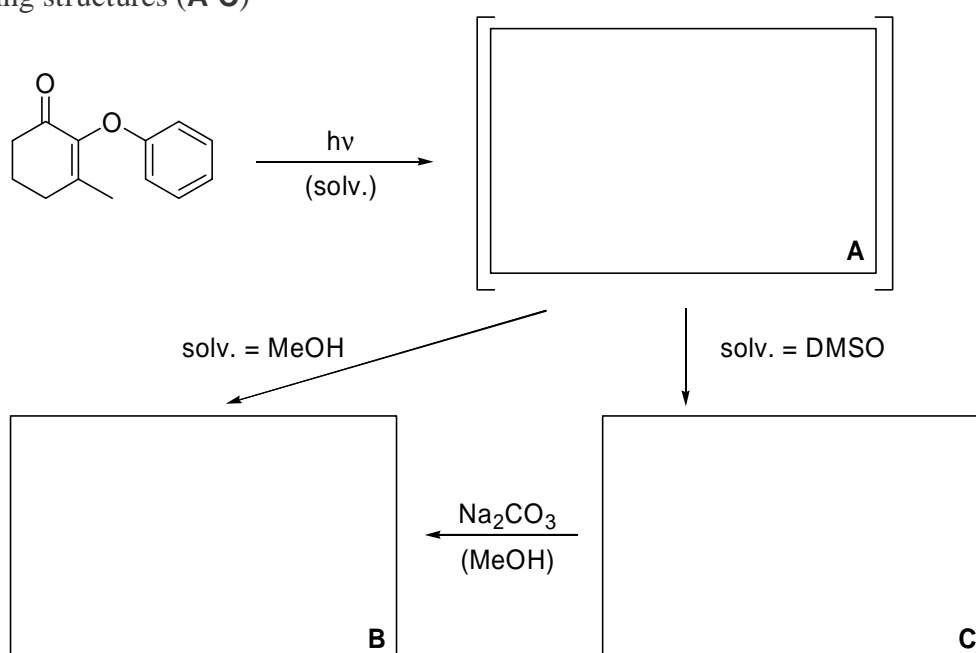
(2. continued)



3. Give the reaction products in the following pericyclic reactions.

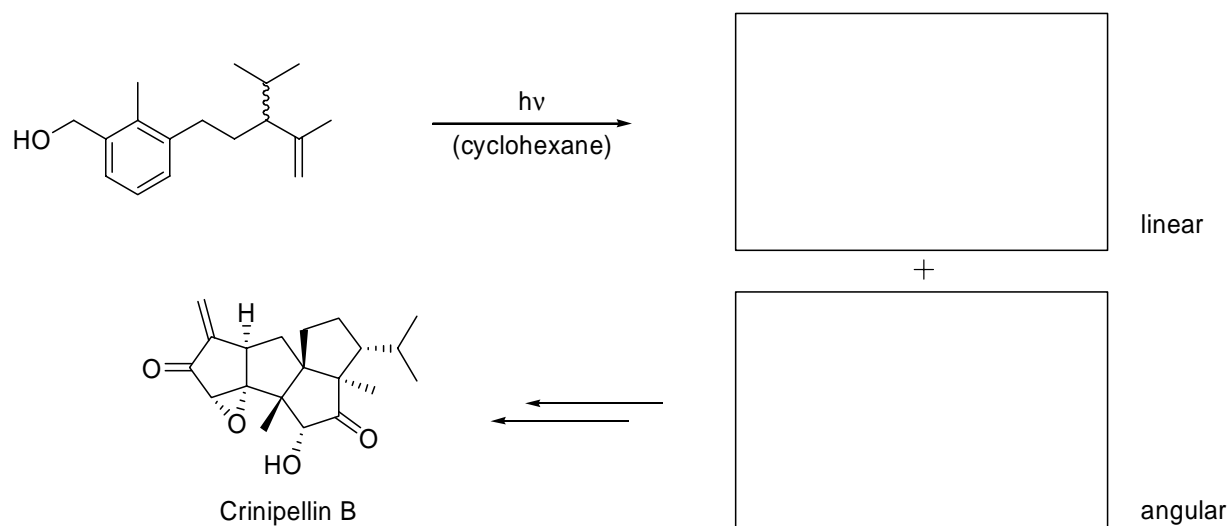


4. In the following pericyclic reaction a zwitterionic intermediate is formed (**A**). In a protic solvent (MeOH) Product **B** is formed, in an aprotic solvent (DMSO) Product **C** is formed, which can be epimerized to yield the desired thermodynamically more stable product **B**. Give all missing structures (**A-C**)

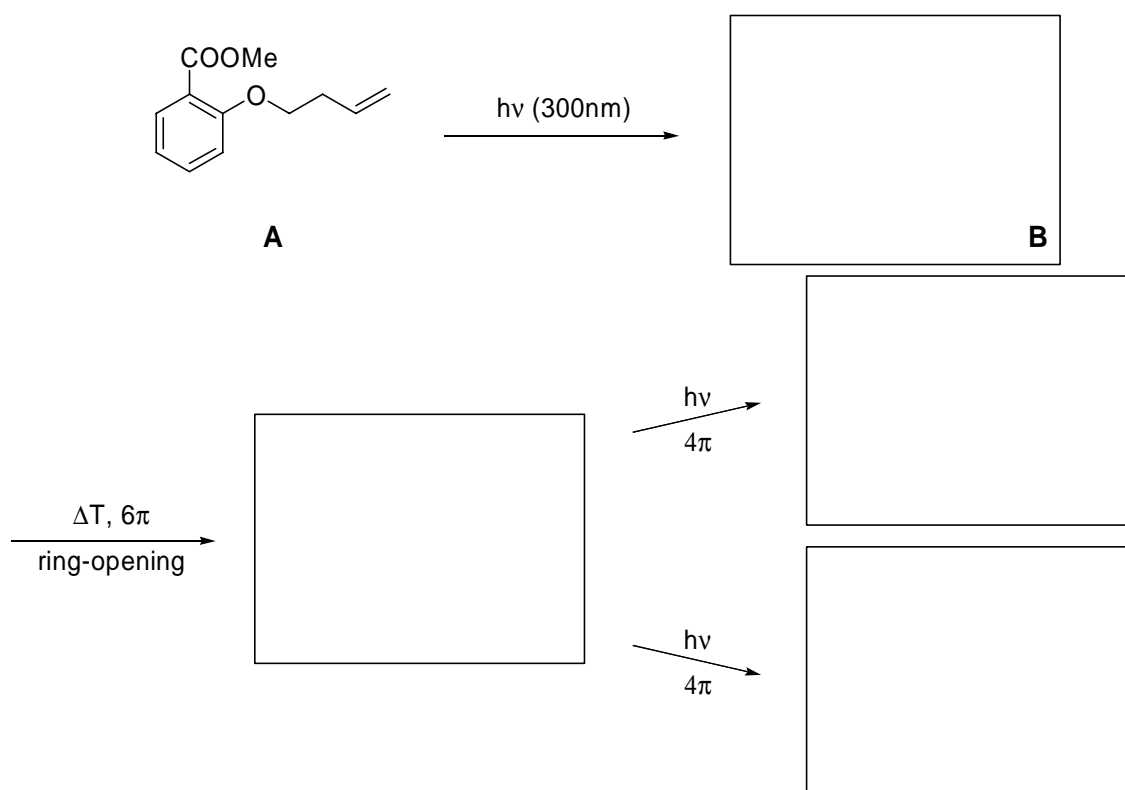


Exercise 4 - Part 1: Photochemical Reactions of Aromatic Compounds
- Part 2: General Repetition

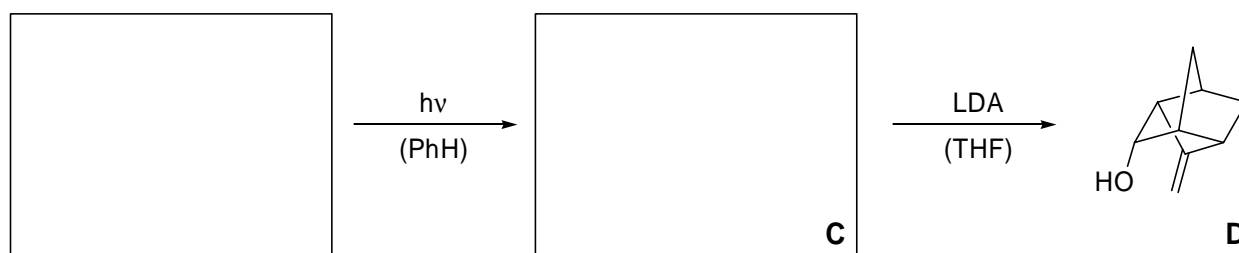
2. Give the expected photoproducts in this key step in the total synthesis of Crinipellin B.



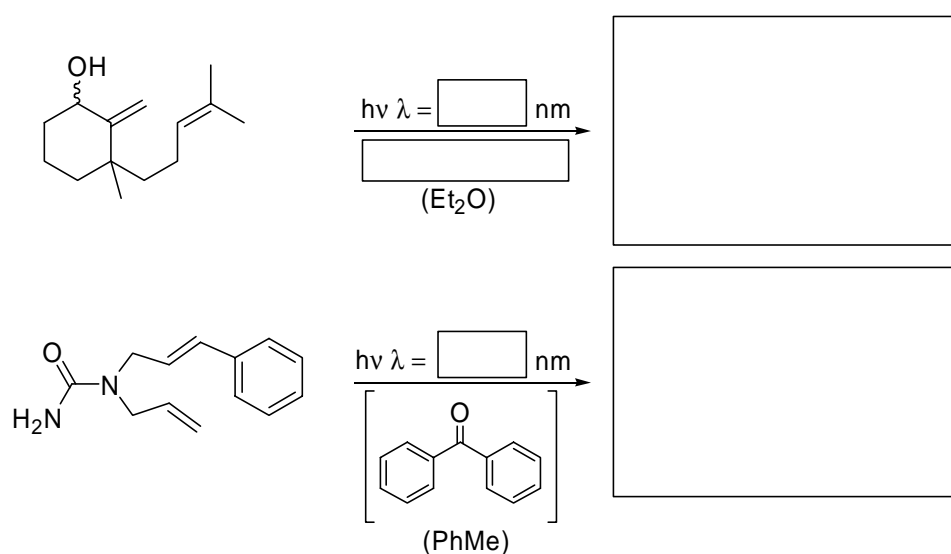
2. The ortho-Photocycloaddition of **A** leads to intermediate **B**. In a disrotatory 6π -ring-opening a cyclooctatriene is formed which is further converted under irradiation. Give all missing structures.



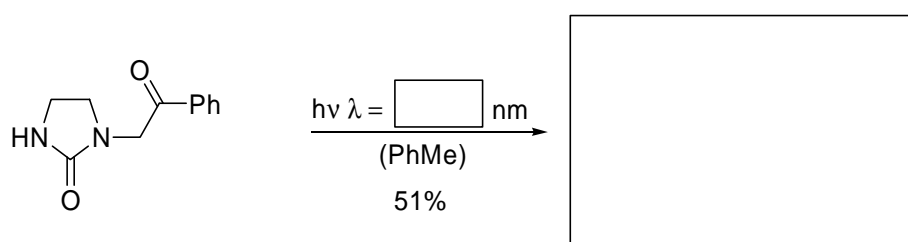
2. Compound **D** was synthesized by treating Paternò-Büchi photoproduct **C** with LDA. Give the missing structures.



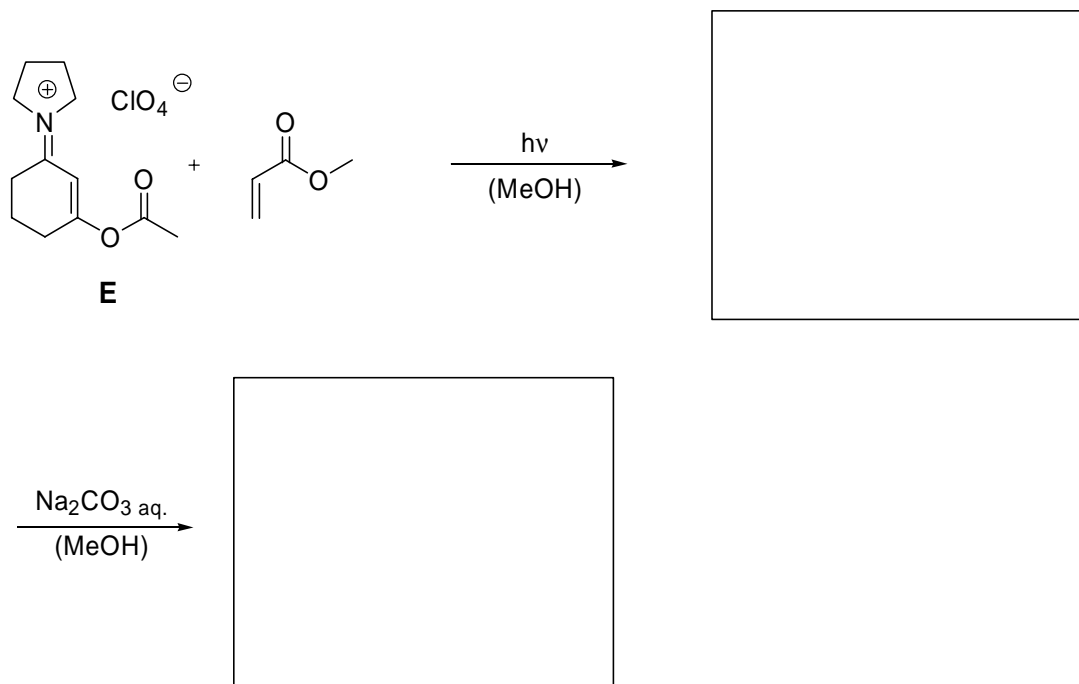
3. Give the reaction products with the expected stereochemistry and the conditions in the following [2+2]-photocycloaddition reactions.



4. In the following Norrish-Yang cyclisation two diastereomeric products are formed. Give the main diastereoisomer and an explanation for the low yield in this reaction.



5. Iminium perchlorate **E** undergoes an intramolecular [2+2]-PCA. Upon treatment with base the acetyl group is hydrolyzed and a retro-aldol reaction is induced.



What is a sequence of [2+2]-PCA and retro-aldol reaction called?

Information about exam weighting

Physical aspects of photochemistry.....	22%
- absorption wavelengths of various chromophores	
- photophysical fundamentals	
<i>Norrish-Yang</i> -cyclisation.....	6%
<i>Paternò-Büchi</i> reaction and synthetical application of oxetanes	17%
[2+2]-photocycloaddition – simple and facial diastereoselectivity.....	35%
- Enones	
- Copper-catalyzed	
- Sensitized	
Rearrangement of β,γ -unsaturated carbonyl compounds.....	6%
Pericyclic reactions.....	10%
Arene-photochemistry	4%