

Organische Chemie IV: Organische Photochemie

Wintersemester 2019/20 – Technische Universität München

Klausur am 19.02.2020

Name, Vorname Matrikel-Nr.
(Druckbuchstaben)

geboren am in

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(Eigenhändige Unterschrift)

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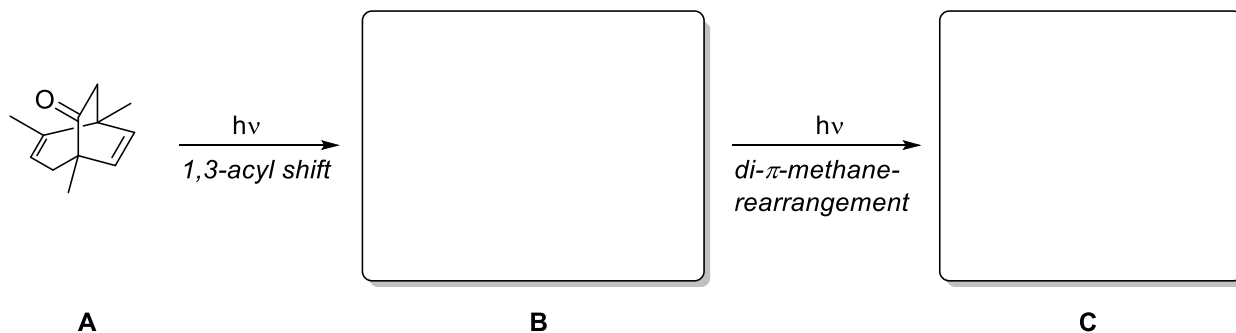
Hinweise zur Klausur:

1. Die Klausur besteht aus insgesamt 11 Blättern (Deckblatt plus 10 Aufgabenblätter). Bitte kontrollieren Sie sofort, ob die Klausurunterlagen vollständig sind.
2. Es dürfen nur die vordruckten Bögen (einschließlich Rückseite) genutzt werden. Antworten sind zu kennzeichnen, sonst werden sie nicht bewertet. Bitte kurze Antworten!
3. Es sind keine Hilfsmittel erlaubt. Täuschungen und Täuschungsversuche führen zum Nichtbestehen der Klausur.
4. Bitte schreiben Sie mit einem Kugelschreiber oder Füller. Verwenden Sie keinen Bleistift und keine rote Tinte!
5. Jede richtig und vollständig beantwortete Aufgabe wird mit der jeweils angegebenen Anzahl von Punkten bewertet. Es können Teilpunkte gegeben werden. Die Klausur ist bestanden, wenn mindestens 50 Punkte erreicht worden sind.

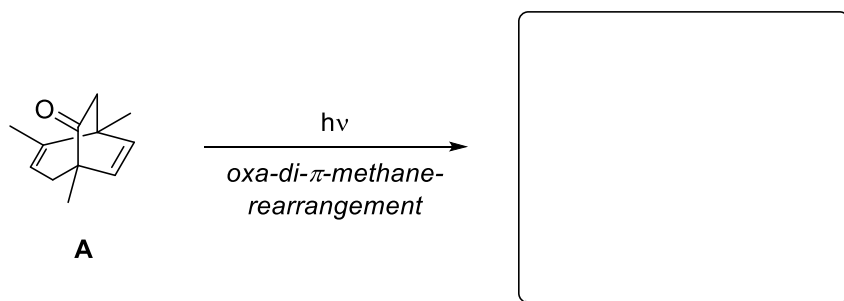
Information

1. The exam is comprised of 11 sheets (cover page, plus 10 question pages). Please check immediately that the exam paper is complete.
2. You may use both sides of the distributed paper to give your answers, but no additional sheets will be allowed. Make sure you indicate clearly which question you are answering, otherwise it will not be counted. Short answers please!
3. No additional sources of information are allowed. Cheating, and cheating attempts will result in the candidate failing the exam.
4. Please write clearly in ink or ballpoint pen. Do not use pencil or red colours!
5. Every correct and fully answered question will be awarded the number of points shown. It is possible to obtain only some of the points if the answer is not completely satisfactory. A pass is obtained if at least 50 points are awarded.

1. a) The bicyclic compound **A** undergoes upon direct irradiation a 1,3-acyl shift to intermediate **B**, which reacts further *via* a di- π -methane-rearrangement to the tricyclic compound **C**. Please give the structure of products **B** and **C** with their absolute configuration (note: the stereogenic centers formed in the second reaction step can be neglected). (6 points)

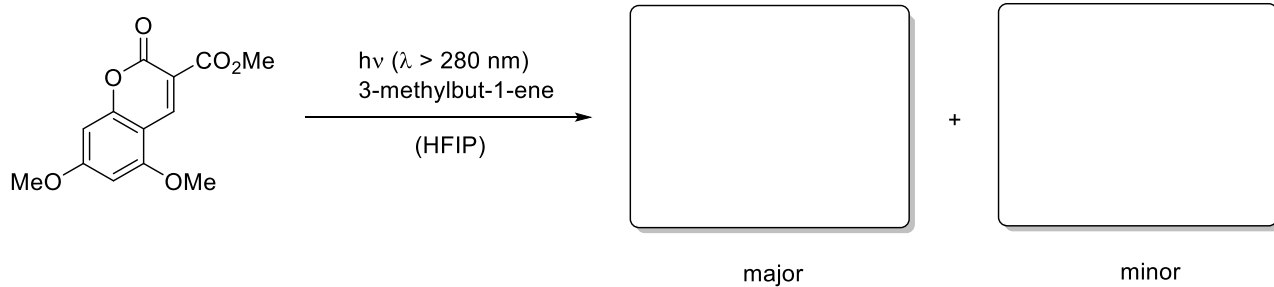


b) The very same bicyclic compound **A** undergoes an oxa-di- π -methane rearrangement upon sensitization. Please draw the respective reaction product with its absolute configuration. Which sensitizer could be used for this reaction? (6 points)



2. In the total synthesis of (\pm)-linderol A by *Ohta* an intermolecular [2+2] photocycloaddition was the key step. Therefore, the depicted coumarin was irradiated in the presence of 3-methylbut-1-ene in HFIP. (HFIP = hexafluoroisopropanol)

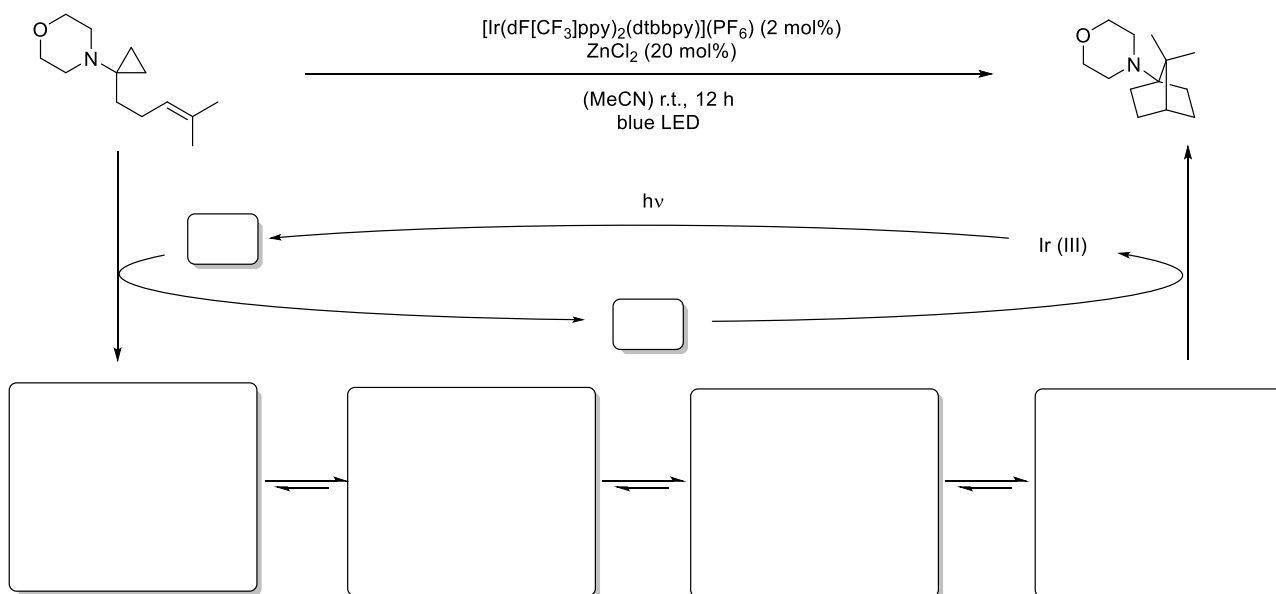
a) Give the expected major and minor diastereomer with the correct relative configuration. (5 points)



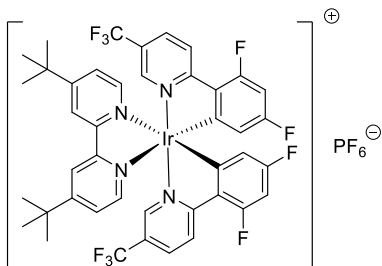
b) Explain the observed regioselectivity of the above mentioned photocycloaddition with the reaction mechanism. In this case, neglect the stereoinformation. Take the polarization of the C-C double bonds into consideration and name the involved processes. (4 points)

3. 1-Aminonorbornanes represent a class of molecules that are well suited to serve as bioisosteres for anilines which makes them compounds of interest to the pharmaceutical sector. *Stephenson* and coworkers reported a method which includes the application of photoredox catalysis to access a formal [3 + 2] cycloaddition of aminocyclopropanes with tethered olefins.

a) Provide the structures of the formed intermediates as well as the different states of the photoredox catalyst. Neglect the influence of $ZnCl_2$ in the reaction. (7 points)



b) In cyclic voltammetry measurements, with a Hg/HgO electrode in NaOH as the reference, the redox potentials of the ground state and the triplet energy of the above used catalyst have been determined. Calculate the redox potentials in the ground state and of M^*/M^- against SCE. For that purpose use the given conversion table. (2 points)



$$E_{1/2}(M/M^*) = -1.29 \text{ V [vs. Hg/HgO, NaOH (0.1M)]}$$

$$\lambda_{\text{max}}(\text{emission, Phos}) = 470 \text{ nm}$$

$$E_T = 254 \text{ kJ/mol} = 2.6 \text{ V}$$

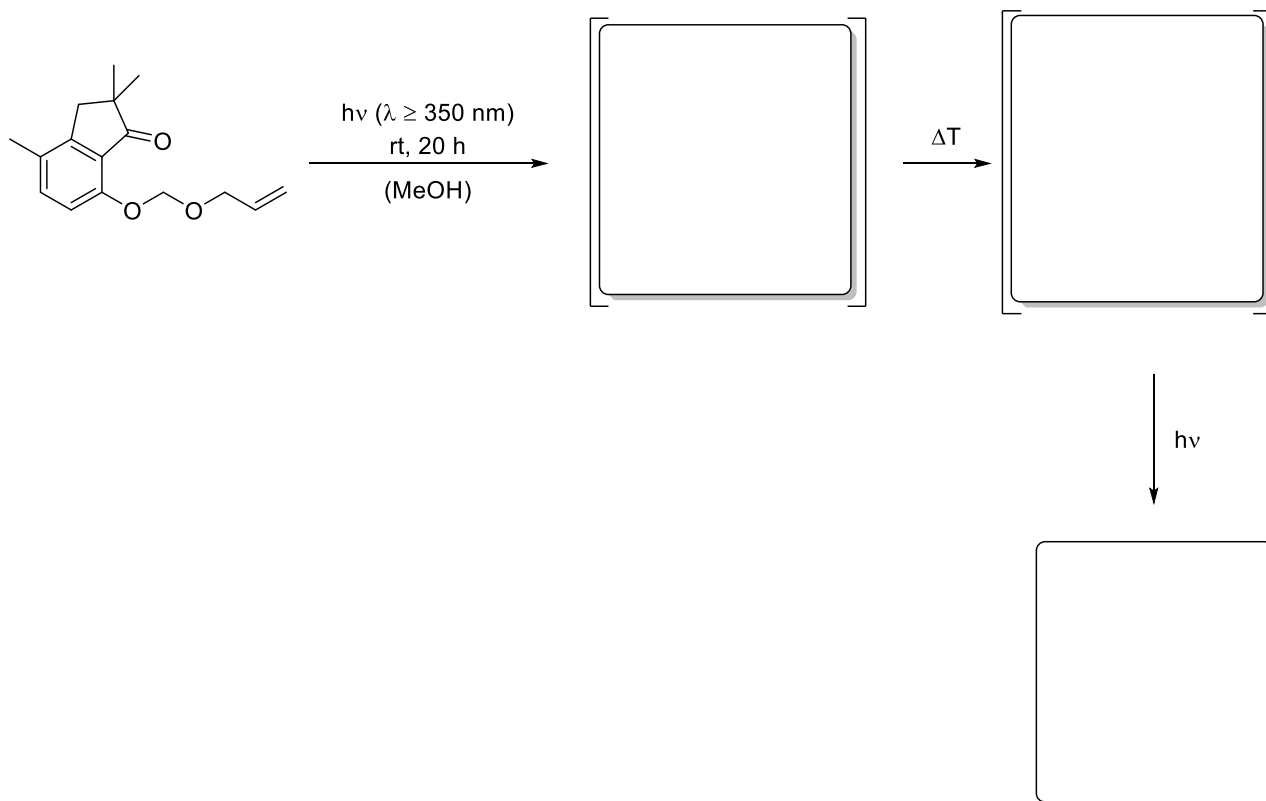
	Potential @ 25 °C	
	vs. NHE (in V)	vs. SCE (in V)
Cu/CuSO ₄ (sat'd)	0.316	0.074
Hg/HgO, NaOH (0.1 M)	0.165	-0.08
Ag/Ag ₂ SO ₄ , H ₂ SO ₄ (0.5 M)	0.72	0.48
Ag/AgNO ₃ (0.01 M) in MeCN	-na-	0.3
SCE	0.25	0

NHE: normal hydrogen electrode

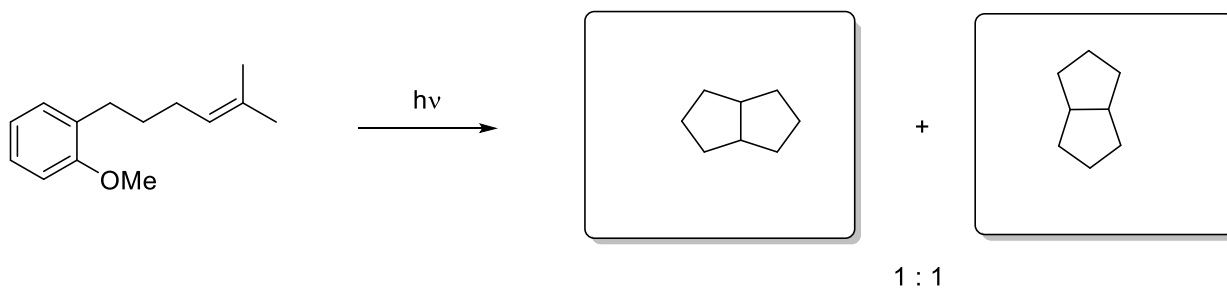
SCE: standard calomel electrode

4. Photocycloaddition of an olefin to an arene core leads to photoproducts, which are often prone to undergo consecutive reactions.

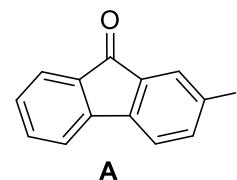
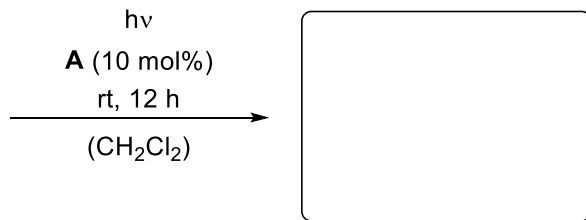
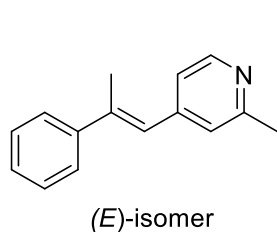
a) Give the expected photoproduct with the correct relative configuration. This product is not stable under the reaction conditions and isomerizes to an intermediate, which upon irradiation forms the final product. Draw the primary photoproduct, intermediate and final product. (10 points)



b) Donor-substituted arenes and olefins also lead to useful photoproducts. Draw the two photoproducts, which are formed in this intramolecular reaction in a 1:1 ratio. Give the expected photoproduct with the correct relative configuration. (6 points)



5. The *E,Z*-isomerization of alkenes can be initiated both thermally and photochemically. Draw the product of the following photochemical reaction. Briefly explain the mechanism of this type of reaction. What is the role of **A** in this reaction and what energetic requirements have to be fulfilled by **A**, the substrate and the formed product. Furthermore, complete the sentences below. (5 points)

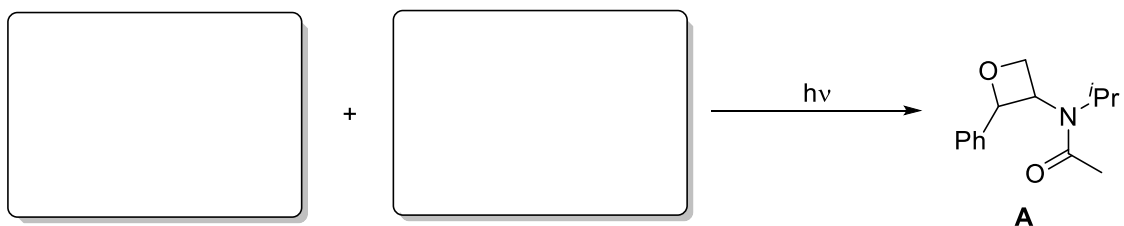


Mechanism:

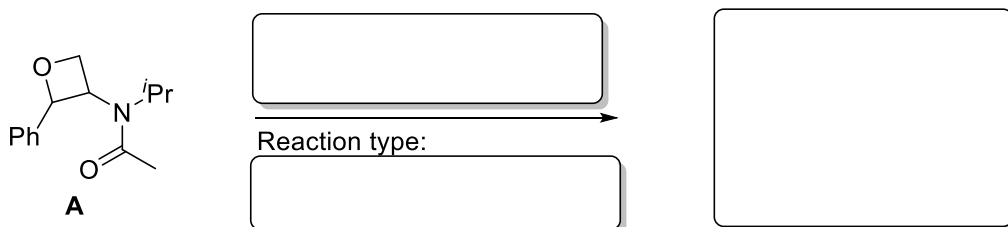
Role of **A**:

Requirements for **A**:

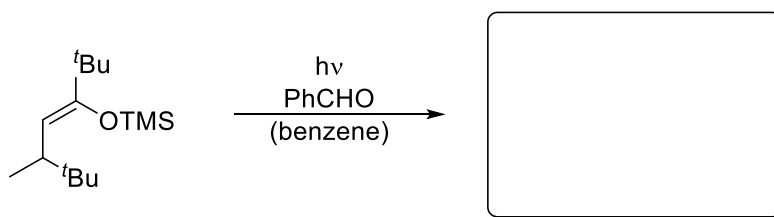
6. a) Give the structure of the starting materials of the following photocycloaddition and add the relative configuration of the product. (3 points)



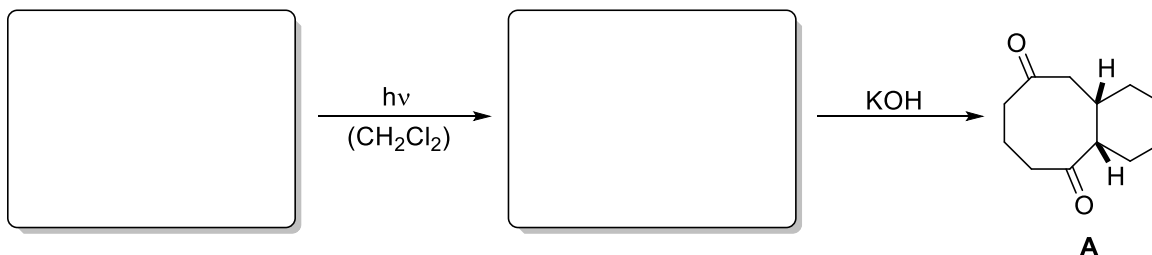
b) Oxetanes can be easily cleaved under various conditions. Name one reaction type to cleave oxetane **A** and give appropriate reaction conditions as well as the structure of the formed product. (4 points)



c) Give the expected product and pay attention to the regio- and stereoselectivity. *Hint: Think about the preferred conformation of the reacting olefin.* (5 points)

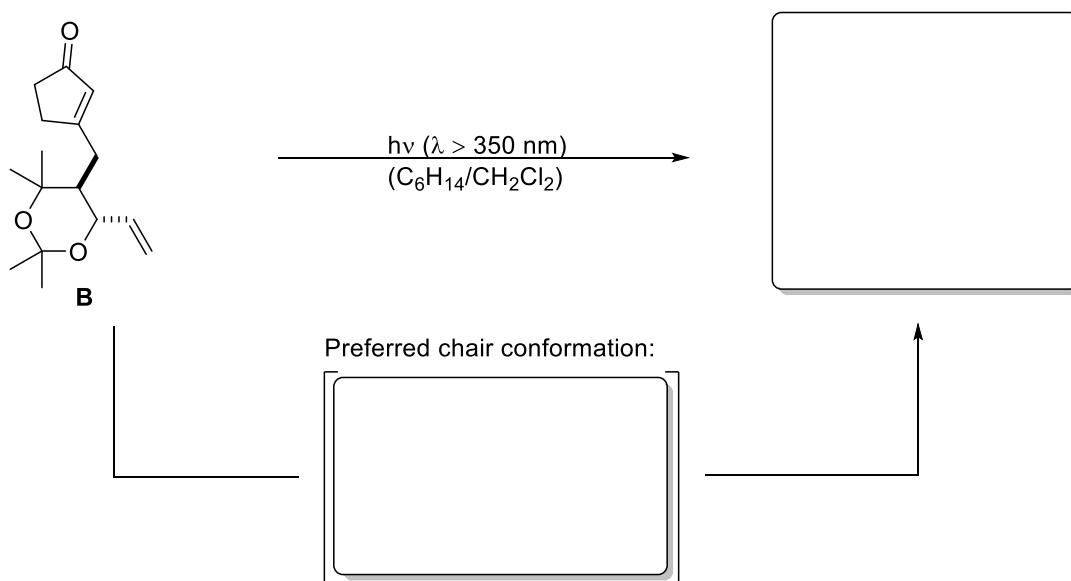


7. a) Diketone **A** can be synthesized by a two-step sequence including an intramolecular photocycloaddition. Give the structure of the starting material and the photoproduct. Indicate all stereocenters. (5 points)

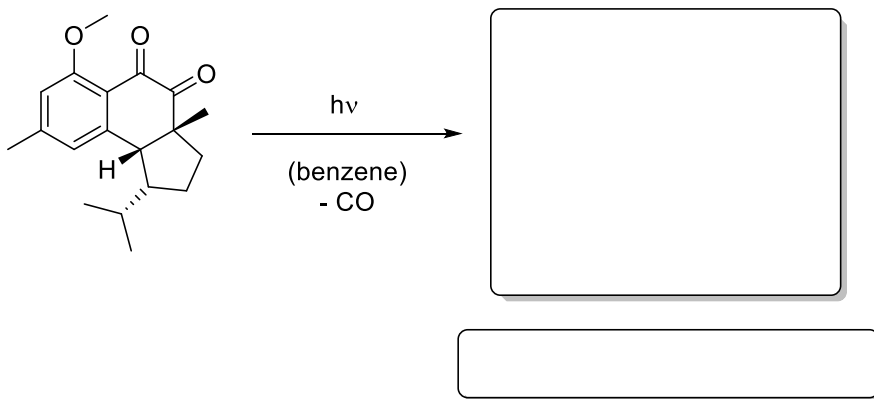


b) High facial diastereoselectivity can be achieved in many intramolecular [2+2] photocycloadditions. Analysis of the preferred conformation of the respective substrate frequently leads to a reliable prediction about the stereochemical outcome.

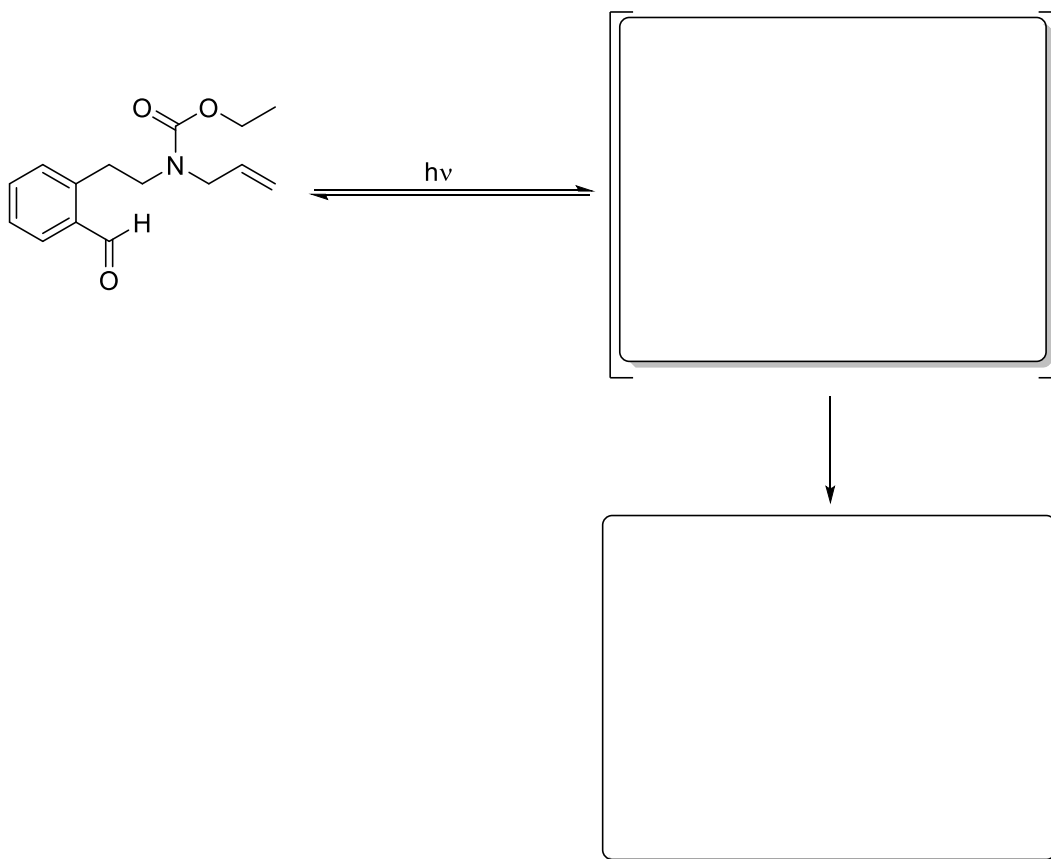
Substrate **B** contains two stereogenic centers in the tether, which connects the olefin with the 2-cyclopentenone core. Give the structure of the formed product. Also draw the preferred six-membered chair conformation of the substrate and predict all stereogenic centers of the product. (8 points)



8. a) Please give the product and name of the depicted photochemical fragmentation. (3 points)



(b) Please give the intermediate and the product formed in the following photochemically induced cycloaddition. Give a reason for the relative configuration of the preferred product. (7 points)



9. Rigby *et al.* successfully performed the enantioselective total synthesis of the antitumor alkaloid (+)-narciclasine using a stereocontrolled photocyclization involving the grey marked carbon atom of aryl enamide **A**. Please fill in the missing structures. Explain the stereoselectivity of this reaction. In a following 1,5-H shift reaction compound **B** was formed. Give the structure of compound **B**. (PMB = 4-methoxybenzyl, 8 points)

