

# Organische Chemie IV: Organische Photochemie

Wintersemester 2018/19 – Technische Universität München

**Klausur am 19.02.2019**

Name, Vorname ..... Matrikel-Nr. ....  
(Druckbuchstaben)

geboren am ..... in .....

.....  
(Eigenhändige Unterschrift)

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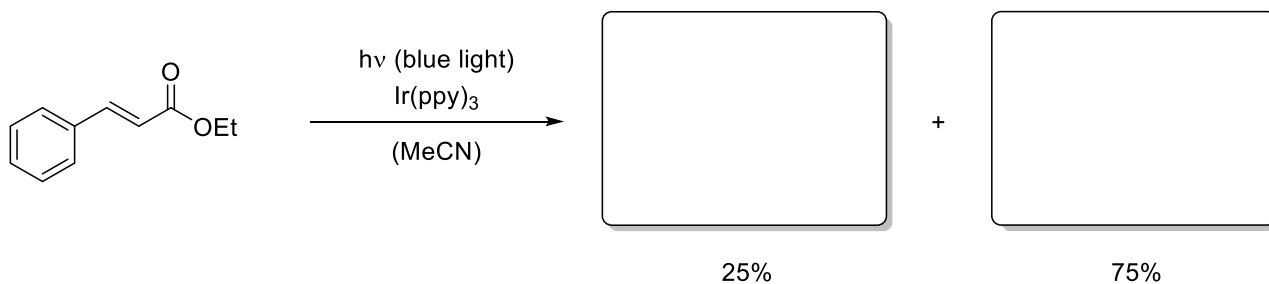
## Hinweise zur Klausur:

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.

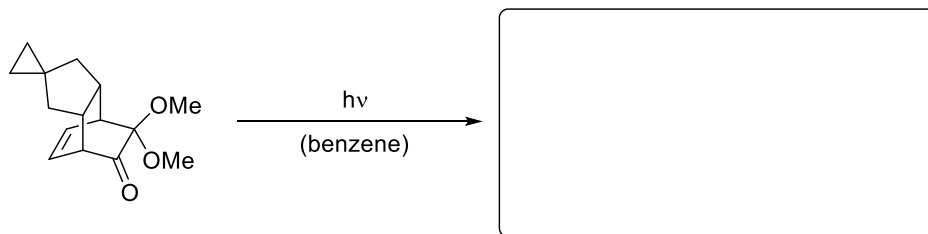
1. The isomerization reaction shown below was used in the synthesis of coumarins. Irradiation of Ir(ppy)<sub>3</sub> as a triplet sensitizer makes it possible to run the reaction under visible light. Give the expected photoproducts. (2 points)



Explain the general mechanism (energy diagram) of sensitization! (3 points)

2. Photochemical induced rearrangement reactions are among the most studied photochemical transformations and therefore their mechanisms are well understood.

a) Give the expected photoproduct with correct relative configuration. What is the name of this photochemical rearrangement reaction, and does it occur from the singlet or triplet hypersurface? How can the reaction be described using the *Woodward-Hoffmann* notation? (7 points)



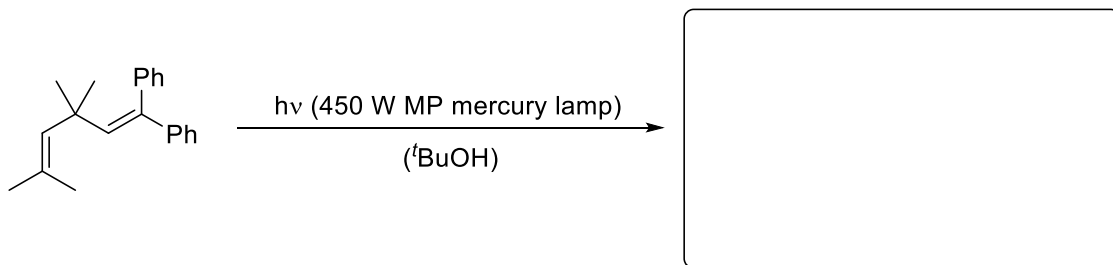
Name:

Woodward-Hoffmann notation:

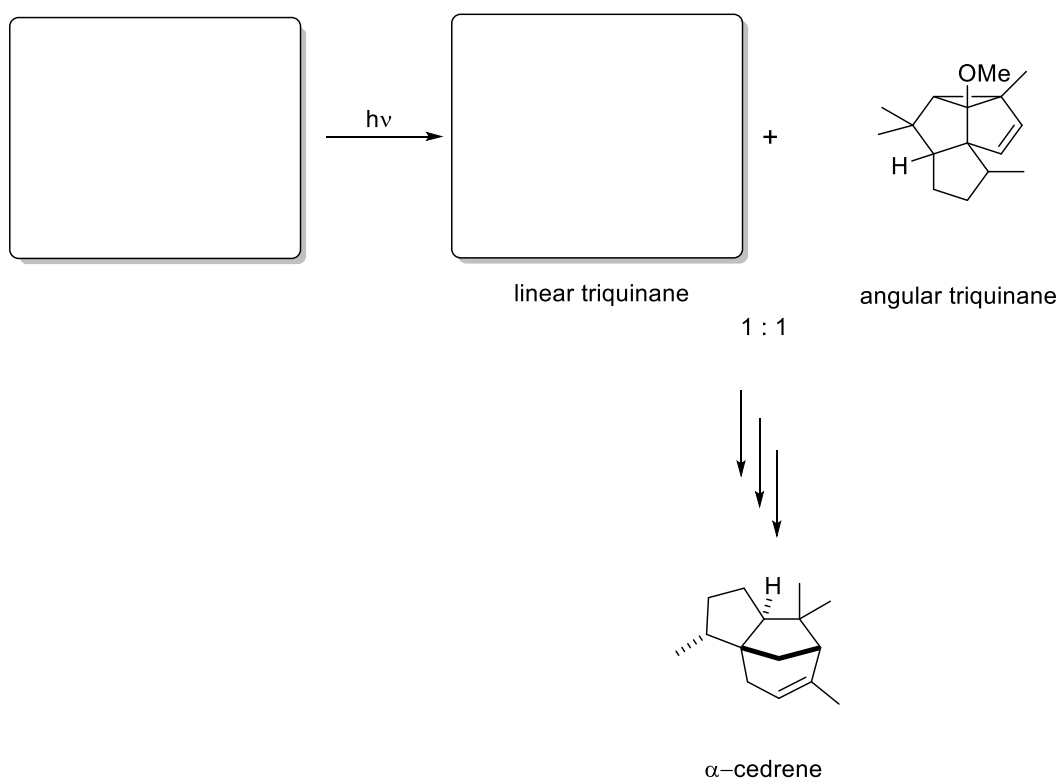
Reaction occurs from: S<sub>1</sub>  T<sub>1</sub>

Which product do you expect if you run the reaction in acetone as solvent? Name the type of reaction and give a short explanation for your assumption. (It is not necessary to give the structure of the product.)

b) In the following rearrangement, the resulting vinylcyclopropane is formed with excellent regioselectivity. Fill in the correct structure and explain the regioselectivity of the reaction. (3 points)

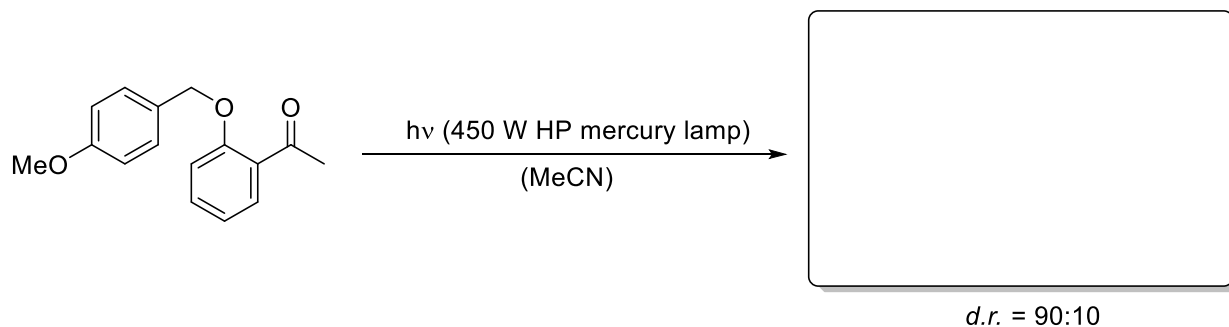


3. Due to its high potential of converting planar molecules into three-dimensional chiral structures, the *meta*-photocycloaddition was employed as photochemical key step in the synthesis of complex natural products. A literature known example is the total synthesis of ( $\pm$ )- $\alpha$ -cedrene published by *Wender et al.* in 1981. The bicyclo[3.2.1]octane core of the natural product was accessible by a simple diastereoselective *meta*-photocycloaddition followed by a ring opening. Give the missing starting material and the structure of the linear triquinane intermediate. Please indicate also, which C-C bond of the linear triquinane has to be cleaved to get access to ( $\pm$ )- $\alpha$ -cedrene. *Note: Do not forget to give all stereocenters with their correct relative configuration.* (6 points)

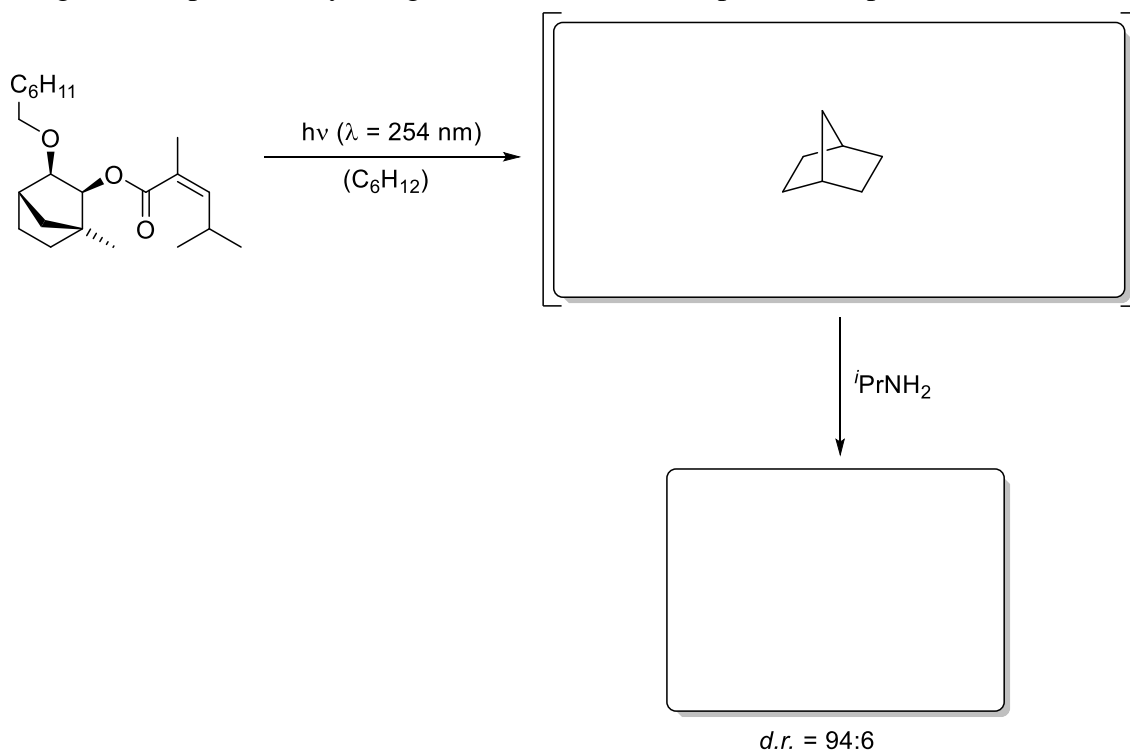


4. Carbonyl compounds are one of the functional groups often employed as chromophores in photochemical reactions in organic chemistry. By tuning the reaction conditions and the structure of the molecule excited by irradiation with light of a suitable wavelength, a variety of different reactions can occur, leading to the formation of products that are difficult to access by thermal reactions.

a) In the following *Norrish-Yang* cyclization, the photoproduct is formed with high diastereoselectivity. Fill in the correct structure with regard to the relative configuration. (3 points)



b) The irradiation of  $\alpha,\beta$ -unsaturated esters derived from (+)-camphor leads to the formation of an intermediate, which can be converted to the corresponding product in the presence of secondary amines with high control of diastereoselectivity. Fill in the missing structure of the intermediate using the given camphor moiety and give the structure of the product. (5 points)

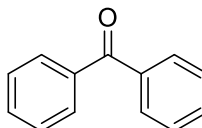


5. a) Below are the chemical structures of five compounds, which are useful chromophores in photochemical reactions. Make a decision, which of the given excitation wavelength ( $\lambda_{\max}$ ) is suitable to excite which chromophore and write the number in the appropriate box. (5 points).

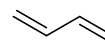
(I) 220 nm (II) 260 nm (III) 325 nm (IV) 345 nm (V) 480 nm



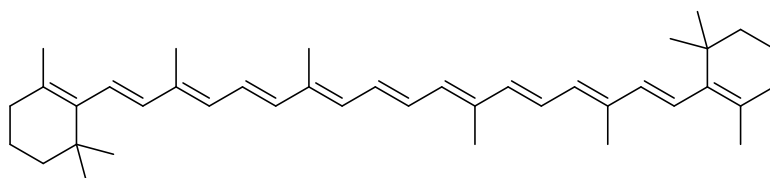
**A**  
( $\pi\pi^*$ )



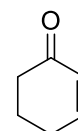
**B**  
( $n\pi^*$ )



**C**  
( $\pi\pi^*$ )



**D**  
( $\pi\pi^*$ )

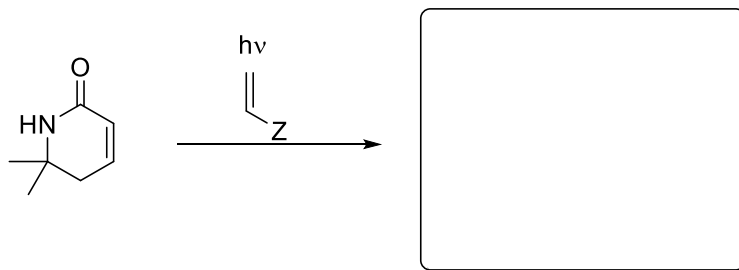


**E**  
( $n\pi^*$ )

b) Considering a simple aliphatic carbonyl compound, what order of magnitude would you expect for the molar absorption coefficient  $\epsilon$  during absorption at  $\lambda \approx 300$  nm? Give a short explanation for your assumption. *Note: Do not forget to consider the correct unit of  $\epsilon$ .* (2 points)

6. Fill in the products of the following photochemical reactions. Pay attention to the regioselectivity of the reactions and the relative configuration of the products.

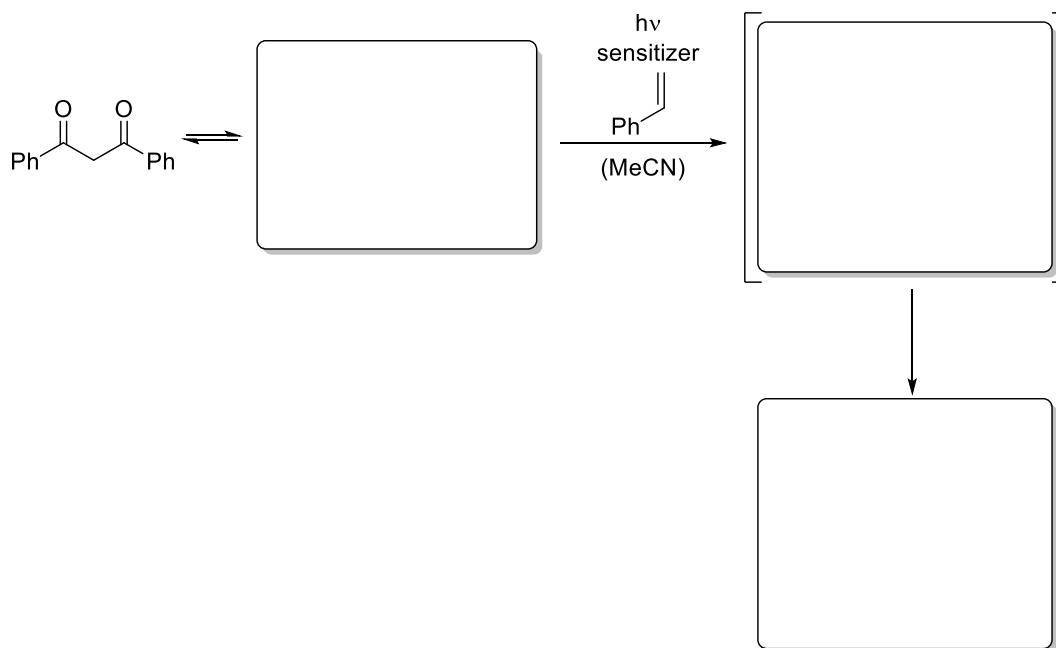
a) (6 points)



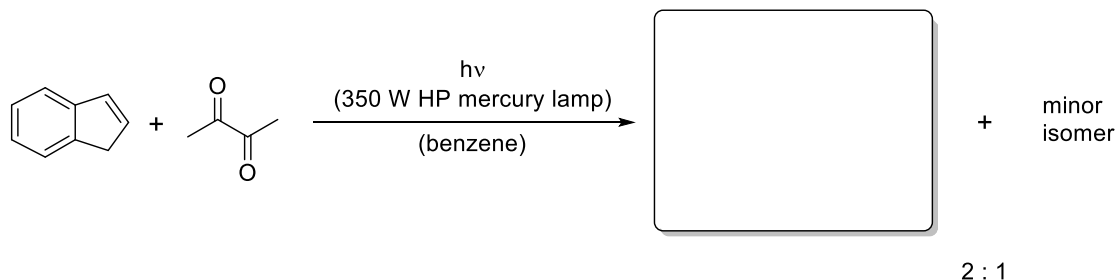
Z = CN: r.r. = 82:18

Which major regioisomer do you expect, if substituent Z = OEt? Give a short explanation.

b) *Hint: The first step includes a tautomerization of the starting material.* (5 points)



c) (4 points)

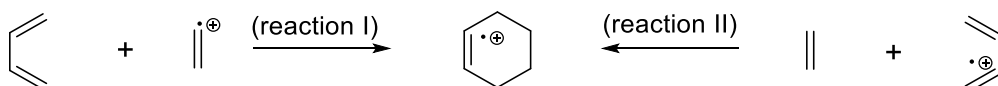




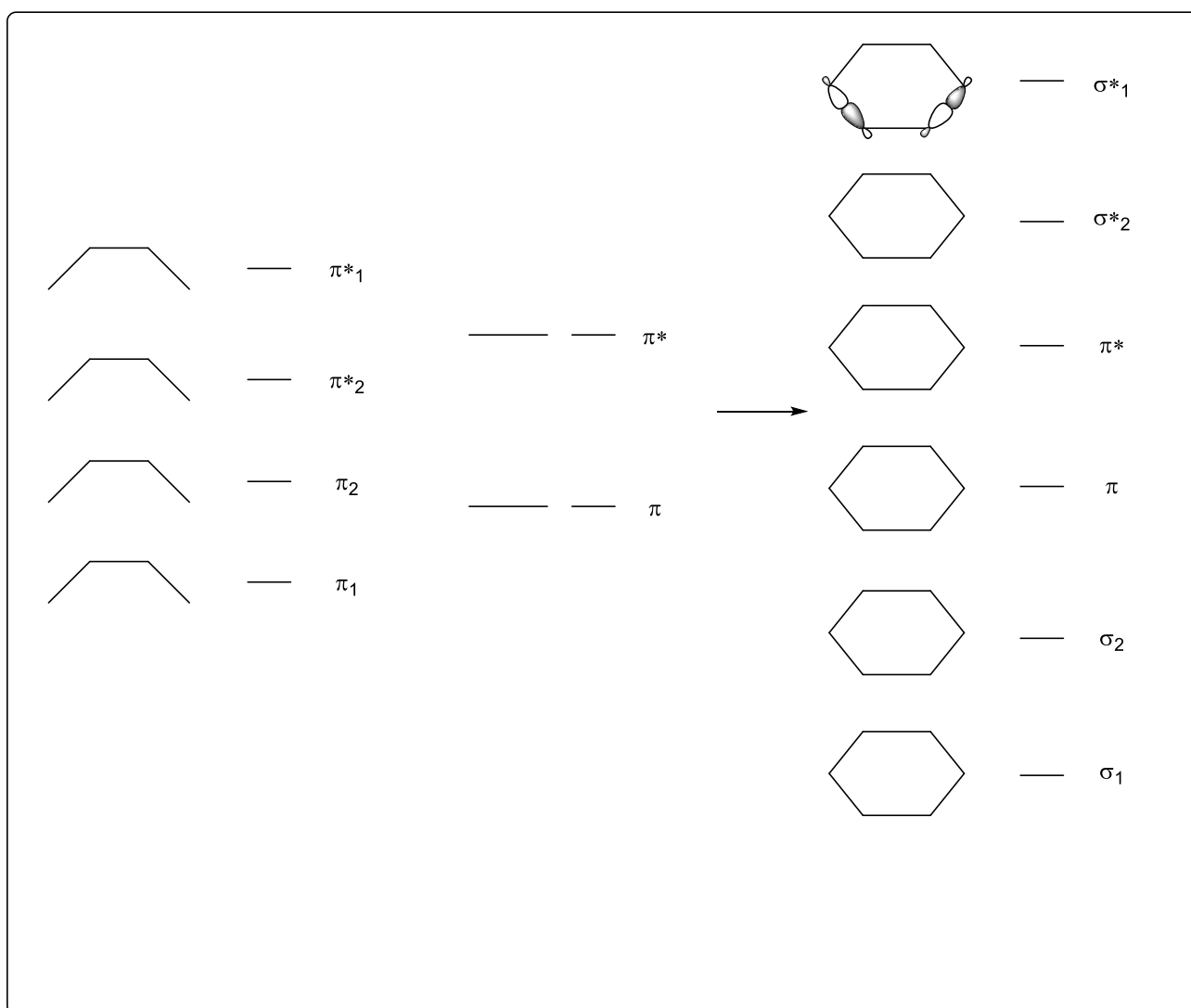


b) Besides neutral pericyclic reactions, cation-radical pericyclic reactions, including the ionic *Diels-Alder* reaction and the ionic *Cope* reaction are known in the literature. In these cases, ionization of one of the reaction partners is found to lower the activation energy of the reaction dramatically. (12 points)

In the cation-radical *Diels-Alder* reaction depicted below, there is a tremendous difference in reactivity between the shown two model reactions (reaction I and reaction II).

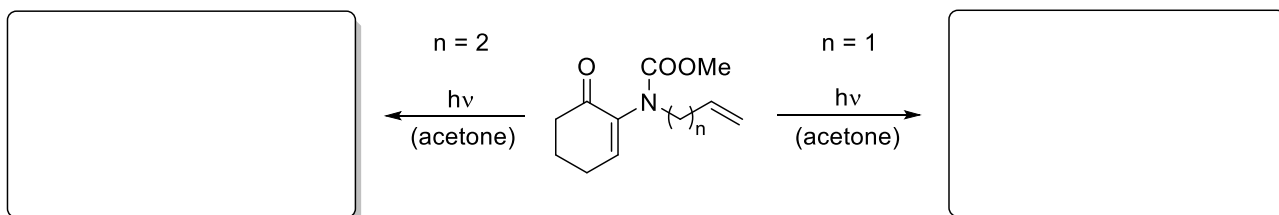


Analyze the symmetry of the orbitals which are involved in reaction I with respect to the *Woodward-Hoffmann* rules. Draw the molecular orbitals with the correct phase in the scheme given below and fill in the appropriate number of electrons. (*Hint: The two newly formed  $\sigma$  bonds have to be considered as one orbital. The highest anti-bonding orbital is given*). Assign the symmetry of each orbital to a mirror plane. Is this reaction thermally allowed?

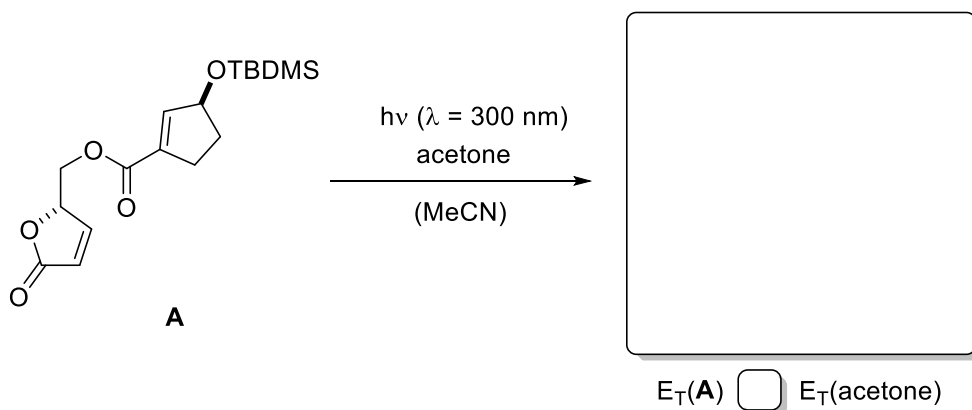


State if the reaction II is thermally allowed. Give a short explanation. (It is not necessary to draw the molecular orbitals a second time.)

9. a) Depending on the chain length of the linker, different photoproducts are formed in the following reactions. Give the expected products and consider the correct relative configuration. (8 points)



b) The following reaction was applied in the total synthesis of stoechospermol. Give the photoproduct including all stereocenters. Give the name of the effect leading to the formation of the preferred product. Further state the role of acetone in this transformation. Which photophysical prerequisites of molecule **A** and acetone have to be fulfilled for this process (fill >, = or < in the two boxes)? (8 points)

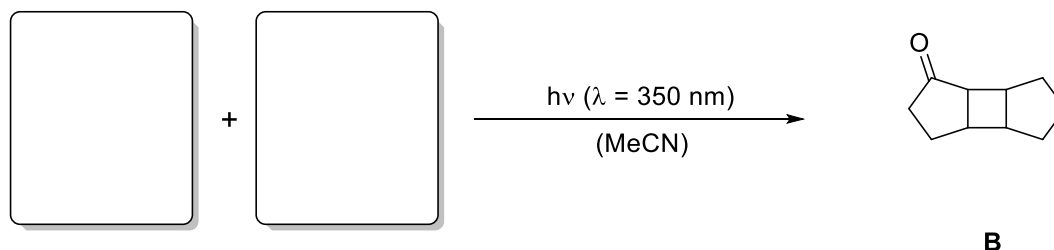


Role of acetone:

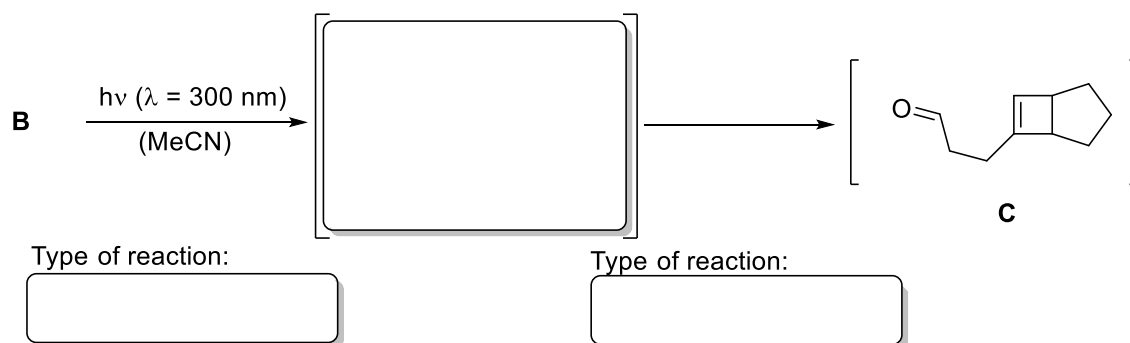
Explanation of relative configuration of the product:

10. The group of *D. J. Aitken* recently reported a cascade photochemical reaction process that formed the final product **A** with a tetracyclic 4:4:4:5 skeleton.

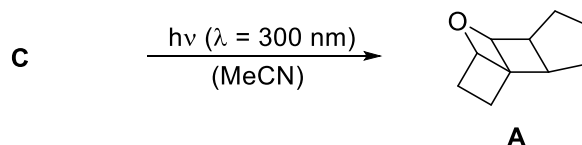
a) It is well known, that the [2+2]-photoproduct **B** can be formed as one single diastereomer upon irradiation of the starting material at  $\lambda = 350$  nm. Fill in the missing structures of the starting materials. (2 points)



b) In the recent publication light of shorter wavelength ( $\lambda = 300$  nm) was used and under these conditions the primary photoproduct **B** was also excited and the depicted intermediate **C** was formed. Fill in the missing intermediate with the correct relative configuration and give the type of reaction for each step. (5 points)



c) The final product **A** of the reaction at  $\lambda = 300$  nm was formed from intermediate **C** in one step. Give the name of this reaction and explain in a few words the mechanism of this reaction. (3 points)



Name reaction:

Mechanism: