

# Organische Chemie IV: Organische Photochemie

Wintersemester 2013/14 – Technische Universität München

**Klausur am 11.02.2014**

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

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

.....  
(Eigenhändige Unterschrift)

1	2	3	4	5	6	7	8	9	10	11	$\Sigma$	Note

## Hinweise zur Klausur:

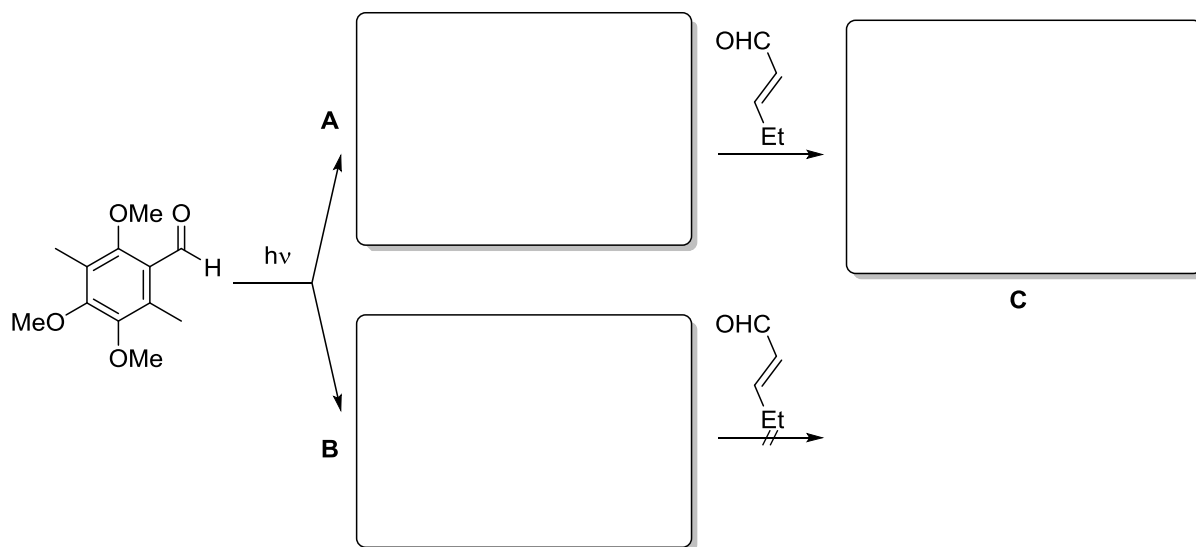
1. Die Klausur besteht aus insgesamt 10 Blättern (Deckblatt plus 9 Aufgabenblätter). Bitte kontrollieren Sie sofort, ob die Klausurunterlagen vollständig sind.
2. Es dürfen nur die vordruckten Bögen (einschließlich Rückseite) genutzt werden. Antworten sind zu kennzeichnen, sonst werden sie nicht bewertet. 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 10 sheets (cover page, plus 9 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.

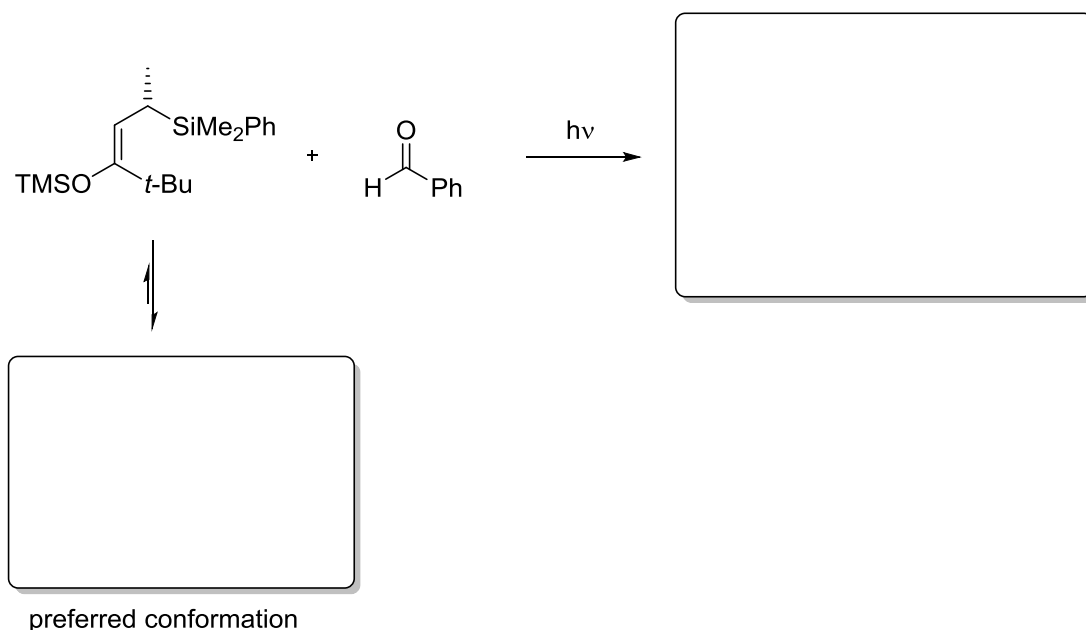
1. In the reaction given below irradiation of the aromatic aldehyde leads to the formation of two isomers **A** and **B** which have the same connectivity but different configuration. Isomer **A** can be trapped with an electron-deficient olefin in a thermal reaction to form cycloaddition product **C** in a regioselective and diastereoselective way. Isomer **B**, however, does not react in this transformation.

a) Give the structure of the intermediates **A** and **B** and of the product **C**. (8 points)



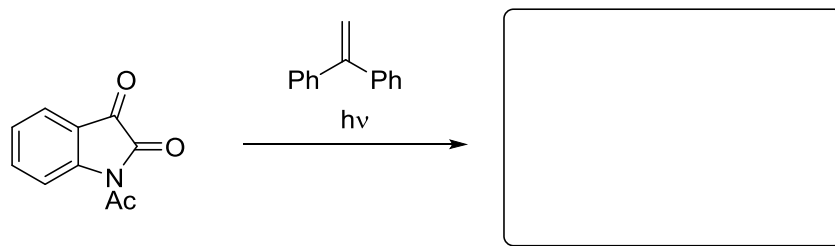
b) Why can intermediate **B** not be trapped in contrast to intermediate **A**? (1 point)

2. Draw the product of the following Paternò-Büchi reaction and explain the facial diastereoselectivity by giving the preferred conformation of the reacting olefin. (5 points)

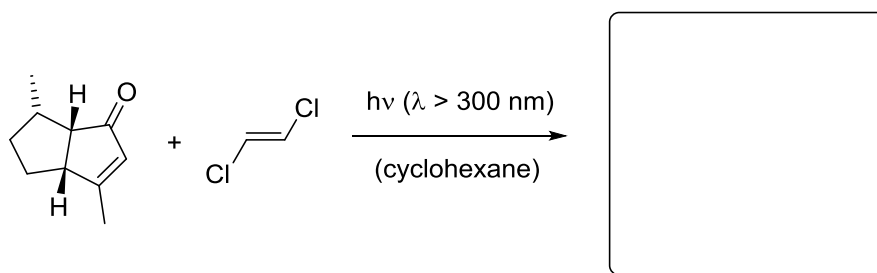


3. In the following intermolecular photocycloadditions, give the expected products with the correct regio- and diastereoselectivity where applicable. (9 points)

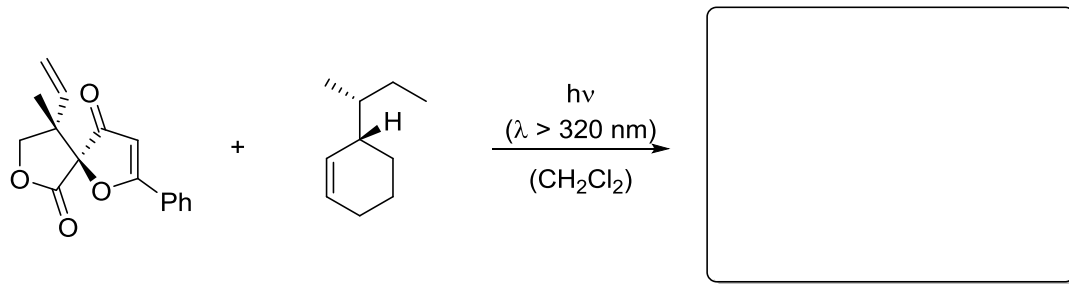
a)



b) Hint: the stereocenters bearing the chlorine atoms cannot be defined.



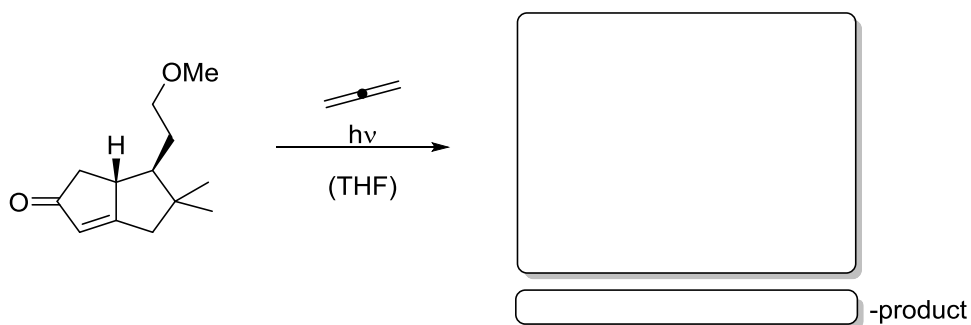
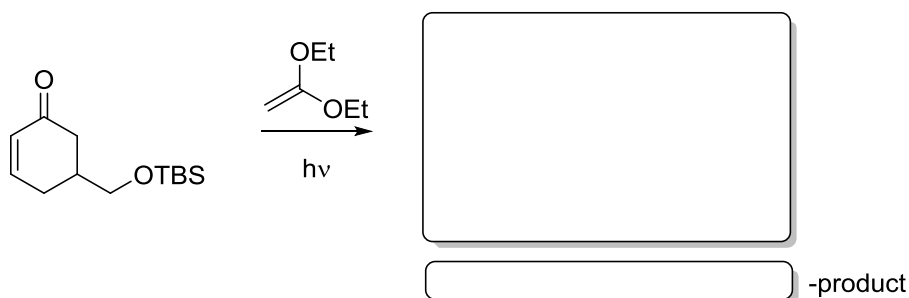
c) Hint: regioselectivity is determined by large substituents avoiding each other.



4. For donor- or acceptor-substituted olefins, the regioselectivity of photocycloaddition reactions needs to be taken into account. Depending on the connectivity of the product, the two terms “head-to-head” and “head-to-tail” are used to describe the different products.

a) Give the products of the following [2+2] photocycloaddition reactions and classify the obtained products. (7 points)

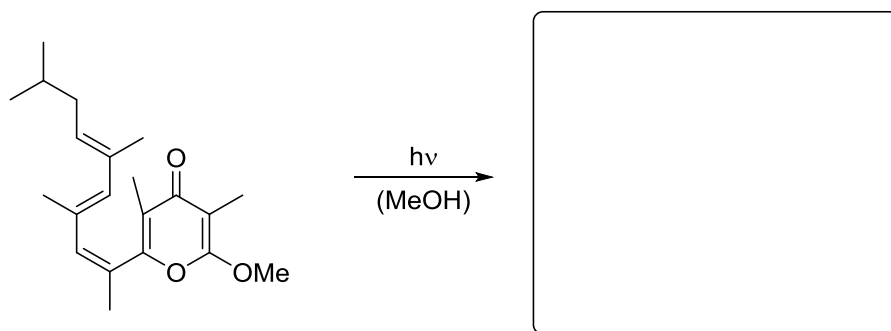
Hint: allenes show a reactivity similar to acceptor-substituted olefins.



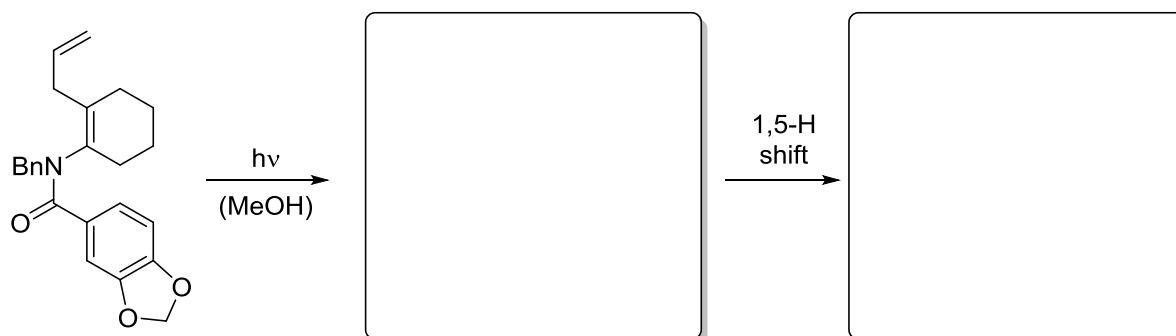
b) Briefly explain the observed regioselectivity of the addition in the first reaction. (2 points)

5. Photocyclisations constitute a simple method for the construction of annelated ring systems. Apart from trienes, enamides may also be used as substrates leading, after a hydrogen shift, to dihydropyridones. In the examples below, give the products with the correct relative stereochemistry. (8 points)

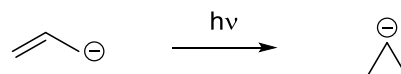
a)



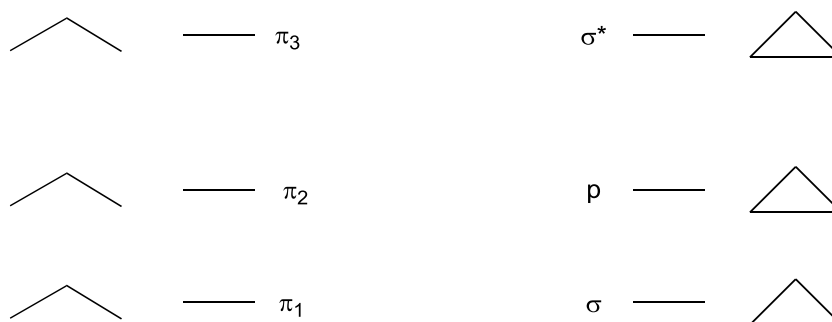
b)



- c) Upon irradiation, the allyl anion may cyclize to the cyclopropyl anion as depicted in the scheme below. Is the conrotatory ring closure photochemically allowed? (10 points)

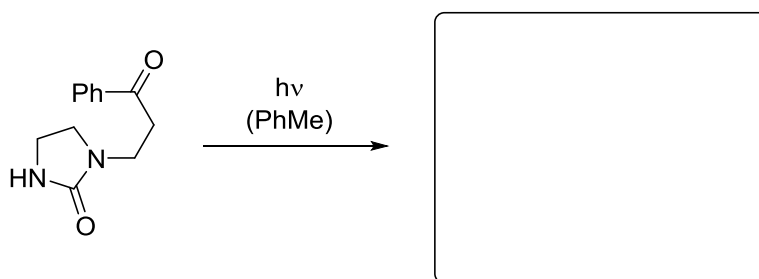


To analyze the reaction, draw the molecular orbitals of the starting material and the corresponding orbitals in the product. Determine if they are symmetric (S) or antisymmetric (A) regarding the symmetry operation of the conrotatory ring closure ( $C_2$  axis). How many electrons occupy the symmetric and antisymmetric molecular orbitals in the starting material and in the product in the first excited singlet state? Is the conrotatory ring closure photochemically allowed? Justify your decision.



6. Simple carbonyl compounds can only undergo a limited range of reactions, one of which is very often used to form four- to six-membered rings.

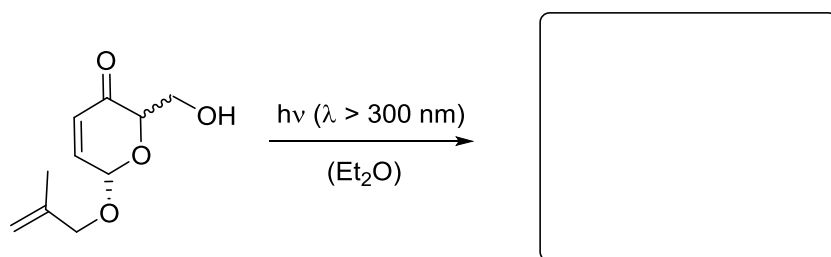
- a) Give the product of the following reaction. (3 points)



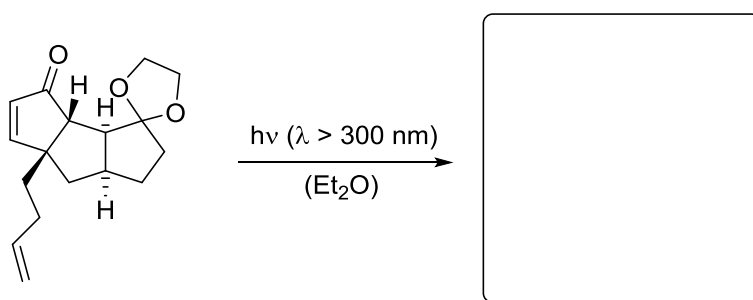
b) Draw the structure of the intermediate which is formed in the first step of the photoreaction. Give a short explanation why this intermediate cannot undergo a Norrish type II cleavage as a side reaction. (3 points)

7. In the following intramolecular photocycloadditions, give the expected products. Pay attention to the correct diastereoselectivity. (8 points)

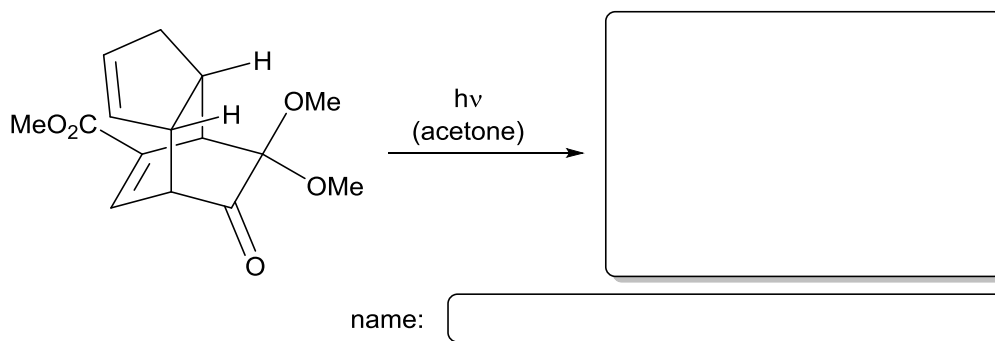
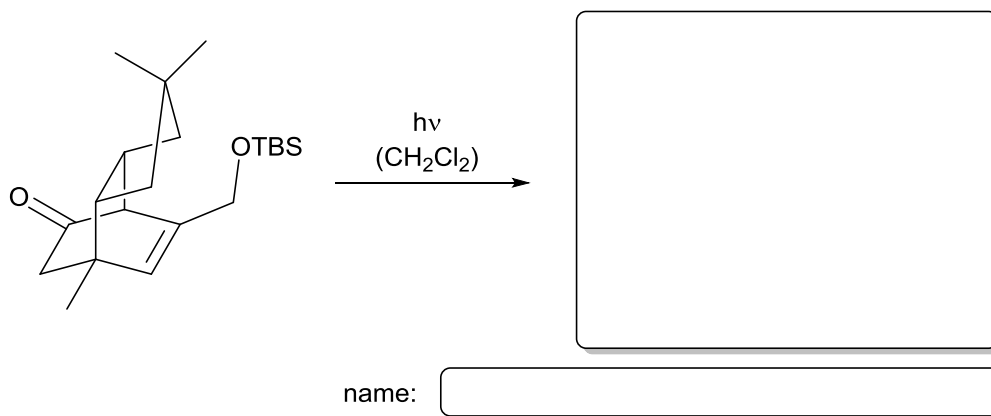
a)



b)



8. Draw the products of the following photochemical reactions in the correct relative configuration. What are the names of these photoreactions? (10 points)

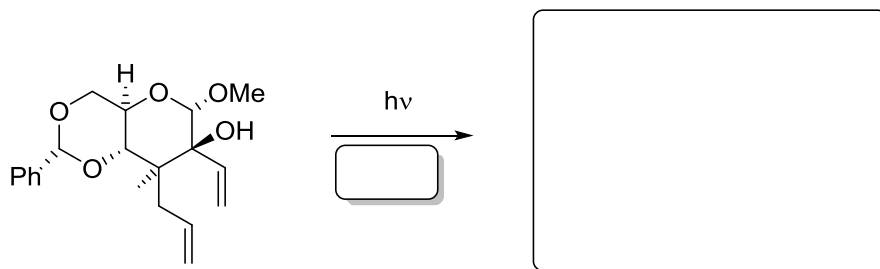


b) Although the chromophore of the two precursors is the same, different photoreactions occur. What is the most important difference between these two reactions? Give a short explanation. (3 points)

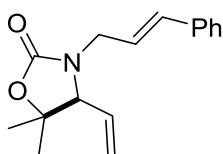


9. Photoreactions of isolated, non-activated double bonds are only possible if certain conditions are applied.

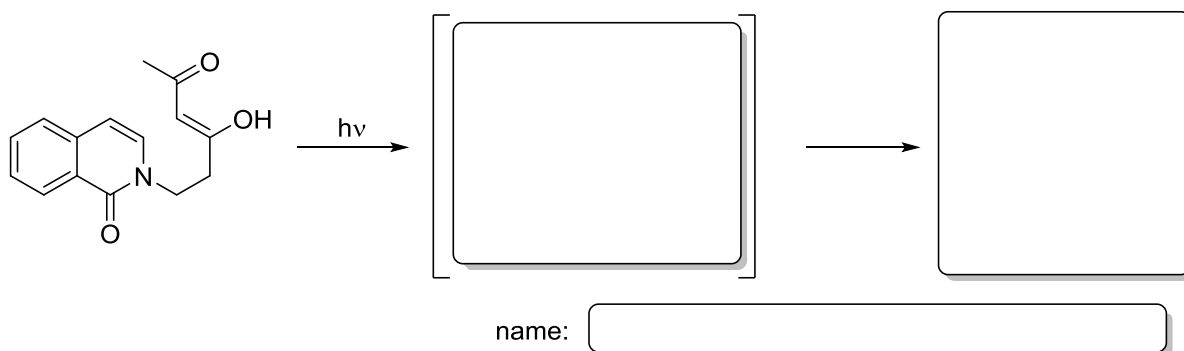
- a) In the reaction given below, draw the expected product and give the reagent (general form is sufficient) that enables this transformation. Briefly explain its role in the reaction. (6 points)



- b) Apart from the method given above, by what means can the photocycloaddition of the following substrate be enabled? Give the keyword and draw one exemplary reagent that can be used for the reaction. Which non-productive side reaction may occur? (3 points)



10. The photocycloaddition of enolizable 1,3-diketones leads, after a consecutive reaction, to products lacking the typical cyclobutane retron. In the following transformation, the substrate is converted to a primary photoproduct, which immediately undergoes a ring-opening reaction to release the high ring strain. Give the intermediary and the final product and name this reaction sequence. (6 points)



11. The *meta*-photocycloaddition is a very powerful reaction since it allows for the construction of highly complex skeletons from planar precursors. The reaction given below was used as the first step in the total synthesis of Crinipellin B. After irradiation of the starting material, two regioisomeric products were obtained as a 1:1 mixture. Give the products with the correct relative stereochemistry (the effect of the allylic stereocenter may be neglected). (8 points)

