Organische Chemie IV: Organische Photochemie

Wintersemester 2016/17 – Technische Universität München

Klausur am 17.02.2016

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

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

.....
(Eigenhändige Unterschrift)

1	2	3	4	5	6	7	8	9	10	11	12	13	Σ	Note

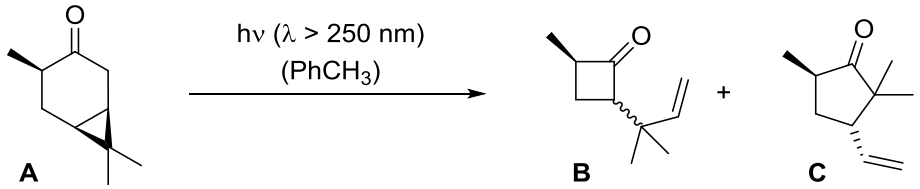
Hinweise zur Klausur:

1. Die Klausur besteht aus insgesamt 7 Blättern (Deckblatt plus 6 Aufgabenblätter). Bitte kontrollieren Sie sofort, ob die Klausurunterlagen vollständig sind.
2. Es dürfen nur die vorgedruckten 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.

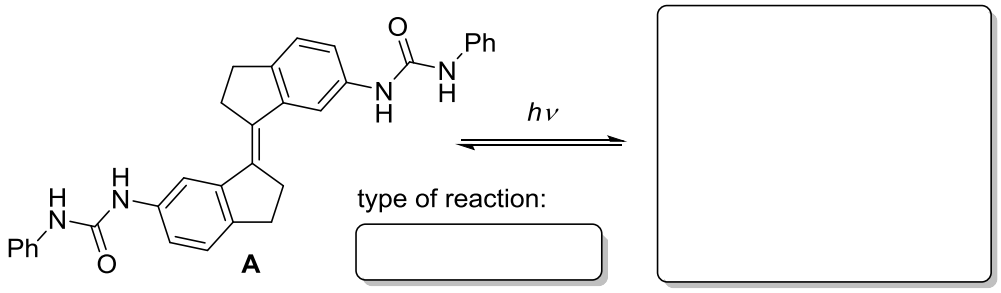
Information

1. The exam is comprised of 7 sheets (cover page, plus 6 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.

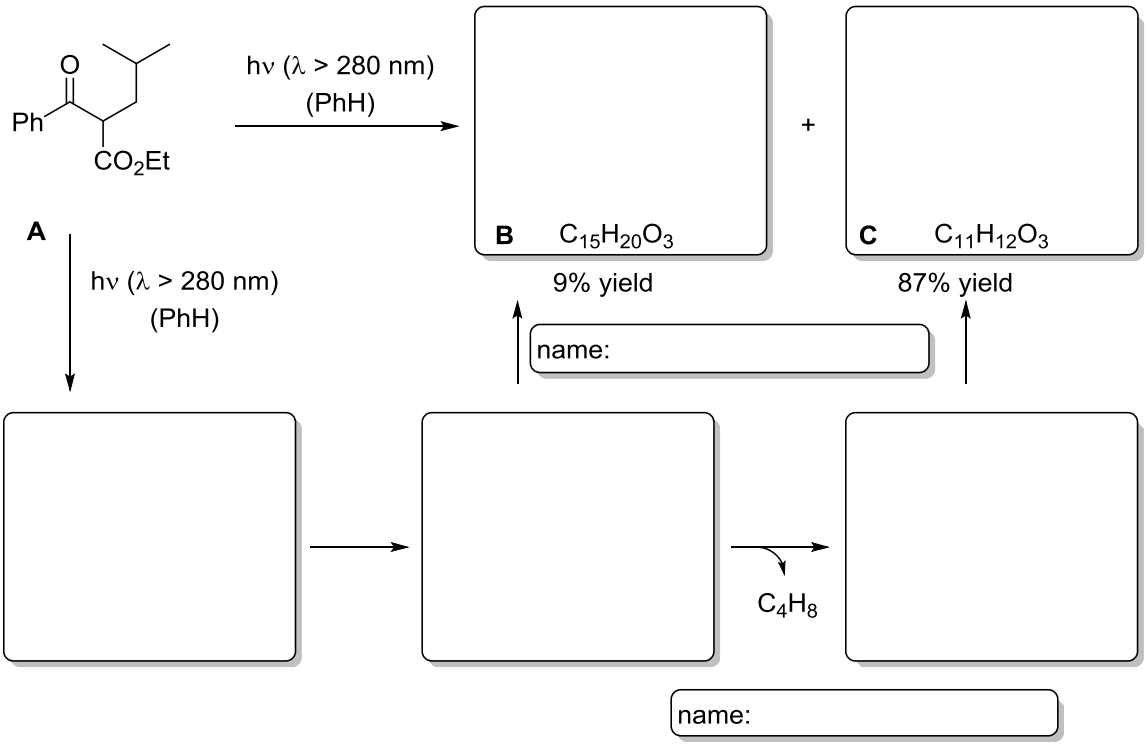
1. Irradiation of compound **A** with a Hanovia 200 W high-pressure mercury lamp yields the cyclobutanone derivative **B** and the cyclopentanone derivative **C**. Propose a reasonable mechanism for the formation of both products (including electron arrows and at least <u>three</u> intermediates) and explain which product (**B** or **C**) should be preferably formed (7 points).



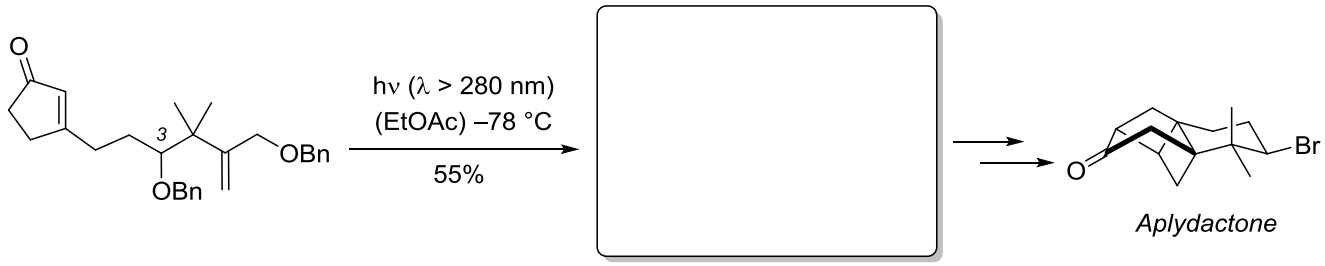
2. The bis-urea receptor **A** can coordinate to anions such as dihydrogen phosphate and acetate. The affinity can be intensified upon irradiation. Please draw the missing structure. (4 points)



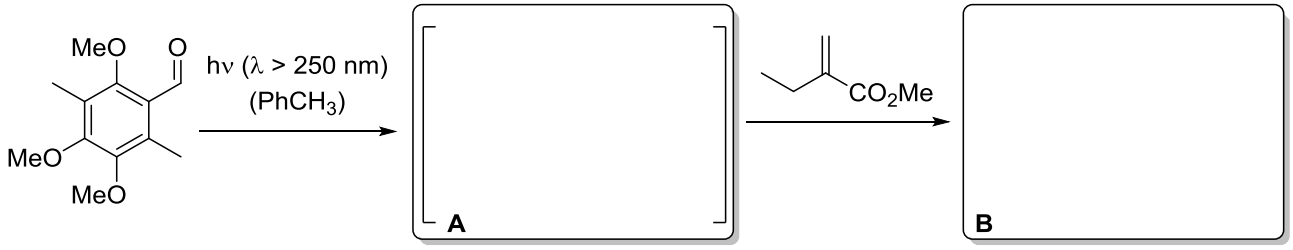
3. Irradiation of compound **A** with a Hanovia 450 W high-pressure mercury lamp through a Pyrex® filter gave a mixture of two UV-active compounds **B** and **C**. Propose a reasonable mechanism for the formation of both products (including electron arrows and the <u>three</u> intermediates). You can neglect the relative configuration. (10 points)



4. On their way to the natural product *Aplydactone* the *Trauner* group used a photochemical key step to form the skeleton of this highly strained sesquiterpenoid. Give the main product of this transformation with the cyclobutane relative configuration. Hint: You can neglect the relative configuration of <u>carbon atom C-3</u> in the product. (5 points)

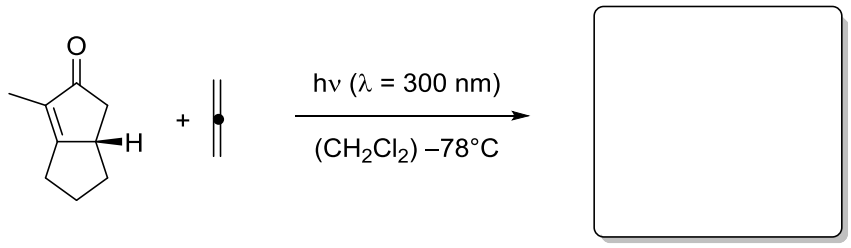


5. *Nicolaou* and *Gray* employed a photochemical step in their total synthesis of *Hybocarpone*. The intermediate **A** can be trapped with an electron-deficient olefin in a thermal reaction to form cycloaddition product **B** in a regioselective and diastereoselective way. Give the structure of the intermediate **A** and of the product **B**. (7 points)

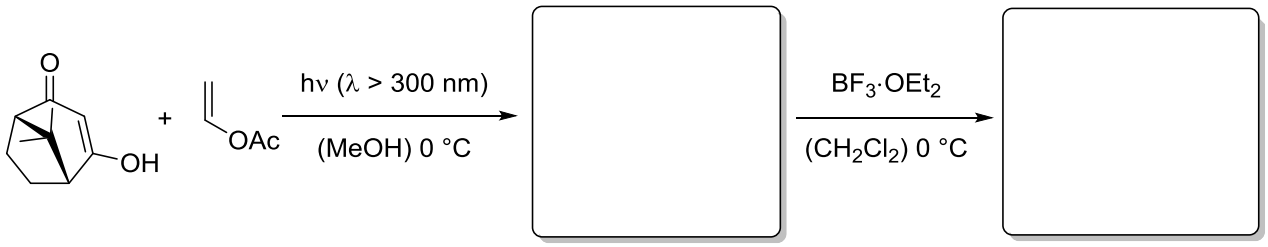


6. Fill in the missing structures of the following intermolecular reactions. (11 points)

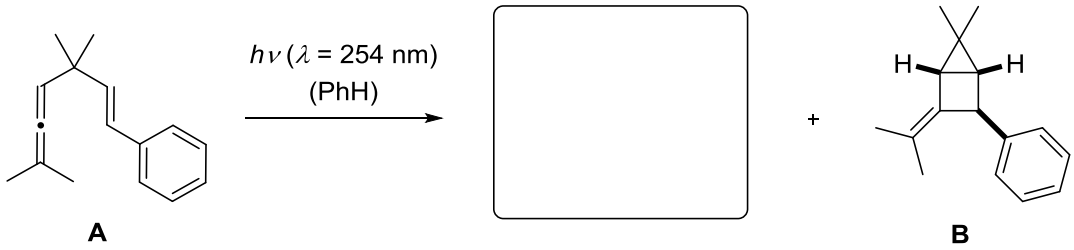
a) Hint: Allenes show similar behaviour as acceptor-substituted alkenes.



b) In this sequence the primary *endo* photoproduct is further converted into a bicyclic structure upon treatment with a *Lewis* acid.

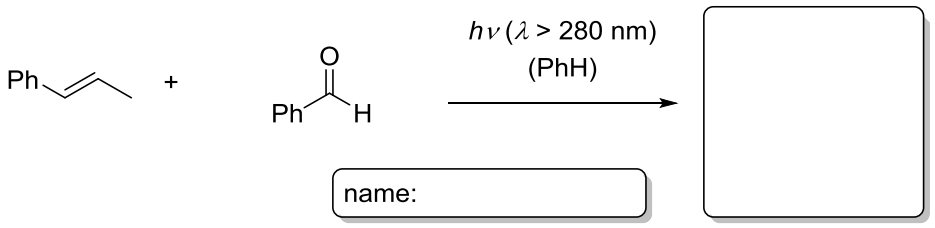


7. a) The irradiation of compound **A** was supposed to lead to the missing product. Interestingly, the major product found was compound **B**. How does the expected product look like? Please indicate the correct relative configuration. (3 points)



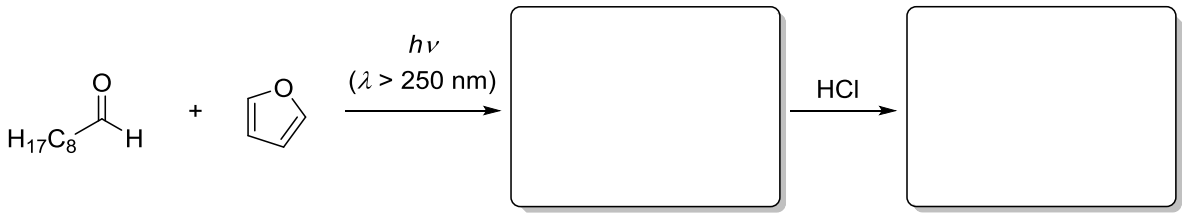
b) What kind of reaction occurred to form compound **B**? (1 point)

8. Benzaldehyde was irradiated in the presence of (*E*)-1-phenylpropene. Fill in the name of the reaction as well as the stable product with the correct relative configuration. (5 points)



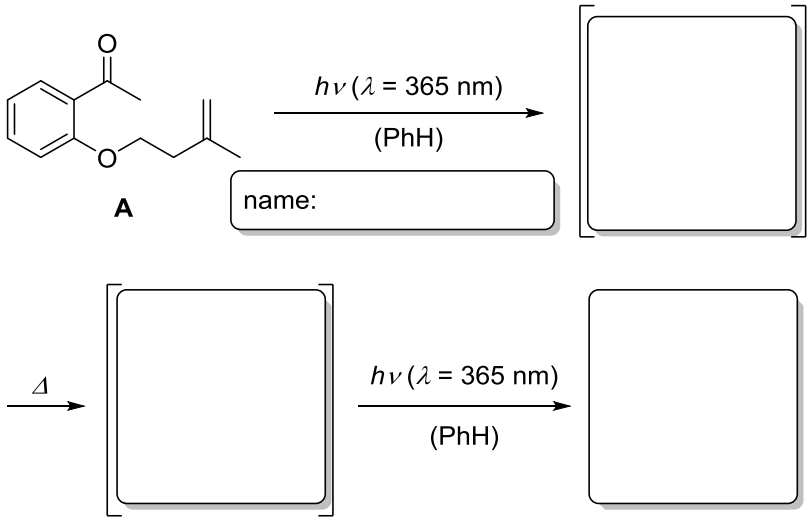
9. Irradiaton of furan in the presence of nonanal leads to an acetal. The formed acetal undergoes acid-catalyzed hydrolysis. (8 points)

a) Fill in the missing acetal as well as the final product with the correct relative configuration.

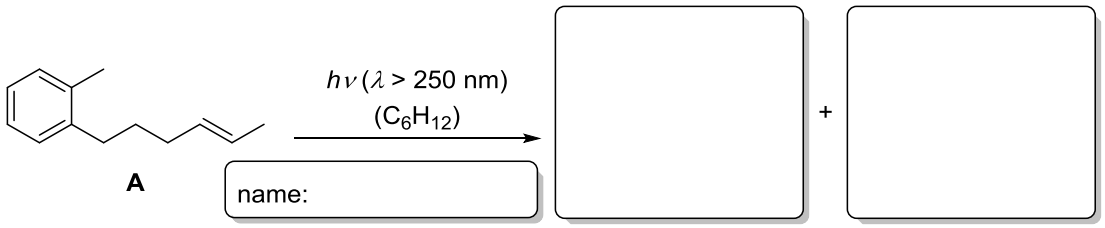


b) Explain briefly the observed regioselectivity in the first step.

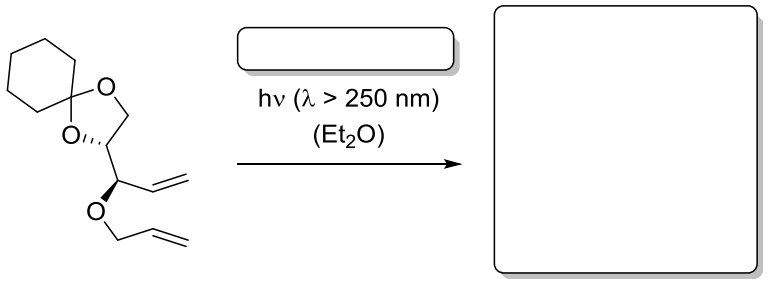
10. Irradiation of the acetophenone derivative **A** leads to a cascade of reactions including a photochemical and thermal reaction. Please draw the intermediates and the product with the correct relative configuration. Name the type of the first reaction. (12 points)



11. In an intramolecular reaction, arene **A** reacts to form two different regioisomers. Which reaction type is involved? (11 points)

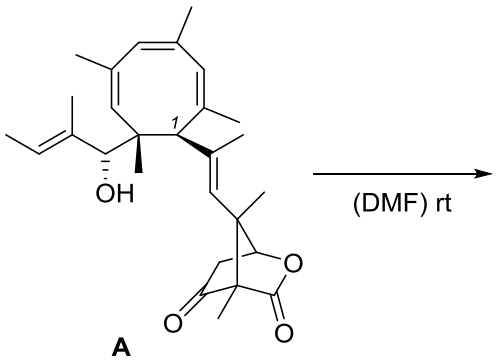


12. To undergo a [2+2]-photocycloaddition reaction alkenes need to be activated by a metal-based catalyst. Please give a typical metal salt and draw the missing structure with the correct relative configuration. (5 points)



13. The total synthesis of *shimalactone A* was achieved by a disrotatory [6π] cyclisation of the cyclooctatrien **A** under thermal conditions. (11 points)

a) Draw the right structure of *shimalactone A*. Hint: For the observed diastereoselectivity only pay attention to the tertiary stereogenic center at carbon atom C-1 and assume that a methyl group is sterically more demanding than the formed carbocycle.



b) Analyze this reaction with respect to the Woodward-Hoffmann rules and show that the disrotatory [6π] cyclisation is thermally allowed. Therefore, first draw all the molecular orbitals with the correct phase in the scheme given below and fill in the appropriate number of electrons. Then, assign the symmetry of each orbital to a mirror plane.