Organische Chemie IV: Organische Photochemie

Wintersemester 2015/16 – Technische Universität München

Klausur am 19.02.2016

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:

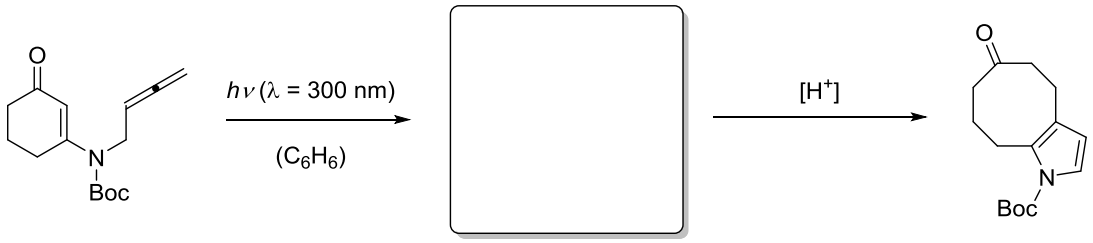
1. Die Klausur besteht aus insgesamt 7 Blättern (Deckblatt plus 6 Aufgabenblätter). Bitte kontrollieren Sie sofort, ob die Klausurunterlagen vollständig sind.
2. Es dürfen nur die vorgedruckten Bögen (einschließlich Rückseite) genutzt werden. Antworten sind zu kennzeichnen, sonst werden sie nicht bewertet. 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.

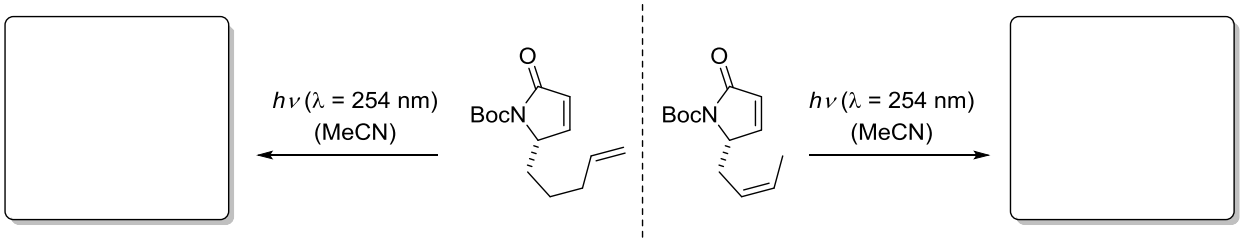
1. Complete the following intramolecular [2+2]-photocycloaddition reactions and define the relative configuration where necessary. Also classify the sequence of part a) by comparing it to a well-known photochemical name reaction. (13 points)

a)

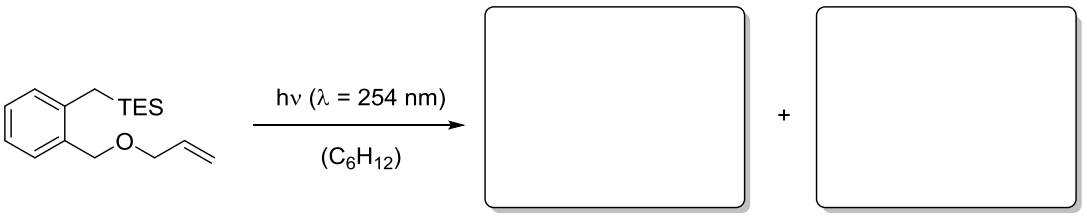


Name:

b)



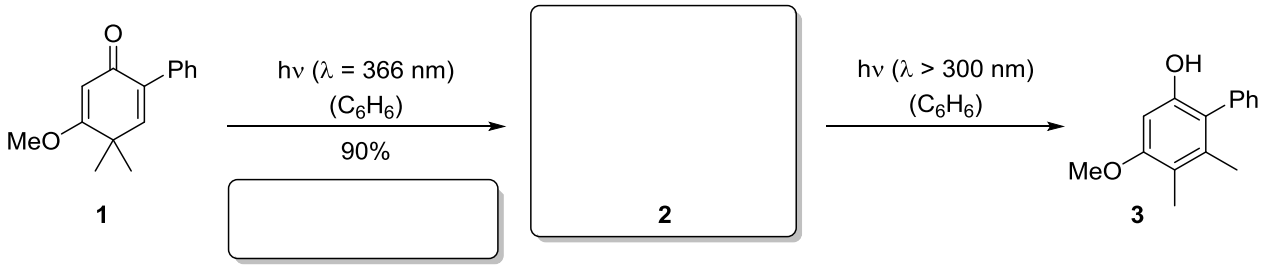
2. Irradiation of the shown *ortho*-substituted benzene results in the formation of two isomeric polycyclic compounds. Draw the structures of the photoproducts using a triquinane skeleton and consider the occurring diastereoselectivity. (8 points)



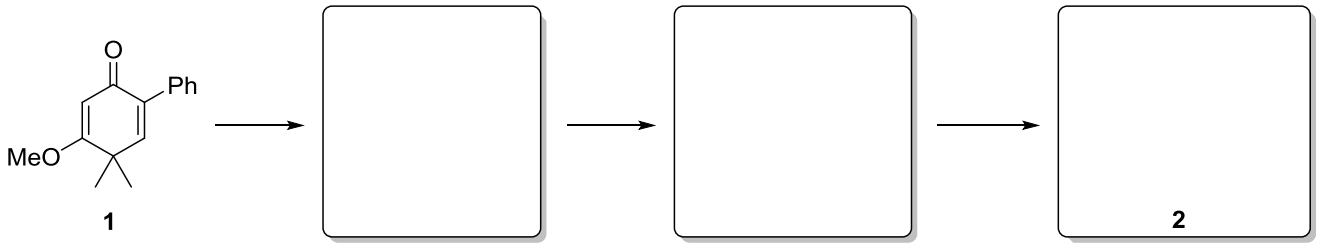
TES = $SiEt_3$

3. Irradiation of compound **1** yields a rearrangement product in 90% yield. Further irradiation of **2** through Pyrex glass results in a type B photorearrangement to give phenol **3**.

a) Draw the respective intermediate with the correct relative configuration and give the name of the first reaction. (4 points)

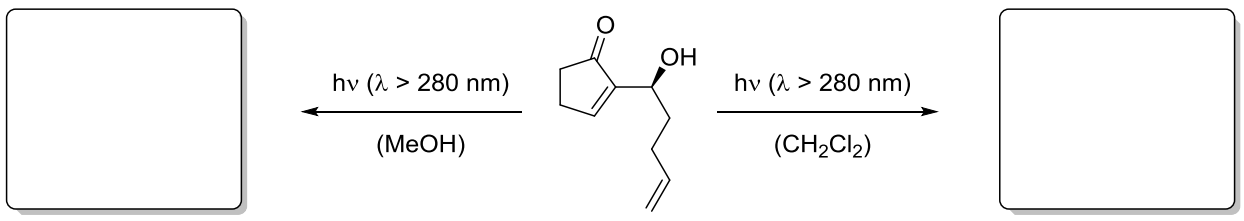


b) Suggest a mechanism for the formation of **2** and explain briefly why this product is formed. (5 points)



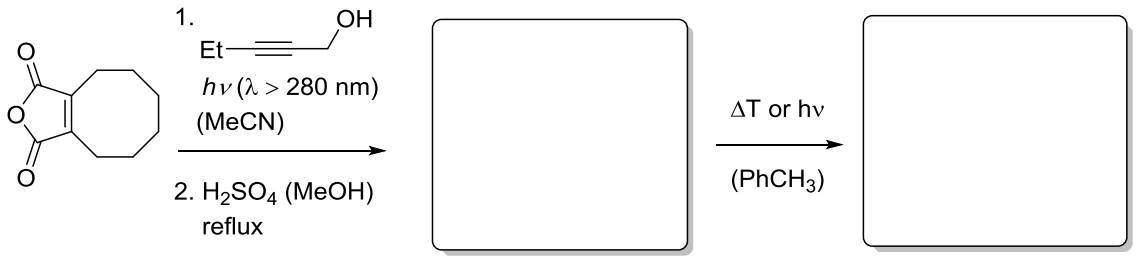
4. In many photochemical transformations, particularly in the example shown here, the choice of the solvent is crucial for the reaction outcome. Try to determine the important difference of the chosen solvents and consider how they can influence the diastereoselectivity. (6 points)

Hint: In Methanol there is no intramolecular hydrogen bond formation.

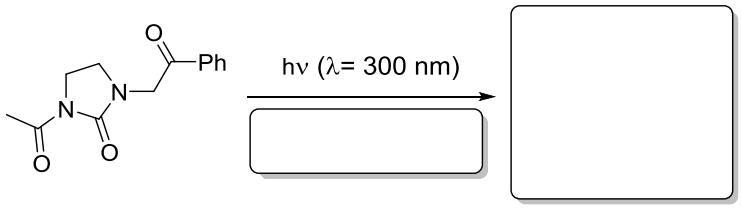


5. Photocycloaddition reactions of maleic anhydride derivates with alkynes can be utilized to construct highly strained ring systems. They can further undergo a conrotatory electrocyclic ring opening to yield cyclic structures with ring sizes up to 17 members. Give the structure of the intermediate and product. Does the conrotatory ring opening occur photochemically or thermally? (9 points)

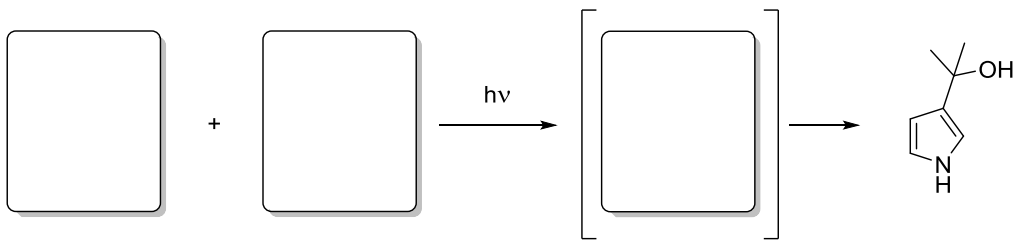
Hint: Only one product is observed due to lactone formation.



6. Draw the product of the following intramolecular photoreaction with the correct relative configuration and name the reaction. (5 points)

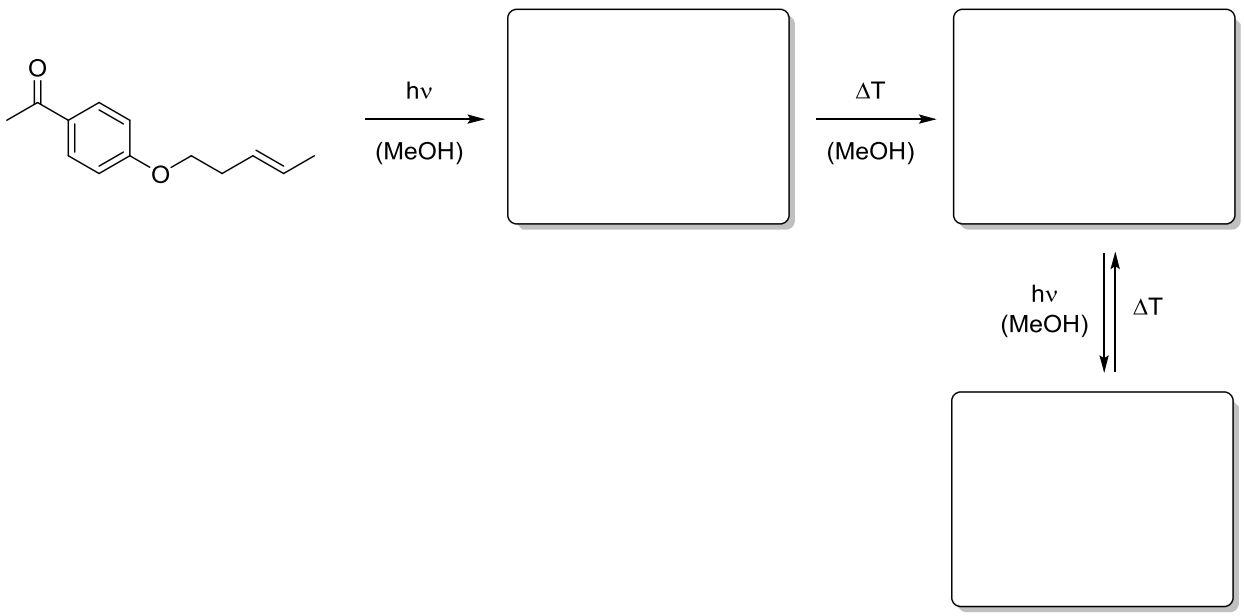


7. In the synthesis of 3-substituted pyrroles a Paternò-Büchi reaction has been applied. Fill in the missing starting materials and the oxetane intermediate. (6 points)



8. The group of *Wagner* stumbled across an interesting reaction cascade in which they combine photochemical and thermal transformations to get access to strained tricyclic scaffolds in a diastereoselective manner. Complete the reaction sequence by showing both intermediates and the final product. (9 points)

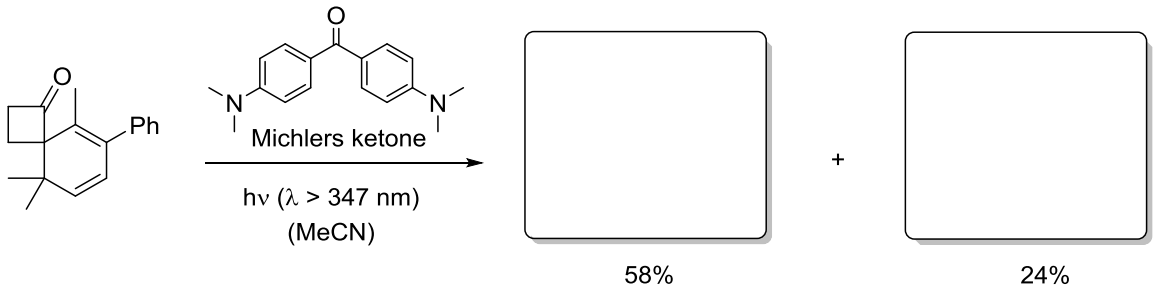
Hint: The final product contains two quarternary brigdehead carbon atoms.



9. *E,Z*-Isomerizations of alkenes can be initiated both thermally and photochemically. After equilibration, a thermal process delivers a mixture of the two isomers which reflects their relative thermodynamic stabilities. In contrast, the ratio of the photoisomerization of an alkene is affected by different characteristic properties. Give two properties on which the ratio in the photostationary state (PSS) depends and explain briefly how the formation of a large excess of the thermodynamically less stable *Z*-isomer in a photochemical reaction can be explained. (3 points)

10. The shown spirocyclobutanone forms two products after irradiation in the presence of Michlers ketone.

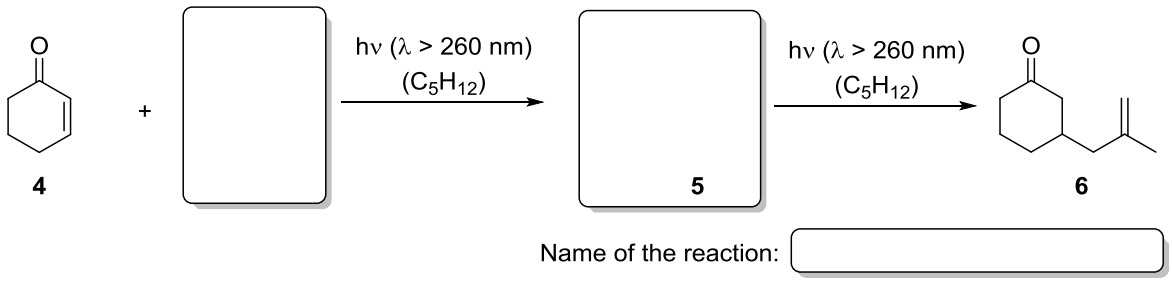
a) Draw the structures of the products without discussion of the relative configuration. Hint: Both products contain a cyclopropane ring. (4 points)



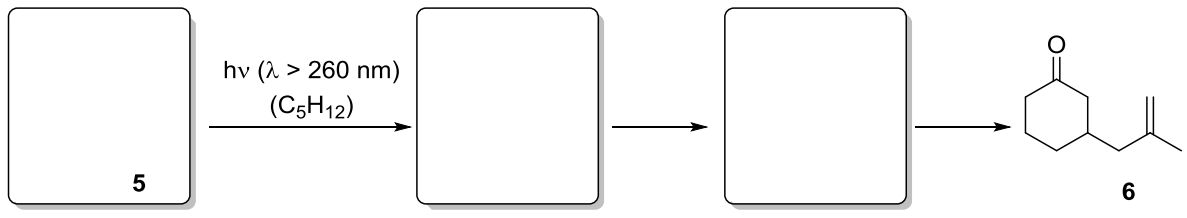
b) What important role does Michlers ketone play in this reaction and which side reaction could occur without the use of this additive? (2 points)

11. The photochemical reactions of 2-cyclohexenone and other derivatives was extensively studied by Corey and coworkers in the 1960s. During these studies they observed a product the formation of which can be explained by a fragmentation.

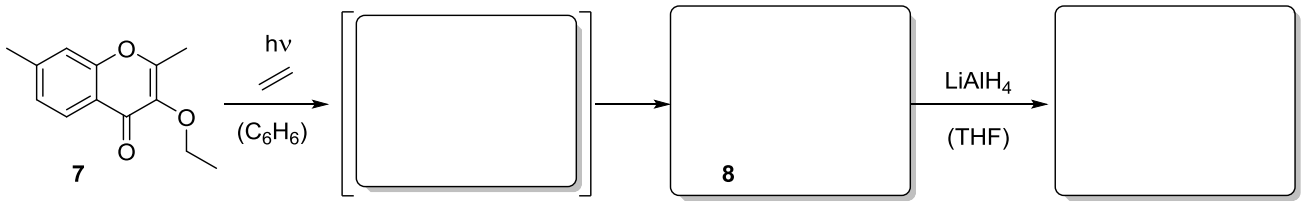
a) Draw the structure of the missing starting material and the product **5** with the correct relative configuration and give the name of the second cleavage reaction. (7 points)



c) Give a mechanistic explanation of how compound **5** is converted into compound **6**. (4 points)



12. Irradiation of compound **7** leads to a photoproduct which undergoes a further transformation without being isolated. The obtained oxetane product **8** is further treated with $LiAlH_4$. Complete the reaction sequence and consider the correct relative configuration of the products. (8 points)



13. Irradiation of the crystalline compound **9** leads to an enantiomerically pure product. Draw the expected product as well as the intermediate with the correct absolute configuration. Performing this reaction in solution may cause a problem. Which? (7 points)

Hint: CO is evolved as by-product.