Organische Chemie IV: Organische Photochemie

Wintersemester 2009/10 – Technische Universität München

Klausur am 18.02.2010

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

geboren am .....…… in .....

.....
(Eigenhändige Unterschrift)

1	2	3	4	5	6	7	8	9	10	11	Σ	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 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.

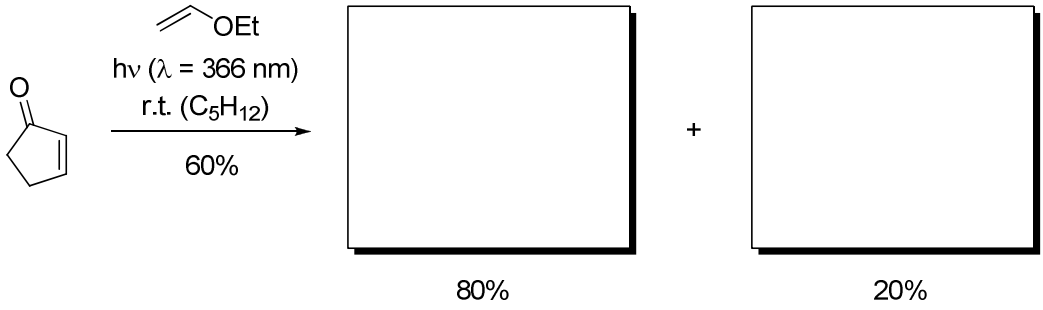
Information

1. The exam is comprised of 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.

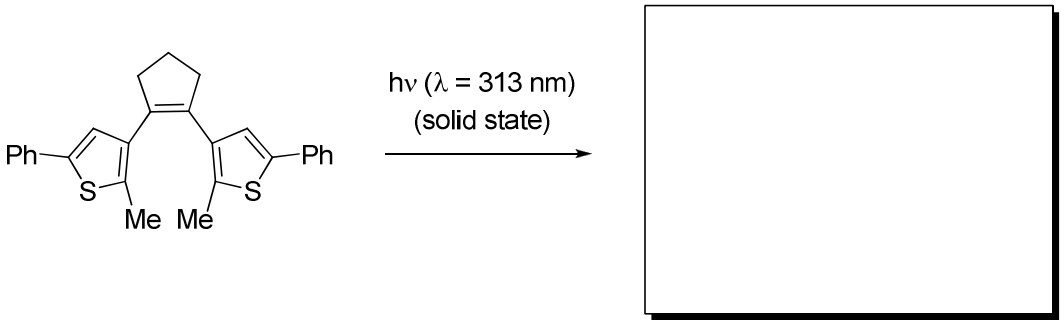
Give the expected main products in the following reactions. Pay attention to the regio- and stereoselectivity!

a) Which two regioisomers are formed?



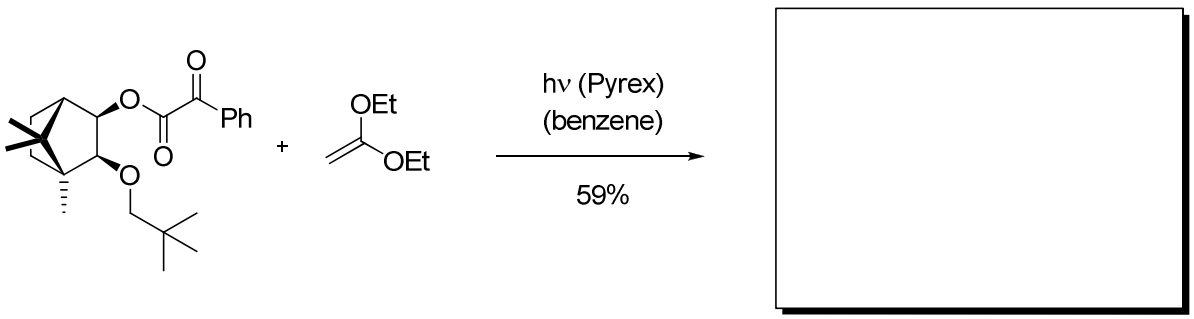
(/ 5)

b)



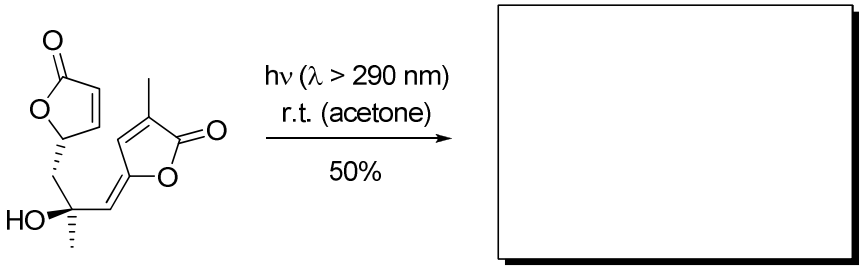
(/ 2)

c)



(/ 3)

d)

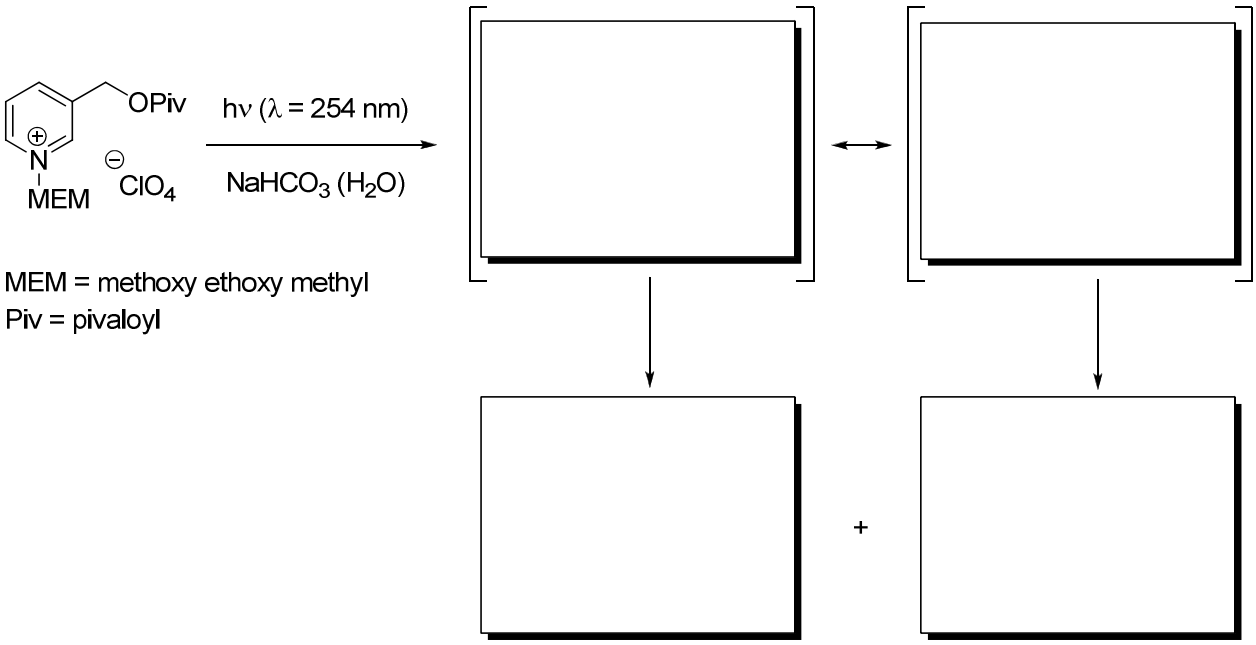


(/ 3)

(/ 13)

2.

If a pyridininum salt with an alkylated nitrogen atom is irradiated, the generated aziridine can be isolated.



MEM = methoxy ethoxy methyl
Piv = pivaloyl

a) Draw the two resonance forms of the intermediate cation that is formed upon photocyclisation.

b) Give the structures of the isolated aziridines.

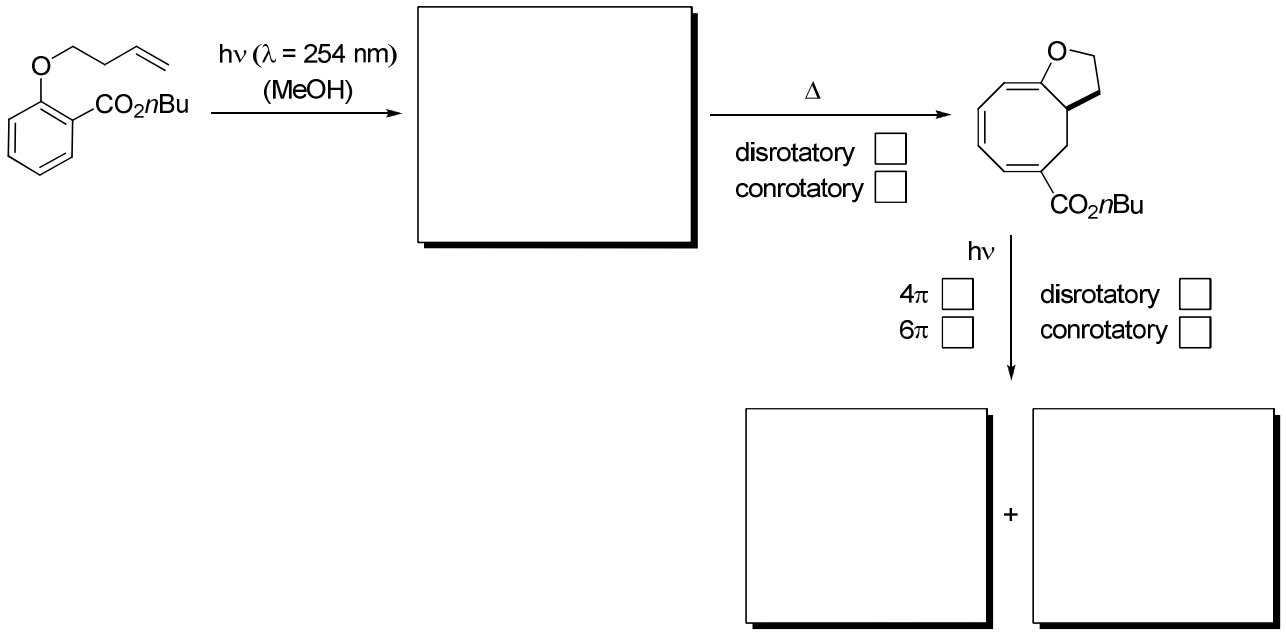
(/ 8)

3.

Name two possible ways to carry out enantioselective photoreactions. No structures needed!

(/ 2)

4.



a) Draw the structure of the primary photoproduct.

(/ 3)

b) This undergoes a thermally promoted ring opening reaction. Is this a disrotatory on conrotatory process? Tick the correct box.

(/ 1)

c) The ring opened product undergoes a photochemically induced process to afford two regioisomeric products. Draw the products and tick the boxes that correctly describe this reaction.

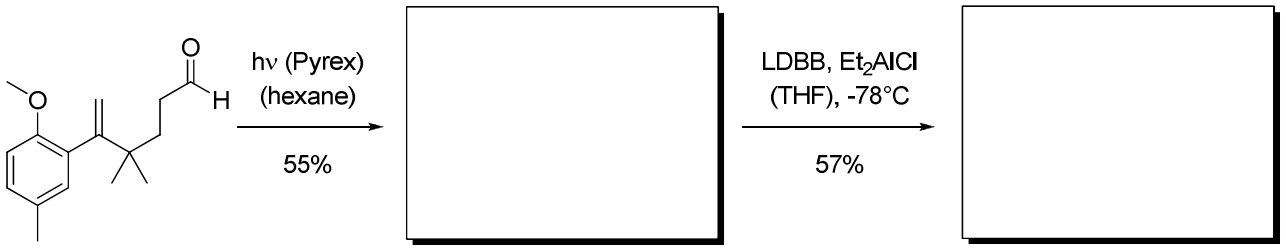
(/ 8)

_____

(/ 12)

5.

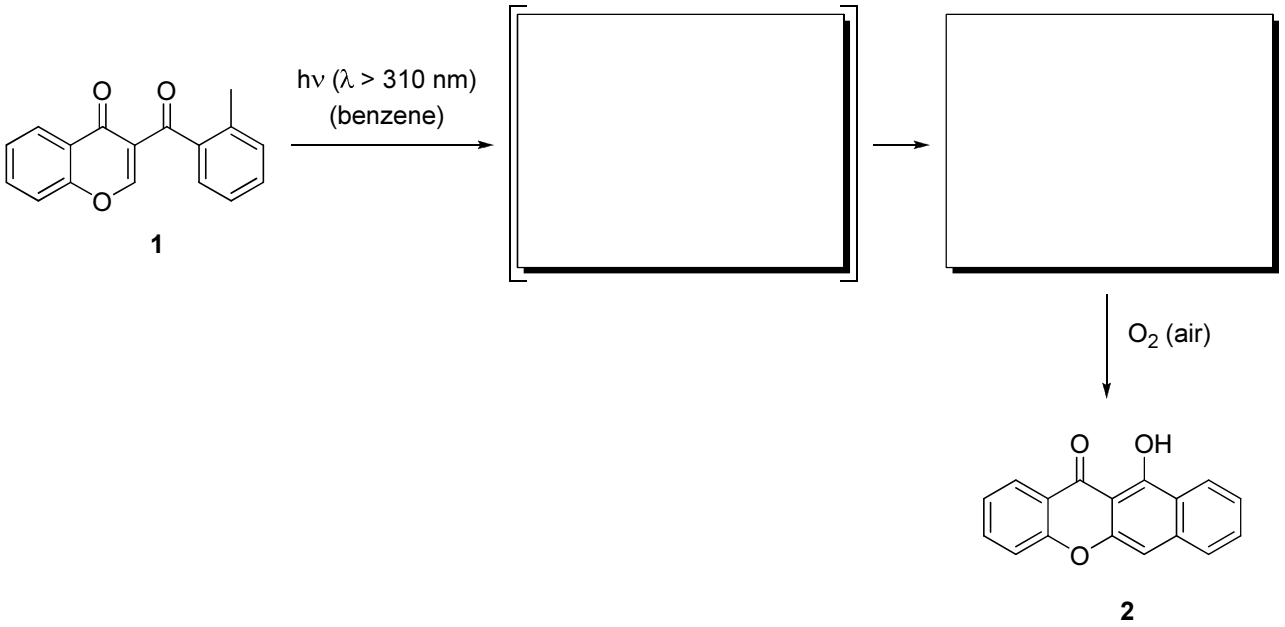
Which products do you expect from the following sequence?
LDBB = Lithium-4,4'-di-tert-butylbiphenyliden = Li(0)



(/ 4)

6.

Upon irradiation, the chromone **1** forms an intermediate that cyclizes to give a tetracycle. This product is subsequently oxidized by atmospheric oxygen.



1 **2**

a) Draw the intermediate and the tetracycle that is formed prior to oxidation.

(/ 5)

b) Explain mechanistically how the intermediate (i.e. the compound in brackets) is formed.

(/ 3)

c) The cyclisation of the intermediate is a

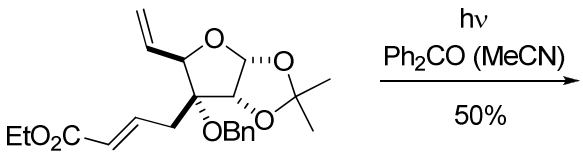
- ☐ 4π cyclisation.
- ☐ 6π cyclisation.
- ☐ 8π cyclisation.

(/ 1)

(/ 9)

7.

a) Give the product of the following reaction.



(/ 2)

b) Why was benzophenone added to the reaction mixture? Which wavelength would you use for this reaction?

(/ 2)

c) Explain the mechanism (energy diagram, name of mechanism) of this kind of [2+2]-photocycloaddition in detail.

(/ 6)

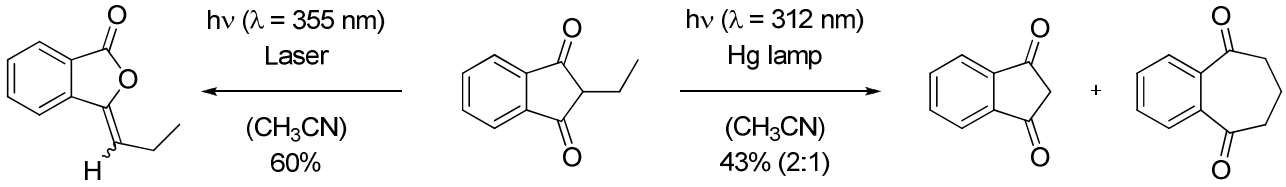
d) Name two alternative sensitizers and order them (incl. benzophenone) in order of their triplet energies. (e.g. A > benzophenone > B)

(/ 3)

(/ 13)

8.

Recently it was discovered that irradiation of the 1,3-indanedione **3** with a Laser or a Hg lamp gave rise to different products.



4 **3** **5** **6**

Draw a reasonable mechanism for each transformation and name the individual reactions.

a) **3 → 4**

(/ 5)

b) **3 → 5**

(/ 3)

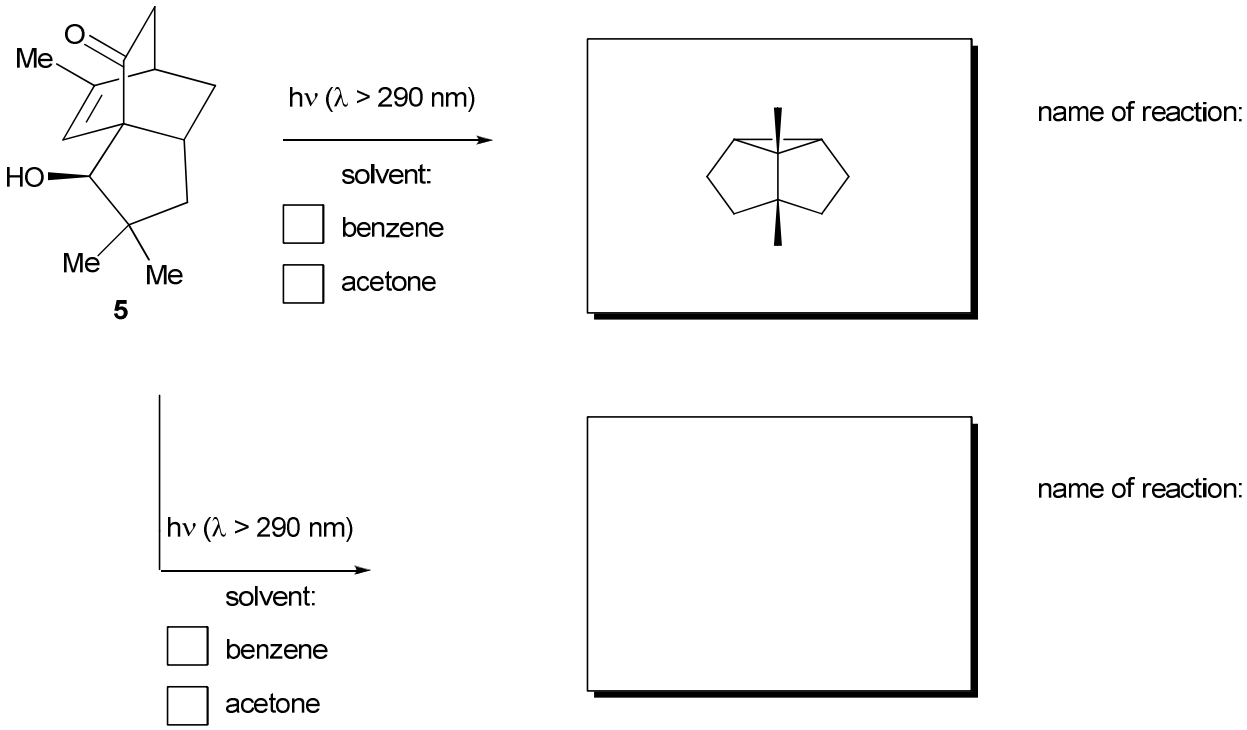
c) **3 → 6**

(/ 4)

(/ 12)

9.

The outcome of the irradiation of substrate **5** was highly dependent on the solvent. One of the reactions afforded a triquinane structrure, whereas another tricyclic compound was formed upon irradiation in a different solvent.



a) Tick the appropriate boxes representing the choice of the solvents and name the corresponding reaction.

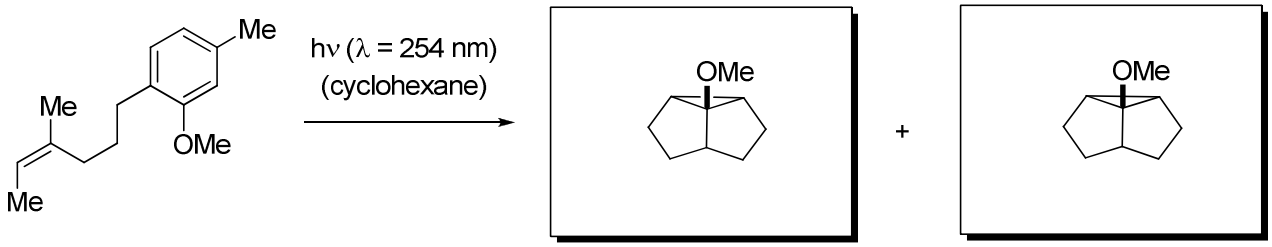
(/ 4)

b) Draw the structures of the products. Use the given diquinane core to display the structure of the triquinane. Don't forget to indicate the substituents at the solid wedged bonds!

(/ 6)

(/ 10)

10.



a) Why does this cycloaddition reaction occur at the positions *ortho* to the methoxy substituent rather than the methyl group?

(/ 1)

b) The configuration of the alkene is retained during this reaction. Explain why.

(/ 1)

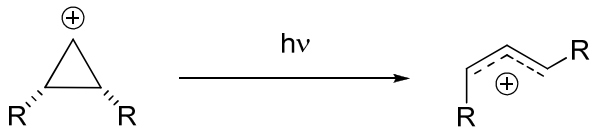
c) Complete the structures of the two photoproducts.

(/ 7)

_____

(/ 9)

11.



The photochemical ring opening of a cyclopropyl cation to an allyl cation occurs in a conrotatory manner.
Using the theory of conservation of orbital symmetry show why this process is photochemically allowed but thermally disallowed.

a) Draw the molecular orbitals of both the starting material and the product.

(/ 3)

b) Assign the symmetry of each molecular orbital. State whether this is assigned using mirror plane symmetry or C_2 symmetry.

(/ 3)

c) Using the diagram you have drawn, explain why this conrotatory process is photochemically allowed but thermally disallowed.

(/ 2)

_____

(/ 8)