Organische Chemie IV: Organische Photochemie

Wintersemester 2000/2001 – Technische Universität München

Klausur am 30.07.2004

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

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

.....
(Eigenhändige Unterschrift)

☐ The questions will be answered in english.

☐ Die Fragen werden auf Deutsch beantwortet.

1	2	3	4	5	6	7	S

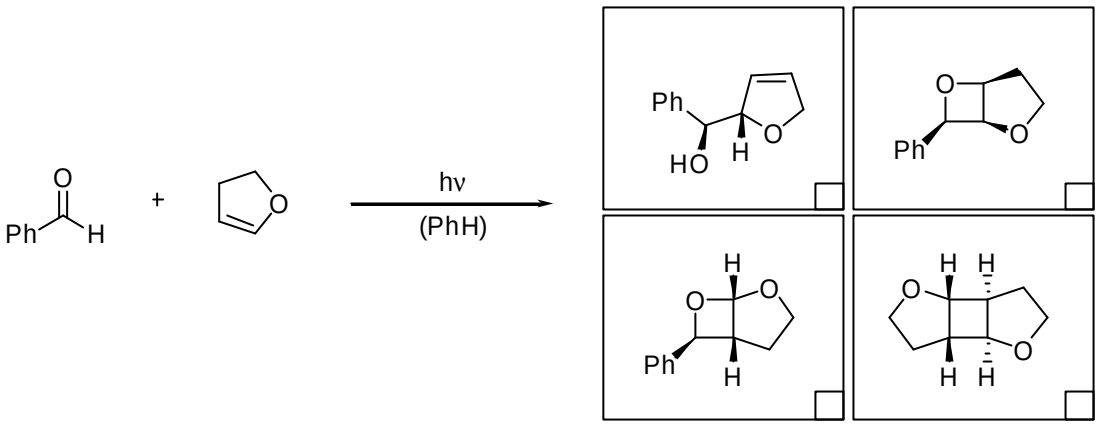
Hinweise zur Klausur:

1. Die Klausur besteht aus insgesamt 8 Blättern (Deckblatt plus 7 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.

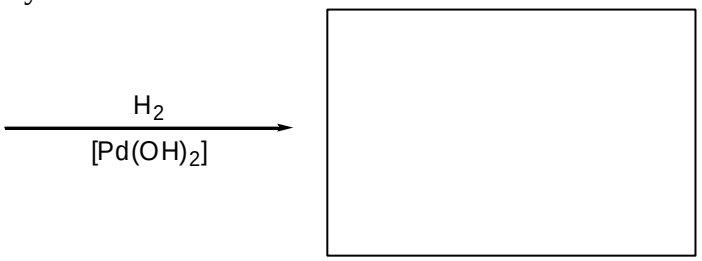
Information

1. The exam is comprised of 8 sheets (cover page, plus 7 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.

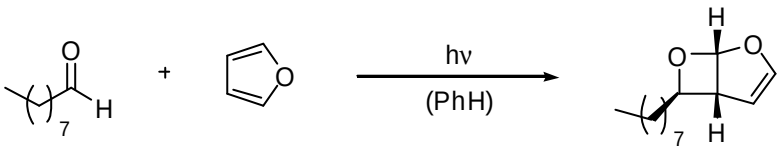
1. a) Only one of the depicted products is formed in the following *Paternò-Büchi* reaction. Select the expected product (mind the regioselectivity). (2)



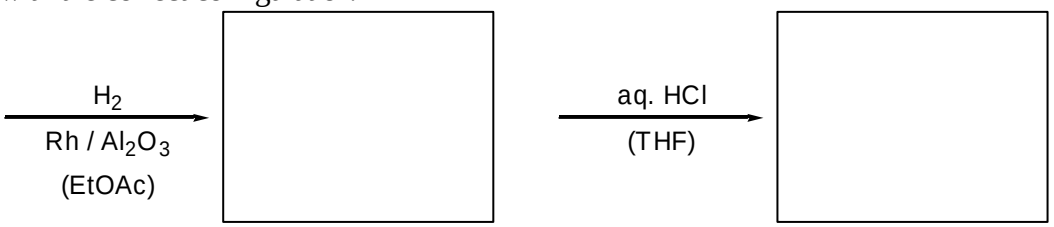
The product was further converted by selectively cleaving *one* Carbon-Oxygen bond hydrogenolytically. (3)



(b) The observed regio- and stereoselectivity is reversed using furane as alkene-component. Explain this observation with the mechanism of the *Paternò-Büchi* reaction. (6)

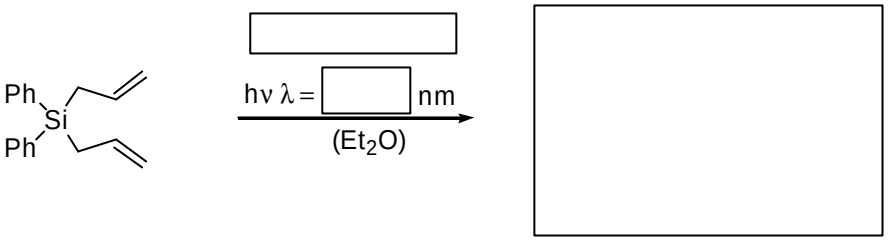


Again the product was further converted. In the first step the double bond was hydrogenated, the saturated product was then treated with acid. Give the intermediate and the final product with the correct configuration. (6)

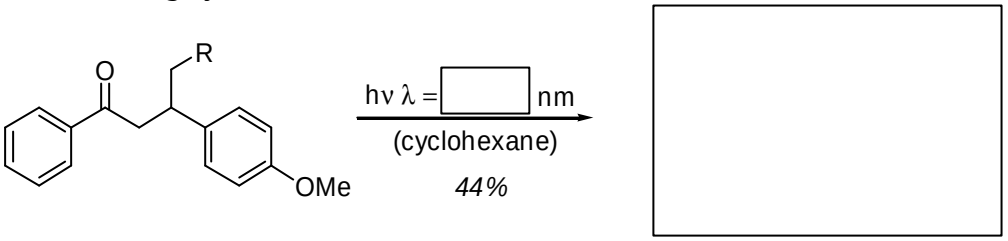


2. Fill in the products and conditions in the following photochemical reactions. Mind the *simple* diastereoselectivity.

a) Intramolecular [2+2]-photocycloaddition (6)

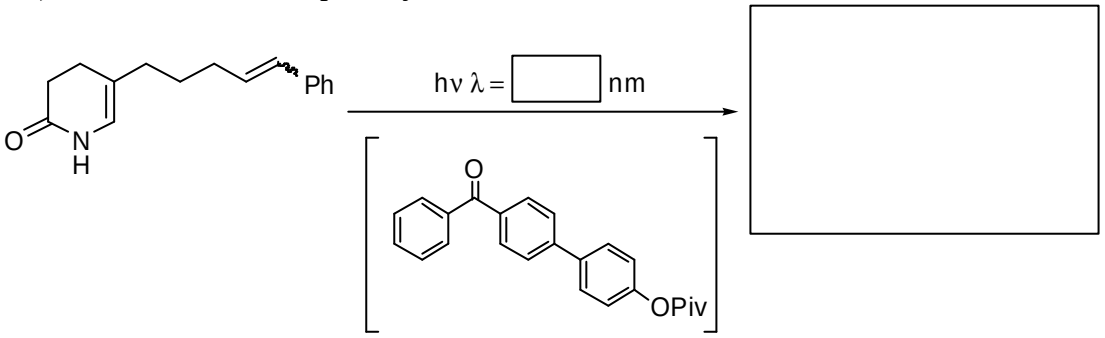


b) *Norrish-Yang* cyclization (5)

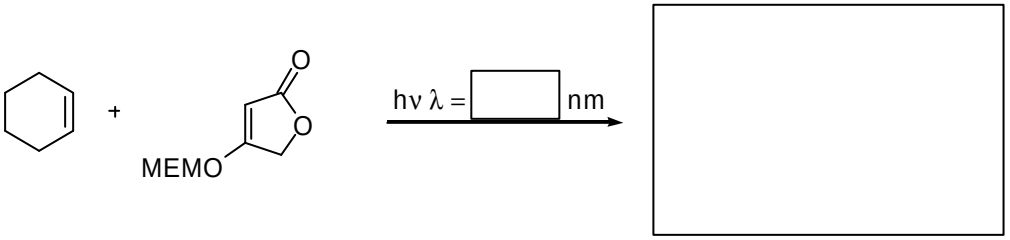


Name the side-reaction responsible for the observed low yield: (1)

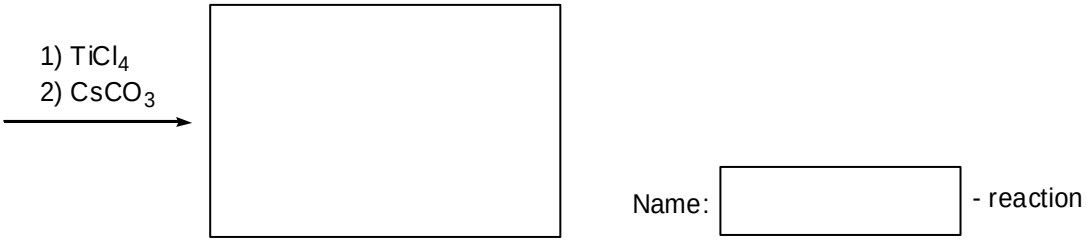
c) Intramolecular [2+2]-photocycloaddition (5)



d) Intermolecular [2+2]-photocycloaddition (5)

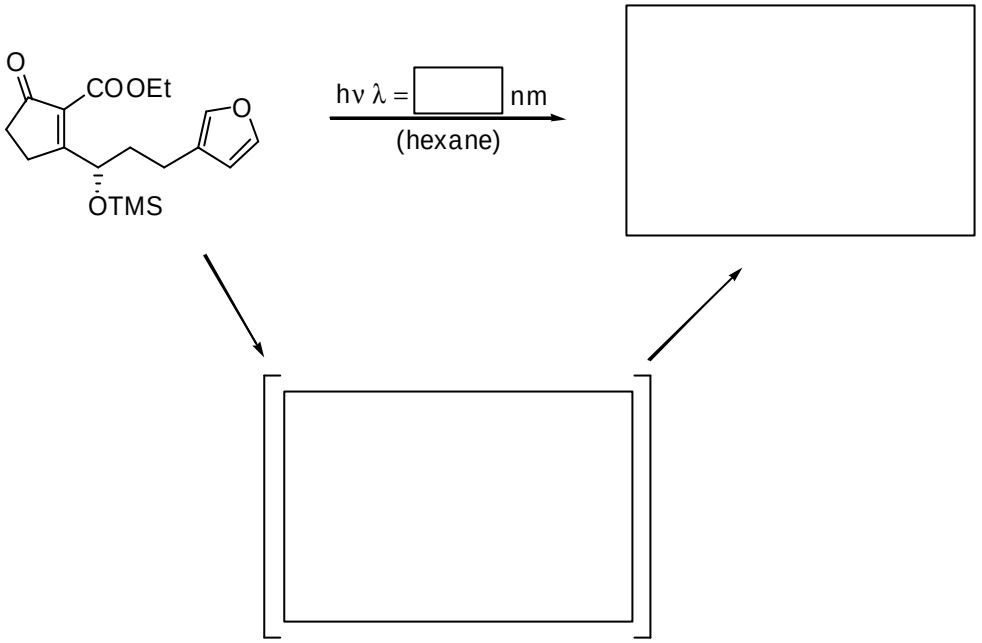


After cleavage of the MEM-protecting group with $TiCl_4$ the photoproduct is treated with Cs_2CO_3. Give the expected product. What is the reaction sequence called? (3)

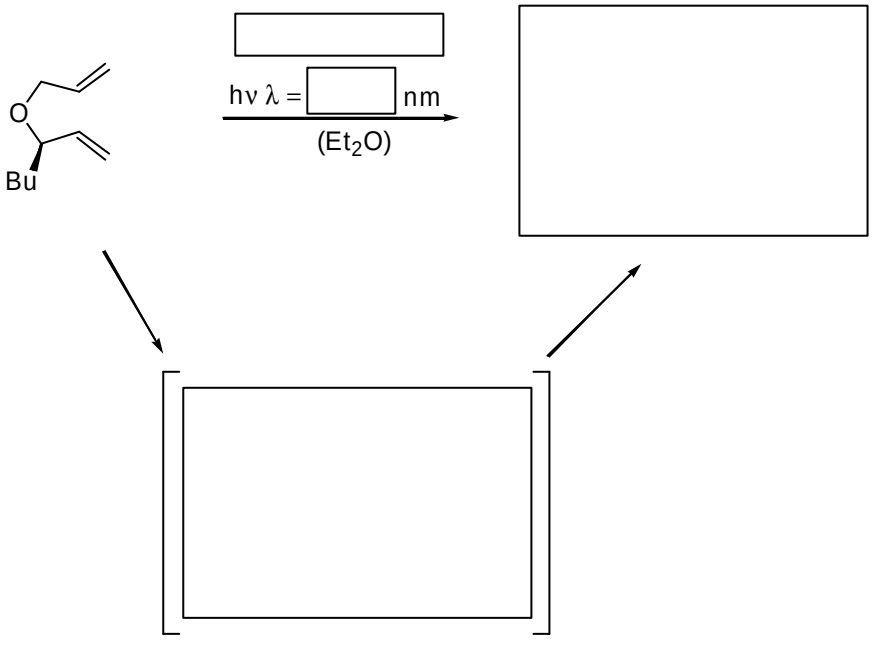


3. Fill in the transition-state, products and conditions in the following photochemical reactions. Mind the *facial* diastereoselectivity. (2 x 8)

a)



b)



4. Underneath are the chemical structures of five compounds **1**-**5**, which are photochemical chromophores. There are also five excitation wavelengths (λ_{max}) given. Decide which wavelength will excite which chromophore, and write this in the appropriate box. (2 points each).

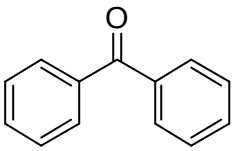
(a) 230 nm (b) 260 nm (c) 300 nm

(d) 340 nm (e) 480 nm

1

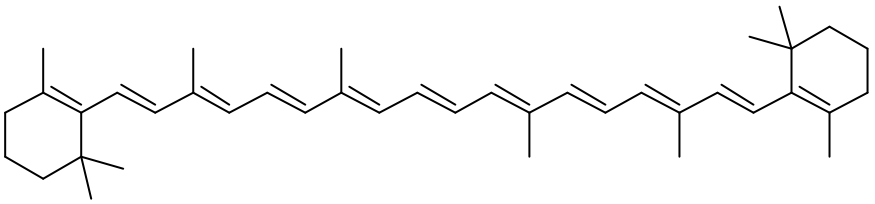
($\pi\pi^*$) ☐

2



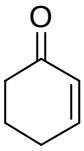
($n\pi^*$) ☐

3



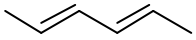
($\pi\pi^*$) ☐

4



($n\pi^*$) ☐

5



($\pi\pi^*$) ☐

5. Below are a series of statements about the physical aspects of photochemistry. Please state which are true and which are false, simply by ticking the correct box. (1 point each)

a) Fluorescence …

	true	false
… occurs from the T_1-state	☐	☐
… occurs at shorter wavelength than the absorption	☐	☐
… is a spin-allowed process	☐	☐
… is a vertical transition	☐	☐

b) Intersystem crossings …

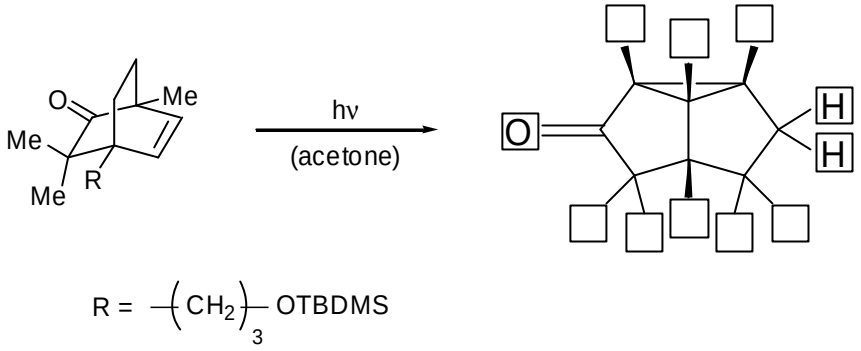
	true	false
… are spin allowed processes	☐	☐
… are horizontal transitions	☐	☐
… are fast in aromatic ketones	☐	☐
… change the electronic energy	☐	☐

According to the Rule of *El Sayed* only two of the following four transitions are allowed. Tick the right answers.

	forbidden	allowed
$^1n\,\pi^* \rightarrow {}^3\pi\,\pi^*$	☐	☐
$^1\pi\,\pi^* \rightarrow {}^3\pi\,\pi^*$	☐	☐
$^1n\,\pi^* \rightarrow {}^3n\,\pi^*$	☐	☐
$^1\pi\,\pi^* \rightarrow {}^3n\,\pi^*$	☐	☐

6. Two photochemical transformations can be used to build up a diquinane-skeleton.

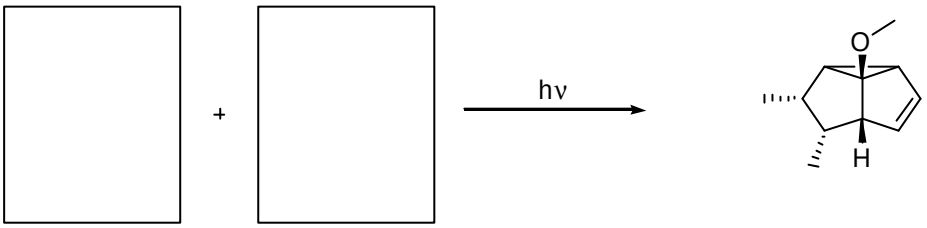
a) Oxadi-π-methane-rearrangement: Fill in the missing substituents (H, Me, R). (4)



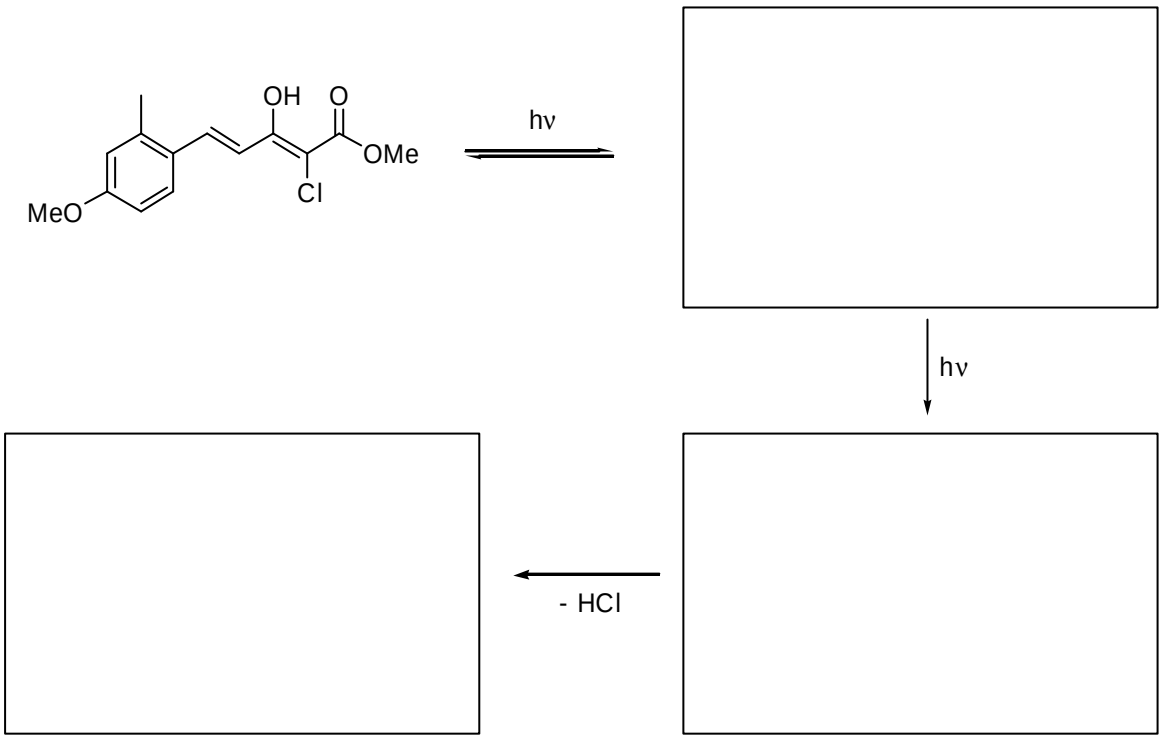
R = $-\left(CH_2\right)_3-$ OTBDMS

Why is acetone used as solvent? (2)

b) meta-Photocycloaddition: Give the two starting materials. (4)



7. The substrate depicted below is *not* directly suited for a pericyclic ring-closure. Under irradiation it is converted to an isomeric compound which undergoes a photochemical cyclisation. The primary photoproduct is rearomatized by elimination of HCl. Give all missing structures and mind the stereochemistry where necessary. (8)



This cyclisation is a …

… 4 π conrotatory... ☐

… 6 π disrotatory... ☐

… 4 π disrotatory... ☐

… 6 π conrotatory... ☐

... process. (2)