Organische Chemie IV: Organische Photochemie

Wintersemester 2008/09 – Technische Universität München

Klausur am 12.02.2009

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

geboren am .....…… in .....

.....
(Eigenhändige Unterschrift)

1	2	3	4	5	6	7	8	9	Σ	Note

Hinweise zur Klausur:

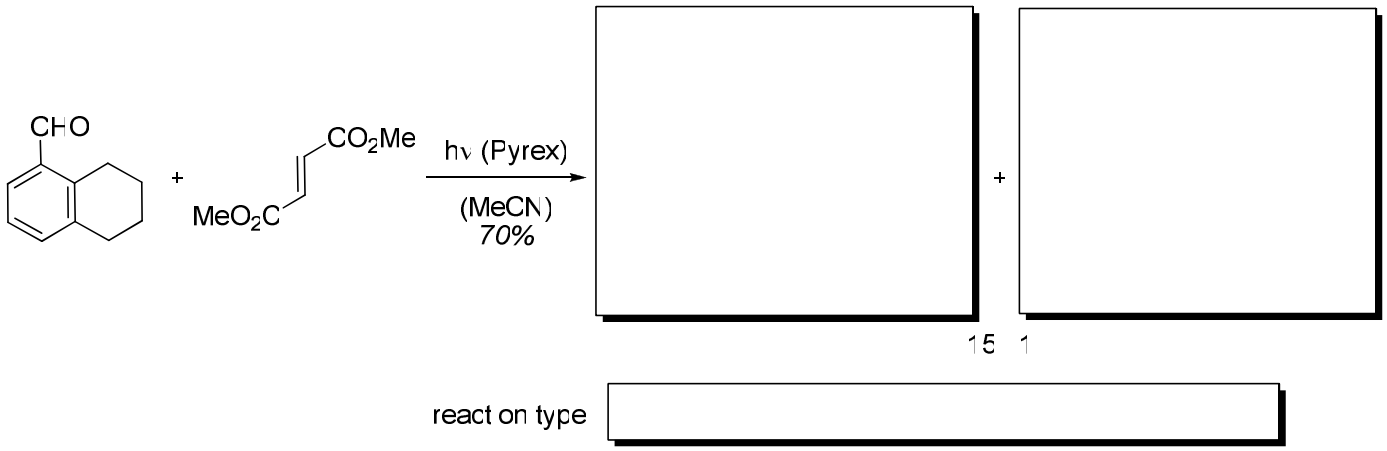
1. Die Klausur besteht aus insgesamt 11 Blättern (Deckblatt plus 10 Aufgabenblätter). Bitte kontrollieren Sie sofort, ob die Klausurunterlagen vollständig sind.
2. Es dürfen nur die vorgedruckten Bögen (einschließlich Rückseite) genutzt werden. Antworten sind zu kennzeichnen, sonst werden sie nicht bewertet. 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 11 sheets (cover page, plus 10 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.

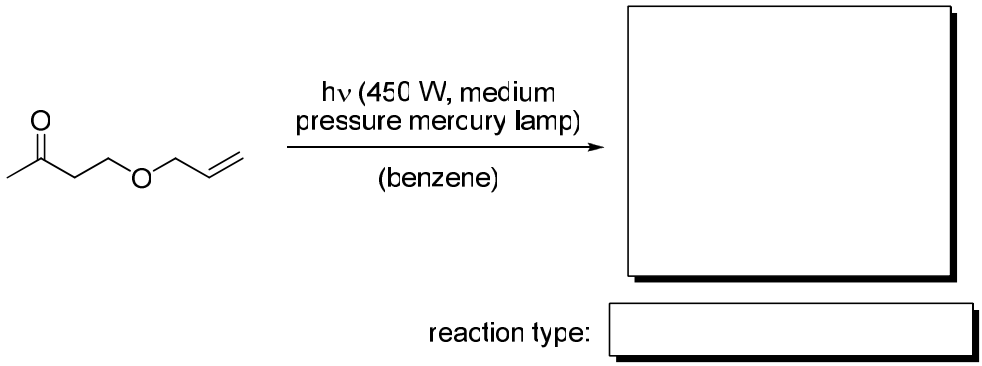
1. Give the expected products and the information asked for in the following reactions. Pay attention to the regio- and stereoselectivity.

a)



(/ 6)

b)



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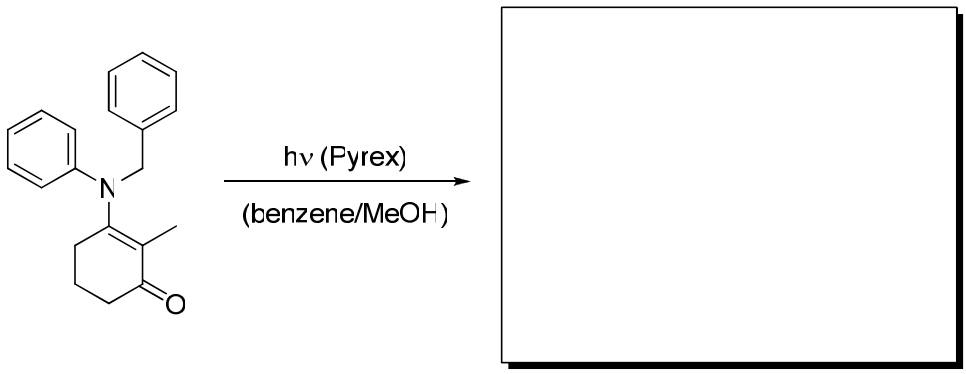
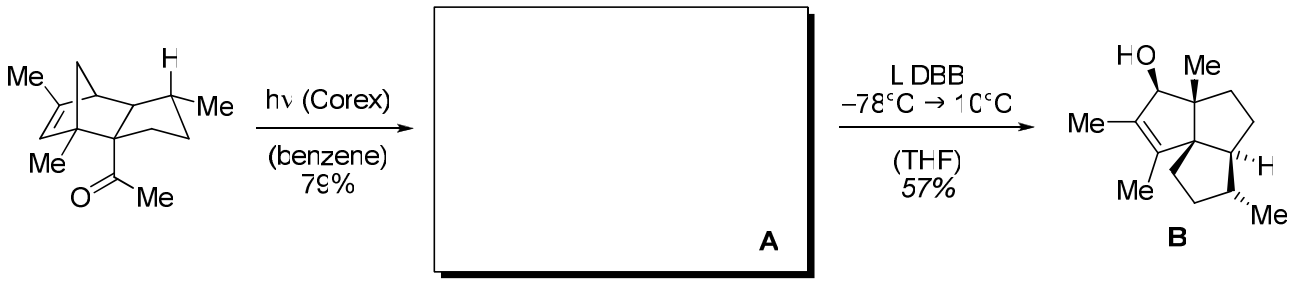
c)



(/ 2)

d)



L DBB = lithium di-*tert*-butylbiphenyl

name

Draw the mechanism of the reductive fragmentation which leads to **B**. (2 points)

(/ 6)

(/ 17)

2. Irradiation of the following compound in the presence of a chiral acid yielded two diastereomeric products in low ee. Depict the two diastereoisomers irrespective of the absolute configuration. (4 points)

DTTA = (+)-di(*p*-toluoyl)tartaric acid

This reaction is a

□ conrotatory [4π] cyclization

□ disrotatory [4π] cyclization

□ conrotatory [6π] cyclization

□ disrotatory [6π] cyclization

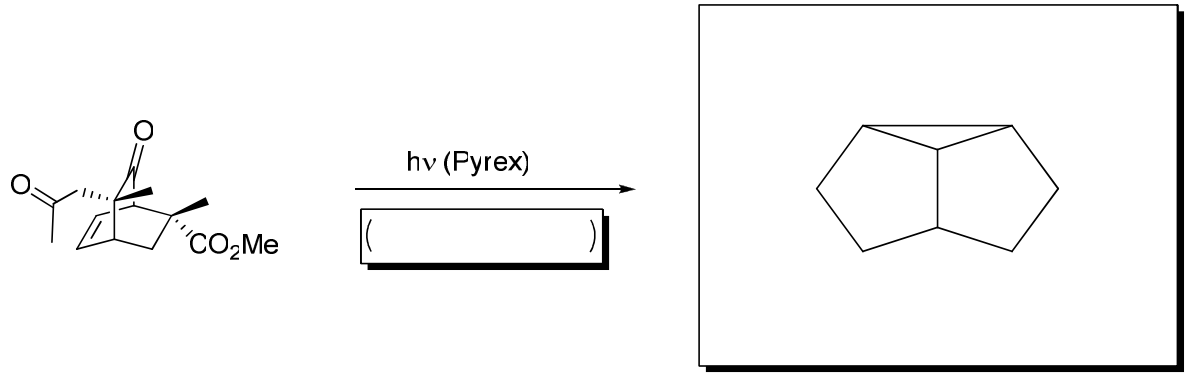
(1 point)

Explain mechanistically why there are two diastereoisomers formed. (4 points)

Make a suggestion how this reaction might be run enantioselectively in solution instead of using DTTA. (1 point)

(/ 10)

3. Complete the structure of the reaction product and give a solvent for the irradiation reaction. (3 points)



Give the name of the reaction. (1 point) _____

Give a detailed explanation (energy diagrams and name of this mechanism) why the reaction was cariied out in this solvent. (5 points)

Assign the correct absorption maxima (in hexane) to the corresponding compounds:
(280 nm, 321 nm, 328 nm, 344 nm) (2 points)

Acetophenone: λ_{max} = _____

Benzophenone: λ_{max} = _____

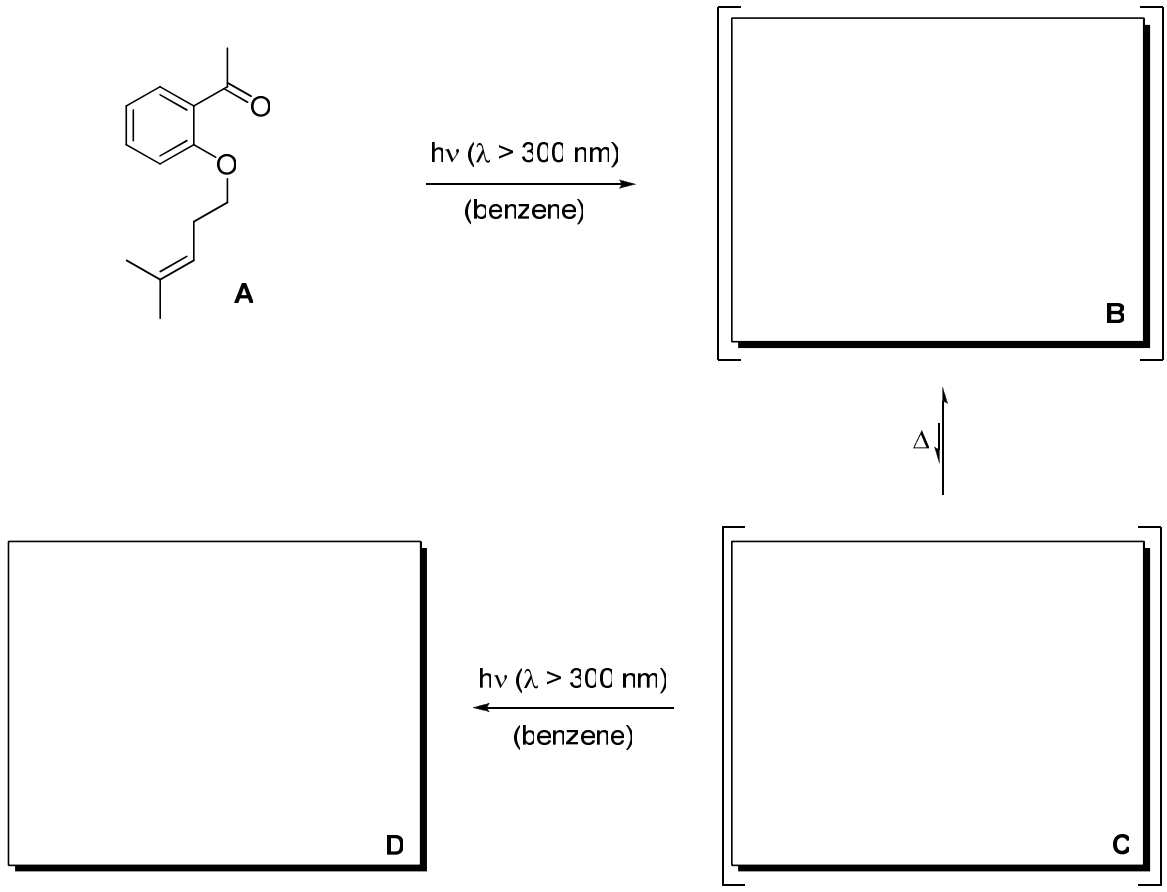
Acetone: λ_{max} = _____

Benzaldehyde: λ_{max} = _____

Which transition is responsible for all of these absorptions? _____ (1 point)

(/ 12)

4. Complete this reaction sequence. (6 points)



Explain each individual step.

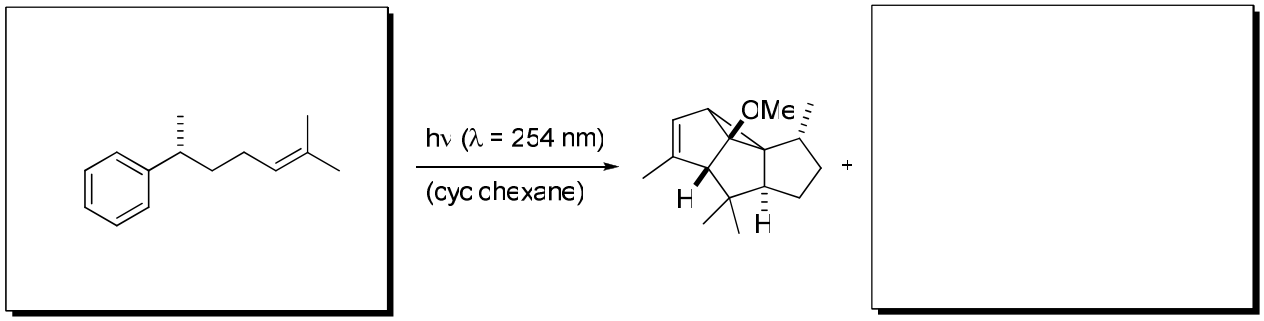
A → B:
(2 points)

B → C:
(3 points)

C → D:
(2 points)

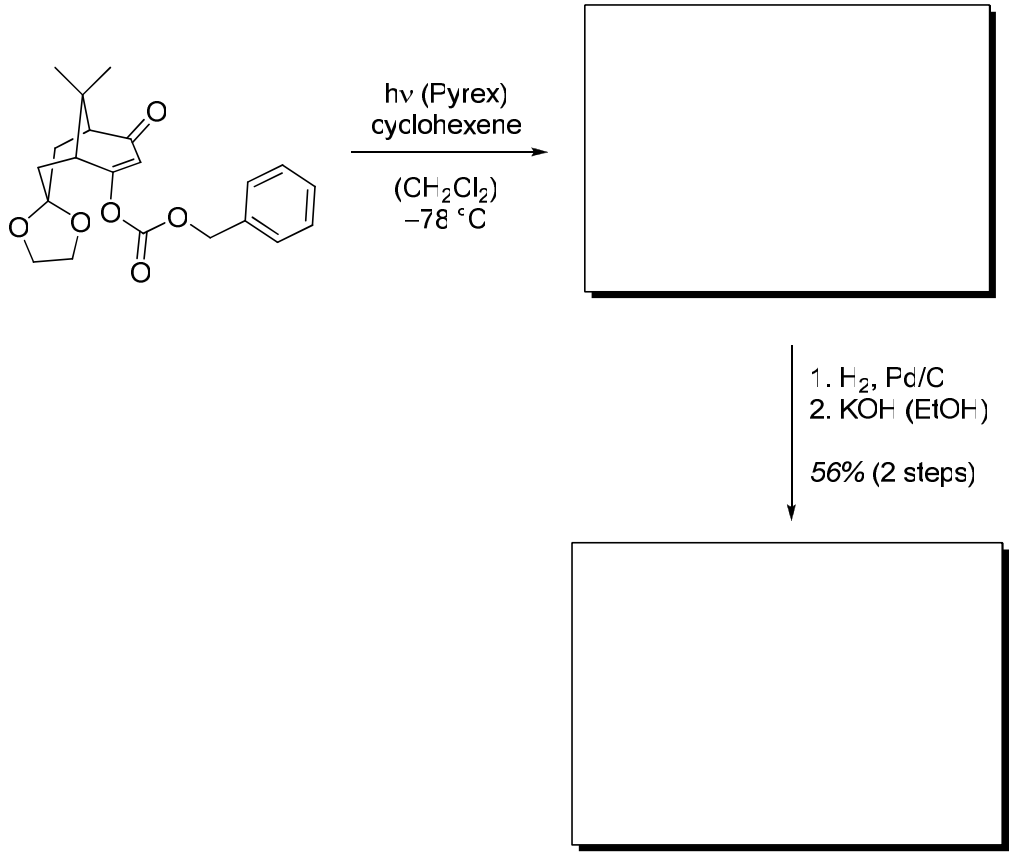
(/ 13)

5. Complete the structure of the starting material and give the structure of the second product formed in this reaction (it is not a diastereomer of the given product).



(/ 6)

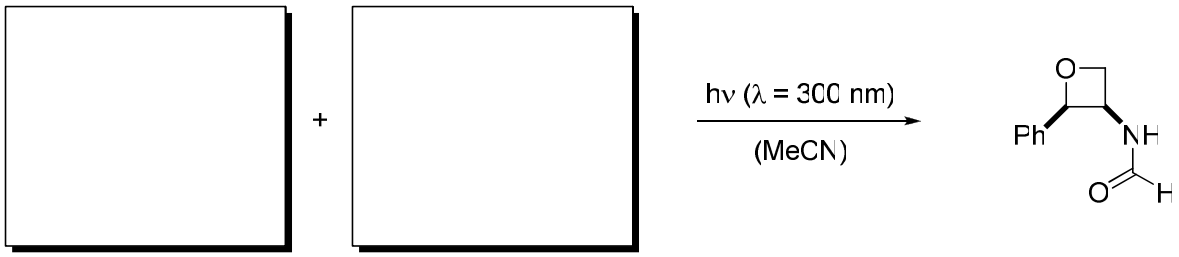
6. Draw the main products of the two reaction steps.



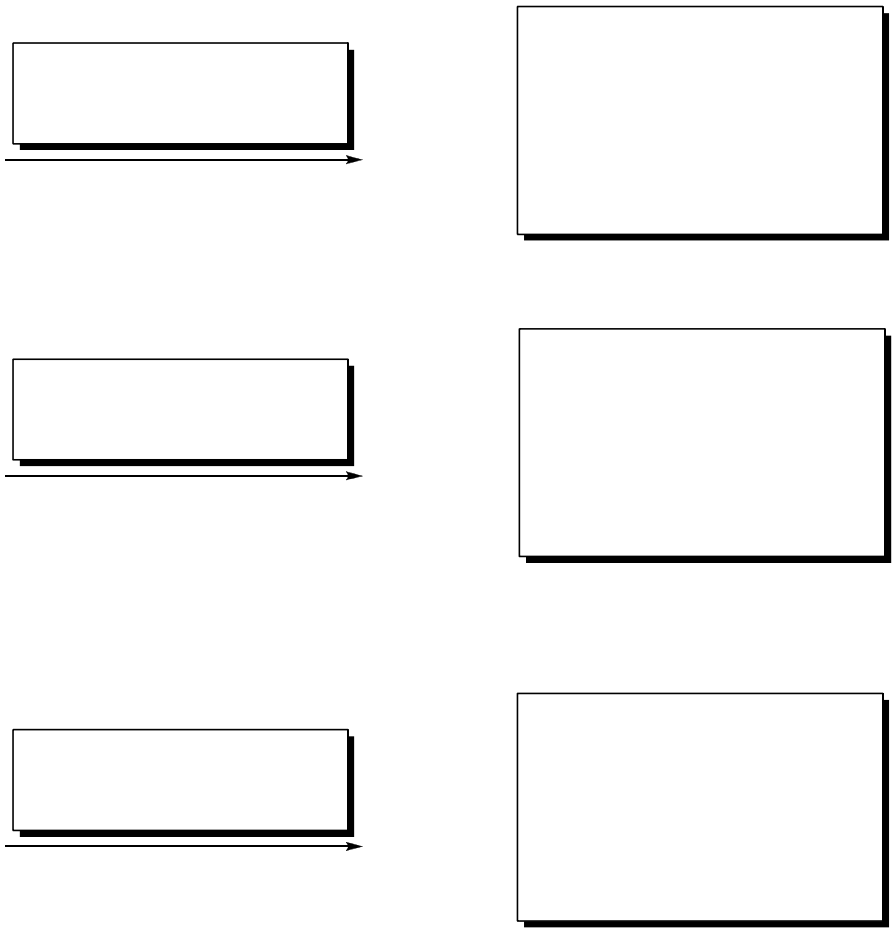
(/ 5)

7.

a) Give the correct starting materials of the following photocycloaddition. (2 points)

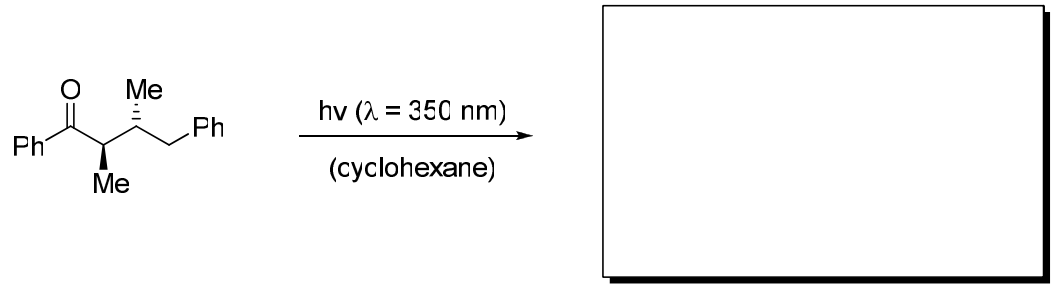


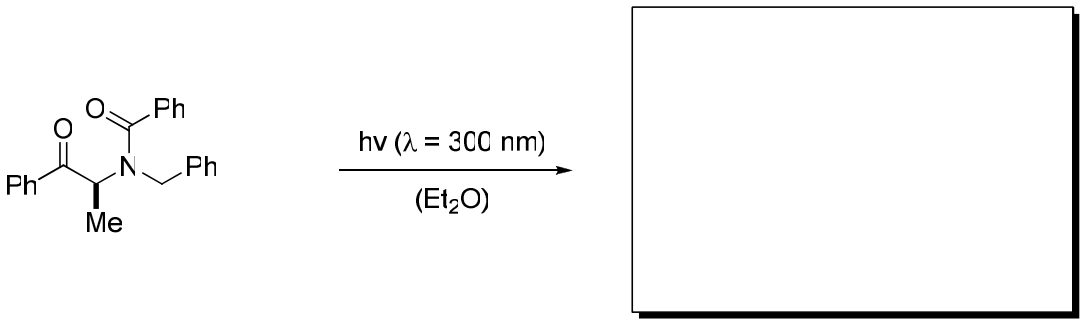
b) Name three possible reagents to open the oxetane ring and draw the appropriate products. (9 points)



(/ 11)

8. The following compounds were irradiated at 300 and 350 nm, respectively. One compound underwent a Norrish type II cleavage, the other compound underwent a Norrish-Yang cyclization. Give a detailed mechanism for each reaction. Explain why the fragmentation is favoured in only one of these reactions.

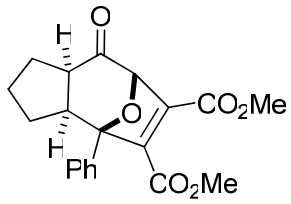




(/ 9)

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

a)

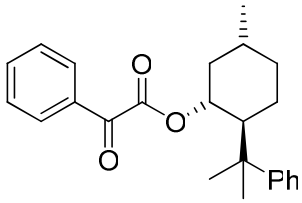


hν (Pyrex)

(benzene)
79%

(/ 3)

b)

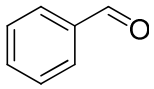


hν (Pyrex)
6 °C

(furan)
95%, 95% de

(/ 3)

c)



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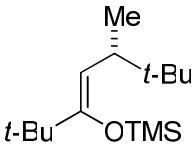
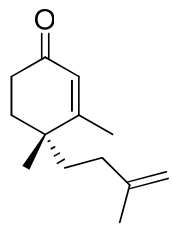


hν (λ = 300 nm)

(benzene)
58%

(/ 2)

d)

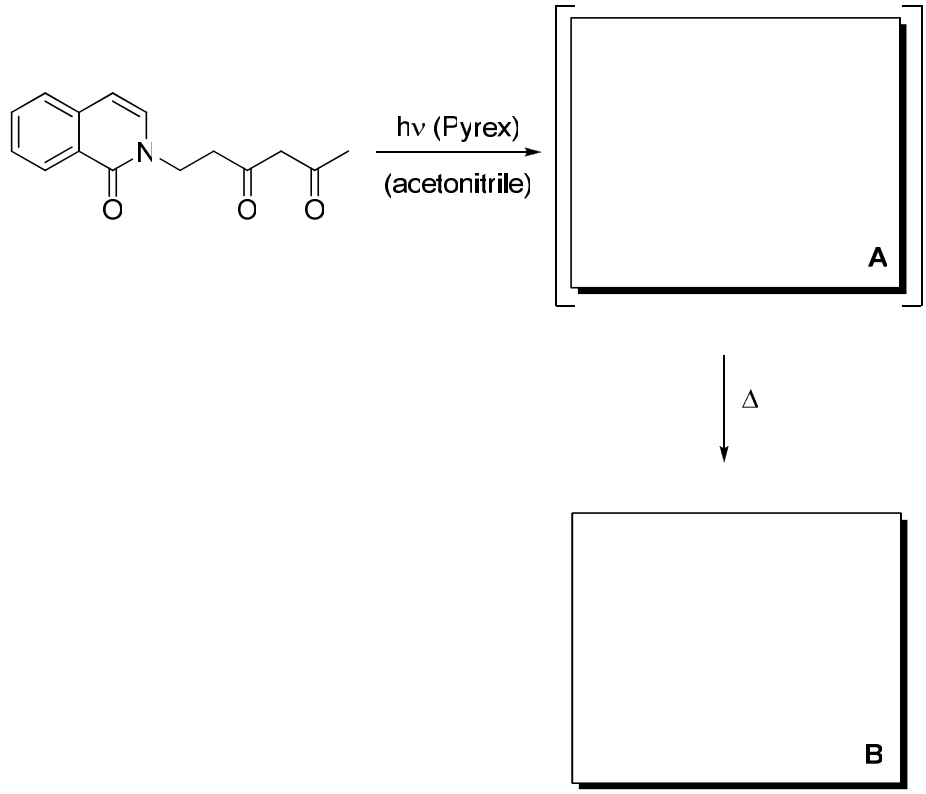


hν (Pyrex)

(hexane)

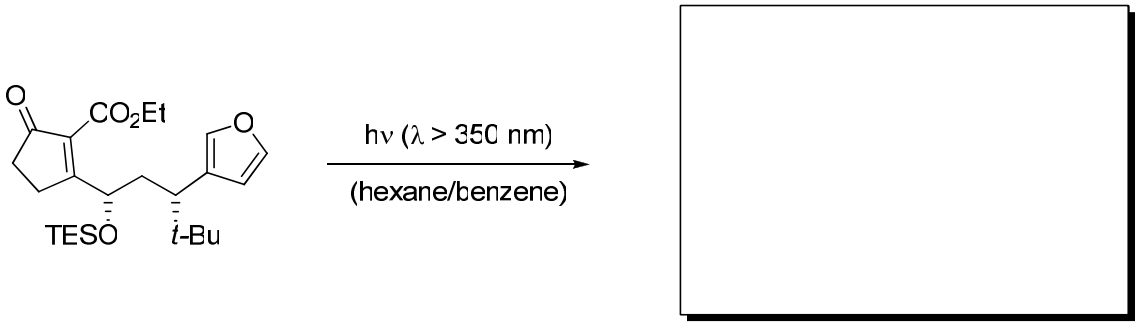
(/ 2)

e) In the following reaction the intermediate cyclization product **A** spontaneously fragmented to give product **B**.



(/ 4)

f)



(/ 3)

(/ 17)