Organische Chemie IV: Organische Photochemie

Wintersemester 2012/13 – Technische Universität München

Klausur am 14.02.2013

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

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

.....
(Eigenhändige Unterschrift)

1	2	3	4	5	6	7	8	9	10	Σ	Note

Hinweise zur Klausur:

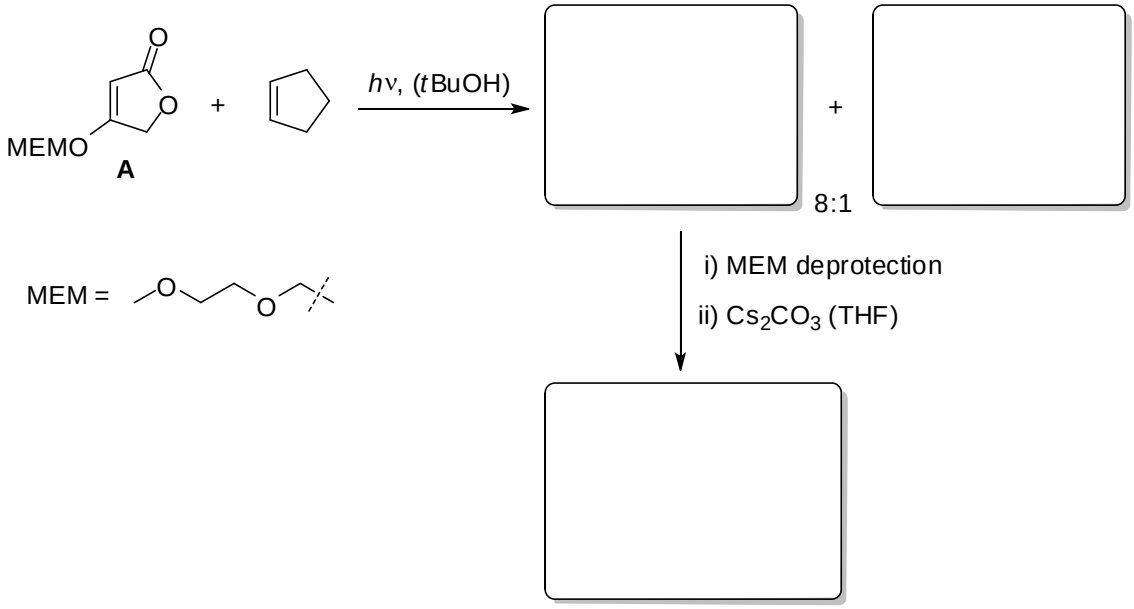
1. Die Klausur besteht aus insgesamt 10 Blättern (Deckblatt plus 9 Aufgabenblätter). Bitte kontrollieren Sie sofort, ob die Klausurunterlagen vollständig sind.
2. Es dürfen nur die vorgedruckten Bögen (einschließlich Rückseite) genutzt werden. Antworten sind zu kennzeichnen, sonst werden sie nicht bewertet. 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. Upon irradiation of a mixture of tetronate **A** and cyclopentene, two diastereoisomers are formed (8:1 ratio). The major product was further transformed into a new product after deprotection and treatment with base.

a) Give the structures of the three products!



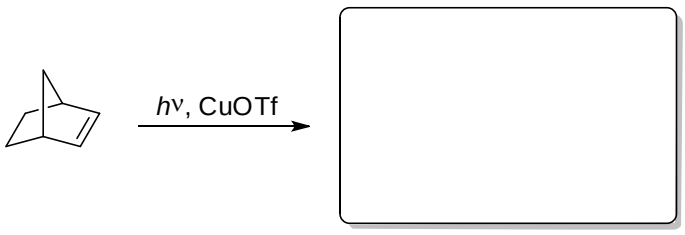
(/ 8)

(b) What is the name of this reaction sequence?

(/ 1)

(/ 9)

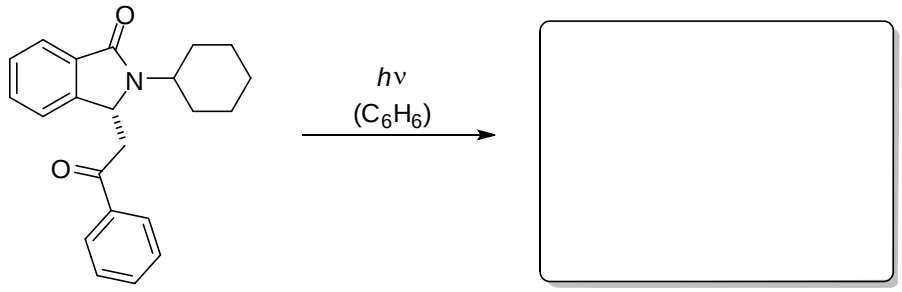
2. Upon irradiation in the presence of copper(I) triflate, norbornene undergoes dimerisation. Give the structure of the product and explain the effect of the copper salt!



(/ 5)

3. Complete the following reactions and consider the correct relative configuration of the products!

a)



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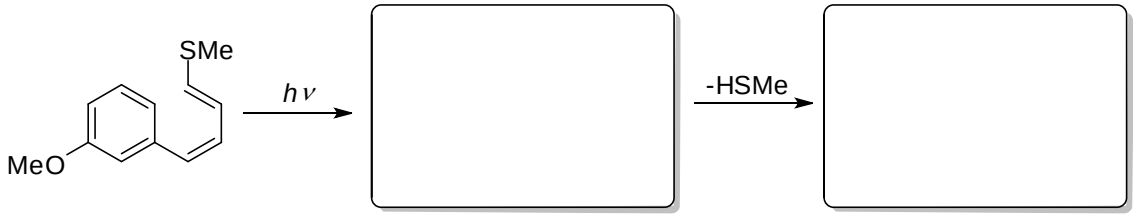
b)



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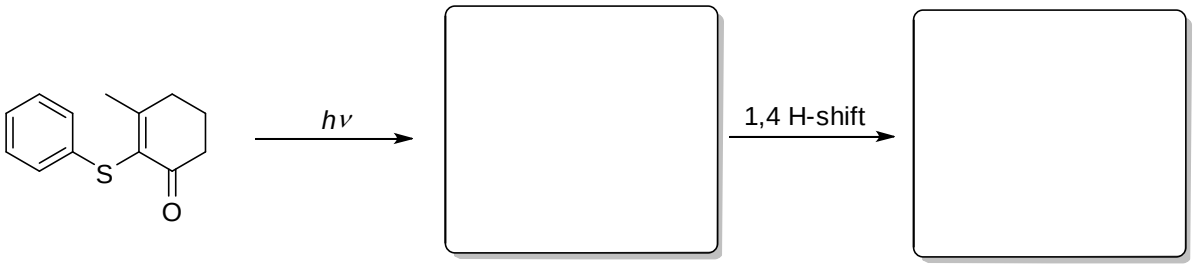
c)



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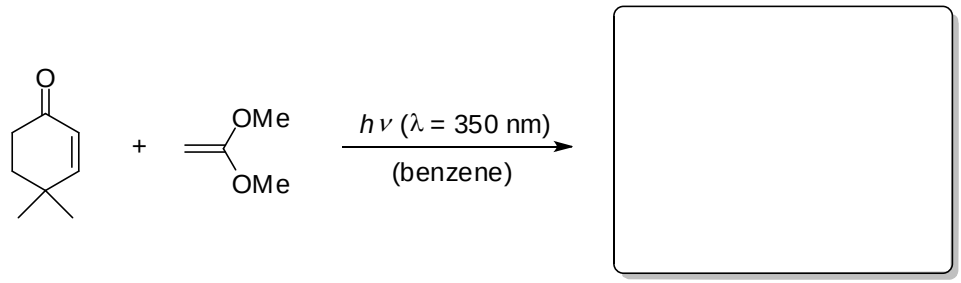
d)

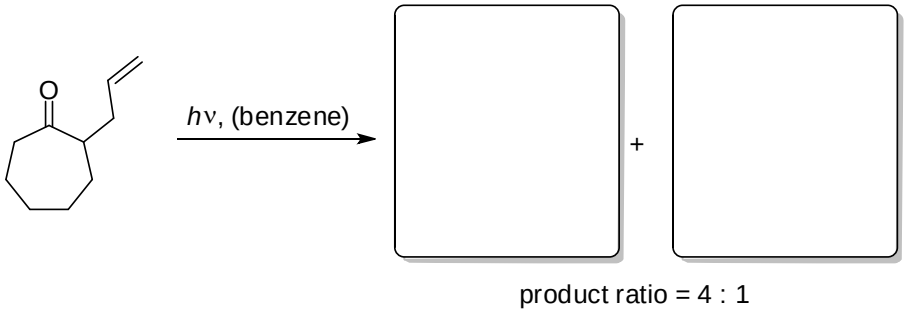


(/ 3)

(/ 15)

4. Complete the following *Paternò-Büchi* reactions, paying attention to the regio- and stereoselectivity! *Hint*: reaction b) delivers only a 1:1 adduct!

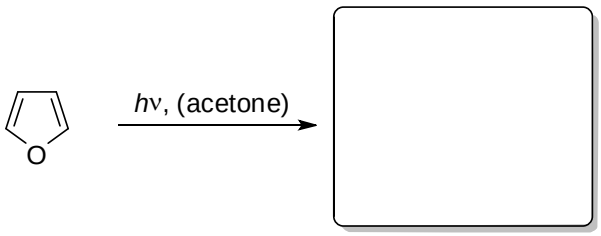
a)



product ratio = 4 : 1

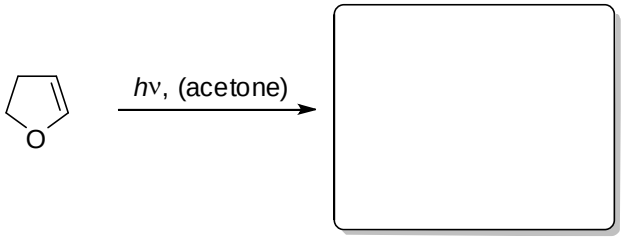
(/ 6)

b)



(/ 2)

c)

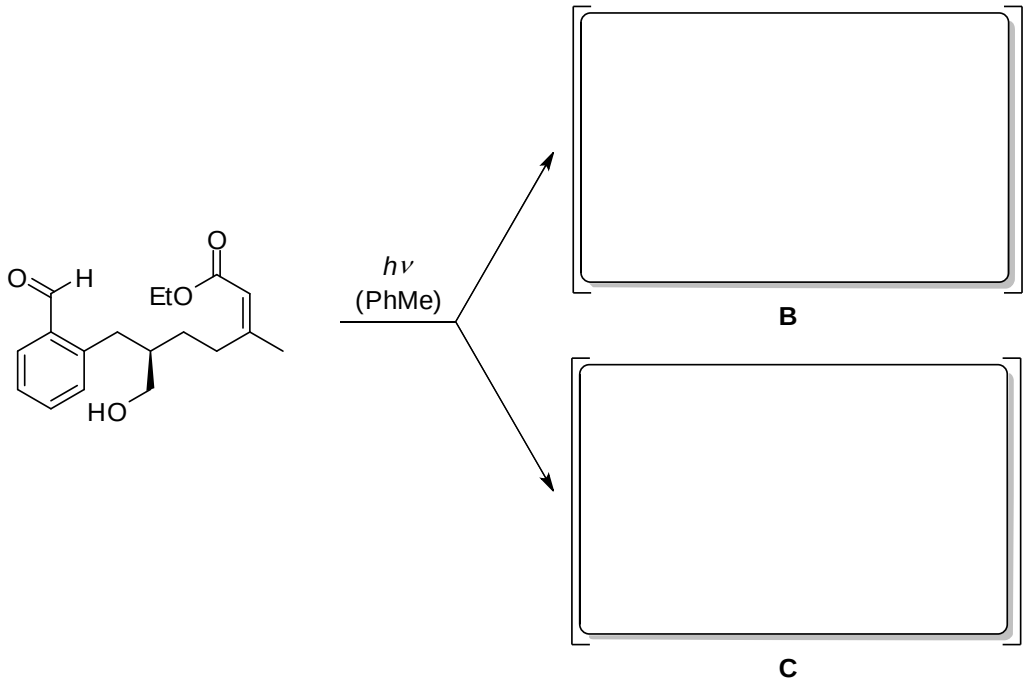


(/ 2)

(/ 10)

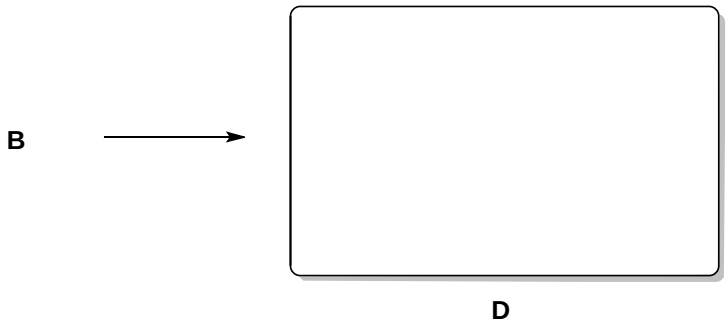
5. Irradiation of the given *ortho*-substituted benzaldehyde leads to two reactive intermediates with the same constitution but different configuration. Intermediate **B** is transformed to the tricyclic compound **D** in a *thermal* reaction, while intermediate **C** is rapidly converted back to the starting material.

a) Give the structure of the intermediates **B** and **C**!



(/ 4)

b) Draw the structure of product **D**!



(/ 3)

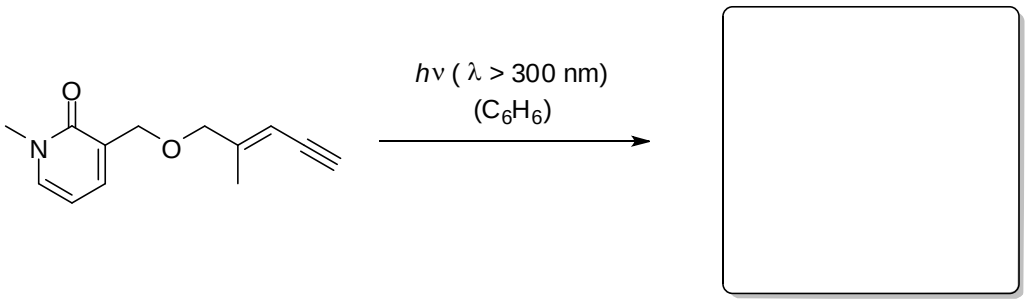
c) Why can't intermediate **B** be trapped and is transformed back to the starting material? Give a short explanation!

(/ 2)

(/ 9)

6. Intramolecular [2+2] photocycloaddition reactions can occur with high simple and facial diastereoselectivity. Give the following products in the correct relative configuration!

a) *Hint*: the configuration of the olefin is retained!



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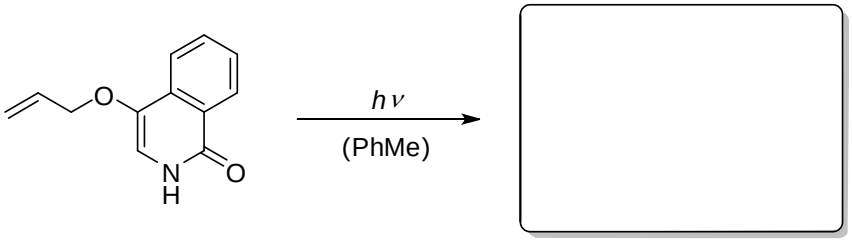

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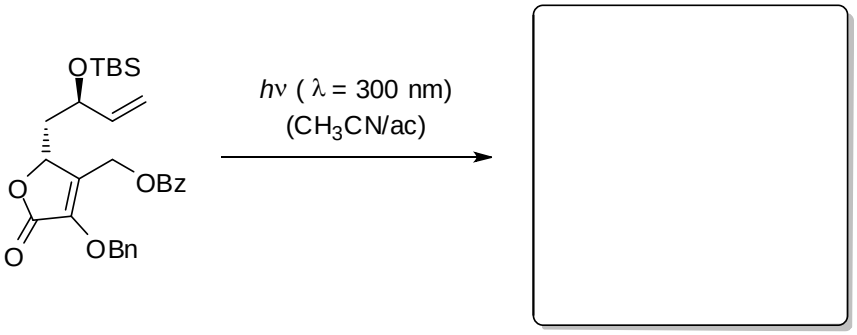
c)



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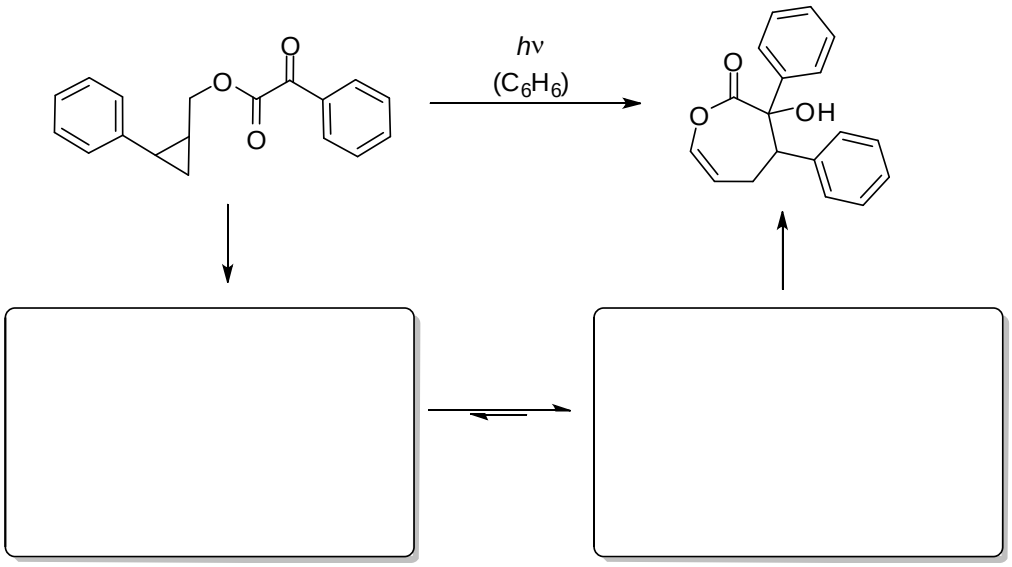
(/ 10)

7. Explain the mechanisms by giving the intermediates of the following photochemical reactions!

a)



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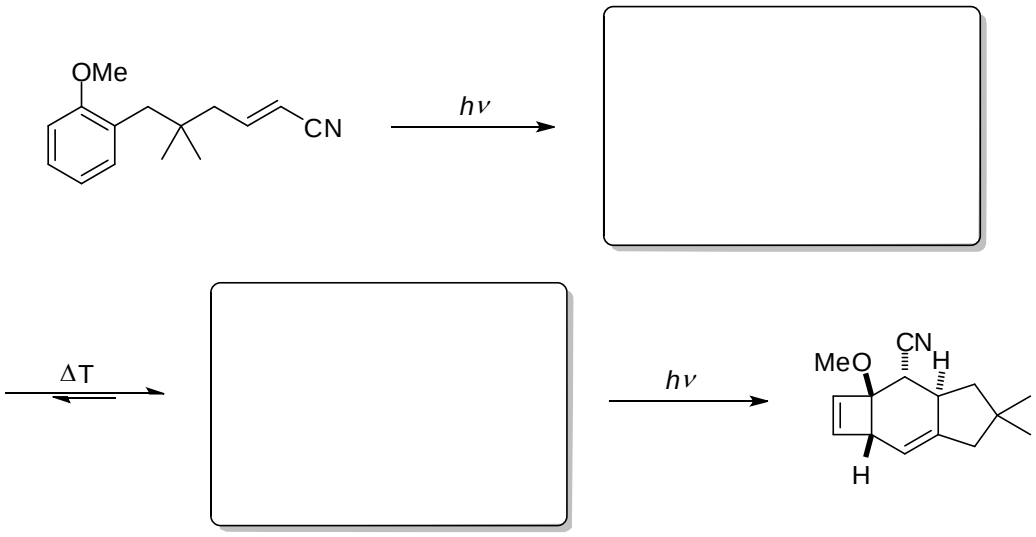
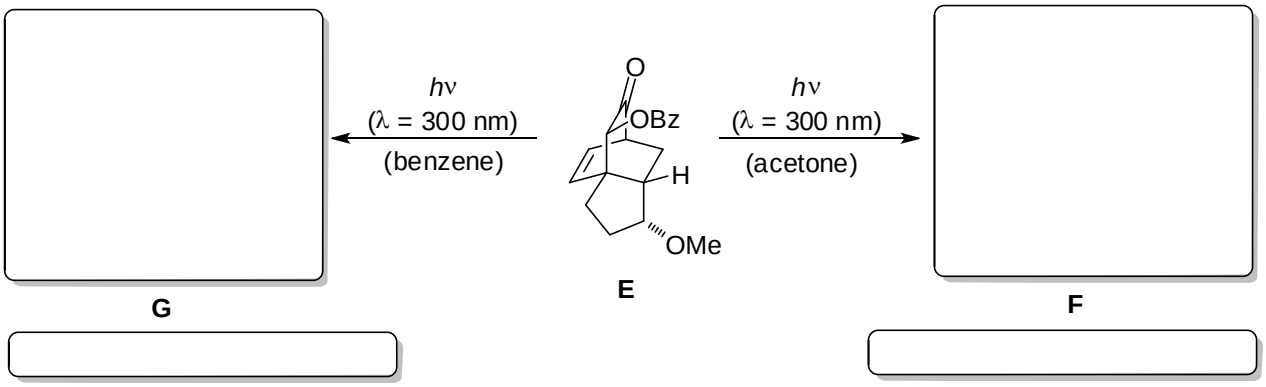
b)



(/ 5)
(/ 9)

8. The irradiation of compound **E** in acetone selectively generates a triquinane product **F**, whilst irradiation in benzene generates a different compound **G**.



a) Give the structures of the products and the names of the reactions!

(/ 8)

b) Rationalise the choice of solvent in each case!

(/ 2)

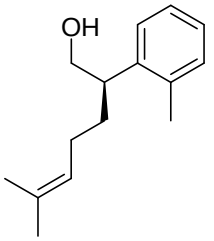
c) Explain the mechanism of the formation of compound **F** by drawing the important intermediates!

(/ 4)

(/ 14)

9. In a total synthesis of penifulvin A a diastereoselective *meta*-photocycloaddition is implemented as key step starting from an aromatic precursor.

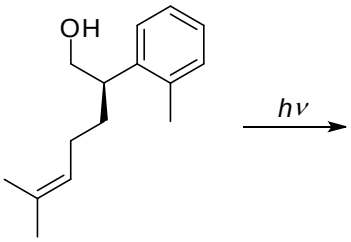
a) Draw the preferred conformation, which determines the diastereoselectivity of the reaction! Give the name of the effect leading to this conformation!



name of the effect:

(/ 3)

b) Draw the structures of the two regioisomeric photoproducts!

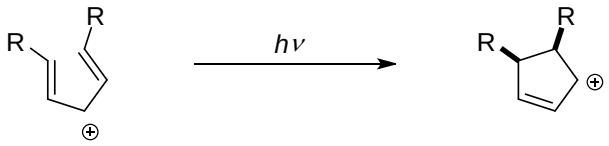


+

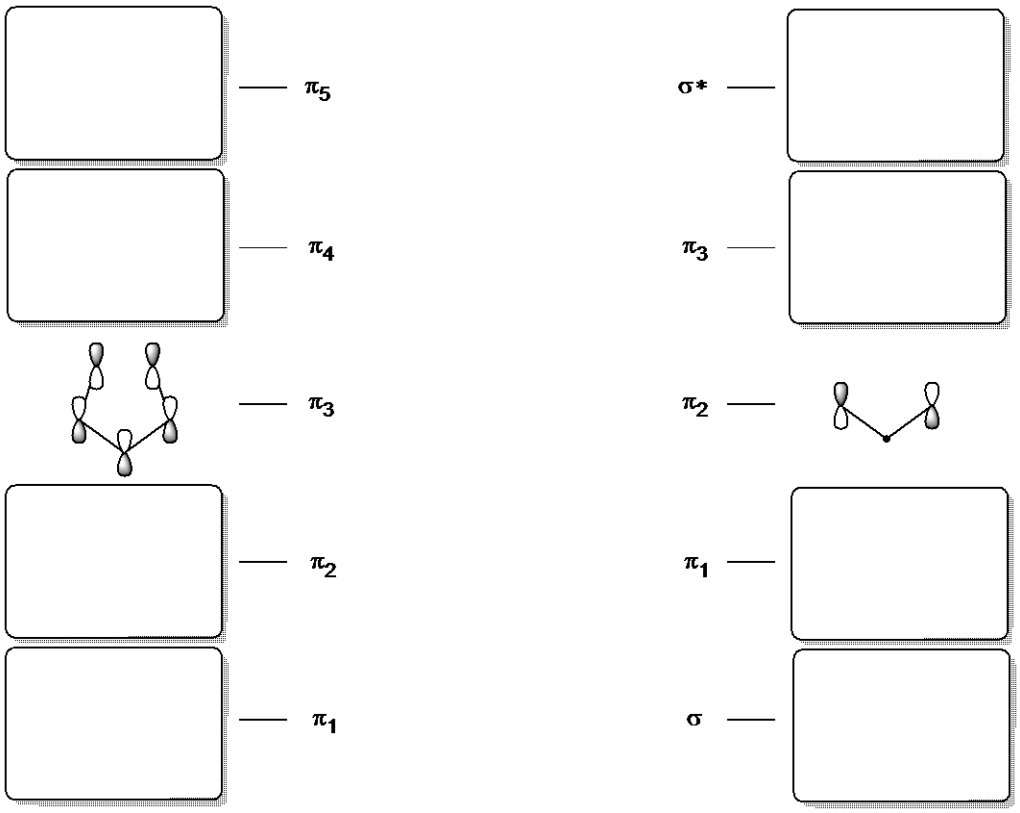
(/ 8)

(/ 11)

10. Irradiation of a pentadienyl cation leads to a disrotatory photocyclization. The stereochemical outcome of this kind of reaction is depicted below.



Draw a MO correlation diagram for this conversion (σ symmetry!), i.e. draw the π orbitals of the starting material and the corresponding orbitals of the product (one of each is given blow) which are involved in this reaction! Identify the orbitals as symmetric (S) or antisymmetric (A). How many electrons occupy the orbitals in the first excited singlet state of the starting material and the product? Give a short explanation why the orbital symmetry is conserved in this reaction!



(/ 8)