

Organische Chemie IV: Organische Photochemie

Wintersemester 2011/12 – Technische Universität München

Klausur am 16.02.2012

Name, Vorname Matrikel-Nr.
(Druckbuchstaben)

geboren am in

.....
(Eigenhändige Unterschrift)

1	2	3	4	5	6	7	8	9	Σ	Note

Hinweise zur Klausur:

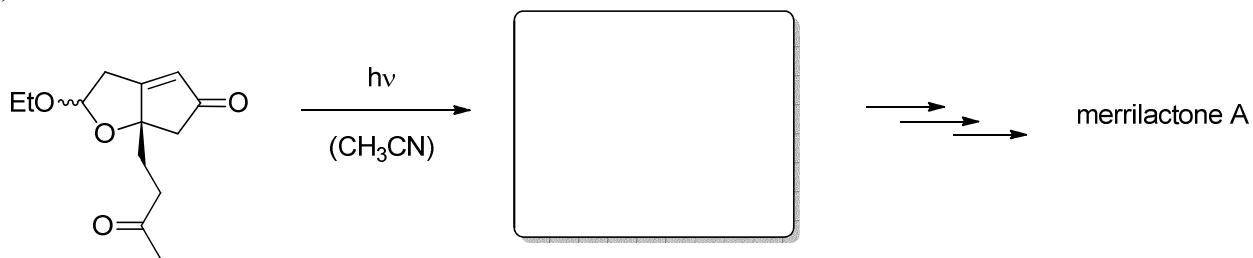
1. Die Klausur besteht aus insgesamt 10 Blättern (Deckblatt plus 9 Aufgabenblätter). Bitte kontrollieren Sie sofort, ob die Klausurunterlagen vollständig sind.
 2. Es dürfen nur die vordruckten Bögen (einschließlich Rückseite) genutzt werden. Antworten sind zu kennzeichnen, sonst werden sie nicht bewertet. 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.
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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.

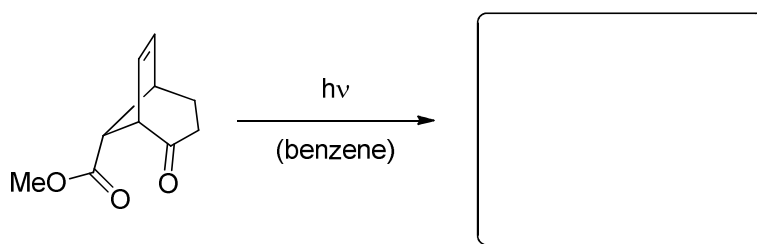
1. Give the expected products and reaction names in the following reactions. Pay attention to the regio- and stereoselectivity!

a)



(/ 2)

b)



Name of reaction:

(/ 4)

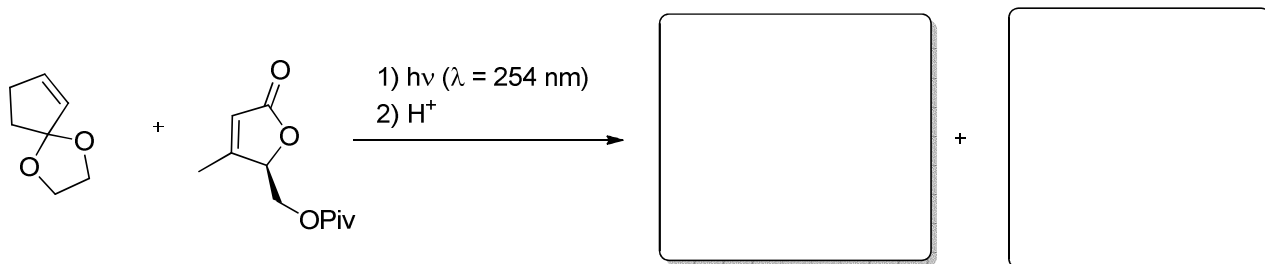
c) Which diastereoisomers would you expect in the following reaction towards the natural product Ikarugamycin? Is the ring-closure disrotatory or conrotatory?



Rotation:

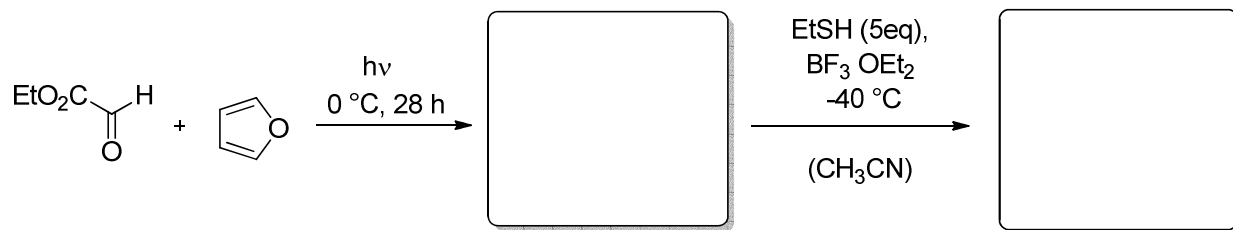
(/ 4)

d) The following reaction leads to **regioisomers** with perfect facial diastereoselectivity. Give the two isomers!



(/ 5)
(/ 15)

2.



a) Complete the given two-step reaction sequence!

(/ 4)

b) Explain the regioselectivity of the first reaction step by the mechanism of this photochemical reaction.

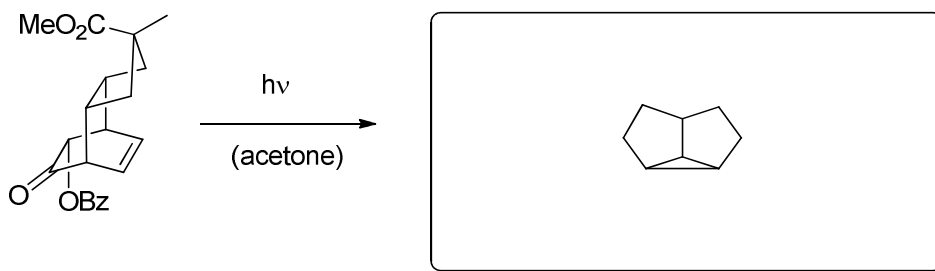
(/ 5)

c) What happens if dihydrofuran is used instead of furan in the first reaction step? Explain why!

(/ 1)

(/ 10)

3. The following photochemical rearrangement was implemented in a total synthesis of (+)-hirsutic acid.



a) Draw the structure of the product in the correct configuration!

(/ 4)

b) Give the name of the reaction!

(/ 1)

c) Why is acetone used as solvent? Give a short explanation!

(/ 1)

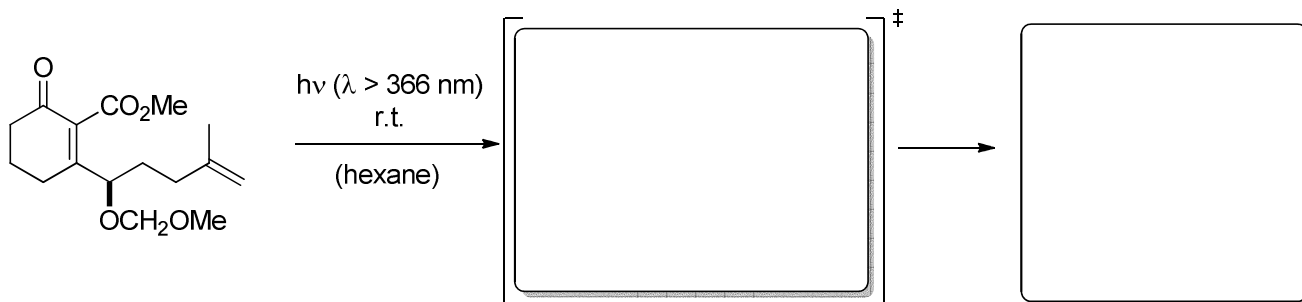
d) Give the name of the process occurring between acetone and the substrate! Explain this process by using an orbital energy diagram of the involved species!

(/ 4)

(/ 10)

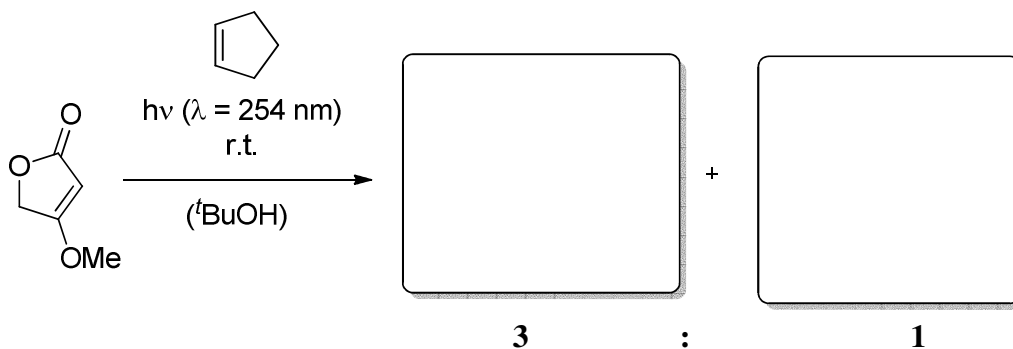
4.

a) The following compound was irradiated in hexane. As expected only one diastereoisomer was observed. Complete the reaction scheme and explain the facial diastereoselectivity by the preferred conformation of the starting material.



(/ 5)

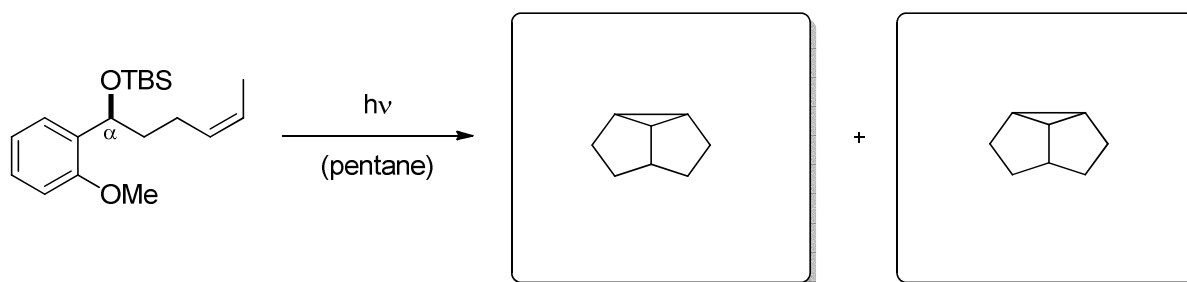
b) Draw the diastereoisomers, which are formed upon irradiation of the methyltetronate. Decide which one is the major diastereoisomer!



(/ 4)

(/ 9)

5.



a) Draw the regioisomers, which are formed upon irradiation of the arene system! Consider the correct configuration of all stereogenic centers in the products!

(/ 8)

b) Why is the configuration of the olefin retained in the reaction?

(/ 1)

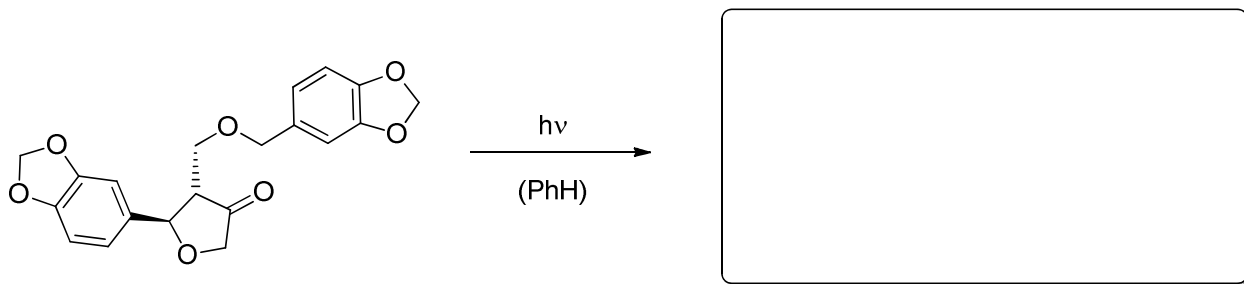
c) The protected alcohol at α -position to the arene determines the configuration of all stereogenic centers in the corresponding products. Give the name of this effect!

(/ 1)

(/ 10)

6. The following photoreactions are used in natural product synthesis. Draw the expected products and give the reaction names:

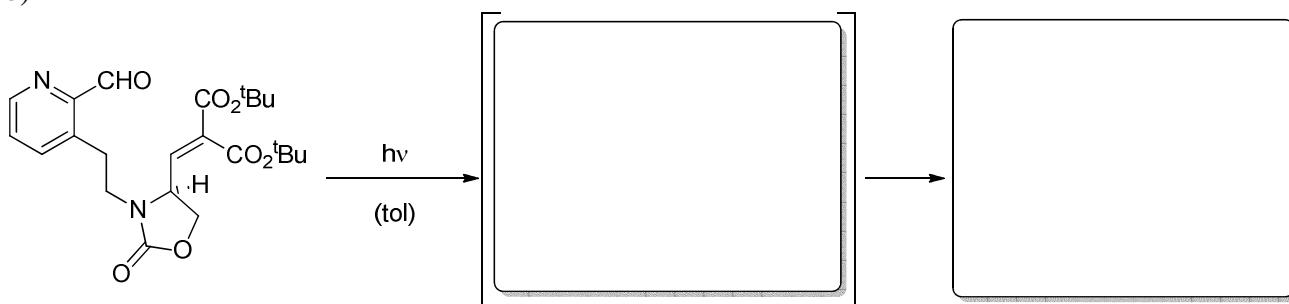
a)



Name of reaction:

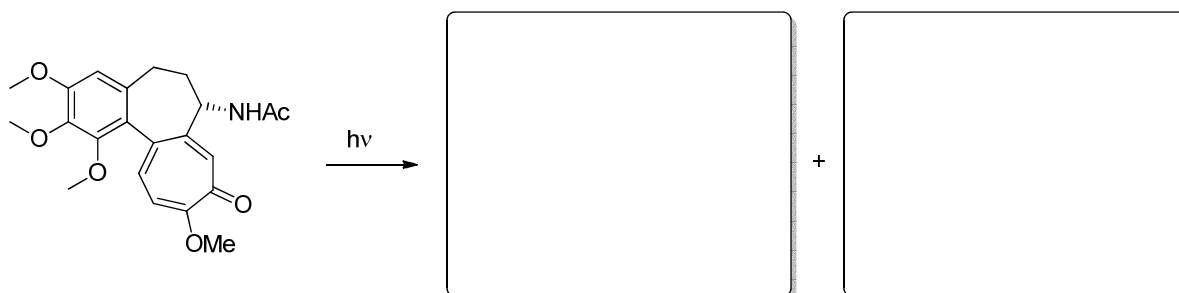
(/ 3)

b)



(/ 6)

c) Colchicine is a natural alkaloid which is used in inflammatory diseases especially in gout. It inhibits the microtubule polymerization and functions as a spindle poison. Under irradiation Colchicine reacts to Lumicolchicine β and γ . Which structures would you suggest for Lumicolchicine?

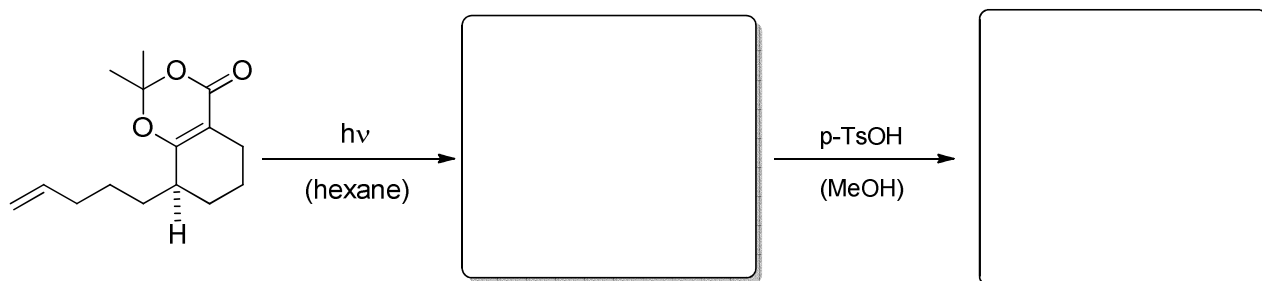


(/ 4)

(/ 13)

7.

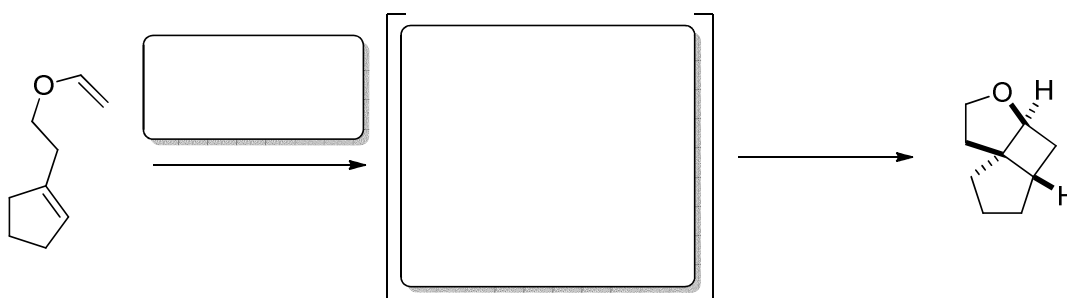
a) Give the products of the reaction sequence and its name. Do **not** discuss the relative product configuration.



Name of reaction:

(/ 5)

b) What reagents and reaction conditions would you use for the following [2+2]-photocycloaddition? Explain your choice and give the correct transition state.



(/ 5)

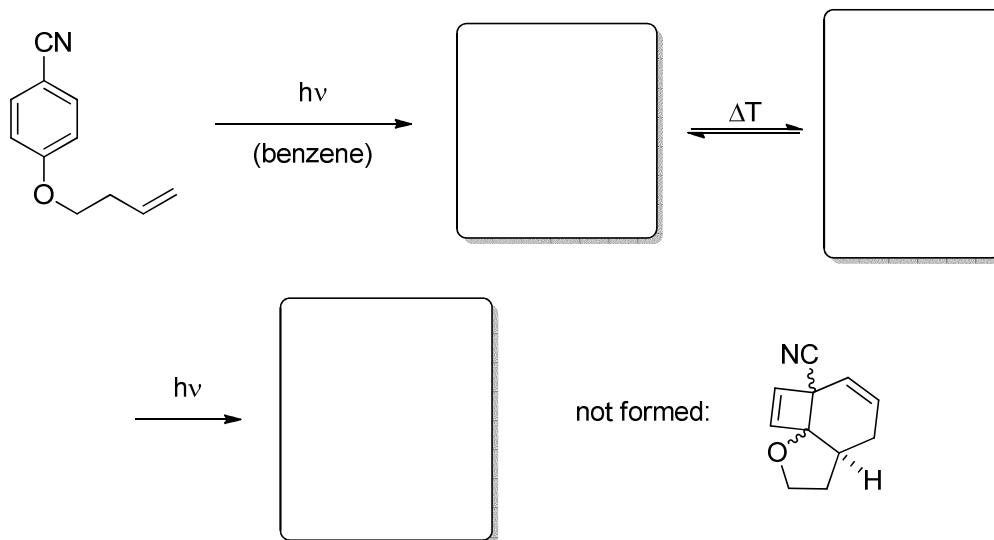
c) Generally speaking there is a second option – apart from Cu-catalysis – for the activation of olefins towards [2+2]-photocycloadditions. How is it called and which reagents would you use!

(/ 3)

(/ 13)

8.

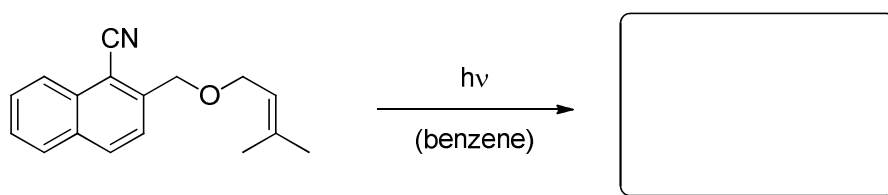
After irradiation of the given arene, a tricyclic product is isolated, which is formed after a sequence of a photochemically induced cycloaddition and thermally and photochemically induced ring-opening and ring closing reactions. The isomer of the final product, which is not formed, is also depicted.



a) Draw the structures of the intermediates and the isolated product!

(/ 6)

b) Give the product of the following reaction! Why is this photoproduct stable towards thermally and photochemically induced ring-opening reactions?

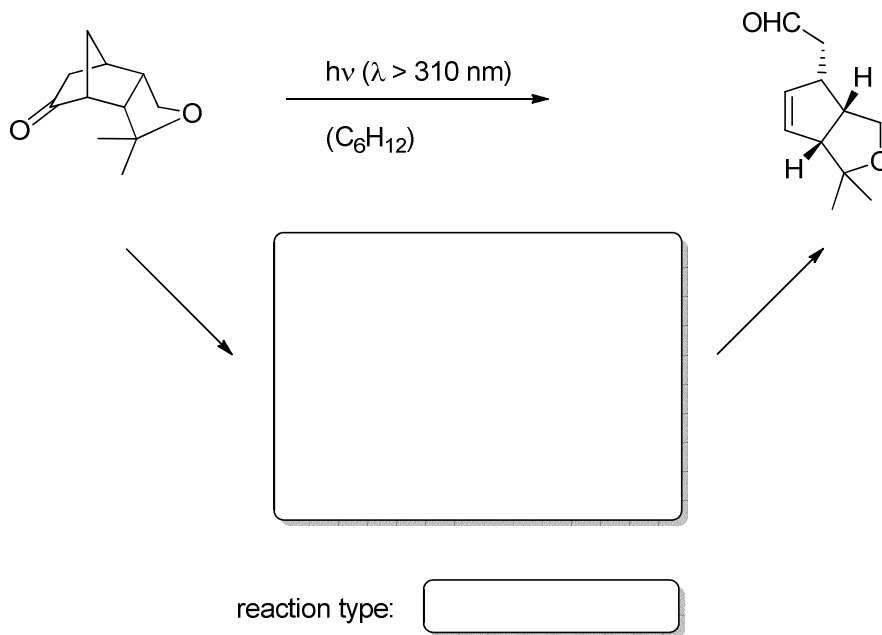


(/ 3)

(/ 9)

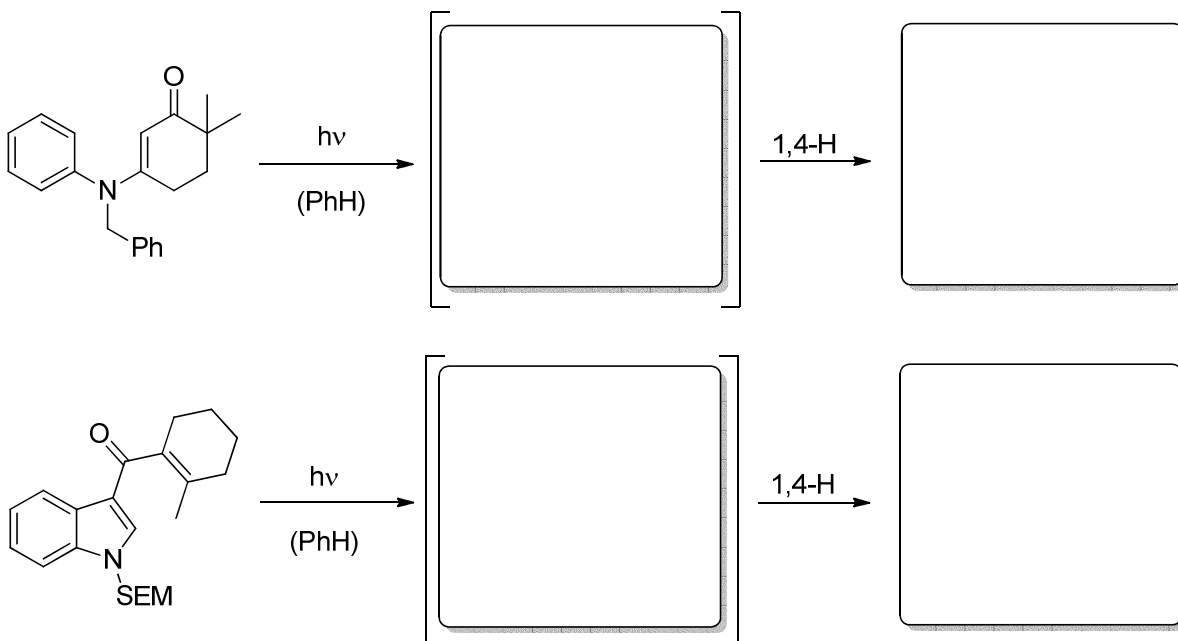
9.

a) The described structure below is irradiated in cyclohexane above 310 nm. Give a suggestion for the intermediate and name the reaction.



(/ 3)

b) Here are some cyclizations to form five-membered rings. Propose the intermediate and the product with the correct configuration.



(/ 8)

(/ 11)