

Organische Chemie IV: Organische Photochemie

Sommersemester 2006 – Technische Universität München

Klausur am 04.08.2006

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	8	Σ

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.
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1. Draw a potential energy curve for the ground state and the first two excited states of a carbonyl compound. Include absorption, intersystem crossing and fluorescence.

(7)

- a) Which of these processes is normally the fastest? _____
- b) Which electronic transition takes place during absorption? _____
- c) What order of magnitude would you expect for the molar absorption coefficient ϵ ?

- Why? _____
- d) Which transition will take place during ISC? _____
Which rule governs this? _____
- e) Which wavelength (approximately) is required to excite an aromatic carbonyl compound? _____
- f) Do aliphatic carbonyls require longer or shorter wavelengths? _____

Some photochemical reactions cannot occur in the presence of light only!

- g) Give the name or a structure of a sensitizer: _____
- h) The oxa-di- π -methane-rearrangement is a ..
- ...thermal...
- ...sensitized ...
- ...non sensitized reaction.

i) The 1,3-acyl shift is a ..

...thermal...

...sensitized ...

...non sensitized ...

... reaction.

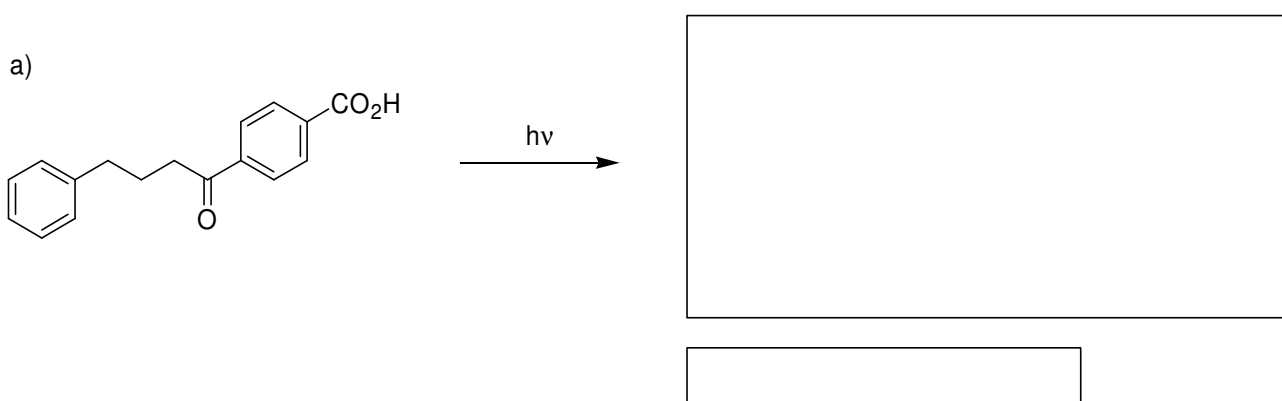
j) Give the name or structure of a triplet quencher: _____

k) Is the 1,3-acyl shift influenced by such a quencher? _____

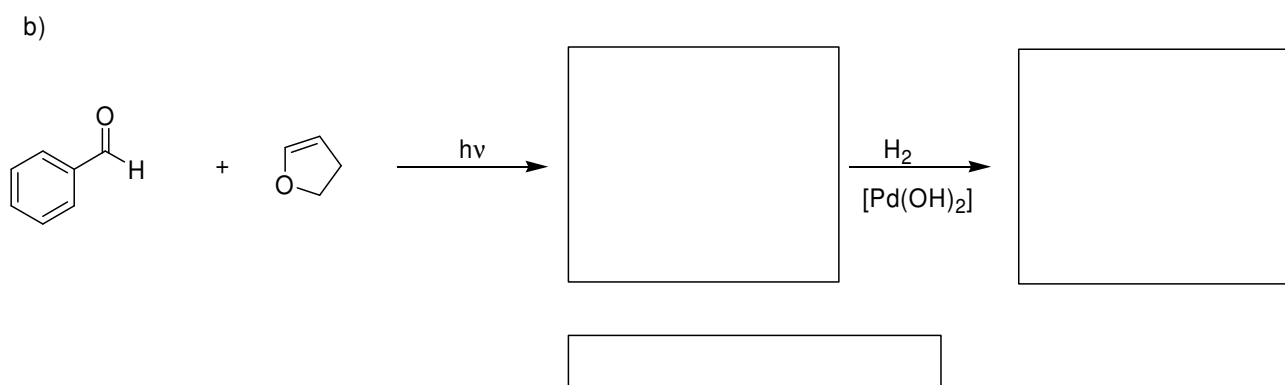
Is the oxa-di- π -methane rearrangement influenced by such a quencher? _____

(14)

2. Give the expected products in the following reactions. Give the names of the reactions, and any other information asked for. Pay attention to the regio- and stereochemistry!

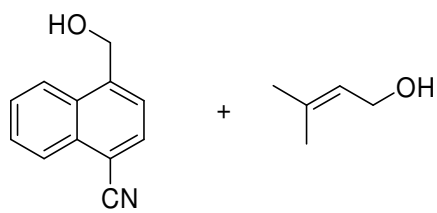


(3)



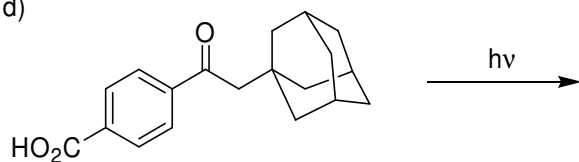
(4)

c)



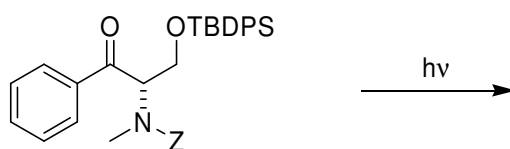
(3)

d)



(3)

e)

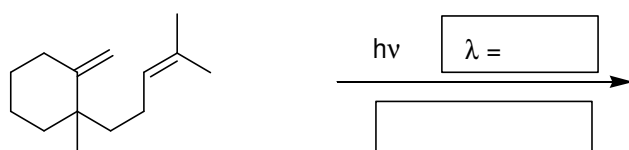


TBDPS = *t*-butyldiphenylsilyl
 Z = benzyloxycarbonyl



(3)

f)

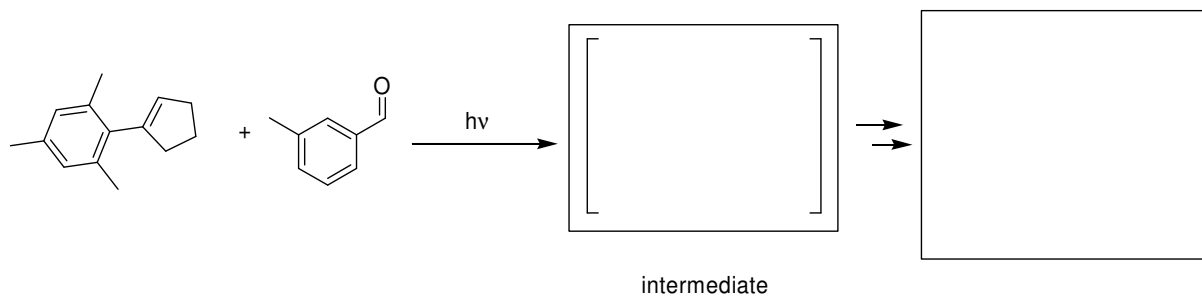


(4)

3. Paternò-Büchi Reaction

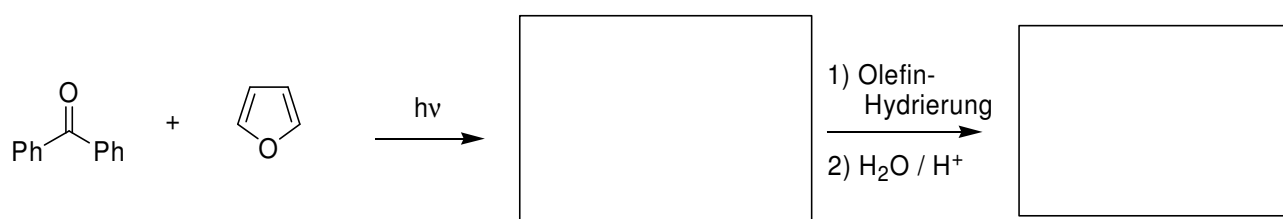
- a) Discuss the mechanism of the following Paternò-Büchi reaction briefly and explain the regio- and stereoselectivity! What spin state does the intermediate have? Which two processes are involved in the oxetane formation?

(3)



(4)

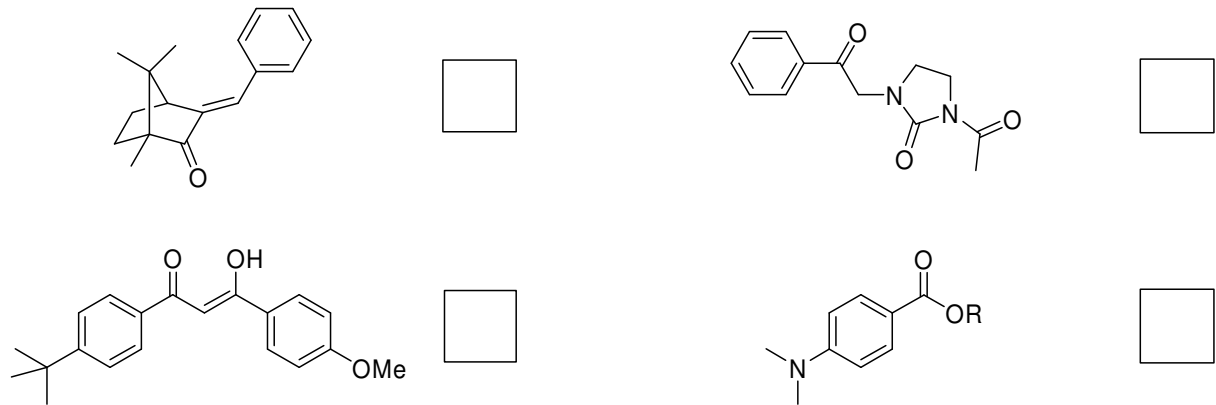
- b) Complete the reaction scheme giving the Paternò-Büchi product and the product of the subsequent ring opening.



(3)

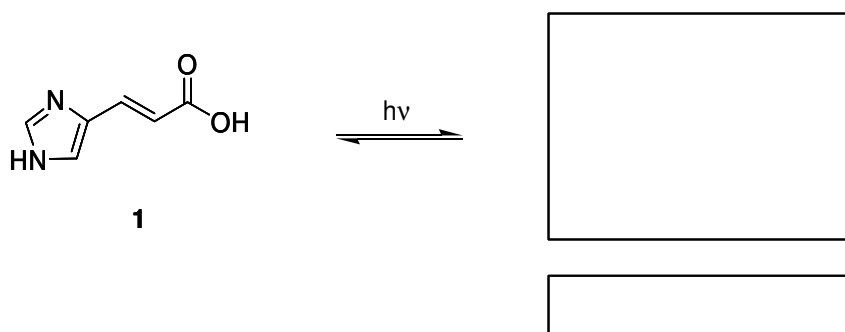
4. 13 000 cases of skin cancer are reported every year by the WHO. One way of reducing the risk associated with sun exposure is to apply a chemical sun screen.

a) Which of the following structures does **not** represent a chemical sun screen?



(1)

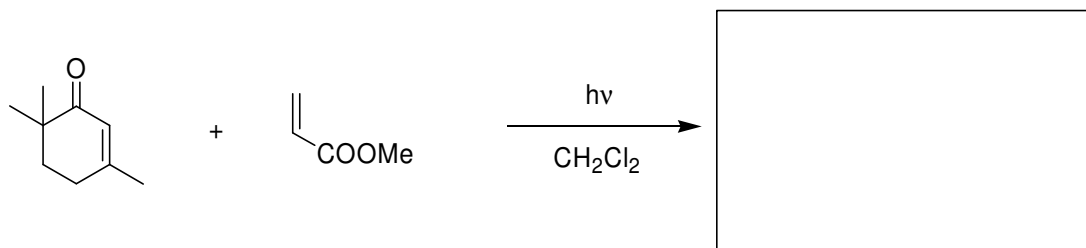
b) Two types of natural sun protection exist in humans: melanine pigmentation and urocanic acid (**1**) formation. What is the mechanism of action of this natural sun screen? Give the product of the reaction, as well as the name of the process.



(3)

5. Enone-Alkene Photocycloaddition

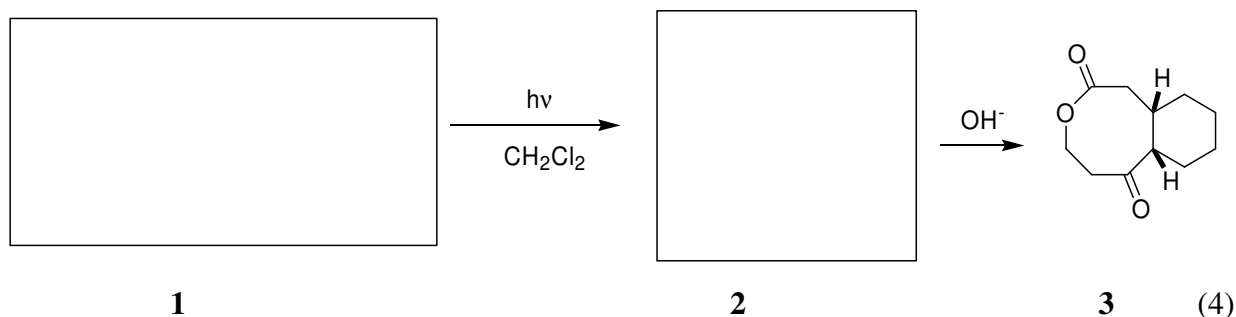
- a) Give the thermodynamically more stable product! Mind the regiochemistry and simple diastereoselectivity.



(2)

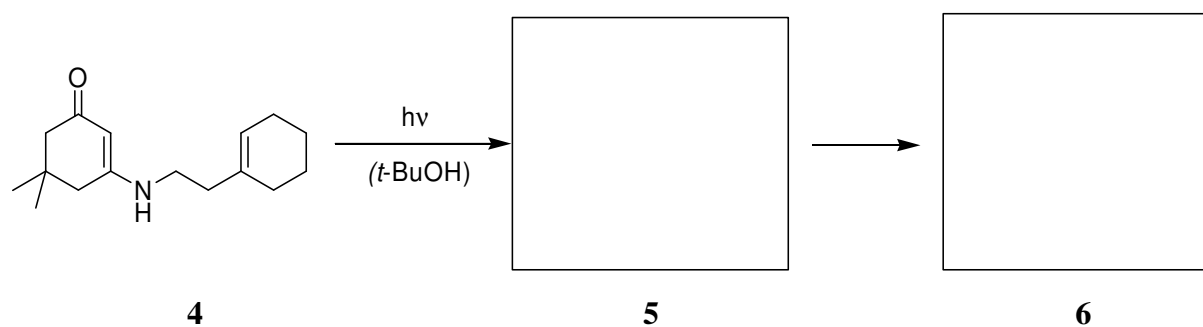
- b) Is the favored product the *endo* or *exo* product? _____ (1)

- c) Lactone **3** is accessible by a two-step sequence including an intramolecular [2+2]-photocycloaddition. Give a possible starting material **1** and the photoproduct **2**.



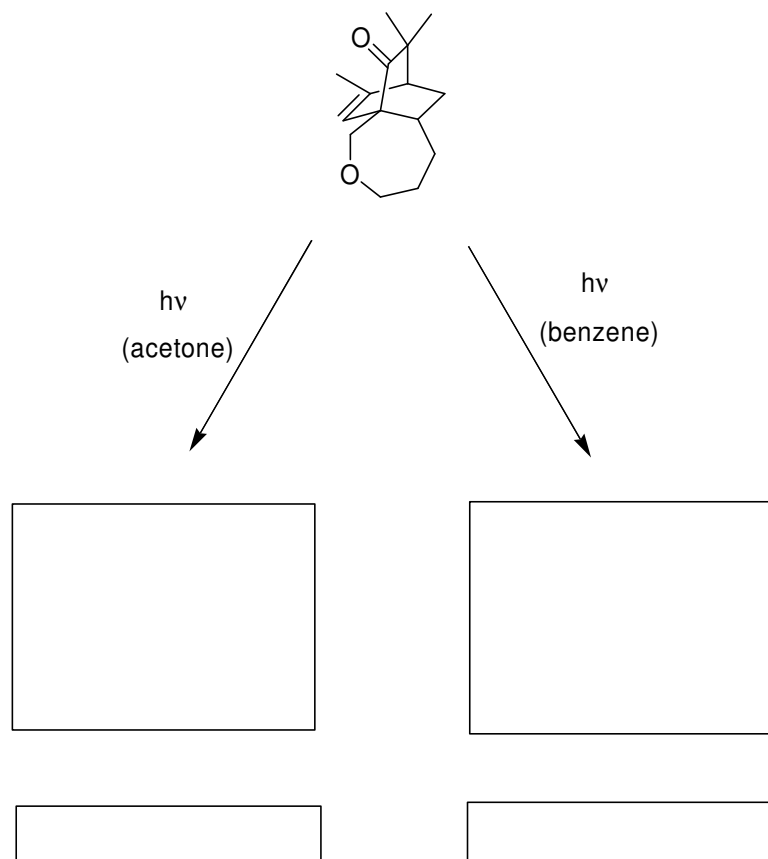
- d) What is the name reaction associated with this sequence? _____ (1)

- e) The final product **6** of the following two-step sequence arises from molecule **5**. The latter is the product of an intramolecular [2+2]-photocycloaddition. The second step is a ring opening reaction analogous to the *retro-aldol* ring opening reaction. Please give **5** and **6** with the correct relative configuration.



- f) What would you call this ring opening reaction in analogy to the *retro-aldol* reaction? _____ (1)

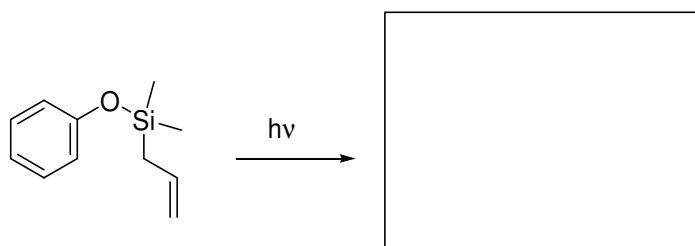
6. Irradiation of the following compound in different solvents yields two different products! Give the names of these rearrangements as well as the expected products. Pay attention to the stereochemistry.



(8)

7. Arene Photochemistry and Pericyclic Reactions

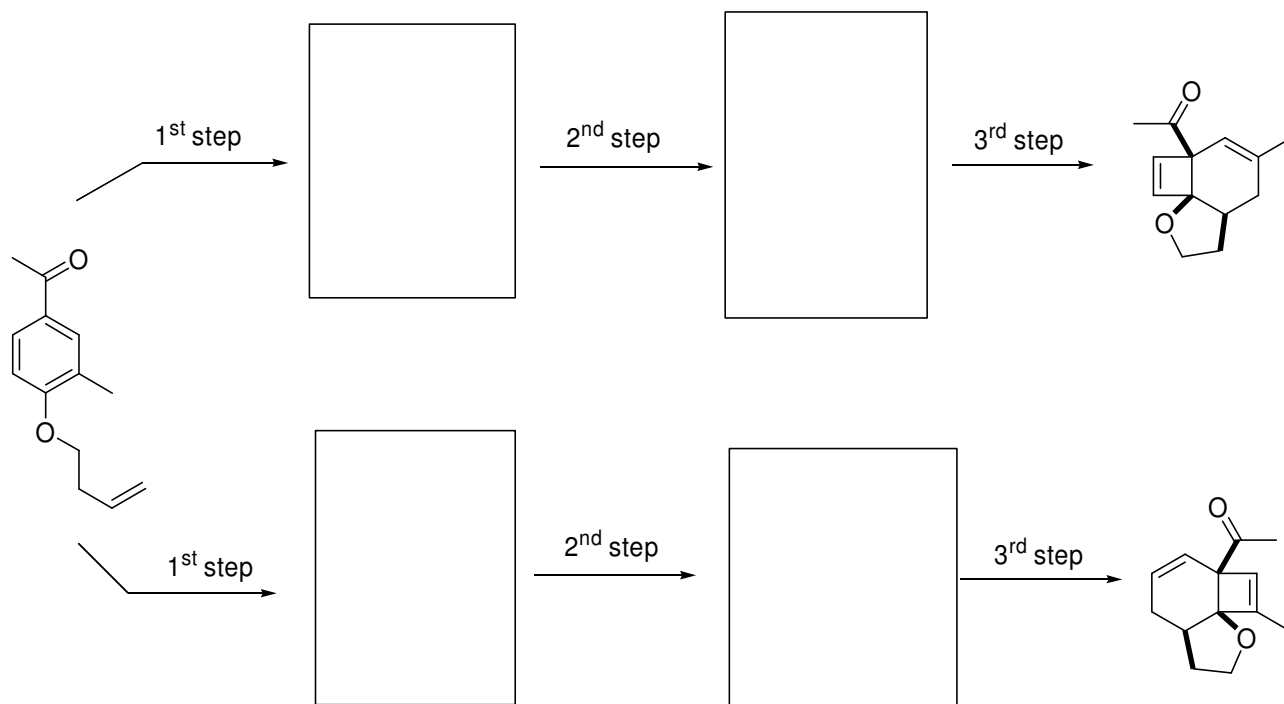
a) Fill in the correct product. Which kind of photoreaction is taking place and why?



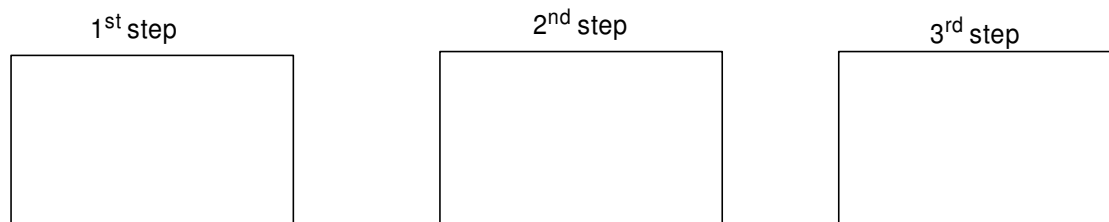
(2)

(2)

b) The following overall reaction can be described by a three step sequence. Fill in the missing intermediates, give the conditions for all three steps, and the names of the reactions taking place.



(8)

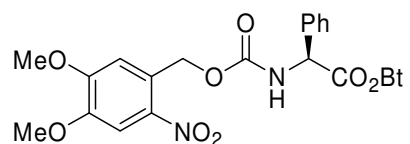


(6)

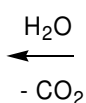
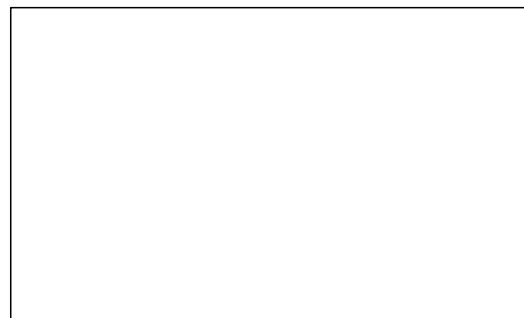
c) Which one is the regioselectivity determining step? _____

(1)

8. Photolabile protecting groups had a renaissance in recent years, because their deprotection is clean and occurs with high quantum yields. For example, 6-nitroveratryloxycarbonyl (NVOC) is used as a protecting group for either the N or the O terminus of polypeptides. Please complete the mechanism for the cleavage of NVOC from the N terminus of the shown amino acid!



Bt = benzotriazolyl



(5)