

Organische Chemie IV: Organische Photochemie

Wintersemester 2014/15 – Technische Universität München

Klausur am 05.02.2015

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(Druckbuchstaben)

geboren am in

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(Eigenhändige Unterschrift)

1	2	3	4	5	6	7	8	9	10	Σ	Note

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 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.

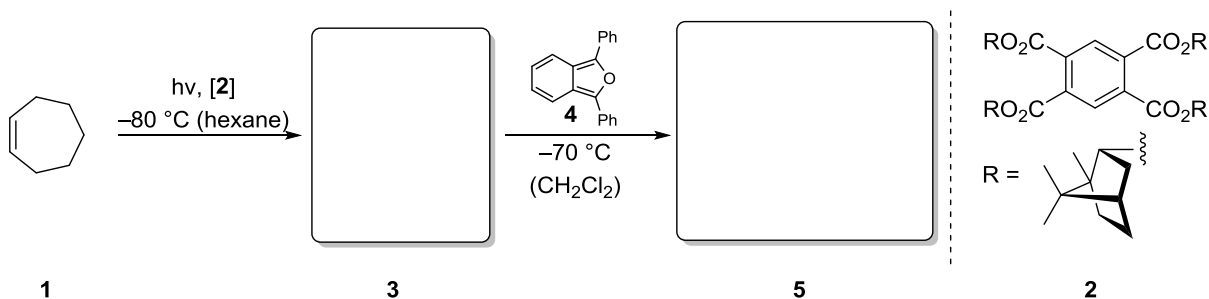
Information

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. Alkenes only have a limited applicability as substrates in photochemical reactions, since they are usually difficult to excite. In this example, (*Z*)-cycloheptene (**1**) is sensitized by **2**, which acts via an exciplex as a singlet sensitizer. The photoproduct **3** is then trapped by 1,3-diphenyl isobenzofuran (**4**).

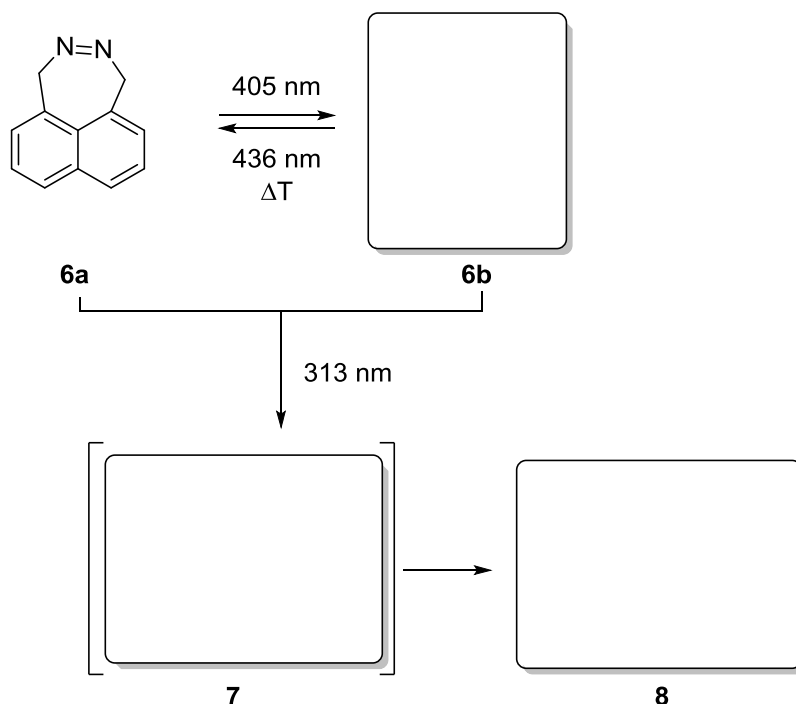
a) Which relaxation process, here from the $S^1 \rightarrow S^0$, is responsible for the formation of **3**? (1 point)

b) Give the structure of the photoproduct **3** and the product of the thermal reaction, with the correct relative configuration, after addition of the trapping agent **4**. (7 points)



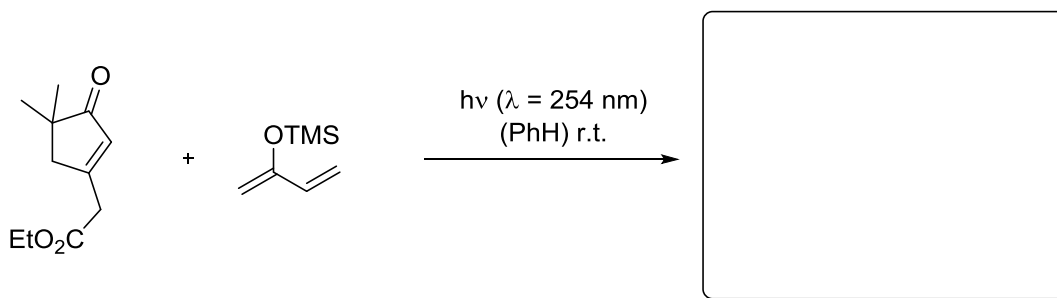
2. The choice of the appropriate wavelength is crucial for a successful photochemistry experiment. Irradiation with different wavelengths can trigger different photochemical transformations of the very same substrate.

Whereas irradiation of the $n\pi^*$ -transition of azocompound **6a** at $\lambda > 400\text{ nm}$ leads to a geometrical change in its structure, excitation of the $\pi\pi^*$ -absorption band at $\lambda = 313\text{ nm}$ leads, via a radical intermediate **7**, to photoproduct **8**, also exhibiting a tricyclic structure. Give the structure of **6b**, intermediate **7** and photoproduct **8**. (6 points)

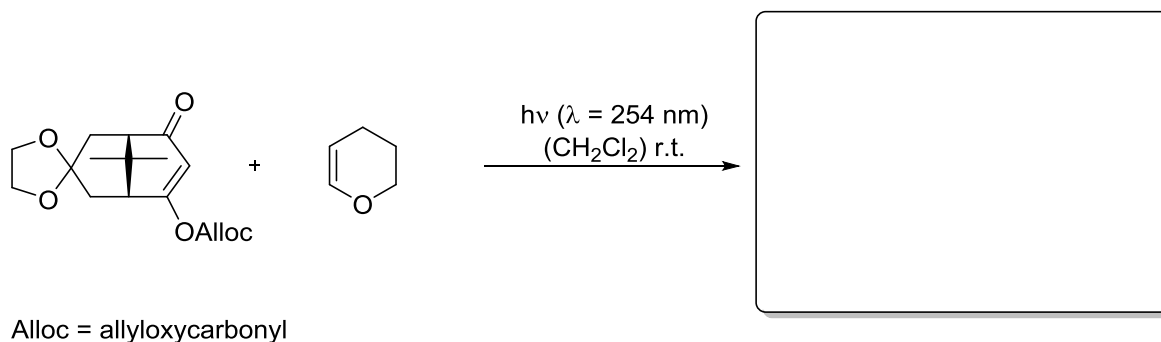


3. The [2+2] photocycloaddition of olefins is one of the most frequently applied reactions in photochemistry due to its potential to create complex ring systems in a single step. In the following reactions, give the respective product with the correct configuration, where applicable. Briefly explain why the copper salt is necessary for the reaction in c). (16 points)

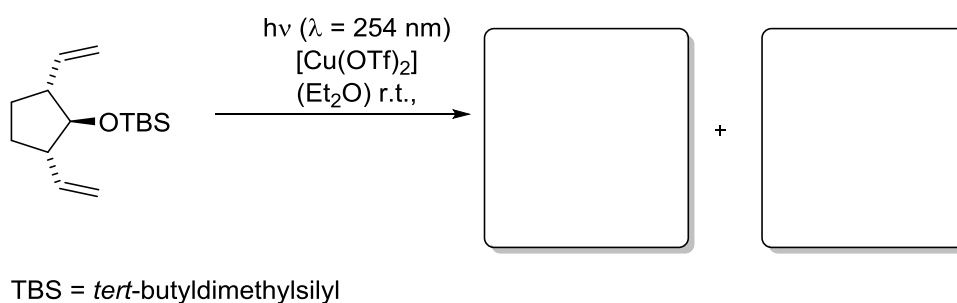
a)



b)



c) Hint: two diastereomeric products are obtained.

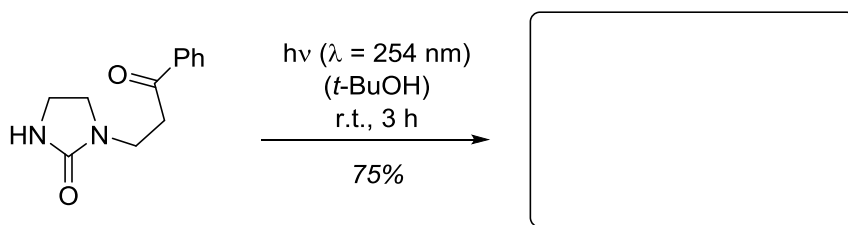


Explanation for the use of the copper salt (1 point):

d) In a), only one regioisomer is observed. Briefly explain the observed selectivity taking suitable molecular orbitals into account and classify the product as head-to-head or head-to-tail. (3 points)

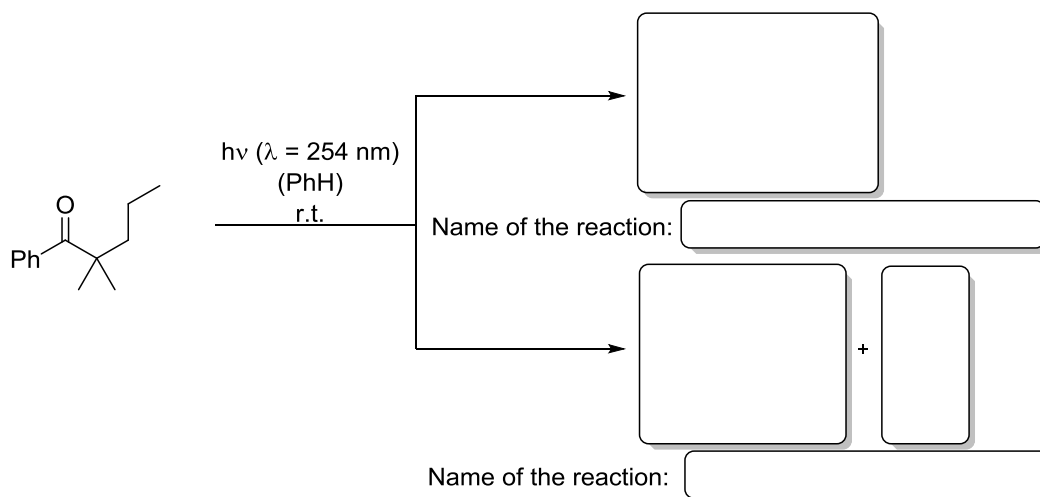
4. Carbonyl compounds can undergo a variety of fragmentation or addition reactions. In the examples below, give the products and the name of the reaction, when requested. You can neglect the relative configuration. (11 points)

a)

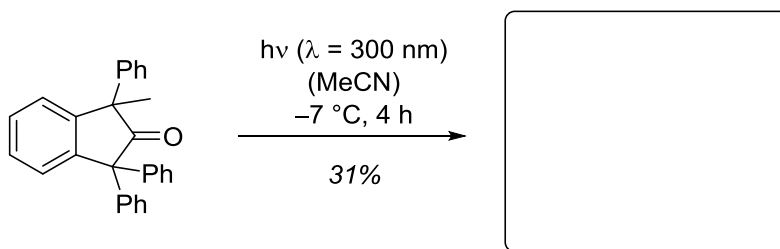


Name of the reaction:

b)

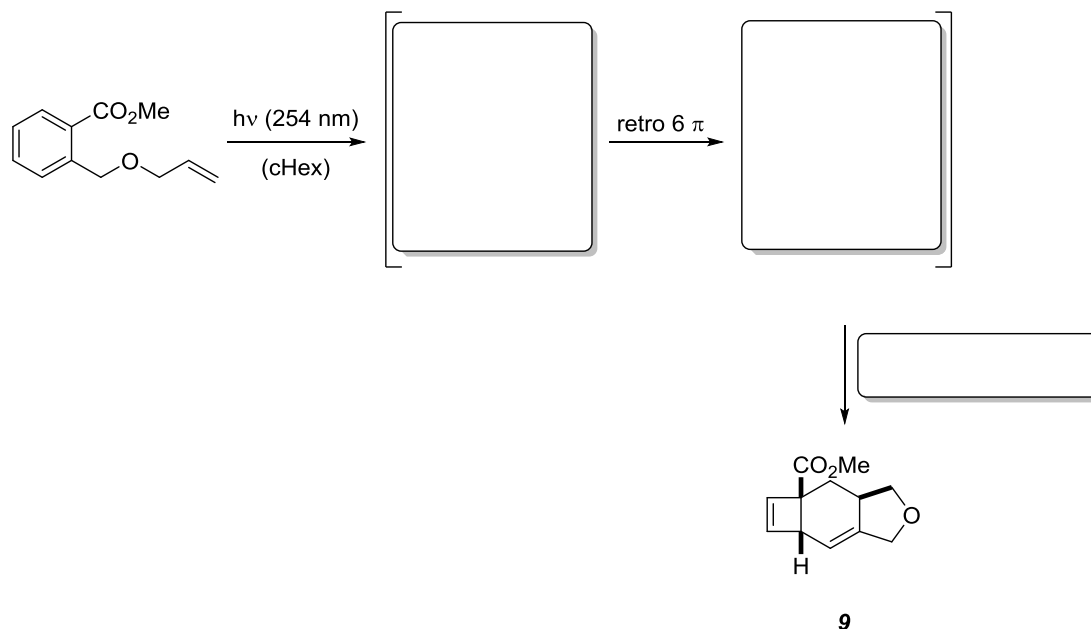


c)

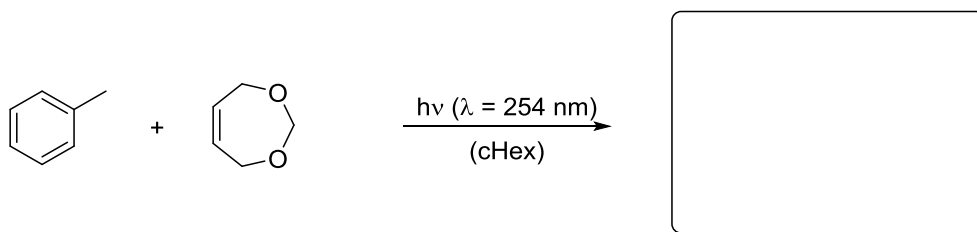


5. Photocycloadditions of an olefin to an arene core can occur in two major modes, leading to highly complex structures from relatively simple precursors. The mode selectivity mostly depends on the substitution pattern within the reacting compounds.

a) Give the expected photocycloaddition product with correct relative configuration. This product is not stable at the reaction conditions and transforms into a bicyclic intermediate, which, in turn reacts in a pericyclic reaction to product **9**. Also, specify the occurring pericyclic reaction. (8 points)

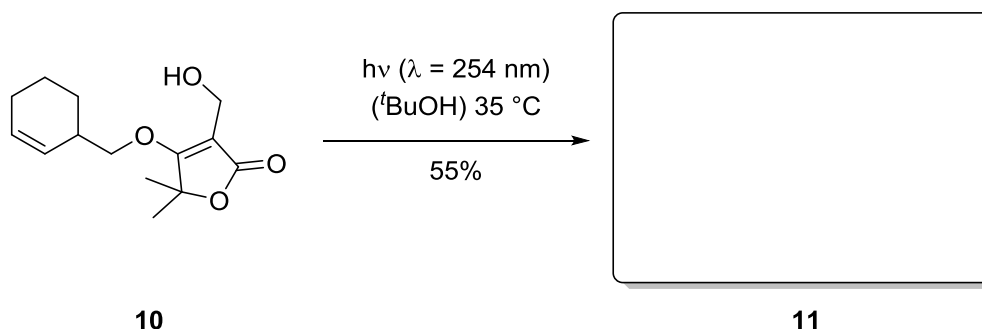


b) Give the expected product of the following intermolecular photocycloaddition. (4 points)

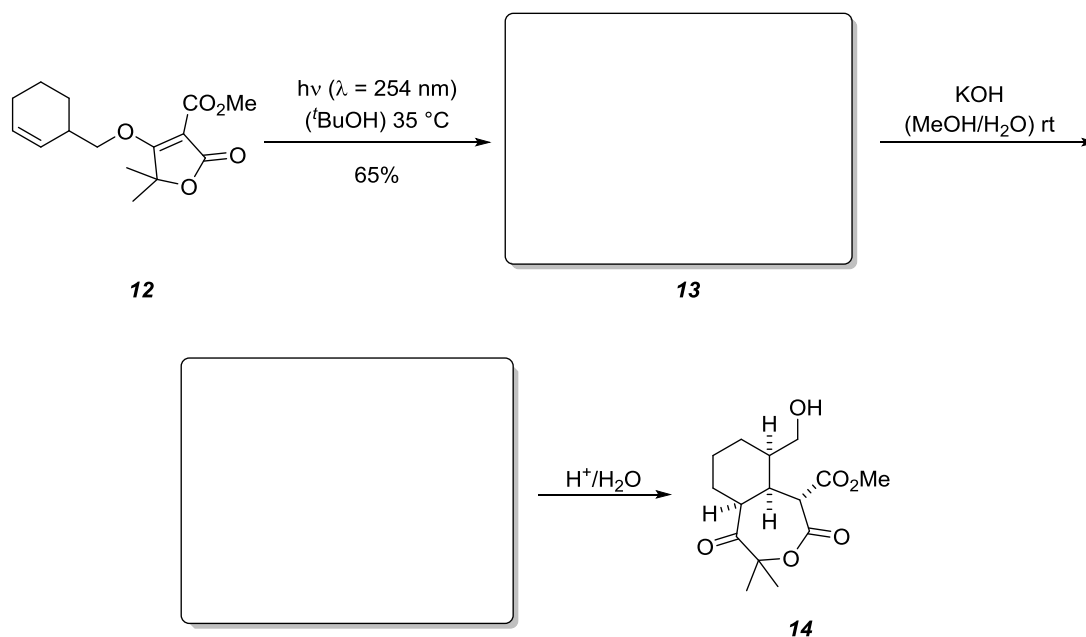


6. In the intramolecular photochemical reactions shown below, compound **10** exclusively forms the straight product **11** (a). However, the similar tetronate **12** only forms the corresponding crossed product **13**. Further treatment of compound **13** under basic conditions and a final acidic work-up, yields the bicyclic product **14** (b). Draw the missing structures. (14 points)

a)

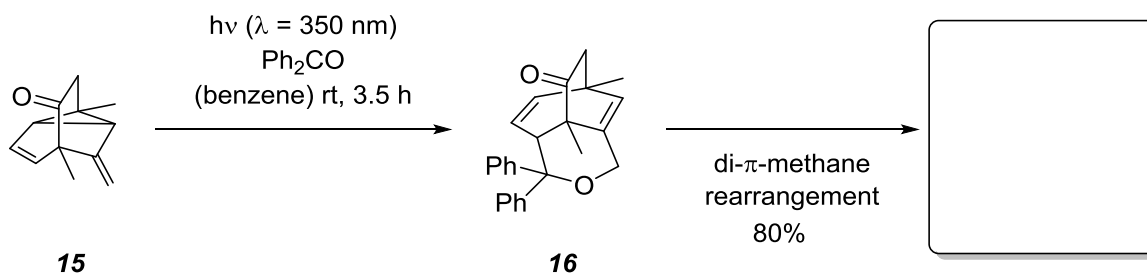


b)



8. Irradiation of compound **15** yields the di- π -methane rearrangement product in 80% yield.

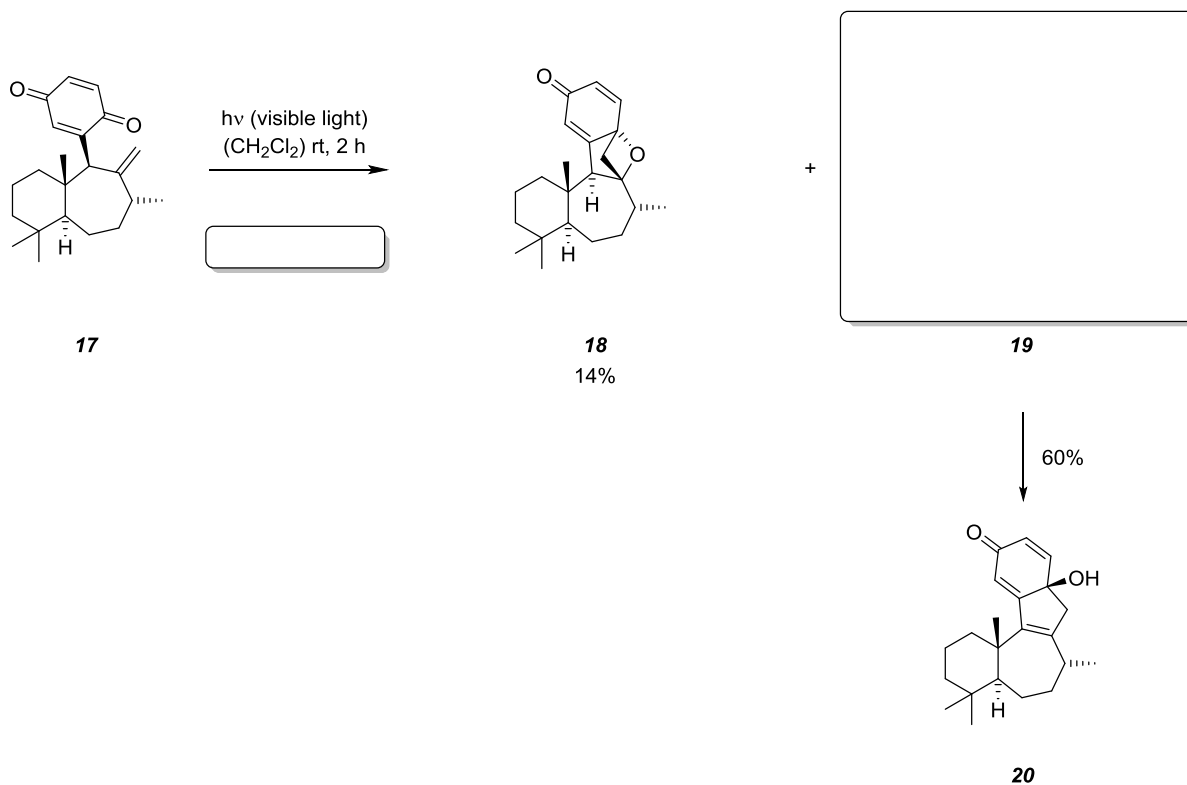
a) Draw the respective product with the correct absolute configuration. (4 points)



b) Suggest a mechanism for the formation of **16**. (4 points)

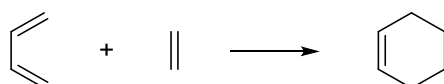
9. Under optimized reaction conditions, compound **17** was found to undergo a slow conversion into two diastereomeric products. Both compounds possess a highly strained bicyclic oxetane ring system, but only **19** can undergo a subsequent reaction to give **20**.

a) Draw the missing structure for **19** and give the name of the photoreaction. (5 points)



b) Give a mechanistic explanation of how compound **19** is converted into compound **20**. Why can't this occur with compound **18**? (3 points)

10. Consider the following general scheme of a Diels-Alder reaction.



Analyze this reaction with respect to the Woodward-Hoffman rules. Therefore, first draw all the molecular orbitals with the correct phase in the scheme given below and fill in the appropriate number of electrons (hint: the two newly formed σ bonds have to be considered as **one** orbital. The second highest anti-bonding orbital is given). Then, assign the symmetry of each orbital to a mirror plane. Finally, explain why the Diels-Alder reaction is thermally allowed but photochemically forbidden. (13 points)

