

# Organische Chemie IV: Organische Photochemie

Wintersemester 2017/18 – Technische Universität München

**Klausur am 16.02.2018**

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

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

.....  
(Eigenhändige Unterschrift)

1	2	3	4	5	6	7	8	9	10	11	12	$\Sigma$	Note

## Hinweise zur Klausur:

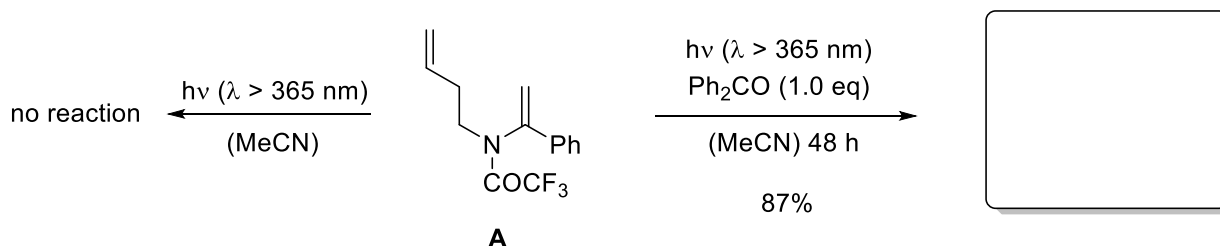
1. Die Klausur besteht aus insgesamt 8 Blättern (Deckblatt plus 7 Aufgabenblätter). Bitte kontrollieren Sie sofort, ob die Klausurunterlagen vollständig sind.
2. Es dürfen nur die vordruckten Bögen (einschließlich Rückseite) genutzt werden. Antworten sind zu kennzeichnen, sonst werden sie nicht bewertet. 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. Enamide (**A**) does not undergo a photochemical reaction by irradiation at  $\lambda = 365$  nm. However, in the presence of benzophenone a new product was obtained.

a) Fill in the missing structure. (3 points)



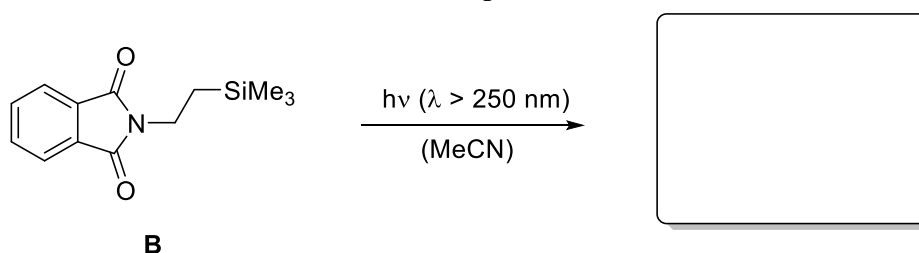
b) What important role does benzophenone play in this reaction? (1 point)

c) Which photophysical properties of molecule **A** and benzophenone have to be fulfilled for this process (fill >, <, or = in the two boxes). (2 points)

$\lambda_{\text{abs}}$  (**A**)   $\lambda_{\text{abs}}$  ( $\text{Ph}_2\text{CO}$ )

$E_{\text{T}}$  (**A**)   $E_{\text{T}}$  ( $\text{Ph}_2\text{CO}$ )

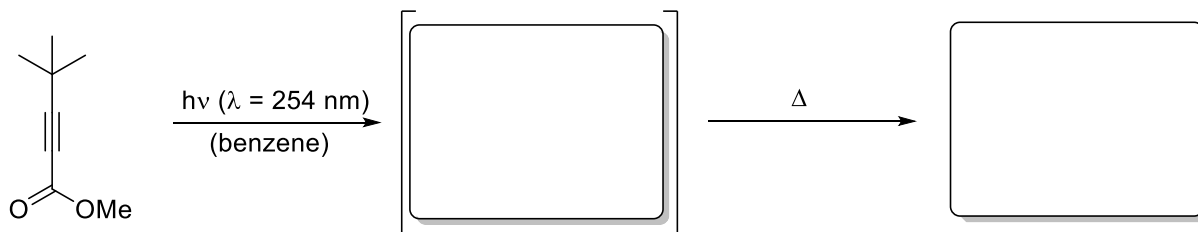
2. Irradiation of imide **B** with a Hanovia 200 W high-pressure mercury lamp yields a seven-membered lactam. Propose a reasonable mechanism for the formation of the product including electron arrows and at least three intermediates. (6 points)



Mechanism:

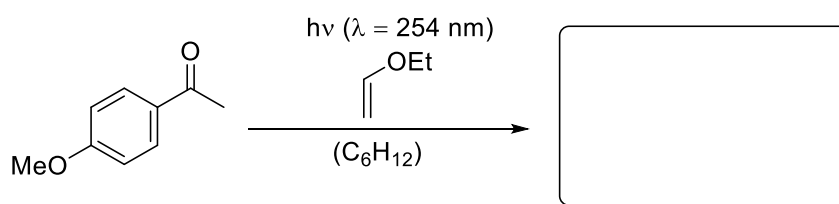
3. Photocycloaddition of an olefin to an arene core leads to photoproducts, which are often prone to consecutive reactions. Draw the primary photoproduct as well as the final product.

a) Give the expected photoproduct with the correct relative configuration. This product is not stable and isomerizes to a final product. Draw the final product and classify the thermal reaction according to the Woodward-Hoffmann notation. *Hint: Alkynes show a reactivity similar to olefins.* (6 points)

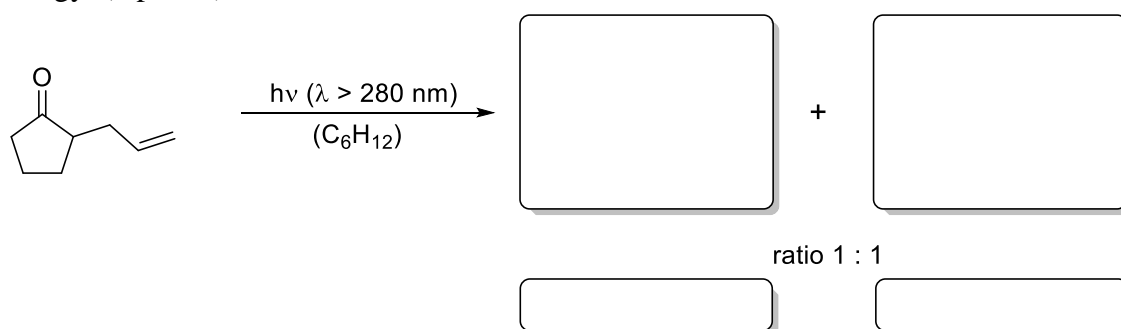


Classification of thermal reaction:

b) Substituted arenes and olefins lead to useful photoproducts. Fill in the missing structure. In this example neglect the relative configuration of the photoproduct. *Hint: The head-to-head product is formed.* (2 points)

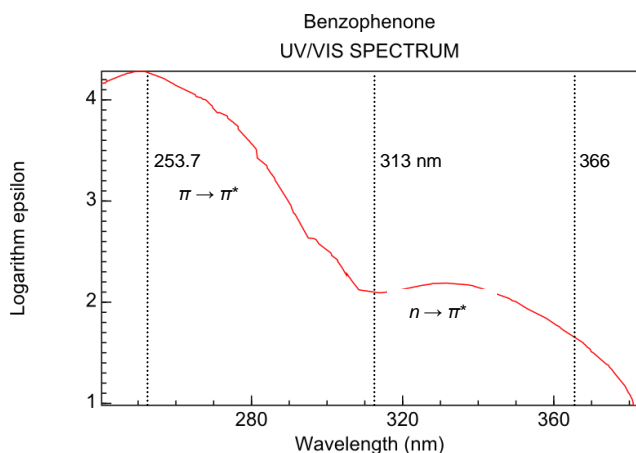


4. 2-Allylcyclopentan-1-one can be converted in a *Paternò-Büchi* reaction to a 1:1 mixture of two different regioisomers. Complete the reaction and label the photoproducts using the straight/crossed terminology. (8 points)

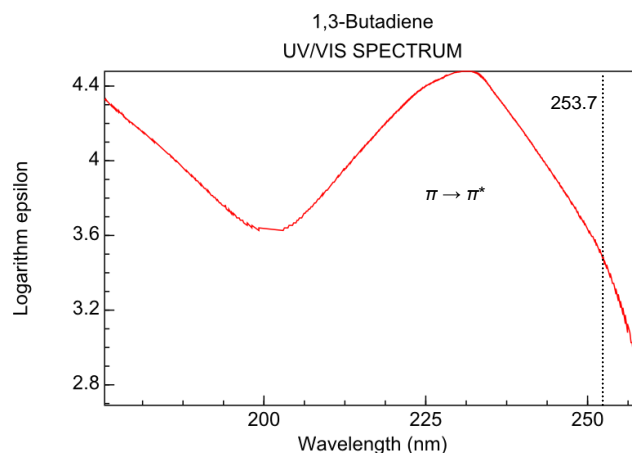


5. The UV/Vis spectra of benzophenone ( $S_1 = 296$  kJ/mol;  $T_1 = 276$  kJ/mol) and 1,3-butadiene ( $S_1 = 428$ -496 kJ/mol;  $T_1 = 240$  kJ/mol) are shown below. A solution consisting of benzophenone and 1,3-butadiene is irradiated with a high-pressure mercury lamp, which shows intense emission at 313 nm (approx. 382 kJ/mol) and at 366 nm (approx. 327 kJ/mol).

Propose a reasonable mechanism for the formation of the main product and explain the energy transfer processes graphically (in a scheme). (8 points)



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Answer:

Main Product:

Mechanistic explanation:

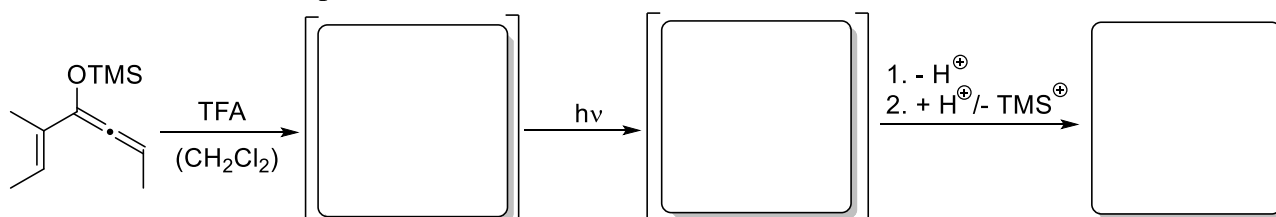
Scheme:

6. Photocyclisation reactions are a very important group of reactions often leading to interesting cyclic products.

a) Fill in the following table using the conrotatory/disrotatory notation. (2 points)

$\pi$ -electrons	thermally allowed
$4n$	
$4n + 2$	

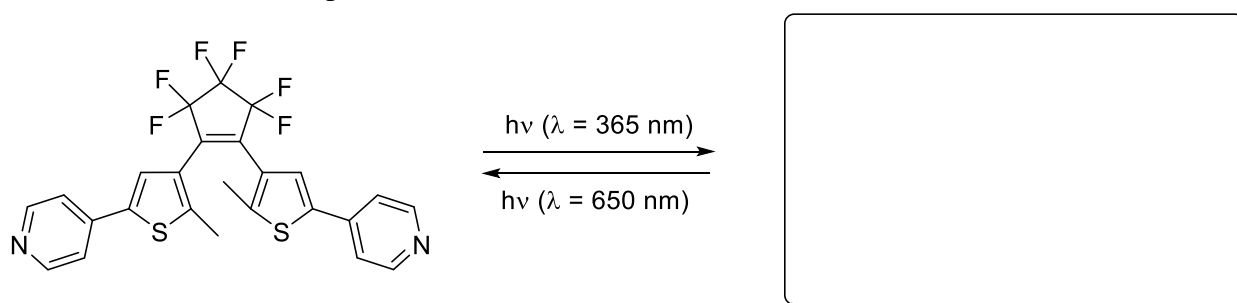
b) The *Nazarov* reaction and its photochemical counterpart can be used to synthesize cyclopentenones. In the first step of the shown reaction a cationic intermediate is formed which can be photochemically converted to a cyclic molecule. A thermal reaction leads to the final product with the formula  $C_8H_{12}O$ . Give all missing structures and indicate the relative configuration of the formed stereocenters. (7 points)



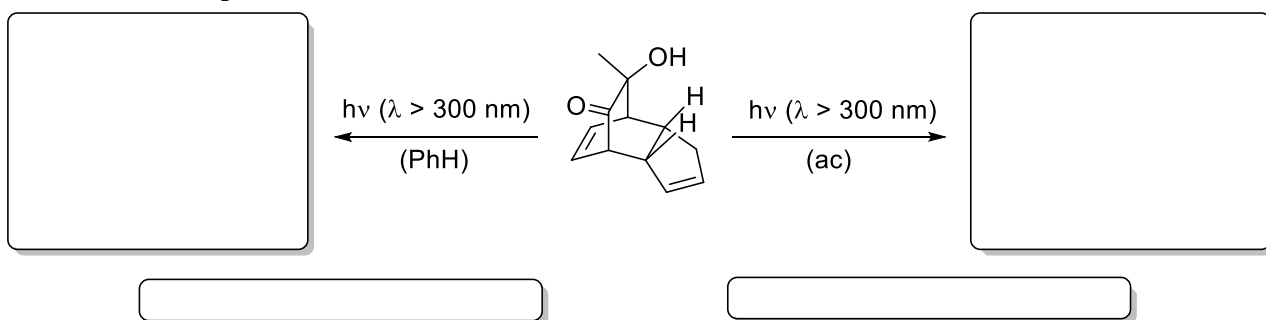
TMS = trimethylsilyl

TFA = 2,2,2-trifluoroacetic acid

c) Diarylethenes are commonly used photochromic species in materials science and device applications. Photochromic compounds are defined by reversible changes in chemical structure with absorption UV or visible light. Draw the product structure when the diarylethene shown on the left is irradiated at 365 nm. (3 points)

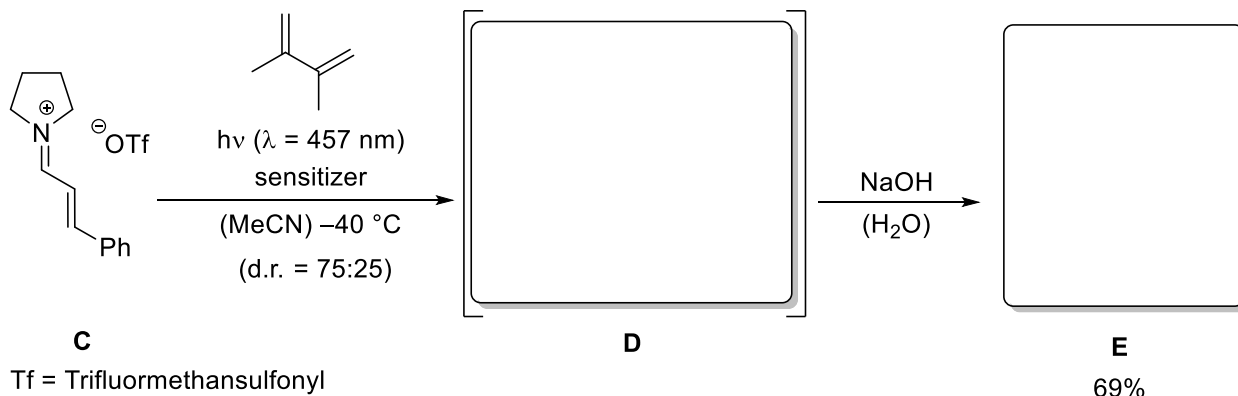


7. *Hirao et al.* investigated the photochemical behaviour of tricyclo[5.2.2.0]undecadienones that are easily accessible via *Diels-Alder* reactions. Irradiation with a 100 W high-pressure mercury lamp through a Pyrex filter gave two different rearrangement products depending on the solvent used. Give the structure of both photoproducts including the relative configuration and give the name of each reaction. (9 points)



8. a) Eniminium ions react in a similar manner as the corresponding  $\alpha,\beta$ -unsaturated carbonyl compounds. The photoexcited intermediate of an eniminium ion **C**, derived from a secondary amine, can undergo an intermolecular reaction with an olefin leading to the corresponding [2+2]-photoproduct. Give the structure of the intermediate **D** and of the final product **E**. Indicate the correct relative configuration.

Is the *head-to-head* or *head-to-tail* product formed? Give an explanation for the observed regioselectivity. Furthermore, how can the relative configuration be explained? (6 points)

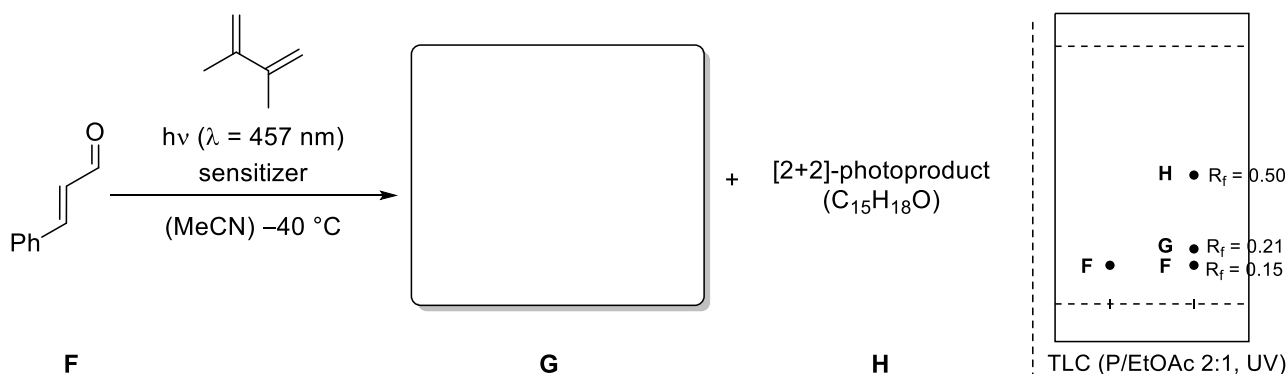


Answer:

Explanation of regioselectivity:

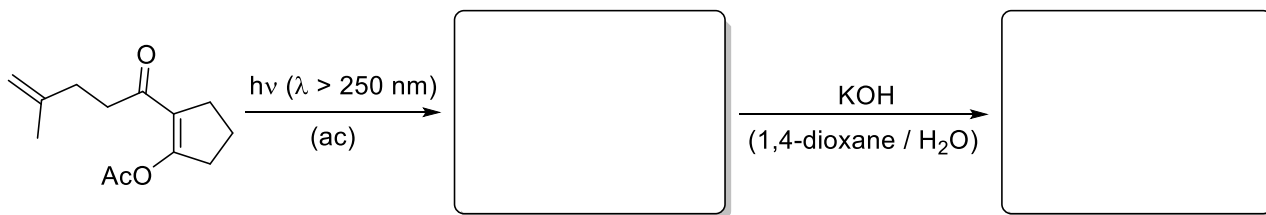
Explanation of stereoselectivity:

b) While monitoring the photocycloaddition reaction of cinnamic aldehyde **F** and 2,3-dimethylbutadiene an additional spot to the starting material and the [2+2]-photoproduct was observed on the TLC plate. The retention factors of the starting material **F** is  $R_f = 0.15$ , of the [2+2]-photoproduct **H**  $R_f = 0.50$  and of the unknown side product **G**  $R_f = 0.21$ . What kind of side reaction can occur during the irradiation? Draw the structure of the product **G** and give the name of the side reaction. (3 points)



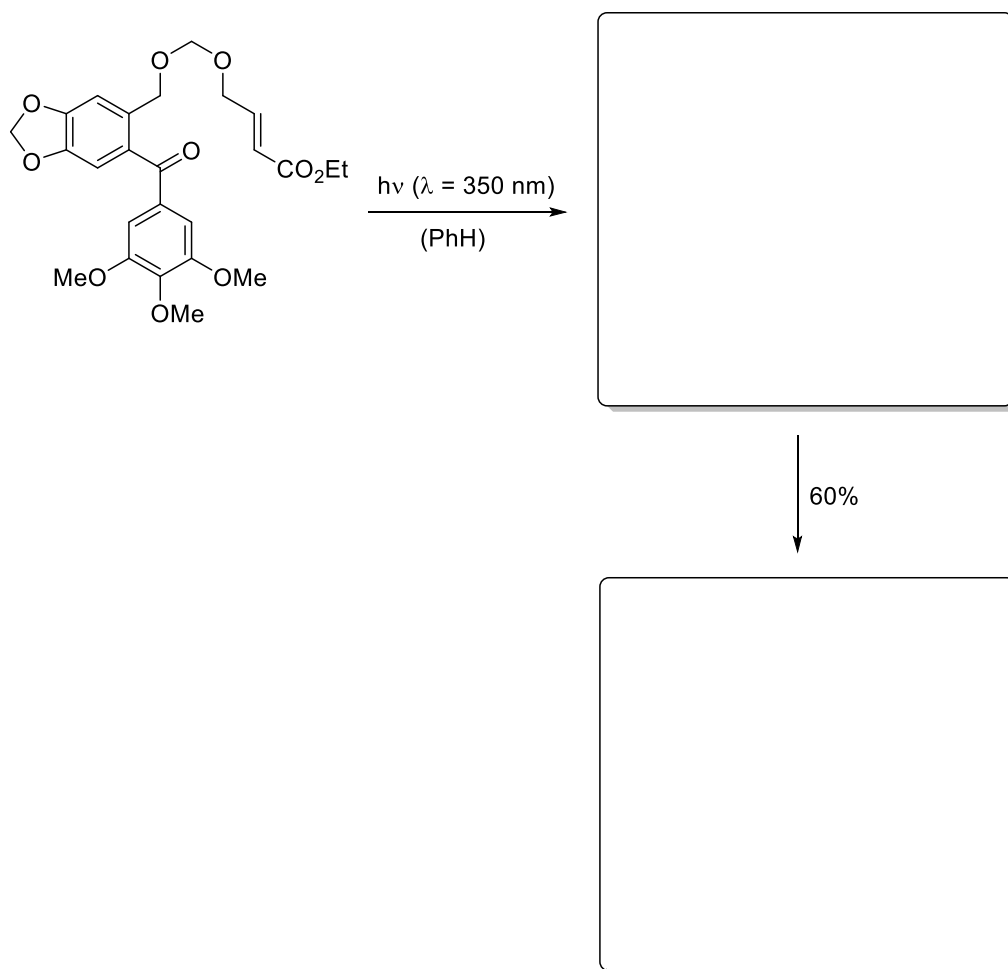
Type of reaction:

9. In studies towards the total synthesis of ( $\pm$ )-*daucene* a [2+2]-photocycloaddition reaction was a key step. Draw the missing structures and name the reaction sequence. (7 points)

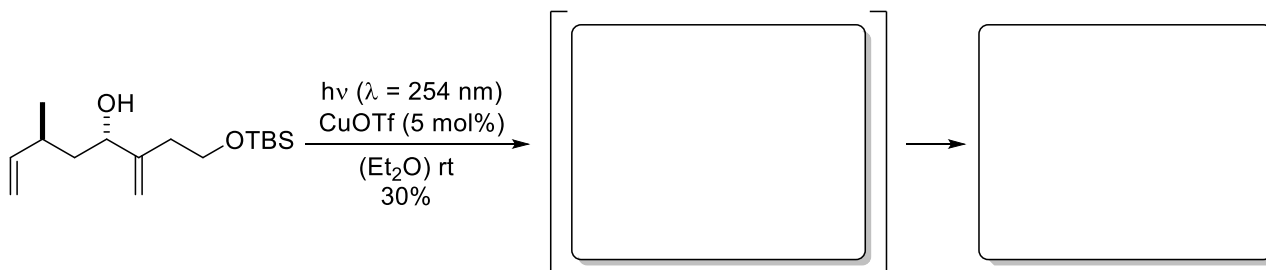


Name of the reaction sequence:

10. On their way to the natural product *podophyllotoxin*, G. A. Kraus and Y. Wu employed a photochemical reaction as a key step. Irradiation of the shown benzophenone derivative in a 350 nm *Rayonet* reactor generated an intermediate, which directly reacted to the desired product in a thermal, intramolecular cycloaddition reaction. Give the structure of the intermediate and the product. Indicate all formed stereocenters. (8 points)



**11.** Non conjugated olefins absorb light at very short wavelength. By complexation with Cu(I) their absorption is shifted to longer wavelength and the complex can be excited with low-pressure mercury lamps ( $\lambda = 254$  nm). Draw the complex in its correct conformation and give the reaction product. (7 points)



TBS = *tert*-Butyldimethylsilyl

**12.** Frequently, fenestranes have been the target of total synthesis by *meta*-photocycloaddition reactions. Here a two step approach toward one specific fenestrane is shown. Draw the two expected primary photoproducts. Which one can be converted to the shown fenestrane by further irradiation? The proposed mechanism for this conversion involves a homolytic cleavage of the cyclopropane ring of photoproduct **J** to afford the linear triquinane biradical, which undergoes addition to the double bond. Additionally, name the type of triquinane **I** (12 points)

