Organic Photochemistry – Exercise 1: 26/10/2023, 11.00 am

German group: CH22210

1. a) The allene amide below shows phosphorescence at $\lambda = 440$ nm. Calculate the triplet energy (in kJ mol⁻¹).



b) UV/Vis spectroscopy is the method to determine at which wavelength a compound absorbs light and therefore at which wavelength it can be promoted to the excited state by direct irradiation. The spectrum of the depicted compound was recorded using a 1.0 mm quartz cuvette with a concentration of 1.0 mM. Please calculate the corresponding extinction coefficients for the maxima at 232 nm and 281 nm.



UV/Vis spectrum of the depicted compound in MeOH (1.0 mM), measured in a 1.0 mm quartz cuvette.

2. a) Complete the following *Jablonski* diagram. Define every energy transfer noted on the diagram.



b) Draw an energy diagram to explain the Franck Condon principle and Kasha's rule.

3. Draw the MO diagram for benzophenone (C=O, π -n- π *) in the ground state, after excitation with light and intersystem crossing processes (ISC).



4. a) Shown below is the photoinduced spirocyclization of an indole-3-carboxamide. Provide a plausible mechanism for the formation of the two observed diastereoisomeric products.



b) Explain the diastereoselectivity observed.

Organic Photochemistry – Exercise 2: 21/11/2023, 09.00 am

German group: CH27402

English group: CH42306

1. a) To this day, the Paternò-Büchi reaction is one of the most useful photoreactions. Please fill in the missing intermediates and products and provide (if necessary) explanations for the observed selectivities.





2. Upon irradiation at 350 nm, cyclohept-1-ene-1-carbaldehyde undergoes $E \rightarrow Z$ isomerization to a reactive intermediate that can undergo subsequent transformations. Write down the isomerized product and the compounds obtained after the subsequent reactions. What are the names of these reactions?



3. The Paternò-Büchi reaction has found many applications in the field of natural product synthesis. One example is the total synthetis of Merrilactone A. Fill in the blank with the correct Paternò-Büchi product.



Organic Photochemistry – Exercise 3: 23/11/2023, 11.00 am

German group: CH22210

English group: CH42306

1. a) Shown below is the isomerization of (E/Z)-stilbene to form one of the isomers as the major product. Which is the major isomer formed in this reaction? What conditions are required to allow for isomerization to happen?

Ph
$$(\lambda = 313 \text{ nm})$$
 Ph $(\lambda = 313 \text{ nm})$ Ph $(\lambda = 313 \text{ nm})$

b) Give the key intermediate structures for the isomerization of alkenes and explain the cause of the energy difference in the two intermediate states. State the type of process that leads to the final product in the final step.



2. a) Sensitizers play an important role in the excitation of alkenes into their respective triplet states. For what reasons do alkenes not undergo efficient ISC to form triplet states from their singlet states, and why are triplet sensitizers (often aromatic carbonyl-bearing compounds) ideally suited for this process? Draw an energy diagram to demonstrate this.

b) Dexter energy transfer explains how the energy of a triplet sensitizer in its excited state can be transferred to another molecule in the ground state. Fill in the molecular orbitals to demonstrate how this is achieved. What are the conditions required to allow energy transfer?



3. [2+2]-cycloadditions are one of the most used photochemical reactions. Fill in the products and intermediates of the following examples.

a)





4. Singlet oxygen is employed in the synthesis of DL-Bishomoinositol. Complete the synthesis.

a)



TPP: Tetraphenylporphyrin

b) You are about to design a new singlet oxygen sensitizer. How would you design the triplet energy of your compound? Draw some examples of common singlet oxygen sensitizers.

Organic Photochemistry – Exercise 4: 12/12/2023, 09.00 am

German group: CH27402

English group: CH42306

1. Give the products of the following reactions.

a)



major minor



The product of the following reaction sequence is a key intermediate in the total syntheses of (±)-Sollasin A and (±)-Sollasin D. Complete the reaction with the intermediate and the product. What is the name of this reaction sequence?



3. In 2023, the *Bach* group published an enantioselective chiral *Lewis* acid-catalyzed variant of a photochemical rearrangement reaction. Give the name of the reaction and fill in the missing structures of the racemic variant with achiral BF_3 as *Lewis* acid.



4. Photochemical rearrangement reactions are a powerful tool to access complex structures. Fill in the missing starting materials and products and give the names of the reactions.



Organic Photochemistry – Exercise 5: 21/12/2023, 11.00 am

German group: CH22210

English group: CH42306

1. The theory described by Woodward and Hoffmann was the first model that successfully explained and predicted the outcome of pericyclic reactions.

- a) Pericyclic reactions are the consequence of orbital interactions. What are the underlying assumptions for these orbital–orbital interactions?
- b) Consider hexa-1,3,5-triene as a model system for cyclizations. Does the photochemical $[6\pi]$ cyclization to cyclohexa-1,3-diene occur in a conrotatory or disrotatory fashion? In the figure below, draw the molecular orbitals of both compounds and fill in the electrons for the S₁ state. Then, analyze the orbital symmetry for both conrotatory and disrotatory cyclization using the Woodward-Hoffmann rules, i.e. if the orbital is symmetric or asymmetric regarding the symmetry operation (conrotatory = C₂-symmetric, disrotatory = mirror-symmetric).



2. What major product is formed by subjecting the substrate shown below to thermal conditions and what is the major product formed by subjecting it to photochemical conditions?



3.

a) Photochemical pericyclic reactions have been used extensively in the synthesis of cyclobutane containing compounds. Draw the intermediates that are formed in the synthesis of piperarborenine B, and include all stereochemical information.



piperarborenine B

b) Is the cyclization a con- or dis- rotatory process? Draw molecular orbitals to demonstrate this.

Organic Photochemistry – Exercise 6: 18/01/2024, 11.00 am

German group: CH22210

English group: CH42306

1. You have learned about the photochemistry of aromatic compounds. Fill in the missing structures of the reactions below and give the names of the reactions.



The following reaction was performed in the presence of the chiral triplet sensitizer **A**. Fill in the correct product for the reaction. Explain the enantioselectivity by drawing the substrate-sensitizer complex.



2.

Organic Photochemistry – Exercise 6: 30/01/2024, 09.00 am

German group: CH27402

English group: CH42306

1. a) The following sp²-sp² coupling reaction happens through a redox neutral process. Suggest a mechanism for this reaction. What is the role of the acid?



2. The following reaction enables an sp²-sp³ addition, followed by carbonylation and esterification. Suggest a mechanism for this.



3. Complete the following simplified molecular orbital representation for a typical photoredox catalyst and the corresponding reductive and oxidative quenching cycles (PC = photocatalyst; A = electron acceptor; D = electron donor; ISC = intersystem crossing).



4. In 2016, the group of Stephenson reported a reductive debromination of unactivated alkyl and aryl bromides. Draw the mechanistic cycle for the reaction and propose a suitable photocatalyst.



Organic Photochemistry – Exercise 8: 08/02/2024, 11.00 am

German group: CH22210

English group: CH42306

1. In 2013, the group of Gouverneur developed this elegant synthetic way of introducing the CF₃ group on various alkenes and alkynes. Fill in the missing intermediates and products of this light mediated transformation. Is this process going through oxidative or reductive quenching?



2. The following light mediated reaction allows the selective C-H γ -functionalization of various ketones. Fill in the missing intermediates and products of this light mediated transformation. Is this process going through oxidative or reductive quenching? Which term describes what happens in step A?





3. The following example depicts a net reductive photoredox catalyzed cyclization reaction using *Michael*-acceptors as substrates. Draw the mechanism including the photocatalytic cycle and explain what serves as an external reductant in this reaction and what side product is formed.

