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

German group: CH22210

English group: CH42306

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



 $E = (h \cdot c)/\lambda$ $h = Planck's \ constant = 6.626 \ x \ 10^{-34} \ J \cdot s$ $c = speed \ of \ light = 3 \ x \ 10^8 \ m/s$ $\lambda = 440 \ nm \ (given \ in \ the \ question \ above)$ $N_A = 6.022 \ x \ 10^{23} \ /mol$

 $E(kJ/mol) = (h \cdot c \cdot N_A)/\lambda = 272 \ kJ/mol$

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.

 $\mathcal{E} = A / (c \times d)$

 $\mathcal{E}_{232 nm} = 0.165 / (1.0 \cdot 10^{-3} \text{ mol/L} \times 0.1 \text{ cm}) = 1650 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ $\mathcal{E}_{281 nm} = 0.056 / (1.0 \cdot 10^{-3} \text{ mol/L} \times 0.1 \text{ cm}) = 560 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$

Absorbances can be read from UV/Vis spectra.

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



<u>Absorption:</u> The absorption of electromagnetic radiation is how matter (typically electrons bound in atoms) takes up a photon's energy — and so transforms electromagnetic energy into internal energy of the absorber (for example, thermal energy).

<u>Internal conversion (IC)</u>: IC denotes the isoenergetic and therefore radiationless transition from the vibrational ground state of an electronically excited state (e.g. S1) to a highly excited vibrational state of the next lower electronic state (e.g. the electronic ground state S0). Occurs without changing the multiplicity of the spin.

<u>Fluorescence</u>: It is the spontaneous emission of radiation by an excited molecule, typically in the first excited singlet state (S1), with retention of spin multiplicity.

<u>Intersystem crossing (ISC)</u>: Isoenergetic radiationless process involving a transition between the two electronic states with different states spin multiplicity.

The dominant mechanism for the ISC in organic molecules is the interaction between the magnetic moment of the spin and that of the associated orbital (spin-orbit coupling). In the case of diradicals, direct interaction between two spins is also possible (spin-spin coupling). The spin-orbit coupling depends to the fourth power on the atomic numbers of the atoms involved. The ISC is thus significantly accelerated in the presence of heavy elements.

<u>Phosphorescence</u>: It is the spontaneous emission of radiation by an excited molecule, typically in the first excited triplet state (T_1) , involving a change in spin multiplicity.

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



E: potential energy; r_{xv}: bond distance (diatomic molecule)

<u>Kasha's rule:</u> The rule states that photon emission (fluorescence or phosphorescence) occurs in appreciable yield only from the lowest excited state of a given multiplicity. This is due to fast relaxation of excited vibrational states.

Franck Condon principle: The principle states that during an electronic transition, a change from one vibrational energy level to another will be more likely to happen if the two vibrational wave functions overlap more significantly.

 \rightarrow Electronic transitions are orthogonal!

Maybe we can also explain Born Oppenheimer in this regard. (\rightarrow For calculation of electronic movements, the movement of the nuclei does not have to be taken into account since it is much slower.)

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 and the regioselectivity 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.







explanation for regio- and diastereoselectivity

-stability of 1,4 biradical

-90° orientation of the two orbitals, prefered ISC geometry,

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?

J. Org. Chem. 2023, 88, 12844-12852.



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.

Org. Lett. 2005, 7, 3969-3971.



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?



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 sensitizers (carbonyl-bearing compounds) ideally suited for this process? Draw an energy diagram to demonstrate this.



Carbonyls

- Non-bonding orbital allows for excitation into low energy S_1 state (n- π^* vs π - π^*)
- Singlet and triplet states are of similar energy levels allowing for efficient ISC

Alkenes

- high electron-electron repulsion in S₁
- no electron-electron repulsion in T₁

Consequence: - no $S_1 \rightarrow T_1$ isc for alkenes

- facile energy transfer from compounds with low T_1

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?



- no energy transfer for r > 1.5 nm (1500 pm, 15 Å) -
- triplet states (π^* orbitals) must have similar energies. -



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

a)



Tetrahedron Lett. 2003, 44, 1401.

major

minor

b)





JACS 2018, 140, 3228 - 3231.

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

a)



Tetrahedron 2003, 59, 2063 - 2066.

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

Low lying E_T is important for the energy transfer.

or





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

German group: CH27402

English group: CH42306

1. Give the products to the following reactions.

a) Eur. J. Org. Chem. 2002, 2002, 645–654.



b) Chem. - Eur. J. 2013, 19, 14098-14111.



c) Tetrahedron Lett. 1997, 38, 1045–1048.



d) Synlett 2009, 2009, 562-564.



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?

Chem. Lett. 1998, 27, 113–114.



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.



ACS Catal. 2023, 13, 9, 5896-5905

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.

a) Chem. Rev. 1996, 96, 3065-3112





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

German group: CH22210

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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?
 - interaction is stronger the closer the corresponding orbitals are in energy and/or the better the orbital overlap is
 - filled shell repulsion: occupied orbitals repeal, occupied and unoccupied orbitals attract each other
 - Coulombic attraction: positive charge on one molecule attracts any negative charge on the other (and repels any positive).
- 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).



Diels-Alder reaction: $[\pi 4_s + \pi 2_s]$ Wagner-Meerwein shift of carbocation: $[_{\omega}0_s + {}_{\sigma}2_s]$ **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.

J. Org. Chem., 2014, 79, 2430-2452



piperarborenine B

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

Conservation of Orbital Symmetry (Woodward-Hoffmann rules 1969)



disrotatory \rightarrow S₁ symmetry element

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.



J. Am. Chem. Soc. 1995, 117, 6801–6802.



meta-photocycloadditon

Tetrahedron Lett. 1990, 31, 2517-2520.





J. Heterocyclic Chem. 2005, 42, 227.

2. 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.



Angew. Chem. Int. Ed. 2014, 53, 7661.

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.





Org. Lett. 2018, 20, 15, 4663-4666

3. Complete and correct 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.





ACS Catal. 2016, 6, 9, 5962–5967.

Organic Photochemistry – Exercise 6: 08/02/2024, 11.00 am

German group: CH27402

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?



J. Am. Chem. Soc. 2013, 135, 2505.

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?





Angew. Chem. Int. Ed. 2018, 57, 1692.

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.



Chem. Rev. 2016, 116, 10075-10166.