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Organic Photochemistry

Exam:CH3038 / EndtermExaminer:Prof. Dr. Thorsten Bach

Date: Tuesday 20th February, 2024 **Time:** 08:30 – 10:00

Working instructions

- This exam consists of **14 pages** with a total of **5 problems**. Please make sure now that you received a complete copy of the exam.
- The total amount of achievable credits in this exam is 100 credits.
- Detaching pages from the exam is prohibited. You may only use the distributed paper to give your answers; no additional sheets are allowed. There is additional space at the end of the exam but make sure to clearly indicate which question you are answering. **Short answers please!**
- · Allowed resources:
 - one non-programmable pocket calculator
 - one analog dictionary English ↔ native language

No other resources are allowed (also no molecule models). Cheating and cheating attempts will result in the candidate failing the exam.

- Do not write in red or green nor use pencils.
- Every correctly and fully answered problem will be awarded the number of credits shown. It is possible to obtain only a fraction of the credits if the answer is not completely satisfactory.
- · Consider the relative and absolute configuration of molecules, unless otherwise noted.
- Physically turn off all electronic devices, put them into your bag and close the bag.

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Problem 1 Multiple Choice Questions (10 credits)

There is only one correct answer option. Please answer multiple choice questions in the following way:

Mark correct answers with a cross To undo a cross, completely fill out the answer option To re-mark an option, use a human-readable marking



a) The Franck Condon principle...

	states that all	vibronic transitions	have the	same probability.
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- states that a transition is more likely the more the wave functions of the two states overlap.
- describes whether an electronic transition is photochemically allowed.
- describes whether a reaction is thermally allowed.
- b) For enone photocycloadditions, why do chemists usually use cyclic enones rather than acyclic ones?
 - Acylic enones usually do not engage in photocycloadditions due to steric reasons.
 - Intersystem crossing rates for acyclic enones are significantly slower than for cyclic ones.
 - In acyclic enones, the energy from the absorbed photon is dissipated by E/Z isomerization before the photocycloadditon can take place.
 - In acylic enones, the triplet biradical is too short-lived and immediately returns to the ground state *via* phosphorescence.
- c) Which excitation pathway does a substrate of an oxa-di- π -methane rearrangement reaction undergo?
 - Direct excitation of S_0 to S_1 ($n\pi^*$).
 - Sensitization from S_0 to T_1 ($n\pi^*$).
 - **Sensitization from S**₀ to T₁ ($\pi\pi^*$).
 - Direct excitation of S_0 to S_1 ($\pi\pi^*$).
- d) According to the Woodward-Hoffmann rules, a conrotatory [4 π] cyclization reaction...
 - is photochemically allowed.
 - is thermally allowed.
 - exclusively occurs on the triplet hypersuface.
 - \square maintains orbital symmetry in S₁ state.

e) The *meta*-photocycloaddition of alkenes to aromatic compounds is generally favored over the *ortho*-photocycloaddition when...

- the alkene bears a donor substituent and the aromatic a donor substituent.
- the alkene bears an acceptor substituent and the aromatic an acceptor substituent.
- the alkene bears a donor substituent and the aromatic an acceptor substituent.
- the alkene bears an acceptor substituent and the aromatic a donor substituent.

- f) Enantioselective photoreactions with chiral Lewis acid catalysts are feasible because of the...
 - the facilitated energy transfer from the Lewis acid to the substrate.
 - the high extinction coefficient of the Lewis acid catalyst.
 - the hypsochromic shift of the substrate-Lewis acid complex.
 - the bathochromic shift of the substrate-Lewis acid complex.
- g) Which statement about Dexter energy transfer is true?
 - Dexter energy transfer is spin allowed as no spin flip is required.
 - Dexter energy transfer can occur either in a concerted or in a stepwise fashion.
 - Dexter energy transfer is highly distance dependent.
 - All of the statements are true.
- h) Upon irradiation, a carbonyl compound is typically excited to the...
 - \square n π^* state.
 - \square $\pi\pi^*$ state.
 - \square n σ^* state.
 - $\Box \sigma \sigma^*$ state.
- i) What is a common method to decrease the reduction potential of α , β -unsaturated carbonyl compounds?
 - Addition of a Lewis base.
 - Addition of a Lewis acid.
 - Use of photoredox catalysts with heavy transition metals.
 - Use of chelating ligands on the photoredox catalyst.

j) In a [Ru(bpy)₃(BF₄)₂] photocatalyzed Pschorr reaction, rearomatization occurs via...

- oxidation of the radical intermediate and deprotonation.
- oxidation of the radical intermediate and tautomerization.
- reduction of the radical intermediate and deprotonation.
- reduction of the radical intermediate and tautomerization.

Problem 2 Fundamentals of Photochemistry (14 credits)

To successfully conduct photochemical reactions, fundamental processes and properties of organic and organometallic compounds upon irradiation need to be studied and understood. **Constants:** Avogadro constant = 6.0221×10^{23} /mol, Planck constant = 6.6261×10^{-34} J s, speed of light = 299.79×10^6 m/s.

Important: Provide equations for all your calculations and all numbers with three significant digits.

a) For what reason are carbonyl compounds excited into the π^* system at longer wavelengths compared to their alkene counterparts?

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3	

0

1

2 3

4 5 b) Give four differences between the fluorescence and phosphorescence emission. Which non-radiative process is required for phosphorescence to occur?

0	
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2	

c) What is Kasha's rule?

d) The wavelength found for the triplet emission spectrum of 2,7-dibromothioxanthone was 469 nm. Calculate the triplet energy in kJ/mol.

0 1 2



e) How does the reduction potential of a metal complex generally change upon the introduction of more electrondeficient ligands? What is the reason for this?

0 1 2

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Problem 3 Direct Excitation (26 credits)

Many photochemical processes are induced by the absorption of light by an organic substrate.

a) In 1985, Kakisawa *et al.* utilized a photochemical reaction to obtain the bicyclic ring system of the taxane skeleton. Draw the missing structures and give the name of the reaction sequence.







Name of the reaction:

c) Antroalbocin A, first isolated in 2018, was recently synthesized employing two photochemical steps. The enone is first deconjugated as you can see in the scheme below. Further irradiation under the same conditions then leads to the product. Draw the short-lived intermediate of this rearrangement reaction as well as the final product. What is the name of this reaction?



d) Sesquiterpenes comprise a class of natural products and photochemistry offers elegant ways for the synthesis of their complex carbon skeletons. Give the structures and the names of the two triquinane products obtained by the Zhu group as they synthesized silphinane derivatives. What is the name of this reaction?





Problem 4 Photoredox Chemistry (20 credits)

In recent years, the field of photoredox chemistry has experienced a rapid gain in importance and attention.

a) In 2015, the Zhang group reported this visible light mediated synthesis of nitrogen-containing heterocycles using fac-[Ir(ppy)₃] as the photocatalyst. Please complete the catalytic cycle of the reaction. Does the catalyst undergo an oxidative or a reductive quench?



b) Give the correct product structures of the reactions shown below.



74%



Problem 5 Diverse Reactivity (30 credits)

Organic photochemistry gives rise to a diverse set of chemical reactions.

 a) The formation of which product can be observed, when the shown α , β -unsaturated ketone is irradiated in deuterated methanol?



b) Give the correct structures of the intermediate and the final product of the reaction sequence shown below.



c) The group of Opatz reported a remarkable example of a three-step cascade reaction. In the first step, a photochemical ring contraction leads to an azirine intermediate, which subsequently reacts with acetylacetone to a pyrrole in a thermal fashion. Further irradiation of the pyrrole leads to the formation of the final product. Fill in the boxes. What type of reaction occurs in the second photochemical step?



Type of reaction:	

d) Shown below is an enantioselective Cu(I)-catalyzed photoreaction reported by Sarkar *et al.* in 2004. Draw the correct product and the transition state that determines its relative configuration. Shortly explain the function of the Cu-catalyst in the reaction.



e) Give the structure of the product in the reaction shown below as well as the structure of the intermediate. What are the reasons for the observed regioselectivity and stereoselectivity? Try to rationalize the latter with the relative geometry of the relevant orbitals. What is the name of this reaction?



Reason for diastereoselectivity:	
Reason for regioselectivity:	
Name of the reaction:	

f) Give the correct structure for the product of the reaction shown below. What is the name of this reaction?





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Additional space for solutions-clearly mark the (sub)problem your answers are related to and strike out invalid solutions.

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