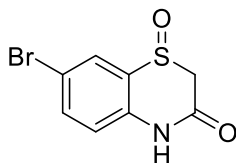


Organic Photochemistry – Exercise 1: 27/10/2022, 11.00 am

German group: CH22210

English group: CH42306

1. The benzothiazine derivative below shows phosphorescence at $\lambda = 413$ nm.



a) Calculate the triplet energy (in kJ/mol).

$$E = (h \cdot c) / \lambda$$

$$h = \text{Planck's constant} = 6.626 \times 10^{-34} \text{ J}\cdot\text{s}$$

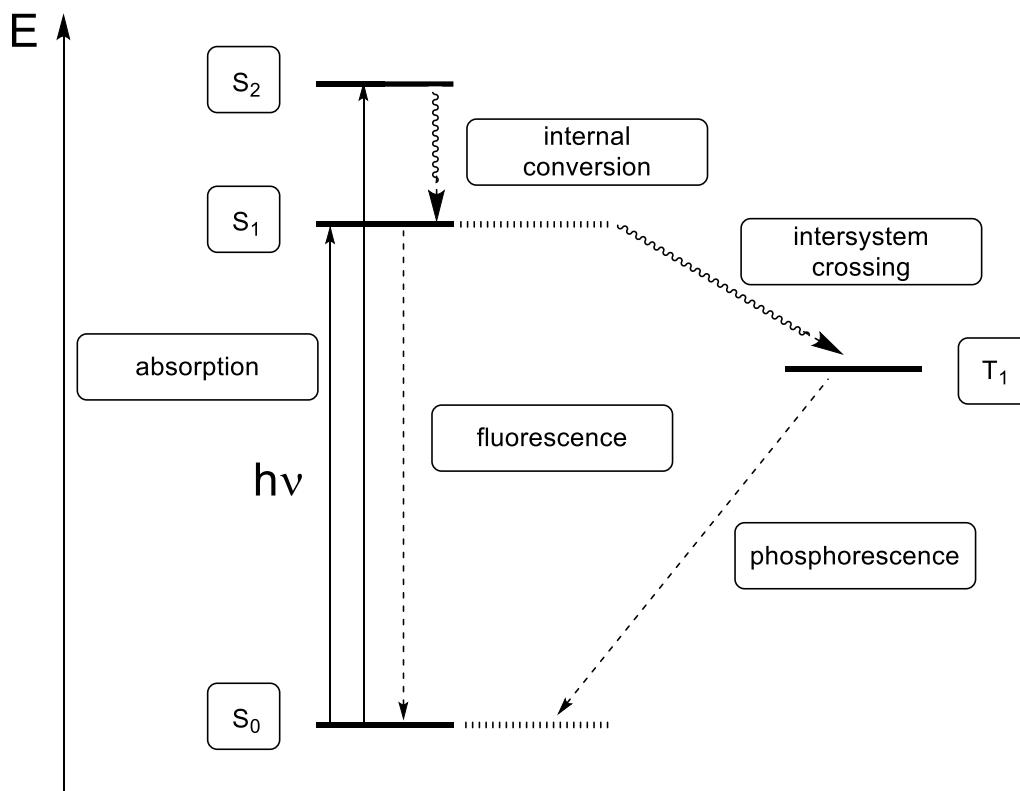
$$c = \text{speed of light} = 3 \times 10^8 \text{ m/s}$$

$$\lambda = 413 \text{ nm (given in the question above)}$$

$$N_A = 6.022 \times 10^{23} \text{ 1/mol}$$

$$E(\text{kJ/mol}) = (h \cdot c \cdot N_A) / \lambda = 290 \text{ kJ/mol}$$

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



Absorption: 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).

Internal conversion (IC): 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.

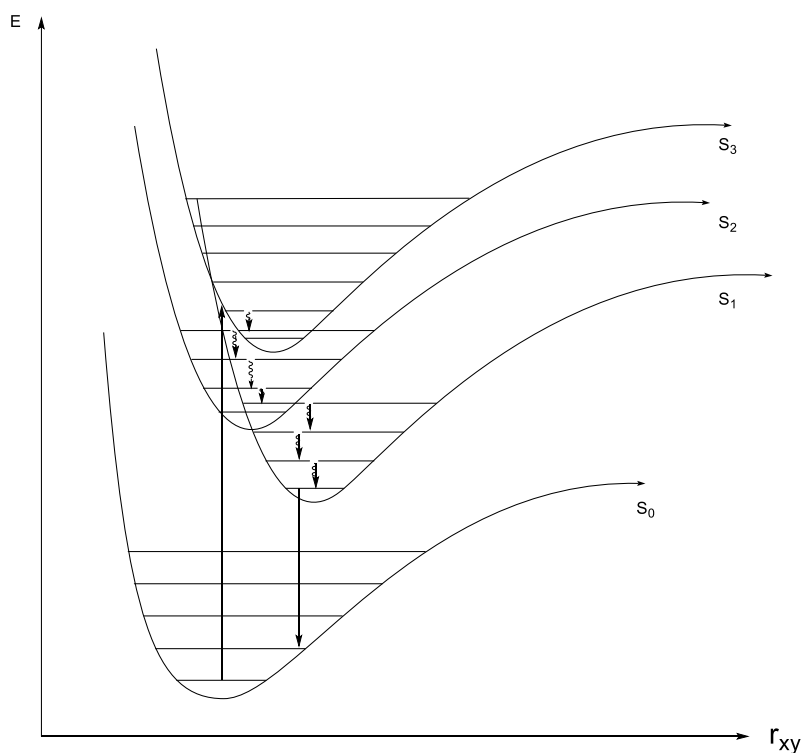
Fluorescence: It is the spontaneous emission of radiation by an excited molecule, typically in the first excited singlet state (S₁), with retention of spin multiplicity.

Intersystem crossing (ISC): 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.

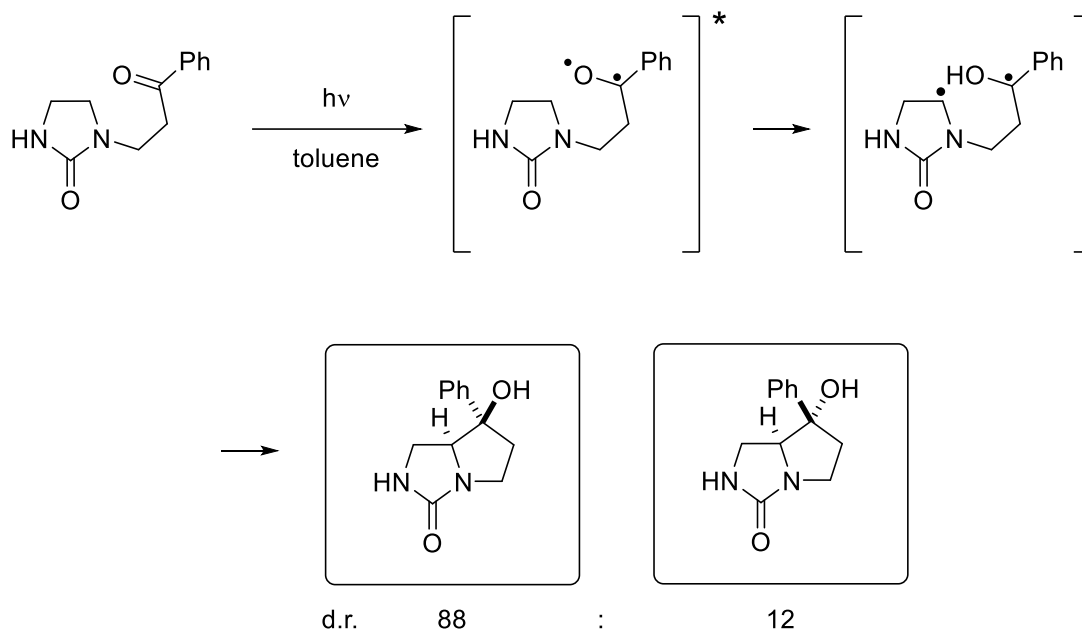
Phosphorescence: It is the spontaneous emission of radiation by an excited molecule, typically in the first excited triplet state (T₁), involving a change in spin multiplicity.

c) Draw an energy diagram to explain the Kasha's rule.

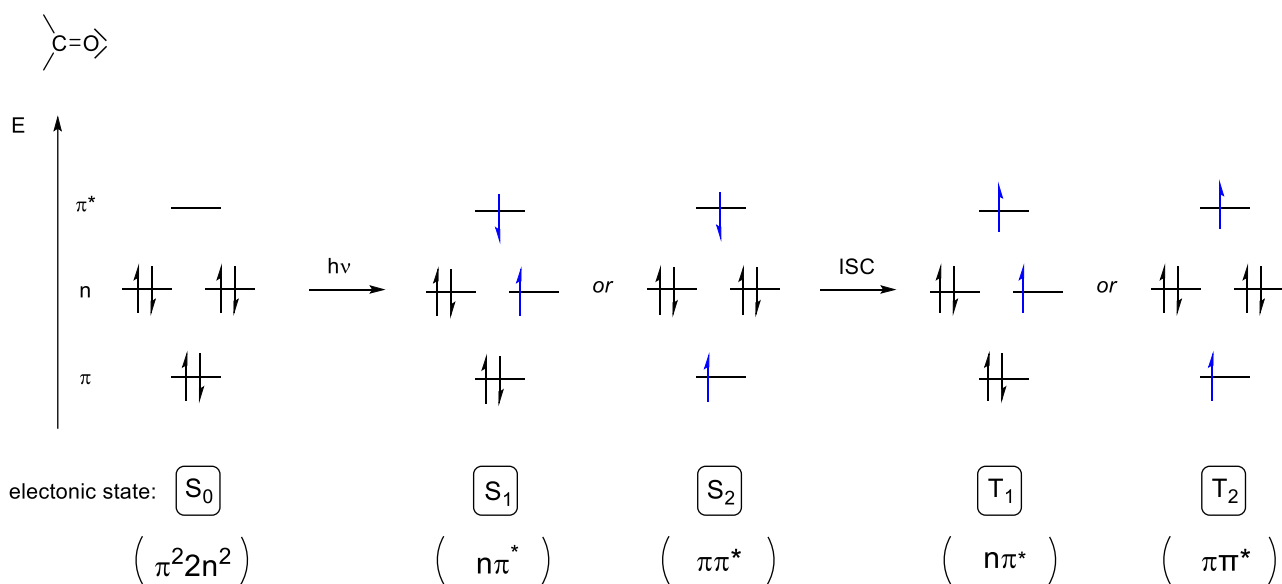


E: potential energy; r_{xy} : bond distance (diatomic molecule)

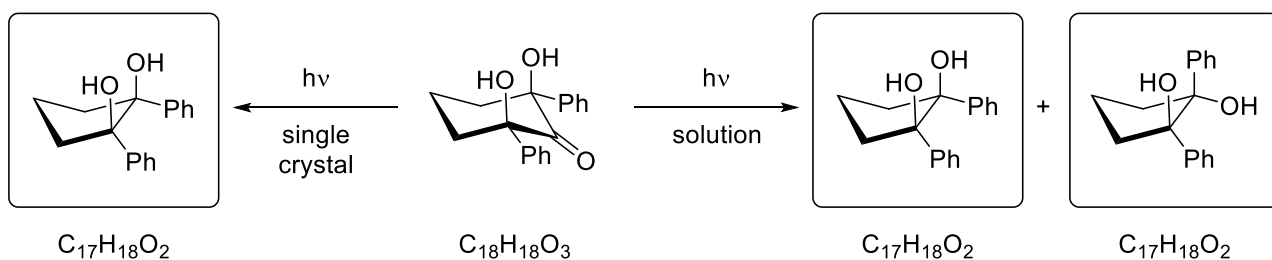
2. a) Provide the mechanism and the two diastereoisomers formed in this reaction. Explain the diastereoselectivity.



b) Draw the MO diagram for the ketone (not the urea) ($C=O$, π - n - π^*) in the ground state, after excitation with light and intersystem crossing processes (ISC).



3. The irradiation of this ketone derivative was performed both in solution and in a single-crystal form. In the latter case, only one isomer was obtained, while two different stereoisomers were obtained when irradiation was performed in solution. Complete the scheme with the appropriate compounds, and explain the difference in reactivity.

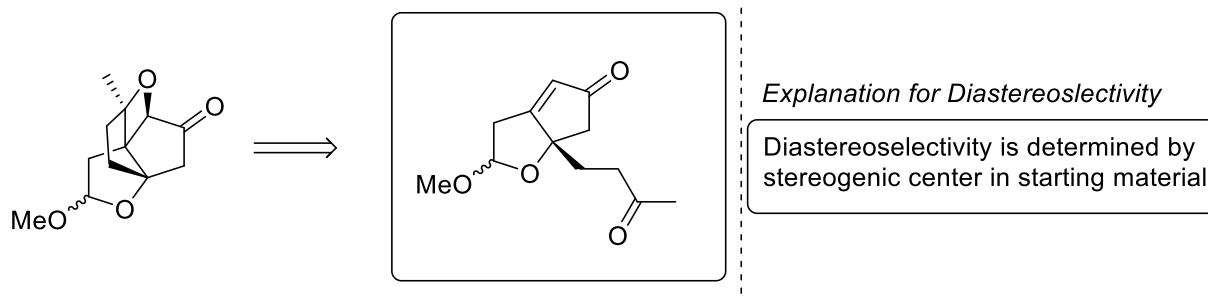


Organic Photochemistry – Exercise 2: 17/11/2022, 11.00 am

German group: CH22210

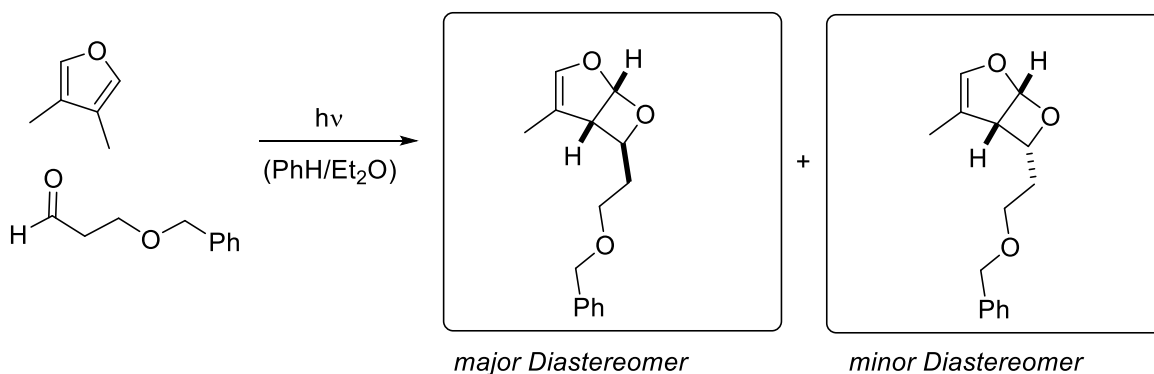
English group: CH42306

1. The tetracyclic core of the merrilactone A was synthesized by *Greaney* and coworkers utilizing an elegant intramolecular Paternò Büchi Reaction. Please provide the structure of the irradiation precursor and an explanation for the observed diastereoselectivity.



2. The synthetic utility of the Paternò-Büchi Reaction originates not only from the possibility to access densely functionalized furans, but also from the option to further transform these products. Please fill in the missing structures and provide an explanation for the observed selectivity.

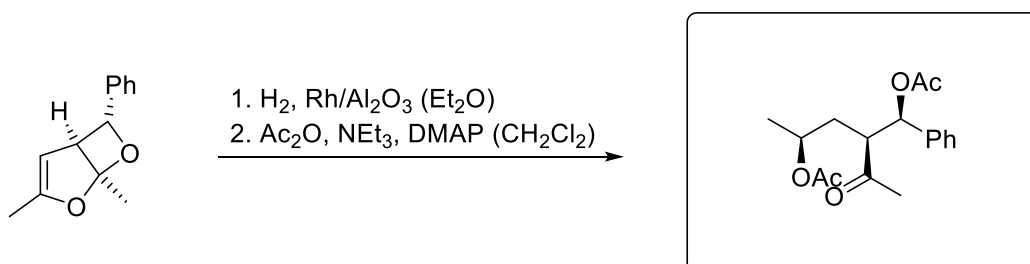
a)



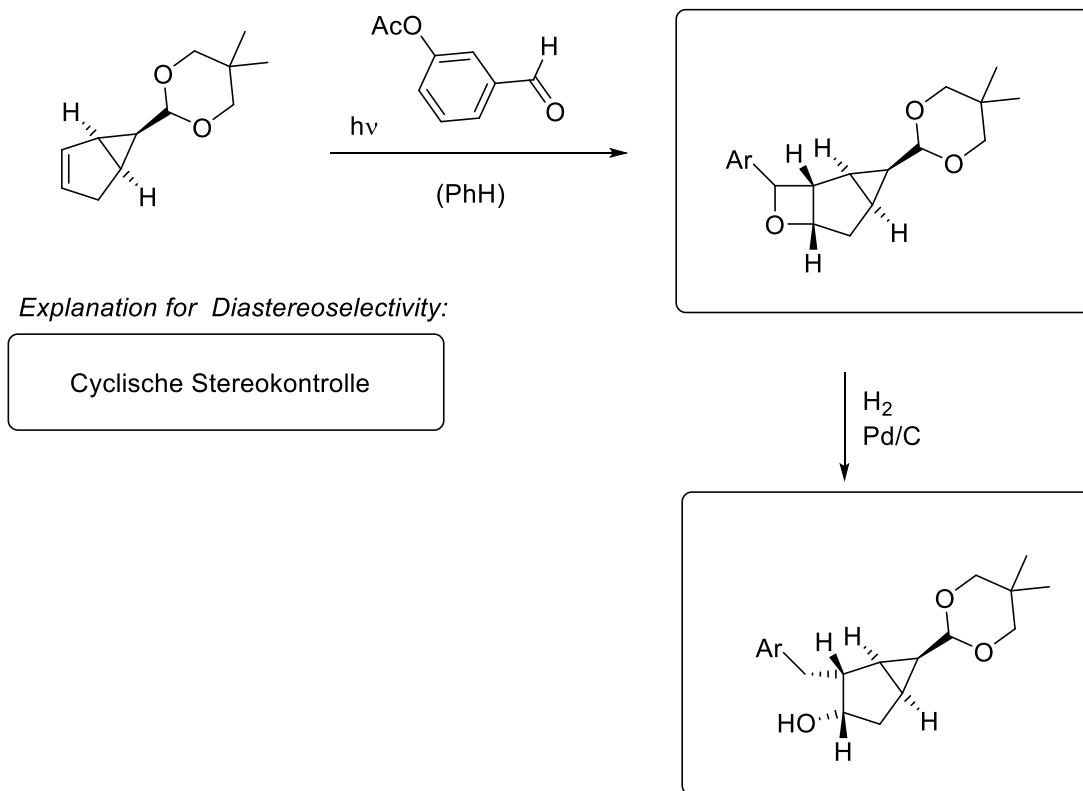
Explanation for Regioselectivity and Diastereoselectivity:

Stability of 1,4 diradical
large substituents trans to each other

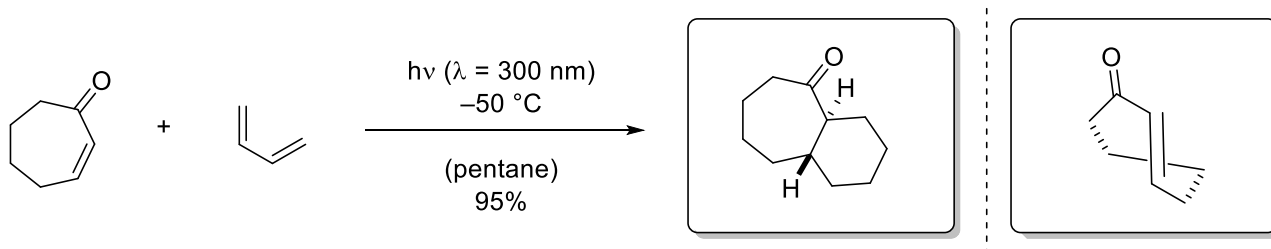
b)



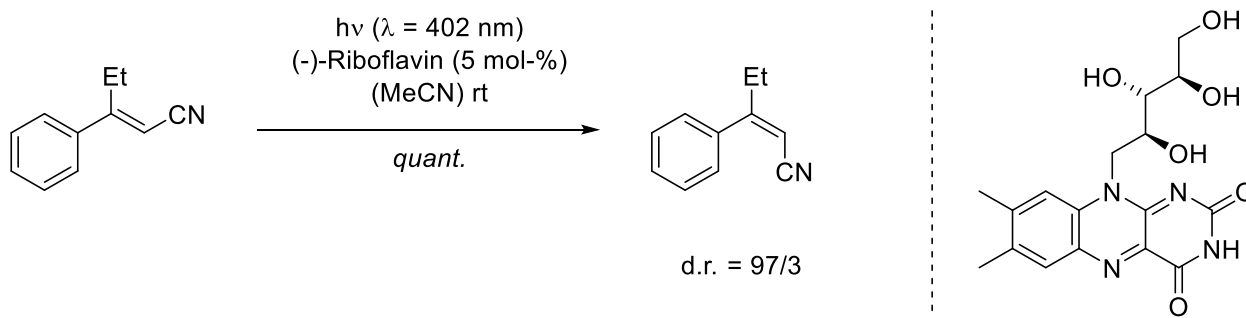
c)



3. In 2022 the Bach group published a paper on Diels-Alder reactions of cyclohept-2-enones. The depicted cyclic enone does not undergo a reaction without irradiation. Upon irradiation a reactive intermediate leads to a Diels-Alder-reaction. Please explain this observation and fill in the blanks.



4. a) The following photocatalytic $E \rightarrow Z$ isomerization of cinnamionitriles in the presence of (-)-Riboflavin was observed. Explain this phenomenon by drawing a rough scheme of the possible energy distribution of the electronic states involved in the reaction.

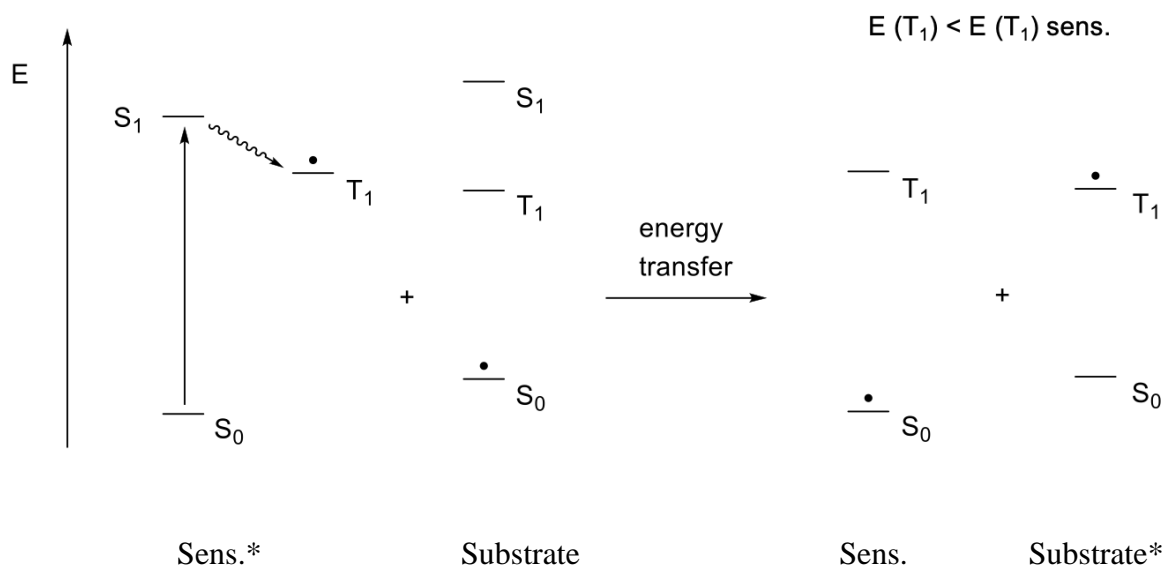


b) What is the role of (-)-Riboflavin? Explain the mechanism behind it (name of mechanism?).

$$E(T_1)[cis] > E(T_1)[Sens.] > E(T_1)[trans]$$

Riboflavin acts as the sensitizer.

Dexter Energy Transfer Mechanism:



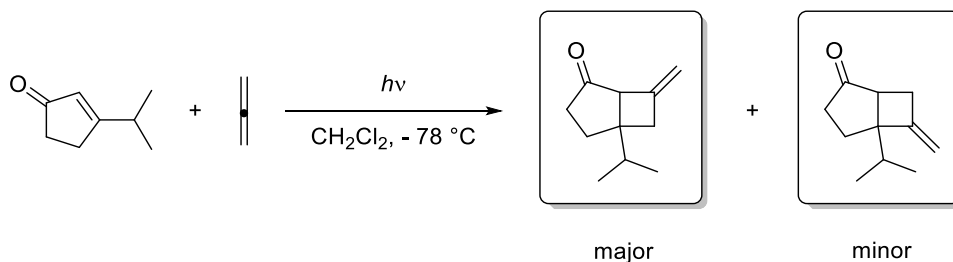
Organic Photochemistry – Exercise 3: 01/12/2022, 11.00 am

German group: CH22210

English group: CH42306

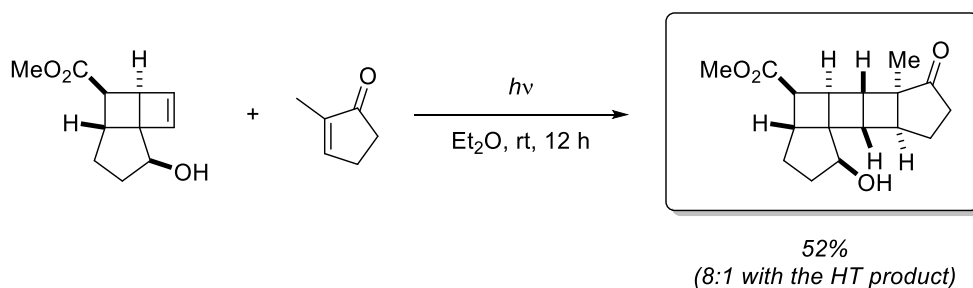
1. Give the products of the following [2+2] photocycloadditions.

a) Hint: Allenes react similar to acceptor-substituted olefins



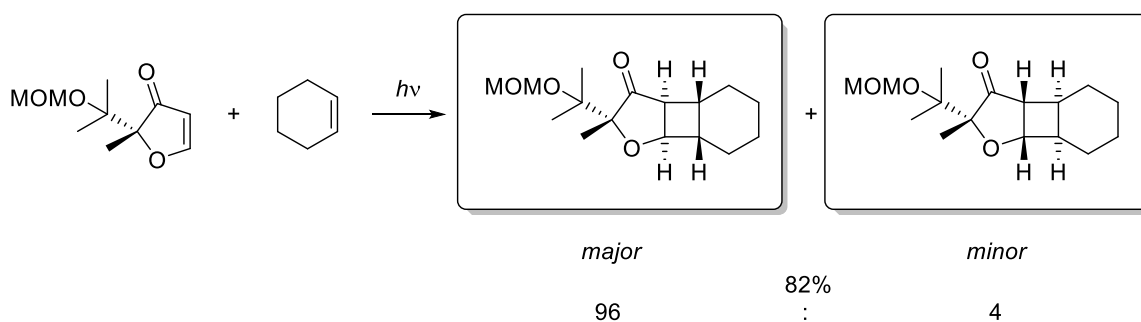
Tetrahedron Lett. **2003**, *44*, 1401.

b)



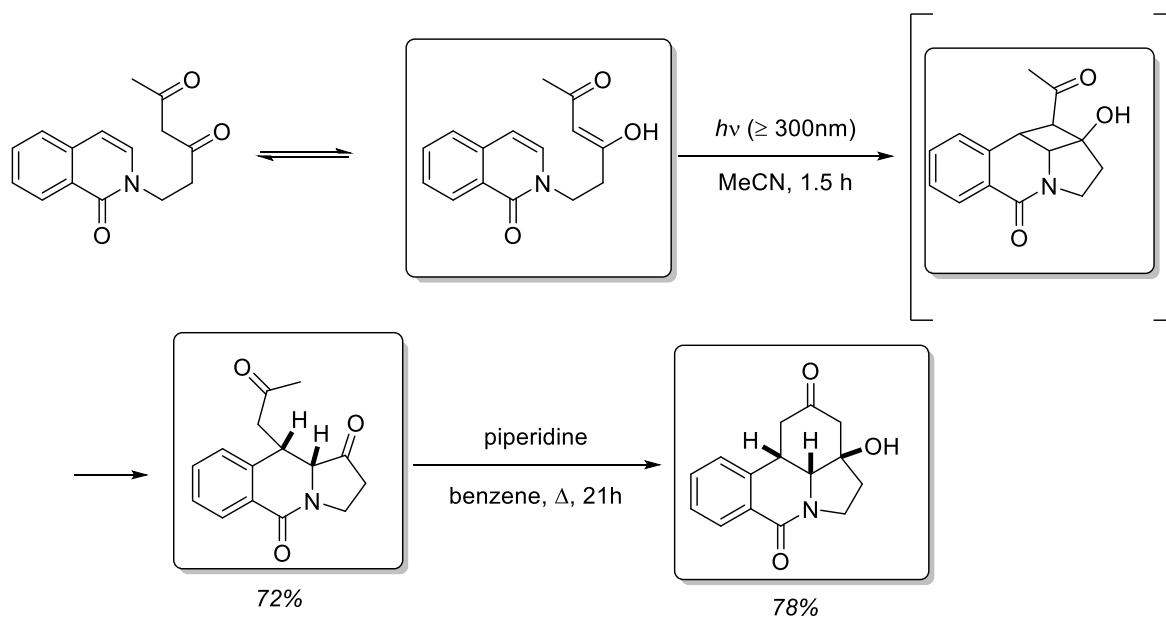
J. Am. Chem. Soc. **1999**, *121*, 4534.

c)



Tetrahedron Lett. **1986**, *27*, 5975.

2. The following reaction sequence is a great way to build up Galanthan-type tetracyclic skeletons. Which form of the diketone is capable of undergoing [2+2] photocycloadditions? Draw the correct form of the diketone and the reaction intermediate. The photoproduct then undergoes a subsequent thermal reaction to the final compound. Name the reaction sequence and the following thermal reaction.

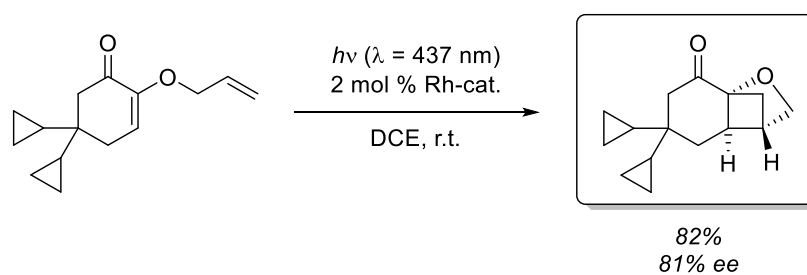


Reaction sequence:

Thermal reaction:

J. Org. Chem. **2004**, *69*, 160.

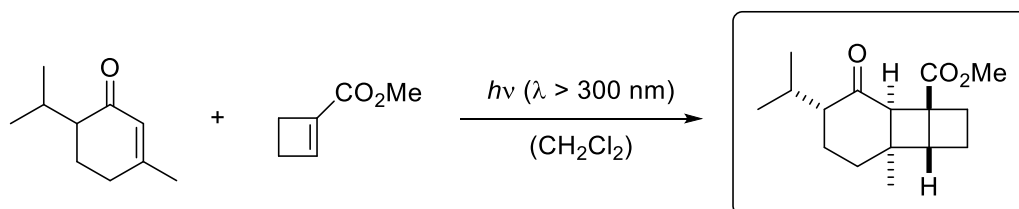
3. The following cyclic enone was shown to undergo enantioselective sensitized [2+2] photocycloaddition in the presence of a chiral rhodium-based triplet sensitizer. Draw the product of the reaction (both enantiomers will be accepted).



Chem. Sci. **2022**, *13*, 2378.

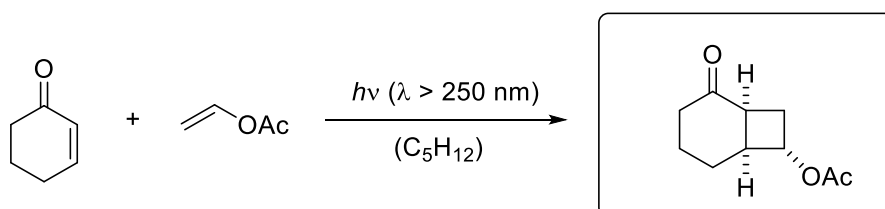
4. Give the products of the following [2+2] photocycloaddition reactions and explain the regioselectivity.

a)



J. Am. Chem. Soc. **1979**, 101, 7373.

b)



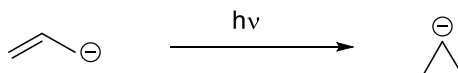
J. Am. Chem. Soc. **1964**, 86, 5570.

Organic Photochemistry – Exercise 4: 15/12/2022, 11.00 am

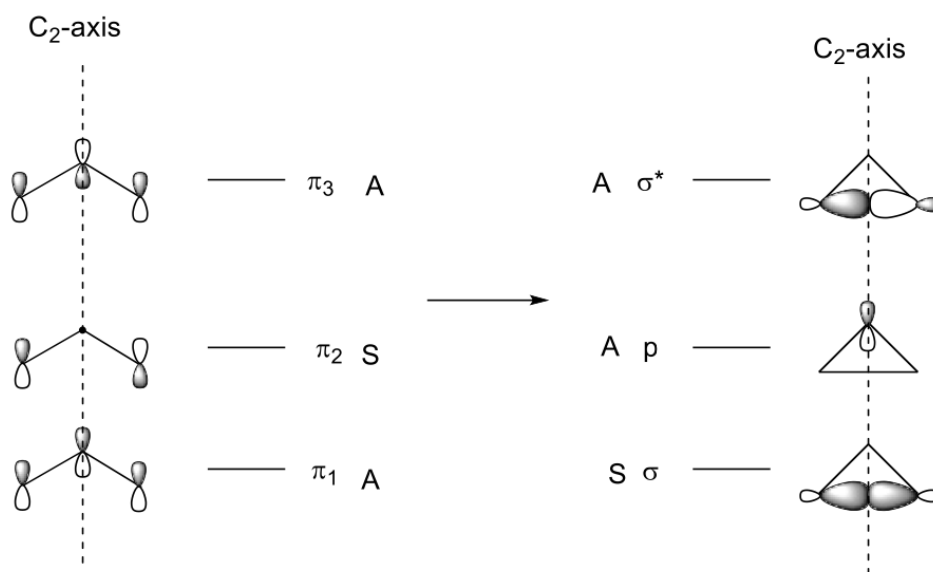
German group: CH22210

English group: CH42306

1. Upon irradiation, the allyl anion may cyclize to the cyclopropyl anion as depicted in the scheme below.



To analyze the reaction, draw the molecular orbitals of the starting material and the corresponding orbitals in the product. Determine if they are symmetric (S) or antisymmetric (A) regarding the symmetry operation of a conrotatory ring closure (C_2 axis). How many electrons occupy the symmetric and antisymmetric molecular orbitals in the starting material and in the product in the first excited singlet state? Is the conrotatory ring closure photochemically allowed? Justify your decision.



[π^4 a]-system

In the ground state: $(\pi_1)^2(\pi_2)^2 \rightarrow (\sigma_1)^2(\pi)^2$

A S \rightarrow S A

Orbital symmetry is conserved: thermally allowed

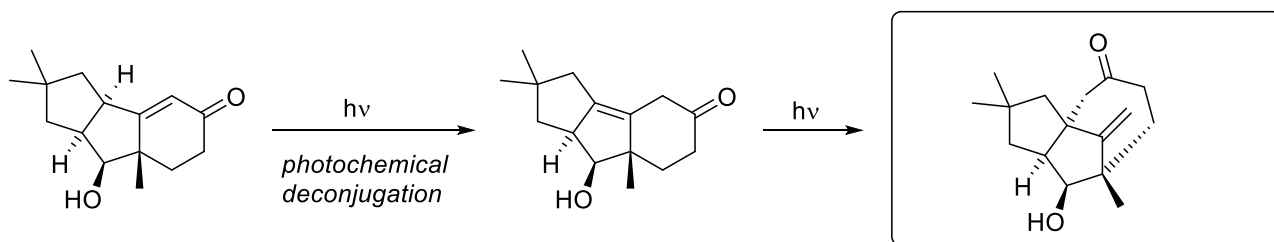
In the excited state: $(\pi_1)^2(\pi_2)^1(\pi_3)^1 \rightarrow (\sigma_1)^2(\pi)^1(\sigma^*)^1$

A S A \rightarrow S A A

Orbital symmetry is not conserved: photochemically forbidden

2. Rearrangement reactions of β,γ -unsaturated molecules can lead to a broad range of complex structures: Please provide the missing molecules.

a)

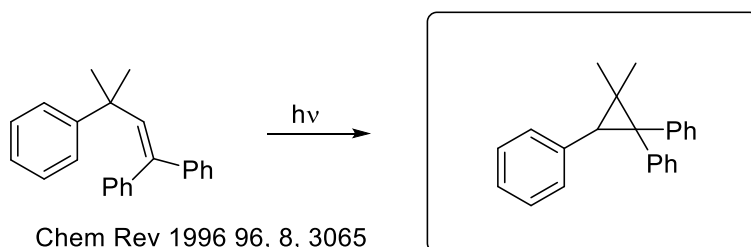


Org Lett 2022, 24, 31, 5812

Name of the photoreaction:

1,3-Acyl Shift

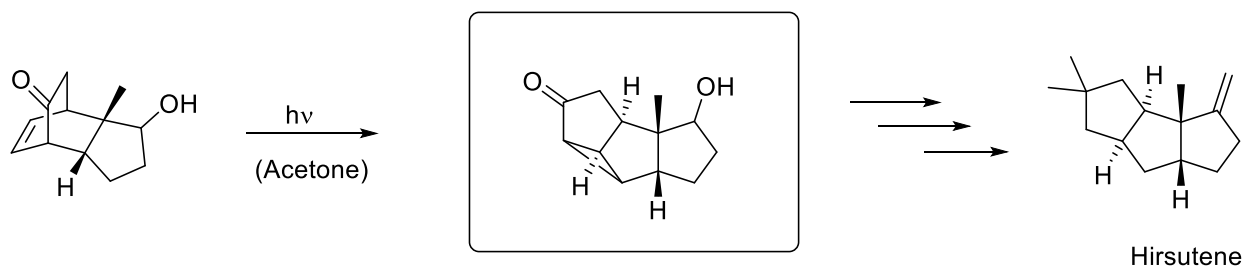
b)



Name of the photoreaction:

Di- π -methane rearrangement

c)



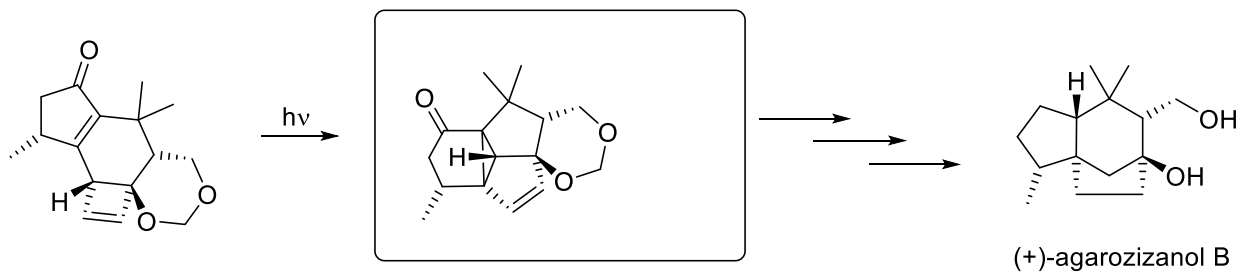
Name of the photoreaction: Oxa-di- π -methane rearrangement

Name of the carbon skeleton present in hirsutene:

triquinane

Tetrahedron 60 (2004) 8161–8169

3. The total synthesis of (+)-agarozizanol B was accomplished by a complex photochemical cascade reaction. One of the steps of the photochemical cascade involves a di- π -methane rearrangement, which leads to a key compound that later could be converted to the desired natural product. Please provide the structure of the missing compound.



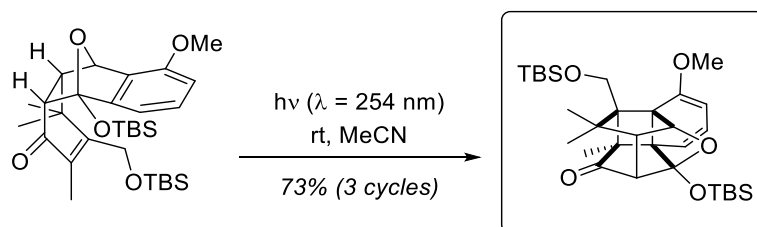
Organic Photochemistry – Exercise 5: 12/01/2023, 11.00 am

German group: CH22210

English group: CH42306

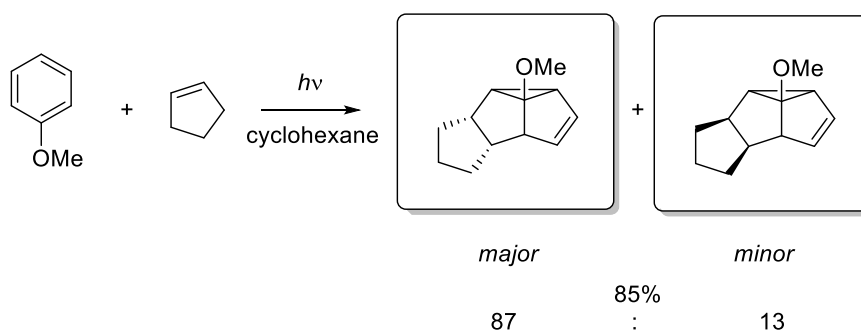
1. Give the products of the following arene photocycloadditions.

a)



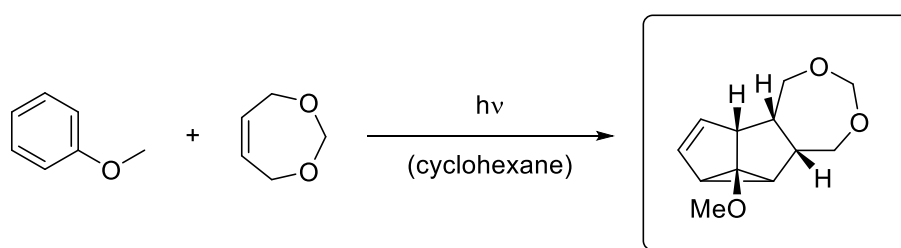
Science **2020**, 367, 676.

b)



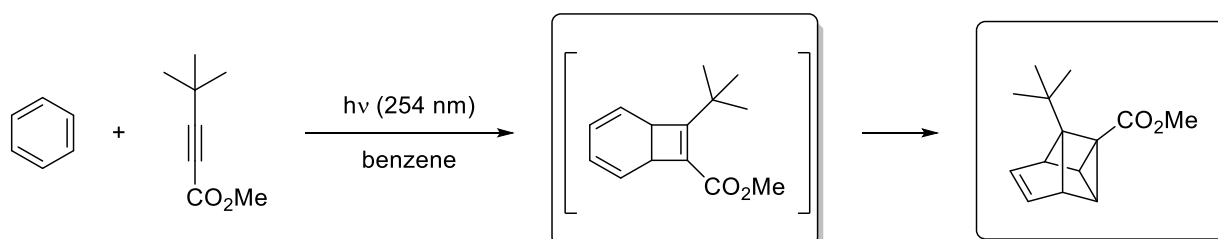
J. Org. Chem. **1977**, 42, 1321.

c)



Chem. Commun. **2013**, 49, 1106.

2. Give the intermediate and the product of the following arene photocycloaddition.

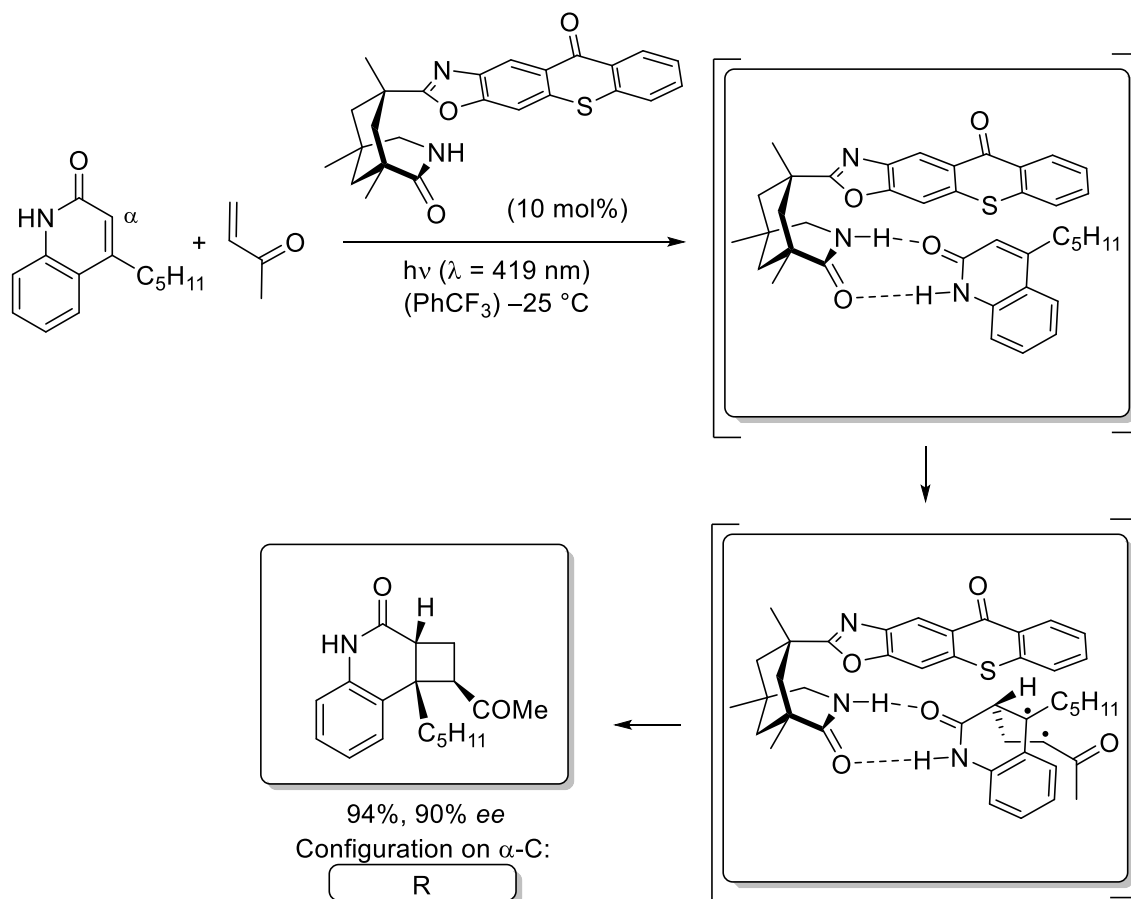


Synthesis **1982**, 661.

3.

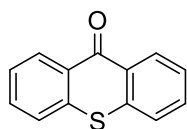
a) Enantioselective photocycloadditions are a major research topic in recent studies. One opportunity for enantioselective photocycloaddition is the reaction with a chiral organocatalyst.

Draw the hydrogen bond complex of the substrate and the catalyst, the resulting 1,4-diradical and the preferred enantiomer of the product. Determine the configuration of the new formed stereogenic centre on the α -carbon atom according to the *Cahn-Ingold-Prelog* sequence rules (CIP priority rules).



J. Am. Chem. Soc. **2016**, *138*, 7808–7811

b) The used chiral catalyst has a sensitizer as shield. What is the sensitizer? Please draw the structure of the sensitizer and explain briefly the principle of a sensitized photoreaction.



Thioxanthone:

The substrate (here quinolone) does not absorb light but is indirectly excited to a higher energetic state through a photosensitizer (i.e. a molecular entity that absorbs radiation and transfers the energy to another molecular entity, while not being consumed in the reaction). From this excited state, the reaction (here [2+2] PCA) takes place. To achieve energy transfer, the energy of the acceptor molecule's excited state needs to be lower than the energy of the donor molecule's (long-living) excited state.

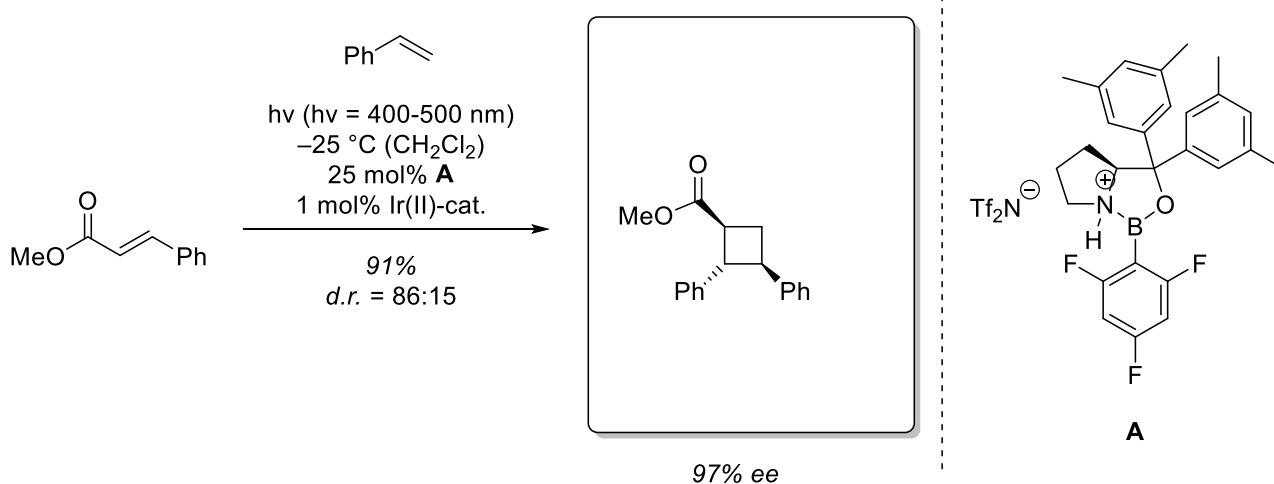
Organic Photochemistry – Exercise 6: 26/01/2023, 11.00 am

German group: CH22210

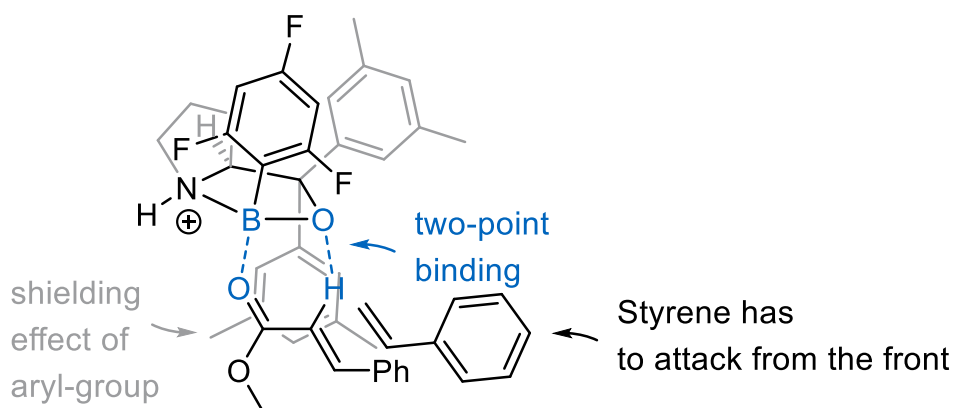
English group: CH42306

1. Yoon, Baik and co-workers studied the activation of cinnamic acid esters by chiral Lewis acids. Lewis acid **A** was able to enantioselectively catalyze the triplet sensitized reaction depicted below. An iridium complex served as an achiral sensitizer in this dual catalytic reaction.

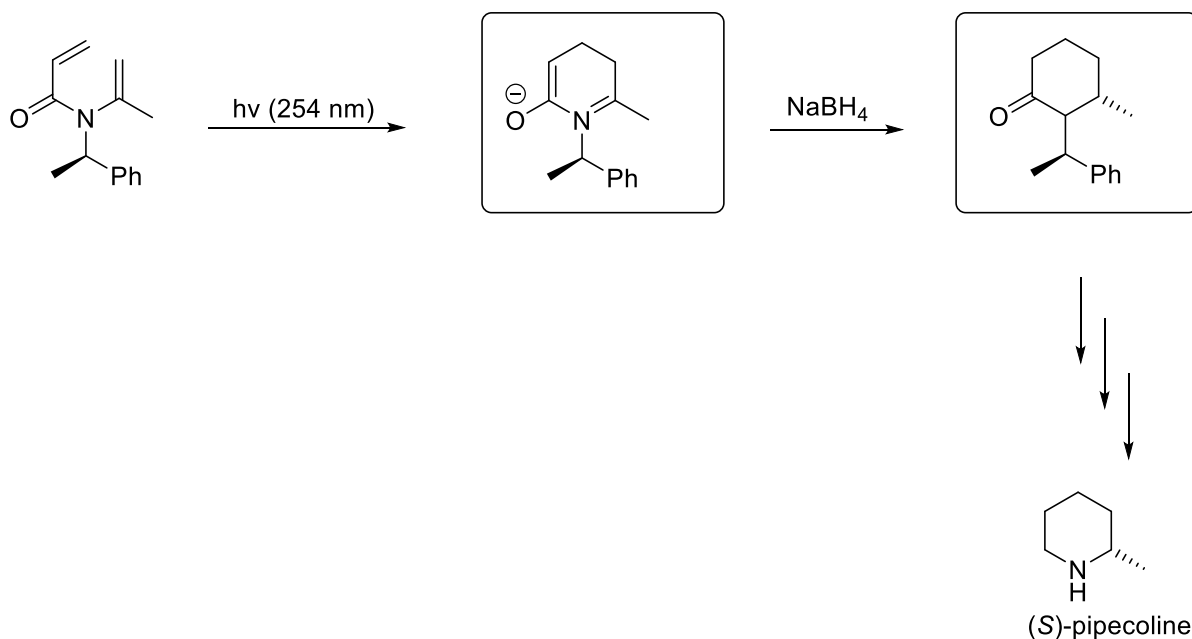
a) Draw the product in its correct relative and absolute configuration.



b) Draw the substrate-catalyst complex which indicates the enantioselectivity of the reaction.



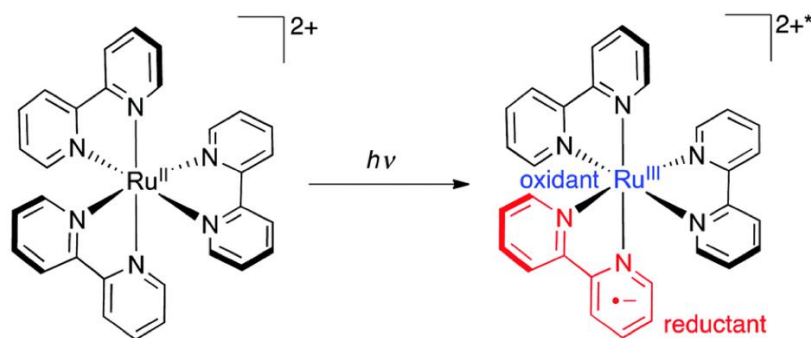
c) Not only catalytic methods can lead to enantioenriched products: In the following example an auxiliary assisted diastereoselective reaction was used for the total synthesis of (*S*)-pipercoline. Please provide the missing structures.



2. The *MacMillan* group described useful applications for ruthenium complexes in the field of visible light photoredox catalysis. A commonly used catalyst is the polypyridyl complex of ruthenium $\text{Ru}(\text{bpy})_3^{2+}$.

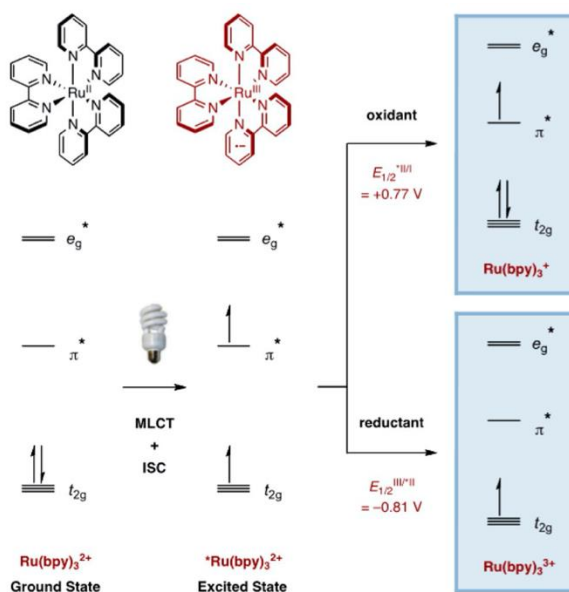
a) Explain what photo- and electrochemical properties of $\text{Ru}(\text{bpy})_3^{2+}$ make the complex a good photoredox catalyst.

1. $\text{Ru}(\text{bpy})_3^{2+}$ absorbs visible light, absorption maximum $\lambda_{\text{max}} = 452 \text{ nm}$
2. Forms a stable, long-lived excited state upon excitation and ISC
3. Can act as a single electron transfer catalyst (SET)
4. Effective excited state oxidant and reductant
5. Key for the redox activity of the excited state is the spatial separation of charge within the molecule following light absorption:

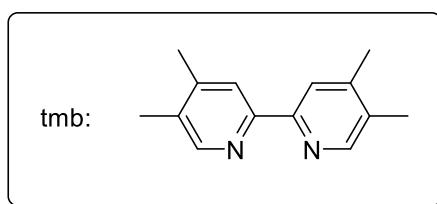


“Nature of excitation”

b) Draw a MO-scheme of $\text{Ru}(\text{bpy})_3^{2+}$, before and after excitation, illustrating its oxidant and reductant properties.



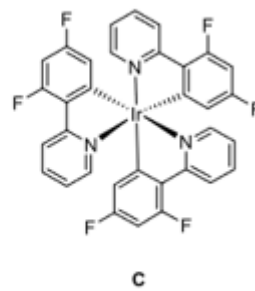
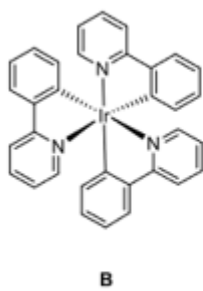
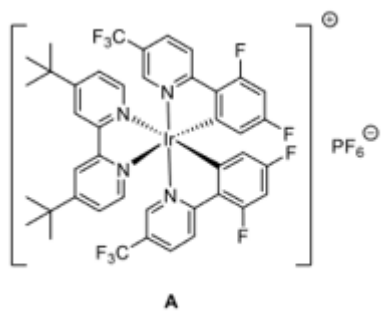
c) What effect has a more electron rich ligand as tmb?



Positive charge is better stabilized by the metal (electron rich ligand)
 $E_{1/2}(\text{Ru}^{\text{III}}/\text{Ru}^*)$ decreases: -1.01 V instead of -0.70 V with bpy

d) Please order the photoredox catalysts depicted below according to their redox potential $E_{1/2}(\text{M}/\text{M}^{\cdot-})$. Give a short explanation for the observed trend.





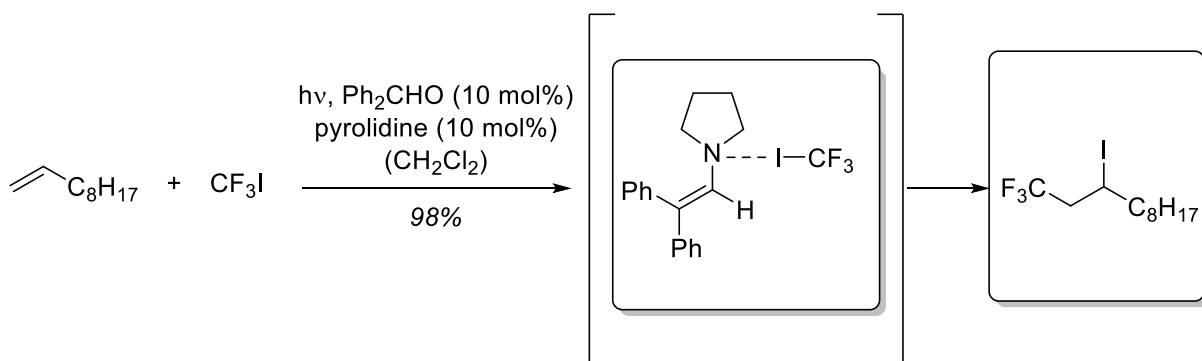
$B < C < A$

Organic Photochemistry – Exercise 7: 09/02/2023, 11.00 am

German group: CH22210

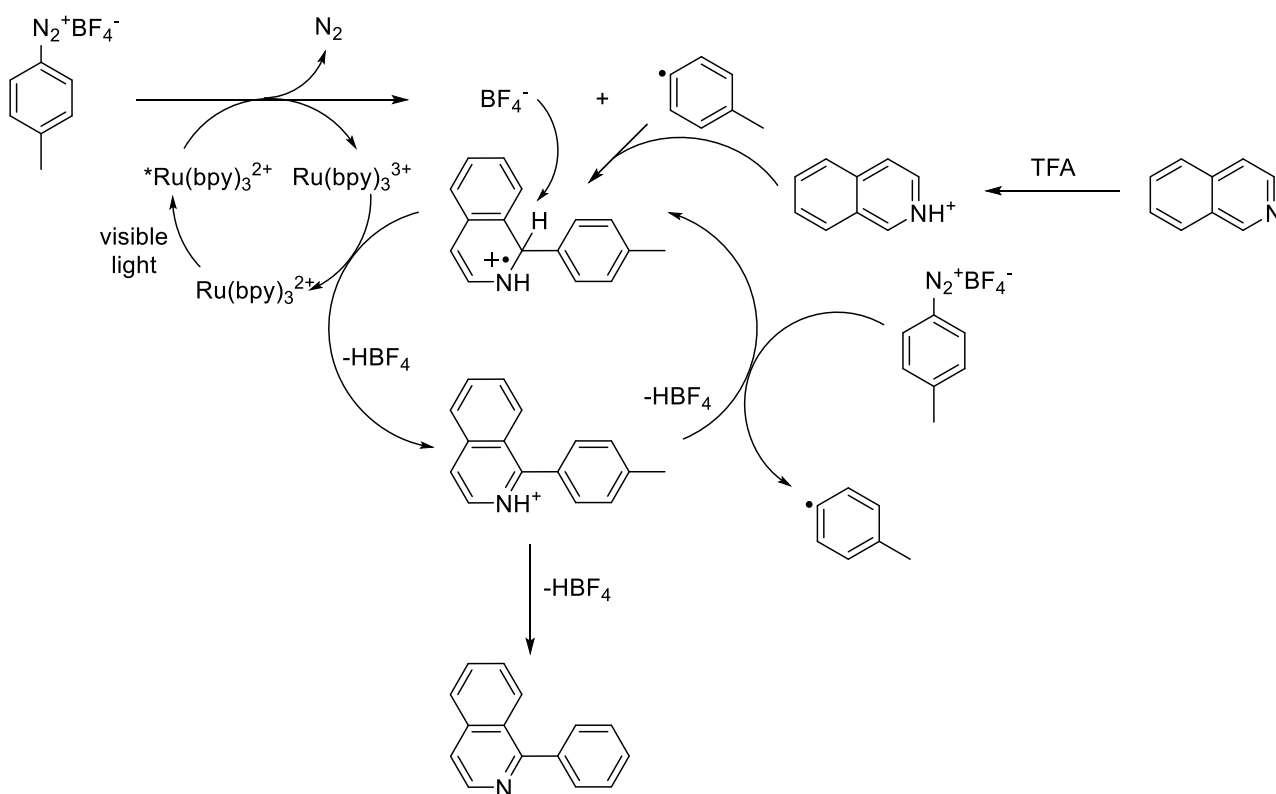
English group: CH42306

1.



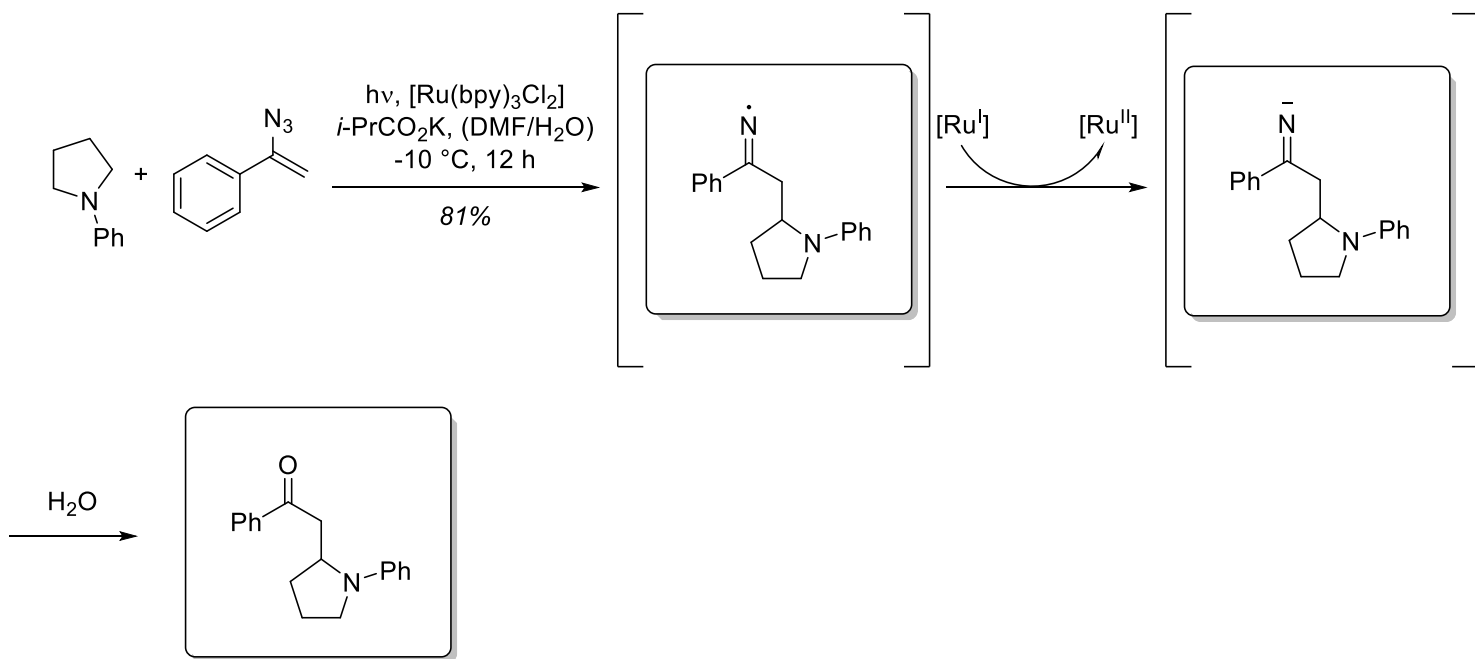
Eur. J. Org. Chem. **2020**, 3808.

2.



J. Org. Chem. **2014**, 79, 10682.

3.



Redox-neutral.

J. Org. Chem. **2019**, *84*, 14760.

4.

