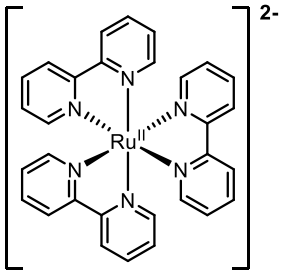
Synthetic Organic Photochemistry

Covered in today's problem class;
- Underlying physical chemistry principles of photochemistry.
- The fate of excited states of photoredox catalysts.
- Practical considerations when carrying out photochemical reactions.
- Common name reactions in synthetic organic photochemistry.

Before starting have a read through the Burns group slideshow that I will circulate . The first 7 slides are very useful.

Principles of Photochemistry



1) Draw a Jablonski diagram, labelling each electronic state and the transitions between them.
1) Define the following terms: *extinction coefficient*, *quantum yield*, *photosensitizer*, *quencher*.
2) How would you determine whether a photochemical reaction/process proceeds through a singlet or a triplet excited state?
3) The photo-redox catalyst $[Ru(bpy)_3]Cl_2$ has a λ_{max} = 452 nm. What is the excited state energy (in $kJmol^{-1}$) of this transition metal complex?
4) Have a look at *Chem. Rev.* **2013**, *113*, 5322-5363 (pages 5323-5324). Explain why the excited state of $[Ru(bpy)_3]Cl_2$ is both a powerful oxidant and reductant, showing the relevant molecular orbitals.

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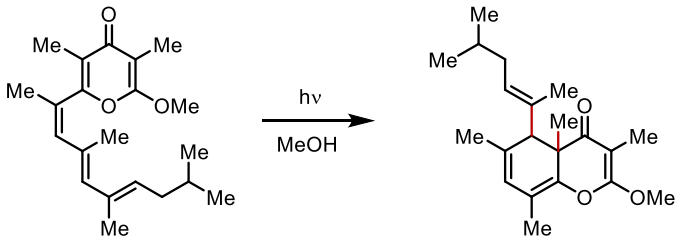
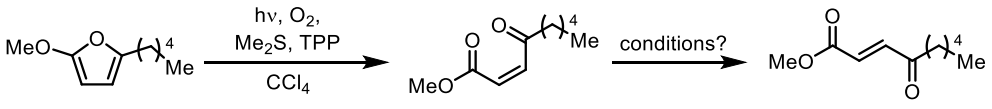
6) i) What are the Woodward-Hoffmann rules? How does this change under photochemical control?
ii) The [6π] electrocyclic reaction below (Moses et al. *Org. Lett.* **2008**, *10*, 4025) is under photochemical control. What is the expected diastereoselectivity?
iii) What would the be the expected diastereoselectivity under thermal control?

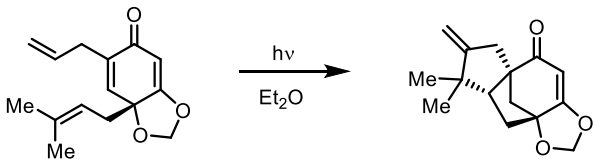


(±)-tridachiahydropyrone

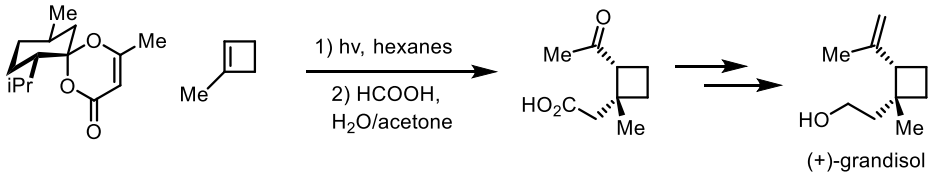
7) i) What is the mechanism of the following transformation? (*Synth. Commun.* **2008**, *38,* 212-216)
ii) What is the role of the tetraphenylporphyrin (TPP)?
iii) Suggest some conditions to for the conversion of the Z-alkene to the E-alkene.



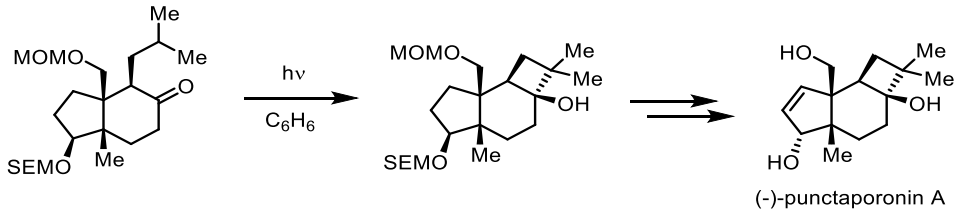
8) i) What are Beckwith's rules?
ii) Using this information, suggest a mechanism for the following transformation. (Danishefsky et al. *Tetrahedron Lett.* **2008**, *49*, 6383-6385)



9) Look up the DeMayo reaction. Suggest a mechanism for the following transformation. (Demuth et al. *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 1117-1119.)



10) What is the following name reaction? Provide a mechanism. (Paquette et al. *J. Am. Chem. Soc.* **1986**, *108*, 3841-3842.)



11) (time permitting) Using your knowledge of the above name reactions, give a mechanism for the following (hint. Consider the imide in alternative tautomer) (Booker-Milburn et al. *Org. Lett.* **2004**, *6*, 1481-1484.)