

PHOTOCHEMISTRY AND PHOTOCATALYSIS IN ORGANIC SYNTHESIS.

Objective

The aim of the course is to give the student the basic concept to understand a photochemical reaction, the methodology to study it and the synthetic possibilities of photoinduced reactions to applied them in the synthesis of a target compound.

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Date: 1-3.11.17 and 6-7.11.17

Contents

Topic 1: A crash course in photophysics and a classification of primary photoreactions. Photophysical processes. Energy transfer, electron transfer, quenching and sensitization. classification of photochemical reaction pathways. Photochemical reaction mechanisms and reaction intermediates. Problems.

Topic 2: Techniques and methods. Light sources, filters and detectors Preparative irradiation. Steady-state and Time-resolved Absorption and emission spectroscopy. Quantum yields.

Topic 3: Chemistry of excited molecules. Alkenes and alkynes. Aromatic compounds photosubstitution. Carbonyl compounds. Nitrogen compounds. Sulfur compounds. Organic halogen compounds. Molecular oxygen. Retrosynthetic photochemistry. Problems.

Topic 4: Photocatalysis in organic synthesis. Basic Concepts in Photocatalysis: Energy transfer and electron transfer mechanism. *Energy Transfer Photocatalysis:* Single Oxygen as Reagent in Organic Synthesis, enantioselective catalysis of photochemical reaction. *Electron Transfer Photocatalysis:* Photoredox Catalysis with visible light, homogeneous photocatalysis with transitions metal catalysts and organic dyes, heterogeneous

photocatalysis with semiconductors. Consecutive photoredox catalysis and photon-up conversions. Combination of Photoredox catalysis with other catalysis (dual or synergistic catalysis). Problems.

References

- (1) Turro, N. J., Ramamurthy, V., and Scaiano, J. C. *Principles of Molecular Photochemistry: An Introduction*, University Science Publishers, New York, N.Y. **2009**.
- (2) *Handbook of Synthetic Photochemistry*; Albini, A., Fagnoni, M., Eds.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, **2009**.
- (3) *Principles of Fluorescence Spectroscopy*; Lakowicz, J. R., Ed.; Springer US: Boston, MA, **2006**.
- (4) *Chemical Photocatalysis*; König, B., Ed.; DE GRUYTER: Berlin, Boston, **2013**.
- (5) Staveness, D.; Bosque, I.; Stephenson, C. R. J. Free Radical Chemistry Enabled by Visible Light-Induced Electron Transfer. *Acc. Chem. Res.* **2016**, *49* (10), 2295–2306 DOI: 10.1021/acs.accounts.6b00270.
- (6) Tellis, J. C.; Kelly, C. B.; Primer, D. N.; Jouffroy, M.; Patel, N. R.; Molander, G. A. Single-Electron Transmetalation via Photoredox/Nickel Dual Catalysis: Unlocking a New Paradigm for sp^3 – sp^2 Cross-Coupling. *Acc. Chem. Res.* **2016**, *49* (7), 1429–1439 DOI: 10.1021/acs.accounts.6b00214.
- (7) Romero, N. A.; Nicewicz, D. A. Organic Photoredox Catalysis. *Chem. Rev.* **2016**, *116* (17), 10075–10166 DOI: 10.1021/acs.chemrev.6b00057.
- (8) Reiser, O. Shining Light on Copper: Unique Opportunities for Visible-Light-Catalyzed Atom Transfer Radical Addition Reactions and Related Processes. *Acc. Chem. Res.* **2016**, *49* (9), 1990–1996 DOI: 10.1021/acs.accounts.6b00296.
- (9) Chatterjee, T.; Iqbal, N.; You, Y.; Cho, E. J. Controlled Fluoroalkylation Reactions by Visible-Light Photoredox Catalysis. *Acc. Chem. Res.* **2016**, *49* (10), 2284–2294 DOI: 10.1021/acs.accounts.6b00248.
- (10) Jamison, C. R.; Overman, L. E. Fragment Coupling with Tertiary Radicals Generated by Visible-Light Photocatalysis. *Acc. Chem. Res.* **2016**, *49* (8), 1578–1586 DOI: 10.1021/acs.accounts.6b00284.
- (11) Koike, T.; Akita, M. Fine Design of Photoredox Systems for Catalytic Fluoromethylation of Carbon–Carbon Multiple Bonds. *Acc. Chem. Res.* **2016**, *49* (9), 1937–1945 DOI: 10.1021/acs.accounts.6b00268.

- (12) Ghosh, I.; Marzo, L.; Das, A.; Shaikh, R.; König, B. Visible Light Mediated Photoredox Catalytic Arylation Reactions. *Acc. Chem. Res.* **2016**, *49* (8), 1566–1577 DOI: 10.1021/acs.accounts.6b00229.
- (13) Fabry, D. C.; Rueping, M. Merging Visible Light Photoredox Catalysis with Metal Catalyzed C–H Activations: On the Role of Oxygen and Superoxide Ions as Oxidants. *Acc. Chem. Res.* **2016**, *49* (9), 1969–1979 DOI: 10.1021/acs.accounts.6b00275.
- (14) Hopkinson, M. N.; Tlahuext-Aca, A.; Glorius, F. Merging Visible Light Photoredox and Gold Catalysis. *Acc. Chem. Res.* **2016**, *49* (10), 2261–2272 DOI: 10.1021/acs.accounts.6b00351.
- (15) Majek, M.; Jacobi von Wangelin, A. Mechanistic Perspectives on Organic Photoredox Catalysis for Aromatic Substitutions. *Acc. Chem. Res.* **2016**, *49* (10), 2316–2327 DOI: 10.1021/acs.accounts.6b00293.
- (16) Schultz, D. M.; Yoon, T. P. Solar Synthesis: Prospects in Visible Light Photocatalysis. *Science* (80). **2014**, *343* (6174), 1239176–1239176 DOI: 10.1126/science.1239176.
- (17) Hopkinson, M. N.; Sahoo, B.; Li, J.-L.; Glorius, F. Dual Catalysis Sees the Light: Combining Photoredox with Organo-, Acid, and Transition-Metal Catalysis. *Chem. - A Eur. J.* **2014**, *20* (14), 3874–3886 DOI: 10.1002/chem.201304823.
- (18) Prier, C. K.; Rankic, D. a; MacMillan, D. W. C. Visible Light Photoredox Catalysis with Transition Metal Complexes: Applications in Organic Synthesis. *Chem. Rev.* **2013**, *113* (7), 5322–5363 DOI: 10.1021/cr300503r.
- (19) Ravelli, D.; Fagnoni, M.; Albini, A. Photoorganocatalysis. What for? *Chem. Soc. Rev.* **2013**, *42* (1), 97–113 DOI: 10.1039/C2CS35250H.
- (20) Narayanam, J. M. R.; Stephenson, C. R. J. Visible light photoredox catalysis: applications in organic synthesis. *Chem. Soc. Rev.* **2011**, *40* (1), 102–113 DOI: 10.1039/B913880N.