

Project 2.2. Sustainable photochemical transformations of diazo reagents as a source of reactive intermediates

Supervisor: professor Dorota Gryko

Institute: Institute of Organic Chemistry PAS

Unit: group XV

WWW: https://ww2.icho.edu.pl/gryko_group/index.html

Background:

Drawing inspiration from photosynthesis, scientists challenged the use of visible light for the activation of organic molecules and the discovery unknown solar-driven transformations. Plethora of organic compounds have been investigated in terms of their photochemical activity. However, the fact that diazo compounds possess their intrinsic chromophore ($-C=N^+=N^-$) puts them in a unique position among many reagents that can absorb visible light and hence are suitable for solar-driven transformations. To date, they are extensively studied in metal catalyzed reactions and proved to undergo a range of unusual transformations, furnishing even complex molecules with impressive stereoselectivities. As traces of toxic metals are unacceptable by pharmaceutical industry, greener methodologies are in high demand.

Aim:

The main objective of this proposal is to unveil general reactivity modes of diazo compounds under visible light-irradiation. We will develop their solar-driven reactions and determine reactive intermediates (singlet or triplet carbenes, radicals, others) generated during these processes. To this end, we will elaborate direct photolysis of diazo compounds which absorb in the blue region in C-H insertions. For compounds unreactive under visible light-irradiation, photocatalyzed transformations in the presence of a photosensitizer or a photoredox catalyst represent an alternative.

In particular, the main tasks will involve:

- design, preparation of diazo compounds absorbing visible light and determination of their optical properties;
- studying reactions of diazo compounds in the presence of photoredox catalysts;
- scope and limitation studies;
- analytical characterization of synthesized;
- preparation of manuscripts.

Requirements:

- master degree in chemistry;
- experience in organic or related;
- other skills include analysis and interpretation of experimental data (NMR, MS, UV/Vis);
- demonstrated experience in research work will be an asset;
- effective written and oral communication in English