

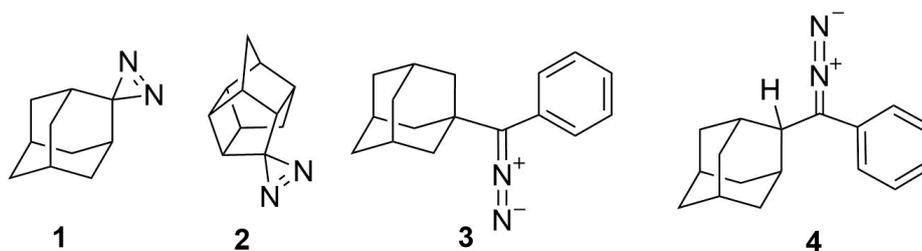
PHOTOCHEMICAL ELIMINATION OF NITROGEN FROM DIAZIRINES AND DIAZO COMPOUNDS

Nikola Basarić

Department of Organic Chemistry and Biochemistry, Ruđer Bošković Institute, Bijenička cesta 54, HR-10000 Zagreb, Croatia
nbasaric@irb.hr

Elimination of nitrogen from diazo compounds and diazirines that delivers carbenes is a well known reaction, which can be initiated thermally or photochemically.^[1] Prompted by our interest in the synthesis of polycyclic strained molecules,^[2] we studied photoelimination of nitrogen from adamantane **1** and pentacycloundecane (PCU) diazirine derivative **2**. Combined preparative irradiations, spectroscopic study and computations for **1** and **2** indicated that photoproducts were formed *via* singlet and triplet carbenes, even though singlet carbenes are more stable than the triplets. Complexation of diazirines with macrocyclic host molecules changed the distribution of singlet and triplet photoproducts.^[3] Furthermore, upon irradiation of **2** in CH₃OH we isolated some products with rearranged PCU skeleton, which indicated that carbenes undergo protonation in CH₃OH, and not O-H bond insertion, changing the paradigm for the mechanism of the reaction of carbenes with alcohols.

Combined experimental and theoretical investigation of photoelimination of nitrogen from diazo compounds **3** and **4** unraveled hitherto undisclosed pathway involving higher excited singlet states. Fluorescence takes place from S₂, whereas the photoelimination of nitrogen upon excitation to S₂ proceeds more efficiently than upon excitation to S₁, due to efficient deactivation to S₀ *via* a conical intersection.^[4] The discovery of anti-Kasha photochemical pathways is interesting due to its fundamental value, as well as for potential applications, since the photoreaction can be tuned by appropriate choice of light wavelength.



REFERENCES

- [1] A.-M. A. Abdel-Wahab, S. A. Ahmed and H. Dürr, Carbene, In *CRC Handbook of Photochemistry and Photobiology 2nd Ed.*, (Eds.: W. Horspool and F. Lenci), CRC Press, Boca Raton, 2004.
- [2] K. Mlinarić-Majerski, Molecules with Inverted Carbon Atoms, in *Strained Hydrocarbons*, (Ed.: H. Dodziuk), Wiley-VCH, Weinheim, 2009, and references cited therein.
- [3] T. Šumanovac, M. Alešković, M. Šekutor, M. Matković, T. Baron, K. Mlinarić-Majerski, C. Bohne, N. Basarić, *Photochem. Photobiol. Sci.* 2019, 18, 1806–1822.
- [4] M. Alešković, T. Piteša, K. Becker, C. Bohne, N. Basarić, N. Došlić, *unpublished results*.