

## Photoredox catalytic transformations of pyrazoles

Redox reactions, which take place after photon absorption, enable preparation and functionalization of heterocyclic compounds under mild reaction conditions. Under visible light irradiation in the presence of eosin, a photoredox catalyst, and oxygen, an oxidant, 1-substituted pyrazolidin-3-ones were successfully oxidized. So formed azomethine imines are useful building blocks in the synthesis of heterocyclic compounds, as demonstrated by a one-pot photocatalyzed oxidation and cycloaddition of ensuing dipoles with ynones. After optimization of reaction conditions, a plethora of azomethine imines and pyrazolo[1,2-*a*]pyrazoles were synthesized. 1-Arylpyrazolidin-3-ones were also successfully oxidized to 1-arylpyrazol-3-ones. Aldehydes and ketones, which are formed from N1 substituent of azomethine imines, were identified as side products of pyrazolidin-3-one oxidation.

Pyrazolo[1,2-*a*]pyrazoles are fluorescent compounds, which can absorb visible light. Some of the optical properties of these bicyclic compounds were measured. Their instability in solutions was for the first time attributed to exposure to visible light as pyrazole ring opening takes place. With optimization of reaction conditions, 6 distinct transformations into substituted pyrazoles were achieved. The selectivity of the reactions is dependent on the substituents on the pyrazolo[1,2-*a*]pyrazole and the added reagents. The combined research proved crucial in the use of pyrazolo[1,2-*a*]pyrazoles as fluorescent markers.

Attempts to sulfonate pyrazoles with photoredox catalyzed radical addition with sulfonyl chlorides, which were synthesized under photoredox catalyzed conditions as well, were unsuccessful. The research was concluded with an unexpected two-step formation of dialkenyl sulfones with sequential radical additions between triflyl chloride and arylacetylenes. This transformation has not yet been explored despite already investigated reactions involving alkenes.

Keywords: pyrazoles, pyrazolo[1,2-*a*]pyrazoles, photoredox catalysis, visible light, photoreactions