OP-17

SUBSTITUENT EFFECTS ON THE PHOTOCHEMISTRY OF 5-AMINOTETRAZOLES

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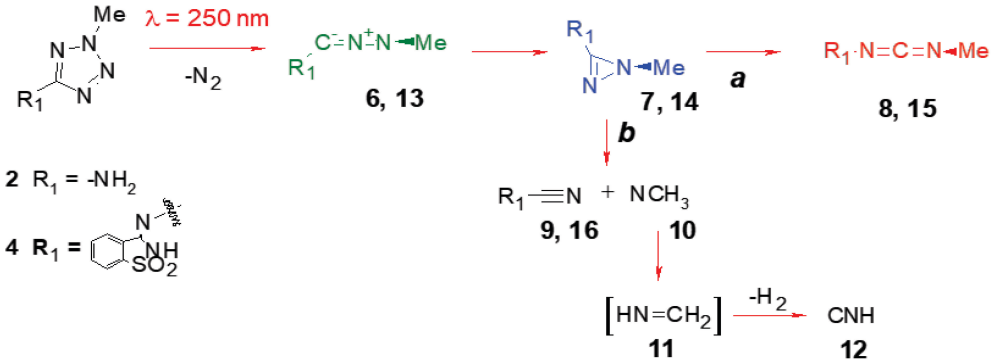
The applications of 2-methyl-(2*H*)-tetrazole-5-amino-saccharinate (**4**; Scheme 1) in catalysis and chelant-based chemotherapy stimulated investigations on its photostability.[1a] The photochemistry of **4** in solid argon (15 K) was compared with those of 2-methyl-(2*H*)-tetrazole-5-amine (**2**) and 1-methyl-(2*H*)-tetrazole-5-amine.[1b] Compounds were subjected to *in situ* narrowband UV-irradiation at different wavelengths. Reactions were followed by infrared spectroscopy, supported by B3LYP/6-311++G(d,p) calculations. Photochemical pathways for **2** and **4** proved similar but photodegradation of **4** was 20x slower, unraveling the photo-stabilizing effect of the saccharyl moiety that extends into the nitrilimine **6**, formed from **4**, and its antiaromatic 1*H*-diazirene isomer **7**, which proved photostable at 290 nm, unlike the 1*H*-diazirene **14**, formed from **2**. Analysis of the photochemistry of **2**/**4** (250 nm), including energy trends calculated for the isomeric $C_2H_5N_3$ species postulated/observed from photolysis and EPR results, enabled a deeper insight into the photodegradation mechanisms of 2,5-substituted tetrazoles. We postulate a pivotal singlet state imidoylnitrene species as common intermediate, which undergoes a Wolff-type isomerization to a stable carbodiimide (**8**, **15**; Scheme 1).[2]



Scheme 1.

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[2] A. Ismael, M. Abe, R. Fausto, M. L. S. Cristiano, *Pure Appl. Chem.* **2019**, *in press*.