

Fakulteta za znanosti o okolju vabi

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Interconversion of nitrenes, diradicals and ylides

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Aromatic and heteroaromatic nitrenes undergo several interrelated unimolecular reactions: ring expansion to azacyclohepatetraenes or to a new class of bond-switch isomers which are zwitterionic cumulenes (cyclic nitrile ylides), ring opening to nitrile ylides, nitrile imines, diradicals or dienylnitrenes, and ring contraction to 5-membered ring nitriles.

2-Quinazolylnitrenes undergo diradicaloid and ylidic ring openings. Argon matrix photolysis of tetrazolo[1,5-a]quinazoline/2-azidoquinazoline affords 2-quinazolylnitrene, which has been characterized by ESR, UV and IR spectroscopy. A diradical is formed rapidly by ring opening and characterized by ESR spectroscopy; it decays thermally at 15 K with a half-life of ca. 47 min due to its facile intersystem crossing (triplet to open-shell singlet) followed by cyclization to 1-cyanoindazole and H-shift to N-cyanoanthranilonitrile.

Furthermore, benzotriazacycloheptatetraene can photochemically interconvert with the ring opened product, 2-isocyano- α -diazo- α -phenyltoluene as determined by IR and UV spectroscopy.

Vljudno vabljeni!