Nitron: From Bench Stable Carbene to Blatter-type Radical

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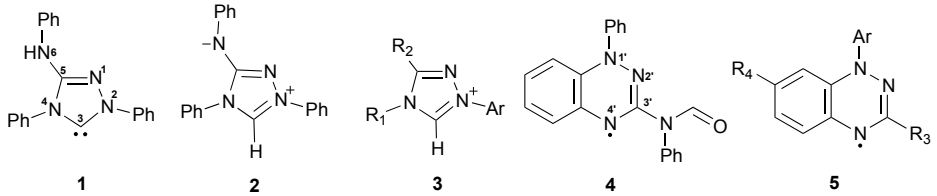
In 2012, Färber *et al* showed that the analytical reagent Nitron exhibits some reactivity consistent with NHC-type tautomer **1** rather than the conventional representation as Lewis structure **2**.[1] We now report C(3)-H deuterium exchange studies of Nitron, and compare these with our results for a large series of 1,2,4-triazolium ions **3**.[2]

During these studies, we noted that stock solutions of Nitron in CD_3CN changed colour over 1 day at room temperature. Black crystals were observed to form upon concentration of the aged solution, which, after isolation and purification, proved to be stable in air and at room temperature for months. X-Ray crystallographic analysis identified product **4**, which is similar to the stable Blatter-type 1,2,4-benzotriazinyl radicals **5** first described in 1968[3] as 'beautiful black needles'. EPR analysis supports the radical nature of **4**, which is the first example with a C(3')-amido substituent to our knowledge. Literature examples of stable Blatter organic radicals **5** have been mostly restricted to R_3 = alkyl, aryl or alkenyl. To explore the versatility of this route towards functionalized stable organic radicals, a range of Nitron derivatives was prepared and analysed. Our synthetic results and mechanistic proposals for radical formation will be presented.



1 **2** **3** **4** **5**

1. C. Färber, M. Leibold, C. Bruhn, M. Maurer and U. Siemeling, *Chem. Commun.*, **2012**, *48*, 227-229.

2. (a) R. S. Massey, C. J. Collett, A. G. Lindsay, A. D. Smith and A. C. O'Donoghue, *J. Am. Chem. Soc.*, **2012**, *134*, 20421-20432; (b) D. E. Tucker, P. Quinn, R. S. Massey, C. J. Collett, D. J. Jasiewicz, C. R. Bramley, A. D. Smith, A. C. O'Donoghue, *J. Phys. Org. Chem.* **2015**, *28*, 108-115.

3. H. M. Blatter and H. Lukaszewski, *Tet. Lett.*, **1968**, *22*, 2701-2705.