

# First generation of pentazole (HN<sub>5</sub>, pentazolic acid), the final azole, and a zinc pentazolate salt in solution: A new *N*-dearylation of 1-(*p*-methoxyphenyl) pyrazoles, a 2-(*p*-methoxyphenyl) tetrazole and application of the methodology to 1-(*p*-methoxyphenyl) pentazole†

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Ceric ammonium nitrate (CAN) in methanol–water gave a new *N*-dearylation of a series of substituted 1-(*p*-methoxyphenyl) pyrazoles and a 2-(*p*-methoxyphenyl)tetrazole producing *p*-benzoquinone and the parent azole in a mole for mole ratio. Application of this reaction to 1-(*p*-methoxyphenyl) pentazole at  $-40\text{ }^{\circ}\text{C}$  produced *p*-benzoquinone. <sup>15</sup>N NMR spectra suggest that pentazole, HN<sub>5</sub>, was also produced and held in solution as N<sub>5</sub><sup>-</sup> with Zn<sup>2+</sup> ion. The <sup>15</sup>N signal from N<sub>5</sub><sup>-</sup> was  $-10.0 \pm 2.0$  ppm in agreement with calculated values.

The existence of an all-nitrogen aromatic azole ring, R–N<sub>5</sub>, the pentazoles, was proved by Clusius and Hurzeler<sup>1</sup> in Zurich and Huisgen and Ugi<sup>2</sup> in Munich.<sup>3</sup> Since then a significant goal of heterocyclic chemistry has been to prepare the parent pentazole, HN<sub>5</sub>. Ozonolytic degradation of the aryl ring was attempted<sup>4</sup> and recently revisited with controlled limited amounts of ozone,<sup>5</sup> but HN<sub>5</sub> or its anion N<sub>5</sub><sup>-</sup> was not found. Following the recent discovery of N<sub>5</sub><sup>+</sup> as a reasonably stable cation in inorganic salts<sup>6,7</sup> there has been renewed experimental interest in allotropes of nitrogen and in N<sub>5</sub><sup>-</sup> in particular. There has also been much theoretical interest in these types of species.<sup>8–12</sup> Metallocene pentazole derivatives have been predicted as viable forms of N<sub>5</sub><sup>-</sup>, but bidentate forms MN<sub>5</sub> (M = Na, K, MgCl<sup>+</sup>, CaCl<sup>+</sup>) and M(N<sub>5</sub>)<sub>2</sub> (M = Na, K, Mg, Ca) and unidentate Zn(N<sub>5</sub>)Cl and Zn(N<sub>5</sub>)<sub>2</sub> are calculated to have lower energy.<sup>13</sup> Recently it has been suggested the N<sub>5</sub><sup>+</sup>.N<sub>5</sub><sup>-</sup> is a viable entity.<sup>14</sup>

Following our recent establishment of the mechanism of formation of aryl pentazoles from aryldiazonium ions and azide ion,<sup>15</sup> we have been endeavouring to generate HN<sub>5</sub> and its anion N<sub>5</sub><sup>-</sup>. Recently N<sub>5</sub><sup>-</sup> has been detected for the first time from high voltage collisions of 4-pentazolyphenolate ion, N<sub>5</sub>-C<sub>6</sub>H<sub>4</sub>O<sup>-</sup>, in the mass spectrometer.<sup>16</sup> We are therefore prompted to make a preliminary report of our work.

To remove an aryl group from an arylpentazole without destruction of the pentazole ring a mild oxidizing agent and the appropriate aryl pentazole must be chosen. Ceric (iv) ammonium nitrate (CAN) has been used to remove *p*-MeOC<sub>6</sub>H<sub>5</sub>-groups from *p*-methoxyphenyl ethers<sup>17,18</sup> and *N*-*p*-methoxyphenyl azetidines.<sup>19–20</sup> The methoxyphenyl ring is removed as *p*-benzoquinone and the use of H<sub>2</sub><sup>18</sup>O has proved that the two quinone oxygens arise from water in the solvent.<sup>18</sup> Successive one-electron oxidations are considered to produce a quinone-imine dication which is hydrolysed.<sup>20</sup> We tested this reaction for the first time with an azole substrate using the 1-*N*-*p*-methoxyphenyl pyrazole series shown in Fig. 1. It proved successful and was optimised at low temperatures. The *p*-benzoquinone is easily detected and estimated. Its presence indicates a mole for mole presence of the azole. High temperatures are not appropriate for this reaction because the azole generated may undergo addition reactions with *p*-benzoquinone.<sup>21</sup> We also attempted the reaction with the non-

metallic one-electron acceptor tetracycanoethylene,<sup>22</sup> but this gave no dearylation. A similar CAN oxidation of the tetrazole **4** gave *p*-benzoquinone and 5-phenyltetrazole **5**.

A theoretical study was carried out<sup>13</sup> to determine the <sup>15</sup>N NMR shift expected for N<sub>5</sub><sup>-</sup> and to identify the best cation to retain it, which proved to be Zn<sup>2+</sup>. An analysis of LCAO-MO coefficients showed considerable interaction between Zn d orbitals and the N<sub>5</sub><sup>-</sup> lone pairs and π MOs.<sup>13</sup> A Mulliken population analysis indicated much more of a covalent interaction between Zn and N<sub>5</sub><sup>-</sup> than the other metals. The Mulliken charges on the metal calculated with the basis set used in our study are Na +0.805, K +0.914 for MN<sub>5</sub>, and Mg +0.756, Ca +0.869, Zn +0.300 for M(N<sub>5</sub>)Cl. Kaszynski et al.<sup>5</sup> have concluded that HN<sub>5</sub> has a half-life of only 10 min and hence it could probably not be directly detected. It has also been suggested that HN<sub>5</sub> is a stronger acid than nitric acid,<sup>23</sup> hence if generated a significant portion would be converted to the anion and held were an appropriate cation such as Zn<sup>2+</sup> present.

When the CAN dearylation was applied to 1-(*p*-methoxyphenyl) pentazole at  $-40\text{ }^{\circ}\text{C}$ , *p*-benzoquinone was readily detected in the solution by tlc and confirmed by direct detection with <sup>1</sup>H and <sup>13</sup>C NMR spectra. Proton NMR and GC calibration against standard benzoquinone solutions gave yields of up to 25% quinone. The benzoquinone was also isolated as yellow crystals by sublimation. The presence of the benzoquinone suggests that HN<sub>5</sub> has been generated. The pentazole used was prepared as described by Huisgen and Ugi.<sup>2</sup> When NMR spectra were measured however there was always some *p*-methoxyphenyl azide present but ratios of pentazole to azide as high as 11 : 1 were achieved. Fig. 3a shows the <sup>15</sup>N NMR spectrum of **6** where signals from the pentazole only are seen. The proton NMR spectrum of the same solution (Fig. 3a, inset) shows the presence of 7% *p*-methoxyphenyl azide. Control reactions of CAN with *p*-methoxyphenyl azide produced effectively no measurable *p*-benzoquinone and the small impurity of aryl azide could not account for the observed results from the reaction of CAN with **6**.

The key experiments shown in Fig. 2 were then performed.† The <sup>15</sup>N-labelled derivative **6** was prepared from the reaction of *p*-methoxyphenyl diazonium ion with terminal <sup>15</sup>N-labelled

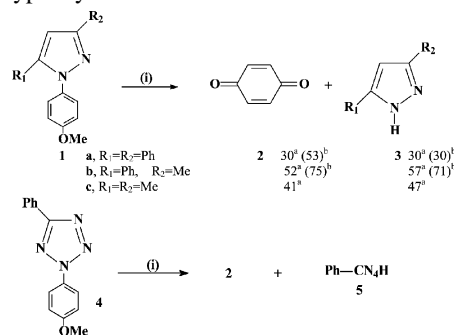
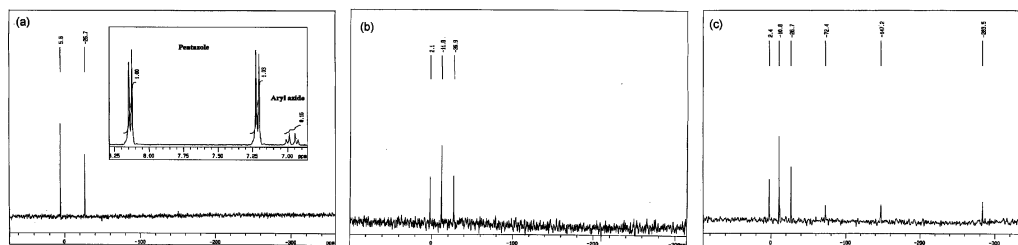


Fig. 1 <sup>a</sup> Isolated yield (%) at ambient temperature. <sup>b</sup> Isolated yield (%) at  $-10\text{ }^{\circ}\text{C}$ . Reagents: (i) Ce(NH<sub>4</sub>)<sub>2</sub>(NO<sub>3</sub>)<sub>6</sub> in MeCN:H<sub>2</sub>O, (83:17 v/v) or MeOH:H<sub>2</sub>O (80:20 v/v).

† Electronic supplementary information (ESI) available: experimental details. See <http://www.rsc.org/suppdata/cc/b3/b301491f/>



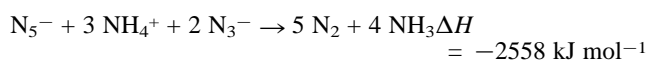
**Fig. 3** (a)  $^{15}\text{N}$  NMR spectrum of  $^{15}\text{N}$ -labelled **6** (see Fig. 2) with inset  $^1\text{H}$  NMR spectrum showing 7% arylazide (cf. ref. 24). (b)  $^{15}\text{N}$  NMR spectrum of reaction mixture of CAN and compound **6** when held at  $-40\text{ }^\circ\text{C}$  for up to 2 weeks. (c)  $^{15}\text{N}$  NMR spectrum of reaction mixture after 7 days at  $-40\text{ }^\circ\text{C}$  followed by 68 h at  $-20\text{ }^\circ\text{C}$ , showing  $^{15}\text{N}_2$  ( $-72\text{ ppm}$ )<sup>24</sup> and  $^{15}\text{N}_3^-$  ( $-283\text{ ppm}$ ,  $-147\text{ ppm}$ ). Larger version of spectra available in ESI.†

azide ion which places  $^{15}\text{N}$  atoms at the 2-, 3-, 4- and 5-pentazole positions.<sup>15</sup> Solutions of **6** in  $\text{CD}_3\text{OD}:\text{D}_2\text{O}$  containing excess  $\text{Zn}(\text{NO}_3)_2$  were treated with CAN at  $-40\text{ }^\circ\text{C}$  and followed by  $^{15}\text{N}$  NMR spectra.† Only  $^{15}\text{N}$  labelled nitrogen atoms are detected. As the signals of the pentazole declined a new signal appeared at  $-10.0 \pm 2.0\text{ ppm}$  in different runs (Fig. 3b). The calculated  $^{15}\text{N}$  shift for  $\text{Zn}(\text{N}_5)\text{Cl}$  is  $-16.6\text{ ppm}$ .<sup>13</sup> This is an average of the five values reported for the  $^{15}\text{N}$  shifts. Geometry optimization of  $\text{Zn}(\text{N}_5)\text{NO}_3$  using the same procedure<sup>13</sup> leads to the unidentate, planar configuration and an average  $^{15}\text{N}$  shift of  $-17.5\text{ ppm}$ . The spread in the signal position,  $-10.0 \pm 2.0\text{ ppm}$  in different runs, may be due to the mix of ions present in the solution. The cations present are  $\text{Zn}^{2+}$ ,  $\text{NH}_4^+$ ,  $\text{Ce}(\text{iv})$  and  $\text{Ce}(\text{iii})$  and the anions are  $\text{NO}_3^-$  and  $\text{N}_5^-$ .  $\text{Ce}(\text{iii})$  is expected to be detrimental to  $\text{N}_5^-$ . When the solution was warmed to  $-20\text{ }^\circ\text{C}$  for ca. 24 h a signal at  $-72\text{ ppm}$  due to  $^{15}\text{N}$ -labelled nitrogen gas appeared along with signals at  $-283\text{ ppm}$  and  $-147\text{ ppm}$ , the terminal and central atoms of  $^{15}\text{N}_3^-$  respectively (Fig. 3c). When the solution was warmed above  $0\text{ }^\circ\text{C}$  these three signals disappeared. At the end of the reaction there were no signals for  $^{15}\text{N}$ -labelled azide ion and careful work-up of aqueous and organic extracts showed no traces of  $\text{N}_3^-$  ion in the IR spectra of the residue. The anion  $\text{N}_5^-$  would be expected to break down to  $^{15}\text{N}_2$  and  $^{15}\text{N}_3^-$  (as observed herein and also in gas phase<sup>16</sup>) since  $\text{ArN}_5$  breaks down to  $\text{ArN}_3$  and  $\text{N}_2$ . We had expected the  $^{15}\text{N}_3^-$  to grow and remain in the solutions. Optimising the geometries of the reactants and products at the B3LYP/6-11++Gdp level of theory<sup>13</sup> gives a reaction energy of

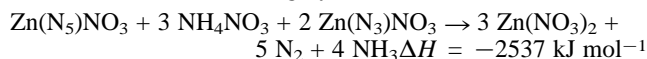


( $-60\text{ kJ mol}^{-1}$  at the CCSD(T)/aug-cc-pVTZ level of theory<sup>14</sup>).

However the presence of excess  $\text{NH}_4^+$  ions in the solutions can give rise to the following highly exothermic removal of azide ion:

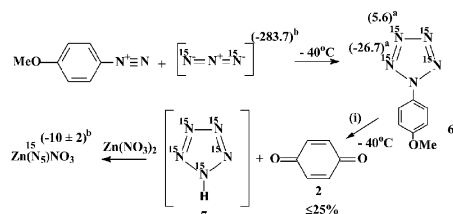


Even when considering the effect of counter ions as ion pair structures the reaction is highly exothermic:



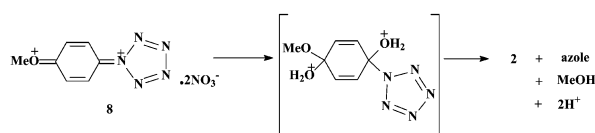
The totality of the experimental results we have observed suggest that in these solutions we have generated  $\text{HN}_5$  and held it for a time in a zinc(ii) salt.

From literature work<sup>17–20</sup> we believe the key intermediate in these dearylation reactions is the species **8**. This must not be



**Fig. 2** a  $^{15}\text{N}$  shifts ppm from  $\text{MeNO}_2$  in  $\text{CD}_3\text{OD}$ . b  $^{15}\text{N}$  shifts ppm in  $\text{CD}_3\text{OD}:\text{D}_2\text{O}$  77:23 (v/v). Reagents: (i)  $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$  (2.8 mol),  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (6 mol),  $\text{CD}_3\text{OD}:\text{D}_2\text{O}$  77:23 (v/v).

looked upon as an unstable organic dication. When two  $\text{NO}_3^-$  ions pairs above and below the benzene ring of species **8** are included in B3LYP/3-611 + G(d) geometry optimisations (cf. ref. 13 for details of the method), considerable stabilisation of the organic component is found. Bond lengths resemble much more a neutral aromatic system than a quinone structure. The 1,4-benzene carbons remain positive enough to favour nucleophilic  $\text{H}_2\text{O}$  addition which leads to the separation of the two aromatic rings.



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