First generation of pentazole ( $HN_5$ , 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<sup>†</sup>

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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 °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  $HN_5$  or its anion  $N_5^-$  was not found. Following the recent discovery of N5+ 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  $N_5^-$ , but bidentate forms  $MN_5$  ( $M = Na, K, MgCl^+$ , CaCl<sup>+</sup>) and  $M(N_5)_2$  (M = Na, K, Mg, Ca) and unidentate  $Zn(N_5)Cl$  and  $Zn(N_5)_2$  are calculated to have lower energy.<sup>13</sup> Recently it has been suggested the N5+.N5- is a viable entity.14

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-pentazolylphenolate 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*-methox-yphenyl azetidines.<sup>19–20</sup> The methoxyphenyl ring is removed as *p*-benzoquinone and the use of  $H_2^{18}O$  has proved that the two quinone oxygens arise from water in the solvent.18 Successive one-electron oxidations are considered to produce a quinoneimine dication which is hydrolysed.<sup>20</sup> We tested this reaction for the first time with an azole substrate using the 1-N-pmethoxyphenyl pyrazole series shown in Fig. 1. It proved successful and was optimised at low temperatures. The pbenzoquinone 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 pbenzoquinone.<sup>21</sup> We also attempted the reaction with the non-

† Electronic supplementary information (ESI) available: experimental details. See http://www.rsc.org/suppdata/cc/b3/b301491f/ 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  $N_5^-$  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  $N_5^-$  lone pairs and  $\pi$  MOs.<sup>13</sup> A Mulliken population analysis indicated much more of a covalent interaction between Zn and  $N_5^-$  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 °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 HN5 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.<sup>†</sup> 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** a Isolated yield (%) at ambient temperature. <sup>b</sup> Isolated yield (%) at -10 °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).



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

azide ion which places <sup>15</sup>N atoms at the 2-,3-,4- and 5-pentazole positions.<sup>15</sup> Solutions of **6** in CD<sub>3</sub>OD:D<sub>2</sub>O containing excess  $Zn(NO_3)_2$  were treated with CAN at -40 °C and followed by <sup>15</sup>N NMR spectra.<sup>†</sup> Only <sup>15</sup>N labelled nitrogen atoms are detected. As the signals of the pentazole declined a new signal appeared at  $-10.0 \pm 2.0$  ppm in different runs (Fig. 3b). The calculated <sup>15</sup>N shift for  $Zn(N_5)Cl$  is -16.6ppm.<sup>13</sup> This is an average of the five values reported for the <sup>15</sup>N shifts. Geometry optimization of  $Zn(N_5)NO_3$  using the same procedure<sup>13</sup> leads to the unidentate, planar configuration and an average <sup>15</sup>N shift of -17.5 ppm. The spread in the signal position, -10.0 + 2.0 ppm in different runs, may be due to the mix of ions present in the solution. The cations present are  $Zn^{2+}$ ,  $NH_4^+$ , Ce(IV) and Ce(III)and the anions are  $\hat{NO}_3^-$  and  $N_5^-$ . Ce(III) is expected to be detrimental to  $N_5^{-}$ . When the solution was warmed to -20 °C for ca. 24 h a signal at -72 ppm due to <sup>15</sup>N-labelled nitrogen gas appeared along with signals at -283 ppm and -147 ppm, the terminal and central atoms of  ${}^{15}N_3$  – respectively (Fig. 3c). When the solution was warmed above 0 °C these three signals disappeared. At the end of the reaction there were no signals for <sup>15</sup>N-labelled azide ion and careful work-up of aqueous and organic extracts showed no traces of N<sub>3</sub><sup>-</sup> ion in the IR spectra of the residue. The anion  $N_5^-$  would be expected to break down to  ${}^{15}N_2$  and  ${}^{15}N_3$  (as observed herein and also in gas phase<sup>16</sup>) since ArN<sub>5</sub> breaks down to ArN<sub>3</sub> and N<sub>2</sub>. We had expected the  $^{15}N_3^{-}$  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

$$N_5^- \rightarrow N_2 + N_3^- \Delta H = -59 \text{ kJ mol}^-$$

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

However the presence of excess  $NH_4^+$  ions in the solutions can give rise to the following highly exothermic removal of azide ion:

$$N_5^- + 3 NH_4^+ + 2 N_3^- \rightarrow 5 N_2 + 4 NH_3\Delta H$$
  
= -2558 kJ mol<sup>-1</sup>

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

$$\begin{array}{l} {\rm Zn}({\rm N}_5){\rm NO}_3+3\ {\rm NH}_4{\rm NO}_3+2\ {\rm Zn}({\rm N}_3){\rm NO}_3 \rightarrow 3\ {\rm Zn}({\rm NO}_3)_2+\\ 5\ {\rm N}_2+4\ {\rm NH}_3\Delta H\ =\ -2537\ {\rm kJ\ mol^{-1}} \end{array}$$

The totality of the experimental results we have observed suggest that in these solutions we have generated  $HN_5$  and held it for a time in a zinc(II) salt.

From literature work  $^{17-20}$  we believe the key intermediate in these dearylation reactions is the species **8**. This must not be



**Fig. 2** <sup>a</sup> <sup>15</sup>N shifts ppm from MeNO<sub>2</sub> in CD<sub>3</sub>OD. <sup>b</sup> <sup>15</sup>N shifts ppm in CD<sub>3</sub>OD:D<sub>2</sub>O 77:23 (v/v). *Reagents*: (i) Ce(NH<sub>4</sub>)<sub>2</sub>(NO<sub>3</sub>)<sub>6</sub> (2.8 mol), Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (6 mol), CD<sub>3</sub>OD:D<sub>2</sub>O 77:23 (v/v).

looked upon as an unstable organic dication. When two  $NO_3^-$  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 H<sub>2</sub>O addition which leads to the separation of the two aromatic rings.



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