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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†

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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. ^{15}N NMR spectra suggest that pentazole, HN_5, was also produced and held in solution as N_5^- with Zn^{2+} ion. The ^{15}N signal from N_5^- was -10.0 ± 2.0 ppm in agreement with calculated values.

The existence of an all-nitrogen aromatic azole ring, R–N_5, the pentazoles, was proved by Clusius and Hurzeler[1] in Zurich and Huisgen and Ugi[2] in Munich.[3] Since then a significant goal of heterocyclic chemistry has been to prepare the parent pentazole, HN_5. Ozonolytic degradation of the aryl ring was attempted[4] and recently revisited with controlled limited amounts of ozone,[5] but HN_5 or its anion N_5^- was not found. Following the recent discovery of N_5^+ as a reasonably stable cation in inorganic salts[6,7] there has been renewed experimental interest in allotropes of nitrogen and in N_5^- in particular. There has also been much theoretical interest in these types of species.[8–12] Metallocene pentazole derivatives have been predicted as viable forms of N_5^-, but bidentate forms MN_5 (M = Na, K, $MgCl^+$, $CaCl^+$) 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.[13] Recently it has been suggested the $N_5^+.N_5^-$ is a viable entity.[14]

Following our recent establishment of the mechanism of formation of aryl pentazoles from aryldiazonium ions and azide ion,[15] we have been endeavouring to generate HN_5 and its anion N_5^-. Recently N_5^- has been detected for the first time from high voltage collisions of 4-pentazolylphenolate ion, N_5-$C_6H_4O^-$, in the mass spectrometer.[16] 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*-$MeOC_6H_5$-groups from *p*-methoxyphenyl ethers[17,18] and *N*-*p*-methoxyphenyl azetidines.[19–20] 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 quinone-imine dication which is hydrolysed.[20] 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.[21] We also attempted the reaction with the non-metallic one-electron acceptor tetracycanoethylene,[22] 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[13] to determine the ^{15}N NMR shift expected for N_5^- and to identify the best cation to retain it, which proved to be Zn^{2+}. An analysis of LCAO-MO coefficients showed considerable interaction between Zn d orbitals and the N_5^- lone pairs and π MOs.[13] 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_5, and Mg +0.756, Ca +0.869, Zn +0.300 for $M(N_5)Cl$. Kaszynski et al.[5] have concluded that HN_5 has a half-life of only 10 min and hence it could probably not be directly detected. It has also been suggested that HN_5 is a stronger acid than nitric acid,[23] hence if generated a significant portion would be converted to the anion and held were an appropriate cation such as Zn^{2+} 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 ^1H and ^{13}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_5 has been generated. The pentazole used was prepared as described by Huisgen and Ugi.[2] 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 ^{15}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 ^{15}N-labelled derivative **6** was prepared from the reaction of *p*-methoxyphenyl diazonium ion with terminal ^{15}N-labelled

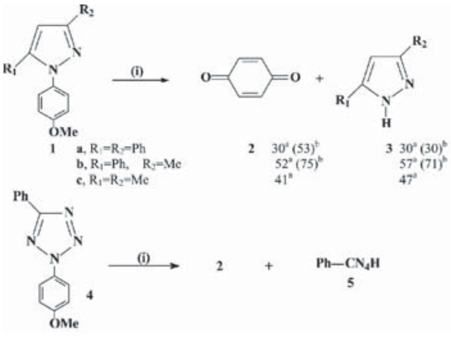

Fig. 1 [a] Isolated yield (%) at ambient temperature. [b] Isolated yield (%) at −10 °C. *Reagents*: (i) $Ce(NH_4)_2(NO_3)_6$ in MeCN : H_2O, (83 : 17 v/v) or MeOH : H_2O (80 : 20 v/v).

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

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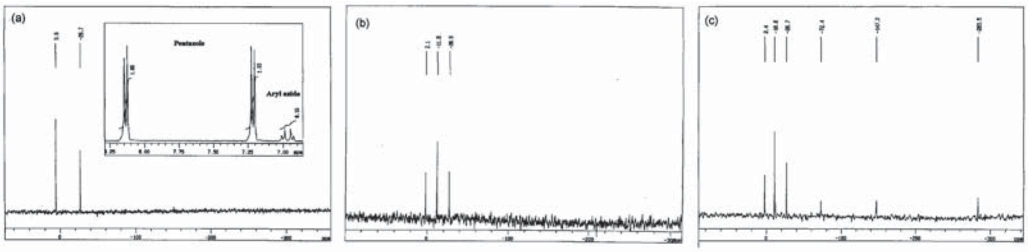


Fig. 3 (a) ^{15}N NMR spectrum of ^{15}N-labelled **6** (see Fig. 2) with inset ^1H NMR spectrum showing 7% arylazide (cf. ref. 24). (b) ^{15}N NMR spectrum of reaction mixture of CAN and compound **6** when held at −40 °C for up to 2 weeks. (c) ^{15}N NMR spectrum of reaction mixture after 7 days at −40 °C followed by 68 h at −20 °C, showing $^{15}N_2$ (−72 ppm)[24] and $^{15}N_3^-$(−283 ppm, −147 ppm). Larger version of spectra available in ESI.†

azide ion which places ^{15}N atoms at the 2-,3-,4- and 5-pentazole positions.[15] Solutions of **6** in $CD_3OD{:}D_2O$ containing excess $Zn(NO_3)_2$ were treated with CAN at −40 °C and followed by ^{15}N NMR spectra.† Only ^{15}N labelled nitrogen atoms are detected. As the signals of the pentazole declined a new signal appeared at −10.0 ± 2.0 ppm in different runs (Fig. 3b). The calculated ^{15}N shift for $Zn(N_5)Cl$ is −16.6ppm.[13] This is an average of the five values reported for the ^{15}N shifts. Geometry optimization of $Zn(N_5)NO_3$ using the same procedure[13] leads to the unidentate, planar configuration and an average ^{15}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 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 ^{15}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 ^{15}N-labelled azide ion and careful work-up of aqueous and organic extracts showed no traces of N_3^- 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[16]) since ArN_5 breaks down to ArN_3 and N_2. 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[13] gives a reaction energy of

$$N_5^- \rightarrow N_2 + N_3^- \Delta H = -59 \text{ kJ mol}^{-1}$$

(−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:

$$N_5^- + 3\,NH_4^+ + 2\,N_3^- \rightarrow 5\,N_2 + 4\,NH_3 \Delta H = -2558 \text{ kJ mol}^{-1}$$

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

$$Zn(N_5)NO_3 + 3\,NH_4NO_3 + 2\,Zn(N_3)NO_3 \rightarrow 3\,Zn(NO_3)_2 + 5\,N_2 + 4\,NH_3 \Delta H = -2537 \text{ kJ mol}^{-1}$$

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 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_2O addition which leads to the separation of the two aromatic rings.

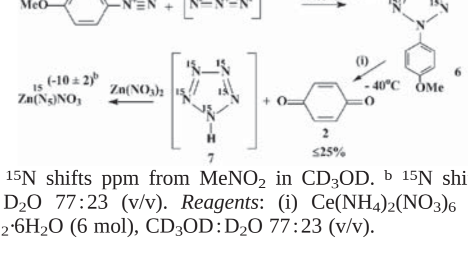
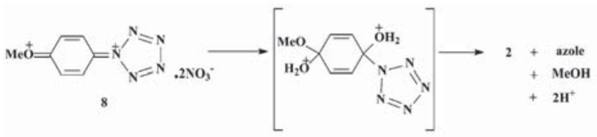


Fig. 2 ᵃ ^{15}N shifts ppm from $MeNO_2$ in CD_3OD. ᵇ ^{15}N shifts ppm in $CD_3OD{:}D_2O$ 77:23 (v/v). *Reagents*: (i) $Ce(NH_4)_2(NO_3)_6$ (2.8 mol), $Zn(NO_3)_2{\cdot}6H_2O$ (6 mol), $CD_3OD{:}D_2O$ 77:23 (v/v).



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Notes and references

1 K. Clusius and H. Hurzeler, *Helv. Chim. Acta*, 1954, **37**, 798.
2 R. Huisgen and I. Ugi, *Chem. Ber.*, 1957, **90**, 2914; R. Huisgen and I. Ugi, *Angew. Chem.*, 1956, **68**, 705.
3 A review, R. N. Butler, *Comprehensive Heterocyclic Chemistry II*, Series eds., A. R. Katritzky, C. W. Rees, E. F. V. Scriven, Pergamon Press, Oxford, 1996, **vol. 4** (ed. R. C. Storr), p. 897.
4 I. Ugi, *Angew. Chem.*, 1961, **73**, 172.
5 V. Benin, P. Kaszynski and J. G. Radziszewski, *J. Org. Chem.*, 2002, **67**, 1354.
6 K. O. Christe, W. W. Wilson, J. A. Sheehy and J. A. Boatz, *Angew. Chem., Int. Ed.*, 1999, **38**, 2004.
7 A. Vij, W. W. Wilson, V. Vij, F. S. Tham, J. A. Sheehy and K. O. Christe, *J. Am. Chem. Soc.*, 2001, **123**, 6308.
8 M. T. Nguyen, M. Sana, G. Leroy and J. Elguero, *Can. J. Chem.*, 1983, **61**, 1435.
9 M. T. Nguyen, M. A. McGinn, A. F. Hegarty and J. Elguero, *Polyhedron*, 1985, **4**, 1721.
10 R. J. Bartlett, *Chem. Ind. (London)*, 2000, 140; K. F. Ferris and R. J. Bartlett, *J. Am. Chem. Soc.*, 1992, **114**, 8302.
11 G. A. Olah, G. K. Surya Prakash and G. Rasul, *J. Am. Chem. Soc.*, 2001, **123**, 3308.
12 A. Hammerl and T. M. Klapötke, *Inorg. Chem.*, 2002, **41**, 906.
13 L. A. Burke, R. N. Butler and J. C. Stephens, *J. Chem. Soc., Perkin Trans. 2*, 2001, 1679.
14 M. T. Nguyen and T. K. Ha, *Chem. Phys. Lett.*, 2001, **335**, 311; S. Fau, K. J. Wilson and R. J. Bartlett, *J. Phys. Chem. A*, 2002, **106**, 4639.
15 R. N. Butler, A. Fox, S. Collier and L. A. Burke, *J. Chem. Soc., Perkin Trans. 2*, 1998, 2243; R. N. Butler, S. Collier and A. Fleming, *J. Chem. Soc., Perkin Trans. 2*, 1996, 801.
16 A. Vij, J. G. Pavlovich, W. W. Wilson and K. O. Christe, *Angew. Chem., Int. Ed.*, 2002, **41**, 3051, cf. *Chem. Eng. News*, August 19, 2002, p.8.
17 G. A. Molander, *Chem. Rev.*, 1992, **92**, 29.
18 P. Jacob III, P. S. Callery, A. T. Shulgin and N. Castagnoli Jr., *J. Org. Chem.*, 1976, **41**, 3627.
19 D. R. Kronenthal, C. Y. Han and M. K. Taylor, *J. Org. Chem.*, 1982, **47**, 2765.
20 J. Fetter, E. Keskeny, T. Czuppon, K. Lempert, M. Kajtár-Perody and J. Tamás, *J. Chem. Soc., Perkin Trans. 1*, 1992, 3061.
21 P. Ballesteros, R. M. Claramunt, C. Escolástico, M. D. Santa Maria and J. Elguero, *J. Org. Chem.*, 1992, **57**, 1873.
22 R. N. Butler, J. Oakes and M. C. R. Symons, *J. Chem. Soc. Section A*, 1968, 1134.
23 C. Cheng, *Int. J. Quantum Chem.*, 2000, **80**, 27.
24 R. Müller, J. D. Wallis and W. von Philipsborn, *Angew. Chem., Int. Ed.*, 1985, **24**, 513.