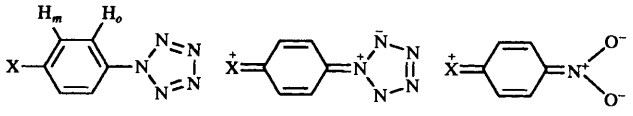
Pentazoles: proton and carbon-13 NMR spectra of some 1-arylpentazoles: kinetics and mechanism of degradation of the arylpentazole system

Richard N. Butler,* Seamus Collier and Adrienne F. M. Fleming

Chemistry Department, University College, Galway, Ireland

The proton and carbon-13 NMR spectra of a range of 1-(*p*-substituted-phenyl)pentazoles are reported. The influence of the $-N_5$ group on the aryl shifts is compared with that of the $-NO_2$ and $-N_3$ groups. Direct kinetic measurements of the degradation of 1-arylpentazoles in CD_3OD–CD_2Cl_2 (1 : 1, v/v) gave a Hammett ρ value of + 1.25. For 1-(*p*-chlorophenyl)pentazole values of $\Delta E^{\ddagger}$, 88.6 kJ mol^{-1}, $\Delta H^{\ddagger}$ 86.3 kJ mol^{-1} and $\Delta S^{\ddagger}$ + 19.9 J mol^{-1} K^{-1} are obtained at − 10–0 °C. These data suggest a polar two-step mechanism with rate-determining cleavage of the 1–2 bond giving an unstable azido–azo (pentazene) intermediate, the nitrogen analogue of the azido–azomethine species of tetrazole ring-opening.

The pentazole ring is the full isoelectronic nitrogen analogue of the cyclopentadienylide anion and the final member of the azole series. The only known pentazoles are aryl derivatives. Since the discovery of the existence of the pentazole ring at low temperatures[1,2] many theoretical calculations have been performed on these systems[3–10] but measured experimental data are less plentiful. The most stable of the known pentazoles, 1-(*p*-dimethylaminophenyl)pentazole, **1a**, has been the most amenable and both an X-ray crystal structure[11] and a nitrogen NMR spectrum[12,13] have been reported for this compound. The UV spectra of a number of 1-arylpentazoles were reported shortly after their discovery.[14] No proton or carbon-13 NMR spectra of arylpentazoles have been previously reported. From the X-ray crystal structure of **1a** it was suggested that the influence of the pentazole ring was comparable to that of a nitro group,[11] while for the same compound the nitrogen-15 NMR



1a X = Me_2N
1b X = MeO
1c X = Me
1d X = H
1e X = Cl
1f X = Br
1g X = NO_2

2 **3**

spectrum[12] led to suggestions that the pentazole ring was more akin to an aldehyde group in its effect. Herein we report the low-temperature proton and carbon-13 NMR spectra for some 1-arylpentazoles, including 1-(*p*-dimethylaminophenyl)pentazole, **1a**, and 1-(*p*-chlorophenyl)pentazole, **1e**, and also a proton NMR kinetic study of the influence of substituents on the degradation of the pentazole ring for the series **1a**–**1e**.

Results and discussion

NMR spectra

The pentazoles were prepared at below −10 °C by coupling diazonium salts with azide ions following the procedure of Huisgen and Ugi.[1] The pentazoles were soluble in 1 : 1 (v/v) mixtures of methanol–dichloromethane as suggested by Witanowski *et al.*[13] and spectra were measured in this solvent mixture using fully deuteriated solvents. Spectra were measured up to the range 0–15 °C where the pentazole disappeared being replaced by the corresponding azide. The chemical shifts were not influenced by temperature or the presence of the azide over the range −40 to 15 °C. All of the compounds listed in Table 1 were measured in the same solvent mixture under the same conditions as the pentazole derivative. Normal NMR concentrations (10–30 mg cm^{-3}) were used and the shifts were not influenced by the quantity of sample in this range.

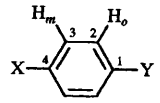
The chemical shifts and the incremental effects of the pentazole ring are summarised in Table 1 along with those for NO_2 and N_3 substituents. In its effects on the aryl proton shifts the pentazole ring is similar to a nitro group.† For the *p*-chlorophenyl series the *ortho* protons are deshielded by 1.12 ppm for $-N_5$ and by 1.13 ppm for $-NO_2$. The deshielding of the *meta* protons is 0.53 ppm for $-N_5$ and 0.39 ppm for $-NO_2$ (Table 1, entries 1, 2, 4). The similarity of the effects of the pentazole and nitro groups does not extend to the carbon-13 shifts. The incremental effect of the pentazole ring in **1e** is C-*ipso*, +11.4; *ortho*, −5.75; *meta*, +1.2 and *para*, −0.55. These values are significantly different to the NO_2 group particularly at C-*ipso* and C-*para* and they suggest that resonance contributions such as **2** are less important for the pentazole case relative to the forms **3** which contribute significantly for the nitro compounds. Comparable deshielding effects were observed for the pentazole ring in **1c** and **1f** (Table 1, entries 5, 6) but for 1-(*p*-dimethylaminophenyl)pentazole, **1a**, the shifts were somewhat smaller and this may be due to the strong resonance electron-donating effects of the Me_2N substituent.

Kinetics

It proved possible to measure the rates of disappearance of the proton signals for a series of *p*-substituted 1-arylpentazoles at −5 °C (Fig. 1). These rates were measured for solutions made up at −40 °C and raised to −5 °C for the kinetic measurements which were reproducible to ±3%. Varying quantities of aryl azides were present in all cases but these did not influence the rates suggesting that the azide is produced in a slow step after the rate-determining step in the degradation of the pentazole. This was important for the rate measurements since we could not produce solutions of pentazoles which did not contain azides. To measure a series of rates it was necessary to find a

† For 1-phenylpentazole, **1d**, the proton signals for H_m and H_p appeared as an overlapping multiplet at δ 7.69–7.76 in both $CDCl_3$ and CD_3OD–CD_2Cl_2 (1 : 1, v/v) at −30 °C. (The correlation of δH_p shifts in $CDCl_3$ for monosubstituted benzenes against Hammett σ_p values ignoring temperature would suggest a tentative σ_p value for the pentazol-1-yl ring in the range 0.87–1.1; σ_p, CH=O, 0.42; σ_p, NO_2, 0.78. We thank a referee for suggesting that this be included.)

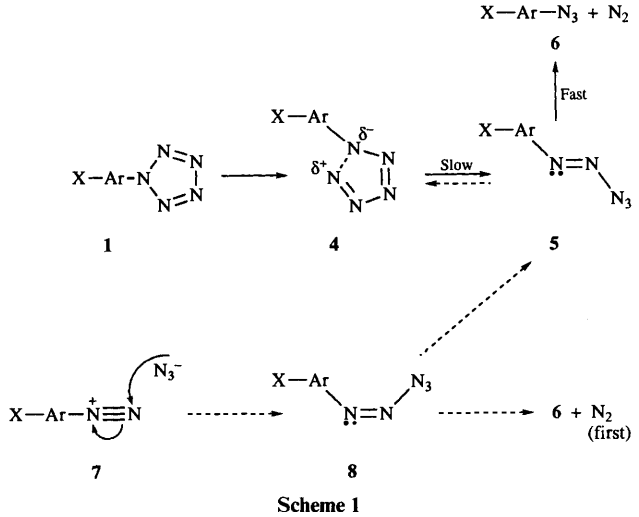
Table 1 NMR shifts[a]



	Compound		^{1}H Shifts		^{13}C Shifts[c]			
Entry	X	Y	H_o (ΔH_o)[b]	H_m (ΔH_m)[b]	C_1 (ΔC_1)	C_2 (ΔC_2)	C_3 (ΔC_3)	C_4 (ΔC_4)
1	Cl	H	7.06 (0.00)	7.18 (0.00)	126.7 (0.00)	128.7 (0.00)	130.0 (0.00)	134.2 (0.00)
2	Cl	NO_2	8.19 (1.13)	7.57 (0.39)	147.4 (20.7)	125.7 (−3.0)	130.3 (0.3)	142.05 (7.8)
3	Cl	N_3	7.00 (−0.06)	7.33 (0.15)	139.6 (12.9)	121.05 (−7.65)	130.5 (0.5)	130.8 (−3.45)
4	Cl	N_5	8.18 (1.12)	7.71 (0.53)	138.1 (11.4)	122.95 (−5.75)	131.2 (1.2)	133.7 (−0.55)
5	Br	N_5	8.14 (1.02)	7.88 (0.48)	—	—	—	—
6	Me	N_5	8.05 (1.05)	7.55 (0.45)	134.9 (8.7)	121.3 (−8.6)	131.8 (2.6)	136–137 (−1.5–−0.5)[e]
7	Me_2N	H	7.13 (0.00)	6.60–6.68 (0.0)	117.9 (0.00)	130.10 (0.00)	114.0 (0.00)	151.95 (0.00)
8	Me_2N	N_3	6.94 (−0.18)	6.80 (0.14–0.20)	129.5 (11.8)	120.5 (−9.6)	115.3 (1.3)	149.4 (−2.55)
9	Me_2N	N_5	8.00 (0.87)	6.91 (0.23–0.31)	*d*	122.4 (−7.7)	112.2 (−1.8)	*d*

[a] Solvent CD_3OD–CD_2Cl_2 (1:1, v/v) measured at −30 °C. For AA'BB' systems J_{AB} was 8.6–8.8 Hz. [b] Parentheses contain the shifts change (Δ) relative to the parent monosubstituted benzene (shown for entries 1 and 7 only). Positive away from TMS; negative towards TMS. [c] Shifts to 0.05 ppm. [d] Signal too weak. [e] Weak signals at limits of detection.

propitious temperature and −5 °C proved best. Nevertheless it was not possible to measure the disappearance of 1-(*p*-nitrophenyl)pentazole **1g** at this temperature because it was far too fast, nor that of the 1-(*p*-dimethylaminophenyl)pentazole because it was just about too slow. A rate value for the latter was obtained from separate rates measured in the range 0–12 °C and extrapolated back to −5 °C. The behaviour of these two extreme substituted pentazoles readily showed the qualitative substituent trend; strongly electron-donating aryl substituents stabilised the system and slowed the degradation while electron-withdrawing substituents destabilised the ring and enhanced the degradation. The rates were first-order with the following values at 268 K, substrate, 10^4k s^{-1} (Hammett σ_p from C. Hansch, A. Leo and R. W. Taft, *Chem. Rev.*, 1991, **91**, 165): **1a**, 0.48 (−0.83); **1b**, 2.1 (−0.27); **1c**, 2.7 (−0.17); **1d**, 6.6 (0.0); **1e**, 9.2 (0.23). These values correspond to a Hammett ρ of +1.25 (r = 0.989). The trends are in agreement with results obtained from measurements of nitrogen evolution reported by Huisgen and Ugi.[15] For 1-(*p*-chlorophenyl)pentazole **1e** further rate constants at 263 K and 270 K were 4.3×10^{-4} and 12.0×10^{-4} s^{-1} respectively giving $\Delta E^{\ddagger}$ 88.6 kJ mol^{-1}, $\Delta H^{\ddagger}$ 86.3 (±0.05) kJ mol^{-1} and $\Delta S^{\ddagger}$ +19.9 (±0.15) J K^{-1} mol^{-1} in this temperature range. These data suggest a ring-opening process **4** as shown in Scheme 1 followed by a rapid degradation of the pentazene



Scheme 1

(azido–azo) chain in the intermediate **5**. This mechanism is analogous to the ring-opening of 1,5-disubstituted tetrazoles to azido–azomethines which is a common feature of tetrazole chemistry.[16,17] Rate constants reported[17] for the thermal ring opening to azido–azomethines (isomerisation) of 1-aryl-5-aminotetrazoles supported the similarity. They allow us to determine a ρ value of +1.53 and $\Delta S^{\ddagger}$ +8.0 (±0.2) J K^{-1} mol^{-1} at 390–410 K for 1-(*p*-chlorophenyl)-5-aminotetrazole. It is likely that the ring-opening of the pentazoles is heavily influenced by the presence of the 1-aryl substituent. High level calculations on the degradation of the unknown parent pentazole, HN_5, clearly suggest quite a different mechanism for this species namely a concerted cycloreversion.[6] Care is therefore required in considering the behaviour of the known 1-arylpentazoles and the as yet unknown 1-alkyl or 1*H*-pentazoles.§ Principles of reversibility would allow that the formation of 1-arylpentazoles from aryldiazonium and azide ions may be the reverse of the ring-opening, *i.e.* **5** ⟶ **4**, rather than a cycloaddition. If this is so it could only arise after an isomerisation in the initial pentazene **8** in which the new β-lone pair should be *trans* to the N_3 group in accordance with the stereoelectronic effects[18] which operate in the addition of nucleophiles to triple bonds (Scheme 1). Hence the degradation of the species **8** would be the source of the *first* nitrogen evolution[1] in the formation of arylpentazoles and this degradation would be competing with an isomerisation of **8** to **5** on the route to **4**. A close similarity is then evident in the formation and ring-opening of 1-arylpentazoles and 1-aryltetrazoles.

Experimental

NMR spectra were measured on a JEOL GX-FT 270 NMR spectrometer. Temperatures (±0.5 °C) were measured with a copper constantin thermocouple and checked before and after each kinetic measurement with standard methanol and

§ The kinetic data would fit a cycloreversion process with a dominant orbital interaction ArN_3(LUMO)–N_2(HOMO) where electron-withdrawing groups in Ar would lower the activation energy. Such an interaction is highly unlikely because the orbital gap is *ca.* 15.4 eV. The ionisation potential (HOMO energy) for N_2 is −15.576 eV (*Handbook of Chemistry and Physics*, CRC Press, Boca Raton, 1st student edn., 1988, p. E-73) and the electron affinity value (LUMO energy) is thought to be *ca.* 0 eV. For PhN_3 CNDO/2 calculated orbital energies are HOMO, −9.5 eV and LUMO −0.2 eV (I. Fleming, *Frontier Orbitals and Organic Chemical Reactions*, Wiley, Chichester, 1978, p. 156). Even with alkynes PhN_3, reacts significantly through the dipole HOMO orbital and for a reaction with N_2 the closest orbital interaction for a concerted cycloreversion is ArN_3(HOMO)–N_2(LUMO) and such a process would give the reverse of the observed kinetic substituent effects.

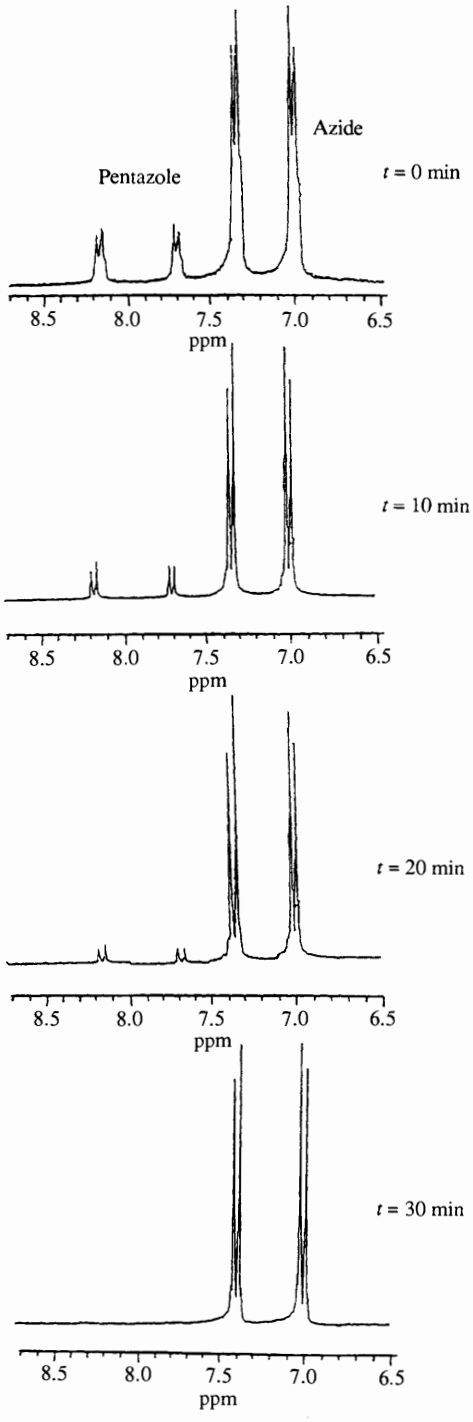


Fig. 1 Points from a kinetic measurement on **1e** at −5 °C

propane-1,3-diol samples. The pentazoles were prepared as described by Huisgen and Ugi [1] and separated at −40 °C at a phase boundary between light petroleum (bp 40–60 °C) and the aqueous component. However filtering the samples at −40 °C from this mixture proved problematic and when the samples were dissolved in the NMR solvent, CD_2Cl_2–CD_3OD (1:1, v/v), some aryl azide was always found to be present. Hence the presence of aryl azide was accepted and the following simpler procedure was used to produce the solutions for the NMR work. Typical example: *p*-chloroaniline (1.42 g, 0.0125 mol) in water (10 cm^3) was treated dropwise with conc. HCl (2.5 cm^3) at 0–2 °C and the mixture was treated with sodium nitrite (0.96 g, 0.014 mol) in water (6 cm^3) also at 0–2 °C. The solution was cooled to below −10 °C (*ca.* −15 °C) and treated at this temperature dropwise with a precooled solution of NaN_3 (0.9 g, 0.014 mol) and $NaOAc{\cdot}3H_2O$ (1.9 g) in water (17 cm^3). An evolution of N_2 occurred (the *'first'* [1] evolution) and a solid mixture of *p*-chloroazidobenzene and 1-(*p*-chlorophenyl)pentazole separated. The solid was filtered off using a filter funnel which had been pre-cooled in liquid nitrogen and taken up in CD_2Cl_2–CD_3OD (1.0 cm^3) (1:1, v/v) at −40 °C (Table 1). For kinetic runs the temperature was raised to −5 °C. Separately varying the quantity of aryl azide in these solutions had no influence on the data. Only in one case, 1-phenylpentazole **1d**, was a modification of this procedure needed. In this case the solid did not separate and the pentazole–azide mixture was extracted into CD_2Cl_2 at −15 °C. An aliquot of the extract was made up to 1:1 v/v CD_2Cl_2–CD_3OD at −40 °C and used for kinetic measurements at −5 °C. The rates of disappearance of pentazole were obtained from plots of log $(I_t - I_\infty)$ for the aromatic signals (Fig. 1) *vs.* time. The plots were linear with slopes of $-k/2.303$ where k is the rate constant for the degradation of the arylpentazole. All experiments and measurements were repeated many times from the arylamine starting material. The rate constant quoted for compound **1a** at −5 °C was extrapolated from the following values, T/°C, 10^4k s^{-1}: 2, 2.5; 5, 5.3; 7, 5.9; 12, 7.0.

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Paper 5/07330H
Received 7*th November* 1995
Accepted 17*th January* 1996