Pentazole chemistry: the mechanism of the reaction of aryldiazonium chlorides with azide ion at −80 °C: concerted *versus* stepwise formation of arylpentazoles, detection of a pentazene intermediate, a combined ^{1}H and ^{15}N NMR experimental and *ab initio* theoretical study

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The reaction of *p*-chlorophenyldiazonium chloride with azide ion at −80 °C has been examined by ^{1}H and ^{15}N NMR spectra. The main product, *p*-azidochlorobenzene, was present in the earliest spectra. Spectra were obtained before the appearance of the second product, *p*-chlorophenylpentazole and an intermediate was observed. Correlated *ab initio* calculations at the MP2/6-31G* level on 1*H*-pentazole and 1-phenylpentazole agree with the NMR spectra. An (*E*,*Z*)-arylpentazene **3** is the key intermediate leading to the 1-arylpentazole products. A (*Z*,*E*)-arylpentazene **2** leads directly to the aryl azide and is not convertible to the *E*-isomer. Three isomeric arylpentazenes, *Z*,*E*, *E*,*E* and *E*,*Z* are formed from initial azide ion attack at the diazonium β-atom.

The formation of arylpentazoles in the reaction of aryldiazonium salts with azide ion[1–4] has engendered discussion as to whether the pentazole ring arises from a concerted (3+2) cycloaddition or a stepwise process involving cyclisation of a pentazene intermediate. Huisgen[5] has favoured a pentazene intermediate as the route to the arylpentazoles which he and his coworkers discovered. Because of experimental difficulties and the expected fleeting nature of a pentazene species (often represented as a linear resonance hybrid) the possibility of exploring this question directly has seemed remote. Recently we reported[6] the first proton and carbon-13 NMR spectra of arylpentazoles. Our experience combined with a consideration of the expected non-linear structural features of a pentazene (diazo azide) intermediate suggested that a direct NMR search for it would be worthwhile.

Stereoelectronic effects established[7–9] for the addition of nucleophiles to triple bonds, and particularly for nitrilium ions[7,8] indicate that azide ion attack on the triple bond of a diazonium ion **1** might preferentially produce the diazo-*Z*-isomer **2**. Indeed in the reactions of cyanide ion with aryldiazonium ion readily detectable (*Z*)-aryldiazocyanides are first formed and they isomerise subsequently to the *E*-isomers.[10–12] Attack by oxygen and sulfur nucleophiles at the terminal nitrogen of diazonium ions also gives initial *Z*-diazo compounds.[13] The *Z*-isomer **2** would have the wrong structure for pentazole formation since the azido group needs to be *cis* to the β-lone pair, as in **3**, for pentazole ring-closure. Hence an azo $Z \rightarrow E$ isomerisation might be necessary before pentazole formation could occur. For Ph–N=N–Ph the $Z \rightarrow E$ barrier is reported as 23.7 kcal mol^{-1} and for F–N=N–F the barrier is increased to 35.2 kcal mol^{-1} since electron withdrawing groups inhibit isomerisation by increasing sp^2 character on the N-atoms thereby disfavouring the sp-character necessary for the linear inversion mechanism of *E*,*Z*-isomerization.[14] The HN_5 system, including the parent pentazenes **2** and **3** (H for Cl–C_6H_4), was studied some time ago by the *ab initio* LCAO-SCF-MO method using the STO-3G basis set and limited electron correlation.[15] The results gave a $Z \rightarrow E$ inversion barrier higher than for the unsubstituted diazocyanide as well as an E_{act} value of 65 kcal mol^{-1} for the pentazene degradation HN_5 (*Z*)→HN_3 + N_2 and a particularly high E_{act} for HN_5 (*Z*)→HN_5 (*E*) of 116 kcal mol^{-1}. These considerations suggested to us that a species such as **2** might be detectable at low enough temperatures. We initially sought a *p*-NO_2 group on the phenyldiazonium ion but experimental difficulties including solubility problems prevented it. The *p*-chlorophenyldiazonium species **1** was more manageable. We examined its reactions with azide ion in the temperature range −80 to −85 °C in CD_3OD–D_2O (4:1 v/v) using 400 MHz ^{1}H NMR and also ^{15}N NMR with samples prepared from ^{15}N-labelled *p*-chloroaniline. In the event it was the intermediate **3A/3** that proved to be detectable.

Results and discussion

(a) Formation of the arylpentazole

(i) Experimental results. Solutions of *p*-chlorophenyldiazonium chloride salt in CD_3OD–D_2O (4:1, v/v) were made up by dissolving ether-moistened solid samples (*ca.* 180 mg) in CD_3OD (2.0 cm^3)–D_2O (0.5 cm^3) (mixed at 25 °C) at −40 °C and cooled to −90 °C in the probe of a JEOL GX400 NMR spectrometer. The spinning gas used was dry N_2 and temperatures were measured with both standard MeOH samples and the probe thermostat. Separate solutions of NaN_3 (160 mg) in the same solvent (2.5 cm^3) were cooled to −90 °C and added dropwise to the raised NMR tube containing the diazonium solutions while still within the probe. This is the critical stage and if the temperature rises above *ca.* −75 °C on mixing the experiment is lost insofar as pentazole is already well present in the first spectra measured. The tube containing the mixture was lowered immediately and spectra measured against time. An alternative approach was also used in which the diazonium solution was frozen solid in a tilted NMR tube and the azide solution, at −80 to −90 °C, was introduced and also frozen solid to allow for mixing when the temperature of the solid mixture was raised to *ca.* −85 °C. For ^{1}H spectra 8 scans (~40 s) were normally sufficient to obtain a spectrum and for ^{15}N-spectra 14 scans (~112 s) were necessary to obtain the first

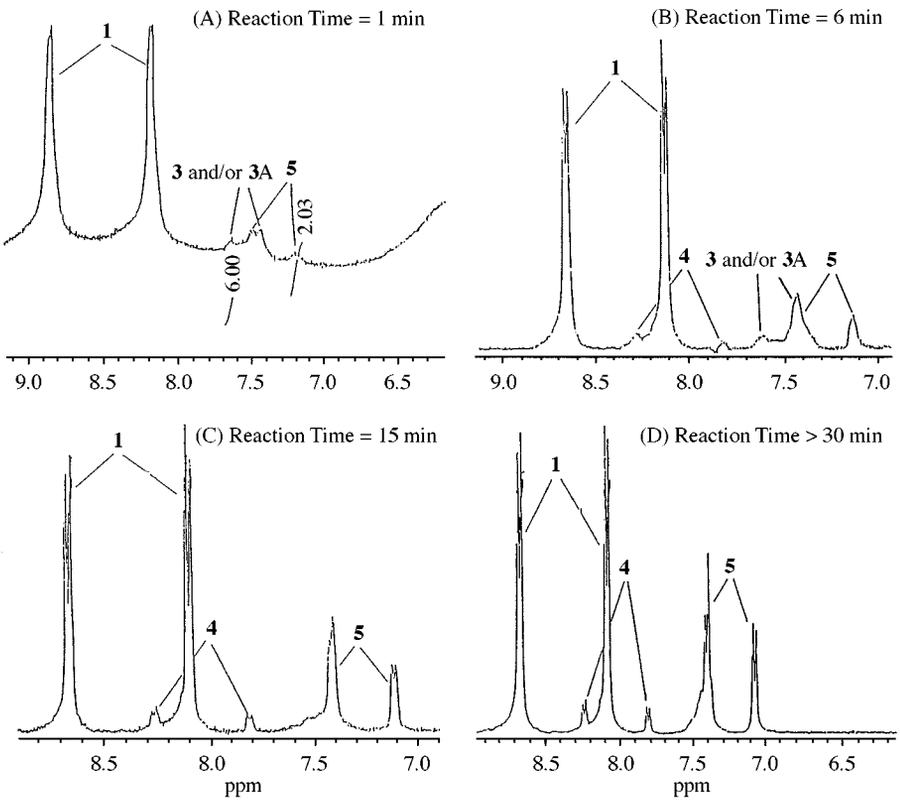


Fig. 1 ^{1}H Spectra (at −80 °C) for the reaction of *p*-chlorophenyldiazonium chloride with azide anion.

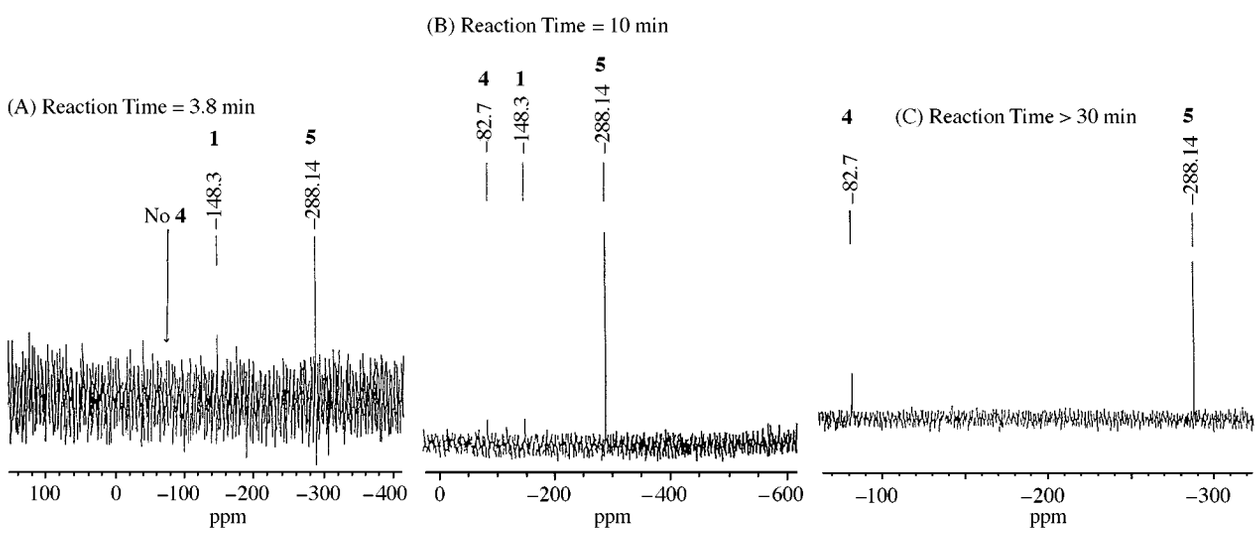
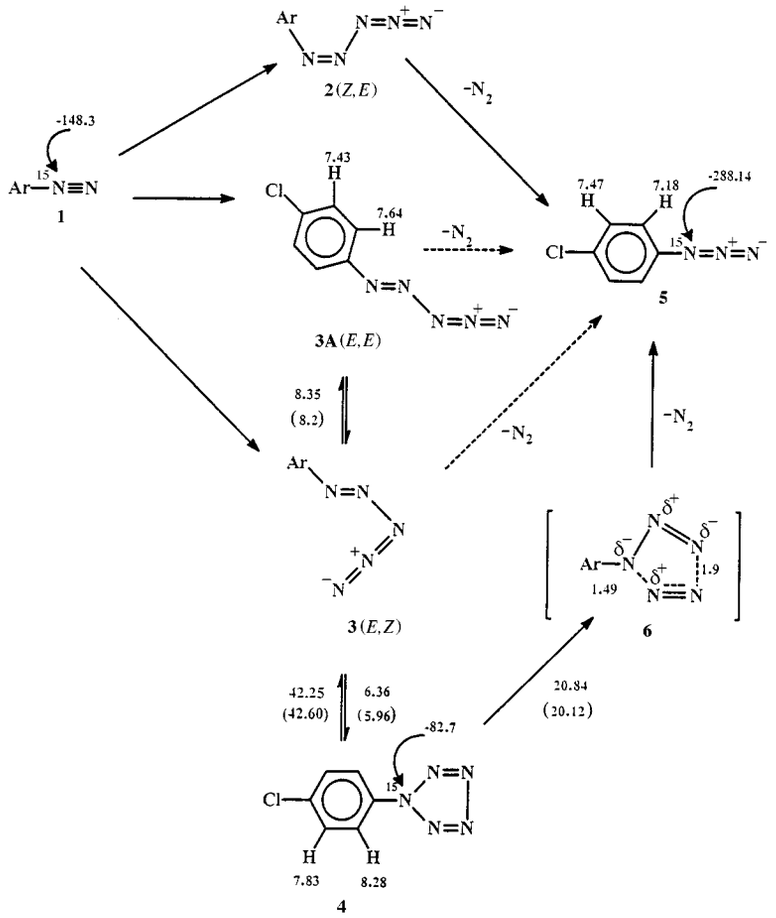


Fig. 2 ^{15}N Spectra (at −80 °C) for the reaction of *p*-chlorophenyldiazonium chloride with azide anion.

spectrum. In both cases it was possible to measure spectra either before any pentazole signals were present or when the pentazole was in the early stages of growth (Figs. 1 and 2). This is a most important experimental observation. It means the pentazole is formed late in the reaction. In all cases the aryl azide **5** was strongly present in the earliest spectra. In these early spectra where pentazole signals were first seen typical ratios of pentazole **4** to azide **5** were *ca.* 1 : 10 and these changed to a final consistent ratio of 1 : 4 with time. Ratios were obtained by direct integration of signals. In the proton NMR spectra the presence of an intermediate species prior to the appearance of pentazole was seen with signals at 7.43 and 7.64 ppm which we assign to the (*E*)-pentazene **3A** and/or **3** (Scheme 1)(Fig. 1A). In the earliest spectra the ratio of this intermediate to the azide **5** was *ca.* 1 : 2 and no pentazole signals were visible.

As the pentazole signals at δ 7.83 and 8.28 grew into the spectra the signals at δ 7.43 and 7.64 faded away. These changes took place over about 15 minutes at −80 °C and they could be induced also by raising the temperature to −70 °C. These proton spectra were reproduced starting from *p*-chloroaniline many times. In any one run up to six NMR tubes of diazonium ion were prepared ready to be separately treated with azide ion. In some cases if the early stages were lost at the mixing step due to inadvertent heating above −75 °C the next tube was used and so on. The results were successfully reproduced many times but in the earliest spectra (Fig. 1A) the resolution was poor due to the fact that N_2 gas is necessarily bubbling from the solution at this stage. The chemical shifts of the signals however are clear and do not change after subsidence of the gas evolution when the resolution returns (Fig. 1B,C,D). The ethereal moistening of the diazonium salt was important as the traces of ether appeared to prevent precipitation of the azide and/or pentazole



Scheme 1 ^{1}H and ^{15}N NMR shifts at −80 °C shown. E_{act} values, kcal mol^{-1} shown for H in place of Ar and in parentheses for C_6H_5 in place of Ar. Ar = *p*-ClC_6H_4.

from the solution in the NMR tube. The species **3/3A** is a diazo azide and it is of interest that the oxygen analogue nitrosyl azide, O=N–N_3, has recently been observed as a pale yellow solid at −110 °C.[16]

For the ^{15}N experiment ^{15}N-labelled *p*-chloroaniline was synthesised by standard procedures from *p*-chlorobenzene using ^{15}N-labelled nitric acid.[17] This should then produce only one ^{15}N signal for each of the species present in the solution (Scheme 1). In this case the ^{15}N signals for the diazonium ion **1**, azide **5** and pentazole **4** were observed (Fig. 2) and the results showed that the ^{15}N atom remained bonded to the aryl group throughout the reaction. Spectra were again obtained before the pentazole had fully grown confirming its late appearance in the reaction, and the observed ratios of **4** to **5** agreed with those of the proton spectra. However a ^{15}N signal from the intermediate species **3A/3** was not reproduceably detected. The necessary longer acquisition time plus the fact that there is but one ^{15}N atom as against two protons per mole of **3A/3** appears to have prevented its observation.

(ii) Theoretical calculations. The mechanisms that involve the proposed intermediates include rotations about single bonds, electrocyclic ring closures and retro-cycloadditions. The first two can be relatively well described energetically at the SCF level. However, Ferris and Bartlett[18] have shown that correlation is needed to describe the decomposition of pentazole to HN_3 and N_2. All theoretical pathways were calculated using the GAUSSIAN94 series of programs.[19] In the case of 1*H*-pentazole the effect of the basis set was studied by using the MP2/6-31G* and MP2/6-311+G** levels. The latter basis set is similar to that in the Bartlett[18] study but has an extra, diffuse set of valence orbitals. Eigenvector following methods were used to find transition states and vibrational analyses were performed to demonstrate one single imaginary frequency at these points. The equilibrium and transition state geometries for 1*H*-pentazole were then used as starting points in the search for the corresponding phenylpentazole at the MP2/6-31G* level. Frequency calculations were not carried out for phenylpentazole as the geometries were not found to be far from those in the unsubstituted case and the size of the calculations are prohibitive at this stage. Details of the calculations as well as theoretical vibrational spectra can be found at http://camchem.rutgers.edu/~burke.

As this is a study of possible pathways among intermediates, the energies of **1** and **5** are not needed, thus the problem of basis set superposition error does not arise. Pentazene **3** is taken as a reference point for the relative energies and entropies given in Table 1. Table 2 gives the activation energies for the reactions **3** to **3A**, **3** to **4** and **4** to **5**. The electronic energies of a van der Waals' molecular complex of **5** and N_2 were calculated to be *ca.* 70 kcal mol^{-1} more stable than **3**. Due to the large energy fall from **4** further geometry optimizations of the possible molecular complexes were not necessary for this study.

All attempts to find a concerted transition state to form the pentazole **4** failed but led instead to the head to tail formation of pentazene. This addition is without an activation barrier. The pentazenes **2**, **3** and **3A** can be considered to be two-step intermediate structures in the cycloadditions to **1** by azide ion leading ultimately to pentazole **4**. The attack of the azide group can possibly form four configurations of pentazene, *E*,*Z* (**3**), *E*,*E* (**3A**), *Z*,*E* (**2**) and *Z*,*Z*. The last form could not be found and optimization searches for it lead to **2**. In both the 1*H*- and 1-phenyl-pentazenes, all three configurations **2**, **3** and **3A** lie nearby in relative energy with little difference between them (Table 1).

The barriers from **3** to **3A** were found to be nearly 8 kcal mol^{-1} for both the *H*- and phenyl-pentazenes. In an older,

Table 1 Standard state energies and entropies relative to form **3** calculated with the MP2/6-31G* method. The values found for the MP2/6-311+G** method are in parentheses. $\Delta G^\circ = \Delta H^\circ - 298.15\ \Delta S^\circ$.

Form	ΔE°/kcal mol^{-1} [a]	ΔE°/kcal mol^{-1} [b]	ΔH°/kcal mol^{-1} [b]	ΔS°/cal mol^{-1} K^{-1} [b]	ΔG°/kcal mol^{-1} [b]
2	0.01	0.10	−0.01	0.41	−0.13
		(0.54)	(0.40)	(0.35)	(0.29)
3A	0.02	0.25	0.44	−0.13	0.48
		(−0.79)	(−0.55)	(−0.18)	(−0.50)
4	−36.64	−35.89	−34.71	−5.76	−32.99
		(−32.63)	(−31.40)	(−6.04)	(−29.61)

[a] R = Ph. [b] R = H.

Table 2 Standard state activation barriers calculated with the MP2/6-31G* method. The values found for the MP2/6-311+G** method are in parentheses. $\Delta G^\circ = \Delta H^\circ - 298.15\ \Delta S^\circ$

Barrier	ΔG°/kcal mol^{-1} [a]	ΔE°/kcal mol^{-1} [b]	ΔE°/kcal mol^{-1} [a]	ΔH°/kcal mol^{-1} [a]	ΔS°/cal mol^{-1} K^{-1} [a]
3 to **3A**	8.20	8.34	7.81	−2.21	8.48
		(7.91)	(7.43)	(−2.44)	(8.16)
3 to **4**	5.96	6.36	5.36	−3.50	6.40
		(7.16)	(6.05)	(−3.40)	(7.06)
4 to **5**	20.12	20.84	17.96	3.25	16.99
		(19.77)	(16.75)	(3.51)	(15.72)

[a] R = H. [b] R = Ph.

STO-3G(55x55CI) study that did not include optimization with a force method, Leroy *et al*.[15] found a barrier in excess of 110 kcal mol^{-1} for the conversion of **2** to **3A**. It is not expected, however, that increasing the basis set and refining the optimization method would make the **2** to **3A** conversion competitive with loss of N_2 from **2**.

Eigenvector following from 1*H*-pentazole **4** leads to the electrocyclic transition state structure between **4** and **3** as well as the reverse-cycloaddition loss of N_2 to form **5** as found previously.[18] The barriers for the electrocyclic reactions of **3** to **4** are 6.36 and 5.96 kcal mol^{-1} for 1*H*- and phenyl-pentazene to pentazole. This can be compared with the stability of at least 30 kcal mol^{-1} for **4** compared to **3**. Loss of N_2 from **4** to form **5** proceeds through a nonsynchronous transition state and activation barrier of at least 20 kcal mol^{-1}.

With the aid of the calculations † we interpret these results as shown in Scheme 1. Attack by the azide ion on the diazonium salt **1** gives the *Z*,*E*-pentazene **2** which is not a normal planar *cis*-isomer but a twisted structure with the azide out of the plane of the arylazo group. This intermediate loses N_2 with steric assistance from the aryl group almost as it is forming. The high barrier to isomerization (>60 kcal mol^{-1}) of **2** to the *E*,*E*-**3A** directs all of the *Z*,*E*-isomer **2** to the azide **5**. This is the source of the azide present in the earliest spectra. Concommitant with the formation of **2** from **1** is the alternative path, also with zero activation energy, resulting in the formation of the *E*,*E* and *E*,*Z* isomers **3A** and **3** which are similar in energy to **2** (Table 1). At −80 °C these intermediates are just detectable (Fig. 1). On the basis of the spectral integration this represents about one-third of the reaction and it probably occurs due to secondary factors such as the possible influence of the counter ion and solvent. Known pentazole chemistry would not exist but for this fortuitous side-reaction. Thus the *E*,*E*/*E*,*Z*-pentazene isomer mixture of **3A** and **3** then proceeds in *ca*. 60% conversion to the pentazole **4**, with about 40% conversion to the azide **5** giving an overall ratio of **4**:**5** of 1:4 as observed on both ^{1}H and ^{15}N NMR spectra. The energy fall from **3A/3** to **5** is >70 kcal mol^{-1} and a competition with pentazole formation is not unexpected.

† We wish to record that a referee has stated "the very important role of solvation energy differences for these polar compounds has not been included in these calculations and the solvation energy differences for these compounds could easily be *ca*. 5 kcal/mol". In reply we state that (i) the structures and energies of the species, **2**, **3A** and **3** are so close that we expect the solvation effect to be similar for each of these (but it could influence the **2/3** balance) and (ii) the differences (fall) in energy between **2**, **3A**, **3** and the products **4**,**5** are too large for the solvation effect to be significant

(b) Degradation of arylpentazole

In the present work numerous solutions of 1-*p*-chlorophenylpentazole **4** were produced and the opportunity was taken to recheck the thermodynamic parameters of activation for its degradation to **5** and N_2 over a 20° temperature range from +5 °C to −15 °C. The values obtained from the proton spectra were ΔE_{act} 87 kJ mol^{-1} (20.8 kcal mol^{-1}), ΔH_{act} 85 kJ mol^{-1} and ΔS_{act} + 17 J mol^{-1} K^{-1}. From measurements at 0 to −10 °C we previously reported[6] ΔE_{act} 88.6 kJ mol^{-1}, ΔH_{act} 86.3 kJ mol^{-1} and ΔS_{act} +19.9 J mol^{-1} K^{-1}. We wish to amend these earlier values to the slightly different values herein. The measured E_{act} value is very close to the calculated value (20.12 kcal mol^{-1}) for 1-phenylpentazole (Scheme 1). The degradation of the 1-arylpentazoles displays a Hammett ρ value of +1.1[4] to +1.25[6] and we previously[6] compared it to the ring-opening of 1-aryltetrazoles. Because of the large difference in energy between the species **4** and **3** the calculations suggest an E_{act} value of 42.6 kcal mol^{-1} for a pathway from **4** to **5** *via* **3**. Hence the ring-opening route **4**→**5**→**3** is unlikely, despite the kinetic similarities to tetrazole ring-opening,[6] and we now favour a transition state of type **6** (Scheme 1) in which the key feature is the development of minus charge on the pentazole 1-N as the 1,2-bond cleaves (positive ρ value) concomitant with a cleavage of the 3,4-bond. Structure **6**, which represents a calculated transition state with the elongated bonds shown, is consistent with the kinetic data and is not a frontier orbital-controlled cycloreversion.

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