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Arylpentazoles Revisited: Experimental and Theoretical Studies of 4-Hydroxyphenylpentazole and 4-Oxophenylpentazole Anion

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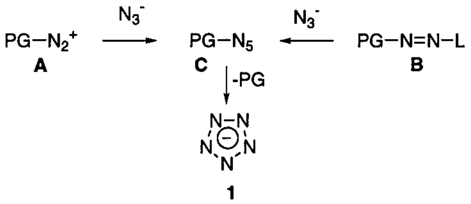
Kinetic measurements for the degradation of 4-hydroxyphenylpentazole (**2a**) and its salt **2b-NBu$_4$** in CD_3OD and in CD_2Cl_2 provided a set of activation parameters. The resulting free energies of activation in methanol ($\Delta G^{\ddagger}_{298} = 19.7$ kcal/mol for **2a** and $\Delta G^{\ddagger}_{298} = 20.6$ kcal/mol for **2b-NBu$_4$**) were compared with previous results for the 4-chloro derivative, **2c**, and collectively correlated with results of gas-phase calculations at the B3LYP/6-31+G(d,p) level of theory. This, and another linear correlation of the seven computed $\Delta G^{\ddagger}_{298}$ values with the previously reported kinetic data of Ugi and Huisgen, gave the basis for the estimation of the stability of pentazole anion (**1**) and its derivatives in solutions. Thus, $N_5(-)$ is predicted to have $t_{1/2} = 2.2$ d, while the half-lifetime for HN_5 is expected to be only about 10 min in methanol at 0 °C. Controlled ozonolysis of **2b-NBu$_4$** followed by ^{1}H and ^{15}N NMR spectroscopy shows a preferential destruction of the N_5 ring, which excludes it from possible methods for preparation of the parent pentazole.

Introduction

Current interest in allotropes of nitrogen[1−4] and nitrogen analogues of metallocenes[5,6] has identified pentazole $N_5(-)$ (**1**) as a possible precursor. Several gas-phase calculations predict anion **1** to be an isolable stable species separated by a barrier of at least 19 kcal/mol from the thermodynamically stable $N_3(-)$ and N_2.[5,7,8] Despite experimental efforts, the anion has remained elusive, and only arylpentazoles have been isolated and extensively characterized to date.[8,9]

In a simple scenario, the preparation of the parent pentazole anion **1** can be envisioned as a two-step process shown in Scheme 1. In the first step, a substituted pentazole **C** is formed by the reaction of $N_3(-)$ with an electrophilic two-nitrogen fragment as in **A** or **B**. Subsequently, the protecting group PG, such as carboxyl,[10] in pentazole **C** is removed to form **1**. Unfortunately, the choice of stable diazonium cation **A** appears to be limited to aryl derivatives, and our attempts to use other compounds with electrophilic two-nitrogen fragments such as azenes with a leaving group L (**B** in Scheme 1) have been discouraging thus far.[11−13]

Scheme 1



Removal of a benzene ring from **C** to form **1** was first attempted on 4-dimethylaminophenylpentazole by saturation of the solutions with ozone.[14] Mass spectrometric analysis of the reaction mixture did not find $N_5(-)$ among the products, but it is unclear whether a more controlled approach, with limited amounts of ozone, would be more successful.

We decided to reinvestigate the ozonolysis route to **1** and focused on two arylpentazoles, 4-hydroxyphenylpentazole (**2a**) and 4-oxophenylpentazole anion (**2b**), which were only briefly mentioned in the literature.[15−17] The

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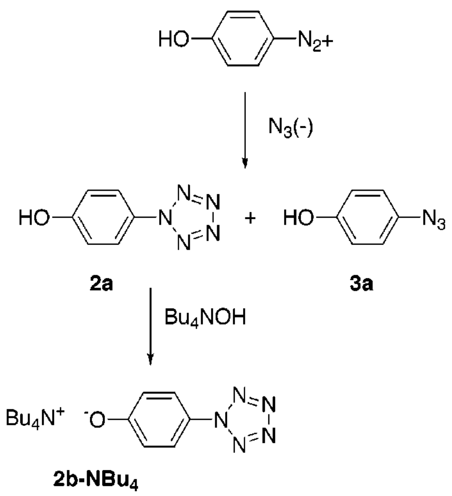
Scheme 2



choice for anion **2b** was dictated by the reported high thermal stability of the pentazole ring,[17] and enhanced reactivity of the benzene ring toward ozone when substituted with an electron-donating group.

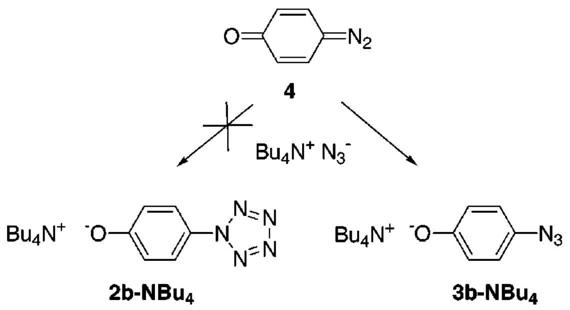
Here we report the synthesis of 4-hydroxyphenylpentazole (**2a**) and its O-anion **2b-NBu$_4$**, derive activation parameters for their thermal decomposition, and discuss the reaction of anion **2b** with ozone. The analysis of experimental results is aided with DFT calculations, which allow the prediction of the stability of **1** and other pentazole derivatives.

Results

Synthesis. 4-Hydroxyphenylpentazole (**2a**) was prepared in about 40% yield as shown in Scheme 2, according to a general procedure reported by Ugi and Huisgen.[16] For reasons of stability and handling, the 4-hydroxybenzenediazonium was prepared as the trifluoroacetate salt[18] rather than the chloride. Upon reaction of the salt with sodium azide at −25 °C, 4-hydroxyphenylpentazole (**2a**) preferentially precipitated, together with some of 4-hydroxyphenyl azide (**3a**). The latter was removed from the solid of **2a** by washing it with cold methanol. The solid pentazole **2a** was carefully dried in a vacuum at low temperature. The ^{15}N-labeled pentazole **2a-^{15}N** was prepared in an analogous manner using partially labeled sodium azide, Na^{15}N^{14}N^{14}N. On the basis of the proposed mechanism of the reaction,[15,19] the ^{15}N isotope is expected to be incorporated either in position 2 or 3 of the pentazole ring.

Careful ^{1}H NMR monitoring of the reaction between 4-hydroxyphenyldiazonium trifluoroacetate and sodium azide in a CD$_3$OD/D$_2$O mixture revealed that the formation of pentazole **2a** was very slow below −40 °C and accelerated only at higher temperatures. As reported before,[19] the parallel formation of aryl azide is inevitably observed. Interestingly, the ratio of pentazole **2a** to azide **3a** is temperature dependent and gradually changed from about 1:2.0 at −30 °C to about 1:1.3 at 0 °C.

Scheme 3



Scheme 4

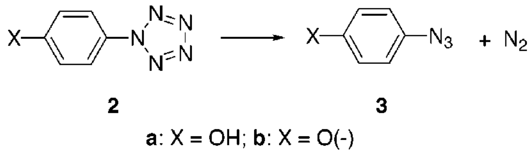


Table 1. Activation Parameters for Arylpentazoles 2

compound	solvent	$\Delta H^{\ddagger}$, [kcal/mol]	$\Delta S^{\ddagger}$, [cal/mol·K]	$\Delta G^{\ddagger}_{298}$, [kcal/mol]
4-OHC$_6$H$_4$N$_5$ (**2a**)	CD$_3$OD	28.4	29.1	19.7
4-(−)OC$_6$H$_4$N$_5$ (**2b**)	CD$_3$OD	24.1	11.8	20.6
	CD$_2$Cl$_2$	30.2	32.1	20.6
4-ClC$_6$H$_4$N$_5$ (**2c**)[a]	CD$_3$OD/D$_2$O[b]	20.3	4.1	19.1

[a] Data from ref 19. [b] 4:1 (v/v) ratio.

4-Oxophenylpentazole anion (**2b**) was prepared by deprotonation of the hydroxyl group in **2a** with 1 equiv of tetrabutylammonium hydroxide, giving ion pair **2b-NBu$_4$** soluble in organic solvents (Scheme 2). Attempts at preparation of pentazole salt **2b-NBu$_4$** directly, by addition of azide anion to *p*-diazobenzoquinone (**4**), resulted in the formation of the aryl azide **3b-NBu$_4$** as the sole product (Scheme 3) as evident from ^{1}H NMR spectra of the reaction mixture.

Stability of Pentazoles. Kinetic Studies. The thermal decomposition of arylpentazoles **2a** and **2b-NBu$_4$** to azides **3b** and **3b-NBu$_4$**, respectively (Scheme 4), was run in methanol at several temperatures and monitored by ^{1}H NMR spectroscopy. The kinetic results yielded activation parameters which are collected in Table 1 and compared to the recent results on 4-chlorophenylpentazole (**2c**).[19,20] For **2b-NBu$_4$** the kinetic measurements were also done in methylene chloride in order to establish a possible solvent effect on the pentazole ring stability. Unfortunately, 4-hydroxy derivative **2a** was insufficiently soluble in CD$_2$Cl$_2$ to conduct comparative kinetic measurements.

The order of free energy of activation $\Delta G^{\ddagger}_{298}$ for the three pentazoles in methanol follows the general trend of stability established by Ugi and Huisgen. As expected, the energy of 20.6 kcal/mol obtained for anion **2b** is the highest in the series. Plotting the three experimental activation energies against the Hammett constants gave the ρ_{exptl} value of +0.87 ($R^2 = 0.980$) at 25 °C,[21] which compares to +1.00 obtained from rate constants[17] at 0 °C for eight derivatives **2**.

A comparison of results for **2b-NBu$_4$** obtained in methanol and methylene chloride shows the same $\Delta G^{\ddagger}_{298}$

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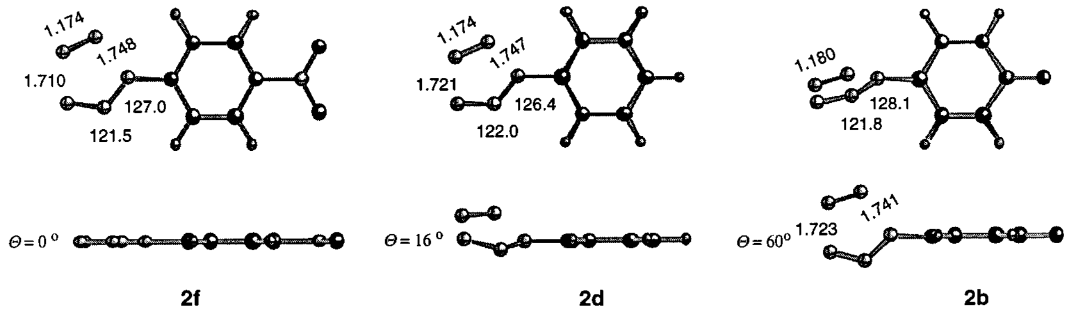

Figure 1. DFT-optimized transition structures for decomposition of (a) 4-nitrophenyl- (**2f**), (b) phenyl- (**2d**), (c) oxyphenylpentazole anion (**2b**). Distances are in Å and the angles for N(3)−N(2)−N(1) and N(2)−N(1)−C(1) in degrees. Θ is defined as the N(2)−N(1)−C(1)−C(2) dihedral angle.

for decomposition, within experimental error, but different kinetic parameters. The rate of decomposition of the salt in methanol at 5 °C increased 3-fold relative to that in CD_2Cl_2, which is reflected in lower E_a and lnA values by about 6 kcal/mol and 10, respectively. The observed solvent effect is consistent with the reported 1.1 times increase of the rate constant for phenylpentazole (**2d**) upon transition from chloroform to methanol at 0 °C.[16]

DFT Calculations. Gas-phase decomposition processes for several 4-substituted phenylpentazoles **2a**−**g** were modeled using the B3LYP/6-31+G(d,p) level of theory. All ground-state structures were found to be planar with C_{2v} symmetry except for **2a**, which has C_s molecular symmetry. In the transition state structures the aryl and N_5 rings are no longer coplanar (C_1 symmetry) except for the CN and NO_2 derivatives, **2e** and **2f** (Figure 1). The dihedral angle between the rings was found to correlate with the ability of the phenyl ring to accommodate a negative charge that develops on the N(1) atom in the TS as the dipolar azide is formed. Thus, the aryl and pentazole rings are coplanar ($\Theta = 0°$) for strongly electron-withdrawing substituents such nitro ($\sigma_p = +0.78$), moderately twisted ($\Theta = 14°$) for the parent phenylpentazole ($\sigma_p = 0.0$), and significantly twisted ($\Theta = 60°$) for 4-oxyphenylpentazole ($\sigma_p = -0.97$).[21]

The calculated activation energies $\Delta G^{\ddagger}_{298}$ for the gas-phase decomposition processes of 4-substituted phenylpentazoles **2** increase in the expected order from the lowest for **2f** ($X = NO_2$) to the highest for **2b** ($X = O^-$). The calculated $\Delta G^{\ddagger}_{298}$ values correlate well with the Hammett σ parameters ($\rho_{calcd} = +1.98$, $R^2 = 0.987$), experimental solution activation energy for **2a**−**c**, and kinetic data[17] for a series of aryl derivatives measured at 0 °C. The last two correlations are shown in Figure 2.

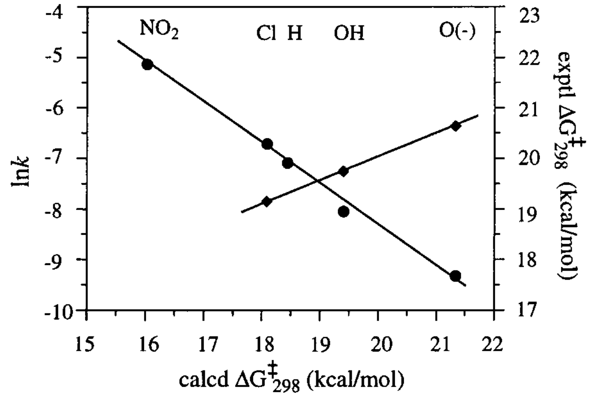

Figure 2. Plots of the calculated free energy of activation $\Delta G^{\ddagger}_{298}$ (calcd) vs experimental activation energy $\Delta G^{\ddagger}_{298}$ (exptl) (diamonds) and kinetic data from ref 17 (circles). Best fit functions: $\Delta G^{\ddagger}_{298}$ (exptl) = 0.462 × $\Delta G^{\ddagger}_{298}$ (calcd) + 10.75 (R^2 = 0.999, diamonds) and ln k = −0.799 × $\Delta G^{\ddagger}_{298}$ (calcd) + 7.65 (R^2 = 0.995, circles).

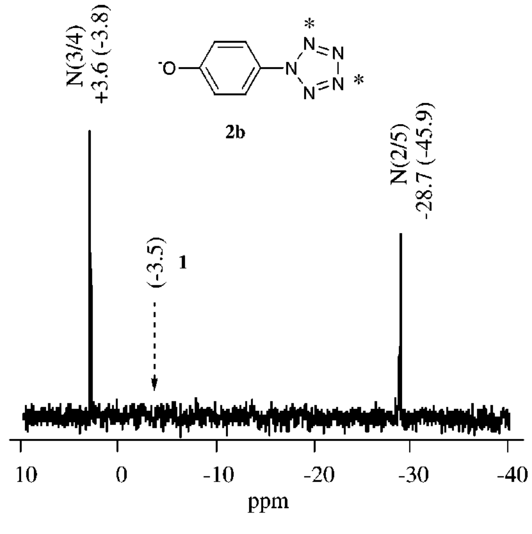

Figure 3. ^{15}N NMR spectrum for 4-oxyphenylpentazole anion (**2b-15N-NBu₄**) in CD_2Cl_2. The arrow shows the expected chemical shift for pentazole anion **1**. Experimental and calculated (in parentheses) chemical shifts are listed above the signals.

^{15}N NMR Spectroscopy. The NMR spectrum of the ^{15}N-labeled 4-oxophenylpentazole anion (**2b-^{15}N-NBu$_4$**) shows two signals (Figure 3) whose chemical shifts are consistent with values reported for other arylpentazoles.[19,22,23] The results of DFT calculations differ from the experimental data by up to 17 ppm, but nevertheless they clearly support the structural assignment shown in Figure 3.[24] The predicted ^{15}N chemical shifts for pentazole **1** is −3.5 ppm, which is close to the N(3) resonance in arylpentazoles. Upon protonation, the N(1) and N(2/5) atoms in HN_5 are significantly shielded (−113.8 and −19.5 ppm, respectively), while the N(3/4) atoms are deshielded (+15.4 ppm). These results are consistent with the recently reported gas-phase chemical shifts obtained

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(24) ^{15}N NMR chemical shifts show a generally large solvent effect up to 40 ppm (ref 28), which partially accounts for the observed difference between the results obtained for gas phase and CH_2Cl_2 solutions. Nevertheless, these computational results appear to be significantly closer to the experiment than those obtained wth the IGLO method in ref 2.

for **1** and other pentazole derivatives at the B3LYP/6-311++G(2d,p) level of theory.[23]

Ozonolysis of 4-Oxophenylpentazole. The experiment was performed on an NMR scale sample of ^{15}N-labeled 4-oxophenylpentazole salt **2b-^{15}N-NBu$_4$**, in CD_2Cl_2 at −78 °C in the presence of excess NBu_4OH. After 3 min of passing ozone/air mixture through the solution, the ^{1}H NMR spectrum showed a virtually unaltered pattern, characteristic for 1,4-disubstituted benzenes, but considerably shifted, relative to the signals of the starting **2b-^{15}N-NBu$_4$**. ^{15}N NMR, however, clearly showed the complete absence of the two initial signals assigned to the pentazole moiety (Figure 3). In fact, there were no signals detected at all, indicating that no compound with labeled nitrogen remained in the solution. The latter result, combined with the possible distribution of labeled nitrogen in the pentazole unit, led to the conclusion that the remaining material contained most likely only the nitrogen directly bound to the aromatic ring. The nature of this new aromatic product remains unclear. By comparison with authentic samples, we excluded 4-nitrophenol or its anion as possible products.

Discussion and Conclusions

The calculated activation energies $\Delta G^{\ddagger}$ (but not $\Delta H^{\ddagger}$) for arylpentazoles show excellent correlation with experimental data (Figure 2), which validates the computational results. The significant difference between the observed and theoretical values is presumably largely due to the difference between the gas phase and the polar and protic environment of methanol. The slope of 0.462 for the $\Delta G^{\ddagger}$ (calcd)/$\Delta G^{\ddagger}$ (exptl) correlation in Figure 2 and the ratio of $\rho_{\mathrm{exptl}}/\rho_{\mathrm{calcd}} = 0.44$ suggest that arylpentazoles are generally stabilized in methanol solution relative to gas phase except for those with strongly electron-donating substituents. This is consistent with the calculated polarity of the ground and transition structures **2**. Thus, polarity of the ground state increases for derivatives with substituent of increasing electron-donating ability (e.g., **2f**: $\mu_{\mathrm{GS}} = 0.35$ D and **2a**: $\mu_{\mathrm{GS}} = 6.16$ D). Also the transition state is more polar than the ground state for derivatives with electron-withdrawing substituents and less polar for derivatives with electron-donating substituents (e.g., **2f**: $\mu_{\mathrm{TS}} - \mu_{\mathrm{GS}} = +1.56$ D and **2a**: $\mu_{\mathrm{TS}} - \mu_{\mathrm{GS}} = -1.32$ D). More experimental datapoints, especially for electron-deficient derivatives such as **2e** and **2f**, would be helpful to extend the correlation of free energies of activation. It should be pointed out, however, that the excellent correlation for ln$k$ with the computed $\Delta G^{\ddagger}$ over a broad range of σ_p values strongly suggests a cogency of the free energy correlation in Figure 2.

Assuming that the correlations in Figure 2 are general, one can estimate the stability of other pentazole derivatives and the parent pentazole **1**. Some of the results are shown in Table 2. Not surprisingly, 4-thiophenylpentazole anion (**2g**), with the very negative σ_p value of −1.21, is expected to be more stable than the oxo anion **2b**. Its rate of decomposition in MeOH at 0 °C can be estimated to be 1.2 times lower than that for **2b**, the most stable pentazole derivative known. The same correlations allow estimation of the stability of pentazole anion **1** in methanol solution, which is a likely medium for its generation and study. Thus, the estimated half-lifetime $t_{1/2}$ for **1** is about 2.2 days in methanol at 0 °C, which offers encouragement for future experimental work. The parent hydrogen pentazole, HN_5, is predicted to be as stable as 4-chlorophenylpentazole (**2c**), while 1-aminopentazole[1] has a predicted half-lifetime $t_{1/2}$ of less than 1 min at 0 °C.

Table 2. Calculated Free Energy of Activation for Selected Pentazole Derivatives and Predicted Stability in Methanol[a]

	calculated[b]	predicted[a]	
compound	$\Delta G^{\ddagger}_{298}$, [kcal/mol]	$\Delta G^{\ddagger}_{298}$, [kcal/mol]	$k\cdot10^4$ at 0 °C, [s^{-1}]
4-(−)$SC_6H_4N_5$ (**2g**)	21.43	20.65	0.77
N_5(−) (**1**)	25.25	22.42	0.036
N_5H	17.95	19.04	12.4
1-NH_2N_5	14.90	17.63	142.0

[a] Predictions made based on correlations in Figure 2. [b] At the B3LYP/6-31+G(d,p) level of theory.

The results from ozonolysis of **2b** suggest that O_3 reacts much faster with pentazole than with the benzene ring, which eliminates this method from possible routes to **1**. Other precursors need to be considered, especially those that lead to the N_5-COO(−), silicon or sulfur derivatives of **1**. This approach hinges, however, upon the ability to construct a linear or cyclic array of nitrogen atoms by methods such as those shown in Figure 1.

Computational Details

Quantum-mechanical calculations were carried out at the B3LYP/6-31+G(d,p)[25] level of theory using the Linda-Gaussian 98 package[26] on a Beowulf cluster of 16 processors. Geometry optimizations were undertaken using appropriate symmetry constraints and default convergence limits. Transition structures were located using the QST2 keyword. Vibrational frequencies were used to characterize the nature of the stationary points and to obtain thermodynamic parameters. Zero-point energy (ZPE) corrections were scaled by 0.9806.[27]

Nuclear magnetic shielding tensors were calulated for molecules at ground-state geometry using the NMR keyword and the default GIAO method at the B3LYP/6-31+G(d,p) level of theory. The resulting energies and absolute shielding tensors are listed in the Supporting Information.

Experimental Section

^{1}H NMR spectra were recorded at 400 MHz and referenced to the solvent. ^{15}N NMR spectra were recorded at 40.56 MHz in CD_2Cl_2, and externally referenced to the ^{15}N signals of doubly labeled $^{15}NH_4{}^{15}NO_3$ ($^{\mathbf{15}}\mathbf{N}H_4$ δ −360.4, $^{\mathbf{15}}\mathbf{N}O_3$ δ −4.00) which was indirectly referenced to neat CH_3NO_2 ($\delta = 0.0$

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ppm).[28] Labeled sodium azide was purchased from Cambridge Isotope Laboratories. Ozone was generated using a Griffin Ozonia G-TC-0.5 instrument.

Thermolysis of 2. Kinetic Measurements. Pentazole **2a** or **2b-NBu₄** (approximately 0.06 mmol) was dissolved in deuterated solvent (0.5 mL) and transferred into an NMR tube at low temperature. The sample was kept at a constant temperature, and ^{1}H NMR spectra were taken at regular time intervals, until the virtual disappearance of the starting material. A ratio of intensities of the signals of the aromatic hydrogens in the starting material (**2a**: (CD_3OD) δ 7.04 and 8.01 ppm; **2b-NBu$_4$** (CD_2Cl_2) δ 6.58 and 7.69 ppm, (CD_3OD) δ 6.74 and 7.79 ppm) to that in the forming azide (**3a**: (CD_3OD) δ 6.78 and 6.90 ppm; **3b-NBu$_4$** (CD_2Cl_2) δ 6.47 and 6.65 ppm, (CD_3OD) δ 6.59 and 6.69 ppm) was used to calculate the rate constants. Four kinetic measurements were done in the range of temperatures between −10 to +20 °C. Full kinetic data is listed in the Supporting Information.

4-Hydroxybenzenediazonium Trifluoroacetate.[18] The salt was prepared in 65% yield as a 1:1 complex with trifluoroacetic acid according to a general literature procedure.[18] ^{1}H NMR (CD_3CN) δ 7.16 (d, $J = 9.4$ Hz, 2H), 8.17 (d, $J = 9.4$ Hz, 2H), 8.70 (bs, 2H).

4-Hydroxyphenylpentazole (2a). 4-Hydroxybenzenediazonium trifluoroacetate (0.42 g, 1.26 mmol) was dissolved in methanol (3.40 mL) at −23 °C (dry ice−carbon tetrachloride bath) and petroleum ether (3.40 mL) was added to the solution. Sodium azide (0.16 g, 2.46 mmol), in water (0.65 mL), was added dropwise and the stirring continued for about 0.5 h at the same temperature. The solid material was separated using a jacketed funnel for low temperature filtration and carefully washed with a small amount of cold methanol. The remaining solid was collected at low temperature and vacuum-dried to give 0.08 g (40% yield) of the product as a gray solid, which was 90% pure by NMR: ^{1}H NMR (CD_3OD) δ 7.04 (d, $J = 6.4$ Hz, 2H), 8.01 (d, $J = 6.5$ Hz, 2H).

The second major product was identified as 4-hydroxyphenyl azide (**3a**): ^{1}H NMR (CD_3OD) δ 6.78 (d, $J = 8.8$ Hz, 2H), 6.90 (d, $J = 8.8$ Hz, 2H); ($CDCl_3$) δ 6.83 (d, $J = 8.9$ Hz, 2H), 6.92 (d, $J = 8.9$ Hz, 2H). Lit.[29] ($CDCl_3$) δ 6.83 (d, $J = 9$ Hz, 2H), 6.92 (d, $J = 9$ Hz, 2H).

4-Oxophenylpentazole, Tetrabutylammonium Salt (2b-NBu$_4$). Pentazole **2a** (0.01 g, 0.06 mmol) was suspended in a solution of tetrabutylammonium hydroxide (0.02 g, 0.08 mmol) in deuterated dichloromethane (0.5 mL) at − 78 °C. Temperature was raised to − 35 °C and stirring continued until the full dissolution of the solid and formation of **2b**: ^{1}H NMR (CD_2Cl_2) δ 0.92 (t, $J = 7.2$ Hz, 12H), 1.24−1.34 (m, 8H), 1.41−1.52 (m, 8H), 2.99−3.06 (m, 8H), 6.58 (d, $J = 6.8$ Hz, 2H), 7.69 (d, $J = 6.8$ Hz, 2H); ^{15}N NMR (CD_2Cl_2) δ −28.7 (s, 1N), 3.2 (s, 1N).

Attempted Preparation of 4-Oxophenylpentazole, Tetrabutylammonium Salt (2b-NBu$_4$). *p*-Diazobenzoquinone[18,30] (**4**, 10 mg, 0.09 mmol) was dissolved in CD_3OD (0.25 mL) and the solution cooled to −78 °C. A solution of tetrabutylammonium azide (30 mg, 0.10 mmol) in CD_3OD (0.25 mL) was added dropwise and the temperature gradually raised to 0 °C during 1 h period. The solution was transferred to an NMR tube and a spectrum was accumulated immediately at ambient temperature. The spectral data were consistent with the sole presence of azide **3b-NBu$_4$**.

Ozonolysis of 4-Oxophenylpentazole, Tetrabutylammonium Salt (2b-NBu$_4$). A solution of ^{15}N-labeled 4-oxophenylpentazole salt **2b-15N-NBu$_4$** (30 mg, 0.07 mmol) and Bu_4NOH (35 mg, 0.14 mmol) in deuterated dichloromethane was cooled to −78 °C. A slow stream of ozone was passed through the solution for 3 min after which both ^{1}H and ^{15}N NMR spectra were measured. A new set of peaks in the ^{1}H NMR spectrum: ^{1}H NMR (CD_2Cl_2) δ 7.15 (d, 2H), 7.87 (d, 2H). No signals were detected in the ^{15}N NMR spectrum. The data were compared with measurements on CD_2Cl_2 solutions of original samples of *p*-nitrophenol (δ 6.95 (d, 2H), 8.16 (d, 2H)) and tetrabutyammonium *p*-nitrophenolate (δ 6.21 (d, 2H), 7.87 (d, 2H)).

4-Oxophenyl Azide, Tetrabutylammonium Salt (3b-NBu$_4$). ^{1}H NMR (CD_3OD) δ 6.59 (d, $J = 9.0$ Hz, 2H), 6.69 (d, $J = 9.0$ Hz, 2H); (CD_2Cl_2) δ 6.47 (d, $J = 8.8$ Hz, 2H), 6.65 (d, $J = 8.8$ Hz, 2H); ^{15}N NMR (CD_2Cl_2) δ −148.4 (s, 1N), −131.7 (s, 1N).

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Supporting Information Available: Listing of full kinetic data and computational results including isotropic shielding tensors are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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