Supporting Information

Aberrant $S_{RN}1$ Reaction of 4-Aminophenol with α,p-Dinitro-cumene: EPR Observation of Intermediates

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Materials and manipulations. Because of the sensitivity of radical reactions and highly basic anions to oxygen and water, extreme care was taken to work under an argon atmosphere. Apparatus was baked at 110 ºC for several hours prior to use. Reactions vessels containing weighed samples were fitted with a 3-way stopcock and degassed repeatedly by evacuating to 0.05 mm Hg or less and purging with dried, deoxygenated argon. Liquids were transferred by reaching through the stopcock with a degassed, gas-tight syringe with a stream of argon flowing through the side opening of the stopcock.

The DMSO was carefully purified as previously described and stored under argon.[1] Potassium t-butoxide was purified by sublimation then placed in a RB flask fitted with a 3-way stopcock and handled as described above. DMSO was added by syringe and aliquotes of the resulting clear, colorless solution were titrated. α,p-Dinitrocumene(**1**) was prepared by the method of Norris, et. al.[2]

Standard procedure for reactions of nucleophiles with 1. Nucleophile conjugate acid (1.00 mmol) and **1** (1.00 mmol) were placed in separate reaction vessels fitted with 3-way stopcocks and pump-flushed 5-6 times with argon. Potassium t-butoxide solution (1.00 mmol) was added to the nucleophile vessel by syringe followed by sufficient DMSO to make 5.0 mL of

solution. DMSO (5.0 mL) was added to **1**, and the resulting solution was added to the nucleophile by syringe. In most cases an intense color change immediately occurred. After 2 h water (10 mL) was added and the contents of the vessel poured into ice water (50 mL). The mixture was extracted with ether (3 x), and the combined ether extracts were washed with water (3 x), and dried with anhydrous magnesium sulfate. In experiments for yield determination, an internal standard was added to the reaction mixture before the extraction process. Removal of solvent yielded the crude reaction mixture which was separated by column chromatography to isolate pure products, and/or analyzed by HPLC or NMR for yield determinations.

Reaction of 6b and 1. The reaction of of **6b** (135.2 mg, 1.09 mmol) and **1** (234.0 mg, 1.11 mmol) was carried out in the dark for 2 h as described above and gave 340 mg of yellow oil. The oil was adsorbed onto a 15 g silica gel column and eluted first with 1% ether-petroleum ether. The first two 30 mL fractions gave 54 mg of elimination product 2-(4-nitrophenyl)propene as a yellow oil: ^{1}H NMR ($CDCl_3$) 2.18 (broad s, 3H), 5.27 (m, 1H), 5.47 (broad s, 1H), and 7.5-8.3 (two AB doublets, 4H). Fraction 3 was blank and fractions 4 and 5 contained 112 mg of **5b** as a yellow oil. Fractions 6 and 7 (3% ether-petroleum ether) contained 77 mg of a mixture of **5b** and **1**. Fractions 4 and 5 were rechromatographed to give an analytical sample of **5b** as a bright yellow oil: ^{1}H NMR ($CDCl_3$) δ 1.62 (s, 6H), 3.68 (s, 3H, OMe), 6.55 (s, 4H), 7.5-8.3 (2 AB doublets, 4H); IR (neat) ν/cm^{-1} 2975, 2815, 1600, 1505, 1350, 1225, 1155, 1105, 960, 870, 760, and 710; m/z 287 (M^+) and 124 (base). Anal. Calcd for $C_{16}H_{17}NO_4$: C, 66.88; H, 5.97; N, 4.88. Found: C, 66.93; H, 6.11; N, 4.82.

In an identical experiment with 1.00 mmol of **6b** the ether extracts were spiked with 69.3 mg (0.449 mmol) of biphenyl and analyzed by HPLC (C-18 column, 90% MeOH-10% water). Detected were **1** (0.100 mmol, 10%), **5b** (0.576 mmol, 58%) and 2-(4-nitrophenyl)propene (0.268 mmol, 25%).

2-(4-Hydroxyanilino)-2-(4-nitrophenyl)propane (10). Reaction of **1**, **7** and KOBu-t (each 1.0 mM) in DMSO (10 mL) under argon for 2 h in the dark gave 2-(4-hydroxyanilino)-2-(4-nitrophenyl)propane (**10**) (0.92 mmol, 92%). Trituration of the original product oil in benzene-

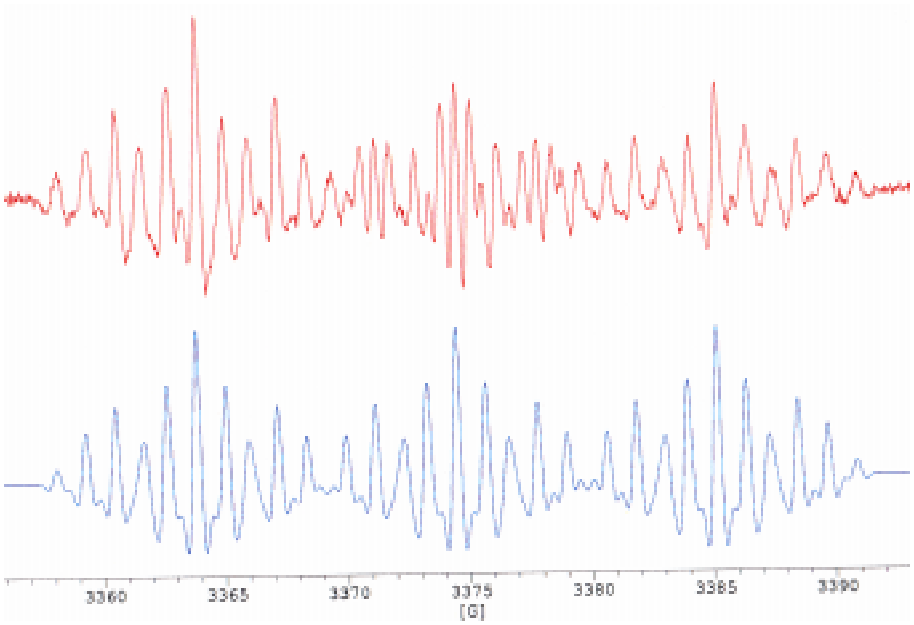
petroleum ether gave a brownish solid, mp 104-108 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.62 (s, 6H), 4.73 (broad s, 2H), 6.00-6.87 (broad d, 4H), 7.52-8.40 (2 AB doublets, 4H). Attempts to purify **10** led to decomposition so it was characterised as the O-acetyl derivative. Treatment of **10** with acetic anhydride in benzene and pyridine gave the O-acetyl ester of **10**, mp 147-148 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.65 (s, 6H), 2.20 (s, 3H), 4.08 (broad s, 1H), 6.52 (2 AB doublets, 4H), 7.87 (2 AB doublets, 4H); ν/cm^{-1} (KBr) 3379 (NH), 1745 (C=O); M^+ Calcd for $C_{17}H_{18}N_2O_4$: 314.1267. Found: 314.1258 (13.4%). Anal. Calcd for $C_{17}H_{18}N_2O_4$: C, 64.95; H, 5.77; N, 8.91. Found: C, 64.82; H, 5.66; N, 8.83.

[1]. (a) Scamehorn, R.G.; Hardacre, J.M.; Lukanich, J.M.; Sharpe, L.R. *J. Org. Chem.* **1984**, *49*, 4881. (b) Ritchie, C.D.; Skinner, G.A.; Badding, V.G. *J. Am. Chem. Soc.* **1967**, *89*, 2069.

[2]. Burt, B.L.; Freeman, D.J.; Gray, P.G.; Norris, P.K.; Randles, D. *Tetrahedron Lett.* **1977**, 3063.

EPR spectrum of the radical anion of 2-(4-hydroxyanilino)-2-(4-nitrophenyl)propane (9)

Reaction of α,p-dinitrobenzene (**1**) with 4-aminophenol in DMSO at 295 K was monitored by EPR spectroscopy and a well resolved, though slightly anisotropic, spectrum (upper trace) was obtained which persisted for several hours. This spectrum contained two components and the major one was well matched by a computer simulation (lower trace) with the following hyperfine splittings: a(N) = 10.6, a(2H) = 3.34, a(2H) = 1.2, a(N) = 1.2 G.



The EPR spectra of radical anions derived from nitrobenzene, 4-nitrocumene and related nitroaromatics display hfs of very similar magnitudes for N and the two sets of ring hydrogens, and hence we assign the above spectrum to the radical anion **9**. The fact that a small hfs from an additional N was observed confirmed that the nucleophile was attached via the NH group.