JOC The Journal of Organic Chemistry

J. Org. Chem., 1998, 63(13), 4390-4391, DOI:10.1021/jo980173v

DMD Oxidation of *in-situ*-Generated σ^H Adducts Derived From Nitroarenes and the Carbanion of 2-Phenylpropionitrile to Phenols: The First Direct Substitution of a Nitro by a Hydroxy Group

SUPPLEMENTARY INFORMATION

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General Aspects

^{1}H and ^{13}C NMR spectra were measured on a Brucker AC 200 and a Varian Gemini (^{1}H: 200 MHz, ^{13}C: 50 MHz) spectrometer with deuteriochloroform as internal standard. *J* values are given in Hz. IR spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrophotometer. MS spectra were measured on a Finnigan MAT 8200 spectrometer. Elemental analyses were carried out by the Microanalytical Division of the Institute of Inorganic Chemistry, University of Würzburg and Microanalysis Laboratory of the Insitute of Organic Chemistry, Polish Academy of Sciences. Melting points were taken on a Büchi B-545 apparatus, and are not corrected. TLC analyses were conducted on precoated silical-gel foils Polygram SIL G/UV$_{254}$ (40 × 80 mm) from Macherey & Nagel. Spots were identified on UV-light exposure and/or by iodine vapor. Silical gel (63-200 μm, Woelm) was used for column chromatography. THF was freshly distilled over potassium benzophenone ketyl. DMF was distilled over CaH. ^{t}BuOK was freshly sublimed prior to use. DMD solutions were prepared according to literature[5b] and were dried over fresh molecular sieves (4Å) two

times for two days each. All chemicals were commercial products from Aldrich or Fluka and were used as received, except 3,5-dichloronitrobenzene, which was prepared from 2,6-dichloro-4-nitroaniline[10].

General Procedure for the DMD Oxidation of σ^H Adducts

To 123 mg (1.10 mmol) of ^{t}BuOK, cooled at -70 °C under an argon gas atmosphere in a 100-mL, oven-dried flask, was added slowly 20 mL THF while magnetically stirring. A solution of 131 mg (1.00 mmol) of 2-phenyl-propionitrile and 123 mg (1.00 mmol) of nitrobenzene in 1.0 mL of DMF was added at -70 °C within 2 min by means of a syringe. The resulting mixture was stirred for 5 min, before 14.5 mL (0.083 M, 1.2 mmol) of DMD solution (precooled at -70 °C) was added in one portion. After 5 min, 18 μL (1.0 mmol) of water was added. The mixture was further stirred for 5 min and then hydrolyzed with 1.0 mL saturated aq. NH_4Cl solution. The cooling bath was removed and after the temperature of the mixture rose to *ca.* 20 °C, $MgSO_4$ was added to remove the water. After filtration and washing with THF (3×20 mL), the solvent was removed (30 °C/12 mbar). The residue was purified by chromatography on silica gel (4:1 n-hexane/EtOAc and then 2:1 n-hexane/EtOAc) to give 16 mg (6%) of the nitro compound **4a** (which was identical with a sample prepared according to literature[3b]) and 185 mg (83%) of the phenol **5a**.

2-(4-Hydroxyphenyl)-2-phenylpropionitrile (**5a**, 83%): white flakes, m.p. 84-86 °C (CH_2Cl_2/hexane). δ_H(200 MHz; $CDCl_3$) 2.05 (s, 3H, CH_3), 6.83-6.87 (m, 2H, Ar), 6.70-7.20 (br. s, 1H, OH), 7.20-7.23 (m, 2H, Ar), 7.32-7.38 (m, 5H, Ph) ppm. δ_C(50 MHz, $CDCl_3$) 28.1 (q), 45.3 (s), 115.6 (d), 123.6 (s), 126.3 (d), 127.7 (d), 127.8 (d), 128.7 (d), 132.4 (s), 141.3 (s), 157.7 (s) ppm. ν_{max}(KBr wafer)/cm^{-1}: 3400, 2241, 1612, 1597, 1510, 1503, 1438, 1370, 1269, 1178, 1105, 831. Anal. Calcd. for $C_{15}H_{13}NO$(223.3): C, 80.69; H, 5.87; N, 6.27. Found: C, 80.63; H, 5.67; N, 6.29. MS (EI), m/z: 223(M^+), 208(100%), 190, 181, 153, 91, 77.

2-(2,6-Dichloro-4-hydroxyphenyl)-2-phenylpropionitrile (**5b**, 69%): white powder, m.p. 155-156 °C (CH_3Cl). δ_H(200 MHz; $CDCl_3$) 2.70 (s, 3H, CH_3), 7.10 (br. s, 1H, OH), 7.20 (s, 2H, Ar), 7.56-7.69 (m, 5H, Ph) ppm. δ_C(50 MHz, $CDCl_3$) 31.5 (q), 47.7 (s), 118.7 (d), 122.5 (s), 124.6 (s), 125.4 (d), 127.6 (d), 129.0 (d), 136.1 (s), 142.4 (s), 156.1 (s) ppm. ν_{max}($CHCl_3$)/cm^{-1}: 3581, 3332, 2238, 1605, 1568, 1493, 1450, 1416, 1269, 1219, 1183, 955, 854. Anal. Calcd. for $C_{15}H_{11}Cl_2NO$(292.2): C, 61.67; H, 3.79; N, 4.79. Found: C, 61.97; H, 3.57; N, 4.70.

2-(3,6-Dibromo-4-hydroxyphenyl)-2-phenylpropionitrile (**5c**, 72%): white powder, m.p. 123-124 °C (CH_2Cl_2/hexane). δ_H(200 MHz; $CDCl_3$) 2.10 (s, 3H, CH_3), 5.90 (br. s, 1H, OH), 7.22-7.35 (m, 6H, Ph, Ar), 7.71 (s, 1H, Ar) ppm. δ_C(50 MHz, $CDCl_3$) 30.3 (q), 46.2 (s), 109.1 (s), 121.3 (s), 122.8 (d), 124.1 (s),

125.9 (d), 127.7 (d), 128.9 (d), 131.1 (s), 131.4 (d), 140.7 (s), 153.1 (s) ppm. $\nu_{max}(CHCl_3)/cm^{-1}$: 3515, 3318, 3024, 2239, 1594, 1556, 1476, 1387, 1299, 1188, 1081, 1053, 875. Anal. Calcd. for $C_{15}H_{11}Br_2NO$(381.1): C, 47.28; H, 2.91; N, 3.68. Found: C, 46.91; H, 2.69; N, 3.63. MS (EI), m/z: 383, 381(M^+), 287, 285, 221, 206(100%), 177, 151, 103, 43.

2-(3-Fluoro-4-hydroxyphenyl)-2-phenylpropionitrile (**5d**, 81%): colorless oil. δ_H(200 MHz; $CDCl_3$) 2.05 (s, 3H, CH_3), 6.05-6.20 (br. s, 1H, OH), 6.93-7.09 (m, 3H, Ar), 7.31-7.39 (m, 5H, Ph) ppm. δ_C(50 MHz, $CDCl_3$) 28.0 (q), 45.3 (s), 114.2 and 114.6 (d, J = 19.9), 117.6 and 117.7 (d, J = 2.5), 122.9 and 123.0 (d, J = 3.0), 126.4 (d), 127.7 (d), 128.1(s), 129.0 (d), 134.0 and 134.1 (s, J = 6.1), 140.9 (s), 143.1 and 143.4 (s, J = 13.9), 148.4 and 153.1 (s, J = 239) ppm. ν_{max}(KBr wafer)/cm^{-1}: 3351, 2240, 1625, 1520, 1434, 1365, 1298, 1250, 1200 Anal. Calcd. for $C_{15}H_{12}FNO$(241.3): C, 74.68; H, 5.01; N, 5.81. Found: C, 74.62; H, 5.01; N, 5.76. MS (EI), m/z: 241(M^+), 226(100%), 206, 199, 178, 151, 89, 71.

2-(2-Chloro-4-hydroxyphenyl)-2-phenylpropionitrile (**5e**, 87%): white flakes, m.p. 180-182 °C (CH_2Cl_2). δ_H(200 MHz; $CDCl_3$) 2.09 (s, 3H, CH_3), 5.69 (br. s, 1H, OH), 6.81-6.89 (dd, J_1 = 8.6, J_2= 2.6, 1H, Ar) 6.91-6.94 (d, J_2= 2.6, 1H, Ar), 7.20-7.39 (m, 5H, Ph), 7.42-7.50 (d, J = 8.6, 1H, Ar) ppm. δ_C(50 MHz, $CDCl_3$) 29.6 (q), 44.8 (s), 113.9 (d), 118.9 (d), 122.0 (s), 125.8 (d), 127.5 (d), 128.6 (s), 128.8 (d), 129.0 (d), 135.3 (s), 141.3 (s), 156.5 (s) ppm. ν_{max}(KBr wafer)/cm^{-1}:

3375, 2236, 1607, 1575, 1495, 1430, 1312, 1291, 1215. Anal. Calcd. for $C_{15}H_{12}ClNO$(257.7): C, 69.91; H, 4.69; N, 5.43; Cl, 13.76. Found: C, 69.74; H, 4.43; N, 5.29; Cl, 13.83. MS (EI), m/z: 257(M^+), 242 (100%), 222, 215, 207, 206, 195, 177, 165, 152, 89, 77.

Additional Reference

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