Oxidation of Electron Deficient Anilines by HOF. A Route to Nitro-Containing Compounds for Molecular Electronic Devices

Shawn M. Dirk, Edward T. Mickelson, Jay C. Henderson, and James M. Tour*

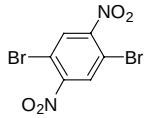
Department of Chemistry and Center for Nanoscale Science and Technology, MS 222, Rice University, 6100 Main Street, Houston, TX 77005

tour@rice.edu

Supporting Information

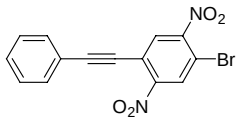
Experimental

General HOF Oxidation Procedure. To a 125 mL polyethylene bottle were added H_2O (2 mL) and CH_3CN (60 mL) and the mixture was cooled to –20 ^oC. F_2 (20% in He) was then bubbled through the solution at a rate of 50 sccm for 2 h. The resulting HOF/CH_3CN solution was then purged with He for 15 min. The species to be oxidized was then added in acetone or ethyl acetate (10 mL) and mixed at –20 ^oC for 5 min before being neutralized by pouring into a saturated $NaHCO_3$ solution.

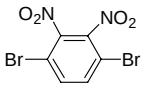


1,4-Dibromo-2,5-dinitrobenzene. 2,5-Dibromo-4-nitroaniline (415 mg, 1.40 mmol) in acetone was oxidized according to the general procedure to yield 397 mg (87 %) of a yellow solid. IR (KBr) 3461.6, 3354.2, 3093.4, 1703.9, 1615.5, 1539.3, 1452.8,

1368.8, 1340.4, 1263.6, 1064.7, 894.2, 841.5, 736.6, 650.3, 532.2, 466.4, 403.6 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.5, 131.9, 114.5. HRMS Calc'd for 323.8382. Found: 323.8383.

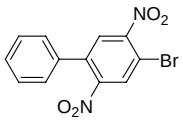


1-Bromo-4-ethynylphenyl-2,5-dinitrobenzene. 2-Bromo-4-nitro-5-ethynylphenylaniline (490 mg, 1.48 mmol) in ethyl acetate was oxidized according to the general procedure to yield 320 mg (60 %) of a yellow solid. IR (KBr) 3442.7, 3101.4, 2216.8, 1610.6, 1540.9, 1461.3, 1384.8, 1358.7, 1337.1, 1264.4, 906.2, 849.6, 824.4, 760.2, 689.8 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1 H), 8.09 (s, 1 H), 7.60-7.58 (m, 2 H), 7.41-7.39 (m, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.1, 150.4, 132.7, 131.7, 131.0, 130.7, 129.1, 121.5, 119.8, 113.9, 102.0, 82.8. HRMS Calc'd for 345.9589. Found: 345.9585.

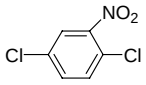


1,4-Dibromo-2,3-dinitrobenzene. 2,5-Dibromo-5-aminoaniline (203 mg, 0.77 mmol) in acetone was oxidized according to the general procedure to yield 247 mg (98 %) of a yellow solid. IR (KBr) 3083.2, 1555.0, 1536.0, 1440.2, 1391.5, 1349.2, 1274.5, 1179.6, 1096.9, 884.0, 829.5, 767.8, 749.9, 699.4 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$)

δ 7.72 (s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 136.8, 114.3. HRMS Calc'd for 323.8382. Found: 323.8382.



1-Bromo-2,5-dinitro-4-phenylbenzene. 2-Bromo-5-phenyl-4-nitroaniline (373 mg, 1.28 mmol) in ethyl acetate was oxidized according to the general procedure to yield 407 mg (99 %) of a orange solid. IR (KBr) 3446.7, 3090.4, 1542.8, 1461.1, 1443.1, 1347.3, 1257.7, 1114.6, 1076.2, 1051.8, 1021.0, 904.5, 842.5, 768.8, 743.7, 699.9, 551.0, 485.16 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1 H), 7.89 (s, 1 H), 7.47-7.45 (m, 3 H), 7.31-7.29 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.5, 150.6, 137.2, 134.4, 130.8, 130.1, 129.7, 128.9, 128.1, 114.1. HRMS Calc'd for 321.9589. Found: 321.9592.



2,5-Dichloronitrobenzene. 2,5-Dichloroaniline (243 mg, 1.5 mmol) in ethyl acetate was oxidized according to the general procedure to yield 280 mg (97%) of a pale yellow solid. IR (KBr) 3090.0, 3077.2, 1588.6, 1565.9, 1532.6, 1466.0, 1353.2, 1274.3, 1251.9, 1158.8, 1138.6, 1099.4, 1051.2, 882.3, 831.7, 768.4, 752.1, 690.3, 661.9, 611.8, 544.3, 490.6, 416.8. cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6) δ 702 (dd, J = 2.2, 0.3, 1 H), 6.39

(dd, J = 8.7, 2.2, 1 H), 6.36 (dd, J = 8.6, 0.4, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4, 133.9, 133.8, 133.3, 126.0, 125.9. HRMS Calc'd for 190.9541. Found: 190.9543.