

SUPPORTING INFORMATION

Photochemical Preparation of 1,3,5,7-Tetracyanoadamantane and Its Conversion to 1,3,5,7-Tetrakis(aminomethyl)adamantane

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Experimental Section

General Methods. All reactions were carried out under a dry nitrogen atmosphere and were stirred magnetically. Reagents were obtained from commercial suppliers and used without purification unless otherwise indicated. Solvents were purified by standard methods. Photolyses were performed in a Southern New England Rayonet RPR-100 ultraviolet photochemical reactor. Purification of crude products was done by flash chromatography on Merck 60Å silica gel. Melting points were recorded on an Electrothermal digital capillary melting point apparatus and are reported uncorrected. NMR data were obtained on a Bruker 300 MHz FT instrument, with spectra referenced to proton residues of deuterated solvents. Infrared spectra were recorded on a Nicolet Avitar 320 FT-IR instrument.

1,3,5,7-Tetrabromoadamantane (7). A mixture of 120.00 g anhydrous AlCl_3 (87.61 mmol) and 60 mL bromine (109.52 mmol) was cooled to 0°C. Adamantane (30.00 g, 21.90 mmol) was added in small portions through a solid addition funnel. The mixture was then refluxed 9 h. HBr gas that evolved was passed through second flask containing concentrated aqueous sodium bisulfite. When no more HBr evolved, the reaction mixture was treated first with 100 mL saturated sodium bisulfite solution, and then with 100 mL 6N HCl. The resulting dark yellow precipitate was taken up in chloroform, washed with distilled water and brine, and dried over anhydrous magnesium sulfate. The organic solution was filtered and evaporated at reduced pressure; the residue was recrystallized from acetone/water to afford 71.23 g (94%) of **7** as white crystals: mp 246-248 °C (lit. 245-247 °C¹²); ^1H NMR (300 MHz, CDCl_3) δ 2.71 (s, 12H); ^{13}C NMR (CDCl_3) δ 54.62, 54.78; IR (KBr) ν_{max} 487 cm^{-1} ; UV λ_{max} = 262nm.

1,3,5,7-Tetrachloroadamantane (9). A mixture of 5.00 g adamantane (0.03 mol) and 10.00 g AlCl_3 (0.07 mol) in 45 mL carbon tetrachloride was refluxed 1 h. After cooling, the mixture was treated with 20 mL of 6N HCl. The organic product was extracted into 150 mL of chloroform, washed with distilled water and brine, and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure, affording 10.03 g (98%) of **9** as an off-white solid: mp

191-193 °C (lit 194 °C¹⁸); ¹H NMR (300 MHz, CDCl₃) δ 2.35 (s, 12H); ¹³C NMR (CDCl₃) δ 46.56, 53.58; IR (KBr) ν_{max} 502 cm⁻¹.

1,3,5,7-Tetraiodoadamantane (10). A mixture of 100 mg tetrabromoadamantane (0.22 mmol), 58 mg AlBr₃ (0.44 mmol), and 3 mL iodomethane was stirred at room temp for 15 h. The resulting pink-brown solution was treated with 50 mL concentrated sodium bisulfite solution, then with 25 mL of 6N HCl. The organic product was taken into 50 mL of chloroform, washed with distilled water and brine, and dried over anhydrous magnesium sulfate. The solvent was removed at reduced pressure, to give 130 mg (91%) of **10** as a white solid: mp >360 °C (lit 370 °C¹⁹); ¹H NMR (300 MHz, CDCl₃) δ 3.22 (s, 12H); ¹³C NMR (300 MHz, CDCl₃) δ 57.21, 59.22; IR (KBr) ν_{max} 479cm⁻¹.

1,3,5,7-Tetracyanoadamantane (1). Tetrabromoadamantane (**7**) (10.00 g, 0.07mol), and sodium cyanide (17.20 g, 0.42 mol) were dissolved in 700 mL DMSO in a cylindrical quartz vessel. The mixture was irradiated at 254 nm 6 h in a Rayonet photochemical reactor. DMSO was removed by distillation at reduced pressure. The residue was washed with 500 mL water and the solid product isolated by vacuum filtration, with the filtrate collected directly into a solution of 6% sodium hypochlorite (commercial bleach) to decompose excess cyanide. Flash chromatography, initially with methylene chloride, removed unreacted **7** and partially cyanated products; **1** eluted with 1:4 methylene chloride:acetone as an off-white powder (3.52 g, 63% yield). Alternatively, recrystallization of the crude product from acetone/water afforded **1** in 73% yield: mp > 400 °C; ¹H NMR (300 MHz, DMSO-d₆) δ 2.38 (s, 12H); ¹³C NMR (DMSO-d₆) δ 29.37, 36.19, 120.96; IR (KBr) ν_{max} 2240cm⁻¹; HRMS-FAB (m/z): [M⁺] calcd 236.1062; found 236.1630; UV λ_{max} = 257nm.

1,3,5,7-Tetrakis(aminomethyl)adamantane tetra(hydrochloride) (2•4HCl). A mixture of tetracyanoadamantane **1** (500 mg, 2.08 mmol) in 10 mL dry THF was refluxed 2 h. Monochloroborane-methyl sulfide (BMS-Cl) (2.12 mL, 6.28 mmol) was then added dropwise over 10 min, with removal of dimethyl sulfide by distillation. After 24 h at reflux, the reaction mixture was cooled to room temp. After further cooling in an ice bath, 12 mL of 1.0 M methanolic HCl were carefully added over 15 min, with vigorous evolution of hydrogen. The solution was heated, allowing the methyl borate to distill off. Anhydrous ethanol was added and distilled off sequentially three times to remove residual borates. Recrystallization from ethanol gave 710 mg of **2•4HCl** (98%): mp > 400 °C, ¹H NMR (300 MHz, D₂O) δ 1.27 (s, 8H), 2.77 (s, 12H); ¹³C NMR (D₂O) δ 39.00, 33.39, 48.98; IR (KBr) ν_{max} 3387, 2917, 1614, 1318 cm⁻¹.

1,3,5,7-Tetrakis(aminomethyl)adamantane (2). A solution of 100 mg (0.25 mmol) 1,3,5,7-tetrakis(aminomethyl)adamantane tetra(hydrochloride) in 5 mL water was treated with concentrated NaOH to pH 13. Water was removed at reduced pressure, and the residue taken up in CH₂Cl₂. The solution was filtered, shaken with brine, dried over magnesium sulfate, and evaporated to give 55 mg (86%) of **2** as a colorless oil: ¹H NMR (300 MHz, D₂O) δ 0.89 (s, 8H), 2.11 (s, 12H); ¹³C NMR (D₂O) δ 32.65, 38.99, 50.26; ¹H NMR (300 MHz, CDCl₃) δ 1.09 (s, 8H), 2.45 (s, 12H); IR (cast) ν_{max} 3646, 3444, 2914, 1556, 1320 cm⁻¹; HRMS-FAB (m/z): [MH⁺] calcd 253.2391; found 253.2388.

1,3,5,7-Tetra(carbomethoxy)adamantane (11). A mixture of 100 mg (0.42 mmol) 1,3,5,7-tetracyanoadamantane (**1**) and 50 mL of 1.0M anhydrous methanolic HCl was refluxed 3 days. Evaporation of solvent afforded 112 mg (72%) of **11**^{3b, 4}. ¹H NMR (300 MHz, CDCl₃) δ 3.65 (s, 12H), 2.66 (s, 12H) ; IR (cast) ν_{max} 2985, 2878, 1736, 1179 cm⁻¹.