A Novel Type of Nucleophilic Substitution Reactions on Non-Activated Aromatic Compounds and Benzene Itself with Trimethylsiliconide Anions

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Experimental

General Methods: Gas chromatographic analyses were performed on a Hewlett-Packard 5890 Series II instrument with a flame ionization detector, a Hewlett-Packard 3396 Series III integrator, an one of the following columns: HP1 5 m x 0.17 mm column, and a DB-1, 30 m x 0.17 mm column. ^{1}H NMR (200.13 MHz) and ^{13}C NMR (50.32 MHz) were conducted on a Bruker AC 200 spectrometer in deuterochloroform as solvent. Coupling constants (J) are given in Hz units. GC/MS analyses were carried out on a Shimadzu GC/MS QP 5050 spectrometer equipped with a DB-5, 30 m x 0.18 mm ID column.

Determination of the relative concentrations of deuterated and nondeuterated products were carried out by GC/MS analysis (Shimadzu GC-17 A Series, DB5-MS 30 m x 0.2 mm x 0.18 mm film column, coupled to a Shimadzu GCMS-QP 5050 mass selective detector) by mass selective integration.

Materials: Iodobenzene, bromobenzene, chlorobenzene, fluorobenzene, bromomesitylene, mesitylene, 4-methylchorobenzene, 1,4-dichlorobenzene, hexamenthyldisilane, methyl iodide, trimethylsilylbenzene, *p*-bis-trimethylsilylbenzene, eicosane, pentadeuterofluorobenzene, and pyridine were all purchased from Aldrich Chemical Company and used as received from the supplier.

Hexamethylphosphoramide was purchased from Fluka AG and distilled twice under reduced pressure. Benzene-d_6, 99%, and sodium methoxide were obtained from Strem Chemicals. Ethyl chloroformate was obtained from Fluka AG and used as received.

Reactions of Halobenzenes with Sodium Trimethylsiliconide in HMPA: Into a 5 mL tube previously flamed, sodium methoxide (7.5×10^{-4} moles) and HMPA (2.5 mL) were introduced and the tube sealed with a rubber septum. The suspension was stirred with a micro stir bar and was de-oxygenated and blanketed with a nitrogen atmosphere thrice, and left under N_2. The stirred suspension was cooled in an ice bath when hexamethyldisilane (7×10^{-4} moles) was slowly introduced by syringe and the solution left stirring for 20 minutes. Further degassing the solution and filling with N_2 was done one more time. A deep orange solution was obtained, indicating the formation of trimethylsiliconide anion. At this time, the reaction tube was covered with aluminum foil to protect it from laboratory light, and the

halobenzene (2.5×10^{-4} moles) was slowly introduced by syringe through the rubber septum. Reaction times range from 15 minutes to a few hours, depending on the substrate. The mixtures were then cooled down in an ice bath and quenched slowly with water or iodomethane and extracted three times into pentane. The pentane layers were washed twice with doubly distilled water. The organic layers were gathered and dried over sodium sulfate, filtered, evaporated and chromatographed (for isolation purposes, the number of moles of the reactants was scaled up by a factor of 10, and the solvent volume, HMPA, was 7.5 mL) over a 2 mm-thickness plate using a chromatotron (solvent of elution was hexane). The isolated compounds were characterized by standard spectroscopic techniques (^{1}H / ^{13}CNMR, and MS). For GC quantification, the internal standard method was used, employing eicosane as internal standard.

Characterization of Compounds:

Trimethylsilylbenzene, *p-bis*-trimethylsilylbenzene, and mesitylene were characterized by GC/MS analysis and compared with authentic samples.

p-Chlorotrimethylsilylbenzene, *p*-trimethylsilyltoluene , *p*-fluoro-trimethylsilylbenzene, trimethyl mesityl silane, and *p*-trimethylsilylanisole were isolated as described above, and their spectroscopic data matched well with those found in the literature.[1]

***p*-Chloro-trimethylsilylbenzene**. GC/MS EI, m/z:184 (17), 171 (30), 169 (100), 155 (2), 141 (3), 119 (1), 93 (2), 91 (6), 65 (5), 63 (8).

***p*-Trimethylsilyltoluene**. GC/MS EI, m/z:164 (18), 150 (16), 149 (100), 121 (13), 105 (3), 73 (3), 58 (3), 45 (5).

***p*-Fluorotrimethylsilylbenzene.**[1] NMR δ_H (200.133 MHz; $CDCl_3$; Me_4Si): 0.17 (s, 9H), 7.08 (dt, 2H), 7.40 (dt, 2H). GC/MS EI, m/z: 168 (17), 153 (100), 137 (5), 125 (6), 91 (14), 77 (9), 63 (2).

***o*- Fluorotrimethylsilylbenzene.**[2] NMR δ_H (200.133 MHz; $CDCl_3$; Me_4Si): 0.41 (s, 9H), 7.03 (cplx m., 2 H), 7.43 (cplx.m, 2H). GC/MS EI, m/z: 168 (19), 153 (100), 137 (8), 125 (6), 91 (17), 77 (11), 63 (5).

4-Trimethylsilylpyridine.[3] NMR δ_H (200.133 MHz; $CDCl_3$; Me_4Si): 0.28 (s, 9H), 7.36 (dd, 2H, J = 1.5, J = 5.8), 8.55 (dd, 2H, J = 1.5, J = 5.8). NMR δ_C (50.32 MHz; $CDCl_3$;

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[1] Haubold, W.; Herdtle, J.; Gollinger, W. Einholz, W *J.Organomet.Chem.* **1986**, 1-8. Freeburger, M.E.; Hughes, M.; Buell, G.R.; Tierman, T.O.; Splatter, L. *J.Org.Chem.*, **1971**, *36*, 933-937. Moerlin, S.M. *J.Organomet. Chem*, **1987**, *319*, 29-39.

(2) Freeburger, M.E.; Hughes, M.; Buell, G.R.; Tierman, T.O.; Splatter, L. *J.Org.Chem.*, **1971**, *36*, 933-937.

Me_4Si): -1.78, 128.1, 148.7, 150.3. GC/MS EI, m/z: 151 (31), 136 (100), 120 (3), 106 (5), 93 (4), 83 (26), 68 (2), 43 (16).

N-Ethylformate-4-trimethylsilyl-4-hydropyridine.[4] . NMR δ_H (200.133 MHz; $CDCl_3$; Me_4Si): 0.15 (s, 9H), 1.34 (t, 3H), 2.23 (q, 2H), 4.51 (dd, 1H), 5.05 (dd, 2H), 6.31 (dd, 2H). GC/MS EI, m/z: 225 (2), 196 (9), 153 (4), 152 (42), 136 (12), 108 (12), 80 (100), 73 (37), 53 (4), 45 (7). $M^{+\cdot}$ 225.365.

4-Trimethylsilyl-1,4-dihydropyridine.[2] (aromatizes in the isolation process) GC/MS EI, m/z: 153 (25), 152 (50), 138 (5), 79 (41), 73 (100), 59 (11), 52 (25), 43 (11).

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(4) Fowler, F. *J.Org.Chem.*, **1972**, *37*, 1321-1323. Sundberg, R.J.; Hamilton, G.; Trindle, C. *J.Org.Chem.*, **1986**, *51*, 3672-3679.