Radical Reduction of Aromatic Azides to Amines with Triethylsilane

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General Procedure for the Preparation of Azides 1a-u. The already known aryl azides **1a-u** were prepared by diazotization of the corresponding anilines **3a-u**, all commercially available, followed by treatment with sodium azide, according to a standard procedure.¹ All the azides were characterized on the basis of physical and/or spectral data (**1a**,² **1b**,² **1c**,² **1d**,³ **1e**,² **1f**,⁴ **1g**,⁵ **1h**,⁶ **1i**,⁷ **1j**,⁸ **1k**,⁵ **1l**,⁹ **1m**,¹⁰ **1n**,⁹ **1o**,² **1p**,⁷ **1q**,¹¹ **1r**,¹² **1s**,⁹ **1t**,¹³ **1u**¹⁴).

1a: R= OMe

1b: R= Me

1c: R= H

1d: R= CN

1e: R= F

1f: R= Cl

1g: R= Br

1h: R= I

1i: R= COMe

1j: R= COOMe

1k: R= COOH

1l: R= NO₂

1m: R=OMe

1n: R= Cl

1o: R= OMe

1p: R= Me

1q: R= Ph

1r: R= F

1s: R= Cl

1t

1u

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General Procedure for the Preparation of Azides 4a-c. The already known alkyl azides **4a-c** were prepared from the corresponding commercially available bromo-derivatives. An acetone / water (25 mL / 25 mL) solution of the halogenated compound (2 mmol) and sodium azide (6 mmol) was stirred at room temperature until disappearance of the starting reagent. The acetone was removed at reduced pressure and the residue extracted with diethyl ether. Purification on silica-gel using a hexane / diethyl ether (90:10) mixture gave the pure azide in nearly quantitative yield (**4a**,¹⁵ **4b**,¹⁶ **4c**¹⁷).

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GC-MS Spectra of Anilinosilanes 2a-u.

4-methoxy-N-(triethylsilyl)benzenamine 2a:¹⁸ *m/z* (rel. inten.) 237 (80), 208 (100), 180 (48), 152 (34).

4-methyl-N-(triethylsilyl)benzenamine 2b:¹⁸ *m/z* (rel. inten.) 221 (50), 192 (100), 164 (41), 136 (27), 134 (17).

N-(triethylsilyl)benzenamine 2c:¹⁸ *m/z* (rel. inten.) 207 (33), 178 (100), 150 (50), 122 (37), 120 (28).

4-(triethylsilylamino)benzonitrile 2d:¹⁸ *m/z* (rel. inten.) 232 (28), 203 (100), 175 (53), 147 (51), 145 (33).

4-fluoro-N-(triethylsilyl)benzenamine 2e:¹⁸ *m/z* (rel. inten.) 225 (35), 196 (100), 168 (61), 140 (54), 138 (28).

4-chloro-N-(triethylsilyl)benzenamine 2f:¹⁸ *m/z* (rel. inten.) 241 (39), 214 (34), 212 (100), 186 (20), 184 (56), 158 (16), 156 (50), 154 (18).

1-(4-(triethylsilylamino)phenyl)ethanone 2i: *m/z* (rel. inten.) 249 (44), 220 (100), 192 (34).

methyl 4-(triethylsilylamino)benzoate 2j: *m/z* (rel. inten.) 265 (40), 236 (100), 208 (32), 180 (14).

4-(triethylsilylamino)benzoic acid 2k: *m/z* (rel. inten.) 251 (6), 222 (100), 178 (15), 150 (25), 120 (63).

4-nitro-*N*-(triethylsilyl)benzenamine 2l:¹⁸ *m/z* (rel. inten.) 252 (22), 223 (100), 195 (37), 167 (28), 120 (12).

3-methoxy-*N*-(triethylsilyl)benzenamine 2m: *m/z* (rel. inten.) 237 (49), 208 (100), 180 (50), 152 (23), 150 (17).

3-chloro-*N*-(triethylsilyl)benzenamine 2n:¹⁸ *m/z* (rel. inten.) 241 (34), 212 (100), 184 (52), 156 (52).

2-methoxy-*N*-(triethylsilyl)benzenamine 2o: *m/z* (rel. inten.) 237 (21), 208 (18), 193 (100), 164 (37), 136 (12), 135 (12).

2-methyl-*N*-(triethylsilyl)benzenamine 2p:¹⁸ *m/z* (rel. inten.) 221 (39), 192 (100), 164 (30), 162 (16), 134 (17).

2-Phenyl-*N*-(triethylsilyl)benzenamine 2q: *m/z* (rel. inten.) 283 (38), 254 (100), 224 (34), 196 (33).

2-fluoro-*N*-(triethylsilyl)benzenamine 2r: *m/z* (rel. inten.) 225 (29), 196 (24), 168 (100), 140 (28).

2-chloro-*N*-(triethylsilyl)benzenamine 2s:¹⁸ *m/z* (rel. inten.) 241 (28), 212 (100), 186 (20), 184 (60), 156 (44).

***N*-(triethylsilyl)naphthalen-1-amine 2t:** *m/z* (rel. inten.) 257 (44), 228 (100), 198 (20), 170 (30), 143 (13).

***N*-(triethylsilyl)naphthalen-2-amine 2u:** *m/z* (rel. inten.) 257 (62), 228 (100), 200 (44), 172 (19), 170 (21), 143 (22), 129 (30).

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GC-MS spectra for alkylaminosilanes 5a-c.

3-phenyl-*N*-(triethylsilyl)propan-1-amine 5a: *m/z* (rel. inten.) 249 (16), 220 (100), 144 (35), 116 (45), 91 (25).

***N*-(triethylsilyl)undecan-1-amine 5b:** *m/z* (rel. inten.) 285 (4), 256 (100), 144 (47), 116 (10).

5-(triethylsilylamino)pentanenitrile 5c: *m/z* (rel. inten.) 183 ($M^+ - 29$, 100), 142 (35), 128 (44).

Reaction of 4-Methoxyphenyl Azide **1a** in C₆D₅CD₃.

The reaction of 4-methoxyphenyl azide **1a** was also performed in C₆D₅CD₃ solution; in such case, direct ¹H and ¹³C NMR analysis of the resulting reaction mixture monitored the virtually exclusive presence of 4-methoxy-*N*-(triethylsilyl)benzeneamine **2a**¹⁸ [¹H NMR (400 MHz, C₆D₅CD₃) δ 0.55 (q, 6 H, *J* = 8.1 Hz), 0.97 (t, 9 H, *J* = 8.1 Hz), 2.83 (br s, 1 H), 3.41 (s, 3 H), 6.49 (part of AA'BB' system, 2 H, *J* = 8.9 Hz), 6.65 (part of AA'BB' system, 2 H, *J* = 8.9 Hz); ¹³C NMR (100 MHz, C₆D₅CD₃) δ 55.1, 115.1, 117.6, 141.2 (C), 152.9(C)].