A General and Convenient Procedure for the Synthesis of *N*-Alkylarylamines and *N*-Alkylheteroarylamines by Electrophilic Amination of Cuprates with *N*-Alkylhydroxylamines

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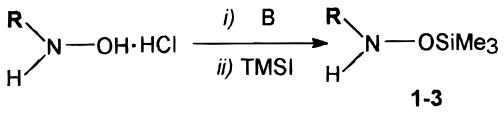
N-Alkylarylamines ArNHR can be prepared by the direct alkylation of primary aromatic amines with alkyl halides,[1] aryl sulfonates,[2] dialkyl phosphites,[3] or dimethyl oxalate,[4] provided that a large excess of the starting amine is used. However, the separation of the product from the reaction mixture is difficult. Tertiary *N*,*N*-(dialkyl)arylamines are invariably byproducts[5] because the *N*-alkylarylamines produced in the first step are more nucleophilic than the starting primary amines.[6] This problem intensifies when *N*-alkylheteroaylamines are considered. Besides the difficulties encountered in the mono-alkylation of 2-aminopyridine in which a competing alkylation reaction at the endocyclic N atom occurs,[7] the N-alkylation of 2-aminothiophene appears to be difficult.[8]

The N-arylation route provides an alternative strategy which might allow one to overcome some of the above-mentioned drawbacks. Direct amination of aromatic compounds remains however a challenging problem of pratical importance in organic synthesis. Although several methods have been reported for N-phenylation of amines in recent years[9] and a noteworthy advancement has been achieved with new methodic developments for hetero-Heck reactions by Hartwig[10] and Buchwald,[11] there is still the need for a general and simple procedure directed at the synthesis of N-substituted anilines.

Scheme 1



1-3

1 : **R** = Me; B = 2, 4, 6-trimethylpyridine; 68% yield
2 : **R** = *i*-Pr; B = Et 3N; 80 % yield
3 : **R** = *t*-Bu; B = Et 3N; 77 % yield

In an earlier paper,[12] we reported that the electrophilic amination of cyanocuprates with bis(trimethylsilyl)hydroxylamine provides suitable entry to primary amines, some of which are otherwise not easily accessible. Commercially available *O*-(trimethylsilyl)hydroxylamine and *O*-benzylhydroxylamine, easily obtained from the corresponding hydrochlorides, upon reaction with cyanocuprates also proved to be highly useful as aminating agents, with no variations being observed with respect to the bis(trimethylsilyl)hydroxylamine in the formation of primary amines.[13] Moreover, the use of our oxidative coupling protocol[14] for the synthesis of secondary amines led in several cases to the formation of overoxidation byproducts. These results prompted us to extend the hydroxylamine-based methodology to the synthesis of *N*-alkylarylamines and -heteroarylamines using *N*-alkyl-*O*-silylhydroxylamines as starting materials. In this paper we disclose a convenient and general method for the synthesis of *N*-methyl-, *N*-isopropyl-, and *N*-*tert*-butyl-substituted arylamines and heteroarylamines through the formation of new N−aryl or N−heteroaryl bonds.

Hydroxylamines **1**−**3** were synthesized in good yields (Scheme 1) from the commercially available hydrochlorides by using 1-(trimethylsilyl)imidazole (TMSI) as the silylating reagent and a suitable base according to a modification of the procedure reported[15] in the literature.

Compounds **1**−**3** reacted under mild conditions with cyanocuprates bearing aromatic and heteroaromatic transferable ligands. Attempts at modifying the organometallic reagent by Cu to Zn transmetalation[14b] did not substantially improve the yields of the reactions. Along with the desired secondary amines (**4**), small amounts of C−C homocoupling byproducts were found in the reaction mixture. The relevant results of the N-arylation and -heteroarylation of *N*-alkylhydroxylamines with organocopper reagents are reported in Table 1.

From hydroxylamines **1**−**3** a wide range of N-arylated and N-heteroarylated secondary amines (**4a**−**s**) could be obtained in satisfactory to good yields. Key features of this N-arylation procedure are the simplicity and the mildness of the reaction conditions. Moreover, the wide applicability of this methodology highlights its synthetic value since for secondary arylamines only scattered

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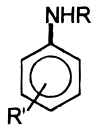
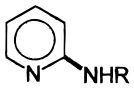
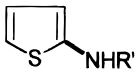
Table 1. N-Arylation and N-Heteroarylation of Hydroxylamines 1−3 with $Ar_2Cu(CN)Li_2$

$(R'\text{-}C_6H_4)_2Cu(CN)Li_2$ + RNH-OSiMe3 (**1-3**) → R'-C_6H_4-NHR (**4**)

Entry	Reagent	Product	4	R	R'	yield[a] (%)
1	**1**		**a**[b]	Me	H	58
2			**b**[c]		*p*-Me	57
3			**c**		*m*-OMe	59
4			**d**[b]		*p*-OMe	88
5	**2**		**e**[d]	*i*-Pr	H	64
6			**f**[c]		*p*-Me	67
7			**g**		*p*-OMe	73
8			**h**		*p*-F	45
9	**3**		**i**[e]	*t*-Bu	H	53
10			**l**[e]		*p*-Me	65
11			**m**[e]		*m*-OMe	73
12			**n**[e]		*p*-F	45
13	**1**		**o**[f]	Me		65
14	**2**		**p**[g]	*i*-Pr		68
15	**3**		**q**[h]	*t*-Bu		70
16	**1**		**r**	Me		60
17	**2**		**s**	*i*-Pr		65

[a] Yields are of isolated products. [b] Reference 16. [c] Reference 17. [d] Reference 18. [e] Reference 19. [f] Reference 20. [g] Reference 21. [h] Reference 22.

methods based on multistep N-alkylation processes in the most favorable cases concerning highly homogeneous series of compounds have appeared in the literature. So far the reported procedure[18] for the preparation of *N*-isopropylarylamines such as **4e**−**h** (entries 5−8) based on the system alcohol/aluminum *tert*-butoxide/Raney nickel appears limited to primary and secondary amines and cannot be employed with MeOH or with tertiary alcohols. On the other hand, the use[17] of environmentally unfriendly solvents such as HMPA or, as in the case of the direct *tert*-butylation,[19] of not easily handled isobutylene or of an excess of reagents under hard reaction conditions, which may pose problems for reactions involving thermally sensitive molecules, makes these procedures scarcely competitive with that herein reported (entries 9−12). The advantage of employing commercially available starting materials may also counterbalance the fact that in several cases the yields in Table 1 are lower (entries 1−3) or comparable (entry 4) with respect to those previously reported.

When applied to the formation of *N*-heteroaryl derivatives, the methodology based on the use of *N*-alkylhydroxylamines appears particularly valuable. Therefore the benzotriazole chemistry,[20] even though successful for the N-alkylation among others of the 2- and 3-aminopyridines with a range of primary and secondary alkyl groups, cannot be applied to the formation of compounds such as RNH−Py, where R is a *tert*-butyl moiety. Moreover, the proposed oxidative variant of this route[22] leads through a multistep sequence only to 20% of 2-(*tert*-butylamino)pyridine. By contrast the compounds **4o**−**q** are obtained in good yields (entries 13−15 in Table 1) according to the one-step N-heteroarylation methodology herein reported. Finally, the hydroxylamine-based electrophilic heteroarylamination provides a unique entry to the new 2-(*N*-alkylamino)thiophene derivatives **4r**,**s** previously not accessible through the N-alkylation route due to the high unstability of 2-aminothiophene.[8]

In summary, we have developed a convenient and highly general method to synthesize *N*-alkyl aromatic and heteroaromatic amines from the corresponding *N*-alkylhydroxylamines and aryl- and heteroarylcuprates which circumvents the restricted range of applicability of most of the previously reported methodologies

Experimental Section

General. Solvents were dried by distillation from a drying agent and stored over 3 Å molecular sieves. All reactions were carried out under nitrogen. Column chromatography was performed on silica gel (70−230 mesh) at normal pressure, or on silica gel (230−400 mesh) at 0.2−0.4 mPa, using the solvent mixtures mentioned below. GC was performed on a chromatograph equipped with a 25 m × 0.25 mm, cross-linked 5% methylphenylsilicone capillary column. CG-MS and HRMS (EI/DP) spectra were obtained at 70 eV. ^{1}H (200 MHz) and ^{13}C (50.3 MHz) NMR spectra were measured in $CDCl_3$ and in C_6D_6 with TMS as internal standard.

Materials. 2-Bromopyridine, 3-bromopyridine, *o*-, *m*-, and *p*-bromotoluenes, *o*-, *m*-, and *p*-bromoanisoles, 1-fluoro-4-iodobenzene,1-(trimethylsilyl)imidazole, *N*-methylhydroxylamine hydrochloride, *N*-isopropylhydroxylamine hydrochloride, *N*-*tert*-butylhydroxylamine hydrochloride, and CuCN, were commercially available and were used without any further purification. The purity of organolithium derivatives was checked according to Gilman.[23]

General Procedure for the Preparation of *N*-Alkyl-*O*-(trimethylsilyl)hydroxylamines 1−3. To a suspension of N-alkylhydroxylamine hydrochloride (50 mmol) in pentane (15 mL) at room temperature was added 60 mol of a suitable base (see Scheme 1 in the text), and after 12 h the mixture was treated dropwise with 7.1 mL (50 mmol) of 1-(trimethylsilyl)-imidazole and stirred for additional 9 h. Then the suspension was filtered through a Celite pad and the solution was evaporated at atmospheric pressure. The crude material was purified by distillation to give the expected product

***N*-Methyl-*O*-(trimethylsilyl)hydroxylamine (1)**: 3.1 g (68%), colorless oil, bp 95 °C. ^{1}H NMR ($CDCl_3$): δ 5.12 (br, 1H,), 2.67 (d, 3H, J = 2.16 Hz), 0.13 (s, 9H). MS *m*/*z* (relative intensity): 119 (M^+, 20), 104 (76), 75 (100), 73 (74), 59 (20), 45 (61), 43 (18). Anal. Calcd for $C_4H_{13}NOSi$: C, 40.29; H, 10.99. Found: C, 40.08; H, 10.66.

***N*-Isopropyl-*O*-(trimethylsilyl)hydroxylamine (2)**: 4.78 g (80%), colorless oil, bp 123 °C. ^{1}H NMR ($CDCl_3$): δ 4.78 (br, 1H), 3.06 (m,1H), 1.00 (d, 6H), 0.13 (s, 6H). MS *m*/*z* (relative intensity): 147 (M^+, 9), 132 (51), 116 (36), 75 (100), 73 (23), 59 (16), 45 (28), 43 (20). Anal. Calcd for $C_6H_{17}NOSi$: C, 48.93; H, 11.63. Found: C, 48.82; H, 11.66.

***N*-*tert*-Butyl-*O*-(trimethylsilyl)hydroxylamine (3)**: 5.13 g (77%), colorless oil, bp 130 °C. ^{1}H NMR ($CDCl_3$): δ 4.51 (br, 1H), 1.01 (s, 9H), 0.13 (s, 9H). MS *m*/*z* (relative intensity): 161 (M^+, 7), 146 (73), 130 (35), 90 (83), 75 (39), 73 (41), 57 (37), 56

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(100). Anal. Calcd for $C_7H_{19}NOSi$: C, 52.13; H, 11.88. Found: C, 52.30; H, 11.47.

General Procedure for the Preparation of Secondary Amines 4a−s. The cyanocuprates were prepared by rapidly adding CuCN (2.00 mmol, 0.179 g) under N_2 flow to the lithium compound (4.00 mmol) in THF (15 mL), cooled at −40 °C. The reaction mixture was stirred until dissolution of the salt, which was generally complete after 20 min. The secondary amines were prepared by adding dropwise the *N*-alkyl-*O*-(trimethylsilyl)-hydroxylamines (2.00 mmol) to a THF solution of cyanocuprate (2.00 mmol) at −50 °C. The temperature was allowed to rise to rt, and after 2 h the dark reaction mixture was filtered through a Celite pad. The solution was evaporated, and the residue was purified by flash chromatography.

***N*-Methylaniline (4a).**[16] The crude product was purified by flash chromatography (benzene/ethyl acetate, 8:2), to give 0.124 g (58%) of a pale yellow liquid whose spectral data were identical to those of the commercial product.

***N*-Methyl-4-methylaniline (4b).**[17] The residue was purified by flash chromatography (petroleum ether/ethyl acetate 9:1) to give 0.139 g (57%) of a yellow oil. The spectral data were identical to those of the commercial product.

***N*-Methyl-3-methoxyaniline (4c).** The crude material was purified by flash chromatography (light petroleum ether/ethyl ether 1:1) to give 0.162 g (59%) of a pale yellow oil. ^{1}H NMR ($CDCl_3$): δ 7.1−6.6 (m, 4H), 3.8 (s, 3H), 3.7 (s, 1H), 2.8 (s, 3H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 147.0, 139.5, 121.4, 116.3, 109.4, 55.5, 30.4. HRMS: calcd for $C_8H_{11}NO$ 137.0841, found 137.0840

***N*-Methyl-4-methoxyaniline (4d).**[16] The crude material was purified by flash chromatography (benzene/ethyl acetate 8:2) to give 0.241 g (88%) of a low melting point material. ^{1}H NMR ($CDCl_3$): δ 6.84−6.79 (m, 2H), 6.64−6.57 (m, 2H), 3.76 (s, 3H), 3.32 (br, 1H), 2.81 (s, 3H). ^{13}C NMR (50.3 MHz,$CDCl_3$): δ 152.22, 143.8, 115.1, 113.7, 55.9, MS *m*/*z* (relative intensity): 137 (M^+, 70), 122 (100), 94 (25), 77 (11), 65 (24), 52 (19).

***N*-Isopropylaniline (4e).**[18] Evaporation of the solvent led to 0.173 g (64%) of a yellow oil whose analytical data matched those of an authentic sample.

***N*-Isopropyl-4-methylaniline (4f).**[17] The crude material was purified by flash chromatography (benzene) to give 0.200 g (67%) of a yellow oil. ^{1}H NMR ($CDCl_3$): δ 7.10−6.59 (m, 4H), 3.78−3.59 (m, 1H), 3.29 (br, 1H), 2.39 (s, 3H), 1.30−1.26 (d, 6H, J = 6.2 Hz). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 145.3, 129.7, 126.2, 113.6, 44.6, 23.1, 20.3. MS *m*/*z* (relative intensity): 149 (M^+, 28), 134 (100), 119 (7), 106 (12), 91 (10), 77 (8), 65 (6), 51 (3).

***N*-Isopropyl-4-methoxyaniline (4g)**. The crude material was purified by flash chromatography (benzene/ethyl acetate 8:2) to give 0.241 g (73%) of a low melting solid. ^{1}H NMR ($CDCl_3$): δ 6.82−6.58 (m, 4H), 3.76 (s, 3H), 3.63−3.50 (m, 1H), 3.18 (br, 1H), 1.22−1.19 (d, 6H, J = 6.3 Hz). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 152.0, 141.8, 114.9, 55.7, 45.2, 23.0. HRMS: calcd for $C_{10}H_{15}NO$ 165.1154, found 165.1155.

***N*-Isopropyl-4-fluoroaniline (4h)**. The crude material was purified by flash chromatography (benzene/ethyl ether 9:1) to give 0.138 g (45%) of a white oil. ^{1}H NMR ($CDCl_3$): δ 6.93−6.64 (m, 2H), 6.56−6.49 (m, 2H), 3.59−3−53 (m, 1H), 3.14 (br, 1H), 1.21−1.18 (d, 6H, J = 6.3 Hz). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 158.0, 144.0, 115.4, 114.3, 45.0, 23.0. HRMS: calcd for $C_9H_{12}NF$ 153.0954, found 153.0953.

***N*-*tert*-Butylaniline (4i)**. The residue was purified by flash chromatography (benzene/ethyl acetate 8:2) to give 0.158 g (53%) of a yellow liquid whose analytical data matched those previously reported in the literature.[19]

***N*-*tert*-Butyl-4-methylaniline (4l).** The crude material was purified by flash chromatography (ethyl acetate/light petroleum ether 9:1) to give 0.212 g (65%) of a pale yellow oil whose analytical data matched those previously reported in the literature.[19]

***N*-*tert*-Butyl-3-methoxyaniline (4m)**. The crude material was purified by flash chromatography (benzene/ethyl ether 8:2) to give 0.262 g (73%) of a low melting point solid whose analytical data matched those previously reported in the literature.[19]

***N*-*tert*-Butyl-4-fluoroaniline (4n)**. Following the usual procedure and workup, the crude material was purified by flash chromatography (benzene/ethyl ether 9:1) to give 0.150 g (45%) of a white oil whose analytical data matched those previously reported in the literature.[19]

2-Methylaminopyridine (4o).[20] To 2 mmol of 2-pyridylcyanocuprate prepared as previously described[10] was added 0.238 mL (2 mmol) of **1** at −60 °C, and the reaction mixture was slowly allowed to reach rt. The dark mixture subjected to the usual workup gave a dark oil that was purified by flash chromatography (ethyl acetate), affording 0.140 g (65%) of a yellow oil. ^{1}H NMR ($CDCl_3$): δ 8.09−8.06 (d, 1H, J = 4.6 Hz), 7.47−7.39 (m, 1H), 6.60−6.53 (m, 1H), 6.40−6.36 (d, 1H, J = 4.6 Hz), 2.90 (s, 3H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 159.6, 148.0, 137.4, 112.7, 106.2, 29.1. MS *m*/*z* (relative intensity): 108 (M^+, 100), 107 (56), 92 (2), 79 (93), 67 (11), 65 (6), 52 (35), 41 (5).

2-Isopropylaminopyridine (4p).[21] The crude material was purified by flash chromatography (benzene/ethyl acetate 9:1) to give 0.185 g (68%) of a yellow oil. ^{1}H NMR ($CDCl_3$): δ 8.12−7.96 (m, 1H), 7.42−7.30 (m, 1H), 6.58−6.21 (m, 2H), 4.49 (br, 1H), 3.95−3.70 (m, 1H), 1.21−1.18 (d, 6H, J = 6.3 Hz). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 158.2, 148.1, 137.2, 112.3, 106.8, 43.0, 22.9. MS *m*/*z* (relative intensity): 136 (M^+, 28), 121 (100), 94 (34), 78 (36), 67 (21), 58 (27), 51 (12).

2-*tert*-Butylaminopyridine (4q).[22] The crude material was purified by flash chromatography (benzene/ethyl acetate 8:2) to give 0.210 g (70%) of a brown oil. ^{1}H NMR ($CDCl_3$): δ 8.06−8.03 (m, 1H), 7.39−7.36 (m, 1H), 6.53−6.41 (m, 2H), 4.49 (br, 1H), 1.41 (s, 9H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 158.5, 148.1, 136.7, 112.3, 108.6, 50.7, 29.6. MS *m*/*z* (relative intensity): 150 (M^+, 24), 135 (100), 95 (33), 994 (98), 78 (28), 67 (49), 57 (7), 52 (7).

2-Methylaminothiophene (4r). The dark violet residue was purified by Kugelrohr distillation (80 °C/ 12 mmHg) to give 0.119 g (60%) of a pale yellow liquid that slowly darkened on exposure to light. ^{1}H NMR ($CDCl_3$): δ 6.7−6.0 (m, 3H), 3.72 (br, 1H), 2.84 (s, 3H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 156.5, 126.3, 110.3, 103.2, 34.4. HRMS: calcd for C_5H_7NS 113.0299, found 113.0297.

2-Isopropylaminothiophene (4s). The solvent was evaporated, and the dark violet residue was purified by Kugelrohr distillation (100 °C/ 12 mmHg) to give 0.165 g (65%) of a pale yellow liquid that slowly darkened on exposure to light. ^{1}H NMR ($CDCl_3$): δ 6.74−6.02 (m, 3H), 3.59 (br, 1H), 3.50−3.38 (m, 1H), 1.24−1.20 (d, 6H, J = 6.3 Hz). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 154.2, 126.1, 110.8, 105.4, 49.4, 22.9. HRMS: calcd for $C_7H_{11}NS$ 141.0612, found 141.0616.

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