

First Regioselective C-2 Lithiation of 3- and 4-Chloropyridines

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We have shown that the BuLi/LiDMAE reagent promotes the clean and regioselective C2 lithiation of 3- and 4-chloropyridines, while other reagents such as LDA or BuLi/TMEDA lead to classical *ortho* lithiation products or mixtures of re-

gioisomers. The method was successfully applied to the preparation of various reactive 2,3- and 2,4-disubstituted pyridines.

Introduction

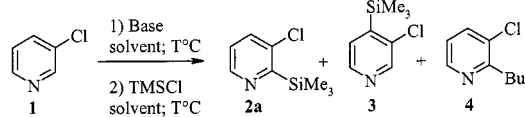
Chloropyridines are particularly versatile compounds. Indeed, their C–Cl bond makes them suitable for subsequent S_NAr ^[1] or organometallic coupling reactions,^[2] while the presence of acidic protons on the pyridine ring offers additional sites for the introduction of new functional groups. Thus, the design of methods allowing for the metallation of chloropyridines with retention of the C–Cl bond is of great synthetic value. Recently, we reported that the BuLi/Me₂N-(CH₂)₂OLi (BuLi/LiDMAE)^[3] reagent performed the regioselective C-6 lithiation of 2-chloropyridine with complete retention of the C–Cl bond.^[4] This unprecedented high level of C–Cl bond tolerance by a BuLi-containing reagent^[5] prompted us to further investigate the lithiation of 3- and 4-chloropyridines. We now report that the BuLi/LiDMAE superbases promotes the clean regioselective C-2 metallation of 3- and 4-chloropyridines, opening a route to new reactive 2,3- and 2,4-disubstituted pyridines.

Results and Discussion

Selective Lithiation and Functionalisation of 3-Chloropyridine (1)

The reaction of 3-chloropyridine with various lithiating agents was investigated. The reactivity of our BuLi/LiDMAE basic system was compared to those of classic reagents by performing some relevant experiments found in the literature (Table 1).

Table 1. Reaction of **1** with lithiating reagents^[a]



Metallation conditions			Condensation conditions			Yields [%] ^[b]			
Base (equiv.)	Solvent	T [°C]	TMSCl (equiv.)	Solvent	T [°C]	1	2a	3	4
LDA (1)	THF	-78	1	THF	-78	-	-	80	-
BuLi (1)/ TMEDA (1)	Et ₂ O	-60	2.2	Et ₂ O	-60	-	60	9	20
BuLi (3)/ LiDMAE (3)	hexane	-60	4	THF	-60	-	80	-	-

^[a] Reaction performed on 2.7 mmol of **1**. – ^[b] Isolated yields after purification on a Chromatotron.

In agreement with previous work, it was shown that LDA^[6a,6b] leads to exclusive lithiation at C-4 and **3** was isolated in 80% yield. On the other hand, the BuLi/TMEDA complex^[7] led mainly to the C-2-substituted product **2a** (60%). However, the latter reaction was found to be less selective. Indeed, careful analysis of the reaction products revealed the presence of **3** as well as a significant amount of the addition product **4** (9 and 20%, respectively).

The results of the BuLi/LiDMAE reaction is in sharp contrast to those obtained above. Indeed, after a short preliminary study (not reported here), we were pleased to find that clean and exclusive C-2 lithiation of **1** could be obtained by performing the metallation at –60 °C in hexane with 3 equiv. of the basic reagent. Under these conditions, no side-products were detected and **2a** was isolated as a single product in 80% yield. It is noteworthy that no addition products were detected, thus underlining the high basicity/nucleophilicity ratio of BuLi/LiDMAE.

The fact that this reaction was particularly clean and regioselective strongly encouraged us to further investigate the lithiation of 4-chloropyridine (**5**).

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Selective Lithiation and Functionalisation of 4-Chloropyridine (**5**)

For comparison, the lithiation of **5** was performed with the BuLi/LiDMAE basic system as well as with classic lithiating reagents (Table 2).

Table 2. Reaction of **5** with lithiating reagents^[a]

Reaction scheme: 4-chloropyridine (**5**) reacts with 1) Base, solvent; T°C and 2) ClSiMe₃, solvent; T°C to form 2-chloro-2-(trimethylsilyl)pyridine (**6a**) and 3-chloro-2-(trimethylsilyl)pyridine (**7**).

Metallation conditions			Condensation conditions			Yields [%] ^[b]		
Base (equiv.)	Solvent	T [°C]	TMSCl (equiv.)	Solvent	T [°C]	5	6a	7
LDA (1)	THF	-70	1	THF	-70	-	-	70
BuLi (1)/ TMEDA (1)	Et ₂ O	-70	1	Et ₂ O	-70	-	-	75
BuLi (3)/ LiDMAE (3)	hexane	-60	3.5	THF	-60	-	50	-
BuLi (4)/ LiDMAE (4)	hexane	-78	5	THF	-78	-	85	-

^[a] Reaction performed on 2.7 mmol of **1**. — ^[b] Isolated yields after purification on a Chromatotron.

Surprisingly, BuLi/LiDMAE led to lithiation exclusively at C-2 of **5**. This unprecedented selectivity strongly contrasted with the classical C-3 lithiation found with LDA^[6a] or BuLi/TMEDA.^[8] Furthermore, while the introduction of a substituent at C-2 had been performed only by means of bromine/magnesium exchange on 2-bromo-4-chloropyridine,^[9] our method simply involved the parent 4-chloropyridine. Note that the conditions previously determined for the lithiation of **1** led to **6a** only in 50% yield without recovery of starting **5**. These differences could be attributed to a lower thermal stability of the 4-chloro-2-lithiopyridine at -60 °C which was then more prone to undergo degradation (see below). Finally, after adjusting the conditions, we found that the temperature of the metallation reaction had to be decreased (-78 °C), and that the amount of base had to be increased (4 equiv.) to obtain **6a** in a very good 85% isolated yield.

Synthesis of C-2-Substituted Chloropyridines

In order to illustrate the versatility and synthetic value of our new methodology for the preparation of C-2-substituted 3- and 4-chloropyridines, we have examined the condensation of various representative electrophiles (see Table 3).

Table 3. Preparation of C-2-substituted 3- and 4-chloropyridines^[a]

Substrate	Electrophile	Product, E =	GC yield [%] ^[b]	Isolated yield [%] ^[c]	
	DCI/D ₂ O ^[d]	D	2b	-	66 (96) ^[e]
	MeSSMe	SMc	2c	90	83
	<i>t</i> -BuCHO	<i>t</i> -BuCH(OH)	2d	86	60
	PhCONMe ₂	COPh	2e	85	69
	I ₂	I	2f	80	66
	CBr ₄	Br	2g	71	47
	C ₂ Cl ₆	Cl	2h	70	60
	DCI/D ₂ O ^[b]	D	6b	-	58 (98) ^[e]
	MeSSMe	SMc	6c	80	64
	<i>t</i> -BuCHO	<i>t</i> -BuCH(OH)	6d	75	51
	PhCONMe ₂	COPh	6e	78	56
	I ₂	I	6f	77	70
	CBr ₄	Br	6g	69	49
	C ₂ Cl ₆	Cl	6h	73	44

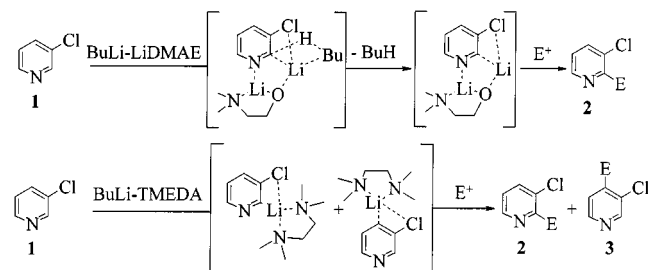
^[a] Reactions performed on 2.7 and 2 mmol of **1** and **5**, respectively. — ^[b] GC yields relative to an internal standard. — ^[c] Isolated yields after column chromatography on silica gel. — ^[d] 10 equiv. were used. — ^[e] In parentheses, deuterium content determined by ¹H NMR.

As shown, the functional derivatives **2b–h** and **6b–h** were prepared in acceptable to very good yields. The deuteration experiments led to high rates of deuterium incorporation, an indication of the formation of chloro-2-lithiopyridines as intermediates. The method was found to be particularly efficient for the preparation of compounds **2f–h** and **6f–h** which have to be considered as useful reactive precursors for further functionalisations. It is worth noting that 4-chloropyridine generally led to good but lower GC yields than 3-chloropyridine, once again underlining the lower stability of the corresponding lithiated intermediate. As a general trend, all the prepared products appeared to be sensitive,^[10] as shown by deviations between the GC and the isolated yields obtained after purification on silica gel. All attempts to optimise the isolated yields by other purification methods, such as chromatography on alumina or distillation, proved to be unsuccessful. After having demonstrated the synthetic usefulness of our methodology, we turned to the explanation of the observed selectivities.

Origin of the Selectivities

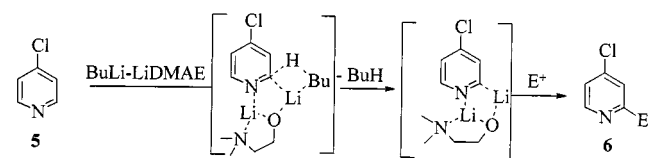
We thought that the exclusive lithiation at C-2 of 3-chloropyridine (**1**) was probably a result of a strong cooperative

complexation of lithium by BuLi/LiDMAE aggregates, and pyridine nitrogen and chlorine atoms (Scheme 1). Such a strong complexation was hardly conceivable with the BuLi/TMEDA complex, thus allowing for the formation of the C-4 isomer in significant amounts when this reagent was used.



Scheme 1

With 4-chloropyridine (**5**), a similar complexation pathway could be postulated. However, the absence of additional complexation of lithium by the chlorine atom in this case offered a weaker stabilisation of the lithium aggregates. This stabilisation was probably favoured by a decrease in the temperature of the metallation reaction from -60 to -78 °C, thus promoting the selective functionalisation at C-2 of **5** (Scheme 2). This interpretation agreed with our previous observations during the metallation of 2-methoxypyridine and pyridine.^[3a,3b]



Scheme 2

Conclusion

In summary, we have shown that BuLi/LiDMAE promoted the clean lithiation at C-2 of 3-chloropyridine and an unprecedented lithiation at C-2 of 4-chloropyridine. The retention of the C–Cl bond obtained in the reaction opens the way to new reactive functional pyridines. Synthetic applications are now under investigation.

Experimental Section

^1H and ^{13}C NMR spectra were recorded with a Bruker spectrometer at 400 and 100 MHz, respectively, with TMS as internal standard and CDCl_3 as solvent; J values are given in Hz. – GC analyses were performed (with an internal standard) with a Shimadzu GC-14A apparatus using an HP1 20-m column and temperature programming. – GC/MS (EI) spectra were recorded with an HP5871 spectrometer. – Melting points were performed with a Tottoli apparatus and are uncorrected. – HRMS analyses were performed by the Service Central d'Analyse du CNRS (Vernaison, France). – Commercially available hexane solutions of BuLi (1.6 M) were used. 4-Chloropyridine (**5**) was prepared by neutralisation (K_2CO_3) of 4-chloropyridine hydrochloride. 3-Chloropyridine (**1**)

and 2-dimethylaminoethanol were distilled before use. All other reagents were used as received. Hexane, THF, and xylene were distilled and stored over sodium wire before use.

General Procedure for C-2 Functionalisation of 3-Chloropyridine (**1**):

A solution of 2-(dimethylamino)ethanol (0.72 g, 8 mmol) in hexane (5 mL) was cooled to ca. -5 °C and BuLi (10 mL, 16 mmol) was added dropwise under nitrogen. After 30 min at 0 °C, the solution was cooled to -60 °C and a solution of 3-chloropyridine (0.306 g, 2.67 mmol) in hexane (5 mL) was added dropwise. After 1 h of stirring, the orange solution was treated dropwise with a solution of the appropriate electrophile (10.67 mmol) in THF (20 mL). The reaction medium was then allowed to warm slowly to room temperature (1 h) and the mixture was hydrolysed at 0 °C with H_2O (20 mL). The aqueous layer was then extracted with dichloromethane (20 mL). The organic layer was dried (MgSO_4) and the solvents were evaporated under reduced pressure. The crude product was analysed by GC and purified by column chromatography. (3-Chloro-2-pyridyl)trimethylsilane (**2a**),^[11] 3-chloro-2-pyridyl methyl sulfide (**2c**),^[1b] and 2-bromo-3-pyridyl chloride (**2g**)^[12] were found to be identical (spectroscopic data) to authentic samples.

3-Chloro-[2- ^2H]pyridine (2b**):** 201 mg (66%), colourless oil; eluent: hexane/AcOEt (95:5). – ^1H NMR (400 MHz, CDCl_3): δ = 7.25 (dd, J = 8.0 and 4.40 Hz, 1 H), 7.7 (d, J = 8.0 Hz, 1 H), 8.5 (d, J = 4.70 Hz, 1 H). – ^{13}C NMR (100 MHz, CDCl_3): δ = 122.9, 131.8, 139.7, 150.7, 152.8, 153.5, 154.2. – MS (EI); m/z (%): 115 (21) [$\text{M}^+ + 1$], 114 (86) [M^+], 79 (100), 51 (20).

1-(3-Chloro-2-pyridyl)-2,2-dimethyl-1-propanol (2d**):** 320 mg (60%), white solid, m.p. 67 – 68 °C; eluent: hexane/AcOEt (75:25). – ^1H NMR (400 MHz, CDCl_3): δ = 0.95 (s, 9 H), 3.75 (d, J = 9.7 Hz, 1 H), 4.90 (d, J = 9.9 Hz, 1 H), 7.15 (dd, J = 8.0 and 4.6 Hz, 1 H), 7.65 (dd, J = 8.0 and 1.2 Hz, 1 H), 8.50 (dd, J = 4.6 and 1.1 Hz, 1 H). – ^{13}C NMR (100 MHz, CDCl_3): δ = 25.8, 37.8, 75.7, 123.1, 131.0, 137.1, 146.2, 158.0. – MS (EI); m/z (%): 199.00 (1) [M^+], 168 (2), 166 (6), 151 (4), 146 (2), 143 (85), 142 (100), 127 (4), 114 (13), 107 (4), 89 (2), 87 (3), 78 (34), 63 (3), 57 (27), 51 (21). – HRMS: calcd. for $\text{C}_{10}\text{H}_{14}\text{ClNO}$ requires 199.0764, found 199.0762.

(3-Chloro-2-pyridyl)(phenyl)methanone (2e**):** 400 mg (69%), yellow oil; eluent: hexane/AcOEt (75:25). – ^1H NMR (400 MHz, CDCl_3): δ = 7.40 (dd, J = 8.3 and 4.8 Hz, 1 H), 7.50 (t, J = 7.7 Hz, 2 H), 7.6 (t, J = 8.4 Hz, 1 H), 7.8 (m, 3 H), 8.55 (dd, J = 4.6 and 1.3 Hz, 1 H). – ^{13}C NMR (100 MHz, CDCl_3): δ = 125.3, 128.5, 129.4, 130.1, 133.9, 135.0, 137.8, 146.9, 154.3, 192.4. – MS (EI); m/z (%): 217 (14) [M^+], 216 (22) [$\text{M}^+ - 1$], 191 (16), 189 (48), 154 (24), 105 (100), 77 (66), 51 (15). – HRMS: calcd. for $\text{C}_{12}\text{H}_8\text{ClNO}$ requires 217.0294, found 217.0290.

2-Iodo-3-pyridyl Chloride (2f**):** 422 mg (66%), yellow solid, m.p. 82 – 84 °C; eluent: hexane/AcOEt (90:10). – ^1H NMR (400 MHz, CDCl_3): δ = 7.30 (dd, J = 7.9 and 4.6 Hz, 1 H), 7.75 (dd, J = 7.9 and 1.7 Hz, 1 H), 8.25 (dd, J = 4.0 and 1.6 Hz, 1 H). – ^{13}C NMR (100 MHz, CDCl_3): δ = 121.4, 123.5, 136.9, 138.1, 148.6. – MS (EI); m/z (%): 239 (48) [M^+], 238 (33), 126 (82), 113 (19), 111 (95), 85 (19), 76 (100), 62 (8), 51 (27). – HRMS: calcd. for $\text{C}_5\text{H}_3\text{ClIN}$ requires 238.9000, found 238.9001.

2,3-Dichloropyridine (2h**):** 237 mg (60%), white solid, m.p. 77 – 79 °C; eluent: hexane/AcOEt (90:10). – ^1H NMR (400 MHz, CDCl_3): δ = 7.25 (dd, J = 7.9 and 4.8 Hz, 1 H), 7.7 (dd, J = 7.9 and 1.6 Hz, 1 H), 8.3 (dd, J = 4.8 and 1.6 Hz, 1 H). – ^{13}C NMR (100 MHz, CDCl_3): δ = 123.1, 130.5, 138.6, 147.1, 149.0. – MS (EI); m/z (%): 148 (62%) [M^+], 147 (100), 114 (31), 112 (98), 85 (13), 76 (33), 51 (10).

General Procedure for C-2 Functionalisation of 4-Chloropyridine (5):

A solution of 2-(dimethylamino)ethanol (0.72 g, 8 mmol) in hexane (5 mL) was cooled to ca. -5°C and BuLi (10 mL, 16 mmol) was added dropwise under nitrogen. After 30 min at 0°C , the solution was cooled to -78°C and a solution of 4-chloropyridine (0.299 g, 2 mmol) in hexane (5 mL) was added dropwise. After stirring for 1 h, the orange solution was treated dropwise with a solution of the appropriate electrophile (10 mmol) in THF (20 mL). The reaction medium was then allowed to warm slowly to room temperature (1 h) and the mixture was hydrolysed at 0°C with H_2O (20 mL). The aqueous layer was then extracted with dichloromethane (20 mL). The organic layer was dried (MgSO_4) and the solvents were evaporated under reduced pressure. The crude product was analysed by GC and purified by column chromatography. (4-Chloro-2-pyridyl)trimethylsilane (**6a**)^[9] and (4-chloro-2-pyridyl)-(phenyl)methanone (**6e**)^[13] were found to be identical (spectroscopic data) to authentic samples.

4-Chloro-[2- ^2H]pyridine (6b): 132 mg (58%), colorless oil; eluent: hexane/AcOEt (95:5). – ^1H NMR (400 MHz, CDCl_3): δ = 7.30 (s, 2 H), 8.50 (s, 1 H). – ^{13}C NMR (100 MHz, CDCl_3): δ = 124.2, 142.5, 151.2, 151.9, 152.6, 154.6. – MS (EI); m/z (%): 115 (24) [$\text{M}^+ + 1$], 114 (75) [M^+], 79 (100), 51 (27).

4-Chloro-2-pyridyl Methyl Sulfide (6c): 204 mg (64%), colorless oil; eluent: hexane/AcOEt (95:5). – ^1H NMR (400 MHz, CDCl_3): δ = 2.55 (s, 3 H), 7.00 (dd, J = 5.3 and 1.9 Hz, 1 H), 7.20 (d, J = 2.0 Hz, 1 H), 8.30 (d, J = 5.32 Hz, 1 H). – ^{13}C NMR (100 MHz, CDCl_3): δ = 13.3, 120.9, 143.6, 149.9, 161.8. – MS (EI); m/z (%): 159 (67) [M^+], 158 (58), 113 (77), 82 (32), 78 (100), 76 (51), 73 (15), 51 (47). – HRMS: calcd. for $\text{C}_6\text{H}_6\text{ClNS}$ requires 158.9909, found 158.9910.

1-(4-Chloro-2-pyridyl)-2,2-dimethyl-1-propanol (6d): 203 mg (51%), viscous yellow oil; eluent: hexane/AcOEt (80:20). – ^1H NMR (400 MHz, CDCl_3): δ = 0.95 (s, 9 H), 4.05 (d, J = 7 Hz, 1 H), 4.35 (d, J = 7 Hz, 1 H), 7.2 (dd, J = 5.3 and 2 Hz, 1 H), 7.25 (s, 1 H), 8.45 (d, J = 5.3 Hz, 1 H). – ^{13}C NMR (100 MHz, CDCl_3): δ = 26.1, 36.3, 80.4, 122.5, 122.9, 143.6, 148.7, 162.0. – MS (EI); m/z (%): 199 (1) [M^+], 184 (1), 166 (2), 113 (17), 77 (22), 56 (25), 50 (20). – HRMS: calcd. for $\text{C}_{10}\text{H}_{14}\text{ClNO}$ requires 199.0764, found 199.0764.

2-Iodo-4-pyridyl Chloride (6f):^[14] 335 mg (70%), yellow oil; eluent: hexane/AcOEt (90:10). – ^1H NMR (400 MHz, CDCl_3): δ = 7.3 (dd, J = 5.3 and 1.8 Hz, 1 H), 7.75 (d, J = 1.84 Hz, 1 H), 8.25 (d, J = 5.32 Hz, 1 H). – ^{13}C NMR (100 MHz, CDCl_3): δ = 117.7, 123.6, 134.5, 144.4, 151.0. MS (EI); m/z (%): 239 (96) [M^+], 127 (13), 114 (32), 76 (100), 51 (6).

2-Bromo-4-pyridyl Chloride (6g):^[15] 189 mg (49%), yellow oil; eluent: hexane/AcOEt (90:10). – ^1H NMR (400 MHz, CDCl_3): δ = 7.30 (dd, J = 5.3 and 1.8 Hz, 1 H), 7.55 (d, J = 1.83 Hz, 1 H), 8.3 (d, J = 5.32 Hz, 1 H). – ^{13}C NMR (100 MHz, CDCl_3): δ = 123.2, 127.2, 142.4, 145.3, 150.6. – MS (EI); m/z (%): 192 (24) [M^+], 191 (19), 112 (81), 106 (8), 81 (74), 76 (100), 75 (43), 51 (57).

2,4-Dichloropyridine (6h):^[15] 131 mg (44%), yellow oil; eluent: hexane/AcOEt (90:10). – ^1H NMR (400 MHz, CDCl_3): δ = 7.25 (d, J = 5.3 and 1.7 Hz, 1 H), 7.35 (d, J = 1.83 Hz, 1 H), 8.3 (d, J = 5.32 Hz, 1 H). – ^{13}C NMR (100 MHz, CDCl_3): δ = 122.8, 124.3, 145.7, 150.1, 152.2. – MS (EI); m/z (%): 149 (36) [M^+], 147 (58), 114 (30), 112 (100), 85 (35), 76 (74), 62 (32), 51 (54).

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