ORTHO-LITHIATION OF 2-(BENZOTHIAZOL-2-YLTHIO)PYRIDINE. PREPARATION OF 2,3-DISUBSTITUTED PYRIDINES

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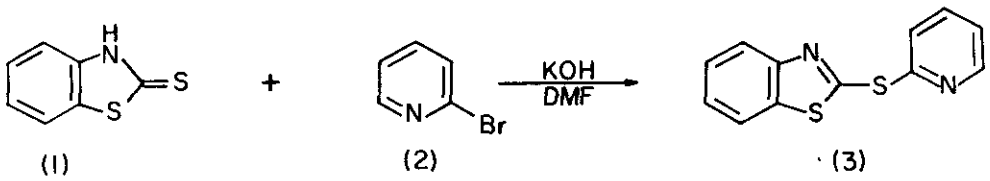
Abstract- 2-(Benzothiazol-2-ylthio)pyridine undergoes lithiation exclusively at the 3-position. The products of reaction with electrophiles of the lithiated species undergo sulfide cleavage to give 3-substituted 2-alkylthiopyridines and/or 3-substituted pyridine-2-thiones.

The introduction of substituents into a pyridine ring is not easy: direct electrophilic substitution is difficult due to the deactivating effect of the pyridine nitrogen[1], and the formation of pyridyl nucleophilic organometallic species also presents various problems. Thus, halopyridines do not form organomagnesium reagents,[2] and organolithiums normally add across the C=N bond rather than metallate a ring CH.[3] Lithio-pyridines (prepared by lithium-halogen exchange) react with electrophiles but, even at very low temperatures, this results in poor yields of substituted pyridines.[2] Recently, the direct metallation of pyridine has been reported;[4] however, this leads to the formation of mixtures of 2-, 3- and 4-pyridyl species.

In recent years, a variety of substituted pyridines has been shown[5] to undergo regioselective ortho metallation.[6] The benzothiazol-2-ylsulphenyl group can stabilize adjacent carbanions by a combination of inductive plus coordinating effects.[7] As an extension of this work, we have now studied the ortho-lithiation of 2-(benzothiazol-2-ylthio)pyridine (3) and subsequent reactions with electrophiles. Further manipulation of the benzothiazole moiety allows the preparation of various 2,3-disubstituted pyridines.

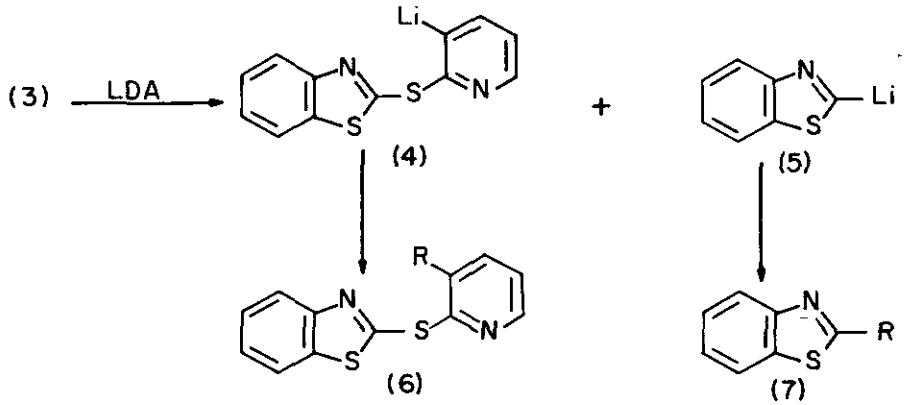
Pyridine (3) had been previously prepared[8] by reaction of 2-bromobenzothiazole with pyridine-2-thione, but is more conveniently available from 2-bromopyridine (2) and benzothiazole-2-thione (1) by refluxing in DMF in the presence of potassium hydroxide (Scheme I).



(1) (2) (3)

Scheme I

The ortho-lithiation of (3) is achieved with LDA/THF at -78°C and the resulting 3-lithio-derivative (4) is trapped at the same temperature with electrophiles to give the corresponding 3-substituted pyridines (6) (Scheme II). Only moderate (52 to 66%) yields of (6) are obtained (Table I) due to the competing attack by the base at the exocyclic sulfur atom resulting in the formation of 2-lithiobenzothiazole (5). The formation of (5) is evidenced by the isolation of the alcohol (7a),[9] when p-tolualdehyde was used as electrophile, as well as benzothiazole (7c) and 2-deuteriobenzothiazole (7d), when trimethylsilyl chloride[10] and CD_3OD were the electrophiles, respectively (see Table I). Benzyl bromide and ethyl p-methylbenzoate as electrophiles gave complex mixtures.



a R = p-$MeC_6H_4CH(OH)$; b R = $SiMe_3$; c R = H; d R = D

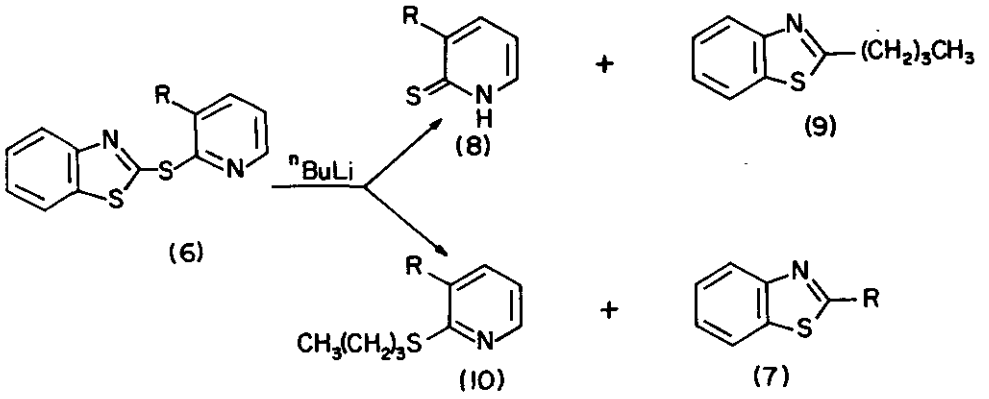
Scheme II

Table I. The Reaction of (3) with LDA and Electrophiles.

Electrophile	Product (6) R	Yield (%)	Product (7) R	Yield (%)
p-MeC_6H_4CHO	p-$MeC_6H_4CH(OH)$	66	p-$MeC_6H_4CH(OH)$	16
Me_3SiCl	Me_3Si	52	H	30
CD_3OD	D	53	D	26

The 2,3-disubstitution pattern in pyridines (6) is demonstrated by the ^{1}H- and ^{13}C-NMR spectra. Thus, the 300 MHz ^{1}H-NMR spectrum of the alcohol (6a) showed a double doublet at δ 8.53, assigned to the pyridine 6-H; the coupling constants ($J_{5,6}$ = 4.7 Hz and $J_{4,6}$ = 1.7 Hz) were in agreement with typical values for reported pyridines.[11] Comparison of the ^{13}C-NMR spectra of the trimethylsilyl derivative (6b) and of the parent pyridine (3) characterized the former. Thus, two doublets (off resonance) were observed for the pyridine C-6 and C-4 in (6b) at δ 149.5 and 143.5, respectively.[12] Additionally, a large downfield shift[13] was observed for the pyridine C-3 carrying the trimethylsilyl group (δ 137.1) with respect to the same carbon in (3) (δ 125.8-120.6). The presence of the deuterium atom at the 3-position of the pyridine (6d) was clearly established from the 200 MHz ^{1}H-NMR spectrum. This showed the pyridine H-4 as a doublet (J = 7 Hz) at δ 7.5, as compared with the parent (3) where H-4 resonated as a triplet (J = 8 Hz) at δ 7.6.

We have recently shown[7] that 2-alkylthiobenzothiazoles are attacked by alkyllithiums at the benzothiazole 2-position to give the corresponding 2-alkylbenzothiazoles and alkyl mercaptans. Application of this reaction to the disubstituted pyridines (6) was expected to lead to the formation of previously unknown 3-substituted pyridine-2-thiones (8) (Scheme III). However, the reaction of the pyridines (3) and (6) with n-butyllithium took different courses depending on the substituent at the 3-position. When this position was unsubstituted (R = H), none of the expected 2-butylbenzothiazole (9) and pyridine-2-thione (8c) were obtained. Instead, 2-butylthiopyridine (10c) (59%) and 2-lithiobenzothiazole (5) were formed; the lithio-derivative (5) was conveniently trapped with p-tolualdehyde to afford the alcohol (7a) (62%). The formation of (7a) and (10c) is a result of the base attacking the exocyclic sulfur atom rather than the benzothiazole 2-carbon, an example of the known tendency of organolithium reagents to cleave sulfur-carbon bonds in sulfides when a stable carbanion can be expelled.[14]



a R = p-$MeC_6H_4CH(OH)$; b R = $SiMe_3$; c R = H

Scheme III

This striking difference with respect to the reaction course in the 2-alkylthiobenzothiazole series is perhaps due to the higher coordinating effect of the pyridine nitrogen (compared with the benzothiazole nitrogen),[15] that directs the attack to the exocyclic sulfur, cf. Figure I.

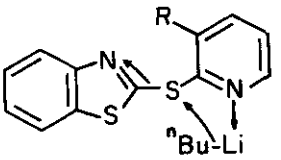


Figure I

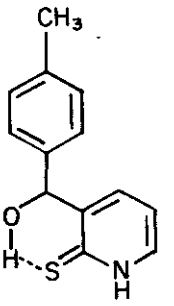
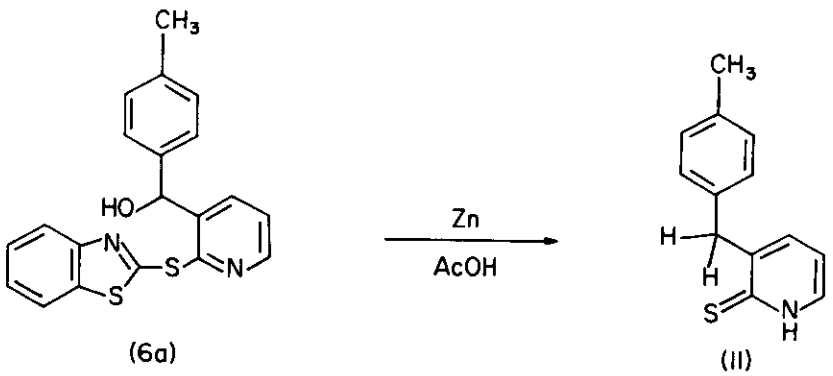


Figure II

The trimethylsilyl derivative (6b), when reacted with n-butyllithium, similarly afforded benzothiazole (7c) (72%) and 2-(butylthio)-3-(trimethylsilyl)pyridine (10b) (75%) as major products. These were accompanied by a small amount (15%) of 2-butylbenzothiazole (9) and, presumably, the pyridinethione (8b). However, this compound was not stable enough (vide infra) to allow its isolation.

Surprisingly, the reaction of the alcohol (6a) with n-butyllithium did give as major products of the reaction 2-butylbenzothiazole (9) (51%) and the pyridinethione (8a) (62%), derived from the attack at the benzothiazole 2-

position, with only small amounts of benzothiazole (7c) (24%) and the sulfide (10a) (28%). We cannot explain the difference in behaviour between (6a) and the other pyridines (3) and (6b).



(6a) (11)

Scheme IV

Desulfurization of the 2,3-disubstituted pyridines would in principle lead to the corresponding 3-substituted pyridines. Simple alkylthiopyridines have been desulfurized with zinc in boiling 50% acetic acid.[16] However, the alcohol (6a) under these conditions gave the pyridinethione (11) (85%) (Scheme IV), characterized by its spectral (^{1}H- and ^{13}C-NMR) properties (decomposed before analysis). The ^{1}H-NMR spectrum of (11) displayed a broad signal for the 6-H at δ 7.5. The broadening of the signal is due to coupling to the adjacent NH proton. A triplet at δ 6.6 was assigned to the pyridine H-5 and the rest of the aromatic protons appeared as a multiplet at δ 7.2-7.1. The benzylic CH_2 protons resonated as a singlet at δ 3.95, whereas the methyl protons gave a singlet at δ 2.2. The ^{13}C-NMR spectrum of (11) showed the thiocarbonyl group at δ 177.2. The pyridine C-3, bearing the p-methylbenzyl group, resonated at δ 142.8 and the pyridine C-5 was characteristically shielded[12] at δ 112.4. In the aliphatic region, the methylene and methyl carbons appeared at δ 38.7 and 20.5, respectively. A product whose TLC characteristics were comparable to (11) was obtained under similar conditions from the trimethylsilyl derivative (6b) but this compound, presumably (8b), could not be characterized since it decomposed during work-up. The stability of the pyridinethione (8a), with respect to (8b) and (11) is probably due to intramolecular hydrogen bonding interactions (Figure II).

EXPERIMENTAL

Melting points were determined on a Kofler hot-stage microscope, and are uncorrected. IR spectra were recorded on a Perkin-Elmer 283B spectrophotometer. ^{1}H-NMR spectra were obtained on a Jeol JNM-PMX60 (60 MHz, continuous wave mode) spectrometer, if unspecified, and Jeol JNM-FX100 (100 MHz, FT mode), Varian XL200 (200 MHz, FT mode) or Nicolet NT300 (300 MHz, FT mode) spectrometers, as specified. ^{13}C-NMR spectra were run on a Jeol JNM-FX100 (25 MHz) or Varian XL200 (50 MHz) spectrometer. Mass spectra were obtained on a AEI MS 30 spectrometer at 70 eV. N,N-Dimethylformamide (DMF) was kept over 4 Å molecular sieves. Tetrahydrofuran (THF) and diethyl ether were dried by distillation from sodium-benzophenone ketyl. Diisopropylamine was distilled over calcium hydride, and then stored over sodium hydroxide under an argon atmosphere. All reactions involving alkyllithium reagents were carried out in a dry argon atmosphere. Flash chromatography was carried out using MCB silica gel (230-400 mesh).

Preparation of 2-(Benzothiazol-2-ylthio)pyridine (3).

Benzothiazol-2-thione (31.5 g, 188 mmol) was added to a solution of potassium hydroxide (12.4 g) in ethanol (100 ml), and the mixture stirred until complete disolution took place. The solvent was evaporated under reduced pressure (20 mmHg) and the remaining solid dried in vacuo (60 °C/1 mmHg). The solid was dissolved in DMF (70 ml) and 2-bromopyridine (20 g, 126 mmol) added to the solution. The mixture was stirred and refluxed for 22 h. The solvent was removed under reduced pressure (10 mmHg) and the residue extracted between benzene and water. The organic layer was washed with 1 N NaOH, followed by water, and dried over $MgSO_4$. Evaporation of the solvent gave an oil that solidified on standing. The solid was triturated in cyclohexane to afford the product (3) as a white-cream solid, mp 63-65 °C; recrystallized from methanol (20 g, 60%), needles, mp 67-68 °C; IR ($CHBr_3$) 1570 (m), 1510 (w), 1450 (m), 1410 (s), 1310 (w), 1280 (w), 1240 (w), 1090 (w), 1040 (w), 1020 (w), 1020 (w), 1000 (m), 990 (m), 760 (s), 720 (m) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 8.7 (d, J=4Hz, 1 H), 8.2-7.1 (m, 7 H); ^{13}C-NMR (25 MHz) ($CDCl_3$) δ 162.1, 154.2, 152.3, 149.5, 137.0, 135.8, 125.8, 124.6, 122.0, 120.6. Found: C, 59.20; H, 3.24; N, 11.46. $C_{12}H_8N_2S_2$ requires C, 59.01; H, 3.27; N, 11.47.

General Method for the Lithiation of (3) and Reactions with Electrophiles.

A solution of (3) (1.22 g, 5 mmol) in THF (10 ml) was added to a solution of LDA [from diisopropylamine (0.92 ml) and 2.0 M (in hexane) n-butyllithium (3 ml, 6 mmol) in THF (40 ml) at -78°C. The resulting strong red solution was stirred at -78°C for 1 h. The electrophile (6 mmol) was added, and the solution stirred at -78°C for the appropriate time (see below). The reaction mixture was poured into saturated aqueous ammonium chloride (100 ml), extracted with chloroform (3 x 50 ml) and the organic extracts washed with water and dried ($MgSO_4$). Evaporation of the solvents left an oily residue that was purified as indicated below to give the products (6) and (7).

Reaction with p-Tolualdehyde.

Reaction time, 90 min. The residue after evaporation was stirred in hexanes, upon which crystallization took place to afford 2-(benzothiazol-2-ylthio)-3-[hydroxy(4-methylphenyl)methyl]pyridine (6a) (0.76 g). The remaining hexanes solution was evaporated and the residue subjected to flash chromatography (benzene-ethyl acetate, 19:1) to afford further 0.30 g of (6a) (total yield, 66%). Also eluted during the chromatography was (7a) (0.20 g, 16%), mp 124-126°C (lit.[7] mp 127-130°C), identical in spectral (IR, ^{1}H- and ^{13}C-NMR) properties and R_f value with an authentic sample.[7] Data for (6a): mp (benzene) 152-153°C; IR ($CHBr_3$) 3400-3100 (m, b, OH), 1570 (m), 1560 (m), 1500 (w), 1440 (m), 1410 (s), 1400 (s), 1310 (m), 1270 (m), 1240 (m), 1200 (w), 1170 (m), 1080 (s), 1030 (s), 1010 (m), 850 (m), 810 (s), 790 (m), 760 (m), 750 (s), 740 (m), 720 (m) cm^{-1}; ^{1}H-NMR (300 MHz) (DMSO-d_6) δ 8.53 (dd, J = 4.7, 1.7 Hz, 1 H), 8.00 (m, 2 H), 7.90 (dd, J = 7.0, 1.1 Hz, 1 H), 7.50-7.40 (m, 3 H), 7.23 (d, J = 8 Hz, 2 H), 7.12 (d, J = 8 Hz, 2 H), 6.18 (d, J = 4.4 Hz, 1 H, OH), 5.97 (d, J = 4.4 Hz, 1 H), 2.24 (s, 3 H); ^{13}C-NMR (25 MHz) (DMSO-d_6) δ 161.1, 149.7, 148.7, 145.8, 138.7, 137.7, 134.8, 133.7, 133.5, 126.9, 125.3, 124.2, 122.8, 121.0, 119.8, 119.3, 68.9, 18.9. Found: C, 66.24; H, 4.42; N, 7.60. $C_{20}H_{16}N_2OS_2$ requires C, 65.93; H, 4.39; N, 7.69.

Reaction with trimethylsilyl chloride.

Reaction time, 4 h. The residue after evaporation was purified by flash chromatography (dichloromethane). This gave in succesive order of elution benzothiazole (7c) (0.20 g, 30%) (identified by comparison with an authentic sample of the commercially available material) and 2-(benzothiazol-2-ylthio)-3-(trimethylsilyl)pyridine (6b) (0.82 g, 52%), needles from hexanes, mp 97-98°C; IR ($CHBr_3$) 2960 (m), 2800 (w), 1550 (m), 1510 (w), 1450 (m), 1420 (m), 1410 (m), 1360 (s), 1310 (m), 1260 (w), 1250 (s), 1200 (m), 1180 (m), 1160 (m), 1130 (m), 1010 (m), 1000 (s), 840 (s), 790 (m), 750 (s), 720 (m) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 8.7 (m, 1 H), 8.2-7.1 (m, 6 H), 0.4 (s, 9 H); ^{13}C-NMR (25 MHz) ($CDCl_3$) δ 164.4, 158.3, 152.1, 149.5, 143.4, 137.1, 135.6, 125.8, 124.3, 122.1, 121.9, 120.6, -0.87. Found: C, 56.84; H, 5.15; N, 8.65. $C_{15}H_{16}N_2S_2Si$ requires C, 56.96; H, 5.06; N, 8.86.

Reaction with Deuteriomethanol.

Reaction time, 3 h. The oil that was obtained after evaporation was subjected to flash cromatography (benzene-ethyl acetate, 20:1) to yield in successive order of elution 2-deuteriobenzothiazole (7d) (0.18 g, 26%) (ca. 90% deuterium incorporation) and 2-(benzothiazol-2-ylthio)-3-deuteriopyridine (6d) (0.65 g, 53%) (ca. 85% deuterium incorporation). Data for (7d): ^{1}H-NMR ($CDCl_3$) δ 9.1 (s, ca. 0.1 H), 8.4-7.8 (m, 2 H), 7.7-7.3 (m, 2 H). Data for (6d): ^{1}H-NMR (200 MHz) ($CDCl_3$) δ 8.56 (b, 1 H), 7.97 (d, J = 8 Hz, 1 H), 7.76 (d, J = 8 Hz, 1 H), 7.56 (d, J = 7 Hz, 1 H), 7.48-7.11 (m, 3 H); ^{13}C-NMR (50 MHz) (CDC13) δ 162.01, 153.75, 152.05, 149.29, 136.88, 136.77, 135.59, 125.67, 124.51, 121.95, 121.84, 120.50.

Cleavage of (3) with n-Butyllithium.

n-Butyllithium (2.2 mmol) was added dropwise to a stirred solution of (3) (0.49 g, 2 mmol) in diethyl ether (20 ml) at -78°C and the solution was stirred at -78°C for 1 h. A solution of p-tolualdehyde (0.26 ml, 2.2 mmol) in ether (2 ml) was added and the mixture stirred at -78°C for 4 h. The reaction mixture was poured into water (20 ml) and the whole extracted with dichloromethane (3 x 15 ml). The organic extracts were washed with water and dried ($MgSO_4$). Evaporation of the solvents left an oily solid that was stirred in cyclohexane and filtered to afford (7a) (0.32 g, 62%), mp 124-126°C (lit.[7] mp 127-130°C), identical in spectral (IR, ^{1}H- and ^{13}C-NMR) properties and R_f value with an authentic sample.[7] Evaporation of the filtrate gave an oil that was treated with dilute hydrochloric acid (3 ml) and extracted with ether (3 x 5 ml). The aqueous layer was treated with 1 N NaOH until alkaline, and extracted with ether (3 x 5 ml). These organic extracts were dried ($MgSO_4$) and the solvent evaporated to give 2-butylthiopyridine (10c) (0.20 g, 59%); IR (neat) 3060 (w), 3040 (w), 2950 (s), 2920 (s), 2860 (s), 1575 (s), 1550 (m), 1450 (s), 1410 (s), 1375 (w), 1275 (m), 1140 (m), 1120 (s), 1040 (m), 980 (m), 905 (w), 885 (w), 870 (w), 750 (s), 720 (s) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 8.6 (d, 1 H), 7.7-6.8 (m, 3 H), 3.2 (t, J = 7.5 Hz, 2 H), 2.9-0.7 (m, 7 H); ^{13}C-NMR (50 MHz) ($CDCl_3$) δ 159.49, 149.25, 135.60, 121.94, 118.96, 31.30, 29.67, 21.93, 13.56. Found: M^+ 167.0768. Calc. for $C_9H_{13}NS$ M^+ 167.0768.

Cleavage of (6a) with n-Butyllithium.

n-Butyllithium (3.3 mmol) was added dropwise to a solution of (6a) (0.55 g, 1.5 mmol) in THF (30 ml) at -78°C and the solution was stirred at that temperature for 1 h. The resulting red solution was poured into saturated aqueous ammonium chloride (30 ml) and the whole extracted with chloroform (3 x 30 ml). The organic extracts were washed with water, dried ($MgSO_4$) and the solvents evaporated to give an oil that was stirred with cyclohexane to afford 3-[hydroxy(4-methylphenyl)methyl]pyridine-2-thione (8a) (0.22 g, 62%), plates from chloroform, mp 174-175°C; IR ($CHBr_3$) 3440 (m), 3005 (s), 1600 (m), 1560 (w), 1430 (w), 1280 (w), 1130 (s), 1010 (w), 795 (m), 780 (w), 755 (w), 730 (w), 685 (s) cm^{-1}; ^{1}H-NMR (200 MHz) (DMSO-d_6) δ 7.72 (d, J = 7.5 Hz, 1 H), 7.60 (b, 1 H), 7.35 (d, J = 7.5 Hz, 2 H), 7.05 (d, J = 7.5 Hz, 2 H), 6.83 (t, 1 H), 6.28 (s, 1 H), 5.82 (bs, 1 H), 3.4 (b, NH), 2.26 (s, 3 H); ^{13}C-NMR (50 MHz) (DMSO-d_6) δ 175.15, 146.62, 140.85, 136.34, 135.70, 134.65, 128.21, 126.57, 112.85, 70.18, 20.67. Found: C, 67.28; H, 5.66; N, 5.89. $C_{13}H_{13}NOS$ requires C, 67.50; H, 5.66; N, 6.05.

The cyclohexane filtrate was evaporated to dryness and the remaining oil subjected to flash chromatography (hexanes-ethyl acetate, 19:1). In successive order of elution were obtained: 2-butylbenzothiazole (9) (0.15 g, 51%) (identical in R_f, IR, ^{1}H- and ^{13}C-NMR with an authentic sample[7]), benzothiazole

(0.05 g, 24%) (characterized as above) and 2-butylthio-3-[hydroxy(4-methylphenyl)methyl]pyridine (10a) (0.12 g, 28%), as an oil; IR (neat) 3500-3200 (m, OH), 3040 (w), 3020(w), 2950 (s), 2920 (s), 2860 (s), 1570 (s), 1555 (m), 1505 (m), 1450 (m), 1400 (s), 1170 (s), 1120 (m), 1105 (w), 1070 (m), 1020 (s), 1010 (s), 985 (w), 900 (w), 855 (w), 800 (s), 760 (s), 735 (m), 720 (m) cm^{-1}; ^{1}H-NMR (100 MHz) ($CDCl_3$) δ 8.30 (dd, J = 2, 5 Hz, 1 H), 8.25 (dd, J = 2, 8 Hz, 1 H), 7.15 (AB q, J = 8 Hz, 4 H), 6.95 (dd, J = 5, 8 Hz, 1 H), 5.96 (s, 1 H), 3.40-2.80 (m, 3 H), 2.29 (s, 3 H), 1.55 (m, 4 H), 0.90 (t, J = 7 Hz, 3 H); ^{13}C-NMR (25 MHz) ($CDCl_3$) δ 156.6, 147.8, 138.7, 137.5, 137.1, 133.6, 129.1, 127.0, 119.2, 71.4, 31.3, 30.1, 22.0, 21.0, 13.6. Found: C, 70.90; H, 7.40; N, 4.79. $C_{17}H_{21}NOS$ requires C, 71.05; H, 7.36; N, 4.87.

Cleavage of (6b) with n-Butyllithium.

n-Butyllithium (1.5 mmol) was added dropwise to a solution of (6b) (0.47 g, 1.5 mmol) in THF (15 ml) at -78°C and the solution was stirred at that temperature for 1 h. The same work-up as for the reaction of (6a) gave an oil that, after flash chromatography (hexanes-ethyl acetate, 19:1), afforded in successive order of elution: (7c) (0.14 g, 72%) (characterized as above), 2-(butylthio)-3-(trimethylsilyl)pyridine (10b) (0.26 g, 75%) and (9) (0.04 g, 15%) (characterized as above). Data for (10b): oil; IR (neat) 3030 (w), 2950 (s), 2920 (s), 2870 (m), 2850 (m), 1540 (s), 1460 (w), 1400 (w), 1360 (s), 1245 (s), 1200 (w), 1135 (s), 1060 (m), 1035 (w), 845 (s), 840 (s), 835 (s), 785 (w), 760 (s), 680 (w), 640 (m), 610 (w) cm^{-1}; ^{1}H-NMR (200 MHz) ($CDCl_3$) δ 8.37 (dd, J = 2, 5 Hz, 1 H), 7.57 (dd, J = 2, 7 Hz, 1 H), 6.92 (dd, J = 5, 7 Hz, 1 H), 3.23 (t, J = 7 Hz, 2 H), 1.76-1.36 (m, 4 H), 0.92 (t, J = 7 Hz, 3 H), 0.37 (s, 9 H); ^{13}C-NMR (50 MHz) ($CDCl_3$) δ 157.44, 142.19, 135.03, 126.34, 111.74, 24.48, 23.61, 15.12, 6.73, -8.01. Found: C, 60.04; H, 8.84; N, 5.82. $C_{12}H_{21}NSSi$ requires C, 60.19; H, 8.83; N, 5.84.

Reduction of (6a).

To a solution of (6a) (0.36 g, 1 mmol) in 50% acetic acid (4 ml)was added zinc foil (0.3 g) and the mixture was refluxed for 4 h. Evaporation of the solvent gave a gummy solid that was treated with 1 N NaOH (4 ml) and extracted with ether (3 x 4 ml). The organic extracts were washed with water and dried ($MgSO_4$). The solvent was evaporated and the residue was purified by flash chromatography (benzene-ethyl acetate, 9:1) to afford 3-[(4-methylphenyl)methyl]pyridine-2-thione (11) (0.18 g, 85%); ^{1}H-NMR (200 MHz) (DMSO-d_6) δ 7.52 (b, 1 H), 7.2-7.0 (m, 5 H), 6.64 (t, 1 H), 3.95 (s, 2 H), 3.48 (b, 1 H, NH), 2.20 (s, 3 H); ^{13}C-NMR (25 MHz) (DMSO-d_6) δ 177.2, 142.8, 136.4, 135.9, 135.7, 134.9, 128.8, 112.4, 38.7, 20.5.

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