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# Metalation Reactions. XXIV. Metalation of (Vinylthio)benzene

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**Abstract:** The addition of organolithium compounds to (vinylthio)benzene (**1**) and then an electrophilic quenching followed by a further metalation/electrophilic quenching is a general method to prepare in one pot (alkylthio)benzenes *ortho,alpha*-substituted with equal or different groups. The direct dimetalation of **1** affords the *ortho, alpha*-dilithiated species **15** besides other by-products. Starting from **15** it is possible to obtain in one step *ortho,alpha*-substituted (vinylthio)benzenes and heterocyclic compounds. © 1998 Elsevier Science Ltd. All rights reserved.

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It was previously shown that (alkylthio)benzenes undergo mono and dimetalation by butyllithium or superbases to yield mono and dianionic intermediates useful to prepare, after electrophilic quenching, benzenes bearing new substituents on the ring or in the *alpha* position of the thioethereal group.[1-3]

We have now examined the synthetic power of the reactions between organolithium compounds and (vinylthio)benzene (**1**). Our interest in this molecule is connected to the synthesis of natural products[4] and is due to its three potential reactive sites: the *alpha* and the *ortho* carbon and the double bond. Moreover, its derivatives can be considered as precursors of carbonyl compounds and their derivatives.[5-9]

The literature reports only studies on the α-metalation of this substrate, and on the metalated intermediates derived from addition of the organolithium to the double bond.[5,7-10] Nothing at all is reported about the direct dimetalation reaction. We now report our studies on these topics with the aim to obtain 1,2-disubstituted benzenes with an α-substituted thiovinyl or thioalkyl group and benzocondensed heterocycles containing an exocyclic double bond available of further functionalization. The α-lithiation of (vinylthio)benzene is a well-known reaction: it can be achieved through various procedures and by various lithiating reagents. Parham and Motter[9] using butyllithium in diethyl ether at 0°C obtained the product derived from the addition of the organolithium to the carbon-carbon double bond. To avoid this side reaction Ager[8] used the same reagent at -90°C, while Cookson[4] and Magnus[7] proposed lithium diisopropylamide (LDA) as α-metallating reagent: in this way α-substituted


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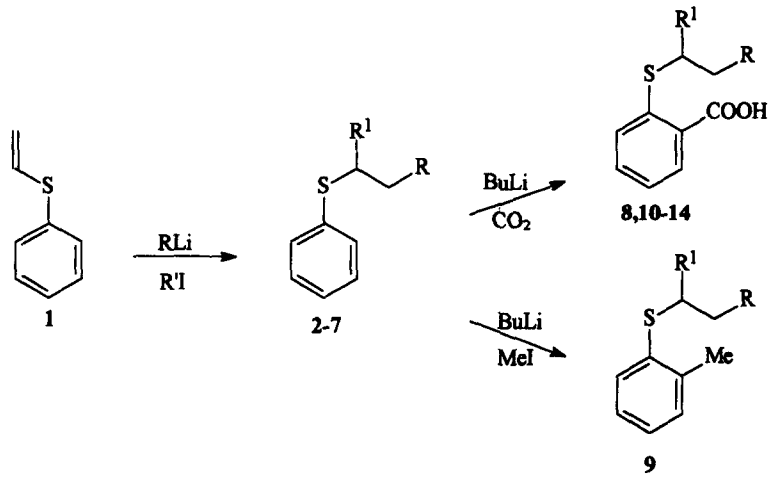
products can be prepared in high yield. Schlosser α-metalated (vinylthio)benzene using the superbases.[10]

The reaction between one molar equivalent of the 1:1 mixture butyllithium/TMEDA and an ethereal solution of (vinylthio)benzene at 0°C affords the (α-lithiohexylthio)benzene that, after quenching with iodomethane or iodoethane, yields the α-hexylthio derivatives **2** and **3**, respectively. These compounds can be monometalated in one-pot and then quenched with another electrophile (carbon dioxide, or iodomethane) to give the *ortho,alpha*-disubstituted products **8-10** (Scheme 1). Analogously, treatment of **1** with one molar equivalent of propyllithium/TMEDA followed by quenching with iodomethane or iodoethane affords the α-methyl- and α-ethylpentylthio derivatives **4** and **5**, which are converted in one pot into the *ortho*-substituted benzoic acids **11** and **12** by further metalation and quenching with carbon dioxide. A similar procedure employing one molar equivalent of methyllithium/TMEDA gives the α-substituted propylthio derivatives **6** and **7** that are easily converted into the corresponding acids **13** and **14**.



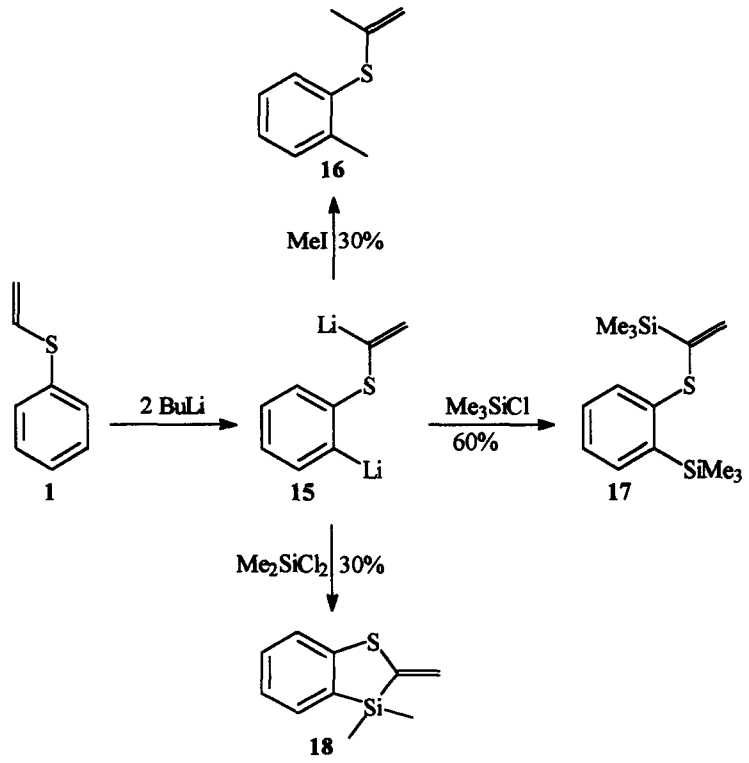

| Compound | R | $R^1$ | Yield (%) | Compound | R | $R^1$ | Yield (%) |
|---|---|---|---|---|---|---|---|
| **2** | Bu | Me | 88 | **9** | Bu | Me | 64 |
| **3** | Bu | Et | 84 | **10** | Bu | Et | 68 |
| **4** | Pr | Me | 86 | **11** | Pr | Me | 74 |
| **5** | Pr | Et | 82 | **12** | Pr | Et | 66 |
| **6** | Me | Me | 85 | **13** | Me | Me | 75 |
| **7** | Me | Et | 79 | **14** | Me | Et | 61 |
| **8** | Bu | Me | 71 | | | | |

Scheme 1

Then we examined the direct dimetalation reaction using various metallating reagents.

The use of LDA yields a mixture of α-metalation and elimination products even employing a large excess of this reagent (two, three, four moles of LDA per mole of sulphide). This result is not surprising since LDA is not basic enough to abstract an aromatic

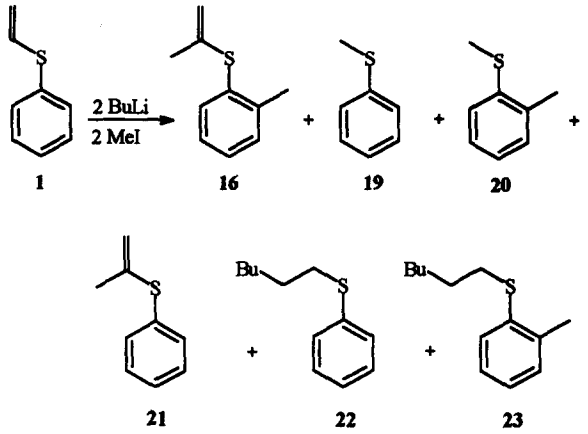
hydrogen, less acidic than the *alpha* one. The use of LITMP (lithium 2,2,6,6-tetramethylpiperidide) yields the α-metalated product with 100% selectivity. Trying to suppress the unwanted addition of butyllithium to the double bond,[7,8] we first worked at -80°C: we obtained the α-metalation product (30%) besides starting material (17%) and other side products. We obtained unsatisfactory results even operating at -10°C or using *tert*-butyllithium. So we employed two molar equivalents of butyllithium at 0°C. In this way we prepared the *ortho,alpha*-dilithiated intermediate **15** (Scheme 2) that, after quenching with iodomethane or chlorotrimethylsilane allowed us to prepare the *ortho,alpha*-disubstituted products **16, 17**.




Scheme 2

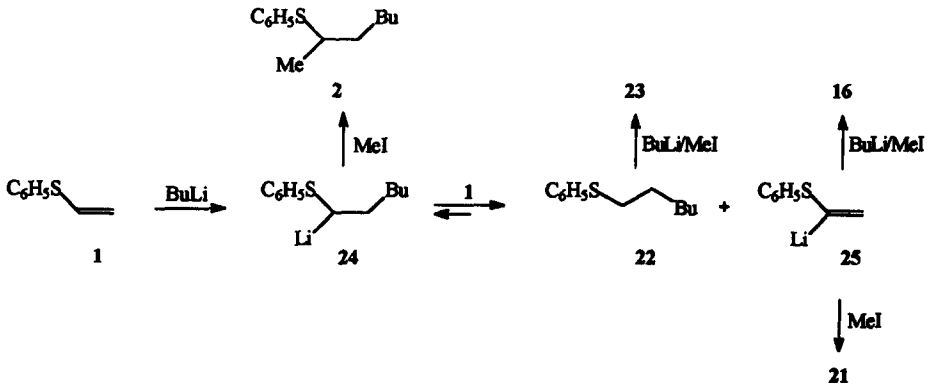
Quenching the intermediate **15** with dichlorodimethylsilane we prepared the heterocyclic compound **18** containing an exocyclic double bond.

Unfortunately the yields of the wanted products were always lowered by many by-products as showed by the GC/MS analysis of the reaction mixture. The products obtained from quenching with iodomethane (Scheme 3) were, besides **16**, (methylthio)benzene (**19**), 1-methyl-2-(methylthio)benzene (**20**), [(1-methylvinyl)thio]benzene (**21**), (hexylthio)benzene (**22**) and 2-(hexylthio)-1-methylbenzene (**23**) in the following ratios: **16**:**19**:**20**:**21**:**22**:**23** = 26:11:10:3:5:18.




Scheme 3

The product **19** can arise from the reaction of iodomethane with the thiophenoxide formed by an elimination process. The same thiophenoxide can undergo a further *ortho*-metalation to give **20** after quenching with iodomethane.[11] Another alternative route to **20** can be an elimination in the compound **16** to give lithium 2-(methylthio)phenoxide and then **20** after quenching with iodomethane. The presence of **22** can be explained (Scheme 4) supposing the primary formation of the intermediate **24** by an addition of butyllithium to **1**. This intermediate can in its turn react with **1** to give **22** and the α-metalated **25**. This last hypothesis is supported by an experiment in which we reacted the sulphide **1** (Scheme 4) with one mole of butyllithium at 0°C: the monolithiated intermediate **24** was revealed by quenching with iodomethane to obtain **2**. This intermediate was then reacted with another portion of **1**: now acting as the metallating reagent gave the α-lithiated **25** and was converted into **22**. The intermediate **25** can react with iodomethane to give the monosubstituted **21** or it can be metalated to give **16** after quenching. Finally **23** can be formed by a further *ortho*-metalation/quenching with iodomethane of **22**.




Scheme 4

## EXPERIMENTAL

The GC-MS analyses were performed at 70 eV with a Hewlett Packard 5989A GC-MS system with HP 5890 GC fitted with a capillary column (50 m x 0.2 mm) packed with DH 50.2 Petrocol (0.50 μm film thickness). $^{1}H$ and $^{13}C$ NMR spectra spectra were recorded on a Varian VXR-300 spectrometer with tetramethylsilane as internal reference. δ values were given in ppm and J in Hz. IR spectra were recorded on a Perkin-Elmer 1310 grating spectrophotometer. Microanalyses were carried out on a Carlo Erba model 1106 Elemental Analyzer. The TLC analyses were carried out on silica gel 60 F254 plates (Merck). All flash-chromatographies were performed on silica G60 (Merck) columns.

Commercially available reagent-grade starting materials and solvents were used. Solutions of butyllithium in hexane (1.6 M) and methyllithium in diethyl ether (1.5 M) were obtained from Aldrich Chemical Company. Solutions of propyllithium in diethyl ether (1.4 M) were prepared from literature methods.[12,13] All the organolithium solutions were analysed by the Gilman double titration method before use.[14] *N,N,N',N'*-tetramethyl-1,2-diaminoethane (TMEDA) was obtained from the Aldrich Chemical Company and distilled from calcium hydride before use. Diethyl ether and tetrahydrofuran were dried by distillation from sodium benzophenone ketyl before use.

*Starting material*

(Vinylthio)benzene (**1**) was a commercial product (Aldrich Chemical Company).

*Authentic samples*

(Methylthio)benzene (**19**) was a commercial product (FLUKA AG). 1-Methyl-2-(methylthio)benzene (**20**), [(1-methylvinyl)thio]benzene (**21**) and (hexylthio)benzene (**22**) were prepared by reported methods.[9-11]

*2-(Hexylthio)-1-methylbenzene (23).* This compound was obtained starting from 2-methylbenzenethiol and 1-bromohexane. Yield 78%; bp 165-168/30 mm Hg; $^{1}H$ NMR ($CDCl_3$): δ 0.93 (t, 3H, $CH_3CH_2$, J = 7.5), 1.34 (m, 4H, $CH_3CH_2CH_2$, J = 7.5), 1.48 (m, 2H, $CH_2CH_2CH_2S$), 1.70 (m, 2H, $CH_2CH_2S$), 2.40 (s, 3H, $CH_3$-Ar), 2.93 (t, 2H, $CH_2S$, J = 7.5), 7.20 (m, 4H, Ar-*H*); $^{13}C$ NMR ($CDCl_3$): δ 136.8, 134.5, 130.0, 126.1, 125.5, 124.2, 34.8, 32.6, 30.8, 28.3, 22.7, 17.1, 14.0; MS *m/z* 208 ($M^+$).
Anal. Calcd for $C_{13}H_{20}S$: C, 74.94; H, 9.67; S, 15.39. Found: C, 74.87; H, 9.61; S, 15,20.

*General Procedure for the Introduction of Two Different Electrophiles on 1.*

A solution of **1** (2 g, 15 mmol) in anhydrous diethyl ether (50 ml) was gradually added under nitrogen to a vigorously stirred solution of the proper organolithium (16 mmol) and TMEDA (1.8 g, 16 mmol) in anhydrous diethyl ether (20 ml) and stirring was continued at the same temperature for almost 2 hours. The resulting mixture was then treated dropwise with the first electrophile (16 mmol) in anhydrous diethyl ether (10 ml), allowed to warm and left

at room temperature for 2 hours with stirring. Butyllithium in hexane (12.5 ml, 20 mmol) was added dropwise at 0°C to this solution. When the addition was complete, the mixture was stirred at the same temperature for almost 2 hours and then poured onto *ca.* 50 g of crushed solid carbon dioxide. After 24 hours the residue was treated with 10% aqueous sodium hydroxide and then with diethyl ether. The alkali layer was separated, washed with diethyl ether and then acidified with cold concentrated hydrochloric acid. The crude product was filtered and crystallized. In this way the following compounds were obtained:

*2-[(1-Methylhexyl)thio]benzoic Acid (8).* Prepared using butyllithium as first organolithium and iodomethane as first electrophile. Yield 71%; crystallized from aqueous ethanol, mp 83-86°C; IR (nujol): 3450-3060 (OH), 1690 $cm^{-1}$ (C=O); $^1H$ NMR ($CDCl_3$): δ 0.89 (t, 3H, $CH_3CH_2$, J = 7.0), 1.30 (m, 4H, $CH_3CH_2CH_2$, J = 7.0), 1.35 (d, 3H, $CH_3CH$, J = 6.6), 1.48 (m, 2H, $CH_2CH_2CHS$), 1.71 (m, 2H, $CH_2CHS$), 3.36 (m, 1H, CHS), 7.64 (m, 4H, Ar-*H*), 10.28 (s, br, 1H, COO*H*, $D_2O$ exchanged); $^{13}C$ NMR ($CDCl_3$): δ 171.6, 136.2, 133.4, 130.9, 128.3, 125.7, 123.8, 40.1, 39.7, 32.7, 26.0, 22.3, 21.1, 14.5; MS *m/z* 252 ($M^+$).
Anal. calcd for $C_{14}H_{20}O_2S$: C, 66.63; H, 7.99; S, 12.70. Found: C, 66.55; H, 7.94; S, 12.63.

If the reaction mixture was hydrolysed before the second metalation *[(1-methylhexyl)thio]benzene (2)* was obtained. Yield 88%; yellow oil; bp 153-155°C/30 mm Hg; $^1H$ NMR ($CDCl_3$): δ 0.91 (t, 3H, $CH_3CH_2$, J = 6.9), 1.29 (d, 3H, $CH_3CH$, J = 6.9), 1.31 (m, 4H, $CH_3CH_2CH_2$, J = 6.9), 1.48 (m, 2H, $CH_3CH_2CH_2CH_2$), 1.64 (m, 2H, $CH_3CHCH_2$), 3.23 (q, 1H, CH, J = 6.9), 7.30 (m, 5H, Ar-*H*); $^{13}C$ NMR ($CDCl_3$): δ 135.8, 129.3, 128.8, 126.8, 126.4, 123.8, 40.3, 39.0, 32.4, 25.8, 22.3, 21.1, 14.3; MS *m/z* 208 ($M^+$).Anal. calcd for $C_{13}H_{20}S$: C, 74.94; H, 9.67; S, 15.39. Found: C, 74.88; H, 9.61; S, 15.27.

*2-[(1-Methylhexyl)thio]-1-methylbenzene (9).* In the first step butyllithium as first organolithium and iodomethane as first electrophile were used. The resulting solution was metalated at 0°C with butyllithium (12.5 ml, 20 mmol) as above described, then treated with iodomethane (3.1 g, 22 mmol) in diethyl ether (5 ml), allowed to warm with stirring, left at room temperature for 4 hours and poured into water. The organic layer was separated and the aqueous layer extracted with diethyl ether. The organic solutions were combined, dried over calcium chloride and concentrated. The crude product was distilled. Yield 64%; bp 168-170°C/27 mm Hg; $^1H$ NMR ($CDCl_3$): δ 0.88 (t, 3H, $CH_3CH_2$, J = 6.9), 1.26 (d, 3H, $CH_3CH$, J = 6.6), 1.29 (m, 4H, $CH_3CH_2CH_2$, J = 6.9), 1.48 (m, 2H, $CH_2CH_2CHS$), 1.63 (m, 2H, $CH_2CHS$), 2.39 (s, 3H, $CH_3Ar$), 3.20 (m, 1H, CHS), 7.20 (m, 4H, Ar-*H*); $^{13}C$ NMR ($CDCl_3$): δ 136.1, 135.4, 129.0, 127.1, 125.7, 124.2, 40.5, 39.3, 29.7, 25.9, 23.1, 21.4, 17.2, 14.4; MS *m/z* 222 ($M^+$).Anal. calcd for $C_{14}H_{22}S$: C, 75.61; H, 9.97; S, 14.42. Found: C, 75.53; H, 9.93; S, 14.30.

*2-[(1-Ethylhexyl)thio]benzoic Acid (10).* Prepared using butyllithium as first organolithium and iodoethane as first electrophile. Yield 68%; viscous pale yellow oil; IR ($CHCl_3$): 3350-3070 (OH), 1690 $cm^{-1}$ (C=O); $^1H$ NMR ($CDCl_3$): δ 0.95 (t, 3H, $CH_3CH_2CH_2$, J = 7.2), 1.06 (t, 3H, $CH_3CH_2CHS$, J = 6.6), 1.35 (m, 2H, $CH_3CH_2CH_2$, J = 7.2), 1.52 (m, 4H,

$CH_3CH_2CH_2CH_2$), 1.68 (m, 4H, $CH_2CHCH_2$), 3.17 (m, 1H, CHS), 7.63 (m, 4H, Ar-*H*), 11.48 (s, br, 1H, COO*H*, $D_2O$ exchanged); $^{13}C$ NMR ($CDCl_3$): δ 172.4, 136.7, 133.3, 130.8, 128.2, 126.0, 124.1, 46.9, 35.7, 31.4, 29.8, 26.1, 23.8, 14.3, 10.4; MS *m/z* 266 ($M^+$).

Anal. calcd for $C_{15}H_{22}O_2S$: C, 67.63; H, 8.32; S, 12.03. Found: C, 67.51; H, 8.25; S, 11.90.

If the reaction mixture was hydrolysed before the second metalation *[(1-ethylhexyl)thio]benzene (3)* was obtained. Yield 84%; pale yellow oil; bp 174-176°C/2 mm Hg; $^1H$ NMR ($CDCl_3$): δ 0.92 (t, 3H, $CH_3CH_2CH_2$, J = 6.6), 1.04 (t, 3H, $CH_3CH_2CHS$, J = 7.2), 1.31 (m, 2H, $CH_3CH_2CH_2$, J = 6.6), 1.51 (m, 4H, $CH_3CH_2CH_2CH_2$), 1.62 (m, 4H, $CH_2CHCH_2$), 3.07 (m, 1H, CHS), 7.38 (m, 5H, Ar-*H*); $^{13}C$ NMR ($CDCl_3$): δ 135.1, 128.1, 128.0, 126.6, 126.3, 125.5, 46.9, 36.8, 32.7, 28.8, 26.2, 23.7, 14.4, 10.2; MS *m/z* 222 ($M^+$).Anal. calcd for $C_{14}H_{22}S$: C, 75.61; H, 9.97; S, 14.42. Found: C, 75.55; H, 9.90; S, 14.25.

*2-[(1-Methylpentyl)thio]benzoic Acid (11).* Prepared using propyllithium as first organolithium and iodomethane as first electrophile. Yield 74%; viscous pale yellow oil; IR ($CHCl_3$): 3300-3070 (OH), 1690 $cm^{-1}$ (C=O); $^1H$ NMR ($CDCl_3$): δ 0.95 (t, 3H, $CH_3CH_2CH_2$, J = 7.2), 1.10 (t, 3H, $CH_3CH_2CHS$, J = 7.2), 1.38 (m, 2H, $CH_3CH_2CH_2$, J = 7.2), 1.55 (m, 4H, $CH_3CH_2CH_2CH_2$), 1.68 (m, 4H, $CH_2CHCH_2$), 3.17 (m, 1H, CHS, J = 7.2), 7.61 (m, 4H, Ar-*H*), 11.80 (s, br, 1H, COO*H*, $D_2O$ exchanged); $^{13}C$ NMR ($CDCl_3$): δ 172.4, 137.8, 133.3, 130.7, 129.5, 126.0, 124.4, 40.1, 38.9, 28.4, 22.2, 21.1, 13.8; MS *m/z* 238 ($M^+$).

Anal. calcd for $C_{13}H_{18}O_2S$: C, 65.51; H, 7.61; S, 13.45. Found: C, 65.40; H, 7.54; S, 13.29.

If the reaction mixture was hydrolysed before the second metalation *[(1-methylpentyl)thio]benzene (4)* was obtained. Yield 86%; pale yellow oil; bp 164°C/35 mm Hg; $^1H$ NMR ($CDCl_3$): δ 0.91 (t, 3H, $CH_3CH_2$, J = 7.2), 1.28 (d, 3H, $CH_3CHS$, J = 7.2), 1.46 (m, 4H, $CH_3CH_2CH_2$, J = 7.2), 1.63 (q, 2H, $CH_2CHS$), 3.22 (m, 1H, CHS, J = 7.2), 7.36 (m, 5H, Ar-*H*); $^{13}C$ NMR ($CDCl_3$): δ 135.2, 129.5, 128.1, 126.6, 126.0, 124.2, 40.2, 38.4, 29.3, 22.2, 21.3, 14.2; MS *m/z* 194 ($M^+$).

Anal. calcd for $C_{12}H_{18}S$: C, 74.17; H, 9.34; S, 16.49. Found: C, 74.10; H, 9.29; S, 16.33.

*2-[(1-Ethylpentyl)thio]benzoic Acid (12).* Prepared using propyllithium as first organolithium and iodoethane as first electrophile. Yield 66%; viscous pale yellow oil; IR ($CHCl_3$): 3340-3050 (OH), 1690 $cm^{-1}$ (C=O); $^1H$ NMR ($CDCl_3$): δ 0.94 (t, 3H, $CH_3CH_2CH_2$, J = 7.2), 1.06 (t, 3H, $CH_3CH_2CHS$, J = 6.6), 1.31 (m, 2H, $CH_3CH_2CH_2$, J = 7.2), 1.48 (m, 4H, $CH_3CH_2CH_2CH_2$), 1.63 (m, 4H, $CH_2CHCH_2$), 3.20 (m, 1H, CHS), 7.69 (m, 4H, Ar-*H*), 11.20 (s, br, 1H, COO*H*, $D_2O$ exchanged); $^{13}C$ NMR ($CDCl_3$): δ 172.7, 137.8, 133.5, 129.7, 128.4, 126.0, 124.1, 46.7, 36.6, 32.6, 29.8, 26.2, 23.5, 14.3, 10.5; MS *m/z* 252 ($M^+$).Anal. calcd for $C_{14}H_{20}O_2S$: C, 66.63; H, 7.99; S, 12.70. Found: C, 66.51; H, 7.92; S, 12.58.

If the reaction mixture was hydrolysed before the second metalation *[(1-ethylpentyl)thio]benzene (5)* was obtained. Yield 82%; yellow oil; bp 154°C/30 mm Hg; $^1H$ NMR ($CDCl_3$): δ 0.89 (t, 3H, $CH_3CH_2CH_2$, J = 7.2), 1.00 (t, 3H, $CH_3CH_2CH$, J = 7.2), 1.27 (m, 2H, $CH_3CH_2CH_2$, J = 7.2), 1.45 (m, 2H, $CH_3CH_2CH_2$), 1.57 (m, 4H, $CH_2CHCH_2$, J = 7.2), 3.02 (m, 1H, CHS), 7.28 (m, 5H, Ar-*H*); $^{13}C$ NMR ($CDCl_3$): δ 135.1, 128.3, 127.9,

126.8, 126.1, 124.2, 46.8, 36.5, 32.7, 29.9, 26.2, 22.7, 13.8, 10.4; MS *m/z* 208 ($M^+$).Anal. calcd for $C_{13}H_{20}S$: C, 74.94; H, 9.67; S, 15.39. Found: C, 74.88; H, 9.60; S, 15.21.

*2-[(1-Methylpropyl)thio]benzoic Acid (13).* Prepared using methyllithium as first organolithium and iodomethane as first electrophile. Yield 75%; viscous pale yellow oil; IR (nujol): 3410-3030 (OH), 1700 $cm^{-1}$ (C=O); $^1H$ NMR ($CDCl_3$): δ 1.08 (t, 3H, $CH_3CH_2$, J = 7.2), 1.39 (d, 3H, $CH_3CHS$, J = 7.2), 1.66 (m, 2H, $CH_3CH_2$, J = 7.2), 3.30 (m, 1H, CHS, J = 7.2), 7.58 (m, 4H, Ar-*H*), 10.20 (s, br, COO*H*, $D_2O$ exchanged); $^{13}C$ NMR ($CDCl_3$): δ 172.6, 137.8, 133.4, 130.6, 128.1, 126.2, 124.0, 42.3, 31.1, 20.9, 10.6; MS *m/z* 210 ($M^+$).Anal. calcd for $C_{11}H_{14}O_2S$: C, 62.83; H, 6.71; S, 15.25. Found: C, 62.74; H, 6.64; S, 15.11.

If the reaction mixture was hydrolysed before the second metalation *[(1-methylpropyl)thio]benzene (6)* was obtained. Yield 85%; pale yellow oil; bp 130-131°C/40 mm Hg; $^1H$ NMR ($CDCl_3$): δ 1.03 (t, 3H, $CH_3CH_2$, J = 7.2), 1.29 (d, 3H, $CH_3CHS$, J = 7.2), 1.57 (m, 2H, $CH_3CH_2$, J = 7.2), 3.18 (m, 1H, CHS, J = 7.2), 7.32 (m, 5H, Ar-*H*); $^{13}C$ NMR ($CDCl_3$): δ 135.1, 128.2, 127.8, 126.1, 125.7, 124.3, 42.5, 31.2, 21.8, 10.7; MS *m/z* 166 ($M^+$).

Anal. calcd for $C_{10}H_{14}S$: C, 72.23; H, 8.49; S, 19.28. Found: C, 72.18; H, 8.44; S, 19.11.

*2-[(1-Ethylpropyl)thio]benzoic Acid (14).* Prepared using methyllithium as first organolithium and iodoethane as first electrophile. Yield 61%; viscous pale yellow oil; IR ($CHCl_3$): 3350-3080 (OH), 1690 $cm^{-1}$ (C=O); $^1H$ NMR ($CDCl_3$): δ 1.02 (t, 6H, $CH_3$, J = 7.2), 1.73 (m, 4H, $CH_2$, J = 7.2), 3.18 (m, 1H, CHS, J = 7.2), 7.87 (m, 5H, Ar-*H*), 10.17 (s, br, COO*H*, $D_2O$ exchanged); $^{13}C$ NMR ($CDCl_3$): δ 172.6, 137.8, 134.5, 130.5, 128.2, 126.0, 124.3, 48.1, 29.9, 10.9; MS *m/z* 224 ($M^+$).Anal. calcd for $C_{12}H_{16}O_2S$: C, 64.25; H, 7.19; S, 14.29. Found: C, 64.18; H, 7.14; S, 14.13. If the reaction mixture was hydrolysed before the second metalation *[(1-ethylpropyl)thio]benzene (7)* was obtained. Yield 79%; pale yellow oil; bp 125-128°C/15 mm Hg; $^1H$ NMR ($CDCl_3$): δ 1.03 (t, 6H, $CH_3$, J = 7.2), 1.63 (m, 4H, $CH_2$, J = 7.2), 3.02 (m, 1H, CHS, J = 7.2), 7.60 (m, 5H, Ar-*H*); $^{13}C$ NMR ($CDCl_3$): δ 135.1, 128.2, 127.7, 126.1, 125.6, 124.4, 48.0, 29.4, 10.2; MS *m/z* 180 ($M^+$).

Anal. calcd for $C_{11}H_{16}S$: C, 73.28; H, 8.94; S, 17.78. Found: C, 73.19; H, 8.89; S, 17.59.

*General Procedure for the One-step Introduction of Two Electrophiles in 1*

A vigorously stirred solution of **1** (1 g, 7.34 mmol), TMEDA (2.09 g, 18 mmol) and anhydrous diethyl ether (10 ml) was treated dropwise with a 1.6 M solution of butyllithium in hexane (11.9 ml, 19 mmol) at 0°C under nitrogen. After 2 h, to the resulting solution of **15** the proper electrophile (19 mmol) was added at 0°C and the reaction completed by stirring overnight. The reaction mixture was poured into water, the organic layer separated and the aqueous layer extracted with diethyl ether. The combined organic extracts were dried ($Na_2SO_4$), filtered and evaporated. The crude product was chromatographed using petroleum ether as eluent.

In this way, using iodomethane, chlorotrimethylsilane and dichlorodimethylsilane as electrophiles, the following compounds were obtained:

*1-Methyl-2-[(1-methylvinyl)thio]benzene (16).* Yield 30%; $^1$H NMR ($CDCl_3$): δ 2.01 (s, 3H, C*H*$_3$-C=), 2.46 (s, 3H, C*H*$_3$-Ar), 4.62 (s, 1H, C=C*H*), 5.06 (s,1H, C=C*H*), 7.25 (m, 4H, Ar-*H*); $^{13}$C NMR ($CDCl_3$): δ 151.2, 136.9, 135.4, 129.0, 125.9, 125.1, 124.3, 98.0, 24.6, 17.4; MS *m/z* 164 ($M^+$).

Anal. calcd for $C_{10}H_{12}S$: C, 73.12; H, 7.36; S, 19.52. Found: C, 73.06; H, 7 31; S, 19.32.

The GC-MS analysis of the overall reaction mixture revealed, besides **16**, products **19**, **20**, **21**, **22**, and **23** (**16**:**19**:**20**:**21**:**22**:**23** = 26:11:10:3:5:18). These compounds were identified by comparison of their mass spectra with those of authentic samples.

*[2-[[1-(Trimethylsilyl)vinyl]thio]phenyl]trimethylsilane (17).* Yield 60%; $^1$H NMR ($CDCl_3$): δ 0.25 (s, 9H, C*H*$_3$-Si-Ar), 0.34 (s, 9H, C*H*$_3$-Si-C), 4.78 (s, 1H, C=C*H*), 4.99 (s, 1H, C=C*H*), 7.40 (m, 4H, Ar-*H*); $^{13}$C NMR ($CDCl_3$): δ 158.5, 140.1, 138.6, 133.4, 129.6, 125.2, 123.7, 112.1, 1.8, -3.5; MS *m/z* 280 ($M^+$).

Anal. calcd for $C_{14}H_{24}SSi_2$: C, 59.93; H, 8.62; S, 11.43. Found: C, 59.83; H, 8.57; S, 11.27.

Running the reaction at -80°C, only 1-phenylthio-1-trimethylsilylethene[8] was obtained in 30% yield besides a 17% of the starting material.

*2-Methylene-3,3-dimethyl-1,3-benzothiasilole (18).* Yield 30%; $^1$H NMR ($CDCl_3$): δ 0.43 (s, 6H, C*H*$_3$-Si), 5.66 (s, 1H, C=C*H*), 5.96 (s, 1H, C=C*H*), 7.25 (m, 4H, Ar-*H*); $^{13}$C NMR ($CDCl_3$): δ 158.8, 140.3, 138.4, 133.1, 129.8, 125.4, 124.3, 111.9, -3.9; MS *m/z* 192 ($M^+$).

Anal calcd for $C_{10}H_{12}SSi$: C, 62.44; H, 6.29; S, 16.67. Found: C, 62.33; H, 6.23; S, 16.51.

*Reaction of [(1-Lithiohexyl)thio]benzene on 1*

A solution of **1** (1 g, 7.5 mmol) in anhydrous diethyl ether (10 ml) was gradually added under nitrogen to a vigorously stirred 1.6 M solution of butyllithium (9 ml, 15 mmol) and TMEDA (1.75 g, 15 mmol) in anhydrous diethyl ether (10 ml) and stirring was continued at the same temperature for 2 hours. The resulting solution was treated dropwise with **1** (1 g, 7.5 mmol) in anhydrous diethyl ether, the reaction mixture stirred for 2 hours at 0°C, treated with iodomethane (1 g, 7.5 mmol) in diethyl ether (5 ml) and left to warm to room temperature with stirring. The mixture was poured into water, extracted with diethyl ether and dried over calcium chloride. The GC-MS analysis revealed two products which were identified as [(1-methylvinyl)thio]benzene (**21**) and (hexylthio)benzene (**22**) by comparison of their mass spectra with those of authentic samples.

If a portion of the reaction mixture was hydrolysed before the second treatment with **1**, [(1-methylhexyl)thio)benzene (**2**) was obtained, identified by comparison with an authentic sample.

*Reaction of 1 with LDA.*

A solution of diisopropylamine (2.5 g, 25 mmol) in anhydrous diethyl ether was treated with butyllithium (15.6 ml, 25 mmol) at 0°C under nitrogen; after 10 min **1** was added (1.5 g, 11 mmol) and after 1 h the solution was quenched with iodomethane (4.3 g, 30 mmol). After 24 h the reaction mixture was poured into a solution of $NH_4Cl$, extracted with diethyl ether,

dried ($Na_2SO_4$) and concentrated. The GC/MS analysis of the mixture revealed the presence of the α-metalated product **21** (30%) besides **19** (10%) and the starting material **1** (60%).

*Reaction of 1 with LITMP.*

A solution of butyllithium (9.4 ml, 15 mmol) and anhydrous THF (30 ml) was treated with 2,2,6,6-tetramethyl piperidine (2.1 g, 15 mmol) at -30°C under argon. After 5 min **1** was added (1 g, 7.6 mmol) and the resulting solution was stirred for 2 h. Then iodomethane was added (2.1 g, 15 mmol) and after 15 h the solution was poured into water, extracted with diethyl ether, dried ($Na_2SO_4$) and concentrated. The GC/MS analysis of the mixture revealed the presence of the α-metalated product **21** (62%) besides 1,2,2,6,6-pentamethylpiperidine (38%).

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