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Metallation Reactions. XX. Regioselective Metallation of (Alkylthio)methoxybenzenes by Superbases *Versus* Organolithium Compounds

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Abstract - (Alkylthio)methoxybenzenes have been metallated using two different metallating agents The results show that sometimes superbases and butyllithium do not functionalize the same sites Superbases monometallate the thiomethylic carbon of *meta* and *para* (methylthio)methoxybenzenes The same substrates on the other hand are metallated by butyllithium in *ortho* to the methoxy group One-step dimetallation performed with either superbases or butyllithium occurs at the thiomethylic carbon and at the aryl carbon *ortho* to the methoxy group. Two consecutive one-pot monometallations of the *para* isomer (**1c**) with superbases occur at the thiomethylic carbon and at the annular carbon *ortho* to the methoxy group, in this order A similar procedure with butyllithium metallates the two *ortho* positions to the methoxy group Monometallation of (ethylthio) derivative (**1d**) yields products substituted in *ortho* to the methoxy group using either superbases or butyllithium Dimetallation of this compound always substitutes the hydrogen *ortho* to the methoxy group and a thiomethylenic hydrogen

The development of new methods for the selective functionalization of aromatic compounds is of great interest in synthetic organic chemistry.[1-5] In the past decades the great utility of heteroatom mediated *ortho*-metallation of aromatic rings in the synthesis of complex aromatic systems was shown [1-7] During our works we recently studied the substituent effect of the *ortho*-directing thioethereal group [8] It was noted that without other substituents the thiomethylic carbon atom of the thiomethyl group is metallated while higher (alkylthio)benzenes promote the metallation of the position *ortho* to the thioethereal function.[8] In the presence of other substituents, such as alkoxy groups or fluorine atoms, the metallation occurs in *ortho* to these groups thus showing the weaker coordinating power of the sulfur atom [8,9] It was recently shown that superbases metallate in *alpha* also the higher (alkylthio)benzenes [10]

The aim of the present work is to investigate the possibility of changing the regiochemistry of the alkoxy(alkylthio)benzenes by superbases

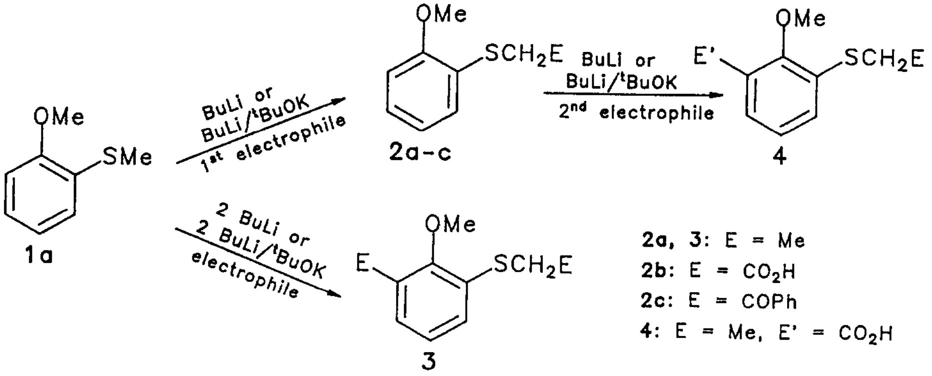
Results and discussion

All monometallation reactions were performed by treating the substrates **1a-d** with an equimolar amount of the superbase mixture of butyllithium and potassium *t*-butoxide. Dimetallations were carried out with two equivalents of the same reagent The intermediates were identified, after reaction with iodomethane, using GC/MS comparison with authentic samples.

The results show that:

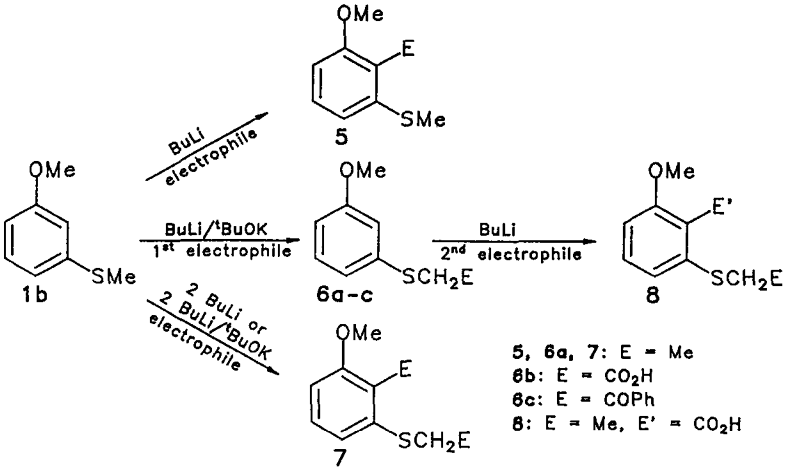
i) monometallation of 1-methoxy-2-(methylthio)benzene (**1a**) occurs only on the thiomethylic carbon (Scheme 1), as shown by the formation of the products **2a-c** after treatment of the metallated intermediate with iodomethane, carbon dioxide or benzoyl chloride. The direct one-step bimetallation leads to the substitution of a thioalkylic hydrogen atom and of the ring hydrogen atom *ortho* to the ethereal group yielding, after treatment with iodomethane, derivative **3**. Two different functional groups can be introduced in the same sites through two consecutive one-pot monometallations each followed by treatment with an electrophile, as shown by the preparation of the product **4**

Scheme 1



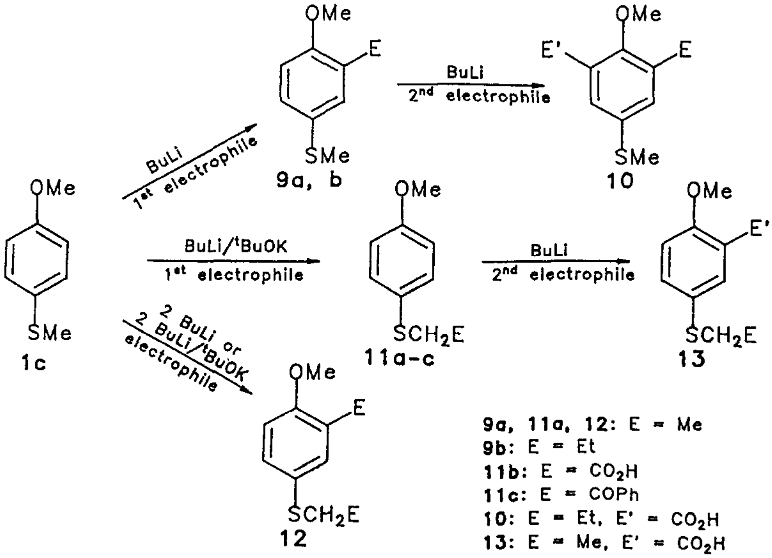
ii) Monometallation of 1-methoxy-3-(methylthio)benzene (**1b**) yields derivatives **6a-c** by the substitution of the thiomethylic hydrogen atom (Scheme 2); the direct one-step bimetallation substitutes a thiomethylic hydrogen and the ring hydrogen *ortho* to both substituents (methoxy and alkylthio) yielding the product **7** after reaction with iodomethane. On the other hand, two consecutive, one-pot monometallations allow the introduction of two different electrophiles as shown by the preparation of **8** by using first iodomethane and then carbon dioxide as electrophiles

Scheme 2



iii) Monometallation of 1-methoxy-4-(methylthio)benzene (**1c**) yields the products, **11a-c**,[11] deriving from the substitution of the thiomethylic hydrogen atom (Scheme 3) One-step bimetallation yields the substitution product **12** at both the thiomethylic and the annular hydrogen *ortho* to the methoxy group

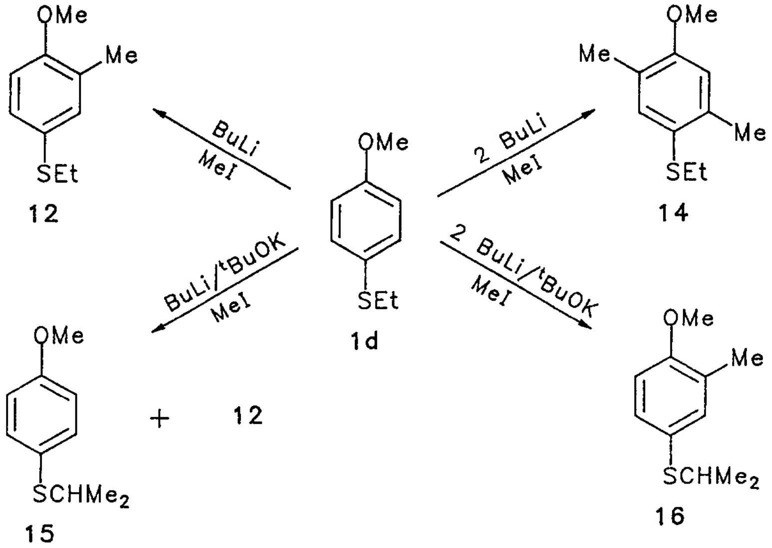
Scheme 3



Two consecutive monometallations, each followed by treatment with an electrophile, functionalize the same sites with two different groups, as shown by the preparation of **13**. On the other hand, two consecutive one-pot butyllithium monometallation/electrophile addition reactions, yield the product **10**, where the two functional groups both enter *ortho* to the ethereal function.[8]

iv) Monometallation of 1-(ethylthio)-4-methoxybenzene (**1d**) followed by treatment with iodomethane yields **12** as main product, where a ring hydrogen *ortho* to the methoxy group has been substituted (Scheme 4); direct one-step bimetallation/treatment with iodomethane of the same substrate substitutes also the thiomethylenic hydrogen yielding **16**.

Scheme 4



The above results show that with the *ortho*-substituted derivative **1a** the use of superbases does not change the monometallation pattern (Scheme 1). On the other hand, the *meta* and *para* isomers, **1b** and **1c**, react with a different regiochemistry of metallation compared with the normal lithiating agents,[8] since the reactive site is not the arylic hydrogen *ortho* to the ethereal group, but the thiomethylic one (Schemes 2 and 3).

With the aim of verifying if the initial site of metallation was the same for both organometallic reagents (superbases and butyllithium), all reactions were repeated employing superbases in the same operative conditions used with butyllithium alone[8] (*i.e* keeping the metallation mixture for 12 h at room temperature before functionalisation) The results confirmed that superbases and butyllithium do not functionalize the same sites as stated above

We had suggested the acidity of the hydrogen atoms of the substrates was more important with superbases than with butyllithium in directing the metallation.[10] In the present work the presence of a methoxy group in the substrate shows the coordinating power of the oxygen atom is important also for superbases. Metallation of **1d** occurs in *ortho* to the methoxy group even though the aromatic *ortho* hydrogen is less acidic than the hydrogen *alpha* to the sulfur atom In the derivative **1d** the thiomethylenic hydrogen competes for a small amount (5%) to the metallation yielding **15** with iodomethane (Scheme 4) This suggests that with superbases the reactivity of this site is not very different from that in *ortho* to the methoxy group

The above results emphasize the synthetic potential of superbases that allow the functionalization of the thiomethylic carbon in the monometallation, or, with two consecutive one-pot monometallations, the functionalization of the thiomethylic and *ortho* (to the methoxy) carbon atoms with two different groups. It was thus possible to prepare: i) 1,2,αS-trisubstituted benzene derivatives **2a-c** starting from **1a**, ii) 1,3,αS-trisubstituted benzene derivatives **6a-c** starting from **1b**, iii) 1,4,αS-trisubstituted benzene derivatives **11a-c** starting from **1c**; iv) 1,2,3,αS-tetrasubstituted benzene derivatives starting from **1a** and **1b** as proved by attainment of **3**, **4**, **7**, **8**, v) 1,2,4,αS-tetrasubstituted benzene derivatives starting from **1c** and **1d** as proved by attainment of **12**, **13**, **16**

It is worth noticing that two consecutive monometallations performed with butyllithium regioselectively substitute the two *ortho* positions to the methoxy group[8] Thus, the two reagents are complementary and allow the regioselective substitution of different sites of the molecule

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 μ film thickness) ^{1}H NMR spectra were recorded on a Varian VXR-300 spectrometer with tetramethylsilane as internal reference. The following abbreviations are used to describe the signal multiplicity s· singlet; d· doublet; t: triplet, q quartet; m· multiplet, br broad. IR spectra were recorded on a Perkin-Elmer 1310 grating spectrophotometer The TLC analyses were carried out on a silica gel 60 F254 plates (Merck) All flash chromatographies were performed on silica G60 (Merck) columns. Microanalyses were carried out with a Carlo Erba 1106 elemental analyser Melting points were obtained on a Kofler hot stage microscope and are uncorrected

Commercially available reagent-grade starting materials and solvents were used. Solutions of *n*-butyllithium in hexane were obtained from Aldrich Chemical Company and were analysed by the Gilman double titration method before use [12]

Starting materials

2-(Methylthio)- (**1a**), 3-(methylthio)- (**1b**), and 4-(methylthio)-1-methoxybenzene (**1c**) and 1-(ethylthio)-4-methoxybenzene (**1d**) were prepared by published methods starting from the corresponding arenethiols and dimethylsulfate or diethylsulfate.[13-17]

Authentic samples

1-Methoxy-2-methyl-3-methylthio- (**5**), 1-(ethylthio)-2-methoxy- (**2a**) 1-(ethylthio)-3-methoxy- (**6a**) 1-(ethylthio)-3-methoxy-2-methyl- (**7**), 1-methoxy-2-methyl-4-(methylthio)-(**9a**) and 1-methoxy-4-(isopropylthio)-benzene (**15**) were prepared by published methods [14,18-22]

3-(Ethylthio)-2-(methoxy)benzoic acid (4). - To a vigorously stirred solution of **2a** (6 g, 36 mmol), anhydrous TMEDA (4.6 g, 39 mmol) and anhydrous hexane (100 ml) cooled to 0°C a 1.2 M solution of *n*-butyllithium in hexane (33 ml, 39 mmol) was gradually added under nitrogen, and stirring was continued at room temperature for 12 h The resulting solution was poured onto ca 100 g of crushed solid carbon dioxide. After 24 h the residue was treated successively with 12% aqueous sodium bicarbonate and then with ethyl ether The alkali layer was separated, washed with ethyl ether, and then acidified with cold concentrated hydrochloric acid, extracted with ethyl ether, dried (Na_2SO_4), and concentrated. The crude product was purified by flash-chromatography on silica gel with ethyl acetate as eluent Yield 68%; crystallised from aqueous ethanol mp 84-85°C (lit [8] 84-86°C)

6-(Ethylthio)-2-methoxybenzoic acid (8). This compound was prepared as described for **4** starting from **6a**. The crude product was crystallised from water, yield 73%, mp 135-136°C, IR (nujol, cm^{-1}): 3050 (OH), 1700 (C=O) ^1H NMR ($CDCl_3$) δ 1 27 (3H, t, CH_3CH_2), 2 90 (2H, q, CH_3CH_2), 3 84 (3H, s, OCH_3), 7.04 (3H, m, Ar-*H*), 10 7 (1H, s, br, CO_2H, D_2O exchanged) *m/z* 212 (M^+) (Found C, 56.46, H, 5 64, S, 14.98 $C_{10}H_{12}O_3S$ requires C, 56.58, H, 5 70, S, 15 10).

5-(Ethylthio)-2-methoxybenzoic acid (13). This compound was prepared as described for **4** starting from **1d**.[11] The crude product was crystallised from aqueous ethanol Yield 81%, mp 60°C. IR (nujol, cm^{-1}) 3080 (OH), 1710 (C=O) ^1H NMR ($CDCl_3$) δ 1 73 (3H, t, CH_3CH_2), 2 80 (2H, q, CH_3CH_2), 3 14 (3H, s, OCH_3), 7 44 (3H, m, Ar-*H*), 9 90 (1H, s, br, CO_2H, D_2O exchanged) *m/z* 212 (M^+). (Found C, 56 43, H, 5 66, S, 15 01 $C_{10}H_{12}O_3S$ requires C, 56 58, H, 5 70, S, 15 10)

1-(Ethylthio)-2-methoxy-3-methylbenzene (3). To a vigorously stirred solution of **2a** (5 5 g, 36 mmol), anhydrous TMEDA (4 5 g, 39 mmol) and anhydrous hexane (100 ml) cooled to 0°C a 1 2 M solution of *n*-butyllithium in hexane (33 ml, 39 mmol) was gradually added under nitrogen, and stirring was continued at room temperature for 12 h To this solution iodomethane (5 1 g, 36 mmol) was gradually added at 0°C After the addition was completed the mixture was allowed to warm to room temperature, kept 12 h with stirring and poured into water, and the pH was adjusted to 5-6 by addition of 10% hydrochloric acid The organic layer was separated, the aqueous layer extracted with ethyl ether, and the organic solutions combined were dried (Na_2SO_4) and concentrated. The crude product was purified by flash-chromatography on silica gel using hexane/ethyl acetate (20·1) as eluent. Yield 90%, bp 98-100°C (0.3mm Hg); ^1H NMR ($CDCl_3$) δ: 1 34 (3H, t, CH_3CH_2), 2 29 (3H, s, CH_3Ar), 2 92 (2H, q, CH_3CH_2), 3 82 (3H, s, OCH_3), 7 04 (3H, m, Ar-*H*). *m/z* 182 (M^+) (Found C, 65 80; H, 7.69; S, 15 48 $C_{10}H_{14}OS$ requires C, 65.89; H, 7 74; S, 17 59)

4-(Ethylthio)-1-methoxy-2-methylbenzene (12). This compound was prepared as described for **3** starting from **1d** The crude product was flash-chromatographed on silica gel using hexane/ethyl acetate (10 1) as eluent Yield 88%; bp 108-109°C (0.4mm Hg), ^1H NMR ($CDCl_3$) δ 1 28 (3H, t, CH_3CH_2), 2.25 (3H, s, CH_3Ar), 2.86 (2H, q, CH_3CH_2), 3 80 (3H, s, OCH_3), 7 18 (3H, m, Ar-*H*) *m/z* 182 (M^+). (Found C, 65.80; H, 7.70, S, 17 47 $C_{10}H_{14}OS$ requires C, 65 89, H, 7 74, S, 17.59)

5-(Ethylthio)-2-methoxy-1,4-dimethylbenzene (14) - To a vigorously stirred solution of **1d** (6 g, 36 mmol), anhydrous TMEDA (10 g, 87 mmol) and anhydrous hexane (100 ml) cooled to 0°C a 1 2 M solution of *n*-butyllithium in hexane (74 ml, 87 mmol) was gradually added under nitrogen, and stirring was continued at room temperature for 15 h To this mixture iodomethane (12 3 g, 87 mmol) was gradually added at 0°C and the resulting solution worked up in the same manner described for **3** The crude product was flash-chromatographed on silica gel using hexane/ethyl acetate (20.1) as eluent. Yield 48%, bp 118-120°C (0 3mm Hg), ^1H NMR ($CDCl_3$) δ 1 29 (3H, t, CH_3CH_2), 2 23 (3H, s, CH_3Ar), 2 45 (3H, s, CH_3Ar), 2 85 (2H, q, CH_3CH_2), 3 83 (3H, s, OCH_3), 7.02 (2H, m, Ar-*H*). *m/z* 196 (M^+) (Found C, 67 21, H, 8 15; S, 16.20 $C_{11}H_{16}OS$ requires C, 67 30; H, 8 22, S, 16.33)

1-Methoxy-2-methyl-4-(isopropylthio)benzene (16) - This compound was prepared as described for **3** starting from **15** The crude product was flash-chromatographed on silica gel using petroleum ether (bp 40-70°C) as eluent Yield 79%, bp 114-115°C (0 2mm Hg), ^1H NMR ($CDCl_3$) δ 1 26 (6H, d, $(CH_3)_2CH$), 2 21 (3H, s, CH_3Ar), 3 20 (1H, m, $(CH_3)_2CH$), 3 82 (3H, s, OCH_3), 7 00 (3H, m, Ar-*H*) *m/z* 196 (M^+) (Found C, 67 23, H, 8 14, S, 16 17 $C_{11}H_{16}OS$ requires C, 67 32, H, 8 22, S, 16 30).

Monometallation procedure

A solution of *n*-butyllithium in hexane (35 ml, 50 mmol) was cooled to -60°C under nitrogen and a solution of the starting sulfide **1a-d** (43 mmol) in hexane (20 ml) was added Finely powdered potassium *t*-butoxide (5.6 g, 50 mmol) was added and the temperature allowed to rise to -20°C The mixture was kept for 1 h at -20°C, after which the temperature was allowed to rise to -10°C. After 3 h, an excess of iodomethane (12.8 g, 90 mmol) was slowly added, the cooling bath removed and the reaction completed by stirring overnight at room temperature. The reaction mixture was poured into water, the organic layer separated and the aqueous layer extracted with ether The combined organic extracts were dried (Na_2SO_4), filtered and evaporated The products were distilled and identified by GC/MS comparison with authentic samples

In this manner, starting from **1a**, **1b**, **1c** and **1d**, respectively, the following compounds were obtained

a) **1-(Ethylthio)-2-methoxybenzene (2a)**. - Yield 64%, bp 120-122°C (10mm Hg).

b) **1-(Ethylthio)-3-methoxybenzene (6a)** - Yield 66%; bp 117-118°C (10mm Hg).

c) **1-(Ethylthio)-4-methoxybenzene (11a = 1d)**. - Yield 78%; bp 128-129°C (10mm Hg)

d) **4-(Ethylthio)-1-methoxy-2-methylbenzene (12)**. - Yield 67%; bp 100-101°C (0.3mm Hg). The GLC analyses of the reaction mixture show also the presence of **15** The ratio of **12**:**15** is 95:5

The same results were obtained when the reaction mixture was allowed to warm and kept at room temperature for 12 h before the electrophilic quenching

The following compounds were similarly obtained from **1a**, **1b** and **1c**, respectively, and carbon dioxide or benzoyl chloride:

f) **[(2-Methoxyphenyl)thio]acetic acid (2b)** - The metallated mixture of **1a** was poured onto ca 100 g of crushed solid carbon dioxide After 24 h the residue was treated successively with 10% aqueous sodium bicarbonate and then with ethyl ether The alkali layer was separated, washed with ethyl ether, and then acidified with cold concentrated hydrochloric acid, extracted with ethyl ether, and dried (Na_2SO_4) The ethyl ether was evaporated and the crude product was crystallised from water Yield 69%, mp 120-121°C (lit.[23] mp 121-122°C) IR (nujol, cm^{-1}) 3080 (OH), 1700 (C=O). ^1H NMR ($CDCl_3$) δ· 3 61 (2H, s, SCH_2), 3 81 (3H, s, OCH_3), 7 10 (4H, m, Ar-*H*), 10 83 (1H, s, CO_2H, br, D_2O exchanged).

g) **2-[(2-Methoxyphenyl)thio]-1-phenylethanone (2c)** - The crude product was flash-chromatographed using hexane/ethyl acetate (5 1) as eluent Yield 65%, crystallised from aqueous ethanol, mp 65-67°C. IR (nujol, cm^{-1}) 1670 (C=O). ^1H NMR ($CDCl_3$) δ 3.80 (3H, s, OCH_3), 4 21 (2H, s, SCH_2), 7 37 (9H, m, Ar-*H*) *m/z* 258 (M^+). (Found C, 69 69, H, 5 41, S, 12 24. $C_{15}H_{14}O_2S$ requires C, 69.75; H, 5 47, S, 12 39).

h) **[(3-Methoxyphenyl)thio]acetic acid (6b)** - The crude product was flash-chromatographed on a silica gel column using hexane/ethyl acetate (5 1) as eluent Yield 71%, crystallised from hexane, mp 62-63°C (lit [24] mp 64°C) IR (nujol, cm^{-1}) 3100 (OH), 1710 (C=O) ^1H NMR ($CDCl_3$) δ 3 67 (2H, s, SCH_2), 3 76 (3H, s, OCH_3), 6.99 (4H, m, Ar-*H*), 10 9 (1H, s, CO_2H, br, D_2O exchanged)

i) **2-[(3-Methoxyphenyl)thio]-1-phenylethanone (6c)** - The product was flash-chromatographed on silica gel using hexane as eluent Yield 63%, mp 45-46°C (lit [25] mp 47°C). IR (neat, cm^{-1}) 1680 (C=O) ^1H NMR ($CDCl_3$) δ: 3 65 (3H, s, OCH_3), 4.24 (2H, s, SCH_2), 7 28 (9H, m, Ar-*H*)

j) **[(4-Methoxyphenyl)thio]acetic acid (11b)** - The crude product was flash-chromatographed on silica gel using petroleum ether (bp 40-70°C)/ethyl ether (1 1) as eluent Yield 76%, crystallised from benzene, mp 76-77°C (lit [26] mp 76-78°C) IR (nujol,

cm^{-1}): 3140 (OH), 1710 (C=O). ^1H NMR ($CDCl_3$) δ· 3 52 (2H, s, SCH_2), 3.77 (3H, s, OCH_3), 7.12 (4H, m, Ar-*H*), 10.8 (1H, s, CO_2H, br, D_2O exchanged).

k) **2-[(4-Methoxyphenyl)thio]-1-phenylethanone (11c)**. The crude product was flash-chromatographed on silica gel using hexane/ethyl acetate (5·1) as eluent. Yield 61%; bp 200-201°C (0 4mm Hg) (lit.[25] bp 196-198°C (0.2mm Hg)) IR (neat, cm^{-1})· 1680 (C=O). ^1H NMR ($CDCl_3$) δ 3 70 (3H, s, OCH_3), 4 10 (2H, s, SCH_2), 7 38 (9H, m, Ar-*H*)

Bimetallation procedure

A solution of *n*-butyllithium in hexane (70 ml, 100 mmol) was cooled to -60°C under nitrogen, then a solution of the starting thioethers **1a-d** (43 mmol) in hexane (20 ml), and, successively, finely powdered potassium *t*-butoxide (11 2 g, 100 mmol) was added. After the usual work-up, an excess of iodomethane (25.6 g, 180 mmol) was added slowly and the mixture worked up as described above The products were distilled and identified by GC/MS comparison with authentic samples.

In this manner, starting from **1a**, **1b**, **1c** and **1d**, respectively, the following compounds were obtained

a) **1-(Ethylthio)-2-methoxy-3-methylbenzene (3)**. - Yield 60%, bp 99-100°C (0.3mm Hg).

b) **1-(Ethylthio)-3-methoxy-2-methylbenzene (7)**. - Yield 57%; bp 104-105°C (3mm Hg), sulphone, mp 43 5-44°C (lit·[22] mp 44-45°C).

c) **4-(Ethylthio)-1-methoxy-2-methylbenzene (12)** - Yield 59%; bp 100-101 (0 3mm Hg).

d) **1-Methoxy-2-methyl-4-(isopropylthio)benzene (16)** - Yield 58%; bp 114-115°C (0 2mm Hg)

The same results were obtained when the reaction mixture was allowed to warm and kept at room temperature for 12 h before the electrophilic quenching

Sequential, one-pot introduction of two different electrophiles on 1a-c

A solution of *n*-butyllithium in hexane (35 ml, 50 mmol) was cooled to -60°C under nitrogen and a solution of the starting thioethers **1a-c** (43 mmol) in hexane (20 ml) was added Finely powdered potassium *t*-butoxide (5 6 g, 50 mmol) was added and the resulting mixture worked up as described above The mixture was successively treated dropwise with iodomethane (7 1 g, 50 mmol), allowed to warm and left at room temperature for 4 h with stirring The mixture was then cooled to 0°C and treated dropwise with *n*-butyllithium in hexane (35 ml, 50 mmol) After the usual work-up, the resulting solution was poured onto ca 100 g of crushed solid carbon dioxide and worked-up in the same manner described for **2b** The products were identified by comparison with authentic samples

In this manner starting from **1a**, **1b** and **1c** the following compounds were prepared.

a) **3-(Ethylthio)-2-methoxybenzoic acid (4)**. - Yield 55%, mp 84-85°C

b) **6-(Ethylthio)-2-methoxybenzoic acid (8)**. - Yield 51%, mp 135-136°C.

c) **(5-Ethylthio)-2-methoxybenzoic acid (13)**. - Yield 68%; mp 60°C

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11 For the sake of clarity a different number has been assigned to each compound, even though compound **11a** is identical with **1d**

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