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METALATION REACTIONS.

IV *. METALATION OF *o*-ALKYL- AND *o,o'*-DIALKYL-SUBSTITUTED ALKYLTHIOBENZENES

S. CABIDDU, S. MELIS, P.P. PIRAS and F. SOTGIU

Istituto Chimico and Istituto di Chimica Farmaceutica e Tossicologica, Università,
09100 Cagliari (Italy)

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Summary

Metalation of *o*-alkyl- and *o,o'*-dialkyl-substituted alkylthiobenzenes with n-butyllithium, in the presence and absence of TMEDA, has been investigated. The results showed that metalation at the thioalkyl carbon probably occurs by direct attack of the organolithium reagent, although a transmetalation reaction cannot be excluded in some cases. It has also been found that benzylic, thiomethylic, and ring metalation occurs in ether alone, whereas mainly thiomethylic or ring metalation occurs in the presence of TMEDA.

Introduction

In a previous paper [2] we reported that metalation of several (alkoxy)(alkylthio)benzenes occurred at various positions depending on the relative orientation power of the two substituents.

It has been suggested by Shirley and Reeves [3] that metalation of (methylthio)benzene is a two step reaction, with an initial step involving hydrogen abstraction from the ring being followed by metalation of the thioalkyl carbon by the aryllithium. Other authors [4,5] have reported that with *o*-methylanisole there is competition between ring and side-chain metalation.

We describe below the reactions between n-butyllithium and *o*-alkyl- or *o,o'*-dialkyl-substituted alkylthiobenzenes, which were examined in order to throw more light on the possible existence of a transmetalation equilibrium [3], and to see whether there is competition between alkylic, thioalkylic and ring positions.

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* For Part III see ref. [1].

Results and discussion

(Alkylthio)benzenes (Ia, Ib; IIa, IIb; IIIa, IIIb) were examined. The reactions were carried out by treating the ethereal solutions with an equimolar amount of n-butyllithium in hexane both in the presence and in the absence of an equimolar amount of *N,N,N',N'*-tetramethylethylenediamine (TMEDA). The aryllithium compounds were then carbonated, and the resulting acids analyzed by GLC and characterized by comparison of the acids or of their desulfuration products with authentic samples, or through analysis of their IR and ^{1}H NMR spectra.

The results, listed in Table 1, show that:

(i) Metalation of 1-methyl-2-(methylthio)benzene (Ia) in ether gives a mixture of three acids (Scheme 1): IVa (29%), IVb (68%) and IVc (3%). When the reaction is carried out in the presence of TMEDA only IVb is obtained, along with traces of IVc.

(ii) 1-Methoxy-2-(isopropylthio)benzene (Ib) gives in ether the two acids Va (57%) and Vb (43%) (Scheme 2). When TMEDA is present Va and Vb are found in a ratio of 5/95. Unexpectedly, benzoic acid is also formed, in approximately the same yield as Vb.

(iii) 1,3-Dimethyl-2-(methylthio)benzene (IIa) gives two acids (Scheme 3), VIa and VIb, in a ratio of 70/30 with n-BuLi and 4/96 with n-BuLi and TMEDA. Metalation of IIa with phenyllithium and TMEDA gives only the acid VIb.

(iv) 1,3-Dimethyl-2-(isopropylthio)benzene (IIb) in the absence of TMEDA gives exclusively acid VII (Scheme 4), but in the presence of TMEDA the yield is rather low and 3-methylbenzoic acid is also obtained.

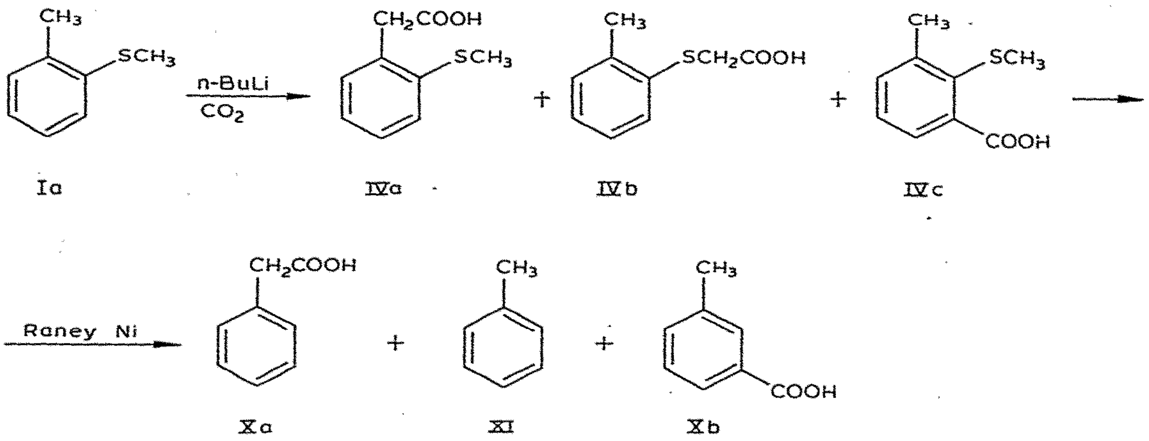
TABLE 1

METALATION OF ALKYLTHIOBENZENES (I, II and III) [a]

Starting material	Products	Fraction (%)	
		without TMEDA	with TMEDA
1-Methyl-2-(methylthio)benzene (Ia)	[2-(Methylthio)benzene]acetic acid (IVa)	29	—
	[2-(Methylphenyl)thio]acetic acid (IVb)	68	97
	3-Methyl-2-(methylthio)benzoic acid (IVc)	3	3
1-Methyl-2-(isopropylthio)benzene (Ib)	[2-(Isopropylthio)benzene]acetic acid (Va)	57	3
	3-Methyl-2-(isopropylthio)benzoic acid (Vb)	43	52
	Benzoic acid	—	45
1,3-Dimethyl-2-(methylthio)benzene (IIa)	[3-Methyl-2-(methylthio)benzene]acetic acid (VIb)	70	4
	[(2,6-Dimethylphenyl)thio]acetic acid (VIb)	30	96
1,3-Dimethyl-2-(isopropylthio)benzene (IIb)	[3-Methyl-2-(isopropylthio)benzene]acetic acid (VII)	100	89
	3-Methylbenzoic acid	—	11
1-Ethyl-2-(methylthio)benzene (IIIa)	[(2-Ethylphenyl)thio]acetic acid (VIIIa)	95	94
	3-Ethyl-2-(methylthio)benzoic acid (VIIIb)	5	6
1,3-Diethyl-2-(methylthio)benzene (IIIb)	[(2,6-Diethylphenyl)thio]acetic acid (IX)	100	100

[a] All percentages were obtained by GLC analysis.

SCHEME 1



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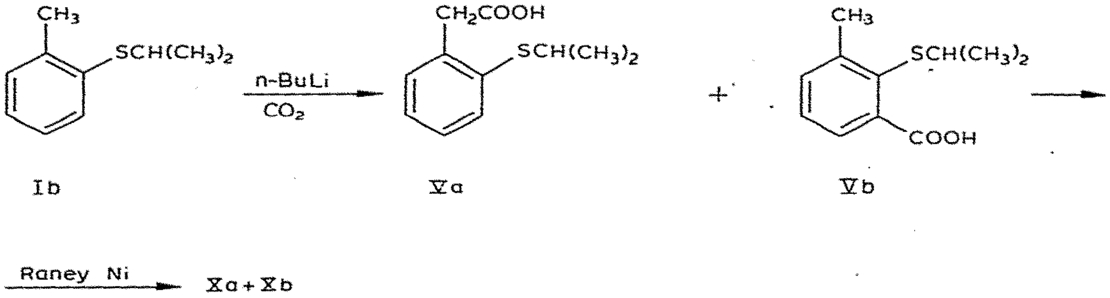

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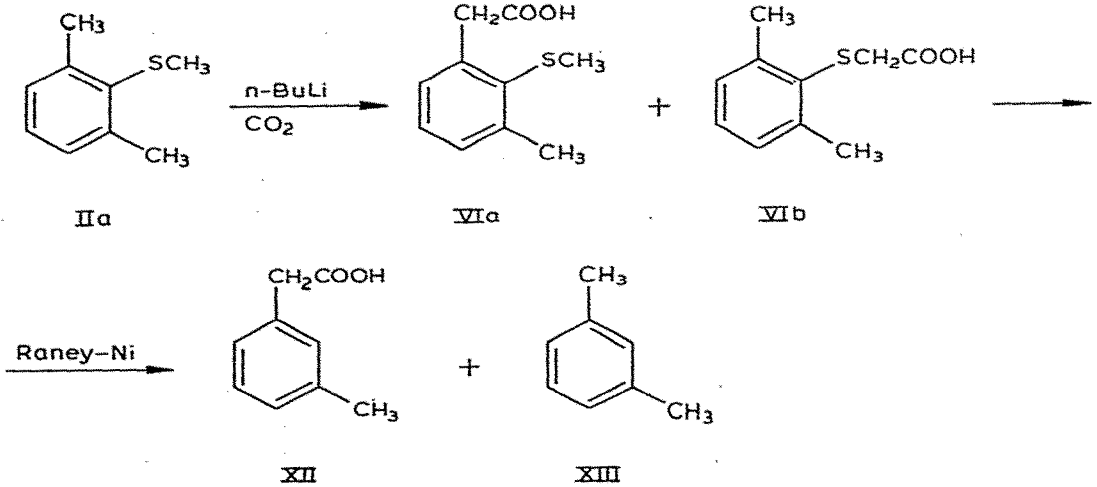

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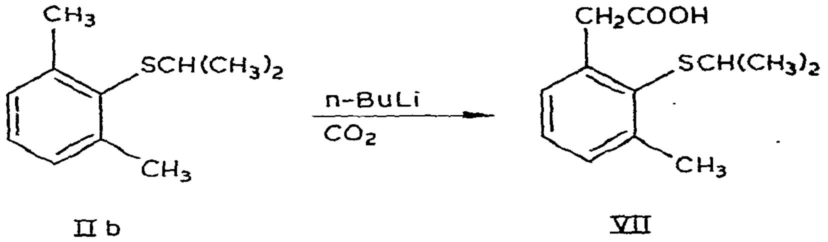

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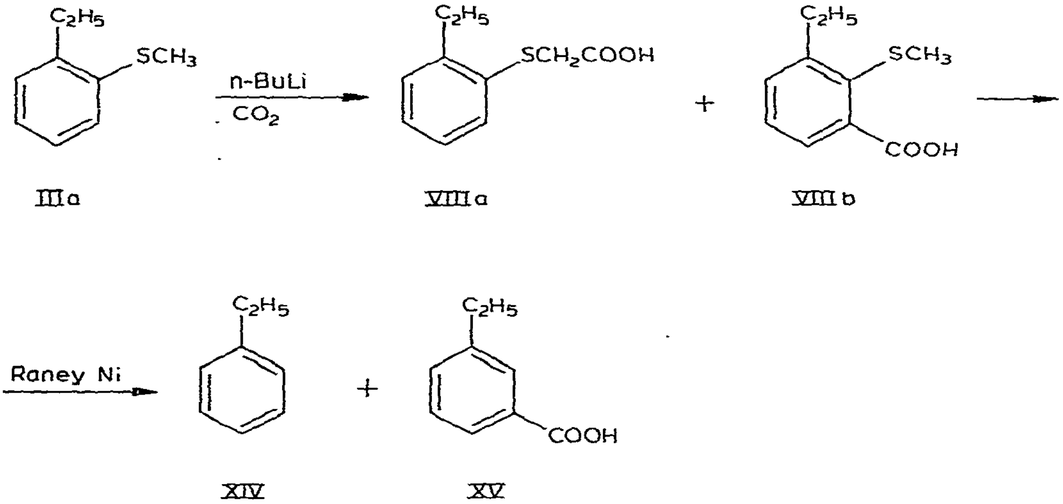
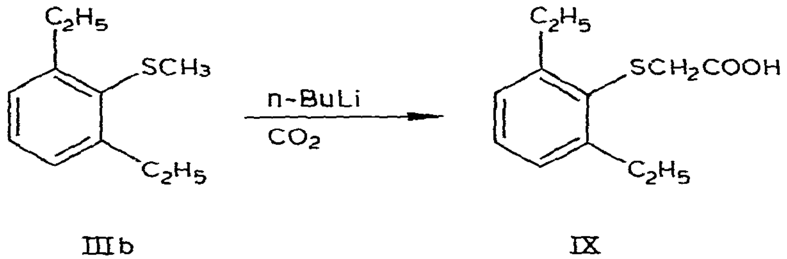


SCHEME 6



(v) Metalation of 1-ethyl-2-(methylthio)benzene (IIIa) (Scheme 5) both in the presence and in the absence of TMEDA gives mainly the acid VIIIa, with traces of VIIIb.

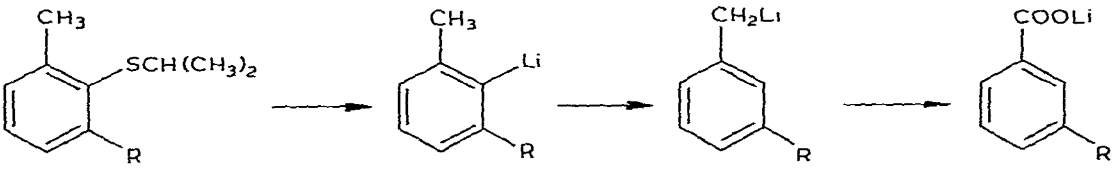
(vi) Only the acid IX is obtained under both conditions from metalation of 1,3-diethyl-2-(methylthio)benzene (IIIb) (Scheme 6).

These results show that in the substrates used, there are three types of site which may undergo metalation, viz. benzylic, thioalkylic, and ring positions.

The presence of the acids IVb, IVc and VIIIb seems to support participation of a transmetalation reaction; the first step is ring metalation *ortho* to the sulphur atom (kinetically controlled step), and this is followed by metalation of the thiomethylic carbon by the aryllithium (thermodynamically controlled step) [3]. The formation of Vb in the metalation of Ib is also consistent with such a transmetallation; in this case the absence of an acid derived from metalation of the thioisopropylic carbon is not surprising because of the destabilization of the thioalkylic carbanion by the two attached methyl groups [2,6]. However, such a transmetalation does not account for the products derived from attachment of the lithium at the thiomethylic position of IIa and IIIb, since there is no ring hydrogen *ortho* to the thioalkylic group available for metalation; the products were VIb and IX, and VIb was the main product in the presence of TMEDA. We believe that these products cannot come from transmetalation by an aryllithium with the lithium *meta-* or *para-* to the methylthio group, since we were unable to detect traces of the corresponding substituted benzoic acids. Moreover it seems unlikely that a benzyllithium is involved in the transmetalation, since we obtained IX from the reaction of IIIb without any traces of benzylic metalation product. Thus it is probable that metalation of the thiomethyl group occurs by direct attack of by n-butyllithium, although transmetalation cannot be excluded when possible.

Another feature of interest is the concurrent benzylic and thiomethylic substitution in compounds Ia and IIa, and concurrent benzylic and ring substitution in compound Ib. When the reaction is carried out with n-BuLi-TMEDA the extent of benzylic metalation decreases, and the thiomethylic and ring positions appear be more readily attacked. The basicity order n-BuLi < n-BuLi-TMEDA may account for this observation [5,7]. It was found that the reactivities of the thiomethylic (in Ia and IIa) and of the ring positions (in Ib) are increased with respect to that of the benzylic position as the base-strength of the reagent is increased [5,6]. If one assumes that the transition state involving the weakest base involves a greater degree of breaking of the C—H bond, it follows that stabilization due to electron-delocalization will be larger the weaker the base [8,9,10]. Thus metalation by the more basic n-BuLi-TMEDA will mainly occur at the ring or thiomethylic positions, while the less basic n-BuLi will predominantly attack the benzylic position, since delocalization of charge stabilizes the benzylic carbanion [5,6]. Support for this explanation is provided by the observations that reaction of IIa with phenyllithium-TMEDA gives only VIb, through a thioalkylic metalation, and that a low yield of VII is obtained in the reaction with n-BuLi-TMEDA.

The unexpected formation of benzoic or 3-methylbenzoic acid in the reaction of Ib or IIb with n-BuLi-TMEDA merits comment. Probably the first step is the cleavage of the sulfur—phenyl bond with formation of the corresponding aryllithium [3]. Subsequently the aryllithium would isomerize to a benzyllithium derivative, in which the carbanion is probably stabilized by coordination of the metal with TMEDA and delocalization of the negative charge on the aromatic ring [11]. The benzyllithium derivative would give rise to acid by oxidation [12,13].



R = H, CH$_3$

Experimental

General

Melting points were determined with a Tottoli apparatus (capillary method) and are uncorrected. Analyses by GLC were carried out with a Carlo Erba Fractovap C Gas Chromatograph equipped with a flame ionization detector, and a 10% Apiezon L column, using nitrogen as the carrier gas. Infrared spectra were recorded on a Perkin—Elmer 157 G spectrophotometer using potassium bromide mulls or neat liquids between sodium chloride plates. ^{1}H NMR spectra were recorded on a JEOL C-60 HL spectrometer working at 60 MHz with tetramethylsilane as internal reference. Microanalysis for C and H were carried out with a Perkin—Elmer model 240 Elementary Analyzer; analyses for S were carried out by the standard procedures [14,15]. Solutions of n-butyllithium in hexane were obtained from Aldrich Chemical Company and were analyzed by the Gilman double titration method before use [16]. *N,N,N′,N′*-Tetramethylethylenediamine (TMEDA) was obtained from Aldrich Chemical Company and was distilled from dry potassium hydroxide before use. All reactions were carried out in dried glassware under an atmosphere of dry, purified nitrogen. All compounds used were shown to be pure by GLC analysis.

Starting materials

1-Methyl-2-(methylthio)- (Ia), 1-methyl-2-(isopropylthio)- (Ib), 1,3-dimethyl-2-(methylthio)- (IIa) and 1-ethyl-2-(methylthio)-benzene (IIIa) were prepared by published methods [17—20].

1,3-Dimethyl-2-(isopropylthio)benzene (IIb). 2,6-Dimethylbenzenethiol [21] (0.2 mol), 2-bromopropane (0.21 mol), anhydrous potassium carbonate (0.23 mol) and dry acetone (60 cm^3) were refluxed together for 15 h. The mixture was then poured into water and the organic product extracted with diethyl ether. The ethereal solution was dried (CaCl$_2$), the solvent evaporated, and the residue distilled. Yield 77%, b.p. 83—84°C/2 mmHg; n_D^{18} 1.5430 (Found: C, 73.18; H, 8.89; S, 17.61. C$_{11}$H$_{16}$S calcd.: C, 73.27; H, 8.95; S, 17.78%). ^{1}H NMR (CCl$_4$): δ 6.80 (m, 3 H, Ar—H), 2.95 (m, 1 H, CH$_3$—*CH*—CH$_3$), 2.40 (s, 6 H, (*CH*$_3$)$_2$Ar) and 1.10 ppm (d, 6 H, *CH*$_3$—CH—*CH*$_3$).

1,3-Diethyl-2-(methylthio)benzene (IIIb). To a well stirred solution of 2,6-diethylbenzenethiol [22] (0.06 mol) and sodium hydroxide (0.072 mol) in water (25 cm^3) dimethyl sulfate (0.061 mol) was added dropwise. When the addition was complete, the mixture was stirred under reflux for two hours, then poured into water and extracted with diethyl ether. After drying (CaCl$_2$) the solvent was evaporated and the residue distilled. Yield 72%; b.p. 110—

111°C/5 mmHg; n_D^{20} 1.5630. (Found: C, 73.07; H, 8.88; S, 17.61. $C_{11}H_{16}S$ calcd.: C, 73.27; H, 8.95; S, 17.78%). ^{1}H NMR (CCl_4): δ 7.05 (m, 3 H, Ar — H), 2.90 (q, 4 H, *CH*$_2$—CH$_3$), 2.14 (s, 3 H, SCH$_3$) and 1.15 ppm (t, 6 H, CH$_2$—*CH*$_3$). *CH*$_3$).

Authentic samples

[2-(Methylthio)benzene]acetic acid (IVa), [(2-methylphenyl)thio]acetic acid (IVb) and [(2-ethylphenyl)thio]acetic acid (VIIIa), 3-methyl-2-(methylthio)-benzoic acid (IVc) and 3-ethylbenzoic acid (XV) were prepared by published procedures [23—27]. Benzeneacetic acid (Xa), (3-methylbenzene)acetic acid (XII), 3-methylbenzoic acid (Xb), toluene (XI), *m*-xylene (XIII) and ethylbenzene (XIV) were commercial products (Aldrich Chemical Company).

[(2,6-Dimethylphenyl)thio]acetic acid (VIb). A solution of 2,6-dimethylbenzenethiol (0.036 mol), chloroacetic acid (0.036 mol), sodium hydroxide (0.09 mol) and water (35 ml) was stirred under reflux for 3 hours. After cooling, the solution was acidified with 10% hydrochloric acid and extracted with diethyl ether. The combined extracts were dried (Na_2SO_4), filtered and concentrated in vacuo. The crude product was recrystallized from ligroin to constant melting point. Yield 71%, m.p. 74°C. (Found: C, 61.07; H, 6.11; S, 16.22. $C_{10}H_{12}O_2S$ calcd.: C, 61.19; H, 6.16; S, 16.34%). ^{1}H NMR ($CDCl_3$): δ 10.70 (s, 1 H, COOH, D_2O exchanged), 7.00 (m, 3 H, Ar—H), 2.90 (s, 2 H, *CH*$_2$—COOH) and 2.00 ppm (s, 6 H, Ar—*CH*$_3$). IR: 3100 (O—H), 1705 cm^{-1} (C=O).

[(2,6-Diethylphenyl)thio]acetic acid (IX). This was prepared as above from 2,6-diethylbenzenethiol. Yield 45%; b.p. 155—157°C/3 mmHg; n_D^{20} 1.5660 (Found: C, 64.11; H, 7.13; S, 14.08. $C_{12}H_{16}O_2S$ calcd.: C, 64.25; H, 7.19; S, 14.29%). ^{1}H NMR ($CDCl_3$): δ 9.00 (s, 1 H, COOH, D_2O exchanged), 7.05 (m, 3 H, Ar—H), 3.27 (s, 2 H, *CH*$_2$—COOH), 2.90 (q, 4 H, *CH*$_2$—CH$_3$) and 1.15 ppm (t, 6 H, CH$_2$—*CH*$_3$). IR: 3050 (O—H), 1710 cm^{-1} (C=O).

Metalation of 1-methyl-2-(methylthio)benzene (Ia)

A solution of Ia (0.0195 mol) in dry diethyl ether (25 cm^3) was blanketed with dry nitrogen and then treated dropwise at room temperature with n-butyllithium in hexane (0.02 mol, 11.3 cm^3). After the addition was complete, the mixture was stirred under reflux for 4 h. After cooling, the mixture was poured onto ca. 70 g of crushed solid carbon dioxide and allowed to stand for 15 hours. The residue was treated successively with 10% aqueous sodium bicarbonate and diethyl ether (50 cm^3). The alkali layer was separated, washed with diethyl ether, and then acidified with cold concentrated hydrochloric acid, extracted with diethyl ether, and dried (Na_2SO_4). A portion of this solution was treated with ether containing a 30% molar excess of diazomethane. The diethyl ether and excess diazomethane were allowed to evaporate off. The resulting methyl esters were analyzed by GLC, which gave three peaks with retention times identical to those of authentic sample of the methyl esters of IVa, IVb, IVc, in the ratio 29/68/3.

When the TMEDA-n-butyllithium complex was employed, this was first formed by treating TMEDA (0.02 mol) in diethyl ether (10 cm^3) with n-butyllithium in hexane (0.02 mol, 11.3 cm^3). After stirring for 1 h, a solution of Ia (0.0195 mol) in diethyl ether (25 cm^3) was added and the reaction continued as previously described. GLC analysis showed that the methyl esters of IVb and IVc were obtained in a ratio of 97/3.

Action of Raney nickel catalyst on mixture of acids IVa, IVb, IVc

A solution of acids IVa, IVb, IVc (0.01 mol) in 10 cm^3 of 95% ethanol was refluxed 2 h with 2 g of Raney nickel [28]. The mixture was filtered and evaporated. The residue was diluted with diethyl ether and treated with diazomethane. GLC gave three peaks which had retention times identical with those of XI and methyl esters of Xa and Xb.

Metalation of 1-methyl-2-(isopropylthio)benzene (Ib)

A solution of Ib (0.022 mol) in dry diethyl ether (28 cm^3) was treated dropwise at room temperature with n-butyllithium in hexane (0.023 mol, 15 cm^3). The mixture was worked up as described for Ia. GLC analysis of the methyl esters of the mixture from the sodium bicarbonate phase showed two peaks in the ratio 57/43. Identification of the components (Va and Vb) responsible for these peaks was accomplished after desulfuration with Raney nickel.

After metalation using n-butyllithium-TMEDA, the GLC of methyl esters of the products showed three peaks, with retention times identical with those of methylbenzoate and the methyl esters of Va and Vb, in the ratio of 45/3/52.

Action of Raney nickel catalyst on mixture of acids Va and Vb

A solution of the acids Va and Vb (0.01 mol) in 95% ethanol (10 cm^3) was treated with Raney nickel (2 g) and the products worked up as described above. GLC analysis showed two peaks, with retention times identical to those of the methyl esters of Xa and Xb.

Metalation of 1,3-dimethyl-2-(methylthio)benzene (IIa)

A solution of IIa (0.032 mol) in dry diethyl ether (50 cm^3) was treated dropwise at room temperature with n-butyllithium in hexane (0.034 mol, 17.8 cm^3). The mixture was stirred under reflux for 4 h and then worked up as described above. From the bicarbonate phase a mixture of acids was obtained, the methyl esters of which exhibited two peaks in GLC in the ratio 70/30. The minor component was identified as [(2,6-dimethylphenyl)thio]acetic acid (VIb) by comparison with an authentic sample. The major component, which was identified as 3-methyl-2-(methylthio)benzeneacetic acid (VIa), was isolated by chromatography on a silica gel column, using petroleum ether (40—70°)/ acetone (2/1) as eluent. Yield 47%, m.p. 86—87°C. (Found: C, 61.05; H, 6.11; S, 16.18. $C_{10}H_{12}O_2S$ calcd.: C, 61.19; H, 6.16; S, 16.34%). ^1H NMR ($CDCl_3$): δ 7.90 (s, 1 H, COOH, D_2O exchanged), 7.00 (m, 3 H, Ar—H), 3.70 (s, 3 H, SCH_3), 3.60 (s, 2 H, CH_2—COOH) and 2.25 ppm (s, 3 H, Ar—CH_3). IR: 3500 (O—H), 1730 (C=O), 760 cm^{-1} (1,2,3-trisubstituted benzene).

After metalation using n-butyllithium-TMEDA, GLC showed two peaks, with retention times identical to those of the methyl esters of VIa and VIb, in the ratio 4/96.

Action of Raney nickel catalyst on mixture of acids VIa and VIb

A solution of acids VIa and VIb (0.01 mol) in 95% ethanol (10 cm^3) was treated with Raney nickel (2 g) and the products were worked up as described above. GLC analysis showed two peaks with retention times corresponding to XIII and methyl ester of XII.

Metalation of IIa using phenyllithium

To a mixture of phenyllithium in diethyl ether [29] (0.025 mol, 16 cm^3) and TMEDA (0.025 mol) a solution of IIa (0.019 mol) in dry diethyl ether (40 cm^3) was added dropwise at room temperature. The mixture was stirred under reflux for 6 h and then worked up as described above. GLC analysis of methyl esters from the bicarbonate phase showed two peaks which were identified as methylbenzoate and VIb. No VIa was detected.

Metalation of 1,3-dimethyl-2-(isopropylthio)benzene (IIb)

A solution of IIb (0.027 mol) in dry diethyl ether (50 cm^3) was treated dropwise at room temperature with n-butyllithium in hexane (0.03 mol, 17.2 cm^3). The mixture was worked up as described above. The GLC analysis of the methyl esters from the sodium bicarbonate phase exhibited one peak. The component responsible for this peak was identified as [3-methyl-2-(isopropylthio)-benzene]acetic acid (VII), and was purified by chromatography on a silica gel column, using petroleum ether (40—70°)-diethyl ether (1/1) as eluent. Yield 48%, m.p. 74—75°C. (Found: C, 64.15; H, 7.11; S, 14.18. $C_{12}H_{16}O_2S$ calcd.: C, 64.25; H, 7.19; S, 14.29%). ^{1}H NMR ($CDCl_3$): δ 10.05 (s, 1 H, COOH, D_2O exchanged), 7.10 (m, 3 H, Ar—H), 4.00 (s, 2 H, CH_2—COOH), 3.05 (m, 1 H, CH_3—CH—CH_3), 2.50 (s, 3 H, Ar—CH_3) and 1.10 ppm (d, 6 H, CH_3—CH—CH_3). IR: 3500 (O—H), 1765 (C=O), 760 cm^{-1} (1,2,3-trisubstituted benzene).

Metalation of 1-ethyl-2-(methylthio)benzene (IIIa)

Metalation of IIIa was performed as described above. GLC analysis of methyl esters of a portion of the mixture of acids showed two peaks, in the ratio 95/5. The major component was identified as VIIIa by comparison with an authentic sample. The minor component, VIIIb was identified after desulfuration with Raney nickel.

GLC analysis of the product mixture from n-butyllithium-TMEDA showed only the two peaks, from VIIIa and VIIIb, in the ratio 96/4.

Action of Raney nickel catalyst on mixture of acids VIIIa and VIIIb

A solution of the mixture of acids VIIIa and VIIIb (0.01 mol), 95% ethanol (10 cm^3) was refluxed with Raney nickel (2 g) for 2 h and the products worked up as described above. GLC analysis gave two peaks, with the retention times of XIV and the methyl ester of XV.

Metalation of 1,3-diethyl-2-(methylthio)benzene (IIIb)

IIIb (0.032 mol) in dry diethyl ether (50 cm^3) was metalated with a solution of n-butyllithium in hexane (0.034 mol, 17.8 ml). The products were worked up as described above. GLC analysis of the methyl esters from an aliquot of the mixture of acids showed one peak, which was identified as being due to the methyl ester of IX by comparison with an authentic sample.

GLC analysis of the products from metalation with n-butyllithium-TMEDA showed only the peak due to IX.

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