Pergamon

Tetrahedron Vol. 51, No. 43, pp. 11883-11890, 1995
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0040-4020/95 $9.50+0.00

0040-4020(95)00749-0

3-Lithiopropyl *tert*-Butyl Thioether: A New γ-Functionalised Organolithium Compound (d^3-Reagent) in Synthetic Organic Chemistry

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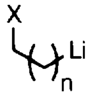
Abstract: The reaction of 3-bromo or 3-chloropropyl *tert*-butyl thioether (**1a** or **1'a**) with an excess of lithium powder and a catalytic amount of naphthalene (2,5 mol %) in THF at -78°C followed by treatment with an electrophile (H_2O, D_2O, Me_2S_2, CO_2) at the same temperature leads, after hydrolysis, to the expected products **2**. Alternatively the process can be carried out under Barbier-type reaction conditions [lithiation in the presence of the electrophile: Me_3SiCl, Bu^tCHO, PhCHO, Me_2CO, $(CH_2)_4CO$, $(CH_2)_5CO$, PhCOMe, c-C_3H_5COPh] and using DTBB as the arene catalyst at 0°C. De-*tert*-butylation of products **2** with mercury(II) acetate and sulfhydric acid yields different sulfurated derivatives depending on the structure of the starting thioether.

INTRODUCTION

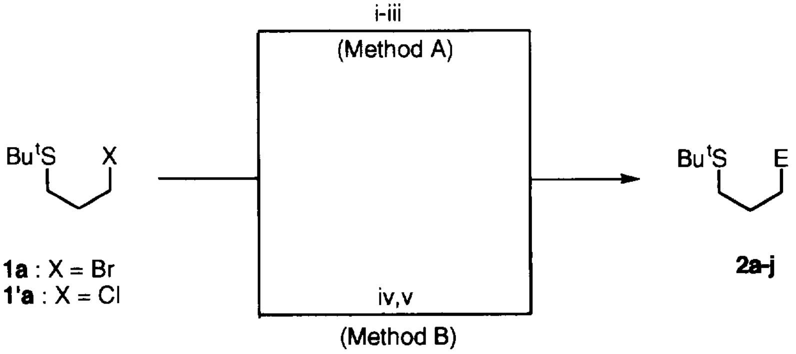
Functionalised organolithium compounds[1] of the type **I** (d^n-reagents[2]) are interesting intermediates in synthetic organic chemistry because by reaction with electrophilic reagents they yield directly polyfunctionalised molecules[3]. The corresponding β-substituted oxygenated or nitrogenated derivatives (d^2-reagents[2]: **I**, n=1, X=RO, R_2N, respectively) have been prepared at low temperature by three different methods: (a) mercury/lithium transmetallation[4]; (b) chlorine/lithium exchange[5,6]; (c) reductive opening of the corresponding saturated heterocycles (epoxides[7] or aziridines[8]). Oxygen- or nitrogen-containing γ-functionalised organolithium intermediates (d^3-reagents[2]: **I**, n=2) have been prepared following the routes (b)[9,10] and (c)[11,12] and by tin/lithium transmetallation[13] starting from the appropriate precursors. For intermediates of the type **I** with n>2 (d^n-reagents[2]), the so-called remote-functionalised organolithium compounds, the most common procedure is the halogen/lithium exchange [way (b)][14,15]. Whilst sulfur-containing organolithium compounds of the type **I** with n=1 or 2 are not accessible by the above described routes (a)[16], (b)[17] or (c)[18], the corresponding remote-functionalised derivatives (n>2) have been obtained by a different way: a sulfur/lithium exchange[19]. In this paper we apply the recently reported arene-catalysed lithiation procedure[20,21] to the preparation, for the first time, of a γ-functionalised sulfur-containing organolithium compound of the type **I** with n=2 and X=RS from the corresponding brominated or chlorinated precursor.



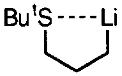
I (n = 1,2,...)

RESULTS AND DISCUSSION

The reaction of 3-bromopropyl *tert*-butyl thioether (**1a**) with an excess of lithium powder (1:10 molar ratio) and a catalytic amount of naphthalene (2.5 mol %) in THF at -78°C led to the intermediate **3**, which by reaction with different electrophiles (H_2O, D_2O, Me_2S_2, CO_2) at the same temperature yielded, after hydrolysis with water, the corresponding products **2a-d** (Method A; Scheme 1 and Table 1, entries 1-4). Alternatively the reaction can be carried out under Barbier-type conditions: in this case the lithiation step was performed in the presence of the electrophile [Me_3SiCl, Bu^tCHO, PhCHO, Me_2CO, $(CH_2)_5CO$, *c*-C_3H_5COPh] using 4,4'-di-*tert*-butylbiphenyl (DTBB) as the arene catalyst at room temperature affording, after hydrolysis, the expected products **2e-j** (Method B; Scheme 1 and Table 1, entries 5-10). The presence of the *tert*-butyl group attached to the sulfur atom is important in order to get a stable species: when the same reaction shown in the Scheme 1 was carried out with the starting material **1b** or **1c** no product of the type **2** was isolated (using both Methods A or B), although the corresponding precursor **1b** or **1c** disappeared.



Scheme 1. *Reagents and conditions*: i, Li excess, naphthalene cat. (2.5 mol %), THF, -78°C, 1 h; ii, E^+=H_2O, D_2O, Me_2S_2, CO_2, -78°C; iii, H_2O, -78 to 20°C; iv, Li excess, DTBB cat. (2.5 mol %), E^+=Me_3SiCl, Bu^tCHO, PhCHO, Me_2CO, $(CH_2)_5CO$, *c*-C_3H_5COPh, THF, 20°C, 4 h; v, H_2O.



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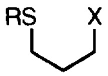
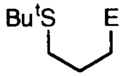


1b : R = Ph, X = Cl
1c : R = $PhCH_2$, X = Br



2k : E = $(CH_2)_4COH$ (87%)
2l : E = PhC(OH)Me (53%)

Table 1. Preparation of Compounds **2**

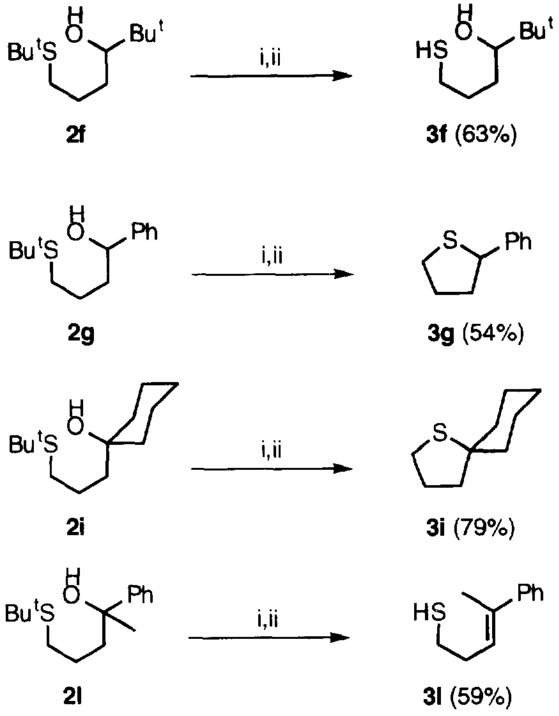
Entry	Method	Electrophile E^+	Product[a] No.	E	Yield (%)[b]	R_f[c]
1	A	H_2O	**2a**	H	79	0.29[d]
2	A	D_2O	**2b**	D	81	0.29[d]
3	A	Me_2S_2	**2c**	MeS	65	0.40[e]
4	A	CO_2	**2d**	CO_2H	60	0.42[f]
5	B	Me_3SiCl	**2e**	Me_3Si	55	0.40[g]
6	B	Bu^tCHO	**2f**	Bu^tCHOH	82	0.30[h]
7	B	PhCHO	**2g**	PhCHOH	49[i]	0.23[h]
8	B	Me_2CO	**2h**	Me_2COH	45	0.25[h]
9	B	$(CH_2)_5CO$	**2i**	$(CH_2)_5COH$	69	0.28[h]
10	B	*c*-C_3H_5COPh	**2j**	*c*-$C_3H_5C(OH)Ph$	52	0.43[h]

[a] All products **2** were >95% pure (GLC and 300 MHz ^1H NMR). [b] Isolated yield after column chromatography (silica gel, hexane/ethyl acetate) based on the starting bromothioether **1**. [c] Silica gel. [d] Hexane/ethyl acetate: 20/1. [e] Hexane/ethyl acetate: 10/1. [f] Hexane/ethyl acetate: 2/1. [g] Hexane. [h] Hexane/ethyl acetate: 5/1. [i] A 74% yield was obtained starting from **1'a** (see text).

The reaction shown in Scheme 1 can be alternatively carried out starting from the corresponding chlorinated thioether; thus, using *tert*-butyl 3-chloropropyl thioether (**1'a**) as starting material and Method A, compounds **2g**, **2k** and **2l** were isolated when benzaldehyde, cyclopentanone or acetophenone were used, respectively, as electrophilic reagents.

Starting materials **1** were prepared by nucleophilic substitution reaction of lithium *tert*-butanethiolate with 1,3-dibromo or 1,3-dichloropropane.

Finally, we studied the de-*tert*-butylation of products **2** by successive treatment with mercury(II) acetate-trifluoroacetic acid and sulfhydric acid[22] finding that the reaction products depend strongly of the alcoholic moiety in **2**. Thus, applying this methodology only hydroxythiol **3f** was obtained from the pivalaldehyde derivative **2f**. From benzaldehyde derivative **2g** a cyclisation to the corresponding tetrahydrothiophene **3g** took place, this behaviour being also observed for the cyclohexanone derivative **2i** to give spirothioether **3i**. Finally, a dehydration occurred when acetophenone derivative **2l** was submitted to the same procedure, affording the unsaturated (*E*)-thioether **3l** as the only diastereoisomer[23]. All these apparently strange behaviours can be easily explained considering that the acidic reaction medium used for the reaction can transform the corresponding hydroxythiol (*eg*. **3f**) into the corresponding carbenium ion, which suffers either an intramolecular nucleophilic attack of the sulfur atom (to give compounds **3g** and **3i**) or a proton elimination (to yield compound **3l**) depending on the substitution at the alcoholic carbon atom (Scheme 2).



Scheme 2. *Reagents and conditions*: i, $Hg(OAc)_2$, CF_3CO_2H, 0°C; ii, H_2S, H_2O, THF.

In conclusion, we have developed a simple methodology to prepare a sulfur-containing γ-functionalised organolithium compound (d^3-reagent[2]) of the type **I**, with n=2.

EXPERIMENTAL PART

General.- For general information see reference 8b.

Preparation of Halothioethers **1**. *General Procedure.*- To a cooled (-50°C) solution of the corresponding thiol (5.0 mmol) in THF (10 ml) under argon was added a 1.6 M hexane solution (5.5 mmol) of Bu^nLi. The temperature was allowed to rise to 20°C during *ca.* 1 h. The reaction mixture was transfered *via cannula* to a cooled (-50°C) solution of the corresponding 1,3-dihalopropane (2.0 mmol) in THF (20 ml) and the temperature was allowed to rise to 20°C over a period of 3 h. The resulting mixture was hydrolysed with water and extracted with ethyl acetate. The organic layer was dried over anhydrous sodium sulfate and evaporated (15 mmHg). The resulting residue was purified by column chromatography (silica gel; hexane/ethyl acetate) and/or distillation under reduced pressure (Kugelrohr) to give the tittle compounds **1**. Yields, physical and spectroscopic data as well as literature references follow.

3-Bromopropyl 1,1-Dimethylethyl Thioether (**1a**): (31%) bp 65°C/1mm Hg; ν_{max} (film) 2960 cm^{-1} (CH); δ_H 1.33 [9H, s, $(CH_3)_3C$], 2.06-2.15 (2H, m, $CH_2CH_2CH_2$), 2.68 (2H, t, *J*=7.0, CH_2S), 3.52 (2H, t, *J*=6.4, CH_2Br); δ_C 26.5 ($CH_2CH_2CH_2$), 30.9 [$(CH_3)_3C$], 32.6, 32.7 (CH_2S, CH_2Br), 42.1 [$(CH_3)_3C$]; *m/z* 212 [$M^+(^{81}Br)$, 6%], 210 [$M^+(^{79}Br)$, 6%], 156 (11), 57 (100), 45 (10), 41 (51) (Found: M^+, 210.0088. $C_7H_{15}BrS$ requires M, 210.0078).

3-Chloropropyl Phenyl Thioether (**1b**): (85%) R_f=0.55 (hexane/ethyl acetate, 10:1); ν_{max} (film) 3030, 1580, 740, 690 cm^{-1} (ArH); δ_H 1.99-2.08 (2H, m, $CH_2CH_2CH_2$), 3.04 (2H, t, *J*=6.9, CH_2S), 3.62 (2H, t, *J*=6.2, CH_2Cl), 7.14-7.34 (5H, m, ArH); δ_C 30.5, 31.5, 43.2 (3xCH_2), 126.1, 128.9, 129.3, 135.6 (ArC); *m/z* 188 [M$^+$(^{37}Cl), 28%], 186 [M$^+$(^{35}Cl), 75%], 123 (100), 110 (76), 109 (22), 77 (11), 65 (14), 51 (10), 45 (14) (Found: M$^+$, 186.0281. $C_9H_{11}ClS$ requires M, 186.0270).

Benzyl 3-Bromopropyl Thioether (**1c**): (43%) R_f=0.51 (hexane/ethyl acetate, 10:1); ν_{max} (film) 3020, 1590, 760, 690 cm^{-1} (ArH); δ_H 1.99-2.08 (2H, m, $CH_2CH_2CH_2$), 2.54 (2H, t, *J*=6.9, CH_2S), 3.44 (2H, t, *J*=6.4, CH_2Br), 3.70 (2H, s, ArCH_2), 7.21-7.31 (5H, m, ArH); δ_C 29.4, 31.9, 32.1, 36.2 (4xCH_2), 127.0, 128.5, 128.7, 138.1 (ArC); *m/z* 246 [M$^+$(^{81}Br), 55%], 244 [M$^+$(^{79}Br), 54%], 92 (30), 91 (100), 89 (12), 65 (41), 63 (13), 51 (10), 45 (27), 41 (18) (Found: M$^+$, 243.9914. $C_{10}H_{13}BrS$ requires M, 243.9921).

3-Chloropropyl 1,1-Dimethylethyl Thioether (**1'a**)[24]: (96%) R_f=0.29 (*n*-pentane); ν_{max} (film) 2960 cm^{-1} (CH); δ_H 1.33 [9H, s, $(CH_3)_3C$], 1.98-2.07 (2H, m, $CH_2CH_2CH_2$), 2.68 (2H, t, *J*=7.0, CH_2S), 3.65 (2H, t, *J*=6.2, CH_2Cl); δ_C 25.2 ($CH_2CH_2CH_2$), 30.9 [$(CH_3)_3C$], 32.6 (CH_2S), 42.1 [$(CH_3)_3C$], 43.8 (CH_2Cl); *m/z* 168 [M$^+$(^{37}Cl), 54%], 166 [M$^+$(^{35}Cl), 70%], 153 (12), 151 (30), 45 (10), 41 (51).

Preparation of Compounds **2**. *Method A*.- To a cooled (-78°C) blue suspension of lithium powder (0.14 g, 20.0 mmol) and a catalytic amount of naphthalene (0.013 g, 0.1 mmol) in THF (10 ml) was added the halothioether **1** (2.0 mmol) under argon and the mixture was stirred at -78°C for 1 h. Then, the corresponding electrophile (2.1 mmol; 0.5 ml in the case of water or deuterium oxide; CO_2 was bubbled for 1 h) was added and the temperature was allowed to rise to 20°C for *ca.* 3 h. The resulting mixture was hydrolysed with water and extracted with ethyl acetate. The organic layer was dried over anhydrous sodium sulfate and evaporated (15 mmHg). The resulting residue was purified by column chromatography (silica gel; hexane/ethyl acetate) and/or distillation under reduce pressure (Kugelrohr) to yield pure compounds **2a-d**. Yields are included in Table 1 and text; R_f values for compounds **2a-d** are included in Table 1; analytical and spectroscopic data follow.

1,1-Dimethylethyl Propyl Thioether (**2a**): ν_{max} (film) 2940 cm^{-1} (CH); δ_H 0.99 (3H, t, *J*=7.3, CH_3CH_2), 1.32 [9H, s, $(CH_3)_3C$], 1.59 (2H, sextet, *J*=7.3, CH_3CH_2), 2.50 (2H, t, *J*=7.4, CH_2S); δ_C 13.8 (CH_3CH_2), 23.2 (CH_3CH_2), 30.3 (CH_2S), 30.9 [$(CH_3)_3C$], 41.6 [$(CH_3)_3C$]; *m/z* 132 (M$^+$, 8%), 57 (100), 56 (18), 41 (51) (Found: M$^+$, 132.0966. $C_7H_{16}S$ requires M, 132.0973).

3-Deuteriopropyl 1,1-Dimethylethyl Thioether (**2b**): ν_{max} (film) 2920 cm^{-1} (CH); δ_H 0.97-1.02 (2H, m, CH_2D), 1.32 [9H, s, $(CH_3)_3C$], 1.56-1.61 (2H, m, $CH_2CH_2CH_2$), 2.50 (2H, t, *J*=7.4, CH_2S); δ_C 13.5 (t, J_{CD}=19.3, CH_2D), 23.1 ($CH_2CH_2CH_2$), 30.3 (CH_2S), 30.9 (3xCH_3), 41.6 [$(CH_3)_3C$]; *m/z* 133 (M$^+$, 22%), 75 (11), 57 (100), 56 (24), 45 (11), 42 (13), 41 (80) (Found: M$^+$, 133.1036. $C_7H_{15}DS$ requires M, 133.1036).

1-(1,1-Dimethylethylthio)-3-methylthiopropane (**2c**): ν_{max} (film) 2940 cm^{-1} (CH); δ_H 1.32 [9H, s, $(CH_3)_3C$], 1.86 (2H, quintet, *J*=7.2, $CH_2CH_2CH_2$), 2.09 (3H, s, CH_3S), 2.59, 2.63 (4H, 2 t, *J*=7.2, 2xSCH_2); δ_C 15.3 (CH_3S), 27.0, 29.1 (2xCH_2), 30.9 [$(CH_3)_3C$], 33.3 (CH_2S), 41.9 [$(CH_3)_3C$]; *m/z* 178 (M$^+$, 10%), 122 (11), 121 (100), 74 (18), 73 (37), 61 (30), 59 (14), 57 (57), 47 (16), 46 (12), 45 (28), 41 (60) (Found: M$^+$, 178.0851. $C_8H_{18}S_2$ requires M, 178.0850).

4-(1,1-Dimethylethylthio)butanoic Acid (**2d**): ν_{max} (film) 3700-2300 (CO_2H), 1700 cm^{-1} (C=O); δ_H 1.31 [9H, s, $(CH_3)_3C$], 1.90 (2H, quintet, *J*=7.3, $CH_2CH_2CH_2$), 2.49 (2H, t, *J*=7.3, CH_2CO_2H), 2.58 (2H, t, *J*=7.3, CH_2S), 11.44 (1H, br s, CO_2H); δ_C 24.8, 27.4 (2xCH_2), 30.9 [$(CH_3)_3C$], 33.0 (CH_2S), 42.0 [$(CH_3)_3C$], 179.7 (CO_2H); *m/z* 176 (M$^+$, 67%), 121 (14), 120 (61), 103 (44), 102 (81), 87 (26), 75 (22), 73 (30), 61 (14), 60 (26), 59 (44), 58 (28), 57 (100), 56 (35), 55 (37), 47 (23), 46 (21), 45 (83), 43 (14), 42 (31), 41 (88) (Found: M$^+$, 176.0874. $C_8H_{16}O_2S$ requires M, 176.0871).

1-[3-(1,1-Dimethylethylthio)propyl]cyclopentanol (**2k**): R_f=0.23 (hexane/ethyl acetate, 5:1); ν_{max} (film) 3720-3080 cm^{-1} (OH); δ_H 1.32 [9H, s, $(CH_3)_3C$], 1.53-1.81 (13H, m, 4xring CH_2, OH, $SCH_2CH_2CH_2$), 2.57 (2H, t, J=6.3, CH_2S); δ_C 23.7, 25.0, 28.8 (2xring CH_2, $SCH_2CH_2CH_2$), 30.9 [$(CH_3)_3C$], 39.6, 40.9 (2xring CH_2, $SCH_2CH_2CH_2$), 41.8 [$(CH_3)_3C$], 82.2 (COH); *m/z* 216 (M^+, 1%), 141 (18), 116 (16), 113 (12), 85 (10), 67 (11), 58 (13), 57 (100), 55 (21), 43 (11), 41 (45) (Found: M^+, 216.1548. $C_{12}H_{24}OS$ requires M, 216.1548).

1-Methyl-4-(1,1-dimethylethylthio)-1-phenyl-1-butanol (**2l**): R_f=0.35 (hexane/ethyl acetate, 5:1); ν_{max} (film) 3660-3130 cm^{-1} (OH); δ_H 1.26 [9H, s, $(CH_3)_3C$], 1.38-1.62 (2H, m, $SCH_2CH_2CH_2$), 1.54 (3H, s, CH_3COH), 1.87-1.98 (3H, m, CH_2COH), 2.45 (2H, t, J=7.3, CH_2S), 7.18-7.43 (5H, m, ArH); δ_C 24.3, 28.5, ($SCH_2CH_2CH_2$), 30.2 (CH_3COH), 30.9 [$(CH_3)_3C$], 41.8 [$(CH_3)_3C$], 43.5 (CH_2S), 74.4 (COH), 124.7, 126.5, 128.1, 147.6 (ArC); *m/z* 252 (M^+, 4%), 177 (16), 163 (22), 121 (60), 116 (52), 105 (13), 103 (10), 101 (10), 91 (11), 77 (19), 57 (100), 43 (97), 41 (39) (Found: M^+, 252.1550. $C_{15}H_{24}OS$ requires M, 252.1548).

Preparation of Compounds **2**. *Method B*.- To a blue suspension of lithium powder (0.140 g, 20.0 mmol) and a catalytic amount of 4,4'-di-*tert*-butylbiphenyl (0.026 g, 0.1 mmol) in THF (5 ml) was slowly added (*ca.* 2 h) a solution of **1a** (0.422 g, 2.0 mmol) and the corresponding electrophile (3.0 mmol) in THF (4 ml) at 20°C. The resulting mixture was hydrolysed with water and extracted with ethyl acetate. The organic layer was dried over anhydrous sodium sulfate and evaporated (15 mmHg). The resulting residue was purified by column chromatography (silica gel; hexane/ethyl acetate) to yield pure compounds **2e-j**. Yields and R_f values are included in Table 1; analytical and spectroscopic data follow.

3-(1,1-Dimethylethylthio)-1-trimethylsilylpropane (**2e**): ν_{max} (film) 830 cm^{-1} [$Si(CH_3)_3$]; δ_H 0.00 [9H, s, $Si(CH_3)_3$], 0.01-0.15 (2H, m, $SiCH_2$), 1.33 [9H, s, $(CH_3)_3C$], 1.53-1.64 (2H, m, $CH_2CH_2CH_2$), 2.55 (2H, t, J=7.4, CH_2S); δ_C -1.8 [$Si(CH_3)_3$], 16.8, 24.6 (2xCH_2), 31.0 [$(CH_3)_3CS$], 32.0 (CH_2), 41.7 [$(CH_3)_3C$]; *m/z* 204 (M^+, 9%), 134 (10), 133 (73), 91 (27), 75 (13), 74 (10), 73 (100), 59 (10), 57 (76), 45 (13), 41 (22) (Found: M^+, 204.1372. $C_{10}H_{24}SSi$ requires M, 204.1368).

2,2-Dimethyl-6-(1,1-dimethylethylthio)-3-hexanol (**2f**): ν_{max} (film) 3620-3080 cm^{-1} (OH); δ_H 0.84 [9H, s, $(CH_3)_3CCH$], 1.26 [9H, s, $(CH_3)_3CS$], 1.47-1.86 [4H, m, $(CH_2)_2CHOH$], 2.51 (2H, t, J=7.0, CH_2S), 3.13 (1H, dd, J=9.6, 0.9, $CHOH$), 3.19 (1H, br s, OH); δ_C 25.6 [$(CH_3)_3CCH$], 26.5, 27.3, 28.3 (3xCH_2), 30.9 [$(CH_3)_3CS$], 34.9 [$(CH_3)_3CCH$], 41.8 [$(CH_3)_3CS$], 79.5 (CHOH); *m/z* 218 (M^+, 2%), 143 (18), 127 (14), 105 (11), 87 (34), 69 (10), 57 (100), 43 (14), 41 (51) (Found: M^+, 218.1709. $C_{12}H_{26}OS$ requires M, 218.1704).

4-(1,1-Dimethylethylthio)-1-phenyl-1-butanol (**2g**): ν_{max} (film) 3600-3100 cm^{-1} (OH); δ_H 1.28 [9H, s, $(CH_3)_3CS$], 1.49-1.90 (4H, m, 2xCH_2), 2.15 (1H, br s, OH), 2.51 (2H, t, J=7.2, CH_2S), 4.63 (1H, dd, J=7.2, 5.7, $CHOH$), 7.24-7.35 (5H, m, ArH); δ_C 26.0, 28.1, (2xCH_2), 30.9 [$(CH_3)_3CS$], 38.4 (CH_2S), 41.8 [$(CH_3)_3CS$], 74.1 (CHOH), 125.8, 127.4, 128.3, 144.5 (ArC); *m/z* 238 (M^+, 4%), 181 (12), 147 (51), 107 (16), 105 (24), 79 (30), 77 (33), 57 (100), 51 (10), 41 (48) (Found: M^+, 238.1386. $C_{14}H_{22}OS$ requires M, 238.1391).

2-Methyl-5-(1,1-dimethylethylthio)-2-pentanol (**2h**): ν_{max} (film) 3600-3020 cm^{-1} (OH); δ_H 1.21 [6H, s, $(CH_3)_2C$], 1.32 [9H, s, $(CH_3)_3C$], 1.53-1.72 (4H, m, 2xCH_2), 1.92 (1H, br s, OH), 2.54 (2H, t, J=7.0, CH_2S); δ_C 24.5, 28.6 (2xCH_2), 29.1 [$(CH_3)_2C$], 30.8 [$(CH_3)_3C$], 41.7 [$(CH_3)_3C$], 43.2 (CH_2S), 70.5 (COH); *m/z* 190 (M^+, 5%), 116 (17), 115 (20), 101 (46), 59 (36), 58 (11), 57 (100), 55 (11), 43 (26), 41 (37) (Found: M^+, 190.1398. $C_{10}H_{22}OS$ requires M, 190.1391).

1-[3-(1,1-Dimethylethylthio)propyl]cyclohexanol (**2i**): ν_{max} (film) 3600-3080 cm^{-1} (OH); δ_H 1.27 [9H, s, $(CH_3)_3C$], 1.30-1.64 [15H, m, 5xring CH_2, $(CH_2)_2COH$], 2.49 (2H, t, J=7.0, CH_2S); δ_C 22.2, 23.3, 25.7, 28.6 [5xring CH_2, $(CH_2)_2COH$], 30.9 [$(CH_3)_3C$], 37.4 (CH_2S), 41.8 [$(CH_3)_3C$], 71.2 (COH); *m/z* 230 (M^+, 2%), 155 (32), 116 (26), 113 (14), 99 (11), 85 (25), 57 (100), 55 (23), 43 (12), 41 (49) (Found: M^+, 230.1702. $C_{13}H_{26}OS$ requires M, 230.1704).

1-Cyclopropyl-4-(1,1-dimethylethylthio)-1-phenyl-1-butanol (**2j**): ν_{max} (film) 3600-3100 cm^{-1} (OH); δ_H 0.08-0.63 (5H, m, 2xring CH_2, 1xringCH), 0.75-0.97 (2H, m, $CH_2\mathit{CH_2}CH_2$), 1.27 [9H, s, $(CH_3)_3C$], 1.42-2.07 (3H, m, CH_2COH), 2.47 (2H, t, *J*=7.2, CH_2S), 7.09-7.46 (5H, m, ArH); δ_C 0.6, 1.4, 3.1 (2xring CH_2), 21.9, 24.0, 28.6 (3xCH_2), 30.9 [$(\mathit{C}H_3)_3C$], 41.7 [$(CH_3)_3\mathit{C}$], 74.8 (COH), 125.5, 126.8, 127.9, 146.1 (ArC); *m/z* 278 (M^+, 4%), 147 (39), 129 (11), 116 (33), 105 (64), 103 (10), 91 (19), 77 (28), 69 (16), 57 (100), 55 (10), 41 (36) (Found: M^+, 278.1701. $C_{17}H_{26}OS$ requires M, 278.1704).

*De-*tert*-butylation of compounds* **2f,g,i,l**. *Isolation of compounds* **3**. *General procedure.-* To a solution of the corresponding thioether **2** (0.5 mmol) in trifluoroacetic acid (5 ml) was added mercury (II) acetate (0.160 g, 0.5 mmol) at 0°C and the mixture was stirred for 3 (compounds **2f** and **2i**) or 15 h (compounds **2g** and **2l**). The solvent was then evaporated (15 Torr) and to the resulting residue water (3 ml) and THF (1 ml) were added. Through the resulting mixture hydrogen sulfide was bubbled for 1 h. Then, the black precipitate was filtered off (celite) and washed with ethyl acetate (30 ml). After decantation of the aqueous layer, the organic one was dried with anhydrous sodium sulfate and evaporated (15 Torr). The obtained residue was purified by column chromatography (silica gel; hexane/ethyl acetate) yielding the titled compounds **3**. Yields are included in Scheme 2; analytical and spectroscopic data as well as literature references for known compounds follow.

6-Mercapto-2,2-dimethyl-3-hexanol (**3f**): R_f=0.27 (hexane/ethyl acetate, 5:1); ν_{max} (film) 3680-3080 cm^{-1} (OH); δ_H 0.90 [9H, s, $(CH_3)_3C$], 1.31-1.43 (2H, m, $HSCH_2\mathit{CH_2}$), 1.63-2.11 (4H, m, $\mathit{CH_2}CHO\mathit{H}$, SH), 2.95-3.08 (2H, m, $\mathit{CH_2}SH$), 3.23 (1H, dd, *J*=10.4, 1.8, $C\mathit{H}OH$); δ_C 25.6 [$(\mathit{C}H_3)_3C$], 26.7, 30.1 (2xCH_2), 35.0 [$(CH_3)_3\mathit{C}$], 39.8 (CH_2S), 79.5 (CHOH); *m/z* 144 (M^+-H_2O, 2%), 105 (10), 104 (28), 101 (18), 87 (100), 71 (66), 69 (17), 61 (10), 60 (30), 57 (58), 55 (12), 47 (14), 45 (18), 43 (72), 42 (10), 41 (60).

2-Phenyl tetrahydro thiophene (**3g**)[25]: R_f=0.16 (pentane); ν_{max} (film) 3060, 3026, 1599, 759, 699 cm^{-1} (ArH); δ_H 1.18-2.58 (4H, m, $SCH_2\mathit{CH_2CH_2}$), 2.97-3.14 (1H, m, $\mathit{H}CHS$), 3.13-3.19 (1H, m, $HC\mathit{H}S$), 4.51 (1H, dd, *J*=8.2, 6.1, CHPh), 7.18-7.43 (5H, m, ArH); δ_C 31.0, 33.4, 40.5 (3xCH_2), 52.7 (CHPh), 126.9, 127.6, 128.3, 143.0 (ArC); *m/z* 164 (M^+, 15%), 121 (16), 117 (18), 115 (11), 103 (12), 91 (17), 78 (27), 77 (33), 65 (10), 63 (17), 62 (10), 60 (23), 59 (38), 58 (35), 52 (10), 51 (54), 50 (31), 47 (45), 46 (91), 45 (100), 42 (19), 41 (51).

1-Thiaspiro[4.5]decane (**3i**)[26]: R_f=0.38 (hexane); ν_{max} (film) 2930 cm^{-1} (CH); δ_H 1.22-1.61 (10H, m, 5xring CH_2), 1.75 (2H, t, *J*=6.5, $SCH_2CH_2\mathit{CH_2}C$), 2.04 (2H, quintet, *J*=6.5, $SCH_2\mathit{CH_2}CH_2C$), 2.85 (2H, t, *J*=6.5, SCH_2); δ_C 24.9, 25.7, 29.0, 32.0, 40.9, 44.1 (8xCH_2), 59.7 (CS); *m/z* 156 (M^+, 18%), 128 (12), 114 (12), 113 (100), 100 (46), 87 (22), 85 (13), 81 (28), 79 (35), 77 (15), 71 (12), 67 (45), 65 (13), 59 (13), 58 (15), 55 (23), 54 (11), 53 (26), 51 (10), 47 (14), 45 (25), 41 (59).

(E)-4-Phenyl-3-pentene-1-thiol (**3l**): R_f=0.38 (hexane); ν_{max} (film) 2567 cm^{-1} (SH); δ_H 1.46 (1H, t, *J*=7.6, SH), 2.06 (3H, d, *J*=1.4, CH_3), 2.49-2.69 (4H, m, $HS\mathit{CH_2CH_2}$), 5.75 (1H, tq, *J*=7.0, 1.4, $C\mathit{H}$=CPh), 7.20-7.40 (5H, m, ArH); δ_C 16.1 (CH_3), 24.5, 33.1 ($HSCH_2CH_2$), 125.4, 125.6, 126.8, 128.2, 137.0, 143.4 (CH=CArC); *m/z* 178 (M^+, 7%), 163 (30), 132 (10), 131 (100), 129 (22), 128 (15), 116 (18), 115 (20), 91 (50), 77 (17), 51 (15), 47 (13) (Found: M^+, 178.0820. $C_{11}H_{14}S$ requires M, 178.0816).

ACKNOWLEDGEMENTS

This work was supported by DGICYT (no. PB91-0751). J. A. thanks the Ministerio de Educación y Ciencia of Spain for a fellowship.

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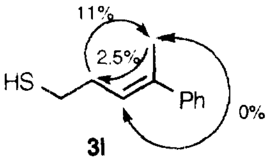

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(*Received in UK* 7 *August* 1995; *revised* 5 *September* 1995; *accepted* 8 *September* 1995)