Pergamon

Tetrahedron, Vol. 53, No. 15, pp. 5563-5572, 1997

0040-4020/97 $17.00 + 0.00

PII: S0040-4020(97)00211-1

Reductive Opening of Phenyl Substituted Thiacycloalkanes: New Way for Sulphur-containing Organolithium Compounds

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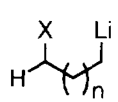
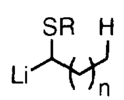
***Abstract*:** The reaction of 2-phenyl substituted four, five and six membered thiacycloalkanes (**1**, **4** and **7**) with lithium and a catalytic amount of DTBB (5 mol %) in THF at -78°C leads to the corresponding sulphur-containing benzylic organolithium compounds (**2**, **5** and **8**), which by reaction with different electrophiles [D_2O, Me_3SiCl, Bu^tCHO, Me_2CO, Et_2CO, $(CH_2)_4CO$, CO_2] followed by hydrolysis with water afford the expected functionalised mercaptans (**3**, **6** and **9**) in a regioselective manner. Some reaction products (**3**, **6**) are cyclised under acidic conditions (85% phosphoric acid) to yield the corresponding homologous substituted sulphur-containing saturated heterocycles (**10**, **11**).

INTRODUCTION

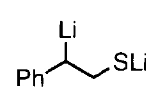
Functionalised organolithium compounds of the general type **I**[1] are versatile intermediates in synthetic organic chemistry because they react with different electrophiles to give in one reaction step polyfunctionalised organic structures, which are widely represented in nature. In general, oxygen- and nitrogen-containing species of type **I** (with X=RO, R_2N) have been prepared by four ways: (a) mercury-lithium transmetallation;[2] (b) direct deprotonation;[3] (c) chlorine-lithium exchange;[4] and (d) reductive opening of heterocycles.[5] However, the problem with the analogous sulphur-containing intermediates of type **I** (with X=RS) comes from the fact that α-protons with respect to the sulphur atom are far more acidic than the ω-ones, so sulphur-containing species of type **I** are unstable and undergo intra or intermolecular deprotonation to give the more stable α-lithiated intermediates of type **II**. In the last few years we have used an arene-catalysed lithiation[6] for the preparation of organolithium compounds from non-halogenated materials,[7a] functionalised organolithium compounds by chlorine-lithium exchange[7b] or by reductive opening of heterocycles[7c] and polylithiumsynthons.[7d] Among these procedures, only two ways for the preparation of sulphur-containing organolithium compounds have been described by halogen-lithium exchange[8a] and by reductive opening of thiophthalan and thiochroman[8b] or thioisochroman[8c] at low temperature or under Barbier-type reaction conditions. In the present paper we describe a general method for the preparation of benzylic dianions intermediates of type **I** with X=SLi starting from four, five, or six membered 2-phenyl thiacycloalkanes using a DTBB-catalysed lithiation at low temperature.



I



II

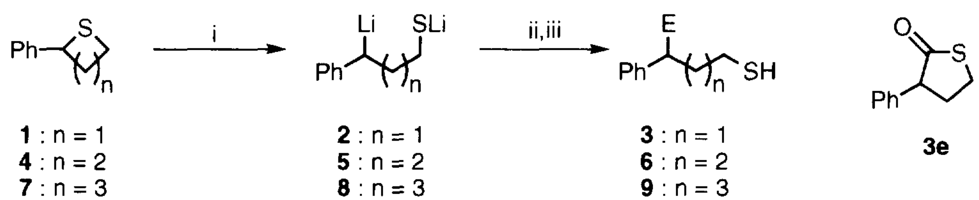


III

RESULTS AND DISCUSSION

We first studied the reductive ring opening of phenylthiirane[9] with lithium and 4,4'-di-*tert*-butylbiphenyl (DTBB) as electron carrier catalyst in THF: under different reaction conditions [Barbier-type reaction conditions (lithiation in the presence of the electrophile) or in a two-step reaction (tandem lithiation/S_E reaction with the electrophile at 0 or -78°C] the only reaction product isolated was ethylbenzene. We think that the ring opening takes place (the starting material disappears) giving the corresponding more stable benzylic organolithium compound **III**, which suffers β-elimination of lithium sulphide to yield styrene; under the reaction conditions (excess of lithium) and after final hydrolysis with water this compound is reduced to ethylbenzene.

When the same reaction was applied to 2-phenylthietane (**1**) using an excess of lithium powder (1:15) and a catalytic amount of DTBB (5 mol %) in THF; after 30 min at -78°C a solution of the corresponding dilithio intermediate **2** was formed, which is stable under these reaction conditions without suffering γ-elimination. Treatment of dianion **2** with different electrophiles [D_2O, Bu^{t}CHO, Et_2CO, $(CH_2)_4CO$, CO_2] at the same temperature led, after hydrolysis with water, to the expected functionalised mercaptans **3a-e** in a complete regioselective manner (Scheme 1 and Table 1, entries 1-4). In the case of using carbon dioxide as electrophile thiolactone **3e** was directly obtained after work-up (Table 1, entry 5). The presence of the phenyl group in the heterocyclic ring is indispensable: the same process applied to 3-methylthietane[10] (-78°C, 45 min) gave the starting material unchanged.



Scheme 1. *Reagents and conditions*: i, Li, DTBB cat. (5 %), THF, -78°C; ii, E^+ = D_2O, Bu^{t}CHO, Et_2CO, $(CH_2)_4CO$, CO_2, -78°C; iii, H_2O.

Applying the same protocol used for the four membered ring **1** to the corresponding 5-membered ring **4** [electrophiles E^+ = D_2O, Bu^{t}CHO, Me_2CO, Et_2CO, $(CH_2)_4CO$, CO_2] we obtained the expected final compounds **6a-f** through the corresponding dianion **5** (Scheme 1 and Table 1, entries 6-11). Also here when the phenyl group is not present in the heterocyclic ring the reductive opening did not work: even at room temperature the DTBB-catalysed lithiation or tetrahydrothiophene for 4 h yielded the starting material unaltered.

Finally we studied the DTBB-catalysed lithiation of 2-phenylthian **7**. Thus, the reaction of this material under the reaction conditions above described led to the corresponding intermediate **8**, which by reaction with different electrophiles (D_2O, Me_3SiCl, CO_2) afforded, after hydrolysis with water, the expected products **9c-e** (Scheme 1 and Table 1, entries 12-14). In the case of starting material **7** the reaction can be carried out at 0°C and in the presence of carbonyl compounds [Bu^{t}CHO, Me_2CO, Et_2CO, $(CH_2)_4CO$] for 1 h, the expected compounds **9d-g** were isolated, after hydrolysis with water, as the only reaction products (Table 1, entries 15-18 and footnote o).

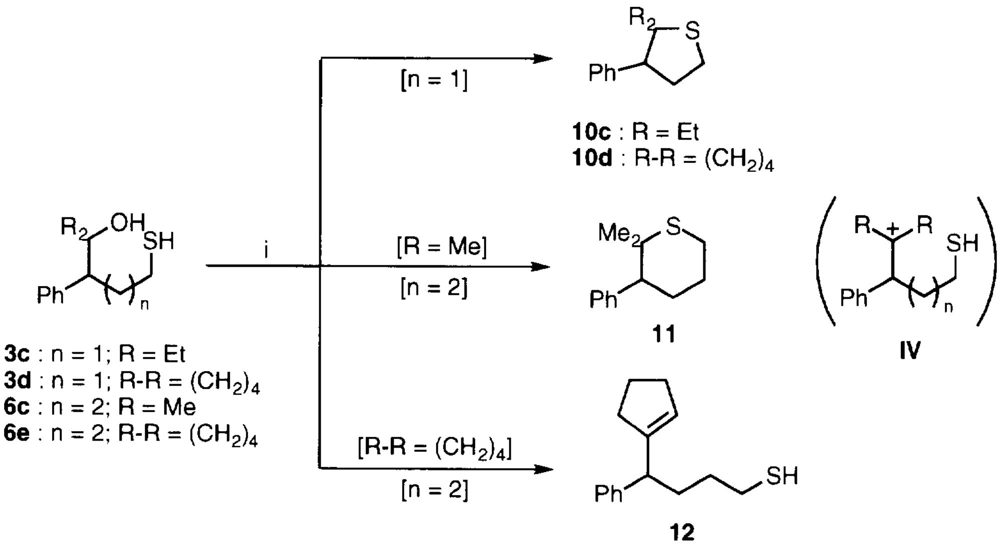
Table 1. Preparation of Compounds **3**, **6** and **9**

Entry	Starting Material	Electrophile E^+	Lithiation time	Product[a] No.	E	Yield(%)[b]	Mp (°C)[c] or R_f[d]
1	**1**	D_2O	30 min	**3a**	D	86[e]	0.20[f]
2	**1**	Bu^tCHO	30 min	**3b**	Bu^tCHOH	50[g]	0.18[h]/0.24[i]
3	**1**	Et_2CO	30 min	**3c**	Et_2COH	62	0.17
4	**1**	$(CH_2)_4CO$	30 min	**3d**	$(CH_2)_4COH$	52	0.20
5	**1**	CO_2	30 min	**3e**	---	59	52-53[j]
6	**4**	D_2O	45 min	**6a**	D	89	0.24[f]
7	**4**	Bu^tCHO	45 min	**6b**	Bu^tCHOH	61[k]	0.45[h]/0.49[i]
8	**4**	Me_2CO	45 min	**6c**	Me_2COH	54	0.60[l]
9	**4**	Et_2CO	45 min	**6d**	Et_2COH	51	0.43
10	**4**	$(CH_2)_4CO$	45 min	**6e**	$(CH_2)_4COH$	53	0.21
11	**4**	CO_2	45 min	**6f**	CO_2H	82	0.41[m]
12	**7**	D_2O	2h	**9a**	D	78[e]	0.21[f]
13	**7**	Me_3SiCl	2h	**9b**	Me_3Si	58	0.20[f]
14	**7**	CO_2	2h	**9c**	CO_2H	80	0.38[n]
15[o]	**7**	Bu^tCHO	2h	**9d**	Bu^tCHOH	70[p]	0.30/0.36
16[o]	**7**	Me_2CO	2h	**9e**	Me_2COH	69	0.14
17[o]	**7**	Et_2CO	2h	**9f**	Et_2COH	72	0.28
18[o]	**7**	$(CH_2)_4CO$	2h	**9g**	$(CH_2)_4COH$	71	0.36

[a] All products **3**, **6** and **9** were >94% pure (GLC and/or 300 MHz ^1H NMR). [b] Isolated yield after column chromatography (silica gel, hexane/ethyl acetate) based on the starting sulphur-containing heterocycle **1**, **4** or **7**. [c] From dichloromethane/pentane. [d] Silica gel, hexane/ethyl acetate: 5/1. [e] >90% Deuterium incorporation (mass spectrum). [f] Silica gel, hexane. [g] 3.1/1 Diastereoisomers mixture (deduced by weight after chromatographic separation). [h] Major diastereoisomer. [i] Minor diastereoisomer. [j] After acidic work-up the thiolactone **3e** was directly isolated. [k] 3/1 Diastereoisomers mixture (deduced by weight after chromatographic separation). [l] Silica gel, hexane/ethyl acetate: 2/1. [m] Silica gel, hexane/ethyl acetate: 1/2. [n] Silica gel, hexane/ethyl acetate: 1/1. [o] The reaction was performed under Barbier-type reaction conditions at 0°C (see text). [p] 1/1 Diastereoisomers mixture (deduced by weight after chromatographic separation).

Starting materials **1**, **4**[11] and **7**[12] were prepared from commercially available or easily prepared[13] ω-chloroalkyl phenyl ketones by successive reduction with sodium borohydride,[14] chlorination with thionyl chloride[15] and final treatment with hydrated sodium sulphide.[16]

In the last part of this study we considered some products **3** and **6** in order to get cyclisation reactions. Thus, treatment of compounds **3c** and **3d** with 85% phosphoric acid under toluene reflux yielded the expected substituted five membered heterocycles **10c** and **10d**, respectively (Scheme 2 and Table 2, entries 1 and 2), this process combined with the reductive opening of the four membered ring **4** being a homologation of this last heterocycle. A similar result was obtained starting from compound **6c**: under the same reaction conditions the six membered heterocycle **11** was isolated (Scheme 2 and Table 2, entry 3). However, using the same procedure with compound **6c** a dehydration reaction yielding product **12** took place instead of the corresponding cyclisation (Scheme 2 and Table 2, entry 4). In all cases a carbenium ion of type **IV** is probably formed, which suffered intramolecular nucleophilic attack by the sulphur atom (to give compounds **10** and **11**) or deprotonation (to yield the endocyclic olefin **12**).



Scheme 2. *Reagents and conditions*: i, 85% H_3PO_4, PhMe reflux.

Table 2. Preparation of Compounds **10-12**

Entry	Starting Material	Product[a] No.	Yield (%)[b]	R_f[c]
1	**3c**	**10c**	81	0.17
2	**3d**	**10d**	78	0.19
3	**6c**	**11**	54	0.31[d]
4	**6e**	**12**	41	0.20

[a] All products **10-12** were >96% pure (GLC and/or 300 MHz ^{1}H NMR). [b] Isolated yield after column chromatography (silica gel, hexane/ethyl acetate) based on the starting materials **3** or **6**. [c] Silica gel, hexane. [d] Silica gel, hexane/ethyl acetate: 20/1.

As a conclusion, we report here a new way to prepare dianionic sulphur-containing organolithium compounds by reductive opening of four, five or six membered 2-phenyl thiacycloalkanes, which are stable at low temperature and react with electrophiles giving functionalised mercaptans. The interest of species of type **2**, **5** and **8**, which can be considered d^n reagents following Seebach nomenclature,[17] comes from the fact that they do not suffer α-deprotonation with respect to the sulphur atom, probably due to the negative carge located on the heteroatom, which decreases the acidity of the α-protons.

EXPERIMENTAL PART

General.- M.p.s are uncorrected and were measured on a Reichert Thermovar apparatus. IR spectra were determined with a FT-IR Nicolet 400 D spectrometer. ^{1}H and ^{13}C NMR spectra were recorded in a Brucker AC-300 using $CDCl_3$ as solvent and $SiMe_4$ as internal standard; chemical shifts are given in δ (ppm) and the coupling constants (*J*) are measured in Hz. MS (EI) were recorded with a Shimazdu QP-5000 spectrometer. Thin layer chromatography (TLC) was carried out on Scheleicher & Schnell F1500/LS 254 plates coated with a 0.2 mm layer of silica gel, using hexane or a mixture of hexane/ethyl acetate as eluant; R_f values are given under these conditions. Microanalyses were performed by the Microanalyses Service of the University of Alicante. High resolution mass spectra were performed by the corresponding service at the University of Zaragoza. Solvents were dried by standard procedures.[18] Starting materials for the preparation of compounds **1**, **4** and **7**, as well as other reagents and electrophiles, were commercially available (Aldrich or Fluka) and were used as received.

Preparation of Starting Materials **1**, **4** *and* **7**. *General Procedure.-* To a suspension of sodium bicarbonate (1 g) and the corresponding ω-chlorophenone (3-chloropropiophenone, 4-chlorobutyrophenone or 5-chloro-valerophenone) (10 mmol) in ethanol (10 ml) was added dropwise a water solution (5 ml) of sodium borohydryde (0.19 g, 5 mmol) at room temperature. The resulting mixture was stirred at the same temperature for 1h.[14] The ethanol was evaporated and the residue was acidified with 3 M hydrochloric acid and extracted with diethyl ether (3x10 ml). The organic layer was dried over anhydrous sodium sulphate and evaporated (15 Torr). To a stirred chloroform (20 ml) solution of the resulting brown oil (*ca.* 5 mmol) was added thionyl chloride (1 ml, 13.7 mmol) at 0°C.[15] The reaction mixture was heated at 60°C for 3 h. The reaction mixture was then carefully hydrolysed with water (5 ml), basified with 2.5 M sodium hydroxide and extracted with diethyl ether (3x10 ml). The organic layer was evaporated (15 Torr) and the resulting residue was treated with nona-hydrated sodium sulphide (1.2 g, 5 mmol) in a solution of ethanol/water (25 ml/5 ml) at 120°C for 15 h.[16] Then, it was extracted with hexane (3x10 ml) and the organic layer was dried over anhydrous sodium sulphate and evaporated (15 Torr). The residue was then purified by column chromatography (silica gel; hexane) to yield pure products **1**, **4** and **7**. Yields, physical and spectroscopic date as well as literature references follow.

2-Phenylthietane (**1**):[19] (27%, 3 steps) R_f = 0.19 (silica gel, hexane); ν (film) 3082, 3060, 3026, 759, 697 cm^{-1} (C=CH); δ_H 2.94 (1H, td, *J* = 8.5, 3.6, *H*CHCHPh), 3.04-3.20 (2H, m, CH_2S), 3.37 (1H, q, *J* = 8.5, HC*H*CHPh), 4.92 (1H, t, *J* = 8.5, C*H*Ph), 7.20-7.48 (5H, m, ArH); δ_C 20.9 (*C*H_2CHPh), 36.2, (CH_2S), 44.4 (*C*HPh), 127.0, 127.2, 128.3, 143.6 (ArC); *m/z* 151 (M$^+$+1, 13%), 150 (M$^+$, 100), 135 (24), 122 (80), 121 (65), 117 (24), 115 (33), 104 (93), 103 (37), 91 (24), 78 (55), 77 (43), 63 (21), 51 (43), 50 (21), 45 (39).

2-Phenyltetrahydrothiophene (**4**):[11] (55%, 3 steps) R_f = 0.16 (silica gel, pentane); ν (film) 3060, 3026, 1599, 759, 699 cm^{-1} (C=CH); δ_H 1.18-2.58 (4H, m, $SCH_2CH_2CH_2$), 2.97-3.14 (1H, m, *H*CHS), 3.13-3.19 (1H, m, HC*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 (*C*HPh), 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).

2-Phenyltetrahydro-2H-thiopyran (**7**):[12] (34%, 4 steps) mp 50-51°C (pentane); ν (film) 3078, 3056, 3027, 1598, 1489, 757, 698 cm^{-1} (C=CH); δ_H 1.38-2.17 (6H, m, $CH_2CH_2CH_2$CHPh), 2.66 (1H, ddd, J = 13.4, 5.2, 3.3, *H*CHS), 2.86 (1H, ddd, J = 13.4, 12.3, 2.4, HC*H*S), 3.84 (1H, dd, J = 11.6, 2.4, C*H*Ph), 7.18-7.36 (5H, m, ArH); δ_C 26.7, 26.9, 30.8, 35.1 (4xCH_2), 47.3 (*C*HPh), 127.1, 127.3, 128.4, 142.8 (ArC); *m/z* 178 (M^+, 62%), 129 (24), 121 (19), 117 (26), 115 (18), 91 (44), 87 (100), 78 (12), 77 (15), 65 (12), 51 (17), 45 (32).

Preparation of Compounds **3**, **6** *and* **9a-c**. *General Procedure*.- To a cooled (-78°C) blue suspension of lithium powder (0.105 g, 15 g atoms) and a catalytic amount of 4,4'-di-*tert*-butylbiphenyl (0.026 g, 0.1 mmol) in THF (8 ml) was added the corresponding 2-phenylthiacycloalkane (compounds **1**, **4** or **7**; 1 mmol) under argon and the mixture was stirred at -78°C (see Table 1 for the lithiation time). Then, the corresponding electrophile (1.5 mmol; 0.5 ml in the case of water or deuterium oxide; CO_2 was bubbled for 1 h) was added. The mixture was stirred at the same temperature for 15 min and it was hydrolysed at -78°C with water (5 ml). The resulting mixture was extracted with diethyl ether (3x10 ml). The organic layer was dried over anhydrous sodium sulphate and evaporated (15 Torr). The residue was then purified by column chromatography (silica gel; hexane ethyl acetate) to yield pure products **3**, **6** and **9a-c**. Yields and R_f values are included in Table 1; analytical and spectroscopic data as well as literature references follow.

3-Deuterio-3-phenyl-1-propanethiol (**3a**): ν (film) 2567 cm^{-1} (SH); δ_H 1.34 (1H, t, J = 7.6, SH), 1.88-1.95 (2H, m, CH_2CHD), 2.52 (2H, q, J = 7.6, HSCH_2), 2.67-2.74 (1H, m, CHD), 7.16-7.31 (5H, m, ArH); δ_C 23.9 (CH_2CHD), 36.9 (t, J_{CD} = 19.5, CHD), 35.3 (CH_2SH), 125.9, 128.3, 128.4, 141.2 (ArC); *m/z* 153 (M^+, 29%), 119 (58), 118 (100), 117 (71), 93 (41), 92 (99), 91 (38), 78 (18), 77 (18), 66 (33), 65 (26), 63 (15), 61 (43), 51 (29), 47 (17), 45 (21), 42 (18), 40 (29) (Found: M^+, 153.0715. $C_9H_{11}DS$ requires M, 153.0723).

6-Mercapto-2,2-dimethyl-4-phenyl-3-hexanol (**3b**):[20] (Major diastereoisomer) ν (film) 3715-3190 (OH), 2568 cm^{-1} (SH); δ_H 0.90 [9H, s, $(CH_3)_3C$], 1.25 (1H, t, J = 7.6, SH), 1.78 (1H, br s, OH), 2.22-2.43 (4H, m, HSCH_2CH_2), 3.00 (1H, dt, J = 11.0, 3.9, C*H*Ph), 3.47 (1H, d, J = 3.9, C*H*OH), 7.17-7.31 (5H, m, ArH); δ_C 22.8 ($HSCH_2CH_2$), 26.6 [$(CH_3)_3C$], 35.3 ($HSCH_2$), 36.4 [$(CH_3)_3C$], 45.7 (*C*HPh), 83.0 (CHOH), 126.3, 128.0, 128.5, 144.9 (ArC); *m/z* 146 (M^+-C_6H_5-CH_3, 1%), 118 (100), 117 (43), 108 (19), 92 (14), 91 (43), 87 (20), 69 (21), 57 (29), 47 (16), 45 (25), 43 (17), 41 (51). (Minor diastereoisomer) ν (film) 3700-3150 (OH), 2568 cm^{-1} (SH); δ_H 0.79 [9H, s, $(CH_3)_3C$], 0.89-0.92 (2H, m, $HSCH_2CH_2$), 1.26 (1H, t, J = 7.3, SH), 1.50 (1H, br s, OH), 2.10-2.44 (3H, m, HSCH_2, C*H*Ph), 3.44 (1H, d, J = 2.4, C*H*OH), 7.17-7.34 (5H, m, ArH); δ_C 22.7 ($HSCH_2CH_2$), 26.6 [$(CH_3)_3C$], 36.1 [$(CH_3)_3C$], 40.1 ($HSCH_2$), 45.6 (*C*HPh), 82.5 (CHOH), 126.7, 128.4, 129.7, 140.9 (ArC); *m/z* 146 (M^+-C_6H_5-CH_3, 1%), 118 (100), 117 (41), 105 (18), 92 (14), 91 (39), 87 (19), 69 (21), 57 (33), 47 (16), 45 (23), 43 (19), 41 (51), 40 (34).

3-Ethyl-6-mercapto-4-phenyl-3-hexanol (**3c**):[20] ν (film) 3680-3200 (OH), 2565 cm^{-1} (SH); δ_H 0.81, 0.89 (6H, 2t, J = 7.3, 2xCH_2CH_3), 1.09-1.40 (5H, m, 2xCH_2CH_3, SH), 1.60 (2H, q, J = 7.3, CH_2SH), 1.91-2.42 (3H, m, OH, CH_2CHPh), 2.87 (1H, dd, J = 11.6, 3.3, C*H*Ph), 7.20-7.33 (5H, m, ArH); δ_C 7.5, 7.9 (2xCH_3), 23.1, 27.8, 29.3, 33.0 (4xCH_2), 50.4 (*C*HPh), 76.1 (COH), 126.6, 128.2, 129.7, 140.1 (ArC); *m/z* 209 (M^+-CH_2CH_5, 0.6%), 152 (68), 118 (89), 117 (49), 115 (15), 105 (24), 91 (50), 87 (100), 77 (18), 69 (40), 57 (65), 47 (37), 45 (90), 43 (52), 41 (58).

1-(3-Mercapto-1-phenylpropyl)-1-cyclopentanol (**3d**):[20] ν (film) 3700-3170 (OH), 2564 cm^{-1} (SH); δ_H 1.11-1.18 (2H, m, CH_2CHPh), 1.25 (1H, t, J = 7.6, SH), 1.56-2.06 (9H, m, 4xring CH_2, OH), 2.13-2.47 (2H, m, CH_2SH), 2.80 (1H, dd, J = 11.6, 3.0, C*H*Ph), 7.20-7.33 (5H, m, ArH); δ_C 23.0, 23.2, 23.5, 34.4, 38.4, 39.7 (6xCH_2), 53.7 (*C*HPh), 84.4 (COH), 126.7, 128.3, 129.0, 140.9 (ArC); *m/z* 218 (M^+-H_2O, 2%), 152

(49), 118 (100), 117 (38), 105 (16), 91 (31), 85 (76), 67 (55), 57 (25), 55 (23), 47 (20), 43 (23), 41 (43), 40 (15).

3-Phenyltetrahydrothiophen-2-one (**3e**): ν (film) 1692 cm^{-1} (C=O); δ_H 2.36-2.50 (1H, m, *H*CHCHPh), 2.65-2.74 (1H, m, HC*H*CHPh), 3.32-3.46 (2H, m, CH_2SH), 3.69 (1H, dd, *J* = 11.3, 7.0, C*H*Ph), 7.19-7.38 (5H, m, ArH); δ_C 30.3 (CH_2CHPh), 34.2 (CH_2S), 57.6 (*C*HPh), 127.5, 128.1, 128.7, 137.1 (ArC), 208.1 (C=O); *m/z* 178 (M+, 69%), 150 (26), 122 (38), 118 (41), 117 (100), 115 (25), 104 (53), 103 (20), 91 (25), 78 (24), 77 (22), 63 (15), 58 (19), 57 (18), 51 (28), 45 (20), 44 (34), 43 (22) (Found: C, 67.47; H, 5.89; S, 18.14. $C_{10}H_{10}OS$ requires: C, 67.38; H, 5.65; S, 17.99).

4-Deuterio-4-phenyl-1-butanethiol (**6a**): ν (film) 2568 cm^{-1} (SH); δ_H 1.32 (1H, t, *J* = 7.8, SH), 1.53-1.75 (4H, m, CH_2CH_2CHD), 2.49-2.63 (3H, m, HSCH_2, CHD), 7.15-7.30 (5H, m, ArH); δ_C 24.4, 30.0, 33.5 (3xCH_2), 34.9 (t, J_{CD} = 19.5, CHD), 125.8, 128.2, 128.3, 142.0 (ArC); *m/z* 167 (M+, 90%), 106 (17), 105 (86), 104 (89), 93 (22), 92 (100), 91 (71), 78 (18), 66 (25), 65 (21), 51 (19), 47 (21), 45 (16) (Found: M+, 167.0875. $C_{10}H_{13}DS$ requires M, 167.0879).

7-Mercapto-2,2-dimethyl-4-phenyl-3-heptanol (**6b**):[20] (minor diastereoisomer) ν (film) 3700-3180 (OH), 2567 cm^{-1} (SH); δ_H 0.78 [9H, s, $(CH_3)_3C$], 1.23-2.04 (6H, m, 2xCH_2, OH, SH), 2.46 (2H, q, *J* = 7.3, HSCH_2), 2.83 (1H, ddd, *J* = 10.0, 5.2, 2.7, C*H*Ph), 3.45 (1H, d, *J* = 4.3, C*H*OH), 7.15-7.31 (5H, m, ArH); δ_C 24.6 (CH_2), 26.6 [$(CH_3)_3C$], 32.2, 35.0 (2xCH_2), 36.0 [$(CH_3)_3C$], 46.9 (*C*HPh), 82.5 (CHOH), 126.5, 128.3, 129.6, 141.8 (ArC); *m/z* 252 (M+, 0.8%), 166 (76), 132 (26), 131 (18), 117 (18), 105 (17), 104 (100), 91 (87), 87 (40), 69 (24), 57 (39), 45 (29), 43 (18). (Major diastereoisomer) ν (film) 3695-3200 (OH), 2566 cm^{-1} (SH); δ_H 0.89 [9H, s, $(CH_3)_3C$], 1.25 (1H, t, *J* = 7.6, SH), 1.30-2.07 (5H, m, CH_2CH_2CHPh, OH), 2.36-2.49 (2H, m, HSCH_2), 2.74 (1H, dt, *J* = 11.3, 3.6, C*H*Ph), 3.44 (1H, d, *J* = 3.9, C*H*OH), 7.15-7.30 (5H, m, ArH); δ_C 24.7 (CH_2), 26.6 [$(CH_3)_3C$], 29.8, 32.1 (2xCH_2), 36.3 [$(CH_3)_3C$], 47.1 (*C*HPh), 83.2 (CHOH), 126.1, 127.9, 128.4, 145.7 (ArC); *m/z* 234 (M+-H_2O, 0.7%), 166 (71), 132 (25), 131 (17), 117 (18), 105 (17), 104 (100), 91 (83), 87 (39), 69 (21), 57 (31), 45 (27), 43 (18).

6-Mercapto-2-methyl-3-phenyl-2-hexanol (**6c**):[20] ν (film) 3725-3130 (OH), 2564 cm^{-1} (SH); δ_H 1.16, 1.17 (6H, 2s, 2xCH_3), 1.25 (1H, t, *J* = 7.6, SH), 1.32-2.03 (5H, m, CH_2CH$_2$CHPh, OH), 2.39-2.51 (2H, m, HSCH_2), 2.56 (1H, dd, *J* = 11.6, 3.4, C*H*Ph), 7.19-7.35 (5H, m, ArH); δ_C 24.6 (CH_2), 27.8, 27.9 (2xCH_3), 28.0, 32.4 (2xCH_2), 56.7 (*C*HPh), 72.6 (COH), 126.6, 128.1, 129.4, 140.8 (ArC); *m/z* 206 (M+-H_2O, 4%), 166 (43), 163 (23), 132 (16), 131 (26), 129 (23), 117 (19), 115 (16), 105 (17), 104 (82), 91 (73), 77 (15), 59 (100), 44 (16), 43 (39).

3-Ethyl-7-mercapto-4-phenyl-3-heptanol (**6d**):[20] ν (film) 3735-3195 (OH), 2564 cm^{-1} (SH); δ_H 0.81, 0.88 (6H, 2t, *J* = 7.6, 2xCH$_2$CH_3), 1.16-1.41 (6H, m, CH_2CH$_3$, SH, OH, CH_2CH$_2$CHPh), 1.60 (2H, q, *J* = 7.6, CH_2CH$_3$), 1.83-1.91 (2H, m, CH_2CHPh), 2.16-2.53 (2H, m, HSCH_2), 2.64 (1H, dd, *J* = 7.9, 7.3, C*H*Ph), 7.19-7.32 (5H, m, ArH); δ_C 7.6, 8.0 (2xCH_3), 24.6, 27.4, 27.9, 29.2, 32.4 (5xCH_2), 51.7 (*C*HPh), 76.1 (COH), 126.5, 128.1, 129.7, 141.0 (ArC); *m/z* 234 (M+-H_2O, 5%), 166 (53), 163 (22), 159 (18), 131 (15), 129 (18), 117 (45), 115 (15), 105 (14), 104 (46), 91 (56), 87 (100), 69 (18), 57 (34), 45 (86), 43 (28).

1-(4-Mercapto-1-phenylbutyl)-1-cyclopentanol (**6e**):[20] ν (film) 3700-3130 (OH), 2563 cm^{-1} (SH); δ_H 1.13-2.07 (14H, m, 6xCH_2, SH, OH), 2.39-2.52 (2H, m, CH_2SH), 2.58 (1H, dd, *J* = 11.4, 3.8, C*H*Ph), 7.19-7.33 (5H, m, ArH); δ_C 23.2, 23.6, 24.6, 28.8, 32.3, 38.3, 39.7 (7xCH_2), 54.9 (*C*HPh), 84.6 (COH), 126.6, 128.2, 128.9, 141.7 (ArC); *m/z* 250 (M+, 0.7%), 232 (M+-H_2O, 13), 230 (18), 166 (58), 163 (42), 157 (37), 141 (21), 132 (21), 131 (18), 129 (66), 128 (22), 117 (21), 115 (43), 105 (15), 104 (74), 91 (100), 85 (66), 79 (19), 77 (28), 67 (52), 65 (18), 55 (24), 51 (16), 45 (15), 44 (29), 43 (18).

5-Mercapto-2-phenylpentanoic Acid (**6f**):[20] ν (film) 3750-2287 cm^{-1} (CO_2H); δ_H 1.23 (1H, t, *J* = 7.0, SH), 1.44-2.16 (4H, m, CH_2CH_2CHPh), 2.56-2.63 (2H, m, CH_2SH), 3.49-3.56 (1H, m, C*H*Ph), 7.21-7.32 (5H, m, ArH), 9.16 (1H, br s, CO_2H); δ_C 26.8, 31.6, 38.4 (3xCH_2), 51.0 (*C*HPh), 127.5, 127.9, 128.6, 138.0 (ArC), 179.4 (CO_2H); *m/z* 192 (M^+-H_2O, 13%), 164 (100), 163 (30), 136 (37), 135 (20), 131 (25), 121 (35), 117 (91), 115 (41), 104 (98), 103 (28), 91 (44), 78 (33), 77 (34), 65 (30), 64 (19), 63 (21), 58 (18), 51 (44), 50 (18), 45 (28), 44 (28).

5-Deuterio-5-phenyl-1-pentanethiol (**9a**): ν (film) 2569 cm^{-1} (SH); δ_H 1.30 (1H, t, J = 7.6, SH), 1.35-1.67 (6H, m, $CH_2CH_2CH_2$CHD), 2.46-2.62 (3H, m, HSCH_2, CHD), 7.14-7.29 (5H, m, ArH); δ_C 24.5, 27.9, 30.7, 33.8 (4xCH_2), 35.3 (t, J_{CD} = 19.5, CHD), 125.6, 128.2, 128.3, 142.3 (ArC); *m/z* 181 (M^+, 19%), 118 (24), 117 (21), 105 (24), 104 (26), 93 (24), 92 (100), 91 (41), 90 (19), 89 (40), 88 (16), 66 (19), 65 (16), 55 (40), 47 (38), 44 (44) (Found: M^+, 181.1033. $C_{11}H_{15}DS$ requires M, 181.1036).

5-Phenyl-5-trimethylsilyl-1-pentanethiol (**9b**): ν (film) 2571 cm^{-1} (SH); δ_H 0.20 [9H, s, $(CH_3)_3Si$], 1.52-2.15 (7H, m, SH, 3xCH_2), 2.27 (1H, dd, J = 11.6, 3.9, C*H*Ph), 2.65-2.91 (2H, m, HSCH_2), 7.26-7.52 (5H, m, ArH); δ_C -3.0 [$(CH_3)_3Si$], 24.4, 28.0, 28.7, 34.0 (4xCH_2), 36.8 (*C*HPh), 124.3, 127.6, 128.0, 143.5 (ArC); *m/z* 252 (M^+, 3%), 146 (24), 117 (15), 104 (20), 91 (25), 73 (100), 45 (25), 44 (10), 43 (10) (Found: M^+, 252.1367. $C_{14}H_{24}SSi$ requires M, 252.1368).

5-Mercapto-2-phenylhexanoic Acid (**9c**):[20] ν (film) 3740-2129 cm^{-1} (CO_2H); δ_H 1.22-2.12 (7H, m, 3xCH_2, SH), 2.43-2.51 (2H, m, CH_2SH), 3.53 (1H, t, J = 7.6, C*H*Ph), 7.24-7.34 (5H, m, ArH), 10.16 (1H, br s, CO_2H); δ_C 24.2, 26.1, 32.4, 33.6 (4xCH_2), 51.4 (*C*HPh), 127.5, 127.9, 128.6, 138.2 (ArC), 180.2 (CO_2H); *m/z* 206 (M^+-H_2O, 35%), 178 (30), 145 (57), 136 (51), 118 (24), 117 (22), 115 (15), 103 (21), 91 (100), 89 (18), 87 (34), 79 (18), 77 (27), 55 (37), 51 (19), 47 (48), 45 (22).

Preparation of Compounds **9d-g**. *General Procedure*.- To a cooled (0°C) blue suspension of lithium powder (0.105 g, 15 g atoms) and a catalytic amount of 4,4'-di-*tert*-butylbiphenyl (0.026 g, 0.1 mmol) in THF (5 ml) was added compound **7** (0.178 g, 1 mmol) and the electrophile (2 mmol) disolved in THF (3 ml) under argon. The addition was complete within 1 h. Then, the mixture was hydrolysed at 0°C with water (5 ml). The resulting mixture was extracted with diethyl ether (3x10 ml). The organic layer was dried over anhydrous sodium sulphate and evaporated (15 Torr). The residue was then purified by column chromatography (silica gel, hexane/ethyl acetate) to yield pure products **9d-g**. Yields and R_f values are included in Table 1; analytical and spectroscopic data as well as literature references follow.

8-Mercapto-2,2-dimethyl-4-phenyl-3-octanol (**9d**):[20] (First diastereoisomer) ν (film) 3725-3140 (OH), 2568 cm^{-1} (SH); δ_H 0.88 [9H, s, $(CH_3)_3C$], 1.08-1.95 (8H, m, 3xCH_2, SH, OH), 2.35-2.47 (2H, m, HSCH_2), 2.73 (1H, dt, J = 11.3, 3.6, C*H*Ph), 3.40-3.48 (1H, m, C*H*OH), 7.16-7.30 (5H, m, ArH); δ_C 24.4, 26.3 (2xCH_2), 26.6 [$(CH_3)_3C$], 30.4, 34.1 (2xCH_2), 36.3 [$(CH_3)_3C$], 47.3 (*C*HPh), 83.2 (CHOH), 126.0, 127.9, 128.3, 146.0 (ArC); *m/z* 248 (M^+-H_2O, 0.7%), 180 (100), 146 (79), 145 (18), 131 (16), 118 (17), 117 (64), 115 (16), 105 (29), 104 (65), 92 (31), 91 (87), 89 (81), 88 (63), 87 (65), 77 (17), 69 (41), 57 (46), 55 (40), 47 (34), 45 (44), 43 (32). (Second diastereoisomer) ν (film) 3720-3150 (OH), 2567 cm^{-1} (SH); δ_H 0.77 [9H, s, $(CH_3)_3C$], 1.06-1.34 (3H, m, *H*SCH$_2$CH$_2$CH_2), 1.48-1.93 (5H, m, HSCH$_2$CH_2CH$_2$CH_2, OH), 2.39-2.47 (2H, m, HSCH_2), 2.82 (1H, ddd, J = 10.0, 5.2, 2.7, C*H*Ph), 3.39-3.47 (1H, m, C*H*OH), 7.17-7.31 (5H, m, ArH); δ_C 24.4, 26.4 (2xCH_2), 26.6 [$(CH_3)_3C$], 33.9, 35.6 (2xCH_2), 35.9 [$(CH_3)_3C$], 47.1 (*C*HPh), 82.4 (CHOH), 126.4, 128.2, 129.5, 142.0 (ArC); *m/z* 180 (M^+-Bu^tCHOH, 56%), 146 (42), 117 (37), 105 (17), 104 (40), 92 (19), 91 (100), 89 (79), 88 (42), 87 (47), 69 (26), 57 (40), 55 (27), 47 (23), 45 (31), 43 (22).

7-Mercapto-2-methyl-3-phenyl-2-heptanol (**9e**):[20] ν (film) 3735-3145 (OH), 2567 cm^{-1} (SH); δ_H 1.16 (6H, s, 2xCH_3), 1.24 (1H, t, J = 7.9, SH), 1.66-1.90 (7H, m, OH, $CH_2CH_2CH_2$CHPh), 2.35-2.48 (2H, m,

$HSCH_2$), 2.56 (1H, dd, J = 11.0, 3.6, C*H*Ph), 7.19-7.32 (5H, m, ArH); δ_C 24.3, 26.9 (2xCH_2), 27.7, 27.8 (2xCH_3), 28.7, 34.0 (2xCH_2), 57.0 (*C*HPh), 72.6 (COH), 126.5, 128.0, 129.4, 141.0 (ArC); *m/z* 220 (M^+ - H_2O, 8%), 180 (62), 177 (22), 146 (41), 131 (46), 129 (18), 117 (63), 115 (24), 105 (32), 104 (61), 92 (27), 91 (97), 89 (78), 88 (41), 87 (21), 77 (19), 59 (100), 55 (39), 47 (36), 43 (55).

3-Ethyl-8-mercapto-4-phenyl-3-octanol (**9f**):[20] ν (film) 3735-3175 (OH), 2567 cm^{-1} (SH); δ_H 0.78, 0.89 (6H, m, 2xCH_2CH_3), 1.05-1.86 (12H, m, 5xCH_2, SH, OH), 2.34-2.47 (2H, m, $HSCH_2$), 2.64 (1H, dd, J = 11.0, 4.1, C*H*Ph), 7.19-7.32 (5H, m, ArH); δ_C 7.6, 8.0 (2xCH_3), 24.4, 26.8, 27.9, 28.1, 29.2, 34.1 (6xCH_2), 52.0 (*C*HPh), 76.1 (COH), 126.4, 128.0, 129.7, 141.2 (ArC); *m/z* 248 (M^+-H_2O, 11%), 180 (29), 159 (32), 146 (15), 131 (15), 117 (56), 104 (16), 91 (57), 89 (35), 88 (21), 87 (100), 69 (17), 57 (33), 55 (22), 47 (19), 45 (74), 43 (31).

1-(5-Mercapto-1-phenylpentyl)-1-cyclohexanol (**9g**):[20] ν (film) 3690-3135 (OH), 2567 cm^{-1} (SH); δ_H 1.24-1.86 (18H, m, 8xCH_2, SH, OH), 2.35-2.46 (2H, m, CH_2SH), 2.52 (1H, dd, J = 10.9, 3.9, C*H*Ph), 7.19-7.31 (5H, m, ArH); δ_C 21.8, 21.9, 24.3, 25.7, 26.9, 27.8, 34.1, 35.4, 35.8 (9xCH_2), 56.4 (*C*HPh), 72.9 (COH), 126.4, 128.0, 129.6, 141.1 (ArC); *m/z* 260 (M^+-H_2O, 9%), 180 (20), 171 (27), 129 (29), 99 (77), 91 (51), 89 (21), 81 (45), 55 (44), 44 (100), 43 (34).

Cyclisation of Compounds **3c**,**d** *and* **6c**,**e**. *General Procedure*.- To a solution of the corresponding compound **3c**,**d** or **6c**,**e** (0.5 mmol) in toluene (5 ml) was added 85% phosphoric acid (0.3 ml). The reaction mixture was heated at 110°C for 1 h. Then toluene was removed by distillation and the resulting residue was hydrolysed with water (5 ml) and extracted with diethyl ether (3x10 ml). The organic layer was dried over anhydrous sodium sulphate and evaporated (15 Torr). The resulting residue was purified by column chromatography (silica gel, hexane/ethyl acetate) to yield pure products **10-12**. Yields and R_f values are included in Table 2; analytical and spectroscopic data follow.

2,2-Diethyl-3-phenyltetrahydrothiophene (**10c**): ν (film) 3086, 3061, 3028, 763, 701 cm^{-1} (C=CH); δ_H 0.73, 1.11 (6H, 2t, J = 7.3, 2xCH_2CH_3), 1.41-1.84 (4H, m, 2xCH_2CH_3), 2.30-2.57 (2H, m, CH_2CHPh), 2.86-2.91 (2H, m, CH_2SH), 3.22 (1H, dd, J = 11.9, 5.2, C*H*Ph), 7.17-7.32 (5H, m, ArH); δ_C 9.3, 9.8 (2xCH_3), 29.1, 29.2, 31.2, 35.0 (4xCH_2), 54.2 (*C*HPh), 63.6 (CS), 126.6, 128.0, 128.8, 139.7 (ArC); *m/z* 220 (M^+, 29%), 191 (100), 129 (17), 118 (36), 117 (50), 116 (20), 115 (21), 102 (32), 101 (23), 91 (37), 73 (26), 45 (30), 41 (50) (Found: M^+, 220.1296. $C_{14}H_{20}S$ requires M, 220.1286).

4-Phenyl-1-thiaspiro[4,4]nonane (**10d**): ν (film) 3084, 3060, 3026, 765, 702 cm^{-1} (C=CH); δ_H 1.25-1.95 (8H, m, 4xring CH_2), 2.39-2.47 (2H, m, CH_2CHPh), 2.99-3.05 (2H, m, CH_2SH), 3.25 (1H, t, J = 8.2, C*H*Ph), 7.20-7.34 (5H, m, ArH); δ_C 23.1, 23.2, 29.1, 35.8, 36.7, 39.2 (6xCH_2), 56.7 (*C*HPh), 66.9 (CS), 126.7, 128.0, 129.2, 139.7 (ArC); *m/z* 218 (M^+, 100%), 190 (53), 189 (51), 129 (28), 128 (24), 118 (63), 117 (78), 116 (47), 114 (40), 100 (55), 91 (62), 77 (32), 67 (94), 65 (29), 51 (28), 45 (37), 41 (57) (Found: M^+, 218.1127. $C_{14}H_{18}S$ requires M, 218.1129).

*2,2-Dimethyl-3-phenyltetrahydro-2*H*-thiopyran* (**11**): ν (film) 3059, 3025, 767, 703 cm^{-1} (C=CH); δ_H 1.08, 1.34 (6H, 2s, 2xCH_3), 1.71-2.20 (4H, m, CH_2CH_2CHPh), 2.47-2.54 (1H, m, *H*CHS), 2.89-3.02 (2H, m, HC*H*S, C*H*Ph), 7.13-7.29 (5H, m, ArH); δ_C 21.9 (CH_3), 26.9, 28.4, 29.0 (3xCH_2), 29.9 (CH_3), 42.8 (S*C*CHPh), 55.1 (*C*HPh), 126.4, 127.7, 129.1, 142.9 (ArC); *m/z* 206 (M^+, 43%), 130 (26), 117 (24), 115 (24), 104 (66), 91 (41), 89 (100), 77 (14), 75 (28), 74 (49), 59 (26), 55 (19), 47 (14) (Found: M^+, 206.1118. $C_{13}H_{18}S$ requires M, 206.1129).

4-(1-Cyclopentenyl)-4-phenyl-1-butanethiol (**12**): ν (film) 2568 cm^{-1} (SH); δ_H 1.29 (1H, t, J = 7.6, SH), 1.43-2.34 (10H, m, 5xCH_2), 2.49 (2H, q, J = 7.6, CH_2SH), 3.28 (1H, t, J = 7.3, C*H*Ph), 5.48-5.50 (1H, m, C=CH), 7.13-7.30 (5H, m, ArH); δ_C 23.2, 24.6, 32.3, 32.7, 33.6 ($5xCH_2$), 47.3 (*C*HPh), 123.8 (C=*C*H), 126.1, 127.8, 128.2, 143.7, 147.1 (ArC, *C*=CH); *m/z* 232 (M^+, 19%), 166 (56), 157 (75), 142 (17), 141 (20), 131 (15), 130 (17), 129 (100), 128 (23), 115 (52), 91 (80), 79 (17), 77 (23), 67 (15), 44 (31) (Found: M^+, 232.1282. $C_{15}H_{20}S$ requires M, 232.1286).

ACKNOWLEDGEMENTS

This work was generously supported by DGICYT (no. PB94-1514). J. A. thanks the Ministerio de Educación y Ciencia of Spain for a fellowship.

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(*Received in UK* 31 *December* 1996; *revised* 25 *February* 1997; *accepted* 27 *February* 1997)