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New Homologation of 2-Hydroxy and 2-Mercapto Benzylic Alcohols†

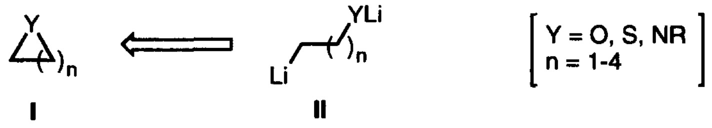
Prabir K. Choudhury, Juan Almena, Francisco Foubelo and Miguel Yus*

Departamento de Química Orgánica, Facultad de Ciencias, Universidad de Alicante, Apdo. 99, E-03080-Alicante, Spain

Abstract: The reaction of benzo-1,3-dioxanes or benzo-1,3-oxathianes **1** [easily prepared from 2-hydroxy or 2-mercapto benzylic alcohols (**3** or **4**, respectively) and carbonyl compounds] with an excess of lithium and a catalytic amount of DTBB (4.5 mol %) in THF at room temperature or -78°C leads, after hydrolysis with water, to the corresponding homobenzylic alcohols **2**. Cyclisation of compounds **2** under acidic (85% H_3PO_4) or neutral (Ph_3P/DIAD) conditions affords the expected heterocycles **5**.

INTRODUCTION

Homologation reactions are classical processes in synthetic organic chemistry since they allow the preparation of a target molecule starting from the same structure containing one less carbon atom, this process having the possibility to become iterative. Recently, we have applied an arene-catalysed lithiation[1] under very mild reaction conditions for the reductive opening of different oxygen-,[2] sulphur-[3] or nitrogen-containing[4] saturated heterocyclic compounds[5] of the general type **I** in order to prepare a wide series of functionalised organolithium compounds[6] of the type **II**, which are interesting reagents in organic synthesis. In this paper we describe the application of the above mentioned methodology, arene-catalysed lithiation, to the reductive opening of benzocondensed 1,3-dioxanes or 1,3-oxathianes. This process allows the easy homologation of the precursor benzylic systems in a way which, to our best knowledge, represents a new methodological route for this transformation.



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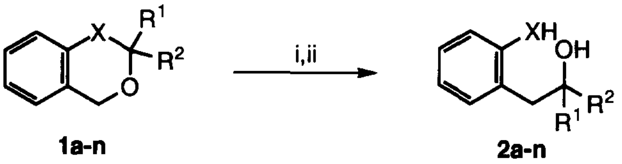
† This paper is dedicated to Professor Pascual Royo on occasion of his 60th birthday

RESULTS AND DISCUSSION

The reaction of 1,3-dioxane or 1,3-oxathiane **1** with an excess of lithium powder (1:9 molar ratio) and a catalytic amount of 4,4'-di-*tert*-butylbiphenyl (DTBB; 1:0.09 molar ratio; 4.5 mol %) in THF at room temperature (X=O) or at -78°C (X=S) led after *ca.* 2h stirring and final hydrolysis with water to the corresponding 2-substituted homobenzylic alcohols **2** in moderate yields (Scheme 1 and Table 1).



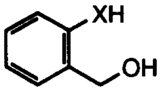
Scheme 1. *Reagents and conditions*: i, Li, DTBB cat. (4.5 mol %), THF, 20°C (X=O) or -78°C (X=S) , 1.5-2 h; ii, H_2O.

Table 1. Preparation of Alcohols **2**.

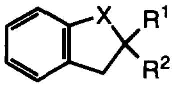
	Starting Material				Product		
Entry	No.	X	R^1	R^2	No.	Yield (%)[a]	R_f or mp (°C)
1	**1a**	O	H	Me	**2a**	46	0.21[b]
2	**1b**	S	H	Me	**2b**	49	0.17[c]
3	**1c**	O	Me	Me	**2c**	47	0.36[b]
4	**1d**	S	Me	Me	**2d**	60	0.27[c]
5	**1e**	O	H	Pr^i	**2e**	41	74-77[d]
6	**1f**	S	H	Pr^i	**2f**	43	54-56[d]
7	**1g**	O	H	Bu^i	**2g**	40	87-88[d]
8	**1h**	S	H	Bu^i	**2h**	50	0.35[c]
9	**1i**	O	H	Bu^t	**2i**	39	96-100[d]
10	**1j**	S	H	Bu^t	**2j**	43	36-40[d]
11	**1k**	O	$-(CH_2)_5-$		**2k**	44	0.44[b]
12	**1l**	S	$-(CH_2)_5-$		**2l**	47	0.41[c]
13	**1m**	O	H	$Ph(CH_2)_2$	**2m**	41	0.29[b]
14	**1n**	S	H	$Ph(CH_2)_2$	**2n**	49	0.25[c]

[a] Isolated yield of pure compounds (>95% by GLC and/or 300 MHz ^1H NMR) after column chromatography (silica gel; hexane/ethyl acetate). [b] Silica gel, hexane/ethyl acetate: 5/1. [c] Silica gel, hexane/ethyl acetate: 10/1. [d] From dichloromethane/pentane.

Starting heterocycles **1** were prepared from the corresponding 2-substituted benzylic alcohols **3** or **4** by reaction with different carbonyl compounds under *p*-toluenesulfonic acid catalysis (Table 2).



3 : X = O
4 : X = S



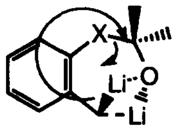
5

Table 2. Preparation of Heterocycles **1**.

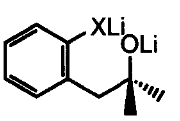
Entry	Starting Alcohol	Carbonyl compound		Reaction conditions		Product		
		R^1	R^2	Solvent	T (°C)	No.	Yield (%)[a]	R_f or mp (°C)
1[b]	**3**	H	Me	MeCHO	40	**1a**	42	0.51[c]
2[b]	**4**	H	Me	MeCHO	40	**1b**	91	0.42[d]
3[e]	**3**	Me	Me	Me_2CO	40	**1c**	99[f]	0.52[c]
4[e]	**4**	Me	Me	Me_2CO	40	**1d**	99[f]	0.44[d]
5	**3**	H	Pr^i	CH_2Cl_2	50	**1e**	84	35-39[g]
6	**4**	H	Pr^i	CH_2Cl_2	50	**1f**	96	0.51[d]
7	**3**	H	Bu^i	PhH	90	**1g**	92	0.58[c]
8	**4**	H	Bu^i	PhH	90	**1h**	94	0.50[d]
9	**3**	H	Bu^t	CH_2Cl_2	50	**1i**	99[f]	33-34[g]
10	**4**	H	Bu^t	CH_2Cl_2	50	**1j**	95[f]	64-66[g]
11	**3**	$-(CH_2)_5-$		PhH	100	**1k**	39	0.56[c]
12	**4**	$-(CH_2)_5-$		PhH	100	**1l**	93	0.46[d]
13	**3**	H	$PhCH_2$	PhH	100	**1m**	95	0.51[c]
14	**4**	H	$PhCH_2$	PhH	100	**1n**	98	0.42[d]

[a] Isolated yield of pure compounds (>95% by GLC and/or 300 MHz ^{1}H NMR) after column chromatography (silica gel; hexane/ethyl acetate), unless otherwise stated, based on the starting materials **3** or **4**. [b] An equimolecular amount of 1,1-diethoxyethane was used without *p*-TsOH as catalyst. [c] Silica gel, hexane/ethyl acetate: 20/1. [d] Silica gel, hexane/ethyl acetate: 50/1. [e] An equimolecular amount of 2,2-dimethoxypropane was used. [f] Isolated crude yield (purity>95% by GLC and/or 300 MHz ^{1}H NMR). [g] From dichloromethane/pentane.

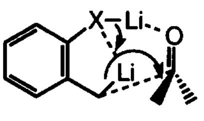
Concerning a possible mechanistic pathway for the formation of compounds **2**, we think that in the first step a benzylic cleavage takes place[2e,f, 3a,b, 4a-d] giving a dianionic intermediate of the type **III**, which either



III



IV



V

could afford directly the homobenzylic dianion **IV** (precursor of the final product **2**) or could give a complex of type **V**, between a benzylic dianion and the carbonyl compound, which afford the same intermediate of type **IV**. At this moment we can not decide if the complex **V** takes really place in the process.

In the last part of this work we studied the cyclisation of 2-substituted homobenzylic alcohols **2** either under acidic reaction conditions, with 85% phosphoric acid in refluxing toluene (method A) or under Mitsunobu-type reaction conditions, with triphenylphosphine and diisopropylazodicarboxylate (DIAD) in THF (method B), giving the expected oxygen- or sulphur-containing heterocycles **5** (Table 3).

Table 3. Preparation of Compounds **5**.

Entry	Starting Material	Method[a]	Product					
			No.	X	R^1	R^2	Yield (%)[b]	R_f[c]
1	**2a**	A	**5a**	O	H	Me	57	0.43
2	**2b**	A	**5b**	S	H	Me	66	0.44
3	**2c**	A	**5c**	O	Me	Me	65	0.19
4	**2d**	A	**5d**	S	Me	Me	62	0.46
5	**2e**	B	**5e**	O	H	Pr^i	66	0.18
6	**2f**	B	**5f**	S	H	Pr^i	74	0.46
7	**2g**	B	**5g**	O	H	Bu^i	69	0.25
8	**2h**	B	**5h**	S	H	Bu^i	70	0.51
9	**2i**	B	**5i**	O	H	Bu^t	52	0.27
10	**2j**	B	**5j**	S	H	Bu^t	19	0.43
11	**2k**	A	**5k**	O	$-(CH_2)_5-$		79	0.25
12	**2l**	A	**5l**	S	$-(CH_2)_5-$		83	0.48
13	**2m**	B	**5m**	O	H	$Ph(CH_2)_2$	68	0.11
14	**2n**	B	**5n**	S	H	$Ph(CH_2)_2$	61	0.31

[a] Method A: H_3PO_4 (85%), PhMe, 115°C, 1-3 h; Method B: Ph_3P, DIAD, THF, 20°C, overnight. [b] Isolated yield of pure compounds (>95% by GLC and/or 300 MHz ^1H NMR) after column chromatography (silica gel; hexane/ethyl acetate) based on the starting materials **2**. [c] Silica gel, hexane.

Finally we tried also to prepare the corresponding systems of type **2** and **5** for X = NR. However, in this case the problem was the preparation of the *N*-protected starting material **1**: either the ketalisation of *N*-Boc-2-hydroxymethylaniline or the *N*-protection (as Boc-, methyl-, benzyl- or trimethylsilyl-derivatives) of the heterocycles of the type **1** with X = NH, failed under different reaction conditions.

In summary, we have described in this paper a new homologation methodology, which allows the transformation of benzylic alcohol derivatives **3** or **4** into the corresponding homobenzylic ones **2** using as the key step a DTBB-catalysed lithiation of the heterocyclic derivatives **1**. Moreover, compounds **2** are able to be cyclised to the corresponding heterocycles **5** under acidic or neutral reaction conditions.

EXPERIMENTAL PART

General.- Melting points were obtained with a Reichert Thermovar apparatus. FT-IR spectra were obtained on a Nicolet Impact 400D spectrophotometer. NMR spectra were recorded on a Bruker AC-300 (300 MHz for ^{1}H and 75 MHz for ^{13}C) using $CDCl_3$ as solvent and TMS as internal standard; chemical shifts are given in δ (ppm) and coupling constants (J) in Hz. ^{13}C-NMR assignments were made on the basis of DEPT experiments. Mass spectra (EI) were obtained at 70 eV on a Shimazdu QP-5000 spectrometer, fragment ions in m/z with relative intensities (%) in parentheses. Elemental analyses were performed by the Microanalyses Service at the University of Alicante. High resolution mass spectra were performed by the corresponding service at the University of Zaragoza. The purity of volatile products and the chromatographic analyses (GLC) were determinated with a Hewlett Packard HP-5890 instrument equipped with a flame ionization detector and a 12 m capillary column (0.2 mm diam, 0.33 mm film thickness), using nitrogen (2 ml/min) as carrier gas, $T_{injector}$ = 275°C, T_{column} = 60°C (3 min) and 60-270°C (15°C/min). Thin layer chromatography (TLC) was carried out on Schleicher & Schuell F1500/LS 254 plates coated with a 0.2 mm layer of silica gel; R_f values are given under these conditions. Column chromatography was performed using silica gel 60 of 35-70 mesh. All starting materials were commercially available (Acros, Aldrich, Fluka) of the best grade and were used without further purification. THF was dried over benzophenone ketyl under an argon atmosphere and destilled before use.

Preparation of Starting Heterocycles **1**. *General Procedure.*- A mixture of 2-hydroxy- or 2-mercapto-benzyl alcohol (**3** or **4**,[7] respectively) (5 mmol), the corresponding carbonyl compound (or the corresponding ketal in case of acetaldehyde or acetone; see Table 2, footnotes b and c) (5-7.5 mmol), anhydrous Na_2SO_4 (2 g) and a catalytic amount of *p*-toluenesulphonic acid was heated overnight at the temperature and in the solvent (20 ml) shown in Table 2. After removal of the solvent *in vacuo* (15 Torr) the resulting residue was hydrolysed with water (10 ml), extracted with ethyl acetate, the organic layer dried with anhydrous Na_2SO_4 and evaporated (15 Torr) to give a residue, which was purified by column chromatography (silica gel, hexane/ethyl acetate) or recrystallised affording the title compounds. Reaction conditions, yields and physical data are included in Table 2; spectroscopic and analytical data, as well as literature references for known compounds follow.

*2-Methyl-4*H*-benzo[a][1,3]dioxine* (**1a**): ν (film) 3047, 2995, 1616, 1588, 1489 cm^{-1} (C=CH); δ_H 1.54 (3H, d, J = 6.1, CH_3), 4.80, 4.98 (2H, 2d, J = 14.6, PhCH_2), 5.17 (1H, q, J = 5.2, OCHO), 6.82-6.95 (3H, m, ArH), 7.11-7.16 (1H, m, ArH); δ_C 20.6 (CH_3), 66.3 (PhCH$_2$), 97.0 (OCHO), 116.55, 120.7, 120.9, 124.8, 127.9, 152.9 (ArC); m/z 150 (M$^+$, 72%), 106 (82), 78 (100), 63 (10), 51 (49), 50 (28) (Found: M$^+$, 150.0686. $C_9H_{10}O_2$ requires M, 150.0680).

*2-Methyl-4*H*-benzo[a][1,3]oxathiine* (**1b**): ν (film) 3060, 2980, 2841, 1590, 1479, 1439 cm^{-1} (C=CH); δ_H 1.62 (3H, d, J = 6.1, CH_3), 4.91 (2H, s, PhCH_2), 5.24 (1H, q, J = 6.1, SCHO), 6.86-7.16 (4H, m, ArH), δ_C 21.8 (CH_3), 69.8 (PhCH$_2$), 77.6 (SCHO), 124.5, 125.7, 127.15, 127.2, 129.3, 131.9 (ArC); m/z 166 (M$^+$, 27%), 137 (58), 122 (100), 91 (12), 78 (29), 51 (13) (Found: M$^+$, 166.0460. $C_9H_{10}OS$ requires M, 166.0452).

*2,2-Dimethyl-4*H*-benzo[a][1,3]dioxine* (**1c**):[8] ν (film) 3046, 2990, 1614, 1590 cm^{-1} (C=CH); δ_H 1.53 [6H, s, C(CH_3)$_2$], 4.83 (2H, s, PhCH_2), 6.79-7.23 (4H, m, ArH) ; δ_C 24.7 [C(CH$_3$)$_2$], 60.8 (PhCH$_2$), 99.4 [C(CH$_3$)$_2$], 117.0, 119.1, 120.3, 124.55, 128.0, 151.1 (ArC); m/z 164 (M$^+$, 36%), 106 (85), 78 (100), 63 (10), 52 (37), 51 (41), 43 (45).

*2,2-Dimethyl-4*H*-benzo[a][1,3]oxathiine* (**1d**): ν (film) 3066, 2975, 2853, 1590, 1449 cm^{-1} (C=CH); δ_H 1.65 [6H, s, C(CH_3)$_2$], 4.85 (2H, s, PhCH_2), 6.98-7.19 (4H, m, ArH) ; δ_C 29.4 [C(CH$_3$)$_2$], 64.2 (PhCH$_2$), 81.9 (SCO), 124.4, 125.45, 127.2, 127.9, 129.9, 132.2 (ArC); m/z 180 (M$^+$, 18%), 136 (10), 122 (100), 121 (59), 78 (19), 77 (10), 51 (10) (Found: M$^+$, 180.0602. $C_{10}H_{12}OS$ requires M, 180.0608).

*2-Isopropyl-4*H*-benzo[a][1,3]dioxine* (**1e**): ν (film) 3058, 2980, 2870, 1587, 1493 cm^{-1} (C=CH); δ_H 1.04-1.07 [6H, m, CH(CH_3)$_2$], 1.97-2.08 [1H, m, CH(CH$_3$)$_2$], 4.74 (1H, d, J = 4.6, OCHO), 4.81 (1H, d, J = 14.6, PhCH$_2$), 4.94 (1H, d, J = 14.3, PhCH$_2$), 6.83-6.91 (3H, m, ArH), 7.10-7.15 (1H, m, ArH); δ_C 16.5 (CH_3), 16.6 (CH_3), 32.3 [CH(CH$_3$)$_2$], 66.6 (PhCH$_2$), 103.1 (OCHO), 116.65, 120.7, 121.0, 124.8, 127.8, 153.2 (ArC); m/z 178 (M$^+$, 24%), 149 (25), 106 (100), 97 (46), 83 (54), 78 (95), 57 (100), 51 (13) (Found: M$^+$, 178.0999. $C_{11}H_{14}O_2$ requires M, 178.0993).

2-Isopropyl-4H-benzo[a][1,3]oxathiine (**1f**): ν (film) 3060, 2963, 2872, 1569, 1439 cm^{-1} (C=CH); δ_H 1.05-1.10 [6H, m, CH(CH_3)$_2$], 2.09 [1H, octet, J = 6.6, CH(CH$_3$)$_2$], 4.85 (1H, d, J = 14.9, PhCHH), 4.92 (1H, d, J = 17.0, PhCHH), 4.96 (1H, d, J = 5.8, SCHO), 6.87-7.15 (4H, m, ArH); δ_C 18.0, 18.1 [CH(CH$_3$)$_2$], 33.7 [CH(CH$_3$)$_2$], 70.3 (PhCH$_2$), 87.6 (SCHO), 124.3, 125.6, 127.1, 127.6, 129.9, 132.2 (ArC); *m/z* 194 (M$^+$, 24%), 151 (71), 137 (10), 122 (100), 121 (51), 78 (26), 57 (10), 51 (10) (Found: M$^+$, 194.0761. $\mathrm{C_{11}H_{14}OS}$ requires M, 194.0765).

2-Isobutyl-4H-benzo[a][1,3]dioxine (**1g**): ν (film) 3047, 2960, 2850, 1616, 1589, 1489 cm^{-1} (C=CH); δ_H 0.98 [6H, d, J = 6.7, CH(CH_3)$_2$], 1.71-1.75 [2H, m, CH_2CH(CH$_3$)$_2$], 1.96 [1H, septet, J = 6.7, CH(CH$_3$)$_2$], 4.81, 4.97 (2H, 2d, J = 14.6, PhCH_2), 5.06 (1H, t, J = 5.5, OCHO), 6.82-6.96 (3H, m, ArH), 7.10-7.16 (1H, m, ArH); δ_C 22.8, 22.3 [CH(CH$_3$)$_2$], 23.8 [CH(CH$_3$)$_2$], 43.1 [CH$_2$CH(CH$_3$)$_2$], 66.4 (PhCH$_2$), 99.1 (OCHO), 116.0, 120.8, 121.0, 124.8, 127.8, 153.1 (ArC); *m/z* 192 (M$^+$, 20%), 135 (10), 106 (100), 85 (10), 78 (77), 57 (14), 51 (10) (Found: M$^+$, 192.1144. $\mathrm{C_{12}H_{16}O_2}$ requires M, 192.1150).

2-Isobutyl-4H-benzo[a][1,3]oxathiine (**1h**): ν (film) 2956, 2870, 1596, 1468, 1439 cm^{-1} (C=CH); δ_H 0.92-1.00 [6H, m, CH(CH_3)$_2$], 1.55-1.73 [1H, m, CH(CH$_3$)$_2$], 1.83-2.02 [2H, m, CH_2CH(CH$_3$)$_2$], 4.87 (2H, s, PhCH_2), 5.18 (1H, t, J = 6.1, SCHO), 6.88-7.15 (4H, m, ArH); δ_C 22.3, 22.68 [CH(CH$_3$)$_2$], 24.7 [CH(CH$_3$)$_2$], 44.65 [CHCH$_2$CH(CH$_3$)$_2$], 69.85 (PhCH$_2$), 80.6 (SCHO), 124.4, 125.6, 127.1, 127.4, 129.65, 132.0 (ArC); *m/z* 208 (M$^+$, 17%), 137 (13), 136 (12), 122 (100), 121 (41), 78 (14), 57 (10) (Found: M$^+$, 208.0932. $\mathrm{C_{12}H_{16}OS}$ requires M, 208.0921).

2-(tert-Butyl)-4H-benzo[a][1,3]dioxine (**1i**): ν (film) 2959, 2870, 1616, 1589, 1490 cm^{-1} (C=CH); δ_H 1.05 [9H, s, C(CH$_3$)$_3$], 4.60 (1H, s, OCHO), 4.81, 4.93 (2H, 2d, J = 14.3, PhCH_2), 6.80-6.95 (3H, m, ArH), 7.07-7.20 (1H, m, ArH); δ_C 24.3 [C(CH$_3$)$_3$], 34.8 [C(CH$_3$)$_3$], 66.8 (PhCH$_2$), 105.1 (OCHO), 116.7, 120.6, 121.05, 124.7, 127.8, 153.5 (ArC); *m/z* 192 (M$^+$, 22%), 135 (100), 106 (82), 78 (83), 57 (32), 51 (10) (Found: M$^+$, 192.1152. $\mathrm{C_{12}H_{16}O_2}$ requires M, 178.1150).

2-(tert-Butyl)-4H-benzo[a][1,3]oxathiine (**1j**): ν (film) 3066, 2959, 2866, 1594, 1439 cm^{-1} (C=CH); δ_H 1.07 [9H, d, J = 0.6, C(CH$_3$)$_3$], 4.85 (1H, d, J = 14.9, PhCHH), 4.92 (1H, s, SCHO), 4.93 (1H, d, J = 14.9, PhCHH), 6.89-7.18 (4H, m, ArH); δ_C 25.65 [C(CH$_3$)$_3$], 35.9 [C(CH$_3$)$_3$], 70.8 (PhCH$_2$), 91.35 (SCHO), 124.2, 125.55, 127.1, 127.8, 129.95, 132.6 (ArC); *m/z* 208 (M$^+$, 42%), 151 (78), 122 (100), 121 (98), 78 (50), 57 (48), 45 (51). Anal. Calcd. for $\mathrm{C_{12}H_{16}OS}$: C, 69.19; H, 7.74; S, 15.39. Found: C, 69.01; H, 7.82; S, 15.68.

Spiro[4H-benzo[a][1,3]dioxine-2,1'-cyclohexane] (**1k**): ν (film) 3045, 2950, 1614, 1589, 1490 cm^{-1} (C=CH); δ_H 1.45-1.50 (2H, m, ring CH$_2$), 1.59-1.65 (4H, m, 2 x ring CH$_2$), 1.67-1.82 (4H, m, 2 x ring CH$_2$), 4.81 (2H, s, PhCH_2), 6.82-6.94 (3H, m, ArH), 7.11-7.16 (1H, m, ArH); δ_C 22.1, 25.3, 33.5 [(CH$_2$)$_5$], 60.1 (PhCH$_2$), 99.65 (OCO), 117.0, 120.0, 120.2, 124.55, 127.9, 151.05 (ArC); *m/z* 204 (M$^+$, 90%), 186 (12), 106 (100), 97 (17), 78 (94), 55 (42) (Found: M$^+$, 204.1158. $\mathrm{C_{13}H_{16}O_2}$ requires M, 204.1150).

Spiro[4H-benzo[a][1,3]oxathiine2,1'-cyclohexane] (**1l**): ν (film) 3053, 2935, 2855, 1570, 1439 cm^{-1} (C=CH); δ_H 1.37-1.51 (2H, m, ring CH$_2$), 1.52-1.79 (4H, m, 2 x ring CH$_2$), 1.83-2.08 (4H, m, 2 x ring CH$_2$), 4.85 (2H, s, PhCH_2), 6.95-7.20 (4H, m, ArH); δ_C 22.5, 25.25, 37.8 [(CH$_2$)$_5$], 63.3 (PhCH$_2$), 85.3 (SCO), 124.3, 125.4, 127.2, 127.9, 130.7, 132.0 (ArC); *m/z* 220 (M$^+$, 75%), 135 (10), 122 (100), 121 (96), 78 (48), 69 (13), 55 (21) (Found: M$^+$, 220. 0918.$\mathrm{C_{13}H_{16}O_2}$ requires M, 220.0921).

1-(4H-Benzo[a][1,3]dioxin-2-yl)-2-phenylethane (**1m**): ν (film) 3026, 2958, 2931, 2857, 1615, 1588, 1489 cm^{-1} (C=CH); δ_H 2.11-2.19 (2H, m, CH_2CH$_2$Ph), 2.86 (2H, t, J = 7.9, CH$_2$CH_2Ph), 4.82 (1H, d, J = 14.3, PhCHH), 4.95 (1H, d, J = 14.9, PhCHH), 4.98 (1H, t, J = 5.0, OCHO), 6.84-6.94 (3H, m, ArH), 7.10-7.30 (6H, m, ArH); δ_C 29.7 (CHCH$_2$CH$_2$Ph), 35.8 (CH$_2$$CH_2$Ph), 66.4 (Ph$CH_2$), 98.9 (OCHO), 116.6, 120.9, 121.0, 124.85, 125.95, 127.9, 128.4, 128.4, 141.2, 153.0 (ArC); *m/z* 240 (M$^+$, 48%), 222 (10), 107 (63), 91 (62), 78 (100), 51 (21) (Found: M$^+$, 240.1153. $\mathrm{C_{16}H_{16}O_2}$ requires M, 240.1150).

1-(4H-Benzo[a][1,3]oxathiin-2-yl)-2-phenylethane (**1n**): ν (film) 3060, 2947, 2857, 1595, 1440 cm^{-1} (C=CH); δ_H 2.03-2.37 (2H, m, CH_2CH$_2$Ph), 2.77-2.94 (2H, m, CH$_2$CH_2Ph), 4.85 (1H, d, J = 15.3, PhCHH), 4.93 (1H, d, J = 15.0, PhCHH), 5.08 (1H, t, J = 6.1, SCHO), 6.85-7.38 (9H, m, ArH) ; δ_C 31.1 (CHCH$_2$CH$_2$Ph), 37.25 (CH$_2$$CH_2$Ph), 69.8 (Ph$CH_2$), 80.7 (SCHO), 124.5, 125.7, 126.1, 127.2, 127.4, 128.5, 129.6, 131.8, 140.7 (ArC); *m/z* 256 (M$^+$, 31%), 238 (10), 210 (10), 133 (12), 122 (100), 121 (90), 91

(36), 78 (50), 65 (16), 45 (25). Anal. Calcd. for $C_{16}H_{16}OS$: C, 74.96; H, 6.29; S, 12.51. Found: C, 75.16; H, 6.34; S, 12.12.

DTBB-Catalysed Lithiation of Heterocycles **1**. *Preparation of Homobenzylic Alcohols* **2**. *General Procedure*.- To a blue suspension of lithium powder (0.12 g, 18 mmol) and a catlytic amount of DTBB (0.047 g, 0.18 mmol) in THF (8 ml) was added the corresponding heterocycle **1** (2 mmol) at room temperature (for X=O) or -78°C (for X=S) and the resulting mixture was stirred for 2 h at the same temperature. Then it was hydrolysed with water, extracted with ethyl acetate (3 x 25 ml), dried over anhydrous Na_2SO_4 and evaporated (15 Torr) giving a residue, which was purified by column chromatography (silica gel, hexane/ethyl acetate) to yield the pure title compounds. Yields and physical data are included in Table 1. Spectroscopic and analytical data, as well as literature references for known compounds follow.

1-(2-Hydroxyphenyl)-2-propanol (**2a**): ν (film) 3721-3061 (OH), 1709, 1585 cm^{-1} (C=CH); δ_H 1.21 (3H, d, *J* = 6.1, CH$_3$), 2.69-2.85 (2H, m, PhC*H*$_2$), 3.31 [1H, br s, CH(O*H*)CH$_3$], 4.12-4.21 (1H, m, CH$_2$C*H*OH), 6.80-6.88 (2H, m, ArH), 6.99-7.14 (2H, m, ArH), 8.51 (1H, br s, PhO*H*) ; δ_C 23.0 (CH$_3$), 40.5 (Ph*C*H$_2$), 70.0 (CHOH), 116.9, 120.3, 125.25, 128.2, 131.7, 155.2 (ArC); *m/z* 152 (M+, 54%), 134 (20), 119 (16), 108 (100), 91 (29), 77 (50), 51 (16) (Found: M+, 152.0841. $C_9H_{12}O_2$ requires M, 152.0837).

1-(2-Sulfanylphenyl)-2-propanol (**2b**):[9] ν (film) 3550-3100 (OH), 2563 cm^{-1} (SH); δ_H 1.24 (3H, d, *J* = 6.1, CH$_3$), 2.07 (1H, br s, PhS*H*), 2.69-2.93 (2H, m, PhC*H*$_2$), 3.46 (1H, br s, CHO*H*), 4.00-4.21 (1H, m, C*H*OH), 6.99-7.38 (4H, m, ArH) ; δ_C 22.9 (CH$_3$), 44.0 (Ph*C*H$_2$), 67.4 (CHOH), 126.0, 127.1, 130.9, 130.9, 131.0, 137.0 (ArC); *m/z* 169 (M++1, 1.2%), 168 (M+, 10), 150 (38), 124 (36), 91 (100).

1-(2-Hydroxyphenyl)-2-methyl-2-propanol (**2c**): ν (film) 3708-3029 (OH), 1585 cm^{-1} (C=CH); δ_H 1.29 [6H, s, C(CH$_3$)$_2$], 2.72 (1H, br s, CH$_2$CO*H*), 2.82 (2H, s, PhC*H*$_2$), 6.72-7.34 (4H, m, ArH), 8.73 (1H, br s, PhO*H*); δ_C 29.6 [C(*C*H$_3$)$_2$], 45.4 (Ph*C*H$_2$), 74.15 (CH$_2$COH), 117.3, 120.0, 124.8, 128.3, 132.4, 155.6 (ArC); *m/z* 166 (M+, 10%), 148 (14), 133 (42), 108 (100), 91 (10), 77 (26), 59 (96), 51 (10) (Found: M+, 166.0992. $C_{10}H_{14}O_2$ requires M, 166.0993).

2-Methyl-1-(2-sulfanylphenyl)-2-propanol (**2d**):[9] ν (film) 3566-3113 (OH), 2543 cm^{-1} (SH); δ_H 1.26 [6H, s, C(CH$_3$)$_2$], 2.90 (2H, s, PhC*H*$_2$), 3.72 (1H, s, OH), 6.97-7.37 (4H, m, ArH); δ_C 29.4 [C(*C*H$_3$)$_2$], 46.9 (Ph*C*H$_2$), 72.1 (CH$_2$COH), 125.8, 127.0, 131.4, 131.8, 132.0, 136.7 (ArC); *m/z* 182 (M+, 2%), 164 (22), 149 (51), 124 (61), 91 (58), 59 (100).

1-(2-Hydroxyphenyl)-3-methyl-2-butanol (**2e**): ν (film) 3499-3106 (OH), 2960, 1585 cm^{-1} (C=CH); δ_H 0.97 [6H, d, *J* = 7.0, CH(C*H*$_3$)$_2$], 1.73 [1H, septet, *J* = 6.7, C*H*(CH$_3$)$_2$], 2.86 (2H, dd, *J* = 14.6, 8.5, PhC*H*$_2$), 3.58-3.71 (1H, m, C*H*OH), 6.79-7.14 (4H, m, ArH), 8.46 (1H, br s, PhO*H*) ; δ_C 17.5, 18.5 [CH(*C*H$_3$)$_2$], 33.5 [*C*H(CH$_3$)$_2$], 36.3 (Ph*C*H$_2$), 79.7 (CHOH), 117.6, 120.2, 126.0, 128.1, 131.3, 155.5 (ArC); *m/z* 180 (M+, 10%), 162 (13), 147 (16), 108 (100), 91 (30), 77 (31). Anal. Calcd. for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 72.95; H, 8.94.

3-Methyl-1-(2-sulfanylphenyl)-2-butanol (**2f**):[9] ν (film) 3718-3113 (OH), 2556 cm^{-1} (SH); δ_H 1.02 [6H, d, *J* = 6.7, CH(C*H*$_3$)$_2$], 1.77 [1H, septet, *J* = 6.7, C*H*(CH$_3$)$_2$], 2.67 (1H, dd, *J* = 13.7, 9.7, PhCH*H*), 2.92 (1H, dd, *J* = 13.7, 2.4, PhC*H*H), 3.45 (1H, s, CHO*H*), 3.55-3.71 (1H, m, C*H*OH), 7.02-7.33 (4H, m, ArH); δ_C 17.4, 18.6 [C(*C*H$_3$)$_2$], 33.65 [*C*H(CH$_3$)$_2$], 39.2 (Ph*C*H$_2$), 76.0 [CH$_2$*C*H(OH)], 124.0, 126.1, 127.1, 130.9, 131.1, 137.7 (ArC); *m/z* 196 (M+, 8%), 178 (30), 163 (16), 149 (10), 124 (87), 91 (100).

1-(2-Hydroxyphenyl)-4-methyl-2-pentanol (**2g**): ν (film) 3400-3068 (OH), 2950, 1590 cm^{-1} (C=CH); δ_H 0.88-0.93 [6H, m, CH(C*H*$_3$)$_2$], 1.22-1.48 [2H, m, C*H*$_2$CH(CH$_3$)$_2$], 1.65-1.78 [1H, m, C*H*(CH$_3$)$_2$], 2.73 (1H, dd, *J* = 14.6, 7.3, PhCH*H*), 2.83 (1H, dd, *J* = 14.6, 2.7, PhC*H*H), 3.03 [1H, br s, CHO*H*], 4.01-4.14 (1H, m, C*H*OH), 6.80-6.90 (2H, m, ArH), 7.00-7.03 (1H, m, ArH), 7.10-7.15 (1H, m, ArH), 8.48 (1H, br s, PhO*H*); δ_C 22.0, 23.0 [CH(*C*H$_3$)$_2$], 24.6 [*C*H(CH$_3$)$_2$], 39.4 [*C*H$_2$CH(CH$_3$)$_2$], 45.8 (Ph*C*H$_2$), 72.2 (CHOH), 117.0, 120.2, 125.4, 128.2, 131.6, 155.4 (ArC); *m/z* 194 (M+, 2%), 133 (20), 108 (54), 91 (11), 77 (18), 44 (100). Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 73.52; H, 9.29.

4-Methyl-1-(2-sulfanylphenyl)-2-pentanol(**2h**):[9] ν (film) 3678-3120 (OH), 2565 cm^{-1} (SH); δ_H 0.88-0.99 [6H, m, CH(C*H*$_3$)$_2$], 1.28-1.37, 1.47-1.56 [2H, 2m, C*H*$_2$CH(CH$_3$)$_2$], 1.82 [1H, septet, *J* = 6.7, C*H*(CH$_3$)$_2$], 2.70 (1H, dd, *J* = 14.0, 8.5, PhC*H*H), 2.89 (1H, dd, *J* = 14.0, 3.7, PhCH*H*), 3.47 (1H, br s, OH), 3.97 (1H, septet, *J* = 4.2, C*H*OH), 6.98-7.40 (4H, m, ArH); δ_C 22.0, 23.4 [CH(*C*H$_3$)$_2$], 24.6 [*C*H(CH$_3$)$_2$], 43.1

$[CH_2CH(CH_3)_2]$, 46.35 ($PhCH_2$), 69.4 (CHOH), 126.1, 127.1, 131.0, 131.05, 131.1, 137.2 (ArC); *m/z* 210 (M^+, 5%), 192 (36), 149 (27), 124 (100), 91 (98), 41 (15).

1-(2-Hydroxyphenyl)-3,3-dimethyl-2-butanol (**2i**): ν (film) 3335-3006 (OH), 2956, 1596 cm^{-1} (C=CH); δ_H 0.97 [9H, s, $C(CH_3)_3$], 2.61 (1H, d, *J* = 14.0, PhC*H*H), 2.79 (1H, dd, *J* = 14.0, 9.7, PhCH*H*), 3.46 (1H, d, *J* = 9.7, C*H*OH), 6.79-6.86 (2H, m, ArH), 6.99 (1H, d, *J* = 1.2, ArH), 7.02-7.12 (1H, m, ArH); δ_C 25.4 $[C(CH_3)_3]$, 34.0 $[C(CH_3)_3]$, 36.2 ($PhCH_2$), 83.2 (CHOH), 117.0, 120.4, 127.0, 128.0, 130.9, 155.5 (ArC); *m/z* 194 (M^+, 6%), 133 (13), 108 (100), 91 (14), 77 (21). Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 73.97; H, 9.38.

3,3-Dimethyl-1-(2-sulfanylphenyl)-2-butanol (**2j**):[9] ν (film) 3537-3375 (OH), 2549 cm^{-1} (SH); δ_H 1.04 [9H, s, $C(CH_3)_3$], 2.61 (1H, dd, *J* = 13.7, 10.7, PhC*H*H), 2.97 (1H, dd, *J* = 13.7, 1.8, PhCH*H*), 3.42-3.56 (2H, m, CHOH), 7.03-7.33 (4H, m, ArH); δ_C 25.7 $[C(CH_3)_3]$, 35.2 $[C(CH_3)_3]$, 36.9 ($PhCH_2$), 79.0 (CHOH), 126.1, 127.0, 131.0, 131.05, 131.1, 138.3 (ArC); *m/z* 210 (M^+, 8%), 192 (30), 177 (10), 149 (87), 124 (100), 91 (88).

1-(2-Hydroxybenzyl)-1-cyclohexanol (**2k**): ν (film) 3563-3090 (OH), 2932, 1585 cm^{-1} (C=CH); δ_H 1.41-1.66 (10H, m, 5 x ring CH_2), 2.48 (1H, s, COH), 2.83 (2H, s, $PhCH_2$), 6.71-7.34 (4H, m, ArH), 8.69 (1H, br s, PhO*H*); δ_C 22.4, 25.4, 37.4 [$(CH_2)_5$], 43.7 ($PhCH_2$), 75.0 (CH_2COH), 117.3, 119.9, 124.0, 128.3, 132.3, 155.8 (ArC); *m/z* 206 (M^+, 11%), 188 (42), 108 (100), 99 (68), 91 (10), 81 (90) (Found: M^+, 206.1308. $C_{13}H_{18}O_2$ requires M, 206.1306).

1-(2-Sulfanylbenzyl)-1-cyclohexanol (**2l**):[9] ν (film) 3684-3134 (OH), 2537 cm^{-1} (SH); δ_H 1.39-1.70 (10H, m, 5 x ring CH_2), 2.91 (2H, s, $PhCH_2$), 3.77 (1H, s, COH), 7.01-7.36 (4H, m, ArH); δ_C 21.9, 25.7, 37.5 $[(CH_2)_5]$, 46.8 ($PhCH_2$), 72.7 (COH), 125.7, 127.0, 131.4, 132.0, 132.2, 136.25 (ArC); *m/z* 222 (M^+, 0.6%), 204 (53), 149 (10), 147 (47), 124 (79), 91 (32), 81(100).

1-(2-Hydroxyphenyl)-4-phenyl-2-butanol (**2m**): ν (film) 3708-3118 (OH), 2940, 1584 cm^{-1} (C=CH); δ_H 1.81-1.91 (2H, m, CH_2CH_2Ph), 2.42 (1H, br s, CHO*H*), 2.74 (2H, dt, *J* = 7.6, 2.4, $PhCH_2CH_2$), 2.83-2.86 (2H, m, $PhCH_2CH$), 3.97-4.08 (1H, m, C*H*OH), 6.79-7.34 (9H, m, ArH), 8.02 (1H, br s, PhO*H*); δ_C 32.0 (CH_2CH_2Ph), 38.3 (CH_2CH_2Ph), 39.6 ($PhCH_2CH$), 73.9 (CHOH), 117.2, 120.3, 125.1, 126.2, 128.3, 128.3, 128.4, 131.6, 141.1, 155.5 (ArC); *m/z* 242 (M^+, 8%), 133 (13), 108 (100), 91 (81), 77 (20) (Found: M^+, 242.1317. $C_{16}H_{18}O_2$ requires M, 242.1306).

4-Phenyl-1-(2-sulfanylphenyl)-2-butanol (**2n**):[9] ν (film) 3523-3194 (OH), 2563 cm^{-1} (SH); δ_H 1.77-2.02 (2H, m, CH_2CH_2Ph), 2.61-2.97 (4H, m, $PhCH_2CH_2$ and $PhCH_2CH$), 3.42 (1H, br s, CHO*H*), 3.85-3.99 (1H, m, C*H*OH), 7.02-7.35 (9H, m, ArH); δ_C 32.0 (CH_2CH_2Ph), 38.6 (CH_2CH_2Ph), 42.6 ($PhCH_2CHOH$), 70.8 (CHOH), 125.8, 126.1, 127.2, 128.3, 128.4, 130.95, 131.0, 131.15, 137.0, 141.9 (ArC); *m/z* 258 (M^+, 0.5%), 240 (51), 149 (41), 124 (52), 91 (100).

Cyclisation of Homobenzylic Alcohols **2**. *Preparation of Heterocycles* **5**. *Method A*.- A mixture of the corresponding homobenzylic compound **2** (1 mmol) and 85% phosphoric acid (0.4 ml) in toluene (5 ml) was heated at reflux for 1-3 h. Toluene was then removed *in vacuo* (15 Torr) and the resulting residue was hydrolysed with water (4 ml) and extracted with ethyl acetate (3 x 15 ml). The organic layer was dried over anhydrous Na_2SO_4 and evaporated (15 Torr) giving a residue, which was purified by column chromatography (silica gel, hexane/ethyl acetate) affording the pure title compounds.

Method B.- To a solution of the corresponding homobenzylic alcohol **2** (1 mmol) and triphenylphosphine (1.2 mmol) in THF (5 ml) was dropwise added DIAD (1.5 mmol) at room temperature and the mixture was stirred for *ca.* 12 h. Then, THF was removed *in vacuo* (15 Torr), the resulting residue being purified by column chromatography (silica gel, hexane/ethyl acetate) to afford the pure title compounds.

Yields and physical data are included in Table 3. Spectroscopic and analytical data, as well as literature references for known compounds follow.

2-Methyl-2,3-dihydrobenzo[b]furan (**5a**):[10] ν (film) 2969, 1596, 1233 cm^{-1} (C=CH); δ_H 1.46 (3H, d, *J* = 6.1, CH_3), 2.80 (1H, dd, *J* = 15.2, 7.6, PhCH*H*), 3.30 (1H, dd, *J* = 15.2, 8.8, PhC*H*H), 4.76-4.93 (1H, m, $CHCH_3$), 6.68-6.89 (2H, m, ArH), 7.03-7.20 (2H, m, ArH); δ_C 21.7 (CH_3), 37.1 ($PhCH_2$), 79.4 (OCH), 109.3, 120.1, 124.9, 127.0, 127.9, 159.5 (ArC); *m/z* 134 (M^+, 100%), 119 (61), 105 (20), 91 (64).

2-Methyl-2,3-dihydrobenzo[b]thiophene (**5b**):[11] ν (film) 2959, 1589, 1461, 1447, 742 cm^{-1} (C=CH); δ_H 1.43 (3H, d, *J* = 6.7, CH_3), 2.93 (1H, dd, *J* = 15.4, 6.7, PhC*H*H), 3.36 (1H, dd, *J* = 15.5, 7.3, PhCH*H*), 3.96 (1H, sextet, *J* = 6.7, SC*H*CH_3), 6.90-7.29 (4H, m, ArH); δ_C 21.7 (CH_3), 44.3 (Ph*C*H_2), 45.4 (SCH), 122.15, 123.9, 124.6, 127.2, 139.4, 141.2 (ArC); *m/z* 150 (M$^+$, 75%), 135 (100), 115 (17), 91 (58).

2,2-Dimethyl-2,3-dihydrobenzo[b]furan (**5c**):[12] ν (film) 2971, 1598, 1259 cm^{-1} (C=CH); δ_H 1.47 [6H, s, $C(CH_3)_2$], 3.00 (2H, s, PhC*H*$_2$), 6.67-6.86 (2H, m, ArH), 7.04-7.17 (2H, m, ArH); δ_C 28.2 [C(*C*H_3)$_2$], 42.8 (Ph*C*H_2), 86.4 [*C*(CH_3)$_2$], 109.5, 119.9, 125.1, 127.0, 127.9, 158.8 (ArC); *m/z* 148 (M$^+$, 57%), 133 (100), 105 (55), 77 (25).

2,2-Dimethyl-2,3-dihydrobenzo[b]thiophene (**5d**):[13] ν (film) 2956, 1582, 1461, 1447, 740 cm^{-1} (C=CH); δ_H 1.55 [6H, s, $C(CH_3)_2$], 3.07 (2H, s, PhC*H*$_2$), 6.91-7.19 (4H, m, ArH); δ_C 29.6 [C(*C*H_3)$_2$], 51.1 (Ph*C*H_2), 56.8 [*C*(CH_3)$_2$], 122.3, 123.9, 124.8, 127.2, 139.6, 141.7 (ArC); *m/z* 164 (M$^+$, 50%), 149 (100), 134 (35), 115 (13), 91 (11).

2-Isopropyl-2,3-dihydrobenzo[b]furan (**5e**): ν (film) 2962, 1776, 1235 cm^{-1} (C=CH); δ_H 0.96 (3H, d, *J* = 6.7, CHC*H*$_3$), 1.03 (3H, d, *J* = 6.4, CHC*H*$_3$), 1.95 [1H, septet, *J* = 6.7, C*H*(CH_3)$_2$], 2.93 (1H, dd, *J* = 15.6, 8.5, PhC*H*H), 3.16 (1H, dd, *J* = 15.6, 9.1, PhCH*H*), 4.49 (1H, ddd, *J* = 15.9, 8.8, 1.8, OCH), 6.69-6.87 (2H, m, ArH), 7.02-7.21 (2H, m, ArH); δ_c 17.75, 18.2 [CH(*C*H_3)$_2$], 21.6 [*C*H(CH_3)$_2$], 32.8 (Ph*C*H_2), 74.3 (OCH), 109.0 119.9, 124.8, 127.1, 127.8, 159.9 (ArC); *m/z* 162 (M$^+$, 55%), 147 (50), 133 (18), 119 (40), 107 (100) (Found: M$^+$, 162.1042. $C_{11}H_{14}O$ requires M, 162.1044).

2-Isopropyl-2,3-dihydrobenzo[b]thiophene (**5f**): ν (film) 2953, 1582, 1463, 1446, 739 cm^{-1} (C=CH); δ_H 1.00 [6H, d, *J* = 24.0, CH(C*H*$_3$)$_2$], 1.94 [1H, septet, *J* = 6.7, C*H*(CH_3)$_2$], 3.04 (1H, dd, *J* = 15.7, 8.8 PhCH*H*), 3.30 (1H, dd, *J* = 15.5, 7.6, PhC*H*H), 3.76 [1H, ddd, *J* = 15.6, 8.2, 1.2, SC*H*CH(CH_3)$_2$], 6.90-7.19 (4H, m, ArH); δ_C 20.6, 21.0 [CH(*C*H_3)$_2$], 33.8 [*C*H(CH_3)$_2$], 40.4 (Ph*C*H_2), 58.7 [S*C*HCH(CH_3)$_2$], 121.7, 123.85, 124.2, 127.2, 140.1, 141.4 (ArC); *m/z* 178 (M$^+$, 42%), 135 (100), 91 (50) (Found: M$^+$, 178.0821. $C_{11}H_{14}S$ requires M, 178.0816).

2-Isobutyl-2,3-dihydrobenzo[b]furan (**5g**): ν (film) 2956, 1598, 1232 cm^{-1} (C=CH); δ_H 0.93-1.06 [6H, m, CH(C*H*$_3$)$_2$], 1.38-1.53 [1H, m, C*H*(CH_3)$_2$], 1.73-1.97 [2H, m, C*H*$_2$CH(CH_3)$_2$], 2.81 (1H, dd, *J* = 15.3, 7.9, PhC*H*H), 3.26 (1H, dd, *J* = 15.3, 8.8, PhCH*H*), 4.72-4.92 (1H, m, OCH), 6.65-6.89 (2H, m, ArH), 7.02-7.19 (2H, m, ArH); δ_C 22.3, 23.0 [CH(*C*H_3)$_2$], 25.0 [*C*H(CH_3)$_2$], 35.9 [*C*H_2CH(CH_3)$_2$], 45.2 (Ph*C*H_2), 81.7 (OCH), 109.3, 120.0, 124.9, 126.9, 127.8, 159.4 (ArC); *m/z* 176 (M$^+$, 80%), 133 (89), 119 (46), 107 (100) (Found: M$^+$, 176.1205. $C_{12}H_{16}O$ requires M, 176.1201).

2-Isobutyl-2,3-dihydrobenzo[b]thiophene (**5h**): ν (film) 2955, 1588, 1462, 1447, 742 cm^{-1} (C=CH); δ_H 0.93 [6H, d, *J* = 30.5, CH(C*H*$_3$)$_2$], 1.49-1.82 [3H, m, C*H*(CH_3)$_2$ and C*H*$_2$CH(CH_3)$_2$], 2.95 (1H, dd, *J* = 15.2, 7.6, PhCH*H*), 3.32 (1H, dd, *J* = 15.2, 7.3, PhC*H*H), 3.90-4.05 (1H, m, SC*H*CH_2], 6.91-7.24 (4H, m, ArH); δ_C 21.9, 22.9 [CH(*C*H_3)$_2$], 27.1 [*C*H(CH_3)$_2$], 42.7 [*C*H_2CH(CH_3)$_2$], 45.0 (Ph*C*H_2), 49.4 (SCH), 122.1, 123.9, 124.4, 127.2, 139.6, 141.0 (ArC); *m/z* 192 (M$^+$, 54%), 135 (100), 91 (37) (Found: M$^+$, 192.0969. $C_{12}H_{16}S$ requires M, 192.0972).

*2-(*tert*-Butyl)-2,3-dihydrobenzo[b]furan* (**5i**): ν (film) 2958, 1596 cm^{-1} (C=CH); δ_H 0.97 [9H, d, *J* = 0.9, $C(CH_3)_3$], 3.00 (1H, dd, *J* = 15.5, 8.8, PhC*H*H), 3.07 (1H, dd, *J* = 15.5, 9.1, PhCH*H*), 4.45 (1H, dt, *J* = 9.1, 0.9, OCH), 6.70-6.85 (2H, m, ArH), 7.03-7.18 (2H, m, ArH); δ_C 25.1 [C(*C*H_3)$_3$], 30.8 (Ph*C*H_2), 34.3 [*C*(CH_3)$_3$], 90.85 (OCH), 108.9, 119.8, 124.7, 127.2, 127.8, 160.1 (ArC); *m/z* 176 (M$^+$, 79%), 161 (20), 133 (92), 119 (84), 107 (100), 91 (91) (Found: M$^+$, 176.1203. $C_{12}H_{16}O$ requires M, 176.1201).

*2-(*tert*-Butyl)-2,3-dihydrobenzo[b]thiophene* (**5j**): ν (film) 2960, 1589, 1464, 1445, 741 cm^{-1} (C=CH); δ_H 1.01 [9H, s, $C(CH_3)_3$], 3.15 (1H, dd, *J* = 15.6, 9.1, PhCH*H*), 3.22 (1H, dd, *J* = 15.5, 8.5, PhC*H*H), 3.91 (1H, dt, *J* = 8.8, 0.6, SCH), 6.90-7.19 (4H, m, ArH); δ_C 27.5 [C(*C*H_3)$_3$], 34.2 [*C*(CH_3)$_3$], 37.5 (Ph*C*H_2), 62.8 (SCH), 121.6, 123.8, 124.1, 127.1, 140.1, 141.4 (ArC); *m/z* 192 (M$^+$, 29%), 135 (100), 91 (34) (Found: M$^+$, 192.0971. $C_{12}H_{16}S$ requires M, 192.0972).

Spiro[2,3-dihydrobenzo[b]furan-2,1'-cyclohexane] (**5k**):[12] ν (film) 2932, 1597, 1240 cm^{-1} (C=CH); δ_H 1.36-1.55 (4H, m, 2 x ring CH_2), 1.57-1.89 (6H, m, 3 x ring CH_2), 2.97 (2H, s, PhC*H*$_2$), 6.68-6.88 (2H, m, ArH), 7.02-7.20 (2H, m, ArH); δ_C 23.0, 25.2, 37.1 [$(CH_2)_5$], 40.9 (Ph*C*H_2), 88.3 (O*C*CH_2), 109.45, 119.7, 125.1, 126.7, 127.8, 158.8 (ArC); *m/z* 188 (M$^+$, 81%), 133 (10), 131 (21), 107 (100), 91 (16).

Spiro[2,3-dihydrobenzo[b]thiophene-2,1'-cyclohexane] (**5l**): ν (film) 2927, 1589, 1461, 1446, 741 cm^{-1} (C=CH); δ_H 1.48-1.73 (8H, m, 4 x ring CH_2), 1.92-2.06 (2H, m, ring CH_2), 3.09 (2H, s, $PhC\mathit{H}_2$), 6.89-7.18 (4H, m, ArH); δ_C 24.3, 25.6, 38.6 [$(CH_2)_5$], 49.6 ($PhCH_2$), 63.0 ($SCCH_2$), 122.1, 123.8, 124.8, 127.0, 139.2, 140.9 (ArC); *m/z* 204 (M$^+$, 100), 161 (84), 147 (87), 135 (32), 91 (17) (Found: M$^+$, 204.0978. $C_{13}H_{16}S$ requires M, 204.0972).

1-(2,3-Dihydrobenzo[b]furan-2-yl)-2-phenylethane (**5m**): ν (film) 2929, 1598, 1232 cm^{-1} (C=CH); δ_H 1.85-2.05, 2.06-2.29 (2H, 2m, $PhCH_2C\mathit{H}_2$), 2.71-2.90 (3H, m, $PhCH\mathit{H}CH$ and $PhC\mathit{H}_2CH_2$), 3.27 (1H, dd, J = 15.2, 8.5, $PhC\mathit{H}HCH$), 4.76 (1H, dquintet, J = 7.3, 1.8, OCH), 6.76-6.84 (2H, m, ArH), 7.07-7.32 (7H, m, ArH); δ_C 31.8 ($PhCH_2CH_2$), 35.4 ($PhCH_2CH_2$), 37.8 ($PhCH_2CH$), 82.3 (OCH), 109.3, 120.1, 124.9, 125.9, 126.8, 127.9, 128.4, 128.45, 133.6, 133.8, 141.5, 159.5 (ArC); *m/z* 224 (M$^+$, 100%), 133 (92), 117 (10), 107 (64), 91 (90) (Found: M$^+$, 224.1209. $C_{16}H_{16}O$ requires M, 224.1201).

1-(2,3-Dihydrobenzo[b]thiophen-2-yl)-2-phenylethane (**5n**): ν (film) 2932, 1582, 1461, 1446, 743 cm^{-1} (C=CH); δ_H 1.99-2.12 (2H, m, $PhCH_2C\mathit{H}_2$), 2.63-2.86 (2H, m, $PhC\mathit{H}_2CH_2$), 3.02 (1H, dd, J = 15.5, 7.0, $PhC\mathit{H}HCH$), 3.37 (1H, dd, J = 15.5, 7.6, $PhCH\mathit{H}CH$), 3.84 (1H, quintet, J = 7.3, SCH), 6.93-7.35 (9H, m, ArH); δ_C 34.4 ($PhCH_2CH_2$), 37.9 ($PhCH_2CH_2$), 42.5 ($PhC\mathit{H}_2CH$), 50.3 (SCH), 122.2, 124.1, 124.5, 126.0, 127.3, 128.4, 128.5, 139.4, 140.75, 141.2 (ArC); *m/z* 240 (M$^+$, 78%), 149 (51), 135 (100), 91 (63) (Found: M$^+$, 240.0975. $C_{16}H_{16}S$ requires M, 240.0972).

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REFERENCES AND NOTES

1. (a) First account: Yus, M.; Ramón, D. J. *J. Chem. Soc., Chem. Commun.* **1991**, 398-400. (b) For a recent review, see: Yus, M. *Chem. Soc. Rev.* **1996**, 155-161.
2. For arene-catalysed reductive opening of oxiranes,[2a,b] oxetanes,[2c] tetrahydrofurans[2d,e] or tetrahydropyrans,[2f] see: (a) Bachki, A.; Foubelo, F.; Yus, M. *Tetrahedron: Asymm.* **1995**, *6*, 1907-1910. (b) Bachki, A.; Foubelo, F.; Yus, M. *Tetrahedron: Asymm.* **1996**, *7*, 2997-3008. (c) Bachki, A.; Falvello, L. R.; Foubelo, F.; Yus, M. *Tetrahedron: Asymm.*, in press. (d) Ramón, D. J.; Yus, M. *Tetrahedron* **1992**, *48*, 3585-3588. (e) Almena, J.; Foubelo, F.; Yus, M. *Tetrahedron* **1995**, *51*, 3351-3364. (f) Almena, J.; Foubelo, F.; Yus, M. *Tetrahedron* **1995**, *51*, 3365-3374.
3. For arene-catalysed reductive ring opening of thietans,[3a] tetrahydrothiophenes[3a,b] and thiacyclohexanes,[3a] see: (a) Almena, J.; Foubelo, F.; Yus, M. *Tetrahedron* **1997**, *53*, 5563-5572. (b) Almena, J.; Foubelo, F.; Yus, M. *J. Org. Chem.* **1996**, *61*, 1859-1862.
4. For arene-catalysed reductive ring opening of aziridines,[4a,b] azetidines,[4c] pyrrolidines[4d] and piperidines,[4d] see: (a) Almena, J.; Foubelo, F.; Yus, M. *Tetrahedron Lett.* **1993**, *34*, 1649-1652. (b) Almena, J.; Foubelo, F.; Yus, M. *J. Org. Chem.* **1994**, *59*, 3210-3215. (c) Almena, J.; Foubelo, F.; Yus, M. *Tetrahedron* **1994**, *50*, 5775-5782. (d) Almena, J.; Foubelo, F.; Yus, M. *Tetrahedron* **1996**, *52*, 8545-8564.
5. For a review, see: Foubelo, F.; Yus, M. *Rev. Heteroatom. Chem.*, in press.
6. For reviews, see: (a) Nájera, C.; Yus, M. *Trends Org. Chem.* **1991**, *2*, 155-181. (b) Nájera, C.; Yus, M. *Recent Res. Devel. Org. Chem.* **1997**, *1*, 67-96.
7. Arnoldi, A; Carughi, M. *Synthesis* **1988**, 155-157.
8. Sala, T.; Sargent, M. V. *J. Chem. Soc., Perkin Trans. 1* **1981**, 877-882.
9. For this compound, microanalysis and HRMS could be performed, but gave unsatisfactory results.
10. Brust, D. P.; Tarbell, D. S. *J. Org. Chem.* **1966**, *31*, 1251-1255.
11. Meyers, C. Y.; Rinaldi, C.; Bonoli, L. *J. Org. Chem.* **1963**, *28*, 2440-2442.
12. Martini, J. C.; Franke, N. W.; Singerman, G. M. *J. Org. Chem.* **1970**, *35*, 2904-2907.
13. Kwart, H.; Evans, E. R. *J. Org. Chem.* **1966**, *31*, 413-419.
14. Antus, S.; Baitz-Gács, E.; Snatzke, G.; Vas, J. *Tetrahedron* **1986**, *42*, 5637-5640.

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