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Di(lithiomethyl)benzenes from Di(chloromethyl)benzenes by a DTBB-Catalysed Lithiation under Barbier-type Conditions

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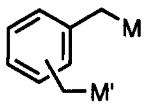
Abstract: The reaction of 1,2-, 1,3- and 1,4-di(chloromethyl)benzenes (**1a-c**) and different electrophiles [Pr^{i}CHO, Bu^{t}CHO, PhCHO, $(CH_2)_5CO$, PhCOMe, Me_3SiCl] with an excess of lithium powder and a catalytic amount of DTBB (4 mol%) in THF at 0°C leads, after hydrolysis with water, to the expected dioles or disilylated compounds **2aa-cf**. © 1997 Elsevier Science Ltd.

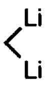
INTRODUCTION

One inherent problem when preparing very reactive organolithium compounds,[1] such as benzyllithium, from the corresponding halogenated precursors is their spontaneous Wurtz-type coupling to give the corresponding dimers. For this reason, methodologies involving (a) direct benzylic deprotonation using superbases or an alkyllithium in the presence of an amine (leading to 'mixed' carbanions or amine complexes, respectively),[1,2a] (b) a mercury-lithium transmetallation[2b] or (c) mesylate-lithium exchange[2c] have been developed. The use of benzyl halides under Barbier-type conditions (lithiation in the presence of the electrophile) gives also, in general, bad results.[3] To the best of our knowledge, only route (a) has been attempted to generate dianions[4] of the type **I** [by using the Lochmann-Schlosser base (potassium *tert*-butoxide and *n*-butyllithium)[5]], studying their reaction with alkylating agents, yields being, in general, moderate.[6,7] A few years ago we developed a lithiation methodology consisting of using an excess of lithium powder and a catalytic amount of an arene, naphthalene and 4,4'-di-*tert*-butylbiphenyl being the most commonly used.[8] Applying this methodology, we have been able to find new procedures for preparing organolithiums from non-halogenated materials[9a] as well as for the preparation of very unstable functionalised organolithium intermediates[10] (from chlorinated precursors,[9b] heterocyclic compounds[9c] and carbonylic derivatives[9d]) or polylithium synthons.[9e] Concerning these last intermediates, we have recently prepared polylithiated species **II-VIII**[11] as polyanionic intermediates combining an arene-catalysed lithiation at low temperature with performing the reaction under Barbier-type reaction conditions, so obtaining directly polyfunctionalised molecules. In the present paper we apply the former methodology to generate dilithiated synthons of the type **I** (M = M'= Li) and study their *in situ* reaction with electrophilic reagents.

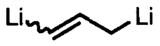


I

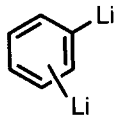
(M = or = M'= Li, K)



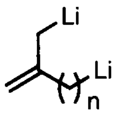
II[11a,b]



III[11c]



IV[11d]

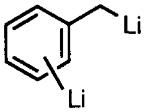


V

(n = 0,[11e,f] 1[11g,h])

VI[11i]

VII[11j]



VIII[11k]

RESULTS AND DISCUSSION

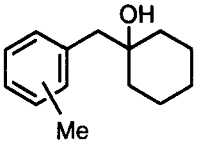
The reaction of di(chloromethyl)benzenes **1a-c** with an excess of lithium powder (1:14 molar ratio; theoretical 1:4 molar ratio) and a catalytic amount of DTBB (4 mol %) in the presence of different electrophiles [Pr^iCHO, Bu^tCHO, PhCHO, $(CH_2)_5CO$, PhCOMe, Me_3SiCl] (Barbier-type reaction conditions) in THF at 0°C for *ca.* 1 h led, after hydrolysis with water, to the formation of the corresponding difunctionalised products **2aa-cf** (Scheme 1 and Table 1). In the case of using prochiral carbonyl compounds such as aldehydes (Table 1, entries 1-3, 7, 10 and 11) or acetophenone (Table 1, entries 5 and 13) the corresponding *ca.* 1:1 diastereisomeric mixture was isolated.

1a : 1,2-
1b : 1,3-
1c : 1,4-

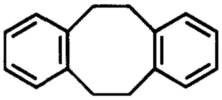
2aa-cf

Scheme 1. *Reagents and conditions*: i, Li, DTBB cat. (4 mol %), E^+ = Pr^iCHO, Bu^tCHO, PhCHO, $(CH_2)_5CO$, PhCOMe, Me_3SiCl, THF, 0°C, 1 h; ii, H_2O, 0 to 20°C.

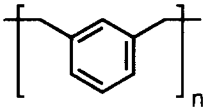
Concerning the reaction conditions shown in Scheme 1, in absence of the catalyst, even having conversions of around 80%, yields of the desired compounds **2** are rather lower than those of the catalysed process, the reaction being less clean for the uncatalysed one. As an example, the lithiation of **1a-c** with cyclohexanone without DTBB gave 44%, 44% and 16% yields for compounds **2ad**, **2bd** and **2cd**, respectively (compare to Table 1, entries 4, 8 and 12), the corresponding by-products **3a-c** being isolated in 32%, 25% and 26%, respectively. On the other hand, the two-step reaction (tandem DTBB-catalysed lithiation/reaction with the electrophile) gave very poor results. Thus, using cyclohexanone as electrophile, the two-step reaction with compound **1a** gave dibenzo-1,5-cyclooctadiene (**4**) as the major product (38%)[12] together with compounds **2ad** (23%)[12] and **3a** (21%).[11] In the case of starting materials **1b,c** a polymeric material was the main product isolated, which probably has structure **5b,c**.[13,14] Finally, working at temperatures lower than 0°C, the yields of compound **2** are much lower obtaining variable amounts of compounds **3**, using cyclohexanone as electrophile.



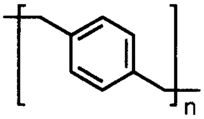
3a-c



4



5b



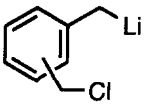
5c

Table 1. Preparation of Compounds **2**

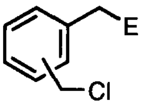
Entry	Starting material	Electrophile E+	Product[a]			
			No.	E	Yield (%)[b]	Mp (°C)[c] or R_f[d]
1	**1a**	Pr^{i}CHO	**2aa**	Pr^{i}CHOH	43[e,f]	0.63[g]
2	**1a**	Bu^{t}CHO	**2ab**	Bu^{t}CHOH	45[e,f]	0.90
3	**1a**	PhCHO	**2ac**	PhCHOH	53[e,f]	0.57[g]
4	**1a**	$(CH_2)_5CO$	**2ad**	$(CH_2)_5COH$	86[f]	106
5	**1a**	PhCOMe	**2ae**	PhC(OH)Me	42[e,f]	0.73[g]
6	**1a**	Me_3SiCl	**2af**	Me_3Si	72[h]	0.44[i]
7	**1b**	Pr^{i}CHO	**2ba**	Pr^{i}CHOH	30[e,f]	0.55[g]
8	**1b**	$(CH_2)_5CO$	**2bd**	$(CH_2)_5COH$	84[f]	104
9	**1b**	Me_3SiCl	**2bf**	Me_3Si	82[h]	0.44[i]
10	**1c**	Pr^{i}CHO	**2ca**	Pr^{i}CHOH	38[e,j]	0.60
11	**1c**	PhCHO	**2cc**	PhCHOH	55[e,f]	0.55
12	**1c**	$(CH_2)_5CO$	**2cd**	$(CH_2)_5COH$	62[f]	133
13	**1c**	PhCOMe	**2ce**	PhC(OH)Me	52[e,f]	0.63
14	**1c**	Me_3SiCl	**2cf**	Me_3Si	88[h]	0.41[i]

[a] All compounds **2** were >95% pure (GLC and 300 MHz ^{1}H NMR). [b] Isolated yield based on the starting material **1**. [c] From hexane/ethyl acetate. [d] Silica gel, hexane/ethyl acetate: 1/1 unless otherwise stated. [e] *ca.* 1:1 Diastereoisomers mixture (GLC and/or 300 MHz ^{1}H NMR). [f] After recrystallisation (hexane/ethyl acetate). [g] Both diastereoisomers could not be separated by TLC. [h] Isolated crude yield of essentially pure product (>90%, GLC). [i] Silica gel, hexane. [j] After column chromatography (silica gel, hexane/ethyl acetate).

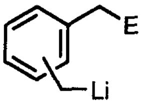
From the results obtained we deduce that the probable mechanistic pathway would involve intermediates **IX-XI**, so the initially monolithiated species **IX** would prefer to react with the electrophile present in the reaction medium, to give compound **X**, instead of dimerising (to compound **4**) or polymerising (to compounds **5b,c**). Final lithiation to intermediate **XI** followed by condensation with another molecule of the electrophile affords the obtained products **2**. If intermediate **XI** is formed in the absence of the electrophile it can abstract a proton from the reaction medium giving compounds **3**. The participation of dilithiated intermediates **XII** can not be ruled out; however, their instability,[4] together with the existence of the electrophile in the reaction medium support the pathway including species **IX-XI**.



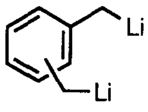
IX



X



XI



XII

As a conclusion, DTBB-catalysed lithiation of di(chloromethyl)benzenes **1** has to be performed in the presence of electrophiles (Barbier-type conditions) giving difunctionalised products **2**, the method being to be chosen for these compounds. In the case of carbonyl derivatives (**2**, E = RR'COH) the corresponding *o*-systems (from **1ab**), 1,6-diols, are adequate to be cyclised to the corresponding oxepanes.[11k]

EXPERIMENTAL PART

General.- Melting points are uncorrected. IR spectra were recorded using NaCl for neat liquids or KBr pellets for solid samples. Only structurally most important peaks (IR, cm^{-1}) are listed. ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively, using $CDCl_3$ as solvent and TMS (0.00 ppm, ^{1}H) and $CDCl_3$ (77.00 ppm, ^{13}C) as internal standards; chemical shifts are given in δ (ppm) and coupling constants (J) are measured in hertz. The purity of volatile distilled products and the chromatographic analysis (GLC) were determined with a flame ionisation detector and a 12-m HP-1 capillary column (0.2 mm diam, 0.33 mm film thickness) with nitrogen (2 mL/min) as the carrier gas, T_{injector} = 270 °C, T_{column} = 60 °C (3 min), and 60-270 °C (15 °C/min). 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. 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. All reagents were commercially available (Aldrich, Acros) and of the best grade. Reaction solvents were dried and distilled under argon using standard procedures.[15] Merck silica gel 60 (70-230 mesh) was employed for column chromatography.

General Procedure for the DTBB-Catalysed Lithiation of Di(chloromethyl)-benzenes in the Presence of Electrophiles. Isolation of Compounds **2**.- To a cooled (0 °C) green suspension of lithium powder (*ca.* 0.20 g, 28 mmol) and DTBB (0.090 g, 0.34 mmol) in THF (5 ml) was slowly added (*ca.* 1 h) a mixture of the corresponding dichlorinated starting material (**1**; 0.35 g, 2 mmol) and the electrophile (4 mmol) in THF (2 ml). The resulting mixture was hydrolysed with water (5 ml) at 0 °C and extracted with ethyl acetate (3 x 10 ml). The organic layer was dried over anhydrous Na_2SO_4 and evaporated (15 Torr). The resulting residue was purified by recrystallisation or column chromatography (silica gel, hexane/ethyl acetate) to yield pure products **2**. Compound **2ab**, which was isolated as a *ca.* 1:1 diastereoisomers mixture (GLC), was identified by GLC-MS, by comparison with an authentic sample, already prepared by us.[16] For compounds **2**, yields and physical data are included in Table 1; spectroscopic and analytical data follow.

1,2-Di-(3'-methyl-2'-hydroxybutyl)benzene (**2aa**):[17] 1:1 Diastereomers mixture (GLC); ν (film) 3385 (OH), 3058, 3025, 1672, 1602 (C=CH), 1067 cm^{-1} (C-O); δ_H 0.93, 0.95, 1.02 (24H, 3d, *J* = 13.7, 8xMe), 1.79, 1.97 (4H, 2m, 4xC*H*Me), 2.65, 2.68, 2.88, 2.89 (8H, 4dd, *J* = 13.7, 1.2, 4xCH_2), 3.40, 3.61, (4H, 2m, 4xCHO), 7.21 (8H, m, ArH); δ_C 16.0, 17.7, 18.7, 20.1 (8xMe), 33.6, 37.1 (4xCH_2), 76.75, 76.8 (4xCHO), 126.6, 130.7, 137.8 (ArC); *m/z.* 232 (M^+ - H_2O, 1%), 145 (74), 129 (11), 117 (27), 115 (11), 106 (100), 105 (53), 104 (92), 103 (10), 91 (32), 79 (11), 77 (14), 73 (60), 71 (10), 55 (36), 45 (10), 43 (60).

1,2-Di-(2'-hydroxy-2'-phenylethyl)benzene (**2ac**): 1:1 Diastereomers mixture (GLC); ν (KBr) 3401 (OH), 3061, 3029, 1601, 1493 (C=CH), 1045 cm^{-1} (C-O); δ_H 2.59 (2H, 2br s, 2xOH), 3.01 (8H, d, *J* = 6.4, 4xCH_2), 4.91 (4H, t, *J* = 6.4, 4xCHO), 7.10-7.37 (28H, m, ArH); δ_C 42.2, 42.3, 42.35 (4xCH_2), 74.6, 75.5, 77.6, 78.8 (4xCHO), 125.6, 125.65, 126.4, 126.9, 126.95, 127.3, 127.8, 128.2, 128.3, 130.6, 136.7, 139.6, 143.9 (ArC); first diastereomer (t_r 17.40 min)[18] *m/z* 300 (M^+ - H_2O, 5%), 282 (25), 202 (10), 195 (17), 194 (90), 193 (21), 192 (17), 191 (64), 189 (12), 180 (16), 179 (100), 178 (43), 165 (16), 117 (11), 116 (86), 115 (40), 107 (56), 105 (55), 103 (14), 91 (37), 79 (59), 78 (14), 77 (65), 65 (11), 51 (25), 44 (19); second diastereomer (t_r 17.45 min)[18] *m/z* 300 (M^+ - H_2O, 5.8%), 282 (21), 195 (16), 194 (91), 193 (21), 192 (16), 191 (59), 189 (11), 180 (15), 179 (100), 178 (42), 165 (14), 117 (11), 116 (91), 115 (41), 107 (66), 106 (19), 105 (55), 104 (10), 103 (13), 91 (39), 79 (67), 78 (15), 77 (72), 65 (12), 51 (25), 44 (18) (Found: C, 81.28; H, 7.11. $C_{22}H_{22}O_2 \cdot 1/3H_2O$ requires: C, 81.45; H, 7.04).

1,2-Di-[(1'-hydroxycyclohexyl)methyl)benzene (**2ad**): ν (KBr) 3442 (OH), 3056, 3025, 1601, 1483 (C=CH), 1148 cm^{-1} (C-O); δ_H 1.21-1.59 (20H, m, 10xring CH_2), 2.93 (4H, s, 2xCH_2Ar), 7.20 (4H, m, ArH); δ_C 22.0, 25.8, 37.7 (10xring CH_2), 45.5 (2x*C*H_2Ar), 71.9 (2xCO), 126.0, 132.0, 136.9 (ArC); *m/z* 266 (M+ - $2H_2O$, 25%), 186 (22), 184 (24), 183 (79), 182 (18), 169 (10), 155 (14), 143 (15), 142 (39), 141 (100), 129 (27), 128 (25), 117 (21), 115 (23), 105 (22), 104 (13), 99 (34), 91 (25), 81 (43), 80 (20), 79 (23), 77 (15), 67 (17), 55 (37), 53 (14), 44 (16), 43 (15) (Found: C, 79.59; H, 10.22. $C_{20}H_{30}O_2$ requires: C, 79.42; H, 10.00).

1,2-Di-(2'-phenyl-2'-methyl-2'-hydroxyethyl)benzene (**2ae**):[17] 1:1 Diastereomers mixture (GLC); ν (film) 3385 (OH), 3058, 3025, 1672, 1602 (C=CH), 1067 cm^{-1} (C-O); δ_H 1.56, 1.64 (12H, 2s, 4xMe), 3.05, 3.07 (8H, 2s, 4xCH_2Ar), 6.87, 7.04, 7.33 (28H, 3m, ArH); δ_C 29.8, 29.9 (4xMe), 46.2 (4x*C*H_2Ar), 74.9, 74.95 (4xCO), 124.9, 126.2, 126.6, 126.65, 128.05, 128.1, 131.7, 131.8, 136.6, 147.9, 148.0 (ArC); *m/z* 310 (M^+ - $2H_2O$, 21%), 219 (15), 217 (11), 208 (13), 206 (19), 205 (71), 204 (28), 203 (17), 202 (13), 193 (14), 192 (12), 191 (14), 178 (13), 130 (10), 121 (27), 115 (17), 105 (32), 103 (14), 91 (39), 77 (27), 51 (13), 44 (16), 43 (100).

1,2-Di-(trimethylsilylmethyl)benzene (**2af**): ν (film) 3066, 3013, 1599, 1574 (C=CH), 857, 837 cm^{-1} (SiC); δ_H 0.02 (18H, s, 6xMe), 2.04 (4H, s, 2xCH_2), 6.95 (4H, m, ArH); δ_C -1.32 (6xMe), 24.1 (2xCH_2), 123.8, 128.9, 136.9 (ArC); *m/z* 252 (M$^+$ + 2, 1.7%), 251 (M$^+$ + 1, 2), 250 (M$^+$, 18), 162 (52), 147 (46), 74 (18), 73 (100), 45 (53), 43 (15) (Found: M$^+$, 250.1575. $C_{14}H_{26}Si_2$ requires M, 250.1573).

1,3-Di-(3'-methyl-2'-hydroxybutyl)benzene (**2ba**): 1:1 Diastereomers mixture (GLC); ν (film) 3416 (OH), 3058, 3010, 1616 (C=CH), 1043 cm^{-1} (C-O); δ_H 0.99 (24H, d, *J* = 6.7, 8xMe), 1.67 (4H, br s, 4xOH), 1.74 (4H, m, 4xC*H*Me), 2.56 (4H, dd, *J* = 13.4, 9.1, 2xC*H*$_2$Ar), 2.83 (4H, dd, *J* = 13.4, 3.4, 2xC*H*$_2$Ar), 3.57 (4H, m, 4xCHO), 7.10 (2H, s, 2xArH), 7.25 (6H, m, 6xArH); δ_C 17.4, 17.45, 18.85, 18.9 (8xMe), 33.2, 33.25 (4x*C*HMe), 40.7 (4xCH_2), 77.4, 77.45 (4xCHO), 127.3, 127.35, 128.7, 130.4, 130.5, 139.5 (ArC); *m/z* 250 (M$^+$, 1.2%), 160 (21), 145 (44), 117 (11), 106 (23), 105 (33), 104 (75), 91 (22), 79 (12), 77 (12), 73 (28), 71 (19), 69 (26), 55 (35), 45 (13), 44 (38), 43 (100) (Found: M$^+$, 250.1922. $C_{16}H_{26}O_2$ requires M, 250.1933).

1,3-Di-[(1'-hydroxycyclohexyl)methyl)benzene (**2bd**): ν (KBr) 3385 (OH), 3049, 3024, 1614 (C=CH), 974 cm^{-1} (C-O); δ_H 1.24-1.60 (20H, 2m, 10xring CH_2), 2.73 (4H, s, 2xC*H*$_2$Ar), 7.08, 7.25 (4H, 2m, ArH); δ_C 22.0, 25.7, 37.2 (10xring CH_2), 48.5 (*C*H$_2$Ar), 71.0 (CO), 127.5, 128.4, 133.25, 136.8 (ArC); *m/z* 266 (M$^+$ - 2H_2O, 32%), 186 (32), 185 (19), 184 (11), 172 (14), 171 (31), 143 (21), 141 (15), 129 (34), 128 (19), 117 (13), 115 (15), 106 (11), 105 (25), 104 (23), 99 (39), 95 (14), 94 (16), 91 (38), 81 (100), 80 (46), 79 (47), 77 (20), 67 (28), 65 (11), 55 (37), 53 (22), 44 (19), 43 (20) (Found: C, 79.59; H, 10.27. $C_{20}H_{30}O_2$ requires: C, 79.42; H, 10.00).

1,3-Di-(trimethylsilylmethyl)benzene (**2bf**): ν (film) 3053, 3009, 1602, 1582 (C=CH), 849 cm^{-1} (SiC); δ_H -0.02 (18H, s, 6xMe), 2.01 (4H, s, 2xCH_2), 6.67 (4H, m, ArH); δ_C -1.76 (6xMe), 26.95 (2xCH_2), 123.75, 127.8, 140.1 (ArC); *m/z* 252 (M$^+$ + 2, 1.4%), 251 (M$^+$ + 1, 4), 250 (M$^+$, 15), 163 (10), 162 (57), 147 (25), 74 (19), 73 (100), 59 (14), 45 (52), 43 (15) (Found: M$^+$, 250.1582. $C_{14}H_{26}Si_2$ requires M, 250.1573).

1,4-Di-(3'-methyl-2'-hydroxybutyl)benzene (**2ca**): 1:1 Diastereomers mixture (GLC); ν (film) 3351 (OH), 3086, 3048, 1606, 1570 (C=CH), 1041, 1018 cm^{-1} (C-O); δ_H 0.99 (24H, d, *J* = 6.7, 8xMe), 1.56 (2H, br s, 2xOH), 1.74 (4H, m, 4xC*H*Me), 2.57 (4H, dd, *J* = 13.4, 9.4, 2xC*H*$_2$Ar), 2.84 (4H, dd, *J* = 13.4, 3.5, 2xC*H*$_2$Ar), 3.56 (4H, m, 4xCHO), 7.17 (8H, m, ArH); δ_C 17.35, 17.4, 18.9 (8xMe), 33.1 (4x*C*HMe), 40.3 (4xCH_2), 77.4 (4xCHO), 129.5, 137.1 (ArC); *m/z* 214 (M$^+$ - 2H_2O, 0.7%), 160 (11), 117 (10), 106 (49), 105 (34), 104 (100), 91 (17), 73 (31), 57 (13), 55 (32), 43 (37) (Found: M$^+$, 250.1922. $C_{16}H_{26}O_2$ requires M, 250.1933).

1,4-Di-(2'-hydroxy-2'-phenylethyl)benzene (**2cc**): 1:1 Diastereomers mixture (GLC); ν (KBr) 3394 (OH), 3087, 3060, 1518, 1492 (C=CH), 1051 cm^{-1} (C-O); δ_H 2.99 (8H, m, 4xCH_2), 4.87 (4H, m, 4xCHO), 7.12, 7.31 (28H, 2m, ArH); δ_C 31.4, 37.5, 45.5, 45.7 (4xCH_2), 75.25, 75.3 (4xCHO), 125.9, 127.5, 127.6, 128.4, 128.6, 129.4, 129.6, 135.5, 136.3, 140.1, 143.8, 143.85 (ArC); *m/z* 300 (M$^+$ - H_2O, 1.5%), 283 (75), 282 (100), 265 (11), 203 (24), 202 (17), 195 (13), 194 (68), 193 (28), 191 (18), 189 (10), 179 (38), 178 (53), 165 (14), 141 (13), 132 (14), 115 (12), 107 (48), 106 (22), 105 (39), 104 (12), 103 (15), 91 (18), 79 (61), 78 (13), 77 (64), 51 (25), 44 (34) (Found: C, 83.64; H, 7.18. $C_{22}H_{22}O_2$ requires: C, 82.99; H, 6.96).

1,4-Di-[(1'-hydroxycyclohexyl)methyl)benzene (**2cd**): ν (KBr) 3373 (OH), 3087, 3046, 3013, 1514 (C=CH) cm^{-1}; δ_H 1.23-1.60 (20H, 2m, 10xring CH_2), 2.72 (4H, s, 2xCH_2Ar), 7.14 (4H, br s, ArH); δ_C 22.1, 25.8, 37.3 (10xring CH_2), 48.3 (2xCH_2Ar), 71.2 (2xCO), 130.4, 135.2 (ArC); *m/z* 266 (M^+ - $2H_2O$, 20%), 186 (13), 185 (21), 171 (12), 129 (18), 117 (13), 105 (12), 104 (23), 99 (16), 91 (19), 81 (24), 79 (20), 67 (13), 55 (17), 53 (10), 44 (100), 43 (18) (Found: C, 79.54; H, 10.38. $C_{20}H_{30}O_2$ requires: C, 79.42; H, 10.00).

1,4-Di-(2'-phenyl-2'-methyl-2'-hydroxyethyl)benzene (**2ce**): 1:1 Diastereomers mixture (GLC); ν (film) 3565, 3503 (OH), 3046, 3022, 1604, 1510 cm^{-1} (C=CH); δ_H 1.54 (12H, s, 4xMe), 2.81 (4H, s, 2xCH_2), 2.98, 3.10 (4H, 2d, J = 13.4, 2xCH_2), 6.89, 6.99 (8H, 2d, J = 8.0, 8xArH), 7.31 (20H, m, 20xArH); δ_C 29.5, 37.5 (4xMe), 50.3 (4xCH_2), 74.8 (4xCO), 125.6, 127.3, 128.7, 128.9, 131.2, 134.9, 140.9, 148.5 (ArC); *m/z* 310 (M^+ - $2H_2O$, 46%), 208 (17), 207 (15), 205 (23), 193 (37), 192 (22), 191 (14), 178 (14), 121 (18), 115 (29), 105 (11), 103 (40), 91 (29), 77 (34), 57 (11), 51 (13), 44 (23), 43 (100), 42 (10) (Found: C, 84.01; H, 7.58. $C_{24}H_{26}O_2$ requires: C, 83.20; H, 7.56).

1,4-Di-(trimethylsilylmethyl)benzene (**2cf**): ν (film) 3078, 3044, 1508 (C=CH), 847 cm^{-1} (SiC); δ_H -0.04 (18H, s, 6Me), 1.35 (4H, s, 2xCH_2), 6.83 (4H, br s, ArH); δ_C -1.9 (6xMe), 26.3 (2xCH_2), 127.8, 135.5 (ArC); *m/z* 252 (M^+ + 2, 3.7%), 251 (M^+ + 1, 10), 250 (M^+ , 38), 251 (10), 250 (38), 235 (15), 163 (12), 162 (74), 147 (32), 75 (12), 74 (26), 73 (100), 59 (13), 45 (64), 43 (20) (Found: $M^{+\cdot}$ 250.1576. $C_{14}H_{26}Si_2$ requires M, 250.1573).

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17. For this liquid compound was not possible to achieve the corresponding HRMS due to the absence of the M$^+$ signal.
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