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C,O-Dilithiated Diarylmethanols: Easy and Improved Preparation by Naphthalene-Catalysed Lithiation of Diaryl Ketones and Reactivity Toward Electrophiles

David Guijarro, Balbino Mancheño and Miguel Yus*

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

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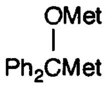
Abstract: The lithiation of different diaryl ketones 1 with an excess of lithium powder and a catalytic amount (8 mol %) of naphthalene in tetrahydrofuran at -30°C leads to the formation of the corresponding dianions of the type I, with Met=Li, which react with several electrophiles (E^+=MeI, EtBr, Pr^iCHO, PhCHO, cyclohexanone, MeCN) to give, after hydrolysis, the expected substituted diarylmethanols 2.

Introduction

Although the reaction of benzophenone with sodium to give the corresponding dianion of the type I, with Met=Na, is an old known process[1], this intermediate has found a limited interest from a synthetic point of view[2]. Recently[3], Fry and coworkers have studied the preparation and reactivity of dianions of the type I, with Met=Li, which have been obtained by direct lithiation of the corresponding diaryl ketones with lithium powder in the presence of 4,4'-di-*t*-butylbiphenyl and under ultrasonic irradiation. On the other hand, we have recently described that the use of lithium powder and a catalytic amount of naphthalene represents a very efficient and powerful procedure for the lithiation of different organic substrates[4]. In this paper we report the application of this last methodology for the preparation of dianions of the type I, with Met=Li, avoiding the use of sonication and studied their reactivity toward different electrophiles. In addition, intermediates of the type I can be consider as d^1-reagents with umpolung reactivity[5], which are, in general, of difficult access by other methodologies[6].

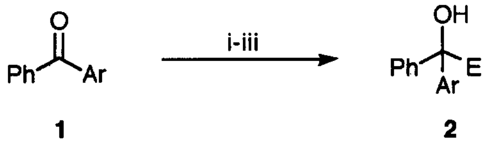


$$\begin{array}{c} OMet \\ | \\ Ph_2CMet \end{array}$$

I

Results and Discussion

The reaction of different diaryl ketones **1** with an excess of lithium powder (1:10 molar ratio) and a catalytic amount of naphthalene [1:0.16 molar ratio (8%)] in tetrahydrofuran at -30°C led to the corresponding dianions of the type **I**, with Met=Li, which by treatment with several electrophiles afforded, after hydrolysis, the expected products **2** (Scheme 1 and Table 1).



Scheme 1. *Reagents and conditions*: i, Li powder/$C_{10}H_8$ cat. (8 mol %), -30°C; ii, E^+=MeI, EtBr, Pr^iCHO, PhCHO, $(\overline{CH_2)_5C}O$, MeCN, -30 to 20°C; iii, H_2O-HCl.

Two strange results were obtained when the electrophile was methyl iodide and the starting materials were the diaryl ketones **1b** or **1e**. Thus, in the first case 2-[4-(methylphenyl)methyl]toluene **3** was isolated (51%) together with the expected reaction product **2ba** (Table 1, entry 7). If the reaction mechanism involves a SET process[3], the first intermediate **4** can be transformed into the dianion **5**, which in the form **5b** suffers annular methylation to give the corresponding lithium diarylmethanolate **6**, which undergoes final benzylic reduction to afford the product **3**. This last benzylic dehydroxylation, which is a known process carried out by dissolving metals[7], has been observed only in this case. On the other hand, the non-participation of the *o*-substituted ring in the annular methylation could be explained by steric hindrance (Chart 1).

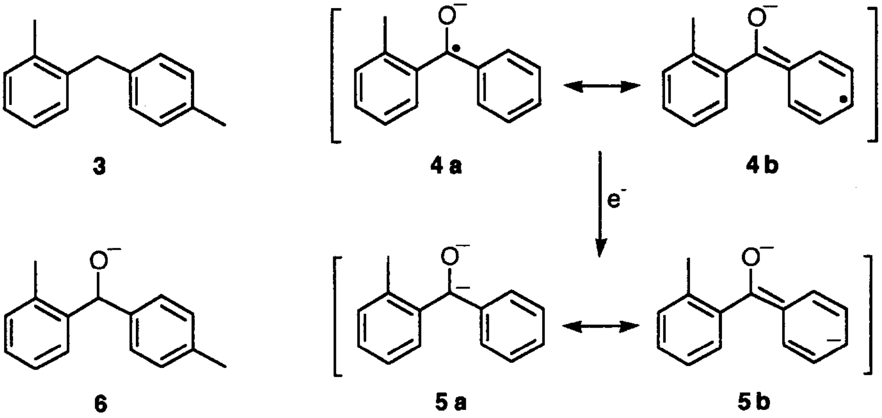
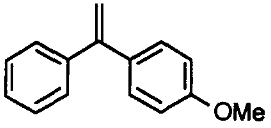


Chart 1.

Table 1. Catalysed Lithiation of Diaryl Ketones **1** and Reaction with Electrophiles E^+. Obtention of Compounds **2**, **3** and **7**.

Entry	Starting ketone no.	Starting ketone Ar	Electrophile E^+	Products[a] no.	Products[a] E	Products[a] yield (%)[b]	Products[a] R_f[c]	Products[a] m.p. (°C)
1	**1a**	Ph	MeI	**2aa**	Me	92	0.34	-[d]
2	**1a**	Ph	EtBr	**2ab**	Et	96	0.40	91-2[e]
3	**1a**	Ph	$\mathrm{Pr^iCHO}$	**2ac**	$\mathrm{Pr^iCHOH}$	95	0.27	123-4[e]
4	**1a**	Ph	PhCHO	**2ad**	PhCHOH	57	0.48	167-8[e]
5	**1a**	Ph	$\mathrm{(CH_2)_5CO}$	**2ae**	$\mathrm{(CH_2)_5COH}$	80	0.48	128[f]
6	**1a**	Ph	MeCN	**2af**	MeCO	21	0.36	-[d]
7	**1b**	$\mathrm{2\text{-}MeC_6H_4}$	MeI	**2ba**	Me	32[g]	0.38	-[d]
8	**1b**	$\mathrm{2\text{-}MeC_6H_4}$	$\mathrm{Pr^iCHO}$	**2bb**[h]	$\mathrm{Pr^iCHOH}$	61[h]	0.30[h,i]	-[d]
9	**1c**	$\mathrm{3\text{-}MeC_6H_4}$	MeI	**2ca**	Me	93	0.30	-[d]
10	**1c**	$\mathrm{3\text{-}MeC_6H_4}$	$\mathrm{Pr^iCHO}$	**2cb**[h]	$\mathrm{Pr^iCHOH}$	96[h]	0.32[h,i]	92-7[e,h]
11	**1d**	$\mathrm{4\text{-}MeC_6H_4}$	MeI	**2da**	Me	80	0.32	-[d]
12	**1d**	$\mathrm{4\text{-}MeC_6H_4}$	$\mathrm{Pr^iCHO}$	**2db**[j]	$\mathrm{Pr^iCHOH}$	77[j]	0.29[j]	140[e,j]
13	**1d**	$\mathrm{4\text{-}MeC_6H_4}$	PhCHO	**2dc**[h]	PhCHOH	50[h]	0.17[h,i]	182-7[e,h]
14	**1d**	$\mathrm{4\text{-}MeC_6H_4}$	$\mathrm{(CH_2)_5CO}$	**2dd**	$\mathrm{(CH_2)_5COH}$	86	0.41	121-2[f]
15	**1e**	$\mathrm{4\text{-}MeOC_6H_4}$	MeI	**7**	Me	43	0.50	-[d]
16	**1e**	$\mathrm{4\text{-}MeOC_6H_4}$	$\mathrm{(CH_2)_5CO}$	**2ea**	$\mathrm{(CH_2)_5COH}$	55	0.30	105-6[f]
17	**1f**	$\mathrm{2,4\text{-}Me_2C_6H_3}$	$\mathrm{(CH_2)_5CO}$	**2fa**	$\mathrm{(CH_2)_5COH}$	13	0.41	153-4[f]

[a] All products were >95% pure (GLC and 300 MHz ^{1}H NMR). [b] Isolated yields after flash chromatography (silica gel, hexane/ethyl acetate) based on the starting diaryl ketone **1**. [c] Hexane/ethyl acetate: 6/1. [d] Oil. [e] From hexane/ethyl acetate. [f] From hexane/dichloromethane. [g] Compound **3** (see text) was also obtained in 51% isolated yield; R_f=0.64 (hexane/ethyl acetate: 6/1). [h] Mixture of two diastereoisomers (*ca.* 1:1, from 300 MHz ^{1}H NMR). [i] Both diastereoisomers could not be separated under these conditions. [j] Only one diastereoisomer could be detected by GLC and ^{1}H NMR.



7

The second rare result was obtained in the reaction of the diaryl ketone **1e** with methyl iodide (Table 1, entry 15): in this case the dehydration product **7** was the only compound isolated after work-up. The facile formation of the olefin has to be attributable to the electronic effect of the methoxy group at the *para* position in one of the aromatic rings in the starting material.

Two more comments to the results described in the Table 1 are: (a) the low yields in the process with acetonitrile or starting from the diaryl ketone **1f** (Table 1, entries 6 and 17, respectively) due to undesirable by-processes; (b) the obtention of a mixture of diastereoisomers (*ca.* 1:1) in the cases in which this is possible (Table 1, entries 8, 10 and 13), except in the case of compound **2db**, in which only one diastereoisomer could be detected (Table 1, entry 12). We do not find any explanation to this last behaviour.

Finally, the presence of two aryl groups in the starting ketone seems to be necessary in order to avoid pinacolinic coupling reactions: the corresponding pinacol was the only reaction product isolated when acetophenone was used as starting material.

From the study presented in this paper we conclude that the here described methodology represents an improvement respect to the already reported procedure using sonication. We find specially interesting the "mixed pinacols" **2ac**, **2ad**, **2ae**, **2bb**, **2cb**, **2db**, **2dc**, **2dd**, **2ea** and **2fa**, which are difficult to be prepared by other procedures and impossible by crossed pinacolinic condensation.

Experimental Part

General.- For general information see reference 4d. Microanalyses were performed by the Microanalyses Service of the University of Alicante. All the starting diaryl ketones and electrophiles were commercially available (Aldrich, Fluka) and were used without further purification.

Catalytic Lithiation of Diaryl Ketones 1 and Reaction with Electrophiles. Isolation of Compounds 2, 3 and 7. General Procedure.- To a stirred green suspension of lithium powder (70 mg, 10 mmol) and naphthalene (20 mg, 0.16 mmol) in dry tetrahydrofuran (5 ml) was added a solution of the corresponding diaryl ketone **1** (1 mmol) in tetrahydrofuran (2 ml) for 10 min at -30°C under an argon atmosphere. After 30 min of additional stirring at the same temperature the corresponding electrophile E^+ (1.2 mmol) was added and the mixture was stirred for *ca.* 4 h allowing the temperature to rise to 20°C. The resulting mixture was then hydrolyzed with water (5 ml), neutralyzed with 2 M hydrochloric acid and extracted with ether (2x20 ml). The organic layer was then dried with anhydrous sodium sulfate and evaporated (15 Torr). The resulting residue was purified by flash chromatography (silica gel, hexane/ethyl acetate) yielding the products **2**, **3** or **7**. Yields, R_f values and m.p.'s are included in Table 1; analytical and spectral data, as well as literature references for known compounds follow.

1,1-Diphenylethanol (2aa)[8]: ν_{max} (film) 3400 (OH), 3050, 3020, 1595 and 1490 cm^{-1} (HC=C); δ_H 1.90 (3 H, s, Me), 2.29 (1 H, br s, OH) and 7.16-7.39 (10 H, m, ArH); δ_C 30.7 (Me), 76.1 (CO), 125.8, 126.85, 128.05 and 147.9 (ArC); *m/z* 199 (M^++1, 2%), 198 (M^+, 9), 184 (22), 183 (100), 121 (16), 105 (77), 78 (14), 77 (49), 51 (16) and 43 (31).

1,1-Diphenyl-1-propanol (**2ab**)[9]: ν_{max} (CH_2Cl_2) 3580 (OH), 3050, 1595 and 1485 cm^{-1} (HC=C); δ_H 0.86 (3 H, t, *J*=7.3, Me), 2.03 (1 H, br s, OH), 2.29 (2 H, q, *J*=7.3, CH_2), 7.15-7.21, 7.25-7.31 and 7.37-7.41 (10 H, 3m, ArH); δ_C 8.1 (Me), 34.4 (CH_2), 78.4 (CO), 126.05, 126.7, 128.05 and 146.85 (ArC); *m/z* 212 (M^+, <1%), 184 (14), 183 (100), 105 (82) and 77 (35).

3-Methyl-1,1-diphenyl-1,2-butanediol (**2ac**)[10]: ν_{max} (CH_2Cl_2) 3470 (OH), 3040, 3010, 1585 and 1480 cm^{-1} (HC=C); δ_H 0.89, 0.93 (6 H, 2 d, *J*=6.8, 2xMe), 1.71 (1 H, septet d, *J*=6.8, 2.4, C*H*Me), 1.94 (1 H, d, *J*=4.1, CHO*H*), 3.07 (1 H, s, COH), 4.45 (1 H, dd, *J*=4.1, 2.4, C*H*OH), 7.14-7.33 (6 H, m, 6xArH), 7.43 (2 H, d, *J*=7.6, 2xArH) and 7.58 (2 H, d, *J*=7.6, 2xArH); δ_C 16.2 (1xMe), 22.4 (1xMe), 28.55 (*C*HMe), 78.3 (CHO), 80.8 (CO), 125.45, 126.15, 126.55, 127.0, 128.05, 128.45, 144.2 and 146.9 (ArC); *m/z* 184 (M^+-72, 15%), 183 (7), 182 (12), 105 (100), 79 (19), 78 (31), 77 (55) and 51 (20).

1,1,2-Triphenyl-1,2-ethanediol (**2ad**)[11]: ν_{max} (CH_2Cl_2) 3550, 3440 (OH), 3050, 3015, 1590 and 1485 cm^{-1} (HC=C); δ_H 2.45 (1 H, d, *J*=3.2, CHO*H*), 3.14 (1 H, s, COH), 5.60 (1 H, d, *J*=3.2, CHO), 7.02-7.17, 7.24-7.32, 7.36-7.41 and 7.66-7.69 (15 H, 4 m, ArH); δ_C 77.95 (CHO), 80.75 (CO), 126.15, 126.7, 127.0, 127.35, 127.45, 127.6, 127.7, 128.05, 128.45, 138.75, 143.35 and 145.05 (ArC); *m/z* 183 (M^+-107, 15%), 105 (61), 78 (28) and 77 (100).

1-(Hydroxydiphenylmethyl)cyclohexanol (**2ae**)[12]: ν_{max} (CH_2Cl_2) 3560 (OH), 3040, 1590 and 1485 cm^{-1} (HC=C); δ_H 1.45-1.75 (10 H, m, 5xCH_2 ring), 1.85 (1 H, s, 1xOH), 2.79 (1 H, s, 1xOH), 7.18-7.29 (6 H, m, 6xArH) and 7.65 (4 H, d, *J*=7.2, 4xArH); δ_C 21.6 (2C), 25.45, 32.3 (2C)(5xCH_2 ring), 77.05 (CH_2*C*O), 82.4 (Ph*C*O), 126.8, 127.5, 128.35 and 144.25 (ArC); *m/z* 184 (M^+-98, 28%), 183 (10), 107 (12), 106 (10), 105 (98), 79 (49), 78 (37), 77 (100), 63 (10), 52 (13), 51 (68) and 50 (21).

1-Hydroxy-1,1-diphenylpropanone (**2af**)[13]: ν_{max} (film) 3410 (OH), 3050, 3020, 1590, 1485 (HC=C) and 1700 cm^{-1} (CO); δ_H 2.26 (3 H, s, Me), 4.83 (1 H, s, OH) and 7.36 (10 H, s, ArH); δ_C 26.15 (Me), 85.7 (COH), 128.0, 128.15, 128.4, 141.25 (ArC) and 208.6 (C=O); *m/z* 184 (M^+-42, 5%), 183 (39), 105 (100), 77 (84), 51 (17) and 43 (14).

1-(2-Methylphenyl)-1-phenylethanol (**2ba**)[14]: ν_{max} (film) 3540, 3440 (OH), 3050, 3010, 1595 and 1480 cm^{-1} (HC=C); δ_H 1.92 (3 H, s, MeCO), 1.98 (3 H, s, *Me*Ph), 2.12 (1 H, s, OH), 7.08-7.11, 7.19-7.32 and 7.67-7.70 (1 H, 7 H and 1 H, respectively, 3 m, ArH); δ_C 21.35 (*Me*CO), 32.1 (*Me*Ph), 76.8 (CO), 125.25, 125.35, 125.95, 126.55, 127.65, 128.1, 132.4, 137.15, 144.55 and 147.95 (ArC); *m/z* 213 (M^++1, 2%), 212 (M^+, 9), 198 (15), 197 (100), 194 (21), 179 (31), 178 (11), 121 (27), 119 (45), 105 (90), 92 (15), 91 (50), 89 (11), 77 (47), 65 (17), 51 (12) and 43 (57).

3-Methyl-1-(2-methylphenyl)-1-phenyl-1,2-butanediol (**2bb**): ν_{max} (film) 3460 (OH), 3040, 3010, 1590 and 1485 cm^{-1} (HC=C); δ_H 0.84 (6 H, d, *J*=7.0, 2x*Me*CH), 0.95, 0.98 (6 H, 2 d, *J*=6.9, 2x*Me*CH), 1.47 (1 H, septet d, *J*=6.9, 2.2, 1xC*H*Me), 1.56 (1 H, septet d, *J*=6.9, 1.8, 1xC*H*Me), 1.89, 2.10 (6 H, 2 s, 2x*Me*Ph), 2.24 (1 H, d, *J*=4.8, 1xCHO*H*), 2.43 (1 H, d, *J*=7.8, 1xCHO*H*), 2.75, 3.12 (2 H, 2 s, COH), 4.39 (1 H, dd, *J*=4.8, 2.2, 1xC*H*OH), 4.67 (1 H, dd, *J*=7.8, 1.8, 1xC*H*OH), 7.00 (1 H, d, *J*=7.9, 1xArH), 7.08 (2 H, dd, *J*=7.4, 1.5, 2xArH), 7.11-7.33 (10 H, m, 10xArH), 7.44-7.47 (3 H, m, 3xArH), 7.64 (1 H, d, *J*=7.7, 1xArH) and 7.99 (1 H, dd, *J*=7.9, 1.4, 1xArH); δ_C 15.05, 15.9 (1x*Me*CH), 21.55, 21.65 (*Me*Ph), 22.25, 22.6 (1x*Me*CH), 28.15, 29.5 (*C*HMe), 75.8, 78.1 (CHO), 81.25, 81.85 (CO), 125.15, 125.4, 125.7, 126.05, 126.15, 126.45, 127.25, 127.3, 127.35, 127.5, 127.75, 128.3, 131.85, 133.5, 135.1, 139.25, 142.9, 143.25, 143.55 and 146.2 (ArC); *m/z* 270 (M^+, <1%), 198 (44), 197 (100), 119 (28), 105 (67), 91 (25) and 77 (23).

1-(3-Methylphenyl)-1-phenylethanol (**2ca**)[15]: ν_{max} (film) 3420 (OH), 3040, 3010, 1595 and 1480 cm^{-1} (HC=C); δ_H 1.92 (3 H, s, MeCO), 2.26 (1 H, br s, OH), 2.31 (3 H, s, *Me*Ph), 7.03-7.06, 7.17-7.24, 7.27-7.32 and 7.38-7.42 (1 H, 4 H, 2 H and 2 H, respectively, 4 m, ArH); δ_C 21.55 (*Me*CO), 30.8 (*Me*Ph), 76.1 (CO), 122.9, 125.75, 126.45, 126.8, 127.65, 128.0, 128.05, 137.7, 147.9 and 148.05 (ArC); *m/z* 213 (M^++1, 3%), 212 (M^+, 15), 198 (16), 197 (100), 119 (30), 105 (95), 91 (36), 77 (29), 65 (13) and 43 (42).

3-Methyl-1-(3-methylphenyl)-1-phenyl-1,2-butanediol (**2cb**): ν_{max} (Nujol) 3470 (OH), 3060, 1590 and 1495 cm^{-1} (HC=C); δ_H 0.88-0.95 (12 H, m, 4x*Me*CH), 1.65-1.78 (2 H, m, 2xC*H*Me), 1.90-1.92 (2 H, m, 2xCHO*H*), 2.30, 2.32 (6 H, 2 s, 2x*Me*Ph), 3.02, 3.03 (2 H, 2 s, 2xCOH), 4.45 (2 H, dd, *J*=4.6, 2.5, 2xC*H*OH), 6.97-7.04, 7.13-7.34 and 7.36-7.60 (2 H, 14 H and 2 H, respectively, 3 m, ArH); δ_C 16.25 (1x*Me*CH), 21.65 (*Me*Ph), 22.45 (1x*Me*CH), 28.55, 28.55 (*C*HMe), 78.3, 78.35 (CHO), 80.8 (CO), 122.6, 123.0, 125.4, 126.0, 126.15, 126.5, 126.9, 126.95, 127.35, 127.85, 127.95, 128.05, 128.35, 128.45, 137.65, 138.2, 144.15, 144.25, 146.85 and 146.95 (ArC); *m/z* 198 (M^+-72, 73%), 197 (95), 165 (13), 119 (28), 105 (100), 91 (35), 77 (50) and 65 (11). Anal. calcd for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 80.0; H, 8.3.

1-(4-Methylphenyl)-1-phenylethanol (**2da**)[15]: ν_{max} (film) 3540, 3420 (OH), 3040, 3010, 1590 and 1480 cm^{-1} (HC=C); δ_H 1.90 (3 H, s, MeCO), 2.26 (1 H, s, OH), 2.30 (3H, s, *Me*Ph), 7.08-7.11, 7.20-7.31 and 7.37-7.40 (2 H, 5 H and 2 H, respectively, 3 m, ArH); δ_C 20.95 (*Me*CO), 30.8 (*Me*Ph), 76.0 (CO), 125.75, 126.75, 128.05, 128.8, 136.5, 145.1 and 148.15 (ArC); *m/z* 213 (M^++1, 2%), 212 (M^+, 9), 198 (12), 197 (100), 135 (11), 119 (34), 105 (35), 91 (23), 77 (28), 65 (12) and 43 (34).

3-Methyl-1-(4-methylphenyl)-1-phenyl-1,2-butanediol (**2db**): ν_{max} (Nujol) 3520, 3460 (OH), 3065, 3040 and 1590 cm^{-1} (HC=C); δ_H 0.89, 0.94 (6 H, 2 d, *J*=6.9, 2x*Me*CH), 1.69 (1 H, septet d, *J*=6.9, 2.5, C*H*Me), 1.90 (1 H, d, *J*=4.9, CHO*H*), 2.29 (3 H, s, *Me*Ph), 2.97 (1 H, s, COH), 4.43 (1 H, dd, *J*=4.9, 2.5, C*H*OH), 7.11-7.19, 7.23-7.29 and 7.40-7.48 (9 H, 3 m, ArH); δ_C 16.2 (1x*Me*CH), 20.9 (*Me*Ph), 22.45 (1x*Me*CH), 28.6 (*C*HMe), 78.35 (CHO), 80.75 (CO), 125.45, 126.1, 126.5, 128.05, 129.2, 136.7, 144.0 and 144.45 (ArC); *m/z* 198 (M^+-72, 25%), 197 (60), 165 (10), 119 (37), 105 (100), 91 (33), 77 (48), 65 (10) and 55 (12). Anal. calcd for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 80.9; H, 8.4.

1-(4-Methylphenyl)-1,2-diphenyl-1,2-ethanediol (**2dc**)[16]: ν_{max} (CH_2Cl_2) 3510, 3440 (OH), 3040, 3010, 1590 and 1480 cm^{-1} (HC=C); δ_H 2.20, 2.34 (6 H, 2 s, 2xMe), 2.48, 2.51 (2 H, 2 d, *J*=3.0, 2xCHO*H*), 3.09, 3.12 (2 H, 2 s, 2xCOH), 6.89-7.22 (20 H, m, ArH), 7.27 (2 H, t, *J*=7.3, ArH), 7.36 (2 H, t, *J*=7.5, ArH), 7.54 (2 H, d, *J*=8.1, ArH) and 7.63 (2 H, d, *J*=7.5, ArH); δ_C 20.9 (1xMe), 21.0 (1xMe), 77.95 (2xCHO), 80.65 (2xCO), 126.1, 126.15, 126.6, 126.85, 126.9, 127.2, 127.35, 127.4, 127.55, 127.6, 128.05, 128.15, 128.3, 128.35, 129.15, 136.25, 137.0, 138.8, 138.9, 140.5, 142.15, 143.5 and 145.15 (ArC); *m/z* 195 (M^+-109, 1%), 184 (44), 183 (81), 165 (12), 105 (100) and 77 (63).

1-[Hydroxy(4-methylphenyl)phenylmethyl]cyclohexanol (**2dd**): ν_{max} (CH_2Cl_2) 3520 (OH), 3050, 3010, 1595 and 1485 cm^{-1} (HC=C); δ_H 1.50-1.73 (10 H, m, 5xCH_2 ring), 1.85 (1 H, s, CH_2COH), 2.30 (3 H, s, Me), 2.74 (1 H, s, PhCO*H*), 7.08 (2 H, d, *J*=8.1, 2xArH), 7.17-7.29 (3 H, m, 3xArH), 7.53 (2 H, d, *J*=8.2, 2xArH) and 7.64 (2 H, d, *J*=7.2, 2xArH); δ_C 20.85 (Me), 21.6 (2C), 25.45, 32.25, 32.3 (5xCH_2 ring), 77.05 (CH_2*C*O), 82.3 (Ph*C*O), 126.7, 127.45, 128.2, 128.25, 128.3, 136.4, 141.35 and 144.4 (ArC); *m/z* 198 (M^+-98, 69%), 197 (34), 183 (31), 119 (58), 106 (10), 105 (100), 99 (67), 92 (17), 91 (55), 81 (80), 79 (20), 77 (69), 65 (20), 57 (13), 55 (32), 53 (10), 43 (17) and 41 (22). Anal. calcd for $C_{20}H_{24}O_2\cdot 1/4\ H_2O$: C, 79.83; H, 8.20. Found: C, 80.2; H, 8.1.

1-[Hydroxy(4-methoxyphenyl)phenylmethyl]cyclohexanol (**2ea**): ν_{max} (CH_2Cl_2) 3500 (OH), 3040, 1600 and 1495 cm^{-1} (HC=H); δ_H 1.40-1.78 (10 H, m, 5xCH_2 ring), 1.89 (1 H, s, CH_2COH), 2.73 (1 H, s, PhCO*H*), 3.75 (3 H, s, Me), 6.79-6.82, 7.21-7.30 and 7.56-7.65 (2 H, 3 H and 4 H, respectively, 3 m, ArH); δ_C 21.6 (2C), 25.45, 32.25, 32.35 (5xCH_2 ring), 55.1 (Me), 77.1 (CH_2*C*O), 82.2 (Ph*C*O), 112.8, 126.7, 127.45, 128.25, 129.65, 136.55, 144.45 and 158.25 (ArC); *m/z* 214 (M^+-98, 78%), 213 (94), 135 (50), 109 (21), 105 (100), 99 (27), 92 (14), 81 (26) and 77 (42). Anal. calcd for $C_{20}H_{24}O_3\cdot 1/4\ H_2O$: C, 75.80; H, 7.79. Found: C, 76.2; H, 7.7.

1-[(2,4-Dimethylphenyl)hydroxyphenylmethyl]cyclohexanol (**2fa**): ν_{max} (CH_2Cl_2) 3520, 3460 (OH), 3040, 3010, 1600 and 1480 cm^{-1} (HC=C); δ_H 1.10 (1 H, br s, CH_2COH), 1.48-1.80 (10 H, m, 5xCH_2 ring), 1.91, 2.28 (6 H, 2 s, 2xMe), 2.71 (1 H, br s, PhCO*H*), 6.89 (1 H, s, 1xArH), 6.97 (1 H, d, *J*=8.2, 1xArH), 7.20-7.27 (3 H, m, 3xArH), 7.36 (2 H, d, *J*=6.8, 2xArH) and 8.12 (1 H, br s, 1xArH); δ_C 20.7 (1xMe), 21.6, 21.85 (2C), 25.5 (2C)(5xCH_2 ring), 22.4 (1xMe), 77.55 (CH_2*C*O), 83.1 (Ph*C*O), 124.7, 126.45, 127.15, 128.2, 129.35, 134.05, 136.7, 138.75, 139.55 and 143.7 (ArC); *m/z* 213 (M^+-97, 15%), 212 (86), 211 (37), 197 (26), 178 (10), 133 (32), 107 (11), 106 (14), 105 (100), 99 (25), 81 (25), 79 (13) and 77 (49). Anal. calcd for $C_{21}H_{26}O_2\cdot 1/4\ H_2O$: C, 80.09; H, 8.48. Found: C, 79.8; H, 8.3.

2-[4-(Methylphenyl)methyl]toluene (**3**)[17]: ν_{max} (film) 3040, 3010, 1600 and 1490 cm^{-1} (HC=C); δ_H 2.23, 2.30 (6 H, 2 s, 2xMe), 3.93 (2 H, s, CH_2) and 6.99-7.20 (8H, m, ArH); δ_C 19.65 (1xMe), 20.95 (1xMe), 39.0 (CH_2), 125.95, 126.3, 128.6, 129.05, 129.85, 130.2, 135.35, 136.55, 137.25 and 139.15 (ArC); *m/z* 198 (M^++2, 1%), 197 (M^++1, 14), 196 (M^+, 73), 182 (17), 181 (100), 179 (14), 178 (13), 166 (34), 165 (30), 105 (17), 104 (72), 78 (10) and 77 (11).

1-(4-Methoxyphenyl)-1-phenylethylene (**7**)[14]: ν_{max} (film) 3060, 3030, 1645, 1595 and 1490 cm^{-1} (HC=C); δ_H 3.79 (3 H, s, Me), 5.34, 5.38 (2 H, 2 d, *J*=1.2, 2xCH_2), 6.85 (2 H, d, *J*=8.8, 2xArH) and 7.25-7.34 (7 H, m, ArH); δ_C 55.2 (Me), 112.9 (CH_2), 113.5, 127.6, 128.1, 128.25, 129.35, 133.95, 141.8, 159.3 (ArC) and 149.5 (*C*=CH_2); *m/z* 212 (M^++2, 1%), 211 (M^++1, 16), 210 (M^+, 100), 209 (11), 195 (52), 179 (13), 178 (15), 167 (16), 166 (16), 165 (30), 152 (21), 89 (15), 77 (13), 63 (11) and 51 (10).

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