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Direct Transformation of Dialkyl Sulfates into Alkyllithium Reagents by a Naphthalene-Catalysed Lithiation

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Abstract: **The lithiation of primary and secondary dialkyl sulfates with an excess of lithium powder in the presence of a catalytic amount of naphthalene (4 mol %) in THF at -78°C leads to the corresponding alkyllithium reagents (1:2 molar ratio) which react with different electrophiles, mainly carbonyl compounds, to yield after hydrolysis, the expected coupling products. This methodology represents an indirect way to transform alcohols into organolithium compounds through the corresponding dialkyl sulfates. When the same procedure is applied to five or six member cyclic sulfates (derived from 1,2- or 1,3-diols) only products arising from a β- or γ-elimination process (giving olefins or cyclopropanes), respectively, are obtained.**

INTRODUCTION

Organolithium compounds are powerful intermediates in organic synthesis due to their great reactivity toward electrophilic reagents, above all in carbon-carbon bond formation processes, in general under mild reaction conditions[1]. Although methods such as mercury- or tin-lithium transmetallation, reductive cleavage of ethers and thioethers or the Shapiro reaction can be eventually used for preparing organolithium reagents, the most common procedures for these important intermediates are the halogen- and hydrogen-lithium exchanges[1]. From these last two possibilities are alkyl bromides or chlorides the most general starting materials for alkyllitium since the deprotonation requires some acidity in the carbon-hydrogen bond, which is going to be lithiated. However, the presence of lithium halide in the solution of the organolithium compounds prepared from the corresponding alkyl halides represents in some cases changes in the reactivity of the organometallic reagent. For this reason it is interesting to develop methodologies, which permit the preparation of halogen-free organolithium compounds. With this purpose in mind, we found recently[2] that allylic and benzylic mesylates can be transformed into the corresponding organolithium derivatives by a naphthalene-catalysed lithiation with lithium powder[3,4]. However, this method does not work for alkylic systems. In this paper we report the conversion of dialkyl sulfates into alkyllithium compounds following the above described methodology. If one consider that the starting dialkyl sulfates are easily accessible from the corresponding alcohols (see *infra*) this route represents an indirect and new transformation of alcohols into alkyllithium reagents[5].

RESULTS AND DISCUSSION

The reaction of different primary and secondary dialkyl sulfates **1** with an excess of lithium powder (1:14 molar ratio) and a catalytic amount of naphthalene (1:0.16 molar ratio; 4 mol %) in THF at -78°C led to a solution of the corresponding organolithium reagent **2**, which reacted with several electrophiles, mainly carbonyl compounds, to yield, after hydrolysis with aqueous hydrochloric acid, the expected products **3** (Scheme 1 and Table 1). In the absence of the catalyst the reaction took place with much poorer yields (Table 1, footnote c). On the other hand, it is important to keep the temperature at -78°C in order to avoid secondary processes, mainly coupling reactions between the obtained organolithium compound and the starting dialkyl sulfate; as an example, the above described reaction using diethyl sulfate **1b** as the starting material and benzaldehyde as electrophile carried out at room temperature afforded the corresponding product **3ba** in only 14% yield (compare to Table 1, entry 4).

$$\underset{\mathbf{1}}{(RO)_2SO_2} \xrightarrow{i} \underset{\mathbf{2}}{2\,RLi} \xrightarrow{ii,iii} \underset{\mathbf{3}}{2\,RE}$$

Scheme 1. *Reagents and conditions*: i, Li powder (excess), $C_{10}H_8$ cat. (4 mol %), THF, -78°C; ii, E^+=Pr^iCHO, PhCHO, Et_2CO, Pr^nCOMe, $(CH_2)_5CO$, Ph_2CO, $(PhCH_2S)_2$, -78 to 20°C; iii, H_2O-HCl.

In general, the reaction works nicely except in the case of enolizable carbonyl compounds such as isobutanal, 3-pentanone or cyclohexanone, in which the yields are considerably lower (Table 1, entries 5, 8, 10, 12 and 15): with these substrates the organolithium intermediate **2** abstracts mainly the α-proton of the carbonyl compound instead acting as a nucleophile, under the tried reaction conditions.

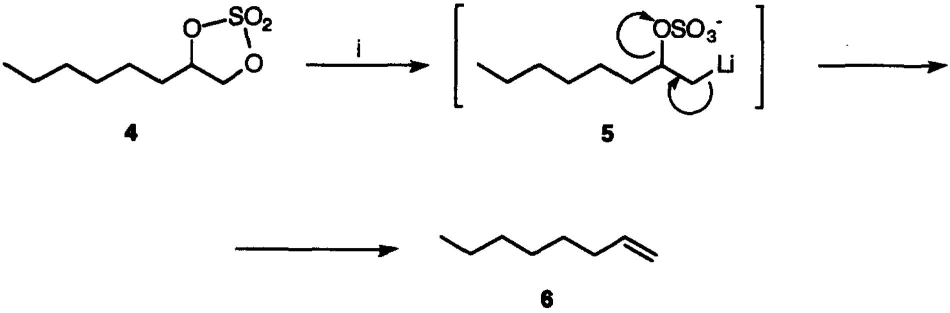
The here described method is general for primary (Table 1, entries 1-6 and 10-13) and secondary (Table 1, entries 7-9 and 14-17) dialkyl sulfates. We could not obtain tertiary dialkyl sulfates by the conventional methods, so we were not able to test the above mentioned methodology with these starting materials. In general, starting dialkyl sulfates were prepared from the corresponding alcohols following the Sharpless procedure[6].

With the above results in hand we tried to prepare dilithio compounds starting from cyclic sulfates[7]. Thus, the lithiation of the sulfate **4**, derived from 1,2-octanediol, under the above described reaction conditions, followed by treatment with benzaldehyde or cyclohexanone, yielded 1-octene **6** as the only reaction product detected in GLC (*ca.* 40% yield). In this case, the first formed monoorganolithium derivative (presummably the most stable primary carbanion **5**), which is a β-functionalised organolithium compound[8,9] (d^2 reagent following Seebach's nomenclature[10]), suffers spontaneous β-elimination [11] to give the obtained olefin[12] (Scheme 2).

Table 1. Transformation of Dialkyl Sulfates **1** into Organolithium Compounds **2** and Reaction with Electrophiles E^+. Preparation of Products **3**.

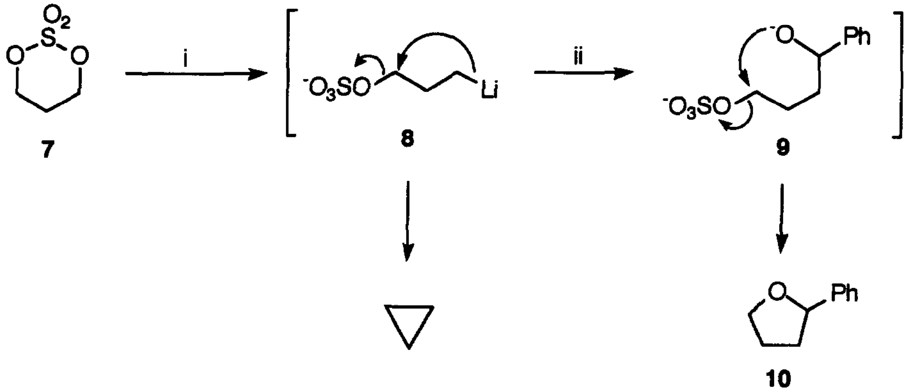
	Starting sulfate		Electrophile	Product[a]		
Entry	No.	R	E^+	No.	E	Yield (%)[b]
1	**1a**	Me	PhCHO	**3aa**	PhCHOH	52[c]
2	**1a**	Me	Ph_2CO	**3ab**	Ph_2COH	99
3	**1a**	Me	$(PhCH_2S)_2$	**3ac**	$PhCH_2S$	64
4	**1b**	Et	PhCHO	**3ba**	PhCHOH	73
5	**1b**	Et	$\overline{(CH_2)_5C}O$	**3bb**	$\overline{(CH_2)_5C}OH$	41
6	**1b**	Et	Ph_2CO	**3bc**	Ph_2COH	70
7	**1c**	*i*-Pr	PhCHO	**3ca**	PhCHOH	40
8	**1c**	*i*-Pr	$\overline{(CH_2)_5C}O$	**3cb**	$\overline{(CH_2)_5C}OH$	20
9	**1c**	*i*-Pr	Ph_2CO	**3cc**	Ph_2COH	55
10	**1d**	*n*-Bu	*i*-PrCHO	**3da**	*i*-PrCHOH	25
11	**1d**	*n*-Bu	PhCHO	**3db**	PhCHOH	55
12	**1d**	*n*-Bu	Et_2CO	**3dc**	Et_2COH	15
13	**1d**	*n*-Bu	Ph_2CO	**3dd**	Ph_2COH	33
14	**1e**	n-$C_6H_{13}CHMe$	PhCHO	**3ea**	PhCHOH	31[d]
15	**1e**	n-$C_6H_{13}CHMe$	Et_2CO	**3eb**	Et_2COH	23
16	**1e**	n-$C_6H_{13}CHMe$	*n*-PrCOMe	**3ec**	*n*-PrC(Me)OH	18[e]
17	**1e**	n-$C_6H_{13}CHMe$	Ph_2CO	**3ed**	Ph_2COH	48

[a] All products **3** were >95% pure (GLC and 300 MHz ^1H NMR). [b] Isolated yield after flash chromatography (silica gel, hexane/ethyl acetate) based on the starting dialkyl sulfate **1** and corresponding to the stoichiometry **1**→2 **2**. [c] 28% isolated yield in absence of naphthalene under the same reaction conditions. [d] 1.2:1 diastereoisomers mixture (from 300 MHz ^1H NMR). [e] 1:1 diastereoisomers mixture (from 300 MHz ^1H NMR).



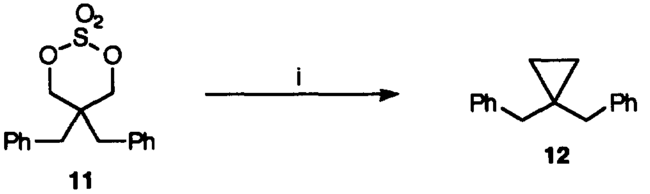
Scheme 2. ***Reagents and conditions***: i, Li powder (excess), $C_{10}H_8$ cat. (4 mol %), THF, -78°C.

We then tried to lithiate the cyclic sulfate **7** derived from 1,3-propanediol under the reaction conditions indicated for **1** and using benzaldehyde as electrophile. In this case the only reaction product isolated was the substituted tetrahydrofuran **10** in 7% isolated yield, after flash chromatography. We suppose that the main reaction product is cyclopropane resulting from a γ-elimination[13] of sulfate from the first formed γ-functionalised organolithium intermediate **8**[8,14] (*d^3* reagent following Seebach's nomenclature[10]). A small amount (<10%) of the dianion **8** survives the reaction conditions and reacts with the carbonyl compound used as electrophile giving another dianion **9**, which finally undergoes an easy intramolecular S_N-type reaction affording the corresponding 2-phenyltetrahydrofuran **10** in poor isolated yields (Scheme 3).



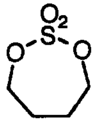
Scheme 3. *Reagents and conditions*: i, Li powder (excess), $C_{10}H_8$ cat. (4 mol %), THF, -78°C; ii, PhCHO, -78 to 20°C.

In order to demonstrate that the main process in Scheme 3 is the γ-elimination we prepared the dibenzylic sulfate **11** (by dibenzylation of diethyl malonate followed by reduction with lithium aluminium hydride and final cyclization to the corresponding sulfate). Its lithiation under the standard reaction conditions yielded the expected 1,1-dibenzylcyclopropane **12** in 75% isolated yield (Scheme 4).



Scheme 4. ***Reagents and conditions***: i, Li powder (excess), $C_{10}H_8$ cat. (4 mol %), THF, -78 to 20°C.

Finally, we prepared also the cyclic sulfate **13** derived from 1,4-butanediol and submited it to lithiation as above in order to study the posible preparation of δ-functionalised organolithium compounds of the type **14**[8,15] and their δ-elimination. In this case the reaction failed: although the starting material disappeared no reaction products could be isolated after the final treatment with benzaldehyde or cyclohexanone.



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From the results described in this paper we conclude that the naphthalene-catalysed lithiation of primary and secondary dialkyl sulfates is an adequate new route for halide-free organolithium compounds. The methodology is not applicable to cyclic sulfates, in order to prepare dilithio compounds, due to the great tendency of the monolithiated intermediates to undergo β- or γ-elimination yielding olefins or cyclopropanes, when starting from five or six member ring substrates, respectively.

EXPERIMENTAL SECTION

General.- M.p.s are uncorrected and were measured on a Reichert thermovar apparatus. IR spectra were determined with a Pye Unicam SP3-200 spectrometer. ^1H and ^{13}C NMR spectra were recorded in a Bruker AC-300 (unless otherwise stated: Varian EM-360L at 60 MHz) 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 Hewlett Packard EM/CG HP-5988A spectrometer. The purity of volatile distilled products and the chromatographic analyses (GLC) were determined with Hewlett Packard HP-5890 instrument equiped with a flame ionization detector (FID) and a 12 m HP-1 capillary column (0,2 mm diam., 0.33 μm film thickness), using 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); retention times (t_r) are given under these conditions. 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 a mixture of hexane/ethyl acetate as eluant; R_f values are given under these conditions. Solvents were dried by standard procedures[16]. Electrophiles, alcohols and diols precursors of the corresponding sulfates, dimethyl and diethyl sulfates and the other commercially available (Aldrich, Fluka) chemicals were of the best grade and used as delivered.

Preparation of Starting Sulfates **1**, **4**, **7**, **11** and **13**. *General Procedure.*- To a solution of the corresponding alcohol (10 mmol) in carbon tetrachloride (5 ml) was added thionyl chloride (0.45 ml, 6 mmol) and the resulting solution was refluxed for 45 min. The solution was then cooled at 0°C and diluted with acetonitrile (5 ml). To the mixture was added ruthenium trichloride trihydrate (1 mg, 0.004 mmol), sodium periodate (2.0 g, 7.5 mmol) and water (7.5 ml), and it was stirred at room temperature for 2 h. The mixture was then extracted with ether (2x20 ml). The organic layer was washed with water, saturated aqueous sodium hydrogen carbonate and brine. After drying over anhydrous sodium sulfate the solution was filtered through a small pad of silica gel to remove the brown color. The filtrate was evaporated *in vacuo* (15 torr) to yield the pure sulfates **1c**-**1e**. Sulfates **4**, **7**, **11** and **13** were prepared following the Sharpless procedure[6]. [CAUTION: dialkyl sulfates are harmful chemicals and should be handled with special precautions].

Diisopropylsulfate (**1c**)[17]: t_r 6.63 min; ν_{max} (film) 1370 and 1190 cm^{-1} (SO_2); δ_H 1.38 (12 H, d, J=6.3, 4xMe) and 4.84 (2 H, septet, J=6.3, 2xCH); δ_C 22.4 (4 C, 4xMe) and 79.8 (2 C, 2xCO); *m/z* 167 (M^+-15, 6%), 87 (17), 45 (100), 43 (94), 42 (11) and 41 (22).

*Di-*n*-butylsulfate* (**1d**)[18]: t_r 10.06 min; ν_{max} (film) 1395 and 1190 cm^{-1} (SO_2); δ_H (60 MHz) 0.95 (6 H, t, J=6.5, 2xMe), 1.1-2.0 (8 H, m, 4xMeCH_2CH_2) and 4.2 (4 H, t, J=6.0, 2xCH$_2$O).

Bis(2-octyl)sulfate (**1e**): R_f 0.55 (hexane/ethyl acetate: 6/1); ν_{max} (film) 1375 and 1185 cm^{-1} (SO_2); δ_H 0.89 (6 H, t, J=6.7, 2x*Me*CH$_2$), 1.20-1.41 [16 H, m, 8x(CH_2)$_4$Me], 1.42 (6 H, d, J=6.3, 2x*Me*CH), 1.49-1.80 (4 H, m, 2xCH_2CH) and 4.76 (2 H, sextet, J=6.3, 2xCH); δ_C 13.9 (2 C), 20.3 (2 C)(4xMe), 22.45 (2 C), 24.75 (2C), 28.85 (2 C), 31.55 (2 C), 36.3 (2 C)(10xCH$_2$) and 83.35 (2 C, 2xCO); *m/z* 265 (M^+-57, <1%), 157 (24), 113 (64), 112 (98), 97 (13), 84 (25), 83 (35), 82 (10), 71 (61), 70 (77), 69 (49), 67 (10), 57 (55), 56 (57), 55 (100), 53 (11), 45 (11), 43 (39), 42 (25) and 41 (71).

*4-(*n*-Hexyl)-1,3,2-dioxathiolane-2,2-dioxide* (**4**): R_f 0.23 (hexane/ethyl acetate: 6/1); t_r 11.86 min; ν_{max} (film) 1375 and 1200 cm^{-1} (SO_2); δ_H 0.89 (3 H, t, J=6.7, Me), 1.20-1.55, 1.72-1.81, 1.87-2.00 [8 H, 1 H and 1 H, respectively, 3 m, 5xMe(CH_2)$_5$], 4.35 (1 H, t, J=8.4, 1xCH$_2$O), 4.73 (1 H, dd, J=8.7, 6.0, 1xCH$_2$O) and 4.94-5.03 (1 H, m, CHO); δ_C 13.85 (Me), 22.3, 24.4, 28.55, 31.3, 32.05, 72.9 (6xCH$_2$) and 83.15 (CHO); *m/z* 208 (M^+, <1%), 123 (10), 95 (20), 82 (28), 81 (99), 79 (13), 70 (100), 69 (53), 68 (62), 67 (66), 57 (21), 56 (20), 55 (64), 54 (41), 43 (51), 42 (28) and 41 (64).

1,3,2-Dioxathiane-2,2-dioxide (**7**)[7]: t_r 7.49 min; ν_{max} (film) 1380 and 1195 cm^{-1} (SO_2); δ_H (60 MHz) 2.1 (2 H, quint, J=6.0, CH_2CH$_2$O) and 4.65 (4 H, t, J=6.0, 2xCH$_2$O).

5,5-Dibenzyl-1,3,2-dioxathiane-2,2-dioxide (**11**): R_f 0.27 (hexane/ethyl acetate: 4/1); t_r 18.71 min; m.p. 109-111°C (diethyl ether); ν_{max} (CH_2Cl_2) 3050, 3020, 1595, 1490 (HC=C), 1395 and 1195 cm^{-1} (SO_2); δ_H 2.85 (4 H, s, 2xC*H*$_2$Ph), 4.40 (4 H, s, 2xCH_2O) and 7.14-7.38 (10 H, m, ArH); δ_C 37.2 (*C*CH_2Ph), 37.7 (2 C, 2x*C*H_2Ph), 78.1 (2 C, 2xCH_2O), 127.45, 128.8, 130.5 and 134.25 (ArC); *m/z* 318 (M^+, 2%), 130 (18), 129 (60), 115 (13), 91 (100) and 65 (16).

1,3,2-Dioxathiepane-2,2-dioxide (**13**)[7]: R_f 0.23 (hexane/ethyl acetate: 2/1); t_r 8.98 min; m.p. 42-43°C (hexane/diethyl ether); ν_{max} (CH_2Cl_2) 1375 and 1200 cm^{-1} (SO_2); δ_H 1.95-2.03 (4 H, m, 2xC*H*$_2$$CH_2$O) and 4.31-4.38 (4 H, m, 2xCH_2O); δ_C 27.1 (2 C, 2x*C*$H_2$$CH_2$O) and 71.95 (2 C, 2xCO); *m/z* 152 (M^+, <1%), 123 (34), 91 (26), 71 (81), 55 (18), 54 (75), 43 (20), 42 (100) and 41 (77).

Catalytic Lithiation of Sulfates **1**, **4**, **7**, **11** *and* **13** *and Reaction with Electrophiles. Isolation of Compounds* **3**, **10** *and* **12**. *General Procedure*.- A suspension of lithium powder (100 mg, 14 mmol) and naphthalene (20 mg, 0.16 mmol) in tetrahydrofuran (5 ml) was stirred under argon until a dark green colour appeared and then it was cooled at -78°C. To the resulting suspension was added a solution of the corresponding sulfate (1 mmol)[CAUTION: see above] in tetrahydrofuran (2 ml) for 15 min. After 1 h of additional stirring at -78°C the corresponding electrophile (2 mmol) was added and the mixture was stirred for *ca.* 5 h allowing the temperature to rise to 20°C. The resulting mixture was then hydrolyzed with water (5 ml), neutralyzed with 2 N hydrochloric acid and extracted with diethyl ether (2x20 ml). The organic layer was dried over anhydrous sodium sulfate and the solvents were evaporated *in vacuo* (15 torr). The resulting residue was purified by flash chromatography (silica gel, hexane/ethyl acetate) affording the corresponding products **3**, **10** and **12**.

1-Phenylethanol (**3aa**)[19]: R_f 0.34 (hexane/ethyl acetate: 4/1); t_r 6.44 min; ν_{max} (film) 3350 (OH), 3050, 3020, 1595 and 1485 cm^{-1} (ArH); δ_H 1.46 (3 H, d, *J*=6.5, Me), 2.28 (1 H, br s, OH), 4.84 (1 H, q, *J*=6.5, CHO) and 7.23-7.38 (5 H, m, ArH); δ_C 25.05 (Me), 70.25 (CO), 125.3, 127.35, 128.4 and 145.75 (ArC); *m/z* 122 (M^+, 53%), 107 (100), 105 (11), 79 (90), 78 (18), 77 (57), 51 (17) and 43 (14).

1,1-Diphenylethanol (**3ab**)[20]: R_f 0.34 (hexane/ethyl acetate: 9/1); t_r 12.27 min; 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).

Benzyl Methyl Sulfide (**3ac**)[21]: R_f 0.25 (hexane); t_r 7.70 min; ν_{max} (film) 3050, 3020, 1595 and 1485 cm^{-1} (HC=C); δ_H 1.92 (3 H, s, Me), 3.60 (2 H, s, CH_2) and 7.20-7.27 (5 H, m, ArH); δ_C 14.85 (Me), 38.3 (CH_2), 126.9, 128.4, 128.8 and 138.3 (ArC); *m/z* 140 (M^++2, 2%), 139 (M^++1, 4), 138 (M^+, 41), 91 (100) and 65 (13).

1-Phenyl-1-propanol (**3ba**)[19]: R_f 0.35 (hexane/ethyl acetate: 6/1); t_r 7.68 min; ν_{max} (film) 3350 (OH), 3055, 3020, 1600 and 1490 cm^{-1} (HC=C); δ_H 0.85 (3 H, t, *J*=7.4, Me), 1.59-1.83 (2 H, m, CH_2), 2.60 (1 H, br s, OH), 4.48 (1 H, t, *J*=6.6, CHO) and 7.22-7.29 (5 H, m, ArH); δ_C 10.0 (Me), 31.7 (CH_2), 75.7 (CO), 125.9, 127.2, 128.15 and 144.5 (ArC); *m/z* 137 (M^++1, 4%), 136 (M^+, 46), 108 (16), 107 (100), 105 (12), 79 (88), 78 (14), 77 (68) and 51 (19).

1-Ethylcyclohexanol (**3bb**)[22]: R_f 0.30 (hexane/ethyl acetate: 9/1); t_r 5.65 min; ν_{max} (film) 3370 cm^{-1} (OH); δ_H 0.90 (3 H, t, *J*=7.5, Me), 1.48 (2 H, q, *J*=7.5, C*H*$_2$Me) and 1.20-1.70 (10 H, m, 5xCH_2 ring); δ_C 7.2 (Me), 22.25 (2C), 25.9, 36.9 (2C)(5xCH_2 ring), 34.75 (*C*H_2Me) and 71.45 (CO); *m/z* 128 (M^+, 1%), 99 (100), 85 (68), 81 (54), 72 (21), 57 (26), 55 (17), 43 (35) and 41 (16).

1,1-Diphenyl-1-propanol (**3bc**)[23]: R_f 0.40 (hexane/ethyl acetate: 9/1); t_r 12.98 min; m.p. 91-92°C (hexane/ethyl acetate); 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, 3 m, 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).

2-Methyl-1-phenyl-1-propanol (**3ca**)[24]: R_f 0.76 (hexane/ethyl acetate: 6/1); t_r 8.25 min; ν_{max} (film) 3370 (OH), 3050, 3020, 1595 and 1485 cm^{-1} (HC=C); δ_H 0.79 (3 H, d, *J*=6.8, 1xMe), 0.99 (3 H, d, *J*=6.7, 1xMe), 1.85 (1 H, s, OH), 1.95 (1 H, octet, *J*=6.8, C*H*Me), 4.35 (1 H, d, *J*=6.9, CHO) and 7.24-7.36 (5 H, m, ArH); δ_C 18.2, 18.95 (2xMe), 35.25 (*C*HMe), 80.0 (CO), 126.55, 127.4, 128.15 and 143.6 (ArC); *m/z* 151 (M^++1, 1%), 150 (M^+, 5), 107 (100), 79 (63), 77 (43) and 51 (14).

1-Isopropylcyclohexanol (**3cb**)[25]: R_f 0.53 (hexane/ethyl acetate: 6/1); t_r 6.92 min; ν_{max} (film) 3420 cm^{-1} (OH); δ_H 0.91 (6 H, d, *J*=6.9, 2xMe) and 1.10-1.70 (11 H, 3 m, CH y 5xCH_2 ring); δ_C 16.65 (2 C, 2xMe), 21.9 (2C), 25.9, 34.1 (2C)(5xCH_2 ring), 37.55 (CH) and 73.05 (CO); *m/z* 142 (M^+, 1%), 99 (100), 81 (56), 55 (14), 43 (47) and 41 (14).

2-Methyl-1,1-diphenyl-1-propanol (**3cc**)[26]: R_f 0.42 (hexane/ethyl acetate: 9/1); t_r 13.39 min; ν_{max} (film) 3560, 3490 (OH), 3050, 3015, 1595 and 1485 cm^{-1} (HC=C); δ_H 0.89 (6 H, d, *J*=6.7, 2xMe), 1.95 (1 H, s, OH), 2.88 (1 H, septet, *J*=6.7, C*H*Me), 7.13-7.18, 7.23-7.30 and 7.47-7.51 (10 H, 3 m, ArH); δ_C 17.15 (2 C, 2xMe), 35.0 (*C*HMe), 80.45 (CO), 125.7, 126.35, 128.05 and 146.7 (ArC); *m/z* 226 (M^+, <1%), 184 (11), 183 (100), 105 (86) and 77 (43).

2-Methyl-3-heptanol (**3da**)[27]: R_f 0.41 (hexane/ethyl acetate: 9/1); t_r 5.03 min; ν_{max} (film) 3360 cm^{-1} (OH); δ_H 0.90-0.93 (9 H, m, 2x*Me*CH and *Me*CH_2), 1.20-1.48 (6 H, m, 3xCH_2), 1.60-1.70 (1 H, m, C*H*Me) and 3.33-3.38 (1 H, m, CHO); δ_C 14.05 (*Me*CH_2), 17.05, 18.85 (2x*Me*CH), 22.75, 28.2, 33.8 (3xCH_2), 33.4 (*C*HMe) and 76.7 (CO); *m/z* 112 (M^+-18, 2%), 87 (55), 86 (16), 73 (47), 69 (100), 57 (15), 55 (21), 45 (10), 43 (20) and 41 (30).

1-Phenyl-1-pentanol (**3db**)[19]: R_f 0.17 (hexane/ethyl acetate: 6/1); t_r 9.74 min; ν_{max} (film) 3310 (OH), 3050, 3020, 1590 and 1485 cm^{-1} (HC=C); δ_H 0.87 (3 H, t, *J*=7.0, Me), 1.14-1.42 (4 H, m, C*H*$_2$C*H*$_2$Me), 1.61-1.83 (2 H, m, C*H*$_2$CHO), 2.72 (1 H, br s, OH), 4.59 (1 H, t, *J*=7.0, CHO) and 7.05-7.35 (5 H, m, ArH); δ_C 13.95 (Me), 22.5 (*C*H_2Me), 27.9 (*C*$H_2$$CH_2$Me), 38.65 (*C*$H_2$CO), 74.65 (CO), 125.85, 127.4, 128.35 and 144.9 (ArC); *m/z* 165 (M^++1, 1%), 164 (M^+, 8), 107 (100), 79 (36) and 77 (18).

3-Ethyl-3-heptanol (**3dc**)[28]: R_f 0.56 (hexane/ethyl acetate: 9/1); t_r 6.20 min; ν_{max} (film) 3420 cm^{-1} (OH); δ_H 0.86 (6 H, t, *J*=7.5, 2x*Me*CH_2CO), 0.91 (3 H, t, *J*=6.6, *Me*$CH_2$$CH_2$), 1.20-1.44 [6 H, m, Me(C*H*$_2$)$_3$] and 1.46 (4 H, q, *J*=7.5, 2xMeC*H*$_2$CO); δ_C 7.75 (2 C, 2x*Me*CH_2CO), 14.1 (*Me*$CH_2$$CH_2$), 23.35 (Me*C*$H_2$$CH_2$), 25.6 (*C*$H_2$$CH_2$CO), 31.0 (2 C, 2xMe*C*$H_2$CO), 37.9 ($CH_2$*C*$H_2$CO) and 74.6 (CO); *m/z* 115 (M^+-29, 100%), 97 (10), 87 (55), 69 (10), 59 (20), 57 (20), 55 (25), 45 (23), 43 (14) and 41 (15).

1,1-Diphenyl-1-pentanol (**3dd**)[29]: R_f 0.58 (hexane/ethyl acetate: 9/1); t_r 14.30 min; ν_{max} (film) 3460 (OH), 3050, 3020, 1590 and 1485 cm^{-1} (HC=C); δ_H 0.86 (3 H, t, *J*=7.0, Me), 1.20-1.40 (4 H, m, C*H*$_2$C*H*$_2$Me), 2.13 (1 H, s, OH), 2.23-2.28 (2 H, m, CH_2CO), 7.16-7.21, 7.25-7.28 and 7.30-7.41 (2 H, 4 H and 4 H, respectively, 3 m, ArH); δ_C 14.0 (Me), 23.05 (*C*H_2Me), 25.9 (*C*$H_2$$CH_2$Me), 41.7 (*C*$H_2$CO), 78.2 (CO), 126.0, 126.65, 128.05 and 147.15 (ArC); *m/z* 222 (M^+-18, 43%), 194 (15), 193 (100), 191 (10), 179 (13), 178 (35), 165 (26), 116 (10), 115(93) and 91 (39).

2-Methyl-1-phenyl-1-octanol (**3ea**)[30]: R_f 0.83 (hexane/ethyl acetate: 6/1); t_r 12.96 min; ν_{max} (film) 3380 (OH), 3050, 3010, 1595 and 1490 cm^{-1} (HC=C); δ_H 0.66 (3 H, d, *J*=6.8, 1x*Me*CH), 0.76-0.83 (9 H, m, 1x*Me*CH and 2x*Me*CH_2), 0.96-1.36 (20 H, m, 10xCH_2), 1.48-1.58, 1.64-1.79 (1 H each, 2 m, 2xC*H*Me), 1.86 (1 H, br s, OH), 4.32, 4.42 (1 H each, 2 d, *J*=6.9, 5.7, respectively, 2xCHO) and 7.16-7.24 (10 H, m, 2xArH); δ_C 14.04, 14.06, 14.3, 15.6 (4xMe), 22.6, 22.65, 26.95, 27.1, 29.4, 29.6, 31.8, 31.85, 32.2, 33.1 (10xCH_2), 40.05, 40.1 (2x*C*HMe), 78.1, 79.0 (2xCO), 126.3, 126.65, 127.1, 127.3, 128.05, 143.55 and

143.85 (ArC); *m/z* 107 (M^+-113, 28%), 105 (100), 79 (15), 77 (57) and 51 (21).

3-Ethyl-4-methyl-3-decanol (**3eb**): R_f 0.85 (hexane/ethyl acetate: 9/1); t_r 10.54 min; ν_{max} (film) 3460 cm^{-1} (OH); δ_H 0.83-0.91 (12 H, m, 4xMe), 1.17-1.35 [10 H, m, Me(C*H*$_2$)$_5$] and 1.40-1.56 (5 H, m, 2xCH$_2$CO and CH); δ_C 7.45, 7.55 (2x*Me*CH$_2$CO), 13.6 (*Me*CH), 14.1 (*Me*CH$_2$CH$_2$), 27.95, 28.05 (2x*C*H$_2$CO), 22.7, 28.45, 29.75, 30.8, 31.95 [Me(*C*H$_2$)$_5$], 39.25 (CH) and 76.3 (CO); *m/z* 182 (M^+-18, 4%), 98 (67), 97 (29), 83 (14), 70 (13), 69 (55), 67 (13), 56 (10), 55 (100), 43 (16) and 41 (43).

4,5-Dimethyl-4-undecanol (**3ec**): R_f 0.40 (hexane/ethyl acetate: 9/1); t_r 10.38 min; ν_{max} (film) 3350 cm^{-1} (OH); δ_H 0.78-0.88 (18 H, m, 4x*Me*CH$_2$ and 2x*Me*CH), 1.00, 1.01 (3 H each, 2 s, 2xMeCO) and 1.19-1.40 (30 H, m, 14xCH$_2$ and 2xCH); δ_C 13.65, 14.1 (2 C), 14.35, 14.7, 14.75, 16.4, 16.55 (8xMe), 22.65 (2 C), 23.3, 23.7, 28.3, 28.4, 29.65, 29.7, 30.9, 31.45, 31.9 (2 C), 41.8, 42.35 (14xCH$_2$), 42.4, 42.45 (2xCH), 75.0 and 75.05 (2xCO); *m/z* 185 (M^+-15, 1%), 87 (100), 71 (10), 69 (15), 57 (13), 55 (11), 45 (50), 43 (38) and 41 (29).

2-Methyl-1,1-diphenyl-1-octanol (**3ed**)[31]: R_f 0.65 (hexane/ethyl acetate: 95/5); t_r 16.56 min; ν_{max} (film) 3500 (OH), 3050, 3020, 1595 and 1485 cm^{-1} (HC=C); δ_H 0.85 (3 H, t, J=6.8, *Me*CH$_2$), 0.86 (3 H, d, J=6.7, *Me*CH), 1.06-1.50 (10 H, m, 5xCH$_2$), 2.04 (1 H, s, OH), 2.62 (1 H, dqd, J=10.4, 6.7, 1.6, C*H*Me), 7.13-7.18, 7.22-7.30 and 7.45-7.50 (2 H, 4 H and 4 H, respectively, 3 m, ArH); δ_C 14.05 (2 C, 2xMe), 22.6, 28.0, 29.45, 31.2, 31.8 (5xCH$_2$), 40.35 (CHMe), 81.15 (CO), 125.6, 125.7, 126.2, 126.35, 128.05, 128.1, 146.8 and 146.85 (ArC); *m/z* 183 (M^+-113, 100%), 105 (56), 77 (32) and 43 (10).

2-Phenyltetrahydrofuran (**10**)[32]: R_f 0.58 (hexane/ethyl acetate: 4/1); t_r 8.78 min; ν_{max} (film) 3060, 3030, 1590 and 1485 cm^{-1} (HC=C); δ_H 1.77-1.84, 1.98-2.04, 2.29-2.40 (1 H, 2 H and 1 H, respectively, 3 m, CHC*H*$_2$C*H*$_2$), 3.90-3.97, 4.06-4.13 (1 H each, 2 m, CH$_2$O), 4.89 (1 H, t, J=7.2, CHO) and 7.27-7.40 (5 H, m, ArH); δ_C 26.0, 34.6, 68.65 (3xCH$_2$), 80.65 (CHO), 125.6, 127.1, 128.25 and 143.45 (ArC); *m/z* 149 (M^++1, <1%), 148 (M^+, 58), 147 (74), 117 (14), 115 (14), 106 (12), 105 (100), 91 (28), 78 (19), 77 (47), 63 (12), 51 (28), 50 (13), 42 (15) and 41 (15).

1,1-Dibenzylcyclopropane (**12**): R_f 0.46 (hexane); t_r 14.02 min; ν_{max} (film) 3050, 3020, 1595 and 1490 cm^{-1} (HC=C); δ_H 0.51 (4 H, s, 2xCH$_2$ ring), 2.55 (4 H, s, 2xC*H*$_2$Ph) and 7.10-7.35 (10 H, m, ArH); δ_C 10.75 (2 C, 2xCH$_2$ ring), 20.85 (*C*CH$_2$Ph), 41.55 (2 C, 2x*C*H$_2$Ph), 125.95, 128.05, 129.45 and 140.1 (ArC); *m/z* 223 (M^++1, 1%), 222 (M^+, 6), 131 (47), 130 (17), 129 (15), 128 (10), 116 (13), 115 (28), 92 (17), 91 (100), 77 (10), 65 (23) and 51 (10) (Found: M^+, 222.141305. $C_{17}H_{18}$ requires M, 222.140851).

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