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Synthesis of Substituted Cyclopropanes from 1,3-Diols Through the Corresponding Cyclic Sulfates

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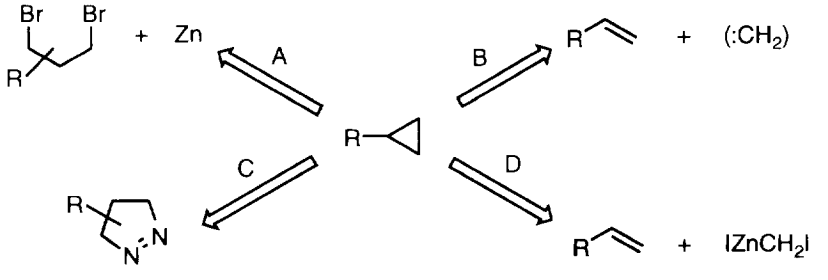
Abstract: The reaction of different cyclic sulfates **2** (easily prepared from the corresponding 1,3-diols **1** following the Sharpless methodology) with an excess of lithium powder and a catalytic amount of DTBB (5 mol %) leads to the corresponding substituted cyclopropanes **3** through a γ-elimination process, the sulfate ion acting as leaving group.

INTRODUCTION

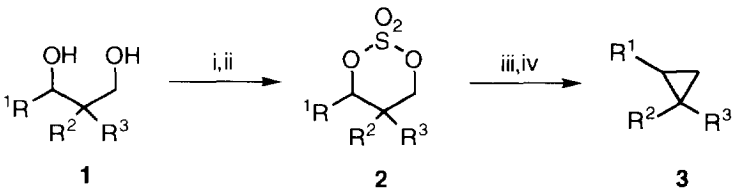
Among the methodologies to prepare cyclopropane derivatives[1], the most important are: (1) 1,3-elimination from 1,3-dihalides and metals (Method A)[1,2], (2) carbene addition to olefins (Method B)[3], (3) thermal or photochemical decomposition of 1-pyrazolines (Method C)[4], and (4) the Simmons-Smith reaction (Method D)[5] (Scheme 1). To the best of our knowledge there is only one precedent described in the literature[6] for the transformation of 1,3-diols into cyclopropane derivatives by using McMurry's method ($TiCl_3$-$LiAlH_4$); two important limitations of this reaction are: (a) it works only with benzylic derivatives (*eg.* 1,3-diphenyl-1,3-propanediol) and (b) a mixture of cyclopropanes together with the corresponding alkenes, alkane and alcohol is obtained. On the other hand, we have recently applied the arene-catalysed lithiation procedure[7] for the transformation of dialkyl sulfates into organolithium reagents[8]; however, when this method was applied to cyclic sulfates, instead of the corresponding dilithiocompounds an elimination process took place[8b]. In this paper we explore this last reaction in order to obtain cyclopropane derivatives from 1,3-diols[9] through the corresponding cyclic sulfates[10].



Scheme 1.

RESULTS AND DISCUSSION

1,3-Diols **1** were easily transformed into the corresponding cyclic sulfates **2** by the Sharpless methodology[11]. The reaction of these materials **2** with an excess of lithium powder (1:14 molar ratio) and a catalytic amount of 4,4'-di-*tert*-butylbiphenyl (DTBB; 1:0.1 molar ratio, 5 mol %) in THF at 0°C gave, after hydrolysis with water, the corresponding substituted cyclopropanes **3** (Scheme 2 and Table 1). In the case of sulfate **2b**, the corresponding *ca.* 1:1 diastereoisomeric mixture (obtained from diol **1b**, which was also a 1:1 diastereoisomeric mixture) could be separated by flash chromatography; independent lithiation of both diastereoisomers gave the following result: *trans*-**2b** and *cis*-**2b** afforded a *trans:cis*-**3b** mixture of 3:1 and 4.8:1, respectively, the reaction being clearly not stereospecific (Table 1, entry 2 and footnotes e-h). In addition, both diol **1h** and sulfate **2h** were isolated as a *ca.* 2:1 diastereoisomeric mixture; however, when the mentioned mixture **2h** was submitted to lithiation as above, only the *cis* bicyclic compound **3h**[12] was isolated in 91% yield, so the preparation of **3h** is independent of the stereochemistry of sulfate **2h** (Table 1, entry 8 and footnote i).



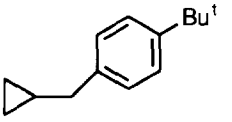
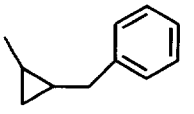
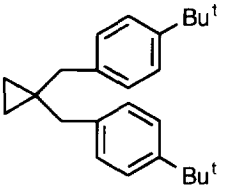
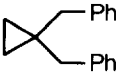
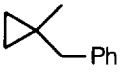
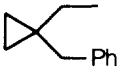
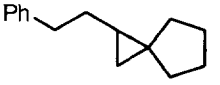
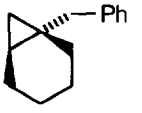
a : R^1=R^2=H, R^3=4-Bu^t$C_6H_4CH_2$
b : R^1=Me, R^2=H, R^3=$PhCH_2$
c : R^1=H, R^2=R^3=4-Bu^t$C_6H_4CH_2$
d : R^1=H, R^2=R^3=$PhCH_2$
e : R^1=H, R^2=Me, R^3=$PhCH_2$
f : R^1=H, R^2=Et, R^3=$PhCH_2$
g : R^1=$PhCH_2CH_2$, R^2-R^3=$(CH_2)_4$
h : R^1-R^2=$(CH_2)_4$, R^3=$PhCH_2$

Scheme 2. *Reagents and conditions*: i, $SOCl_2$, CCl_4, reflux; ii, $NaIO_4$, $RuCl_3$ cat. (*ca.* 0.1%), MeCN, H_2O, 0 to 20°C; iii, Li, DTBB cat. (5 mol %), THF, 0°C; iv, H_2O.

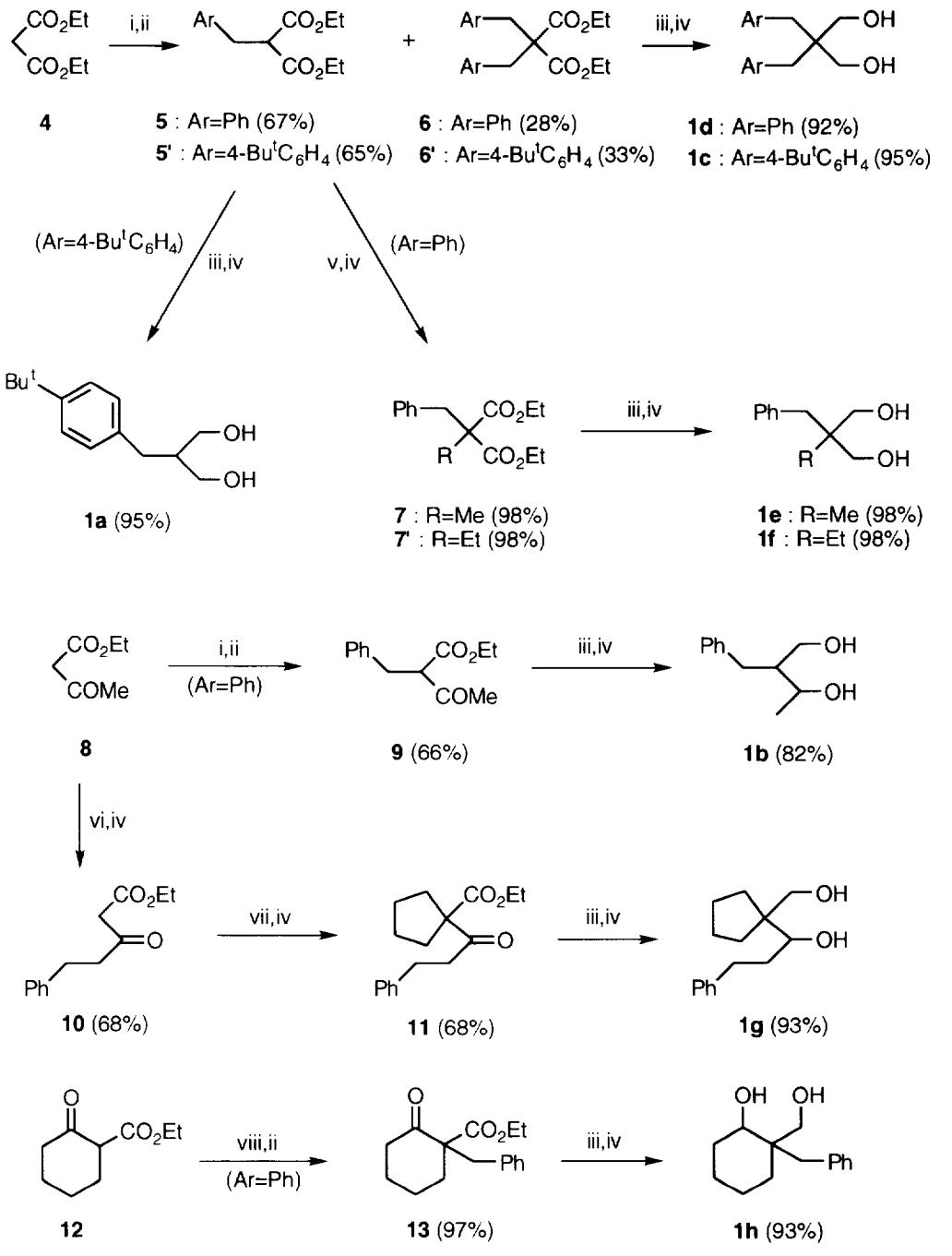
Starting 1,3-diols were prepared by different routes as summarised in Scheme 3, in which the corresponding isolated yields are also included. From diethyl malonate (**4**) a mixture of compounds **5+6** or **5'+6'** was obtained by tandem deprotonation with sodium hydride followed by benzylation. After chromatographic separation, compound **5'** was reduced with lithium aluminum hydride (LAH) to give diol **1a**. Compound **5** was alkylated to yield first diesters **7** and **7'**, which after reduction with LAH gave diols **1e** and **1f**. Direct reduction of diesters **6** and **6'** afforded diols **1d** and **1c**, respectively. Starting from ethyl acetylacetate (**8**), diols **1b** and **1g** were prepared as follows: tandem benzylation (to give 9)-reduction yielded diol **1b** as a *ca.* 1:1 diastereoisomers mixture, which could not be separated chromatographically. Double deprotonation of the same starting material **8** followed by benzylation afforded ketoester **10**, which was converted into compound **11** using 1,4-dibromobutane as alkylating agent and sodium ethoxide as deprotonation

reagent; the final reduction of this compound gave diol **1g**. Finally, diol **1h** was prepared from ketoester **12** by benzylation (to give **13**) followed by reduction with LAH, yielding a 2:1 diastereoisomers mixture, which could not be separated by flash chromatography (Scheme 3).

Table 1. Preparation of Compounds **3**

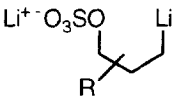
Entry	Starting diol **1**	Cyclic sulfate **2** [yield (%)][b]	Cyclopropane **3**[a] No.	Structure	Yield (%)[c]	R_f[d]
1	**1a**	**2a** [89]	**3a**		85	0.47
2	**1b**[e]	**2b**[95][f]	**3b**		84[g]	0.49[h]
3	**1c**	**2c** [60]	**3c**		78	0.29
4	**1d**	**2d** [85]	**3d**		83	0.46
5	**1e**	**2e** [81]	**3e**		60	0.41
6	**1f**	**2f** [88]	**3f**		81	0.36
7	**1g**	**2g** [97]	**3g**		96	0.26
8	**1h**[i]	**2h** [93]	**3h**		91	0.25

[a] All compounds **3** were >95% pure (GLC and 300 MHz ^{1}H NMR). [b] Isolated crude yield based on the starting diol **1**; compounds **2** were >90% pure (300 MHz ^{1}H NMR). [c] Isolated yield after flash chromatography (silica gel, hexane) based on the cyclic sulfate **2**. [d] Silica gel, hexane. [e] Isolated as a *ca.* 1:1 diastereoisomers mixture (GLC), which could not be separated chromatographically. [f] A *ca.* 1:1 *trans*:*cis* diastereoisomers mixture was obtained, which was separated by chromatography (see text). [g] A 3-4.8:1 *trans*:*cis* mixture of diastereoisomers was obtained (see text). [h] R_f value corresponding to the major (*trans*) diastereoisomer. [i] Isolated as a *ca.* 2:1 diastereoisomers mixture (300 MHz ^{1}H NMR).



Scheme 3. *Reagents and conditions*: i, NaH, THF, then $ArCH_2Br$ (Ar=Ph, 4-$Bu^tC_6H_4$); ii, NH_4Cl, H_2O; iii, $LiAlH_4$, THF reflux; iv, H_2O; v, NaH, THF, then RI (R=Me, Et); vi, 2 LDA, THF, then $PhCH_2Br$; vii, 2 EtONa, EtOH reflux, then $Br(CH_2)_4Br$; viii, as step i but at reflux.

Concerning a possible mechanistic pathway, we think that the first lithiation step of sulfates **2** should be the formation of a γ-functionalised organolithium compound[13] of the type **I**, which suffers a rapid γ-elimination[1,2] to yield the cyclopropane structure, the sulfate anion acting as leaving group. The behaviour observed either in the transformation of each diastereoisomer **2b** into a mixture of compounds **3b** or in the conversion of the *cis/trans* mixture **2h** into a single product **3h** would indicate that both a primary and a secondary carbanionic centre are formed in the first lithiation step. The secondary intermediate would suffer inversion in the configuration, so the whole process is not stereospecific, giving the corresponding thermodinamic control reaction product(s).



I

As a conclusion, we think that the described methodology here represents an adequate way for the indirect transformation of 1,3-diols to cyclopropanes through the corresponding cyclic sulfates. This procedure is applicable to the preparation of cyclopropanyl spiranes or bicyclic systems (*e.g.* compounds **3g** or **3h**).

EXPERIMENTAL SECTION

General.- For general considerations see reference 8b. High resolution mass spectra were measured in the corresponding service at the University of Valencia.

*Alkylation of Diethyl Malonate (**4**) and Ethyl Acetylacetate (**8**). Isolation of Compounds* **5**, **5'**, **6**, **6'**, **7**, **7'**, **9**, **10**, **11**, and **13**. *General Procedure.*- To a suspension of sodium hydride (10 mmol) in dry THF (15 ml) was dropwise added the starting material **4** or **8** (10 mmol). When the gas evolution finished the corresponding alkyl bromide (10 mmol) was added and the reaction mixture was stirred for 1 h. The resulting mixture was then hydrolysed with a saturated aqueous solution of ammonium chloride and extracted with ethyl acetate (2x20 ml). The organic layer was dried over anhydrous sodium sulfate and evaporated at reduced pressure (15 Torr), giving a residue which was purified by flash chromatography (silica gel, hexane/ethyl acetate), giving products **5**, **5'**, **6**, **6'**, and **9**. Compound **5** was again alkylated using methyl or ethyl iodide (1:1.1 molar ratio) following the same protocol as it was described above, affording compounds **7** and **7'**. Compounds **10** and **11** were prepared from the starting material **8** following the procedure described in the literature[14]. In the case of compound **13**, it was necessary to reflux the reaction mixture after adding benzyl bromide. Yields are included in Scheme 3. Compounds **5**[15], **5'**[16], **6**[17], **7**[18], **7'**[19], **9**[20], **10**[21] and **13**[22] were characterised by comparison of their spectroscopic and physical data with the literature ones. Physical, analytical and spectroscopic data for new compounds **6'** and **11** follow.

*Diethyl Bis(4-*tert*-butylbenzyl)malonate* (**6'**): R_f 0.54 (ethyl acetate); t_r 22.84 min; m.p. 75-76°C (hexane/ethyl acetate); ν (film) 3056, 3029, 1513 (HC=C) and 1733 cm^{-1} (C=O); δ_H 1.13 (6 H, t, *J*=7.2 Hz, 2x*Me*CH_2), 1.30 (18 H, s, 6xMeC), 3.19 (4 H, s, 2xCH_2Ar), 4.10 (4 H, q, *J*=7.2 Hz, 2xCH_2O), 7.11 and 7.28 (4 H each, 2 d, *J*=8.5 Hz each, ArH); δ_C 13.8 (2 C, 2x*Me*CH_2), 31.3 (6 C, 6x*Me*C), 34.35 (2 C, 2xCMe), 38.45 (2 C,

2xCH_2Ar), 60.2 (CCH_2), 61.05 (2 C, 2xCH_2O), 125.05 (4 C), 129.75 (4 C), 133.25 (2 C), 149.55 (2 C)(ArC) and 171.1 (C=O); *m/z* 305 (M^+-147, 32 %), 260 (13), 259 (100), 147 (27), 132 (13), 117 (20) and 57 (24). Anal. calcd. for $C_{29}H_{40}O_4$: C, 76.94; H, 8.91. Found: C, 77.1; H, 9.0.

Ethyl α-(3-Phenylpropionyl)cyclopentanecarboxylate (**11**): R_f 0.58 (ethyl acetate); t_r 15.23 min; ν (film) 3063, 3028, 1604, 1497 (HC=C), 1739 and 1713 cm^{-1} (C=O); δ_H 1.20 (3 H, t, *J*=7.2 Hz, Me), 1.53-1.68, 2.02-2.08 (4 H each, 2 m, 4xCH_2 ring), 2.70-2.77, 2.86-2.94 [2 H each, 2 m, Ph(CH_2)$_2$], 4.12 (2 H, q, *J*=7.2 Hz, CH_2O) and 7.14-7.29 (5 H, m, ArH); δ_C 13.95 (Me), 25.5 (2 C), 32.8 (2 C)(4xCH_2 ring), 30.15, 40.7 [Ph(CH_2)$_2$], 61.25 (CH_2O), 66.65 (*C*C=O), 126.05, 128.3, 128.4, 140.95 (ArC), 173.35 (CO_2Et) and 205.15 (C=O); *m/z* 275 (M^++1, 1 %), 274 (M^+, 5), 142 (65), 133 (15), 114 (14), 105 (82), 104 (11), 103 (13), 96 (18), 95 (12), 91 (100), 79 (16), 78 (12), 77 (18), 68 (19), 67 (32), 65 (22), 51 (11) and 41 (23).

Lithium Aluminum Hydride Reduction of Compounds **5'**, **6**, **6'**, **7**, **7'**, **9**, **11** and **13**. *Isolation of 1,3-Diols* **1a-h**. *General Procedure*.- A mixture of the corresponding title diester or cetoester (5 mmol) and lithium aluminum hydride (1:1.5 molar ratio) in THF (10 ml) was refluxed for 1 h. After cooling at room temperature, the resulting mixture was hydrolysed with water (10 ml) and extracted with ethyl acetate (3x20 ml). The organic layer was dried with anhydrous sodium sulfate and evaporated (15 Torr). The crude products 1,3-diols were in all cases > 90 % pure (300 MHz ^{1}H NMR) and were used for the preparation of cyclic sulfates **2** without further purification. Yields are included in Scheme 3. Analytical, physical and spectroscopic data, as well as literature references for known compounds, follow.

*2-(4-*tert*-Butylbenzyl)-1,3-propanediol* (**1a**): R_f 0.29 (ethyl acetate); t_r 13.94 min; m. p. 74-75°C (hexane/diethyl ether); ν (KBr) 3340 (OH), 3050, 3010 and 1510 cm^{-1} (HC=C); δ_H 1.29 (9 H, s, 3xMe), 1.98-2.05 (1 H, m, C*H*CH_2O), 2.54 (2 H, d, *J*=7.6 Hz, CH_2Ph), 3.07 (2 H, br s, 2xOH), 3.62 (2 H, dd, *J*=10.7, 7.0 Hz, 2xC*H*HO), 3.75 (2 H, dd, *J*=10.7, 4.0 Hz, 2xC*H*HO), 7.09 and 7.29 (2 H each, 2 d, *J*=8.2 Hz each, ArH); δ_C 31.35 (3 C, 3xMe), 33.65 (CH_2Ph), 34.3 (*C*Me), 43.75 (*C*HCH_2O), 65.1 (2 C, 2xCO), 125.25, 128.6, 136.65 and 148.85 (ArC); *m/z* 223 (M^++1, 1 %), 222 (M^+, 9), 208 (14), 207 (100), 204 (62), 190 (12), 189 (83), 173 (29), 147 (40), 145 (35), 132 (21), 131 (33), 130 (12), 129 (35), 128 (14), 119 (11), 118 (10), 117 (50), 116 (10), 115 (24), 105 (20), 92 (15), 91 (38), 77 (10), 57 (42) and 41 (17). Anal. calcd. for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.9; H, 10.5.

2-Benzyl-1,3-butanediol (**1b**)[23] (diastereoisomers ratio 1:1): R_f 0.38 (ethyl acetate); t_r 11.98 and 12.05 min; ν (film) 3372, 3362 (OH), 3062, 3026, 1603 and 1495 cm^{-1} (HC=C); δ_H 1.23 (3 H, d, *J*=6.4 Hz, 1xMe), 1.28 (3 H, d, *J*=6.7 Hz, 1xMe), 1.67-1.74, 1.93-2.00 (1 H each, 2 m, 2xC*H*CO), 2.54 (1 H, dd, *J*=13.7, 9.5 Hz, 1xC*H*HPh), 2.59-2.67 (2 H, m, 2xC*H*HPh), 2.79 (1 H, dd, *J*=13.7, 5.8 Hz, 1xC*H*HPh), 3.36-3.70 (7 H, m, 3xCHO and 4xOH), 3.82-3.93, 4.03-4.08 (2 H and 1 H, respectively, 2 m, 3xCHO) and 7.15-7.29 (10 H, m, ArH); δ_C 19.1, 21.85 (2xMe), 32.05, 34.85 (2xCH_2Ph), 47.0, 47.65 (2xCHCO), 63.0, 63.4 (2xCH_2O), 70.15, 70.85 (2xCHO), 125.9, 125.95, 128.3, 128.35, 128.85, 129.0, 140.2 and 140.3 (ArC); *m/z* (1st. diastereoisomer) 162 (M^+-18, 4 %), 117 (10), 91 (23), 45 (100) and 43 (34); (2nd. diastereoisomer) 162 (M^+-18, 5 %), 91 (30), 45 (100) and 43 (42).

*2,2-Bis(4-*tert*-butylbenzyl)-1,3-propanediol* (**1c**): R_f 0.60 (ethyl acetate); t_r 23.91 min; m. p. 172-173°C (hexane/acetone); ν (KBr) 3350, 3240 (OH), 3050, 3020, 1510 cm^{-1} (HC=C); δ_H [$(CD_3)_2CO$] 1.30 (18 H, s, 6xMe), 2.73 (4 H, s, 2xCH_2Ar), 3.27 (4 H, s, 2xCH_2O), 3.76 (2 H, br s, 2xOH), 7.25 and 7.31 (4 H each, 2 d,

J=8.7 Hz each, ArH); δ_C [$(CD_3)_2CO$] 31.7 (6 C, 6xMe), 34.8 (2 C, 2x*C*Me), 38.35 (2 C, 2x*C*H_2Ar), 44.85 (*C*CO), 64.15 (2 C, 2xCO), 125.3, 131.3, 136.35 and 149.05 (ArC); *m/z* 368 (M^+, 2 %), 169 (11), 147 (37), 133 (14), 132 (11), 129 (17), 117 (19), 92 (12), 91 (12), 57 (100) and 41 (12). Anal. calcd. for $C_{25}H_{36}O_2$: C, 81.47; H, 9.85. Found: C, 81.4; H, 9.9.

2,2-Dibenzyl-1,3-propanediol (**1d**)[24]: R_f 0.54 (ethyl acetate); t_r 17.15 min; ν (film) 3380 (OH), 3060, 3020, 1600 and 1495 cm^{-1} (HC=C); δ_H 2.44 (2 H, br s, 2xOH), 2.71 (4 H, s, 2x*C*H_2Ph), 3.52, 3.53 (2 H each, 2 s, 2xCH_2O) and 7.17-7.30 (10 H, m, ArH); δ_C 39.2 (2 C, 2x*C*H_2Ph), 43.4 [*C*$(CH_2)_4$], 66.85 (2 C, 2xCO), 126.25, 128.1, 130.5 and 137.65 (ArC); *m/z* 147 (M^+-109, 1 %), 115 (10), 92 (14), 91 (100), 65 (30), 51 (10) and 41 (10).

2-Benzyl-2-methyl-1,3-propanediol (**1e**)[25]: R_f 0.37 (ethyl acetate); t_r 12.14 min; ν (film) 3355, 3299 (OH), 3084, 3028, 1602 and 1493 cm^{-1} (HC=C); δ_H 0.74 (3 H, s, Me), 2.67 (2 H, s, C*H*$_2$Ph), 3.21 (2 H, br s, 2xOH), 3.52 (4 H, s, 2xCH_2O) and 7.17-7.29 (5 H, m, ArH); δ_C 18.45 (Me), 39.75 (*C*H_2Ph), 40.0 (*C*Me), 69.55 (2 C, 2xCO), 126.05, 127.9, 130.5 and 137.7 (ArC); *m/z* 131 (M^+-49, 7 %), 115 (15), 92 (21), 91 (100), 89 (13), 78 (10), 77 (19), 65 (54), 63 (21), 57 (12), 51 (29), 50 (12), 43 (33) and 41 (43).

2-Benzyl-2-ethyl-1,3-propanediol (**1f**): R_f 0.47 (ethyl acetate); t_r 13.04 min; ν (film) 3360 (OH), 3060, 3020, 1605 and 1495 cm^{-1} (HC=C); δ_H 0.92 (3 H, t, *J*=7.5 Hz, Me), 1.24 (2 H, q, *J*=7.5 Hz, C*H*$_2$Me), 2.64 (2 H, s, C*H*$_2$Ph), 2.95 (2 H, br s, 2xOH), 3.53, 3.57 (2 H each, 2 d, *J*=10.8 Hz each, 2xCH_2O) and 7.16-7.29 (5 H, m, ArH); δ_C 7.5 (Me), 23.25 (*C*H_2Me), 36.6 (*C*H_2Ph), 42.3 (*C*CH_2O), 67.85 (2 C, 2xCO), 126.05, 128.0, 130.35 and 137.75 (ArC); *m/z* 176 (M^+-18, 2 %), 145 (18), 107 (12), 104 (11), 92 (81), 91 (100), 77 (10), 70 (16), 65 (23), 57 (20), 55 (26), 43 (29) and 41 (29).

1-[1-(Hydroxymethyl)cyclopentyl]-3-phenyl-1-propanol (**1g**): R_f 0.52 (ethyl acetate); t_r 15.05 min; ν (film) 3355 (OH), 3062, 3026, 1603 and 1496 cm^{-1} (HC=C); δ_H 1.14-1.34, 1.49-1.65, 1.70-1.85 (2 H, 5 H and 3 H, respectively, 3 m, 4xCH_2 ring and C*H*$_2$C*H*$_2$Ph), 2.63 (1 H, dt, *J*=13.9, 8.1 Hz, 1xC*H*HPh), 2.92-3.01 (1 H, m, 1xC*H*HPh), 3.37-3.49 (4 H, m, CH_2O and 2xOH), 3.72 (1 H, dd, *J*=10.4, 2.4 Hz, CHO) and 7.15-7.31 (5 H, m, ArH); δ_C 25.15, 25.4, 31.55, 33.1, 33.15, 34.85 (4xCH_2 ring and *C*H_2*C*H_2Ph), 50.5 [*C*$(CH_2)_3$], 68.45 (CH_2O), 79.85 (CHO), 125.75, 128.35, 128.4 and 142.25 (ArC); *m/z* 216 (M^+-18, 5 %), 134 (28), 118 (10), 117 (10), 111 (14), 105 (15), 104 (40), 92 (42), 91 (100), 82 (47), 81 (23), 79 (17), 78 (14), 77 (14), 67 (63), 65 (16), 55 (13) and 41 (18).

2-Benzyl-2-(hydroxymethyl)cyclohexanol (**1h**) (diastereoisomers ratio 2:1): R_f 0.52 (ethyl acetate); t_r 14.53 min; ν (film) 3345 (OH), 3061, 3027, 1602 and 1495 cm^{-1} (HC=C); δ_H (major diast.) 0.65 (1 H, td, *J*=13.4, 4.0 Hz, 1xC*H*HCCH_2O), 1.12-1.84 [7 H, m, $(CH_2)_3$CHO and 1xC*H*HCCH_2O], 2.75, 3.13 (1 H each, 2 d, *J*=13.7 Hz each, C*H*$_2$Ph), 3.25-3.39, 3.52-3.60, 3.79-3.84 (2 H, 2 H and 1 H, respectively, 3 m, 3xCHO and 2xOH) and 7.18-7.31 (5 H, m, ArH); (minor diast.) 0.82-0.91, 1.12-1.84 [1 H and 7 H, respectively, 2 m, $(CH_2)_4$], 2.80, 3.07 (1 H each, 2 d, *J*=13.3 Hz each, C*H*$_2$Ph), 3.25-3.39, 3.52-3.60, 3.79-3.84 (1 H, 1 H and 2 H, respectively, 3 m, CH_2O and 2xOH), 4.13 (1 H, d, *J*=11.3 Hz, CHO) and 7.18-7.31 (5 H, m, ArH); δ_C (major diast.) 20.35, 24.35, 28.3, 29.85 (4xCH_2 ring), 40.9 (*C*CO), 42.3 (*C*H_2Ph), 71.05 (CH_2O), 78.85 (CHO), 125.8, 127.85, 130.65 and 138.3 (ArC); (minor diast.) 20.9, 24.0, 29.4, 31.05 (4xCH_2 ring), 41.75 (*C*CO), 42.3 (*C*H_2Ph), 65.05 (CH_2O), 76.35 (CHO), 125.9, 127.75, 130.85 and 137.7 (ArC); *m/z* 220 (M^+, 1%), 202 (17), 171 (16), 143 (12), 133 (12), 129 (17), 117 (12), 111 (22), 93 (17), 92 (53), 91 (100), 83 (12),

81 (12), 77 (10), 67 (18), 65 (14), 55 (31) and 41 (14) (Found: M^+, 220.1457. $C_{14}H_{20}O_2$ requires M, 220.1463).

Preparation of Cyclic Sulfates **2**. *General Procedure*.- Compounds **2** were prepared following the literature procedure[11]. Yields are included in Table 1. Analytical, physical and spectroscopic data, as well as literature references for known compounds, follow.

*5-(4-*tert*-Butylbenzyl)-1,3,2-dioxathiane-2,2-dioxide* (**2a**): R_f 0.25 (hexane/ethyl acetate: 4/1); t_r 16.77 min; m. p. 132-133°C (hexane/ethyl acetate); ν (KBr) 3040, 1510 (HC=C), 1390 and 1190 cm^{-1} (SO_2); δ_H 1.32 (9 H, s, 3xMe), 2.36-2.48 (1 H, m, C*H*CH_2O), 2.77 (2 H, d, *J*=7.9 Hz, CH_2Ph), 4.51 (2 H, dd, *J*=11.3, 7.0 Hz, 2xC*H*HO), 4.67 (2 H, dd, *J*=11.3, 3.7 Hz, 2xC*H*HO), 7.11 and 7.38 (2 H each, 2 d, *J*=8.2 Hz each, ArH); δ_C 31.25 (3 C, 3xMe), 32.7 (*C*H_2Ph), 34.45 (*C*Me), 34.6 (*C*HCH_2O), 76.25 (2 C, 2xCO), 125.9, 128.45, 133.45 and 150.2 (ArC); *m/z* 286 (M^++2, 1 %), 285 (M^++1, 4), 284 (M^+, 22), 270 (15), 269 (100), 171 (24), 143 (28), 132 (11), 131 (59), 129 (29), 128 (13), 117 (22), 115 (17), 91 (24), 57 (13) and 41 (19). Anal. calcd. for $C_{14}H_{20}O_4S$: C, 59.13; H, 7.09; S, 11.27. Found: C, 58.9; H, 7.4; S, 10.9.

*(4*S**, 5*R**)-5-Benzyl-4-methyl-1,3,2-dioxathiane-2,2-dioxide* (**2b**): R_f 0.40 (hexane/ethyl acetate: 2/1); t_r 14.77 min; ν (film) 3050, 3020, 1600, 1495 (HC=C), 1395 and 1195 cm^{-1} (SO_2); δ_H 1.55 (3 H, d, *J*=6.4 Hz, Me), 2.30-2.45 (2 H, m, 1xC*H*HPh and C*H*CO), 2.89 (1 H, m, 1xC*H*HPh), 4.20 (1 H, dd, *J*=11.6, 4.2 Hz, 1xC*H*HO), 4.45 (1 H, t, *J*=11.6 Hz, 1xC*H*HO), 4.83 (1 H, dd, *J*=9.8, 6.4 Hz, CHO), 7.13 (2 H, d, *J*=6.7 Hz, 2xArH) and 7.24-7.36 (3 H, m, 3xArH); δ_C 19.05 (Me), 33.0 (*C*H_2Ph), 40.8 (*C*HCH_2), 75.3 (CH_2O), 86.1 (CHO), 127.25, 128.5, 129.0 and 136.0 (ArC); *m/z* 243 (M^++1, 1 %), 242 (M^+, 7), 144 (22), 131 (11), 129 (74), 117 (28), 115 (12), 92 (11), 91 (100) and 65 (16) (Found: M^+, 242.0613. $C_{11}H_{14}O_4S$ requires M, 242.0613).

*(4*R**, 5*R**)-5-Benzyl-4-methyl-1,3,2-dioxathiane-2,2-dioxide* (**2b**): R_f 0.34 (hexane/ethyl acetate: 2/1); t_r 14.63 min; m. p. 79°C (hexane/diethyl ether); ν (KBr) 3050, 3020, 1595, 1490 (HC=C), 1385 and 1195 cm^{-1} (SO_2); δ_H 1.57 (3 H, d, *J*=6.6 Hz, Me), 1.92-1.98 (1 H, m, C*H*CO), 2.86 (1 H, dd, *J*=13.7, 11.6 Hz, 1xC*H*HPh), 3.01 (1 H, dd, *J*=13.7, 4.6 Hz, 1xC*H*HPh), 4.24 (1 H, dd, *J*=11.6, 1.2 Hz, 1xC*H*HO), 4.63 (1 H, d, *J*=11.6 Hz, 1xC*H*HO), 5.29 (1 H, qd, *J*=6.6, 2.3 Hz, CHO) and 7.18-7.37 (5 H, m, ArH); δ_C 17.6 (Me), 28.5 (*C*H_2Ph), 39.0 (*C*HCH_2), 73.85 (CH_2O), 84.8 (CHO), 126.95, 128.95, 129.15 and 137.5 (ArC); *m/z* 243 (M^++1, 1 %), 242 (M^+, 5), 144 (25), 131 (13), 129 (76), 117 (32), 115 (11), 92 (22), 91 (100) and 65 (17). Anal. calcd. for $C_{11}H_{14}O_4S$: C, 54.53; H, 5.82; S, 13.23. Found: C, 54.2; H, 6.1; S, 13.2.

*5,5-Bis(4-*tert*-butylbenzyl)-1,3,2-dioxathiane-2,2-dioxide* (**2c**): R_f 0.57 (hexane/ethyl acetate: 2/1); t_r 27.97 min; m. p. 174°C (hexane/diethyl ether); ν (KBr) 3050, 3020, 1510 (HC=C), 1400 and 1200 cm^{-1} (SO_2); δ_H 1.33 (18 H, s, 6xMe), 2.82 (4 H, s, 2xCH_2Ph), 4.42 (4 H, s, 2xCH_2O), 7.11 and 7.36 (4 H each, 2 d, *J*=8.4 Hz each, ArH); δ_C 31.3 (6 C, 6xMe), 34.5 (2 C, 2x*C*Me), 37.0 (2 C, 2xCH_2Ph), 37.35 (*C*CH_2O), 78.4 (2 C, 2xCO), 125.7, 130.25, 131.25 and 150.35 (ArC); *m/z* (DIP) 431 (M^++1, 3 %), 430 (M^+, 10), 415 (25), 200 (14), 148 (12), 147 (100), 132 (38), 131 (46), 129 (23), 128 (13), 117 (53), 115 (24), 105 (14), 104 (12), 91 (29), 57 (35) and 41 (30). Anal. calcd. for $C_{25}H_{34}O_4S$: C, 69.73; H, 7.96; S, 7.45. Found: C, 69.5; H, 8.3; S, 7.2.

5,5-Dibenzyl-1,3,2-dioxathiane-2,2-dioxide (**2d**)[8b]: R_f 0.27 (hexane/ethyl acetate: 4/1); t_r 18.71 min; m. p. 109-111°C (diethyl ether); ν (KBr) 3050, 3020, 1595, 1490 (HC=C), 1395 and 1195 cm^{-1} (SO_2); δ_H 2.85 (4 H, s, 2xCH_2Ph), 4.40 (4 H, s, 2xCH_2O) and 7.14-7.38 (10 H, m, ArH); δ_C 37.2 (CCH_2Ph), 37.7 (2 C, 2xCH_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). Anal. calcd. for $C_{17}H_{18}O_4S \cdot 1/4\ H_2O$: C, 63.24; H, 5.78; S, 9.91. Found: C, 63.6; H, 6.0; S, 9.7.

5-Benzyl-5-methyl-1,3,2-dioxathiane-2,2-dioxide (**2e**): R_f 0.24 (hexane/ethyl acetate: 4/1); t_r 14.36 min; m. p. 91-92°C (hexane/diethyl ether); ν (KBr) 3060, 3020, 1600, 1495 (HC=C), 1380 and 1190 cm^{-1} (SO_2); δ_H 0.96 (3 H, s, Me), 2.87 (2 H, s, CH_2Ph), 4.33, 4.41 (2 H each, 2 d, *J*=11.3 Hz each, 2xCH_2O), 7.16 (2 H, dd, *J*=7.8, 1.7 Hz, 2xArH) and 7.25-7.37 (3 H, m, 3xArH); δ_C 17.2 (Me), 34.1 (*C*Me), 39.4 (CH_2Ph), 79.9 (2 C, 2xCO), 127.2, 128.55, 130.4 and 134.75 (ArC); *m/z* 242 (M^+, 1 %), 144 (15), 129 (26), 117 (11), 115 (15), 91 (100), 78 (10), 77 (15), 65 (43), 63 (12), 51 (20) and 41 (29). Anal. calcd. for $C_{11}H_{14}O_4S$: C, 54.53; H, 5.82; S, 13.23. Found: C, 54.3; H, 6.1; S, 12.9.

5-Benzyl-5-ethyl-1,3,2-dioxathiane-2,2-dioxide (**2f**): R_f 0.44 (hexane/ethyl acetate: 2/1); t_r 14.70 min; m. p. 60°C (hexane/ethyl acetate); ν (KBr) 3050, 3020, 1600, 1495 (HC=C), 1400 and 1195 cm^{-1} (SO_2); δ_H 1.01 (3 H, t, *J*=7.6 Hz, Me), 1.40 (2 H, q, *J*=7.6 Hz, CH_2Me), 2.89 (2 H, s, CH_2Ph), 4.34, 4.47 (2 H each, 2 d, *J*=11.6 Hz each, 2xCH_2O) and 7.14-7.36 (5 H, m, ArH); δ_C 7.2 (Me), 22.4 (CH_2Me), 35.55 (CH_2Ph), 36.6 [$C(CH_2)_4$], 78.85 (2 C, 2xCO), 127.2, 128.65, 130.3 and 134.75 (ArC); *m/z* 256 (M^+, 1 %), 129 (23), 115 (12), 91 (100), 65 (27), 55 (25), 51 (13) and 41 (17). Anal. calcd. for $C_{12}H_{16}O_4S$: C, 56.23; H, 6.30; S, 12.49. Found: C, 56.0; H, 6.6; S, 12.1.

6-(2-Phenylethyl)-7,9-dioxa-8-thiaspiro[4,5]decane-8,8-dioxide (**2g**): R_f 0.66 (ethyl acetate); ν (film) 3062, 3027, 1496 (HC=C), 1396 and 1198 cm^{-1} (SO_2); δ_H 1.13-1.39, 1.55-1.88 (2 H and 7 H, respectively, 2 m, 4xCH_2 cyclopentane and 1xC*H*HCH$_2$Ph), 1.98-2.08 (1 H, m, 1xC*H*HCH$_2$Ph), 2.67 (1 H, dt, *J*=13.7, 8.2 Hz, 1xC*H*HPh), 2.94 (1 H, ddd, *J*=13.7, 9.2, 4.6 Hz, 1xC*H*HPh), 4.08, 4.44 (1 H each, 2 d, *J*=11.3 Hz each, CH_2O), 4.75 (1 H, dd, *J*=10.7, 1.5 Hz, CHO) and 7.19-7.34 (5 H, m, ArH); δ_C 25.45, 25.95, 28.9, 30.35, 31.15, 31.25 (4xCH_2 cyclopentane and CH_2CH_2Ph), 44.85 [$C(CH_2)_3$], 80.0 (CH_2O), 91.5 (CHO), 126.35, 128.55, 128.65 and 140.15 (ArC); *m/z* (DIP) 297 (M^++1, 1 %), 296 (M^+, 5), 118 (23), 117 (99), 105 (18), 104 (100), 92 (21), 91 (85), 81 (25), 79 (28), 78 (15), 77 (19), 67 (47), 65 (27), 55 (15), 53 (14), 51 (11) and 41 (42).

1-Benzyl-3,5-dioxa-4-thiabicyclo[4,4,0]decane-4,4-dioxide (**2h**) (diastereoisomers ratio 2:1); R_f 0.62 (ethyl acetate); ν (film) 3063, 3029, 1602, 1497 (HC=C), 1398 and 1198 cm^{-1} (SO_2); δ_H (major diast.) 0.88 (1 H, td, *J*=13.5, 4.1 Hz, 1xC*H*HCCH$_2$O), 1.45-2.06 [7 H, m, $(CH_2)_3$CHO and 1xC*H*HCCH$_2$O], 3.01, 3.08 (1 H each, 2 d, *J*=14.0 Hz each, CH_2Ph), 4.07 (1 H, d, *J*=11.3 Hz, 1xC*H*HO), 4.16 (1 H, dd, *J*=11.3, 1.2 Hz, 1xC*H*HO), 4.81-4.89 (1 H, m, CHO) and 7.06-7.35 (5 H, m, ArH); (minor diast.) 1.45-2.06 [8 H, m, $(CH_2)_4$], 2.55, 2.96 (1 H each, 2 d, *J*=14.0 Hz each, CH_2Ph), 3.79, 4.65 (1 H each, 2 d, *J*=11.6 Hz each, CH_2O), 4.81-4.89 (1 H, m, CHO) and 7.06-7.35 (5 H, m, ArH); δ_C (major diast.) 19.25, 23.95, 26.5, 29.0 [$(CH_2)_4$], 36.95 (*C*CO), 38.45 (CH_2Ph), 78.85 (CH_2O), 90.45 (CHO), 126.95, 128.55, 130.65 and 135.45 (ArC); (minor diast.) 18.95, 20.0, 24.45, 25.4 [$(CH_2)_4$], 35.75 (*C*CO), 38.45 (CH_2Ph), 80.15 (CH_2O), 88.3 (CHO), 127.4, 128.65, 129.95 and 134.05 (ArC); *m/z* (DIP) 283 (M^++1, < 1%), 282 (M^+, < 1), 93 (14), 92 (21), 91 (100), 79 (13), 65 (17) and 41 (15).

DTBB-Catalysed Lithiation of Cyclic Sulfates **2**. *Isolation of Cyclopropanes* **3**. *General Procedure*.- To a blue suspension of lithium powder (100 mg, 14 mmol) and DTBB (26 mg, 0.1 mmol) in THF (5 ml) was added the corresponding sulfate **2** (1 mmol) in THF (3 ml) during 30 min, at 0°C, under Ar. After 10 min of additional stirring at the same temperature, the resulting mixture was hydrolysed with water (5 ml) and extracted with ether (2x20 ml). The organic layer was dried over anhydrous sodium sulfate and evaporated (15 Torr). The resulting residue was purified by flash chromatography (silica gel, hexane) to give the pure title compounds **3**. Yields and R_f values are given in Table 1. Analytical, physical and spectroscopic data, as well as literature references for known compounds, follow.

*(4-*tert*-Butylbenzyl)cyclopropane* (**3a**): t_r 10.72 min; ν (film) 3070, 3000 (CH cyclopropane) and 1510 cm^{-1} (HC=C); δ_H 0.20 (2 H, dt, *J*=5.5, 4.6 Hz, 2xC*H*HCH$_2$), 0.52 (2 H, ddd, *J*=7.8, 5.5, 4.6 Hz, 2xC*H*HCH$_2$), 0.89-1.05 (1 H, m, CH$_2$C*H*CH$_2$), 1.32 (9 H, s, 3xMe), 2.52 (2 H, d, *J*=6.7 Hz, C*H*$_2$Ph), 7.21 and 7.32 (2 H each, 2 d, *J*=8.2 Hz each, ArH); δ_C 4.65 (2 C, 2xCH$_2$ cyclopropane), 11.75 (CH$_2$*C*HCH$_2$), 31.4 (3 C, 3xMe), 34.35 (*C*Me), 39.8 (*C*H$_2$Ph), 125.1, 127.95, 139.1 and 148.55 (ArC); *m/z* 189 (M^++1, 3 %), 188 (M^+, 23), 174 (14), 173 (100), 147 (45), 145 (17), 132 (26), 131 (29), 117 (16), 115 (11), 91 (16) and 55 (18) (Found: M^+, 188.1563. $C_{14}H_{20}$ requires M, 188.1565).

1-Benzyl-2-methylcyclopropane (**3b**)[26] (diastereoisomers ratio 3:1): t_r 7.73 (major diast.) and 8.28 min (minor diast.); ν (film) 3060, 3020 (CH cyclopropane), 1600 and 1490 cm^{-1} (HC=C); δ_H (major diast.) 0.25, 0.35 (1 H each, 2 dt, *J*=8.2, 4.6 Hz each, CH$_2$ ring), 0.58-0.76 (2 H, m, 2xCH ring), 1.05 (3 H, d, *J*=5.8 Hz, Me), 2.55 (2 H, d, *J*=6.7 Hz, C*H*$_2$Ph) and 7.15-7.32 (5 H, m, ArH); (minor diast.) -0.11 (1 H, dd, *J*=10.1, 5.2 Hz, 1xC*H*H ring), 0.58-0.76 (1 H, m, 1xCH*H* ring), 0.83-1.03 (2 H, m, 2xCH ring), 1.11 (3 H, d, *J*=6.1 Hz, Me), 2.56-2.71 (2 H, m, C*H*$_2$Ph) and 7.15-7.32 (5 H, m, ArH); δ_C (major diast.) 12.95 (1xCH ring), 13.0 (1xCH$_2$ ring), 18.8 (Me), 20.4 (1xCH ring), 39.9 (*C*H$_2$Ph), 125.7, 128.15, 128.2 and 142.3 (ArC); (minor diast.) 9.85 (1xCH ring), 12.25 (CH$_2$ ring), 13.5 (Me), 16.5 (1xCH ring), 34.25 (*C*H$_2$Ph), 125.6, 128.15, 128.2, 142.7 (ArC); *m/z* (major diast.) 148 (M^++2, < 1 %), 147 (M^++1, 2), 146 (M^+, 14), 131 (14), 117 (29), 115 (16), 105 (62), 104 (87), 103 (13), 92 (21), 91 (100), 78 (12), 77 (12), 65 (19) and 51 (11); (minor diast.) 147 (M^++1, < 1 %), 146 (M^+, 6), 117 (17), 105 (35), 104 (66), 92 (12), 91 (100) and 65 (14).

*1,1-Bis(4-*tert*-butylbenzyl)cyclopropane* (**3c**): t_r 17.58 min; m. p. 71-72°C (hexane/diethyl ether); ν (KBr) 3070, 3020 (CH cyclopropane), 3050 and 1510 cm^{-1} (HC=C); δ_H 0.50 (4 H, s, 2xCH$_2$ cyclopropane), 2.54 (4 H, s, 2xC*H*$_2$Ph), 7.13 and 7.30 (4 H each, 2 d, *J*=8.5 Hz each, ArH); δ_C 10.75 (2 C, 2xCH$_2$ cyclopropane), 20.9 (*C*CH$_2$Ph), 31.45 (6 C, 6xMe), 34.35 (2 C, 2x*C*Me), 41.05 (2 C, 2x*C*H$_2$Ph), 124.9, 129.15, 137.1 and 148.6 (ArC); *m/z* 335 (M^++1, 3 %), 334 (M^+, 11), 147 (56), 132 (12), 131 (19), 129 (25), 128 (21), 117 (48), 116 (11), 115 (35), 105 (15), 104 (16), 103 (10), 91 (58), 77 (11), 57 (100) and 41 (75). Anal. calcd. for $C_{25}H_{34}$·1/4 H_2O : C, 88.56; H, 10.26. Found: C, 88.8; H, 10.7.

1,1-Dibenzylcyclopropane (**3d**)[8b]: t_r 14.02 min; ν (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^+, 222.1413. $C_{17}H_{18}$ requires M, 222.1409).

1-Benzyl-1-methylcyclopropane (**3e**)[27]: t_r 7.48 min; ν (film) 3070, 3020 (CH cyclopropane), 1605, 1495 (HC=C); δ_H 0.31, 0.46 (2 H each, 2 dd, *J*=5.8, 4.0 Hz each, 2xCH_2 cyclopropane), 0.98 (3 H, s, Me), 2.56 (2 H, s, CH_2Ph), 7.19-7.30 (5 H, m, ArH); δ_C 12.5 (2 C, 2xCH_2 cyclopropane), 16.35 (*C*Me), 22.95 (Me), 45.05 (*C*H_2Ph), 125.85, 128.0, 129.25 and 140.7 (ArC); *m/z* 147 (M^++1, 1 %), 146 (M^+, 13), 131 (11), 118 (13), 117 (27), 115 (23), 92 (11), 91 (100), 89 (12), 77 (15), 65 (42), 63 (21), 55 (11), 51 (29), 50 (16) and 41 (12).

1-Benzyl-1-ethylcyclopropane (**3f**): t_r 8.72 min; ν (film) 3060, 3020 (CH cyclopropane), 1605 and 1490 cm^{-1} (HC=C); δ_H 0.29-0.34, 0.37-0.42 (2 H each, 2 m, 2xCH_2 ring), 0.90 (3 H, t, *J*=7.3 Hz, Me), 1.20 (2 H, q, *J*=7.3 Hz, CH_2Me), 2.58 (2 H, s, CH_2Ph) and 7.16-7.29 (5 H, m, ArH); δ_C 10.65 (Me), 11.15 (2 C, 2xCH_2 ring), 21.4 [*C*$(CH_2)_4$], 28.55 (*C*H_2Me), 41.3 (*C*H_2Ph), 125.85, 128.0, 129.3 and 140.5 (ArC); *m/z* 161 (M^++1, 4 %), 160 (M^+, 29), 131 (25), 117 (27), 115 (13), 104 (20), 92 (17), 91 (100), 69 (14), 68 (15), 65 (14) and 41 (11) (Found: M^+, 160.1257. $C_{12}H_{16}$ requires M, 160.1252).

1-(2-Phenylethyl)spiro[2,4]heptane (**3g**): t_r 12.17 min; ν (film) 3061, 3026 (CH cyclopropane), 3049 and 1496 cm^{-1} (HC=C); δ_H 0.05 (1 H, dd, *J*=5.2, 4.0 Hz, 1xC*H*H cyclopropane), 0.56 (1 H, dd, *J*=8.6, 4.0 Hz, 1xC*H*H cyclopropane), 0.65-0.74 (1 H, m, C*H*CH_2), 1.31-1.72 (10 H, m, 4xCH_2 cyclopentane and C$H_2$$CH_2$Ph), 2.68 (2 H, t, *J*=7.8 Hz, CH_2Ph) and 7.13-7.29 (5 H, m, ArH); δ_C 19.85, 26.15, 26.55, 30.15, 33.15, 36.35, 37.55 (7xCH_2), 23.15 (*C*HCH_2), 26.95 [*C*$(CH_2)_3$], 125.55, 128.2, 128.45 and 142.8 (ArC); *m/z* 201 (M^++1, 2 %), 200 (M^+, 13), 118 (14), 117 (16), 109 (21), 104 (48), 92 (14), 91 (100), 81 (10), 79 (13), 77 (15), 67 (73), 65 (32), 55 (11), 53 (10) and 41 (22) (Found: M^+, 200.1560. $C_{15}H_{20}$ requires M, 200.1565).

1-Benzylbicyclo[4.1.0]heptane (**3h**): t_r 11.01 min; ν (film) 3084, 3027 (CH cyclopropane), 3060, 1604 and 1495 cm^{-1} (HC=C); δ_H 0.24 (1 H, dd, *J*=5.5, 4.3 Hz, 1xCC*H*HCH), 0.54 (1 H, dd, *J*=9.2, 4.3 Hz, 1xCC*H*HCH), 0.90 (1 H, dddd, *J*=9.2, 7.3, 5.5, 1.8 Hz, C*H*CH_2), 1.05-1.47, 1.55-1.63, 1.90-1.97 (4 H, 3 H and 1 H, respectively, 3 m, 4xCH_2 ring), 2.51, 2.58 (1 H each, 2 d, *J*=14.2 Hz each, CH_2Ph) and 7.15-7.29 (5 H, m, ArH); δ_C 16.55 (CH_2 cyclopropane), 17.6 (CH cyclopropane), 19.85 (C cyclopropane), 21.5, 21.65, 24.05, 28.25 (4xCH_2 ring), 47.15 (*C*H_2Ph), 125.8, 127.95, 129.15 and 140.7 (ArC); *m/z* 187 (M^++1, 1 %), 186 (M^+, 9), 104 (12), 95 (100), 94 (63), 91 (42), 79 (17), 67 (26), 65 (13) and 41 (10) (Found: M^+, 186.1406. $C_{14}H_{18}$ requires M, 186.1409).

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