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Reductive ring opening of *cis*- and *trans*-2,3-diphenyloxirane: a common intermediate

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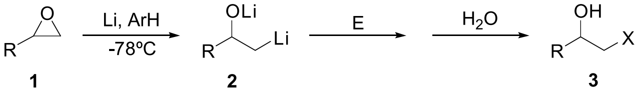
Abstract—The reaction of both *cis*- and *trans*-2,3-diphenyloxirane (**7** and **4**, respectively) with an excess of lithium and a catalytic amount of 4,4′-di-*tert*-butylbiphenyl (DTBB, 2.5 mol%) in the presence of different carbonyl compounds as electrophiles (Barbier conditions) in THF at temperatures ranging between −80 and −50 °C gives the same organolithium intermediate **5** and consequently, the same 1,3-diols **6**. In the case of *cis*-epoxide an inversion of the configuration at the benzylic carbanionic center can explain the obtained results. Only for the dicyclopropyl ketone derivative (**6h**) some amount (14%) of the corresponding epimer (**6′h**) resulting from a process with retention of the configuration of the intermediate is obtained. In representative cases, the structure of the final products (**6**) was unequivocally determined by X-ray diffraction analysis.

1. Introduction

In the last few years, functionalized organolithium compounds[1] have emerged as synthetically useful intermediates able to transfer their functionality to electrophilic reagents, making accessible polyfunctionalized molecules in only one synthetic operation. One problem associated to this type of compounds is that, due to their high reactivity, they have to be prepared and manipulated at low temperature, so the lithiation step is a crucial process. For this reason, about ten years ago, we developed an arene-catalyzed lithiation[2–5] as a convenient methodology in order to perform lithiation reactions under very mild reaction conditions. Among the different applications of this methodology is the ring opening of heterocycles, which is a direct way to generate functionalized organolithium intermediates.[6] For instance, epoxide **1** can be opened using a lithium-arene (stoichiometric version)[7] or lithium and a catalytic amount of an arene (catalytic version)[8] at low temperature, so a regioselective ring opening takes place to give the most stable primary β-oxide functionalized organolithium intermediate **2**, which by reaction with electrophiles gives, after hydrolysis, the expected products **3** (Scheme 1).



Scheme 1.

In this paper we describe the application of the arene-catalyzed lithiation to the ring opening of *cis*- and *trans*-2,3-diphenyloxirane in order to study the stereochemistry of the process, specially in the lithiation step.[9]

2. Results and discussion

The treatment of *trans*-2,3-diphenyloxirane (**4**) with an excess of lithium powder (1:7 molar ratio; theoretical 1:4) and a catalytic amount of 4,4′-di-*tert*-butylbiphenyl (DTBB, 1:0.05 molar ratio) in the presence of the corresponding carbonyl compound as electrophile[10] (1:2 molar ratio) in THF at temperatures ranging between −80 and −50 °C

Keywords: Epoxides; Reductive ring opening; DTBB-catalyzed lithiation; 1,3-Diols.

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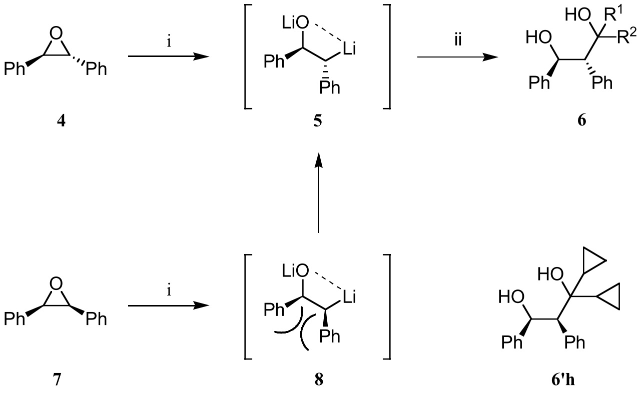
gave, after hydrolysis with water, the expected 1,3-diols **6** (Scheme 2). Both the intermediate **5** and the final products **6** keep the stereochemistry of the initial stereocenters of the starting material **4**. Surprisingly, when we started from *cis*-2,3-diphenyloxirane (**7**), the same process (under the same reaction conditions and using the same electrophiles) afforded the same products **6** with the same stereochemistry than before. In this reaction, the corresponding intermediate **8**, which (like in the case of **5**) possesses a rather rigid structure due to the coordination of the negatively charged oxide with the lithium atom (CIPE),[11] suffers a benzylic inversion at the carbanionic center[12] giving the more stable intermediate **5**, so the same products **6** obtained from the epoxide **4** were isolated (Scheme 2 and Table 1). Concerning reaction conditions, higher temperature (0 °C) gave worse results because variable amounts of the corresponding pinacol were obtained, their separation from the desired product being not easy. On the other hand, when the reaction shown in Scheme 2 was carried out step-by-step (Grignard conditions), yields were slightly lower than those obtained with Barbier conditions.



Scheme 2. Reagents and conditions: (i) Li, DTBB (2.5% molar), E (R^1R^2CO)=Bu^tCHO, c-$C_6H_{11}CHO$, PhCHO, Me_2CO, Et_2CO, $(CH_2)_5CO$, Pr^i_2CO, $(c$-$C_3H_5)_2CO$, THF −78 to −50 °C; (ii) H_2O, −50 °C to rt.

As it can be seen in Table 1, yields are in general modest. In spite the complete conversion (total disappearance of the starting material at the end of the reaction), important amounts of the 'reduced' product 1,2-diphenyl-1-ethanol (resulting from a proton abstraction of intermediate **5** or/and **8** from the reaction media)[13] are obtained together with products **6**. Even so, the reaction can be used for synthetic purposes because the separation of both products is very easy by flash chromatography. On the other hand, it is worthy to note that no products having the configuration of the intermediate **8** (from the starting epoxide **7**) have been detected from the reaction crude, except in the case of using dicyclopropyl ketone as electrophile, in which a 7:1 mixture of diastereomers (**6h**:**6′h**) was obtained in favor of compound **6h**. The minor diastereomer **6′h** was isolated from the corresponding mixture mechanically (at the microscope plate) in order to get its whole characterization. Finally, when benzaldehyde was used as prostereogenic electrophile, only one diastereomer (**6c**) was isolated having (1*S**,3*S**) configuration, its structure having been determined by NMR experiments. We do not have any explanation for this result.

Due to the stereochemical aspects of the reaction shown in Scheme 2 the structure of some compounds **6** (and **6′h**) was determined not only by NMR experiments, but also by X-ray crystallography (Chart 1 and Table 2), in which a hydrogen-bond is observed in the solid state in all cases. The same observation was found by NMR in solution (see Section 4).

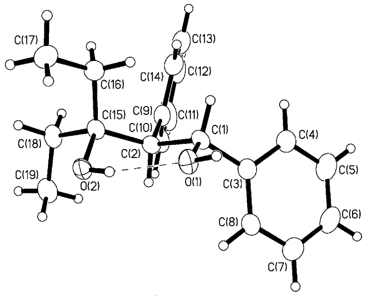
3. Conclusion

In conclusion, we report here that the DTBB-catalyzed lithiation of both *cis*- and *trans*-2,3-diphenyloxirane (**7** and **4**, respectively) gives the same intermediate **5**, so after reaction with different carbonyl compounds the same 1,3-diols **6** were stereoselectively obtained, these products being the expected ones coming from the *trans*- starting material **4** without changing the configuration of both oxiranyl stereocenters. In the case of the *cis*-epoxide **7**, a benzylic

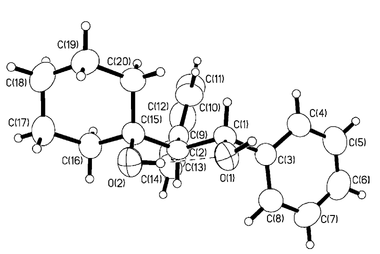
Table 1. Preparation of compounds **6**

Entry	Electrophile	Product			Yield (%)[a]	
		No.	R^1	R^2	From **4**	From **7**
1	Bu^tCHO	**6a**	H	Bu^t	35[b]	32[c]
2	c-$C_6H_{11}CHO$[d]	**6b**	H	c-C_6H_{11}[d]	20[e]	30[f]
3	PhCHO	**6c**	H	Ph	20[g]	31[g]
4	Me_2CO	**6d**	Me	Me	35	50
5	Et_2CO	**6e**	Et	Et	60	40
6	$(CH_2)_5CO$	**6f**	$(CH_2)_5$		41	38
7	Pr^i_2CO	**6g**	Pr^i	Pr^i	25	76
8	$(c$-$C_3H_5)_2CO$[h]	**6h**	c-C_3H_5	c-C_3H_5[h]	31	79[i]

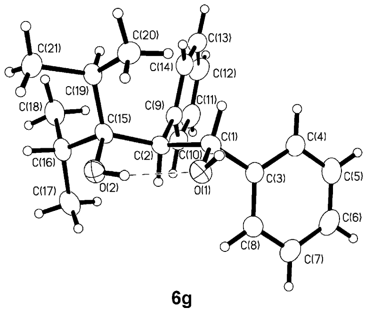
[a] Isolated yield after flash chromatography (silica gel, hexane/ethyl acetate) based on the starting epoxides **4** or **7**.
[b] 2.8:1 Diastereomeric mixture (^{1}H NMR).
[c] 2.1:1 Diastereomeric mixture (^{1}H NMR).
[d] c-C_6H_{11} = cyclohexyl.
[e] 1.3:1 Diastereomeric mixture (^{1}H NMR).
[f] 1.5:1 Diastereomeric mixture (^{1}H NMR).
[g] Only the diastereomer with the (1*S**,3*S**) configuration was obtained (^{1}H NMR from the crude mixture).
[h] c-C_3H_5 = cyclopropyl.
[i] A 7:1 mixture of compounds **6**:**6′h** was obtained (^{1}H NMR).



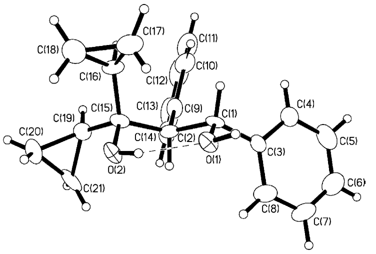
6e



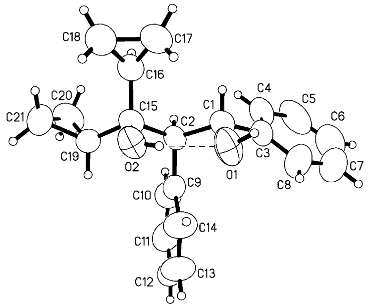
6f



6g



6h



6′h

Chart 1.

inversion in the initially obtained organolithium intermediate **8** leads to the same intermediate **5**. Only in the case of the dicyclopropyl ketone an small amount (about 14%) of the corresponding product **6′h** without inversion was obtained.

4. Experimental

4.1. General

For general information see Ref. 5. X-ray analyses were performed at the Universities of Zaragoza and Purdue, the corresponding details being given below. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AC-300 using $CDCl_3$ as solvent and TMS as internal standard.

4.2. DTBB-catalyzed lithiation of *cis*- and *trans*-2,3-diphenyloxirane 4 and 7. Preparation of compounds 6

To a cooled green suspension of lithium (49 mg, 7 mmol) and DTBB (13 mg, 0.05 mmol) in THF (3 mL) at −80 °C was slowly added (ca. 45 min) a solution of the corresponding electrophile (2 mmol) and *cis* or *trans*-2,3-diphenyloxirane (200 mg, 1 mmol) in THF (2 mL). The resulting mixture was stirred for 2 h allowing the temperature to rise to −50 °C and then it was hydrolyzed with water (5 mL) allowing the temperature to rise to 20 °C. The resulting mixture was extracted with ethyl acetate (3×10 mL). The organic layer was dried over anhydrous $MgSO_4$ and evaporated (15 Torr). The resulting residue was then purified by flash chromatography (silica gel, hexane/ethyl acetate) to give the desired compounds **6**, which were recrystallized in hexane/ethyl acetate. Yields are given in Table 1; physical, analytical spectroscopic data as well as literature references for the known compounds **6c** and **6d** follow.

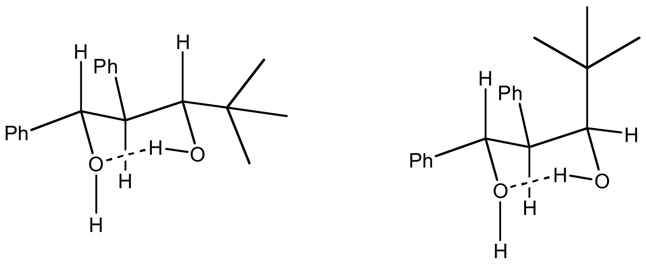
4.2.1. (1*S,2*R**,3*R**/*S**)-4,4-Dimethyl-1,2-diphenyl-1,3-pentanediol (6a).** Diastereomeric mixture. 1:2.78. t_r= 15.3 (major), 15.5 (minor) min; R_f (hexane/ethyl acetate 8:2)=0.13, 0.14; mp 166 °C; ν (film) 3261 (OH), 3085, 3060, 3026, 1603 cm^{-1} (C=CH); δ_H 0.69 [9H, s, $(CH_3)_3$, minor], 0.85 [9H, s, $(CH_3)_3$, major], 3.06–3.11 (2H, m,

Table 2. Crystallographic data of compounds **6e–h** and **6′h**

	6e	**6f**	**6g**	**6h**	**6′h**
Crystallized from	Hexane/ethyl acetate	Hexane/ethyl acetate	Hexane/ethyl acetate	Hexane/ethyl acetate	Hexane/ethyl acetate
Empirical formula	$C_{19}H_{24}O_2$	$C_{20}H_{24}O_2$	$4(C_{21}H_{28}O_2)$, C_6H_{14}	$C_{21}H_{24}O_2$	$C_{21}H_{24}O_2$
Formula weight [g mol^{-1}]	284.38	296.39	1335.91	308.40	308.40
Crystal color, habit	Colorless, plate	Colorless, block	Colorless, block	Colorless, block	Colorless, block
Crystal dimensions [mm]	0.20×0.12×0.07	0.18×0.13×0.11	0.22×0.21×0.13	0.20×0.150×0.125	0.15×0.07×0.06
Temperature [K]	100(1)	291(1)	100(1)	150(1)	291(1)
Crystal system	Orthorhombic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_12_12_1$	$C2/c$	$P\bar{1}$	Cc	$P2_1/c$
Z	4	8	2	4	4
Reflections for cell determination	2192	1453	3000	1475	575
2θ Range for cell determination [°]	4.62–42.68	5.2–40.10	4.48–49.94	5.7–49.32	4.8–31.4
Unit cell parameters					
a [Å]	9.8420(7)	23.324(2)	14.6635(10)	11.3406(17)	9.9482(11)
b [Å]	10.5542(8)	8.3651(8)	14.6931(10)	17.198(3)	20.549(2)
c [Å]	15.8826(12)	17.2572(17)	18.8287(13)	9.1699(14)	9.2011(10)
α, β, γ [°]	90, 90, 90	90, 100.457(2), 90	84.3680(10), 76.3420(10), 89.8380(10)	90, 102.953(10), 90	90, 110.290(2), 90
V [Å^3]	1649.8(2)	3311.1(5)	3922.1(5)	1742.9(5)	1764.2(3)
D_x [g cm^{-3}]	1.145	1.189	1.131	1.175	1.161
$\mu(\mathrm{MoK}_\alpha)$ [mm^{-1}]	0.072	0.075	0.070	0.074	0.073
Transmission factors (min; max)	0.799; 0.995	0.9217; 0.9918	0.8875; 0.9909	—; —	0.9151; 0.9956
$2\theta_{\max}$ [°]	50	50	50	49.32	50
Total reflections measured	12,196	11,828	29,044	1475	12,861
Symmetry-independent reflections	1691	2925	13,809	1475	3105
Reflections with $I>2\sigma(I)$	1479	1859	7715	1280	1064
Reflections used in refinement	1691	2925	13,809	1475	3105
Parameters refined	194	201	909	210	211
$R(F)$ [$I>2\sigma(I)$ reflections]	0.0367	0.0435	0.0568	0.0880	0.0647
$wR(F^2)$ (all data)	0.0905	0.1137	0.1213	0.2677	0.1264
Weighting parameters [a;b][a]	0.05; 0.0963	0.0539; 0.0722	0.0330; 0.0	0.2; 1.6929	0.03; 0.0
Goodness-of-fit	1.066	1.014	0.990	1.049	0.950
Secondary extinction coefficients	—	—	—	—	0.0058(10)
Final $\Delta_{\max}/\sigma$	0.005	0.000	0.001	0.013	0.008
$\Delta\rho$ (max; min) [eÅ^{-3}]	0124; −0.162	0.115; −0.170	0.214; −0.208	0.306; −0.321	0.151; −0.134

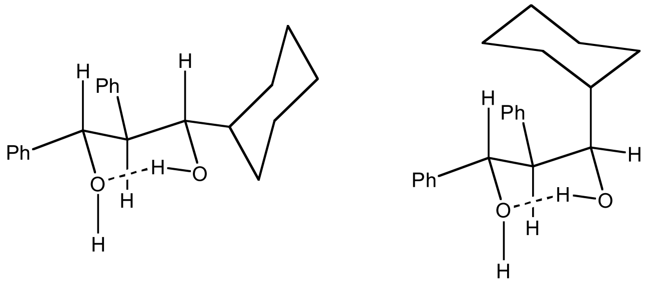
[a] $w=[\sigma^2(F_o^2)+(aP)^2+bP]^{-1}$, where $P=(F_o^2+2F_c^2)/3$.

PhC*H*COH), 3.62 (4H, br s, 2×OH), 3.99 (1H, d, $J=6.9$ Hz, Me_3CC*H*OH, major), 4.02 (1H, d, $J=1.9$ Hz, Me_3CC*H*OH, minor), 4.98 (1H, d, $J=9.5$ Hz, PhC*H*OH, major), 5.03 (1H, d, $J=7.1$ Hz, PhC*H*OH, minor), 6.84–7.33 (20H, m, ArH); δ_C 26.1, 26.8 (CH_3), 35.5, 37.0 (Me_3*C*), 53.7, 54.7 (Ph*C*HCOH), 77.7, 79.0 (Me_3C*C*OH), 84.7 (Ph*C*HOH), 125.9, 126.3, 126.9, 127.0, 127.1, 127.6, 127.9, 128.0, 129.0, 130.5 (ArCH), 140.1, 142.6, 143.4 (ArC); *m*/*z* (minor) 251 (M^+-H_2O-Me, 1%), 181 (17), 180 (30), 179 (11), 160 (62), 146 (12), 145 (100), 105 (13), 91 (27), 79 (13), 77 (17), 57 (14); HRMS (minor): M^+-H_2O, found 266.1691. $C_{19}H_{22}O$ requires 266.1671; *m*/*z* (major) 266 (M^+-H_2O, 1%), 180 (27), 179 (11), 160 (59), 146 (12), 145 (100), 120 (10), 107 (17), 105 (10), 91 (28), 79 (16), 77 (18), 57 (15); HRMS (major): M^+-H_2O, found 266.1707. $C_{19}H_{22}O$ requires 266.1671. Anal. Calcd for $C_{19}H_{24}O_2\cdot H_2O$: C, 75.46; H, 8.67. Found: C, 75.69; H, 7.98%.



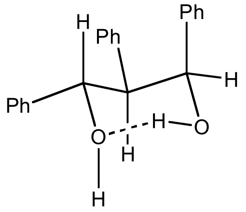
(major) **6a** (minor)

4.2.2. (1*S,2*R**,3*R**/*S**)-1-Cyclohexyl-2,3-diphenyl-1,3-propanediol (6b).** Diastereomeric mixture. 1:1.35. $t_r=17.5$ (minor), 17.6 (major) min; R_f (hexane/ethyl acetate 8:2)=0.21, 0.22; mp 186 °C; ν (film) 3402 (OH), 3093, 3060, 3026 cm^{-1} (C=CH); δ_H 0.79–0.90, 1.02–1.48, 1.55–1.67 (22H, 3m, ringCH, 5×ringCH_2), 3.01–3.11 (2H, m, Ph*CH*COH), 3.24 (4H, br s, 2×OH), 4.04 (1H, br d, J=8.8 Hz, Cy*CH*OH, minor), 4.15 (1H, br d, J=8.2 Hz, Cy*CH*OH, major), 5.03 (1H, d, J=9.2 Hz, Ph*CH*OH, major), 5.35 (1H, d, J=3.2 Hz, Ph*CH*OH, minor), 6.81–7.17 (20H, m, ArH); δ_C 24.3, 25.4, 25.9, 26.3, 26.4, 29.4, 29.7, 30.5, 30.6 (ringCH$_2$), 40.2, 40.4 (ringCH), 54.8, 55.7 (Ph*C*HCOH), 74.9, 76.9 (Cy*C*OH), 80.6, 80.7 (Ph*C*HOH), 126.4, 126.9, 127.0, 127.2, 127.7, 127.8, 127.9, 128.1, 128.8, 129.9 (ArCH), 138.2, 139.2, 142.4, 142.8 (ArC); m/z (minor) 292 (M^+-H_2O, 1%), 186 (47), 180 (52), 179 (17), 129 (11), 107 (11), 105 (21), 104 (100), 95 (10), 91 (27), 79 (16), 77 (17), 55 (17); HRMS (minor): $M^+-2\times H_2O$, found 274.1680. $C_{21}H_{22}$ requires 274.1721; m/z (major) 274 ($M^+-2\times H_2O$, 1%), 186 (50), 180 (23), 129 (11), 107 (14), 105 (20), 104 (100), 95 (10), 91 (25), 79 (17), 77 (16), 55 (15); HRMS (major): $M^+-2\times H_2O$, found 274.1715. $C_{21}H_{22}$ requires 274.1721. Anal. Calcd for $C_{21}H_{26}O_2\cdot 1/3H_2O$: C, 79.71; H, 8.49. Found: C, 79.68; H, 8.29%.



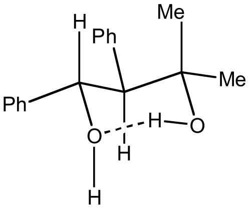
(major) **6b** (minor)

4.2.3. (1*S,3*S**)-1,2,3-Triphenyl-1,3-propanediol (6c).**[14] t_r=17.7 min; R_f (hexane/ethyl acetate 8:2)=0.13; mp 130 °C; ν (film) 3408 (OH), 3085, 3061, 3028, 1602 cm^{-1} (C=CH); δ_H 3.22 [1H, dd, J=3.2, 7.8 Hz, Ph*CH*(COH)$_2$], 3.50 (2H, br s, 2×OH), 5.18 (1H, d, J=7.8 Hz, Ph*CH*OH), 5.34 (1H, d, J=3.2 Hz, Ph*CH*OH), 6.84–7.19 (15H, m, ArH); δ_C 59.2 [Ph*C*H(COH)$_2$], 74.2, 76.0 (Ph*C*HOH), 126.4, 126.5, 126.9, 127.0, 127.5, 127.7, 128.1, 130.1 (ArCH), 137.4, 142.1, 142.9 (ArC); m/z 268 ($M^+-2\times H_2O$, 1%), 181 (15), 180 (100), 179 (32), 178 (11), 165 (16), 107 (14), 105 (21), 91 (13), 79 (18), 77 (26); HRMS: M^+-H_2O, found 286.1315. $C_{21}H_{18}O$ requires 286.1358. Anal. Calcd for $C_{21}H_{20}O_2$: C, 82.85; H, 6.63. Found: C, 82.52; H, 6.40%.



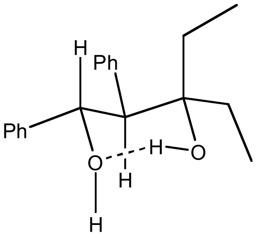
6c

4.2.4. (1*S,2*R**)-3-Methyl-1,2-diphenyl-1,3-butanediol (6d).**[15] t_r=14.6 min; R_f (hexane/ethyl acetate 8:2)=0.13; mp 98 °C; ν (film) 3328 (OH), 3026, 1602 cm^{-1} (C=CH); δ_H 0.94, 1.54 (3H, 3H, 2s, 2×CH$_3$), 3.09 (1H, d, J=10.8 Hz, Ph*CH*COH), 4.45, 4.70 (2H, 2br s, 2×OH), 5.26 (1H, d, J=10.8 Hz, Ph*CH*OH), 7.06–7.14 (10H, m, ArH); δ_C 24.4, 30.6 (CH$_3$), 62.6 (Ph*C*HCOH), 74.8 (Me$_2$*C*OH), 77.3 (Ph*C*HOH), 126.5, 127.1, 127.3, 127.9 (ArCH), 139.2, 143.1 (ArC); m/z 238 (M^+-H_2O, 1%), 181 (12), 180 (82), 179 (40), 178 (17), 165 (20), 133 (11), 132 (100), 117 (47), 115 (10), 107 (12), 105 (16), 91 (24), 79 (16), 77 (25), 59 (11); HRMS: $M^+-2\times H_2O$, found 220.1532. $C_{17}H_{16}$ requires 220.1552. Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.94; H, 7.94%.



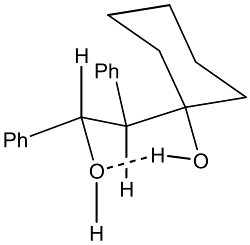
6d

4.2.5. (1*S,2*R**)-3-Ethyl-1,2-diphenyl-1,3-pentanediol (6e).** t_r=15.8 min; R_f (hexane/ethyl acetate 8:2)=0.76; mp 141 °C; ν (film) 3261 (OH), 3080, 3066, 3026, 1602 cm^{-1} (C=CH); δ_H 0.76 (3H, t, J=7.3 Hz, CH$_3$), 0.99 (3H, t, J=7.3 Hz, CH$_3$), 1.09, 1.57, 1.76, 2.12 (4H, 4m, 2×CH$_2$), 3.23 (1H, d, J=10.2 Hz, Ph*CH*COH), 3.82 (2H, br s, 2×OH), 5.24 (1H, d, J=10.2 Hz, Ph*CH*OH), 7.08 (10H, br s, ArH); δ_C 7.3, 7.6 (CH$_3$), 27.9, 30.0 (CH$_2$), 59.8 (Ph*C*HCOH), 77.4 (Et$_2$*C*OH), 78.2 (Ph*C*HOH), 126.4, 126.9, 127.1, 127.8 (ArCH), 139.2, 143.6 (ArC); m/z 266 (M^+-H_2O, 1%), 181 (15), 180 (100), 179 (32), 178 (13), 165 (16), 160 (51), 131 (15), 107 (10), 105 (13), 91 (24), 79 (14), 77 (18), 57 (30); HRMS: $M^+-2\times H_2O$, found 248.1580. $C_{19}H_{20}$ requires 248.1565.



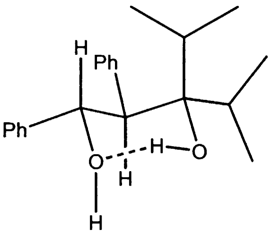
6e

4.2.6. (1*S,2*R**)-1-(2-Hydroxy-1,2-diphenylethyl)-1-cyclohexanol (6f).** t_r=17.2 min; R_f (hexane/ethyl acetate 8:2)=0.24; mp 205 °C; ν (film) 3248 (OH), 3087, 3026, 1602 cm^{-1} (C=CH); δ_H 0.82–1.04, 1.28–1.80, 2.14–2.17 (10H, 3m, 5×ringCH$_2$), 2.97 (2H, br s, 2×OH), 3.13 (1H, d, J=10.6 Hz, Ph*CH*COH), 5.35 (1H, d, J=10.6 Hz, Ph*CH*OH), 7.06–7.17 (10H, m, ArH); δ_C 21.2, 21.6, 25.6, 31.5, 38.0 (ringCH$_2$), 63.4 (Ph*C*HCOH), 75.4 [(CH$_2$)$_5$*C*OH], 76.8 (Ph*C*HOH), 126.5, 127.0, 127.4, 127.8, 127.9 (ArCH), 139.1, 143.4 (ArC); m/z 278 (M^+-H_2O, 1%), 181 (15), 180 (100), 179 (30), 178 (13), 172 (49), 165 (16), 129 (13), 107 (10), 105 (14), 104 (16), 91 (25), 81 (23), 79 (19), 77 (20); HRMS: $M^+-2\times H_2O$, found 260.1545. $C_{20}H_{20}$ requires 260.1565. Anal. Calcd for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16. Found: C, 81.94; H, 8.40%.



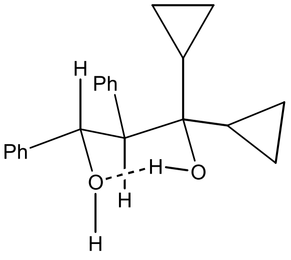
6f

4.2.7. (1*S,2*R**)-3-Isopropyl-4-methyl-1,2-diphenyl-1,3-pentanediol (6g).** $t_r = 16.7$ min; R_f (hexane/ethyl acetate 8:2) = 0.45; mp 142 °C; ν (film) 3261 (OH), 3087, 3066, 3033, 1609 cm^{-1} (C=CH); δ_H 0.44 (3H, d, $J = 6.9$ Hz, CH_3), 0.92 (3H, d, $J = 6.7$ Hz, CH_3), 1.04 (3H, d, $J = 6.9$ Hz, CH_3), 1.35 (3H, d, $J = 6.7$ Hz, CH_3), 1.79, 2.52 (2H, 2m, 2× CH), 3.39 (1H, d, $J = 10.3$ Hz, PhC*H*COH), 4.44 (2H, br s, 2×OH), 5.34 (1H, d, $J = 10.3$ Hz, PhC*H*OH), 6.93–7.30 (10H, m, ArH); δ_C 17.6, 18.8, 19.3 (CH_3), 32.1, 37.0 (CH), 57.3 (Ph*C*HCOH), 79.6 (Ph*C*HOH), 82.1 (Pr^i_2*C*OH), 126.2, 126.9, 127.5, 127.6 (ArCH), 139.2, 144.3 (ArC); *m/z* 276 ($M^+ - 2\times H_2O$, 1%), 188 (12), 181 (15), 180 (100), 179 (26), 178 (11), 165 (13), 146 (10), 145 (83), 107 (13), 105 (15), 91 (29), 79 (16), 77 (19), 71 (48); HRMS: $M^+ - 2\times H_2O$, found 276.1865. $C_{21}H_{24}$ requires 276.1878. Anal. Calcd for $C_{21}H_{28}O_2$: C, 80.72; H, 9.04. Found: C, 80.09; H, 9.06%.



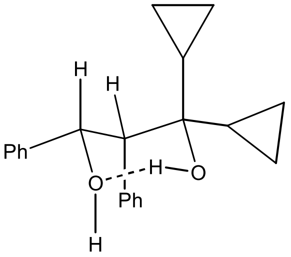
6g

4.2.8. (1*S,2*R**)-1,1-Dicyclopropyl-2,3-diphenyl-1,3-propanediol (6h).** $t_r = 16.96$ min; R_f (hexane/ethyl acetate 8:2) = 0.41; mp 115 °C; ν (film) 3335 (OH), 3087, 3060, 3006, 1690 cm^{-1} (C=CH); δ_H 0.13–0.19, 0.22–0.29, 0.35–0.41, 0.47–0.60, 0.74–0.78, 1.43–1.58 (10H, 6m, 2× ringCH, 4×ringCH$_2$), 3.27 (1H, d, $J = 10.9$ Hz, PhC*H*COH), 1.58, 3.63 (2H, 2br s, 2×OH), 5.61 (1H, d, $J = 10.9$ Hz, PhC*H*OH), 7.04–7.35 (10H, m, ArH); δ_C −1.3, −0.2, 1.2, 1.3 (ringCH$_2$), 15.8, 19.0 (ringCH), 62.3 (Ph*C*HCOH), 74.2 (Ph*C*HOH), 126.3, 127.3, 127.4, 127.9 (ArCH), 138.7, 143.1 (ArC); *m/z* 184 (17), 181 (15), 180 (100), 179 (28), 178 (10), 169 (19), 165 (16), 156 (10), 155 (26), 154 (11), 153 (13), 143 (28), 142 (14), 141 (41), 129 (18), 128 (45), 127 (11), 115 (33), 106 (47), 105 (51), 91 (37), 79(10), 78 (15), 77 (57), 69 (21), 51 (26); HRMS: $M^+ - 2\times H_2O$, found 272.1581. $C_{21}H_{20}$ requires 272.1565.



6h

4.2.9. (1*R,2*R**)-1,1-Dicyclopropyl-2,3-diphenyl-1,3-propanediol (6′h).** $t_r = 17.01$ min; R_f (hexane/ethyl acetate 8:2) = 0.39; mp 156 °C; ν (film) 3335 (OH), 3089, 3058, 3003, 1690 cm^{-1} (C=CH); δ_H 0.01–0.09, 0.22–0.27, 0.33–0.40, 0.41–0.51, 0.54–0.61, 0.72–0.85 (10H, 6m, 2×ringCH, 4×ringCH$_2$), 2.94 (1H, d, $J = 2.5$ Hz, PhC*H*COH), 2.48, 3.32 (2H, 2br s, 2×OH), 6.01 (1H, d, $J = 2.3$ Hz, PhC*H*OH), 6.98–7.14 (10H, m, ArH); δ_C 0.0, 0.2, 1.2, 1.6 (ringCH$_2$), 16.7, 20.8 (ringCH), 62.6 (Ph*C*HCOH), 74.6 (Ph*C*HOH), 125.9, 126.3, 126.6, 127.2, 127.6, 131.4 (ArCH), 137.4, 143.0 (ArC); *m/z* (major) 249 ($M^+ - H_2O–C_3H_5$, 1%), 184 (19), 181 (16), 180 (100), 179 (23), 169 (17), 165 (13), 154 (21), 143 (25), 142 (11), 141 (31), 129 (14), 128 (33), 115 (25), 111 (15), 106 (31), 105 (41), 91 (34), 79 (13), 78 (11), 77 (46), 69 (33), 51 (19); HRMS: $M^+ - 2\times H_2O$, found 272.1579. $C_{21}H_{20}$ requires 272.1565.



6′h

4.3. X-ray analysis

Diffraction data were taken in a Bruker Smart CCD diffractometer (for compounds **6e**, **6f**, **6g** and **6′h**) at the University of Zaragoza and in a Kappa CCD apparatus (for compound **6h**) at Purdue University. Crystal data are summarized in Table 2 and have been deposited at the Cambridge Crystallographic Data Centre.

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