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Arene-catalysed lithiation of phenyl- and 1,1-diphenylcyclopropane: synthetic applications

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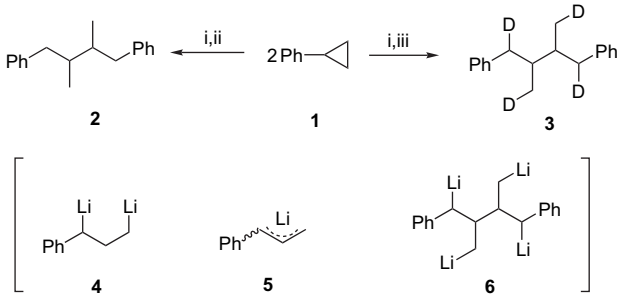
This paper is dedicated to Professor Adalbert Maercker, a pioneer in dilithium compounds chemistry, on the occasion of his 75th birthday

Abstract—The reaction of phenylcyclopropane (**1**) with an excess of lithium and a catalytic amount of DTBB (2.5% molar) in THF at room temperature, followed by treatment with an electrophile [Me_3SiCl, $PhMe_2SiCl$, *t*-BuCHO, PhCHO, Me_2CO, Et_2CO, $(CH_2)_5CO$, adamantan-2-one, *i*-Pr_2CO, di(cyclopropyl)ketone] and final hydrolysis with water leads to allylic products **10** or **11** depending on the structure of the electrophile: whereas for chlorosilanes or crowded ketones γ-products **11** are isolated, for aldehydes and non-congested ketones α-products **10** are formed. The application of the same protocol to 1,1-diphenylcyclopropane (**7**) leads to a mixture of products **13**–**15** resulting from the introduction of one or two electrophilic fragments to the open-chain mono- or dilithiated intermediate: also in this case the regiochemistry of the reaction is governed by steric reasons.

1. Introduction

From an electronic point of view, cyclopropanes are more similar to olefins than to other cycloalkanes: in fact, instead of having a 25% s-character (corresponding to a pure sp^3-hybridised carbon atom) in the simplest cyclopropane the carbon–hydrogen bonds have a 33% s-character whereas the carbon–carbon bonds have a 17% s-character.[1] These electronic characteristics are a consequence of the great strain of the small cyclopropane ring, which also has an important influence on its reactivity, so the cyclopropane ring usually suffers easy ring opening by means of different reagents. Concerning the lithiation of cyclopropane derivatives with lithium metal, it does not work with non-activated systems (cyclopropane itself or alkylated derivatives),[2] but cyclopropanes substituted by unsaturated groups, such as vinyl or phenyl moieties, can be used for the reductive ring opening: in this case, the electron transfer from the metal goes to the π* orbital of the substituent and from there it is transferred to the low energy adjacent σ* orbital of a carbon–carbon bond of the cyclopropane ring, thus facilitating its cleavage giving initially the corresponding radical anion stabilised by resonance.[3] Recently Maercker et al. reported[4] that the lithiation of phenylcyclopropane (**1**) with lithium metal in THF at room temperature required ultrasonication and more than one day to take place. After quenching with MeOH or MeOD the dimer **2** or **3** was obtained, intermediates **4**–**6** being proposed to be involved in the process (Scheme 1). It is supposed that after generation of the dilithio derivative **4** a β-elimination of lithium hydride took place (it was isolated and characterised) giving the delocalised allyllithium derivative **5**, which under the assayed reaction conditions, and through a new electron transfer process, undergoes dimerisation to form the corresponding dimeric tetralithio intermediate **6** as a mixture of diastereomers. Final treatment with MeOH or MeOD affords the final product **2** or **3** (Scheme 1).



Scheme 1. Reagents and conditions: (i) Li, THF,))), 20 °C; (ii) MeOH; (iii) MeOD.

In the case of 1,1-diphenylcyclopropane (**7**), its lithiation took place under milder reaction conditions (Li, THF, −30 °C, 5 h) than for phenylcyclopropane giving, after

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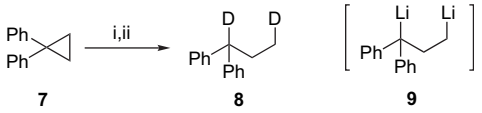
quenching with MeOD, the dideuterio compound **8** with high deuterium incorporation (96%). Here the proposed more stable dilithio intermediate **9** behaves differently than **4** not suffering dimerisation (Scheme 2).[4]



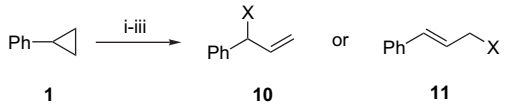
Scheme 2. Reagents and conditions: (i) Li, THF, −30 °C; (ii) MeOD.

In this paper we study the application of an arene-catalysed lithiation[5] to the reductive ring opening of both phenyl- and 1,1-diphenylcyclopropane (**1** and **7**, respectively) in order to trap the intermediates **4** (or **5**) and **9**,[6] respectively, with different electrophiles to explore the synthetic possibilities of the reductive ring opening of the starting materials **1** and **7**.

2. Results and discussion

2.1. Lithiation of phenylcyclopropane (1)

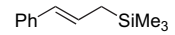
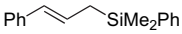
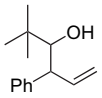
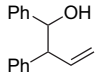
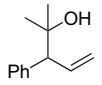
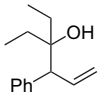
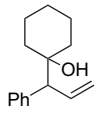
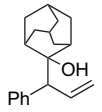
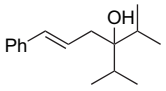
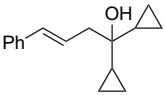
The reaction of commercially available phenylcylopropane (**1**) with an excess of lithium (1/7 molar ratio; theoretical 1/2 molar ratio)[7] and a catalytic amount of 4,4′-di-*tert*-butylbiphenyl (DTBB; 1/0.05 molar ratio; 2.5% molar) in THF for 4 h at room temperature afforded, after treatment with a chlorosilane or a carbonyl compound as electrophile [E=Me_3SiCl, $PhMe_2SiCl$, *t*-BuCHO, PhCHO, Me_2CO, Et_2CO, $(CH_2)_5CO$, adamantan-2-one, *i*-Pr_2CO, di(cyclopropyl)ketone] at 0 °C and final hydrolysis with water, the corresponding allylic compounds **10** or **11** (Scheme 3 and Table 1).[8]



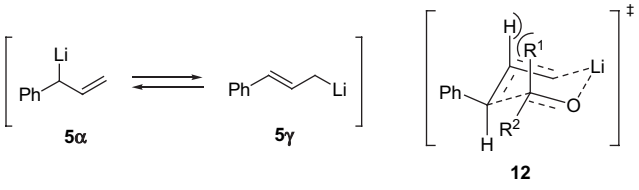
Scheme 3. Reagents and conditions: (i) Li, DTBB (2.5% molar), THF, rt, 4 h; (ii) E=Me_3SiCl, $PhMe_2SiCl$, *t*-BuCHO, PhCHO, Me_2CO, Et_2CO, $(CH_2)_5CO$, adamantan-2-one, *i*-Pr_2CO, di(cyclopropyl) ketone, 0 °C, 30 min; (iii) H_2O, 0 °C to rt, 1 h.

The result of this reaction clearly indicates that under the assayed conditions, the initially formed dilithio intermediate **4** suffers rapid lithium hydride elimination to give the allylic intermediate **5**, which is the real lithium reagent in the reaction with the electrophile. The reaction is rather regioselective depending on the nature and/or structure of the electrophile and is governed by steric reasons: with bulky chlorosilanes only (*E*)-allylic products **11a**,**b** were isolated (γ-substitution; Table 1, entries 1 and 2), no other products from the reaction with the electrophile [either **10c**,**d** or (*Z*)-**11c**,**d**] being detected (<5%) from the crude reaction mixture.[9] When a sterically non-hindered carbonyl compound was used as electrophile an α-substitution was always observed yielding compounds **10c–h** (Table 1, entries 3–8), whereas for crowded ketones like di(cyclopropyl) ketone or di(isopropyl) ketone products **11i**,**j** resulting from a γ-attack were the only reaction products isolated (Table 1, entries 9 and 10). It seems that for non-bulky carbonyl compounds the reaction works through the intermediate **5α** and the chair-like transition state **12**,[10] since for bulky electrophiles the less congested intermediate **5γ** takes part exclusively in the reaction.[11] In the case of using aldehydes as electrophiles, the corresponding mixture of diastereomers was obtained (Table 1, entries 3 and 4), the major one being the *anti*-configurated, the expected one according to the model **12** for the corresponding transition state.

Table 1. Lithiation of phenylcyclopropane (**1**) and reaction with electrophiles—isolation of products **10** or **11**

Entry	Electrophile	Product[a]	No.	Yield[b] (%)
1	Me_3SiCl		**11a**	44
2	$PhMe_2SiCl$		**11b**	40
3	*t*-BuCHO		**10c**	42[c]
4	PhCHO		**10d**	34[d]
5	Me_2CO		**10e**	59
6	Et_2CO		**10f**	45
7	$(CH_2)_5CO$		**10g**	56
8	Adamantan-2-one		**10h**	38
9	*i*-Pr_2CO		**11i**	42[e]
10	Di(cyclopropyl) ketone		**11j**	51[f]

[a] All products **10** and **11** were >95% pure (GLC and 300 MHz ^{1}H NMR).
[b] Isolated yield after purification by column chromatography (silica gel, hexane/ethyl acetate) based on the starting phenylcyclopropane (**1**).
[c] A 4/1 *anti*/*syn* diastereomer (^{1}H NMR) mixture was obtained.
[d] A 1.5/1 *anti*/*syn* diastereomer (^{1}H NMR) mixture was obtained.
[e] A ca. 10% of the corresponding saturated alcohol was also detected (GC–MS).
[f] A 9% of the corresponding saturated alcohol was also detected (GC–MS).

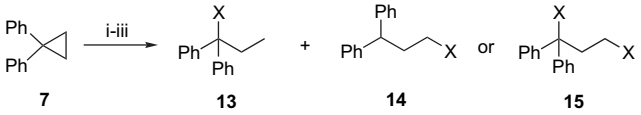


Concerning the role of the arene as catalyst in the electron transfer reaction from the metal to the substrate to be lithiated, in the absence of DTBB the starting material **1** was

recovered under the same reaction conditions shown in Scheme 3. The use of a stoichiometric amount of lithium (**1**/Li, 1/2.1 molar ratio) and the same amount of the arene (2.5% molar) led to a low conversion (less than 40%) under the same reaction conditions. Finally, when the stoichiometric version of the DTBB-promoted reaction was used (**1**/LiDTBB, 1/2.1 molar ratio) under the same reaction conditions, only about 30% conversion was observed.[7,12]

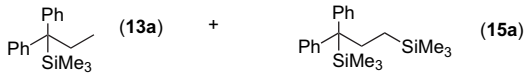
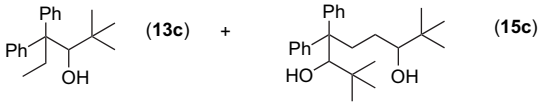
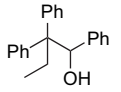
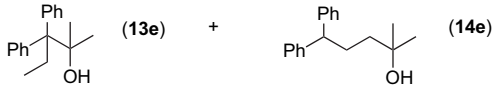
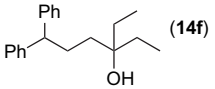
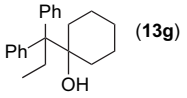
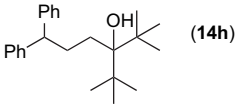
2.2. Lithiation of 1,1-diphenylcyclopropane (7)

When the same reaction shown in Scheme 3 was applied to 1,1-diphenylcyclopropane (**7**),[13] but using a little bit more catalyst loading (ca. 4% molar ratio) and lower temperature (−50 °C) for the S_E step, compounds **13–15** were obtained (Scheme 4 and Table 2). In this case, the intermediate **9** initially formed, instead of suffering elimination of lithium hydride, takes partially or totally a proton from the reaction medium[14] to generate the monolithiated intermediates **16**, which afford final compounds **13** and **14**. In some cases, for very reactive electrophiles such as chlorosilanes (Table 2, entries 1 and 2) and pivalaldehyde (Table 2, entry 3) the dianion **9** could be trapped, so the corresponding disubstituted compounds **15** were also isolated. In general for carbonyl compounds, products **13** (resulting from the intermediate **16α**) were mainly (Table 2, entries 3 and 5) or exclusively (Table 2, entries 4 and 7) obtained, except for dialkyl ketones for which compounds **14** (resulting from the intermediate **16γ**) were partially (Table 2, entry 5) or totally (Table 2, entries 6 and 8) formed. Thus, for the lithiated intermediates from 1,1-diphenylcyclopropane (**7**) (see species **9** and **16**) we found a reactivity parallel to that reported in Table 1: for hindered ketones the less congested γ-attack is preferred to the corresponding α-one indicating that steric factors play an important role in the regiochemistry of the process. From a preparative point of view it is worthy to note that in general compounds **13–15** have been separated and purified chromatographically, so they could be easily isolated in pure form.



Scheme 4. Reagents and conditions: (i) Li, DTBB (4% molar), THF, 0 °C, 1.5 h; (ii) E=Me_3SiCl, $PhMe_2SiCl$, *t*-BuCHO, PhCHO, Me_2CO, Et_2CO, *i*-Pr_2CO, $(CH_2)_5CO$, −50 °C, 30 min; (iii) H_2O, −50 °C to rt, 1 h.

Table 2. Lithiation of 1,1-diphenylcyclopropane (**7**) and reaction with electrophiles (E)—isolation of products **13–15**

Entry	Electrophile	Products[a]	Yield[b] (%)
1	Me_3SiCl		19+36
2	$PhMe_2SiCl$		15+54
3	*t*-BuCHO		55+23[c]
4	PhCHO		47
5	Me_2CO		56+6
6	Et_2CO		50
7	$(CH_2)_5CO$		42
8	*t*-Bu_2CO		48

[a] All products **13–15** were >95% pure (GLC and 300 MHz ^{1}H NMR).
[b] Isolated yield after purification by column chromatography (silica gel, hexane/ethyl acetate) based on the starting material **7**.
[c] Only one diastereomer was detected by NMR and GLC.

3. Conclusions

The chemistry described here showed that the reductive opening of both phenylcyclopropane and 1,1-diphenylcyclopropane using an arene-catalysed lithiation could have synthetic applications where the cyclopropyl ring starting materials are readily available. This procedure is applicable to the preparation of polyfunctionalised molecules, especially alcohol derivatives, the regioselectivity of the process being rationalised considering mainly steric factors of both the lithiated intermediate and the electrophile used.

4. Experimental

4.1. General

For general information, see Ref. 15. All lithiation reactions were carried out under argon atmosphere in oven-dried glassware. All commercially available reagents (Acros, Aldrich, Fluka) were used without further purification (chlorotrimethylsilane and benzaldehyde were distilled before use). Commercially available anhydrous THF (99.9%, water content $\leq$0.006%, Fluka) was used as solvent in all the lithiation reactions. IR spectra were measured (film) with a Nicolet Impact 400 D-FT Spectrometer. NMR spectra were recorded in the Technical Services of the University of Alicante with a Bruker AC-300 or Bruker AC-400 spectrometer using $CDCl_3$ as solvent and TMS as internal standard; chemical shifts are given in parts per million and coupling constants (J) are given in hertz. ^{13}C NMR assignments were made on the basis of DEPT experiments. LRMS were measured with Shimadzu GC/HS QP-5000 and Hewlett–Packard EM/CG-5973A spectrometers, and HRMS were measured in the Technical Services of the University of Alicante with a Finnigan MAT95 S spectrometer, fragment ions in m/z with relative intensities (%) in parentheses. The purity of volatile products and the chromatographic analyses (GLC) were determined with a Hewlett–Packard HP-6890 instrument equipped with a flame ionisation detector and a 30 m HP-5 capillary column (0.32 mm diam., 0.25 μm film thickness), using nitrogen (2 mL/min) as carrier gas, $T_{injector}$=275 °C, $T_{detector}$=300 °C, T_{column}=60 °C (3 min) and 60–270 °C (15 °C/min), P=40 kPa; retention times (t_R) are given under these conditions. Thin layer chromatography (TLC) was carried out on Merck plastic sheets coated with silica gel 60 F_{254}. Melting points were obtained with an MPA100 Optimelt SRS apparatus. Lithium powder, which can be prepared from commercially available lithium granules (99%, high sodium content, Aldrich) as it was already reported by us,[16] was supplied by Medalchemy S.L. and Chemetall GmbH.

4.2. DTBB-catalysed lithiation of cyclopropylbenzene (1). Isolation of compounds 10 and 11. General procedure

To a green suspension of lithium powder (49 mg, 7 mmol), and DTBB (13 mg, 0.05 mmol) in THF (3 mL) was added dropwise cyclopropylbenzene (0.130 mL, 1 mmol) at room temperature and the resulting mixture was stirred for 4 h at the same temperature. To the resulting deep red solution was added the corresponding electrophile (1.2 mmol) and the solution was stirred at 0 °C for 30 min. Then it was hydrolysed with water (5 mL) allowing the temperature to rise to room temperature. The resulting mixture was extracted with diethyl ether (3×5 mL) and the organic layer was dried over anhydrous $MgSO_4$ and evaporated (15 Torr). The resulting residue was then purified by column chromatography (silica gel, hexane/ethyl acetate) to yield the title products. Yields are included in Table 1; physical, spectroscopic and analytical data, as well as literature references for known compounds, follow.

4.2.1. (*E*)-3-Trimethylsilyl-1-phenyl-1-propene (11a). Colourless oil, 88 mg; t_R=10.5 min; R_f (hexane/ethyl acetate 8/2)=0.89; ν (film) 3061 (=CH) cm^{-1}; δ_H (300 MHz) 0.00 (9H, s, 3×CH_3), 1.62 (2H, d, J=6.7, CH_2), 6.18–6.22 (2H, m, CH=CH), 7.08–7.28 (5H, m, 5×ArH); δ_C (75 MHz) −1.9 (CH_3), 23.9 (CH_2), 125.5, 126.2, 127.8, 128.2, 128.4 (CH=CH, ArCH), 138.5 (ArC); m/z 190 (M^+, 31%), 115 (11), 73 (100).[17]

4.2.2. (*E*)-3-Dimethylphenylsilyl-1-phenyl-1-propene (11b). Colourless oil, 106 mg; t_R=15.4 min; R_f (hexane/ethyl acetate 8/2)=0.73; ν (film) 3068 (=CH) cm^{-1}; δ_H (400 MHz) 0.32 (6H, s, 2×CH_3), 1.90 (2H, d, J=6.8, CH_2), 6.20–6.24 (2H, m, CH=CH), 7.14–7.54 (10H, m, 10×ArH); δ_C (100 MHz) −3.3 (CH_3), 23.0 (CH_2), 125.5, 126.3, 127.1, 127.8, 128.4, 128.9, 129.1, 133.6 (CH=CH, ArCH), 138.4, 138.5 (ArC); m/z 252 (M^+, 11%), 136 (14), 135 (100).[18]

4.2.3. *syn/anti*-2,2-Dimethyl-4-phenyl-5-hexen-3-ol (10c). Colourless oil, 90 mg; t_R (*anti*-isomer)=11.7 min, t_R (*syn*-isomer)=11.5 min; R_f (hexane/ethyl acetate 8/2)=0.86 (*anti*+*syn*-isomers); ν (film) 3456 (OH), 3062 (=CH) cm^{-1}; δ_H (400 MHz) 0.88 [9H, s, $C(CH_3)_3$ *syn*-isomer], 0.91 [9H, s, $C(CH_3)_3$ *anti*-isomer], 1.46 (1H, d, J=4.1, CHO*H* *syn*-isomer), 1.75 (1H, d, J=4.6, CHO*H* *anti*-isomer), 3.53–3.63 (2H, m, C*H*CH=CH_2, C*H*OH *anti*+*syn*-isomers), 5.00–5.17 (2H, m, CHCH=CH_2 *anti*+*syn*-isomers), 6.11–6.18 (1H, m, CHC*H*=CH_2 *syn*-isomer), 6.20–6.30 (1H, m, CHC*H*=CH_2 *anti*-isomer), 7.17–7.32 (5H, m, 5×ArH, *anti*+*syn*-isomers); δ_C (100 MHz) 26.7 (CH_3 *anti*-isomer), 26.8 (CH_3 *syn*-isomer), 35.9 [*C*$(CH_3)_3$ *syn*-isomer], 36.0 [*C*$(CH_3)_3$ *anti*-isomer], 52.8 (*C*HCH=CH_2 *anti*-isomer), 53.8 (*C*HCH=CH_2 *syn*-isomer), 81.5 (CHOH *syn*-isomer), 81.6 (CHOH *anti*-isomer), 114.8 (CH_2 *syn*-isomer), 117.2 (CH_2 *anti*-isomer), 126.3, 127.9, 128.6 (ArCH *anti*-isomer), 126.7, 128.7, 128.9 (ArCH *syn*-isomer), 138.9 (CH*C*H=CH_2 *anti*+*syn*-isomers), 141.6 (ArC *syn*-isomer), 144.5 (ArC *anti*-isomer); m/z (*anti*-isomer) 186 (M^+-H_2O), 119 (10), 118 (100), 117 (61), 115 (21), 91 (17), 87 (17), 69 (14); m/z (*syn*-isomer) 186 (M^+, 1%), 129 (10), 119 (11), 118 (100), 117 (61), 115 (19), 91 (15), 87 (16), 69 (13).[19]

4.2.4. *syn/anti*-1,2-Diphenyl-3-buten-1-ol (10d). Colourless oil, 80 mg; t_R (*anti*+*syn*-isomers)=14.7 min; R_f (hexane/ethyl acetate)=0.34; ν (film) 3425 (OH), 3061 (=CH) cm^{-1}; δ_H (300 MHz) 1.95 (1H, s, OH *anti*-isomer), 2.32 (1H, s, OH *syn*-isomer), 3.55 (1H, dd, J=8.3, C*H*CH=CH_2 *anti*-isomer), 3.63 (1H, dd, J=8.1, 8.0, C*H*CH=CH_2 *syn*-isomer), 4.82–5.00 (3H, m, C*H*OH *anti*+*syn*-isomers, CH=CH_2 *anti*+*syn*-isomers), 5.84–5.96 (1H, m, C*H*=CH_2 *syn*-isomer), 6.18–6.31 (1H, m, C*H*=CH_2

anti-isomer), 7.33–7.43 (10H, m, 10×ArH *anti*+*syn*-isomers); δ_C (75 MHz) 58.5 (C*H*CH=CH_2 *syn*-isomer), 59.2 (C*H*CH=CH_2 *anti*-isomer), 117.2 (CH_2 *syn*-isomer), 118.4 (CH_2 *anti*-isomer), 126.6, 126.6, 127.0, 127.4, 127.8, 127.9, 128.1, 128.3, 128.7, 128.7 (ArCH *anti*+*syn*-isomers), 137.6 (*C*H=CH_2 *anti*-isomer), 137.8 (*C*H=CH_2 *syn*-isomer), 140.6, 141.8 (ArC *anti*+*syn*-isomers); *m/z* (*anti*-isomer) 206 (M^+-H_2O, 6%), 119 (10), 118 (100), 117 (45), 116 (10), 115 (28), 107 (78), 91 (14), 79 (48), 77 (29); *m/z* (*syn*-isomer) 206 (M^+-H_2O, 5%), 119 (10), 118 (100), 117 (45), 116 (10), 115 (28), 107 (79), 91 (14), 79 (45), 77 (27).[20]

4.2.5. 2-Methyl-3-phenyl-4-penten-2-ol (10e). Colourless oil, 108 mg; t_R=10.0 min; R_f (hexane/ethyl acetate 8/2)=0.20; ν (film) 3440 (OH), 3062 (=CH) cm^{-1}; δ_H (400 MHz) 1.17 (3H, s, CH_3), 1.21 (3H, s, CH_3), 1.60 (1H, s, OH), 3.27 (1H, d, *J*=9.7, C*H*CH=CH_2), 5.12–5.22 (2H, m, CH=CH_2), 6.25–6.37 (1H, m, C*H*=CH_2), 7.20–7.35 (5H, m, 5×ArH); δ_C (100 MHz) 27.6, 27.8 (CH_3), 61.8 (*C*HCH=CH_2), 72.2 (COH), 117.8 (CH=*C*H_2), 126.7, 128.3, 129.1 (ArCH), 137.7 (*C*H=CH_2), 141.1 (ArC); *m/z* 161 (M^+-CH_3, 1%), 119 (10), 118 (100), 117 (87), 116 (12), 115 (35), 91 (18), 59 (57).[21]

4.2.6. 3-Ethyl-4-phenyl-5-hexen-3-ol (10f). Colourless oil, 97 mg; t_R=12.0 min; R_f (hexane/ethyl acetate 8/2)=0.53; ν (film) 3479 (OH), 3062 (=CH) cm^{-1}; δ_H (400 MHz) 0.82 (3H, dd, *J*=7.6, 7.3, CH_3), 0.88 (3H, dd, *J*=7.6, 7.3, CH_3), 1.20–1.29 (1H, m, C$H_2$$CH_3$), 1.30–1.38 (1H, m, C$H_2$$CH_3$), 1.58 (1H, s, OH), 3.34 (1H, d, *J*=9.6, C*H*CH=CH_2), 5.07–5.15 (2H, m, CH=CH_2), 6.27–6.37 (1H, m, C*H*=CH_2), 7.19–7.33 (5H, m, 5×ArH); δ_C (100 MHz) 7.6, 7.7 (CH_3), 28.1, 28.7 (CH_2CH_3), 57.3 (*C*HCH=CH_2), 76.0 (COH), 116.7 (CH=*C*H_2), 126.5, 128.3, 129.2 (ArCH), 138.0 (*C*H=CH_2), 141.4 (ArC); *m/z* 186 (M^+-H_2O, 1%), 119 (10), 118 (100), 117 (49), 116 (11), 115 (33), 91 (17), 87 (84), 69 (15), 57 (36).[22]

4.2.7. 1-(1-Phenylallyl)-1-cyclohexanol (10g). Colourless oil, 127 mg; t_R=13.7 min; R_f (hexane/ethyl acetate 8/2)=0.44; ν (film) 3443 (OH), 3061 (=CH) cm^{-1}; δ_H (300 MHz) 1.11–1.73 (10H, m, 5×ring CH_2), 3.24 (1H, d, *J*=9.7, C*H*CH=CH_2), 5.07–5.18 (2H, m, CH=CH_2), 6.25–6.38 (1H, m, C*H*=CH_2), 7.19–7.33 (5H, m, 5×ArH); δ_C (75 MHz) 21.8, 25.6, 35.5, 35.8 (4×ring CH_2), 61.0 (*C*HCH=CH_2), 72.6 (COH), 117.3 (CH=*C*H_2), 126.5, 128.2, 129.2 (ArCH), 137.6 (*C*H=CH_2), 140.9 (ArC); *m/z* 198 (M^+-H_2O, 1%), 119 (11), 118 (100), 117 (38), 115 (26), 99 (59), 91 (13), 81 (53), 55 (11).[23]

4.2.8. 2-(1-Phenylallyl)-2-adamantanol (10h). White solid, 107 mg; mp 117 °C; t_R=17.2 min; R_f (hexane/ethyl acetate 8/2)=0.62; ν (KBr) 3574 (OH), 3061 (=CH) cm^{-1}; δ_H (400 MHz) 0.67–2.35 (14H, m, 10×ring CH_2, 4×ring CH), 3.97 (1H, d, *J*=9.5, C*H*CH=CH_2), 5.06–5.15 (2H, m, CH=CH_2), 6.27–6.37 (1H, m, C*H*=CH_2), 7.02–7.36 (5H, m, 5×ArH); δ_C (100 MHz) 27.0, 27.1 (2×ring CH), 32.9, 33.2, 33.4, 34.1 (4×ring CH_2), 34.4, 34.9 (2×ring CH), 38.4 (1×ring CH_2), 53.6 (*C*HCH=CH_2), 75.9 (COH), 116.5 (CH=*C*H_2), 126.5, 128.3, 129.2, 137.6 (*C*H=CH_2, ArCH), 141.2 (ArC); *m/z* 250 (M^+-H_2O, 5%), 152 (12), 151 (100), 118 (33), 117 (10), 91 (14).[24]

4.2.9. (*E*)-3-Isopropyl-2-methyl-6-phenyl-5-hexen-3-ol (11i). Colourless oil, 102 mg; t_R=14.7 min; R_f (hexane/ethyl acetate 8/2)=0.38; ν (film) 3485 (OH), 3059 (=CH) cm^{-1}; δ_H (400 MHz) 0.96–1.01 [12H, m, 2×CH(CH_3)$_2$], 1.98 [2H, m, C*H*(CH_3)$_2$], 2.47 (2H, d, *J*=7.5, CH_2), 6.22–6.29 (1H, m, ArCH=C*H*), 6.44 (1H, d, *J*=15.9, ArC*H*=CH), 7.17–7.36 (5H, m, 5×ArH); δ_C (100 MHz) 17.3, 17.6 [CH(CH_3)$_2$], 34.2 [*C*H(CH_3)$_2$], 37.6 (CH_2), 77.4 (COH), 126.0, 126.8, 127.0, 128.5, 132.4 (CH=CH, ArCH), 137.5 (ArC); *m/z* 214 (M^+-H_2O, 2%), 189 (27), 118 (42), 117 (36), 116 (11), 115 (72), 91 (21), 71 (100), 55 (13).[19]

4.2.10. (*E*)-1,1-Dicyclopropyl-4-phenyl-3-buten-1-ol (11j). Brownish oil, 120 mg; t_R=15.3 min; R_f (hexane/ethyl acetate 8/2)=0.36; ν (film) 3576, 3474 (OH), 3088 (=CH) cm^{-1}; δ_H (300 MHz) 0.30–0.46 (8H, m, 4×ring CH_2), 0.85–0.92 (2H, m, 2×ring CH), 2.50 (2H, d, *J*=6.1, CH=CHCH_2), 6.36–6.49 (2H, m, CH=CH), 7.20–7.38 (5H, m, 5×ArH); δ_C (75 MHz) −0.5, 0.8 (ring CH_2), 18.8 (ring CH), 46.3 (CH=CH*C*H_2), 70.9 (COH), 126.0, 126.2, 127.1, 128.5, 132.9 (CH=CH, ArCH), 137.6 (ArC); *m/z* 211 (M^+-OH, 15%), 210 (84), 195 (22), 182 (16), 181 (37), 179 (13), 178 (13), 169 (12), 168 (17), 167 (87), 166 (29), 165 (53), 155 (11), 154 (22), 153 (29), 152 (31), 141 (33), 129 (22), 128 (29), 119 (43), 117 (26), 116 (10), 115 (48), 105 (13), 103 (10), 92 (11), 91 (100), 79 (10), 77 (19), 65 (10); HRMS: M^+-H_2O, found 210.1400, $C_{16}H_{18}$ requires 210.1409.

4.3. Preparation of 1,1-diphenylcyclopropane (7)

To a mixture of $LiAlH_4$ (20 mmol) in THF (30 mL) at 0 °C, was added dropwise a solution of 1,1-dibromo-2,2-diphenylcyclopropane[12] (15 mmol) in THF (15 mL) and the solution was stirred at room temperature overnight. The resulting mixture was cooled at 0 °C and was hydrolysed with H_2O (1 mL), NaOH 10% (1 mL) and H_2O again (3 mL), filtered through Celite, dried over anhydrous $MgSO_4$ and evaporated (15 Torr). The resulting white solid was dissolved in THF (30 mL) and the solution was cooled at −30 °C, then 18 mL of *n*-butyllithium (1.6 M in hexane) was added dropwise, the mixture was stirred for 45 min and then it was hydrolysed with water (10 mL) allowing the temperature to rise to room temperature. The solution was extracted with hexane (3×10 mL) and the organic layer was dried over $MgSO_4$ and evaporated (15 Torr) to obtain 13.1 mmol of pure 1,1-diphenylcyclopropane (>95% GLC). Its spectroscopic and chromatographic data are similar to those described in the literature.[13]

4.4. DTBB-catalysed lithiation of 1,1-diphenylcyclopropane (7). Isolation of compounds 13–15. General procedure

To a green suspension of lithium powder (49 mg, 7 mmol), and DTBB (20 mg, 0.075 mmol) in THF (2 mL) was added dropwise 1,1-diphenylcyclopropane (1 mmol) at 0 °C and the resulting mixture was stirred for 1.5 h at the same temperature. Then the red solution was cooled at −50 °C and the corresponding electrophile (2 mmol) was added dropwise and stirred for 30 min. The resulting mixture was hydrolysed with water (5 mL) allowing the temperature to rise to room temperature, and then it was extracted with

diethyl ether (3×5 mL), the organic layer was dried over anhydrous $MgSO_4$ and evaporated (15 Torr). The resulting residue was then purified by column chromatography (silica gel, hexane/ethyl acetate) to yield the title compounds. Yields are included in Table 2; physical, spectroscopic and analytical data, as well as literature references for known compounds, follow.

4.4.1. 1,1-Diphenylpropyl(trimethyl)silane (13a). Colourless oil, 54 mg; t_R=14.8 min; R_f (hexane/ethyl acetate 8/2)=0.78; δ_H (300 MHz) 0.05 [9H, s, Si(CH_3)$_3$], 0.78 (3H, t, J=7.2, CH_2CH_3), 2.23 (2H, q, J=7.2, CH_2), 7.15–7.33 (10H, m, 10×ArH); δ_C (75 MHz) −1.0 [Si(CH_3)$_3$], 9.0 (CH_2CH_3), 28.4 (CH_2), 45.1 (CSi), 124.7, 127.5, 129.7 (ArCH), 145.7 (ArC); *m/z* 268 (M^+, 14%), 240 (11), 195 (22), 194 (80), 193 (11), 165 (16), 135 (29), 115 (12), 91 (16), 73 (100); HRMS: M^+, found 268.1687, $C_{18}H_{24}Si$ requires 268.1647.

4.4.2. 1,1-Diphenyl-1,3-bis(trimethylsilyl)-propane (15a). Colourless oil, 129 mg; t_R=16.0 min; R_f (hexane/ethyl acetate 8/2)=0.83; ν (film) 3056 (=CH) cm^{-1}; δ_H (300 MHz) 0.00 [9H, s, Si(CH_3)$_3$], 0.05 [9H, s, Si(CH_3)$_3$], 0.30–0.37 (2H, m, CH_2Si), 2.14–2.20 (2H, m, CCH_2), 7.15–7.32 (10H, m, 10×ArH); δ_C (75 MHz) −1.8, −0.9 [Si(CH_3)$_3$], 10.4 (CH_2Si), 29.9 (CCH_2), 46.0 (CSi), 124.7, 127.5, 129.7 (ArCH), 145.7 (ArC); *m/z* 340 (M^+, 16%), 267 (15), 266 (53), 252 (25), 224 (35), 135 (22), 73 (100); HRMS: M^+, found 340.2063, $C_{21}H_{32}Si_2$ requires 340.2043.

4.4.3. 1,1-Diphenylpropyl(dimethyl)phenylsilane (13b). Colourless oil, 52 mg; t_R=18.7 min; R_f (hexane/ethyl acetate 8/2)=0.77; ν (film) 3052 (=CH) cm^{-1}; δ_H (300 MHz) 0.29 [6H, s, Si(CH_3)$_2$], 0.65 (3H, t, J=7.2, CH_2CH_3), 2.24 (2H, q, J=7.2, CH_2), 7.09–7.36 (15H, m, 15×ArH); δ_C (75 MHz) −2.9 [Si(CH_3)$_2$], 8.7 (CH_2CH_3), 28.6 (CH_2), 45.8 (CCH_2), 124.9, 127.2, 127.4, 127.7, 128.7, 129.9, 133.0, 135.0 (ArCH), 138.2, 144.6 (ArC); *m/z* 330 (M^+, 4%), 194 (30), 136 (14), 135 (100); HRMS: M^+, found 330.1805, $C_{23}H_{26}Si$ requires 330.1804.

4.4.4. 1,1-Diphenyl-1,3-bis(dimethylphenylsilyl)-propane (15b). Colourless oil, 261 mg; t_R=28.5 min; R_f (hexane/ethyl acetate 8/2)=0.71; ν (film) 3067, 3051 (=CH) cm^{-1}; δ_H (300 MHz) 0.19 [6H, s, Si(CH_3)$_2$], 0.23 [6H, s, Si(CH_3)$_2$], 0.40–0.50 (2H, m, CH_2Si), 2.12–2.19 (2H, m, CCH_2), 7.01–7.43 (20H, m, 20×ArH); δ_C (75 MHz) −3.3, −2.9 (CH_3), 9.1 (CH_2Si), 30.3 (CCH_2), 46.7 (CCH_2), 124.8, 127.2, 127.4, 127.7, 128.7, 128.8, 129.9, 133.6, 134.9 (ArCH), 138.1, 139.0, 144.5 (ArC); *m/z* 464 (M^+, 1%), 328 (15), 314 (13), 253 (11), 252 (45), 136 (14), 135 (100); HRMS: M^+, found 464.2365, $C_{31}H_{36}Si_2$ requires 464.2356.

4.4.5. 2,2-Dimethyl-4,4-diphenyl-3-hexanol (13c). Colourless oil, 160 mg; t_R=16.7 min; R_f (hexane/ethyl acetate 8/2)=0.61; ν (film) 3585 (OH), 3057 (=CH) cm^{-1}; δ_H (400 MHz) 0.61 (3H, dd, J=7.3, 7.1, CH_2CH_3), 0.77 [9H, s, C(CH_3)$_3$], 2.02 (1H, dt, J=14.2, 7.1, CH_2), 2.13 (1H, d, J=4.4, OH), 2.60 (1H, dt, J=14.2, 7.3, CH_2), 4.29 (1H, d, J=4.4, CH), 7.24–7.41 (8H, m, 8×ArH), 7.55–7.57 (2H, m, 2×ArH); δ_C (100 MHz) 10.1 (CH_2CH_3), 28.4 [C(CH_3)$_3$], 31.4 (CH_2), 37.0 [C(CH_3)$_3$], 57.6 (CCH_2), 82.6 (CH), 125.8, 126.4, 127.4, 128.0, 128.7, 130.6 (ArCH), 141.2, 146.3 (ArC); *m/z* 264 (M^+-H_2O, 1%), 197 (10), 196 (59), 195 (17), 168 (14), 167 (100), 165 (14), 117 (11), 91 (19); HRMS: M^+-H_2O, found 264.1861, $C_{20}H_{24}$ requires 264.1878.

4.4.6. 2,2,8,8-Tetramethyl-4,4-diphenyl-3,7-nonanediol (15c). Colourless oil, 88 mg; t_R=20.3 min; R_f (hexane/ethyl acetate 8/2)=0.42; ν (film) 3454 (OH), 3056 (=CH) cm^{-1}; δ_H (400 MHz) 0.65 [9H, s, C(CH_3)$_3$], 0.69 [9H, s, C(CH_3)$_3$], 1.01–1.09 (2H, m, CH_2CH), 1.35 (1H, d, J=5.5, CH_2CHOH), 1.73–1.81 (1H, m, CCH_2), 2.16 (1H, d, J=4.1, Ph_2CCHOH), 2.85–2.88 (1H, m, CH_2CH), 2.93–3.01 (1H, m, CCH_2), 4.22 (1H, d, J=4.1, Ph_2CCH), 7.16–7.56 (10H, m, 10×ArH); δ_C (100 MHz) 25.4 (CH_3), 27.5 (CH_2CH), 28.4 (CH_3), 34.8, 36.6 [C(CH_3)$_3$], 37.0 (CCH_2), 57.3 (CCH_2), 80.8 (CH_2CH), 83.2 (Ph_2CCH), 126.0, 126.4, 127.4, 128.1, 128.5, 130.7 (ArCH), 141.1, 146.4 (ArC); *m/z* 293 [$M^+-H_2O-C(CH_3)_3$, 2%], 193 (23), 181 (16), 180 (100), 179 (11), 165 (15); HRMS: $M^+-2\times H_2O-C(CH_3)_3$, found 275.1856, $C_{21}H_{23}$ requires 275.1800.

4.4.7. 1,2,2-Triphenyl-1-butanol (13d). Colourless oil, 149 mg; t_R=19.3 min; R_f (hexane/ethyl acetate 8/2)=0.50; ν (film) 3558, 3455 (OH), 3056 (=CH) cm^{-1}; δ_H (400 MHz) 0.67 (3H, t, J=7.3, CH_3), 1.80–1.87 (1H, m, CH_2), 1.90–1.97 (1H, m, CH_2), 2.16 (1H, d, J=4.6, OH), 5.61 (1H, d, J=4.6, CH), 6.64 (2H, d, J=7.5, 2×ArH), 7.05–7.36 (13H, m, 13×ArH); δ_C (100 MHz) 9.2 (CH_3), 30.9 (CH_2), 56.9 (CCH_2), 77.0 (CH), 126.0, 126.4, 126.9, 127.1, 127.5, 127.8, 128.1, 129.3, 130.8 (ArCH), 140.6, 141.6, 144.9 (ArC); *m/z* 284 (M^+-H_2O, 2%), 197 (12), 196 (80), 195 (100), 179 (10), 178 (13), 167 (57), 165 (27), 117 (30), 115 (21), 107 (15), 91 (40), 79 (12), 77 (13); HRMS: M^+-H_2O, found 284.1532, $C_{22}H_{20}$ requires 284.1565.

4.4.8. 2-Methyl-3,3-diphenyl-2-pentanol (13e). Colourless oil, 150 mg; t_R=15.7 min; R_f (hexane/ethyl acetate 8/2)=0.34; ν (film) 3480 (OH), 3055 (=CH) cm^{-1}; δ_H (300 MHz) 0.67 (3H, t, J=7.2, CH_2CH_3), 1.24 [6H, s, C(CH_3)$_2$], 2.34 (2H, q, J=7.3, CH_2), 7.17–7.29 (6H, m, 6×ArH), 7.46–7.49 (4H, d, J=7.2, 4×ArH); δ_C (75 MHz) 10.1 (CH_2CH_3), 27.5 (CH_2), 28.5 [C(CH_3)$_2$], 59.7 (CCH_2), 77.0 (COH), 125.7, 126.9, 131.2 (ArCH), 144.2 (ArC); *m/z* 236 (M^+-H_2O, 2%), 196 (47), 168 (14), 167 (100), 165 (20), 117 (11), 115 (12), 91 (18), 59 (19).[25]

4.4.9. 2-Methyl-5,5-diphenyl-2-pentanol (14e). Colourless oil, 16 mg; t_R=15.7 min; R_f (hexane/ethyl acetate 8/2)=0.23; ν (film) 3391 (OH), 3060 (=CH) cm^{-1}; δ_H (300 MHz) 1.20 (6H, s, 2×CH_3), 1.40–1.47 (2H, m, CH_2C), 2.09–2.17 (2H, m, $CHCH_2$), 3.85 (1H, t, J=7.7, CH), 7.14–7.31 (10H, m, 10×ArH); δ_C (75 MHz) 29.2 (CH_3), 30.3 ($CHCH_2$), 42.3 (CH_2C), 51.7 (CH), 70.9 (COH), 126.1, 127.8, 128.4 (ArCH), 145.0 (ArC); *m/z* 236 (M^+-H_2O, 4%), 181 (15), 180 (100), 179 (10), 168 (13), 167 (89), 166 (14), 165 (43), 152 (17).[26]

4.4.10. 3-Ethyl-6,6-diphenyl-3-hexanol (14f). Colourless oil, 148 mg; t_R=17.2 min; R_f (hexane/ethyl acetate 8/2)=0.34; ν (film) 3441 (OH), 3060 (=CH) cm^{-1}; δ_H (300 MHz), 0.78 (6H, t, J=7.5, CH_3), 1.34–1.47 (6H, m, CH_2CH_2C, 2×CH_2CH_3), 2.01–2.09 (2H, m, $CHCH_2$), 3.82

(1H, t, J=7.6, CH), 7.12–7.30 (10H, m, 10×ArH); δ_C (75 MHz) 7.7 (CH_3), 29.5 (CHCH_2), 30.9 (CH_2CH_3), 36.6 (CH_2CH_2C), 51.9 (CH), 74.6 (COH), 126.1, 127.7, 128.4 (ArCH), 145.0 (ArC); m/z 264 (M^+-H_2O, 3%), 181 (16), 180 (100), 175 (11), 167 (41), 165 (28), 152 (10), 57 (13); HRMS: M^+-H_2O, found 264.1877, $C_{20}H_{24}$ requires 264.1878.

4.4.11. 1-(1,1-Diphenylpropyl)-1-cyclohexanol (13g). Colourless oil, 130 mg; t_R=18.6 min; R_f (hexane/ethyl acetate 8/2)=0.53; ν (film) 3578 (OH), 3054 (=CH) cm^{-1}; δ_H (300 MHz) 0.62 (3H, t, J=7.3, CH_3), 0.82–1.93 (10H, m, 5×ring CH_2), 2.32 (2H, q, J=7.3, CH_2CH_3), 7.17–7.28 (6H, m, 6×ArH), 7.48 (4H, d, J=7.3, 2×ArH); δ_C (75 MHz) 10.0 (CH_3), 21.9, 25.3, 26.9, 33.2 (3×ring CH_2, CH_2CH_3), 60.6 (CCH_2CH_3), 77.5 (COH), 125.6, 126.8, 131.5 (ArCH), 143.7 (ArC); m/z 294 (M^+, 1%), 197 (12), 196 (74), 168 (14), 167 (100), 165 (20), 117 (10), 115 (11), 99 (40), 91 (16), 81 (24); HRMS: M^+-H_2O, found 276.1861, $C_{21}H_{24}$ requires 276.1878.

4.4.12. 3-(*tert*-Butyl)-2,2-dimethyl-6,6-diphenyl-3-hexanol (14h). Colourless oil, 169 mg; t_R=19.6 min; R_f (hexane/ethyl acetate 8/2)=0.61; ν (film) 3626 (OH), 3060 (=CH) cm^{-1}; δ_H (300 MHz) 0.87 (18H, s, 6×CH_3), 1.45–1.51 (2H, m, CH_2C), 2.01–2.10 (2H, m, $CHCH_2$), 3.72 (1H, t, J=7.6, CH), 7.06–7.08 (2H, m, 2×ArH), 7.16–7.19 (8H, m, 8×ArH); δ_C (75 MHz) 28.5 (CH_3), 31.7, 32.4 ($CHCH_2$, CH_2C), 42.5 [$C(CH_3)_3$], 52.3 (CH), 79.6 (COH), 126.0, 127.8, 128.3 (ArCH), 145.2 (ArC); m/z 338 (M^+, 1%), 282 (12), 281 (55), 204 (13), 203 (81), 194 (15), 193 (84), 181 (22), 180 (100), 168 (10), 167 (56), 166 (18), 165 (46), 152 (18), 143 (11), 118 (10), 117 (94), 115 (12), 91 (13), 87 (22), 57 (51); HRMS: $M^+-C(CH_3)_3$, found 281.1882, $C_{20}H_{25}O$ requires 281.1905.

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