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# Naphthalene-Catalysed Lithiation of Allylic and Benzylic Mesylates: A New Method for Allyl, Methallyl, and Benzyl Lithium

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***Abstract:** The reaction of allylic or benzylic mesylates (1) with an excess of lithium powder and a catalytic amount of naphthalene (4 mol %) in THF at -78°C leads to a solution of the corresponding organolithium derivatives, which by treatment with different electrophiles yield the expected products 2-7. As an alternative route, the process can be carried out at 0°C by adding the corresponding mesylate together with the electrophile to a suspension of the activated lithium in THF, in a Barbier-type reaction.*

## Introduction

Conventional methods involving halogen-lithium interchange are not useful for preparing allylic or benzylic lithium reagents due to the almost exclusive formation of Wurtz-type products[1]. Other alternative routes have been developed: (a) the direct deprotonation of the corresponding hydrocarbons, which needs the use of a co-reactant such as an alkoxide or an amine (e.g. TMEDA or DABCO) and leads to the corresponding "mixed" carbanions or the complex organolithium compound-amine, respectively[1c,2]; (b) a mercury-lithium[3] or tin-lithium[4] transmetallation, which has been used for the preparation of benzyl or allyl lithium, respectively; (c) the reductive cleavage of allyl phenyl ether with lithium is a useful procedure in the case of allyllithium[5].

On the other hand, we have recently described[6] that an arene such as naphthalene acts as an effective catalyst in lithiation reactions using lithium powder as lithiation agent. This procedure has been succesfully employed above all for chlorine-lithium exchange at low temperature, in general for the preparation of very reactive functionalized organolithium compounds[7]. In the present paper we describe a new route for allylic and benzylic organolithium reagents by naphthalene-catalysed lithiation of the corresponding mesylates.

## Results and discussion

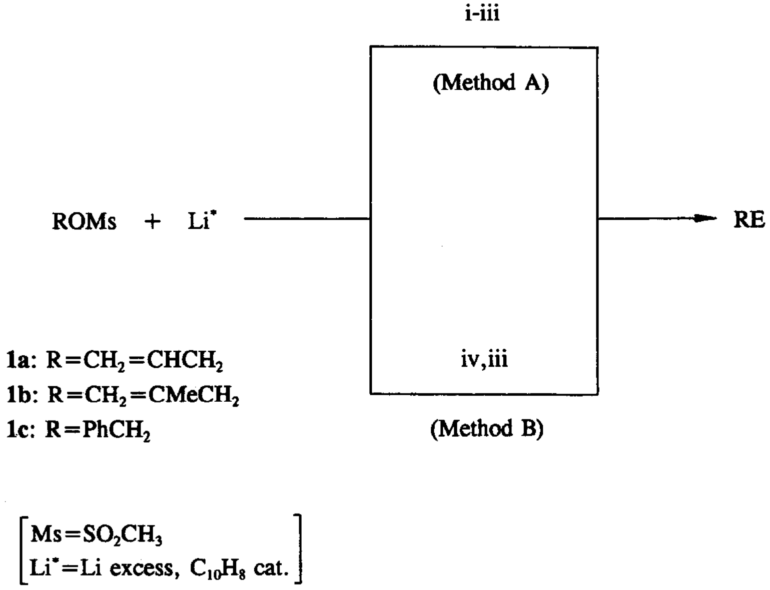
The reaction of allyl, methallyl or benzyl mesylate **1** (easily prepared by treatment of the corresponding alcohols with mesyl chloride/triethylamine in THF) with an excess of lithium powder (1:10 molar ratio) and a catalytic amount of naphthalene (1:0.04 molar ratio) in THF at -78°C led, after 30 min, to a solution of the corresponding organolithium compound, which by reaction with different electrophilic reagents afforded, after hydrolysis, the expected products **2a-6a**, **2b-5b**, and **2c-7c**, respectively (Method A; Scheme 1 and Table 1). In the absence of naphthalene the lithiation did not take place under the same reactions conditions (Table 1, footnote j).

**Table 1.** **Preparation of Allyl, Methallyl and Benzyl Lithium and Reaction with Electrophiles. Obtention of compounds 2-7.**

| | | | Product[a] | | | |
|---|---|---|---|---|---|---|
| | Starting | Electrophile | | | Yield (%)[b] | |
| Entry | mesylate | $E^+$ | No. | E | Method A/B | $R_f$[c] |
| 1 | **1a** | PhCHO | **2a** | PhCHOH | 69/45 | 0.54[d] |
| 2 | **1a** | $Et_2CO$ | **3a** | $Et_2COH$ | 38/75 | 0.57[e] |
| 3 | **1a** | $\overline{(CH_2)_5C}O$ | **4a** | $\overline{(CH_2)_5C}OH$ | 48/55 | 0.46[d] |
| 4 | **1a** | $Ph_2CO$ | **5a** | $Ph_2COH$ | -/72 | 0.54[f] |
| 5 | **1a** | $(PhCH_2S)_2$ | **6a** | $PhCH_2S$ | 42/80 | 0.71[g] |
| 6 | **1b** | PhCHO | **2b** | PhCHOH | 42/21 | 0.45[d] |
| 7 | **1b** | $Et_2CO$ | **3b** | $Et_2COH$ | 46/- | 0.37[h] |
| 8 | **1b** | $\overline{(CH_2)_5C}O$ | **4b** | $\overline{(CH_2)_5C}OH$ | 45/23 | 0.61[d] |
| 9 | **1b** | $Ph_2CO$ | **5b** | $Ph_2COH$ | 71/- | 0.63[h] |
| 10 | **1c** | $Pr^iCHO$ | **2c** | $Pr^iCHOH$ | 35/45 | 0.54[f] |
| 11 | **1c** | PhCHO | **3c** | PhCHOH | 58/35 | 0.54[f,i] |
| 12 | **1c** | $Et_2CO$ | **4c** | $Et_2COH$ | 47/41 | 0.44[f] |
| 13 | **1c** | $\overline{(CH_2)_5C}O$ | **5c** | $\overline{(CH_2)_5C}OH$ | 38[j]/39[k] | 0.40[f] |
| 14 | **1c** | $Ph_2CO$ | **6c** | $Ph_2COH$ | -/63 | 0.52[f,l] |
| 15 | **1c** | $(PhCH_2S)_2$ | **7c** | $PhCH_2S$ | 71/68 | 0.61[h] |

[a] All products were >95% pure (GLC and 300 MHz $^1H$ NMR). [b] Isolated yields after column chromatography (silica gel, hexane/ethyl acetate or hexane/diethyl ether) based on the starting mesylate **1**. [c] Hexane/ethyl acetate. [d] 4/1. [e] 3/1. [f] 6/1. [g] Hexane/ether: 4/1. [h] 9/1. [i] Mp. 64-65°C. [j] 0% yield without naphthalene. [k] 13% Yield without naphthalene. [l] Mp. 88-89°C.

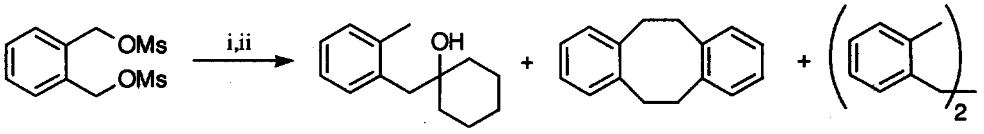
An alternative procedure involves a Barbier-type process: to a suspension of an excess of lithium and a catalytic amount of naphthalene (see above) in THF was added a solution of the corresponding mesylate and the electrophile in THF at 0°C. After 2h at the same temperature the expected products **2-7** were isolated, after hydrolysis (Method B; Scheme 1 and Table 1). In the absence of naphthalene the yields are much lower (Table 1, footnote k).



**Scheme 1.** *Reagents and conditions*: i, -78°C, 30 min; ii, E$^+$=$Pr^iCHO$, PhCHO, $Et_2CO$, $(CH_2)_5CO$, $Ph_2CO$, $(PhCH_2S)_2$, -78°C to 20°C; iii, $H_2O$-HCl; iv, E$^+$, 0°C, 2 h.

In all the described reactions the corresponding coupling product, diallyl, dimethallyl or dibenzyl, is obtained as by-product. The separation of these by-products could be easily performed by simple evaporation or by column chromatography.

Finally, we tried to prepare a dibenzylic derivative such as **13** starting from the corresponding dimesylate **8** and following the here described methodology. Thus, the catalytic lithiation of compound **8** at -78°C in the presence of cyclohexanone yields a mixture of the product of monoaddition **9** together with the "dimers" **10** and **11** (Scheme 2). The obtained results can be rationalized considering that the first lithiation gives the intermediate **12**, which can follow two different processes: (a) reaction with the electrophile followed by a tandem lithiation-proton abstraction from the reaction media[9] yielding the product **9**, or (b) double coupling to **10** or monocoupling followed to a tandem lithiation-proton abstraction, to give the product **11**. In the absence of the electrophile only products **10** and **11** were obtained: catalytic lithiation of starting material **8** at 0°C

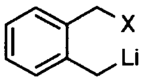


**8** **9** (49%) **10** (15%) **11** (12%)

**Scheme 2:** *Reagents and conditions*: i, Li*, $\overline{(CH_2)_5CO}$, -78°C; ii, $H_2O$-HCl.

followed by acid hydrolysis yielded compounds **10** (18%) and **11** (16%).

We think that the here described methodology presents a convenient *via* for allyl, methallyl and benzyl lithium. Moreover, it represents a new method for obtaining alkyllithium derivatives indirectly from alcohols through their corresponding mesylates. Studies on the application of this reaction to other alcohols and other different electrophiles are in course.



**12**: X=OMs
**13**: X=Li

## Experimental Part

*General.*- M.p.s are uncorrected and were measured on a Reichert thermovar apparatus. I.r. spectra were determined with a Pye Unicam SP3-200 spectrometer. $^1H$ and $^{13}C$ n.m.r. spectra were recorded in a Bruker AC-300 (unless otherwise stated) using $CDCl_3$ as solvent and $SiMe_4$ as internal standard; chemical shifts are given in $\delta$ (ppm) and the coupling constants ($J$) are measured in Hz. M.s. (e.i.) were recorded with a Hewlett Packard EM/CG HP-5988A spectrometer. The purity of volatile distilled products and the chromatographic analysis (g.l.c.) were determined with a Hewlett Packard HP-5890 instrument equipped with a flame ionization detector and a 12 m HP-1 capillary column (0.2 mm diam., 0.33 $\mu$m film thickness), using nitrogen (2 ml/min) as the carrier gas, $T_{injector}$=270°C, $T_{column}$=60°C (3 min) and 60-270°C (15°C/min); retention times ($t_r$) are given under these conditions. Thin layer chromatography (t.l.c.) was carried out on Scheleicher & Schnell F1500/LS 254 plates coated with a 0.2 mm layer of silica gel, using a mixture of hexane/ethyl acetate as eluant; $R_f$ values (see Table 1) are given under this conditions. Solvents for the reaction with lithium or organolithium compounds were dried as usually.

*Preparation of Starting Mesylates* **1** *and* **8**.- Compounds **1** and **8** were prepared according to the literature procedure[8] from the corresponding commercially available alcohols (Aldrich):

*Allyl Mesylate* (**1a**)[10]: $t_r$=5.64 min; $\nu_{max}$ (film) 3015, 1630 (HC=C), 1345, and 1170 $cm^{-1}$ ($SO_2$); $\delta_H$ (60 MHz)[11] 3.05 (3 H, s, Me), 4.7 (2 H, d, $J$=5.5, $CH_2O$), and 5.2-6.35 (3 H, m, $CH_2$=CH).

*Methallyl Mesylate* (**1b**)[10]: $t_r$=6.88 min; $\nu_{max}$ (film) 3050, 1630 (HC=C), 1350, and 1170 $cm^{-1}$ ($SO_2$); $\delta_H$ (60 MHz)[11] 1.8 (3 H, s, MeC), 3.0 (3 H, s, MeS), 4.6 (2 H, s, $CH_2O$), and 4.95-5.2 (2 H, m, $CH_2$=C).

*Benzyl Mesylate* (**1c**)[10]: $t_r$=10.90 min; $\nu_{max}$ (film) 3010, 1490, (HC=C), 1350, and 1170 $cm^{-1}$ ($SO_2$); $\delta_H$ (60 MHz)[11] 2.9 (3 H, s, Me), 5.2 (2 H, s, $CH_2$), and 7.4 (5 H, s, ArH).

*2-(Mesyloximethyl)benzyl Mesylate* (**8**): $t_r$=13.45 min, $R_f$=0.56 (hexane/ethyl acetate: 1/1); $\nu_{max}$ (film) 3010, 1600, (HC=C), 1340, and 1165 ($SO_2$); $\delta_H$ 2.98 (6 H, s, 2xMe), 5.35 (4 H, s, 2x$CH_2$), and 7.43-7.51 (4 H, m, ArH); $\delta_C$ 37.8 (2xMe), 68.6 (2x$CH_2$), 130.0, 130.85, and 132.45 (ArC).

*Preparation of Compounds* **2-7**. *General Procedure. Method A*.- A suspension of lithium powder (Aldrich; 140 mg, 20 mmol) and naphthalene (10 mg, 0.08 mmol) in THF (5 ml) was stirred under Ar until a dark-green colour appeared. To the resulting mixture cooled at -78°C was added a solution of the corresponding mesylate **1** (1 mmol) in THF (2 ml) during *ca.* 30 min. After 30 min stirring at the same temperature the corresponding electrophile (1.2 mmol) was added. The mixture was stirred for 4-5 h allowing the temperature to rise to 20°C. The resulting suspension was then hydrolyzed with water (5 ml), neutralyzed with 2N hydrochloric acid and extracted with ether (2x20 ml). The organic layer was dried over $Na_2SO_4$ and evaporated. The resulting residue was purified by column chromatography (silica gel; hexane/ethyl acetate[12]) to yield the expected products **2-7**.

*Method B*.- To a dark-green suspension of lithium (140 mg, 20 mmol) and naphthalene (10 mg, 0.08 mmol) in THF (5 ml) prepared as it was described in method A was added a solution of the mesylate **1** (1 mmol) and the corresponding electrophile (1.2 mmol) in THF (2 ml) during *ca.* 15 min at 0°C. After 2 h stirring the mixture was hydrolyzed and worked up as above. Yields, $R_f$ values and m.p.s for products **2-7** are reported in Table 1. Physical and spectral data follow:

*1-Phenyl-3-buten-1-ol* (**2a**)[13]: $t_r$=8.56 min; $\nu_{max}$ (film) 3370 (OH), 3065, 3025, 1635, 1600, and 1490 $cm^{-1}$ (HC=C); $\delta_H$ 2.25 (1 H, s, OH), 2.42-2.56 (2 H, m, $CH_2CO$), 4.67-4.71 (1 H, m, CHO), 5.11, 5.13 (1 H each, 2d, *J*=9.7, 17.7 respectively, $CH_2$=C), 5.78 (1 H, ddt, *J*=17.7, 9.7, 7.1, $CH{=}CH_2$), and 7.27-7.34 (5 H, m, ArH); $\delta_C$ 43.7 ($CH_2CO$), 73.25 (CO), 118.2 ($CH_2$=C), 134.4 ($CH{=}CH_2$), 125.75, 127.45, 128.3, and 143.8 (ArC); *m/z* 129 ($M^+$-19, 1%), 107 (16), 79 (68), 78 (24), 77 (100), 51 (38), and 41 (36).

*3-Ethyl-5-hexen-3-ol* (**3a**)[14]: $t_r$=4.49 min; $\nu_{max}$ (film) 3410 (OH), 3060, and 1635 $cm^{-1}$ (HC=C); $\delta_H$ 0.88 (6 H, t, *J*=7.5, 2xMe), 1.48 (4 H, q, *J*=7.5, 2x$CH_2$Me), 1.60 (1 H, br s, OH), 2.21 (2 H, d, *J*=7.4, $CH_2C{=}C$), 5.11, 5.12 (1 H each, 2d, *J*=17.0, 10.3 respectively, $CH_2$=C), and 5.80-5.89 (1 H, m, CH); $\delta_C$ 7.7 (2xMe), 30.9 (2x$CH_2$Me), 42.85 ($CH_2C{=}C$), 74.15 (CO), 118.25 ($CH_2$=C), and 133.95 (CH); *m/z* 99 ($M^+$-29, 12%), 87 (71), 69 (22), 57 (100), and 45 (57).

*1-Allylcyclohexanol* (**4a**)[15]: $t_r$=6.77 min; $\nu_{max}$ (film) 3410 (OH), 3060, and 1630 $cm^{-1}$ (HC=C); $\delta_H$ 1.39-1.66 (10 H, m, 5x$CH_2$ ring), 2.22 (2 H, d, *J*=7.4, $CH_2C{=}C$), 5.11, 5.15 (1 H each, 2d, *J*=16.4, 8.8 respectively, $CH_2$=C), and 5.89 (1 H, ddt, *J*=16.4, 8.8, 7.4, CH); $\delta_C$ 22.15 (2C), 25.75, 37.35 (2C)(5x$CH_2$ ring), 46.6 ($CH_2C{=}C$), 70.9 (CO), 118.6 ($CH_2$=C), and 133.7 (CH); *m/z* 122 ($M^+$-18, <1%), 99 (100), 81 (72), and 55 (24).

*1,1-Diphenyl-3-buten-1-ol* (**5a**)[16]: $t_r$=13.64 min; $\nu_{max}$ (film) 3460 (OH), 3050, 3020, 1635, 1595, and 1490 $cm^{-1}$ (HC=C); $\delta_H$ 2.55 (1 H, br s, OH), 3.06 (2 H, d, *J*=7.1, $CH_2CO$), 5.15, 5.21 (1 H each, 2d, *J*=10.1, 17.2 respectively, $CH_2$=C), 5.65 (1 H, ddt, *J*=17.2, 10.1, 7.1, $CH{=}CH_2$), and 7.17-7.44 (10 H, m, ArH); $\delta_C$ 46.65 ($CH_2C{=}C$), 76.85 (CO), 120.35 ($CH_2$=C), 133.4 ($CH{=}CH_2$), 125.95, 126.8, 128.1, and 146.45 (ArC);

*m/z* 206 ($M^+$-18, <1%), 183 (77), 105 (100), 77 (65), and 51 (13).

*Allyl Benzyl Sulfide* (**6a**)[17]: $t_r$=9.70 min; $\nu_{max}$ (film) 3065, 3045, 3010, 1625, 1595, and 1485 $cm^{-1}$ (HC=C); $\delta_H$ 3.01 (2 H, d, *J*=7.1, $CH_2$CH), 3.64 (2 H, s, $CH_2$Ph), 5.07, 5.11 (1 H each, 2d, *J*=17.1, 9.9 respectively, $CH_2$=C), 5.78 (1 H, ddt, *J*=17.1, 9.9, 7.1, *CH*=$CH_2$), and 7.15-7.29 (5 H, m, ArH); $\delta_C$ 33.95 ($CH_2$CH), 34.8 ($CH_2$Ph), 117.15 ($CH_2$=C), 134.1 (*C*H=$CH_2$), 126.8, 128.35, 128.9, and 138.2 (ArC); *m/z* 166 ($M^+$+2, 1%), 165 ($M^+$+1, 2), 164 ($M^+$, 16), 122 (23), 91 (100), 77 (21), and 65 (42).

*3-Methyl-1-phenyl-3-buten-1-ol* (**2b**)[18]: $t_r$=9.43 min; $\nu_{max}$ (film) 3380 (OH), 3060, 3020, 1635, 1595, and 1485 $cm^{-1}$ (HC=C); $\delta_H$ 1.77 (3 H, s, Me), 2.29 (1 H, br s, OH), 2.35-2.47 (2 H, m, $CH_2$C=C), 4.78 (1 H, dd, *J*=7.3, 6.3, CHO), 4.83, 4.90 (1 H each, 2s, $CH_2$=C), and 7.20-7.39 (5 H, m, ArH); $\delta_C$ 22.25 (Me), 48.2 ($CH_2$C=C), 71.4 (CO), 113.9 ($CH_2$=C), 142.3 (*C*=$CH_2$), 125.7, 127.35, 128.3, and 144.05 (ArC); *m/z* 162 ($M^+$, 4%), 108 (12), 107 (100), 105 (16), 79 (78), 77 (50), and 51 (10).

*3-Ethyl-5-methyl-5-hexen-3-ol* (**3b**): $t_r$=5.75 min; $\nu_{max}$ (film) 3410 (OH), 3060, and 1630 $cm^{-1}$ (HC=C); $\delta_H$ 0.88 (6 H, t, *J*=7.5, 2x*Me*$CH_2$), 1.49 (4 H, q, *J*=7.5, 2xC*H*$_2$Me), 1.84 (3 H, s, *Me*C=C), 2.17 (2 H, s, $CH_2$C=C), 4.75, and 4.92 (1 H each, 2s, $CH_2$=C); $\delta_C$ 8.05 (*Me*$CH_2$), 25.1 (*Me*C=C), 30.95 ($CH_2$Me), 46.2 ($CH_2$C=C), 74.4 (CO), 114.7 ($CH_2$=C), and 142.85 (*C*=$CH_2$); *m/z* 113 ($M^+$-29, 8%), 87 (100), 69 (17), 57 (61), and 45 (28).

*1-(2-Methyl-2-propenyl)cyclohexanol* (**4b**)[19]: $t_r$=7.90 min; $\nu_{max}$ (film) 3450 (OH), 3060, and 1635 $cm^{-1}$ (HC=C); $\delta_H$ 1.23-1.71 (10 H, m, 5x$CH_2$ ring), 1.84 (3 H, s, Me), 2.19 (2 H, s, $CH_2$C=C), 4.75, and 4.93 (1 H each, 2s, $CH_2$=C); $\delta_C$ 22.3 (2C), 25.75, 37.85 (2C)(5x$CH_2$ ring), 25.3 (Me), 71.0 (CO), 114.65 ($CH_2$=C), and 142.6 (*C*=$CH_2$); *m/z* 154 ($M^+$, <1%), 100 (11), 99 (100), 81 (88), 79 (14), 55 (24), and 41 (15).

*3-Methyl-1,1-diphenyl-3-buten-1-ol* (**5b**)[18]: $t_r$=14.07 min; $\nu_{max}$ (film) 3510 (OH), 3050, 3010, 1630, 1590, and 1485 $cm^{-1}$ (HC=C); $\delta_H$ 1.23 (3 H, s, Me), 2.79 (1 H, s, OH), 3.00 (2 H, s, $CH_2$), 4.69, 4.83 (1 H each, 2s, $CH_2$=C), 7.05-7.10, 7.15-7.21, and 7.35-7.39 (10 H, 3m, ArH); $\delta_C$ 24.2 (Me), 49.75 ($CH_2$C=C), 75.9 (CO), 116.65 ($CH_2$=C), 142.1 (*C*=$CH_2$), 125.8, 126.65, 128.0, and 146.95 (ArC); *m/z* 220 ($M^+$-18, <1%), 183 (63), 182 (10), 105 (100), 77 (49), and 51 (10).

*3-Methyl-1-phenyl-2-butanol* (**2c**)[20]: $t_r$=9.38 min; $\nu_{max}$ (film) 3400 (OH), 3050, 3020, 1595, and 1485 $cm^{-1}$ (HC=C); $\delta_H$ 0.99 (6 H; d, *J*=6.8, 2xMe), 1.60 (1 H, br s, OH), 1.71-1.77 (1 H, m, C*H*Me), 2.59, 2.84 (1H each, dd=13.6, 9.4, and dd=13.6, 3.4 respectively, $CH_2$), 3.55-3.61 (1 H, m, CHO), and 7.21-7.33 (5 H, m, ArH); $\delta_C$ 17.35, 18.85 (2xMe), 33.05 (CHMe), 40.7 ($CH_2$), 77.45 (CO), 126.3, 128.5, 129.3, and 139.15 (ArC); *m/z* 164 ($M^+$, 2%), 121 (9), 92 (100), 91 (95), 77 (19), 65 (33), and 41 (27).

*1,2-Diphenylethanol* (**3c**)[21]: $t_r$=13.03 min; $\nu_{max}$ ($CH_2Cl_2$) 3380 (OH), 3070, 3050, 3020, 1590, and 1485 $cm^{-1}$ (HC=C); $\delta_H$ 2.04 (1 H, br s, OH), 2.99, 3.01 (1 H each, 2d, *J*=8.0, 5.3 respectively, $CH_2$), 4.87 (1 H, dd, *J*=8.0, 5.3, CHO), and 7.16-7.34 (10 H, m, ArH); $\delta_C$ 46.0 ($CH_2$), 75.3 (CO), 125.85, 126.55, 127.55, 128.35, 128.45, 129.45, 138.0, and 143.75 (ArC); *m/z* 198 ($M^+$, 2%), 107 (28), 91 (55), 79 (83), 77 (100), 65 (50), and 51 (40).

*3-Benzyl-3-pentanol* (**4c**)[22]: $t_r$=10.18 min; $\nu_{max}$ (film) 3430 (OH), 3050, 3020, 1600, and 1490 cm$^{-1}$ (HC=C); $\delta_H$ 0.92 (6 H, t, $J$=7.5, 2xMe), 1.35 (1 H, br s, OH), 1.46 (4 H, q, $J$=7.5, 2xC$H_2$Me), 2.74 (2 H, s, C$H_2$Ph), and 7.21-7.32 (5 H, m, ArH); $\delta_C$ 7.95 (2xMe), 30.4 (2x$CH_2$Me), 44.75 ($CH_2$Ph), 74.55 (CO), 126.3, 128.15, 130.55, and 137.95 (ArC); *m/z* 178 (M$^+$, <1%), 149 (30), 92 (100), 91 (92), 87 (93), 65 (30), and 57 (38).

*1-Benzylcyclohexanol* (**5c**)[23]: $t_r$=11.89 min; $\nu_{max}$ (film) 3380 (OH), 3080, 3050, 3020, 1600, and 1490 cm$^{-1}$ (HC=C); $\delta_H$ 1.34 (1 H, br s, OH), 1.38-1.56 (10 H, m, 5xCH$_2$ ring), 2.72 (2 H, s, C$H_2$Ph), and 7.18-7.30 (5 H, m, ArH); $\delta_C$ 22.05 (2C), 25.7, 37.2 (2C)(5xCH$_2$ ring), 48.65 ($CH_2$Ph), 71.05 (CO), 126.25, 128.0, 130.55, and 137.15 (ArC); *m/z* 190 (M$^+$, 1%), 99 (93), 92 (100), 91 (79), 81 (61), 65 (24), and 55 (18).

*1,1,2-Triphenylethanol* (**6c**)[24]: $t_r$=16.86 min; $\nu_{max}$ ($CH_2Cl_2$) 3545 (OH), 3050, 3020, 1590, and 1485 cm$^{-1}$ (HC=C); $\delta_H$ 2.28 (1 H, br s, OH), 3.62 (2 H, s, CH$_2$), and 6.86-7.41 (15 H, m, ArH); $\delta_C$ 47.85 (CH$_2$), 77.85 (CO), 126.15, 126.7, 126.8, 127.95, 128.0, 130.85, 135.75, and 146.5 (ArC); *m/z* 256 (M$^+$-18, 2%), 183 (100), 105 (96), 91 (21), 77 (78), 65 (12), and 51 (14).

*Dibenzyl Sulfide* (**7c**)[25]: $t_r$=14.00 min; $\nu_{max}$ (film) 3055, 3020, 1600, and 1490 cm$^{-1}$ (HC=C); $\delta_H$ 3.49 (4 H, s, 2xCH$_2$), and 7.18 (10 H, s, ArH); $\delta_C$ 35.5 (2xCH$_2$), 126.9, 128.35, 128.9, and 138.1 (ArC); *m/z* 216 (M$^+$+2, 1%), 215 (M$^+$+1, 4), 214 (M$^+$, 27), 123 (20), 91 (100), 77 (23), and 65 (48).

*Catalytic Lithiation of Dimesylate* **8** *and Reaction with Cyclohexanone. Isolation of Compounds* **9-11**.-To a dark-green suspension of lithium (140 mg, 20 mmol) and naphthalene (10 mg, 0.08 mmol) in THF (5 ml) prepared as it was described in Method A was added a solution of the dimesylate **8** (1 mmol) and cyclohexanone (2.2 mmol) in THF (2 ml) at -78°C. After 5 h stirring allowing the temperature to rise to 20°C the mixture was hydrolyzed and worked up as in Method A.

*1-(o-Methylbenzyl)cyclohexanol* (**9**): $R_f$=0.42 (hexane/ethyl acetate: 9/1), $t_r$=12.71 min; $\nu_{max}$ (film) 3430 (OH), 3050, 3010, 1590, and 1480 cm$^{-1}$ (HC=C); $\delta_H$ 1.16 (1 H, br s, OH), 1.34-1.52 (10 H, m, 5xCH$_2$ ring), 2.29 (3 H, s, Me), 2.70 (2 H, s, C$H_2$Ph), and 7.03-7.11 (4 H, m, ArH); $\delta_C$ 20.5 (Me), 21.95 (2C), 25.8, 37.5 (2C)(5xCH$_2$ ring), 45.4 ($CH_2$Ph), 72.15 (CO), 125.4, 126.45, 130.5, 131.55, 135.55, and 137.7 (ArC); *m/z* 204 (M$^+$, 1%), 106 (100), 105 (15), 99 (31), 91 (18), and 81 (28).

*Dibenzo-1,5-cyclooctadiene* (**10**)[26]: $R_f$=0.77 (hexane/ethyl acetate: 9/1), $t_r$=13.58 min, m.p. 108-109°C (hexane/ethyl acetate); $\nu_{max}$ ($CH_2Cl_2$) 3040, 3000, 1590, and 1480 cm$^{-1}$ (HC=C); $\delta_H$ 3.06 (8 H, s, 4xCH$_2$), and 6.92-7.09 (8 H, m, ArH); $\delta_C$ 35.15 (4xCH$_2$), 126.05, 129.65, and 140.55 (ArC); *m/z* 210 (M$^+$+2, 1%), 209 (M$^+$+1, 10), 208 (M$^+$, 61), 194 (16), 193 (100), 180 (12), 179 (22), 178 (41), 165 (12), 117 (10), 116 (25), 115 (30), 104 (45), 103 (32), 91 (15), 89 (10), 78 (40), 77 (21), 65 (10), 63 (12), and 51 (12).

*1,2-Bis(2-methylphenyl)ethane* (**11**)[27]: $R_f$=0.83 (hexane/ethyl acetate: 9/1), $t_r$=13.22 min, m.p. 65-66°C (hexane/ethyl acetate); $\nu_{max}$ ($CH_2Cl_2$) 3040, 3000, 1590, and 1485 cm$^{-1}$ (HC=C); $\delta_H$ 2.24 (6 H, s, 2xMe), 2.78 (4 H, s, 2xCH$_2$), and 7.03-7.09 (8 H, m, ArH); $\delta_C$ 19.25 (2xMe), 34.1 (2xCH$_2$), 126.05, 126.1, 128.85, 130.2, 135.9, and 140.15 (ArC); *m/z* 211 ($M^+$+1, 3%), 210 ($M^+$, 22), 105 (100), 103 (10), 79 (13), and 77 (18).

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