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Direct Transformation of Allylic and Benzylic Alcohols or Their Silylated Derivatives into Organolithium Compounds

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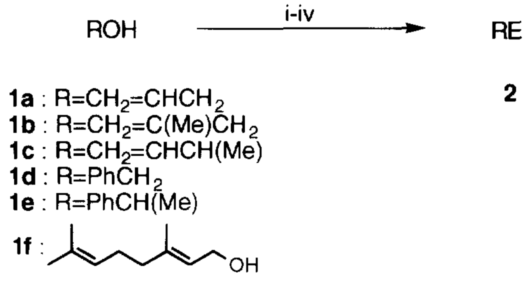
Abstract: The reaction of allylic or benzylic alcohols **1** with *n*-butyllithium followed by treatment with lithium powder and a catalytic amount of DTBB (5 mol %) in THF at room temperature gives a solution of the corresponding alkyllithium reagent, which reacts *in situ* with different electrophiles to yield the expected products **2**. Alternatively, the *O*-silylated derivatives of the same alcohols are lithiated under Barbier-type reaction conditions to afford the same reaction products with better yields.

INTRODUCTION

The most important methodology for the preparation of organolithium reagents uses a halogenated compound as starting material[1]. Other less general procedures involving deprotonation reactions[2], transmetallation processes[3], reductive cleavage of ethers or thioethers[4] and the Shapiro reaction[5] are of limited application. Concerning lithiation methodologies, we have recently discovered[6] that a mixture of lithium powder and a catalytic amount of an arene [naphthalene, biphenyl or 4,4'-di-*tert*-butylbiphenyl (DTBB)] in THF is an excellent combination in order to lithiate different substrates under very mild reaction conditions. Thus, it has been possible to transform for the first time mesylates[7a], sulfates[7b,c], phosphates[7d], nitriles[7e], thioethers[6], phenylsulfones[7f,g] and phenylsulfoxides[7g] into alkyllithium compounds. By this methodology functionalised organolithium compounds[8] are prepared from the corresponding saturated heterocycles, such as aziridines[9a,b], azetidines[9c], tetrahydrofuran[9d], dioxolanes[9e,f], phthalan[9g] and isochroman[9h]. Finally, we could prepare polylithium synthons from the corresponding polychlorinated precursors and explored their synthetic applications under Barbier-type reaction conditions[10]. In this paper we study the direct transformation of allylic and benzylic alcohols through their corresponding alcoholates or their *O*-silyl derivatives into organolithium compounds, this process being, to our best knowledge, a new route to transform alcohols into alkyllithium intermediates.

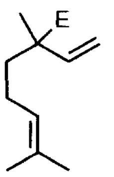
RESULTS AND DISCUSSION

The treatment of different allylic or benzylic alcohols **1a-f** with *n*-butyllithium in THF at 0°C followed by lithiation with an excess of lithium powder and a catalytic amount of DTBB (5 mol %) at ambient temperature led to the formation of the corresponding alkyllithium, which by *in situ* reaction with several electrophiles [PhCHO, Et_2CO, $(CH_2)_5CO$, Me_3SiCl] at temperatures ranging between -30 and 20°C yielded, after hydrolysis with water, the expected compounds **2** (Scheme 1 and Table 1, entries 1, 4, 7, 9-11, 15 and 19). The corresponding process performed either in absence of the catalyst or under Barbier-type conditions (lithiation step in the presence of the electrophile; see below) did not work.

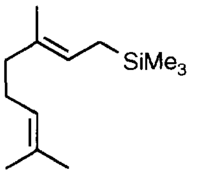


Scheme 1. *Reagents and conditions*: i, Bu^nLi, 0°C, 15 min; ii, Li, DTBB cat (5 mol %), 20°C, 2 h; iii, E^+=PhCHO, Et_2CO, $(CH_2)_5CO$, Me_3SiCl, -30 to 20°C; iv, H_2O.

In order to improve the modest yields obtained starting from the mentioned alcohols **1** we studied the same reaction using the corresponding silylated alcohols **1'**. Thus, the direct DTBB-catalysed lithiation of these *O*-silyl alcohols **1'** under the reaction conditions shown in Scheme 1, but in the presence of different electrophiles [PhCHO, Et_2CO, $(CH_2)_5CO$, Pr^iCHO, Me_3SiCl] (Barbier-type process) led, after hydrolysis with water, to the same expected products **2** (Scheme 2 and Table 1, entries 2, 3, 5, 6, 8, 12-14, 16-18 and 20-22), The obtained results under these reaction conditions were better than the corresponding ones for a two-step process (compare Table 1, entries 12 and 13, and footnote g). In all cases yields were much better than those of the same reaction starting from the corresponding alcohols shown in Scheme 1. (compare, for instance, Table 1, entries 1 and 2, 4 and 6 or 19 and 22). On the other hand, in the absence of the catalyst the reaction worked worse giving, in general, lower yields (Table 1, entries 3, 6, 13, 16 and footnote e). Only in one case, the reaction with the benzylic material **1'd**, both yields (for the catalysed or uncatalysed reaction) were closed (Table 1, entry 12 and footnote e); however, either the reaction time (40 min or 2 h, respectively) or the cleanness of the reaction mixture (much more clean in the catalysed reaction: only solvents and product are present) advise the use of the catalyst. Finally, it is worthy to note the difference found in the reaction of starting material **1'f** with carbonyl compounds or chlorotrimethylsilane; while in the second case both starting materials **1f** and **1'f** yielded the same α-product **2fe** (Table 1, entries 19 and 22) in the reaction of **1'f** with 3-pentanone or isobutyraldehyde γ-products **2fb'** and **2fd'** were the only ones isolated (Table 1, entries 20 and 21).



2fb' : E=Et_2COH
2fd' : E=Pr^iCHOH

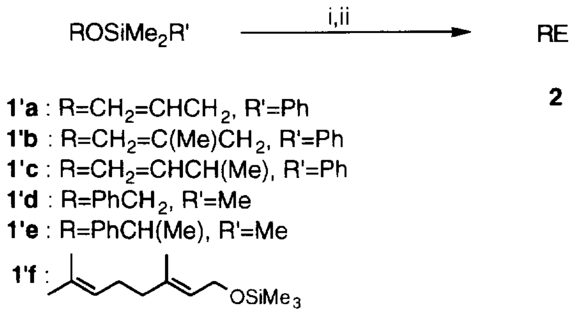


2fe

Table 1. Preparation of Compounds **2** from Alcohols **1** or Their Silyl Derivatives **1'**

Entry	Starting material	Electrophile E^+	Product[a]			
			No.	R	E	Yield (%)[b]
1	**1a**	PhCHO	**2aa**	$CH_2=CHCH_2$	PhCHOH	22
2	**1'a**	PhCHO	**2aa**	$CH_2=CHCH_2$	PhCHOH	47
3	**1'a**	Et_2CO	**2ab**	$CH_2=CHCH_2$	Et_2COH	31 (19)[c]
4	**1b**	$(CH_2)_5CO$	**2bc**	$CH_2=C(Me)CH_2$	$(CH_2)_5COH$	28
5	**1'b**	PhCHO	**2ba**	$CH_2=C(Me)CH_2$	PhCHOH	53
6	**1'b**	$(CH_2)_5CO$	**2bc**	$CH_2=C(Me)CH_2$	$(CH_2)_5COH$	42 (10)[c]
7	**1c**	Et_2CO	**2cb**	$CH_2=CHCH(Me)$	Et_2COH	≈40[d,e]
8	**1'c**	Et_2CO	**2cb**	$CH_2=CHCH(Me)$	Et_2COH	32[d,f]
9	**1d**	PhCHO	**2da**	$PhCH_2$	PhCHOH	47
10	**1d**	$(CH_2)_5CO$	**2dc**	$PhCH_2$	$(CH_2)_5COH$	45
11	**1d**	Me_3SiCl	**2de**	$PhCH_2$	Me_3Si	83
12	**1'd**	PhCHO	**2da**	$PhCH_2$	PhCHOH	58 (56)[c] (53)[g]
13	**1'd**	Et_2CO	**2db**	$PhCH_2$	Et_2COH	67 (35)[c] (49)[g]
14	**1'd**	Me_3SiCl	**2de**	$PhCH_2$	Me_3Si	85
15	**1e**	Et_2CO	**2eb**	PhCH(Me)	Et_2COH	44
16	**1'e**	Et_2CO	**2eb**	PhCH(Me)	Et_2COH	55 (15)[c]
17	**1'e**	Pr^iCHO	**2ed**	PhCH(Me)	Pr^iCHOH	45
18	**1'e**	Me_3SiCl	**2ee**	PhCH(Me)	Me_3Si	60
19	**1f**	Me_3SiCl	**2fe**	-[h]	Me_3Si	15
20	**1'f**	Et_2CO	**2fb'**	-[h]	Et_2COH	43
21	**1'f**	Pr^iCHO	**2fd'**	-[h]	Pr^iCHOH	22
22	**1'f**	Me_3SiCl	**2fe**	-[h]	Me_3Si	56

[a] All isolated products **2** were >95% pure (GLC and 300 MHz ^1H NMR). [b] Isolated yield after column chromatography (silica gel, hexane/ethyl acetate) based on the starting material **1** or **1'**. [c] Isolated yield for the non-catalysed reaction. [d] This compound decomposes partially in the chromatographic column. [e] GLC yield. [f] Isolated yield corresponding to a 4 mmol scale reaction. [g] Isolated yield corresponding to the two-step process (see text). [h] See figures in text and Schemes 1 and 2.



Scheme 2. *Reagents and conditions*: i, E^+=PhCHO, Et_2CO, $(CH_2)_5CO$, Pr^iCHO, Me_3SiCl, Li, DTBB cat. (5 mol %), 20°C, 45 min; ii, H_2O.

As a conclusion, we describe here a new methodology for transforming either allylic and benzylic alcohols or their *O*-silyl derivatives into alkyllithium intermediates and reaction with electrophilic reagents. In general, the reaction works better using silylated alcohols.

EXPERIMENTAL PART

General.- For general considerations see the precedent paper in this issue.

Preparation of O-*Silyl Alcohols* **1'**. *General Procedure.-* To a solution of the corresponding alcohol (10 mmol) and triethylamine (20 mmol) in THF (20 ml) was dropwise added the corresponding chlorosilane (10 mmol) at 0°C. After 1 h stirring at temperatures ranging between 0 and 20°C the resulting mixture was hydrolysed with water (10 ml) and extracted with ether (2x20 ml). The organic layer was washed with water (1x10 ml) and dried over anhydrous sodium sulfate. Solvents were evaporated (15 Torr) and the resulting residue contained the title compounds **1'** (>90% pure by 300 MHz ^1H NMR), which were submitted to lithiation without further purification. Yields, physical, analytical and spectroscopic data, as well as literature references for known compounds, follow.

(Allyloxy)phenyldimethylsilane (**1'a**)[11]: 75% yield; R_f 0.49 (hexane/diethyl ether: 9/1); t_r 8.86 min; ν (film) 3060, 3000, 1640, 1590 (HC=C), 1250 (SiMe) and 1115 cm^{-1} (SiO); δ_H 0.39 (6 H, s, 2xMe), 4.14 (2 H, dt, *J*=5.1, 1.7 Hz, CH_2O), 5.09 (1 H, dq, *J*=10.3, 1.7 Hz, 1xC*H*H=CH), 5.25 (1 H, dq, *J*=17.1, 1.7 Hz, 1xC*H*H=CH), 5.91 (1 H, ddt, *J*=17.1, 10.3, 5.1 Hz, C*H*=CH_2), 7.33-7.44 and 7.55-7.61 (3 H and 2 H, respectively, 2 m, ArH); δ_C -1.7 (2 C, 2xMe), 64.05 (CO), 114.65 (CH_2=CH), 127.8, 129.6, 133.45, 137.0 and 137.65 (ArC and CH=CH_2); m/z 193 (M^++1, 1%), 192 (M^+, 7), 177 (38), 162 (10), 159 (16), 135 (25), 121 (33), 117 (13), 115 (10), 105 (13), 99 (100), 91 (14), 77 (12), 75 (35), 61 (11), 59 (13), 51 (10), 45 (31), 43 (23) and 41 (19).

(Methallyloxy)dimethylphenylsilane (**1'b**): 99% yield; R_f 0.51 (hexane/ethyl acetate: 9/1); t_r 9.09 min; ν (film) 3060, 3040, 1655, 1585, 1480 (HC=C), 1250 (SiMe) and 1110 cm^{-1} (SiO); δ_H 0.39 (6 H, s, 2xMeSi), 1.68 (3 H, t, *J*=0.8 Hz, *Me*C), 4.01 (2 H, s, CH_2O), 4.80-4.82, 4.98-5.00 (1 H each, 2 m, CH_2=C), 7.35-7.38 and 7.57-7.60 (3 H and 2 H, respectively, 2 m, ArH); δ_C -1.8 (2 C, 2xMeSi), 19.0 (*Me*C), 66.75 (CO), 109.8 (*C*H_2=C), 127.8, 129.6, 133.45, 137.75 and 144.15 (ArC and *C*=CH_2); m/z 207 (M^++1, 1%), 206 (M^+, 5), 191 (41), 138 (12), 137 (98), 136 (10), 135 (80), 121 (22), 119 (10), 115 (23), 114 (11), 113 (93), 107 (12), 105 (20), 91 (23), 77 (18), 75 (100), 59 (13), 55 (20), 53 (17), 51 (14), 45 (33), 43 (30) and 41 (15) (Found: M^+, 206.1126. $C_{12}H_{18}OSi$ requires M, 206.1127).

Dimethyl(1-methylallyloxy)phenylsilane (**1'c**)[12]: 82% yield; R_f 0.55 (hexane/diethyl ether: 1/1); t_r 8.57 min; ν (film) 3050, 1630, 1580 (HC=C), 1240 (SiMe) and 1110 cm^{-1} (SiO); δ_H 0.38 (6 H, s, 2xMeSi), 1.20 (3 H, d, *J*=6.4 Hz, *Me*CH), 4.23-5.00 (1 H, m, CHO), 4.98 (1 H, dt, *J*=10.4, 1.5 Hz, 1xC*H*H=CH), 5.12 (1 H, dt, *J*= 17.1, 1.5 Hz, 1xC*H*H=CH), 5.84 (1 H, ddd, *J*=17.1, 10.4, 5.5 Hz, C*H*=CH_2), 7.32-7.41 and 7.52-7.61 (3 H and 2 H, respectively, 2 m, ArH); δ_C -1.2, -0.9 (2xMeSi), 24.0 (*Me*CH), 69.8 (*C*HMe), 113.0 (*C*H_2=CH), 127.7, 129.5, 133.5, 138.2 and 142.35 (ArC and *C*H=CH_2); m/z 208 (M^++2, 1%), 207 (M^++1, 2), 206 (M^+, 16), 191 (42), 177 (13), 162 (17), 138 (18), 137 (92), 136 (15), 135 (100), 128 (11), 121 (10), 119 (13), 117 (13), 115 (22), 113 (88), 107 (17), 105 (28), 91 (33), 78 (10), 75 (67), 59 (11), 55 (27), 53 (18), 51 (19), 45 (45) and 43 (43).

Benzyloxytrimethylsilane (**1'd**)[13]: 89% yield; R_f 0.31 (hexane/ethyl acetate: 9/1); t_r 8.00 min; ν (film) 3050, 3020, 1490 (HC=C), 1240 (SiMe) and 1060 cm^{-1} (SiO); δ_H 0.15 (9 H, s, 3xMe), 4.69 (2 H, s, CH_2) and 7.20-7.42 (5 H, m, ArH); δ_C -0.42 (3 C, 3xMe), 64.5 (CH_2), 126.5, 127.05, 128.25 and 140.9 (ArC); m/z 182 (M^++2, 1%), 181 (M^++1, 3), 180 (M^+, 21), 166 (13), 165 (92), 136 (11), 135 (75), 92 (11), 91 (100), 73 (27), 65 (31), 45 (22) and 43 (12).

(1-Methylbenzyloxy)trimethylsilane (**1'e**)[14]: 91% yield; R_f 0.57 (hexane/diethyl ether: 9/1); t_r 7.88 min; ν (film) 3050, 3010, 1490 (HC=C). 1245 (SiMe), and 1095 cm^{-1} (SiO); δ_H 0.01 (9 H, s, 3xMeSi), 1.37 (3 H, d, *J*=6.4 Hz, *Me*CH), 4.79 (1 H, q, *J*=6.4 Hz, C*H*Me) and 7.12-7.28 (5 H, m, ArH); δ_C 0.08 (3 C, 3xMeSi), 26.85 (*Me*CH), 70.6 (CO), 125.35, 126.8, 128.1, and 146.45 (ArC); m/z 196 (M^++2, <1%), 195 (M^++1, <1), 194 (M^+, 1), 180 (18), 179 (74), 105 (24), 79 (12), 77 (29), 76 (10), 75 (100), 74 (14), 73 (72), 51(11), 45 (27) and 43 (16).

E-*(3,7-Dimethyl-2,6-octadienyloxy)trimethylsilane* (**1'f**)[15]: 81% yield; R_f 0.34 (hexane); t_r 9.68 min; ν (film) 1670 (HC=C), 1250 (SiMe) and 1065 cm^{-1} (SiO); δ_H 0.12 (9 H, s, 3xMeSi), 1.60, 1.64, 1.67 (3 H each, 3 br s, 3xMeC=C), 1.98-2.13 (4 H, m, CH_2CH_2), 4.14-4.16 (2 H, m, CH_2O), 5.06-5.12 (1 H, m, C*H*=CMe_2) and 5.29-5.35 (1 H, m, C*H*CH_2O); δ_C -0.32 (3 C, 3xMeSi), 16.25, 17.6, 25.65 (3x*Me*C=C), 26.3, 39.5 (CH_2CH_2), 59.5 (CO), 123.8, 124.05 (2x*C*H=C), 131.5 and 137.6 (2x*C*=CH); m/z 227 (M^++1, 1%), 226 (M^+, 3), 156 (10), 143 (24), 136 (10), 123 (11), 121 (33), 93 (24), 75 (68), 73 (100), 69 (37), 67 (10), 45 (11) and 41 (29).

Lithiation of Alcohols **1** *and their Silyl Derivatives* **1'** *and Reaction with Electrophiles. Isolation of Compounds* **2**. *General Procedures*.- To the corresponding alcohol **1** (1 mmol) in THF (2 ml) was added a 1.6 M hexane solution of *n*-butyllithium (1.1 mmol) at 0°C for 15 min. The resulting solution was added to a blue suspension of lithium powder (100 mg, 14 mmol) and DTBB (26 mg, 0.1 mmol; 5 mol %) in THF (5 ml) at room temperature, stirring the mixture for 2 additional h at the same temperature. Then the electrophilic reagent (1.2 mmol) was added at 20°C (except for benzaldehide, for which the temperature was -78°C) and, after 1 h stirring, the mixture was hydrolysed with water (5 ml). It was then extracted with ether (2x20 ml), the organic layer was dried over anhydrous sodium sulfate and evaporated (15 Torr). The resulting residue was chromatographied (silica gel, hexane/ethyl acetate) to give pure title compounds **2**. In the case of *O*-Silylated alcohols **1'** (1 mmol), to a blue suspension of lithium powder (100 mg, 14 mmol) and DTBB (26 mg, 0.1 mmol; 5 mol %) in THF (5 ml) was added a solution of the corresponding starting material **1'** (1 mmol) and the electrophilic reagent (1.2 mmol) in THF (2 ml) for 30 min, at 0°C. After 10 min the resulting mixture was hydrolysed and worked up as above. Yields in both cases are indicated in Table 1. Compounds **2aa**[7a,16], **2ab**[7a,17], **2ba**[7a,18], **2bc**[7a,16], **2da**[7a,19], **2db**[7a,20], **2dc**[7a,21] and **2de**[7f,g,22] were described by us[7a,f,g] and others[16-22] and were characterised by comparison of their physical and spectroscopic data with those reported in the literature. For the other compounds **2**, physical, analytical and spectroscopic data follow.

*3-Ethyl-4-methyl-5-hexen-3-o*l (**2cb**)[23]: R_f 0.28 (hexane); t_r 5.09 min; ν (film) 3422 (OH), 3069, 3050 and 1648 cm^{-1} (HC=C); δ_H 0.86 (6 H, t, *J*=7.5 Hz, 2x*Me*CH$_2$), 1.00 (3 H, d, *J*=7.0 Hz, *Me*CH), 1.22 (1 H, br s, OH), 1.49, 1.50 (2 H each, 2 q, *J*=7.5 Hz each, 2xC*H*$_2$Me), 2.34 (1 H, quintet, *J*=7.0 Hz, C*H*Me), 5.03-5.10 (2 H, m, C*H*$_2$=C), 5.80-5.92 (1 H, m, C*H*=CH$_2$); δ_C 7.35, 7.5 (2x*Me*CH$_2$), 14.15 (*Me*CH), 27.8, 28.35 (2x*C*H$_2$Me), 44.25 (*C*HMe), 75.0 (CO), 115.5 (*C*H$_2$=C) and 140.45 (*C*H=CH$_2$); m/z 113 (M$^+$-29, 5%), 87 (67), 69 (17), 57 (100), 55 (20), 53 (10), 45 (49), 43 (22) and 41 (23).

3-Ethyl-2-phenyl-3-pentanol (**2eb**)[9e]: R_f 0.41 (hexane/ethyl acetate: 6/1); t_r 10.62 min; ν (film) 3470 (OH), 3040, 3010, 1595 and 1485 cm^{-1} (HC=C); δ_H 0.83 (3 H, t, *J*=7.3 Hz, 1x*Me*CH$_2$), 0.88 (3 H, t, *J*=7.6 Hz, 1x*Me*CH$_2$), 1.05 (1 H, s, OH), 1.22 (1 H, dq, *J*=14.4, 7.6 Hz, 1xC*H*HMe), 1.29 (3 H, d, *J*=7.0 Hz, *Me*CH), 1.37 (1 H, dq, *J*=14.4, 7.6 Hz, 1xC*H*HMe), 1.57 (2 H, q, *J*=7.3 Hz, 1xC*H*$_2$Me), 2.86 (1 H, q, *J*=7.0 Hz, C*H*Me) and 7.18-7.32 (5 H, m, ArH); δ_C 7.6, 7.95 (2x*Me*CH$_2$), 15.25 (1x*Me*CH), 27.3, 29.05 (2x*C*H$_2$Me), 45.4 (1x*C*HMe), 75.85 (CO), 126.25, 128.0, 129.15 and 143.65 (ArC); m/z 192 (M$^+$, <1%), 163 (17), 106 (51), 105 (35), 103 (12), 91 (47), 87 (100), 79 (19), 77 (28), 69 (15), 57 (26), 45 (62), 43(67) and 41 (65).

2-Methyl-4-phenyl-3-pentanol (**2ed**)[24] (1st. diastereoisomer): R_f 0.29 (hexane/ethyl acetate: 6/1); t_r 9.41 min; ν (film) 3488 (OH), 3084, 3060, 3027, 1601 and 1493 cm^{-1} (HC=C); δ_H 0.91 (3 H, d, *J*=6.7 Hz, 1x*Me*$_2$CH), 0.94 (3 H, d, *J*=7.0 Hz, 1x*Me*$_2$CH), 1.30 (3 H, d, *J*=7.0 Hz, *Me*CHPh), 1.40 (1 H, s, OH), 1.54-1.65 (1 H, m, C*H*Me$_2$), 2.90 (1 H, quintet, *J*=7.0 Hz, C*H*Ph), 3.39-3.43 (1 H, m, CHO) and 7.18-7.33 (5 H, m, ArH); δ_C 15.6, 16.7 (2x*Me*$_2$CH), 19.95 (*Me*CHPh), 30.15 (*C*HMe$_2$), 42.75 (*C*HPh), 81.15 (CO), 126.25, 127.6, 128.5 and 145.15 (ArC); m/z 178 (M$^+$, <1%), 106 (100), 105 (18), 91 (80), 77 (10), 73 (15), 55 (12) and 43 (12).

2-Methyl-4-phenyl-3-pentanol (**2ed**)[24] (2nd. diastereoisomer): R_f 0.42 (hexane/ethyl acetate: 6/1); t_r 9.47 min; ν (film) 3488 (OH), 3084, 3060, 3027, 1601 and 1493 cm^{-1} (HC=C); δ_H 0.94, 1.03 (3 H each, 2 d, *J*=6.7 Hz each, 2x*Me*$_2$CH), 1.25 (3 H, d, *J*=7.3 Hz, *Me*CHPh), 1.59 (1 H, s, OH), 1.75-1.85 (1 H, m, C*H*Me$_2$), 2.84 (1 H, quintet, *J*=7.3 Hz, C*H*Ph), 3.44 (1 H, dd, *J*=7.3, 4.3 Hz, CHO) and 7.20-7.35 (5 H, m, ArH); δ_C 15.3, 18.6 (2x*Me*$_2$CH), 20.4 (*Me*CHPh), 30.0 (*C*HMe$_2$), 43.4 (*C*HPh), 80.45 (CO), 126.6, 128.15, 128.55 and 144.05 (ArC); m/z 135 (M$^+$-43, 4%), 106 (98), 105 (32), 103 (14), 91 (100), 79 (20), 57 (16), 55 (27), 51 (22), 45 (16), 43 (83) and 41 (59).

Trimethyl(1-phenylethyl)silane (**2ee**)[25]: R_f 0.50 (hexane); t_r 8.18 min; ν (film) 3082, 3061, 3024, 1601, 1494 (HC=C), 1248 and 837 cm^{-1} (SiMe); δ_H 0.00 (9 H, s, 3xMeSi), 1.42 (3 H, d, *J*=7.5 Hz, *Me*CH), 2.22 (1 H, q, *J*=7.5 Hz, C*H*Me) and 7.07-7.45 (5 H, m, ArH); δ_C -3.35 (3 C, 3xMeSi), 14.75 (*Me*CH), 29.7 (*C*HMe), 124.2, 126.95, 127.9 and 145.9 (ArC); m/z 180 (M$^+$+2, 1%), 179 (M$^+$+1, 3), 178 (M$^+$, 16), 135 (11) and 73 (100).

E-*(3,7-Dimethyl-2,6-octadienyl)trimethylsilane* (**2fe**)[26]: R_f 0.35 (hexane); t_r 9.02 min; ν (film) 1653 (HC=C) and 1247 cm^{-1} (SiMe); δ_H -0.01 (9 H, s, 3xMeSi), 1.41 (2 H, d, *J*=8.5 Hz, CH_2Si), 1.56, 1.62, 1.69 (3 H each, 3 br s, 3xMeC=C), 2.01-2.10 (4 H, m, CH_2CH_2), 5.08-5.15 (1 H, m, C*H*=CMe_2) and 5.15-5.22 (1 H, m C*H*CH_2Si);δ_C -1.75 (3 C, 3xMeSi), 15.7, 17.7, 25.75 (3x*Me*C=C), 18.6 (CH_2Si), 26.85, 40.0 (CH_2CH_2), 120.3, 124.5 (2x*C*H=C), 131.05 and 132.2 (2x*C*=CH); m/z 210 (M$^+$, 3%), 73 (100), 69 (21), 67 (14), 53 (11), 45 (18), 43 (10) and 41 (26).

3-Ethyl-4,8-dimethyl-4-vinyl-7-nonen-3-ol (**2fb'**): R_f 0.26 (hexane); t_r 11.55 min; ν (film) 3503 (OH), 3080, 3059 and 1635 cm^{-1} (HC=C); δ_H 0.90 (3 H, t, *J*=7.6 Hz, 1x*Me*CH_2), 0.91 (3 H, t, *J*=7.5 Hz, 1x*Me*CH_2), 1.04 (3 H, s, *Me*CCH_2), 1.29-1.91 (15 H, m, 4xCH_2, 2x*Me*C=C and OH), 5.01 (1 H, dd, *J*=17.7, 1.5 Hz, 1xC*H*H=C), 5.06-5.13 (1 H, m, C*H*=CMe_2), 5.18 (1 H, dd, *J*=11.0, 1.5 Hz, 1xC*H*H=C) and 5.91 (1 H, dd, *J*=17.7, 11.0 Hz, C*H*=CH_2); δ_C 9.25, 9.30 (2x*Me*CH_2), 16.9, 17.55, 26.65 (2x*Me*C=C and *Me*CCH_2), 23.3, 27.1, 27.3, 35.05 (4xCH_2), 48.6 (*C*CO), 77.0 (CO), 114.9 (*C*H_2=C), 125.15, 144.25 (2x*C*H=C) and 131.0 (*C*Me_2); m/z 206 (M$^+$-18, <1%), 123 (20), 95 (44), 87 (100), 69 (81), 68 (11), 67 (14), 57 (37), 55 (17), 45 (36), 43 (12) and 41 (36) (Found: M$^+$-H_2O, 206.2035. $C_{15}H_{26}$ requires M-H_2O, 206.2035).

2,4,8-Trimethyl-4-vinyl-7-nonen-3-ol (**2fd'**)[27] (diastereoisomers ratio 1:1): R_f 0.28 (hexane); t_r 10.46 min; ν (film) 3488 (OH), 3080 and 1635 cm^{-1} (HC=C); δ_H 0.85, 0.88 (3 H each, 2 d, *J*=6.7 Hz each, 2x*Me*CH), 0.97, 1.00 (3 H each, 2 d, *J*=7.0 Hz each, 2x*Me*CH), 1.02, 1.06 (3 H each, 2 s, 2x*Me*CCO), 1.59 (6 H, s, 2x*Me*$_2$C=C), 1.67 (6 H, s, 2x*Me*$_2$C=C), 1.21-1.49, 1.82-2.00 (4 H and 6 H, respectively, 2 m, 2xC*H*$_2$C*H*$_2$ and 2xC*H*Me_2), 3.18 (1 H, d, *J*=4.9 Hz, 1xCHO), 3.19 (1 H, d, *J*=5.2 Hz 1xCHO), 5.02, 5.03 (1 H each, 2 dd, *J*=17.7, 1.5 Hz each, 2xC*H*H=CH), 5.07-5.11 (2 H, m, 2xC*H*=CMe_2), 5.14, 5.16 (1 H each, 2 dd, *J*=11.0, 1.5 Hz each, 2xC*H*H=CH), 5.80 and 5.84 (1 H each, 2 dd, *J*=17.7, 11.0 Hz each, 2xC*H*=CH_2); δ_C 16.6, 16.9, 17.6, 18.0 (4x*Me*CH), 19.1 (2 C, 2x*Me*CCH_2), 22.7 (2 C, 2x*C*H_2C), 23.4, 23.6, 25.65 (2 C)(4x*Me*$_2$C), 28.5, 28.9 (2x*C*HMe_2), 38.2, 38.55 (2x*C*H_2CH), 45.5, 45.6 (2x*C*CO), 81.1, 81.65 (2xCO), 114.25 (2 C, 2x*C*H_2=CH), 124.85 (2 C), 143.95, 144.5 (4x*C*H=C) and 131.3 (2 C, 2x*C*Me_2); m/z 211 (M$^+$+1, <1%), 210 (M$^+$, <1), 123 (21), 95 (49), 82 (12), 73 (19), 70 (15), 69 (100), 68 (14), 55 (27), 43 (16) and 41 (36).

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