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PAPER

One-pot multicoupling reaction of silylcopper reagents, organolithium compounds and α,β-unsaturated nitriles†

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The silylcupration of allene using a lower order silylcopper species gives an allylsilane–vinyl copper intermediate **2** which, in conjunction with an organolithium reagent, is able to participate in a one-pot multicoupling reaction with α,β-unsaturated nitriles. The scope of this tandem reaction is studied and a possible mechanism pathway is outlined.

Introduction

The development of new strategies directed to the efficient introduction of various functionalized groups into a molecule, with a minimum of chemical steps, constitutes one of the subjects of increasing interest in the synthesis of complex structures.
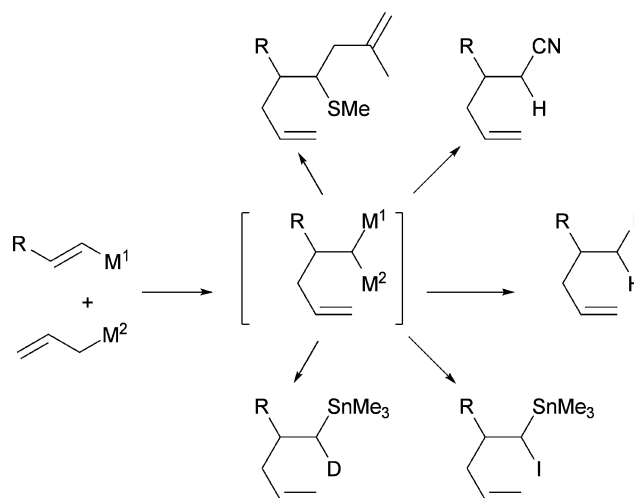
In this sense, there have been many attempts to achieve the consecutive introduction of various reagents into a substrate in a single operation, the so-called multicomponent one-pot-reactions. Thus, Gaudemar,[1] Knochel,[2,3] and Normant's groups[4,5] have described the synthesis of *gem*-dimetallic reagents *via* a carbometallation process of vinyl organometallics with allylic zinc bromides.[6] The dimetallic reagents, containing two metals of different nature and reactivity, show good chemoselectivity in the presence of two different electrophiles to give the corresponding multicoupled products in good yields. This reaction works even when the two different electrophiles are added simultaneously to the dimetallic reaction media (Scheme 1).

On the other hand, Nakamura[7] has reported that the simultaneous addition of two different electrophiles to a novel dimetallated hydrazone provides chemoselectively the product of double trapping, in nearly quantitative yield.

A different approach to a one-pot multicoupling reaction has been described by de Meijere[8] in his synthesis of primary amines by the consecutive addition of two equivalents of a Grignard reagent to a nitrile, in the presence of Ti(OiPr)$_4$. However, the reaction is low-yielding when two different Grignard reagents are used.

Another example of this strategy has been reported by Shimizu,[9,10] who developed an efficient method for the introduction of two different nucleophiles into an α,β-unsaturated aldimine, to give functionalized amines in a one-pot procedure.

On the other hand, allylsilanes have been extensively used as building blocks in the construction of natural products,[11,12] due

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† We are pleased to dedicate this article to Professor Carmen Nájera on the occasion of her 60th birthday.

Scheme 1 Reactivity of *gem*-dimetallic reagents.

to their remarkable versatility and synthetic utility. For the last decade, we have been involved in the study of the silylcupration of allenes[13,14] and in the development of new strategies, using the allylsilanes thus obtained, for the synthesis of carbocycles[15,16] of close structure to some natural products (Scheme 2).

Thus, in the course of the study of the silylcupration of allene, followed by capture of the intermediate allylsilane–vinylcuprate **2** with α,β-unsaturated nitriles[17] we discovered an interesting stepwise one-pot conversion of alkenenitriles to the corresponding products of double 1,2 and 1,4-diaddition.
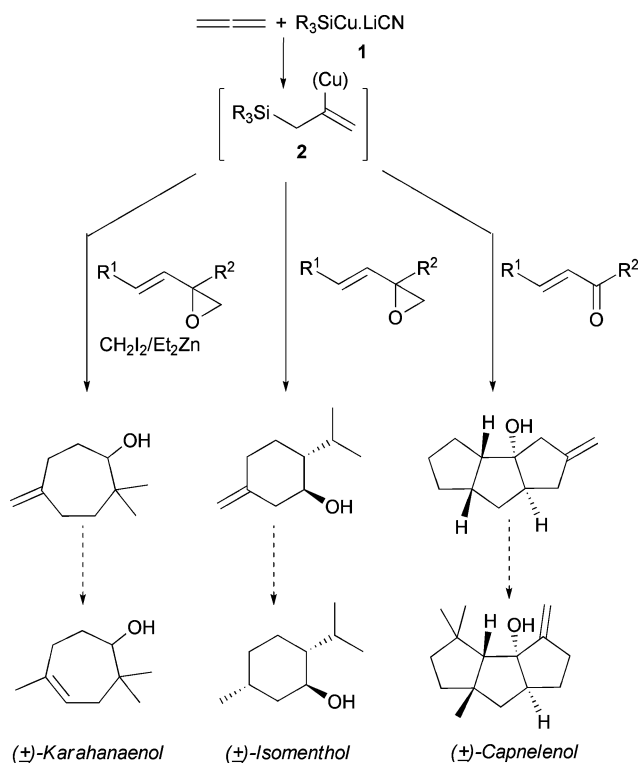
In this paper we describe an efficient method for the selective double nucleophilic addition of two different organometallics to α,β-unsaturated nitriles to give the products of double addition in an efficient one-pot procedure.

Results and discussion

Thus, the addition of α,β-unsaturated nitriles to an equimolar mixture of an organolithium reagent and an allylsilane—vinylcopper intermediate **2**, generated by reaction of allene with the lower

Scheme 2 Allylsilanes as intermediates in the synthesis of carbocycles.

order *tert*-butyldiphenylsilylcopper or phenyldimethylsilylcopper **1**, provides functionalized ketones **3** in good yields over two steps (Scheme 3).
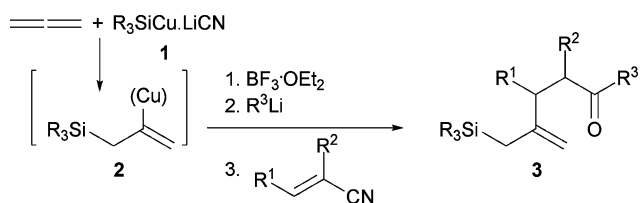
Scheme 3 Double nucleophilic addition of different organometallics to α,β-unsaturated nitriles.

To study the scope of this interesting process we have used a wide variety of organolithium reagents, different substituted nitriles and silyl groups of different nature (Table 1). As we observe from results quoted in Table 1, both aryl-substituted and alkyl-substituted acrylonitriles undergo this sequential double addition. On the other hand, the use of alkyllithium reagents provides the best yields of the double addition product, though the reaction also works when aryllithium or allyllithium is used. Moreover, both phenyldimethylsilyl and *tert*-butyldiphenylsilyl groups give satisfactorily the tandem reaction (Table 1).

Interestingly, the different nature of the two metals (lithium and copper) in both organometallics was used in a chemoselective manner to create successively two new bonds in their reaction with alkenenitriles. Thus, since carbon–copper and carbon–lithium (or carbon–magnesium) bonds show very different reactivities, they are able to add stepwise to an electrophile with two reactive sites, such as the α,β-unsaturated nitrile, affording the products of double 1,2- and a 1,4-diaddition. We couldn't isolate either

Table 1 Scope of the multicoupling reaction

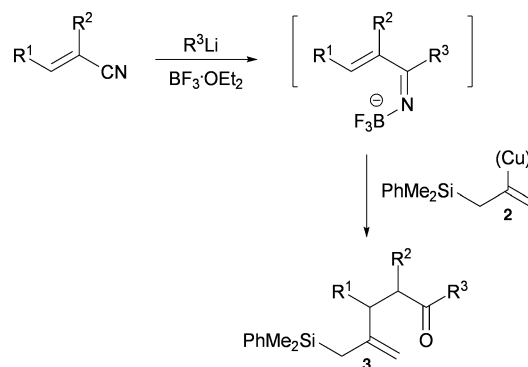| Nitrile		Organolithium			
R^1	R^2	R^3	SiR_3	Product	Yield (%)^a
H	Me	Me	SiPh$_2$^{t}Bu	**3a**	58
H	Me	Bu	SiPh$_2$^{t}Bu	**3b**	50
Me	H	Bu	SiPh$_2$^{t}Bu	**3c**	55
Et	H	Bu	SiPh$_2$^{t}Bu	**3d**	60
Ph	H	Bu	SiPh$_2$^{t}Bu	**3e**	57
H	Me	Bu	SiPh$_2$^{t}Bu	**3f**	50
H	Me	Ph	SiMe$_2$Ph	**3g**	49
H	Me	Allyl	SiMe$_2$Ph	**3h**	40
Me	H	Me	SiMe$_2$Ph	**3i**	51

^{a} The allylsilane of hydrolysis R$_3$Si⌇ was isolated, as the major byproduct.

the products of 1,4-monoaddition **4** or the products of 1,2-monoaddition **5** (Scheme 4), which seems to indicate that the reaction of the intermediate monoaddition product with the remaining organometallic is very fast.
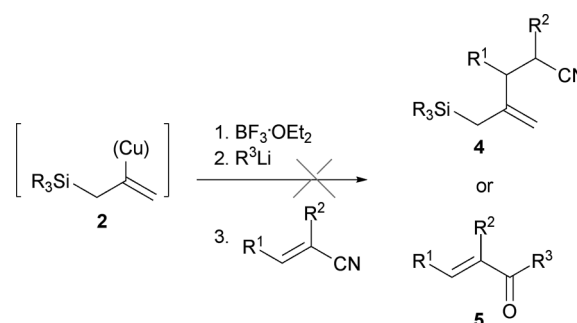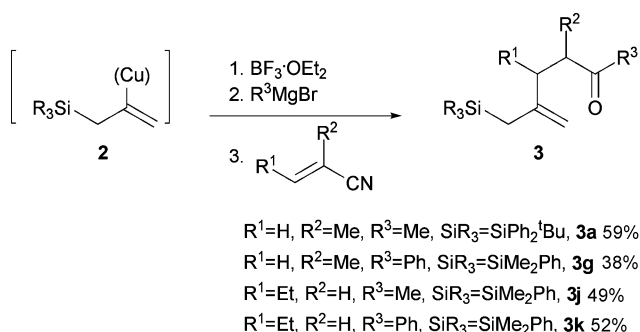

Scheme 4 The products of monoaddition couldn't be isolated.

From these results we propose a plausible reaction mechanism as shown in Scheme 5. Thus, the initial 1,2-addition of the more reactive organolithium reagent to the vinyl nitrile would generate an α,β-unsaturated imine intermediate, which in turn is attacked by the allylsilane–vinylcopper **2** in a conjugate addition to give, after final hydrolysis, the product of double nucleophilic addition **3** (Scheme 5).

Scheme 5 Mechanism of the reaction.

Finally, we examined the validity of this protocol when a Grignard reagent is used instead of the organolithium reagents. Results are summarized in Scheme 6. As we can see organomagnesium

Scheme 6 Multicoupling reaction using Grignard reagents.

R[1]=H, R[2]=Me, R[3]=Me, SiR$_3$=SiPh$_2$^{t}Bu, **3a** 59%
R[1]=H, R[2]=Me, R[3]=Ph, SiR$_3$=SiMe$_2$Ph, **3g** 38%
R[1]=Et, R[2]=H, R[3]=Me, SiR$_3$=SiMe$_2$Ph, **3j** 49%
R[1]=Et, R[2]=H, R[3]=Ph, SiR$_3$=SiMe$_2$Ph, **3k** 52%

reagents are also effective for promoting the reaction, though yields are slightly lower (Scheme 6).

Conclusions

In summary, this paper describes a four component reaction by a double nucleophilic addition of two different organometallics (organolithium/organomagnesium and an allylsilane–vinylcopper reagent) to α,β-unsaturated nitriles to give, in a one-pot procedure, functionalized oxoallylsilanes. This methodology provides a quick one-pot assembly of equimolar amounts of four substrates: allene, a silylcopper reagent, an organolithium reagent and a nitrile.

Experimental

General experimental

All the reactions were carried out under an atmosphere of argon or nitrogen in dried glassware unless otherwise indicated. Materials were obtained from commercial suppliers and used without further purification except when otherwise noted. Solvents were dried and distilled according to the standard protocols. Flash column chromatography was performed on silica gel using the indicated solvent.

General procedure for one-pot double addition

A solution of dimethylphenylsilyl-lithium (6 mmol) in THF was added by syringe to a stirred suspension of copper(I) cyanide (6 mmol) in THF at 0 °C. After 30 min at this temperature the solution of silylcopper 1 (6 mmol) was cooled at −40 °C and a slight excess of allene was added from a balloon. The mixture was stirred for 1 h and then used immediately.

The organolithium or Grignard reagent (6 mmol) was added to this solution at −60 °C and then 6 mmol of BF$_3$·Et$_2$O was added to the mixture and stirred for an additional period of 10 min. The nitrile (6 mmol) in THF was slowly dropped in at −60 °C and stirred at this temperature for 1 h. The reaction mixture was allowed to warm to 0 °C, quenched with basic saturated ammonium chloride solution and extracted with ether. The organic layer was dried (MgSO$_4$), evaporated and chromatographed to give the corresponding products.

5-[(*tert*-Butyldiphenylsilyl)methyl]-3-methyl-5-hexen-2-one (3a). Colorless oil; Yield (58%); IR ν_{max}(film)/cm^{-1} 1715, 1633, 1105,

885; ^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): 7.76–7.27 (m, 10H, 2×Ph), 4.74 (s, 1H, C*H*H=), 4.60 (s, 1H, CH*H*=), 2.56–2.44 (m, 1H, CH), 2.31 (d, J = 13.7 Hz, 1H, C*H*H–Si), 2.16 (d, J = 13.7 Hz, 1H, CH*H*-Si), 2.02 (dd, J = 14.5 and 6.5 Hz, 1H, C*H*H–C=), 1.90 (s, 3H, CH$_3$-CO), 1.63 (dd, J = 14.5 and 7.9 Hz, 1H, CH*H*-C=), 1.11 (s, 9H, ^{t}Bu), 0.84 (d, J = 6.9, 3H, C*H$_3$*-CH); ^{13}C NMR (75 MHz, CDCl$_3$) δ (ppm): 212.3, 143.9, 136.1, 134.6, 129.2, 127.5, 112.3, 44.9, 41.3, 27.7, 20.0, 18.6, 15.8; MS (EI): *m/z* 349 (M$^+$ − CH$_3$, 34%), 307 (M$^+$ − ^{t}Bu, 5%), 239 (^{t}BuPh$_2$Si, 12%); Anal. Calcd for C$_{24}$H$_{32}$OSi: C, 79.06; H, 8.85; Found: C, 79.45; H, 8.56%.

2-[(*tert*-Butyldiphenylsilyl)methyl]-4-methyl-1-nonen-5-one (3b). Colorless oil; Yield (50%); IR ν_{max}(film)/cm^{-1} 1714, 1632, 1256, 1105, 885; ^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): 7.68–7.27 (m, 10H, 2×Ph), 4.71 (s, 1H, CH*H*=), 4.57 (s, 1H, C*H*H=), 2.55–2.44 (m, 1H, CH-CO), 2.25 (d, J = 14.3 Hz, 1H, CH*H*-Si), 2.20 (d, J = 14.3 Hz, 1H, C*H*H–Si), 2.15 (t, J = 7.3 Hz, 2H, C*H$_2$*-CO), 2.00 (dd, J = 14.3 and 6.8 Hz, 1H, CH*H*-CH), 1.57 (dd, J = 14.3 and 7.8 Hz, 1H, C*H*H-CH), 1.49-1.41 (m, 2H, CH$_2$), 1.39–1.15 (m, 2H, C*H$_2$*-CH$_3$), 1.09 (s, 9H, 3×CH$_3$), 0.89 (t, J = 7.2 Hz, 3H, C*H$_3$*-CH$_2$), 0.80 (t, J = 6.9 Hz, 3H, C*H$_3$*-CH); ^{13}C NMR (75 MHz, CDCl$_3$) δ (ppm): 214.3, 144.0, 136.1, 134.7, 129.1, 127.5, 112.3, 44.1, 41.3, 40.5, 27.7, 25.5, 22.2, 20.0, 18.6, 15.9, 13.9; MS (EI): *m/z* 406 (M$^+$, 10%), 391 (M$^+$ − CH$_3$, 5%), 349 (M$^+$ − Bu, 17%), 239 (^{t}BuPh$_2$Si, 10%); Anal. Calcd for C$_{27}$H$_{38}$OSi: C, 79.74; H, 9.42; Found: C, 80.11; H, 9.73%.

2-[(*tert*-Butyldiphenylsilyl)methyl]-3-methyl-1-nonen- 5-one (3c). Colorless oil; Yield (55%); IR ν_{max}(film)/cm^{-1} 1713, 1633, 1106, 925; ^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): 4.60 (s, 1H, CH*H*=), 4.55 (s, 1H, C*H*H=), 2.30–2.09 (m, 5H, CH$_3$–C*H*, 2×CH$_2$-CO), 2.19 (s, 2H, CH$_2$-Si), 1.45 (quintet, J = 7.3 Hz, 2H, C*H$_2$*-CH$_2$), 1.40–1.10 (m, 2H, CH$_2$–C*H$_2$*), 1.06 (s, 9H, 3×CH$_3$), 0.89 (t, J = 7.2 Hz, 3H, C*H$_3$*-CH$_2$), 0.79 (d, J = 6.2 Hz, 3H, C*H$_3$*-CH); ^{13}C NMR (75 MHz, CDCl$_3$) δ (ppm): 210.4, 150.5, 136.2, 134.4, 129.0, 127.4, 108.8, 48.9, 42.4, 36.6, 27.8, 25.7, 22.2, 19.2, 18.6, 18.5, 13.8; MS (EI): *m/z* 406 (M$^+$, 7%), 391 (M$^+$ − CH$_3$, 7%), 349 (M$^+$ − Bu, 20%), 239 (^{t}BuPh$_2$Si, 13%).

2-[(*tert*-Butyldiphenylsilyl)methyl]-3-ethyl-1-nonen- 5-one (3d). Colorless oil; Yield (60%); IR ν_{max}(film)/cm^{-1} 1714, 1636, 1256, 1105, 876; ^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): 7.69–7.27 (m, 10H, 2×Ph), 4.62 (s, 1H, CH*H*=), 4.55 (s, 1H, C*H*H=), 2.33–2.10 (m, 3H, CH and CH–C*H$_2$*-CO), 2.17 (t, J = 7.1 Hz, 2H, C*H$_2$*-CO), 2.17 (s, 2H, CH$_2$- Si), 1.45-1.3 (m, 2H, C*H$_2$*-CH), 1.28–0.9 (m, 4H, C*H$_2$*-C*H$_2$*), 1.03 (s, 9H, 3×CH$_3$), 0.88 (t, J = 7.3 Hz, 3H, C*H$_3$*-CH$_2$), 0.65 (t, J = 7.4 Hz, 3H, C*H$_3$*-CH$_2$-CH); ^{13}C NMR (75 MHz, CDCl$_3$) δ (ppm): 210.6, 147.9, 136.2, 134.4, 129.0, 127.4, 111.4, 46.8, 43.7, 42.5, 27.8, 25.8, 25.7, 22.3, 18.4, 17.6, 13.9, 11.0; MS (EI): *m/z* 420 (M$^+$, 2%), 391 (M$^+$ − Et, 12%), 363 (M$^+$ − Bu, 15%), 239 (^{t}BuPh$_2$Si, 13%); Anal. Calcd for C$_{28}$H$_{40}$OSi: C, 79.94; H, 9.58; Found: C, 79.58; H, 9.85%.

2-[(*tert*-Butyldiphenylsilyl)methyl])-3-phenyl-1-nonen-5-one (3e). Colorless oil; Yield (57%); IR ν_{max}(film)/cm^{-1} 1717, 1632, 1245, 1104, 925; ^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): 7.67–7.27 (m, 10H, 2×Ph), 7.25–6.98 (m, 5H, Ph), 4.75 (s, 1H, CH*H*=), 4.73 (s, 1H, C*H*H=), 3.37 (dd, J = 9.6 and 5.2 Hz, 1H, CH-Ph), 2.62 (dd, J = 15.5 and 9.6 Hz, 1H, CH*H*-CH), 2.43 (dd, J = 15.5 and 5.2 Hz, 1H, C*H*H-CH), 2.19 (d, J = 15.0 Hz, 1H, CH*H*-Si), 2.11–1.92 (m, 2H, CH$_2$–CO), 1.87 (d, J = 15.0 Hz, 1H, C*H*H–Si), 1.34–1.16

(m, 2H, CH_2- CH$_2$), 1.15–1.04 (m, 2H, CH_2-CH$_3$), 1.00 (s, 9H, 3×CH$_3$), 0.79 (t, J = 7.2 Hz, 3H, CH_3-CH$_2$); ^{13}C NMR (75 MHz, CDCl$_3$) δ (ppm): 209.1, 148.1, 142.3, 136.3, 136.2, 134.5, 134.3, 129.1, 129.0, 128.2, 127.4, 126.4, 110.1, 47.9, 47.8, 42.6, 27.7, 25.4, 22.1, 19.1, 18.4, 13.7; MS (EI): m/z 391 (M$^+$ – Ph, 8%), 411 (M$^+$ – Bu, 20%), 239 (^{t}BuPh$_2$Si, 19%); Anal. Calcd for C$_{32}$H$_{40}$OSi: C, 81.99; H, 8.60; Found: C, 82.32; H, 8.89%.

2-[(Dimethylphenylsilyl)methyl)]-4-methyl-1-nonen-5-one (3f).
Colorless oil; Yield (50%); IR ν_{max}(film)/cm^{-1} 1714, 1631, 1249, 1112, 885; ^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): 7.56–7.27 (m, 5H, Ph), 4.58 (s, 2H, CH$_2$=), 2.67–2.59 (m, 1H, CH), 2.33–2.26 (m, 2H, CH$_2$-CO), 2.19 (dd, J = 14.4 and 6.7 Hz, 1H, CHH-CH), 1.76 (d, J = 13.6 Hz, 1H, CHH-Si), 1.75 (dd, J = 14.4 and 7.8 Hz, 1H, CHH-CH), 1.71 (d, J = 13.6 Hz, 1H, CHH-Si), 1.52–1.44 (m, 2H, CH$_2$), 1.34–1.23 (m, 2H, CH$_2$), 0.96 (d, J = 6.8 Hz, 3H, CH_3-CH), 0.90 (t, J = 7.2 Hz, 3H, CH_3-CH$_2$), 0.33 (s, 6H, 2×CH$_3$–Si); ^{13}C NMR (75 MHz, CDCl$_3$) δ (ppm): 214.4, 144.1, 138.8, 133.5, 129.2, 127.5, 110.0, 44.2, 41.3, 40.9, 26.9, 25.6, 22.3, 16.1, 13.9, –3.0, –3.2; MS (EI): m/z 302 (M$^+$, 28%), 287 (M$^+$ – CH$_3$, 8%), 273 (M$^+$ – Et, 4%), 245 (M$^+$ – Bu, 18%), 167 (M$^+$ – SiMe$_2$Ph, 13%), 135 (SiMe$_2$Ph, 100%), 57 (Bu, 5%); Anal. Calcd for C$_{19}$H$_{30}$OSi: C, 75.43; H, 10.00; Found: C, 75.78; H, 9.67%.

3-[(Dimethylphenylsilyl)methyl)]-1-methyl-3-butenyl phenyl ketone (3g). Colorless oil; Yield (49%); IR ν_{max}(film)/cm^{-1} 1688, 1630, 1251, 1110, 878; ^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): 7.58–7.27 (m, 10H, 2×Ph), 4.63 (s, 1H, CHH=), 4.59 (s, 1H, CHH=), 3.61 (sextet, J = 6.9 Hz, 1H, CH), 2.44 (dd, J = 14.8 and 6.5 Hz, 1H, CHH-C=), 1.95 (dd, J = 14.8 and 7.3 Hz, 1H, CHH–C=), 1.82 (d, J = 13.7 Hz, 1H, CHH-Si), 1.76 (d, J = 13.7 Hz, 1H, CHH–Si), 1.14 (d, J = 6.9 Hz, 3H, CH_3-CH), 0.34 (s, 3H, CH$_3$–Si), 0.32 (s, 3H, CH$_3$–Si); ^{13}C NMR (75 MHz, CDCl$_3$) δ (ppm): 215.2, 144.2, 136.5, 133.5, 132.8, 129.0, 128.6, 128.2, 127.7, 109.7, 41.6, 38.7, 26.0, 17.3, –3.0; MS (EI): m/z 322 (M$^+$, 5%), 307 (M$^+$ – CH$_3$, 19%), 245 (M$^+$ – Ph, 25%), 135 (SiMe$_2$Ph, 100%); Anal. Calcd for C$_{21}$H$_{26}$OSi: C, 78.21; H, 8.13; Found: C, 77.89; H, 8.41%.

7-[(Dimethylphenylsilyl)methyl)]-5-methyl-1,7-octadien-4-one (3h). Colorless oil; Yield (40%); IR ν_{max}(film)/cm^{-1} 1710, 1634, 1251, 1112, 885; ^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): 7.60–7.27 (m, 5H, Ph), 5.86 (ddt, J = 17.1, 10.3 and 6.9 Hz, 1H, CH=), 5.15 (d, J = 10.3 Hz, 1H, CHH=), 5.08 (d, J = 17.1 Hz, 1H, CHH=), 4.59 (s, 2H, CH$_2$=), 3.08 (d, J = 6.9 Hz, 2H, CH$_2$-CO), 2.72–2.63 (m, 1H, CH-CO), 2.19 (dd, J = 14.5 and 6.7 Hz, 1H, CHH–C=), 1.78 (dd, J = 14.5 and 7.7 Hz, 1H, CHH-C=), 1.76 (d, J = 13.8 Hz, 1H, CHH-Si), 1.69 (d, J = 13.8 Hz, 1H, CHH–Si), 0.97 (d, J = 6.9 Hz, 3H, CH_3-CH), 0.33 (s, 6H, 2×CH$_3$–Si); ^{13}C NMR (75 MHz, CDCl$_3$) δ (ppm): 211.9, 143.9, 138.8, 133.5, 130.8, 129.1, 127.8, 118.4, 110.2, 46.0, 43.8, 41.2, 25.6, 16.0, –2.9, –3.2; MS (EI): m/z 286 (M$^+$, 13%), 271 (M$^+$ – CH$_3$, 10%), 135 (SiMe$_2$Ph, 100%).

5-[(Dimethylphenylsilyl)methyl)]-4-methyl-5-hexen-2-one (3i). Colorless oil; Yield (51%); IR ν_{max}(film)/cm^{-1} 1720, 1633, 1240, 1114, 878; ^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): 7.58–7.27 (m, 5H, Ph), 4.63 (s, 1H, CHH=), 4.57 (s, 1H, CHH=), 2.52 (dd, 1H, J = 15.3 and 4.2 Hz, CHH-CO), 2.44–2.33 (m, 1H, CH), 2.27 (dd, J = 15.3 and 8.8 Hz, 1H, CHH-CO), 2.04 (s, 3H, CH$_3$-CO), 1.81 (d, J = 14.7 Hz, 1H, CHH-Si), 1.76 (d, J = 14.7 Hz, 1H, CHH-Si),

0.97 (d, J = 6.6 Hz, 3H, CH_3-CH), 0.35 (s, 3H, CH$_3$–Si), 0.34 (s, 3H, CH$_3$–Si); ^{13}C NMR (75 MHz, CDCl$_3$) δ (ppm): 208.2, 150.9, 138.9, 133.6, 129.0, 127.7, 106.6, 49.8, 36.3, 30.2, 25.0, 19.4, –2.9; MS (EI): m/z 260 (M$^+$, 10%), 245 (M$^+$ – CH$_3$, 100%), 217 (M$^+$ – CH$_3$ – CO, 40%); Anal. Calcd for C$_{16}$H$_{24}$OSi: C, 73.79; H, 9.29; Found: C, 74.18; H, 9.58%.

5-[(Dimethylphenylsilyl)methyl)]-4-ethyl-5-hexen-2-one (3j). Colorless oil; Yield (49%); IR ν_{max}(film)/cm^{-1} 1710, 1630, 1241, 1111, 878; ^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): 7.56–7.27 (m, 5H, Ph), 4.76 (s, 1H, CHH=), 4.73 (s, 1H, CHH=), 2.48–2.22 (m, 3H, CH$_2$-CO, CH), 2.04 (s, 3H, CH$_3$-CO), 1.73 (s, 2H, CH$_2$-Si), 1.55 (quint, J = 6.5 Hz, 2H, CH_2-CH$_3$), 0.80 (t, J = 7.5 Hz, 3H, CH_3-CH$_2$), 0.36 (s, 3H, CH$_3$–Si), 0.35 (s, 3H, CH$_3$–Si); ^{13}C NMR (75 MHz, CDCl$_3$) δ (ppm): 211.5, 146.1, 138.3, 133.5, 129.2, 127.8, 109.6, 48.9, 44.0, 27.8, 25.3, 21.3, 11.1, –2.9; MS (EI): m/z 274 (M$^+$, 8%), 259 (M$^+$ – CH$_3$, 100%), 231 (M$^+$ – CH$_3$ – CO, 20%); Anal. Calcd for C$_{17}$H$_{26}$OSi: C, 74.39; H, 9.55; Found: C, 74.73; H, 9.86%.

3-[(Dimethylphenylsilyl)methyl)]-2-ethyl-3-butenyl phenyl ketone (3k). Colorless oil; Yield (52%); IR ν_{max}(film)/cm^{-1} 1720, 1635, 1243, 1110, 881; ^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): 7.61–7.24 (m, 10H, 2×Ph), 4.66 (s, 1H, CHH=), 4.64 (s, 1H, CHH=), 2.96 (dd, J = 16.2 and 6.1 Hz, 1H, CHH-CO), 2.89 (dd, J = 16.2 and 7.0 Hz, 1H, CHH-CO), 2.41-2.32 (m, 1H, CH), 1.76 (s, 2H, CH$_2$–Si), 1.08–1.01 (m, 2H, CH_2-CH$_3$), 0.79 (t, J = 7.4 Hz, 3H, CH_3-CH$_2$), 0.34 (s, 6H, 2×CH$_3$–Si); ^{13}C NMR (75 MHz, CDCl$_3$) δ (ppm): 206.0, 149.1, 139.6, 133.2, 133.0, 129.0, 128.6, 128.1 127.6, 109.5, 53.6, 43.2, 29.4, 24.6, 10.9, 3.1; MS (EI): m/z 336 (M$^+$, 12%), 321 (M$^+$ – CH$_3$, 100%), 259 (M$^+$ – Ph, 30%).

Acknowledgements

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