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Note

Bismetalated carbon for tandem Wittig-type reaction via allylgallation of magnesium acetylides: A convenient and efficient method to allyl allenes

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Abstract

A tandem Wittig-type reaction via allylgallation of magnesium acetylides to afford allyl allenes was reported. As a result of the ready availability of starting materials and the simple and convenient operation, this reaction would have potential utility in organic synthesis.

Keywords: Bismetalation; Wittig-type reaction; Allylgallation; Magnesium acetylide; Allyl allene

1. Introduction

In the past decade, organogallium chemistry, considered as "young chemistry" [1], has attracted increasing attention [2,3]. Early in 1997, Yamaguchi reported the addition of allylic gallium compounds to alkynes [2a] and in 2002, Takai reported a tertiary amine-accelerated allylgallation of alkynes [2b]. In these references an interesting 1, 1-bismetalated intermediate was proposed, but no further synthetic applications were developed. Although the 1,1-bismetalated intermediate was not isolated, both Yamaguchi and Takai group gave enough and reliable evidence to prove it (Scheme 1).

During our study, we observed that the organogallium intermediate could be trapped by electrophiles, such as acid chlorides [4]. Normant and Marek reported many useful reactions about *gem*-dismetallic compounds in organic synthesis (Scheme 2) [5].

These facts stimulated us to further investigate the possibility of a tandem reaction of the 1,1-bismetalated compound with a suitable electrophile, to afford a simple and efficient method to new carbon–carbon double bond and useful compounds.

2. Results and discussion

As a first attempt, we used 1 mmol of hept-1-yne, 1 mmol of EtMgBr and 3 mmol of allylgallium to produce the 1,1-bismetalated-2-allyl-hept-1-ene [2b]. We isolated 2-allyl-hept-1-ene (**1a**) in 93% yield after the reaction mixture was quenched with saturated NH_4Cl. However, considering that the excessive allylgallium will react with aldehydes and give theoretically 2 equiv. of homoallylic alcohols [6], we decreased the amount of allylgallium to 1.2 equiv. and obtained **1a** in 88% yield. Then a series of electrophiles were chosen for trapping 1,1-bismetalated-2-allyl-hept-1-ene. The results were summarized in Table 1.

For the reaction of 1,1-bismetalated-2-allyl-hept-1-ene with 4-chlorobenzaldehyde, most of aldehyde was recovered, indicating that 1,1-bismetalated-2-allyl-hept-1-ene might be lower reactive than normal Grignard reagent. Thus, we conducted this reaction at higher temperature and got much better results (Scheme 3).

Encouraged by this result, we chose 60 °C as the reaction temperature and a series of 3-allyl allenes (**3**) were synthesized smoothly in moderate yields (Table 2).

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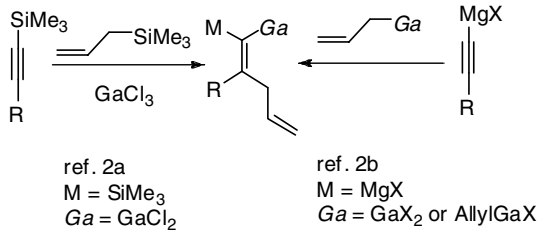
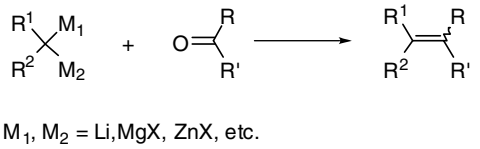


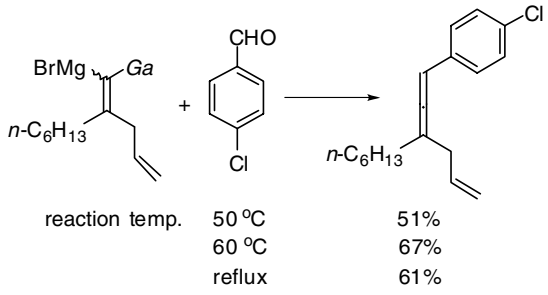
Scheme 1.



Scheme 2.

It is notable that 1,1-bisgallated-2-allyl-hept-1-ene, prepared by the reaction of hept-1-yne with excessive allylgallium [2b], could not react with aldehyde, demonstrating that at least one C–Mg bond of the 1,1-bismetalated intermediate was essential (Scheme 4).

A plausible mechanism proposal is shown in Scheme 4. At first a Grignard reaction occurs, affording the β-gallium alkoxide intermediate A. The intermediate A, probably via a four-membered ring intermediate B, eliminates a gallium(III) bromide oxide to produce allyl allene (Scheme 5) [7].



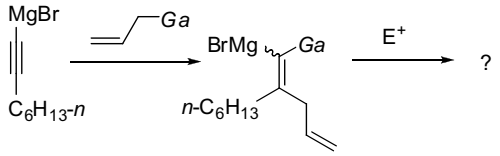
Scheme 3.

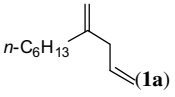
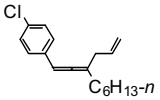
In summary, we have reported a simple and efficient protocol for the synthesis of 3-allyl allenes, which are useful building blocks in organic synthesis [8]. Although the delicate, complicated and exquisite synthetic methods are of interest for organic community, this type of reaction presented here, as a result of the ready availability of starting materials and the simple and convenient operation, has potential utility in organic synthesis.

3. Experimental

All ^{1}H NMR spectra were measured in $CDCl_3$ and recorded on Bruker Avance-400 (400 MHz) spectrometer

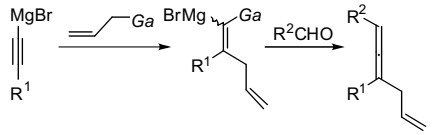
Table 1
Reaction of 1,1-bismetalated-2-allyl-hept-1-ene of electrophiles[a]



Entry	E^+	Equiv.	Time (h)	Product	Yield (%)
1	CH_3COCl	1.2	2	Mixture of mono- and diacylation	32(1:3)[b]
2	CH_3COCl	2.4	2		56(1:5.6)[b]
3	PhCOCl	2.4	2		61(1:6)[b]
4	EtOAc	3.0	24	 (**1a**)	77
5	$PhCOCH_3$	1.5	24	**1a**	72[c]
6	PhCOPh	1.5	24	**1a**	59[d]
7	*p*-Cl–PhCHO	1.5	24		19[e]
8	*n*-PrCHO	1.5	48	**1a**	80

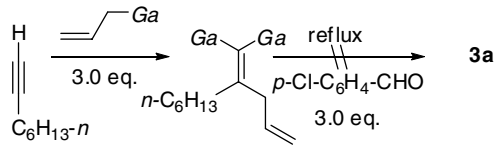
[a] All reactions were carried out in 5 mL of THF under N_2 at r.t.
[b] The ratio of monoacylation/diacylation.
[c] The iodine-quenching of the reaction mixture gave monoiodide and diiodides with a ratio of 1:3.
[d] An unidentified mixture was observed.
[e] 51% of **1a** was isolated and 63% of aldehyde was recovered.

Table 2
Synthesis of 3-allyl allenes[a,b]

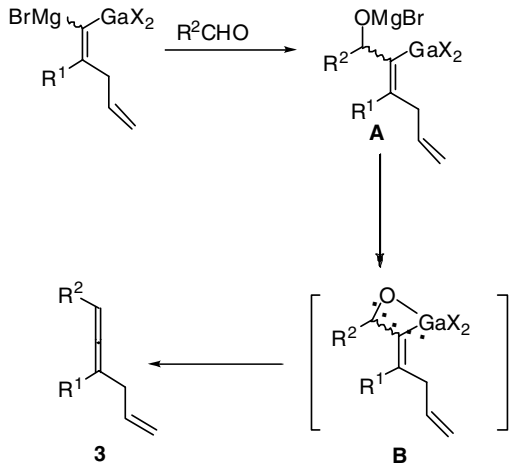


Entry	R^1	R^{2c}	Yield of **3**
1	*n*-Hex	*p*-Cl–C_6H_4–	67(**3a**)
2	*n*-Hex	*p*-Br–C_6H_4–	69(**3b**)
3	*n*-Hex	*p*-Me–C_6H_4–	59(**3c**)
4	*n*-Hex	*o*-Br–C_6H_4–	62(**3d**)
5	*n*-Pent	*p*-Cl–C_6H_4–	65(**3e**)
6	*n*-Pent	*p*-Br–C_6H_4–	64(**3f**)
7	*n*-Pent	*p*-Me–C_6H_4–	60(**3g**)
8	*n*-Pent	*o*-Br–C_6H_4–	72(**3h**)
9	*n*-Pent	C_6H_5–	62(**3i**)
10	C_6H_5–	*p*-Cl–C_6H_4–	51(**3j**)
11	C_6H_5–	*p*-Br–C_6H_4–	53(**3k**)

[a] All reactions were carried out in 1 mmol scale in 5 mL of THF under N_2 at 60 °C.
[b] Allylgallium was prepared according to Ref. [2b].
[c] Bis(4-fluorophenyl)methanone was examined and did not give allene.



Scheme 4.



Scheme 5.

with TMS as the internal standard. ^{13}C NMR spectra were measured in $CDCl_3$ and recorded on Bruker Avance-400 (100 MHz) spectrometer with TMS as the internal standard. Chemical shifts are expressed in ppm and *J* values are given in Hz. IR spectra were run on a Bruker vector 22 spectrometer. EIMS were determined with a HP5989B mass spectrometer. All the reactions in this paper were performed under nitrogen atmosphere.

3.1. General procedure for the synthesis of allylgallium

To 100 mmol of gallium metal (powder) and 5 mmol of metal indium were added 90 mL THF and 150 mmol of allyl bromide under a nitrogen atmosphere at 10 °C. When the gallium dissolved after about 3 h, the solution of allyl gallium (ca. 1.0 M solution) was stored in a refrigerator for use.

3.2. General procedure for the synthesis of 3-allyl allenes (*3a–3k*)

To the solution of 1.2 mmol of allylgallium in THF was added 1 mmol of magnesium acetylide under a N_2 atmosphere at room temperature, followed by stirring for 4 h. Then 1.5 mmol of aldehyde were added to the reaction mixture, followed by a warming to 60 °C for 24 h. The reaction mixture was cooled to room temperature, quenched with saturated NH_4Cl, extracted with petroleum ether, and dried over anhydrous Na_2SO_4. After evaporation, chromatography on silica gel (eluent: petroleum ether) of the crude product afforded the desired product.

*Compound **3a**:* Liquid; ^1H NMR (400 MHz, $CDCl_3$) δ 7.26–7.24 (m, 2H), 7.21–7.18 (m, 2H), 6.10–6.09 (t, $J = 2.8$ Hz, 1H), 5.87–5.79 (m, 1H), 5.13–5.02 (m, 2H), 2.85–2.83 (dd, $J_1 = 6.8$ Hz, $J_2 = 0.8$ Hz, 2H), 2.10–2.05 (m, 2H), 1.49–1.41 (m, 2H), 1.33–1.24 (m, 6H), 0.88–0.84 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 202.7, 135.5, 134.4, 131.8, 128.5, 127.5, 116.1, 107.6, 94.5, 37.4, 32.2, 31.6, 29.0, 27.4, 22.5, 13.9. MS (*m/z*) 274 (M^+, 16.8), 276 (M + 2, 6.6), 169 (100); IR (neat, cm^{-1}) 1949, 1709. HRMS calcd for $C_{18}H_{23}Cl$: 274.1488. Found: 274.1496.

*Compound **3b**:* Liquid; ^1H NMR (400 MHz, $CDCl_3$) δ 7.40–7.37 (m, 2H), 7.14–7.11 (m, 2H), 6.08–6.07 (t, $J = 2.8$ Hz, 1H), 5.87–5.78 (m, 1H), 5.12–5.01 (m, 2H), 2.84–2.83 (d, $J = 7.6$ Hz, 2H), 2.10–2.05 (m, 2H), 1.48–1.40 (m, 2H), 1.31–1.24 (m, 6H), 0.87–0.83 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 202.9, 135.6, 134.9, 131.5, 128.0, 120.0, 116.1, 107.8, 94.7, 37.4, 32.2, 31.6, 29.0, 27.5, 22.6, 14.0. MS (*m/z*) 318 (M^+, 8.8), 320 (M + 2, 8.2), 169 (100);IR (neat, cm^{-1}) 1949, 1727. HRMS calcd for $C_{18}H_{23}Br$: 318.0983. Found: 318.0992.

*Compound **3c**:* Liquid; ^1H NMR (400 MHz, $CDCl_3$) δ 7.17–7.12 (m, 2H), 7.10–7.07 (m, 2H), 6.12–6.09 (t, $J = 2.8$ Hz, 1H), 5.90–5.79 (m, 1H), 5.11–5.00 (m, 2H), 2.83–2.82 (d, $J = 6.4$ Hz, 2H), 2.33 (s, 3H), 2.09–2.03 (m, 2H), 1.47–1.43 (m, 2H), 1.34–1.21 (m, 6H), 0.86–0.83 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 202.3, 136.1, 136.0, 132.9, 129.2, 126.3, 115.9, 107.0, 95.2, 37.7, 32.3, 31.7, 29.1, 27.5, 22.6, 21.1, 14.0. MS (*m/z*) 254 (M^+, 21.8), 255 (M + 1, 4.8), 143 (100); IR (neat, cm^{-1}) 1949, 1726. Anal. Calc. for $C_{19}H_{26}$: C, 89.70; H, 10.30. Found: C, 89.35; H, 10.50%.

*Compound **3d**:* Liquid; ^1H NMR (400 MHz, $CDCl_3$) δ 7.53–7.51 (d, $J = 8.4$ Hz, 1H), 7.45–7.42 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.2$ Hz, 1H), 7.25–7.21 (t, $J = 7.6$ Hz, 1H), 7.05–7.01

(m, 1H), 6.59–6.58 (t, $J = 2.8$ Hz, 1H), 5.92–5.82 (m, 1H), 5.15–5.05 (m, 2H), 2.87–2.86 (d, $J = 7.6$ Hz, 2H), 2.12–2.08 (m, 2H), 1.51–1.44 (m, 2H), 1.35–1.30 (m, 6H), 0.89–0.85 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 203.7, 135.5, 135.1, 132.9, 128.0, 127.7, 127.2, 122.3, 116.2, 107.4, 94.4, 37.4, 32.1, 31.6, 29.0, 27.4, 22.6, 14.0. MS (*m*/*z*) 318 (M^+, 3.6), 320 (M + 2, 3.5), 169 (100);IR (neat, cm^{-1}) 1949, 1733. Anal. Calc. for $C_{18}H_{23}Br$: C, 67.71; H, 7.26. Found: C, 67.39; H, 7.52%.

Compound ***3e****:* Liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25–7.22 (m, 2H), 7.19–7.17(m, 2H), 6.09-6.08 (t, $J = 3.2$ Hz, 1H), 5.86–5.78 (m, 1H), 5.12–5.01 (m, 2H), 2.84–2.82 (dd, $J_1 = 7.2$ Hz, J2 = 0.8 Hz, 2H), 2.09–2.05 (m, 2H), 1.48–1.41 (m, 2H), 1.33–1.25 (m, 4H), 0.86–0.83 (t, $J = 6.4$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 202.7, 135.5, 134.3, 131.8, 128.5, 127.5, 116.0, 107.6, 94.4, 37.4, 32.0, 31.4, 27.0, 252.3, 22.5, 13.9. MS (*m*/*z*) 260 (M^+, 20.8), 262 (M + 2, 5.5), 169 (100); IR (neat, cm^{-1}) 1949, 1710. Anal. Calc. for $C_{17}H_{21}Cl$: C, 78.29; H, 8.12. Found: C, 78.02; H, 8.26%.

Compound ***3f****:* Liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.39 (m, 2H), 7.16–7.13 (m, 2H), 6.10–6.09 (t, $J = 2.8$ Hz, 1H), 5.89–5.80 (m, 1H), 5.15–5.03 (m, 2H), 2.87–2.85 (dt, $J_1 = 6.8$ Hz, $J_2 = 1.2$ Hz, 2H), 2.12–2.07 (m, 2H), 1.49–1.45 (m, 2H), 1.33–1.28 (m, 4H), 0.90–0.86 (t, $J = 7.6$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 202.8, 135.6, 134.9, 131.5, 127.9, 120.0, 116.2, 107.8, 94.6, 37.5, 32.2, 31.5, 27.1, 22.5, 14.0. MS (*m*/*z*) 304 (M^+, 11.6), 306 (M + 2, 10.8), 169 (100); IR (neat, cm^{-1}) 1948, 1717. HRMS calcd for $C_{17}H_{21}Br$: 304.0827. Found: 304.0818.

Compound ***3g****:* Liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24–7.22 (d, $J = 8.0$ Hz, 2H), 7.16–7.14 (d, $J = 7.6$ Hz, 2H), 6.18–6.17 (t, $J = 2.8$ Hz, 1H), 5.95–5.87 (m, 1H), 5.19–5.06 (m, 2H), 2.91–2.89 (dd, $J_1 = 6.8$ Hz, $J_2 = 0.8$ Hz, 2H), 2.39 (s, 3H), 2.16–2.10 (m, 2H), 1.56–1.50 (m, 2H), 1.40–1.31 (m, 4H), 0.97–0.90 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 202.3, 136.1, 135.9, 132.9, 129.2, 126.3, 115.9, 107.0, 95.2, 37.7, 32.3, 31.6, 27.2, 22.5, 21.1, 14.0. MS (*m*/*z*) 240 (M^+, 24.5), 241 (M + 1, 4.6), 169 (100); IR (neat, cm^{-1}) 1947, 1718. Anal. Calc. for $C_{18}H_{24}$: C, 89.94; H, 10.06. Found: C, 89.68; H, 10.20%.

Compound ***3h****:* Liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51–7.49 (d, $J = 8.0$ Hz, 1H), 7.42–7.40 (dd, $J_1 = 8.0$ Hz, $J_2 = 0.8$ Hz, 1H), 7.22–7.19 (t, $J = 7.6$ Hz, 1H), 7.02–6.98 (m, 1H), 6.57–6.56 (t, $J = 2.8$ Hz, 1H), 5.88–5.81 (m, 1H), 5.13–5.02 (m, 2H), 2.85–2.84 (d, $J = 6.0$ Hz, 2H), 2.09–2.06 (m, 2H), 1.49–1.44 (m, 2H), 1.33–1.25 (m, 4H), 0.86–0.83 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 203.7, 135.5, 135.1, 132.9, 128.0, 127.7, 127.2, 122.3, 116.3, 107.4, 94.4, 37.4, 32.1, 31.6, 27.4, 22.6, 14.0. MS (*m*/*z*) 304 (M^+, 4.8), 306 (M + 2, 4.9), 169 (100); IR (neat, cm^{-1}) 1948, 1699. Anal. Calc. for $C_{17}H_{21}Br$: C, 66.89; H, 6.93. Found: C, 66.66; H, 7.08%.

Compound ***3i****:* Liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.26 (m, 4H), 7.18–7.15 (m, 1H), 6.14–6.12 (t, $J = 2.8$ Hz, 1H), 5.89–5.82 (m, 1H), 5.13–5.01 (m, 2H), 2.85–2.84 (d, $J = 6.8$ Hz, 2H), 2.10–2.05 (m, 2H), 1.50–1.45 (m, 2H), 1.32–1.25 (m, 4H), 0.879–0.833 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 202.3, 135.5, 135.4, 128.0, 126.0, 126.0, 115.5, 106.7, 95.0, 37.2, 31.8, 31.2, 26.8, 22.0, 13.6. MS (*m*/*z*) 226 (M^+, 10.6), 129 (100); IR (neat, cm^{-1}) 1949, 1719. HRMS calcd for $C_{17}H_{22}$: 226.1722. Found: 226.1738.

Compound ***3j****:* Liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.49 (m, 4H), 7.34–7.31 (m, 2H), 7.26–7.23 (m, 2H), 6.51–6.50 (t, $J = 3.0$ Hz, 1H), 6.00–5.94 (m, 1H), 5.22–5.07 (m, 2H), 3.34 (d, $J = 0.8$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 207.1, 135.5, 135.2, 133.7, 133.3, 131.9, 128.6, 128.5, 127.6, 126.1, 116.8, 108.9, 97.1, 34.8. MS (*m*/*z*) 266 (M^+, 21.8), 268 (M + 2, 9.6), 105 (100); IR (neat, cm^{-1}) 1934, 1698. HRMS calcd for $C_{18}H_{15}Cl$: 266.0862. Found: 266.0869.

Compound ***3k****:* Liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.41 (m, 4H), 7.38–7.34 (m, 2H), 7.25–7.19 (m, 2H), 6.49 (s, 1H), 6.00–5.93 (m, 1H), 5.22–5.07 (m, 2H), 3.34 (d, $J = 0.8$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 207.0, 135.2, 135.1, 133.3, 131.8, 128.5, 128.3, 127.3, 126.1, 120.7, 116.7, 108.8, 97.2, 34.7. MS (*m*/*z*) 310 (M^+, 68), 312 (M + 2, 66), 189 (100); IR (neat, cm^{-1}) 1934, 1699. Anal. Calc. for $C_{18}H_{15}Br$: C, 69.47; H, 4.86. Found: C, 69.21; H, 5.10%.

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