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Trialkylmanganate Mediated Radical Addition of Triphenylgermane to Carbon–Carbon Multiple Bonds

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Treatment of 1-dodecyne with triphenylgermane in the presence of catalytic amounts of tributylmanganate at 25 °C provided 1-triphenylgermyl-1-dodecene in good yield. The reaction proceeded in a radical pathway and treatment of diene afforded the corresponding radical cyclization product.

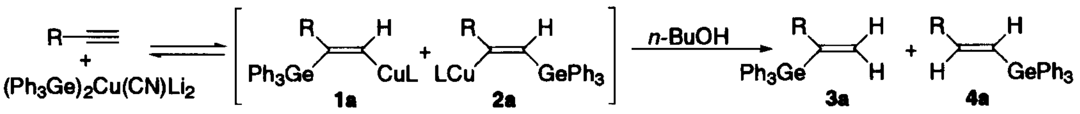
We have reported that bis(triphenyl)- or (trialkylgermyl)-cuprate(I) added to an acetylenic linkage in the presence of proton donor such as 1-butanol or pentanal.[1] The reaction has proceeded as follows. The addition reaction is reversible and the equilibrium favors the original system more than the intermediary alkenylcopper species, which consists of 2-germyl-1-alkenylcopper **1a** and its regio isomer **2a**. The coexistent weakly acidic proton donor reacts easily only with the alkenylcopper to give the adduct (**3a**+**4a**) and is reluctant to react with bis(triphenylgermyl)cuprate(I) (Scheme 1).

Here we examined the reaction of the corresponding manganese ate complex, tris(triphenylgermyl)manganate(II) with carbon-carbon multiple bond. Treatment of 1-dodecyne (0.5 mmol) with $Li[Mn(Ph_3Ge)_3]$ (0.6 mmol), generated from $MnCl_2$ and three molar amounts of triphenylgermyllithium,[2] in THF in the presence of 1-butanol (2.0 mmol) gave (*E*)-1-triphenylgermyl-1-dodecene (**4a**) quantitatively (Scheme 2). In contrast to the copper reaction with $(Ph_3Ge)_2Cu(CN)Li_2$ which provided a regioisomeric mixture of 2-triphenylgermyl-1-dodecene (**3a**) and 1-triphenylgermyl-1-dodecene (**4a**) (**3a**/**4a** = 1/4), no regioisomer **3a** could be observed in the reaction mixture of triphenylgermylmanganate and 1-dodecyne.

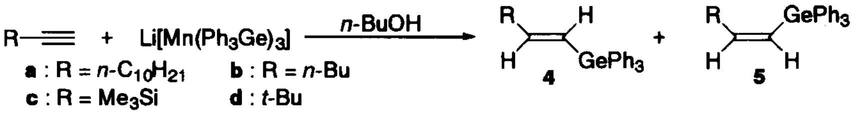
The reaction did not proceed at all in the absence of 1-butanol. The stereochemical outcome heavily depended on the molar ratio between the manganese reagent and the acetylenic compound. Whereas (*E*)-1-triphenylgermyl-1-alkene **4** was produced exclusively in the presence of excess reagent (manganate reagent/acetylene = 1.2/1), (*Z*)-isomer **5** became the main product in the case of the reaction with excess acetylenic compound. For instance, treatment of 1-hexyne (0.33 g, 2.0 mmol) with a quarter molar amount of germylmanganate (0.5 mmol) in the presence of 1-butanol (126 mg, 1.7 mmol) afforded a mixture of (*Z*)-1-triphenylgermyl-1-hexene (**5b**) and (*E*)-isomer **4b** (0.54 g, 1.4 mmol, **5b**/**4b** = 94/6) in 93% combined yield. Similar results were observed in the reaction of 1-trimethylsilylacetylene and 3,3-dimethyl-1-butyne with germylmanganate. The reaction of 1-trimethylsilylacetylene (0.5 mmol) with triphenylgermylmanganate (0.75 mmol) in the presence of 1-butanol (2.0 mmol) gave (*E*)-1-trimethylsilyl-2-triphenylgermylethene (**4c**) exclusively in 76% yield. In contrast, treatment of 1-trimethylsilylacetylene (2.0 mmol) with manganate (0.5 mmol) provided a mixture of (*Z*)-1-trimethylsilyl-2-triphenylgermylethene (**5c**) and (*E*)-isomer **4c** (**5c**/**4c** = 89/11) in 88% combined yield. In the presence of excess manganate reagent, the sequential addition-elimination of second triphenylgermyl radical could convert the (*Z*)-1-germyl-1-alkene into (*E*)-1-germyl-1-alkene (See Scheme 4 in Ref. 6). The internal acetylenes as well as terminal acetylenic compounds provided the corresponding adducts effectively. Again, the molar ratio of the reagent/acetylene had a large influence on the stereochemical result. Whereas (*Z*)-6-triphenylgermyl-6-dodecene was generated as a single product in the reaction of 6-dodecyne (2.0 mmol) with manganate (0.5 mmol), a mixture of (*Z*)- and (*E*)-isomer (1 : 1) was obtained in the reaction with large excess of manganate reagent. Treatment of 1-dodecene with triphenylgermylmanganate gave 1-triphenylgermyldodecane in 89% yield.

Based on these stereo- and regiochemical results which are very similar to those of the Et_3B induced addition of triphenylgermane to acetylenic compounds,[3] we concluded that the reaction with germylmanganate in the presence of 1-butanol would not proceed via germylmanganation, as we had expected, but in a radical pathway.[4] The formation of a mixture of (*E*)- and (*Z*)-1-germyl-1-alkene could be explained as follows. A proton donor such as 1-butanol would react with tris(triphenylgermyl)manganate(II) to generate triphenylgermane.[5] Then triphenylgermane could add to acetylenic linkage via a radical pathway to give alkenylgermane under the catalysis of the remaining tris(triphenylgermyl)manganate(II). Thus, tris(triphenylgermyl)manganate(II) would play a critical role in the reaction as a radical initiator like triethylborane.[6] So it was anticipated that tributylmanganate(II) also could be an initiator,[8] as well as triphenylgermylmanganate, for the radical addition of triphenylgermane to carbon–carbon multiple bond. This was indeed the case, and treatment of a solution of 1-dodecyne (1.0 mmol) and triphenylgermane (1.5 mmol) with a catalytic amount of tributylmanganate(II)[9] (0.1 mmol), derived from *n*-BuLi and $MnCl_2$, at 25 °C for 11 h provided a stereoisomeric mixture of (*E*)-1-triphenylgermyl-1-dodecene (**4a**) and (*Z*)-isomer **5a** (**4a**/**5a** = 9/91) in 89% yield (Scheme 3). Some representative results are shown in Table 1.

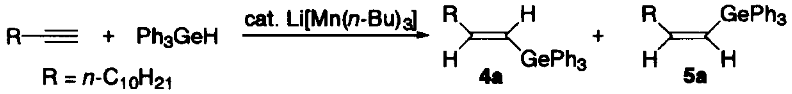
Several comments are worth noting. (1) Not only acetylenic linkage but also terminal alkenes reacted with triphenylgermane in the presence of a catalytic amount of manganate. For instance, treatment of 1-dodecene with Ph_3GeH under



Scheme 1.

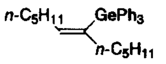
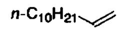
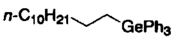
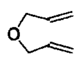
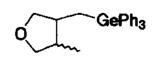
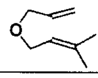
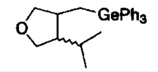


Scheme 2.



Scheme 3.

Table 1. n-Bu$_3$MnLi-mediated Radical Addition of Ph$_3$GeH to Acetylene or Alkene

Entry	Acetylene or Alkene	Product	Yield
1	n-C$_{10}$H$_{21}$—≡		89% (*E*/*Z* = 9/91)
2	Me$_3$Si—≡		86% (*E*/*Z* = 20/80)
3	*t*-Bu—≡		84% (*E*/*Z* = 20/80)
4	n-C$_5$H$_{11}$—≡—n-C$_5$H$_{11}$		61% (Z only)
5			99%
6			97% (*trans*/*cis* = 24/76)
7			94% (*trans*/*cis* = 39/61)

Li[Mn(n-Bu)$_3$] catalysis gave 1-triphenylgermyldodecane in 99% yield. (2) Treatment of diene provided the corresponding cyclized products (Entries 6 and 7). (3) In contrast to the Et$_3$B induced reaction of Ph$_3$GeD with acetylenic compounds which has afforded 1-triphenylgermyl-2-deuterio-1-alkenes in good yields, tributylmanganate-mediated addition of Ph$_3$GeD to 1-dodecyne did not proceed and both starting materials were recovered completely. The reaction of 1-dodecyne with Ph$_3$SnH, or n-Bu$_3$SnH also resulted in a recovery of the starting materials. Thus, tributylmanganate proved to be a less effective radical initiator than Et$_3$B for the addition of Ph$_3$GeD and Ph$_3$SnH to acetylenes.

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References

1 H. Oda, Y. Morizawa, K. Oshima, and H. Nozaki, *Tetrahedron Lett.*, **25**, 3217 (1984).

2 Triphenylgermyllithium was prepared in situ from Ph$_3$GeH and butyllithium.

3 K. Nozaki, Y. Ichinose, K. Wakamatsu, K. Oshima, and K. Utimoto, *Bull. Chem. Soc. Jpn.*, **63**, 2268 (1990).

4 The reaction did not proceed in the presence of galvinoxyl or TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) as a radical scavenger.

5 An addition of CD$_3$OD (1.7 mmol) to a solution of Li[Mn(Ph$_3$Ge)$_3$] (0.5 mmol) followed by aqueous workup gave Ph$_3$GeD (83%-*d*) quantitatively.

6 Single electron transfer from lithium tris(triphenylgermyl)manganate(II) or tributylmanganate(II) to triphenylgermane would produce triphenylgermyl radical. Then this germyl radical adds to carbon-carbon triple bond to give an alkenyl radical, which abstracts hydrogen from triphenylgermane to produce (*Z*)-1-germyl-1-alkene and regenerate triphenylgermyl radical. The selective formation of thermodynamically favored (*E*)-1-germyl-1-alkene might be attributed to the sequential addition-elimination of second triphenylgermyl radical to the preformed (*Z*)-1-germyl-1-alkene.[7] The attack of the germyl radical on the carbon–carbon double bond at the carbon-bearing triphenylgermyl group could be supported by the experimental result described in Ref. 3. However, the possibility of isomerization via the addition-elimination of the second germyl radical on the double bond at the opposite carbon could not be denied.

7 The following results also support this mechanism. The stereochemical outcome heavily depended on the reaction time. Stirring a THF solution of 1-dodecyne and triphenylgermylmanganate in the presence of 1-butanol at 25 °C for 4.5 h afforded (*E*)-1-triphenylgermyl-1-dodecene exclusively. Meantime, the reaction for 30 min gave the mixture of **4a** and **5a** (**4a**/**5a** = 57/43) (Scheme 4).

Scheme 4.

8 Trialkylmanganate-induced cyclization of allyl 2-iodophenyl ether and 2-iodoethanal acetal has been reported. R. Inoue, J. Nakao, H. Shinokubo, and K. Oshima, *Bull. Chem. Soc. Jpn.*, **70**, 2039 (1997).

9 The use of n-Bu$_3$MnMgBr (0.1 mmol), generated from n-BuMgBr and MnCl$_2$, in place of n-Bu$_3$MnLi afforded *Z*-isomer **5a** exclusively in 44% yield. The manganese reagents i-Pr$_3$MnMgBr or Ph$_3$MnMgBr gave 1-triphenylgermyl-1-dodecene in 71% (*E*/*Z* = 6/94) or 28% (*Z* only) yield, respectively.