

Linear Trimerization Reaction of Silylacetylene Promoted by GaCl₃

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Conjugated trienes are attractive compounds in the fields of biological and material sciences, and linear trimerization of acetylenic compounds is potentially one of the most straightforward methods to prepare these compounds. However, cyclic trimerization generally predominates over linear trimerization, giving benzene derivatives.¹ Exceptionally, a low yield of triene was obtained when excess 1-phenyl-4,4-dimethyl-1-butyne was treated with (*i*-Bu)₂AlH without solvent at 140–160 °C for 4 days.² Since 1-phenylpropyne did not give the acyclic compound, linear trimerization was restricted to the hindered disubstituted acetylene. The reaction could not be used in organic synthesis because of the slow reaction rate and the limitation of the trienes that can be synthesized. During our studies on the chemistry of novel organogallium compounds, another group 13 element,³ we found that silylacetylene trimerized rapidly, giving acyclic conjugated trienes. A noteworthy aspect of the reaction is that a terminal carbon atom of the hexatriene can be alkylated with organometallic reagents while the other terminal carbon atom is attached to the gallium metal.

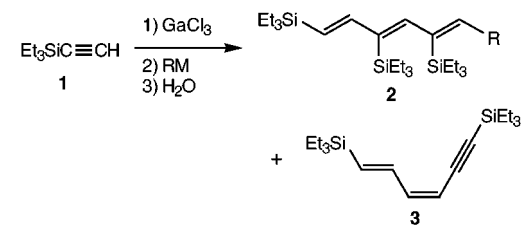
(Triethylsilyl)acetylene (**1**) was treated with GaCl₃ in dichloromethane and methylcyclohexane at –78 °C for 90 min, and methylmagnesium bromide in ether was then added. The mixture was warmed to 0 °C, and aqueous workup gave heptatriene **2a**, hexadienyne **3**, and allene **4a** (Table 1, Scheme 2). The structures of **2a** and **3** were determined by spectroscopic methods including the NOE technique. While **2a** possessed the 1*E*,3*Z*,5*Z* structure, **3** was shown to be a 1*E*,3*Z* isomer. Notably, a methyl group was transferred to the terminal carbon atom of **2a** from the Grignard reagent. In contrast, **3** did not possess any such methyl group. The allene structure of **4a** was deduced by IR absorption at 1915 cm⁻¹ and ¹³C NMR chemical shift at δ 210.72, and the *E* configuration of the double bond was determined by the NMR coupling constant. A methyl group was also transferred to **4a** from the Grignard reagent. When the organometal treatment was conducted in THF, **4a** was not formed. The formation of the conjugated triene **2a** involves two C(sp²)–C(sp²) bond formations and Grignard alkylation at the terminal sp² carbon. Although the yield of **2a** was in the range of 20%, the yield based on the consumed **1** was calculated to be approximately 40%. The total yield of the trimerized products **2a** and **3** based on the consumed **1** exceeded 50%. The reaction terminated for the most part at the trimerization. Furthermore, the reaction could be conducted with 1 g of **1**. Other Grignard reagents and alkynyllithium reagents also gave the conjugated trienes (Table 1).

(1) Wilke, G.; Müller, H. *Liebigs Ann. Chem.* **1960**, 629, 222. Eisch, J. J.; Harrell, R. L., Jr. *J. Organomet. Chem.* **1969**, 20, 257. Also see the following reviews for the transition-metal-catalyzed cyclic trimerization reactions. Keim, W.; Behr, A.; Röper, M. *Alkene and Alkyne Oligomerization, Cooligomerization and Telomerization Reactions*. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, 1982; Vol. 8, Chapter 52, p 371. Grotjahn, P. D. B. *Transition Metal Alkyne Complexes: Transition Metal-catalyzed Cyclotrimerization*. In *Comprehensive Organometallic Chemistry II*; Abel, E. A., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, 1995; Vol. 12, Chapter 7.3, p 741.

(2) Eisch, J. J.; Amtmann, R. *J. Org. Chem.* **1972**, 37, 3410.

(3) Yamaguchi, M.; Kido, Y.; Hayashi, A.; Hiram, M. *Angew. Chem., Int. Ed. Engl.* **1997**, 36, 1313.

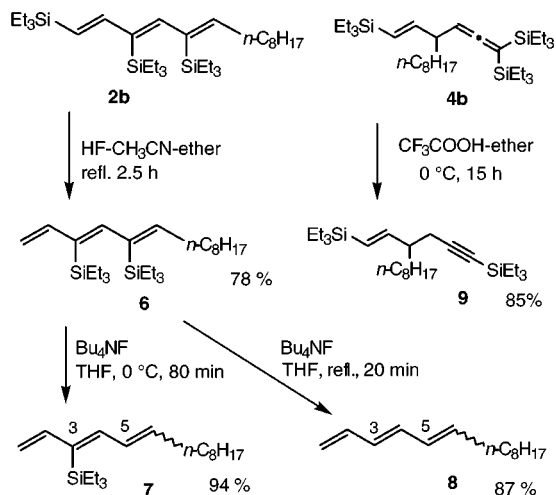
Table 1. Trimerization of Silylacetylene **1**



RM	yield ^a /%	
	2	3
MeMgBr	19 (36)	9 (18)
MeMgBr ^b	20 (40)	7 (12)
EtMgBr	20 (41)	14 (28)
<i>n</i> -C ₄ H ₉ MgBr	22 (39)	11 (20)
<i>n</i> -C ₈ H ₁₇ MgBr	13 (24)	9 (17)
<i>n</i> -C ₈ H ₁₇ MgBr ^c	13 (22)	4 (7)
<i>n</i> -C ₄ H ₉ C≡CLi	14 (25)	10 (18)
PhC≡CLi	12 (23)	<i>d</i>
<i>t</i> -BuMe ₂ SiO(CH ₂) ₈ MgBr	8 (15)	<i>d</i>

^a Isolated yield based on **1**. Shown in parentheses are yields based on the consumed **1**. ^b Grignard reagent in ether was used, and allene **4b** was obtained in 3% yield. ^c Grignard reagent in ether was used, and allene **4b** was obtained in 4% yield. ^d Not determined.

Scheme 1



The triene **2b** derived from octylmagnesium bromide was monodesilylated to **6** by treatment with HF in acetonitrile–ether at reflux (Scheme 1). The desilylation occurred selectively at the terminal carbon atom. Other silyl groups could be removed by treatment with tetrabutylammonium fluoride, giving **7** or **8** depending on the reaction conditions. Both **7** and **8** were obtained as 1.5:1 mixtures of 3*E*,5*E* isomers and 3*E*,5*Z* isomers. Thus, the trimerization of the silylacetylene provided a novel and convenient method for the synthesis of conjugated trienes. (*E*)-Allene **4b** was desilylated with trifluoroacetic acid, giving (*E*)-enyne **9** via the SE2' reaction.

Formation of vinylgallium intermediates before the aqueous workup was confirmed by deuteration experiments. When the reaction mixture formed by the Grignard methylation was quenched with D₂O, **2a-d**, **3-d**, and **4a-d** were obtained (Scheme 2). These experiments clearly showed the formation of vinylgallium intermediates **13**, **15**, and **16**.

The proposed mechanism of the trimerization is shown in Scheme 2. The reaction was initiated with the formation

