Linear Trimerization Reaction of Silylacetylene Promoted by GaCl₃

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Received July 14, 1998

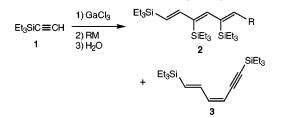
Conjugated trienes are attractive compounds in the fields of biological and material sciences, and linear trimerization of acetylenic compounds is potentially one of the most straightforward methods to prepare these compounds. However, cyclic trimerization generally predominates over linear trimerization, 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 1E,3Z,5Z structure, 3 was shown to be a 1E,3Z 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).

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

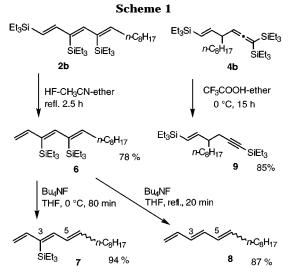
(3) Yamaguchi, M.; Kido, Y.; Hayashi, A.; Hirama, M. Angew. Chem., Int. Ed. Engl. 1997, 36, 1313.





| 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) |
| $n-C_8H_{17}MgBr^c$ | 13 (22) | 4 (7) |
| $n-C_4H_9C \equiv CLi$ | 14 (25) | 10 (18) |
| PhC≡CLi | 12 (23) | d |
| t-BuMe ₂ SiO(CH ₂) ₈ MgBr | 8 (15) | d |

^{*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.

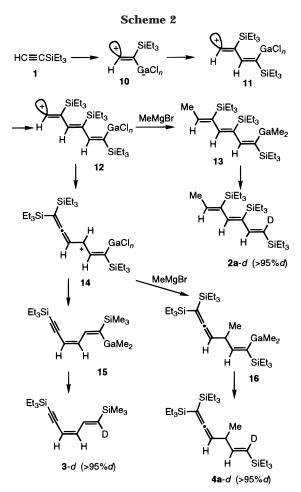


The triene **2b** derived from octylmagnesium bromide was monodesilylated to **6** by treatment with HF in acetonitrile– ether at reflux (Scheme 1). The desilylation occurred selectively at the terminal carbon atom. Other silyl groups could be removed by treatment with tetrabutylammonium fluoride, giving **7** or **8** depending on the reaction conditions. Both **7** and **8** were obtained as 1.5:1 mixtures of 3E,5Eisomers and 3E,5Z 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 D_2O , 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

⁽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.



of vinyl cationic species **10**. This may be a reasonable assumption since electrophilic aromatic β -silylvinylation took place³ when this reaction was conducted in the presence of nucleophilic aromatic hydrocarbons. Electrophilic head-to-tail trimerization then converted **10** to trienyl cation **12** via dienyl cation **11**. Treatment of **12** with methylmagnesium bromide gave vinylgallium **13**, which was transformed to **2a**-*d* by workup with D₂O. Some part of **12** probably rearranged to allenyl cation **14** via an as yet unknown mechanism. Cation **14** was desilylated to dienylgallium **15**, which was isolated after D₂O workup to give **3**-*d*. In contrast, methylation of **14** followed by D₂O treatment gave **4a**-*d*.

To obtain further information on the intermediates, NMR studies of the reaction mixtures were conducted before the organometal treatment. The structure of the trienic compound 12 was elucidated by COSY, NOE difference spectroscopy, and COLOC (Figure 1). The experiment was conducted at -70 °C to suppress decomposition. The terminal carbon atom attacked by organometal showed characteristic low-field chemical shifts, ¹H NMR δ 9.94 and ¹³C NMR δ 204.6, indicative of an electron-deficient state. The ¹³C NMR chemical shift is within the range reported for known vinyl cations.⁴ Formation of vinyl chloride could be excluded on the basis of the chemical shift and the ability of the intermediate to react with the organomagnesium compounds. To our knowledge, this is the first spectroscopic detection of a vinyl cation attached to a hydrogen atom. A C-H coupling constant of J = 180 Hz was obtained by

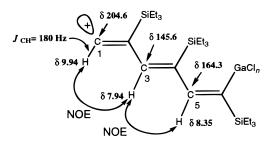


Figure 1.

heteronuclear J spectroscopy at the cationic carbon atom, which revealed an sp² carbon structure. Probably, ionpaired sp² vinyl cationic species were formed in the nonpolar solvent. The observation of NOE between 1-H and 3-H was consistent with this interpretation. Facile formation of such cationic intermediates appears to be one of the interesting aspects of organogallium compounds.

Another intriguing aspect of this reaction was the origin of the selective trimerization. The bulkiness of the silyl group was not essential, since (trimethylsilyl)acetylene also gave the corresponding trimer in 9% yield. No dimers or tetramers were isolated. When the reaction mixture containing **12** was treated with excess *m*-xylene, no electrophilic substitution product was obtained. Since **10** reacted with the aromatic hydrocarbon,³ **12** apparently is less reactive than **10**. It is assumed that the inertness of the trienyl cation can be one of the reasons for the termination of the oligomerization.

Under an argon atmosphere, dichloromethane (20 mL) was cooled to $-\overline{78}$ °C, to which a solution of GaCl₃ (1.0 M in methylcyclohexane, 5.0 mmol) was added dropwise (contact of GaCl₃ with dichloromethane at room temperature caused decomposition). Then (triethylsilyl)acetylene (1, 1.05 g, 7.5 mmol) in dichloromethane (5 mL) was added, and the mixture was stirred at -78 °C for 90 min. After the addition of methylmagnesium bromide (0.87 M in THF, 15 mmol), the reaction mixture was allowed to warm to 0 °C and stirred for 30 min. Water was added, and the organic layer was separated and dried over MgSO4. The recovery of (triethylsilyl)acetylene was checked by GC analysis using nitrobenzene as the internal standard. The crude product was purified by flash column chromatography and preparative recycling GPC giving 2a (204 mg, 19% yield based on 1 used and 36% yield based on consumed 1) and 3 (72 mg, 9% based on 1 used and 18% yield based on consumed 1).

Acknowledgment. The fellowship to Y.K. from the Japan Society of Promotion of Science for young Japanese scientists is gratefully acknowledged. This work was supported by grants from the Japan Society of Promotion of Science (RFTF 97P00302) and the Ministry of Education, Science, Sport, and Culture, Japan (Nos. 08404050 and 10132204).

Supporting Information Available: Spectra data (¹H NMR, ¹³C NMR, IR, MS) and ¹³C NMR spectra of triene derivatives (19 pages).

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