

Allylgallation reaction of carbon–carbon triple bonds with allylsilanes and GaCl₃

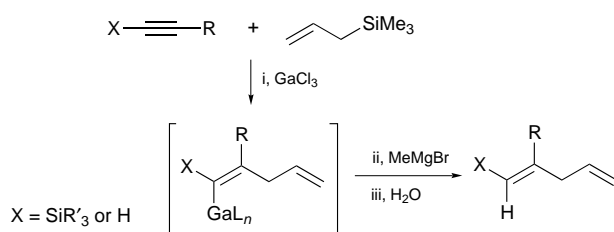
Masahiko Yamaguchi,*† Takayuki Sotokawa and Masahiro Hirama

Department of Chemistry, Graduate School of Science, Tohoku University, Aoba, Sendai 980-77, Japan

Treatment of alkynes with allyltrimethylsilanes in the presence of GaCl₃ gives 1,4-dienes via allylgallation.

Allylmetallation reactions of carbon–carbon triple bonds are known for organometallic compounds of magnesium, boron, aluminium, indium, zinc, titanium, zirconium and tantalum.¹ Metal-induced allylation reactions with allyltrimethylsilanes were also recently reported.² During our studies on the chemistry of novel organogallium compounds,^{3,4} allylgallation reaction of silylalkynes or alk-1-yne was found to take place upon treatment with allylsilanes and GaCl₃.

A mixture of an alkynyltrimethylsilane and allyltrimethylsilane in methylcyclohexane was treated with GaCl₃ at room temp. for 30 min. Then methylmagnesium bromide was added at –78 °C and 1-trimethylsilyl-2-substituted-1,4-diene was obtained after aqueous workup (Scheme 1 and Table 1). Although silylalkynes undergo self-dimerization in the presence of GaCl₃,³ the cross-coupling reaction with allylsilane is more rapid. C–C bond formation occurs regioselectively at the β-carbon atom of silylalkynes, and the (*E*)-relation between the silyl and allyl groups was determined by NOE. Primary and secondary aliphatic alkynes, and aromatic alkynes reacted



Scheme 1

Table 1 Allylgallation reactions of silylacetylenes and alk-1-yne

X	R	Yield (%)
SiMe ₃	<i>n</i> -C ₅ H ₁₁	81 ^a
	<i>n</i> -C ₉ H ₁₉	79 ^a
	Bu ^t Me ₂ SiO(CH ₂) ₂	68
	–(CH ₂) ₁₀ –	55 ^b
	<i>cyclo</i> -C ₆ H ₁₁	77 ^a
	Ph	86 ^a
	<i>p</i> -BrC ₆ H ₄	76 ^a
SiEt ₃	<i>p</i> -MeOC ₆ H ₄	63
	H	75
H	<i>cyclo</i> -C ₆ H ₁₁	30
	<i>n</i> -C ₉ H ₁₉	74
	Bu ^t Me ₂ SiO(CH ₂) ₂	47 ^c
	<i>n</i> -C ₉ H ₁₉ CHMe	52
	<i>cyclo</i> -C ₆ H ₁₁	56
	1-Adamantyl (1-Ad)	56
	Ph	56
<i>p</i> -MeOC ₆ H ₄	45 ^c	

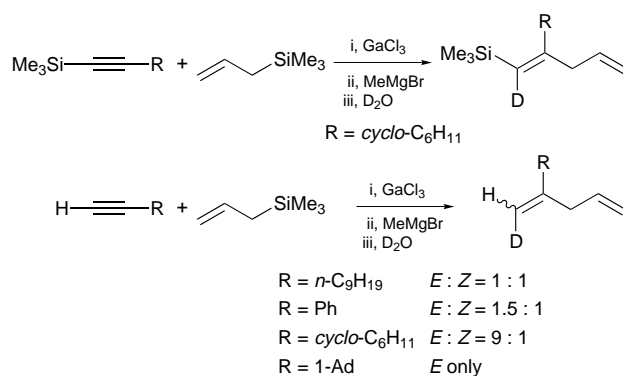
^a (*E*)-Configuration was determined by NOE. ^b 4 mol equiv. of allylsilane was used, and yield of diallylated product is shown. ^c Reaction was conducted in chlorobenzene.

smoothly. A tertiary aliphatic alkyne, however, was inert to the reaction. Triethylsilylethyne also reacted at the β-carbon atom giving a 1-silylpenta-1,4-diene with (*E*)-configuration (*J* 18.6 Hz). Since reaction of triethylsilylalkynes and allyltrimethylsilane gave 1-triethylsilylpenta-1,4-dienes and not trimethylsilyl derivatives, the silyl groups in the products are derived from silylalkynes. The allylation took place with alk-1-yne as well as silylalkynes giving 2-substituted-1,4-dienes. Aliphatic and aromatic alk-1-yne including a tertiary alkyl derivative could be allylated. The reaction was also carried out in other non-coordinating solvents such as benzene, chlorobenzene and dichloromethane. Some examples are shown in Table 1 in which chlorobenzene gave better results than methylcyclohexane because of the higher solubility of the substrates. Disubstituted alkynes, diphenylacetylenes and oct-4-yne, gave rise to oligomerization, and allylation products could not be detected.

Deuteriation experiments indicated the formation of vinylgallium intermediates (Scheme 2). Thus, the present allylation takes place *via* allylgallation with carbon–carbon triple bonds. The organometal treatment before the aqueous workup is essential to attain satisfactory yields, which probably is required for the effective protonation of the vinylgallium intermediates.⁴ While the allylgallation of silylalkynes gave *cis*-addition products, mixtures of isomers were obtained from alk-1-yne depending on the substituents. *cis*-Addition took place predominantly with secondary and a tertiary alk-1-yne, while comparable amounts of *trans* isomers formed for primary and aryl derivatives. The stereochemistries appear to reflect the relative thermodynamic stability of *E*- and *Z*-vinylgallium intermediates.

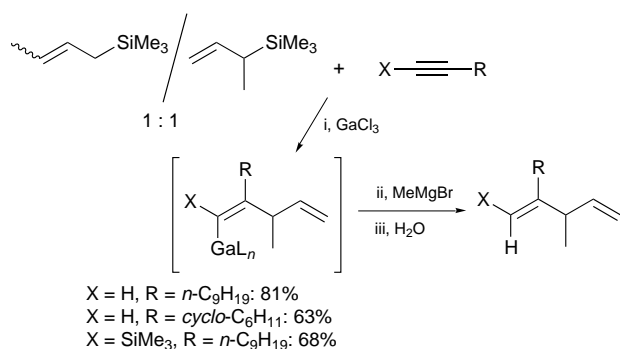
Substituted allylsilanes added to alkynes at the more hindered site irrespective of the structure of the starting organosilicon compounds. A 1 : 1 mixture of but-2-enylsilane and but-3-en-2-ylsilane⁵ gave 3-methyl-1,4-diene exclusively (Scheme 3). Both oct-1-en-3-ylsilane **1** and oct-2-ene-1-ylsilane **2**⁶ reacted similarly (Scheme 4).

Two mechanisms (I or II) are conceivable for the allylgallation reaction: (I) formation of an allylgallium intermediate by the transmetalation of allylsilane with GaCl₃ followed by the

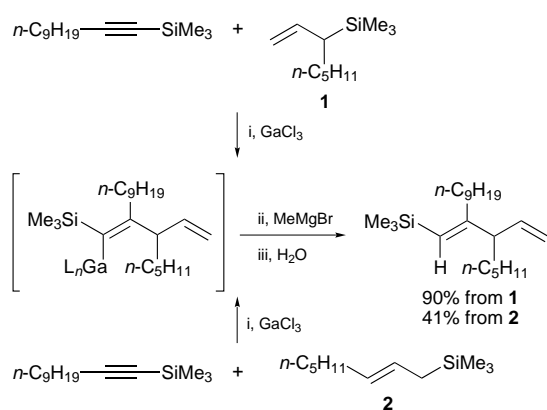


Scheme 2

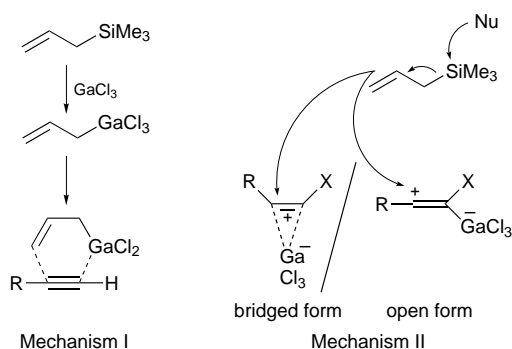
addition to a carbon-carbon triple bond or (II) attack of allylsilane to alkyne activated by GaCl₃, the structure of which can be either open or bridged (Scheme 5). Our recent studies showed both examples of the carbogallation reaction. The dimerization reaction of silylalkynes with GaCl₃ may involve an alkynylgallium intermediate formed by the transmetalation reaction (mechanism I).³ In the aromatic β-silylvinylation reaction, attack of aromatic hydrocarbons to GaCl₃-activated silylethyne is a probable pathway (mechanism II).⁴ The regioselectivity of substituted allylsilanes can be a probe to discriminate between the two mechanisms in the present system. Isomeric allylsilanes would give the same products *via* mechanism I provided that the allyl transposition of the allylgallium intermediate is rapid enough. Mechanism II would involve an S_E2' pathway *via* allyl transposition of allylsilanes; C-C bond formation taking place at the γ-carbon atom of the silicon group. The reactions of substituted allylsilanes are consistent with mechanism I (Scheme 4). The lower yield in the reaction of **2** compared to **1** may be due to the inefficiency of the transmetalation. Well documented *cis*-stereochemistry of such



Scheme 3



Scheme 4



Scheme 5 Possible mechanisms of the allylgallation reaction

allylmetallations,^{1,2} however, was not observed in some reactions of alk-1-yne; primary and aromatic alk-1-yne gave mixtures of *cis*- and *trans*-addition products (Scheme 2). We tentatively ascribed this to the isomerization of the initially formed *cis*-adducts to the thermodynamic equilibrium.

Allylmetallation reactions of other group 13 elements except for gallium are known. It is now known that allylgallation takes place with both silylalkynes and alk-1-yne. Treatment of alk-1-yne with allylsilane and a catalytic amount of AlCl₃ or EtAlCl₂ was recently reported to give the allylsilylation product. Jung proposed a mechanism involving allylation of silicon-stabilized vinyl cations,^{2a} while Yamamoto proposed allylaluminum related to our mechanism II (Scheme 5).^{2b} In spite of the use of a similar allylating reagent system, allylsilane and a Lewis acid of the group 13 element, different mechanisms are proposed in these reactions and for our reaction. Determination of the precise mechanisms will be subject of future work.

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Footnotes

* E-mail: yama@mail.pharm.tohoku.ac.jp

† Present address: Pharmaceutical Institute, Tohoku University, Aoba, Sendai 980-77, Japan.

‡ *Typical experimental procedure:* under an argon atmosphere, a 1.0 M solution of GaCl₃ in methylcyclohexane (1 ml, 1.0 mmol) was added dropwise over 10 min to a mixture of 1-trimethylsilyl-2-cyclohexylacetylene (0.18 g, 1.0 mmol) and allyltrimethylsilane (0.23 g, 2.0 mmol) in methylcyclohexane (10 ml) at room temp. After stirring for 30 min, the mixture was cooled to -78 °C, and 0.92 M methylmagnesium bromide in thf (6.4 ml, 6.0 mmol) was added dropwise. The cooling bath was removed, and stirring was continued for 1 h at room temp. Water was then added, and organic materials were extracted twice with hexane. The combined extracts were washed with saturated aqueous NH₄Cl and brine, dried over Na₂SO₄, and concentrated. Flash column chromatography on silica gel (hexane) gave (*E*)-1-trimethylsilyl-2-cyclohexylpenta-1,4-diene (0.17 g, 77%).

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