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Aluminum chloride catalyzed stereo- and regiospecific allylsilylation of alkynes: a convenient route to silyldienes [☆]

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Abstract

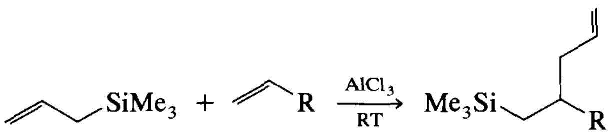
Allyltrimethylsilane reacts with phenylalkynes in the presence of aluminum chloride catalyst under mild conditions to afford silylphenyldienes in moderate yield. In this allylsilylation reaction, the silyl group adds regioselectively to the terminal carbon and the allyl group to the inner carbon of the triple bond. The allylsilylation of phenylacetylene gives the allylsilylated product having the silyl and allyl groups in the *cis*-position, while diphenylacetylene gives the *trans* product. The allylic inversion was also observed in the allylsilylation with the stereohomogeneous (*Z*)-crotyltrimethylsilane. These results are consistent with the initial formation of trimethylsilyl cation intermediate and a stepwise process of allylsilylation.

Keywords: Alkylsilylation; Alkynes; Allylic inversion; Allylsilanes; Stereoselectivity; Regioselectivity

1. Introduction

The allylmetalation of alkynes using allyl containing metals such as Li, Mg, B, Zn, and Al is an important synthetic method for dienes, [1]. Mechanistic studies of the allylations suggested that a six- or four-membered intermediate stage was plausible [2]. Zirconium-catalyzed allylalumination reactions and zirconium-mediated allylzincation of alkynes have also been reported [3]. To our knowledge, however, the addition reactions of both allyl and silyl groups of allylsilanes to alkynes have not been reported.

We recently reported a novel aluminum chloride-catalyzed allylsilylation of alkenes with allyltriorganosilanes [4]. Allylsilanes react with terminal olefins in the presence of aluminum chloride catalyst under the mild conditions to afford 5-silyl-1-alkenes in good yield. In the allylsilylation reaction, the silyl group regioselectively adds to the terminal carbon and the allyl group to the inner carbon of the double bond of alkenes. The allylsilylation of cycloalkenes gives the allylsilylated product having the silyl and allyl groups in mutually *trans* positions.



We have attempted to add allylsilanes to alkynes and report here the first examples of the allylsilylation of alkynes.

2. Results and discussion

2.1. Allylsilylation of phenylacetylenes

The addition of allyltrimethylsilane **1a** (2.2 g, 19 mmol) to phenylacetylene **2a** (1.9 g, 19 mmol) in benzene solution in the presence of anhydrous aluminum chloride as catalyst at 24°C gave (*E*)-1-trimethylsilyl-2-phenyl-1,4-pentadiene **3a** (1.38 g) as the major product in 34% yield on the basis of **1a** consumed. Besides **3a**, several other by-products also were obtained and identified as 4,6,6-trimethyl-6-silahept-1-ene **4a** (1%), hexamethyldisiloxane (18%), 2-phenyl-1,4-pentadiene, **5** (10%), 1-phenyl-2-(trimethylsilyl)acetyl-

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[☆] Dedicated to Prof. Hideki Sakurai on the occasion of his retirement from Tohoku University.

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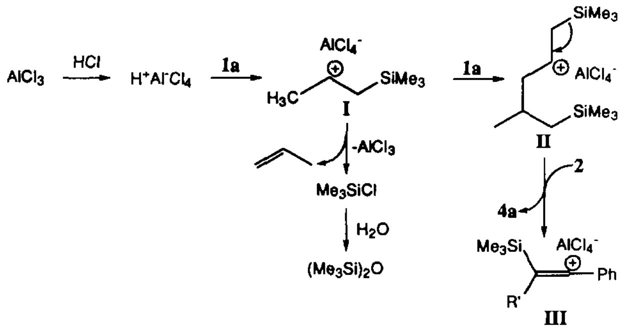


Scheme 1.

ene **6** (9%) 2-phenyl-6,6-dimethyl-6-silahepta-1,3-diene, **7** (0.6%) and unidentified polymeric materials (28%).

The hexamethyldisiloxane by-product, apparently produced by hydrolysis of trimethylchlorosilane, was obtained in the every allylsilylation reaction, indicating that cleavage of the allyl group from allyltrimethylsilane was involved. Protodesilylation of allyltrimethylsilane by acids has been reported [5]. In the Friedel–Crafts alkylation with alkenes in the presence of aluminum chloride, a small amount of hydrogen chloride resulting from the reaction of anhydrous aluminum chloride with adventitious water in the reaction mixture is responsible for this well-known [6] and well-understood [7,8] cleavage reaction. The stabilized carbocation intermediate, **I**, generated by the protonation of **1a** either undergoes desilylation to give propylene and the trimethylsilyl cation [5,9], or reacts with **1a** to give the cation adduct, **II**, which gives the by-product, **4a**, by donating a trimethylsilyl cation to **1a**. Electrophilic attack on electron-rich systems by trialkylsilyl cations has been reported for other systems [10]. GC–MS analysis of the evolved gas indeed showed the presence of propylene, indicating the occurrence of the desilylation of **1a**. This type of intermediate, i.e. **II**, was proposed to be formed during the allylsilylation of alkenes [4]. At the final stage of the allylsilylation, the cation intermediate, **II** would interact with $AlCl_4^-$ to give trimethylchlorosilane which is hydrolyzed to hexamethyldisiloxane during the workup. These results are consistent with the initial formation of trimethylsilyl cation intermediates by protodesilylation. The reaction pathways for the by-products are proposed in Scheme 1.

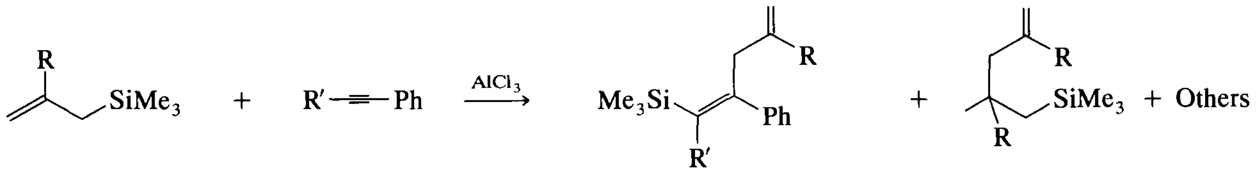
The fact that the products **5** and **6** are obtained in approximately equal amounts from the allylsilylation of **2a** suggests that an exchange reaction between the ethynyl proton of **2a** and the trimethylsilyl group of the product **3a** might have been taken place. In order to check this possibility, a mixture of **2a** and **3a** was equilibrated under the same reaction conditions, but neither **5** nor **6** was obtained. This result suggests that **5** and **6** might have been produced from the exchange reaction between the ethynyl proton of **2a** and the trimethylsilyl group of **1a**.

A similar allylsilylation was carried out using 1-phenylpropyne **2b** having no ethynyl proton gave (*E*)-2-trimethylsilyl-3-phenyl-2,5-hexadiene **3b** as the major product in 66% yield. Several other by-products were also obtained and identified as hexamethyldisiloxane (10%) **4a** (3%), and 4-phenyl-1,4-hexadiene **8** (5%). The compounds **5** and **6** were indeed not obtained from the allylsilylation of **2b**, which has no ethynyl protons. This result supports the hypothesis that **5** and **6** are obtained from the exchange reaction between the ethynyl proton and the trimethylsilyl group of **2a**. This exchange reaction is consistent with the fact that a trimethylsilyl cation is involved in the allylsilylation.

2.2. *Stereoselectivity of allylsilylation*

In order to study the stereochemistry of **3a** and confirm the exchange reaction between the trimethylsilyl group of **1a** and the ethynyl proton of **2a**, 1-deutero-2-phenylacetylene **2a'** was prepared by lithiation of **2a** with *n*-butyllithium followed by quenching with deuterium oxide and allylsilylated with **1a**. This allylsilylation gave the same type of products as obtained from **2a**. GC–MS and NMR analysis showed that the products **3a'**, **5'** and **7'** contained deuterium, but **4a** did not. This indicates that **4a** was formed at the beginning stage of the reaction before the exchange started. The compound **5'** was identified as 1,1-dideutero-2-phenyl-1,4-pentadiene and **7'** as 1,1-dideutero-2-phenyl-6,6-dimethyl-6-silahepta-1,3-diene.

The geometric structure of **3a** was deduced from the structure of **5''** which was obtained from protodesilylation [11] of deuterated **3a'** by anhydrous hydrogen chloride. It is well known that protodesilylation of vinylsilanes by acid takes place with retention of configuration [12]. The compound **5''** was the only product from the protodesilylation of stereohomogeneous **3a'**



1a, R = H
b, R = Me

2a(a'), R' = H(D)
b, R' = Me

3a(a'), R = R' = H (R' = D)
b, R = H, R' = Me

4a, R = H
b, R = Me

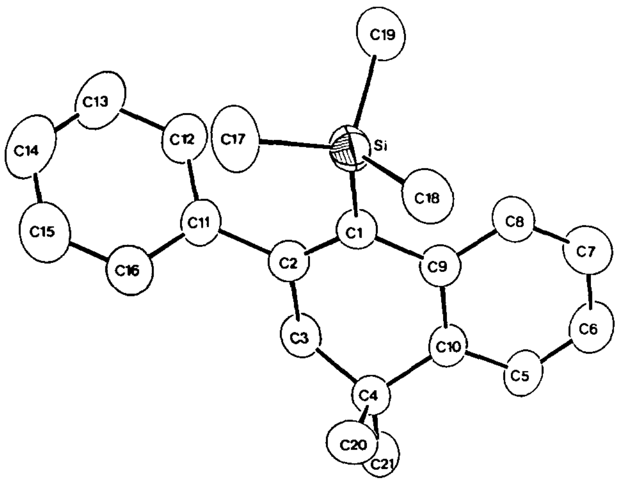
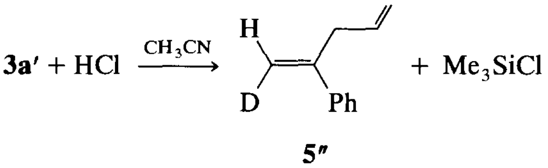


Fig. 1. Molecular structure of **3c′** showing full atom labeling scheme. Hydrogen atoms have been omitted for clarity.

and the ^{1}H NMR peak due to the vinyl proton appeared at 5.42 ppm. Considering that *cis*- and *trans*-vinyl protons relative to the phenyl group of **5** appear at 5.12 and 5.42 ppm [13], respectively, the vinyl proton of **5″** is assigned *trans* to the phenyl while the deuterium is assigned as *cis*. This result is consistent with the fact that the trimethylsilyl group of **3a** is located on *trans* to the phenyl group, probably to minimize the steric repulsion between two bulky groups. This result also indicates that the trimethylsilyl and allyl groups are added to the triple bond in *cis*-positions. The stereochemistry of **3b** has been assigned analogously to be (*E*)-2-trimethylsilyl-3-phenyl-2,5-hexadiene.



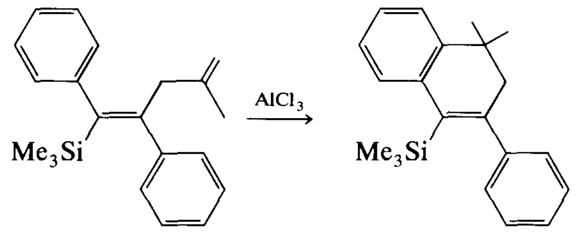
5″

The silyl group also adds to the terminal carbon and the (*E*)-isomeric product indicates that the allylsilylation is regiospecific, as observed in the allylsilylations of alkenes [4] and also stereospecific.

2.3. Allylsilylation of diphenylacetylene

The allylsilylation of diphenylacetylene **2c** with 2-methyl-2-propenyl trimethylsilane **1b** instead of **1a** under the same reaction conditions gave (*Z*)-1-trimethylsilyl-1,2-diphenyl-4-methyl-1,4-pentadiene **3c** in 48% yield, as expected. Other by-products were identified as hexamethyldisiloxane (16%) and 2,4,4,6,6-pentamethyl-6-silahept-1-ene **4b** (17%).

When the reaction mixture was stirred at room temperature for 20 h and then quenched, a secondary product 3,4-benzo-5,5-dimethyl-1-phenyl-2-trimethylsilylcyclohex-1-ene **3c′** was produced. In order to confirm the secondary reaction, **3c** was separated and stirred with aluminum chloride in benzene for 15 min at 40°C. The cyclized compound **3c′** was also obtained in 75% yield based on **3c**. This intramolecular cyclization of alkenylbenzenes catalyzed by Lewis acid is well-known [14].



3c **3c′**

Compound **3c′** was characterized by ^{1}H and ^{13}C NMR spectra and by HRMS. (see Section 3). The structure of **3c′** was also confirmed by X-ray crystal structure analysis. A perspective view of the molecular structure of **3c′** is shown in Fig. 1. Interatomic distances and selected bond angles are given in Table 1 and positional parameters and isotropic temperature factors in Table 2. Fig. 1 clearly indicates the configuration of the benzo and phenyl groups located as mutually *trans*. The configuration of **3c** was deduced from that of **3c′**, determined by X-ray analysis.

In the allylsilylation of diphenylacetylene, the trimethylsilyl and allyl groups are added to the triple bond in the *trans*-position. This result is opposite to those observed for the allylsilylation of phenylacetylenes, suggesting that the allylsilylation is not a concerted reaction but a stepwise one. The steric repul-

Table 1
Interatomic distances (Å) and selected bond angles (deg) for **3c′**

Interatomic distances (Å)			
Si–C19	1.866(2)	Si–C17	1.868(2)
Si–C18	1.873(2)	Si–C1	1.896(2)
C1–C2	1.349(3)	C1–C9	1.495(2)
C2–C11	1.491(2)	C2–C3	1.508(3)
C3–C4	1.525(3)	C4–C10	1.522(3)
C4–C21	1.530(3)	C4–C20	1.534(3)
C5–C6	1.380(3)	C5–C10	1.388(2)
C6–C7	1.368(3)	C7–C8	1.382(3)
C8–C9	1.398(3)	C9–C10	1.406(2)
C11–C12	1.385(3)	C11–C16	1.390(3)
C12–C13	1.380(3)	C13–C14	1.368(3)
C14–C15	1.377(3)	C15–C16	1.388(3)
Angle (deg)			
C19–Si–C17	108.22(11)	C19–Si–C18	110.81(11)
C17–Si–C18	104.83(11)	C19–Si–C1	112.71(9)
C17–Si–C1	113.89(9)	C18–Si–C1	106.09(9)
C2–C1–C9	116.7(2)	C2–C1–Si	124.55(14)
C9–C1–Si	118.26(13)	C2–C1–C11	124.0(2)
C1–C2–C3	120.6(2)	C11–C2–C3	115.3(2)
C8–C9–C10	117.9(2)	C8–C9–C1	120.7(2)
C10–C9–C1	121.3(2)		

sion between two bulky phenyl groups might be responsible for the *trans* addition. This indicates that the steric interaction between two phenyl groups in the *cis* position is larger than that between a phenyl and a trimethylsilyl group.

2.4. Allylic inversion

We extended the allylsilylation to diphenylacetylene **2c** and the stereohomogeneous (*Z*)-crotyltrimethylsilane [15] **1c**. (*Z*)-1-trimethylsilyl-1,2-diphenyl-3-methyl-1,4-pentadiene **3d** was obtained in 26% yield. The stereochemistry of **3d** has been assigned analogously to be (*Z*)-isomer. The product having a methyl group at the carbon α to the double bond, which comes from the terminal carbon of the starting allylsilane, indicates that an allylic inversion occurs during the allylsilylation. This type of allylic inversion was reported in the allylation of carbonyl compounds [15b] and the allylsilylation of alkenes [4]. It implies that the allylsilylation reaction is not concerted but stepwise, as observed in the allysilylation of alkenes.

This allylic inversion is consistent with the interaction of the cation intermediate **III** generated by the addition of trimethylsilyl cation to alkyne **2** with the electron-rich double bond of the allylsilane and then elimination of a silyl cation from the incoming allylsilane to give the allylsilylated products. The weak stabilization of β-trimethylsilylphenylvinyl cation compared with the corresponding carbocation has recently been reported [16]. The *trans*-position of the trimethylsilyl group relative to the phenyl group in **3a** may be explained by the addition of trimethylsilyl cation to phenylacetylene to give a β-trimethylsilylphenylvinyl cation, followed by reaction with **1c** to give the more stable *trans*-adduct.

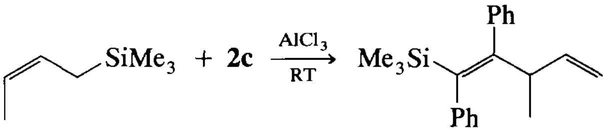
Table 2
Positional parameters and isotropic temperature factor (Å^2) for Non-hydrogen atoms of **3c′**

Atom	x	y	z	U_{eq}
Si	0.2059(0)	0.1019(0)	0.8103(0)	0.0473
C1	0.2804(1)	0.2701(2)	0.7671(1)	0.0427
C2	0.2670(1)	0.4243(2)	0.7855(1)	0.0448
C3	0.3083(2)	0.5523(2)	0.7855(1)	0.0501
C4	0.3108(1)	0.5078(2)	0.6470(1)	0.0472
C5	0.4331(2)	0.3133(3)	0.5797(1)	0.0536
C6	0.4831(2)	0.1693(3)	0.5751(1)	0.0594
C7	0.4668(2)	0.0586(3)	0.6317(1)	0.0591
C8	0.3999(2)	0.0911(2)	0.6925(1)	0.0523
C9	0.3487(1)	0.2362(2)	0.6989(1)	0.0427
C10	0.3666(1)	0.3497(2)	0.6408(1)	0.0436
C11	0.2180(1)	0.4801(2)	0.8591(1)	0.0474
C12	0.2590(2)	0.4351(3)	0.9309(1)	0.0572
C13	0.2165(2)	0.4880(3)	0.9999(1)	0.0715
C14	0.1316(2)	0.5865(3)	0.9981(1)	0.0756
C15	0.0896(2)	0.6343(3)	0.9276(2)	0.0728
C16	0.1329(2)	0.5825(2)	0.8582(1)	0.0591
C17	0.0872(2)	0.1647(3)	0.8677(2)	0.0728
C18	0.1539(2)	−0.0198(3)	0.7300(1)	0.0640
C19	0.2986(2)	−0.0198(3)	0.8795(1)	0.0687
C20	0.1988(2)	0.4905(3)	0.6148(1)	0.0658
C21	0.3665(2)	0.6395(2)	0.6026(1)	0.0647

Table 3
Results on allylsilylation of phenylacetylenes with allylsilanes [a]

Allylsilanes	Alkynes	Reaction time (min)	Product	B.p. [b] (°C)	Yield [c] (%)
1a	**2a**	10	**3a**	54–56	34
1a	**2b**	25	**3b**	58–60	66
1b	**2c**	540	**3c**	107–110	48
1c	**2c**	25	**3d**	106–109	26

[a] A 24°C water bath was used.
[b] Distilled at 0.6 mmHg.
[c] Isolated yields based on allylsilanes consumed.

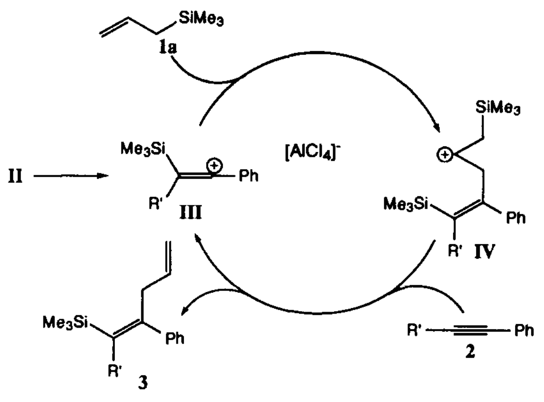


1c **3d**

The allylsilylation of phenylacetylenes proceeds in the presence of aluminum chloride catalyst under mild conditions with moderate yields and high stereo- and regioselectivities. The results of allylsilylations of phenylacetylenes with allylsilanes in the presence of aluminum chloride in benzene solution are summarized in Table 3.

2.5. Reaction mechanism

We propose a mechanism for the allylsilylation in which a carbocation intermediate **I** generated by the protonation of **1a**, either undergoes desilylation to give propylene and the trimethylsilyl cation [5,9] or reacts with **1a** to give the cation adduct **II** which gives the by-product **4a** by donating a trimethylsilyl cation to **2**. When a trimethylsilyl cation adds to phenylacetylene, the more stable secondary vinyl cation formation, the β stabilization effect by the silyl group, and the resonance stabilization by phenyl group would be responsible for the regiochemistry of the products [16]. The exchange reaction between the trimethylsilyl group of **1a** and the ethynyl proton can be explained by the elimination of a proton from β-trimethylsilylphenylvinyl cation **III** to form **6**. Several persistent β-silyl-substituted vinyl cations were characterized by Siehl and coworkers in solution at low temperatures [17]. The proton eliminated from the exchange reaction adds to phenylacetylene to form the phenylvinyl cation, which reacts with **1a** and then eliminates a trimethylsilyl cation to give **5**. When the cation **III** interacts with the double bond of **1a** to



Scheme 2. A catalytic cycle of allylsilylation.

form a new carbon–carbon bond, a carbenium ion center at the carbon β to silicon is generated. When the intermediate **IV** interacts with **2**, the allylsilylated products **3** are obtained by transfer of the trimethylsilyl cation to **2** to regenerate the intermediate **III**. The allylic inversion can be best explained by formation of a new double bond between the carbons α and β to the silicon of the incoming allylsilane and elimination of the trimethylsilyl cation, as illustrated in Scheme 2. When R′ is a phenyl group (Scheme 2) the phenyl and silyl groups on the same carbon will be switched owing to the larger steric interactions between two phenyl groups in the *cis* configuration. This may explain the *trans* addition of allylsilane to diphenylacetylene. All the results are consistent with the initial formation of trimethylsilyl cation intermediates by protodesilylation as proposed in the allylsilylation of alkenes [4].

3. Experimental details

The solvents benzene and acetonitrile were dried over sodium benzophenone ketyl or calcium hydride, respectively, and distilled before use. Allyltrimethylsilane was purchased from Hüls America Inc. and used without further purification. 2-Methyl-2-propenyltrimethylsilane and (*Z*)-crotyltrimethylsilane were prepared using the Grignard reaction and by literature methods [15], respectively. Anhydrous aluminum chloride, phenylacetylenes and other simple chemicals were purchased from Aldrich Chemical Co. and used without further purification. Hydrogen chloride (99.0%, anhydrous) was obtained from Matheson Gas Products Inc. The hydrogen chloride flow rate was controlled with a rotameter (Model FM-1051S-HA with 600 tube cube) manufactured by Matheson Gas Products Inc.

Products obtained from the allylsilylation of various alkynes were analyzed by GLC using a capillary column (SE-54, 30-m) or a packed column (10% OV-101 on 80–100 mesh Chromosorb W/AW, 1.5 m × 1/8 in.) on a Varian 3300 gas chromatograph equipped with a flame ionization detector or a thermal conductivity detector. The samples for characterization were purified by a preparative GLC using a Varian Aerograph Series 1400 gas chromatograph with a thermal conductivity detector and a 2-m by 1/8 in. stainless steel column packed with 20% OV-101 on 80–100 mesh Chromosorb P/AW. NMR spectra were recorded using $CDCl_3$ as internal reference (δ 7.26) on a Varian Gemini 300 spectrometer. Mass spectra were obtained using a Hewlett-Packard 5890 Series II gas chromatograph equipped with a 5972 mass selective detector. High resolution mass spectra (70 eV, EI) were performed by the Analytical Chemistry Laboratory of the Korea Research Institute of Chemical Technology, Daejon, Korea.

3.1. Allylsilylation of 2a with 1a

To a stirred solution of 0.25 g (1.9 mmol) of anhydrous aluminum chloride and 10.0 ml of dried benzene in a 50 ml three-necked round-bottomed flask equipped with an addition funnel, a reflux condenser, and a gas inlet tube was added dropwise a mixture of 2.2 g (19 mmol) of **1a** and 1.9 g (19 mmol) of **2a** under dry nitrogen at 24°C (water bath). The mixture was stirred for 10 min then quenched with 5 ml of water. The upper layer was separated and dried over anhydrous magnesium sulfate. The solvent and low-boiling factions were removed by simple distillation, and the products mixture was distilled under vacuum to give (*E*)-trimethylsilyl-2-phenyl-1,4-pentadiene **3a** (1.4 g, b.p. 54–56°C/0.6 Torr) in 34% yield, on the basis of **1a** consumed. Besides **3a**, several other by-products were obtained by vacuum distillation and identified as 4,6,6-trimethyl-6-silahept-1-ene **4a** (1%), hexamethyldisiloxane (18%), 2-phenyl-1,4-pentadiene **5** (10%) 1-phenyl-2-(trimethylsilyl)acetylene **6** (9%), 2-phenyl-6,6-dimethyl-6-silahepta-1,3-diene **7** (0.6%), and unidentified polymeric materials (28%). For **3a**: ^{1}H NMR δ ($CDCl_3$, ppm): -0.17 (s, 9H, Si–CH_3), 3.16 (dq, $J = 6.9$ Hz, 1.3 Hz, 2H, CH_2), 5.01–5.07 (m, 2H, CH_2=), 5.62 (t, $J = 1.3$ Hz, 1H, CH), 5.79–5.86 (m, 1H, CH), 7.15–7.35 (m, 5H, ArH); ^{13}C NMR δ ($CDCl_3$, ppm) 0.1 (Si–CH_3), 46.8 (CH_2), 116.5 (CH_2=), 127.0, 127.8, 128.0, 144.1 (Ar), 136.0 (CH), 157.4 (C). HRMS (m/e): Calc. for $C_{13}H_{17}Si$ (M^+–CH_3), 201.1099; found, 201.1098. For **5**: ^{1}H NMR δ ($CDCl_3$, ppm): 3.28 (dq, $J = 6.2$ Hz, 1.0 Hz, 2H, CH_2), 5.15–5.35 (m, 2H, =CH_2), 5.12 (s, 1H, =CH^aH), 5.42 (s, 1H, =CHH^b), 5.86–6.00 (m, 1H, CH), 7.23–7.48 (m, 5H, ArH). For **7**: ^{1}H NMR δ ($CDCl_3$, ppm): 0.01 (s, 9H, Si–CH_3), 1.56 (d, $J = 16.0$ Hz, 2H, CH_2), 4.97 (s, 1H, =CH^aH), 5.10 (s, 1H, =CHH^b), 5.59–5.69 (m, 1H, CH), 6.16 (d, $J = 15.4$ Hz, 1H, CH), 7.20–7.50 (m, 5H, ArH).

3.2. Allylsilylation of 2b with 1a

Using the reaction procedure described above, (*E*)-2-trimethylsilyl-3-phenyl-2,5-hexadiene **3b**, 2.9 g (bp 58–60°C/0.6 Torr, 66% yield) was obtained from the reaction of a mixture of 4.3 g (36 mmol) of **1a** and 2.2 g (19 mmol) of **2b** using 0.25 g (1.9 mmol) of anhydrous aluminum chloride in benzene. Other by-products were identified as hexamethyldisiloxane (10%), **4a** (3%), 4-phenyl-1,4-hexadiene, **8** (5%). For **3b**: ^{1}H NMR δ ($CDCl_3$, ppm): -0.22 (s, 9H, Si–CH_3), 1.84 (s, 3H, CH_3), 3.18 (d, $J = 6.3$ Hz, 2H, CH_2), 4.94–5.03 (m, 2H, CH_2=), 5.67–5.80 (m, 1H, CH), 7.07–7.31 (m, 5H, ArH); ^{13}C NMR δ ($CDCl_3$, ppm): -0.1 (Si–CH_3), 17.9 (CH_3), 40.6 (CH_2), 115.2 (CH_2=), 126.6, 127.8, 129.0, 145.9 (*Ar*), 134.9 (*C*H), 133.7, 148.9 (C). HRMS (*m/e*): Calc. for $C_{14}H_{19}Si$ (M^+), 230.1491; found, 230.1497. For **8**: ^{1}H NMR δ ($CDCl_3$, ppm): 1.82 (d, $J = 6.9$ Hz, 3H, CH_3), 3.28 (d, $J = 5.6$ Hz, 2H, CH_2), 4.99–5.14 (m, 2H, =CH_2), 5.81–5.94 (m, 1H, CH), 5.95 (q, $J = 6.9$ Hz, 1H, CH), 7.19–7.40 (m, 5H, ArH); ^{13}C NMR δ ($CDCl_3$, ppm) 14.2 (CH_3), 34.2 (CH_2), 115.1 (=CH_2), 124.2, 126.0, 128.2, 141.8 (*Ar*), 126.5, 135.7 (*C*H), 141.8 (*C*).

3.3. Allylsilylation of 2c with 1b

Using the reaction procedure described above, (*Z*)-1-trimethylsilyl-1,2-diphenyl-4-methyl-1,4-pentadiene **3c**, 2.5 g (b.p. 107–110°C/0.6 Torr, 48% yield) was obtained from the reaction of a mixture of 2.4 g (19 mmol) of **1b** and 3.4 g (19 mmol) of **2c** using 0.25 g (1.9 mmol) of anhydrous aluminum chloride in benzene. Other by-products were identified as hexamethyldisiloxane (16%) and 2,4,4,6,6-pentamethyl-6-silahept-1-ene **4b** (17%). For **3c**: ^{1}H NMR δ ($CDCl_3$, ppm): -0.20 (s, 9H, Si–CH_3), 1.59 (s, 3H, CH_3), 3.05 (s, 2H, CH_2), 4.55 (s, 1H, =CH^aH), 4.67 (s, 1H, =CHH^b), 7.14–7.41 (m, 10H, ArH); ^{13}C NMR δ ($CDCl_3$, ppm) 0.4 (Si–CH_3), 22.8 (CH_3), 45.5 (CH_2), 112.6 (=CH_2), 125.3, 127.0, 127.7, 128.0 128.2, 129.1, 142.8, 143.8 (*Ar*), 131.8, 144.6, 151.1 (*C*). HRMS (*m/e*): Calc. for $C_{21}H_{26}Si$ (M^+), 306.1804; found, 306.1797.

3.4. Allylsilylation of 2c with 1c

Using the reaction procedure described above, (*Z*)-1-trimethylsilyl-1,2-diphenyl-3-methyl-1,4-pentadiene **3d**, 1.5 g (b.p. 106–109°C/0.6 Torr, 26% yield) was obtained from the reaction of a mixture of 2.5 g (19 mmol) of **1c** and 3.4 g (19 mmol) of **2c** using 0.25 g (1.9 mmol) of anhydrous aluminum chloride in benzene. Other by-products were identified as hexamethyldisiloxane (16%) and 4-ethyl-3,6,6-trimethyl-6-silahept-1-ene **4c** (11%). For **3d**: ^{1}H NMR δ ($CDCl_3$, ppm): -0.28 (s, 9H, Si–CH_3), 0.96 (d, $J = 6.9$ Hz, 3H, CH_3), 3.39 (p, $J = 6.8$ Hz, 2H, CH_2), 4.81–4.98 (m, 2H, =CH_2), 5.70–5.81 (m, 1H, CH), 7.12–7.65 (m, 10H, ArH); ^{13}C NMR δ ($CDCl_3$, ppm) 0.1 (Si–CH_3), 18.3 (CH_3), 42.3 (CH), 113.4 (=CH_2), 125,4, 126.8, 127.2, 128.3, 128.4, 130.6, 140.5, 141.7 (*Ar*), 141.7 (*C*H, overlapped peak), 144.3, 155.6 (*C*). HRMS (*m/e*): Calc. for $C_{21}H_{26}Si$ (M^+), 306.1804; found, 306.1798.

3.5. Friedel–Crafts reaction of 3c

Compound **3c** (0.2 g) was reacted with anhydrous aluminum chloride in 3 ml of benzene solution. The mixture was stirred for 15 min at 40°C (water bath) and then quenched with 2 ml of water. Usual workup and separation by preparative GLC gave 3,4-benzo-5,5-dimethyl-1-phenyl-2-trimethylsilylcyclohex-1-ene **3c′** in 75% yield based on **3c** used. For **3c′**: ^{1}H NMR δ ($CDCl_3$, ppm): -0.01 (s, 9H, Si–CH_3), 1.40 (s, 6H, –CH_3), 2.48 (s, 2H, –CH_2–), 7.22–7.44 (m, 9H, ArH). ^{13}C NMR δ ($CDCl_3$, ppm): 2.0 (Si–CH_3), 27.2 (CH_3), 33.4 (*C*), 48.3 (CH_2), 123.2, 125.3, 126.5, 127.5, 127.8, 128.0, 128.9, 134.3, 138.3, 143.9 (*Ar*), 145.6, 152.4 (*C*). HRMS (*m/e*): Calc. for $C_{21}H_{26}Si$ (M^+), 306.1804; found, 306.1804.

3.6. Allylsilylation of 2a′ with 1a

1-Deuterio-2-phenylacetylene **2a′** was prepared and reacted with **1a** by using the reaction procedure described for the synthesis of **3a**. A major product was **3a′** and by-products were identified as 1,1-dideuterio-2-phenyl-1,4-pentadiene **5′** and 1,1-dideuterio-2-phenyl-6,6-dimethyl-6-silahepta-1,3-diene **7′**. Because only a small amount of **7′** was obtained, it was identified only by GC–MS analysis. For **3a′**: ^{1}H NMR δ ($CDCl_3$, ppm): -0.17 (s, 9H, Si–CH_3), 3.16 (dt, $J = 6.9$ Hz, 1.3 Hz, 2H, CH_2), 5.01–5.07 (m, 2H, CH_2=), 5.79–5.86 (m, 1H, CH), 7.15–7.35 (m, 5H, ArH); ^{13}C NMR δ ($CDCl_3$, ppm) 0.1 (Si–CH_3), 46.7 (CH_2), 116.4 (CH_2=), 127.0, 127.8, 128.0, 144.1 (*Ar*), 136.0 (*C*H), 157.4 (*C*). For **5′**: ^{1}H NMR δ ($CDCl_3$, ppm): 3.28 (d, $J = 6.5$ Hz, 1.3 Hz, 2H, CH_2), 5.15–5.35 (m, 2H, =CH_2), 5.86–6.00 (m, 1H, CH), 7.23–7.48 (m, 5H, ArH).

3.7. Protodesilylation of 3a′

3a (0.18 g, 0.83 mmol) reacted with ca. 3 mmol of anhydrous hydrogen chloride, in a rotameter in dry acetonitrile solution. Gas chromatographic analysis showed this reaction was quantitative. After separation of the product by preparative GLC, the major product was identified as (*Z*)-1-deuterio-2-phenyl-1,4-pentadiene **5″** by ^{1}H NMR analysis, with trimethylchlorosilane as a by-product. For **5″**: ^{1}H NMR δ ($CDCl_3$, ppm): 3.28 (d, $J = 6.5$ Hz, 2H, CH_2), 5.15–5.35 (m, 2H, =CH_2), 5.42 (s, 1H, =CHD), 5.86–6.00 (m, 1H, CH), 7.23–7.48 (m, 5H, ArH).

Table 4
Crystallographic data for **3c′**

Empirical formula	$C_{21}H_{26}Si$
fw	306.51
Temperature (K)	293
Radiation source	Mo Kα
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	12.7540(10)
b (Å)	8.4814(7)
c (Å)	17.1384(10)
β (deg)	90.580(10)
Vol. (Å^3)	1853.8(2)
Z	4
Density (calc.) (g cm^{-3})	1.098
Abs. coeff. (mm^{-1})	0.122
$F(000)$	664
Crystal size (mm)	0.5×0.5×0.5
θ range for data collection (deg)	$4 \leqslant 2\theta \leqslant 45$
Scan type	$\omega/2\theta$
Index range	$0 \leqslant h \leqslant 13$, $0 \leqslant k \leqslant 9$, $-13 \leqslant l \leqslant 13$
No. of reflections collected	2668
No. of independent reflections	2261
No. of observed reflections	2076 ($\lvert F_o \rvert > 4.0\sigma(F_o)$)
No. of parameters refined	206
R_1 ($\lvert F_o \rvert > 4.0\sigma(F_o)$) [a]	0.0332
wR_2 ($\lvert F_o \rvert > 4.0\sigma(F_o)$) [b]	0.0886
GOF ($\lvert F_o \rvert > 4.0\sigma(F_o)$)	1.062
Max and min peak (eÅ^3)	+0.14, −0.15

[a] $R_1 = \Sigma \lvert\lvert F_o \rvert - \lvert F_c \rvert\rvert / \Sigma \lvert F_o \rvert$.

[b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (0.0450P)^2 + 0.5771P)^2]$, $P = (F_o^2 + 2F_c)^2/3$.

3.8. X-ray crystallography

A colorless single crystal of compound **3c′** suitable for X-ray analysis was obtained by crystallization from the slowly cooled diethylether/ethanol solution. Reflection data were collected on an Enraf-Nonius CAD4TSB diffractometer with graphite-monochromated Mo-Kα radiation at 20°C. Accurate cell parameters and an orientation matrix were determined from the least-square fit of 25 accurately centered reflections in the range $10.62° \leq \theta \leq 15.08°$ (SET4). All data were collected with the $\omega/2\theta$ scan mode and corrected for Lorentz polarization effects. No absorption correction was applied. Details of crystal data, data collection and data refinement are listed in Table 4. The structure of this compound was solved by direct methods (SHELXS-86). Nonhydrogen atoms were refined by full-matrix least-squares techniques (SHELXL-93) with anisotropic displacement parameters. Hydrogen atoms were placed at their geometrically calculated positions ($d_{CH} = 0.970$ Å for methylene hydrogens, $d_{CH} = 0.960$ Å for methyl hydrogens, $d_{CH} = 0.930$ Å for aromatic hydrogens) and refined riding on the corresponding carbon atoms with isotropic thermal parameters ($U = 1.5\ U$ (C_{methyl}) and $1.2\ U$ ($C_{methylene}$ and aromatic)). The final R_1 and weighted wR_2 where $R_1 = \Sigma \lVert F_o \rvert - \lvert F_c \rVert / \Sigma \lvert F_o \rvert$. $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$, were 0.0332 and 0.0886 for 2076 reflections with $\lvert F_o \rvert > 4.0\sigma(F_o)$, respectively. All calculations were performed on an IBM RISC/6000 workstation.

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