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A General Synthesis of β-Silylallenes from Allylsilanes

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Abstract : β-Trimethylsilyl allenes have been prepared in fair to good yields from allylsilanes by successive dibromocarbene addition and rearrangement of the cyclopropylidenes. In the case of 3,6-bis(trimethylsilyl)cyclohexa-1,4-diene, insertion of dibromocarbene occurs in the silicon-carbon bond leading to α-bromobenzyltrimethylsilane. © 1997 Published by Elsevier Science Ltd.

While allylsilanes have received considerable attention,[1] their homologous β-trimethylsilylallenes have not been extensively studied from a synthetic point of view.[2] This results probably from the difficulty of their availability. Thus, only reported in fair yields, the synthesis of this class of compounds has only been performed by displacement of propargylic acetates or tosylates with the Grignard reagent of chloromethyltrimethylsilane in the presence of a copper salt[3] or from 1-substituted-4-trimethylsilyl-2-tributylstannylbut-2-en-1-ol through a conjugative acidic β-elimination of tributylstannyl-hydroxide.[4] However, these two approaches present major drawbacks: the difficulty to access in good yield to a general preparation with a large number of substituents and the impossibility to introduce functional groups. For these two reasons, it was desirable to develop an alternative procedure that would be general, expeditive and inexpensive. Moreover, Creary *et al*, in a study related to the silyl-substituted cyclopropyl rearrangement, have described the formation of β-silylallenes from β-silylated dibromocyclobutanes.[5] This prompted us to report our results in this field.

Taking into account the numerous possibilities offered by the compounds bearing two allysilanes functions as, for example, BISTRO [1,8-bis(trimethylsilyl)-2,6-octadiene] **1f**,[6] we projected the synthesis of 1,5-bis(trimethylsilyl)-penta-2,3-diene **3e** from 1,4-bis(trimethylsilyl)but-2-ene **1e** by a dibromocarbene addition and cyclopropylidene rearrangement sequence; **1e** being readily prepared from lithium, chlorotrimethylsilane and butadiene in 65% yield.[7]

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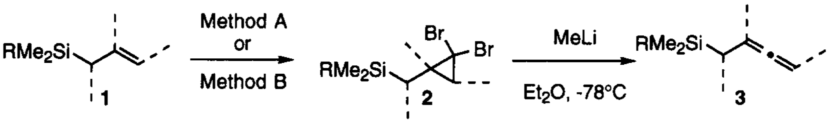
We started an exploratory study with allyltrimethylsilane **1a** (see table 1). Reaction of allylsilane **1a** with aqueous sodium hydroxide and bromoform under phase transfer conditions in the presence of benzyltriethylammonium chloride (TEBA) leads to the corresponding *gem*-dibromocyclopropane **2a** in 85% yield (procedure A).[8] Using bromoform and potassium *tert*-butoxyde in pentane, the reaction takes place with similar yield (procedure B).[9]



A: $CHBr_3$, NaOH aq 50%, Et_3BnNCl 5%, 0°C
B: $CHBr_3$, *t*-BuOK (1eq.), pentane, 0°C

In order to extend this result, other allylsilanes were submitted to dibromocarbene addition. For allylsilanes **1a-c,f**, phase transfer catalysis seems to be the more adapted method. In contrast, disilyl derivative **1e** needs the use of procedure B which gives high yields (method A leaving **1e** unchanged). This is certainly due to steric reasons imputable to the difference of solvatation of the reactive species (H_2O *vs* *t*-BuOH-pentane). Furthermore, high degree of symmetry leads to a low polarization of the double bond which inhibits the addition reaction.[10] For such reasons, tetrakis(trimethylsilyl)but-2-ene **1h** was found unreative under both conditions.[11]

Depending on their structure, rearrangement of cyclopropylidenes (or the corresponding carbenoids) can give allenes[12] or bicyclobutanes.[13] Due to the structure of the β-silyl dibromocyclopropanes **2a-g**, the first evocated process should be the favoured one. Generation of the cyclopropylidenes was done by halogen-lithium exchange[14] with methyllithium at low temperature and the rearrangement led in good yields to β-trimethylsilylallenes **3a-g** as the sole products.[15] Note that the presence of the hydroxy function does not affect the rearrangement reaction (compound **3i** from **1i**).[16]

Surprisingly, dibromocarbene addition into 3,6-bis(trimethylsilyl)cyclohexa-1,4-diene does not lead to the desired dibromocyclopropane adduct but to α-bromobenzyltrimethylsilane in 69% yield. As a possible explanation to rationalize this result, we think that the tribromomethyl anion adds to silicon and generates a siliconate. The latter then evolves by 1,2-migration giving the product equivalent to dibromocarbene insertion into the allylic carbon-silicon bond. Finally, successive dehydrobromination and protolysis of bisallylic carbon-silicon bond reactions lead to **4**.

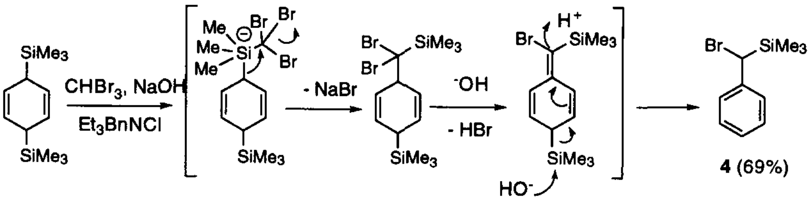
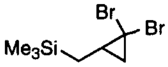
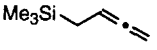
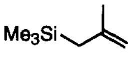
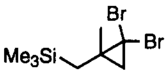
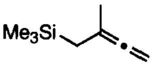
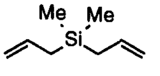
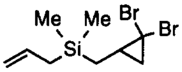
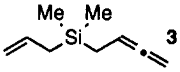
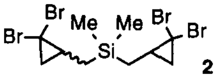
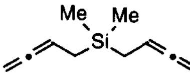
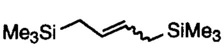
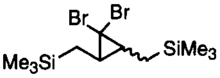
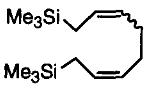
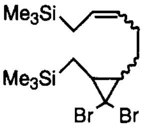
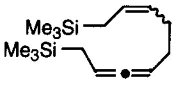
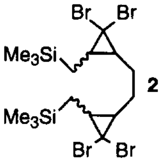
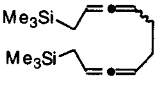
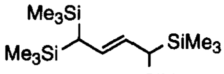
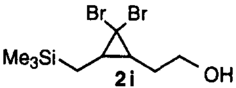
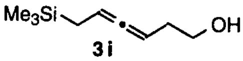


Table 1 : Synthesis of β-allenylsilanes

Allylsilanes 1	Exp. Cond	Dibromocyclopropanes 2	yield	β-allenylsilanes 3	yield
 **1 a**	A B	 **2 a**	85 83	 **3 a**	80
 **1 b**	A	 **2 b**	80	 **3 b**	72
 **1 c**	A 1 eq.*	 **2 c**	74	 **3 c**	88
"	A 2 eq.	 **2 d**	85**	 **3 d**	90
 **1 e**	A B	 **2 e**	0 93**	 **3 e**	70
 **1 f**	A 1 eq.*	 **2f**	63	 **3 f**	86
"	A 2.2 eq.	 **2 g**	65**	 **3g**	95**
 **1 h**	A B	- -	0 0	- -	- -
 **1 i**	B	 **2 i**	82	 **3 i**	70***

* obtained as a separable mixture (80/20) of mono and diaddition products.

** obtained as an equimolar mixture of diastereomers.

*** 2.5 equivalents of MeLi have been used.

In summary, we have investigated a new general route to β-trimethylsilyl allenes. Studies to modify the nature of the metal (Sn, B) and to investigate the synthetic properties of the various cyclopropylsilanes **2** and silylallenes **3** are currently underway.

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References and notes

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11- PM3 semi-empirical calculation method applied to **1h** reveals a high HOMO level compared to HOMO level of allyltrimethylsilane. In spite of this, for the HOMO, the sp2 carbons exhibit very weak orbital coefficients leading to a bad overlapping that can explained the unreactivity of **1h** toward dibromocarbene.

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14- All new reported compounds exhibit satisfactory analysis (^{1}H and ^{13}C NMR, MS).

15- Preparation of 1,5-bis(trimethylsilyl)penta-2,3-diene **3e**: Bromoform (17 mmol) was added, at 0° C, to 1,4-bis(trimetylsilyl)but-2-ene (10mmol) and potassium *tert*-butoxide (17mmol) in suspension in pentane (10mL). The mixture was stirred for 1h., warmed to room temperature for 10 mn, extracted with ether (3x10 mL) and the combined organic layers dried. The solvents were removed to give **2e**. Chromatography on silica gel eluting with light petroleum ether gave a colorless oil.

Dibromocyclopropane **2e** (8 mmol) was dissolved in dry ether (10mL) and was stirrred at –78° C. Methyl lithium (8.8 mmol) was added dropwise then the mixture was warmed to –10° C in 1 h. then quenched with 10mL of H_2O. After usual treatments, chromatography on silica gel eluting with light petroleum ether gave 2,01 g of a colorless oil **3e** (70%). NMR ^{1}H ($CDCl_3$) $\delta = 0.0$ (s, 9H); 1.26 (m, 4H); 4.99 (ddd, $J = 4.3$, 6.6, 10.9 Hz, 2H). NMR ^{13}C ($CDCl_3$) $\delta = 0.0$ (6C); 18.5 (2C); 86.4 (2C); 204.8. IR (meaningfull signal) = 1955 cm^{-1}.

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