Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 1994, **4(2)**, 55–57
Mendeleev Communications

Synthesis of 5-Trimethylsilyl-1,4-enynes from Ethoxy(trimethylsilyl)acetylene and Mono- and Diboron Allylic Compounds

Yurii N. Bubnov,* Alexei V. Geiderikh, Sergei B. Golovin, Mikhail E. Gursky, Marina Yu. Etinger, Larisa I. Lavrinovich, Peter Yu. Meleshkin, Sergei V. Ponomarev and Valentina I. Zheludeva

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 117913 Moscow, Russian Federation. Fax: +7 095 135 5328

Allylic boranes and diboranes add to ethoxy(trimethylsilyl)acetylene with full rearrangement of the allylic moiety to give a series of new trimethylsilyl-substituted cyclic and acyclic 1,4-enynes and polyenynes with a terminal double bond.

A key step in the most convenient synthetic pathways to the 1,4-pentenynes (allylacetylenes) with terminal double and triple bonds,[1] as well as to their trimethylsilyl analogues[2] **4**, (R = H, Me), involves allylboration of ethoxyacetylene and trimethylsilylethoxyacetylene **1**, respectively (Scheme 1).

cis-Addition **2** of an allylboron fragment to the triple bond of acetylenic compound **1** results in formation of boron–silicon adducts **3**, which are unstable and undergo β-elimination[2] at room temperature, yielding enynes **4** and R'_2BOEt.

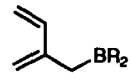
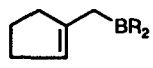
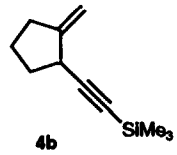
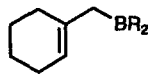
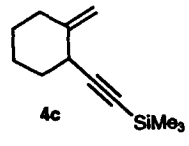
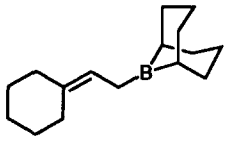
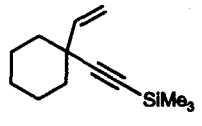
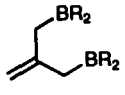
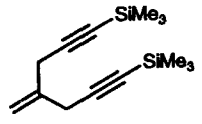
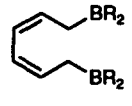
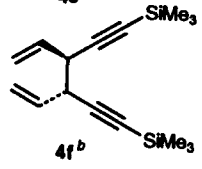
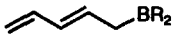
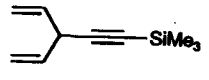
We applied this method to the synthesis of novel linear and cyclic silicon-containing 1,4-enynes **4a–g** with terminal double bond(s) (see Table 1) using new allylic boranes and diboranes[3,4] **5a–g** as starting materials (Scheme 2).

Addition of **5** to **1** proceeds with full rearrangement of the allylic moiety *via* a six-membered transition state **6**. It is noteworthy that boranes **5** react with **1** significantly more slowly than allylic and crotylic boron derivatives.[2] The reaction was monitored by IR spectroscopy.

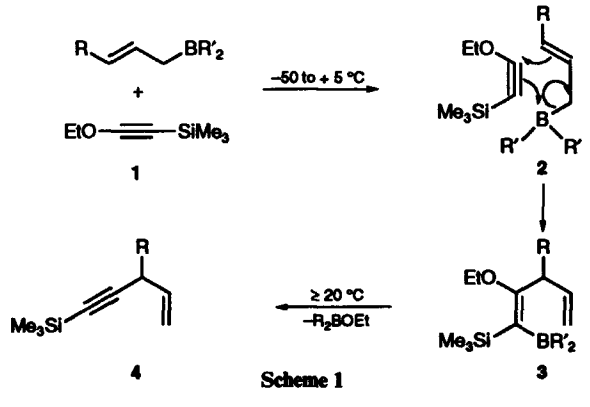
On mixing boranes **5a–e** with **1**, a weak self-heating is observed (due to complexing B←O). After 10–15 min a band at

Mendeleev Commun., 1994, 4(2), 55–57

Table 1 Synthesis of enynes **4a–g** from allylic boranes and diboranes.

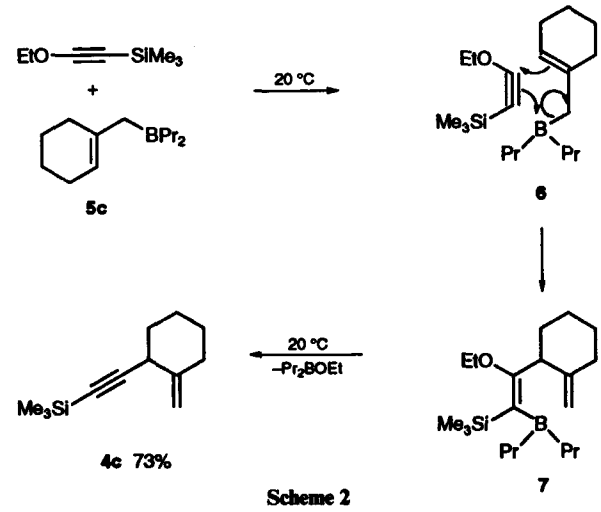
Starting borane	Product (1,4-enyne)	Time	Yield (%)	B.p. /°C (Torr)	n_D^{20}
 **5a**	 **4a**	2 days	92(43)[a]	77.5–78 (22)	1.4695
 **5b**	 **4b**	4 hours	46.6[a]	37–39 (1)	1.4680
 **5c**	 **4c**	5 days	73.3[a]	45–47 (1)	1.4749
 **5d**	 **4d**	25 days	48[a]	54–55 (2)	1.4658
 **5e**	 **4e**	4 days	68[a]	84–85 (1)	1.4679
 **5f**	 **4f**[b]	2 days	74	73–77 (1)	1.4608
 **5g**	 **4g**	7 days	58	47–49 (16)	1.4491

[a] The product was isolated by distillation and purified by column chromatography on SiO_2, eluent pentane or hexane. [b] The product is a mixture of diastereomers, ratio being 4:1 (not assigned).



Scheme 1

1600–1610 cm^{-1} appears in the IR-spectrum of the reaction mixture, due to the B–C=C–OEt fragment in the adduct **7** formed; the intensity of the band increases and then decreases to zero. This takes place because of the accumulation of the corresponding adduct **7** followed by its transformation to enyne **4a–e** and R_2BOEt.



Scheme 2

Among the boranes **5a–e** investigated, the cyclopentenic derivative **5b** is the most active. Its reaction with **1** (addition–β-

elimination) is completed in 4 h at ~20 °C. Under the same conditions **5c** and **5e** react with **1** for 4–5 days. Borane **5d** reacts with **1** slowly (25 days at ~20 °C); moreover, no absorption at 1600 cm^{-1} in the IR spectra of the reaction mixture recorded after different time intervals was observed. One may conclude that in this case addition product **7d** undergoes fast β-elimination just after formation.

The isolated yields of the silylated 1,4-enynes **4a–g** are quite good (Table 1). Therefore, the reaction of allylic boranes with 1-ethoxy-2-trimethylsilylacetylene is a general method for the preparation of various compounds of this type.[†,‡]

This work was partly supported by the Russian Fundamental Research Foundation (grant no. 93–03–18193).

[†] *Typical procedure:* 1,6-Bis(dipropylboryl)hexadiene **5f** (1.64 g, ~6 mmol) was mixed with **1** (1.72 g, 12 mmol) in 5 ml of pentane at ~20 °C. The reaction was monitored by IR spectroscopy. After 2 days the reaction mixture was evaporated under reduced pressure and the product was isolated by short-run distillation *in vacuo* (1 mmHg), yield 1.21 g (see Table 1). (Found: C, 70.34; H, 9.65; Si, 20.03%. Calc. for $C_{16}H_{26}Si_2$: C, 70.0; H, 9.54; Si, 20.46%).

^{13}C NMR spectrum ($CDCl_3$, δ ppm): 0.1, 41.8 (41.3), 89.7, 104.3, 117.2 (117.3), 134.7 (134.1) (the chemical shifts of the minor stereoisomer are given in parentheses, the ratio major/minor being *ca.* 4/1).

[‡] ^1H NMR spectroscopic data for enynes **4a–g**; δ (ppm); *J*/Hz. **4a** 0.16 (s, 9 H, $SiMe_3$); 3.15 (s, 2 H, $-CH_2-$); 5.15–5.50 (4 H, $=CH_2$); 6.40–6.55 (2 H, $=CH-$). **4b** 0.16 (s, 9 H, $SiMe_3$); 1.46–2.43 (6 H, ring); 3.2 (m, 1H, $H-C-C\equiv$); 4.98 s and 5.18 s (2 H, $=CH_2$). **4c** 0.17 (s, 9 H, $SiMe_3$); 1.34–2.06 and 2.42 (8 H, ring); 3.05 (d.d., 1 H, $H-C-C\equiv$); 4.78 and 5.06 (s, 2 H, $=CH_2$). **4d** 0.18 (s, 9 H, $SiMe_3$); 1.1–1.4 and 1.5–1.8 (10 H, ring); 5.02 (d.d., 1H, $J_{cis} = 10.2$, $J_{AB} = 2.0$); 5.36 (d.d., 1 H, $J_{trans} = 17.0$, $=CH_2$); 5.76 (dd, 1 H, $=CH-$). **4e** 0.18 (s, 18 H, $SiMe_3$); 3.02 (br.s, 4 H, CH_2); 5.21 (br.s, 2H, $=CH_2$). **4f** 0.16 (s, 18 H, $SiMe_3$); 3.20 (m, 2H, CH aliph.); 5.20 and 5.37 (m, 4 H, $=CH_2$); 5.80–5.97 (2 H, $=CH-$). **4g** 0.19 (s, 18 H, $SiMe_3$); 3.80 (m, 1 H, CH aliph.); 5.14 and 5.33 (m, 4 H, $=CH_2$); 5.70–5.87 (2 H, $=CH-$).

References

1 Yu. N. Bubnov, A. V. Tsyban' and B. M. Mikhailov, *Synthesis*, 1980, 904.

2 S. V. Ponomarev, Yu. N. Bubnov and B. M. Mikhailov, *Izv. Akad. Nauk SSSR., Ser. Khim.*, 1981, 1859 (*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1981, **30**, 1528).

3 Yu. N. Bubnov, *Pure Appl. Chem.*, 1987, **59**, 895; 1991, **63**, 361.

4 Yu. N. Bubnov, M. E. Gurskii and A. V. Geiderikh, *Metalloorg. Khim.*, 1989, **2**, 1433 (*Organomet. Chem. USSR*, 1989, **2**, 761).

Received: Moscow, 13th December 1993
Cambridge, 21st January 1994; Com. 3/07669E