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Tris(trimethylsilyl)silyl Radical Induced Bicyclization of 1,6-Dienes and 1,6-Enynes Providing 3,3-Bis(trimethylsilyl)-3-silabicyclo[3.3.0]octanes and 3-Silabicyclo[3.3.0]oct-1-enes

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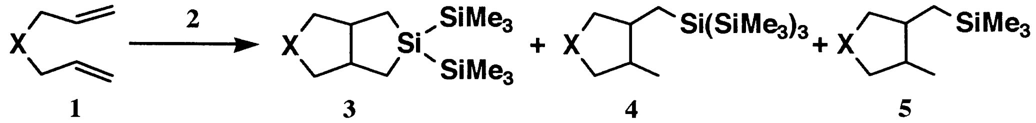
Treatment of 1,6-dienes with tris(trimethylsilyl)silane in the presence of triethylborane or AIBN afforded 3,3-bis(trimethylsilyl)-3-silabicyclo[3.3.0]octanes in addition to monocyclized cyclopentanes. Bicyclization of 1,6-enynes provided the corresponding 3-silabicyclo[3.3.0]oct-1-enes.

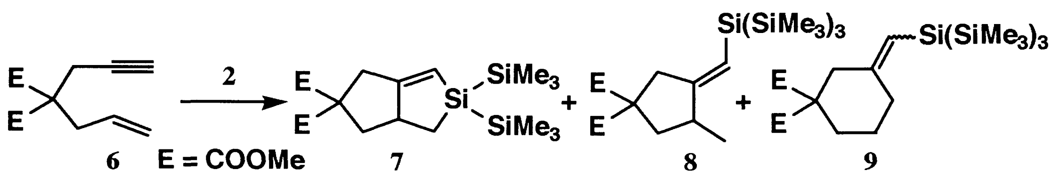
A recent publication[1)] on homolytic substitution reaction at a silicon atom prompts us to report our independent results along similar lines. When a benzene solution of diene **1a** and tris(trimethylsilyl)silane (**2**, TTMSS)[2)] was treated at 25 °C with a catalytic amount of triethylborane,[3)] bicyclized product **3a** (11%) was isolated along with monocyclized product **4a** (87%) after chromatography. The ratio **3a**/**4a** had increased to 81/19 and the isolated yields of **3a** and **4a** were 71% and 17%, respectively, upon treatment of **1a** (1.0 mmol) with TTMSS (1.3 mmol) at 80 °C using an initial concentration of substrate of 0.02 M with intermittent addition of azobis(isobutyronitrile) (AIBN, 0.1 mmol x 5) over 5 h. In addition to the formation of **3a** and **4a**, trimethylsilylmethyl-substituted monocyclized product **5a** was obtained in 8% yield.



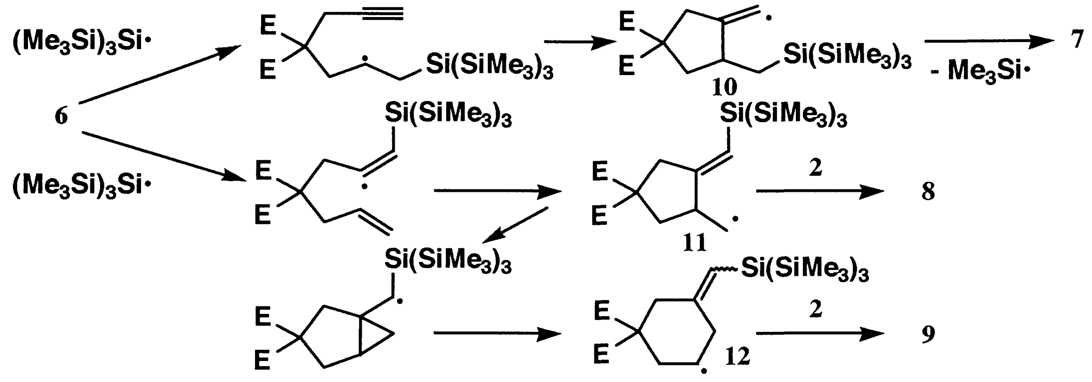
	X	Yield/% (cis/trans)		
a:	$C(COOMe)_2$	71 (15/1)	17 (1/2)	8 (5/1)
b:	CH_2	62 (6/1)	27 (1/5)	4 (3/1)
c:	O	53 (cis only)	26 (1/8)	3 (3/1)

In a similar manner, dienes **1b** and **1c** were converted into the corresponding bicyclized products **3b** and **3c**, respectively. Two types of monocyclized products **4b** and **5b** (or **4c** and **5c**) were also obtained as mixtures of *cis* and *trans* compounds.[4)] Whereas **3c** was produced in an isomerically pure form (*cis*-fused compound), **3a** and **3b** were obtained as isomeric mixtures of *cis*-fused and *trans*-fused 3-silabicyclooctanes under similar reaction conditions.[5)]

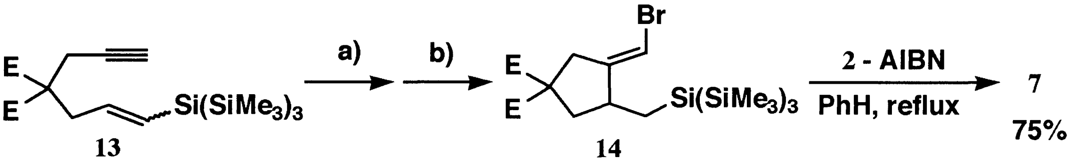
Then, the cyclization of 1,6-enynes has been examined. Heating a benzene (5 ml) solution of 1,6-enyne **6** (1.0 mmol) and **2** (1.3 mmol) in the presence of AIBN (0.1 mmol) at reflux for 2.5 h gave bicyclized product **7** (48%) in addition to monocyclized ones, **8** (6%) and **9** (39%).



We assume following reaction mechanism for bicyclization of enynes. The tris(trimethylsilyl)silyl radical can attack either terminal olefinic carbon or terminal acetylenic carbon. The attack on terminal olefinic carbon gives silabicyclo product **7** *via* olefinic radical **10**. On the other hand, an addition of tris(trimethylsilyl)silyl radical to terminal acetylenic carbon provides cyclopentylmethyl radical **11** which can not undergo cyclization because of its (*E*) stereochemistry. Thus, the radical **11** abstracts hydrogen from **2** to provide **8**. Alternatively, **11** rearranges to cyclohexyl radical **12** which reacts with **2** to give **9**.



The Si-Si bond fission by the intramolecular attack of carbon radical was confirmed by the experiments shown below. Radical abstraction of bromine from **14**, prepared from 1,6-enyne **13**, afforded 3-silabicyclo[3.3.0]oct-1-ene **7** in 75% yield.



a) *n*-Bu_3SnH-AIBN, PhH, reflux; b) Br_2, CH_2Cl_2, -78 °C

References

1) a) K. J. Kulicke, C. Chatgilialoglu, B. Kopping, and B. Giese, *Helv. Chim. Acta*, **75**, 935 (1992); b) B. Kopping, C. Chatgilialoglu, M. Zehnder, and B. Giese, *J. Org. Chem.*, **57**, 3994 (1992).

2) C. Chatgilialoglu, D. Griller, and M. Lesage, *J. Org. Chem.*, **53**, 3641 (1988); C. Chatgilialoglu, A. Guarini, A. Guerrini, and G. Seconi, *ibid.*, **57**, 2208 (1992).

3) K. Nozaki, K. Oshima, and K. Utimoto, *Tetrahedron*, **45**, 923 (1989).

4) The ratio of *cis*-**4c**/*trans*-**4c** = 3/1 has been reported in Ref 1a. In contrast, a mixture of *cis*-**4c**/*trans*-**4c** = 1/8 was obtained in our method.

5) *trans*-**3b**: ^{1}H NMR ($CDCl_3$) δ 0.11 (s, 18H), 0.40 (dd, *J* = 13.4, 12.1 Hz, 2H), 0.91 (dd, *J* = 13.4, 5.6 Hz, 2H), 0.99-1.13 (m, 2H), 1.34-1.51 (m, 2H), 1.67-1.77 (m, 2H), 1.86-1.96 (m, 2H); ^{13}C NMR ($CDCl_3$) δ -0.86, 11.15, 27.48, 31.05, 54.39.

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