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1,1-Diethynylsilacycloalkanes and Propellanes Based Thereon

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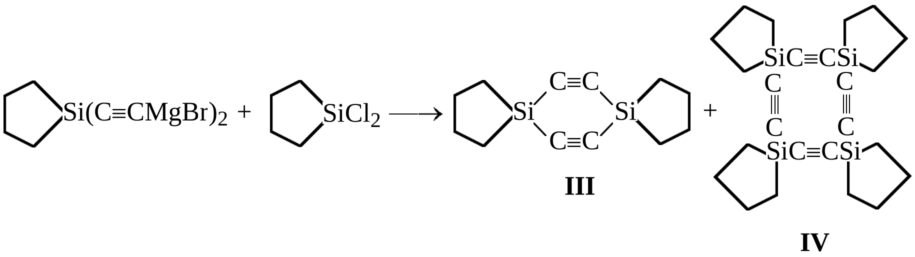
Abstract—Previously unknown 1,1-diethylnylsilacycloalkanes $(CH_2)_nSi(C\equiv CH)_2$ (n = 3, 4) were prepared by the reaction of $HC\equiv CMgBr$ with 1,1-dichlorosilacycloalkanes $(CH_2)_nSiCl_2$ (n = 3, 4). The reaction of $(CH_2)_4Si(C\equiv CMgBr)_2$ with $(CH_2)_4SiCl_2$ in THF under conditions of high dilution gives cyclo(tetramethylene)silethynes $[(CH_2)_4SiC\equiv C]_4$ with an admixture of cyclodi(tetramethylene)silethyne $[(CH_2)_4SiC\equiv C]_2$. The reaction of $Me_2Si(C\equiv CSiMe_2C\equiv CMgBr)_2$ with $(CH_2)_4SiCl_2$ was used to prepare 1,1,4,4,7,7-hexamethyl-10,10-tetramethylene-1,4,4,10-tetrasilacyclododeca-2,5,8,11-tetrayne.

Earlied we described 1-ethynyl-1-methylsilacyclobutane and 1-ethynyl-1-methylsilacyclopentane [1, 2]. Proceeding with these studies, we synthesized 1,1-diethylnylsilacyclobutane (**I**) and 1,1-diethynylsilacyclopentane (**II**). They were obtained by the reactions of ethynylmagnesium bromides with respectively 1,1-dichlorosilacyclobutane and 1,1-dichlorosilacyclopentane in THF.

$$(CH_2)_nSiCl_2 + 2BrMgC\equiv CH \longrightarrow \underset{\textbf{I, II}}{(CH_2)_nSi(C\equiv CH)_2},$$

$$n = 3\ (\textbf{I}),\ 4\ (\textbf{II}).$$

1,1-Diethynylsilacyclobutane and 1,1-diethynylsilacyclopentane are colorless liquids with a specific ethynylsilane odor. Due to presence of a mobile acetylenic hydrogen atom they can be easily converted to highly reactive organomagnesium derivatives. The reaction of 1,1-bis(bromomagnesioethynyl)silacyclopentane with 1,1-dichlorosilacyclopentane in THF under conditions of high dilution gives a mixture of bi- and tetracyclo(tetramethylene)silethynes: 1,1,4,4-di(tetramethylene)-1,4-disilacyclohexa-2,5-diyne and 1,1,4,4,7,7,10,10-tetra(tetramethylene)-1,4,7,10-tetrasilacyclododeca-2,5,8,11-tetrayne, respectively.



Propellane **IV** was isolated as crystals (Table 1) and characterized by ^1H, ^{13}C, and ^{29}Si NMR spectroscopy (Table 2). The mass spectrum of the resulting sample contains, along with the base peak at *m/e* 432 (compound **IV**), a lower intensity peak at *m/e* 216 assignable to propellane **III**. This assignment is supported by the observation in the ^1H and ^{13}C NMR spectra of signals due to both **III** and **IV** (Table 2).

Bis(bromomagnesiodimethylsilylethynyl)dimethylsilane was reacted with 1,1-dichlorosilacyclopentane to obtain 1,1,4,4,7,7-hexamethyl-10,10-tetramethylene-1,4,7,10-tetrasilacyclododeca-2,5,8,11-tetrayne (**V**).

Macrocyclic ethynylsilanes **IV, V** are colorless high-melting (>200°C) crystals insoluble in nonpolar solvents. The yields, constants, and elemental analyses of all the synthesized compounds are listed in Table 1. The structures of the compounds were

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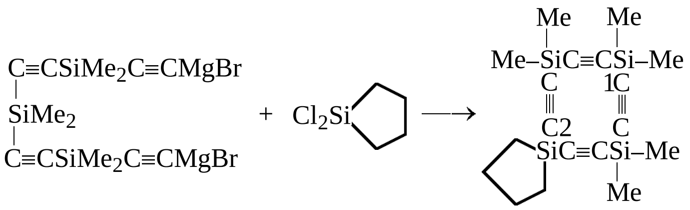


V

established based on their ^{1}H, ^{13}C, and ^{29}Si NMR (Table 2) and mass spectra (Table 1).

EXPERIMENTAL

The mass spectra were obtained on an LKB-2091 GC–MS system with direct inlet, ion sorce temperature 250°C, ionizing energy 60 eV. The NMR spectra were measured on a Jeol FX-90Q spectrometer for 15% solutions in $CDCl_3$, internal reference TMS.

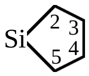
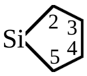
1,1-Dichlorosilacyclobutane was prepared by the reaction of trichloro(3-chloropropyl)silane with magnesium in ether. 1,1-Dichlorosilacyclopentane was

Table 1. Yields, elemental analyses, and physicochemical characteristics of the synthesized compounds

Comp. no.	Yield, %	bp, °C (p, mm)	d_4^{20}	n_D^{20}	Found, %			Formula	Calculated, %			m/e (I_{rel}, %)
					C	H	Si		C	H	Si	
I	65.0	46 (50)	0.8996	1.4860	69.82	6.68	23.37	C_7H_8Si	69.93	6.70	23.36	–
II	61.0	64 (25)	0.9066	1.4790	71.05	8.18	20.16	$C_8H_{10}Si$	71.57	7.51	20.92	–
IV[a]	8.5	[b]	–	–	66.57	7.43	25.30	$C_{24}H_{32}Si_4$	66.60	7.45	25.25	432 (100)
V	9.0	[c]	–	–	60.46	7.40	31.88	$C_{18}H_{26}Si_4$	60.94	7.39	31.67	354 (100)

[a] Contains an admixture of compound **III**, *m/e* 216 (13). [b] Decomposes at 370°C. [c] mp 237°C.

Table 2. ^{1}H, ^{13}C, and ^{29}Si NMR spectra of the synthesized compounds

Comp. no.	^{1}H NMR spectrum, δ, ppm		^{13}C NMR spectrum, δ_C, ppm			^{29}Si NMR spectrum, δ_{Si1}, ppm
		≡CH		SiC≡	≡CH	
I [a]		2.68	–	84.03	95.99	–35.83
II	0.90 s (2, 5)	2.52	13.57 s (2, 5)	84.81	95.78	–27.40
	1.54 s (3, 4)		26.67 s (3, 4)			
III	1.08 s (2, 5)	–	11.26 s (2, 5)	114.83	–	–29.67
	1.68 s (3, 4)		27.00 s (3, 4)			
IV	0.87 s (2, 5)	–	12.83 s (2, 5)	114.83	–	–29.67
	1.62 s (3, 4)		26.62 s (3, 4)			
V [b]	0.86 s (2, 5)	–	12.94 s (2, 5)	112.70	–	–30.00
				113.87		
	1.62 s (3, 4)		26.60 s (3, 4)	114.06		
				115.76		

[a] ^{1}H NMR spectrum, δ, ppm: 1.34 (2, 4) (J_{HH} 8.5 Hz), 2.21 t (3) (J_{HH} 8.5 Hz) (). ^{13}C NMR spectrum, δ_C, ppm: 15.4 s (2, 4), 18.1 s (3). [b] ^{1}H NMR spectrum, δ, ppm: 0.31 s (SiMe). ^{13}C NMR spectrum, δ_C, ppm: –0.85 s (SiMe). ^{29}Si NMR spectrum, δ_{Si}, ppm: –41.60 (Si).

prepared by the reaction of 1,4-dibromobutane with a mixture of magnesium with tetrachlorosilane. Their constants were consistent with published data [3, 4].

1,1-Diethynylsilacyclobutane (I). To 7.05 g of 1,1-dichlorosilacyclobutane in 50 ml of ether we added dropwise with stirring HC≡CMgBr obtained from 2.43 g of Mg, 10.9 g of EtBr, and acetylene in 100 ml of THF. The mixture was heated for 0.5 h and then decomposed with water and 5% HCl. Usual workup followed by drying with calcined $CaCl_2$, removal of the solvents in a water-jet-pump vacuum, and vacuum distillation of the residue gave 3.9 g (65%) of compound **I** (Table 1).

Compound **II** (Table 1) was prepared in a similar way.

1,1,4,4,7,7-Hexamethyl-10,10-tetramethylene-1,4,7,10-tetrasilacyclododeca-2,5,8,11-tetrayne (V). To 50 ml of ether we simultaneously added, dropwise with stirring, $Me_2Si(C{\equiv}CSiMe_2C{\equiv}CMgBr)_2$ (prepared from 2.43 g of Mg, 10.9 g of EtBr, and 13.6 g of $Me_2Si(C{\equiv}CSiMe_2C{\equiv}CH)_2$ in 75 ml of THF) and 7.6 g of 1,1-dichlorosilacyclopentane in 75 ml ether. Further workup was performed as described above. High-vacuum (10^{-4} mm) distillation gave 1.3 g (9.0%) of compound **V** (Table 1).

Compound **IV** was prepared in a similar way (Table 1). According to the mass spectrum, it contained an admixture of compound **III**.

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