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Cyclosilethynes Containing Exocyclic Cyclopentyl and Cyclohexyl Groups

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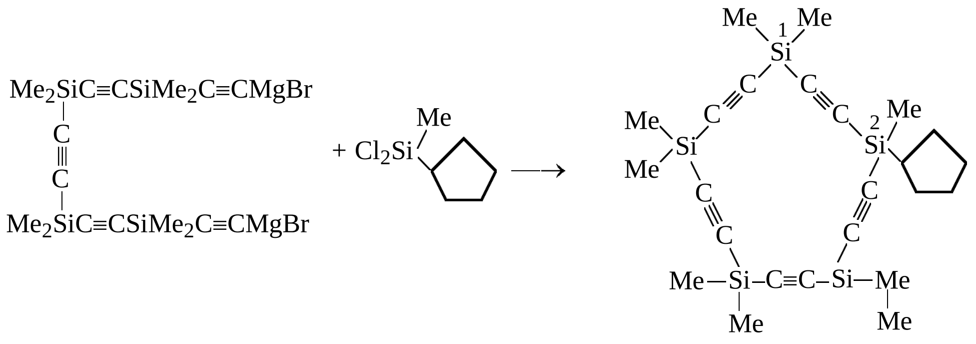
Abstract—The reaction of $BrMgC{\equiv}CSiMe_2C{\equiv}CSiMe_2C{\equiv}CSiMe_2C{\equiv}CSiMe_2C{\equiv}CMgBr$ with chloro(cyclopentyl)(methyl)silane in a large excess of THF gave 1-cyclopentyl-1,4,4,7,7,10,10,13,13-nonamethyl-1,4,7,10,13-pentasilacyclopentadeca-2,5,8,11,14-pentayne. Similarly, 1,10-di(cyclopentyl)- or 1,6-di(cyclopentylmethyl)-1,4,4,7,7,10,13,13,16,16-decamethyl-1,4,7,10,13,16-hexasilacyclooctadeca-2,5,8,11,14,17-hexaynes were synthesized from $BrMgC{\equiv}CSiMe_2C{\equiv}CSiMe_2C{\equiv}CMgBr$ and dichloro(cyclopentyl)methylsilane or dichloro(cyclopentylmethyl)(methyl)silane. Condensation of $Me_2Si(C{\equiv}CMgBr)_2$ with dichloro(cyclohexyl)methylsilane afforded 1,7-di(cyclohexyl)-1,4,4,7,10,10-hexamethyl-1,4,7,10-tetrasilacyclododeca-2,5,8,11-tetrayne.

Proceeding with the research into perorganylcyclosilethynes $[R_2SiC{\equiv}C]_n$ [1, 2] and coming nearer to the synthesis of macrocyclic propellanes, we have prepared new representatives of this class of compounds, containing cyclic peripheral groups. Thus, the reaction of bis[[(bromomagnesioethynyl)dimethylsilylethynyl]dimethylsilyl]ethyne with dichloro(cyclopentyl)methylsilane in THF under conditions of high dilution gave 1-cyclopentyl-1,4,4,7,7,10,10,13,13-nonamethyl-1,4,7,10,13-pentasilacyclopentadeca-2,5,8,11,14-pentayne (**I**).



I

Similarly, 1,10-dicyclopentyl)- or 1,6-di(cyclopentylmethyl)-1,4,4,7,7,10,13,13,16,16-decamethyl-1,4,7,10,13,16-hexasilacyclooctadeca-2,5,8,11,14,17-hexaynes (compounds **II** and **III**, respectively) were synthesized from bis[(bromomagnesioethynyl)dimethylsilyl)ethyne and dichloro(cyclopentyl)methylsilane or dichloro(cyclopentylmethyl)(methyl)silane.

Finally, the reaction of bis(bromomagnesioethynyl)dimethylsilane with dichloro(cyclohexyl)(methyl)silane under the same conditions resulted in preparation of 1,7-di(cyclohexyl)-1,4,4,7,10,10-hexamethyl-1,4,7,10-tetrasilacyclododeca-2,5,8,11-tetrayne (**IV**).

Compounds **I**–**IV** are colorless high-melting crys-

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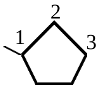
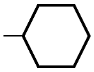
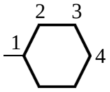
Table 1. Properties of compounds **I–IV**

Comp. no.	Yield, %	mp, °C	[*M*], *m/e* (I_{rel}, %)	Found, %			Formula	Calculated, %		
				C	H	Si		C	H	Si
I	10.2	167	474 (20)	62.12	8.02	29.91	$C_{24}H_{36}Si_5$	61.99	7.08	30.20
II	8.8	186	600 (16)	63.57	8.24	27.67	$C_{32}H_{48}Si_6$	63.93	8.05	28.02
III	8.5	173	628 (16)	64.25	8.43	26.74	$C_{34}H_{52}Si_6$	64.89	8.33	26.78
IV	4.4	193	464 (20)	67.14	8.88	23.53	$C_{26}H_{40}Si_4$	67.32	8.67	24.19

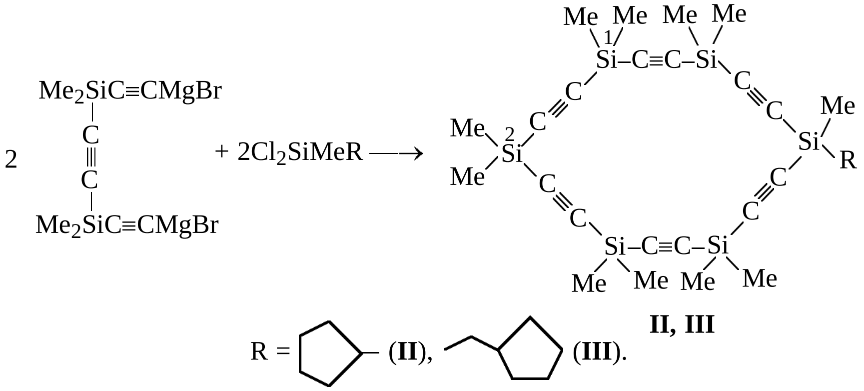
Table 2. ^{1}H, ^{13}C, and ^{29}Si NMR spectra of compounds **I–IV**

Comp. no.	^{1}H NMR spectrum, δ, ppm			^{13}C NMR spectrum, δ_C, ppm				^{29}Si NMR spectrum, δ_{Si}, ppm	
	Si^1CH_3	Si^2CH_3	$Si–C_5H_9$	Si^1CH_3	Si^2CH_3	C≡C		Si^1	Si^2
I	0.33	0.29	1.56	0.11	–2.56	110.07, 110.85, 111.11	25.01 (C^1), 27.22 (C^2), 27.93 (C^3)	–41.6	–36.8
II	0.33	0.28	1.58	0.00	–2.73	109.90, 110.68, 110.94	24.84 (C^1), 26.99 (C^2), 27.70 (C^3)	–41.4	–36.7
III	0.33	0.28	1.00 (CH_2Si), 1.57	0.02	–1.00	110.71, 110.92, 111.16	22.54 (CH_2Si), 24.93 (C^2), 35.33 (C^3), 35.56 (C^1)	–41.58	–41.55
IV[a]	0.34	0.33		–0.95	–4.88	112.55, 114.55		–41.92	–36.86

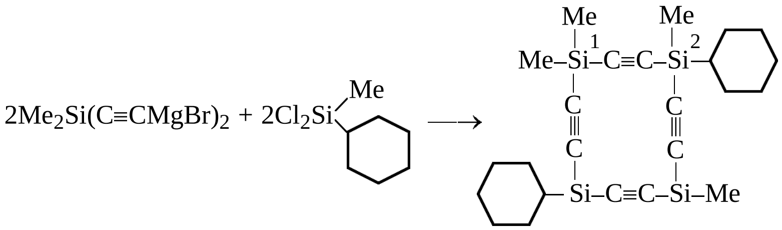
[a] Other signals: ^{1}H NMR spectrum, δ, ppm: 1.81 (); ^{13}C NMR spectrum, δ_C, ppm: 22.35 (C^1), 26.33 (C^4), 26.51 (C^3), 27.33 (C^2) ().

tals insoluble in nonpolar solvents. Their melting points, yields, and elemental analyses are listed in Table 1. The structure of the products was proved by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy (Table 2) and mass spectrometry (Table 1).

Dichloro(cyclohexyl)(methyl)silane was prepared by the addition of dichloro(methyl)silane to cyclo-



II, III



IV

hexene in the presence of H_2PtCl_6 under autopressure at 180°C, yield 45%, bp 68°C (2 mm Hg), d_4^{20} 1.1344, n_D^{20} 1.4695. The other starting materials were described earlier [3–5].

EXPERIMENTAL

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

1-Cyclopentyl-1,4,4,7,7,10,10,13,13-nonamethyl-1,4,7,10,13-pentasilacyclopentadeca-2,5,8,11,14-pentayne (I). To 50 ml of ether we added with stirring simultaneously from two dropping funnels the Iotsich reagent prepared from 0.96 g of Mg and 4.36 g of EtBr, $HC\equiv CSiMe_2C\equiv CSiMe_2C\equiv CSiMe_2C\equiv CSiMe2C\equiv CH$, 7.8 g, in 50 ml of THF, and 3.68 g of dichloro(cyclopentyl)methylsilane in 50 ml of ether. The mixture was stirred for 1 h and decomposed with water and 5% HCl. Conventional workup, drying over calcined $CaCl_2$, removal of the solvents, and high-vacuum distillation (10^{-4} mm Hg) gave 0.95 g (10%) of compound **I** (Table 1). Compounds **II**–**IV** were prepared in a similar way (Table 1).

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