Russian Journal of General Chemistry, Vol. 74, No. 12, 2004, pp. 1895–1899. Translated from Zhurnal Obshchei Khimii, Vol. 74, No. 12, 2004, pp. 2007–2011.
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Hydrosilylation of Cyclohexene, 1-Methylcyclohexene, and Isopropylidenecyclohexane

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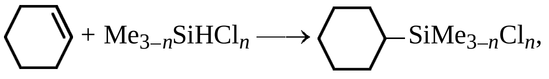
Received February 12, 2003

Abstract—Hydrosilylation of cyclohexene and isopropylidenecyclohexane with chloro(methyl)silanes $Me_{3-n}SiHCl_n$ (n = 1–3) gives rise to cyclohexyl- and chloro(2-cyclohexylpropyl)methylsilanes. Hydrosilylation of 1-methylcyclohexene with chlorodimethylsilane (n = 1) occurs anomalously and involves double-bond migration to form a mixture of seven compounds: the *cis* and *trans* isomers of 2-, 3-, 4-chlorodimethyl(methylcyclohexyl)silanes and chlorodimethyl(cyclohexylmethyl)silane. Chlorodimethylsilane (n = 2) adds to 1-methylcyclohexene to form a mixture of the *cis* and *trans* isomers of dichloro(methyl)(2-methylcyclohexyl)silane and dichloro(cyclohexylmethyl)methylsilane. With trichlorosilane (n = 3), no other products than trichloro(cyclohexylmethyl)silane are formed. The hydrosilylation products were reacted with ethynylmagnesium bromide to synthesize the corresponding ethynyl derivatives.

Hydrosilylation of cycloalkenes and alkylidenecycloalkenes has poorly been studied [1–5]. It is known that cyclopentene and 1-methylcyclopentene react with hydrosilanes to form respectively chloro(cyclopentyl)methyl- and chloro(cyclopentylmethyl)methylsilanes, which were then converted into ethynyl derivatives [6, 7].

Petrov *et al.* [8] showed that dichloro(methyl)silane adds to cyclohexene in the presence of platinum on carbon (0.5%) at 220°C to form dichloro(cyclohexyl)methylsilane in a low (6%) yield [8]. The nickel complex catalyst $Ni(PPhMe_2)Cl_2$ is more active: Dichloro(methyl)silane adds to cyclohexene (120°C, 20 h) to give a mixture of dichloro(cyclohexyl)methylsilane (34%) and chloro(cyclohexyl)methylsilane (41%) [9]. The addition of dichloro(methyl)silane to 1-methylcyclohexene in the presence of H_2PtCl_6 gives rise to chloro(cyclohexylmethyl)methylsilane [10]. The reactions of trichlorosilane with 1- or 3-methylcyclohexene provide trichloro(cyclohexylmethyl)silane [11].

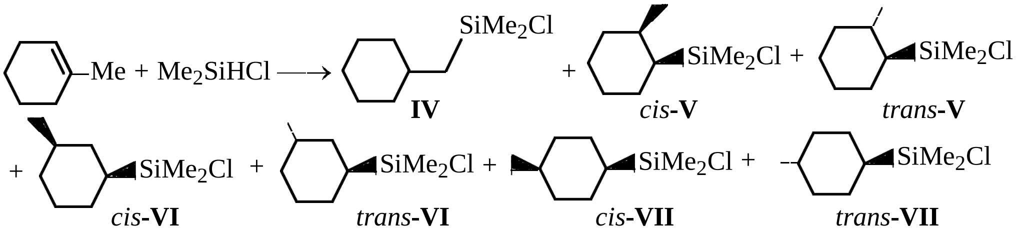
We performed a systematic study of hydrosilylation of cyclohexene, 1-methylcyclohexene, and isopropylidenecyclohexane with chlorodimethyl-, dichloro(methyl)-, and trichlorosilanes of the general formula $Me_{3-n}SiHCl_n$ (n = 1–3) in the presence of H_2PtCl_6. The reaction occurs at 180°C. The yields of hydrosilylation products are 15–30, 40–50, and 45–60%, respectively. The reactions of cyclohexene with $Me_{3-n}SiHCl_n$ at all n afford chloro(cyclohexyl)methylsilanes.



I–III

n = 1 (**I**), 2 (**II**), 3 (**III**).

1-Methylcyclohexene is hydrosilylated regio- and stereoselectively. The structures of the adducts are determined by the number of chlorine atoms (n) in the hydrosilylating agent. Thus chlorodimethylsilane forms a mixture of seven hydrosilylation products: chloro(cyclohexylmethyl)dimethylsilane (**IV**), *cis*- and *trans*-chloro(2-methylcyclohexyl)dimethylsilane (**V**), *cis*- and *trans*-chloro(3-methylcyclohexyl)dimethylsilane (**VI**), and *cis*- and *trans*-chloro(4-methylcyclohexyl)dimethylsilane (**VII**).



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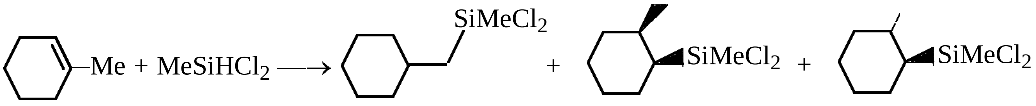
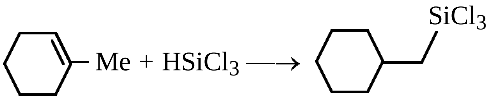
The reaction of dichloro(methyl)silane with 1-methylcyclohexene gave dichloro(cyclohexylmethyl)methylsilane (**VIII**) and *cis*- and *trans*- dichloro-(2-methylcyclohexyl)methylsilanes (**IX**).



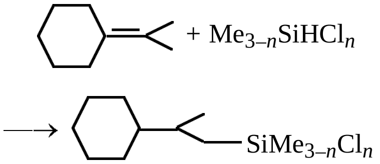
VIII *cis*-**IX** *trans*-**IX**

Trichlorosilane reacts with 1-methylcyclohexene to form exclusively trichloro(cyclohexylmethyl)silane (**X**), yield 60%.



X

The reaction of isopropylidenecyclohexane with all the hydrosilylating agents gives chloro(2-cyclohexylpropyl)methylsilanes **XI**–**XIII**.

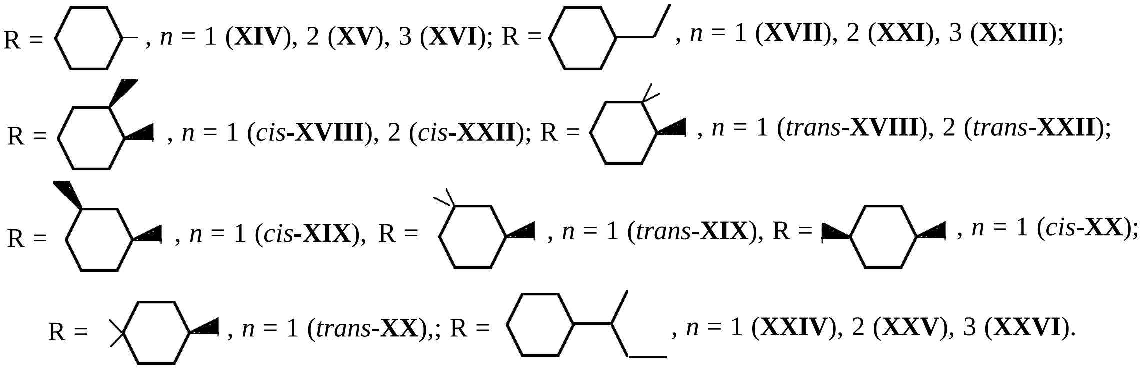


XI–**XIII**

Compounds **I**–**XIII** were reacted with ethynylmagnesium bromide in THF to synthesize ethynyl derivatives **XIV**–**XXVI**.

$$\text{R–SiMe}_{3-n}\text{Cl}_n + n\text{BrMgC≡CH} \longrightarrow \text{R–SiMe}_{3-n}(\text{C≡CH})_n,$$

XIV–**XXVI**



(Cyclohexylmethyl)triethynylsilane (**XXIII**) is a colorless substance (mp 66°C), and the other ethynyl derivatives **XIV**–**XXII** and **XIV**–**XXVI** are colorless liquids distillable in a vacuum and stable to handling. The yields and constants of hydrosilylation products **I**–**XIII** and their ethynyl derivatives **XIV**–**XXVI** are listed in Tables 1 and 2, respectively. The structures of compounds **XIV**–**XXVI** are established by ^{1}H, ^{13}C, and ^{29}Si spectroscopy (Table 3).

EXPERIMENTAL

The NMR spectra were recorded on a Bruker DPX-400 spectrometer (400 MHz) for 15% solutions in CDCl$_3$, internal reference HMDS.

Trichloro(cyclohexylmethyl)silane (X). A mixture of 9.6 g of 1-methylcyclohexene, 13.55 g of trichlorosilane, and 0.02 ml of H$_2$PtCl$_6$ in 2-propanol was

Table 1. Yields and constants of chlorosilanes **I**–**XIII**

Comp. no.	Yield, %	bp, °C (p, mm Hg)	d_4^{20}	n_D^{20}
I	17	74 (10)	0.9853	1.4525
II	46	68 (2)	1.1344	1.4695
III	51	67 (1)	1.2469	1.4755
IV–**VII**	21	80 (4)	0.9721	1.4508
VIII, IX	51	83 (3)	1.0759	1.4735
X	60	85 (4)	1.1765	1.4755
XI	32	99 (1)	0.9528	1.4640
XII	41	110 (3)	1.0569	1.4740
XIII	46	115 (4)	1.1896	1.4775

heated (5 h at 120°C and 5 h at 180°C) in an ampule housed in an autoclave and then distilled in a vacuum. Yield 13.8 g (60%) (Table 1).

Compounds **I**–**IX** and **XI**–**XIII** were prepared in a similar way (Table 1).

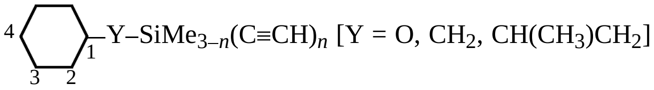
(Cyclohexylmethyl)triethynylsilane (XXIII). To 11.6 g of compound **X** in 50 ml of ether we added dropwise with stirring ethynylmagnesium bromide prepared from 3.65 g of Mg, 16.5 g of EtBr, and cetylene in 120 ml of THF. After 30-min stirring, the mixture was decomposed with water and 5% HCl, subjected to usual workup, dried with $CaCl_2$, the solvents were removed at reduced pressure (water-jet vacuum), and the residue was sublimed in a vacuum

Table 2. Yields, constants, and elemental analyses of ethynylsilanes **XIV**–**XXVI**

Comp. no.	Yield, %	bp, °C (p, mm Hg)	d_4^{20}	n_D^{20}	Found, %			Formula	Calculated, %		
					C	H	Si		C	H	Si
XIV	67	83 (10)	0.8762	1.4550	71.73	10.68	17.20	$C_{10}H_{18}Si$	72.20	10.90	16.89
XV	65	80 (4)	0.9187	1.4760	74.15	9.33	16.01	$C_{11}H_{16}Si$	74.92	9.15	15.33
XVI	64	85 (1)	0.9310	1.4895	77.17	7.78	15.29	$C_{12}H_{14}Si$	77.34	7.57	15.08
XVII–**XX**	71	70 (10)	0.8846	1.4465	72.80	10.92	16.02	$C_{11}H_{20}Si$	73.25	11.18	15.57
XXI, XXII	66	55 (1)	0.9034	1.4730	75.78	9.54	14.59	$C_{12}H_{18}Si$	75.71	9.53	14.75
XXIII	63	66[a]	–	–	78.16	8.00	13.99	$C_{13}H_{16}Si$	77.92	8.05	14.02
XXIV	67	95 (1)	0.8664	1.4645	74.97	11.72	13.79	$C_{13}H_{24}Si$	74.91	11.61	13.48
XXV	69	103 (1)	0.8958	1.4765	75.68	10.15	12.71	$C_{14}H_{22}Si$	76.98	10.15	12.86
XXVI	65	110 (1)	0.9245	1.4860	77.78	9.14	11.73	$C_{15}H_{20}Si$	78.88	8.82	12.30

[a] Melting point.

Table 3. 1H, ^{13}C, and ^{29}Si NMR parameters of compounds **XIV**–**XXVI**



–Y–$SiMe_{3-n}(C{\equiv}CH)_n$ [Y = O, CH_2, $CH(CH_3)CH_2$]

Comp. no.	^{1}H NMR spectrum, δ, ppm			^{13}C NMR spectrum, δ_C, ppm				^{29}Si NMR spectrum, δ_{Si}, ppm
	SiMe	R	≡CH	SiMe	R	≡CH	SiC≡	
XIV	0.07 s	0.63 m, 1.16 m, 1.69 m	2.29	–3.95	25.38 (C^1), 26.76 (C^4), 27.02 (C^3), 27.81 (C^2)	93.64	88.56	–13.40
XV	0.28 s	0.80 m, 1.23 m, 1.76 m	2.41	–3.65	26.19 (C^1), 26.31 (C^4), 26.79 (C^3), 27.76 (C^2)	95.19	84.96	–34.21
XVI	–	0.92 m, 1.28 m, 1.80 m	2.54	–	25.27 (C^1), 26.22 (C^4), 26.69 (C^3), $^{27}.^{52}$ (C^2)	96.24	81.63	–60.09
XVII–	0.07 s,	0.61 d ($SiCH_2$), 0.86 d.d.d	2.29,	–0.88	22.68 ($SiCH_2$), 26.21	92.03,	89.75,	–19.50, –19.24,

Table 3. (Contd.)

Comp. no.	^{1}H NMR spectrum, δ, ppm			^{13}C NMR spectrum, δ_C, ppm				^{29}Si NMR spectrum, δ_{Si}, ppm
	SiMe	R	≡CH	SiMe	R	≡CH	SiC≡	
XX	0.10 s, 0.12 s, 0.16 s	($4H_a$), 0.96 q.t ($4H_a$), 1.04 d.t ($3H_a$), 1.18 d.t ($4H_e$), 1.28 m ($3H_e$)	2.30, 2.34, 2.35		(C^4), 26.48 (C^3), 35.48 (C^1), 36.58 (C^2), 35.89 (C^1), 37.74 (C^2)	93.26, 93.48, 93.69	89.85	–19.01, –17.47, –16.75, –16.48
XXI	0.35 s	0.75 d ($SiCH_2$), 0.98 d.d.d ($2.6H_a$)	2.41	–0.66	23.14 ($SiCH_2$), 26.25	94.89	86.11	–38.25
XXII	–	1.18 q.t ($4H_a$), 1.25 q.t ($3.5H_a$), 1.60 m ($4H_e$), 1.66 d.t ($3.5H_e$), 1.70 m ($1H_a$), 1.82 m ($2.6H_e$)	2.42, 2.43	–	(C^4), 26.49 (C^4), 26.68 (C^3), 26.84 (C^3), 33.86 (C^1), 34.15 (C^1), 35.15 (C^1), 35.34 (C^2), 35.48 (C^2), 36.40 (C^2)	95.07, 96.24		–34.29, –33.89
XXIII	–	0.90 d ($SiCH_2$), 1.04 d.d.d ($2.6H_a$), 1.65 q.t ($4H_a$), 1.27 q.t ($3H_a$), 1.63 m ($4H_e$), 1.67 m ($1H_e$), 1.71 m ($3H_e$), 1.86 d.q ($2H_e$)	2.55	–	23.93 ($SiCH_2$), 25.96 (C^4), 26.19 (C^3), 33.67 (C^1), 35.96 (C^2)	95.60	82.68	–63.97
XXIV	0.17 s	0.49 d.d [*A* part of the *AB* system of $SiCH_2$, $^2J_{AB}$ 14.69, $^3J(H_ACCH)$ 9.72 Hz], 0.76 d.d [*B* part of the *AB* system of $SiCH_2$, $^2J_{AB}$ 14.69, $^3J(H_BCCH)$ 4.3 Hz], 0.90 d (CH_3, *J* 6.8 Hz), 0.99 m ($2H_a$), 1.18 m ($3H_a$, C*H*, $1H_a$), 1.62 m ($4H_a$, $4H_e$, $3H_e$), 1.72 d.t ($2H_e$)	2.34	–0.85	19.21 (CH_3), 21.15 ($SiCH_2$), 26.92 (C^4), 27.05 (C^3), 34.61 (C^1) [30.36 (C^2), 28.81 (C^2)] (nonequiv.), 45.39 (*C*HCH_3)	93.60	89.99	–15.74
XXV	0.34 s	0.63, 0.90 [$SiCH_2$, *AB* spectrum, $^2J_{AB}$ 14.55, $^3J(H_ACCH)$ 9.78, $^3J(H_BCCH)$ 4.5 Hz], 0.95 d (CH_3CH), 0.99 m ($2H_a$), 1.3–0.98 ($1H_a$, $3H_a$, $2H_a$, CH), 1.79–1.56 ($4H_a$, $4H_e$, $3H_e$, $2H_e$)	2.45	–0.86	18.92 (CH_3), 20.69 ($SiCH_2$), 26.74 (C^4), 26.89 (C^3), 34.38 (C^1) [30.25 (C^2), 28.62 (C^2)] (nonequiv.) 44.99 (*C*HCH_3)	94.84	86.06	–37.10
XXVI	–	0.77, 0.88 ($SiCH_2$), 0.99 d (*C*H_3CH), 1.3– 0.98 ($1H_a$, $3H_a$, $2H_a$, CH), 1.79–1.56 ($4H_a$, $4H_e$, $3H_e$, $2H_e$)	2.55	–	18.74 (CH_3), 20.80 ($SiCH_2$), 26.63 (C^4), 26.83 (C^3), 34.14 (C^1) [30.21 (C^2), 28.54 (C^2)] (nonequiv.), 44.74 (*C*HCH_3)	95.87	82.79	–62.86

(1 mm Hg) on a boiling water bath to isolate 6.6 g (63%) of compound **XXIII** (Table 2).

Compounds **XIV**–**XXII** and **XXIV**–**XXVI** were prepared in a similar way (Table 2).

ACKNOWLEDGMENTS

The work was financially supported by the Russian Foundation for Basic Research (project no. 00-15-97395).

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