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Table 1

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Abstract

Full Text

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SYNTHESIS OF CERTAIN ALKYLHALOSILANES AND SILICON HYDROCARBONS

The present communication is a continuation of our work on the study of reactions for the formation of organosilicon compounds from unsaturated hydrocarbons and silicon compounds containing the Si–H bond ([1–3]). In this work, the addition reactions of trichlorosilane and tribromosilane to isoamylene, 1-nonene, and 1-decene were studied. The addition reactions of tribromosilane were carried out under conditions analogous to those for the addition of trichlorosilane.

Table 1

Experiment no.	Formula	B.p., °C/mm Hg	Reaction temperature, °C	Duration of experiment, h	Yield, %
1	*u*-$C_5H_{11}SiCl_3$	147.5–149/754	40	15	5.1
1	*u*-$C_5H_{11}SiCl_3$	147.5–149/754	100	3.5	11.7*
2	*u*-$C_5H_{11}SiBr_3$	196–198/751	40	15	8.5
3	$C_9H_{19}SiCl_3$	121–123/5	85	30	60.9
4	$C_9H_{19}SiBr_3$	154–157/5	85	30	79.4
5	$C_{10}H_{21}SiCl_3$	133–137/5	100	20	62.7
6	$C_{10}H_{21}SiBr_3$	167–168/5	100	20	74.0
7	$C_{10}H_{33}SiCl_3$	208–210/5	60	14	29.7
8	$C_9H_{19}SiCH_3Cl_2$	115–117/5	80	36	22.2
9	$C_{10}H_{21}SiCH_3Cl_2$	126–129/5	80	40	38

* The experiment was carried out in an autoclave under a pressure of 100 atm.

It is seen from Table 1 that both tribromosilane and trichlorosilane add to 1-nonene and 1-decene in the presence of benzoyl peroxide with high yields

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(60–70%), and to isoamylene with low yields (5–8%). The reduced yields of isoamyltrichlorosilane and isoamyltribromosilane may have depended on the reaction temperature, owing to the low boiling point of isoamylene.

In order to eliminate the influence of temperature, we carried out an experiment on the addition of trichlorosilane to isoamylene under pressure, at 100° in the presence of benzoyl peroxide. The yield of isoamyltrichlorosilane, as is evident from Table 1, increased only slightly. Comparing the yields of the products of addition of tribromosilane and trichlorosilane to olefinic hydrocarbons, one may note the somewhat greater activity of the bromide.

Experiments carried out by us on the addition of methyldichlorosilane to 1-nonene and 1-decene showed that the reactions proceed with considerably lower yields in comparison with the addition of trichlorosilane to the same hydrocarbons.

On the basis of the alkylhalosilanes obtained, silicon hydrocarbons were synthesized; their properties are given in Table 2.

Table 2

Experiment No.	Formula	B.p., °C/mm Hg	d_4^{20}	n_D^{20}	MR_D found	MR_D calc.
1	n-$C_5H_{11}Si(CH_3)_3$	133–134/751	0.7295	1.4064	48.63	48.8
2	$C_9H_{19}Si(CH_3)_3$	83–85/5	0.7801	1.4321	67.32	66.52
3	$C_9H_{19}SiCH_3(C_4H_9)_2$	160–162/5	0.8115	1.4521	94.76	95.10
4	$C_{10}H_{21}SiCH_3(C_4H_9)_2$	162–164/5	0.8121	1.4529	99.13	99.73
5	$C_7H_{15}Si(C_4H_9)_3$	144–146/2	0.8053	1.4508	99.75	99.73
6	$C_9H_{19}Si(C_4H_9)_3$	166–168/5	0.8138	1.4532	108.77	108.99
7	$C_{10}H_{21}Si(C_4H_9)_3$	176–178/5	0.8139	1.4538	113.44	113.62
8	$C_{16}H_{33}Si(C_4H_9)_3$	219–233/5	0.8313	1.4609	140.17	141.40

* Literature data for n-$C_5H_{11}Si(CH_3)_3$: b.p. 131.5–132.5°/758.6; d_4^{20} 0.7281; n_D^{20} 1.4057.

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Experimental Part

Addition of silicon compounds containing an Si–H bond to olefin hydrocarbons

1. **Isoamyltribromosilane.** From 30 g of isoamylene (2-methylbutene-3) and 42 g of technical-grade tribromosilane (b.p. 108–120°), in the presence of 3 g of benzoyl peroxide, 4.4 g of isoamyltribromosilane was obtained (yield 8.5%); b.p. 196–198°/751 mm.

Found, %: Br 70.01; 70.73
$C_5H_{11}SiBr_3$. Calculated, %: Br 70.79

2. **Isoamyltrichlorosilane.** a) From 70 g of isoamylene and 136 g of trichlorosilane, in the presence of 5 g of benzoyl peroxide, 13.3 g (yield 5.1%) of isoamyltrichlorosilane was obtained.

b) In an autoclave, a mixture of 41.5 g of isoamylene and 81.5 g of trichlorosilane was heated in the presence of 2 g of benzoyl peroxide at 100° and a pressure of 100 atm.; 13.6 g (yield 11.14%) of isoamyltrichlorosilane was obtained; b.p. 147°/754 mm.

Found, %: Cl 52.15; 51.56
$C_5H_{11}SiCl_2$. Calculated, %: Cl 51.77

3. **Nonyltribromosilane.** From 15 g of nonene-1 and 32 g of technical-grade tribromosilane (b.p. 110–120°), in the presence of 4 g of benzoyl peroxide, 36 g (yield 79.4%) of nonyltribromosilane was obtained; b.p. 154–157°/5 mm; d_4^{20} 1.4590; n_D^{20} 1.4764; MR_D 76.40, calc. 75.21.

Found, %: Br 59.91; 60.22;
$C_9H_{19}SiBr_3$. Calculated, %: Br 60.79

4. **Nonyltrichlorosilane.** From 84 g of nonene-1 and 90 g of trichlorosilane, in the presence of 5 g of benzoyl peroxide, 106 g (yield 60.99) of nonyltrichlorosilane was obtained; b.p. 121–123°/5 mm; d_4^{20} 1.0645; n_D^{20} 1.4498; MR_D 66.05, calc. 66.25.

Found, %: Cl 40.42; 40.46;
$C_9H_{19}SiCl_3$. Calculated, %: Cl 40.72.

5. **Decyltribromosilane.** From 17 g of decene-1 and 30 g of technical-grade tribromosilane, in the presence of 3 g of benzoyl peroxide, 33 g (yield 74%) of decyltribromosilane was obtained; b.p. 166–169°/5 mm; d_4^{20} 1.3896; n_D^{20} 1.4692; MR_D 80.27, calc. 79.84.

Found, %: Br 57.94; 58.78;
$C_{10}H_{21}SiBr_3$. Calculated, %: Br 58.69.

6. **Decyltrichlorosilane.** From 80 g of decene-1 and 80 g of trichlorosilane, in the presence of 5 g of benzoyl peroxide, 92 g (yield 62.7%) of decyl-

trichlorosilane was obtained; b.p. 137°/10 mm; d_4^{20} 1.0540; n_D^{20} 1.4528; MR_D 70.95; calc. 70.84.

Found, %: Cl 38.81; 38.41
$C_{10}H_{21}SiCl_3$. Calculated, %: Cl 38.66

Literature data (4) for $C_{10}H_{21}SiCl_3$: b.p. 189°/84 mm.

7. **Hexadecyltrichlorosilane.** From 28.7 g of hexadecene-1 and 93 g of trichlorosilane, in the presence of 5 g of benzoyl peroxide, 13.3 g (yield 29.7%) of hexadecyltrichlorosilane was obtained; b.p. 208°/5 mm.

Found, %: Cl 29.52; 29.64
$C_{16}H_{33}SiCl_3$. Calculated, %: Cl 29.62

Literature data (5) for $C_{16}H_{33}SiCl_3$: b.p. 194–196°/7.5 mm.

8. **Nonylmethyldichlorosilane.** From 21 g of nonene-1 and 110 g of methyldichlorosilane, in the presence of 5 g of benzoyl peroxide, 8.5 g (yield 21.2%) of nonylmethyldichlorosilane was obtained; b.p. 115–117°/5 mm; d_4^{20} 0.9931; n_D^{20} 1.4548; MR_D 65.91, calc. 66.58.

Found, %: Cl 28.47; 28.55
$C_{10}H_{22}SiCl_2$. Calculated, %: Cl 29.21

9. **Decylmethyldichlorosilane.** From 24 g of decene-1 and 100 g of methyldichlorosilane, in the presence of 5 g of benzoyl peroxide, 15.7 g (yield 38%) of decylmethyldichlorosilane was obtained; b.p. 126–129°/5 mm; d_4^{20} 0.9859; n_D^{20} 1.4542; MR_D 70.17, calc. 71.21.

Found, %: Cl 27.75; 27.82;
$C_{11}H_{24}SiCl_2$. Calculated, %: Cl 27.84.

Preparation of Silicon Hydrocarbons

Silicon hydrocarbons were obtained with the aid of organolithium compounds. To a previously prepared ethereal solution of the organolithium compound, the organosilicon halogen derivative was added. The reaction mixture was heated at the boiling point of ether for 10 h. The isolated silicon hydrocarbons were treated by shaking with concentrated sulfuric acid and by distillation over metallic sodium. The principal properties of the silicon hydrocarbons obtained by us are given in Table 2.

1. **Isoamyltrimethylsilane.** From 7 g of lithium, 70 g of methyl iodide, and 18 g of isoamyltrichlorosilane, 11.7 g (yield 96.3%) of isoamyltrimethylsilane was obtained; b.p. 133–134°/751 mm;

Found, %: C 66.64; 66.61; H 14.04; 13.98
$C_8H_{20}Si$. Calculated, %: C 66.58; H 13.37

2. **Nonyltrimethylsilane.** From 4.5 g of lithium, 45 g of methyl iodide, and 16 g of nonyltribromosilane, 7.2 g (yield 88.8%) of nonyltrimethylsilane was obtained; b.p. 83–85°/5 mm;

Found, %: C 72.54; 72.59; H 13.92; 13.82
$C_{12}H_{28}Si$. Calculated, %: C 71.91; H 14.08

3. **Nonylmethyldibutylsilane.** From 6 g of lithium, 55 g of butyl bromide, and 5 g of nonylmethyldichlorosilane, 4.2 g (yield 71.2%) of nonylmethylbutylsilane was obtained; b.p. 160–162°/5 mm;

Found, %: C 76.88; 76.85; H 13.89; 13.87
$C_{18}H_{40}Si$. Calculated, %: C 75.98; H 14.17

4. **Decylmethyldibutylsilane.** From 4 g of lithium, 50 g of butyl bromide, and 7 g of decylmethyldichlorosilane, 5.2 g (yield 63.4%) of decylmethyldibutylsilane was obtained; b.p. 162-164°/5 mm;

$C_{19}H_{42}Si$.	Found, %:	C 76.47; 76.30; H 14.02; 14.07
	Calculated, %:	C 76.42; H 14.18

5. **Heptyltributylsilane.** From 14 g of lithium, 140 g of butyl bromide, and 74 g of heptyltribromosilane, 42 g (yield 70%) of heptyltributylsilane was obtained; b.p. 144-146°/2 mm.

$C_{19}H_{42}Si$.	Found, %:	C 76.22; 76.24; H 14.16; 14.17
	Calculated, %:	C 76.42; H 14.18

6. **Nonyltributylsilane.** From 15 g of lithium, 140 g of butyl bromide, and 50 g of nonyltrichlorosilane, 42.4 g (yield 68%) of nonyltributylsilane was obtained; b.p. 167-168°/5 mm;

$C_{21}H_{46}Si$.	Found, %:	C 77.06; 77.10; H 14.46; 14.32
	Calculated, %:	C 77.22; H 14.37

7. **Decyltributylsilane.** From 9 g of lithium, 90 g of butyl bromide, and 30 g of decyltrichlorosilane, 25.7 g (yield 67%) of decyltributylsilane was obtained; b.p. 176-178°/5 mm.

$C_{22}H_{48}Si$.	Found, %:	C 77.59; 77.56; H 13.94; 14.01
	Calculated, %:	C 77.56; H 14.20

8. **Hexadecyltributylsilane.** From 4 g of lithium, 42 g of butyl bromide, and 9 g of hexadecyltrichlorosilane, 6.4 g (yield 60.4%) of hexadecyltributylsilane was obtained; b.p. 219-223°/5 mm.

$C_{28}H_{60}Si$.	Found, %:	C 79.03; 78.95; H 14.09; 14.12
	Calculated, %:	C 79.24; H 14.15

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