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Abstract

Full Text

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Corresponding Member of the Academy of Sciences of the USSR N. S. NAMETKIN, T. I. CHERNYSHEVA,
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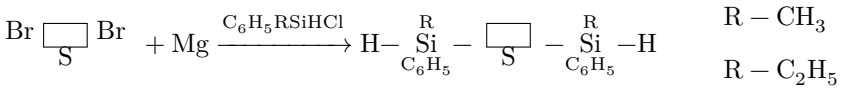
ORGANOSILICON COMPOUNDS

WITH THIENYLENECARBON CHAIN UNITS

Continuing investigations in the field of studying the addition reaction of hydrosilanes to various unsaturated compounds, and also for the purpose of synthesizing organosilicon compounds containing thienylenecarbon units in the main chain, we carried out the synthesis of a series of dihydridethienylenesilanes and studied some of their reactions. Dihydridethienylenesilanes were obtained by an organomagnesium synthesis, starting from 2,5-dibromothiophene and chlorohydridosilane, according to the following scheme:



The properties of the compounds obtained are given in Table 1. It seemed of interest to us, using the addition reaction of the dihydridosilanes obtained to alkenylsilanes, to obtain organosilicon compounds containing a thienylenecarbon bridge:

Table 1

Hydridethienylenesilanes

Compound	Boiling temp., °C/mm Hg	d_4^{20}	n_D^{20}	MRD found	MRD calculated	Molecular weight found	Molecular weight calculated	Yield, %
H—Si(CH_3)(C_6H_5)—[2,5-thienylene]—Si(CH_3)(C_6H_5)—H	205/2	1.085	1.5980	103.37	103.37	338.0	324.4	55.6
H—Si(C_2H_5)(C_6H_5)—[2,5-thienylene]—Si(C_2H_5)(C_6H_5)—H	230/2	1.059	1.5892	112.39	112.39	320.0	352.5	33.0

—Si—C_x—Si— [S] —Si—C_x—Si—

The addition reaction of hydridethienylenesilanes to alkenylsilanes was carried out at atmospheric pressure, using chloroplatinic acid as catalyst (0.1 *N* solution of $H_2PtCl_6 \cdot 6H_2O$ in absolute isopropyl alcohol), with a hydrosilane-to-alkenylsilane ratio of 1 : 3.

Thus, the addition of 2,5-di-(methylphenylsilyl)-thiophene to trimethylvinylsilane and to trimethylallylsilane was carried out; 2,5-di-(ethylphenylsilyl)-thiophene adds to triethylvinylsilane, triethylallylsilane

and trimethylallylsilane. In all cases addition occurred at both Si—H bonds of hydridthienylenesilane:

$$\mathrm{H{-}Si(R)(C_6H_5){-}C_4H_2S{-}Si(R)(C_6H_5){-}H} + \begin{matrix} \xrightarrow{\mathrm{R'_3SiCH{=}CH_2}} \\ \xrightarrow{\mathrm{R'_3SiCH_2CH{=}CH_2}} \end{matrix}$$

$$\longrightarrow \mathrm{R'_3SiCH_2CH_2Si(R)(C_6H_5){-}C_4H_2S{-}Si(R)(C_6H_5)CH_2CH_2SiR_3}$$

$$\longrightarrow \mathrm{R'_3SiCH_2CH_2CH_2Si(R)(C_6H_5){-}C_4H_2S{-}Si(R)(C_6H_5)CH_2CH_2CH_2SiR_3}$$

It was shown earlier that, in the addition of dihydriddiphenylsilanes to allyl derivatives of silicon, more severe conditions are required than in their addition to vinyl derivatives of silicon ([1]). Dihydridthienylenesilanes add in high yields both to vinyl and to allyl derivatives of silicon. The addition products are viscous oils. Some physicochemical properties of the addition products obtained are given in Table 2.

Table 2

Compound	b.p., °C/mm Hg	d_4^{20}	n_D^{20}	MR_D, found	MR_D, calculated	Molecular weight, found	Molecular weight, calculated	Yield, %
$(CH_3)_3SiCH_2CH_2Si(CH_3)(C_6H_5){-}C_4H_2S{-}Si(CH_3)(C_6H_5)CH_2CH_2Si(CH_3)_3$	258–260/2	0.9944	1.5489	167.96	168.40	523; 521	524	76.7
$(C_2H_5)_3SiCH_2CH_2Si(C_2H_5)(C_6H_5){-}C_4H_2S{-}Si(C_2H_5)(C_6H_5)CH_2CH_2Si(C_2H_5)_3$	307–310/2	0.9938	1.5370	205.10	204.49	631; 636	653	50.3
$(CH_3)_3SiCH_2CH_2CH_2Si(CH_3)(C_6H_5){-}C_4H_2S{-}Si(CH_3)(C_6H_5)CH_2CH_2CH_2Si(CH_3)_3$	277–280/2	0.9792	1.5415	177.57	177.67	550; 554	552	57

Compound	b.p., °C/mm Hg	d_4^{20}	n_D^{20}	MR_D, found	MR_D, calculated	Molecular weight, found	Molecular weight, calculated	Yield, %
$(CH_3)_3SiCH_2CH_2Si(C_2H_5)(C_6H_5){-}C_4H_2S{-}Si(C_2H_5)(C_6H_5)CH_2CH_2Si(CH_3)_3$	280–285/2	0.9952	1.5430	184	186	576; 574	581	54.5
$(C_2H_5)_3SiCH_2CH_2Si(C_2H_5)(C_6H_5){-}C_4H_2S{-}Si(C_2H_5)(C_6H_5)CH_2CH_2Si(C_2H_5)_3$	325–330					665; 663	665.1	69.6

To confirm the mode of addition, IR spectra of the addition products were recorded.

The spectra were recorded on a UR-10 spectrograph in the region 700–2900 cm^{-1}. On the basis of the absorption bands (1135, 1055 cm^{-1}), characteristic of the structural group

$$-Si-CH_2-CH_2-Si-$$

in the products of addition of dihydridthienylenesilanes to vinylsilanes, and of the absorption bands (1140–1142; 900–

908 cm^{-1}), characteristic of the structural group

$$-Si-CH_2-CH_2-CH_2-Si-$$

in the products of addition of dihydridethienylenesilanes to allylsilanes, it may be asserted that the addition of dihydridethienylenesilanes to alkenylsilanes proceeds according to Farmer' s rule (i.e., silicon adds to the terminal carbon atom).

Experimental Part

Preparation of dihydridethienylenesilanes

2,5-Di-(methylphenylsilyl)thiophene. To 2,5-dimagnesiobromothiophene, prepared from 72.6 g (0.3 mole) of 2,5-dibromothiophene and 15 g (0.6 mole) of magnesium in absolute diethyl ether, 93.6 g (0.6 mole) of methylphenylchlorosilane was added dropwise. Yield of 2,5-di-(methylphenylsilyl)thiophene 55.6% (53.5 g). B.p. 200–205° at 2 mm, d_4^{20} 1.0851, n_D^{20} 1.5980.

Found, %: C 66.44, 66.25; H 6.68, 6.74; Si 17.00, 17.39; active H 0.64, 0.65. $C_{18}H_{20}Si_2S$. Calculated, %: C 66.63; H 6.21; Si 17.30; active H 0.61.

2,5-Di-(ethylphenylsilyl)thiophene. To 2,5-dimagnesiobromothiophene, prepared from 72.6 g (0.3 mole) of 2,5-dibromothiophene and 15 g (0.6 mole) of

magnesium in absolute diethyl ether, 16.23 g (0.6 mole) of ethylphenylchlorosilane was added dropwise. Yield of 2,5-di-(ethylphenylsilyl)thiophene 58.5% (62). B.p. 228-230° at 2 mm, d_4^{20} 1.0599, n_D^{20} 1.5860.

Found, %: C 68.47, 68.20; H 7.30, 7.00; Si 15.92, 15.62; active H 0.62, 0.56.
$C_{20}H_{24}Si_2S$. Calculated, %: C 68.14; H 6.86; Si 15.91; active H 0.57.

Addition of dihydridethienylenesilanes to alkenylsilanes

2,5-Bis-(tetramethylphenyldisilylethyl)thiophene. To 30 g (0.3 mole) of trimethylvinylsilane in the presence of 0.5 ml of catalyst (0.1 *N* solution of $H_2PtCl_6 \cdot 6H_2O$ in absolute isopropyl alcohol), 32.4 g (0.1 mole) of 2,5-di-(methylphenylsilyl)thiophene was added at such a rate that the temperature of the reaction mixture did not exceed 70°. The reaction mixture was then heated for 10 h at 180°. Yield 76.7% (39.2 g). B.p. 258-260° at 2 mm, d_4^{20} 0.9944, n_D^{20} 1.5489.

Found, %: C 64.46, 64.61; H 9.06, 9.10; Si 22.25, 22.19.
$C_{28}H_{44}Si_4S$. Calculated, %: C 64.07; H 8.45; Si 21.34.

2,5-Bis-(tetramethylphenyldisilpropyl)thiophene. To 34.2 g (0.3 mole) of trimethylallylsilane in the presence of 0.5 ml of catalyst, 32.4 (0.1 mole) of 2,5-di-(methylphenylsilyl)thiophene was added. The reaction mixture was heated for 10 h. The maximum temperature was 180°. Yield 77% (42.5 g). B.p. 277-280° at 2 mm, d_4^{20} 0.9792, n_D^{20} 1.5415.

Found, %: C 65.32, 65.37; H 8.46, 8.53; Si 19.95, 20.58.
$C_{30}H_{48}Si_4S$. Calculated, %: C 65.17; H 8.75; Si 20.29.

2,5-Bis-(tetraethylphenyldisilylethyl)thiophene. To 42.2 (0.3 mole) of triethylvinylsilane in the presence of 0.5 ml of catalyst, 38 g (0.1 mole) of 2,5-di-(ethylphenylsilyl)thiophene was added. The reaction mixture was heated for 10 h; the maximum temperature was 200°. Yield 50.3% (5 g). B.p. 307-310 at 2 mm, n_D^{20} 1.5370; d_4^{20} 0.9938.

Found, %: C 67.56, 67.88; H 9.66, 9.44; Si 17.44, 17.07.
$C_{36}H_{60}Si_4S$. Calculated, %: C 67.88; H 9.49; Si 17.52.

2,5-Bis-(trimethylethylphenyldisilylpropyl)-thiophene. To 34 g (0.3 mole) of trimethylallylsilane in the presence of 0.5 ml of catalyst, 35.2 g (0.1 mole) of 2,5-di-(ethylphenylsilyl)-thiophene was added. The reaction mixture was heated for 10 hours at a temperature of 180-200°. Yield 54.5% (30 g). B.p. 280-287° at 2 mm. n_D^{20} 1.5430, d_4^{20} 0.9952. MR_D 184.07.

Found, %: C 66.57, 66.27; H 9.91, 10.27; Si 18.27, 18.80
$C_{32}H_{52}Si_4S$. Calculated, %: C 66.16; H 9.02; Si 19.32

2,5-Bis-(tetraethylphenyldisilylpropyl)-thiophene. To 47 g (0.3 mole) of triethylallylsilane in the presence of 0.5 ml of catalyst, 35.2 g (0.1 mole) of 2,5-di-(ethylphenylsilyl)-thiophene was added. The reaction mixture was heated

for 10 hours at a temperature of 180–200°. Yield 69.6%. B.p. 325–330°/2 mm (thick yellow oil).

Found, %: C 68.09, 67.79; H 9.92, 9.87; Si 17.00, 17.25
$C_{38}H_{64}Si_4S$. Calculated, %: C 68.61; H 9.70; Si 16.88

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Note: Figure translations are in progress. See original paper for figures.