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1957

SovietRxiv

Abstract

Full Text

CHEMISTRY

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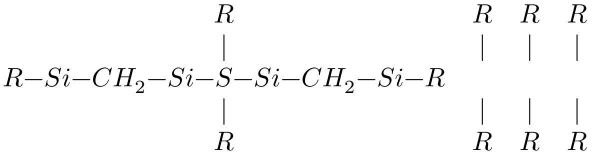
PREPARATION OF COMPOUNDS WITH SILTHIANOCARBON CHAIN UNITS

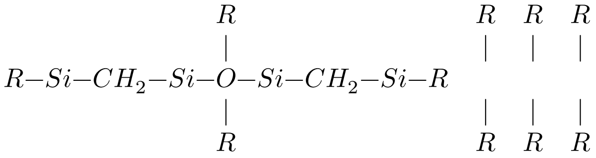
In recent years a number of works have appeared on the synthesis of organosilicon compounds containing sulfur bonded to a silicon atom. It has been proposed to obtain such compounds by the interaction of silicon halide derivatives with metal sulfides ([1,2]), and also by the action of hydrogen sulfide on primary aminosilanes ([3,4]) or on trialkylchlorosilanes ([5]).

It seemed of interest to us to synthesize compounds with silthianocarbon chain units

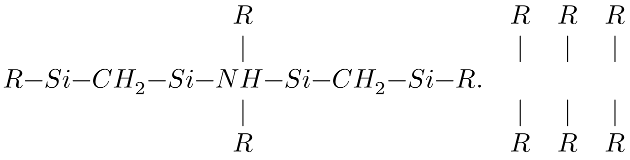


$$R{-}Si{-}CH_2{-}Si{-}\overset{\overset{R}{|}}{\underset{\underset{R}{|}}{S}}{-}Si{-}CH_2{-}Si{-}R \qquad \begin{matrix} R & R & R \\ | & | & | \\ | & | & | \\ R & R & R \end{matrix}$$

and to study their properties in comparison with the compounds of analogous structure described by us earlier, containing siloxanocarbon ([6–8]) and silazanocarbon units ([9]):



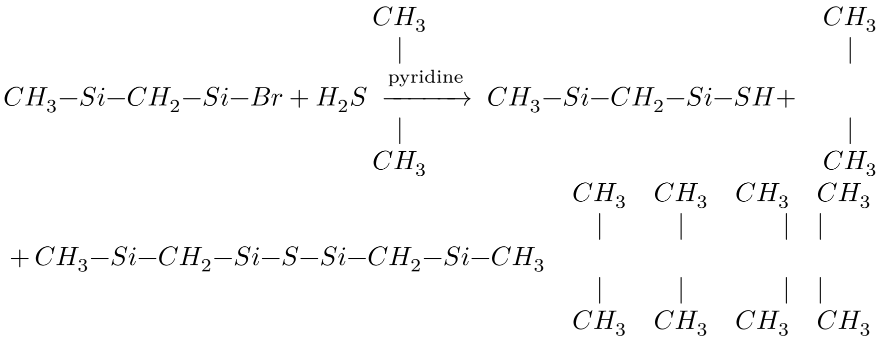
$$R{-}Si{-}CH_2{-}Si{-}\overset{\overset{R}{|}}{\underset{\underset{R}{|}}{O}}{-}Si{-}CH_2{-}Si{-}R \qquad \begin{matrix} R & R & R \\ | & | & | \\ | & | & | \\ R & R & R \end{matrix}$$



$$R{-}Si{-}CH_2{-}Si{-}\overset{\overset{R}{|}}{\underset{\underset{R}{|}}{N}}H{-}Si{-}CH_2{-}Si{-}R. \qquad \begin{matrix} R & R & R \\ | & | & | \\ | & | & | \\ R & R & R \end{matrix}$$

For the synthesis of compounds with silthianocarbon chain units, the starting materials used were the pentaalkyl bromo derivatives of disilanemethane described by us earlier (6), obtained by the interaction of pentaalkyl derivatives of disilanemethane with bromine.

We have shown that, upon treating pentamethylbromodisilane methane with hydrogen sulfide in the presence of pyridine, a mixture of pentamethylthiodisilanemethane and bis-(pentamethyldisilanemethane)-sulfide is formed according to the scheme:



$$CH_3{-}Si(CH_3)_2{-}CH_2{-}Si(CH_3)_2{-}Br + H_2S \xrightarrow{\text{pyridine}} CH_3{-}Si(CH_3)_2{-}CH_2{-}Si(CH_3)_2{-}SH +$$

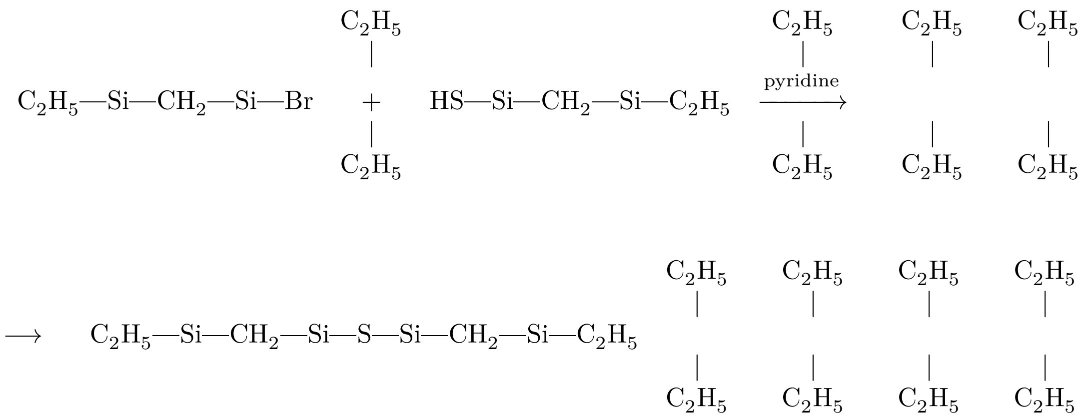
$$+ CH_3{-}Si(CH_3)_2{-}CH_2{-}Si(CH_3)_2{-}S{-}Si(CH_3)_2{-}CH_2{-}Si(CH_3)_2{-}CH_3$$

Table 1

Pentaalkylthiol derivatives of disilanemethane and bis-(pentaalkyldisilanemethane) sulfides

Compound	Formula	b.p., °C	b.p., mm Hg	m.p., °C	d^{20}	n_D^{20}	MR_D, found	MR_D, calc.
Pentamethylthiodisilanemethane	$CH_3{-}Si(CH_3)_2{-}CH_2{-}Si(CH_3)_2{-}SH$	58–60	14		0.8632	1.4604	56.53	56.75
Pentaethylthiodisilanemethane	$C_2H_5{-}Si(C_2H_5)_2{-}CH_2{-}Si(C_2H_5)_2{-}SH$	113–114	3		0.8989	1.4852	79.02	80.3
Bis(pentamethyldisilanemethane) sulfide	$CH_3{-}Si(CH_3)_2{-}CH_2{-}Si(CH_3)_2{-}S{-}Si(CH_3)_2{-}CH_2{-}Si(CH_3)_2{-}CH_3$	117–118	3.5	−9.8	0.8774	1.4771	103.84	104.96
Bis(pentaethyldisilanemethane) sulfide	$C_2H_5{-}Si(C_2H_5)_2{-}CH_2{-}Si(C_2H_5)_2{-}S{-}Si(C_2H_5)_2{-}CH_2{-}Si(C_2H_5)_2{-}C_2H_5$	202–204	3		0.9108	1.4980	149.06	150.06

Pentaethylbromodisilanylmethane, when treated with hydrogen sulfide, forms only pentaethylthiodisilanylmethane. Bis(pentaethyldisilanylmethane) sulfide was obtained by us through the interaction of pentaethylbromodisilanylmethane with pentaethylthiodisilanylmethane in the presence of pyridine:



$$C_2H_5—\overset{C_2H_5}{\underset{C_2H_5}{Si}}—CH_2—Si—Br + HS—Si—CH_2—Si—C_2H_5 \xrightarrow{\text{pyridine}}$$

$$\longrightarrow C_2H_5—Si—CH_2—Si—S—Si—CH_2—Si—C_2H_5$$

The properties of the sulfur-containing organosilicon compounds obtained by us are given in Table 1.

Experimental Part

I. A solution of 13.6 g (0.17 mole) of pyridine in 100 ml of ether was saturated for 30 min with hydrogen sulfide dried over calcium chloride. Then a solution of 40 g (0.17 mole) of pentaethylbromodisilanylmethane in 50 ml of ether was added. The mixture was heated for 5 hours to boiling while a weak stream of hydrogen sulfide was passed through. After cooling, the precipitate of pyridine hydrobromide was filtered off, and after removal of the ether the liquid reaction products were distilled in vacuo into the following main fractions:

1. Fraction 58-60° at 14 mm, corresponding to pentaethylthiodisilanylmethane; 11 g was obtained (yield 36.4%).

$C_6H_{18}SSi_2$. Found %: C 41.02; 41.02; H 9.71; 9.81; S 17.34; 17.80
Calculated %: C 40.39; H 10.17; S 17.98

2. Fraction 117-118° at 3.5 mm, corresponding to bis(pentaethyldisilanylmethane) sulfide; 11.5 g was obtained (yield 41.9%).

$C_{12}H_{34}SSi_4$. Found %: C 44.82; 44.84; H 10.60; 10.59; S 10.39; 9.84
Calculated %: C 44.76; H 10.64; S 9.93

Molecular weight (cryoscopic method; solvent benzene): found *M* 315; 324; calculated *M* 322.7.

II. 1. Hydrogen sulfide was passed for 30 min through a solution of 20 g (0.25 mole) of pyridine in 150 ml of toluene, after which 72 g (0.25 mole) of pentaethylbromodisilanylmethane was added. The reaction mixture was heated for 12 hours to boiling while a weak stream of hydrogen sulfide was passed through. After cooling, the precipitate of pyridine hydrobromide was filtered off and the filtrate was distilled. After removal of the toluene, 48 g (yield 80.3%) of a substance corresponding to pentaethylthiodisilanylmethane was obtained; b.p. 113-114° at 3.5 mm.

$C_{11}H_{28}SSi_2$.	Found %:	C 53.52; 53.72;	H 10.69; 10.77;	S 12.52; 12.39
	Calculated %:	C 54.26;	H 9.52;	S 13.27

2. To a mixture of 17.5 g (0.07 mole) of pentaethylthiodisilanylmethane and 5.6 g (0.07 mole) of pyridine in 50 ml of toluene was added 30 g (0.07 mole) of pentaethylbromodisilanylmethane in 25 ml of toluene. The reaction mixture was heated for 16 hours to boiling. After cooling, pyridine hydrobromide was filtered off and the toluene was distilled off. On distillation of the liquid pro-

of the reaction products, 10.5 g (yield 32.4%) of a substance with b.p. 202-204° at 3 mm, corresponding to bis(pentaethyldisilylmethane) sulfide, was obtained.

$C_{22}H_{44}SSi_4$.	Found, %:	C 57.61; 57.39;	H 11.87; 11.70;	S 6.44; 6.55
	Calculated, %:	C 57.08;	H 11.76;	S 6.92

Molecular weight (cryoscopic method; solvent: benzene): found *M* 457; 469; calculated *M* 463.

Received
30 XI 1956

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

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