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G. V. ODABASHYAN, T. A. ZHURAVLEVA, and Corresponding Member of the Academy of Sciences of the USSR A. D. PETROV

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## Abstract

## Full Text

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# STUDY OF THE ADDITION REACTION OF DICHLOROSILANE TO ALKENYLSILANES

At the present time, organosilicon polymers containing alternating siloxane and carbon-carbon bonds in their chains are of definite interest, since their properties are intermediate between those of polysiloxanes and organic polymers ([1,2]). The literature describes various methods for the synthesis of such monomers, which under certain conditions are capable of giving bridged organosilicon polymers ([3–19]). Of these methods for synthesizing bridged organosilicon compounds, the reaction of addition of silicon hydrides to alkenylsilanes in the presence of chloroplatinic acid is of greatest interest ([15–19]).

$$\text{a) } X_3Si(CH_2)_{nCH}=CH_2+HSiX_3\rightarrow X_3Si(CH_2)_{nCH}2CH_2SiX_3,$$

$$\text{b) } X_2Si[(CH_2)_{nCH}=CH_2]_2+2HSiX_3\rightarrow X_2Si[(CH_2)_{nCH}2CH_2SiX_3]_2,$$

where $X=CH_3,C_2H_5,C_3H_7,C_4H_9,C_6H_5,Cl;\ n=0,1.$

The interaction of silicon hydrides with alkenylsilanes according to the schemes given proceeds smoothly under relatively mild conditions, with good yields of the addition products.

**Table 1**

**Addition of dichlorosilane to vinyl- and allylsilanes in the presence of $H_2PtCl_6\cdot 6H_2O$**
**(amount of 0.1 M solution of $H_2PtCl_6\cdot 6H_2O$, 0.1 ml; time from the start of heating of the reaction mixture, 1.5 hours)**

| No. | Starting substances | Amount, g | Amount, mol | Max. temp., °C | Max. pressure, atm | Isolated from the reaction products | Yield, g | Yield, % |
|---|---|---|---|---|---|---|---|---|
| 1 | $H_2SiCl_2$ + $CH_2{=}CHSiCl_3$ | 10.1 + 32.3 | 0.1 + 0.2 | 190 | 15.0 | $Cl_2Si(CH_2CH_2SiCl_3)_2$ | 17.0 | 27 |
| 2 | $H_2SiCl_2$ + $CH_2{=}CHSi(CH_3)Cl_2$ | 10.1 + 28.2 | 0.1 + 0.2 | 199 | 8.0 | $Cl_2Si[CH_2CH_2Si(CH_3)Cl_2]_2$ | 20.0 | 52 |
| 3 | $H_2SiCl_2$ + $CH_2{=}CHSi(CH_3)_3$ | 10.1 + 20.0 | 0.1 + 0.2 | 175 | 8.0 | $Cl_2Si[CH_2CH_2Si(CH_3)_3]_2$ | 22.5 | 75 |
| 4 | $H_2SiCl_2$ + $CH_2{=}CHSi(C_2H_5)Cl_2$ | 10.1 + 31.2 | 0.1 + 0.2 | 179 | 14.0 | $Cl_2Si[CH_2CH_2Si(C_2H_5)Cl_2]_2$ | 19.0 | 46 |
| 5 | $H_2SiCl_2$ + $CH_2{=}CHSi(C_2H_5)_3$ | 10.1 + 28.4 | 0.1 + 0.2 | 175 | 10.0 | $Cl_2Si[CH_2CH_2Si(C_2H_5)_3]_2$ | 24.0 | 62 |
| 6 | $H_2SiCl_2$ + $CH_2{=}CHCH_2SiCl_3$ | 10.1 + 35.1 | 0.1 + 0.2 | 148 | 4.0 | $Cl_2Si[CH_2CH_2CH_2SiCl_3]_2$** | 23.0 | 51 |
| 7 | $H_2SiCl_2$ + $CH_2{=}CHCH_2Si(CH_3)Cl_2$ | 7.4 + 22.7 | 0.7 + 1.46 | 168 | 3.0 | $Cl_2Si[CH_2CH_2CH_2Si(CH_3)Cl_2]_2$ | 15.0 | 45 |
| 8 | $H_2SiCl_2$ + $CH_2{=}CHCH_2Si(CH_3)_3$ | 10.1 + 22.8 | 0.1 + 0.2 | 142 | 1.0 | $Cl_2Si[CH_2CH_2CH_2Si(CH_3)_3]_2$ | 21.0 | 65 |
| 9 | $H_2SiCl_2$ + $CH_2{=}CHSi(C_2H_5)_3$ | 10.1 + 14.20 | 0.1 | 157 | 11.0 | $(C_2H_5)_3SiCH_2CH_2Cl_2Si[CH_2CH_2Si(C_2H_5)_3$ | 6.5 | 14 |
| 10 | $(C_2H_5)_3SiCH_2CH_2SiHCl_2$ + $CH_2{=}CHCH_2Si(CH_3)_3$ | 6.0 + 2.85 | 0.025 + 0.025 | 150 | 4.0 | $Cl_2Si[CH_2CH_2Si(C_2H_5)_3]\cdot[CH_2CH_2CH_2Si(CH_3)_3]$ | 3.0 | 33 |

* Yields were calculated on the alkenylsilanes taken into the reaction.
** The compound has been described in the literature.

Therefore, in the present work we investigated the possibility of obtaining organosilicon monomers by the addition of dichlorosilane to alkenylsilanes in the presence of chloroplatinic acid, according to the general equation:

$$\mathrm{H_2SiCl_2 + 2CH_2 = CH(CH_2)_{nSiX}3 \rightarrow Cl_2Si[CH_2CH_2(CH_2)_{nSiX}3]_2},$$

where $X = \mathrm{CH_3}, \mathrm{C_2H_5}, \mathrm{Cl}$; $n = 0, 1$.

As can be seen from Table 1, dichlorosilane adds to alkenylsilanes in the presence of chloroplatinic acid chiefly in good yields (up to 75%). However, the structure of the alkenylsilane has a substantial effect on the yield of the addition products. The yield of the addition products decreases both with an increase in the number of electronegative groups at the silicon atom in the alkenylsilane and on passing from vinylsilanes to allylsilanes.

It is interesting to note that, according to the data of A. V. Topchiev, N. S. Nametkin, and S. G. Durgaryan ([18]), in the case of the addition of trichlorosilane to diallylsilanes in the presence of chloroplatinic acid, the opposite picture is observed: the yield of the addition products decreases with a decrease in the number of electronegative groups at the silicon atom in the diallylsilane. Dichlorosilane adds to alkenylsilanes stepwise. First one Si—H bond reacts, and then the other; here the relative rate of reaction of the first Si—H bond is greater than that of the second, which is in agreement with the data of A. D. Petrov, V. A. Ponomarenko, and G. V. Odabashyan ([20,21]) on the addition of silicon dihydrides to olefins. This feature of the reaction of addition of silicon dihydrides to unsaturated compounds in the presence of chloroplatinic acid makes it possible to synthesize organosilicon monomers with various bridges:

$$\text{a) } H_2SiCl_2 + CH_2 = CHSiX_3 \rightarrow H(Cl_2)SiCH_2CH_2SiX_3,$$
$$\text{b) } H(Cl_2)SiCH_2CH_2SiX_3 + CH_2 = CHCH_2SiX_3 \rightarrow$$
$$\rightarrow Cl_2Si(CH_2CH_2SiX_3)(CH_2CH_2CH_2SiX_3).$$

Investigation of the IR spectra* of the obtained organosilicon bridged compounds showed that dichlorosilane adds to vinyl- and allylsilanes against Markovnikov' s rule, i.e., the hydrogen adds to the less hydrogenated carbon atom of the double bond.

## Experimental Part

1. **Di-($\beta$-trichlorosilylethyl)-dichlorosilane**— $Cl_2Si(CH_2CH_2SiCl_3)_2$**.** Into a stainless-steel autoclave, precooled with dry ice, of 50 ml capacity, were charged 10.10 g (0.1 mole) of $H_2SiCl_2$, 32.30 g (0.2 mole) of $CH_2 = CHSiCl_3$, and 0.1 ml of a 0.1 M solution of $H_2PtCl_6 \cdot 6H_2O$ in isopropyl alcohol. The time from the start of heating of the reaction mixture was 1.5 hours. The maximum furnace temperature was 160°. The maximum temperature of the reaction mixture was 190°. The maximum pressure was 15 atm. From 42.20 g of crude reaction-product mixture, distillation in vacuum gave 11.5 g (27%) of di-($\beta$-trichlorosilylethyl)-dichlorosilane; b.p. 140—142° (6 mm), m.p. 58—60°.

Found, %: C 11.20, 11.40; H 1.89, 2.10; Si 19.50, 19.72; Cl 67.00, 66.80
$C_4H_8Si_3Cl_8$. Calculated, %: C 11.33; H 1.90; Si 19.87; Cl 66.89

2. **Di-($\beta$-methyldichlorosilylethyl)-dichlorosilane**— $Cl_2Si[CH_2CH_2Si(CH_3)Cl_2]_2$. From 36.40 g of crude reaction-product mixture, distillation in vacuum gave 20.00 g (52.0%) of di-($\beta$-methyldichlorosilylethyl)-dichlorosilane, b.p. 165—166° (13 mm), m.p. 80—81°.

* We express our deep gratitude to E. D. Lubuzh for carrying out the spectral analysis of the compounds obtained.

** All reactions for the addition of dichlorosilane to alkenylsilanes were carried out under the conditions of experiment No. 1.

Found, %: C 18.91, 19.00; H 4.02, 3.89; Si 22.1, 22.23; Cl 55.6, 55.41
$C_6H_{14}Si_3Cl_6$. Calculated, %: C 18.8; H 3.68; Si 21.99; Cl 55.51

**3. Di-($\beta$-trimethylsilylethyl)-dichlorosilane**–$Cl_2Si[CH_2CH_2Si(CH_3)_3]_2$. From 29.00 g of the crude mixture of reaction products, vacuum distillation gave 22.50 g (75.0%) of di-($\beta$-trimethylsilylethyl)-dichlorosilane; b.p. 135° (17 mm), m.p. 66-68°.

Found, %: Cl 23.50, 23.70
$C_{10}H_{26}Si_3Cl_2$. Calculated, %: Cl 23.52

**4. Di-($\beta$-ethyldichlorosilylethyl)-dichlorosilane**–$Cl_2Si[CH_2CH_2Si(C_2H_5)Cl_2]_2$. From 42 g of the crude mixture of reaction products, vacuum distillation gave 19.0 g (46%) of di-($\beta$-ethyldichlorosilylethyl)-dichlorosilane; b.p. 171-172° (8 mm), solidification point 29-32°.

Found, %: Cl 51.50; 51.35
$C_{12}H_{18}Si_3Cl_6$. Calculated, %: Cl 51.73

**5. Di-$\beta$-triethylsilylethyl)-dichlorosilane**–$Cl_2Si[CH_2CH_2Si(C_2H_5)_3]_2$. From 37.50 g of the crude mixture of reaction products, vacuum distillation gave 24.00 g (62%) of di-($\beta$-triethylsilylpropyl)-dichlorosilane; b.p. 176-178° (6 mm), $d_4^{20}$ 0.9639, $n_D^{20}$ 1.4775, $MR_D$ found 113.15, calculated 112.9.

Found, %: C 50.01, 50.20; H 9.90, 9.82; Si 21.65, 21.78; Cl 18.91; 18.99
$C_{16}H_{38}Si_3Cl_2$. Calculated, %: C 49.83; H 9.93; Si 21.85; Cl 18.38

**6. Di-($\gamma$-trichlorosilylpropyl)-dichlorosilane**–$Cl_2Si(CH_2CH_2CH_2SiCl_3)_2$. From 45.10 g of the crude mixture of reaction products, vacuum distillation gave 23.10 g (51.0%) of di-($\gamma$-trichlorosilylpropyl)-dichlorosilane; b.p. 172-173° (12 mm), solidification point 28°, $d_4^{20}$ 1.4160, $n_D^{20}$ *1.4934*; $MR_D$ found 92.85, calculated 92.88.

Found, %: C 15.80; 15.98; H 2.87, 2.93; Si 18.84, 18.75; Cl 62.9, 63.0
$C_6H_{12}Si_3Cl_8$. Calculated, %: C 15.94; H 2.67; Si 18.64; Cl 62.74

**Literature data:** b.p. 210-212 (2 mm) (18).

**7. Di-($\gamma$-methyldichlorosilylpropyl)-dichlorosilane**–$Cl_2Si[CH_2CH_2CH_2Si(CH_3)Cl_2]_2$. From 29.35 g of the crude mixture of reaction products, vacuum distillation gave 18.50 g (45%) of di-($\gamma$-methyldichlorosilylpropyl)-dichlorosilane; b.p. 198-200° (16 mm), m.p. 47-48°.

Found, %: Cl 51.98, 51.61
$C_8H_{18}Si_3Cl_6$. Calculated, %: Cl 51.73

**8. Di-($\gamma$-trimethylsilylpropyl)-dichlorosilane**–$Cl_2Si[CH_2CH_2CH_2Si(CH_3)_3]_2$. From 32.70 g of the crude mixture of reaction products, vacuum distillation

gave 21.60 g (65.5%) of di-($\gamma$-trimethylsilylpropyl)-dichlorosilane; b.p. 121-122° (4 mm), $d_4^{20}$ 0.9386, $n_D^{20}$ 1.4560, $MR_D$ found 95.44, calculated 95.10.

Found, %: C 44.76, 44.30; H 10.24, 9.28; Si 25.65, 25.85; Cl 21.54, 21.40 $C_{12}H_{30}Si_3Cl_2$. Calculated, %: C 43.73; H 9.17; Si 25.57; Cl 21.51

**9. $\beta$-Triethylsilylethyldichlorosilane**–$(C_2H_5)_3SiCH_2CH_2SiHCl_2$. From 23.6 g of the crude mixture of reaction products, vacuum distillation gave 6.1 g (25%) of $\beta$-triethylsilylethyldichlorosilane; b.p. 109-111 (12 mm), $d_4^{20}$ 1.0066, $n_D^{20}$ 1.4650, $MR_D$ found 66.83, calculated 66.85.

**10. $\beta$-Triethylsilylethyl-$\gamma$-trimethylsilylpropyldichlorosilane**–$Cl_2Si[CH_2CH_2Si(C_2H_5)_3][CH_2CH_2CH_2Si(CH_3)_3]$. From

* For a supercooled liquid.

8.3 g of the crude mixture of reaction products, on vacuum distillation, gave 3 g (33%) of $\beta$-triethylsilylethyl-$\gamma$-trimethylsilylpropyldichlorosilane; b.p. 165-167° (10 mm), $d_4^{20}$ 0.9573, $n_D^{20}$ 1.4680, $MR_D$ found 103.84, calculated 104.00.

11. **Di-($\gamma$-trimethylsilylpropyl)dimethylsilane** –$(CH_3)_2Si[CH_2CH_2CH_2Si(CH_3)_3]_2$. Obtained by the reaction of di-($\gamma$-trimethylsilylpropyl)dichlorosilane $Cl_2Si[CH_2CH_2CH_2Si(CH_3)_3]_2$ with methylmagnesium bromide, prepared from 5 g of Mg and $CH_3Br$ in 100 ml of absolute ether by the usual method. Vacuum distillation gave 8.0 g (66.5%) of di-($\gamma$-trimethylsilylpropyl)dimethylsilane; b.p. 116-118° (8 mm), $d_4^{20}$ 0.7960, $n_D^{20}$ 1.4410, $MR_D$ found 95.77, calculated 95.84. Literature data: $d_4^{20}$ 0.7972, $n_D^{20}$ 1.4420 ([19]).

12. **Di-($\beta$-trimethylsilylethyl)dimethylsilane** –$(CH_3)_2Si[CH_2CH_2Si(CH_3)_3]_2$.

Obtained by the reaction of di-($\beta$-trimethylsilylethyl)dichlorosilane $Cl_2Si[CH_2CH_2Si(CH_3)_3]_2$ with methylmagnesium bromide, prepared from 3 g of Mg and $CH_3Br$ in 100 ml of absolute ether by the usual method. Vacuum distillation gave 5.0 g (72%) of di-($\beta$-trimethylsilylethyl)dimethylsilane; b.p. 101-103° (14 mm), $d_4^{20}$ 0.7952, $n_D^{20}$ 1.4402, $MR_D$ found 86.42, calculated 86.58.

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## REFERENCES

1. K. A. Andrianov, Proceedings of the Technical Conference "Chemistry and Practical Application of Organosilicon Compounds," vol. 2, L., 1958, p. 13.

2. P. D. George, H. Prober, I. R. Elliot, Chem. Rev., 56, 1065 (1956).

3. L. H. Sommer, G. M. Goldberg et al., J. Am. Chem. Soc., 69, 980 (1947).

4. L. H. Sommer, F. A. Mitch, G. M. Goldberg, J. Am. Chem. Soc., 71, 2746 (1949).

5. L. H. Sommer, G. R. Ansul, J. Am. Chem. Soc., 77, 2482 (1955).

6. A. V. Topchiev, N. S. Nametkin, O. P. Solovova, DAN, 86, 965 (1952).

7. N. S. Nametkin, A. V. Topchiev, O. P. Solovova, DAN, 93, 285 (1953).

8. S. I. Sadykhzade, A. D. Petrov, DAN, 96, 765 (1954).

9. A. D. Petrov, S. I. Sadykhzade, E. A. Chernyshev, V. F. Mironov, ZhOKh, 26, 1248 (1956).

10. A. D. Petrov, G. I. Nikishin, N. P. Smetankina, ZhOKh, 28, 2085 (1958).

11. C. A. Burkhard, R. H. Krieble, J. Am. Chem. Soc., 69, 2687 (1947).

12. A. D. Petrov, V. A. Ponomarenko, B. A. Sokolov, G. V. Odabashyan, Izv. AN SSSR, OKhN, 1957, 1206.

13. A. V. Topchiev, N. S. Nametkin, T. I. Chernysheva, S. G. Durgaryan, DAN, 110, 97 (1956).

14. V. M. Vdovin, R. Sultanov, E. D. Lubuzh, A. D. Petrov, DAN, 138, 831 (1961).

15. A. V. Topchiev, N. S. Nametkin, S. G. Durgaryan, ZhOKh, 30, 927 (1960).

16. A. D. Petrov, V. M. Vdovin, Izv. AN SSSR, OKhN, 1959, 1139.

17. V. M. Vdovin, A. D. Petrov, ZhOKh, 30, 838 (1960).

18. A. V. Topchiev, N. S. Nametkin, S. G. Durgaryan, DAN, 130, 105 (1960).

19. V. M. Vdovin, K. S. Pushchevaya, A. D. Petrov, Izv. AN SSSR, OKhN, 1961, 1275.

20. A. D. Petrov, V. A. Ponomarenko, G. V. Odabashyan, DAN, 126, 1009 (1959).

21. V. A. Ponomarenko, G. V. Odabashyan, A. D. Petrov, DAN, 130, 333 (1960).

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

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