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Abstract

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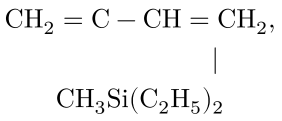
HIGH-TEMPERATURE CONDENSATION OF CHLOROPRENE WITH METHYLDICHLOROSILANE

In a series of studies (^{1}) it was shown that reactions of high-temperature condensation of alkenyl- (or aryl-) halides with hydrosilanes offer broader possibilities for the synthesis of alkenylchlorosilanes than the so-called direct synthesis. Thus, for example, under the conditions of direct synthesis vinyltrichlorosilane is obtained in a yield of ~4%, whereas by high-temperature condensation of vinyl chloride with $HSiCl_3$ it was obtained in a yield of 60%, etc. An attempt (^{2}) to obtain 2-trichlorosilylbutadiene from chloroprene by the direct-synthesis method was not successful. Only cyclodimerization of chloroprene to dichlorides I and II was observed:

[structural formulas I and II]

but neither chloroprene itself nor the dichlorides reacted with silicon. In the present study we carried out high-temperature condensation of chloroprene with methyldichlorosilane.

The first experiment was conducted at 550-580°. The condensate obtained was treated with C_2H_5MgBr and the reaction product was fractionated. In one of the fractions we found the expected methyldiethylsilylbutadiene,



$$\begin{array}{c} CH_2 = C - CH = CH_2, \\ \qquad\qquad | \\ CH_3Si(C_2H_5)_2 \end{array}$$

which contained a considerable amount (by spectroscopic estimate, not less than 50%) of the allene isomer. On the basis of elemental-analysis data this fraction contained up to 5% chlorine. Chlorine was also present in the dimer fraction $[CH_3(C_2H_5)_2Si—CH = CH—CH = CH_2]_2$.

The second experiment, carried out at 590-600°, gave a higher yield of condensate (up to 50%, calculated on the chloroprene that entered into the reaction). In this case the reaction product was methylated (by the action of

CH_3MgBr). In this experiment it was possible to isolate and identify, in addition to $CH_2 = C[Si(CH_3)_3]—CH = CH_2$ (a mixture of isomers), styrene (formed in a yield of 10%, calculated on the chloroprene that entered into the reaction). The formation of styrene indicates partial reduction of the chlorine of chloroprene and also the occurrence of dehydrogenation reactions, since styrene is apparently formed here through vinylcyclohexene*. In addition, a disilane was isolated to which, on the basis of elemental analysis, the formula $C_{10}H_{22}Si_2$ may be assigned (fraction I).

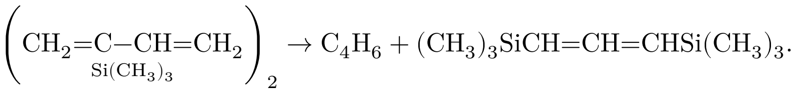
We were unable to establish unambiguously the structure of this disilane. On the basis of spectroscopic data it may be assumed that conjugation of two C=C bonds located in the α-position to silicon is present (bands at 1590 and 1570 cm^{-1}). This is consistent with the presence of a band at 3005 cm^{-1} (=CH=C) and bands at 1250, 846, and 756 cm^{-1}, characteristic of $Si(CH_3)_3$ groups.

The following formula may be proposed tentatively:

$$(CH_3)_3SiCH = CH—CH = CHSi(CH_3)_3$$

* Styrene could also have been formed from butadiene according to the scheme given below.

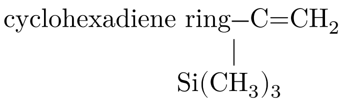
and formation of disilane from the dimer according to scheme I:



$$\left(\underset{Si(CH_3)_3}{CH_2{=}C}{-}CH{=}CH_2\right)_2 \rightarrow C_4H_6 + (CH_3)_3SiCH{=}CH{=}CHSi(CH_3)_3. \quad I$$

However, the presence in the spectrum, alongside the band at 1410 cm^{-1}, of a band at 1445 cm^{-1} contradicts this formula, since the latter band is evidently associated with the presence of $C{-}CH_3$ or $-CH_2$-groups. Disilane adds both two and four bromine atoms. One of the fractions (D), according to analytical data, proved to be

very close to α-trimethylsilylvinylcyclohexadiene.



$$\text{cyclohexadiene ring}{-}\underset{\displaystyle Si(CH_3)_3}{\overset{}{C}}{=}CH_2$$

In the IR spectrum, bands of CH vibrations of the vinyl group were found at 3025 and 3065 cm^{-1}, and in the region of C=C frequencies the bands 1520, 1590, 1610 cm^{-1}, whose lowered values may be caused by conjugation, as well as by the influence of the Si atom (C=C in the α-position to Si). Along with the bands at about 758, 845, 1255, and 1415 cm^{-1}, characteristic of the $Si(CH_3)_3$ group, there is a strong band at 1465 cm^{-1}, probably indicating $-CH_2-$(or C

$-CH_3$) groups. The higher-boiling fractions contained halogen and were not studied in detail.

Experimental Part*

Condensation of $CH_2{=}C(Cl){-}CH{=}CH_2$ **with** CH_3Cl_2SiH

Experiment 1. Into an empty glass tube 20 mm in diameter and 600 mm long, heated to 550-580°, a mixture of 395.0 g of chloroprene and 560.0 g of methyldichlorosilane was added dropwise at a rate of 2-3 drops per second. In a receiver cooled with ice, 750.0 g of condensate collected, from which 385.0 g of the initial mixture (b.p. 40-60°) was distilled off. The residue in the flask, without fractionation, was treated with ethylmagnesium bromide, and after distillation on a column two main fractions were isolated:

Fraction I (40-45.0 g), b.p. 68.5-70°/18 mm, n_D^{20} 1.4606, d_4^{20} 0.8466.

Found, %: C 68.62; 68.34; H 11.26; 10.95; Si 14.74; 14.99; Cl 5.51; 5.95
$C_9H_{18}Si$. Calculated, %: C 70.11; H 11.70; Si 18.18

IR spectrum (ν cm^{-1}): 747 (v.s.), 789 (v.s.), 820 (s.), 841 (m.), 866 (w.), 946 (m.), 962 (m.), 1010 (m.), 1061 (w.), 1086 (w.), 1150 (m.), 1230 (m.), 1249 (w.), 1370 (m.), 1390 (m.), 1410 (m.), 1460 (s.), 1575 (v.w.), 1610 (v.w.), 1925 (w.), 2820 (w.), 2880 (s.), 2917 (s.), 2960 (s.), 3021 (w.).

The frequencies 1610 and 1575 cm^{-1} may be assigned to C=C–C=C, and the frequency 1925 cm^{-1} to C=C=C groups, which agrees with what was said above about the composition of compound I.

Fraction II (40.0 g), after distillation over Na, had the following constants: b.p. 88-90°/0.5 mm, n_D^{20} 1.4939, d_4^{20} 0.8845; MR_D found 101.52, MR_D calculated 101.66. Literature data for $(CH_3(C_2H_5)_2SiCH{=}CH{-}CH{=}CH_2)_2$ (2): b.p. 139-141°/3 mm, n_D^{20} 1.4930, d_4^{20} 0.8849. Intermediate fractions were not investigated.

Experiment 2. By the same procedure, condensation was carried out of 815.0 g (9.21 mol) of chloroprene and 1107.0 g (9.62 mol) of methyldichlorosilane at 585-600°. In the receiver, 1300.0 g of condensate was collected, from which 380.0 g of the initial mixture was distilled off and then, in vacuum, 695.0 g of higher-boiling products. After many distillations on a column, 11 fractions were isolated, each of which was methylated and the products then distilled on a column. The following fractions were isolated:

Fraction A (35.0 g), b.p. 111.5-113°/748, n_D^{20} 1.4311, d_4^{20} 0.7539; MR_D found 43.35, calculated 43.23.

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* R. I. Pal' chik took part in the experimental part of the work.

Found, %:	C 66.73;	H 11.78;	Si 21.23
$C_7H_{14}Si$. Calculated, %:	C 76.57;	H 11.18;	Si 22.22

In the IR spectrum, bands at 1635 and 1585 cm^{-1}, assigned to the group C=C–C=C, and a band at 1940 cm^{-1}, corresponding to an admixture of the allene isomer (apparently not less than 30%), were found. A weak band at about 2180 cm^{-1} was also observed, probably associated with the formation of the corresponding silicon acetylene. Thus, the compound of fraction A is a mixture of isomers.

Fraction B (33.0 g), b.p. 71°/64 mm, n_D^{20} 1.5380, d_4^{20} 0.9012.

Found, %:	C 91.49;	H 8.13
C_8H_8. Calculated, %:	C 92.25;	H 7.74

As a result of bromination, crystals with m.p. 72-73° were obtained (recrystallized twice from 80% alcohol). A mixed-melting-point test with known dibromoethylbenzene gave m.p. 72°. The IR spectrum also agreed well with the literature data for the spectrum of styrene.

Fraction C (20.0 g), b.p. 75/30-74/28 mm, n_D^{20} 1.4830, d_4^{20} 0.8605.

Found, %: C 71.75; 71.80; H 9.23; 9.59; Si 19.15; 19.31

In the IR spectrum, the bands 2960, 2900, 1263, 1250, 853, 840, and 754 cm^{-1} indicate $Si(CH_3)_3$ groups; the splitting of the band at 1250 and 840 cm^{-1} may be associated with the existence of two differently situated groups in the molecule. The bands 1585, 1493, 1433, and 1113 cm^{-1} are characteristic of the group

Si–⟨benzene ring⟩.

The presence of a benzene ring also accounts for the appearance in the group of bands at 1770, 1820, 1875, 1910, and 1970 cm^{-1}. The bands 3020, 3065, and 3075 cm^{-1} are associated with C–H vibrations in the ring (and, possibly, with $C=CH_2$, although the presence of a vinyl group could not be established reliably). At the same time, no evidence could be found for the existence of CH_3- and CH_2-groups other than $Si(CH_3)_3$. It may be assumed that this is a mixture of two silicon-containing hydrocarbons.

Fraction G (60.0 g), b.p. 86°/20 mm, n_4^{20} 1.4580, d_D^{20} 0.8277.

Found, %:	C 59.95; 60.29;	H 10.97; 10.83;	Si 29.13; 29.08
$C_{10}H_{22}Si_2$. Calculated, %:	C 60.60;	H 11.11;	Si 28.28

IR spectrum (ν, cm^{-1}): 728 (weak), 756 (medium), 786 (weak), 805 (strong), 846 (very, very strong), 870 (strong), 906 (weak), 940 (weak), 962 (medium), 1010 (very strong), 1035 (weak), 1100 (medium), 1150 (strong), 1250 (very strong), 1320 (weak), 1410 (strong), 1445 (medium), 1570 (medium), 1590 (strong), 2795 (weak), 2880, 2900 (strong), 2960 (strong), 3005 (medium).

Fraction D (30-35.0 g), b.p. 62-64°/3 mm, n_D^{20} 1.5090, d_4^{20} 0.9070; MR_D found 58.71, MR_D calculated 59.15.

Found, %:	C 73.50; 73.57;	H 9.17; 9.32;	Si 15.35; 15.48
$C_{11}H_{18}Si$. Calculated, %:	C 74.15;	H 10.11;	Si 15.72

Apparently, formation occurred according to scheme II:

$$\text{[substituted benzene ring bearing CH=CH}_2\text{, Si(CH}_3)_3\text{, Si(CH}_3)_3\text{]}$$
$$\longrightarrow (CH_3)_3Si{-}Si(CH_3)_3 + \text{[substituted benzene ring bearing CH=CH}_2\text{, Si(CH}_3)_3\text{]} \qquad \text{II}$$

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

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