# Chemistry

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## Abstract

## Full Text

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# THERMAL TELOMERIZATION OF METHYLDICHLOROSILANE WITH OLEFINS

Silicon hydrides $HSiCl_3$, $HSiBr_3$, $HSiCl_2R$, $HSiClR_2$, $RSiH_3$ are capable of adding to the double bond of unsaturated compounds $^{(1-4)}$ under the action of acyl and alkyl peroxides, ultraviolet light, and also on platinum contact.

Reactions initiated by peroxides or irradiation apparently have a chain radical character. For the interaction of trichlorosilane with olefins in the presence of acetyl peroxide, the following reaction mechanism has been proposed $^{(1)}$:

$$(CH_3COO)_2 \rightarrow 2CH_3COO^\bullet \rightarrow CH_3{}^\bullet + CO_2$$

$$CH_3{}^\bullet + HSiCl_3 \rightarrow CH_4 + SiCl_3{}^\bullet$$

$$RCH{=}CH_2 + SiCl_3{}^\bullet \rightarrow R\dot{C}HCH_2SiCl_3$$

$$R\dot{C}HCH_2SiCl_3 + HSiCl_3 \rightarrow RCH_2CH_2SiCl_3 + SiCl_3{}^\bullet$$

The thermal addition of trichlorosilane and alkyldichlorosilanes to olefins at 160–400° has also been described. The authors $^{(3)}$ consider that the reaction proceeds through a transition state in which electron-accepting silicon binds to the methylene group of the olefin $RCH{=}CH_2$, and the chlorine atom—to the neighboring carbon atom, after which its exchange with the labile hydrogen atom of the silane gives the final product.

Recently there appeared a report on carrying out a photochemical telomerization reaction of trichlorosilane and perfluoroethylene with formation of a mixture of products of the structure $SiCl_3(CF_2CF_2)_{nH}$, where $n = 1$—$3$. Carrying out this reaction thermally led to the production of perfluorocyclobutane and a small amount of organosilicon compounds $^{(7)}$.

We have found that methyldichlorosilane, in a thermal reaction with ethylene and propylene under pressure under conditions of an excess of olefin, forms a mixture of substances of the structure $CH_3SiCl_2(CH_2CH_2)_{nH}$ in the first case and $CH_3SiCl_2(C_3H_6)_{nH}$ in the second. Since dialkyldichlorosilanes are not capable of interacting with olefins under the reaction conditions (3), the formation of the mixture of the indicated products excludes the above-mentioned molecular mechanism of the thermal reaction. It is evident that the thermal reaction studied by us has a chain character.

The structure of the methylalkyldichlorosilanes obtained is confirmed by determination of the molecular refraction of these compounds. For those of the compounds obtained by us that are described in the literature, only boiling points are known, and these coincide with those found by us. The yields of methylalkyldichlorosilanes show a certain regularity characteristic of a telomerization reaction: the maximum yield was obtained for compounds where $n = 2$; with increasing $n$, the yields decrease. Preliminary data concerning the reaction of methyldichlorosilane with propylene make it possible to suppose that this reaction does not proceed unequivocally. The yield given in Table 2 is calculated for broad fractions boiling within a range of 10–20°.

The reaction between methyldichlorosilane and ethylene was carried out in a half-liter autoclave made of EYa-1T steel. Into the autoclave were charged 123 g of $CH_3SiCl_2H$

**Table 1**

$CH_3SiCl_2(CH_2CH_2)_{nH}$

| $n$ | Yield, % of the sum of all products | $n_D^{20}$ | $d_4^{20}$ | $MR$, found | $MR$, calculated | B.p., °*/mm | Cryst. temp., °C/mm Hg | Source | C, %, calculated | C, %, found | H, %, calculated | H, %, found | Si, %, calculated | Si, %, found | Cl, %, calculated | Cl, %, found |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 23.6 | – | | | | 100 | 100 | (10) | | 35.20 | | 7.00 | | 16.60 | | 41.44 |
| 2 | 25.6 | 1.4311 | 1.0424 | 43.48 | 43.26 | 147–148 | 147.5–148 | (2) | 35.08 | 35.37 | 7.01 | 7.08 | 16.40 | 16.64 | 41.52 | 40.52 |
| 3 | 17.7 | 1.4390 | 0.9935 | 52.75 | 52.59 | 91/32 | 192 | (2) | 42.21 | 42.64;<br>42.71 | 8.10 | 8.24;<br>8.33 | | | | |
| 4 | 13.4 | 1.4440 | 0.9766 | 61.83 | 61.88 | 94/6 | 100–110/20 | (2) | 47.57 | 47.73;<br>47.76 | 8.81 | 9.01;<br>9.00 | | | | |
| 5 | 4.7 | 1.4490 | 0.9607 | 71.32 | 71.18 | 111–114/3 | – | | 51.76 | 51.67;<br>51.79 | 9.41 | 9.36;<br>9.45 | 11.00 | 11.00;<br>10.99 | 27.83 | 27.64;<br>27.25 |
| 6 | 3.8 | 1.4532 | 0.9558 | 80.20 | 80.47 | 124–127/3 | – | | 55.12 | 55.28;<br>55.32 | 9.83 | 9.90;<br>9.93 | 9.91 | 9.80;<br>9.57 | 25.08 | 25.22;<br>24.70 |

| $n$ | Yield, % of the sum of all products | $n_D^{20}$ | $d_4^{20}$ | $MR$, found | $MR$, calculated* | B.p., °/mm | Cryst. temp., °C/mm Hg | Source | C, %, calculated | C, %, found | H, %, calculated | H, %, found | Si, %, calculated | Si, %, found | Cl, %, calculated | Cl, %, found |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $n > 6$ | 8.5 | | | | | | | | | | | | | | | |

* The calculated value of the refraction was computed on the basis of Vogel’ s data on bond refractions (11).

and, after purging with nitrogen, ethylene was introduced. The reaction mixture was heated to 260°; the pressure rose to 560 atm. The reaction was carried out at 260–270° for 2 h. In this process almost all the ethylene was absorbed. The experiment was repeated three times, the reaction products were combined and subjected to fractional distillation. In all, 331 g of methyldichlorosilane was charged. The weight of the reaction products was 499 g. On distillation, 51 g of unreacted methyldichlorosilane was obtained. The conversion of methyldichlorosilane approaches 80%. From the mixture, methylalkyldichlorosilanes of the structure $CH_3SiCl_2(CH_2CH_2)_{nH}$, where $n = 1$–6, were isolated individually. The properties and yields of the methylalkyldichlorosilanes are summarized in Table 1.

**Table 2**

$CH_3SiCl_2(C_3H_6)_{nH}$

| $n$ | Yield, % of the sum of all products | $n_D^{20}$ | B.p., °/mm | Si, %, found | Si, %, calculated |
|---|---|---|---|---|---|
| 1 | 49 | 1.4240 | 123–124* | | |
| 2 | 26.2 | 1.4400 | 82/32 | 14.01;<br>14.07 | 14.10 |
| 3 | 3.9 | 1.4540 | 80–82/2 | 11.77;<br>11.82 | 11.64 |
| $n > 3$ | 10 | | | | |

* Literature data (3): b.p. 123–124°.

The reaction between methyldichlorosilane and propylene was carried out at 260–275° for 3 h at a maximum pressure of 100 atm. In two experiments, with a total charge of 151 g of methyldichlorosilane, 216 g of reaction products was obtained. On fractional distillation of this mixture, 21 g of unreacted methyldichlorosilane was obtained. From the mixture, methylalkyldichlorosilanes of composition $CH_3SiCl_2(C_3H_6)_{nH}$, where $n = 1$–3, were isolated. The properties and yields of the methylalkyldichlorosilanes obtained from propylene are summarized in Table 2.

The extension of this reaction to other silicon hydrides and other olefins will be reported separately.

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