HIGH TEMPERATURE CONDENSATION OF SILICOCHLOROFORM AND CHLOROFORM WITH SOME ORGANIC COMPOUNDS

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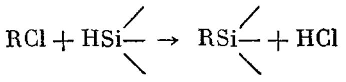
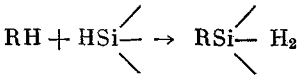
In previous papers it was shown that the "high-temperature condensation method" is not only a new general method for the synthesis of organosilicon compounds, but in principle is also a new way of forming the C–Si bond [1-8]. In essence, this method consists in reacting the chloro derivatives of unsaturated or aromatic hydrocarbons with silicon hydrides by passing their stoichiometric mixture through an empty quartz tube heated to 550-650°.



$$RCl + HSi\equiv \rightarrow RSi\equiv + HCl$$

Later it proved that the condensation of silicon hydrides with hydrocarbons can also go under the described conditions [1, 9-11].

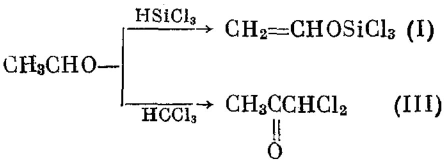


$$RH + HSi\equiv \rightarrow RSi\equiv \; H_2$$

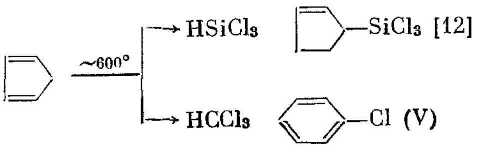
To determine the limits of application of the high-temperature condensation method, in the present paper we studied the reaction of silicon hydrides with other classes of compounds under the conditions of this method. In addition, we compared the condensation of $HSiCl_3$ and $HCCl_3$ with the same compounds. Here it was found that in principle various reactions take place, probably due to the variable thermal decomposition of these compounds.

$$HSiCl_3 \xrightarrow{t} H\cdot + \cdot SiCl_3$$
$$HCCl_3 \xrightarrow{t} :CCl_2 + HCl$$

For example, we found that if vinyloxytrichlorosilane is formed when acetaldehyde is reacted with trichlorosilane, then with chloroform this reaction leads to the formation of dichloroacetone.



With cyclopentadiene the reactions also go in various directions.

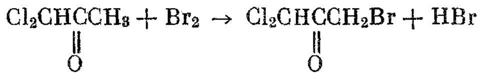


The structure of compound (I) was proved by its counter synthesis employing the reaction of Nesmeyanov, Lutsenko and Bratsev [13].

$$Hg(CH_2CHO)_2 + SiCl_4 \rightarrow CH_2 = CHOSiCl_3$$

Difficulty was encountered in proving the structure of compound (III), since the properties given in the literature for this compound relate to a substance that is highly contaminated with monochloroacetone [14]. The physical and chemical properties of the unsymmetrical dichloroacetone obtained by us confirm its structure. Compounds (I) and (III) react with bromine at room temperature.

$$CH_2{=}CHOSiCl_3 + Br_2 \rightarrow BrCH_2BrCHOSiCl_3 \qquad (II)$$

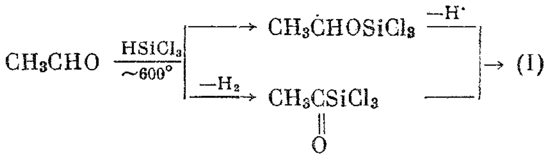


$$Cl_2CH\underset{\displaystyle O}{\underset{\|}{C}}CH_3 + Br_2 \rightarrow Cl_2CH\underset{\displaystyle O}{\underset{\|}{C}}CH_2Br + HBr \qquad (IV)$$

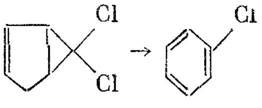
The formation of compound (I) is most probably associated with the enolization of acetaldehyde, since compound (I) is also formed when the reaction is run with $SiCl_4$ under analogous conditions.

$$CH_3CHO \xrightarrow{t} (CH_2{=}CHOH) \xrightarrow{SiCl_4} (I) + HCl$$

However, in the case of trichlorosilane the formation of (I) by other schemes is also not excluded.



The mechanism for the formation of compound (III) is plausibly explained by the attachment of dichlorocarbene to the C−H bond, while the formation of compound (V) is explained by the addition of dichlorocarbene to the double bond and subsequent dehydrochlorination.



EXPERIMENTAL

Vinyloxytrichlorosilane $CH_2{=}CHOSiCl_3$ (I). A. With stirring, a suspension of 16.7 g of $Hg(CH_2CHO)_2$ in 100 ml of nonane was added in 3 h to 40 g of $SiCl_4$. The flask contents were heated on the boiling water bath for 2 h. The precipitate was filtered and washed with absolute ether. Fractional distillation of the filtrates through a column gave 17 g (98%) of (I) with b. p. 87° (760 mm); n_D^{20} 1.4140; d_4^{20} 1.2978. See Fig. 1 for the infrared spectrum. Found: C 13.39; 13.07; H 1.98; 1.87; Si 15.29; 14.85; Cl 60.1; 60.57%; MR 34.1. $C_2H_3Cl_3SiO$. Calculated: C 13.53; H 1.70; Si 15.82; Cl 59.9%; MR 34.2.

Raman Spectrum of (I) ($\Delta\nu$, cm^{-1}): 148 (2), 170 (8w), 222 (4w), 269 (0w), 350 (2), 406 (3w), 425 (0), 452(5vw), 503 (2sh), 611 (0), 787 (1), 1320 (9), 1404 (0), 1641 (10), 2990 (0w), 3072 (0w).

B. A mixture composed of 135 g of $HSiCl_3$ and 88 g of CH_3CHO was passed at a rate of 20 g/h through an empty quartz tube, heated to 600°. The mixture was made up, stored, and fed into the tube at −60°. The obtained condensate was distilled from a flask, and then through a column. We isolated 57 g (46%) of (I) with b. p. 87.5° (757 mm); n_D^{20} 1.4155; d_4^{20} 1.2915. See Fig. 2 for the infrared spectrum. The Raman spectrum coincides with the spectrum of (I). Found: Si 15.88; 15.72; Cl 59.89; 60.05%; MR 34.4. $C_2H_3SiOCl_3$. Calculated: Si 15.82; Cl 59.9%; MR 34.2.

Chromatographic analysis of the (I) obtained from experiments A and B revealed the identity of these substances and the presence of an impurity (5%) of variable character in each substance. The infrared spectrum of the (I) obtained from Expt. B, in contrast to the (I) obtained from Expt. A, contains superfluous lines at 2054 and 740 cm^{-1}. The 2054 cm^{-1} line does not disappear when (I) was refluxed with H_2PtCl_6, for which reason it probably belongs to an impurity that contains the triple bond, and not the Si−H bond (it is possibly $Cl_3SiOC{\equiv}CH$).

C. A mixture composed of 85 g of $SiCl_4$ and 22 g of CH_3CHO, cooled to −70°, was passed through the above described quartz tube, heated to 650-670°, for 3 h. We obtained 6 g of (I) with b. p. 86° (755 mm); n_D^{20} 1.4130; d_4^{20} 1.2985. Chromatographic analysis confirmed the identity of this substance with the (I) obtained in the preceding experiments.

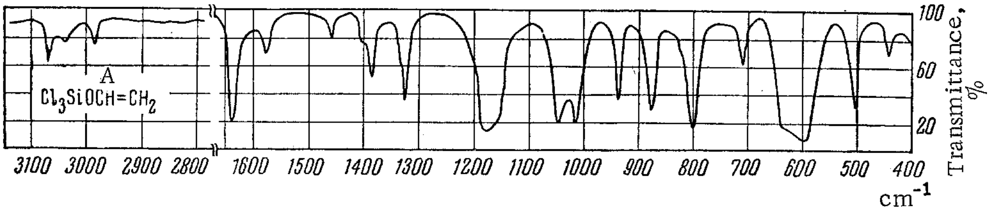


Fig. 1

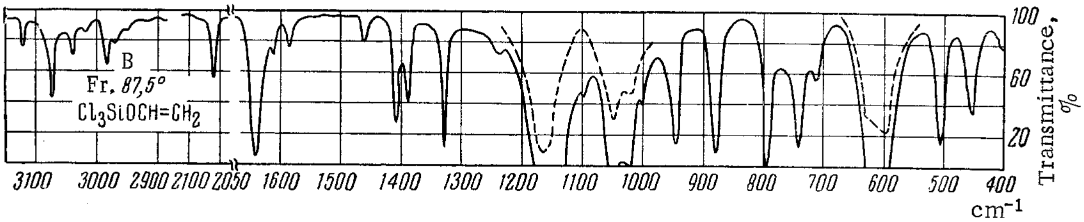


Fig. 2

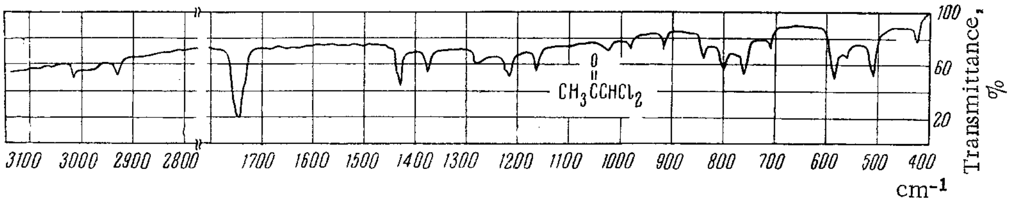


Fig. 3

α,β-Dibromoethoxytrichlorosilane $BrCH_2BrCHOSiCl_3$ (II). The addition of 9 g of bromine to 10 g of (I) went slowly when an incandescent lamp was used for illumination. We obtained 18 g (94%) of (II) with b. p. 78° (8 mm); n_D^{20} 1.5062; d_4^{20} 1.9949. Found: Si 8.50; 8.70%; MR 48.97. $C_2H_3Br_2Cl_3OSi$. Calculated: Si 8.33%; MR 50.25.

Raman Spectrum of (II) ($\Delta\nu$, cm^{-1}): 149 (I), 188 (6sh), 208 (5sh), 235 (2), 292 (0), 350 (I), 404 (I), 438 (0), 475 (0), 495 (I), 691 (10vw), 769 (Iw), 1026 (I), 1134 (0), 1248 (3), 1422 (0), 2875 (0), 2971 (1w).

1,1-Dichloroacetone $CH_3\overset{O}{\overset{\|}{C}}CHCl_2$ (III). A mixture composed of 220 g of acetaldehyde and 359 g of chloroform was passed through an empty quartz tube, heated to 480°, for 18 h. Fractional distillation of the condensate through a column gave 150 g of acetaldehyde, 200 g of chloroform and 140 g (84.5τ when based on reacted $HCCl_3$) of (III) with b. p. 117° (757 mm); n_D^{20} 1.4460; d_4^{20} 1.2985. See Fig. 3 for the infrared spectrum. Found: C 28.24; 28.51; H 3.13; 3.12; Cl 55.81; 55.54%; MR 26.0. $C_3H_4Cl_2O$. Calculated: C 28.38; H 3.18; Cl 55.85%; MR 25.7.

Raman Spectrum of (III) ($\Delta\nu$, cm^{-1}): 149 (2), 181 (1w), 241 (1w), 273 (4), 422 (10), 447 (2), 581 (5), 706 (3), 731 (3w), 753 (0w), 792 (1), 829 (3), 977 (0), 1170 (1w), 1220 (0), 1421 (1w), 1579 (1), 1618 (0), 1741 (3w), 2925 (10w), 2973 (1w), 3003 (3w), 3077 (0).

The NMR spectrum (III) contains only two signals, τ = 4.00 and 7.59 ppm, in a 1 : 3 ratio.

1,1-Dichloro-3-bromoacetone $Cl_2HC\overset{O}{\overset{\|}{C}}CH_2Br$ (IV). To 18 g of (III), illuminated with a 100-watt lamp, was added 22.6 g of bromine in 3 h. Fractional distillation gave 26 g (89.6%) of (IV) with b. p. 98-99° (20 mm); m. p. 27°. Found: C 16.64; 16.82; H 1.60; 1.48; Cl + Br 73.92%. $C_3H_3Cl_2OBr$. Calculated: C 17.5; H 1.46; Cl + Br 73.23%.

Raman Spectrum of (IV) ($\Delta\nu$, cm^{-1}): 181 (2w), 243 (1), 268 (10), 303 (0), 325 (7), 423 (9), 503 (2w), 556 (I), 619 (2), 642 (2), 724 (3w), 806 (2w), 1047 (1w), 1121 (1w), 1213 (2w), 1278 (1w), 1394 (1w), 1746 (6), 1768 (1), 2875 (3w), 2951 (5w), 2976 (2), 3010 (4w).

Only two signals, τ = 3.60 and 5.49 ppm, in a 1 : 2 ratio, were observed in the NMR spectrum of (IV).

Chlorobenzene C_6H_5Cl (V). A mixture composed of 33 g of cyclopentadiene or its dimer and 60 g of chloroform was passed through an empty quartz tube, heated to 460°, for 2 h. Fractional distillation gave 26 g (46%) of chlorobenzene with b. p. 131° (752 mm); n_D^{20} 1.5240; d_4^{20} 1.1050. Found: C 64.93; 64.64; H 5.16; 5.11; Cl 30.23; 31.02%; MR 31.17. C_6H_5Cl. Calculated: C 64.07; H 4.57; Cl 31.4%; MR 31.21.

The chromatographic and spectral analyses also confirm the fact that (V) is chlorobenzene.

SUMMARY

A new method was found for obtaining vinyloxy-substituted silanes and dichloroacetone, which are respectively formed by the short heating of acetaldehyde with hydrochlorosilanes or with chloroform at 500°.

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