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Abstract

Full Text

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THE ORDER OF ADDITION OF SILICON HYDRIDES TO PROPARGYL CHLORIDE

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In the literature ([1–3]) there are reports that silicon hydrides add to monosubstituted acetylenes in most cases according to the following scheme:

$$RC \equiv CH + HSi < \rightarrow \; RCH = CHSi <, \quad \text{where } R = C_3H_7;\; C_4H_9;\; C_5H_{11};\; C_6H_5;$$

$$\textit{iso}\text{-}C_3H_7;\; \text{tert.} - C_4H_9;\; R_3Si;\; CH_2 = CH;\; HOCH_2.$$

Only in the case of dimethylethynylcarbinol and some of its analogues was a change in the indicated order of addition of silicon hydrides to the reverse order observed ([4–7]):

$$HO{-}C(CH_3)_2C \equiv CH + HSi(C_2H_5)_3 \rightarrow (C_2H_5)_3SiC(= CH_2)C(CH_3)_2OH.$$

In the present work it was established that silicon hydrides add to propargyl chloride with formation, in equal amounts, of two isomeric compounds corresponding to different orders of addition of the silicon hydride*:

$$ClCH_2C \equiv CH + HSiCl_2R \xrightarrow{H_2PtCl_6} \begin{cases} ClCH_2CH = CHSiCl_2R, \\ ClCH_2C(= CH_2)SiCl_2R; \end{cases}$$

$$R = Cl;\; CH_3;\; C_2H_5.$$

Both types of compounds obtained possess increased mobility of the halogen atom in the alkyl chain and, upon methylation with an excess of Grignard reagent, readily replace it by a methyl group:

$$Cl_3SiCH = CHCH_2Cl \xrightarrow{CH_3MgCl} \begin{cases} (CH_3)_3SiCH = CHCH_2Cl \\ (CH_3)_3SiCH = CHCH_2CH_3 \end{cases} \qquad (I)$$

$$Cl_3SiC(=CH_2)CH_2Cl \xrightarrow{CH_3MgCl} \begin{cases} (CH_3)_3SiC(=CH_2)CH_2Cl \\ (CH_3)_3SiC(=CH_2)CH_2CH_3. \end{cases} \quad \text{(II)}$$

It is interesting to note that compound (II), upon methylation, does not undergo any decomposition of the kind characteristic of all other β-chloroalkylsilane chlorides:

$$Cl_3SiCH_2CH_2Cl \xrightarrow{RMgCl} R_4Si + CH_2 = CH_2.$$

* This had previously been assumed only on the basis of spectral analysis ([8]).

The compound $(CH_3)_3SiCH{=}CHCH_2Cl$ undoubtedly contains an admixture of the product of its allylic rearrangement, i.e. $(CH_3)_3SiCHClCH{=}CH_2$, since frequencies of 1633 and 3082 cm^{-1} are observed in the Raman spectrum. The first frequency is characteristic of the β-position of a multiple bond relative to the silicon atom, and the second of a terminal $= CH_2$ group.

Methyl- and ethyldichlorosilane, as well as trichlorosilane, add to propargyl chloride considerably more vigorously than to allyl chloride ([9]). Finally, it was established that trichlorosilane also adds to propargyl bromide; however, only one compound could be isolated in this case:

$$BrCH_2C{\equiv}CH + HSiCl_3 \rightarrow \underset{\displaystyle CH_2}{\overset{}{Cl_3Si\underset{\|}{C}{-}CH_2Br}}$$

Thus, silicon hydrides, on adding to propargyl chloride, form equal amounts of two compounds corresponding to different modes of their addition.

Experimental Part

Addition of trichlorosilane to propargyl chloride.

In a one-liter flask equipped with a reflux condenser, thermometer, and dropping funnel, a portion ($\sim$ 20 ml) of a mixture composed of 223.5 g of $ClCH_2C{\equiv}CH$ and 406.4 g of $HSiCl_3$ was placed. After the addition of 1 ml of a 0.1 *N* solution of H_2PtCl_6 in isopropyl alcohol and boiling of the mixture for three hours, its boiling temperature rose from 35 to 100°. The remainder of the mixture was added at such a rate that the boiling temperature of the contents of the flask did not fall below $\sim$ 80°. When the boiling temperature reached 120°, boiling was stopped and the contents of the flask were first distilled under vacuum and then on a 30-plate column.

200 g (yield 32%) of β-chloroisopropenyltrichlorosilane were obtained,

$$Cl_3SiC(=CH_2)CH_2Cl,$$

b.p. 165.2° (760); n_D^{20} 1.4810; d_4^{20} 1.4000, MR_D found 42.68; calculated 42.80. Literature data ([10]): b.p. 164° (750 mm); n_4^{20} 1.4794; d_4^{20} 1.3967. See Fig. 1A for the IR spectrum.

Raman spectrum (cm^{-1}): $Cl_3SiC(=CH_2)CH_2Cl$. 170(2), 196(5 sh), 222(2), 264(0), 292(3), 359(6 sh), 381(0), 457(19), 496(5), 591(1 sh), 647(1), 695(1 sh), 723(0), 760(6 sh), 939(1), 969(0), 1114(0), 1144(0), 1170(0), 1192(0), 1244(1), 1269(1), 1305(1), 1361(1), 1418(5 sh), 1447(0), 1611(4), 2878(0), 2945(3), 2970(4 sh), 2997(3), 3086(1), 3086(4 sh).

Also obtained were 201 g (yield 32%) of γ-chloropropenyltrichlorosilane ($Cl_3SiCH{=}CHCH_2Cl$), b.p. 176.5° (748 mm); n_D^{20} 1.4855, d_4^{20} 1.3951, MR_D found 43.18, calculated 42.80. See Fig. 1B for the IR spectrum.

Raman spectrum (cm^{-1}): $Cl_3SiCH{=}CHCH_2Cl$. 153(3), 173(4 sh), 203(1), 242(1), 314(2), 336(3), 400(0), 442(10), 495(2), 547(1), 590(0 sh), 696(8 sh), 765(1), 820(1), 933(0), 987(0), 1064(0), 1144(0), 1239(1), 1270(1 sh), 1316(8), 1421(2), 1625(10), 2878(1 sh), 2940(2), 2959(0), 3004(2 sh).

Addition of methyldichlorosilane to propargyl chloride.

In the apparatus described above, gentle heating of a small portion (~ 20 ml) of a mixture composed of 61 g of propargyl chloride and 94 g of methyldichlorosilane causes a vigorous reaction with a rapid rise of the temperature to ~ 120°. The remainder of the mixture is added at such a rate that the boiling temperature of the contents of the flask does not fall below ~ 70°. The reaction mixture is then boiled for about an hour and distilled under vacuum. Repeated rectification on a column gave 55 g (yield 35.5%) of

$$\begin{array}{c} CH_3Cl_2SiCCH_2Cl \\ \| \\ CH_2 \end{array}$$

b.p. 163.8° (735 mm);

$$n_D^{20}\ 1.4730, \quad d_4^{20}\ 1.2156, \quad MR_D \text{ found } 43.75, \text{ calculated } 43.17.$$

$$\begin{array}{c} CH_2 \\ \| \\ Cl_2CH_3SiC{-}CH_2Cl \end{array}$$

Raman spectrum (cm^{-1}): $Cl_2CH_3SiC{=}CH_2CH_2Cl$, 152(2), 176(1), 210(4 b), 229(1), 287(0), 309(1), 331(1), 370(0), 396(2), 438(0), 468(10 b), 495(10), 558(1 b), 610(1), 679(10 b), 741(5), 762(6 b), 932(1), 956(0), 995(0), 1112(0), 1146(1), 1173(0), 1239(0), 1270(1), 1301(2), 1336(1), 1410(7 b), 1609(4), 1640(4), 2914(10), 2985(4 b), 3021(1), 3078(1 b).

The frequency 1640 (4) indicates the presence of an impurity of an unknown unsaturated compound. In addition, 52 g was isolated (yield 33.5%). $Cl_2CH_3SiCH{=}CHCH_2Cl$, b.p. 176.8° (745 mm); n_D^{20} 1.4782; d_4^{20} 1.2403; MR_D found 43.28, calculated 43.17.

Fig. 1. IR spectra.
A $-Cl_3SiC(=CH_2)CH_2Cl$; $-Cl_3SiCH{=}CHCH_2Cl$; $-(CH_3)_3SiC(=CH_2)CH_2CH_3$; $-(CH_3)_3SiC(=CH_2)CH_2Cl$; $-(CH_3)_3SiCH{=}CHCH_2CH_3$. The ordinate is percent transmittance; the abscissa is cm^{-1}.

Raman spectrum (cm^{-1}): $CH_3Cl_2SiCH{=}CHCH_2Cl$. 177(2); 196(1); 215(1); 243(1 b); 297(1 b); 334(1); 349(2); 400(1 b); 426(0); 456(5); 485(2); 500(1); 527(1 b); 556(0); 680(8 b); 719(0); 751(1 b); 780(1 b); 829(1 b); 931(0); 992(1); 1059(0); 1144(3 b); 1175(0); 1214(1 b); 1244(1); 1270(3); 1294(0); 1315(5); 1408(1); 1423(2); 1442(0); 1622(10 b); 2890(0); 2919(10); 2949(1); 2967(1); 2993(8 b); 3029(0).

Methylation of *β*-chloroisopropenyltrichlorosilane. To CH_3MgCl, prepared from 24 g of magnesium in 0.4 l of ether, 65 g of

$$\begin{array}{c} Cl_3SiCCH_2Cl \\ \| \\ CH_2 \end{array}$$

was added. After two hours of boiling, the contents of the flask were decomposed with water. The ether layer was dried over $CaCl_2$, and the ether was distilled off from it. Rectification of the liquid residue on a column gave 13 g (yield 33%) of

$$\begin{array}{c} (CH_3)_3SiCCH_2CH_3 \\ \| \\ CH_2 \end{array}$$

b.p. 109° (764 mm); n_D^{20} 1.4200, d_4^{20} 0.7412, MR_D found 43.81, calculated 43.20. Literature data ([10]): b.p. 110° (771 mm); n_D^{20} 1.4195; d_4^{20} 0.7482. For the IR spectrum see Fig. 1 .

$$\begin{array}{c} CH_2 \\ \| \\ (CH_3)_3SiCCH_2CH_3 \end{array}$$

Raman spectrum (cm^{-1}): $(CH_3)_3SiCCH_2CH_3$. 158(3 very broad); 212(4 broad); 235(3); 338(1 broad); 379(2 broad); 515(1 broad); 568(4 broad); 610(9); 652(2); 695(4); 757(1); 792(0); 835(1 broad); 884(1); 930(1); 1011(2); 1052(1); 1075(1); 1137(2 broad); 1181(0); 1202(2 broad); 1260(2 broad); 1320(1 broad); 1415(8 broad); 1454(2); 1607(1); 2904(10 broad); 2945(1); 2968(10 broad); 3060(0).

In addition, 21 g (yield 45.5%) of

$$\begin{array}{c} CH_2 \\ \| \\ (CH_3)_3SiCCH_2Cl \end{array}$$

was obtained, b.p. 141.8° (766 mm); n_D^{20} 1.4491, d_4^{20} 0.9048, MR_D found 44.10, calculated 43.91. See the IR spectrum in Fig. 1 G.

$$\begin{array}{c} CH_2 \\ \| \\ (CH_3)_3SiCCH_2Cl \end{array}$$

Raman spectrum (cm^{-1}): $(CH_3)_3SiCCH_2Cl$. 152(3); 223(5 broad); 245(1); 299(1); 343(0); 365(1); 488(7); 560(8 broad); 612(10); 633(1); 670(3 broad); 698(4 broad); 741(3 very broad); 766(4); 846(0); 932(1); 1138(2 broad); 1195(2 very broad); 1233(1); 1260(2 broad); 1414(4 broad); 1446(0); 1609(3 broad); 2904(20); 2965(20 broad); 3068(0).

Methylation of γ-chloropropenyltrichlorosilane. Under the conditions of the preceding experiment, from 42 g of $Cl_3SiCH{=}CHCH_2Cl$ and CH_3MgCl, 9 g (yield 35%) of $(CH_3)_3SiCH{=}CHCH_2CH_3$ was obtained, b.p. 111.5° (744 mm); n_D^{20} 1.4170, d_4^{20} 0.7317, MR_D found 44.10; calculated 43.70. See the IR spectrum in Fig. 1 D.

Raman spectrum (cm^{-1}): $(CH_3)_3SiCH{=}CHCH_2CH_3$. 210(very broad); 229(1 broad); 267(0); 330(0); 377(2 broad); 620(10); 697(3 broad); 732(0); 810(0); 837(1 broad); 902(1); 1029(1 broad); 1074(1); 1137(2 broad); 1200(2 broad); 1261(10 broad); 1307(4); 1325(4); 1380(1); 1414(2); 1438(2); 1460(1); 1622(8); 2905(10 broad); 2943(1); 2970(9 broad).

In addition, 12 g (yield 36%) of $(CH_3)_3SiCH{=}CHCH_2Cl$ was obtained, b.p. 145° (758 mm); n_D^{20} 1.4465; d_4^{20} 0.8951; MR_D found 44.35; calculated 43.91.

Raman spectrum (cm^{-1}): $(CH_3)_3SiCH{=}CHCH_2Cl$. 147(1); 170(0); 201(4 broad); 220(3); 336(3); 390(3); 488(0); 531(0 broad); 610(7); 632(1); 666(9 broad); 695(2 broad); 745(1 broad); 798(1 broad); 835(1); 986(0); 1053(1 broad); 1079(0); 1109(1 broad); 1137(4 broad); 1191(2 broad); 1237(2); 1247(1); 1266(2 broad); 1293(1); 1314(1 broad); 1376(1); 1406(2); 1430(0); 1615(10); 1633(3); 2900(10 broad); 2959(9 broad); 3007(1 broad); 3082(1).

β-Trichlorosilylallyl bromide

$$\begin{array}{c} Cl_3SiCCH_2Br \\ \| \\ CH_2 \end{array}$$

A mixture consisting of 32 g of propargyl bromide, 37 g of trichlorosilane, and 2 ml of a 0.1 *N* solution of H_2PtCl_6 in isopropyl alcohol was boiled for 20 h, with interruptions overnight. The temperature of the mixture thereby rose from 31 to 145°. After vacuum distillation and rectification on a column, 21 g (yield 30%) of

$$\begin{array}{c} Cl_3SiCCH_2Br \\ \| \\ CH_2 \end{array}$$

was obtained, b.p. 183.1° (751 mm); n_D^{20} 1.4980; d_4^{20} 1.5983. MR_D found 46.66, calculated 45.64.

$$\begin{array}{c} CH_2 \\ \| \\ Cl_3SiC{-}CH_2Br \end{array}$$

Raman spectrum (cm^{-1}): $Cl_3SiC{-}CH_2Br$.* 150(1 broad); 169(1); 193(10 broad); 217(1); 243(0); 311(1); 355(1 broad); 414(0); 436(10); 482(doublet); 512(0); 568(2); 609(4 broad); 662(2); 692(0); 724(2); 756(1 broad); 812(0 broad); 933(0); 962(0); 1063(0 broad); 1121(2); 1152(0); 1215(5 broad); 1240(0); 1260(0); 1314(3); 1413(2); 1614(8 broad); 2941(0); 2965(2); 2991(1); 3018(1 broad); 3077(1 broad).

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* The recording and interpretation of the Raman and IR spectra were performed by L. A. Leites.

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