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Abstract

Full Text

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Academician A. V. TOPCHIEV, N. S. NAMETKIN, and S. G. DURGARYAN

ON THE ADDITION OF TRICHLOROSILANE TO DIALKYL-(PHENYL, CHLORO)-DIALLYLSILANES IN THE PRESENCE OF $H_2PtCl_6 \cdot 6H_2O$

The study of the possibility of obtaining organosilicon compounds by the addition of hydrosilanes to various unsaturated compounds has in recent years attracted the attention of a large number of investigators. Benzoyl peroxide, acetyl peroxide ([1–6]), platinum on carbon, chloroplatinic acid ([7–13]), and others ([9–14]) are used as catalysts for this reaction.

In 1953, Kanazashi ([15]) described the reaction of alkylvinylsilanes with trichlorosilane in the presence of acetyl peroxide, proceeding according to the schemes:

$$R_3SiCH{=}CH_2 + HSiCl_3 \rightarrow R_3SiCH_2CH_2SiCl_3.$$

$$R_2Si{\begin{matrix}CH{=}CH_2\\CH{=}CH_2\end{matrix}} + 2HSiCl_3 \rightarrow R_2Si{\begin{matrix}CH_2CH_2SiCl_3\\CH_2CH_2SiCl_3\end{matrix}}$$

In the reaction of trichlorosilane with vinyltrichlorosilane, styrene, and octene-1 in the presence of $NiCl_2 \cdot 5C_5H_5N$, addition of trichlorosilane was observed both according to Markovnikov' s rule and against this rule ([16]). For example, in the reaction of trichlorosilane with vinyltrichlorosilane two isomers were isolated:

$$Cl_3SiCH{=}CH_2 + HSiCl_3 \rightarrow Cl_3SiCH_2CH_2SiCl_3 + Cl_3SiCH(CH_3)SiCl_3.$$

In the addition of methyldichlorosilane to butyl acrylate in the presence of platinized carbon, an isomer was also isolated ([17]):

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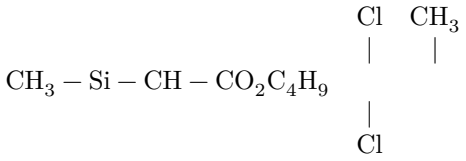

We studied the addition of trichlorosilane to various diallyl derivatives of silicon in the presence of chloroplatinic acid. Under the reaction conditions we selected, addition of trichlorosilane was observed both at one double bond and at two double bonds. The overall yield of addition products varied from 55 to 75% (see Table 1).

The investigation carried out showed that the activity of the double bond in diallyl derivatives of silicon toward addition reactions depends on the pri-

Table 1

Compound	b.p., °C/mm	Cl analysis: found	Cl analysis: calculated	Yield, %
$(CH_3)_2(CH_2{=}CHCH_2)Si(CH_2CH_2CH_2SiCl_3)_2$	158/7	38.43	38.66	28.5
$(C_2H_5)_2(CH_2{=}CHCH_2)Si(CH_2CH_2CH_2SiCl_3)_2$	124/2	34.80	35.05	29.0
$(C_3H_7)_2(CH_2{=}CHCH_2)Si(CH_2CH_2CH_2SiCl_3)_2$	167/3	32.70	32.84	29.7
$(C_4H_9)_2(CH_2{=}CHCH_2)Si(CH_2CH_2CH_2SiCl_3)_2$	188/3	26.80	27.04	28.8
$(C_6H_5)_2(CH_2{=}CHCH_2)Si(CH_2CH_2CH_2SiCl_3)_2$	222/2	26.20	26.37	17.6
$C_6H_5(CH_3)(CH_2{=}CHCH_2)Si(CH_2CH_2CH_2SiCl_3)_2$	180/2	31.67	31.80	13.8
$Cl_2(CH_2{=}CHCH_2)Si(CH_2CH_2CH_2SiCl_3)_2$	156/4	38.53	38.48	38.61	8.3
$(CH_3)_2Si(CH_2CH_2CH_2SiCl_3)_2$	163/5	51.93	52.13	51.77	27.9
$(C_2H_5)_2Si(CH_2CH_2CH_2SiCl_3)_2$	176/3	48.49	48.83	48.47	32.0
$(C_3H_7)_2Si(CH_2CH_2CH_2SiCl_3)_2$	198/3	45.79	45.47	45.56	32.6
$(C_4H_9)_2Si(CH_2CH_2CH_2SiCl_3)_2$	210/2	42.49	42.82	42.98	34.1
$(C_6H_5)_2Si(CH_2CH_2CH_2SiCl_3)_2$	268/2	39.72	39.68	39.77	52.4
$C_6H_5(CH_3)Si(CH_2CH_2CH_2SiCl_3)_2$	202/2	44.78	44.60	44.97	41.4
$Cl_2Si(CH_2CH_2CH_2SiCl_3)_2$	218/2	62.40	62.51	62.77	67.3

the nature of the atoms and groups bonded to the silicon atom. With increasing alkyl radicals, and also upon replacing them by a phenyl radical or a chlorine atom, the activity of the double bond in dialkyl-(phenyl, chloro)-diallylsilanes increases.

For example, trichlorosilane adds to dimethyl-, diethyl-, dipropyl-, and dibutyldiallylsilane with an overall yield of addition products of 56 to 63%, and to diphenyl- and dichlorodiallylsilane with overall yields of 70 and 75%, respectively (Table 1). In the reaction of the chloro derivatives obtained by addition of trichlorosilane to dialkyl-(phenyl, chloro)-diallylsilanes at the two double bonds with lithium alkyls, a series of organosilicon hydrocarbons was obtained.

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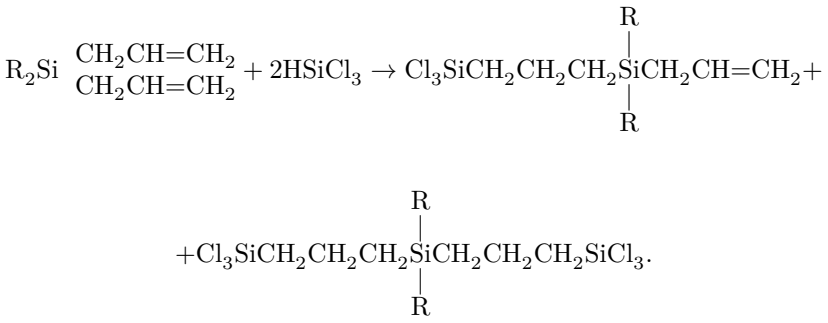
The infrared spectra* of these organosilicon hydrocarbons showed that addition of trichlorosilane to dialkyl-(phenyl, chloro)-diallylsilanes proceeds against Markovnikov' s rule according to the following scheme:



* The spectral study was carried out by Yu. P. Egorov.

Experimental Part

Dialkyl-(phenyl, chloro)-diallylsilanes were obtained by the interaction of allylmagnesium bromide with the corresponding chlorinated silicon derivatives.

Addition of trichlorosilane to diallyl derivatives of silicon. The corresponding diallyl derivative of silicon and chloroplatinic acid—a 0.1 M solution of $H_2PtCl_6 \cdot 6H_2O$ in isopropyl alcohol—were charged into a three-necked flask equipped with a stirrer, a reflux condenser, and a dropping funnel. With stirring, trichlorosilane was added slowly. Heating was carried out at 50° for 10 h and then at 80° for 2 h.

1. **Addition of trichlorosilane to dimethyldiallylsilane.** From 42 g (0.3 mol) of dimethyldiallylsilane and 95 g (0.7 mol) of trichlorosilane, in the presence of 1 ml of chloroplatinic acid solution, there were obtained 23.8 g (yield 28.5%) of dimethylallyl-(trichlorosilylpropyl)-silane $[(CH_3)_2(CH_2{=}CHCH_2)SiCH_2CH_2CH_2SiCl_3]$ and 34.5 g (yield 27.9% of theory) of dimethyldi-(trichlorosilylpropyl)-silane $[(CH_3)_2Si(CH_2CH_2CH_2SiCl_3)_2]$.
2. **Addition of trichlorosilane to diethyldiallylsilane.** From 42 g (0.25 mol) of diethyldiallylsilane and 82 g (0.6 mol) of trichlorosilane, in the presence of 1 ml of chloroplatinic acid solution, there were obtained 22.0 g (yield 29.0%) of diethylallyl-(trichlorosilylpropyl)-silane $[(C_2H_5)_2(CH_2{=}CHCH_2)SiCH_2CH_2CH_2SiCl_3]$ and 33.1 g (yield 30.2% of theory) of diethyldi-(trichlorosilylpropyl)-silane $[(C_2H_5)_2Si(CH_2CH_2CH_2SiCl_3)_2]$.
3. **Addition of trichlorosilane to dipropyldiallylsilane.** From 39 g (0.2 mol) of dipropyldiallylsilane and 82 g (0.6 mol) of trichlorosilane,

in the presence of 1 ml of chloroplatinic acid solution, there were obtained 19.7 g (yield 29.7%) of dipropylallyl-(trichlorosilylpropyl)-silane $[(C_3H_7)_2(CH_2{=}CHCH_2)SiCH_2CH_2CH_2SiCl_3]$ and 30.4 g (yield 32.6% of theory) of dipropyldi-(trichlorosilylpropyl)-silane $[(C_3H_7)_2Si(CH_2CH_2CH_2SiCl_3)_2]$.

4. **Addition of trichlorosilane to dibutyldiallylsilane.** From 45 g (0.2 mol) of dibutyldiallylsilane and 82 g (0.6 mol) of trichlorosilane, in the presence of 1 ml of chloroplatinic acid solution, there were obtained 20.7 g (yield 28.8%) of dibutylallyl-(trichlorosilylpropyl)-silane $[(C_4H_9)_2(CH_2{=}CHCH_2)SiCH_2CH_2CH_2SiCl_3]$ and 33.7 g (yield 34.1% of theory) of dibutyldi-(trichlorosilylpropyl)-silane $[(C_4H_9)_2Si(CH_2CH_2CH_2SiCl_3)_2]$.

5. **Addition of trichlorosilane to diphenyldiallylsilane.** From 40 g (0.15 mol) of diphenyldiallylsilane and 68 g (0.5 mol) of trichlorosilane, in the presence of 1 ml of chloroplatinic acid solution, there were obtained 10.6 g (yield 17.6%) of diphenylallyl-(trichlorosilylpropyl)-silane $[(C_6H_5)_2(CH_2{=}CHCH_2)SiCH_2CH_2CH_2SiCl_3]$ and 42.3 g (yield 52.4% of theory) of diphenyldi-(trichlorosilylpropyl)-silane $[(C_6H_5)_2Si(CH_2CH_2CH_2SiCl_3)_2]$.

6. **Addition of trichlorosilane to phenylmethyldiallylsilane.** From 42 g (0.2 mol) of phenylmethyldiallylsilane and 82 g (0.6 mol) of trichlorosilane, in the presence of 1 ml of chloroplatinic acid solution, there were obtained 9.7 g (yield 13.8%) of phenylmethylallyl-(trichlorosilylpropyl)-silane $[C_6H_5(CH_3)(CH_2{=}CHCH_2)SiCH_2CH_2CH_2SiCl_3]$ and 40.7 g (yield 41.4% of theory) of diphenyldi-(trichlorosilylpropyl)-silane $[C_6H_5(CH_3)Si(CH_2CH_2CH_2SiCl_3)_2]$.

7. **Addition of trichlorosilane to dichlorodiallylsilane.** From 36 g (0.2 mol) of dichlorodiallylsilane and 82 g (0.6 mol) of trichlorosilane, in the presence of 1 ml of chloroplatinic acid solution, there were obtained 5.2 g (yield 8.3%) of dichloroallyl-(trichlorosilylpropyl)-silane $[Cl_2(CH_2{=}CHCH_2)SiCH_2CH_2CH_2SiCl_3]$ and 60.8 g (yield

67.3%) dichlorodi-(trichlorosilylpropyl)silane $[Cl_2Si(CH_2CH_2CH_2SiCl_3)_2]$. Analyses for Cl were performed by I. I. Karelova.

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