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Abstract

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SYNTHESIS AND SOME TRANSFORMATIONS OF SILANOLS OF THE VINYLACETYLENE SERIES

The most important and promising field of the chemistry of organosilicon compounds is that of oxygen-containing compounds, among which polyorganosiloxanes, silanols, and organosilicon alcohols are of special interest.

In earlier investigations we described the synthesis and transformations of various saturated and acetylenic organosilicon alcohols ([1]) and silanols ([2]). In the literature ([3],[4]) there are some indications of the interaction of Grignard reagents with polyorganosiloxanes; however, there are no data whatever on the reaction of polyorganosiloxanes with Iotsich reagents. In the present communication only the first results are given of a systematic study of the reaction of various Iotsich reagents with diverse polyorganosiloxanes.

In the present investigation, the interaction of the Iotsich reagent with polyorganosiloxanes was studied using as an example the reaction of magnesium bromovinylacetylene with polydimethyl- and polydiethylsiloxanes:

$$\mathrm{CH_2{=}CH{-}C{\equiv}CMgBr + (RR'SiO)_x \rightarrow CH_2{=}CH{-}C{\equiv}C(R)_2SiOH},$$

where R and R' are like and unlike radicals ($\mathrm{H, CH_3, C_2H_5}$, etc.).

To prove the structure of the compounds obtained, a reverse synthesis of dimethylvinylethynylsilanol was carried out by saponification of dimethylvinylethynyldichlorosilane:

$$\mathrm{CH_2{=}CH{-}C{\equiv}C(CH_3)_2SiCl + NaOH \rightarrow CH_2{=}CH{-}C{\equiv}C(CH_3)_2SiOH + NaCl}.$$

Thus, two methods were found for preparing vinylacetylenic silanols, which constitute a new class of organosilicon compounds.

Dimethylvinylethynylchlorosilane was prepared by the reaction of magnesium bromovinylacetylene with dimethyldichlorosilane:

$$\mathrm{CH_2{=}CH{-}C{\equiv}CMgBr + (CH_3)_2SiCl_2 \rightarrow CH_2{=}CH{-}C{\equiv}C(CH_3)_2SiCl + MgClBr}.$$

In addition, the synthesis of dimethylvinylethynylchlorosilane was carried out by us according to the following scheme:

$$CH_2{=}CH{-}C{\equiv}C(CH_3)_2SiOH + SOCl_2 \rightarrow CH_2{=}CH{-}C{\equiv}C(CH_3)_2SiCl + SO_2 + HCl.$$

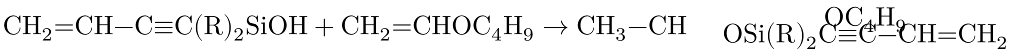
Under the action of thionyl chloride on dimethylvinylethynylsilanol, cleavage of the Si–C bond is not observed.

Boiling of vinylacetylenic silanols in the presence of potash, as well as slow distillation of these compounds, leads to their dehydration to the corresponding vinylacetylenic disiloxanes:

$$2CH_2{=}CH{-}C{\equiv}C(R)_2SiOH \rightarrow [CH_2{=}CH{-}C{\equiv}C(R)_2Si]_2O + H_2O.$$

Vinylacetylenic silanols readily add to vinyl alkyl ethers in the presence of traces of concentrated hydrochloric acid with forma-

with the formation of organosilicon acetals of the vinylacetylene series, not described in the literature:



$$CH_2{=}CH{-}C{\equiv}C(R)_2SiOH + CH_2{=}CHOC_4H_9 \rightarrow CH_3{-}CH\begin{smallmatrix}OC_4H_9\\ OSi(R)_2C{\equiv}C{-}CH{=}CH_2\end{smallmatrix}$$

Vinylacetylene silanols, chlorosilanes, disiloxanes, and acetals are readily polymerized compounds. Their polymerization and copolymerization are being studied.

Experimental Part

Synthesis of dimethylvinylethynylsilanol. To the Iotsich reagent, prepared from 163.5 g (1.5 g-mol) of ethyl bromide, 36.5 g (1.5 gram-atoms) of magnesium in 400 ml of abs. ether, and 78 g (1.5 g-mol) of vinylacetylene, with heating on a water bath and stirring, 50 g of polydimethylsiloxane was added. The mixture was heated with stirring for another 10–12 hr. Then, with cooling to 0°, it was carefully decomposed with 10% HCl, and after the usual workup 36.7 g (43.4%) of a substance was isolated, b.p. 56–57°/10 mm, n_D^{20} 1.4800, d_4^{20} 0.8943; MR found 40.09, calculated 38.00.

Found, %: Si 22.43
$C_6H_{10}SiO$. Calculated, %: Si 22.25

In an analogous manner ethylvinylethynylsilanol and diethylvinylethynylsilanol were obtained; their physicochemical constants are presented in Table 1. Vinylacetylene silanols are colorless liquids with a carbinol odor, readily soluble in most organic solvents and poorly soluble in water. On storage in the light they turn yellow, liberate water, and polymerize.

Table 1

Physicochemical constants of the compounds obtained

No.	Formula of compound	B.p., °C / mm Hg	n_D^{20}	d_4^{20}	MR found	MR calc.	Si, % found	Si, % calc.	Yield, %
1	$(CH_2{=}CH{-}C{\equiv}C)(CH_3)_2SiOH$	56-57/10	1.4800	0.8943	40.09	38.00	22.43	22.25	43.4
2	$(CH_2{=}CH{-}C{\equiv}C)(C_2H_5)SiOH$	64-65/22	1.4716	0.8960	39.41	39.26	22.55	22.25	23.2
3	$(CH_2{=}CH{-}C{\equiv}C)(C_2H_5)_2SiOH$	60-62/13	1.4875	0.9181	48.62	47.28	18.51	18.20	30.0
4	$(CH_2{=}CH{-}C{\equiv}C)(CH_3)_2SiCl$	53-54/26	1.4694	0.9570	42.15	41.72	19.23	19.42	53.4
5	$[(CH_2{=}CH{-}C{\equiv}C)(CH_3)_2Si]_2O$	98.5-100.5/12	1.4730	0.8981	73.80	72.54	24.21	23.96	33.3
6	$(CH_2{=}CH{-}C{\equiv}C)(CH_3)_2SiOCH(CH_3)OC_3H_7$-*iso*	71.5-73/8	1.4504	0.8846	64.56	63.14	13.02	13.23	56.4
7	$(CH_2{=}CH{-}C{\equiv}C)(CH_3)_2SiOCH(CH_3)OC_4H_9$-*n*	111-113/26	1.4511	0.8819	69.12	67.77	12.37	12.41	32.9
8	$(CH_2{=}CH{-}C{\equiv}C)(C_2H_5)_2SiOCH(CH_3)OC_4H_9$-*n*	90-91/9	1.4558	0.8816	78.52	77.03	11.20	11.04	61.4

Synthesis of dimethylvinylethynylchlorosilane. In a 50-ml synthesis apparatus were placed 19 g (0.15 g-mol) of freshly distilled dimethylvinylethynylsilanol and 1 g of pyridine. With cooling and stirring, 26 g (0.21 g-mol) of thionyl chloride was added dropwise. The mixture was stirred for 10 hr with cooling and for 12 hr while being heated to 60°, and then distilled in vacuum. This gave 11 g (53.4%) of a substance with b.p. 53-54°/26 mm, n_D^{20} 1.4694, d_4^{20} 0.9570; MR found 42.15, calculated 41.72.

Found, %: Si 19.23
C_6H_9SiCl. Calculated, %: Si 19.42

Dimethylvinylethynylchlorosilane was also obtained by the reaction of vinylacetylene magnesium bromide with dimethyldichlorosilane in a yield of 19.4%.

Synthesis of dimethylvinylethynylsilanol. Into a synthesis apparatus of 0.5 l capacity were placed 11.2 g (0.075 g-mole) of dimethylvinylethynylchlorosilane, 2 drops of phenolphthalein, and 50 ml of absolute ether. The mixture was cooled to −5° and, with vigorous stirring, 0.25 N NaOH solution was gradually added until a faint-pink, persistent coloration of the mixture appeared. The aqueous layer was separated from the ether layer, and after the usual workup of the latter, 6.2 g (65.5%) of dimethylvinylethynylsilanol and 2.1 g (22%) of tetramethylbis-(vinylethynyl)-disiloxane were isolated.

Synthesis of tetramethylbis-(vinylethynyl)-disiloxane. Into a 50 ml round-bottom flask fitted with a reflux condenser were placed 35 g (0.28 g-mole) of dimethylvinylethynylsilanol and 5 g of calcined potash. The mixture was heated at 80-90° for 1 hour, then cooled, filtered, and distilled in vacuo. Distillation gave 12 g of dimethylvinylethynylsilanol, b.p. 60-61°/12 mm, with n_D^{20} 1.4780, and 11 g (33.3%) of tetramethyl-di-(vinylethynyl)-disiloxane, b.p. 98.5-100.5°/12 mm, n_D^{20} 1.4730, d_4^{20} 0.8911; MR found 73.80, calculated 72.54.

Found, %: Si 24.21

$C_{12}H_{18}Si_2O$. Calculated, %: Si 23.96

Synthesis of diethylvinylethynylsilyl butyl acetal. Into a synthesis apparatus was placed a mixture of 4 g (0.03 g-mole) of diethylvinylethynylsilanol and 3.0 g (0.03 g-mole) of vinyl butyl ether. Then, with stirring, one drop of conc. HCl was added. The temperature of the mixture rose sharply to 49°. To complete the reaction, the mixture was heated for another 1.5-2 hours at 60-70°. The reaction mixture was then neutralized with calcined potash, filtered, and distilled in vacuo. Distillation yielded 4.21 g (61.4%) of a substance with b.p. 90-91°/9 mm, n_D^{20} 1.4558, d_4^{20} 0.8816, MR found 78.52, calculated 77.03.

Found, %: Si 11.20

$C_{14}H_{16}SiO_2$. Calculated, %: Si 11.04

In an analogous manner, dimethylvinylethynylsilyl isopropyl acetal and dimethylvinylethynylsilyl butyl acetal were obtained. Organosilicon vinylacetylene acetals are colorless liquids, soluble in organic solvents and insoluble in water; they have a pleasant odor, and on prolonged storage they turn yellow and polymerize.

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