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Abstract

Full Text

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Studies in the Synthesis and Transformations of Unsaturated Organosilicon Compounds

Synthesis of Branched Silicon Hydrocarbons of the Diacetylene Series

(Presented by Academician B. A. Arbuzov, 16.VI.1961)

In our previous studies, we investigated the synthesis and reactivity of organosilicon acetylenic and diacetylenic alcohols ([1]) and silicon hydrocarbons of the vinylacetylene series ([2]).

In the present work, with the aim of further developing our investigations, a new method is described for the synthesis of branched diacetylenic silicon hydrocarbons from halogen derivatives of organosilicon acetylenic alcohols and tert-butylacetylene according to the scheme:

$$\mathrm{R{-}COH{-}\underset{\mathrm{CH_3}}{C{\equiv}C}{-}Si(CH_3)_3} \xrightarrow{\mathrm{HCl}} \mathrm{R{-}\underset{\mathrm{CH_3}}{CCl}{-}C{\equiv}C{-}Si(CH_3)_3} \xrightarrow{(\mathrm{CH_3})_3C{-}C{\equiv}CMgBr} \longrightarrow (\mathrm{CH_3})_3C{-}C{\equiv}C{-}\underset{\mathrm{R}}{\overset{\mathrm{CH_3}}{\overset{|}{C}}}{-}C{\equiv}C{-}Si(CH_3)_3,$$

where $R = CH_3$; C_2H_5; and tert-C_4H_9.

The presence of two triple bonds in the diacetylenic silicon hydrocarbons obtained was proved by hydrogenating them to saturation. As a result of the investigations carried out, we have for the first time obtained and characterized three representatives of organosilicon acetylenic chlorides ([1–3]) and three representatives of branched diacetylenic silicon hydrocarbons ([4–6]), the constants of which are given in Table 1.

Experimental Part

In the synthesis of acetylenic chlorides, the reaction was carried out in a three-necked round-bottom flask of 150 ml capacity, equipped with a reflux condenser and a thermometer.

Synthesis of 5-trimethylsilyl-3-methylpent-4-yn-3-yl chloride (1). Into the reaction flask containing 21.25 g of 5-trimethylsilyl-3-methylpent-4-yn-3-ol (b.p. 61-62°/2 mm), gaseous hydrogen chloride was passed at 30°. At this temperature the temperature in the reaction mixture rose to 48°. After 45 min, two layers had formed in the flask and the reaction was stopped. The upper layer was separated from the lower (aqueous) layer, dried over $CaCl_2$, and distilled in vacuo. This gave 15 g (63.8%) of 5-trimethylsilyl-3-methylpent-4-yn-3-yl chloride with b.p. 38-40° (2 mm). By this method two further representatives of acetylenic monochlorides of different structure were obtained. The constants of all three chlorides obtained are given in Table 1.

Synthesis of 1-trimethylsilyl-3,6,6-trimethyl-3-ethylheptadiyne-1,4 (5). To the Grignard reagent (prepared from 2.4 g

Table 1

No.	Compound	b.p., °C (mm Hg)	d_4^{30}	n_D^{20}	MR_D calc.	MR_D found	Yield, %	C, % calc.	C, % found	H, % calc.	H, % found	Si, % calc.	Si, % found	Cl, % calc.	Cl, % found
1	$(CH_3)_2CCl-C\equiv C-Si(CH_3)_3$	32–35 (5)	0.9043	1.4505	52.03	51.95	55.4	54.96	54.81	8.65	8.67 8.78	16.07	15.41 15.61	20.30	20.47 20.10
2	$CH_3CCl(C_2H_5)-C\equiv CSi(CH_3)_3$	38–40 (2)	0.9011	1.4505	56.66	56.30	63.8	57.24	57.49 57.04	9.07	9.22 9.14	14.87	14.50 14.81	18.80	18.84 18.71
3	$(CH_3)_3C-C(CH_3)Cl-C\equiv CSi(CH_3)_3$	54–55 (2) m.p. 41	–	–	–	–	63.0	60.91	61.10 61.20	9.87	9.12 9.89	12.51	12.36	15.40	15.40 15.60
4	$(CH_3)_3C-C\equiv C-C(CH_3)(CH_3)-C\equiv C-Si(CH_3)_3$	53–54 (4)	0.8245	1.4527	73.36	72.21	50.0	76.28	76.00 76.10	11.20	11.70	12.35	12.20	–	–
5	$(CH_3)_3C-C\equiv C-C(CH_3)(C_2H_5)-C\equiv C-Si(CH_3)_3$	56–58 (2)	0.8035	1.4367	77.99	76.39	59.7	76.84	77.18 77.06	11.29	11.36	11.98	11.65 11.78	–	–

No.	Compound	b.p., °C (mm Hg)	d_4^{30}	n_D^{20}	MR_D calc.	MR_D found	Yield, %	C, % calc.	C, % found	H, % calc.	H, % found	Si, % calc.	Si, % found	Cl, % calc.	Cl, % found
6	$(CH_3)_3C-C\equiv C-C(CH_3)(C(CH_3)_3)-C\equiv C-Si(CH_3)_3$	70–72 (4) m.p. 55	—	—	—	—	45.5	77.77	77.84	11.80	11.70	10.76	10.11	10.25	—

Mg, 10.9 g of C_2H_5Br) over the course of 25 min, with constant stirring and cooling, 8.5 g of tert-butylacetylene in 20 ml of ether was added. After standing for 40 h, the contents of the flask were heated on a water bath to 35° and kept at this temperature until the evolution of ethane ceased. To the resulting complex —magnesium bromo-tert-butylacetylene—1 g of Cu_2Cl_2 and 0.5 g of $HgCl_2$ were added as catalyst[(3)]. After 0.5 h of stirring, the mixture was cooled to −2° and acetylene chloride[(2)] was added to it in an amount of 21.68 g. The contents of the flask were then left at room temperature with stirring for 58 h, after which they were heated for 6 h and decomposed with dilute HCl. The ethereal solution and the extract were dried over ignited Na_2SO_4. After distillation of the ether, double distillation gave 14 g (59.7%) of 1-trimethylsilyl-3,6,6-trimethyl-3-ethylheptadiyne-1,4, b.p. 56–58° (2 mm). By an analogous method, two more representatives of diacetylenic silicon hydrocarbons were obtained, the constants of which are given in Table 1.

Hydrogenation of the diacetylenic silicon hydrocarbon (5)*.
0.2 g of Raney Ni catalyst was taken in 5 ml of methyl alcohol. The mixture was saturated with hydrogen, after which 0.123 g of silicon hydrocarbon (5) was introduced.

In the first 13 min, addition of hydrogen proceeded vigorously and 11 ml was absorbed; thereafter the absorption of hydrogen proceeded very slowly, and a further 34.61 ml of hydrogen was absorbed. In all, 43.61 ml of hydrogen was absorbed. Theoretically, 47 ml of hydrogen is required for complete hydrogenation of two triple bonds.

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* The hydrogenation of the diacetylenic silicon hydrocarbon was carried out in the laboratory of Prof. L. Kh. Freidlin with the participation of I. F. Zhukova, for which we express our gratitude.

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