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Abstract

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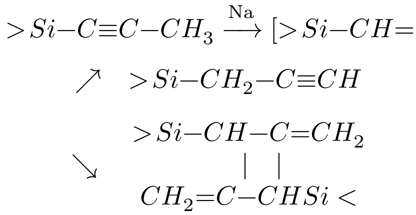
ALLENE-ACETYLENE ISOMERIC TRANSFORMATIONS IN THE ORGANOSILICON SERIES

The isomeric transformations of disubstituted acetylenic hydrocarbons into monosubstituted ones, and vice versa, discovered by A. E. Favorskii (^{1}), as well as the mechanism of these transformations, proceeding through the stage of allenic hydrocarbons, have by now been covered in numerous studies (^{2}). The synthesis of organosilicon acetylenic hydrocarbons has also been described in a number of works ($^{3-8}$); as for the isomeric transformations of acetylenic organosilicon compounds, there is only a single study devoted to this reaction. It was shown (^{7}) that disubstituted organosilicon acetylenic hydrocarbons with the triple bond in the σ-position to silicon (trialkyl-β-methylacetylene silanes), when heated with Na, isomerize to monosubstituted organosilicon acetylenic hydrocarbons, but in low yield, since the α-β-silicon allenic hydrocarbons formed as intermediates undergo cyclodimerization to compounds of type (2).



$$>Si{-}C{\equiv}C{-}CH_3 \xrightarrow{\text{Na}} [>Si{-}CH{=}C{=}CH_2]$$

$$\nearrow\ >Si{-}CH_2{-}C{\equiv}CH \qquad (1)$$

$$\searrow\ \begin{array}{c} >Si{-}CH{-}C{=}CH_2 \\ \quad | \quad | \\ CH_2{=}C{-}CHSi< \end{array} \qquad (2)$$

In the present investigation we obtained, for the first time, β-γ-organosilicon allenic hydrocarbons by condensation of Grignard reagents from α-organosilicon halides with propargyl bromide. It is interesting to note that, in this case, only organosilicon allenic hydrocarbons were obtained in 60–70% yield, probably according to the scheme:

$$>Si{-}CH_2MgCl{+}BrCH_2{-}C{\equiv}CH \rightarrow [BrCH{=}C{=}CH_2] \rightarrow >Si{-}CH_2{-}CH{=}C{=}CH_2.$$

In contrast, in the condensation with propargyl bromide of Grignard reagents from halides not containing silicon, a mixture of acetylenic and allenic hydrocarbons is formed (9). When heated with Na, the β-γ-organosilicon allenic hydrocarbons were converted in high yield (about 40%) into monosubstituted organosilicon acetylenic hydrocarbons with the triple bond in the γ-position to silicon. These organosilicon hydrocarbons gave a white precipitate with an ammoniacal silver nitrate solution. Monosubstituted acetylenic hydrocarbons with the triple bond in the γ-position relative to silicon, unlike organosilicon acetylenic hydrocarbons with the triple bond in the α- and β-positions (3,6), undergo hydration with formation of the corresponding ketones. In particular, we hydrated, in the presence of $HgSO_4$ in methanol solution, $(CH_3)_3Si{-}CH_2{-}CH_2{-}C{\equiv}CH$ and $(CH_3)(C_2H_5)_2Si{-}CH_2{-}CH_2{-}C{\equiv}CH$.

The sodium derivatives of the acetylenic organosilicon compounds readily condensed with haloalkyls:

$$>Si{-}CH_2{-}CH_2{-}C{\equiv}CNa + RCl \rightarrow > Si{-}CH_2{-}CH_2{-}C{\equiv}C{-}R$$

Experimental Part

Trimethylsilylmethylallene (siliconeopentylallene) $(CH_3)_3Si{-}CH_2{-}CH = C = CH_2$ (I). To a Grignard reagent prepared from 26.4 g of Mg and 134.6 g of $(CH_3)_2SiCH_2Cl$ in 350 ml of ether, with stirring for 3 hr, 119 g of propargyl bromide was added. Owing to the strong heating that occurred during addition of the propargyl bromide, the flask had to be cooled vigorously. After completion of the addition of the bromide, the contents of the flask were heated on a water bath for 3 hr. After separation of the residue, the ethereal layer was dried with $CaCl_2$. After removal of the ether, the reaction product, isolated in an amount of 130 g, was fractionated on a column with a glass packing. A 90 g fraction with b.p. 119.5-119.7° was isolated; according to the analytical data (Table 1), and also to the spectral study, it proved to be $(CH_3)_3Si{-}CH_2{-}CH = C = CH_2$. In the Raman spectrum the following frequencies were found (in cm^{-1}): 148 (4 sh), 173(4), 212(4), 240(4), 513(5), 612(8), 698(5 sh), 769(2), 836(3), 872(2), 940(3 sh), 1124(8), 1160(4), 1195(3), 1220(4), 1250(2), 1282(2), 1330(4), 1383(2), 1413(3), 1444(3), 2116(1), 2900(10), 2925(3), 2960(7), 2988(9), 3048(2). In the spectrum of I, as well as of II and III*, a very intense line at 1124 cm^{-1} is observed, corresponding to the (10,11) symmetric vibration of the cumulated bonds. The absence of noticeable lines in the region 1600-1640 cm^{-1} rules out the possibility of formation of diene compounds. At the same time a weak line 2116(1), attributable to the frequency $C \equiv C$ (IV), was found. The impurity (IV) is insignificant, ~ 5%.

Under analogous conditions, **dimethylethylsilylmethylallene** $(CH_3)_2(C_2H_5)Si{-}CH_2{-}CH = C = CH_2$ (II) and **methyldiethylsilylmethylallene** $(CH_3)(C_2H_5)_2Si{-}CH_2{-}CH = C = CH_2$ (III) were also synthesized; their properties are also given in Table 1.

Trimethylsilylethylacetylene $(CH_3)_3Si{-}CH_2{-}CH_2{-}C \equiv CH$ (IV). Into a flask fitted with a reflux condenser were placed 26 g of $(CH_3)_3Si{-}CH_2{-}CH = C = CH_2$, 5 g of finely cut metallic sodium, and 50 ml of *o*-xylene with b.p.

144°**. The contents of the flask were boiled for 10 hr. During this time evolution of hydrogen was observed, and the color of the mixture became brown. The unreacted allenic silicon hydrocarbon and part of the *o*-xylene were distilled off. Then, to isolate the acetylenic silicon hydrocarbon and to quench the excess sodium, the residue was treated first with methyl alcohol and then with water. The organic reaction products were extracted with ether. By fractionation on a column, a 10 g fraction with b.p. 115.5-116° was isolated; the analytical data and properties of this fraction are given in Table 1. In the spectrum of IV the following lines were found (in cm^{-1}): 173(1), 212(2 sh), 241(3 sh), 278(0), 312(1), 336(3), 360(4), 460(4), 575(7), 608(7), 695(5), 835(1 sh), 898(2 sh), 945(2 sh), 1010(4), 1126(4 sh), 1155(3 sh), 1186(3 sh), 1252(3), 1280(1), 1321(3), 1411(4), 1437(2), 2116(10), 2845(3 sh), 2895(10), 2910(3), 2954(8), 3305(2). Characteristic are the frequencies ($C \equiv C$) 2116 and ($\equiv C—H$) 3305 cm^{-1} (^{12}). Under analogous conditions, 4-(dimethylethylsilyl)-1-butyne $(CH_3)_2(C_2H_5)Si—CH_2—CH_2—C \equiv CH$ (V) and (methyldiethylsilyl)-1-butyne $(CH_3)(C_2H_5)_2Si—CH_2—CH_2—C \equiv CH$ (VI) were also obtained; their properties are presented in Table 1. All three representatives of the series of silicon-acetylenic hydrocarbons distilled without polymerization. As for the isomeric allenic silicon hydrocarbons, here only the first member of the series distilled without polymerization.

Siliconeopentyl acetone $(CH_3)_3Si—CH_2—CH_2—C(=O)—CH_3$ (VII). Into a flask fitted with a stirrer and reflux condenser, 50 mg of metallic—

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* The spectra of (II), (III), (V), and (VI) will be published later.

** In subsequent experiments *o*-xylene was replaced by a fraction of distilled kerosene with b.p. 220-230°.

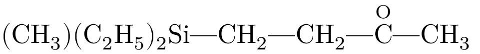
Table 1

No.	Compound	B.p., °C	Press., mm Hg	n_D^{20}	d_4^{20}	*MR* found	*MR* calculated	Yield, %	C, % found	C, % calculated	H, % found	H, % calculated	Si, % found	Si, % calculated
I	$(CH_3)_3Si—CH_2—CH=C=CH_2$	119.5–119.7	755	1.4452	0.7865	42.73	42.56	72	66.12, 66.17	65.59	11.52, 11.72	11.18	21.81, 22.28	22.22
II	$(CH_3)_2(C_2H_5)_2Si—CH_2—CH=C=CH_2$	63	15	1.4632	0.8041	52.87	52.49	79	70.20, 69.90	70.05	11.90, 11.80	11.69	—	—

No.	Compound	B.p., °C	Press., mm Hg	n_D^{20}	d_4^{20}	MR found	MR calculated	Yield, %	C, % found	C, % calculated	H, % found	H, % calculated	Si, % found	Si, % calculated
III	$(CH_3)_2(C_2H_5)Si-CH_2-CH=C=CH_2$	145	752	1.4478	0.7911	47.46	47.87	83	67.62; 67.55	68.51	11.56; 11.53	11.49	19.29; 20.01	20.00
IV	$(CH_3)_3Si-CH_2-CH_2-C\equiv CH$	115.5–116	754	1.4235	0.7620	42.1	42.56	50	66.03; 66.19	66.59	11.22; 11.30	11.18	21.85; 21.67	22.22
V	$(CH_3)_2(C_2H_5)Si-CH_2-CH_2-C\equiv CH$	142	745	1.4310	0.7863	46.41	47.19	50	67.52; 67.42	68.51	11.60; 11.40	11.49	19.78; 19.54	20.00
VI	$(CH_3)(C_2H_5)_2Si-CH_2-CH_2-C\equiv CH$	59–60	15	1.4435	0.8020	51.06	51.81	50	69.71; 69.80	70.05	11.95; 12.02	11.69	17.88	18.18

nol, 10 g of $(CH_3)_3SiCH_2—CH_2—C \equiv CH$, and 0.1 g of $HgSO_4$. With stirring, the contents of the flask were heated to the boiling point of methanol for 3 hours. Every hour an additional 0.01 g of $HgSO_4$ was added to the mixture. The liquid was decanted from the gray precipitate of catalyst, the methanol was distilled off, and the reaction product was fractionated. There were isolated 7 g of a fraction with b.p. 82–83° at 64 mm, $n_D^{20} = 1.4223$, $d_4^{20} = 0.8331$; MR_{found} 44.0; $MR_{\text{calc.}}$ 44.10. The ketone formed a 2,4-dinitrophenylhydrazone with m.p. 102°. The properties given closely coincide with the properties of this ketone obtained by us earlier by another reaction (^{13}).

1-Methyl-diethylsilylbutanone-3



$$(CH_3)(C_2H_5)_2Si—CH_2—CH_2—\overset{O}{C}—CH_3 \qquad \text{(VIII)}$$

was obtained by hydration of $(CH_3)(C_2H_5)_2Si—CH_2—CH_2—C \equiv CH$ under the conditions for the synthesis of (VII), b.p. 85° at 10 mm, n_D^{20} 1.4410, d_4^{20} 0.8624.

Found, %: C 62.09; H 11.98; Si 15.70
$C_9H_{21}SO$. Calculated, %: C 62.34; H 12.21; Si 16.20

The 2,4-dinitrophenylhydrazone of this ketone had m.p. 78–79°.

Found, %: N 16.21
$C_{15}H_{24}SiN_4O_4$. Calculated, %: N 15.90

1-(Methyl-diethyl)-silyloctyne-3 $(CH_3)(C_2H_5)_2Si—CH_2—CH_2—C \equiv C—CH_2—CH_2—CH_2—CH_3$ (IX). To the sodium derivative of $(CH_3)(C_2H_5)_2Si—CH_2—CH_2—C \equiv CH$, obtained by the method described above from 15.4 g of $(CH_3)(C_2H_5)_2Si—CH_2—CH = C = CH_2$, 27.4 g of C_4H_9Br was added. The mixture was boiled for 2 hours. The organic reaction products were extracted with ether. Fractionation gave 6 g of a fraction with b.p. 90–91.5° at 2 mm, $n_D^{20} = 1.4578$; d_4^{20} 0.8227; MR_{found} 69.77; $MR_{\text{calc.}}$ 70.34.

Found, %: C 73.67; H 12.46; Si 13.39
$C_{13}H_{26}Si$. Calculated, %: C 74.19; H 12.45; Si 13.35

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