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Abstract

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SYNTHESIS AND DEHYDRATION OF UNSATURATED SILICON-CONTAINING ALCOHOLS

As is known, the character of the dehydration of alcohols is determined by their structure and by the nature of the alcohol group (tertiary alcohols are usually dehydrated more readily than others; after them come secondary alcohols, and primary alcohols are dehydrated with the greatest difficulty). In the case of silicon-containing alcohols, the influence of the silicon atom is added to the indicated factors.

In a number of studies ([1]) it was shown that alcohols with the alcohol group in the β-position relative to Si, both saturated and unsaturated, depending on their structure, usually undergo, along with dehydration, a greater or lesser β-cleavage. Unsaturated alcohols with the alcohol group in the γ-position, as well as alcohols with the alcohol group in the β-position that do not undergo cleavage, to which the present investigation is devoted, have as yet been studied very little. The first unsaturated alcohols with γ- and β-position of the OH group were synthesized by the reactions ([2,4]):

$$\mathrm{CH_3{-}C(Cl){=}CH{-}CH_2OH + ClSiR_3} \xrightarrow{\mathrm{C_5H_5N}} \mathrm{CH_3{-}C(Cl){=}CH{-}CH_2{-}O{-}SiR_3} \xrightarrow[\mathrm{ClSiR_3}]{\mathrm{Na}}$$

$$\rightarrow \mathrm{R_3Si{-}C(CH_3){=}CH{-}CH_2OSiR_3} \xrightarrow[\mathrm{HCl}]{\mathrm{H_2O}} \mathrm{R_3Si{-}C(CH_3){=}CH{-}CH_2OH}.$$

Their dehydration has not yet been studied.

The first unsaturated alcohol with the β-position of the OH group and not undergoing cleavage was obtained ([3]) by the reaction:

$$\mathrm{HO{-}C(CH_3)_2{-}C{\equiv}CH + (C_2H_5)_3SiH \rightarrow HO{-}C(CH_3)_2{-}C(Si(C_2H_5)_3){=}CH_2}.$$

Its dehydration with $KHSO_4$ proceeded very readily and gave the first silicon analog of methylisoprene.

$$HO{-}C(CH_3)_2{-}C(Si(C_2H_5)_3){=}CH_2 \xrightarrow{-H_2O} CH_2{=}C(CH_3){-}C(Si(C_2H_5)_3){=}CH_2.$$

Continuing this investigation, in the present work we synthesized cyclic analogs of the indicated alcohol and silicon hydrocarbon by the reactions:

$$\text{I.}\quad -\underset{OH}{\overset{H}{C}}{\equiv}CH + (C_2H_5)_3SiH \longrightarrow -C(Si(C_2H_5)_3){=}CH_2 \xrightarrow[KHSO_4]{-H_2O} {=}C(Si(C_2H_5)_3){=}CH_2$$

As early as 1953 it was shown [4] that, after the reaction of dimethylethynylcarbinol with an excess of Grignard reagent, the resulting product reacts with R_3SiCl. Of the two possible pathways for this reaction:

$$\begin{array}{l} CH_3 \\ | \\ C{-}C{\equiv}CMgX \\ | \quad | \\ CH_3 \quad OMgX \end{array} + R_3SiCl \rightleftarrows \begin{array}{l} CH_3 \\ | \\ C{-}C{\equiv}CH \\ | \quad | \\ CH_3 \quad OSiR_3 \end{array} \qquad (1)$$

$$\begin{array}{l} CH_3 \\ | \\ C{-}C{\equiv}C{-}SiR_3 \\ | \quad | \\ CH_3 \quad OH \end{array} \qquad (2)$$

at that time, owing to the inability of the resulting compound to undergo dehydration with iodine and on the basis of certain spectral data, preference was given to the first pathway.

We repeated the synthesis of the above-mentioned compound for $R = CH_3$ and obtained a series of its analogs. All these compounds were readily dehydrated with $KHSO_4$. The indicated results and the refined spectral data make it possible to consider that this reaction proceeds according to equation (2).

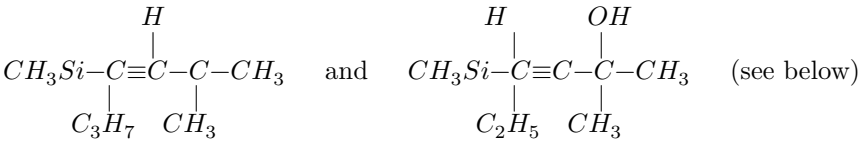
$$\text{II.}\quad (CH_3)_2C(OMgX){-}C{\equiv}CMgX + (CH_3)(C_2H_5)\cdot H\cdot SiCl \longrightarrow (CH_3)_2C(OH){-}C{\equiv}C{-}Si(H)(CH_3)(C_2H$$
$$\xrightarrow{-H_2O} (CH_3)(C_2H_5)\cdot H\cdot Si{-}C{\equiv}C{-}C(CH_3){=}CH_2$$

$$\text{III.}\quad \begin{array}{l} H \\ | \\ -C{\equiv}CMgX \\ | \\ OH \end{array} + (C_2H_5)_3SiCl \longrightarrow \begin{array}{l} H \\ | \\ -C{\equiv}C{-}Si(C_2H_5)_3 \\ | \\ OH \end{array}$$

Confirmation that the reaction proceeds according to equation (2) by a spectral method became possible thanks to the Raman spectra recently obtained

by us for a series of standard organosilicon compounds containing a triple bond. The position of the characteristic frequency $C{\equiv}C$ proved to be as follows: $(CH_3)_3SiC{\equiv}C{-}CH_3$ 2186 cm^{-1}, $(CH_3)_3SiC{\equiv}C{-}C_4H_9$ 2175 cm^{-1}, $(CH_3)_3Si{-}C{\equiv}C{-}CH{=}CH_2$ 2154 cm^{-1}, $(CH_3)_3SiCH_2{-}CH_2C{\equiv}CH$ 2116 cm^{-1}. From these figures it is evident that when the $C{\equiv}C$ bond is in the α-position to Si (and not at the end of the chain), a line is observed in the region 2170-2190 cm^{-1}; when the $C{\equiv}C$ and $C{=}C$ bonds are conjugated the frequency decreases to $\sim$ 2155 cm^{-1}, and when it is shifted to the end of the chain (and removed from the Si atom) it decreases to 2116 cm^{-1}. The last figure is close to the value observed in alkynes-1 (for example, $R{-}C{\equiv}CH \sim 2120$ cm^{-1}).

In the Raman spectra obtained for the alcohols



and

(see below)

an intense frequency of 2167 cm^{-1} was found. The position of this frequency is somewhat below the region previously indicated for the group

$$> Si{-}C{\equiv}C{-}R,$$

but considerably higher than at the end of the chain, as might have been expected on the basis of equation (1). In addition, in the infrared spectra of these same alcohols a typical band of the OH group was found in the region of 2.75 μ.

Another confirmation of the structure was the formation of enyne-type compounds. In the spectra of two compounds of this series

$(CH_3)_3Si{-}C{\equiv}C{-}C(CH_3){=}CH_2$ and $(C_2H_5)(CH_3)(H)Si{-}C{\equiv}C{-}C(CH_3){=}CH_2$

frequencies were found–

Table 1

Properties of unsaturated organosilicon alcohols and the corresponding silicon hydrocarbons

Compound	B.p., °C/mm	M.p., °C	n_D^{20}	d_4^{20}	MR, found	MR, calc.	Yield, %	Found C, %	Found H, %	Found Si, %	Calculated C, %	Calculated H, %	Calculated Si, %	OH number
Alcohols														

Compound	B.p., °C/mm	M.p., °C	n_D^{20}	d_4^{20}	MR, found	MR, calc.	Yield, %	Found C, %	Found H, %	Found Si, %	Calculated C, %	Calculated H, %	Calculated Si, %	OH number
$CH_3(C_2H_5)Si(H)-C\equiv C-C(OH)(CH_3)_2$	82.5/18.5		1.4510	0.8604	48.85	49.00	65	61.63	10.44	18.12	61.54	10.30	17.95	–
$CH_3(C_3H_7)Si(H)-C\equiv C-C(OH)(CH_3)_2$	86/12		1.4515	0.8568	53.87	53.61	66	63.60	10.67	16.40	63.53	10.59	16.47	–
cyclohexyl-$C(OH)(H)-C\equiv C-Si(CH_3)_3$	127/24	71.5–72.5	–	–	–	–	–	–	–	–	–	–	–	1.06
cyclohexyl-$C(OH)(H)-C\equiv C-Si(C_2H_5)_3$	161.5–162/12	–	1.4822	0.9195	73.94	74.39	43	–	–	–	–	–	–	0.92
cyclohexyl-$C(OH)(H)(Si(C_2H_5)_3)-C{=}CH_2$	169.5–170.5/23	–	1.4875	0.9163	75.55	75.53	95	–	–	–	–	–	–	0.97
$(C_6H_5)_3Si-C\equiv C-C(OH)(CH_3)_2$	236/5	117.5–118.5					85							0.98
Hydrocarbons														
$CH_3Si-C\equiv C-C(CH_3){=}CH_2$	130/755		1.4505	0.7867	47.37	46.72	80	69.60	10.27	20.40	69.6	10.15	20.29	
$CH_3(C_2H_5)Si(H)-C\equiv C-C(CH_3){=}CH_2$	141.5–142/745		1.4580	0.7948	47.49	46.98	95	67.77	9.74	22.67	67.66	9.73	22.60	
$CH_3(C_3H_7)Si(H)-C\equiv C-C(CH_3){=}CH_2$	56–57/9		1.4590	0.8007	51.96	51.61	75	71.14	10.54	18.30	71.05	10.53	18.42	
$C_6H_5-C(=CH_2)-Si(C_2H_5)_3$	161.5–163.5/24		1.5028	0.8817	74.59	73.51	70	75.64	12.15	–	75.60	11.79	–	

frequencies corresponding to both double and triple bonds, namely: $\nu(C=C)$ 1610 cm^{-1} and $\nu(C\equiv C)$ 2152 cm^{-1}. The values obtained are close to those previously indicated by us for vinylethynylsilanes $R_3SiC\equiv C-CH=CH_2$ (5).

It is interesting to note that in the Raman spectrum of

$$\text{cyclohexene ring}-\underset{|\atop Si(C_2H_5)_3}{C}{=}CH_2$$

the frequency of the $C=C$ bond is raised to 1633 cm^{-1}, which is considerably higher than in

$$CH_3-\underset{|\,Si(CH_3)_3}{C}{=}CH_2$$

(1605 cm^{-1}).

1. Synthesis of

$$\text{cyclohexane ring}\overset{OH}{}-C(OH){=}CH_2 \quad Si(C_2H_5)_3$$

. Into an autoclave were placed 15 g of ethynylcyclohexanol, 15 g of triethylsilane, and catalytic amounts of Pt/C. The autoclave was heated for 24 hours at 200-210°. After fractionation, an alcohol was isolated, the constants of which are given in Table 1.

2. Synthesis of

$$\begin{array}{c}\text{cyclohexene ring} - \text{C}\equiv\text{C} - \text{Si}(\text{C}_2\text{H}_5)_3\\ \text{OH}\end{array}$$

. From 7.2 g of magnesium and 33.0 g of ethyl bromide in ether, ethylmagnesium bromide was prepared, to which 19.0 g of ethynylcyclohexanol dissolved in ether was then added. On the following day 27.0 g of triethylbromosilane was added; the reaction mixture was stirred with heating for 3 hours, after which the ether was distilled off and the residue was heated on an oil bath at 100-130° for 3 hours. It was then decomposed with water while cooling with ice and extracted with ether. The ether extracts were dried with potash, the ether was distilled off, and fractionation gave a product with the properties presented in Table 1.

All the organosilicon alcohols were obtained by an analogous method. The Raman spectra were obtained on an apparatus with an ISP-51 spectrograph and a camera with $f = 270$ mm.

It was also possible to synthesize the ether

$$\begin{array}{l}\text{CH}_3\\ \text{CH}_3\end{array}\!\!> \text{C} - \text{C}\equiv\text{CH}$$
$$\text{OSi}(\text{C}_2\text{H}_5)_3$$

under the following conditions. To a mixture of 15 g of dimethylethynylcarbinol and 12 g of pyridine, with stirring, 25 g of triethylchlorosilane was added gradually. To complete the reaction, the flask was heated for 1.5 hours on a water bath. After cooling, the precipitate was filtered off and the filtrate was distilled. An ether was isolated with b.p. 93.5° (183.7-184.2° at 758.8 mm), $n_D^{20} = 1.4310$, $d_4^{20} = 0.8414$.

$\text{C}_{11}\text{H}_{22}\text{SiO}$.	Found, %:	H—11.39;	C—66.83;	Si—13.92
	Calculated, %:	H—11.11;	C—66.66;	Si—14.14

The isomeric tertiary alcohol, which we had previously taken for the ether (4), has b.p. 121.8° at 27 mm, $n_D^{20} = 1.4557$, $d_4^{20} = 0.8638$.

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