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Abstract

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SYNTHESIS AND PROPERTIES OF CERTAIN ORGANOSILICON β-ALCOHOLS (β-HYDROXYALKYLTRIMETHYLSILANES)

Organosilicon alcohols with the hydroxyl group in the β-position have been little studied (2,7). Under the influence of well-known work on β-cleavage (1,2), a somewhat exaggerated notion arose concerning the exceptional instability of organosilicon compounds of the type

$$> \text{Si—C—C—X} \quad (\text{X} = \text{Cl}, \text{Br}, \text{OH and other electronegative atoms and groups}),$$

including β-hydroxyalkylsilanes, leading, upon the action on them of electrophilic and nucleophilic reagents, to β-cleavage according to the scheme

$$> \text{Si—C—C—X} \to > \text{Si—X} + \text{C} = \text{C}.$$

Thus, when $(CH_3)_3SiCH_2CH(OH)CH_3$ was heated with several drops of 10% sulfuric acid, Whitmore, Sommer, Gold, and Van Strien (2) observed vigorous β-cleavage with evolution of propylene. The data that have accumulated by the present time on reactions of β-halosilanes (dehydrochlorination (3), action of Grignard reagents (4), direct synthesis (5), Friedel–Crafts reaction (6)) show that, in general, the accepted ideas about their instability require serious additions and sometimes corrections.

In a series of previous works we showed that electronegative groups attached to Si substantially influence the reactivity of β-halosilanes. In this connection, attention was drawn to the role of the stabilizing influence of chlorosilyl groups (8).

Thus, the question naturally arose of a more detailed study of the properties of β-hydroxyalkylsilanes: their susceptibility not only to β-cleavage but also to dehydration, the influence of neighboring atoms and groups on the behavior of the hydroxyl group situated in the β-position to Si, the thermal stability of β-alcohols, etc. The aim of the present work was to take a first step in this direction.

From $(CH_3)_3SiCH_2MgCl$ and a series of carbonyl compounds—methyl ethyl ketone, ethyl formate, chloral, and benzil—we obtained β-alcohols, the properties of which are presented in Table 1.

Analysis of the reaction products of $(CH_3)_3SiCH_2MgCl$ with the indicated carbonyl compounds makes it possible to note the formation not only of the desired β-alcohols, but also of products of dehydration of the alcohols and products of β-cleavage. Thus, in the preparation and purification of

$$(CH_3)_3SiCH_2C(OH)(C_2H_5)\ (I)$$
$$CH_3$$

to isolate, in a considerable amount, an alkenylsilane of the structure

$$(CH_3)_3SiCH_2C(CH_3) = CH - CH_3 \quad (A),$$

in which, according to the Raman spectra, another isomeric dehydration product is also present in a very small amount,

$$(CH_3)_3SiCH_2C(C_2H_5) = CH_2 \quad (B).$$

The dehydration of alcohol I proceeded, evidently, both during decomposition of the reaction mixture with water and drying of the ethereal solution over Na_2SO_4, and during distillation of the ether on a column and fractionation under vacuum.

Table 1

No.	Formula of alcohol	Yield, %	B.p., °C	Pressure, mm Hg	d_4^{20}	n_D^{20}	MR found	MR calc.
I	$(CH_3)_3SiCH_2C(OH)(C_2H_5)(CH_3)$	1.9	52	33	0.8451	1.4410	50.10	50.35
II	$[(CH_3)_3SiCH_2]_2CHOH$	7.9	74.5	7	1.4401	0.8369	64.36	64.61
III	$(CH_3)_3SiCH_2CH(OH)CCl_3$	17.0	87–88	9	1.1730*	1.4700**	56.04	55.61
IV	$(CH_3)_3SiCH_2C(OH)(C_6H_5)C(=O)(C_6H_5)$	69.5	m.p. 92–93°	—	—	—	—	—

$* d_4^{40} \qquad ** n_D^{40}$

As a result of dehydration, the yield of the β-alcohol proved to be very low. Attention should be drawn to the order of elimination of the elements of water: although it obeys Zaitsev's rule, the preferential formation of (A), in the absence of $(CH_3)_3SiCH = CH(CH_3) - CH_2CH_3$ (B) and with a very small amount of (B), indicates that, apparently, in the γ-methylene group the C—H bonds are the least strong. The fact of dehydration of β-alcohol I thus introduces a new, substantial addition to Whitmore' s scheme.

In the preparation and isolation of alcohols II and III, formation of small amounts of β-cleavage products was observed: $(CH_3)_3SiCH_2CH_2 = CH_2$ from II and $(CH_3)_3SiOH$ from III. No cleavage or dehydration products were isolated from alcohol IV. At the same time, the yields of alcohols III and, especially, IV themselves were higher than those of alcohols I and II. It is quite probable that, under the conditions of the Grignard reaction and isolation from the mixture of reaction products, they are more stable both toward β-cleavage and toward dehydration. Thus, it must be assumed that the nature of the radicals adjacent to the β-hydroxyl group can substantially influence its reactivity.

Also deserving attention is the behavior of the obtained β-alcohols upon heating, which was carried out in a Sivolobov apparatus (^{9}) for determining the boiling point of small quantities of substance. On heating alcohols I, II, and III to boiling, no decomposition was observed. Alcohol IV, when heated to 230°, was converted, without decomposing, into a viscous substance which after some time crystallized again. The heating product of the keto alcohol melted over a broad range close to the melting temperature of the original keto alcohol.

Data on the behavior of alcohols I-III upon heating are given in Table 2.

Trimethylsilylmethyl-(methyl)-(ethyl)carbinol (I). To the Grignard reagent prepared from 60 g of $(CH_3)_3SiCH_2Cl$ and 12 g of magnesium

in ether, 35 g of methyl ethyl ketone was added. Heating of the reaction mixture was observed, with formation of a precipitate. After 4 h of heating and standing, the reaction mixture was decomposed with water. The ether layer was dried over Na_2SO_4, and the ether was distilled off. This gave 42 g of a mixture of reaction products. 28 g

Table 2

Alcohol	B.p., °C	Pressure, mm Hg	n_D^{20} before heating	n_D^{20} after heating	Duration of heating, min	Notes
I	~169–171	754	1.4372	1.4382	30	Colorless before and after heating
II	~206–210	753	1.4392	1.4392	60	–
III	~213–217	754	1.4740*	1.4735*	60	After heating turns slightly yellow

* At 30°.

of this mixture, after additional drying over Na_2SO_4, was fractionated under vacuum. The following were isolated:

1. Fraction with b.p. 18–24° (50 mm), n_D^{20} 1.3912,–apparently a mixture of β-cleavage products: $(CH_3)_3SiOH$, etc.
2. 10 g of $(CH_3)_3SiC_5H_9$, b.p. 57° (49 mm), d_4^{20} 0.7620, n_D^{20} 1.4320. Found MR 48.43, calculated MR 48.33.

	Found, %:	C 67.46; 67.37;	H 12.65; 12.70;	Si 19.55; 19.42
$C_8H_{18}Si$.	Calculated, %:	C 67.53;	H 12.75;	Si 19.72

At atmospheric pressure the substance has b.p. 134° (747.5 mm). In the Raman spectrum of $(CH_3)_3SiC_5H_9$,* the following frequencies (in cm^{-1}) were found: 164(4sh), 191(4sh), 242(4sh), 299(1), 396(3sh), 485(4), 606(8), 659(1), 692(4), 790(1), 862(3sh), 957(2), 1045(2), 1144(3), 1165(4), 1217(3), 1250(3), 1339(4), 1382(3), 1417(4), 1450(4sh), 1640(1), 1665(7), 2867(4), 2900(10sh), 2920(3), 2961(8), 3076(1).

In the region of multiple bonds there are two frequencies: one–the principal one–1665 cm^{-1}, and the second–a very weak one–1640 cm^{-1}. As a result of dehydration of the alcohol, three alkenylsilanes could have formed: A, B, and V.

The frequency 1665 cm^{-1}, together with the frequencies 1165 cm^{-1} and 1382 cm^{-1}, indicates that the alkenylsilane has structure A, since all these frequencies are characteristic of a double bond located in the β-position to Si (^{10}) and having a methyl group at the end (^{11}). The frequency 1640 cm^{-1} and the weak line 3076 cm^{-1} indicate an admixture of compound B with a terminal $=CH_2$ group, which, as is known, is characterized by the frequency 1638 cm^{-1}. Formation of V is spectrally refuted by the absence of lines in the region 1590–1620 cm^{-1}, characteristic of a double bond in vinylsilanes (^{12}).

From 14 g of the remaining mixture of reaction products, by fractionation in a higher vacuum, it was possible to isolate 1.5 g (1.9%) of alcohol I.

Found, %: H 12.35; 12.44; C 60.19; 60.21; Si 17.41; 17.38
$C_8H_{20}OSi$. Calculated, %: H 12.58; C 59.94; Si 17.50

Bis-(trimethylsilylmethyl)-carbinol (II). To the Grignard reagent obtained from 75 g of $(CH_3)_3SiCH_2Cl$ and 14.7 g of Mg in 225 ml of absolute ether, 18.5 g of ethyl formate was added dropwise. After carrying out the usual operations (heating for 3 h, decomposition with water, extraction of the aqueous layer with ether, drying of the ether solution of the reaction products with Na_2SO_4), 25.3 g of a mixture of reaction products was obtained, from of which, after three vacuum distillations, 5 g (7.9%) of pure alcohol II was obtained.

Found, %: H 11.67; 11.88; C 52.75; 52.86; Si 27.70; 27.82
$C_9H_{24}OSi_2$. Calculated, %: H 11.83; C 52.88; Si 27.46

In the more volatile portion of the reaction products, collected in the trap (−70°), during distillation on a column it was possible to establish reliably only the presence of trimethylallylsilane (1.3 g), b.p. 83-85° (743.7 mm), d_4^{20} 0.7216, n_D^{20} 1.4030. Literature data (^{13}): b.p. 84.9° (737 mm), d_4^{20} 0.7193, n_D^{20} 1.4074.

Trimethylsilylmethyl-trichloromethyl-carbinol (III). To $(CH_3)_3SiCH_2MgCl$, obtained from 92 g of $(CH_3)_3SiCH_2Cl$ and 18.1 g of Mg in 300 ml of ether, 110.8 g of chloral was added dropwise with stirring. After operations analogous to those described above, and four vacuum distillations, 30 g (17%) of alcohol III was obtained, melting at a temperature slightly above room temperature.

Found, %: H 5.79; 5.55; C 30.89; 30.84; Cl 44.99; 45.17; Si 11.73; 14.96
$C_6H_{13}Cl_3OSi$. Calculated, %: H 5.56; C 30.59; Cl 45.15; Si 11.91

Keto alcohol (IV). The keto alcohol was obtained by the reaction of $(CH_3)_3SiCH_2MgCl$ (67 g of $(CH_3)_3SiCH_2Cl$ and 15 g of Mg in 300 ml of absolute ether) with benzil* (53 g). After 6.5 h of heating, decomposition with

* The optical analysis was carried out by Yu. P. Egorov, to whom we express our gratitude.

water, and removal of the ether by distillation, the reaction product (52.4 g) crystallized. After three recrystallizations from ether it melted at 92–93°.

Found, %: H 7.32; 7.46; C 72.38; 72.59; Si 10.06; 9.98
$C_{18}H_{22}O_2Si$. Calculated, %: H 7.44; C 72.43; Si 9.40

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* Benzil was added to the Grignard reagent in solid form in small portions.

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

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