SYNTHESIS OF PRIMARY γ -ORGANOSILICON

ACETYLENE ALCOHOLS

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In previous papers [1-4], we described methods of preparing mono-, di-, and trihydric γ -silicon- and germanium-containing secondary and tertiary acetylene alcohols. Continuing the investigation in this direction, in the present work we developed a method for preparing primary γ -silicon-containing alcohols. The basis of the synthesis of primary γ -silicon-containing alcohols was the reaction of the dibromodimagnesium derivative of propargyl alcohol with an alkyl(aryl)chlorosilane:

$$R_3SiC1+BrMgC\equiv C-CH_2OMgBr \longrightarrow R_3SiC\equiv C-CH_2OH$$

(where R is alkyl or aryl). The structure of the alcohols obtained was demonstrated by hydrogenation and acetal formation according to the scheme:



 γ -Hydroxypropyltrimethylsilane has been described in the literature [5]. The constants of the alcohol we obtained by hydrogenation of 3-trimethylsilylpropyn-2-ol-1 agreed completely with literature data.

EXPERIMENTAL

Synthesis of 3-trimethylsilylpropyn-2-ol-1 (CH₃)₃SiC \equiv C-CH₂OH. Into a 2-liter, three-necked, roundbottomed flask fitted with a mechanical stirrer, dropping funnel, reflux condenser, and thermometer, were placed 48.6 g (2 g-atom) of magnesium turnings and 500 ml of dry ether. Then 218 g (2 moles) of ethyl bromide was added dropwise with stirring and cooling. To the Grignard reagent formed was added 56 g (1 mole) of propargyl alcohol dropwise with stirring and cooling. Gas was evolved and a white, curdy precipitate formed. The reaction mixture was stirred for 2 hr with cooling and for 3 hr with heating on a water bath. Then 2 g of cuprous chloride was introduced into the flask and 108.5 g (1 mole) of trimethylchlorosilane added gradually with cooling and stirring. The mixture formed was stirred for 2 hr at room temperature and for 8 hr with heating on a water bath. At the end of the synthesis, the reaction mixture was cooled and stirred and treated with 150 ml of moist ether and then 5% aqueous hydrochloric acid until the precipitate dissolved completely. The ether

TABLE

Physicochemical Constants of Organosilicon Compounds Obtained

כוייייוס	B. p. in °C	20	0 ^{%7}		MR	Si	in %	E .: Ploiv
r Ullilua	(p in mm Hg)	Q_{μ}	۴ ۳	found	calculated	found	calculated	
(CH₁)\$SIC≡C - CH₁OH	61 (2)	1,4523	0,8806	39,31	39,48	21,39 21,52	21,9	40,2
(C₄H₂)₃SICΞC - CH₂OH	109-110 (6)	1,4670	0, 8932	52,92	53,37	$16,12 \\ 16,30$	16,49	44,7
(CH₃)₄C₄H₅SIC≘C∴ CH₂OH OC₄H₅	131-132 (2)	1,5335	0,9996	59,13	59,15	$14,51 \\ 14,62$	14,76	67 , 8
CH,- CH OCH,C≂CSIICH,).	95 (5)	1,4378	0,8683	69,02	69,25	11,95 11,87	12,29	71,0
(CH ₃ ,SiCH ₂ CH ₂ CH ₂ OH*	6162 (10)	1,4295	0,8406	40,61	41,09	. 1		0,00
• Described in the literature.								

layer was separated from the aqueous layer and the latter was extracted with ether. The ether layer and ether extracts were combined, washed with distilled water until neutral, and dried over calcium chloride. The ether was removed and the residue vacuum distilled.

Fractions were obtained: Fraction I had b.p. 30-61° (2 mm); n_D^{20} 1.4465;6 g, Frac. II ; b.p. 61-62° (2 mm); n_D^{20} 1.4523; 54.8 g.

Redistillation of the last fraction yielded 51.5 g (40.2%) of substance with b.p. 61° (2 mm); $n_{\rm D}^{20}$ 1.4523; d_4^{20} 0.8806. Found: MR 39.31. C₆H₁₂SiO. Calculated: MR 39.48. Found: Si 21.39; 21.52%. Calculated: Si 21.9%.

3-Triethylsilylpropyn-2-ol-1 and 3-dimethylphenylsilylpropyn-2-ol-1 were synthesized analogously and their physicochemical constants are given in the table.

<u>Synthesis of 3-trimethylsilylpropyn-2-yl butyl</u> <u>acetal</u> $CH_3 - CH \xrightarrow{OC_4H_5}$ Into a $OCH_2C \equiv CSi(CH_3)_3.$

25-ml, three-necked, round-bottomed flask, fitted with a mechanical stirrer, reflux condenser, and thermometer were placed 5 g (0.05 mole) of vinyl butyl ether and 6.4 g (0.05 mole) of 3-trimethylsilylpropyn-2-ol-1. Then 1 drop of concentrated hydrochloric acid was added with stirring. The mixture was heated up to 79°. For completion of the reaction the mixture was heated for a further 2 hr at 100° and left overnight. The reaction mixture was then neutralized with baked potassium carbonate, filtered, and vacuum distilled. Fractions were obtained: Fraction I had b.p. 75-94° (5 mm); n_D^{20} 1.4308; 1.9 g; Fraction II had b.p. 94-95° (5 mm); n_D^{20} 1.4378; 8.8 g.

Redistillation of fraction II yielded 8.1 g (71%) of a substance with b.p. 95° (5 mm); n_D^{20} 1.4378; d_4^{20} 0.8683. Found MR 69.02.C₁₂H₂₄SiO₂. Calculated MR 69.25. Found: Si 11.95; 11.87%. C₁₂H₂₄SiO₂. Calculated: Si 12.29%.

Synthesis of 3-trimethylsilylpropanol-1 (CH₃)₃-SiCH₂CH₂CH₂OH. The hydrogenation was carried out in an autoclave in ethanol over Raney nickel. For the hydrogenation we used 12.8 g (0.1 mole) of 3-trimethylsilylpropyn-2-ol and ~1 g of Raney Ni in 50 ml of ethanol. The usual treatment yielded 11.6 g (90%) of a substance with b.p. 61-62° (10 mm); n_D^{20} 1.4295; d_4^{20} 0.8406. Literature data [5]: b.p. 62-63° (10 mm); n_1^{20} 1.4238; d_4^{20} 0.8408.

SUMMARY

1. The reaction of trialkyl(aryl)chlorosilanes with the dimagnesium derivative of propargyl alcohol was studied. A method was developed for preparing primary γ -silicon-containing acetylene alcohols.

2. 3-Trimethylsilylpropyn-2-ol-1, 3-dimethylphenylsilylpropyn-2-ol-1, 3-triethylsilylpropyn-2-ol-1, and 3-trimethylsilylpropyn-2-yl butyl acetal were obtained for the first time.

LITERATURE CITED

- 1. M.F. Shostakovskii, I.A. Shikhiev, and N.V. Komarov, Doklady Akad, Nauk SSSR 109, 344 (1956).*
- 2. M.F. Shostakovskii, I.A. Shikhiev, and N.V. Komarov, Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk, 1271 (1956).*
- 3. I.A. Shikhiev, M.F. Shostakovskii, N.V. Komarov, and L.A. Katyutenko, Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1139 (1957).*

4. M.F. Shostakovskii, I.A. Shikhiev, N.V. Komarov, and I.A. Aslanov, Author's Cert. 117493 (1958).

5. M.F. Shostakovskii and I.A. Shikhiev, Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk 795 (1954).

*Original Russian pagination. See C.B. translation.