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Abstract

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Chemistry

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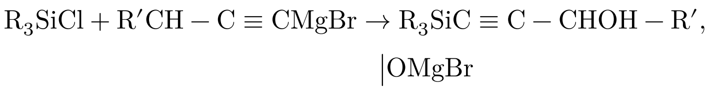
Synthesis and Some Transformations of Secondary γ-Silicon-Containing Acetylenic Alcohols

In our earlier investigations ($^{1-3}$), a method was developed for obtaining primary and tertiary silicon-, tin-, and germanium-containing acetylenic alcohols. Study of the chemical properties of the indicated compounds showed that they are highly reactive substances. Their chemical properties resemble those of organic analogs; however, along with this, they differ significantly from the latter and exhibit a number of distinctive features.

In the present work we investigated the reaction of chlorosilanes with dimagnesium bromide derivatives of secondary acetylenic alcohols. On the basis of this reaction, a method was developed for obtaining secondary γ-silicon-containing acetylenic alcohols according to the scheme:



$$R_3SiCl + \underset{|\text{OMgBr}}{R'CH} - C \equiv CMgBr \rightarrow R_3SiC \equiv C - CHOH - R',$$

where R and R' are CH_3, C_2H_5, etc., organic radicals.

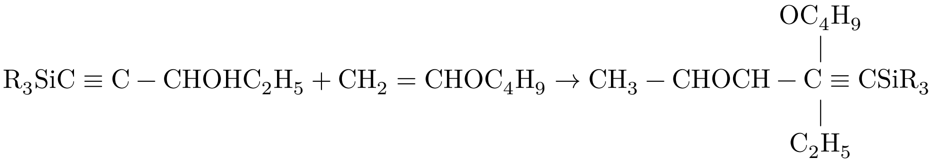
The interaction of the compounds obtained with thionyl chloride and simple vinyl ethers was investigated.

The interaction of secondary γ-silicon-containing alcohols with thionyl chloride showed that the exchange reaction of the hydroxyl group for a chlorine atom proceeds under relatively mild conditions. The principal reaction products are the corresponding silicon-acetylenic chlorides.

$$R_3SiC \equiv C - CHOHC_2H_5 + SOCl_2 \rightarrow R_3SiC \equiv C - CHClC_2H_5 + SO_2 + HCl,$$

where $R = CH_3$ and C_2H_5. Cleavage of the Si − C bond was not observed.

The reaction with simple vinyl ethers proceeds smoothly with formation of the corresponding acetals



$$R_3SiC \equiv C - CHOHC_2H_5 + CH_2 = CHOC_4H_9 \rightarrow CH_3 - CHOCH - \underset{\displaystyle C_2H_5}{\underset{|}{\overset{\displaystyle OC_4H_9}{\overset{|}{C}}}} \equiv CSiR_3$$

$R = CH_3$ and C_2H_5.

5-Trimethylsilylpentyn-4-ol-3 $(CH_3)_3SiC \equiv C - CHOHC_2H_5$. To a Grignard reagent prepared from 65.4 g (0.6 g-mole) of ethyl bromide and 14.58 g (0.6 g-atom) of magnesium in 200 ml of anhydrous ether, 25.2 g (0.3 g-mole) of ethylethynylcarbinol is added dropwise with stirring and cooling. After this, the mixture is stirred for another 2 hours with ice-water cooling and for 5–6 hours at room temperature. Then 0.5 g of Cu_2Cl_2 is introduced into the reaction mixture, and at $-5°$ 32.5 g (0.3 g-mole) of trimethylchlorosilane is gradually added. The mixture is stirred for another 3 hours at room temperature and for 5–6 hours while heating on a water bath. After completion of the synthesis, the reaction mass is decomposed, with cooling, by 10% hydrochloric acid until the precipitate dissolves completely.

The aqueous layer is separated from the ether layer, and after the usual workup, by distillation in vacuo, 25.2 g (55%) of 5-trimethylsilylpentyn-4-ol-3 is isolated with b.p. 57.5°/3 mm, n_D^{20} 1.4452, d_4^{20} 0.8604. MR_D found 48.37; for $C_8H_{16}OSi$ calculated MR_D 48.74. Found %: Si 18.13; for $C_8H_{16}OSi$ calculated %: Si 17.97.

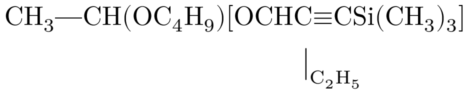
5-Triethylsilylpentyn-4-ol-3 $(C_2H_5)_3SiC \equiv C—CHOHC_2H_5$. The synthesis is carried out analogously to that described above. For the synthesis there were taken: 65.4 g (0.6 g-mole) of ethyl bromide, 14.58 g (0.6 g-atom) of magnesium, 200 ml of absolute ether, 25.2 g (0.3 g-mole) of ethynylethylcarbinol, 0.5 g of Cu_2Cl_2, and 45.2 g (0.3 g-mole) of triethylchlorosilane. 25.6 g (44.6%) of 5-triethylsilylpentyn-4-ol-3 was isolated with b.p. 106°/7 mm, n_D^{20} 1.4601, d_4^{20} 0.8851. MR_D found 61.37; for $C_{11}H_{22}OSi$ calculated MR_D 61.38. Found %: Si 14.58; for $C_{11}H_{22}OSi$ calculated %: Si 14.2.

3-Chloro-5-trimethylsilylpentyn-4 $(CH_3)_3SiC \equiv C—CHClC_2H_5$.

Into a three-necked round-bottom flask of 50 ml capacity, equipped with a reflux condenser, dropping funnel, mechanical stirrer, and thermometer, are placed 7.8 g (0.05 g-mole) of 5-trimethylsilylpentyn-4-ol-3 and 1 g of pyridine. The mixture is then cooled and, with stirring, 8.92 g (0.075 g-mole) of thionyl chloride is gradually added to it, and stirring of the mixture is continued for another 2 h. On the following day the mixture is first stirred for 2–3 h at room temperature, and then with heating to 60° to remove SO_2. Upon completion of the synthesis the mixture is treated, with cooling, with 15 ml of water. The organic layer is separated from the aqueous layer, dried over calcium chloride, and by distillation in vacuo 4.52 g (60%) of 3-chloro-5-trimethylsilylpentyn-4 is isolated with b.p. 46–47°/5 mm, n_D^{20} 1.4540, d_4^{20} 0.9090. MR_D found 52.34; for $C_8H_{15}SiCl$ calculated MR_D 52.03. Found %: Si 15.65; for $C_8H_{15}SiCl$ calculated %: Si 15.89.

3-Chloro-5-triethylsilylpentyn-4 $(C_2H_5)_3SiC \equiv C{-}CHClC_2H_5$. The synthesis was carried out analogously to that described above. For the synthesis there were taken: 5.84 g (0.03 g-mole) of 5-triethylsilylpentyn-4-ol-3, 1 g of pyridine, and 5.35 g (0.045 g-mole) of thionyl chloride. 4.1 g (60.6%) of 3-chloro-5-triethylsilylpentyn-4 was obtained with b.p. 96.5–98.5°/8 mm, n_D^{20} 1.4641, d_4^{20} 0.9048. MR_D found 66.10; for $C_{11}H_{21}SiCl$ calculated 65.92. Found %: Si 12.54; for $C_{11}H_{21}SiCl$ calculated %: Si 12.96.

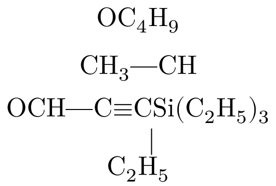
Butyl-(3-trimethylsilyl-1-ethylpropyn-2)-acetal



$$CH_3{-}CH(OC_4H_9)[O\underset{\substack{|\\ C_2H_5}}{CH}C{\equiv}CSi(CH_3)_3]$$

Into the apparatus described above are placed 4.68 g (0.03 g-mole) of 5-trimethylsilylpentyn-4-ol-3 and 3 g (0.03 g-mole) of vinyl butyl ether. Then, with stirring, 1–2 drops of conc. hydrochloric acid are introduced. The temperature of the reaction mixture rises sharply to +58°. After this the contents of the flask are stirred for 3 h at 80° and left overnight. On the following day the reaction mass is neutralized with ignited potash, filtered, and by distillation in vacuo 3.2 g (41.6%) of substance is isolated with b.p. 102–103°/8 mm, n_D^{20} 1.4368, d_4^{20} 0.8580. MR_D found 78.11; for $C_{14}H_{28}O_2Si$ calculated MR_D 78.51. Found %: Si 11.48; for $C_{14}H_{28}O_2Si$ calculated %: Si 10.95.

Butyl-(3-triethylsilyl-1-ethylpropyn-2)-acetal



$$\begin{array}{c} OC_4H_9 \\ CH_3{-}CH \\ OCH{-}C{\equiv}CSi(C_2H_5)_3 \\ | \\ C_2H_5 \end{array}$$

Obtained in an analogous manner. For the synthesis there were taken 5.95 g (0.03 g-mole) of 5-triethylsilylpentyn-4-ol-3 and 3 g (0.03 g-mole) of vinyl butyl ether. Self-heating of the mixture reached 53.5°. As a result of the synthesis, 4.3 g (48%) of substance was isolated with b.p. 138–139°/2.5 mm, n_D^{20} 1.4500, d_4^2 0.8736. Found: MR_D 91.81; for $C_{17}H_{34}O_2Si$ calculated: MR_D 92.40. Found, %: Si 9.40; for $C_{17}H_{34}O_2Si$ calculated, %: Si 9.57.

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