



Preliminary communication

An unusual rearrangement of 1-trimethylsiloxy-3-bromomagnesium-2-propyne

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Abstract

3-Trimethylsilyl-2-propyn-1-ol (4) was synthesized via the rearrangement of 1-trimethylsiloxy-3-bromomagnesium-2-propyne and followed by hydrolysis of the latter. The yield of compound 4 depends largely on the solvent used. © 1998 Elsevier Science S.A.

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The general method for the preparation of triorganylsilylethynyl-alkanols R₃SiC≡CCH₂OH is the reaction of trialkylhalosilanes with bis(bromomagnesium) derivatives of acetylenic alcohols [1]. Recently, we have developed a method for the preparation of 3-trialkylsilyl(trialkylgermyl)-2-propyn-1-ols by reaction of 1-trimethylsiloxy-3-bromomagnesium-2-propyne with triorganylchlorosilanes or -germanes (yield 85−87%) [2]. The application of trimethylsilyl ethers of acetylenic alcohols in synthetic chemistry is mainly connected with blocking or protecting of hydroxyl by trimethylsiloxy group [3].

Silyl protected cyclopropan alkanols and alkenols containing a tin substituent were found to undergo transmetalation followed by 1,4-silyl migration from oxygen to carbon in the presence of methyllithium [4]. An unusual transformation of 1-trimethylsiloxy-2-propyne (1) to isomeric alcohol 3-trimethylsilyl-2-propyn-1-ol (4) in the presence of Grignard reagent has been found by us.

1,4-Migration of trimethylsilyl group $O \rightarrow C_{sp}$ in 1 probably proceeds by this scheme.

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$$Me_{3}SiOCH_{2}C = CH \xrightarrow{EtMgBr} Me_{3}SiOCH_{2}C = CMgBr$$

$$\downarrow 1$$

$$THF(Et_{2}O) \rightarrow BrMgOCH_{2}C = CSiMe_{3} Me_{3}$$

$$\downarrow HOCH_{2}C = CSiMe_{3}$$

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The rearrangement occurs under reflux of intermediate 2 in the solvent. The subsequent hydrolysis of the reactive complex with 5% HCl leads to the isolation of alcohol 4 in 80% yield with THF as the solvent and 24% in ether. The promotion of the reaction with THF is likely to be due to the good solubility of Iotsitch's reagent 1. On 10-fold dilution of the reaction mixture (in ether) the yield of 4 is five times lower. This fact counts in favor of the intermolecular character of the transformation of 1 to 4. The described reaction is a new convenient route to the preparation of alcohol 4 widely used in the synthesis of carbofunctional trimethylsilyl ethynyl silanes [5–7].

1. Experimental details

1.1. Typical procedure for the synthesis of 4

To a solution of Grignard reagent (1.95 g, 80 mmol Mg, 8.72 g, 80 mmol EtBr, 100 ml THF) reagent **1** (10.26 g, 80 mmol) was added dropwise, then the reaction mixture was heated at reflux for 9 h. The reaction mixture was treated with 5% hydrochloric acid and extracted with ether. Organic solution was dried over MgSO₄, concentrated and distilled in vacuo to give the alcohol **4** (8.21 g, 80%), b.p. $70-71^{\circ}\text{C}/11$ mm Hg, n_D^{20} 1.4510. Lit. [3]: b.p. $76^{\circ}\text{C}/11$ mm Hg, n_D^{20} 1.4508. IR-spectrum (film): $\nu(\text{cm}^{-1})$ 1240 (Si-C), 2172 (C=C), 3300 (OH). ¹H NMR (CDCl₃): δ 0.16 (s, 9H, (CH₃)₃Si); 2.88 (s, 1H, OH); 4.25 (s, 2H, CH). Anal.

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Found: C 56.40; H 9.77; Si 21.79. $C_6H_{12}OSi$. Calc.: C 56.18; H 9.45; Si 21.50. IR-spectra were recorded on a Specord IR-75 spectrometer. ¹H NMR (89.5 MHz) were recorded on a JEOL-FX-90 spectrometer (HMDS). GLC analysis were performed on a LKhM-80 chromatograph with heat conduction detector on a $(1500 \times 3 \text{ mm})$ column, packed with 10% polymethylsiloxane on Chromaton.

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