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SHORT COMMUNICATIONS

1,4-Migration of Et_3Ge Group in 1-Triethylgermoxypropyne[*]

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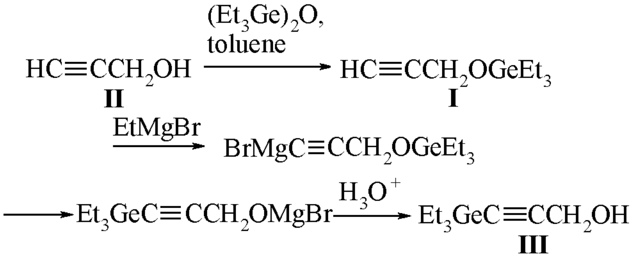
In our previous studies was established a 1,4-migration of trimethylsilyl group $O \rightarrow C_{sp}$ in 1-trimethylsiloxy-2-propyne when treated with ethylmagnesium bromide. On hydrolysis was obtained 3-trimethylsilyl-2-propyn-1-ol in 85% yield [1–3]. It was also shown that the same reagent produced analogous migration of the trimethylsilyl group in 1-trimethylsilylthio-2-propyne, $S \rightarrow C_{sp}$ [4]. In the propargyl esters $HC{\equiv}CCH_2XSiMe_3$ (X = O, S) the migration of the trimethylsilyl group $X \rightarrow C_{sp}$ is facilitated on going from the oxygen to sulfur atom. In extension of the studies on the regular trends in the rearrangement of compounds of a general composition $HC{\equiv}CCH_2XMR_3$ (where X = O, S; M = Si, Ge) we report here on transformation suffered by 1-triethylgermoxy-2-propyne under treatment of the Grignard reagents. We planned that the results of this study w would allow estimation of the role of the element from silicon subgroup in the propargyl alcohol derivatives with O–Si and O–Ge bonds on the efficiency of 1,4-migration $X \rightarrow C_{sp}$ of the MR_3 group.

1-Triethylgermoxy-2-propyne (I) was prepared by reaction of 2-propyn-1-ol (**II**) with hexaethyldigermoxane in toluene [5]. Under optimal conditions for its silicon-containing analog, 1-trimethylsiloxy-2-propyne, i.e. at boiling with ethylmagnesium bromide in tetrahydrofuran, the expected 3-triethylgermyl-2-propyn-1-ol (**III**) was obtained in 12% yield.



$$\underset{\mathbf{II}}{HC{\equiv}CCH_2OH} \xrightarrow[\text{toluene}]{(Et_3Ge)_2O,} \underset{\mathbf{I}}{HC{\equiv}CCH_2OGeEt_3} \xrightarrow{EtMgBr} BrMgC{\equiv}CCH_2OGeEt_3$$

$$\longrightarrow Et_3GeC{\equiv}CCH_2OMgBr \xrightarrow{H_3O^+} \underset{\mathbf{III}}{Et_3GeC{\equiv}CCH_2OH}$$

The low yield of the isomerization product **III** may be due to the prevailing cleavage with ethylmagnesium bromide of the Ge–O bond in ether **I** and not of the Iotzitsch complex as we assumed for the rearrangement mechanism [2]. This guess is confirmed by the increase in the yield of alcohol **III** to 48% at applying a milder nucleophile, phenylmagnesium bromide (THF, boiling for 1.5 h). Moreover, the reaction of compound **I** with phenylmagnesium bromide at room temperature within 15 h afforded alcohol **III** in 43% yield. Since the migration of Et_3Ge group in compound **I** occurred under milder conditions than the migration of the Me_3Si group in its analog the heterolysis of the Ge–O bond was easier than that of Si–O bond in compounds $HC{\equiv}CCH_2OMR_3$ effected by the corresponding Iotzitsch complex. Thus the efficiency of the 1,4-migration $X \rightarrow C_{sp}$ of the MR_3 group in compounds $HC{\equiv}CCH_2XMR_3$ essentially depends on the character of the heteroatom and the element in the M–X bond, and also on the Grignard reagent used. The combination of these results confirms that the limiting stage of the rearrangement of the terminal organoelemental derivatives of the propargyl alcohol and of its thioanalog into triorganylsilyl- or -germylacetylene alcohols or thiols is the heterolysis of the M–X bond under the action of Iotzitsch complex.

Isomerization of 1-triethylgermoxy-2-propyne (**I**) under treatment with Grignard reagent. (a) To a Grignard reagent prepared from 0.48 g of magnesium and 1.18 g of ethyl bromide in 20 ml of anhydrous THF was added 4.3 g of compound **I** in 5 ml of THF. The reaction mixture was refluxed at stirring for 9 h and left standing at 20°C for 12 h. The reaction mixture was hydrolyzed with water solution of ammonium chloride, the reaction product was extracted into ethyl ether, and the extract was dried

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with $MgSO_4$. The residue after evaporation of the solvent was analyzed by GLC. The yield of alcohol **III** was determined against the authentic compound **III** prepared by method [6]; it amounted to 12%. IR spectrum (from thin film, ν, cm^{-1}): 2164(C≡C), 3300 (OH).

(b) To a solution of phenylmagnesium bromide prepared from 0.28 g of magnesium and 1.48 g of bromobenzene in 12 ml of anhydrous THF was added solution of 2 g of compound **I** in 3 ml of THF. The reaction mixture was refluxed at stirring for 1.5 h, hydrolyzed with water solution of ammonium chloride. The reaction product was extracted into ethyl ether, and the extract was dried with $MgSO_4$. The residue after evaporation of the solvent was analyzed by GLC. The yield of alcohol **III** was determined against the authentic compound **III**; it amounted to 48%.

(c) To a solution of phenylmagnesium bromide prepared from 0.48 g of magnesium and 3.14 g of bromobenzene in 20 ml of anhydrous THF was added solution of 4 g of compound **I** in 5 ml of THF. The reaction mixture was stirred at room temperature for 15 h and then treated as above. Yield of alcohol **III** 43% (GLC).

IR spectra were recorded on spectrometer Specord IR75 from thin film. The GLC analyses were performed on chromatograph LKhM-80 equipped with conductivity detector, column 1500 × 3.0 mm, stationary phase 10% of polymethylsiloxane on Chromaton, carrier gas helium.

REFERENCES

1. Medvedeva, A.S., Novokshonov, V.V., Demina, M.M., and Voronkov, M.G., *Zh. Org. Khim.*, 1994, vol. 64, no. 7, p. 1224.
2. Novokshonov, V.V., Medvedeva, A.S., Demina, M.M., Sherstyannikova, L.V., and Voronkov, M.G., *Zh. Org. Khim.*, 1996, vol. 32, no. 12, pp. 1828–1831.
3. Medvedeva, A.S., Novokshonov, V.V., Demina, M.M., and Voronkov, M.G., *J. Organometal. Chem.*, 1998, vol. 553, nos. 1–2, pp. 481–482.
4. Medvedeva, A.S. and Novokshonov, V.V., *Zh. Org. Khim.*, 1998, vol. 34, no. 9, pp. 1412–1413.
5. Shchelkunov, A.V., Vasil’eva, R.A., and Krichevskii, L.A., *Sintez i vzaimnye prevrashcheniya monozameshchennykh atsetilenov* (Synthesis and Mutual Transformation of Acetylene), Alma-Ata: Nauka, 1976.
6. Medvedeva, A.S., Margorskaya, O.I., and Voronkov, M.G., *USST Inventor*’s Certificate 1705297, 1991; SSSR Byull. Izobr., 1992, no. 2.