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Abstract

Full Text

CHEMISTRY

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ON THE INTERACTION OF TETRAHYDROFURAN WITH SILICON TETRACHLORIDE

A number of investigators have established that the tetrahydrofuran ring can undergo cleavage under the action of various halogen-containing agents, with the formation of 1,4-dihalogen-substituted aliphatic hydrocarbons. Thus, Frobé and Hochstetter ([1]), Starr and Hixon ([2]), and Fried and Kline ([3]), in studying the action of hydrogen halides on tetrahydrosilvan, tetrahydrofuran, and 2,5-dimethyltetrahydrofuran, found that, as a result of the ring opening occurring in this process, 1,4-dihalogen derivatives of butane, pentane, and hexane are formed. Paul ([4]), by the action of HBr on α-propyl-, α-butyl-, and α-benzyltetrahydrofurans in acetic-acid solution at 120–130°, obtained, respectively, 1,4-dibromoheptane, 1,4-dibromooctane, and 1-phenyl-2,5-dibromopentane. Wilson ([5]) investigated the cleaving action of HBr in the presence of acetic anhydride on tetrahydrofuran and a series of its functional derivatives, and also on tetrahydropyran. As a result, he obtained bromo derivatives of butane or pentane. Kluge and Evers ([6]) showed that, in the interaction of phosphorus tribromide with tetrahydrofuran, 1,4-dibromobutane is formed in a yield of 53%. Grimm and Schimpfle, in a patent ([7]), reported the preparation of 1,4-dichlorobutane in high yields (up to 90%) by the action of phosgene on tetrahydrofuran at 40–150° in the presence of catalysts that split off acids and water (Al_2O_3, $ZnCl_2$, MoO_3, activated carbon, etc.).

We found ([8], [9]) that the tetrahydrofuran ring is cleaved under the action of aluminum chloride or bromide, titanium tetrachloride, and antimony pentachloride. In this process, 1,4-dihaloalkanes are formed. In the present work we investigated the action of silicon tetrachloride on tetrahydrofuran. It turned out that tetrahydrofuran and silicon tetrachloride, in the absence of catalysts, do not enter into reaction even upon heating for 5 hr. However, under the catalytic influence of anhydrous zinc chloride, the reaction between these compounds proceeds rather rapidly and leads to the formation of 1,4-dichlorobutane and of an organosilicon compound to which the following structure must be assigned:

SovietRxiv

$$OCH_2CH_2CH_2CH_2Cl$$

$$Cl_2Si$$

$$OCH_2CH_2CH_2CH_2Cl$$

This organosilicon compound is readily hydrolyzed by water with evolution of heat, being converted into 4-chlorobutanol-1 and silicic acid. If the reaction is carried out with equimolar amounts of tetrahydrofuran and silicon tetrachloride, all of the tetrahydrofuran and about one half of the total amount of silicon tetrachloride enter into the reaction. This fact proves the correctness of the structure we have assigned to the organosilicon compound.

compounds. Thus, as a result of the reaction between tetrahydrofuran and silicon tetrachloride, the principal products formed are 1,4-dichlorobutane and di-(δ-chlorobutoxy)-dichlorosilane:

$$\begin{matrix} CH_2CH_2CH_2CH_2 \\ | \qquad\quad | \\ Cl \qquad Cl \end{matrix} + SiO_2$$

$$\text{tetrahydrofuran} + SiCl_4 \xrightarrow{(ZnCl_2)} \begin{cases} ClCH_2CH_2CH_2CH_2Cl + SiO_2 \\ Cl_2Si(OCH_2CH_2CH_2CH_2Cl)_2 \end{cases}$$

$$Cl_2Si(OCH_2CH_2CH_2CH_2Cl)_2 \xrightarrow{H_2O} HOCH_2CH_2CH_2CH_2Cl + SiO_2 \cdot nH_2O + HCl$$

The reaction between tetrahydrofuran and silicon tetrachloride was carried out as follows. Into a flask fitted with a reflux condenser were placed 1 g-mol of tetrahydrofuran, 1 g-mol of $SiCl_4$, and only 1 g of anhydrous zinc chloride. The reaction mixture was heated to boiling for 5 hours, and then, after distillation of the unreacted $SiCl_4$, was fractionated under reduced pressure.

Fraction I, with b.p. 50–51° (9 mm), in an amount of 18 g, had d_4^{20} 1.1294 and n_D^{20} 1.4516. Found: MR_D 30.32; for $C_4H_8Cl_2$, calculated MR_D 30.41. This fraction, obtained in a yield of about 15%, was 1,4-dichlorobutane.

Fraction II distilled with slight decomposition within the range 150–153° (8 mm). It was a colorless liquid fuming in air. Hydrolysis of this fraction was carried out in a flask fitted with a stirrer, a dropping funnel, and a reflux condenser. A dilute soda solution was slowly added from the dropping funnel to an ethereal solution of the fraction. The hydrolysis products were extracted several times with ether. After drying with anhydrous potash and distilling off the ether, the hydrolysis products were distilled under reduced pressure. As a result of hydrolysis, silicic acid and 4-chlorobutanol-1 were obtained, the latter having

SovietRxiv

the following properties: b.p. 80–81° (10 mm), d_4^{20} 1.0883 and n_D^{20} 1.4515. Found: MR_D 26.92; for C_4H_9ClO, calculated MR_D 27.06. The yield of 4-chlorobutanol-1, obtained in an amount of 65 g, was about 65%, calculated on the initial tetrahydrofuran.

Thus, as a result of the investigation carried out, it has been established that, in the interaction of tetrahydrofuran with silicon tetrachloride in the presence of anhydrous zinc chloride as catalyst, 1,4-dichlorobutane and di-(δ-chlorobutoxy)-dichlorosilane are formed. This reaction may serve as a method for obtaining oxygen-containing organosilicon compounds and chlorine-substituted aliphatic alcohols.

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