K. E. PIOTROVSKII and M. P. STOTSKAYA

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Abstract

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K. E. PIOTROVSKII and M. P. STOTSKAYA

DECOMPOSITION OF CERTAIN SIMPLE VINYL ETHERS AND 1,4-DIOXANE BY BUTYLLITHIUM

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P. P. Shorygin, as early as 1910, discovered the reaction of decomposition of simple ethers by organosodium compounds, proceeding according to scheme ([1]):

$$(C_{nH_{2n+1}})_2O + C_{mH_{2m+1}}Na \rightarrow C_{nH_{2n+1}}ONa + C_{nH_{2n}} + C_{mH_{2m+2}}.$$

Comparatively recently, studies began in the field of the interaction of simple ethers with organolithium compounds ([2]-[5]). In the work of Wittig and Harborth ([6]) there is an indication that, upon interaction of phenyllithium with certain vinyl ethers, acetylene was detected among the reaction products. The authors do not provide data on the quantitative determination of the latter. We undertook a study of the interaction of simple vinyl ethers (ethyl and isopropyl vinyl ethers) and 1,4-dioxane with butyllithium. Acetylene was detected in the gaseous decomposition products of all three of the above-mentioned compounds (see Table 1). Butyllithium was synthesized by the interaction of butyl chloride with metallic lithium in benzene medium (benzene suitable for cryoscopic determinations).

Table 1

Results of experiments on the decomposition of vinyl ethers and 1,4-dioxane by butyllithium

Ether	Duration of decomposition, hr	Taken for reaction, mol: ether	Taken for reaction, mol: butyllithium	Acetylene found in decomposition products, mg	Acetylene found in decomposition products, mol	Decomposed to acetylene, %: ether	Decomposed to acetylene, %: butyllithium
Ethyl vinyl ether	3	0.0417	0.0595	8.35	0.0003	0.7	1.5
»	5	0.0417	0.0640	48.20	0.0018	4.3	9.1
»	7	0.0417	0.0640	84.8	0.0033	7.9	16.6
Isopropyl vinyl ether	3	0.0174	0.0400	44.5	0.0017	9.6	13.1
Same	5	0.0174	0.0400	55.5	0.0021	12.4	16.5
»	7	0.0174	0.0400	64.6	0.0025	14.4	19.23
1,4-Dioxane	1.5	0.0469	0.0835	55.2	0.0024	4.6	10.4
	3	0.0469	0.0835	73.3	0.0028	5.9	13.2
	5	0.0469	0.0835	93.68	0.0036	7.7	17.3

Note. The decomposition of ethyl vinyl ether and isopropyl vinyl ether was carried out at 60°, the decomposition of 1,4-dioxane at 70°.

All operations for the synthesis, analysis, and dosing of butyllithium solutions were carried out in a stream of nitrogen free from traces of oxygen and moisture. The butyllithium solution was stored in a Schlenk vessel under nitrogen. Solutions 0.6–0.8 N in butyllithium were used for the work.

The ethers and dioxane were thoroughly washed (the dioxane was additionally freed from peroxides), dried over potassium hydroxide, distilled, and dried over metallic sodium.

The decomposition of the ethers and dioxane was carried out in an apparatus consisting of a three-necked flask with a reflux condenser and equipped with a thermometer and a siphon with a stopcock, through which a solution of butyllithium was fed into the flask, while during the decomposition nitrogen was periodically passed through to stir the reaction mixture. A three-way adapter with a dropping funnel and two stopcocks was mounted on the upper end of the condenser; one of the stopcocks was connected to a gasometer, and the other to a vacuum pump. The dropping funnel ended in a long glass tube passing through the entire condenser. The ethers and dioxane were introduced into the reaction mixture from the dropping funnel. To remove traces of moisture and air from the system before the experiment, the apparatus was thoroughly evacuated on an oil vacuum pump with heating and gradual cooling. The vacuum in the apparatus was equalized with nitrogen.

After completion of the decomposition, the apparatus was thoroughly purged with nitrogen in order to displace from the reaction medium and the system into the gasometer all gaseous reaction products. The quantitative determination of acetylene was carried out by a known method (7), based on argentometry. After a specified time from the beginning of the decomposition, the reaction mixture was treated with ethyl alcohol.

Analyses established that the main amount of acetylene is liberated precisely during this treatment. Thus, in an experiment on the decomposition of vinyl ethyl ether by butyllithium over 3 hours, 1.7 mg of acetylene was liberated; after treatment of the reaction mixture with ethyl alcohol, 8.35 mg of acetylene was collected. On the basis of this observation, the decomposition reaction of vinyl ethers by butyllithium may in general be represented by the following scheme:

$$R'{—}O{—}CH{=}CH_2 + LiR \rightarrow R'{—}O{—}Li + CH{\equiv}CH + RH,$$

$$CH{\equiv}CH + 2LiR \rightarrow LiC{\equiv}CLi + 2RH.$$

The acetylene formed as a result of the interaction of butyllithium with the vinyl ether reacts with butyllithium, forming lithium acetylide, which decomposes with liberation of acetylene only after treatment of the reaction mixture with alcohol. In studying the interaction of 1,4-dioxane with butyllithium, in addition to the quantitative determination of acetylene, proof was obtained for the presence of dilithium glycolate in the decomposition products by treating the reaction products with benzoyl chloride, followed by isolation and identification of ethylene glycol dibenzoate.

Its constants: melting point found 70-71° (according to literature data (8), 73-74°); molecular weight calculated 270.29, from the ester number 265.4, found cryoscopically 260.1.

In addition, butane was found in the gaseous products after decomposition of the reaction mixture with alcohol.

The sum of the experimental data makes it possible to represent the decomposition of 1,4-dioxane by butyllithium by the following scheme, which provides for the formation, as an intermediate compound, of a vinyl ether derivative:

a) $O< \begin{matrix} CH_2—CH_2 \\ \\ CH_2—CH_2 \end{matrix} >O + LiR \rightarrow Li—O—CH_2—CH_2—O—CH{=}CH_2 + RH,$

b) $LiO—CH_2—CH_2—O—CH{=}CH_2 + LiR \rightarrow LiO—CH_2—CH_2—OLi+$
$+CH\equiv CH + RH,$

c) $HC\equiv CH + 2LiR \rightarrow LiC\equiv CLi + 2RH.$

On the basis of the data obtained, one can give a very probable explanation of the widely known fact (9) of the regulation by vinyl ethers and 1,4-dioxane of the molecular weight in the polymerization of diene hydro-

hydrogens by alkali metals or their organic compounds. The growing polymer chain in this case is, in essence, an organometallic compound of the alkali metals and, reacting with vinyl ethers and 1,4-dioxane, causes the formation of acetylene. The latter reacts with the active centers of the growing chain and deactivates them, leading to the formation of lower-molecular-weight products.

The data obtained on the decomposition of 1,4-dioxane by butyllithium also make it possible to conclude that it is inadvisable to use dioxane as a solvent in the synthesis and storage of organolithium compounds.

All-Union Scientific Research Institute
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Note: Figure translations are in progress. See original paper for figures.