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ALKYLATION OF ANIONOID INTERMEDIATES IN THE REACTION OF BENZOFURAN WITH LITHIUM IN HEXAMETAPOL

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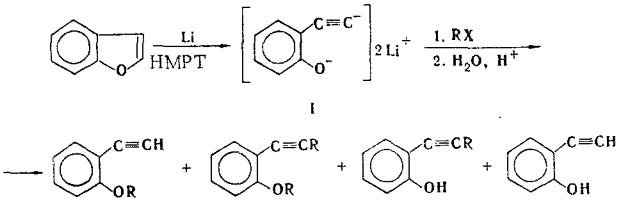
UDC 547.728.1:542.953

It is shown that the principal pathway in the reaction of benzofuran with a solution of lithium in hexametapol is opening of the furan ring of benzofuran to give a dilithium derivative. Mono- and dialkylation products are formed when the reaction mixture is treated with alkylating agents. It was established by the use of alkylating agents with different degrees of hardness that the oxygen atom is a softer polarizable center than the sp-hybridized carbanion center.

The reaction of benzofuran with a solution of sodium in liquid ammonia leads to hydrogenolysis of the furan ring of benzofuran to give o-ethylphenol [1].

We have investigated the reaction of benzofuran with a solution of lithium in hexametapol [hexamethylphosphoric triamide (HMPT)]. It is known that aryl alkyl ethers undergo cleavage in an alkali metal–hexametapol medium [2]. An investigation of the products of alkylation of the anionoid intermediates formed in the reaction of benzofuran with a solution of lithium in hexametapol shows that in our case the principal pathway is opening of the furan ring to give a dianion (I) or its dilithium derivative. Anion I is evidently formed as a result of the addition of two electrons to the benzofuran molecule, since only 50% of the benzofuran undergoes reaction with one equivalent of lithium.



I

II III IV V

Mono- and dialkylation products are formed in the case of alkylation with alkylating agents with different degrees of hardness and subsequent treatment of the reaction mixture with water (Table 1).

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TABLE 1. Alkylation of Benzofuran in the Presence of Lithium in Hexametapol

Alkylating agent	Composition of the alkylation products, %		
	II	III	IV
Benzofuran : lithium : alkylating agent ratio			1 : 2 : 3
Methyl bromide	3	78	—
Ethyl bromide	5	80	—
Isopropyl bromide	39	9	—
Allyl bromide	75	—	—
Propargyl bromide	83	—	—
Methyl tosylate	Traces	75	—
Benzofuran : lithium : alkylating agent ratio			1 : 1 : 3
Methyl bromide	2	42	—
Ethyl bromide	2	44	—
Benzofuran : lithium : alkylating agent ratio			1 : 2 : 1
Methyl bromide	1	22	45
Ethyl bromide	1	31	48
Methyl tosylate	2	5	69
Ethyl tosylate	1	10	70

The only reaction pathway is O-monoalkylation with the softest alkylating agents (allyl bromide and propargyl bromide). The fraction of O-monoalkylation products decreases on passing to harder alkylating agents (alkyl halides).

It should be noted that except for the experiments with isopropyl bromide, phenols are absent in the products of exhaustive alkylation of dianion I. In the case of isopropyl bromide the formation of o-ethynylphenol (27%) is explained by the ability of isopropyl bromide to eliminate hydrogen bromide under the influence of bases, which leads to neutralization of the organic anion.

The peculiarities of the alkylation make it possible to assume that the oxygen atom in dianion I is a softer polarizable center than the sp-hybridized carbanion center. The experimental data obtained when one equivalent of the alkylating agent was used are in good agreement with this conclusion. The fraction of C-monoalkylation products increases sharply in the case of harder leaving groups (methyl and ethyl tosylates).

o-Ethylphenol ethers are side products in all of the experiments; this may be associated with the peculiarity of the hexametapol anion radical to give up hydrogen atoms to the reaction medium [3].

EXPERIMENTAL

Chromatographic analysis was carried out with a Tsvet-4 chromatograph with a flame-ionization detector and a column (*l* 3 m, d 0.4 cm) filled with a PÉG-20000 stationary phase (10%) applied to Chromosorb W (30-60 mesh); the column temperature was 160°C. The PMR spectra were recorded with a Varian T-60 spectrometer. The mass spectra were recorded with a Varian (Gnom) MAT-111 spectrometer.

Cleavage of Benzofuran. A 40-ml sample of hexametapol and 2.36 g (0.02 mole) of benzofuran were placed in a reaction flask, 0.28 g (0.04 mole) of finely cut lithium metal was added, and the mixture was stirred at room temperature for 2 h. It was then cooled to 0°C, and excess alkylating agent was added dropwise. The mixture was treated with water, acidified with 10% hydrochloric acid, and extracted with ether. The combined ether extracts were washed successively with 10% sodium hydroxide solution and water (until the wash waters were neutral) and dried over magnesium sulfate. The alkaline extracts were acidified with 10% hydrochloric acid solution and extracted with ether. The extract was washed with water and dried over magnesium sulfate. The solvent was removed by distillation, and the reaction products were analyzed by gas–liquid chromatography, PMR spectroscopy, and mass spectrometry.

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