

cycloadducts, and with unsaturated donating type compounds as a 1,3-dipolar conjugated system to give products of [2 + 4]-cycloaddition regio- and stereo-selectively.

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STUDIES IN THE CROWN ETHER SERIES.

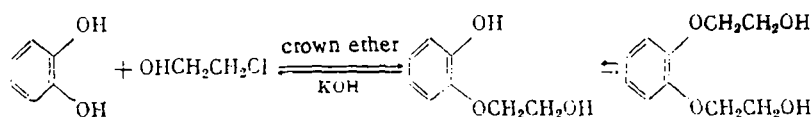
3. CATALYTIC ACTIVITY OF CROWN ETHERS AND THEIR "HETEROGENATED" ANALOGS

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UDC 541.128.34:547.898:542.91:547.562

The immobilization of crown ethers on carriers is a method for preparing synthetic models of ionophoric and enzymatic systems with a prolonged and multiply repeated action [1]. Modeling the catalytic function of benzo-crown ethers and their heterogenated analogs in the nucleophilic substitution reaction has already been carried out in [2, 3].

In continuation of the investigation on these subjects, already commenced, we studied the influence of functionalization and immobilization factors of benzo-crown ethers on their catalytic activity in the synthesis of esters according to Williamson, in particular in the reaction of hydroxyethylation of pyrocatechol by ethylene chlorohydrin in the presence of an alkali



EXPERIMENTAL

For the investigation, we used dicyclohexyl-18-crown-6 (I) from the firm "Fluka," benzo-18-crown-6 (II) [4], dibenzo-18-crown-6 (III) and 18-crown-6 (VII), produced at the Scientific-Research Institute of General Chemistry of the Siberian Branch of the Academy of Sciences of the USSR, 4,4'-diaminodibenzo-18-crown-6 (IV) and 4,4'-dinitrodibenzo-18-crown-6 (VI) [5, 6], 4'-nitrobenzo-18-crown-6 (V), and 4-aminobenzo-18-crown-6 (VIII) [7]. The immobilized derivatives of crown ethers (IV) and (VIII) were obtained according to [2, 3].

The GLC was carried on a "Chrom-5" chromatograph in an isothermal regime, the flow rate of He, H₂ and air was 40, 40, 400 ml/min, respectively, using a 2.5 m × 4 mm glass column, a chromatone N-AW-HmDS carrier (0.2-0.25 mm) with 10% Lucoprene G-1000 as stationary phase, the temperature of the carrier 200°C, of the thermostat and the columns 170°C, and of the flame ionization detector 220°C.

Hydroxyethylation of Pyrocatechol. Potassium hydroxide (2 g, 0.035 mole) was added in portions in an inert atmosphere to a solution of 1.1 g (0.01 mole) of pyrocatechol and 0.002 mole of a crown ether in 15 ml of ethanol. Then, 2.5 g of ethylene chlorohydrin were added dropwise to the boiling mixture. The mixture was boiled for 2 h, then cooled, the KCl precipitate was filtered and washed with 10 ml of ethanol. In the filtrate, the content of 1,2-

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TABLE 1. Catalytic Activity of Crown Ethers in Hydroxyethylation Reaction of Pyrocatechol

Crown ether	Yield	Conversion	Selectivity
	%		
Dicyclohexyl-18-crown-6 (I)	99	100	99
Benzo-18-crown-6 (II)	84.3	85.5	98.7
Dibenzo-18-crown-6 (III)	68.9	84.2	78.2
4,4'-Diamino-dibenzo-18-crown-6 (IV)	4.6	63	7.3
4'-Nitrobenzo-18-crown-6 (V)	8	50.9	15.4
4,4'-Dinitrodibenzo-18-crown-6 (VI)	3.5	99	3.5
18-Crown-6 (VII)	72	90.0	80.0
4'-Aminobenzo-18-crown-6 (VIII)	12.6	49.0	25.7

TABLE 2. Catalytic Activity of Immobilized Crown Ethers

Crown ether	Content of crown ether groups on polymer, mg-eq/g	Yield	Conversion	Selectivity
		%		
VIII on chloromethylated copolymer of styrene with DVB (8%) (IX)	1.12	78	88	89
VIII on silica, modified by SOCl_2 (X)	0.16			
VIII on carboxylorganoaerosil (XI)	0.45	28	85	33
IV on chloromethylated copolymer of styrene with DVB (2%) (XII)	0.64	64	100	64
IV on chloromethylated copolymer of styrene with DVB (8%) (XIII)	0.495	58	79	73
IV on silica, modified (XIV)	0.25	69	28	71
IV on carboxylorganoaerosil (XV)	0.66	16	85	18
VIII on chloromethylated copolymer of styrene with DVB (2%) (XVI)	1.35	83	90	92

di-(2-hydroxyethoxy)benzene and pyrocatechol was determined by GLC, and the yield, conversion, and selectivity were calculated. The data obtained are given in Tables 1 and 2.

RESULTS AND DISCUSSION

The experimental data given in Table 1 show that the yield, conversion and selectivity of the process are very dependent on the structure of the crown ethers. According to the influence on the reaction parameters, the crown ethers can be arranged in the following order: (I) > (II) > (VII) > (III) > (VIII) > (V) > (IV) > (VI). In this reaction, the role of the dianion of the ion pair separated by the crown ether increases with increase in the force holding the cation inside the polyether ring, or with increase in the thermodynamic stability constant of the complex of the crown ether with the cation. In this respect, the experimental data agree with the results of the investigation of the complexing ability of derivatives of DBC. According to these, the introduction of nitro groups considerably decreases the activity of the complexone [8]. As far as the use of the amino derivatives of crown ethers (IV) and (VIII) as catalysts is concerned, in this case the catalyst itself reacts with the substrate to form byproducts. Analysis of the experimental data shows that functionalization of the aromatic ring of the crown ether negatively influences the catalytic activity of the benzo-crown ethers.

Among the immobilized derivatives of crown ethers, crown ether (VIII), immobilized on a chlorinated silica gel and on a chloromethylated copolymer of styrene with divinylbenzene (DVB) with a degree of crosslinking of 2%, is the most effective catalyst.

An appreciable disadvantage of crown ethers on inorganic carriers (silicas) is the solubility of the latter in strongly alkaline medium. Catalysts on an organic polymer were no less effective, and did not decrease the activity after fourfold use. Thus, the catalysts obtained can be used several times, and their operating capacity is very dependent on the mechanical stability of the polymeric matrix. A compromise between the opposite factors (ensuring a sufficient degree of freedom for the polyether ring while retaining the mechanical strength) could be achieved by using a chloromethylated copolymer of styrene with DVB, with a content of about 8% of the crosslinking agent.

The least active were crown ethers immobilized on a carboxylated aerosil (XI), (XV). In this case, the active center, the polyether ring, is most remote from the support. Judging from the data in [9], this should favorably affect the catalytic activity of the immobilized crown ether. Decrease in the activity of (XI), (XV) is possibly due to screening of the destabilizing amino group. When this group is most screened by the polyether ring and the support, the yield and the selectivity of the catalyzed process are high.

CONCLUSIONS

1. The yield, conversion and selectivity of ethers in the Williamson reaction depend on the structure of the crown ether used as catalyst, the nature of the support, and the distance of the polyether ring from it.

2. The optimal catalyst is 4'-aminobenzo-18-crown-6 on a chloromethylated copolymer of styrene and divinylbenzene with a degree of crosslinking of 8%.

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