CATALYTIC ALKYLATION OF BENZOFURANS

III.* ALKYLATION OF BENZOFURAN BY ISOBUTYLENE AND TERT-BUTYL ALCOHOL

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The alkylation of benzofuran by isobutylene and tert-butyl alcohol in an autoclave in a flow system on $ZnCl_2$ applied to Al_2O_3 was studied. The major reaction products are 2- and 3-tert-tert-butylbenzofurans, the ratio of which depends on the conditions used to carry out the reaction. The product yield depends on the acidity of the catalyst used. The predominant formation of 2-tert-butylbenzofuran in the flow system is explained by the isomerization of 3-tert-butylbenzofuran via an intermolecular mechanism.

Continuing our investigations of the catalytic alkylation reactions of benzofuran [1,2], we have alkylated it with isobutylene and tert-butyl alcohol in the presence of zinc chloride applied to aluminum oxide. We ascertained the effect of the alkylating agent, the reaction conditions, and the acidity of the catalyst on the yield of alkylation products in the liquid and vapor phases. Zinc chloride was applied to aluminum oxide in

TABLE 1. Acidity of the Catalyst Sample

Sample No.	$ZnCl_2$ content in the catalyst, wt. %	Catalyst acidity, milliequivalents of butylamine per gram of catalyst
I	0 (Al_2O_3)	0,2
II	5	1,0
III	10	1,5
IV	20	3,0

TABLE 2. Alkylation of Benzofuran by Isobutylene in an Autoclave

Expt. No.	$ZnCl_2$ content on aluminum oxide, %	Temp.	Yield of reaction products, %				Isomer Ratio	Total yield of alkylated products
			2-tert-Butylbenzofuran	3-tert-Butylbenzofuran	2-n-Butylbenzofuran	Phenols		
1	5	100	—	—	—	—		
2		150	—	—	—	—		
3		200	2	2	—	—	1 : 1	4
4		250	4	5	—	—	1 : 1,2	9
5	10	100	—	—	—	—		
6		150	—	—	—	—		
7		200	19	21	Traces	Traces	1 : 1,1	40
8		250	26	30	2	8	1 : 1,15	58
9	20	100	12	15	2	4	1 : 1,25	29
10		150	20	28	—	6	1 : 1,4	48
11		200	27	25	2	17	1 : 1,08	54
12		250	35	42	3	15	1 : 1,2	80

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*See [1,2] for communications I and II.

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TABLE 3. Alkylation of Benzofuran by Isobutylene in a Flow System *

Expt. No.	Temp.	Yield of reaction products (%) relative to unchanged benzofuran			Ratio of the alkylbenzofurans formed
		2-tert-Butylbenzofuran	3-tert-Butylbenzofuran	Phenols	
1	200	24	3	8	8 : 1
2	230	32	6	8	5 : 1
3	245	33	6	10	8 : 1
4	265	8	1	40	8 : 1

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* The space velocity was 0.36 h^{-1}, and the catalyst was 20% ZnC12/A1203.

TABLE 4. Alkylation of Benzofuran by tert-Butyl Alcohol *

Expt. No.	Catalyst sample No.	Temp.	Degree of conversion of benzofuran, wt. %	Yield of alkylation products (%) based on unchanged benzofuran				Ratio of 2- 3-tert-butyl.-benzofurans
				2-tert-Butylbenzofuran	3-tert-Butylbenzofuran	Not interpreted	Phenol	
1	II	200	5	4	3	2	—	1,3 : 1
2		260	5	4	3	—	—	1,3 : 1
3		300	6	6	3	—	—	2 : 1
4	III	200	47	40	3	2	4	13 : 1
5		260	47	64	9	2	16	7 : 1
6		300	46	26	4	—	36	6 : 1
7	IV	200	62	52	5	7	29	10 : 1
8		260	58	68	9	4	25	7 : 1
9		300	65	30	2	2	62	15 : 1

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*The catalyst was 20% $ZnCl_2/Al_2O_3$ (IV), and the space velocity was 0.4 h^{-1}.

amounts from 5 to 20%, which made it possible to vary the catalyst acidity (Table 1). In the alkylation of benzofuran by isobutylene in a steady-state system (autoclave), it turned out that a definite catalyst acidity is required to accomplish the reaction at one or another temperature; the acidity has a substantial effect on the yield of alkylation products (Table 2). The products of the alkylation of benzofuran were 2- and 3-tert-butylbenzofurans, which are formed in an approximately constant ratio of 1:1.20. In addition to them, small amounts (2-3%) of 2-n-butylbenzofuran and 2-ethylphenol and phenol, the total yield of which did not exceed 17%, were detected in the catalyzate.

The ratio of the isomers formed changes substantially when the reaction is carried out in a flow system on a sample of catalyst IV at 200-265 deg (Table 3). It should be noted that virtually no alkylation occurs on catalysts I-III.

The sources of the phenol in the catalyzates are apparently the products of condensation of the starting benzofuran on the catalyst, the formation of which is promoted by raising the temperature above 250-260 deg.

The predominance of 2-tert-butylbenzofuran in the catalyzates when the reaction is carried out in the flow system is associated with isomerization of 3-tert-butylbenzofuran to 2-tert-butylbenzofuran, which was established by specially designed experiments. The isomerization of 3-tert-butylbenzofuran apparently proceeds via an intermolecular mechanism, since benzofuran and isobutylene are detected in the reaction products.

The alkylation of benzofuran by isobutylene probably proceeds through the formation of a tert-butyl cation on the acid centers of the catalyst [3]. The presence of 2-n-butylbenzofuran in the catalyzates is also evidence in favor of this.

In contrast to the alkylation by isobutylene, the alkylation by tert-butyl alcohol in a flow system also proceeds on a catalyst of lower activity (Table 4), which is apparently associated with the relatively great ease of formation of the tert-butyl cation from the alcohol.

EXPERIMENTAL

The experiments under steady-state conditions were carried out in autoclaves mounted in a tilting furnace with a heater. The experiments in the vapor phase were carried out in an automated apparatus of the flow type at atmospheric pressure in a stream of nitrogen that was fed in at a constant rate. To obtain comparable data, a fresh portion of catalyst was used in each experiment, and the catalyzate was removed during stable operation of the catalyst. The liquid catalyzates were analyzed by the method described in [1]. Isobutylene and a small amount of hydrogen were detected during the analysis of the gaseous reaction products in the experiments with tert-butyl alcohol.

The acidity of the catalyst was determined by anhydrous titration in the presence of an ethoxychrysoidine indicator [4].

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