REACTIONS OF 2- AND 3-METHYLBENZOTHIOPHENES IN THE PRESENCE OF HETEROGENEOUS ACID CATALYSTS

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In the presence of catalysts (Al_2O_3, Al_2O_3 activated by HCl, and 5, 10, and 20% $ZnCl_2/Al_2O_3$), 2- and 3-methylbenzothiophenes undergo mutual isomerization, dealkylation, and disproportionation to benzothiophene and 2,3-dimethylbenzothiophene at 250-450°C and space velocities of 0.1 and 0.8 h^{-1}. An ionic mechanism is proposed for the isomerization reaction.

Very little study has been devoted to the reactions of alkylbenzothiophenes in the presence of heterogeneous acid catalysts. The available information on them is restricted to our two earlier studies [1, 2], in which we noted the fact of mutual isomerization of 2- (I) and 3-methylbenzothiophenes (II) at 300°C on contact with 20% $ZnCl_2/Al_2O_3$.

In the present research we observed the mutual isomerization of benzothiophenes I and II at 250-450°C in the presence of a number of acid catalysts – aluminum oxide, aluminum oxide activated by hydrochloric acid, and zinc chloride (various concentrations) deposited on aluminum oxide. Both compounds were converted to mixtures (with close quantitative compositions) of identical substances, the dependence of the yields of which on the temperature are identical for both isomers (the dependence for 2-methylbenzothiophene is presented in Fig. 1 as an example). The degree of conversion of methylbenzothiophenes I and II also changes identically as the experimental parameters are varied (Table 1 and Fig. 2).

The acidity of the catalyst has a substantial effect on the degree of isomerization. Thus isomerization does not proceed at all on Al_2O_3 at 350°C, but in the presence of 10 or 20% $ZnCl_2/Al_2O_3$ the migration of the methyl group from one position to the other occurs to a sufficiently appreciable extent (Table 1). This dependence is also retained when the experiments are carried out in a sealed ampul (Table 2) rather than in a flow system.

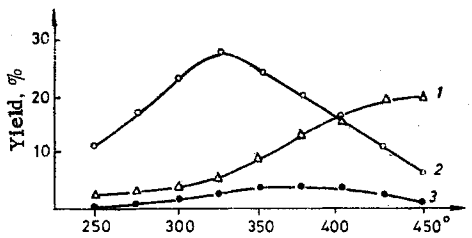

Fig. 1

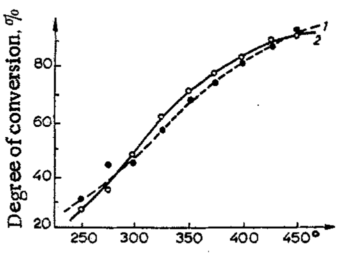

Fig. 2

Fig. 1. Dependence of the yield of products of the conversion of 2-methylbenzothiophene on the temperature (20% $ZnCl_2/Al_2O_3$, 0.1 h^{-1}): 1) benzothiophene; 2) 3-methylbenzothiophene; 3) 2,3-dimethylbenzothiophene.

Fig. 2. Dependence of the degree of conversion of methylbenzothiophenes on the temperature (20% $ZnCl_2/Al_2O_3$, 0.1 h^{-1}): 1) 2-methylbenzothiophene; 2) 3-methylbenzothiophene.

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TABLE 1. Dependence of the Conversion of Isomeric Methylbenzothiophenes on the Acidity of the Catalyst (at 350°C and 0.1 h^{-1})

Compound	Catalysts	Degree of conversion, %	Catalysate composition, %/yield, %					
			I	II	III	IV	V	Unidentified substances[a]
I	Al_2O_3	11	97	—	3/3	—	—	—
II	Al_2O_3	11	97	3/3	Trace	—	Trace	—
II	5% $ZnCl_2/Al_2O_3$	14	95	4/4	1/1	—	—	—
I	HCl/Al_2O_3	14	93	5/5	2/2	—	—	—
II	HCl/Al_2O_3	17	92	7/6	1/1	—	—	—
I	10% $ZnCl_2/Al_2O_3$	44	66	23/20	6/5	3/2	1/1	Traces
II	10% $ZnCl_2/Al_2O_3$	40	67	24/22	5/5	3/3	—	Traces
I	20% $ZnCl_2/Al_2O_3$	44[b]	65	27/23	3/3	2/2	2/2	Traces
II		47[b]	27/22	64	4/4	3/2	1/1	Traces
II		54[c]	29/23	58	6/5	4/3	2/2	Traces
I		69	43	34/24	12/9	6/4	1/1	4
I		44[d]	67	20/17	5/5	3/2	1/1	4
II		67	34/26	43	13/11	6/4	1/1	4
I		76[e]	37	31/20	19/13	7/4	Trace	6
I		65[f]	52	26/17	13/10	4/2	1/1	4
II		77[e]	24/23	34	22/16	6/4	Trace	4
I		83[g]	31	29/16	27/16	6/3	Trace	7
I		72[h]	43	31/20	17/12	5/3	—	4

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[a] Apparently benzene ring-alkylated benzothiophenes.

[b] 300°C.

[c] 300°C, indol.

[d] 0.8 h^{-1}.

[e] 375°C.

[f] 375°C, 0.8 h^{-1}.

[g] 400°C.

[h] 400°C, 0.8 h^{-1}.

TABLE 2. Transformations of the Isomeric Methylbenzothiophenes under Static Conditions

Compound	Catalyst	Time, h	Catalysate composition, %					
			I	II	III	IV	V	VI
I	20% $ZnCl_2/Al_2O_3$	5	87	7	1	—	5	—
I	20% $ZnCl_2/Al_2O_3$	30	58	25	4	—	14	2
II	Al_2O_3	5	2	98	—	—	—	—
II	20% $ZnCl_2O_3/Al_2O_3$	5	10	82	1	—	1	6
II		30	20	61	1	—	6	12
Mix. of I, II (1 : 1)		23	42	38	2	Traces	13	5
Mix. of I, II (1 : 1)		43	38	36	2	7	11	4

TABLE 3. Transformations of a Mixture of Isomeric Methylbenzothiophenes (1 : 1) (20% $ZnCl_2/Al_2O_3$, 0.1 h^{-1})

Temp., °C	Catalysate yield, %	Catalysate composition, %						Ratio in the Catalysate, %	
		I	II	III	IV	V	unidentified substances	I	II
300	90	47	46	3	2	1	1	50,3	49,7
350	78	40	39	12	6	1	3	50,9	49,1
400	61	31	30	25	9	Traces	5	50,8	49,2

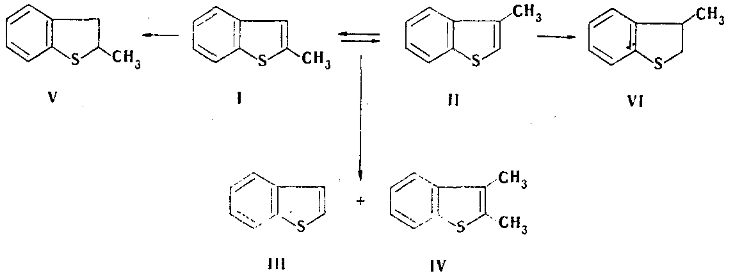
In addition to isomerization of I and II in the presence of catalysts that have sufficient aprotic acidity, one also observes disproportionation to benzothiophene (III) and 2,3-dimethylbenzothiophene (IV). The reaction proceeds primarily in a flow system but does take place under static conditions under the most severe conditions (Table 2).

The formation (due to disproportionation of hydrogen on acid catalysts) of small amounts of 2-methyl-

2,3-dihydrobenzothiophene (V) is also observed in the case of benzothiophene I. Benzothiophene V is also found in the products of conversion of benzothiophene II (Table 1). 3-Methyl-2,3-dihydrobenzothiophene (VI) is formed, in addition to dihydro derivative V, from II only when the reaction is carried out in a static system (Table 2). Its absence in the catalysates obtained in the flow system is evidently associated with the higher rates of competitive processes – isomerization, disproportionation, and dealkylation. Evidence for the occurrence of the latter is provided by the formation of benzothiophene III in greater amounts than the amounts formed as a result of disproportionation of I and II (Tables 1 and 2).

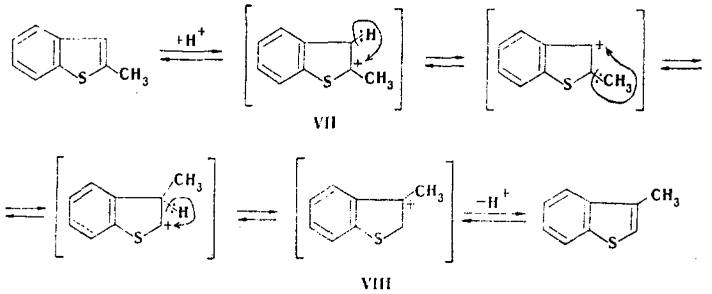
It was established in the case of benzothiophene I that only its degree of conversion decreases as the space velocity of the process increases, whereas the direction of the reactions does not change (Table 1).

Thus the transformations of benzothiophenes I and II can be represented by the following general scheme:



The isomerization of substituted benzothiophenes in the presence of strong protic acids has been investigated in [3], in which the ability of 3-substituted benzothiophenes to undergo isomerization to 2-substituted compounds was established, but the reverse reaction was not noted. Kost and co-workers [3] proposed an ionic mechanism for the reaction including protonation of the double bond of the heterocyclic ring of the benzothiophene molecule in the 3 position.

Later one of us [4] demonstrated that the direction of protonation of alkylbenzothiophenes, as in the case of alkylbenzofurans [5], depends on the position of the substituent in the heteroring: 2-methylbenzothiophene (I) is protonated in the 3 position, whereas 3-methylbenzothiophene (II), on the other hand, is protonated in the 2 position. In this case isomerization can be represented by the following scheme:



In the present research it was established that the isomerization of benzothiophenes I and II proceeds on both a catalyst with protic acidity (Al_2O_3 activated by HCl) and on a catalyst with primarily aprotic acidity ($ZnCl_2/Al_2O_3$) (Table 1). Consequently, both the protic and aprotic centers of the catalyst act as active centers. In the latter case the isomerization may also proceed in conformity with the scheme presented above. These facts, together with the absence of isomerization on Al_2O_3, indicate that the general acidity of the catalyst rather than the character of the acidity is important for isomerization.

Carbonium ions VII and VIII evidently have close stabilities, and this also explains the formation at 300-400°C of both isomers in approximately equal amounts (Tables 1 and 3).

The ionic character of the isomerization of benzothiophenes I and II is also confirmed by an experiment carried out in the presence of an inhibitor (ionol), during which the process was not slowed down (Table 1).

EXPERIMENTAL

2-Methylbenzothiophene (I) was obtained by the method in [6] and had mp 50-51°C and bp 95°C (7 mm). 3-Methylbenzothiophene (II) was synthesized by the method in [7] and had bp 77-78° (2.5 mm), d_4^{20} 1.1223, and n_D^{20} 1.6248.

TABLE 4. General Acidities and Specific Areas of the Catalysts

Catalyst	Acidity, mmole of n-butylamine/g of catalyst	Specific area, m^3/g
Al_2O_3	0,41	262
5% $ZnCl_2/Al_2O_3$	0,58	225
HCl/Al_2O_3	0,61	232
10% $ZnCl_2/Al_2O_3$	0,76	204
20% $ZnCl_2/Al_2O_3$	1,12	133

Preparation of the Catalysts (Table 4). The aluminum oxide, aluminum oxide activated by hydrochloric acid, and zinc chloride deposited on aluminum oxide were prepared by the methods in [8]. The general acidities of the catalysts were determined by the method in [9], and the specific areas were determined by the method in [10].

Experimental Method. The flow apparatus and its method of operation were described in [11]. The experiments in the static system were carried out in a sealed heat-resistant ampul, which was heated for 5 or 30 h in a tubular electric oven at 250°C.

Analysis of the Catalysts. The reaction products were analyzed by gas–liquid chromatography (GLC) with KhL-4, KhL-6, and UKh-1 chromatographs with columns 700- and 180 cm long and 0.4 cm in diameter; the liquid phase was Apiezon N and polyethylene glycol adipate applied on Chromosorb W (60-80 mesh) in 15 and 10% amounts, respectively. The chromatograms were interpreted and calculated by the methods in [12], and the internal standard was 3-methylbenzothiophene.

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