

ISOMERIZATION OF OXYGEN-CONTAINING HETEROCYCLES IN THE
 PRESENCE OF ACTIVATED CHARCOAL

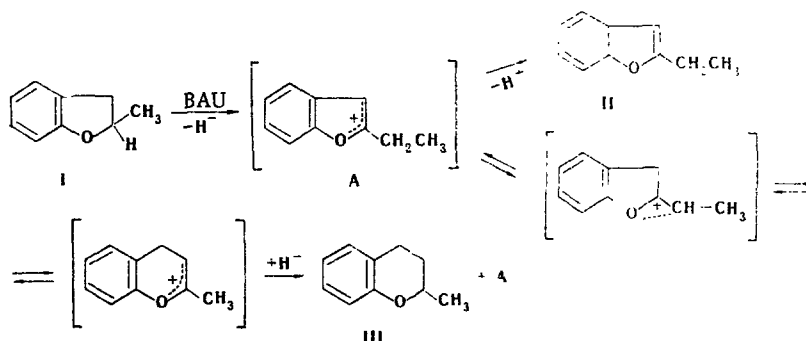
É. A. Karakhanov, M. V. Vagabov,
 S. K. Dzhamalov, and E. A. Viktorova

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Alkyl-2,3-dihydrobenzofurans, octahydrobenzofuran, and chromans undergo skeletal isomerization, dehydroisomerization, cis-trans isomerization, and dehydrogenation in the presence of BAU-activated charcoal. An ionic mechanism including initial stripping of a hydride ion from the starting compounds is proposed for the reactions. It is shown by means of ESR spectroscopy that there is no correlation between the catalyst activity and the concentration of paramagnetic centers on it. It is assumed that quinoid groupings on the charcoal surface are the active centers.

We have previously shown that 2,3-dihydrobenzofurans, octahydrobenzofuran, and chromans undergo similar transformations — dehydrogenation, isomerization, and dehydroisomerization — in the presence of both catalysts with aprotic activity ($ZnCl_2/Al_2O_3$) [1] and hydride-ion acceptors [2]. 2,3-Dihydrobenzofurans are dehydrogenated to give high yields of products also in contact with activated charcoal, during which the dehydrogenation proceeds via an ionic mechanism and one of the steps in the reaction is detachment of a hydride ion from the substrate molecule [3].

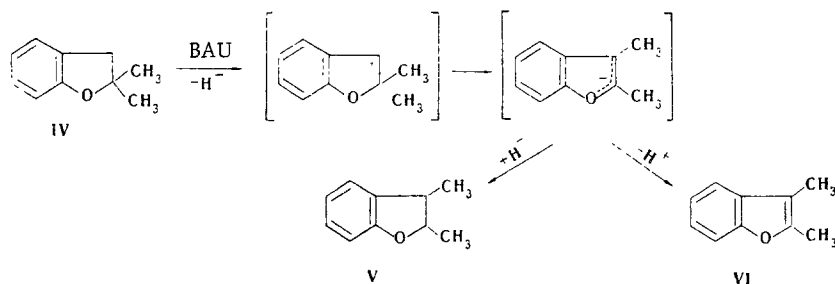
In the present research it was shown that activated charcoal at 300–400°C is a catalyst for the isomerization of oxygen-containing heterocyclic compounds. Thus 2-ethyl-2,3-dihydrobenzofuran (I), in addition to undergoing dehydrogenation to 2-ethylbenzofuran (II), is isomerized to 2-methylchroman (III) (Table 1):



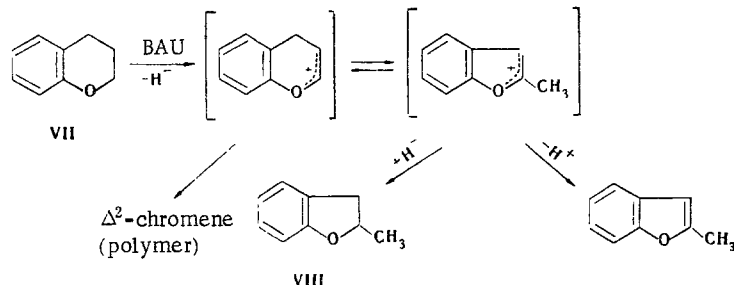
2,2-Dimethyl-2,3-dihydrobenzofuran (IV) undergoes isomerization to 2,3-dimethyl-2,3-dihydrobenzofuran (V) and dehydroisomerization to 2,3-dimethylbenzofuran (VI) (Table 2): (see scheme on following page).

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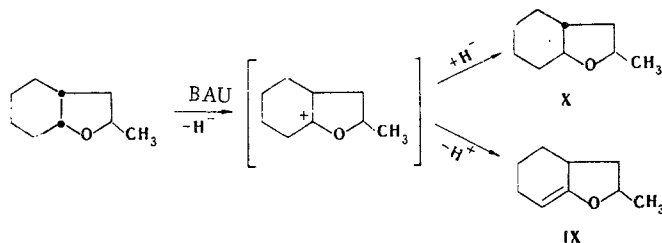
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Chromans VII and III are isomerized, respectively, to 2-methyl-2,3-dihydrobenzofuran (VIII) and I and 2-alkylbenzofurans (Tables 3 and 4):



At 200° and a space velocity of 0.1 h⁻¹ in the presence of BAU cis-2-methyloctahydrobenzofuran (IX) undergoes 25% conversion to trans isomer X; 2-methyl-2,3,4,5,6,8-hexahydrobenzofuran (XI) is simultaneously formed [4]:



The processes described above are accompanied by the formation of phenols, the amount of which increases as the temperature is raised. Alkylphenols with the same number of carbon atoms as in the starting material constitute the principal component of the phenols.

Functional groups of the BAU surface, particularly quinoid groups, the presence of which was demonstrated in [5, 6], may participate in hydride transfer reactions.

The IR reflection spectra of the BAU samples used contain maxima corresponding to carbonyl groups bonded to a polynuclear aromatic system (1750 cm⁻¹), carboxyl groups (1585 cm⁻¹), and hydroxyl groups (1070 cm⁻¹).

The literature contains indications regarding the presence on the charcoal surface of paramagnetic centers [6]. The ESR spectra of the BAU samples used and a carbon sample obtained by carbonization of sucrose showed that the concentration of paramagnetic centers on the sucrose carbon is higher by two orders of magnitude than on the BAU surface. However the catalytic activity of BAU in the dehydrogenation and isomerization reactions is higher than that of sucrose charcoal. The absence of a correlation between the charcoal activity and the paramagnetic center concentrations shows that radical processes made practically no contribution to these reactions.

EXPERIMENTAL

Industrial-activated birch charcoal was treated with nitric acid and then with distilled water until the wash waters gave a negative reaction for the nitrate ion. According to the results of emission analysis the treated charcoal contained the following microimpurities: 0.001% Si, 0.0001% Mg, and 0.0001% Cu. The specific area of the BAU, determined by thermal desorption of nitrogen, was 670 m²/g. All of the experiments were

TABLE 1. Transformations of 2-Ethyl-2,3-dihydrobenzofuran

Temp., °C	Yield, %		
	II	III	phenols
250	20	6	6
300	22	5	19
350	32	2	22
400	48	1	29

TABLE 3. Transformations of Chroman

Temp., °C	Yield, %		
	VIII	2-methylbenzofuran	phenols
250	—	—	—
300	Traces	1	Traces
350	Traces	6	15
400	1	28	40

TABLE 2. Transformations of 2,2-Dimethyl-2,3-dihydrobenzofuran

Temp., °C	Yield, %		
	v	VI	phenols
250	2	1	—
300	4	3	10
350	7	5	24
400	5	10	35

TABLE 4. Transformations of 2-Methylchroman

Temp., °C	Yield, %		
	I	II	phenols
250	2	Traces	Traces
300	4	1	5
350	1	8	29
400	—	20	40

carried out in a flow system with an integral reactor in a stream of oxygen-free nitrogen. The rate of feeding of the starting materials into the system was 0.1 h^{-1} . The liquid reaction products were analyzed with a Tsvet-4 chromatograph with a thermal conductivity detector. The liquid phase was polyethylene glycol 20,000, the solid support was Chromosorb W (60-80 mesh), the column length was 4 m, the temperature was 150° , and the helium flow rate was 40 ml/min.

The IR spectra were recorded with a IKS-20 spectrometer by the MNPVO method. The ESR spectra were recorded with an RE-1301 radiospectrometer at 9380 MHz. The derivative absorption line was recorded. The concentration of paramagnetic centers was determined by comparison with a standard sample through an intermediate standard (Cr^{3+} in corundum) with the aid of a double-integration nomogram.

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