HYDROGENATION AND DEHYDROGENATION REACTIONS OF BENZOFURAN AND ITS DERIVATIVES (REVIEW)

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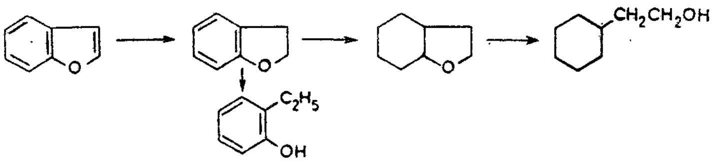
The literature data relative to the hydrogenation and dehydrogenation of benzofuran and its hydrogenated derivatives in the presence of different types of catalysts are examined. The problems involved in the formation, stability, and transformations of carbonium ions in the benzofuran series under the conditions of ionic hydrogenation and reactions with hydride-ion acceptors are discussed.

The interest in compounds of the benzofuran series is associated, on the one hand, with their physiological activity, participation in plant metabolism processes, antioxidant activity, etc., and, on the other, with the presence of potential resources of these compounds in the products of petroleum and coal refining. The combination of benzene and heterocyclic rings in benzofuran derivatives determines the certain specific character of their chemical (particularly, catalytic) transformations, which up to now have not been adequately studied. Benzofuran and its hydrogenated derivatives are extremely interesting subjects for a study of ionic processes that give rise to cationoid and anionoid particles.

The aim of the present review is an analysis of the literature data devoted to catalytic and noncatalytic hydrogenation, dehydrogenation, and isomerization in the benzofuran series.

Hydrogenation of Benzofurans

Catalysts based on group VIII metals and their oxides bring about hydrogenation not only of the heterocyclic ring of benzofurans but also of the benzene ring even under relatively mild conditions, and hydrogenation in a number of cases is accompanied by hydrogenolysis of the oxide ring of the resulting octahydrobenzofuran. A similar sequence of reactions was observed in the hydrogenation of benzofuran in the presence of palladized asbestos both in the liquid phase under pressure and at atmospheric pressure in a flow system (175°C) [1]. The predominant process was hydrogenolysis of the oxide ring.



Platinum oxide gives rise to the same processes at an even lower temperature (50°), in which case the rate of hydrogenation of the benzene ring is considerably lower than the rate of hydrogenation of the double bond of the heterocyclic ring.

The rate of hydrogen absorption for benzofuran at 25° in the presence of palladized carbon is considerably lower than the rate observed for indene and furan but is appreciable as compared with the rate observed for benzene, which does not absorb hydrogen at all under these conditions [2].

Raney nickel is most active in the hydrogenation of benzofuran to 2,3-dihydrobenzofuran; palladized (10%) carbon and copper oxide on chromium oxide display lower activities [2]. The selectivity of the process decreases as the temperature is raised in all cases, and the hydrogenation product is also octahydrobenzofuran.

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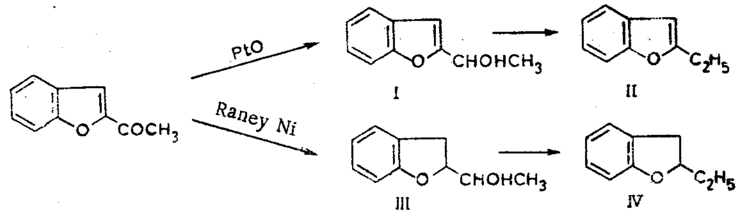
Platinum oxide displays high selectivity: Only successive reduction of the acetyl group occurs in the hydrogenation of 2-acetylbenzofuran [3], whereas Raney nickel also brings about hydrogenation of the carbon–carbon double bond of the heterocycle. Replacement of platinum oxide by colloidal platinum destroys the selectivity (a mixture of I-IV is formed).

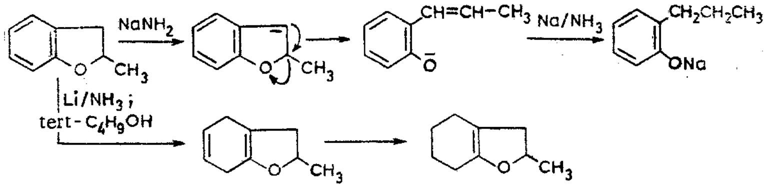


Benzofuran and its 2- and 3-alkyl-substituted derivatives can be arranged in the following order with respect to the relative rates of hydrogenation in the presence of Raney nickel and platinized carbon (15%) at 50° [4]: benzofuran > 2-methylbenzofuran > 2-ethylbenzofuran > 3-methylbenzofuran > 2,3-dimethylbenzofuran. 2-Phenylbenzofuran is not hydrogenated under these conditions. The effect of the presence, position, and volume of a substituent on the rate of hydrogenation of substituted benzofurans is thus apparent. The results are satisfactorily explicable from the position of π-complex adsorption [5-7] of aromatic compounds on group VIII metals. An increase in the number of alkyl groups, on the one hand, by lowering the ionization potential, promotes the formation of a π complex of the substrate with the metal and, on the other, creates steric hindrance to this sort of interaction [8]. Similar regularities were observed during a study of the competitive hydrogenation of alkylbenzenes [9].

Catalysts based on ruthenium proved to be highly effective in the hydrogenation of 2,3-dihydrobenzofuran [10]. Ruthenium on aluminum oxide and ruthenium on carbon hydrogenate dihydrobenzofuran at 50° in hexahydrocoumaran without causing hydrogenolysis of the oxide ring. A study of the kinetic principles of the hydrogenation at 1-120 atm showed that hydrogenation proceeds at a higher rate in the presence of Ru/Al_2O_3 than on Ru/C. Up to 90 atm, a reaction that is zero order with respect to 2,3-dihydrobenzofuran and first order with respect to hydrogen is observed, and an overall zero-order reaction occurs at higher pressures.

The data from research on the catalytic hydrogenation of benzofurans presented above show that it does not always proceed selectively to give 2,3-dihydro derivatives and is complicated by the formation of octahydro derivatives and products of hydrogenolysis of the heterocyclic ring.

The reduction of benzofurans and their derivatives with alkali metals in liquid ammonia [11-14] proceeds in several directions to give ring cleavage products (alkylphenols) and tetrahydro and hexahydro derivatives:

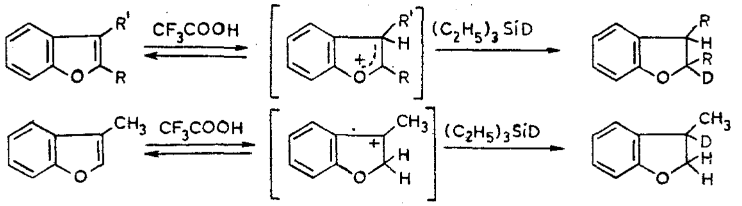


The ionic hydrogenation of benzofurans, which consists in the successive addition of a proton and a hydride ion to the molecule, may serve as a method for the noncatalytic hydrogenation of benzofurans to 2,3-dihydrobenzofurans [15]. Inasmuch as carbonium ions, the properties of which determine the extent and direction of the processes, are formed in the first step of the reaction, only compounds that, upon protonation, give carbonium ions that are sufficiently stable to exist in the form of kinetically independent particles undergoing ionic hydrogenation.

The ionic hydrogenation of benzofuran and its homologs [16] with a trifluoroacetic acid–triethylsilane pair showed that this reaction may serve as a preparative method for the synthesis of 2,3-dihydrobenzofurans (the yields are close to quantitative). Inasmuch as the first step in ionic hydrogenation is protonation of the substrate, a question naturally arises regarding the site of initial attack of the proton; up until recently, this problem had remained unresolved for compounds of the benzofuran series. The computational [17-19] and experimental [20, 21] data on the relative activities of the 2 and 3 positions of the molecules in electrophilic substitution reactions (particularly alkylation) are extremely contradictory.

The direction of protonation of benzofuran was established in experiments with hydrogenating pairs in which one of the substances contained deuterium [22, 23]. In the base of benzofuran and its 2-alkyl- and

2,3-dialkyl-substituted derivatives attack of the proton is directed to the 3 position, whereas 3-methylbenzofuran is protonated in the 2 position:



$R=R'=H$; $R=D, R'=H$; $R=CH_3, R'=H$; $R=C_2H_5, R'=H$; $R=R'=CH_3$

However, individual monodeutero-2,3-dihydrobenzofurans can be obtained only when the trifluoroacetic acid–triethyldeuterosilane pair is used (Table 1), whereas when deuterated trifluoroacetic acid is used as the deuterium source, a certain amount of polydeuterated analogs are also formed along with the monodeuterated compounds.

The NMR spectra and mass spectra indicate that the 2,3-dihydrobenzofurans obtained in this way have a strictly fixed position of the deuterium atom, and, consequently, 1,2-hydride and methyl migrations are absent in the intermediate carbonium ions.

The data in [22] make it possible to draw a conclusion that is of fundamental importance – the protonation of benzofuran is determined by the position of the alkyl substituent in the heteroring. The presence and position of the substituent determine the reactivities of these compounds in ionic hydrogenation: Thus the relative rates of hydrogenation of benzofuran and 3- and 2-methylbenzofurans are 1, 8, and 16, respectively.

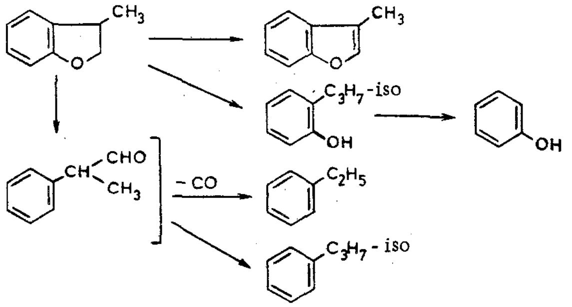
Dehydrogenation of 2,3-Dihydrobenzofurans

Both dehydrogenating agents (sulfur) and various types of catalysts such as group VIII metals and catalysts with active centers of an acceptor nature (aluminum oxide, zinc oxide on aluminum oxide, aluminum silicates, and activated carbon) have been used for the dehydrogenation of 2,3-dihydrobenzofurans.

Klarmann [24] obtained benzofuran in 45-50% yield by heating 2,3-dihydrobenzofuran with sulfur or selenium at 220°.

Lesiak [25] was able to obtain benzofuran in 77% yield by carrying out the dehydrogenation of 2,3-dihydrobenzofuran in the vapor phase (600-630°) in contact with alumogel (promoted by iron oxide) at reduced pressure and repeated recirculation of the unchanged 2,3-dihydrobenzofuran.

Platinum, palladium, or rhodium on carbon have proved to be extremely effective catalysts for the dehydrogenation of 2,3-dihydrobenzofuran [26]. The yields of benzofurans (70-95%) depend on the structures of the starting compounds, the catalysts, and the temperature [27-29]. Rhodium is the most selective catalyst [28]. Hydrogenolysis of the oxide ring to give alkylphenols is a side reaction in this case.



It is extremely interesting that the position of the substituent in the heteroring changes the direction of opening of the oxide ring. Substances that provide evidence for cleavage of the oxide ring not only at the 1–2 bond but also at the 1–9 bond were detected in the products of conversion of 3-methyl-1,2-dihydrobenzofuran (for example, in the presence of Pt/C) [30].

The investigated compounds are arranged in the following order with respect to their ease of dehydrogenation on group VIII metals: 2,3-dihydrobenzofuran > 3-methyl-2,3-dihydrobenzofuran > 2-methyl-2,3-dihydrobenzofuran > 2,3-dimethyl-2,3-dihydrobenzofuran (Table 2) [31].

TABLE 1. Ionic Hydrogenation of Benzofurans [CF_3COOH–$(C_2H_5)_3SiD$ hydrogenating pair, reaction time 3 h at 70°C]

Substituent in the starting benzofuran	Substituent in the 2,3-dihydrobenzofuran product	Yield, %	Deuterium content, %
H	2-D	81	98
2-D	$2,2\text{-}D_2$	80	94
$2\text{-}CH_3$	$2\text{-}D\text{-}2\text{-}CH_3$	96	100
$2\text{-}C_2H_5$	$2\text{-}D\text{-}2C_2H_5$	96	98
$2,3\text{-}(CH_3)_2$	$2\text{-}D\text{-}2,3\text{-}(CH_3)_2$	94	98
$3\text{-}CH_3$	$3\text{-}D\text{-}3\text{-}CH_3$	96	97

TABLE 2. Apparent Energies of Activation in the Dehydrogenation of 2,3-Dihydrobenzofurans

Compound	E_{app}, kcal/mole			
	Pd/C	Pd black	Pt/C	Rh/C
2,3-Dihydrobenzofuran	5,0	5,7	8,5	6,7
2-Methyl-2,3-dihydrobenzofuran	10,1	9,2	12,3	10,1
3-Methyl-2,3-dihydrobenzofuran	8,2	8,5	—	—
2,3-Dimethyl-2,3-dihydrobenzofuran	14,5	12.6	—	—

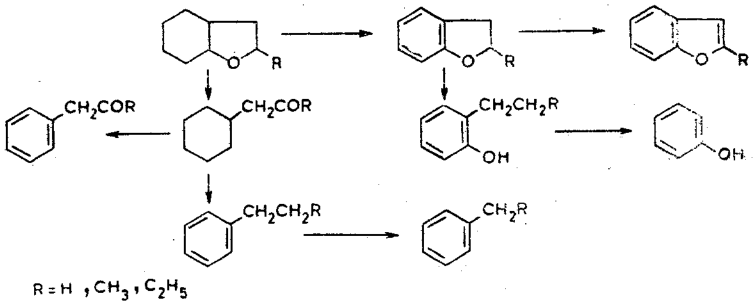
TABLE 3. Yields of Alkylphenols (%) as a Function of the Structure of the Starting 2,3-Dihydrobenzofuran (reaction temperature 290°C)

Catalyst	Substituent in the 2,3-dihydrobenzofuran						
	H	$3\text{-}CH_3$	$3,3,5\text{-}(CH_3)_3$	$2\text{-}CH_3$	$2\text{-}C_2H_5$	$2,3\text{-}(CH_3)_2$	$2,2\text{-}(CH_3)_2$
Pd/C	18	16	18	5	9	6	0
Pt black	31	23	—	15	17	13	8

Thus an increase in the degree of substitution of the heteroring lowers the reaction rate, i.e., an effect similar to the ortho-deactivation effect [7, 32] evidently occurs in the dehydrogenation of 2,3-dihydrobenzofurans. In addition, one should take into account the fact that the oxygen in 2,3-dihydrobenzofurans gives rise to an additional interaction with the catalyst's surface [33], which also shows up in the difference in the kinetic parameters of dehydrogenation of unsubstituted 2 3-dihydrobenzofuran and its 2- and 3-alkyl derivatives. The effect of steric hindrance also shows up in the hydrogenolysis of the oxygen-containing ring (Table 3). The yields of alkylphenols (the hydrogenolysis products) are substantially lower for 2,3-dihydrobenzofurans that have an alkyl substituent in the 2 position [34].

2,3-Dihydrobenzofurans are not only dehydrogenated to benzofurans in a stream of hydrogen in the presence of platinized carbon at 200-300° but are also hydrogenated to octahydrobenzofurans. The equilibrium is shifted to favor the hydrogenated derivatives, which then undergo rather complex transformations.

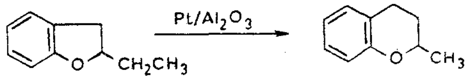
It is interesting that octahydrobenzofurans undergo mainly dehydrogenation on contact with group VIII metals [29, 30, 35, 36]; this distinguishes them from tetrahydrofurans, which are isomerized to carbonyl compounds of the aliphatic series under similar conditions [37]. This behavior of octahydrobenzofurans is associated with the possibility of conversion of the alicyclic fragment of the molecule to a benzene ring, which stabilizes the oxide ring. The dehydrogenation of octahydrobenzofurans is accompanied by side processes, the sequence of which is depicted by the following scheme in the case of catalysis by platinum, rhodium, and palladium deposited on carbon:



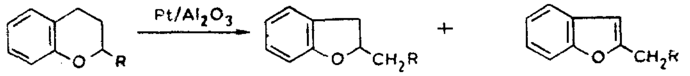
R = H, CH_3, C_2H_5

The carbon used as the support was prepared in such a way that it did not have catalytic activity in the indicated reactions and did not give rise to isomerization of the heteroring.

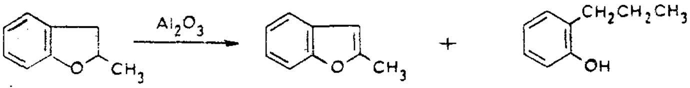
In contrast to platinized carbon, platinum on aluminum oxide, in addition to causing dehydrogenation of 2-alkyl-2,3-dihydrobenzofurans, also brings about their isomerization. Thus 2-ethyl-2,3-dihydrobenzofuran forms 2-methylchroman in up to 38% yields on contact with this catalyst [38].



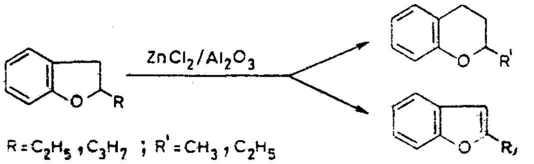
The isomerization reaction is reversible, and chroman undergoes dehydroisomerization with contraction of the heteroring under similar conditions [39-41]:



Aluminum oxide itself has not only isomerizing but also dehydrogenating activity, and 2,3-dihydrobenzofurans undergo the same transformations as on group VIII metals when it is present [42]:



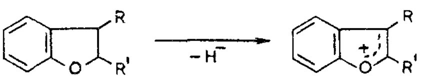
Other catalysts with aprotic acidity also display similar activity. Thus zinc chloride on aluminum oxide dehydrogenates and isomerizes (with expansion of the oxide ring) 2-alkyl-2,3-dihydrobenzofurans [43, 44]:



2,2-Dimethyl- and 3,3-dimethyl-2,-3-dihydrobenzofurans undergo dehydroisomerization under similar conditions [45, 46]:

Alumosilicate catalysts are more stable and selective than the $ZnCl_2/Al_2O_3$ catalyst, and this makes it possible to obtain dehydrogenation products in up to 80% yields [47]. The formation of phenols in their presence was observed only at temperatures above 400°.

A peculiarity of the transformations of 2,3-dihydrobenzofurans on all acid catalysts is the absence of hydrogen in the gas phase, whereas a stoichiometric amount of hydrogen is detected in the gaseous reaction products in the case of dehydrogenation on group VIII metals. In this connection, a question arose regarding the mechanism of dehydrogenation of 2,3-dihydrobenzofurans on acid catalysts. Concepts have been developed regarding the ionic mechanism of processes that occur on contact of 2,3-dihydrobenzofurans with catalysts of an acidic nature, according to which a hydride ion is detached from the 2,3-dihydrobenzofuran molecule in the first step of the reaction under the influence of the acceptor centers of the catalyst. The carbonium ions thereby generated are quite stable owing to the participation of the oxygen in delocalization of the positive charge.



The transformations of the carbonium ions determine the final composition of the reaction products. One such transformation is stabilization of them by ejection of a proton, which leads to the dehydrogenation products. In addition, the carbonium ion may react via different pathways: In particular, it may undergo skeletal isomerization.

Oxidized activated carbon is an effective catalyst for the dehydrogenation of 2,3-dihydrobenzofurans, and, as in the case of acid catalysts, hydrogen is absent in the gas phase [48, 49]. Taking into account the presence on the activated carbon surface of quinoid groups that have an acceptor effect, Karakhanov and co-workers feel that the transformations of 2,3-dihydrobenzofurans proceed via an ionic mechanism in

TABLE 4. Effective Rate Constants and Apparent Energies of Activation for Dehydrogenation on Activated Carbon (BAU)

Temp., °C	Effective rate constants, $kK \cdot 10^4$ moles/atm · sec			
	2,3-dihydrobenzofuran	2-methyl-2,3-dihydrobenzofuran	3-methyl-2,3-dihydrobenzofuran	2,3-dimethyl-2,3-dihydrobenzofuran
290	4,0	6,3	3,8	4,6
320	5,4	7,9	5,9	6,4
350	7,1	8,9	7,3	8,3
380	9,8	12,0	9,8	11,0
E_{app}, kcal/mole	8,5	5,7	7,3	6,8

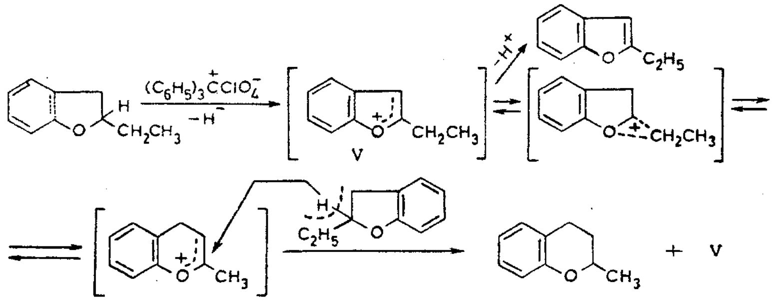
this case also. The absence of a correlation between the activity of the carbon in the indicated reactions and the concentration of the paramagnetic centers on its surface demonstrates and there is practically no contribution of radical processes to dehydrogenation and isomerization [50].

The kinetic principles of the dehydrogenation of 2,3-dihydrobenzofurans on carbon [51] and alumosilicate [47] provide evidence in favor of ionic initiation of the processes (Table 4).

Thus, with respect to the ease of dehydrogenation on activated carbon, 2,3-dihydrobenzofurans are arranged in an order opposite to the order obtained in dehydrogenation on group VIII metals [31]. The reactivities of 2,3-dihydrobenzofurans correlate with the hydride lability of the hydrogen in their molecules. Similar results were obtained in experiments with an alumosilicate catalyst [47].

The specific character of the adsorption of 2,3-dihydrobenzofuran on an alumosilicate catalyst was investigated to obtain a more detailed explanation of the mechanism of the described transformation [52]. The IR spectra of 2,3-dihydrobenzofuran adsorbed on the original sample of alumosilicate and on a sample obtained as a result of H—D exchange in its surface silanol groups and a mass-spectral analysis of the products of H—D exchange desorbed from the surface of the catalyst showed that the deuterium is concentrated in the 2 position of the 2,3-dihydrobenzofuran molecule. In the case of the hydrocarbon analog of 2,3-dihydrobenzofuran — indane — H—D exchange occurs at a minimum of two carbon atoms of the five-membered ring. The presence of deuterium atoms only in the 2 position in the 2,3-dihydrobenzofuran molecule, in contrast to indane, made it possible to draw a conclusion regarding the specific character of the adsorption of 2,3-dihydrobenzofuran, consisting in the fact that the plane of the molecule forms a certain angle with the surface of the adsorbent, and the hydrogen atoms in the 2 position prove to be closer to the surface than those in the 3 position. This sort of orientation of the molecule may be associated with pronounced interaction of the oxygen atom of the five-membered ring with the tricoordinated aluminum of the alumosilicate, and it is also responsible for splitting out of a hydride ion primarily from the 2 position of the molecule. Karakhanov and co-workers [53] and Lysenko [54] associate the formation of phenols from 2,3-dihydrobenzofurans in the presence of acid catalysts with redistribution of the hydrogen in the polymerized complex, which is formed in turn from the alkylphenols — products of opening of the oxygen ring of 2,3-dihydrobenzofurans.

The ionic character of the transformations of 2,3-dihydrobenzofurans on acid catalysts and activated carbon suggests hydride lability of the hydrogen atoms in 2,3-dihydrobenzofuran molecules, information regarding which was obtained in [16, 55-57] during a study of the reaction of 2,3-dihydrobenzofurans with classical hydride-ion acceptors — stable carbonium ions.



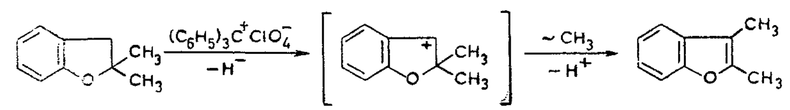
Drawing analogies between the catalyzed and noncatalyzed processes in a number of cases makes it possible to construct extremely useful models, by means of which one can explain many experimental facts.

A study of the generative conditions and the character of the subsequent transformations of the carbonium ions of the benzofuran series [16, 55, 57] made it possible to model processes that occur on the active centers of acid catalysts.

2,3-Dihydrobenzofurans under ionic dehydrogenation and skeletal isomerization on reaction with triphenylmethyl perchlorate. An ion-chain process is realized.

On the basis of the scheme presented above one should expect a considerably lower capacity of 2-methyl-2,3-dihydrobenzofuran to undergo isomerization with expansion of the oxide ring, inasmuch as the isomerization of the cations is unlikely in this case. This is confirmed by the absence of chroman in the products of the reaction of 2-methyl-2,3-dihydrobenzofuran with hydride-ion acceptors.

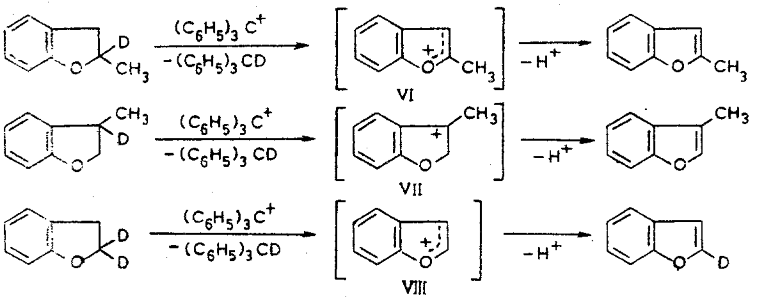
2,2-Dimethyl-2,3-dihydrobenzofuran is dehydrogenated to 2,3-dimethylbenzofuran in reactions with hydride-ion acceptors.



2,3-Dihydrobenzofurans react similarly with triphenylmethyl tetrafluoroborate and chloranil.

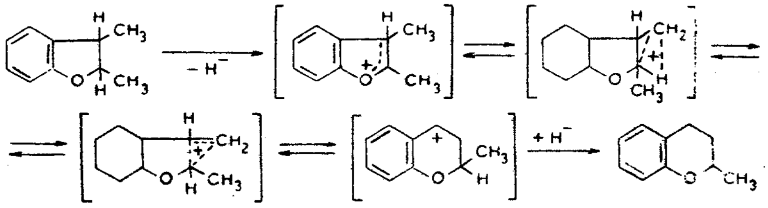
The hydride lability of the hydrogens in 2,3-dihydrobenzofurans was also estimated from their activity as hydride-ion donors in the hydrogenation of cyclic olefins and the reduction of triphenylmethylcarbinol [56, 57]. The investigated 2,3-dihydrobenzofurans are arranged in the same order with respect to the case of extraction of a hydride ion as the order obtained during an investigation of their transformations on acid catalysts and activated carbon.

The results and the structure of the 2,3-dihydrobenzofurans made it possible to assume that the hydride ion is detached from the 2 position. However, Karakhanov and co-workers [56, 57] did not exclude the possibility of detachment of a hydride ion also from the 3 position, inasmuch as the benzene ring may participate in charge stabilization in the resulting carbonium ion in this case. As a result of experiments with labeled 2,3-dihydrobenzofurans, Dem'yanova [16] unambiguously established the site of detachment of the hydride ion:

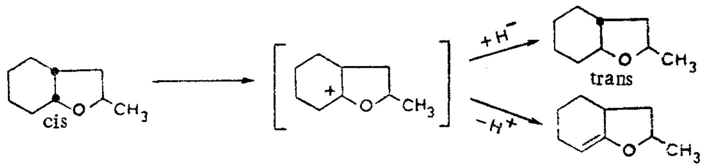


The deuterium content in the triphenylmethane formed as a result of hydride transfer was close to quantitative. When an alkyl substituent participates in stabilization of the intermediately formed carbonium ions, the hydride ion is split out from the same carbon atom to which this substituent is attached. Thus the site of detachment of a hydride ion from the starting 2,3-dihydrobenzofurans is determined by the position of the alkyl substituents. In the case of unsubstituted 2,3-dihydrobenzofuran, the hydride ion is split out only from the 2 position, and this constitutes evidence that the positive charge is stabilized to a greater extent by the oxygen p electrons than by the π system of the benzene ring. The carbonium ions that are generated by detachment of a hydride ion are arranged in the order VI > VII > VIII with respect to their relative stabilities, and this correlates with the ease of dehydrogenation of 2,3-dihydrobenzofurans under the influence of both hydride-acceptors and catalysts that are acidic in nature. In [16] it was shown by means of ESR and NMR methods (chemical polarization of the nuclei) that the reactions under discussion did not proceed through a step involving one-electron transfer.

Experiments with 2,3-dimethyl-2,3-dihydrobenzofuran on alumosilicate, in which 2-methylchroman – the product of expansion of the oxide ring – if formed along with 2,3-dimethylbenzofuran, constitutes an extremely interesting illustration of the ionic character of the transformations of 2,3-dihydrobenzofurans on acid catalysts [58]:



The cis,trans-isomerization of octahydrobenzofurans [59] under the influence of Al_2O_3 and $ZnCl_2$/ Al_2O_3 also apparently proceeds via an ionic mechanism:



The material from the papers cited above persuasively demonstrates the existence of a correlation between the activities of 2,3-dihydrobenzofurans, in their transformations on catalysts with acceptor centers, and the hydride lability of the hydrogen of the heterocyclic ring and, consequently, the ionic character of processes that occur on catalysts on this sort. Thus the reaction of 2,3 dihydrobenzofurans with hydride-ion acceptors and their transformations on acid catalysts can be used for the preparation of the corresponding benzofurans in high yields. Of particular interest are catalysts such as activated carbon and alumosilicate, which are quite stable in the experiments and bring about highly selective dehydrogenation.

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