(0.07-0.1)]. The catalyst was activated prior to the experiments in a stream of hydrogen at 400°C for 4 h.

Analytical-grade 1,4-butanediol was used. The reaction products were condensed in a mixture of dry ice and acetone. The condensate was analyzed by gas—liquid chromatography (GLC) with a Varian Aerograph-2800 chromatograph with Cilicon DC-702 applied to Cellite-545 in 30% amounts as the stationary phase. The detector was a flame-ionization device, the vaporizer temperature was 220°C, the carrier-gas (helium) flow rate was 60 ml/min, and the column temperatures were 90 and 150°C. Isoamyl alcohol was used as the internal standard.

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ISOTOPE EXCHANGE OF HETEROCYCLIC COMPOUNDS WITH D_2O IN THE PRESENCE OF TRANSITION METALS

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During a study of deuterium-hydrogen exchange of two-ring condensed heterocycles in the presence of a Pt catalyst it was observed that the degree of deuteration decreases in the order benzofuran ≫ naphthalene > benzothiophene. It was found that the degree of deuteration of 2-acetylbenzofuran is 80%, whereas for 2-propylbenzofuran it is only 8%. The degree of deuteration of hydrogenated derivatives decreases in the order coumarin > chromene > dihydrocoumarin; the formation of polydeuterated derivatives is observed for coumarin, whereas products of replacement of one hydrogen atom by deuterium predominate for chromene and dihydrocoumarin.

In the present research we investigated H—D exchange with D_2O of a number of heterocyclic compounds in the presence of Pt, Cu, Fe, Co, and Ni blacks.

In contrast to benzene [1], which undergoes intensive exchange with D_2O, furan and thiophene undergo exchange considerably less vigorously under similar conditions (see Table 1), and they can be arranged in the order benzene > thiophene > furan with respect to their degree of deuteration.

The "introduction" of another benzene ring in the molecules named above changes the picture substantially. Benzofuran, benzothiophene, and naphthalene are arranged in the order benzofuran ≫ naphthalene > benzothiophene with respect to their degree of deuteration.

The difference in the behavior of one-ring and two-ring compounds can be explained within the framework of the concepts of π-complex adsorption [1]. During π-complex adsorption benzene is flatly disposed on the surface and participates actively in the adsorption—desorption process [1]. Furan and thiophene, due to the strong interaction of the n electrons of the heteroatoms with the metal, evidently are vertically oriented on the surface [2, 3], and this leads to a significant decrease in the degree of deuteration.

In the case of two-ring systems the presence of two aromatic rings will increase the strength of π-complex adsorption [1], and, as noted above, this should give rise to a de-

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TABLE 1. Compositions of the Reaction Mixtures after H—D Exchange of Organic Compounds with D_2O according to Data from Mass-Spectrometric Analysis

No.	Substance	Catalyst	Distribution, D, %						Σd_i, %	D_∞*, %
			d_0	d_1	d_2	d_3	d_4	d_5		
1	Benzofuran	Pt	50	43	7				50	100
2	"	Cu	99	1					1	100
3	"	Fe	98	2					2	100
4	"	Co	97	3					3	100
5	"	Ni	89	11					11	100
6	2-Propylbenzofuran	Pt	92	8					8	100
7	2-Acetylbenzofuran	Pt	20	28	25	16	8	3	80	75
8	Furan	Pt	96	4					4	100
9	Thiophene	Pt	90	7	3				10	100
10	Benzothiophene	Pt	100	0					0	100
11	2-Methyl-2,3-dihydrobenzothiophene	Pt	98	2					2	100
12	Naphthalene	Pt	97	3					3	75
13	Chroman	Pt	83	8	3	3	2	1	17	60
14	Chromene	Pt	44	32	14	8	2		56	75
15	Coumarin	Pt	6	20	30	24	15	5	94	100
16	Dihydrocoumarin	Pt	55	43	2				45	75

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*The expression "D_∞ = 100%" means that the reagents were used in such amounts that half of the D atoms from D_2O were sufficient for 100% deuteration of the substrate.

crease in deuteration. Thus, in contrast to benzene, naphthalene undergoes only 3% exchange, during which the naphthalene molecule is horizontally oriented on the surface [1].

The presence in two-ring heteroaromatic compounds of a heteroatom, the electrons of which also can interact with the metal surface, leads to a slanted orientation [4, 5]. This orientation promotes a decrease in the strength of bonding with the surface, as a result of which the substrate molecules can actively participate in the adsorption—desorption process [4]. This explains the intensive deuteration of benzofuran as compared with naphthalene (see Table 1). It is apparent from Table 1 that two-ring sulfur compounds virtually do not participate in H—D exchange. A vertical orientation on the metal surface is evidently also realized in this case for them [4].

It has been shown [5] that the hydrogen atoms of the $C_2—C_3$ bond are primarily exchanged in benzofuran, whereas the hydrogen atoms of the benzene ring are primarily exchanged in the case of 2,3-dihydrobenzofurans. Mono- and dideutero derivatives are primarily present in the products of H—D exchange of chromene with D_2O (see Table 1), whereas the distribution of the deuterium label in the exchange products is approximately uniform in chroman. It may be assumed that whereas chroman, like 2,3-dihydrobenzofuran [5], is oriented on the catalyst surface in such a way that the hydrogen atoms of the benzene ring undergo exchange, in the case of chromene primarily the n electrons of the heteroatom and the π electrons of the $C_3—C_4$ bond interact with the catalyst, and this leads to primarily H—D exchange in the heteroring.

It is apparent from Table 1 that the presence and nature of substituents in the substrate molecules have a substantial effect on both the character of H—D exchange and on the degree of deuteration. It has been shown that alkyl substituents slow down H—D exchange on heterogeneous catalysts, leading to ortho-deactivation effects both in the case of hydrocarbons [1] and in the case of heterocycles [5]. The effect of the nature of the substituent on isotope exchange was investigated in this research. 2-Propylbenzofuran, which contains an electron-donor substituent, and 2-acetylbenzofuran, which contains an electron-acceptor substituent, were selected as models. It follows from the data in Table 1 that 2-propylbenzofuran undergoes only 8% deuteration, i.e., the propyl substituent has a negative effect on H—D exchange that is similar to the effect described in [5]. At the same time, the degree of deuteration of 2-acetylbenzofuran reaches 80% (see Table 1), and polydeuterated derivatives are present in the reaction products; according to data from mass-spectrometric analysis, the hydrogen atoms of the methyl group did not participate in H—D exchange. Thus the hydrogen atoms of the benzene ring in 2-acetylbenzofuran participate in exchange. This difference in the effect of the substituents can be explained as follows.

As we noted above, alkyl substituents lead to ortho-deactivation effects [1, 5] in the case of π-complex adsorption. The presence in the heteroring of the benzofuran molecule of a strong acceptor group such as an acetyl group reduces the ability of the π electrons of the C_2–C_3 bond to participate in a donor–acceptor interaction with the metal, and, as a result, primarily the π electrons of the benzene ring and the electrons of the heteroatom interact with the catalyst surface, i.e., the 2-acetylbenzofuran molecule interacts with the metal in the same way as 2,3-dihydrobenzofuran [5]. This promotes exchange of the hydrogen atoms in the benzene ring.

The reasoning presented above is confirmed by data on the H–D exchange of chromene, coumarin, and dihydrocoumarin (see Table 1). The indicated compounds are arranged in the order coumarin > chromene > dihydrocoumarin with respect to their degree of deuteration.

In contrast to chromene, in the products of H–D exchange of which mono- and dideuterated derivatives predominated, tri-, tetra-, and pentadeuterated analogs are also present in the reaction mixture in the case of coumarin, i.e., as in the case of 2-acetylbenzofuran, the hydrogen atoms of the benzene ring also participate in exchange in the case of coumarin. The above-noted effect of the carbonyl group on the ability of the hydrogen atoms of the benzene ring to undergo exchange in systems of the benzofuran and chromene type is confirmed by the results of H–D exchange of dihydrocoumarin (see Table 1), in which the carbonyl group has no effect on the benzene ring. It is apparent from Table 1 that, in contrast to coumarin, dihydrocoumarin undergoes exchange considerably less intensively, and virtually only monodeuterated derivatives are present in the reaction products.

Isotope exchange of heterocyclic compounds was investigated in the presence of Pt, Cu, Co, Fe, and Ni metals (see Table 1). With respect to their activity, which is defined as $\Sigma d_i/S$ (where S is the area of a weighed sample of the catalyst), in H–D exchange of heterocycles the investigated metals are arranged in the order Pt $\gg$ Ni > Co $\sim$ Fe $\sim$ Cu. The specific areas of the metals were as follows: Pt 25 m^2/g, Ni 66 m^2/g, Cu 20 m^2/g, Co 34 m^2/g, and Fe 31 m^2/g, i.e., the specific areas varied in a different order. Thus platinum, which has one of the smallest areas in the investigated series of metals, had the maximum activity, which exceeds by far that of the other metals. This may be associated with both the concentration of active centers of the metals and with their efficiencies. It is apparent from Table 1 that Fe, Co, and Cu virtually do not catalyze H–D exchange, and the determination of the number of active centers was therefore carried out for Pt and Ni.

The active surface of the metal and the number of active centers were determined from the number of diphenylpicrylhydrazyl radicals formed in the reaction of diphenylpicrylhydrazine with the oxygen chemisorbed on the metal surface. The number of active centers on the Pt surface for the given samples of the catalysts was $0.82 \cdot 10^{19}$ centers/m^2. The development of radicals was not established in the case of Ni. The absence of sufficiently active catalytic centers on the Ni surface may explain its insignificant activity in H–D exchange of heteroaromatic compounds. A similar assumption can also be made for the other metals.

EXPERIMENTAL

The catalytic experiments were carried out in evacuated ampuls at 120°C for 20 h. The experimental method was described in [4]. The percentage of deuterium in the reaction products was determined with a Varian MAT-111 (Gnom) chromatographic mass spectrometer at an ionization energy of 80 eV and a temperature of 50°C; the 1.5-m chromatographic column was filled with 10% SE-30 on chromosorb W and had d = 1.8 mm. The percentage of deuterium was calculated with a correction for the monoisotope effect, which was determined from the mass spectrum of the unlabeled compound. The specific area of the metals was determined by the volumetric method in [8].

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REACTIONS OF 4-(o-CARBORANYL)PYRYLIUM SALTS WITH NUCLEOPHILIC AGENTS. SYNTHESIS OF NITROGEN HETEROCYCLES WITH AN o-CARBORANYL SUBSTITUENT

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Nitrogen heterocycles, viz., pyridines, pyridinium salts, diazepine, and pyrazoles, with an o-carboranyl substituent were obtained by reaction of 4-(o-carboranyl)-pyrylium perchlorates with nitrogen-containig nucleophilic agents, viz., ammonia, primary amines, hydrazine, and phenylhydrazine. Opening of the pyrylium ring without involvement of the carborane ring occurs under the influence of bases.

Despite the fact that the synthetic chemistry of 12-carboranes has undergone active development in recent years, few carboranyl-substituted heterocycles are known [1-6]. The described heterocycles generally contain a carboranylmethyl grouping; the presence of a separating CH_2 group substantially reduces the effect of the carborane ring on the heterocyclic fragment as a consequence of the pronounced decrease in the inductive effect [7].

It seemed of interest to us to introduce a carboranyl grouping directly bonded to the heterocyclic ring as a substituent in nitrogen heterocycles. For this, we used carboranylpyrylium salts, which, like other pyrylium salts [8], should form various heterocyclic derivatives under the influence of N-containing nucleophilic agents.

The starting 4-(o-carbornayl)pyrylium perchlorates contained phenyl or tert-butyl groups in the 2 and 6 positions. Little study has generally been devoted to the transformations of pyrylium salts that contain bulky tert-butyl groups in the α,α'-positions of the pyrylium ring [9-11]. It is assumed that the outcome of the reaction is determined by the size of the α substituents rather than by their electronic effect [11].

Under the influence of ammonia, 2,6-diphenyl-4-(phenyl-o-carboranyl)pyrylium (Ia) and 2,6-di-tert-butyl-4-(methyl-o-carboranyl)pyrylium (Ib) salts are converted readily and in high yields to the corresponding pyridines, which can be used as characteristic derivatives for the identification of carboranylpyrylium perchlorates, since the latter explode when they are heated.

The action of primary amines of the aliphatic and aromatic series, viz., methylamine and aniline, leads to the production of the corresponding N-methyl- and N-phenylpyridinium perchlorates only when there are phenyl groups in the α,α' positions of the pyrylium ring. The presence of bulky tert-butyl groups in these positions hinders the indicated transformations. The reaction is realized in ethanol in the case of methylamine, while the use of glacial acetic acid as the solvent gave good results in the case of aniline.

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