CATALYTIC CONVERSIONS OF COUMARANS

I. Conversions of 2-Methylcoumaran on Group VIII Metal Catalysts

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The dehydrogenation of 2-methylcoumaran on platinum, palladium, and rhodium catalysts deposited on carbon (content of the metal 5%), has been studied. The maximum yields of 2-methylbenzofuran at 300–350° C were 89, 95, and 81%, respectively, for Pt, Rh, and Pd, the yield of catalyzates being 98–99%.

Tetrahydrofuran, unlike the other five-membered heterocycles pyrrolidine and thiophene, does not undergo dehydrogenation on a platinum catalyst at 350–400° C [1]. At the same time, such compounds as 2,3- and 2,5-dihydrofurans are converted into the corresponding furan homologs on contact with a platinum catalyst at a temperature as low as 200–300° C [2]. The formation of a double (conjugated) bond takes place more readily than the formation of the first (isolated) double bond. The dehydrogenation of coumaran was first effected by Klarmann [3]. When coumaran was heated with sulfur or selenium at 220° C for 15 hr,

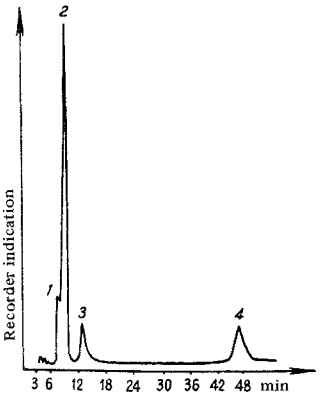


Fig. 1. Chromatogram of the catalysate from experiment No. 7 on the dehydrogenation of 2-methylcoumaran on Pt/C: 1) 2-methylcoumaran; 2) 2-methylbenzofuran; 3) chromane; 4) 2-propylphenol.

benzofuran was obtained with a yield of 45–50%. Lesiak [4] obtained benzofuran from coumaran with a yield of 77% at a temperature of 600–630° C under reduced pressure (10 mm Hg) in the presence of ferric oxide on alumina. The conversions of the coumarans in the presence of metal catalysts have not previously been studied. As the subject of our investigations we selected 2-methylcoumaran. We have studied the conversions of 2-methylcoumaran on low-percentage (5%) catalysts—platinum, palladium, and rhodium deposited on carbon. Under the conditions studied, the latter possesses no catalytic activity. The experiments were carried out in the vapor phase in the range of temperature from 250–350° C. In view of the closeness of the boiling points of 2-methylcoumaran and 2-methylbenzofuran, it was impossible to separate them by distillation. The catalysates were studied by gas-liquid chromatograph, UV spectroscopy, and nuclear mag-

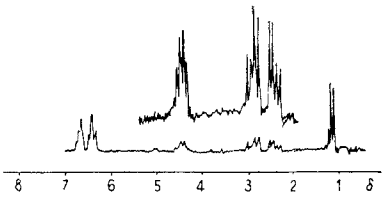
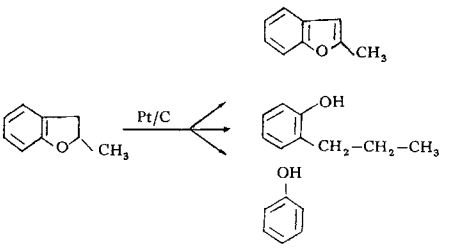


Fig. 2. Proton resonance spectrum of 2-methylcoumaran.

netic resonance. The products of the conversion of 2-methylcoumaran on a platinum catalyst were shown to contain 2-methylbenzofuran, unchanged 2-methylcoumaran, 2-propylphenol, and phenol (see table).



The maximum yield of 2-methylbenzofuran (89%) was obtained at 350° C. The propylphenol present in the catalysts obtained at 250 and 300° C in considerable amounts (32–20%) is formed as a result of the opening of the heterocyclic ring of the 2-methylcoumaran.

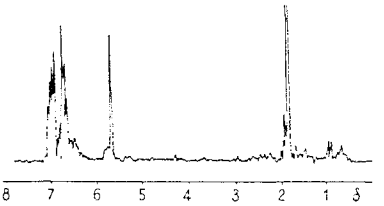


Fig. 3. Proton resonance spectrum of 2-methylbenzofuran.

The rate of the opening of the heterocyclic ring at the temperatures given is comparable with the rate of its dehydrogenation, while at 350° C the latter reaction predominates.

In addition to the compounds mentioned, the catalyzates obtained on working with platinum contained a substance with a retention time similar to that of chromane. However, the mechanism of its formation under these conditions requires a detailed study.

Results of Experiments on the Dehydrogenation of 2-Methyl Coumaran over Rh/C, Pd/C, and Pt/C Catalysts

Expt. No.	Catalyst	Temp., °C	Yield of catalyzate, %	Composition of catalysate, %				
				2-methylcoumaran	2-methylbenzofuran	2-propylphenyl	phenol	chromane
1	Rh/C	250	99	14	69	15	2	—
2	Rh/C	300	99	3	95	1	1	—
3	Pd/C	350	99	12	74	7	7	—
4	Pd/C	250	99	4	58	38	—	—
5	Pd/C	300	99	8	81	11	—	—
6	Pd/C	350	99	13	74	6	8	—
7	Pt/C	250	99	7	51	32	—	10
8	Pt/C	300	99	4	66	20	Traces	10
9	Pt/C	350	99	3	39	4	1	3

The main direction of the conversion of 2-methylcoumaran at 250–350° C in the presence of palladium and rhodium catalysts is its dehydrogenation to 2-methylbenzofuran. In addition to 2-methylbenzofuran and unchanged 2-methylcoumaran, the catalysates also contain 2-propylphenol and phenol. The table gives

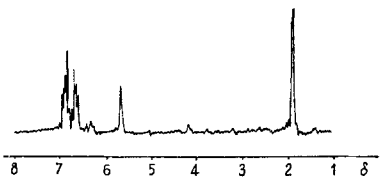


Fig. 4. Proton resonance spectrum of the catalysate from experiment No. 2.

figures showing the yield of 2-methylbenzofuran as a function of the temperature of the experiment on working with the catalysts mentioned. The highest yields (95%) of 2-methylbenzofuran were obtained in experiments at 300-350° C in the presence of rhodium deposited on carbon and lower yields–81 and 89%, respectively–were obtained with the use of platinum and palladium catalysts. From the experiments on the conversion of 2-methylcoumaran on the three group VIII metal catalysts it follows that its dehydration is the process predominating at temperatures of 250–350° C. Of the three catalysts studied, the best is rhodium, which gives the maximum yield of 2-methylbenzofuran (at 300° C). Under these conditions platinum and palladium bring about the hydrogenolysis of 2-methylcoumaran to 2-propylphenol to a considerable extent, this property being most pronounced in the case of palladium.

EXPERIMENTAL

All experiments on the catalytic conversion of 2-methylcoumaran were carried out in a flow apparatus placed in an oven with a controlled heater. The catalysts containing 5% of metal were prepared by Kaffer's method [5]. The reactor was charged with 10 cm^3 of catalyst (a fresh portion being used for each experiment), and hydrogen was passed through for 24 hr. After cooling, the hydrogen was displaced by nitrogen, the temperature was raised to the predetermined level, and 10 ml of 2-methylcoumaran was passed through at a space velocity of 0.1 hr^{-1}.

The dehydrogenation products were identified by gas-liquid chromatography (column 2.5 m × 4 mm; stationary phase: poly(ethylene sebacate), 20% on Celite; temperature: 150° C; carrier gas: helium; rate of flow: 2.7 l/hr) and also by NMR spectroscopy.

The compositions of the catalysate calculated from the chromatograms (mean figures from two parallel experiments) are given in the table.

Figures 2–4 show the proton spectra of 2-methylcoumaran, 2-methylbenzofuran, and the catalysate obtained from experiment No. 2.

The following were used as standards for the gas-liquid chromatography and for recording the NMR spectra:

2-Methylcoumaran, synthesized as described by Adams and Rindfusz [6], bp 84–88° C (15 mm); d_4^{20} 1.0319; n_D^{20} 1.5310. Literature data [6]: bp 197–198° C (760 mm); d_4^{20} 1.0320; n_D^{20} 1.5310.

2-Methylbenzofuran, obtained by Claisen's method [7], bp 85–86° C (15 mm); [8]: bp 196–198° C (760 mm); d_4^{20} 1.0424; n_D^{25} 1.5460.

Chromane, obtained by Maitte's method [9], bp 252° C (760 mm); d_4^{20} 1.0613; n_D^{20} 1.5457. Literature data [10]: bp 214° C (742 mm); d_4^{20} 1.0610; n_D^{20} 1.5440.

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