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HYDROGENATION AND DISPROPORTIONATION OF HYDROGEN IN 3-CARENE

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The hydrogenation of 3-carene (I) on Pt gives a mixture of cis- and trans-caranes together with very small amounts (2-5%) of 1,1,4-trimethylcycloheptane (II) [1]. Conversely, the hydrogenation of (I) on Pd gives (II) as the main product (74%) and smaller amounts of carenes [2]. Since the hydrogen disproportionation reaction in olefins may be considered as the combinations of two reactions — dehydrogenation and rehydrogenation — it must be expected that the products of the hydrogenation stage in the disproportionates obtained on Pt and Pd will be different.

In the present communication we give the results of a study of the hydrogen disproportionation reaction in (I) in Pt. The reaction was performed in sealed tubes with Pt/C (0.5% of Pt) as catalyst with a ratio of substrate to catalyst of 10:1 (by weight) at a temperature of 180-200°C, for 5-240 min. Analysis was performed by the GLC method [3].

With the complete conversion of the 3-carene, a disproportionate of the following composition was obtained: 2-carene, 5%; 1,4,4- and 1,4,5-trimethylcycloheptenes, 20% each; cis- and trans-caranes, 4%; p- and m-menthanes, 1%; p- and m-cymenes, 25 and 15%, respectively; and p- and m-methylisopropenylbenzenes, 5% each. A mixture of similar composition has been obtained previously in the hydrogen disproportionation of (I) on Pd [2].

A study of the composition of the hydrogen disproportionation reaction products in (I) when it had undergone incomplete conversion showed that the disproportionates always contained small amounts (up to 4%) of 3,7,7-trimethylcyclohepta-1,3,5-triene (III). This gives grounds for assuming that the stage determining the transition to compounds with a cycloheptane ring is the dehydrogenation of the 2-carene formed under the conditions of this reaction [2] to cara-2,4-diene (IV). Compound (IV) is present in rapid equilibrium with its tautomer (III), the equilibrium being strongly shifted in the direction of the monocyclic compound [4]. The hydrogenation of (III) also gives products with a trimethylcycloheptane skeleton.

A similar scheme probably applies in the hydrogenation of (I), also, since Pd and Pt catalyze not only the forward but also the reverse reaction. Raising the temperature should favor the endothermic dehydrogenation reaction competing with the hydrogenation of (I), i.e., it should increase the yield of products with the cycloheptane skeleton. Such a situation is known for Pd [2]. We observed an analogous pattern when the hydrogenation of (I) was performed at elevated temperatures (70-100°C). The formation of different products in the hydrogenation of (I) on Pt and Pd at room temperature is most probably due to the high activation energy of dehydration on Pt as compared with the same reaction on Pd.

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