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CATALYTIC HYDROGENATION OF METHYLCYCLOHEX-2-ENYLAMINES

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A series of methylcyclohex-2-enylamines was hydrogenated using Ni, Pd, and Pt catalysts. The product determining steps were discussed on the basis of the variations of the isomer distribution in the products.

Although the stereochemistry of the catalytic hydrogenation of allyl alcohols has been a subject of discussion in recent years,$^{1-4)}$ there has been no report on that of allylamines. We now present a first example of the stereochemistry of the hydrogenation of some allylamines: methylcyclohex-2-enylamines.

The hydrogenations were carried out in ethanol at 25°C under 1 atm of hydrogen. The product compositions were determined by gas chromatographic analyses: the products from I and IV were analysed after the acetylation with acetic anhydride and sodium carbonate, and the analyses in the case of II were conducted after the N-methylation with formalin and hydrogen over Raney Ni. Percentages of cis-methylcyclohexylamines are listed in the Table. The hydrogenations over Ni gave in all cases trans-amines as the main products. Over Pd, thermodynamically more stable isomers were mainly obtained: trans from I, II, and III, or cis from IV. However, the hydrogenations over Pt differed from those over Ni and Pd: trans-amines were favored in the cases of I, II, and IV, while III gave cis-amine as the main saturated product. The hydrogenations of the hydrochlorides of I, III, and IV led mainly cis-isomers over Pt. The hydrogenations of III over Pd and Pt also yielded methylcyclohexane and 1-methylcyclohexene: percentages of these hydrocarbons were 34% on Pd and 24% on Pt. However, scarcely any hydrogenolysis was observed over Ni.

The hydrogenations of allylamines and allyl alcohols$^{1)}$ over Ni always gave trans-isomers as the main products. The substrate will be adsorbed preferentially from the side of the amino or hydroxyl group; these groups will act as the anchors. This fact is ascribed to the high affinity of N and O atoms for Ni. Therefore, the product determining step will be the adsorption of the substrate on the catalyst.$^{1)}$

Siegel and Smith$^{5)}$ found that the hydrogenation of 1,2- and 2,3-dimethylcyclohexenes over Pd gave thermodynamically more stable isomer: trans-1,2-dimethylcyclohexane as the main product, and considered that the product determining step was the conversion of the half-hydrogenated state to the saturated product. Our findings are also compatible with Siegel and Smith rationalization.

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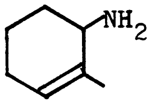
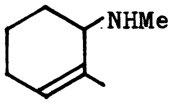
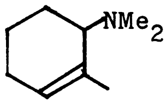
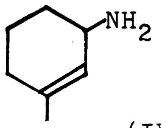
Table. Percentages of Cis-Isomer in Saturated Products

Catalyst	 (I)	 (II)	 (III)	 (IV)
Raney Ni	17	9	24	26
$Pd(OH)_2$	38(40*)	25	29	57(85*)
PtO_2	28(74*)	18	70(74*)	16(64*)

* The equimolar mixture of the amine and HCl was hydrogenated.

Product compositions with Pt were distinct from those with Ni and Pd: the primary and secondary amines, I, II, and IV, yielded mainly trans-amines, while cis-amine was predominant in the case of the tertiary amine III. The hydrochlorides of I, III, and IV gave mainly cis-isomers. Siegel and Smith[5)] concluded that the product determining step was the formation of the half-hydrogenated state in the PtO_2 catalysed hydrogenation of dimethylcyclohexenes at the moderate pressures of hydrogen. Similar discussion has been done in the case of methylcyclohex-2-enols.[1)] The isomer distribution in the product from the primary and secondary amines suggests that the adsorption of the amino groups lowers the free-energy level of the transition state to form the half-hydrogenated state. The result of this effect is to increase the formation of trans-amines from I, II, and IV. On the other hand, the predominance of cis-amine from the tertiary amine indicates that the steric effect is more operative than the anchor effect owing to the bulkiness of dimethylamino group. The hydrogenation of the hydrochlorides will be governed by the catalyst hindrance, and yield predominantly cis-isomers. These facts demonstrate that the product determining step over Pt is also the formation of the half-hydrogenated state in our case.

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