ISOMERIZATION OF THIACYCLOHEXANE AND DEHYDROGENATION OF 2-METHYLTHIACYCLOPENTANE ON ACID CATALYSTS

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The isomerization of thiacyclohexane (with ring contraction) and the dehydrogenation of monocyclic sulfides in the presence of acid catalysts have not been described in the literature.

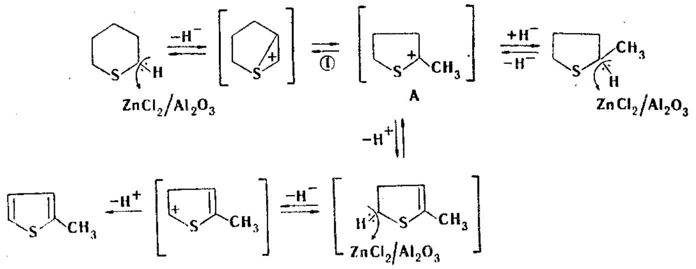
We have studied the behavior of thiacyclohexane and 2-methylthiacyclopentane on contact with catalysts that have protic and aprotic acidity: γ-Al_2O_3, 5-30% $ZnCl_2/Al_2O_3$, 1% HCl/Al_2O_3, and $Al_2O_3-SiO_2$ (at 250-400°C and a space velocity of 0.2-0.8 h^{-1}).

The primary reaction of thiacyclohexane is skeletal isomerization to thiacyclopentane, while the principal direction of the transformations of 2-methylthiacyclopentane is dehydrogenation to 2-methylthiophene. Both of these reactions proceed to the greatest extent in the presence of catalysts with high aprotic acidity. Thus with 20% $ZnCl_2/Al_2O_3$, the percentages of products of the isomerization of thiacyclohexane and products of the dehydrogenation of 2-methylthiacyclopentane in the catalyzate reach 32% (at 400' and 0.3 h^{-1}) and 39% (at 300° and 0.22 h^{-1}), respectively.

In addition, both sulfides undergo partial decomposition with the production of hydrogen sulfide (4-5%) and unsaturated hydrocarbons, and condensation products, the amount of which reaches 16-28% of the weight of the starting compound, also form on the catalyst.

The primary products of the transformations of thiacyclohexane and 2-methylthiacyclopentane partially undergo secondary transformations: isomerization of 2-methylthiophene to 3-methylthiophene, dealkylation of methyl-substituted sulfides, and formation of aliphatic sulfides from hydrogen sulfide and the gaseous cracking hydrocarbons.

The direct dependence of the isomerization of thiacyclohexane and the dehydrogenation of 2-methylthiacyclopentane on the acidity of the catalyst makes it possible to assume that these reactions proceed through a step involving removal of a hydride ion under the influence of the catalyst to give carbonium ions:



This assumption is confirmed by the presence of hydride lability in oxygen analogs of the investigated compounds [1].

Reverse isomerization of the five-membered sulfide to a six-membered compound was not observed. Of the three possible directions of stabilization of cation A, reaction 1 is apparently not realized under the given conditions.

LITERATURE CITED

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