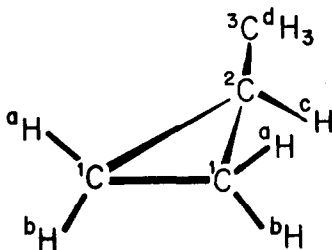


LETTERS TO THE EDITORS

Mechanism of Methylcyclopropane Isomerization over Silica-Alumina

The tracer studies of Larson, Gerberich, and Hall (1) revealed that the mechanism of cyclopropane isomerization to propylene over silica-alumina could be explained in either of two ways, viz., by a bimolecular hydride transfer (I) or by a protonic mechanism (II). These possibilities required either a $C_3H_5^+$ (Lewis site) or a $C_3H_7^+$ (Bronsted site) intermediate surface complex, respectively. Studies of the isomerization of methylcyclopropane (MCP) and the dimethylcyclopropanes over similar catalysts have provided new evidence which strongly favors II.

Consider the isomers resulting from isomerization of



by classical mechanisms, making the single assumption that primary carbonium ions will not be formed.

Mechanism I

a. Loss of either $^aH^-$ (or either $^bH^-$) would yield a secondary ion which would rearrange through $^1C-^2C$ cleavage to an allylic carbonium ion and ultimately form the three *n*-butenes.

b. Loss of $^cH^-$ would result exclusively in formation of isobutene through $^1C-^1C$ cleavage.

c. Loss of one of the $^aH^-$ would lead to the formation of the resonance-stabilized bicyclobutonium ion (2). Return of this species to the gas phase would yield only cyclobutane and/or 1-butene as primary products. The 2-butenes could form only as a result of secondary reactions.

Mechanism II

a. Proton addition to 1C would always result in the formation of the *n*-butenes through $^1C-^2C$ cleavage.

b. Proton addition to 2C is not allowed since it would involve formation of an unstable primary carbonium ion.

The only products observed from MCP isomerization over silica-alumina (Houdry M-46 catalyst which had been oxidized and outgassed at 550°) in both micro-catalytic and static reactors between 0° and 100° were the *n*-butenes. All three isomers were primary products in the approximate ratio 1-butene:*cis*-2-butene:*trans*-2-butene = 1:1:2. Since MCP was isomerized much faster than any of the *n*-butenes under similar conditions, the butene product ratios, even though not in thermodynamic equilibrium, did not change significantly during the entire course of the reaction.

On the basis of these results, hydride abstraction mechanisms appear unlikely. Although Ia by itself would explain the products, there is no reason why $^aH^-$ or $^bH^-$ should be the only ions lost. In fact, $^cH^-$ should be lost more readily than $^aH^-$ or $^bH^-$ since the more stable *tertiary*, rather than a *secondary*, carbonium ion would be

formed. If a hydride transfer mechanism were operative at all, the most likely position for hydride abstraction is at ^3C , to form the bicyclobutonium ion (2). This mechanism would predict only cyclobutane and/or 1-butene as initial products; cyclobutane was not observed and 1-butene made up only 25% of the products. When cyclobutane was tested as a reactant, it was found to be completely inert over the catalyst at temperatures below 400° .

Mechanism II accounts for all the *n*-butenes and also explains the absence of isobutene among the products. A similar proton addition mechanism explained semiquantitatively the selectivities and relative reactivities for interconversion among the three *n*-butenes over the same catalyst, as well as the magnitudes of their equilibrium constants (3). However, in MCP isomerization the reaction coordinates probably do not involve the same classical 2-butyl-carbonium ion which explained the *n*-butene isomerization, because the product distribution was not that expected for this intermediate from earlier work (3).

Ethylcyclopropane also yielded only *n*-pentenes when isomerized over silica-alumina. In this case, the 2-pentenes predominated, the product ratios at room temperature being about 1-pentene:*cis*-2-pentene:*trans*-2-pentene = 1:10:10. Since 1-pentene formation involved either a 2,3-hydride shift or a primary carbonium ion, it would be expected to form only in small quantities, if at all.

Finally, classical proton addition mechanisms accounted qualitatively for all the observed products from isomerization of the three dimethylcyclopropane isomers. Certain C_5 olefins (e.g., 2-methyl-1-butene from *cis*- or *trans*-1,2-dimethylcyclopropane), which could not be formed by classical mechanisms without passing through a primary carbonium ion or involving a hydride shift, were not observed in signif-

icant quantities. There was no interconversion between *cis*- and *trans*-1,2-dimethylcyclopropane. By analogy with the alkylcyclopropane reactions, we conclude that the isomerization of cyclopropane must also involve a protonated intermediate, probably the nonclassical C_3H_7^+ ion of Baird and Aboderin (4).

When slugs of MCP were passed in a stream of helium over a catalyst which had been saturated with butene- d_8 , deuterium appeared in the isomerized products, but only a small fraction of the butene molecules contained more than one D atom. There was essentially no deuterium in the unisomerized MCP. These results are in accord with observations made with the *n*-butenes (5). They suggest that the required protons are furnished by "residue" or "coke" formed by chemisorption of substrate.

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