On the Non-Interconversion of C_5-C_6 Rings in the Methylindan-Tetralin System

Csicsery recently studied the cyclization of phenylbutanes (*1*). He proposed that the cyclization over Pt-SiO_2-Al_2O_3 was independently catalyzed by the metallic and acidic functions. Six-carbon rings leading to tetralin (and naphthalene) were formed only over the metal; five-carbon rings leading to methylindans were formed over the acid function as well as the metal function. This proposal was valid provided five and six-member rings, once formed, did not undergo interconversion. In a later communication (*2*), Csicsery provided evidence that the five and six-ring intermediates were not interconverted after formation by showing that tetralin was dehydrogenated to naphthalene but not converted to methylindans. This was accepted as proof for non-interconversion.

Methylcyclopentane is converted to benzene under reaction conditions similar to those used by Csicsery; but cyclohexane forms little methycyclopentane due to its rapid dehydrogenation to benzene (*3*). The methylcyclopentane-cyclohexane system is analogous to the methylindan-tetralin system. The rapid dehydrogenation of tetralin may not enable one to observe the five-six carbon ring interconversion.

A more severe test for the proposal of non-interconversion could be performed with methylindan. We have made this test and report the results in this note.

EXPERIMENTAL

The 2 wt % Pt on white Mobil silica-alumina bead catalyst (see Ref. *1* for preparation) was reduced *in situ* at 500°C in a flow reactor. The reaction conditions were similar to those in Ref. *1*; 36 cc H_2/min 0.5 g catalyst, 2.4 cc hydrocarbon/hr, and a reaction temperature of 371°C. Three consecutive 0.4 cc liquid samples were collected.

The liquid products were analyzed by g.c. using a Carbowax 20M column. We did not attempt to identify all minor products; tetralin, methylindan, methylindenes, and naphthalene were well separated and could be determined quantitatively.

1-Methylindan was prepared by the Clemmensen reduction of the 3-methyl-1-indanone obtained by the $AlCl_3$ catalyzed alkylation of benzene with crotonic acid (*4*).

RESULTS AND DISCUSSION

The methylindan/tetralin system is similar to that of methylcyclopentane/cyclohexane. The dual functional nature of the methylcyclopentane/cyclohexane system has been widely studied. It has been established that the isomerization of the alkylcyclopentane by the acid function to a cyclohexane compound is slower than the dehydrogenation of cyclohexane (*3*). The conversion of methylcyclopentane to benzene is readily accomplished at atmospheric pressure over a mechanical mixture of platinum bearing particles and silica-alumina. But the conversion of cyclohexane under the same conditions would produce little methylcyclopentane because the dehydrogenation of cyclohexane to benzene is too rapid to allow much methylcyclopentane to be formed. The cyclohexane reaction would, in general, be a poor test for the interconversion of five- and six-carbon member rings whereas the methylcyclopentane conversion to benzene would be a better test. Csicsery's experiment with tetralin corresponds to the cyclohexane case, the dehydrogenation may be so rapid that six to five carbon ring isomerizations would be difficult to observe (note that conversion of tetralin to naphthalene was nearly complete in Csicsery's test over Pt-catalysts).

In our study with 1-methylindan, the liquid products for the first sample contained 7.1 wt % methylindene but less than 0.5 wt % naphthalene. There were other minor peaks in the chromatogram but their total amount was less than 1 wt %. The catalyst activity declined slowly during the run. The methylindan and methylindene peaks were trapped from the gas chromatography effluent. The nmr analysis of the methylindan peak indicated there was little, if any, isomerization of the 1-methylindan to 2-methylindan. The mass spectra of the methylindene agreed well with the spectra published for 1-methylindene (*5*). Our results thus show that there was metal activity to provide the olefin intermediate required for the cyclo-C_5/cyclo-C_6 ring interconversion but there was very little such interconversion. Naphthalene did not appear to be held up on the catalyst by adsorption since the naphthalene content for sample 1 was greater than in samples 2 and 3. Furthermore, the nmr and mass spectra of the methylindan and methylindenes suggest that there was little, if any, methyl migration from the 1 to the 2 position. Methylcyclopentane was found to produce about 10 wt % benzene when passed over the same catalyst under similar conditions.

Our data with the more demanding test support Csicsery's conclusion that the five and six-carbon ring compounds in the methylindan-tetralin system do not interconvert at 371°C under his experimental conditions. The olefin, methylindene, was present in a much larger quantity than would be expected to be necessary for the intermediate in a dual functional reaction pathway over metal impregnated acid catalysis (*3*). The interconversion of five- to six-carbon rings did occur at temperatures considerably higher than used by Csicsery (371°C) over the metal function (on a non-acidic support) or over the dual function catalyst (475°C).

REFERENCES

1. CSICSERY, S. M., *J. Catal.* **12**, 183 (1968).
2. CSICSERY, S. M., *J. Catal.* **12**, 212 (1968).
3. WEISZ, P. B., *Advan. Catal.* **13**, 137 (1962).
4. ENTEL, J., RUOF, C. H., AND HOWARD, H. C., *Anal. Chem.* **25**, 1303 (1953).
5. "Index of Mass Spectral Data," A.S.T.M. Special Publication No. 356, American Society for Testing and Materials, 1963.

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