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reaction scheme: methylcyclooctane transformations to methyl-cis-pentalanes and hydrogenolysis products

Figure 1: reaction scheme: methylcyclooctane transformations to methyl-cis-pentalanes and hydrogenolysis products

## Abstract

## Full Text

## Chemistry

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# TRANSFORMATIONS OF METHYLCYCLOOCTANE IN THE PRESENCE OF PLATINUM CATALYSTS

It was shown earlier that, in the presence of platinum catalysts, cyclooctane undergoes $C_5$-dehydrocyclization to cis-pentalane ([1,2]).

It was of interest to study the reaction of transannular dehydrocyclization of methylcyclooctane and to determine whether the presence of hydrogen at the tertiary carbon atom of the ring affects the preferential direction of dehydrocyclization, or whether this reaction is determined by the conformational features of the methylcyclooctane molecule.

The methylcyclooctane synthesized by us was passed over 5% platinized carbon in the absence of a carrier gas. The degree of conversion of methylcyclooctane was approximately 90%. The catalyzate was distilled on a column at 80 theoretical plates, and individual fractions were analyzed on a gas–liquid chromatograph with a capillary column.

The analysis showed that the products of methylcyclooctane transformations consist of exo-2-methyl-cis-pentalane ($\sim$ 34%), endo-2-methyl-cis-pentalane ($\sim$ 6%), exo-3-methyl-cis-pentalane ($\sim$ 17%), endo-3-methyl-cis-pentalane ($\sim$ 11%), 1-methyl-cis-pentalane ($\sim$ 8%), hydrogenolysis products of 1-methyl-cis-pentalane ($\sim$ 11%), and hydrogenolysis products of 1-methyl- and 2-methyl-cis-pentalanes ($\sim$ 12%). Apparently, the catalyzate also contained isomeric methyloctanes (less than 1%), which were formed by direct hydrogenolysis of the eight-membered ring in methylcyclooctane.

The principal directions of the transformations of methylcyclooctane in the presence of platinized carbon may be represented by the following scheme:

schematic structure of methylcyclooctane showing numbered carbon atoms 1-8 and a $CH_3$ substituent at carbon 1

Figure 2: schematic structure of methylcyclooctane showing numbered carbon atoms 1-8 and a $CH_3$ substituent at carbon 1

Methylcyclooctane over platinized carbon undergoes transannular $C_5$-dehydrocyclization with the formation of all isomeric methyl-cis-pentalanes. Of these, 2-methyl-cis-pentalane is formed predominantly; 3-methyl-cis-pentalane and 1-methyl-cis-pentalane are formed in smaller amounts. The hydrogenolysis products of the five-membered ring in the methylpentalanes formed amounted to 23%, and, in order to reduce their quantity, methylcyclooctane was subjected to catalysis in the presence of an iron-platinum catalyst at 300°. Appreciable conversion of the hydrocarbon was observed at a rate of 0.4 $h^{-1}$. The degree of conversion was 63%.

The converted portion of the catalyzate contained isomeric methyl-cis-pentalanes in approximately the same ratios as in the case of platinized ...

hydrocarbons: exo-2-methyl-cis-pentalane $\sim$ 35%, endo-2-methyl-cis-pentalane $\sim$ 8%, exo-3-methyl-cis-pentalane $\sim$ 18%, endo-3-methyl-cis-pentalane $\sim$ 15%, 1-methyl-cis-pentalane $\sim$ 13%. The total amount of hydrogenolysis products of the methylpentalanes decreased to 11%.

Comparing the analysis data for the two catalysts, it should be noted that the ratio of the methyl-cis-pentalanes formed in the primary transformations of methylcyclooctane does not depend on the nature of the platinum catalysts studied. It is apparently determined by the conformational features of the methylcyclooctane molecule. In the most stable crown-shaped conformation of the eight-membered ring there are, approximately, two types of hydrogen atoms (3): 1) eight axial hydrogen atoms, of which four are directed upward and four downward from the mean plane of the molecule; 2) eight equatorial hydrogen atoms, which differ very little from one another. Literature data (4) and consideration of a model of this conformation of cyclooctane show that in monosubstituted cyclooctane the equatorial position of the substituent is the most favorable. The methyl group in methylcyclooctane can apparently occupy any of the eight equatorial positions.

In transannular dehydrocyclization of methylcyclooctane there are two possibilities for the formation of 2-methylpentalane—the elimination of two hydrogen atoms located at carbons $C_2, C_6$ and $C_4, C_8$—and one possibility each for the formation of 3-methylpentalane and 1-methylpentalane (elimination of hydrogen atoms at $C_3, C_7$ in the case of 3-methylpentalane and at $C_1, C_5$ for 1-methylpentalane). If it is assumed that the indicated possibilities for the formation of methylpentalanes are equally probable, then the methylcyclooctane catalyzate should contain twice as much 2-methylpentalane as 3-methylpentalane or schematic structures labeled (I) and (II), with $CH_3$ in the exo form and $H/CH_3$ in the endo form

Figure 3: schematic structures labeled (I) and (II), with $CH_3$ in the exo form and $H/CH_3$ in the endo form

1-methylpentalane. The experimental data obtained by us show that in transannular dehydrocyclization of methylcyclooctane the formation of 2-methyl-cis-pentalane predominates (more than 40%), while smaller amounts of 3-methyl-cis-pentalane and 1-methyl-cis-pentalane are formed. Thus, the preferential direction of dehydrocyclization of methylcyclooctane is determined by the conformational features of the molecule, and not by the presence of hydrogen at the tertiary carbon atom.

It should be noted that, among the exo- and endo-2-methyl-cis-pentalanes formed in the case of both platinum catalysts studied, the exo isomer predominates ($\sim$ 34–35%). The amount of the endo isomer is only 6–7%, whereas exo- and endo-3-methyl-cis-pentalanes are formed in comparable amounts: exo form $\sim$ 17–18%; endo form 12–15%. The preferential formation of the exo form (I) of 2-methyl-cis-pentalane compared with the endo form (II) is apparently due to the spatial structure of this hydrocarbon. In the endo form (II), the methyl group and the hydrogen located at $C_6$ are so close to one another that the repulsive forces between them make this form of the molecule more strained than the exo form (I).

In 3-methyl-cis-pentalane and in the endo and exo forms, the molecules have equally favorable positions of the methyl group, as a result of which the isomers are probably almost equally stable and are formed in approximately equal amounts.

## Experimental Part

Into the catalytic tube were placed 60 ml (15 g) of 5% platinized carbon, and over it, at 310°, at a rate of 0.2 $h^{-1}$, 41.6 g of methylcyclooctane was passed, b.p. 167-167.4° (740 mm); $n_D^{20}$ 1.4532; $d_4^{20}$ 0.8285. This yielded 6 liters of gas consisting of hydrogen, and 38 g of liquid catalyzate with $n_D^{20}$ 1.4452; $d_4^{20}$ 0.8272. The catalyzate contained small amounts of aromatic hydrocarbons (0.2 g; $n_D^{20}$ 1.4920). After their removal by chromatography on silica gel, the catalyzate was distilled on a column into 80 narrow fractions. The results of the distillation (36 g of material) are shown in Table 1.

**Table 1**

| Fraction No. | B.p., °C at 736 mm | Weight of fraction | $n_D^{20}$ | $d_4^{20}$ |
|---:|---:|---:|---:|---:|
| 1 | 126–144.6 | 5.6 | 1.4240 | 0.7695 |

| Fraction No. | B.p., °C at 736 mm | Weight of fraction | $n_D^{20}$ | $d_4^{20}$ |
|---|---|---|---|---|
| 2 | 144.6–147.5 | 3.8 | 1.4348 | 0.7973 |
| 3 | 147.5–148.9 | 1.7 | 1.4434 | 0.8214 |
| 4 | 148.9–150.0 | 2.1 | 1.4500 | 0.8383 |
| 5 | 150.0–150.2 | 4.0 | 1.4535 | 0.8472 |
| 6 | 150.2–151.0 | 6.2 | 1.4540 | 0.8483 |
| 7 | 151.0–151.4 | 1.7 | 1.4540 | 0.8484 |
| 8 | 151.4–151.8 | 2.0 | 1.4540 | 0.8480 |
| 9 | 151.8–154.4 | 2.6 | 1.4545 | 0.8490 |
| 10 | 154.4–159.5 | 1.7 | 1.4570 | 0.8517 |
| 11 | Residue | 2.4 | 1.4536 | 0.8280 |
|  | Losses | 2.5 |  |  |

Analysis of the fractions was carried out on a gas–liquid chromatograph with a flame-ionization detector. The length of the steel capillary was 90 m, diameter 0.25 mm; squalane served as the stationary phase. Thermostat temperature 94°. Carrier gas—helium; inlet pressure 1.5 atm.

1-Methyl-cis-pentalane and the endo- and exo-2-methyl-cis-pentalanes were identified by the retention times of the transformation products contained in the fractions, and by the retention times of individual hydrocarbons synthesized by us (5), as well as with the aid of mixed samples of these hydrocarbons with individual catalyzate fractions.

**Table 2**

| Endo-2- | Exo-2- | Endo-3- | Exo-3- |
|---|---|---|---|
| 147.5 | 120.5 | 119 | 126 |
| 148 | 121 | 118.5 | 126 |
| 150 | 121 | 119 | 127 |

For the isomeric methyl-cis-pentalanes, relative retention times were calculated. Table 2 gives the relative retention times from three parallel determinations. The relative retention time of 1-methyl-cis-pentalane was taken as 100 (methane was used as the standard substance).

**Table 3**

| Hydrocarbon | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | Content in the catalyzate, % calculated on the converted portion |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Methyloctanes | 3 | — | — | — | — | — | — | — | — | — | — | 1 |
| Hydrogenation products of 2- and 3-methylpentalane | 59 | 6 | 19 | — | — | — | — | — | — | — | — | 12 |
| Hydrogenation products of 1-methyl-cis-pentalane | 24 | 52 | — | — | — | — | — | — | — | — | — | 11 |
| 1-Methyl-cis-pentalane | 13 | 32 | 24 | 10 | — | — | — | — | — | — | — | 8 |
| Endo-3-methyl-cis-pentalane | — | 2 | 15 | 22 | 23 | 20 | 13 | 10 | 4 | — | — | 11 |

| Hydrocarbon | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | Content in the catalyzate, % calculated on the converted portion |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Exo-3-methyl-cis-pentalane | — | — | — | — | 5 | 20 | 48 | 60 | 62 | 15 | — | 17 |
| Exo-2-methyl-cis-pentalane | — | 7 | 42 | 68 | 72 | 60 | 39 | 30 | 7 | — | — | 34 |
| Endo-2-methyl-cis-pentalane | — | — | — | — | — | — | — | — | 23 | 70 | — | 6 |
| Methylcyclooctane | — | — | — | — | — | — | — | — | — | — | 100 | — |

Endo- and exo-3-methyl-cis-pentalanes were identified by comparing the relative retention times of the pentalane hydrocarbons contained in the catalyzate with those reported in the literature ([6]). The products of hydrogenolysis of methyl-cis-pentalanes in the methylcyclooctane catalyzate were identified by chromatographic analysis of mixed samples of individual fractions of the methylcyclooctane catalyzate with the hydrogenolysis products of individual 1-methyl-cis-pentalane and fraction VI of the methylcyclooctane catalyzate, consisting of 40% 2-methyl-cis-pentalane and 60% 3-methyl-cis-pentalane.

**Table 4**

| Fraction No. | B.p., °C at 740 mm | $n_D^{20}$ | Weight, g |
|---:|---:|---:|---:|
| 1 | 141.5–155 | 1.4450 | 6.0 |
| 2 | 155–166 | 1.4528 | 4.0 |
| 3 | Residue | 0.4535 | 1.7 |
| 3 | Losses | – | 0.6 |

Hydrogenolysis of 1-methyl-cis-pentalane and fraction VI of the methylcyclooctane catalyzate was carried out over platinized carbon at 300° in a stream of hydrogen.

The composition of the methylcyclooctane catalyzate is given in Table 3.

## Catalytic transformations of methylcyclooctane over an iron-platinum catalyst

13.5 g of methylcyclooctane was passed over 40 ml (10.7 g) of iron-platinum catalyst (7) at 300°, with a space velocity of 0.4 $h^{-1}$. 12.8 g of catalyzate with $n_D^{20}$ 1.4535 was obtained; after removal of traces of aromatic hydrocarbons it was distilled on a 40 theoretical-plate column. The results of the distillation (12.32 g of catalyzate) are given in Table 4.

**Table 5**

| Hydrocarbons | Percentage content, I fraction | Percentage content, II fraction | In the catalyzate, calculated for the converted portion |
|---|---:|---:|---:|
| Hydrogenolysis products of methyl-cis-pentalanes | 13 | – | 11 |
| 1-Methyl-cis-pentalane | 15 | – | 13 |
| Endo-3-methyl-cis-pentalane | 15 | 3 | 45 } 33 |
| Exo-3-methyl-cis-pentalane | 17 | 6 | 48 } 33 |
| Exo-2-methyl-cis-pentalane | 34 | 8 | 35 } 43 |
| Endo-2-methyl-cis-pentalane | 5 | 7 | 8 } 43 |
| Methylcyclooctane | 1 | 76 | |

Analysis of the catalyzate fractions was carried out under the conditions described above. On the basis of the chromatogram, the distillation residue contained methylcyclooctane. The composition of the catalyzate is given in Table 5.

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*Note: Figure translations are in progress. See original paper for figures.*