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Abstract

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MUTUAL INTERCONVERSIONS OF cis- AND trans-1,2-DIMETHYLCYCLOPENTANES IN THE PRESENCE OF A PLATINUM CATALYST

Recently we undertook a study of the kinetics of hydrogenolysis of alkylcyclopentanes in the presence of platinized carbon (^{1}). The results obtained prompted us to extend these investigations to stereoisomeric dialkylcyclopentanes, first of all to cis- and trans-1,2-dimethylcyclopentanes. In the course of this work, however, it became clear that it is impossible to study the kinetics of hydrogenolysis of the individual stereoisomers, since under the experimental conditions each of them is immediately converted into a mixture of both stereoisomers. The composition of the mixture formed does not depend on which of the stereoisomers has undergone catalysis and, in the temperature range 150—280°, is very close to the composition of the thermodynamically equilibrium mixture for the corresponding temperature*. The rate of this transformation considerably exceeds the rate of hydrogenolysis. Thus, whatever individual stereoisomer we take, the kinetics of hydrogenolysis are studied with an equilibrium mixture of stereoisomers, and it is not possible to determine the rate of hydrogenolysis of each of them separately. Nevertheless, it seems to us that this isomerization reaction itself deserves attention.

The possibility of conversion of geometrical isomers of cyclopentane hydrocarbons from one configuration into another in the presence of platinized carbon has already been noted, although in a more complicated case. Indeed, as early as 1948 Kazanskii and co-workers (^{3}), studying the hydrogenolysis of individual stereoisomeric 1,2,3-trimethylcyclopentanes, observed that their isomerization occurs simultaneously. At that time, of course, there was no possibility of studying this transformation quantitatively, and it was difficult to foresee that the reaction under discussion proceeds at a high rate. At present, study of the products of transformation of cis- and trans-1,2-dimethylcyclopentanes by gas–liquid chromatography has enabled us to examine their transformations in greater detail.

The results of this investigation, summarized in Table 1, show that the reaction rate is sufficiently high that, in the temperature interval studied, at a space velocity of 0.2 hr^{-1}, from trans-1,2-dimethylcyclopentane one obtains catalyzates close in composition to equilibrium mixtures. The same may be said of the cis form as well, although in this case, because of the shortage of the initial hydrocarbon, it was not possible to carry out experiments below 240°. It is very noteworthy that the isomerization, studied by us mainly in an atmosphere of hydrogen, also proceeds in the absence of the latter (experiments 26 and 29). It is true that the impression is created that without hydrogen the reaction proceeds somewhat more slowly, but this requires further experimental verification. It is also interesting that isomerization occurs even at such a temperature (200° and below) at which hydrogenolysis of the five-membered ring can no longer be detected at all.

* Calculated from Rossini' s data (^{2}).

The starting hydrocarbons were obtained from adipic acid via cyclopentanone according to the scheme:

[reaction scheme]

All stages of this synthesis are well developed, and here it is necessary to dwell on only one fact. It turned out that hydrogenation of 1,2-dimethylcyclopentene on platinized charcoal at room temperature gave a mixture consisting of 39% cis- and 61% trans-form, whereas at 150° the content of the cis-form decreased to 20%.

[chromatograms]

Fig. 1. Chromatogram of the catalyzate obtained from cis-1,2-dimethylcyclopentane at 240° (*A*) and at 280° (*B*). *I* —hydrogenolysis products, *II* —trans-1,2-dimethylcyclopentane, *III* —cis-1,2-dimethylcyclopentane

This fact leads to very important conclusions about the mechanism of hydrogenation of cycloolefins in the presence of a platinum catalyst. Since in the catalyzate obtained at room temperature the ratio of cis- and trans-forms (0.64) exceeds the equilibrium value (0.051) by an order of magnitude, it cannot be excluded that cis-addition of hydrogen occurs considerably more readily than trans-addition. It is possible that this is the predominant or even the only direction of the reaction, while the trans-form is the result of a secondary isomerization process. The higher the reaction temperature, the faster the isomerization proceeds and the closer the concentration of the trans-form approaches the equilibrium value. In addition, it should be emphasized that, for the preparative production of the relatively difficultly accessible cis-isomer of 1,2-dimethylcyclopentane, a low temperature proves preferable.

Experimental Part

Preparation of the starting hydrocarbons. The synthesis was carried out according to the scheme given above. In this procedure, dehydration of 1-methylcyclopentanol-1 and 1,2-dimethylcyclopentanol-1 was performed with the aid of sha-

Table 1

Dependence of the composition of trans- and cis-1,2-dimethylcyclopentanes on the experimental temperature

No.	Experiment No.	Temp., °C	n_D^{20} of the catalyzate	Catalyzate composition, %: trans-1,2-dimethylcyclopentane	Catalyzate composition, %: cis-1,2-dimethylcyclopentane	Catalyzate composition, %: hydrogenolysis products	(cis)/(trans) in the catalyzate	Calculated equilibrium constant K_p
trans-1,2-dimethylcyclopentane								
1	3	280	1.4058	56.9	12.0	31.1	0.21	0.195
2	13	280	1.4079	62.9	13.6	23.5	0.21	
3	26*	280	1.4142	83.75	16.25	0.0	0.19	
4	4	270	1.4072	63.8	12.5	23.7	0.20	0.189
5	5	270	1.4074	63.3	12.9	23.8	0.20	
6	11	270	1.4102	70.7	15.0	14.3	0.21	
7	12	270	1.4100	68.8	15.2	16.0	0.22	
8	6	260	1.4098	72.1	15.2	12.7	0.21	0.183
9	7	260	1.4098	74.2	16.0	9.8	0.22	
10	8	250	1.4100	79.3	15.7	5.0	0.20	0.178
11	9	250	1.4122	78.8	15.7	5.5	0.20	
12	10	250	1.4123	78.3	16.6	5.1	0.21	
13	27	200	1.4139	83.95	16.05	0.0	0.19	0.150
14	30	200	1.4137	84.9	15.1	0.0	0.18	
15	28	150	1.4130	90.3	9.7	0.0	0.11	0.121
16	29*	150	1.4128	92.6	7.4	0.0	0.08	
cis-1,2-dimethylcyclopentane								
17	15	280	1.4065	59.4	12.8	27.8	0.21	0.195
18	21	280	1.4080	64.5	13.7	21.8	0.21	
19	22	280	1.4078	62.5	13.4	24.1	0.21	
20	16	270	1.4108	71.3	15.7	13.0	0.22	0.189
21	23	270	1.4104	70.4	16.2	13.4	0.23	
22	17	260	1.4120	76.1	16.1	7.8	0.21	0.183
23	20	260	1.4126	77.0	16.6	6.4	0.21	
24	18	250	1.4128	80.5	15.5	4.0	0.19	0.178
25	24	250	1.4127	79.3	16.7	4.0	0.21	
26	19	240	1.4130	79.0	17.8	3.2	0.22	0.173

No.	Experiment No.	Temp., °C	n_D^{20} of the catalyzate	Catalyzate composition, %: trans-1,2-dimethylcyclopentane	Catalyzate composition, %: cis-1,2-dimethylcyclopentane	Catalyzate composition, %: hydrogenolysis products	(cis)/(trans) in the catalyzate	Calculated equilibrium constant K_p
27	25	240	1.4132	80.9	17.4	1.7	0.21	

* Experiments Nos. 26 and 29 were carried out in the absence of hydrogen.

of levulinic acid; methylcyclopentene-1 was oxidized to 2-methylcyclopentanone according to the procedure of A. F. Plate and A. A. Melnikov (4); hydrogenation of 1,2-dimethylcyclopentene over platinized charcoal was carried out at atmospheric pressure. The resulting 1,2-dimethylcyclopentane was chromatographed on silica gel and then separated into stereoisomers by distillation on a column with an efficiency of 100 theoretical plates. A comparison of the constants of the stereoisomers obtained with the most reliable literature data is given in Table 2.

Experimental procedure. All experiments were carried out in a flow system over one portion (10 ml) of platinized charcoal (20% Pt), prepared according to the procedure of N. D. Zelinskii and M. B. Turova-Polyak (5) and stabilized by carrying out on it the hydrogenolysis of cyclopentane for 55 h. The hydrocarbon was passed over the catalyst in a stream of hydrogen at a practically constant volumetric rate (~0.2). The duration of each experiment was 2 h; the catalyzate collected during the first hour—during the so-called preliminary period—was sepa-

was discarded, and only the catalyst collected during the last hour was subjected to analysis. The analysis was carried out by gas-liquid chromatography on an SKB IOKh AN SSSR chromatograph in a stream of helium at 60-62° on a 5.5 m column filled with triethylene glycol butyrate (20%) on diatomaceous brick.

Table 2

Physical properties of the starting hydrocarbons

Hydrocarbon	B.p., °C at 760 mm	n_D^{20}	d_4^{20}
Trans-1,2-dimethylcyclopentane	92.0	1.4120	0.7514
Literature data (2)	91.869	1.41200	0.75144
Cis-1,2-dimethylcyclopentane	99.6	1.4221	0.7726
Literature data (2)	99.532	1.42217	0.77262

Fig. 1 gives, as an example, chromatograms of catalysts obtained from cis-1,2-dimethylcyclopentane at 240 and 280° (experiments Nos. 25 and 22, respectively).

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