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Abstract

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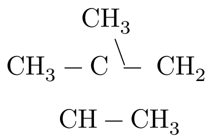
CATALYTIC TRANSFORMATIONS OF 1,1,2-TRIMETHYLCYCLOPROPANE IN THE PRESENCE OF PALLADIZED CHARCOAL AND ACTIVATED CHARCOAL

It has been noted more than once that cyclopropane and its homologues, in the presence of certain catalysts—aluminum oxide ([1–3]), silica gel ([4,5]), platinum black ([6,1])—are capable of undergoing isomerization to olefins. It should be noted that not in all the cases described have the hydrocarbons formed as a result of isomerization been identified with sufficient clarity; moreover, the data concerning the conditions under which the reactions are carried out are often contradictory.

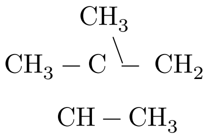
In studying the hydrogenolysis of hydrocarbons of the cyclopropane series ([7–9]) in the presence of palladized and platinized charcoal, we decided to determine whether these catalysts can bring about isomerization of a three-membered ring. The object of the present investigation was 1,1,2-trimethylcyclopropane; the reaction was carried out in a flow system in the absence of hydrogen (in a stream of nitrogen) at a temperature of 220° and a volumetric feed rate of the hydrocarbon equal to 0.2 hr^{-1}.

It was found that palladized charcoal under these conditions causes isomerization of 1,1,2-trimethylcyclopropane to a mixture of olefins. The isomerization proceeds to approximately 55%, and the bond that is cleaved is mainly the bond between the most and the least hydrogenated carbon atoms of the ring and, to a lesser extent, the other bond adjacent to the quaternary carbon atom.

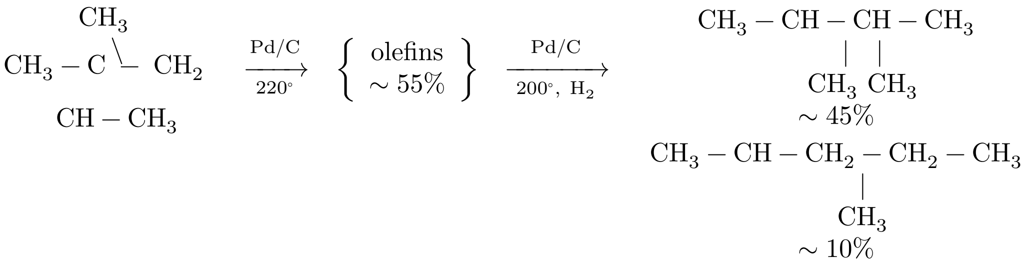


$$\begin{array}{c} CH_3 \\ CH_3 - C \diagdown - \; CH_2 \\ CH - CH_3 \end{array}$$

The bond between the two most hydrogenated carbon atoms—the bond that is cleaved during hydrogenolysis—remains unaffected during isomerization.



To determine more precisely the direction of cleavage of the three-membered ring during isomerization, we hydrogenated the olefins formed and fractionated the hydrogenation product on an efficient column. The reaction can be represented by the following scheme:



According to the data available to us, platinized carbon behaves in this reaction analogously to palladized carbon; experimental material relating to this catalyst will be published later.

We also studied the behavior of 1,1,2-trimethylcyclopropane in a stream of nitrogen at the same temperature and space velocity in the presence of activated carbon—the support used for preparing platinum and palladium catalysts. It turned out that carbon is an even more active isomerizing agent than these catalysts. Thus, in the presence of carbon, 1,1,2-trimethylcyclopropane was converted completely into a mixture of olefins, hydrogenation of which and distillation gave about 80% 2,3-dimethylbutane and about 20% 2-methylpentane. We also investigated the behavior of 1,1,2-trimethylcyclopropane by passing it, under the same conditions, over activated carbon, but not in a stream of nitrogen, rather in a stream of hydrogen. It was found that under these conditions, in addition to isomerization of 1,1,2-trimethylcyclopropane, hydrogenation of the mixture of olefins formed took place. It should be noted that carbon was not an active hydrogenation catalyst and was noticeably poisoned as the hydrocarbon was passed through. Only when small portions of hydrocarbon were passed did saturated catalyzate form from the first pass. To obtain 25 ml of saturated catalyzate, three successive passages through a fresh portion of activated carbon were required. Distillation of the catalyzate obtained showed that a mixture of 2,3-dimethylbutane and 2-methylpentane was formed. Thus, the scheme of the process is as follows:

$$\text{1,1,2-trimethylcyclopropane} \xrightarrow[220^\circ;\ H_2]{C} \begin{cases} CH_3{-}CH(CH_3){-}CH(CH_3){-}CH_3, \\ CH_3{-}CH(CH_3){-}CH_2{-}CH_2{-}CH_3. \end{cases}$$

Comparison of this reaction with the hydrogenolysis reaction of 1,1,2-trimethylcyclopropane (7) in the presence of platinized carbon makes it possible to draw the following conclusions.

$$\text{1,1,2-trimethylcyclopropane} \xrightarrow[100^\circ;\ H_2]{Pt/C} CH_3{-}C(CH_3)_2{-}CH_2{-}CH_3$$

1. In the catalytic addition of hydrogen to alkylcyclopropanes, two processes may occur: the hydrogenolysis reaction of the three-membered ring with ring opening, and the isomerization reaction to olefins with their subsequent hydrogenation.
2. Hydrogenolysis of alkylcyclopropanes does not proceed through intermediate isomerization of them into olefins; otherwise, the final products of both reactions would be identical.
3. Activated carbon can catalyze not only the isomerization reaction of alkylcyclopropanes, but also the hydrogenation reaction of the olefinic hydrocarbons formed in this process.

Experimental Part

Isomerization of 1,1,2-trimethylcyclopropane in the presence of palladized carbon

Into the catalytic tube were placed 50 ml of 20% palladized carbon prepared by the Zelinsky method (10). The catalyst was reduced in a stream of hydrogen at 300°, after which the temperature was lowered to the desired value, the hydrogen feed was stopped, and the hydrogen adsorbed by the catalyst was displaced from its surface by a definite portion of 1,1,2-trimethylcyclopropane, which was thereby partially hydrogenated and then discarded. After this, 1,1,2-trimethylcyclopropane was passed over the catalyst at a space velocity of 0.2 h^{-1} in a weak stream of nitrogen.

1,1,2-trimethylcyclopropane was passed through. The catalyst had n_D^{20} 1.3940 and intensely decolorized bromine water. After hydrogenation in a duck-shaped flask at room temperature in the presence of palladized charcoal, 78.0 g of the mixture was fractionated on a column with an efficiency of 100 theoretical plates. The results of the fractionation are presented in Table 1 and in Fig. 1 (curve *a*); Table 2 gives the constants of the original 1,1,2-trimethylcyclopropane and of the hydrocarbons that may be present in the mixture.

Table 1

Fig. 1

Figure 1: Fig. 1

Fraction	Amount, g	B.p., °C (at 760 mm)	n_D^{20}	d_4^{20}
I	8.9	48.6–52.0	1.3800	0.6790
II	20.4	52.0–52.8	1.3860	0.6944
III	10.9	52.8–57.6	1.3810	
IV	25.4	57.6–57.7	1.3750	0.6612
V	4.6	57.7–59.8	1.3730	0.6565
VI	1.4	59.8–61.0	1.3717	0.6537*
VII	5.3	61.0–86.4	1.3730	0.6548

Note. Loss 1.1 g.

* 20 ml of *n*-octane was added to the distillation flask as a displacing agent.

Table 2

Hydrocarbon	B.p., °C (at 760 mm)	n_D^{20}	d_4^{20}
1,1,2-Trimethylcyclopropane	52.5	1.3862	0.6947
2,2-Dimethylbutane ([11])	49.741	1.36876	0.64915
2,3-Dimethylbutane ([11])	57.988	1.37495	0.66164
2-Methylpentane ([11])	60.271	1.37145	0.65316

From a comparison of the data in Tables 1 and 2 it may be concluded that fraction IV is 2,3-dimethylbutane, while fraction VI and, in part, fraction VII are 2-methylpentane. Fraction II is 1,1,2-trimethylcyclopropane that did not enter into the reaction; fractions III and V are transitional. Fraction I contains 1,1,2-trimethylcyclopropane and small amounts of 2,2-dimethylbutane, which could have formed as a result of hydrogenolysis of 1,1,2-trimethylcyclopropane by hydrogen dissolved in the palladium.

Fig. 1

Thus, judging from the fractionation data, isomerization proceeded to approximately 55%. Of this amount, about 45% was 2,3-dimethylbutane and about 10% was 2-methylpentane.

Isomerization of 1,1,2-trimethylcyclopropane in the presence of activated charcoal. The activated charcoal was subjected to the preliminary treatment usually employed by us in preparing catalysts—platinized and palladized charcoal. The treatment procedure consisted in heating with an alkali solution, thorough washing with water to neutral reaction, heating with dilute nitric acid, thorough washing with distilled water until the wash waters gave a negative reaction with diphenylamine, and drying the charcoal.

The ash content of the charcoal was 0.2%; activity toward ether, 24%.

Isomerization of 1,1,2-trimethylcyclopropane was carried out exactly as described above; n_D^{20} of the isomerizate was 1.4035. After hydrogenation in a duck-shaped flask in the presence of palladized charcoal, 28.2 g of the hydrocarbon mixture of the isomerization product was fractionated on a column with an efficiency of 100 theoretical plates. The results of the fractionation are given in Table 3 and in Fig. 1 (curve *b*).

Comparison of the data of Table 3 with the constants given in Table 2 shows that fraction II is 2,3-dimethylbutane, fraction IV consists mainly of 2-methylpentane, and fraction III is intermediate.

Thus, judging from the distillation data, isomerization in the presence of activated carbon proceeded completely. The hydrogenated isomerizate is a mixture of $\sim$ 80% 2,3-dimethylbutane and $\sim$ 20% 2-methylpentane.

Hydrogenation of 1,1,2-trimethylcyclopropane in the presence of activated carbon. The experiments were carried out at a temperature of 220° and a space velocity of 0.2 h^{-1}, similarly to that described above, with the only difference that 1,1,2-trimethylcyclopropane was passed over activated carbon in a stream of hydrogen. The results of the experiments are given in Table 4. 28.0 ml of the combined catalyzates were distilled on a column with an efficiency of 50 theoretical plates. The results of the distillation are given in Table 5 and in Fig. 1 (curve *b*).

Table 3

Fraction	Amount, g	B.p., °C (at 760 mm)	n_D^{20}	d_4^{20}
I	1.3	58.0–58.2	1.3751	0.6624
II	16.5	58.2	1.3750	0.6616
III	6.5	58.2–60.7	1.3746	0.6595*
IV	2.9	60.7	1.3725	0.6556
V	1.0	60.7–81.8	1.3721	0.6550

Note. Losses 0.9 g.

* 20 ml of *n*-octane was added to the distillation flask as a displacing agent.

Table 4

Exp. no.	Amount of 1,1,2-trimethylcyclopropane taken, ml	n_D^{20}	d_4^{20}	Catalyst: aniline point	Catalyst: reaction with bromine water
1	2	1.3748	0.6606	71.4	does not decolorize
2	3	1.3745	0.6602	–	””
3	6	1.3750	0.6612	69.8	””
4	30	1.3750*	–	–	””

* Constants are given for the catalyzate obtained by threefold passage over activated carbon.

Table 5

Fraction	Amount, ml	B.p., °C (at 760 mm)	n_D^{20}	d_4^{20}
1	5.0	56.5–57.9	1.3750	0.6616
2	7.5	57.9–58.1	1.3749	0.6612
3	3.5	58.1–58.5	1.3745	0.6610
4	3.0	58.6–59.1	1.3739	0.6589
5	3.0	59.1–60.3	1.3735	0.6571

Comparison of the data of Tables 5 and 2 shows that fractions nos. 1, 2, and 3 consist mainly of 2,3-dimethylbutane; fractions nos. 4 and 5 contain a mixture of 2,3-dimethylbutane and 2-methylpentane.

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