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Abstract

Full Text

Chemistry

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HYDROGENATION OF VINYLCYCLOPROPANE AND 1-METHYL-1-ISOHEXENYLCYCLOPROPANE IN THE PRESENCE OF PLATINUM AND PALLADIUM

It has recently been found (^{1}) that isopropenylcyclopropane, in the presence of palladium black at room temperature, readily adds two moles of hydrogen with formation of 2-methylpentane. It was shown that the reaction proceeds through the intermediate formation of 2-methylpentene-1 and 2-methylpentene-2 according to the scheme:

$$\text{isopropenylcyclopropane} \xrightarrow[20^\circ]{\text{Pd; H}_2} \left\{ \begin{array}{l} CH_3 - CH_2 - CH_2 - C(CH_3) = CH_2 \\ CH_3 - CH_2 - CH = C(CH_3) - CH_3 \end{array} \right\} \xrightarrow[20^\circ]{\text{Pd; H}_2} CH_3 - CH_2 - CH_2 - C \tag{1}$$

Isopropylcyclopropane is not formed at all under these conditions.

This peculiar behavior of isopropenylcyclopropane led us to suggest that the presence of a double bond in the side chain of this hydrocarbon lowers the stability of the C—C bonds of the three-membered ring, situated adjacent to the substituent, toward their cleavage with addition of hydrogen, apparently owing to a special conjugation between the cyclopropane ring and the double bond.

Hydrogenation of isopropenylcyclopropane in the presence of platinum black (^{2}) proceeds differently: 1.3 moles of hydrogen are added, and a mixture is obtained consisting of 70% isopropylcyclopropane and 30% 2-methylpentane:

$$\text{isopropenylcyclopropane} \xrightarrow[20^\circ]{\text{Pt; H}_2} \begin{cases} \text{isopropylcyclopropane} & (70\%), \\ CH_3 - CH_2 - CH_2 - CH(CH_3) - CH_3 & (30\%). \end{cases} \tag{2}$$

Thus, in the presence of platinum black, cleavage of the three-membered ring with addition of hydrogen according to the scheme given for palladium (1) pro-

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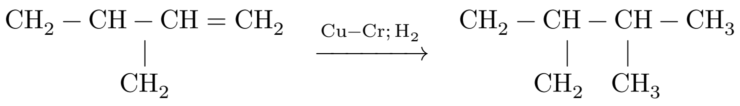
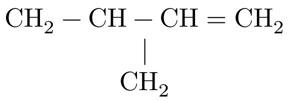
ceeds more slowly than the addition of hydrogen at the double bond with preservation of the cyclopropane ring. The first reaction consumes 0.6 mole, and the second 0.7 mole, of hydrogen. It is known from the literature (3) that one molecule of hydrogen can be selectively added to isopropenylcyclopropane with formation of isopropylcyclopropane in the presence of a copper-chromium catalyst at a comparatively high temperature and under elevated-

under hydrogen pressure:



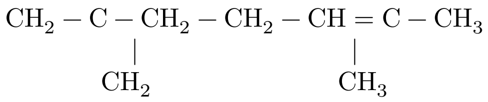
$$\mathrm{CH_2 - \underset{\begin{array}{c}|\\ CH_2\end{array}}{CH} - CH = CH_2 \xrightarrow{Cu-Cr;\, H_2} CH_2 - \underset{\begin{array}{c}|\\ CH_2\end{array}}{CH} - \underset{\begin{array}{c}|\\ CH_3\end{array}}{CH} - CH_3} \qquad (3)$$

It should be noted that, with both palladium black and platinum black, isopropylcyclopropane at room temperature does not add hydrogen at all. In the present work we studied the addition of hydrogen in the presence of palladium and platinum black to two other hydrocarbons of the cyclopropane series containing a double bond in the side chain: vinylcyclopropane (I), in which the double bond is in a position conjugated with the three-membered ring, and 1-methyl-1-isohexenylcyclopropane (II), in which it is separated from the ring by two methylene groups.



$$\mathrm{CH_2 - \underset{\begin{array}{c}|\\ CH_2\end{array}}{CH} - CH = CH_2}$$

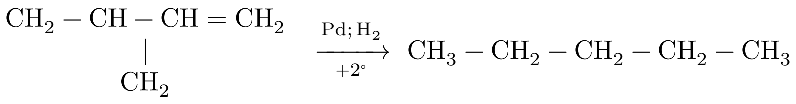
I



$$\mathrm{CH_2 - \underset{\begin{array}{c}|\\ CH_2\end{array}}{C} - CH_2 - CH_2 - CH = \underset{\begin{array}{c}|\\ CH_3\end{array}}{C} - CH_3}$$

II

Vinylcyclopropane in the presence of palladium black readily (at +2°) adds two molecules of hydrogen, being converted into *n*-pentane; that is, in this case there occurs the same easy cleavage of the three-membered ring with addition of hydrogen and hydrogenation of the double bond of the side chain as was observed earlier for isopropenylcyclopropane (1):



$$\mathrm{CH_2 - \underset{\begin{array}{c}|\\ CH_2\end{array}}{CH} - CH = CH_2 \xrightarrow[+2^\circ]{Pd;\, H_2} CH_3 - CH_2 - CH_2 - CH_2 - CH_3} \qquad (4)$$

If the hydrogenation is interrupted after only one molecule of hydrogen has been added, a more complex mixture is formed, not yet studied in detail, but, judging from the distillation curve and the physical properties of the fractions, containing unreacted vinylcyclopropane, *n*-pentane, pentene-1, and pentene-2.

In the hydrogenation of vinylcyclopropane in the presence of platinum black, as in the case of isopropenylcyclopropane (2), about 1.3 moles of hydrogen is added, and a mixture of ethylcyclopropane and *n*-pentane is formed.

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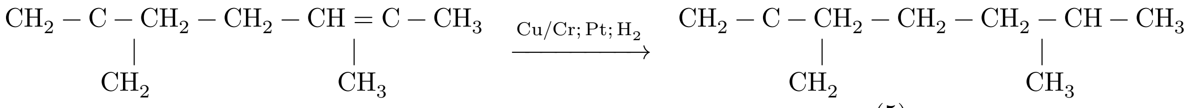
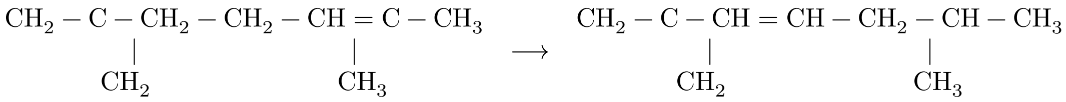
1-Methyl-1-isohexenylcyclopropane, both in the presence of platinum black at room temperature and in the presence of a copper-chromium catalyst at 100° and pressures up to 130 atm, is smoothly converted into 1-methyl-1-isohexylcyclopropane, hitherto not described in the literature.



$$CH_2 - \underset{\underset{CH_2}{|}}{C} - CH_2 - CH_2 - CH = \underset{\underset{CH_3}{|}}{C} - CH_3 \xrightarrow{Cu/Cr;\,Pt;\,H_2} CH_2 - \underset{\underset{CH_2}{|}}{C} - CH_2 - CH_2 - CH_2 - \underset{\underset{CH_3}{|}}{CH} - CH_3 \qquad (5)$$

In the presence of palladium black at room temperature, 1-methyl-1-isohexenylcyclopropane absorbs about 1.6 moles of hydrogen and is converted, as may be judged from the properties of the hydrogenation product, into a mixture of 1-methyl-1-isohexylcyclopropane with 2,6-dimethyloctane. This result of hydrogenation may be explained as follows: part of the hydrogen that has added is used for hydrogenation of the double bond in the side chain according to equation (5); another part is expended in addition to an isomeric hydrocarbon in which the double bond, under the influence of contact with palladium black, has shifted into a position conjugated with the cyclopropane ring.



$$CH_2 - \underset{\underset{CH_2}{|}}{C} - CH_2 - CH_2 - CH = \underset{\underset{CH_3}{|}}{C} - CH_3 \longrightarrow CH_2 - \underset{\underset{CH_2}{|}}{C} - CH = CH - CH_2 - \underset{\underset{CH_3}{|}}{CH} - CH_3 \qquad (6)$$

A similar shift in the presence of palladium had previously been observed (1) for 2-methylpentene-1, and in that case a mixture of 2-methylpentene-1 and 2-methylpentene-2 was obtained. The 1-methyl-1-iso- formed as a result of isomerization···

hexenylcyclopropane with a double bond conjugated with respect to the cyclopropane ring should evidently behave in the presence of palladium and hydrogen analogously to vinylcyclopropane and isopropenylcyclopropane, i.e., add two molecules of hydrogen and be converted into 2,6-dimethyloctane.

$$CH_2{-}C{-}CH{=}CH{-}CH_2{-}CH(CH_3){-}CH_3 \xrightarrow[H_2]{Pd} CH_3{-}CH_2{-}CH(CH_3){-}CH_2{-}CH_2{-}CH_3{-}CH(CH_3)_2 \qquad (7)$$

In the presence of platinum black, migration of the double bond does not occur, and therefore the result of hydrogenation is only 1-methyl-1-isohexylcyclopropane. At 180° in the vapor phase in the presence of platinized carbon, 1-methyl-1-isohexylcyclopropane, with addition of hydrogen, is converted into 2,2,6-trimethylheptane; i.e., hydrogenolysis of the three-membered ring in this case also proceeds, as for other alkylcyclopropanes (4,5), with rupture of the C—C bond located opposite the substituent.

$$\text{1-methyl-1-isohexylcyclopropane} \xrightarrow[180^\circ]{\text{Pt/C; H}_2} \text{2,2,6-trimethylheptane} \qquad (8)$$

Experimental Part

Vinylcyclopropane was synthesized according to Slabey (6) and had the following properties: b.p. 40–40.2°/760 mm; n_D^{20} 1.4140; d_4^{20} 0.7197.

1-Methyl-1-isohexenylcyclopropane was obtained according to Kizhner (7) and had the following properties: b.p. 161–161.5°/760 mm; n_D^{20} 1.4400; d_4^{20} 0.7770.

Table 1

Name of hydrocarbon	b.p., °C (760 mm)	n_D^{20}	d_4^{20}	Aniline point, °C
Ethylcyclopropane (8)	35.94	1.3786	0.6839	–
n-Pentane (9)	36.0	1.3575	0.6262	–
2-Methylbutane (9)	27.85	1.3537	0.6196	–
1-Methyl-1-isohexylcyclopropane*	155.1	1.4193	0.7544	57.2
2,6-Dimethyloctane (9)	158.54	1.4113	0.7285	78.1 (crit.)
2,2,6-Trimethylheptane (9)	148.2	1.4059	0.7195	81 (crit.)

* Obtained by us by hydrogenating 1-methyl-1-isohexenylcyclopropane in the presence of a copper-chromium catalyst.

Table 1 gives the properties of hydrocarbons that could be obtained in the catalytic addition of hydrogen to these two hydrocarbons, if it is assumed that the hydrogenation reaction proceeds in all possible directions. The procedure for adding hydrogen and isolating the reaction products was the same as in our previous work (1). Palladium and platinum black were prepared according to Zelinsky (10).

1. **Hydrogenation of vinylcyclopropane.** 7.2 g of hydrocarbon, in the presence of palladium black, added hydrogen in an amount corresponding to 2 mol. The isolated reaction product was distilled on a column of 40 theoretical plates. The properties of the fractions obtained are given in Table 2. The results of the distillation show that hydrogenation gave almost pure *n*-pentane, probably with some admixture of unreacted vinylcyclopropane.

7.2 g of vinylcyclopropane in the presence of platinum black added an amount of hydrogen corresponding to 1.29 moles. Distillation on the same column gave a product having the following properties: b.p. 35.6-35.9°/760 mm; n_D^{20} 1.3738; d_4^{20} 0.6723. Comparison of the catalyst constants with the data of Table 1 shows that it is a mixture of ethylcyclopropane and *n*-pentane, which cannot be separated by distillation.

Table 2

Fraction No.	B.p., °C (760 mm)	Weight, g	n_D^{20}	d_4^{20}
1	36.0-36.1	0.6	1.3585	0.6285
2	36.1-36.2	2.2	1.3578	0.6270
3	36.2-36.3	1.3	1.3576	0.6270
Residue, after distillation from Favorskii' s column	36.3-36.4	1.3	1.3581	0.6275
Losses	–	0.7	–	–

2. Hydrogenation of 1-methyl-1-isohexenylcyclopropane. 19.0 g of the hydrocarbon in the presence of platinum black added an amount of hydrogen corresponding to one mole. The reaction product was distilled on a 40 t.t. column at 154.8-155.0°/760 mm and had n_D^{20} 1.4193; d_4^{20} 0.7544, i.e., it was pure 1-methyl-1-isohexylcyclopropane (see Table 1).

Table 3

Fraction No.	B.p., °C (760 mm)	Weight, g	n_D^{20}	d_4^{20}	Aniline point, °C
1	154.5-154.8	0.4	1.4178	0.7517	–
2	154.8-155.3	1.1	1.4166	0.7493	59.2
3	155.3	7.0	1.4165	0.7468	63.9

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Fraction No.	B.p., °C (760 mm)	Weight, g	n_D^{20}	d_4^{20}	Aniline point, °C
4	155.3–155.6	2.2	1.4150	0.7438	65.2
5	155.6–156.0	2.5	1.4143	0.7401	67.1
Losses	–	1.3	–	–	–

15.5 g of 1-methyl-1-isohexenylcyclopropane was hydrogenated in the presence of palladium black. The amount of hydrogen taken up corresponds to 1.63 moles. After isolation, the reaction product was distilled on a column. The results of the fractionation are given in Table 3.

Comparing the data of Tables 1 and 3, one may conclude that the catalyst consists of a mixture of 1-methyl-1-isohexylcyclopropane and 2,6-dimethyloctane.

4.5 g of 1-methyl-1-isohexylcyclopropane was passed in a stream of hydrogen, at a space velocity of 0.2 h^{-1}, through a tube with platinized charcoal heated to 180°. The catalyst was distilled from Favorskii' s flask and had the following properties: b.p. 147.6°/760 mm; n_D^{20} 1.4058; d_4^{20} 0.7191. Judging from these, the hydrocarbon obtained is 2,2,6-trimethylheptane.

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