IONIC HYDROGENATION OF ALKENYL- AND ALKYLIDENECYCLOPROPANES

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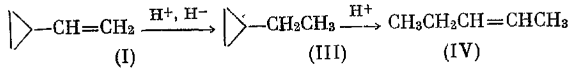
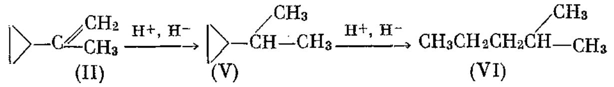
The present paper is devoted to a study of the reaction for the ionic hydrogenation of cyclopropane hydrocarbons, containing a double bond in conjugation with the ring (alkenylcyclopropanes), and of cyclopropane hydrocarbons containing a semicyclic double bond (alkyldienecyclopropanes). Previously we had shown [1] that the ionic hydrogenation of vinylcyclopropane (I) and isopropenylcyclopropane (II), which contain a double bond in conjugation with a three-membered ring, proceeds in a stepwise manner. Initially the double bond is hydrogenated and the alkylcyclopropane is formed. Depending on the structure of the alkylcyclopropane, it then either isomerizes to the olefin or is converted to the saturated hydrocarbon.

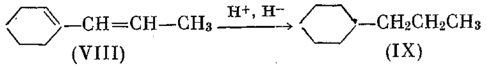
In the present paper we made a more detailed study of the reaction for the ionic hydrogenation of alkenylcyclopropanes (I) and (II), and we also studied the yield of the formed hydrocarbons as a function of the length of experiment, the amount of trifluoroacetic acid, and the temperature. In the ionic hydrogenation of vinylcyclopropane (I), resulting in the formation of ethylcyclopropane (III), in not one of the studied cases were we able to isolate an ethylcyclopropane that was not contaminated with trans-2-pentene (IV) (Table 1).

Isopropenylcyclopropane (II) behaves in a different manner when hydrogenated (Table 2). At −10°C and a twofold excess of trifluoroacetic acid we obtained isopropylcyclopropane (V) in approximately 80% yield, which was not contaminated with either the ethylenic or the saturated hydrocarbon [2-methylpentane (VI)]





It is interesting to compare the results of the ionic hydrogenation of alkenylcyclopropanes (I) and (II) with the previously studied ionic hydrogenation of conjugated dienes [2]. Thus, the unsubstituted diene, and specifically 1,3-cyclohexadiene (VII), practically does not hydrogenate. 1-Propenylcyclohexene (VIII), which has branching at one of the double bonds, is hydrogenated completely, i. e., selectivity is absent



As a result, the main characteristic difference in the ionic hydrogenation of alkenylcyclopropane hydrocarbons and dienic hydrocarbons consists in the possibility of the selective hydrogenation of a double bond that is conjugated with a three-membered ring. This selectivity can be explained by the intermediate formation of the cyclopropylcarbonium ion (A), which possesses a high stability due to conjugation with a three-membered ring [3]. The addition of hydride ion from triethylsilane to ion (A) leads to the formation

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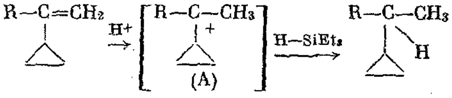
TABLE 1. Yield of Hydrocarbons (in %), Obtained in the Ionic Hydrogenation of Vinylcyclopropane (I)

Reaction time, h	Reaction temperature, °C	Amount of CF_3COOH, moles			
		2,5		4	
		(III)	(IV)	(III)	(IV)
0,1	0	—	—	15	2,0
0,5	20	27	3,6	41	6,3
1,0	20	33	2,8	40	10,8
1,5	20	35	2,8	34	13,5
4,0	20	39	6,0	27	15,0
15,0	20	31	10,0	20	7,7

TABLE 2. Yield of Hydrocarbons (in %), Obtained in the Ionic Hydrogenation of Isopropenylcyclopropane (II)

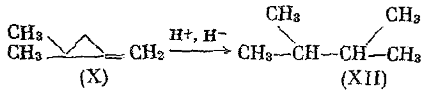
Reaction time, h	Reaction temperature, °C	Amount of CF_3 COOH, moles			
		2		3	
		(V)	(VI)	(V)	(VI)
0,1	0	48	0	62	0
0,5	—10	78	0	59	0,5
1,0	20	50	0	53	1,0
3,0	20	52	2	17	8,6
50,0	20	40	—	—	—

of alkylcyclopropanes*

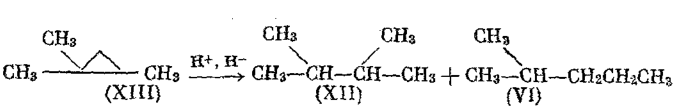


The differences in the results of hydrogenating (I) and (II) are probably explained by the fact that the carbonium ion that is obtained from (II), which is stabilized by conjugation with the cyclopropyl group, is in addition a tertiary ion, which makes it more stable than the secondary ion that is formed from (I). For this reason the ionic hydrogenation of the ethylenic linkage in (II) proceeds at a faster speed than in (I). This can explain the difference between the hydrogenation rate of the double bond and the rate of opening the ring in isopropenylcyclopropane and vinylcyclopropane. For this reason isopropylcyclopropane can be obtained without contamination by the saturated hydrocarbon.

In order to make a comparison with the results of hydrogenating alkenylcyclopropanes, we studied under the same conditions the behavior of two alkylidenecyclopropane hydrocarbons, and specifically 1,1-dimethyl-2-methylenecyclopropane (X) and 1,1-dimethyl-2-isopropylidenecyclopropane (XI), in which the double bond is semicyclic. They also take part in the ionic hydrogenation reaction and are converted to saturated hydrocarbons with an open chain, but in contrast to alkenylcyclopropanes (I) and (II), the formation of alkylcyclopropane hydrocarbons is not observed during the course of their hydrogenation, i.e., the semicyclic double bond in these compounds does not hydrogenate selectively. 2,3-Dimethylbutane (XII) is obtained in 65% yield as the result of the hydrogenation of hydrocarbon (X)



The absence of the intermediate formation of 1,1,2-trimethylcyclopropane (XIII) is corroborated by the following data. Previously it was shown [5] that 1,1,2-trimethylcyclopropane (XIII) during ionic hydrogenation is converted to a mixture, which is composed of 75% of 2,3-dimethylbutane (XII) and 25% of 2-methylpentane (VI), whereas the reaction with (X) leads to the formation of only 2,3-dimethylbutane (XII)



As the result of the reaction of 1,1-dimethyl-2-isopropylidenecyclopropane (XI) the main hydrogenation product proved to be 2,5-dimethylhexane (XIV); 2,5-dimethyl-2-hexene (XV) and 2,5-dimethyl-3-hexene (XVI) were also detected. The latter predominated under incomplete hydrogenation conditions

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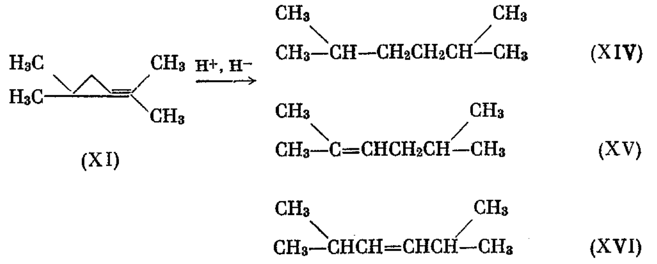
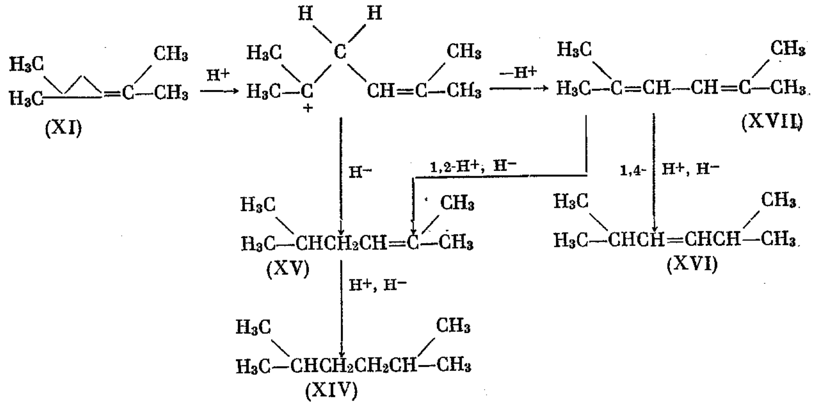
* The authors of [4] failed to observe the formation of saturated hydrocarbons with an open chain when cyclopropylcarbinols were reacted with silicon hydrides and trifluoroacetic acid. Apparently, this is associated with the fact that the reaction was run using inadequate amounts of acid and silane, and also a short contact time.



The formation of these hydrocarbons is possible only when the ring attached to the bond between the two substituted carbon atoms is cleaved. The course of the reaction can be depicted by the following scheme, which postulates the intermediate formation of 2,5-dimethyl-2,4-hexadiene (XVII)



The following facts serve to corroborate the presented scheme. By means of special experiments* it was shown that, together with the saturated hydrocarbon (XIV), the symmetrical olefin (XVI) is formed in the ionic hydrogenation of diene (XVII), and traces of olefin (XV) were also detected. These results testify to the fact that the hydrogenation of diene (XVII) proceeds at the 1,2- and 1,4-directions, and corroborate the possibility of its intermediate formation during the hydrogenation of (XI).

EXPERIMENTAL

Vinylcyclopropane (I) and isopropenylcyclopropane (II) were obtained as described in [6], and had the following constants: vinylcyclopropane, bp 40.1°, n_D^{20} 1.4142; isopropenylcyclopropane, bp 70.3°, n_D^{20} 1.4255.

The commercial grade of trifluoroacetic acid was refluxed for 2 h with conc. H_2SO_4 (volume ratio 2 : 1) in a dry argon stream, and then distilled through a column filled with glass packing and having an efficiency of 15 theoretical plates; bp 72.5°; mp 15.2. The triethylsilane (Et_3SiH) was obtained by the reaction of ethylmagnesium bromide with silicochloroform [7]; bp 108-109°; n_D^{20} 1.4093.

1,1-Dimethyl-2-isopropylidenecyclopropane (XI) was obtained by the addition of isopropylidenecarbene to isobutylene [8]. With stirring, 21 g of isobutylene dibromide was dissolved in 200 ml of liquid isobutylene. The solution was cooled to −10° and, in a dry argon stream, an ether solution of 0.1 mole of methyllithium was added in 1 h. The mixture was stirred at 0° for 1.5 h, decomposed with water, and dried over $MgSO_4$. After distilling off the solvent the residue was distilled; bp 58.5° (200 mm); n_D^{20} 1.4240; yield 57%. NMR spectrum (δ, ppm): 1.75 (6 protons), 1.15 (6 protons), 0.77 (2 protons). Infrared spectrum: 1780, 1450, 1370, 1150, 1140, 1000 cm^{-1}.

1,1-Dimethyl-2-methylenecyclopropane (X) was obtained by the stepwise reduction of 1,1-dimethyl-2,2-dibromo-3-methylenecyclopropane with tri-n-butyl hydride [9]. To 31.7 g of the dibromide [bp 78-79.5° (26 mm)] in a dry argon stream, with stirring, was added an equimolar amount of 17.0 g of $n\text{-}Bu_3SnH$. After 3 days (at 22°) the monobromide was distilled off and the reduction was repeated. The 1,1-dimethyl-2-methylenecyclopropane (X) had bp 46-48° [10]. NMR spectrum (δ, ppm): 1.22 (6 protons), 5.25 (2 protons), 0 (2 protons).

Ionic Hydrogenation. To a mixture of 0.01 mole of the hydrocarbon and 0.01 mole of Et_3SiH was gradually added 0.02 mole of CF_3COOH (due to exothermic reaction, in the case of hydrocarbons (I) and (II) the acid was

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*The experiments were run with the collaboration of G. I. Bolestova.

added at 0°). The mixture was kept at a temperature of −10, 20, or 50° and, at the end of reaction, was either decomposed with water, extracted with benzene and neutralized with solid K_2CO_3, or a sample was taken directly from the reaction mixture and analyzed by GLC.

Hydrocarbon (X), using a molar ratio of the reactants of hydrocarbon : silane : acid = 1 : 2 : 4, at 20°, in 90 h, gives a 65% yield of 2,3-dimethylbutane.

From hydrocarbon (XI), using a 1 : 2 : 4 ratio of the reactants, at 50°, in 16 h, is formed: 63% of 2,5-dimethylhexane (XIV), 18.5% of 2,5-dimethyl-3-hexene (XVI), and 1.6% of 2,5-dimethyl-2-hexene (XV), and also 7% of 2,5-dimethyl-2-hexanol trifluoroacetate. Using a reactant ratio of 1 : 1 : 2, at 50°, in 12 h, gives 19% of (XVI), 4.7% of (XI), 4.0% of (XV), and 55% of 2,5-dimethyl-2-hexanol trifluoroacetate.

The hydrogenation of diene (XVII) using a reactant ratio of 1 : 2 : 3, at 20°, in 172 h, gives 30% of (XIV), 10% of (XVI) and traces of (XV). 2,5-Dimethyl-3-hexene (XVI) was isolated by preparative GLC. NMR spectrum (δ, ppm): 0.96 (6 protons), 2.17 (2 protons), 5.28 (2 protons).

The GLC analysis of the products was run by comparing with standard compounds of known structure, while the quantitative analysis was run using an internal standard. n-Pentane served as the standard for hydrocarbon (I), n-hexane for (II) and (X), and isooctane for (XI). The GLC was run on a "Khrom-3" apparatus, using nitrogen as the carrier gas, and a glass capillary with a length of 43 m and an inside diameter of 0.25 mm. Silicone elastomer E-301 served as the liquid phase. The preparative isolation was run on a Varian-Aerograph 1868/4 instrument at 100°, using an aluminum column with a length of 6 m and an inside diameter of 9 mm; diethylene glycol dicyanide served as the liquid phase.

CONCLUSIONS

1. A study was made of the ionic hydrogenation of cyclopropane hydrocarbons, containing a double bond in the side chain.

2. On the example of the ionic hydrogenation of the vinyl- and isopropenylcyclopropanes it was shown that the selective hydrogenation of a double bond, conjugated with a three-membered ring, is possible.

3. In the ionic hydrogenation of alkylidenecyclopropane hydrocarbons, and specifically 1,1-dimethyl-2-methylenecyclopropane and 1,1-dimethyl-2-isopropylidenecyclopropane, the selective hydrogenation of the semicyclic double bond fails to occur and the hydrogenation products are saturated hydrocarbons with an open chain, and specifically 2,3-dimethylbutane and 2,5-dimethylhexane.

4. A reaction scheme was proposed for the ionic hydrogenation of 1,1-dimethyl-2-isopropylidenecyclopropane, which includes the intermediate formation of 2,5-dimethyl-2,4-hexadiene, which compound is capable of taking part in the ionic hydrogenation reaction, both by the 1,2- and by the 1,4-mechanism.

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