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COMPARISON OF THE IONIC HYDROGENATION OF THE UNSATURATED ANALOGS OF COMPOUNDS OF THE BICYCLO[2.2.1]HEPTANE SERIES AND OF THE CYCLOHEXANE SERIES

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The intermediate formation of tertiary carbenium ions with trifluoroacetic acid and triethylsilane is a necessary condition for the ionic hydrogenation of olefins [1]; for example, this takes place during the protonation of trisubstituted ethylenes. Olefins which yield secondary carbocations do not react.\*

Secondary bicyclo[2.2.1]heptyl cations possess enhanced stability. In connection with this we investigated the feasibility of the ionic hydrogenation of bicyclo[2.2.1]heptene hydrocarbons, and a comparison with monocyclic unsaturated compounds was carried out to clarify the role of the bridge structure of the substrate in this process. For this, unsaturated hydrocarbons (I)-(V) and hydrocarbons (VI)-(XI), which are close to them in the degree of substitution and the number and position of the double bonds in the molecule, were introduced into the reaction (Table 1).

Cyclohexene (VI) is not hydrogenated by the action of  $Et_3SiH$  and  $CF_3COOH$  on it even in the presence of additions of  $BF_3 \cdot Et_2O$ , which accelerate ionic hydrogenation [2]. Cyclohexyl trifluoroacetate, which is formed slowly, is the only reaction product; this is connected with the low stability of the secondary cyclohexyl cation.

Bicyclo[2.2.1]heptene (I) is reduced to bicyclo[2.2.1]heptane (XII) with a 3.5% yield by the action of Et<sub>3</sub>SiH and CF<sub>3</sub>COOH. Bicyclo[2.2.1]heptyl trifluoroacetate (XIII) is the principal reaction product. When  $BF_3 \cdot Et_2O$  is added to the reaction mixture, the yield of (XII) reaches 22%. An increase in the duration of the reaction and also the amount of the hydrogenating agents does not result in an increase in the yield of (XII) in both cases; this indicates that the step in which trifluoroacetate (XIII) is formed is irreversible. It follows from this that two competing irreversible processes take place during the reaction: the addition of the CF<sub>3</sub>COO<sup>-</sup> anion to the bicyclo[2.2.1]heptyl cation (A) and the interaction of cation (A) with the hydride silane:



\*Secondary carbocations which are stabilized by conjugation with the benzene or cyclopropane ring are an exception.

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carbons (20°C, 24 h)			
Hydro- carbon	Ratio in moles of hydrocarbon; Et <sub>3</sub> SiH:CF <sub>3</sub> COOH: BF <sub>3</sub> • OEt <sub>2</sub>	Hydrogenation product	Y ie l <b>d,</b> %
(I)	1,0 : 5,0 : 10,0 : 0,4	(XII)	22
(VI)	1,0 : 5,0 : 10,0 : 0,4	Cyclohexane	0
(II)	1,0:5,1:13,1:0	(XIV)	45
(VII)	4,0:5,1:13,1:0	(XXIV)	0
(VIII)	1,0:5,1:13,1:0	(XVI)	20
(III)	1,0:10,2:20,3:0	(XIII)	17
(IX)	1,0:10,2:20,3:0	1(XX)	0
(X)	1,0:10,2:20,3:0	1(XX)	65
(IV) (V) (XI)	1,0:6,5:12,1:1 1,0:6,5:12,1:1 1,0:6,5:12,1:1 1,0:6,5:12,1:1	(XIV) (XXI) (XXIV)	85 80 25

TABLE 1. Ionic Hydrogenation of the Mono- and Bicyclic Unsaturated Hydrocarbons (20°C, 24 h)

Reaction (2) considerable exceeds reation (1) in rate [3]. It is probable that this fact and not the low stability of cation (A) is the reason for the low yield of (XIII).

5-Methylbicyclo[2.2.1]hept-2-ene (II) should also form a secondary cation during protonation. However, hydrocarbon (II), in contrast to (I), is hydrogenated by  $CF_3COOH$  and  $Et_3SiH$  in the absence of a catalyst forming endo-2-methylbicyclo[2.2.1]heptane (XIV) with a 37% yield (within 5 min). An increase in the reaction time to 24 h increases the yield of (XIV) to 45%, which does not change further evidently because of the irreversible conversion of the remaining amount of hydrocarbon (II) to a mixture of the secondary exo-methylbicyclo[2.2.1]heptyl trifluoroacetates (XV) (three isomers according to GLC). The difference in behavior of hydrocarbons (I) and (II) is connected with the possibility of intramolecular hydride shifts in the bicyclo[2.2.1]heptyl cations to which they are quite inclined. For (II), conversion of the secondary cation (C) to the more stable tertiary one (D) takes place as a result of the hydride migration. The latter is reduced by the hydride silane and as a result of the exo addition of the hydride ion the endo isomer (XIV) forms



The starting hydrocarbon (II) was a mixture of the exo and endo isomers and their ratio did not affect the overall course of the reaction. Evidently this is due to ability of carbocations (B) and (C) to undergo a Wagner-Meerwein rearrangement which alters the spatial orientation of the CH<sub>3</sub> group.

If substance (XIV) is actually formed through cation (D), then the hydride ion from the silane should add to the tertiary carbon atom.

The use of the deuterosilane for the hydrogenation of (II) and the presence of a broadened singlet signal from the protons in the  $CH_3$  group ( $\delta 0.73$  ppm) in the PMR spectrum of the hydrogenation product, to which the doublet ( $\delta 0.72$  ppm, J = 6.66 Hz) corresponds in the spectrum of compound (XIV) containing no deuterium, permit one to conclude that the deuterium in (XIV-D) is to be found at the tertiary carbon atom, i.e., an intramolecular hydride transfer took place during the reaction forming a tertiary carbonium ion. Allylcyclohexane (VII), as for II, contains a tertiary C atom in the  $\beta$  position to the C=C bond; however, it does not react with the hydride silane in the presence of CF<sub>3</sub>COOH. A comparison of the behavior of the mono- and bicyclic hydrocarbons (VII) and (II) under ionic hydrogenating conditions shows that the 2-methylbicyclo[2.2.1]heptyl cation (C), in which the distance between the C<sup>2</sup> and C<sup>6</sup> carbons converges, is disposed to a 6,2-(1,3)-hydride shift, whereas the 1,3-hydride conversion in the allylcyclohexyl cation does not take place.

The ionic hydrogenation of an olefin of the cyclohexane series occurs when it does not contain branching at the C=C bond except when the latter is arranged next to a tertiary carbon atom. Thus, vinylcyclohexane (VIII) is converted to ethylcyclohexane (XVI) with a 20% yield and to the trifluoroacetate (XVII) by the action of CF<sub>3</sub>COOH and Et<sub>3</sub>SiH:



The formation of hydrocarbon (XVI) evidently takes place through tertiary cation (F) obtained from the 1,2-hydride shift from the secondary ion (E). A similar isomerization of a carbocation had been previously observed during the ionic hydrogenation of isopropylcyclo-propane [4].

Bicyclo[2.2.1]hepta-2,5-diene (III) under the ionic hydrogenation conditions yields a mixture of three trifluoroacetates: that of bicyclo[2.2.1]hepten-2-o1 (XVIII), tricyclo-[2.3.1.0<sup>2,6</sup>]heptan-3-o1 (XIX), and bicyclo[2.2.1]heptan-2-o1 (XIII) in a 62:20:17 ratio respectively. The formation of (XIII) indicates that hydrogenation of one C=C bond takes place in diene (III). Hydrocarbon (I) obtained at this time adds a molecule of CF<sub>3</sub>COOH. Trifluoroacetates (XVIII) and (XIX) are formed from the interaction of diene (III) and CF<sub>3</sub>COOH



Under analogous conditions, cyclohexa-1,4-diene (IX) is not hydrogenated. At the same time, cyclohexa-1,3-diene (X) with conjugated C=C bonds is hydrogenated with  $CF_3COOH$  and  $Et_3SiH$  to cyclohexene (VI) (65% yield), from which cyclohexyl trifluoroacetate (XX) is then formed



It follows from this that thanks to the homoallyl conjugation the bicyclo[2.2.1]heptenyl cation (G) approaches the cyclohexenyl cation (H) of the allyl type in stability.

Homoconjugated C=C bonds exist in 5-methylenebicyclo[2.2.1]hept-2-ene (IV) and 5-ethylidenebicyclo[2.2.1]hept-2-ene (V) as in diene (III); however, in contrast to (III), one of them is heptacyclic. During the ionic hydrogenation of dienes (IV) and (V), completely hydrogenated products are formed: endo-2-methyl- (XIV) and endo-2-ethylbicyclo[2.2.1]heptane (XXI) (yield 85%, 24 h at 20°C). At 50°C this yield of hydrogenation products is reached in 3 h. The reaction is strictly stereoselective and can be used for preparative purposes. The methylene or ethylene group is the most probable site of attack by the proton in compounds (IV) or (V), because the tertiary carbenium ion (U) is the most stable of the possible ones obtained in this case. The charge on it is distributed between the  $C^2$  and  $C^5$  carbons due to the homoconjugation. 1-Methyl- (XXII) or 1-ethyltricyclo[2.2.1.0<sup>2,6</sup>]heptane (XXIII) should be formed as a result of the addition of the hydride ion to the  $C^2$  carbon; one of its fragments is a gem-substituted cyclopropane



The gem-substituted cyclopropanes are easily hydrogenated by  $CF_3COOH$  and  $Et_3SiH$  with ring opening and the formation of saturated hydrocarbons [5]. Probably compounds (XXII) and (XXIII) are analogously hydrogenated to the endo-2-alkylbicyclo[2.2.1]heptanes. The hydrogenation of 1-ethyltricyclo[2.2.1.0<sup>2,6</sup>]heptane (XXIII) by  $CF_3COOH$  and  $Et_3SiH$  to the endo isomer (XXI) with a 90% yield in 15 min supports the proposed scheme. We did not succeed in detecting the formation of the tricyclene (XXII) or (XXIII) during the hydrogenation of dienes (IV) and (V); this is due to the considerably higher hydrogenation rate of a tricyclene compared to the alkylidenebicyclo[2.2.1]heptenes.

The C=C bonds in 1-allylcyclohex-1-ene (XI) are found in the 1,4-positions, just as in (V). In addition, the molecules of both hydrocarbons contain a trisubstituted ethylene group. The completely hydrogenated product, n-propylcyclohexane (XXIV), is formed during the ionic hydrogenation of (XI); however, the yield of the latter does not exceed 25%. Allylcyclo-hexane (VII) is the other reaction product



At the same time, propenylcyclohexane forms the completely hydrogenated product (XXIV) with a 75% yield [6]

$$\bigcirc -CH = CHCH_3 \xrightarrow{CF_3COOH}_{HSiEt_3} (XXIV)$$

Thus, homoconjugation is manifested during the ionic hydrogenation of the dienes of bicyclio[2.2.1]heptane series (IV), (V) analogously to the conjugation in the dienic hydro-carbons of the cyclohexane series.

The data obtained agree with the concept of the capability of the unsaturated compounds of the bicyclo[2.2.1]heptane series to form a carbocation possessing enhanced stability due to the characteristics of their structure.

## EXPERIMENTAL\*

The CF<sub>3</sub>COOH was purified by distillation over concentrated  $H_2SO_4$ . Triethylsilane was synthesized according to [7]; hydrocarbons (I) and (III) were synthesized condensing cyclopentadiene with ethylene [8] and acetylene [9]. Hydrocarbons (II), (IV), and (V) were prepared by reacting cyclopentadiene with the appropriate dienophiles followed by a number of subsequent conversions [10-12]. The synthesis of 1-ethyltricyclo[2.2.1.0<sup>2,6</sup>]heptane (XXIII) is described in [13]. See [10, 14] for the preparation of saturated hydrocarbons (XIV) and (XXI), the standards for the identification of the hydrogenation products. The purity of the compounds used was checked by their physical constants and GLC.

The analysis of the reaction products was carried out by GLC (Khrom-3 and Tsvet-5 instruments). Parameters of the packed columns: 1) 10% polyethylene glycol adipate on Risorb VLK, 0.2 to 0.3 mm, 3.5 m  $\times$  6.0 mm column; 2) 25%  $\beta$ , $\beta$ '-hydroxydipropionitrile on Chromosorb PAW, 80-100 mesh, 2.5 m  $\times$  3.7 mm column; 3) 25% OV-17 on Chromosorb W, 80-100 mesh, 2.6 m  $\times$ 4.0 mm column. Capillary column, 45 m  $\times$  0.25 mm, polyethylene glycol 6000. The standards were used to identify the peaks. Internal standards were used for the quantitative analysis.

\*A. B. Torchinov participated in carrying out the experiment.

The PMR spectra were run on a Perkin-Elmer R-12 (60 MHz), solvent CC14, external standard TMS.

The ionic hydrogenation was carried out by a standard method: a mixture of the hydrocarbon, CF<sub>3</sub>COOH, Et<sub>3</sub>SiH, and the standards necessary for performing the quantitative analysis were maintained at 20°C for a given time. A total of 0.02 to 0.2 g of the hydrocarbon was introduced into the experiment (if the reaction products were not to be isolated) or 2-5 g of the hydrocarbon (if the hydrogenation products were to be isolated). The ratios of the reagents and experimental results are given in Table 1. During the hydrogenation of compounds (I) and (VI) in the presence of a catalyst, a solution of BF<sub>3</sub>·OEt<sub>2</sub> in CF<sub>3</sub>COOH was added to the mixture of hydrocarbon, silane, and the standard. In order to isolate the hydrogenation reaction products, the reaction mixture was poured into water, neutralized with a NaHCO<sub>3</sub> solution, washed with ether, and the organic layer was dried with MgSO<sub>4</sub>. The solvent was distilled off, and the remainder was fractionally distilled. Hydrocarbon (XIV) had a bp of 127°C (760 mm),  $n_D^{2^\circ}$  1.4548; (XXI) had a bp of 151°C (750 mm),  $n_D^{2^\circ}$  1.4562.

The structure of trifluoroacetate (XIII) was established by converting it to the corresponding alcohol. The latter was identified by comparing it with a standard by GLC. The determination of the products of the reaction between diene (III) and CF<sub>3</sub>COOH and Et<sub>3</sub>SiH was carried out by GLC on the corresponding acetates obtained by the addition of CH<sub>3</sub>COOH to diene (III). In order to convert the trifluoroacetates to the acetates, the reaction mixture was neutralized with a NaHCO<sub>3</sub> solution, and boiled with an alcoholic alkali solution. Then toluene was added to the mixture, the organic layer was separated, washed with water, and boiled with glacial CH<sub>3</sub>COOH in the presence of catalytic amounts of  $p-CH_3C_6H_4SO_3H$ . The mixture was washed with water, a sodium carbonate solution, dried with MgSO<sub>4</sub>, and analyzed by GLC.

## CONCLUSIONS

The ionic hydrogenation of unsaturated compounds of the bicyclo[2.2.1]heptane series proceeds more easily than for the unsaturated compounds of the cyclohexane series with a related structure.

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