MASS SPECTROMETRIC INVESTIGATION AND SYNTHESIS OF HYDROCARBONS OF THE BICYCLO[2.2.1]HEPTANE SERIES WITH THE COMPOSITIONS C₁₀H₁₈ AND C₁₁H₂₀

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In a continuation of research on the behavior of hydrocarbons of the bicyclo[2.2.1]heptane series under the influence of electron impact [1], in the present communication we are examining the features of mass spectral decomposition of tri- and tetramethylbicyclo[2.2.1]heptanes (I)-(XII).

The structure of these hydrocarbons is shown below in schematic form. The hydrocarbons (V), (IX), and (X) were synthesized by the procedures given below. The other structures were obtained by methylenation [2].



 $\begin{aligned} &R^1 = R^3 = R^6 = Me \ (I); \quad R^1 = R^2 = R^6 = Me \ (II); \quad R^1 = R^6 = R^{12}(R^{11}) = Me \ (III); \\ &R^1 = Me, \ R^6 = Et \ (IV); \quad R^1 = R^{11} = R^{12} = Me \ (V); \quad R^1 = R^6 = R^{11} = R^{12} = Me \ (VI); \\ &R^1 = R^5 = R^{11} = R^{12} = Me \ (VII); \quad R^1 = R^4 = R^{11} = R^{12} = Me \ (VIII); \quad R^1 = R^3 = R^{11} = R^{12} = Me \ (III); \\ &R^1 = R^1 = Me \ (IX); \quad R^1 = R^2 = R^{11} = R^{12} = Me \ (X); \quad R^1 = R^{11} = Me, \quad R^{12} = Et \ (XI); \\ &R^{11} = R^{12} = Me, \quad R^1 = Et \ (XII). \end{aligned}$

EXPERIMENTAL

1,7,7-Trimethylbicyclo[2.2.1]heptane (V) was obtained by the reduction of 1,7,7-trimethylbicyclo[2.2.1]heptanone-2 (camphor) by the Wolff-Kishner method; yield 80%, mp 147°C. The compounds endo- and exo-1,2, 7,7-tetramethylbicyclo[2.2.1]heptane (IX) and (X) were obtained by the Grignard reaction from 1,7,7-trimethylbicyclo[2.2.1]heptanone-2 with subsequent dehydration of the tertiary alcohol on Al_2O_3 and hydrogenation of the unsaturated hydrocarbon on Raney nickel at 100°C and a hydrogen pressure of 60 kgf/cm². The hydrocarbon that was obtained was a mixture of endo and exo isomers in a 17/83 ratio. The exo isomer was isolated by preparative gas-liquid chromatography, mp - 92°C.*

The 1,2,4-trimethyl-, 1,4,7-trimethyl-, and 1-methyl-4-ethylbicyclo[2.2.1]heptanes (I)-(IV) were obtained by methylenation of 1,4-dimethylbicyclo[2.2.1]heptane, and the 1,4,7,7-, 1,2,7,7-, and 1,3,7,7-tetramethylbicyclo[2.2.1]heptanes, the 1,7-dimethyl-7-ethylbicyclo[2.2.1]heptane, and the 7,7-dimethyl-1-ethylbicyclo[2.2.1]heptane (VI)-(XII) were obtained by methylenation of 1,7,7-trimethylbicyclo[2,2,1]heptane (V).

The composition of the products from methylenation was deciphered by chromatographic matching with individual samples of the hydrocarbons, and also by isomerization of the methylenated products in the presence of Pt/C at 300°C under hydrogen pressure, so that the configuration could be determined from the isomers of the 1,2,4-trimethyl- and 1,3,7,7-tetramethylbicyclo[2.2.1]heptane. The assignment of configuration for the isomers of the 1,2,7,7-tetramethylbicyclo[2.2.1]heptane was based on the equilibrium characteristics of the isomers obtained under analogous conditions. The structures (III), (XI), and (XII) were assigned on the basis of the statistical distribution rule in methylenation reactions. The order of elution of the hydrocarbons and the composition of the methylenated products are shown in Fig. 1. The equilibrium compositions of the isomers

* As in Russian original – Translator.

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Fig. 1. Chromatograms of products from methylenation of 1,4-dimethylbicyclo[2.2.1]heptane (a) and 1,7,7-trimethylbicyclo[2.2.1]heptane (b): (I) endo-1,2,4-trimethyl-; (II) exo-1,2,4-trimethyl-; (III) 1,4,7-trimethyl-; (IV) 1methyl-4-ethyl-; (V) 1,7,7-trimethyl-; (VI) 1,4,7,7-tetramethyl-; (VI) endo-1,3,7,7-tetramethyl-; (VIII) exo-1,3, 7,7-tetramethyl-; (IX) endo-1,2,7,7-tetramethyl-; (X) exo-1,2,7,7-tetramethyl-; (XI) 1,7-dimethyl-7-ethyl-; (XII) 1-ethyl-7,7-dimethylbicyclo[2.2.1]heptane.

TABLE 1. Equilibrium Concentrations of Steroisomeric Tri- and Tetramethylbicyclo[2.2.1]heptanes at 300°C, Pt/C

Hydrocarbon	Equilibrium concentration, %
1,2,4-Trimethyl-endo (I)	51
» exo (II)	49
1,2,7,7-Tetramethyl-endo(IX)	87
» exo(X)	13
1,3,7,7-Tetramethyl-endo(VII)	76
» exo(VIII)	24

of the 1,2,4-trimethyl- and the 1,2,7,7- and 1,3,7,7-tetramethylbicyclo[2.2.1]heptanes (I), (II) and (VII)-(X) are listed in Table 1. Here, in the case of hydrocarbons with geminal CH_3 groups at the C^7 , contrary to the situation for the 2-alkyl- or 1,3-dialkylbicyclo[2.2.1]heptanes [3], of the two stereoisomers, the most stable are the endo(VII) and the endo (IX).

It is interesting to note that the 1,2,7,7-tetramethylbicyclo[2.2.1]heptane is a convenient model for determining the magnitude of the interaction of exo and syn CH₃ in the C² and C⁷ positions, respectively. As a consequence of the equality between the sums of the interactions in exo- and endo-1,2-dimethylbicyclo[2.2.1]heptanes ($\Delta E = H \approx 0$), the energy of conversion of exo-1,2,7,7-into endo-1,2,7,7-tetramethylbicyclo[2.2.1]heptane represents the sought quantity, 2.2 kcal/mole. This interaction, which appears in 1,2,7,7- and 1,3, 7,7-tetramethylbicyclo[2.2.1]heptanes and is absent in cis- and trans-1,3-dimethylcyclopentanes, is evidence of severe deformation of the bond angles in the five-membered rings making up the structure of the bicyclic molecule.

Chromatographic mass spectrometric studies of the synthesized hydrocarbons was performed in an LKB-2091 instrument (Sweden) with an ionizing electron energy of 70 eV and an ionization chamber temperature of 250°C. The peak intensities (Table 2) are expressed as percentages of the total ion flux. The separation of these hydrocarbons was performed in a capillary column with a length of 50 m with squalane as the stationary phase and helium as the carrier gas; the column temperature was $90-100^{\circ}$ C, and the pressure of the carrier gas at the inlet was 1.2 kgf/cm^2 gauge.

DISCUSSION OF RESULTS

The basic relationships in the decomposition of molecular ions (MI) under electron impact that were noted for the monosubstituted and disubstituted bicyclo[2.2.1]heptanes [1] remain the same for the trialkyl and tetraalkyl derivatives that we have examined (Table 2). As shown in [1], the bicyclo[2.2.1]heptane is characterized by the presence of several isomeric MI forms: Bicyclic M_1 and monocyclic M_2 and M_3 (Scheme 1). The predominance of one form or another, which determines the subsequent path of MI decomposition, is governed by the type of substituent and by the number and relative location of the substituents. TABLE 2. Relative Intensities for Characteristic Ion Peaks in Mass Spectra of Bicyclo[2.2.1]heptanes with Compositions $C_{10}H_{18}$ and $C_{11}H_{20}$

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C10H18	138 M	123 [M-15]+	110 [M-28]+	109 [M-29]+	96 [M-42]+	$\begin{bmatrix} 95\\ [M-43] + \end{bmatrix}$	82 [M-56]+	[M-57]+	68 [M-70]+	67 [M-71]+		
ΞĒ	4,3	4,0 3,9	1,9	10,7 12,2	$^{3,2}_{3,0}$	28,5 25,6	5,0 4,2	6'9 6'9	50 750 757	5,7 5,5		1,1 1,2
	4,4 4,8	3,0 2,8	7,0 3,3	17,9 36,3	2,4 0,9	15,0 1,6	3,9 3,9	4,2 7,3	7,8 3,1	5,9 8,2		1,5
ŝ	6,2	6,4	1,0	1,5	4,0	22,7	4,6	6,7	4,1	5,7		1,0
C ₁₁ H ₁₈	152 M	137 [M-15]+	$^{123}_{[M-29]+}$	110 [M-42]+*	109 [M-43]+	96 [M-56]+*	95 [M-57]+	82 [M-70]+*	81 [M-71]+	68 [M-84]+	67 [M-85]+	
(IV)	1,7	2,7	1,0	2,4	26,0	5,3	4,3	2,2	4,6	5,4	4,4	0,6
EXX EXX EXX EXX EXX EXX EXX EXX EXX EXX	4.6 4.6 4.6 4.0	0,4 0, 0,0 2 2	1,1 0,6 13,1	3,3 0,8 0,7 8	16,4 17,5 4,0 4,0	800°	8,1 14,4 15,3	41,4 35,5 4,4	₩ ₩ ₩ ₩ ₩ ₩ ₩ ₩ ₩ ₩ ₩ ₩ ₩ ₩ ₩ ₩ ₩ ₩ ₩	2,000 3,1,00 3,300	4.0.0 4.2 2,2 2,2 2,2	0,0,0 9,2,8,8 9,2,8
(XII)	6,1	2,9	4,9	2,1	12,3	2,9	11,8		6,1	1,6	11,0	2,1

241

The presence of a substituent in (I)-(XII) at the bridgehead also determines the main direction of decomposition of these MIs, i.e., rupture of bonds at the quaternary C atom. The stability of the MIs of these compounds is approximately equal to that of the MIs of mono- and dialkylbicyclo[2.2.1]heptanes with a bridgehead substituent. An exception is the 1,4,7,7-tetramethylbicyclo[2.2.1]heptane, for which the MI stability is very low, possibly because of the high level of stress in the system, unusual for diangular structures (eight butane interactions) and the features of structure of its MI. In contrast to the 1,7-, 1,4-, 1,7,7-, and 1,4,7-substituted compounds, the M₂ form of (VI) is formed by rupture of both C^1-C^7 and C^4-C^7 bonds and contains the geminal grouping $1-CH_3 - 1-i-C_3H_7$. This tends to give very easy removal of the \dot{C}_3H_7 radical from the M₂, and thus reduces the stability of this ion. For all of the mono-, di-, tri-, and tetraalkylbicyclo[2.2.1]heptanes that were studied, the ratio I_M/I_{M-15} depends not on the number of CH_3 groups, but only on their spatial arrangement in the molecule.

The mass spectrum of (IV) is similar to those of the 1-alkyl- and 1,4-dialkylbicyclo[2.2.1]heptanes that were examined in [1]. The spectrum of (IV) is characterized by a very marked predominance of the peak for the ion $[M-C_2H_5]^+$ with m/e 109, which is related to preferential ionization of the bonds at the quaternary C atom. The high intensity of the $[M-C_2H_5]^+$ ion peak in comparison with the intensity of this peak for 1,4-dimethylbicyclo[2.2.1]heptane is explained by the presence of two paths for the formation of this ion in the case of (IV), i.e., elimination of a C_2H_5 radical and detachment of the bridge part of the molecule in the form of C_2H_5 .

The spectra of (I) and (II) are similar to those of the stereoisomers of 2-methyl- and 1,2-dimethylbicyclo-[2.2.1]heptane [1]. The maximum-intensity peaks in these spectra are those of a C_7H_{13} ion with m/e 95, formed by elimination of a substituted ethylene bridge from the MI in the form of a C_3H_7 radical. The presence of two angular CH₃ groups leads to an increase in the intensity of the $[M-C_2H_5]^+$ ion peak that is formed by elimination of the unsubstituted ethylene bridge. The spectra of the endo compound (I) and the exo compound (II) are similar, and this correlates with the small differences in their thermodynamic stabilities.

For the compounds (III), (V)-(VII), (IX), and (X), which have a substituent on the C^7 , the main direction of MI decomposition is rupture of the $C^1 - C^7$ bond, leading to the rearranged form M_2 (see Scheme 1) [1]. Removal of the C^7 atom with its substituent groups from the M_2 leads to the appearance of a peak for the type **b** ion that is the maximum peak for (III), (V)-(VII), (IX), and (X).



In accordance with the proposed scheme, the intensity of odd-electron ions of type **a** increases in comparison with the norbornanes that do not have a substituent on the C^{7} . This ion has m/e 68 if the diene that is formed contains one CH₃ group, and is shifted to m/e 82 if the diene contains one C₂H₅ group or two CH₃ groups.

For the spectra of (V) and (VI), containing respectively two and three neighboring quaternary C atoms, similar to the spectra of bicyclanes with a bridgehead substituent, a characteristic feature is the considerable predominance of one peak, i.e., the type b peak. A feature of the spectrum of (VI) is the predominance of the peak of the odd-electron ion in the groups of ions with five and seven C atoms (m/e 68 and 96, ions of types a and e, respectively) (Scheme 1).

In contrast to the spectra described above, the mass spectrum of compound (III), which does not have any neighboring quaternary carbon atoms, contains, along with the maximum peak of the $[M-C_2H_5]^+$ ion^{*} a peak of

* The $[M-C_2H_5]^+$ ion is formed by two paths: by elimination of the ethylene bridge from the MI in the form of a C_2H_5 radical and by removal of the C^7 atom with an CH₃ group from M₂.

TABLE 3. Characteristic Indicators in Mass Spectra of Bicyclo[2.2.1]heptanes with Compositions $C_{10}H_{18}$ and $C_{11}H_{20}$

Compound	Maximum peak, m/e	Characteristic indicators of bi- cyclo[2, 2, 1]heptanes with compo- sition $C_{10}H_{18}$ and $C_{11}H_{20}$
****		$C_{10}H_{18}$
(I), (II)	95	1108>1M
(III)	109	$I_{109} \approx I_{95}$. High intensity of odd electron ions (m/e 68 and 110)
(IV)	109	$I_{109} \gg I$ of other fragment ions
(V)	95	I109 <im< td=""></im<>
		C11H20
(VI)	109	$I_{109} \gg I$ of other fragment ions
(VII)	109	I ₈₂ >I ₈₁
(IX)	109	$I_{109} \approx I_{95} \approx I_{82}$. I_{82} is 2.5 times that
(X)	82	$I_{109} \approx I_{95} \approx I_{82}$
(XI)	95	$I_{95} \approx I_{123}$
(XII)	109	$I_{109} \approx I_{95} \approx I_{67}$

similar intensity for a type d ion (C_7H_{11} , m/e 95). The existence of two paths for the formation of this ion is confirmed by the corresponding metastable transitions ($123 \rightarrow 95$, *73.4; $110 \rightarrow 95$, *82.1). The favorability of C_7H_{11} ion formation is related to the ease of bond rupture at the quaternary C atoms.

The intensity of the peak for the odd-electron ion C_8H_{14} (m/e 110, type c ion) is approximately equal to that of the peak of the other primary odd-electron ion C_5H_8 (m/e 68, type a ion). The formation of these ions proceeds along two parallel paths from the MI and M_2 (Scheme 1). In both cases, interactions between the C^7 CH_3 and the exo-hydrogens on the C^2 are eliminated, and this explains the favorability of these decomposition paths.

The spectra of the structural isomers (XI) and (XII) are considerably different; this is well explained by the difference in structure between the form M_2 and the molecular ions (Scheme 2). Thus, decomposition of the form M_2 with the formation of a maximum ion of type **b**, in the case of the isomers (XI) and (XII), leads to the appearance of ions with respective m/e 95 and 109 in their mass spectra. It should be noticed that, in contrast to (XI), the ion with m/e 95 in the case of (XII) is apparently formed solely as a result of two-step decomposition (Scheme 2). Also, the spectra of these norbornanes differ in the intensity of the peaks for the $[M-C_2H_5]^+$ ions (m/e 123) and $[M-CH_3]^+$ (m/e 137). The existence of a double bond in the M_2 form in the vinyl position with respect to the C_2H_5 group in the case of (XII) hinders its removal, and the intensity of the peak with m/e 123 is low in comparison with its intensity in the spectrum of (XI), for which removal of the $\dot{C}_{2}H_5$ radical proceeds from the i- C_4H_9 substituent. Thus, removal of a \dot{C}_2H_5 radical from the quaternary C^7 atom proceeds to a greater degree than from the C^1 at the bridgehead. The elimination of the CH₃ group is more favorable in the case of (XII). For the formation of the $[M-CH_3]^+$ ion from the form M_2 of this hydrocarbon, there are three possibilities, one of which is initiated by the presence of the allyl bond. In the case of (XI), only two CH₃ groups can be the main participants in formation of the $[M-CH_3]^+$ ion. The presence of a double bond in the vinyl position relative to one of these groups does not favor the occurrence of this process.



Scheme 2

The stability of the MIs of the stereoisomers (IX) and (X) correlates with their thermodynamic stability. We were not able to achieve a clean separation of the stereoisomers of 1,3,7,7-tetramethylbicyclo[2.2.1]hep-tane, and hence we will not discuss the mass spectrum of the exo-(VIII). We were able to obtain the spectrum of the endo-(VII), since it is the main component in the equilibrium mixture of the stereoisomers.

The introduction of a CH_3 group on the C^2 (IX) and (X) or C^3 (VII) affects primarily the intensity of the peak for the C_6H_{10} ion with m/e 82. For these hydrocarbons, this ion can be formed both directly from M_2 (type **a** ion) and from M_1 (type **e** ion). The appearance of a substituent at C^2 (or C^3) favors rupture of the $C^1 - C^2$ bond (or $C^3 - C^4$) and the formation of the ion $[M - C_3H_6]^{+*}$, the subsequent decomposition of which with elimination of **a** C_2H_4 molecule leads to an ion with m/e 82. Hence, even though the process of formation of the type **b** ion is still the main process, and the peak of this ion is maximum in the spectra of the isomers (VII) and (IX), we also observe an intense peak of a C_6H_{10} ion, which becomes the maximum peak in the spectrum of the most sterically hindered hydrocarbon (X). This is the only spectrum among those examined for the 7-substituted norbornanes in which the peak of the type **b** ion is not maximum.

The presence of a CH₃ group on C^2 or C^3 leads to the appearance of an intense peak for a C_7H_{11} ion with m/e 95. In the case of (VI), which does not have any such substituents, the peak of this ion is much less intense. The metastable transition (110 \rightarrow 95, *82.1), as well as the low intensity of this peak in the low-voltage spectrum (12 eV), indicates that it is secondary in character.

Thus, from the features observed in the mass spectra of structural isomers of the compositions $C_{10}H_{18}$ and $C_{11}H_{20}$, these isomers can be identified quite reliably (Table 3).

CONCLUSIONS

1. 1,7,7-Trimethyl- and 1,2,7,7-tetramethylbicyclo[2.2.1]heptanes have been synthesized. The stereochemistry and equilibrium ratios of the stereoisomers have been investigated.

2. The mass spectra of bicyclo[2.2.1]heptanes with the compositions $C_{10}H_{18}$ and $C_{11}H_{20}$ have been studied and analyzed. The features of the spectra for the structural isomers offer the possibility of identifying these isomers quite reliably.

3. The mass spectra of the stereoisomers show differences if their relative thermodynamic stabilities differ by a factor of more than 2.

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