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Mass Spectrometry of Saturated Hydrocarbons

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The decomposition by electron impact of saturated acyclic and cyclic (mono-, bi-, tri-, tetra-, penta-, and hexa-cyclic) hydrocarbons having condensed, bridged, and single-bonded structures is examined and the reaction mechanisms, the characteristics of the decomposition due to structural and stereochemical factors, and the possibilities for the identification of the hydrocarbons by analysing their mass spectra are discussed.
The bibliography includes 204 references.

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I. INTRODUCTION

The basis on which mass spectrometry has been established as an analytical method has been its successful application in qualitative and quantitative analyses of hydrocarbon mixtures, in particular, petroleum and its processing products as well as the products of the petrochemical and organic synthesis. The subsequent stage in the development of this method was determined by the combined employment of highly effective procedures for the separation of mixtures and the automation of the interpretation of the mass spectrum which led to the development of fundamentally new mass-spectrometric analytical methods.

Chromato-mass-spectrometry has become irreplaceable in the analysis of hydrocarbons and their mixtures by virtue of the large amount of information derivable by this procedure, its sensitivity, and the speed and accuracy of the determinations. The advances in this field are based on the systematic study of the characteristics of the mass-spectrometric decomposition of individual hydrocarbons. In contrast to compounds with functional groups, where the heteroatom is generally the site of the preferential localisation of charge and hence determines which particular bond is ruptured preferentially, for a hydrocarbon molecule it is difficult to isolate such a decisive factor, i.e. it is difficult to interpolate the mass spectrum even within the limits of a narrow group of compounds. The low predictive power of the mass spectra of hydrocarbons (with the exception of n-alkanes), where the appearance of even one non-bonding interaction can lead to significant changes in the spectrum, the large number of isomeric and stereoisomeric structures, the monotonic variation of their mass spectra, and the associated difficulty of the computer search in their identification necessitate a detailed investigation and periodic systematic treatment of the mass spectra of hydrocarbons as well as the analysis and survey of the information in this field, which is constantly being renewed and expanded.

The review below is devoted to the characteristic features of the decomposition of saturated hydrocarbons under electron impact.

II. ALKANES

Alkanes constitute a large proportion of petroleum and their mass spectra have been described in the greatest detail.[1-7] The spectra of unbranched normal alkanes are very similar. The curve for the distribution of the peak intensities in their spectra (Fig.1) decreases smoothly from a maximum in the region of mass numbers of 43, 57, and 71 to the peak of the molecular ion (MI). The appearance of a maximum at any position on this curve implies the presence of a branch in the alkane molecule (Fig.2). The above features of the mass spectra of normal alkanes and alkanes substituted at different sites (including isoprenoid alkanes) are used for analytical purposes[8-13] although the information obtained from the consideration of the mass spectrum is insufficiently specific for the complete identification of any alkane.

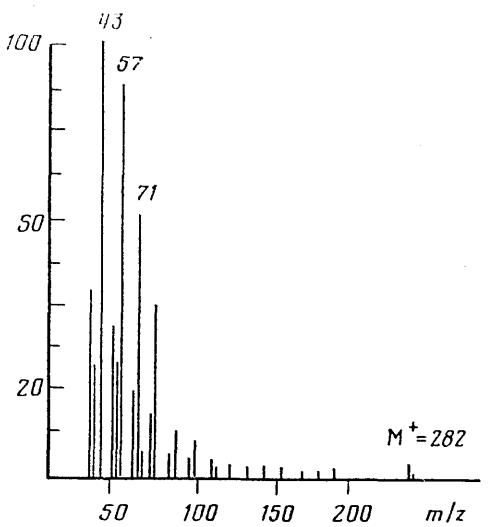


Figure 1. The mass spectrum of n-eicosane.[41]

The intensity of the MI peaks of n-alkanes is low and decreases exponentially with increased molecular weight of the alkane.[14] The intensities of the MI peaks of branched alkanes depend on the number and relative positions of the methyl groups and decrease with increase in the degree of branching.[1,8,14]

A whole series of communications (among them also reviews),[9,15-29] including the analysis of the mass spectra of n-alkanes labelled with ^2H [15,17-19] and ^{13}C,[20-23] thermochemical data for the molecular and fragment ions,[24,25] low-temperature spectra,[29] ionisation efficiency curves,[5] reactions occurring on collision with a gas molecule,[16,23] etc. have been devoted to the structure and mechanism of the decomposition of molecular and fragment ions derived from n-alkanes. This analysis permitted the conclusion that the reactive configuration of the MI retains to a large extent the structure of the neutral molecule, while fragment ions decompose via complex skeletal rearrangements, which accounts for the observed loss of identity of the peaks of labelled ions in a series of mass spectra of lower n-alkanes.[15]

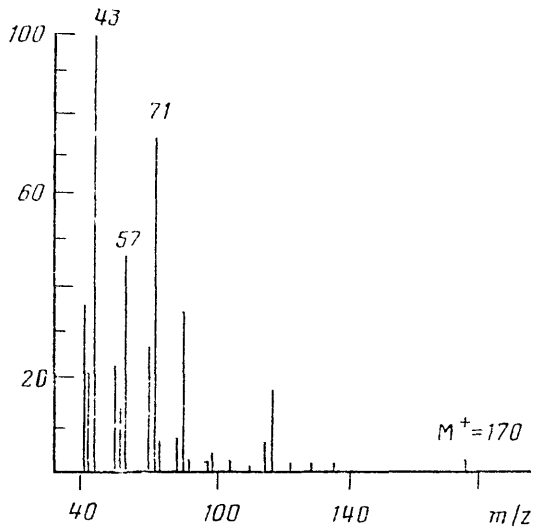
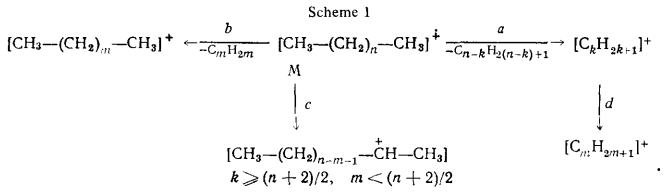


Figure 2. The mass spectrum of 4,7-dimethyldecane.[2]

The alkyl ions C_kH_{2k+1} are formed with the highest probability by simple rupture of the C–C bonds in the MI (Scheme 1, pathway *a*). This process is most favoured in the formation of large ions [$k \geq (n+2)/2$].[9,15,20]

Scheme 1



The study of the mass spectra of a large series of n-alkanes showed that there is a relation between the intensity of the peak of the alkyl ion C_kH_{2k+1} and the number of carbon atoms in the molecule (n) and fragment (k) ions.[9,15] The study of metastable transitions and ionisation efficiency curves[5] and comparison of the low-temperature mass spectra obtained for high (70 eV) and low ionisation energies[29] have shown that small alkyl ions are formed mainly via secondary processes, i.e. as a result of the decomposition of heavier primary alkyl ions (Scheme 1, pathway *d*). The few ions which are formed directly from the MI are produced from its central component (Scheme 1, pathways *b* and *c*) in the non-specific dissociation of the C–C bonds with recombination of the terminal methyl groups.[15,20] The contribution of this pathway increases with increasing chain length.

The probability of the loss of the methyl group is low and diminishes with increase in the n-alkane chain length.[22] The elimination of the CH_3 group proceeds to a large extent non-specifically: the formation of $[M-CH_3]^+$ is associated with the elimination of both terminal carbon atoms (pathway *a*) and the carbon atoms in the central component of the molecule (pathway *c*).[22] The formation of ions with an odd number of electrons is associated with the rearrangement of H atoms[28] or CH_3 groups.[18]

III. MONOCYCLIC SATURATED HYDROCARBONS

1. Unsubstituted Monocyclic Hydrocarbons

The mass spectra of unsubstituted monocyclic hydrocarbons having the general formula  are known for compounds with n = 3–14 and 24.[2,30-41] The character of the variation of the MI peak intensities in the series of C_3–C_{14} cycloalkanes is described by a curve[30] having maxima in the region of n = 3, 6, and 13 and a distinct minimum in the region of n = 9 and 10. The molecular ion of cyclopropane is the most stable in the series of cycloalkanes and its intensity is a maximum in the spectrum. A distinctive feature of this spectrum is the presence of a peak due to the ion $[M-3H]^+$,[2,32] whose high intensity can be explained by the aromatic character of the cyclopropenyl cation $[C_3H_3]^+$ formed.[33]

The study of the mechanisms of the fragmentation of cycloalkanes with the aid of deuterated analogues,[34,35] the measurement of the ionisation potentials and the heats of formation of their molecular ions,[36,37] and the study of the kinetics of the isomerisation of the MI [38,39] showed that, under the conditions of electron impact, the MI of cycloalkanes with three–five-membered rings undergo intensive isomerisation to linear ions, while the MI of hydrocarbons with six–eight-membered rings mainly retain the cyclic structure.

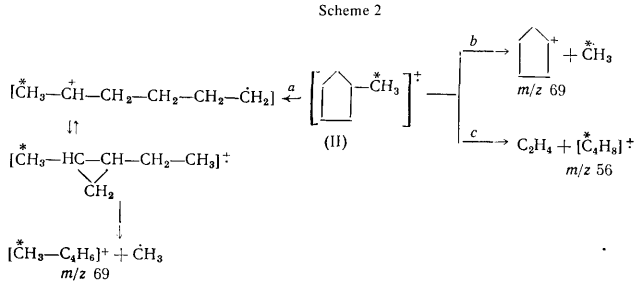
Despite the different structures of the MI of hydrocarbons with different ring sizes, the mass spectra of compounds with four–eight-membered rings are in many respects similar. They are characterised by the intense peak of the ion $[M-CH_3]^+$ and the peak for one of the odd-electron ions (m/z 56, 70, etc.) is the most intense in their spectra.[2,30,40] An increase of ring size alters appreciably the pattern in the decomposition of the MI and the character of the spectrum of the hydrocarbon containing more than eight carbon atoms in the molecule becomes similar to that of the spectrum of the corresponding alkane: the stability of the MI is low and the peaks of the even-electron ions (m/z 57, 71, etc.) predominate in the spectrum.[2,30,31] The high intensity of the MI peak in the spectrum of cyclotetracosane should be noted as an exception.[41]

2. Monosubstituted Monocyclic Hydrocarbons

The introduction of the methyl substituent into the cycloalkane molecule does not eliminate the differences noted between the structures of the molecular ions of unsubstituted

hydrocarbons. It has been suggested[40,42–44] that the ionisation of the MI of methylcyclopropane (I) and methylcyclopentane (II) entails the rupture of the endocyclic bond adjoining the methyl group and that, after the migration of the proton, an alkene ion with a straight-chain structure is formed [the n-butene ion for (I) and the n-hexane ion for (II)]. For methylcyclopropane, this conclusion has been confirmed by the identity of the spectra of compound (I) and its acyclic isomers.[42] Analysis of the spectra of methylcyclopentane and methylcyclohexane (III) analogues deuterated in all positions and labelled with ^{13}C permitted a detailed study of all the possible pathways leading to the formation of the fragment ions (Scheme 2; the ^{13}C isotope is marked with an asterisk) and also an estimate of the contribution of each pathway to the overall peak intensity of the ion having the given mass.[43–46]

Scheme 2

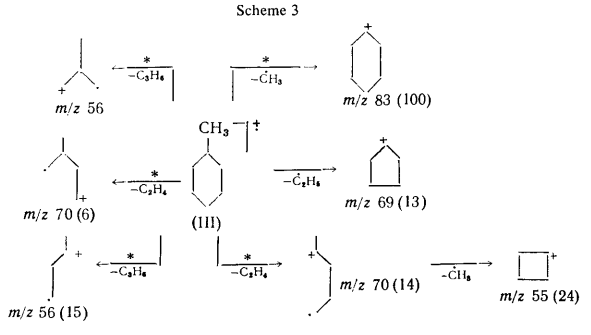


The data obtained for compound (II) show that the molecular ion decomposes with a higher probability via pathway *a*.[43–44]

Another intense process involving the decomposition of the molecule of compound (II) is the elimination of ethylene from the MI. The study of the mass spectra of the deuterated analogue of compound (II) showed[45] that the C_2H_4 molecule is ejected mainly from the cyclic component of the MI (Scheme 2, pathway *c*).

In methylcyclohexane, whose MI retains mainly the cyclic structure, the elimination of the methyl group takes place only from the side chain.[45] Scheme 3† presented below, constitutes the generalised result of a study which showed[46] that more than 90% of the primary fragment ions are formed on dissociation of the C–C bond at the tertiary carbon atom of the MI (the relative peak intensities expressed as percentages are indicated in brackets):

Scheme 3



The ratios $I_{[M]^+}/I_{[M-CH_3]^+} < 1$ have been obtained for methylcycloheptane and methylcyclo-octane, as for compound (II) and (III). On further increase of ring size, the $[M-CH_3]^+$ peak diminishes and is not observed at all in the spectra of methylcyclodecane, methylcyclododecane, and methylcyclotetracosane.[2,41]

The existence of the isomeric linear form of the MI has also been noted for ethyl and propyl derivatives of cyclopropane and cyclopentane,[45–47] although it has been shown for ethylcyclopentane[45] that the weakening of the bond between the ring and the substituent results in an equal probability of the two processes involving the abstraction of the substituent from the MI (pathways *a* and *b* in Scheme 2). The intensity of the MI peak in the spectra of monoalkylcyclopentanes [Alk = n-Pr, n-Bu, t-Bu, n-C_3H_{11}, iso-C_5H_{11}, n-$C_{16}H_{33}$, or $CH(C_9H_{19})_2$] and cyclohexanes (Alk = C_2H_5–$C_{10}H_{21}$, iso-Pr, s-Bu, iso-Bu, or t-Bu)[48] varies appreciably as a function of the length and structure of the substituting group.[48,49] The most intense peak in the spectra of monoalkylmonocyclanes is that of the ion $[M-R]^+$. The intense peak of the ion $[M-RH]^+$ accompanies it. This pair of peaks (*m/z* 83, 82 for alkylcyclohexanes and *m/z* 69, 68 for alkylcyclopentanes) is used for the qualitative and quantitative analyses of these two types of hydrocarbons in mixtures.[50–55] There are also literature data on the mass spectra of alkylcyclohexanes and alkylcyclopentanes obtained using different energies of ionising electrons.[50,51,56]

3. Polysubstituted Monocyclic Hydrocarbons

Among polysubstituted monocyclanes, alkylcyclopentanes (ACP) and alkylcyclohexanes (ACH) have been studied in greatest detail. Analysis of the mass spectra of the structural and geometrical isomers revealed the influence of ring size and the number, nature, and relative disposition of the substituents in the molecule on the mechanism of the decomposition of the MI.[57–68]

An increase of the number of methyl groups in the methylcycloalkane molecule as a rule decreases the peak for the ion $[M-CH_3]^+$ and increases the intensity of the peaks due to the ions formed on decomposition of the ring, but has little influence on the stability of the MI[68] (Table 1). The appearance in the molecule of a more stable group R entails a decrease of the intensity of the MI peak and an increase of the intensity of the peak due to the ion $[M-R]^+$.

Table 1. The peak intensities of the ions M^+ and $[M-R]^+$ in the mass spectra of alkylcyclopentanes (ACP) and alkylcyclohexanes (ACH).[68]

N	$I_{[M]^+}$		$I_{[M-CH_3]^+}$		$I_{[M-C_2H_5]^+}$	
	ACP	ACH	ACP	ACH	ACP	ACH
1	3.0–0	9.2–0.3	9.5	22.5	16.2	27.3
2	3.7–0.6	6.3–0.3	4.7–2.5	26.8–13.1	18.2–13.0	31.7–26.6
3	3.1–1.2	6.4–1.1	2.6–0.9	24.0–3.5	11.8–2.4	24.5–14.0
4	2.3–0.1	5.4–3.4	0.7–0.2	16.8–0.7	8.3–1.3	––
5	3.2–0.6	4.9–2.4	1.5–0.2	9.2–0.5	—	––
6	—	5.8–2.1	—	8.5–0	––	––
gem	2.4–0.1	2.8–0	15.0–3.0	31.6–5.5	—	30.9–18.0

Remarks: R = CH_3 for the methyl-substituted derivatives and R = C_2H_5 for the ethyl and methylethyl-substituted derivatives; *N* is the number of substituents in the molecule. Here and henceforth the peak intensities are quoted as percentages of the total ion current.

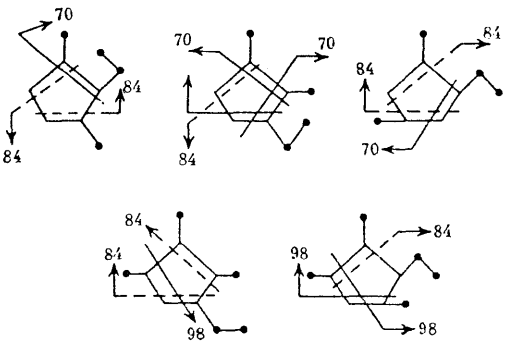
The molecular ions of hydrocarbons of the cyclopentane series, whose molecules contain a ring more strained than in cyclohexanes, decompose via two competing pathways with

†In Scheme 3 and henceforth the asterisk denotes the presence of a peak due to a metastable ion (MSP).

equal probabilities: (1) abstraction of the alkyl substituent R from the molecular ion with subsequent decomposition of the ion $[M-R]^+$ formed; (2) decomposition of the cyclic component of the molecule. The decomposition of the cyclic component leads mainly to the formation of ions with an odd number of electrons (Scheme 2, pathway c).

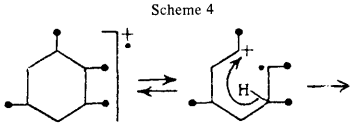
The mass spectra of the structural isomers of dialkylcyclopentanes differ only in the intensities of the peaks due to ionic species M^+ and $[M-RH]^{\ddagger}$, the first peak being more intense in the spectra of 1,2-substituted derivatives and the second in those of the 1,3-substituted derivatives.[49,65]

The differences between the spectra of the structural isomers of tri- [57] and tetra-alkylcyclopentanes[58] are expressed mainly in the different intensities of the peaks for ions with *m/z* 70, 84, 98 formed on decomposition of the cyclic component of the molecule.

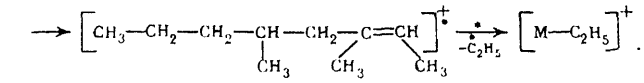


In contrast to alkylcyclopentanes, the decomposition of the cyclic components of the molecules of alkylcyclohexanes occurs only for structures having a vicinal disposition of the methyl groups in the molecule. It involves the formation of both odd-electron ions, for example, $[M-C_2H_4]^{\ddagger}$ and $[M-C_3H_6]^{\ddagger}$, and even-electron ions, for example, $[M-C_2H_5]^+$. The appearance of the latter can be explained by the decomposition of the isomeric linear form of the MI whose formation is initiated by the presence of vicinal substituents.[60,67,68] This also accounts for the appearance of the peak due to the ion $[M-C_2H_5]^+$ in the spectra of hydrocarbons with the MI (IV), which lack an unsubstituted dimethylene unit whose elimination together with the proton might also lead to the formation of the ion $[M-C_2H_5]^+$ (Scheme 4).[60]

Scheme 4



M, (IV)



Additional evidence for the existence of the isomeric form of the MI is provided by the absence of correlation between the stability of the MI and the relative stabilities# in the series of geometrical isomers as well as the presence of such correlation for the primary ions formed in the competing decomposition reactions of the isomeric forms of the MI.[60]

#Here and henceforth thermochemical stability (ΔH) is referred to.

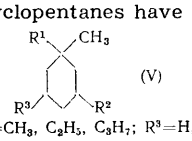
In the series of structural isomers of di-, tri-, and tetramethylcyclohexanes the peak intensities of the ionic species formed on decomposition of the cyclic component of the molecule, namely $[M-C_2H_5]^+$ and $[M-C_3H_6]^{\ddagger}$, increase and the intensity of the ion $[M-CH_3]^+$ formed in a competing process falls as the stability of the isomer diminishes.[60] For the 1,3- and 1,4-dimethyl- and 1,3,5-trimethyl-cyclohexanes, which have no vicinal methyl groups in the molecule, the MI decomposes only via the first pathway. They are characterised by the maximum intensity of the peak due to the ion $[M-CH_3]^+$ in the series of structural isomers.

The quantitative differences between the spectra of the structural isomers of di-, tri-, tetra-methylcyclohexanes, reflecting the contribution of a particular pathway in the decomposition of the MI, make it possible to identify each isomer, with the exception of 1,3-, and 1,4-dimethylcyclohexanes, on the basis of the criteria presented (Table 2).[68]

Table 2. Diagnostic features of the mass spectra of structural isomers of di-, tri-, and tetra-methylcyclohexanes.

Di-	I_{70}/I_{69}	Tri-	I_{84}/I_{83}	I_{97}	Tetra-	I_{84}/I_{97}	I_{98}/I_{97}
1,2-	$\geqslant 1$	1,2,3-	$\leqslant 1$	8,6—2,2	1,2,4,5-	>1	>1
1,3-	$\leqslant 1$	1,2,4-	>1	5,0—1,2	1,2,3,5-	$=1$	$\leqslant 1$
1,4-	$\leqslant 1$	1,3,5-	$\leqslant 1$	0,7—0,5	1,2,3,4-	<1	$\geqslant 1$

For cyclohexanes having a substituent R other than the methyl group, the decomposition of the MI take place mainly in accordance with the first pathway. The differences between the spectra of these structures are associated solely with the intensity of the peaks for the ionic species M^+, $[M-R]^+$, and $[M-RH]^{\ddagger}$ and as a rule have no diagnostic value.[60] However, the position of the group R in the molecules of geminal-substituted cyclohexanes (V) can be readily determined mass-spectrometrically.[2,68] The spectra of geminally substituted cyclopentanes have been little studied.[2]



(V)

R^1, R^2=CH_3, C_2H_5, C_3H_7; R^3=H, CH_3

Systematic study of the mass spectra of monocyclic hydrocarbons has shown no possibility for an unambiguous assignment of the hydrocarbon to the cyclopentane or cyclohexane series solely on the basis of one characteristic feature. However, when the molecule contains at least one methyl substituent, this can be achieved on the basis of a number of features which are proposed in Table 3. The same data permitted conclusions concerning the number *N* of substituents in the ring.

The presence of two and more substituents in the ring implies the possibility of the existence of stereoisomers. Under these conditions, in the case of compounds without heteroatoms, the influence of the steric structure on the decomposition of the molecule can be very considerable and in a number of instances[68] can swamp the effect of structural isomerism. This influence is natural if one takes into account the absence of a site of preferential localisation of the charge in the saturated hydrocarbon molecule—a factor which is as a rule of decisive importance in the decomposition of heteroatomic compounds. Thus only the energy state of the molecules of isomeric hydrocarbons, determined by the

number of non-bonding interactions, determines the mass-spectrometric properties.

The idea of a relation between the relative stabilities of the stereoisomers and the differences between their spectra was put forward by Biemann[69] as early as 1962 and was then developed in a whole series of studies by Natalis and co-workers.[70-74] Subsequently Meyerson[75] related these differences to the thermochemical stabilities, i.e. the enthalpies of the ground states of the ions, which determine the ease of the fragmentation reactions, and not to the thermodynamic stability of the isomer—a factor which is significant for the relative proportions of the isomers under equilibrium conditions. This conclusion is consistent with the ionisation energies (IE) and appearance energies (AE).[71,76]

Table 3. Diagnostic features in the mass spectra of hydrocarbons of the cyclopentane and cyclohexane series and the values of m/z for the peak with maximum intensity.

Cyclopentanes			Cyclohexanes	
N	(m/z)	diagnostic features	(m/z)	diagnostic features
		C_9H_{18} (M=126)		
1	69	intense peaks of ions with m/z 68, 69	83	intense peaks of ions with m/z 82, 83
2	83, 55	intense peaks of ions with m/z 83, 55; $I_{97}<2$	97, 55	intense peaks of ions with m/z 97, 55
3	55, 56, 70	I_{97}=2.4—11.8	69	intense peaks of ions with m/z 69, 111*
4	84, 69, 70, 98	$I_{97}\leqslant 1.5$; $I_{111}<1$	—	—
		$C_{10}H_{20}$ (M=140)		
1	69	intense peaks of ions with m/z 68, 69	83	intense peaks of ions with m/z 82, 83
2	—	—	97, 55	intense peaks of ions with m/z 97, 55; absence of peaks of ions with m/z 70,84
3	97, 55	I_{84}=3.5—3.8; I_{70}=8.7—9.6	69	intense peaks of ions with m/z 69, 111; $I_{97}>I_{98}$; $I_{125}<1$**
4	69, 98	$I_{98}\gg I_{97}$; $I_{125}<1$	69	I_{125}=2.0—12.2
5	84	—	—	—

*The spectrum of 1,2,3-trimethylcyclohexane is an exception, but for this spectrum $I_{83}>I_{84}$, in contrast to the spectra of trialkylcyclopentanes.

**The spectrum of 4-ethyl-1,2-dimethylcyclohexane is an exception. It resembles the spectra of the series of stereoisomers of tetramethylcyclohexane.

Measurements performed with the aid of photoionisation for a series of 1,2-dimethylcyclopentanes and cyclohexanes have shown[71] that the IE of the stereoisomers do not differ, while the AE of the ions $[M-CH_3]^+$ {for dimethylcyclopentanes, also the ions $[M-C_2H_4]^+$, $[M-C_2H_5]^+$, $[M-C_3H_5]^+$, and $[M-C_3H_6]^+$} change by 0.1 eV on passing from the *cis*- to the *trans*-isomer. Within the limits of experimental error, this difference is in each case equal in magnitude (but opposite in sign) to the difference between the heats of formation of the stereoisomer. Somewhat different values but showing the same type of variation as a function of the relative positions of the substituents have been obtained for the stereoisomers of 1,2-dimethylcyclohexane by other methods.[77,78]

The interrelation of the stereochemistry of the molecule and of the characteristic features of its decomposition under electron impact has been traced in detail and systematically for almost all the stereoisomers in the series of polymethylcyclopentanes and polymethylcyclohexanes.[2-5,49,57-68] The character of the variation of the quantitative characteristics of the spectrum remains the same as in the series of structural isomers: the intensity of the peaks due to the ions $[M-R]^+$ is a maximum in the spectrum of the isomer showing the highest thermochemical stability and decreases with decrease of the stability in the series of stereoisomers; there is a simultaneous increase of the intensities of the peaks due to the ions formed on decomposition of the cyclic component of the molecule.

The differences between the quantitative characteristics of the spectra of the stereoisomers are greater the larger the difference between the stabilities of their molecules. In a number of instances these differences are of diagnostic value.[57-60] The spectra of stereoisomers whose stabilities are similar are virtually identical.

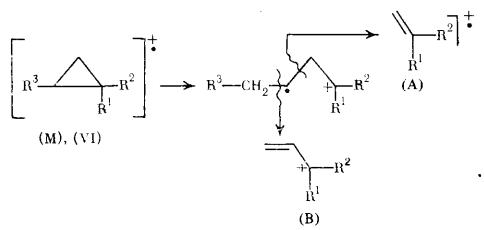
The available information about the decomposition of substituted cycloalkanes C_nH_{2n} (where $n\neq 5$ or 6) under electron impact is limited to data concerning alkylcyclopropanes. In the spectra of geminally (R^1=R^2=CH_3, R^3=H) and vicinally (R^1=R^3=CH_3, R^2=H) substituted dimethylcyclopropanes (VI)[132] the peak for the ion $[M-CH_3]^+$ shows the highest intensity. The absence of appreciable differences between their spectra has been attributed to[32] the pseudo-ethylenic character of the bonds in the cyclopropane ring. This hypothesis is supported by the large number of peaks due to doubly charged ions.[69]

The mass spectra of isomeric cyclopropanes differing in the lengths of the alkyl substituents R^1 and R^2 (i.e. in the position of the cyclopropane ring in the aliphatic chain) also proved to be similar.[79] The absence of differences between the spectra of dialkylcyclopropanes (VI) and the corresponding olefins (there are differences only in the stabilities of the MI) demonstrates the possibility of the isomerisation of the MI compound (VI) to an ion having a linear structure.

A distinctive feature of the spectra of the hydrocarbons (VI) is the presence of intense peaks of the ions formed on dissociation of the C—C bonds in the ring at one of the carbon atoms [ions of types (A) and (B), Scheme 5].

The peaks for the ions (A) and (B) are characterised by having the maximum intensity in the majority of spectra.[79]

Scheme 5



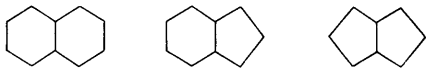
Analysis of the spectra of deuterated analogues of compound (VI) permitted the conclusion that the formation of the ions (A) and (B) involves the ionisation of the most highly substituted cyclopropane bond with localisation of the positive charge on the most substituted carbon atom.[79]

IV. BICYCLIC SATURATED HYDROCARBONS

1. Hydrocarbons with a Condensed Type of Junction between the Rings

(a) Unsubstituted hydrocarbons. In the series of compounds of this type attention has been concentrated on the mass spectra of hydrocarbons consisting of five- and/or six-membered rings belonging to the bicyclo[4.4.0]decane (VII),

bicyclo[4.3.0]nonane (VIII), and bicyclo[3.3.0]octane (IX) series.[2,31,80–86] Data have been published also for the spectra of hydrocarbons with cyclopropane (X) and cyclobutane (XI) rings.[86–93]

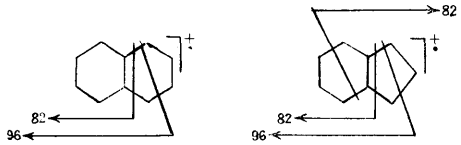


(VII) (VIII) (IX)

The stability of the MI of the bicycloalkanes considered decreases in the sequence (VII) > (VIII) > (IX) in parallel with the increased strain in the molecules.[80–82] In contrast to the spectra of unsubstituted monocyclic hydrocarbons, the intensity of the peak due to the ion $[M-CH_3]^+$ in the spectra of compounds (VII)–(IX) is low. In the case of compounds (VIII) and (IX) the abstraction from the molecular ion of a fragment containing two carbon atoms takes place mainly in the form of the ethylene molecule. This process is not characteristic of compounds (VII). The ratio of the ionic species $[M-C_3H_6]^{+\cdot}$ and $[M-C_3H_7]^+$ is influenced by the number of methylene units in the ring. Thus the presence of only cyclopentane rings in the molecules of compounds (IX) entails the preferential elimination of a three-carbon fragment in the form of the propyl radical; the intensity of the peak for the ion $[M-C_3H_7]^+$ becomes a maximum§, much greater than the intensity of the peak in the ionic species $[M-C_3H_6]^{+\cdot}$. In the case of the hydrocarbon (VII), containing only cyclohexane rings, there is a high probability of the elimination of a propene molecule and the ratio of the intensities of the above peaks changes ($I_{[M-C_3H_6]^{+\cdot}} > I_{[M-C_3H_7]^+}$). On the other hand, for the molecules of compounds (VIII), consisting of five- and six-membered rings, the peaks of the ionic species $[M-C_3H_6]^{+\cdot}$ and $[M-C_3H_7]^+$ (*m/z* 82 and 81 respectively) have similar intensities and their ratio depends on the type of junction between the rings: $I_{82} > I_{81}$ for *trans*-(VIII), while the opposite relation obtains for *cis*-(VIII).

The differences between the thermochemical stabilities of the *cis*- and *trans*-isomers of compounds (VII) and (VIII) [compounds (IX) exist solely as the *cis*-isomers[94]] are clearly reflected in their spectra.[80–84] Thus a much higher intensity of the MI peak and a lower intensity of the peaks due to the primary ions are observed in the spectra of the more stable *trans*-isomers of compounds (VII) and (VIII) compared with the spectra of the *cis*-isomers. With decrease in the energy of the ionising electrons, the above differences become more pronounced.

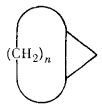
Interesting results have been obtained from the comparison of the IE and AE of the *cis*- and *trans*-isomers. The IE of the molecular ions for the two isomers proved identical but the AE of some of the ions (*m/z* 96, 82) are higher for the *trans*-isomers, while those for other ions (*m/z* 95, 68, 67) are higher for the *cis*-isomers. The AE measured with a high accuracy can be used to determine the differences between the enthalpies of formation of the *cis*- and *trans*-isomers of compounds (VII) and (VIII).[95] The difference between the ΔH of the stereoisomers should then be correlated quantitatively to the differences between the AE of only those ions which are formed from the MI in a single stage as a result of simple bond rupture. From this standpoint, the ions with *m/z* 96 and 82 are of greatest interest:



(VII) (VIII)

The equality of the differences between the AE and ΔH for the stereoisomers of compounds (VII) and (VIII) is observed only for the ion with *m/z* 96. The absence of such clear-cut quantitative correlation for the ion with *m/z* 82 can be associated with the difference between the pathways leading to its formation on decomposition of the stereoisomers, while for other ions it can be associated with the fact that they are in the nature of rearrangements (*m/z* 109, 95, 81) or with the multistage character of their formation (*m/z* 67. 68).[95]

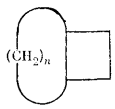
The differences between the spectra of hydrocarbons of type (X) are associated with the size of the polymethylene ring:[87–91]



(X); n = 3-10

The stability of the MI decreases from 11 to 0.5% with increase of the size of this ring from $n = 3$ to $n = 8$ and then increases slightly. The decomposition of the MI of hydrocarbons (X) takes place as a result of the simultaneous occurrence of two processes—the contraction of the polymethylene ring and the opening of the cyclopropane ring.[87] The intensity of the peak due to the ion $[M-CH_3]^+$ is a maximum in the spectrum of bicyclo[3.1.0]hexane and diminishes with increase of the size of the larger ring. Comparision of the spectra of compounds (X) and their halogeno-derivatives suggests[87] that the methyl radical split off from the MI is derived from a methylene unit of the three-membered ring. The peak of the ion $C_5H_7^+$ with *m/z* 67 shows the maximum intensity in the majority of the spectra.

Bicyclo[*n*.2.0]alkanes (XI) are characterised by a low stability of the MI (1.6–0.2%) and, in contrast to bicyclo-[*n*.1.0]alkanes (X), the stability of their MI is independent of the size of the larger ring of the molecule.[92,93]



(XI); n = 2–6

On the other hand, the intensity of the peak due to the ion $[M-CH_3]^+$ diminishes with increase in the size of the above ring. The MI of the bicycloalkanes (XI) decompose with the preferential cleavage of the C–C bonds in the cyclobutane ring, while the intensity of the peak of the radical-ion $[M-C_2H_4]^{+\cdot}$, formed as a result of this process, is a maximum in the majority of the spectra.

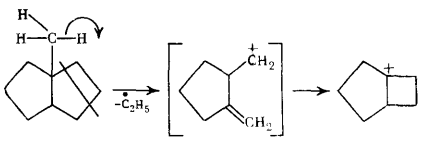
(b) Monosubstituted hydrocarbons. The mass spectra of a large number of structural and geometrical isomers of the methyl derivatives of compounds (VII)–(IX) have been described in the literature.[65,85,86,96,97] It has been observed that the MI of methylbicyclo[4.4.0]decanes (XII) are more resistant to electron impact than the MI of methylbicyclo-[4.3.0]nonanes (XIII) and methylbicyclo[3.3.0]octanes (XIV). In the series of structural isomers of compounds (XIII) and (XIV) the greatest stability of the MI is observed for the

§There is a possibility of a two-stage pathway to the formation of the ion $[M-C_3H_7]^+$—from the radical-ion $[M-C_2H_4]^{+\cdot}$ or the ion $[M-CH_3]^+$.

angular position of the methyl group.[85,86] The spectra of compounds (XII) with angular substituents have not been described.

The introduction of the methyl group into the molecules, of the unsubstituted hydrocarbons (VII)–(IX) does not entail significant changes in the intensity of the MI peak. The intensity of the peak of the ion $[M-CH_3]^+$ in the spectra of compounds (XII)–(XIV) is higher compared with that observed in the spectra of compounds (VII)–(IX), the only exception being 7-methylbicyclo[4.3.0]nonane. The intensity of the $[M-CH_3]^+$ peak then changes markedly as a function of both the position of the substituent and the stereochemistry of the molecule.

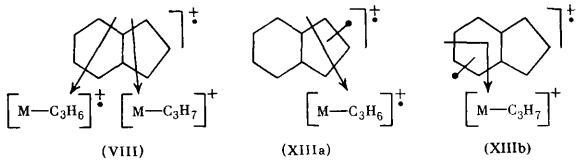
The abstraction from the MI of a fragment consisting of two carbon atoms takes place in the case of hydrocarbons (XIII)–(XIV) mainly in the same manner as in the unsubstituted structures—in the form of the ethylene molecule. The fact that the elimination of the ethyl radical from structures with angular substituents is favoured by energy factors has been explained[85,86] by the disposition of the methyl group convenient for the migration of a proton:



(XIV) *m/z* 95

The abstraction of a two-carbon fragment from the molecular ion is not characteristic of compounds (XII).

The main pathways leading to the fragmentation of the MI of methylbicycloalkanes (XII)–(XIV) are associated with the rupture of the bond at the tertiary (quaternary) carbon atoms.[85,86,96] The peaks of the ionic species $[M-C_4H_8]^{+\cdot}$, $[M-C_4H_9]^+$, $[M-C_5H_{10}]^{+\cdot}$, and $[M-C_5H_{11}]^+$ are the most intense in the spectra of compounds (XII), while the $[M-C_3H_6]^{+\cdot}$ and $[M-C_3H_7]^+$ peaks are the most intense in the spectra of compounds (XIII)–(XIV). The ratio of the latter peak intensities depends on the position of the methyl group in the cyclopentane or cyclohexane ring of the molecule: for structures with the substituent in the cyclopentane ring [structures (XIIIa)], a propene molecule is eliminated preferentially, while the presence of a substituent in the cyclohexane ring [structures (XIIIb)] promotes the ejection of a propyl radical from the MI¶. As a consequence, the ratio $I_{[M-C_3H_6]^{+\cdot}}/I_{[M-C_3H_7]^+}$ becomes diagnostic: it is greater than unity for compounds (XIIIa) and less than unity for compounds (XIIIb).



(VIII) (XIIIa) (XIIIb)

The differences between the spectra of the *cis*- and *trans*-isomers of compounds (XII)–(XIV) are correlated with their relative stabilities.[85,86,96] Thus a more stable MI is formed also in the case of the more stable bicycloalkane stereoisomers. The abstraction of the methyl substituent from the MI proceeds as a rule also more vigorously for the more stable stereoisomers, while an increase of strain in the molecules entails an increase of the contribution by the competing dissociation of endocyclic bonds. The attempt to explain these differences for the stereoisomers of compounds (XII) as a consequence of the stronger decomposition of the ion $[M-CH_3]^+$ in the case of the less stable isomer[65] appears little justified, since the difference between the enthalpies of the stereoisomers influences mainly the rates of the primary and not secondary MI decomposition reactions[98]—those which can result in an excess of internal energy, which is characteristic of the less stable isomer. The features discussed above are more likely to be a consequence of differences between the energy relations of the competing MI decomposition reactions. For the less stable isomer with an axial methyl group, the decomposition of the cyclic system consuming less energy obtains more readily, while in the case of the more stable stereoisomers with an equatorial substituent the probability of the rupture of the exocyclic bond increases, which results in an increase of the peak intensity of the ion $[M-CH_3]^+$ in its spectrum. If the radial abstraction process were energetically more favourable than the cleavage of the ring, the peak of the ion $[M-R]^+$ in the spectrum of the stable isomer would have had a greater intensity.

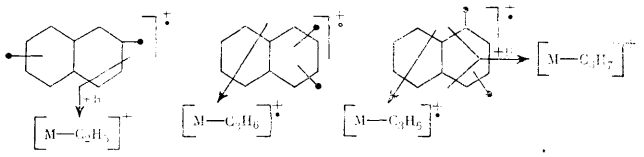
In order to confirm this hypothesis, studies were made of the mass spectra of ethylbicyclo[4.4.0] decanes,[98] because the dissociation energy of the $C-C_2H_5$ exocyclic bond is much lower than that of the $C-CH_3$ bond. Indeed the peak intensity of the ion $[M-C_2H_5]^+$ in the spectra of ethylbicyclo-[4.4.0]decanes is much higher than the peak intensity of the ion $[M-CH_3]^+$ in the spectra of compounds (XII) and the differences between their intensities in the spectra of the stereoisomers are reduced, as was to be expected. Nevertheless, this peak still remains more intense in the spectrum of the stereoisomer with an equatorial ethyl group.

The measurements of the IE and AE for the ions of 2- and 3-methylbicyclo[4.4.0]decanes with a *trans*-junction between the rings also failed to throw light on the above equation.[97]

(c) Disubstituted hydrocarbons. The spectra of dimethylbicycloalkanes have been studied in detail only for compounds (VII).[99–101] In addition, the spectra of 7,7-, and 7,9-, and 1,9-dimethyl derivatives of compounds (VIII)[85,102] and the 1,2-, 1,3-, 2,4-, and 3,7-dimethyl derivatives of compounds (IX)[86] have been described. The stability of the MI of dimethylbicycloalkanes with angular substituents is higher than that of the MI of all the methyl-substituted compounds (XII)–(XIV), while for the remaining dimethyl derivatives it is lower than for compounds (XII)–(XIV). The peak intensity of the ion $[M-CH_3]^+$ varies within broad limits. The presence of a geminal group leads to a sharp increase in the intensity of this peak, with the exception of 7,7-dimethylbicyclo[4.3.0]nonane, while the angular position of one of the methyl groups has little influence on its magnitude.

The decomposition of the cyclic system takes place preferentially via the rupture of the bonds at the tertiary and quaternary carbon atoms. The abstraction of a two-carbon fragment from the MI of dimethylbicyclo[4.4.0]decane (XV) takes place mainly in the form of a radical from the substituted ring of the molecule, while the peak intensity of the ion $[M-C_2H_5]^+$ is greatest in the spectra of structures of type (XVa) in which the disposition of the substituents is favourable for this purpose. On the other hand, the peak of the ion $[M-C_2H_5]^+$ is virtually absent from the mass spectra of compounds (XV) with angular and geminal substituents:

¶ The opposite ratio of the intensities of these peaks has been observed for unsubstituted structures on decomposition of the rings in compounds (VIII).



M, (XVa) M, (XVb) M, (XVc)

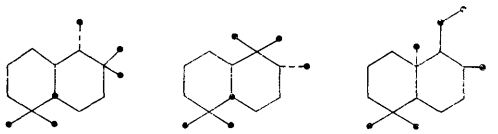
C_9 ions are present in the spectra of all dimethylbicyclo-[4.4.0]decanes. For structures of type (XVb), where both substituents are in the same ring, the peak intensities of these ions are comparatively low and that of the radical-ion $[M-C_3H_6]^+$ is somewhat greater than that of the ion $[M-C_3H_7]^+$, as in the spectra of unsubstituted compound (VII). It has been suggested[100] that the formation of the radical-ion $[M-C_3H_6]^+$ is associated with the cleavage of the unsubstituted ring. This hypothesis is supported by the higher peak intensity of the ion $[M-C_3H_7]^+$ compared with that of $[M-C_3H_6]^+$ in the spectra of 2,4- and 2,5-dimethylbicyclo[4.4.0]decanes (XVc), which also have one unsubstituted ring, but the disposition of the methyl groups in the second ring is favourable for the elimination of the C_3H_6 and C_3H_7 fragments.

The formation of C_8 (m/z 109, 110) and C_7 (m/z 95, 96) ions takes place most vigorously for the hydrocarbons (XV); the corresponding peaks have as a rule the maximum intensity in the spectra. Geminally substituted structures, in the spectra of which the peak of the ion $[M-CH_3]^+$ predominates, are an exception. Structures of type (XVb) are distinguished by a higher peak intensity of the ions $[M-C_4H_9]^+$ compared with those of $[M-C_4H_8]^+$ ($I_{109} \gg I_{110}$). For hydrocarbons with a different disposition of the methyl groups in the molecule, the ratio of these peaks is reversed to a marked extent ($I_{109} \ll I_{110}$). The peaks of C_7 ions have a high intensity in the spectra of all the structural isomers with the exception of 2,5-dimethylbicyclo[4.4.0]decane, for which their formation in a single stage is impossible without skeletal rearrangement.[99]

As a consequence of the limited number of spectra of dimethyl derivatives of compounds (VIII) and (IX), it is difficult to isolate any group characteristics of the structural isomers.[82,85] One can only note that the presence or absence of an angular methyl group in the molecule can be inferred from the ratio of the peak intensities of the ionic species $[M-C_3H_7]^+$ (m/z 95) and $[M-C_3H_6]^+$ (m/z 96) in the spectra of dimethyl derivatives of compound (IX): $I_{95}/I_{96} > 1$ for the 1,2- and 1,3-dimethyl derivatives and $I_{95}/I_{96} < 1$ in the absence of a substituent at C(1).

In the series of dimethylbicycloalkane stereoisomers examined the same dependence of the MI intensity on the stability of the molecule is observed as for the monosubstituted structures: in the mass spectrum of the sterically less hindered stereoisomer the peaks of the ionic species M^+ and $[M-CH_3]^+$ are as a rule more intense than those observed in the spectra of the more hindered isomer. The differences between the peak intensities of the primary ions in the series of stereoisomers of certain hydrocarbons are then found to be sufficiently large to be employed for diagnostic purposes.[85,86,99-102]

(d) Polyalkyl-substituted hydrocarbons. The mass spectra of compounds having more than two substituents in the molecule are known only for the most stable bicyclo[4.4.0]decane system—compounds (XV)–(XVII).[103-105]



(XVI) (XVII) (XVIII)

The difference between the positions of the geminal and methyl groups in the molecules of the structural isomers of compounds (XVI) and (XVII) does not affect the character of the decomposition of their molecular ions—the spectra of compounds (XVI) and (XVII) proved to be similar:[103] they are both characterised by a low-intensity peak of the molecular ion (m/z 208) and the maximum peak intensity of the ion $[M-CH_3]^+$. Fragments corresponding to the abstraction of two and three carbon atoms from the molecular ion are absent. Despite the presence of the geminal group in the molecule of compound (XVIII), its mass spectrum is characterised by a small peak due to the ion $[M-CH_3]^+$ and an intense MI peak (m/z 222).[105] The peak intensity for the ion $[M-C_2H_5]^+$ is also high and the peak for the ion with m/z 123 has the highest intensity.

2. Hydrocarbons with a Bridge Type of Junction between the Rings

(a) Unsubstituted hydrocarbons. The vast majority of the mass spectra quoted in the literature[91,106-119] refer to hydrocarbons consisting of five–six-membered rings [compounds (XIX)–(XXII)]. The only exception is bicyclo[1.1.1]-pentane (XXIII),[120] whose mass spectrum contains, apart from the MI peak with the maximum intensity, also the peak of the ion $[M-H]^+$. The study of the decomposition of the deuteriated analogue of compound (XXIII) led to the conclusion that hydrogen is eliminated not only from the methylene but also from the methylidyne unit. The peak intensities of the remaining fragment ions are low.



(XIX) (XX) (XXI) (XXII) (XXIII)

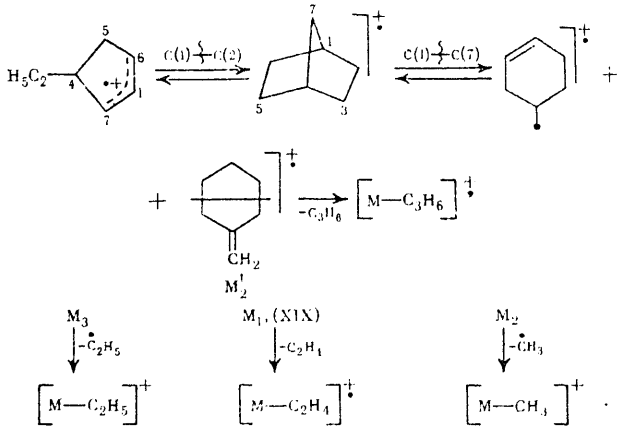
Table 4.

Compound	$I_{[M]^+}$	$I_{[M-CH_3]^+}$
(XIX)	3.8	14.7
(XX)	7.5	3.9
(XXI)	11.9	0.5
(XXII)	12.3	3.3

The stability of the MI and the ion $[M-CH_3]^+$ in the spectra of the unsubstituted bicycloalkanes (XIX)–(XXII) varies within wide limits (Table 4).[106,108,117,119] A molecule of the hydrocarbon (XIX) is subject to an intense strain arising as a consequence of the distortion of the C(1)–C(7)–C(4) angle (~90°) and an appreciable "Pitzer" interaction between the hydrogen atoms [C(2), C(3) and C(5), C(6)], which is characteristic of a six-membered ring in the boat conformation. Under the conditions of electron impact, these difficulties initiate the formation of isomeric forms of the molecular

ion (M_2 and M_3, Scheme 6), whose subsequent decomposition leads to the appearance of the intense peaks of $[M-CH_3]^+$ and $[M-C_2H_5]^+$ (maximum peak).[117,118] The decomposition of the form M_1 leads to the appearance of the intense peak of the radical-ion $[M-C_2H_4]^{+\cdot}$.

Scheme 6



In the spectra of the hydrocarbons (XX) and (XXII), whose molecules also contain the dimethylene bridge, the peak of the ion $[M-C_2H_5]^+$ is one of the most intense. In the spectra of compounds (XX)–(XXII) the maximum intensity is shown by the peak of the ion $[M-C_3H_7]^+$. For compound (XX), the formation of this ion is attributed to the successive elimination of a methyl radical and an ethylene molecule from the MI,[106] in the case of compound (XXI) it is believed to arise as a consequence of the ejection of a propyl radical from the monocyclic form of the MI,[119] while for compound (XXII) the formation of the ion is believed to be due to the contributions of both decomposition pathways.[108]

Table 5. The peak intensities of the characteristic ions in the spectra of monomethylbicycloalkanes.[106,108,117–119]

Ions	(XIX)	(XX)	(XXI)	(XXII)
M^+	2.0—4.2	1.5—6.7	5.0—8.6	10.1—11.1
$[M-CH_3]^+$	5.8—9.8	2.7—12.8	3.2—18.1	4.3—10.8
$[M-C_2H_5]^+$	10.6—32.5	3.7—28.6	0.4—5.4	13.8—22.5
$[M-C_3H_7]^+$	9.5—16.6	3.2—24.3	3.8—32.2	7.3—12.8
$[M-C_4H_9]^+$	—	6.3—14.6	7.3—14.9	9.8—14.3

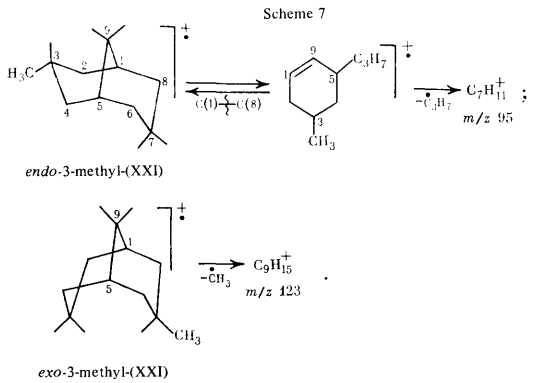
(b) Monosubstituted hydrocarbons. The introduction of the methyl substituent into the molecules of compounds (XIX)–(XXII) lowers somewhat the stability of their MI. The highest stability of the MI is then shown for bicyclo[2.2.2]octanes (Table 5), which makes it possible to distinguish them from the isomeric bicyclo[3.2.1]octanes.[106–108,112,117–119] The peak intensity of the ion $[M-CH_3]^+$ derived from the methyl derivative of compound (XXII) is higher compared with the unsubstituted structure; nevertheless the ratio $I_{[M]^+}/I_{[M-CH_3]^+}$ remains greater than unity. For the remaining members of the series, the ratio of the intensities of these peaks is determined by the position of the methyl group in the molecule.

The decomposition of the cyclic components of the bridged bicyclo-octanes takes place preferentially with the abstraction from the molecular ion of fragments containing two and three carbon atoms. A two-carbon fragment is ejected mainly as a result of the decomposition of the unsubstituted dimethylene bridge. This process proceeds very vigorously for the methyl derivatives of compounds (XIX), (XX), and (XXII), with the exception of 6-methylbicyclo[3.2.1]octane, but is not characteristic of compounds (XXI) (Table 4). A distinctive feature of the spectra of the 6- and 8-methyl derivatives of compound (XX), in which the substituent is attached to the most strained part of the molecule, is the prominance of the peak due to the primary odd-electron ionic species, namely $[M-C_3H_6]^{+\cdot}$ and $[M-C_2H_4]^{+\cdot}$ respectively, whose intensity in the spectra of the remaining structural isomers does not exceed 50% of the maximum value.

The monosubstituted hydrocarbons (XIX)–(XXI) exist in the form of two (*exo*- and *endo*-) geometrical isomers, apart from compounds (XIX)–(XXI) substituted in the angular position. As a consequence of the high symmetry of the molecule of hydrocarbon (XXII), its monosubstituted derivatives have no geometrical isomers. The stereochemical characteristics of the molecules are reflected in the spectra of the stereoisomers differing greatly in their thermochemical stabilities. These differences are particularly clear in the spectra of the *exo*- and *endo*-isomers of the 3-methyl derivative of compound (XXI).[119] The molecule of compound (XXI) exists in the "chair–chair" conformation, in which there is a strong *trans*-annular interaction with the axial hydrogen atoms at C(3) and C(7) and for this reason the additional interactions in the molecule, arising following the introduction of substituents [in particular, the interaction of the 3-*endo*-methyl group with the hydrogen atom at C(7) in the molecules of 3-methyl substituted derivatives], force one of the rings to adopt the boat conformation.

Thus the decomposition of the MI of the *endo*-epimer is determined by the removal of the "bowsprit" interactions, which is achieved, according to the authors,[119] by the efficient formation of the isomeric monocyclic form of the MI. The subsequent decomposition of this form yields the ion with *m/z* 95, the peak intensity of which is a maximum in the spectrum. The main pathway in the decomposition of the *exo*-epimer involves the elimination of the methyl group. The peak of the ion $[M-CH_3]^+$ in its spectrum has the maximum intensity (Scheme 7).

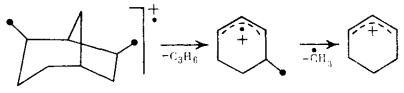
Scheme 7



(c) Disubstituted hydrocarbons. The introduction of a second methyl group into the molecules of compounds (XIX)–(XX) and (XXII) reduces somewhat the stability of the MI.[106,108,117] In the case of compound (XXI) it hardly changes.[119] On the other hand, no regularity is observed in the variation

of the peak intensity of the ion $[M-CH_3]^+$ and the ratio $I_{[M]^+}/I_{[M-CH_3]^+}$ in a series of structural isomers. The peaks of the ionic species $[M-C_2H_5]^+$, $[M-C_3H_7]^+$, and $[M-C_4H_8]^{+\cdot}$ are the most intense in the spectra of the dimethyl derivatives of compounds (XIX)–(XXI) and one of these actually has the maximum intensity. Analysis of the mass spectra of structural isomers available in the literature does not allow unambiguous conclusions about the structural elements of the molecule (such as the structure of the bicyclic skeleton, substitution in one or different rings, and vicinal or geminal disposition of the methyl groups).

However, the spectra of hydrocarbons (XIX) and (XX) substituted in the angular position stand out somewhat. They are as a rule characterised by a considerable predominance of one [the 1,2-, 1,6-, and 1,7-dimethyl derivatives of compound (XX) and the 1,4-dimethyl derivative of compound (XIX)] or two [the 1,3-, 1,4-, and 1,5-dimethyl derivatives of compound (XX) and the 1,2- and 1,3-dimethyl derivatives of compound (XIX)] decomposition pathways as a result of the preferential rupture of the bond at the quaternary carbon atom. The intensities of the peaks of the remaining ions under these conditions do not exceed 25% of the intensity of the main peak. An exception is provided by the 1,8-dimethyl derivative of compound (XX), which is characterised by an intense decomposition of the molecular ion to an equal extent via all the pathways as a consequence of the considerable strain in the molecule. For the remaining dimethyl derivatives of hydrocarbon (XX), each having three tertiary carbon atoms, the fragmentation of the molecular ion proceeds with equal probability via several pathways; according to some investigators[106] the methyl substituents are retained in the charged fragments and their subsequent abstraction leads to the strong formation of secondary ions.



2,7-$(CH_3)_2$-(XX) m/z 96 m/z 81

In the series of geometrical isomers of dimethylbicyclooctanes the spectrum of the most stable stereoisomer of each structure also exhibits the most intense peaks of the ions M^+ and $[M-CH_3]^+$. In other respects the spectra of the stereoisomers are very similar.[106,108,117–119]

3. Other Bicyclic Systems

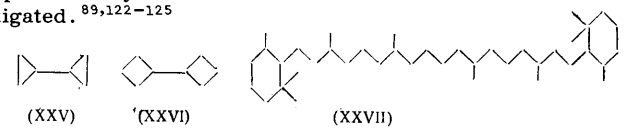
(a) Spiran hydrocarbons. Spiropentane (XXIV) is the only representative of this class whose mass spectrum has been described.[2,121]



(XXIV)

It is of interest that at 70 eV the peak of the ion $(M-H)^+$ is the most intense in the spectrum of compound (XXIV), while at 15 eV the peak of the radical-ion $(M-C_2H_4)^{+\cdot}$ is the most intense. The intensity of the peak for the ion $(M-CH_3)^+$ is low in both spectra.

(b) Hydrocarbons with single-bonded rings. The mass spectra of hydrocarbons of this class have been little investigated.[89,122–125]

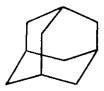


(XXV) (XXVI) (XXVII)

The MI peak in the spectra of compounds (XXV)–(XXVII) is insignificant. The strongest peak in the spectra of bicyclopropyl (XXV) [89] and bicyclobutyl (XXVI) [122] {the radical-ions $[M-C_2H_4]^{+\cdot}$ and $[M-C_3H_6]^{+\cdot}$} corresponds to the ionic species formed on dissociation of endocyclic bonds at a tertiary carbon atom. The strongest peak in the spectrum of perhydro-β-carotene (XXVII) is that of the secondary ion with m/z 69.[123–125] The height of the peak due to the ion $[M-CH_3]^+$ is considerable (90% of the maximum value) only in the spectrum of compound (XXV).

V. TRICYCLIC SATURATED HYDROCARBONS

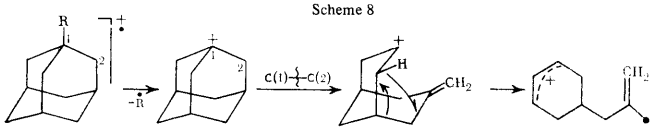
The greatest number of studies on the mass spectrometry of tricyclic hydrocarbons have been devoted to compounds of the adamantane series. Adamantane (XXVIII) itself is the first among tricyclic hydrocarbons to have been identified in petroleums; much attention has been devoted to hydrocarbons of the adamantane series in the chemistry of petroleum.[126] The adamantane system is the most stable among tricyclic systems, which is due to the absence of any internal strains, since all three rings have the chair conformation. In the spectrum of compound (XXVIII) the MI peak has the maximum intensity. The easiest decomposition reaction of the MI of adamantane involves the elimination from it of fragments containing three and four carbon atoms, but the peak intensities of the ions formed do not exceed 50% of the maximum value:[127]



(XXVIII)

Regardless of the energy of the ionising electrons, the decomposition of the MI of alkyladamantanes leads to the formation of the adamantyl ion $C_{10}H_{15}^+$ with m/z 135 [Scheme 8, ion (C)] from the monoalkyl derivative of compound (XXIX) [128–132] or of its homologues from polyalkyladamantanes.[132–134] The peaks of these ions have the maximum intensity. It has been suggested[130,133] that the ion (C) does not retain the tricyclic structure with a positive charge on the carbon atom at the bridgehead but actually undergoes an extensive rearrangement to the cyclic allyl ion (D) which accounts for its high stability.

Scheme 8



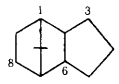
M, (XXIX) (C) (D)

Examination of the mass spectra of 1- and 2-alkyladamantanes demonstrated a considerable decrease in the stability of the MI with increase in the length of the substituent group[128,129,132] and, for the same length of the substituent group, the stability of the MI is higher for the 2-substituted structures than for the 1-substituted structures. As a result, the ratio $I_{[M]^+}/I_{[M-R]^+}$ can be used as a criterion in determining the position of the substituent in the adamantane nucleus: it is 5–7 times higher for the 2-substituted derivatives than for the 1-substituted derivatives.

An increase in the number of substituents in the adamantane molecule leads to a decrease of the stability of the MI and an increase of the peak intensity of the ion $[M-R]^+$.[129, 132,133] In contrast to the spectra of monomethyladamantanes, the peaks of the ions $[M-C_2H_5]^+$ appear in the spectra of the tri- and tetrasubstituted derivatives, which indicates,

according to the authors,[129] the additional elimination of the CH_2 fragment from the other methyl group. The peak intensity of the above ion increases with increased number of methyl groups in the molecule.

Apart from the mass spectrum of adamantanes, a detailed study has been made of the spectrum of the isomeric tricyclo[5.2.1.$0^{2,6}$]decane (XXX) and its methyl and ethyl derivatives,[135,136] for which the IE have been measured.[137]

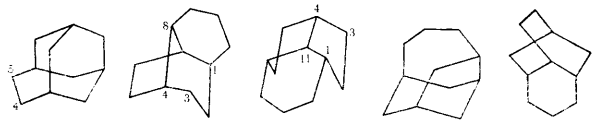


(XXX)

The peak for the ion $[M-C_3H_5]^+$ with m/z 95, formed following the abstraction of the CH_2=CH−CH_2 fragment from the MI, has the maximum intensity in the spectra of the *exo*- and *endo*-isomers of compound (XXX).

The introduction of a substituent into the molecule of compound (XXX) (the 3-, 4-, 8-, and 10-methyl derivatives have been studied) decreases the stability of the MI. On the other hand, the peak intensity of the ion $[M-CH_3]^+$ increases relative to that noted for the unsubstituted structure. The peak for the ion $[M-C_2H_5]^+$ has the maximum intensity only in the spectrum of 10-methyltricyclo[5.2.1.$0^{2,6}$]-decane. Apparently it arises in the spectrum of this compound via a mechanism analogous to that described for 7-substituted bicyclo[2.2.1]heptanes.[118] In all the remaining spectra the peaks of the secondary ions have the maximum intensities.[135,136]

As regards tricyclic hydrocarbons having the composition $C_{11}H_{18}$ (tricycloundecanes), there exist literature data for a fairly large number of structures,[138–145] many of which have been identified in petroleum.[146] The mass spectrum of homoadamantanes (XXXI) resembles that of adamantane—the MI peak is more than twice as intense as the remaining peaks in the spectrum.[138] The main difference between the spectra of compounds (XXVIII) and (XXXI) is associated with the presence in the latter of the intense peak of the ion $[M-CH_3]^+$. The spectra of the hydrocarbon labelled with ^{13}C have shown[139] that each atom in the C(4)−C(5) dimethylene bridge is involved in the abstraction of the methyl group from the MI to the extent of ~25%.



(XXXI) (XXXII) (XXXIII) (XXXIV) (XXXV)

The maximum intensity of the MI peak is observed in the spectrum of tricyclo[5.4.0.$0^{4,8}$]undecane (XXXII),[140] but a high intensity of the main fragment ions is also characteristic of this compound. The decomposition of the MI of tricyclo[5.3.1.$0^{4,11}$]undecane (XXXIII) takes place with the preferential ejection of an ethylene molecule.[140] The molecule of 4-homoprotoadamantane (XXXIV), containing the cycloheptane ring, decomposes via many pathways under electron impact.[141] The peak of the secondary ion $[C_6H_7]^+$ with m/z 79 has the maximum intensity in its spectrum.

Among the hydrocarbons having the composition $C_{11}H_{18}$, the most interesting is tricyclo[5.3.1.$0^{3,8}$]undecane—homoisotwistane (XXXV).[142–144] This hydrocarbon is the only one among the tricycloundecanes investigated which is formed solely from six-membered rings and the valence angles in its molecule are completely undistorted. The characteristics of the structure of homoisotwistane are reflected in its high thermal stability[104] and the high intensity of the MI peaks in its spectrum, which exceeds by a factor of almost two the intensities of the remaining peaks. The maximum intensity of the MI peak persists also in the spectrum of 1-methyltricyclo[5.3.1.$0^{3,8}$]undecane,[145] which is not characteristic of methyl-substituted saturated hydrocarbons.

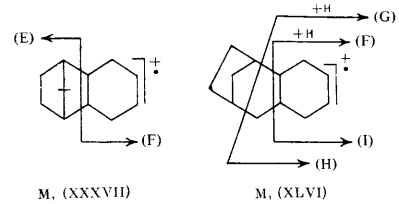
Systematic mass-spectrometric studies of a series of unsubstituted tricycloundecanes[144] and tricyclododecanes,[147] made up of five- and six-membered rings, demonstrated the possibility of identifying structural and in many instances also geometrical isomers. The mass spectra of tricyclo-[6.3.0.$0^{2,6}$]undecane (XXXVI), tricyclo[6.2.1.$0^{2,7}$]undecane (XXXVII), tricyclo[5.2.2.$0^{2,6}$]undecane (XXXVIII), tricyclo-[5.3.1.$0^{2,6}$]undecane (XXXIX), tricyclo[6.2.1.$0^{2,6}$]undecane (XL), tricyclo[5.3.1.$0^{3,7}$]undecane (XLI), tricyclo-[6.2.1.$0^{1,6}$]undecane (XLII), tricyclo[5.2.2.$0^{1,5}$]undecane (XLIII), tricyclo[6.3.0.$0^{1,5}$]undecane (XLIV), tricyclo-[7.3.0.$0^{3,8}$]dodecane (XLV), tricyclo[7.2.1.$0^{2,7}$]dodecane (XLVI), tricyclo[6.3.1.$0^{2,6}$]dodecane (XLVII), tricyclo-[6.2.2.$0^{2,7}$]dodecane (XLVIII), tricyclo[6.3.1.$0^{4,12}$]dodecane (XLIX), tricyclo[7.2.1.$0^{1,6}$]dodecane (L), tricyclo[6.3.1.$0^{1,6}$]-dodecane (LI), tricyclo[6.3.1.$0^{1,5}$]dodecane (LII), and tricyclo[5.3.1.$1^{4,11}$]dodecane (LIII) have been investigated.

The stability of the MI of the tricyclanes investigated varied within wide limits (1.8–13.3%) and is lower the greater the number of cyclopentane rings in the molecule. The mass spectra of all the tricyclanes contain the peaks of the ions $[M-CH_3]^+$ and $[M-C_2H_5]^+$, the intensity of the latter being particularly high in the spectra of compounds containing the dimethylene bridge. The abstraction of a three-carbon fragment from the MI takes place strongly only in the decomposition of tricyclododecanes.

All the hydrocarbons (XXXV)–(LIII) investigated can be divided into two groups according to the absence (group 1) or presence (group 2) of a carbon atom common to all three rings. The quantitative differences between the spectra of the hydrocarbons in groups 1 and 2 reflect the fundamental difference between the pathways in the decomposition of their MI.

The first significant difference for tricycloundecanes consists in the peak intensity for the ion $C_5H_7^+$ with m/z 67 [ion (E), Scheme 9], which is more than twice as high in the spectra of the group 1 hydrocarbons (XXXVI)–(XL) as in the spectra of the group 2 compounds (XLI)–(XLIV). This is apparently associated with the fact that the formation of the ion (E) from compounds (XXXVI)–(XL) requires the rupture of two C–C bonds (Scheme 9, on the left), while in compounds (XLI)–(XLIV) three such bonds must be broken, which is less probable.

Scheme 9



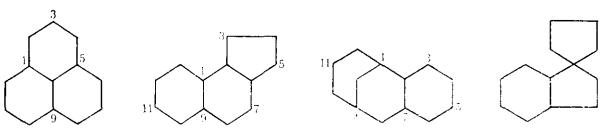
M, (XXXVII) M, (XLVI)

The second difference is the absence from the spectra of group 2 hydrocarbons of the peak of the ion $C_6H_{11}^+$ with m/z 83 [ion (F)]. In the case of group 1 hydrocarbons this ion is formed directly from the molecular ion. Among group 2 hydrocarbons, its formation requires, apart from the rupture of the C–C bonds, the migration of at least one hydrogen atom to the C_6 fragment. The impossibility of such migration for steric or other reasons apparently leads

to the absence of the peak of the ion (F) from the spectra of group 2 hydrocarbons.

The spectra of group 1 tricyclododecanes (XLV)–(XLVIII) contain intense peaks for the ionic species $C_6H_{11}^+$ (m/z 83), $C_7H_{13}^+$ (m/z 97), $C_7H_{12}^+$ (m/z 96), and $C_6H_{10}^+$ (m/z 82) [ionic species (F), (G), (H), and (I), Scheme 9, on the right], whereas in the spectra of group 2 hydrocarbons the first two peaks are missing and the intensities of the last two are insignificant. The above differences are associated with the impossibility of the formation of these ions as a result of the simple rupture of two bonds in the molecules of group 2 hydrocarbons. Their formation following the dissociation of three bonds, is firstly, less favourable on energy grounds and, secondly, requires the migration of at least one hydrogen atom.

The mass spectra of tricyclic hydrocarbons having the composition $C_{13}H_{22}$ have been obtained for tricyclo[7.3.1.$0^{5,13}$]-tridecane (LIV),[107] tricyclo[7.4.0.$0^{2,6}$]tridecane (LV),[148] tricyclo[7.3.1.$0^{2,7}$]tridecane (LVI),[149] and 1,2-tetramethylene-spiro[4,4]nonane (LVII).[148]



(LIV) (LV) (LVI) (LVII)

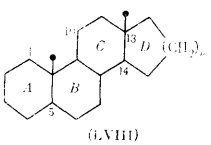
The intensity of the MI peak for the first three compounds is high, while that of the peaks for the ions $[M-CH_3]^+$ and $[M-C_2H_5]^+$ is insignificant. The main pathway in the decomposition of the MI of compounds (LIV)–(LVIII) involves the abstraction of fragments containing three carbon atoms: in the spectra of compounds (LV) the peak of the ion $[M-C_3H_7]^+$ has the maximum intensity. The mass spectrum of the hydrocarbon (LVII) is characterised by a high peak intensity of the ion $[M-C_4H_9]^+$ greatly exceeding that observed for the remaining peaks in the spectrum.

VI. HYDROCARBONS WITH FOUR AND MORE RINGS IN THE MOLECULE

The decomposition of the molecule of a polycyclic compound of this type under electron impact conditions has been examined in greatest detail for hydrocarbons of the steroid and triterpenide types, which is due primarily to their widespread occurrence in nature and the important role which they play in the solution of many geochemical problems.[150]

1. Tetracyclic Hydrocarbons of the Steroid Type

The extensive experimental data obtained in the mass-spectrometric study of the hydrocarbons (LVIII)–(LXI) with the aid of ^{13}C-labelled and deuteriated analogues made it possible to formulate the main pathway leading to the decomposition of the MI and to determine the mechanism of the formation and the structure of the main fragment ions as well as the type of A/B and C/D junctions between the rings in molecules of compound (LXI).[151–156]

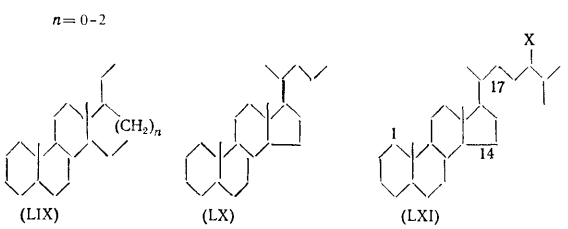


(LVIII)

(LVIIIa): n = 0 (D-norandrostane); (LVIIIb): n = 1 (androstane); (LVIIIc): n = 2 (D-homoandrostane); (LVIIId): n = 3 (D-bishomoandrostane)

The principal pathway in the decomposition of the unsubstituted structure (LVIII) is determined by the structure of the D ring.[41,151,153] The MI peak is intense in the spectra of all the compounds with the exception of compound (LVIIIa). The peak intensity of the ion $[M-CH_3]^+$ in the spectra of compound (LVIII, a, c, and d) is approximately half the maximum value, while in the spectrum of compound (LVIIIb) this is the main peak.

The decomposition of the cyclic component of the molecule of compound (LVIII) takes place with the preferential rupture of the C–C bonds in the A and D rings. Studies of the deuteriated analogues have shown[41,151] that the decomposition of the A ring in compound (LVIIIb) predominates over the decomposition of the D ring, while in compounds (LVIII, a and d) the opposite behaviour obtains. In the case of compounds (LVIII, a, c, and d) this leads to the preferential formation of ions with m/z 217 and 218 [(K) and (L), Scheme 10], while in the case of compound (LVIIIb) ions with m/z 203 and 204 are formed preferentially. The appearance in the D ring of a substituent at the carbon atom adjoining C(13) [pregnanes (LIX), cholanes (LX), and steranes (LXI) have also been investigated][151,156–162] promotes the preferential rupture of the bond between these two atoms, as a result of which the peaks for the ions with m/z 217 and 218 have the maximum intensity in the spectra of compounds (LIX)–(LXI)†.



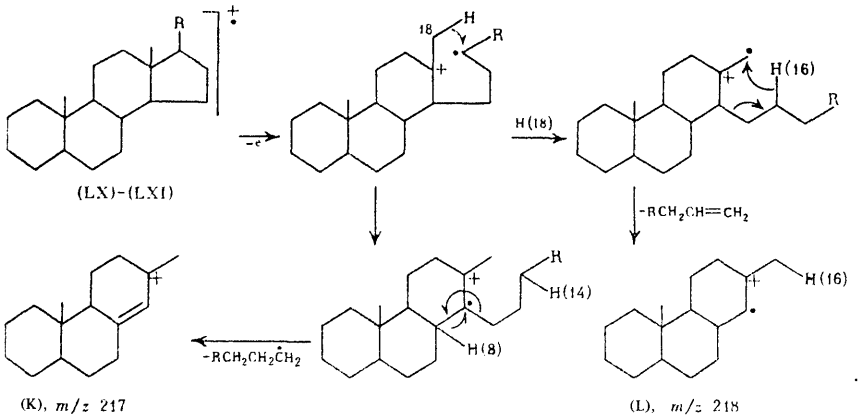
(LIX) (LX) (LXI)

(LVIIIa): (cholestane); (LXIb): X = CH_3 (ergostane); (LXIc): X = C_2H_5 (sitostane)

Attempts to determine structures of this type have been frequently made,[158,159] but only by the analysis of the spectra of deuteriated compounds was it possible to formulate a mechanism of the formation of these ions and to determine their structure (Scheme 10).[151,157]

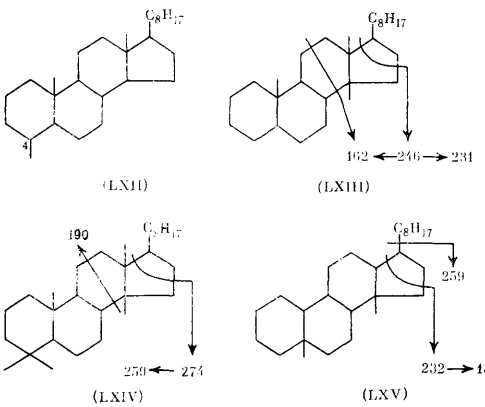
†The presence in the spectra of steranes of intense peaks due to the ions with m/z 217 and 218 makes it possible to determine unambiguously their presence in complex mixtures, which is widely used in the chromato-mass-spectrometric analysis of petroleum fractions.[163–173]

Scheme 10



The ratio of the peak intensities for the ions with m/z 217 and 218 and also the ions with m/z 149 and 151, formed on cleavage of the *C* ring,[156] plays an important role in the determination of the stereochemical features of molecules of the steranes (LXI, a–c). Thus the first of these characterises the type of *C*/*D* junction between the rings (*trans*-junction for $I_{217}/I_{218} > 1$ and *cis*-junction for $I_{217}/I_{218} < 1$), while the second characterises the type of *A*/*B* junction between the rings (*cis*-junction for $I_{149}/I_{151} \geq 1$ and *trans*-junction for $I_{149}/I_{151} < 1$).[150]

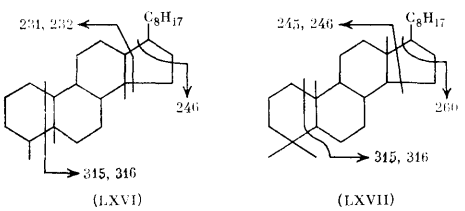
Apart from the hydrocarbons (LVIII)–(LXI) examined above, studies have been made of the spectra of a large group of compounds retaining the skeleton of the molecule of cholestane (LXI), but having methyl groups in other positions in the molecule.



The study of the 4α-methylcholestane (LXII) fragmentation pathway showed[172–174] that the appearance of an additional substituent in the *A* ring does not alter the principal pathways leading to the decomposition of the molecular ion and characteristic of steranes, merely displacing the mass numbers of the fragment ions incorporating the *A* ring by 14 a.m.u. towards higher values.

On the other hand, the presence of a substituent at C(14) in 14α-methylcholestane (LXIII) and lanostane (LXIV) [172] alters significantly the MI decomposition pattern. The study of the (LXIII) and (LXIV) fragmentation pathways with the aid of deuteriated analogues showed[175] that the ion with the maximum peak intensity in their spectra [with m/z 231 for (LXIII) and m/z 259 for (LXIV)] is formed from the fragment ions and not from the MI as in the case of cholestane.

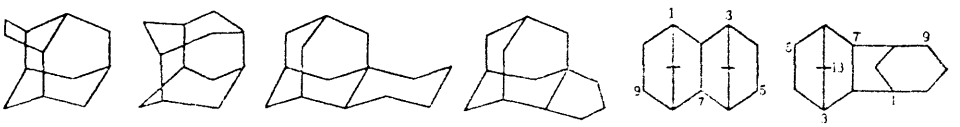
The mass spectra of the stereoisomers of the rearranged cholestane (LXV) are characterised by a high peak intensity of the ions with m/z 189 and 259.[176] The methyl group in the C(5) position in the molecule of compound (LXV) not only shifts by 14 a.m.u. the mass number of the fragments containing the *A* ring, as in the case of compound (LXII), but also alters sharply the quantitative picture of the spectrum.[174] A characteristic feature of the spectra of the rearranged 4-methylcholestanes (LXVI) is the presence of the intense peaks for the ions with m/z 315 and 316 formed on degradation of the *A* ring. As for compound (LXV), this is accompanied by the decomposition of the *D* ring with formation of ions having m/z 232, 231, and 246.



The decomposition of 4,4-dimethylcholestanes (LXVII) under electron impact resembles the decomposition of cholestanes.[175] The mass number of the ions incorporating the *A* ring is displaced by 28 a.m.u. relative to the corresponding peaks in the spectrum of compound (LXI). Ions which do not incorporate the *A* ring have the same mass number as for compound (LXIa). For the hydrocarbons (LXV)–(LXVII), there is a possibility, as for cholestane, of the mass-spectrometric determination of the type of *A*/*B* and *C*/*D* junctions between the rings.[174,176]

2. Other Tetracyclic Hydrocarbons

The molecule of tetracyclo[6.3.1.$0^{2,6}$.$0^{5,10}$]dodecane (LXVIII) can be regarded as the molecule of adamantane having an ethane bridge in the 2,5-positions.



(LXVIII) (LXIX) (LXX) (LXXI) (LXXII) (LXXIII)

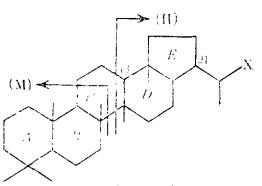
This modification of the adamantane structure does not alter the decomposition of its MI.[177] The MI peak again has the maximum intensity in the spectrum of compound (LXVIII), while the peak of the ion $[M-C_2H_5]^+$ is insignificant. The replacement of the dimethylene bridge by the methylene bridge, as in tetracyclo[5.3.1.$1^{2,6}$.$0^{4,9}$]dodecane, is also hardly reflected in the character of the fragmentation of the MI and the spectrum of compound (LXIX) retains the features characteristic of that of adamantane.[178]

The MI peak intensity remains a maximum also in the spectra of the hydrocarbons (LXX) and (LXXI).[179] However, the stability of the parent ion is greatly reduced compared with its stability in the adamantane spectrum.

The decomposition of the molecules of tetracyclo[6.2.1.$0^{2,7}$.$1^{3,6}$]-dodecane (LXXII) and tetracyclo[6.3.1.$0^{2,7}$.$1^{3,6}$]tridecane (LXXIII) proceeds with formation of the ionic species M^+, $[M-C_2H_4]^+$, $[M-C_2H_5]^+$, and $[M-C_3H_7]^+$, which correspond to intense peaks.[180] The peaks of the secondary ions [*m/z* 80, 121 for (LXXII) and *m/z* 41 for (LXXIII)] have the maximum intensity in the spectra of compounds (LXXII) and (LXXIII).

3. Pentacyclic Hydrocarbons of the Triterpane Series

The study of the fragmentation of hydrocarbons of the triterpane series (LXXIV) (the hopane series) under electron impact showed[172,181,182] that it proceeds with the preferential formation of ions of two types—(M) and (H).

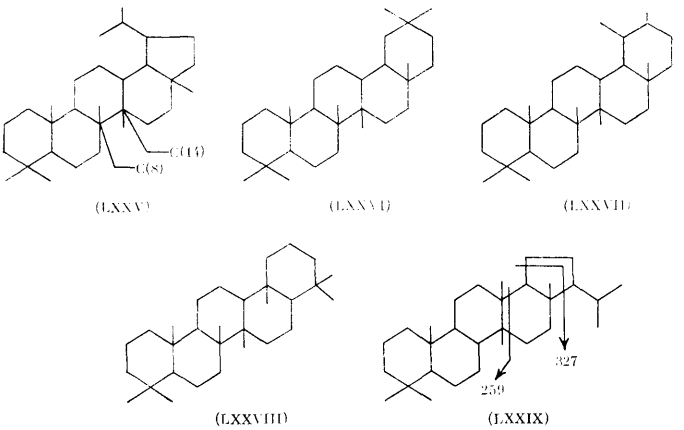


(LXXIV)

(LXXIVa): X = H (adiantane); (LXXIVb): X = CH_3 (hopane); (LXXOVc): X = C_2H_5 (homohopane)

In the case of hopane these ions have equal masses (*m/z* 191). The presence in the spectra of pentacyclic hydrocarbons of the peaks due to the ions (M) and (H), whose intensity greatly exceeds that of the remaining peaks in the spectrum {the peaks of the ions M^+ and $[M-CH_3]^+$ have as a rule low intensities}, has been widely used for the identification of compounds of the "hopane series" in petroleum.[152,183-193] On the other hand, the ratio of the intensities of these peaks is diagnostic for the type of *D/E* ring junction—$I_{(M)}/I_{(H)} > 1$ for the *trans*-junction and $I_{(M)}/I_{(H)} < 1$ for the *cis*-junction.

A change in the position of the substituent in the *E* ring of the hopane molecule does not entail any changes in the spectrum of compound (LXXV).[181,183,184]



(LXXV) (LXXVI) (LXXVII)

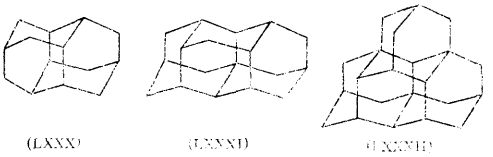
(LXXVIII) (LXXIX)

The rupture of the C(8)–C(14) bond is the main process also for compounds with a six-membered *E* ring [oleanane (LXXVI), ursane (LXXVII), and gammacerane (LXXVIII)][181,185] which retain the methyl groups C(8) and C(14).

The transfer of the methyl group from the C(8) position to the C(13) position in structures of type (LXXIX) leads to a sharp decrease of the peak intensity for the ion with *m/z* 191.[172,181] Intense peaks due to the ions with *m/z* 259 and 327, which are absent from the spectra of compounds (LXXIV)–(LXXIX), then appear and there is also a sharp increase of the intensity of the peaks in the region of low masses, which in fact attain maximum values (*m/z* 69, 81, 109).

4. Other Hydrocarbons with Five and More Rings in the Molecule

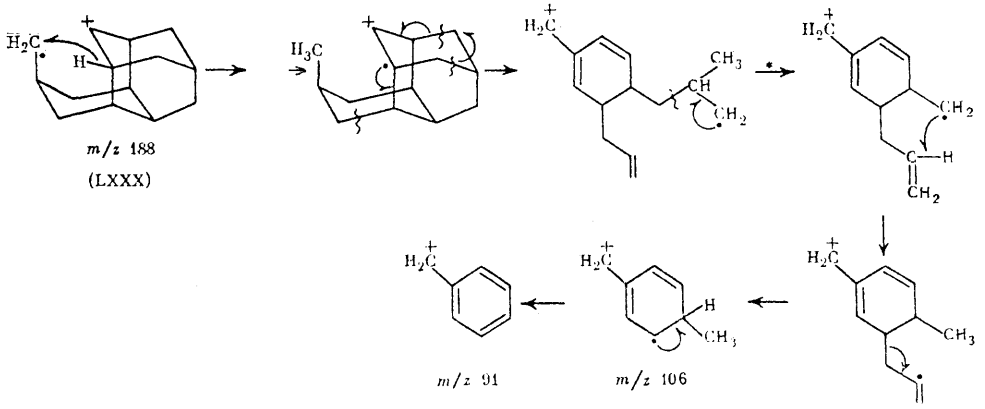
Polycyclic hydrocarbons having adamantane-like structures (LXXX)–(LXXXII) have been studied in detail. As in the spectrum of adamantane, the maximum intensity in their spectra is that of the molecular ion.[193-200]



(LXXX) (LXXXI) (LXXXII)

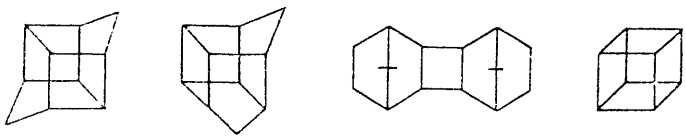
In the diamantane (LXXX) spectrum the intensity of the MI peak is a maximum, being approximately five times greater than that of any other peak.[194,195] The study of the metastable ion peaks in the spectrum of compound (LXXX) showed[196] that the ion with *m/z* 91 which has the next largest peak is not primary, but is formed as a result of a multistage decomposition of the MI and apparently has the structure of the phenylalkyl cation (Scheme 11).

Scheme 11



The spectra of 1-, 3-, and 4-methyldiamantanes retain the type of behaviour in the decomposition of the MI described previously for alkyladamantanes.[197,198] The ratio $I_{[M]^+}/_{[M-CH_3]^+}$ can also be used in this instance for the determination of the position of the methyl group in the diamantane nucleus: it is greater for 3-methyldiamantane than for the 1- and 4-methyldiamantanes.

The decomposition of the MI into two symmetrical fragments with dissociation of the bonds in the cyclobutane rings is characteristic of two pentacyclic hydrocarbons—pentacyclo-[5.3.0.$0^{2,6}$.$0^{3,9}$.$0^{4,8}$]decane (LXXXIII) and pentacyclo-[5.3.0.$0^{2,6}$.$0^{3,9}$.$0^{5,8}$]decane (LXXXIV).[201] The ion with the cyclopentadiene structure (*m/z* 66) formed under these conditions exhibits the maximum intensity for both compounds, which is much higher than for the remaining peaks in the spectrum (more than 50% of the total ionic current).



(LXXXIII) (LXXXIV) (LXXXV) (LXXXVI)

The possibility of the symmetric cleavage of the molecule into two fragments of equal mass (with *m/z* 91) has also been discussed in connection with the dissociation of pentacyclo-[8.2.1.$1^{4,7}$.$0^{2,9}$.$0^{3,8}$]tetradecane (LXXXV).[202] However, consideration of the metastable transitions and the spectra of deuteriated analogues showed that the ion $C_7H_7^+$ with *m/z* 91 is formed as a result of the successive ejection also of C_2 and C_5 fragments from the MI.[202] The ion does not then retain the norbornane structure, but isomerises to a tropylium ion.

The spectrum of "cubane" (LXXXVI), a hexacyclic hydrocarbon with four carbon atoms in the rings, proved to be interesting.[203] The peak for the ion $(M-H)^+$ shows the maximum intensity (this had been observed earlier only in the spectrum of spiropentane[121]).

Mass-spectrometric study of linked-ring adamantane derivatives, containing two adamantyl groups, namely biadamantyls (R–Ad–Ad–R) and diadamantylethanes (Ad–CH_2–CH_2–Ad), showed[204] that the dissociation of the bond between the adamantyl residue Ad and the carbon chain is accompanied by the formation of the radical-ion $[M-AdH]^+$ having an intense peak is characteristic of diamantylethanes, while in the case of biadamantyls the most intense peak in the spectrum corresponds to the rupture of the bond between the adamantyl residues {the $[RAd]^+$ ion}. The above differences persist also for the alkyl derivatives of these structures.

In conclusion one must note yet again that the characteristic features of the decomposition of saturated hydrocarbons under electron impact, mentioned in the present review, necessitate much caution in the approach to the interpretation of the mass spectra and the identification of compounds of this class on that basis. The data available to us do not allow unambiguous conclusions concerning individual structural elements of the molecule, such as the presence (or absence) of a substituent, of a quaternary or tertiary carbon atom, and of bridge type, condensed, or single bond type of connection between the rings in the molecule of the polycyclic hydrocarbon. The solution of these problems is so far possible only in some cases and within the limits of groups of compounds which have been studied systematically.

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