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MASS SPECTRA OF 1- AND 2[a]-SUBSTITUTED 1,3,5,7-TETRAMETHYL-2,4,6,8-TETRATHIAADAMANTANES

V. I. Khvostenko, E. G. Galkin, E. M. Vyrypaev, B. M. Lerman, and G. A. Tolstikov

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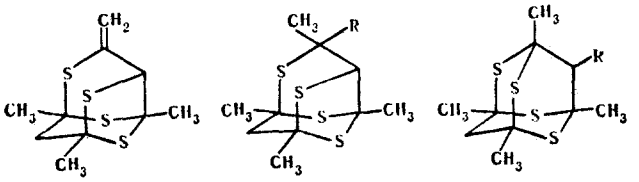
A comparative analysis was made of the mass spectra of monosubstituted 1,3,5,7-tetramethyl-2,4,6,8-tetrathiaadamantanes (TMTTA). It is shown that the pathways of monomolecular fragmentation depend on the character of the substituent and the isomeric form of the TMTTA. The principal lines in the mass spectra of the investigated compounds indicate the occurrence of competitive processes of fragmentation of the molecular ions (M^+) with detachment of the substituent from the M^+ ion or with cleavage of the cellular structure. The first process makes it possible to form a judgement regarding the mechanism of the fragmentation of the molecular ion and the site of primary localization of the charge on the fragment ions as a function of the donor—acceptor properties of the substituents, and the second process enables one to form a judgement regarding the character of the fragmentation of the cellular structures of the various isomeric forms.

The mass spectra of hydroxythiaadamantanes, 1,3,5,7-tetramethyl-2,4,6,8-tetrathiaadamantane (TMTTA) [1-3], and mono-, di-, tri-, and tetrasubstituted adamantanes [4, 5] have been described. In the present research we studied the mass spectra of 1- and 2a-substituted TMTTA derivatives that correspond to two isomeric forms — the proto (A) and thia (B) forms.



I (A) A B

II R=NHC_6H_5; III R=$NH(CH_2)_2OH$; IV R=$O(CH_2)_2OH$; V R=$SCOCH_3$; VI R=SC_4H_9; VII R=SCH_2OH; VIII R=OH; IX R=$OCOC_6H_5$; X R=$OCOC(CH_3)=CH_2$; XI R=$OCOCH_3$; XII R=$SCOCH_3$; XIII R=Br; XIV R=Cl

The hypothetical compositions of the principal fragments and the relative intensities (in percent of the total ion current) of the most characteristic lines in the mass spectra of the investigated compounds with respect to the single-isotope compounds are presented in Table 1.

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It was established that the fragmentation pathways indicated in [2, 3] are realized for all of the investigated compounds and that the difference between TMTTA and hydroxythiaadamantanes and tetrathiaadamantane consists in the fact that the relative intensities of the M^+, $[M - SH]^+$, and $[M - S_2H]^+$ ion peaks decrease when a substituent is introduced in the tetrathiaadamantane ring and that the pathways of fragmentation of the molecular ion in the first steps of fragmentation also change.

The pathways of fragmentation of the primary fragment ions depend on the site of attachment of the substituent and its donor–acceptor properties. Thus groupings that contain heteroatoms with unshared electron pairs (N and O) promote the formation of $[M - R]^+$ and $[R]^+$ ions, and fragmentation of substituent R at the β bond relative to the ring of TMTTA is also observed in the case of II, V, and X. In the case of compounds with acceptor (XIII and XIV) and sulfur-containing substituents (V-VII and XII) all of the intense peaks in the spectra are due to sulfur-containing ions.

Like polysubstituted adamantanes, with respect to the type of fragmentation of the molecular ion, the investigated compounds can be divided into two groups: 1) the substituent is split out in the form of a neutral fragment (VI, VII, XIII, and XIV); 2) the substituent is incorporated in the structure of the ions that give the maximum peak in the mass spectra (II-V and VIII-XII). However, because of the presence of sulfur atoms in the skeleton, it will be more convenient to separate the TMTTA derivatives into two groups as a function of the character of the fragmentation of M^+ in the first steps of the fragmentation.

The first group includes II-VII, X, and XII with low stabilities with respect to electron impact (W_M values from 1.2 to 5.6*) for which the primary fragmentation process is detachment of the substituent.

The second group includes I, VIII, IX, and XI with increased stabilities with respect to electron impact (W_M values from 4.7 to 9.9), in the mass spectra of which the intensities of the $[M - SH]^+$ and $[M - S_2H]^+$ ion peaks surpass the intensities of the $[M - R]^+$ ion peaks.

In the case of compounds of the proto form a monomolecular fragmentation reaction of the first type leads to the formation of intense peaks of $[M - R]^+$ ions with m/e 262, whereas in the case of compounds of the thia form it leads to the formation of ions with m/e 264 and 263; this is associated with the migration of hydrogen atoms from the substituent to the ring of TMTTA. The predominant detachment of a substituent at the α or β bonds and the formation of $[R_\alpha]^+$ or $[R_\beta]^+$ ions can evidently be explained by the stabilities of these fragments and the lower ionization potentials of these groups as compared with the ionization potentials of $\cdot SH$ and $\cdot S_2H$ radicals. In the case of fragmentation of V detachment of substituent R at the β bond predominates, whereas in the case of X α detachment of R is not observed at all. In the case of IV the γ-C–C bond in the substituent is cleaved instead of the β bond; however, an appreciable ion peak with m/e 262 (α cleavage) appears only when the ionizing-electron energy is lowered to 25-30 eV.

The intensities of the $[M - SH]^+$ and $[M - S_2H]^+$ ion peaks are low (0.3-0.9%) in the case of compounds that undergo fragmentation via the second pathway; they are, nevertheless, higher than the intensities of the $[M - R]^+$ ion peaks (0.1-0.4%). β Detachment of the substituent is observed in the spectra of IX and XI, and the positive charge is more likely retained on the $[R_\beta]^+$ fragments (the intensities of the $PhCO^+$ and CH_3CO^+ ion peaks in the mass spectra of these compounds are 26.5 and 9.5%, respectively) than on $[M - R_\beta]^+$. This fact can be explained, on the one hand, by the increased stabilities of the carbonyl-containing ions and their ability to localize the positive charge on the carbonyl carbon atom and, on the other, by the fact that compounds with oxygen-containing (and, to a lesser extent, nitrogen-containing) substituents (IV and IX-XII) split out an R_β fragment while retaining one oxygen (nitrogen) atom in the structures of the ions that give the principal peak in the spectrum; this probably also explains the appearance in the mass spectra of these compounds of ion peaks with m/e 170-173 and the superimpositions in the region of the signals of $[D + S]^+$ ion peaks (Scheme 1). For example, in the case of IV the heteroatom (oxygen) may be contained in the fragment with m/e 192 (i.e., it may replace one CH_3 group in an ion of the $[D + S]^+$ type), which, as a result of subsequent fragmentation, gives intense ion peaks with m/e 149 ($[192 - CH_3CO]^+$ 5.3%) and m/e 43 ($[CH_3CO]^+$ 11.4%).

*The W_M value is the fraction of the current of the molecular ions in the total ion current in percent.

TABLE 1. Mass Spectra of I-XIV: m/e Values (relative intensities of the peaks of the ions in percent relative to the total ion current with a correction for the single-isotope effect)

Compound	m/e values (relative intensities in percent)
I	262 (9,6), 229 (0,4), 197 (0,6), 189 (0,8), 171 (1,2), 170 (1,6), 158 (0,6), 157 (2,7), 139 (2,5), 131 (14,1), 130 (6,3), 127 (4,9), 126 (1,8), 125 (4,3), 117 (3,5), 99 (1,3), 98 (1,2), 97 (2,7), 85 (1,1), 71 (0,9), 59 (26,6)
II	355 (1,8), 278 (0,7), 264 (0,5), 262 (11,9), 229 (0,5), 197 (0,6), 192 (0,3), 191 (0,4), 190 (0,8), 189 (0,6), 170 (1,3), 158 (0,7), 157 (2,0), 139 (1,1), 132 (0,5), 131 (6,7), 130 (6,4), 127 (3,0), 126 (1,0), 125 (2,7), 117 (1,9), 99 (0,9), 98 (2,0), 97 (0,6), 93[a] (12,4), 85 (0,6), 77[b] (1,2), 73 (0,4), 71 (0,9), 59 (6,6)
III	323 (1,2), 290 (0,3), 262 (0,5), 230 (0,6), 198 (0,4), 192 (0,4), 191 (5,7), 189 (0,5), 173 (2,4), 171 (0,4), 159 (2,4), 158 (3,6), 144 (0,3), 143 (0,4), 139 (0,7), 131 (17,9), 130 (1,1), 126 (6,2), 125 (1,1), 117 (1,0), 100 (0,9), 99 (1,5), 98 (0,7), 97 (0,8), 85 (0,8), 59 (12,5), 45[b] (3,5)
IV	324 (2,8), 293 (0,9), 263 (1,2), 259 (0,7), 198 (0,3), 192 (1,1), 173 (0,5), 159 (0,5), 158 (0,3), 157 (0,3), 149 (5,3), 145 (0,3), 139 (1,7), 131 (17,0), 130 (1,0), 127 (2,6), 126 (0,6), 125 (1,1), 117 (2,0), 99 (1,4), 98 (0,8), 97 (1,0), 73 (0,8), 72 (0,5), 71 (0,5), 61[a] (1,7), 59 (16,7), 45[b] (2,4), 43 (11,4)
V	338 (5,6), 295 (0,8), 263 (0,4), 262 (8,0), 229 (1,1), 197 (0,5), 191 (0,5), 190 (0,4), 189 (2,7), 173 (0,6), 172 (0,6), 171 (3,9), 158 (0,9), 157 (1,0), 145 (0,3), 139 (3,4), 132 (1,1), 131 (20,5), 130 (1,4), 127 (1,2), 125 (1,5), 117 (1,1), 99 (0,9), 98 (0,9), 97 (1,5), 76[a] (1,1), 71 (0,6), 59 (10,9)
VI	352 (1,5), 264 (5,0), 263 (1,9), 262 (0,9), 231 (1,4), 199 (2,2), 191 (0,7), 189 (0,7), 171 (2,7), 157 (0,6), 145 (0,6), 139 (4,0), 132 (1,8), 131 (12,5), 126 (1,8), 125 (2,6), 117 (2,9), 99 (1,7), 98 (1,1), 97 (2,2), 85 (0,9), 73 (1,6), 71 (0,7), 59 (8,1), 57[b] (3,1)
VII	326 (1,9), 262 (4,1), 189 (1,5), 171 (3,5), 158 (0,5), 157 (0,8), 145 (0,4), 139 (1,9), 131 (37,6), 130 (1,4), 127 (0,9), 125 (1,3), 117 (1,2), 99 (0,9), 98 (0,9), 97 (0,8), 85 (0,5), 73 (0,4), 59 (30,0)
VIII	280 (9,9), 247 (0,8), 191 (4,8), 171 (0,3), 159 (2,6), 158 (1,0), 157 (0,7), 145 (0,8), 143 (0,5), 139 (0,3), 131 (6,6), 127 (10,6), 126 (2,2), 125 (1,8), 117 (2,1), 99 (3,0), 98 (1,0), 97 (1,6), 85 (1,0), 59 (32,1)
IX	384 (7,2), 351 (0,8), 246 (0,4), 191 (4,9), 159 (3,5), 145 (1,0), 139 (1,3), 131 (8,2), 127 (8,8), 117 (2,3), 105[b] (26,5), 99 (2,1), 77[c] (5,3), 59 (19,9)
X	348 (3,3), 315 (0,5), 279 (4,6), 246 (1,9), 191 (5,0), 159 (2,7), 158 (0,3), 145 (0,7), 139 (0,6), 131 (5,4), 127 (5,0), 126 (1,0), 125 (1,0), 117 (1,9), 99 (1,6), 98 (0,7), 97 (0,6), 69[b] (19,1), 59 (18,6), 41[c] (14,7)
XI	322 (4,7), 289 (0,9), 262 (0,4), 257 (0,3), 197 (1,4), 191 (4,7), 171 (1,0), 159 (3,4), 158 (1,0), 157 (1,5), 145 (1,2), 139 (2,5), 132 (0,4), 131 (12,5), 130 (1,2), 127 (8,6), 126 (2,1), 125 (3,0), 117 (2,7), 99 (2,4), 98 (1,5), 97 (1,9), 85 (1,0), 59 (23,6), 43[b] (9,5)
XII	338 (3,2), 305 (0,4), 273 (0,5), 264 (6,3), 263 (0,5), 262 (4,4), 231 (2,5), 199 (3,8), 189 (1,3), 171 (0,7), 170 (0,8), 159 (0,6), 158 (0,9), 157 (2,5), 139 (4,8), 132 (0,4), 131 (8,5), 130 (2,9), 127 (2,6), 126 (3,2), 125 (4,8), 117 (4,4), 99 (2,1), 98 (1,3), 97 (1,6), 85 (1,0), 76[a] (1,7), 73 (1,0), 71 (0,6), 59 (15,8), 43[b] (1,0)
XIII	342 (2,4), 309 (0,4), 263 (0,9), 231 (0,8), 199 (0,8), 191 (0,4), 189 (0,8), 171 (1,3), 158 (1,8), 157 (2,8), 139 (12,5), 131 (21,9), 127 (1,1), 125 (2,0), 117 (1,7), 99 (1,3), 98 (1,7), 97 (1,3), 85 (0,8), 73 (0,8), 59 (39,5)
XIV	298 (2,6), 265 (0,4), 263 (2,2), 233 (1,4), 191 (1,3), 189 (0,6), 172 (0,8), 171 (0,6), 159 (1,5), 158 (1,5), 157 (1,3), 143 (0,4), 139 (2,6), 131 (23,9), 127 (3,1), 126 (2,0), 125 (2,4), 117 (2,2), 99 (1,4), 98 (1,2), 85 (0,6), 73 (1,1), 59 (39,8)

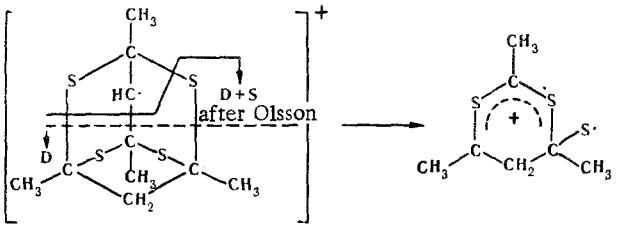
a) These are the $[R]^+$ fragments. b) These are the $[R_\beta]^+$ fragments. c) These are the $[R_\gamma]^+$ fragments.

The appearance of appreciable peaks in the m/e 170-173 region is associated not only with replacement of one sulfur atom by a heteroatom of the substituent, since a comparison of the relative intensities of these peaks in the spectra of the proto (0.5-3.9%) and thia (0.3-1.3%) compounds makes it possible to assume the possibility of the formation of $[C_8H_{11}S_2]^+$ fragments in the case of the proto compounds. Evidence for this is also provided by the presence in the spectra of V-VII of appreciable ion peaks with m/e 171 (2.7-3.9%), which cannot be explained by replacement of the sulfur atom of the TMTTA ring by a heteroatom of the substituent (since the heteroatom in these compounds is sulfur).

The charge in II is localized on both the $[M - R_\alpha]^+$ fragment with m/e 262 (11.9%) and on $[R_\alpha]^+$ with m/e 93 (12.4%), the peaks of which are the maximum peaks in the mass spectrum. This attests to high stability of these fragments, which for the $[R_\alpha]^+$ fragment (where R_α is aniline) is due not only to the nitrogen atom but also to the benzene ring, and provides evidence that the ionization potentials of TMTTA and aniline are close to one another.

Owing to the existence of two isomeric forms, the substituents can be found in the 1 and 2^a positions. The mass spectra of compounds belonging to the different forms differ with respect to different intensity ratios of the ion peaks with m/e 131 ($[E - H]^+$) and m/e 59 ($[CH_3{-}C{\equiv}S]^+$). The presence of a 1,3-dithiapentanone structure in the proto form promotes the formation of an ion with m/e 131, the relative intensity of the peak of which exceeds the intensity of the ion peak with m/e 59 in the spectra of all of the proto-substituted TMTTA. The elimination of a substituent probably makes the β- and γ-C—S bonds more labile relative to the 1 and 2^a carbon atoms, and this leads to cleavage of the TMTTA ring and the formation of stable fragments of the $[D + S]^+$, $[D]^+$, $[E - H]^+$, and $[CH_3{-}C{\equiv}S]^+$ type (Scheme 2). Whereas the peaks of rearranged $[D + S]^+$ ions are of low intensity in the spectra of hydroxythiaadamantanes, in the given series of compounds their intensities are close to the intensities of the $[D]^+$ ion peaks and even exceed the intensities of the peaks of compounds in the thia form.

Scheme 1

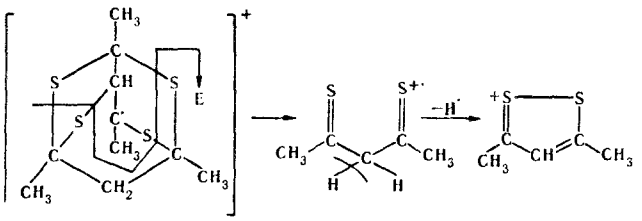


$[M-R_\alpha]^+$ $[D+S]^+$

In the case of compounds in the thia form the [D + S] ion peaks (0.8-5.0%) are more intense than the $[D]^+$ ion peaks (1.5-3.5%). The formation of $[D + S]^+$ fragments may take place through detachment of $^{\cdot}SH$ and $^{\cdot}C_3H_3$ radicals or elimination of dehydrogenated thiaacetone, whereas the formation of $[D]^+$ fragments may be the result of both detachment of $HCS^{\cdot}$ and $CH_3CS^{\cdot}$ radicals and elimination of an $^{\cdot}SH$ radical and thiaacetone via a mechanism that is the reverse of the McLafferty rearrangement. The possibility that all of the indicated processes occur is not excluded, and considering the possible migration of hydrogen during detachment of the substituent, one may therefore assume the appearance of ions of the $[D + S]^+$, $[D]^+$, and $[D - S]^+$ type, respectively, over m/e ranges of 189-191, 157-159, and 125-127.

In addition to the above-indicated groups of ions, primarily $[E - H]^+$ fragments with m/e 131 are formed in the case of compounds in the proto form.

Scheme 2



$[M-R]^+$ $[E]^+$ $[E-H]^+$

It might be assumed that the $[E - H]^+$ ion would be formed from $[D + S]^+$ ions as a result of the loss of $CH_3CS^{\cdot}$ and subsequent rearrangement; however, this sort of fragmentation of the ring is evidently less likely than detachment of a sulfur atom from the side chain. The formation of $[CH_3{-}C{\equiv}S]^+$ ions most likely occurs in later steps of the fragmentation of the $[M - R]^+$ fragments.

Thus the mass spectral difference in the proto and thio forms is manifested not only in the different ratios of the ion peaks with m/e 131 and 59 but also in the entire fragmentation process. In some cases (II, III, V, and VII) substituent R leads to deviations from the indicated schemes, apparently as a result of migration of hydrogen atom from the 2^a position of TMTTA to the substituent.

EXPERIMENTAL

The mass spectra of I-XIV were obtained with an MKh-1303 mass spectrometer equipped for direct introduction of the samples at 50-100°C and an ionizing-electron energy of 70 eV.

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ACETYLENIC α-AZIRIDINYLCARBINOLS IN REACTIONS WITH HYDRAZINE AND METHYL-SUBSTITUTED HYDRAZINES

A. V. Eremeev, D. A. Tikhomirov, V. A. Tyusheva, and É. É. Liepin'sh

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It is shown that hydrazones of phenylpropiolaldehyde are formed in the reaction of an acetylenic α-aziridinylcarbinol — 1-hydroxy-1-aziridinyl-3-phenyl-2-propyne — with hydrazine and methyl — and 1,1-dimethylhydrazine. The reaction of this carbinol with sym-dimethylhydrazine leads to the formation of phenylacetylene and 1-formyl-1,2-dimethylhydrazine, 1-aziridinyl-1-hydrazino-3-phenyl-2-propyne, or 3,6-diphenylethynyl-1,2,4,5-tetramethyltetrazine, depending on the reaction conditions. It was established that the reaction of 1-hydroxy-1-aziridinyl-3-phenyl-2-propyne and 1-hydroxy-1-(2-methylaziridinyl)-2-propyne with hydrazine and methyl-substituted hydrazines is realized through an intermediate step involving the decomposition of the acetylenic aziridinylcarbinols to an α-alkynyl aldehyde and ziridine.

Acetylenic α-aziridinylcarbinols, which we have previously obtained [1], are the first representatives of α-aziridinylcarbinols of the unsaturated series. In the present research we studied the reactions of 1-hydroxy-1-(2-methylaziridinyl)-2-propyne (I) and 1-hydroxy-1-aziridinyl-3-phenyl-2-propyne (II) with hydrazine and methyl-substituted hydrazines.

The currently available data [2] provide evidence that saturated α-aziridinylcarbinols react with primary and secondary amines to give aminals only through an intermediate step involving the decomposition of the aziridinylcarbinols to aldehydes and aziridines. However, no data at all are available on the reactivities of aziridinylcarbinols in reactions with hydrazine and its derivatives.

We have established by PMR and IR spectroscopy that the corresponding hydrazones of phenylpropiolaldehyde (III, IV, and V) are formed in the reaction of acetylenic α-aziridinylcarbinol II with hydrazine and methyl- and 1,1-dimethylhydrazine (see the scheme below). The hydrazones are oily liquids and were found to be mixtures of syn and anti isomers (Table 1). However, the less stable anti isomers gradually undergo isomerization to the syn isomers. The rate of conversion of the anti isomers to the syn isomers of hydrazones III, IV, and V increases as the number of methyl groups attached to the amine nitrogen atom increases.

From the data in [1, 2] it may be assumed that the reaction of hydrazine and methyl-substituted hydrazines with acetylenic aziridinylcarbinol II is realized through an intermediate step involving the decomposition of the indicated aziridinylcarbinol to an aldehyde and aziridine (see the scheme below). The experimental data provide evidence for this premise.

Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, Riga 226006.

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