

Characteristic differences in EI mass spectra of 2,2,6,6-tetramethylpiperidine derivatives

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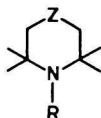
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Received 23 November 1984

The characteristic differences in the fragmentation pathways in the mass spectra of the studied derivatives of 2,2,6,6-tetramethylpiperidine have been found. The subsequent loss of methyl, ammonia or hydroxylamine and $\cdot\text{C}\equiv\text{CH}$ fragment is the most characteristic feature for the amines and the hydroxylamines of interest.

Обнаружены характеристические различия в масс-спектрах при фрагментации изучаемых производных 2,2,6,6-тетраметилпиперидина. Последующая потеря метила, аммиака или гидроксилamina и $\cdot\text{C}\equiv\text{CH}$ фрагмента является самой характеристической чертой изучаемых аминов и гидроксиламинов.

In this paper the possible fragmentation pathways in EI mass spectra of the title compounds were compared. A general formula of the compounds of interest is



I-XII

R	Z			
	$-\text{CH}_2-$	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}- \end{array}$	$\begin{array}{c} \text{OH} \\ \\ -\text{CH}- \end{array}$	$\begin{array}{c} \text{OCOPh} \\ \\ -\text{CH}- \end{array}$
H	I	IV	VII	X
O \cdot	II	V	VIII	XI
OH	III	VI	IX	XII

The mass spectra of the nitroxides II, V, and VIII (EI, 70 eV) were described by Morrison and Davies in [1]. The spectra of the amines I, IV, VII and the radicals II, V, VIII (EI, 30 eV) were described in [2]. To our knowledge the spectra of

hydroxylamines and benzoates *III*, *VI*, *IX—XII* have never been reported.*

The mass spectra (EI, 70 eV) of the compounds *I—XII* were measured. The metastable transitions arranged in the table and the bar graphs will be sent to the interested by the authors on request. The spectra of *I*, *II*, *IV*, *V*, *VII*, and *VIII* were in accordance with those in [1, 2]. We noticed a small difference between the spectrum of *VIII* taken in our laboratory and that reported in [1]. The intensity of the peaks at $m/z=57$ and $m/z=71$ was inverted.

The loss of the fragment with the relative molecular mass $M_r=17$ was observed in the spectra of all amines. This transition was confirmed by the metastable peaks. In our opinion this fragment is NH_3 (in opposition to [2]). For the hydroxylamines *III*, *IX*, and the radical *II* the loss of NH_2OH ($M_r=33$) was confirmed. The fragmentation pathway for the amines *I*, *IV*, *VII*, *X* and the hydroxylamines *III*, *IX* is proposed in Scheme 1.

In *I*, *III*, *IV* the ion *a* is formed from the parent ion by the loss of $\cdot\text{CH}_3$ and in *VII*, *IX*, *X* by the subsequent loss of $\cdot\text{CH}_3$ and H_2O or PhCOOH . The structures *b—d* may be proved by the hyperconjugation mechanism. The cyclization of the intermediate *e* may lead to the formation of a 5-membered (g_1 , g_2 , g_3) or 6-membered ring (f_1 , f_2). The 5-membered structure g_3 is proposed in [1] as the structure of the ion at $m/z=109$ forming in another rearrangement.

The formation of the intermediate structure *e* for the ion at $m/z=107$ (observed in the spectrum of the amine *X*) is caused by the loss of the fragment $\cdot\text{CH}\equiv\text{C}$ ($M_r=25$). It was confirmed by the metastable peak.

The sequence of the ions at $m/z=107$, 82, 67 was present in the spectra of *VII*, *IX*, and *XII*. The sequence at $m/z=109$, 84, 69 was observed in the spectra of *I*, *II*, and *III*.

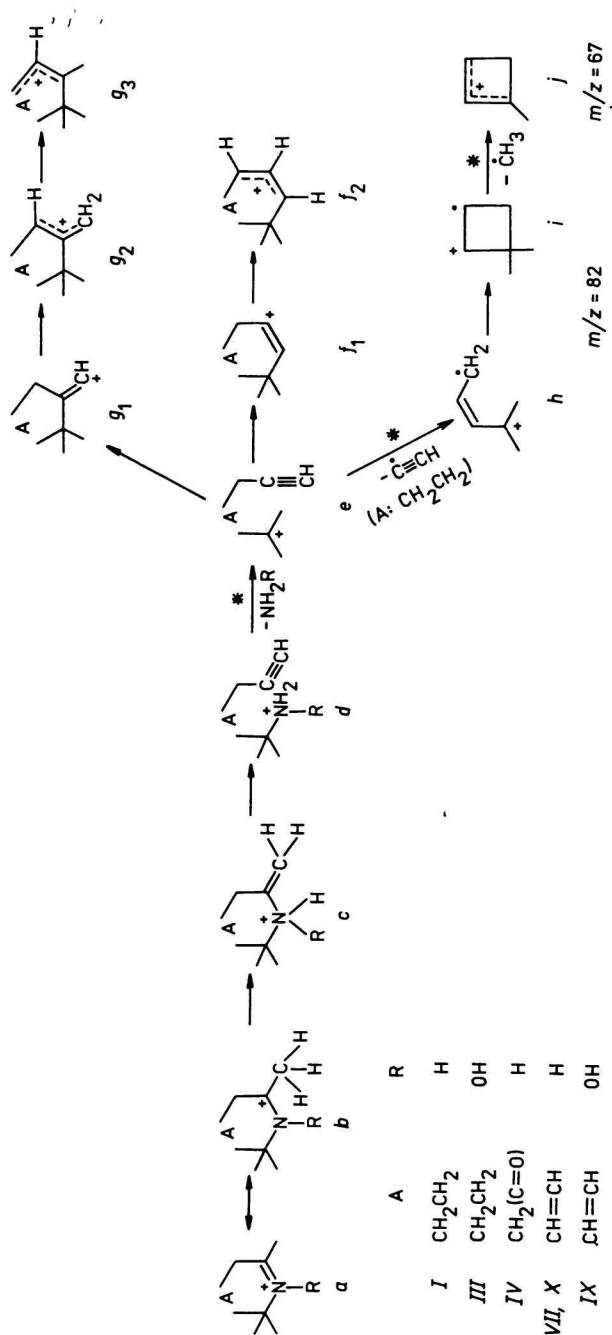
Another fragmentation pathway seems to be confirmed by the metastable peak analysis for the loss of NH_2OH from the parent ion of the radical *II* (Scheme 2).

The formula C_9H_{15} for *k* has already been reported in [1]. The loss of HNO is the typical fragmentation pathway for all hydroxylamines (*III*, *VI*, *IX*, and *XII*) [2], whereas the elimination of $\cdot\text{NO}$ is characteristic feature for the molecular ions of the nitroxyl radicals *II*, *V*, *VIII*, and *XI* [1, 3, 4]. The loss of HNO was observed in the following steps (Scheme 3).

The structure of the ion o_1 was also confirmed in the fragmentation pathway of the radical *V*, but in another way — by the subsequent elimination of $\cdot\text{NO}$ and $\cdot\text{CH}_3$ from the ion at $m/z=116$.

In [2] a simultaneous loss of the $\cdot\text{NO}$ and CO fragments from the ion at $m/z=114$ was described. To our knowledge the elimination does not occur

* Recently the mass spectra of at least *I*, *II*, *V*, *VII*, *VIII* were reported in [14]. (Note added in proof.)

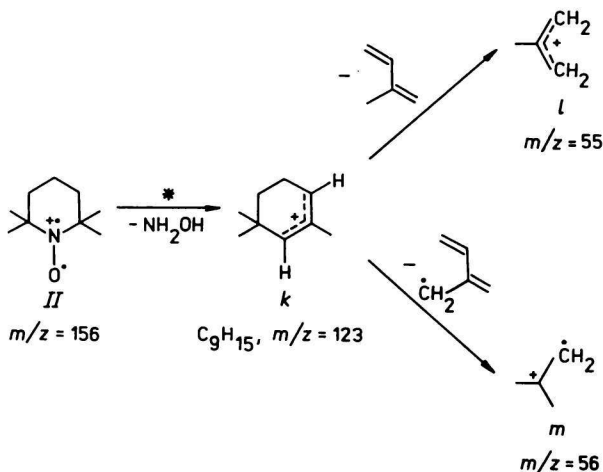


Scheme 1

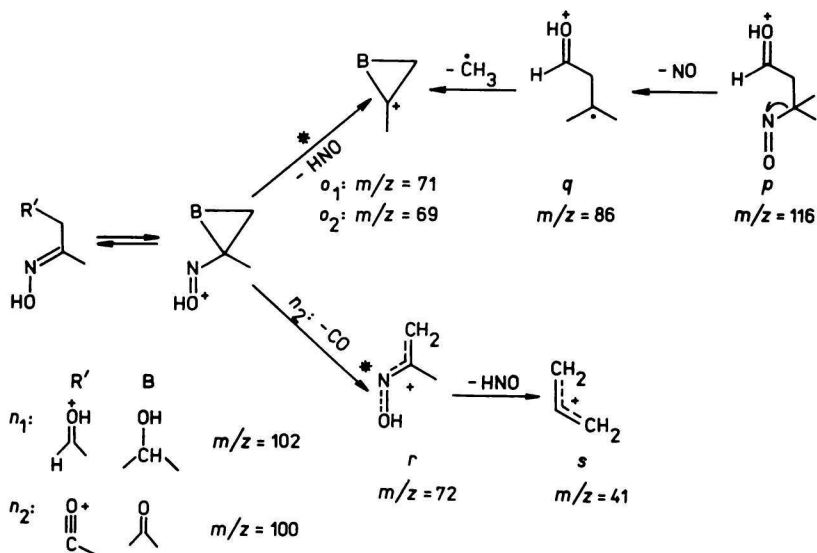
e, f or g :
 I, III $m/z = 109$
 IV $m/z = 124$
 VII, IX, X $m/z = 107$

simultaneously but subsequently. It was confirmed by the metastable peaks. It is in accordance with our former investigations [5]. The presence of the peak at $m/z = 112$ in IV may be also explained by the loss of CO from the ion t . The ion u loses acetoneimine and the allyl-stabilized ion l is formed (Scheme 4).

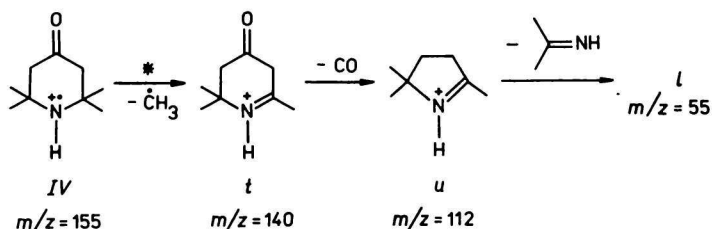
The loss of acetoneimine ($M_r = 57$) is typical for the amines, while the elimination



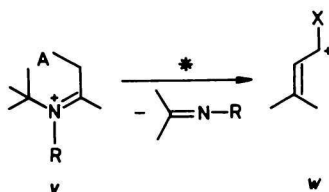
Scheme 2



Scheme 3



Scheme 4



A	R	X
CH ₂ CH ₂	H	H
CH ₂ (C=O)	=O	H
CH ₂ CHOH	OH	H
CH ₂ CH ₂	H	O [•]
CH ₂ CH ₂	H	OH
CH ₂ (C=O)	=O	OH

Scheme 5

of acetone oxime ($M_r = 73$) is typical for the hydroxylamines. The loss of fragment with $M_r = 72$ (probably $(CH_3)_2C=N-O\cdot$) was observed for the radical *II* (Scheme 5).

In the case of benzoates *X–XII* this type of elimination was not observed. In the spectra of these compounds the presence of $PhC\equiv O^+$, Ph^+ , and $C_4H_3^+$ ions (typical for the benzoyl derivatives) was recorded.

In almost all the compounds the characteristic loss of $CH_2=C=O$ or $CH_2=CH-X$ ($X = H, OH, OCOPh$) was observed. It is McLafferty's rearrangement with formation of the ion at $m/z = 98$ [1, 2], and the isobutene ($M_r = 56$) elimination. Water or benzoic acid was easily eliminated from the alcohols or the benzoates. The respective alkene was formed [1, 2].

The $[M - \cdot CH_3]^+$ peak is the characteristic feature of the amines and the hydroxylamines. It is more abundant than the parent one. In the spectra of the nitroxides the $[M - \cdot CH_3]^+$ peak is less intense than the molecular one, as well as the $[M - M(M_r = 14)]^{+ \cdot}$ (e.g. $[M + M(M_r = 1) - \cdot CH_3]^+$) one [1]. It is caused by the possibility of the elimination of the second methyl group and formation of the stable $[M - M(M_r = 30)]^{+ \cdot}$ ion [1].

The ions at $m/z = 58$ and $m/z = 42$ which are present in the spectra of all amines and hydroxylamines, are identified as $(\text{CH}_3)_2\text{C}=\text{N}^+\text{H}_2$ [2] and $\text{CH}_3\text{C}=\text{N}^+\text{H}$ ($\text{M}(\text{M}_r = 58) - \text{CH}_4$), respectively. In the spectra of the nitroxides both the above-mentioned ions are absent.

Experimental

The electron impact mass spectra were obtained at 70 eV using an LKB 9000 A mass spectrometer; ion source temperature 250 °C; accelerating voltage 3.5 kV; trap current 60 μA . The compounds *III*—*XII* were introduced by direct inlet at 25—65 °C. The compounds *I** and *II* were introduced as 5 % acetone solutions (1 μl) through the GLC column (length 4 m, 3 % SE-30 on Chromosorb G) and the molecular separator of Becker—Ryhage type was used; carrier gas — helium. The temperature of injector 180 °C, of column 130 °C, of separator 235 °C.

The title compounds were obtained according to the respective literature: the amines *I* [6], *IV*, *VII*, *X* [7]; the nitroxides *II* [8], *V* [9], *VIII* [10], *XI* [11]; the hydroxylamines *III*, *VI*, *IX*, *XII* [12].

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* When the volatile amine *I* was introduced by DI, only the spectrum of the triacetone (*IV*) azine was obtained. Both *I* and azine are the products in the Wolff—Kishner reduction of *IV* [6, 13].