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THE MASS SPECTRAL LOSS OF N - SUBSTITUENTS IN α,ω - DIAMINOALKANES

Part 13. Mass Spectral Behaviour of Nitrogen Containing Compounds (1)

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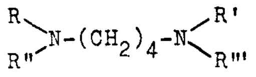
The mass spectral loss of N-acyl and N-alkyl residues from N-acylated or N-alkylated amines or their fragments has been discussed previously, see e.g. (2). Such N-substituents are usually eliminated under hydrogen rearrangement as neutral molecules (e.g., as ketene in case of N-acetyl derivatives). N-Alkylated compounds favour the elimination of the corresponding alkenes (or cycloalkanes) if the nitrogen is quaternary and therefore charged. The elimination of N-substituents without hydrogen rearrangement is rare; e.g. in the mass spectrum of trimethylhydrazine an intense M - CH_3 signal is registered (α-cleavage).

In connection with our work on the structure elucidation of spermidine alkaloids (3), we investigated an interesting class of compounds, which show unusual mass spectral behaviour. N-Di-, tri-, and tetra-substituted derivatives of putrescine show predominant peaks which correspond to the loss of N-substituents from the molecular ion without hydrogen rearrangement; this is exemplified by the spectrum of N,N'-diethyl-N,N'-diacetyl putrescine (Fig. 1). In the spectrum measured at 70ev (Fig. 1a) there are some other fragmentation reactions (e.g. α-cleavage) but at 12ev (Fig. 1b) the elimination of $\cdot COCH_3$ is the predominant reaction. The corresponding peaks of some other putrescine derivatives are given in the Table.

 $R(R'')N-(CH_2)_4-N(R')R'''$				70 ev rel. %			12 ev rel. %		
R	R'	R"	R"'	M^+	M-R	M-R'	M^+	M-R	M-R'
CH_2Ø	H	H	H	<1	10	-	<1	45	-
C_2H_5	C_2H_5	H	H	7	5	-	26	56	-
$COCH_3$	$COCH_3$	H	H	8	15	-	15	30	-
CH_2Ø	CH_2Ø	H	H	9	15	-	12	58	-
COØ	COØ	H	H	4	7	-	39	90	-
COØ	CH_2Ø	H	H	<1	<1	7	1	<1	31
CH_2Ø	COØ	COØ	H	<1	<1	36	<1	<1	100
$(CH_2)_3$-O-$COCH_3$	$COCH_3$	$COCH_3$	H	41	-	6	13	-	100
$(CH_2)_3$-O-Ø	$COCH_3$	$COCH_3$	H	*) <1	-	4	2	-	6
CH_3	CH_3	CH_3	CH_3	25	6	-	47	12	-
C_2H_5	$COCH_3$	$COCH_3$	C_2H_5	3	-	60	3	-	100
CH_2CD_3	CH_2Ø	CH_2Ø	CH_2CD_3	7	5	16	42	18	100
$COCH_3$	CH_2Ø	CH_2Ø	$COCH_3$	3	47	4	7	100	11
$COCD_3$	CH_2Ø	CH_2Ø	$COCD_3$	1	37	3	3	100	12
$(CH_2)_3$-O-Ø	$COCH_3$	$COCH_3$	$(CH_2)_3$-O-Ø	*) 1	-	20	3	-	26

*) In these compounds the main reaction is the S_Ni-type fragmentation, see (4).

Table : The loss of N-substituents in the mass spectra of putrescine derivatives.

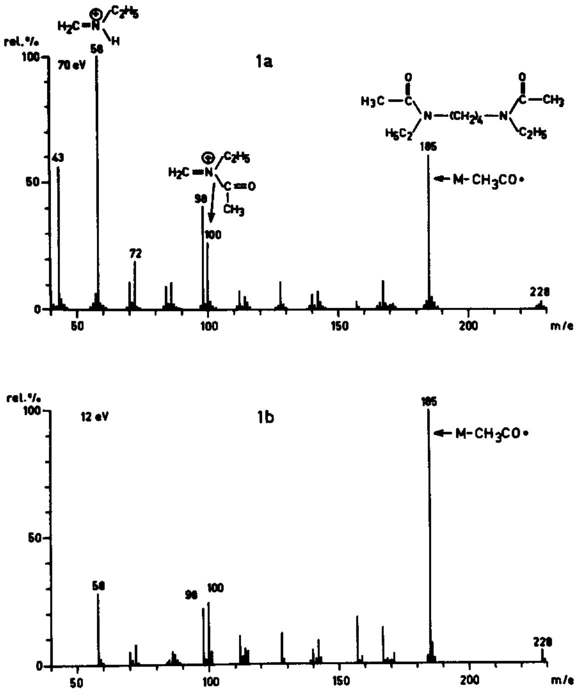
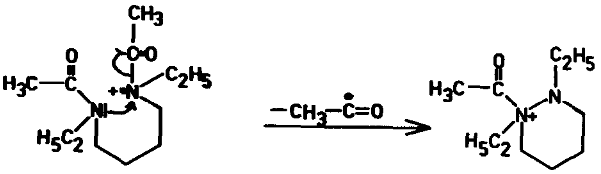


Fig. 1. Mass spectrum of N,N'-diethyl-N,N'-diacetyl putrescine;
Fig. 1a at 70ev, 1b at 12ev.

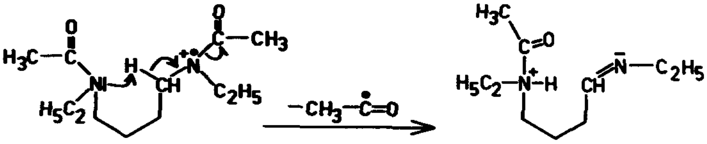
The elimination of these substituents is a one step process (metastable peaks; in all cases signals corresponding to alternative transitions like $M^+ \longrightarrow (M-1) \longrightarrow (M-R)$ or $M \longrightarrow (M-R+1) \longrightarrow (M-R)$ are missing). By high resolution mass spectrometry it was found that the tabulated peaks are singlets with the expected elemental composition. D-shifts (substituent ⟶ amine residue) were not observed. These results are contradictory to the mass spectra of N-substituted monoamines (2). The different behaviour of both groups of compounds must be due to the second nitrogen function.

On the basis of our results it is not possible to differentiate between the following two reaction mechanism:

1.



2.



We prefer mechanism 2 because of the "internal M -1 peak" which is analogous to the M -1 peak in the spectra of the corresponding monoamines. A detailed analysis of this mechanism is in progress. The mass spectral loss of N-substituents is not limited to putrescine derivates. It is also observed in the mass spectra of spermine and spermidine derivatives in N,N'-disubstituted α,ω-diaminoalkanes and N-substituted ω-aminoalkane carboxylic esters. In derivatives of α,ω-diaminoalkanes an intense signal corresponding to $M-(CH_2-N<^{R}_{R'})$ is found in addition (5) (6).

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References

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(6) The $M-(CH_2-N<^{R}_{R'})$ peak corresponds to the loss of 73 u in the spectrum of methyl 10-amino-undecanoate (7).
(7) R.E. Wolff and A. Caspar, Tetrahedron Letters 1970, 1807.