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MASS SPECTRAL STUDIES. V. FRAGMENTATION OF AMIDINES (1)

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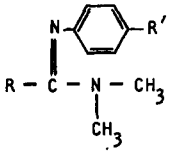
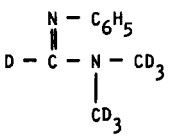
Recently we have reported on the skeletal rearrangement of various types of molecules under electron impact (1c,2). We wish to report here on the rearrangement of several N,N,N′-tri-substituted amidines (I - VI).

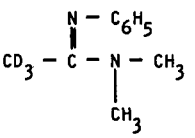


I, R = R′ = H
II, R = CH_3 ; R′ = H
III, R = C_6H_5 ; R′ = H
IV, R = H ; R′ = NO_2
V, R = H ; R′ = OCH_3
VI, R = CH_3 ; R′ = OCH_3

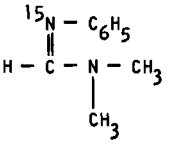
Detailed information on the fragmentation modes of these amidines was obtained from a study of the isotope-labeled compounds VII, VIII, IX and X.



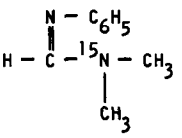
VII



VIII



IX

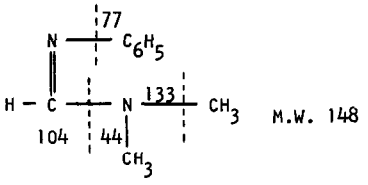


X

All the amidines (I - X) show an intense molecular ion, M^+ and also a significant $[M - 1]^+$ peak. The fact that VII displays a $[M - 1]^+$ peak rather than a $[M - 2]^+$ peak signifies that the formation of this peak involves the loss of an aryl proton.

The most intense peak is at m/e 44 for amidines I, IV and V, but in the spectra of II and VI, M - 44 is the strongest peak. In the spectrum of

III, M - 44 is a prominent peak although the most intense peak is at m/e 77. The strongest peak for X is at m/e 45 and that for VII at m/e 50 showing that a facile cleavage occurs between the amino nitrogen and the trigonal carbon. Other expected major fragments from the straight cleavage were also observed (for example, see XI for the fragments from N,N-dimethyl-N'-phenyl-formamidine, I).

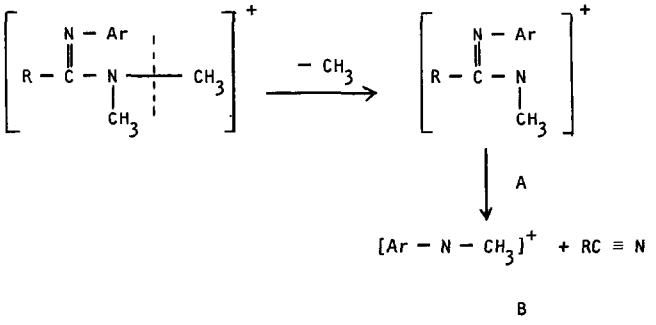


M.W. 148

XI

The strong $[M - 15]^+$ peak in I and $[M - 18]^+$ peak in VII indicate the ease of scission of an $N - CH_3$ bond. In amidine II where there is a choice between the cleavage of $C - CH_3$ and $N - CH_3$ bonds, the scission of the latter continues to be significant. Evidence for this is provided by the spectrum of VIII in which the $[M - 15]^+$ peak is strong.

Besides the fragments formed by simple cleavage there are peaks that can be explained only on the basis of skeletal rearrangement. Thus, the fragment A formed by the cleavage of an $N - CH_3$ bond must undergo a rearrangement and a scission to produce fragment B .



The rearrangement of ion A to ion B is supported by the appropriate metastable peaks in the spectra of I (calcd. 84.4, found 85), II (calcd. 76.4, found 77), V (calcd. 113.4, found 114) and VI (calcd. 104.5, found 105).

The composition B assigned to the peak at m/e 106 in the spectrum of I is supported by the observation that substitution on the phenyl ring produces the expected shift in the m/e of fragment B : to m/e 151 in the spectrum of IV and m/e 136 in the spectra of V and VI. Furthermore, the spectrum of VII shows a prominent peak at m/e 109. Evidence for aryl migration is also provided by the spectrum of N-methyl-N,N′-diphenyl formamidine (XII). A peak is observed at m/e 168 corresponding to the expected fragment C .

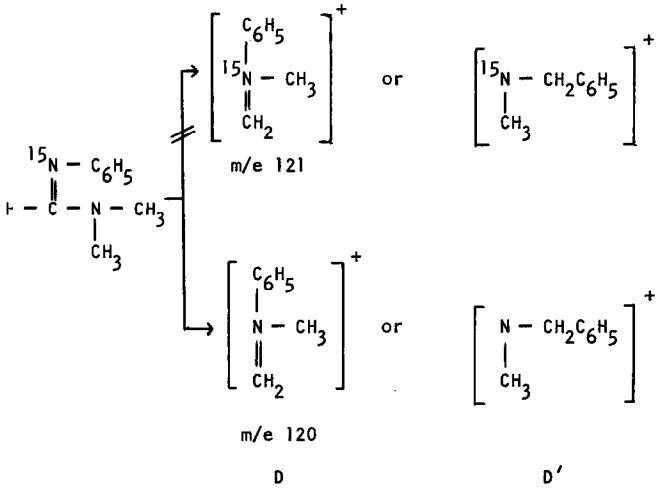
XII C

The fragment B could be produced from I in two different ways: (a) by the migration of a methyl group to the imino nitrogen, (b) by the migration of the aryl group to the amino nitrogen. The peak at m/e 107 in the spectrum of IX (see Fig. 1) indicates that the fragment C arises, at least in part, by mechanism (a).

In the spectrum of I the peak at m/e 120 must correspond to the fragment D or D′* since a peak is found at m/e 165 in the spectrum of

* The representation $[\overset{CH_3}{\overset{|}{N}} - CH_2 - C_6H_5]^+$ has been used to avoid implying preference between $[H - \overset{+}{\underset{\|}{N}} - CH_2 - C_6H_5]$, $[H - \overset{+}{\underset{|}{N}} = CH - C_6H_5]$ and other forms that are reasonable on the basis of concepts valid for the ground state. The requirements of an excited state may be quite different from those of the ground state (3).

IV, a peak at m/e 150 in the spectrum of V and VI and a peak at m/e 125 in the spectrum of VII. It is reasonable to expect that D (or D') arises by the migration of the aryl group to the amino nitrogen containing moiety rather than the migration of two alkyl groups to the imino nitrogen containing moiety. The spectrum of the ^{15}N – labeled amidine IX (Fig. 1) shows a peak at m/e 120 and not 121, whereas the amidine X does show the corresponding peak at m/e 121. This constitutes conclusive evidence for the presence of the amino nitrogen in the fragment D (or D').



The mass spectrum of I was recorded at different values of the ionization potential. It was found that even at 10 ev the peak at m/e 120 was prominent while many of the other peaks became insignificant.

A detailed account of the present work and further investigations in progress will appear elsewhere.

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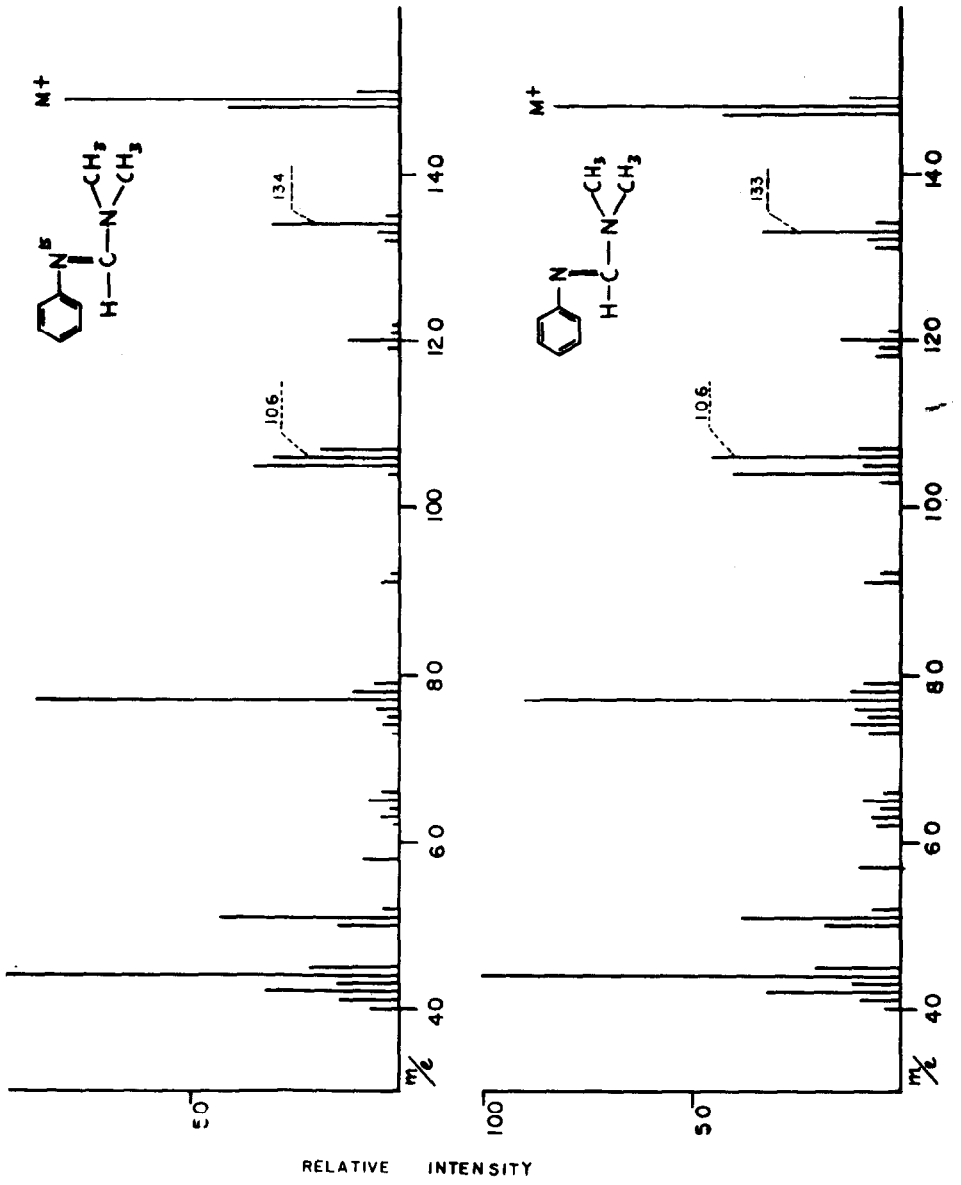
M+
134
106
133
106
100
50
40
60
80
100
120
140
m/e
RELATIVE INTENSITY

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