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THE ELECTRON-IMPACT INDUCED FRAGMENTATION OF SOME DIOXAMIDOXIME DERIVATIVES

by

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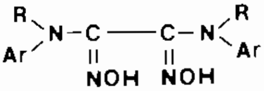
Abstract: *The mass spectra of five symmetric N,N'-bis-aryl- and four symmetric N,N'-bis-alkyl-N,N'-bis-aryl-dioxamidoxime derivatives are reported and compared with those of two 3,4-diamino-1,2,5-oxadiazoles, prepared from the corresponding dioxamidoximes by thermal dehydration. Attempts were made for deuterium labelling for some of the studied compounds, but the partly deuterated products didn't provide more evidence in favour of the proposed mechanism.*

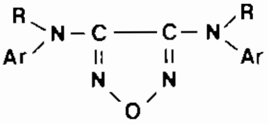
INTRODUCTION

Although the electron-impact induced fragmentation of aldoximes and ketoximes has been reported in detail in some relatively early papers[1], only two papers dealing with the mass spectrometric behaviour of simple benzamidoximes have been published so far[2,3].

In this paper the mass spectra of some symmetric N,N'-bis- and N,N,N'-N'-tetrasubstituted derivatives of dioxamidoxime of the general type I are reported. These compounds were prepared through a double 1,3-dipolar addition of cyanogen di-N-oxide with primary and secondary amines[4]. The observed fragmentation pattern is further compared with that of two 3, 4-diamino-1, 2, 5-oxadiazole derivatives II, prepared from the corresponding compounds I by heating.



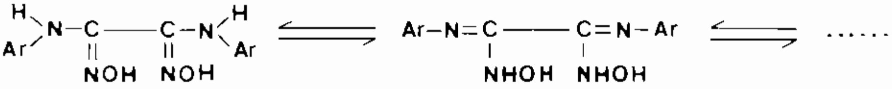
I(a–i)



II(h,i)

I, II: (a) Ar = C_6H_5, R = H; (b) Ar = 2-CH_3-C_6H_4, R = H;
(c) Ar = 3-CH_3-C_6H_4, R = H; (d) Ar = 4-CH_3-C_6H_4, R = H;
(e) Ar = 2,4,6-$(CH_3)_3C_6H_2$, R = H; (f) Ar = C_6H_5, R = CH_3;
(g) Ar = C_6H_5, R = C_2H_5; (h) Ar = 2-CH_3-C_6H_4, R = CH_3;
(i) Ar = 3-CH_3-C_6H_4, R=C_2H_5;

Although compounds $I_{(a-e)}$ (R=H) can exist in several tautomeric forms (like III, etc) it has been suggested[4] that they adopt the dioximino structure I.



I III

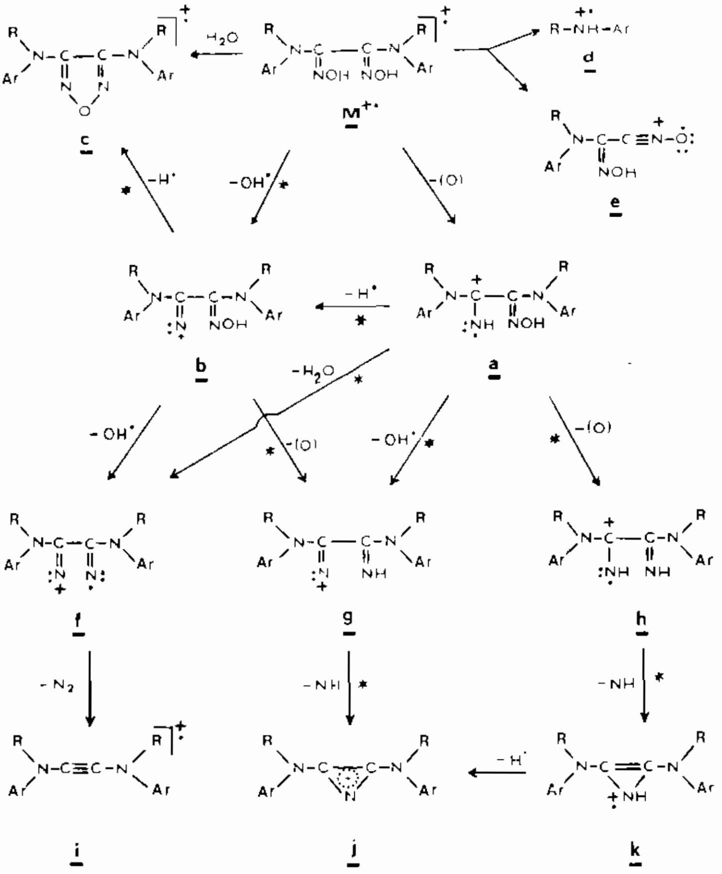
This is further supported by the study of the NMR spectra of compounds I in dimethyl-d_6 sulfoxide, where it was observed that the hydroxyl protons of all compounds studied resonate at very similar τ values[5]. For example the hydroxyl protons of compounds $I_{(b)}$ and $I_{(h)}$ appear at τ=-0.30 and -0.32 respectively. Furthermore, it was found that both hydroxyl protons in each of the compounds studied are equivalent. From the present mass spectral data it is concluded that tautomeric forms like III participate possibly in the structure of the molecular ion $M^{+\cdot}$ of compounds $I_{(a-e)}$, before fragmentation.

The fragmentation processes which will be mainly discussed in this study are concerned with the loss of O, $OH^{\cdot}$ and H_2O from the molecular ions, as well as from the ions produced by these primary fragmentation reactions. The recorded mass spectra of all studied compounds are given in Fig. 1-5 and in tabular form in Table I. Relative intensities are given in parentheses.

RESULTS — DISCUSSION

Although bis-aryl-dioxamidoximes $I_{(a-e)}$ and bis-alkyl-bis-aryl-dioxamidoximes $I_{(f-i)}$ show a number of similar primary fragmentation reactions, general for all of them, it is easily noticeable that compounds $I_{(a-e)}$ show also some substantial differences. The comparison is mainly refered to the fragmentation pathway of the central dioximino group leading to fragments observed in the higher mass number region of the recorded mass spectra.

The general primary fragmentation pathway of compounds I is given in scheme I. It is necessary to state that the ions given in all schemes can exist in more than one structural forms.



Scheme I

A similar fragmentation pattern has been suggested for the primary fragmentation reactions of some mono-amidoximes[3], where it is reported that the molecular ions were found in all cases with moderate relative intensities, while loss of O, OH˙ and H_2O were the most interesting fragmentations, leading to the very abundant ions M-16, M-17 and M-18 respectively. It has also been reported that aniline

$(C_6H_5\overset{+\cdot}{N}H_2)$, which appears as the base peak in the mass spectrum of benzanilide oxime, formed directly from the molecular ion by elimination of a benzonitrile oxide molecule, as it is evidenced by the appropriate metastable ion[3].

Like in the case of mono-amidoximes tbe molecular ions of compounds $I_{(a-e)}$ were found in all cases with moderate relative intensities and the molecular ions of compounds $I_{(f-i)}$ were found with lower abundance. The same differences between compounds $I_{(a-e)}$ and $I_{(f-l)}$ were also observed in the relative intensities of ions *a*, while ions *b* and *c* were found more abundant in the recorded mass spectra of compounds $I_{(f-l)}$. Ions *d* were found in all cases with very high relative abundance. On the other hand ions *e* were found in very low abundance. These two transitions were not followed by the appropriate metastable ions and it is possible for ions *d* to be formed by alternative pathways. Further fragmentation of the primary formed ions *a* and *b* gave the fragments *g*, *f* and *h* as it is evidenced by the appropriate metastable ions, confirmed in almost all studied mass spectra. Ions *g*, *f* and *h* were again found with higher relative intensities in the spectra of compounds $I_{(a-e)}$.

The fragment M-18 is the most interesting of all the others given in scheme I and is attributed to 3,4-diamino-1,2,5-oxadiazole ion of the general structure *c*. As it is shown in scheme I ions *c* can be formed in one step from $M^{+\cdot}$ by loss of H_2O or from ions *b* by loss of $H^\cdot$ However the former transition was not followed by any metastable ion in the studied spectra. The suggested structure *c* is supported by the fact that the fragmentation of $I_{(i)}$ and of the corresponding diaminofurazan $II_{(i)}$ follows a closely similar pathway. The same was also observed for compounds $I_{(h)}$ - $II_{(h)}$. This aspect is also in agreement with the reported formation of 1,2,5-oxadiazole ions as the dehydration fragments of the molecular ions in the mass spectra of some aryl- and aroyl derivatives of glyoxime[6]. Compounds $II_{(h,l)}$ were prepared by thermal dehydration of compounds $I_{(h,l)}$. Efforts for the analogous preparation of $II_{(a)}$ and $II_{(e)}$ failed.

The proposed fragmentation pathway of ion c is given in scheme II and the mass spectra of compounds $I_{(i)}$ and $II_{(i)}$ in Fig. 1 and 2 respectively. Fragments *j*, *l*, *n* and *o* were found in recorded mass spectra of all studied compounds $I_{(a-l)}$. The proposed fragmentation mechanisms are in agreement with those reported for 3,4-bis-alkyl-[7] and 3-amino-4-phenyl-1,2,5-oxadiazole[8]. A very interesting feature in the

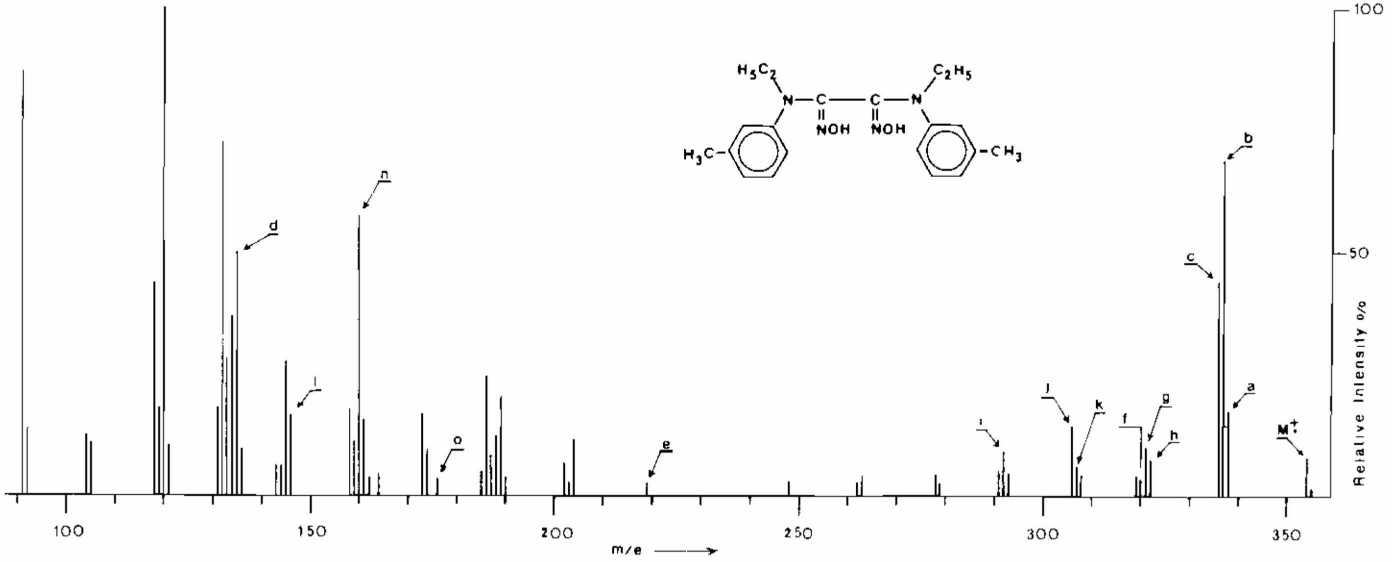


Fig. 1. Mass spectrum of N,N'-diethyl-N,N'-bis(m-methyl-)phenyl-dioxamidoxime (Ii).

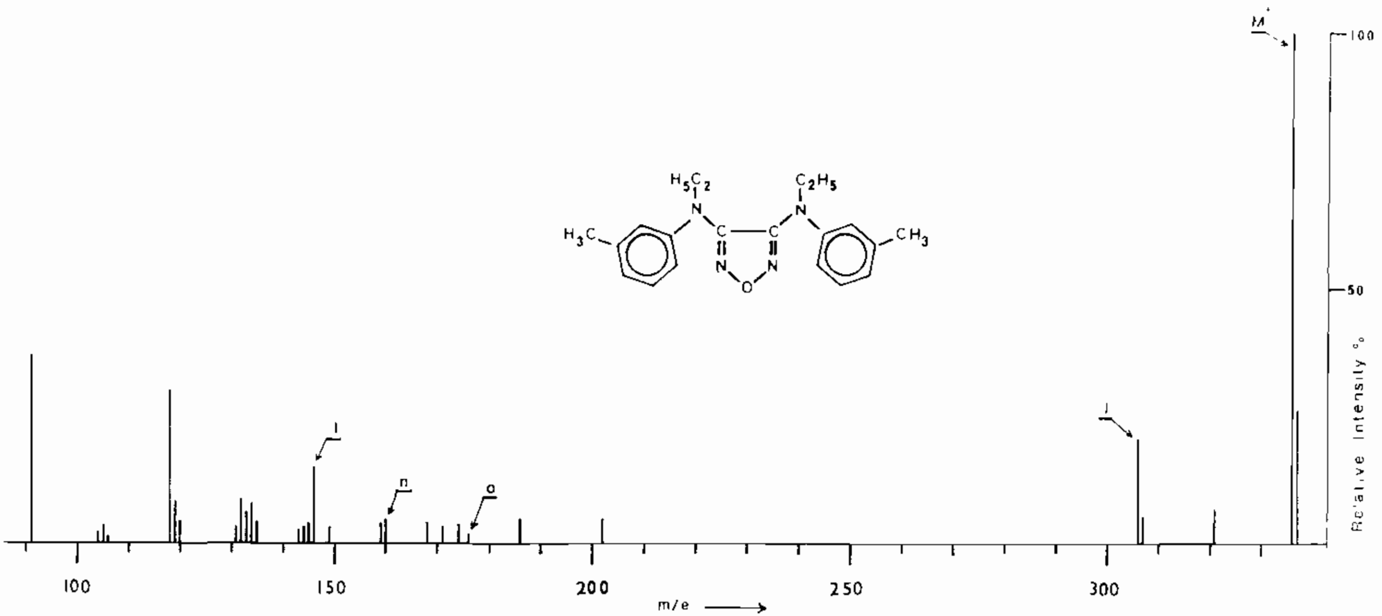
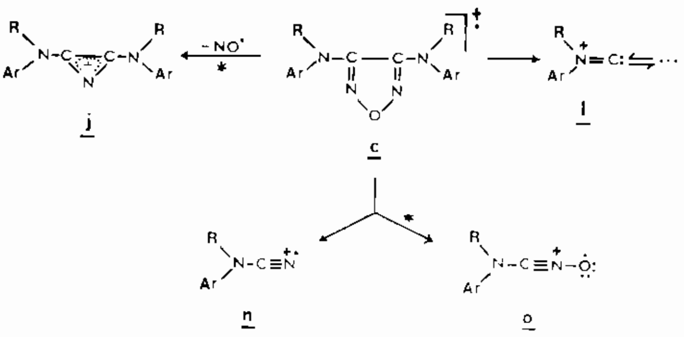


Fig. 2. Mass spectrum of N,N'-diethyl-N,N'-bis(m-methyl-)phenyl-3,4-diamino-1,2,5-oxadiazole (IIi).

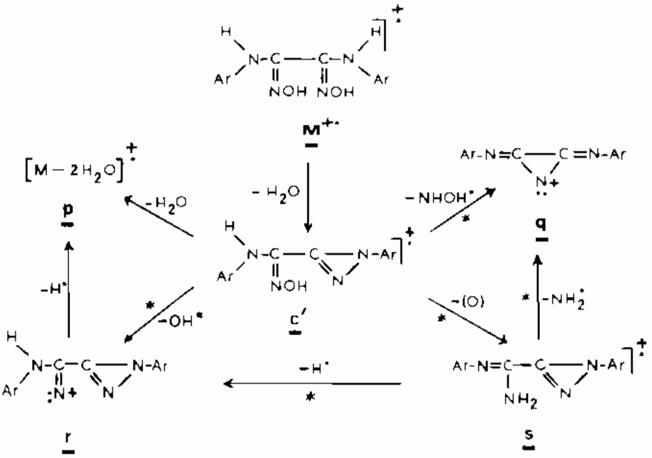


Scheme II

mass spectra of compounds $II_{(h,i)}$ is the fact that oxygen is not lost from their molecular ions.

The suggested fragmentation pattern in schemes I-II explains well the formation of the most abundant ions observed in the high mass number region of compound $I_{(i)}$ (Fig. 1). The other abundant recorded fragments can be easily explained considering the participation of the alkyl and aryl groups in the fragmentation reactions, as well as the known eliminations of amine and nitrile fragments of amidoximes[2]. For example the ions m/e 308, 293 and 291 can be formed from ions *b*, *h* and *f* respectively by elimination of the radical $C_2H_5^{\cdot}$ and the ions m/e 204, 203, 202, 188, 187 and 186 by loss of $3\text{-}CH_3\text{-}C_6H_4\text{-}\dot{N}\text{-}C_2H_5$ from the ions *a*, *b*, *c*, *h*, *g* and *f* respectively. The base peak m/e 120 is attributed to the cation $3\text{-}CH_3\text{-}C_6H_4\text{-}\overset{+}{N}\text{-}CH_3$ formed from ion *d* by loss of $CH_3^{\cdot}$ as it is evidenced by the appropriate metastable ion. The same transition was also observed in the mass spectrum of $I_{(g)}$ ($R = C_2H_5$). The very abundant ion m/e 91 is assigned to the tropylium cation.

Although the suggested fragmentation reactions in schemes I-II explain the recorded ions of $I_{(i)}$ and generally of compounds $I_{(f-l)}$ they don't give a completely satisfactory explanation for the mass spectra of compounds $I_{(a-e)}$ and especially for some ions observed in the high mass number region. In the case of compounds $I_{(a-e)}$ it is also possible an alternative pathway for the primary dehydration of their molecular ions, with the participation in this process of only the two active hydrogens of the same oximino group ($HON{=}\overset{|}{C}\text{-}NH\text{-}$). Two alternative pathways for the primary fragmentation reactions of compounds $I_{(a-e)}$ are given in schemes III-IV. The proposed structure *c'* for the ion M-18 explains the formation of some ions observed in high abundance only in the spectra of compounds I$_{(a\text{-}e)}$. These transitions in almost all cases are followed by the appropriate metastable ions (Scheme III).



Scheme III

The other abundant ions observed in the high mass number region in the recorded spectra of compounds I$_{(a\text{-}e)}$ can be formed by fragmentation mechanisms given in scheme IV. It is important to note that ions *t* (M-NHOH$^{\cdot}$) and *h* [M-2(O)] have the same mass number (both of them correspond to M-32) and high resolution mass spectra are necessary to distinguish them. The same happens for ions v and *g* (both of them correspond to M-33), while ions *y* and *j* are isomeric forms (when R=H). Ions *t* can be formed in one step from the molecular ions by elimination of the radical NHOH$^{\cdot}$ or from fragments *a* and *b* by loss of NH$_2^{\cdot}$ or NH respectively. The elimination of NHOH$^{\cdot}$ has been reported as a primary fragmentation reaction of the molecular ion of benzanilide oxime[3].

The general fragmentation pathway of the title compounds appears very complicated, especially in respect to the mechanisms and positions of the ejected hydrogens. Furthermore some fragments of the same mass number may have a different composition. In the suggested fragmentation we considered that only the original active hydrogens of >NH and =NOH participate in the leaving fragments OH$^{\cdot}$, H$_2$O, NH, NH$_2^{\cdot}$ and NHOH$^{\cdot}$. This is in agreement with the observed elimination M$^{+\cdot}$ -NHOH$^{\cdot}$ in the mass spectrum of benzanilide oxime, where it is re-

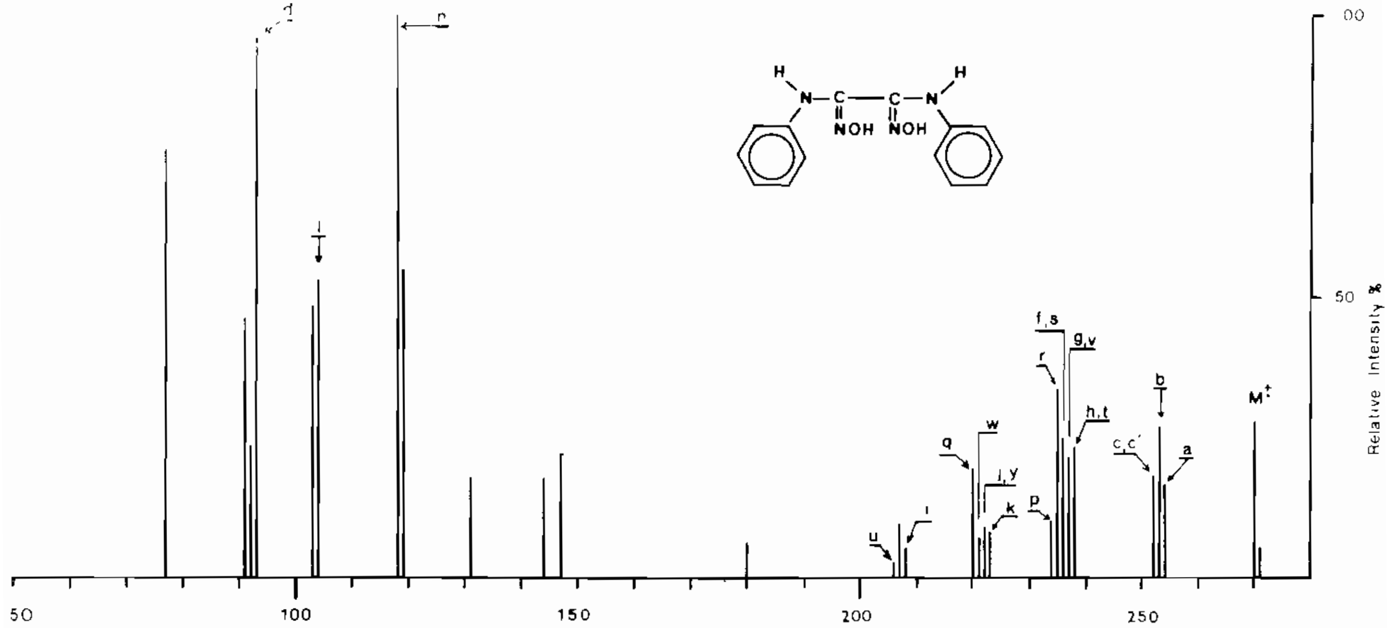
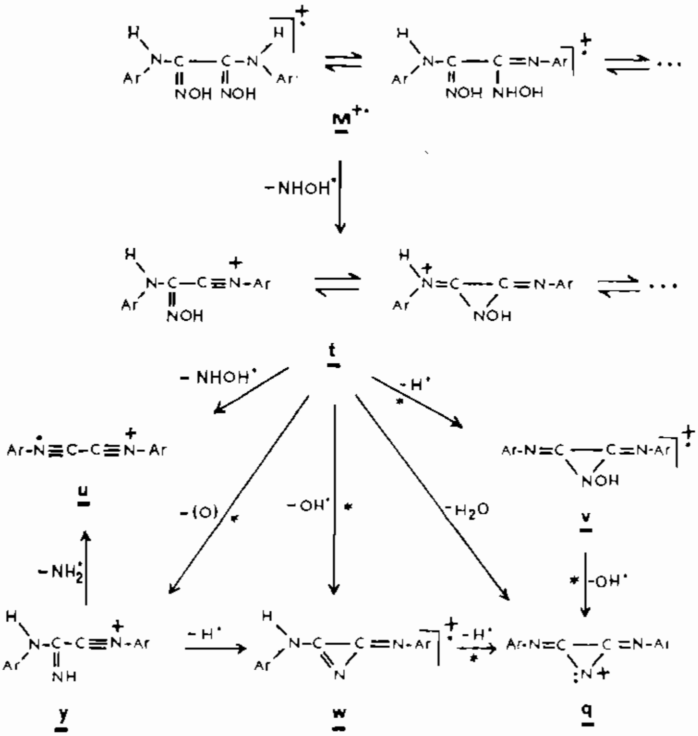


Fig. 3. Mass spectrum of N,N′-diphenyl-dioxamidoxime (Ia).



Scheme IV

ported that the oxime hydroxyl and the amine hydrogen are the only ones involved in this process with no scrambling of hydrogens from either phenyls[3]. On the other hand in another mass spectral study of benzamidoximes it is proposed, in respect to the ejection $\overset{+}{M^{\cdot}}-H_2O$ (in one or more steps) that occurs extended degree of randomization of hydrogens in the molecular ion before fragmentation and in this process participate the two active hydrogens ($>$NH, $=$NOH), the o-hydrogens of the aniline ring and to a lower extent the o-hydrogens of the benzal ring[2]. However, only selective deuterium labelling of the title compounds in hydroxyl, amino and phenyl groups would conclusively provide evidence as to which hydrogens participate to these eliminations. Efforts to these directions were unsuccessful. Repeated recrystallisation of compounds $I_{(a)}$ and $I_{(i)}$ from CH_3OD gave mixtures consisting from completely and partly deuterated species of the oximino group,

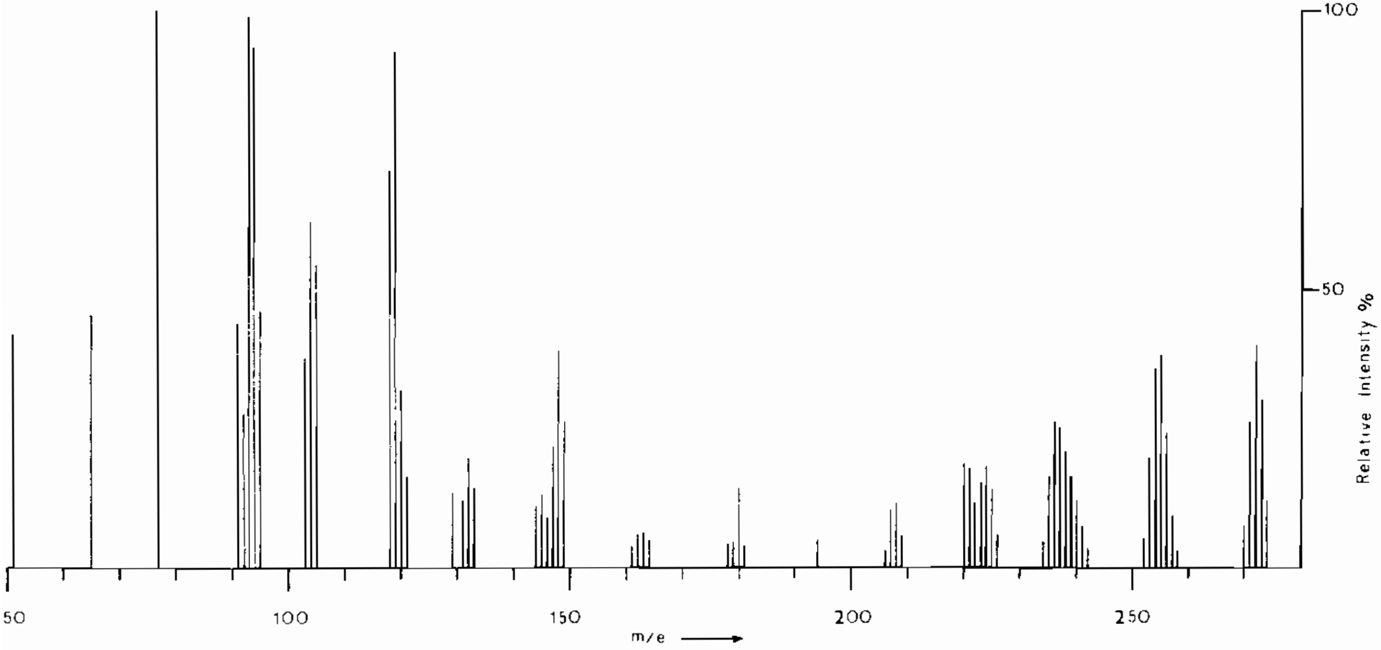


Fig. 1. Mass spectrum of deuterated Ia.

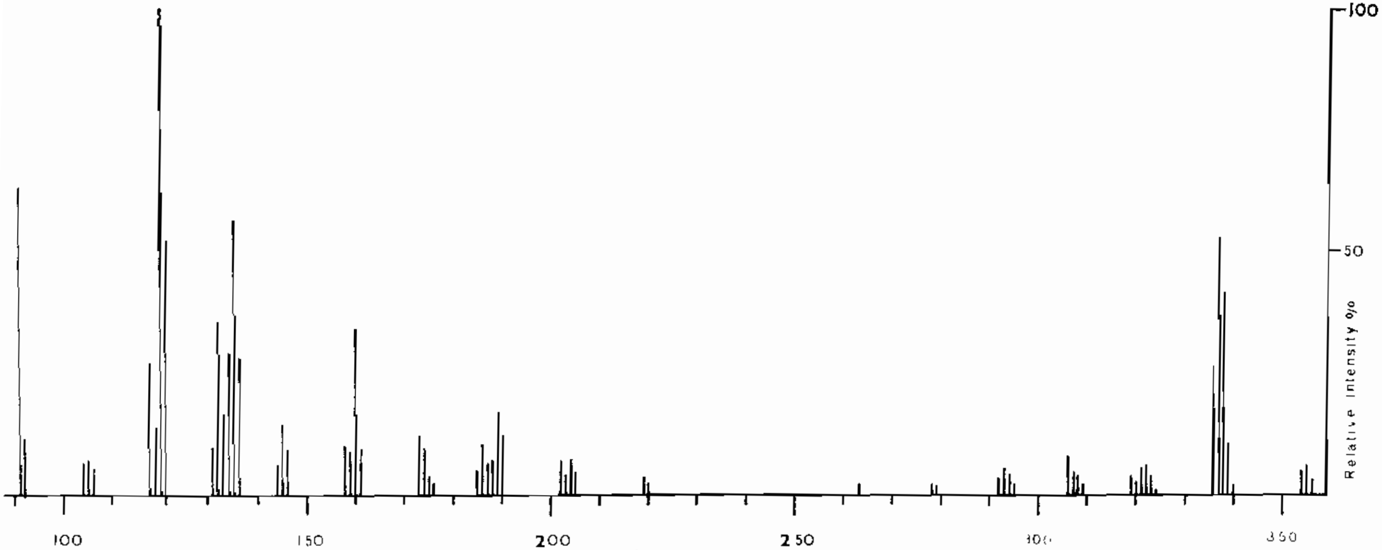


Fig. 5. Mass spectrum of deuterated Ii.

TABLE I.

Principal fragment ions in the mass spectra of compounds I and II (% relative intensities).

Ib: 299 (7), $M^{+\cdot}$ 298 (35), 283 (5), 282 (19), 281 (27), 280 (16), 267 (7), 266 (22), 265 (12), 264 (16), 263 (17), 262 (8), 251 (13), 250 (11), 249 (20), 248 (27), 247 (11), 236 (6), 235 (8), 234 (10), 233 (8), 192 (8), 191 (20), 176 (10), 161 (16), 160 (8), 159 (7), 158 (7), 149 (8), 148 (6), 147 (6), 146 (10), 145 (17), 143 (9), 133 (44), 132 (73), 131 (48), 118 (67), 117 (43), 116 (25), 107 (100), 106 (85), 105 (19), 104 (60), 91 (46), 90 (26), 89 (23), 79 (16), 78 (21), 77 (32).

Ic: 299 (8), $M^{+\cdot}$ 298 (39), 282 (34), 281 (88), 280 (16), 266 (22), 265 (23), 264 (31), 263 (42), 262 (10), 251 (15), 250 (12), 249 (15), 248 (37), 236 (5), 235 (15), 234 (11), 233 (8), 208 (9), 191 (3), 176 (6), 175 (5), 161 (44), 160 (9), 159 (13), 158 (22), 148 (6), 146 (10), 145 (29), 143 (8), 134 (12), 133 (56), 132 (100), 131 (44), 119 (8), 118 (71), 117 (52), 116 (35), 108 (14), 107 (93), 106 (78), 105 (18), 104 (22), 92 (12), 91 (77), 90 (27), 89 (23), 79 (23), 78 (19), 77 (37), 65 (32).

Id: 299 (8), $M^{+\cdot}$ 298 (38), 282 (16), 281 (23), 280 (14), 267 (5), 266 (18), 265 (17), 264 (22), 263 (27), 262 (9), 251 (7), 250 (9), 249 (7), 248 (21), 236 (9), 235 (11), 234 (5), 191 (3), 176 (9), 175 (6), 161 (24), 160 (7), 159 (11), 158 (17), 148 (5), 146 (8), 145 (22), 143 (7), 133 (49), 132 (82), 131 (56), 118 (68), 117 (42), 116 (29), 108 (12), 107 (96), 106 (100), 105 (17), 104 (20), 91 (78), 90 (22), 89 (20), 79 (22), 78 (19), 77 (38).

Ie: 355 (7), $M^{+\cdot}$ 354 (27), 338 (9), 337 (18), 336 (17), 335 (7), 323 (10), 322 (23), 321 (8), 320 (8), 319 (7), 307 (16), 306 (16), 305 (29), 304 (19), 303 (8), 292 (8), 291 (8), 290 (21), 289 (19), 288 (20), 220 (7), 219 (11), 204 (16), 203 (8), 189 (2), 188 (7), 187 (10), 176 (4), 173 (7), 172 (6), 171 (9), 162 (10), 161 (41), 160 (69), 159 (45), 147 (12), 146 (64), 145 (86), 144 (30), 136 (22), 135 (100), 134 (67), 133 (51), 132 (16), 131 (20), 121 (12), 120 (65), 119 (22), 118 (14), 117 (20), 116 (10), 115 (14), 105 (10), 104 (9) 103 (16), 91 (33), 79 (10), 78 (8), 77 (22), 65 (14).

If: 299 (3), $M^{+\cdot}$ 298 (10), 282 (9), 281 (34), 280 (46), 266 (6), 265 (4), 264 (4), 251 (10), 250 (25), 236 (7), 191 (2), 161 (21), 159 (10), 158 (37), 157 (10), 148 (4), 145 (17), 133 (18), 132 (91), 131 (24), 118 (50), 117 (19), 107 (66), 106 (86), 105 (18), 104 (26), 91 (46), 77 (100).

Ig: 327 (3), $M^{+\cdot}$ 326 (6), 310 (12), 309 (49), 308 (48), 294 (7), 293 (12), 292 (3), 280 (4), 279 (7), 278 (18), 264 (7), 250 (4), 235 (4), 220 (3), 205 (1), 203 (4), 190 (11), 188 (4), 175 (15), 174 (12), 173 (7), 172 (24), 162 (4), 160 (7), 159 (13), 147 (14), 146 (59), 145 (11), 144 (16), 132 (18), 131 (29), 121 (41), 120 (32), 119 (33), 118 (88), 106 (82), 105 (13), 104 (48), 93 (8), 92 (9), 91 (28), 79 (9), 78 (13), 77 (100), 65 (15).

Ih: 327 (5) $M^{+\cdot}$ 326 (20), 310 (12), 309 (48), 308 (22), 296 (6), 293 (4), 292 (2), 291 (2), 280 (10), 279 (21), 278 (26), 264 (7), 263 (5), 262 (4), 248 (4), 205 (7), 190 (10), 189 (5), 188 (16), 175 (11), 174 (10), 173 (6), 172 (13), 171 (4), 162 (3), 161 (5), 160 (10), 159 (18), 158 (23), 157 (11), 150 (15), 147 (26), 146 (86), 145 (44), 144 (7), 133 (9) 132 (37), 131 (62), 130 (16), 122 (19), 121 (100), 120 (91), 119 (31), 118 (87) 117 (33), 116 (12), 107 (15), 106 (83), 105 (15), 104 (37), 103 (8), 93 (9), 92 (20), 91 (80), 90 (15), 89 (20), 79 (16), 78 (22), 77 (45), 65 (52).

IIh: 309 (22), $M^{+\cdot}$ 308 (100), 279 (9), 278 (29), 262 (2), 248 (2), 188 (6), 175 (1), 172 (4), 167 (4), 162 (3), 149 (9), 147 (6), 146 (10), 145 (6), 132 (73), 131 (11), 121 (12), 120 (11), 118 (18), 117 (16), 116 (7), 106 (4), 105 (6), 92 (5), 91 (37), 78 (3), 77 (7), 65 (18).

along with some of the original compounds as it is obvious from their mass spectra (Fig. 4, 5).

It is pointed that in favour to our consideration on the fragmentation mechanisms is the fact that in the mass spectrnm of compound $I_{(e)}$, where the four o-positions of two phenyl groups are occupied by methyl groups, the decisive ions *p* (3%), *q* (19%), *r* (7%), *u* (21%) and v (17%) are also observed, even in lower, sometimes, abundance to those of the corresponding ions of $I_{(a-d)}$. These differences in the relative intensities of the same type ions are also observed in many other cases in the studied mass spectra and can arise from conformational differences, cansed by the substituents. It is also important to note that the observed weak ion m/e 319 in the mass spectrum of $I_{(i)}$, corresponding to M-35, can be formed only by the ejection of at least three hydrogens from the molecular ion, as for example through the transition *f* - $H^{\cdot}$. This process leads probably to the formation of the corresponding ion of a tropylium cation derivative.

In conclusion it may be pointed out that there are some characteristic mass spectral distinctions between compounds $I_{(a-e)}$ and $I_{(f-i)}$. Only compounds $I_{(a-e)}$ show in their mass spectra abundant ions of the types *p*, *q*, *r*, *s* and *w*.

EXPERIMENTAL

Compounds $I_{(a-i)}$ were prepared by earlier reported procedures^{4}. Compounds $II_{(h,i)}$ were prepared from compouds $I_{(h,i)}$ by their thermal dehydration at 200-205° for 3 min and were separated from the reaction mixture by preparative T.L.C. on silica gel, as the faster moving band, eluting with petroleum spirit - ether (1:1). Their spectral data (NMR, IR, MS) were in agreement with the proposed structures.

All mass spectra were run at 70 eV on a RMU-6L Hitachi-Perkin-Elmer single focusing mass spectrometer using the direct insertion probe of the samples in the range 160 to 200°.

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ΠΕΡΙΛΗΨΙΣ

ΜΕΛΕΤΗ ΦΑΣΜΑΤΩΝ ΜΑΖΩΝ ΩΡΙΣΜΕΝΩΝ ΠΑΡΑΓΩΓΩΝ ΤΗΣ ΔΙΟΞΑΜΙΔΟΞΙΜΗΣ

Ὑπὸ

ΔΗΜΗΤΡΙΟΥ Ν. ΝΙΚΟΛΑΪΔΗ

(Ἐργαστήριον Ὀργανικῆς Χημείας Πανεπιστημίου Θεσσαλονίκης)

Μελετῶνται τὰ φάσματα μαζῶν πέντε συμμετρικῶν N,N′-δις-αρυλο- καὶ τεσσάρων συμμετρικῶν N,N′-δις-αλκυλο-N,N′-δις-αρυλο-παραγώγων τῆς διοξαμιδοξίμης τοῦ γενικοῦ τύπου I καὶ συγκρίνονται μὲ τὰ φάσματα μαζῶν δύο N,N′-δις-αλκυλο-N,N′-δις-αρυλο-παραγώγων τοῦ 3,4-διαμινο-1,2,5-οξαδιαζολίου τοῦ τύπου II, παρασκευασθέντων διὰ θερμικῆς ἀφυδατώσεως τῶν ἀντιστοίχων διοξαμιδοξιμῶν I. Ἡ μελέτη ἀφορᾶ κυρίως τὸν τρόπον διασπάσεως τῆς διοξιμινο-ομάδος τῶν ἐνώσεων τοῦ τύπου I. Κατ᾽ αὐτὴν διαπιστοῦται ὅτι αἱ ἐν λόγω ἐνώσεις διασπῶνται ἀρχικῶς ἀναλόγως πρὸς τὰς βενζαμιδοξίμας ὑπὸ ἀπόσπασιν ἐκ τοῦ μοριακοῦ ἰόντος O, $OH^{\cdot}$, $NHOH^{\cdot}$, H_2O. Τὸ γενικὸν ὅμως σχῆμα διασπάσεως τῶν I ἐμφανίζεται πολυπλοκώτερον τοῦ τῶν βενζαμιδοξιμῶν.

Εἰς τὸ σχῆμα I δίδονται οἱ προτεινόμενοι τρόποι σχηματισμοῦ τῶν μεγάλης ἐντάσεως καὶ μεγάλου μαζικοῦ ἀριθμοῦ (m/e) ἰόντων, τὰ ὁποῖα ἐμφανίζονται εἰς τὰ φάσματα μαζῶν ὅλων τῶν ἐνώσεων I. Εἰδικῶς εἰς τὸ σχῆμα II δίδεται ὁ προτεινόμενος μηχανισμὸς περαιτέρω διασπάσεως τοῦ πρωτογενῶς σχηματιζομένου ἰόντος M-18, (*c*), διὰ τὸ ὁποῖον γίνεται δεκτὴ ἡ δομὴ διαμινο-διοξαζολίου τοῦ τύπου II. Ὑπὲρ τῆς προτεινομένης δομῆς συνηγορεῖ τὸ γεγονὸς ὅτι αἱ παραλλήλως μελετηθεῖσαι ἐνώσεις $II_{(h,i)}$ ἔδειξαν ἀνάλογον τρόπον διασπάσεως. Διὰ τῶν μηχανισμῶν διασπάσεως τῶν σχημάτων I καὶ II ἐξηγεῖται ἕνας μεγάλος ἀριθμός, ἀλλὰ ὄχι τὸ σύνολον, τῶν ἰόντων πού ἐμφανίζονται εἰς τὴν ἀντίστοιχον περιοχὴν τῶν φασμάτων μαζῶν τῶν ἐνώσεων $I_{(a-e)}$. Προκειμένου νὰ ἐξηγηθῇ ὁ σχηματισμὸς τῶν ἐν λόγω ἐπὶ πλέον παρατηρουμένων ἰόντων προτείνονται διὰ τὰς ἐνώσεις $I_{(a-e)}$ καὶ οἱ μηχανισμοὶ διασπάσεων τῶν σχημάτων III-IV, οἱ ὁποῖοι προφανῶς χωροῦν παραλλήλως πρὸς τοὺς τῶν σχ. I-II.

Ἐκ τῆς ὅλης μελέτης διαπιστοῦται ὅτι τὰ σχηματιζόμενα ἰόντα δύναν-

ται νὰ ἀποδοθοῦν μὲ περισσοτέρους τύπους (συντονισμοῦ ἢ ταυτομερεῖς), διὰ τῶν ὁποίων ἐξηγοῦνται ἱκανοποιητικῶς αἱ προτεινόμεναι διασπάσεις. Ἐπὶ πλέον ὡρισμένα ἰόντα δύνανται νὰ ἀποδοθοῦν μὲ διαφόρους τύπους, ἀντιστοιχοῦντας εἰς τὸν αὐτὸν μαζικὸν ἀριθμόν, ἀλλὰ εἰς διάφορον στοιχειομετρικὴν σύστασιν, ὡς π.χ. τὰ ἰόντα *t* καὶ *h*.

Ἐν τούτοις ἡ ἐμφάνισις ὡρισμένων μετασταθῶν ἰόντων προσφέρει σημαντικὰ διευκρινιστικὰ στοιχεῖα διὰ τὴν σύστασιν καὶ τὸν τρόπον σχηματισμοῦ πολλῶν ἐξ αὐτῶν.

Προκειμένου νὰ διευκρινισθῇ ἂν εἰς τὰ ἀποσπώμενα θραύσματα $OH^{\cdot}$, H_2O, $NHOH^{\cdot}$, NH, $NH_2^{\cdot}$ συμμετέχουν μόνον τὰ ἐνεργὰ ἀμινικὰ καὶ ὑδροξυλικὰ ὑδρογόνα τῆς διοξιμινικῆς ὁμάδος, ὅπως ἐθεωρήθη εἰς τοὺς προτεινομένους μηχανισμούς, ἢ καὶ ἄλλα ὑδρογόνα ἐκ τοῦ ὑπολοίπου μορίου τῶν I, ἐγένετο προσπάθεια ἀντικαταστάσεως τῶν ὡς ἄνω ἐνεργῶν ὑδρογόνων μὲ δευτέριον, δι᾿ ἐπανειλημμένων ἀνακρυσταλλώσεων τῶν $I_{(a,l)}$ ἀπὸ CH_3OD. Κατὰ τὴν προσπάθειαν αὐτὴν ἐλήφθησαν μίγματα ἐκ πλήρως, μερικῶς καὶ οὐδόλως δευτεριωμένων προϊόντων I, ἄνευ οὐσιαστικῆς σημασίας.

Συμπερασματικῶς ἀναφέρεται ὅτι οἱ προτεινόμενοι μηχανισμοὶ διασπάσεως ἐξηγοῦν ἱκανοποιητικῶς τὰ μελετηθέντα φάσματα, προσφέρουν στοιχεῖα διακρίσεως μεταξὺ τῶν ἑνώσεων ποὺ περιλαμβάνονται εἰς τὰς κατηγορίας $I_{(a-e)}$ καὶ $I_{(f-l)}$ καὶ δεικνύουν ὅτι τὸ μοριακὸν ἰὸν τῶν $I_{(a-e)}$ δύνανται νὰ συμμετέχουν καὶ ταυτομερεῖς δομαὶ τοῦ τύπου III.