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MASS-SPECTROMETRIC BEHAVIOR OF 2-METHYL-3-OXO-3,4-DIHYDROQUINOXALINE DERIVATIVES

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UDC 543.51:547.863

The mass spectra of 20 derivatives of 2-methyl-3-oxo(thioxo)-3,4-dihydroquinoxaline, as well as 2-nitromethylquinoxaline and 2-ethoxycarbonyl-3-oxopiperazine, were recorded in order to study the possibility of detection of a ketimine-enamine equilibrium in the gas phase. It was established that the mass-spectrometric criteria for the identification of the tautomeric forms that were previously proposed for analogous structures are inapplicable in the case of the investigated compounds. The mass spectra of all of the compounds are presented, and correlated schemes for their fragmentation are given.

We recently investigated the ketimine-enamine equilibrium of derivatives of 2-ethoxycarbonylmethylene- (I) and 2-cyanomethylene-3-oxo-1,2,3,4-tetrahydroquinoxalines (II) in solution in dimethyl sulfoxide (DMSO) by means of PMR spectroscopy [1]. However, under these conditions the solvation effect of the solvent may have had an appreciable effect on the shift of the tautomeric equilibrium. We therefore became intereseted in the research of Inagaki and Iwanami [2], who investigated the same equilibrium by means of mass spectrometry. They assert that intense F_2 peaks are characteristic for the fragmentation of the enamine form of ester I (Scheme 1), while the fragmentation of the molecular ions of ketimines takes place with detachment of the substituent from the 2 position as a whole (the F_5 ion).

Scheme 1

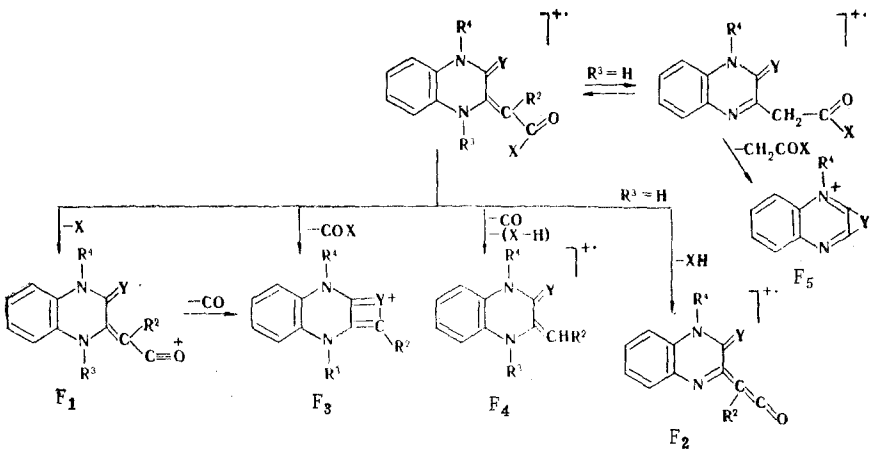

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TABLE 1. Mass Spectra of II-XII and XIV-XXIV*

Compound	Recording temp., °C	m/e values (relative intensities of the ion peaks, %)
II	190	185 (100), 157 (37), 156 (15), 131 (5), 130 (5), 103 (11), 90 (13), 84 (8), 83 (10), 82 (8), 81 (11)
III	220	292 (100), 247 (13), 246 (37), 220 (25), 219 (58), 207 (19), 191 (21), 137 (19), 136 (14), 135 (16), 134 (59)
IV	110	262 (65), 217 (13), 216 (24), 191 (3), 190 (16), 189 (30), 188 (100), 175 (3), 145 (3), 144 (4), 81 (3)
V	160	308 (23), 263 (11), 262 (75), 236 (19), 235 (100), 207 (13), 206 (40), 205 (20), 91 (11), 90 (4), 77 (3)
VI	140	206 (8), 191 (8), 173 (2), 161 (7), 160 (100), 132 (17), 131 (14), 119 (1), 104 (2), 90 (7), 77 (5)
VII	200	300 (2), 235 (22), 160 (17), 159 (100), 132 (10), 131 (42), 97 (12), 91 (9), 81 (10), 78 (18), 77 (49)
VIII	100	174 (100), 147 (11), 146 (85), 145 (58), 131 (54), 104 (18), 92 (8), 90 (19), 78 (12), 77 (34), 76 (11)
IX	80	250 (29), 215 (37), 180 (21), 179 (32), 178 (92), 177 (100), 143 (23), 142 (64), 141 (8), 102 (62), 89 (11)
X	60	232 (96), 174 (16), 173 (47), 172 (25), 145 (33), 144 (31), 143 (100), 130 (25), 103 (31), 102 (20), 90 (98)
XI	120	262 (87), 190 (14), 189 (100), 188 (3), 161 (14), 160 (61), 159 (5), 134 (12), 133 (5), 132 (12), 131 (5)
XII	100	246 (100), 201 (35), 200 (88), 174 (55), 173 (84), 172 (23), 146 (35), 145 (94), 93 (15), 91 (45), 77 (68)
XIV	200	260 (100), 215 (76), 214 (52), 189 (11), 188 (81), 187 (25), 173 (8), 172 (8), 160 (21), 159 (15), 145 (10)
XV	180	199 (100), 172 (26), 170 (23), 156 (27), 144 (17), 118 (16), 97 (15), 95 (13), 90 (28), 82 (14), 81 (22)
XVI	120	199 (100), 171 (5), 170 (12), 144 (6), 143 (7), 131 (37), 102 (7), 90 (12), 81 (8), 77 (24), 76 (8)
XVII	100	213 (100), 173 (29), 170 (21), 145 (57), 131 (14), 102 (23), 103 (12), 90 (23), 85 (14), 78 (14), 77 (50)
XVIII	180	217 (42), 200 (32), 174 (100), 172 (18), 146 (72), 145 (60), 131 (32), 117 (12), 90 (23), 78 (13), 77 (64)
XIX	120	231 (28), 200 (24), 174 (100), 173 (7), 172 (8), 146 (35), 145 (25), 144 (3), 143 (3), 131 (12), 117 (3)
XX	130	245 (31), 202 (10), 201 (29), 200 (100), 174 (40), 173 (15), 172 (15), 145 (25), 81 (15), 77 (13), 72 (55)
XXI	180	202 (100), 187 (67), 160 (28), 159 (30), 132 (17), 131 (32), 130 (3), 103 (4), 90 (13), 87 (12), 77 (10)
XXII	190	205 (10), 160 (10), 159 (100), 132 (9), 131 (69), 116 (5), 105 (6), 104 (8), 103 (8), 91 (11), 90 (37)
XXIII	100	189 (9), 144 (15), 143 (100), 137 (2), 116 (3), 103 (4), 102 (51), 90 (4), 89 (15), 83 (5), 76 (13)
XXIV	120	184 (100), 139 (62), 138 (28), 113 (9), 112 (89), 111 (12), 110 (36), 109 (7), 106 (12), 84 (20), 81 (22)

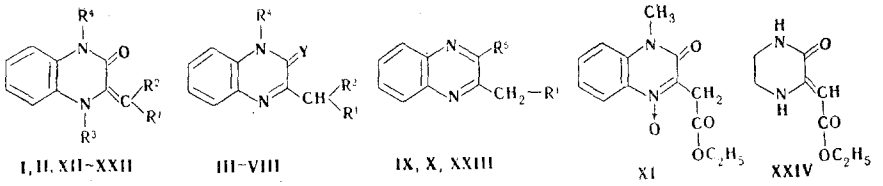
*The molecular-ion peak and the 10 most intense peaks are presented.

TABLE 2. Intensities of the Peaks of the Principal Characteristic Ions in the Mass Spectra of II-XII and XIV-XXIV ($\%\Sigma_{39}$)

Compound	w_M	F_1	F_2	F_3	F_4	F_5	F_6	F_7
II	20,3	—	—	—	—	—	6,8	—
III	9,2	1,0	3,0	4,8	2,0	0,8	—	—
IV	25,8	4,2	8,0	10,0	5,3	1,0	—	—
V	8,2	—	21,6	28,9	—	—	—	—
VI	5,1	—	—	—	56,7	—	—	—
VII	0,5	—	—	—	20,9	—	—	—
VIII	19,2	—	—	—	—	—	14,4	8,6
IX	5,6	0,8	—	18,6	14,8	—	—	—
X	14,2	0,7	0,6	6,7	0,7	0,8	—	—
XI	28,2	—	—	28,3	0,8	0,3	—	—
XII	11,9	2,6	9,5	8,9	5,0	—	—	—
XIV	20,8	12,2	9,1	4,4	14,1	1,4	0,2	1,7
XV	15,0	—	—	—	—	1,0	0,5	—
XVI	27,1	—	—	—	—	—	1,0	9,5
XVII	19,1	—	—	—	—	4,9	0,8	9,6
XVIII	6,4	—	4,5	1,1	14,3	—	—	—
XIX	10,8	—	8,6	2,5	36,0	—	—	—
XX	6,6	3,3	19,4	2,9	7,8	—	—	—
XXI	30,8	19,2	—	9,1	7,6	0,6	0,9	—
XXII	3,4	—	—	34,1	—	—	—	—
XXIII	3,1	—	—	31,6	—	0,3	—	—
XXIV	22,5	12,3	5,7	2,0	18,3	1,2	—	—

In order to verify the correctness and general character of this conclusion we studied the mass spectra (Table 1) of a series of derivatives of 2-methyl-3-oxo-3,4-dihydroquinoxaline (III-XI, XXIII) and 2-methylene-3-oxo-1,2,3,4-tetrahydroquinoxaline (I, II, XII-XXII, XXIV).

An analysis of the processes involved in the fragmentation of the molecular ions of the investigated compounds makes it possible to propose a general scheme for the fragmentation for all of the carbonyl-containing compounds I, III-V, IX-XIV, and XVIII-XXI with the formation of F_1-F_5 ions (Scheme 1). In the dissociative ionization of II, VI-VIII, and XV-XVII, in addition to the formation of F_3 and F_5 fragments, one observes processes involving the initial elimination of a CO molecule (to give the F_6 ion) by the molecular ion with subsequent loss of the substituent (to give the F_7 ion in Scheme 2).



I, II, XII-XXII III-VIII IX, X, XXIII XI XXIV

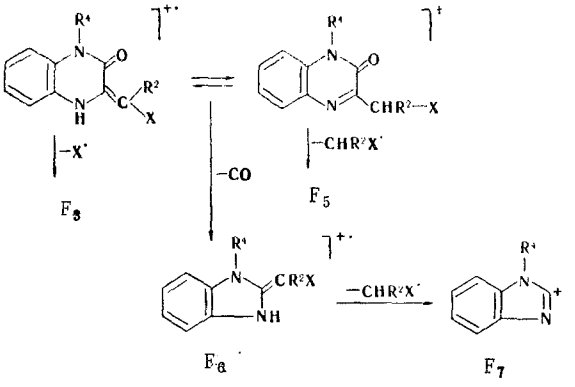
I $R^2=R^3=R^4=H$, $R^1=COOC_2H_5$; II $R^1=CN$, $R^2=R^3=R^4=H$; III $R^1=COOC_2H_5$, $R^2=R^4=H$, Y=O(6,7-dimethoxy); IV $R^1=COOC_2H_5$, $R^2=H$, $R^4=CH_3$, Y=S; V $R^1=COOC_2H_5$, $R^2=C_6H_5$, $R^4=H$, Y=O; VI $R^1=SCH_3$, $R^2=R^4=H$, Y=O; VII $R^1=SO_2C_6H_5$, $R^2=R^4=H$, Y=O; VIII $R^1=R^2=H$, $R^4=CH_3$, Y=O; IX $R^1=COOC_2H_5$, $R^5=Cl$; X $R^1=COOCH_3$, $R^5=OCH_3$; XII $R^1=COOC_2H_5$, $R^2=R^3=H$, $R^4=CH_3$; XIII $R^1=COOC_2H_5$, $R^2=H$, $R^3=D$, $R^4=CH_3$; XIV $R^1=COOC_2H_5$, $R^2=H$, $R^3=R^4=CH_3$; XV $R^1=CN$, $R^2=CH_3$, $R^3=R^4=H$; XVI $R^1=CN$, $R^2=R^3=H$, $R^4=CH_3$; XVII $R^1=CN$, $R^2=H$, $R^3=R^4=CH_3$; XVIII $R^1=CONH_2$, $R^2=R^3=H$, $R^4=CH_3$; XIX $R^1=CONHCH_3$, $R^2=R^3=H$, $R^4=CH_3$; XX $R^1=CON(CH_3)_2$, $R^2=R^3=H$, $R^4=CH_3$; XXI $R^1=COCH_3$, $R^2=R^3=R^4=H$; XXII $R^1=NO_2$, $R^2=R^3=R^4=H$; XXIII $R^1=NO_2$, $R^5=H$

An examination of the data in Table 2 makes it possible to note that intense peaks of F_5 ions, which, according to [2], characterize the presence of the ketimine form, are observed both in the mass spectra of genuine "ketimines" (X and XI) and in the spectra of compounds with fixed enamine structures (XIV and XVII). At the same time, F_5 ions are absent in the mass spectra of "ketimines" such as VI-IX.

Moreover, the loss of an XH molecule by the molecular ion is observed in the dissociative ionization not only of compounds in which the existence of a tautomeric equilibrium is formally possible (III-V, XII, and XVIII-XXII) but also in the case of compounds with a fixed "ketimine" structure (X) or in the case of compounds that do not have a hydrogen atom attached to the nitrogen atom in the 1 position (XIV).

It should be noted that in the case of deuterium-containing XII only 80% of the deuterium is lost during elimination of a molecule of alcohol, and this indicates possible randomization of the protons of the NH and methylidyne groups. This process takes place in the gas phase, since the $[M - C_2H_5OH]^+$ ions contain some deuterium (∿20%) when the mass spectra of an undeuterated sample of XII is recorded in the spectrometer in an atmosphere of deuteromethanol. Let us note that similar processes occur in solution only in the presence of traces of acid [1]. At the same time, deuterium exchange of the methylene protons in X is not observed even when a solution of the latter in deuteromethanol is allowed to stand for 30 days.

Scheme 2



Thus the data obtained in this research make it possible to conclude that mass spectrometry is inapplicable for the determination of the position of the tautomeric equilibrium in compounds of this series.

EXPERIMENTAL

We described the synthesis of III, IV, X, XII, XIV, XV, XXII, and XXIV in [3]. Compounds VI, XI, and XVII-XX were synthesized by the method in [5]. The preparation of V and IX was accomplished by the method in [4], whereas the data in [6] (VII), [7] (VIII), [8] (II), [9] (XVI), [10] (XXI), and [11] (XXIII) were used for the preparation of the remaining compounds. Deuterium derivative XIII was obtained by two recrystallizations of XII from deuteromethanol.

The mass spectra were obtained with MKh-1303 and Varian MAT-44S spectrometers with direct introduction of the samples into the ion source at ionization energies of 50 and 70 eV, respectively.

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SYNTHESIS AND THERMAL DECOMPOSITION OF HALOALKOXY-sym-TRIAZINES. 7.* THERMAL DECOMPOSITION OF 2-DIALKYLAMINO-4-(2-CHLOROETHOXY)-6-METHOXYAMINO-sym-TRIAZINES

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UDC 547.873'785.5.07

Two 2-dialkylamino-4-(2-chloroethoxy)-6-methoxyamino-sym-triazines were synthesized. It was established that when they are heated at 120°C, the 2-chloroethoxy group undergoes rearrangement with cyclization to give 2-dialkylamino-4-oxo-8-methoxy-6,7-dihydroimidazo[1,2-a]-sym-triazines, the structure of which was confirmed by data from the IR, PMR, and mass spectra.

Continuing our research on the thermal decomposition of 2-chloroethoxy derivatives of the sym-triazine series [1-5] we studied the specificity of the rearrangement-cyclization reaction in the case of 2-dialkylamino-4-(2-chloroethoxy)-6-methoxyamino-sym-triazines (IIa, b).

We established that, in contrast to the corresponding alkylamino derivatives, methoxyamino-sym-triazines are NH acids owing to the electronegative inductive effect of the methoxy group. In order to avoid the formation of salts due to the hydrogen atom of the methoxy-

*See [6] for Communication 6.

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