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COMPARATIVE MASS SPECTROMETRIC BEHAVIOR OF o-HYDROXYNITROSO DERIVATIVES OF THE QUINOLINE, ISOQUINOLINE, AND COUMARIN SERIES

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Benzo-substituted ortho-hydroxynitrosoquinoline and isoquinoline are found in the gas phase predominantly as the hydroxyimino-ortho-quinoid tautomeric form and under electron bombardment they do not undergo a second order Beckmann rearrangement. Molecular ions of 4-hydroxy-3-nitrosocarbostyryls and coumarin have almost exclusively the structure of the corresponding 2,4-dioxo-3-hydroxyiminohetarene; they also do not undergo rearrangement and decompose predominantly by retrodiene cleavage.

It has been shown repreatedly that many rearrangements of organic compounds which take place in solution are also observed in the gas phase in the molecular ions of the same compounds. Beckmann [1, 2], Wagner–Meerwin [3], and Fischer [4] rearrangements have thus been observed under mass spectroscopic conditions together with several other processes [5, 6]. We have recently demonstrated that isatin monooxime undergoes a second order Beckmann rearrangement under electron bombardment [7]. However, a study of the dissociative ionization of ortho-nitrosonaphthols [8] together with ortho-nitrosoindazoles and benzotriazoles [9] have shown that in this case an analogous rearrangement does not occur. We therefore considered it of interest to study the mass spectrometric behavior of derivatives of quinoline, isoquinoline, and coumarin, which contain an ortho-hydroxynitroso fragment in both the carbo- and the heterocyclic ring (compounds I-V). For comparison we ran mass spectra of the products of a second order Beckmann rearrangement of compounds I and II,* the corresponding β-pyridylacrylic acids (VIa,b, VIIb) and also 4-nitrosoantipyrine (VIII) which contains an ortho-nitrosooxo fragment but cannot act in the hydroxyimino tautomeric form and hence cannot undergo rearrangement in solution. The preparation of compounds I, III, IV, VI, and VII has been described previously by one of us [10, 11] and compounds II, V, and VIII were prepared by us by nitrosotization of 1-hydroxyisoquinoline, 4-hydroxycoumarin, and antipyrine respectively. Rearrangement of the isoquinoline II to the trans-acid VIIb was effected by the action of a mixture of benzenesulfonyl chloride and sodium hydroxide solution.

An examination of the mass spectra of the nitrosocompounds I-V which we studied (Table 1) shows that their molecular ions (M^+) have considerable stability (Table 2) and cleavage

*The rearrangement of compounds III and IV was described in [11], and compound V forms the nitrile of salicylic acid under the conditions for the rearrangement.

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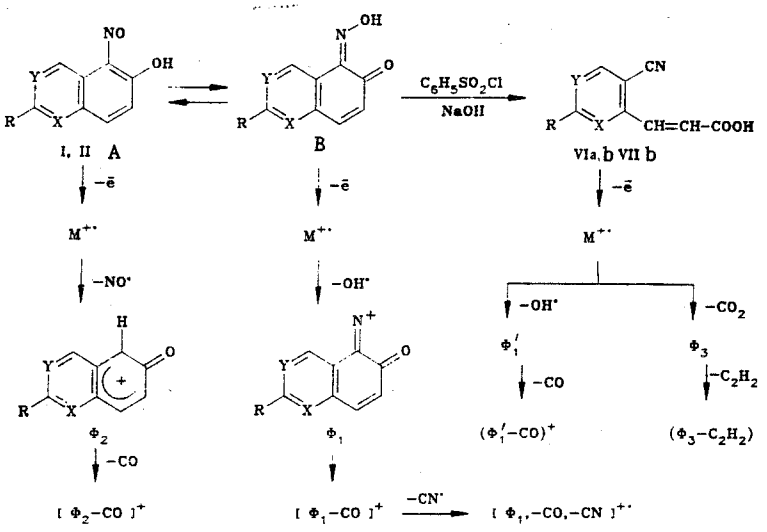
TABLE 1. Mass Spectra of Compounds I-VIII*

Compound	m/z (I_{rel}, %)
I	188 (100), 171 (76), 158 (25), 143 (33), 130 (58), 103 (36), 103 (36), 76 (28), 63 (22), 52 (15), 51 (18)
II	174 (100), 157 (35), 145 (18), 130 (17), 129 (39), 119 (19), 118 (19), 116 (39), 89 (38), 75 (28), 63 (26)
III	204 (100), 187 (86), 159 (34), 146 (28), 132 (58), 116 (32), 105 (34), 104 (36), 91 (38), 77 (61), 67 (55)
IV	266 (100), 149 (72), 221 (26), 308 (18), 196 (21), 195 (80), 180 (14), 167 (30), 166 (21), 77 (61), 51 (44)
V	191 (100), 174 (32), 121 (94), 120 (52), 105 (18), 93 (16), 92 (32), 77 (27), 64 (20), 63 (24), 51 (25)
VIa	188 (1), 144 (100), 143 (38), 118 (34), 117 (13), 91 (7), 90 (10), 89 (7), 64 (9), 63 (12), 52 (7)
VIb	188 (58), 144 (100), 143 (91), 142 (29), 118 (39), 117 (24), 116 (15), 90 (21), 64 (17), 63 (20), 52 (17)
VIIb	174 (100), 157 (20), 130 (57), 129 (75), 128 (74), 103 (32), 102 (32), 76 (50), 75 (53), 51 (29), 50 (31)
VIII	217 (100), 121 (14), 119 (82), 106 (11), 93 (16), 91 (22), 77 (48), 67 (78), 56 (66), 65 (16), 51 (19)

*M^+ and the 10 most intense peaks are shown.

takes place either with primary loss of a hydroxyl group (ion Φ_1) which is characteristic for oximes of oxocompounds of alicyclic and heterocyclic series [12, 13], or with loss of a nitroso group (ion Φ_2). However, as the results in Table 2 show, the probability of the formation of the first from these fragments is considerably higher than that of the second since the ratio Φ_2/Φ_1 falls along the series I > II > III > IV > V. From this one can conclude that for the molecular ions of compounds I and II the hydroxyimino-ortho-quinoid tautomeric form B is characteristically preferred (scheme 1). In the case of compounds III, and IV, the fraction of M^+ of nitroso form A becomes even smaller and compound V in the gas phase exists exclusively in form B.

Scheme 1



I, VIa, b X=N, Y=CH, R=CH_3; II, VIIb X=CH, Y=N, R=H; a cis-, b trans-

The sharp increase in the saturated form B of the molecular ion in the case of carbostyryl and coumarin derivatives leads to the appearance of a new fragmentation route – retrodiene cleavage (RDC, scheme 2), which is characteristic for derivatives of tetrahydroquinolones and tetrahydrocoumarins [14, 15].

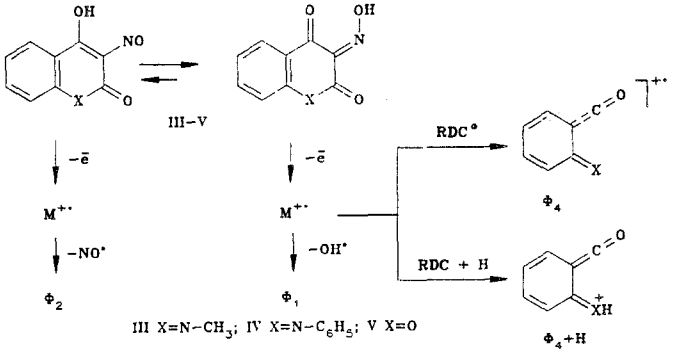
It is important to note that in the mass spectra of compounds I-V the peaks for the $[M - CO_2]^+$ ions are absent which could indicate that there is only partial rearrangement of their M^+ into the corresponding ortho-cyanocarboxy-containing derivatives. In fact, in the mass spectra of the known products of the rearrangement of the nitroso derivatives I and II of the acids VIa,b and VIIb, intense peaks of the Φ_3 ions are observed.

TABLE 2. Intensity of Peaks of Characteristic Ions in the Mass Spectra of Compounds I-V, VIa,b, VIIb ($\%\Sigma_{50}$)

Ion	Compound							
	I	II	III	IV	V	VIa	VIb	VIIb
$M-(W_M)$	15,9	14,9	10,5	11,5	18,4	0,4	10,2	10,2
$[M-OH]^+$ (Φ_1)	10,7	6,0	8,7	8,2	5,9	1,2	2,2	1,8
$[M-NO]^+$ (Φ_2)	3,5	1,2	0,7	1,0	<0,1	—	—	—
$[\Phi_1-CO]^+$	4,7	5,1	3,5	2,9	0,8	11,0	14,0	6,7
$[\Phi_2-CO]^+$	8,2	5,2	2,8	1,9	0,1	—	—	—
$[\Phi_1-CO, -H]^+$	0,5	0,4	—	0,4	—	1,5	4,4	6,6
$[\Phi_1-CO, -C_2H_2]^+$	1,1*	1,4*	—	—	—	3,6	3,7	2,8
$[M-CO_2]^+$ (Φ_3)	—	1,7**	—	—	—	28,6	15,4	5,1
$[\Phi_3-C_2H_2]^+$	—	—	—	—	—	9,7	5,9	0,7
$(RDC)^{\cdot}\Phi_4$	—	—	0,7	9,0	9,4	—	—	—
Φ_4+H	—	—	—	0,9	16,2	—	—	—
Φ_4-H	—	—	5,8	—	—	—	—	—
$Z=\Phi_2/\Phi_1$	0,3	0,2	0,1	0,1	—	—	—	—

*From MCBP evidence, ion (Φ_1–CO–CN).
**From MCBP evidence, ion (M–OH–HCN).

Scheme 2

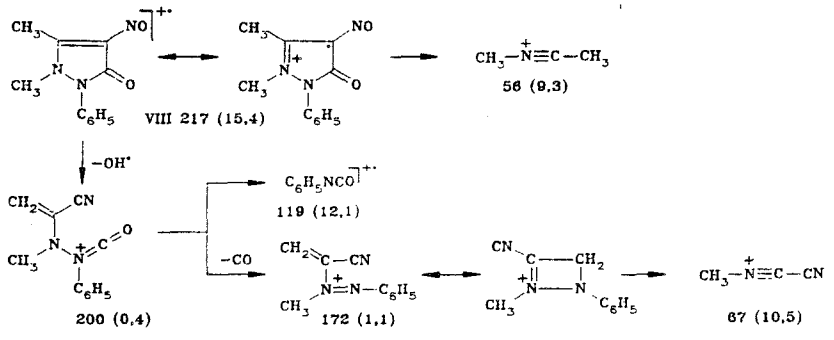


*RDC-retrodiene cleavage

Here, in the case of the primary product of the rearrangement – cis-β-(6-methyl-3-cyanopyridyl-2)acrylic acid (VIa)† – M^+ is relatively unstable and the ions $[M-CO_2]^+$ comprise more than a quater of the ion current which is characteristic for picolinic acid derivatives [16].

In the mass spectrum of compound VIII, the Φ_1 ion peak has very low intensity (the hydroxyimino form is absent) and besides this its formation is apparently connected with transfer of a hydrogen atom from a neighboring methyl group to the oxygen atom of the nitroso group which is characteristic for ortho-nitrotoluene and its analogs [13]. The further breakdown of this ion is set out in Scheme 3.

Scheme 3*



*Peak intensities are given as percentages of the total ion current.

†In the case of the rearrangement of compound II, the cis-acid VIIa is not recorded.

Thus, from an examination of the mass spectra of the ortho-hydroxy-nitroso compounds studied one can identify in the gas phase the presence of their hydroxyimino-ortho-quinoid tautomeric forms and demonstrate the absence of second order Beckmann rearrangement processes in their molecular ions.

EXPERIMENTAL

Mass spectra were run on an LKB-2091 instrument with direct introduction of the sample into the ion source at an ionization energy of 70 eV. The elemental composition of the ions was determined on an MAT-212 apparatus with a resolving power of 10,000. TLC was carried out on Silufol UV-254 plates in 4:1 isopropanol-10% aqueous ammonia with visualization by iodine vapor.

The preparation of compounds I and VIa,b has been described by us in [10] and the method of [11] was used for the preparation of the hydroxynitrosocarbostyryls.

The results of the elemental analyses for C, H, N were in agreement with those calculated.

7-Hydroxy-8-nitrosoisoquinoline (II). To a solution of 0.48 g (3 mmole) 7-hydroxyisoquinoline [17] in 0.36 ml (3 mmole) conc. HCl and 3 ml water at 2°C was added with stirring a solution of 0.21 g (3 mmole) sodium nitrite in 2 ml water. After 2 h the solution was made alkaline with 5% $NaHCO_3$ and the yellow-green deposit recovered by suction, washed with water and dried. Yield 0.47 g (87%), mp 180-181°C (from ethyl acetate), R_f 0.46. From the results of [18], mp 181.7-182.7°C.

3-Nitroso-4-hydroxycoumarin (V, $C_9H_5NO_4$). To a suspension of 9.8 g (60 mmole) 4-hydroxycoumarin in 50 ml water was added 4.5 g (64 mmole) sodium nitrite in 10 ml water. The solution acquired a blue color and after 1 h with vigorous stirring the solution became deep blue. While cooling in ice, 12% HCl, was added to a pH of 3-4 and the yellow-green crystals removed by suction and washed with water. Yield 8.8 g (75%), mp 153-154°C (from chloroform). From the results of [19], mp 149°C.

trans-β-(3-Cyanopyridyl-4)acrylic Acid (VIIb, $C_9H_6N_2O_2$). To a boiling solution of 1.74 g (10 mmole) compound II and 2.65 g (15 mmole) benzene sulfonyl chloride in 30 ml acetone was added, over 3-4 min with stirring, 70 ml 10% NaOH, boiled for 10 min, cooled, neutralized with 10% HCl to pH 7 and the acetone distilled off. The solution was filtered, the filtrate acidified with 12% HCl to pH 4, the precipitate removed and dissolved in 50 ml 10% $NaHCO_3$, boiled with activated carbon, filtered and again precipitated by the addition of 12% HCl to pH 4. The precipitate was filtered off, washed with water, and dried. Yield 1.6 g (93%), mp 236-237°C (from 1:1 water-ethanol).

4-Nitrosoantipyrine (VIII, $C_{11}H_{11}N_3O_2$). To a solution of 1.9 g (10 mmole) antipyrine in 10 ml acetic acid cooled to 0 to +5°C was added a solution of 0.8 g (12 mmole) sodium nitrite in 5 ml water, stirred 20 min, diluted with 20 ml water, and the emerald-colored crystals which formed removed by suction. Yield 1 g (23%), mp 185-190°C.

Rearrangement of 3-nitroso-4-hydroxycoumarin (V). To a solution of 2.83 g (15 mmole) compound V and 3.81 g (20 mmole) p-toluenesulfonyl chloride in 50 ml acetone was added a solution of 2.04 g NaOH in 20 ml water, boiled 10 min, cooled, 12% HCl added to pH 8, the acetone distilled off, the solution purified with activated carbon and filtered. The filtrate was acidified with 12% HCl to pH 3, the precipitate removed, washed with water, and reprecipitated from 15 ml $NaHCO_3$. Product 2.0 g (96%) salicylic acid with mp 157-158°C. From [20], mp 159.5°C.

4-Nitrosoantipyrine did not react in this way; the starting material was recovered unchanged.

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SYNTHESIS AND PROPERTIES OF ANALOGS OF 5(4)-AMINOIMIDAZOLE-4(5)-CARBOXAMIDE AND PURINES.

15.* RING OPENING IN IMIDAZO[4,5-d]-1,2,3-TRIAZINES

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It has been shown that 4-methylthio-, ethoxy-, and methoxyimidazotriazines and imidazotriazin-4-ones, unlike benzo-1,2,3-triazines, do not display cryptodiazonium behavior. A novel type of fission of the triazine ring to give esters and thioesters of 5-aminoimidazole-4-carboxylic acid is described.

It is known that imidazotri- and -tetrazoles and -triazines [2-4], like benzotriazines [5], undergo cleavage of the triazine ring in acid media or on treatment with nucleophiles to give diazo-compounds. We report here some aspects of the behavior of 4-chloro-, thio-, and alkoxyimidazotriazines (Ia-d) in aqueous acid media.

On heating the chloroimidotriazine (Ia) with dimethylaniline in aqueous hydrochloric acid, there was obtained the expected imidazole (III), identical (IR and UV spectra) with that reported previously [3].

With aniline, on the other hand, N- rather than C-azocoupling of 5-diazoimidazole-4-carbonitrile (II), formed by fission of the $N_{(2)}$–$N_{(3)}$ bond in the triazine ring in (Ia), takes place. The resulting monosubstituted triazine (IV), like 5-(3-methyl-1-triazeno)-imidazole-4-carbonitrile [3], is then converted under the reaction conditions into the 4-iminotriazine (V). (Formula, top, following page.)

Confirmation of this reaction scheme was provided by the isolation from the reaction mixture of the aminoimidazolecarbonitrile (VI), and by the formation of (V) directly from the diazoimidazole (II) and aniline [3].

For Communication 14, see [1].

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