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MASS-SPECTROMETRIC IDENTIFICATION OF THE TAUTOMERIC FORMS OF BISTHIOCARBONOHYDRAZONES OF KETONES IN THE GASEOUS PHASE

V. V. Lashin, P. B. Terent'ev, K. N. Zelenin,
G. A. Bulakhov, and V. V. Alekseev

Electron-impact mass spectrometry was used to identify the 2-hydrazono-1,3,4-thiadiazolidone form and linear tautomeric forms of bisthiocarbonohydrazones of acetone, pinacolone, and acetophenone. For the derivatives para-nitro- and para-methoxyacetophenone in the gaseous phase, a third possible 1,2,4-triazolidine-3-thione tautomer was detected in addition to the other two. Ions characterizing each of the tautomeric forms were found in the mass spectra of bisthiocarbohydrazones of acetophenones.

Earlier, we successfully applied the method of electron-impact (ET) mass spectrometry to the identification in the gaseous phase of a linear and two cyclic (2-amino-1,3,4-thiadiazolidine and 1,2,4-triazolidine-3-thione) tautomeric forms of thiosemicarbazones of carbonyl compounds [1-3]. The appearance of an additional NH group in monothiocarbonohydrazones has made possible the formation of a fourth, hexahydro-1,2,4,5-tetrazine-3-thione tautomeric form. However, despite the fact that we recorded the linear and thiadiazolidine tautomers mass-spectrometrically in the gaseous phase [4, 5], we were unable to distinguish the five-membered from the six-membered nitrogenous heterocyclic tautomers on the basis of mass-spectral data for monothiocarbonohydrazones unsubstituted at the nitrogen atoms, since the $[M-NHCS]^{+\cdot}$ and $[M-CH_2N_2S]^{+\cdot}$ ions are formed during mass-spectral breakdown of the two forms. For bisthiocarbonohydrazones, the formation of the tetrazine tautomer is excluded, making it possible to distinguish mass-spectrometrically three possible (but not bicyclic) tautomeric forms from one another. Therefore, we chose bisthiocarbonohydrazones I-V (see Scheme 1) as the subject of the present study (see top of the following page).

According to the data of ^1H and ^{13}C spectra (Table 1), these substances in DMSO solution exist entirely in canonic linear form A (Scheme 1) without manifesting any signs of transitions to any of the cyclic tautomeric forms.

As is evident from a comparison of the data of Tables 2 and 3, the peaks of the characteristic ions in the mass spectra of these compounds (Table 3) were of moderate strength. This is due to the fact that the high-intensity peaks of the $(M-\Phi_1)^{+\cdot}$ and $(M-\Phi_2)^+$ ions and their protonated analogues $(M-R)^+$ (for derivatives of acetone I and pinacolone II) and $C_6H_5^+$ (for derivatives of acetophenone III, para-nitro- IV and para-methoxyacetophenone V) do not provide sufficient information to permit one to distinguish the tautomeric forms. At the same time, the peaks of the $\Phi_3-\Phi_7$ ions, despite their low strength, permitted a precise identification of the different tautomers.

The EI mass spectra (Tables 2 and 3, Scheme 1) of bisthiocarbonohydrazones of acetone I and pinacolone II had the peaks of the $\Phi_1-\Phi_4$ ions indicating the presence in the gaseous phase of only two tautomeric forms, A and B. Since the Φ_3 and Φ_4 fragments could only be formed from tautomer B after breakdown of its molecular ion via paths A and B, respectively (Scheme 1), the presence of this tautomer in the gaseous phase was unquestionable. However, the Φ_1 and Φ_2 fragments could have originated both from linear tautomeric form A and from heterocyclic compound B after rupture of the C−N and N−N single bonds (Scheme 1), i.e., the Φ_1 and Φ_2 ions cannot be characteristic of tautomer A and hence, for compounds I and II we were unable to distinguish the linear A and thiadiazolidine B tautomeric forms.

M. V. Lomonosov Moscow State University, Moscow 119899. S. M. Kirov Military Medical Academy, St. Petersburg 194175. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 563-566, April, 1994. Original article submitted April 7, 1994.

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TABLE 1. Parameters of the PMR Spectra of Compounds I-V in DMSO-d_6

Compound	Chemical shifts δ, ppm		
	CH_3, s	R	NH_2, s
I	2,01	2,08 s	9,95
II	1,94	1,12 s	9,82
III	2,42	7,4...8,1 m	10,80
IV	2,40	8,0...8,3 m	11,05
V	2,34	3,72 s, 7,04 d & 7,90 d	10,71

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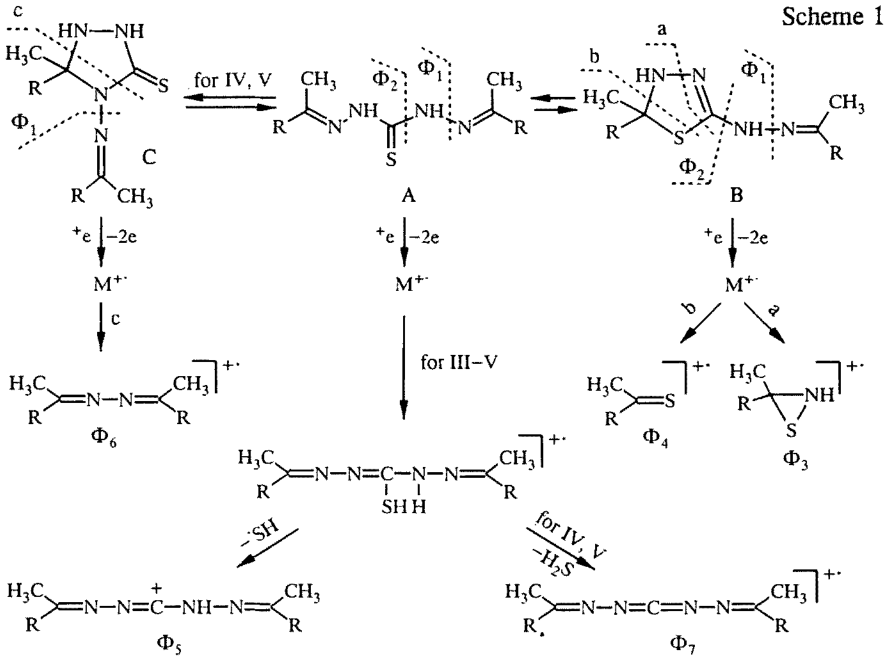
*^{13}C NMR spectra (DMSO-d_6): III 14.1 (CH_3), 126.5, 128.5, 129.6, 137.8 (C_{arom}), 150.0 (C=N), 175.6 (C=S); V 13.8 (CH_3), 55.2 (CH_3O), 113.8, 127.9, 130.1, 160.5 (C_{arom}), 151.0 (C=N), 175.2 (C=S).

Scheme 1



I R = CH_3, II t-Bu, III Ph, IV 4-$NO_2C_6H_4$, V 4-$CH_3OC_6H_4$

In the mass spectrum of the acetophenone derivatives III, in addition to the peaks of the $\Phi_1-\Phi_4$ ions, the Φ_5 fragment was observed (Table 3, Scheme 1), which could only have formed from linear tautomer A as a result of the ions of a sulfhydryl radical by its iminethiol form. Since in the case of compound III we were able to distinguish the two tautomers present in the gaseous phase, we next studied bisthiocarbonohydrazones of substituted acetophenones IV and V. A study of the mass spectra of these compounds enabled us to conclude that a third tautomeric form C was present in the gaseous phase, as evidenced by the peak of the Φ_6 ion (Table 3, Scheme 1), formed from the molecular ion via path c. At the same time, the Φ_5 fragment in this case can no longer be characteristic of linear tautomer A, since it could have formed from the heterocyclic compound C also after transfer of a hydrogen atom to the thiocarbonyl group. However, in addition to the loss of a sulfhydryl radical by the molecular ions of compounds IV and V, we observed the formation of the Φ_7 fragment (Table 3, Scheme 1). This ion could only have formed from linear tautomer A as a result of the loss of a hydrogen sulfide molecule.

Thus, a careful study of the EI mass spectra of bisthiocarbonohydrazones of para-nitro- and para-methoxyacetophenones has made it possible to prove the presence in the gaseous phase of three possible tautomeric forms, A, B, and C, of these compounds.

TABLE 2. Mass Spectra of Compounds I-V*

Compound	m/z (relative intensity, %)
I	186(100) M, 171(27), 115(28), 98(8), 89(12), 72(24), 71(21), 58(39), 57(28), 56(69), 42(45)
II	270(6) M, 213(67), 116(17), 100(6), 84(5), 83(5), 69(11), 57(100), 55(9), 43(7), 42(41)
III	310(57) M, 295(20), 134(28), 133(32), 120(40), 119(35), 118(46), 104(50), 103(23), 77(100), 51(33)
IV	400(1) M, 221(63), 179(90), 164(34), 163(70), 118(45), 117(100), 77(26), 76(67), 75(22), 50(29)
V	370(13) M, 206(81), 164(92), 149(100), 148(54), 134(20), 133(35), 108(22), 107(36), 92(30), 77(57)

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*Shown are the peak of the molecular ion and the ten strongest peaks.

TABLE 3. Strengths of Peaks of Certain Characteristic Ions (% Σ_{40}) of Compounds I-V

Compound	w_M	$\Phi 1$	Φ_2	Φ_3	Φ_4	Φ_5	Φ_6	Φ_7
I	19,9	2,3	5,4	2,3	0,8	—	—	—
II	2,6	0,2	0,4	7,8	0,3	—	—	—
III	8,8	1,5	2,6	1,1	1,1	0,2	—	—
IV	0,3	0,1	1,0	0,1	0,3	0,1	0,2	0,1
V	2,0	0,2	1,6	0,1	0,5	0,1	0,5	0,4

EXPERIMENTAL

The ^{1}H NMR spectra were recorded with a Tesla BS-497 instrument (100 MHz), and the ^{13}C NMR spectra, with a Gemini-200 instrument (50.29 MHz). The chemical shifts were measured against TMS as the internal standard.

The mass spectra of compounds I-V were recorded by directly inserting the substance into the ion source in an MX-1321A instrument at an ionizing electron energy of 70 eV and an ionization chamber temperature of 200°C.

Bisthiocarbonohydrazones I-V were obtained by means of the method described in [6]: compound I — by boiling the thiocarbonohydrazide in acetone, and compounds II-V — by reacting the thiocarbonohydrazide (0.05 mole) with the corresponding ketone (0.11 mole) in 75% aqueous ethanol. Compound I: yield, 60%; m.p. 185°C [6]; II: yield, 72%; mp 142°C; III: yield, 82%; mp 184-185°C [6]; IV: yield, 60%; mp 210-212°C; V: yield, 65%: mp 205-206°C.

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