MESOIONIC 1-AMINO-1,3,4-TRIAZOLE-2-THIONES AND THEIR AZOMETHINE DERIVATIVES

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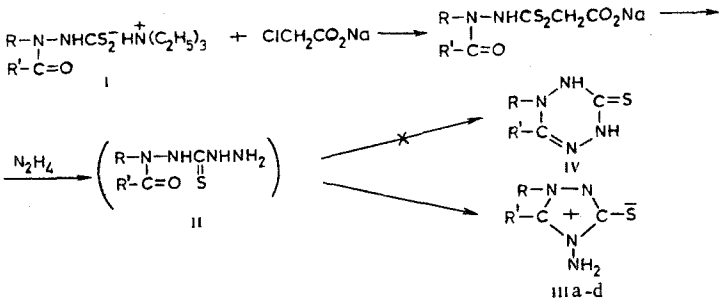
The reaction of triethylammonium salts of α-acyldithiocarbazic acids with sodium chloroacetate and hydrazine leads to the formation of mesoionic 1-amino-1,3,4-triazole-2-thiones, which react with aldehydes to give the corresponding azomethine derivatives.

In an attempt to synthesize 1-benzoyl-1-phenylthiocarbohydrazide (II) by the Jensen method [1, 2] we obtained a cyclization product, to which we assigned the mesoionic 1-amino-4,5-diphenyl-1,3,4-triazole-2-thione structure (IIIa) [3].



IIIa R=R′=C$_6$H$_5$; b R=C$_6$H$_5$, R′=*p*-ClC$_6$H$_4$, c R=CH$_3$, R′=H; d R=C$_6$H$_5$CH$_2$, R′=H

1,4-Dihydro-1,2,4,5-tetrazine-3-thione structure IV may serve as an alternative structure for aminotriazole III [4]. However, nitrosation of the reaction product gives 4,5-diphenyl-3H-1,3,4-triazole-2-thione (VI), and reaction with aldehydes gives the corresponding azomethine derivative [3]; this is characteristic for 1-amino-1,3,4-triazole-2-thiones [5].

V a R=R′=R″=C$_6$H$_5$; b R=CH$_3$, R′=H, R″=C$_6$H$_5$; c R=C$_6$H$_5$CH$_2$, R′=H, R″=C$_6$H$_5$; d R=R′=C$_6$H$_5$, R″=3-CH$_3$O-4-HOC$_6$H$_3$; e R=R′=C$_6$H$_5$, R″=*p*-(CH$_3$)$_2$NC$_6$H$_4$; f R=R′=C$_6$H$_5$, R″=*o*-HOC$_6$H$_4$; g R=R′=C$_6$H$_5$, R″=furyl

The mesoionic sym-triazolo[3,4-b]-1,3,4-thiadiazole system (VII) is formed in the reaction of IIIa with benzimidocarbonyl dichloride and phosgene; this reaction is characteristic for thioacylhydrazines [6].

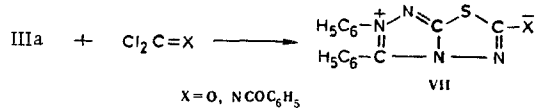


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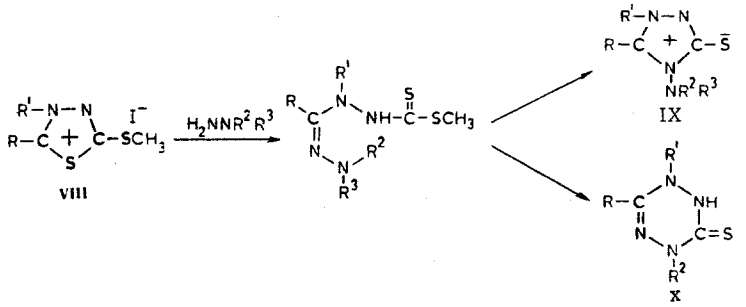
TABLE 1. Mesoionic 1-Amino-1,3,4-triazole-2-thiones (III) and Their Azomethine Derivatives (V)

Compound	mp, °C	Empirical formula	Found, %				Calculated, %				UV spectrum, λ_{max}, nm (log ε)	IR spectrum, cm^{-1}	PMR spectrum, δ, ppm	Yield, %
			C	H	N	S	C	H	N	S				
IIIa	215—216 (dec.)	$C_{14}H_{12}N_4S$	62,4	4,5	20,7	12,0	62,6	4,5	20,9	12,0	328 (3,48) 252 (4,29)	3290, 3240, 3220, 3080, 1635, 1610, 1525, 1390, 1365	7,16 m (C_6H_5)	51
IIIb	158—158,5	$C_{14}H_{11}N_4SCl$	55,7	3,6	18,7	10,5	55,5	3,7	18,5	10,6	334 (4,48) 254 (4,72)	3280, 3220, 3100, 1630, 1600, 1515, 1488, 1380, 1360	7,12 m (arom.)	29
IIIc	192,5	$C_3H_6N_4S$	28,0	4,5	42,9	24,8	27,7	4,6	43,0	24,6	248 (4,56) 234 (4,52)	3250, 3170, 3080, 3050, 2960, 1635, 1590, 1505, 1390, 1360	8,96 s (C—H); 3,62 s (CH_3—N)	30
IIId	220—221	$C_9H_{10}N_4S$	52,2	4,9	27,4	15,3	52,4	4,9	27,2	15,5	248 (4,57)	3290, 3200, 3180, 3130, 3070, 3010, 2910, 1660, 1500, 1370, 1340	8,82 s (C—H); 7,00 s (C_6H_5) 5,00 s (CH_2)	16
Va	224	$C_{20}H_{16}N_4S$	69,7	4,7	16,1	9,0	69,8	4,7	16,3	9,3	350 (3,46) 258 (4,49)	1615, 1520, 1490, 1465, 1380, 1330, 1325	7,08 m (C_6H_5)	87
Vb	198,5—199	$C_{10}H_9N_4S$	55,5	4,1	26,0	14,7	55,3	4,2	25,8	14,8	348 (3,15) 244 (4,67)	1630, 1602, 1488, 1460, 1362, 1340	8,25 s (C—H); 7,18 m (C_6H_5) 3,72 s (CH_3—N)	89
Vc	188	$C_{16}H_{14}N_4S$	65,5	4,9	19,1	11,1	65,3	4,8	19,0	10,9	342 (3,41) 266 (4,52)	1612, 1580, 1485, 1460, 1370, 1342	8,17 s (C—H); 7,04 m (C_6H_5) 5,08 s (CH_2)	74
Vd	181,5	$C_{22}H_{19}N_4SO_2$	65,3	4,8	13,7	7,9	65,5	4,7	13,9	8,0	318 (4,50) 292 (4,41) 234 (4,66)	1600, 1515, 1480, 1435, 1380	7,10 m (arom.) 3,53 s (O—CH_3)	94
Ve	199—199,5	$C_{23}H_{21}N_5S$	69,2	5,3	17,2	8,1	69,1	5,3	17,5	8,0	348 (4,07) 248 (4,76)	1620, 1595, 1540, 1520, 1485, 1378	7,16 m (arom.); 3,04 s (N—CH_3)	71
Vf	198—198,5	$C_{21}H_{16}N_4SO$	67,9	4,4	14,9	8,8	67,7	4,3	15,0	8,6	332 (3,84) 256 (4,40)	1630, 1610, 1515, 1490, 1390	7,12 m (arom.)	73
Vg	198	$C_{19}H_{14}N_4SO$	66,1	4,2	16,4	9,5	65,9	4,1	16,2	9,3	296 (4,57) 258 (4,68)	1622, 1605, 1520, 1490, 1478, 1380	7,10 m (C_6H_5); 7,52 s 6,75; 6,22 m (furan ring protons)	77

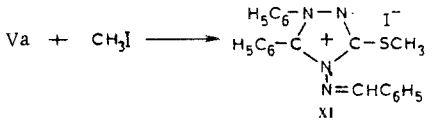


In addition, in [4] Grashey and co-workers were able to obtain either mesoionic aminotriazole IX or 1,4-dihydrotetrazinethione X by reaction of 2-methylthio-1,3,4-thiadiazolium salts VIII with substituted hydrazines, depending on the reaction conditions and the hydrazine used.

No physical constants whatsoever of the synthesized compounds nor concrete reaction conditions, except for the PMR spectra, which differs substantially for these two reaction products, are presented in [4]. In the PMR spectra of the III and V that we synthesized, the signal of the protons of the methyl group (CH_3–N, δ 3.62-3.72 ppm) coincides with the signal of the protons of the methyl group of the aminotriazoles presented in [4] (3.40-3.75 ppm), whereas the signal of the protons of the methyl group of X is found at stronger field – 2.80-2.92 ppm.

Inasmuch as we have previously described only one representative of mesoionic aminotriazoles (IIIa) [3], in the present research we have synthesized several representatives of this class of compounds and a number of their azomethine derivatives.

Compounds III and V have two absorption bands in their UV spectra (Table 1) – a shortwave band at 234-254 nm and, when aromatic substituents are present, a second band in the longwave portion of the spectrum at 296-350 nm. Similar UV spectra have been described for other mesoionic triazoles [7-9]. The IR spectra of III and V contain a very intense band at 1325-1390 cm^{-1}, which is characteristic for the NC=S grouping of mesoionic triazolethiones [9]. The absorption at 1400-1630 cm^{-1} is extremely characteristic for these compounds. Infrared spectra of similar character have been described for mesoionic triazoles [9, 10]. Bands of stretching vibrations of an NH_2 group at 3100-3300 cm^{-1}, which are absent in the spectra of V, are observed in the IR spectra of III. Methiodide XI was obtained from azomethine derivative Va; the absorption of a thione group is absent in the IR spectrum of XI, whereas its UV spectrum is similar to the spectra of salts of mesoionic triazolethiones [6].



The PMR signal of the ring protons in the 5 position of mesoionic triazoles is usually found at very weak field – from 10.3 to 9.0 ppm [8, 9]. The ring proton in III gives a signal in the same region, whereas it gives a signal at somewhat stronger field in the spectra of V (see Table 1).

The mass spectrum of IIIa, the probable pathways of fragmentation of the molecular ion of which are represented in Fig. 1 on the following page,* may serve as an example of the fragmentation of III under the influence of electron impact.

Intense molecular ions are observed in the mass spectra of all compounds of the III type. Splitting out of an NH fragment and the formation of a disubstituted triazole ring from the trisubstituted ring are also characteristic for them. The ion with mass number 253 in the mass spectrum of Va is the most intense ion, and this confirms the presence of identical triazole rings in IIIa and Va.

*The numbers under the formulas are the m/e values, the intensities with respect to the maximum ion are given in parentheses, and the numbers with asterisks denote the apparent mass of the metastable ion.

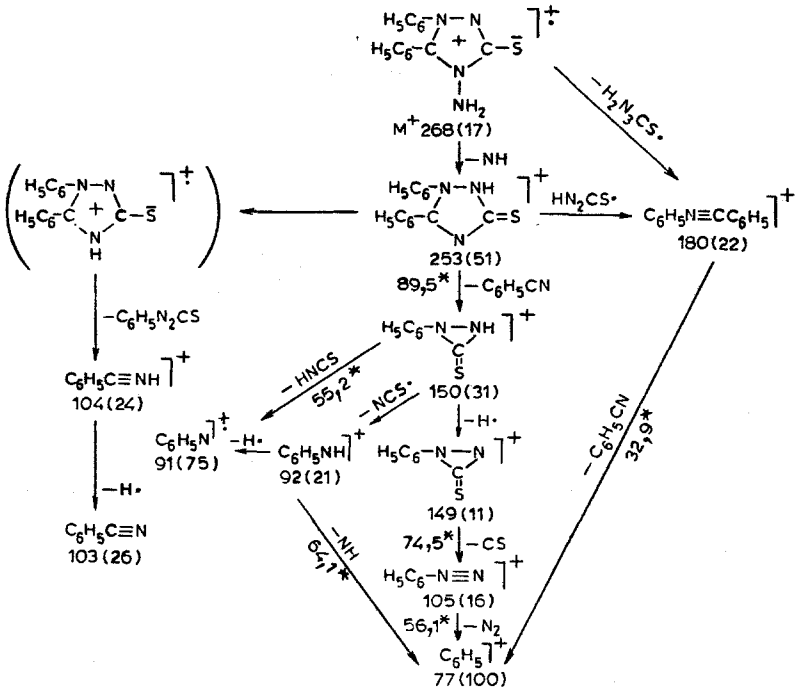


Fig. 1. Mass-spectral characteristics of 1-amino-4,5-substituted-1,3,4-triazole-2-thiones (III) and 1-benzylideneamino-4,5-diphenyl-1,3,4-triazole-2-thione (Va).

IIIa 268 (17), 253 (51), 180 (22), 150 (31), 149 (11), 105 (16), 104 (24), 103 (26), 92 (21), 91 (75), 77 (100).

IIIb 304 (18), 302 (55), 272 (17), 270 (52), 255 (10), 139 (20), 137 (71), 133 (32), 111 (14), 102 (12), 91 (100), 77 (45).

IIIc 130 (52), 88 (45), 87 (22), 73 (27), 60 (16), 59 (11), 59 (9), 45 (21), 43 (60), 42 (60).

IIId 206 (20), 191 (19), 103 (14), 91 (100).

Va 253 (100), 221 (18), 180 (37), 150 (45), 149 (14), 129 (18), 118 (13), 105 (14), 104 (20), 103 (24), 92 (20), 91 (79), 77 (83).

EXPERIMENTAL

The melting points were determined with a Kofler block and were not corrected. The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The UV spectra of acetonitrile solutions were recorded with an SF-4 spectrophotometer. The PMR spectra of CF_3CO_2H solutions were recorded with a Tesla BS 487C spectrometer (80 MHz) with hexamethyldisiloxane as the internal standard. The mass spectra were obtained with an MKh-1303 spectrometer with a system for direct introduction of the samples into the ion source at an ionizing voltage of 70 V (the vaporization temperature of IIIa-IIId was ~115°, as compared with ~180° for Va).

Mesoionic 1-Amino-1,3,4-triazole-2-thiones (IIIa-d). The triethylammonium salts of acyldithiocarbazic acids (I) (40 mmole) were added in portions to a heated (to 40°) solution of 4.45 g (45 mmole) of sodium chloroacetate in 20 ml of water, and the mixture was stirred until all of the solid dissolved. The resulting solution was filtered, treated with 2.24 g (45 mmole) of hydrazine hydrate, and heated on a boiling-water bath for 40 min. The resulting precipitate was removed by filtration, washed with water, dried, and recrystallized from dimethylformamide (DMF)–alcohol. The physical constants, yields, and spectral characteristics of III are presented in Table 1.

Mesoionic 1-Azomethine-1,3,4-triazole-2-thiones (Va-g). A solution of 3 mmole of III and 3 mmole of aldehyde in 5 ml of glacial acetic acid containing 0.1 g of anhydrous sodium acetate was refluxed for 1 h, after which the mixture was cooled, and the resulting precipitate was removed by filtration, washed with ether, dried, and recrystallized from DMF–alcohol. See Table 1 for the physical constants, yields, and spectral characteristics of V.

S-Methyl-1-benzylideneamino-4,5-diphenyl-1,3,4-triazoline-2-thione Iodide (XI). A solution of 0.61 g (1.8 mmole) of IVa in 5 ml of absolute alcohol was heated on a boiling-water bath in a sealed ampul with 1 ml of methyl iodide for 4 h, after which the mixture was allowed to crystallize overnight. The resulting crystals were washed with absolute ether to give 0.68 g (80%) of analytically pure XI with mp 148-150°. UV spectrum, λ_{max} (log ε): 246 nm (4.73). IR spectrum: 1625, 1612, 1527, and 1490 cm^{-1}. PMR spectrum, ppm: 7.08 (multiplet, C_6H_5) and 2.43 (singlet, $S-CH_3$). Found: N 11.7%. $C_{21}H_{19}N_4SI$. Calculated: N 11.5%.

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