SYNTHESIS OF DERIVATIVES OF 4-IMINO-2-AMINO-2-IMIDAZOLINE. NEW EXAMPLE OF A MULTICOMPONENT CONDENSATION INVOLVING ISONITRILES

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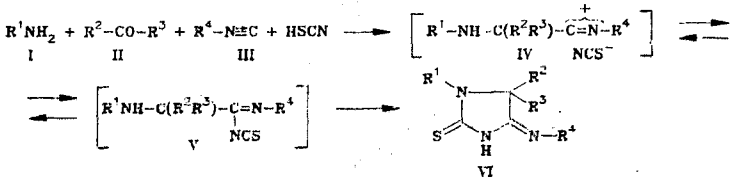
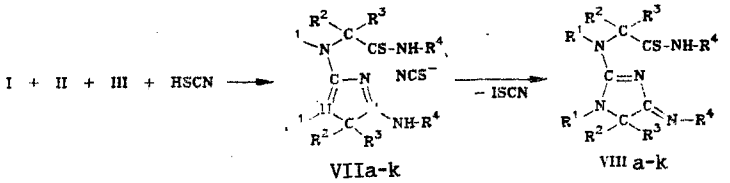
Isonitriles have been found to react with ketones and ammonium and methylammonium thiocyanates in methanol or ethyleneglycol at 20°C to form derivatives of 4-imino-2-amino-2-imidazoline and 2,4-diaminoimidazolium salts.

Ugi [1] has shown the possibility of preparing 2-thiohydantoin-4-imines by the condensation of amines I and ketones II with isonitriles III and thiocyanic acid by the scheme



Upon using this reaction for the preparation of hydantoins VI with R^1 = H and CH_3, we found an unusual multicomponent condensation leading to imidazole derivatives VII and VIII, which were more complex than previously assumed [2].



The condensation products are, as a rule, imidazolium salts VII, have strong IR bands for the S—C≡N group at 2030-2080 cm^{-1} and give a positive test for the thiocyanate ion with $FeCl_3$ solution.

Compounds such as VIIa and VIIe formed from acetone, p-tolylisonitrile and benzylisonitrile contain two molecules of bound HSCN, apparently as a result of the reaction 2 VII → VII•HSCN + VIII. This is supported by the elemental analysis and IR spectral data (Table 1). The site of the addition of the second HSCN molecule could not be determined but is most likely $N_{(2)}$ of the imidazole ring.

Imidazole derivatives VII and VIII are readily interconverted upon the corresponding change in solution pH. Their structures were established finally only by x-ray diffraction structural analysis. The x-ray diffraction structural data for model compounds VIIj and VIIIe are given in Fig. 1 and in the Experimental.

Since the conditions for the reaction studied are identical to those for a well-investigated four-component condensation, we assume, that differences in the reaction mechanism between them may arise only in the step involving stabilization of intermediates IV and V. Assuming the formation of aziridinimine IX as an intermediate, the preparation of VII and VIII may, in our opinion be explained by the following scheme:

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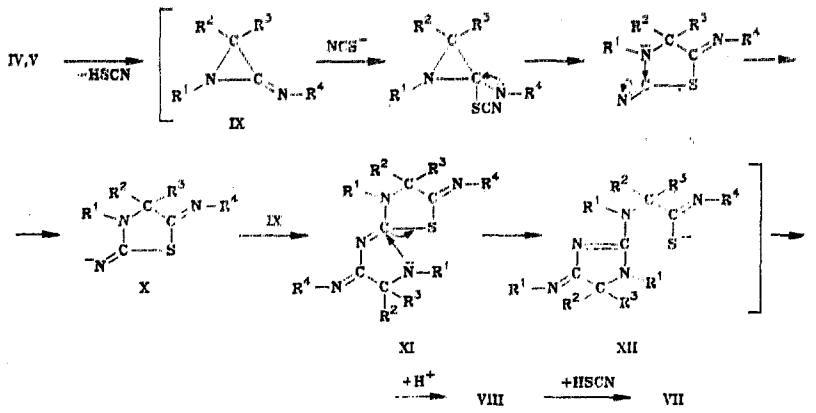
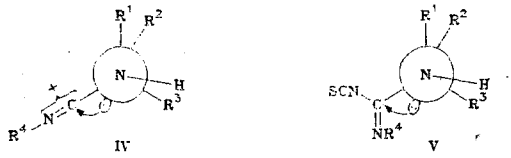


The reaction of thiazolidine X with IV or V may be presented analogously to the formation of VII and VIII.

The rate of consumption of X in the abovementioned reactions is apparently rather high and, as a result, the corresponding 2,5-diimino-1,3-thiazolidines are not found among the products.

Thus, the key compound controlling the condensation is aziridinimine IX. Conformations of the reaction site close to eclipsed must precede the formation of both IX and VI from intermediate IV or V. These conformations for IV and V may be represented along the C—N bond as follows:

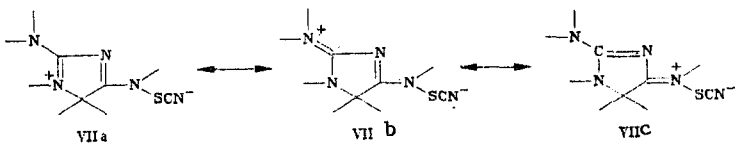


The steric hindrance which is important for realization of the conformation leading to the formation of aziridinimine IX is minimal for R^1 = H and CH_3. Thus, the steric factor apparently determines the nature of the reaction such that multicomponent condensation is found upon slight repulsion between R^1, R^2 and R^3, while four-component condensation is found in the case of strong repulsion of these substituents.

The IR spectra of all imidazolium salts VII and imino-2-imidazolines VIII taken in KBr pellets are in full accord with the x-ray diffraction structural data. An increase in the intensity of the C=N band at 1620-1660 cm^{-1} by almost a factor of 2 in going from VII to VIII is characteristic for the IR spectra of these compounds. This increase is probably a consequence of the extension of the conjugation chain involving the two azomethine groups.

This conclusion is in accord with the x-ray diffraction structural data. The delocalization of the π-electron density leads to the levelling out of the lengths of the C—N double and single bonds (Fig. 1).

The bond lengths found indicate a definite contribution, for example, of the following resonance forms of imidazolium salts VII:



Special interest is found in the results of the spectral studies of solutions of these two groups of compounds (Tables 1 and 2). This is related, especially for iminoimidazolines VIII, to the expectation of a tautomeric equilibrium involving at least two forms; thioamide (A) and thiolimide (B). The formation of tautomer VIIIB, although this form was not found in the usual state for thioamides [3], might have been expected due to the possible stabilization of the thiol form by the nitrogen atoms of the guanidine group.

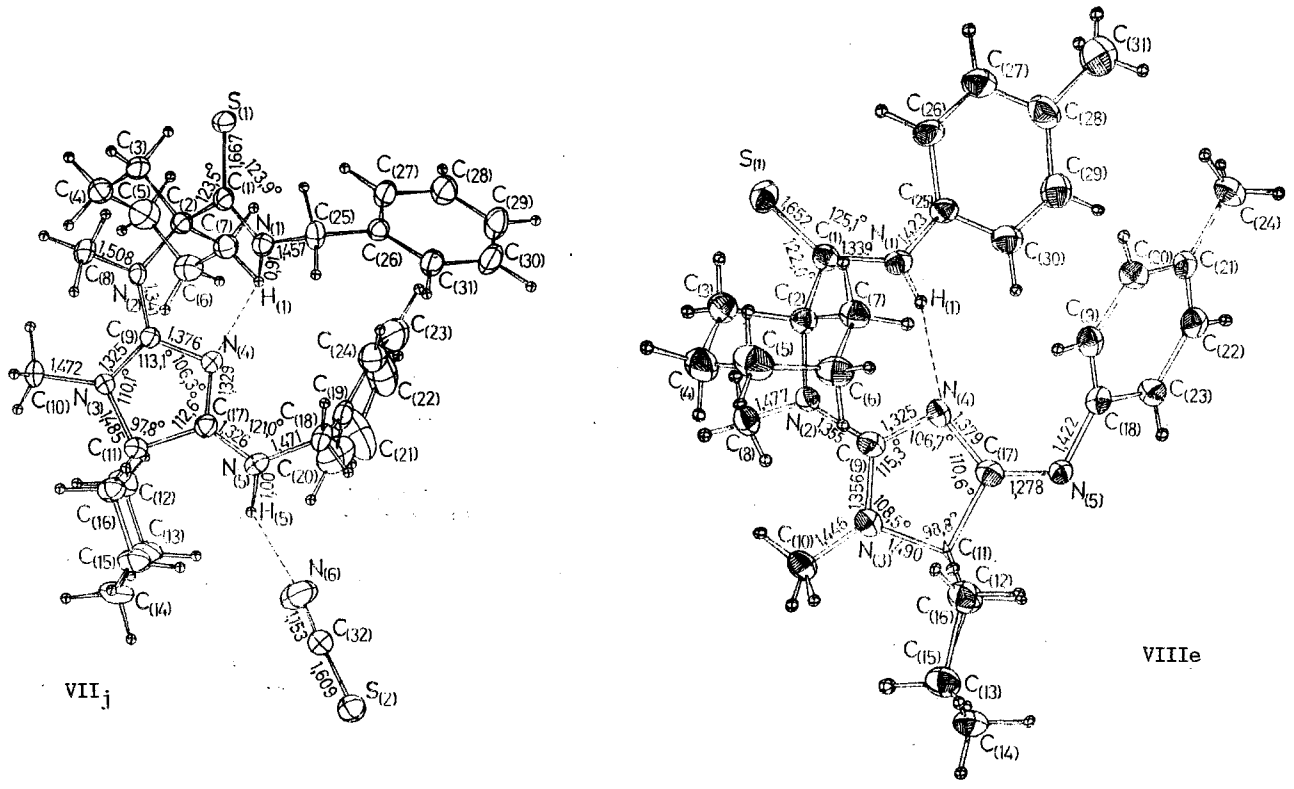


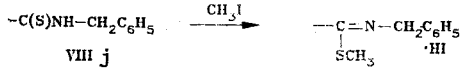
Fig. 1. Structure of the products of the multicomponent condensation, imidazolium salt VIIj and imino-2-imidazoline VIIIe.

According to the spectral data, derivatives VII in media of different polarity such as $CHCl_3$ and DMSO are virtually in a single tautomeric form A, containing an NH group in either the free or bound state. The IR spectra of solutions of salts VII in $CHCl_3$ do not contain a band characteristic for the SH group.

We should note the absence of coupling of the $NH-CH_3$ group protons in the PMR spectra of VIIa, c, h-j, which indicates that the azomethine group nitrogen atom is also protonated in solution.

The spectral data for iminoimidazolines VIII are rather complex in nature. Thus, the IR spectra of VIIIe, f, h, j in $CHCl_3$ show weak bands for a bound SH group at 2400-2600 cm^{-1}, signals for a free NH group at 3440-3490 cm^{-1} and lack the absorption characteristic for a bound NH group.

Some support for the equilibrium proposed above for solutions of VIII was obtained in the ^{13}C NMR spectrum of VIIIj. In addition to the signals for the carbon atoms of the thioamide, guanidine and amidine groups at 203.9 and 170.2 (double signal), in contrast to salt VIIj, there is a broad signal at 140.2 ppm for the base, which is apparently a result of the overlap of the signal for the thiolimide group S—C=N bond and of the aromatic carbon atoms. To support this assignment, we studied the possibility of the synthesis of a model compound with fixed tautomeric structure B. On the basis of elemental analysis and PMR spectral data, the iodomethylate obtained from VIIIj is a monoalkylated compound whose ^{13}C NMR spectrum lacks a thioamide group signal. Thee these findings indicate that reaction according to the scheme



The spectrum has a signal at 145.4 ppm assigned to the thiolimide group. The somewhat upfield shift of this signal is due to the salt character of this compound.

The iodomethylate thereby obtained has a structure analogous to imidazolium salts VII. As in compounds such as VII, it contains two similar $NH-CH_2$ group doublets in the PMR spectrum (see Experimental) and two C=N bond signals in the ^{13}C NMR spectrum.

TABLE 1. Physicochemical Indices for VIIa-k and VIIIa-k

Compound*	Mp, °C	IR spectrum, cm^{-1}			Found, %				Chemical formula	Calculated, %				Yield, %
		NH	SCN	C=N, C=C	C	H	N	S		C	H	N	S	
VII[a]	152—153	3420 br.	2040, 2070	1600, 1650, 1695	58,0	6,6	17,5	17,8	$C_{27}H_{35}N_7S_3$	58,5	6,4	17,7	17,4	53
VIII[a]	239—240	3440 †, 3350	—	1625, 1610	—	—	16,3	7,8	$C_{25}H_{33}N_5S$	—	—	16,1	7,4	75
VII[b]	205—207	3440	2040	1670, 1615, 1580	—	—	16,0	12,1	$C_{28}H_{36}N_6S_2$	—	—	16,1	12,3	64
VIII[b]	110—111	3440 †, 3400	—	1610, 1565	70,9	7,5	15,0	6,5	$C_{27}H_{33}N_5S$	70,6	7,2	15,2	7,0	80
VII[c]	238—239	3360, 3200 br.	2030	1665, 1615, 1580	—	—	15,4	11,7	$C_{30}H_{38}N_6S_2$	—	—	15,4	11,7	66
VIII[c]	222—224	3430 †, 3400, 3300 br.	—	1660, 1600, 1570	—	—	14,1	6,6	$C_{29}H_{37}N_5S$	—	—	14,35	6,6	65
VII[d]	190—191	3420	2080	1655, 1610, 1575	65,7	7,0	16,0	11,6	$C_{30}H_{38}N_6S_2$	65,9	7,0	15,9	11,7	55
VIII[d]	148—149	3440 †, 3420	—	1670, 1625, 1600	—	—	14,4	6,1	$C_{28}H_{37}N_5S$	—	—	14,7	6,7	47
VII[e]	160—161	3440 br., 3210	2065	1650, 1595	66,0	7,4	14,2	10,8	$C_{32}H_{42}N_6S_2$	66,7	7,4	14,6	11,1	62
VIII[e]	159—160	3440 †, 3410, 3260 br.	—	1660, 1600	72,2	7,9	13,1	6,8	$C_{31}H_{41}N_5S$	72,2	8,0	13,6	6,2	41
VII[f]	151—152	3360 br.	2040, 2070 cl	1660, 1620, 1580	—	—	17,6	17,2	$C_{27}H_{35}N_7S_3$	—	—	17,7	17,4	55
VIII[f]	208—209	3450 †, 3320	—	1625, 1580	—	—	16,2	7,0	$C_{25}H_{33}N_5S$	—	—	16,1	7,4	65
VII[g]	oil	3200 br.	2060	1685, 1600, 1580	—	—	15,9	11,9	$C_{28}H_{36}N_6S_2$	—	—	16,1	12,3	82
VIII[g]	105—106	3440 †, 3400	—	1610, 1570	—	—	15,0	6,8	$C_{27}H_{33}N_5S$	—	—	15,2	7,0	84
VII[h]	91—93	3220 br.	2060	1660, 1600, 1580	—	—	14,9	11,6	$C_{30}H_{38}N_6S_2$	—	—	15,4	11,7	57
VIII[h]	174—176	3440 †, 3420, 3300 br.	—	1600, 1535	—	—	13,9	6,4	$C_{29}H_{37}N_5S$	—	—	14,3	6,6	63
VIII[i]	176—177	3440, 3220 br.	2065	1655, 1580	66,1	7,2	15,6	11,7	$C_{30}H_{38}N_6S_2$	66,0	7,0	15,4	11,7	40
VII[j]	193—194	3440, 3240	2060	1640, 1575	66,7	7,3	14,8	11,2	$C_{32}H_{42}N_6S_2$	66,9	7,4	14,6	11,2	92
VIII[j]	150—151	3480	—	1620, 1585	72,2	7,8	13,3	6,3	$C_{31}H_{41}N_5S$	72,2	8,0	13,6	6,2	60
VII[k]	136—137	3440, 3280	2050	1730, 1685, 1580	54,8	7,9	14,6	10,9	$C_{26}H_{42}N_6O_4S_2$	55,2	7,4	14,5	11,3	54
VIII[k]	155—157	3450 †, 3440	—	1755, 1730	—	—	13,8	6,4	$C_{25}H_{41}N_5O_4S$	—	—	13,8	6,3	57

*VIIa and VIIf contain two HSCN molecules.
†In CCl_4.

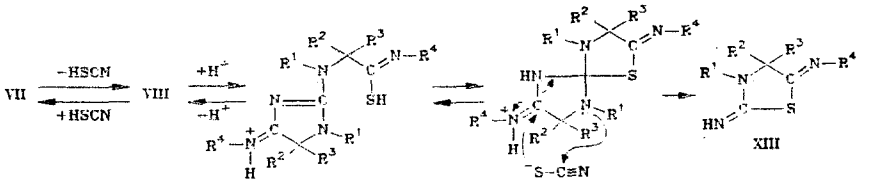
TABLE 2. PMR Spectra of VII and VIII

Compound	Chemical shift, δ, ppm
VII a	1,31; 1,44; 1,62; 1,65 (4×3H, 4 s, CH_3); 2,28; 2,49 (2×3H, 2 s, Ar—CH_3); 3,10 (6H, br.s N—CH_3); 6,97; 7,13 (2×4H, 2 d, C_6H_4); 9,01; 10,28 (NH, br.s)
VIII a	0,48; 1,24 (2×3H, 2 s, CH_3); 1,44 (6H, br.s CH_3); 2,14; 2,36 (2×3H, 2 s N—CH_3); 2,21 (6H, br.s Ar—CH_3); 7,14 (8H, m, C_6H_4); 8,48 (NH, br.s)
VII c	1,69 (20H, m, *cyclo*-C_6H_{10}); 2,25 (6H, br.s Ar—CH_3); 7,39 (8H, m C_6H_4); 7,87; 9,41; 10,90 (NH, br.s)
VII h	At 250 MHz 1,43—2,26 (20H, m, *cyclo*-C_6H_{10}); 4,40; 4,75 (2×2H, 2 d. CH_2N); 7,18; 7,27 (10H, m, C_6H_5); 7,80; 9,16; 10,05 (NH, br.s)
VIII h	(At 250MHz) 1,05—1,84 (20H, m, *cyclo*-C_6H_{10}); 4,45; 4,80 (2×2H, 2 d, CH_2N); 7,21; 7,28 (10H, m, C_6H_5); 6,32; 8,19; 9,56 (NH, br.s)
VII i	1,91 (16H, m *cyclo*-C_5H_8); 3,13; 3,22 (2×3H, 2 s CH_3—N); 4,36 (2H, br.s. CH_2—N); 4,73 (2H, d, CH_2—N); 7,15; 7,24 (2×5H, 2 s, C_6H_5); 9,72; 10,02 (NH, br.s)
VIIIj	[in $(CD_3)_2CO$] 1,72 (16H, m, *cyclo*-C_5H_8); The NCH_3 signals fall in the region of the solvent signals 4,25; 4,33 (2H, 2 d CH_2N); 4,42; 4,67 (2H, 2 s, CH_2N); 7,17 (10H, br.s C_6H_5); 6,15; 9,26 (NH, br.s)
VII j	1,48—2,06 (20H, m, *cyclo*-C_6H_{10}); 3,07; 3,26 (2×3H, 2 s, CH_3N); 4,27 (2H, br.d CH_2N); 4,70 (2H, d, CH_2N); 7,21 (10H, br.s C_6H_5); 7,75; 9,72 (NH, br.s)
	(br.d 250 MHz) 1,13—2,41 (20H, m, *cyclo*-C_6H_{10}); 3,17; 3,32 (2×3H, 2 s, CH_3—N); 4,37 (2H, br.d CH_2N); 4,82 (2H, d, CH_2N); 7,04—7,20 (10H, m C_6H_5); 9,68; 9,83 (NH, br. t)
	(HCL salt, 80°) 1,12—1,92 (20H, m *cyclo*-C_6H_{10}); 3,07; 3,26 (2×3H, s, CH_3N); 4,26 (2H, br. d, CH_2N); 4,70 (2H, d CH_2N); 7,19 (10H, m, C_6H_5); 9,96; 10,4 (NH, br.s)
VIII	1,61 (20H, m, *cyclo*-C_6H_{10}); 1,88; 2,06 (2×3H, 2 s CH_3N); 4,21; 4,27 (2×2H, 2 in CH_2N); 7,12; 7,17 (10H, 2 s C_6H_5); 8,53 (NH, br.s)
	[in $(CD_3)_2CO$] 1,65 (20H, m *cyclo*-C_6H_{10}); The NCH_3 signals fall in the region of the solvent signals 4.27; 4,35 (2H, 2 d CH_2N); 4,50; 4,76 (2H, 2s, CH_2N); 7,12; 7,16 (10H, 2s, C_6H_5); 8,62 (NH, br.s)

The PMR spectra of solutions of VIIIg and VIIIj in DMSO-d_6 show a significant downfield shift of the N—H and N—CH_3 group signals in comparison with VIIg and VIIj. This difference is attributed to the lack of the deshielding effect of the positive charge of the quanidine fragment upon going to the free base. The broadening of the NH signals in the PMR spectra of these compounds is also more pronounced relative to the salts, which complicates the detection of the thiolimide group.

Imidazolidines VIII are stable upon heating, but gradually decompose upon heating at reflux in water–ethanol solutions of KOH with the release of H_2S and formation of unidentified compounds.

Upon brief heating at reflux in benzene or toluene, salt VII is converted to thiazolidine XIII. On the whole, we propose the following scheme for this reaction:



The conversion of VII to 2 XIII in the case of R^4 = p-$CH_3C_6H_4$ proceeds more rapidly than in the case of R^4 = $CH_2C_6H_5$. Thus, one of the steps of this conversion presumably involves the thiolimide form, whose formation is especially facilitated in the case of R^4 = p-$CH_3C_6H_4$ by the conjugation of the aromatic ring electrons with the C=N bond.

Pseudoanalogs of thiazolidinimines XIII, namely, iminothiohydantoins VI, were not found among the reaction products.

A mass spectrometric study of VIIIh-j and XIIIa showed that VIIIi and VIIIj do not give molecular ion peaks, even at 15 eV, while the (M + 1) peak is present in these spectra. On

the other hand, the presence of peaks for the $(M - C_2H_4)$ and $(M - C_2H_5)$ ions (487 and 486 for VIIIj and 459 and 458 for VIIIi) in these spectra indicates their molecular mass (515 for VIIIj and 487 for VIIIi) in accord with the structures proposed for these compounds on the basis of the above results.

As expected, the mass spectra of these compounds have ion peaks* 91 ($C_6H_5CH_2^+$) while the (M + 1) peaks are 3-5 times stronger at 15 eV than at 70 eV. In addition, VIIIi and VIIIj give strong peaks for ions 272 and 286, which apparently, are formed as a result of M − [CH_3—N—C(CH_2)$_n$—C—NH$CH_2C_6H_5$], where n = 4 and 5, respectively, for VIIIi and VIIIj. The mass spectrum of VIIIh, in contrast to VIIIj, contains not only an M^+ peak (487) but also a greater number of strong peaks for ions with high mass numbers. The effect of structure of these similar compounds on the mass spectral intensity distribution clearly requires a separate discussion.

EXPERIMENTAL

The IR spectra were taken on a Perkin-Elmer 457 spectrometer in KBr pellets and $CHCl_3$ and CCl_4 solutions. The PMR and ^{13}C NMR spectra were taken on Bruker HX-90E (90MHz), Varian, and WM-250 (250 MHz) spectrometers for solutions in $(CD_3)_2SO$ with TMS as the internal standard. The mass spectra were taken on an LKB-2091 mass spectrometer at 70 eV.

The reaction course and compound purities were monitored by thin-layer chromatography on Silufol UV-254 plates in 1:5 acetone—benzene and 1:2 acetone—hexane solvent systems.

The isoitriles were obtained according to Ugi [1]. The x-ray diffraction structural analyses were carried out for monocrystals of VIIj and VIIIe. The major crystallographic data for VIIj, $C_{32}H_{42}N_6S_2$, M = 574.54 are a = 14.899(5), b = 18.875(8), c = 12.247(3) Å, α = 90, β = 90, γ = 65.23(2)°, V = 3127.22 Å^3, d_{calc} = 1.22 g/cm^3, z = 4, space group $P2_1/b$. The major crystallographic data for VIIIe, $C_{31}H_{41}N_5S$, M = 515.76 are a = 10.743(5), b = 11.185(6), c = 12.052(3) Å, α = 79.98(4), β = 80.88(3), γ = 89.62(4)°, V = 1407.77 Å^3, d_{calc} = 1.22 g/cm^3, z = 2, space group P1. Sets of 2846 reflections for VIIj and 2914 reflections for VIIIe with $I > 2\sigma$ were measured on DAR-UM (for VIIj) and Syntex P1 (for VIIIe) diffractometers. Absorption was not taken into account.

The structures were determined by the direct method according to Andrianov et al. [4]. The hydrogen atoms were localized from the R maps. The refinement was carried out by the method of least squares in the full-matrix approximation according to Andrianov et al. [4] assuming anisotropy for the S, N, and C atoms and isotropy for the hydrogen atoms to R = 0.056-0.055. Molecular representations were obtained using the ELLIDS program [5].

Structural parameters for the hydrogen bonds: VIIj, bond lengths: $N_{(4)}...H_{(1)}$ 2.04 (3); $N_{(4)}...N_{(1)}$ 2.891 (3); $N_{(6)}...H_{(5)}$ 1.93 (4); $N_{(6)}...N_{(5)}$ 2.814 (4) Å; angle $N_{(4)}H_{(1)}N_{(1)}$ 156 (3), $C_{(9)}N_{(4)}H_{(1)}$ 99.3 (9), $C_{(17)}N_{(4)}H_{(1)}$ 146.7 (8), $N_{(6)}H_{(5)}N_{(5)}$ 146 (3), $C_{(32)}N_{(6)}H_{(5)}$ 161 (1)°; VIIIe, $N_{(4)}...H_{(1)}$ 1.92 (3); $N_{(4)}...N_{(1)}$ 2.809 (3); $N_{(4)}H_{(1)}N_{(1)}$ 160 (3); $C_{(9)}N_{(4)}H_{(1)}$ 103.7 (9); $C_{(17)}N_{(4)}H_{(1)}$ 146.3 (9)°. VII, VIIa, d-f, i-k $R^1 = CH_3$, b, c, g, h $R^1 = H$; a, f $R^2 + R^3 = 2CH_3$, b, d, g, i $R^2 + R^3 = (CH_2)_4$, c, e, h, j, k $R^2 + R^2 = (CH_2)_5$, a-e R^4 = p-CH_3-C_6H_4, f-j $R^4 = C_6H_5CH_2$, k $R^4 = C_2H_5O_2CCH_2$.

2-4-Diaminoimidazolium Derivatives VIIa, d-f, i-k. A sample of 0.01 mole isonitrile was added dropwise with stirring to an equimolar mixture of 0.01 mole ketone, $CH_3NH_2 \cdot HCl$ + KSCN (NH_4SCN was used in the case of VIIb, c, g, h) in 8 ml ethyleneglycol or methanol at 20°C. The reaction mixture was stirred for 6 h and left overnight to yield a single, chromatographically-pure product as lightly colored crystals, which were washed with hexane and dried. In the preparation of VIId, the reaction mixture contained VIIId, which was isolated upon evaporation of the solution and washing of the residue with water (0.8 g).

The condensation with acetone and p-tolylisonitrile has several special features: only VIIIa is formed in ethyleneglycol while both VIIa and VIIIa are obtained in methanol. In the latter case, 0.65 g VIIIa in the precipitate was filtered off and VIIa was obtained by precipitation from water. This precipitate was extracted with three 20 ml portions of chloroform and the extract was dried over $MgSO_4$. The solvent was evaporated and the precipitate was filtered off and dried with 5 ml acetone and then hexane to yield 1.46 g (53%) VIIa. By analogy, 1.53 g (55%) VIIf and 0.7 g VIIIf were obtained in the reaction with benzylisonitrile in methanol.

*Here and subsequently, the ion peaks are given in units of m/z.

These compounds are insoluble in water, benzene, ether, and most organic solvents but are partially soluble in acetone, $CHCl_3$, dimethylsulfoxide, and DMF. ^{13}C NMR spectrum of VIIj: 204.3 (C=S), 181.3 (guanidine C=N), 170.0 (amidine (C=N), 130.3 (SCN), 137.1, 136.8, 128.5, 128.2, 127.4, 126.9 (C_6H_5), 72.9, 72.0 (C_{spiro}), 48.7, 46.3 ($N-CH_2C_6H_5$), 37.9, 36.8 ($N-CH_3$), 34.7, 33.0, 24.6, 22.7, 21.9, 20.4 (cyclo-C_6H_{10}).

2-Amino-4-imino-2-imidazoline Derivatives (VIIIa-k (Table 1). A sample of 10 ml 0.015 mmole 10% aqueous NaOH was added to a solution of 0.01 mmole VII in chloroform and stirred for 0.5 h. The chloroform solution of VIII was separated, dried over Na_2SO_4 and evaporated. These compounds are soluble in acetone, ethanol and chloroform.

^{13}C NMR spectrum of VIIj: 203.9 (C=S), 170.2 (double signal as a result of overlap of the guanidine and amidine C=N signals), 140.1 br, 136.9, 127.9, 127.3, 127.1, 126.4, 125.9, 117.3 (C_6H_5), 68.3, 63.5 (C_{spiro}), 45.5, 45.1 ($N-CH_2C_6H_5$), 38.5, 38.1 ($N-CH_3$), 35.6, 35.3, 31.4, 31.0, 27.7, 26.9, 24.8, 23.9, 22.2, 22.0, 21.8 (cyclo-C_6H_{10}). Mass spectra*: VIIIh, 91 (98), 92 (9), 98 (10), 107 (7), 215 (9), 245 (8), 257 (100), 258 (19), 281 (91), 336 (19), 337 (56), 338 (20), 354 (9), 362 (17), 453 (30), 454 (10), M^+ 487 (16); VIIIi, 65 (6), 68 (9), 91 (55), 92 (7), 96 (10), 98 (14), 125 (5), 176 (7), 230 (21), 271 (14), 272 (100), 273 (14), 380 (9), 381 (11), $(M + 1)^+$ 488 (13). VIIIj, 34 (6), 68 (5), 111 (14), 117 (16), 232 (5), 286 (100), 365 (9), 405 (7), $(M + 1)^+$ 516 (18).

The iodomethylate of VIIIj was obtained by treating VIIIj with a five-fold excess of CH_3I for 48 h. The product was obtained in 70% yield, mp 87°C. Found: C, C, 58.2; H, 69; N, 10.3; S, 4.9%. Calculated for $C_{32}H_{44}IN_5S$: C, 58.4; H, 6.7; N, 10.7; S, 4.9%. IR spectrum (KBr): 16.0, 1640 (C=N), 3160-3650 cm^{-1} (br. NH). PMR spectrum: 1.46-1.74 (20H, m, cyclo-C_6H_{10}), 2.22 (3H, s, $S-CH_3$), 3.24 (6H, br. s, NCH_3), 4.29 (2H, d, ($NHCH_2$), 4.68 (2H, br. d, $NHCH_2$), 7.13 (10H, br. s, C_6H_5), 9.62 ppm (NH, br. s). ^{13}C NMR spectrum: 178.7 (quanidine C=N), 166.0 (amidine C=N), 145.4 (S-C=N), 135.6, 134.6, 132.3, 129.4 (br. s), 121.8, 118.7 (br. s, C_6H_5), 71.49, 71.24 (C_{spiro}), 37.4, 36.3 (NCH_3), 32.8-20.47 (cyclo-C_6H_{10}), 13.20, 12.95 ppm (SCH_3).

1.3-Thiazolidin-5-imines (XXXa,e,j) were obtained from VIIa,e,j by heating at reflux in 2% toluene solution. The reaction was monitored by thin-layer chromatography. Products XIIIa and XIIIe were isolated from the oil obtained after solvent removal. XIIIa was dissolved in a minimum amount of acetone and separated by thin-layer chromatography using 1:3 acetone–benzene as eluent. XIIIe was obtained by crystallization of the oil from hexane. Thiazolidinimine XIIIj was crystallized from toluene upon cooling.

Thiazolidinimine XIIIa was obtained in 65% yield, mp 185°C. Found: N, 16.8; S, 13.3%. Calculated for $C_{13}H_{17}N_3S$: N, 17.0; S, 13.5%. Mass spectrum: 41 (7), 56 (100), 57 (7), 65 (7), 70 (7), 91 (14), 116 (27), 118 (7), 132 (14), 159 (9), 173 (7), 232 (33), M^+ 247 (99). IR spectrum (KBr): 1610, 1640 (C=N), 3435 cm^{-1} (NH).

Thiazolidinimine XIIIe was obtained in 70% yield, mp 155°C. Found: N, 14.8; S, 11.2%. Calculated for $C_{16}H_{21}N_3S$: N, 14.7; S, 11.2%. IR spectrum (KBr): 3415 (NH), 1695 cm^{-1} (br, C=N). ^{13}C NMR spectrum: 179.2, 178.7 (NC=NH), 157.8, 157.3 (C=N–Ar), 145.8, 138.6, 136.3, 133.4, 131.6, 129.5, 120.8, 119.0 (C_6H_4), 70.1, 65.5 (C_{spiro}), 37.9, 37.1 (NCH_3), 31.4-19.8 (cyclo-C_6H_{10}, CH_3-Ar).

Thiazolidinimine XIIIj was obtained in 100% yield, mp 205°C. Found: C, 66.4; H, 7.4; N, 14.4; S, 11.2%. Calculated for $C_{16}H_{21}N_3S$: C, 66.7; H, 7.3; N, 14.6; S, 11.2%. IR spectrum (KBr): 1585-1600 (C=C, C=N), 3420 cm^{-1} (NH). PMR spectrum: 1.66 (10H, m, cyclo-C_6H_{10}), 3.01, 3.15 (3H, 2 s, CH_3N), 4.29, 4.48 (2H, 2 s, CH_2N), 7.03-7.14 (5H, 2 s, C_6H_5), 8.33 ppm (NH, br. s). The ratio of the E and Z isomers was 1:5.

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*Here and subsequently, the ion peaks with intensity greater than 5% of the strongest peak are given; the intensities are given in parentheses.