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SYNTHESIS AND PROPERTIES OF 5-FURYL(ARYL)-Δ^2-1,2,4-TRIAZOLINES AND -Δ^2-1,3,4-THIADIAZOLINES. MOLECULAR AND CRYSTAL STRUCTURE OF 2-ACETYLAMINO-5-PHENYL-Δ^2-1,3,4-THIADIAZOLINE

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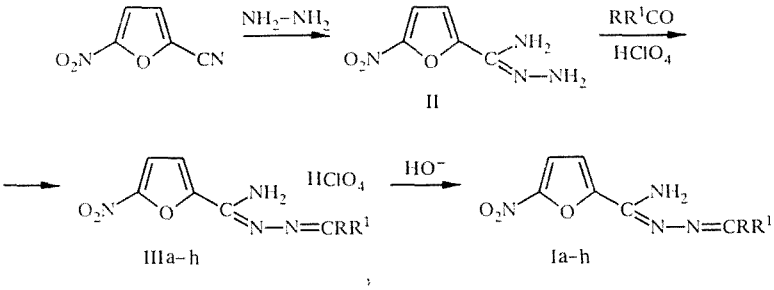
We show that upon acylation of arylidene amidrazones of 5-nitro-2-furancarboxylic acid, 3-(5-nitro-2-furyl)-Δ^2-1,2,4-triazolines or 5-(5-nitro-2-furyl)-1,2,4-triazole are formed (depending on the structure of the arylidene moiety). Δ^2-1,3,4-thiadiazolines are obtained by reaction of thiosemicarbazones of aromatic and furaldehydes and furan ketones. We discuss schemes for closure of the triazolidine, triazole, and thiadiazoline rings. We describe the molecular structure of 2-acetylamino-4-acetyl-5-phenyl-Δ^2-1,3,4-thiadiazoline.

Earlier we obtained 3-(5-nitrofurfuryl)-Δ^2-1,2,4-triazolines by reaction of S-(5-nitrofurfuryl)thiosemicarbazonium salts [1, 2]. With the goal of obtaining compounds for which the nitrofuran ring is directly bonded to the triazoline ring, we carried out acylation of arylidene amidrazones of 5-nitro-2-furancarboxylic acid (I). The amidrazones I, like thiosemicarbazonium salts, contain a 1,5-ambiphilic moiety [3], which is responsible for the possibility of constructing the 1,2,4-triazoline ring. We know of formation of triazolines upon fusion of the corresponding amidrazones [4], but such an approach is inapplicable for synthesis of nitrofuryltriazolines.

The starting arylidene amidrazones Ia-h were synthesized according to a scheme including synthesis of the amidrazone of 5-nitro-2-furancarboxylic acid (II) and its subsequent condensation with carbonyl compounds.



II

IIIa–h Ia–h

I, IIIa–f R^1 = H; I, IIIg,h R^1 = CH_3; I, IIIa R = C_6H_5; b R = 4-CH_3O—C_6H_4; c R = 4-$N(CH_3)_2$—C_6H_4; d,g R = 2-furyl; e,h ,3 R = 5-methyl-2- furyl; f R = 5- nitro -2-furyl

The amidrazone II is formed upon reaction of 5-nitro-2-cyanofuran with hydrazine hydrate in ethanol. Compound II is high-melting red crystals, difficultly soluble in most organic solvents but dissolving well in acid aqueous solutions. Therefore condensation of amidrazone II and the corresponding carbonyl compound was done in acid aqueous alcohol solution. The free bases Ia-h were isolated by treatment of the perchlorates IIIa-h with an aqueous solution of sodium hydroxide.

Compounds Ia-h are deeply colored high-melting crystalline substances with low solubility in most organic solvents (Table 1). The IR spectra of amidrazones Ia-h contain a set of bands characterizing absorption of the NH-bonds (3300-3600 cm^{-1}) and C=N-groups (1600-1620 cm^{-1}).

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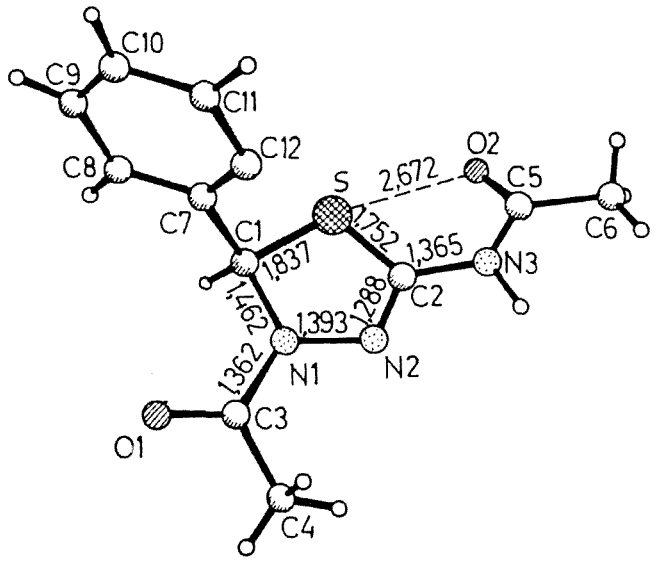
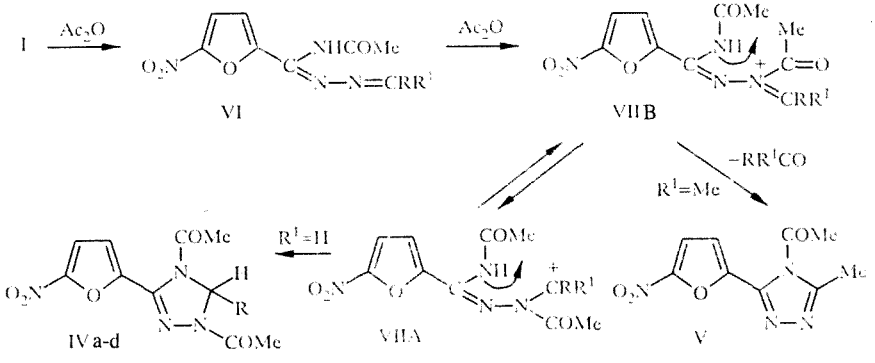


Fig. 1. Projection of a three-dimensional model of the 2-acetylamino-4-acetyl -5-phenyl-Δ^2-1,3,4-thiadiazoline (IXf) molecule.

In the PMR spectra, there are signals corresponding to nitrofuran and aryl (furyl) protons. The presence downfield of a signal from the azomethine proton (8.22-8.68 ppm) suggests an acyclic structure for the compound I [5].

We studied acylation of amidrazones Ia-H and established that they react with the acetic anhydride in different ways. Heating amidrazones Ia-c, e, h (derivatives of aldehydes and containing a donor arylidene moiety) in acetic anhydride at 100°C leads to triazolines IVa-d. Compounds Ig, h (ketone derivatives) react with acetic anhydride at high temperature (140°C) and in this case undergo ring closure to form triazole V, liberating a molecule of the corresponding ketone. (The ketones were identified by TLC.) The triazole V was also obtained by an alternate route to confirm its identity: acylation of amidrazone II. Compounds Id, f do not react under the conditions we used.



IV a) R = C_6H_5; b) R = 4-OCH_3—C_6H_4; c) R = 4-$N(CH_3)_2$—C_6H_4; d) R = 5-methyl-2-furyl

It seems to us that acylation of compound I proceeds through formation of monoacyl derivatives VI. We could not isolate the compounds VI, but similar products have been obtained and characterized upon acylation of thiosemicarbazonium salts [2, 6, 7].

Subsequent acylation of VI at the azomethine nitrogen atom leads to intermediate VII, which is a 1,3-bielectrophilic reagent owing to the presence in it of positive carbonyl and azomethine carbon atoms competing for the nucleophilic nitrogen atom.

When R^1 = H, the higher electrophilicity of the azomethine carbon compared with the electrophilicity of the carbonyl carbon atom is responsible for the nucleophilic attack by the amide nitrogen atom on the azomethine carbon, ending in formation of the triazoline ring IV.

For R^1 = CH_3, the electrophilicity of the azomethine carbon of intermediate VII is somewhat less, which makes possible competitive reaction with the amide nitrogen atom of the carbonyl carbon, leading to closure of the energetically more

TABLE 1. Physicochemical Characteristics of Synthesized Compounds Ia-h, IVa-d, IXa-f

Compound	Empirical formula	mp, °C	UV spectrum (ethanol), λ_{max}, nm (lg ε)	IR spectrum, ν, cm^{-1}	Yield, %
Ia	$C_{12}H_{10}N_4O_3$	167...169	307 (4,16), 380 (4,17)	1615, 3300, 3400, 3600	84
Ib	$C_{13}H_{12}N_4O_4$	153...155	305 (4,14), 397 (4,13)	1605, 3300, 3400	80
Ic	$C_{14}H_{15}N_5O_3$	196...197	338 (4,15), 432 (4,14)	1615, 3280, 3380, 3610	78
Id	$C_{10}H_8N_4O_4$	173...174	311 (4,18), 393 (4,21)	1600, 3380, 3480	75
Ie	$C_{11}H_{10}N_4O_4$	148...150	312 (4,15), 402 (4,20)	1620, 3380, 3500	74
If	$C_{10}H_7N_5O_3$	210...212	295 (4,08), 418 (4,43)	1600, 3360, 3440, 3500	70
Ig	$C_{11}H_{10}N_4O_4$	143...144	311 (4,08), 402 (4,20)	1600, 3450, 3520, 3600	80
Ih	$C_{12}H_{12}N_4O_4$	145...146	312 (4,17) 409 (4,17)	1600, 3300, 3400	82
IVa	$C_{16}H_{14}N_4O_5$	141...143	338 (4,16)	1725, 1735	67
IVb	$C_{17}H_{16}N_4O_6$	189...190	288 (4,08), 360 (3,99)	1650, 1670	40
IVc	$C_{18}H_{10}N_5O_5$	206...208	270 (4,04), 366 (3,98)	1660, 1680	55
IVd	$C_{15}H_{14}N_4O_6$	156...158	270 (4,35), 360 (4,02)	1660, 1700	60
IXa	$C_{10}H_{11}N_3O_3S$	192...193		1610, 1680, 1695, 3200	75
IXb	$C_{11}H_{13}N_3O_3S$	173...174		1610, 1675, 1690, 3200	74
IXc	$C_{10}H_{10}N_4O_5S$	205...206		1600, 1660, 3200	72
IXd	$C_{11}H_{13}N_3O_3S$	160...162		1605, 1670, 3200	78
IXe	$C_{12}H_{15}N_3O_3S$	170...171		1610, 1670, 3200	74
IXf	$C_{12}H_{13}N_3O_2S$	227...228		1600, 1680, 3200	71

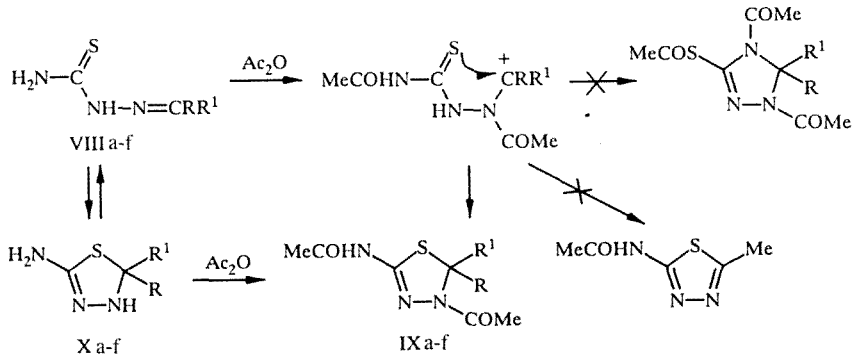
favorable aromatic triazole ring V. More vigorous temperature conditions promote participation of the carbonyl carbon atom in the reaction.

The triazolines IVa-d are high-melting crystalline materials, soluble in most organic solvents (Table 2).

A shortening of the conjugation chain in triazolines IVa-d, connected with transition of the sp^2-hybridized azomethine carbon to sp^3-hybridized, is apparent in the hypsochromic shift of the long-wavelength absorption maximum of compounds IVa-d compared with that for the corresponding amidrazones Ia-c, e. The IR spectra of compounds IVa-d contain two intense absorption bands in the 1670-1725 region due to stretching vibrations of the amide carbonyl groups. In the PMR spectra of triazolines IVa-d, the signal from the azomethine proton is missing while there is a signal from the 5-H proton of the triazoline ring in the 7.18-7.38 ppm region.

The triazole V is a colorless crystalline compound, the IR spectrum of which contains an intense absorption band for the amide carbonyl (1725 cm^{-1}) and a characteristic absorption band for the C–H bonds of the furan ring (3110 cm^{-1}). The PMR spectrum contains singlets from the two methyl groups and two doublet signals from the β-protons of the furan ring.

Like arylidene amidrazones, thiosemicarbazones are also 1,5="ambiphiles" but, in contrast to compound I, they have two terminal nucleophilic centers (the thione sulfur and the amide nitrogen atom) capable of taking part in cyclization. In analogy with compounds I, we carried out acylation of the thiosemicarbazones VIIIa-f. The reaction with acetic anhydride of thiosemicarbazones of both aldehydes and ketones leads only to Δ^2-1,3,4-thiadiazolines IXa-f, which is determined to all appearances by the greater nucleophilicity of the sulfur atom. The fact that the result of acylation of thiosemicarbazones VIII is independent of the nature and structure of the arylidene moiety is possibly explained [8] by participation in the reaction of the cyclic tautomeric form X, the structure of which is confirmed by acylation of the nitrogen atom.



VIII, IX a-c,f R^1 = H; d,e R^1 = CH_3; VIII, IXa,d R = 2-furyl; b,e R = 5-methyl-2-furyl; c R = 5-NO_2-2-furyl; f R = C_6H_5

TABLE 2. PMR Spectra of Synthesized Compounds Ia-h, IVa-d, IXa-f

Compound	Chemical shifts, δ, ppm, J, Hz*					
	nitrofuran		R	R^1	Ac	NH
	3-H	4-H**2				
Ia	7,66	7,93	7,35...8,00 (5H, m, C_6H_5)	d, 8,68		
Ib	7,20	7,48	6,90 (2H, d, 3-H and 5-H), 7,73 (2H, d, 2-H and 6-H), $J_{2,3} = J_{5,6} = 9,0$, 3,75(3H, s, OCH_3)	8,32		
Ic	7,17	7,50	6,67 (2H, d, 3-H and 5-H), 7,67(2H, d, 2-H and 6-H), $J_{2,3} = J_{5,6} = 9,0$, 2,95 [6H, s, $N(CH_3)_2$]	8,28		
Id	7,65	7,87	6,58 (1H, d.d, 4-H), $J_{3,4} = 3,6$, 7,17 (1H, d, 3-H), $J_{3,5} = 1,5$, 7,80 (1H, d.d, 5-H), $J_{4,5} = 2,0$	8,45		
Ie	7,45	7,85	6,37 (1H, d, 4-H), $J_{3,4} = 3,6$, 7,00 (1H, d, 3-H), 2,30 (3H, s, 5-CH_3)	8,22		
If	7,60	7,87	6,30 (1H, d, 3-H), $J_{3,4} = 4,0$, 6,40 (1H, d, 4-H)	8,48		
Ig	7,65	7,82	6,37 (1H, d.d, 4-H), $J_{3,4} = 3,6$, 7,23 (1H, d.d, 3-H), $J_{3,5} = 1,5$, 7,32 (1H, d, d, 5-H), $J_{4,5} = 2,0$	2,48		
Ih	7,67	7,88	6,23 (1H, d, 4-H), $J_{3,4} = 4,0$, 7,30 (1H, d, 3-H), 2,32 (3H, s, 5-CH_3)	2,48		
IVa	6,90	7,30	7,68 (5H, s, C_6H_5)	7,38	2,17, 2,55	
IVb	7,20	7,33	6,85 (2H, d, 3-H and 5-H), 7,38 (2H, d, 2-H and 6-H), $J_{2,3} = J_{5,6} = 9,0$, 3,72(3H, s, OCH_3)	7,13	2,06, 2,30	
IVc	7,25	7,50	7,70 (4H, s, C_6H_4), 3,48 [6H, s. $N(CH_3)_2$]	7,18	2,08, 2,25	
IVd	7,42	7,85	6,18 (1H, d, 4-H), $J_{3,4} = 3,6$, 6,61 (1H, d, 3-H), 2,30 (3H, s, 5-CH_3)	7,35	2,21, 2,30	
IXa			6,25 (2H, d, 3-H and 4-H), 7,25 (1H, d, d, 5-H), $J_{3,4} = J_{4,5} = 1,4$, $J_{3,5} = 1,2$	6,81	2,12, 2,22	11,30
IXb			5,88 (1H, m, 4-H), $J_{3,4} = 3,5$, 6,08 (1H, d, 3-H), 2,15 (3H, s, 5-CH_3)	6,77	2,03, 2,10	11,32
IXc			6,53 (1H, d, 3-H), $J_{3,4} = 4,0$, 7,17 (1H, d, 4-H)	6,72	2,16, 2,26	10,40
IXd			6,25 (2H, m, 3-H and 4-H), 7,30(1H, m, 5-H)	1,90	2,18, 2,23	10,70
IXe			5,60 (1H, d, 4-H), $J_{3,4} = 3,6$, 5,87 (1H, d, 3-H), 1,95 (3H, s, 5-CH_3)	1,68	1,95, 2,02	10,50
IXf			6,92 (5H, s, C_6H_5)	6,45	1,88, 2,02	10,80

*The spectra of compound Ia-h were recorded in CF_3COOH; IV, IX, in $CDCl_3$.

**The spin–spin coupling constant for the β protons of the nitrofuran ring is equal to 4.0 Hz.

The thiadiazolines IXa-f are crystalline materials with clear melting points. In the IR spectra of the acyl derivatives IXa-f, there are intense absorption bands from the amide carbonyls (1660-1695 cm^{-1}) and the azomethine bond (1600-1610 cm^{-1}). In most cases, ν_{CO} of the two acetyl groups appears as a single band. The PMR spectra of compounds IXa-f contain two upfield singlets from the acetyl protons, a set of signals belonging to the substituent R, and a characteristic singlet from the 5-H proton at 6.45-6.90 ppm, supporting a thiadiazoline structure [2]. In the ^{13}C NMR spectrum of compound IXe there is a signal in the 74.1 ppm region (corresponding to a cyclic structure) due to resonance of the sp^3-hybridized carbon atom bonded to the electron-acceptor sulfur and nitrogen atoms [9, 10].

The structure of one of the synthesized compounds, 2-acetylamino-4-acetyl-5-phenyl-Δ^2-1,3,4-thiadiazoline (IXf), was investigated by x-ray diffraction.

The thiadiazoline ring, like the triazoline ring [2], has an envelope conformation. The short bond in the heterocycle is located between the 2 and 3 atoms of the ring, ensuring that the S, $C_{(2)}$, $N_{(2)}$, and $N_{(1)}$ atoms are located in the same plane (plane 1, average deviation 0.0033 Å). The $C_{(1)}$ atom deviates from this plane by 0.35 Å, and as a result the angle between the planes of the envelope is 19.9°. The $N_{(3)}$ and $C_{(3)}$ atoms belong to plane 1, but the planar acetylamine $N_{(3)}$, $C_{(5)}$, $C_{(6)}$,

TABLE 3. Coordinates of Atoms (C, O, N, S × 10^4; H × 10^3) and Temperature Factors (Å^2 × 10^3) in the IXf Molecule

Atom	x	y	z	U
S	3217(2)	4017(1)	4061(1)	49(1)*
$O_{(1)}$	5844(5)	785(3)	3837(3)	56(2)*
$O_{(2)}$	2598(6)	5880(3)	5153(4)	76(2)*
$N_{(1)}$	4667(6)	2220(4)	4804(4)	42(2)*
$N_{(2)}$	4506(6)	2855(3)	5811(4)	42(2)*
$N_{(3)}$	3483(6)	4538(4)	6393(5)	45(2)*
$C_{(1)}$	3715(7)	2597(4)	3781(5)	41(2)*
$C_{(2)}$	3778(8)	3779(5)	5540(5)	48(3)*
$C_{(3)}$	5694(7)	1302(5)	4758(5)	39(2)*
$C_{(4)}$	6560(10)	946(6)	5854(7)	49(3)*
$C_{(5)}$	2829(8)	5562(4)	6163(5)	52(3)*
$C_{(6)}$	2502(16)	6247(6)	7238(8)	69(4)*
$C_{(7)}$	2324(7)	2099(4)	3665(5)	40(2)*
$C_{(8)}$	2031(8)	1637(5)	2603(5)	47(3)*
$C_{(9)}$	720(10)	1186(5)	2513(7)	64(3)*
$C_{(10)}$	-170(10)	1133(6)	3465(8)	70(4)*
$C_{(11)}$	135(9)	1578(6)	4532(7)	69(3)*
$C_{(12)}$	1394(9)	2046(5)	4620(6)	59(3)*
$H_{(1)}$	435(6)	248(4)	308(4)	4(1)
$H_{(3)n}$	397(8)	433(5)	712(6)	8(3)
$H_{(8)}$	275(7)	168(4)	190(5)	6(2)
$H_{(9)}$	49(6)	97(4)	173(5)	5(2)
$H_{(10)}$	-109(6)	90(4)	350(4)	4(2)
$H_{(11)}$	-55(9)	159(6)	528(7)	12(3)
$H_{(12)}$	165(6)	237(4)	542(5)	5(2)
$H_{(41)}$	585(9)	82(6)	644(7)	12(3)
$H_{(42)}$	692(8)	155(5)	628(6)	10(3)
$H_{(43)}$	726(8)	38(6)	576(6)	10(3)
$H_{(61)}$	149(12)	637(8)	722(9)	16(6)
$H_{(62)}$	273(9)	679(6)	707(7)	10(3)
$H_{(63)}$	284(11)	593(7)	792(8)	16(4)

*Equivalent isotropic factors U were determined as one-third of the projection of the orthogonalized (U_{ij}) tensor.

$O_{(2)}$ and acetyl $C_{(3)}$, $C_{(4)}$, $O_{(1)}$ groups bonded to them are rotated relative to plane 1 by 9.6° and 13.4° so that the oxygen atoms $O_{(1)}$ and $O_{(2)}$ deviate from plane 1 on the other side of the $C_{(1)}$ atom. Note the fact that in this molecule, as in the 2-acetylaminothiazole molecule [8], an "O,S-cis" conformation is realized for the relative arrangement of the sulfur and the oxygen of the amide group $O_{(2)}$.

The plane of the benzene ring is almost perpendicular to plane 1 (the dihedral angle between the planes is equal to 94.2°). The torsional angle $H_{(1)}-C_{(1)}-C_{(7)}-C_{(8)}$, characterizing the degree of screening of the benzene ring by the $\beta-C-H$ bond, is equal to 5.5° (see Fig. 1).

EXPERIMENTAL

The UV spectra were recorded on the Specord M-40 spectrophotometer. The IR spectra were recorded in vaseline oil on the IR-71 instrument. The PMR spectra were obtained on the Tesla BS-467 spectrometer (60 MHz), internal standard HMDS. The ^{13}C NMR spectra were recorded on the Bruker AM-300 in $CDCl_3$, internal standard TMS.

The elemental analysis data for C, H, H for compounds Ia-h, IVa-d, IVa-f correspond to the calculated values.

X-ray diffraction analysis was done on the Nicolet P3 diffractometer in monochromatic MoKα radiation, $\Delta/2\Delta$ scanning. Monoclinic crystals of compound IXf were obtained by recrystallization from ethanol. The unit cell parameters were:

a = 8.921(2), b = 12.936(3), c = 12.273(3) Å, γ = 79.46(2)°, V = 1279.0 Å^3, space group $P2_1/b$, Z = 4. The structure was deciphered by the direct method using the SHELXTL package [12] and refined in the anisotropic approximation (isotropic for hydrogen atoms) to R = 0.048 (R_W = 0.048) for 957 reflections with I > 3σ(I). The coordinates of the atoms are presented in Table 3.

5-Nitro-2-cyanofuran. 5-Nitrofurfurol oxime (7 g, 0.044 moles) was added to 40 ml thionyl chloride in portions. The mixture was stirred at room temperature until the oxime was completely dissolved. Some of the thionyl chloride was distilled off, the remaining amount was evaporated at room temperature. The residue was recrystallized from ethanol. Obtained: 4.9 g (80%) 5-nitro-2-cyanofuran. mp 65-67°C.

Amidrazone of 5-Nitro-2-furancarboxylic Acid (II, $C_5H_6N_4O_3$). Hydrazine hydrate (0.9 g, 18 mmoles) was added dropwise to a solution of 2.1 g (15 mmoles) 5-nitro-2-cyanofuran in 30 ml ethanol with stirring at room temperature. The mixture was held in a cold place for twenty-four hours. The precipitate was filtered off and washed with cold ethanol. Obtained: 1.2 g (71.5%) compound II. mp 220°C (decomp.).

1-Benzylidene Amidrazone of 5-Nitro-2-furancarboxylic Acid (Ia). Benzaldehyde (1.06 g, 0.01 moles) was added in portions to a solution of 1.68 g (0.01 moles) amidrazone II in 30 ml of a 15% aqueous solution of perchloric acid. The mixture was stirred at room temperature for 1 h. The precipitate was filtered off and washed with water, and then transferred to a solution of 0.4 g (0.01 moles) NaOH in 50 ml water. The suspension was stirred for 20 min, and then the precipitate was filtered off, washed with water, and dried in air. Obtained: 2.2 g compound Ia.

The amidrazones Ib, d, e, g, h were obtained similarly (Tables 1 and 2).

1-(5-Nitro-2-furfurylidene)amidrazone of 5-Nitro-2-furancarboxylic Acid (If). A solution of 1.4 g (0.01 moles) 5-nitrofurfurol in 20 ml ethanol was added to a solution of 1.7 g (0.01 moles) amidrazone II in 30 ml of a 15% aqueous solution of perchloric acid. The mixture was stirred at room temperature for 1 h. The oil falling out was gradually recrystallized. The precipitate was filtered off and washed with water, and then treated as described above. Obtained: 2 g compound If.

Compound Ic was obtained similarly (Tables 1 and 2).

1,4-Diacetyl-3-(5-nitro-2-furyl)-5-phenyl-Δ^2-1,2,4-triazoline (IVa). A solution of 1 g (4 mmoles) amidrazone Ia in 10 ml acetic anhydride was heated at 100°C for 0.5 h. The solution was cooled and the anhydride was hydrolyzed; the precipitate was filtered off and washed with water. Obtained: 0.7 g compound IVa.

The triazolines IVb-d were obtained similarly (Tables 1 and 2).

4-Acetyl-3-methyl-5-(5-nitro-2-furyl)-1,2,4-triazole (V). A. A solution of 0.8 g (3 mmoles) amidrazone Ig in 20 ml acetic anhydride was boiled for 2-3 min and then cooled; the anhydride was hydrolyzed and then the precipitate was filtered off, washed with water, and recrystallized from ethanol. Obtained: 0.5 g (70%) compound V. mp 220°C (decomp.). UV spectrum, λ_{max} (lgε): 228 (4.0), 340 (4.05) nm. IR spectrum: 1725, 3110 cm^{-1}. PMR spectrum ($CDCl_3$): 2.73 (3H, s, 5-CH_3), 2.84 (3H, s, CH_3CO), 7.23 and 7.38 ppm — doublets of β protons of the nitrofuran ring, $J_{3,4}$ = 4.0 Hz.

B. A solution of 0.85 g (5 mmoles) amidrazone II in 20 ml acetic anhydride was heated at 100°C for 0.5 h. The solution was cooled, the anhydride was hydrolyzed, and the precipitate was washed with water. Obtained: 0.9 g (75%) compound V.

2-Acetylamino-4-acetyl-5-methyl-5-(5-methyl-2-furyl)-Δ^2-1,3,4-thiadiazoline (IXe). A solution of 2.8 g (0.01 moles) thiosemicarbazone VIIIe in 25 ml acetic anhydride was boiled for 10-15 min and then cooled; the anhydride was hydrolyzed, the precipitate was filtered off and then recrystallized from ethanol. Obtained: 2.1 g compound IXe. ^{13}C NMR spectrum ($CDCl_3$): 13.50 (5-CH_3), 23.60 and 22.46 (CH_3CO), 25.79 (5-CH_3 on the furan ring), 74.01 (5-C), 106.46, 107.71, 150.09, and 152.25 (3-C, 4-C, 2-C, 5-C of the furan ring), 144.02 (C=N), 169.62 and 169.92 ppm (CH_3CO).

The thiadiazolines IXa-d, f were obtained similarly.

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