2-PHENYL-1,3,4-THIADIAZOL-2-INES

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According to data from the ^1H and ^{13}C NMR spectra in nonpolar media and the mass spectra, alkylidene derivatives of thiobenzhydrazide have a 1,3,4-thiadiazol-2-ine structure rather than a thiobenzhydrazone structure. The products of condensation of thiobenzhydrazide with acetone and anisaldehyde in methanol undergo partial isomerization to thiobenzhydrazones. The hydrochlorides of the compounds under discussion are the corresponding 1,3,4-thiadiazolinium salts, in which the proton is coordinated with the N_4 atom. The 2-phenyl-5,5-dimethyl-1,3,4-thiadiazol-2-ine anion has a noncyclic thioenolate structure.

Of the alkylidene derivatives of thioacylhydrazines, the products of condensation of carbonyl compounds with thiobenzhydrazide (I) have been investigated most thoroughly [1, 2]. The IR and UV spectra of individual compounds of this series have been discussed, and quantum-chemical calculations have been made [3]; the mass spectra are presented in [4]. On the basis of these data, the substances were regarded to be thiobenzhydrazones II, whereas another possibility, viz. the existence of the products in cyclic 1,3,4-thiadiazoline form III [10], should also be taken into consideration from the standpoint of the available concepts regarding the isomeric ring-chain transformations of related compounds such as semicarbazones [5-7], alkylidene derivatives of amidrazones [8], and thiosemicarbazones [9]. The validity of this assumption has been demonstrated for the products of condensation of thiobenzhydrazide I with acetone and methyl ethyl ketone [11]. In the present paper we present detailed information on the products of the reaction of thiobenzhydrazide with saturated and aromatic aldehydes, aliphatic and aliphatic-aromatic ketones, and cyclohexanone.

We found that monoaddition products III are formed in the majority of cases (Tables 1 and 2). The only exception was the reaction of thiobenzhydrazide I with formaldehyde, in which, despite the data in [1], a 3:2 compound, which, according to our data (see the experimental section), has the bis(2-phenyl-1,3,4-thiadiazol-2-in-4-yl)methane structure (IV), is obtained. In individual cases (IIIg,k,l) we showed that the alkylidene derivatives of thiobenzhydrazide can be synthesized just as easily also by thioacylation of the corresponding hydrazones V with dithiobenzoic acid carboxymethyl ester.

From the set of spectral characteristics (Table 2) of the synthesized alkylidene derivatives it may be asserted that they all, without exception, are the corresponding 2-phenyl-1,3,4-thiadiazol-3-ines (IIIa-n) in the crystalline state and in low-polarity media (CCl_4, $CDCl_3$). In particular, this follows from the presence in the ^{13}C NMR spectra of signals of C_2 and C_5 atoms at 138.4-147.6 and 74.4-84.5 ppm, from the anomalously high chemical shifts of the signals of the substituents in the 5 position in the PMR spectra, and from the magnetic equivalence of identical substituents or the diastereotopic character of the protons and carbon atoms of the prochiral groups in the same position in the ^1H and ^{13}C NMR spectra. In addition, coupling between the 5-H and NH protons with spin–spin coupling constants (SSCC) of 0.5-3.0 Hz is observed in the PMR spectra in the case of aldo derivatives IIId-f.

The IR spectra of III in mineral oil and chloroform are characterized by absorption of C=N bonds at 1600-1625 cm^{-1} and NH bonds at ~3350 cm^{-1}. Two maxima at 232-242 and 300-315 nm are present in their UV spectra; the position of the bands and their intensities are insensitive to the nature of the solvent and to acidification of the solution.

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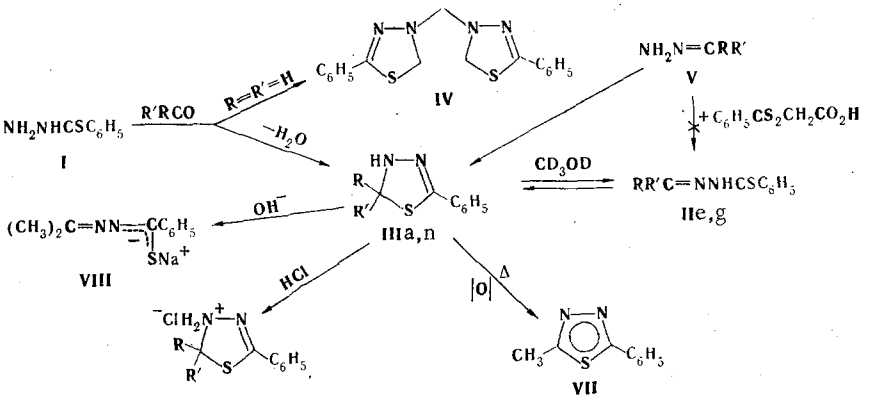
TABLE 1. 5-Phenyl-1,3,4-thiadiazol-2-ines (III)

Compound	mp, °C (from hexane)	R_f	UV spectrum in CH_3OH, λ_{max}, nm (log ε)	Found, % N	Found, % S	Empirical formula	Calc., % N	Calc., % S	Yield, %
IIIa	Oil	0,40	235 (4,12), 310 (3,84)	15,7	18,1	$C_9H_{10}N_2S$	15,7	18,0	20
IIIb	Oil[a]	0,30	236 (4,07), 317 (3,66)	14,5	16,7	$C_{10}H_{12}N_2S$	14,6	16,7	25
IIIc	45—46	0,25	236 (4,47), 317 (4,01)	13,5	15,6	$C_{11}H_{14}N_2S$	13,6	15,5	35
IIId	81—82[b]	0,50	242 (4,14), 305 (4,06)	11,7	13,4	$C_{14}H_{12}N_2S$	11,7	13,3	60
IIIe	82—83[b]	0,50	236 (4,19), 308 (4,07)	10,6	12,0	$C_{15}H_{14}N_2OS$	10,5	12,0	90
IIIf	111—112[b]	0,65	235 (4,30), 277 (4,29)	14,7	11,1	$C_{14}H_{11}N_3O_2S$	14,7	11,2	80
IIIg	52—53	0,55	236 (4,10), 309 (3,87)	14,6	16,8	$C_{10}H_{12}N_2S$	14,6	16,7	80
IIIh	35—40	0,45	236 (4,10), 313 (3,80)	13,5	15,5	$C_{11}H_{14}N_2S$	13,6	15,5	85
IIIi	Oil[a]	0,55	235 (4,21), 315 (3,97)	12,6	14,6	$C_{12}H_{16}N_2S$	12,7	14,5	25
IIIj	35—40	0,55	235 (3,75), 312 (3,14)	12,1	13,7	$C_{13}H_{16}N_2S$	12,0	13,7	25
IIIk	48—49	0,70	239 (4,10), 312 (3,72)	12,1	13,7	$C_{13}H_{18}N_2S$	12,0	13,7	40
IIIl	55—56	0,55	235 (4,27), 312 (3,95)	11,0	12,6	$C_{15}H_{18}N_2S$	11,0	12,6	50
IIIm	Oil[a]	0,25	232 (3,98), 302 (3,67)	11,3	12,9	$C_{12}H_{14}N_2O_2S$	11,2	12,8	35
IIIn	55—56	0,30	237 (4,22), 298 (3,88)	12,6	14,6	$C_{12}H_{16}N_2S$	12,7	14,5	55

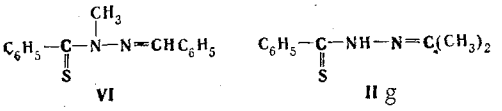
[a]From 50% aqueous ethanol. [b]From methanol.

To achieve more nearly complete substantiation of the conclusion that III have a cyclic structure we obtained information from their mass spectra. The mass spectra of the investigated compounds and the relative intensities of the peaks of the common fragment ions are presented in Tables 3 and 4. The most intense F_1 ion is, as a rule, the product of fragmentation of the molecular ion due to the loss of the heavier substituent in the 5 position (Table 3). The remaining peaks can be regarded as being the result of further fragmentation of the M^+ or F_1 ions.



III a R=H, R′=CH_3, b R=H, R′=C_2H_5; c R=H, R′=i-C_3H_7; d R=H, R′=C_6H_5; e R=H, R′=4-$CH_3OC_6H_4$; f R=H, R′=4-$NO_2C_6H_4$; g R=CH_3, R′=CH_3; h R=CH_3, R′=C_2H_5; i R=CH_3, R′=n-C_3H_7; j R=CH_3, R′=i-C_4H_9; k R=CH_3, R′=t-C_4H_9; l R=CH_3, R′=C_6H_5; m R=CH_3, R′=$COOC_2H_5$; n R—R′=$(CH_2)_5$

The mass spectra of VI and the product of condensation of thiobenzhydrazide (I) with acetone are discussed in [4].



It is difficult to propose that VI exists in the thiadiazoline form, since migration of a methyl group from one nitrogen atom to another should occur for its formation. The maximum peak in the mass spectrum of this compound is the peak of $C_6H_5 \equiv \overset{+}{S}$ (F_4) ions, which, in the opinion of the authors, are formed from $C_6H_5C(=S)N(CH_3)N{=}CH$ ($[M - C_6H_5]^+$) ions by cleavage of the thioamide bond. The intensity of the F_4 daughter ion peak exceeds the intensity of the peak of the parent F_1 peak by a factor of 2.2. According to our data, this pattern is reversed when the methyl group is replaced by a hydrogen atom (IIId, see Tables 3 and 4), and the peak of F_4 ions is 3.3 times less intense than the peak of F_1 ions. However, if one proceeds from

TABLE 2. NMR Spectra of III ($CDCl_3$)

Compound	^{13}C NMR spectrum, δ, ppm; J, Hz				PMR spectrum, δ, ppm (J, Hz)		
	C_2	C_5	R	R′	NH_2^+ (1H, c)	R	R′
IIIa					6,30	5,30 q (6, 1H)	1,35 d (6, 3H)
IIIb[a]	147,6	76,0	—	11,0; 31,8	6,20	5,08t (6, 1H)	1,56 m (2H), 0,75 t (6, 3H)
IIIc	146,1	79,3; $^1J_{CH}$=160,6, $^2J_{CCH}$=4,7	—	17,7; $^1J_{CH}$=132,3 17,8; $^1J_{CH}$=132,3 34,3; $^1J_{CH}$=130,7	6,13	5,16 dd (6, 0,5, 1H)	1,85 m (1H), 0,95 d (6, 6H)
IIId	143,3	77,2; $^1J_{CH}$=138,8	—	—	6,38 d (2 Hz)	6,25 d (2)	—[b]
IIIe[a]	145,8	74,4	—	52,0 (CH_3O)	6,35	6,15 s (1H)	3,55 s (3H, OCH_3)[b]
IIIf[a]	147,5	73,0	—	—	6,50 d (3Hz)	6,30d (3)	—[b]
IIIg	138,4	79,7	34,6; $^1J_{CH}$=134,7, $^2J_{CCH}$=3,8	34,6; $^1J_{CH}$=134,7; $^2J_{CCH}$=3,8	6,25	1,70 s (3H)	1,70 s (3H)
IIIh	145,7	84,1	27,0; $^1J_{CH}$=127,5	9,2; $^1J_{CH}$=123,0 34,0; $^1J_{CH}$=125,0	6,30	1,52 s (3H)	1,75 m (2H), 0,92 t (3H)
IIIi	145,0	83,5	27,5; $^1J_{CH}$=135,4	13,4; 18,5; 43,5	5,85	1,60 s (3H)	1,86 m (2H); 1,50 m (2H); 0,92 t (3H, 8)
IIIj					6,00	1,53 s (3H)	0,95 d (6, 6H), 1,80 m (1H), 1,85 m (2H)
IIIk					5,88	1,63 s (3H)	1,08 s (9H)
IIIl	139,1	78,9	29,2; $^1J_{CH}$=126,9	—	6,30	1,95s (3H)	—[b]
IIIm	144,9	80,0; $^2J_{CCH}$=4,7	25,2; $^1J_{CH}$=136,1	13,4; $^1J_{CH}$=135,5; $^2J_{CCH}$=9,0 61,9; $^1J_{CH}$=155,9; $^2J_{CCH}$=4,7	6,82	1,85 s (3H)	1,27 t (7, 3H), 4,20 q (7, 2H)
IIIn	144,1	84,5	23,1; $^1J_{CH}$=136,4, 23,3; 37,4; $^1J_{CH}$=136,4		5,95	1,20—2,00 m (6H), 2,1 m (4H)	

[a]The ^{13}C NMR spectrum was recorded with complete suppression of ^{13}C—H coupling. [b]Superposition of the signals of the phenyl rings attached to 2-C and 5-C.

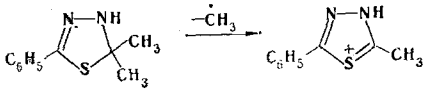
TABLE 3. Relative Intensities of the M^+ Peaks and the Common Fragment Ions in the Mass Spectra of III

Compound	M^+	F_1	F_2 (PhCSN)	F_3 (PhCSN)	F_4 (PhCS)	F_5 (PhS)	F_6 (PhCNH)	F_7 (PhCN)	F_8 (Ph)	F_9 (C_4H_3)
IIIb	10,9	100	9,6	4,2	18,4	4,5	37,0	13,0	47,7	35,1
IIIc	6,7	100	10,8	1,8	12,7	4,6	22,6	6,4	30,1	14,1
IIId	49,2	100	15,5	9,5	34,3	4,9	78,8	16,5	96,5	38,0
IIIe	53,1	30,8[a]	11,7	10,8	60,5	4,0	29,2	11,6	59,3	24,8
IIIf	44,4	100	12,9	5,2	30,6	4,8	60,9	30,2	49,0	25,2
IIIg	14,8	100	7,2	3,5	16,4	6,5	13,1	8,8	25,1	15,3
IIIj	4,5	92,2[b]	3,1	4,0	23,7	5,1	27,8	8,8	65,7	33,9
IIIk	2,8	100	6,7	9,8	16,1	5,0	17,8	7,5	54,6	21,8
IIIl	—	100	3,2	3,2	20,2	3,2	17,2	10,1	33,9	22,8
IIIm	3,0	100	7,4	3,6	9,6	6,6	16,4	9,5	30,4	13,7

[a]The maximum peak is the peak of $CH_3OC_6H_4C\equiv\overset{+}{N}H$ ions. [b]The peak of the $C_6H_5C\overset{+}{N}H_2$ ions is the maximum peak.

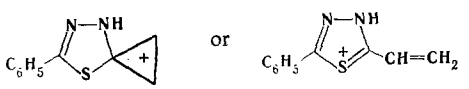
the analogy of the structures of the F_1 and F'_1 ions, one should have expected a decrease in the stability of the F_1 ion, since the electron-donor group that stabilizes the F_1 ion is replaced by a hydrogen atom in the case of IIId. The indicated regularity is retained in the case of an alternative pathway for the formation of F_4 ions, viz., directly from M^+. In addition, peaks of F_2 and F_3 ions are completely absent in the mass spectrum of VI, while the peaks of F_6 and F_7 ions have insignificant (<5%) relative intensities (compare with Table 3). Consequently, the M^+ ions of VI and IIId have different structures and undergo fragmentation via different pathways. The bulk of the M^+ ions of IIId have a cyclic structure, and only a very small amount of opening of the heteroring occurs prior to fragmentation of M^+.

In the opinion of Duffield and co-workers [4], the product of condensation of thiobenzhydrazide with acetone is linear isomer IIg; however, its mass spectrum and the mass spectrum that we obtained for thiadiazoline IIIg (see Tables 3 and 4) virtually coincide, differing only slightly with respect to the relative intensities of some ions. Although the mass spectrum of this thiobenzhydrazide is not discussed in [4] (only the process $M^+ \rightarrow [M - CH_3]^+$ is noted), Duffield and co-workers, while rejecting a linear structure for the molecule, also assign a linear structure to the $[M - CH_3]^+$ (F_1) ion, whereas the intensity of the peak of F_1 ions in the mass spectrum of this compound exceeds the intensity of the peak of F_4 ($C_6H_5C\equiv S^+$) ions by a factor of nine (as compared with a factor of seven according to our data), which makes it possible to assign the 2-phenyl-5,5-dimethyl-1,3,4-thiadiazol-2-ine structure (IIIg) to it. The splitting out of a methyl group from M^+ can then be represented by the scheme



Peaks of $[M - C_6H_5CN]^+$ (156, 8.8%), $4\text{-}CH_3OC_6H_4CH{=}S^{+\bullet}$ (152, 11.5%), and $4\text{-}CH_3OC_6H_4C\equiv S^+$ (151, 8.8%) ions, the formation of which is possible only from the 1,3,4-thiadiazoline structure of M^+, are subsequently recorded in the mass spectrum of IIIe.

Finally, the maximum peak in the mass spectrum of IIIn is the peak of ions with m/z 189, which are formed as a result of splitting out of a C_3H_7 radical from the cyclohexane ring with the formation of



ions. This fragmentation is typical for the analogous spiro compounds [12].

The indicated mass-spectrometric data make it possible to conclude that the M^+ ions of all of the investigated compounds basically have a 1,3,4-thiadiazoline structure.

1,3,4-Thiadiazol-2-ines (III) have basic properties and, under the influence of HCl, form hydrochlorides (Table 5), in which the proton is coordinated with the N_4 atom. This follows from the fact that the NH_2^+ signal in the PMR spectra of the hydrochlorides is a singlet in various solvents and when the temperature is varied.

A distinctive peculiarity of aldo derivatives III (R = H) is their tendency to undergo oxidation to give the corresponding 1,3,4-thiadiazoles, as previously noted in [13]. It is interesting that keto derivatives III (R, R' ≠ H) also undergo aromatization when they are heated, which was demonstrated in the case of IIIg, from which 2-methyl-5-phenyl-1,3,4-thiadiazole (VII), which is identical to the product of oxidation of thiadiazoline IIIa, was synthesized.

Starting from the data in [10] and the fact of the thioacylhydrazone—thiadiazoline ring-chain tautomerism that we observed in the case of the benzylidene derivative of thiophenylacetylhydrazine [14], one should also take into account the possibility of the II ⇄ III transformation. An indirect confirmation of this is the 1-thiobenzoyl-5-hydroxy-2-pyrazoline—5-(2-oxo)alkyl-1,3,4-thiadiazol-2-ine ring-chain tautomerism [15], which is most likely realized through the thiobenzoylhydrazone tautomeric form.

This partial isomerization actually occurs in strongly polar media (CD_3OD) in the case of IIIe,g. Two singlets of equal intensity of the syn- and anti-CH_3 groups of linear tautomer IIg appear at 2.02 and 1.77 ppm, respectively, in the PMR spectrum of IIIg in CD_3OD, in addition to a strong-field signal of the methyl groups of cyclic form IIIg at 1.65 ppm. In precisely the same way, signals of an azomethine proton at 8.45 ppm and of a methoxy group at 4.58 ppm are present in the spectrum of a methanol solution of anisaldehyde thiobenzhydrazone IIe, in addition to signals of a 5-H proton (6.38 ppm) and a methoxy group (3.75 ppm), which correspond to thiadiazoline IIIe [10]. The percentage of the hydrazone form is small and does not exceed 7-10%. The formation of hydrazone tautomer II was not observed under the same conditions for IIId,f,k,l.

The effect of structural factors on the position of the II ⇄ III tautomeric equilibrium is currently under investigation.

EXPERIMENTAL

The IR spectra of solutions of the compounds in chloroform were recorded with a UR-20 spectrometer. The UV spectra of solutions in methanol were recorded with an SF-8 spectrophotometer. The PMR spectra were obtained with a Tesla BS 497 spectrometer (100 MHz) with hexamethyldisiloxane as the internal standard. The ^{13}C NMR spectra were recorded with a GFT-20 spectrometer with tetramethylsilane as the internal standard. The mass spectra were obtained with an MAT-44S mass spectrometer with direct introduction of the samples into the ion source; the ionizing voltage was 75 V, the emission current was 0.5 mA, and the temperature was 80-170°C. The individuality of all of the compounds obtained was confirmed by chromatography in a thin layer of Silufol in chloroform.

The aldehydes and ketones (commercial-grade preparations) were purified prior to synthesis by distillation or recrystallization.

2-Phenyl-1,3,4-thiadiazol-2-ines (IIIa-n). A) A 0.05-mole sample of hydrazide I [16] was refluxed with a 1.5-fold excess of the corresponding carbonyl component in benzene with a Dean—Stark adapter until all of the hydrazide had undergone reaction according to the results of thin-layer chromatography (TLC). The volatile components were removed in vacuo, and the residue was recrystallized. This method was used to obtain IIIj-n.

B) A 0.05-mole sample of the corresponding carbonyl component was added with stirring at 0°C to 0.05 mole of hydrazide I in 25 ml of 2 N HCl. After 24 h, the precipitated hydrochlorides of thiadiazolines IIIa,b,g,l were removed by filtration, recrystallized from acetonitrile, and dried in vacuo (Table 5). Free bases IIIa,b,g,l were isolated by neutralization of 0.025 mole of the hydrochloride in 20 ml of methanol in which 0.025 mole of sodium had been dissolved. The methanol was removed in vacuo, and the residue was extracted with ether (three 25-ml portions). The extract was dried with $CaCl_2$, the solvent was removed, and the residue was recrystallized.

The dihydrochloride of IV, with mp 123-125°C and R_f 0.25, was isolated under the same conditions in the reaction with formalin. PMR spectrum (C_6H_5CN): 4.85 (4H, s, CH_2), 5.02 (2H, s, CH_2), and 10.63 ppm (2H, s, NH). Found: C 49.5; Cl 17.1; N 13.6%. $C_{17}H_{16}N_4S_2 \cdot 2HCl$. Cal-

TABLE 4. Mass Spectra of III

Compound	m/z values (relative intensities of the ion peaks in percent of the maximum peak)
IIIb	192 (11), 164 (11), 163 (100), 121 (18), 104 (37), 103 (13), 77 (48), 76 (17), 69 (40), 56 (11), 51 (35)
IIIc	206 (7), 164 (16), 163 (100), 136 (11), 121 (13), 105 (23), 104 (23), 103 (6), 77 (30), 69 (7), 51 (14)
IIId	240 (49), 239 (28), 163 (100), 136 (14), 121 (34), 104 (79), 103 (17), 77 (97), 69 (14), 57 (15), 51 (38)
IIIe	270 (53), 269 (38), 163 (31), 135 (22), 134 (100), 121 (61), 108 (25), 107 (22), 104 (29), 77 (59), 51 (25)
IIIf	285 (44), 284 (17), 164 (15), 163 (100), 121 (30), 104 (61), 103 (30), 91 (17), 77 (49), 76 (21), 51 (25)
IIIg	192 (15), 178 (15), 177 (100), 136 (7), 121 (16), 104 (13), 103 (9), 77 (25), 74 (7), 56 (40), 51 (15)
IIIj	234 (5), 178 (17), 177 (92), 121 (24), 105 (100), 104 (28), 77 (66), 76 (11), 57 (20), 55 (11), 51 (34)
IIIk	234 (5), 222 (11), 178 (15), 177 (100), 135 (10), 121 (16), 105 (95), 104 (17), 77 (55), 57 (30), 51 (21)
IIIl	192 (15), 178 (15), 177 (100), 121 (21), 104 (17), 103 (10), 77 (34), 76 (9), 74 (8), 56 (55), 51 (23)
IIIm	250 (4), 177 (100), 121 (10), 117 (36), 105 (27), 104 (17), 103 (9), 89 (25), 77 (30), 61 (83), 51 (14)
IIIn	232 (26), 190 (21), 189 (100), 176 (18), 121 (18), 104 (27), 103 (12), 77 (33), 55 (20), 54 (29), 51 (21)

TABLE 5. Hydrochlorides of III

Compound	mp, °C	PMR spectrum (DMF), δ, ppm (J, Hz)			Found, %		Empirical formula	Calc., %		Yield, %
		NH_2^+ (2H, c)	R	R′	Cl	N		Cl	N	
IIIa	107—109	10,41	5,60 q (6, 1H)	1,50 d (6, 3H)	16,5	13,0	$C_9H_{10}N_2S \cdot HCl$	16,6	13,1	75
IIIb	120—121	11,53	5,45 t (6, 1H)	0,85 t (6, 3H)	15,5	12,4	$C_{10}H_{12}N_2S \cdot HCl$	15,6	12,3	80
IIIg	120	10,29	1,75 s (6H)		15,6	12,3	$C_{10}H_{12}N_2S \cdot HCl$	15,6	12,3	90
IIIl	105	10,58	—	1,75 s (3H)	12,3	9,8	$C_{15}H_{14}N_2S \cdot HCl$	12,2	9,7	65

culated: C 49.6; Cl 17.2; N 13.6%. Free base IV was isolated as indicated above and had mp 85-86°C and R_f 0.85. PMR spectrum (CCl_4): 4.78 (4H, s, CH_2), 4.85 (2H, s, CH_2), and 7.2-7.6 ppm (10H, s, C_6H_5). Found: C 63.6; H 4.9; N 16.6%. $C_{17}H_{16}N_4S_2$. Calculated: C 63.5; H 4.9; N 16.5%.

C) A 0.05-mole sample of the corresponding carbonyl component was added to 0.05 mole of hydrazide I in 25 ml of methanol. After 24 h, the methanol was removed in vacuo, and the residue was recrystallized. This method was used to synthesize thiadiazolines IIIc-n.

D) A 0.05-mole sample of dithiobenzoic carboxymethyl ester [16] in 25 ml of water was neutralized to pH ~ 8 by the action of $NaHCO_3$, and 0.05 mole of acetone [17], pinacolone [18], or acetophenone [17] hydrazone was added. The next day, the precipitate of the corresponding thiadiazoline IIIg,k,l was separated, dried in vacuo, and recrystallized.

2-Methyl-5-phenyl-1,3,4-thiadiazole (VII). A) Oxygen was bubbled through a solution of 0.01 mole of thiadiazoline IIIa for 5 h, after which the solvent was removed, and the residue was recrystallized from hexane to give a product with mp 107-108°C [1] and R_f 0.55. PMR spectrum (CCl_4): 2.72 (3H, s, CH_3) and 7.2-7.6 ppm (5H, s, C_6H_5).

B) A 0.01-mole sample of thiadiazoline IIIg was heated at 140°C in 10 ml of DMF for 2 days, after which the DMF was removed in vacuo, and the residue was recrystallized from hexane. The reaction product (55% yield) was identical to the compound obtained by method A.

Thioenolate VIII. This compound was obtained by the method in [19] and had mp 163°C and R_f 0.10. PMR spectrum (D_6-DMSO): 1.75 (3H, s, CH_3), 1.95 (3H, s, CH_3), and 7.1-8.3 ppm (5H, m, C_6H_5). Found: C 56.2; H 5.2; N 13.0%. $C_{10}H_{11}N_2NaS$. Calculated: C 56.1; H 5.1; N 13.1%.

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