SYNTHESIS OF DERIVATIVES OF 1,2,4-TRIAZIN-3-THIONE AND 5-AMINO-2-ACYL-2,3-DIHYDRO-1,3,4-THIADIAZOLIUM SALTS FROM 1,2-DICARBONYL COMPOUNDS AND 4-SUBSTITUTED THIOSEMICARBAZIDES

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The reactions of methyl- and phenylglyoxal with 2,4-disubstituted thiosemicarbazides and of diacetyl with 4-monosubstituted thiosemicarbazides gave monothiosemicarbazones which were converted in trifluoroacetic acid into previously unknown 5-amino-2-acyl-2,3-dihydro-1,3,4-thiadiazolium salts. Diacetyl monosemithiocarbazones are cyclized to 5-methylene-1,2,4-triazin-3-thiones which are also obtained in the reaction of diacetyl with 2,4-disubstituted thiosemicarbazides. In particular cases the monothiosemicarbazones are converted into the corresponding 5-alkoxy-1,2,4-triazin-3-thiones in the presence of alcohols. The 3-thio-1,2,4-triazinium cations are formed from the 5-methylene- and 5-alkoxy derivatives in trifluoroacetic acid.

The condensation products from 1,2-dicarbonyl compounds with thiosemicarbazides with a linear structure, mono- and bisthiosemicarbazones, are valuable sources of physiologically active substances [1, 2]. This reaction is valuable as a method for the synthesis of 1,2,4-triazin-3-thiones [3], however, their preparation is excluded when thiosemicarbazides with substituents in the 4-position are used. On this account data are available only for the preparation of isomeric monoaldothiosemicarbazones and the corresponding 5-hydroxy-5-phenyl-1,2,4-triazin-3-thiones from the reaction between phenylglyoxal and 4-methyl- and 2,4-dimethyl thiosemicarbazides [4]. We have recently shown for some examples that the reaction of diacetyl with 4-mono- and 2,4-disubstituted thiosemicarbazides led to the unknown 4-alkyl-5-methylene-1,2,4-triazin-3-thione or to 5-methoxy-4-alkyl-1,2,4-triazin-3-thione [5].

Results of the reactions of methyl- and phenylglyoxal and diacetyl with some 4-mono- and 2,4-disubstituted thiosemicarbazides are presented in the present paper.

The bisthiosemicarbazones Ia and Ib (see Experimental) are formed from the reaction of methylglyoxal with 4-substituted thiosemicarbazides at room temperature. Under the same conditions methylglyoxal and phenylglyoxal react with 2,4-disubstituted thiosemicarbazides to give the monoaldothiosemicarbazones IIa and IIb just as diacetyl does with 4-monosubstituted thiosemicarbazides (IIc-f, Table 1).

The difference between the mono- and bisthiosemicarbazones was established by elemental analysis and ^{1}H NMR spectroscopy. The aldohydrazone structure of the monothiosemicarbazones IIa and IIb was demonstrated by their ^{1}H NMR spectra (Table 1) in which the signal for the CH=N proton appeared at 6.94 and 7.45 ppm respectively. It was necessary to consider the possibility of the alternative 5-hydroxy-1,2,4-triazin-3-thione III. However, this was unambiguously excluded by observation of spin—spin interaction in the $N_4H—R^3$ fragment which is only possible for the thiosemicarbazone isomer II.

The different course of the reactions is readily explained by steric effects, namely the decrease in rate of formation of the hydrazones with increasing substitution in the carbonyl and hydrazine components.

The reaction of 2,4-disubstituted thiosemicarbazides with diacetyl under the same conditions led to the corresponding 5-methylene-1,2,4-triazin-3-thiones (IV) which are most likely secondary products from the thiosemicarbazone intermediates.

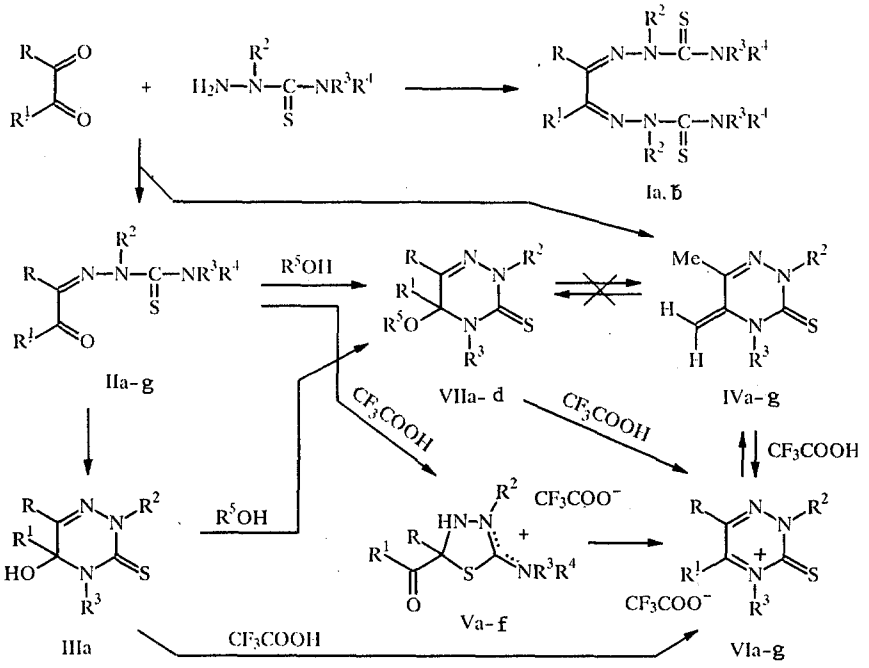
Academy of Military Medicine, St. Petersburg 194175. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp.1418-1425, October, 1992. Original article submitted July 3, 1991.

0009-3122/92/2810-1211$12.50

In any case, the diacetyl monothiosemicarbazones IIc-f are also converted into the 5-methylene-1,2,4-triazin-3-thiones IVa-d when heated in the presence of the dehydrating agent CaO.

Their ^{1}H NMR spectra are characterized by olefinic proton signals forming an AB system (Table 2). The structure of 2,4,6-trimethyl-5-methylene-1,2,4-triazin-3-thione IVe is demonstrated unambiguously by its ^{15}N NMR spectrum (2 signals for the sp^3-hybridized nitrogen atoms at 132.8 and 169.1 ppm, and a signal the C=N nitrogen atom at 312.0 ppm) and agreement with the carbon spectrum [5].

The double bonds of 5-methylene-1,2,4-triazin-3-thiones do not react with nucleophiles (water, alcohols, amines, hydrazines), in contrast to 5-methylene-2-pyrazolines and 5-methylene-2-isoxaazolines [6, 7], however, they are instantaneously and quantitatively converted to the red-brown 3-thio-1,2,4-triazinium cations on dissolution in trifluoroacetic acid (Table 3).



Ia R = R^2 = R^4 = H, R^1 = R^3 = CH$_3$; b R = R^2 = R^4 = H, R^1 = CH$_3$, R^3 = CH$_2$C$_6$H$_5$; IIa R = R^4 = H, R^1 = R^2 = = CH$_3$, R^3 = CH$_2$C$_6$H$_5$; b R = R^4 = H, R^1 = C$_6$H$_5$, R^2 = R^3 = CH$_3$; c R^2 = R^4 = H, R = R^1 = R^3 = CH$_3$; d R^2 = R^4 = = H, R = R^1 = CH$_3$, R^3 = C$_2$H$_5$; e R^2 = R^4 = H, R = R^1 = CH$_3$, R^3 = CH$_2$C$_6$H$_5$; f R^2 = R^4 = H, R = R^1 = CH$_3$, R^3 = = C$_6$H$_5$; g R^2 = H, R = R^1 = R^3 = R^4 = CH$_3$; IIIa R = R^4 = H, R^1 = C$_6$H$_5$, R^2 = R^3 = CH$_3$; IVa R^2 = R^4 = H, R = = R^1 = R^3 = CH$_3$; b R^2 = R^4 = H, R = R^1 = CH$_3$, R^3 = C$_2$H$_5$; c R^2 = R^4 = H, R = R^1 = CH$_3$, R^3 = CH$_2$C$_6$H$_5$; d R^2 = = R^4 = H, R = R^1 = CH$_3$, R^3 = C$_6$H$_5$; e R^4 = H, R = R^1 = R^2 = R^3 = CH$_3$; f R^4 = H, R = R^1 = R^2 = CH$_3$, R^3 = CH$_2$C$_6$H$_5$; g R^4 = H, R = R^1 = R^3 = CH$_3$, R^2 = C$_2$H$_5$; V a R = R^4 = H, R^1 = R^2 = CH$_3$, R^3 = CH$_2$C$_6$H$_5$; b R = R^4 = H, R^1 = = C$_6$H$_5$, R^2 = R^3 = CH$_3$; c R^2 = R^4 = H, R = R^1 = R^3 = CH$_3$; d R^2 = R^4 = H, R = R^1 = CH$_3$, R^3 = C$_2$H$_5$; e R^2 = R^4 = H, R = R^1 = CH$_3$, R^3 = CH$_2$C$_6$H$_5$; f R^2 = R^4 = H, R = R^1 = CH$_3$, R^3 = C$_6$H$_5$; g R^2 = H, R = R^1 = R^3 = R^4 = CH$_3$; VI a R = R^4 = H, R^1 = R^2 = CH$_3$, R^3 = CH$_2$C$_6$H$_5$; b R = R^4 = H, R^1 = C$_6$H$_5$, R^2 = R^3 = CH$_3$; c R^2 = R^4 = H, R = R^1 = = R^3 = CH$_3$; d R^2 = R^4 = H, R = R^1 = CH$_3$, R^3 = CH$_2$C$_6$H$_5$; e R^2 = R^4 = H, R = R^1 = CH$_3$, R^3 = C$_6$H$_5$; f R^4 = H, R = = R^1 = R^2 = R^3 = CH$_3$; g R^4 = H, R = R^1 = R^2 = CH$_3$, R^3 = CH$_2$C$_6$H$_5$; VII a R^1 = R^4 = H, R = R^2 = CH$_3$, R^3 = = CH$_2$C$_6$H$_5$, R^5 = C$_2$H$_5$; b R = R^4 = H, R^1 = C$_6$H$_5$, R^2 = R^3 = R^5 = CH$_3$; c R = R^4 = H, R^1 = C$_6$H$_5$, R^2 = R^3 = CH$_3$, R^5 = C$_2$H$_5$; d R^2 = R^4 = H, R = R^1 = CH$_3$, R^3 = C$_6$H$_5$, R^5 = CH$_3$

In principle the possibility of recyclization under the influence of CF_3COOH into the corresponding 1,3,4-triazinium cation should be considered, but the ^{1}H (Table 3), ^{13}C, and ^{15}N NMR spectra (see Experimental) are in complete accord with structures VI, although it is strictly impossible to eliminate compounds with a sulfur containing heterocycle. Moreover we have shown that deprotonation of the salt VIg with pyridine gave the initial 2,6-dimethyl-4-benzyl-5-methylene-1,2,4-triazin-3-thione (IVf).

The formation of 5-methylene-1,2,4-triazin-3-thiones may be explained as follows. According to the ^{1}H NMR data, monothiosemicarbazones exist as a single form, preferentially as the *E* form, which cannot cyclize into a triazine ring. However, it is known that the barrier to *syn—anti* isomerization for thiosemicarbazones is not large as a result of their ready ring—chain conversions [8].

TABLE 1. Characteristics of the Thiosemicarbazones III

Compound	Molecular formula	mp., °C, solvent	R_f*	^{1}H NMR Spectra in $CDCl_3$, δ, ppm (splitting, Hz)					Yield, %
				R	R^1	R^2	R^3	R^4	
a	$C_{12}H_{15}N_3OS$	98...99, benzene	0,61	6,94 (1H, s)	2,22 (3H, s)	3,69 (3H,s)	4,83 (2H,d, 5,0); 7,27 (5H,s)	8,36 (1H, br)	46
b	$C_{11}H_{13}N_3OS$; [12]	141...142, benzene-hexane	0,68	7,45 (1H,s)	7,28...7,52 (3H,m) 7,78...7,90 (2H, m)	3,74 (3H,s)	3,03 (3H,d, 5,0)	8,00 (1H, br)	94
c	$C_6H_{11}N_3OS$	173...174, ethanol	0,61	1,98 (3H,s)	2,37 (3H, s)	8,82 (1H,s)	3,21 (3H,d, 5,0)	7,55 (1H,q, 5,0)	82
d	$C_7H_{13}N_3OS$	127...128,benzene	0,72	1,97 (3H,s)	2,37 (3H, s)	8,75 (1H,s)	3,57...3,85 (2H,m); 1,26 (3H,t, 7,0)	7,48 (1H,br)	91
e	$C_{12}H_{15}N_3OS$	132...134, methanol	0,79	1,94 (3H,s)	2,27 (3H,s)	8,75 (1H,s)	4,90 (2H,d, 6,0); 7,29 (5H; s)	7,73 (1H, br)	87
f	$C_{11}H_{13}N_3OS$; [13]	163...164, methanol	0,77	1,96 (3H,s)	2,38 (3H,s)	8,79 (1H,s)	7,04...7,63 (5H, m)	9,19 (1H, s)	96
g	$C_7H_{13}N_3OS$; [13]	129...130, ethyl acetate	0,56	1,93 (3H,s)	2,33 (3H,s)	8,47 (1H,s)	3,41 (6H,s)		93

*Sorbfil, ether—hexane, 4:1.

TABLE 2. Characteristics of 5—Methylene-1,2,4-triazin-3-thiones IV

Compound	Molecular formula	mp., °C, solvent	R_f*	^{1}H NMR Spectra in $CDCl_3$, δ, ppm (splitting, Hz)				Yield, %
				CH_3—C (3H,	CH_2= (2H)	R^2	R^3	
a	$C_6H_9N_3S$	126...127, methanol	0,77	2,05	4,38 & 4,46 (J_{AB}=2,0)	9,85 (1H, s)	3,48 (3H, s)	80
b	$C_7H_{11}N_3S$	96...97, benzene-hexane	0,78	2,00	4,43 s	10,19 (1H s)	4,19 (2H, q, 7,0); 1, (3H, t, 7,0)	78
c	$C_{12}H_{13}N_3S$	161...163, methanol-acetonitrile	0,77	2,00	4,32 & 4,38 (J_{AB}=3,0)	9,90 (1H, s)	5,45 (2H, s); 7,26 (5H, s)	84
d	$C_{11}H_{11}N_3S$	163...165, methanol	0,72	2,01	3,74 (1H, d, 2,5); 4,31 (1H, d, 2,5)	9,76 (1H, s)	7,10...7,50 (5H, m)	76
e	$C_7H_{11}N_3S$	102...104, methanol	0,89	2,05	4,22 & 4,36 (J_{AB}=3,0)	3,73 (3H, s)	3,52 (3H, s)	53
f	$C_{13}H_{15}N_3S$	120...121, benzene	0,92	1,93	4,10 & 4,22 (J_{AB}=3,0)	3,74 (3H, s)	5,48 (2H, s); 7,20 (5H, s)	68
g	$C_8H_{13}N_3S$	54...56, benzene	0,90	2,08	4,20...4,41 (4H, 1,30 (3H, t, 7,0)		3,56 (3H, s)	59

*Sorbfil, ether—hexane, 3:2

TABLE 3. Spectra of 3-Thio-1,2,4-1,2,4-triazinium Cations in CF_3COOH, ppm

Compound	R, s	R^1, s	R^2	R^3
a	2,10 (3H)	8,15 (1H)	3,90 (3H, s)	5,27 (2H,s); 6,94...7,14 (5H,m)
b	8,15 (1H)	7,38 (5H)	3,94 (3H, s)	3,78 (3H, s)
c	2,16 (3H)	2,41 (3H)	4,46 (1H,br)	3,75 (3H,s)
d	2,14 (3H)	2,48 (3H)	4,39 (1H,br)	5,70 (2H, s); 6,94 (5H,s)
e	1,83 (3H)	2,20 (3H)	4,55 (1H,br)	6,84...7,40 (5H,m)
f*	2,08 (3H)	2,27 (3H)	3,73 (3H,s)	3,61 (3H,s)
g	2,20 (3H)	2,49 (3H)	3,89 (3H,s)	5,80 (2H, s); 6,80...7,00 (5H, m)

TABLE 4. ^1H NMR Spectra of 5-Alkylamino-2-acyl-2,3-dihydro-1,3,4-thiadiazolium Cations in CF_3COOH, ppm (splitting, Hz)*

Compound	R	R^1	R^3	R^4
a	5,31 (1H, s)	1,98 (3H, s)	4,14 & 4,29 (2H, ABX, J_{AB}=15,5, J_{AX}=J_{BX}=5,5); 6,80...7,02 (5H, m)	7,67 (1H, ABX, J_{AX}=J_{BX}=5,5)
b	6,35 (1H, s)	7,06...7,34 (3H, m); 7,48...7,66 (2H, m)	2,78 (3H,d, 5,0)	**
c	1,62 (3H, br)	2,06 (3H, br)	2,80 (3H, br)	7,94 (1H, br)
d	1,62 (3H, br)	2,08 (3H, br)	0,93 (3H,t, 7,0) 3,12 (2H,br)	7,90 (1H, br)
e	1,60 (3H, br)	2,06 (3H, s)	4,23 (2H,br) 6,96 (5H,br)	8,26 (1H, br)
f	1,61 (3H, s)	2,07 (3H,s)	6,86...7,18 (5H,m)	9,73 (1H, br)
g	1,59 (3H, s)	2,09 (3H,s)	2,89 (3H,s)	2,98 (3H, s)

*The signals for R^2 = H were not observed as a result of exchange with CF_3COOH. For compound Va $CH_3—N_{(2)}$ 3.03 (3 H, s) and for Vb $CH_3—N_{(2)}$ 3.04 (3 H, s).

**Signal not observed because of exchange with CF_3COOH.

In fact, monothiosemicarbazones are able to form the cyclic 5-alkylamino-2,3-dihydro-1,3,4-thiadiazolium cations (V) rapidly and quantitatively on solution in CF_3COOH. Their ^1H (Table 4) and ^{13}C NMR spectra (see Experimental) are in complete agreement with the spectroscopic characteristics of known 5-alkylamino-2,3-dihydro-1,3,4-thiadiazolium salts [9]. Signal broadening in the ^1H NMR spectra and doubling in the ^{13}C NMR spectrum of compound Vd is apparently caused by retardation of rotation about the C—N_{exo} bond. It is possible to recyclize 5-alkylamino-2,3-dihydro-1,3,4-thiadiazolium cations to 3-thio-1,2,4-triazinium cations on prolonged heating as we demonstrated for compound Ve.

Hence it is probable isomerization of the thiosemicarbazones occurs on heating, after which the *Z* isomer is cyclized to a 5-hydroxy-1,2,4-triazin-3-thione. This is confirmed by the isomerization phenylglyoxal 2,4-dimethylthiosemicarbazone into 5-hydroxy-2,4-dimethyl-5-phenyl-1,2,4-triazin-3-thione (Table 5) [4].

In the case of diacetyl the intermediate 5-hydroxy-1,2,4-triazin-3-thione is rapidly dehydrated to the corresponding 5-methylene-1,2,4-triazin-3-thione. This conversion is not unexpected since 5-alkyl-1,2,4-triazin-3-thiones [10] and 5-methyl-1,2,4-triazin-3-thiones [11] with no substituent at position 4 tend to tautomerize with migration of the double bond into the exocyclic position of the 5-alkyl substituent.

We have shown further that 5-hydroxy-2,4-dimethyl-1,2,4-triazin-3-thione (IIIa) reacts readily with ethanol to give 5-ethoxy-2,4-dimethyl-1,2,4-triazin-3-thione (VIIc). In agreement with the work mentioned above, we also synthesized it and the 5-methoxy analog VIIb by prolonged heating of phenylglyoxal 2,4-dimethylthiosemicarbazone in the corresponding alcohol in the presence of CF_3COOH. Following these results, we prepared 5-ethoxy-2,6-dimethyl-6-benzyl-1,2,4-triazin-3-thione (VIIa) from 2-methyl-4-benzylthiosemicarbazide and methylglyoxal and 5-methoxy-6-methyl-4-phenyl-1,2,4-triazin-3-thione (VIId) from diacetyl and 4-phenylthiosemicarbazide (Table 5). As shown previously [5], the ^{15}N NMR spectrum of compound VIId has two signals for sp^3 nitrogen atoms at 140.1 and 170.2 ppm and a signal for the C=N nitrogen atom at 308.4 ppm.

TABLE 5. Characteristics of 5-Hydroxy- and 5-Alkoxy-1,2,4-triazin-3-thione

Compound	Molecular formula	mp, °C solvent	R_f	^{1}H NMR spectra in $CDCl_3$, δ, ppm (splitting H_3)					Yield, %
				R	R^1	R^2	R^3	R^5	
IIIa	$C_{11}H_{13}N_3OS$; [12]	132...133, Benzene–Hexane	0,85	6,68 (1H, s)	7,35 (5H, s)	3,73 (3H, s)	3,08 (3H, s)	**	78
VIIa	$C_{14}H_{19}N_3OS$	Oil	0,84	4,88 (1H, s)	1,87 (3H, s)	3,72 (3H, s)	4,47 & 6,07 (2H, J_{AB}=15,0); 7,26 (5H, s)	1,04 (3H, t, 7,0); 3,11 (2H, q, 7,0)	32
VII	$C_{12}H_{15}N_3OS$	Oil	0,94	6,48 (1H, s)	7,34 (5H, s)	3,79 (3H, s)	3,01 (3H, s)	3,24 (3H, s)	73
VII	$C_{13}H_{17}N_3OS$	Oil	0,94	6,50 (1H, s)	7,35 (5H, s)	3,78 (3H, s)	3,01 (3H, s)	1,26 (3H, t, 7,0); 3,22...3,55 (2H	76
VII	$C_{12}H_{15}N_3OS$; [5]	138, ethanol	0,92	2,00 (3H, s)	1,24 (3H, s)	9,75 (1H, s)	7,00...7,50 (5H, m)	3,20 (3H, s)	46

It is interesting that 5-ethoxy-5-phenyl-1,2,4-triazin-3-thione (VIIc) is converted quantitatively into the corresponding methoxy derivative VIId when heated for a short while in methanol with a catalytic amount of trifluoroacetic acid, while the reverse conversion is brought about by treatment of VIId with an excess of ethanol. This phenomenon may be interpreted in terms of a crypto-ionic mechanism with intermediate dissociation of the alkoxy compound VIIc into the cation VIb.

It is worth noting that 5-hydroxy- and 5-alkoxy-1,2,4-triazin-3-thiones IIIa and VIIb-d also give the cations VIb and VIe on solution in trifluoroacetic acid.

Hence the reaction between 1,2-dicarbonyl compounds and 4-substituted thiosemicarbazides serves as synthetic method for the previously unknown 5-alkylamino-2-acyl-2,3-dihydro-1,3,4-thiadiazolium salts or 5-methylene(alkoxy)-1,2,4-triazin-3-thiones and 3-thio-1,2,4-triazinium salts.

EXPERIMENTAL

The ^1H (100 MHz) and ^{13}C (20.41 MHz) NMR spectra were recorded with a Tesla BS—497 instrument with HMDS as internal standard. ^{15}N NMR spectra* were obtained with a Bruker AM-500 (50.69 MHz) machine. Chemical shifts were measured relative to an external standard (90% formamide in DMSO) and converted to the NH_3 scale (δ_{HCONH_2} = 112.5 ppm). Reactions were monitored and the purity of the compounds obtained used TLC on Sorbfil plates with ether—hexane mixtures in suitable ratios as eluents.

The C, H, N, and S analyses for new compounds corresponded to the calculated values.

Reaction of 1,2-dicarbonyl Compounds with Thiosemicarbazides. A 1,2-dicarbonyl compound (methylglyoxal and phenylglyoxal, 0.02 mole in water; diacetyl, 0.05 mole without solvent) was mixed at room temperature with the corresponding thiosemicarbazide (0.01 mole; in ethanol (20 ml) for methylglyoxal, in water (50 ml) for phenylglyoxal, and without solvent for diacetyl). The bisthiosemicarbazones Ia and Ib and the monothiosemicarbazones IIb-g precipitated, were filtered off and recrystallized. In the reaction with methylglyoxal 2-methyl-4-benzyl-thiosemicarbazone (IIIa) and 5-ethoxy-2,6-dimethyl-4-benzyl-1,2,4-triazin-3-thione (VIIa) were isolated by preparative TLC on Al_2O_3 (eluent ether) after removal of the solvent. 5-Methylene-1,2,4-triazin-3-thiones IVe-g were recrystallized after removal of the excess diacetyl. The characteristics of compounds I, IV, and VII are given in Tables 1, 2, and 5.

Methylglyoxal Bis-4-methylthiosemicarbazone (Ia). mp 254-255°C (dec.) (from methanol), yield 78%. ^1H NMR spectrum (in DMF-D_7): 2.20 (3H, s, CH_3-C); 3.08 (6H, d, J = 5.0 Hz, 2 CH_3—N); 7.28 (1H, s, CH), 8.55 (2H, br, 2 NH—CH_3); 10.25 (1H, s, NH); 11.60 ppm (1H, s, NH).

Methylglyoxal Bis-4-benzylthiosemicarbazone (Ib). m.p. 204-206° C (ethanol), yield 83%. ^1H NMR spectrum (1:1 $CDCl_3$+DMSO-D_6): 2.08 (3H, s, CH_3), 4.85 (4H, d, J = 5.0 Hz, 2 CH_2), 7.27 (10H, s, 2 C_6H_5), 7.63 (1H, s, CH), 8.10 (1H, br, NH), 8.30 (1H, s, NH), 8.30 (1H, s, NH), 11.60 ppm (1H, s, NH).

6-Methyl-4-R^3-5-Methylene-1,2,4-triazin-3-thiones IVa-d. The thiosemicarbazone IIc-f (0.01 mole) in benzene (50 ml) was boiled over CaO (2 g) for 15 h. The solution was filtered, the benzene evaporated in vacuum, and the residue recrystallized. Characteristics of the compounds are given in Table 2.

5-Hydroxy-2,4-dimethyl-5-phenyl-1,2,4-triazin-3-thione (IIIa) was obtained by standing methylglyoxal 2,4-dimethylthiosemicarbazone (0.01 mole) in benzene with a catalytic amount of CF_3COOH for 15 h. After removal of the solvent, the oily residue was extracted with hexane. Compound IIIa (Table 5) precipitated on cooling the extract.

5-Methoxy- and 5-ethoxy-2,4-dimethyl-5-phenyl-1,2,4-triazin-3-thiones (VIIb and c) were obtained by heating phenylglyoxal 2,4-dimethylthiosemicarbazone in the corresponding alcohol with a catalytic amount of CF_3COOH for 8 h. The solvent was removed and the oil purified by reprecipitation from hexane. Characteristics of the compounds are given in Table 5.

Compound Vd. ^{13}C NMR spectrum in CF_3COOH: 11.8 and 12.7 (2 $CH_2\underline{C}H_3$), 18.9 ($\underline{C}H_3$—C(2) in two forms), 23.3 and 23.5 (2 $\underline{C}H_3$—CO), 41.6 and 46.0 (2 CH_2), 86.1 and 87.2 (2 $C_{(2)}$), 172.5 and 176.3 (2 C=N^+), 206.3 ppm (C=O in two forms).

Compound Vg. ^{13}C NMR spectrum in CF_3COOH: 19.0 (CH_3—C(2)), 23.3 ($\underline{C}H_3$—CO), 39.8 and 45.6 (2 CH_3—N), 87.5 ($C_{(2)}$), 174.8 (C=N^+), 204.4 ppm (C=O).

* We thank our co-worker T. I. Pekhk, NIIKhBF, for measuring the spectra and participating in discussion of the results.

Compound Vf. ^{13}C NMR spectrum in CF_3COOH: 18.5 and 19.7 (2 $C\underline{C}H_3$), 42.6 and 51.1 (2 CH_3—N), 144.3 (C=N), 164.1 and 167.0 ppm (C=N^+ and C=S). ^{15}N NMR spectrum in CF_3COOH: 219.3 and 230.6 ($N_{(2)}$ and $N_{(4)}$), 372.3 ppm ($N_{(1)}$).

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