INTERACTION OF THERMAL ACYLACETYLENES WITH THIOSEMICARBAZIDE AND 4-METHYL- AND 4-PHENYLTHIOSEMICARBAZIDES

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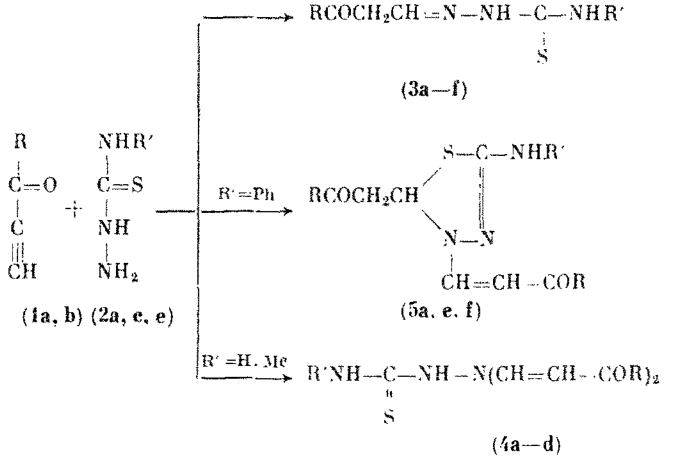
By the reaction of thiosemicarbazide and 4-methyl- and 4-phenylthiosemicarbazides with terminal α-acetylenic ketones, depending on the conditions, thiosemicarbazones of acylacetic aldehyde, 1,1-bis(acylvinyl)thiosemicarbazides, and 5-phenylamino-2-acylmethyl-3-acylvinyl-1,3,4-thiadiazolines are obtained. Ring-chain tautomerism of the 1,1-bis(acylvinyl)thiosemicarbazides has been investigated.

Keywords: *acylacetylenes, thiosemicarbazide, 4-methylthiosemicarbazide, 4-phenylthiosemicarbazide, 1,1-bis(acylvinyl)thiosemicarbazides, thiosemicarbazones of acylacetic aldehyde, 5-amino(phenylamino)-2-acylmethyl-3-acylvinyl-1,3,4-thiadiazolines.*

It is known that the reaction of terminal α-acetylenic ketones with 1-phenylthiosemicarbazide leads to the formation of 2-acylmethyl-5-imino-3-phenyl-4H-1,3,4-thiadiazoles [1], and that the reaction of 1-acyl-2-phenylacetylenes with thiosemicarbazide leads to the formation of 2-amino-7-hydroxy-6,7-dihydro-1,3,4-thiadiazepines [2]. The dimethyl ester of acetylenedicarboxylic acid with thiosemicarbazide and its 1-substituted derivatives gives 2-hydrazino-5-methoxycarbonylmethylene-1,3-thiazolin-4-ones [3], and with 4-substituted derivatives of thiosemicarbazide it gives 3-amino-2-imino-6-methoxycarbonyl-1,3-thiazin-4-ones [4]. However, in the reaction of the diethyl ester of acetylenedicarboxylic acid with thiosemicarbazide in ethanol, 3-thioxo-6-ethoxycarbonylmethylenehexadro-1,2,4-triazin-5-one is obtained [5].

In continuation of our research on reactions of acylacetylenes with ambifunctional N,S-containing reagents [1, 6-9], we have investigated the reaction of terminal α-acetylenic ketones (**1a, b**) with thiosemicarbazide (**2a**), 4-methylthiosemicarbazide (**2c**), and 4-phenylthiosemicarbazide (**2e**).



R = Ph, R' = H (**a**); R = 2-thienyl R' = H (**b**); R = Ph, R' = Me (**c**); R = 2-thienyl R' = Me (**d**); R = R' = Ph (**e**); R = 2-thienyl R' = Ph (**f**).

By the reaction of equimolar quantities of benzoyl- or thenoylacetylenes **1a, b** with thiosemicarbazide **2a** and 4-methylthioemicarbazide **2c** in methanol at 20°C, 45-66% yields were obtained of the thiosemicarbazones of acylacetic aldehyde

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TABLE 1. Characteristics of Synthesized Compounds

Compound	Yield, %	Mp, °C	Empirical formula	Found/Calculated, %			
				C	H	N	S
3a	51	139–140	$C_{10}H_{11}N_3OS$	54.1/54.3	5.0/4.5	14.5/14.5	18.7/19.0
3b	45	141–142	$C_6H_9N_3OS_2$	42.4/42.3	4.1/4.5	18.7/19.0	28.0/28.2
3c	66	123–124	$C_{11}H_{13}N_3OS$	56.1/56.2	5.5/5.5	17.8/17.9	13.9/13.6
3d	64	110–112	$C_9H_{11}N_3OS_2$	44.7/44.8	4.6/4.6	17.3/17.4	27.0/26.6
3e	41	111–112	$C_{16}H_{15}N_3OS$	64.3/64.7	5.0/5.1	14.1/14.1	10.7/10.8
3f	43	114–115	$C_{14}H_{13}N_3OS_2$	55.4/55.4	4.0/4.3	14.1/13.9	21.2/21.2
4a	68	144–145	$C_{19}H_{17}N_3O_2S$	64.8/65.0	5.1/4.8	11.6/12.0	9.2/9.1
4b	63	144–146	$C_{15}H_{13}N_3O_2S_3$	49.4/49.6	3.9/3.6	11.8/11.6	26.2/26.4
4c	70	143–144	$C_{20}H_{19}N_3O_2S$	65.5/65.8	5.3/5.2	11.8/11.5	9.0/8.8
4d	66	144–145	$C_{16}H_{15}N_3O_2S_3$	50.7/50.9	3.8/4.0	11.0/11.1	25.5/25.5
5a	77	129–130	$C_{19}H_{17}N_3O_2S$	64.7/65.0	4.7/4.8	11.7/12.0	9.2/9.1
5e	93	163–164	$C_{25}H_{21}N_3O_2S$	70.4/70.3	4.8/4.9	9.9/9.8	7.5/7.5
5f	86	165–166	$C_{21}H_{17}N_3O_2S_3$	57.4/57.4	3.9/3.9	9.6/9.6	21.6/21.9

3a-d, and 16-23% yields of 1,1-bis(acylvinyl)thiosemicarbazides **4a-d**. Under analogous conditions, with a 2:1 ratio of **1a** or **1b** to **2a**, only the compounds **4a-d** were obtained, with 63-70% yields.

The interaction of the α-acetyleneic ketones **1a, b** with 4-phenylthiosemicarbazide **2e** was carried out at −30°C with equimolar quantities of the reagents, in methanol. The yields of compounds **3e** and **3f** were 41% and 43%, respectively. When this reaction was carried out at 20°, no reaction products could be isolated, as the reaction mixture was largely converted to tar.

When the reaction of the ketone **1a** or **1b** with **2e** was carried out with a 2:1 mole ratio at −30°C in methanol, the picture was completely different. In this case, the only reaction product, obtained in high yield (86-93%) was a 5-phenylamino-2-acylmethyl-3-acylvinyl-1,3,4-thiadiazoline **5e** or **5f**. When this reaction was carried out at 20°C, the respective yields of the compounds **5e, f** were 67% and 78%.

The structures of the synthesized compounds were confirmed by elemental analysis (Table 1), IR spectroscopy, ^1H and ^{13}C NMR spectrometry (Table 2), and mass spectrometry.

In the IR spectra of the hydrazones **3a-f**, absorption bands are observed for the carbonyl group (1640-1680 cm^{-1}), stretching vibrations of NH and NH_2 groups (3155-3370 cm^{-1}), and C=N and C=C bonds (1515-1605 cm^{-1}). In the IR spectra of compounds **4a-d**, bands are present corresponding to absorption by the conjugated carbonyl group (1625-1640 cm^{-1}), the C=C bond (1580-1600 cm^{-1}), and NH and NH_2 groups (3100-3300 cm^{-1}). In the IR spectra of the substituted 1,3,4-thiadiazolines **5e, f**, two absorption bands are observed, corresponding to carbonyl groups at 1670-1685 cm^{-1} ($COCH_2$) and 1640 cm^{-1} (COCH=), the =C bond (1575-1600 cm^{-1}), and the exocyclic NH group (3270-3280 cm^{-1}).

In the ^1H NMR spectra of compounds **3a-f**, doublets are observed from protons of the CH_2 group at 4.04-4.06 ppm, and singlets from a proton of the amino group of the hydrazine fragment at 11.31-11.37 ppm. The signals from the proton of the N=CH group and the amino group of the thioamide fragment are overlapped by signals from aromatic ring protons, and

TABLE 2. ^1H and ^{13}C NMR Spectra of Synthesized Compounds

Compound	PMR spectrum δ, ppm, J, Hz	^{13}C NMR spectrum δ, ppm
3a	4.06 d (2H, CH_2), 7.58—8.00 m (8H, C_6H_5, CH=N, NH_2), 11.31 c (1H, NH)	40.96 (CH_2), 195.63 (C=O) 176.99 (C=S), 140.8 (CH=N), 127.1—135.06 (C_6H_5)
3b	4.05 d (2H, CH_2), 7.28—8.21 m (6H, C_4H_3S, CH=N, NH_2), 11.35 s (1H, NH)	—
3c	2.95 d (3H, CH_3), 4.06 d (2H, CH_2), 7.54—7.99 m (6H, C_6H_5, CH=N), 8.19 s (1H, $N\underline{H}CH_3$), 11.35 s (1H, =N—NH)	—
3d	3.00 d (3H, CH_3), 4.04 d (2H, CH_2), 7.60 t (1H, CH=N), 7.32—8.23 m (5H, C_4H_3S, $N\underline{H}CH_3$, CH=N), 11.37 s (1H, =N—NH)	31.01 (CH_3), 42.59 (CH_2), 143.06 (CH=), 178.39 (C=S), 188.40 (C=O), 128.49—139.62 (C_4H_3S)
3e	4.17 d (2H, CH_2), 7.33—8.02 m (11H, $2C_6H_5$, CH=), 9.85 s (1H, $N\underline{H}—C_6H_5$), 11.75 s (1H, =N—NH)	44.91 (CH_2), 195.85 (C=O) 174.93 (C=S), 141.35 (CH=N), 123.79—137.99 ($2C_6H_5$)
4a	6.53 d (2H, 2COCH=, ^3J = 13.5), 10.64 s (1H, NH), 7.61—8.64 m (14H, $2C_6H_5$, =CH—N—CH=, NH_2)	—
4b	6.32 d (2H, 2COCH=, ^3J = 12), 7.29—8.47 m (10H, $2C_4H_3S$, =CH—N—CH=, NH_2), 10.48 s (1H, NH)	—
4c	2.95 d (3H, CH_3), 6.46 d (2H, 2COCH=, ^3J = 12), 7.63—8.52 m (13H, $2C_6H_5$, =CH—N—CH=, $N\underline{H}—CH_3$), 10.46 s (1H, NH—N)	31.41 (CH_3), 102.08 (COCH=), 148.1 (N=CH), 180.43 (C=S), 188.35 (C=O) 127.77—138.38 (C_6H_5)
4d	2.95 d (3H, CH_3), 6.35 d (2H, 2COCH=, ^3J = 12), 7.30—8.50 m (9H, $2C_4H_3S$, =CH—N—CH=, $N\underline{H}—CH_3$), 10.42 s (1H, NH—N)	—
5a	3.77—3.90 m (2H, CH_2), 6.10 m (2H, COCH=, CH_x), 7.11 br.s (2H, NH_2), 7.51—7.80 m (10H, $2C_6H_5$), 8.00 d (1H, N—CH=, ^3J = 12.2)	—
5e	3.75—4.22 m (2H, CH_2, $^2J_{AB}$ = 17.8, $^3J_{AX}$ = 7.75, $^3J_{BX}$ = 5.2), 6.31 m (2H, CH_x, COCH=, ^3J = 12.0), 7.07—8.02 m (16H, $3C_6H_5$, N—CH=), 10.00 s (1H, NH)	47.38 (CH_2), 67.40 (CH), 93.17 ($CO\underline{C}H$=), 144.93 (N—CH=), 151.58 (S—C=N), 186.39 ($\underline{C}OCH$=), 197.52 ($\underline{C}OCH_2$), 118.12—140.38 (C_6H_5)
5f	3.98 m (2H, CH_2), 6.32—6.45 m (2H, COCH=, CH_x, ^3J = 12), 7.32—8.14 m (12H, $2C_4H_3S$, C_6H_5, N—CH=), 10.09 m (1H, NH)	—

TABLE 3

Exp. No.	Solvent	Temp., °C	Ratio 1a/2a	Yield, %		Ratio 4a/5a
				3a	4a—5a	
1	MeOH	20	1/1	51	21	100/–
2	MeOH	20	2/1	0	68	100/–
3	MeOH	60	1/1	55	16	100/–
4	MeOH	60	2/1	0	40	100/–
5	MeCN	20	1/1	50	22	60/40
6	MeCN	20	2/1	0	68	60/40
7	MeCN	60	2/1	0	68	40/60
8	MeCN	75	1/1	48	22	10/90
9	MeCN	75	2/1	0	70	10/90

are observed at 7.23-8.23 ppm. In the spectra of compounds **4a-d** there are doublets from α-protons of the group =CH−CO at 6.32-6.53 ppm (the value of the SSCC, ^3J = 12-13.5 Hz, indicates the *trans* configuration for both double bonds). The doublets from β-protons of the =CH−N−CH= group and signals from protons of the thioamide groups are overlapped by signals from aromatic ring protons, and lie in the interval δ 7.29-8.64 ppm. The signals from protons of the amino groups of the hydrazine fragment are observed at 10.42-10.64 ppm. In the ^1H NMR spectra of the substituted 1,3,4-thiadiazolines **5e, f** we observe multiplets from methyl-group protons at 3.9-4.1 ppm; triplets from methyl-group protons are imposed on doublets from α-protons of the acylvinyl group and are observed in the form of a multiplet at 6.31-6.45 ppm. Signals from the aromatic ring protons and β-protons of the vinyl group lie in the interval δ 7.32-8.14 ppm (^3J = 12 Hz, *trans* isomer); singlets from the amino group protons are observed at 10.00-10.09 ppm.

In the example of the reaction of benzoylacetylene **1a** with **2a**, we investigated the influence of the solvent, temperature, and reactant ratio on the yields and ratio of reaction products (Table 3). In these experiments, the reaction time was 2 h.

As can be seen from Table 3, an increase of the reaction temperature to 60-75°C, a change of the solvent (MeOH or MeCN), or changes in the reactant ratio do not result in any substantial changes of the overall yield of reaction products. At the same time, however, replacement of the protic solvent MeOH by the polar aprotic solvent MeCN, regardless of the reactant ratio, results in the appearance of the substituted 1,3,4-thiadiazoline **5a** in the reaction mixture along with compound **4a**; and an increase of the reaction temperature (in MeCN) from 20 to 75°C results in much higher contents of **5a** in the reaction mixture (Table 3).

The ratio of compounds **4a** and **5a** in the reaction mixture was calculated from the integral curve of the ^{1}H NMR spectrum of solutions in DMSO-d_6.

The pure 1,3,4-thiadiazoline **5a** was obtained by the interaction of the thiosemicarbazone **3a** with an equimolar quantity of the ketone **1a** in MeCN at 75°C (Table 2). We were not successful in obtaining the individual compounds **5b-d** by reaction of the corresponding thiosemicarbazones **3b-d** with the ketones **1a, b** under these same conditions.

We applied ^{1}H NMR spectrometry in an investigation of the ring–chain tautomeric transitions **4a** $\rightleftarrows$ **5a** in polar solvents. Upon heating compound **4a** in MeCN for 7 h at 75°C, 10% of compound **4a** and 90% **5a** were found in the solution. In the ^{1}H NMR spectrum, along with the proton signals that are characteristic for 1,1-bis(benzoylvinyl)thiosemicarbazide **4a** (Table 1), a multiplet appeared from protons of the $COCH_2$ groups (δ 3.77-3.90 ppm), and a multiplet from protons of CH_x and COCH= groups (δ 6.10 ppm). In solutions obtained by analogous treatment of compounds **4b** and **4c**, we found 40% **4b** and 60% **5b** in the first case, and 66% **4c** and 34% **5c** in the second case. In the ^{1}H NMR spectra of the solutions, along with signals from protons that are characteristic for compounds **4b** and **4c** (Table 2), multiplets from protons of the $COCH_2$ group were observed at 3.60-3.72 ppm (for **5b**) and 3.67-3.82 ppm (for **5c**), and multiplets from COCH= and CH_x groups at 6.00-6.13 ppm (for **5b**) and 6.14 ppm (for **5c**).

Ring–chain tautomeric conversions **4a** $\rightleftarrows$ **5a** were also observed upon heating compound **4a** in other polar solvents. In DMSO-d_6 at 110°C, the solution was found to contain 50% **4a** and 50% **5a**. In pyridine at 20°C the solution was found to contain 75% **4a** and 25% **5a**; at 60°C, the contents were 60% **4a** and 40% **5a**; and at 110°C, 40% **4a** and 60% **5a**.

Thus we can note that the ability of the 1,1-bis(acylvinyl)thiosemicarbazides **4a-c** to undergo tautomeric conversions to the substituted 1,3,4-thiadiazolines **5a-c** upon heating in polar aprotic solvents depends on the nature of the substituents R and R′.

EXPERIMENTAL

The IR spectra were taken in a UR-20 spectrometer in tablets with KBr. The ^{1}H NMR spectra of solutions in $(CD_3)_2SO$ were obtained in a Tesla BS-487C spectrometer with a working frequency of 80 MHz; the ^{13}C NMR spectra were obtained in an FX-90Q spectrometer (22.49 MHz). The mass spectra (EI) were taken in an MKh-1303 mass spectrometer with direct introduction of the sample into the ion source; the ionizing electron energy was 30 or 70 eV, and the ionization chamber temperatures was 100-170°C.

Reaction of Benzoylacetylene 1a with Thiosemicarbazide 2a. Experiment 1. To a suspension of 0.46 g (5 mmoles) of thiosemicarbazide in 20 ml of MeOH, a solution of 0.65 g (5 mmoles) of **1a** in 10 m of MeOH was added slowly with stirring, after which the stirring was continued for 2 h at 20°C. The precipitate was filtered off, washed with ether, and vacuum-dried. Obtained 0.18 g (21%) of 1,1-bis(benzoylvinyl)thiosemicarbazide **4a** — a yellow, amorphous powder with mp 144-145°C (from MeOH).

The solution was chilled to 0°C and held at that temperature for 24 h. The precipitate was filtered off, washed with ether, and vacuum-dried. Obtained 0.57 g (51%) of the thiosemicarbazone of benzoylacetic aldehyde **3a** — light yellow needles with mp 139-140°C (from a 2:1 mixture of EtOH and water). Mass spectrum, *m/z*, I_{rel}, %): 221 (50) $[M]^{+\bullet}$, 105 (100) $[PhCO]^+$, 102 (8) $[M - PhCOCH_2]^+$, 59 (30) $[S{=}C{=}NH]^{+\bullet}$.

The reaction of benzoylacetylene **1a** with **2a** was also carried out in methanol (experiments 2-4) and in acetonitrile (experiments 5-9) (Table 3).

Thiosemicarbazone of 2-Thenoylacetic Aldehyde 3b was obtained in the same manner as compound **3a**, in MeOH at 20°C, from 0.46 g (5 mmoles) of **2a** and 0.68 g (5 mmoles) of **1b**. Obtained 0.51 g (45%) of compound **3a** — a light brown powder with mp 141-142°C — and 0.25 g (23%) of compound **4b** — a yellow powder with mp 144-146°C.

4-Methylthiocarbazone of Benzoylacetic Aldehyde 3c was obtained in the same manner as compound **3a**, in MeOH at 20°C, from 0.53 g (5 mmoles) of **2c** and 0.65 g (5 mmoles) of **1a**. Yield 0.75 g (66%), white crystals with mp 123-124°C (from EtOH). Also recovered from the reaction mixture was 0.15 g (16%) of compound **4c**, yellow powder with mp 143-144°C.

4-Methylthiosemicarbazone of 2-Thenoylacetic Aldehyde 3d was obtained in the same manner as compound **3a**, in EtOH at 20°C, from 0.53 g (5 mmoles) of **2c** and 0.68 g (5 mmoles) of **1b**. Yield 0.77 g (64%), yellow crystals with mp 110-112°C. Also recovered from the reaction mixture was 0.17 g (18%) of compound **4d**, light brown powder with mp 144-145°C.

4-Phenylthiosemicarbazone of Benzoylacetic Aldehyde 3e. To a solution of 1.3 g (10 mmoles) of **1a** in 30 ml of MeOH, chilled to −30°C, 1.67 g (10 mmoles) of **2e** was added with stirring, and the solution was gradually warmed to 0°C. Stirring was continued for 15 min; then the precipitate was rapidly filtered off, washed with cold ether, and vacuum-dried. Obtained 1.22 g (41%) of **3e**, yellow crystals with mp 111-112°C (from EtOH). The reaction was accompanied by considerable tar formation in the reaction mixture.

Compound **3f** was obtained analogously (Table 1).

1,1-Bis(2-thenoylvinyl)thiosemicarbazide 4b was obtained in the same manner as compound **4a**, in MeOH at 20°C, from 1.36 g (10 mmoles) of **1b** and 0.46 g (5 mmoles) of **2a**. Obtained 1.15 g (63%) of **4b**, yellow powder with mp 144-146°C (from MeOH).

1,1-Bis(benzoylvinyl)-4-methylthiosemicarbazide 4c was obtained in the same manner as compound **4a**, in EtOH at 20°C, from 1.3 g (10 mmoles) of **1a** and 0.53 g (5 mmoles) of **2c**. Yield 1.3 g (70%), yellow powder with mp 143-144°C (from EtOH). Mass spectrum, *m/z* (I_{rel}, %): 365 (8) $[M]^{+\bullet}$, 235 (60) $[M - PhCOC{\equiv}CH]^+$, 260 (100) $[M - PhCO]^+$, 105 (60) $[PhCO]^+$.

1,1-Bis(2-thenoylvinyl)-4-methylthiosemicarbazide 4d was obtained in the same manner as **4a**, in EtOH at 20°C, from 1.36 g (10 mmoles) of **1b** and 0.53 g (5 mmoles) of **2c**. Yield 1.24 g (66%), yellow powder with mp 144-145°C (from a 3:1 mixture of EtOH and MeCN).

5-Amino-3-benzoylvinyl-2-benzoylmethyl-1,3,4-thiadiazoline 5a. To a solution of 0.221 g (1 mmole) of the thiosemicarbazone **3a** in 20 ml of MeCN, heated to 75°C, a solution of 0.13 g (1 mmole) of **1a** in 5 ml of MeCN was added slowly with stirring. The mixture was stirred for 0.5 h at 75°C, chilled to 0°C, and held at that temperature for 24 h. The precipitate was filtered off, washed with ether, and vacuum-dried. Obtained 0.27 g (77%) of the 1,3,4-thiadiazoline **5a**, gold-colored crystals with mp 129-130°C.

2-Benzoylmethyl-3-benzoylvinyl-5-phenylamino-1,3,4-thiadiazoline 5e. To a solution of 1.3 g (10 mmoles) of **1a** in 30 ml of MeOH, chilled to −30°C, 0.84 g (5 mmoles) of **2e** was added with stirring, after which the mixture was warmed to 0°C and stirred for an additional 15 min. The precipitate was filtered off, washed with cold ether, and dried. Obtained 1.99 g (93%) of **5e**, gold-colored needles with mp 163-164°C (from EtOH). When the reaction was carried out in MeOH at 20°C obtained 1.67 g (78%) of compound **5e**.

3-(Thenoyl-2)-vinyl-2-(thenoyl-2)-methyl-5-phenylamino-1,3,4-thiadiazoline 5f was obtained in the same manner as **5e**, from 1.36 g (10 mmoles) of **1b** and 0.84 g (5 mmoles) of **2c**. Yield 1.89 g (86%), dark yellow crystals with mp 165-166°C (from EtOH). When the reaction was carried out in MeOH at 20°C, obtained 1.47 g (67%) of compound **5f**.

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