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Multicomponent Heterocyclization of Carboxamides with H_2S and CH_2O

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Abstract—Multicomponent heterocyclization of aliphatic amides with H_2S and CH_2O (1:3:2) in water-organic solvent mixture in the presence of BuONa led to the formation of 1,3,5-dithiazinane in high yield (30–95%) and with high selectivity (100%). Under these conditions benzamide gave 3,5-dibenzoyl-1,3,5-thiadiazinane in 74% yield, whereas due to *ortho*-effect the acetylsalicylamide with H_2S and CH_2O in a system BuOH–H_2O without BuONa formed N-acetylsalicyloyl-1,3,5-dithiazinane (80%). Heterocyclization of α-aminosuccinic acid monoamide depending on the H_2S and CH_2O concentration occurred either at one or both NH_2 yielding respectively mono- or bisdithiazinanes.

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Nowadays the interest still exist to synthetic heterocycles containing sulfur and nitrogen applicable as catalysts in the phase transfer processes, efficient extractants, sorbents, flotation reagents, and also as antibacterial, anticancer, and antiHIV agents [1, 2].

One of promising methods of preparation of N,S-containing heterocycles, namely, 1,3,5-dithiazinanes and 1,3-thiazetidines is the cyclothiomethylation of primary amines with H_2S and CH_2O [3–10]. Until our studies carboxamides were not involved into the cyclocondensation with H_2S and CH_2O.

Taking into consideration the practical significance of dithiazinanes, thiadiazinanes, and their derivatives as selective sorbents and also aiming at the development of preparation methods for these classes compounds we studied the multicomponent condensation of aliphatic and aromatic carboxamides with H_2S and CH_2O.

We selected for objects of investigation formamide, acetamide, caproamide, 2-cyanoacetamide, trifluoroacetamide, acrylamide, benzamide, acetylsalicylamide, and 2-aminosuccinic acid monoamide (*D*-asparagine) (**Ia–Ii**).

To develop the optimum conditions of the synthesis of *N*-acyl-1,3,5-dithiazinanes we studied by an example of the cyclothiomethylation of acetamide (**Ib**) the effect of temperature, the sequence of the reagents and catalyst addition to the reaction mixture. Mineral acids and bases were applied as catalysts.

It was established that acetamide (**Ib**) brought into the reaction under the chosen conditions and at the reagents ratio acetamide (**Ib**)–CH_2O–H_2S 1:3:2 was not involved into the cyclothiomethylation. However on adding to the reaction mixture BuONa in amount 2 mol per mol of the initial amide the lability of hydrogen atoms in the initial amide notably grew and therefore it was involved into the cyclocondensation with H_2S and CH_2O giving the corresponding 1,3,5-dithiazinane **IIb** in a sufficiently good yield.

In the presence of other bases (Et_3N, NaOH, K_2CO_3, NaOH/BuOH, NaOH/EtOH, and EtONa/EtOH) independent of the temperature (0–80°C) the reaction of amide **Ib** with H_2S and CH_2O resulted in trithiolane **IX** [8]. Similar results were also obtained at acidifying the reaction mixture (**Ib**–CH_2O–H_2S, 1:3:2) with HCl.

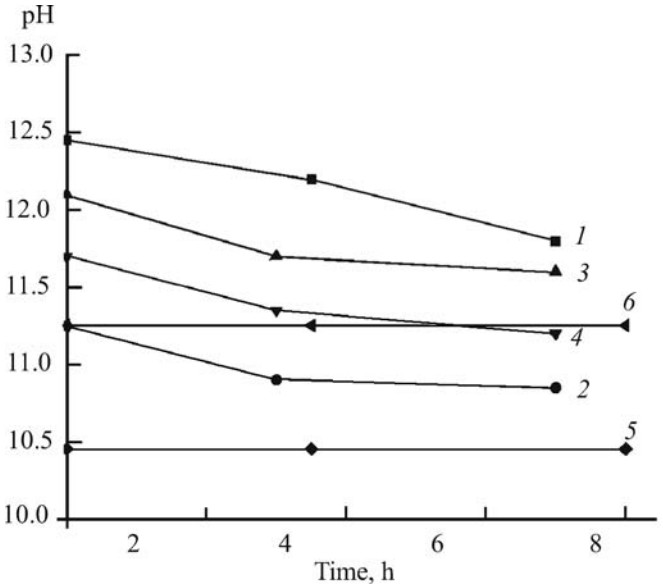
The basic properties of amino group in amides are known to be considerably weakened due to the replacement of a hydrogen by an acid residue [11]. As a result strong mineral acids and bases form salts with amides that decompose under the action of water giving the initial amide and the corresponding acid. It was also established [12] that potassium salts of heterylcyano-

amides were stable compounds and *N*-alkylheteryl-cyanoamides were obtained therefrom.

Potentiometric analysis showed that under the treatment of bases like NaOH, K_2CO_3, NaOH/BuOH, and NaOH/EtOH acetamide (**Ib**) was hydrolyzed to acetic acid (see the figure), whereas bases EtONa/EtOH and BuONa/BuOH conserved the amide group, and the activity of the alcoholates in the formation of molecular complexes with amides depended on the positive charge value on the sodium atom and on the structure of the initial alcoholate growing in going from methylate (sodium charge in the units of ionic character of the chemical bond +1.335) to butylate (Na +2.385) [13, 14].

In this connection we chose as the optimum activating system for amides a solution of sodium butylate in butanol (pH 11.25). As optimum reaction temperature was found to be 40°C. At higher temperature tarring occurred, at lower temperature the target dithiazinanes were obtained in lower yields (10–20%).

In order to elucidate the mechanism of activation by BuONa in amides cyclocondensation with H_2S and CH_2O we studied the interaction of acetamide with BuONa dissolved in BuOH by means of IR and ^1H and ^{13}C NMR spectroscopy. For instance in the ^1H NMR spectrum of acetamide (**Ib**) the characteristic signals of the methyl group protons appeared at δ 2.21 ppm, and of amino group protons, at δ 7.07–7.78 ppm. After adding the reagent BuONa/BuOH in a ratio **Ib**–BuONa 1:2 (Scheme 1) the signals suffered an upfield shift, namely the CH_3 group to δ 1.78 ppm, NH_2 group to δ 5.19–5.55 ppm. In the ^{13}C NMR spectrum thesignal of the methyl group of acetamide shifted downfield, from δ 20.27 ppm for compound **Ib** to δ 20.59 ppm for the complex (**Ib**)·$[BuONa]_2$ (**A**), and the signal of the carboxy group, upfield from δ 174.87 to 173.96 ppm. At the same time we registered the proton and carbon signals from the butyl group in BuONa molecule. Thus in the ^1H NMR spectrum signals were observed at 0.69, 1.24, and 3.35 ppm with the ratio of ontegral intensities 3:4:2, and in the ^{13}C NMR spectrum appeared signals at δ 12.45, 17.93, 33.85, and 60.35 ppm belonging to the methyla and the methylene carbon atoms.

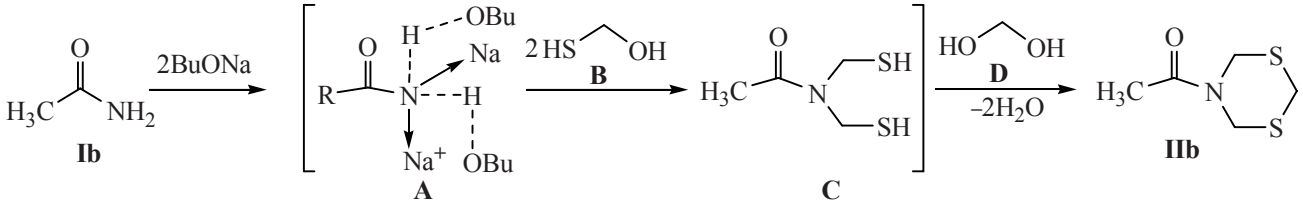


Variation of the medium pH depending on the reaction time and catalytic system: NaOH + H_2O (*1*), K_2CO_3 (*2*), NaOH + BuOH (*3*), NaOH + EtOH (*4*), EtONa/EtOH (*5*), BuONa/BuOH (*6*).

In the IR spectrum the absorption band of the carbonyl group of amide **Ib**, ν 1660 cm^{-1}, is conserved in complex **A**, whereas the bending vibrations of the amino group of amide **Ib**, ν 1630–1645 cm^{-1}, in complex **A** shift to short-wave region by 10–20 cm^{-1} with simultaneous decrease in intensity. Monodentate ligands with the coordination center on the nitrogen atom in complex with metals were described [15].

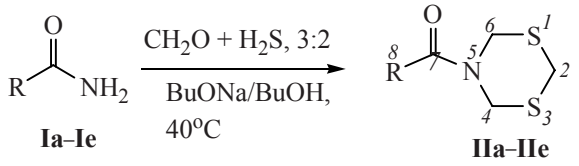
Complex (**Ib**)·$[BuONa]_2$ apparently is of **A** structure where the chelating of ions Na occurs at the nitrogen. As a result the lability of hydrogen atoms of the amide group grows in reaction with thioacetals **B** formerly found by GC-MS analysis as intermediates in the thiomethylation of aliphatic amines with a mixture CH_2O–H_2S [7]. Obviously in the coordinated amide **A** the lability of protons originates rom the Coulomb repulsion from the positively charged sodium ions [16]. Further cyclocondensation of *N,N*-bis(mercapto-methyl)acetamide **C** with methylene glycol **D** resulted in *N*-acetyl-1,3,5-dithiazinane (**IIb**) (Scheme 1).

Scheme 1.



Thus under the condition chosen by us for the heterocyclization of acid amides **Ia–Ie** with H_2S and CH_2O the reaction of initial amides **Ia–Ie** in the presence of BuONa with water solution of formaldehyde (37%) saturated with the hydrogen sulfide proceeded at the reagents ratio amide–H_2S–CH_2O 1:2:3 for 6 h at 40°C. Aliphatic amides **Ia–Ie** provided exclusively 1,3,5-dithiazinanes **IIa–IIe** in 30–95% yields (Scheme 2).

Scheme 2.



Ia–Ie **IIa–IIe**

R = H (**a**), CH_3 (**b**), $CH_2CH_2CH_2CH_2CH_3$ (**c**), $NCCH_2$ (**d**), CF_3 (**e**).

We found that the yields of the target dithiazinanes **IIa–IIe** grew in the series of amides having in the hydrocarbon chain of the molecule the following groups: n-C_5H_{11}<CH_3<H<$CNCH_2$<CF_3, therefore with the growing electron-withdrawing quality of the latter grew the activity of initial amides in the cyclo-condensation with H_2S and CH_2O. It was established that amides with electron-withdrawing substituents were capable to enter into the multicomponent condensation with H_2S and CH_2O in the absence of BuONa, but in this case the conversion decreased to 20–30%.

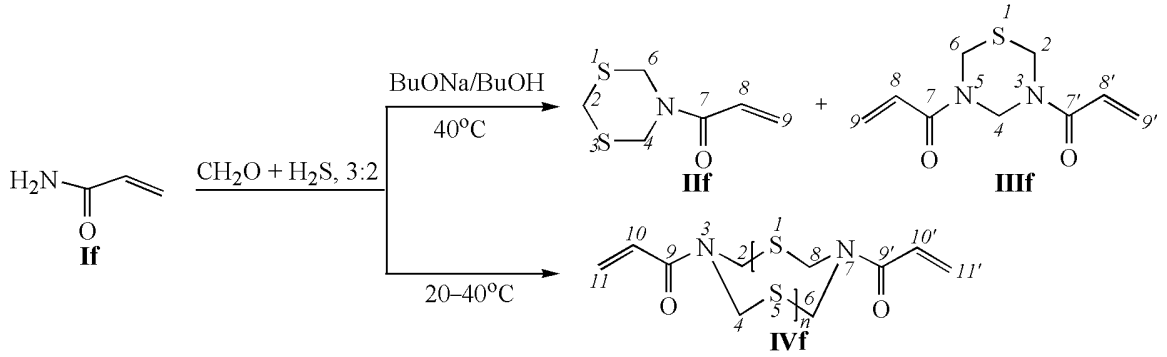
We showed formerly [10] that at the decrease in the basicity of the amino group in the initial amines grew the efficiency of the cyclothiomethylation, but diminished the selectivity. The basicity of aromatic and unsaturated carboxamides is reduced compared to the aliphatic saturated amides due to the conjugation of the lone pair of the nitrogen with the π-electrons of the aromatic ring or the double bond. Therefore the heterocyclization of acrylamide (**If**) alongside the 1,3,5-dithiazinane **IIf** gave 1,3,5-thiadiazinane **IIIf**. In thiomethylation of acrylamide (**If**) in the absence of BuONa two and more molecules of compound **If** were involved into the cyclocondensation leading to the formation of heterocycle **IVf**. With growing reaction temperature (40°C) the number of acrylamide units in compound **IVf** increased and therefore the macroheterocycles **IVf** obtained possessed lower solubility (Scheme 3).

The formation of compound **IVf** is indicated by the presence in its ^{13}C NMR spectrum of signals characteristic of methylene groups located between nitrogen and sulfur atoms, δ 39.79 and 40.84 ppm, and also of carbon atoms of the double bond at δ 127.45 and 131.45 ppm and of a carbonyl carbon at δ 166.23 ppm. In the ^1H NMR spectrum of compound **IVf** the hydrogen atoms of the methylene group give rise to a multiplet in the region 4.65–4.75 ppm, and the signals of the hydrogens at the double bond appear as a multiplet in the region 5.71–6.24 ppm.

Compounds **IIf** and **IIIf** were separated by column chromatography on SiO_2 (eluent – $CHCl_3$–ether–C_2H_5OH, 10:1:1).

Condensation of benzamide (**Ig**) with H_2S and CH_2O in a ratio 1:2:3 in water medium at 20–70°C is accompanied by the hydrolysis of amide **Ig** to benzoic acid **VIg** (60%) (Scheme 4). Under these conditions at 0°C dithiazinane **II g** and thiazetidine **Vg** formed only in minor amounts (11 and 5% respectively). Therewith in the reaction mixture trithiolane **IX** and tetrathiepane **VIII** were also detected. However the condensation of compound **Ig** in the presence of BuONa followed by the treatment with the mixture H_2S–CH_2O, 2:3, led to the

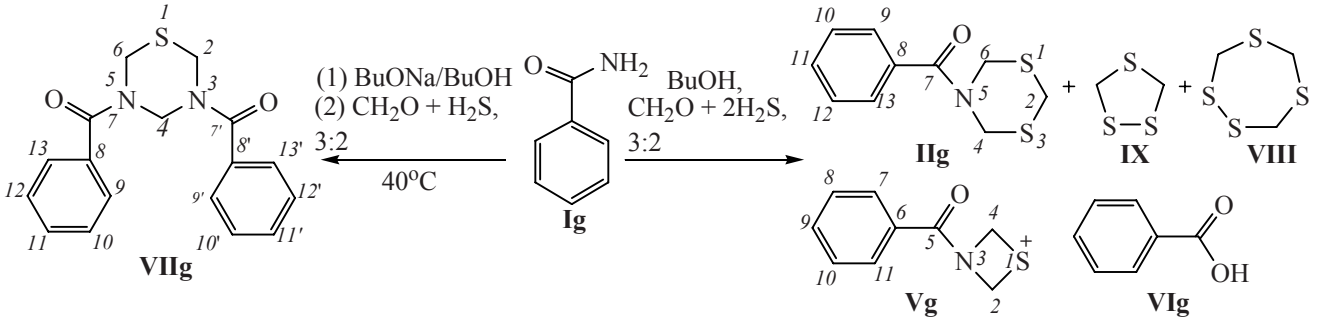
Scheme 3.



If **IIf** **IIIf** **IVf**

20°C, n =1; 40°C, n_{av} = 4.

Scheme 4.



exclusive formation of 1,3,5-thiadiazinane **VIIg** in ~74% yield.

Unlike benzamide (**Ig**) acetylsalicylamide (**Ih**) presumably due to the *ortho*-effect [17] reacted with H_2S and CH_2O (1:2:3) in BuOH–H_2O regioselectively forming 5-acetylsalicyloyl-1,3,5-dithiazinane (**IIh**) in ~80% yield.

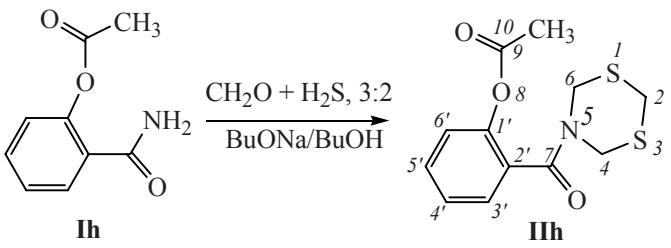
The cyclothiomethylation of α-aminosuccinic acid monoamide (**Ii**) with H_2S and CH_2O under the chosen optimum conditions (**Ii**–CH_2O–H_2S, 1:6:4, 20–40°C) occurred selectively providing 2,4-bis(1,3,5-dithiazinan-5-yl)-4-oxobutyric acid (**XIi**) in ~65% yield (see the table, Scheme 6). At a higher temperature the initial asparagine (**Ii**) formed a crystal hydrate and did not enter into the cyclothiomethylation. The cyclothiomethylation of asparagine (**Ii**) with CH_2O–H_2S in a ratio 1:3:2 resulted in a mixture of compounds **XIi** and **Xi** in yields 15% each (see the table), whereas at 0°C exclusively 2-(1,3,5-dithiazinan-5-yl)-4-succinic acid monoamide (**Xi**) was obtained in 40% yield, and at 40°C, bisdithiazinane **XIi** in ~42% yield.

The structure of compounds obtained **IIa–IIe, III–XI** was proved by ^1H and ^{13}C, IR spectroscopy, and GC-MS method.

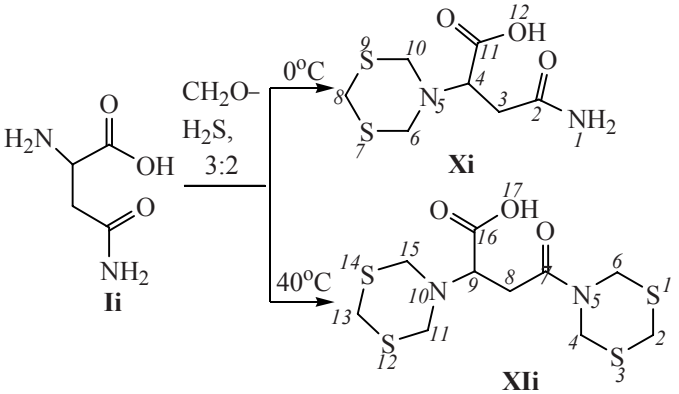
The mass spectra of compounds **IIa, IIb, IIg**, and **Vg** contained the corresponding molecular ion peaks and the peaks of fragment ions originating from the successive elimination from $[M]^+$ of fragments CH_2S, CH_2SCH_2S.

Thus the heterocyclization of aliphatic carboxamides with H_2S and CH_2O occurred with best yields in the presence of BuONa and led to the formation of the corresponding N-acyl-1,3,5-dithiazinanes in high yields. Benzamide under these conditions gave exclusively 3,5-dibenzoyl-1,3,5-thiadiazinane in 74% yield, whereas acetylsalicylamide due to the *ortho*-effect in BuOH–H_2O mixture formed selectively *N*-acetylsalicyloyl-1,3,5-dithiazinane in up to 80% yield.

Scheme 5.



Scheme 6.



Effect of temperature and the ratio of initial compounds on yield and composition of reaction procucts in thiomethylation of asparagine (**Ii**)

Temperature, °C	Ratio of **Ii**:CH_2O:H_2S	Yield, %	
		Xi	**XIi**
0	1:3:2	40	–
20		15	1542
40		–	
0	1:6:4	10	20
20		–	30
40		–	65

EXPERIMENTAL

In experiments were used compounds of purity no less than 95%. The solvents were purified, dried, and distilled as described in [18].

^{1}H and ^{13}C NMR spectra were registered on spectrometers Bruker AM-300 with operating frequency 300 MHz and Jeol FX 90 Q with operating frequencies 89.55 and 22.50 MHz (for ^{1}H and ^{13}C respectively), internal reference TMS. IR spectra were recorded on a spectrophotometer Specord 75IR from mulls in mineral oil. Mass spectra of compounds **IIa** and **IIb** were obtained on MKh 1320 instrument with direct admission of a sample into the ion source at 100–150°C and voltage 70 V. GC-MS analysis of compounds **IIg, Vg,** and **VIg** was carried out on Finnigan 4021 instrument equipped with a glass capillary column 50000 × 0.25 mm, stationary phase HP-5, carrier gas helium, ramp from 50 to 300°C at a rate 5 deg/min, vaporizer temperature 280°C, ion source temperature 250°C. Elemental analysis of the substances was performed on Karlo Erba 1106 analyzer. The melting points were measured on a device RNMK 80/2617; pH of solutions was determined on a pH-meter pH-340. Molecular weight of compound **IVe** was determined by cryoscopy [19].

Acetamide complex with sodium butylate in butanol (A) [$CH_3CONH_2(BuONa)_2$]. A solution of 1.7 mmol (100 mg) of acetamide (**Ib**) in butanol was charged into a reactor containing 5.1 mmol (0.43 ml) of freshly prepared BuONa in BuOH, and the mixture obtained was transferred into a cell of IR spectrophotometer. On adding to the complex **A** thus obtained 0.05 ml of deuterium oxide the proton signals were registered. Then under the conditions of continuous registering 6 drops of acetone were added, and the ^{13}C NMR spectrum was recorded. IR spectrum, ν, cm^{-1}: 650, 1030–1060, 1370–1450, 1610, 1660, 2910, 3300–3350. ^{1}H NMR spectrum (D_2O), δ, ppm: 0.69 t (6H, $H^{4,42}$), 1.24 m (8H, $H^{2,22,3,32}$), 1.78 s (3H, H_3C), 3.35 t (4H, $H^{1,12}$), 5.19–5.55 br.s (2H, NH_2). ^{13}C NMR spectrum [D_2O, $(CH_3)_2CO$], δ, ppm: 12.46 m ($C^{4,42}$), 17.93 t ($C^{3,32}$), 20.59 t (H_3C), 33.85 t ($C^{2,22}$), 60.35 t ($C^{1,12}$), 173.96 s (CO).

Cyclothiomethylation of carboxamides with H_2S and CH_2O. *a*. Into a glass reactor equipped with a magnetic stirrer, a reflux condenser, an adapter for gas input, and a dropping funnel was charged at 40°C 3 mol of 37% formaldehyde water solution, and it was saturated with hydrogen sulfide by bubbling the gas through the solution for 1 h. In another reactor the initial amide was mixed at room temperature (20°C) with BuONa dissolved in BuOH in a molar ratio 1:2, and then was added dropwise the prepared water solution of CH_2O–H_2S. The reaction mixture was stirred for 4 h maintaining the desired temperature (40°C), then it was neutralized with dilute HCl. The separated crystals of compounds **IIa–IIe** were filtered off, washed with water, and dried.

b. Bubbling of H_2S through 37% formaldehyde water solution to a desired reagent ratio was carried out for 1 h. Then to the thiomethylating mixture 1 mol of an appropriate amide in solution was added dropwise, and the reaction mixture was stirred for 5 h at a desired temperature (0, 20, 40, 80°C). The precipitate formed was filtered off and washed with a large volume of water. Compounds **IIf** and **IIIf** were separated on a column packed with SiO_2 (eluent $CHCl_3$–ether–C_2H_5OH, 10:1:1).

5-Formyl-1,3,5-dithiazinane (IIa). Yield 1.86 g (40%), colorless crystals, mp 84–86°C. IR spectrum, ν, cm^{-1}: 695, 1085, 1385, 1455, 1600, 2910, 3350. ^{1}H NMR spectrum (C_6D_6, CF_3COOH), δ, ppm: 2.97 s (2H, H^2), 3.62 s (4H, $H^{4,6}$), 10.50 s (1H, H^8). ^{13}C (C_6D_6, CF_3COOH), δ, ppm: 29.57 t (C^2), 50.01 t ($C^{4,6}$), 161.47 s (C^7). Mass spectrum, *m/z* (I_{rel}, %): 149 $[M]^+$, 116 $[M - S]^+$, 102 $[M - CH_2S]^+$, 70 $[M - SCH_2S]^+$, 56 $[M - CH_2SCH_2S]^+$, 42 $[CH_2{=}N{-}N]^+$. Found, %: C 32.10; H 4.70; N 9.45; S 43.15. $C_4H_7NOS_2$. Calculated, %: C 32.22; H 4.69; N 9.40; S 42.95. *M* 149.23.

5-Acetyl-1,3,5-dithiazinane (IIb). Yield 1.24 g (35%), colorless crystals, mp 111–113°C. IR spectrum, ν, cm^{-1}: 700, 1100, 1380–1460, 1660, 2900. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.55 s (2H, H^2), 3.15 s (4H, $H^{4,6}$), 3.95 t (3H, H^8). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 34.87 t (C^2), 60.73 t ($C^{4,6}$), 15.50 s (C^8), 185.05 s (C^7). Mass spectrum, *m/z* (I_{rel}, %): 163 $[M]^+$, 120 $[M - CH_3CO]^+$, 78 $[SCH_2S]^+$, 57 $[M - CH_2SCH_2SCH_2]^+$, 43 $[CH_3CO]^+$. Found, %: C 35.97; H 5.73; N 8.42; S 40.15. $C_5H_9NOS_2$. Calculated, %: C 36.78; H 5.56; N 8.58; S 39.28. *M* 163.26.

5-Caproyl-1,3,5-dithiazinane (IIc). Yield 1.34 g (30%), colorless crystals, mp 98–100°C. IR spectrum, ν, cm^{-1}: 710, 1010, 1185, 1380, 1460, 1540, 1645, 2905. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.29 br.s (3H, H^{12}), 1.73 br.s (6H, $H^{9,10,11}$), 2.50 br.s (2H, H^8), 2.98 s (2H, H^2), 4.40 s (4H, $H^{4,6}$). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 13.74 t (C^{12}), 24.72 t (C^9), 30.87 t (C^{10}), 32.92 t (C^8), 34.80 t (C^2), 63.23 t ($C^{4,6}$), 179.67 s (C^7). Found, %: C 48.79; H 7.54; N 5.86; S 29.72. $C_9H_{17}NOS_2$. Calculated, %: C 49.28; H 7.81; N 6.39; S 29.23.

3-Oxo-3-(1,3,5-dithiazinan-5-yl)propionitrile (IId). Yield 1.34 g (67%), yellow crystals, mp 139–141°C. IR spectrum, ν, cm^{-1}: 730, 1170, 1375, 1460, 1600, 2300–2350, 2910, 3360. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.93 br.s (2H, H^2), 3.95 s (2H, H^8), 4.25 br.s (2H, H^4), 4.60 br.s (2H, H^6). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 32.36 t (C^8), 32.92 t (C^2), 66.68 t (C^{4,6}), 129.21 d (C^9), 157.01 s (C^7). Found, %: C 37.65; H 4.78; N 15.10; S 34.46. $C_6H_8N_2OS_2$. Calculated, %: C 38.29; H 4.26; N 14.89; S 34.04.

5-Trifluoroacetyl-1,3,5-dithiazinane (IIe). Yield 3.10 g (95%), colorless crystals, mp 123–124°C. IR spectrum, ν, cm^{-1}: 690, 1090, 1195, 1375–1465, 2920. ^{1}H NMR spectrum (C_6D_6, CF_3COOH), δ, ppm: 3.90 C (2H, H^2), 4.5 c (4H, H^{4,6}). ^{13}C NMR spectrum (C_6D_6, CF_3COOH), δ, ppm: 34.64 t (C^2), 50.12 t (C^{4,6}), 115.01 q (C^8, $^1J_{C–F}$ 1231.0 Hz), 160.00 q (C^7, $^2J_{C–F}$ 171.0 Hz). Found, %: C 27.62; H 2.80; N 6.42; S 30.05. $C_5H_6F_3NOS_2$. Calculated, %: C 27.64; H 2.78; N 6.45; S 29.52.

5-(Acryloyl)-1,3,5-dithiazinane (IIf) obtained by method *b* (40°C). Yield 1 g (40%), colorless crystals, mp 136–138°C, R_f 0.85 (eluent $CHCl_3$–ether–C_2H_5OH, 10:2:1). IR spectrum, ν, cm^{-1}: 725, 1020, 1185, 1370–1460, 1540, 1650, 2910, 3300. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.86 s (2H, H^2), 4.92 s (4H, H^{4,6}), 7.44–7.89 m (3H, H^{8,9}). ^{13}C (DMSO-d_6), δ, ppm: 31.07 t (C^2), 55.56 t (C^{4,6}), 114.00 t (C^9), 126.40 d (C^8), 178.20 s (C^7). Found, %: C 40.05; H 4.86; N 8.14; S 37.07. $C_6H_9NOS_2$. Calculated, %: C 41.12; H 5.18; N 7.99; S 36.59.

***N*-Benzoyl-1,3,5-dithiazinane (IIg)** obtained by method *b* (20°C). Yield 0.21 g (11%), colorless crystals, mp 123–125°C. IR spectrum, ν, cm^{-1}: 600–700, 1010, 1115, 1400–1450, 1580, 1610–1650, 2910. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.79 s (2H, H^2), 4.79 s (4H, H^{4,6}), 7.53–7.96 m (5H, H^{9,10,11,12,13}). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 33.12 t (C^2), 63.53 t (C^{4,6}), 127.51 d (C^{10,12}), 128.19 d (C^{9,13}), 131.23 d (C^{11}), 134.32 d (C^8), 168.31 s (C^7). Mass spectrum, *m/z* (I_{rel}, %): 225 (5) [*M*]$^+$, 148 (2) [*M* – Ph]$^+$, 121 (7) [*M* – PhCO]$^+$, 105 (100) [*M* –$NCH_2SCH_2SCH_2$]$^+$, 92 (3) [SCH_2S]$^+$, 77 (70) [Ph]$^+$, 46 (20) [CH_2S]$^+$. Found, %: C 52.78; H 5.01; N 5.93; S 29.06. $C_{10}H_{11}NOS_2$. Calculated, %: C 53.33; H 4.88; N 6.22; S 28.44. *M* 225.33.

5-Acetylsalisyloyl-1,3,5-dithiazinane (IIh) obtained by method *b* (40°C). Yield 0.5 g (80%), colorless crystals, mp 105–107°C. IR spectrum, ν, cm^{-1}: 740, 1010, 1380–1460, 1660, 2910. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.85 s (3H, H^{10}), 3.50 s (2H, H^2), 5.70 s (4H, H^{4,6}), 7.87–8.80 m (4H, H^{3,4,5,6}). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 14.59 br.s (C^{10}), 33.02 t (C^2), 63.39 t (C^{4,6}), 117.42 d (C^6), 118.49 d (C^4), 128.19 d (C^3), 130.31 d (C^2), 134.12 d (C^5), 152.94 d (C^1), 161.99 s (C^7), 172.02 s (C^9). Found, %: C 51.17; H 4.16; N 4.98; S 23.39. $C_{12}H_{13}NO_3S_2$. Calculated, %: C 50.86; H 4.62; N 4.94; S 22.63.

3,5-Bis(acryloyl)-1,3,5-thiadiazinane (IIIf) obtained by method *b* (40°C). Yield 54 g (20%), colorless crystals, R_f 0.53 (eluent $CHCl_3$–ether–C_2H_5OH, 10:2:1). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 63.01 t (C^{2,6}), 85.77 t (C^4), 126.37 d (C$^{8,8'}$), 132.11 t (C$^{9,9'}$), 165.89 s (C^{7,72}). Found, %: C 50.94; H 5.66; N 13.21; S 15.09. $C_9H_{12}N_2O_2S$. Calculated, %: C 50.86; H 5.42; N 14.01; S 16.04.

3,7-Bis(acryloyl)-1,5-dithia-3,7-diazacyclooctane (IVf, *n* = 1) obtained by method *b* (20°C). Yield 3.15 g (86%), colorless resinous substance. IR spectrum, ν, cm^{-1}: 690, 810, 1020, 1110, 1230, 1540, 1660, 2900, 3330. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 4.75 s (8H, $H_2C^{2,4,6,8}$), 5.71 br.s (2H, $H_2C^{10,10'}$), 6.24 br.s (4H, $H_2C^{11,112}$). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 39.79 t (C^{2,4}), 40.84 t (C^{6,8}), 127.45 t (C^{11,112}), 131.45 d (C^{10,102}), 166.23 s (C^{9,92}). Found, %: C 46.10; H 5.50; N 11.40; S 25.05. *M* 267±10. $C_{10}H_{14}N_2O_2S_2$. Calculated, %: C 46.49; H 5.46; N 10.84; S 24.82.

N-Benzoyl-1,3-thiazetidine (Vg) obtained by method *b* (20°C). Yield 5%, colorless crystals. Mass spectrum, *m/z* (I_{rel}, %): 179 (2) [*M*]$^+$, 148 (2) [*M* – S]$^+$, 133 (45) [*M* – CH_2S]$^+$, 119 (5) [*M* – CH_2SCH_2]$^+$, 105 (100) [*M* – NCH_2SCH_2]$^+$, 77 (65) [Ph]$^+$, 46 (8) [*M* – $PhCONCH_2$]$^+$. C_9H_9NOS. Calculated: *M* 179.23.

Benzoic acid (VIg) obtained by method *b* (80°C). Yield 1.05 γ (60%), colorless needle crystals, mp 121–123°C [20]. IR spectrum, ν, cm^{-1}: 700, 930, 1060, 1180, 1310, 1580, 1680, 1785, 2750, 2810. Mass spectrum, *m/z* (I_{rel}, %): 122 (87) [*M*]$^+$, 105 (100) [*M* – OH]$^+$, 77 (65) [Ph]$^+$, 44 (22) [*M* – Ph]$^+$. Found, %: C 69.05; H 4.45. $C_7H_6O_2$. Calculated, %: C 65.85; H 4.92. *M* 122.12.

3,5-Bis(benzoyl)-1,3,5-thiadiazinane (VIIg) obtained by method *a*. Yield 1.98 g (74%), colorless crystals, mp 215–217°C. IR spectrum, ν, cm^{-1}: 720, 1010, 1175, 1365, 1495, 1645, 2920, 3360. ^{1}H NMR spectrum (C_6D_6, CF_3COOH), δ, ppm: 3.95 s (H^{2,6}), 4.73 s (2H, H^4), 7.42–7.90 m (10H, H^{8,82,9,92,10,102,11,112,12,122,13,132}). ^{13}C NMR spectrum (C_6D_6, CF_3COOH), δ, ppm: 55.66 t (C^{2,6}), 63.18 t (C^4), 127.26 d (C^{10,102,12,122}), 128.28 d (C^{9,92,13,132}), 131.34 d (C^{11,112}), 134.27 d (C^{8,82}), 166.21 s

($C^{7,72}$). Found, %: C 65.19; H 5.27; N 8.48; S 11.73. $C_{17}H_{16}N_2O_2S$. Calculated, %: C 65.38; H 5.13; N 8.97; S 10.25.

1,2,4,6-Tetrathiepane (VIII). Yield 10%, mp 95–96°C (95–96°C [8]). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 5.30 s (4H, $H^{3,7}$), 4.46 s (2H, H^5). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 37.6 t ($C^{3,7}$), 36.4 t (C^5). Found, %: C 21.33; H 3.28; S 75.39. $C_3H_6S_4$. Calculated, %: C 21.17; H 3.53; S 75.30.

1,2,4-Trithiolane (IX). Yield 40%, mp 74–75°C [8]. ^{1}H NMR spectrum, δ, ppm: 4.30 s ($H^{3,5}$). ^{13}C NMR spectrum, δ, ppm: 38.8 t ($C^{3,5}$). Found, %: C 19.52; H 3.38; S 77.10. $C_2H_4S_3$. Calculated, %: C 19.35; H 3.23; S 77.42.

2-(1,3,5-Dithiazinan-5-yl)succinic acid monoamide (Xi) obtained by method *b* (0°C). Yield 1.05 g (40%), colorless crystals, mp 208–210°C. IR spectrum, ν, cm^{-1}: 750, 1005, 1120, 1300, 1370, 1455, 1620, 1695, 2910, 3350. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.12 s (2H, H^1), 2.52 br.s (2H, H^3), 2.58 t (1H, H^4), 3.94 s (2H, H^8), 4.61 s (1H, H^{12}), 4.76 s (4H, $H^{6,10}$). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 31.00 m (C^3), 32.86 t (C^8), 55.81 t (C^4), 63.30 d ($C^{6,10}$), 166.65 s (C^2), 172.64 s (C^{11}). Found, %: C 35.71; H 4.85; N 12.15; S 27.03. $C_7H_{12}N_2O_3S_2$. Calculated, %: C 35.59; H 5.08; N 11.86; S 27.12.

2,4-Bis(1,3,5-dithiazinan-5-yl)-4-oxobutyric acid (XIi) obtained by method *b* (40°C). Yield 1.85 g (65%), colorless crystals, mp 147–149°C. IR spectrum, ν, cm^{-1}: 700, 750, 1030, 1120, 1175, 1300, 1360, 1455, 1615, 1685, 2910. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.49 br.s (2H, H_2C^8), 3.35 br.s (1H, H^9), 3.66 s (2H, H^{13}), 3.78 s (2H, H^2), 4.18 s (4H, $H^{11,15}$), 4.56 s (4H, $H^{4,6}$), 5.77 s (1H, H^{17}). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 31.91 m (C^8), 32.89 t (C^{13}), 33.28 t (C^2), 55.03 t (C^4), 57.41 t ($C^{11,15}$), 58.71 t (C^6), 63.79 d (C^9), 169.29 s (C^7), 172.97 C (C^{16}). Found, %: C 33.27; H 4.74; N 9.23; S 35.67. $C_{10}H_{16}N_2O_3S_4$. Calculated, %: C 33.71; H 4.53; N 9.16; S 34.91.

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