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Dedicated to Full Member of the Russian Academy of Sciences I. P. Beletskaya on occasion of her jubilee

Sulfonylimines of Polychloroaldehydes in Reaction with Thioamides

G. N. Rosentsveig, Yu. A. Aizina, I. B. Rosentsveig, G. G. Levkovskaya, G. I. Sarapulova, A. N. Mirskova, and T. I. Drozdova

Faworsky Irkutsk Institute of Chemistry, Siberian Division, Russian Academy of Sciences 664033, Irkutsk, Russia e-mail: i_roz@irioch.irk.ru

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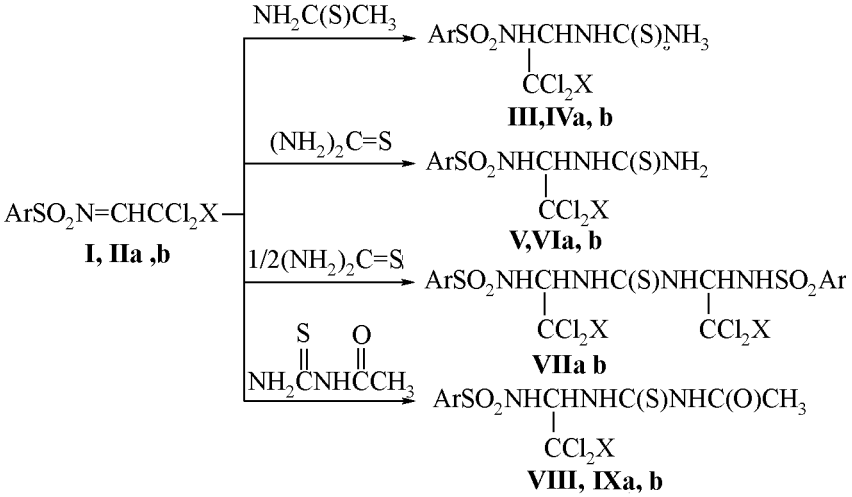
Abstract—*N*-(2,2,2-Trichloroethylidene)- and *N*-(2-phenyl-2,2-dichloroethylidene)amides of aromatic sulfonic acids react with thioacetamide, thiourea, and *N*-acetylthiourea at equimolar reagents ratio to furnish *N*-(1-arenesulfonamido-2,2,2-trichloroethyl)- and *N*-(1-arenesulfonamido-2-phenyl-2,2-dichloroethyl)thioamides. The reaction with deficient amount of thiourea results in *N*,*N*'-bis(1-arenesulfonamido-2-polychloroethyl)-thiocarbamides.

The reactivity of polychloroaldehydes sulfonylimines originating from the presence in their structure of electron-withdrawing polyhalomethyl and arenesulfonyl groups was amply demonstrated on their reactions with oxygen-, nitrogen-, sulfur-, and phosphorus-centered nucleophiles [1]. The reactions of polyhaloimines with amides of sulfonic, phosphonic, carboxylic, and carbamic acids are well documented [1–3]. However similar reactions with acid thioamides are poorly investigated, and their examples are limited to addition of amides and *N*-thioacetylamides of thiophosphonuc acids to chloral acetylimine [4].

In extension of systematic studies on reactivity of *N*-(2,2,2-trichloroethylidene)-arenesulfonamides (**Ia, b**) [1, 5] and *N*-(2-phenyl-2,2-dichloroethylidene)arenesulfonamides (**IIa, b**) [6, 8], we examined their reactions with thiourea, *N*-acetylthiourea, and thioacetamide. It should be elucidated whether the NH_2 group of thioamides would be involved into the addition process or they would react in an isothiouronium form and a thiol function would take part in the reaction.

It was established that the above thioamides are highly active in reations with compounds **Ia, b** and **IIa, b**. The process occurred involving the NH_2



X = Cl: Ar = Ph (**Ia, IIIa, Va, VIIa**), Ar = 4-ClC_6H_4 (**Ib, IIIb, Vb VIII**); X = Ph: Ar = Ph (**IIa, IVa, VIa, IXa**), Ar = 4-ClC_6H_4 (**IIb, IVb, VIb, VIIb, IXb**).

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group of thioamides and resulted in formation of *N*-(1-arenesulfonamido-2-polychloroethyl)amides of thiocarboxylic acids **III–IX**. At the use of two equiv of amides **Ia, b, IIa, b** with thiourea both NH_2 groups of the reagent were involved into reaction.

The thioamides addition to the highly electrophilic trichloroethylideneamides **Ia, b** occurred under mild conditions: The reaction was completed within 1–3 h at room temperature. The derivatives of dichlorophenylacetic aldehyde **IIa, b** are less active in these processes than chloral derivatives **Ia, b** due to less pronounced electron-withdrawing properties of dichlorophenylmethyl group compared to trichloromethyl one. Compounds **IIa, b** react with thioamides only at heating to 80°C within 4–8 h. Yields of reaction products **III–IX** amount 64–92%.

We failed to obtain carboximidothioates, products of compounds **I, II** addition to the isothiouronium form of thioamides under study. The attempt to obtain products of simultaneous addition of NH_2 and SH groups of thiocarbamides to two equiv of amides **I, II** also was unsuccessful. The variation of solvents (tetrachloromethane, benzene, 1,4-dioxane, DMF) did not affrect the direction of reaction.

The composition and structure of compounds **III–IX** were confirmed by elemental analyses (Table 1), and IR (Table 2), ^{1}H NMR (Table 3), and ^{13}C NMR (Table 4) spectra.

IR spectra of compounds **III–IX** contain characteristic absorption bands confirming their structure (Table 2). The assignment of bands according to vibration types is based on [9, 10]. The bands of the terminal primary amino group NH_2 in the spectra of compounds **IVa**, **b–VIa, b** appear at 3330 and 3400 cm^{-1}, and overlapping with the stretching vibrations bands of the secondary amino groups NH result in a complicated form of the overall absorption band . Low values of νNH, νNH_2 (at recording in KBr pellets) and the presence of low-frequency components in the νSO_2 bands show that these groups are involved in hydrogen bonds. Since the molecules of the amides in question contain several proton(electron)-donor(acceptor) moieties, possess several degrees of freedom, and rotation therein around formally ordinary thioamide bonds (S)C–N is hampered, the arising hydrogen bonds may be both inter- and intramolecular. These types of molecular interaction determine mainly the character of IR spectra of the compounds under study.

The IR spectra of compounds **VIII, IXa, IXb** contain additional absorption bands at 1660 and 1700 cm^{-1} corresponding to the stretching vibrations of C=O groups. The bands apeear as doublets due either to the presence of free carbonyls and those taking part in the hydrogen bonds or to the conformational inequality.

In the ^{1}H NMR spectra (DMSO-d_6) of addition products **III–IX** the protons belonging to SO_2NHCHNHC=S moiety appear as a characteristic group of signals: triplet at 6.78–7.04 ppm (CH) and two doublets of equal intensity in a weaker field (SO_2NH) and (NHC=S) (Table 3). It is clear that in isothiouronium derivatives, carboximidothioates, the proton of CH group should have appeared as a doublet with another chemical shift.

As a rule the chemical shift of the methine proton in the spectra of aromatic sulfonic acids polychloroethylamides $(ArSO_2NH)_2CHCCl_2X$, where X = Ph, Cl) is around 5.0–5.5 ppm, and for *N*-(1-acetamido-2,2,2-trichloroethyl)amides of arenesulfamides it is 6.15–6.20 ppm [2]. The significant downfield shift of the proton signal from the ($CHCCl_2X$) group in compounds **III–VI**, **VIII**, **IX** (Table 3) (up to 6.99 ppm for amide **IVa**) is due to thiocarbonyl group influence.

In the ^{1}H NMR spectra of compounds **VIIa, b** obtained by reaction of two equiv of amides **Ia** and **IIb** with one equiv. of thiourea the signal of the methine proton is shifted a little more downfield, and the signals from NH protons are strongly displaced as compared to the spectra of amides **VIa** and **Va**; therewith the broadened singlet from the protons NH_2 group is lacking.

In the ^{1}H NMR spectra of amides **III–IX** are present also the signals from aromatic protons, and in the spectra of compounds **III, IV, VIII, IX** also signals of protons from methyl groups with relative integral intensity consistent with the assumed structures **III–IX**.

In the ^{13}C NMR spectra of compounds **IV, VI** (Table. 4) are seen signals corresponding to the carbons from the thiocarbonyl group, from the polyhalomethyl group, from aromatic rings, and from NHCHNH fragment.

The obtained products **III–IX** of thioamides addition to chloral and dichlorophenylacetic aldehyde arenesulfonimines are white and gray crystalline substances, well soluble in DMSO, acetone, aqueous alkalis, insoluble in water. The presence in the structure of these compounds of NHC=S and C–Cl fragments suggests that they may be promising semiproducts in the synthesis of thiazole derivatives.

Table 1. Yields, melting points, and elemental analyses of compounds **III**–**IX**

Compd. no.	Yield, %	mp, °C	Found, %				Formula	Calculated, %			
			C	Cl	N	S		C	Cl	N	S
IIIa	78	106–108	32.41	30.03	7.35	18.01	$C_{10}H_{11}Cl_3N_2O_2S_2$	33.21	29.41	7.75	17.73
IIIb	83	98–99	29.89	37.00	6.25	14.99	$C_{10}H_{10}Cl_4N_2O_2S_2$	30.32	35.88	7.07	16.19
IVa	91	150–151	47.35	17.26	7.01	15.73	$C_{16}H_{16}Cl_2N_2O_2S_2$	47.65	17.58	6.95	15.90
IVb	88	154–155	43.72	24.01	6.64	14.46	$C_{16}H_{15}Cl_3N_2O_2S_2$	43.90	24.29	6.40	14.65
Va	88	153–155	30.97	29.61	10.30	18.15	$C_9H_{10}Cl_3N_3O_2S_2$	29.81	29.33	11.59	17.68
Vb	75	147–148	27.68	35.47	9.74	15.23	$C_9H_9Cl_4N_3O_2S_2$	27.22	35.71	10.58	16.15
VIa	88	128–129	44.35	10.02	10.42	15.68	$C_{15}H_{15}Cl_2N_3O_2S_2$	44.56	17.54	10.39	15.86
VIb	92	149–150	40.89	24.15	9.61	14.51	$C_{15}H_{14}Cl_3N_3O_2S_2$	41.06	24.24	9.58	14.61
VIIa	97	169–172	31.39	32.52	8.41	14.88	$C_{17}H_{16}Cl_6N_4O_4S_3$	31.45	32.77	8.63	14.82
VIIb	79	100–102	43.15	25.32	6.78	12.09	$C_{29}H_{24}Cl_6N_4O_4S_3$	43.46	26.54	6.99	12.00
VIII	67	154–155	28.95	31.06	9.48	14.16	$C_{11}H_{11}Cl_4N_3O_3S_2$	30.09	32.29	9.57	14.60
IXa	64	143–144	45.58	15.79	9.56	14.24	$C_{17}H_{17}Cl_2N_3O_3S_2$	45.74	15.89	9.41	14.36
IXb	69	146–147	42.32	21.99	8.63	13.21	$C_{17}H_{16}Cl_3N_3O_3S_2$	42.47	22.12	8.74	13.34

Table 2. Frequencies corresponding to absorption bands of main functional groups in the IR spectra of amides **III**–**IX** (cm^{-1})

Compd. no.	νNH, $νNH_2$	$νC=C_{aryl}$	δC(S)NH	$ν^{as}SO_2$, $δ^sSO_2$	$νS–C_{aryl}$	νS–N	νC–Cl	$ωSO_2$
IIIa	3220, 3340	1580	1540	1340, 1160	1080	920	740	550
IIIb	3200, 3330	1580	1520	1340, 1160	1080	920	750	540
IVa	3200, 3300, 3330, 3400	1600	1540	1320, 1150	1080	930	740	550
IVb	3200, 3300, 3340, 3400	1590	1550	1330, 1150	1080	930	745	540
Va	3220, 3300, 3330, 3400	1585	1550	1340, 1160	1085	925	750	550
Vb	3200, 3300, 3340	1580	1540	1330, 1160	1080	930	760	560
VIa	3200, 3300, 3330, 3400	1590	1540	1340, 1150	1085	940	750	550
VIb	3200, 3300, 3330, 3400	1580	1530	1330, 1160	1080	925	740	540
VIIa	3270, 3340	1580	1530	1340, 1170	1090	935	740	560
VIIb	3220, 3330	1600	1540	1340, 1160	1085	930	740	540
VIII	3200, 3300	1580	1540	1330, 1160	1085	930	745	550
IXa	3200, 3300	1590	1530	1340, 1155	1080	920	750	560
IXb	3200, 3300	1580	1530	1340, 1150	1080	925	740	540

EXPERIMENTAL

^1H and ^{13}C NMR spectra were registered on spectrometer Bruker DPX-400 (400.6, 100.61 MHz for ^1H and ^{13}C respectively) in DMSO-d_6, concentration of the compound 5–10%, internal reference HMDS.

IR spectra were recorded on spectrophotometer Specord 75IR from samples pelletized with KBr.

***N*-(2,2,2-Trichloroethylidene)arenesulfonamides (Ia, b)** used in the study were synthesized by procedure [5], *N*-(2,2-dichloro-2-phenylethylidene)arenesulfonamides (**IIa, b**) were prepared as in [6, 7].

***N*-(1-Benzenesulfonamido-2,2,2-trichloroethyl)-thioacetamide (IIIa).** A mixture of 2.87 g (0.01 mol) of amide **Ia** and 2.25 g (0.03 mol) of thioacetamide in 10 ml of benzene was stirred for 3 h at room temperature. The separated precipitate was filtered off and washed with warm water (30–40 ml). Yield of amide **IIIa** was 2.82 g.

***N*-[1-(4-Chlorobenzene)sulfonamido-2,2,2-trichloro-ethyl]thioacetamide (IIIb)** was similarly

Table 3. ^{1}H NMR spectra of compounds **III**–**IX**

Compd. no.	^{1}H NMR spectrum (DMSO-d_6), δ, ppm				J(SO_2NHCH), Hz	J(C(S)NHCH), Hz
	CH_3	CH	NH	Ar		
IIIa	2.14 s	6.91 t	9.16 d, 10.34 d	7.51–7.82 m	10.0	9.0
IIIb	2.21 s	6.84 t	9.35 d, 10.46 d	7.57, 7.81 (AA'BB' 4-ClC_6H_4)	9.6	9.2
IVa	2.08 s	6.99 t	8.66 d, 10.10 d	7.37–7.74 m	9.8	9.0
IVb	2.06 s	6.95 t	8.79 d, 10.14 d	7.39–7.66 m (Ph), 7.54, 7.71 (AA'BB' 4-ClC_6H_4)	9.9	9.1
Va	–	6.95 t	7.47 d, 9.18 d	7.65–7.93 m	10.4	9.4
Vb	–	6.78 t	7.82 d, 9.34	7.57, 7.92 (AA'BB' 4-ClC_6H_4)	10.0	9.0
VIa	–	6.92 t	7.10 br.s, 7.70 d, 8.60 d	7.37–7.85 m	9.6	10.0
VIb	–	6.89 t	7.13 br.s, 7.87 d, 8.76 d	7.48–7.85 (AA'BB' 4-ClC_6H_4), 7.39–7.72 m (Ph)	9.6	10.0
VIIa	–	6.93 t	8.81 d, 9.14 d	7.47–7.97 m	9.5	9.3
VIIb	–	7.04 t	8.69 d, 8.76 d	7.32–7.84 m	9.3	9.2
VIII	2.02 s	6.68 d.d	9.64 d, 11.36 d, 11.48 s	7.59–7.88 (AA'BB' 4-ClC_6H_4)	10.1	9.7
IXa	1.96 s	6.84 t	8.99 d, 11.14 s, 11.25 d	7.42–7.79 m	9.9	9.6
IXb	6.95 t		9.12 d, 11.07 s, 11.22 d	7.42–7.79 (AA'BB' 4-ClC_6H_4), 7.55–7.77 m (Ph)	9.8	9.5

Table 4. ^{13}C NMR spectra of compounds **IVa, b, VIa, b**

Compd. no.	^{13}C NMR spectrum (DMSO-d_6), δ, ppm				
	Ar	Me	CH	CCl_2	C=S
IVa	126.71–128.63 (C^2, C^3, C^5, C^6, C^8, C^9, C^{11}, C^{12}), 129.54 (C^{10}), 132.38 (C^7), 138.37 (C^1), 140.81 (C^4)	32.44	71.57	93.77	202.96
IVb	127.18–128.77 (C2, C^3, C^5, C^6, C^8, C^9, C^{11}, C^{12}), 129.57 (C^{10}), 137.34 (C^7), 138.27 (C^1), 139.67 (C^4)	32.39	71.55	93.62	203.08
VIa	126.69–128.75 (C^2, C^3, C^5, C^6, C^8, C^9, C^{11}, C^{12}), 129.41 (C^{10}), 132.15 (C^7), 139.11 (C^1), 141.86 (C^4)	–	72.36	95.85	183.56
VIb	127.02–128.53 (C2, C^3, C^5, C^6, C^8, C^9, C^{11}, C^{12}), 129.07 (C^{10}), 136.77 (C^7), 138.79 (C^1), 140.49 (C^4)	–	72.18	95.40	183.50

prepared from 3.21 g (0.01 mol) of trichloroethylideneamide **Ib** and 2.25 g (0.03 mol) of thioacetamide. Yield of amide **IIIb** was 3.29 g.

***N*-(1-Benzenesulfonamido-2-phenyl-2,2-dichloroethyl)thioacetamide (IVa).** Within 5 h was heated at reflux while vigorous stirring a mixture of 1.64 g (0.005 mol) of compound **IIa** and 0.75 g (0.01 mol) of thioacetamide in 30 ml of benzene. Then the reaction mixture was evaporated, the solid residue was washed with 50 ml of hot water. Yield of amide **IVa** was 1.83 g.

***N*-[1-(4-Chlorobenzene)sulfonamido-2-phenyl-2,2-dichloroethyl]thioacetamide (IVb)** was obtained as described above from 1.81 g (0.005 mol) of compound **IIb** and 0.75 g (0.01 mol) of thioacetamide. Yield of amide **IVb** was 1.93 g.

***N*-(1-Benzenesulfonamido-2,2,2-trichloroethyl)-thiocarbamide (Va).** A mixture of 2.87 g (0.01 mol) of compound **Ia**, 1.14 g (0.015 mol) of thiourea and 10 ml of unhydrous dioxane was stirred for 3 h. Then the reaction mixture was evaporated, the residue was washed with hexane and then with warm water (30–40 ml). Yield of amide **Va** was 3.19 g.

***N*-[1-(4-Chlorobenzene)sulfonamido-2,2,2-trichloro-ethyl]thiocarbamide (Vb)** was prepared similarly from 3.21 g (0.01 mol) of compound **Ib** and

1.14 g (0.015 mol) of thiourea. Yield of amide **Vb** was 2.98 g.

***N*-(1-Benzenesulfonamido-2-phenyl-2,2-dichloroethyl)thiocarbamide (VIa).** A mixture of 1.64 g (0.005 mol) of compound **IIa** and 0.38 g (0.005 mol) of thiourea in 10 ml of benzene was stirred for 6 h. Then the solvent was evaporated, the solid residue was washed with water and recrystallized from ethanol. Yield of amide **VIa** was 1.78 g.

***N*-[1-(4-Chlorobenzene)sulfonamido-2-phenyl-2,2-dichloroethyl]thiocarbamide (VIb)** was obtained as described above from 1.81 g (0.005 mol) of compound **IIb** and 0.38 g (0.005 mol) of thiourea. Yield of amide **VIb** was 1.93 g.

***N,N'*-Bis(1-benzenesulfonamido-2,2,2-trichloroethyl)thiocarbamide (VIIa).** A mixture of 11.3 g (0.05 mol) of *N*-dichlorobenzenesulfonamide and 26.91 ml (0.3 mol) of trichloroethylene was stirred at 87°C for 9 h. Then the reaction mixture was cooled to 35°C, and by portions was added thereto 1.90 g (0.025 mol) of thiourea. Yield of compound **VIIa** was 15.74 g.

***N,N'*-Bis(1-benzenesulfonamido-2-phenyl-2,2-dichloroethyl)thiocarbamide (VIIb).** To a solution of 1.64 g (0.005 mol) of compound **IIb** in 10 ml of benzene was added 0.19 g (0.0025 mol) of thiourea. The reaction mixture was stirred at heating to 80°C for 8 h. Then the benzene was evaporated, the residue was dissolved in acetone and precipitated into water. The resin formed was separated by decanting, stored for a week at cold, and recrystallized from ethanol. Yield of compound **VIIb** was 1.56 g.

***N*-[1-(4-Chlorobenzene)sulfonamido-2,2,2-trichloroethyl]-*N'*-acetylthiocarbamide (VIII).** To a solution of compound **Ib** in trichloroethylene, prepared from 1.30 g (0.005 mol) of dichloroamide of chlorobenzenesulfonic acid [5] was added 0.59 g (0.005 mol) of acetylthiourea. The reaction mixture was stirred at heating to 70–80°C for 1 h and then left standing for 24 h at room temperature.. The separated precipitate was filtered off and washed with tetrachloromethane. Yield of amide **VIII** was 1.47 g.

***N*-(1-Benzenesulfonamido-2-phenyl-2,2-dichloroethyl)-*N'*-acetylthiocarbamide (IXa).** A mixture of 1.64 g (0.005 mol) of compound **IIa** and 0.59 g (0.005 mol) of acetylthiourea in 10 ml of benzene was stirred while heating at reflux for 4 h. Then the solvent was evaporated, and the residue was recrystallized from ethano. Yield of amide **IXa** was 1.43 g.

***N*-[1-(4-Chlorobenzene)sulfonamido-2-phenyl-2,2-dichloroethyl]-*N'*-acetylthiocarbamide (IXb)** was obtained analogously from 1.81 g (0.005 mol) of compound **IIb** and 0.59 g (0.005 mol) of acetylthiourea. Yield of amide **IXb** was 1.66 g.

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