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Reactions of α-Sulfenyl-*N*-anions with Nitrogen Participation. Reactions of N-Substituted Sulfenylamide Salts with Isothiocyanates

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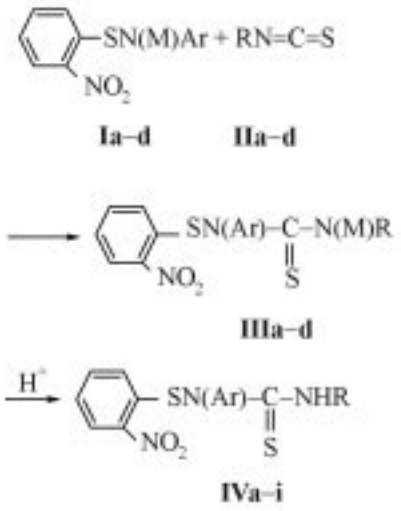
Abstract—Reaction of *N*-aroyl- and *N*-arylsulfonylarenesulfenylamide salts with aryl isothiocyanates in acetone results in salts of *N*-arenesulfenyl-*N*-aroyl(arylsulfonyl)-*N*'-arylthioureas that in the presence of mineral acids are transformed into the corresponding thioureas.

Reactions of sulfenylamides with isothiocyanates can provide N-sulfenylated thioureas that cannot yet be prepared by alternative methods. It is known that sulfenylation of thiourea and its derivatives occurs at sulfur atom. However the analysis of publications [2, 3] showed that the reaction between sulfenylamides and isothiocyanates did not provide unambiguous results presumably due both to the character of sufenylamide and isothiocyanate. For instance, sulfenylamides  (R = Et, *t*-Bu) react with phenyl isothiocyanate with the rupture of S–N bond and addition of the amidyl fragment to the carbon atom and the sulfenyl moiety to the sulfur of the isothiocyanate group [2]. Similarly reacts with the phenyl isothiocyanate also sulfenylamide $C_6Cl_5SNMe_2$; however the resulting product suffers a rearrangement with migration of the sulfenyl moiety from sulfur to nitrogen atom yielding the corresponding N-sulfenylated thiourea. As was reported [3], *N*-monosubstituted sulfenylamides R^1SNHR^2 (R^1, R^2 = Alk, Ar) also react with the phenyl isothiocyanate via S–N bond cleavage, sulfenyl fragment addition to the sulfur atom, and amidyl moiety addition to the carbon in the isothiocyanate group.

In extension of the previous research [4–6] on ambidental properties of α-sulfenyl-*N*-anions we investigated in this study reactions of *N*-aroyl- and *N*-arylsulfonyl-2-nirobenzenesulfenylamides alkali metal salts with isothiocyanates. Therewith we used as reaction medium anhydrous acetone that was inert with respect to the initial reagents and due to high polarity facilitated dissolution and dissociation of N-substituted arenesulfenylamide salts and promoted their reactions with isothiocyanates at the ionized N–M bond. We established that reaction between alkali metal salts of N-substituted 2-nitrobenzenesulfenylamides **Ia–d** and isothiocyanates **IIa–d** at room temperature took from several hours to several



I, Ar = $SO_2C_6H_5$: M = Na (**a**), K (**b**); Ar = $SO_2C_6H_4CH_3$-*p*, M = Na (**c**); Ar = $C(O)C_6H_5$, M = K (**d**); **II**, R = 2,4-$(NO_2)_2C_6H_3$ (**a**), $C_6H_5C(O)$ (**b**), *p*-$CH_3C_6H_4SO_2$ (**c**), C_6H_5 (**d**); **III**, M = Na, R = 2,4-$(NO_2)_2C_6H_3$: Ar = $SO_2C_6H_5$ (**a**), $SO_2C_6H_4CH_3$-*p* (**b**); R = $C_6H_5C(O)$: Ar = $SO_2C_6H_5$ (**c**), $SO_2C_6H_4CH_3$-*p*(**d**); R = *p*-$CH_3C_6H_4SO_2$, Ar = $SO_2C_6H_5$ (**e**), $SO_2C_6H_4CH_3$-*p* (**f**); M = K, R = C_6H_5, Ar = $SO_2C_6H_5$ (g), $C(O)C_6H_5$ (**h**); R = $C_6H_5C(O)$, Ar = $SO_2C_6H_5$ (**i**); R = 2,4-$(NO_2)_2C_6H_3$, Ar = $SO_2C_6H_5$ (**j**); R = *p*-$CH_3C_6H_4SO_2$, Ar = $SO_2C_6H_5$ (**k**); **IV**, R = 2,4-$(NO_2)_2C_6H_3$: Ar = $SO_2C_6H_5$ (**a**), $SO_2C_6H_4CH_3$-*p* (**b**); R = $C_6H_5C(O)$: Ar = $C(O)C_6H_5$ (**c**), $SO_2C_6H_5$ (**d**), $SO_2C_6H_4CH_3$-*p* (**e**); R = *p*-$CH_3C_6H_4SO_2$: Ar = $SO_2C_6H_5$ (**f**), $SO_2C_6H_4CH_3$-*p* (**g**); R = C_6H_5: Ar = $C(O)C_6H_5$ (**h**), $SO_2C_6H_5$ (**i**).

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Table 1. Yields, melting points, IR spectra, and elemental analyses of salts of *N*-2-nitrobenzenesulfenyl-*N*-aroyl(arylsulfonyl)-*N*'-arylthioureas **IIIa**–**k**

Compd. no.	Yield, %	mp, °C	IR spectrum, ν, cm^{-1}						Found N, %	Formula	Calculated N, %
			SO_2		NO_2		C=O	C=S			
			sym.	asym.	sym.	asym.					
IIIa	45	199–200	1160	1310	1320	1560		1090	12.68	$C_{19}H_{12}N_5NaO_8S_3$	12.57
IIIb	41	202–203	1150	1320	1330	1530		1095	12.40	$C_{20}H_{14}N_5NaO_8S_3$	12.25
IIIc	45	204–205	1160	1320	1330	1545	1670	1050	9.01	$C_{20}H_{14}N_3NaO_5S_3$	8.48
IIId	68	200–201	1180	1310	1330	1560	1680	1052	8.31	$C_{21}H_{16}N_3NaO_5S_3$	8.25
IIIe	89	194–195	1152	1310	1320	1530		1050	7.80	$C_{20}H_{16}N_3NaO_6S_4$	7.71
IIIf	72	184–185	1160	1310	1330	1550		1060	7.61	$C_{21}H_{18}N_3NaO_6S_4$	7.51
IIIg	50	161–162	1150	1320	1340	1530		1050	8.87	$C_{19}H_{14}KN_3O_4S_3$	8.70
IIIh	56	203–204	1160	1310	1330	1530	1670	1060	9.49	$C_{20}H_{14}KN_3O_3S_2$	9.40
IIIi	65	139–140	1160	1310	1320	1525	1670	1060	8.31	$C_{20}H_{14}KN_3O_5S_3$	8.22
IIIj	74	144–145	1160	1320	1330	1530		1050	12.30	$C_{19}H_{12}KN_5O_8S_3$	12.22
IIIk	72	255–256	1150	1310	1330	1530		1050	7.60	$C_{20}H_{16}KN_3O_6S_4$	7.49

Table 2. Yields, melting points, IR spectra, and elemental analyses of *N*-2-nitrobenzenesulfenyl-*N*'-aroyl(arylsulfonyl)-*N*'-arylthioureas **IVa**–**i**

Compd. no.	Yield, %	mp, °C	IR spectrum, ν, cm^{-1}							Found N, %	Formula	Calculated N, %
			SO_2		NO_2		C=O	C=S	N–H			
			sym.	asym.	sym.	asym.						
IVa	87	137–138	1155	1310	1330	1580		1080	3110	13.20	$C_{19}H_{13}N_5O_8S_3$	13.08
IVb	64	145–146	1150	1310	1330	1560		1070	3100	12.70	$C_{20}H_{15}N_5O_8S_3$	12.75
IVc	69	115–116	1130	1320	1340	1535	1690	1060	3110	14.71	$C_{21}H_{15}N_3O_4S_2$	14.64
IVd	86	125–126	1130	1310	1335	1535	1670	1060	3110	9.01	$C_{20}H_{15}N_3O_5S_3$	8.87
IVe	66	135–136	1135	1310	1330	1535		1070	3100	8.70	$C_{21}H_{17}N_3O_5S_3$	8.62
IVf	77	130–131	1130	1310	1330	1560		1070	3090	8.10	$C_{20}H_{17}N_3O_6S_4$	8.03
IVg	62	140–141	1135	1315	1340	1560		1060	3100	7.90	$C_{21}H_{19}N_3O_6S_4$	7.83
IVh	36	171–172	1140	1310	1335	1560	1670	1070	3100	10.91	$C_{20}H_{15}N_3O_3S_2$	10.58
IVi	68	192–193	1130	1310	1340	1550		1060	3110	9.50	$C_{19}H_{15}N_3O_4S_3$	9.40

days and resulted in the corresponding salts of *N*-2-nitrobenzenesulfenyl-*N*-aroyl(arylsulfonyl)-*N*'-arylthioureas **IIIa**–**k** that by treatment with mineral acids were converted into the corresponding thioureas **IVa**–**i**.

It should be noted that the reactivity of salts **Ia**–**d** toward isothiocyanates and the yields of respective thioureas decrease in going from *N*-arylsulfonyl-2-nirobenzenesulfenylamides to *N*-aroyl-2-nirobenzenesulfenylamides. This fact may be ascribed to the decreasing stability of mesomeric N-anion and to the increasing lability of the S–N bond at this transition as is also indicated by the comparison of force constants corresponding to stretching vibrations of this bond in *N*-phenylsulfonyl-2-nitrobenzenesulfenylamide and *N*-acetyl-2-nitrobenzenesulfenylamide (1946.3×10^{-17} and 1894.7×10^{-17} J mol^{-1} m^2 respectively) [7].

Thioureas salts **IIIa**–**k** (Table 1) are crystalline substances colored from light yellow to orange, well soluble in water, acetone, methanol, ethanol, worse soluble in 2-propanol, insoluble in hydrocarbons. In

the IR spectra of salts **IIIa–k** appear characteristic absorption bands of stretching vibrations of sulfo group at 1320–1330 and 1155–1165 cm^{-1}, nitro group at 1530–1580, 1330–1350 cm^{-1}, and also of groups C=O (1650–1690 cm^{-1}) and C=S (1080–1095 cm^{-1}).

The treatment of water or acetone solutions of compounds **IIIa–k** with diluted (1:1) hydrochloric acid affords thioureas **IVa–i** (Table 2), yellow or orange crystalline compounds, well soluble in acetone, dimethylformamide, methanol, soluble at heating in aromatic hydrocarbons and 2-propanol, insoluble in water and saturated hydrocarbons. In the IR spectra of thioureas **IVa–i** are observed the absorption bands of stretching vibrations of nitro group (1535–1580, 1330–1340 cm^{-1}), sulfo group (1310–1320, 1130–1150 cm^{-1}), C=O (1670–1680 cm^{-1}), C=S (1070–1094 cm^{-1}), and NH groups (3090–3110 cm^{-1}).

Salts **IIIa–k** and thioureas **IVa–i** were tested as thermal stabilizers of microsuspension poly(vinyl chloride). The experiments showed that all compounds provide thermal stabilization when taken in amount of ~0.5% and over 2% per weight of the polymer. Some of compounds **IIIa–k** under the experimental conditions nearly reached the thermal stabilizing effect of the common industrial stabilizer, cadmium stearate.

EXPERIMENTAL

IR spectra were recorded on spectrophotometer Specord from KBr pellets. The reaction progress was monitored by TLC on Silufol UV-254 plates, eluent hexane–acetone, 3:1. The titration of salts **IIIa–k** was carried out on IONOMETR-75 device. The thermal stabilization with the use of compounds synthesized was evaluated by the "Congo Red" method [8].

***N*-Phenylsulfonyl-2-nitrobenzenesulfenylamide sodium salt (Ia).** To a solution of 5 mmol (1.55 g) of *N*-phenylsulfonyl-2-nitrobenzenesulfenylamide in 60 ml of anhydrous acetone was added a solution of sodium methylate (5 mmol of sodium metal dissolved in 5 ml of methanol). The dark-red solution obtained was filtered, the filtrate was evaporated in air and dried in a desiccator over anhydrous calcium chloride to yield salt **Ia**.

Salt **Ic** was obtained in a similar way.

***N*-Phenylsulfonyl-2-nitrobenzenesulfenylamide potassium salt (Ib).** To a solution of 10 mmol (3.1 g) of *N*-phenylsulfonyl-2-nitrobenzenesulfenylamide in 80 ml of anhydrous acetone an alcoholic solution of 10 mmol (0.56 g) of potassium hydroxide) was added. The reaction mixture was stirred at room temperature for 5–10 min, filtered, the solvent was partially evaporated on a water bath (to about a half of the initial volume), then the mixture was evaporated in air, and the residue was dried in a desiccator over anhydrous calcium chloride or potassium hydroxide at room temperature to furnish salt **Ib**. Salt **Id** was prepared analogously. The sulfenylamides salts **Ia–d** were stored in a desiccator over anhydrous calcium chloride.

Aryl isothiocyanates **IIa–c** were prepared by a known method [9] from the corresponding chloro derivatives and potassium thiocyanate in anhydrous acetone.

***N*-2-Nitrobenzenesulfenyl-*N*-phenylsulfonyl-*N*'-2,4-dinitrophenylthiourea sodium salt (IIIa).** To a solution of 5 mmol (1.66 g) of sodium salt **Ia** in 50 ml of anhydrous acetone was added a solution of 10 mmol (2.25 g) of 2,4-dinitrophenyl isothiocyanate (**IIa**) in 10 ml of anhydrous acetone. The reaction mixture was stirred and then stored at room temperature till negative test for sulfenylamide (no red color with 10% water solution of potassium hydroxide). Then the solution was evaporated in air to 1/2–1/3 of the initial volume, the precipitated crystals of salt **IIIa** were filtered off, washed on the filter with a small volume of acetone (the salt was soluble!). The repeated partial evaporation of the filtrate furnished some more salt **IIIa**. Compounds **IIIb–k** were prepared in a similar way.

***N*-2-Nitrobenzenesulfenyl-*N*-phenylsulfonyl-*N*'-2,4-dinitrophenylthiourea (IVa).** (a) To a solution of 10 mmol (3.32 g) of sodium salt **Ia** in 100 ml of anhydrous acetone a solution of 15 mmol (3.37 g) of isothiocyanate **IIa** in 25 ml of anhydrous acetone was added, and the mixture was left standing at room temperature till negative test for sulfenylamide. The reaction mixture was acidified with dilute hydrochloric acid till pH 3–4. The acetone solution was partially evaporated in air to achieve more complete precipitation of sodium chloride, and then the mixture was filtered. The filtrate was evaporated in air to furnish thiourea **IVa**. Compounds **IVb–i** were prepared similarly. (b) Salt **IIIa** (5 mmol, 2.74 g) was dissolved in 80 ml of acetone, diluted (1:1) hydrochloric acid was added to pH ~3–4, acetone solution was evaporated to a half of the initial volume, the precipitated sodium chloride was filtered off. Complete removal of acetone from the filtrate

gave thiourea **IVa** in a quantitative yield. The sample gave no depression of melting point with the substance prepared by procedure (a).

Mixed samples of compounds **IVb–i** prepared by methods (a) and (b) melted also with no depression; the IR spectra of the compounds were identical.

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