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N-Arylsulfanyl-*N*-arylsulfonyl(acyl)-*N'*-phenylthiourea Sodium Salts

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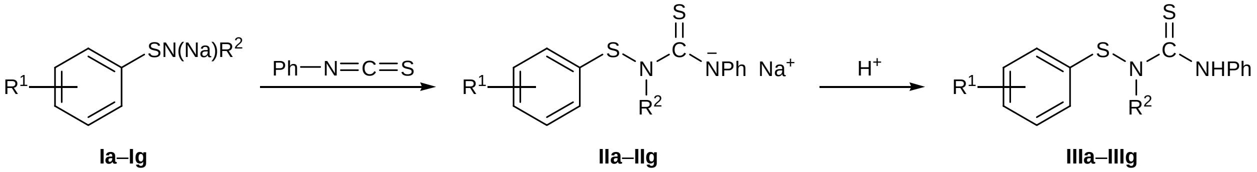
Abstract—Reactions of *N*-arylsulfonyl(acyl)arenesulfenamide sodium salts with phenyl isothiocyanate afforded *N*-arylsulfanyl-*N*-arylsulfonyl(acyl)-*N'*-phenylthioura sodium salts which were found to increase thermal stability of finely dispersed poly(vinyl chloride).

Thioureas having a sulfenyl group on the nitrogen atom attract interest as potential additives increasing thermal stability of polymers, sorbents for noble metals, curing agents, pharmaceuticals, etc. [1, 2]. However, the number of these compounds still remains limited due to the lack of efficient methods for their preparation. It is known [3] that sulfenylation of thiourea and its homologs with sulfenyl chlorides and other sulfenylating agents occurs at the sulfur rather than nitrogen atom; therefore, the products are unsymmetrical disulfides. On the other hand, it was shown in [4] that sulfenylation of *S*-alkylisothioureas with arenesulfenyl chlorides readily occurs at the nitrogen atom to give *S*-alkyl-*N*-arylsulfenylisothioureas which cannot be converted into the corresponding *N*-(arylsulfenyl)thioureas. While studying ambident reactivity of α-sulfenyl-substituted N-centered anions [5] we found that reactions of *N*-arylsulfonyl-2-nitrobenzenesulfenamides with aryl isothiocyanates smoothly afforded *N*-2-nitrophenylsulfenyl-*N*-arylsulfonyl-*N'*-arylthiourea sodium salts which were converted into the corresponding thioureas by the action of mineral acids.

With the goal of extending the series of available N-sulfenylated thioureas, optimizing the procedure for their synthesis, and extending the scope of its application, in the present work we studied reactions of *N*-arylsulfonyl(acyl)arenesulfenamides **Ia**–**Ig** containing one or two nitro groups with phenyl isothiocyanate. We found that salts **Ia**–**Ig** relatively smoothly react with phenyl isothiocyanate in acetone, yielding *N*-arylsulfanyl-*N*-arylsulfonyl(acyl)-*N'*-phenylthiourea sodium salts **IIa**–**IIg** (Scheme 1, see table). Among the examined solvents (benzene, chloroform, carbon tetrachloride, acetone, etc.), anhydrous acetone turned out to be the best solvent. It is inert toward the initial reactants, and its relatively high polarity favors dissolution and dissociation of salts **Ia**–**Ig** and their reaction with phenyl isothiocyanate, which involves ionized N–Na bond. The reaction occurs at room temperature, and takes from a few hours to 24 h, depending on the reactant nature. Rise in the temperature is undesirable, for it promotes various side processes. Salts **IIa**–**IIg** are bright yellow (one nitro group) or orange (two nitro groups) crystalline substances, which are readily soluble in water, soluble in acetone, sparingly soluble in methanol, ethanol, and (on heating) in 1-propanol and 2-propanol, and insoluble in aromatic and saturated hydrocarbons.

The IR spectra of salts **IIa**–**IIg** contain absorption bands typical of stretching vibrations of nitro groups

Scheme 1.



I–**III**, R^1 = 4-NO$_2$, R^2 = 4-MeC$_6$H$_4$SO$_2$ (**a**), 4-ClC$_6$H$_4$SO$_2$ (**b**); R^1 = 2-NO$_2$, R^2 = PhSO$_2$ (**c**), 4-MeC$_6$H$_4$SO$_2$ (**d**), MeCO (**e**), PhCO (**f**); R^1 = 2,4-(NO$_2$)$_2$, R^2 = PhSO$_2$ (**g**).

Yields, melting points, IR spectra, and elemental analyses of *N*-arylsulfanyl-*N*-arylsulfonyl(acyl)-*N'*-phenylthioureas **IIIa**–**IIIg** and their sodium salts **IIa**–**IIg**

Comp. no.	Yield, %	mp, °C	IR spectrum, ν, cm^{-1}					Found N, %	Formula	Calculated N, %
			SO_2	NO_2	C=S	NC(=S)N	NH			
IIa	60.3	194–195	1140, 1310	1340, 1520	1055	1440		8.89	$C_{20}H_{16}N_3NaO_4S_3$	8.73
IIb	84.9	210–211	1100, 1305	1335, 1520	1095	1442		8.51	$C_{19}H_{13}ClN_3NaO_4S_3$	8.37
IIc	65.8	205–206	1140, 1310	1330, 1540	1095	1440		8.85	$C_{19}H_{14}N_3NaO_4S_3$	8.99
IId	83.2	201–202	1160, 1315	1342, 1510	1055	1448		8.81	$C_{20}H_{16}N_3NaO_4S_3$	8.73
IIe[a]	71.1	203–204 (decomp.)	1120, 1335	1350, 1520	1097	1445		11.50	$C_{15}H_{12}N_3NaO_3S_2$	11.38
IIf[a]	52.1	198–199 (decomp.)	1122, 1340	1350, 1522	1035	1450		9.87	$C_{20}H_{14}N_3NaO_3S_2$	9.74
IIg	55.8	195–197	1108, 1313	1340, 1515	1074	1460		11.10	$C_{19}H_{13}N_4NaO_6S_3$	10.93
IIIa	43.6	175	1161, 1315	1342, 1510	1095	1248	3350	9.43	$C_{20}H_{17}N_3O_4S_3$	9.15
IIIb	88.9	182	1110, 1310	1340, 1530	1085	1242	3385	8.61	$C_{19}H_{14}ClN_3O_4S_3$	8.76
IIIc	71.3	192	1135, 1310	1340, 1550	1062	1300	3120	–	$C_{19}H_{15}N_3O_4S_3$	9.40
IIId	55.8	169	1120, 1315	1340, 1520	1062	1302	3150	9.34	$C_{20}H_{17}N_3O_4S_3$	9.15
IIIe[a]	42.5	141	1122, 1340	1360, 1522	1040	1235	3530	12.21	$C_{15}H_{13}N_3O_3S_2$	12.10
IIIf[a]	53.4	171	1135, 1308	1340, 1560	1035	1210	3220	–	$C_{20}H_{15}N_3O_3S_2$	10.58
IIIg	25.3	178	1152, 1310	1330, 1562	1060	1310	3360	11.81	$C_{19}H_{14}N_4O_6S_3$	11.43

[a] ν(C=O), cm^{-1}: 1690 (**IIe**), 1696 (**IIf**), 1708 (**IIIe**), 1695 (**IIIf**).

(1510–1530 and 1335–1360 cm^{-1}), sulfonyl groups (1310–1340 and 1108–1130 cm^{-1}), and NC(=S)N moiety (1440–1460 cm^{-1}). Compunds **IIb** showed in the spectrum a strong absorption band at 741 cm^{-1} due to stretching vibrations of the C–Cl bond; compounds **IIe** and **IIf** displayed an absorption band at 1690–1696 cm^{-1}, which belongs to the carbonyl group stretching vibrations. No absorption assignable to N–H stretching vibrations was present.

Salts **IIa**–**IIg** slowly decompose on storage to give a complex mixture of products, among which only 2,2'-dinitro- or 2,2',4,4'-tetranitrodiphenyl disulfides were identified. The decomposition process is appreciably accelerated in the presence of hydrochloric acid vapor at room temperature, and 2,2'-dinitrodiphenyl disulfide is also formed in this case. Treatment of salts **IIa**–**IIg** with acids in water, aqueous alcohol, acetone, or aqueous acetone gives the corresponding *N*-arylsulfanyl-*N*-arylsulfonyl(acyl)-*N'*-phenylthioureas **IIIa**–**IIIg** (see table) which are yellow crystalline substances, their color depending on the number of nitro groups in the molecule. Compounds **IIIa**–**IIIg** are insoluble in water and aromatic and saturated hydrocarbons and soluble in acetone, alcohols, and dimethylformamide. In the IR spectra of **IIIa**–**IIIg** we observed absorption bands typical of stretching vibrations of N–H bond (3110–3350 cm^{-1}; 3539–3606 cm^{-1} for **IIIf**), NO_2 group (1510–1525 and 1340–1360 cm^{-1}), SO_2 group (1315–1340 and 1122–1161 cm^{-1}), C=O bond (1695–1710 cm^{-1}), and NC(=S)N fragment (1440–1400 cm^{-1}, 1210–1230 cm^{-1} for **IIIe** and **IIIf**).

Compounds **IIIa**–**IIIg** are more stable at room temperature than the corresponding sodium salts **II**; however, they undergo gradual decomposition on prolonged storage to give a mixture of products, among which we succeeded in isolating and identifying 2,2'-dinitro- and 2,2',4,4'-tetranitrodiphenyl disulfides. Thioureas **IIIa**–**IIIg** also decompose on heating or on attempted recrystallization from high-boiling solvents.

Salts **IIa**–**IIg** and thioureas **IIIa**–**IIIg** were tested as additives for stabilization of dispersed poly(vinyl chloride) (PVC) against thermal degradation. The stabilizing effect was estimated by measuring the induction period τ, i.e., the time elapsed from the start of heating of a sample to appearance of distinct signs of its decomposition (evolution of hydrogen chloride). Compounds **IIIa**–**IIIg** showed no stabilizing effect; by contrast, they initiated thermal degradation of PVC (see figure). More promising for further study are salts **IIa**, **IIb**, and **IIg** which increased the induction period at very low concentrations (0.1–0.4 wt %). Cadmium stearate, which is a commercial agent for thermal stabilization of polymers, shows almost no effect at that concentration. Presumably, extension of the induction period in the presence of salts **IIa**–**IIg** results from participation of their anions in ionic polymer degradation processes occurring in PVC on heating on exposure to atmospheric oxygen.

Sharp reduction in the stabilizing effect and initiation of degradation of PVC at increased concentrations of compounds **IIa**–**IIg** and **IIIa**–**IIIf** may be due to thermal instability of these compounds; their thermal decomposition could give rise to a number of reactive radical species which promote radical processes of PVC degradation.

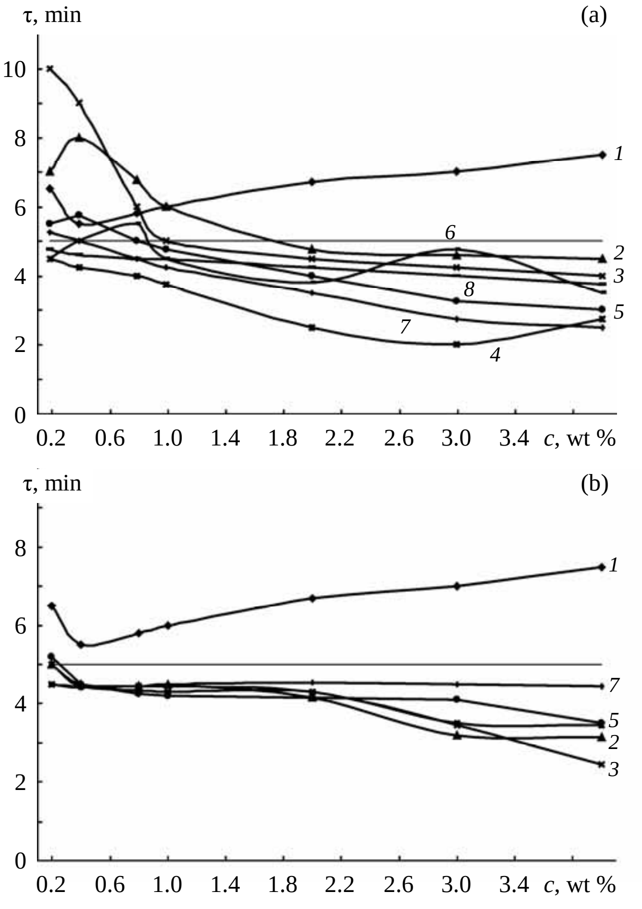
EXPERIMENTAL

The IR spectra were recorded in KBr on a Specord spectrophotometer. The progress of reactions was monitored by thin-layer chromatography on Silufol UV-254 plates (solvent system hexane–acetone, 3 : 1, by volume). Salts **IIa**–**IIc** and **IIf** were titrated using an Ionometr-75 instrument. The stabilizing effect against thermal degradation was determined as described in [6].

***N*-Arylsulfonyl(acyl)arenesulfenamide sodium salts Ia–Ig.** Appropriate arenesulfenamide, 1 mmol, was dissolved in 10 ml of acetone, and a solution of an equimolar amount of sodium hydroxide in a minimal volume of hot distilled water was added. The resulting dark cherry solution of salt **Ia**–**Ig** was filtered, the filtrate was evaporated, and salts **Ia**–**Ig** were stored in a desiccator over anhydrous calcium chloride.

***N*-Arylsulfanyl-*N*-arylsulfonyl(acyl)-*N*′-phenylthiourea sodium salts IIa–IIg.** Salt **Ia**–**Ig**, 2 mmol, was dissolved in 15 ml of acetone, 7–10 equiv of phenyl isothiocyanate was added, and the mixture was stirred and kept for a few hours to 24 h at room temperature until salt **IIa**–**IIg** separated from the solution. The precipitate was filtered off and washed with a small amount of acetone. An additional amount of salt **IIa**–**IIg** was isolated by partial evaporation of the filtrate. After careful washing with acetone, salts **IIa**–**IIg** required no additional purification by recrystallization; they showed no depression of the melting point on mixing with samples prepared as described in [5].

***N*-Arylsulfanyl-*N*-arylsulfonyl(acyl)-*N*′-phenylthioureas IIIa–IIIg.** *a*. Compound **Ia**–**Ig**, 2 mmol, was dissolved in a minimal amount of acetone, the solution was filtered, and 6–9 equiv of phenyl isothiocyanate was added to the filtrate. The resulting solution was stirred until a crystalline solid separated, the solvent was partially evaporated, the mixture was filtered, the precipitate was washed on a filter with warm acetone, and the filtrate was acidified to pH 3–4 with dilute hydrochloric acid. The precipitate was filtered off, and the filtrate was evaporated in air to obtain compounds **IIIa**–**IIIg** which were repeatedly washed with water until neutral washings.



Plots of the induction period τ versus concentration *c* of (a) *N*-arylsulfanyl-*N*-arylsulfonyl(acyl)-*N*′-phenylthioureas and (b) their sodium salts: (*1*) cadmium stearate (reference), (*2*) **IIa** and **IIIa**, (*3*) **IIb** and **IIIb**, (*4*) **IIc** and **IIIc**, (*5*) **IId** and **IIId**, (*6*) **IIe**, (*7*) **IIf** and **IIIf**, and (*8*) **IIg**.

b. Salt **IIa**–**IIg**, 1 mmol, was dissolved in acetone, and the solution was acidified to pH 3–4 with dilute hydrochloric acid. The precipitate was allowed to coagulate, the solvent was partially evaporated (by no more than 1/3 of the initial volume), the mixture was filtered, and the filtrate was evaporated to obtain compounds **IIIa**–**IIIg** which were contaminated with inorganic impurities. The products were repeatedly washed with distilled water, dried in air at room temperature, and reprecipitated from acetone. Thioureas **IIIa**–**IIIg** showed no depression of the melting point on mixing with samples prepared as described in [5].

Decomposition of compound IIc in the presence of hydrochloric acid vapor. A desiccator was charged with 20% hydrochloric acid and was kept for 5 days for equilibration to establish. A container was charged with a sample of compound **IIc** and was placed in the desiccator for 1–3 months. The formation of 2,2'-dinitrodiphenyl disulfide was detected by TLC. After 3 months, the sample was withdrawn from the desiccator and was treated with several small portions of acetone to extract decomposition products. The residue was 2,2'-dinitrodiphenyl disulfide which was washed with acetone, dried, and identified by mixing with an authentic sample (no depression of the melting point was observed).

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