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Reactions of α-Sulfenyl-*N*-anions at the Nitrogen Atom. Reactions of *N*-Substituted Arenesulfenamide Sodium Salts with Isocyanates

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Abstract—*N*-Arylsulfonylarenesulfenamide sodium salts react with isocyanates in acetone to give *N*-arylsulfonyl-*N*-arylsulfenyl-*N*′-substituted urea sodium salts which are converted into the corresponding ureas by the action of mineral acids.

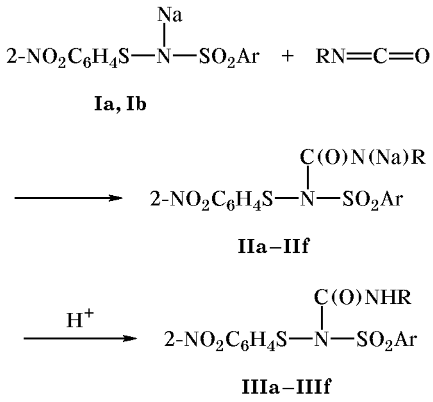
An important problem of preparative organic chemistry is search for and detailed study of various intermediates which are formed in many chemical reactions. In this connection we thought it reasonable from both theoretical and practical viewpoints to develop methods of generation and examine the properties of previously discovered [1, 2] α-sulfenyl-*N*-anions. In the preceding communications [3–17] we have described some procedures for generation of α-sulfenyl-*N*-anions and their reactions at the sulfur atom. As a result, such reactions with sulfenamides as alkoxylation [7, 16], oxidative amidation [10, 13], and oxidative imidation [9, 14] have become available. As noted in reviews [18, 19], α-sulfenyl-*N*-anions exhibit dual reactivity toward electrophiles; depending on the electrophile nature, they can react either at the sulfur or at the nitrogen atom.

The alkylation of α-sulfenyl-*N*-anions with alkyl halides is known as the only example of their reactions occurring at the nitrogen atom. With the goal of extending the series of reactions of α-sulfenyl-*N*-anions at the nitrogen atom, in the present work we examined their reactions with isocyanates. As substrates we used *N*-arylsulfonyl-substituted 2-nitrobenzenesulfenamides. α-Sulfenyl-*N*-anions were generated via transformation of the sulfenamides into sodium salts. The reactions were carried out in anhydrous acetone which is an inert solvent with respect to the reactants and is sufficiently polar to ensure dissolution and dissociation of sulfenamide sodium salts **Ia** and **Ib**. The reactions occurred at room temperature and were complete in several hours to several days, yielding *N*,*N*,*N*′-trisubstituted urea sodium salts **IIa**–**IIf** (Scheme 1; see table). The reaction rate increases in going from 2,4-dinitrophenyl isocyanate to benzoyl and *p*-tolylsulfonyl isocyanate due to increase in the electrophilicity of the carbon atom in the isocyanato group.

Salts **IIa**–**IIf** are light to dark yellow crystalline substances which are readily soluble in water, acetone, and dimethylformamide, sparingly soluble in ethanol and 2-propanol, and insoluble in saturated hydrocarbons. The IR spectra of **IIa**–**IIf** contain bands due to stretching vibrations of the NO_2 (1380–1395 and 1550–1570 cm^{-1}), SO_2 (1130–1135 and 1365–1375 cm^{-1}), and C=O groups (1595–1650 cm^{-1}).

Acidification of solutions of sodium salts **IIa**–**IIf** in acetone, water, or alcohol with dilute hydrochloric acid gives the corresponding substituted ureas

Scheme 1.



I, Ar = Ph (**a**), 4-MeC_6H_4 (**b**); **II**, **III**, Ar = Ph, R = Ts (**a**), 2,4-$(NO_2)_2C_6H_3$ (**b**), PhCO (**c**); Ar = 4-MeC_6H_4, R = Ts (**d**), 2,4-$(NO_2)_2C_6H_3$ (**e**), PhCO (**f**).

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Yields, melting points, IR spectra, and elemental analyses of sodium salts **IIa**–**IIf** and ureas **IIIa**–**IIIf**

Comp. no.	Yield, %	mp, °C	IR spectrum, ν, cm^{-1}						Found N, %	Formula	Calcd. N, %
			SO_2		NO_2		NH	C=O			
			sym.	asym.	sym.	asym.					
IIa	56	230–231	1130	1365	1382	1560	–	1595	7.95	$C_{20}N_{16}N_3NaO_7S_3$	7.94
IIb	75	174–175	1130	1370	1385	1560	–	1600	13.19	$C_{19}H_{12}N_5NaO_9S_2$	12.94
IIc	74	204–205	1130	1365	1385	1570	–	1650	8.89	$C_{20}H_{14}N_3NaO_6S_2$	8.77
IId	84	224–225	1135	1365	1395	1560	–	1600	7.81	$C_{21}H_{18}N_3NaO_7S_3$	7.73
IIe	77	184–185	1130	1365	1390	1560	–	1620	12.75	$C_{20}H_{14}N_5NaO_9S_2$	12.61
IIf	76	189–190	1130	1375	1395	1565	–	1650	8.58	$C_{21}H_{16}N_3NaO_6S_2$	8.52
IIIa	51	149–150	1135	1365	1375	1560	3250	1595	8.35	$C_{20}H_{17}N_3O_7S_3$	8.28
IIIb	58	104–105	1130	1360	1375	1560	3255	1600	13.60	$C_{19}H_{13}N_5O_9S_2$	13.49
IIIc	72	129–130	1130	1370	1395	1570	3250	1660	9.27	$C_{20}H_{15}N_3O_6S_2$	9.19
IIId	85	139–140	1135	1360	1380	1560	3220	1650	8.04	$C_{21}H_{19}N_3O_7S_3$	8.06
IIIe	80	94–95	1130	1365	1375	1565	3250	1595	13.24	$C_{20}H_{15}N_5O_9S_2$	13.13
IIIf	74	119–120	1130	1365	1380	1560	3250	1650	8.81	$C_{21}H_{17}N_3O_6S_2$	8.92

IIIa–**IIIf** (see table). Compounds **IIIa**–**IIIf** are colorless or light yellow crystalline substances which are insoluble in water and saturated hydrocarbons, soluble in DMF, acetone, and ethanol, and sparingly soluble in 2-propanol. They showed in the IR spectra absorption bands belonging to stretching vibrations of the SO_2 (1130–1135 and 1360–1370 cm^{-1}), NO_2 (1375–1395 and 1560–1570 cm^{-1}), C=O (1595–1660 cm^{-1}), and NH groups (3220–3250 cm^{-1}).

Following the procedure described in [20], compounds **IIa**–**IIf** and **IIIa**–**IIIf** were tested as thermal stabilizers for suspension polyvinylchloride. Ureas **IIIa**–**IIIf** showed almost no thermostabilizing activity, whereas some sodium salts **II** may be recommended for further testing.

EXPERIMENTAL

The IR spectra were recorded on UR-20 (KBr) and Specord 75IR spectrometers (mineral oil). The progress of reactions was monitored by TLC on Silufol UV-254 plates using 3:1 hexane–acetone as eluent; development with iodine vapor. The molecular weights of compounds **IIIa**–**IIIf** were determined according to Rust.

Isocyanates were prepared by reaction of the corresponding halogen derivatives with silver isocyanate in anhydrous acetone [21].

***N*-Phenylsulfonyl-2-nitrobenzenesulfenamide sodium salt (Ia).** To a solution of 10 mmol of *N*-phenylsulfonyl-2-nitrobenzenesulfenamide in 100 ml of anhydrous acetone we added a solution of sodium ethoxide, prepared from 10 mmol of sodium and 10 ml of anhydrous ethanol. The originally light yellow solution quickly turned dark red. It was stirred for 5–10 min at room temperature and evaporated to 0.1 of the initial volume, and the dark red tar-like residue crystallized on drying in a desiccator over calcium chloride. Yield 98%, mp 137–138°C.

Dark orange salt **Ib** was synthesized in a similar way. Yield 99%, mp 105–106°C.

***N*-(2-Nitrophenylsulfenyl)-*N*-phenylsulfonyl-*N*′-(*p*-tolylsulfonyl)urea sodium salt (IIa).** To a solution of 1 mmol of salt **Ia** in 25 ml of anhydrous acetone we added a solution of an equimolar amount of *p*-tolylsulfonyl isocyanate in 10 ml of anhydrous acetone. The mixture was kept at room temperature until a negative test for sulfenamide (a sample of the mixture should not give a red color with a 10% aqueous solution of potassium hydroxide; the end of the reaction was determined by TLC). The originally dark red mixture turned yellow. A part of the solvent was allowed to evaporate in air, and the precipitate of salt **IIa** was filtered off and dried in air. Compounds **IIb**–**IIf** were obtained in a similar way.

***N*-(2-Nitrophenylsulfenyl)-*N*-phenylsulfonyl-*N*′-(*p*-tolylsulfonyl)urea (IIIa).** *a*. To a solution of 1 mmol of salt **Ia** in 30 ml of anhydrous acetone we added a solution of an equimolar amount of *p*-tolylsulfonyl isocyanate in 4 ml of anhydrous acetone. The mixture was kept at room temperature until a negative color test for sulfenamide and the latter was not detected by TLC. It was then acidified with dilute (1 : 1) hydrochloric acid to pH 3–4, the precipitate of sodium chloride was filtered off, and the filtrate was evaporated in air.

b. A solution of 1 mmol of salt **IIa** in 25 ml of acetone was acidified with dilute (1 : 1) hydrochloric acid to pH 3–4. The precipitate of sodium chloride was filtered off, the filtrate was evaporated to 3/4–1/2 of the initial volume and filtered again to remove residual sodium chloride, and the solvent was allowed to evaporate in air.

Compounds **IIIb**–**IIIf** were synthesized in a similar way, following method *a* or *b* (see table). Samples of **IIIb**–**IIIf** obtained by the two methods showed no depression of the melting point on mixing.

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[*] Wrong reference.—*Publisher.*