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Imination of Sulfur-containing Compounds: XXXV.* New Preparation Method and Oxidative Benzenesulfonylimination of Unsymmetrical Disulfides

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Abstract—A new preparative method of synthesis was developed for unsymmetrical and symmetrical disulfides. This method involves sulfenylation of sodium thiolates with *N*-arenesulfenyl-*N*,*N*'-bis(arenesulfonyl)sulfinamidines. Imination of unsymmetrical disulfides with sodium chloroamides of sulfonic acids occurs at the more nucleophilic sulfur atom, affording *N*,*N*'-bis(arenesulfonyl)sulfinamidines and symmetrical disulfides.

Sulfenylation reactions are of great preparative importance and are widely used to obtain sulfides [2], disulfides [3], sulfenamides [4], and the other valuable products of the fine organic synthesis, and also for creating protective groups in the syntheses of peptides and natural substances [5]. The role of sulfenylating agents in these processes played till recently predominantly sulfenyl chlorides [6], although their application was not always convenient due to low stability, relative unavailability and too high activity resulting sometimes in various undesirable side reactions. Therefore now a considerable attention is being given to search for new sulfenylating agents, and some of these investigations have brought positive results. For instance, it was shown [7] that in the synthesis of sulfides for sulfenylation of aromatic compounds could be successfully used sulfenamides and sulfenyl acetates activated respectively with SO_3 and $AlBr_3$. For sulfenylation of alkenes [8] and aromatic hydrocarbons with strong electron-donor groups attached to the benzene ring [9] were applied sulfenamides activated with $POCl_3$. As reported in [10, 11], the syntheses of unsymmetrical disulfides for thiols sulfenylation are carried out with the use of sulfenyl thiocyanates, sulfenamides, symmetrical disulfides, thiosulfonates, and Bunte salts, but these methods are not yet widely applied, and the only preparative method for the synthesis of unsymmetrical disulfides is now thiols sulfenylation with sulfenyl chlorides in the presence of organic bases [12]. As shown in [12] this method of disulfide synthesis has significant disadvantages especially for aliphatic-aromatic disulfides, for the sulfenylation of aliphatic thiols with aromatic sulfenyl chlorides is accompanied by oxidation and formation of symmetrical disulfides resulting in low yield of unsymmetrical disulfides. In this connection the search for new agents of thiols sulfenylation is urgent both from preparative and theoretical viewpoint.

In extension of these investigations we report here on reaction between sodium thiolates and compounds we have been first to describe [13, 14], *N*-arenesulfenyl-*N*,*N*'-bis(benzenesulfonyl)sulfinamidines **Ia, b**. We showed in [14] that these compounds are efficient transfer agents for sulfenyl groups in reactions with nucleophilic reagents. The study of this reaction demonstrated that compounds **Ia, b** vigorously reacted with sodium thiolates in organic solvents to afford depending on the thiolate character either symmetrical or unsymmetrical disulfides **IIa–d** in 43–92% yield. As side products the reaction gave rise to *N*,*N*'-bis(benzenesulfonyl)sulfinamidines (**IIIa, b**) sodium salts (**IIIa, b**). Benzene is the preferable

$$\begin{array}{l} RS{-}NSO_2Ph \\ \quad | \qquad\qquad + \quad R'SNa \\ R{-}S{=}NSO_2Ph \end{array}$$

Ia, b

$$\rightarrow \quad RSSR' + RS{=}NSO_2Ph)N(Na)SO_2Ph$$

IIa–f **IIIa, b**

I, R = Ph (**a**), 4-MeC_6H_4 (**b**); **II**, R = R' = Ph (**a**); R = R' = 4-MeC_6H_4 (**b**); R = Ph, R' = Bu (**c**); R = Ph,R' = 2-$NO_2C_6H_4$ (**d**); R = Ph, R' = 4-$NO_2C_6H_4$ (**e**); R = 4-MeC_6H_4, R' = 2-$NO_2C_6H_4$ (**f**); **III**, R = Ph (**a**), 4-MeC_6H_4 (**b**).

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solvent for preparative syntheses since disulfides are well soluble therein and the sodium salts of *N*,*N*'-bis(benzenesulfonyl)sulfinamidines are insoluble, and thus the separation is easy.

Disulfides **IIa–f** are described in the literature [12, 15], and their identification was performed with the help of a mixed sample melting point or by refraction index (for the liquid compounds). The melting (boiling) points and yields of compounds **IIa–f** compared with the yields obtained in [12] are presented in a table.

As seen from the table, the yield of compounds **IIa–f** tends to diminish in going from aliphatic thiolates to thiophenolates and nitrothiophenolates apparently due to decrease in sulfur nucleophilicity in this series.

N-(Arenesulfenyl)l-*N*,*N*'-bis(benzenesulfonyl)-sulfinamidines **Ia, b** were prepared along our procedure [13, 14], namely, by oxidative imination of sodium thiophenolates with benzenesulfonyldichloroamide in CCl_4.

$$4RSNa + 2PhSO_2NCl_2 \xrightarrow[-(RS)_2,\ -4NaCl]{} \textbf{Ia, b}$$

It was shown [16, 17] that compounds of analogous composition arise at oxidative imination of symmetrical diaryl disulfides with sodium chloroamides of sulfonic acids in anhydrous media. It is presumed [17] that these compounds are intermediates in reaction between disulfides and sodium chloroamides of sulfonic acids in water solutions that is known [18] to afford *N*,*N*'-bis(arenesulfonyl)sulfinamidines. Therefore it was of interest to investigate the reactions of unsymmetrical disulfides **IIc, d** with sodium benzenesulfonylchloroamide in order to reveal which sulfur atom suffered oxidative imination. We established that similar to the reaction of unsymmetrical disulfides with dichloroamides of sulfonic acids [19] the imination with sodium benzenesulfonylchloroamide occurred at the more nucleophilic sulfur atom to furnish *N*,*N*'-bis(benzenesulfonyl)sulfinamidines (**IVa, b**) and symmetrical disulfides **Va, b**.

$$\textbf{IIc, d} + 2PhSO_2NNaCl - 2H_2O \rightarrow RS(=NSO_2Ph)NHSO_2Ph + R'SSR'$$

IVa, b **Va, b**

IV, R = 2Bu (**a**), Ph (**b**); **V**, R' = Ph (**a**), 2-$NO_2C_6H_4$ (**b**).

Physical constants and yields of disulfides **IIa–f**

Compd. no.	mp, °C (solvent for crystallization)	Yield, %	Yield, % [12]
IIa	61–62 (CCl_4)	89	–
IIb	45–48 (CCl_4)	89	–
IIc	132–135 (5)[a]	92	21
IId	53–54 (AcOH)	52	86
IIe	56–57 (AcOH)	49	43
IIf	70–71 (EtOH)	44	89

[a] bp (*p*, mm Hg).

According to the assumption from [17] compounds **I** arising in the first stage of the reaction are decomposed by the crystallization water and alkali traces present to afford compounds **IV** and sulfenic acid as we have experimentally proved in [14]

$$\textbf{I} \xrightarrow{H_2O\ (\bar{O}H)} \textbf{IV} + R'SOH$$

The sulfenic acid in its turn undergoes disproportionation under the reaction conditions according the following equation [14].

$$5R'SOH \rightarrow R'SO_3H + 2(R'S-)_2 + 2H_2O$$

Thus the symmetrical disulfides in the above reaction arise through disproportionation of the sulfenic acid and not from recombination of two sulfenyl fragments. Therefore in the oxidative imination of disulfides with sodium chloroamides of sulfonic acids disregarding the amount of the latter the disulfide always is present in the reaction mixture as has been already mentioned in earlier publications [20].

N,*N*'-Bis(benzenesulfonyl)sulfinamidines (**IVa, b**) are described in the literature [15], and their identification was performed with the help of a mixed sample melting point with authentic samples prepared by oxidative imination of sodium thiolates with dichloroamides of sulfonic acids, and also by IR and ^{1}H NMR spectra. In the IR spectra of compounds **IVa, b** are present the absorption bands of symmetric (1150–1160 cm^{-1}) and asymmetric (1310–1320 cm^{-1}) stretching vibrations of SO_2 group, and also the bands of stretching vibrations of NH group (3050–3100 cm^{-1}). The ^{1}H NMR spectrum of compound **IVa** contains two multiplets from protons on groups

C_6H_5 and $-CH_2-CH_2-$ (δ 7.1–7.7 and 1.04 ppm respectively) and two triplets from groups CH_3 (δ 0.31 ppm) and $(CH_2)_3$ (δ 3.34 ppm).

The tests for biological activity established that compound **IVb** in small concentrations showed a relatively high fungicidal activity with respect to spores of fungi *Puccinia triticina* and a moderate fungicidal activity against the spores of *Phytophtora infestans*.

EXPERIMENTAL

IR spectra were recorded on spectrophotometer UR-20 from samples pelleted with KBr. ^{1}H NMR spectra were registered on JEOL C-60 instrument at operating frequency 60 MHz from solutions in CF_3COOH internal reference HMDS, the chemical shifts were presented in the δ scale. *N*-arenesulfenyl-*N*,*N*'-bis(arenesulfonyl)sulfinamidines **Ia, b** were prepared along procedure described in [13, 14].

Disulfides IIa–f. To a solution of 0.01 mol of compound **Ia** or **Ib** in 75 ml of anhydrous benzene was added at vigorous stirring 0.01 mol of an appropriate sodium thiolate. The reaction mixture became a solution, and then separated a fine precipitate. The reaction mixture was stirred for 15–30 min and filtered. Disulfides **IIa–f** were obtained from the filtrate by evaporation of benzene in air and crystallization of the residue from an appropriate solvent (or by a vacuum distillation in the case of liquid products). The precipitate obtained by filtration of the reaction mixture was dissolved in 100 ml of water and filtered. On acidification of filtrate were precipitated the corresponding sulfinamidines identified by mixed sample melting point [15].

Oxidative benzenesulfonylimination of unsymmetrical disulfides IIc, d. To a solution of 0.001 mol of disulfide **IIc** in 10 ml of pyridine was added 0.002 mol of sodium benzenesulfonylchloroamide, the mixture was stirred by shaking for 30 min and then left standing for several hours till negative reaction for active chlorine. The reaction mixture was poured into 80 ml of 10% hydrochloric acid, the separated precipitate was filtered off, treated with 20 ml of 10% sodium hydrogen carbonate, and filtered. On acidifying the filtrate *N*,*N*'-bis(benzenesulfonyl)butanesulfinamidine (**IVa**) was separated in amount 0.18 g (45%). The product was identified by mixed sample melting point, IR, and ^{1}H NMR spectra. The precipitate filtered off after treating with sodium hydrogen carbonate was washed with petroleum ether, dried, and recrystallized from CCl_4. We obtained 0.09 g (41%) of diphenyl disulfide identified by melting with an authentic sample.

Similarly was carried out the oxidative benzenesulfonylimination of disulfide **IId**. In this case we isolated 0.16 g (38%) of sulfinamidine **IVb** and 0.15 g (50%) of 2,2'-dinitrodiphenyl disulfide identified by melting with an authentic sample.

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