Russian Journal of Organic Chemistry, Vol. 41, No. 3, 2005, pp. 386–389. Translated from Zhurnal Organicheskoi Khimii, Vol. 41, No. 3, 2005, pp. 396–399.
Original Russian Text Copyright © 2005 by Koval'.

Imination of Sulfur-Containing Compounds: XXXVI.* A New Method of Synthesis and Oxidative Arylsulfonylimination of Sulfenamides

I. V. Koval'

Ukrainian State University of Chemical Technology, pr. Gagarina 8, Dnepropetrovsk, 49005 Ukraine

Received July 8, 2003

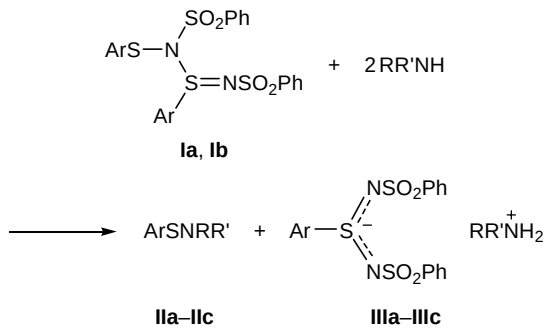
Abstract—Sulfenylation of ammonia, amines, and arenesulfonamide sodium salts with *N*-(arylsulfenyl)-*N*,*N'*-bis(arylsulfonyl)sulfinimidamides afforded unsubstituted and *N*-substituted arenesulfenamides. Oxidation of the latter with *N*-chloro sulfonamide sodium salts gave the corresponding sulfinimidamides.

Sulfenylation reactions are important from the preparative viewpoint and are widely used for the synthesis of sulfides [2], disulfides [3], sulfenamides [4], and other valuable products, as well as for introduction of protecting groups in peptide syntheses and syntheses of natural compounds [5]. Until recently, sulfenyl chlorides were mainly used as sulfenylating agents [6]. However, these reagents are not always convenient because of their low stability and relatively poor accessibility. In addition, their high reactivity often gives rise to various undesirable side processes. Therefore, a number of new sulfenylating agents have been proposed in the recent years. According to the data of [7], sulfenamides and sulfenyl acetates activated by SO_3 and $AlBr_3$, respectively, can be successfully used for sulfenylation of aromatic hydrocarbons to obtain sulfides. Sulfenamides activated by $POCl_3$ were proposed as sulfenylating agents with respect to alkenes [8, 9], alkynes [10], and aromatic hydrocarbons having strong electron-donor groups in the aromatic ring [11].

Apart from sulfenyl chlorides, thiols [12], disulfides activated by metal salts [3, 4], thiosulfonic acid *S*-esters, and sulfenyl thiocyanates [4, 5] were sometimes used as sulfenylating agents in the synthesis of sulfenamides. However, these reactions are not general, and they have not found wide application. At present, the only preparative method for the synthesis of sulfenamides is based on reactions of sulfenyl chlorides with compounds containing N–H or N–M bonds (M = Na, K, Li, Ag). Search for new sulfenylating agents effective toward N–H or N–M compounds is important from both preparative and theoretical viewpoints. In the preceding communication [1] it was shown that previously unknown *N*-arylsulfenyl-*N*,*N'*-bis(phenylsulfonyl)sulfinimidamides are effective sulfenylating agents with respect to thiols and that these compounds can be used for the preparation of both symmetric and asymmetric disulfides. Proceeding with studies in this line, in the present work we examined reactions of *N*-arylsulfenyl-*N*,*N'*-bis(phenylsulfonyl)-sulfinimidamides **Ia** and **Ib** with compounds having N–H or N–M bonds. As the latter we used ammonia, primary and secondary amines, and arenesulfonamide sodium salts.

We have found that compounds **Ia** and **Ib** vigorously react with ammonia and primary and secondary amines in anhydrous inert organic solvents to give, respectively, unsubstituted and *N*-mono- and *N*,*N*-disubstituted arenesulfenamides **IIa**–**IIc** (Scheme 1). The

Scheme 1.



I, Ar = Ph (**a**), 4-MeC_6H_4 (**b**); **II**, **III**, Ar = Ph, R = R' = H (**a**); R = R' = Et (**b**); R = H, R' = Ph (**c**).

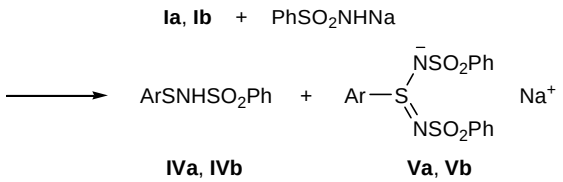
* For communication XXXV, see [1].

1070-4280/05/4103-0386 © 2005 Pleiades Publishing, Inc.

corresponding *N*,*N*′-bis(phenylsulfonyl)arenesulfinimidamide ammonium salts **IIIa**–**IIIc** were also formed as by-products; they were identified via transformation into sulfinimidamides by acidification.

By reaction of compounds **Ia** and **Ib** with arenesulfonamide sodium salts in anhydrous acetone we obtained *N*-(arylsulfonyl)arenesulfenamides **IVa** and **IVb** and *N*,*N*′-bis(arylsulfonyl)arenesulfinimidamide sodium salts **Va** and **Vb** (Scheme 2).

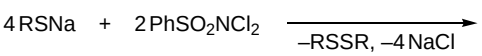
Scheme 2.



IV, **V**, Ar = Ph (**a**), 4-MeC_6H_4 (**b**).

Sulfenamides **IIa**–**IIc**, **IVa**, and **IVb** were reported previously [13–15]; they were identified by the melting points (by mixing with authentic samples) or refractive indices (for liquid substances). *N*-(Arylsulfenyl)-*N*,*N*′-bis(phenylsulfonyl)sulfinimidamides **Ia** and **Ib** were prepared by the procedure developed by us previously [16, 17], namely by oxidative imination of sodium benzenethiolates with *N*,*N*-dichlorobenzenesulfonamide in carbon tetrachloride (Scheme 3).

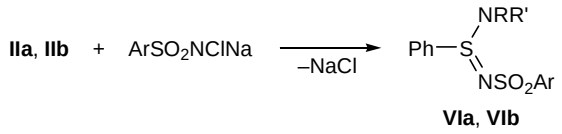
Scheme 3.



It is known that *N*-(arylsulfenyl)-*N*,*N*′-bis(arylsulfonyl)sulfinimidamides react with an equimolar amount of sodium thiolate to give 1 equiv of the corresponding disulfide and 1 equiv of *N*,*N*′-bis(phenylsulfonyl)sulfinimidamide. Presumably, the latter are formed as intermediate products in reactions of sodium thiolates with *N*,*N*-dichloro sulfonamides at a ratio of 5:2; these reactions underlie a number of preparative procedures for the synthesis of *N*,*N*′-disubstituted sulfinimidamides [18]. Another equally important reaction leading to sulfinimidamides is oxidative imination of sulfenamides with *N*-halo derivatives [4, 5]. Here, the ability of sulfenamides to undergo imination with *N*-halo compounds is determined by the structure of the initial sulfenamide [19], nucleophilicity of the sulfur atom therein [20, 21], acidity of the substrate [22], strength of the C–S bond [23], solvent nature [13, 24], and other factors which should be taken into account in each particular case. Therefore, it was interesting to study oxidative imination of sulfenamides **IIa** and **IIb** with *N*-chloro-arenesulfonamide sodium salts.

We have found that sulfenamides **IIa** and **IIb** relatively readily undergo imination with *N*-chloroarenesulfonamide sodium salts in acetone to afford the corresponding sulfinimidamides **VIa** and **VIb** (Scheme 4).

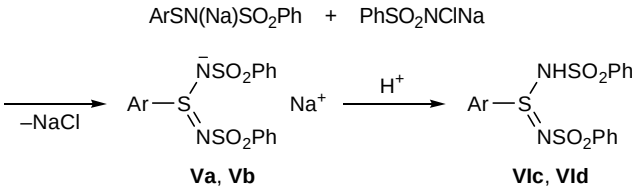
Scheme 4.



VI, R = R′ = H, Ar = Ph (**a**); R = R′ = Et, Ar = 4-MeC_6H_4 (**b**).

Imination of sulfenamides **IVa** and **IVb** can also be effected using *N*-chloro sulfonamide sodium salts in acetone [15]; however, the imination of the corresponding sodium salts occurs more smoothly due to enhanced nucleophilicity of the sulfur atom in the sulfenamide *N*-anion [22] (Scheme 5).

Scheme 5.



VI, Ar = Ph (**c**), 4-MeC_6H_4 (**d**).

The reaction of sulfenamide **IIc** with *N*-chlorobenzenesulfonamide sodium salt in acetone was not selective. It resulted in formation of a mixture of several products, from which only *N*,*N*′-bis(phenylsulfonyl)sulfinimidamide and diphenyl disulfide were isolated and identified. The observed reaction pattern may be rationalized in terms of insufficient nucleophilicity of the sulfur atom in sulfenamide **IIc**, on the one hand, and weakness of the S–N bond therein, on the other. Cleavage of that bond during the process gives rise to subsequent imination of the PhS fragment, as was observed previously in the imination of bis(arylsulfenyl)imides [23]. According to [23], anomalous imination with cleavage of the S–N bond occurs as a rule with N-substituted sulfenamides; the force constant for stretching vibrations of that bond does not exceed 1920.5×10^{-17} J mol^{-1} m^2. In the IR spectrum of sulfenamide **IIc**, stretching vibration fre-

quency of the S–N bond is 743 cm^{-1}; using the formula given in [25], the corresponding force constant was estimated at 1910×10^{-17} J mol^{-1} m^2.

Arenesulfinimidamides **VIa**–**VId** were reported previously [1, 13, 15, 26]; they were identified by the melting points (by mixing with authentic samples) and IR and mass spectra. The IR spectrum of **VIa** contains two strong absorption bands in the region 3250–3350 cm^{-1}, which belong to stretching vibrations of the free NH_2 group. Absorption bands due to stretching vibrations of the sulfonyl group appear at about 1160 cm^{-1}. In the IR spectra of **VIc** and **VId**, absorption bands corresponding to symmetric and antisymmetric stretching vibrations of the sulfonyl group (1150–1160 and 1310–1320 cm^{-1}, respectively) and stretching vibrations of the N–H bond (3050–3100 cm^{-1}) were present.

Like *N*-aroyl-*N'*-arylsulfonyltrichloromethanesulfinimidamides [19], compounds **VIc** and **VId** showed no molecular ion peak in the mass spectra. Presumably, their molecular ions are unstable because of the large size. The most abundant were fragment ions corresponding to the aryl and arylsulfonyl residues.

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrometer. The mass spectra were obtained on an CB-9000 instrument with direct sample admission into the ion source.

Sulfenamides IIa–IIc. Compound **Ia**, 0.01 mol, was dissolved in 100 ml of anhydrous benzene, and 0.02 mol of the corresponding amine was added or (in the synthesis of **IIa**) dry gaseous ammonia was passed through the solution. A tarry material precipitated, the mixture was stirred for 15–30 min, and the solution was separated from the tarry residue by decanting. The solvent was evaporated in air, and the residue was crystallized from appropriate solvent or distilled under reduced pressure (for liquid products) to obtain sulfenamides **IIa**–**IIc**. The tarry material was dissolved in 100 ml of water, the solution was filtered, and the filtrate was acidified to isolate *N*,*N'*-bis(phenylsulfonyl)benzenesulfinimidamide which was identified by comparing with an authentic sample [15].

Sulfenamides IVa and IVb. Anhydrous benzenesulfonamide sodium salt, 0.01 mol, was added under vigorous stirring to a solution of 0.01 mol of compound **Ia** or **Ib** in 100 ml of anhydrous acetone. The mixture turned homogeneous and was stirred for 40 min. The solvent was evaporated in air, the residue was treated with 100 ml of water, and the precipitate was filtered off, dried, and recrystallized from appropriate solvent to obtain sulfenamide **IVa** or **VIb**. The aqueous filtrate was acidified to isolate sulfinimidamide **Va** or **Vb** which was identified by comparing with an authentic sample [15].

Oxidative arylsulfonylimination of sulfenamides IIa and IIb. *N*-Chlorobenzenesulfonamide sodium salt, 0.001 mol, was added to a solution of 0.001 mol of sulfenamide **IIa** in 10 ml of acetone, and the mixture was stirred until complete disappearance of active chlorine. The mixture was filtered, the filtrate was evaporated in air, and the residue was recrystallized from benzene to obtain 0.26 g (92%) of *N*-phenylsulfonylbenzenesulfinimidamide (**VIa**) which was identified by comparing with an authentic sample [13] and by IR spectroscopy. The reaction with sulfenamide **IIb** was performed in a similar way to isolate 0.22 g (62%) of *N*-*p*-tolylsulfonyl-*N*,*N'*-diethylbenzenesulfinimidamide (**VIb**) which was identified by the melting point [26].

Oxidative phenylsulfonylimination of sulfenamide IVa and IVb sodium salts. Sulfenamide **IVa** or **IVb**, 0.001 mol, was added to a solution of 0.001 mol of sodium methoxide in 10 ml of methanol. The solvent was distilled off under reduced pressure, the residue was dissolved in 15 ml of anhydrous acetone, and 0.001 mol of *N*-chlorobenzenesulfonamide sodium salt was added to the solution. The mixture spontaneously warmed up, and finely dispersed sodium chloride precipitated. The mixture was shaken for 15 min until complete disappearance of active chlorine and filtered, the filtrate was evaporated in air, and the residue was dissolved in 50 ml of water. The solution was filtered, and the filtrate was acidifed with 5% hydrochloric acid to isolate *N*,*N'*-bis(phenylsulfonyl)benzenesulfinimidamide (**VIc**) or *N*,*N'*-bis-(phenylsulfonyl)-*p*-toluenesulfinimidamide (**VId**) (yield quantitative) which were identified by comparing with authentic samples [15] and by the IR and mass spectra.

REFERENCES

1. Koval', I.V., *Russ. J. Org. Chem.*, 2002, vol. 38, p. 232.
2. Koval', I.V., *Usp. Khim.*, 1994, vol. 63, p. 338.
3. Koval', I.V., *Usp. Khim.*, 1994, vol. 63, p. 776.
4. Koval', I.V., *Russ. J. Org. Chem.*, 1996, vol. 32, p. 1239.
5. Koval', I.V., *Usp. Khim.*, 1996, vol. 65, p. 452.

6. Koval', I.V., *Usp. Khim.*, 1995, vol. 64, p. 781.
7. Zefirov, N.S., Zyk, N.V., Beloglazkina, E.K., and Tyurin, V.S., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 1995, p. 324.
8. Beloglazkina, E.K., Zyk, N.V., Tyurin, V.S., Titanyuk, I.D., and Zefirov, N.S., *Dokl. Ross. Akad. Nauk*, 1995, vol. 344, p. 487.
9. Zyk, N.V., Beloglazkina, E.K., Belova, M.A., and Dubinina, N.S., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 2002, p. 1816.
10. Zyk, N.V., Beloglazkina, E.K., Belova, M.A., and Zefirov, N.S., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 2000, p. 1874.
11. Zyk, N.V., Beloglazkina, E.K., and Belova, M.A., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 2000, p. 178.
12. Koval', I.V., *Usp. Khim.*, 1993, vol. 62, p. 813.
13. Koval', I.V., Oleinik, T.G., and Kremlev, M.M., *Zh. Org. Khim.*, 1981, vol. 17, p. 2174.
14. Kharasch, N., Potempa, S.J., and Wehrmeister, H.L., *Chem. Rev.*, 1946, vol. 39, p. 269.
15. Koval', I.V., Oleinik, T.G., and Kremlev, M.M., *Zh. Org. Khim.*, 1979, vol. 15, p. 2319.
16. Kremlev, M.M., Kodachenko, G.F., Burmistrov, S.I., and Koval', I.V., USSR Inventor's Certificate no. 245771, 1969; *Byull. Izobret.*, 1969, no. 20.
17. Kremlev, M.M. and Koval', I.V., *Zh. Org. Khim.*, 1970, vol. 6, p. 1457.
18. Koval, I.V., *Sulfur Rep.*, 1993, vol. 14, p. 149.
19. Koval', I.V., Tarasenko, A.I., Kremlev, M.M., and Molchanova, N.R., *Zh. Org. Khim.*, 1981, vol. 17, p. 533.
20. Koval', I.V., Goncharuk, V.N., and Oleinik, T.G., *Zh. Org. Khim.*, 1993, vol. 29, p. 2002.
21. Koval', I.V., *Russ. J. Org. Chem.*, 1995, vol. 31, p. 889.
22. Koval', I.V., Oleinik, T.G., Tarasenko, A.I., and Kremlev, M.M., *Zh. Org. Khim.*, 1985, vol. 21, p. 2578.
23. Koval', I.V., Tarasenko, A.I., Kremlev, M.M., and Naumenko, R.P., *Zh. Org. Khim.*, 1986, vol. 22, p. 1178.
24. Koval', I.V., Oleinik, T.G., and Novikova, L.B., *Zh. Org. Khim.*, 1993, vol. 29, p. 1822.
25. Yanovskaya, L.A., *Sovremennye teoreticheskie osnovy organicheskoi khimii* (Modern Theoretical Foundations of Organic Chemistry), Moscow: Khimiya, 1978, p. 35.
26. Goerdeler, J. and Redies, B., *Chem. Ber.*, 1959, vol. 92, p. 1.