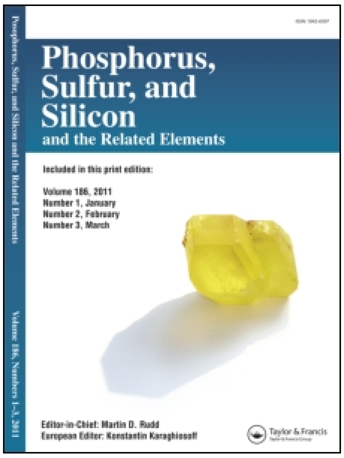

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A CONVENIENT SYNTHESIS OF N-PHENYLSULFONYL-S-ARYL-S-CHLOROSULFOXIMINES

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A CONVENIENT SYNTHESIS OF N-PHENYLSULFONYL-S-ARYL-S-CHLOROSULFOXIMINES

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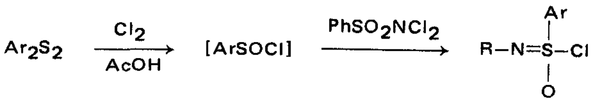
ABSTRACT

N-Phenylsulfonyl-S-phenyl-S-chlorosulfoximine and N-phenylsulfonyl-S-(*p*-nitrophenyl)-S-chlorosulfoximine are prepared in 40–50% yields from corresponding disulfides, chlorine and N,N-dichlorobensenesulfonamide.

The suggested procedure is of advantage because it uses the stable and simply purified iminating reagent (N,N-dichlorobensenesulfonamide) and excludes the isolation of unstable reaction intermediates (sulfinyl chlorides).

S-Aryl-S-chlorosulfoximines (arenesulfonimidoyl chlorides) **1** were usually prepared by oxidative imination of corresponding sulfinyl chlorides[1] with (*i*) Na salts of N-chloroarenesulfonamides[2a,b] (R=$ArSO_2$), N-chloroacetamide[3a] (R=MeCO) and N-chlorodiethylurethane[3b] (R=εtOOC) and (*ii*) free N-chloroamides in the presence of tertiary amines.[4,5] Among the known N,N-dichloro compounds, only N,N-dichloroalkylamines[6,7a–c] and N,N-dichloro-α-cyanoalkylamines[8] were used in the preparation of corresponding **1** (R=Alk and $Alk_2C(CN)$). It must be noted, however, that similar to **1**, S-aryl-S-chlorosulfilimines ($ArSO_2$-N=S(Ar′)Cl) were prepared either from Na N-chloroarenesulfonamides and Ar′SCl or from N,N-dichloroarenesulfonamides and Ar′SCl or Ar'_2S_2;[9] the last procedure was regarded to be the most convenient because it does not involve the preparation of Ar′SCl.[9]

We wish to report here a simple method of one-step preparation of S-aryl-S-chlorosulfoximines, **1** (R=$PhSO_2$; **1a**: Ar = *p*-O_2NPh; **1b**: Ar = Ph) from corresponding disulfides, chlorine and N,N-dichlorobenzenesulfonamide.



$$Ar_2S_2 \xrightarrow[AcOH]{Cl_2} [ArSOCl] \xrightarrow{PhSO_2NCl_2} R{-}N{=}\overset{Ar}{\underset{O}{S}}{-}Cl$$

1a: R = $PhSO_2$, Ar = *p*-O_2NPh

1b: R = $PhSO_2$, Ar = Ph

1

The procedure involves an oxidative chlorination of aryl disulfides to sulfinyl chlorides (see *e.g.* references 10 and 11) and the following treatment of reaction mixture with N,N-dichlorobenzenesulfonamide. This reagent seems to be more convenient as compared to Na-salt of N-chlorobenzenesulfonamide due to the simplicity of its purification and drying.[12] The suggested procedure is also of advantage because it does not involve the isolation of unstable and easily hydrolyzed sulfinyl chlorides.

The substances **1a, b** are characterized by their mp's, uv, and ir absorbtion spectra.

Experimental Section

Compound 1a

A shaked mixture of *p*-nitrophenyl disulfide (0.05 mol), glacial AcOH (0.1 mol) and absol $CHCl_3$ (50 ml) was saturated at –5–10° with dry chlorine until the solid completely disappeared and the initial red color of a solution turned to bright-yellow. The mixture was warmed to 20° and allowed to stand overnight. 0.1 Mol. of N,N-dichlorobenzenesulfonamide and 50 ml of absol $CHCl_3$ were added and the whole was refluxed for 4 hours. The solution was filtered and evaporated in vacuo; the resulting solid was washed with $εt_2O$:heptane (2:1, 2 x 50 ml) yielding 95% of crude product. Recrystallization from εtOH[13] or εtOH:heptane (1:1) affords

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1. Obtained from $ArSO_2H$ and $SOCl_2$, see Ref. 2*b*.
2. *a.* E. S. Levchenko, N. Ya. Derkach, A. V. Kirsanov, *Zh. Obshch. Khim.*, **30**, 1971 (1960);
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   b. **Ger. 1,212,525** (1966); *Chem. Abstr.* **65**:P3799b;
   c. **Fr. 1,413,596** (1965), *Chem. Abstr.* **64**:P5001f.
8. A. M. Pinchuk, L. N. Markovskii, E. S. Levchenko, V. I. Shevchenko, *Zh. Obshch. Khim.*, **37**, 852 (1967).
9. *e.g.*, E. S. Levchenko, L. V. Seleznenko, *Zh. Org. Khim.*, **2**, 92 (1966).
10. I. B. Douglass, B. S. Farah, E. G. Thomas, *J. Org. Chem.*, **26**, 1996 (1961).
11. S. Oae, K. Ikura, *Bull. Chem. Soc. Jap.*, **39**, 1306 (1966).
12. $PhSO_2NCl_2$ can be dried in a vacuum dessicator, *cf.* a special procedure for preparation of anhydrous Na N-chloroarenesulfonamides:
    A. V. Kirsanov, *Zh. Obshch. Khim.*, Coll. Vol. II, 1046 (1953).
13. A solution must not be heated for a long time due to the possibility of partial alcoholysis.

40–50% of pure **1a**, colorless needles, mp 125–6° (uncorr), (lit[2b] 125–6°). UV max (in $CHCl_3$) 256 nm (ϵ = 19300); ir bands (nujol) 1358 m, 1334 s, 1300 s, 1169 m, 1135 s, 1092 m, 1080 m, 1010 m, 975 w cm^{-1}.

Compound 1b

The saturation of a cooled solution of phenyl disulfide (0.005 mol) and glacial AcOH (0.01 mol) in 5 ml of absol $CHCl_3$ with dry chlorine and the above operations lead to pale-yellow oil, which crystallizes on long standing. The yield of crude product was 80% (after washing with ϵt_2O: heptane (2 : 1, 3 x 5 ml)). Recrystallization from ϵtOH : heptane (1:1) affords 40–50% of pure **1b**, mp 93–94° (uncorr), (lit[2a] 93–94°) uv max (in $CHCl_3$) 246 nm (ϵ = 9700); ir bands (nujol) 1348 s, 1332 m, 1278 m, 1185 m, 1166 m, 1104 m, 1086 m, 1070 m, 1027 w, 998 w cm^{-1}.