

SHORT COMMUNICATIONS

Dedicated to Full Member of the Russian Academy of Sciences
N.S. Zefirov on His 70th Anniversary

First Example of Synthesis of *N,N'*-Bis(trichloroethylidene)- arene disulfonamides

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We previously developed methods for the synthesis of *N*-sulfonyl-substituted polyhalogenated aldehyde imines via reaction of *N,N'*-dichlorosulfonamides with polyhaloethenes [1, 2]. In the present communication we report for the first time on the application of the same approach to the preparation of *N,N'*-bis(trichloroethylidene)-*p,p'*-biphenyl- and *p,p'*-oxydibenzene disulfonamides. For this purpose, *p,p'*-biphenyldisulfonamide and *p,p'*-oxydibenzene disulfonamide were chlorinated in the presence of sodium hydroxide to obtain the corresponding *N,N,N',N'*-tetrachloro derivatives **Ia** and **Ib**, and the latter were brought into reaction with trichloroethylene. As a result, we obtained in high yields *N,N'*-bis(trichloroethylidene)-*p,p'*-biphenyldisulfonamide (**IIa**) and *N,N'*-bis(trichloroethylidene)-*p,p'*-oxydibenzene disulfonamide (**IIb**). Molecules of **IIa** and **IIb** possess highly electrophilic azomethine groups; therefore, these compounds attract interest from the viewpoint of their further transformations.

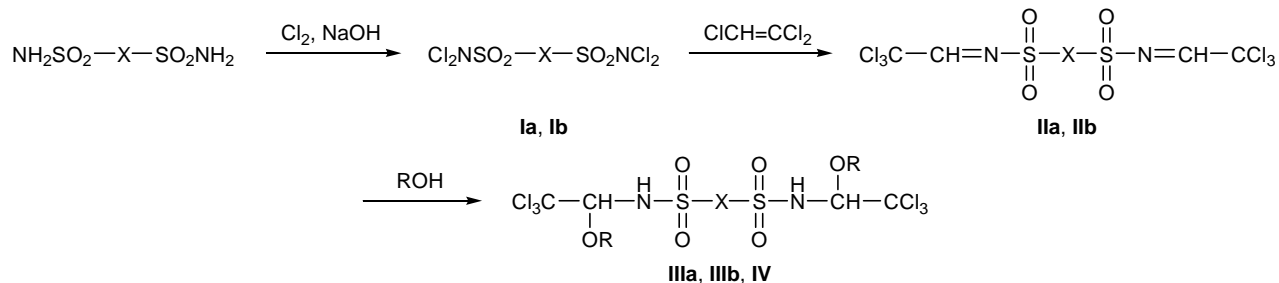
The high reactivity of bis-imines **IIa** and **IIb** is demonstrated by exothermic addition of oxygen-centered nucleophiles. Compounds **IIa** and **IIb** vigorously react with methanol, and they take up water even upon

contact with atmospheric moisture. It seems to be reasonable to use Schiff bases **IIa** and **IIb** without isolation from the reaction mixture to avoid formation of hydroxy derivatives **IIIa** and **IIIb** as impurity.

Halogenated Schiff bases having several CH=N bonds activated by electron-withdrawing substituents may be convenient starting compounds in the synthesis of polyfunctional cyclic or acyclic haloalkylamide ensembles containing pharmacophoric fragments, which are promising as strong NH acids, ligands, and reagents for asymmetric synthesis and supramolecular chemistry.

N,N,N',N'-Tetrachlorodisulfonamides **Ia** and **Ib** were prepared by chlorination of alkaline solutions of the corresponding disulfonamides [3].

N,N'-Bis(2,2,2-trichloroethylidene)-*p,p'*-biphenyldisulfonamide (**IIa**). A mixture of 4.50 g (0.01 mol) of compound **Ia** and 18 ml (0.20 mol) of trichloroethylene was heated under reflux in a continuous stream of argon until chlorine no longer evolved (10–12 h). According to the ¹H NMR data, product **IIa** was formed in quantitative yield. IR spectrum, ν , cm⁻¹:



I–III, X = *p*-C₆H₄C₆H₄-*p* (**a**), *p*-C₆H₄OC₆H₄-*p* (**b**); **III**, R = OH; **IV**, R = MeO, X = *p*-C₆H₄OC₆H₄-*p*.

1150, 1335 (SO₂); 1635 (C=N). ¹H NMR spectrum (CDCl₃), δ, ppm: 7.98 and 8.22 (8H, AA'BB' system, H_{arom}), 8.85 s (2H, N=CH).

N,N'-Bis(2,2,2-trichloroethylidene)-*p,p'*-oxydibenzenedisulfonamide (**IIb**) was synthesized in a similar way. IR spectrum, ν, cm⁻¹: 1145, 1330 (SO₂); 1630 (C=N). ¹H NMR spectrum (CDCl₃), δ, ppm: 7.24 and 8.02 (8H, AA'BB' system, H_{arom}), 8.50 s (2H, N=CH). ¹³C NMR spectrum (CDCl₃), δ_C, ppm: 96.47 (CCl₃); 119.74, 130.07, 136.61, 160.77 (C₆H₄); 159.08 (N=C).

N,N'-Bis(2,2,2-trichloro-1-hydroxyethyl)-*p,p'*-biphenyldisulfonamide (**IIIa**). Water, 1 ml (0.05 mol), was added to the reaction mixture containing Schiff base **IIa**, and the resulting mixture was shaken for 20–30 min. The precipitate was filtered off and dried. Yield 90%, mp 176–178°C. IR spectrum, ν, cm⁻¹: 1140, 1330 (SO₂); 3250 (NH); 3450 (OH). ¹H NMR spectrum (DMSO-*d*₆), δ, ppm: 5.24 d (1H, NCH, *J* = 11 Hz), 7.90 and 8.01 (8H, AA'BB' system, H_{arom}), 9.02 d (1H, NH, *J* = 11 Hz). Found, %: C 31.73; H 2.38; Cl 35.33; N 4.75; S 10.69. C₁₆H₁₄Cl₆N₂O₆S₂. Calculated, %: C 31.65; H 2.32; Cl 35.04; N 4.61; S 10.56.

N,N'-Bis(2,2,2-trichloro-1-hydroxyethyl)-*p,p'*-oxydibenzenedisulfonamide (**IIIb**) was synthesized as described above for **IIIa**. Yield 95%, mp 182–185°C. IR spectrum, ν, cm⁻¹: 1145, 1330 (SO₂); 3230 (NH); 3480 (OH). ¹H NMR spectrum (acetone-*d*₆), δ, ppm: 5.46 d (1H, NCH, *J* = 11 Hz), 7.24 and 7.99 (8H, AA'BB' system, H_{arom}), 7.77 d (1H, NH, *J* = 11 Hz). ¹³C NMR spectrum (acetone-*d*₆), δ_C, ppm: 86.83 (NCH); 102.55 (CCl₃); 119.80, 130.63, 138.42,

160.43 (C₆H₄). Found, %: C 30.95; H 2.31; Cl 34.28; N 4.67; S 10.41. C₁₆H₁₄Cl₆N₂O₇S₂. Calculated, %: C 30.84; H 2.26; Cl 34.14; N 4.50; S 10.29.

N,N'-Bis(2,2,2-trichloro-1-methoxyethyl)-*p,p'*-oxydibenzenedisulfonamide (**IV**) was synthesized as described above for **IIIa** using compound **IIb** and methanol instead of water. Yield 86%, mp 143–146°C. IR spectrum, ν, cm⁻¹: 1140, 1330 (SO₂); 3250 (NH). ¹H NMR spectrum (CDCl₃), δ, ppm: 3.60 s (3H, OCH₃), 4.97 d (1H, NCH, *J* = 12 Hz), 5.69 d (1H, NH, *J* = 12 Hz), 7.10 and 7.94 (8H, AA'BB' system, H_{arom}). ¹³C NMR spectrum (CDCl₃), δ_C, ppm: 58.49 (OCH₃); 92.69 (NCH); 99.03 (CCl₃); 119.34, 129.94, 136.26, 159.78 (C₆H₄). Found, %: C 33.32; H 2.85; Cl 32.92; N 4.43; S 9.97. C₁₈H₁₈Cl₆N₂O₇S₂. Calculated, %: C 33.20; H 2.79; Cl 32.67; N 4.30; S 9.85.

The ¹H and ¹³C NMR spectra were recorded from 5–10% solutions on a Bruker DPX-400 spectrometer at 400.6 and 100.61 MHz, respectively, using hexamethyldisiloxane as internal reference. The IR spectra were measured in KBr on a Specord 75IR instrument.

REFERENCES

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