

Synthesis of 2-Methyl-*N*-(2,2,2-trichloroethylidene)- and 2-Methyl-*N*-(2,2,2-trichloroethyl)benzenesulfonamides from *N,N*-Dichloro-2-methylbenzenesulfonamide and Trichloroethylene

Yu. A. Aizina^a, I. B. Rozentsveig^a, S. K. Petkevich^b, V. I. Potkin^b, and G. G. Levkovskaya^a

^a Favorskii Irkutsk Institute of Chemistry, Siberian Branch, Russian Academy of Sciences,
ul. Favorskogo 1, Irkutsk, 664033 Russia
e-mail: ggl@irioch.irk.ru

^b Institute of Physical Organic Chemistry, National Academy of Sciences of Belarus,
ul. Surganova 13, Minsk, 220072 Belarus

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Abstract—The reaction of *N,N*-dichloro-2-methylbenzenesulfonamide with trichloroethylene gave a new representative of highly electrophilic *N*-sulfonyl polyhaloaldehyde imines, 2-methyl-*N*-(2,2,2-trichloroethylidene)benzenesulfonamide. High reactivity of the product was demonstrated in the addition of water and 2-methylbenzenesulfonamide and reactions with benzene, toluene, anisole, thiophene, and 2-chlorothiophene. *N,N*-Dichlorobenzenesulfonamides and *N,N*-dichlorotrifluoromethanesulfonamide failed to react with 1,1,3,3,4,4-hexachlorobut-1-ene and 1,1,2,3,4-pentachlorobuta-1,3-diene under the conditions ensuring formation of *N*-(2,2,2-trichloroethylidene)arenesulfonamides from *N,N*-dichloroarenesulfonamides and trichloroethylene.

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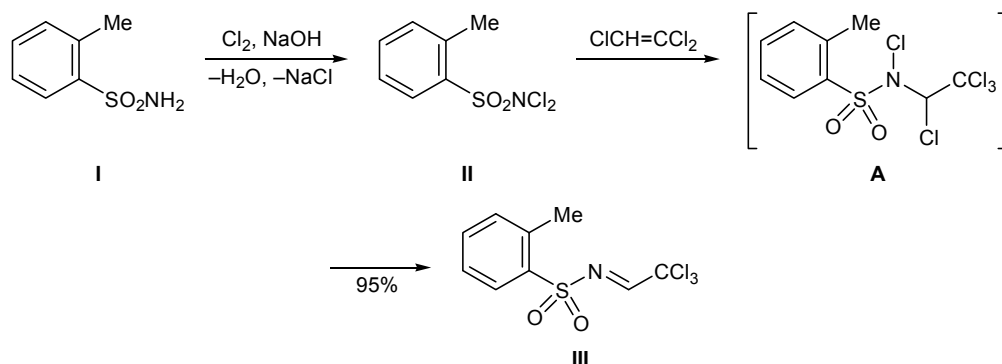
Sulfonamide derivatives are widely used as medicinal agents exhibiting antidiabetic [1, 2], diuretic [1, 3], analgesic [1, 4], anti-inflammatory [1, 5], and anti-tumor activity [6]; efficient enzyme inhibitors were also found among these compounds [7]. Sulfonamides are also known as herbicides, insecticides, fungicides [8], and dyes (including those for medical purposes) [9]. Furthermore, sulfonamides are important reagents in modern organic synthesis, specifically in the preparation and identification of amines [10] and synthesis of new sulfonamides [11] and Schiff bases [12]; they were also used as enantioselective catalysts [13], ligands for metal complex catalysts [14], etc.

One of the most efficient methods for the preparation of highly reactive *N*-sulfonyl polyhaloaldehyde imines and a broad series of sulfonamide derivatives based thereon utilizes the reaction of *N,N*-dichloroarene-, phenylmethane-, and perfluoroalkanesulfonamides with 1,2-polyhaloethenes [15–20]. However, the chemical behavior of such an accessible 2-toluene-sulfonamide derivative as *N,N*-dichloro-2-methylben-

zenesulfonamide [21] has been studied very poorly. There are published data only on the reduction of this compound with DMSO [22] and its electrochemical (cathodic) reduction to 2-methylbenzenesulfonamide [23]. Up to now, reactions of *N,N*-dichloro-2-methylbenzenesulfonamide with 1,2-polyhaloethenes have not been studied.

With a view to develop selective procedures for the synthesis of new important precursors of biologically active substances and practically valuable products of the sulfonamide series, including heterocyclic derivatives, in the present work *N,N*-dichloro-2-methylbenzenesulfonamide (**II**) was brought into reaction with trichloroethylene, as well as with 1,1,3,3,4,4-hexachlorobut-1-ene and 1,1,2,3,4-pentachlorobuta-1,3-diene synthesized from trichloroethylene. Amide **II** was prepared in 68% yield by treatment of an alkaline solution of 2-methylbenzenesulfonamide (**I**) with gaseous chlorine, by analogy with the synthesis of isomeric *N,N*-dichloro-4-methylbenzenesulfonamide [24] (Scheme 1).

Scheme 1.



We tried to synthesize previously unknown 2-methyl-*N*-(2,2,2-trichloroethylidene)benzenesulfonamide (**III**) by reaction of *N,N*-dichloro amide **II** with trichloroethylene under the conditions ensuring quantitative formation of *N*-(2,2,2-trichloroethylidene)-arenesulfonamides [15, 18, 20]. Compound **II** reacted with trichloroethylene in 10–12 h to afford amide **III** in a good yield (95%); the reaction was accompanied by formation of an equimolar amount of pentachloroethane as a result of chlorine addition to trichloroethylene. The reaction followed a radical chain mechanism and involved intermediate formation of unstable saturated adduct **A** which readily underwent dechlorination (Scheme 1).

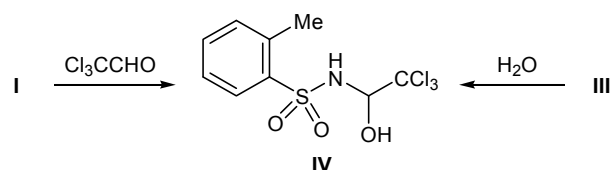
N,N-Dihalo amides derived from arenesulfonic and trifluoromethanesulfonic acids were reacted with 1,1,3,3,4,4-hexachlorobut-1-ene and 1,1,2,3,4-pentachlorobut-1,3-diene. It was expected that these reactions would give rise to the corresponding highly reactive polyhaloaldehyde imines (by analogy with the reaction of *N,N*-dichloro sulfonamides with 1,2-polyhaloethenes, which was studied by us in detail [15]) and 1-amido-substituted chlorobutanes as intermediate products for the synthesis of chloroaziridines [15, 16]. However, under the conditions optimal for the synthesis of *N*-sulfonyl polyhaloaldehyde imines or adducts of ethenes and *N,N*-dichloro amides [15–20], *N,N*-dichloro sulfonamides, including the most reactive *N,N*-dichlorotrifluoromethanesulfonamide [17, 19], failed to react with the above polychloroalkenes.

In continuation of our systematic studies on the reactivity of *N*-(polychloroethylidene)arenesulfonamides we examined some reactions of amide **III** with a view to develop synthetic approaches to new *N*-(haloalkyl)sulfonamides containing additional heteroatom, aromatic, and heterocyclic fragments. These compounds attract interest from the viewpoints of their further transformations and potential biological ac-

tivity. Newly synthesized 2-methyl-*N*-(2,2,2-trichloroethylidene)benzenesulfonamide (**III**) was brought into reactions with water and amide **I** and amidoalkylation of benzene, toluene, anisole, thiophene, and 2-chlorothiophene, which are typical of chloral imines.

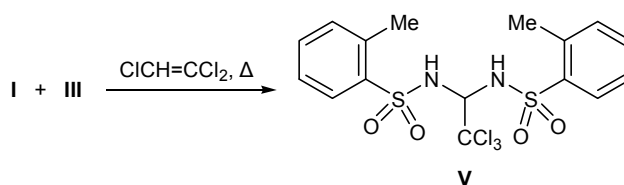
Imine **III** was quantitatively converted into hydroxy derivative **IV** on exposure to air for 24 h or on addition of water (Scheme 2), which indicated high electrophilicity of the CH=N group in **III** activated by strong electron-withdrawing substituents. Compound **IV** was also synthesized from amide **I** and trichloroacetaldehyde in the presence of a catalytic amount of concentrated sulfuric acid, but the yield was somewhat lower. In this case, no imine **III** was detected in the reaction mixture by ^1H and ^{13}C NMR spectroscopy.

Scheme 2.

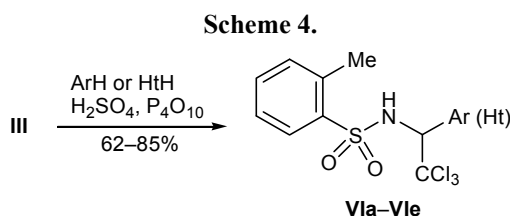


Imine **III** reacted with amide **I** in trichloroethylene at 90–92°C in the absence of a catalyst to produce bis-amide **V** in quantitative yield (Scheme 3). The ability of imine **III** to react with aromatic and heteroaromatic compounds under acid catalysis was demonstrated using benzene, toluene, anisole, thiophene, and 2-chlorothiophene as substrates. As a result, the corresponding *N*-[1-aryl(hetaryl)-2,2,2-trichloroethyl]-

Scheme 3.



2-methylbenzenesulfonamides **VIa–VIe** were obtained in good yields (Scheme 4). When fuming sulfuric acid (10–20% SO₃) was used as catalyst [25], the reaction was accompanied by tarring and side sulfonation of the aromatic substrate, while no compounds **VIa–VIe** were formed in the presence of concentrated sulfuric acid alone. Efficient C-amidoalkylation was achieved when imine **III** was added to excess aromatic substrate and a mixture of 90–94% sulfuric acid and phosphoric anhydride (0.4–0.5 g of H₂SO₄ and 0.25–0.3 g of P₄O₁₀ per 0.01 mol of **III**; see table).



Ar = Ph (**a**), 4-MeC₆H₄ (**b**), 4-MeOC₆H₄ (**c**); Ht = 2-thienyl (**d**), 5-chlorothiophen-2-yl (**e**).

The reactions were carried out at room temperature under vigorous stirring using the substrate (in the synthesis of **VIa–VIc**) or halogenated hydrocarbon as solvent (in the synthesis of thiophene derivatives **VI d** and **Ve**). The substitution in arenes and hetarenes was regioselective with formation of 4-substitued benzenes **VIb** and **VIc** and 2-substitued thiophenes **VI d** and **Ve**; the optimal reaction time was 3–5 h. No bis-amide **V** was detected in the reaction mixtures under these conditions.

The proposed approach to the synthesis of 2-methylbenzenesulfonamide derivatives via transformations of 2-methyl-*N*-(2,2,2-trichloroethylidene)benzenesulfonamide features high chemo- and regioselectivity. Undoubtedly, the products attract interest from the viewpoint of preparation of various 2-methylbenzenesulfonamide derivatives, including *N*-protected aryl- and hetarylglycines [26] and polyfunctional [15, 27] and heterocyclic compounds [15, 28], by analogy with the transformations of other *N*-arylsulfonyl imines derived from polyhalogenated aldehydes.

Compounds **III–VI** are colorless crystalline substances, which are readily soluble in polar organic solvents and insoluble in water. The structure of **II–VI** was proved by spectral data and elemental analyses. All compounds **II–VI** displayed in the IR spectra absorption bands typical of SO₂ group. In the spectra of substituted amides **III–VI** we observed absorption bands due to stretching vibrations of the NH group,

Yields of amide **VIa** in the reaction of benzene with sulfonamide **III**^a

Catalyst (amount)	Time, h	Yield, %
AlCl ₃ (1.33 g, 10 mmol)	50	0
BF ₃ ·Et ₂ O (1.42 g, 10 mmol)	50	0
P ₄ O ₁₀ (2.84 g, 10 mmol)	50	0
100% H ₂ SO ₄ (0.98 g, 10 mmol)	7	25 ^b
Oleum, 10% SO ₃ (1.0 g)	7	45 ^c
Oleum, 20% SO ₃ (1.0 g)	7	40 ^c
94% H ₂ SO ₄ (1.0 g), P ₄ O ₁₀ (1.0 g)	5	78
94% H ₂ SO ₄ (1.0 g), P ₄ O ₁₀ (0.5 g)	5	80
94% H ₂ SO ₄ (0.5 g), P ₄ O ₁₀ (0.5 g)	3	81

^a The reactions were carried out according to the procedure described in Experimental for the synthesis of amide **VIa**.

^b Sulfonamide **I** and bis-amide **V** were also formed.

^c Toluene- and benzenesulfonic acids were also formed.

and the spectrum of hemiaminal **IV** also contained OH vibration band.

The ¹H NMR spectra of **II–VI** contained signals from protons in the methyl group, and the NH–CH fragment of amides **IV–VI** was represented in the spectra by two doublets with a coupling constant of 9.5–10.5 Hz. Signals from the aromatic protons in **VIb** and **VIc** appeared as an *AA'**BB'* pattern, indicating *para* substitution of the aromatic ring. The signal intensities in the ¹H NMR spectra of **II–VI** and the position of signals in the ¹³C NMR spectra of **III–VI** were fully consistent with the assumed structures.

EXPERIMENTAL

The ¹H and ¹³C NMR spectra were measured on a Bruker DPX-400 instrument at 400.61 and 100.13 MHz, respectively, using tetramethylsilane as internal reference. The IR spectra were recorded in KBr on a Bruker IFS-25 spectrometer. 2-Methylbenzenesulfonamide and *N,N*-dichloroarenesulfonamides were commercial products. 1,1,3,3,4,4-Hexachlorobut-1-ene and 1,1,2,3,4-pentachlorobuta-1,3-diene were synthesized according to the procedures reported in [29, 30]. *N,N*-Dichlorotrifluoromethanesulfonamide was prepared as described in [31].

***N,N*-Dichloro-2-methylbenzenesulfonamide (II).** Amide **I**, 1.71 g (10 mmol), was added under stirring to a solution of 1.60 g (40 mmol) of sodium hydroxide in 20 mL of water, gaseous chlorine was passed through the solution until saturation, and the mixture was kept for 2 h at room temperature. The tarry precipitate was

separated, washed with water, and dried. Yield 1.63 g (68%); mp 33°C (CHCl₃) [21]. IR spectrum, ν , cm⁻¹: 3064 (C–H_{arom}); 1331, 1164 (SO₂). ¹H NMR spectrum (CDCl₃), δ , ppm: 2.71 s (3H, CH₃); 7.42 t, 7.64 t, 8.14 d (4H, C₆H₄). ¹³C NMR spectrum (CDCl₃), δ , ppm: 21.1 (CH₃); 123.8, 126.6, 133.3, 133.7, 135.8, 141.5 (C₆H₄). Found, %: C 34.87; H 2.81; Cl 30.09; N 5.58; S 12.87. C₇H₇Cl₂NO₂S. Calculated, %: C 35.02; H 2.94; Cl 29.53; N 5.83; S 13.35.

Amide **II** was extracted from the reaction mixture into chloroform (2 × 30 mL), the extracts were combined and dried over calcium chloride, and the resulting solution was used to prepare imine **III**.

Reaction of *N,N*-dichloro sulfonamides with polychloroalkenes (general procedure). A mixture of 0.01 mol of *N,N*-dichloro sulfonamide and 0.01–0.02 mol of 1,1,3,3,4,4-hexachlorobut-1-ene or 1,1,2,3,4-pentachlorobut-1,3-diene was heated for 10–12 h in anhydrous carbon tetrachloride under reflux or in chlorobenzene at 110–120°C. The reactions were also carried out under analogous conditions with addition of 4–10% of benzoyl peroxide. Evaporation of the mixture under reduced pressure gave the initial *N,N*-dichloro sulfonamide.

2-Methyl-*N*-(2,2,2-trichloroethylidene)benzenesulfonamide (III). A mixture of 2.40 g (10 mmol) of amide **II** and 10.50 g (80 mmol) of trichloroethylene was heated for 10–12 h under reflux in an argon atmosphere until chlorine no longer evolved (starch-iodine test) and was then evaporated under reduced pressure. Yield 2.85 g (95%), mp 128–130°C. ¹H NMR spectrum (CDCl₃), δ , ppm: 2.67 s (3H, CH₃); 7.33 t, 7.53 t, 8.03 d (4H, C₆H₄); 8.50 s (1H, N=CH). ¹³C NMR spectrum (CDCl₃), δ , ppm: 21.0 (CH₃), 81.3 (CCl₃); 123.8, 126.6, 129.0, 133.2, 133.7, 135.8 (C₆H₄); 141.5 (C=N). Found, %: C 35.87; H 2.81; Cl 35.09; N 4.58; S 10.87. C₉H₈Cl₃NO₂S. Calculated, %: C 35.96; H 2.68; Cl 35.38; N 4.66; S 10.67.

Imine **III** was brought into further transformations without isolation.

2-Methyl-*N*-(2,2,2-trichloro-1-hydroxyethyl)benzenesulfonamide (IV). *a.* A mixture of 1.71 g (10 mmol) of 2-methylbenzenesulfonamide (**I**), 3.26 g (20 mmol) of trichloroacetaldehyde, and 1 mL of concentrated sulfuric acid was vigorously stirred for 15 min at 60–65°C. The mixture was then kept for 15 min at room temperature, and the precipitate was filtered off, washed with water until neutral washings, and dried. Yield 3.16 g (95%), mp 128–130°C; published data [32]: mp 148°C. IR spectrum, ν , cm⁻¹: 3380

(OH), 3259 (NH), 3098 (C–H_{arom}), 1314 (SO₂), 1152. ¹H NMR spectrum (DMSO-*d*₆), δ , ppm: 2.57 s (3H, CH₃), 5.07 d (1H, NHCH, ³*J* = 9.2 Hz); 7.33 t, 7.46 d, 7.90 d (4H, C₆H₄); 9.04 d (1H, NH, ³*J* = 9.2 Hz). ¹³C NMR spectrum (DMSO-*d*₆), δ , ppm: 20.8 (CH₃), 85.7 (NCH), 102.0 (CCl₃); 128.2, 128.4, 129.5, 130.9 (C_{arom}). Found, %: C 35.02; H 3.12; Cl 33.75; N 4.53; S 10.02. C₉H₁₀Cl₃NO₃S. Calculated, %: C 34.93; H 3.16; Cl 33.38; N 4.40; S 10.06.

b. Imine **III**, 1.50 g (5 mmol), was kept for 24 h on exposure to air. Yield of **IV** 1.59 g (100%).

***N,N'*-(2,2,2-Trichloroethane-1,1-diyl)bis-(2-methylbenzenesulfonamide) (V).** A mixture of imine **III** [prepared from 2.40 g (10 mmol) of amide **II** and 10.50 g (80 mmol) of trichloroethylene] and 1.71 g (10 mmol) of amide **I** was stirred for 3 h on heating to 90–92°C. The mixture was cooled to room temperature, the solvent was distilled under reduced pressure, and the residue was washed with water and dried. Yield 4.51 g (96%), mp 158–161°C. IR spectrum, ν , cm⁻¹: 3302, 3253 (NH); 2988 (C–H_{aliph}); 1329, 1161 (SO₂). ¹H NMR spectrum (CDCl₃), δ , ppm: 2.65 s (6H, CH₃), 5.38 t (1H, NHCH, ³*J* = 8.8 Hz), 7.28–7.41 m (8H, C₆H₄); 7.99 d (2H, NH, ³*J* = 8.8 Hz). ¹³C NMR spectrum (CDCl₃), δ , ppm: 19.9 (CH₃), 74.6 (CH), 100.7 (CCl₃); 125.5, 128.6, 131.8, 131.9, 136.5, 138.4 (C₆H₄). Found, %: C 40.21; H 3.52; Cl 22.98; N 5.71; S 12.91. C₁₆H₁₇Cl₃N₂O₄S₂. Calculated, %: C 40.73; H 3.63; Cl 22.54; N 5.94; S 13.59.

2-Methyl-*N*-(2,2,2-trichloro-1-phenylethyl)benzenesulfonamide (VIa). A mixture of imine **III** [prepared from 2.40 g (10 mmol) of *N,N*-dichloro amide **II** and 10.50 g (7.2 mL, 80 mmol) or 8.0 g (5.4 mL, 60 mmol) of trichloroethylene], 0.5–0.6 mL of 96% H₂SO₄, and 0.4–0.5 g of P₄O₁₀ in 10 mL of benzene was stirred for 3 h. The mixture was evaporated under reduced pressure, and the residue was washed with water, 30 mL of 20% aqueous ammonia, and water again (until neutral washings) and dried in air at room temperature. Yield 3.18 g (81%), mp 125–127°C. IR spectrum, ν , cm⁻¹: 3259 (NH); 3061 (C–H_{arom}); 1330, 1168 (SO₂). ¹H NMR spectrum (CDCl₃), δ , ppm: 2.41 s (3H, CH₃), 5.04 d (1H, NHCH, ³*J* = 10.4 Hz); 7.08 d, 7.18 m, 7.31 t, 7.48 d, 7.76 d (9H, H_{arom}); 9.27 (1H, NH, ³*J* = 10.4 Hz). ¹³C NMR spectrum (CDCl₃), δ , ppm: 19.8 (CH₃), 71.6 (CH), 100.9 (CCl₃); 125.1, 127.8, 128.4, 128.7, 131.1, 131.5, 131.8, 136.6, 137.9 (C_{arom}). Found, %: C 47.87; H 4.08; Cl 27.21; N 3.42; S 8.24. C₁₅H₁₄Cl₃NO₂S. Calculated, %: C 47.57; H 3.73; Cl 28.08; N 3.70; S 8.47.

2-Methyl-*N*-[2,2,2-trichloro-1-(4-methylphenyl)ethyl]benzenesulfonamide (VIb) was synthesized in a similar way from 2.40 g (10 mmol) of *N,N*-dichloro amide **II**, 8.0 g (5.4 mL, 60 mmol) of trichloroethylene, and 10 mL of toluene using 0.5 mL of 96% H₂SO₄ and 0.5 g of P₄O₁₀. Yield 3.18 g (81%), mp 80–83°C. IR spectrum, ν , cm⁻¹: 3254 (NH); 1338, 1153 (SO₂). ¹H NMR spectrum (CDCl₃), δ , ppm: 2.24 s (3H, CH₃), 2.77 s (3H, CH₃), 4.67 d (1H, NHCH, ³*J* = 10.2 Hz), 6.73 d and 7.00 d (4H, *AA'*/*BB'*, C₆H₄); 6.77 t, 6.89 t, 7.53 d (4H, C₆H₄); 8.21 (1H, NH, ³*J* = 10.2 Hz). ¹³C NMR spectrum (CDCl₃), δ , ppm: 19.7 (CH₃), 20.5 (CH₃), 71.6 (CH), 100.9 (CCl₃); 125.1, 127.8, 128.4, 128.7, 131.1, 131.5, 131.8, 136.6, 137.9 (C_{arom}). Found, %: C 48.87; H 4.08; Cl 27.21; N 3.42; S 8.24. C₁₆H₁₆Cl₃NO₂S. Calculated, %: C 48.93; H 4.11; Cl 27.08; N 3.57; S 8.16.

2-Methyl-*N*-[2,2,2-trichloro-1-(4-methoxyphenyl)ethyl]benzenesulfonamide (VIc) was synthesized in a similar way from 2.40 g (10 mmol) of *N,N*-dichloro amide **II**, 7.2 mL (80 mmol) of trichloroethylene, and 3 mL of anisole in 10 mL of carbon tetrachloride containing 0.5 mL of 96% H₂SO₄ and 0.5 g of P₄O₁₀. Yield 3.55 g (87%), mp 134–136°C. IR spectrum, ν , cm⁻¹: 3293 (NH); 3062 (C–H_{arom}); 2964 (C–H_{aliph}); 1336, 1164 (SO₂). ¹H NMR spectrum (DMSO-*d*₆), δ , ppm: 2.44 s (3H, CH₃), 3.71 s (3H, OCH₃), 4.99 d (1H, CH, ³*J* = 10.5 Hz); 6.76 d and 7.42 d (4H, *AA'*/*BB'*, CH₃OC₆H₄); 7.12 d, 7.22 t, 7.36 t, 7.76 d (4H, CH₃C₆H₄); 9.17 d (1H, NH, ³*J* = 10.4 Hz). ¹³C NMR spectrum (DMSO-*d*₆), δ , ppm: 20.4 (CH₃), 55.7 (OCH₃), 71.6 (CH), 102.6 (CCl₃); 126.4, 127.03, 129.3, 131.4, 132.6, 133.0, 137.1, 139.1, 159.9 (C_{arom}). Found, %: C 47.23; H 3.88; Cl 26.17; N 3.55; S 7.93. C₁₆H₁₆Cl₃NO₃S. Calculated, %: C 47.02; H 3.95; Cl 26.02; N 3.43; S 7.85.

2-Methyl-*N*-[2,2,2-trichloro-1-(2-thienyl)ethyl]benzenesulfonamide (VIId) was synthesized in a similar way from 3 mL of thiophene using 0.7 g of H₂SO₄ and 0.7 g of P₄O₁₀. Yield 2.37 g (62%), mp 125–127°C. IR spectrum, ν , cm⁻¹: 3250 (NH); 1335, 1168 (SO₂). ¹H NMR spectrum (DMSO-*d*₆), δ , ppm: 2.40 s (3H, CH₃), 5.49 d (1H, CH, ³*J* = 9.5 Hz); 7.04, 7.36, 7.40 m (3H, thiophene); 7.52 d (1H, NH, ³*J* = 9.5 Hz), 7.35 m and 7.47 m (4H, C₆H₄). ¹³C NMR spectrum (acetone-*d*₆), δ , ppm: 20.6 (CH₃), 66.7 (CH), 100.8 (CCl₃); 128.2, 128.8, 128.9, 129.1, 130.7, 130.9, 131.0, 144.1 (C_{arom}). Found, %: C 40.73; H 3.08; Cl 27.17; N 3.51; S 16.33. C₁₃H₁₂Cl₃NO₂S₂. Calculated, %: C 40.58; H 3.14; Cl 27.65; N 3.64; S 16.67.

2-Methyl-*N*-[2,2,2-trichloro-1-(5-chlorothiophen-2-yl)ethyl]benzenesulfonamide (VIe) was synthesized in a similar way from 3 mL of 2-chlorothiophene using 0.6 mL of 96% H₂SO₄ and 0.5 g of P₄O₁₀. Yield 3.14 g (75%), mp 108–110°C. IR spectrum, ν , cm⁻¹: 3254 (NH), 1330 (SO₂), 1166. ¹H NMR spectrum (DMSO-*d*₆), δ , ppm: 2.40 s (3H, CH₃), 5.28 d (1H, CH, ³*J* = 10.2 Hz), 6.87 d and 7.02 d (2H, 3'-H, 4'-H); 7.21 d, 7.28 t, 7.43 t, 7.82 d (4H, C₆H₄), 9.36 d (1H, NH, ³*J* = 10.2 Hz). ¹³C NMR spectrum (DMSO-*d*₆), δ , ppm: 19.9 (CH₃), 67.6 (CH), 100.6 (CCl₃); 125.8, 126.1, 129.0, 129.8, 132.2, 132.8, 135.2, 136.8, 138.2 (C_{arom}). Found, %: C 38.22; H 2.85; Cl 33.33; N 3.45; S 15.89. C₁₃H₁₁Cl₄NO₂S₂. Calculated, %: C 37.25; H 2.65; Cl 33.83; N 3.34; S 15.30.

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