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Synthesis and Properties of *N*-(2,2,2-Trichloroethylidene)-trifluoromethanesulfonamide and Its Derivatives*

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Abstract—The reaction of *N*,*N*-dichloromethanesulfonamide with trichloroethylene gave *N*-(2,2,2-trichloroethylidene)trifluoromethanesulfonamide which showed high reactivity toward oxygen- and nitrogen-centered nucleophiles, as well as in C-alkylation of aromatic compounds.

The reactivity of nitrogen-centered radicals like $R\dot{N}Cl$ toward halogenated ethenes is determined by the electrophilicity of the radical center. For example, *N*-halo- and *N*,*N*-dihaloamines (R = Alk) do not add to trichloroethylene [1]. By contrast, N-centered radicals derived from *N*,*N*-dihaloacylamines (R = R′CO, R′SO_2, R'_2PO) react with polyhaloethenes, resulting in formation of Schiff bases [2, 3]. Thus increase in electron-acceptor properties of the R substituent enhances the reactivity of nitrogen-centered radicals toward haloethenes. It might be expected that, among *N*,*N*-dichloro derivatives, *N*,*N*-dichloro sulfonamides and especially *N*,*N*-dichloroperfluoroalkanesulfonamides should exhibit high reactivity with respect to ethenes.

In continuation of our systematic studies on the reactivity of compounds possessing an N–Hlg bond and polyhalogenated ethenes, we examined the reaction of *N*,*N*-dichlorotrifluoromethanesulfonamide [4] with trichloroethylene in order to reveal the effect of the trifluoromethyl group on the properties of the initial *N*,*N*-dichloro amide and the resulting Schiff base. The reaction was carried out with excess trichloroethylene at a reactant ratio of 1 : (8–10). Unlike previously studied reactions of *N*,*N*-dichloro sulfonamides [2, 3], the reaction of *N*,*N*-dichlorotrifluoromethanesulfonamide with trichloroethylene required neither the presence of radical initiators nor thermal or photochemical initiation. The reaction occurred on mixing the reactants at room temperature and was accompanied by heat evolution. The process was complete in 20–25 h to afford *N*-(2,2,2-trichloroethylidene)trifluoromethanesulfonamide (**I**), chlorine, and pentachloroethane (Scheme 1).

Scheme 1.

$$CF_3SO_2NCl_2 + ClCH{=}CCl_2 \longrightarrow \underset{\mathbf{I}}{CF_3SO_2N{=}CHCCl_3} + Cl_2CH{-}CCl_3 + Cl_2$$

In the ^1H NMR spectrum ($CDCl_3$) of the reaction mixture we observed a signal at δ 6.44 ppm from trichloroethylene, a singlet at δ 8.65 ppm from the CH=N proton, and a singlet at δ 6.09 ppm from the dichloromethyl group of pentachloroethane. The formation of Schiff base **I** is also confirmed by the IR data (Table 1). Its IR spectrum contains absorption bands typical of –N=CH– and CF_3SO_2 fragments.

The mechanism of reactions of *N*,*N*-dichloro sulfonamides with polyhaloethenes was studied in [5]. Judging by the structure of the products, in our case an analogous mechanism is operative.

Schiff base **I** very readily reacts with oxygen- and nitrogen-centered nucleophiles, yielding addition products at the CH=N bond. The addition is favored by strong electron-acceptor character of the trifluoromethylsulfonyl and trichloromethyl groups. Compound **I** undergoes fast hydrolysis on exposure to atmospheric moisture and takes up alcohols with a strong exothermic effect. It also reacts with arene-

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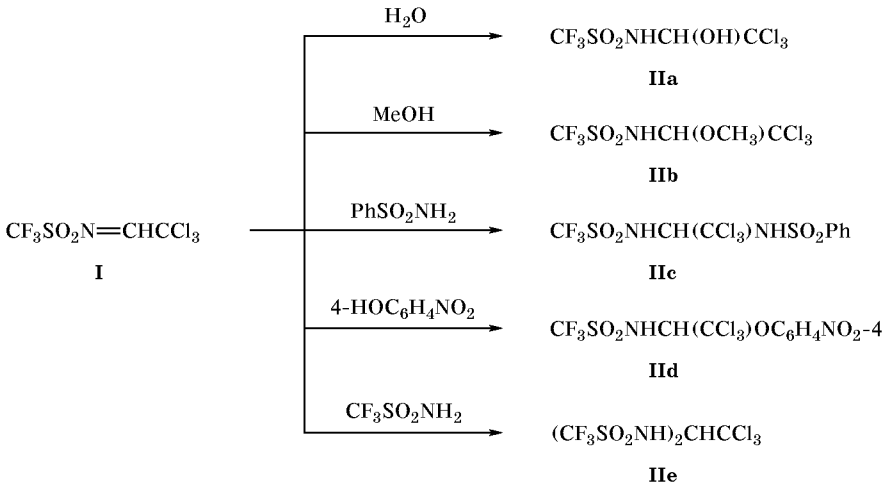
Scheme 2.

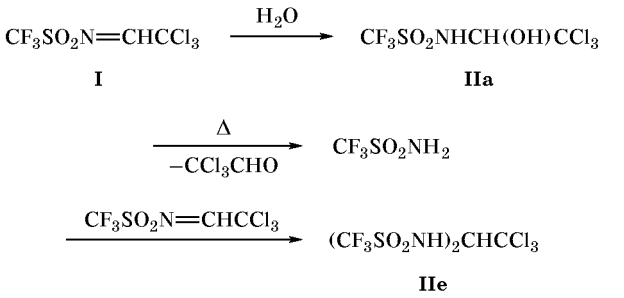


sulfonamides on keeping for 24 h and (on heating) with 4-nitrophenol and trifluoromethanesulfonamide (Scheme 2). It should be noted that known Schiff bases derived from sulfonamides and polyhalogenated aldehydes do not react even with chlorophenols [6]; also, we failed to react *N*-(2,2,2-trichloroethylidene)-arenesulfonamides with trifluoromethanesulfonamide.

Our attempts to synthesize *N*-(2,2,2-trichloro-1-hydroxyethyl)trifluoromethanesulfonamide (**IIa**) by independent method, namely by reaction of trichloroacetaldehyde or its hydrate with trifluoromethanesulfonamide were unsuccessful, although such reactions with arenesulfonamides occur fairly readily [7]. Presumably, this is the result of reduced nucleophilicity of the amide nitrogen atom due to electron-acceptor effect of the trifluoromethylsulfonyl group.

Distillation of product **I** at a temperature exceeding 60°C resulted in partial formation of 1,1,1-trichloro-2,2-bis(trifluoromethylsulfonylamino)ethane (**IIe**). Probably, when contacted with air, compound **I** is converted into hydroxy derivative **IIa** which decomposes to give trifluoromethanesulfonamide on heating above 60°C. Addition of the latter to Schiff base **I** yields 1,1,1-trichloro-2,2-bis(trifluoromethylsulfonylamino)ethane (**IIe**) (Scheme 3).

Scheme 3.

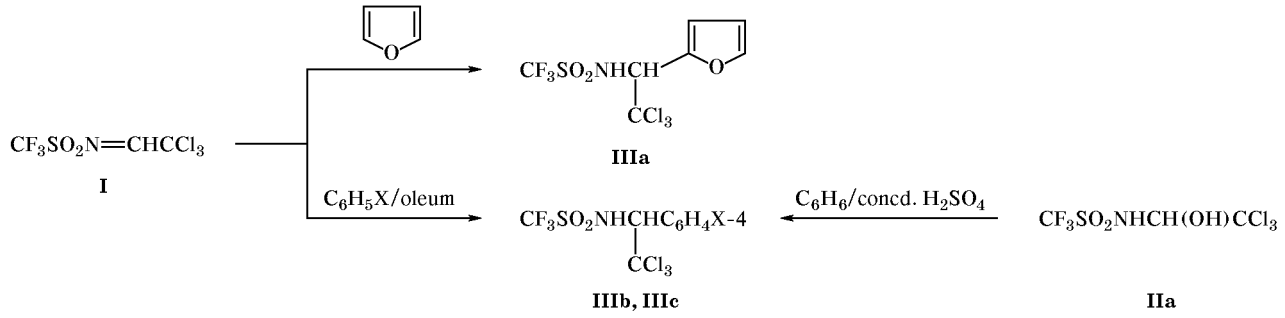


The structure of *N*-(trichloroethyl)trifluoromethanesulfonamides **II**–**IIe** was proved by the ^{1}H NMR and IR spectra (Table 1). Compounds **IIa**, **IIc**, and **IId** showed in the ^{1}H NMR spectra characteristic doublets from protons of the CH−NH moiety; signals from the CH and NH protons of bis-sulfonamide **IIe** appeared as broadened singlets. The NH proton in **IIb** is readily replaced by deuterium in $CDCl_3$, and the CH signal becomes a singlet. Likewise, fast H–D exchange occurs in the trifluoromethanesulfonamide moiety of **IIc**; however, the less labile NH proton in the benzenesulfonamide moiety is retained. The resulting −ND−CH−NH− fragment gives rise to two doublets in the ^{1}H NMR spectrum. In the spectrum of **IIb** a singlet from the methoxy group was also present, the spectra of amides **IIc** and **IId** contained signals from aromatic protons. The intensity of the doublet NH signal of bis-amide **IIe** was twice as large as the intensity of the CH multiplet.

In the IR spectra of compounds **IIa**–**IIe** we observed absorption bands belonging to C_{aliph}−H and N−H bonds; the CF_3SO_2 fragment gives rise to a broad band at 1380 cm^{-1} and three bands in the region 1150–1230 cm^{-1}; hydroxy derivative **IIa** showed absorption of the hydroxy group.

N-(2,2,2-Trichloroethylidene)trifluoromethanesulfonamide (**I**) is also capable of alkylating aromatic and heteroaromatic compounds. Its reaction with furan requires no catalyst and is accompanied by evolution of heat, yielding *N*-[2,2,2-trichloro-1-(2-furyl)ethyl]-trifluoromethanesulfonamide (**IIIa**). The reactions of **I** with benzene and chlorobenzene occur only in the

Scheme 4.



IIIb, X = H; **IIIc**, X = Cl.

presence of oleum. The products are *N*-(1-aryl-2,2,2-trichloroethyl)trifluoromethanesulfonamides **IIIb** and **IIIc**. Compound **IIIb** was also synthesized from *N*-(2,2,2-trichloro-1-hydroxyethyl)trifluorosulfonamide (**IIa**) and benzene in the presence of sulfuric acid [8, 9] (Scheme 4).

The structure of amides **IIIa**–**IIIc** was proved by the IR and ^{1}H NMR spectra (Table 1) and elemental analyses (Table 2). The IR spectra of **IIIa**–**IIIc** contain absorption bands due to the CF_3SO_2 and NH groups. In the ^{1}H NMR spectra of these compounds, apart from signals of aromatic protons, a signal from the $CHCCl_3$ fragment was present at δ 5.2–5.3 ppm, in keeping with published data for *N*-(2,2,2-trichloroethyl) sulfonamides [8–10].

N-(2,2,2-Trichloroethylidene)trifluoromethanesulfonamide (**I**) is a colorless liquid with a specific odor; it is readily soluble in organic solvents. Nucleophile addition products and C-aryl derivatives **IIIa**–**IIIc** are liquids or crystalline substances having an odor typical of trichloroacetaldehyde. They readily sublime or decompose on heating and are insoluble in water and soluble in organic solvents.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on Bruker DPX-400 (400 MHz) and Jeol FX-90Q (90 MHz) instruments from 5–10% solutions in deuterated solvents; the chemical shifts were measured relative to HMDS as internal reference. The IR spectra were obtained on a Specord 75IR spectrometer from samples prepared as KBr pellets or thin films.

N,*N*-Dichlorotrifluoromethanesulfonamide was synthesized by the procedure reported in [4].

***N*-(2,2,2-Trichloroethylidene)trifluoromethanesulfonamide (I).** A solution of 4.18 g (0.02 mol) of *N*,*N*-dichlorotrifluoromethanesulfonamide in 12–15 ml (0.16–0.20 mol) of freshly distilled anhydrous trichloroethylene was purged with argon for 1 h, and the mixture was left to stand for 20–25 h at room temperature until the yellow color disappeared. The product can be used in further syntheses without isolation. Pure Schiff base **I** was isolated by vacuum distillation, a fraction with bp 27–33°C (18–22) being collected. Yield 1.93 g (35%), n_D^{20} 1.4538. According to the ^{1}H NMR data, fractions with a lower boiling point were contaminated with pentachloroethane, and those boiling at higher temperature contained an admixture of 1,1,1-trichloro-2,2-bis(trifluoromethylsulfonylamino)ethane (**IIe**).

***N*-(2,2,2-Trichloro-1-hydroxyethyl)trifluoromethanesulfonamide (IIa).** *a*. Compound **I** was prepared as described above from 2.09 g (0.01 mol) of *N*,*N*-dichlorotrifluoromethanesulfonamide and 6–7 ml (0.08–0.1 mol) of trichloroethylene, and the solution was left to stand on exposure to air. After 20 h, the precipitate of **IIa** was filtered off and washed with dry chloroform. Yield 1.54 g (52%).

b. Water, 0.9 ml (0.05 mol), was added to 1.39 g (0.005 mol) of compound **I**. The mixture spontaneously warmed up to 60–70°C. The product was dried under reduced pressure (~100 mm) over P_2O_5. Yield 1.8 g (95%).

***N*-(2,2,2-Trichloro-1-methoxyethyl)trifluoromethanesulfonamide (IIb).** To a solution of Schiff base **I**, prepared as described above in *a*, 0.5 ml of anhydrous methanol was added, and the mixture warmed up to 40–50°C. The product was isolated by vacuum distillation, a fraction with bp 85–87°C (10 mm) being collected. Yield 1.18 g (38%), n_D^{20} 1.4395.

***N*-(2,2,2-Trichloro-1-phenylsulfonylaminoethyl)-trifluoromethanesulfonamide (IIc).** To a solution of compound **I** (see above) 1.57 g (0.01 mol) of benzenesulfonamide was added. The mixture was stirred for

Table 1. IR and ^{1}H NMR spectra of *N*-(2,2,2-trichloroethylidene)trifluoromethanesulfonamide (**I**) and *N*-(2,2,2-trichloroethyl)trifluoromethanesulfonamides **II** and **III**

Comp. no.	IR spectrum, ν, cm^{-1}			^{1}H NMR spectrum, δ, ppm				$J_{NH,CH}$, Hz
	N–H	CF_3SO_2	other bands	solvent	CH	NH	H_{arom}	
I	–	1390, 1230, 1210, 1130	1650 (C=N)	$CDCl_3$	8.65 s	–	–	–
IIa	3220	1380, 1230, 1200, 1130	3400 (OH)	C_6D_6	5.12 d	6.52 d	–	9.5
IIb[a]	3280	1380, 1230, 1200, 1130	2950 (CH_{aliph})	$CDCl_3$	4.95 s	–	–	–
IIc	3240–3280	1380, 1230, 1200, 1130		DMSO-d_6	5.61 d	9.38 d	7.11–7.87 m	9.5
IId	3280	1350, 1230, 1200, 1130	3000 (CH_{aliph})	$CDCl_3$	5.97 d	6.89 d	7.09, 8.18 (*AA′BB′*)	8.4
IIe	3250	1380, 1230, 1200, 1130	2950 (CH_{aliph})	DMSO-d_6	5.54[b]	11.51[b]	–	–
IIIa	3270	1380, 1230, 1200, 1140	2850 (CH_{aliph})	$CDCl_3$	5.34 d	6.37 d	7.46 d (2-H), 6.44 d.d (3-H), 6.59 d (4-H)	9.0
IIIb	3280	1380, 1220, 1200, 1130		$CDCl_3$	5.24 d	6.41 d	7.42–7.93 m	9.0
IIIc	3280	1380, 1230, 1200, 1140	2980 (CH_{aliph})	CD_3COCD_3	5.30 d	9.11 d	7.65, 7.37 (*AA′BB′*)	9.0

[a] $\delta(CH_3)$ 3.67 ppm, s.
[b] Broadened signal.

8 h, and the precipitate was filtered off, washed with chloroform, dried under reduced pressure, and examined by ^{1}H NMR spectroscopy. The product was a mixture of benzenesulfonamide, hydroxy derivative **IIa**, and addition product **IIc**. The latter was formed in 51% yield (2.22 g).

***N*-(2,2,2-Trichloro-1-*p*-nitrophenoxyethyl)trifluoromethanesulfonamide (IId).** *p*-Nitrophenol, 1.39 g (0.01 mol), was added to a solution of compound **I**, prepared from *N*,*N*-dichlorotrifluoromethanesulfonamide and trichloroethylene as described above. The mixture was heated for 50 h at 50–60°C with occasional shaking, and *p*-nitrophenol dissolved. When the reaction was complete, the liquid part was separated from undissolved *p*-nitrophenol by decanting and was analyzed by ^{1}H NMR spectroscopy. The yield of addition product **IId** was 1.59 g (38%). In addition, the mixture contained initial *p*-nitrophenol and hydroxyethyl amide **IIa**.

1,1,1-Trichloro-2,2-bis(trifluoromethylsulfonylamino)ethane (IIe). Trifluoromethanesulfonamide, 1.49 g (0.01 mol), was added to a solution of amide **I**, prepared as described above from *N*,*N*-dichlorotrifluoromethanesulfonamide and trichloroethylene. The mixture was kept for 60 h at 60–70°C and then for 20 h at room temperature. The large transparent crystals of bisamide **IIe** were separated by decanting and dried. Yield 1.08 g (37%).

***N*-[2,2,2-Trichloro-1-(2-furyl)ethyl]trifluoromethanesulfonamide (IIIa).** To a solution of Schiff base **I**, prepared as described above, 0.68 g (0.01 mol) of furan was added. A slight exothermic effect was observed. The mixture was kept for 24 h at room temperature and then for 24 h in the cold. The precipitate was filtered off and dried under reduced pressure. Yield of amide **IIIa** 1.84 g (53%).

***N*-(2,2,2-Trichloro-1-phenylethyl)trifluoromethanesulfonamide (IIIb).** *a*. Dry benzene, 5 ml, was added to a solution of Schiff base **I** (see above), and 0.5–0.7 ml of oleum (15–20% of SO_3) was then added under vigorous stirring. The mixture was stirred for 5–6 h at room temperature, 5 ml of chloroform was added, the mixture was shaken, and the organic phase was separated by decanting and evaporated.

Table 2. Yields, melting points, and elemental analyses of *N*-(2,2,2-trichloroethyl)trifluoromethanesulfonamides **II** and **III**

Comp. no.	Yield, %	mp, °C	Found, %				Formula	Calculated, %			
			C	Cl	N	S		C	Cl	N	S
IIa	95	107–110	11.97	35.15	4.81	10.94	$C_3H_3Cl_3F_3NO_3S$	12.15	35.87	4.72	10.81
IIb[a]	38		15.41	34.08	4.43	10.48	$C_4H_5Cl_3F_3NO_3S$	15.47	34.25	4.51	10.33
IIe	37	151–152	11.18	30.47	6.73	15.07	$C_4H_3Cl_3F_6N_2O_4S_2$	11.24	24.88	6.55	15.00
IIIa	53	88–90	24.17	30.59	4.11	9.37	$C_7H_5Cl_3F_3NO_3S$	24.26	30.69	4.04	9.25
IIIb	70[b] 78[c]	118–120	30.25	29.70	4.01	9.12	$C_9H_7Cl_3F_3NO_2S$	30.32	29.83	3.93	8.99
IIIc	72	174–175	27.56	36.19	3.62	8.34	$C_9H_6Cl_4F_3NO_2S$	27.65	36.27	3.58	8.20

[a] For boiling point, see Experimental.

[b] From *N*-(2,2,2-trichloroethylidene)trifluoromethanesulfonamide (**I**).

[c] From *N*-(2,2,2-trichloro-1-hydroxyethyl)trifluoromethanesulfonamide (**IIa**).

The solid residue was washed with water, dried over P_2O_5, and recrystallized from benzene. Yield of amide **IIIb** 2.5 g (70%).

b. A mixture of 2.97 g (0.01 mol) of *N*-(2,2,2-trichloro-1-hydroxyethyl)trifluoromethanesulfonamide (**IIa**), 10 ml of dry benzene, and 3–4 ml of concentrated sulfuric acid was vigorously stirred for 5 h. The organic phase was separated by decanting and was then treated as described above. Yield of amide **IIIb** 2.78 g (78%).

***N*-(2,2,2-Trichloro-1-*p*-chlorophenylethyl)trifluoromethanesulfonamide (IIIc)** was synthesized as described above for compound **IIIb** (method *a*) from Schiff base **I** and 5 ml of dry chlorobenzene in the presence of 0.5–0.7 ml of oleum. Yield 2.82 g (72%).

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