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Synthesis and Properties of *N*-(2,2,2-Trichloroethylidene)- and *N*-(2,2,2-Trichloroethyl)nitrobenzenesulfonamides

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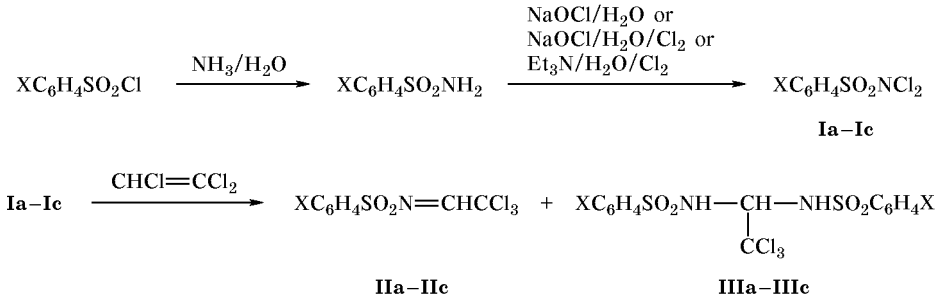
Abstract—Highly reactive *N*-(2,2,2-trichloroethylidene)nitrobenzenesulfonamides were synthesized by reaction of *N*,*N*-dichloronitrobenzenesulfonamides with trichloroethylene. Reactions of *N*-(2,2,2-trichloroethylidene)nitrobenzenesulfonamides with oxygen and nitrogen nucleophiles gave products of addition at the double C=N bond; with arenes and haloarenes, the corresponding C-amidoalkylation products were obtained.

Previously unknown *N*-(2,2,2-trichloroethylidene)-nitrobenzenesulfonamides may be convenient model compounds for studying the effect of strong electron-acceptor substituents in the arylsulfonyl group on the reactivity of *N*-(alkylidene)arenesulfonamides. These compounds are available via several approaches [1]. However, *N*-(2,2,2-trichloroethylidene)nitrobenzenesulfonamides cannot be obtained from *N*-(2,2,2-trichloro-1-hydroxyethyl)nitrobenzenesulfonamides, for the latter are not formed by condensation of trichloroacetaldehyde with nitrobenzenesulfonamides. Procedures based on condensations of sulfonamide and carboxamide derivatives with trichloroacetaldehyde are very laborious [1]. Therefore, it seemed most reasonable to develop a procedure for preparation of *N*-(2,2,2-trichloroethylidene)nitrobenzenesulfonamides by reaction of *N*,*N*-dichloronitrobenzenesulfonamides with trichloroethylene. *N*-(2,2,2-Trichloroethylidene)-arenesulfonamides were previously synthesized from trichloroethylene and *N*,*N*-dichloro derivatives of benzenesulfonamide, 4-toluenesulfonamide, and 4-chlorobenzenesulfonamide [1, 2]. Xu and Shu [3] also reported on the reaction of trichloroethylene with *N*,*N*-dichloroperfluoroalkanesulfonamides.

We have synthesized *N*,*N*-dichloronitrobenzenesulfonamides **Ia**–**Ic** as shown in Scheme 1 and studied their reactions with trichloroethylene. The chlorination of amides with freshly prepared sodium hypochlorite by the procedure described in [4] gave the corresponding *N*,*N*-dichloro derivatives **Ia**–**Ic** in 38–53% yield. Following another procedure [5], namely by passing gaseous chlorine through alkaline solutions of nitrobenzenesulfonamides, we obtained dichloro amides **Ia**–**Ic** in even poorer yield which did not exceed 30%. This may be due to ready hydrolysis of the SO_2NH group in the presence of a strong base; in this case, the major products were the corresponding salts of nitrobenzenesulfonic acids. We succeeded in slightly

Scheme 1.



X = 2-NO_2 (**a**), 3-NO_2 (**b**), 4-NO_2 (**c**).

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increasing the yield of the target *N*,*N*-dichloro derivatives (by 5–10%) when the reaction was carried out at low temperature (down to –15°C).

We have found that *N*,*N*-dichloro amides **Ia**–**Ic** are formed in up to 92% yield by chlorination of nitrobenzenesulfonamides in aqueous triethylamine. However, products **Ia**–**Ic** thus obtained are contaminated with triethylamine and its derivatives which are difficult to separate. As a result, the stability of compounds **Ia**–**Ic** to storage decreases. Purification of *N*,*N*-dichloro-2-nitrobenzenesulfonamide (**Ia**) was the most difficult. It should be also kept in mind that triethylamine is capable of promoting haloform cleavage of the target trichloroethylidene derivatives **IIa**–**IIc** (by analogy with reactions of trichloroacetaldehyde and its derivatives with strong bases [6, 7]). Therefore, in the reaction with trichloroethylene we used dichloro amide **Ia** which was synthesized by treatment of 2-nitrobenzenesulfonamide with sodium hypochlorite [5] at low temperature. The reactions of compounds **Ib** and **Ic** with trichloroethylene were carried out at reactant ratios of 1:4 and 1:8, respectively, using azobis(isobutyronitrile) as radical initiator or under UV irradiation.

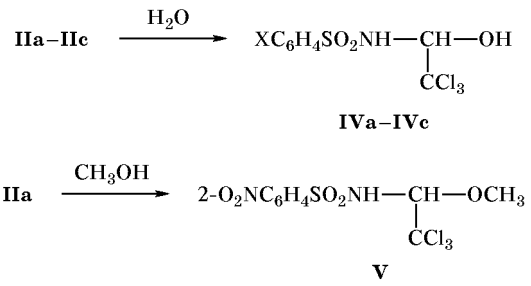
In all cases, the target *N*-(2,2,2-trichloroethylidene)-nitrobenzenesulfonamides **IIb** and **IIc** were formed in 90–92% yield. Also, 1,1,1-trichloro-2,2-bis(nitrophenylsulfonylamino)ethanes **IIIb** and **IIIc** were isolated as by-products (yield ≤10%). Diamide **IIIa** was formed from dichloro amide **Ia** only on prolonged (up to 15 h) boiling of the reaction mixture. By heating compound **Ia** with trichloroethylene for 8 h we obtained amide **IIa** and 2-nitrobenzenesulfonamide. According to our previous data [1, 2], compounds like **IIIa**–**IIIc** were not formed by reactions of *N*,*N*-dichloroarenesulfonamides with trichloroethylene under similar conditions. Presumably, the presence of a strong electron acceptor group in the benzene ring of **Ia**–**Ic** favors electrophilic chlorination of trichloroethylene to afford tetrachloroethylene and nitrobenzenesulfonamides. The latter add at the C=N bond of amides **IIa**–**IIc**, yielding diamides **IIIa**–**IIIc**. We can also state that the ability of 2-nitrobenzenesulfonamide to add across the C=N bond of *N*-(2,2,2-trichloroethylidene) derivatives **II** is considerably lower than that of the 4- and 3-nitro isomers.

UV irradiation did not appreciably change the yield of the products. However, the formation of by-products, diamides **IIIa**–**IIIc**, was reduced to 2% when the reaction was carried out in the presence of azobis(isobutyronitrile).

The structure of *N*,*N*-dichloro amides **Ia**–**Ic**, *N*-(trichloroethylidene) sulfonamides **IIa**–**IIc**, and diamides **IIIa**–**IIIc** was confirmed by elemental analysis (Table 1) and IR and ^{1}H NMR spectroscopy (Table 2). The IR spectra of compounds **Ia**–**Ic**, **IIa**–**IIc**, and **IIIa**–**IIIc** contained absorption bands due to SO_2 and NO_2 groups. Nitrobenzenesulfonamides characteristically showed doublet peaks due to NH_2 groups, which were absent in the spectra of *N*,*N*-dichloro derivatives **Ia**–**Ic** (see Experimental). In addition, the IR spectra of **IIa**–**IIc** and **IIIa**–**IIIc** contained absorption bands due to vibrations of the C=N and N–H bonds, respectively. In the ^{1}H NMR spectra of products **IIa**–**IIc** and **IIIa**–**IIIc** we observed multiplet signals from aromatic protons and signals from the CH=N or NHCHNH fragment.

Amides **IIa**–**IIc** readily react with water to give *N*-(2,2,2-trichloro-1-hydroxyethyl)nitrobenzenesulfonamides **IVa**–**IVc**; the hydrolysis occurs even on storage in air by the action of atmospheric moisture. Addition of water to amides **IIa**–**IIc** or their solutions in trichloroethylene promotes a strongly exothermic reaction (the mixture warms up to 50–60°C). Compounds **IIa**–**IIc** react with methanol in a similar way (Scheme 2). Product **V** is readily hydrolyzed on storage in a moist atmosphere or by the action of aqueous acids and bases. The hydrolysis product is hydroxy derivative **IVa**. Compounds **IVa**–**IVc** and **V** react with aqueous acids and alkalies to release the corresponding nitrobenzenesulfonamides in quantitative yield.

Scheme 2.



IV, X = 2-NO_2 (**a**), 3-NO_2 (**b**), 4-NO_2 (**c**).

Amides **IIa**–**IIc** are also active as amidoalkylating agents toward aromatic compounds. Anisole reacts with amide **IIa** in the presence of Lewis acids; the reactions with benzene, toluene, and halobenzenes occur in the presence of oleum (Scheme 3). These reactions were carried out without isolation of amides **IIa** and **IIb**, by adding excess aromatic compound to the reaction mixture.

The structure of products **IV**–**VIII** was confirmed by the elemental analyses (Table 1) and IR and ^{1}H

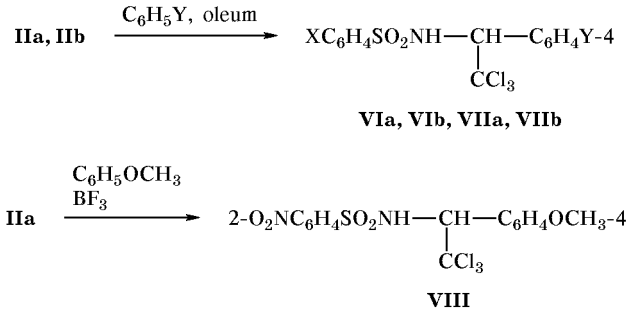
Table 1. Yields, melting points, and elemental analyses of compounds **II**–**VIII**

Comp. no.	Yield, %	mp, °C	Found, %				Formula	Calculated, %			
			C	Cl	N	S		C	Cl	N	S
IIa	90	136–138	28.73	31.51	8.03	9.13	$C_8H_5Cl_3N_2O_4S$	28.98	32.08	8.45	9.67
IIb	92	152–154	28.60	31.72	8.15	9.21	$C_8H_5Cl_3N_2O_4S$	28.98	32.08	8.45	9.67
IIc	90	148–151	28.78	31.65	8.09	9.19	$C_8H_5Cl_3N_2O_4S$	28.98	32.08	8.45	9.67
IIIa	2	218–220	31.35	19.15	10.29	12.07	$C_{14}H_{11}Cl_3N_4O_8S_2$	31.50	19.93	10.50	12.01
IIIb	5	204–208	31.37	19.43	10.41	12.18	$C_{14}H_{11}Cl_3N_4O_8S_2$	31.50	19.93	10.50	12.01
IIIc	7	212–215	31.30	19.31	10.37	12.11	$C_{14}H_{11}Cl_3N_4O_8S_2$	31.50	19.93	10.50	12.01
IVa	98	108–110	27.35	31.15	7.91	8.83	$C_8H_7Cl_3N_2O_5S$	27.49	30.43	8.01	9.17
IVb	98	153–154	27.28	31.11	7.80	8.95	$C_8H_7Cl_3N_2O_5S$	27.49	30.43	8.01	9.17
IVc	98	245–248	27.41	30.95	7.93	9.01	$C_8H_7Cl_3N_2O_5S$	27.49	30.43	8.01	9.17
V	92	104–106	29.54	30.06	7.53	8.26	$C_9H_9Cl_3N_2O_5S$	29.73	29.25	7.70	8.82
VIa	63	130–132	40.93	25.83	6.77	7.60	$C_{14}H_{11}Cl_3N_2O_4S$	41.05	25.96	6.84	7.83
VIb	71	107–110	37.51	31.48	6.23	7.13	$C_{14}H_{10}Cl_4N_2O_4S$	37.86	31.93	6.31	7.22
VIIa	45, 77[a]	150–152	42.48	25.05	6.51	7.48	$C_{15}H_{13}Cl_3N_2O_4S$	42.52	25.10	6.61	7.57
VIIb	73	165–168	39.18	24.68	6.43	7.23	$C_{14}H_{10}Cl_3FN_2O_4S$	39.32	24.87	6.55	7.50
VIII	76	158–160	40.69	24.17	6.21	7.14	$C_{15}H_{13}Cl_3N_2O_5S$	40.97	24.19	6.37	7.29

[a] From *N*-(2,2,2-trichloro-1-hydroxyethyl)-3-nitrobenzenesulfonamide (**IVb**), method *b*.

NMR spectra (Table 2). In the IR spectra of **IV**–**VIII** we observed bands typical of SO_2, NO_2, and NH groups. Hydroxy derivatives **IVa** and **IVb** also show OH group absorption. The ^{1}H NMR spectra of amides **IV**–**VIII** contain doublets typical of the NHCH group. Aromatic protons (YC_6H_4) in **VI**–**VIII** give rise to an *AA′BB′* spin system, indicating formation of *para*-substituted products.

Scheme 3.

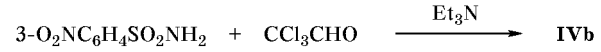


VI, X = 2-NO_2, Y = H (**a**); X = 2-NO_2, Y = Cl (b);
VII, X = 3-NO_2, Y = Me (**a**); X = 3-NO_2, Y = F (b).

We showed in [8] that *N*-(2,2,2-trichloro-1-hydroxyethyl) sulfonamides act as C-amidoalkylating agents in reactions with aromatic compounds [8]. We have synthesized compound **VIa** by reaction of hydroxy derivative **IVa** with toluene in the presence of concentrated sulfuric acid. The reaction was carried out under vigorous stirring using excess toluene as solvent. The optimal reaction time was 5 h. Nitrobenzenesulfonamides (5–10%) and sulfonation products of toluene were also formed.

It is known that a number of *N*-(trichloroethyl) sulfonamides can be obtained from the corresponding *N*-(2,2,2-trichloroethyl-1-hydroxy) derivatives [8, 9]. In some cases, the latter are more convenient starting compounds than *N*-(2,2,2-trichloroethylidene) sulfonamides which are unstable to storage. *N*-(2,2,2-Trichloro-1-hydroxyethyl) sulfonamides are in turn available through condensation of sulfonamides with trichloroacetaldehyde or trichloroacetaldehyde hydrate [6]. These data prompted us to examine the reaction of nitrobenzenesulfonamide with trichloroacetaldehyde. However, we failed to effect the condensation using concentrated sulfuric acid as catalyst; heating of the reaction mixture was also unsuccessful. We succeeded in reacting with trichloroacetaldehyde only 3-nitrobenzenesulfonamide in the presence of triethylamine (Scheme 4). The corresponding *N*-(2,2,2-trichloro-1-hydroxyethyl) sulfonamide **IVb** was formed in 70% yield, and it required additional purification. We failed to find conditions to effect the condensation of trichloroacetaldehyde with 4- and 2-nitrobenzenesulfonamides. Presumably, the reason is strong electron acceptor effect of the nitro group in the *ortho*- and *para*-positions.

Scheme 4.



Amides **II**–**VIII** are yellow or colorless crystalline substances which are soluble in DMSO, acetone, and aqueous alkalies and insoluble in water. *N*,*N*-Dichloro amides **Ia**–**Ic** are soluble in halogenated hydrocarbons; they react with acetone and diethyl ether with strong exothermic effect which can lead to inflammation. On heating above 130°C amides **Ia**–**Ic** decompose to produce a large amount of gaseous products and soot.

Thus, like known *N*-(polyhaloethylidene) sulfonamides, *N*-(2,2,2-trichloroethylidene)nitrobenzenesulfonamides synthesized from *N*,*N*-dichloronitrobenzenesulfonamides and trichloroethylene are highly reactive toward nucleophiles, including such weak nucleophilic reagents as nitrobenzenesulfonamides and aromatic compounds (as C-amidoalkylating agents). The obtained products are promising for preparation of other derivatives of the nitrobenzenesulfonamide series.

EXPERIMENTAL

The ^{1}H NMR spectra were obtained on a Tesla BS-487C instrument operating at 80 MHz; the chemical shifts were measured relative to hexamethyldisiloxane as internal reference. The IR spectra were recroded in KBr on a UR-20 spectrometer.

***N*,*N*-Dichloro-2-nitrobenzenesulfonamide (Ia)**. *a*. Gaseous chlorine was passed through a solution of 4 g of NaOH in 50–60 ml of water until the mixture no longer warmed up (1–1.5 h). The mixture was cooled to 5–10°C, and 10 g of 2-nitrobenzenesulfonamide was added with stirring. An additional amount of chlorine (0.2–0.3 mol) was passed through the mixture over a period of 1 h under stirring, and the undissolved material (compound **Ia**) was filtered off, washed with water, and dried under reduced pressure over P_2O_5. The product was dissolved in 40–50 ml of chloroform, the solution was filtered and evaporated, and the residue was additionally recrystallized from chloroform or carbon tetrachloride. Yield 5.17 g (38%), mp 65–67°C. IR spectrum, ν, cm^{-1}: 3100 (=C–H); 1520, 1310 (NO_2); 1350, 1160 (SO_2).

In a similar way, from 10 g of 3-nitrobenzenesulfonamide we obtained 7.21 g (53%) of dichloro amide **Ib**, mp 120–122°C. IR spectrum, ν, cm^{-1}: 3090 (=C–H); 1510, 1320 (NO_2); 1350, 1160 (SO_2).

N,*N*-Dichloro-4-nitrobenzenesulfonamide (**Ic**) was synthesized in a similar way from 10 g of 4-nitrobenzenesulfonamide. Yield 6.53 g (48%), mp 135°C. IR spectrum, ν, cm^{-1}: 3100 (C–H_{arom}); 1520, 1320 (NO_2); 1330, 1160 (SO_2).

b. 2-Nitrobenzenesulfonamide, 10 g, was dissolved at 5°C in 50–60 ml of a 2 M aqueous solution of sodium hydroxide, and the solution was filtered. The filtrate was cooled to –5 to –10°C, and gaseous chlorine was passed through the solution until a solid material no longer separated (2.5–3 h). The precipitate was filtered off, washed with 100 ml of water, dried under reduced pressure over P_2O_5, and purified by recrystallization from carbon tetrachloride or chloroform. Yield of **Ia** 4.90 g (36%).

In a similar way, from 10 g of 3-nitrobenzenesulfonamide we obtained 6.12 g (45%) of product **IIb**. Dichloro amide **Ic** was synthesized by the same procedure; yield 6.85 g (43%).

c. A mixture of 10 g of 2-nitrobenzenesulfonamide, 14 ml of triethylamine, and 100 ml of water was stirred until the sulfonamide dissolved. The mixture was filtered off, and gaseous chlorine was passed through the filtrate until a solid no longer separated (2–3 h), maintaining the temperature below 25°C. The precipitate was filtered off, washed with 200 ml of water, and recrystallized from carbon tetrachloride. Yield of **Ia** 7.89 g (58%).

Following the same procedure, compounds **Ib** and **Ic** were synthesized in 92 and 90% yield, respectively.

***N*-(2,2,2-Trichloroethylidene)-2-nitrobenzenesulfonamide (IIa)**. A mixture of 2.71 g of dichloro amide **Ia**, 8–10 ml of trichloroethylene (distilled over P_2O_5), and 0.01 g of azobis(isobutyronitrile) was heated in a strong stream of argon until chlorine no longer evolved (10–12 h). The mixture was filtered while hot to separate undissolved diamide **IIIa**. The filtrate was evaporated under reduced pressure in a nitrogen or argon atmosphere.

N-(2,2,2-Trichloroethylidene)nitrobenzenesulfonamides **IIb** and **IIc** were obtained in a similar way.

***N*-(2,2,2-Trichloro-1-hydroxyethyl)-3-nitrobenzenesulfonamide (IVb)**. *a*. Amide **IIb** prepared from 2.71 g of *N*,*N*-dichloro amide **Ib** and 8–10 ml of trichloroethylene was kept in air for 72 h.

Compounds **IVa** and **IVc** were obtained in a similar way.

b. Triethylamine, 0.5 ml, was added with stirring to a mixture of 5 g of 3-nitrobenzenesulfonamide and 3 ml (0.03 mol) of trichloroacetaldehyde in 20 ml of dry chloroform. The mixture warmed up to 40°C. It was stirred for 5 h at 40–45°C and was kept for 12 h at room temperature. The precipitate was filtered off, washed on a filter with 50 ml of water, and dried in

Table 2. IR and ^{1}H NMR spectra of nitrobenzenesulfonamides **II**–**VIII**

Comp. no.	IR spectrum, ν, cm^{-1}				^{1}H NMR spectrum (DMSO-d_6), δ, ppm, J, Hz			
	NH	NO_2	SO_2	other groups	CH	NH	H_{arom}	$J_{NH, CH}$
IIa	–	1520, 1360	1350, 1160	3100 (C−H_{arom}), 1650 (C=N), 1600 (C=C_{arom})	8.52 s	–	7.85 m, 8.38 m	–
IIb	–	1520, 1360	1340, 1160	3110 (C−H_{arom}), 1630 (C=N), 1600 (C=C_{arom})	8.85 s	–	7.82, 8.32, 8.57 m	–
IIc	–	1530, 1350	1340, 1160	3100 (C−H_{arom}), 1640 (C=N), 1600 (C=C_{arom})	8.56 s	–	8.15 m, 8.50 m (*AA′BB′*)	–
IIIa	3250	1540, 1350	1350, 1160	3110 (C−H_{arom}), 1600 (C=C_{arom})	5.28 t	9.45 d	7.88–8.83 m	11
IIIb	3250	1520, 1350	1340, 1170	3100 (C−H_{arom}), 1600 (C=C_{arom})	5.25 t	9.48 d	7.89–8.60 m	11
IIIc	3250	1520, 1350	1340, 1160	3110 (C−H_{arom}), 1600 (C=C_{arom})	5.26 t	9.42 d	8.20 m, 8.45 m (*AA′BB′*)	10.5
IVa	3260	1520, 1350	1340, 1170	3490 (OH), 3110 (C−H_{arom}), 1600 (C=C_{arom})	5.20 d	9.25 d	7.92–8.11 m	10
IVb	3220	1520, 1350	1340, 1160	3510 (OH), 3110 (C−H_{arom}), 1600 (C=C_{arom})	5.18 d	9.23 d	7.47–8.12 m	10
IVc	3220	1520, 1350	1340, 1160	3500 (OH), 3110 (C−H_{arom}), 1600 (C=C_{arom})	5.20 d	9.44 d	7.82–8.09 m (*AA′BB′*)	10
V[a]	3300	1540, 1360	1350, 1180	2750–3010 (C−H_{aliph}), 3100 (C−H_{arom}), 1600 (C=C_{arom})	5.15 s	–	7.89–8.15 m	–
VIa[b]	3250	1515, 1420	1340, 1165	3090 (C−H_{arom}), 1600 (C=C_{arom})	5.23 d	6.74 d	7.23–7.83 m	10.2
VIb	3300	1550, 1380	1360, 1180	3095 (C−H_{arom}), 1600 (C=C_{arom})	5.40 d	8.10 d	7.65–7.84 m (3-$NO_2C_6H_4$), 7.17–7.55 m (*AA′BB′*, 4-ClC_6H_4)	12
VIIa[c]	3250	1510, 1420	1340, 1160	2910–2950 (C−H_{aliph}), 3090 (C−H_{arom}), 1600 (C=C_{arom})	5.10 d	9.22 d	7.38–8.27 m (3-$NO_2C_6H_4$), 6.80–7.25 m (*AA′BB′*, 4-MeC_6H_4)	10
VIIb[b]	3250	1510, 1430	1350, 1170	2900–2950 (C−H_{aliph}), 3100 (C−H_{arom}), 1600 (C=C_{arom})	5.23 d	6.41 d	7.50–7.83 m (3-$NO_2C_6H_4$), 6.81–7.47 m (*AA′BB′*, 4-FC_6H_4)	10.5
VIII[d]	3250	1510, 1350	3345, 1160	2750–3010 (C−H_{aliph}), 3100 (C−H_{arom}), 1600 (C=C_{arom})	5.18 d	9.45 d	7.82–8.10 m (*AA′BB′*, 4-$NO_2C_6H_4$) 6.66–7.36 m (*AA′BB′*, 4-$MeOC_6H_4$)	10.5

[a] $\delta(CH_3)$ 3.55 ppm.
[b] The ^{1}H NMR spectrum was recorded in $CDCl_3$.
[c] $\delta(CH_3)$ 2.17.
[d] $\delta(CH_3)$ 3.63.

air. According to the ^{1}H NMR data, the product was a mixture of amide **IVb**, 6.11 g (70%), and 3-nitrobenzenesulfonamide.

2-Nitro- and 4-nitrobenzenesulfonamides failed to react with trichloroacetaldehyde under the same conditions and were recovered from the reaction mixtures.

***N*-(2,2,2-Trichloro-1-methoxyethyl)-2-nitrobenzenesulfonamide (V).** Anhydrous methanol, 4 ml, was added to amide **IIa** prepared from 2.71 g of **Ia** and 8–10 ml of trichloroethylene. The mixture spontaneously warmed up. It was kept for 12 h and evaporated, and the solid residue was recrystallized from methanol–chloroform (1 : 3).

***N*-(2,2,2-Trichloro-1-phenylethyl)-2-nitrobenzenesulfonamide (VIa).** A mixture of amide **IIa**, prepared from 2.71 g of **Ia** and 8–10 ml of trichloroethylene, 3–5 ml of dry benzene, and 0.5–1 ml of oleum (10–30% SO_3) was vigorously stirred for 5 h under argon. The organic phase was separated by decanting and evaporated. The solid residue was washed with 3–5% aqueous ammonia (10 ml) and dried. The remaining oleum was diluted with 10 ml of ice water, the mixture was stirred for 5 min, and the precipitate was filtered off, washed with aqueous ammonia, and dried in air. The products obtained from the organic and oleum phases were combined and recrystallized from benzene.

***N*-[2,2,2-Trichloro-1-(4-chlorophenyl)ethyl]-2-nitrobenzenesulfonamide (VIb)** was synthesized in a similar way from 2.71 g of dichloro amide **Ia** and excess chlorobenzene. Yield 3.15 g (71%).

***N*-[2,2,2-Trichloro-1-(4-methylphenyl)ethyl]-3-nitrobenzenesulfonamide (VIIa).** *a*. A mixture of amide **IIb**, prepared from 2.71 g of **Ib** and 8–10 ml of trichloroethylene, 3–5 ml of dry toluene, and 0.5–1 ml of oleum (10–30% SO_3) was vigorously stirred for 4–5 h. Ice water, 20 ml, was added, the mixture was stirred for 10 min, and the precipitate was filtered off, washed on a filter with 3–5% aqueous ammonia until slightly alkaline washings (~30 ml), dried in air, and recrystallized from benzene.

***N*-[2,2,2-Trichloro-1-(4-fluorophenyl)ethyl]-3-nitrobenzenesulfonamide (VIIb)** was synthesized in a similar way from 2.71 g of **Ib** and excess fluorobenzene.

b. A mixture of 3.5 g of amide **IVb**, 7 ml of toluene, and 3–5 ml of concentrated sulfuric acid was vigorously stirred for 5 h. Water, 15 ml, was added, and the mixture was stirred for 10 min. The precipitate was filtered off, washed on a filter with 5% aqueous ammonia until slightly alkaline washings (15–20 ml), dried in air, and purified by recrystallization from benzene.

***N*-[2,2,2-Trichloro-1-(4-methoxyphenyl)ethyl]-4-nitrobenzenesulfonamide (VIII).** Anhydrous methyl phenyl ether, 2 ml, and 5 drops of freshly distilled boron trifluoride–ether complex were added to the solution of amide **IIIc**, obtained from 2.71 g of **Ic** and 10 ml of trichloroethylene. The mixture was heated for 8 h at 40–50°C, evaporated by half under reduced pressure, and kept for 12 h in the cold (–10°C). The precipitate was filtered off, dried under reduced pressure, and recrystallized from ethanol.

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