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*Dedicated to Full Member of the Russian Academy of Sciences B.A. Trofimov on the 65th Anniversary of His Birth*

# *N*-Chloro-*N*-(1,2,2,2-tetrachloro- and 1,2,2-trichloroethyl)-sulfonamides from *N*,*N*-Dichlorosulfonamides and 1,2-Polychloroethenes

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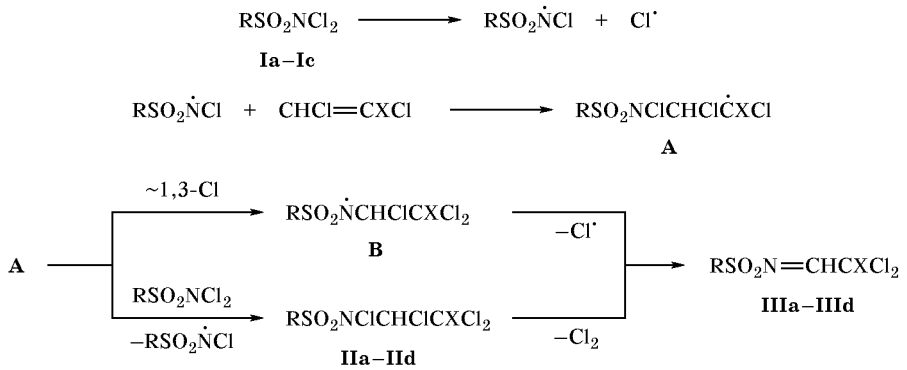
**Abstract**—*N*,*N*-Dichlorosulfonamides react with trichloroethylene and 1,2-dichloroethylene at a temperature not exceeding 20°C to afford unstable addition products, *N*-chloro-*N*-(1,2,2,2-tetrachloroethyl)- and *N*-chloro-*N*-(1,2,2-trichloroethyl)sulfonamides. The latter undergo elimination of chlorine on heating, irradiation, or prolonged storage to give the corresponding *N*-(2,2-di- or 2,2,2-trichloroethylidene)arene(or trifluoromethane)-sulfonamides.

*N*,*N*′-Dihalo amides **Ia**–**Ic** are known to react with aliphatic [1], cyclic [2], and functionally substituted ethylene derivatives [3, 4] to give the corresponding addition products, *N*-halo-*N*-β-haloalkyl amides. As a rule, such products are unstable and are readily reduced to *N*-(β-haloalkyl) amides. By contrast, the reaction of *N*,*N*-dihalo amides with 1,2-polyhaloethenes leads to formation of different products. We have found that, under conditions of thermal or UV initiation, the reaction yields *N*-(polyhaloethylidene)-carboxamides, -sulfonamides, -carbamates, or -amidophosphonates [5].

Using the CIDNP and ESR methods, we previously showed that the mechanism of reaction of *N*,*N*-dihalo amides with 1,2-polyhaloethenes includes intermediate formation of radical adduct **A** (Scheme 1); however, it remained unclear how intermediate **A** is transformed into the final Schiff base. Two possible ways of stabilization of radical **A** were discussed. The first of these is 1,3-chlorotropic rearrangement to give radical **B** which then loses chlorine atom from the α-position with respect to the radical center. The second way involves formation of unstable *N*-chloro-*N*-(1,2,2,2-tetrachloroethyl)amide **II** and its subsequent dehalo-

**Scheme 1.**




X = Cl: R = Ph (**a**), 4-$ClC_6H_4$ (**b**), $CF_3$ (**c**); X = H, R = $CF_3$ (**d**).

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genation [6]. We failed to detect radical **B** in the reaction mixture by physical methods. Also, unsuccessful attempts to synthesize addition products like **II** were reported. Thus, no proofs for any of the above reaction paths were obtained.

In the present work we succeeded in obtaining for the first time products of addition of *N*,*N*-dichlorosulfonamides **Ia**–**Ic** to 1,2-dichloroethylene and 1,1,2-trichloroethylene, *N*-chloro-*N*-(1,2,2-trichloro- and 1,2,2,2-tetrachloroethyl)sulfonamides **IIa**–**IId**. We found that strict adherence to temperature conditions is the main factor ensuring successful results. Compounds **IIa**–**IId** were synthesized by reaction of *N*,*N*-dichloro amides **Ia** and **Ib** with trichloroethylene at a temperature not exceeding 15°C; the reaction lasted several days. The addition also occurs in the dark at the same temperature, but it takes a longer time.

The addition of *N*,*N*-dichlorotrifluoromethanesulfonamide (**Ic**) to 1,2-dichloroethylene and 1,1,2-trichloroethylene occurred on exposure to light at room temperature using 3–6 equiv of polychloroethene; the reaction was complete in 15 min, and the yields of amides **IIc** and **IId** were quantitative. The process was accompanied by heat evolution. No effect of the isomeric composition of 1,2-dichloroethylene was observed (both pure *cis* and *trans* isomers and their mixture were used).

*N*-Chloro amides **IIa**–**IId** are unstable. On heating above 20°C, as well as on storage, they are converted into the corresponding Schiff bases **IIIa**–**IIId**. Presumably, the low stability of compounds like **II** is responsible for the failure to obtain the respective addition products from *N*,*N*-dichloro amides **Ia** and **Ib** and 1,2-dichloroethylene. For the same reason, only amide **IIb** was isolated in the pure state. Compound **IIa** was isolated as a mixture with Schiff base **IIIa**, and trifluoromethanesulfonamide derivatives **IIc** and **IId** were obtained as solutions in haloethenes.

The formation of *N*-chloro-*N*-(polychloroethyl)-sulfonamides **IIa**–**IId** was proved by NMR data. In the $^1$H NMR spectra of amides **IIa**–**IId** we observed characteristic singlets at δ 6.4–7.2 ppm (**IIa**–**IIc**) or a doublet at δ 6.4 ppm (**IId**), which belong to the CHCl proton. The corresponding carbon signal appears in the $^{13}$C NMR spectra of **IIa**–**IId** at $\delta_C$ 80–85 ppm. In addition, the spectra of **IIa**–**IId** contained signals from aromatic rings or $CF_3$ group and from the $CXCl_2$ moiety. The structure of amide **IIb**, which was isolated as individual substance, was also confirmed by IR spectroscopy and elemental analysis. The spectral parameters and physical constants of Schiff bases **IIIa**–**IIId** were in agreement with those reported in [7–9].

Thus we were the first to demonstrate that *N*,*N*-dichlorosulfonamides react with 1,2-dichloroethylene and trichloroethylene at a temperature not exceeding 20°C in the absence of a catalyst through intermediate formation of unstable adducts which undergo dechlorination to afford *N*-polychloroethylidenesulfonamides. It should be noted that our results do not rule out reaction path involving 1,3-chlorotropic rearrangement in the reaction of *N*,*N*-dichloro amides with 1,2-polyhaloethenes on heating or irradiation.

## EXPERIMENTAL

The IR spectra were recorded on a Specord 75IR spectrometer from samples pelleted with KBr or dispersed in mineral oil. The $^1$H and $^{13}$C NMR spectra were obtained on Bruker DPX-400 and Varian VXR-500S instruments using HMDS as internal reference.

***N*-Chloro-*N*-(1,2,2,2-tetrachloroethyl)benzenesulfonamide (IIa).** *N*,*N*-Dichlorobenzenesulfonamide (**Ia**), 2.26 g (0.01 mol), was dissolved in ~5.5 ml (0.06 mol) of trichloroethylene, and the mixture was kept for 24 h at 10–15°C and then for 3 days at –15°C. The precipitate was filtered off, dried under reduced pressure, and analyzed by NMR spectroscopy. According to the $^1$H NMR data, the product was a mixture of compounds **IIa** and **IIIa** at a ratio of 1:1; yield of **IIa** 37%. $^1$H NMR spectrum ($CDCl_3$), δ, ppm: **IIa**: 7.23 s (1H, CHCl), 7.47–7.75 m (5H, $H_{arom}$); **IIIa**: 8.40 s (1H, N=CH), 7.82–8.05 m (5H, $H_{arom}$).

***N*,4-Dichloro-*N*-(1,2,2,2-tetrachloroethyl)benzenesulfonamide (IIb).** *N*,*N*,4-Trichlorobenzenesulfonamide (**IIb**), 2.62 g (0.01 mol), was dissolved in ~5.5 ml (0.06 mol) of trichloroethylene, and the solution was kept for 4 days at 10–15°C and was then treated as described above. Yield 3.33 g (85%), mp 122–125°C (decomp.). IR spectrum, ν, cm$^{-1}$: 1180, 1380 ($SO_2$); 2980 ($C-H_{aliph}$), 3085–3090 ($C-H_{arom}$). $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 7.24 s (1H, CHCl), 7.53 and 7.91 (4H, *AA′BB′*, $C_6H_4$). $^{13}$C NMR spectrum ($CDCl_3$), $\delta_C$, ppm: 85.52 (CHCl); 98.49 ($CCl_3$); 129.33, 131.21, 132.40, 142.36 ($C_6H_4$). Found, %: C 24.22; H 1.30; Cl 53.85; N 3.77; S 8.05. $C_8H_5Cl_6NO_2S$. Calculated, %: C 24.52; H 1.29; Cl 54.28; N 3.57; S 8.18.

***N*-Chloro-*N*-(1,2,2,2-tetrachloroethyl)trifluoromethanesulfonamide (IIc).** Trichloroethylene, 0.9 ml (0.01 mol), was added to 0.44 g (0.002 mol) of *N*,*N*-dichlorotrifluoromethanesulfonamide (**Ic**) [10], and the solution was kept for 5–15 min on exposure to direct sunlight, maintaining the temperature below

30°C. The progress of the reaction was monitored by NMR spectroscopy. $^1$H NMR spectrum ($CCl_2$=CHCl), δ, ppm: 6.41 s (1H, CHCl), 6.43 s (4H, excess $CCl_2$=CHCl). $^{13}$C NMR spectrum ($CCl_2$=CHCl), $\delta_C$, ppm: 82.16 (CHCl); 97.97 ($CCl_3$); 114.84, 118.07, 121.30, 124.53 q ($CF_3$, $J_{CF}$ = 325 Hz); 116.95, 124.25 ($CCl_2$=CHCl).

***N*-Chloro-*N*-(1,2,2-trichloroethyl)trifluoromethanesulfonamide (IId)** was synthesized as described above for compound **IIc** from 0.44 g (0.002 mol) of *N*,*N*-dichlorotrifluoromethanesulfonamide (**Ic**) and 0.90 ml (0.01 mol) of 1,2-dichloroethylene. $^1$H NMR spectrum (ClCH=CHCl), δ, ppm: 5.84 d (1H, NCHCl, $^3J_{HH}$ = 8.31 Hz), 6.1 d (1H, $CHCl_2$, $^3J_{HH}$ = 8.31 Hz), 6.33 s and 6.38 s (*cis*- and *trans*-ClCH=CHCl). $^{13}$C NMR spectrum (ClCH=CHCl), $\delta_C$, ppm: 71.35 ($CHCl_2$); 79.73 (NCHCl); 114.42, 117.62, 120.82, 124.02 q ($CF_3$, $J_{CF}$ = 322 Hz); 120.45 and 120.88 (*cis*- and *trans*-ClCH=CHCl).

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