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Oxidation of *N*-(1-Hydroxypolychloroethyl)sulfonamides

I. B. Rozentsveig, G. N. Rozentsveig, G. G. Levkovskaya, and A. N. Mirskova

Favorskii Irkutsk Institute of Chemistry, Siberian Division, Russian Academy of Sciences, ul. Favorskogo 1, Irkutsk, 664033 Russia
fax: (3952) 396 046

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Abstract—*N*-(2,2,2-Trichloro-1-hydroxyethyl)- and *N*-(2,2-dichloro-1-hydroxy-2-phenylethyl)arenesulfonamides are oxidized with chromium(VI) oxide to give, respectively, *N*-(arylsulfonyl)trichloroacetamides and *N*-(arylsulfonyl)dichloro(phenyl)acetamides. Under analogous conditions *N*-(2,2,2-trichloro-1-hydroxyethyl)-trifluoromethanesulfonamide is converted into 1,1,1-trichloro-2,2-bis(trifluoromethylsulfonylamino)ethane.

N-(1-hydroxy-2-polyhaloethyl)amides are important intermediate products in the synthesis of Schiff bases from polyhalogenated aldehydes and also of polyhaloethylamides which possess biological activity and are useful from the synthetic viewpoint [1–4].

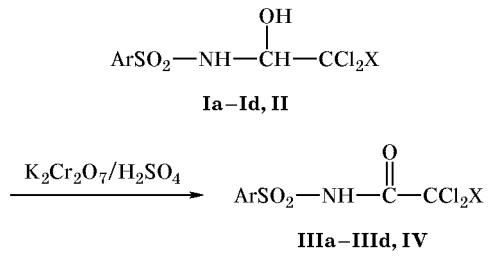
We previously performed a systematic study of the reactivity of *N*-(1-hydroxy-2-polychloroethyl)arenesulfonamides [5] and found that these compounds are unstable toward aqueous solutions of acids and bases: their decomposition leads to formation of arenesulfonamides. We also showed [2, 3] that *N*-(1-hydroxy-2-polychloroethyl)arenesulfonamides do not undergo decomposition in concentrated sulfuric acid but react with aromatic and heteroaromatic compounds.

The present communication reports for the first time on the behavior of a series of *N*-(1-hydroxy-2-polychloroethyl)sulfonamides in reactions with oxidants. *N*-(2,2,2-Trichloro-1-hydroxyethyl)arenesulfonamides **Ia**–**Id** and *N*-(2,2-dichloro-1-hydroxy-2-phenylethyl)-*p*-chlorobenzenesulfonamide (**II**) are readily oxidized with potassium dichromate in concentrated sulfuric acid to give, respectively, *N*-(arylsulfonyl)trichloroacetamides **III** and *N*-(*p*-chlorophenylsulfonyl)dichloro(phenyl)acetamide (**IV**). The reaction is exothermic, and the yields of the oxidation products attain 70–95% in 3–5 h (Scheme 1). Raising the temperature or increasing the reaction time did not result in increased yield of target products. Overheating of the reaction mixture was accompanied by vigorous evolution of NO_2.

We failed to obtain mixed amides **III** and **IV** by the action of other oxidants, such as hydrogen peroxide in acetic acid and potassium permanganate in the presence of alkali. In these cases, only the corresponding arenesulfonamides were isolated as a result of decomposition of initial *N*-(1-hydroxy-2-polychloroethyl)arenesulfonamides **Ia**–**Id** and **II**.

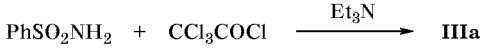
The structure of products **IIIa**–**IIId** and **IV** was proved by IR and NMR spectroscopy and analytical data. The structure of amide **IIIa** was additionally proved by independent synthesis via condensation of trichloroacetyl chloride with benzenesulfonamide in the presence of triethylamine (Scheme 2).

Scheme 1.



I, **III**, X = Cl; **Ia**, **IIIa**, Ar = Ph; **Ib**, **IIIb**, Ar = 4-ClC_6H_4; **Ic**, **IIIc**, Ar = 4-MeC_6H_4; **Id**, **IIId**, Ar = 3-$NO_2C_6H_4$; **II**, **IV**, X = Ph, Ar = 4-ClC_6H_4.

Scheme 2.



The spectral parameters and melting points of samples of **IIIa** obtained by the two methods were identical, but the yield of **IIIa** according to Scheme 2 did not exceed 20%; moreover, the product required a laborious multistep purification procedure.

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Yields, melting points, IR spectra, and elemental analyses of compounds **IIIa**–**IIId**, **IV**, and **VI**

Compound no.	Yield, %	mp, °C	IR spectrum, ν, cm^{-1}		
			C=O	NH	SO_2
IIIa	95	163–165	1200, 1380	3220	1700, 1780
IIIb[a]	86	187–189	1170, 1380	3200	1720
IIIc	77	215–218[b]	1200, 1380	3210	1730
IIId	56	172–175	1190, 1340	3220	1710
IV	69	123–124	1180, 1350	3260	1730
VI[c]	9	151–152	–	3250	–

Compound no.	Found, %				Formula	Calculated, %			
	C	H	N	S		C	H	N	S
IIIa	31.02	2.13	10.58	4.49	$C_8H_6Cl_3NO_3S$	31.76	2.00	10.60	4.63
IIIb[a]	28.13	1.75	0.02	4.19	$C_8H_5Cl_4NO_3S$	28.51	1.50	9.51	4.16
IIIc	30.80	2.02	10.45	4.45	$C_9H_8Cl_3NO_3S$	34.15	2.55	10.13	4.42
IIId	28.01	1.83	9.79	8.61	$C_8H_5Cl_3N_2O_5S$	27.65	1.45	9.22	8.06
IV	43.12	3.15	9.99	4.62	$C_{14}H_{10}Cl_3NO_3S$	44.41	2.66	8.47	3.70
VI[c]	11.18	0.93	6.73	15.07	$C_4H_3Cl_3F_6N_2O_4S_2$	11.24	0.71	6.55	15.00

[a] ^{1}H NMR spectrum, δ, ppm: 7.89, 7.60 (*AA'BB'*); ^{13}C NMR spectrum, δ_C, ppm: 100.00 (CCl_3), 129.34 (*o*- and *m*-C^2, C^3), 137.28 (CCl_2), 140.92 (CSO_2), 163.03 (C=O).

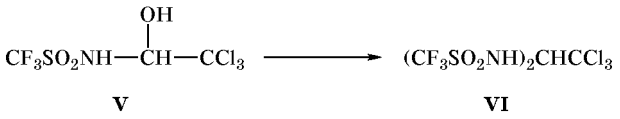
[b] Melts with decomposition.

[c] ^{1}H NMR spectrum, δ, ppm (the signals are broadened): 5.54 (CH), 11.51 (NH); IR spectrum, ν(CF_3SO_2), cm^{-1}: 1380, 1230, 1200, 1130.

Amides **III** and **IV** showed in the IR spectra absorption bands belonging to stretching vibrations of the carbonyl group (1710–1720 cm^{-1}), N–H bond (3230–3250 cm^{-1}), and SO_2 group (1150, 1370 cm^{-1}); hydroxy group absorption typical of initial hydroxyethylamides (3500 cm^{-1}) was absent. The ^{13}C NMR spectrum of sulfonamide **IIIb** contained a signal at δ_C 163.03 ppm, belonging to the carbonyl carbon atom. In the ^{1}H NMR spectra of oxidation products **III** and **IV** only signals of aromatic protons were observed. The NH proton did not appear in the spectrum, presumably because of fast H–D exchange. By contrast, the ^{1}H NMR spectra of initial *N*-(1-hydroxypolychloroethyl)amides **I** and **II** contain two doublets with a coupling constant of 10–11 Hz due to the NH–CH fragment [2, 3].

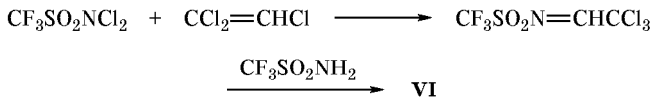
The oxidation of *N*-(2,2,2-trichloro-1-hydroxyethyl)trifluoromethanesulfonamide (**V**) takes a different pathway. Instead of the expected *N*-(trifluoromethylsulfonyl)trichloroacetamide we isolated 1,1,1-trichloro-2,2-bis(trifluoromethylsulfonylamino)ethane (**VI**) in a small yield (Scheme 3). The structure of compound **VI** was established by IR and ^{1}H NMR spectroscopy and was confirmed by elemental analysis (see table). The IR spectrum of **VI** contained absorption bands due to NH group and CF_3SO_2 fragment. In the ^{1}H NMR spectrum, the intensity of the NH signal was twice as large as that of the CH signal. Compound **VI** was also synthesized by reaction of *N*-(2,2,2-trichloroethylidene)trifluoromethanesulfonamide with trifluoromethanesulfonamide as shown in Scheme 4. Samples of **VI** obtained by the two methods had identical melting points and spectral parameters.

Scheme 3.



V **VI**

Scheme 4.



N-(arylsulfonyl)amides **III** and **IV** are crystalline substances, soluble in polar organic solvents, aromatic

hydrocarbons, and aqueous alkalies and insoluble in water.

Thus, the oxidation of accessible [1–3] *N*-(2,2,2-trichloro-1-hydroxyethyl)- and *N*-(2,2-dichloro-1-hydroxy-2-phenylethyl)arenesulfonamides with potassium dichromate in concentrated sulfuric acid can be recommended as a convenient method for preparation of *N*-arylsulfonylpolychloroacetamides which are promising intermediate products in the synthesis of oxygen- and nitrogen-containing heterocycles.

EXPERIMENTAL

The ^{1}H NMR spectra were obtained on Bruker DPX-400 (400 MHz) and Jeol FX-90Q spectrometers (90 MHz); samples were prepared as 5–10% solutions in appropriate solvents; HMDS was used as internal reference. The IR spectra were recorded on a Specord 75IR instrument from samples pelleted with KBr.

***N*-(Trichloroacetyl)benzenesulfonamide (IIIa).** *N*-(2,2,2-Trichloro-1-hydroxyethyl)benzenesulfonamide (**Ia**), 6.09 g (0.02 mol), was added in small portions under stirring to a mixture of 20 ml of concentrated sulfuric acid, 5 ml of acetic acid, and 12 g (0.04 mol) of potassium dichromate in such a way that the temperature did not exceed 25°C (above that temperature vigorous evolution of NO_2 occurs, and the mixture can overflow the reaction flask). The mixture was stirred for 5 h and poured into 50 ml of water, and the precipitate of *N*-(trichloroacetyl)benzenesulfonamide (**IIIa**) was filtered off, washed on a filter with water until it became colorless, and dried. Yield 5.61 g (93%). An additional amount of product **IIIa**, 0.11 g (2%), precipitated from the filtrate on storage.

***N*-(Trichloroacetyl)-*p*-chlorobenzenesulfonamide (IIIb)** was synthesized in a similar way from 3.4 g (0.01 mol) of *N*-(2,2,2-trichloro-1-hydroxyethyl)-*p*-chlorobenzenesulfonamide (**Ib**). Yield 2.91 g (86%).

***N*-(Trichloroacetyl)-*p*-toluenesulfonamide (IIIc)** was synthesized in a similar way from 3.19 g (0.01 mol) of *N*-(2,2,2-trichloroethyl)-*p*-toluenesulfonamide (**Ic**). Yield 3.44 g (77%).

***N*-(Trichloroacetyl)-*m*-nitrobenzenesulfonamide (IIId)** was synthesized in a similar way from 3.18 g (0.01 mol) of *N*-(2,2,2-trichloro-1-hydroxyethyl)-*m*-nitrobenzenesulfonamide (**Id**). Yield 1.77 g (56%).

***N*-[Dichloro(phenyl)acetyl]-*p*-chlorobenzenesulfonamide (IV)** was synthesized in a similar way from 3.81 g (0.01 mol) of *N*-(2,2-dichloro-1-hydroxy-2-phenylethyl)-*p*-chlorobenzenesulfonamide (**II**). Yield 2.6 g (69%).

1,1,1-Trichloro-2,2-bis(trifluoromethylsulfonylamino)ethane (VI). *a*. Following the above procedure, from 2.97 g (0.01 mol) of *N*-(2,2,2-trichloro-1-hydroxyethyl)trifluoromethanesulfonamide (**V**) 0.18 g (9%) of compound **VI** was obtained.

b. A strong stream of argon was passed over a period of 20–30 min through a solution of 2.18 g (0.01 mol) of *N*,*N*-dichlorotrifluoromethanesulfonamide [6] in 6–7 ml (0.08–0.1 mol) of trichloroethene which was preliminarily distilled over P_2O_5. The mixture was exposed to sunlight for 20–25 h, and 1.49 g (0.01 mol) of trifluoromethanesulfonamide was added to the resulting colorless solution. The mixture was heated for 60 h at 60–70°C and was then kept for 20 h at room temperature. The large transparent crystals of compound **VI** were separated and dried. Yield 1.08 g (37%).

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