*Russian Journal of Organic Chemistry, Vol. 41, No. 10, 2005, pp. 1558–1560. Translated from Zhurnal Organicheskoi Khimii, Vol. 41, No. 10, 2005, pp. 1588–1590.*


## SHORT COMMUNICATIONS

# Synthesis of *N*-(1-Sulfonylamino-2-polychloroethyl)acrylamides

**I. B. Rozentsveig, I. V. Ushakova, E. V. Kondrashov, G. N. Rozentsveig, G. G. Levkovskaya, and A. N. Mirskova**

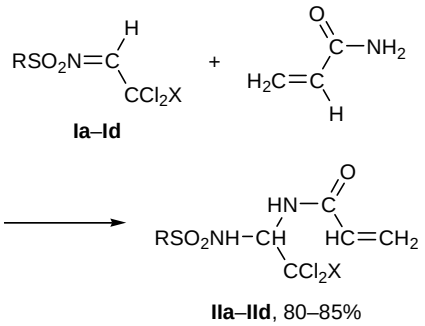
*Favorskii Irkutsk Institute of Chemistry, Siberian Division, Russian Academy of Sciences, ul. Favorskogo 1, Irkutsk, 664033 Russia*
*e-mail: i_roz@irioch.irk.ru*

Received March 23, 2005

Acrylamide and N-substituted acrylamides are used in both fine organic synthesis and industry as intermediate products for the preparation of carbo- and heterochain polymers and copolymers and polyfunctional acyclic and heterocyclic compounds. While performing our systematic studies on the synthetic potential of halogen-containing *N*-sulfonyl imines, which have become readily accessible as a result of development of methods for their synthesis from *N*,*N*-dichlorosulfonamides, polyhaloethenes, and phenylacetylene [1], we examined reactions of *N*-(2,2,2-trichloroethylidene)trifluoromethane- and -arenesulfonamides **Ia**–**Ic** and *N*-(2-phenyl-2,2-dichloroethylidene)-4-chlorobenzenesulfonamide (**Id**) with acrylamides.

We previously showed that carboxamides, ureas, and sulfonamides add to *N*-sulfonyl imines derived from polychlorinated aldehydes to give the corresponding symmetric and asymmetric 1,1-bis(acylamino)polychloroalkanes [1].

In the present work we found for the first time that Schiff bases **Ia**–**Id** obtained from the corresponding *N*,*N*-dichloro sulfonamides, trichloroethylene, and phenylacetylene readily take up acrylamide (within 2–3 h) to give *N*-(1-sulfonylamino-2-polychloroethyl)-acrylamides **IIa**–**IId**. Heating of the reaction mixture to 40–50°C accelerates the process. We observed no formation of poly(acrylamide), though acrylamide is known to readily undergo polymerization in the presence of radical initiators.




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

The structure of acrylamide derivatives **IIa**–**IId** was proved by spectral data and elemental analyses. The IR spectra of **IIa**–**IId** contained absorption bands due to stretching vibrations of the amide NH, carbonyl, and sulfonyl groups. Amides **IIa**–**IId** showed in the $^1$H NMR spectra signals corresponding to protons in the aromatic rings, NH–CH–NH fragment, and vinyl group. The latter appeared as an *ABX* spin system. In the $^{13}$C NMR spectra of **IIa**–**IId** we observed signals from carbon atoms in the polyhaloethyl fragment and carbonyl group; the $CF_3$ signal in the spectrum of **IIa** was split into a quartet due to coupling with fluorine nuclei.

Compounds **IIa**–**IId** are colorless crystalline substances which are insoluble in water, poorly soluble in nonpolar organic solvents, and readily soluble in acetone, DMSO, and aqueous alkali. The presence of proton-donor and proton-acceptor substituents, polyhalomethyl fragments, and a double bond in molecules **IIa**–**IId** makes these compounds potential ligands for complex formation with metals and promising intermediate products for fine organic synthesis, specifically for the preparation of nitrogen-containing acyclic and heterocyclic compounds and carbo- and heterochain polymers and copolymers having labile hydrogen atoms. Structural features of amides **IIa**–**IId** could give rise to formation of strong intra- and intermolecular hydrogen bonds; therefore, these compounds may

1070-4280/05/4110-1558 

be interesting models for spectroscopic studies. The synthesis of new *N*-[sulfonylamino(chloro)alkyl]acrylamides and study on their structure, heterocyclization, and polymerization are now in progress.

Commercial *N*,*N*-dichloroarenesulfonamides were preliminarily recrystallized from carbon tetrachloride. *N*,*N*-Dichlorotrifluoromethanesulfonamide was synthesized by the procedure described in [2]. Commercial acrylamide was preliminarily evacuated for 24 h over phosphoric anhydride.

***N*-(2,2,2-Trichloro-1-trifluoromethylsulfonylaminoethyl)acrylamide (IIa).** A solution of 2.18 g (0.01 mol) of *N*,*N*-dichlorotrifluoromethanesulfonamide (**Ia**) in 5–7 ml (0.40–0.60 mol) of trichloroethylene was kept on exposure to light under argon until chlorine no longer evolved (20–25 h) [3]. Acrylamide, 0.85 g (0.012 mol), was added, and the mixture was stirred for 3–4 h and evaporated under reduced pressure. The residue was washed first with hexane and then with water. Yield 2.86 g (82%), mp 163°C. IR spectrum, ν, $cm^{-1}$: 1120, 1195, 1220, 1370 ($CF_3SO_2$); 1610 (C=C); 1660 (C=O); 3110 br, 3370 (NH). $^1$H NMR spectrum, δ, ppm: 5.75 d.d (1H, $=CH_2$, $^2J$ = 1.5, $^3J_{cis}$ = 10.2 Hz), 6.17 d (1H, $CHCCl_3$, $^3J$ = 9.5 Hz), 6.25 d.d (1H, $=CH_2$, $^2J$ = 1.5, $^3J_{trans}$ = 17.2 Hz), 6.52 d.d (1H, CH=, $^3J_{cis}$ = 10.2, $^3J_{trans}$ = 17.2 Hz), 9.38 d (1H, $NHSO_2$, $^3J$ = 9.5 Hz). $^{13}$C NMR spectrum, $\delta_C$, ppm: 70.84 (CHN), 100.33 ($CCl_3$), 114.92, 118.11, 121.31, 124.52 ($CF_3$, $^1J_{CF}$ = 322.3 Hz), 129.06 (**C**H=$CH_2$), 130.34 (CH=**C**$H_2$), 164.84 (C=O). Found, %: C 20.15; H 1.70; Cl 31.15; N 8.15; S 9.05. $C_6H_6Cl_3F_3N_2O_3S$. Calculated, %: C 20.62; H 1.73; Cl 30.43; N 8.01; S 9.17.

***N*-(2,2,2-Trichloro-1-phenylsulfonylaminoethyl)acrylamide (IIb).** A solution of 2.26 g (0.01 mol) of *N*,*N*-dichlorobenzenesulfonamide (**Ib**) in 7–10 ml (0.06–0.09 mol) of trichloroethylene was heated at the boiling point in a stream of argon until chlorine no longer evolved (10–12 h) [4]. Acrylamide, 1.07 g (0.015 mol), was added, the mixture was stirred for 3 h at 50–60°C and kept for 24 h in the cold, and the precipitate was filtered off, washed with diethyl ether and water, dried, and recrystallized from chloroform. Yield 2.86 g (80%), mp 187–190°C. IR spectrum, ν, $cm^{-1}$: 1160, 1330 ($SO_2$); 1610 (C=C); 1670 (C=O); 3220, 3350 (NH). $^1$H NMR spectrum, δ, ppm: 5.57, 6.05, 6.18 (3H, *ABX* system, CH=$CH_2$); 6.13 d.d (1H, $CHCCl_3$, $^3J$ = 9.6, 9.9 Hz); 7.49 m, 7.61 m, 7.76 m (5H, $C_6H_5$); 8.73 d (1H, NHCO, $^3J$ = 9.6 Hz), 9.05 d (1H, $NHSO_2$, $^3J$ = 9.9 Hz). $^{13}$C NMR spectrum, $\delta_C$, ppm: 69.68 (CHN); 100.52 ($CCl_3$); 127.61 (CH=**C**$H_2$); 126.52, 128.84, 129.94, 140.75 ($C_{arom}$); 132.57 (**C**H=$CH_2$); 164.32 (C=O). Found, %: C 36.85; H 3.12; Cl 29.35; N 7.87; S 8.78. $C_{11}H_{11}Cl_3N_2O_3S$. Calculated, %: C 36.94; H 3.10; Cl 29.74; N 7.83; S 8.96.

***N*-[2,2,2-Trichloro-1-(4-chlorophenylsulfonylamino)ethyl]acrylamide (IIc)** was synthesized as described above for compound **IIb** from 2.61 g (0.01 mol) of *N*,*N*,4-trichlorobenzenesulfonamide (**Ic**). Yield 3.33 g (85%), mp 212–215°C. IR spectrum, ν, $cm^{-1}$: 1150, 1310 ($SO_2$); 1620 (C=C); 1670 (C=O); 3260, 3340 (NH). $^1$H NMR spectrum, δ, ppm: 5.58 d.d (1H, $=CH_2$, $^2J$ = 2.0, $^3J_{cis}$ = 9.9 Hz), 6.02 d.d (1H, $=CH_2$, $^2J$ = 2.0, $^3J_{trans}$ = 17.0 Hz), 6.05 d.d (1H, $CHCCl_3$, $^3J$ = 9.6, 9.8 Hz), 6.17 d.d (1H, CH=, $^3J_{cis}$ = 9.9, $^3J_{trans}$ = 17.0 Hz), 7.55 d and 7.75 d (2H each, *AA'BB'* system, $C_6H_4$), 8.73 d (1H, CONH, $^3J$ = 9.6 Hz), 9.16 d (1H, $SO_2NH$, $^3J$ = 9.8 Hz). $^{13}$C NMR spectrum, $\delta_C$, ppm: 69.67 (CHN); 100.25 ($CCl_3$); 127.75 (CH=**C**$H_2$); 137.59 (**C**H=$CH_2$); 128.64, 129.02, 129.81, 139.43 ($C_{arom}$); 164.40 (C=O). Found, %: C 33.78; H 2.51; Cl 36.05; N 7.20; S 8.35. $C_{11}H_{10}Cl_4N_2O_3S$. Calculated, %: C 33.70; H 2.57; Cl 36.17; N 7.14; S 8.18.

***N*-[2,2-Dichloro-1-(4-chlorophenylsulfonylamino)-2-phenylethyl]acrylamide (IId).** A mixture of 3.63 g (0.01 mol) of *N*-(2,2-dichloro-2-phenylethylidene)-4-chlorobenzenesulfonamide (**Id**) [5] and 1.42 g (0.02 mol) of acrylamide in carbon tetrachloride was stirred on heating for 2 h. The mixture was evaporated, and the residue was washed with water and dried. Yield 3.56 g (82%), mp 164–166°C. IR spectrum, ν, $cm^{-1}$: 1150, 1320 ($SO_2$); 1620 (C=C); 1660 (C=O); 3140 br, 3320 (NH). $^1$H NMR spectrum, δ, ppm: 5.46 d.d (1H, $=CH_2$, $^2J$ = 2.0, $^3J_{cis}$ = 10.1 Hz), 5.86 d.d (1H, $=CH_2$, $^2J$ = 2.0, $^3J_{trans}$ = 17.0 Hz), 6.07 d.d (1H, CH=, $^3J_{cis}$ = 10.1, $^3J_{trans}$ = 17.0 Hz), 6.18 d.d (1H, NCH, $^3J$ = 9.6, 10.0 Hz), 8.47 d (1H, NHCO, $^3J$ = 9.6 Hz), 8.75 d (1H, $NHSO_2$, $^3J$ = 10.0 Hz). $^{13}$C NMR spectrum, $\delta_C$, ppm: 67.46 (NCH); 94.29 ($CCl_2$); 126.87 (CH=**C**$H_2$); 138.83 (**C**H=$CH_2$); 126.99, 128.17, 128.62, 128.83, 129.55, 130.15, 137.28, 139.74 ($C_{arom}$); 163.89 (C=O). Found, %: C 46.85; H 3.39; Cl 24.45; N 6.25; S 7.05. $C_{17}H_{15}Cl_3N_2O_3S$. Calculated, %: C 47.08; H 3.49; Cl 24.52; N 6.46; S 7.39.

The NMR spectra were recorded on a Bruker DPX-400 spectrometer at 400.6 and 100.61 MHz for $^1$H

and $^{13}C$, respectively, from solutions in DMSO-$d_6$ ($c$ = 5%); the chemical shifts were measured relative to hexamethyldisiloxane as internal reference. The IR spectra were measured on a Specord 75IR spectrometer from samples prepared as KBr pellets.

## REFERENCES

1. Levkovskaya, G.G., Drozdova, T.I., Rozentsveig, I.B., and Mirskova, A.N., *Usp. Khim.*, 1999, vol. 68, p. 638.
2. Nazaretyan, V.P., Radchenko, O.A., and Yagupol'skii, L.M., *Zh. Org. Khim.*, 1974, vol. 10, p. 2460.
3. Rozentsveig, I.B., Levkovskaya, G.G., Kondrashov, E.V., Evstaf'eva, I.T., and Mirskova, A.N., *Russ. J. Org. Chem.*, 2001, vol. 37, p. 1559.
4. Mirskova, A.N., Levkovskaya, G.G., Drozdova, T.I., Kalikhman, I.D., and Voronkov, M.G., *Zh. Org. Khim.*, 1982, vol. 18, p. 452.
5. Drozdova, T.I., Levkovskaya, G.G., and Mirskova, A.N., *Zh. Org. Khim.*, 1992, vol. 28, p. 1236.