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SHORT COMMUNICATIONS

N-(2,2,2-Trichloroethylidene)- and *N*-(2,2-Dichloro-2-phenylethylidene)-4-methoxybenzenesulfonamides from 4-Methoxy-*N*,*N*-dichlorobenzenesulfonamide, Trichloroethylene, and Phenylacethylene

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Abstract—Reaction of 4-methoxy-*N*,*N*-dichlorobenzenesulfonamide with trichloroethylene and phenylacetylene underlies an effective method developed for the synthesis of highly reactive 4-methoxy-*N*-(2,2,2-trichloroethylidene)- and 4-methoxy-*N*-(2,2-dichloro)-2-phenylethylidene)benzenesulfonamides, valuable reagents for the preparation of new difficultly accessible derivatives of the sulfonamide series.

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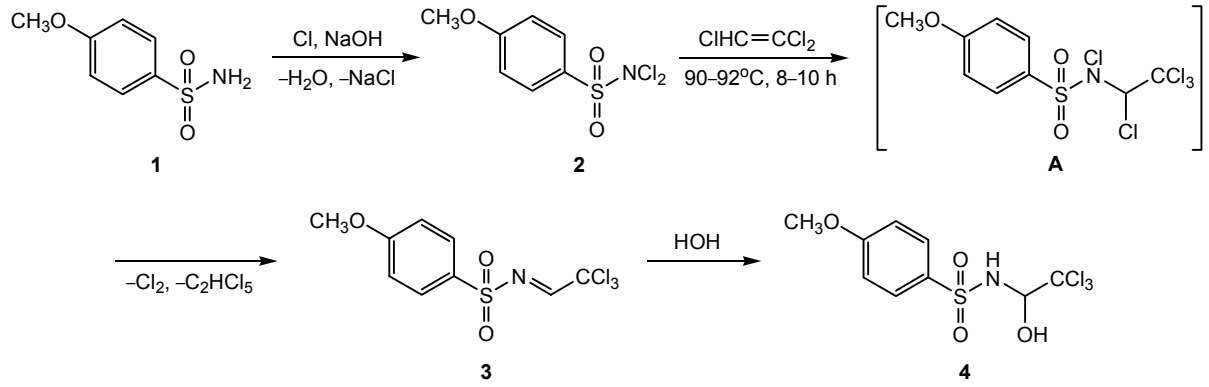
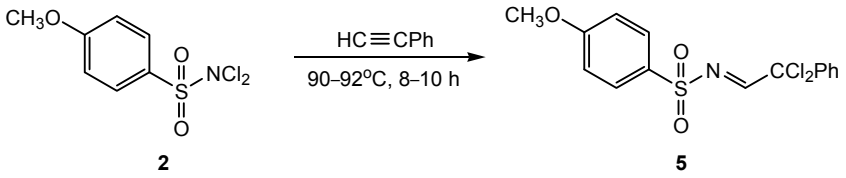
Highly electrophilic halogen-substituted sulfonylimines are valuable reagents for the production of a variety of derivatives of the sulfonamide series [1–7]. The development of methods for the synthesis of activated arylsulfonylimines of halocarbonyl compounds is an urgent task. We are developing one of the most effective approaches to the synthesis of imines of this type, underlain by the reaction of *N*,*N*-dichlorosulfonamides with 1,2-polyhaloethenes or phenylacetylene [2, 3, 8–14]. This approach allows the synthesis of sulfonylimines of polyhaloaldehydes in a single preparative step in high yields.

In extension of the research on the development of the synthesis of highly reactive *N*-(polyhaloethylidene)arenesulfonamides we chlorinated the 4-methoxybenzenesulfonamide **1** and for the first time we studied the interaction of the obtained 4-methoxyphenyl-*N*,*N*-dichlorosulfonamide **2** with trichloroethylene and phenylacetylene (Schemes 1, 2). Previously, dichloroamide **2** was obtained in a lower yield (76%) by chlorination of sulfonamide **1** with a triple amount of calcium hypochlorite [15].

Scheme 1.



Scheme 2.



2 **5**

The reaction of dichloroamide **2** with trichloroethylene was carried out by boiling for 8–10 h at a reagent ratio of 1 : 6–8. Similar conditions were applied in the preparation of other arylsulfonylimines of polychloroaldehydes [8–14].

4-Methoxy-*N*-(2,2,2-trichloroethylidene)benzenesulfonamide **3** was isolated in 80% yield. Imine **3** is apparently formed as a result of a chain radical reaction proceeding through the formation of an unstable adduct **A**, which under the reaction conditions is easily dechlorinated (Scheme 1).The possibility of compound **A** formation in such processes is shown in [9]. Due to the addition of chlorine to trichlorethylene a second reaction product, pentachloroethane, is formed.

Previously the synthesis of imine **3** in the reaction of unstable 4-methoxy-*N*-sulfinylbenzenesulfonamide with chloral was reported [16], but data on the physicochemical properties of compound **3** were not revealed and its yield was not indicated.

Imine **3** adds water with self-heating and forms *N*-(1-hydroxy-2,2,2-trichloroethyl)-4-methoxybenzenesulfonamide **4** in a quantitative yield (Scheme 1). Compound **4** is also formed when the imine **3** is stored for several hours in air as a result of the latter's reaction with atmospheric moisture.

To synthesize 4-methoxy-*N*-(2-phenyl-2,2-dichloroethylidene)benzenesulfonamide **5**, we brought dichloroamide **2** in the reaction with phenylacetylene (Scheme 2). The reaction was carried out under conditions which made it possible to obtain in a similar process a maximum yield of arylsulfonylimines of phenyldichloroacetic aldehyde [17].

The structure of compounds **1–5** is proved by spectral methods and is confirmed by elemental analysis data. Hemiaminal **4** was obtained by authentic synthesis from chloral and sulfonamide **1**. In the IR spectra of sulfonamides **1–5** absorption bands appear corresponding to the assumed structures. The relative integral intensities and position of the signals in ^{1}H and ^{13}C NMR spectra of compounds **1–5** fully correspond to their formulas.

The presence of an electron-donor substituent in the aromatic ring of compounds **3–5** makes it possible to consider them as promising for further studies in the reactions of intramolecular heterocyclization.

4-Methoxy-*N*,*N*-dichlorobenzenesulfonamide (2). The mixture prepared from 1.60 g (40 mmol) of NaOH and 1.87 g (10 mmol) of 4-methoxybenzenesulfonamide **1** in 30 mL of water was filtered, and chlorine was bubbled through the filtrate until the absorption ceased, and the reaction mixture was kept at room temperature for 30 minutes. The precipitate of dichloroamide **2** was filtered off, washed with water, and dried. Yield 2.48 g (97%), mp 48°C (mp 52°C [15]). IR spectrum, ν, cm^{-1}: 2949–3019 (C–H_{Ar}), 1164, 1268 (SO_2). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.95 s (3H, CH_3), 7.11 d, 8.02 d (4H, C_6H_4). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 55.85 (OCH_3), 114.49, 119.57, 133.85, 165.68 (C_6H_4). Found, %: C 32.82; H 2.52; Cl 26.64; N 5.57; S 8.75. $C_7H_7Cl_2NO_3S$. Calculated, %: C 32.83; H 2.75; Cl 27.69; N 5.47; S 12.52.

4-Methoxy-*N*-(2,2,2-trichloroethylidene)benzenesulfonamide (3). The mixture of 2.56 g (10 mmol) of dichloroamide **2** and 10.50 g (80 mmol) of trichloroethylene was boiled for 8–10 h in an argon atmosphere until the chlorine evolution ceased (test with KI starch paper). The solution was kept for 24 h at 5°C, the precipitate of imine **3** was rapidly filtered off in a vacuum on a glass frit filter, washed on the filter with an anhydrous hexane, and dried in a vacuum desiccator at a reduced pressure over P_2O_5. Yield 2.53 g (80%), mp 118–121°C (hydroscopic). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.98 s (3H, CH_3), 7.00 d, 7.81 d (4H, C_6H_4), 7.94 s (1H, N=CH). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 55.41 (CH_3), 71.78 (CCl_3), 100.42, 113.73, 127.88, 131.14, 133.72, 162.74 (C_6H_4), 142.05 (CH=N). Found, %: C 34.27; H 2.81; Cl 33.09; N 4.58; S 10.01. $C_9H_8Cl_3NO_3S$. Calculated, %: C 34.14; H 2.55; Cl 33.60; N 4.42; S 10.13.

***N*-(1-Hydroxy-2,2,2-trichloroethyl)-4-methoxybenzenesulfonamide (4).** *a.* Imine **3**, 1.58 g (5 mmol) was stored in open air for 24 h. Yield 1.67 g (98%).

b. A mixture of 1.87 g (10 mmol) of 4-methoxybenzenesulfonamide **1**, 1.48 g (10 mmol) of chloral, and 0.5 mL of conc. H_2SO_4 was intensively stirred for 25 minutes at 35–40°C. The mixture was cooled to room temperature. The precipitate was repeatedly washed with water till neutral washings, filtered off, and dried. Yield 2.31 g (69%), mp 94°C. IR spectrum, ν, cm^{-1}: 3424 (O–H), 3369 (N–H), 3265, 3208 (C–H, C–H_{Ar}), 1162, 1331 (SO_2). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.89 s (3H, CH_3), 5.32 d (1H, NCH, $^3J_{CH,NH}$ 10.2 Hz), 5.52 d (1H, NH, $^3J_{CH,NH}$ 10.2 Hz), 6.98 d, 7.87 d (4H, C_6H_4). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 55.25 (CH_3), 84.81 (CCl_3), 99.39 (NCH), 113.93, 129.14, 130.89, 163.07 (C_6H_4). Found, %: C 32.63; H 2.88; Cl 32.10; N 4.02; S 9.39. $C_9H_{10}Cl_3NO_4S$. Calculated, %: C 32.31; H 3.01; Cl 31.79; N 4.19; S 9.58.

4-Methoxy-*N*-(2-phenyl-2,2-dichloroethylidene)-benzenesulfonamide (5). A solution of 4.08 g (40 mmol) of phenylacetylene in 30 ml of anhydrous CCl_4 was cooled to –3°C while bubbling with argon. To the solution was added in portions 7.68 g (30 moles) of dichloroamide **2**. The reaction mixture was stirred for 1.5 h at room temperature, then 8–10 h at 70–76°C. To isolate imine **5** in an individual form, the mixture was kept for 24 h at –5°C, the precipitate was filtered off, washed on the filter with anhydrous hexane, and dried in a vacuo over P_2O_5. Yield 1.51g (40%), mp 105°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 4.05 s (3H, CH_3), 7.09 d, 7.97 d (4H, C_6H_4), 7.38 d, 7.44 t, 7.60 d (5H, C_6H_5), 8.83 s (1H, N=CH). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 55.88 (CH_3), 75.65 (CH), 115.08, 126.34, 127.56, 127.32, 129.36, 130.80, 135.47, 137.27, 163.30 (Ar), 159.51 (C=N). Found, %: C 49.57; H 3.81; Cl 18.79; N 3.58; S 9.01. $C_{15}H_{13}Cl_2NO_3S$. Calculated, %: C 50.29; H 3.66; Cl 19.79; N 3.91; S 8.95.

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-400 spectrometer (operating frequencies 400.61, 100.13 MHz, respectively), internal reference TMS. Chemical shifts were measured with respect to TMS with an accuracy of 0.01 and 0.02 ppm, respectively. IR spectra were taken on a Bruker IFS-25 spectrometer from pellets with KBr. Elemental analysis was performed on an automatic CHNS-analyzer Thermo scientific Flash 2000.

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