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Synthesis of *N*-(2-Benzene-2,2-dichloroethylidene)-4-chlorobenzenesulfonamide and *N*-(2-Benzene-2,2-dichloroethylidene)-4-methylbenzenesulfonamide

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Abstract—In reaction of *N*,*N*-dichloro-4-chlorobenzene- and *N*,*N*-dichloro-4-methylbenzenesulfonamides with phenylacetylene were obtained in good yield N-(2-benzene-2,2-dichloroethylidene)arenesulfonamides. The latter undergo nucleophilic addition of water, ethanol, and arenesulfonamides.

We reported formerly [1] on reaction of *N*,*N*-dichlorobenzenesulfonamide with phenylacetylene yielding *N*-(2-benzene-2,2-dichloroethylidene)benzenesulfonamide alongside the other products arising from further transformations and reactions of the latter imine. A.A.Petrov et al [2] obtained *N*-(2-benzene-2,2-dichloroethylidene)-4-chlorobenzenesulfonamide in lower yield by prolonged (25 h) heating of a mixture containing phenylacetylene and *N*,*N*-dichlorobenzenesulfonamide; the other reaction products were not thoroughly investigated. Aiming at further investigation of reactions between phenylacetylene and *N*,*N*-dichloroarenesulfonamides and at refining the synthetic procedures for the above imines we studied the effect of reaction conditions of *N*,*N*-dichloro-4-chlorobenzene- and *N*,*N*-dichloro-4-methylbenzenesulfonamides (**Ia, b**) with phenylacetylene (**II**).

$$\underset{\textbf{Ia,b}}{ArSO_2NCl_2} + \underset{\textbf{II}}{C_6H_5C{\equiv}CH} \rightarrow \underset{\textbf{IIIa,b}}{ArSO_2N{=}CHCCl_2C_6H_5}$$

$$(ArSO_2NH)_2CHCCl_2C_6H_5 + ArSO_2NH_2$$

IVa,b **Va,b**

Ar = 4-ClC_6H_4 (**a**), 4-$CH_3C_6H_4$ (**b**).

It was established that the reaction of *N*,*N*-dichloro-4-chlorobenzene- or *N*,*N*-dichloro-4-methylbenzenesulfonamides (**Ia, b**) with phenylacetylene (**II**) in 1 : 4 ratio proceeded under inert atmosphere (nitrogen or argon) in anhydrous carbon tetrachloride for 0.5–1 h at 15–20°C and 0.5–1 h at 55–60°C to afford N-(2-benzene-2,2-dichloroethylidene)arenesulfonamides (**IIIa, b**) in 80 and 82% yields, respectively. As side products formed amides **IVa, b** in 6–8% yield and amides **Va, b** in 5–7% yield.

The yield of imines **IIIa, b** is strongly affected by the temperature at the initial reaction period: the increase over 20°C reduces the yield of imines by 15–20% with simultaneous growth of side products content: of 1,1-di(arenesulfonamido)-2-phenyl-2,2-dichloroethanes (**IVa, b**) to 12–14%, and of arenesulfonamides (**Va, b**) to 15–20%. To obtain high yields of compounds **IIIa, b** it is desirable to add slowly the phenylacetylene (**II**) to a solution of dichloroamides **Ia, b** in CCl_4 avoiding overheating above 20°C.

The changed order of reagents mixing, namely, addition of dichloroamides **Ia, b** in CCl_4 solution to phenylacetylene also results in strong reduction of imines **IIIa, b** yield due to proceeding of the side processes providing predominantly sulfonamides **Va, b**. After the mixing of reagents is completed the reaction mixture is heated to 55–60°C and stirred for about 1 h. The longer heating of the reaction mixture gives rise to side processes to afford amides **IVa, b, Va, b** at the expense of decrease in the yield of the target products **IIIa, b**.

The previously obtained data [1] on the effect of reagents ratio on the yield of reaction products are in agreement with those obtained in this study of reaction between dichloroamides **Ia, b** and phenylacetylene (**II**). Thus at two-fold excess of phenylacetylene (**II**) the reaction furnishes imines **IIIa, b** in sufficiently high yield (70–75%). The rise in the yield by 7–9% is attained at increasing the excess of phenylacetylene (**II**) from 2-fold to 4-fold. Further increase in phenylacetylene excess to 6-fold does not affect the yield of compounds **IIIa, b**. The attempt to carry out the reaction at equimolar reagents ratio and initiation by UV-irradiation at 30°C did not result in high yield

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Table 1 Yields, melting points, and elemental analyses of *N*-arenesulfonylimines **IIIa, b** and N-substituted arenesulfonamides **IVa, b, VIa, b, VIIa, b**

Compd. no.	Yield, %	mp, °C	Found, %					Formula	Calculated, %				
			C	H	Cl	N	S		C	H	Cl	N	S
IIIa	82	104–105[a]	46.24	2.74	29.24	3.83	8.79	$C_{14}H_{10}Cl_3NO_2S$	46.54	2.79	29.06	3.88	8.86
IIIb	80	105–106	52.37	3.68	20.29	4.37	9.54	$C_{15}H_{13}Cl_2NO_2S$	52.79	3.84	20.51	4.11	9.38
IVa	67	217–219	43.09	3.09	25.52	5.03	11.52	$C_{20}H_{16}Cl_4N_2O_4S_2$	43.48	2.92	25.34	5.07	11.59
IVb	65	200–202	50.98	4.61	13.62	5.29	12.28	$C_{22}H_{22}Cl_2N_2O_4S_2$	51.56	4.33	13.66	5.47	12.50
VIa	79	124–126	44.56	3.40	27.44	4.06	8.27	$C_{14}H_{12}Cl_3NO_3S$	44.33	3.79	27.68	3.70	8.44
VIb	78	115–119	49.91	4.22	19.68	3.80	8.88	$C_{15}H_{15}Cl_2NO_3S$	50.14	4.21	19.48	3.90	8.91
VIIa	78	86–88	47.34	3.78	25.21	3.67	7.35	$C_{16}H_{16}Cl_3NO_3S$	47.18	3.96	25.78	3.44	7.86
VIIb	74	89–91	51.93	4.64	17.73	3.56	8.03	$C_{17}H_{19}Cl_2NO_3S$	52.58	4.93	18.26	3.61	8.26

[a] mp 103.5°C [2].

of imines **IIIa, b**. These compounds were isolated in 25 to 28% yield. Under these reaction conditions a stronger chlorine liberation was observed.

We did not observe under our reaction conditions a formation of 1-(4-chlorophenylsulfonamido)-2-chloro-2-phenylethene; in [2] it was obtained as presumed due to intramolecular 1,3-migration of chlorine in the initially arising adduct, 1-[*N*-chloro-*N*-(4-chlorophenyl)sulfonamido]-2-chloro-2-phenylethene.

Thus under experimental conditions found we succeeded to get an yield of imine **IIIa** by 15% higher than in [2] and to reduce the reaction time from 25 to 1.5–2 h. Under the same conditions we also obtained in high yield and high purity imine **IIIb**.

The formation of *N*-arenesulfonylimines **IIIa, b** occurs apparently along the mechanism previously assumed in [1, 2], namely, by 1,3-migration of chlorine in the initially arising adduct $ArSO_2NClCH{=}CClC_6H_5$. The resulting from the reaction amides **Va, b** in the course of the process add across the azomethine bond of compounds **IIIa, b** to provide amides **IVa, b**.

The compounds synthesized are colorless crystalline substances, well soluble in dimethyl sulfoxide, dimethylformamide, acetone, chloroform, sparingly soluble in benzene, ethyl ether, insoluble in hexane.

Azomethine structure of compounds **IIa, b** was proved by NMR and IR spectroscopy; the composition was confirmed by elemental analysis (Table 1).

In the IR spectra of compounds **IIIa, b** appear characteristic absorption bands from stretching and bending vibrations of bonds in the following regions, cm^{-1}: 1635 and 1640 (C=N), 1170 and 1340 (O=S=O), 1450 and 1455 (C=Carom), 3080 (=C–Harom), 760–820 (C–Cl) respectively.

In the ^1H NMR spectra (in DMSO-d_6) of imines **IIIa, b** alongside the signals of the aromatic rings in the 7.40–7.87 region are observed the singlets of the methine protons at 8.25 and 8.21 ppm respectively, and also a singlet of a methyl group in compound **IIIb** at 2.38 ppm. In the ^1H NMR spectrum of compound **IIIa** in $CDCl_3$ the singlet of the methine proton appears at 8.51 ppm. The spectral characteristics of compound **IIIa** obtained in [2], namely the presence in the ^1H NMR spectrum (in $CDCl_3$) of two peaks belonging to methine protons at 8.67 and 8.49 ppm in 1:5 ratio, were not explained by Petrov *et al*. Probably the signal at 8.67 ppm originated from NH group of amide **VIa** that might have formed if under conditions of the reaction in [2] were present traces of moisture. In the ^1H NMR spectrum (in DMSO-d_6) of specially prepared compound **VIa** appeared a doublet signal at 8.56 ppm from the proton of NH group. To our regret, due to the low solubility of compound **VIa** in $CDCl_3$ we failed to compare the spectral data with those published in [2].

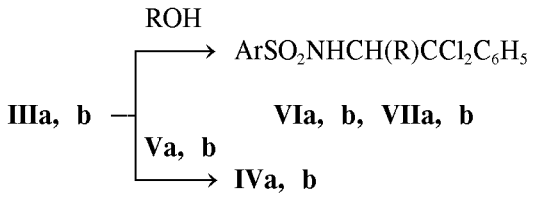
It was previously demonstrated that the azomethine bond of *N*-benzenesulfonylimine of dichlorophenylacetic aldehyde was highly electrophilic toward proton-donor reagents (water, alcohols. carboxylic acids, and amides [1–4], but reactivity of imine **IIIa** was revealed only by one example [2]. *N*-(2-Benzene-2,2-dichloroethylidene)-4-chlorobenzenesulfonamide and *N*-(2-benzene-2,2-dichloroethylidene)-4-methylbenzenesulfonamide (**IIIa, b**) prepared by us add at heating across the N=C bond water, ethanol, arene-

Table 2. IR and ^{1}H NMR spectra of N-substituted arensulfonamides **IVa, b, VIa, b, VIIa, b**

Compd.	^{1}H NMR spectrum, δ, ppm, *J*(NH–CH)						IR spectrum, ν[a], cm^{-1}				
no.	NH	H (arom)	CH	CH_2	CH_3	*J*, Hz	NH	=CH (arom)	C=C (arom)	SO_2	Alk
IVa	8.34 d	7.41–7.88 m	5.35 d			9.2	3220, 3280	3050, 3070	1480, 1420	1165, 1340	
IVb	8.28 d	7.29–7.67 m	5.38 d		2.34 s	9.3	3220, 3280	3045, 3075	1475	1175, 1340	
VIa	8.56 d	7.53–7.81 m	5.44 d			9.76	3250, 3270	3042	1460–1480	1160, 1320	
VIb	8.33 d	7.55–7.74 m	5.42 d		2.35 s	9.65	3245, 3270	3040	1446, 1550	1160, 1320	
VIIa	8.61 d	7.52–7.78 m	5.28 d	3.47 d	0.81 t	9.2	3230	3050	1465	1180, 1325	2860, 2935, 2970
VIIb	8.72 d	7.34–7.83 m	5.31 d	3.39 d	0.79 t, 2.32 s	9.4	3235	3045	1460	1180, 1330	2855, 2940, 2970

[a] For compounds **VIa** and **VIb** ν(OH) respectively 3480, 3520 and 3440 cm^{-1}.

sulfonamides **Va, b** to afford *N*-(2-phenyl-2,2-dichloro-1-hydroxy- or 2-ethoxyethyl)arensulfonamides (**VIa, b, VIIa, b**) and 1,1-di(arensulfonamido)-2-phenyl-2,2-dichloroethanes **IVa, b** in high yields.



VI, VII, R = OH (**VIa, b**), OC_2H_5 (**VIIa, b**); Ar = 4-ClC_6H_4 (**a**), 4-$CH_3C_6H_4$ (**b**).

Synthesized colorless crystalline compounds **IV, VI, VII** are well soluble in acetone, dimethyl sulfoxide, dimethylformamide, sparingly soluble in chloroform, benzene, ethyl ether, insoluble in water. Their composition and structure were proved by elemental analysis, ^{1}H NMR and IR spectroscopy (Tables 1, 2).

In the IR spectra of compounds **IVa, a, VIa, b, VIIa, b** appear the absorption bands of the stretching and bending vibrations of the bonds N–H, O=S=O, and of benzene rings, alkyl and hydroxy groups (Table 2). In the IR spectrum of compounds **IVa, b** are observed two characteristic absorption bands of the N–H bond at 3220 and 3280 cm^{-1}. In the IR spectra of compound **VIa** from KBr pellets the absorption bands of N–H and O–H bonds appear as double bands at 3190 and 3280, 3480 and 3520 cm^{-1} respectively. In solution in CCl_4 the corresponding spectrum contains single bands at 3370 (N–H) and 3575 cm^{-1} (O–H). This absorption of the hydroxy group suggests its participation both in hydrogen bonds and intramolecular cyclization.

The ^{1}H NMR spectra of compounds **VIa, b, VIIa, b** contain signals of protons from groups NH, CH with ^3J(NH–CH) 8–9 Hz, and multiplets from protons in benzene rings (Table 2). In the ^{1}H NMR spectra of compounds **IVa, b** due to coupling the signal of NH proton is split into doublet, that of CH into triplet; also appear the multiplets from benzene ring protons.

EXPERIMENTAL

IR spectra were recorded on spectrophotometer UR-20 from KBr pellets in 400–4000 cm^{-1} region. ^{1}H NMR spectra were registered on Jeol FX-90Q instrument (90 MHz), solvent DMSO-, internal reference HMDS.

***N*-(2-Benzene-2,2-dichloroethylidene)-4-chlorobenzenesulfonamide (IIIa).** To 5.12 g of compound **Ia** dissolved in 15 ml of anhydrous carbon tetrachloride was slowly added dropwise at 15–20°C 9 ml

of phenylacetylene (**II**) (at fast mixing of reagents occurred self-heating to 55–60°C). Then the reaction mixture was vigorously stirred at 55–60°C for 0.5–1 h. Throughout the reaction time nitrogen or argon was bubbled through the reaction mixture. The reaction mixture was cooled to 35–40°C, the precipitated crystals were filtered off, washed with hot petroleum ether, and extracted with hot benzene. The compound insoluble in benzene was filtered off to obtain 0.6 g (6%) of amide **IVa**. From the benzene solution on cooling precipitated amide **Va** (1.9 g, 5%), mp 144°C (mp 143–145°C [5]). The mother liquor in carbon tetrachloride was cooled, and the precipitated compound was filtered off; thus we obtained 5.9 g (82%) of imine **IIIa**.

***N*-(2-Benzene-2,2-dichloroethylidene)-4-methylbenzenesulfonamide (IIIb)** was prepared in a similar way from 4.8 g of amide **Ib** and 9 ml of phenylacetylene (**II**). We obtained 5.4 g (80%) of imine **IIIb**, 0.6 g (8%) of compound **IVb**, and 0.2 g (7%) of amide **Vb**, mp 138°C.

1,1-Di(4-chlorophenylsulfonamido)-2-phenyl-2,2-dichloroethane (IVa). To a solution of 3.6 g of imine **IIIa** in 10 ml of benzene was added 1.9 g of amide **Va**. The reaction mixture was refluxed in benzene for 5 h at vigorous stirring, and then cooled to room temperature. The precipitated crystals were filtered off, washed with hot benzene and then with ethyl ether. The compound that remained after extraction with solvents was dried to yield 3.5 g of amide **IVa**.

1,1-Di(4-methylphenylsulfonamido)-2-phenyl-2,2-dichloroethane (IVb) was similarly prepared from 3.4 g of imine (**IIIb**) and 1.7 g of amide **Vb**. Yield of compound **IVb** 3.3 g.

***N*-(1-Hydroxy-2-phenyl-2,2-dichloroethyl)-4-chlorobenzenesulfonamide (VIa).** To a solution of 3.6 g of imine **IIIa** in 8 ml of chloroform was added 1 ml of water. The reaction mixture was stirred for 1–1.5 h at 35°C and then cooled to 5–10°C. The crystalline reaction product was filtered off to obtain 3 g of compound **VIa**.

***N*-(1-Hydroxy-2-phenyl-2,2-dichloroethyl)-4-methylbenzenesulfonamide (VIb)** was obtained in the same way from 3.4 g of imine IIIb. We separated 2.6 g of compound **VIb**.

***N*-(2-Phenyl-2,2-dichloro-1-ethoxyethyl)-4-chlorobenzenesulfonamide (VIIa) and -4-methylbenzenesulfonamide (VIIb)** were obtained similarly from 3.6 g of imine **IIIa** or 3.4 g of imine **IIIb** and 1 ml of ethanol. We isolated 3.2 g of compound **VIIa** and 2.8 g of compound **VIIb**.

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