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SHORT COMMUNICATIONS

Reaction of *N*-(2,2,2-Trichloroethyl)arenesulfonamides with Activated Alkenes

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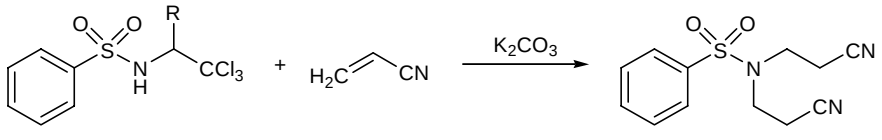
Up to now, convenient synthetic approaches to functionalized halogen-containing *N*-alkylamides of sulfonic, carboxylic, and phosphonic acids have been developed on the basis of reactions of N-functionalized polyhalogenated aldehyde imines with nucleophilic reagents and aromatic and heteroaromatic compounds [1, 2]. The reactivity of these compounds is extensively studied. Their synthetic importance was demonstrated by preparation of oxygen-, nitrogen-, and sulfur-containing heterocyclic systems [1, 3–5] and amino acids [6, 7]. On the other hand, reactions involving the amide group of *N*-(haloalkyl)amides were studied relatively poorly. In particular, there no published data on addition of the NH groups in such amides at multiple bonds, though addition reactions of various amides with unsaturated compounds have been used for functionalization of alkenes [8–10].

In continuation of our systematic studies on the reactivity of *N*-(polyhaloalkyl) sulfonamides, we examined reactions of *N*-(2,2,2-trichloroethyl)arenesulfonamides $ArSO_2NHCH(R)CCl_3$ with alkenes in which the double bond is activated due to the presence of electron-acceptor substituents. We found that, depending on the R substituent, *N*-(2,2,2-trichloroethyl)arenesulfonamides react with methyl vinyl ketone and acrylonitrile in different ways.

In the reactions of amides **Ia**–**Id** (where R is a nucleofugal fragment, i.e., OH, OAlk, OAc, or $NHSO_2Ph$ group) with acrylonitrile in dioxane in the presence of alkali metal carbonate we isolated *N*,*N*-bis(2-cyanoethyl)benzenesulfonamide (**II**). Presumably, in the first stage, the initial *N*-(2,2,2-trichloroethyl)arenesulfonamide undergoes cleavage of the N–C bond, and the arenesulfonamide thus formed takes up two alkene molecules to give N,N-disubstituted sulfonamide **II** (Scheme 1). According to published data, *N*-(1-hydroxycyclohexyl)-*p*-toluenesulfonamide reacts with acrylonitrile in dioxane in the presence of aqueous alkali to afford *N*-(1-hydroxycyclohexyl)-*N*-(2-cyanoethyl)-*p*-toluenesulfonamide in 75% yield as a result of addition of the NH group at the double bond [9].

We succeeded in effecting the reaction of *N*-(2,2,2-trichloroethyl)benzenesulfonamide (**III**) with methyl vinyl ketone in *tert*-butyl alcohol using potassium *tert*-butoxide as base. The reaction was carried out at room temperature (reaction time 3 days), and the product was *N*-(3-oxobutyl)-*N*-(2,2,2-trichloroethyl)benzenesulfonamide (**IV**, yield 75%; Scheme 2). When the reaction was performed at elevated temperature, the process was accompanied by oligomerization of methyl vinyl ketone and tarring; as a result, the yield of **IV** was lower.

Scheme 1.



Ia–Id **II**

R = OH (**a**), OAlk (**b**), OAc (**c**), $NHSO_2Ph$ (**d**).

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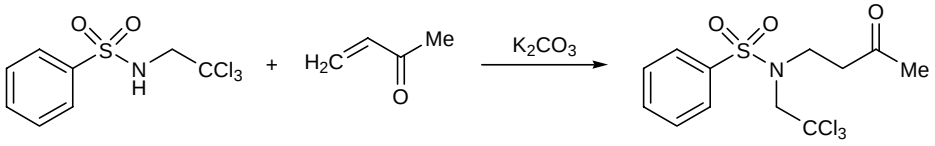
Scheme 2.



III **IV**

Arenesulfonamides **V** with R = Ar or Ht failed to react with the above alkenes despite variation of the conditions. We used water and organic solvents and alkali metal carbonates, hydroxides, and alkoxides as base catalysts. Presumably, the reason is steric shielding of the reaction center by bulky aryl or hetaryl group. The reactions performed under severe conditions resulted in tarring due to polymerization of alkenes.

The structure of compounds **II** and **IV** was confirmed by the spectral data and elemental analyses. The IR spectra of benzenesulfonamides **II** and **IV** contained absorption bands due to vibrations of the sulfonyl group, while N–H absorption typical of initial sulfonamides **I** and **III** was not observed. Compounds **II** and **IV** showed in the spectra absorption bands typical of cyano group (**II**) and carbonyl group (**IV**). In the ^{1}H and ^{13}C NMR spectra of compound **II**, signals from protons and carbon atoms in the benzene ring, four methylene groups, and cyano groups were present. Amide **IV** displayed in the ^{1}H NMR spectrum signals from the aromatic protons and a singlet corresponding to proton in the trichloroethyl fragment, as well as a singlet and two triplets from protons in the oxobutyl substituent. The presence of a trichloromethyl and carbonyl groups in molecule **IV** follows from the ^{13}C NMR data.

Compounds **II** and **IV** are colorless crystalline substances which are soluble in organic solvents and insoluble in water. *N*,*N*-Disubstituted amides **II** and **IV** are appreciably better soluble in weakly polar organic solvents than *N*-(2,2,2-trichloroethyl) sulfonamides like **I**, **III**, and **V** due to the absence of strongly polar NH groups.

***N*,*N*-Bis(2-cyanoethyl)benzenesulfonamide (II).** A mixture of 3.05 g (0.01 mol) of *N*-(2,2,2-trichloro-1-hydroxyethyl)benzenesulfonamide, 5.31 g (0.10 mol) of acrylonitrile, and 13.82 g (0.10 mol) of potassium carbonate in 100 ml of dioxane was stirred for 15 h at 101°C (under reflux). The solvent was distilled off under reduced pressure, and the residue was recrystallized from carbon tetrachloride to obtain 1.97 g (75%) of compound **II**, mp 83–87°C; published data [8]: mp 92°C. IR spectrum (KBr), ν, cm^{-1}: 1130, 1330 (SO_2); 2750 (CN). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.75 t and 3.49 t (8H, CH_2CH_2); 7.57 m, 7.66 m, and 7.83 m (5H, H_{arom}). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 19.13, 46.27 (CH_2CH_2); 117.41 (CN); 127.31, 129.78, 133.85, 137.84 (C_{arom}). Found, %: C 54.65; H 4.91; N 15.83; S 12.01. $C_{12}H_{13}N_3O_2S$. Calculated, %: C 54.74; H 4.98; N 15.96; S 12.18.

***N*-(3-Oxobutyl)-*N*-(2,2,2-trichloroethyl)benzenesulfonamide (IV).** A mixture of 2.89 g (0.01 mol) of *N*-(2,2,2-trichloroethyl)benzenesulfonamide (**III**), 3.50 g (0.05 mol) of methyl vinyl ketone, and 0.11 g (1 mmol) of potassium *tert*-butoxide in 10–12 ml of *tert*-butyl alcohol was stirred for 3 days. The mixture was poured into 50 ml of water, and the precipitate was filtered off, dried, and recrystallized from carbon tetrachloride. Yield 2.67 g (75%), mp 142–144°C. IR spectrum (KBr), ν, cm^{-1}: 1130, 1360 (SO_2); 1700 (C=O). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.06 s (3H, Me); 2.97 t and 3.61 t (4H, CH_2CH_2); 4.42 s (2H, CH_2CCl_3); 7.63 m, 7.71 m, and 7.91 m (5H, H_{arom}). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 30.00 (CH_3); 43.51, 46.20 (CH_2CH_2); 99.20 (CCl_3); 128.35, 130.22, 134.09, 139.75 (C_{arom}); 206.18 (C=O). Found, %: C 40.30; H 3.97; Cl 29.82; N 3.83; S 8.78. $C_{12}H_{14}Cl_3NO_3S$. Calculated, %: C 40.19; H 3.93; Cl 29.65; N 3.91; S 8.94.

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-400 spectrometer at 400.6 MHz for ^{1}H and 100.61 MHz for ^{13}C; the chemical shifts were measured relative to hexamethyldisiloxane as internal reference. The IR spectra were obtained on a Specord 75IR spectrometer.

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