ISSN 1070-4280, Russian Journal of Organic Chemistry, 2011, Vol. 47, No. 4, pp. 611–613. © Pleiades Publishing, Ltd., 2011.
Original Russian Text © I.B. Rozentsveig, A.V. Popov, G.G. Levkovskaya, V.Yu. Serykh, 2011, published in Zhurnal Organicheskoi Khimii, 2011, Vol. 47, No. 4, pp. 605–606.

SHORT COMMUNICATIONS

Reaction of 4-Chloro-*N*-(2,2,2-trichloroethylidene)benzenesulfonamide with Allyl- and Propargylzinc Bromides

I. B. Rozentsveig, A. V. Popov, G. G. Levkovskaya, and V. Yu. Serykh

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 September 20, 2010

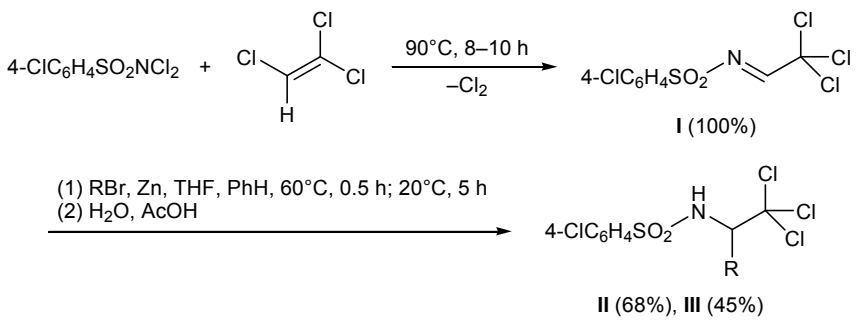
DOI: 10.1134/S1070428011040245

N-(Trichloroethyl)arenesulfonamides are convenient starting compounds for the synthesis of difficultly accessible sulfonamide derivatives. This was demonstrated by the preparation of biologically active N-protected amino acids [1], amidines [2], imides [3], and various heterocyclic derivatives of the sulfonamide series [4–7]. Therefore, synthesis of new *N*-polychloroethyl sulfonamides is an important problem. Convenient synthetic approaches to *N*-(trichloroethyl) sulfonamides are based on transformations of activated *N*-sulfonyl trichloroacetaldehyde imines which possess enhanced electrophilicity due to the presence in their molecules of strong electron-withdrawing substituents and readily take up various nucleophiles at the CH=N bond [8]. Our research activity is directed at developing synthetic approaches to *N*-(polychloroalkyl) sulfonamides on the basis of reactions of polyhalogenated aldehyde imines with carbon-centered nucleophiles.

In the framework of these studies we examined reactions of allylzinc bromide and propargylzinc bromide with 4-chloro-*N*-(2,2,2-trichloroethylidene)-benzenesulfonamide (**I**) which is readily obtained in quantitative yield from *N*,*N*,4-trichlorobenzenesulfonamide and trichloroethylene [9]. Reactions of Schiff bases with organozinc compounds are widely used for the preparation of various amines and amides [10–13]. However, no analogous reactions were reported previously for *N*-sulfonyl imines derived from halogen-containing aldehydes.

We have found that 4-chloro-*N*-(2,2,2-trichloroethylidene)benzenesulfonamide (**I**) reacts with allylzinc bromide and propargylzinc bromide (prepared preliminarily as described in [14–16]) in THF to give previously unknown 4-chloro-*N*-(1,1,1-trichloropent-4-en-2-yl)benzenesulfonamide (**II**) and 4-chloro-*N*-(1,1,1-trichloropent-4-yn-2-yl)benzenesulfonamide (**III**) in poor yields (21–23%). The yield of **II** and **III** was even lower when the reaction was carried out in diethyl ether instead of tetrahydrofuran.

With a view to simplify the procedure for the synthesis of compounds **II** and **III** and improve their yield we also examined transformations of sulfonamide **I** in the presence of zinc dust and allyl bromide or propar-



II, R = CH_2=$CHCH_2$; **III**, R = HC≡CCH_2.

gyl bromide. We anticipated generation of the corresponding organozinc compounds *in situ*. In fact, this procedure was less laborious, and the yield of target sulfonamides **II** and **III** was considerably higher. Thus one-pot procedure involving preparation of organozinc compounds *in situ* is more advantageous than the use of preliminarily prepared organozinc compounds.

It should be specially emphasized that in the examined reactions we did not observe formation of 4-chloro-*N*-(2,2,2-trichloroethyl)benzenesulfonamide as by-product via reduction of the C=N bond. Furthermore, the reaction mixtures contained no products that could be formed via transformations of the trichloromethyl group in Schiff base **I** or sulfonamides **II** and **III**. We failed to obtain compounds **II** and **III** by reaction of **I** with allylmagnesium bromide or propargylmagnesium bromide. In these cases, the reactions involved transformations of the trichloromethyl group, cleavage of the C–N bond with liberation of 4-chlorobenzenesulfonamide, and considerable tarring.

Thus the use of organozinc reagents in reactions with *N*-(arylsulfonyl) trichloroacetaldehyde imines is more appropriate than the use of organomagnesium or other more active organometallic compounds which act as strong reducing agents and are capable of initiating side processes. Analogous results were obtained while studying similar transformations of alkyl trichloroethylidenecarbamates [17].

The structure of amides **II** and **III** was confirmed by spectral methods and elemental analyses. The NCH proton in compounds **II** and **III** resonated in their ^{1}H NMR spectra as a complex multiplet due to spin–spin couplings with diastereotopic protons in the neighboring methylene group.

The presence of a trichloromethyl group, NH group, and multiple bonds in the molecules of sulfonamides **II** and **III** makes these compounds promising as reagents for subsequent transformations, including preparation of various functionalized acyclic derivatives of the sulfonamide series and heterocyclic compounds.

We are now trying to optimize the procedure for the preparation of compounds **II** and **III** and studying their reactivity and biological activity.

4-Chloro-*N*-(2,2,2-trichloroethylidene)benzenesulfonamide (**I**) was synthesized according to the procedure described in [9].

4-Chloro-*N*-(1,1,1-trichloropent-4-en-2-yl)benzenesulfonamide (II). A mixture of 6.42 g (0.02 mol) of compound **I**, 2.42 g (0.02 mol) of allyl bromide, 1.30 g (0.02 mol) of zinc dust, 10 ml of THF, and 10 ml of benzene was stirred first for 0.5 h at 60°C and then for 5 h at 20°C. The mixture was then treated with 20 ml of 30% acetic acid, the organic phase was separated, washed with water (3×30 ml), dried over Na_2SO_4, and evaporated, and the solid residue was recrystallized from hexane. Yield 4.94 g (68%), mp 112–115°C. IR spectrum (KBr), ν, cm^{-1}: 3267 (NH), 1644 (C=C), 1340, 1165 (SO_2). ^{1}H NMR spectrum, δ, ppm: 2.32 m and 2.75 m (1H each, CH_2), 4.12 m (1H, NHC**H**); 4.64, 4.93, 5.38 (3H, CH=CH_2, $^3J_{AB}$ = 17.0, $^3J_{AC}$ = 10.0, $^2J_{BC}$ = 1.2 Hz); 7.63, 7.81 (4H, C_6H_4, *AA′BB′*); 8.76 d (1H, NH, ^3J = 8.8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 35.98 (CH_2), 69.19 (NHCH), 103.63 (CCl_3), 119.19 (=CH_2); 129.18, 129.61, 137.87, 141.67 (C_6H_4); 133.03 (CH). Found, %: C 36.74; H 3.03; Cl 38.93; N 3.69; S 8.69. $C_{11}H_{11}Cl_4NO_2S$. Calculated, %: C 36.39; H 3.05; Cl 39.06; N 3.86; S 8.83.

4-Chloro-*N*-(1,1,1-trichloropent-3-yn-2-yl)benzenesulfonamide (III) was synthesized in a similar way from 2.42 g (0.02 mol) of prop-2-ynyl bromide. The product was purified by washing with cold diethyl ether until its color disappeared. Yield 3.25 g (45%), mp 119–121°C. ^{1}H NMR spectrum, δ, ppm: 2.62 s (1H, ≡CH), 2.93 m and 2.97 m (1H each, CH_2), 4.29 m (1H, CH); 7.63, 7.86 (4H, C_6H_4, *AA′BB′*); 9.00 d (1H, NH, ^3J = 8.9 Hz). ^{13}C NMR spectrum, δ_C, ppm: 21.92 (CH_2), 68.28 (≡CH), 74.09 (NCH), 78.92 (≡C), 101.96 (CCl_3), 128.74, 129.15, 137.46, 141.15 (C_6H_4). Found, %: C 36.72; H 2.48; Cl 39.50; N 3.69; S 8.71. $C_{11}H_9Cl_4NO_2S$. Calculated, %: C 36.59; H 2.51; Cl 39.27; N 3.88; S 8.88.

The IR spectra were recorded on a Bruker IFS-25 spectrometer. The ^{1}H and ^{13}C NMR spectra were measured from solutions in DMSO-d_6 on a Bruker DPX-400 spectrometer at 400.61 and 100.13 MHz, respectively, using tetramethylsilane as internal reference.

REFERENCES

1. Rozentsveig, I.B., Levkovskaya, G.G., Mirskova, A.N., and Kashik, T.V., *Russ. J. Org. Chem*., 2000, vol. 36, p. 1760.
2. Rozentsveig, I.B., Levkovskaya, G.G., Rozentsveig, G.N., Mirskova, A.N., Krivdin, L.B., Larina, L.I., and Albanov, A.I., *Tetrahedron Lett*., 2005, vol. 46, p. 8889.
3. Rozentsveig, I.B., Popov, A.V., Mirskova, A.N., and Levkovskaya, G.G., *Russ. J. Org. Chem*., 2007, vol. 43, p. 1559.

4. Rozentsveig, I.B., Popov, A.V., Brikov, A.V., Chernyshev, K.A., Mirskova, A.N., and Levkovskaya, G.G., *Russ. J. Org. Chem*., 2007, vol. 43, p. 926.
5. Rozentsveig, I.B., Popov, A.V., Rozentsveig, G.N., Chernyshev, K.A., and Levkovskaya, G.G., *Khim. Geterotsikl. Soedin*., 2008, p. 1587.
6. Rozentsveig, I.B., Popov, A.V., Rozentsveig, G.N., Serykh, V.Yu., Chernyshev, K.A., Krivdin, L.B., and Levkovskaya, G.G., *Mol. Diversity*, 2010, vol. 14, p. 533.
7. Drach, B.S., Brovarets, V.S., and Smolii, O.B., *Sintez azotsoderzhashchikh geterotsiklicheskikh soedinenii na osnove amidoalkiliruyushchikh agentov* (Synthesis of Nitrogen-Containing Heterocyclic Compounds on the Basis of Amidoalkylating Agents): Kiev: Naukova Dumka, 1992.
8. Levkovskaya, G.G., Drozdova, T.I., Rozentsveig, I.B., and Mirskova, A.N., *Usp. Khim*., 1999, vol. 68, p. 638.
9. Mirskova, A.N., Levkovskaya, G.G., Drozdova, T.I., Kalikhman, I.D., and Voronkov, M.G., *Zh. Org. Khim*., 1982, vol. 18, p. 452.
10. Traverse, J.F., Hoveyda, A.H., and Snapper, M.L., *Org. Lett*., 2003, vol. 5, p. 3273.
11. Frantz, D.E., Fassler, R., and Carreira, E.M., *J. Am. Chem. Soc*., 1999, vol. 121, p. 11245.
12. Bloh, R., *Chem. Rev*., 1998, vol. 98, p. 1407.
13. Ferraris, D., *Tetrahedron*, 2007, vol. 63, p. 9581.
14. Gaudemar, M., *Ann. Chim*., 1956, p. 161.
15. Gaudemar, M., *C.R. Acad. Sci., Ser. C*, 1958, vol. 246, p. 1229.
16. Yamamoto, Y. and Asao, N., *Chem. Rev*., 1993, vol. 93, p. 2207.
17. Kashima, S., Aoki, Y., and Omoto, Y., *J. Chem. Soc., Perkin Trans. 1*, 1975, p. 2511.