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# NEW METHOD FOR THE SYNTHESIS OF BENZENE- AND PHENYLMETHANESULFONYLMETHYL-SUBSTITUTED 1,3-DITHIOLANES AND 1,3-DITHIANES

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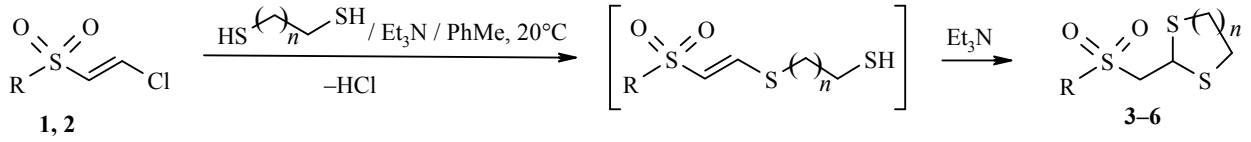
*The reactions of (E)-chlorovinyl sulfones with 1,2-ethanedithiol or 1,3-propanedithiol in the presence of triethylamine in toluene at 80°C lead to the selective formation of 1,3-dithiolane and 1,3-dithiane derivatives with yields of up to 49%.*

**Keywords**: (*E*)-2-chlorovinyl sulfones, 1,3-dithianes, 1,3-dithiolanes,.

1,3-Dithiolanes [1; 2, p. 329] and 1,3-dithianes [1; 2, p. 724; 3] have attracted attention as an important class of heterocyclic compounds widely used in organic synthesis. The 1,3-dithiolane and 1,3-dithiane rings are also used as protecting groups in carbonyl compounds [2, 4]. In addition, there are published data on the insecticidal activity of derivatives of 1,3-dithiolane [5] and 1,3-dithiane [6]. 1,3-Dithiane derivatives have also been tested as agents acting on the central nervous system [7].

In the literature there are only two papers on the synthesis of arylsulfonylmethyl[1,3]dithiolanes and arylsulfonylmethyl[1,3]dithianes and their derivatives. The principal method for the synthesis of 2-benzenesulfonylmethyl[1,3]dithiolane is based on the reaction of (*Z*)-1,2-bis(phenylsulfonyl)ethylene with 1,2-ethanedithiol in the presence of NaH in tetrahydrofuran [8]. Compounds of this type were also obtained by the reaction of the respective arylsulfonylacetylenes with 1,2-etanedithiol or 1,2-benzenedithiol in the NaH–THF system [8, 9]. In many cases, however, the synthesis of arylsulfonylacetylenes is extremely complicated, while the synthesis of arylsulfonyl methyl[1,3]dithiolanes requires the use of fire-hazardous sodium hydride. The aim of our work was therefore to develop a simple method for the synthesis of benzene- and phenylmethanesulfonylmethyl-substituted 1,3-dithiolanes and 1,3-dithianes.




**1, 2** **3–6**

**1,3,4** R = Ph; **2,5,6** R= $PhCH_2$; **3,5** *n* = 1, **4,6** *n* = 2

* Deceased.

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We developed a method for the synthesis of the 1,3-dithiolanes and 1,3-dithianes **3-6** in the 1,2-ethanedithiol (or 1,3-propanedithiol)–$Et_3N$–toluene system at 80°C. The products were isolated by column chromatography with yields of 17-49% (see Experimental).

The reaction mechanism includes the reaction of compounds **1** or **2** with dithiols with the formation of intermediates that add to the activated C=C bond with the formation of compounds **3-6**.

## EXPERIMENTAL

The $^1$H NMR spectra were recorded in $CDCl_3$ on a Varian Mercury-200 instrument (200 MHz) with HMDS as internal standard (δ 0.05 ppm). The mass spectra were obtained on a GC-MS HP 6890 instrument (70 eV). The reactions were monitored on Silufol UV-254 plates. The 1,2-ethanedithiol and 1,3-propanedithiol (Acros) were used without additional purification.

The (*E*)-2-chlorovinyl sulfones **1** and **2** were obtained by the method in [10].

**Synthesis of 1,3-Dithiolanes 3 and 5 and 1,3-Dithianes 4 and 6 by Nucleophilic Addition of 1,2-Ethanedithiol or 1,3-Propanedithiol to 2-Chlorovinyl Sulfones 1 and 2 (General Method)**. To a solution of (*E*)-2-chlorovinyl sulfone **1** or **2** (1 mmol) and triethylamine (0.25 g, 2 mmol) in dry toluene (2 ml) we added 1,2-ethanedithiol or 1,3-propanedithiol (1 mmol). The mixture was stirred at 80°C for 72 h and filtered through a thin layer of silica gel. The toluene was evaporated on a rotary evaporator. The products **3-6** were isolated by column chromatography (eluent 2:1 toluene–ethyl acetate) in the form of yellow liquids and identified by $^1$H NMR and mass spectroscopy. According to the data from gas chromatography the purity of the compounds was higher than 95%.

**2-Benzenesulfonylmethyl[3,1]dithiolane (3)**. The yield 31%. $^1$H NMR spectrum, δ, ppm (*J*, Hz): 2.72-2.79 (4H, m, $CH_2CH_2$); 3.59 (2H, d, *J* = 8.0, $CH_2$); 4.78 (1H, t, *J* = 8.0, SCH); 7.54-7.72 (3H, m, H-3,4,5); 7.91-7.95 (2H, m, H-2,6). Mass spectrum, *m*/*z* ($I_{rel}$, %): 141 $[M-CH_2(dithiolane)]^+$ (5), 118 $[M-SO_2Ph]^+$ (100), 105 (12), 91 (45), 77 (78), 59 (32), 51 (48), 45 (44). Found, %: C 45.61; H 4.63. $C_{10}H_{12}O_2S_3$. Calculated, %: C 46.12; H 4.64.

**2-Benzenesulfonylmethyl[1,3]dithiane (4)**. The yield 49%. $R_f$ 0.37. $^1$H NMR spectrum, δ, ppm (*J*, Hz): 1.80-2.12 (2H, m, $CH_2C\underline{H}_2CH_2$); 2.52-2.95 (4H, m, $SCH_2$); 3.51 (2H, d, *J* = 6.0, $CH_2$); 4.48 (1H, t, *J* = 8.0, SCH); 7.18-7.28 (1H, m, H-4); 7.52-7.67 (2H, m, H-3,5); 7.93-7.97 (2H, m, H-2,6). Mass spectrum, *m*/*z* ($I_{rel}$, %): 274 $[M]^+$ (3), 132 (100), 105 (13), 91 (31), 77 (80), 59 (29), 45 (44). Found, %: C 48.40; H 4.88. $C_{11}H_{14}O_2S_3$. Calculated, %: C 48.14; H 5.14.

**2-Phenylmethanesulfonylmethyl[1,3]dithiolane (5)**. The yield 25%. $R_f$ 0.53. $^1$H NMR spectrum, δ, ppm (*J*, Hz): 2.96-3.07 (4H, m, $CH_2CH_2$); 3.42 (2H, d, *J* = 8.0, $CH_2$); 4.17 (2H, s, $PhC\underline{H}_2$); 4.56 (1H, t, *J* = 8.0, CH); 7.25-7.40 (5H, m, $C_6H_5$). Mass spectrum, *m*/*z* ($I_{rel}$, %): 274 $[M]^+$ (<1), 118 $[M-SO_2CH_2Ph]^+$ (100), 91 (97), 65 (13). Found, %: C 48.16; H 5.11. $C_{11}H_{14}O_2S_3$. Calculated, %: C 48.14; H 5.14.

**2-Phenylmethanesulfonylmethyl[1,3]dithiane (6)**. The yield 17%. $R_f$ 0.5. $^1$H NMR spectrum, δ, ppm (*J*, Hz): 1.80–2.04 (2H, m, $CH_2C\underline{H}_2CH_2$); 2.75–3.04 (4H, m, $SCH_2$); 3.25 (2H, d, *J* = 6.0, $O_2SC\underline{H}_2CH$); 4.43 (2H, s, $PhC\underline{H}_2$); 4.54 (1H, t, *J* = 6.0, CH); 7.35–7.45 (5H, m, $C_6H_5$). Mass spectrum, *m*/*z* ($I_{rel}$, %): 288 $[M]^+$ (<1), 132 (100), 91 (90), 73 (13), 65 (22), 45 (22). Found, %: C 48.31; H 5.00. $C_{12}H_{16}O_2S_3$. Calculated, %: C 49.97; H 5.59.

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