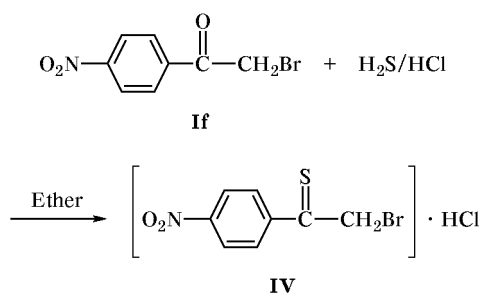


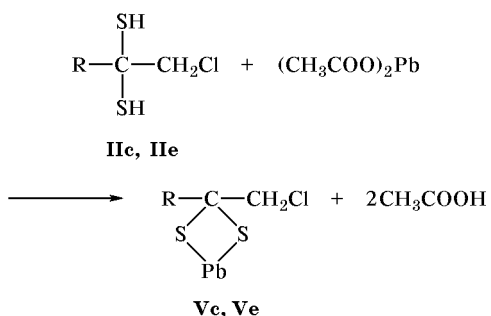
H₂S/HCl in ether gave 1-bromo-2-(4-nitrophenyl)ethane-2-thione hydrochloride (**IV**) instead of the expected geminal dithiol (Scheme 3).

Scheme 3.



Using 1-chloro-2-(4-tolyl)ethane-2,2-dithiol (**IIc**) and 1-chloro-2-(1-naphthyl)ethane-2,2-dithiol (**IIe**) as examples, we demonstrated the possibility for formation of the corresponding lead dithiolates **Vc** and **Ve** via reaction with methanolic lead(II) acetate (Scheme 4). Dithiolates **Vc** and **Ve** turned out to be convenient starting compounds for the synthesis of difficultly accessible dithiirane derivatives [7].

Scheme 4.



EXPERIMENTAL

The IR spectra were recorded on a Specord 75IR spectrometer from samples pelleted with KBr or dispersed in mineral oil. The ¹H NMR spectra were obtained on a Jeol FX-90Q instrument using CDCl₃ as solvent and hexamethyldisiloxane as external reference. The progress of reactions was monitored by TLC on Silufol UV-254 plates with chloroform as eluent.

1-Bromopropane-2,2-dithiol (IIa). Hydrogen sulfide was passed at -70°C over a period of 3 h through a solution of 3 g (21.9 mmol) of 1-bromoacetone (**Ia**) in 15 ml of diethyl ether, which was saturated with hydrogen chloride at -10°C. The mixture was left to stand for 48 h at -40°C until the initial

ketone disappeared and was then purged with nitrogen for 1 h to remove HCl and excess H₂S. The ether solution was washed with ice water until neutral reaction, dried over CaCl₂, and evaporated under reduced pressure to obtain 3.6 g (88%) of almost pure dithiol (**IIa**) as a light yellow oily substance which was stable at -5°C. ¹H NMR spectrum, δ, ppm: 1.78 s (3H, CH₃), 2.83 s (2H, SH), 3.71 s (2H, CH₂Cl). Found, %: Br 42.30; S 34.12. C₃H₇BrS₂. Calculated, %: Br 42.78; S 34.22.

1-Chloro-2-phenylethane-2,2-dithiol (IIb) was synthesized in a similar way from 1 g (6.5 mmol) of 1-chloroacetophenone (**IIb**). The mixture was kept for 48 h at -40°C until initial ketone **IIb** disappeared (TLC). Yield of **IIb** 1.1 g (83%); colorless oily substance, stable at -5°C; mp 26°C. IR spectrum, ν, cm⁻¹: 750 (C-S), 2550 (SH), 2850 (CH₂, ν_s), 2925 (CH₂, ν_{as}). ¹H NMR spectrum, δ, ppm: 3.47 s (2H, SH), 4.27 s (2H, CH₂Cl), 7.37-7.75 m (5H, C₆H₅). Found, %: C 46.80; H 4.37; Cl 17.25; S 31.60. C₈H₉ClS₂. Calculated, %: C 46.94; H 4.40; Cl 17.35; S 31.29.

1-Chloro-2-(4-tolyl)ethane-2,2-dithiol (IIc) was synthesized in a similar way from 1 g (5.9 mmol) of ketone **Ic**. Yield of **IIc** 1.1 g (85%); colorless thick oily liquid, stable at -5°C. ¹H NMR spectrum, δ, ppm: 3.47 s (2H, SH), 4.27 s (2H, CH₂Cl), 7.37-7.75 m (4H, C₆H₄). Found, %: Cl 16.68; S 29.41. C₉H₁₁ClS₂. Calculated, %: Cl 16.24; S 29.29.

1-Bromo-2-(4-tolyl)ethane-2,2-dithiol (IId) was synthesized in a similar way from 1 g (4.7 mmol) of ketone **Id**. Yield 1 g (81%); colorless thick oily liquid, stable at -5°C. ¹H NMR spectrum, δ, ppm: 2.31 s (3H, CH₃), 3.33 s (2H, SH), 4.23 s (2H, CH₂Br), 7.15-7.56 m (4H, C₆H₄). Found, %: Br 30.01; S 24.20. C₉H₁₁BrS₂. Calculated, %: Br 30.41; S 24.33.

1-Chloro-2-(1-naphthyl)ethane-2,2-dithiol (IIe) was synthesized in a similar way from 1 g (4.8 mmol) of ketone **Ie**. Yield 1.12 g (90%); colorless thick oily liquid, stable at -5°C. ¹H NMR spectrum, δ, ppm: 3.59 s (2H, SH), 4.58 s (2H, CH₂Cl), 7.47-7.81 m (7H, C₁₀H₇). Found, %: Cl 13.20; S 25.60. C₁₂H₁₁ClS₂. Calculated, %: Cl 13.94; S 25.17.

1-Bromo-2-(4-nitrophenyl)ethane-2-thione (IV). Hydrogen sulfide was passed at -70°C over a period of 3 h through a solution of 1 g (4.1 mmol) of 1-bromo-2-(4-nitrophenyl)ethan-2-one (**II**) in 15 ml of diethyl ether, which was saturated with hydrogen chloride at -10°C. The mixture was left to stand for 5 days at -40°C until initial ketone **II** disappeared.

The precipitate was filtered off, washed with ether, and dried under reduced pressure. Yield 1.15 g (95%); yellow powder decomposing at 169–170°C. IR spectrum, ν , cm^{-1} : 1200 (C=S), 1350 and 1365 (NO_2 , ν_s), 1510 and 1520 (NO_2 , ν_{as}), 2500–3200 br. ^1H NMR spectrum, δ , ppm: 4.67 s (2H, CH_2Br), 8.08–8.36 m (4H, C_6H_4). Found, %: C 32.70; H 2.26; Br 26.20; Cl 11.34; N 5.10; S 11.02. $\text{C}_8\text{H}_7\text{BrClNO}_2\text{S}$. Calculated, %: C 32.87; H 2.36; Br 26.90; Cl 11.94; N 4.72; S 10.76.

Lead 1-chloro-2-(4-tolyl)ethane-2,2-dithiolate (Vc). A solution of 0.22 g (0.7 mmol) of lead acetate was added at -5°C to a solution of 0.17 g (0.8 mmol) of 1-chloro-2-(4-tolyl)ethane-2,2-dithiol (**IIc**) in 10 ml of anhydrous methanol. The mixture was heated to 20°C and was kept at that temperature for 12 h (until initial compound **IIc** disappeared; TLC). The yellow precipitate was filtered off and dried under reduced pressure. It was dissolved in 10 ml of chloroform, and pure dithiolate **Vc** was precipitated with hexane. Yield 0.2 g (61%), decomposes at $120\text{--}123^\circ\text{C}$. IR spectrum, ν , cm^{-1} : 780 (C–S, ring); 1180, 1450, 1500, 1600 (aromatic ring); 2850 (CH_2 , ν_s), 2925 (CH_2 , ν_{as}). Found, %: C 25.80; H 2.30; Cl 7.90; Pb 48.00; S 15.00. $\text{C}_9\text{H}_9\text{ClPbS}_2$. Calculated, %: C 25.50; H 2.12; Cl 8.38; Pb 48.87; S 15.11.

Lead 1-chloro-2-(1-naphthyl)ethane-2,2-dithiolate (Ve) was synthesized in a similar way from 0.2 g (0.8 mmol) of 1-chloro-2-(1-naphthyl)ethane-2,2-dithiol (**IIe**) and 0.26 g (0.8 mmol) of lead(II) acetate. Yield of **Ve** 0.24 g (67%), orange powder

decomposing at $143\text{--}145^\circ\text{C}$. IR spectrum, ν , cm^{-1} : 780 (C–S, ring); 900–1600 (a number of strong bands, aromatic ring); 2850 (CH_2 , ν_s), 2925 (CH_2 , ν_{as}). Found, %: C 31.20; H 1.80; Pb 44.80; S 13.20. $\text{C}_{12}\text{H}_9\text{ClPbS}_2$. Calculated, %: C 31.30; H 1.97; Pb 45.05; S 13.94.

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