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1-Haloethane-2,2-dithiols

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Abstract—Optimal conditions were found for the synthesis of 1-bromopropane-2,2-dithiol and 1-halo-2-arylethane-2,2-dithiols by low-temperature acid-catalyzed hydrosulfurization of the corresponding 1-haloketones $RCOCH_2X$ (R = CH₃, X = Br; R = C₆H₅, X = Cl; R = 4-CH₃C₆H₄, X = Cl; R = 4-CH₃C₆H₄, X = Br; R = 1-C₁₀H₇, X = Cl). Reaction paths and solvent effect are discussed.

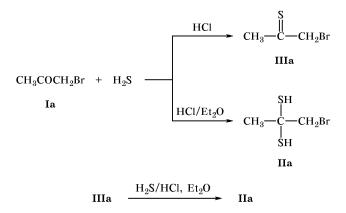
First representatives of 1-haloethane-2,2-dithiols $RC(SH)_2CH_2X$ (R = CH₃, X = Cl; R = C₆H₅, X = Br; R = 5-Cl-2-C₄H₂S, X = Cl) were synthesized by us by the action of hydrogen sulfide on the corresponding α -haloketones in ether solution of hydrogen chloride at -70°C [1]. We also performed analogous reactions with fluoroacetone [2] and bromo- and fluoropinaco-lone [3]. Attempts to obtain 1-iodopropan-2,2-dithiol in a similar way were unsuccessful. Instead, in the latter case the product was 2,2,5,5-hexanetetrathiol which was formed in quantitative yield [4].

In continuation of these studies we examined hydrosulfurization of 1-bromoacetone (**Ia**), 1-chloro-acetophenone (**Ib**), 1-chloro-2-(4-tolyl)ethan-2-one (**Ic**), 1-bromo-2-(4-tolyl)ethan-2-one (**Id**), 1-chloro-2-(1-naphthyl)ethan-2-one (**Ie**), and 1-bromo-2-(4-nitrophenyl)ethan-2-one (**If**) in ether solution of hydrogen chloride at -60° C. From ketones **Ia–Ie** we obtained the corresponding α -halodithiols **IIa–IIe** (Scheme 1).

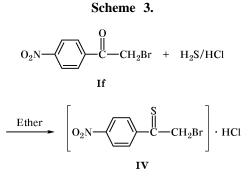
Scheme 1.

The isolation of geminal dithiols **IIa–IIe** involved some experimental difficulties. Attempts to remove hydrogen chloride from the reaction mixture resulted in transformation of dithiols **Ha–He** into the corresponding thioketones which undergo instantaneous trimerization in aqueous medium [5]. Therefore, hydrogen chloride was removed by purging with an inert gas and washing with water at low temperature. Thioketones are likely to be formed as intermediates in the above reaction. For example, bromothioacetone (**HIa**) obtained by reaction of bromoacetone with hydrogen sulfide in the presence of HCl without a solvent [6] was converted into 1-bromopropane-2,2-dithiol (**Ha**) by the action of H_2S and HCl in ether (Scheme 2).

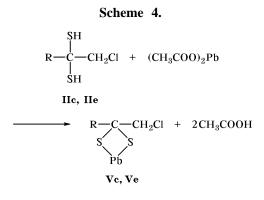
Scheme 2.



These transformations demonstrate a considerable effect of the solvent on the acid-catalyzed hydrosulfurization of α -haloketones. Depending on the conditions, either α -halothioketones **IIIa–IIIe** or α -halodithiols **IIa–IIe** could be obtained. The reaction of 1-bromo-2-(4-nitrophenyl)ethan-2-one (**If**) with H_2S/HCl in ether gave 1-bromo-2-(4-nitrophenyl)ethane-2-thione hydrochloride (**IV**) instead of the expected geminal dithiol (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].



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-bromo-acetone (**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 (**Ha**) 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 (**Ib**). The mixture was kept for 48 h at -40°C until initial ketone **Ib** disappeared (TLC). Yield of **IIb** 1.1 g (83%); colorless oily substance, stable at -5°C; mp 26°C. IR spectrum, v, cm⁻¹: 750 (C-S), 2550 (SH), 2850 (CH₂, v_s), 2925 (CH₂, v_{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 (**If**) 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 **If** 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, v, cm⁻¹: 1200 (C=S), 1350 and 1365 (NO₂, v_s), 1510 and 1520 (NO₂, v_{as}), 2500–3200 br. ¹H NMR spectrum, δ , ppm: 4.67 s (2H, CH₂Br), 8.08–8.36 m (4H, C₆H₄). Found, %: C 32.70; H 2.26; Br 26.20; Cl 11.34; N 5.10; S 11.02. C₈H₇BrClNO₂S. 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 120-123°C. IR spectrum, v, cm⁻¹: 780 (C-S, ring); 1180, 1450, 1500, 1600 (aromatic ring); 2850 (CH₂, v_s), 2925 (CH₂, v_{as}). Found, %: C 25.80; H 2.30; Cl 7.90; Pb 48.00; S 15.00. C₉H₉ClPbS₂. 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 was from 0.2 g (0.8 mmol) of 1-chloro-2-(1-naphthyl)ethane-2,2-dithiole (IIe) and 0.26 g (0.8 mmol) of lead(II) acetate. Yield of Ve 0.24 g (67%), orange powder decomposing at 143–145°C. IR spectrum, v, cm⁻¹: 780 (C–S, ring); 900–1600 (a number of strong bands, aromatic ring); 2850 (CH₂, v_s), 2925 (CH₂, v_{as}). Found, %: C 31.20; H 1.80; Pb 44.80; S 13.20. C₁₂H₉ClPbS₂. Calculated, %: C 31.30; H 1.97; Pb 45.05; S 13.94.

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