

SHORT  
COMMUNICATIONS

## Synthesis of First Examples of $\alpha,\alpha$ -Dihalosubstituted Thiones and Geminal Dithiols

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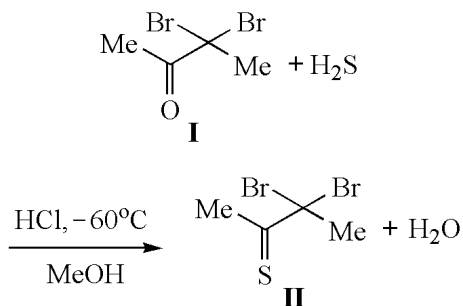
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$\alpha$ -Halosubstituted thiones and geminal dithiols are considered among exceedingly reactive compounds thus suitable for preparation of various heterocyclic systems [1–3]. Introduction of a second halogen atom into the thione and geminal dithiol molecule provides additional opportunities for heterocyclization.

The goal of this study was synthesis of previously unknown  $\alpha,\alpha$ -dihalosubstituted thiones and *gem*-dithiols by acid-catalyzed hydrothiolysis of 1,1-dibromoacetophenone and 3,3-dibromobutan-2-one both without solvent or in a protic or aprotic solvent.

It was established that in the absence of solvent 3,3-dibromobutan-2-one (**I**) virtually did not undergo hydrothiolysis at  $-60^\circ\text{C}$  whereas in an aprotic solvent (anhydrous ethyl ether) saturated with hydrogen chloride at  $-60^\circ\text{C}$  a weak conversion of the ketone was observed to form inseparable mixture of olthiol and thioketone (NMR data). In a system MeOH–HCl at  $-60^\circ\text{C}$  3,3-dibromobutan-2-one (**I**) reacted with hydrogen sulfide to give 3,3-dibromobutane-2-thione (**II**) in 90% yield.



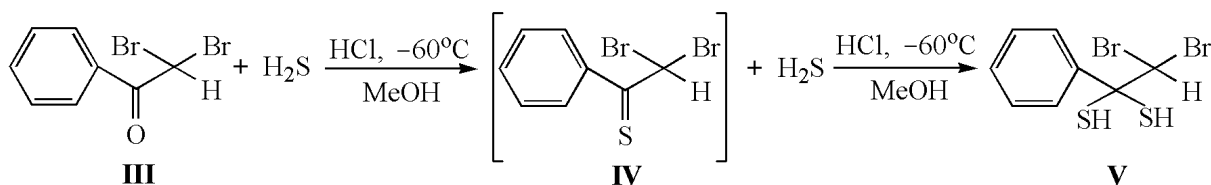
Thione **II** was separated as a dark-red oily substance stable at  $-30^\circ\text{C}$ . The structure of 3,3-dibromobutan-2-thione (**II**) was confirmed by IR and  $^1\text{H}$  and  $^{13}\text{C}$  NMR

spectroscopy. In the  $^{13}\text{C}$  NMR spectrum of thione **II** a signal was observed in the region 241.97 ppm, characteristic of a carbon in a thiocarbonyl group. In the spectrum of the initial ketone the carbonyl group carbon gave rise to a signal at 195.19 ppm. The IR spectrum of thione **II** lacks the signal from the carbonyl group in the region  $1734\text{ cm}^{-1}$ .

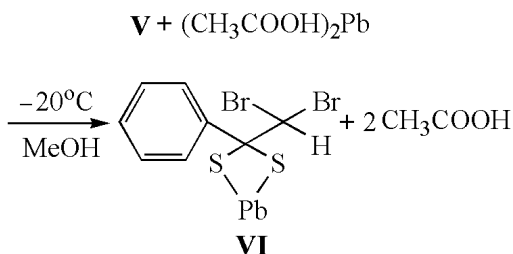
By this reaction we synthesized the first example of thioketone containing in the molecule three highly reactive centers with different properties, therefore it can be regarded as a new promising reagent for designing sulfur-containing acyclic and heterocyclic systems.

Acid-catalyzed hydrothiolysis of 1,1-dibromoacetophenone (**III**) was carried out both in an aprotic and protic solvents. It was found that the reaction of 1,1-dibromoacetophenone (**III**) with hydrogen sulfide in a system ether–HCl at  $-60^\circ\text{C}$  led to the formation of an intractable products mixture. In a protic solvent the reaction of 1,1-dibromoacetophenone (**III**) with hydrogen sulfide in a system methanol–HCl at  $-60^\circ\text{C}$  resulted in 1,1-dibromo-2-phenylethene-2,2-dithiol (**V**) in 85% yield. At the start of reaction the mixture turned dark-blue indicating the formation of 1,1-dibromo-2-phenylethene-2-thione (**IV**). The subsequent decoloration of the reaction mixture in the course of hydrothiolysis evidenced further nucleophilic addition of the hydrogen sulfide to the carbon of the thiocarbonyl group in thione **IV** and formation of 1,1-dibromo-2-phenylethene-2,2-dithiol (**V**).

In the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of dithiol **V** signals were observed in the region 2.11 s (2H, SH), 6.40 s (1H,  $\text{CHBr}_2$ ), 7.48–8.07 m (5H, Ph), 59.89 ( $\text{CHBr}_2$ ), 65.71



(HS-C-SH), 125–134 (6C-Ph) ppm. In the IR spectrum the absorption band of the mercapto group appeared at  $2557\text{ cm}^{-1}$ .



The presence of two mercapto groups in the molecule of 1,1-dibromo-2-phenylethene-2,2-dithiol (**V**) was additionally proved by the formation of lead 1,1-dibromo-2-phenylethene-2,2-dithiolate (**VI**) on treating compound **V** with lead acetate in methanol at  $-20^\circ\text{C}$ . Lead dithiolate **VI** is an orange powder, t.decomp.  $180\text{--}185^\circ\text{C}$ .

The IR spectrum of dithiolate **VI** obtained lacked the signal of mercapto group in the region  $2557\text{ cm}^{-1}$  proving the formation of S-Pb-S bond, namely, the insertion of the lead atom into the two mercapto groups of the dithiol.

**3,3-Dibromobutane-2-thione (II).** Through a solution of 1 g (4.3 mmol) of 3,3-dibromobutane-2-one (**I**) in 10 ml of anhydrous methanol saturated at  $-10^\circ\text{C}$  with HCl within 1.5 h was passed at  $-55$  to  $-60^\circ\text{C}$  a flow of hydrogen sulfide till complete disappearance of the initial ketone (8–12 h). The reaction mixture was flushed with dry argon to remove HCl and  $\text{H}_2\text{S}$  and diluted with 50 ml of ether cooled to  $-60^\circ\text{C}$ . Then the reaction mixture was quickly washed with ice water till neutral washings (the reaction mixture turned from colorless to dark-red) and dried over  $\text{CaCl}_2$  at  $-60^\circ\text{C}$ . On removing the ether in a vacuum we obtained 0.96 g (90%) of virtually pure thione **II**, dark-red oily substance, stable below  $-30^\circ\text{C}$ .  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 2.79 s (3H,  $\text{CH}_3\text{CBr}_2$ ), 3.27 s (3H,  $\text{CH}_3\text{C}=\text{S}$ ).  $^{13}\text{C}$  NMR spectrum,  $\delta$ , ppm: 39.14 ( $\text{CH}_3\text{C}=\text{S}$ ), 40.61 ( $\text{CH}_3\text{CBr}_2$ ), 67.70 ( $\text{CBr}_2$ ), 241.97 ( $\text{C}=\text{S}$ ). Initial 3,3-dibromobutane-2-one (**I**).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 2.55 s (3H,  $\text{CH}_3\text{C}=\text{O}$ ), 2.69 s (3H,  $\text{CH}_3\text{CBr}_2$ ).  $^{13}\text{C}$  NMR spectrum,  $\delta$ , ppm: 23.35 ( $\text{CH}_3\text{C}=\text{O}$ ), 34.97 ( $\text{CH}_3\text{CBr}_2$ ), 62.75 ( $\text{CBr}_2$ ), 195.19 ( $\text{C}=\text{O}$ ). Found, %: Br 65.01; S 13.68.  $\text{C}_4\text{H}_6\text{Br}_2\text{S}$ . Calculated, %: Br 65.04; S 13.01.

### 1,1-Dibromo-2-phenylethene-2,2-dithiol (**V**).

Through a solution of 1 g (3.6 mmol) of 1,1-dibromoacetophenone (**III**) in 10 ml of anhydrous methanol saturated at  $-10^\circ\text{C}$  with HCl within 1.5 h was passed at  $-55$  to  $-60^\circ\text{C}$  a flow of hydrogen sulfide till complete disappearance of the initial ketone (18–20 h). In the course of reaction the solution from colorless turned dark-blue and then gradually suffered decoloration. The reaction mixture was flushed with dry argon to remove HCl and  $\text{H}_2\text{S}$  and diluted with 50 ml of ether cooled to  $-60^\circ\text{C}$ . Then the reaction mixture was quickly washed with ice water till neutral washings (the reaction mixture turned from colorless to dark-red) and dried over  $\text{CaCl}_2$  at  $-60^\circ\text{C}$ . On removing the ether in a vacuum we obtained 1.09 g (85%) virtually pure *gem*-dithiol **V**, light-yellow oily substance, stable below  $-10^\circ\text{C}$ . IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 2557 (SH).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 2.11 s (2H, 2SH), 6.40 s (1H,  $\text{CHBr}_2$ ), 7.34–8.08 m ( $\text{C}_6\text{H}_5$ ).  $^{13}\text{C}$  NMR spectrum,  $\delta$ , ppm: 59.89 (SCS), 65.71 ( $\text{BrCBr}$ ), 125–134 ( $\text{C}_6\text{H}_5$ ). Initial 1,1-dibromoacetophenone (**III**).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 6.70 s (1H,  $\text{CHBr}_2$ ), 7.47–8.07 m (5H,  $\text{C}_6\text{H}_5$ ).  $^{13}\text{C}$  NMR spectrum,  $\delta$ , ppm: 59.89 (SCS), 39.51 ( $\text{BrCBr}$ ), 125–134 ( $\text{C}_6\text{H}_5$ ). Found, %: Br 64.45; S 20.04.  $\text{C}_8\text{H}_{10}\text{Br}_2\text{S}_2$ . Calculated, %: Br 48.78; S 19.51.

**Lead 1,1-dibromo-2-phenylethene-2,2-dithiolate (VI).** To a solution of 0.5 g (1.5 mmol) of compound **V** in 5 ml of anhydrous methanol cooled to  $-30^\circ\text{C}$  was added dropwise at stirring a solution of 0.49 g (1.5 mmol) of lead acetate in 5 ml of anhydrous methanol. The separated yellow precipitate was stirred for 1 h and then filtered off, washed with methanol, ether, and dried in a vacuum. Yield 0.78 g (93%), yellow powder, t.decomp.  $180\text{--}183^\circ\text{C}$ . The IR spectrum of lead dithiolate **VI** lacked the absorption band in the region  $2557\text{ cm}^{-1}$ , characteristic of the mercapto groups of initial *gem*-dithiol **V**. Found, %: Br 29.48; S 11.58.  $\text{C}_8\text{H}_8\text{Br}_2\text{S}_2\text{Pb}$ . Calculated, %: Br 30.02; S 12.00.

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were registered on a spectrometer Bruker DPX-400 in  $\text{CDCl}_3$ . IR spectra were recorded on IFS-25 instrument from KBr pellets. The reaction progress was monitored and the purity of compounds obtained was checked by TLC on Silufol UV-254 plates, chloroform was used as eluent.

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