

Hydrothiolysis of 1,3-Dihaloalkan-2-ones

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Abstract—Acid-catalyzed hydrothiolysis of 1,3-dihaloacetones $(XCH_2)_2CO$ ($X=Cl, Br$) at low temperature was investigated in various solvents. Optimum conditions were found for the formation of 1,3-dichloropropan-2-ol-2-thiol and 1,3-dibromo(dichloro)propan-2-thiones, the first representatives of compounds containing $(XRR'C)_2C(OH)SH$ and $(XRR'C)_2C=S$ ($X=Hlg, R,R'=H, hydrocarbyl$) fragments.

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The acid-catalyzed reaction of ketones with hydrogen sulfide is at present the most general method of preparation of unstable thiones, enethiols, geminal dithiols, trithianes, and polysulfides [1–3]. The direction of the reaction essentially depends on the structure of the initial ketone, character of solvent, on reaction temperature and stability of the final product of the process.

The product of reaction between acetone and hydrogen sulfide in acid medium at $-80^\circ C$ is known to be trithioacetone [4], and the monomeric thioacetone, stable at $-78^\circ C$, already over $-60^\circ C$ suffer spontaneous polymerization into linear polymers [3].

The first example of monohalothioacetones, 1-chloropropan-2-thione, we succeeded to synthesize by treating chloroacetone with hydrogen sulfide without solvent [5]. The structure of the final products of hydrothiolysis of 1-chloropropan-2-one essentially depended on the reaction conditions. For instance, in ether the sole product formed was 1-chloropropan-2,2-dithiol [6, 7], and in a methanol solution of hydrogen chloride 2,5-dimethyl-2,5-endothio-1,4-dithiane was obtained [8].

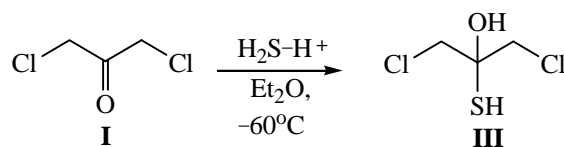
Extending the chemistry of α -halo-substituted thiones [9] we planned to synthesize previously unknown 1,3-dihalothiones and their derivatives. To this end we investigated a cryochemical acid-catalyzed reaction of 1,3-dichloro- (**I**) and 1,3-dibromopropan-2-ones (**II**) with hydrogen sulfide in the presence of HCl in the temperature range -70 to $-10^\circ C$ in protic and aprotic solvents.

The hydrothiolysis of 1,3-dichloropropan-2-one (**I**) was already carried out formerly [10] in two solvents: in

a saturated solution of hydrogen chloride in ethanol at $-10^\circ C$ and in dilute hydrochloric acid (3:1) at $20^\circ C$. In the first event the main product was 1,3-dichloro-2,2-diethoxypropane, in the second, 1,15-dichloro-4,6,12-trithiapentadecene-2,6,10,14-tetraone or 1,5-dithiocyclooctane-3,7-dione.

It was established that reaction of the hydrogen sulfide with 1,3-dichloropropan-2-one (**I**) at $-60^\circ C$ in ethyl ether saturated with HCl gave rise to 1,3-dichloro-propan-2-ol-2-thiol (**III**) (Scheme 1). The structure of *gem*-olthiol **III** was established from 1H and ^{13}C NMR, IR spectroscopy, and elemental analysis data.

Scheme 1.

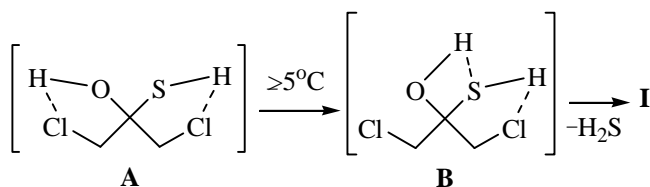


In the 1H and ^{13}C NMR spectra signals appeared characteristic of CH_2 , CSH , COH , and $HSCO$ groups. In the IR spectrum absorption bands were observed of mercapto and hydroxy groups (see EXPERIMENTAL). The synthesized *gem*-olthiol at the temperature over $-5^\circ C$ starts to liberate hydrogen sulfide converting into the initial ketone. Already after some minutes in the IR spectrum of the *gem*-olthiol sample alongside the absorption bands of SH and OH groups appeared the band in the region 1739 cm^{-1} corresponding to vibrations of $C=O$ group. The intensity of this band grows in time. In the

^1H NMR spectrum under these conditions a signal appears at 4.33 s (4H, CH_2); in the ^{13}C NMR spectrum, signals at 46.21 ($\underline{\text{C}}\text{H}_2$) and 195.01 ($\underline{\text{C}}=\text{O}$) ppm characteristic of the initial ketone.

The geminal olthiols are known [11] to be intermediates of the hydrothiolysis. Nobody succeeded to isolate them in these processes. The stabilization of compound **III** obtained is due apparently to intermolecular hydrogen bonds. Considering the structure of 1,3-dichloropropan-2-ol-2-thiol (**III**) having two chlorine atoms in the γ -position with respect to the geminal olthiol moiety it is presumable that owing to the hydrogen bonds spiro-conjugated chelate rings **A** form (Scheme 2) stable below -5°C . On raising the temperature the hydrogen bonds in rings **A** suffer rupture, and new chelate ring **B** forms favoring hydrogen sulfide elimination and appearance of initial ketone **I**.

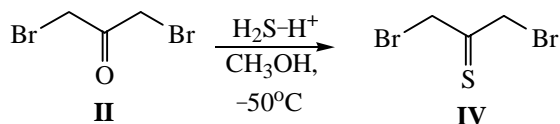
Scheme 2.



In a protic solvent (methanol) the formation of chelate rings is weakened, therefore the hydrothiolysis of 1,3-dibromo- (**II**) and 1,3-dichloropropan-2-ones (**I**) in the system MeOH-HCl at -50°C led to the formation of the corresponding thiones.

1,3-Dibromopropane-2-thione (**IV**) (Scheme 3) we succeeded to isolate from the reaction mixture after an appropriate workup as an oily substance of crimson color, stable below -30°C .

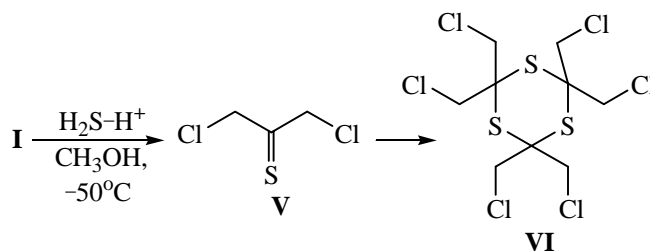
Scheme 3.



At temperature higher than -30°C 1,3-dibromothioacetone (**IV**) starts to polymerize with hydrogen bromide liberation. The structure of 1,3-dibromopropane-2-thione (**IV**) was confirmed by ^1H and ^{13}C NMR spectra and elemental analysis. The NMR spectra of initial dibromoacetone are as follows: 4.14 s (4H, CH_2), 30.49 ($\underline{\text{C}}\text{H}_2$), 193.48 ($\underline{\text{C}}=\text{O}$) ppm.

1,3-Dichloropropane-2-thione (**V**) (Scheme 4) prepared under similar conditions in contrast to its 1,3-dibromosubstituted analog **IV** proved to be less stable and presumably underwent cyclotrimerization (cf. [12]) already at the attempt to isolate it from the reaction mixture. In this case the stability of 1,3-halosubstituted propane-2-thiones is governed apparently by the nature of the halogen, the size of the atom, its electronegativity, and capability of stabilization.

Scheme 4.



Isolated compound **VI** assigned with structure 2,2,4,4,6,6-hexakis(dichloromethyl)-1,3,5-trithiane is poorly soluble in the majority of organic solvents. It was characterized with IR spectrum and elemental analysis.

We failed to isolate individual compounds on hydrothiolysis of 1,3-dibromopropan-2-one (**II**) in aprotic solvents or in liquid hydrogen sulfide. Only dark brown resins containing 10–12% of sulfur were separated from the reaction mixture.

Obviously in event of hydrothiolysis of 1,3-dihalocetones **I** and **II** in methanol at -50°C the conditions of the synthesis proved to be optimum, for we did not find side products of the presumable substitution and alcoholysis reactions (cf. [10]), or trithionbornanes (cf. [13]).

Thus it was established that the direction of acid-catalyzed hydrothiolysis of 1,3-dihalopropan-2-ones **I** and **II** is governed by the following factors: character of solvent, reaction temperature, and nature of the halogen.

EXPERIMENTAL

^1H and ^{13}C NMR spectra were registered in CDCl_3 solutions on a spectrometer Bruker DPX-400. 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.

1,3-Dichloropropan-2-ol-2-thiol (III**).** Through a solution of 1 g (7.9 mmol) of 1,3-dichloropropan-2-one

(I) in 10 ml of anhydrous ether saturated with HCl at -10°C was passed a flow of hydrogen sulfide at $-55\text{...}-60^{\circ}\text{C}$ for 10–12 h till complete disappearance of the initial ketone. The reaction mixture was flushed with dry argon to remove HCl and H_2S . The ether solution of the reaction mixture cooled to -60°C was quickly washed with ice water to neutral reaction and dried with CaCl_2 at -60°C ; ether was removed in a vacuum. Yield 1 g (82%), colorless oily substance stable below -5°C . IR spectrum, ν , cm^{-1} : 2569 (SH), 3449 (OH). ^1H NMR spectrum, δ , ppm: 2.77 s (1H, CSH), 3.90 and 3.91 d (4H, 2CH_2), 3.96 s (1H, COH). ^{13}C NMR spectrum, δ , ppm: 50.57 (CH_2), 82.94 (HSCOH). Found, %: Cl 43.70; S 20.28. $\text{C}_3\text{H}_6\text{Cl}_2\text{OS}$. Calculated, %: Cl 44.10; S 19.88.

In the course of reaction (after 6 h from the start) a sample of reaction mixture was taken for analysis. In the ^1H and ^{13}C NMR spectra of the reaction mixture signals were observed characteristic of 1,3-dichloropropan-2-ol-2-thiol (III). These data proved that this compound was not formed during workup of the reaction mixture from the corresponding thione.

1,3-Dibromopropan-2-thione (IV). Through a solution of 1 g (4.6 mmol) of 1,3-dibromopropan-2-one (II) in 10 ml of anhydrous methanol saturated with HCl at -10°C was passed a flow of hydrogen sulfide at $-45\text{...}-50^{\circ}\text{C}$ for 8–12 h till complete disappearance of the initial ketone. The reaction mixture was flushed with dry argon to remove HCl and H_2S , and 50 ml of ethyl ether cooled to -60°C was added. Then the reaction mixture was quickly washed with ice water to neutral reaction (the reaction mixture turned from colorless to crimson) and dried with CaCl_2 at -60°C ; ether was removed in a vacuum. Yield 0.8 g (75%), oily substance of crimson color stable below -30°C . ^1H NMR spectrum, δ , ppm: 4.70 s (4H, 2CH_2). ^{13}C NMR spectrum, δ , ppm: 38.95 (CH_2), 120.15 (C=S). Found, %: Br 67.85; S 14.23. $\text{C}_3\text{H}_4\text{Br}_2\text{S}$. Calculated, %: Br 68.96; S 13.79.

2,4,6-Hexachloromethylene-1,3,5-trithiane (VI). Through a solution of 1 g (7.9 mmol) of 1,3-dichloropropan-2-one (I) in 10 ml of anhydrous methanol saturated with HCl at -10°C was passed a flow of hydrogen sulfide at $-45\text{...}-50^{\circ}\text{C}$ for 8–12 h till complete disappearance of

the initial ketone. The reaction mixture was flushed with dry argon to remove HCl and H_2S , and 50 ml of ethyl ether cooled to -60°C was added. Then the reaction mixture was quickly washed with ice water to neutral reaction (the reaction mixture first turned crimson, then rapidly decolorized). On removing from the water layer a colorless powder precipitated from the ether solution. The powder was filtered off, washed with ether, and dried in a vacuum. Yield 1.9 g (83%), colorless powder, t. decomp. $171\text{--}173^{\circ}\text{C}$. IR spectrum lacked absorption bands of functional groups C=O, C=S, $\text{C}(\text{SH})_2$. Found, %: Cl 50.25; S 21.83. $\text{C}_3\text{H}_4\text{Cl}_2\text{S}$. Calculated, %: Cl 49.65; S 22.37.

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