

SHORT  
COMMUNICATIONSReactions of 1-Iodo- and 1,3-Diiodoacetone  
with Hydrogen Sulfide

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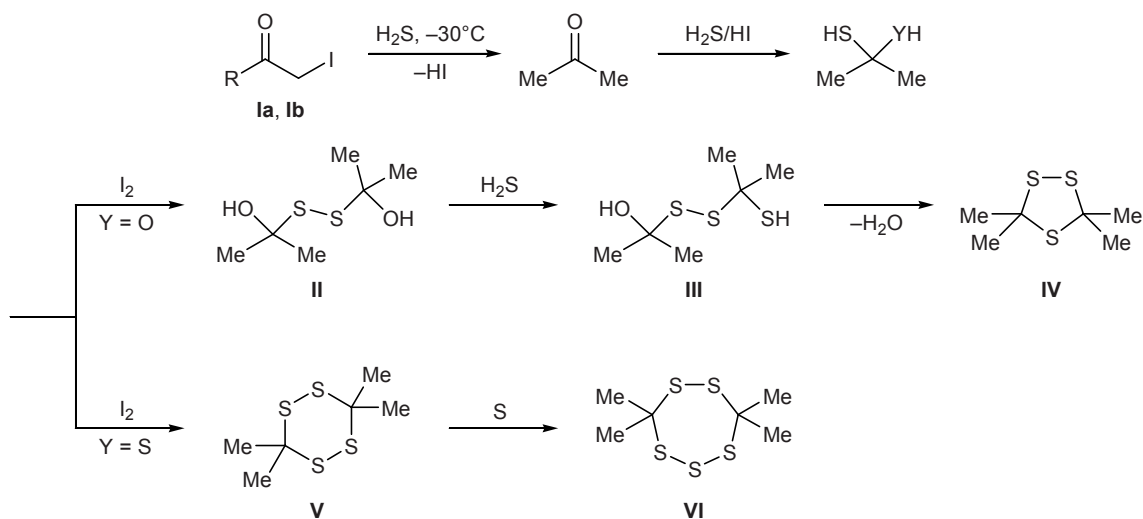
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While developing our studies on reactions of  $\alpha$ -halo ketones with hydrogen sulfide [1, 2], in the present work we examined reactions of iodoacetone (**Ia**) and 1,3-diiodoacetone (**Ib**) with hydrogen sulfide in chloroform at  $-30^\circ\text{C}$ . The reaction of compound **Ia** with  $\text{H}_2\text{S}$  started instantaneously with abundant liberation of molecular iodine. However, instead of the expected formation of  $\text{H}_2\text{C}-\text{CH}_2$  bond, iodoacetone (**Ia**) was reduced to acetone with hydrogen iodide generated *in situ* from  $\text{I}_2$  and  $\text{H}_2\text{S}$  ( $\text{I}_2 + \text{H}_2\text{S} \rightarrow 2\text{HI} + \text{S}$ ). Acetone readily reacted with hydrogen sulfide in the presence of HI to give 3,3,5,5-tetramethyl-1,2,4-trithiolane (**IV**, 77%) and 3,3,6,6-tetramethyl-1,2,4,5-tetrathiane (**V**, 9%) as final products. Monitoring of the reaction course by NMR spectroscopy in  $\text{CDCl}_3$  revealed formation of 2,2'-dithiodi(propan-2-ol) (**II**) in 30 min after the reaction started. The  $^1\text{H}$  NMR spectrum of the reaction mixture contained signals assign-

able to methyl ( $\delta$  2.35 ppm) and methylene protons ( $\delta$  3.76 ppm) in the initial iodo ketone and signals at  $\delta$  2.11 (s, 12H,  $\text{CH}_3$ ) and 4.04 ppm (s, 2H, OH). In the  $^{13}\text{C}$  NMR spectrum of that mixture we observed signals belonging to iodoacetone [ $\delta_{\text{C}}$ , ppm: 7.02 ( $\text{CH}_2\text{I}$ ), 27.09 ( $\text{CH}_3$ ), 200.33 (CO)] and signals at  $\delta_{\text{C}}$  30.87 and 65.82 ppm, corresponding to the methyl and quaternary carbon atoms of disulfide **II**, respectively. After 2.5 h, four new signals appeared in the  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 2.27 and 2.37 (3H each,  $\text{CH}_3$ ), 2.26 (1H, SH), and 4.12 (1H, OH); presumably, these signals belong to 2-(1-methyl-1-sulfanylethyl)disulfanylpropan-2-ol (**III**); also, a signal at  $\delta$  1.89 ppm (6H,  $\text{CH}_3$ ) was present due to 3,3,5,5-tetramethyl-1,2,4-trithiolane (**IV**). The  $^{13}\text{C}$  NMR spectrum contained signals at  $\delta_{\text{C}}$  27.58, 31.19, 49.26, and 67.47 ppm, corresponding to methyl carbon atoms and quaternary carbon atom in disulfide **III**, and signals at  $\delta_{\text{C}}$  31.57 and 53.43 ppm due to

R = Me (**a**),  $\text{ICH}_2$  (**b**); Y = O, S.

trithiolane **IV**. After 4 h, the main signals in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were those typical of trithiolane **IV**:  $\delta$  1.89 ppm (6H,  $\text{CH}_3$ );  $\delta_{\text{C}}$  31.57 ( $\text{CH}_3$ ) and 53.43 ppm (C). The structure of compounds **IV** and **V** was confirmed by the IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR, and mass spectra, which were consistent with published data [3–7].

Diiodoacetone **Ib** reacted with hydrogen sulfide in a similar way, but the major product was previously unknown 4,4,7,7-tetramethyl-1,2,3,5,6-pentathiepane (**VI**, 59%). Presumably, the key intermediate in this reaction is propane-2,2-dithiol whose oxidation gives rise to another intermediate, 3,3,6,6-tetramethyl-1,2,4,5-tetrathiane (**V**). Compound **V** is capable of reacting with molecular sulfur to produce pentathiepane **VI**. The latter could be formed via known insertion of sulfur into the S–S bond in di- and polysulfides [8, 9]. Apart from pentathiepane **VI**, from the reaction mixture we isolated by column chromatography 3,3,5,5-tetramethyl-1,2,4-trithiolane (**IV**, 19%) and 3,3,6,6-tetramethyl-1,2,4,5-tetrathiane (**V**, 10%).

The structure of 4,4,7,7-tetramethyl-1,2,3,5,6-pentathiepane (**VI**) was confirmed by the IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR, and mass spectra. Absorption bands at 553, 486, and 525  $\text{cm}^{-1}$  in the IR spectrum of **VI** can be assigned to stretching vibrations of the S–S bonds in the di- and trisulfide fragments of molecule **VI**. Compound **VI** displayed in the  $^1\text{H}$  NMR spectrum a signal at  $\delta$  1.91 ppm from the methyl protons, while its  $^{13}\text{C}$  NMR spectrum contained signals at  $\delta_{\text{C}}$  30.51 ( $\text{CH}_3$ ) and 76.78 ppm ( $\text{C}^4$ ,  $\text{C}^7$ ). In the mass spectrum of **VI**, the molecular ion peak  $[M]^+$  ( $m/z$  244) had fairly high intensity.

The formation of acetone as primary product in the above reactions was confirmed by independent synthesis of trithiolane **IV** (72%) by reaction of acetone with hydrogen sulfide in the presence of iodine ( $\text{CHCl}_3$ ,  $-30^\circ\text{C}$ ).

Thus we have shown for the first time that the reactions of mono- and diiodoacetones with hydrogen sulfide in chloroform at  $-30^\circ\text{C}$  begin with the reduction of the substrate to acetone with hydrogen iodide generated *in situ*. Hydrogen iodide then catalyzes nucleophilic addition of hydrogen sulfide at the carbonyl group, leading to trithiolane, tetrathiane, and pentathiepane derivatives.

**3,3,5,5-Tetramethyl-1,2,4-trithiolane (IV)**. Hydrogen sulfide was passed through a solution of 2 g (10.8 mmol) of iodoacetone (**Ia**) in 10 ml of chloroform at  $-30^\circ\text{C}$  until the initial ketone disappeared completely (4 h). The mixture was purged with argon to remove  $\text{H}_2\text{S}$ , allowing it to gradually warm up to

room temperature. The solution was evaporated under reduced pressure, and the residue, 3 ml, was subjected to column chromatography on silica gel using chloroform as eluent. Yield 0.5 g (52%), colorless oily substance. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 554 (S–S), 646 (C–S–C) (cf. [1]).  $^1\text{H}$  NMR spectrum:  $\delta$  1.87 ppm, s (12H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR spectrum,  $\delta_{\text{C}}$ , ppm: 31.57 ( $\text{CH}_3$ ), 53.43 ( $\text{C}^3$ ,  $\text{C}^5$ ). Mass spectrum:  $m/z$  180  $[M]^+$ . Found, %: C 39.84; H 6.13; S 52.85.  $\text{C}_6\text{H}_{12}\text{S}_3$ . Calculated, %: C 40.00; H 6.66; S 53.33.

**4,4,7,7-Tetramethyl-1,2,3,5,6-pentathiepane (VI)** was obtained in a similar way from 2 g (6.4 mmol) of 1,3-diiodopropan-2-one (**Ib**). Yield 0.46 g (59%), yellow thick oily substance. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 553 (S–S); 486, 525 (S–S–S).  $^1\text{H}$  NMR spectrum:  $\delta$  1.91 ppm, s (12H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR spectrum,  $\delta_{\text{C}}$ , ppm: 30.51 ( $\text{CH}_3$ ), 66.55 ( $\text{C}^4$ ,  $\text{C}^7$ ). Mass spectrum:  $m/z$  244  $[M]^+$ . Found, %: C 29.18; H 4.36; S 64.98.  $\text{C}_6\text{H}_{12}\text{S}_5$ . Calculated, %: C 29.50; H 4.94; S 65.57.

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded from solutions in  $\text{CDCl}_3$  on a Bruker DPX-400 instrument at 400 and 100 MHz, respectively. The IR spectra were measured in KBr (or thin films) on an IFS 25 spectrometer. The progress of reactions and the purity of products were monitored by TLC on Silufol UV-254 plates using chloroform as eluent. The products were isolated by column chromatography on silica gel L (70–230 mesh) using chloroform as eluent.

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