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SHORT COMMUNICATIONS

New Synthesis of 1,2,4-Trithiolane Derivatives

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Classical reactions of carbonyl compounds with nucleophilic reagents are catalyzed by acids, generally by hydrogen chloride. Hydrogen iodide (which is a stronger acid than hydrogen chloride) was not used to catalyze such reactions.

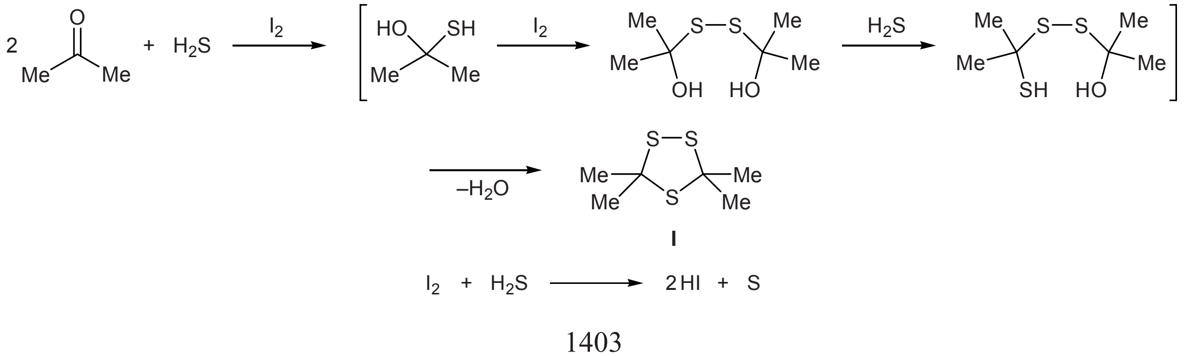
We were the first to accomplish acid-catalyzed addition of hydrogen sulfide to aliphatic, alicyclic, aromatic–aliphatic, and aromatic ketones in the presence of hydrogen iodide generated *in situ*. For this purpose, a required amount of molecular iodine was dissolved in the corresponding ketone or its solution in chloroform, and hydrogen sulfide was passed through the mixture. Hydrogen iodide liberated during the process catalyzed nucleophilic addition of hydrogen sulfide at the ketone carbonyl group. The products were readily isolated by column chromatography on silica gel.

Thus the reaction of acetone with hydrogen sulfide and iodine at –30°C gave 2-sulfanylpropan-2-ol as primary adduct which was converted into 3,3,5,5-tetramethyl-1,2,4-trithiolane (**I**) in 52% yield (Scheme 1). The structure of **I** was confirmed by the IR, ^{1}H and ^{13}C NMR, and mass spectra. In the IR spectrum of **I** (film) we observed an absorption band at 554 cm^{-1}, which may be assigned to stretching vibrations of the S–S bond, and a band at 646 cm^{-1}, corresponding to the C–S–C fragment. The ^{1}H NMR spectrum of this compound contained one signal from methyl protons at δ 1.87 ppm, and signals at δ_C 31.08 and 53.43 ppm from the methyl carbon atoms and C^3 (C^5), respectively, were present in the ^{13}C NMR spectrum. A strong peak from the molecular ion (*m*/*z* 180) was observed in the mass spectrum of 3,3,5,5-tetramethyl-1,2,4-trithiolane (**I**), which is consistent with published data [1, 2].

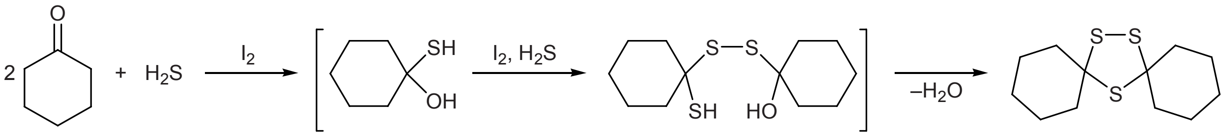
Unlike the known method of synthesis of compound **I** [2] via reaction of acetone with hydrogen sulfide and sulfur in the presence of diisobutylamine (yield 44%), the described one-step procedure is advantageous due to simple manipulations and fast and easy isolation of the target product.

Likewise, cyclohexanone reacted with hydrogen sulfide in the presence of iodine to produce 35.5% of 7,14,15-trithiadispiro[5.1.5.2]pentadecane (**II**) (Scheme 2). Compound **II** displayed in the ^{1}H NMR spectrum signals from the cyclohexane methylene protons as a multiplet in the region δ 1.43–2.40 ppm. The corresponding carbon signals appeared in the ^{13}C NMR spectrum at δ_C 25.22, 26.16, and 39.82 ppm, and the spiro carbon nuclei resonated at δ_C 80.96 ppm. The known procedure for the synthesis of 7,14,15-trithia-

Scheme 1.

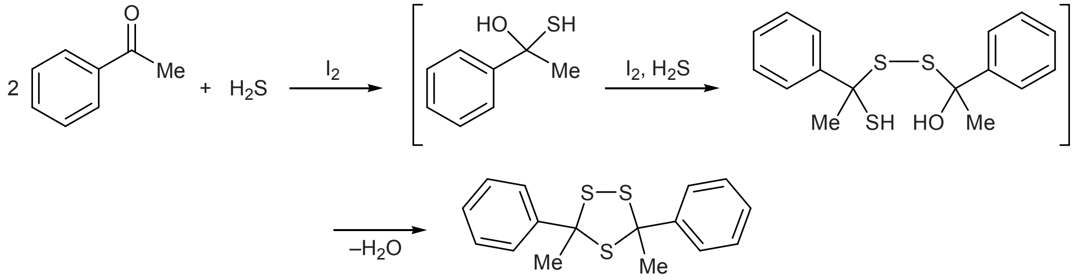


Scheme 2.



II

Scheme 3.



III

dispiro[5.1.5.2]pentadecane (**II**) is based on the reaction of 1-morpholinocyclohexene with hydrogen sulfide in the presence of sulfur [2].

Following the proposed procedure, from acetophenone we obtained previously unknown 3,5-dimethyl-3,5-diphenyl-1,2,4-trithiolane (**III**) in 52% yield (Scheme 3). The structure of **III** was confirmed by the IR, ^{1}H and ^{13}C NMR, and mass spectra. The IR spectrum of **III** (film) contained an absorption band at 545 cm^{-1}, which corresponds to stretching vibrations of the S–S bond, and the band at 673 cm^{-1} may be assigned to the C–S–C moiety. In the ^{1}H NMR spectrum of this compound we observed a signal at δ 2.12 ppm from the methyl groups, and aromatic protons resonated as a multiplet in the region δ 7.31–7.70 ppm. Signals at δ_C 26.75 and 70.96 ppm in the ^{13}C NMR spectrum were typical of the methyl and quaternary (C^3, C^5) carbon atoms, respectively. In the mass spectrum of 3,5-dimethyl-3,5-diphenyl-1,2,4-trithiolane (**III**) a strong peak from the molecular ion (*m*/*z* 304) was present.

Under analogous conditions, benzophenone was converted into 3,3,5,5-tetraphenyl-1,2,4-trithiolane (**IV**) in a poor yield (5–10%). Compound **IV** was synthesized previously by reaction of thiobenzophenone with 2,3,5,6-tetrachlorocyclohexa-2,5-diene-1,4-dione [3], primary or secondary amines [4, 5], or Chloramine-T [6].

Thus we have developed a new simple and convenient procedure for the synthesis of 1,2,4-trithiolane derivatives by reaction of aliphatic, alicyclic, and aromatic–aliphatic ketones with hydrogen sulfide in the presence of molecular iodine.

3,3,5,5-Tetramethyl-1,2,4-trithiolane (I). Iodine, 8.74 g (6.8 mmol), was added to a solution of 2 g (3.4 mmol) of acetone in 5 ml of chloroform. The mixture was cooled to –30°C, and hydrogen sulfide was passed through the mixture until the initial ketone disappeared completely (30 min). The mixture was then purged with nitrogen to remove hydrogen sulfide, allowing it to gradually warm up to room temperature, and evaporated under reduced pressure, and the residue (~3 ml) was subjected to column chromatography on silica gel using chloroform as eluent. Yield 1.6 g (52%), colorless oil. IR spectrum, ν, cm^{-1}: 554 (S–S), 646 (C–S–C) (cf. [1]). ^{1}H NMR spectrum: δ 1.87 ppm, s (CH_3). ^{13}C NMR spectrum, δ_C, ppm: 31.08 (CH_3), 53.43 (C^3, C^5). Mass spectrum: *m*/*z* 180 $[M]^+$.

7,14,15-Trithiadispiro[5.1.5.2]pentadecane (II) was synthesized in a similar way from 2 g (2.0 mmol) of cyclohexanone in the presence of 5.18 g (4.0 mmol) of iodine (hydrogen sulfide was passed over a period of ~1 h). Yield 0.94 g (35.5%), colorless crystals, mp 50–51°C [2]. IR spectrum, ν, cm^{-1}: 534 (S–S), 700 (C–S–C). ^{1}H NMR spectrum: δ 1.43–2.40 ppm, m (CH_2). ^{13}C NMR spectrum, δ_C, ppm: 25.22 (CH_2), 26.16 (CH_2), 39.82 (CH_2), 80.96 (C^3, C^5).

3,5-Dimethyl-3,5-diphenyl-1,2,4-trithiolane (III) was synthesized in a similar way from 1.5 g (1.2 mmol) of acetophenone in the presence of 3 g (2.4 mmol) of iodine (hydrogen sulfide was passed over a period of ~1.5 h). Yield 1 g (52%), colorless thick oil. IR spectrum, ν, cm^{-1}: 545 (S–S), 673 (C–S–C). ^{1}H NMR spectrum, δ, ppm: 2.12 s (6H, CH_3), 7.31–7.70 m (10H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 26.75 (CH_3), 70.96 (C^3, C^5), 126.38–

133.14 m (C_{arom}). Found, %: C 62.85; H 5.16; S 32.03. $C_{16}H_{16}S_3$. Calculated, %: C 63.15; H 5.26; S 31.58.

The ^{1}H and ^{13}C NMR spectra were recorded from solutions in $CDCl_3$ on a Bruker DPX-400 spectrometer at 400 and 100 MHz, respectively. The IR spectra were measured from samples pelleted with KBr or neat substances on an IFS-25 spectrometer. The mass spectra (electron impact, 70 eV) were obtained on a GCMS-QP5050A instrument (quadrupole mass analyzer). The progress of reactions and the purity of products were monitored by TLC on Silufol UV-254 plates using chloroform as eluent; spots were visualized under UV light or by treatment with iodine vapor. Silica gel L (70–230 mesh) was used for column chromatography (eluent chloroform).

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REFERENCES

1. Tjan, S.B., Haakman, J.C., Teunis, C.J., and Peer, H.G., *Tetrahedron*, 1972, vol. 28, p. 3489.
2. Asinger, F., Thiel, M., and Lipfert, G., *Justus Liebigs Ann. Chem*., 1959, vol. 627, p. 195.
3. Schonberg, A. and Konig, B., *Chem. Ber*., 1968, vol. 101, p. 725.
4. Campbell, M.M. and Evgenios, D.M., *J. Chem. Soc. D*, 1971, no. 4, p. 179.
5. Campbell, M.M. and Evgenios, D.M., *J. Chem. Soc., Perkin Trans. 1*, 1973, no. 23, p. 2862.
6. Campbell, M.M. and Evgenios, D.M., *J. Chem. Soc., Perkin Trans. 1*, 1973, no. 23, p. 2866.