

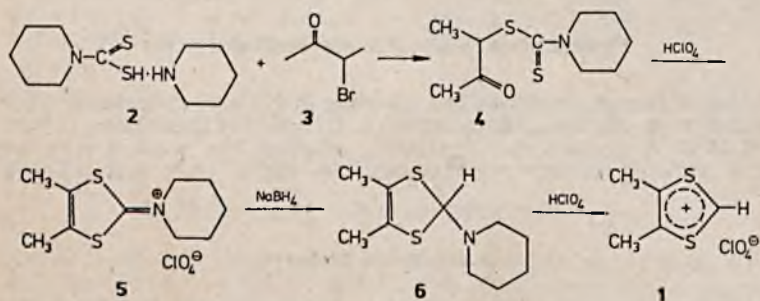
SYNTHESIS OF 4,5-DIMETHYL-1,3-DITHOLIUM PERCHLORATE

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Takamizawa and Hirai have presented a convenient method for preparing 4-*para*-substituted phenyl-1,3-dithiolium salts¹). We have applied this method in the synthesis of 4,5-dimethyl-1,3-dithiolium perchlorate (1) according to Scheme 1. The efforts to use an analogical way to prepare other dialkyl-1,3-dithiolium salts have been reported but not realized²).

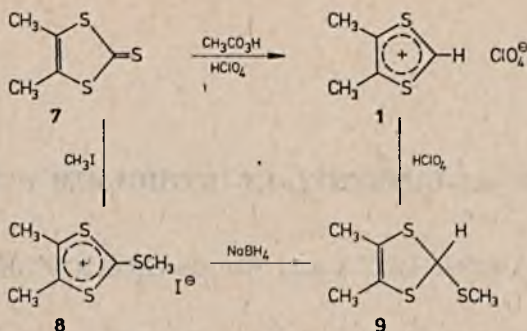
Scheme 1



α -Methylacetonyl 1-piperidinocarbodithioate (4) was easily obtained in condensation of piperidinium 1-piperidinocarbodithioate (2) with 3-bromo-2-butanone (3). Cyclization of 4 with 70% perchloric acid yielded 1-(4,5-dimethyl-1,3-dithiole-2-ylidene)-piperidinium perchlorate (5). Immonium salt 5 was smoothly reduced with sodium borohydride to 2-piperidino-4,5-dimethyl-1,3-dithiole (6) in excellent yield. Treatment of 6 with perchloric acid yielded perchlorate 1.

Other methods of preparing 4,5-dimethyl-1,3-dithiolium salts require 4,5-dimethyl-1,3-dithiole-2-thione (7) as starting material. Perchlorate 1 is obtained by treatment of 7 with peracetic and perchloric acids³). An alternative route includes S-methylation of 7 with methyl iodide, followed by borohydride reduction of resulting 2-thiomethyl-4,5-dimethyl-1,3-dithiolium iodide (8) to 2-thiomethyl-4,5-dimethyl-1,3-dithiole (9), and treatment of 9 with perchloric acid⁴).

Scheme 2



The now reported procedure seems to be a safe and simplified route to 4,5-dimethyl-1,3-dithiolium perchlorate. Complete experimental data for preparing this salt have not yet been made available.

EXPERIMENTAL

^1H NMR spectra were determined at a Jeol JNM MH100 spectrometer using TMS ($\delta = 0$) as internal standard. IR spectra were recorded on a Specord 71 IR spectrometer. All melting and boiling points were uncorrected.

Piperidinium 1-piperidinocarbodithioate (2)

A solution of 38 g (0.5 mole) carbon disulfide in 150 ccm of acetone was dropwise, slowly, added to a stirred solution of 85 g (1 mole) of piperidine in 400 ccm of acetone, at 10°C . A product was separated, collected and washed with acetone to afford 112 g (91%) of colorless crystals, m.p. $169\text{--}173^\circ\text{C}$ (Lit.⁵): m.p. $169\text{--}171^\circ$.

3-Bromobutan-2-one (3)

To a stirred solution of 45 g (0.625 mole) 2-butanone in 350 ccm of carbon tetrachloride 100 g (0.625 mole) of bromine was dropwise, slowly, added at room temperature. The reaction mixture was washed successively with water, aqueous sodium carbonate, water and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure and crude product was purified by vacuum distillation; yield 67 g (71%) of colorless liquid, b.p. $44^\circ\text{C}/25$ mm Hg (Lit.⁶): b.p. $30\text{--}32^\circ\text{C}/9$ mm Hg).

 α -Methylacetyl 1-piperidinocarbodithioate (4)

A sample of 34.7 g (0.23 mole) of 3 was dropped to a stirred suspension of 62.2 g (0.253 mole) of 2 in 500 ccm of ethanol. The mixture was gently refluxed for 3 hrs. After evaporation of the solvent, the residue was diluted with ca. 200 ccm of chloroform, washed with water and dried over anhydrous magnesium sulfate. This solvent was removed under reduced pressure and the crude product was crystallized from *n*-hexane to afford 43 g (81%) of colorless crystals, m.p. $43\text{--}45^\circ\text{C}$. ^1H NMR (CCl_4), δ : 1.40 (d, $J = 7.06$ Hz, 3H), 1.61–1.84 (m, 6H), 2.22 (s, 3H), 3.91–4.29 (m, 4H), 4.92 (q, $J = 7.06$ Hz, 1H); IR (KBr), ν : 1720 cm^{-1} (C=O).

Analysis:

For $C_{10}H_{17}NS_2O$ — Calcd.: 52.0% C, 7.4% H, 6.1% N, 27.7% S;
found: 51.8% C, 7.3% H, 6.1% N, 27.2% S.

1-(4,5-Dimethyl-1,3-dithiole-2-ylidene)-piperidinium perchlorate (5)

To 100 ccm of 70% perchloric acid 23.1 g (0.1 mole) of **4** was slowly added in small portions. The mixture was stirred and warmed to 50°C for 2 hrs. After dilution with 50 ccm acetone and cooling to -10°C ca. 500 ccm of anhydrous ethyl ether was added. Separated crystals were collected, washed with ethyl ether and crystallized from ethanol to yield 27 g (86%) of colorless crystals, m.p. 170–172°C. 1H NMR (CF_3COOD), δ : 1.74–2.03 (m, 6H), 2.33 (s, 6H), 3.72–3.93 (m, 4H); IR (KBr), ν : 1085 cm^{-1} (ClO_4).

Analysis:

For $C_{10}H_{16}NS_2ClO_4$ — Calcd.: 38.3% C, 5.1% H, 4.5% N, 20.4% S, 11.3% Cl;
found: 38.2% C, 5.1% H, 4.5% N, 20.1% S, 10.8% Cl.

2-Piperidino-4,5-dimethyl-1,3-dithiole (6)

To a suspension of 18.8 g (0.06 mole) of ammonium salt **5** in 200 ccm of ethanol (0.18 mole) of sodium borohydride was slowly added in small portions and stirred for 3 hrs at room temperature (not above 30°C). The solution was evaporated under reduced pressure and to the residue ca. 200 ccm of water was added. The mixture was left standing in a refrigerator overnight. The product was extracted with ethyl ether, organic layer was washed with water and dried over anhydrous magnesium sulfate. After evaporation of solvent the crude product was purified by distillation under reduced pressure to yield 11 g (85%) of yellow oil, b.p. 120–122°C/0.6 mm Hg, solidifying in a refrigerator, m.p. 27–31°C. 1H NMR (CCl_4), δ : 1.33–1.63 (m, 6H), 1.87 (s, 6H), 2.35–2.53 (m, 4H), 5.74 (s, 1H).

Analysis:

For $C_{10}H_{17}NS_2$ — Calcd.: 55.8% C, 7.9% H, 6.5% N, 29.8% S;
found: 55.9% C, 7.8% H, 6.2% N, 30.4% S.

4,5-Dimethyl-1,3-dithiolium perchlorate (1)

To a stirred solution of 8 ccm of 70% perchloric acid in 8 ccm of acetone a solution of 2.6 g (0.012 mole) of **6** in 6 ccm of acetone was added dropwise, at room temperature. After 15 minutes the solution was cooled to 0°C and anhydrous ethyl ether (100 ccm) was added to precipitate the product completely. Filtration and washing with ethyl ether yielded pink crystals, 2.1 g (75%), m.p. 119–121°C (Lit.⁴): m.p. 124–126°C, spectral data agree with ⁴): 1H NMR (CD_3CN), δ : 2.73 (s, 6H), 10.87 (s, 1H); IR (KBr), ν : 1085 cm^{-1} (ClO_4).

Received March 13th, 1980.

REFERENCES

- Takamizawa A., Hirai K., *Chem. Pharm. Bull.*, **17**, 1924 (1969).
Calas P., Fabre J.-M., Khalife-El-Saleh M., Mas A., Torrelles E.,
Giral L., *Compt. rend.*, **C281**, 1037 (1975).
Ferraris J. P., Poehler T. O., Bloch A. N., Cowan D. O., *Tetrahedron Letters*, **1973**, 2553.
Krasuski W., Ph.D. Thesis, Polytechnical University, Warszawa 1978.
Maass E., Wolfenstein R., *Chem. Ber.*, **31**, 2687 (1898).
Reppe C., Kumar R., *Arkiv Kemi*, **23**, 475 (1965).