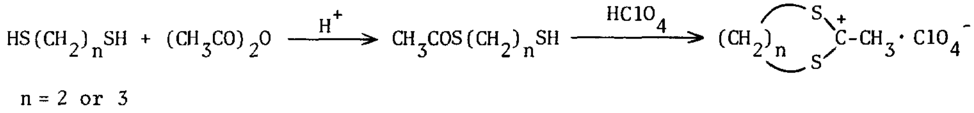
Tetrahedron Letters,Vol.23,No.26,pp 2665-2666,1982 0040-4039/82/262665-02$03.00/0
Printed in Great Britain

# CYCLIC DITHIO-CARBENIUM ION SALTS AND THEIR CONVERSION TO KETENE DITHIOACETALS

Tadashi Okuyama
Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560, Japan

Abstract: 1,2-Ethanedithiol and 1,3-propanedithiol were treated with perchloric acid in acetic anhydride to give 2-methyl-1,3-dithiolan-2-yl and 2-methyl-1,3-dithian-2-yl perchlorates, respectively, which were converted to ketene dithioacetals by deprotonation with tertiary amines.

Dithio-substituted carbocation salts were previously prepared either by hydride transfer from dithioacetals to trityl cation[1] or by dissociation of orthothioesters.[2] Such carbocations have now been isolated as crystalline salts by simply mixing readily-available reagents according to Eq. 1.



(1)

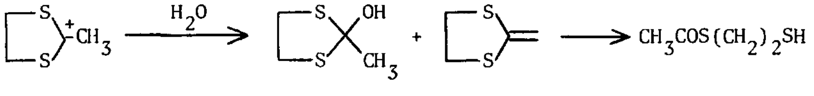
1, n = 2; 2, n = 3

In a typical experiment, 70% perchloric acid (2 ml) was added dropwise to a solution of 1,2-ethanedithiol (1 g) in acetic anhydride (20 ml) under magnetic stirring and cooling in an ice bath. While stirring was continued at room temperature after the addition, the solution gradually turned orange and precipitation started in 1 hr. After 3 hr. reaction, dry ether (30 ml) was added to complete the precipitation of the salt. The precipitates were collected on a glassfilter, washed with ether, and dried under reduced pressure. Yellow crystallines (2.1 g) obtained were identified as 2-methyl-1,3-dithiolan-2-yl perchlorate (1) and found to be essentially pure. UV ($CH_3CN$) $\lambda_{max}$ 328 nm ($\varepsilon \simeq 10^4$). NMR ($CF_3CO_2H$) $\delta$ 3.22 (s, 3H), 4.57 (s, 4H). Reaction of the salt 1 with ethanethiol in acetonitrile afforded almost quantitatively 2-ethylthio-1,3-dithiolane, which substantiates the structure of 1.

The treatment of S-2-mercaptoethyl thioacetate, a presumed intermediate (Eq. 1), with perchloric acid in acetic anhydride gave 1 as expected. The formation of the salt 1 no doubt involves acid-catalyzed thioesterification and cyclization of the thioester. One example of similar reactions is known: Toluene-3,4-dithiol was found to give a very stable cation salt, 5-methyl-1,3-benzodithiolylium perchlorate, on treatment with perchloric acid in formic acid.[3]

1,3-Propanedithiol was treated similarly with perchloric acid in acetic anhydride to give 2-methyl-1,3-dithian-2-yl perchlorate (2). UV ($CH_3CN$) $\lambda_{max}$ 310 nm. NMR ($CF_3CO_2H$) $\delta \sim 2.6$ (m, 2H), 3.05 (s, 3H), 3.75 (t, 4H).

Although all treatments could satisfactorily be performed in the air, the yellow solids turned pink by longer exposure to the air probably owing to the moisture. When the salt 1 was dissolved in water or methanol, vigorous reactions occurred to give tarry pink (or purple) pigments. Under milder conditions, the reaction of 1 with water gave a thioacetate: When a dilute solution of 1 in acetonitrile was introduced into aqueous buffer solutions, the UV absorbance of the cation (328 nm) disappeared immediately and the absorption of S-2-mercaptoethyl thioacetate ($\lambda_{max}$ 232.5 nm) gradually developed in the pH range 0 – 2. 2-Methylene-1,3-dithiolane ($\lambda_{max}$ 244 nm) was found to be formed as well at higher pH.[4]



(2)

The finding that the deprotonation can compete with the hydration in the hydrolysis of 1 would be intriguing in relation to the hydrolysis mechanism of ketene dithioacetals; rate-determining step changes from the initial protonation step to the decay of an intermediate carbocation depending on the structure of the acetal and on the reaction conditions (Eq. 3).[4,5]

$$\mathrm{RCH{=}C(SR')_2} \overset{H^+}{\rightleftharpoons} \mathrm{RCH_2\overset{+}{C}(SR')_2} \xrightarrow{H_2O} \mathrm{RCH_2COSR' + R'SH} \qquad (3)$$

Ketene dithioacetals were preparatively obtained by treating the carbenium salts with tertiary amines. This provides a new synthetic method of ketene dithioacetals.[6] A typical run was carried out as follows. Crude salts (not dried) of 1, obtained from 2 g of 1,2-ethanedithiol was dissolved in dry acetonitrile (30 ml). This solution was added to a solution of diisopropylethylamine[7] (3 ml) in acetonitrile (20 ml) under stirring. The color of the salt solution faded immediately. A usual workup and distillation in the presence of hydroquinone gave 2-methylene-1,3-dithiolane (1.5 g). B.p. 55 °C/9 mmHg. NMR ($CS_2$) $\delta$ 3.31 (s, 4H), 5.00 (s, 2H). A similar treatment of 2 gave 2-methylene-1,3-dithiane. B.p. 97 °C/21 mmHg (lit.[8] 79 – 80 °C/9.5 mmHg). NMR ($CCl_4$) $\delta$ ∿2.15 (m, 2H), 2.86 (t, 4H), 5.27 (s, 2H).

## References and Notes

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(Received in Japan 15 March 1982)