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Isolation of Dithiolanylium Salts and Their Conversion to Ketene Dithioacetals and Ortho Esters

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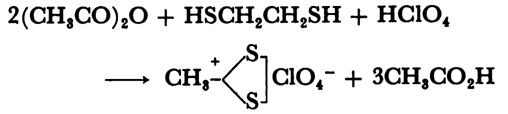
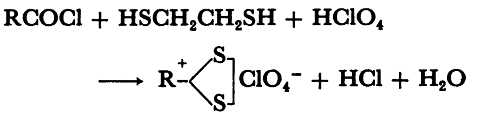
Various 2-substituted 1,3-dithiolan-2-ylium perchlorates (**1**) were prepared by the reaction of 1,2-ethanedithiol with acyl chlorides in the presence of perchloric acid. Treatments of **1** with triethylamine gave 2-alkylidene-1,3-dithiolane (**2**) when the 2-substituent was a primary or secondary alkyl group. 2-Aryl derivatives of **1** were converted to ortho esters by the reaction with methanol in the presence of silver nitrate. 1,3-Dithian-2-ylium perchlorates and 2-alkylidene-1,3-dithianes were also prepared similarly from 1,3-propanedithiol.

We previously described a simple method of preparation of 2-methyl-1,3-dithiolan-2-ylium perchlorate from the reaction of 1,2-ethanedithiol with acetic anhydride in the presence of perchloric acid (Eq. 1).[1] This is extended to a general procedure by using an acyl chloride as one of starting materials (Eq. 2).

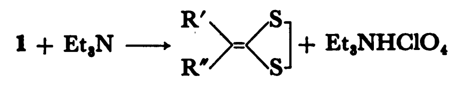

(1)

1a

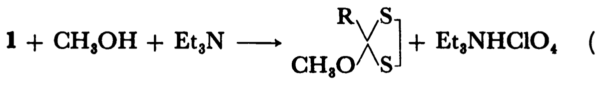

(2)

1 a, R = CH_3 **e**, R = $C_6H_5CH_2$
b, R = C_2H_5 **f**, R = C_6H_5
c, R = $(CH_3)_2CH$ **g**, R = p-$CH_3OC_6H_4$
d, R = $(CH_3)_3C$

The isolated salts can easily be converted to ketene dithioacetals when R is a primary or secondary alkyl group (Eq. 3) and to ortho esters when R is an aryl group (Eqs. 4 and 5).


(3)

2 a, R′ = R″ = H
b, R′ = H, R″ = CH_3
c, R′ = R″ = CH_3
d, R′ = H, R″ = C_6H_5


(4)

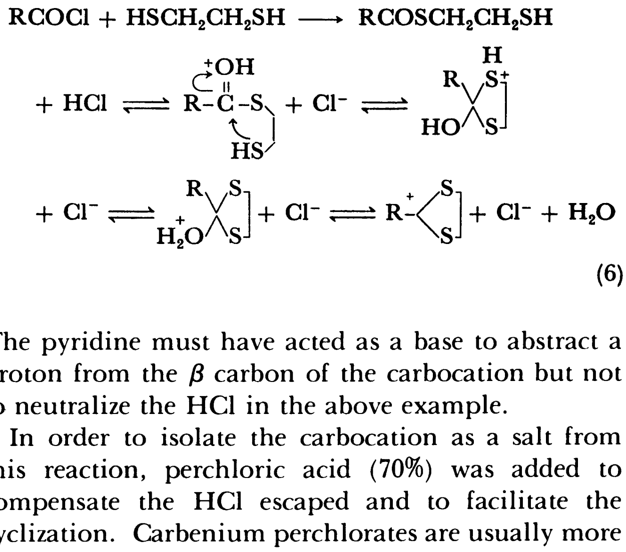
3

$$\mathbf{3} + 2CH_3OH + 2AgNO_3 + 2Et_3N \longrightarrow RC(OCH_3)_3 + AgSCH_2CH_2SAg + 2Et_3NHNO_3 \quad (5)$$

4

Results and Discussion

When equimolar amounts of 1,2-ethanedithiol and isobutyryl chloride were mixed together at room temperature, reaction gradually proceeded with some evolution of HCl gas. Pyridine was added in the final stage of the reaction to neutralize the mixture. A main product isolated was 2-isopropylidene-1,3-dithiolane (**2c**) instead of the thiocarboxylate expected. The monothio ester initially formed is cyclized.[2] The cyclization must be catalyzed by the HCl which is produced in the initial reaction (Eq. 6), although it partly escapes as a gas from the mixture.

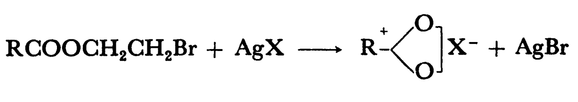

(6)

The pyridine must have acted as a base to abstract a proton from the β carbon of the carbocation but not to neutralize the HCl in the above example.

In order to isolate the carbocation as a salt from this reaction, perchloric acid (70%) was added to compensate the HCl escaped and to facilitate the cyclization. Carbenium perchlorates are usually more stable than the chlorides. Acetic anhydride was used to remove the water and to dissolve the salt. Dry ether was then added to reprecipitate the pure salt. Organic impurities which are soluble in ether are removed in this stage. All the treatments can satisfactorily be done in air and the yellow crystals obtained are practically pure as judged from the NMR spectra.

Salts of dithio carbocations were previously prepared either by hydride transfer from dithioacetals to trityl cation[3] or by dissociation of ortho thio esters.[4–6] The present new procedure involves acid-catalyzed cyclization of thiocarboxylates derived from the dithiol.

Cyclization of acyl derivatives has been used to prepare oxo carbocations.[7,8] In these cases, cyclizing agents may promote formation of the primary carbocations which attack the carbonyl oxygen (Eqs. 7 and 8).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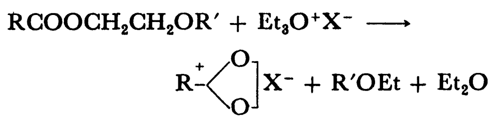
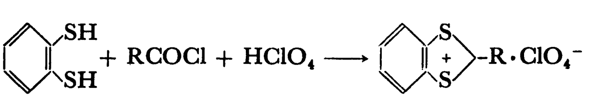
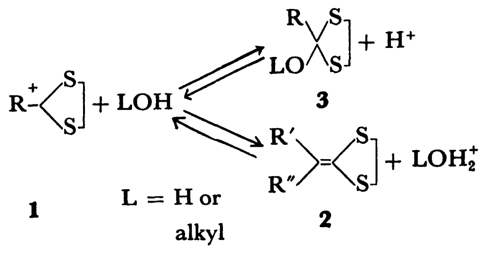

(8)

In the sulfur analogue, the mercapto group is nucleophilic enough even in strongly acidic media to attack the carbonyl carbon which is activated by acid catalysis. A closely related example found in the literature is formation of 1,3-benzodithiolylium salts from the reaction of 1,2-benzenedithiol with acyl chlorides (Eq. 9).[9]


(9)

These unsaturated carbocations are considered to be stable because of aromatic 10π electron delocalization and have been isolated by various methods.[10]

When the dithio carbocations (**1a**—**c**) carrying a primary or secondary alkyl group were treated with methanol, the deprotonated product **2** was obtained as a main product rather than the methanol adduct **3**. Deprotonation from the β carbon occurs more easily than the nucleophilic reaction. This is not unexpected since we have found from kinetic investigations that deprotonation competes well with hydration in aqueous solution[11—15] and even the former predominates in some cases.[16]


(10)

Thus, ketene dithioacetals **2** were prepared quantitatively (as seen by NMR spectra of crude product mixtures) by treating **1** with bases, tertiary amines. Typical procedures are given in Experimental Section.

Ketene dithioacetals are used as versatile intermediates for organic syntheses but general procedures for syntheses of this class of compounds are rather elaborate.[17,18] The present simple procedure starting from readily available reagents would be useful.

The recent two reports[19,20] of new methods for preparation of aryl ortho esters prompted us to examine the possibility of the carbocations **1** leading to this class of compounds. The carbocation **1** derived from benzoyl chloride gave the 2-methoxy derivative **3** by reaction with methanol (Eq. 4).[21] This cyclic ortho thioester **3** could be converted to trimethyl ortho ester **4** by the treatment with two equivalents of $AgNO_3$ in methanol in the presence of excess base (Eq. 5). This is a modification of the method of Breslow[19] where ortho trithioesters are used as a starting material. The present method requires a smaller amount (2/3) of $AgNO_3$ and is much simpler than that of Breslow[19] since preparation of ortho trithioesters is very cumbersome with formation of a large amount of gel during workup which arises from metal halide used.[22] The intermediate ortho thio ester **3** is not necessarily isolated in the present procedure. The carbocation salts **1**, which are just filtered, washed with ether, and still wet, can directly be treated with $AgNO_3$ in methanol to afford the final ortho ester **4** in a satisfactory yield. The 2-*t*-butyl cation **1d** gave the ortho ester **4d** in a low yield.

Derivatives of 1,3-dithiane seem to be prepared in a similar way. Reaction of 1,3-propanedithiol with isobutyryl chloride afforded a 1,3-dithian-2-ylium ion which absorbs light at 311 nm. The salt was then converted to 2-isopropylidene-1,3-dithiane by treatment with triethylamine. Other examples were not examined in detail but brief preliminary experiments seem to give in general satisfactory results.

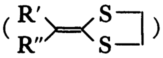
Experimental

Typical procedures are given below. Other derivatives were obtained in the same way. Spectral data and boiling points are summarized in Tables 1 and 2. Temperatures are not

Table 1. Spectral Data of 2-Substituted 1,3-Dithiolan-2-ylium Perchlorates

No.	Substituent	NMR Chemical Shift/ppm[a]	λ_{max}/nm ($10^4\varepsilon$)[b]
	H[c]	4.50(s, 4H), 11.35(s, 1H)	333(0.76)
1a	CH_3	3.22(s, 3H), 4.57(s, 4H)	330(0.80)
1b	C_2H_5	1.62(t, 3H), 3.45(q, 2H), 4.46(s, 4H)	329(0.79)
1c	$(CH_3)_2CH$	1.63(d, 6H), 3.74(m, 1H), 4.47(s, 4H)	331(0.70)
1d	$(CH_3)_3C$	1.68(s, 9H), 4.46(s, 4H)	331(0.77)
1e	$C_6H_5CH_2$	4.40(s, 4H), 4.57(s, 2H), 7.4(broad s, 5H)	332(0.78)
1f	C_6H_5	4.48(s, 4H), 7.6—8.1(m, 5H)	342(2.65)
1g	*p*-$CH_3OC_6H_4$	4.12(s, 3H), 4.36(s, 4H), 7.20(d, 2H), 8.25(d, 2H)	402

a) From internal TMS in $CF_3CO_2D(H)$. b) In $HClO_4$ solution. c) Ref. 21.

Table 2. Boiling Points and Spectral Data of 2-Alkylidene-1,3-dithiolanes ()

R′	R″	Yield/%$^{a)}$	Bp/°C(mmHg)	NMR Chemical Shift/ppm$^{b)}$	λ_{max}/nm($10^4\varepsilon$)$^{c)}$
H	H	36	55(9)	3.31(s, 4H), 5.00(s, 2H)$^{d)}$	243(0.75)
H	CH_3	55	85(10)	1.71(d, 3H), 3.25(s, 4H), 5.40(q, 1H)	235(0.75)
CH_3	CH_3	63	80—81(4)	1.80(s, 6H), 3.31(s, 4H)	230(0.78)
H	C_6H_5	48	143—145(2)	3.1—3.6(m, 4H), 6.49(s, 1H), 7.0—7.4(m, 5H)	304(1.88)

a) Based on the acyl chloride used. b) In CCl_4. c) In aqueous solution. d) In CS_2.

corrected. Proton NMR spectra were recorded on a JNM C60-HL spectrometer.

2-Ethyl-1,3-dithiolan-2-ylium Perchlorate (1b). To an ice-cooled mixture of propionyl chloride (25 mmol) and 1,2-ethanedithiol (25 mmol), 70% perchloric acid (2.5 ml) was added dropwise under stirring. After 5-h reaction on an ice bath, acetic anhydride (15 ml) was added carefully (exothermic) to the viscous mixture. Dry ether (ca. 50 ml) was then added to precipitate the product, which was collected on a sintered-glass filter, washed three times with ether, and dried under reduced pressure. The yellow crystals obtained (4.8 g, 80%) were practically pure as seen by the NMR spectroscopy (Table 1).

2-Phenyl-1,3-dithiolan-2-ylium Perchlorate (1f). 1,2-Ethanedithiol (25 mmol) was added to benzoyl chloride (25 mmol) and stirred on an ice bath for 1 h. Then, 70% perchloric acid (3 ml) was added to the mixture. Stirring was continued for another 1 h at 0 °C. The solidified mixture was dissolved with acetic anhydride (15 ml) and reprecipitated by adding dry ether (50 ml). The yellow crystals were collected on a sintered-glass filter, washed with ether, and dried under vacuum. Yield was 6.2 g (88%).

2-Ethylidene-1,3-dithiolane (2b). The salt of **1b** prepared from 25 mmol of propionyl chloride was dissolved in dry acetonitrile (30 ml). The wet salt was used without drying. The solution was added to excess triethylamine (6 ml). The products were taken up in ether, washed with water, and dried over $MgSO_4$. After the evaporation of the ether, the remaining liquid was distilled. Yield, 1.8 g (55%). Anal. ($C_5H_8S_2$) C, H.

Trimethyl *p*-Methoxyorthobenzoate (4g). The perchlorate **1g**, which was prepared from *p*-methoxybenzoyl chloride (25 mmol) and still wet with ether, was dissolved in acetonitrile (30 ml), and methanol (100 ml) and triethylamine (14 ml) were added to the solution. The solution of silver nitrate (7 g) in acetonitrile (50 ml) was then introduced under stirring. After 10-h stirring at room temperature, precipitates were removed by filtration and the filtrate was concentrated to ca. 20 ml on a rotary evaporator. The products were taken up in ether, washed with aqueous $NaHCO_3$, dried over $MgSO_4$, and distilled. Yield, 2.8 g (53%). Bp 114—116 °C (5 mmHg[†]) [lit,[23] 114—115 °C (5 mmHg)].

Trimethyl Orthopivalate (4d). A solution of $AgNO_3$ (20 mmol) in CH_3CN (20 ml) was added to a solution of triethylamine (3.5 ml) and 2-*t*-butyl-2-methoxy-1,3-dithiolane **3d** (10 mmol) prepared from **1d**[24] in methanol (50 ml). After 12-h of stirring at room temperature, precipitates were filtered away and the filtrate was concentrated to ca. 10 ml. The products were taken up in ether, washed with aqueous $NaHCO_3$, and dried over $MgSO_4$. After evaporation of the ether, the residues were distilled with a Kugelrohr. The fraction collected at the oven temperature of ca. 80 °C and 50 mmHg was solidified on cooling (yield 0.1 g). ^1H NMR (CCl_4) δ=0.92 (s, 9H), 3.36 (s, 9H). Anal. ($C_8H_{18}O_3$) C, H.

2-Isopropylidene-1,3-dithiane. To a mixture of isobutyryl chloride (10 mmol) and 1,3-propanedithiol (10 mmol), 70% $HClO_4$ (1 ml) was added under stirring at room temperature. After 15-h stirring, acetic anhydride (10 ml) and then dry ether (50 ml) were added. Yellow precipitates collected on a sintered-glass filter were washed with ether and dissolved in CH_3CN (20 ml). The solution was added to triethylamine (3 ml). Workup in a similar way to **2b** and the Kugelrohr distillation gave 0.88 g (55%) of the fraction boiling at ca. 95 °C and 5 mmHg. ^1H NMR and IR spectra agree with those reported.[25]

[†] 1mmHg=133.322 Pa.

References

1) T. Okuyama, *Tetrahedron Lett.*, **23**, 2665 (1982).

2) In order to obtain monothioester base should be added in advance although a considerable amount of bis(thioester) $RCOSCH_2CH_2SCOR$ is inevitably formed. Pure mono ester can be obtained by hydrolysis of the isolated salt **1**.

3) E. J. Corey and S. W. Wallinsky, *J. Am. Chem. Soc.*, **94**, 8932 (1972).

4) R. A. Olofson, S. W. Wallinsky, J. P. Marino, and J. L. Jernow, *J. Am. Chem. Soc.*, **90**, 6554 (1968).

5) K. Sakamoto, N. Nakamura, M. Ōki, J. Nakayama, and M. Hoshino, *Chem. Lett.*, **1977**, 1133.

6) L. Hevesi, S. Desauvage, B. George, G. Evrard, P. Blanpain, A. Michel, S. Harkema, and G. J. van Hummel, *J. Am. Chem. Soc.*, **106**, 3784 (1984).

7) H. Meerwein, V. Hederich, and K. Wunderlich, *Arch. Pharmaz.*, **291/63**, 541 (1958).

8) D. J. Raber and W. C. Guida, *Syntheses*, **1974**, 808.

9) L. Sodar and R. Wizinger, *Helv. Chim. Acta*, **42**, 1739 (1959) ; R. Wizinger and D. Dürr, ibid., **46**, 2167 (1963); P. Appriou and R. Guglielmetti, *Bull. Soc. Chim. Fr.*, **1974**, 510.

10) See for reviews, H. Prinzbach and E. Futterer, *Adv. Heterocycl. Chem.*, **7**, 39 (1966); N. Lozac'h and M. Stavaux, ibid., **27**, 151 (1980).

11) T. Okuyama and T. Fueno, *J. Am. Chem. Soc.*, **102**, 6590 (1980); **105**, 4390 (1983).

12) T. Okuyama, S. Kawao, and T. Fueno, *J. Am. Chem. Soc.*, **105**, 3320 (1983).

13) T. Okuyama, S. Kawao, and T. Fueno, *J. Org. Chem.*, **49**, 85 (1984).

14) T. Okuyama, S. Kawao, W. Fujiwara, and T. Fueno, *J. Org. Chem.*, **49**, 89 (1984).

15) T. Okuyama, *J. Am. Chem. Soc.*, **106**, 7134 (1984).

16) T. Okuyama, M. Toyoda, and T. Fueno, *Can. J. Chem.*,

in press.

17) M. Kolb, "The Chemistry of Ketene, Allene and Related Compounds, Part 2," ed by S. Patai, Wiley, New York (1980), Chap. 16.

18) Y. Nagao, K. Seno, and E. Fujita, *Tetrahedron Lett.*, **1979**, 4403.

19) R. Breslow and P. S. Pandey, *J. Org. Chem.*, **45**, 740 (1980).

20) R. A. McClelland, G. Patel, and P. W. K. Lam, *J. Org. Chem.*, **46**, 1011 (1981).

21) T. Okuyama, W. Fujiwara, and T. Fueno, *J. Am. Chem. Soc.*, **106**, 657 (1984).

22) L. C. Rinzema, J. Stoffelsma, and J. F. Arens, *Recl. Trav. Chin. Pays-Bas*, **78**, 354 (1959).

23) H. Kwart and M. B. Price, *J. Am. Chem. Soc.*, **82**, 5123 (1960).

24) T. Okuyama and T. Fueno, *J. Am. Chem. Soc.*, **107**, 4224 (1985).

25) D. Seebach, M. Kolb, and B.-T. Gröbel, *Chem. Ber.*, **106**, 2277 (1973).