they exist as dithiolium salts in 70% perchloric acid, but it appears that the addition of water, ethanol, or reagents such as trifluoroacetic acid to the C-4–C-5 bond, as well as ring cleavage, may be facile and reversible reactions.

Experimental[18]

Phenacyl Dithiobenzoate.—Dithiobenzoic acid[19] (5.1 g.) in ether (90 ml.) was neutralized by the addition of sodium ethoxide solution (sodium, 0.76 g., to ethanol, 20 ml.). Phenacyl chloride (5.1 g.) in ether (30 ml.) was added dropwise and the mixture refluxed for 30 min. After the precipitated sodium chloride was removed and the solvent was evaporated, the residue was recrystallized from ethanol (ten parts) to give phenacyl dithiobenzoate as a brick red solid (compound 1, Table II).

β-Keto N,N-Dimethyl- and N,N-Diethyldithiocarbamates.——Compounds 2–16, Table II, were prepared by the following general method. The phenacyl or acetonyl halide (0.05 mole) dissolved in a minimum of cold ether (or acetone) was added dropwise to a solution of the sodium N,N-dialkyldithiocarbamate (0.055 mole) in ethanol (20 ml.) under reflux. After 30 min., the solvent was removed *in vacuo*, the oily residue was washed with water until crystallization occurred, and the ester was recrystallized from ethanol.

2,4-Diphenyl-1,3-dithiolium Salts. Chloride.[3,4]—Dry hydrogen chloride and hydrogen sulfide were passed simultaneously into a chilled (0–5°) solution of phenacyl dithiobenzoate (0.68 g.) in ether (50 ml.) for 3 hr. After a further 48 hr. at room temperature, the pale yellow-green **2,4-diphenyl-1,3-dithiolium** chloride (62%), m.p. 134–136°, was collected and recrystallized from 3:1 ethyl acetate–ethanol mixture (56 parts) by the further addition of ethanol (150 parts).

Anal. Calcd. for $C_{15}H_{11}ClS_2$: C, 61.95; H, 3.81; S, 22.05. Found: C, 61.75; H, 4.0; S, 21.9.

Perchlorate. A.—70% Perchloric acid (5 ml.) was added to phenacyl dithiobenzoate (0.5 g.) and the mixture gently was heated on the steam bath until solution had occurred (1 min.). The yellow-green product (74%) obtained on chilling the solution was recrystallized from ethanol (220 parts) and had m.p. 207–209°, lit.[4] m.p. 209–209.5°.

B.—The dithiolium chloride was dissolved in ethanol (ten parts) and treated dropwise with 70% perchloric acid until precipitation of the perchlorate was complete. Recrystallized as in A, the product had m.p. 207–209°, undepressed on admixture with the previous specimen.

2-Dimethylamino- and 2-Diethylamino-1,3-dithiolium Perchlorates.[20]—Compounds in Table I were prepared by the following general method. The β-keto N,N-dialkyldithiocarbamate (0.005 mole, *ca.* 1 g.) was dissolved in the minimum of 70% perchloric acid (usually one–three parts). In many instances, ensuing heat of reaction was sufficient to cause dissolution; at other times the mixture had to be warmed on the steam bath for up to 5 min. to complete the reaction. Dithiolium perchlorate was obtained by chilling and triturating with cold water (three parts) or ethyl acetate. Absolute ethanol was the usual solvent for recrystallization, but the exceptions in Table I should be noted.

Partially Deuterated 70% Perchloric Acid.—Anhydrous perchloric acid[21] (62 g.) was diluted with 99.5% deuterium oxide to 100 ml. The excess heavy water was distilled until the temperature of the distillate reached the boiling point of the 70% azeotrope (203° at 760 mm.). The residual liquid was used, where indicated, as a solvent for n.m.r. measurements and was free of spectral detail until 570 cycles downfield from the tetramethylsilane reference.

Acknowledgment.—It is a pleasure to acknowledge the helpful discussions we have had with our colleague Dr. Walter Meyer concerning the interpretation of the n.m.r. measurements. We are also grateful for some technical assistance given by Talmage Bosin (National Science Foundation Undergraduate Research Participant) during the 1962 summer semester.

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[18] All melting points were determined in soft glass capillaries using a Mel-Temp heated-block apparatus and are corrected. Analyses were performed by the Midwest Microlab, Inc., Indianapolis, Ind.

[19] F. Block, *Compt. rend.*, **204**, 1342 (1937).

[20] The inherent danger of an explosion occurring when organic compounds are treated with perchloric acid required the conscientious use of safety screens and face masks. No spontaneous explosions were experienced with the compounds reported in this paper, but, in a related series, two such accidents occurred while using the same experimental procedure. For this reason, all reactions have been limited to relatively small quantities and treated with the utmost care. Attempts were made, as part of a safety program, to induce the 2-dialkylamino-1,3-dithiolium perchlorate derivatives to explode by (a) heating above their melting point, (b) admixing with 70% perchloric acid and heating to dryness, and (c) mechanical grinding with carborundum chips. Only 4-methyl-2-dimethylamino-1,3-dithiolium perchlorate monohydrate (VI, R = CH_3) could be detonated and by b only.

[21] G. F. Smith, *J. Am. Chem. Soc.*, **75**, 184 (1953).

Dithiolium Derivatives. II. Some New 1,3-Dithiolium Perchlorates[1]

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The action of 70% perchloric acid on β-keto S-methyltrithiocarbonates and β-keto O-ethyldithiocarbonates is described. Dithiolium derivatives have been obtained from the trithiocarbonate intermediates. The synthesis of some 4-hydroxyl-1,3-dithiolium perchlorates from appropriate carboxymethyl, carbethoxymethyl, and carbamidomethyl esters is also described, and the ultraviolet and nuclear magnetic resonance spectral characteristics of these new compounds are discussed.

The reports[4,5] of unsuccessful attempts to convert β-keto O-ethyldithiocarbonates and β-keto S-methyltrithiocarbonates into 1,3-dithiolium derivatives have prompted us to try the use of 70% perchloric acid to effect this ring closure. These conditions have recently been used with success in the synthesis of 2-dialkylamino-1,3-dithiolium perchlorates.[6] In this manner, phenacyl methyl trithiocarbonate (I, R = CH_3S; R′ = C_6H_5) and *p*-nitrophenacyl methyltrithiocarbonate (I, R = CH_3S; R′ = *p*-$NO_2C_6H_4$) were converted smoothly into 2-methylthio-4-phenyl-1,3-dithiolium perchlorate (IIa, R = CH_3S; R′ = C_6H_5) and 2-methylthio-4-(*p*-nitrophenyl)-1,3-dithiolium perchlorate (IIb, R = CH_3S; R′ = *p*-$NO_2C_6H_4$), respectively, but no product could be isolated after acetonyl methyltrithiocarbonate (I, R = CH_3S; R′ = CH_3) was similarly treated.

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[2] A portion of the work described is from the forthcoming Ph.D. thesis of R. D. H.

[3] American Chemical Society Petroleum Research Fund Postdoctoral Fellow, 1962–1963.

[4] D. Leaver and W. A. H. Robertson, *Proc. Chem. Soc.*, 252 (1960).

[5] D. Leaver, W. A. H. Robertson, and D. M. McKinnon, *J. Chem. Soc.*, 5104 (1962).

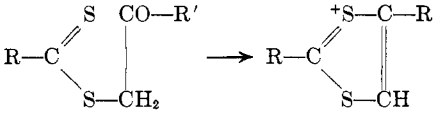
[6] E. Campaigne and N. W. Jacobsen, *J. Org. Chem.*, **29**, 1703 (1964).

TABLE I

ULTRAVIOLET AND N.M.R. DATA

Compound	Ultraviolet,[a] λ_{max} mμ (log ϵ)	N.m.r.[b] signals of substituents at		
		C-2	C-4	C-5
IIa	373 (4.14), 282 (3.89), 240 (4.27)	6.72	2.27 m	1.47
IIb	368 (4.36), 315 (3.90), 268 (3.98), 232 (4.19)	6.70	1.52 d 2.02 d (9)[d]	1.27
IIc	367 (4.18), 275 (3.47), 244 (3.51)	1.90–2.32 m		2.07
IId	242 (4.19)	6.22		5.08
IIe	305 (4.20), 221 (3.29)	6.60		4.80
III	335 (4.14), 243 (4.03)[c]		1.75 d 2.35 d (9)[d]	2.80

[a] Measurements were made in 70% perchloric acid except where otherwise indicated, using the Cary Model 14 recording spectrophotometer. [b] Proton magnetic resonance spectra were determined in trifluoroacetic acid at concentrations between 6–8% w./v. at about 25°, using a Varian A-60 spectrometer operating at 60 Mc./sec. Chemical shifts are recorded on the frequency independent τ-scale relative to an internal tetramethylsilane reference. Unless otherwise indicated, values refer to singlet absorptions; for multiple signals the following abbreviations have been used: d = doublet, m = multiplet. [c] Spectra were measured in 95% ethanol. [d] Spin–spin coupling values (J) are in parentheses; values are in cycles per second measured on the 500-c.p.s. scale.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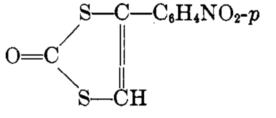
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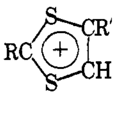
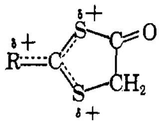
IIa, R = CH_3S; R′ = C_6H_5
b, R = CH_3S; R′ = p-$NO_2C_6H_4$
c, R = C_6H_5; R′ = OH
d, R = $(CH_3)_2N$; R′ = OH
e, R = CH_3S; R′ = OH

The reaction of a series of β-keto O-ethyldithiocarbonates (I, R = OEt; R′ = p-$NO_2C_6H_4$, p-ClC_6H_4, p-BrC_6H_4, p-$CH_3C_6H_4$, p-HOC_6H_4) with perchloric acid was also investigated but much decomposition occurred and in most cases no product was isolated. S-(p-Nitrophenacyl) O-ethyl dithiocarbonate, however, yielded an insoluble product which was shown to be 2-oxo-4-(p-nitrophenyl)-1,3-dithiole (III) on the basis of analysis and infrared and n.m.r. spectroscopy.

Hitherto, such acid-catalyzed cyclizations of β-keto dithio esters of type I (where R = alkyl, aryl, or dialkylamino and R′ = alkyl or aryl) have been the most convenient method for the synthesis of 1,3-dithiolium salts[4–6] but have restricted substituents in position 4 to alkyl or aryl groups. In an attempt to introduce other groups at this position of the hetero ring, we have investigated the reaction of carboxymethyl (I, R′ = OH), carbethoxymethyl (I, R′ = OEt), and carbamidomethyl (I, R′ = NH_2) dithio esters with perchloric acid. Such esters of N,N-dimethyldithiocarbamic acid all gave 2-dimethylamino-4-hydroxy-1,3-dithiolium perchlorate [IId, R = $(CH_3)_2N$; R′ = OH] in high yield. This hydroxydithiolium perchlorate was found to be stable in the crystalline state and in nonhydroxylic solvents, but in water and ethanol it was converted almost quantitatively back into its carboxymethyl and carbethoxymethyl precursors, respectively. In a similar manner, carboxymethyl dithiobenzoate (I, R = C_6H_5; R′ = OH) gave 4-hydroxy-2-phenyl-1,3-dithiolium perchlorate (IIc, R = C_6H_5; R′ = OH), and carboxymethyl methyl trithiocarbonate (I, R = CH_3S; R′ = OH) gave 4-hydroxy-2-methylthio-1,3-dithiolium perchlorate (IIe, R = CH_3S; R′ = OH). These perchlorates were even less stable than the dialkyl analogs, but their decomposition products are yet unknown.

The ultraviolet spectra of IIa, IIb, and IIc show the long wave-length absorption which has been reported for other alkyl and aryl analogs.[5,6] In contrast, however, IId and IIe are optically transparent in this region and, as well, show less of other spectral features (see Table I). An explanation of this is seen from a comparison of the n.m.r. spectra of these compounds when measured in 70% perchloric acid or in trifluoroacetic acid. Those salts exhibiting the long wave-length ultraviolet absorption (IIa, IIb, and IIc) showed the lone C-5 proton signal at low-field strength (τ 1.47, 1.27, and 2.07, respectively) in the region previously reported for dithiolium hetero ring protons,[6] and so must exist in form IV. The colorless dithiolium salts IId and IIe on the other hand showed no single proton signal in this low-field region, but instead they each gave a signal equivalent to two protons in the methylene region (τ 5.08 and 4.80, respectively). Clearly therefore, in these solvents IId and IIe must exist predominantly in the keto form, V.


IV


V

That the C-5 proton signal of IIa occurs at τ 1.47 while the C-5 proton signal of IIb occurs downfield at τ 1.27 is attributed to the decrease in diamagnetic shielding caused by the electron-withdrawing p-nitro substituent. Variation of position of the methyl protons of these derivatives is slight (τ 6.72 and 6.70, respectively), indicating their closer proximity to the positive charge and greater distance from the *para* substituent.

Experimental[7]

2-Methylthio-4-phenyl-1,3-dithiolium Perchlorate (IIa).—Phenacyl methyltrithiocarbonate[6] (1 g.) was reacted with 70% perchloric acid (3 ml.) at 100° for 5 min. The solution was chilled and ethyl acetate (5 ml.) was added to yield IIa (93%). Recrystallized from 70% perchloric acid (three parts) by the addition of ethyl acetate (six parts), it had m.p. 126–127°.

Anal. Calcd. for $C_{10}H_9ClO_4S_3$: C, 36.95; H, 2.8; S, 29.6. *Found:* C, 37.0; H, 2.95; S, 29.5.

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[7] All melting points were determined in soft-glass capillaries using a Mel-Temp heated block apparatus and are corrected. Analyses were performed by the Midwest Microlab, Inc., Indianapolis, Ind.

TABLE II

PREPARATION OF β-KETO O-ETHYLDITHIOCARBONATES (I)

R'	% yield	M.p., °C.	Formula	Analysis, %					
				C		H		S	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
p-BrC$_6$H$_4$	85	81–82	$C_{11}H_{11}BrO_2S_2$					20.1	19.9
p-CH$_3$C$_6$H$_4$	89	86–87	$C_{12}H_{14}O_2S_2$	56.7	56.7	5.55	5.6	25.2	25.3
p-HOC$_6$H$_4$	76	123–124	$C_{11}H_{12}O_3S_2$	51.5	51.6	4.7	4.8	25.0	24.8

2-Methylthio-4-(*p*-nitrophenyl)-1,3-dithiolium Perchlorate (IIb).—*p*-Nitrophenacyl methyltrithiocarbonate (1 g.) and 70% perchloric acid (1.5 ml.) were heated at 100° for 30 min. Addition of ethyl acetate (15 ml.) to the cooled solution gave IIb (75%). After recrystallization from 70% perchloric acid (three parts) by the addition of ethyl acetate (five parts), the heat-sensitive material was dried at room temperature under high vacuum and had m.p. 179–181°.

Anal. Calcd. for $C_{10}H_8ClNO_6S_3$: C, 32.5; H, 2.2; S, 26.0. Found: C, 32.5; H, 2.0; S, 26.0.

S-(*p*-Chlorophenacyl) O-Ethyldithiocarbonate.—A mixture of potassium ethyl xanthate (8 g., 0.05 mole) and *p*-chlorophenacyl chloride (9.5 g., 0.05 mole) in 50% ethanol (150 ml.) was heated on a steam bath until solution was complete (15 min.). The product (87%, m.p. 69–70°) which separated on cooling was recrystallized from *n*-hexane or ethanol.

Anal. Calcd. for $C_{11}H_{11}ClO_2S_2$: C, 48.1; H, 4.0; S, 23.35. Found: C, 48.3; H, 4.2; S, 23.3.

Other analogs prepared by this method are listed in Table II.

2-Oxo-4-(*p*-nitrophenyl)-1,3-dithiole (III).—S-(*p*-Nitrophenacyl) O-ethyldithiocarbonate[8] (2 g.) in 70% perchloric acid (5 ml.) was warmed on a steam bath for 5 min. III crystallized from the hot solution as a yellow solid (73%) and after recrystallization from ethanol (150 parts) had m.p. 205–208°.

Anal. Calcd. for $C_9H_5NO_3S_2$: C, 45.2; H, 2.1; S, 26.8. Found: C, 45.3; H, 2.25; S, 26.6.

4-Hydroxy-2-phenyl-1,3-dithiolium Perchlorate (IIc).—Carboxymethyl dithiobenzoate[9] (1 g.) was heated with 70% perchloric acid (3 ml.) at 100° for 15 min. The solution was chilled and ethyl acetate (3 ml.) was added to induce the product (79%) to crystallize. IIc, an unstable yellow salt, m.p. 129–132° dec., was recrystallized from 70% perchloric acid (two parts) by the addition of ethyl acetate (three parts).

Anal. Calcd. for $C_9H_7ClO_5S_2$: C, 36.65; H, 2.4; S, 21.75. Found: C, 36.65; H, 2.55; S, 21.5.

2-Dimethylamino-4-hydroxy-1,3-dithiolium Perchlorate[10] (IId). A.—Carboxymethyl N,N-dimethyldithiocarbamate[11,12] (0.5 g.) was warmed with 70% perchloric acid (1 ml.) for 15 min. On cooling, ethyl acetate (3 ml.) was added and the perchlorate (98%) was collected. Recrystallized from 70% perchloric acid (two parts) by the addition of ethyl acetate (20 parts), IId had m.p. 172–173°.

Anal. Calcd. for $C_5H_8ClNO_5S_2$: C, 22.95; H, 3.05; S, 24.5. Found: C, 23.1; H, 3.05; S, 24.2.

B.—Carbamidomethyl N,N-dimethyldithiocarbamate[13] (1 g.) and 70% perchloric acid (2 ml.) were heated at 100° for 1 min. The product (95%) was isolated and recrystallized as above and had m.p. 172° unchanged on admixture with IId (above).

C.—Carboethoxymethyl N,N-dimethyldithiocarbamate[11,13] (1 g.) and 70% perchloric acid (2 ml.) were heated at 100° for 5 min. The product (98%, m.p. 172–173°) was also identical with the perchlorates obtained by methods A and B.

Compound IId was unstable in water and alcohol. Recrystallized from the former (ten parts), a quantitative yield of carboxymethyl N,N-dimethyldithiocarbamate (m.p. 149°[11,12]) was obtained. Refluxed in ethanol and then recrystallized from 50% aqueous ethanol (six parts), IId was converted into carbethoxymethyl N,N-dimethyldithiocarbamate (m.p. 60–62°[11,13]) in high yield.

4-Hydroxy-2-methylthio-1,3-dithiolium Perchlorate[10] (IIe).—Carboxymethyl methyltrithiocarbonate (1 g.) dissolved in 70% perchloric acid (3 ml.) was heated on a steam bath for 3 min. Crystallization of IIe (31%) was induced by chilling in a Dry Ice and alcohol mixture and the addition of ethyl acetate (4 ml.). The unstable product (m.p. 97–98°) was recrystallized from 70% perchloric acid (three parts) by the addition of ethyl acetate (five parts).

Anal. Calcd. for $C_4H_5ClO_5S_3$: C, 18.15; H, 1.9; S, 36.35. Found: C, 18.25; H, 2.1; S, 36.4.

Carboxymethyl Methyltrithiocarbonate.—Chloracetic acid (10.6 g.) in ethanol (100 ml.) was added to a cold (0°) solution of sodium methyltrithiocarbonate[5] (0.115 mole) in ethanol (100 ml.). After 1 hr. at room temperature, the precipitated salt was removed and the solution was evaporated. An extract of the residual oil in ether (100 ml.) was washed with water (10 ml.), dried (magnesium sulfate), and evaporated to yield **carboxymethyl methyltrithiocarbonate** (24%). Recrystallized from *n*-hexane (200 parts), it had m.p. 75–76°.

Anal. Calcd. for $C_4H_6O_2S_3$: C, 26.35; H, 3.3; S, 52.75. Found: C, 26.5; H, 3.3; S, 53.0.

Acetonyl Methyltrithiocarbonate.—Chloracetone (9.3 ml.) in ethanol (100 ml.) was added to a solution of sodium methyltrithiocarbonate[5] (0.115 mole) in ethanol (100 ml.) at 0°. After stirring for 1 hr. at room temperature, the mixture was poured into water (300 ml.) and the product (53%) was extracted with ether and distilled (b.p. 109–110° at 1.5 mm.).

Anal. Calcd. for $C_5H_8OS_3$: C, 33.3; H, 4.45; S, 53.35. Found: C, 33.35; H, 4.5; S, 53.5.

***p*-Nitrophenacyl Methyltrithiocarbonate.**—*p*-Nitrophenacyl bromide (12.2 g., 0.05 mole) suspended in ethanol (150 ml.) was added with stirring to a solution of sodium methyltrithiocarbonate[5] (0.05 mole) at $-40°$. The mixture was allowed to warm to room temperature, stirred an additional 2 hr., and then poured into water (1.5 l.). The yellow solid was collected (11.8 g., 85%) and recrystallized twice from alcohol, and melted at 100–102°.

Anal. Calcd. for $C_{10}H_9NO_3S_3$: C, 41.8; H, 3.2; S, 33.5. Found: C, 41.9; H, 3.0; S, 33.5.

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[8] W. E. Parham, E. T. Harper, and R. S. Berger, *J. Am. Chem. Soc.*, **82**, 4932 (1960).

[9] A. Kjaer, *Chem. Abstr.*, **45**, 6160 (1951).

[10] Integration of the n.m.r. spectrum revealed that, when dissolved in 70% perchloric acid or trifluoroacetic acid, this compound exists predominantly in the 4-oxo form.

[11] K. Bodendorf, *Chem. Abstr.*, **24**, 3221 (1930).

[12] K. A. Jenson, *J. prakt. Chem.*, **159**, 189 (1941).

[13] G. Nachmias, *Ann. Chem.*, **7**, 584 (1952).