pressed on admixture of the mesylate (**14a**) of dihydroasperilin (**14b**), m.p. 142–144°. Infrared spectra and rotations, $[\alpha]^{23}D$ +41 (*c* 1.00), were identical.

Formic Acid Dehydration of 5.—A mixture of 0.882 g. of **5** and 10 ml. of formic acid was refluxed for 4 hr., concentrated at reduced pressure, diluted with water, and extracted with ether. The ether extract was washed, dried, evaporated, and chromatographed over alumina (Alcoa F-20). The initial fractions were combined and weighed 0.468 g. The infrared spectrum exhibited bands at 1770, 1710, and 1670 cm.$^{-1}$; the n.m.r. spectrum showed that the eluate was a mixture (**15**) with the $\Delta^{4,5}$-isomer predominating—weak vinyl proton signals at 6.69, 6.55, 5.88, and 5.70 (total intensity one-half proton), 4.5 c (H_8), 1.73 (vinyl methyl singlet, intensity almost three protons), 1.30 (C-10 methyl singlet), and 1.22 d (J = c.p.s., C-11 methyl), with indications of a weak doublet at 1.13 p.p.m. due to the presence of another isomer.

A solution of 0.23 g. of **15** in 6 ml. of acetic acid was hydrogenated with platinum oxide. The oily product was dissolved in benzene and chromatographed over 9 g. of acid-washed alumina. From the benzene eluates was isolated 0.04 g. of somewhat impure dehydrotetrahydroasperilin (**17**), m.p. and m.m.p. 120–122°, infrared spectra superimposable. From the fractions eluted with chloroform there was isolated 0.015 g. of slightly impure tetrahydroasperilin (**16**), m.p. and m.m.p. 144–146°, infrared spectra superimposable.

Anhydrodihydroivalin (12).—Reaction of 0.45 g. of dihydroivalin (**10a**) with methanesulfonyl chloride in the usual manner furnished, after recrystallization from ethanol, 0.5 g. of the mesylate **10b**, m.p. 149–150° dec.; infrared bands at 1765 and 1640 cm.$^{-1}$; n.m.r. signals at 5.02 and 4.72 (exocyclic methylene, the second of these was superimposed on the H_2 resonance, complex multiplet centered at 4.72), 4.53 c (H_8), 2.90 (mesyl), 1.06 d (J = 7 c.p.s., C–11 methyl), and 0.735 p.p.m. (C-10 methyl).

Anal. Calcd. for $C_{16}H_{24}O_5S$: C, 58.51; H, 7.36. Found: C, 58.39; H, 7.55.

A solution of 0.8 g. of the mesylate in 50 ml. of lutidine was refluxed for 24 hr., poured onto crushed ice, neutralized with dilute sulfuric acid, and filtered. The solid was taken up in hot ethanol, treated with charcoal, concentrated, and allowed to cool. The colorless needles melted at 159–161° (m.m.p. 158–164° with **11**), but the infrared (bands at 1775, 1645, and 1610 cm.$^{-1}$) and ultraviolet spectra [λ_{max} 2300 mμ (ϵ 9850), heteroannular diene] clearly differentiated it from **11**. The n.m.r. spectrum could be interpreted most simply on the basis of formula **12**, with signals at 6 c (H_2), 5.44 s, and 4.84 s (exocyclic methylene), the latter partially superimposed on a complex signal centered at 4.7 (H_3), 4.45 c (H_8), 1.23 d (J = 7 c.p.s., C-10 methyl), and 0.83 p.p.m. d (J = 2 c.p.s., C-10 methyl).

Anal. Calcd. for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68; O, 13.77. Found: C, 77.50; H, 8.77; O, 14.02.

Catalytic hydrogenation of **12** furnished tetrahydroalantolactone.

Acknowledgment.—We wish to thank the Research Council of Florida State University for a grant-in-aid.

Dithiolium Derivatives. I. 2-Dialkylamino-1,3-dithiolium Perchlorates[1]

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Contribution No. 1201 from the Chemistry Laboratories of Indiana University, Bloomington, Indiana 47405

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A convenient synthesis of some 4-substituted 2-dialkylamino-1,3-dithiolium perchlorates is described which employs mild conditions. A mechanism for the cyclization is proposed, and the structure of the products is discussed with reference to ultraviolet and n.m.r. spectra.

Leaver and Robertson have reported the synthesis of some 1,3-dithiolium salts by the cyclization of phenacyl carbodithioates (I) in ether saturated with hydrogen sulfide and hydrogen chloride.[3,4] We repeated the synthesis of 2,4-diphenyl-1,3-dithiolium chloride (III, R = R′ = Ph), but the yield was considerably less than previously reported. The reaction was found to be accompanied by an interesting color change. Phenacyl dithiobenzoate (I, R = R′ = Ph) was obtained as a brick red solid by the condensation of sodium dithiobenzoate and phenacyl chloride, while the dithiolium chloride product (III, R = R′ = Ph) obtained from it was pale green. A similar and almost instantaneous change was observed when 70% perchloric acid was added to phenacyl dithiobenzoate. The product proved to be 2,4-diphenyl-1,3-dithiolium perchlorate (III, R = R′ = Ph) and was identical with the perchlorate salt obtained *via* the hydrochloride. This mild method of cyclization of β-keto dithio esters into 1,3-dithiolium salts has been fully confirmed by the preparation of the compounds in Table I. The conditions, however, are in marked contrast to those of Leaver, Robertson, and McKinnon,[4] employing boiling mixtures of acetic and perchloric acids with hydrogen sulfide.

Under the latter conditions the reaction was considered to involve an initial conversion of the β-carbonyl group into a thiocarbonyl function either by the action of the hydrogen sulfide directly or by its generation *in situ* by decomposition of the starting material. Because the reaction has been shown to occur in high yields without the use of hydrogen sulfide, it may be regarded as a direct acid-catalyzed cyclization, I → II followed by dehydration to give the pseudoaromatic cation III[5] (see p. 1704).

To extend the yet limited range of known 1,3-dithiolium compounds,[3-9] preparation of 2-dialkylamino derivatives was investigated. Initial experiments to effect the ring closure of β-keto N,N-dialkyldithiocarbamates [I, R = $(CH_3)_2N$ or $(C_2H_5)_2N$] with hydrogen chloride and hydrogen sulfide did not meet with success. The use of 70% perchloric acid, however, readily gave insoluble perchlorate salts irrespective of the nature of the substituent attached to the ketone group.

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[1] This research was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. We gratefully acknowledge this support.

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

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

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

[5] E. Klingsberg, *J. Am. Chem. Soc.*, **84**, 3410 (1962). (The term "pseudoaromatic," applied to the 1,3-dithiolium cation, seems well justified because the aromatic conjugation can only exist in the cation molecule, and, even in this state, there is incomplete delocalization of π-electrons.)

[6] W. R. H. Hurtley and S. Smiles, *J. Chem. Soc.*, 1821, 2263 (1926).

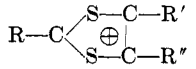
[7] F. Challenger, E. A. Mason, E. C. Holdsworth, and R. Emmott, *Chem. Ind.* (London), 714 (1952); *J. Chem. Soc.*, 292 (1953).

[8] W. Kirmse and L. Horner, *Ann.*, **614**, 4 (1958).

[9] L. Soder and R. Wizinger, *Helv. Chim. Acta*, **42**, 1733, 1779 (1959).

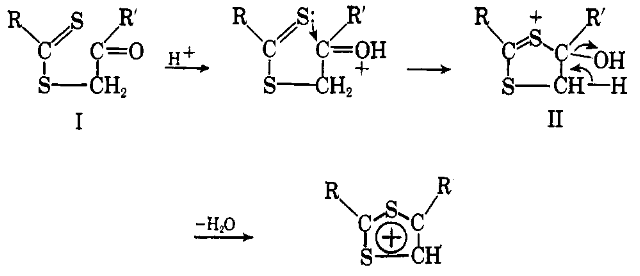
TABLE I

SUBSTITUTED 1,3-DITHIOLIUM PERCHLORATE DERIVATIVES



Compd.				Recrystn.	Yield,			Analysis, %					
				solvent,				Calcd.			Found		
no.	R	R′	R″	ml./g.[a]	%	M.p., °C.	Formula	C	H	S	C	H	S
1	C_6H_5	C_6H_5	H	220	74	207–209	$C_{15}H_{11}ClO_4S_2$	50.75	3.15	18.05	50.95	3.25	18.1
2	$(CH_3)_2N$	CH_3	H	1[b]	81	104–105[c]	$C_6H_{12}ClNO_5S_2$	25.95	4.35	23.1	25.95	4.4	22.8
				25[d]	52	124[e]	$C_8H_{16}ClNO_5S_2$	31.4	5.25	20.95	31.45	5.45	21.2
3	$(CH_3)_2N$	CH_3	CH_3	1.5[b]	95	112–114[c]	$C_7H_{14}ClNO_5S_2$	28.8	4.85	22.0	28.85	4.7	22.05
4	$(CH_3)_2N$	CH_3	C_2H_5	1[b]	85	87–88[c]	$C_8H_{16}ClNO_5S_2$	31.4	5.3	20.95	31.7	5.5	21.0
5	$(CH_3)_2N$	C_6H_5	H	30	95	178–179	$C_{11}H_{12}ClNO_4S_2$	41.05	3.75	19.95	41.3	3.95	19.9
6	$(C_2H_5)_2N$	C_6H_5	H	110	95	176–178	$C_{13}H_{16}ClNO_4S_2$	44.65	4.6	18.35	44.8	4.75	18.6
7	$(CH_3)_2N$	p-$CH_3C_6H_4$	H	120	86	184–185	$C_{12}H_{14}ClNO_4S_2$	42.9	4.2	19.1	43.15	4.2	19.0
8	$(C_2H_5)_2N$	p-$CH_3C_6H_4$	H	53	88	185–186	$C_{14}H_{18}ClNO_4S_2$	46.2	5.0	17.6	46.4	5.2	17.6
9	$(CH_3)_2N$	p-ClC_6H_4	H	125	77	203–204	$C_{11}H_{11}Cl_2NO_4S_2$	37.1	3.1	18.0	37.3	3.25	18.05
10	$(C_2H_5)_2N$	p-ClC_6H_4	H	10	89	122–123	$C_{13}H_{15}Cl_2NO_4S_2$	40.65	3.95	16.7	40.9	4.05	16.8
11	$(CH_3)_2N$	p-$CH_3OC_6H_4$	H	80	87	165–166	$C_{12}H_{14}ClNO_5S_2$	40.95	4.0	18.25	41.1	4.05	18.5
12	$(C_2H_5)_2N$	p-$CH_3OC_6H_4$	H	4	58	154–155	$C_{14}H_{18}ClNO_5S_2$	44.25	4.8	16.9	44.55	4.8	16.9
13	$(CH_3)_2N$	p-HOC_6H_4	H	150	61	208–209	$C_{11}H_{12}ClNO_5S_2$	39.1	3.6	19.0	39.2	3.65	18.8
14	$(C_2H_5)_2N$	p-HOC_6H_4	H	11	79	148–149	$C_{13}H_{16}ClNO_5S_2$	42.65	4.4	17.55	42.75	4.6	17.6
15	$(CH_3)_2N$	p-$NO_2C_6H_4$	H	480	94	207–208	$C_{11}H_{11}ClN_2O_6S_2$	36.0	3.0	17.5	36.3	3.3	17.55
16	$(C_2H_5)_2N$	p-$NO_2C_6H_4$	H	200	95	193–194	$C_{13}H_{15}ClN_2O_6S_2$	39.55	3.85	16.25	39.9	4.1	16.4

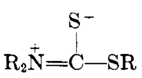
[a] Ml./g. refers to the minimum volume of boiling solvent required to dissolve and recrystallize 1 g. of the compound. Except where otherwise indicated, the solvent was absolute ethanol. [b] 10% perchloric acid. [c] Monohydrate. [d] Ethanol–petroleum ether (b.p. 30–60°) 3:1. [e] Monoethanolate.



I II III

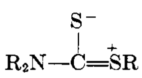
Appropriate N,N-dialkyldithiocarbamoyl esters (Table II) were prepared by the condensation of either sodium N,N-dimethyl- or N,N-diethyldithiocarbamate with the required phenacyl or acetonyl halide. Treatment of these dithiocarbamoyl esters with a minimum (usually one–three parts) of 70% perchloric acid resulted in a considerable heat of reaction, in most cases sufficient to complete solution. The colorless 1,3-dithiolium perchlorates in many instances readily crystallized on cooling; in others, sparing addition of water or ethyl acetate gave the same result. The salts thus obtained were stable enough to be recrystallized from water or ethanol.

The cyclization of β-keto N,N-dialkyldithiocarbamates to give 2-dialkylamino-4-substituted 1,3-dithiolium salts was accompanied by marked changes in spectral features. N,N-dialkyldithiocarbamoyl esters are reported to show two spectral features in the ultraviolet region that have been attributed to transitions to excited states partaking mainly of the character of IV and of V, respectively.[10] An absorption at high wave length (270–280 mμ) has been associated with transition to the immonium state (IV) while a lower wave-length (240–254 mμ) feature is thought to arise from transition to the sulfonium structure (V).[11] Of the N,N-dialkyldithiocarbamates reported in this paper (Table II), those with smaller substituents (compounds **2**–**6**) show both of these absorptions within the ranges indicated. Those dithiocarbamates with *para*-substituted phenyl as a substituent (compounds **7**–**16**) show only one of the spectral features depending on the nature of the *para* substituent. Variations between the dimethylamino and diethylamino series were generally very small, the more basic diethylamino group causing the bathochromic displacement described by Koch.[10]



$$R_2\overset{+}{N}=\overset{S^-}{\overset{|}{C}}-SR$$

IV



$$R_2N-\overset{S^-}{\overset{|}{C}}=\overset{+}{S}R$$

V

In contrast to the open-chain compounds, the ultraviolet spectra of the 1,3-dithiolium derivatives were more complex and subject to variation (Table III). In all aryl derivatives examined, three or four absorptions were found, the longest of these between 315 and 335, and the shortest between 223 and 230 mμ. Those compounds with four spectral features had further bands between 300 and 305 and 235 and 244 mμ. When only three bands were to be found, the third absorption was in the much wider range, 256–292 mμ. *para* substitution of the 4-phenyl group caused an expected bathochromic displacement of the long wave-length feature (315–336 mμ). Those dithiolium salts (**2**–**4**) with only alkyl substituents attached to the dithiolium nucleus showed only two peaks at much reduced intensities. However, we believe that these compounds are chemically quite different from those of the aryl series and that future work will show that, in many environments, they are more truly represented as the intermediate 1,3-dithiolan derivatives (II).

Changes in infrared absorption also reveal the conversion of the open-chain keto dithio esters into 1,3-dithiolium salts upon treatment with 70% perchloric acid. The disappearance of the carbonyl absorption from the region 1656–1689 cm.$^{-1}$ and the appearance of

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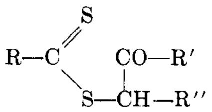
[10] H. P. Koch, *J. Chem. Soc.*, 401 (1949).

[11] K. C. Kennard and D. M. Burness, *J. Org. Chem.*, **24**, 464 (1959).

TABLE II

β-KETO DITHIO ESTERS

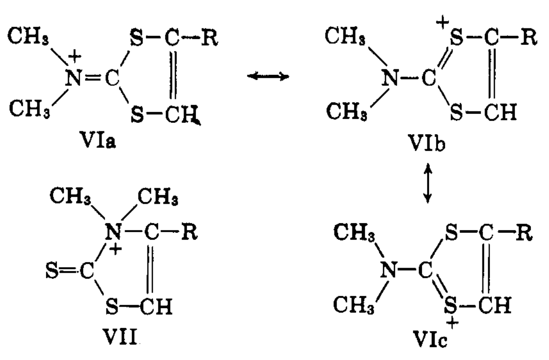


Compd. no.	R	R′	R″	Yield,[a] %	M.p., °C.	Formula	Analysis, % Calcd. C	Calcd. H	Calcd. S	Found C	Found H	Found S	Ultraviolet spectra,[b] λ_{max}, mμ (log ε)
1	C_6H_5	C_6H_5	H	45	79-80	$C_{15}H_{12}OS_2$	66.15	4.45	23.55	66.05	4.25	23.35	297 (4.22); 243 (4.16)
2	$(CH_3)_2N$	CH_3	H	44	54-55[c]	$C_6H_{11}NOS_2$	40.65	6.25	36.15	40.75	6.15	36.45	275 (4.05); 245 (3.97)
3	$(CH_3)_2N$	CH_3	CH_3	45	33-34	$C_7H_{13}NOS_2$	43.95	6.85	33.5	44.0	6.8	33.3	277 (3.93); 248 (3.90)
4	$(CH_3)_2N$	CH_3	C_2H_5	63	42-43	$C_8H_{15}NOS_2$	46.8	7.35	31.2	47.2	7.5	30.9	276 (4.08); 248 (4.06)
5	$(CH_3)_2N$	C_6H_5	H	95	110-111[d]	$C_{11}H_{13}NOS_2$	55.2	5.45	26.8	55.0	5.6	27.1	275 (4.03); 247 (4.32)
6	$(C_2H_5)_2N$	C_6H_5	H	83	103-104[d]	$C_{13}H_{17}NOS_2$	58.4	6.4	24.0	58.5	6.45	23.95	278 (4.10); 248 (4.36)
7	$(CH_3)_2N$	p-$CH_3C_6H_4$	H	79	113-114	$C_{12}H_{15}NOS_2$	56.9	5.95	25.3	57.0	6.05	25.15	254 (4.03)
8	$(C_2H_5)_2N$	p-$CH_3C_6H_4$	H	63	64-65	$C_{14}H_{19}NOS_2$	59.75	6.8	22.8	59.8	6.8	22.6	255 (4.42)
9	$(CH_3)_2N$	p-ClC_6H_4	H	80	88-89	$C_{11}H_{12}ClNOS_2$	48.25	4.4	23.4	48.1	4.55	23.25	254 (4.42)
10	$(C_2H_5)_2N$	p-ClC_6H_4	H	78	66-67	$C_{13}H_{16}ClNOS_2$	51.7	5.35	21.25	52.1	5.55	20.35	254 (4.40)
11	$(CH_3)_2N$	p-$CH_3OC_6H_4$	H	80	96-97	$C_{12}H_{15}NO_2S_2$	53.5	5.6	23.8	53.7	5.5	23.55	275 (4.41)
12	$(C_2H_5)_2N$	p-$CH_3OC_6H_4$	H	46	48-50	$C_{14}H_{19}NO_2S_2$	56.55	6.45	21.55	56.7	6.25	21.5	276 (4.45)
13	$(CH_3)_2N$	p-HOC_6H_4	H	81	203	$C_{11}H_{13}NO_2S_2$	51.75	5.15	25.1	51.8	5.25	25.15	277 (4.41)
14	$(C_2H_5)_2N$	p-HOC_6H_4	H	75	170-171	$C_{13}H_{17}NO_2S_2$	55.1	6.05	22.65	55.05	6.25	22.55	278 (4.42)
15	$(CH_3)_2N$	p-$NO_2C_6H_4$	H	82	146-148	$C_{11}H_{12}N_2O_3S_2$	46.45	4.25	22.65	46.4	4.5	22.6	267 (4.31)
16	$(C_2H_5)_2N$	p-$NO_2C_6H_4$	H	62	106-107	$C_{13}H_{16}N_2O_3S_2$	50.0	5.15	20.55	50.15	5.4	20.45	267 (4.41)

[a] Yields determined after first recrystallization. [b] Ultraviolet spectra were measured in 95% ethanol using a Cary 14 Model spectrophotometer. [c] J. R. Robinson, D. Craig, and R. B. Fowler [*Can. J. Chem.*, **34**, 1596 (1956)] report m.p. 58°; G. Nachmias [*Ann. chim.* (Paris), **7**, 584 (1952)] report m.p. 76°. [d] S. Yoshida and W. Ishizuka [*J. Pharm. Soc. Japan*, **74**, 331 (1954)] report m.p. 111° for **5** and 102° for **6**.

a very strong and broad band (1050–1110 cm.$^{-1}$) due to the perchlorate anion were spectral changes that were used throughout this work to confirm the nature of the reaction products. Also, the one or two additional bands that appeared at frequencies from 1450–1650 cm.$^{-1}$ could be attributed either to the newly introduced C-4–C-5 double bond or to the stretching vibrations associated with a polar $C{=}N^+$ bond.[12]

In the cyclization of N,N-dialkyldithiocarbamoyl esters, it is possible for the products to be quaternary N,N-dialkylthiazoline-2-thiones (VII) on the basis that the order of effective electron donor ability in similar cyclizations is usually considered to be N > S > O.[13] Nevertheless, we have assigned the perchlorates the 1,3-dithiolium structure by analogy with the formation of 2,4-diphenyl-1,3-dithiolium perchlorate, since this system would receive greater stabilization from resonance (VIa–c) than the thiazolinium structure (VII), and on the basis of n.m.r. spectral data.



VIa VIb VII VIc

Attempts to resolve the structure of the products by direct chemical means produced no evidence in favor of the thiazolinium structure. No derivative of a thione group present in VII could be prepared, nor were efforts to hydrolyze any such group with mercuric acetate and acetic acid successful. Nuclear magnetic resonance spectra, moreover, indicated that the perchlorates were unlikely to be thiazoline derivatives. When these measurements were made in trifluoroacetic acid, the N,N-dialkyl substituents were found to be nonequivalent; N,N-dimethyl groups were represented by two peaks and N,N-diethyl groups by two triplet and two quartet features.[14] Such a situation is difficult to envisage as arising out of the structure VII where both alkyl groups would be in similar juxtaposition to the positive charge and hence would suffer identical deshielding effects. On the other hand, if the products existed as dithiolium derivatives, then contributions from the resonance form VIa would produce a barrier to rotation about the C–N bond,[15] and the environments of the two N-alkyl groups would be different (*cis* to S–C–R or *cis* to S–C–H). Further evidence is found in the n.m.r. spectrum of compound **3** (Table III). A single peak, representing six protons, is present in the spectrum taken in 70% perchloric acid. This is the expected resonance for two identical ring methyl groups at C-4 and C-5, in VI, but similar methyl groups in VII would not be expected to be identical. On the basis of this and the aforementioned evidence, the perchlorate products described in this paper are considered as 1,3-dithiolium derivatives (VIa–c).

Contributions from the immonium structure (VIa) are also manifested in the chemical shift of the lone dithiolium proton. The spectrum of 2,4-diphenyl-1,3-dithiolium perchlorate (Fig. 1a) showed only the two anticipated features: a complex signal between τ 1.83 and 2.50 and a singlet at 1.25. Integration of the spectrum showed unequivocally that the broad signal

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(12) J. Chatt, L. A. Duncanson, and L. M. Venanzi, *Chem. Abstr.*, **51**, 5559*d* (1957).

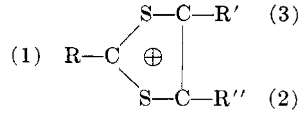
(13) N. J. Leonard, T. W. Milligan, and T. L. Brown, *J. Am. Chem. Soc.*, **82**, 4075 (1960).

(14) This was not so when the n.m.r. spectra were measured in deuterated 70% perchloric acid, for then the N,N-dimethyl protons appeared as a single spectral feature integrating for six protons, while the N,N-diethyl protons were found as one triplet pattern (2 × 3 protons) and as one quartet pattern (2 × 2 protons). This may have been the result of poorer resolution in the more viscous solvent, or the existence of the perchlorates more exclusively in the sulfonium states (VIb and c).

(15) J. D. Roberts, "Nuclear Magnetic Resonance," McGraw-Hill Book Company, Inc., New York, N. Y., 1959, Chapter 3.

TABLE III

SPECTRA OF SUBSTITUTED 1,3-DITHIOLIUM PERCHLORATES



Compd. no.	R	R′	R″	Ultraviolet spectra,[a] λ_{max}, mμ (log ε)	Proton magnetic resonance spectra[b] (J)		
					(1)	(2)	(3)
1	C_6H_5	C_6H_5	H	394 (4.18), 310 (3.72)[c] 277 (3.82), 243 (4.17)	1.83–2.50 m[d]	1.25	1.83–2.50 m[d]
2	$(CH_3)_2N$	CH_3	H	303 (3.49), 245 (2.90)[c]	7.00	3.50 q (2)	8.03 d (2)[c]
3	$(CH_3)_2N$	CH_3	CH_3	312 (3.89), 246 (3.50)[c]	7.03	8.20	8.20[c]
4	$(CH_3)_2N$	CH_3	C_2H_5	312 (3.83), 245 (3.03)[c]	7.05	7.80 q (8) 9.32 t	8.20[c]
5	$(CH_3)_2N$	C_6H_5	H	315 (4.08), 300 (4.03),[a,c] 235 (4.15), 225 (4.21)	6.30 6.35	2.63	2.47
6	$(C_2H_5)_2N$	C_6H_5	H	320 (4.06), 300 (3.95), 236 (4.12), 225 (4.18)	6.00 q, 8.42 t (8) 6.05 q, 8.43 t	2.63	2.47
7	$(CH_3)_2N$	p-$CH_3C_6H_4$	H	320 (4.04), 302 (4.03), 242 (4.13), 228 (4.14)	6.32 6.37	2.70	2.53 d, 2.67 d (9) 7.59[e]
8	$(C_2H_5)_2N$	p-$CH_3C_6H_4$	H	325 (4.04), 302 (4.00), 244 (4.12), 228 (4.12)	6.00 q, 8.42 t (8) 6.05 q, 8.43 t	2.70	2.53 d, 2.67 d (9) 7.59[e]
9	$(CH_3)_2N$	p-ClC_6H_4	H	315 (4.15), 305 (4.16), 237 (4.22), 230 (4.23)	6.28 6.33	2.59	2.50
10	$(C_2H_5)_2N$	p-ClC_6H_4	H	320 (4.13), 305 (4.11), 238 (4.21), 230 (4.20)	6.00 q, 8.42 t (7) 6.05 q, 8.43 t	2.62	2.50
11	$(CH_3)_2N$	p-$CH_3OC_6H_4$	H	326 (4.01), 292 (4.12), 256 (4.10)	6.33 6.38	2.75	2.47 d, 2.88 d (9) 6.03[e]
12	$(C_2H_5)_2N$	p-$CH_3OC_6H_4$	H	330 (3.94), 289 (4.05), 260 (4.06)	5.98 q, 8.40 t (7) 6.03 q, 8.42 t	2.69	2.40 d, 2.80 d (9) 5.97[e]
13	$(CH_3)_2N$	p-HOC_6H_4	H	330 (3.96), 292 (4.11), 261 (4.09)	6.35 6.40	2.78	2.55 d, 2.95 d (9)
14	$(C_2H_5)_2N$	p-HOC_6H_4	H	335 (3.96), 288 (4.12), 264 (4.13)	6.05 q, 8.45 t (7) 6.08 q, 8.47 t	2.78	2.55 d, 2.93 d (9)
15	$(CH_3)_2N$	p-$NO_2C_6H_4$	H	323 (4.32), 255 (3.96), 223 (4.32)	6.27 6.32	2.27	1.60 d, 2.11 d (9)
16	$(C_2H_5)_2N$	p-$NO_2C_6H_4$	H	326 (4.33), 256 (3.95), 225 (4.21)	5.95 q, 8.38 t (7) 5.98 q, 8.40 t	2.28	1.60 d, 2.13 d (9)

[a] Measurements were made in 95% ethanol except where otherwise indicated, using the Cary Model 14 recording spectrophotometer. [b] Proton magnetic resonance spectra were examined in trifluoroacetic acid at concentrations between 6 and 8% w./v. at *ca.* 25°. Where compounds were unstable in this solvent, deuterated 70% perchloric acid was used. Spectral measurements were made with a Varian A-60 spectrophotometer operating at 60 Mc./sec. Chemical shifts are recorded on the frequency independent τ-scale relative to an internal tetramethylsilane reference. When 70% perchloric acid was used as the solvent, it was convenient to calculate chemical shifts by using the perchloric acid proton signal (570 cycles downfield from tetramethylsilane) as the internal reference; values recorded, however, are relative to tetramethylsilane. Spin–spin coupling values (*J*) are in cycles per second measured on the 500-c.p.s. scale. Unless otherwise indicated, values refer to singlet absorptions; for multiple signals the following abbreviations have been used: d = doublet, t = triplet, q = quartet, m = multiplet. [c] Spectra measured in 70% perchloric acid. [d] Approximation; complex multiplet in this range (see Fig. 1a). [e] Absorption due to the *para* substituent.

represented the ten protons of the two aromatic nuclei, and the signal at lower field strength, the lone C-5 proton. Since the resonance of the 2,4-diphenyl derivative is restricted to the equivalent forms of III, τ 1.25 can be taken as the chemical shift to be expected of a proton attached directly to the positively charged dithiolium ring. The dimethylamino protons of 2-dimethylamino-4-phenyl-1,3-dithiolium cation (VI, R = C_6H_5) occurred as two closely spaced peaks at τ 6.35 and 6.30, each integrating for three protons, while the signals arising from the dithiolium and phenyl protons were found at τ 2.63 and 2.47, respectively (Fig. 1b). We suggest that this upfield shift of the dithiolium proton signal is a measure of the increased diamagnetic shielding introduced by the existence of the resonance state VIa in which the positive charge is further removed from the proton in question. The n.m.r. spectra of twelve other dialkylamino derivatives are in accord with this conclusion; in every instance the C-5 proton signals appeared at higher field strength than in the case of the 2,4-diphenyl compound (*cf.* Fig. 1). Variations in the position of the dithiolium and aryl protons within the dialkylamino series appears to be a result of changes in diamagnetic shielding caused by the effect of the *para* aryl substituents.[16] Thus, electron-donating groups were found to increase the shielding in the order OH > OCH_3 > CH_3 > H ⪢ Cl (*cf.* Fig. 1c and Table III), while the electron-withdrawing substituent NO_2 reduced the shielding effect (Fig. 1d). It is important to note that variations in the dialkyl proton signals are much less, and we attribute this to their closer proximity to the positive charge (VIa–c) and greater distance from the *para* substituent.

The preparation of 1,3-dithiolium derivatives without stabilizing aryl substituents introduces some interesting chemistry. For example, 2-dimethylamino-4-methyl-1,3-dithiolium perchlorate [III, R = $(CH_3)_2N$; R′ = CH_3] possessed the unusual property that its salts were only characterized as the monohydrate and

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[16] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Inc., New York, N. Y., 1959, Chapter 4.

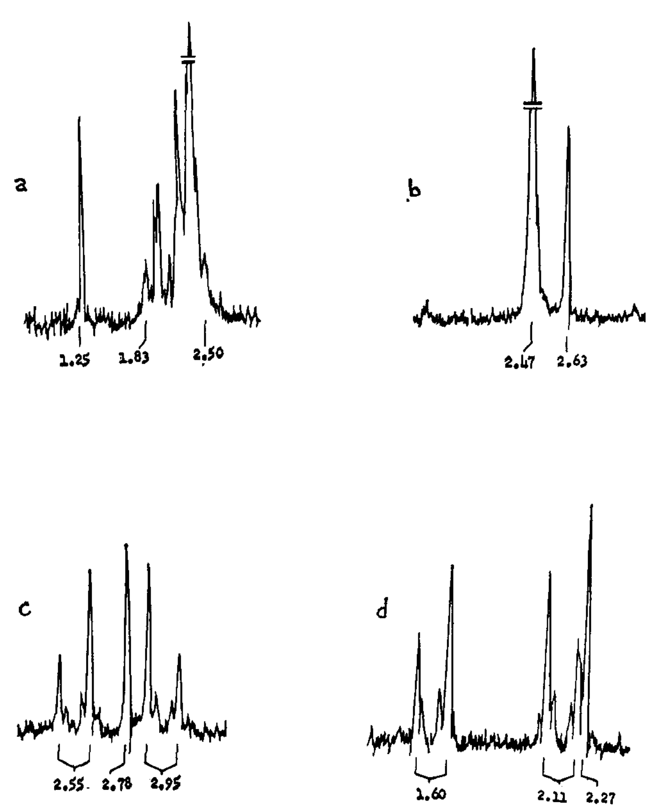
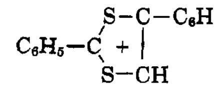
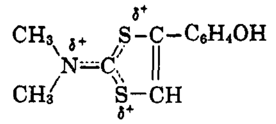


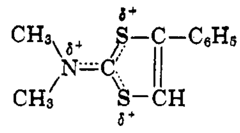
Fig. 1.—N.m.r. spectra showing the signals of the dithiolium and 4-aryl substituent protons measured in trifluoroacetic acid (see a-d below).



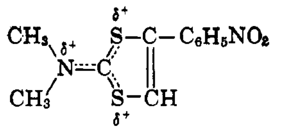
a



c



b



d

as the monoethanolate but could not be obtained free of solvent of crystallization. They were stable in aqueous solution of perchloric acid, but, if their solutions were neutralized to pH 4, ring cleavage occurred to yield the acetonyl N,N-dimethyldithiocarbamate [I, R = $(CH_3)_2N$; R′ = CH_3] from which they had been prepared. Their n.m.r. spectra (Fig. 2a) run in 70% perchloric acid showed the 4-methyl protons as a doublet (τ 8.03) spin coupled (J = 2 c.p.s.) through four bonds to the quartet signal (τ 3.50) from the adjacent C-5 proton. This olefinic-type character of the C-4–C-5 double bond[17] became of greater significance when the spectra of the solvated salts were measured in trifluoroacetic acid (Fig. 2b). Primarily the decoupling of the C-4 methyl and C-5 protons, and the disappearance of the low-field signal suggested that the C-4–C-5 unsaturation no longer existed. In addition, two new coupled signals integrating for two protons appeared at τ 5.76 and 5.93.

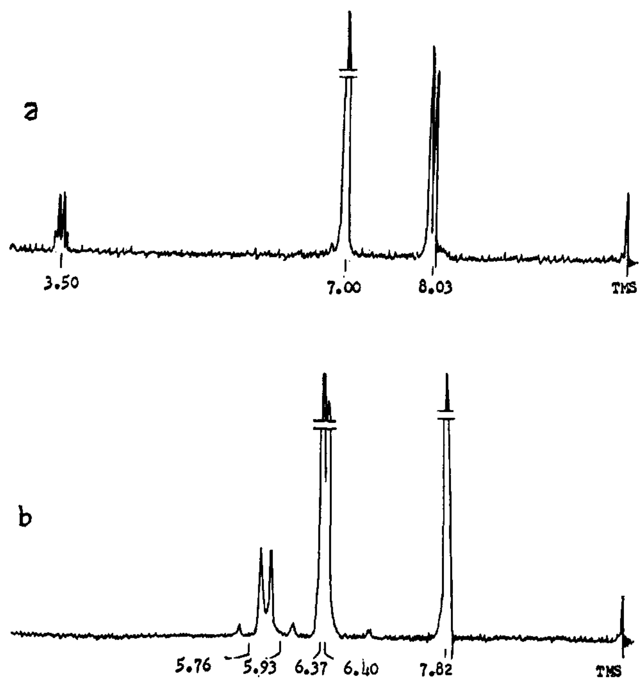
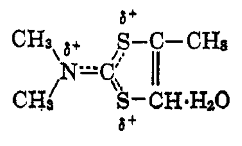
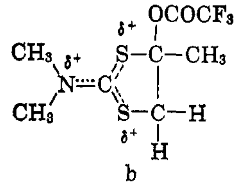


Fig. 2.—N.m.r. spectra of 2-dimethylamino-4-methyl-1,3-dithiolium perchlorate: (a) monohydrate measured in 70% deuterated perchloric acid; (b) in trifluoroacetic acid.



a



b

The characteristic shape of these features was typical of nonequivalent methylene protons splitting each other with a coupling constant (J = 13 c.p.s.) very nearly the same magnitude as their separation (17 c.p.s.)[15] This evidence is compatible with a structure in which normal addition of the trifluoroacetic acid solvent to the C-4–C-5 double bond had occurred. 4,5-Dimethyl-2-dimethylamino- and 2-dimethylamino-4-ethyl-5-methyl-1,3-dithiolium perchlorates (Table I and III, compounds **3** and **4**) likewise could only be isolated as monohydrates and showed evidence of trifluoroacetic acid addition to the C-4–C-5 double bond. Attempts to isolate these adducts have so far been unsuccessful.

2-Dimethylamino-4-methyl-1,3-dithiolium perchlorate monohydrate was also observed to undergo a deuterium exchange in the process of recrystallization from 10% perchloric acid in deuterium oxide. The physical properties of the salt did not alter after this exchange, but the n.m.r. spectra no longer showed the C-5 proton signal and the protons of the methyl substituent then appeared as one peak. This exchange probably occurs *via* hydration or hydrolysis of the ring by deuterium oxide, followed by elimination of deuterium hydroxide or recyclization of deuterated I.

In view of these results, the question arises as to whether these salts are really solvated in their solid state or whether in actual fact they are not the 4-hydroxy- and 4-ethoxydithiolan derivatives [II, R = $(CH_3)_2N$] which are postulated as intermediates in the dithiolium synthesis. Unquestionably the n.m.r. spectra of these 4-alkyl derivatives show that

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[17] Numerous examples showing similar 1,4-coupling of vinyl and allyl hydrogen atoms are given by N. S. Bhacca, L. F. Johnson, and J. N. Schoolery, Varian Associates High Resolution N.M.R. Spectra Catalogue, Varian Associates, Palo Alto, Calif.

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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Contribution No. 1202 from the Chemistry Laboratories of Indiana University, Bloomington, Indiana 47405

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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).