Dithiolium Derivatives. III.[1] Reactions of the 2-Methylthio-4-Substituted 1,3-Dithiolium Cation[2]

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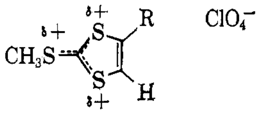
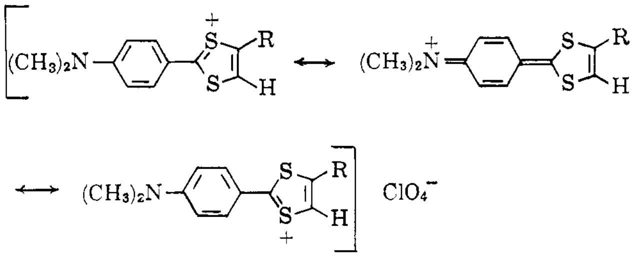
The electrophilic character of the 2-methylthio-4-substituted 1,3-dithiolium cation is demonstrated by condensations with dimethylaniline and with active methylene compounds. Spectral characteristics of the products are discussed. Application of sulfuric acid in the cyclodehydration of β-keto N,N-dialkyl dithiocarbamates, β-keto dithiobenzoates and β-keto methyltrithiocarbonates affords the corresponding 1,3-dithiolium hydrogen sulfates.

The pseudoaromatic 2-methylthio-4-substituted 1,3-dithiolium salts (4-substituted "iso-trithionium salts")[4] have been shown to exist as the charge delocalized species **1** on the basis of n.m.r. and ultraviolet spectral data.[1a] Analogous to these compounds are the 3-methylthio-1,2-dithiolium salts ("trithionium salts"), in which the charge is also distributed between ring and side chain.[5] The electrophilic center of the 1,3-dithiolium cation has been shown experimentally[6,7] and theoretically[8] to be the C-2 carbon atom. In agreement with these results, it has been found that **1** also exhibits electrophilic behavior, attacking dimethylaniline to give the highly colored 2-(p-dimethylaminophenyl)-4-substituted 1,3-dithiolium perchlorates (**2**).



1a, R = p-BrC_6H_4
b, R = C_6H_5
c, R = p-$NO_2C_6H_4$



2a, R = p-BrC_6H_4
b, R = C_6H_5
c, R = p-$NO_2C_6H_4$

These products are readily obtained when **1** is warmed with dimethylaniline in glacial acetic acid for 15–30 min. The intense color of these compounds can be attributed to the large charge separation between the dithiolium resonance forms and the quaternary ammonium dithiol resonance form.[9] The ultraviolet spectral data (Table I) are consistent with this postulate; in a weakly acidic medium, acetic acid, a long wave-length feature in the region 538–540 mμ is observed which can be associated with the quaternary ammonium dithiol resonance form. In 70% perchloric acid, however, protonation of the dimethylamino moiety is possible, thus inhibiting the immonium resonance form and rendering the solution yellow. Klingsberg has reported analogous behavior for some dialkyl aminophenyl-1,2-dithiolium dyes.[9] However, this postulate does not clearly account for the fact that **2** shows the long wave-length absorption (535–538 mμ) in trifluoroacetic acid, since n.m.r. studies indicate protonation of the dimethylamino function in this solvent. Unfortunately, the limited solubility of **2** in acetic acid made comparison of extinction coefficients impossible. Evidence that protonation does occur in trifluoroacetic acid comes from comparison of the chemical shifts of the C-5 proton of 2,4-diphenyl-1,3-dithiolium perchlorate and **2b**, which occur at τ 1.25 and 1.00, respectively. One would expect the dialkyl amino moiety of **2b**—being a strong electron-releasing group ($\sigma_{para} = -0.60$[10])—to cause the C-5 proton to be more shielded (thus further upfield relative to the C-5 proton of 2,4-diphenyl-1,3-dithiolium perchlorate in neutral solvents). In trifluoroacetic acid, however, protonation of the dialkyl amino substituent produces the strongly electron-attracting quaternary nitrogen group ($\sigma_{para} \cong +0.86$[10]) which shifts the position of the C-5 proton downfield as observed.

That the N-methyl protons of **2** occur as a single resonance peak while those of 2-dimethylamino-4-substituted 1,3-dithiolium perchlorates occur as two peaks indicates that in **2** the distant methyl protons are not sufficiently nonequivalent to be resolved under the conditions of measurement although they might be expected to be nonequivalent due to contributions of the immonium form which produces a barrier to rotation about the C–N bond. This point has been discussed[1b] and has been further confirmed by the synthesis of 2-dimethylamino-4,5-diphenyl-1,3-dithiolium perchlorate (**3**), in which both N-methyl groups are in the same electronic environment in the immonium resonance form; as expected, the n.m.r. spectrum in trifluoroacetic acid shows only two resonance peaks, one occurring at τ 2.62 due to the ten equivalent aro-

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[1] (a) Paper II: E. Campaigne, R. D. Hamilton, and N. W. Jacobsen, *J. Org. Chem.*, **29**, 1708 (1964); (b) paper I: E. Campaigne and N. W. Jacobsen, *ibid.*, **29**, 1703 (1964).

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

[3] Abstracted in part from the forthcoming Ph.D. thesis of R. D. H.

[4] A. Lüttringhaus, E. Futterer, and H. Prinzbach, *Tetrahedron Letters*, 1209 (1963).

[5] (a) J. Teste and N. Lozac'h, *Bull. soc. chim. France*, 437 (1955); (b) A. Lüttringhaus and U. Schmidt, *Chem. Ztg.*, **77**, 135 (1953).

[6] E. Klingsberg, *J. Am. Chem. Soc.*, **84**, 3410 (1962).

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

[8] R. Zahradník and J. Koutecký, *Tetrahedron Letters*, 632 (1961).

[9] E. Klingsberg and A. M. Schreiber, *J. Am. Chem. Soc.*, **84**, 2941 (1962).

[10] H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953).

TABLE I

SPECTRAL DATA OF 2-DIMETHYLAMINOPHENYL-4-SUBSTITUTED 1,3-DITHIOLIUM PERCHLORATES[a]

Compound	Ultraviolet, λ_{max} mμ (log ε)			N.m.r., τ-values (J, c.p.s.)		
	70% $HClO_4$	CF_3COOH	HOAc	—$N(CH_3)_2$	C-5 proton	—Ar
2a		537 (3.91)	538	6.42	1.03	1.65 d (9)
	395 (4.11)	405 (4.06)				1.95 d
		305 (4.15)				
	284 (4.15)	285 (4.22)				2.20 d (9)
	253 (4.24)	262 (4.18)				230 d
2b		535 (3.70)	538	6.38	1.00	1.62 d (9)
	390 (4.08)	398 (4.08)				1.90 d
		300 (4.03)				2.10–2.42 m
	278 (4.01)	275 (4.09)				
	243 (4.19)					
2c		538 (4.44)	540	6.38	0.80	1.60 d (9)
	375 (4.30)	370 (4.21)				1.93 d
	295 (4.13)	283 (4.25)				
	262 (4.04)	265 (4.22)				1.47 d (9)
	225 (4.11)					1.87 d

[a] See ref. 15.

TABLE II

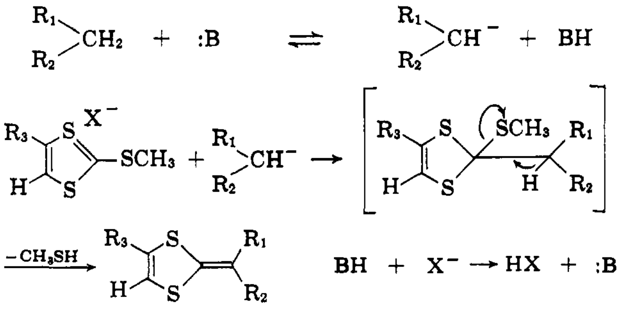
4-SUBSTITUTED 1,3-DITHIOL-2-YLIDENE DERIVATIVES

Compound	Name	% yield	Recrystn. solvent	M.p., °C.	Formula	Analysis, % Calcd. C	Calcd. H	Calcd. S	Found C	Found H	Found S
4a	4-Phenyl-1,3-dithiol-2-ylidenemalononitrile	67	EtOH–EtOAc	167–168	$C_{12}H_6N_2S_2$	59.48	2.50	26.46	59.29	2.68	26.30
4a	Ethyl 4-phenyl-1,3-dithiol-2-ylidenecyanoacetate	45	Abs. alcohol	131–132	$C_{14}H_{11}NO_2S_2$	58.11	3.83	22.16	58.32	3.85	22.48
4c	3-(4-Phenyl-1,3-dithiol-2-ylidene)pentane-2,4-dione	43	Abs. alcohol	144–146	$C_{14}H_{12}O_2S_2$	60.86	4.35	23.21	60.80	4.32	23.12
4d	Ethyl 4-*p*-bromophenyl-1,3-dithiol-2-ylideneacetoacetate	39	Benzene–cyclohexane	195–197	$C_{15}H_{13}BrO_3S_2$	46.76	3.40	16.64	46.86	3.48	16.79
4e	3-(4-*p*-Bromophenyl-1,3-dithiol-2-ylidene)-pentane-2,4-dione	34	EtOAc	221–223	$C_{14}H_{11}BrO_2S_2$	47.33	3.12	18.05	47.56	3.23	18.20
4f	Ethyl 4-*p*-bromophenyl-1,3-dithiol-2-ylidenecyanoacetate	54	EtOH–EtOAc	229–230	$C_{14}H_{10}BrNO_2S_2$	45.65	2.74	17.41	45.85	2.71	17.83
4g	2-(4-Phenyl-1,3-dithiol-2-ylidene)indane-1,3-dione	77	Benzene–cyclohexane	255–256	$C_{18}H_{10}O_2S_2$	67.05	3.13	19.90	67.03	3.25	19.82

matic protons and one occurring at τ 6.33 due to the six equivalent N-methyl protons.

The aromatic regions of **2a** and **2c** consist of four doublets (A_2B_2); **2b** exhibits two doublets (A_2B_2) and a complex multiplet. In **2b**, the doublets (τ 1.62 and 1.90) are due to the four protons on the 2-*p*-dimethylaminophenyl moiety and the multiplet is due to the 4-phenyl substituent. By analogy, the doublets of **2a** and **2c** (τ 1.65, 1.95 and τ 1.60, 1.93, respectively) can be assigned to the 2-*p*-dimethylaminophenyl substituent, and the other A_2B_2 patterns assigned to the 4-*p*-bromophenyl and 4-*p*-nitrophenyl functions, respectively.

The 2-methylthio-4-substituted 1,3-dithiolium cation was allowed to react with several active methylene compounds in order to demonstrate further its electrophilic properties. The reaction was carried out in boiling glacial acetic acid in the presence of pyridine, and may be considered as a nucleophilic attack of the active methylene carbanion on the electron deficient C-2 site of **1**; subsequent elimination of methyl mercaptan gives the product.



This general reaction has been applied to several substituted 3-methylthio-1,2-dithiolium salts,[11,12] and more recently to a substituted 2-methylthio-1,3-dithiolium salt[4] using much milder conditions than those described here. The products (**4**), 4-substituted 1,3-dithiol-2-ylidene derivatives,[13] are formed in yields of 34–77% (Table II).

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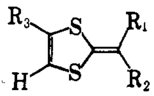
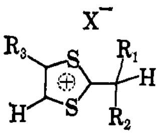
[11] U. Schmidt, R. Scheuring, and A. Lüttringhaus, *Ann.*, **630**, 116 (1960).

[12] Y. Mollier and N. Lozac'h, *Bull. soc. chim. France*, 157 (1963).

[13] This class of compounds has been conveniently termed "1,4-dithiafulvenes" by W. Kirmse and L. Horner [*Ann.*, **614**, 4 (1958)].





4a, $R_1 = R_2 = CN$; $R_3 = C_6H_5$[4]
b, $R_1 = CN$; $R_2 = CO_2Et$; $R_3 = C_6H_5$
c, $R_1 = R_2 = COCH_3$; $R_3 = C_6H_5$
d, $R_1 = COCH_3$; $R_2 = CO_2Et$;
$R_3 = p\text{-}BrC_6H_4$
e, $R_1 = R_2 = COCH_3$; $R_3 = p\text{-}BrC_6H_4$
f, $R_1 = CN$; $R_2 = CO_2Et$; $R_3 = p\text{-}BrC_6H_4$
g, R_1 and R_2 = -*o*-COC_6H_4CO—; $R_3 = C_6H_5$

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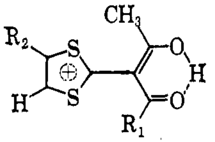
In a strongly acidic medium it is possible for these compounds to exist in the 1,3-dithiol form (**4**) or in the protonated 1,3-dithiolium form (**5**), depending on their relative basicities. Comparison of the n.m.r. chemical shift data of the C-5 proton of these compounds in trifluoroacetic acid (Table III) suggests that **4c** and **4e** (τ 1.88 and 2.08, respectively) exist as the protonated charge-delocalized species **6a** and **6b**, respectively, in which additional stabilization can result from hydrogen bonding with the carbonyl function. The derivatives **4a**, **4b**, and **4f**, being less basic, are apparently not protonated and thus exhibit the C-5 proton resonance upfield at τ 2.73, 2.72, and 2.75, respectively, whereas the C-5 proton resonance in **4d** occurs at an intermediate value, τ 2.22. The chemical shift of the C-5 proton of 2-(4-phenyl-1,3-dithiol-2-ylidene)indane-1,3-dione (**4g**) could not be discerned as its position was obscured in the aromatic region (τ 2.28–2.65).



6a, $R_1 = CH_3$; $R_2 = C_6H_5$
b, $R_1 = CH_3$; $R_2 = p\text{-}BrC_6H_4$

TABLE III

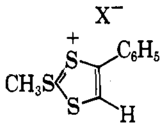
SPECTRAL DATA OF 4-SUBSTITUTED 1,3-DITHIOL-2-YLIDENE DERIVATIVES[a]

Compound	Ultraviolet, λ_{max} mμ (log ε) THF[b]	CF₃COOH	N.m.r. (*J*, c.p.s.) signals of substituents at C-4	C-5	C-2
4a	380 (4.18)	383 (4.37)	2.50	2.73	
	243 (3.99)				
4b	380 (4.39)	383 (4.44)	2.37	2.72	5.55 q
					8.55 t
4c	390 (4.42)	388 (4.36)	2.30–	1.88	7.20
	243 (4.20)	275 (4.23)	2.47 m		
4d	384 (4.49)	390 (4.31)	2.43 d	2.22	7.18
			(9)		
	245 (4.40)		2.57 d		5.43 q
					8.47 t
4e	389 (4.42)	388 (4.28)	2.40 d	2.08	7.15
			(9)		
	243 (4.32)	280 (4.15)	2.50 d		
4f	382 (4.43)	378 (4.56)	2.42 d	2.75	5.55 q
			(9)		
	247 (4.31)		2.58 d		8.55 t
4g	425 (4.43)	420 (4.60)	2.28–	. . .	2.28–
			2.65 m		2.65 m
		300 (4.21)			
		258 (4.37)			

[a] See ref. 15. [b] THF = tetrahydrofuran.

That **4c** and **4e** are protonated in trifluoroacetic acid is also manifested in the ultraviolet region. In a nonacidic medium such as tetrahydrofuran (THF), all of these compounds (except **4b**) exhibit two absorption peaks, a long wave-length feature occurring at 380–390 mμ and a short wave-length band occurring in the region 243–247 mμ. In trifluoroacetic acid, only the long wave-length absorption (378–390 mμ) can be seen in **4a**, **4b**, **4d**, and **4f**, while **4c** and **4e** show the long wave-length feature and, in addition, exhibit new bands at 275 and 280 mμ, respectively. The appearance of these new bands is probably associated with the 1,3-dithiolium form (**5**) since absorption in this region has previously been observed for some 1,3-dithiolium perchlorates in acid solution.[1a]

During the course of this investigation, it was learned that concentrated sulfuric acid could be used in the conversion of phenacyl methyltrithiocarbonate to 2-methylthio-4-phenyl-1,3-dithiolium hydrogen sulfate (**7**). Although **7** was extremely hygroscopic and could not be isolated in pure form, the impure material was used in some of the condensation reactions. Previous communications from this laboratory described the use of 70% perchloric acid to effect this facile cyclodehydration.[1] Conversion of β-keto N,N-dimethyldithiocarbamates and β-keto dithiobenzoates to 2-dimethylamino- (**8b**) and 2-phenyl- (**9b**) 4-substituted 1,3-dithiolium hydrogen sulfates, respectively, was also achieved using sulfuric acid.



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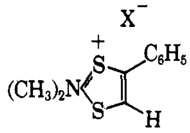
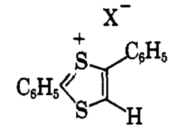


8a, X = ClO_4
b, X = HSO_4
c, X = BF_4
d, X = I
e, X = SCN
f, X = $(NO_2)_3C_6H_2O$



9a, X = ClO_4
b, X = HSO_4
c, X = $(NO_2)_3C_6H_2O$

2-Dimethylamino-4-phenyl-1,3-dithiolium hydrogen sulfate (**8b**) is soluble in water, and addition of another anion (X^-) yields a new water-insoluble 1,3-dithiolium salt in cases where the anion is fluoroborate, iodide, thiocyanate, and picrate. This behavior is analogous to that observed by Klingsberg for the parent 1,3-dithiolium hydrogen sulfate as well as for the 3- and 4-phenyl-1,2-dithiolium hydrogen sulfates.[6,14]

Experimental[15]

2-Dimethylaminophenyl-4-Substituted 1,3-Dithiolium Perchlorates (2a–c).—The general procedure used to prepare these compounds was as follows. To 0.5 g. of 1[1a] in 20 ml. of glacial acetic acid was added a twofold excess of dimethylaniline, and the mixture was warmed at 100° for 15–30 min. The highly colored solid which separated was collected. **2b** could be re-

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[14] E. Klingsberg, *J. Am. Chem. Soc.*, **83**, 2934 (1961).

[15] 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. All n.m.r. measurements were made in trifluoroacetic acid at concentrations from 6–8% w./v. at about 31°, using a Varian A-60 spectrometer operating at 60 Mc./sec. Chemical shifts are recorded on the frequency independent τ-scale relative to internal tetramethylsilane reference. Spin–spin coupling values (*J*) are in cycles per second measured on 500-c.p.s. scale. Unless otherwise indicated, values refer to singlet absorptions; for multiple signals the following abbreviations are used: d = doublet, t = triplet, q = quartet, m = multiplet. All ultraviolet measurements were made with the Cary Model 14 recording spectrophotometer in the solvents indicated.

TABLE IV

1,3-DITHIOLIUM SALTS

Compound	% yield	Recrystn. solvent	M.p., °C.	Formula	Analysis, % Calcd. C	H	S	Found C	H	S
1a	86	70% $HClO_4$–EtOAc	198–200	$C_{10}H_8BrClO_4S_3$	29.75	2.00	23.83	30.02	2.13	23.84
2a	91	HOAc	240–242	$C_{17}H_{15}BrClNO_4S_2$	42.82	3.18	13.45	42.86	3.26	13.54
2b	86	HOAc	219–220	$C_{17}H_{16}ClNO_4S_2$	51.31	4.05	16.12	51.31	4.41	15.98
2c	84	HOAc	280 dec.	$C_{17}H_{15}ClN_2O_6S_2$	46.10	3.41	14.47	45.95	3.45	14.59
3	91	Abs. alc.	221–222	$C_{17}H_{16}ClNO_4S_2$	51.31	4.05	16.12	51.50	4.06	16.30
8a	87	95% alc.	178–179	*a*						
8b	100	EtOH–EtOAc	232–234	$C_{11}H_{13}NO_4S_3$	41.36	4.10	30.11	41.58	4.24	30.29
8c	82	95% alc.	161–163	$C_{11}H_{12}BF_4NS_2$	42.73	3.91	20.74	43.04	3.99	20.85
8d	74	$CHCl_3$	187–189	$C_{11}H_{12}INS_2$	37.83	3.46	18.36	37.95	3.48	18.27
8e	80	Propanol	163–165	$C_{12}H_{12}N_2S_3$	51.39	4.31	34.30	51.30	4.20	34.51
8f	52	MeOH	178–180	$C_{17}H_{14}N_4O_7S_2$	45.33	3.13	14.24	45.18	3.35	14.18
9b	100	Propanol	173–175	$C_{15}H_{12}O_4S_3$	51.11	3.43	27.29	51.24	3.50	27.22
9c	78	MeOH	197–199	$C_{21}H_{13}N_3O_7S_2$	52.17	2.70	13.26	52.10	2.57	13.18

[a] See ref. 1b.

crystallized from acetic acid. Being more insoluble, **2a** and **2c** were washed twice with boiling acetic acid, dried, and submitted for analysis. See Table IV for experimental details.

4-Substituted 1,3-Dithiol-2-ylidene Derivatives.—Compounds **4a–g** were prepared by the following general method.[12] Two or three grams of one of the 2-methylthio-4-substituted 1,3-dithiolium perchlorates (**4a**, **b**, **d**, **g**) or hydrogen sulfates (**4c**, **e**, **f**) and an equal weight of the active methylene compound were refluxed in 50 ml. of glacial acetic acid containing 1.5 ml. of pyridine for 15–20 hr. The solvent was then removed under reduced pressure, and the residue was extracted twice with 100-ml. portions of hot benzene. The benzene solution was decolorized with Norit and evaporated, affording the adduct, which was recrystallized from the appropriate solvent.

2-Methylthio-4-(*p*-bromophenyl)-1,3-dithiolium Perchlorate (1a).—Three grams of methyl *p*-bromophenacyl trithiocarbonate and 10 ml. of 70% perchloric acid were heated to 100° for 30 min. Addition of 20 ml. of ethyl acetate to the cooled solution gave 3.25 g. (86%) of yellow solid, which was recrystallized from 70% perchloric acid by the addition of ethyl acetate. The ultraviolet spectrum showed $\lambda_{\max}^{70\%\ \mathrm{HClO_4}}$, m$\mu$ (log ϵ): 375 (4.16); 287 (4.01); 247 (4.29); and 225 (4.11); the n.m.r. spectrum showed $\tau_{\mathrm{CF_3COOH}}$ 1.53, 2.27 d, 2.43 d (J = 9 c.p.s.), and 6.77.

Methyl *p*-Bromophenacyl Trithiocarbonate.—*p*-Bromophenacyl bromide (13.9 g., 0.05 mole), suspended in 150 ml. of ethanol, was added with stirring to a solution of 0.05 mole of sodium methyl trithiocarbonate[16] at −40°. The mixture was allowed to warm to room temperature, stirred an additional 2 hr., and then poured into 1.5 l. of water. The yellow solid was collected (13.8 g., 87%), and a portion was recrystallized from 95% alcohol. It had m.p. 102–104°.

Anal. Calcd. for $C_{10}H_9BrOS_3$: C, 37.38; H, 2.82; S, 29.94. Found: C, 37.37; H, 2.94; S, 29.85.

α-Phenylphenacyl N,N-Dimethyldithiocarbamate.—α-Chloro-α-phenylacetophenone (4.61 g., 0.02 mole) dissolved in 30 ml. of acetone was added dropwise to a mixture of 3.15 g. (0.022 mole) of sodium N,N-dimethyldithiocarbamate in 35 ml. of refluxing alcohol, and reflux was continued for 30 min. The solvent was evaporated and the oily residue was washed with water several times until crystallization occurred, giving 4 g. (64%) of product. Recrystallization from 95% alcohol gave white needles, m.p. 125–127°; $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ 248 mμ (log ϵ 4.41).

Anal. Calcd. for $C_{17}H_{17}NOS_2$: C, 64.72; H, 5.43; S, 20.33. Found: C, 64.53; H, 5.41; S, 20.28.

2-Dimethylamino-4,5-diphenyl-1,3-dithiolium Perchlorate (3).—One gram of α-phenylphenacyl N,N-dimethyldithiocarbamate and 4 ml. of 70% perchloric acid were warmed together for 5 min. or until complete dissolution occurred. Upon addition of 20 ml. of ethyl acetate to the cooled solution, a white solid separated (1.15 g., 91%). Recrystallization from absolute alcohol afforded white needles, m.p. 221–222°; $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ mμ (log ϵ): 320 (3.98); 315 (4.00); 230 (4.29); and 210 (4.35); $\tau_{\mathrm{CF_3COOH}}$ 2.62, 6.33.

2-Methylthio-4-phenyl-1,3-dithiolium Hydrogen Sulfate (7).—Two grams of phenacyl methyltrithiocarbonate[16] and 2 ml. of concentrated sulfuric acid were warmed (50–60°) together for 5 min. Upon cooling and dilution with 20 ml. of ethyl acetate, a yellow solid separated. This material was quite unstable, and could not be isolated in pure form. An n.m.r. spectrum of the material was identical with that of **1b**. If kept dry, **7** could be stored and used for several weeks.

2-Dimethylamino-4-phenyl-1,3-dithiolium Hydrogen Sulfate (8b).—Ten grams of phenacyl N,N-dimethyldithiocarbamate[1b] was warmed with 10 ml. of concentrated sulfuric acid for 5 min. (temperature never exceeding 65°), and then cooled. Ethyl acetate (100 ml.) was added slowly with stirring, and a quantitative yield of white solid which separated was collected, washed with additional ethyl acetate, and dried. Recrystallization of a portion of the material from ethanol, by the addition of ethyl acetate, raised the melting range to 232–234°.

2-Dimethylamino-4-phenyl-1,3-dithiolium Salts.—Compounds **8a** and **8c–f** were prepared by the following general method. One gram of **8b** dissolved in 5 ml. of water was added to a stoichiometric quantity of the anion salt dissolved in 5 ml. of water. An immediate precipitate of the new dithiolium salt occurred. The solid was washed with ethyl acetate, dried, and recrystallized. Warm alcohol (rather than water) was the solvent used for preparation of **8f**. The n.m.r. spectra of **8a–e** in trifluoroacetic acid are identical, and consist of the C-4 phenyl resonance at τ 2.47, the C-5 proton signal at τ 2.63 and the nonequivalent N-methyl protons occurring as two resonance peaks at τ 6.30 and, 6.35. These derivatives are similar in the ultraviolet region, showing four absorption features at 315, 300, 235 and 225 mμ. Differences arise only in the case of the iodide (**8d**), which lacks an absorption feature at 235 mμ, and the picrate (**8f**) which shows no band at 300 mμ. In the infrared region, **8a** shows an intense absorption at 9.0–9.4 μ (ClO_4^-); **8b** shows three intense peaks in the region 8.1–9.5 μ (HSO_4^-); **8c** features a broad peak at 9.0–9.8 μ and a peak at 2.9 μ (BF_4^-); and **8e** is characterized by a strong absorption at 4.9 μ (SCN^-). Additional experimental data are summarized in Table IV.

2,4-Diphenyl-1,3-dithiolium Hydrogen Sulfate (9b).—One gram of phenacyl dithiobenzoate[1b] and 1 ml. of concentrated sulfuric acid were warmed (50–60°) for 5 min. Upon cooling and addition of 20 ml. of ethyl acetate, a yellow solid separated. The solid was collected, washed with ethyl acetate, dried, and recrystallized three times from propanol, and had m.p. 173–175°. The yield was quantitative (Table IV).

2,4-Diphenyl-1,3-dithiolium Picrate (9c).—Five milliliters of alcohol saturated with picric acid was mixed together with a solution of 0.6 g. of **9b** in 5 ml. of warm alcohol. An immediate precipitation occurred. The solid was collected and recrystallized from methanol. The yellow needles melted at 197–199° and weighed 0.8 g. (78%).

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