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Studies on 1,3-Dithiolium Cations. I. A Novel Synthetic Method of 4-*p*-Substituted Phenyl Derivatives and Related Compounds

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A convenient method for the preparation of 4-*p*-substituted phenyl-1,3-dithiolium salts was presented. 4-*p*-Substituted phenacyl N,N-dialkylaminocarbodithioates easily obtained from the reaction of N,N-dialkylamine N,N-dialkylaminocarbodithioates and *p*-substituted phenacylbromides were cyclized to give 2-immonium 1,3-dithiole salts. Reduction of immonium salts was performed by the action of $NaBH_4$ to give 2-amino-1,3-dithiole and the action of acid to this amine gave 1,3-dithiolium salts immediately. The yield of each step was very high and the operation was simple, giving pure 1,3-dithiolium salts. The properties of intermediates and 4-*p*-substituted phenyl-1,3-dithiolium salts were described.

1,3-Dithiolium cation is iso-π-electronic with tropylium ion from which it can be formally derived by replacement of two C=C bonds by two sulfur atoms.[2] Klingsberg[3] and Leaver, *et al.*[4] obtained 1,3-dithiolium salts from isotrithiones by the action with hydrogen peroxide

Table I. Carbodithioates II

Compd. No.	R R'>N-	R"	R'''	mp (°C)	Yield (%)	Formula	Analysis (%) Calcd. C Found C	H H	N N	λ_{max}^{EtOH} mμ (log ε)
1		H	H	124—125	90	$C_{14}H_{17}ONS_2$	60.20 60.14	6.14 6.12	5.02 4.89	248, 281 (4.24, 4.02)
2		H	H	135—136	90	$C_{13}H_{15}O_2NS_2$	55.51 55.59	5.38 5.33	4.98 5.05	251, 282
3	CH_3 $C_6H_5CH_2$ >N-	H	H	81— 82	70	$C_{17}H_{17}ONS_2$	64.75 64.72	5.43 5.30	4.44 4.48	249, 279 (4.39, 4.09)
4		NO_2	H	130—131	89	$C_{14}H_{16}O_3N_2S_2$	51.85 51.70	4.97 4.88	8.64 8.72	268 (4.39)
5		Br	H	128—129	95	$C_{14}H_{16}ONS_2Br$	46.93 46.93	4.51 4.39	3.91 3.61	259 (4.43)
6		CH_3	H	108—109	73	$C_{15}H_{19}ONS_2$	61.42 61.51	6.53 6.58	4.78 4.63	257, 282 (sh) (4.31, 4.07)
7		CH_3O	H	111—113	88	$C_{15}H_{19}O_2NS_2$	58.24 58.42	6.19 6.22	4.53 4.50	219, 279 (4.29, 4.43)
8		OH	H	195—196	83	$C_{14}H_{17}O_2NS_2$	56.94 56.63	5.80 5.81	4.74 4.58	220, 281.5 (3.88, 4.04)
9		Cl	H	99—100	94	$C_{14}H_{16}ONS_2Cl$	53.54 53.68	5.14 5.06	4.64 4.64	245 (4.42)
10		H	C_6H_5	95	94	$C_{20}H_{21}ONS_2$	67.59 67.81	5.96 5.92	3.94 3.80	251, 282 (4.39, 4.10)

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[1] Location: *Fukushima-ku, Osaka.*

[2] H. Prinzbach and E. Futterer, "Advances in Heterocyclic Chemistry," Vol. 7, ed. by A.R. Katritzky and A.J. Boulton, Academic Press, New York and London, 1966, pp. 39—151.

[3] E. Klingsberg, *J. Am. Chem. Soc.*, **84**, 3410 (1962); **86**, 5290 (1964).

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

or peracid. This is in fact the only method by which unsubstituted compounds in 2-position have been prepared. However, the preparation of isotrithione is somewhat troublesome with unsatisfactory yield.[3–9]

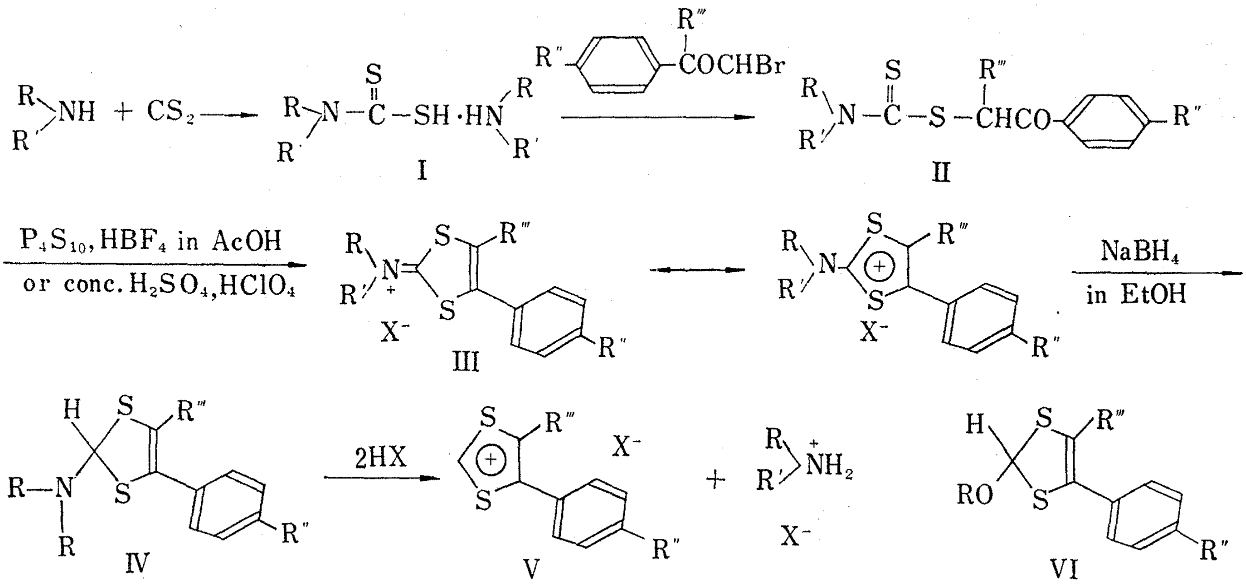
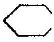
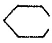


Chart 1

TABLE II. Immonium Salts III

Compd. No.	R R'>N-	R''	R'''	X⁻	mp (°C)	Yield (%)	Formula	Analysis (%) Calcd. C Found C	H H	N N	S S
11	N-	H	H	BF_4	177—178	96	$C_{14}H_{16}NS_2$-BF_4	48.15 48.14	4.62 4.81	4.01 3.88	18.37 18.03
12				HSO_4	215—216	78	$C_{14}H_{17}O_4$-NS_2	46.80 46.65	4.77 4.75	3.91 3.61	26.78 26.54
13	ON-	H	H	BF_4	168—169	94	$C_{13}H_{14}ONS_2$-BF_4	44.99 44.39	4.36 4.51	4.04 3.74	18.48 19.58
14				HSO_4	205—206	96	$C_{13}H_{15}O_5$-$NS_3\cdot 1/2H_2O$	42.20 42.17	4.36 4.13	3.79 3.79	26.00 25.64
15	CH_3 $C_6H_5CH_2$>N-	H	H	BF_4	144—145	93	$C_{17}H_{16}NS_2$-BF_4	53.16 52.40	4.20 4.87	3.65 3.34	16.70 16.50
16	N-	NO_2	H	BF_4	177—180	60	$C_{14}H_{15}O_2N_2$-S_2BF_4	42.67 42.84	3.84 3.94	7.11 6.78	
17				HSO_4	226—229 (decomp.)	73	$C_{14}H_{16}O_6N_2$-$S_3\cdot 1/2H_2O$	40.69 40.40	4.15 3.83	6.80 6.77	23.27 22.34
18	N-	Br	H	BF_4	153—157	77	$C_{14}H_{15}NS_2$-$BrBF_4$	39.28 39.00	3.53 4.26	3.27 3.25	14.98 14.76
19	N-	CH_3	H	HSO_4	216—217	81	$C_{15}H_{19}O_4NS_3$	48.26 48.18	5.13 5.08	3.75 3.58	25.77 25.51
20	N-	CH_3O	H	HSO_4	246 (decomp.)	93	$C_{15}H_{19}O_5NS_3$	46.27 46.26	5.92 4.89	3.50 3.58	24.69 24.57
21	N-	OH	H	HSO_4	245—247 (decomp.)	100	$C_{14}H_{17}O_5NS_3$	44.78 44.74	4.56 4.69	3.74 3.75	25.63 25.41
22	N-	Cl	H	HSO_4	241—242 (decomp.)	98	$C_{14}H_{16}O_3$-NS_3Cl	42.67 42.21	4.09 4.26	3.56 3.59	24.43 24.59
23	N-	H	C_6H_5	ClO_4	249—250 (decomp.)	92	$C_{20}H_{20}O_4$-NS_2Cl	54.84 54.15	4.60 4.62	3.20 3.55	14.64 14.79

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5) R. Mayer and B. Gebhardt, *Chem. Ber.*, **97**, 1298 (1964).
6) L. Soder and R. Wizinger, *Helv. Chim. Acta*, **42**, 1733 (1959).
7) R. Mayer, B. Gebhardt, J. Fabian, and A.K. Miller, *Angew. Chem.*, **76**, 143 (1964).
8) R. Huisgen and V. Weberndrofer, *Experientia*, **17**, 566 (1961).
9) F. Runge, Z. El-Hewehi, H.J. Renner, and E. Taeger, *J. Prakt. Chem.*, **11**, 284 (1960).

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We wish to report a novel and convenient method for the syntheses of 4-*p*-substituted phenyl-1,3-dithiolium salts and relative compounds.

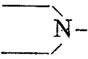
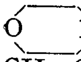
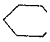
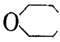
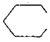
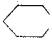
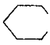
4-*p*-Substituted phenacyl N,N-dialkylaminocarbodithioates (II) were easily obtained from the reactions of N,N-dialkylamine N,N-dialkylaminocarbodithioates ($\begin{smallmatrix}R'\\R\end{smallmatrix}\!>$N-: N-, N-, $\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}\!>$N-,[10] $\begin{smallmatrix}CH_3\\C_6H_5CH_2\end{smallmatrix}\!>$N-) and *p*-substituted phenacyl bromides (R'': H, OH, OCH_3, CH_3, Cl, Br, NO_2; R''': H, C_6H_5) (Table I). II was heated with P_4S_{10} in the presence of HBF_4 in glacial acetic acid to yield N-(4-*p*-substituted phenyl-1,3-dithiole-2-ylidene)-N,N-dialkyl-ammonium fluoroborates (III). Cyclization has also been undergone by treatment with conc. H_2SO_4 or 70% $HClO_4$.[10,11] Table II and III show their properties. Immonium salts III exhibited strong absorption at about 320 mμ in UV spectra and IR spectra showed the strong bands characteristic to anions. The chemical shifts of C-5 protons appeared at higher field (2.3—2.8 τ) than expected from dithiolium ring proton. Therefore, resonance contribution from immonium structure is dominated. *para*-Aryl substituents caused the changes in diamagnetic shielding effects on the

Table III. Spectral Data of Immonium Salts III

Compd. No.	$\begin{smallmatrix}R\\R'\end{smallmatrix}\!>$N-	R''	R'''	X⁻	UV λ_{max}^{EtOH} mμ (log ε)	NMR[a) τ (C-5-H)
11	N-	H	H	BF_4	237, 323 (4.12, 4.08)	2.68
12				HSO_4	322 (4.11)	
13	N-	H	H	BF_4	325 (4.09)	
14				HSO_4	324 (4.09)	
15	$\begin{smallmatrix}CH_3\\C_6H_5CH_2\end{smallmatrix}\!>$N-	H	H	BF_4	322 (4.09)	
16	N-	NO_2	H	BF_4	330 (4.31)	
17				HSO_4	320 (4.23)	2.28
18	N-	Br	H	BF_4	243, 322 (4.20, 4.17)	2.63
19	N-	CH_3	H	HSO_4	225, 326 (4.14, 4.08)	2.75
20	N-	CH_3O	H	HSO_4	261, 292, 333 (4.09, 4.07, 4.00)	2.75
21	N-	OH	H	HSO_4	265, 290, 336 (3.81, 3.81, 3.70)	2.82
22	N-	Cl	H	HSO_4	231, 240, 308, 322 (3.91, 3.91, 3.83, 3.83)	2.63
23	N-	H	C_6H_5	ClO_4	233.5, 320 (4.39, 4.13)	—

a) Spectra were taken in CF_3COOD containing TMS as an internal reference.

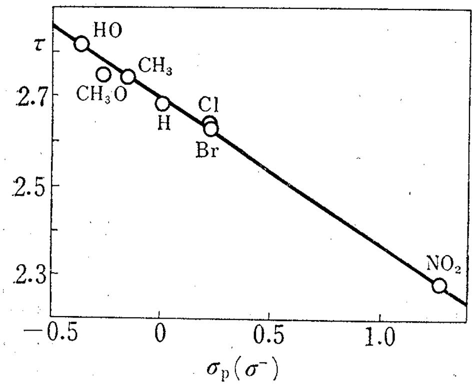


Fig. 1. Correlation of NMR Chemical Shift of C-5-H in III with Hammett's σ_p (σ^- for NO_2) Constant

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10) E. Campaigne, and N.W. Jacobson, *J. Org. Chem.*, **29**, 1703 (1964).
11) E. Campaigne, and R.D. Hamilton, *J. Org. Chem.*, **29**, 1711 (1964).

Table IV. 2-Amino-1,3-dithioles IV

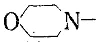
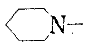
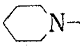
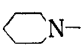
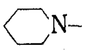
Compd. No.	$\mathrm{R}\atop\mathrm{R'}$>N-	R″	R‴	mp (°C)	Yield (%)	Formula	Analysis (%) Calcd. C Found C	H H	N N	S S
24		H	H	87—88	93	$C_{14}H_{17}S_2N$	63.86 63.78	6.51 6.30	5.32 5.15	24.31 24.15
25		H	H	82—83	93	$C_{13}H_{15}ONS_2$	58.86 59.00	5.70 5.62	5.28 5.29	24.18 24.33
26	$\mathrm{CH_3}\atop\mathrm{C_6H_5CH_2}$>N-	H	H	74—74.5	86	$C_{17}H_{17}NS_2$	68.21 67.65	5.73 5.60	4.68 4.49	21.38 21.32
27	$\mathrm{CH_3}\atop\mathrm{CH_3}$>N-	H	H	67—68	75	$C_{11}H_{13}NS_2$	59.18 58.85	5.87 5.71	6.28 5.81	28.74 28.61
28		NO_2	H	oil	94					
29		Br	H	75—76	87	$C_{14}H_{16}NS_2Br\cdot 1/2H_2O$	48.71 48.32	4.97 4.70	4.06 3.97	18.58 18.31
30		Cl	H	oil	95					
31		CH_3	H	oil	91					
32		CH_3O	H	97—98	95	$C_{15}H_{19}ONS_2$	61.42 61.37	6.53 6.49	4.78 4.68	21.87 22.17
33		OH	H	130—131	81	$C_{14}H_{17}ONS_2$	60.20 59.66	6.14 6.19	5.02 4.83	22.96 22.58
34		H	C_6H_5	110—111	100	$C_{20}H_{21}NS_2$	70.78 70.50	6.24 6.13	4.13 3.83	18.86 18.81

Table V. Spectral Data of 2-Amino-1,3-dithioles V

Compd. No.	$\mathrm{R}\atop\mathrm{R'}$>N-	R″	R‴	UV $\lambda_{\max}^{\mathrm{EtOH}}$ mμ (log ε)	NMR[a) τ (C-5, C-2H)
24		H	H	235, 319 (4.13, 3.89)	3.57, 3.73
25		H	H	317 (3.93)	3.60, 3.80
26	$\mathrm{CH_3}\atop\mathrm{C_6H_5CH_2}$>N-	H	H	234, 318 (4.18, 3.92)	3.53, 3.60
27	$\mathrm{CH_3}\atop\mathrm{CH_3}$>N-	H	H	317	3.58, 3.73
28		NO_2	H	269, 392	3.23, 3.63
29		Br	H	245, 326 (4.19, 4.05)	3.57, 3.72
30		Cl	H	239.5, 324	3.57, 3.72
31		CH_3	H	245, 326 (4.14, 4.08)	3.63, 3.77
32		CH_3O	H	244, 307 (4.11, 4.01)	3.72, 3.77
33		OH	H	242.5, 300 (3.77, 3.71)	3.73, 3.76
34		H	C_6H_5	228.5, 305, 336 (4.20, 3.72, 3.77)	4.03 (C-2-H)

a) Spectra were taken in $CDCl_3$ containing TMS as an internal reference.

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dithiole ring protons, and the electron-withdrawing substituents reduced the shielding effect, while the electron-donating substituents increased the shielding.[10]

Examination of relationship between chemical shifts of C-5 protons of III and Hammett's σ_p values[12] showed that a linear relation is established, as shown in Fig. 1.

Reduction of immonium salts III with $NaBH_4$ in EtOH has smoothly proceeded to yield 2-amino-1,3-dithioles IV in excellent yields. NMR spectra of these compounds showed two singlets due to C-2 and C-5 protons, and the properties were listed in Table IV and V.

To a solution of IV in ethanol, conc. H_2SO_4 or 70% $HClO_4$ was added dropwise to separate the crystals immediately from the solution, and the corresponding 1,3-dithiolium hydrogen sulfates or perchlorates were easily obtained in excellent yields. These salts were stable enough to stand at room temperature.

4-Phenyl-1,3-dithiolium hydrogen sulfate (V: $R''=R'''=H$, $X=HSO_4$) thus obtained was compared with the sample obtained from 4-phenyl-1,3-dithiole-2-thione according to Leaver's method[4] and found to be identical with respect to IR and UV spectra.

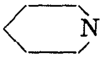
The over-all yield of 4-phenyl-1,3-dithiolium perchlorate from phenacyl piperidinocarbodithioate (II: ${}^{R}_{R'}\!>\!N- =$ , $R''=R'''=H$) is extremely high as to be 80%. Similarly, 4,5-diphenyl-1,3-dithiolium perchlorate (V: $R''=H$, $R'''=C_6H_5$, $X=ClO_4$) was obtained in 83% over-all yield from α-phenylphenacylpiperidinocarbodithioate (II: ${}^{R}_{R'}\!>\!N- =$ , $R''=H$, $R'''=C_6H_5$). The properties of these salts are listed in Table VI and VII. It should be noted that this method for the synthesis of 1,3-dithiolium salts is very convenient because the operation is simple and yield is excellent. NMR spectra of 4-*p*-substituted phenyl-1,3-dithiolium salts V showed two doublets due to C-2 and C-5 protons in 1,3-dithiolium ring. The chemical shifts of C-2 protons appeared at lower field than C-5 protons, showing less electron densities on C-2 positions.[2] Chemical shifts were observed to be effected by polar effects of the substituents, it was also recognized that the electron-donating groups increased the shielding, while the electron-withdrawing substituents reduced the shielding effects, and a more quantitative discussion will be presented in another place.

TABLE VI. 1,3-Dithiolium Perchlorates V

Compd. No.	R''	R'''	X⁻	mp (°C)	Yield[a] (%)	Formula	Analysis (%) Calcd. C Found C	H H	S S
35	H	H	ClO_4	179—180 (decomp.)[b]	94	$C_9H_7O_4S_2Cl$	38.78 38.99	2.53 2.63	23.01 23.39
36	NO_2	H	ClO_4	169 (decomp.)	95	$C_9H_6O_6NS_2Cl\cdot H_2O$	31.64 31.44	2.35 2.16	
37	Br	H	ClO_4	217	90	$C_9H_6O_4S_2BrCl$	30.21 29.93	1.68 1.81	17.93 17.56
38	Cl	H	ClO_4	204	60	$C_9H_6O_4S_2Cl_2$	34.51 34.51	1.92 2.16	20.48 20.52
39	CH_3	H	ClO_4	200—202 (decomp.)	94	$C_{10}H_9O_4S_2Cl$	41.05 41.33	3.10 3.16	21.90 21.92
40	CH_3O	H	ClO_4	193—194	91	$C_{10}H_9O_5S_2Cl$	38.90 39.20	2.94 3.11	20.77 20.32
41	OH	H	ClO_4	204—205	95	$C_9H_7O_5S_2Cl$	36.69 36.92	2.39 2.43	21.77 21.81
42	H	C_6H_5	ClO_4	181	96	$C_{15}H_{11}O_4S_2Cl\cdot$ $1/2H_2O$	49.49 49.15	3.32 3.29	17.62 17.47

a) yield from 2-piperidinol-1,3-dithioles *b*) 161°[4]

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12) L.N. Ferguson, "The Modern Structural Theory of Organic Chemistry," Prentice-Hall, Inc., Englewoods Cliffs, N.J., 1964, p. 415.

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Table VII. Spectral Data of 1,3-Dithiolium Perchlorates V

Compd. No.	R″	R‴	X^-	UV $\lambda_{max}^{50\%\ H_2SO_4}$ mμ (log ε)	NMR[c] (C–5, C–2–H)
35	H	H	ClO_4	241, 265 (sh), 338 (4.23, 3.97, 3.51)[a]	0.80^d, −1.13^d [d]
36	NO_3	H	ClO_4	233 (sh), 254, 285, 323 (sh) (4.04, 4.02, 4.09, 3.93)	0.61^d, −1.27^d
37	Br	H	ClO_4	246.5, 272(sh), 345 (4.25, 4.13, 3.61)	0.80^d, −1.14^d
38	Cl	H	ClO_4	245, 270(sh), 343.5 (4.27, 4.08, 3.60)	0.80^d, −1.14^d
39	CH_3	H	ClO_4	245, 270, 357 (4.19, 4.09, 3.53)	0.84^d, −1.12^d
40	CH_3O	H	ClO_4	247, 283, 377 (4.03, 4.08, 3.47)[b]	0.95^d, −1.02^d [e]
41	OH	H	ClO_4	245, 281.5, 376 (4.08, 4.12, 3.50)	0.98^d, −1.02^d
42	H	C_6H_5	ClO_4	238.5, 349 (4.26, 3.44)	−1.17^s (C-2-H)

a) $\lambda_{max}^{CF_3COOH}$ 347 mμ (ε 2250)[2]

b) $\lambda_{max}^{CF_3COOH}$ 286, 388 mμ (ε 12,600, 2600)[2]

c) Spectra were taken in CD_3CN containing TMS as an internal reference. d expresses doublet and coupling constants are about 2 cps.

d) 0.75^d, −1.31^d (hydrogen sulfate in CF_3COOH)[2]

e) 0.87^d, −1.19^d (hydrogen sulfate in CF_3COOH)[2]

UV spectra measurements were carried out in 50% H_2SO_4 solution and found to be quite different in the measurement in EtOH solutions. Therefore, it was found that UV spectra taken in EtOH[4] were not the spectra of 1,3-dithiolium ions but those of covalent 2-alkoxy-1,3-dithioles VI formed by the nucleophilic attack of alcohol to C–2 position.

Experimental

All melting points were determined in capillary tube and are uncorrected. NMR spectra were taken on a Varian A–60 spectrometer in $CDCl_3$, CF_3COOD, or CD_3CN containing TMS as an internal reference and chemical shifts are presented in a τ value. UV spectra were taken on a Hitachi EPS–3 spectrophotometer in 95% EtOH.

General Procedure for the Preparation of 4-*p*-Substituted Phenacyl N,N-Dialkylaminocarbodithioate (II)——The mixture of phenacyl bromides (0.02 mole), N,N-dialkylamine N,N-dialkylaminocarbodithioates (0.022 mole) (prepared from amine and CS_2), and 50 ml of EtOH was refluxed for 2 hr. After cooling, separated crystals were collected, and recrystallized from EtOH (Table I).

General Procedure for the Preparation of N-(4-*p*-Substituted Phenyl-1,3-dithiole-2-ylidene)-N,N-dialkylammonium Salts (III)——Method A: A mixture of *p*-substituted phenacyl N,N-dialkylaminocarbodithioates (0.01 mole), hydrofluoroboric acid (42%) (2 ml), P_4S_{10} (1.3 g), and glacial AcOH (30 ml) was refluxed for 20 hr. Evaporation of the solvent and addition of EtOH to the residue gave crystals of III as fluoroborate. Recrystallization from acetone gave pale pink prisms (Table II, III).

Method B: 70% perchloric acid (20 ml) was added to *p*-substituted phenacyl N,N-dialkylaminocarbodithioates (0.01 mole) and the mixture was gently heated on the steam bath until solution had occurrerd. The product obtained on chilling the solution was recrystallized from EtOH[10] (Table II, III).

Method C: Conc. H_2SO_4 (5 ml) was added to *p*-substituted phenacyl N,N-dialkylaminocarbodithioates (0.015 mole) and warmed for 5 min and then cooled. AcOEt was added, separated colorless crystals were collected, and washed with EtOH. Recrystallization from MeOH–EtOH gave colorless crystals[11] (Table II, III).

General Procedure for the Preparation of 2-Dialkylamino-4-*p*-substituted Phenyl-1,3-dithioles (IV)——To a suspension of N-(4-phenyl-1,3-dithiole-2-ylidene)piperidinium fluoroborate (1.0 g) in 10 ml of EtOH, 0.3 g of $NaBH_4$ was added and stirred for 2 hr at room temperature. Evaporation of the solvent and addition of H_2O to the residue gave colorless needles of 2-piperidino-4-phenyl-1,3-dithiole. Recrystallization from dil. EtOH gave colorless needles (Table IV, V).

General Procedure for the Preparation of 4-*p*-Substituted Phenyl 1,3-Dithiolium Salts——a) To a suspension of 2-piperidino-4-phenyl-1,3-dithiole (0.5 g) in 30 ml of EtOH, 70% $HClO_4$ was added dropwise to separate pale pink crystals. Collection, washing with a small amount of EtOH–$HClO_4$ and AcOEt gave 4-phenyl-1,3-dithiolium perchlorate (0.5 g). Recrystallization from AcOH–$HClO_4$ gave colorless prisms of mp 179—180° (decomp.) (Table VI, VII).

b) To a suspension of 2.6 g of 2-piperidino-4-phenyl-1,3-dithiole in 35 ml of EtOH, conc. H_2SO_4 was added dropwise to separate crystals. The crystals were collected and washed with EtOH and AcOEt to

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give 2.4 g of pale pink needles. IR and UV spectra were identical with those of authentic sample prepared by Leaver's method.[4]

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