vs, 1624 m, 1600 w, 1587 w, and 1497 cm.$^{-1}$ m. 2-Carbethoxyacetamidoxime hydrochloride[17] had bands at 3377 s, 3138 sh, 2976 vs, 2825 vs, 1749 vs, 1696 vs, 1630 m, and 1545 cm.$^{-1}$ w.

The n.m.r. spectra were determined on a Varian A-60 spectrometer using tetramethylsilane as an internal reference for the chemical shifts which are reported.

Acknowledgment.—The authors acknowledge the support for this work by a grant (CY-4661) from the Cancer Institute of the National Institutes of Health, U. S. Health Service. They would also like to thank Miss Maria Petropoulou for technical assistance.

Dithiolium Derivatives. IV.[1-3] Reaction of Secondary Amines with Substituted 3-Methylthio-1,2- and 2-Methylthio-1,3-dithiolium Perchlorates

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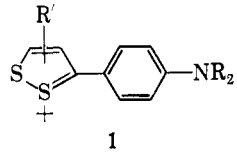
The pseudo-aromatic 3-methylthio-1,2- and 2-methylthio-1,3-dithiolium cationoid systems undergo a facile reaction with secondary amines; aliphatic amines and arylalkylamines yield N,N-disubstituted aminodithiolium derivatives, whereas diphenylamine affords *p*-phenylaminophenyldithiolium adducts. The structures of these products were assigned on the basis of n.m.r. spectra, and by unequivocal syntheses in the cases of methylaniline and diphenylamine. A series of 35 new aminodithiolium derivatives, including a dianion derived from piperazine, are described.

The similarity of electrophilic properties of substituted 1,2- and 1,3-dithiolium cationoid systems has been discussed recently by several investigators. Thus, tertiary aromatic amines such as dimethylaniline can undergo reaction with substituted 1,2-dithiolium salts,[5a] and with 2-methylthio-5-substituted benzo-,[6] 2-methylthio-4-substituted,[1a] and unsubstituted[5b] 1,3-dithiolium salts. The products of these reactions are the highly conjugated and intensely colored N,N-disubstituted *p*-aminophenyl-1,2- and 1,3-dithiolium derivatives, *e.g.*, **1** and **2**. A further common reaction of



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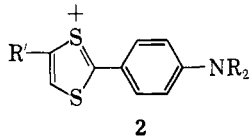

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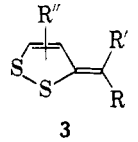

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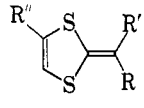

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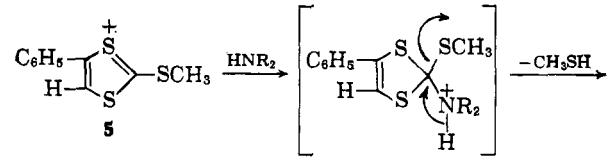
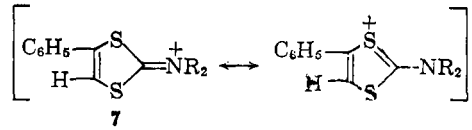
these two systems is condensation with active methylene compounds to yield substituted 1,2-dithiol-3-ylidene (**3**),[7] 1,3-dithiol-2-ylidene (**4**),[1a] and dithiafulvalene[8] derivatives.

That the reactivity of the 1,2- and 1,3-dithiolium systems parallel one another has been further demonstrated in these laboratories. Investigations into the nature of reactivity of 2-methylthio-4-phenyl-1,3-dithiolium perchlorate (**5**) have shown that, when **5** is suspended in tetrahydrofuran (THF) at room temperature in the presence of an aliphatic secondary amine, a good yield of the corresponding 2-dialkylamino-4-phenyl-1,3-dithiolium perchlorate (**7**) is obtained. In view of the susceptibility of the 1,3-dithiolium cation to nucleophilic attack at the C-2 atom, the course of the reaction can be depicted formally as an attack of the secondary amine at C-2 to afford **6**, which can then spontaneously expel methyl mercaptan to form the more stable dialkylamino dithiolium system. In



5 **6**



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analogy to the 1,3-dithiolium series, 3-methylthio-5-phenyl-1,2-dithiolium perchlorate also undergoes reaction with secondary amines to afford the hitherto unknown N,N-disubstituted 3-amino-5-phenyl-1,2-dithiolium perchlorates (**10**).

In intermediate **9**, two competing 1,2-elimination possibilities exist. Pathway 1 involves rupture of the exocyclic C–S bond to eliminate methyl mercaptan and generate the stable dithiolium system **10** whereas, in pathway 2, the endocyclic C–S bond is broken to afford **11**, a species which can undergo further decomposition.[9] Intermediate species similar to **9** and **11** have been postulated by Klingsberg for the reaction of substituted

(1) Previous papers in this series: (a) E. Campaigne and R. D. Hamilton, *J. Org. Chem.*, **29**, 1711 (1964); (b) E. Campaigne, R. D. Hamilton, and N. W. Jacobsen, *ibid.*, **29**, 1708 (1964); (c) E. Campaigne and N. W. Jacobsen, *ibid.*, **29**, 1703 (1964).

(2) A portion of this material was presented before the Division of Organic Chemistry, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April, 1964, Abstracts, p. 28N.

(3) The support of this research by a grant from the Petroleum Research Fund, administered by the American Chemical Society, to Indiana University, and a grant from Mead Johnson and Co., Evansville, Ind., is hereby gratefully acknowledged.

(4) Abstracted in part from the forthcoming Ph.D. Thesis of R. D. H.

(5) (a) E. Klingsberg and A. M. Schreiber, *J. Am. Chem. Soc.*, **84**, 2941 (1962); (b) E. Klingsberg, *ibid.*, **84**, 3410 (1962).

(6) (a) L. Soder and R. Wizinger, *Helv. Chim. Acta*, **42**, 1733 (1959); (b) L. Soder and R. Wizinger, *ibid.*, **42**, 1779 (1959); (c) R. Wizinger and D. Dürr, *ibid.*, **46**, 2167 (1963).

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

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

(9) Attack at the C-5 atom in **8**, a possibility raised by a referee, would similarly lead to ring opening and decomposition, but would seem to be less likely owing to a lesser degree of stabilization of the carbonium ion at this position.

TABLE I

1,2- AND 1,3-DITHIOLIUM PERCHLORATES DERIVED FROM SECONDARY AMINES

Starting material	Amine	% Yield	M.p., °C.	Formula	Calcd., % C	Calcd., % H	Calcd., % S	Found, % C	Found, % H	Found, % S	N.m.r.,[a] τ-units (number of protons); coupling constant (J), c.p.s.
5	Dimethylamine	76	178–179[b]	...		.....			.....		2.47 (5), 2.63 (1), 6.30 (3), 6.35 (3)
	Diethylamine	56	175–177[b]	...		.....			.....		2.47 (5), 2.63 (1), 6.00 q (2), 6.05 q (2) (J = 8), 8.42 t (3), 8.43 t (3) (J = 8)
	Dipropylamine	57	184–185	$C_{15}H_{20}ClNO_4S_2$	47.67	5.33	16.97	47.75	5.28	17.18	2.47 (5), 2.62 (1), 6.10 t (2), 6.13 t (2), (J = 8), 7.58–8.33 m (4), 8.87 t (6) (J = 7)
	Dibutylamine	50	109–110	$C_{17}H_{24}ClNO_4S_2$	50.29	5.96	15.80	50.43	6.11	16.08	2.47 (5), 2.63 (1), 5.90–6.27 m (4), 7.83–8.75 m (8), 8.92 t (6) (J = 6)
	Piperidine	78	167–169	$C_{14}H_{16}ClNO_4S_2$	46.46	4.46	17.72	46.43	4.50	17.68	2.48 (5), 2.70 (1), 6.07 b (4), 8.05 b (6)
	Morpholine	81	198–200	$C_{13}H_{14}ClNO_5S_2$	42.91	3.88	17.63	43.11	3.97	17.83	2.47 (5), 2.60 (1), 5.58–6.08 m (8)
	Pyrrolidine	47	168–169	$C_{13}H_{14}ClNO_4S_2$	44.89	4.06	18.44	45.21	4.09	18.47	2.48 (5), 2.67 (1), 5.92–6.42 m (4), 7.42–7.77 m (4)
	2,5-Dimethylpyrrolidine	69	151–153	$C_{15}H_{18}ClNO_4S_2$	47.93	4.83	17.06	48.10	4.92	17.19	2.48 (5), 2.65 (1), 5.55–5.98 m (2), 7.30–8.05 m (4), 8.39, 8.42 (3), 8.50, 8.53 (3)
	Hexamethyleneimine	74	121–123	$C_{15}H_{18}ClNO_4S_2$	47.93	4.83	17.06	48.17	4.88	17.13	2.48 (5), 2.58 (1), 5.88–6.23 m (4), 7.62–8.38 m (8)
	Ethylcylohexylamine	40	190–191	$C_{17}H_{22}ClNO_4S_2$	50.54	5.49	15.88	50.54	5.46	16.06	2.47 (5), 2.62 (1), 6.03 q (2) (J = 7), 7.70–8.63 m (10), 8.45 t (3) (J = 7)
	Cyanoethylcyclohexylamine	42	199–200	$C_{18}H_{21}ClN_2O_4S_2$	50.40	4.93	14.95	50.66	5.20	15.25	2.47 (5), 2.53 (1), 5.67 t (2), 6.77 t (2) (J = 7), 7.63–8.67 m (10)
	Methylaniline	59	214–215	$C_{16}H_{14}ClNO_4S_2$	50.06	3.68	16.71	49.84	3.90	16.67	2.15–2.75 m (11), 6.00, 6.05 (3)
	Diphenylamine	57	247–248	$C_{21}H_{16}ClNO_4S_2$	56.56	3.62	...	56.34	3.60	...	.....
	Piperazine	90	320 dec.[c]	$C_{22}H_{20}Cl_2N_2O_8S_4$	41.31	3.15	20.05	41.58	3.57	19.62[d]	.....
8	Diethylamine	47	173–174	$C_{16}H_{16}ClNO_4S_2$	44.63	4.61	18.33	44.52	4.51	18.15	2.08–2.55 m (5), 2.50 (1), 5.78–6.33 m (4), 8.47 t (3), 8.50 t (3) (J = 7)
	Piperidine	52	200–201	$C_{14}H_{16}ClNO_4S_2$	46.46	4.46	17.72	46.26	4.55	17.86	2.10–2.50 m (5), 5.82–6.23 m (4), 8.05 b (6)
	Morpholine	54	190–191	$C_{13}H_{14}ClNO_5S_2$	42.91	3.88	17.63	42.80	3.94	17.70	2.08–2.52 m (6), 5.80 b (8)
	2,5-Dimethylpyrrolidine	52	155–156	$C_{15}H_{18}ClNO_4S_2$	47.93	4.83	17.06	47.96	4.86	17.14	2.08–2.50 m (5), 2.55 (1), 5.25–6.00 m (2), 7.33–8.00 m (4), 8.35 (3), 8.45 (3)
	Methylaniline	65	210–211	$C_{16}H_{14}ClNO_4S_2$	50.06	3.68	16.71	50.08	3.79	16.74	2.07–2.58 (11), 6.07 (3)
	Ethylaniline	51	142–143	$C_{17}H_{16}ClNO_4S_2$	51.31	3.55	16.12	51.21	3.97	16.06	2.07–2.60 m (11), 5.65 q (2) (J = 7), 8.47 (3)
17a	Dimethylamine	62	232–233	$C_9H_{10}ClNO_4S_2$	36.54	3.41	21.68	36.50	3.40	21.96	2.00–2.48 m (4), 6.28 (6)
	Diethylamine	75	162–163	$C_{11}H_{14}ClNO_4S_2$	40.80	4.36	19.80	40.84	4.38	20.09	2.00–2.47 m (4), 5.97 q (4) (J = 8), 8.38 t (6) (J = 8)
	Dipropylamine	65	135–137	$C_{13}H_{18}ClNO_4S_2$	44.37	5.16	18.22	44.56	5.17	18.32	2.00–2.48 m (4), 6.08 q (4) (J = 8), 7.62–8.32 m (4), 8.70 (6) (J = 7)
	Piperidine	78	177–178	$C_{12}H_{14}ClNO_4S_2$	42.91	4.20	19.10	43.14	4.38	19.09	2.03–2.48 m (4), 5.83–6.10 m (4), 8.00 b (6)
	Morpholine	87	225–226	$C_{11}H_{12}ClNO_5S_2$	39.11	3.58	18.98	38.90	3.61	19.13	1.97–2.42 (4), 5.57–5.97 m (8)
	2,5-Dimethylpyrrolidine	71	183–184	$C_{15}H_{16}ClNO_4S_2$	44.63	4.61	18.33	44.73	4.79	18.41	1.98–2.52 m (4), 5.43–5.82 m (2), 7.45–8.05 m (4), 8.33 (3), 8.45 (3)
	Methylaniline	72	193–194	$C_{14}H_{12}ClNO_4S_2$	46.99	3.38	17.92	47.02	3.52	17.97	2.00–2.50 m (9), 5.97 (3)
	Ethylaniline	64	184–185	$C_{15}H_{14}ClNO_4S_2$	48.44	3.79	17.24	48.69	3.86	17.30	2.00–2.60 m (9), 5.65 q (2) (J = 8), 8.47 t (3) (J = 8)
	Diphenylamine	43	242–243	$C_{19}H_{14}ClNO_4S_2$	54.34	3.36	15.27	54.19	3.45	15.23	.....

17b	Dimethylamine	81	179–180	$C_{10}H_{12}ClNO_4S_2$	38.77	3.91	20.70	38.95	3.95	20.43	2.12–2.63 (3), 6.27 (6), 7.47 (3)
	Diethylamine	56	106–108	$C_{12}H_{16}ClNO_4S_2$	42.66	4.78	18.98	42.82	4.99	19.34	2.12–2.63 m (3), 5.95 q (4) (J = 7), 7.47 (3), 6.75 t (6) (J = 7)
	Dipropylamine	64	147–148	$C_{14}H_{20}ClNO_4S_2$	45.95	5.51	17.53	45.96	5.69	17.78	2.12–2.63 m (3), 6.03 t (4) (J = 7), 7.48 (3), 7.60–8.27 m (4), 8.85 t (6) (J = 7)
	Dibutylamine	53	110–111	$C_{16}H_{24}ClNO_4S_2$	48.78	6.14	16.28	48.77	6.19	16.20	2.12–2.63 m (3), 6.02 t (4) (J = 7), 7.47 (3), 7.72–8.65 m (8), 8.90 t (6) (J = 6)
	Piperidine	80	218–219	$C_{13}H_{16}ClNO_4S_2$	44.63	4.61	18.33	44.58	4.88	18.35	2.15–2.63 m (3), 5.97 b (4), 7.48 (3), 8.02 b (6)
	Morpholine	76	235–237	$C_{12}H_{14}ClNO_5S_2$	40.96	4.01	18.23	41.07	4.03	18.33	2.12–2.63 m (3), 5.53–6.00 m (8), 7.47 (3)
	Methylaniline	61	157–159	$C_{15}H_{14}ClNO_4S_2$	48.45	3.80	17.25	48.58	3.87	17.47	2.20–2.53 m (8), 6.00 (3), 7.48, 7.52 (3)
	Diphenylamine	44	244–245	$C_{20}H_{16}ClNO_4S_2$	55.36	3.72	14.78	55.26	3.77	14.77	.....

[a] All n.m.r. measurements were made in trifluoroacetic acid at concentrations between 6–10% w./v. at approximately 31°, 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 TMS reference. Spin–spin coupling values (J) are in c.p.s. measured on the 500-c.p.s. scale. Unless otherwise indicated, values refer to singlet absorptions; for multiplet signals the following abbreviations are used: d = doublet, t = triplet, q = quartet, m = multiplet, b = broad signal centered at the τ-value cited. Data are presented as τ-units (number of protons). [b] E. Campaigne and N. W. Jacobsen [*J. Org. Chem.*, **29**, 1703 (1964)] give m.p. 178–179° for the dimethyl derivative and 176–178° for the diethyl derivative. [c] Recrystallized from large quantities of methanol. [d] *Anal.* Calcd. for Cl: 11.09. Found: 11.41.

hydrazines with the 4-phenyl-1,2-dithiolium cation, but, in this case, the species analogous to **11** was capable of recyclization, ultimately leading to substituted pyrazoles.[10] In view of the greater nucleophilicity of sulfur

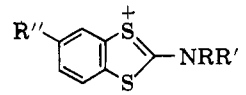
compared to nitrogen, the elimination of methyl mercaptan rather than amine in a reversible process from **6** and **9** may not have been expected *a priori*, although analogous examples are known in the pyrimidine series.[11] The driving force for mercaptan expulsion is ascribed to the greater stability of the N,N-disubstituted aminodithiolium adducts (**7** and **10**) compared to the methylthiodithiolium substrates (**5** and **8**). A reaction path analogous to 2 can be envisioned for the 1,3-system as well; scission of the endocyclic C–S bond in **6** would similarly lead to decomposition products. Experimentally, it appears that path 2 is more important in the 1,2-series than in the 1,3-series. Thus, in general the products are formed in lower yields in the 1,2-series. Moreover, instant development of a dark red-brown color accompanied the addition of amine to the suspension of the 1,2-substrate in THF; this color change, which presumably represents formation of decomposition products, does not occur appreciably in the 1,3-series. In no case was a decomposition product isolated. These reactions were carried out in the presence of a 10% excess of secondary amine in order to ensure complete reaction of the substrate, and were complete after 1 hr. at room temperature.

Although THF proved to be an excellent solvent for reaction of **5** with aliphatic secondary amines, it was undesirable in the cases of the less basic arylalkyl- and diarylamines such as methylaniline and diphenylamine. However, both these reactions could be carried out in the more polar solvent, dimethylformamide (DMF); thus, in DMF the methylaniline adduct was obtained in 59% yield at room temperature after 30 min., and the diphenylamine adduct was obtained in 57% yield after 30 min. at 100°.

Spectral data indicated that the methylaniline adduct was the nonconjugated isomer (**14a**) rather than the *p*-substituted product (**15a**). Cyclization of phenacyl N-methyl-N-phenyldithiocarbamate (**13a**) gave **14a**, identical in every respect with the methylaniline adduct of **5**. That the methyl group occurs as two peaks in the n.m.r. can be rationalized on the basis of the presence of two isomers, since hindered rotation about the C–N bond in the immonium resonance form[1c] would hold the methyl group in different electronic environments (*cis* to SCC_6H_5 and *cis* to SCH) in each of the isomers. Confirmation of this point comes from a comparison of the n.m.r. spectrum of N-methyl-N-phenyl-

(10) E. Klingsberg, *J. Am. Chem. Soc.* **83**, 2934 (1961).

(11) D. J. Brown, "The Pyrimidines," John Wiley and Sons, Inc., New York, 1962, pp. 308, 309.



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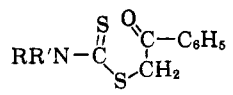
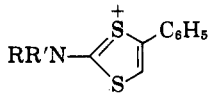
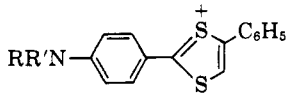


13a, R = CH_3; R′ = C_6H_5
b, R = R′ = C_6H_5



14a, R = CH_3; R′ = C_6H_5
b, R = R′ = C_6H_5



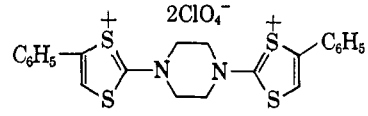
15a, R = CH_3; R′ = H
b, R = C_6H_5; R′ = H
c, R = R′ = CH_3

2-aminobenzo-1,3-dithiolium perchlorate (**12**, R = CH_3; R′ = C_6H_5; R″ = H), in which only one compound is possible; as expected, the methyl protons occur as a single peak at τ 5.97.

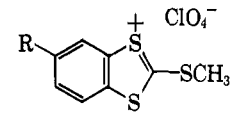
In view of the n.m.r. spectral results, the question arises as to whether these compounds are truly dithiolium salts. Similar compounds have been regarded both as dithiolium derivatives, *e.g.*, 3,5-diamino-4-phenyl-1,2-dithiolium iodide,[12] and as iminium derivatives, *e.g.*, 2-imino-5-methylbenzo-1,3-dithiole hydrochloride.[13] Throughout this work compounds of the type **7** and **10** have been named as amino dithiolium salts rather than as N-substituted ternary iminium salts,[14] although n.m.r. chemical shift data of the C-5 protons indicate that the latter is the predominant resonance form.[1] The dithiolium nomenclature is preferable since it relates these compounds to their precursors and to other similar compounds which are known to be 1,3-dithiolium systems, *e.g.*, 2,4-diphenyl-1,3-dithiolium salts.[1c]

The diphenylamine adduct of **5**, green crystals, m.p. 247–248°, was assigned structure **15b** on the basis of infrared and ultraviolet spectra. The infrared region is very similar to that of 2-(*p*-dimethylaminophenyl)-4-phenyl-1,3-dithiolium perchlorate (**15c**)[1a]; in particular, each spectrum exhibits strong absorption features in the regions 1190–1210, 1310–1340, 1370–1390, and 1590–1600 cm.$^{-1}$. In **15b**, a very weak absorption peak occurs at 3320 cm.$^{-1}$ which is ascribed to N–H stretching. These compounds are also similar in the ultraviolet region, the *p*-dimethylaminophenyl derivative absorbing at 538 and **15b** absorbing at 525 mμ in glacial acetic acid. Attempts to obtain n.m.r. data for **15b** in both trifluoroacetic acid and 70% perchloric acid failed owing to insolubility of the material in these media. 2-Diphenylamino-4-phenyl-1,3-dithiolium perchlorate (**14b**), colorless needles, m.p. 277–278°, was prepared by cyclodehydration of phenacyl N,N-diphenyldithiocarbamate (**13b**). The infrared region of **14b** did not show the four strong absorptions present in **15b**, but did exhibit a strong absorption in the region, 1440–1460 cm.$^{-1}$. Two features were present in the ultraviolet region at 238 and 343 mμ (95% alcohol). Moreover, **14b** was readily soluble in trifluoroacetic acid. Attack at the *para* position of diphenylamine by the dithiolium electrophile can be attributed to steric hindrance as well as to a low degree of basicity of the nitrogen atom.

In this study, new dithiolium perchlorates were prepared from a representative number of secondary amines, listed in Table I.[14a] An interesting compound is the piperazine adduct (**16**), m.p. 320° dec., obtained in 90% yield, which represents the first example of two positively charged dithiolium nuclei in the same molecule. The extreme insolubility of **16** made spectral studies impossible. The structure of this compound was assigned on the basis of analytical data, and by analogy to other secondary amine adducts of **5**.



16



17a, R = H
b, R = CH_3

Compounds of type **7** have been previously prepared in these laboratories[1c] by cyclization of phenacyl N,N-dialkyldithiocarbamates in 70% perchloric acid. However, the dithiocarbamate synthetic route is not applicable to the benzo-1,3-dithiolium system, and hence reaction of 2-methylthiosubstituted benzo-1,3-dithiolium perchlorates (**17**) with secondary amines represents a new and convenient synthesis of compounds of type **12**.

Experimental[15]

Reaction of 3-Methylthio-1,2- and 2-Methylthio-1,3-dithiolium Perchlorates with Aliphatic Secondary Amines.—The following general procedure was employed in the preparation of the N,N-disubstituted amino-1,2- and 1,3-dithiolium perchlorates. One gram of the dithiolium precursor (**5**, **8**, or **17**) and a 10% excess of the appropriate secondary amine were stirred together in 20 ml. of THF at room temperature for 1 hr. Two-thirds of the solvent was removed by a stream of air, and the solid which separated was collected, washed with a small quantity of ethyl acetate, dried and recrystallized (Norit, if necessary) once or twice from 95% ethanol. In some cases, it was necessary to remove all of the solvent and triturate with cold ethyl acetate. In the 1,2-series, instant development of a red-brown color accompanied the addition of the amine to the suspension of dithiolium salt in THF. Additional experimental details are contained in Table I.

Reaction of 3-Methylthio-1,2- and 2-Methylthio-1,3-dithiolium Perchlorates with Arylalkylamines and Diphenylamine.—The procedure used with arylalkylamines such as methylaniline was as follows. To 1 g. of the methylthiodithiolium perchlorate (**5**, **8**, or **17**) suspended in 1–2 ml. of DMF was added a 10% excess of the amine. After standing 30 min. at room temperature, the solution was chilled and diluted with *ca.* 15 ml. of ethyl acetate. The pink solid which separated was collected, washed with ethyl acetate, dried, and recrystallized (Norit) from 95% ethanol or acetic acid. Further experimental details are summarized in Table I.

The general procedure employed with diphenylamine was the following. To 1 g. of the methylthiodithiolium perchlorate (**5**, **8**, or **17**) suspended in 1–2 ml. of DMF was added a 10% excess of diphenylamine dissolved in 2 ml. of DMF. Upon standing at 100° (steam bath) for 15–30 min., the solution developed a deep purple color. Chilling of the solution followed by dilution with *ca.* 15 ml. of ethyl acetate gave a deep green precipitate, which was collected, washed first with ethyl acetate and then with hot acetic acid, dried, and submitted for analysis. Further results are tabulated in Table I.

(12) U. Schmidt, *Chem. Ber.*, **92**, 1171 (1959).
(13) R. W. Addor, *J. Org. Chem.*, **29**, 738 (1964).
(14) N. J. Leonard and J. V. Paukstelis, *ibid.*, **28**, 3021 (1963).

(14a) NOTE ADDED IN PROOF.—Since completion of this paper, similar compounds have been reported by R. Mayer and B. Gebhardt, *Ber.*, **97**, 1298 (1964).

(15) All melting points were determined in soft-glass capillaries using a Mel-Temp heated block apparatus and are corrected. In some cases the compounds charred and/or discolored before melting. Analyses were performed by the Midwest Microlab, Inc., Indianapolis, Ind. All ultraviolet measurements were made with the Cary 14 spectrophotometer in the solvents indicated, and are presented as mμ (log ϵ). Infrared spectra were recorded by a Perkin-Elmer Model 137 Infracord in potassium bromide mulls.

2-Methylthio-5-methylbenzo-1,3-dithiolium Perchlorate (17b).—Six grams of toluene-3,4-dithiol (Eastern Chemical Corp., Newark, N. J.) was dissolved in 15 ml. of methyl chlorothioformate,[16] and 6 ml. of 70% perchloric acid was added dropwise (caution!)[1c] to the rapidly stirring solution. After *ca.* 3 ml. of the acid had been added, evolution of hydrogen chloride was observed, and a strong exothermic reaction ensued. After stirring an additional 15 min., the cooled solution was diluted with 100 ml. of ethyl acetate. The yellow solid which separated was collected and washed with additional ethyl acetate; purification of a portion of the material was effected by precipitation from 70% perchloric acid by the addition of ethyl acetate. The yellow plates, obtained in 33% yield, had m.p. 149–151° (lit.[6a] m.p. 140–142°); τ_{CF_3COOH} 1.78–2.42 m (3), 6.72 (3), 7.35 (3).[17]

Anal. Calcd. for $C_9H_9ClO_4S_3$: C, 34.55; H, 2.90; S, 30.75. Found: C, 34.79; H, 3.02; S, 30.62.

An attempt was made to prepare 2-methylthiobenzo-1,3-dithiolium perchlorate (**17a**) in the preceeding manner. However, insolubility of the reagents gave rise to a heterogeneous mixture, and no reaction occurred upon addition of the acid. A homogenous solution resulted when ethyl acetate was added, and subsequent heating of the mixture at 100° caused a copious evolution of hydrogen chloride. After 1 hr., the solution was cooled and diluted with additional ethyl acetate. A red solid, m.p. 130–140°, obtained in 37% yield, had an infrared spectrum nearly identical with pure **17a**; however, due to the low yield and impurity of product by this procedure, the method of Wizinger and Dürr[6c] was employed. In this manner, **17a** was obtained in an over-all 94% yield starting from benzene-1,2-dithiol.[16]

Phenacyl N-Methyl-N-phenyldithiocarbamate (13a).—The method outlined by Seman[18] was used. In a 300-ml., round-bottom, three-necked flask equipped with reflux condenser, dropping funnel, and magnetic stirrer was suspensed 2.5 g. of 90% practical grade sodium amide in 50 ml. of benzene. Methylaniline (6.3 g., 0.059 mole) in 50 ml. of benzene was added and the mixture was stirred overnight at room temperature. Carbon disulfide (5.4 g., an excess) in 50 ml. of benzene was added, and finally 8.3 g. (0.054 mole) of phenacyl chloride in 50 ml. of benzene was dropped slowly into the stirring mixture. After 15 min., the mixture was refluxed gently for 1 hr., cooled, and poured into 500 ml. of water. The organic layer was separated, washed with water, dried ($MgSO_4$), and evaporated to yield 13.4 g. (83%) of product, which, after recrystallization from 95% ethanol, melted at 157–158°.

Anal. Calcd. for $C_{16}H_{15}NOS_2$: C, 63.75; H, 5.0; S, 21.28. Found: C, 63.84; H, 5.10; S, 21.36.

Phenacyl N,N-Diphenyldithiocarbamate (13b).—**13b** was prepared in the same manner. Thus, 10 g. of diphenylamine yielded 15.5 g. (79%) of product, m.p. 166–167° (95% ethanol).

Anal. Calcd. for $C_{21}H_{17}NOS_2$: C, 69.39; H, 4.72; S, 17.64. Found: C, 69.79; H, 4.93; S, 17.71.

N-Methyl-N-phenyl-2-amino-4-phenyl-1,3-dithiolium Perchlorate (14a).—One gram of **13a** was warmed at 100° in 2 ml. of 70% perchloric acid for 5 min. The solution was then cooled and diluted with *ca.* 200 ml. of ethyl acetate; the colorless solid which separated was collected, dried, and recrystallized from glacial acetic acid. The product, 1.05 g. (83%), melted at 214–215°. A mixture melting point of this material with the methylaniline adduct of **5** was undepressed, and the spectral properties of these compounds were identical: τ_{CF_3COOH} 2.15–2.75 m (11), 6.00, 6.05 (3)[17]; $\lambda_{max}^{95\%\ EtOH}$ 234 mμ (log ε 4.13), 330 (4.03).

2-Diphenylamino-4-phenyl-1,3-dithiolium Perchlorate (14b).—The β-keto dithiocarbamate **13b** (0.6 g.) was warmed at 100° with 5 ml. of 70% perchloric acid for 20 min. The solution was cooled and diluted with ethyl acetate, giving a gray-blue solid (0.64 g., 87%). Recrystallization (Norit) twice from 95% alcohol gave colorless needles: m.p. 277–278°; τ_{CF_3COOH} 2.30 (10), 2.53 (5), 2.63 (1)[17]; $\lambda_{max}^{95\%\ EtOH}$ 238 mμ (log ε 4.21), 343 (3.97).

Anal. Calcd. for $C_{21}H_{16}ClNO_4S_2$: C, 56.56; H, 3.62; S, 14.38. Found: C, 56.46; H, 3.67; S, 14.63.

3-Methylthio-5-phenyl-1,2-dithiolium Perchlorate (8).—Ten grams of 5-phenyl-1,2-dithiole-3-thione[10] was heated in 30 ml. of dimethyl sulfate to 160° for 15 min., and allowed to cool to room temperature. Then 70 ml. of glacial acetic acid was added, followed by 8 ml. of 70% perchloric acid. After stirring thoroughly, 200 ml. of ether was added; the yellow solid (12 g., 78%) which separated was collected and washed with additional quantities of ether and ethyl acetate, and melted at 165–170°. This material was used in the reactions with secondary amines. A portion of the material was recrystallized from 70% perchloric acid by the addition of ethyl acetate, and had m.p. 174–175°; τ_{CF_3COOH} 1.72 (1), 1.98–2.43 m (5), 6.90 (3).[17]

Anal. Calcd. for $C_{10}H_9ClO_4S_3$: C, 36.97; H, 2.79; S, 29.62. Found: C, 36.96; H, 2.72; S, 29.49.

(16) We wish to express our gratitude to Dr. Walter Reifschneider of the Dow Chemical Co., Midland, Mich., for a sample of benzene-1,2-dithiol, and to the Stauffer Chemical Co. for a sample of methyl chlorothioformate.

(17) N.m.r. is reported in τ-units (number of protons).

(18) W. L. Seman, U. S. Patent 2,046,884; *Chem. Abstr.*, **30**, P5592[5,6] (1936).

Quinazolines. I. Formation of a Guanidinoquinazoline during the Three-Component Synthesis of a 4,6-Diamino-1-aryl-1,2-dihydro-s-triazine[1]

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The structure of a high-melting companion product, $C_{14}H_{13}N_5 \cdot HCl$, isolated during the three-component synthesis of 4,6-diamino-2,2-dimethyl-1-(2-naphthyl)-1,2-dihydro-*s*-triazine hydrochloride (I·HCl) from 2-naphthylamine hydrochloride, dicyandiamide, and acetone has been investigated. On the basis of a combination of degradative and synthetic evidence, this by-product has been formulated as the hitherto unreported compound 3-guanidino-1-methylbenzo[*f*]quinazoline hydrochloride (XVII·HCl).

Biologically active 4,6-diamino-1-aryl-1,2-dihydro-*s*-triazines have been synthesized in large numbers since 1951, both in this laboratory[2–4] and elsewhere,[5–9] by either of two general routes (eq. 1). The chemistry of these dihydrotriazines has been surveyed in a recent review,[10] and they have been shown to exhibit a wide variety of significant biological properties, including

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