(trifluoromethyl)phenothiazine was reduced by refluxing for 2 hr. in the presence of 32 g. of reduced iron powder and 1 ml. of concentrated hydrochloric acid. The mixture was made alkaline and filtered hot. The product was isolated from the refrigerated filtrate in 85% yield and recrystallized from toluene, m.p. 235-240° (dec.).

Anal. Calcd. for $C_{13}H_9F_3N_2S$: C, 55.31; H, 3.21; N, 9.93. Found: C, 56.03; H, 3.23; N, 9.93.

2-(Trifluoromethyl)phenothiazine (V). A solution of 4.9 g, of 7-amino-2-(trifluoromethyl)phenothiazine in 120 ml. of isopropyl alcohol and 35 ml. of 2N hydrochloric acid was cooled to 5° and treated with a solution of 1.2 g. of sodium nitrite in 10 ml. of water. The mixture was held at 5-10° for 1 hr. and then refluxed for 16 hr., after which it was made alkaline, cooled to 25°, and diluted with 250 ml. of water. The precipitate was recrystallized from toluene to give 850 mg. (18%) of product with m.p. $185-187^{\circ}$ and infrared spectrum identical to that of authentic 2-(trifluoromethyl)-phenothiazine.

Anal. Caled. for $C_{13}H_{8}F_{8}NS$: C, 58.42; H, 3.02; N, 5.24. Found: C, 58.73; H, 3.44; N, 5.21.

Acknowledgment. The microanalyses were carried out by Mr. T. Alicino and his associates. The authors are furthermore indebted to Dr. H. L. Yale and Dr. J. Bernstein for ideas and discussions stimulating this investigation.

NEW BRUNSWICK, N. J.

[COMMUNICATION NO. 1912 FROM THE KODAK RESEARCH LABORATORIES, EASTMAN KODAK CO.]

2-Substituted-1,3,4-oxa- and thia-diazoline-5-thiones

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Potassium acyl or aroyldithiocarbazates are cyclized in cold $(0-10^\circ)$ concentrated sulfuric acid to thiadiazolinethiones. At higher temperatures, some disulfide is also formed. Mild oxidation of potassium benzoyl dithiocarbazate with iodine produces an unstable linear disulfide corresponding to the thiuram disulfides. This same product forms in solid potassium benzoyl thiocarbazate by air oxidation. Six previously unreported oxadiazolinethiones have been prepared by the usual alkaline cyclization.

Since its preparation and identification in 1904, potassium benzoyldithiocarbazate (I, $R = C_6 H_5$)¹ has been used as an intermediate in a number of syntheses. Busch and Stark¹ prepared several esters (II, $R = C_6 H_5$), while Hoggarth² showed that boiling an alcoholic solution of the salt caused cyclization to 2-mercapto-5-phenyl-1,3,4-oxadiazole (III, $R = C_6 H_5$). He also showed that the latter could be converted to the methylthic derivative $(V, R = C_6H_5, R = CH_3)$. By the use of analogs of potassium benzovldithiocarbazate, Young and Wood³ and Ainsworth⁴ prepared a series of 5-substituted - 2 - mercapto - 1,3,4 - oxadiazoles. However, they pointed out that infrared absorption spectra show the presence of N-H and C=S bands, an observation which indicates that these substances exist as the thiones (IV) rather than the mercapto compounds (III). Further study with the esters (II)³ and amides⁵ of substituted dithiocarbazic acids showed that they could be cyclized by cold concentrated sulfuric acid to 1,3,4-thiadiazoles (VI) in contrast to the 1,3,4-oxadiazoles formed by cyclization of the potassium salts in alkaline solution.

Application of this procedure to substituted po-

(1) M. Busch and M. Stark, J. prakt. Chem., 93, 49 (1916); H. Felin, Inaugural Dissertation, Erlangen University (1904).

(3) R. W. Young and K. H. Wood, J. Am. Chem. Soc., 77, 400 (1955).

(4) C. Ainsworth, J. Am. Chem. Soc., 78, 4475 (1956).

(5) S. Yoshida and M. Asai, J. Pharm. Soc. Japan, 74, 951 (1954); Chem. Abstr., 49, 10937 (1954).



tassium dithiocarbazates has led to a number of 1,3,4-thiadiazoline-5-thiones (Table I).

Although 2-phenyl-1,3,4-thiadiazoline-5-thione (VII, $R = C_6 H_5$)⁶ and its 2-(4-pyridyl) analog

⁽²⁾ E. Hoggarth, J. Chem. Soc., 4811 (1952).

⁽⁶⁾ B. Holmberg, Arkiv Kemi, Mineral. Geol., 17A, 1 (1944); Chem. Abstr., 39, 3524 (1945).

28.3

28.2

29.7

32.7 32.7

1,3,4-Thiadiazoline-5-thiones R-C=N-NH-C=S -S---______ Carbon, % Hydrogen, % Nitrogen, % Sulfur, % Yield, Empirical M.P., °C. R =Calcd. Found Calcd. Found Caled. Found Calcd. Found Formula %p-CH₃OC₆H₄ 35222 - 224 $C_9H_8N_2OS_2$ 48.1 48.23.63.4 12.512.028.6 $\mathrm{C_8H_5N_2S_2Cl}$ $p-\mathrm{ClC}_6\mathrm{H}_4^{a}$ 35 210 - 21241 8 41 8 2.22.212.312.028.1 $n-C_7H_{15}^{b}$ 7356-58 $C_9H_{16}N_2S_2$ 50.2 - 49.97.07.113.112.829.717 221-223 C6H9N2OS2 2-Furoyl 39.139.12.22.115.315.0

TABLE I

a % Cl Calcd./found 15.6/14.9. b Recrystallized from light petroleum. c Recrystallized from 95% ethat	nol.
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 $C_7H_5N_3S_2$

TABLE II

43.1

43.1

1,3,4-Oxadiazoline-5-thiones

R-C=N-NH-C=S	
L0	

Yield,			Empirical	Carbon, %		Hydrogen, %		Nitrogen, %		Sulfur, %	
R==	%	M.P., °C.	Formula	Caled.	Found	Calcd.	Found	Caled.	Found	Caled.	Found
$\overline{m-\mathrm{NO}_{2}\mathrm{C}_{6}\mathrm{H}_{4}^{b}}$	36	132-134	$C_8H_5N_3O_3S$	43.0	43.9°	2.3	2.4	18.8	18.8	14.2	14.5
o-CH ₃ OC ₆ H ₄ ^b	35	223 - 226	$C_9H_8N_2O_2S$	51.9	52.4	3.9	4.3	13.4	13.8		_
o-CH ₃ C ₆ H ₄ ^{<i>a</i>}	37	190 - 191	$C_9H_8N_2OS$	56.2	56.1	4.2	4.3	14.6	14.4	16.7	16.8
m-CH ₃ C ₆ H ₄ ^b	20	158 - 160	$C_9H_8N_2OS$	56.2	56.0	4.2	4.3	14.6	14.3	16.7	16.8
$o-HOC_6H_4^a$	20	212 - 213	$C_8H_5N_2O_2S$	49.5	49.3	3.1	2.9	14.4	14.0	16.5	16.6
$p-\mathrm{HOC}_{6}\mathrm{H}_{4}{}^{a}$	64	252 - 254	$\mathrm{C_8H_5N_2O_2S}$	49.5	49.3	3.1	3.2	14.4	14.7	16.5	16.5

Cyclization conditions ^a KOH in ethanol, ^b pyridine, ^c Several carbon-hydrogen analyses were run on this compound and all results were high.

(VII, R = 4-pyridyl)⁷ have been reported, they were prepared by cyclization of potassium thiobenzoyl- and thioisonicotinoyl-dithiocarbazates (X, $R = C_6H_5$, 4-pyridyl), respectively, with potassium hydroxide in ethanol. The present method offers a distinct advantage, since X ($R = C_6 H_5$) and its homologs are not easy to obtain. Pertinent data for five thiadiazolinethiones and six oxadiazolinethiones hitherto unreported are given in Tables I and II.8

A study of the action of sulfuric acid on potassium benzoyldithiocarbazate revealed that, in addition to the thiadiazolinethione, a second substance is formed. The amount of this substance increases at the expense of the thiadiazolinethione if the temperature exceeds 10°. It increases even more if the potassium benzoyldithiocarbazate is not freshly prepared. Apparently, this by-product is due, in part, to the oxidizing power of sulfuric acid and in part to air oxidation. Reference to Table III shows roughly how the yield of by-product increases under oxidizing conditions.

Further investigation of the by-product showed that it is the disulfide VIII $(R = C_6H_5)$; this was established by oxidation of the thiadiazolinethione

TABLE III

2.9

21.6

22.0

2.6

4 CID	CYCLIZATION	OF POTASSIUM	BENZOYLDITHIOCARBAZATE
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Age	Fre Pre	eshly pared	3 Months Old Sample		
Temperature Viold of this disculing	<10°	40-50°	10°	40-50°	
thione Yield of by-product	67%	40% 13%		51%	

(VII, $R = C_6H_5$) with iodine to a disulfide identical with VIII ($R = C_6 H_5$). Because of the high yield of by-product obtained from aged potassium benzoyldithiocarbazate and because it did not seem reasonable that air oxidation would effect a cyclization, the aged product was investigated for a possible intermediate. Such an intermediate was obtained and it appears to be the non-cyclic disulfide, IX (R = C_6H_5). This same product can be prepared from fresh potassium benzoyldithiocarbazate by oxidation with iodine⁹ and can be cyclized to the disulfide VIII (R = C_6H_5) with sulfuric acid. However, it has not been possible to obtain the non-cyclic product in analytically pure form. Attempts at purification resulted in further reaction with the formation of the oxadiazole and sulfur.

Despite the fact that the assumed intermediate could not be isolated in pure form, such a structure

3-Pyridy]°

30

219 - 221

⁽⁷⁾ H. B. König, W. Siefken, and H. A. Offe, Ber., 87, 825 (1954).

⁽⁸⁾ These substances are described as the thiones because the infrared data are similar to that described by Ainsworth,⁴ who has reported that a more detailed study of the infrared absorption of such compounds will be published by H. Boaz.

⁽⁹⁾ P. Ch. Guha, J. Am. Chem. Soc., 44, 1503 (1922).

DISULFIDES OF 1-OXA- AND THIA-3,4-DIAZOLES R-C=N-N=C-S-S-C=N-N=C-R												
 R=	x	Yield, %	M.P., °C.	Empirical Formula	Carb Calcd.	on, % Found	Hydro Calcd.	gen, <u>%</u> Found	Nitros Calcd.	gen, <u>%</u> Found	$\frac{\text{Sulft}}{\text{Calcd.}}$	ır, % Found
C_6H_5 m -CH $_2C_6H_4$ C_6H_5	0 0 8	$56 \\ 40 \\ 76$	$194-196 \\ 120-121 \\ 160-162$	$\begin{array}{c} C_{16}H_{10}N_4O_2S_2\\ C_{18}H_{14}N_4O_2S_2\\ C_{16}H_{10}N_4S_4 \end{array}$	$54.2 \\ 56.5 \\ 49.7$	54.3 56.9 49.3	2.9 3.7 2.6	2.7 4.0 2.6	$15.8 \\ 14.6 \\ 14.5$	16.3 14.9 14.4	18.1 16.7 33.2	18.4 16.4 33.5

TABLE IV

is not new. The well-known thiuram disulfides (RNHCSSSSCNHR) are not stable compounds.¹⁰ Furthermore, a similar, non-cyclic disulfide (IX, R = 4-pyridyl) has been reported recently,⁷ but details of preparation or isolation are not disclosed.

The S—S— linkage could not be characterized by infrared spectroscopy. However, a polarographic study of potassium benzoyldithiocarbazate and the cyclic and non-cyclic disulfides yielded information¹¹ which, together with the chemical evidence, is consistent with the proposed structure (IX).

EXPERIMENTAL

Potassium 3-aroyl- or 3-acyl-dithiocarbazates (I) were prepared in good yield and quality by a known method.¹ If the salt was not to be used immediately, it was stored in a vacuum desiccator.

2-Substituted-1,3,4-thiadiazoline-5-thiones (VII). Approximately 0.1 mole of the potassium salt (I) was powdered and added in small portions, with vigorous stirring, to cold $(0-2^{\circ})$, concentrated sulfuric acid (d 1.82) (5 ml. per g. of the salt). The temperature was not allowed to exceed 6-8°; the solid dissolves quite rapidly. Stirring was continued 3-5 min. after the addition had been completed.

The solution was poured upon ice (50 g. per g. of potassium salt). The yellowish solid that separated was collected on a filter, washed with water, pressed as dry as possible, and re-

(10) J. v. Braun, Ber., 35, 3368–3388 (1902).

(11) Polarograms of these materials were run by E. P. Przybylowicz, of these Laboratories. The sample was dissolved in a 1:1 mixture of acetone and methanol and diluted to twice its volume with an acetate buffer of pH = 5. The potassium salt (I) produced a well-defined anodic wave which can be assigned to the dithiocarbazate grouping. It also gave a small cathodic wave which could represent the presence of a small amount of disulfide. The product assigned the structure IX and the cyclic disulfide (VIII) gave no anodic waves, but each produced two well-defined cathodic waves. The polarograms of these two samples were virtually identical. From these data it is concluded that products VIII and IX contain similar reducible groups which are not present in I. However, since IX is derived from I by oxidation, it can be concluded that the cathodic waves observed in it and VIII are due to the disulfide grouping.

crystallized (decolorized first with Norit) from 50% ethanol (Table I).

2-Substituted-1,3,4-oxadiazoline-5-thiones (III) were prepared by heating the potassium salts (I) in pyridine² or by boiling an alcoholic (95%) solution of the salt formed by addition of carbon disulfide to an alkaline solution of the hydrazide.⁴ The latter was preferred because it did not involve isolation of the potassium salts and the yields were higher (Table II).

Bis(5-substituted-1,3,4-ora(thia)-diazol-2-yl) disulfides (VIII and XI). The 2-substituted-1,3,4-oxa- or thiadiazoline-5-thione (0.01 to 0.05 mole) was dissolved in 20-35 ml. of 5% aqueous potassium hydroxide. A 1-2% aqueous solution of iodine containing 3% of potassium iodide was added in small portions, with stirring, at room temperature, until the abundant precipitate that formed turned slightly brown. The solid was collected and then recrystallized from ethanol. One disulfide (VIII, $\mathbf{R} = C_6 \mathbf{H}_5$) was also prepared through acid treatment of IX ($\mathbf{R} = C_6 \mathbf{H}_5$), following the same procedure indicated for VII (yield, 73%).

Analytical data for this disulfide and for two disulfides derived from oxadiazolinethiones are given in Table IV.

Bis(3-benzoyldithiocarbazoyl) disulfide (IX, $R = C_6H_5$). (1) A sample of 10 g. of potassium 3-benzoyldithiocarbazate was allowed to stand in an open bottle for 3 months. The sample was then stirred into cold water and the pH adjusted to 8 by addition of a few drops of hydrochloric acid. The undissolved solid (1.0 g., m.p. 210-212°) was not further purified.

Anal. Caled. for $C_{16}H_{14}O_2N_4S_4$: C, 45.4; H, 3.4; N, 13.3; S, 30.3. Found: C, 42.7; H, 2.5; N, 12.8; S, 30.8.

(2) Fresh potassium 3-benzoyldithiocarbazate (5 g.) was treated with a 1% iodine solution (as described for VIII and XI). The yellowish solid (2 g.) obtained had m.p. $210-212^{\circ}$ and showed no depression in melting point on admixture with the product from (1).

Infrared spectra¹² of I and IX. The infrared absorption spectra were obtained on a Baird double-beam spectrophotometer, Model AB-1 (with NaCl prism). The absorption peaks due to —NH at 3μ and to —CONHR at 6.1 and 6.5– 6.6 μ were present, as expected in both the potassium salt (I) and the disulfide (IX). The —NHCS— absorption at 6.8 μ in IX is a more normal position than the band at 7.2 μ in I, for which this group is presumably responsible. This shift may be attributed to the polar potassium salt. The S—S— linkage could not be characterized.

ROCHESTER 4, N. Y.

(12) We are indebted to D. W. Stewart, of these Laboratories, for the infrared data.