92 g. (98%) of cream colored material having a melting point range of 90–95° separated. Recrystallization of this from an ethanol-water system gave 90 g. (96%) of material melting at 95–96°. Additional recrystallizations failed to raise the melting point further. A mixture melting point with an authentic specimen (98°)[7] showed no depression. A 53% yield of this material made by a somewhat similar procedure has been reported.[7]

10-(n-Decyl)phenothiazine-5,5-dioxide. Seventeen grams (0.05 mole) of 10-(*n*-decyl)phenothiazine was dissolved in 290 ml. of glacial acetic acid at 70°. Sixteen milliliters (0.154 mole) of 30% hydrogen peroxide was added causing the formation of a deep red color. Stirring was continued for 1.5 hr. at 80° after which an additional 5 ml. (0.048 mole) of 30% hydrogen peroxide was added. This caused no apparent change in the reaction. One hundred and ninety milliliters of the solvent was removed by distillation. Upon cooling, 13.5 g. (73%) of pink-brown material having a melting point of 93–95.5° separated. Recrystallization of this from an ethanol-water system produced 12.1 g. (67%) of tan material having a melting point of 95.5–96.5°. Additional recrystallization did not raise the melting point.

The infrared spectrum showed the characteristic sulfone absorption bands.

Anal. Calcd. for $C_{22}H_{29}NO_2S$: S, 8.65. Found: S, 8.49, 8.50.

An additional 4.7 g. of a brown semisolid material was recovered by dilution of the acetic acid filtrate from the reaction mixture with water. No effort was made to purify this.

10-(n-Octadecyl)phenothiazine-5,5-dioxide. Twenty-two and one-half grams (0.05 mole) of 10-(*n*-octadecyl)phenothiazine was dissolved in 300 ml. of glacial acetic acid at 80°. Fifteen milliliters (0.147 mole) of 30% hydrogen peroxide was added and the reaction was stirred for 1.5 hr., the temperature being maintained at 80°. An additional 10 ml. (0.098 mole) of 30% hydrogen peroxide was added, causing no change in the reaction. Upon cooling to room temperature, 22 g. (91.5%) of cream colored material melting at 93–93.5° separated. Recrystallization of this from absolute ethanol failed to increase the melting point. The infrared spectrum showed an absorption band characteristic of a sulfone.

Anal. Calcd. for $C_{30}H_{45}NO_2S$: S, 6.63. Found: S, 6.64, 6.71.

10-(n-Decyl)phenothiazine-4-carboxylic acid. Seventeen and one-quarter grams (0.05 mole) of 10-(*n*-decyl)phenothiazine-5-oxide was suspended in 250 ml. of anhydrous ether under an atmosphere of nitrogen. The suspension was cooled to −20° by means of a Dry Ice–acetone bath and 0.05 mole of *n*-butyllithium[16] in 45 ml. of ether was added at such a rate as to maintain the temperature at −20°. After stirring for 2 hr. at −20° another 0.1 mole of *n*-butyllithium in 90 ml. of ether was added and the mixture was permitted to warm to 0° where it was maintained for 4 hr. The reaction mass was then poured jet-wise into an agitated Dry Ice-ether slurry. After this mixture had warmed to room temperature, the ether was extracted with 100 ml. (0.262 mole) of 10% sodium hydroxide in several portions. Acidification of the basic extract with hydrochloric acid caused the separation of a yellow oil which gradually solidified on standing. This weighed 7 g. (36%) and had a melting point of 124–125°. Recrystallization of this from glacial acetic acid gave 6.2 g. (32%) of bright yellow material melting at 128–129°. Additional recrystallizations failed to increase the melting point. The infrared spectrum showed characteristic absorptions bands for the carbonyl group and 1,2,3 trisubstitution.

Anal. Calcd. for $C_{23}H_{29}NO_2S$: S, 8.36. Found: S, 8.21, 8.33.

The sodium salt of this compound was prepared by adding an excess of 10-(*n*-decyl)phenothiazine-4-carboxylic acid to a solution of dilute sodium hydroxide. When the maximum amount of material had dissolved, the solution was filtered and the filtrate was allowed to evaporate slowly. Yellow plate-like crystals having a melting point of 253–254° formed. A flame test indicated the presence of sodium.

Acknowledgment. We wish to thank Mr. E. Miller Layton, Jr., of the Ames Laboratory of the Institute for Atomic Research for the determination of the infrared spectra.

AMES, IOWA

(16) H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn, and L. S. Miller, *J. Am. Chem. Soc.*, **71**, 1499 (1949).

[CONTRIBUTION FROM THE SQUIBB INSTITUTE FOR MEDICAL RESEARCH]

A New Synthesis of 10-(3-Dimethylaminopropyl)-2-(trifluoromethyl)phenothiazine Hydrochloride[1] and 7-Substituted Derivatives[2]

K. FLOREY AND A. R. RESTIVO

Received January 27, 1958

The zinc salt of 2-amino-4-(trifluoromethyl)benzenethiol reacted with 2,4-dinitrochlorobenzene to give 2-amino-4-(trifluoromethyl)-2′,4′-dinitrodiphenylsulfide. The formamido derivative of the latter was cyclized *via* the Smiles Rearrangement to 7-nitro-2-(trifluoromethyl)phenothiazine. By alkylation with dimethylaminopropyl chloride, 10-(3-dimethylaminopropyl)-7-nitro-2-(trifluoromethyl)phenothiazine was obtained. Reduction to the 7-amino analog and reductive deamination *via* the diazonium compound led to 10-(3-dimethylaminopropyl)-2-(trifluoromethyl)phenothiazine in 35% over-all yield. The diazotization of aminophenothiazines is discussed.

The current interest in 10-(3-dimethylaminopropyl)-2-(trifluoromethyl)phenothiazine (VIII) as an ataractic agent[3] prompted us to seek new synthetic approaches to this compound.

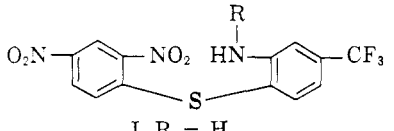
VIII has been synthesized in two laboratories[4,5] by alkylation of 2-(trifluoromethyl)phenothiazine (V). V had been prepared by Smith[6] by thionation of 3-(trifluoromethyl)diphenylamine which led to

(1) The Olin Mathieson Chemical Corp. trademark of this compound is VESPRIN.

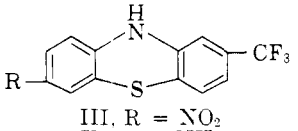
(2) Presented at the 132nd Meeting of the American Chemical Society, New York, September 1957.

a mixture of 2-(trifluoromethyl)phenothiazine (V) in 45% yield and its undesired isomer 4-(trifluoromethyl)phenothiazine in 35% yield. 2-(Trifluoromethyl)phenothiazine has also been synthesized in an unambiguous fashion by Roe and Little[7] *via* the Smiles Rearrangement of 2-formamido-2′nitro-5′-(trifluoromethyl)diphenylsulfide in 59% yield.

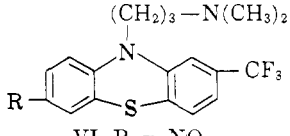
Starting with 2-amino-4-(trifluoromethyl)benzenethiol, the synthesis described in this paper leads to VIII in a 35% over-all yield without the formation of isomers and, furthermore, furnishes means of obtaining 7-substituted derivatives of VIII.



I, R = H
II, R = HCO



III, R = NO_2
IV, R = NH_2
V, R = H



VI, R = NO_2
VII, R = NH_2
VIII, R = H
IX, R = Cl

The zinc salt of 2-amino-4-(trifluoromethyl)-benzenethiol[8] was treated with sodium methylate and 2,4-dinitrochlorobenzene.[9] The resulting 2-amino-4-(trifluoromethyl)-2′,4′-dinitrodiphenylsulfide (I) (85% yield) was converted to its *N*-formamido compound (II) in 90% yield by refluxing in 90% formic acid. II was then cyclized *via* the Smiles Rearrangement[10] to 7-nitro-2-(trifluoromethyl)-phenothiazine (III) in 85% yield. The high yield obtained in this reaction was undoubtedly due to the presence of the second nitro group which facilitated both rearrangement and ring closure. Alkylation of III with dimethylaminopropyl chloride in diethylene glycol dimethyl-ether in the presence of sodamide or sodium hydride proceeded to 10-(3-dimethylaminopropyl)-7-nitro-2-(trifluoromethyl)phenothiazine (VI) in 85% yield. With xylene or toluene as solvents, only erratically low yields were obtained. The hydrochloride of VI was reduced with iron and calcium chloride in 75% ethanol to 7-amino-10-(3-dimethylaminopropyl)-2-(trifluoromethyl)phenothiazine (VII) in 90% yield and recovered as the dihydrochloride. However, isolation of the latter is unnecessary to carry out the next step. Therefore, VII was treated *in situ* with sodium nitrite and hydrochloric acid at 0° and then refluxed for 90 min. The base of 10-(3-dimethylaminopropyl)-2-(trifluoromethyl)-phenothiazine (VIII) was obtained in 70% yield by distillation of the reaction mixture.

The ease with which V could be deaminated was gratifying. Only a few examples of diazotization of phenothiazine derivatives are mentioned in the literature[11] and these have given varying results. The first diazotization described is that of Kehrmann and Vessely[12] who diazotized 3-aminophenothiazine which was then coupled with resorcinol.

A successful reductive deamination has been reported by Krishna and Jain[13] who converted 3-aminophenothiazine to phenothiazine. Baltzly, Harfenist, and Webb,[14] on the other hand, did not succeed in removing the amino group of 7-amino-3-bromophenothiazine by diazotization and reduction.

Successful Sandmeyer reactions have been carried out by Gilman and co-workers[15] who converted 3-amino-10-ethyl-phenothiazine-5-dioxide to 3-chloro-10-ethyl-phenothiazine-5-dioxide in low yield, and by Antonov[16,17] who converted 2-aminophenothiazine-5-dioxide and its *N*-methyl derivative to the corresponding 2-chloro compounds, the latter in 42% yield, the highest yield reported in the literature for any of these diazotiaztion reactions.

When VII was subjected to the Sandmeyer reaction, 7-chloro-10-(3-dimethylaminopropyl)-2-(trifluoromethyl)phenothiazine (IX) was obtained in 35% yield.

Furthermore, 7-amino-2-(trifluoromethyl)phenothiazine (IV), obtained from III by reduction, was deaminated to 2-(trifluoromethyl)phenothiazine (V), albeit in 18% yield. This low yield can be attributed to the fact that the ring-nitrogen is un-

(3) The tranquilizing activity of 10-(3-dimethylaminopropyl)-2-(trifluoromethyl)phenothiazine hydrochloride was first reported by J. C. Burke, H. L. Yale, G. L. Hassert, and J. P. High and by J. J. Piala, J. P. High, K. Greenspan, and J. C. Burke at the 1956 Meeting of the American Society for Pharmacology and Experimental Therapeutics at French Lick Springs, Ind., November 8–10, 1956. For later literature, see *Monographs on Therapy of The Squibb Institute for Medical Research*, **2**, 1957.

(4) P. N. Craig, E. A. Nodiff, J. J. Lafferty, and G. E. Ullyot, *J. Org. Chem.*, **22**, 709 (1957).

(5) H. L. Yale, F. Sowinski, and J. Bernstein, *J. Am. Chem. Soc.*, **79**, 4375 (1957).

(6) N. L. Smith, *J. Org. Chem.*, **15**, 1125 (1950).

(7) A. Roe and W. L. Little, *J. Org. Chem.*, **20**, 1577 (1955).

(8) A. I. Kiprianov and L. M. Yagupolskii, *Zhur. Obshcheĭ Khim.*, **22**, 2209 (1952) as reported in *Chem. Abstr.*, **47**, 4769 (1953).

(9) *Cf.* R. W. Bost, J. O. Turner, and R. D. Norton, *J. Am. Chem. Soc.*, **54**, 1985 (1932).

(10) *Cf.* J. F. Bunnet and R. E. Zahler, *Chem. Revs.*, **49**, 362 (1951).

(11) *Cf.* S. P. Massie, *Chem. Revs.*, **54**, 797 (1954).

(12) F. Kehrmann and O. Vessely, *Ann.*, **332**, 64 (1902).

(13) S. Krishna and M. S. Jain, *Proc. 15th Indian Sci. Cong.*, 153 (1928), as reported in *Chem. Abstr.*, **25**, 3001 (1931).

(14) R. Baltzly, M. Harfenist, and F. J. Webb, *J. Am. Chem. Soc.*, **61**, 2673 (1946).

(15) H. Gilman, R. K. Ingham, J. F. Champaigne, Jr., J. W. Diehl, and R. O. Ranck, *J. Org. Chem.*, **19**, 560 (1954).

(16) D. S. Antonov, *Bull. inst. chim. ac. bulgare sci.*, **2**, 97 (1953) as reported in *Chem. Abstr.*, **49**, 6267 (1955).

(17) D. S. Antonov and E. Karakasheva, *Bull. inst. chim. ac. bulgare sci.*, **2**, 113 (1953) as reported in *Chem. Abstr.*, **49**, 5442 (1955).

protected, leading to side reactions, since nitrous acid was taken up when 2-(trifluoromethyl) phenothiazine (V) was subjected to the conditions of the diazotization reaction. Neither starting material (V) nor any other defined product could be isolated.

These findings, taken together with those of previous investigators, make it apparent that when the ring-nitrogen is protected by alkylation diazotization of aminophenothiazines proceeds without inherent difficulty. However, it should also be pointed out that of the possible replacements of the diazonium group only the substitution by hydrogen (reductive deamination) and chlorine (Sandmeyer Reaction) have been reported in the literature. It may be significant that our attempts to prepare the corresponding hydroxyl, methoxyl, and ethoxyl compounds from VII resulted only in deamination to VIII. It is not clear whether the inability to effect these replacements is characteristic of phenothiazine diazonium compounds in general, or is governed by the influence of ring substituents such as the trifluoromethyl group in VII. This would have to be made the subject of a much broader study.

EXPERIMENTAL[18]

2-Amino-4-(trifluoromethyl)-2′,4′-dinitrodiphenylsulfide (I). At room temperature and under an atmosphere of nitrogen, a slurry of 900 g. of the zinc salt of 2-amino-4-(trifluoromethyl)benzenethiol in 8 liters of methanol was treated with a solution of 216 g. of sodium methylate in 2 l. of dry methanol to form the sodium salt.

The solution of the sodium salt was then added to a solution of 810 g. of 2,4-dinitrochlorobenzene in methanol and the mixture was agitated and refluxed in an atmosphere of nitrogen for 0.5 hr. Then 5 l. of water were added to the hot solutions and, after a cooling period, the crystals of 2-amino-4-(trifluoromethyl)-2′,4′-dinitrodiphenylsulfide, m.p. 170–175°, were collected in 85% yield. By recrystallization from ethanol the melting point was raised to 180–183°.

Anal. Calcd. for $C_{13}H_8F_3N_3O_4S$: N, 11.70; S, 8.92. Found: N, 11.90; S, 9.29.

2-Formamido-4-(trifluoromethyl)-2′,4′-dinitrodiphenylsulfide (II). One kilogram of 2-amino-4-(trifluoromethyl)-2′,4′-dinitrodiphenylsulfide was refluxed in 10 l. of 90% formic acid for one hour. Twenty-three liters of water were added to the cooled solution and the crystals of 2-formamido-4-(trifluoromethyl)-2′,4′-dinitrodiphenylsulfide (II), m.p. 168–170°, were collected in 90% yield. Recrystallization from chloroform raised the melting point to 172–174°.

Anal. Calcd. for $C_{14}H_8F_3N_3O_5S$: N-formyl 7.49; N, 10.85. Found: N-formyl 7.06; N, 10.89.

7-Nitro-2-(trifluoromethyl)phenothiazine (III). At room temperature and in an atmosphere of nitrogen, 950 g. of 2-formamido-4-(trifluoromethyl)-2′,4′-dinitrodiphenylsulfide in 9.5 l. of dry acetone were treated with 2.5 l. of *N* ethanolic NaOH. The mixture was refluxed for 45 min. Addition of 10 l. of warm water caused precipitation of dark red crystals of 7-nitro-2-(trifluoromethyl)phenothiazine, m.p. 205–210° (dec.) in 85% yield.

Anal. Calcd. for $C_{13}H_7F_3N_2O_2S$: C, 50.00; H, 2.25; N, 8.97. Found: C, 50.31; H, 2.16; N, 9.04.

(18) Melting points were taken on the Fischer-Johns apparatus and are uncorrected.

10-(3-Dimethylaminopropyl)-7-nitro-2-(trifluoromethyl)-phenothiazine (VI). To equimolar amounts of sodium amide and 3-dimethylaminopropyl chloride in 500 ml. of diethylene glycol dimethylether were added 100 g. of 7-nitro-2-(trifluoromethyl)phenothiazine in 500 ml. of the same solvent. The mixture was stirred and heated at 135° for 2 hr. under a blanket of nitrogen. The cooled solution was filtered from insoluble material and acidified with hydrogen chloride. The hydrochloride of 10-(3-dimethylaminopropyl)-7-nitro-2-(trifluoromethyl)phenothiazine, m.p. 235–240° (dec.), was collected in 85% yield. By recrystallization from ethanol, the melting point was raised to 240–245° (dec.).

Anal. Calcd. for $C_{18}H_{18}F_3N_3O_2S \cdot HCl$: C, 49.83; H, 4.41; Cl, 8.17; N, 9.69. Found: C, 50.06; H, 4.35; Cl, 8.19; N, 9.44.

7-Amino-10-(3-dimethylaminopropyl)-2-(trifluoromethyl)-phenothiazine (VII). A mixture of 100 g. of 10-(3-dimethylaminopropyl)-7-nitro-2-(trifluoromethyl)phenothiazine hydrochloride, 320 g. reduced iron powder, and 17 g. of calcium chloride in 2 l. of 75% ethanol was agitated and refluxed for 2 hr. The mixture was made strongly alkaline and filtered. The filtrate was either used for reductive deamination (see step VI) or the ethanol was removed. The residue was then taken up in benzene, washed with water, and the crude dihydrochloride of 7-amino-10-(3-dimethylaminopropyl)-2-(trifluoromethyl)phenothiazine was precipitated in 90% yield by addition of hydrogen chloride. By repeated recrystallization from isopropyl alcohol a melting point of 168–170° was obtained.

Anal. Calcd. for dihydrochloride $C_{18}H_{20}F_3N_3S \cdot 2HCl$: C, 49.09; H, 5.04; N, 9.54; Cl, 16.10. Found: C, 49.02; H, 5.04; N, 9.18; Cl, 15.56.

10-(3-Dimethylaminopropyl)-2-(trifluoromethyl)phenothiazine (VIII). The alkaline filtrate from the previous step was brought to pH 6 with concentrated hydrochloric acid and a further 480 ml. of 2*N* hydrochloric acid was added. The solution was cooled to 0°, and 16.0 g. of sodium nitrite in 80 ml. of water was added. The mixture was stirred at 0° for 30 min., and then refluxed for 90 min. After the ethanol was distilled off, the residual aqueous solution was made strongly alkaline, and extracted with benzene. The benzene extract was washed with water, and then the benzene removed *in vacuo*. The base of VIII was obtained in 70% yield by fractionation of the residue: n_D^{23} 1.5780; b.p. 160–165° at 0.7 mm. Both VIII and its hydrochloride were identical with authentic material.[5]

7-Chloro-10-(3-dimethylaminopropyl)-2-(trifluoromethyl)-phenothiazine (IX). To 120 g. of 7-amino-10-(3-dimethylaminopropyl)-2-(trifluoromethyl)phenothiazine dihydrochloride in 700 ml. of 1.5*N* hydrochloric acid was added a solution of 19.0 g. of sodium nitrite in 100 ml. of water at 0°. A wet filter cake of cuprous chloride was prepared by filtration of a mixture of a solution of 136 g. of $CuSO_4 \cdot 5H_2O$ and 36 g. of sodium chloride in 440 ml. of water with a solution of 29 g. of sodium bisulfite and 19 g. of sodium hydroxide in 220 ml. of water. To the filter cake in a solution of 290 ml. of 6*N* hydrochloric acid, the diazotization mixture was added at 0–5°C. Then 1.5 l. of water were added and the mixture was heated to 80° with agitation for 2 hr. The mixture was then made alkaline and extracted with benzene. The benzene layer was dried, the benzene distilled off *in vacuo*, and the residue fractionated to yield 36.0 g. (35%) of a fraction with a boiling point of 160–165° at 70 μ; n_D^{25} 1.5880. Twenty three grams of this material in 250 ml. of anhydrous ether was treated with ethereal hydrochloric acid to give 24.8 g. of 7-chloro-10-(3-dimethylaminopropyl)-2-(trifluoromethyl)phenothiazine, m.p. 208–210°. On recrystallization from isopropyl alcohol, the melting point was raised to 210–212°.

Anal. Calcd. for $C_{18}H_{18}F_3ClN_2S \cdot HCl$: C, 51.07; H, 4.52; N, 6.62; Cl, 16.75. Found: C, 51.00; H, 4.52; N, 6.50; Cl, 16.57.

7-Amino-2-(trifluoromethyl)phenothiazine (IV). In a solution of 300 ml. of 90% isopropyl alcohol, 17.8 g. of 7-nitro-2-

(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 2*N* 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° and infrared spectrum identical to that of authentic 2-(trifluoromethyl)-phenothiazine.

Anal. Calcd. for $C_{13}H_8F_3NS$: 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.]

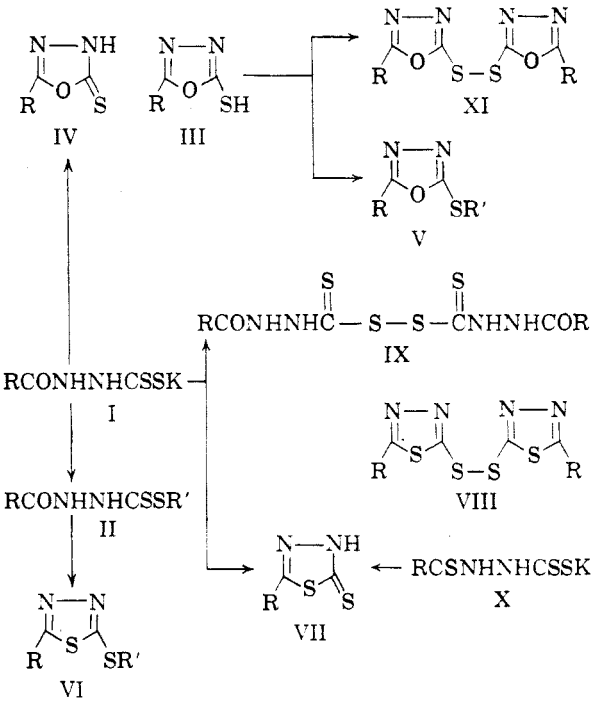
2-Substituted-1,3,4-oxa- and thia-diazoline-5-thiones

MAXIMO BARON AND CHARLES V. WILSON

Received November 22, 1957

Potassium acyl or aroyldithiocarbazates are cyclized in cold (0–10°) 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_6H_5)[1] has been used as an intermediate in a number of syntheses. Busch and Stark[1] prepared several esters (II, R = C_6H_5), while Hoggarth[2] showed that boiling an alcoholic solution of the salt caused cyclization to 2-mercapto-5-phenyl-1,3,4-oxadiazole (III, R = C_6H_5). He also showed that the latter could be converted to the methylthio derivative (V, R = C_6H_5,R' = CH_3). By the use of analogs of potassium benzoyldithiocarbazate, Young and Wood[3] and Ainsworth[4] 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 amides[5] 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 potassium 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_6H_5)[6] and its 2-(4-pyridyl) analog

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

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

(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).

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