

(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  $C_{13}H_5F_3N_3S$ : 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  $C_{13}H_5F_3NS$ : C, 58.42; H, 3.02; N, 5.24. Found: C, 58.73; H, 3.44; N, 5.21.

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

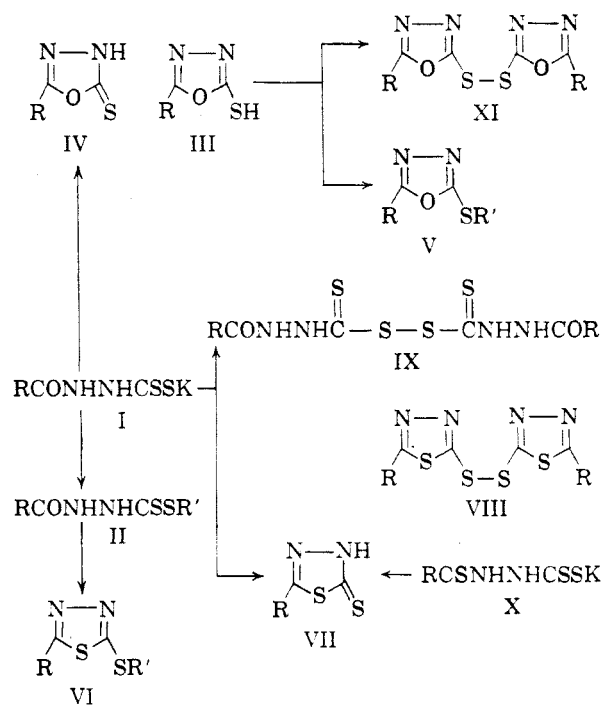
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Potassium acyl or aroyldithiocarbazates are cyclized in cold (0–10°) concentrated sulfuric acid to thiadiazolinethiones. At higher temperatures, some disulfide is also formed. Mild oxidation of potassium benzoyl dithiocarbazate with iodine produces 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,  $R = C_6H_5$ )<sup>1</sup> has been used as an intermediate in a number of syntheses. Busch and Stark<sup>1</sup> prepared several esters (II,  $R = C_6H_5$ ), while Hoggarth<sup>2</sup> 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<sup>3</sup> and Ainsworth<sup>4</sup> 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)<sup>3</sup> and amides<sup>5</sup> 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-



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,  $R = C_6H_5$ )<sup>6</sup> and its 2-(4-pyridyl) analog

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