Five-Membered Heterocyclic Thiones. Part VII (1,2). 1,2,3-Thiadiazole-5-thiolates

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The synthesis of the stable potassium salts of the first known 1,2,3-thiadiazole-5-thiols is described.

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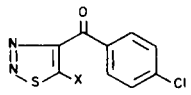
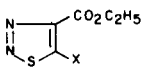
Whereas all of the possible types of 1,2,4- and 1,2,5-thiadiazolethiols are now known (see 3,4, and references therein), no 1,2,3-thidaiazolethiols have ever been reported in the literature. In fact, it is only recently (5,6) that the first alkyl-1,2,3-thiadiazole-5-yl sulfides have been prepared. This publication describes the synthesis of the stable potassium salts of several 1,2,3-thiadiazole-5-thiols including that of the parent member of the series.

It was recently shown (6) that 5-chloro-1,2,3-thiadiazoles bearing a carbonly group at C-4 were obtained as minor products (7) from thiophosgene and α-diazocarbonyl compounds. Displacement of chloride ion therefrom occurred, as expected (8), with a variety of nucleophiles and consequently the use of the chloro compounds as a source of the corresponding thiols was examined. The reaction of the chlorides (**1a**) and (**2a**) with potassium ethyl xanthate proceeded rapidly to give the expected dithiocarbonates (**1b**) and (**2b**). These compounds lost carbon oxysulfide to give the sulfides (**1d**) and (**2d**), even at room temperature, but immediate treatment with an equimolar amount of ethanolic potassium hydroxide provided the stable potassium salts (**1c**) and (**2c**). An additional equivalent of potassium hydroxide converted **2c** into the very insoluble dipotassium salt (**3a**), which could also be obtained directly from **2b** and two equivalents of potash. The structures of these compounds were fully substantiated by their elemental analyses and spectral properties, and by conversion into the sulfides (**1d**), (**2d**), and (**3b**). Compound **3b**, which was identical to the saponification product of **2d** as expected, underwent loss of carbon dioxide at its melting point to furnsih the known (5) 5-ethylthio-1,2,3-thiadiazole (**4a**). Similarly, decarboxylation of **3c**, prepared from the dipotassium salt (**3a**) and benzyl chloride, produced 5-benzylthio-1,2,3-thiadiazole (**4b**).

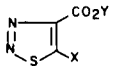
The thiols derived from the above salts were not stable under ordinary conditions since extraction of acidified solutions thereof failed to yield alkali soluble material in any of the cases. Nevertheless, under acidic conditions, in a nitrogen atmosphere, it was possible to trap the thiols from **2c** and **3a** as the Michael adducts (**2e**) and (**3d**) respectively, with methyl acrylate. Subjection of the diester (**2e**) to the action of an equivalent of ethanolic sodium ethoxide effected a reverse Michael reaction and in this way the sodium salt (**2f**) could be generated *in*



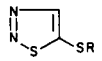
1a, X = Cl
1b, X = $S_2COC_2H_5$
1c, X = SK
1d X = SC_2H_5



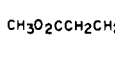
2a, X = Cl
2b, X = $S_2COC_2H_5$
2c, X = SK
2d, X = SC_2H_5
2e, X = $SCH_2CH_2CO_2CH_3$
2f, X = SNa



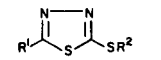
3a, X = SK, Y = K
3b, X = SC_2H_5, Y = H
3c, X = $SCH_2C_6H_5$, Y = H
3d, X = $SCH_2CH_2CO_2CH_3$, Y = H



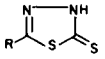
4a, R = C_2H_5
4b, R = $CH_2C_6H_5$
4c, R = $CH_2CH_2CO_2CH_3$
4d, R = K^+
4e, R = $[DBUH]^+$



5a, R = H
5b, R = C(=S)Cl



6a, R^1 = H, R^2 = $CH_2CH_2CO_2CH_3$
6b, R^1 = CH_3, R^2 = $CH_2CH_2CO_2CH_3$



7a, R = H
7b, R = CH_3

situ and converted into the sulfide (**2d**) with ethyl iodide. Inasmuch as decarboxylation of **3d** furnsihed **4c**, the above observation constituted the basis for the generation of salts of the parent 1,2,3-thiadiazole-5-thiol. Thus, addition of **4c** to ethanolic potassium ethoxide gave the crystalline potassium salt (**4d**) which on reaction with ethyl iodide gave the previously described sulfide (**4a**). Alternatively, addition of **4c** to an ethanolic solution of 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) produced a solution of **4e** which was alkylated *in situ* with ethyl iodide.

The knowledge that **4c** readily underwent base induced fragmentation, and that diazomethane reacted (5,6) with ethyl chlorodithioformate to give a mixture of 2-ethylthio-1,3,4-thiadiazole and 5-ethylthio-1,2,3-thiadiazole, set the stage for a much shorter synthesis of 5-methoxycarbonylethylthio-1,2,3-thiadiazole (**4c**). Thus, methyl-3-mercaptopropionate (**5a**) (9) was converted into the corresponding chlorodithioformate (**5b**) with thiophosgene. Condensation of the latter substance with diazomethane, at 0°, gave a 1:2 mixture of **4c** and the isomeric

1,3,4-thiadiazole (**6a**) which was separated by column chromatography on silica gel. The thiolate (**4d**) consequently became available in greater than 25% overall yield from **5b**.

The identity of the 1,3,4-thiadiazole (**6a**) was confirmed by conversion into 1,3,4-thiadiazoline-5-thione (**7a**) (10).

The above two step synthesis of 1,2,3-thiadiazole-5-thiolate was, alas, not applicable to the preparation of homologous members of this group of compounds because diazoethane reacted with **5a** to produce the 1,3,4-thiadiazole (**6b**) as the overwhelmingly major product. The isomeric thiadiazole, if present at all, was formed in less than 0.5% yield. The transformation of **6b** into the thione (**7b**) left no doubt that **6b** was a 1,3,4-thiadiazole.

EXPERIMENTAL (11)

Potassium 4-(4-Chlorobenzoyl)-1,2,3-thiadiazole-5-thiolate (**1c**).

A solution of the 5-chlorothiadiazole (0.128 g., 0.5 mmole) in acetonitrile (20 ml.) containing potassium ethyl xanthate (0.120 g., 0.75 mmole) was stirred at room temperature for 4 hours. The mixture was filtered, the filtrate was evaporated *in vacuo* at a temperature less than 40°, and ether was added to the residue. The ether solution was washed with water, dried over sodium sulfate, and evaporated *in vacuo*. Hexane was added to the crystalline residue and the solid (0.096 g., 55%), m.p. 89-91°, was collected by filtration. This substance decomposed at room temperature to give the sulfide (**1d**) and therefore it was immediately used in the next step. Thus, the dithiocarbonate (0.095 g., 0.27 mmole) in ethanol (5 ml.) containing 85% potassium hydroxide (0.017 g., 0.26 mmole) was stirred at room temperature for 6 hours. The solvent was evaporated, ether was added to the residue, and the yellow solid (0.075 g., 94%) was collected by filtration. After crystalliaztion from ethyl acetate-hexane, the salt had m.p. 170-171°; uv (methanol): 257 (15,500), 360 (9550) nm; ir (potassium bromide): 3430, 1614, 1593 cm^{-1}; nmr (deuterium oxide): 7.44 (d, 2H, J = 8.8 Hz), 7.74 (d, 2H, J = 8.8 Hz).

Anal. Calcd. for $C_9H_4ClKN_2OS_2 \cdot 2/3H_2O$: C, 35.24; H, 1.75; N, 9.14. Found: C, 35.34; H, 1.80; N, 9.09.

Potassium 4-Ethoxycarbonyl-1,2,3-thiadiazole-5-thiolate (**2c**).

Potassium ethyl xanthate (3.84 g., 24 mmoles) was added to a stirred solution of ethyl 5-chloro-1,2,3-thiadiazole-4-carboxylate (**2a**, 3.09 g., 16.1 mmoles) in acetonitrile (50 ml.) at 0°. The solution was maintained at a temperature of 0-10° for 3 hours and then the dithiocarbonate was isolated in the manner described above. The crude mixture was immediately suspended in ethanol and a solution of 85% potassium hydroxide (0.870 g., 13.2 mmoles) in ethanol was added. After 2 hours at room temperature the salt (3.04 g., 83%) was isolated in the manner described above. After crystallization from ethanol-ether the salt had m.p. 216°; uv (methanol): 333 (7950) nm; ir (potassium bromide): 3495, 3390, 1689, 1613 cm^{-1}.

Anal. Calcd. for $C_5H_5KN_2O_2S_2 \cdot 1/2H_2O$: C, 25.30; H, 2.55; N, 11.80. Found: C, 25.30; H, 2.42; N, 11.77.

Dipotassium Salt of 5-Mercapto-1,2,3-thiadiazole-4-carboxylate (**3a**).

(A) From Potassium 4-Ethoxycarbonyl-12,3-thiadiazole-5-thiolate (**2c**).

The thiolate (**2c**, 2.28 g., 10 mmoles) in ethanol (60 ml.) containing 85% potassium hydroxide (0.660 g., 10 mmoles) was stirred at reflux temperature for 5 hours. The di-salt precipitated during the course of the reaction. The mixture was filtered hot; the solid was washed with hot ethyl acetate and dried *in vacuo*. The product thus obtained (2.21 g., 93%) had m.p. 204°; uv (water): 238 (5370), 333 (6610) nm; ir (potassium bromide): 3385, 3220, 1590 cm^{-1}

Anal. Calcd. for $C_3K_2N_2O_2S_2 \cdot H_2O$: C, 14.06; H, 0.79. Found: C, 13.72; H, 0.85.

(B) From the Dithiocarbonate (**2b**).

The crude dithiocarbonate (**2b**), obtained from the chloro compound (**2a**, 10 mmoles) was dissolved in ethanol (50 ml.) containing 85% potassium hydroxide (1.00 g., 15.2 mmoles). After 40 hours at room temperature the solid was collected by filtration, washed well with ethanol and dried. This material (1.30 g., 51%) was identical to the material obtained by method (A).

4-(4-Chlorobenzoyl)-5-ethylthio-1,2,3-thiadiazole (**1d**).

The potassium salt (**1c**) was dissolved in ethanol, an excess of ethyl iodide was added, and the solution was stirred at room temperature for 20 hours. The solvent was removed *in vacuo*, water was added to the residue, the product was extracted with chloroform, the extract was dried over sodium sulfate and evaporated *in vacuo*. The solid residue was crystallized from methanol to give the product (**1d**), m.p. 106-107°, which was spectroscopically indistinguishable from an authentic specimen (6).

Ethyl 5-Ethylthio-1,2,3-thiadiazole-4-carboxylate (**2d**).

(A) By Alkylation of the Potassium Salt (**2c**).

The potassium salt (**2c**) was reacted with ethyl iodide in the manner described above. The crude product was crystallized from hexane to give a solid m.p. 50° which was identical in all respects with an authentic specimen.

(B) From the Michael Adduct (**2e**).

To a solution of sodium ethoxide (prepared from 50% sodium hydride (0.025 g.) in mineral oil) in anhydrous ethanol (7 ml.) was added the diester (**2e**, 0.148 g., 0.53 mmole: see below for synthesis) and the solution was stirred at room temperature with protection from light for 0.5 hour. Ethyl iodide (0.5 ml.) was added and stirring was continued for 3 hours. The solvent was removed *in vacuo*, ethyl acetate was added to the residue and the resultant was washed with water. The solvent was dried and evaporated *in vacuo* to give a residue which after crystallization from hexane gave a crystalline solid (0.090 g., 78%) m.p. 50-51°, underpressed on admixture with an authentic specimen.

Ethylthio-1,2,3-thiadiazole-4-carboxylic Acid (**3b**).

(A) From the Dipotassium Salt (**3a**) and Ethyl Iodide.

A solution of the dipotassium salt monohydrate (0.025 g., 0.1 mmole) in 50% aqueous ethanol (6 ml.) was left at room temperature for 20 hours. The solvent was removed *in vacuo*, water was added to the residue and the solution was washed with ethyl acetate. The aqueous phase was made acidic with hydrochloric acid and the product was extracted into ethyl acetate. The extract was washed, dried, and evaporated *in vacuo*. Hexane was added to the crystalline residue and the solid (0.016 g., 84%) m.p. 169° was collected by filtration. Crystallization of this material from methanol gave a solid m.p. 179-181°; uv (methanol): 233 (5500), 301 (8500) nm; ir (potassium bromide): 3090, 2560, 2425, 1732 cm^{-1}; ms: (relative intensity) 190 (19), 162 (15), 118 (14), 116 (21), 103 (16), 90 (45), 88 (62), 45 (100).

Anal. Calcd. for $C_5H_6N_2O_2S_2$: C, 31.57; H, 3.18; N, 14.73. Found: C, 31.52; H, 3.15; N, 14.67.

(B) By Saponification of Ethyl-5-ethylthio-1,2,3-thiadiazole-4-carboxylate (**2d**).

A solution of the ester (**2d**) (0.927 g., 4.25 mmoles) in ethanol (40 ml.) containing 85% potassium hydroxide (0.281 g., 4.25 mmoles) was left at room temperature for 3 hours. The solvent was removed *in vacuo*, water was added to the residue and the solution was acidified with hydrochloric acid. The product was extracted into ethyl acetate, the extract was dried and evaporated *in vacuo*. The residue (0.670 g., 83%) had m.p. 179-181°, after crystallization from methanol, undepressed on admixture with a specimen prepared in the manner described above.

5-Benzylthio-1,2,3-thiadiazole-5-carboxylic Acid (**3c**).

The alkylation of the dipotassium salt was effected with benzyl chloride in the manner described above except that aqueous acetone was used as the solvent, and that the reaction time was 2 hours. The acid was obtained in quantitative yield and had m.p. 180-182° after crystallization from aqueous methanol; uv (methanol): 240 (6550), 302 (9120) nm; ir (potassium bromide): 2750, 2660, 2580, 2520, 1684 cm^{-1}; nmr ($DMSOd_6$): 4.44 (s, 2H), 7.32 (m, 5H).

Anal. Calcd. for $C_{10}H_8N_2S_2O_2$: C, 47.62; H, 3.20; N, 11.11. Found: C, 47.61; H, 3.21; N, 11.37.

5-Ethylthio-1,2,3-thiadiazole (**4a**) by Decarboxylation of **3b**.

The carboxylic acid (**3b**, 0.200 g.), in a round bottomed flask evacuated to 200 mm, was placed in an oil bath at 170°. The bath temperature was raised to 195° and when the evolution of carbon dioxide was complete the residual oil was evaporatively distilled at 65°/0.05 mm. The product thus obtained (60% yield) was redistilled for analysis; uv (methanol): 240 (1860), 288 (5640), 301 (4260) nm; nmr (deuteriochloroform): 1.40 (t, 3H, J = 7.4 Hz), 3.07 (q, 2H, J = 7.4 Hz), 8.30 (s, 1H); ms: (relative intensity) 146 (10), 118 (17), 103 (48), 90 (59), 76 (11), 64 (15), 57 (36), 45 (100).

Anal. Calcd. for $C_4H_6N_2S_2$: C, 32.88; H, 4.14; N, 19.18. Found: C, 32.96; H, 4.27; N, 19.16.

5-Benzylthio-1,2,3-thiadiazole (**4b**).

The decarboxylation of 5-benzylthio-1,2,3-thiadiazole-4-carboxylic acid (**3c**) was effected in the manner described above but at 185°. The crude product was evaporatively distilled at 85°/0.05 mm and the distillate (60% yield) crystallized spontaneously. Crystallization of this material from hexane, with protection from light, gave a solid m.p. 50-51°; uv (methanol) 282 (2400), 301 (2750) nm; nmr 4.13 (s, 2H), 7.24 (s, 5H), 8.25 (s, 1H).

Anal. Calcd. for $C_9H_8N_2S_2$: C, 51.89; H, 3.87; N, 13.45. Found: C, 51.80; H, 3.88; N, 13.61.

Ethyl 5-Methoxycarbonylethylthio-1,2,3-thiadiazole-4-carboxylate (**2e**).

Nitrogen was bubbled through a solution of the salt (**2c**, 0.30 g., 1.31 mmoles) in water (15 ml.) for a few minutes and then methyl acrylate (2.5 ml.) was added. Aqueous acetic acid (0.1 ml., 1.6 mmoles) in 5 ml. of water was added with stirring, in an atmosphere of nitrogen, over a 1 hour period. After a further 26 hours at room temperature the solution was extracted with ethyl acetate, the extract was washed with water, dried, and evaporated *in vacuo*. The oil (0.180 g.) thus obtained was purified by column chromatography (protection from light) on silica gel. The product (0.153 g., 42%), which was eluted with ethyl acetate-hexane (90:10), crystallized spontaneously and after crystallization from dichloromethane-hexane it had m.p. 32-33°; uv (methanol): 233 (6030), 299 (8910) nm; ir (chloroform): 1743, 1712 cm^{-1}; ms: (relative intensity); 276 (38), 248 (17), 245 (10), 220 (5), 217 (5), 190 (11), 189 (7), 162 (10), 131 (27), 119 (26), 118 (31), 103 (26), 87 (84), 59 (100), 55 (86).

Anal. Calcd. for $C_9H_{12}N_2O_4S_2$: C, 39.11; H, 4.37; N, 10.14. Found: C, 39.09; H, 4.22; N, 10.31.

5-Methoxycarbonylethylthio-1,2,3-thiadiazole-4-carboxylic Acid (**3d**).

A solution of the dipotassium salt monohydrate (0.238 g., 0.93 mmole) in methanol (10 ml.) and water (1 ml.), protected from light, was purged with nitrogen and then methyl acrylate (2 ml.) was added. Acetic acid (0.2 ml.) in water (25 ml.) was added slowly to the stirred solution in a nitrogen atmosphere. After 48 hours the solvent was removed *in vacuo*, the residue was taken up in ethyl acetate and the solution was extracted with 10% sodium bicarbonate solution. The bicarbonate extract was made acidic with 10% hydrochloric acid and the product was extracted into ethyl acetate. The extract was washed with water, dried, and evaporated. Crystallization of the residue from benzene gave a white solid (0.194 g., 84%) m.p. 112-113°; uv (methanol) 231 (5620), 301 (7940) nm; ir (potassium bromide): 2555, 1736 cm^{-1}; ms: (relative intensity); 248 (18), 220 (5), 217 (5), 190 (12), 176 (6), 162 (15), 135 (9), 118 (28), 116 (25), 103 (20), 90 (49), 87 (79), 78 (36), 59 (100), 55 (80), 45 (100).

Anal. Calcd. for $C_7H_8N_2O_4S_2$: C, 33.87; H, 3.25; N, 11.29. Found: C, 33.96; H, 3.27; N, 11.25.

5-Methoxycarbonylethylthio-1,2,3-thiadiazole (**4c**).

(A) By Decarboxylation of the Carboxylic Acid (**3d**).

The above acid (0.300 g., 1.21 mmoles) was decarboxylated at 140°/30 mm. The crude product (0.120 g.) was purified by column chromatography on silica gel using hexane-ethyl acetate (90:10) as the eluant. The pure product (0.105 g., 43%) was evaporatively distilled at 100°/0.1 mm for analysis; uv (methanol): 237 sh. (1900), 280 (3630), 299 (4170) nm; ir (chloroform): 1742 cm^{-1}; nmr (deuteriochloroform): 2.70 (t, 2H, J = 7.2 Hz), 3.25 (t, 2H, J = 7.2 Hz), 3.65 (s, 3H), 8.26 (s, 1H); ms: (relative intensity); 204 (19), 176 (17), 144 (9), 118 (28), 116 (18), 103 (33), 90 (62), 89 (56), 87 (100), 59 (100), 55 (85), 45 (75).

Anal. Calcd. for $C_6H_8N_2O_2S_2$: C, 35.28; H, 3.95; N, 13.72. Found: C, 35.29; H, 3.81; N, 13.79.

(B) By the Condensation of **5b** with Diazomethane.

To a solution of methyl-3-mercaptopropionate (**5a**, 1.15 g., 9.6 mmoles) in carbon disulfide (1 ml.) was added thiophosgene (0.84 ml., 11 mmoles) and the resultant was left at room temperature for 22 hours. The solution was then heated gently at reflux temperature for 6 hours at the end of which time the solvent was removed *in vacuo*. The residual oil was chromatographed on a column of silica gel (33 g.) using hexane-ethyl acetate (96:4) as the eluting solvent. The chlorodithioformate (**5b**), a yellow oil (1.50 g., 79%), was found in the early fractions and used directly in the next step; ir (chloroform): 1738, 1090 cm^{-1}.

The above chlorodithioformate (1.50 g., 7.55 mmoles) was dissolved in ether, cooled to 0° and an ethereal diazomethane solution (prepared from 4.0 g. of nitrosomethylurea) was added. The reaction was allowed to come to room temperature and after 0.5 hour the solvent was removed *in vacuo*. The residue was subjected to column chromatography on silica gel (40 g.) using hexane-ethyl acetate (9:1) as the eluant. The 1,2,3-thiadiazole (**4c**, 0.48 g., 31% based on **5b**) was eluted first and this was closely followed by the 1,3,4-thiadiazole (**6a**, 0.93 g., 60% based on **5b**). Compound **6a** was evaporatively distilled at 110-115°/0.07 mm for analysis; uv (methanol): 266 (5000) nm; ir (chloroform): 1738, 1050 cm^{-1}; nmr (deuteriochloroform): 2.88 (t, 2H, J =

7.2 Hz), 3.58 (t, 2H; J = 7.2 Hz), 3.69 (s, 3H); 8.90 (s, 1H); ms: (relative intensity) 204 (40), 173 (19), 145 (89), 144 (68), 118 (39), 72 (23), 60 (86), 55 (80), 45 (100), 42 (37).

Anal. Calcd. for $C_6H_8N_2O_2S_2$: C, 35.28; H, 3.95. Found: C, 35.45; H, 4.01.

2-Methoxycarbonylethylthio-5-methyl-1,3,4-thiadiazole (**6b**).

The chlorodithioformate (**5b**) (prepared from **5a** (1.15 g., 9.6 mmoles) as described above and used without purification) was dissolved in ether (20 ml.) and ethereal diazoethane (prepared (12) from 7.0 g. of nitrosoethylurea) was added at -30°. The reaction was left to come to room temperature, the excess diazoalkane was destroyed with a few drops of acetic acid and the solvent was then removed *in vacuo*. The residue was subjected to column chromatography on silica gel (50 g.) using hexane-ethyl acetate (4:1) as the eluant. The first product eluted (0.87 g.) had m.p. 97°; uv (methanol): 236 nm; ir (chloroform): 3545, 3425, 1742, 1569 cm^{-1}; nmr (deuteriochloroform): 1.00 (t, 3H, J = 7.2 Hz), 3.82 (q, 2H, J = 7.2 Hz), 6.55 (s, 2H, W_H = 44 Hz). This substance was not investigated further. A very small fraction (0.008 g., 0.4%) was then eluted which may have been the 1,2,3-thiadiazole. The nmr spectrum was slightly different from that of the major product. Spectra: nmr (deuteriochloroform): 2.70 (s, 3H), 2.88 (t, 2H, J = 6.3 Hz), 3.42 (t, 2H, J = 6.3 Hz), 3.70 (s, 3H). The major product (1.32 g.), a crystalline solid, was eluted last. After crystallization from ethyl acetate-hexane this substance (1.12 g., 54%) had m.p. 57-58°. Spectra: uv (methanol): 210 (2950), 267 (6610) nm; ir (chloroform): 1740 cm^{-1}; nmr (deuteriochloroform): 2.70 (s, 3H), 2.85 (t, 2H, J = 7.0 Hz), 3.50 (t, 2H, J = 7.0 Hz), 3.66 (s, 3H).

Anal. Calcd. for $C_7H_{10}N_2O_2S_2$: C, 38.51; H, 4.61; N, 12.83. Found: C, 38.41; H, 4.32; N, 13.02.

Potassium 1,2,3-Thiadiazole-5-thiolate (**4d**).

A solution of the ester (**4c**) (0.28 g., 1.37 mmoles) in anhydrous ethanol (3 ml.) was added, at room temperature, to a solution of potassium ethoxide (prepared from potassium metal (0.06 g.)) in ethanol (3 ml.). The reaction was instantaneous. The solvent was evaporated to a small volume (0.5 ml.), ether (10 ml.) was added, and the crystalline product was collected by filtration. Recrystallization of this material from ethanol-ether gave a solid (0.195 g., 91%) m.p. 80-82° dec.; uv (methanol): 223 (4470), 335 (6610) nm; nmr (deuterium oxide): 8.10 (s, 1H).

Anal. Calcd. for $C_2HKN_2S_2$: C, 15.37; H, 0.64. Found: C, 15.34; H, 0.67.

5-Ethylthio-1,2,3-thiadiazole (**4a**).

(A) From the Potassium Salt (**4d**).

This reaction was effected in the same manner as described for the synthesis of **1d** from **1c**. The sulfide thus obtained (82%) was identical spectroscopically and by tlc with the decarboxylation product of **3b**.

(B) From **4c** *via* **4e**.

This reaction was effected in the same manner as described for the synthesis of **2d** from **2e** except that an equimolar amount of DBU was substituted for sodium ethoxide. The ethylthio compound, obtained in quantitative yield, was identical to the material described in (A).

134- Thiadiazolin-5-thione (**7a**).

To a solution of sodium ethoxide (prepared from 100% sodium hydride (0.30 g.)) in absolute ethanol (3 ml.) was added the ester (**6a**, 0.18 g.). After 0.5 hour at room temperature, water (20 ml.) was added and the solution was washed with ethyl acetate. The aqueous phase was acidified with 10% hydrochloric acid and the product was extracted with ethyl acetate. The extract was washed with water, dried over sodium sulfate and evaporated *in vacuo* The solid residue (0.075 g.) was crystallized from benzene to give material with m.p. 138-141° (lit (10) m.p. 143°).

5-Methyl-1,3,4-thiadiazolin-5-thione (**7b**).

The ester (**6b**) was converted into the thione (**7b**), m.p. 180-183° undepressed on admixture with a commercial sample (Aldrich), prepared in the same manner as described for **7a**.

REFERENCES AND NOTES

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