(10%). One molar equivalent of hydrogen was absorbed. The product crystallized from aqueous ethanol as plates. A thrice crystallized sample melted at 145–147°. It was identical with the substance obtained from the direct oxidation of tetrahydrosolasodine (VIIa), and subsequent catalytic reduction.

Anal. Calcd. for $C_{27}H_{43}ON$: C, 81.55; H, 10.90. Found: C, 81.67; H, 11.01.

Methiodide of 3,16-diacetate of pseudosolasodine B (IX). Compound V (133 mg.) was dissolved in 5 ml. of benzene and 10 ml. of acetone and refluxed with 1 ml. of methyl iodide for 75 min. Excess methyl iodide and solvent were removed *in vacuo* and the residue redissolved in acetone. Upon the addition of *n*-hexane, plates of m.p. 268–270° (dec.), $\lambda_{max}^{chlf.}$ 5.77, 6.00 μ, were obtained in a quantitative yield.

Anal. Calcd. for $C_{32}H_{50}O_4NI$: C, 60.08; H, 7.88; I, 19.85. Found: 60.07; H, 8.02; I, 19.78.

N-Methyl-3,16-diacetate of pseudosolasodine B (X). When IX was treated with a dilute aqueous sodium carbonate solution a compound was obtained which crystallized from aqueous methanol in rods of m.p. 194–197°, $\lambda_{max}^{chlf.}$ 5.77, 6.06 μ.

Anal. Calcd. for $C_{32}H_{49}O_4N$: C, 75.10; H, 9.65; —NCH_3, 2.9. Found: C, 74.91; H, 9.51; —NCH_3, 2.77.

The hydrochloride, $\lambda_{max}^{chlf.}$ 5.77, 5.98 μ, melted at 210–212° (dec.).

N-Methylsolasodine (XI). The methiodide of IX (110 mg.) was dissolved in 20 ml. of 5% methanolic potassium hydroxide and refluxed for 90 min. Although the resulting product was chromatographed over alumina, it appeared to be inhomogeneous, melting partly at 159–162° and partly at 176–180°. Infrared data of the eluates indicated the possible presence of another substance.

Anal. Calcd. for $C_{28}H_{45}O_2N$: C, 78.65; H, 10.60. Found: C, 78.59; H, 10.57.

BETHESDA, MD.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

A Practical Synthesis of Thieno[3,2-*b*]pyrrole*†

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Pyrrole is converted to 3-thiocyanopyrrole (I) in 50% yield by thiocyanation with methanolic thiocyanogen at −70° or with cupric thiocyanate at 0°. Addition of excess dilute potassium hydroxide to a cold methanolic solution of bromoacetic acid and 3-thiocyanopyrrole leads to (3-pyrrolylthio)acetic acid (II), isolated as the ammonium salt in 90% yield. Under similar conditions, methyl iodide and 3-thiocyanopyrrole yield 3-(methylthio)pyrrole (Vc). Ring closure of the acid II with polyphosphoric acid furnishes 2*H*,3*H*-thieno[3,2-*b*]pyrrol-3-one (III) in 36% yield. The structure of III is proved by desulfurization with Raney nickel catalyst, which yields 2-acetylpyrrole. Reduction of III with sodium borohydride leads to thieno[3,2-*b*]pyrrole (IV) in 62% yield.

Thieno[3,2-*b*]pyrrole (IV) is an isostere of indole, having the fused thiophene ring in place of the benzene nucleus of the latter substance. The development of the chemistry of this simple, unsubstituted heterocycle may be expected to add to the fundamental knowledge of the thiophene and pyrrole systems and of interactions between them. Further, the possibility of preparing isosteres of physiologically active indole compounds from thieno[3,2-*b*]pyrrole makes the problem of devising a useful synthesis of the substance an intriguing one.

Although a synthesis of thieno[3,2-*b*]pyrrole (IV) from thiophene has been completed,[2] a great many steps were required and the final product was not obtained in a state of high purity. These difficulties prompted us to investigate the synthesis of thienopyrroles from pyrrole. Notwithstanding the well known sensitivity of pyrrole and such monosubstitution products as chloropyrrole and alkylpyrroles to air, light, and acids,[3] the readiness with which it undergoes electrophilic substitution reactions[3,4] made pyrrole an attractive raw material for the contemplated syntheses.

Thiocyanation appeared to be the most promising method for affixing a suitably substituted sulfur atom to the pyrrole ring. Numerous examples of thiocyanation of active aromatic systems under mild conditions are known.[5] Thiocyanation of carbethoxydimethylpyrroles has been reported.[6] Thiocyanation of pyrrole itself with ammonium thiocyanate and bromine has been reported to yield a dithiocyano derivative of undetermined structure.[6]

The fact that most reagents attack pyrroles at an unsubstituted α-position in preference to an unsubstituted β-position has been accounted for on the basis of the resonance theory.[4] However, recent molecular orbital calculations[7] indicate that the π-electron density in pyrrole is higher at the β-positions than at the α-positions. If, in the transition state, the pyrrole ring and an electrophilic reagent

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[*] This paper is a contribution in honor of Lyndon F. Small, former Editor of the Journal.

[†] For a preliminary communication on this subject, see D. S. Matteson and H. R. Snyder, *J. Am. Chem. Soc.*, **79**, 3610 (1957).

(1) National Science Foundation Predoctoral Fellow, 1954–1957.

(2) H. R. Snyder, L. A. Carpino, J. F. Zack, Jr., and J. F. Mills, *J. Am. Chem. Soc.*, **79**, 2556 (1957).

(3) H. Fischer and H. Orth, *Die Chemie des Pyrrols*, Akademische Verlagsgesellschaft m. b. H., Leipzig, 1934, Vol. I, pp. 23–24, 37–38, 79.

(4) R. C. Elderfield, *Heterocyclic Compounds*, John Wiley and Sons, Inc., New York, 1950, Vol. I, pp. 300–301.

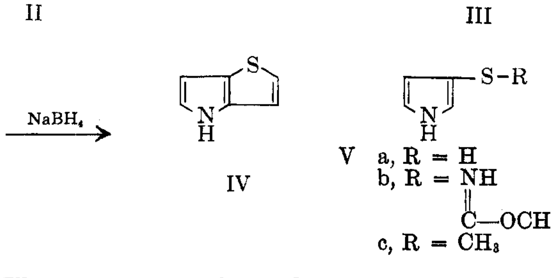
(5) J. L. Wood, *Org. Reactions*, **3**, 240–266 (1946).

(6) P. Pratesi, *Atti reale accad. Lincei*, **16** (6) **9**, 443 (1933); *Chem. Zentralblatt* I, 2815 (1933).

(7) R. D. Brown, *Australian J. Chem.*, **8**, 100 (1955).

are far enough apart that little bond-making has occurred, the π-electron density should determine the orientation and the substituent should enter the β-position. On the other hand, if the pyrrole ring and the reagent are near enough in the transition state to form a bond the π-electrons must be localized, and since localization requires less energy at the α-position the substituent should enter at this point. Thus, according to the molecular orbital view, pyrrole could be attacked preferentially at the α-position by certain electrophilic reagents, but at the β-position by others.

When pyrrole was treated with cupric thiocyanate[8] in methanol at 0°, thiocyanation was apparently complete in a few minutes, and a substance shown to be 3-thiocyanopyrrole (I) by conversion to the bicyclic compounds III and IV described below was obtained in moderate yield. Isolation of 3-thiocyanopyrrole presented no difficulty, as the compound crystallized when the reaction mixture was poured onto ice; saturation of the solvent phase with sodium chloride increased the amount of crystalline material recovered. The use of cupric thiocyanate, although convenient for small-scale exploratory experiments, has disadvantages for the preparation of large amounts of an intermediate for synthetic use. At −75° a methanolic solution of thiocyanogen, conveniently prepared from potassium thiocyanate and bromine, reacts rapidly and exothermically with pyrrole; 3-thiocyanopyrrole (I) was obtained in yields equal to those from the cupric thiocyanate procedure.



The most commonly used process for the conversion of thiocyanates to mercaptans is reduction;[5] 2,4-dimethyl-3-mercapto-5-carbethoxypyrrole has been prepared by reduction of the thiocyanate with zinc and acetic acid.[6] Treatment of thiocyanates with sodium hydroxide usually yields disulfides,[5] but thiophenol has been obtained from phenyl thiocyanate upon treatment with sodium ethoxide.[9] Several attempts to isolate 3-mercaptopyrrole (Va) failed. Zinc and acetic acid appeared not to react with 3-thiocyanopyrrole (I) at 20°. Basic reagents, including sodium hydroxide, sodium carbonate, and liquid ammonia, rapidly decomposed 3-thiocyanopyrrole (I) to dark red materials. When 3-thiocyanopyrrole (I) was treated with a limited amount of sodium hydroxide in methanol at 0°, sodium cyanate, characterized by the infrared spectrum and conversion to the silver salt, crystallized in 83% yield. Treatment of 3-thiocyanopyrrole (I) with methanolic magnesium methoxide furnished *S*-3-pyrrolyl *O*-methyl thioimidocarbonate (Vb) in excellent yield. With basic reagents, the thioimidocarbonate Vb decomposed in the same manner as did the thiocyanate I. Although 3-thiocyanopyrrole (I) appeared unaffected by mild treatment with mineral acids, the thioimidocarbonate was attacked by dilute acetic acid; insufficient effort was expended to obtain any single hydrolysis product in good yield. A more promising route to 3-(alkylthio)pyrroles was found and attempts to isolate 3-mercaptopyrrole (Va) were abandoned.

It was found that the anion of 3-mercaptopyrrole (Va), which apparently decomposes almost as rapidly as it is formed, does have a long enough existence to displace halide ion from a moderately active alkyl halide, if the halide is present in the reaction mixture at the time the anion of Va is generated. Treatment of a methanolic solution of 3-thiocyanopyrrole (I) and methyl iodide at 0° with an excess of dilute potassium or sodium hydroxide furnished 3-(methylthio)pyrrole (Vc) in excellent yield.

Treatment of a methanolic solution of 3-thiocyanopyrrole (I) and chloroacetic, bromoacetic, or iodoacetic acid with dilute potassium hydroxide yielded (3-pyrrolylthio)acetic acid (II). Preliminary experiments, in which the calcium salt of the acid II was isolated, indicated that yields from chloroacetic acid were lower than those from bromoacetic or iodoacetic acid. When cooling in an ice-salt bath was used with large-scale preparations, neutralization at 0° of the bromoacetic acid with potassium hydroxide required a longer time than was considered desirable in view of the possible instability of either the bromoacetic acid or its anion in the reaction mixture. Accordingly, the reaction mixture was cooled in a Dry Ice–acetone bath during addition of the alkali. It appeared that potassium bromoacetate precipitated at the low temperatures and further reaction did not take place until the reaction mixture was allowed to warm to about −20°.

Since the liquid (3-pyrrolylthio)acetic acid (II) decomposed on attempted distillation, it was isolated as a salt. The calcium salt was found to be very soluble in water and difficult to purify. The pure crystalline ammonium salt was obtained in ex-

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[8] H. P. Kaufmann and K. Kuchler, *Ber.*, **67**, 944 (1934).

[9] J. Ross, *J. Am. Chem. Soc.*, **56**, 727 (1934).

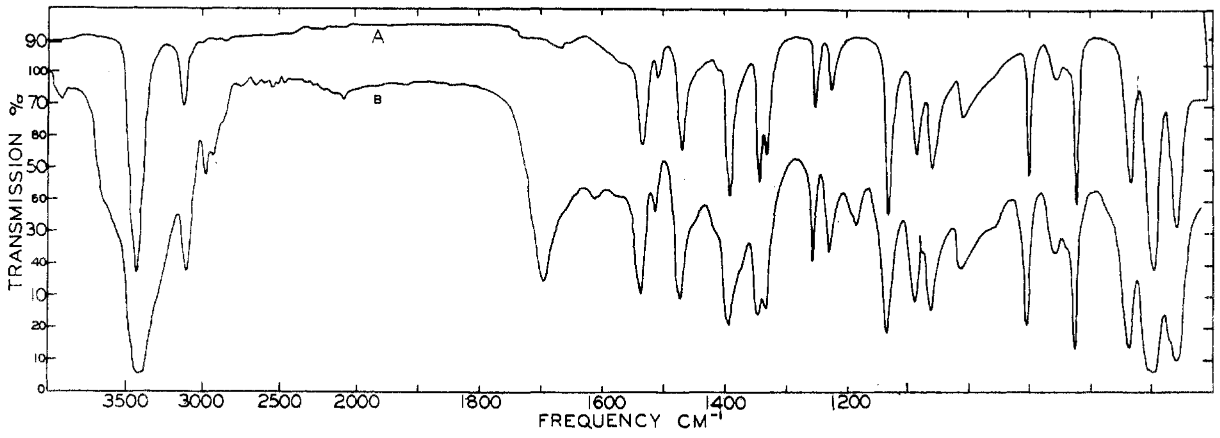

Fig. 1. Curve A: Thieno[3,2-*b*]pyrrole prepared from 2*H*,3*H*-thieno[3,2-*b*]pyrrol-3-one. Curve B: Thieno[3,2-*b*] pyrrole prepared from thieno[3,2-*b*]pyrrole-5-carboxylic acid.

cellent yield when a solution of the acid II in methylene chloride was treated with anhydrous ammonia.

Bromoacetal failed to react with 3-thiocyanopyrrole (I) under the conditions used for the reaction of methyl iodide; evidently, the anion of 3-mercaptopyrrole (Va) decomposed faster than it displaced bromide ion from this reagent. Active alkyl halides, such as phenacyl bromide, ethyl bromoacetate and chloropyruvate ion, appeared to be attacked by hydroxide ion more rapidly than was 3-thiocyanopyrrole, with the result that they also failed to give sulfides.

It was found that 2*H*,3*H*-thieno[3,2-*b*]pyrrol-3-one (III) could be prepared in fair yield by the slow addition of a dilute methylene chloride solution of (3-pyrrolylthio)acetic acid (II) to hot, stirred polyphosphoric acid.[10] A few experiments on the effect of varying the temperature were made; the optimum range appeared to be 120–130°.

Several other methods for cyclizing (3-pyrrolylthio)acetic acid (II) were tested. Trituration of the calcium salt of II with polyphosphoric acid at 80–90° for one hour yielded a small amount of the cyclic ketone III. A black tar resulted when a similar reaction mixture was heated to 120°. Triturating the reagents and allowing the mixture to stand overnight at room temperature yielded none of the ketone. Treatment of the acid II with anhydrous hydrogen fluoride for four hours yielded none of the ketone III. Attempts to prepare the acid chloride of II showed no promise. Thionyl chloride reacted vigorously with the acid II, even in ether solution at −70°, or with the calcium salt, to form black polymeric material. Excess phosphorus oxychloride formed red polymeric material from the calcium salt of II.

Desulfurization of 2*H*,3*H*-thieno[3,2-*b*]pyrrol-3-one (III) with Raney nickel catalyst yields 2-acetylpyrrole. The structure of 2-acetylpyrrole, m.p. 90°, has been proved by degradation;[11] furthermore, 3-acetylpyrrole, m.p. 116°, has been synthesized *via* a ring closure.[12] Other structural features of the ketone III are confirmed by the infrared spectrum (Nujol). The presence of an NH group is indicated by a strong band at 3140 cm.$^{-1}$; every sulfur-substituted pyrrole in the present series exhibits a similar band between 3100 and 3500 cm.$^{-1}$. A carbonyl group conjugated with an electron-donating system is indicated by a strong absorption band at 1635 cm.$^{-1}$ in the infrared spectrum of the ketone III. The high melting point of the compound III and its stability to air and to mild acids are consistent with the properties of other acylpyrroles, but not with those expected of the tautomeric enol form. The 2*H*,3*H*-thieno-[3,2-*b*]pyrrol-3-one structure thus appears to be the better representation of the compound.

Sodium borohydride in methanol reduces 2*H*,3*H*-thieno[3,2-*b*]pyrrol-3-one (III) to thieno[3,2-*b*]-pyrrole (IV) in good yield. Liquid IV darkened after a few hours' exposure to air and light, but in a tightly stoppered container in the refrigerator, solid IV appeared to be stable for weeks. The odor of IV was mild and resembled that of indole; with Ehrlich's reagent, IV gave a deep blue color. The infrared spectra of the analytical sample of the above material (IV) (smear) and a less pure sample synthesized from thiophene[2] are shown in Fig. 1. The major impurity in the latter sample is evidently thieno[3,2-*b*]pyrrole-5-carboxylic acid, from which the sample was prepared by decarboxylation.

EXPERIMENTAL[13]

3-Thiocyanopyrrole (I). Even in very dilute solutions, 3-thiocyanopyrrole (I) reacts with human skin to form deep

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[10] The polyphosphoric acid was generously supplied by the Victor Chemical Works, 141 W. Jackson Blvd., Chicago 4, Ill.

[11] G. Ciamician and P. Silber, *Ber.*, 20, 2594 (1887).

[12] I. J. Rinkes, *Rec. trav. chim.*, 57, 423 (1938).

[13] All melting points are corrected. Microanalyses were performed by J. Nemeth and his associates. Infrared spectra were determined by James Brader and his associates. Ultraviolet spectra were determined by M. S. Chao.

red stains, and more concentrated solutions cause a burning or itching sensation. For this reason, one should always wear rubber gloves when handling 3-thiocyanopyrrole. If contact with the skin is suspected, the affected area should be washed immediately with soap and water and then treated with 3% hydrogen peroxide. This treatment is usually sufficient to prevent serious staining; however, once the red color has formed, it remains until the stained skin has been replaced.

One hundred twenty-five milliliters of methanol was chilled in a Dry Ice-acetone bath, and 159.8 g. (1 mole) of bromine was added. Two hundred grams (2.06 moles) of potassium thiocyanate (free from large lumps) and 250 ml. of methanol were placed in a flask fitted with a mechanical stirrer and an alcohol thermometer, then chilled in a Dry Ice-acetone bath to below −75°. The mixture was stirred vigorously and kept below −60° while the chilled bromine solution was added from a dropping funnel. The solution of thiocyanogen prepared in this manner was light yellow and contained suspended material, presumably potassium bromide.

A solution of 67.1 g. (1 mole) of redistilled pyrrole in 250 ml. of methanol was chilled to −75°. The thiocyanogen solution described above, also chilled to −75°, was stirred very vigorously while the cold pyrrole solution was added as rapidly as possible through a powder funnel. Within a few seconds after the addition of the pyrrole, the temperature of the reaction mixture rose to between −40° and −30°, then began to fall. The cooling bath was removed and the mixture was stirred until it warmed to −25°. It was then poured onto approximately 2 kg. of crushed ice, and 300 g. of sodium chloride was added. The mixture was agitated occasionally for about 0.5 hr., and the 3-thiocyanopyrrole (I) was collected on a Buchner funnel large enough (5–6 in.) to accommodate the unmelted ice. The solids on the funnel were washed freely with water; most of the remaining ice was removed mechanically and the product was rinsed from it. The crude 3-thiocyanopyrrole (I), which darkened on standing, was dried in a vacuum desiccator. The dry material was recrystallized from 100 ml. of methylene chloride and 500 ml. of methylcyclohexane in the following manner. The solid was dissolved in the methylene chloride, about half the methylcyclohexane was added, and the solution was warmed to about 40°. Magnesium sulfate and Darco were added, the solution was filtered, and the solid residue was washed with methylcyclohexane. Since the solution was still red, the treatment with magnesium sulfate and Darco was repeated. The nearly colorless solution was cooled to just above the temperature at which cloudiness appeared, seeded, and left at 0° overnight. The mixture was finally chilled for a half-hour in an ice-salt bath before the long, colorless needles were collected and dried at room temperature. The yield of 3-thiocyanopyrrole (I), m.p. 40–44°, was 62 g. (50%). By chilling the mother liquor to −70°, additional crude product was obtained that weighed 4 g. after recrystallization, m.p. 40–44°.

The infrared spectrum of a sample of 3-thiocyanopyrrole (I) (in carbon tetrachloride) prepared by the above method was identical to that of a sample prepared from cupric thiocyanate and pyrrole.

Thiocyanation of pyrrole with cupric thiocyanate. A solution of 6.71 g. (0.1 mole) of pyrrole in 75 ml. of methanol was kept at 0–5° with an ice bath and stirred under nitrogen while 0.2 mole (on the basis of a thiocyanogen analysis) of cupric thiocyanate was added in several portions over a period of a few minutes. Stirring at 0–5° was continued 50 min., the cuprous thiocyanate was removed by filtration and washed with 50 ml. of methanol, and the filtrate was poured onto approximately 300 g. of crushed ice. One hundred grams of sodium chloride was added. The solids were collected and the 3-thiocyanopyrrole (I) was washed from the excess sodium chloride with 225 ml. of warm methylcyclohexane. After treatment with Darco, the solution was cooled and seeded, and crystallization was allowed to proceed at 0° overnight. The yield of 3-thiocyanopyrrole (I), m.p. 40–43°, was 5.83 g. (47%). An analytical sample was recrystallized twice from methylcyclohexane, m.p. 41.5–43°.

Anal. Calcd. for $C_5H_4N_2S$: C, 48.36; H, 3.25; N, 22.55. Found: C, 48.72; H, 3.15; N, 22.80.

S-3-Pyrrolyl O-methyl thioimidocarbonate (Vb). Under nitrogen, 1.87 g. (0.075 mole) of magnesium turnings was dissolved in 125 ml. of reagent grade methanol. The solution of magnesium methoxide, which contained a small amount of precipitated magnesium hydroxide, was cooled in an ice-salt bath and 6.2 g. (0.05 mole) of 3-thiocyanopyrrole (IX) was added. After the 3-thiocyanopyrrole was dissolved, the mixture was allowed to stand for 1 hr. in the ice-salt bath. The mixture was poured into 500 ml. of water and 200 ml. of ether, and sufficient solid carbon dioxide was added to dissolve the precipitated magnesium hydroxide. The ether phase was separated and the aqueous phase was extracted with additional portions of ether. The combined ether solutions were dried over magnesium sulfate and the ether was evaporated under reduced pressure. The residue sublimed at 75°, 0.1 mm. The yield of *S*-3-pyrrolyl *O*-methyl thioimidocarbonate (Vb) (m.p. 75–80°, softens at 65°) was 6.8 g. (87%). An analytical sample was recrystallized from toluene, resublimed, recrystallized from aqueous methanol and again resublimed (55–65°/0.1 mm.), m.p. 77–80°.

Anal. Calcd. for $C_6H_8N_2OS$: C, 46.14; H, 5.16; N, 17.94. Found: C, 46.14; H, 5.07; N, 17.78.

3-(Methylthio)pyrrole (Vc). A solution of 6.21 g. (0.05 mole) of 3-thiocyanopyrrole (I) and 8.5 g. (0.06 mole) of methyl iodide in 50 ml. of methanol was cooled below 0° in an ice-salt bath and stirred under nitrogen during the addition of a solution of 7.9 g. (0.12 mole) of 85% potassium hydroxide in 20 ml. of water and 20 ml. of methanol over a period of 10 min. The cooling bath was removed and stirring was continued for 1.5 hr. The excess alkali was neutralized with solid carbon dioxide and the reaction mixture was poured into a solution of 100 g. of sodium chloride in 500 ml. of water. The organic material was extracted with three 50-ml. portions of methylene chloride; the solution was dried over potassium carbonate and the solvent was evaporated under reduced pressure. The residue was distilled; the yield of 3-(methylthio)pyrrole (Vc), b.p. 60–66° at 3.5 mm., was 5.1 g. (90%). An analytical sample was redistilled, b.p. 88–89° at 12 to 13 mm.

Anal. Calcd. for C_5H_7NS: C, 53.06; H, 6.24; N, 12.38. Found: C, 52.22; H, 6.27; N, 12.19.

Ammonium (3-pyrrolylthio)acetate (ammonium salt of II). A solution of 62.1 g. (0.5 mole) of 3-thiocyanopyrrole (I) and 83.5 g. (0.6 mole) of bromoacetic acid in 500 ml. of methanol was cooled below −50° in a Dry Ice-acetone bath and stirred rapidly during the addition of a solution of 123 g. (1.87 moles) of 85% potassium hydroxide in 500 ml. of 50% aqueous methanol over a period of 10 min. The cooling bath was removed and stirring was continued for 2 hr.; at the end of this time the mixture had warmed nearly to room temperature. The excess alkali was neutralized (*p*H 8) with solid carbon dioxide and the solvent was evaporated under reduced pressure in a warm water bath (a steam bath caused excessive bumping) until no visible liquid remained. Five hundred milliliters of methylene chloride was added to the solid residue, and the mixture was stirred while 375 ml. of ice-cold 4*N* hydrochloric acid was added at a rate such that carbon dioxide evolution was kept under control. After separation of the methylene chloride phase, the aqueous phase was extracted with two 250-ml. portions of methylene chloride. The combined methylene chloride solutions were dried over magnesium sulfate, treated with Darco, and filtered. An excess of anhydrous ammonia was bubbled into the solution and ammonium (3-pyrrolylthio)acetate (the ammonium salt of II) crystallized. The yield was 78 g. (90%); m.p. 127–133°, softens at 117°. For preparation of an analytical sample, the ammonium salt was treated with 1*N* hydrochloric acid and the free acid II was extracted with methylene chloride. The methylene chloride solution was dried over magnesium sulfate and the ammonium salt of II crystallized upon treatment with anhydrous ammonia, m.p. 125–133°.

Anal. Calcd. for $C_6H_{10}N_2O_2S$: C, 41.35; H, 5.78; N, 16.08. Found: C, 41.59; H, 5.73; N, 15.77.

The calcium salt of II was prepared from the acid II and calcium hydroxide. An analytical sample was recrystallized twice, with much loss of material, from a small amount of water; m.p. 112–120° (dec.). The salt apparently contained two moles of water of crystallization.

Anal. Calcd. for $C_{12}H_{16}N_2O_6S_2Ca$: C, 37.1; H, 4.15; N, 7.20. Found: C, 37.25; H, 4.19; N, 6.95.

The methyl ester of II was prepared in 20% yield by refluxing a dilute methanolic solution of the ammonium salt of II with zinc chloride for 20 hr. The ester was purified by extraction followed by distillation in a sublimation apparatus at 0.1 mm., 80°; the liquid so obtained was submitted for analysis.

Anal. Calcd. for $C_7H_9NO_2S$: C, 49.10; H, 5.30; N, 8.18. Found: C, 49.01; H, 5.30; N, 8.31.

2H,3H-Thieno[3,2-b]pyrrol-3-one (III). Two hundred and fifty milliliters of methylene chloride and 17.42 g. (0.1 mole) of ammonium (3-pyrrolylthio)acetate (ammonium salt of II) were shaken with 30 ml. of ice-cold 6*N* hydrochloric acid. After separation, the aqueous phase was further extracted with two 250-ml. portions of methylene chloride. The combined methylene chloride solutions were treated with magnesium sulfate and Darco and filtered; the magnesium sulfate was washed with 150 ml. of methylene chloride, which was then combined with the filtrate. Four hundred grams of polyphosphoric acid[10] was heated to 120–123° and stirred very vigorously while the methylene chloride solution of (3-pyrrolylthio)acetic acid (II) was allowed to drop directly into the most vigorously agitated region of the polyphosphoric acid over a period of 50 min.; the methylene chloride vapor was allowed to escape (into the hood) through an open neck of the flask. When the addition was complete, the reaction mixture was allowed to cool below 100°; 1200 ml. of water and 750 ml. of ethyl acetate were stirred mechanically while the reaction mixture was added slowly, and stirring was continued for 0.5 hr. afterwards. The aqueous layer, the emulsion, and the ethyl acetate layer were separated. The aqueous layer was extracted with 250 ml. of ethyl acetate; 300 g. of sodium chloride was added, and the aqueous solution was further extracted with two 250 ml. portions of ethyl acetate. The emulsion fraction was neutralized with sodium bicarbonate, warmed on the steam bath, and extracted with three 100-ml. portions of ethyl acetate. The combined ethyl acetate solutions were washed with aqueous sodium bicarbonate until free of acid and dried over magnesium sulfate. The ethyl acetate was evaporated under reduced pressure and the residue was sublimed twice at 0.1 mm. at about 120°. The yield of 2*H*,3*H*-thieno[3,2-*b*]pyrrol-3-one (III) (m.p. 183–188.5°, softens 140°) was 5.0 g. (36%). An analytical sample was resublimed twice, recrystallized twice from aqueous dimethylformamide, again sublimed twice and, after treatment with Darco, recrystallized from methanol; m.p. 187–190°, softens slightly at 165°; ultraviolet spectrum (in 95% ethanol): λ_{max} 330 mμ, ϵ_{max} 7400, λ_{min} 303, ϵ_{min} 3900, λ_{max} 279, ϵ_{max} 16,000, λ_{min} 236, ϵ_{min} 500.

Anal. Calcd. for C_6H_5NOS: C, 51.78; H, 3.62; N, 10.07. Found: C, 52.04; H, 3.82; N, 10.14.

Desulfurization of 2H,3H-thieno[3,2-b]pyrrol-3-one (III). A solution of 0.28 g. (2 millimoles) of 2*H*,3*H*-thieno[3,2-*b*]pyrrole-3-one (III) in approximately 35 ml. of 95% ethanol was heated under reflux with about 2.5 g. of Raney nickel catalyst (W6) for 1 hr. The solution was filtered; the catalyst was washed freely with ethanol, and the washings were combined with the filtrate. The ethanol was evaporated under reduced pressure and the residue was sublimed. The yield of crude acetylpyrrole was 0.06 g. After recrystallization from water, the yield was 23 mg. (10%); m.p. 89–91°, not depressed upon admixture with an authentic sample.[14] The authentic sample of 2-acetylpyrrole was prepared from pyrrolylmagnesium bromide and acetyl chloride; Oddo[14] used pyrrolylmagnesium iodide. The infrared spectra of the sample of 2-acetylpyrrole prepared by the desulfurization described above and of the authentic sample (in chloroform) were identical.

Thieno[3,2-b]pyrrole (IV). A solution of 1.39 g. (0.01 mole) of 2*H*,3*H*-thieno[3,2-*b*]pyrrol-3-one (III) and 1.5 g. of sodium borohydride in 50 ml. of methanol was refluxed 16 hr. under nitrogen. The reaction mixture was poured into 200 ml. of 15% aqueous sodium chloride solution and the product was extracted with three 50-ml. portions of methylene chloride. The methylene chloride solution was dried over magnesium sulfate, the solvent was evaporated under reduced pressure, and the residue was sublimed.

Thieno[3,2-*b*]pyrrole (IV) sublimed rapidly at 60–70°, 0.1 mm.; after a small amount had condensed on the cold finger as an oil, it was induced to crystallize by rubbing it with a spatula that had been chilled with Dry Ice, and when sublimation was resumed the rest of the material condensed as a solid. The yield was 0.76 g. (62%). A considerable amount of less volatile residue remained; after sublimation at 120°, 0.1 mm., followed by recrystallization from methanol, 0.31 g. of the ketone III, m.p. 184–190°, was obtained. The infrared spectrum of this sample (Nujol) was similar to that of the analytical sample of III; small differences were attributed to impurities. The yield of thieno[3,2-*b*]pyrrole (IV) based on the ketone III consumed was 80%. An analytical sample of IV was recrystallized from ether-pentane at −70° and resublimed three times, m.p. 25–28°; u.v. (in 95% ethanol): λ_{max} 260 mμ, ϵ_{max} 11,800, λ_{min} 233, ϵ_{min} 4900.

Anal. Calcd. for C_6H_5NS: C, 58.50; H, 4.09; N, 11.38. Found: C, 58.60; H, 4.27; N, 11.32.

URBANA, ILL.

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(14) B. Oddo, *Ber.*, **43,** 1012 (1910).