

considerably more positive potentials, also have been studied. Again, plots of  $\tau^{1/2}$  vs. concentration show the expected linearity for a chronopotentiometric reaction which is proceeding independent of any previous electrode process. Oxidation reactions with potentials as high as +1.0 v. appear possible with the mercury chloride electrode.

The electrode can also be operated in a more conventional polarographic sense. The halide film is formed by application of an anodic potential for a short period of time. The compound to be oxidized is then introduced and the voltage scanned in an increasing anodic direction using a Leeds and Northrup Electrochemograph. With DPP and ferrocyanide, typical quiet pool polarograms<sup>2</sup> are obtained whose peak heights are proportional to concentration. Investigations are in progress to evaluate the effect of stirring and changing scan rate on peak currents as well as application of the technique to the hanging drop electrode.

A detailed report of this work will be published shortly.

(2) C. A. Streuli and W. D. Cooke, *Anal. Chem.*, **25**, 1691 (1953).

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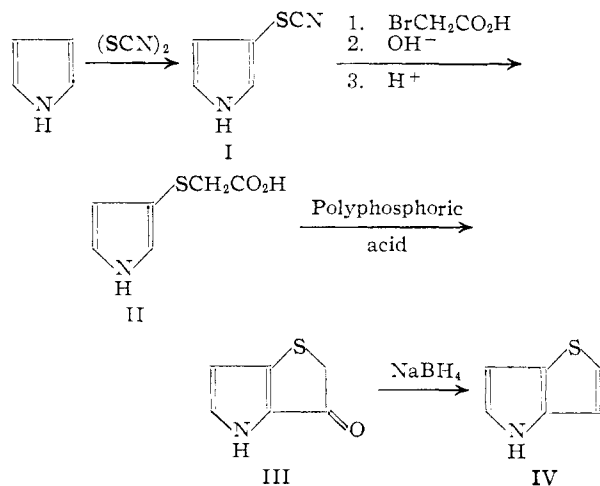
THEODORE KUWANA  
RALPH N. ADAMS

RECEIVED MAY 20, 1957

#### A PRACTICAL SYNTHESIS OF THIENO[3,2-*b*]PYRROLE

Sir:

We have synthesized thieno[3,2-*b*]pyrrole (IV) from pyrrole in four steps. The new synthesis makes this isostere of indole readily available for conversion to various derivatives of biological interest.



From analogous electrophilic substitutions and resonance theory,<sup>1</sup> thiocyanation of pyrrole was expected to occur preferentially at the 2-position. However, recent molecular orbital calculations<sup>2</sup> indicate that the orientation of substitution in the pyrrole nucleus cannot be predicted unambiguously;  $\pi$ -electron localization energy favors 2-substitution

(1) R. C. Elderfield, "Heterocyclic Compounds," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 300-301.

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

but  $\pi$ -electron densities favor 3-substitution. When the reaction was carried out by rapidly mixing cold ( $-75^\circ$ ) methanolic solutions of pyrrole and thiocyanogen (prepared at  $-60^\circ$  from potassium thiocyanate and bromine), the product collected after pouring the reaction mixture onto ice and salt, and amounting to 50% yield after recrystallization from methylene chloride-methylcyclohexane, was 3-thiocyanopyrrole (I), m.p.  $40-44^\circ$ . *Anal.* Calcd. for  $C_4H_4N_2S$ : C, 48.36; H, 3.25; N, 22.55. Found: C, 48.72; H, 3.15; N, 22.80.

Treatment of a cold methanolic solution of I and bromoacetic acid with an excess of potassium hydroxide in aqueous methanol furnished in 90% yield (3-pyrrolylthio)-acetic acid (II), characterized as the ammonium salt which crystallized when anhydrous ammonia was introduced into a methylene chloride solution of the acid. The salt melted at  $127-133^\circ$  (dec.). *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. Addition of a dilute methylene chloride solution of II over 1 hr. to vigorously stirred polyphosphoric acid at  $125^\circ$ , followed by dilution of the mixture with water, extraction with ethyl acetate and sublimation of the product, yielded 36% of 2H,3H-thieno[3,2-*b*]pyrrol-3-one (III), m.p.  $183-188.5^\circ$ . The analytical sample, m.p.  $187-190^\circ$ , was prepared by a series of recrystallizations and resublimations. *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. The infrared spectrum of III (Nujol) contained strong bands at 1635 (C=O) and  $3150\text{ cm}^{-1}$  (NH). The structure of III was proved by desulfurization with Raney nickel catalyst to 2-acetylpyrrole, shown to be identical with an authentic sample<sup>3</sup> by infrared spectra (chloroform), m.p. and mixture m.p. Treatment of III with sodium borohydride in methanol yielded 62% of sublimed thieno[3,2-*b*]pyrrole (IV), m.p., after further purification,  $25-28^\circ$ . *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. The infrared spectrum of IV (smear) was identical with that<sup>4</sup> of a less pure sample prepared<sup>5</sup> unequivocally from thiophene, except for bands due to a carboxylic acid present as an impurity in the latter sample.

(3) (a) B. Oddo, *Ber.*, **43**, 1012 (1911); (b) structure proof of 2-acetylpyrrole, G. Ciamician and P. Silber, *ibid.*, **20**, 2594 (1887).

(4) J. F. Zack, Ph.D. Thesis, University of Illinois, 1956.

(5) H. R. Snyder, L. A. Carpino, J. F. Zack and J. F. Mills, *This Journal*, **79**, 2556 (1957).

(6) National Science Foundation Predoctoral Fellow, 1954-1957.

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#### STUDIES IN THE SYNTHESIS OF THE ANTIRACHITIC VITAMINS. IV. THE SYNTHESIS OF A BIOLOGICALLY ACTIVE VITAMIN D HOMOLOG

Sir:

We wish to report the synthesis of 1-cholestanylidene-2-(5'-methoxy-2'-methylene-1'-cyclohexyli-