

The addition of dibromocarbene to 1,4-cyclohexadiene<sup>9</sup> afforded 7,7-dibromonorcar-3-ene (II), m.p. 36.8–37.0°; *Anal.* Calcd. for C<sub>7</sub>H<sub>8</sub>Br<sub>2</sub>: C, 33.5; H, 3.2; Br, 63.3. Found: C, 33.0; H, 3.5; Br, 63.0. Oxidation converted (II) into *cis*-3,3-dibromocyclopropane-1,2-diacetic acid (III), m.p. 179.4–181.2°; *Anal.* Calcd. for C<sub>7</sub>H<sub>8</sub>O<sub>4</sub>Br<sub>2</sub>: C, 26.8; H, 2.5; Br, 50.5; neut. equiv., 158. Found: C, 26.5; H, 2.2; Br, 50.5; neut. equiv., 159. Hydrogenolysis of (III) gave *cis*-cyclopropane-1,2-diacetic acid (IV), m.p. 131–133°; *Anal.* Calcd. for C<sub>7</sub>H<sub>10</sub>O<sub>4</sub>: C, 53.3; H, 6.4; neut. equiv., 79.4. Found: C, 53.0; H, 6.2; neut. equiv., 79.6. The monomethyl ester chloride of (IV) on treatment with *n*-hexylcadmium followed by alkaline hydrolysis afforded DL-*cis*-6-keto-3,4-methylene-dodecanoic acid which was reduced<sup>10</sup> to DL-*cis*-3,4-methylenedodecanoic acid (V), b.p. 153–154° at 3 mm.; *Anal.* Calcd. for C<sub>13</sub>H<sub>24</sub>O<sub>2</sub>: C, 73.7; H, 11.4; neut. equiv., 213. Found: C, 73.6; H, 11.3; neut. equiv., 208. Conversion of (V) into DL-*cis*-9,10-methyleneoctadecanoic acid (I) was effected by procedures previously described,<sup>8,11</sup> m.p. 38.6–39.6°; *Anal.* Calcd. for C<sub>19</sub>H<sub>36</sub>O<sub>2</sub>: C, 77.0; H, 12.2; neut. equiv., 296. Found: C, 77.0; H, 12.2; neut. equiv., 298. Amide, m.p. 86.4–87.6°; *Anal.* Calcd. for C<sub>19</sub>H<sub>37</sub>ON: C, 77.2; H, 12.6; N, 4.7. Found: C, 77.0; H, 12.3; N, 5.0. Mixed melting point determinations and comparison of the infrared absorption spectra and X-ray diffraction patterns of (I) and dihydrosterculic acid demonstrated the complete identity of these compounds. The X-ray diffraction patterns of the amide of (I) and of dihydrosterculamide were identical also, and admixture of the amides did not result in a depression of the melting point. These findings establish the structure of dihydrosterculic acid.<sup>12</sup>

In connection with studies on the structure of lactobacillic acid, we have converted *cis*-cyclopropane-1,2-diacetic acid (IV) into DL-*cis*-11,12-methylene-octadecanoic acid (VI), m.p. 31.0–33.6°; Found: C, 76.5; H, 12.0; neut. equiv., 294. Amide, m.p. 84.0–85.2°; Found: C, 77.0; H, 12.6; N, 4.8. Although exhibiting an identical infrared absorption spectrum, the synthetic specimen differed from lactobacillic acid in melting point and X-ray diffraction pattern. The non-identity of lactobacillic acid (which has been shown to represent one of the stereoisomeric forms of 11,12-methyleneoctadecanoic acid<sup>13</sup>) with either *cis*- or *trans*-DL-11,12-methyleneoctadecanoic acids demonstrates clearly that lactobacillic acid must be a distinct optical isomer. Synthetic DL-*cis*-11,12-methyleneoctadecanoic acid exhibits approximately one-half the growth promoting activity of natural lactobacillic acid for *Lactobacillus del-*

*brueckii*. DL-*trans*-11,12-Methyleneoctadecanoic acid fails to support growth of this organism under identical experimental conditions.<sup>14</sup> These observations point to either D- or L-*cis*-11,12-methyleneoctadecanoic acid as the structure for lactobacillic acid.

(14) K. Hofmann and C. Panos, *J. Biol. Chem.*, **210**, 687 (1954).

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## OXIDATIONS AT MERCURY HALIDE ANODES

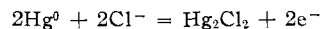
Sir:

It is well known in polarography that the anodic potential range of a mercury electrode is severely limited by oxidation of the mercury itself. A mercury electrode which can be used at highly anodic potentials might well be considered a significant advance in polarographic practice. Such an electrode has been developed as a result of chronopotentiometric studies at a mercury pool in chloride media. This electrode operates through formation of an "inert" film of mercurous chloride prior to oxidation of electroactive species in the bulk of solution. This phenomena has not been observed previously since conventional polarography at the dropping mercury electrode does not allow sufficient time for the proper film formation.

The theory of chronopotentiometry has been thoroughly reviewed by Delahay.<sup>1</sup> The equipment used in the present study was conventional in all respects. The background electrolyte was a solution 0.3 *M* in potassium chloride and 2 × 10<sup>-3</sup> *M* in hydrochloric acid (*pH* 2.7). The anodic chronopotentiogram of this solution (Hg pool area 1.47 cm.<sup>2</sup>, current 350 microamperes) shows four small waves at *ca.* +0.07, 0.5, 0.8, and 1.2 v. *vs.* S.C.E. The first wave is due to formation of mercurous chloride. The variation of *E*<sub>1/4</sub> for this wave follows closely

$$E_{Hg} = E^0 - 0.059 \log [Cl^-]/2$$

where *E*<sup>0</sup> = 0.022 v., the standard potential *vs.* S.C.E. of the reaction



Further interpretation of these potential-time patterns will be reported in the near future.

The chronopotentiogram of a 2 × 10<sup>-3</sup> *M* solution of N,N'-dimethyl-*p*-phenylenediamine (DPP) in the same background electrolyte shows an identical first wave for mercurous chloride formation. It is followed by a clearly defined wave for the oxidation of DPP. The *E*<sub>1/4</sub> of DPP (*ca.* +0.4 v.) wave is identical with that obtained at a platinum electrode under the same *pH* conditions. A plot of *τ*<sup>1/2</sup> *vs.* concentration shows excellent linearity between 4 × 10<sup>-4</sup> to 3 × 10<sup>-3</sup> *M* DPP.

The anodic oxidations of aniline, *o*-phenylenediamine and hydroquinone, which take place at

(1) P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, Inc., New York, N. Y., 1954.

(9) W. von E. Doering and A. K. Hoffmann, *THIS JOURNAL*, **76**, 6162 (1954).

(10) Huang-Minlon, *ibid.*, **68**, 2487 (1946).

(11) S. Stållberg-Stenhagen, *Archiv Kemi Mineral. Geol.*, **A22**, No. 19, 1 (1946).

(12) We wish to express our sincere appreciation to Professor G. A. Jeffrey, Department of Chemistry, University of Pittsburgh, for the X-ray studies. Details of this work will be presented in *THIS JOURNAL*.

(13) G. J. Marco and K. Hofmann, *Federation Proc.*, **15**, 308 (1956).

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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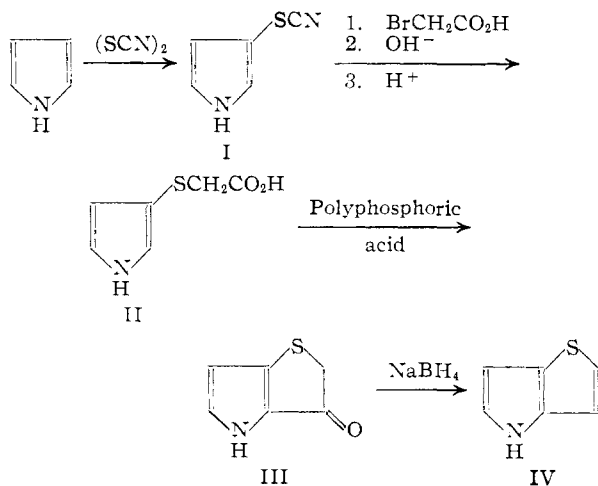
THEODORE KUWANA  
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RECEIVED MAY 20, 1957

#### 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  $\text{C}_5\text{H}_4\text{N}_2\text{S}$ : 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  $\text{C}_6\text{H}_{10}\text{N}_2\text{O}_2\text{S}$ : 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  $\text{C}_6\text{H}_5\text{NOS}$ : 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 ( $\text{C}=\text{O}$ ) 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  $\text{C}_6\text{H}_5\text{NS}$ : 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-