[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE JOHNS HOPKINS UNIVERSITY]

A Proof of Structure for 2-Bromo-3-methyl-4-carbethoxypyrrole[1]

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The scheme described for structural proof established that monobrominated 3-methyl-4-carbethoxypyrrole is predominantly 2-bromo-3-methyl-4-carbethoxypyrrole. This is indicated by the fact that iodination leads to a bromoiodopyrrole which is identical with the 2-bromo-3-methyl-4-carbethoxy-5-iodopyrrole obtained from 2-bromo-3-methyl-4-carbethoxy-5-carbomethoxypyrrole. The isomeric bromoiodopyrrole, 2-iodo-3-methyl-4-carbethoxy-5-bromopyrrole, is prepared from 2,4-dicarbethoxy-3-methyl-5-bromopyrrole. An improved synthetic route for obtaining 3-methyl-4-carbethoxypyrrole in greatly increased yield is also described. This route proceeds *via* 2,5-dicarboxy-3-methyl-4-carbethoxypyrrole and the corresponding 2,5-diiodo compound, which upon hydrogenation undergoes dehalogenation to 3-methyl-4-carbethoxypyrrole.

The previous paper[3] of this series describes an attempt to establish the structure of monobrominated 3-methyl-4-carbethoxypyrrole through formylation to the corresponding bromoaldehyde. However, the Gattermann aldehyde synthesis employing hydrogen chloride or hydrogen bromide with hydrogen cyanide was found in this instance to be complicated by either or both of two anomalous displacement reactions: (1) a halogen interchange reaction leading to the production of chloroaldehydes and (2) a debromination resulting in formation of a halogen-free aldehyde. In view of the ambiguity introduced by these unanticipated displacements, it has been necessary to devise an alternative method of structural proof.

A consideration of various reactions which might be employed to effect an unambiguous and straightforward substitution of the second α-position of monobrominated 3-methyl-4-carbethoxypyrrole led to the selection of iodination as the substitution reaction of choice. Iodine, although a relatively mild reagent, is nevertheless capable of reaction with many pyrroles at room temperature. It was felt, moreover, that the reaction might be carried out in the presence of silver oxide, a substance which tends to prevent the development both of high acidity and of high halide ion concentration during the course of the reaction. This latter consideration is important because hydrogen halides almost certainly play a key role in bringing about both of the anomalous displacements observed[3] during the previously attempted Gattermann aldehyde synthesis.

Iodination of 2-bromo-3-methyl-4-carbethoxypyrrole (I) would be expected to yield bromoiodopyrrole II, while 3-methyl-4-carbethoxy-5-bromopyrrole should under similar conditions afford III. Since neither bromoiodopyrrole II nor its isomer III was known at the outset of this investigation each had to be synthesized by an independent method. The synthesis of bromoiodopyrrole III was accomplished starting from 2,4-dicarbethoxy-3-methyl-5-bromopyrrole (IV).[4,5] Bromodiester IV underwent alkaline hydrolysis to give bromoacid V, which upon iodination in aqueous bicarbonate solution afforded 2-iodo-3-methyl-4-carbethoxy-5-bromopyrrole (III). Hydrogenation of bromoiodopyrrole III produced 3-methyl-4-carbethoxypyrrole (VI)[6,7] thus proving that it is the 2- rather than the 4-carbethoxy group which is attacked during the alkaline hydrolysis of IV.

An analogous synthesis of bromoiodopyrrole II was attempted starting from 2,4-dicarbethoxy-3-methyl-5-carboxypyrrole (VII).[5,8a] Pyrrole acid VII underwent simultaneous decarboxylation and iodination to afford the iododiester VIII. Pyrrole VIII was in turn saponified to an iodoacid which has been assigned structure IX solely upon the basis of presumed analogy with the alkaline hydrolysis of IV to bromoacid V. Bromination of the iodoacid led to an impure product, the carbon analysis of which was significantly lower than that calculated for the anticipated bromoiodopyrrole. This result pointed up the necessity of devising an alternative synthetic route to bromoiodopyrrole II, and, consequently, no attempt was made to prove the structure of the iodoacid.

The synthetic approach to bromoiodopyrrole II which was ultimately successful proceeded from the 2-bromo-3-methyl-4-carbethoxy-5-carbomethoxypyrrole (XII) of Corwin and Straughn.[8b] This bromoester upon alkaline hydrolysis afforded bromoacid XIII, and subsequent iodination provided the desired 2-bromo-3-methyl-4-carbethoxy-5-iodopyrrole (II).

Iodination of monobrominated 3-methyl-4-carbethoxypyrrole in the presence of silver oxide afforded after purification of the crude product a 53% yield of rather pure 2-bromo-3-methyl-4-carbethoxy-5-iodopyrrole (II). Admixture of this product with bromoiodopyrrole II from bromoacid XIII caused no melting point depression, thus indicating identity of the two products. Consequently, monobrominated 3-methyl-4-carbethoxypyrrole is at least predominantly 2-bromo-3-methyl-4-carbethoxypyrrole (I) rather than the 5-bromo isomer.

The fact that the same product is obtained from iodination of either I or XIII also constitutes a proof of structure for bromoacid XIII. If the ethanolic alkaline hydrolysis to which XII was subjected had provided the 4-carboxy-5-carbethoxy isomer of XIII through ester interchange, then subsequent iodination would have produced 2-

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[1] Studies in the Pyrrole Series. XXIV. Paper XXIII, A. H. Corwin and G. G. Kleinspehn, THIS JOURNAL, **75**, 2089 (1953).

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[5] A. H. Corwin, W. A. Bailey and P. Viohl, THIS JOURNAL, **64**, 1272 (1942).

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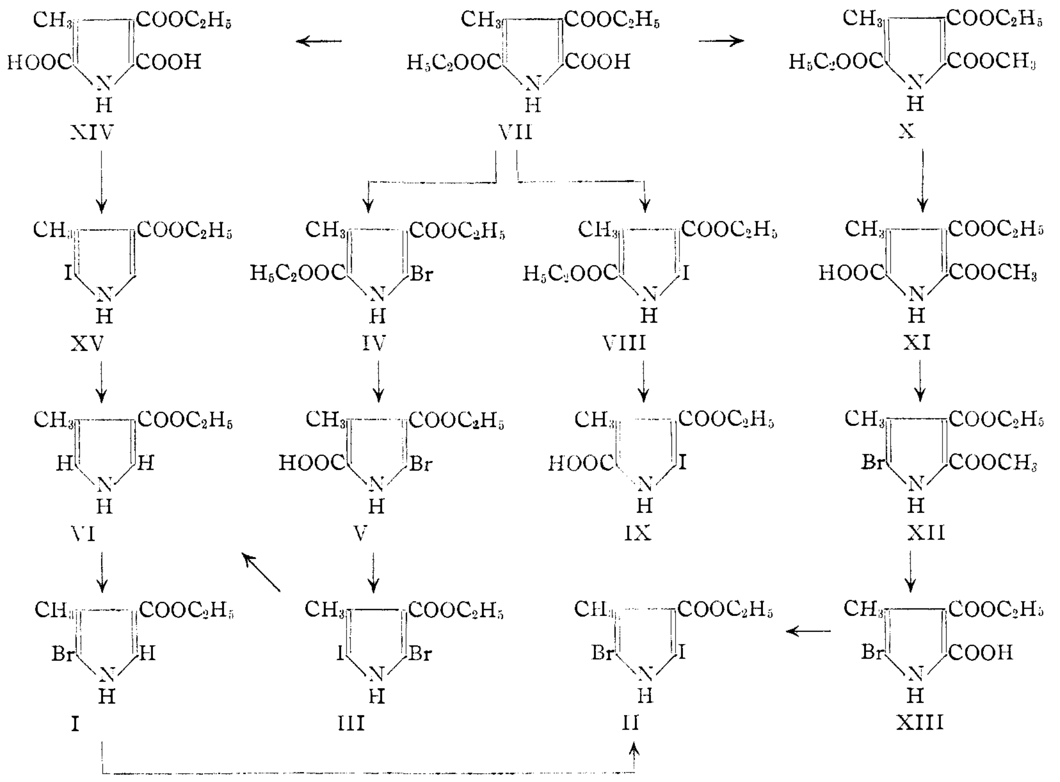
[7] A. H. Corwin and P. Viohl, THIS JOURNAL, **66**, 1145 (1944).

[8] A. H. Corwin and J. L. Straughan, *ibid.*, **70**, (a) 1418, (b) 1419, (c) 2969, (d) 2970 (1948).



bromo-3-methyl-4-iodo-5-carbethoxypyrrole, a substance which could not conceivably result from two consecutive halogenations of 3-methyl-4-carbethoxypyrrole.

During the course of this work an improved synthetic route to 3-methyl-4-carbethoxypyrrole (VI) was devised. Previously accessible from 2,4-dicarbethoxy-3-methyl-5-carboxypyrrole (VII) by a four-step process[5,7] in 32% over-all yield, it is now obtainable from VII in 66% yield *via* 2,5-dicarboxy-3-methyl-4-carbethoxypyrrole (XIV)[8b,8d] and the corresponding 2,5-diiodo compound (XV).

Acknowledgment.—The authors wish to acknowledge the consultation of Dr. James L. A. Webb of Southwestern at Memphis, whose success with the iodinative decarboxylation reaction[9] prompted our use of the reaction in carrying out this structural proof.

Experimental

All melting points were determined on the Fisher–Johns melting point apparatus.

2,4-Dicarbethoxy-3-methyl-5-carboxypyrrole (VII).[5,8a]—This substance was prepared by the method of Corwin, Bailey and Viohl[5] as modified by Corwin and Straughn.[8a] The crude product was recrystallized at least twice from 95% ethanol. The yield of crude product ranges from 65 to 80% of theory in runs employing from 250 g. down to 5 g., respectively, of 2,4-dicarbethoxy-3,5-dimethylpyrrole.

2,4-Dicarbethoxy-3-methyl-5-bromopyrrole (IV).[4,5]—The procedure below describes the bromination of VII in methanolic solution in the presence of excess sodium bicarbonate. It is more rapid and provides IV in better yield than does the procedure of Corwin, Bailey and Viohl[5] upon which it is based.

To a solution of 13.2 g. of 2,4-dicarbethoxy-3-methyl-5-carboxypyrrole in 110 ml. of hot absolute methanol was added 12.0 g. of sodium bicarbonate. After the mixture had been cooled to nearly room temperature, a solution of 3.0 ml. of bromine in 20 ml. of absolute methanol was added with stirring during 5 to 10 minutes. The mixture was stirred an additional 5 minutes, then heated to boiling to discharge the bromine color. Upon pouring the reaction mixture into 650 ml. of ice-water, the bromopyrrole precipitated and after refrigeration was removed by filtration; yield 12.9 g. or 86% of product melting at 143–144.5°.[4,5]

2-Carboxy-3-methyl-4-carbethoxy-5-bromopyrrole (V).—To a warm solution of 14.1 g. of potassium hydroxide in 165 ml. of 95% ethanol was added 10.3 g. of once-crystallized 2,4-dicarbethoxy-3-methyl-5-bromopyrrole. The reaction mixture was heated under reflux for 5 hours, after which the condenser was removed and boiling continued for 30 minutes more to expel some of the solvent. The reaction mixture was then poured into 825 ml. of ice–water mixture, and concentrated hydrochloric acid was added to a *p*H of 2. The resulting precipitate was filtered off and taken up in minimum hot 95% ethanol. Sodium bicarbonate was then added until further addition caused no more effervescence, and the mixture was poured into 725 ml. of water. The precipitate of unchanged bromodiester was allowed to coagulate, then filtered off. Weight of recovered starting material, 1.1 g. or 11%. Acidification of the filtrate to about *p*H 2 with concentrated hydrochloric acid precipitated the bromoacid, which after being allowed to stand for some time to ensure complete precipitation was filtered off. Weight of crude V, 5.9 g. or 63% yield.

In order to ascertain whether or not the crude product might still be contaminated with starting material, a portion of the product was stirred with excess aqueous sodium bicarbonate solution. The crude product ultimately dissolved completely, then was reprecipitated by acidification. Three subsequent recrystallizations from 60% ethanol afforded the analytically pure bromoacid. The substance begins to decompose at about 185–190° and is black by 225°.

Anal. Calcd. for $C_9H_{10}O_4NBr$: C, 39.15; H, 3.65; C_2H_5O, 16.32. Found: C, 39.33; H, 3.73; C_2H_5O, 16.42.

2-Iodo-3-methyl-4-carbethoxy-5-bromopyrrole (III).—Five hundred sixty-four milligrams of the bromoacid V, which had previously been recrystallized once from 60% ethanol, was dissolved by long stirring with a solution of 1.25 g. of sodium bicarbonate in 35 ml. of water. To this was then added during 15 minutes with stirring a solution of 533 mg. of iodine and 1.4 g. of potassium iodide in 15 ml. of water. Stirring was continued for a short period, and the bromoiodopyrrole was filtered off and washed with water. The yield of crude product thus obtained in one run

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(9) J. L. A. Webb, *J. Org. Chem.*, unpublished.

amounted to 93%. Subsequent purification proved difficult. Frequently even after several recrystallizations, the product would still melt over a 10–15° range beginning at 133–134°. Purification was ultimately achieved as follows. The crude product was stirred for some time with aqueous 1% sodium hydroxide solution, filtered, then reprecipitated from the filtrate by acidification with acetic acid. After recrystallizing several times both from ethanol–water and from isoöctane a pure product melting at 151.5–152.5° with decomposition was obtained. The substance melted with decomposition at a lower temperature when observed on a very brightly illuminated hot stage and thus appears to be light-sensitive.

Anal. Calcd. for $C_8H_9O_2NBrI$: C, 26.84; H, 2.53; C_2H_5O, 12.59. Found: C, 26.94; H, 2.83; C_2H_5O, 12.40.

Hydrogenation of III to 3-Methyl-4-carbethoxypyrrole (VI).—Six hundred forty-five milligrams of 2-iodo-3-methyl-4-carbethoxy-5-bromopyrrole, 0.27 g. of 10% palladium on Norit and 0.20 g. of magnesium oxide were placed in a semimicro hydrogenation vessel with 5 to 6 ml. of absolute methanol. Shaking was begun at a pressure of 17.6 lb. hydrogen (2.9 lb. gage). After 29 hours 3 drops of aqueous 0.1 *N* sodium thiosulfate solution was added to prevent reoxidation of the iodide ion, and the catalyst was removed by suction filtration, then gravity filtration. The filtrate and methanol washes were concentrated *in vacuo* to about 2 ml. without heating. Subsequent addition of 20 ml. of ice-water caused oiling out, then rapid solidification of the crude product; weight 203 mg., m.p. 60–61.5°. Two recrystallizations from methanol–water raised the melting point to 75–76°. Mixed melting points with authentic 3-methyl-4-carbethoxypyrrole, m. p. 75–76°, showed no depression.

2,4-Dicarbethoxy-3-methyl-5-iodopyrrole (VIII).—To a hot solution of 13.2 g. of 2,4-dicarbethoxy-3-methyl-5-carboxypyrrole in 70 ml. of 95% ethanol was added 12.0 g. of sodium bicarbonate, then 100 ml. of water. The mixture was heated until solution was complete. A solution of 13.0 g. of iodine and 20 g. of potassium iodide in 150 ml. of water was then added gradually with stirring during 2 hours, the temperature being maintained at about 85°. After stirring for one additional hour the reaction mixture was heated until the iodine color was discharged. Upon the addition of 100 ml. of ice–water mixture, the precipitated product was filtered off and dried; yield 13.2 g. or 77%. Recrystallization from ethanol–water gave an analytically pure product melting at 179–180°.

Anal. Calcd. for $C_{11}H_{14}O_4NI$: C, 37.62; H, 4.02; C_2H_5O, 25.66. Found: C, 37.62, 37.66; H, 4.03, 4.05; C_2H_5O, 25.64.

Monohydrolysis of 2,4-Dicarbethoxy-3-methyl-5-iodopyrrole (VIII).—The procedure employed is essentially that described for the preparation of V. Ten and five-tenths grams of once-crystallized VIII was dissolved in a hot solution of 12.9 g. of potassium hydroxide in 165 ml. of 95% ethanol and refluxed for 5 hours. The condenser was then removed and boiling continued for one additional hour. After precipitating the crude reaction product by pouring into 710 ml. of ice-water and acidifying to a *p*H of 2, the iodoacid was separated from starting diester by taking up the crude product in 35 ml. of hot ethanol, adding excess sodium bicarbonate, then pouring into 640 ml. of water. The resulting precipitate weighed 1.4 g., representing 13% recovery of unchanged diester. Acidification of the filtrate and washes to about *p*H 2 caused the precipitation of 4.9 g. or a 51% yield of the iodoacid. Purification of the crude iodoacid was carried out by the procedure described for bromoacid V, except that the last two crystallizations in the case of the iodoacid were from dioxane–water. The substance softens and decomposes to a dark mass in the range 185–195° when heated at the rate of 2° per minute.

Anal. Calcd. for $C_9H_{10}O_4NI$: C, 33.45; H, 3.12. Found: C, 33.50, 33.84; H, 3.37, 3.26.

2,4-Dicarbethoxy-3-methyl-5-carbomethoxypyrrole (X).[8a,b]—This substance was prepared from 2,4-dicarbethoxy-3-methyl-5-carboxypyrrole by the second method described by Corwin and Straughn. The crude product after a single recrystallization from methanol–water melted at 68–72° and this material was utilized without further purification in the following preparation.

2-Carboxy-3-methyl-4-carbethoxy-5-carbomethoxypyrrole (XI).[8b,c]—This was obtained from X by the procedure[8c] of Corwin and Straughn. One recrystallization from acetone–water afforded a product melting at 207.5–208.5°.

2-Bromo-3-methyl-4-carbethoxy-5-carbomethoxypyrrole (XII).[8b]—The procedure described is a modification of the method of Corwin and Straughn[8b] and affords XII in somewhat improved yield. To a solution of 13.1 g. of once-recrystallized 2-carboxy-3-methyl-4-carbethoxy-5-carbomethoxypyrrole in 100 ml. of hot absolute methanol was added 12.6 g. of sodium bicarbonate. The mixture was stirred briefly, then cooled to room temperature. A solution of 2.9 ml. of bromine in 15 ml. of methanol was then added with vigorous stirring during 15 to 20 minutes at such a rate that the unreacted bromine did not accumulate. The pale yellow reaction mixture was heated briefly to 60°, then poured into 750 ml. of ice-water. After one hour in the refrigerator the crude bromopyrrole was filtered off and washed well with water; yield 13.2 g. or 89%. One crystallization from methanol–water gave 11.3 g. of product melting at 114.5–116° and of sufficient purity for the subsequent alkaline hydrolysis.

2-Bromo-3-methyl-4-carbethoxy-5-carboxypyrrole (XIII).—Nine and eight-tenths grams of 2-bromo-3-methyl-4-carbethoxy-5-carbomethoxypyrrole was refluxed for 4 hours with a solution of 14.1 g. of potassium hydroxide in 165 ml. of 95% ethanol. The condenser was then removed and the mixture was boiled for an additional 30 minutes. After pouring in 825 ml. of ice-water mixture the solution was acidified with concentrated hydrochloric acid to a *p*H of 2 to 3, and the precipitated product was filtered off the next day. Further acidification of the filtrate to a *p*H of 1 or less caused precipitation of additional product. The two crops were combined, taken up in 70 ml. of hot ethanol and after addition of sodium bicarbonate to cessation of effervescence, this was poured into 700 ml. of water. The resulting mixture was stirred for about 30 minutes, then filtered, and the filtrate was acidified to a *p*H of 1 or less. After refrigerating overnight the product was filtered off. Weight of crude product, 3.83 g. Two recrystallizations from ethanol–water followed by two more from 95% ethanol afforded the analytically pure bromoacid.

Anal. Calcd. for $C_9H_{10}O_4NBr$: C, 39.15; H, 3.65. Found: C, 39.02; H, 3.97.

2-Bromo-3-methyl-4-carbethoxy-5-iodopyrrole (II). (a) From **2-Bromo-3-methyl-4-carbethoxy-5-carboxypyrrole (XIII).**—To a mixture of 129 mg. of the analytically pure bromoacid XIII and 0.35 g. of potassium bicarbonate was added 25 drops of methanol and 2 ml. of water. After heating and stirring briefly, then cooling to room temperature, 2 ml. more of water was added and dropwise addition of a solution of 115 mg. of iodine and 0.3 g. of potassium iodide in 4 ml. of water was begun. Addition was completed in about 10–15 minutes, during which time 6 ml. more of water was added in order to ensure sufficient fluidity of the reaction mixture as the flocculent precipitate of product separated. After being allowed to stand for a few minutes, the product was filtered off and washed well with water; yield 154 mg. or 92% of crude bromoiodopyrrole melting at 121–121.5°. The substance was purified for analysis by recrystallization from warm ethanol–water; m.p. 121.5–122°. The substance, like its isomer III, melted with decomposition at a lower temperature when observed on a very brightly illuminated hot stage and thus appears to be light-sensitive.

Anal. Calcd. for $C_8H_9O_2NBrI$: C, 26.84; H, 2.53. Found: C, 26.98; H, 2.71.

Mixtures of II with the isomeric 2-iodo-3-methyl-4-carbethoxy-5-bromopyrrole (III) were prepared. Pyrrole III melts with decomposition at 151.5–152.5°, and the behavior of the mixtures is tabulated below.

Composition of mixture		
II, mg.	III, mg.	Melting range, °C.
7	1.5	117–119
1.3	1.3	117–126
0.8	4.0	127–147

(b) From **2-Bromo-3-methyl-4-carbethoxypyrrole (I).**[3]—Four hundred three milligrams of analytically pure monobrominated 3-methyl-4-carbethoxypyrrole prepared according to the directions of Corwin and Kleinspehn[3] was dissolved in 5 ml. of absolute methanol, and 202 mg. of silver oxide was added. A solution of 442 mg. of iodine in 6 ml. of absolute methanol was then added, followed by 3 ml. of water. Upon agitation the iodine color began to fade. After several minutes an additional 35 mg. of silver oxide was introduced and upon shaking a further decrease in the iodine color was noted. Addition of 20 mg. more of silver oxide caused no visible effect. The silver salts were filtered off and washed with methanol. The combined filtrate and washes were treated with 40–45 drops of aqueous 0.1 *N* sodium thiosulfate solution, then poured into 130 ml. of ice-water from which a white precipitate of the product separated. After refrigerating it was filtered off and purified by dissolving with stirring in 50 ml. of aqueous 1% sodium hydroxide solution. A little Norit A was added and the mixture was filtered. After addition of some ice to the filtrate, the bromoiodopyrrole was precipitated by acidifying gradually with glacial acetic acid until no more precipitate formed. The mixture was refrigerated overnight, then filtered to give 452 mg. or 72% of crude product melting at 114–120° with some softening beginning at about 110°. Recrystallization from warm ethanol–water afforded 309 mg. of product melting at 120–121°, and recrystallization of the crude recovered from the mother liquor gave an additional 21 mg. of product melting at 119.5–120.5°. Total yield of thus purified product, 330 mg. or 53%. One subsequent recrystallization from warm ethanol–water afforded the analytically pure bromoiodopyrrole melting at 121–122°.

Anal. Calcd. for $C_8H_9O_2NBrI$: C, 26.84; H, 2.53. Found: C, 26.90; H, 2.25.

Mixed melting points with the 2-bromo-3-methyl-4-carbethoxy-5-iodopyrrole from XIII showed no depression. Mixed melting point with III (5.8 mg. of II + 1.1 mg. of III), 117–121°.

2,5-Dicarboxy-3-methyl-4-carbethoxypyrrole (XIV).[8b,d]—This was prepared by the alkaline hydrolysis[8b] of 2,4-dicarbethoxy-3-methyl-5-carboxypyrrole. It was found advantageous to extend the reflux period to 3 hours. The product was twice recrystallized from acetone–water before utilization in the next reaction.

2,5-Diiodo-3-methyl-4-carbethoxypyrrole (XV).—Seven and three-tenths grams of sodium bicarbonate and 8.0 g. of 2,5-dicarboxy-3-methyl-4-carbethoxypyrrole were dissolved by stirring with 325 ml. of water. A solution of 17.9 g. of iodine and 23 g. of potassium iodide in 145 ml. of water was then added dropwise with stirring during 65 minutes. At first a white precipitate of the diiodopyrrole formed rapidly, then a dark-colored foam accumulated gradually atop the reaction mixture, preventing efficient mixing of the reactants. Considerable additional water was introduced and the mixture was stirred manually at intervals while the reaction proceeded nearly to completion during several hours. The product was finally filtered off, washed and dried *in vacuo*. Yield 12.5 g. or 93% of crude product melting at 147–151° with decomposition. The substance was recrystallized for analysis from warm ethanol–water; m.p. 151–152.5° with decomposition.

Anal. Calcd. for $C_8H_9O_2NI_2$: C, 23.72; H, 2.24. Found: C, 23.86; H, 2.55.

3-Methyl-4-carbethoxypyrrole (VI).[6,7]—The catalyst for the reduction was prepared by hydrogenation of a mixture of 17.0 g. of 10% palladium chloride solution, 40 ml. of water and 10.2 g. of Norit A for one hour, at 35 lb. gage pressure. The catalyst was filtered off, washed well with water, then methanol, and transferred to a hydrogenation bottle. Eight grams of magnesium oxide, 40.5 g. (100 mmol.) of crude 2,5-diiodo-3-methyl-4-carbethoxypyrrole and 135 ml. of methanol were then added, and the mixture was hydrogenated for 48 hours during which time gage pressure dropped from 39.7 to 24.3 lb. of hydrogen, corresponding to an uptake of approximately 0.2 mole of hydrogen. After addition of a little sodium bisulfite to prevent reoxidation of the iodide ion, the catalyst was removed by suction, then gravity filtration. Gradual addition of the pale yellow filtrate to 775 ml. of ice-water caused the product to separate as a solid. After refrigerating overnight, the crude 3-methyl-4-carbethoxypyrrole was filtered off; weight 12.7 g., m.p. 74–75°. A second crop melting at 73–74° was obtained by freezing, then thawing the filtrate; total yield 13.1 g. or 86% of product.

Baltimore, Maryland

[Contribution from the Chemistry Department, University of Michigan]

Pyrido-2,3-furoxane[1]

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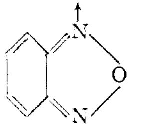
Pyrido-2,3-furoxane (II) has been prepared by the pyrolysis of 8-nitropyridotetrazole (IV). A quinonoid structure with an unsymmetrical arrangement of the N_2O_2 group for II and related furoxanes is in agreement with both analysis of infrared spectra and revised parachor values.

Inasmuch as certain derivatives of benzfuroxane (I), *e.g.*, 5-(or 6)-methylbenzfuroxane,[3] 5-(or 6)-chlorobenzfuroxane[3] and naphtho-1,2-furoxane[3] fail to exist in isomeric forms as required by the generally accepted quinonoid structures, it is recognized that these representations do not adequately describe furoxanes of this type. Not only does pyrido-2,3-furoxane (II) offer a new example in which there appears to be the possibility for two modifications but it also illustrates the hitherto unreported fusion of a heterocyclic aromatic ring to the furoxane moiety. In addition the synthesis of this compound has afforded preliminary investigations on the pyrolysis of pyridotetrazoles, and has offered the possibility of studying an azaquinone structure. Apparently the only previously reported example of this type of compound is 3-aza-*o*-benzoquinone[4] (III) prepared by the oxidation of 2,3-dihydroxypyridine. Certain potential hydroxyazaquinones exist in the keto modification, *e.g.*, alloxan, tetraketopiperazine and phthalonimide.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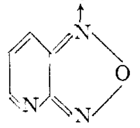
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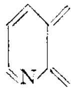
III

Syntheses of pyridotetrazoles have consisted in reactions which would appear to yield the isomeric α-pyridyl azides, *e.g.*, the displacement of halogen by the azido group[5] or the action of nitrous acid upon the hydrazino group.[6] If possible, utiliza-

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