3,5-Cyclo-6β-methoxy-14-androsten-17α-ol (IV) and 5,14-Androstadiene-3β,17α-diol (V).—To a suspension of 0.5 g. of sodium hydride (50% in mineral oil) in 88 ml. of dry tetrahydrofuran under a nitrogen atmosphere was added dropwise a solution of 1.4 g. of III in 50 ml. of dry tetrahydrofuran. The reaction mixture was refluxed for 16 hr. under a nitrogen atmosphere, then cooled to room temperature, and the excess sodium hydride decomposed by dropwise addition of water. An additional 200 ml. of water was added and the mixture was extracted 3 times with 150-ml. portions of chloroform. The chloroform extract was washed with water, dried over sodium sulfate, and taken to dryness under reduced pressure. An infrared spectrum of the residue indicated the absence of carbonyl absorption. The residue was dissolved in benzene and chromatographed on Merck acid washed alumina. Elution with benzene afforded 471 mg. of IV. An analytical sample was prepared by crystallization from hexane, m.p. 128–130°; $[\alpha]^{24}D$ +52; λ_{Nujol} 3.1 μ (–OH); n.m.r.: 8.84 (15-proton), 6.04 doublet (17-proton, J = 5 c.p.s.), 6.65 (methoxy), 8.93 (19-methyl), 8.98 τ (18-methyl).

Anal. Calcd. for $C_{20}H_{30}O_2$: C, 79.42; H, 10.00. Found: C, 79.61; H, 9.79.

Elution with chloroform afforded 70 mg. of V. An analytical sample was prepared by crystallization from acetone–ether, m.p. 193–195°, $[\alpha]^{24}D$ −81°; λ_{Nujol} 3.0 μ (–OH); n.m.r.: 4.62 (6-proton), 4.88 (15-proton), 6.04 doublet (17-proton, J = 6 c.p.s.), 8.96 (19-methyl), and 9.0 τ (18-methyl).

Anal. Calcd. for $C_{19}H_{28}O_2$: C, 79.12; H, 9.52. Found: C, 79.12; H, 9.79.

3,5-Cyclo-6β-methoxy-14-androsten-17α-ol 17-Acetate (IVa).—To a solution of 0.1 g. of IV in 5 ml. of pyridine was added 5 ml. of acetic anhydride. The solution was allowed to stand for 16 hr. and the solvents were removed under reduced pressure. Attempts to crystallize the oil that remained were unsuccessful. An analytical sample was prepared by sublimation at 100° (0.005 mm.), $[\alpha]^{25}D$ +58; λ_{Nujol} 5.75 and 8.0 μ (CH_3COO—).

Anal. Calcd. for $C_{22}H_{32}O_3$: C, 76.70; H, 9.36. Found: C, 76.10; H, 8.61.

3β-Acetoxy-5,14-androstadien-17α-ol (Va).—To a solution of 10 mg. of IV in 1.0 ml. of glacial acetic acid was added 1.0 mg. of *p*-toluenesulfonic acid and the reaction mixture was allowed to stand for 4 hr. The mixture was diluted with water and extracted with ether. The ether extract was washed with water, dried over sodium sulfate, and the ether removed under reduced pressure, affording 10 mg. of a clear oil, λ_{Nujol}, 2.9 (OH), 5.75 and 8.0 μ (CH_3COO—). Thin layer chromatography of this material revealed that it was homogeneous.

3β-Acetoxy-5,14-androstadien-17-one (VI).—To a solution of 10 mg. of the oil Va in 1 ml. of acetone an acidic solution of chromium trioxide[11] was added dropwise until a slight excess was present. The solution was then filtered through Celite, diluted with water, and extracted with chloroform. The chloroform extract was washed with water, dried over sodium sulfate, and the solvent was removed under reduced pressure, affording 10 mg. of a clear oil. Thin layer chromatography revealed that the oil was homogeneous and had thin layer chromatographic mobility in two solvent systems identical to that of an authentic sample of 3β-acetoxy-5,14-androstadien-17-one[3]; λ_{Nujol} 5.75, 8.0 (CH_3COO—), and 5.8 μ (17-ketone).

***p*-Toluenesulfonylhydrazone of 3β-Acetoxy-14α-hydroxy-5-androsten-17-one (IX).**—To a solution of 0.5 g. of 3β-14α-hydroxy-5-androsten-17-one[3] (VIII) in 25 ml. of ethanol was added 0.28 g. of *p*-toluenesulfonylhydrazine and 0.05 g. of *p*-toluenesulfonic acid. The reaction mixture was refluxed for 2 hr. and cooled to room temperature. Under reduced pressure half of the solvent was removed and addition of 50 ml. of ice–water precipitated the product. Filtration and drying afforded 0.389 g. of crude product. An analytical sample was prepared by repeated crystallization from methanol, m.p. 251–252°; λ_{Nujol} 2.8 (14-OH), 3.1, 6.28, 7.1, 7.5, and 8.6 (tosylhydrazone), and 5.75 and 8.0 μ (acetate).

Anal. Calcd. for $C_{27}H_{38}O_5N_2S$: N, 5.5. Found: N, 5.1.

13α,14α-Oxido-5-androsten-3β-ol (X).—To a solution of 0.5 g. of sodium in 75 ml. of dry ethylene glycol under a nitrogen atmosphere was added 0.5 g. of the tosylhydrazone IX. The solution was refluxed for 1 hr. under a nitrogen atmosphere, cooled to room temperature, diluted with 200 ml. of ice–water and extracted with chloroform–ether. The extract was washed with water, dried over sodium sulfate, and the solvent was removed under reduced pressure affording 0.35 g. of residue. An frared spectrum of the residue revealed the absence of carbonyl and tosylhydrazone absorption. Thin layer chromatography showed principally one component. The residue was dissolved in benzene and chromatographed on Merck acid-washed alumina. Elution with ether afforded 127 mg. of X. An analytical sample was prepared by crystallization from dioxane–water, m.p. 139–142°, $[\alpha]^{25}D$ −101°; λ_{Nujol} 2.8 μ (–OH); n.m.r.: 4.57 (6-proton), 9.02 and 9.13 doublet (17-methyl, J = 7 c.p.s.), and 9.02 τ (19-methyl).

Anal. Calcd. for $C_{19}H_{28}O_2$: C, 79.12; H, 9.79. Found, C, 78.86; H, 9.71.

(11) (a) K. Bowden, *et al.*, *J. Chem. Soc.*, 39 (1946); (b) C. Djerassi, *et al.*, *J. Org. Chem.*, **21**, 1548 (1956).

Organoboron Compounds. XVII.[1] Chemistry of a Compound with Neighboring Borono, Ethynyl, and Amine Functional Groups[2]

ROBERT L. LETSINGER AND ALLEN J. WYSOCKI[3]

Department of Chemistry, Northwestern University, Evanston, Illinois

Received May 10, 1963

The synthesis of 2-(*o*-boronophenylethynyl)pyridine (I) and conversion to 2-[β-hydroxy-β-(*o*-boronophenyl)-vinyl]pyridine (II) are reported. Synergetic activity of the borono and amine groups in these molecules was investigated by means of a reaction with chloroethanol.

8-Quinolineboronic acid[4,5] and 2-(2-boronophenyl)-benzimidazole[1] displace chloride from chloroethanol considerably faster than do equimolar mixtures containing benzeneboronic acid and quinoline or 2-phenylbenzimidazole. The enhanced activity of the former compounds was attributed to cooperative action of the borono and amine functions made possible by the proximity of these groups in a given molecule. As a further test of the role of molecular geometry on the chemical properties of the borono and amine groups, we undertook a study of 2-(*o*-boronophenylethynyl)-pyridine (I). In this molecule the groups are sufficiently separated that direct interaction would not be expected[6]; therefore the reaction pathways available to 8-quinolineboronic acid and the boronophenylbenzimidazole should not be available to compound I.

(1) Paper XVI: R. L. Letsinger and D. B. MacLean, *J. Am. Chem. Soc.*, **85**, 2230 (1963).

(2) This research was supported in part by the National Science Foundation.

(3) Dow Chemical Co. Fellow, Lubrizol Corp. Fellow.

(4) R. L. Letsinger and S. Dandegaonker, *J. Am. Chem. Soc.*, **81**, 498 (1958).

(5) R. L. Letsinger, S. Dandegaonker, W. J. Vullo, and J. D. Morrison, *ibid.*, **85**, 2223 (1963).

(6) On the basis of normal bond lengths and angles it is estimated that the minimum distance separating boron and nitrogen in I would be 4.8 Å., while the minimum distance between hydrogen (of BOH) and nitrogen would be 2.9 Å.

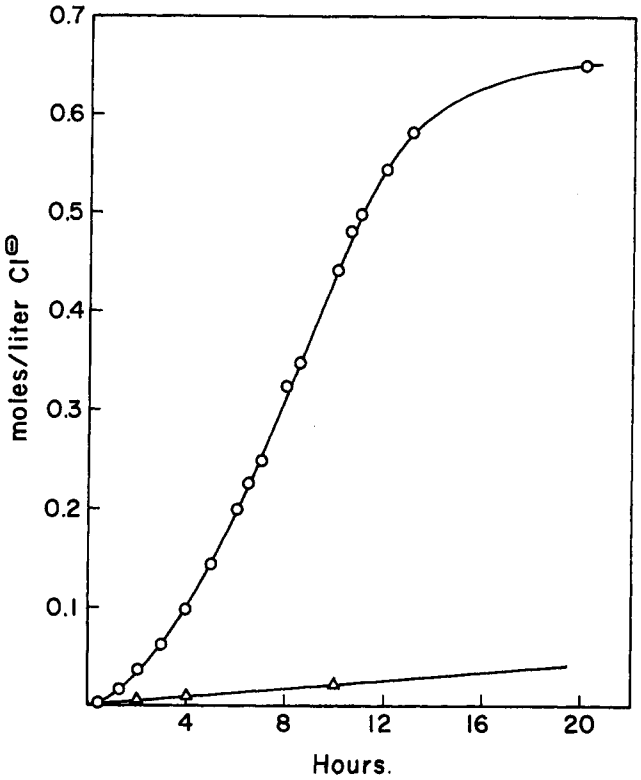
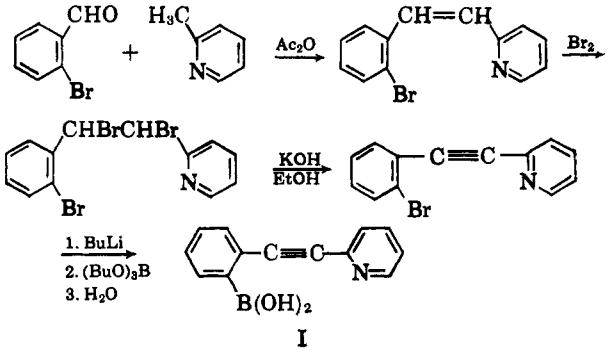


Fig. 1.—Chloride ion formation in the chloroethanol–butanol–collidine system to which 2-(*o*-boronophenylethynyl)pyridine had been added, O; chloride ion formation in a control which did not contain the boron compound, △.

CHART I

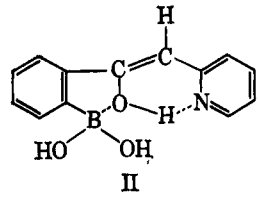


I

2-(*o*-Boronophenylethynyl)pyridine was prepared from *o*-bromobenzaldehyde and 2-picoline by the series of reactions indicated in Chart I. The sequence is similar to that used for the synthesis of 2,2′-tolandiboronic acid.[7] Distinctive bands in the infrared spectrum of I were found at 2.8 (O—H), 4.5 (—C≡C—), and 7.25 and 7.45 μ (region for B—O). Maxima in the ultraviolet region (ethanol solvent) occurred at 274 (ε 16,200), 293 (22,200), 302 (21,700), and 311 mμ (23,000). The compound was further characterized by preparation of a crystalline derivative with *o*-phenylenediamine and by conversion to 2-phenacylpyridine by treatment with hot sulfuric acid.

As in the case of 8-quinolineboronic acid and boronophenylbenzimidazole[1] a chloroethanol–butanol system was used to test for synergetic activity of the borono and amine groups. For this purpose a solution consisting of one millimole of the boron compound, five millimoles of collidine, and five milliliters of 1-butanol, measured at room temperature, was warmed to 88.8° and then brought to a volume of ten milliliters by addition of prewarmed chloroethanol. Aliquots were removed at intervals and titrated for chloride ion by the Volhard procedure. Data from two separate experiments are combined in Fig. 1, along with data for a control reaction in which the boron compound was omitted from the mixture. The curve obtained with this boronophenylethynylpyridine differed in a significant way from those for 8-quinolineboronic acid and the boronophenylbenzimidazole. With the latter compounds the reaction proceeded at a uniform rate from the beginning until the collidine had been converted to the hydrochloride.[1] In contrast, the reaction with compound I was initially very slow, no faster than that of the control. The rate increased over a four-hour period and thereafter was constant until the collidine had been consumed. Throughout the linear portion of the curve the rate (k = 0.60 hr.$^{-1}$)[8] was somewhat greater than that for 8-quinolineboronic acid (k = 0.37 hr.$^{-1}$) and boronophenylbenzimidazole (k = 0.28 hr.$^{-1}$).

This behavior indicates that boronophenylethynylpyridine itself is inactive or of low activity in this system and that in the course of the reaction it is converted to an active compound. In agreement with this idea, a new organoboron compound, assigned structure II, was isolated from a reaction of I with chloroethanol. When this substance was introduced into a fresh portion of the solvent system (chloroethanol–butanol–collidine), the reaction began immediately with no induction period and proceeded at a uniform rate (k = 0.66 hr.$^{-1}$) very close to that corresponding to the linear portion of the curve in Fig. 1.



II

The assignment of structure II rests on analytical data, the formation of a semicarbazone derivative, conversion to 2-phenacylpyridine, and spectral data. The infrared spectrum is consistent with the view that hydroxyl is present (strong absorption at 2.9 μ), that the ethynyl group is absent (no absorption between 4 and 5 μ), that a carbon–carbon double bond is present (strong absorption at 6.2 μ; no bands in the carbonyl region between 5 and 6 μ), and that the boron is tetracoordinated (only weak absorption between 7 and 8 μ). Like 2-phenacylpyridine[9] the substance is yellow; λ_{max}^{EtOH} 383 and 400 (shoulder) mμ.

The transformation of I to II involves addition of –O–H to a carbon–carbon triple bond. An analogous reaction was observed when 2,2′-tolandiboronic acid was heated in an alkaline solution.[7] In that case it was not possible to determine whether the closure involved a five- or six-membered C–B–O ring since

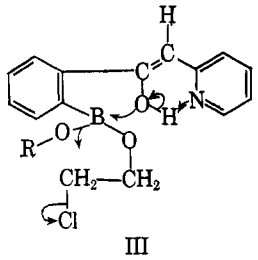
(7) R. L. Letsinger and J. R. Nazy, *J. Am. Chem. Soc.*, **81**, 3013 (1959).

(8) The pseudo zero-order rate constant is 0.062 mole/l./hr.; k is obtained by subtracting the rate for the collidine control reaction and dividing by the molar concentration of the boron compound.

(9) R. F. Branch, *Nature*, **177**, 671 (1956), attributed the yellow color of 2-phenacylpyridine to the presence of an enol tautomer. Since a borono group is a Lewis acid, a neighboring borono group should further stabilize an enol form by coordination with oxygen, as in II.

either type of product would have afforded deoxybenzoin on degradation. With II, however, phenacylpyridine could only reasonably be derived from an intermediate with oxygen alpha to the ring bearing the boron.

The reaction of II with chloroethanol in the presence of excess collidine (relative to II) is a catalytic one since it proceeds until all of the base has been converted to hydrochloride. Though the function of nitrogen in the reaction of II has not yet been uniquely established, formulation III for the operation of the catalyst in the step involving carbon–chlorine fission is attractive. As with 8-quinolineboronic acid[4,10] and the boronophenylbenzimidazole[1] it is assumed that boron functions as a binding site for the alcoholic substrates and that nitrogen serves to increase the nucleophilicity of oxygen bound to boron. Since in II the nitrogen is relatively distant from boron, its effect may be presumed to be transmitted to boron by way of the intervening hydroxyl group. No comparable pathway for interaction of the borono and amine groups is available in compound I, and indeed I appears to be a very poor catalyst for the reaction of chloroethanol with butanol and collidine.



III

Experimental

Infrared spectra were obtained with a Beckman IR-5 spectrometer with the sample in potassium bromide, and ultraviolet spectra were obtained with a Cary Model 11 spectrophotometer. Elemental analyses were performed by Miss Hilda Beck.

o-Bromostilbazole Dibromide.—A mixture of 121.5 g. (0.66 mole) of *o*-bromobenzaldehyde, 61.2 g. (0.66 mole) of 2-picoline and 100 g. (1 mole) of acetic anhydride was refluxed for 10 hr. under a nitrogen atmosphere.[11] The solution was then poured on to ice and acidified with hydrochloric acid. Volatile matter was distilled with steam and the residual solution was made alkaline with sodium hydroxide. The solid which separated on cooling was collected and extracted with hot, dilute hydrochloric acid. *o*-Bromostilbazole hydrochloride separated when the acidic solution was cooled. *o*-Bromostilbazole was liberated by alkaline treatment and was recrystallized from 95% ethanol; weight, 116 g. (68%); m.p. 80–81°. This material was dissolved in carbon disulfide and treated with 25 ml. of bromine. On cooling, 178.6 g. (98% based on bromostilbazole) of bromostilbazole dibromide precipitated, m.p. 153–158°. An analytical sample, m.p. 166–169°, was obtained by recrystallizing a portion of the substance several times from methanol. The remaining material was used for the preparation of *o*-bromophenylethynylpyridine.

Anal. Calcd. for $C_{13}H_{10}Br_3N$: C, 37.1; H, 2.38; N, 3.33. Found: C, 37.1; H, 2.39; N, 3.64.

2-(*o*-Boronophenylethynyl)pyridine.—Dehydrobromination was accomplished by heating 177 g. of *o*-bromostilbazole dibromide with 92 g. of potassium hydroxide in 1600 ml. of absolute ethanol. The solution was then concentrated to about 300 ml., filtered to remove potassium bromide, and further concentrated to 150 ml. Following addition of 200 ml. of water, the mixture was extracted with ether. The crude bromophenylethynylpyridine, obtained as an oil by evaporation of the ether, was purified by formation of the picrate. For this step a solution of bromophenylethynylpyridine (114 g.) in the minimum amount of ethanol was added to 115 g. of picric acid in hot ethanol. The mixture was cooled and filtered, and the precipitate was recrystallized from methanol. The picrate (133 g., m.p. 162–162.5°) was then suspended in 1 l. of water and treated with an aqueous solution containing 13 g. of sodium hydroxide. Extraction with ether, treatment of the ether solution with charcoal, and distillation of the ether afforded 62.5 g. (58.5% based on bromostilbazole dibromide) of 2-(*o*-bromophenylethynyl)pyridine (infrared band, 4.50 μ).

For preparation of the boronic acid, 75 ml. of 1.5 *M* butyllithium in ether was added to 6.2 g. of the bromophenylethynylpyridine in 300 ml. of ether at −70°. A nitrogen atmosphere was used throughout the reaction of the organometallic reagents. After 15 min. an excess (46 g.) of butyl borate was added to the brown solution of the lithium reagent. The solution was stirred an additional 15 min., warmed to 0°, and hydrolyzed by addition of water. Extraction of the ether layer with dilute aqueous potassium hydroxide and neutralization (to pH 6.5) of the extract with hydrochloric acid yielded an oil, which was taken up in chloroform, and extracted with aqueous hydrochloric acid. On addition of sodium carbonate (to pH 6.5) the amphoteric 2-(*o*-boronophenylethynyl)pyridine precipitated; weight, 1.5 g. It was collected by extraction with ether. The analytical sample, obtained by recrystallization from benzene, melted initially at 135°, resolidified on standing, and melted again at 155° on further heating.

Anal. Calcd. for $C_{13}H_{10}BNO_2$: C, 70.0; H, 4.52; N, 6.29; neut. equiv., 223. Found: C,[12] 56.3; H, 4.50; N, 6.04; neut. equiv. (by a potentiometric titration with sodium hydroxide in presence of mannitol), 224.

When hydrogen chloride gas was passed into an ether solution of this boronic acid, an essentially quantitative yield of the amine hydrochloride, m.p. 153.5–154.5°, was obtained. Potentiometric titration of this salt with sodium hydroxide gave a titration curve with two distinct breaks, one for the amine hydrochloride and the other for the boronic acid (mannitol added for second titration). Both gave a value of 263 for the equivalent weight of the hydrochloride, as compared to the calculated value of 260.

***o*-Phenylenediamine Derivative.**—Equimolar amounts of boronic acid I (1.0042 g.) and *o*-phenylenediamine (0.4867 g.) were heated in boiling toluene under conditions to remove the water azeotrope. Concentration of the solution yielded crystals of the *o*-phenylenediamine derivative of 2-(*o*-boronophenylethynyl)-pyridine; weight, 1.0907 g. (82%). It melted at 150–150.5° after recrystallization from carbon tetrachloride.

Anal. Calcd. for $C_{19}H_{14}BN_3$: C, 77.3; H, 4.78; N, 14.24. Found: C[12], 72.2; H, 4.66; N, 13.61.

Conversion to 2-Phenacylpyridine.—A solution of 1.0208 g. of 2-(*o*-boronophenylethynyl)pyridine in 7 ml. of water and 5 ml. of concentrated sulfuric acid was refluxed for 2.5 hr., cooled, diluted with 20 ml. of water, and made alkaline with concentrated ammonium hydroxide. Extraction with ether and recrystallization of the ether soluble material from pentane afforded 0.7411 g. (82%) of 2-phenacylpyridine, m.p. 57–58.5°, lit.[13] m.p. 59°. The oxime melted at 117–118°; for the oxime of 2-phenacylpyridine, lit.[13] m.p. 120°.

2-[β-Hydroxy-β-*o*-(boronophenyl)vinyl]pyridine and Derivatives.—A solution containing 0.5296 g. of compound I in 25 ml. of chloroethanol was warmed at 89° for 20 hr., concentrated at reduced pressure, and made just basic to litmus by addition of aqueous sodium hydroxide. The resulting precipitate was collected and dissolved in methanol. On acidification with hydrochloric acid and concentration of the solution a yellow, crystalline hydrochloride salt separated, m.p. 230–231°, 0.2132 g. The analysis of a sample dried at 65° (1 mm.) for 20 hr. corresponded to an anhydride of 2-(*o*-boronophenacyl)pyrdine hydrochloride.

Anal. Calcd. for $C_{13}H_{11}BClNO_2$: C, 60.2; H, 4.27; N, 5.40. Found: C, 60.9; H, 4.66; N, 5.39.

On heating in a refluxing solution of water (2 ml.) and concentrated sulfuric acid (2 ml.) for 2.5 hr., this compound (25.3 mg.) was converted to **2-phenacylpyridine**, m.p. 50–52°, which was

(10) R. L. Letsinger and J. D. Morrison, *J. Am. Chem. Soc.*, **85**, 2227 (1963).

(11) The procedure was patterned after the preparation of stilbazole described by B. D. Shaw and E. A. Wagstaff, *J. Chem. Soc.*, 77 (1933).

(12) Many of the aromatic B-N compounds have given low carbon analyses as a consequence of incomplete oxidation of carbon at the temperature used in the analytical train.

(13) G. Schering and L. Winterhalder, *Ann.*, **473**, 135 (1929).

isolated in 78% yield (14 mg.) by addition of water to the solution, treatment of the solution with ammonium hydroxide, extraction of the precipitate with ether, and recrystallization from pentane of the solid obtained from the ether extract. The oxime prepared from this sample of phenacylpyridine melted at 115–117°.

2-[β-Hydroxy-β-(*o*-boronophenyl)vinyl]pyridine was obtained by addition of sodium hydroxide in 50% alcohol–water to the hydrochloride salt (0.2940 g.), evaporation of the solution to dryness, extraction of the resulting solid with chloroform, and evaporation of the extract. For further purification, the sample was dissolved in methanol and the solution was filtered and taken to dryness. The resulting pale yellow solid charred and decomposed without melting when heated in the range of 230°. The analysis of the material dried at room temperature corresponded to a dihydrate of compound II.

Anal. Calcd. for $C_{13}H_{12}BNO_3 \cdot 2H_2O$: C, 56.3; H, 5.82; N, 5.06. Found: C, 55.9; H, 5.90; N, 4.92.

After the sample had been heated at 65° (1 mm.) for 24 hr., the analysis agreed with that for 2-[β-hydroxy-β-(*o*-boronophenyl)vinyl]pyridine .

Anal. Calcd. for $C_{13}H_{12}BNO_3$: C, 64.7; H, 5.02; N, 5.81. Found: C, 64.5; H, 5.33; N, 5.99.

A semicarbazone derivative was obtained by warming a solution of 86 mg. of compound II, 0.2 g. of semicarbazide hydrochloride, and 0.3 g. of sodium acetate in 4 ml. of ethanol and 2 ml. of water for 15 min. When the solution was cooled, 60 mg. of the yellow crystalline semicarbazone derivative of compound II was obtained, m.p. 169–172°. The analytical sample was dried at 65° (1 mm.) for 8 hr.

Anal. Calcd. for $C_{14}H_{15}BN_4O_3$: C, 56.4; H, 5.07; N, 18.80. Found: C, 56.5; H, 4.88; N, 18.78.

Notes

Reduction of 1-Methyl-3-acylindole Derivatives with Lithium Aluminum Hydride[1]

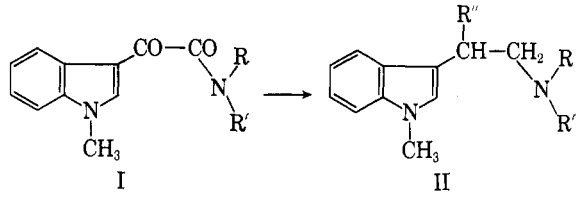
K. T. POTTS AND D. R. LILJEGREN[2]

Department of Chemistry, University of Louisville, Louisville, Kentucky, and Department of Organic Chemistry, University of Adelaide, Adelaide, Australia

Received February 1, 1963

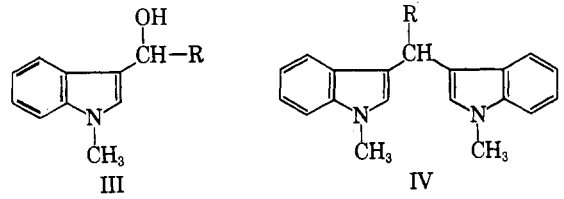
The application of lithium aluminum hydride to the reduction and cyclization of (2–3′-indolylethyl)- or (2–3′-indolyl-2-oxoethyl)pyridinum and isoquinolinium salts has been described in previous papers.[3] This note reports some results obtained in the *ind*-N-methyl series.[4]

The reduction of various 3-acylindoles with lithium aluminum hydride is a well authenticated[5] hydrogenolysis reaction, the 3-alkylindoles being readily obtained. With *ind*-N-methyl-3-acylindoles the reduction has been reported to stop at the intermediate alcohol stage and does not appear to be analogous to the reduction of a disubstituted vinylogous amide. Thus 1,N-dimethyl-3-indoleglyoxamide (I, R = CH_3; R′ = H) and lithium aluminum hydride gave the alcohol[6] II (R = CH_3; R′ = H; R″ = OH). However, conflicting reports have appeared, *e.g.*, the reduction of I (R = R′ = $-CH_2Ph$) with lithium aluminum hydride to give the oxygen-free product[7] II (R = R′ = $-CH_2Ph$; R″ = H); on the other hand, 1-methyl-3-indolylaldehydes have been shown[8] to undergo reduction to 1-methyl-3-hydroxymethyl indoles, in agreement with the former reaction. In attempts to effect the reductive cyclization of 1-[2-(1′-methyl-3′-indolyl)-2-oxoethyl]pyridinium derivatives, no clear-cut results could be obtained and it was decided to investigate the reduction of 1-methyl-3-acetylindole.



I II

Immediately after isolation in the usual way, the product from the lithium aluminum hydride reduction showed intense hydroxyl absorption in its infrared spectrum, indicating the presence of a predominant amount of structure III (R = CH_3). However, no derivative of the alcoholic function could be obtained and, on standing, the crude product developed an odor of acetaldehyde. This was of interest in view of the reported[8] decomposition of 1-methyl-3-hydroxymethylindole (III, R = H) to formaldehyde and the diindolylmethane IV (R = H). However, this decomposition pathway was not followed in the case of our 1-(1′-methyl-3′-indolyl)ethanol. On distillation or on boiling with water it underwent ready dehydration to 1-methyl-3-vinylindole, which immediately polymerized to poly-(1-methyl-3-vinylindole). There was no evidence of the formation of an appreciable amount of 1,1-di(1′-methyl-3′-indolyl)ethane (IV, R = CH_3), authentic



III IV

(1) Regarded as Part IV in the series: Synthetic Experiments Related to the Indole Alkaloids.

(2) Recipient of a C.S.I.R.O. Senior Postgraduate Studentship, 1961–1962.

(3) Part III: K. T. Potts and D. R. Liljegren, *J. Org. Chem.*, **28**, 3066 (1963).

(4) This work was supported in part by PHS Grant H-6475 from the National Heart Institute, Public Health Service.

(5) E. Leete and L. Marion, *Can. J. Chem.*, **31**, 775 (1953).

(6) M. E. Speeter, U. S. Patent 2,815,734; *Chem. Abstr.*, **52**, 12923*f* (1958).

(7) A. Buzas, C. Hoffman, and G. Regnier, *Bull. soc. chim. France*, 643 (1950).

(8) E. Leete, *J. Am. Chem. Soc.*, **81**, 6023 (1959).