Such observations suggest the intermediate formation of I with R = Cl, NR_2', or OR' in all of these reactions which can easily undergo condensation to III. (See col. 2, p. 4701.)

This is substantiated by the following experimental data: (1) refluxing of the diazaboroline (II) in xylene for about thirty minutes provided III in quantitative yield; (2) treatment of I where R = Cl in boiling benzene with triethylamine yields III; (3) although transamination has been found an extremely useful tool for the facile preparation of boron–nitrogen bonded materials,[16] the transamination of the NR_2-group of II could not be effected under relatively mild conditions. At higher temperatures, condensation of three molecules of II occurs yielding again the borazine derivative (III).

On the basis of this evidence it seems understandable that diazaborolines of type II with R other than alkyl or aryl groups are not common. The intermolecular condensation reaction to yield the borazine derivative (III) appears to predominate over normal substitution reactions at the boron atom, thus indicating a preference for this particular ring system.

The transamination reaction illustrated in equation 1 appears to be generally applicable. This is demonstrated by the facile preparation of 2-phenyl-1,3,2-benzodiazaboroline (II. R = C_6H_5) on the interaction of bis(dimethylamino)phenylborane with *o*-phenylenediamine.

Experimental[17]

2-Dimethylamino-1,3,2-benzodiazaboroline (II).—A mixture of 30 g. (0.21 mole) of tris(dimethylamino)borane and 21.6 g. (0.2 mole) of *o*-phenylenediamine was covered with 250 cc. of dry ether and gently heated at reflux for 15 hr. Volatile components were evaporated under reduced pressure and the remaining solid material was sublimed in vacuum at 120–130° using an oil bath. II was obtained as a white crystalline material in 83% yield (26.5 g.), softening at 158–162° and apparently decomposing near 220°. The residue of the sublimation contained a small amount of III.

Anal. Calcd. for $BN_3C_8H_{12}$: B, 6.7; N, 26.2; C, 59.7; H, 7.6. Found: B, 6.7; N, 26.0; C, 59.1; H, 8.0.

2-Phenyl-1,3,2-benzodiazaboroline (I. R = C_6H_5).—In an analogous procedure, a slight excess of bis(dimethylamino)phenylborane reacted with *o*-phenylenediamine to yield 2-phenyl-1,3,2-benzodiazaboroline in 88% yield. The material did not depress the melting point of an authentic sample prepared by a previously described method[7]; their infrared spectra were identical.

5H,12H,19H-Tris(1,3,2-benzodiazaborolo)borazine (III).—(a) Four grams (0.025 mole) of II was covered with 30 cc. of xylene and refluxed for 30 min. After cooling to room temperature, the crude solid product was filtered off and recrystallized from acetone to yield 3.7 g. (94%) of III, softening near 350° and apparently decomposing near 380°. (b) 2-Chloro-1,3,2-benzodiazaboroline (7.6 g., 0.05 mole) was covered with 100 cc. of dry benzene and 10.1 g. (0.1 mole) of triethylamine added. The mixture was refluxed for 10 hr. Recrystallization of the solid residue yielded 4.4 g. (82%) of III, identical with a sample obtained from (a) and a purified sample obtained on thermal decomposition of the 2-chloro-1,3,2-benzodiazaboroline.

Anal. Calcd. for $B_3N_6C_{18}H_{15}$: B, 9.3; N, 24.2; C, 62.2; H, 4.3. Found: B, 9.3; N, 23.9; C, 61.9; H, 4.1.

(16) See and *cf.* ref. 10 and literature cited therein.

(17) Analysis by the Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y. Melting points were taken in sealed capillary tubes on a Mel-Temp block. Infrared spectra were recorded as mulls and potassium bromide pellets on a Perkin–Elmer Model 21 spectrophotometer using sodium chloride optics.

Alkaloid Studies. XXXIX.[1] The Occurrence of Dihydrocorynantheol and Aricine in *Aspidosperma marcgravianum* Woodson

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In the course of our systematic study of the alkaloids of the genus *Aspidosperma*, we have encountered principally alkaloids of the N-acyldihydroindole type.[2–5] In common with the findings of other authors[6] we have also found tetracyclic indoles such as N-methyltetrahydroellipticine[7] and ulein.[8] More recently two alkaloids with the sarpagine skeleton, polyneuridine and normacusine-B, have been isolated from *A. polyneuron* M. Arg.,[9] a species which also synthesizes the biogenetically distinct quebrachamine and aspidospermine. Species of this genus are also able to produce alkaloids of the yohimbine type,[10] and we have found β-yohimbine in an, as yet, unidentified[11] *Aspidosperma species*.

We now wish to report the isolation of two other alkaloid types related to yohimbine from the bark

(1) Paper XXXVIII, C. Djerassi, H. W. Brewer, C. L. Clarke, and L. J. Durham, *J. Am. Chem. Soc.*, **84**, 3210 (1962).

(2) C. Djerassi, A. A. P. G. Archer, T. George, B. Gilbert, and L. D. Antonaccio, *Tetrahedron*, **16**, 212 (1961).

(3) B. Gilbert, J. M. Ferreira, R. J. Owellen, C. E. Swanholm, H. Budzikiewicz, L. J. Durham, and C. Djerassi, *Tetrahedron Letters*, 59 (1962).

(4) C. Djerassi, T. George, N. Finch, H. F. Lodish, H. Budzikiewicz, and B. Gilbert, *J. Am. Chem. Soc.*, **84**, 1499 (1962).

(5) C. Djerassi, L. D. Antonaccio, H. Budzikiewicz, J. M. Wilson, and B. Gilbert, *Tetrahedron Letters*, in press.

(6) For leading references see (a) J. Schmutz, *Pharm. Acta Helv.*, **36**, 103 (1961); (b) M. A. Ondetti and V. Deulofeu, *Tetrahedron*, **15**, 160 (1961).

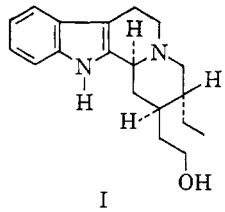
(7) Isolated from *A. parvifolium* A. DC., by Dr. T. George in our laboratory.

(8) B. Gilbert, L. D. Antonaccio, A.A.P.G. Archer, and C. Djerassi, *Experientia*, **16**, 61 (1960).

(9) L. D. Antonaccio, N. A. Pereira, B. Gilbert, H. Vorbrueggen, H. Budzikiewicz, J. M. Wilson, L. J. Durham, and C. Djerassi, *J. Am. Chem. Soc.*, **84**, 2161 (1962).

(10) (a) E. Fourneau and H. Page, *Bull. sci. pharmacol.*, **21**, 7 (1941); (b) K. Biemann, M. Friedmann-Spiteller, and G. Spiteller, *Tetrahedron Letters*, 485 (1961).

(11) Originally identified (see ref. 9) incorrectly as *A. eburneum* F. Allem; a specimen of this as yet unidentified species exists in the Rio de Janeiro Botanical Garden under the number R.B. 11.4085.



I

of the Amazonian tree *A. marcgravianum* Woodson. From the alkaloid fraction extracted from 10% acetic acid solution with benzene, there was isolated aricine by way of its crystalline oxalate in 0.01% yield based on dried bark. The alkaloid was identified with an authentic specimen by mixture melting point, infrared, ultraviolet, and mass spectral[9] comparison.

From the alkaloid fraction extracted at pH 7 by chloroform, we isolated dihydrocorynantheol (I) through its oxalate and hydrochloride. This alkaloid is a known substance[12] but has not been previously encountered in nature, although its methochloride has been isolated from *Hunteria eburnea* Pichon.[13] Its identity was quickly established by mass spectrometry. A very strong (M-1) peak at *m/e* 297 and strong peaks at *m/e* 169 and 170 accompanied by satellite peaks at 156 and 184 indicated at once an alkaloid of the yohimbine type.[9] The empirical formula, $C_{19}H_{26}N_2O$, established by analysis and precise mass spectrometric molecular weight determination, indicated one fewer ring than yohimbine, while the presence of a hydroxyl group was shown by the formation of an acetate. The unchanged positions of the *m/e* 156, 169, 170, and 184 peaks in the mass spectrum of the acetate show that this hydroxyl group is not in the β-carboline portion. The nuclear magnetic resonance spectrum of the acetate shows a multiplet due to two hydrogens at 4.05 δ suggesting that the parent alcohol is primary, and the spectra of both acetate and alcohol show a split C-methyl peak at 0.60 to 0.95 δ which is probably part of an ethyl side chain. A literature search then revealed that the physical constants of the alkaloid were close to those recorded for dihydrocorynantheol (I),[12] identity being established by infrared and mass spectral comparison with an authentic sample.[14]

The occurrence of these two new indole alkaloid types in the genus *Aspidosperma* is of considerable biogenetic interest and represents a further illustration of the remarkable ability of this genus to synthesize a wide variety of (dihydro) indole alkaloids.[15]

(12) C. Vamvacas, W. V. Philipsborn, E. Schlittler, H. Schmid, and P. Karrer, *Helv. Chim. Acta*, **40**, 1793 (1957).

(13) J. D. M. Asher, J. M. Robertson, G. A. Sim, M. F. Bartlett, R. Sklar, and W. I. Taylor, *Proc. Chem. Soc.*, 72 (1962).

(14) We are indebted to Dr. W. I. Taylor (Ciba Pharmaceutical Co.) and Professor E. Wenkert (University of Indiana) for the authentic samples.

(15) Even the simple indole, harman-3-carboxylic acid has now been encountered in *A. polyneuron* Mull. Arg. by L. D. Antonaccio and H. Budzikiewiez [*Monatsh. Chem.*, **93**, 962 (1962)].

Experimental

Isolation Procedure.—Dried bark of *A. marcgravianum* Woodson (10 kg.) was extracted with 95% ethanol and concentrated to a thick syrup. This sirup was dissolved in 10% acetic acid (1.6 l.) and water (1 l.), filtered, and extracted successively with petroleum ether (2.5 l.) and benzene (1.1 l.). The benzene extract was concentrated to a small volume, diluted with ether (200 cc.), filtered, and treated with a saturated solution of oxalic acid in ether (50 cc.) to complete precipitation. The oily precipitate crystallized on trituration with methanol giving aricine oxalate (1.1 g.), which after further crystallization from methanol had m.p. 240–241° (lit.,[16,17] m.p. 234–235°). Liberation of free base with ammonia, ether extraction, evaporation of ethereal solution, and three recrystallizations of residue from methanol–water gave *aricine*, m.p. and m.m.p. 184–185.5°.

The above aqueous acetic acid solution was then extracted with chloroform (1.8 l.), brought to pH 7 with ammonium hydroxide solution, and again extracted with chloroform (2 l.). The pH 7 chloroform extract was treated with excess oxalic acid, and, after standing overnight, decanted from the oily precipitate. From this precipitate the free base was liberated with ammonium hydroxide into ether and the dried ethereal solution treated with hydrogen chloride precipitating an oily hydrochloride, which was crystallized from methanol–ether to give dihydrocorynantheol hydrochloride (3.8 g.) as pale yellow needles, m.p. 260–275° dec., $[\alpha]^{25}D$ +12° (*c*, 1.0 in methanol). The infrared spectrum showed λ_{max}^{Nujol} 2.96 (m), 3.72 (m), 12.96 (s) μ. The ultraviolet spectrum had λ_{max}^{EtOH} 226 and 278 mμ (log ε 4.53, 3.86); λ_{min}^{EtOH} 244 mμ (log ε 3.24).

Anal. Calcd. for $C_{19}H_{27}N_2OCl$: C, 68.14; H, 8.12; N, 8.36; O, 4.78; Cl, 10.58. Found: C, 68.26; H, 7.78; N, 8.55; O, 5.06; Cl, 10.57.

Dihydrocorynantheol (I).[16]—Recovery of the free base by treatment of the hydrochloride with ammonium hydroxide and extraction with ether gave dihydrocorynantheol,[12] m.p. 181–183°, $[\alpha]^{27}D$ −19° (*c*, 1.02 in chloroform); $[\alpha]^{27}D$ −34° (*c*, 0.47 in pyridine). The infrared spectrum showed λ_{max}^{film} 3.1 (s), 6.88 (s), 6.93 (s) μ; λ_{max}^{Nujol} 13.5 (s) μ. The ultraviolet spectrum showed λ_{max}^{EtOH} 226 and 281 mμ (log ε 4.56, 3.87) with a shoulder at 290 mμ (log ε 3.80); λ_{max}^{EtOH} 247 mμ (log ε 3.30); $\lambda_{max}^{EtOH-HCl\ (0.1\ N)}$ 221 and 273 mμ (log ε 4.57, 3.88) with a shoulder at 278 mμ (log ε 3.87); $\lambda_{max}^{EtOH-HCl}$ 242 mμ (log ε 3.27).

Anal. Calcd. for $C_{19}H_{26}N_2O$: C, 76.47; H. 8.78; N, 9.39; O, 5.36; mol. wt., 298.4. Found: C, 76.11; H, 8.54; N, 9.37; O, 5.73; mol. wt. (mass spec.), 298.

Dihydrocorynantheol Acetate Hydrochloride.—Dihydrocorynantheol hydrochloride (201 mg.), acetic anhydride (3 cc.), and pyridine (7.5 cc.) were stirred at room temperature for 40 hr. The solution was poured into a saturated solution of sodium bicarbonate (30 cc.) with ice cooling, neutralized with solid sodium bicarbonate, and the resulting mixture extracted with ether (55 cc.). The ethereal solution was dried ($MgSO_4$), evaporated, and the residue freed of pyridine giving the crude crystalline acetate (150 mg.), m.p. 125–128°, $[\alpha]^{30}D$ 0° (*c*, 1.05 in chloroform), λ_{max}^{film} 3.02 (m), 5.76 (s), and 8.12 (s) μ.

Anal. Calcd. for $C_{21}H_{28}N_2O_2$; mol wt. 340.5. Found: mol. wt. (mass spec.), 340.

Purification was difficult, and the acetate was therefore treated with hydrogen chloride in ethereal solution giving a crystalline precipitate which was recrystallized twice from methanol–ether giving yellow needles, m.p. 253–260° dec.,

(16) (a) R. Goutarel, M. M. Janot, A. le Hir, H. Corrodi, and V. Prelog, *Helv. Chim. Acta*, **37**, 1805 (1954); (b) A. Stoll, A. Hofmann, and R. Brunner, *ibid.*, **38**, 270 (1955).

NOTE ADDED IN PROOF: We have recently also isolated dihydrocorynantheol, m.p. 180–183.5°, $[\alpha]^{27}D$ −18° (chloroform), −37° (pyridine), from *Aspidosperma auriculatum*.

(17) F. A. Hochstein, K. Murai, and W. H. Borgemann, *J. Am. Chem. Soc.* **77**, 3551 (1955).

$[\alpha]^{27}D$ +23° (*c*, 1.07 in methanol). λ_{max}^{Nujol} 3.20 (m), 3.78 (w), 3.88 (m), 3.95 (m), 5.75 (s), 7.94 (s), and 13.58 (s) μ.

Acknowledgment.—We are indebted to Dr. William Rodriguez of the Instituto Nacional de Pesquisas do Amazonas and Dr. Aparicio Duarte of the Rio de Janeiro Botanical Garden for plant collection and identification. Analyses were performed by Dr. Alfred Bernhardt (Mülheim, Germany) while the n.m.r. spectra [$CDCl_3$ solution with tetramethylsilane (δ = 0.00 p.p.m.) as internal standard] were obtained by Dr. Lois J. Durham and the mass spectra were measured by Dr. H. Budzikiewicz and Dr. J. M. Wilson. Financial assistance in support of the joint research effort on Brazilian plants between the Instituto de Quimica Agricola and Stanford University was provided by the Rockefeller Foundation. One of us (L.D.A.) acknowledges receipt of a fellowship from the International Cooperation Administration under a program administered by the U.S. National Academy of Sciences while on leave from the Instituto Nacional de Technologia, Rio de Janeiro, Brazil.

Phosphorus Acids in Organic Systems. III. Specific Pyrophosphoric Acid Catalysis in the Conversion of Resorcinol Dimethyl Ether to Coumarins[1]

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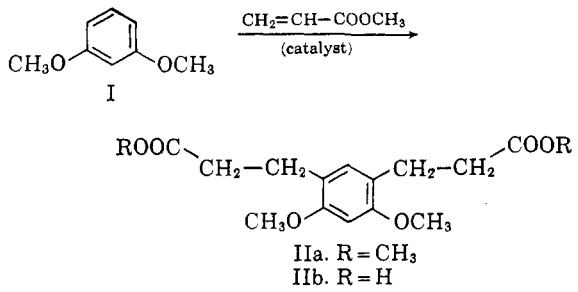
Studies on the composition of polyphosphoric acid[2-6] indicate that the components (H_3PO_4, $H_4P_2O_7$, $H_5P_3O_{10}$, etc.) comprise a spectrum of equilibria which is governed by concentration (% P_2O_5) and, presumably, by temperature. This would perhaps make it seem futile to look for specific catalysis by individual components of these equilibria except for the fact that equilibrium is established rather slowly.[4]

The condensation between pyrogallol trimethyl ether and benzoic acid is catalyzed by polyphosphoric acid and proceeds efficiently to give 2,3,4-trimethoxybenzophenone.[7] This reaction has now been studied semiquantitatively in a series of experiments in which the polyphosphoric acid was varied in composition (% P_2O_5) and the extent of conversion to the product determined after a



IIa. R = CH_3
IIb. R = H

reaction time of ten minutes. Good kinetic studies of polyphosphoric acid systems are precluded by the viscosity of the reagent but the data obtained are meaningful on a relative basis; these are shown graphically in Fig. 1. The change in slope at high phosphorus pentoxide concentrations is undoubtedly due to the increased viscosity of the solution where the already serious diffusion problem approaches the point of control. The most significant feature is the displacement of the pyrophosphoric acid point from the curve. It demonstrates that equilibration of pyrophosphoric acid among the various equilibrium components existent at that phosphorus pentoxide concentration[4] of polyphosphoric acid does not occur to an appreciable extent during ten minutes at 65° and, perhaps more significantly, that pyrophosphoric acid is almost certainly noncatalytic in this process.[8]

It has been observed, on the other hand, that the reaction between resorcinol dimethyl ether (I) and methyl acrylate proceeds in good yield (77%) to give a bispropionate (IIa) when catalyzed by pyrophosphoric acid but in poor yield (34%) when catalysis is by polyphosphoric acid of about the same phosphorus pentoxide content. Identification of the product in each case was through the diacid (IIb).[11]

The most conspicuous catalyst specificity yet observed is that in the reaction of resorcinol dimethyl ether (I) with β-keto esters. It was found that I reacts with ethyl acetoacetate in the presence of pyrophosphoric acid to give 7-methoxy-4-methylcoumarin (III) and methyl *trans*-β-methyl-2,4-dimethoxycinnamate (IVa). Similarly with 2-carbethoxycyclohexanone, I in the presence of pyro-

(1) Part II, P. D. Gardner, *J. Org. Chem.*, **77**, 4675 (1955).
(2) Victor Chemical Co.
(3) R. N. Bell, *Ind. Eng. Chem.*, **39**, 136 (1947); **40**, 1464 (1948).
(4) A. Huhti and P. A. Gartaganis, *Can. J. Chem.*, **34**, 785 (1956).
(5) V. E. Thilo and R. Sauer, *J. prakt. Chem.*, [4] **4**, 324 (1957).
(6) General applications of polyphosphoric acid in condensation reactions and rearrangements have been reviewed; F. D. Popp and W. E. McEwen, *Chem. Rev.*, **58**, 321 (1958).
(7) P. D. Gardner, *J. Am. Chem. Soc.*, **76**, 4550 (1954).

(8) Another illustration of difference is found in the rearrangement of the oxime of fluorenone. Horning, Stromberg, and Lloyd[9] observed that the reaction proceeds readily at 180° in polyphosphoric acid whereas Anet, Bavin, and Dewar[10] report the oxime to be stable at 190° in a 2:1 mixture of sirupy phosphoric acid and phosphorus pentoxide. This mixture contains 74.4% phosphorus pentoxide and corresponds approximately to a reported[4] polyphosphoric acid mixture of 68% orthophosphoric acid, 29% pyrophosphoric acid, and 3% tripolyphosphoric acid. It seems probable that equilibration to this composition occurred at 190° and therefore that orthophosphoric acid and pyrophosphoric acid are noncatalytic in the Beckmann rearrangement.
(9) E. C. Horning, V. L. Stromberg, and H. A. Lloyd, *J. Am. Chem. Soc.*, **74**, 5153 (1952).
(10) F. A. L. Anet, P. M. G. Bavin, and M. J. S. Dewar, *Can. J. Chem.*, **35**, 180 (1957).
(11) The "addition" of aromatics to unsaturated esters has been reported with other Lewis acids. For examples, see "Anhydrous Aluminum Chloride in Organic Chemistry," C. A. Thomas, Reinhold Publishing Corp., New York, N. Y., 1941, pp. 477, 478.