hydrochloric acid. Cooling was necessary to keep the solution from refluxing. The mixture was then heated on the steam-bath for 1 hr. After cooling, the tin double salt was removed and air-dried. The yield was 34 g., 71%.

Five grams of the double salt (0.0106 mole) was dissolved in 50 ml. of 2 *N* hydrochloric acid and cooled to 5–10°. A solution of 1.38 g. (0.02 mole) of sodium nitrite in 25 ml. of water was added dropwise with stirring. Stirring was continued for two more hours. The red precipitate was removed, washed with water and then recrystallized from dimethylformamide–water. The crystals were pale red in color.

PHILADELPHIA, PENNA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

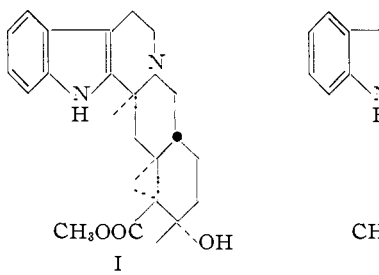
Stereochemistry of Corynantheine, Dihydrocorynantheine and Corynantheidine[1]

BY EUGENE E. VAN TAMELEN, PAUL E. ALDRICH AND THOMAS J. KATZ

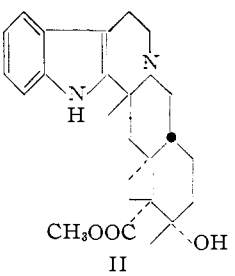
RECEIVED JUNE 7, 1957

On the basis of a stereospecific synthesis of *dl*-corynantheane, as well as interpretations of previously recorded data, the stereoformulas of corynantheine, dihydrocorynantheine and corynantheidine (excluding C-3) are derived. The nature of the isomerism between the corynantheic acids is established and the stereoselectivity of decarboxylation displayed by these acids is discussed.

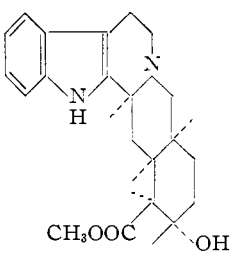
Yohimbe alkaloids which have been isolated from *Pseudocinchona Africana* A. Chev. include the well-known pentacyclic isomers corynanthine (I), pseudoyohimbine (II) and α-yohimbine (rauwolscine, corynanthidine) (III), along with the novel tetracyclic corynantheine (IV), dihydrocorynantheine and corynantheidine (V).[2] The concurrence of the two groups is of particular importance,



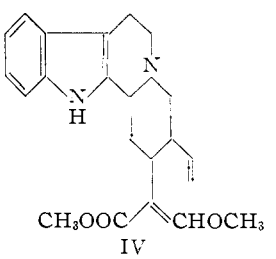
I



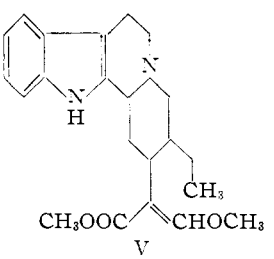
II



III

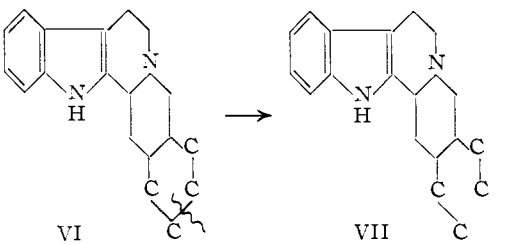


IV



V

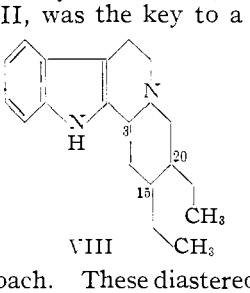
in that it lends further support to the hypothesis of ring-E cleavage[3] of the pentacyclic indole type (VI), which is considered to generate the embryonic skeleta (VII) of several important alkaloid classes, for example, the ajmaline, strychnine, heteroring-E and curare groups. Consequently, illumination of the genealogies and branches in this family becomes of interest; and with the gross structures of many



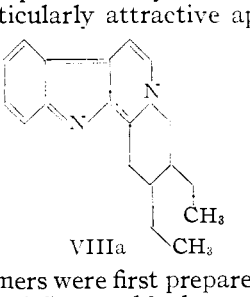
VI VII

members now established, there remains the matter of clarifying the stereochemical relationships involved. Although the nature of all the asymmetric centers in the yohimbine class has been carefully determined,[4] stereochemical structures of the tetracyclic group (IV and V) have not been derived. In this contribution, we describe results which permit assignment of stereochemistry to the corynantheine system.

In assessing the various means by which information about the stereochemistry of these *seco*-alkaloids might be gained, it became clear that a pair of transformation products, dihydrocorynantheane and corynantheidane, both represented by formula VIII, was the key to a particularly attractive approach. These diastereoisomers were first prepared several years ago by Janot and Goutarel,[5] who con-



VIII



VIIIa

(1) Preliminary communication: *Chemistry & Industry*, 793 (1956).

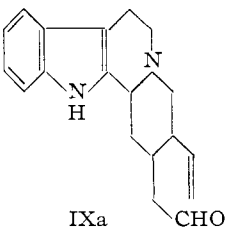
(2) R. H. F. Manske and H. L. Holmes, "The Alkaloids," Vol. II, Academic Press, Inc., New York, N. Y., 1952, p. 420.

(3) R. B. Woodward, *Nature*, **162**, 155 (1948).

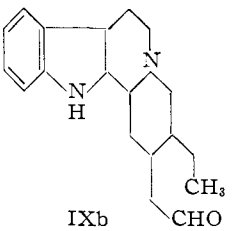
(4) For a review, see J. E. Saxton, *Quart. Revs.*, **10**, 108 (1956). For results requiring the revised stereoformula III for α-yohimbine, see (a) C. Huebner and E. Wenkert, THIS JOURNAL, **77**, 4180 (1955); (b) P. A. Diassi, F. L. Weisenborn, C. M. Dylion and O. Wintersteiner, *ibid.*, **77**, 4687 (1955); (c) E. E. van Tamelen and P. Hance, *ibid.*, **77**, 4692 (1955).

(5) M.-M. Janot and R. Goutarel, *Compt. rend.*, **231**, 152 (1950); *Bull. soc. chim. France*, 588 (1951).

verted, through appropriate hydrolysis and decarboxylation operations, corynantheine and corynantheidine to the aldehydes corynantheal (IXa) and corynantheidal (IXb), respectively; Wolff–Kishner reduction of these aldehydes (along with catalytic



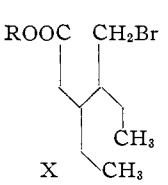
IXa



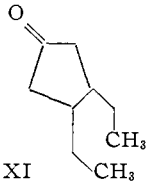
IXb

reduction of the isolated double bond in IXa) completed the reaction sequence. These changes would not be expected to disturb the asymmetric centers 15 and 20; consequently, it was possible to demonstrate, through lead tetraacetate oxidation to a pair of isocarbolines (VIIIa), that corynantheine and corynantheidine are epimeric around these two centers.[6] Therefore, a synthesis which would define unequivocally the relative stereochemistry of either the C-15, C-20-*cis* or -*trans* form of structure VIII and thereby establish the stereochemical nature of the corresponding centers in the parent alkaloids was undertaken.

The synthetic route envisioned required a 3,4-diethyl-5-bromovaleric acid ester (X) of known (*threo* or *erythro*) stereochemistry. Production of the δ-bromoester from 3,4-diethylcyclopentanone (XI) seemed practical, and highly desirable, in



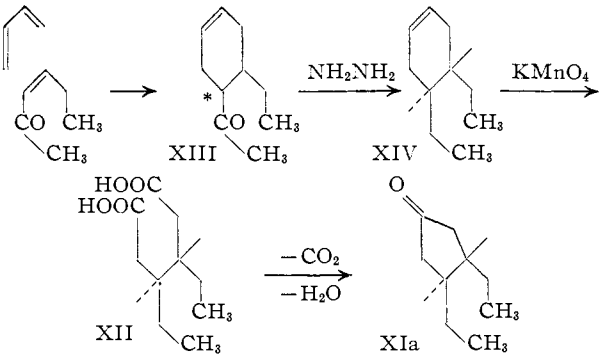
X



XI

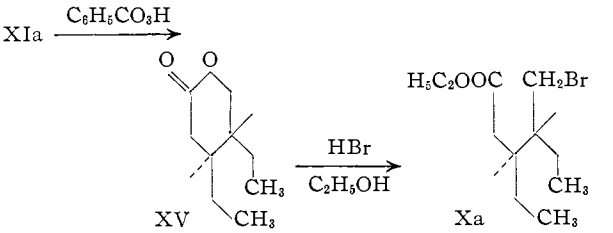
that both diasteroisomeric forms of this ketone had been prepared and the relative configurations had been determined by Koelsch and Stratton, who secured, through decarboxylation–cyclization of a resolvable form of 3,4-diethyladipic acid (XII), the *trans*-cyclopentanone XI; from the *meso*-adipic acid, the *cis* form was prepared.[7]

The diethyladipic acids originally were obtained, as a mixture, through bimolecular chemical reduction of propylidenemalonic ester, followed by hydrolysis and decarboxylation.[7] In our laboratory, the *dl*-acid—unaccompanied by any noticeable amount of the *meso* form—was provided by an alternate approach. 6-Ethyl-3-cyclohexen-1-yl methyl ketone (XIII), previously prepared by means of the Diels–Alder reaction between 1,3-butadiene and 3-hexen-2-one,[8] was reduced by the Wolff–Kishner method (Huang-Minlon modification) to the olefin XIV. Because of the strongly basic conditions employed in this reaction and because of the enolizable center (*) in the ketone XIII, the hydrocarbon undoubtedly has the more

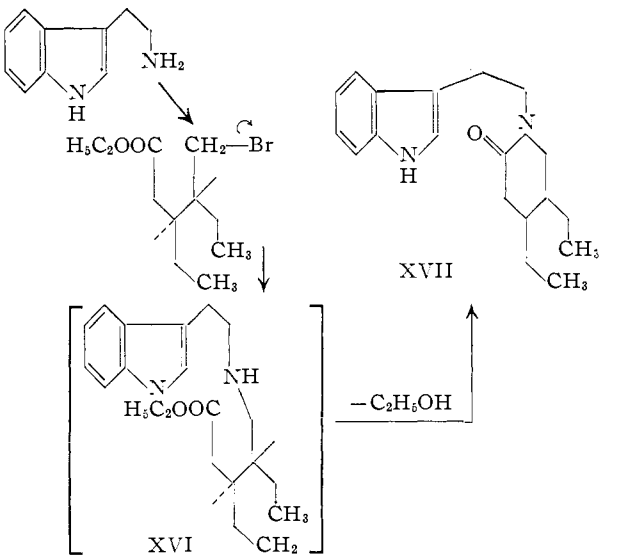


stable diastereoisomeric form. Permanganate oxidation of the olefin led to the *dl*-adipic acid, which was cyclized to the *trans*-ketone XIa, using the conditions employed by the earlier workers.[7]

The remaining steps in the projected synthesis of the indole VIII started with the ring expansion of the *trans*-diethylcyclopentanone to the δ-lactone XV by perbenzoic acid. The lactone was not iso-



lated but was converted by the action of ethanolic hydrogen bromide to the required bromoester Xa, b.p. 123–125° (6 mm.). Following paths already traversed in the pentacyclic series,[9] we then proceeded to N-alkylate tryptamine with the bromoester.



The reaction, accomplished by refluxing an ethanol solution of the components in the presence of potassium carbonate, did not stop at the amino ester stage (XIV) but, as expected,[9] afforded directly the lactam XVII. The latter, isolated and purified by chromatography, melted at 124.5–125° and was the

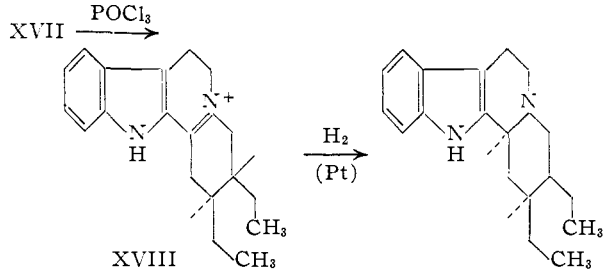
(6) M.-M. Janot, R. Goutarel, A. LeHir, G. Tsatsas and V. Prelog, *Helv. Chim. Acta*, **38**, 1073 (1955).

(7) C. F. Koelsch and C. H. Stratton, THIS JOURNAL, **66**, 1881 (1944).

(8) E. D. Bergmann and C. Resnik, *J. Org. Chem.*, **17**, 1291 (1952).

(9) E. E. van Tamelen, M. Shamma and P. Aldrich, THIS JOURNAL, **78**, 4628 (1956).

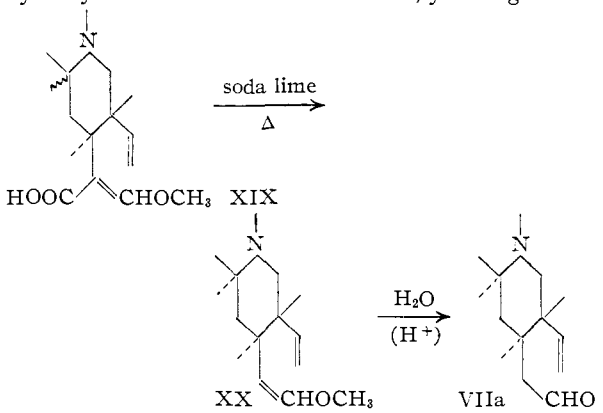
only crystalline intermediate encountered in the series. Completion of the synthesis involved cyclization of the lactam with phosphorus oxychloride which produced the Δ^3-tetracyclic intermediate XVIII; the imine salt was not easily handled or purified and consequently was reduced in the crude



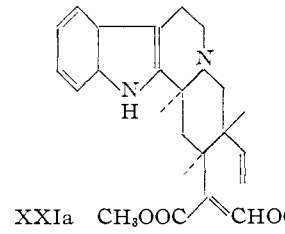
state over Adams catalyst to give a crystalline solid (m.p. 154–156°) which was shown to be *dl*-dihydrocorynantheane, by infrared spectral comparison with *l*-dihydrocorynantheane obtained from the alkaloid. *This outcome thus establishes the C-15, C-20-trans-arrangement in corynantheine and dihydrocorynantheine.*

In order to complete the assignment of stereochemistry, the configuration at C-3 relative to the other centers in the corynantheine molecule must be ascertained. It may be pointed out first of all that corynantheane doubtless belongs to the C-3, C-15-*cis* series, since catalytic reduction of the Δ^3-unsaturated intermediate XVIII would be expected to afford, by analogy to the D–E *trans*-yohimbine series,[9] the more stable product. Unfortunately, the assignment does not extend to corynantheine itself, since one of the operations used in the corynantheine → corynantheane conversion, namely, Wolff–Kishner reduction of corynantheal, employs basic conditions sufficiently drastic to epimerize at C-3, were corynantheine to possess the less stable arrangement at this position. However, by using certain observations made by previous workers, it is possible to deduce the relation of C-3 to the other asymmetric centers.

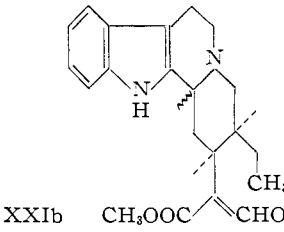
Corynantheal (IXa) has been obtained by two routes.[5] In the first, corynantheic acid (XIX) was subjected to soda lime distillation, affording "Decarboxycorynantheine" (XX); this enol ether was hydrolyzed with dilute mineral acid, yielding the al-



dehyde. Soda lime distillation can, on the basis of observations in the yohimbine family,[10] effect epimerization at C-3; consequently, the changes described imply the more stable conformation (axial hydrogen, *cis* to that at C-15, formula VIIa) at C-3 for corynantheal, although they leave unanswered the question of orientation at this center in the parent alkaloid. Now, corynantheal also can be obtained by direct hydrolysis of corynantheic acid with 0.1 *N* hydrochloric acid at 70°. This fact denotes the C-3, C-15-*cis* relationship in corynantheine, provided that the acidic medium does not concurrently cause inversion at C-3. The mild conditions used make this unlikely, and the possibility was contraindicated by stability studies carried out on a C-2, C-3-axial indole alkaloid, reserpine: the base was recovered unchanged after being subjected to the acidic conditions employed in the conversion of corynantheic acid to corynantheal. Because of the presence of the ring-A methoxyl in the test compound, epimerization at C-3 is more readily brought about here than in the unsubstituted tetrahydro-β-carboline system; and thus this demonstration of C-3 stability in reserpine makes any epimerization process in corynantheine seem remote. Since the basic conditions used to convert corynantheine to corynantheic acid also are not sufficiently drastic to induce inversion at C-3, corynantheine therefore must be the stereochemical equivalent of corynantheal, *i.e.*, C-3, C-15, C-20-*cis*, *trans*, as depicted in formula XXIa.



In view of the established relationship between corynantheine and corynantheidine,[6] the latter may now be formulated as a member of the C-15, C-20-*cis* category (XXIb). However, we have not ac-



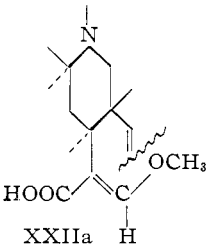
quired evidence sufficient to permit an assignment to C-3 in this alkaloid.[11]

Janot and Goutarel report that the corynantheic acid (levorotatory) obtained by hydrolysis of corynantheine with alkali, could be transformed, on mild treatment with dilute mineral acid, to a dextrorotatory isomer. The relationship between the substances appears to be a subtle one, since they both provided, on further hydrolysis, corynantheal.[5] The demonstration that mild acid treatment does not induce any configurational or gross structural

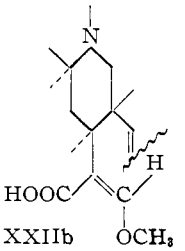
(10) G. Hahn and W. Stern, *Ber.*, **61**, 278 (1928).

(11) On the basis of infrared spectral data, Wenkert and Roychaudhuri tentatively regard (THIS JOURNAL, **78**, 6417 (1956)) the C-3 hydrogen in corynantheidine as *cis* to that at C-15. Also, on the same basis, the C-3 assignment made for corynantheine[1] is supported.

change in corynantheic acid leaves geometrical isomerism, as suggested by Janot and Goutarel, the only basis for a reasonable explanation. Thus the two corynantheic acids must be represented by structures XXIIa and XXIIb. Unfortunately the



XXIIa



XXIIb

data available do not permit a definite assignment of structure: steric considerations strongly imply the structure XXIIa for the stabler isomer, but electronic factors are difficult to assess.

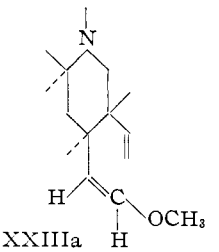
There are a number of simpler analogies for the decarboxylation of the corynantheic acids, *e.g.*, pyrolysis—with or without dry alkali—of β-ethoxycrotonic,[12] β-ethoxymethacrylic[13] and α-methyl-β-alkoxycrotonic acids.[14] Since the geometrical re-

$$CH_3C(OC_2H_5)=CHCOOH \xrightarrow[Ca(OH)_2]{\Delta} C_2H_5OC(CH_3)=CH_2$$

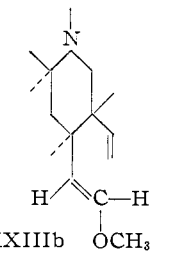
$$CH(OC_2H_5)=C(CH_3)COOH \xrightarrow{\Delta} C_2H_5OCH=CHCH_3$$

$$CH_3C(OR)=C(CH_3)COOH \xrightarrow{\Delta} CH_3(OR)C=CHCH_3$$

lationships implicit in these simple cases have not been determined, it is noteworthy that decarboxylation of the corynantheic acids appears to give different enol ethers. Clearly, "decarboxycorynantheine," derived from the levorotatory acid, and the isomeric "neodecarboxycorynantheine" (poorly defined, but apparently different from decarboxycorynantheine) are geometrical isomers, represented by the formulas XXIIIa and XXIIIb.



XXIIIa H



XXIIIb

Experimental

dl-trans-**6-Ethyl-3-cyclohexen-1-yl Methyl Ketone (XIII).**—The ketone was prepared according to the method of Bergmann and Resnik.[8] The required propylideneacetone, however, was prepared by the method of Eccott and Linstead[15] as for butylideneacetone.

dl-trans-**4,5-Diethylcyclohexene (XIV).**—In a flask equipped with a Cope separator were placed 75 ml. of triethylene glycol, 40 g. (0.263 mole) of XIII, 80 ml. of benzene and 25.5 ml. (25.6 g., 0.800 mole) of anhydrous hydrazine (85% hydrazine hydrate was also found to be equally effective). The entire reaction was carried out in the hood, and the mixture was refluxed until water no longer separated (about 5 hr.). After the mixture had cooled, 10 g. of potassium hydroxide was added, and the mixture was again azeotroped until no more water separated. The flask was then set up for distillation using a short air condenser of large diameter leading into a flask immersed in an ice-bath. The volatile constituents were distilled. The receiver was changed and the temperature of the reaction flask was allowed to rise to 190–200° and held there for 15 hr. At the end of this time the bath temperature was raised still farther. The distillate was diluted with a little water and extracted with petroleum ether. The petroleum ether extracts were washed with saturated salt solution, dried with magnesium sulfate and concentrated.

The above procedure was repeated on another 39 g. of starting material and the products combined. Refluxing over metallic sodium and distillation gave 49.5 g. (69%) of *dl-trans*-diethylcyclohexene, b.p. 171–173° (730 mm.), $n^{25}D$ 1.4562.

Anal. Calcd. for $C_{10}H_{18}$: C, 86.88; H, 13.12. Found: C, 86.64; H, 13.12.

dl-**3,4-Diethyladipic Acid (XII).**[7]—To a solution of 125 g. of potassium permanganate dissolved in 2500 ml. of water was added 25 g. of *dl-trans*-4,5-diethylcyclohexene. The mixture was stirred vigorously at room temperature for 12 hr. Then sodium bisulfite and 6 *N* sulfuric acid were added alternately (so that the amount of precipitated material did not become excessive) with external cooling. When the solution became nearly colorless and acid to congo red, it was extracted five times with ether. The ether extracts were dried with magnesium sulfate, the ether was evaporated and the residue was crystallized from water to give 19.4 g. (53%) of *dl*-3,4-diethyladipic acid, m.p. 131.8–133.8° (reported[7] 133–134°).

dl-trans-**3,4-Diethylcyclopentanone (XI).**—XI was prepared by refluxing the diethyladipic acid with acetic anhydride and pyrolyzing the product according to the procedure described by Koelsch and Stratton (b.p. 202–208°, **semicarbazone** m.p. 208.5–209.5° from ethanol (reported[7] m.p. 203–206°).

Ethyl *threo*-**5-Bromo-3,4-diethylvalerate (X).**—To 2.9 g. (0.0207 mole) of *trans*-3,4-diethylcyclopentanone was added 0.03232 mole of perbenzoic acid in 55 ml. of moist chloroform. The mixture was stoppered and stored in the dark at room temperature. Titration of aliquots of the mixture from time to time showed the reaction to be 95% complete in 3 days. The chloroform was removed at reduced pressure, and the product was taken up in ether. The solution was washed successively with dilute ferrous sulfate (slightly acidified with a little sulfuric acid), with sodium bicarbonate, with slightly acidified water and finally with saturated salt solution. The ether solution was dried over magnesium sulfate and evaporated to give 2.9 g. of the colorless, liquid lactone. No further purification or characterization was carried out—this material was used directly for preparation of the bromoester.

The lactone was washed into a glass bomb tube with 33 ml. of absolute ethanol, placed in an ice-bath and saturated with dry hydrogen bromide (*ca.* 45 g.). The tube was loosely stoppered and allowed to stand overnight at room temperature. Usually after 12–24 hr. standing, two liquid phases had separated. This mixture was again saturated with hydrogen bromide in an ice-bath, but this time the bomb was sealed, allowed to warm to room temperature and shaken gently several days in a mechanical shaker. The glass tube was cooled, opened and the contents were concentrated at reduced pressure. The residue was taken up in ether and water, placed in a large beaker and cautiously neutralized with solid sodium bicarbonate until foaming had ceased. Ether extraction in the usual way gave 3.8 g. of crude bromoester. The liquid was distilled through a Podbielniak spiral metal wire column with a heated jacket to give 2.44 g. (45% from the diethylcyclopentanone) of ethyl *threo*-5-bromo-3,4-diethylvalerate, b.p. 123–125° (6 mm.), $n^{25}D$ 1.4649. For analysis the ester was chromatographed on Alcoa alumina and then distilled in a creased sublimation tube to give the nearly colorless, liquid bromoester.

Anal. Calcd. for $C_{11}H_{21}O_2Br$: C, 49.79; H, 7.98; Br, 30.14. Found: C, 50.26; H, 8.05; Br, 29.94.

dl-trans-**N-(β-3'-Indolylethyl)-4,5-diethyl-2-piperidone (XVII).**—Tryptamine (604 mg., 3.42 mmoles), bromoester (302 mg., 1.14 mmoles), anhydrous potassium carbonate (75.4 mg., 1.25 meq.) and a crystal of potassium iodide were heated in 15–20 ml. of gently refluxing, purified, dry dioxane

(12) L. Claisen, *Ber.*, **26**, 2732 (1893).
(13) A. E. Tschitschibabin, *J. prakt. Chem.*, **2**, 74, 423 (1906).
(14) A. Lapworth and B. S. Mellor, *J. Chem. Soc.*, **107**, 1276 (1915).
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under nitrogen for 42 hr. The dioxane was removed by evaporation at reduced pressure. The residue was taken up in ether, which was washed with sufficient dilute hydrochloric acid to remove the excess tryptamine, washed with saturated salt solution, dried over magnesium sulfate and evaporated. The crude residue was chromatographed on Florisil (eluted with ether and ether–chloroform) to give 264 mg. of crystalline material. Two recrystallizations from ethyl acetate–petroleum ether mixture gave 159 mg. (48%) of the piperidone, m.p. 124.5–125.0°.

Anal. Calcd. for $C_{19}H_{26}ON_2$: C, 76.47; H, 8.78. Found: C, 76.53; H, 8.72.

***dl*-Dihydrocorynantheane.**—The piperidone (159 mg.) and 0.4 ml. of freshly distilled phosphorus oxychloride were heated under reflux protected from moisture in 15–20 ml. of dry benzene for 3 hr. on the steam-bath. The flask was allowed to cool, and the crystals were filtered off and washed with benzene. The intermediate cyclization product was not characterized but hydrogenated directly. It rapidly took up 90% of the theoretical amount of hydrogen over platinum (14 mg. of platinum oxide) in ethanol at atmospheric pressure. The catalyst was filtered off, the solvent evaporated and the residue crystallized from ethanol to give 102 mg. of colorless, crystalline ***dl*-dihydrocorynantheane hydrochloride**, dec. 270°. The free base was prepared by pouring the crystals into a saturated solution of potassium carbonate containing a little potassium hydroxide, covering the mixture with ether, and allowing to stand several hours, *i.e.*, until the crystals had dissolved. From the ether phase was isolated 96 mg. (64% from the piperidone) of *dl*-dihydrocorynantheane, m.p. 147–152°. Recrystallization from ethyl acetate–petroleum ether to constant melting point gave m.p. 154–156°.

Anal. Calcd. for $C_{19}H_{26}N_2$: C, 80.80: H, 9.28. Found: C, 81.00; H, 9.02.

The infrared spectrum of the synthetic product was identical with that of naturally derived dihydrocorynantheane but differed from that of naturally derived corynantheidane. The spectra were all run in chloroform solution on a Perkin–Elmer double-beam spectrophotometer.[16]

Stability of Reserpine in Hydrochloric Acid.—Reserpine (504 mg., m.p. 267–269°, $[\alpha]^{25}D$ −119°) was dissolved in a mixture of 15 ml. in hydrochloric acid and 30 ml. of dioxane with warming. After dissolution was complete, the temperature was held at 70–80° for 2 hr. The solution was cooled and made basic with dilute ammonium hydroxide to give 490 mg. of crude product. Crystallization from methanol gave 286 mg. of reserpine, m.p. 265.5–267°, $[\alpha]^{25}D$ −119°. Chromatography of the mother liquors furnished 42 mg. more of reserpine, m.p. 262.5–266°, $[\alpha]^{25}D$ −118°. The remaining material was an intractable tar. Total recovery of reserpine was 328 mg. (65%).

(16) The authors are indebted to Prof. Prelog for the infrared spectra.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

Azo Compounds.[1] Oxidation of 1,1-Disubstituted Hydrazines. The Synthesis and Oxidation of *cis*- and *trans*-1-Amino-2,6-diphenylpiperidine. A New Stereospecific Ring Closure

BY C. G. OVERBERGER, JOSEPH G. LOMBARDINO[2] AND RICHARD G. HISKEY

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The synthesis, identification and oxidation of the *cis* and *trans* isomers of 1-amino-2,6-diphenylpiperidine is described. Oxidation of these 1,1-disubstituted hydrazines with mercuric oxide gave a theoretical evolution of nitrogen with high yields of 1,2-diphenylcyclopentane. The *trans*-hydrazine yields mostly *trans*-1,2-diphenylcyclopentane, while the *cis*-hydrazine yields only *cis*-1,2-diphenylcyclopentane; a smaller amount of 1,5-diphenyl-1-pentene was obtained from both hydrazines. A stereospecific ring closure is indicated by retention of configuration of the benzyl carbon atoms; the small amount of inversion accompanying oxidation of the *trans*-hydrazine is best explained by the facile isomerization of this hydrazine to the corresponding *cis* isomer before or during oxidation.

The results of many oxidations of 1,1-disubstituted hydrazines as reported in the early literature are summarized in a book on the hydrazines by Wieland.[3] In almost every case a tetrazene was the principal product, and we shall refer to tetrazene formation hereafter as the "normal" oxidation product.

There are, in addition, three examples of abnormal oxidations of 1,1-disubstituted hydrazines where nitrogen gas is eliminated with resultant carbon–carbon bond formation. Busch and Weiss[4] were the first to observe nitrogen evolution and the formation of bibenzyl, when 1,1-dibenzylhydrazine was oxidized in ethanol solution with mercuric oxide. More recently, Hinman and Hamm[5] reported oxidation of *p*-substituted 1,1-dibenzylhydrazines with mercuric oxide in ethanolic solution to give only 4-substituted bibenzyls in varying yields depending on the *p*-substituent.

$$p\text{-}x\text{-}C_6H_4CH_2\text{—}\underset{\displaystyle NH_2}{\overset{\displaystyle |}{N}}\text{—}CH_2C_6H_5 \xrightarrow{[O]} p\text{-}x\text{-}C_6H_4CH_2CH_2C_6H_5 + N_2$$

These authors also report the formation of 2-(β-phenylethyl)-furan in 35% yield on oxidation of 1-benzyl-1-furfurylhydrazine.

Overberger and co-workers[6] reported a 9% yield of bibenzyl and the normal tetrazene acid decomposition products when 1,1-dibenzylhydrazine was oxidized with bromine in aqueous ethanol. Oxidation of 1,1-dibenzylhydrazine with *t*-butyl hypochlorite gave a 12% yield of bibenzyl.[6] These workers also have examined the oxidation behavior of 1-amino-2,6-dicyano-2,6-dimethylpiper-

(1) This is the 19th in a series of papers concerned with the preparation and decomposition of azo compounds. For the previous paper in this series, see C. G. Overberger, N. R. Byrd and R. B. Mesrobian, THIS JOURNAL, **78**, 1961 (1956). For a preliminary report of this work see C. G. Overberger, J. G. Lombardino and R. G. Hiskey, *ibid.*, **79**, 1510 (1957).

(2) This paper comprises a portion of a thesis presented by Joseph G. Lombardino in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the Polytechnic Institute of Brooklyn.

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