THE SYNTHESIS OF PYRIDOCARBAZOLES[1]

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ABSTRACT

7H-Pyrido(2,3-*c*)- (IX, R = H) and 7H-pyrido(3,2-*c*)carbazole (V, R = H) have been synthesized by unambiguous routes and shown to be identical with the products resulting from the Fischer-indole ring closure followed by dehydrogenation of 6- and 7-quinolylhydrazone of cyclohexanone respectively. The cyclization of N-substituted-1,2,3,4-tetrahydro-6- and -7-quinolylhydrazone of cyclohexanone followed by hydrolysis and dehydrogenation resulted in the linear polycyclic systems, 6H-pyrido(3,2-*b*)- (VIII) and 10H-pyrido(2,3-*b*)carbazole (IV) respectively. The 12 possible pyridocarbazoles have now been prepared.

The structure of the Skraup reaction product of 1-phenyl-5-amino-1-benzotriazole (X) has been established.

The fusion of the carbazole nucleus (I) at the *a*, *b*, and *c* positions with the pyridine ring (II) at the 2,3- and 3,4-positions results in 12 isomeric pyridocarbazoles, six belonging to the quinoline and six to the isoquinoline series. The synthesis of the isoquinoline series, namely 11H-pyrido(3,4-*a*)-, 11H-pyrido(4,3-*a*)-, 10H-pyrido(3,4-*b*)-, 6H-pyrido(4,3-*b*)-, 7H-pyrido(3,4-*c*)-, and 7H-pyrido(4,3-*c*)carbazole, has already been reported (9, 10). Of the pyridocarbazoles belonging to the quinoline series, namely 10H-pyrido(2,3-*b*)- (IV), 7H-pyrido(3,2-*c*)- (V), 11H-pyrido(3,2-*a*)- (VI), 11H-pyrido(2,3-*a*)- (VII), 6H-pyrido(3,2-*b*)- (VIII), and 7H-pyrido(2,3-*c*)carbazole (IX), three (VI, VII, and IX) have also been recently synthesized (2,3,6) though the structure of IX was not rigorously established. The purpose of this investigation was to complete the synthesis of the pyridocarbazoles by unambiguous methods.

When 5-, 6-, 7-, and 8-quinolylhydrazone (III) of cyclohexanone undergo a Fischer-indole ring closure the products are tetrahydropyridocarbazoles which on dehydrogenation yield pyridocarbazoles. It will be noted that only 5- and 8-quinolylhydrazones can produce pyridocarbazoles of undoubted structure, the 6- and 7-quinolylhydrazone each being able to undergo cyclization in two directions. It was therefore necessary to block one of the two positions ortho to the hydrazono group in the latter cases before cyclization and to remove the blocking group afterwards, in order to accomplish unequivocal synthesis.

For this purpose 5,8-dichloro-6-quinolylhydrazone of cyclohexanone was prepared and subjected to the Fischer indole reaction. Ring closure was accomplished only under the most drastic conditions and the product was 5-chloro-8,9,10,11-tetrahydro-7H-pyrido(2,3-*c*)carbazole (tetrahydro-IX, R = Cl). Apparently the tendency of the 5,8-dichloro-6-quinolylhydrazone to ring close to the 5-position was so great that the chlorine in that position was eliminated to form the angular pyridocarbazole. The relative ease with which angular aromatic polycyclic compounds form as compared to the linear isomers is a well-known phenomenon (1). The dechlorination of 5-chloro-8,9,10,11-tetrahydro-7H-pyrido(2,3-*c*)carbazole (tetrahydro-IX, R = Cl) yielded tetrahydro-IX (R = H)

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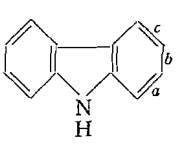
and this was identical with the cyclization product of 6-quinolylhydrazone of cyclohexanone. Dehydrogenation of 8,9,10,11-tetrahydro-IX (R = H) was extremely difficult. Heating it with chloroanil or with platinum catalyst at 350° did not cause any appreciable change. The pyridocarbazole (IX, R = H) was finally obtained by heating the tetrahydro compound with selenium at 350°. This compound (IX, R = H) was also synthesized from 1-phenyl-5-amino-1-benzotriazole (X) (11). In the Skraup reaction X yielded 3-phenyl-3-triazolo(*f*)-quinoline (XI) (5) which on pyrolyses at 400° gave IX (R = H) in 15% yield.



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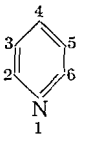

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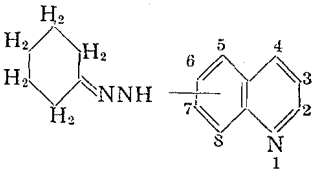

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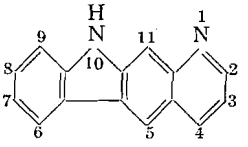

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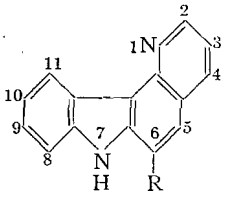

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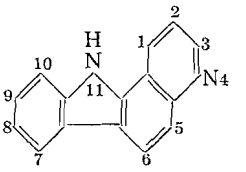

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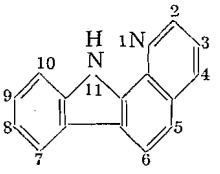

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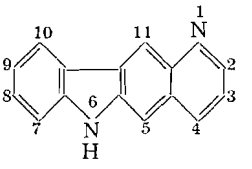
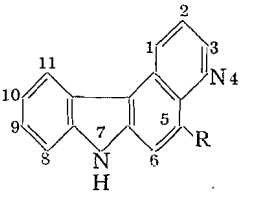
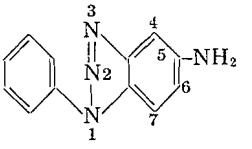


VIII



IX



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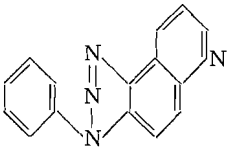

XI

Incidentally, X can theoretically undergo the Skraup reaction in two directions to form 3-phenyl-3-triazolo(*f*)quinoline (XI) and (or) the linear 1-phenyl-1-triazolo(*g*)quinoline. That the angular compound (XI) was formed in this reaction and not the linear isomer is proved indirectly by the fact that it pyrolyzed to IX (R = H) and not to VIII.

6-Chloro-7-quinolylhydrazone of cyclohexanone underwent ring closure with difficulty and in poor yield to 6-chloro-8,9,10,11-tetrahydro-7H-pyrido(3,2-*c*)-carbazole (tetrahydro-V, R = Cl). The identity of the dechlorination product of 8,9,10,11-tetrahydro-V (R = Cl) and the cyclization product of 7-quinolylhydrazone of cyclohexanone showed that the 7-quinolylhydrazone undergoes ring closure to form the angular compound (tetrahydro-V, R = H). The dehydrogenation of the latter compound to V (R = H) was best accomplished by heating with chloroanil in xylene.

The linear pyridocarbazoles IV and VIII could not be synthesized from 6- and 7-quinolylhydrazones (III) because the tendency for angular compound formation could not be suppressed by blocking the reactive positions (5 and 8). However the reactivity of the 5- and 8-positions could be decreased and that of the 6- and 7-positions in III increased by hydrogenating the hetero ring. N-Benzoyl-1,2,3,4-tetrahydro-6-quinolylhydrazone of cyclohexanone was prepared and subjected to acid treatment. A mixture of 1,2,3,4,7,8,9,10-octahydro-6H-pyrido(3,2-*b*)- (octahydro-VIII) and 1,2,3,4,8,9,10,11-octahydro-7H-pyrido-(2,3-*c*)carbazole (octahydro-IX, R = H) in 30 and 18% yield respectively was obtained. These were separated by crystallization and dehydrogenated to VIII and IX (R = H) respectively by heating with platinum catalyst.

A parallel synthesis of IV from 1,2,3,4-tetrahydro-7-quinolylhydrazone of cyclohexanone (III) presented a number of obstacles. When N-*p*-toluenesulphonyl-1,2,3,4-tetrahydro-7-quinolylhydrazone of cyclohexanone was heated in aqueous acid solution or in acetic acid in the presence of sulphuric acid only black resinous material was obtained. The Fischer-indole ring closure of N-benzoyl- and N-acetyl-1,2,3,4-tetrahydro-7-quinolylhydrazone of cyclohexanone to N-benzoyl- (octahydro-N-benzoyl-IV) and N-acetyl-1,2,3,4,-6,7,8,9-octahydro-10H-pyrido-(2,3-*b*)carbazole (octahydro-N-acetyl-IV) respectively could be accomplished by prolonged treatment with hydrochloric acid at room temperature. However attempted hydrolysis of octahydro-N-benzoyl-IV with alcoholic alkali gave only unchanged material and treatment with boiling aqueous hydrochloric acid resulted in decomposition. Octahydro-N-acetyl-IV was also sensitive to hot aqueous acids, but heating a short time with 25% hydrochloric acid resulted in deacetylation and precipitation of the hydrochloride of octahydro-IV. The dehydrogenation of octahydro-IV with platinum catalyst required initial heating at 160–170° for one or two hours before elevating the temperature to 200°. A rapid initial heating above 170° caused a minor explosion even in an atmosphere of nitrogen.

The pyridocarbazoles IV to IX inclusive, like those of the isoquinoline series (9, 10), exhibit a violet fluorescence when in dilute solution. The linear polycyclic systems are less soluble and possess higher melting points than the corresponding

angular isomers. The hydrochlorides of the pyridocarbazoles are all sparingly soluble in water.

The authors are indebted to A. E. Ledingham and R. Mills for the microanalyses.

EXPERIMENTAL

A. 11H-Pyrido(3,2-a)carbazole (VI)

To a hot solution of 7,8,9,10-tetrahydro-11H-pyrido(3,2-*a*)carbazole (tetrahydro-VI) (3) (0.5 gm.) in xylene (100 cc.) was added chloroanil (1.2 gm.) and the reaction mixture was heated under reflux for 24 hr. in a nitrogen atmosphere. The cooled reaction mixture was extracted with two 300 cc. portions of hot dilute hydrochloric acid (VI-HCl is not very soluble in cold water), the aqueous extract filtered, and the filtrate basified with sodium hydroxide. The white precipitate was filtered, washed, and crystallized from pyridine—yield, 0.26 gm. or 50%; m.p. 333–335°, literature (2) m.p. 335°.

B. 11H-Pyrido(2,3-a)carbazole (VII)

7,8,9,10-Tetrahydro-11H-pyrido(2,3-*a*)carbazole (3) (tetrahydro-VII) was dehydrogenated as in Section *A*—yield, 27%; m.p. 172–173°. Tetrahydro-VII could not be dehydrogenated by heating with platinum catalyst at 330° in an inert atmosphere. Clemo and Felton (2) report a melting point of 165° for VII which they obtained by dehydrogenation with palladium. Undoubtedly the low melting point is due to incomplete dehydrogenation.

C. 6-Hydrazino-5,8-dichloroquinoline

A solution of 6-amino-5,8-dichloroquinoline (7) (10 gm.) in concentrated hydrochloric acid (60 cc.) was diazotized at 0° with a solution of sodium nitrite (3.5 gm.) in water (15 cc.). The diazonium salt solution was then gradually added to a chilled solution of stannous chloride dihydrate (35 gm.) in concentrated hydrochloric acid (40 cc.), keeping the temperature below 10°. The reaction mixture was allowed to stand at approximately 7° overnight, the yellow precipitate filtered, dissolved in hot water (400 cc.), and the solution saturated with hydrogen sulphide. The tin sulphides were filtered and the filtrate basified with sodium hydroxide. The filtered precipitate was crystallized from ethanol to give light-yellow needles (6.2 gm. or 60%), m.p. 178° dec. Anal. calc. for $C_9H_7N_3Cl_2$: C, 47.37; H, 3.07; N, 18.42. Found: C, 47.78, 47.65; H, 2.84, 3.09; N, 18.20.

D. 5,8-Dichloro-6-quinolylhydrazone of Cyclohexanone

6-Hydrazino-5,8-dichloroquinoline (6.0 gm.) was suspended in ethanol (150 cc.), cyclohexanone (3.5 cc.) added, and the reaction mixture heated under reflux for one hour. The amber solution was concentrated to about 50 cc. and allowed to cool, yielding golden-yellow needles (7.5 gm. or 90%), m.p. 122–125° dec. Anal. calc. for $C_{15}H_{15}N_3Cl_2$: C, 58.43; H, 4.87; N, 13.63. Found: C, 58.37, 58.38; H, 4.78, 4.82; N, 13.61.

E. 5-Chloro-8,9,10,11-tetrahydro-7H-pyrido(2,3-c)carbazole (Tetrahydro-IX, R = Cl)

Into boiling butanol (50 cc.) dry hydrogen chloride was passed while a solution of 5,8-dichloro-6-quinolylhydrazone of cyclohexanone (4.0 gm.) in warm butanol

(200 cc.) was added through the condenser over a period of one-half hour. The resulting reaction mixture was heated under reflux for five hours while a stream of hydrogen chloride was passed in. The butanol was distilled off, the residue extracted with hot dilute hydrochloric acid, the extract filtered, and the filtrate basified. The filtered precipitate was distilled at 0.3 mm. pressure collecting the fraction boiling at 200–250° bath temperature. The distillate was crystallized from methanol and from acetone (violet fluorescence in dilute solution) to give light-yellow needles (0.65 gm. or 18%), m.p. 254–255°. Anal. calc. for $C_{15}H_{13}N_2Cl$: C, 70.18; H, 5.07; N, 10.91. Found: C, 69.76; H, 5.08; N, 10.95.

Attempts to ring close the hydrazone with aqueous acids at reflux temperatures resulted in a 1% yield of tetrahydro-IX (R = Cl).

F. 8,9,10,11-Tetrahydro-7H-pyrido(2,3-c)carbazole (Tetrahydro-IX, R = H)

(*a*) *From 6-quinolylhydrazone.*—6-Quinolylhydrazone of cyclohexanone was ring closed following the method of Dewar (3), (yield, 30%), m.p. 204–206°, literature, 202°.

(*b*) *By dechlorination of tetrahydro-IX (R = Cl).*—5-Chloro-8,9,10,11-tetrahydro-7H-pyrido(2,3-*c*)carbazole (tetrahydro-IX, R = Cl) (0.12 gm.), Adams platinum catalyst (0.1 gm.), and tetralin (75 cc.) were heated under reflux for 70 hr. while the hydrogen chloride was swept out with a continuous stream of nitrogen. The tetralin was distilled off under reduced pressure and the residue distilled at 0.3 mm. pressure and 220° bath temperature. The distillate was crystallized from acetone yielding light-yellow prisms (0.05 gm. or 40%), m.p. 204–205°; mixed melting point with the product obtained in (*a*) gave no depression.

G. 7H-Pyrido(2,3-c)carbazole (IX, R = H)

(*a*) *From 8,9,10,11-tetrahydro-7H-pyrido(2,3-c)carbazole (tetrahydro-IX, R = H).*—A mixture of tetrahydro-IX (R = H) (0.7 gm.) and selenium powder (3 gm.) was heated at 350–370° for two hours in an atmosphere of nitrogen and then distilled at 0.3 mm. and 250° bath temperature. The distillate on crystallization from acetone yielded light-yellow needles (0.32 gm. or 45%), m.p.211–212°, literature (2), 211°.

(*b*) *From 3-phenyl-3-triazolo(f)quinoline (XI).*—1-Phenyl-5-amino-1-benzotriazole (X) (11) was subjected to the Skraup reaction following the procedure of Fries (5). The resulting 3-phenyl-3-triazolo(*f*)quinoline (XI) (0.2 gm.) (m.p. 126–127°), which was obtained in 20% yield, was heated at 390–400° for 15 min. and then distilled and crystallized as in (*a*). The product (0.026 gm. or 15%) melted at 209–210° either alone or in admixture with that obtained in (*a*).

H. 7-Hydrazinoquinoline

This was prepared from 7-aminoquinoline (8) by the same method as was 6-hydrazino-5,8-dichloroquinoline (Section *C*). A portion of the crude hydrazine which darkened quickly on standing was crystallized from methanol to give light-yellow needles, m.p. 162–163 dec. Anal. calc. for $C_9H_9N_3$: C, 67.92; H, 5.65; N, 26.40. Found: C, 67.76, 68.12; H, 5.58, 5.51; N, 26.22, 26.67.

I. 7-Quinolylhydrazone of Cyclohexanone

Crude 7-hydrazinoquinoline (1.0 gm.) was dissolved in methanol (20 cc.),

cyclohexanone (1 gm.) was added, and the dark amber solution allowed to stand at room temperature for several hours. The precipitated orange plates (1.1 gm. or 73%) were filtered and recrystallized from methanol, m.p. 158–159°. Anal. calc. for $C_{15}H_{17}N_3$: C, 75.29; H, 7.15; N, 17.55. Found: C, 75.43, 75.37; H, 6.83, 6.97; N, 18.08, 18.12.

K. 7-Amino-6-chloroquinoline

To a solution of 7-nitro-6-chloroquinoline (4) (1.5 gm.) in concentrated hydrochloric acid (20 cc.) was added a solution of stannous chloride dihydrate (7 gm.) in concentrated hydrochloric acid (10 cc.), the reaction mixture was heated on the steam bath for one hour and cooled. The yellow precipitate was filtered, dissolved in hot water (200 cc.), and poured into excess dilute sodium hydroxide solution containing cracked ice. The amine was filtered and crystallized from benzene, yielding (0.95 gm. or 75%) white needles, m.p. 151–152°. Anal. calc. for $C_9H_7N_2Cl$: C, 60.50; H, 3.92; N, 15.69. Found: C, 60.49; H, 3.85; N, 15.41.

L. 6-Amino-5-nitroquinoline

To ethanol (100 cc.) containing ammonia (10 gm.) was added 6-chloro-5-nitroquinoline (4) (1.0 gm.) and the reaction mixture was heated in a sealed bomb at 160° for 24 hr. The reaction mixture was taken to dryness, the residue dissolved in dilute hydrochloric acid, the solution filtered, and the filtrate basified with sodium hydroxide. The precipitate was filtered, washed, dried, and crystallized from benzene or methanol to yield orange prisms (0.6 gm. or 70%), m.p. 177–178°. Anal. calc. for $C_9H_7N_3O_2$: C, 57.14; H, 3.70; N, 22.22. Found: C, 57.42, 57.52; H, 3.75, 3.42; N, 21.90.

M. 6-Chloro-8,9,10,11-tetrahydro-7H-pyrido(3,2-c)carbazole (Tetrahydro-V, R = Cl)

7-Amino-6-chloroquinoline (0.90 gm.) was converted to 7-hydrazino-6-chloroquinoline which in turn reacted with cyclohexanone by methods already described (Sections *C* and *D*). The resulting crude 6-chloro-7-quinolylhydrazone of cyclohexanone was dissolved in acetic acid (15 cc.), concentrated sulphuric acid (2 cc.) was added, and the solution heated on the steam bath for one hour. The solution was poured into excess aqueous sodium hydroxide, the precipitated oily material was extracted with ether, the ether removed, and the residue distilled at 0.5 mm. pressure and 200° bath temperature. The oily distillate (0.22 gm.) which could not be induced to crystallize was dissolved in a minimum amount of hot dilute hydrochloric acid and allowed to cool. The precipitated orange needlelike crystals of the hydrochloride were filtered, dissolved in hot water, and the solution basified with sodium hydroxide. The precipitated free base was filtered and crystallized from ethyl acetate to give colorless prisms (0.10 gm. or 10%), m.p. 163–164°. Anal. calc. for $C_{15}H_{13}N_2Cl$: C, 70.18; H, 5.07; N, 10.91. Found: C, 70.48; H, 5.26; N, 11.10.

N. 8,9,10,11-Tetrahydro-7H-pyrido(3,2-c)carbazole (Tetrahydro-V, R = H)

(*a*) *From 7-quinolylhydrazone of cyclohexanone.*—7-Quinolylhydrazone of cyclohexanone (1.0 gm.) was cyclized and the resulting tetrahydro-V (R = H) purified through the hydrochloride in the same manner as described for 6-chloro-8,9,10,11-tetrahydro-7H-pyrido(3,2-*c*)carbazole (Section *M*). The product on

crystallization from dilute methanol and from dibutyl ether yielded stout brown prisms (0.55 gm. or 60%), m.p. 154–155°. Anal. calc. for $C_{15}H_{14}N_2$: C, 81.04; H, 6.34; N, 12.61. Found: C, 81.02, 81.56; H, 6.27, 6.38; N, 12.85, 12.85.

(*b*) *From 6-chloro-8,9,10,11-tetrahydro-7H-pyrido(3,2-c)carbazole (tetrahydro-V, R = Cl).*—Tetrahydro-V (R = Cl) (0.05 gm.) was dechlorinated catalytically by the same method as was 5-chloro-8,9,10,11-tetrahydro-7H-pyrido(2,3-*c*) carbazole (Section *F*). A few crystals were obtained which melted at 149–151° and gave no depression when mixed with the tetrahydro-V (R = H) obtained in (*a*).

O. 7H-Pyrido(3,2-c)carbazole (V, R = H)

8,9,10,11-Tetrahydro-7H-pyrido(3,2-*c*)carbazole (tetrahydro V, R = H) was dehydrogenated with chloroanil in the same manner as described in Section *A*. The crude product was distilled at 0.3 mm. pressure and 220° bath temperature and the distillate on crystallization from methanol and from ethyl acetate gave white prisms (yield 40%), m.p. 173–174°. Anal. calc. for $C_{15}H_{10}N_2$: C, 82.52; H, 4.62; N, 12.83. Found: C, 82.76, 81.99; H, 4.66, 4.56; N, 12.70, 12.94.

P. 6-Hydrazino-1-benzoyl-1,2,3,4-tetrahydroquinoline

A solution of 6-amino-1-benzoyl-1,2,3,4-tetrahydroquinoline (7) (11.4 gm.) in water (50 cc.) and concentrated hydrochloric acid (70 cc.) was diazotized at 0° with a solution of sodium nitrite (3.2 gm.) in water (35 cc.). The diazonium salt solution was then added portionwise to a chilled solution of stannous chloride dihydrate (40 gm.) in concentrated hydrochloric acid (60 cc.), the temperature being maintained below 5°. After it had been allowed to stand at room temperature for two hours the reaction mixture was poured into excess sodium hydroxide solution containing cracked ice. The precipitated hydrazine was filtered (or extracted with 2 liters of ether) and crystallized from benzene to give light-yellow prisms (10.0 gm. or 80%), m.p. 150–152°. Anal. calc. for $C_{16}H_{17}N_3O$: C, 71.91; H, 6.37; N, 15.72. Found: C, 72.25, 72.27; H, 6.16, 6.23; N, 15.31.

Q. 1-Benzoyl-1,2,3,4-tetrahydro-6-quinolylhydrazone of Cyclohexanone

To a solution of 6-hydrazino-1-benzoyl-1,2,3,4-tetrahydroquinoline (10.0 gm.) in methanol (100 cc.) was added cyclohexanone (10 cc.) and the solution was heated under reflux for five minutes. The precipitated almost-white prisms (11.1 gm. or 85%) were filtered from the cooled solution, washed, and dried, m.p. 200–205° dec. Anal. calc. for $C_{22}H_{25}N_3O$: C, 76.08; H, 7.20; N, 12.10. Found: C, 75.37, 75.61; H, 6.91, 6.97; N, 12.16.

R. 1,2,3,4,7,8,9,10-Octahydro-6H-pyrido(3,2-b)carbazole (Octahydro-VIII) and the Angular Isomer

1-Benzoyl-1,2,3,4-tetrahydro-6-quinolylhydrazone of cyclohexanone (10.0 gm.) was dissolved in acetic acid (100 cc.), concentrated hydrochloric acid (100 cc.) added, and the solution allowed to stand at room temperature for three days. The reaction mixture was diluted with water (50 cc.) and heated under reflux for five hours in order to hydrolyze the benzoyl group. It was then cooled and poured into excess sodium hydroxide solution containing cracked ice. The cream-colored precipitate was filtered, washed, dried, and crystallized from

benzene. The yield of the white feathery crystals (m.p. 216–217°) of octahydro-VIII was 2.0 gm. or 30%. Anal. calc. for $C_{15}H_{18}N_2$: C, 79.64; H, 7.96; N, 12.39. Found: C, 79.28, 79.82; H, 7.80, 7.85; N, 11.90.

The benzene mother liquors from the crystallization of octahydro-VIII were taken to dryness, the residual oil mixed with Adams platinum catalyst (0.1 gm.) and heated at 210–220° for five hours in an atmosphere of nitrogen. The product on distillation at 0.3 mm. pressure and 220° bath temperature and crystallization from acetone and from methanol (yield, 1.2 gm. or 18%) melted at 203–205° and gave no depression when mixed with 8,9,10,11-tetrahydro-7H-pyrido(2,3-*c*) carbazole (tetrahydro-IX, R = H) (Section *F*).

S. 6H-Pyrido(3,2-b)carbazole (VIII)

1,2,3,4,7,8,9,10-Octahydro-6H-pyrido(3,2-*b*)carbazole (octahydro-VIII) (0.85 gm.) was mixed with Adams platinum catalyst (0.2 gm.) and the mixture heated at 210–220° for three hours in an atmosphere of nitrogen and then at 270–280° for five hours. The product was distilled at 0.3 mm. pressure and 220° bath temperature. The distillate was mixed with fresh catalyst and re-treated as above. The final product on crystallization from acetone yielded stout yellow prisms (0.28 gm. or 30%), m.p. 282–284°. (Further heating with platinum at 300° did not change the melting point.) Anal. calc. for $C_{15}H_{10}N_2$: C, 82.51; H, 4.63; N, 12.83. Found: C, 82.37, 82.35; H, 4.75, 4.75; N, 12.69.

T. 7-Hydrazino-1-benzoyl-1,2,3,4-tetrahydroquinoline

This was prepared from 7-amino-1-benzoyl-1,2,3,4-tetrahydroquinoline (7) by the same method as was the 6-isomer (Section *P*). Crystallization from methanol yielded (85%) small white needles, m.p. 115–120°, which decomposed rapidly at room temperature. Anal. calc. for $C_{16}H_{17}N_3O$: C, 71.91; H, 6.37; N, 15.72. Found: C, 72.46, 72.64; H, 6.34, 6.20; N, 14.51.

U. 1-Benzoyl-1,2,3,4-tetrahydro-7-quinolylhydrazone of Cyclohexanone

This was prepared from 7-hydrazino-1-benzoyl-1,2,3,4-tetrahydroquinoline by the same method as was the 6-isomer (Section *Q*). It crystallized from methanol as light-yellow prisms (yield, 80%), m.p. 205–207°. Anal. calc. for $C_{22}H_{25}N_3O$: C, 76.08; H, 7.20; N, 12.10. Found: C, 75.98, 76.01; H, 7.08, 7.54; N, 11.70.

V. 1,2,3,4,6,7,8,9-Octahydro-1-benzoyl-10H-pyrido(2,3-b)carbazole (Octahydro-1-benzoyl-IV)

To a solution of 1-benzoyl-1,2,3,4-tetrahydro-7-quinolylhydrazone of cyclohexanone (8.0 gm.) in acetic acid (50 cc.) was added concentrated hydrochloric acid (50 cc.) and the solution was allowed to stand at room temperature for five days. The resulting dark solution was diluted with water, the precipitate filtered, washed, dried, and crystallized from benzene and from ethanol to yield white needlelike crystals (5.5 gm. or 70%), m.p. 242–243°. Anal. calc. for $C_{22}H_{22}N_2O$: C, 80.00; H, 6.67; N, 8.48. Found: C, 80.06, 80.07; H, 6.60, 6.57; N, 8.86.

Attempted hydrolysis of this compound with aqueous acids resulted in decomposition; it was recovered unchanged from boiling alcoholic alkali.

W. 1-Acetyl-1,2,3,4-tetrahydro-7-quinolylhydrazone of Cyclohexanone

7-Hydrazino-1-acetyl-1,2,3,4-tetrahydroquinoline was prepared in 60% yield

from 7-amino-1-acetyl-1,2,3,4-tetrahydroquinoline (7) by the same method as was 6-hydrazino-1-benzoyl-1,2,3,4-tetrahydroquinoline (Section *P*). The resulting oily 7-hydrazino-1-acetyl-1,2,3,4-tetrahydroquinoline was converted to the hydrazone with cyclohexanone (Section *Q*). The almost-white prisms (90% yield) melted at 153–157°. Anal. calc. for $C_{17}H_{23}N_3O$: C, 71.58; H, 8.07; N, 14.74. Found: C, 71.53, 71.26; H, 7.98, 8.04; N, 14.69.

X. 1,2,3,4,6,7,8,9-Octahydro-10H-pyrido(2,3-b)carbazole (Octahydro-IV)

1-Acetyl-1,2,3,4-tetrahydro-7-quinolylhydrazone of cyclohexanone (4.5 gm.) was dissolved in concentrated hydrochloric acid (25 cc.), water (25 cc.) was added, and the resulting reddish solution allowed to stand for three days at room temperature. To the reaction mixture containing precipitated semisolid was added concentrated hydrochloric acid (30 cc.) and the solution was heated under reflux for 15 min. and on the steam bath for 45 min. (The use of more dilute acid or prolonged heating causes excessive decomposition.) The precipitated octahydro-IV-hydrochloride was filtered from the cooled reaction mixture, dissolved in hot water (1 liter), and the solution basified with sodium hydroxide. The crude octahydro-IV (2.5 gm. or 70%) was filtered, washed, dried, and quickly crystallized from benzene. This yielded white needles which darkened on standing, m.p. 175–176°. Anal. calc. for $C_{15}H_{18}N_2$: C, 79.64; H, 7.96; N, 12.39. Found: C, 79.09, 78.98; H, 7.54, 7.55; N, 11.83.

No octahydro-V (R = H) could be found in the mother liquors from octahydro-IV and in those from its hydrochloride.

Y. 6,7,8,9-Tetrahydro-10H-pyrido(2,3-b)carbazole (Tetrahydro-IV)

1,2,3,4,6,7,8,9-Octahydro-10H-pyrido(2,3-*b*)carbazole (octahydro-IV) (2.5 gm.) was mixed with Adams platinum catalyst (0.5 gm.) and heated in an atmosphere of nitrogen at 160–170° for two hours and at 200° for two hours. The product was distilled at 0.3 mm. pressure and 210° bath temperature and the distillate crystallized from ethyl acetate or methanol to yield yellow prisms (1.7 gm. or 68%), m.p. 232–233°. Anal. calc. for $C_{15}H_{14}N_2$: C, 81.04; H, 6.34; N, 12.61. Found: C, 81.71, 81.76; H, 6.19, 6.31; N, 12.34.

Z. 10H-Pyrido(2,3-b)carbazole (IV)

6,7,8,9-Tetrahydro-10H-pyrido(2,3-*b*)carbazole was dehydrogenated with chloroanil as described in Section *A*. The crude product (yield, 10%) on crystallization from methanol yielded yellow needles, m.p. 245–246°. Anal. calc. for $C_{15}H_{10}N_2$; C, 82.51; H, 4.63. Found: C, 82.29; H, 4.77.

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