247. *The* nor*Lupinane–Octahydropyridocoline Relationship. Part III.*

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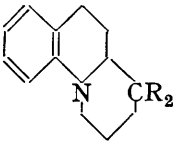
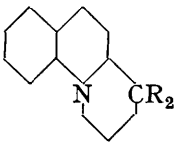
In an endeavour to prepare solid isomers of the *nor*lupinane–octahydropyridocoline types, 5 : 6-*benzo*-1 : 2 : 3 : 4 : 7 : 8-*hexahydropyridocoline* (I, $R_2 = H_2$) and 5 : 6-*benzododecahydropyridocoline* (II, $R_2 = H_2$) have been prepared, but all are oils.

In an attempt to obtain further evidence on the nature of the *nor*lupinane–octahydropyridocoline relationship (J., 1931, 437; 1936, 1429) we were led to prepare 1-keto-5 : 6-benzo-1 : 2 : 3 : 4 : 7 : 8-hexahydro- and 1-keto-5 : 6-benzododecahydro-pyridocolines (I and II; $R_2 = O$) in the hope of obtaining, by the Wolff and Clemmensen reductions,

(I.)   (II.)

solid isomers of the *nor*lupinane and octahydropyridocoline types. These were prepared respectively by condensation of *methyl tetra-* and *deca-hydroquinaldinate* with γ-bromobutyronitrile and subsequent hydrolysis and ring-closure by the Dieckmann method, but, although both ketones gave 'A' and 'B' type bases on reduction, these were all unstable oils. In the case of the dodecahydro-compound, eight bases might have been expected, and the occurrence of only two suggests that the catalytic reduction of the methyl quinaldinate has led to only one of the two theoretically possible racemic forms, and that the Dieckmann ring-closure has again only taken place in one of the possible ways, the ketone (II) only giving one picrolonate and being therefore homogeneous. This is probably the *trans*-form (compare Hückel, *Annalen*, 1925, **441**, 1).

Experimental.

Methyl Deca- and Tetra-hydroquinoline-2-carboxylates.—Methyl quinoline-2-carboxylate (H. Meyer, *Ber.*, 1905, **38**, 2490) (25 g.) in glacial acetic acid (100 c.c.) was shaken for 24 hours with platinum oxide (0·15 g.) in hydrogen at 7 atm. pressure. The solution was filtered, the acetic acid removed, the residual gum basified (saturated potassium carbonate solution), and the yellow oil extracted with ether, dried, and distilled, giving the *decahydro*-ester (7·0 g., b. p. 110—115°/1 mm.) (Found: C, 67·3; H, 9·3. $C_{11}H_{19}O_2N$ requires C, 67·0; H, 9·6%), *picrolonate*, pale yellow prisms, m. p. 221—222° from alcohol (Found: C, 55·1; H, 5·9. $C_{11}H_{19}O_2N,C_{10}H_8O_5N_4$ requires C, 54·7; H, 5·9%), and the *tetrahydro*-ester (16·5 g., b. p. 135°/1 mm.) (Found: C, 69·2; H, 6·6. $C_{11}H_{13}O_2N$ requires C, 69·1; H, 6·9%), *picrolonate*, yellow prisms, m. p. 172° (Found: C, 55·6; H, 4·9. $C_{11}H_{13}O_2N,C_{10}H_8O_5N_4$ requires C, 55·4; H, 4·6%).

Methyl 1-(γ-*Cyanopropyl*)*decahydroquinoline*-2-*carboxylate.*—Methyl decahydroquinoline-2-carboxylate (1·25 g.), γ-bromobutyronitrile (1 g.), and potassium carbonate (1 g.) were heated on a water-bath for 6 hours with frequent stirring. The mixture became light yellow; water (5 c.c.) was added, and the yellow oil extracted with ether, dried, and distilled, giving unchanged reactants (0·85 g., b. p. 100—120°/1 mm.) and *methyl* 1-(γ-*cyanopropyl*)*decahydroquinoline*-2-*carboxylate* (0·9 g., b. p. 170—180°/1 mm.) as a thick oil (Found: C, 67·8; H, 8·8. $C_{15}H_{24}O_2N_2$ requires C, 68·2; H, 9·0%).

Methyl Decahydroquinoline-2-*carboxylate*-1-(γ-*butyrate*).—The above nitrile (0·86 g.) in methyl alcohol (20 c.c.) was cooled in ice and saturated with hydrogen chloride. The solution was kept for 18 hours, refluxed for 2 hours, and the alcohol removed. The residue was basified (saturated potassium carbonate solution) and ether-extracted, and the extract dried and distilled, giving the *dimethyl* ester as a yellow oil (0·8 g., b. p. 160—170°/1 mm.) (Found: C, 64·3; H, 9·3. $C_{16}H_{27}O_4N$ requires C, 64·6; H, 9·1%).

1-*Ketododecahydro*-5 : 6-*benzopyridocoline.*—The diester (1·2 g.) in toluene (4 c.c.) was added to powdered potassium (0·25 g.) in toluene (25 c.c.) and heated for 1 hour on the water-bath. Alcohol (1 c.c.) and concentrated hydrochloric acid (15 c.c.) were added, and the solution similarly heated for a further 6 hours. The solvents were removed under reduced pressure, and the residue basified (40% sodium hydroxide) and ether-extracted. The extract was dried and distilled, giving 1-*ketododecahydro*-5 : 6-*benzopyridocoline* as a light yellow oil (0·53 g., b. p.

130°/1 mm.) (Found: C, 75·7; H, 10·0. $C_{13}H_{21}ON$ requires C, 75·4; H, 10·1%). The *picrolonate* crystallised from alcohol in light yellow prisms, m. p. 216° (Found: C, 59·2; H, 6·4. $C_{13}H_{21}ON,C_{10}H_8O_5N_4$ requires C, 59·6; H, 6·2%).

5 : 6-*Benzododecahydropyridocoline* '*B*' *prepared by the Clemmensen Reduction.*—This reduction was carried out in the manner usually adopted in this series, the ketone (0·5 g.) giving 5 : 6-*benzododecahydropyridocoline* '*B*' as a pale yellow mobile oil (0·25 g., b. p. 100—110°/1 mm.) (Found: C, 80·4; H, 12·0. $C_{13}H_{23}N$ requires C, 80·8; H, 11·9%). The *picrate* crystallised from alcohol in pale yellow prisms, m. p. 128—130° (Found: C, 53·9; H, 6·5. $C_{13}H_{23}N,C_6H_3O_7N_3$ requires C, 54·0; H, 6·2%).

5 : 6-*Benzododecahydropyridocoline* '*A*' *prepared by the Wolff Reduction.*—This reduction was again carried out in the usual way, the ketone (0·5 g.) giving 5 : 6-*benzododecahydropyridocoline* '*A*' as a mobile yellow oil (0·2 g., b. p. 100—110°/1 mm.) (Found: C, 80·5; H, 12·2%). The *picrate* crystallised from alcohol in pale yellow prisms, m. p. 148° (Found: C, 53·7; H, 6·3%).

Methyl 1-(*γ-Cyanopropyl*)*tetrahydroquinoline-2-carboxylate.*—Methyl tetrahydroquinoline-2-carboxylate (1·25 g.), γ-bromobutyronitrile (1 g.), and potassium carbonate (1 g.) were heated on the water-bath for 18 hours with frequent stirring, and worked up as for the decahydro-compound, giving unchanged reactants (0·45 g., b. p. 100—140°/1 mm.) and a thick *oil* (0·9 g., b. p. 190—205°/1 mm.) (Found: C, 69·3; H, 7·2. $C_{15}H_{18}O_2N_2$ requires C, 69·8; H, 7·0%).

Tetrahydroquinoline-2-carboxylate-1-(*γ-butyrate*).—The above nitrile (2·1 g.) was dissolved in methyl alcohol (20 c.c.), cooled in ice and saturated with hydrogen chloride, and treated in the same way as the decahydro-compound. On being worked up, the *dimethyl* ester (1·8 g., b. p. 180—185°/1 mm.) was obtained as a viscous yellow oil (Found: C, 66·7; H, 7·3. $C_{16}H_{21}O_4N$ requires C, 66·0; H, 7·2%).

1-*Keto-5* : 6-*benzo-1* : 2 : 3 : 4 : 7 : 8-*hexahydropyridocoline.*—The diester (2·8 g.) was dissolved in xylene (6 c.c.) and added to powdered potassium (0·6 g.) in xylene (10 c.c.). A vigorous reaction took place and a yellow solid was deposited; this was heated for 1 hour on the water-bath, concentrated hydrochloric acid (20 c.c.) added, and the heating continued for a further 6 hours. The solvents were removed by distillation under reduced pressure, and the residue was basified (saturated potassium carbonate solution) and ether-extracted. The extract was dried and distilled, yielding 1 *keto-5* : 6-*benzo-1* : 2 : 3 : 4 : 7 : 8 *hexahydropyridocoline* as a deep yellow, unstable oil (0·57 g., b. p. 160°/1 mm.) (Found: C 76·9; H, 7·7. $C_{13}H_{15}ON$ requires C, 77·6; H, 7·5%).

5 : 6-*Benzo-1* : 2 : 3 : 4 : 7 : 8-*hexahydropyridocoline* '*A*' *prepared by the Wolff Reduction.*—The above ketone (0·28 g.) was treated in the usual manner and gave a mobile yellow *oil* (0·1 g., b. p. 120°/1 mm.) which decomposed rapidly on standing (Found: N, 7·8. $C_{13}H_{17}N$ requires N, 7·6%). The *picrate* crystallised from alcohol in yellow needles, m. p. 174° (Found: C, 54·7; H, 4·4. $C_{13}H_{17}N,C_6H_3O_7N_3$ requires C, 54·8; H, 4·8%).

5 : 6-*Benzo-1* : 2 : 3 : 4 : 7 : 8-*hexahydropyridocoline* '*B*' *prepared by the Clemmensen Reduction.*—1-Keto-5 : 6-benzo-1 : 2 : 3 : 4 : 7 : 8-hexahydropyridocoline (1·0 g.) was dissolved in concentrated hydrochloric acid (10 c.c.), amalgamated zinc (5·0 g.) added, and the whole refluxed for 18 hours; more concentrated hydrochloric acid (5 c.c.) and amalgamated zinc (2·0 g.) were added and the mixture refluxed for a further 3 hours. The solution was worked up as usual, giving 5 : 6-*benzo-1* : 2 : 3 : 4 : 7 : 8-*hexahydropyridocoline* '*B*' as a pale yellow unstable oil (0·35 g., b. p. 120°/1 mm.) (Found: C, 83·5; H, 8·9; N, 7·5. $C_{13}H_{17}N$ requires C, 83·3; H, 9·1; N, 7·6%). The *picrate* crystallised from alcohol in yellow prisms, m. p. 142° (Found: C, 54·4; H, 4·4%), and the *picrolonate* in brownish-yellow prisms, m. p. 175° (Found: C, 60·3; H, 5·8. $C_{13}H_{17}N,C_{10}H_8O_5N_4$ requires C, 60·9; H, 5·9%).

Attempted Interconversion of '*A*' *and* '*B*'.—5 : 6-Benzo-1 : 2 : 3 : 4 : 7 : 8-hexahydropyridocoline 'A' (0·2 g.), obtained from the Wolff reduction of the 1-keto-compound, was dissolved in concentrated hydrochloric acid (5 c.c.) and refluxed for 6 hours, but was recovered unchanged (0·1 g.; picrate, m. p. alone or mixed with that of the original base, 174°).

The base 'B' obtained from the Clemmensen reduction (0·15 g.) was dissolved in alcohol (2 c.c.) and heated in a sealed tube at 180° with sodium ethoxide (3 g.) for 4 hours. On working the product up as usual, the original base (0·1 g.) was obtained, giving a picrate, m. p. 142° alone or mixed with that of the original base.

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