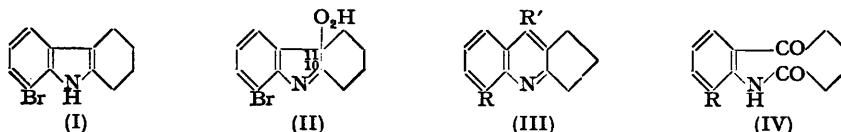


495. *Peroxides of Tetrahydrocarbazole and Related Compounds.*  
 Part V.\* 8-Bromo-1 : 2 : 3 : 4-tetrahydrocarbazole.

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From an examination of 8-bromo-1 : 2 : 3 : 4-tetrahydro-11-carbazolyl hydroperoxide (II) and its transformation products it appears that the compounds (A), (B), and (C) which Barnes, Pausacker, and Badcock (*J.*, 1951, 730) considered to be formed along with 8-bromo-1 : 2 : 3 : 4-tetrahydrocarbazole in the Fischer indole synthesis are the hydroperoxide (II), the lactam of  $\delta$ -(2-amino-3-bromobenzoyl)-*n*-valeric acid, and 8-bromo-4-hydroxy-2 : 3-cyclopentenoquinoline.

By the cyclisation of cyclohexanone *o*-bromophenylhydrazone according to the standard Fischer method Barnes, Pausacker, and Badcock (*J.*, 1951, 730) obtained the expected 8-bromo-1 : 2 : 3 : 4-tetrahydrocarbazole (I) together with three unidentified compounds, (A)  $C_{12}H_{10}O_2NBr$ , (B)  $C_{12}H_{10}O_2NBr$ , and (C)  $C_{12}H_8ONBr$ , which they suggested might be derived from the *o*-bromanilino-radical regarded as an intermediate in the Fischer indole cyclisation according to the mechanism proposed by Pausacker and Schubert (*J.*, 1949, 1384). It seemed to us that peroxidation of (I) was likely to take place under the conditions employed for the isolation of the carbazole (I) and the accompanying products (A), (B), and (C). On the view that (A) is 8-bromo-1 : 2 : 3 : 4-tetrahydrocarbazolyl hydroperoxide,  $C_{12}H_{12}O_2NBr$  (II), and that (B) and (C) are artefacts derived from it a reasonably complete interpretation of the data given by Barnes and his co-workers is possible. Thus (C) is obtained by the action of alkali on (A) under conditions whereby tetrahydrocarbazolyl hydroperoxides are converted into 4-hydroxy-2 : 3-cyclopentenoquinolines (cf., *e.g.*, Part IV\*) and can be formulated as 8-bromo-4-hydroxy-2 : 3-cyclopentenoquinoline (III; R = Br, R' = OH). Further, the properties of the amphoteric compound  $C_{12}H_{11}ON$ , formed by the reductive debromination of (C), closely resemble those of 4-hydroxy-2 : 3-cyclopentenoquinoline (III; R = H; R' = OH) (Part II, *J.*, 1950, 3283), whilst the basic reduction product  $C_{12}H_{11}N$ , m. p. 60°, from (C) can be identified as 2 : 3-cyclopentenoquinoline (III; R = R' = H), m. p. 59–60° (Borsche, *Annalen*, 1910, 377, 120).



In confirmation of the foregoing hypothesis the hydroperoxide (II) was prepared from (I) by the usual method (cf. Part IV) and on treatment with cold aqueous sodium hydroxide was smoothly converted into 8-bromo-4-hydroxy-2 : 3-cyclopentenoquinoline (III; R = Br, R' = OH) which was readily debrominated by hydrogenolysis, giving 4-hydroxy-2 : 3-cyclopentenoquinoline (III; R = H, R' = OH). By the vigorous catalytic reduction procedure employed by Barnes *et al.* 8-bromo-4-hydroxy-2 : 3-cyclopentenoquinoline gave rise to small amounts of (III; R = H, R' = OH) in addition to 2 : 3-cyclopentenoquinoline (III; R = R' = H), an authentic specimen of which was prepared by the reductive dechlorination of (III; R = H, R' = Cl) (cf. Borsche, *loc. cit.*) formed by the action of phosphorus oxychloride on (III; R = H, R' = OH) (Blount and Plant, *J.*, 1937, 376).

The nature of the compound (B) which Barnes *et al.* described as a primary amine soluble in aqueous sodium hydroxide was not immediately clear but its conversion into (C), *i.e.*, (III; R = Br, R' = OH), with alkalis suggested that it was the lactam (IV; R = Br) analogous to (IV; R = H) obtained by Witkop (*J. Amer. Chem. Soc.*, 1950, 72, 1429) from 1 : 2 : 3 : 4-tetrahydrocarbazolyl hydroperoxide. Accordingly the lactam (IV; R = Br) was prepared by ozonolysis of 8-bromo-1 : 2 : 3 : 4-tetrahydrocarbazole and,

\* Part IV, *J.*, 1952, 4946.

although this compound, which formed an acetyl derivative, gave a negative diazo-test for a primary amine, it readily dissolved in warm dilute hydrochloric acid and the solution then gave a positive diazo-test. The compound (B), therefore, is regarded as the lactam (IV; R = Br).

The properties given by Barnes *et al.* for compounds (A), (B), and (C) and for the compounds described in the present work are summarised in the Table. In view of the agreement between the two series we consider that (A), (B), and (C) have the structures (II), (IV; R = Br), and (III; R = Br, R' = OH) respectively, and that their formation has no bearing on the mechanism of the Fischer indole synthesis.

Compounds of Barnes <i>et al.</i> ( <i>loc. cit.</i> )	Compounds described in present paper
(A) C <sub>12</sub> H <sub>10</sub> O <sub>2</sub> NBr, m. p. 146° (deflagration)	(II) 8-Bromo-1 : 2 : 3 : 4-tetrahydro-11-carbazolyl hydroperoxide, C <sub>12</sub> H <sub>12</sub> O <sub>2</sub> NBr, m. p. 146—150° (vigorous decomp.)
(C) C <sub>12</sub> H <sub>8</sub> ONBr, m. p. 253°; semipicrate, m. p. 223—224°	(III; R = Br, R' = OH) 8-Bromo-4-hydroxy-2 : 3-cyclopentenoquinoline, C <sub>12</sub> H <sub>10</sub> ONBr, m. p. 246° (decomp.); semipicrate, m. p. 224°
Amphoteric compound, C <sub>12</sub> H <sub>11</sub> ON, m. p. 341°, from (C)	(III; R = H, R' = OH) 4-Hydroxy-2 : 3-cyclopentenoquinoline, C <sub>12</sub> H <sub>11</sub> ON, m. p. ca. 330° (decomp.)
Base, C <sub>12</sub> H <sub>11</sub> N, m. p. 60°, from (C); picrate, m. p. 190°	(III; R = R' = H) 2 : 3-cyclopentenoquinoline, C <sub>12</sub> H <sub>11</sub> N, m. p. 60—61°; picrate, m. p. 215° (decomp.)
(B) C <sub>12</sub> H <sub>10</sub> O <sub>2</sub> NBr, m. p. 166°; acetyl derivative, m. p. 124°	(IV; R = Br) Lactam of δ-(2-amino-3-bromobenzoyl)valeric acid, C <sub>12</sub> H <sub>12</sub> O <sub>2</sub> NBr, m. p. 164—165°; acetyl deriv., m. p. 126°

## EXPERIMENTAL

For various m. p. see the Table.

[With T. DONAVANIK] 8-Bromo-1 : 2 : 3 : 4-tetrahydro-11-carbazolyl Hydroperoxide (I).—8-Bromo-1 : 2 : 3 : 4-tetrahydrocarbazole, prepared by the method of Barnes *et al.* (*loc. cit.*), was purified by distillation. On being kept, a solution of this compound (2 g.) in a mixture of benzene (10 ml.) and light petroleum (50 ml.) slowly deposited the hydroperoxide (0.5 g.) which, on recrystallisation from ethyl acetate, formed colourless tablets (Found: C, 51.5; H, 4.2; N, 4.9; Br, 27.6. C<sub>12</sub>H<sub>12</sub>O<sub>2</sub>NBr requires C, 51.1; H, 4.3; N, 5.0; Br, 28.4%).

8-Bromo-4-hydroxy-2 : 3-cyclopentenoquinoline (III; R = Br, R' = OH).—A solution of the aforementioned hydroperoxide (1 g.) in methanol (15 ml.) was added to 2N-sodium hydroxide (30 ml.) at room temperature and 24 hr. later the mixture was neutralised with acetic acid. Thus precipitated, 8-bromo-4-hydroxy-2 : 3-cyclopentenoquinoline was purified from benzene and obtained in colourless needles (Found: C, 54.4; H, 4.1; N, 5.2. C<sub>12</sub>H<sub>10</sub>ONBr requires C, 54.6; H, 3.8; N, 5.3%). This amphoteric compound formed a picrate which separated from alcohol in yellow needles.

A solution of the bromo-quinoline (0.25 g.) in 1% methanolic potassium hydroxide (10 ml.) containing Raney nickel (1.0 g.) was agitated in hydrogen for 10 min., filtered, and evaporated. A solution of the residue in water (4 ml.) was neutralised with acetic acid, giving 4-hydroxy-2 : 3-cyclopentenoquinoline, which on purification from alcohol had m. p. 328—330° (decomp.), identified by comparison with an authentic specimen (Part II, *loc. cit.*) and by preparation of the methyl derivative, m. p. and mixed m. p. 218—219°.

4-Chloro-2 : 3-cyclopentenoquinoline.—When the initial reaction between 4-hydroxy-2 : 3-cyclopentenoquinoline (1.6 g.) and phosphoryl chloride (7 ml.) had somewhat subsided the mixture was heated on the steam-bath for 2 hr. and evaporated in a vacuum. A filtered solution of the residue in water (10 ml.) was basified with aqueous ammonia, giving 4-chloro-2 : 3-cyclopentenoquinoline (1.5 g.) which was purified by crystallisation from light petroleum and then by sublimation at 0.01 mm. and obtained in magnificent lustrous rhombs, m. p. 73° (Found: C, 71.0; H, 5.0; N, 6.6; Cl, 17.3. Calc. for C<sub>12</sub>H<sub>10</sub>NCl: C, 70.8; H, 4.9; N, 6.9; Cl, 17.4%) (cf. Blount and Plant, *loc. cit.*, who give m. p. 70°). The picrate separated from alcohol in yellow rods, m. p. 180—181° (Found: C, 49.7; H, 3.3; N, 12.7. C<sub>18</sub>H<sub>13</sub>O<sub>7</sub>N<sub>4</sub>Cl requires C, 49.9; H, 3.0; N, 12.9%).

2 : 3-cyclopentenoquinoline.—(a) A solution of 4-chloro-2 : 3-cyclopentenoquinoline (0.5 g.) in 2% methanolic potassium hydroxide (20 ml.) containing palladised calcium carbonate (0.5 g.;

2% of palladium) was agitated in hydrogen for  $1\frac{1}{2}$  hr. (1 mol. of hydrogen absorbed). On the addition of a little water to the residue left on evaporation of the filtered solution in a vacuum 2 : 3-cyclopentenoquinoline separated as an oil (0.37 g.) which solidified and was purified by sublimation in a vacuum, forming colourless plates, m. p. 60—61° (Found: C, 85.3; H, 6.5; N, 8.1. Calc. for  $C_{12}H_{11}N$ : C, 85.2; H, 6.5; N, 8.3%). Borsche (*loc. cit.*) gives m. p. 59—60°. The *picrate* separated from alcohol in yellow needles (Found: N, 13.7.  $C_{18}H_{14}O_7N_4$  requires N, 14.1%).

(b) A mixture of 8-bromo-4-hydroxy-2 : 3-cyclopentenoquinoline (0.2 g.) and palladised charcoal (0.3 g.; 3% of palladium) was kept in a U-tube in a stream of hydrogen at 280—300° for 2 hr. The sublimate which had collected in the exit limb of the tube was dissolved in a little water, and the solution basified with 2N-sodium hydroxide, giving 2 : 3-cyclopentenoquinoline, m. p. 60—61° after purification as in (a). On being rendered faintly acid with acetic acid the alkaline liquor gave 4-hydroxy-2 : 3-cyclopentenoquinoline, m. p. 329—330° (decomp.).

*Lactam of  $\delta$ -(2-Amino-3-bromobenzoyl)valeric Acid.*—A stream of ozone and oxygen was led into a solution of 8-bromo-1 : 2 : 3 : 4-tetrahydrocarbazole (1.2 g.) in methanol (20 ml.) at  $-50^\circ$  for 1 hr. Triturated with ether, the gum left on evaporation of the solution solidified and on crystallisation from benzene or ethyl acetate gave the *lactam* in colourless needles (0.65 g.) (Found: C, 50.8; H, 4.2; N, 4.7.  $C_{12}H_{12}O_2NBr$  requires C, 51.1; H, 4.3; N, 5.0%). With 2N-sodium hydroxide the lactam was smoothly converted into 8-bromo-4-hydroxy-2 : 3-cyclopentenoquinoline, and on acetylation with acetic anhydride and pyridine gave an acetyl derivative, forming rosettes of needles from light petroleum.