

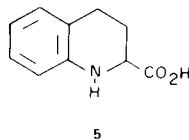
A Synthesis of Pyrrolo[1,2-a]quinoline

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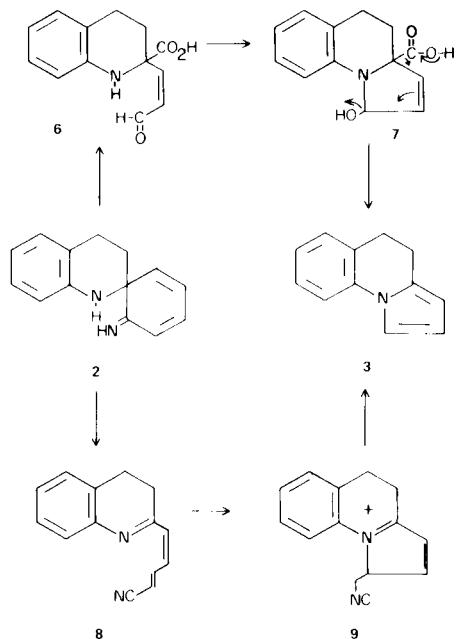
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As part of our continuing study of the chemistry of diazacyclooctatetraenes (1), we recently described the conversion of the tetrahydro-1,2-diazocine **1** to the spiro 1,2,3,4-tetrahydroquinoline derivative **2** (2). The latter compound represents the first example of a stable *o*-semidine rearrangement "intermediate". In attempts to degrade this compound, we subjected it to hydrogen peroxide oxidation in an alkaline medium. To our surprise, the reaction product obtained was neither the expected carboxylic acid **5**, nor quinoline, but a compound

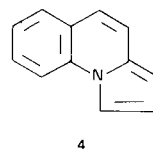


$C_{12}H_{11}N$. The pmr spectrum of this compound shows the presence of a 4-proton multiplet in the aromatic region (τ 2.49-3.10), an ABX pattern (τH_A 4.02, τH_B 3.78, τH_X 2.40) and a 4-proton singlet (τ 7.14). These data are readily accommodated by structure **3**. The compound can be envisioned to be formed by cyclization of an intermediate such as **6**, to form compound **7**, or alternatively, *via* intermediates **8** or **9** (5). Decarboxylation and dehydration,



as indicated by the arrows in structure **7**, finally affords The dihydro-5,6-benzopyrrocoline **3**.

The ultimate structure proof of compound **3** rests upon its conversion to the known pyrrolo[1,2-a]quinoline (**4**) (**3**) by catalytic dehydrogenation with Pd-C in refluxing xylene.



EXPERIMENTAL (4)

Oxidation of Compound **2**

To a solution of 2.1 g. (0.01 mole) of compound **2** in 50 ml. of ethanol was added 10 ml. of 10% sodium hydroxide solution and 5 ml. of 30% hydrogen peroxide. The solution was stirred at 50° for 5 hours and was poured into 200 ml. of water. The aqueous solution was evaporated to dryness to afford a colorless oil (b.p. 138°/0.6 torr) (1.32 g. 78%); pmr (deuteriochloroform) δ 2.49-3.10 (m,4), H_A 3.78, H_B 4.02, H_X 2.40 ($J_{AB} = 3.0$ hz, $J_{AX} = 1.5$ hz, $J_{BX} = 3.0$ hz, 7.14 (s,4); mass spec. mol. wt. 169.

Anal. Calcd. for $C_{12}H_{11}N$: C, 85.17; H, 6.55; N, 8.28. Found, C, 85.40; H, 6.50; N, 8.33.

The oil obtained above was dissolved in 50 ml. of xylene and 200 mg. of 5% palladium on carbon was added. The mixture was stirred and refluxed for 2 days, filtered, and evaporated to dryness to afford 1.15 g. (69% based on compound **2**) of pyrrolo[1,2-a]quinoline, m.p. 107-108° (lit. (3) 108-108.5°).

REFERENCES

- (1) W. W. Paudler and A. G. Zeiler, *J. Org. Chem.*, **34** 2138 (1969).
- (2) W. W. Paudler, A. G. Zeiler and M. M. Goodman, *J. Heterocyclic Chem.*, **10**, 423 (1973).
- (3) E. M. Roberts, M. Gates, and V. Bockelheide, *J. Org. Chem.*, **20**, 1443 (1955).
- (4) The pmr spectra were obtained with a Varian HA-100 instrument as dilute solutions in deuteriochloroform. The mass spectroscopic molecular weights of all compounds were obtained with a Hitachi-Perkin Elmer RMU-6M instrument.
- (5) We wish to thank a referee for suggesting the sequence **2** \rightarrow **8** \rightarrow **9**. We feel, however, that the great hydrolytic ability of the imino group in compound **2**, makes the sequence **2** \rightarrow **6** \rightarrow **7** \rightarrow **3** a more likely one.