

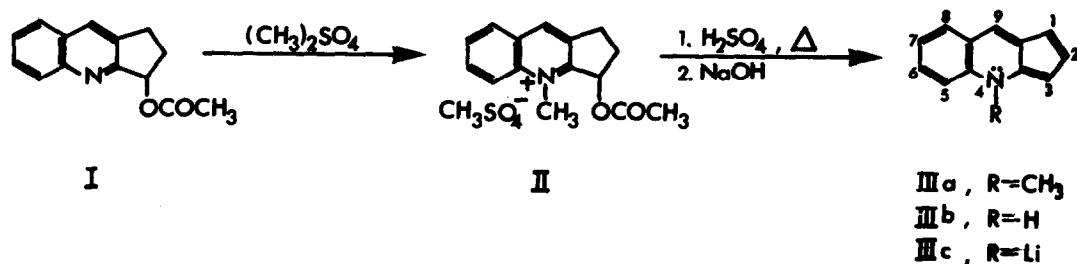
THE SYNTHESIS OF 4-METHYL-4H-CYCLOPENTA[b]QUINOLINE AND ITS  
RESPONSE TO NUCLEOPHILIC ATTACK<sup>1</sup>

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Although several syntheses of substituted cyclopenta[b]quinolines (benzo[b][1]pyrindines) have been reported<sup>2-4</sup>, only recently was the unsubstituted cyclopenta[b]quinoline system synthesized and its tautomeric nature fully characterized<sup>5,6</sup>. Of especial interest was the detection of the 4-H tautomer (IIIb, *ca.* 0.1%), whose fully conjugated, azulene-like character was revealed in its deep violet color<sup>5</sup> and in the electrophilic attack it and its lithium salt (IIIc) underwent at C<sub>1</sub> or C<sub>3</sub><sup>6</sup>. In order to lock the tautomeric cyclopenta[b]quinoline in its 4-H form, we have accordingly prepared the intensely violet-colored, highly reactive 4-methyl derivative (IIIa). We now wish to report on the spectral properties of such an aza-aromatic system and to show that its azulene-like response extends to nucleophilic attack as well.

Since the tautomeric mixture of 1H-, 3H- and 4H-cyclopenta[b]quinolines undergoes both C- and N-methylation with methyl iodide<sup>5</sup>, and since the lithium salt (IIIc) gives principally C-methylation with the same reagent<sup>6</sup>, these approaches did not prove suitable for the synthesis of IIIa. Accordingly, exclusive N-methylation was achieved with a precursor where no C-methyl-



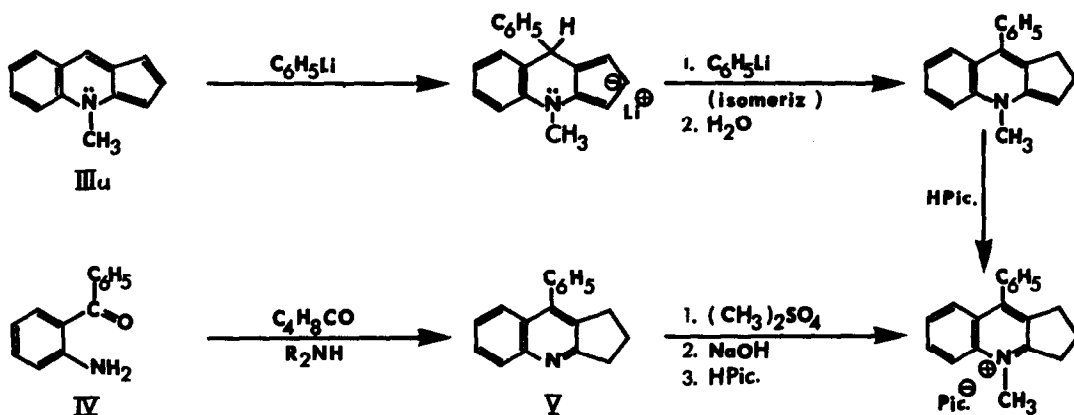
ation was possible. Thus 3-acetoxy-2,3-dihydro-1H-cyclopenta[b]quinoline (I)<sup>5</sup> was treated at

25° with dimethyl sulfate in dry benzene solution to yield the methosulfate II. A solution of II in concentrated sulfuric acid was heated for 4 minutes in a bath preheated to 120° and then, under nitrogen, poured over cracked ice. The thawed mixture was admixed with degassed ether and made basic with 50% aqueous sodium hydroxide solution. The separated and dried ethereal extracts were evaporated under nitrogen to give 55% of 4-methyl-4H-cyclopenta[b]quinoline (IIIa), as a deep violet solid. Although solutions in ether or in  $\text{CCl}_4$  were stable under nitrogen at <0°, the violet color of IIIa rapidly disappeared upon exposure to air and, in the solid state, IIIa tended to form an insoluble, apparently polymeric (no mass spectral peaks at 25°) black solid.

The spectral data for the violet solid are in complete accord with an assignment of structure IIIa: a) mass spectrum at 70 eV with the probe at 25° (mass, relative intensity, assignment): 181, 64, P; 167, 100, P- $\text{CH}_2$ ; 166, 56, P- $\text{CH}_3$ ; 146, 18, P- $\text{C}_2\text{H}$ ; 140, 22, P- $\text{CH}_3\text{-C}_2\text{H}$ ; and 139, 18, P- $\text{CH}_3\text{-C}_2\text{H}_2$ ; b) nmr spectrum in  $\text{CCl}_4$  ( $\delta$ -scale with internal TMS): 3.97, s (N- $\text{CH}_3$ ); 5.83, br. m. ( $\text{C}_7\text{-H}$ , presumably split by  $\text{C}_2\text{-H}$  (ca. 4 Hz) and by  $\text{C}_3\text{-H}$  and  $\text{C}_9\text{-H}$  (ca. 1 Hz); 6.40, center of d. of d. with higher intensity downfield ( $\text{C}_3\text{-H}$ ,  $H_{23} = 5$  Hz,  $H_{13} = 1.5$  Hz); 7.0-7.4, m ( $\text{C}_2\text{-H}$  and  $\text{C}_9\text{-H}$ ); 7.5-7.9, m (3H) and 8.1, br. s ( $\text{C}_6\text{-H}$ ); c) visible spectrum in ether: br. max. 495-555 nm ( $\lambda_{\text{max}}$  525 nm,  $\log \epsilon$  ca. 2.5; and d) infrared spectrum in  $\text{CCl}_4$  ( $\mu$ ): 2.5-3.4, clear; principal bands at 3.4-3.6; 6.3-6.6 br., str; 8.0; 9.2; 9.4; 9.9 and 11.6.

Addition compounds of IIIa were readily formed with sym-trinitrobenzene and with both picric acid and hydriodic acid. However, decomposition accompanied these reactions since only dark solids of uncertain composition could be isolated. Moreover, the products from acid treatment did not cleanly re-form IIIa, when they were subsequently admixed with sodium hydroxide under a nitrogen atmosphere.

On the other hand, we were able to convert IIIa into a stable derivative suitable for analysis by treating it with phenyllithium in ethereal solution. The resulting phenyl adduct was transformed into its methopicrate by means of picric acid and this dark green picrate<sup>7</sup> (m.p. 154-155°) was shown to be that of 2,3-dihydro-9-phenyl-1H-cyclopenta[b]quinoline (V) by spectral and m.p. comparisons with an authentic sample. The previously unreported V was prepared from 2-aminobenzophenone (IV) and cyclopentanone by a procedure adapted from Treibs and Kempter<sup>8</sup>, m.p. 135-136°, 78% yield<sup>7</sup>. The methopicrate of V<sup>7</sup> was prepared by a sequence of quaternizing with dimethyl sulfate, liberating the anhydro base with sodium hydroxide and,



finally, reprotonating with picric acid.

The finding that 4-methyl-4H-cyclopenta[b]quinoline undergoes nucleophilic attack with phenyllithium at C<sub>9</sub> complements neatly our previous characterization of such 1-pyridine systems as analogs of azulene. From the knowledge that organolithium reagents attack azulene at C<sub>4</sub> and C<sub>8</sub><sup>9</sup>, 1-pyridines, as azulene-like systems, would be expected to undergo corresponding attack in the pyridinoid ring gamma to the nitrogen. Our observation of C<sub>9</sub>-phenylation in IIIa is experimental confirmation of this prediction. Therefore, because of their spectral properties and their response to nucleophilic and electrophilic reagents, systems such as the 4-methyl derivative, IIIa, clearly deserve to be treated as close electronic relatives of azulene and benzazulene.

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