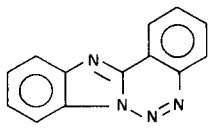
1,2,3-Benzotriazines. III. The Synthesis of Pyrido[2′,2′(3′,2′):4,5]imidazo[1,2-*c*][1,2,3]benzotriazine and Pyrido[3′,4′(4′,3′):4,5]imidazo[1,2-*c*][1,2,3]benzotriazine.

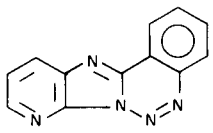
Richard H. Spector and Madeleine M. Joullié

Department of Chemistry, University of Pennsylvania

The benzimidazo[1,2-*c*]benzotriazine ring (I) was first prepared by v. Niementowski in 1898 (1). This ring system received little attention until 1966 when derivatives of this heterocycle were prepared and their reactions studied (2). The internal diazonium salt character of this ring was of particular interest since it offered a new route to 2-(*o*-substituted phenyl)benzimidazoles. We wish now to report two new ring systems (II and III) which are aza analogues of I. The starting materials were 2-*o*-aminophenylimidazo[4,5-*b*]pyridine and 2-*o*-aminophenylimidazo[4,5-*c*]pyridine respectively. Of the many methods available for the synthesis of 2-substituted benzimidazoles, the polyphosphoric acid condensation originally used by Hein and co-workers (3) was chosen, since (2-*o*-aminophenylimidazo[4,5-*b*]pyridine had been prepared by this method (4). Although the usual diazotization reagents (sodium nitrite plus hydrochloric acid and sodium nitrite plus sulfuric acid) were successful to prepare I from the



I



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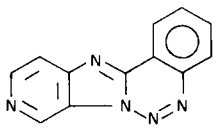

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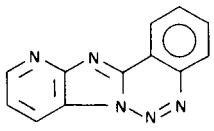

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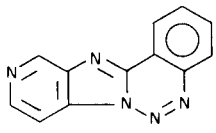

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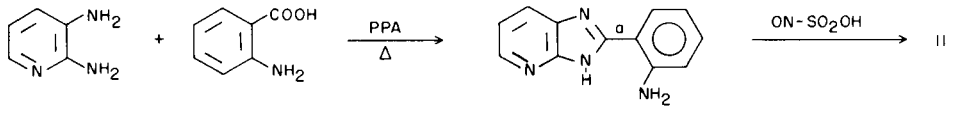
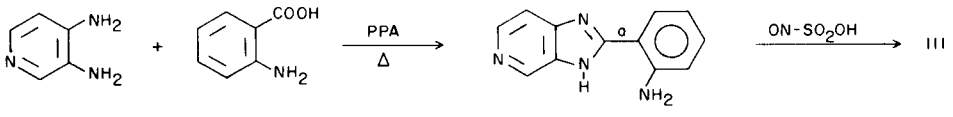


VI



VII

appropriate benzimidazole, they proved ineffective to accomplish a similar ring closure to yield II and III. These compounds were finally obtained by the diazotization of their respective precursors with nitrosylsulfuric acid (5).

The infrared spectra of II and III are identical except in the CH out-of-plane bending region where each compound exhibits its own characteristic pattern for aromatic substitution. The spectrum of II shows two peaks at 775 cm^{-1} and 756 cm^{-1} which can be ascribed to three and four adjacent hydrogens respectively. The spectrum of III exhibits peaks at 880, 825, and 759 cm^{-1} which may be reasonably assigned to one, two and four adjacent hydrogens respectively.

Due to the tautomerism of the imidazole ring of VI and VII and to the free rotation about bond (a) there exists the possibility that two isomeric structures can be formed (IV and V). Thin layer chromatography indicates the formation of only one of these for each system. At the present time we can find no physical or chemical methods to distinguish between the two possible forms.

EXPERIMENTAL

2-*o*-Aminophenylimidazo[4,5-*b*]pyridine (VI).

Compound VI was prepared from 2,3 diaminopyridine and anthranilic acid by the method of Garmaise and Komlossy.

Pyrido[2′,3′,(3′,2′):4,5]imidazo[1,2-*c*][1,2,3]benzotriazine (II or IV).

A solution of 2-*o*-aminophenylimidazo[4,5-*b*]pyridine (6 g., 0.028 moles) in 75 ml. of concentrated sulfuric acid was cooled to 0-5°. Nitrosylsulfuric acid, made by dissolving 3 g. (0.043 moles) of sodium nitrite in 85 ml. of concentrated sulfuric acid, was then added rapidly while maintaining the temperature at 0-5°. Concentrated phosphoric acid (60 ml.) was added immediately with allowing the temperature to exceed 10°. The reaction was stirred with cooling for an additional hour, 2 g. of urea added, and the solution poured in a beaker of ice. The clear solution was neutralized with concentrated sodium hydroxide and the resulting yellow solid washed with water until free of base, and recrystallized from methanol, giving 2.5 g. (40%), m.p. 228-229°; U. V. λ max. (methanol), 223 (ε, 28,177), 277 (ε, 59,022), 287 (ε, 68,000), 325(sh) (ε, 13,155); N.M.R. spectrum (deuterioacetic acid), 7.7-8.9 δ (phenyl protons, multiplet).

Anal. Calcd. for $C_{12}H_7N_5$: C, 65.15; H, 3.19; N, 31.66. Found: C, 65.24; H, 3.30; N, 31.62.

2-*o*-Aminophenylimidazo[4,5-*c*]pyridine (VII).

Compound VII was prepared from 3,4-diaminopyridine and anthranilic acid by the method of Garmaise and Komlossy.

Pyrido[3′,4′,(4′,3′):4,5]imidazo[1,2-*c*][1,2,3]benzotriazine (III or (V).

The procedure employed in the preparation of compound II was used except that 2-*o*-aminophenylimidazo[4,5-*c*]pyridine was employed. The product was recrystallized from 75% ethanol (38%), m.p. 192-194°; U. V. 227 (ε, 20,226), 264(sh) (ε, 27,195), 272 (ε, 31,728), 280 (26,912), 315(sh) (ε, 4,306); N.M.R. spectrum (deuterioacetic acid), 8.0-8.8 δ (phenyl protons, multiplet).

Anal. Calcd. for $C_{12}H_7N_5$: C, 65.15; H, 3.19; N, 31.66. Found: C, 65.29; H, 3.35; N, 31.45.

Acknowledgment.

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