

The Structure of Basic Blue 4. 3,7-Bis(diethylamino)phenazoxonium Chloride

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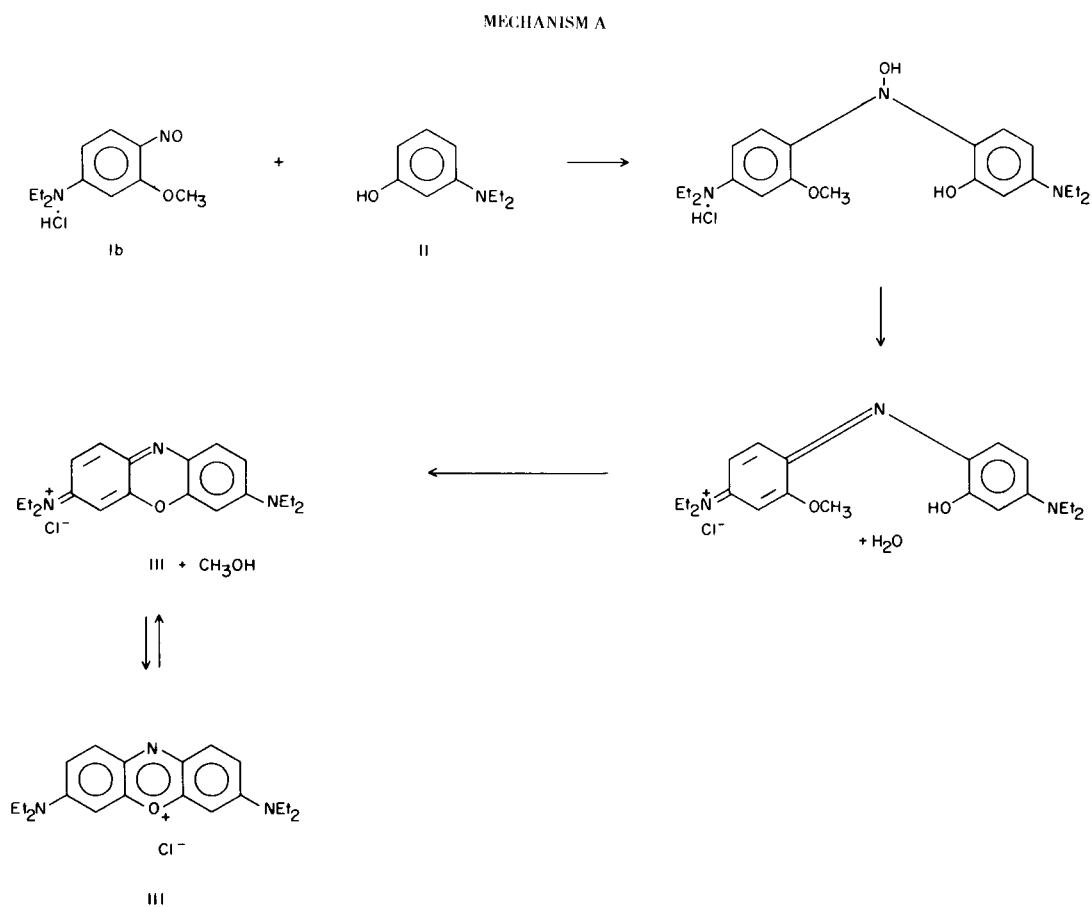
We write to clarify a detail in dye chemistry that has remained unresolved since 1917. In that year Farbenfabriken Bayer & Co. announced a new synthesis (2) of a bright blue basic dye whose structure was interpreted as 3,7-bis(diethylamino)phenazoxonium chloride (III) by the editors of the Beilstein Handbuch (3) on the basis of a private communication from I. G. Farbenindustrie.

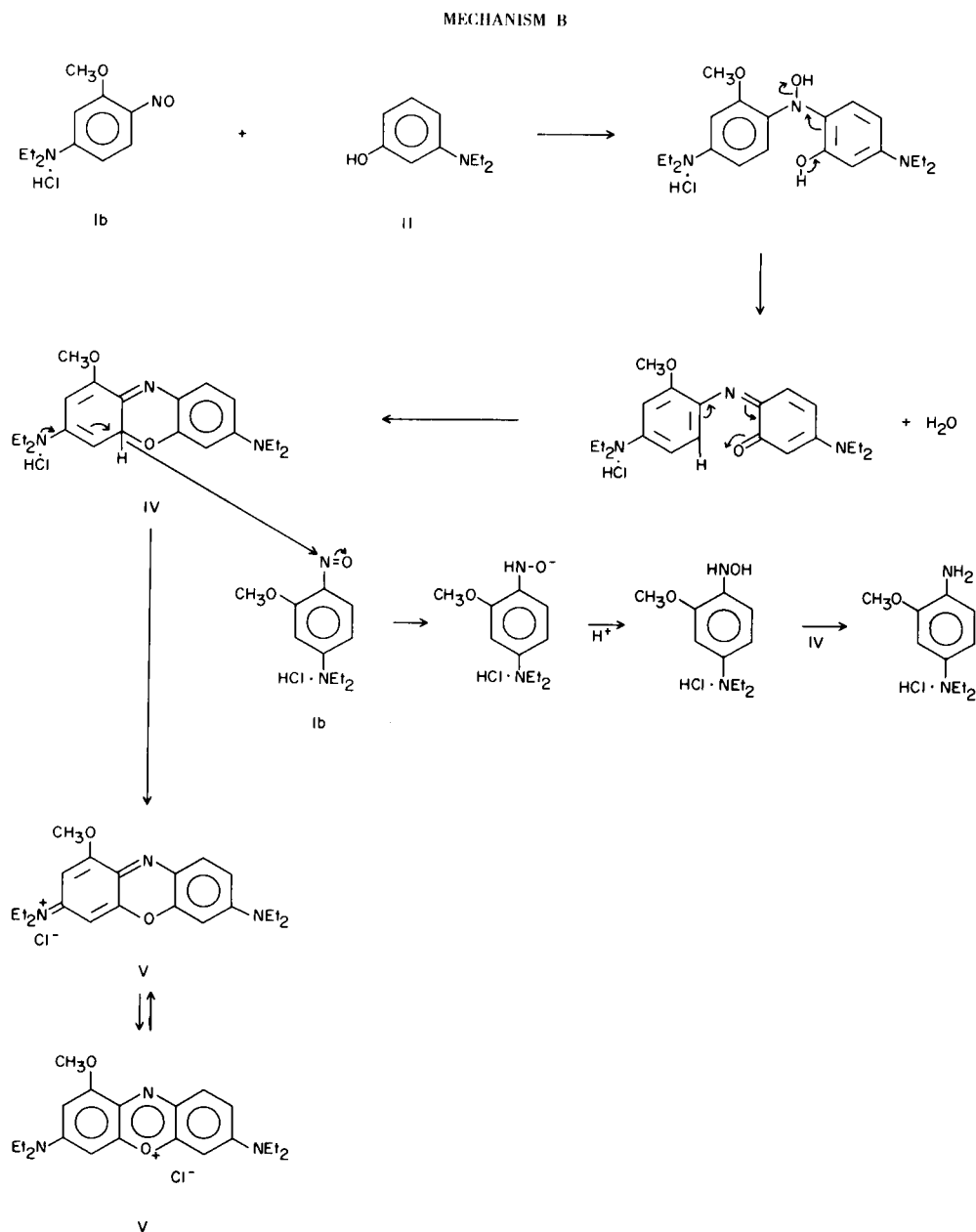
In contrast, a process dated 15 December 1939 for the manufacture of Rhoduline Pure Blue 3G at Hoechst (4) describes the condensation of nitrosated *N,N*-diethyl-*m*-phenetidine (Ia) with *m*-diethylaminophenol (II) to pro-

duce 3,7-bis(diethylamino)-1-ethoxyphenazoxonium chloride (V; C₂H₅O vice CH₃O). On the basis of Reference 4, the editors of the Colour Index (6) portrayed Basic Blue 3, CI 51005, made from Ia, as the 1-ethoxy structure and Basic Blue 4, CI 51004, made from nitrosated *N,N*-diethyl-*m*-anisidine (Ib), as the 1-methoxy structure (V).

Since there is little detectable difference (5) between the properties of these two Basic Blue dyes, it seemed worthwhile to study their structure with current tools.

We have followed the process of Reference 4 in an inert atmosphere, using *N,N*-diethyl-*m*-anisidine (Ib) and





m-diethylaminophenol (II) with 2-propanol as the solvent. The product dye was isolated as the double salt with zinc chloride.

High-resolution mass spectroscopy showed that our product was III, free of the methoxy group. Nuclear magnetic resonance spectroscopy, applied both to the double salt with zinc chloride and to the phenazoxonium picrate, showed no evidence of an alkoxy group.

In the condensation (4) of the hydrochloride of *N,N*-diethyl-4-nitroso-*m*-anisidine (Ib) with *m*-diethylaminophenol (II), two possible mechanisms can be written (A and B). Mechanism A would produce the alkoxy-free structure (III), while Mechanism B would lead to the

alkoxy structure (V).

Mechanism A requires equimolar amounts of Ib and II, while Mechanism B uses 1.5 moles of Ib for each mole of II. Our synthesis of III in an inert atmosphere used equimolar amounts of Ib and II and the yield was 80% of the theoretical. If Mechanism B were operating, equimolar quantities of Ib and II could produce no more than a 67% yield. We therefore believe that our synthesis followed Mechanism A and thus produced a product free of alkoxy groups (III).

Finally, Mechanism A produces an alcohol as a by-product, prior to the dye-forming reaction. A sample of condensed vapor from the refluxing solution of II in

2-propanol, analyzed by gas chromatography, showed only the presence of 2-propanol and water. After the addition of Ib, the blue dye formed and the condensed vapor now contained methanol. In a similar experiment, the evolution of ethanol was detected in the reaction of Ia with II.

We consider that the above evidence supports the alkoxy-free Beilstein structure III for Basic Blue 4 and for Basic Blue 3 as well.

EXPERIMENTAL

Synthesis of Basic Blue 4.

A solution of II (82.6 g., 100% basis, 0.5 mole, 96.0 g. net) in 90% 2-propanol (330 g.) was heated at reflux in a four-necked, one-liter round-bottom flask equipped with a stirrer, thermometer, and a Dean-Stark trap with a condensate sampler. A 130 ml. sample of condensate was collected and the reaction mass was restored to its initial volume by the addition of 130 ml. of 90% 2-propanol. Compound Ib (122.4 g., 100% basis, 0.5 mole, 335 g. net) was added in portions over a 30-minute period while controlling the temperature from 65 to 75°. A blue color formed as the first portion of Ib was added. The mixture was heated to reflux and three 130 ml. samples of condensate were collected over a three-hour period while keeping the volume of the reaction mass constant through the addition of 90% 2-propanol. The dye was then isolated as the zinc chloride double salt by acidification with 2 g. of 30% hydrochloric acid and the slow addition of zinc chloride (85 g., 0.63 mole, as a 40% solution in 75% 2-propanol) at 30 to 35°. The yield was 202 g. of dried crude product. Spectral analysis indicated a purity of 98%. Thus, the yield of zinc chloride double salt (M.W. 495.9) was 80% of theory.

The sample of condensate taken before the addition of Ib contained only water and 2-propanol. The successive samples taken after the addition of Ib contained 2.76, 2.09, and 1.47% respectively, of methanol in addition to the water and 2-propanol. The amount of methanol collected corresponds to 51% of that predicated by the stoichiometry of Mechanism A.

High-Resolution Mass Spectroscopy of Basic Blue 4.

A sample of Basic Blue 4, prepared as described above and isolated as the double salt with zinc chloride, was examined by the direct insertion technique with a Consolidated Electro-dynamics Corp. Model 110 High-Resolution Mass Spectrometer. Perfluorokerosene was used as an internal standard. The peaks found in the vicinity of the cationic mass are given in Table I.

TABLE I

Found	Composition	Calculated Mass
321.1829	C ₂₀ H ₂₃ N ₃ O	321.1831
322.1901	C ₂₀ H ₂₄ N ₃ O	322.1910
323.1991	C ₂₀ H ₂₅ N ₃ O	323.1988
324.2061	C ₂₀ H ₂₆ N ₃ O	324.2066
325.2149	C ₂₀ H ₂₇ N ₃ O	325.2144
326.2172	¹³ CC ₁₉ H ₂₇ N ₃ O	326.2178

No chlorine or zinc was associated with these peaks. The general appearance of the spectrum suggested that the cation was mass 325, presumably a protonated species (7), instead of 324 as represented by structure III.

NMR Spectrum of Basic Blue 4.

The spectrum of Basic Blue 4 showed no evidence of the presence of a methoxyl group. The ratio of methyl/methylene/aromatic protons was 12/7.1/6.1, in good agreement with the 12/8/6 ratio called for by structure III. The chemical shifts (δ , ppm from 3-(trimethylsilyl)propanesulfonic acid sodium salt) for the methyl and the methylene protons were 1.30 and 3.63, respectively.

The nuclear magnetic resonance spectrum of a saturated deuterium oxide solution of our Basic Blue 4 was recorded under optimum instrument conditions on a Varian A-56/60 spectrometer. The sample was run at normal probe temperature (about 35°) in a 5-mm. spinning sample tube with 3-(trimethylsilyl)propanesulfonic acid sodium salt as internal reference. The picrate of the dye was analyzed under similar conditions in a saturated dimethyl-formamide-d₇ solution using internal tetramethylsilane as reference.

Synthesis of Basic Blue 3.

In an experiment similar to that described above for the synthesis of Basic Blue 4, the blue dye from the condensation of II with nitrosated *N,N*-diethyl-*m*-phenetidine hydrochloride (Ia) was prepared and samples of condensate were taken from the refluxing vapors above the reaction mass. Dye tests showed the dye to be similar to Basic Blue 4 prepared as described above. The condensate samples were found to contain ethyl alcohol upon analysis by gas chromatography.

Analysis for Methanol and for Ethanol in 2-Propanol.

These analyses were conducted in a Hewlett-Packard 5751 gas chromatograph equipped with a flame ionization detector. The 4 foot long x 1/4" O.D. glass column was packed with 80/100 mesh Porapak Q (Waters Associates, Inc.) and was maintained at 150°. Helium flow through the column was 75 ml./minute.

Acknowledgment.

For assistance in dye testing the authors extend thanks to John F. Bracelin and Charles W. Harris; for analytical assistance to R. D. Brown (HRMS), Michael S. Fahsel, Jr. (GC), and to Anthony Foris (NMR).

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Received May 5, 1969

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