[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

OPTICALLY ACTIVE DYES. IV. ASYMMETRIC DYES FROM META-AMINOMANDELIC ACID

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In continuation of the work of Porter and Hirst,[2] Porter and Ihrig[3] have prepared a number of asymmetric dyes among which were the phenol and β-naphthol derivatives of diazotized *m*-aminomandelic acid. With the β-naphthol dyes they carried out dyeing experiments which led them to conclude that a chemical reaction was involved in the dyeing process. The work of Brode with Adams[4] in the previous paper has shown that in the case of asymmetric dyes derived from phenylamino-acetic acid there is no selective absorption or other indication of chemical action in the mechanism of dyeing. Inasmuch as the results obtained by Porter and Ihrig on the mandelic acid dyes were in contradiction to these, it was deemed advisable to repeat the experiments on the mandelic acid dyes.

The preparation of *m*-aminomandelic acid was through the *m*-nitromandelic acid and the dyes were then synthesized following the directions of Porter and Ihrig. The melting points obtained were as follows: *dl*-β-naphthol dye, 205–206° (no melting point was given in the publication by Porter and Ihrig but in a private communication Ihrig gave it as 206.5°); the *dl*-phenol dye, 120–121° (Porter and Ihrig gave 119°). Analysis by the titanous chloride method confirmed the identities of these.

The same directions were used in the dyeing experiments that were previously used in the tests by Porter and Ihrig on the same dyes. Duplicate tests were made and the experiments performed on the phenol dye as well as on the β-naphthol dye. One g. of the racemic dye was dissolved in 75 cc. of glacial acetic acid and this was treated with 2.5 g. of wool for 24 hours at 20°. The solution was then filtered, 20 cc. removed for polarimetric observation and the remainder again treated with 2.5 g. of wool under the same conditions for another 24 hours and then filtered, a sample removed and the process again repeated. The dyeing experiments were made by the use of wool flock,[5] a method which gives a much more uniform and greater adsorption than the skein method of dyeing. Wool samples were also treated in acetic acid solutions containing no dye and, after treatment in which the time and temperature were maintained as in the previous experiments, the rotation of these solutions was also measured.

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[1] This communication is an abstract of a portion of a thesis submitted by Wallace R. Brode in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[2] Porter and Hirst, THIS JOURNAL, **41,** 1264 (1919).

[3] Porter and Ihrig, *ibid.,* **45,** 1990 (1923).

[4] Brode with Adams, *ibid.,* **48,** 2193 (1926).

[5] Appel, *Am. Dyestuff Reporter,* **13,** 507 (1924).

These dyeing experiments and the rotational measurements were made at the Bureau of Standards.[6] The observations were made at a wave length of approximately 585 mμ for the colorless and phenol dye solutions, and at about 610 mμ for the naphthol dye solutions. The naphthol dye being a dark red as compared with the yellow color of the phenol dye, it was necessary to use a shorter cell in order to allow enough light to pass through to obtain accurate readings. In the case of the naphthol dye, a 3 cm. cell was used and for the phenol dye a 10 cm. cell. The polarizing angle of the separate Nicol prisms in the polarizer could, of course, be made very small in the case of the clear and phenol-dye solutions, but it had to be much larger in the case of the naphthol dye in order to allow sufficient light to pass through; hence, a greater allowable variation exists in these latter measurements.

The readings recorded below are the average of a number of observations on each solution and in each case the observed rotation is well within the allowable experimental error. In other words, no rotation was observed in any of the solutions.

	Angles of rotation, °			
Solution	0 hrs.	24 hrs.	48 hrs.	72 hrs.
Phenol dye (10cm. tube)	+0.012	+0.021	+0.005	−0.006
β-Naphthol dye (3cm. tube)	+ .006	+ .004	− .008	+ .001
β-Naphthol dye (Porter and Ihrig)	....	− .66	− .91	....

Porter and Ihrig did not publish the tube length used in their polarimetric observations so that it was impossible to verify their data or to reproduce exactly the conditions of their measurements. The concentration of the solution, however, is known, and from experiments made with dye solution of this concentration no satisfactory readings could be made in a 20 cm. cell, since the amount of light that passed through was so small as to require a rather large polarizing angle, thus introducing considerable observational error in the readings. No apparent rotation was observed in acetic acid solutions which had been treated with wool, as evidenced by the reading of +0.004 which was obtained when wool was allowed to stand in acetic acid for 72 hours before being filtered off.

The dyed wool that was filtered off at the end of the first 24 hours should have contained optically active dyes if the theory of Porter and Ihrig is correct. This wool was, therefore, allowed to stand for 48 hours in acetic acid and, after the liquid had been separated by filtering, the rotation of the solution, which had extracted the larger portion of the dye from the fibers, was observed. In the case of the phenol dye, a rotation of —0.001° was observed and in the case of the β-naphthol dye a rotation of +0.003°

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[6] The authors are indebted to the Polarimetric Section of the Bureau of Standards for the use of their apparatus and to Mr. F. P. Phelps for assistance in making these measurements.

was observed, both within the experimental error of the apparatus, considering the fact that the solutions were colored.

Absorption Spectra

In order further to identify and distinguish these dyes, their absorption spectra in the visible and ultraviolet portions of the spectrum were determined. These observations were made in two solvents, namely, alcohol and 3% aqueous sodium hydroxide. These data are presented in Figs. 1 and 2 using the same method of plotting and notation as in previous papers of this series.[7]

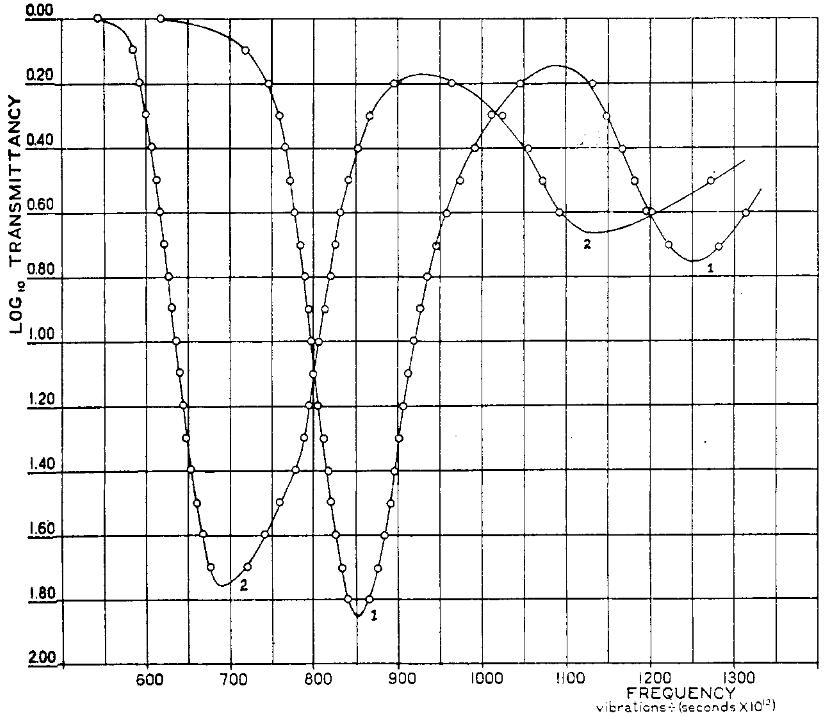

Fig. 1.—The absorption spectra of *dl-m*-azophenolmandelic acid in alcohol (1) and in 3% aqueous sodium hydroxide (2); concn., 0.04 × 576 g. per liter; cell thickness, 0.5 cm.

Experimental Part

***m*-Nitromandelic Acid.**—Much difficulty was encountered in this preparation and consequently details are given.

A solution of 30 g. of *m*-nitrobenzaldehyde (m. p., 34°) in 90 cc. of glacial acetic acid was placed in a round-bottomed flask fitted with a mechanical stirrer and was cooled to 0°. At this temperature the mixture was a mush, due to the solidification

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[7] Brode with Adams, This Journal, **46**, 2032 (1924).

of the acetic acid. To this, during constant stirring, was added 15 g. of potassium cyanide dissolved in a minimum amount of water, about 30 cc. This gave a yellow or greenish pasty mass which was stirred continuously for about four or five hours. After the reaction had been started no more ice was added to the ice-bath and after three or four hours the solution warmed to 8–10° and was of a clear, straw-yellow color. The solution was treated with sodium carbonate, extracted with ether and the ether was removed by evaporation on a steam-bath, care being taken not to heat the liquid cyanohydrin after the ether had been removed. The cyanohydrin was then treated with 150 cc. of concd. hydrochloric acid. This solution, which was still a light yellow, was evaporated on a steam-bath nearly to dryness, more hydrochloric acid added and the evaporation continued. The resulting mush was extracted with ether and about 10 g. of ammonium chloride filtered off from the ether solution. The ether solution was evaporated on a steam-bath to a small volume and the evaporation continued in a vacuum desiccator. On standing for a short time, the viscous liquid solidified to give a light yellow, crystalline solid which crystallized from benzene, and the hot benzene on cooling precipitated light yellow plates of *m*-nitromandelic acid; m. p., 118° (Heller[8] gives 119°). The yields varied widely but averaged about 40–50%.

Fig. 2.—The absorption spectra of *dl*-*m*-azo-β-naphtholmandelic acid in alcohol (1) and in 3% aqueous sodium hydroxide (2); concn., 0.05 × 376 g. per liter; cell thickness, 0.5 cm.

The reduction was carried out as described by Porter and Ihrig and the resulting amine diazotized and coupled to β-naphthol and phenol.

***dl*-*m*-Azo-β-naphtholmandelic acid,** $OH.C_{10}H_6.N:N.C_6H_4.CHOH.COOH$.—This is a

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[8] Heller, *Ber.*, **46**, 3976 (1913).

dark red dye, crystallizing in rosets, m. p. 205–206° (Ihrig gives 206.5°), soluble in alcohol, benzene and ether, and less soluble in acetic acid (a solution of 1 g. in 75 cc., on standing in a closed container, will deposit a large amount of the crystalline solid).

Anal. —N=N—. Calcd.: 8.7. Found: 8.6, 8.8 (by $TiCl_3$ titration).

***dl-m*-Azophenolmandelic acid**, $HO.C_6H_4.N:N.C_6H_4.CHOH.COOH$.—This is a light yellow dye, crystallizing in plates, m. p. 119–120° (Porter and Ihrig give 119°), soluble in alcohol, benzene and in acetic acid, and slightly soluble in water.

Anal. Calcd.: —N=N—, 10.33. Found: 10.30, 10.26 (by $TiCl_3$ titration).

Summary

Two asymmetric dyes, as previously prepared by Porter and Ihrig, have been synthesized.

The absorption spectra of these dyes in various solvents have been determined.

Dyeing experiments have been made with these dyes and the results from these tests have failed to confirm the previous results obtained by Porter and Ihrig. No rotation was observed in any of the solutions examined and no evidence has been obtained which would indicate the selective adsorption of one of the enantiomorphic forms of the racemic dye.

These data agree with previous data obtained by the authors and afford additional proof that the dyeing mechanism is not necessarily a chemical phenomenon.

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THE CHEMICAL PROPERTIES OF CAPROYLRESORCINOL AND SOME OF ITS DERIVATIVES

BY D. TWISS

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Johnson and Lane,[1] and recently Leonard,[2] have announced that certain alkyl resorcinols and especially hexylresorcinol possess high bactericidal strength as compared to phenol, and that these derivatives are relatively non-toxic. Considerable interest has been developed in applying these compounds to the problem of internal antisepsis. A large number of alkyl resorcinols as well as acyl resorcinols, the products from which they are derived, have been made in the laboratories of Sharp and Dohme, Baltimore; the acyl resorcinols by condensing fatty acids with resorcinol by means of zinc chloride, the alkyl resorcinols by reducing these ketones by the method of Clemmensen,[3] which has already been applied by Johnson and Lane to the lower members of this series.

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[1] Johnson and Lane, THIS JOURNAL, **43,** 348 (1921).

[2] Leonard, *J. Am. Med. Assoc.*, **83,** 2005 (1924).

[3] Clemmensen, *Ber.*, **46,** 1837 (1913).