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DYES CONTAINING THE FURANE CYCLE¹

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In the present paper the preparation and properties of certain dyes derived from furfural are described. Preliminary experiments on this line were carried out in the spring of 1915, and it is felt certain that the present authors were the first to isolate stable dyes containing the furane cycle.

On account of the activity of others in this field since the first public announcement of our work was made,² it seems desirable to present these results at this time. Our intention was to enlarge considerably the scope of the work,³ but on account of the entry of one of us into war activities and a subsequent change of location this has been impossible.

Highly colored, unstable condensation products of furfural with primary and secondary aromatic amines have been studied in considerable detail by a number of investigators, notably Stenhouse,⁴ H. Schiff,⁵ de Chalmot,⁶ Ehrhardt,⁷ Knoevenagel,⁸ Zincke and Muhlhausen,⁹ Dieckmann and Beck¹⁰ and Konig.¹¹ None of these products, however, was of any value as a dye.

The condensation of furfural with dimethyl aniline was carried out by O. Fischer¹² at the time that he discovered malachite green by oxidizing the condensation product of benzaldehyde with that base. He found that the leuco base of malachite green, tetramethyl-diamino-triphenyl-methane, was colorless, while the leuco base of the corresponding compound obtained by using furfural instead of benzaldehyde, tetramethyl-diamino-diphenyl-furyl-methane, was light yellow, yet on the oxidation of these two leuco compounds he obtained on the one hand malachite

¹ Read at the Buffalo Meeting of the American Chemical Society, April 6, 1919.

² The results described in this paper furnished part of the material submitted in a thesis for the degree of Master of Science at Iowa State College in June, 1918, by Nellie M. Naylor.

³ In 1913 the senior author began an investigation of corn cobs as a possible source of pentose sugars (U. S. patent 1,190,953) and other materials derived from pentosans, as fermentation products and furfural.

⁴ Stenhouse, *Ann.*, **156**, 199 (1870).

⁵ H. Schiff, *ibid.*, **201**, 355 (1880); **239**, 349 (1887).

⁶ de Chalmot, *ibid.*, **271**, 11 (1892).

⁷ Ehrhardt, *Ber.*, **30**, 2012 (1897).

⁸ Knoevenagel, *ibid.*, **31**, 2613 (1898).

⁹ Zincke and Muhlhausen, *ibid.*, **38**, 3824 (1905).

¹⁰ Dieckmann and Beck, *ibid.*, **38**, 4122 (1905).

¹¹ Konig, *J. prakt. Chem.*, [2] **72**, 555 (1905); **88**, 193 (1913).

¹² O. Fisher, *Ber.*, **10**, 1626 (1877); *Ann.*, **206**, 141 (1883).

green, a bluish-green dye, and on the other a solution of a product which gave a more *yellow-green* color than the former and which was very unstable to light. He supposed this to be the furane analog of malachite green.

On reviewing this work of Fisher the present authors were struck by the apparent inconsistency that the furyl group when substituted for the phenyl group in the leuco base and in the dye had an opposite effect on the absorption of light by the compounds. The furyl group in the leuco compound brought about a greater absorption in the visible spectrum than the phenyl group (yellow and colorless), while in the oxidation product the furyl group seemed to absorb less, that is, the furyl derivative gave a yellow-green color while the phenyl derivative gave a blue-green color.

It was decided to repeat Fisher's work in order to determine with certainty the color of tetramethyl-diamino-diphenyl-furyl-methane. If this were in fact yellow then theory would demand that the dye obtained from it by oxidation (if of analogous structure to malachite green) should absorb more light than the latter. Of course there was the possibility that in the oxidation, the furane nucleus was opened and a compound similar to Konig's azomethin dyes was obtained. However, there is no evidence that such a compound could be formed from tertiary amines.

Experiments proved that tetramethyl-diamino-diphenyl-furyl-methane does absorb light in the visible spectrum and has a light yellow color. Our theoretical considerations were fully borne out as to the color of the salts of its oxidation product. The furane analog of malachite green was obtained both as the zinc chloride double salt and as the oxalate by the oxidation of the leuco compound. These salts and their solutions are more deeply colored than is malachite green, and much to our surprise the colors of fabrics dyed with this substance are indistinguishable as to degree of stability from the former as shown by the standard tests of fastness to light, perspiration, acid, alkali, hydrogen peroxide, milling, stoving, etc.

The dye gives gray-blue shades on silk, wool, and mordanted cotton. Like malachite green the shade on cotton is not a pure tone, but on wool and particularly on silk very handsome effects are obtained.

Attempts were made to prepare other types of dyes containing the furane nucleus. An example of an hydroxy-ketone dye was prepared by the condensation of pyromucic acid with pyrogallol. It is presumably the furane analog of alizarin yellow A, trihydroxyphenyl-furyl-ketone. This has a brown color, and forms brown, gray-brown and yellow-brown lakes with aluminum, chromium and iron, respectively. It gives a dark tan color on cotton mordanted with turkey red.

A number of attempts were made to bring about the condensation of

pyromucic acid with gallic acid to form the furane analog of anthracene brown (anthragallol) without success. The presence of gallic acid seemed, unexpectedly, to augment the carbonization of the pyromucic acid by the condensation agents used, zinc chloride and sulfuric acid.

Experimental

Preparation of Tetramethyl-diamino-diphenyl-furyl-methane.—This product was prepared by the standard procedure using zinc chloride as the condensing agent. The leuco base obtained was subjected to exhaustive purification by solution in acid and precipitation with a base, treating with bone black its solutions in aqueous acids and in neutral organic solvents, and final recrystallizations from petroleum ether. The crystals obtained were light yellow, and the color tone was pure, giving a further indication that the color was an intrinsic property of the substance.

Preparation of the Furane Analog of Malachite Green.—The leuco base was oxidized with lead peroxide in acid solution in the usual manner. It was desirable to keep the reaction mixture cold, and stir continuously for 2 hours or more. After the elimination of the excess of lead salts, a concentrated solution of zinc chloride was added and the zinc chloride double salt of the dye salted out with sodium chloride. It separated as very dark blue crystals having a bronze reflex. The *oxalate* was prepared from a portion of the dye solution. The dye base was precipitated with sodium hydroxide and thoroughly washed and filtered. It was then treated with a warm saturated solution of oxalic acid, and the mixture filtered warm. The oxalate separated as copper colored needle crystals. They were somewhat soluble in cold water, in ethyl and amyl alcohol and in acetone.

The dye was analyzed by dissolving a well-washed sample of the dye base in hydrochloric acid, filtering and precipitating the chloroplatinate with platinic chloride. The precipitate was washed with alcohol, dried and ignited.

Analyses. Calc. for $C_{21}H_{24}ON_2Cl_6Pt \cdot H_2O$: Pt, 26.16. Found: 25.95, 25.96.

The Condensation of Pyromucic Acid with Pyrogallol.—Six g. each of pyromucic acid and pyrogallol were heated with 18 g. of anhydrous zinc chloride. The reaction began at 110° and was almost complete at about 125°. The product was heated to 145° until no more gas was evolved, and then ground with hot water to dissolve the excess of the reagents. It was purified by solution in sodium hydroxide and precipitation with hydrochloric acid. So obtained it is a yellow-brown powder, melting at 160° (uncorr.). It is soluble in alcohol and in acetone, and insoluble in petroleum ether and benzene. These solvents may be used for its purification.

The product was dyed on cotton by the method used for alizarin. A dark tan shade was obtained.

Summary

1. It is believed that the present authors were the first to show that stable dyes could be obtained from furfural aldehyde and from pyromucic acid.
2. Contrary to the results obtained by O. Fisher but in accordance with theory the furane analog of malachite green has a deeper color than the latter. It is an equally stable dye and gives a handsome effect on silk and wool.