tively, and because of their possible utilization in the synthesis of other compounds.

New Haven, Connecticut

[Contribution from the Laboratory of Organic Chemistry, Tulane University]

THE CHEMISTRY OF FURFURAL. THE PREPARATION OF THE FURAN ANALOG OF BENZOFLAVIN OR DIMETHYL-DIAMINO-FURYL-ACRIDINE HYDROCHLORIDE[1,2]

By S. A. Mahood and C. R. Harris

Received July 21, 1924 Published December 13, 1924

Many colored substances have been prepared by the condensation of furfural with aromatic amines[3] but the compounds obtained either are not dyes or give colors which, on the fabric, are fugitive. Condensation has been brought about in three ways. (1) The aldehyde and the unprotected amino groups react to give compounds of the type of Ehrhardt's difuraltolidine. (2) The aldehyde and amine in the presence of free mineral acid give compounds in which the rupture of the furan ring has taken place. The reaction, according to Zincke and Mühlhausen, gives compounds of the general formula $C_6H_5.NH.CH:CH.CH:C(OH)CH:N.C_6H_5.HCl$, which are unstable and readily decompose to give aryl-oxypyridonium salts. (3) The aldehyde and the amine, with the basic groups protected, condense to give derivatives of diphenyl-furyl-methane.

Fischer,[4] in connection with his work on malachite green, thought he had prepared the furan analog of that dye by condensing furfural with dimethylaniline. He described it as being lighter in color than malachite green and very unstable toward light. Recently Renshaw and Naylor[5] have repeated Fischer's work and found that the analog is not only darker than malachite green but is also indistinguishable from it in fastness and stability according to standard tests. At the same time they prepared trihydroxyphenyl-furyl ketone, the furan analog of Alizarin Yellow A, and found it to be a stable dye. A. and E. Lederer[6] have patented certain

---

[1] Read before the Division of Organic Chemistry at the Milwaukee Meeting of the American Chemical Society, Sept. 10–14, 1923.

[2] Abstract of a thesis presented by C. R. Harris to the Faculty of Graduate Studies of Tulane University in partial fulfilment of the requirements for the Degree of Master of Science.

[3] Stenhouse, *Ann.*, **156**, 199 (1870). H. Schiff, *Ann.*, **201**, 355 (1880); **239**, 349 (1887). De Chalmot, *Ann.*, **271**, 11 (1892). Ehrhardt, *Ber.*, **30**, 2012 (1897). Knoevenagel, *Ber.*, **31**, 2585 (1898). Zincke and Mühlhausen, *Ber.*, **38**, 3825 (1905). Dieckmann and Beck, *Ber.*, **38**, 4122 (1905). König, *J. prakt. Chem.*, [2] **72**, 555 (1905); **88**, 193 (1913). O. Fischer, Balling and Aldinger, *ibid.*, **100**, 86 (1919).

[4] Fischer, *Ber.*, **10**, 1626 (1877).

[5] Renshaw and Naylor, This Journal, **44**, 862 (1922).

[6] A. and E. Lederer, Ger. pat. 264,915, March 15, 1915; Aust. pat. 72,235, Aug. 10, 1916.

other dyes of an indefinite nature made from furfural. This paper gives the preparation of a third stable coloring matter containing the furan cycle.

Experimental Part

Preparation of Tetra-amino-ditolyl-furyl-methane.—The sulfate of *m*-toluylene-diamine was prepared by dissolving 20 g. of the purified amine (m. p., 99°) in 70 cc. of water at 60° and then adding 30 cc. of 6 *N* sulfuric acid. On cooling the solution the salt separated practically quantitatively in light brown to colorless crystals. Twenty g. of this sulfate was added to 40 g. of 50% alcohol containing 2.4 g. of furfural and the mixture refluxed until the odor of the aldehyde was lost, which required from eight to ten hours. As the refluxing continued the color became a very deep brown and the condensation product partially separated as a dark brown powder. When the reaction was complete the alcohol was distilled and the solution filtered without the addition of more water because of the appreciable solubility of the compound in water.

Preparation of Dihydro-diamino-dimethyl-furyl-acridine.—Twenty g. of the crude tetra-amino-ditolyl-furyl-methane sulfate was placed in a glass tube, 70 g. of 6 *N* hydrochloric acid added and the tube sealed and jacketed. It was then heated in an electric oven at 140° for four hours. The product obtained was used directly without purification.

Variations were made in the conditions under which this compound is formed in order to determine the effect upon the yield of the dye. The time was varied from two and a half to four hours and the temperature from 110° to 140°. A maximum yield of 60% (calculated from the formula $3C_{19}H_{18}N_3O.3HCl.ZnCl_2$) was obtained with a four-hour heating period at 120°.

Preparation of Dimethyl-diamino-furyl-acridine.—The mass from the tube reaction described just above was dissolved in 500 cc. of 4 *N* hydrochloric acid, the solution filtered, then cooled to 0°, and 70 g. of an ice-cold 30% solution of ferric chloride and 20 g. of zinc chloride in a little water were added. The coloring matter separated as a dark brown powder.

Some difficulty was encountered in the purification of the compound for analysis. The only solvents found in which the dye is appreciably soluble are aniline, quinoline and water. When aniline was used some aniline hydrochloride crystallized with the compound, while quinoline also showed a tendency to remove hydrochloric acid. With water there is a tendency to form tar, due apparently to the removal of hydrochloric acid. The method of purification finally adopted was to dissolve the dye in hot water and precipitate by adding dil. hydrochloric acid.

Table I gives the analysis of several samples of the purified product. Samples 6 and 7 were precipitated twice from water solution while the remaining samples were precipitated four times. Nitrogen was determined by the Kjeldahl method using a sulfuric acid and potassium sulfate oxidizing mixture. Zinc was determined by precipitating the zinc ammonium phosphate and weighing it both as the ammonium phosphate and as the ignited pyrophosphate.

TABLE I

THE ANALYSIS OF THE DYE

Sample	Taken G.	Dried	0.1 *N* HCl Cc.	Nitrogen %	$ZnNH_4PO_4$ G.	Zinc %	$Zn_2P_2O_7$ G.	Zinc %	N in Zn-free, ovendry compound %
1	0.2448	over H_2SO_4	18.25	10.43	0.0358	5.34	....	....	12.36
2	.3234	over H_2SO_4	24.00	10.10	.0443	5.00	0.0385	5.09	12.20
3	.3324	over H_2SO_4	24.80	10.44	.0445	4.88	....	....	12.25
4	.1960	105°	15.20	10.86	.0302	5.61	.0254	5.54	12.27
5	.2110	105°	16.30	10.81	.0322	5.57	.0272	5.58	12.15
6	.2572	105°	19.10	10.40	.0536	7.22	.0441	7.33	12.23
7	.2332	105°	17.40	10.45	.0474	7.42	.0408	7.49	12.34

The results indicate that the amount of zinc chloride retained per molecule is variable and is dependent upon the number of times the product is precipitated, that is, upon the amount of water used in the purification. The samples analyzed approximate the formula $3C_{19}H_{18}N_3O.3HCl.ZnCl_2$ (calc.: N, 10.91%; Zn, 5.63%). The product is somewhat hygroscopic and the samples dried over sulfuric acid gave low values both for zinc and nitrogen, due presumably to the retention of some water. When the percentage of nitrogen is calculated upon a zinc chloride-free basis it is found to be practically constant for all samples and corresponds to the calculated value for dimethyl-diamino-furyl-acridine hydrochloride which is 12.35%.

Properties.—The dye was found to be insoluble in benzene, nitrobenzene, ether, ethyl acetate, petroleum ether, carbon disulfide, carbon tetrachloride and chloroform. It was slightly soluble in 95% ethyl alcohol and very soluble in aniline and quinoline. It is also very soluble in hot water and on cooling the solution a partial separation of very fine particles occurs. When these were examined under the microscope no crystalline structure could be detected.

The coloring matter dyes unmordanted cotton a dull brown and gives to silk, viscose silk and wool a deep rich brown. The fastness of the color to light, washing, milling, alkalies, cross dyeing, perspiration, carbonizing and stoving was tested. It was very resistant in all of these tests and underwent no appreciable change except in the case of cross dyeing. In this it resembled its analog benzoflavin in that it had a slight tendency to bleed into the undyed cotton and wool that were interwoven with the dyed material.

Summary

A new dye containing the furan cycle has been made by the condensation of furfural with *m*-toluylene-diamine. It was obtained as a

double salt of zinc chloride, but the amount of zinc chloride that is retained by the compound is variable. Analysis showed this new compound to be the furan analog of benzoflavin or dimethyl-diamino-furyl-acridine hydrochloride. In its properties it is like a typical acridine dye. It dyes silk, wool and unmordanted cotton and in fastness and stability is indistinguishable from its analog, benzoflavin.

NEW ORLEANS, LOUISIANA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

4-PARA-TOLYLSEMICARBAZIDE AND CERTAIN DERIVATIVES[1]

BY ALVIN S. WHEELER AND R. W. BOST

RECEIVED JULY 23, 1924 PUBLISHED DECEMBER 13, 1924

In certain cases where an aldehyde or ketone is particularly sensitive to alkaline reagents, semicarbazide and phenylsemicarbazide have a great advantage over hydroxylamine as reagents for the carbonyl group. There may be cases where phenylsemicarbazide has an advantage over semicarbazide on account of its increased negativity. Of the three known phenylsemicarbazides the 1-phenylsemicarbazide has not been employed. The 2-phenylsemicarbazide seems to have been used in one case, its condensation with benzaldehyde.[2] The 4-phenylsemicarbazide was first used by Curtius and Hofmann[3] who condensed it with acetone. Its value was further shown by Wheeler and Edwards[4] who prepared a phenylsemicarbazone of tetrahydroxy-naphthalene, an oxime not being obtainable.

In this paper we propose another reagent, 4-*p*-tolylsemicarbazide, describing its preparation and its condensation products with acetone, acetophenone, benzophenone, *p*-quinone and camphor.

Two *p*-tolylsemicarbazides have been described in the literature. Bamberger[5] obtained what should be called 1-*p*-tolylsemicarbazide by the action of potassium cyanate on *p*-tolylhydrazine, analogous to Fischer's method of preparing 1-phenylsemicarbazide. Bamberger states that it crystallizes in silky white leaflets, melting at 190–191°. Pinner[6] treated *p*-tolylhydrazine with urea and obtained what should be called 4-*p*-tolylsemicarbazide as glistening leaves, melting at 157–158°. Young and Stockwell[7] prepared 1-*p*-tolylsemicarbazide by Bamberger's method but

---

[1] This paper is a portion of a thesis submitted by R. W. Bost in partial fulfilment of the requirements for the degree of Master of Arts at the University of North Carolina.

[2] Busch and Walter, *Ber.*, **36**, 1359 (1903).

[3] Curtius and Hofmann, *J. prakt. Chem.*, [2] **53**, 526 (1896).

[4] Wheeler and Edwards, THIS JOURNAL, **38**, 390 (1916).

[5] Bamberger, *Ber.*, **35**, 1424 (1902).

[6] Pinner, *Ber.*, **21**, 1219 (1888).

[7] Young and Stockwell, *J. Chem. Soc.*, **73**, 368 (1898).