[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF TULANE UNIVERSITY]

THE CHEMISTRY OF FURFURAL. THE PREPARATION OF TETRAETHYLDIAMINODIPHENYLFURYLMETHANE HYDROCHLORIDE AND OF DIPHENYLFURYLMETHANE[1]

BY S. A. MAHOOD AND HELEN F. ALDRICH

RECEIVED JULY 21, 1930 PUBLISHED NOVEMBER 5, 1930

Unlike benzaldehyde, furfural does not condense with the hydrogen atoms para to the amino group of two molecules of aniline when furfural and aniline are treated with a dehydrating agent, but condenses with the hydrogens of the amino group. For this reason, in the synthesis of the diphenylfurylmethane dyes, the amino hydrogen atoms must be absent as in the tertiary amines, or protected by the formation of a sulfate or acetyl derivative.

In 1877, at the same time that he made malachite green, Otto Fischer[2] prepared, by the condensation of dimethylaniline and furfural, the first diphenylfurylmethane dye. He described the furyl analog as lighter in color than malachite green and unstable to light. Renshaw and Miss Naylor[3] found it darker than, and as stable as, malachite green.[4]

This paper describes the preparation of tetraethyldiaminodiphenylfurylmethane hydrochloride, from the condensation of diethylaniline and furfural, and the properties of this dye.

From the figures given on the yields in the synthesis of the leuco base of this dye and of the oxidized product, it can be said that in neither case do the reactions involved proceed easily under the conditions maintained. The following conclusions may be added: (1) the replacement of a phenyl group of malachite green by the furyl group causes a change in the stability of the dye; (2) the ease of condensation of an aldehyde with an aromatic amine is decreased when a furyl group is substituted for a phenyl group in the aldehyde; and (3) diethylaniline condenses with furfural less readily than dimethylaniline. There is a possibility that the stability of these dyes might be increased by substitution in the α'-positions of the furan ring.

Mahood and Harris[5] were able to prepare the furan analog of the dye

---

[1] Abstract of a thesis presented by Helen F. Aldrich to the faculty of Graduate Studies of Tulane University in partial fulfilment of the requirements for the Degree of Master of Science, June, 1930.

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

[3] Renshaw and Naylor, THIS JOURNAL, **44**, 862 (1922).

[4] Samples of silk treated with this dye were found by the authors of this paper to be more unstable to light than samples dyed with malachite green, when exposed to bright daylight for two weeks.

[5] Mahood and Harris, THIS JOURNAL, **46**, 2810 (1924).

benzoflavin from *m*-toluylene-diamine sulfate, refluxed with furfural. Mahood and Fenner,[6] however, were able to isolate, only in minute quantities, any diaminodiphenylfurylmethane formed by the condensation of furfural with acetanilide, while Mahood and Martin[7] were unable to isolate any of the above product from the condensation of furfural with aniline sulfate.

Because diaminodiphenylfurylmethane was not isolated in quantity, the preparation of diphenylfurylmethane directly from the latter by diazotization, according to the method used by Otto Fischer to prove the structure of the triphenylmethane dyes, was impossible. Mahood and Jordan[8] attempted to prepare this compound by several methods. In each case they were unsuccessful, either because under the influence of the heat or reagents necessary the furfural polymerized before taking part in the reaction, or because no product could be isolated.[9]

This paper also describes the preparation of the above product, diphenylfurylmethane, by a synthesis which involves first transforming the furfural to a more stable derivative, pyromucic acid, and then treating the ethyl ester of the latter with phenylmagnesium bromide to obtain diphenylfurylcarbinol, which on reduction with zinc and acetic acid gives the desired product.

The combustion values given in the experimental data agree with the calculated values for diphenylfurylmethane. The temperature of the reduction was kept low to prevent the formation of a fluorene linkage between the two phenyl groups.

Experimental Part

Preparation of Tetraethyldiaminodiphenylfurylmethane.—In a 500-cc. flask were placed 61.5 g. of freshly distilled diethylaniline, 18.1 g. of refined furfural and 20 g. of fused zinc chloride, finely pulverized. The flask, connected with a reflux condenser and a mechanical stirrer, was heated on a water-bath for eleven hours. At the end of this time there was still much unchanged diethylaniline, but more prolonged heating did not increase the yield of the product. The somewhat viscous, dark colored reaction mixture was subjected to steam distillation in the same flask, to remove unchanged furfural and diethylaniline. The crystalline leuco base left behind in the flask after steam distillation was washed with water to remove excess zinc chloride, dissolved in alcohol, boiled with boneblack and filtered while hot. Light yellow crystals separated, which darkened on exposure to air. This product, on recrystallization from ligroin, melted

---

[6] Mahood and Fenner, "Tulane Theses," 1927, Vol. 2, p. 152.

[7] Mahood and Martin, "Tulane Theses," 1925, Vol. 3, p. 491.

[8] Mahood and Jordan, *Science*, **60**, 453 (1924).

[9] Recently, Peters and Fischer [THIS JOURNAL, **52**, 2079 (1930)] have isolated impure phenylfurylcarbinol, the product which Jordan failed to isolate, and from which he intended to prepare the corresponding chloride, as a step in the synthesis of diphenylfurylmethane. All efforts to chlorinate this carbinol were found, by Peters and Fischer, to result in the formation of resins.

completely at 78° but softened several degrees below this. A yield of 22 g. or 31% was obtained in this way.

Anal. Calcd. for $C_{25}H_{32}N_2O$: N, 7.45. Found: N, 6.82, 6.91.

Preparation of Tetraethyldiaminodiphenylfurylmethane Hydrochloride.—Following the proportions given by Gattermann[10] for the oxidation of the leuco base of malachite green, the product obtained above was oxidized in acid solution with lead peroxide paste. The oxidation was carried on for two hours in the cold, accompanied by mechanical stirring. After elimination of the lead salts, the dye was precipitated as the double zinc chloride salt by means of a saturated solution of sodium chloride. A yield of 17.2% was obtained.

This dye is crystalline and dark green in color. It dyes silk a yellower color than malachite green, and, in the lighter tones, gives a clear bright green. Dyed samples were fast to washing, but faded somewhat on two week's exposure to bright light, whereas samples dyed with malachite green were unaffected.

Preparation of Diphenylfurylcarbinol.—Phenylmagnesium bromide was prepared according to Gilman,[11] from 10 g. of magnesium and 75 g. of phenyl bromide, in the presence of 200 cc. of ether. When the reaction was complete, 75 cc. of toluene was added and the ether distilled off; 19.6 g. of ethyl pyromucate,[12] prepared from pyromucic acid,[13] was dissolved in 25 cc. of toluene and added to the Grignard reagent with sufficient rapidity to cause vigorous refluxing. The temperature maintained was about 112°.

When the reaction was complete, the cooled mixture was decomposed with ice to which the theoretical amount of 30% acetic acid had been added. The toluene layer was separated. After removal of the toluene and diphenyl by steam distillation, a crystalline mass of a light brown color was left behind. This residue was only slightly soluble in cold ligroin and could be recrystallized from this medium in the form of beautiful, light colored, rhombic crystals, melting at 91° (corr.).[14] Fine white crystals of the same melting point could also be obtained by precipitation from a dilute solution in 87% ethyl alcohol, on the slow addition of water. After standing for a few days, these crystals of diphenylfuryl carbinol soften into a reddish mass. An 85% yield of this carbinol was obtained.

Preparation of Diphenylfurylmethane.—Three grams of the carbinol obtained above was dissolved in about 150 cc. of glacial acetic acid, in a large glass test-tube; 15 g. of zinc dust was added in small amounts to the solution. During this time the contents of the test-tube were heated in a water-bath, the temperature of which was kept below 70°. When the solution had changed in color from red to a pale yellow brown, it was poured into water and partially neutralized with sodium hydroxide. A spongy yellow precipitate, which hardened on drying, collected in a mass and was ground to a powder, washed until neutral and dried. It melted at 51° (corr.). The zinc residue left in the test-tube was further boiled with acetic acid. In this way more of the precipitate was obtained. The product was unstable, softening in a few days to a gummy mass. It was soluble in alcohol, ether, ligroin and hot glacial acetic acid. The yield was 95% of the theoretical, calculated as diphenylfurylmethane.

Anal. Calcd. for $C_{17}H_{14}O$: C, 87.14; H, 6.02. Found: C, 87.23, 86.83; H, 5.77, 5.81.

---

[10] L. Gattermann, "The Practical Methods of Organic Chemistry," translated by Schober and Babasinian, The Macmillan Co., New York, 1921, page 355.

[11] H. Gilman, THIS JOURNAL, 51, 1576 (1929).

[12] J. Malaguti, *Ann.*, **25**, 276 (1838).

[13] "Organic Syntheses," John Wiley and Sons, Inc., New York, **1926**, Vol. VI, p. 44.

[14] Hale, McNally and Pater, *Am. Chem. J.*, **35**, 68 (1906). These authors prepared this carbinol by a method essentially similar. They give 92.4° as its melting point.

Summary

1. A new dye, tetraethyldiaminodiphenylfurylmethane hydrochloride, has been prepared and its properties have been determined.

2. The parent compound of the diphenylfurylmethane dyes, diphenylfurylmethane, has been obtained by reduction of the corresponding carbinol.

NEW ORLEANS, LOUISIANA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

THE DISTILLATION OF GRIGNARD REAGENTS

BY HENRY GILMAN AND ROBERT E. BROWN

RECEIVED JULY 21, 1930 PUBLISHED NOVEMBER 5, 1930

Introduction

Solutions of Grignard reagents are mixtures of RMgX, R_2Mg, MgX_2, R— and —MgX (or MgX_2 + Mg) in a series of equilibria. The following equilibria and dissociation reactions[1] account for the compounds just mentioned.

$$2\ \mathrm{RMgX} \rightleftarrows \mathrm{R_2Mg} + \mathrm{MgX_2} \qquad \text{(I)}$$

$$\mathrm{RMgX} \rightleftarrows \mathrm{R—} + \mathrm{—MgX} \qquad \text{(II)}$$

In order to lend additional support to these reactions, studies have been made on the sublimation and distillation of organomagnesium compounds. First, in an attempted high vacuum distillation of methylmagnesium chloride, a distillate or sublimate of magnesium dimethyl, free of halogen, was obtained.[2a] The magnesium dimethyl, a solid like magnesium diethyl,[3] owes its formation undoubtedly to a displacement of the equilibrium pictured in Reaction I. Second, a search was made for a liquid organomagnesium compound in order to facilitate a study of Reaction I. The relative stability of the liquid beryllium di-*n*-butyl,[4] suggested that greater success might be had with magnesium di-*n*-butyl. Accordingly, magnesium di-*n*-butyl was prepared,[2b] but unfortunately it also is a solid. Like its homologs, magnesium dimethyl and magnesium diethyl, it can also be sublimed in a high vacuum but less smoothly than the lower members of this series because of its lesser volatility or lesser stability at elevated temperatures or for both of these reasons.

With this partial success, we turned to a method of distillation used earlier[4] in a study of organoberyllium compounds, namely, ether distillation. This method, which was highly successful for the distillation of solid

---

[1] Gilman and Fothergill, THIS JOURNAL, 51, 3149 (1929). This article contains leading references to other work.

[2] (a) Gilman and Brown, *Rec. trav. chim.*, 48, 1133 (1929); (b) Gilman and Brown, *ibid.*, 49, 724 (1930).

[3] Gilman and Schulze, THIS JOURNAL, 49, 2328 (1927).

[4] Gilman and Schulze, *J. Chem. Soc.*, 2663 (1927). See also, Gilman and Schulze, THIS JOURNAL, 49, 2904 (1927), for organoberyllium halides.