THE SYNTHESIS OF TEREPHTHAL GREEN AND TEREPHTHAL BRILLIANT GREEN FROM CYMENE

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Introductory.—In 1876, Otto Fischer heated a mixture of o-phthalyl chloride and dimethylaniline at 100° and formed a compound to which he assigned Formula I. In the presence of zinc dust, at the same temperature, he obtained later a "Phthalgruen," whose structure he represented by Formula II, dimethylanilinephthalein (V) being formed simultaneously. Subsequently, this Phthal Green was investigated by Haller and Guyot, who established its constitution as a derivative of 9-phenylanthrone (IV) rather than of the structure shown by Formula III. More recently, Weitz has prepared an o-Phthalaldehyde Green, and Craver has patented Malachite Green types produced from o-xylylaldehyde.

In our search of the literature, we failed to find any record of dyes of this class in the meta- or para-phthalic series, and hence undertook the preparation of such compounds as early as 1917.

In that year, Dr. C. P. Harris, working under the direction of the senior author, conducted some preliminary experiments on the condensation of terephthalyl chloride with dialkylanilines, the object of which was to produce and investigate the terephthalic analogs of the Malachite Green dyes. Green dyes were actually obtained in these preliminary trials, but their investigation was suspended owing to the withdrawal of Dr. Harris to accept an industrial appointment. The present paper is therefore a continuation of the research inaugurated by Bogert and Harris.

The raw material for the synthetic work was the usual one where terephthalic acid is concerned, namely the "spruce turpentine condensate" from the paper mills, a readily available and economical source of cymene.

This hydrocarbon was oxidized to terephthalic acid, the crude acid purified by crystallization of its methyl ester, the pure acid converted into terephthalyl chloride, and the latter condensed with dialkylanilines. The course of the reaction between the acid chloride and the dialkylaniline was determined by the presence or absence of such condensing agents as zinc chloride.

When the terephthalyl chloride and dimethylaniline were heated together at 198–215°, methyl chloride was evolved and the alkylanilide (VI) formed, a reaction similar to that noted by Hess with benzyol chloride and dimethylaniline, and by Staedel in the case of acetyl bromide and dimethylaniline.

In the presence of zinc chloride, however, terephthalyl chloride and
dimethylaniline condensed smoothly, even at 100°, to a deep green dye of Malachite Green type (VII). By using diethyl- instead of dimethylaniline, the analogous Brilliant Green type was secured.

\[ \text{R}_2\text{N.C}_6\text{H}_4.\text{CO.C}_6\text{H}_4.\text{CO.C}_6\text{H}_4.\text{NR}_2\text{HCl} \] (I)

The course of the condensation by which the dye is formed is represented by Series A above, rather than by Series B; for the former assumes that the first step consists in the loss of water, whereas the latter predicates a preliminary removal of hydrogen chloride. Experiments have shown that the dye is formed, not only when zinc chloride is used as the condensing agent, but also when the latter is replaced by phosphorous pentoxide, oxychloride or pentachloride, which are primarily dehydrating agents and not hydrogen chloride eliminants. Further, if the condensation de-
pended upon initial removal of hydrogen chloride, the product should be a colorless diketone (VIII), of Michler ketone type, and not a dye. The presence of hydrochloric acid, or of a phosphorous halide, would be requisite to condense this diketone with a dialkylaniline to a dye.

In tinctorial properties, these new dyes compare favorably with Malachite and Brilliant Green. On wool (1.5% dyeings), the shade is distinctly yellower than the older dyes; in direct sunlight, they are slightly more fugitive; but appear to be superior in fastness to washing, milling, stoving and perspiration tests. Dyeings with Terephthal Brilliant Green are lighter in shade than those made with Terephthal Green, just as Brilliant Green itself gives lighter shades than Malachite Green under similar conditions.

Experimental Part.—“Spruce turpentine condensate,” from the paper mills, was washed with caustic alkali and distilled with steam. The crude cymene so obtained was sufficiently pure for our purposes. It was oxidized by sodium dichromate and sulfuric acid, as recommended by Bogert and Harris. By the use of a large excess of the dichromate (440 g. per 25 g. of cymene), the yield of crude terephthalic acid was increased to 85% of the cymene consumed in the operation. This crude acid contained about 7–8% of $p$-toluic acid and small amounts of chromium salts. It was converted into its methyl ester, using either hydrogen chloride or concd. sulfuric acid as condensing agent, which was crystallized from alcohol; yield, 70%. From the mother-liquors, the $p$-toluic acid was recovered by evaporation of the alcohol, hydrolysis of the ester by boiling it with 10% sodium hydroxide solution, then acidifying and distilling with steam. The $p$-toluic acid thus driven over was crystallized from alcohol and melted at 180° (corr.); yield, 7.1% the weight of crude terephthalic acid employed. Pure terephthalic acid was obtained by hydrolysis (by 10% sodium hydroxide solution) of its methyl ester; yield, 95%, calculated to the ester.

Terephthalyl Chloride was produced from the acid (20 g.), phosphorous oxychloride (56 g.) and pentachloride (90 g.), by the method of Locher; b. p., 263–266°, m. p. 82° (corr.); yield, 90%.

Terephthalmethylanilide (VI).—A mixture of terephthalyl chloride (5 g.) and dimethylaniline (12 g.) was heated for 6 hours at 100°, but no condensation occurred.

When a similar mixture was boiled for 3 hours over a naked flame, the temperature rose gradually from 198° to 215°, at which latter point it remained constant. After continuing the boiling for an hour longer, the mass was dissolved in concd. hydrochloric acid, the solution filtered and the filtrate diluted with 5 volumes of water. The greenish precipitate was collected, boiled for 2 hours with 10% sodium hydroxide solution, removed, washed and dried. It then appeared as a yellow solid; yield,
78%. Crystallized repeatedly from toluene, it formed beautiful pale yellow flat prisms, m. p. 212–213° (corr.); yield, 28%.

Anal. Calc. for C_{12}H_{18}O_{2}Cl_{2}: C, 76.74; H, 5.81; N, 8.14. Found: C, 76.87, 76.77; H, 5.87, 5.82; H, 8.20.

The alkaline filtrate from this product yielded 0.5 g. of terephthalic acid when acidified.

The analytical figures obtained for the product melting at 212–213° (corr.) agree with those calculated for the methylanilide. The reaction was repeated, therefore, using 20 g. of the acid chloride and 48 g. of the dimethylaniline. The effluent gases were past into dry thiophene-free benzene containing some anhydrous aluminum chloride. At the close of the reaction, toluene was detected in the benzene, thus proving the presence of methyl chloride in these effluent gases.

The methylanilide was unchanged when boiled for 7 hours with an excess of acetic anhydride, or when dissolved in alcohol and treated with hydrochloric acid and sodium nitrite at 0°. Boiling concd. hydrochloric acid hydrolyzed it to terephthalic acid and methylaniline, of which the former was identified by conversion into its methyl ester, and the latter by formation of methylacetanilide (m. p. 102°, corr.).

A further proof of the identity of this methylanilide was supplied by its synthesis from terephthalyl chloride and monomethylaniline, in boiling toluene solution. The product isolated was the same in appearance and melting-point as that obtained from dimethylaniline, and a mixture of the two products melted sharply at the same point (212–213°, corr.).

Terephthal Green (VII).—A solution of 5 g. of terephthalyl chloride in 12 g. of dimethylaniline was heated to 100° and 7 g. of finely ground zinc chloride stirred in. After 3 hours' heating, the mixture had congealed to a hard dark green solid. This was dissolved in 200 cc. of warm water and the excess of dimethylaniline removed by distillation with steam. After adding a few drops of acid, to dissolve any basic zinc chloride, the solution was filtered, the filtrate evaporated to about 50 cc. and the dye precipitated by the addition of saturated sodium chloride solution. It was purified by resolution in the minimum quantity of water and reprecipitation by salt, and was finally washed with small amounts of water and dried in a vacuum desiccator. The double zinc chloride thus obtained was a green-black solid, of coppery luster; yield, 50%.

Anal. Calc. for C_{40}H_{44}N_{4}Cl_{2}:3ZnCl_{2}: Zn, 18.47; Cl, 26.79. Found: Zn, 18.09, 18.25; Cl, 27.12.

The proportion of dye to zinc chloride in this and in the succeeding dye differs somewhat from that in the Malachite Green double salt, where the molar ratio of dye to zinc chloride is 3:2.

Terephthal Brilliant Green, prepared similarly, formed a double zinc chloride as a black-green solid, of bronze luster; yield, 48%.
Anal. Calc. for \( C_{48}H_{60}N_4Cl_2 \cdot 3ZnCl_2 \): Zn, 16.72; Cl, 24.23. Found: Zn, 16.37, 16.42; Cl, 24.62.

Comparison of the Dyes.—The following tests were carried out, under as nearly as possible identical conditions, with Malachite Green, Brilliant Green, and the two terephthalic analogs just described. All dyed silk and wool direct, with apparently equal facility, but were not substantive for cotton.

Wool was dyed with a 0.1% solution of the dye containing an amount of dye equal to 1.5% the weight of the fabric used and 20 g. of sodium chloride per 150 cc. of solution. The dyeing was continued at the boiling-point of the solution until the bath was practically exhausted.

1. Shade.—In tinctorial strength, the two classes of dyes seemed about equal. The terephthalic derivatives dyed a yellower green than the corresponding triphenylmethane derivatives, the ethyl derivatives in both cases yielding lighter shades than the methyl.

2. Fastness to Light.—The newer dyes proved even more fugitive than the older ones.

3. Washing Test.—Dyed samples of cloth were wrapped in pieces of undyed cloth and worked for 5 mins. in a solution containing 5 g. of soap per liter of water, then soaked in the same solution for 15 mins. at 40°, rinsed in fresh water and dried. All four dyes lost a little color by this treatment. The older dyes bled into the undyed cloth, but no such bleeding occurred with the newer ones.

4. Milling Test.—Dyed samples wrapped in undyed cloth were stirred and kneaded for 10 mins. at 60° in a solution containing 5 g. of soap and 4 g. of sodium carbonate per liter. Bleeding was much less with the terephthalic dyes than with the triphenylmethane derivatives. Both lost color slightly in the treatment.

5. Fastness to Alkali.—Dyed samples were moistened with dilute and with concd. caustic alkali, dried and brushed off. All four were unchanged by the dilute alkali and turned yellow by the concd.

6. Fastness to Acid.—All four samples were unchanged when boiled for 10 mins. with 10% hydrochloric acid.

7. Perspiration Test.—Dyed samples were wrapt in pieces of undyed cloth, then soaked in a solution containing 100 g. of sodium chloride and 100 g. of acetic acid per liter, removed and heated at 40° for 24 hours. Bleeding occurred with the older dyes, but not with the terephthalic derivatives.

8. Stoving.—Suspended for 12 hours in an atmosphere of sulfur dioxide, the triphenylmethane dyes faded more rapidly than did the terephthalic derivatives; although both were nearly colorless at the end of the exposure.

9. Bleaching.—Dyed samples were soaked for 15 mins. in a solution containing 38 g. of sodium hypochlorite in 2 liters of water. All four samples lost color, but regained it upon exposure to the air.
Summary.—1. New dyes, of Malachite Green type, have been synthesized from terephthalyl chloride (from cymene) and dialkylanilines, in the presence of zinc chloride, which dye wool or silk a yellower green than that produced by Malachite or Brilliant Green. In general, these newer dyes compare favorably with the older triphenylmethane derivatives in tinctorial power, fastness, etc.

2. Terephthalyl chloride and dimethylaniline, in the absence of zinc chloride, react at higher temperatures (198–215°) with evolution of methyl chloride and formation of terephthalanilide.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY, No. 456]

1 The cymene for this investigation was supplied by the Hollingsworth and Whitney Company, Winslow, Maine. We welcome this opportunity to express our appreciation of their courtesy.—M. T. B. and P. S. N.

2 Otto Fischer, Ber., 9, 1753 (1876).


4 Haller and Guyot, Compt. rend., 125, 221, 1153 (1897).

5 Weitz, Ann., 418, 1 (1919).

6 Craver, U. S. Pat. No. 1,470,554 (Oct. 9, 1923); Color Trade J., 14, 12 (1924).

7 C. P. Harris, Dissertation, Columbia Univ., 1917, p. 42.


9 Hess, Ber., 18, 685 (1885).

10 Staedel, Ibid., 19, 1947 (1886).

11 Locher, Bull. soc. chim., (3) 11, 927 (1894).

FURTHER EXPERIMENTS IN THE FIELD OF THE TEREPTHALIC ACID DERIVATIVES1,2

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INTRODUCTORY

Some years ago, Bogert and Harris3 described the synthesis of para-di (hydroxyisopropyl) benzene from methyl terephthalate and methyl magnesium iodide. Its structure suggested the possibility of its possessing hypnotic or local anesthetic properties and, through the coöperation of our good friends, Drs. Arthur W. Dox and Oliver Kamm, of Parke, Davis & Co., and Prof. Arthur D. Hirschfelder, of the University of Minnesota, pharmacodynamic experiments later were carried out. The results of the tests are recorded in the experimental part of this paper.

The lack of physiological activity so disclosed seemed referable, in part at least, to physical and chemical defects which we believed might be