

phosphorus pentachloride for seven hours. After removal of the phosphorus halides under reduced pressure the residue was extracted with warm chloroform. This was evaporated to a small volume whereupon fine needles characteristic of the disulfonyl chloride separated. The yield was 3.7 g. Recrystallization gave a product, m. p. 77.5–78.5°, which showed no depression in melting point when mixed with the unsaturated disulfonyl chloride already described. From the sulfonyl chloride also was prepared the disulfonanilide identical with that obtained from the isobutylenedisulfonic acid.

### Summary

The sulfonation of isobutylene with excess dioxane sulfotrioxide gives the dioxane salt of 2-methylpropene-1,3-disulfonic acid. Evidence for the structure of this compound has been presented, including the synthesis of the corresponding disulfonyl chloride from 2-methyl-1,3-dichloro-2-propanol.

EVANSTON, ILLINOIS

RECEIVED SEPTEMBER 18, 1940

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF LYMAN CHALKLEY]

## Organic Mercury Derivatives of Basic Triphenylmethane Dyes: Dimercuri Derivatives of Malachite Green\*

BY LYMAN CHALKLEY

### Introduction

The various structural formulas which have been proposed for the basic triphenylmethane dyes would indicate that these dyes should mercurate easily. Depending upon the system of notation, these formulas show at least one, and sometimes two or three, para-substituted aniline groups in each molecule. The para-substituted anilines are, in general, quite easy to mercurate. Thus *p*-nitroaniline,<sup>1</sup> *p*-nitromonomethylaniline,<sup>2</sup> *p*-nitromonoethylaniline,<sup>2</sup> *p*-bromodimethylaniline,<sup>3</sup> *p*-toluidine,<sup>4</sup> and dimethyl-*p*-toluidine<sup>4</sup> mercurate with ease.

Nevertheless, most of the basic triphenylmethane dyes do not mercurate readily, if at all.<sup>5</sup> The completely alkylated dyes react only slowly with mercuric acetate, and the observed reaction is a reduction of the mercuric ion. This end result might be produced by the intermediate formation of an inherently unstable organic mercury compound which broke down with reduction of the mercury and oxidation of the dye-stuff. If such were the case it would be impossible to prepare stable mercurated dyes either by direct mercuration or some indirect process.

However, the slowness of the reaction of the

dyes with mercuric acetate speaks against a mechanism which would involve the formation of an intermediate organic mercury compound. For the mercuration of aromatic amines is usually rapid, and therefore a slow reaction, if it involved a mercuration, would indicate a slow decomposition of the organic mercury derivative, and thus time to isolate this derivative. The fact that such derivatives could not be isolated<sup>5</sup> would then suggest that the dyes simply do not react like substituted anilines, but behave more like aromatic quaternary ammonium salts, which are extremely resistant to mercuration.<sup>6</sup>

A similar situation was encountered in attempts to mercurate another basic dye, methylene blue, which reacted with mercuric acetate as do the triphenylmethane dyes.<sup>7</sup> But in the case of methylene blue it was found that a colorless derivative of the dye, the benzoyl leuco base, mercurated smoothly under suitable conditions.

**A Plan for Mercuration.**—It seemed possible, then, that in the case of the triphenylmethane dyes there might also be a profound difference between the behavior of the dyes themselves and the behavior of the colorless derivatives of these dyes toward mercuric salts. There are a number of these colorless derivatives which are in the same stage of oxidation as the dyestuff. In the Fischer notation they have the following general formulas, using Doebner's violet and para-rosaniline as illustrations

\* A preliminary report on a portion of the work described in this paper appeared in *Science*, **91**, 300 (1940).

(1) M. S. Kharasch, F. W. M. Lommen and I. M. Jacobsohn, *THIS JOURNAL*, **44**, 793 (1922).

(2) M. S. Kharasch and I. M. Jacobsohn, *ibid.*, **43**, 1894 (1921).

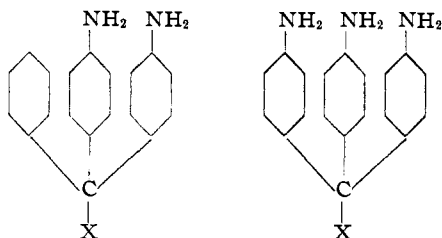
(3) F. C. Whitmore, *ibid.*, **41**, 1841 (1919).

(4) L. Pesci, *Gazz. chim. ital.*, **28**, 11, 101 (1898); see also F. C. Whitmore, "Organic Compounds of Mercury," 1921, p. 243.

(5) F. C. Whitmore and G. J. Leuck, *THIS JOURNAL*, **51**, 2782 (1929).

(6) Reference 2, page 1903.

(7) L. Chalkley, *THIS JOURNAL*, **47**, 2055 (1925).

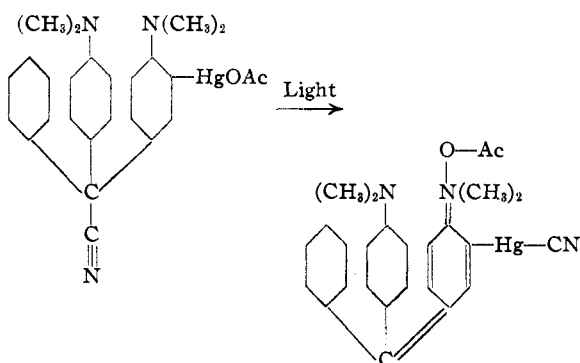


Here "X" is a negative ion, such as  $-\text{OH}$ ,  $-\text{NH}_2$ ,  $-\text{OR}$ ,  $-\text{CN}$ .

Most of these colorless derivatives are sensitive to acids, which convert them back into the dyes. Since mercuration of amines is carried out with mercuric salts, acid is formed in the reaction, and, moreover, is often added in excess to prevent hydrolysis. Therefore, these acid sensitive derivatives would seem to offer little advantage over the dyestuffs themselves.

But there is at least one class of colorless derivatives, the cyanides, which are stable to acid. Thus a dye cyanide appeared to be the logical derivative to attempt to mercurate.

Assuming that the cyanides could be mercurated, then the problem became one of converting the mercurated cyanides back into the dyes. The cyanides are stable to acids, but it was thought that conversion might be effected by a photochemical reaction. J. Lifschitz<sup>8</sup> had observed that the basic triphenylmethane dye cyanides dissolved in suitable solvents gave solutions which were colored while they were exposed to ultraviolet light although the solutions were colorless in the dark.<sup>8</sup> It was also shown that in this reversible reaction the colored form produced by light was ionized, and was probably the true dye,<sup>9</sup> although attempts to demonstrate the presence of cyanide ion by precipitation with silver nitrate were unsuccessful.<sup>10</sup>



(8) J. Lifschitz, *Ber.*, **52B**, 1919 (1919).

(9) J. Lifschitz and L. C. Joffe, *Z. physik. Chem.*, **97**, 426 (1921).

(10) L. C. Joffe, Dissertation, Zürich, 1921, p. 43.

Since organic mercuric cyanides of the type,  $\text{RHgCN}$ , are little ionized, it seemed probable that if a mercurated dye cyanide were exposed to ultraviolet light any cyanide ion formed would be fixed by the mercury, and the acid ion on the mercury would be liberated to form the dye salt, as shown.

**An Experimental Test of this Synthesis.**—The plan just outlined involved two steps. (1) The mercuration of a basic triphenylmethane dye cyanide; and (2) the photochemical conversion of the mercurated cyanide into the dye.

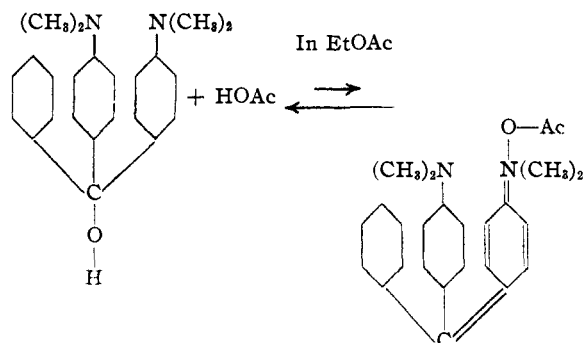
It was found that the cyanide of malachite green, 4,4'-bis-dimethylaminotriphenylacetonitrile, could be mercurated readily. The colorless mercurated nitrile was converted into the dye by the action of ultraviolet light. The reaction was irreversible, as had been anticipated. The conversion of the nitrile into the dyestuff took place without rupture of the mercury-carbon bond.

This synthesis of an organic mercury derivative of malachite green was valuable as showing that at least one colorless derivative of a basic triphenylmethane dye could be mercurated smoothly, and that the mercurated dyestuff was itself capable of existence. But as a preparative procedure the photochemical reaction was cumbersome. Radiation effective in converting the nitrile into the dye lay well out in the ultraviolet. It was not only necessary to use quartz apparatus, but the light sources which produced strong effective radiation also produced much visible light which was not easy to filter out. This visible light caused a decomposition of the dyestuff molecule itself. This, or other side reactions, resulted in a reaction mixture in which some of the organic mercury became unstable and gradually hydrolyzed from the carbon to which it was bound. This instability was not centered in the mercurated dyestuff, since the mercurated malachite green carbinol could be isolated and was found to be stable; but the decomposition of the reaction mixture did complicate the isolation of pure products.

For these reasons a synthesis which would not involve a photochemical conversion was sought.

**A More Direct Method of Synthesis.**—The search for a synthesis which would not involve a photochemical conversion of the initial mercuration product led to a study of the acid sensitive colorless derivatives of malachite green with the hope that it might be possible to find a

mercuration reaction which could be carried out upon these derivatives while they were in some way fixed in their colorless forms and prevented from changing into the dye during the mercuration. It was found that the nature of the solvent used in the mercuration had a profound influence upon the readiness with which the colorless derivatives were converted into the dye by acid. Organic "non-ionizing" solvents, such as ethyl acetate, were found to favor the colorless form. In ethyl acetate the ethyl ether of malachite green carbinol was found to be practically unaffected by the amounts of acetic acid involved in mercuration with mercuric acetate, and the carbinol itself was found to be only a little affected. An equilibrium appeared to be reached in which the carbinol was by far the major constituent



In these non-ionizing solvents there was little hydrolysis of mercuric acetate, and therefore excess acetic acid proved unnecessary in the mercuration.

In such a system mercuration proceeded smoothly. The resulting mercury compound could be converted into the dye by transferring it to an ionizing solvent, such as water or alcohol, and treating it with acid.

**Discussion of Results.**—This method of synthesis is simple and straightforward in principle. In practice it was found to present some interesting problems.

The mercuration of malachite green carbinol in ethyl acetate proceeded smoothly, yet when equimolecular proportions of mercuric acetate and malachite green carbinol were employed the reaction product consisted of a mixture of the expected monomercury compound and considerable amounts of unmercured carbinol and dimercurated carbinol. A similar result was obtained in the mercuration of the bis-dimethylamino-triphenylacetonitrile.

In the mercuration of a mononuclear aromatic compound the introduction of the first mercury atom greatly reduces the reaction speed of the entry of a second mercury atom, and thus monomercury derivatives are usually obtained in good yields. But in these polynuclear dye derivatives the introduction of a mercury atom into one nucleus seemed to have little influence upon the reactivity of the other nuclei in the molecule, with the result that the monomercury and dimercury derivatives were produced in more nearly the probability ratios. This interpretation seems to represent a general rule, since similar behavior was observed in the mercuration of aurin,<sup>5</sup> diphenyl ether,<sup>11</sup> and biphenyl.<sup>12</sup>

In order to simplify separation procedures, the work reported in this paper is limited to mercuration of malachite green derivatives with two molecular equivalents of mercuric acetate—one atom of mercury for each dimethylamino group.

While the mercuration of malachite green carbinol went to completion, and all of the mercury entered into organic combination, the reaction product when transferred to alcohol or water proved sensitive to hydrolysis by even the small amount of acetic acid produced in the mercuration, and considerable amounts of organically bound mercury were converted fairly rapidly into mercuric acetate. The pure malachite green carbinol mercury compound is stable to these concentrations of acetic acid, and therefore it seems probable that some by-product is formed which catalyzes the hydrolysis of the mercury-carbon bond. Whatever the cause, this type of decomposition is always a possibility in these mercurations and can easily lead to erroneous results. When the product precipitates from the reaction mixture, as in the example given in the experimental part, this difficulty is avoided; but when such precipitation does not take place, as for example with monomercured malachite green carbinol, special precautions should be observed in working up the reaction mixture.

Some of the mercury compounds in this group show surprising solubility relationships. For example, diacetoxymercuri-bis-dimethylamino-triphenylacetonitrile is more soluble in alcohol and ethyl acetate than is the unmercured nitrile. On the other hand, the products may form little

(11) W. D. Schroeder and R. Q. Brewster, *THIS JOURNAL*, **60**, 751 (1938).

(12) F. B. Hill, *ibid.*, **60**, 321 (1938).

soluble solvated compounds which are useful in separation, as exemplified in the process of mercuration of the carbinol given in the experimental part.

The dimercury derivatives in the malachite green series generally do not have sharp melting points but decompose when heated. The region of most rapid decomposition is not constant, but may vary many degrees with the rate of heating of the sample.

The conversion of dimercurated malachite green carbinol into the dye by acid is peculiar in that it does not go to completion. Acid solutions of the mercurated dye do not show the depth of color of solutions of unmercurated malachite green of the same molar concentration. The color of the solutions of mercurated malachite green is indistinguishable from that of the parent dye-stuff, and therefore comparisons of depth of color are easily made.

The light absorption of dilute aqueous solutions of dimercurated malachite green varies with hydrogen ion concentration from that of a solution of unmercurated dye having about 20% of the molar concentration of the mercurated dye solution to that of a dye solution of about 50% of the molar strength of the mercury compound. This variation takes place with an increase in acetic acid content of from about  $M/10,000$  acid in a  $M/10,000$  solution of mercury compound to 1.6  $M$  acetic acid in a  $M/10,000$  solution of mercury compound.

The addition of sodium chloride to a colored acid solution of the mercurated malachite green gives a precipitate which is largely dichloromercuri malachite green carbinol. Therefore, the lesser intensity of color of the mercurated dye solutions is probably not due to a lowered molecular absorption power, but to an incomplete conversion of the carbinol into the dye. Thus the mercurated malachite green appears to exist in water solution as an equilibrium mixture of the true dye salt and the carbinol. This would be similar to the equilibrium postulated above for the parent dye in ethyl acetate solution.

If the molecular light absorbing power of the mercurated and unmercurated dyes were the same, then the percentage conversion of the mercurated carbinol into the dye would be given by the color comparisons. Figures mentioned above would indicate a conversion of from 20% to 50% of the carbinol into the dye.

The equilibrium between dye and carbinol seems quite sensitive to temperature, and the color of solutions becomes deeper with rising temperature.

In view of the incomplete conversion of carbinol into dye the preparation of the mercurated dye in pure solid form becomes a problem in itself, which will not be considered here.

Perhaps as a corollary to the incomplete conversion of the carbinol into the dye, a much higher hydrogen ion concentration is required to color an aqueous solution of the mercurated carbinol than is required to color the parent carbinol. Malachite green carbinol in water changes from colorless to blue over the range of  $pH$  13 to  $pH$  11.4, whereas the dimercurated carbinol only begins to turn blue at about  $pH$  7.

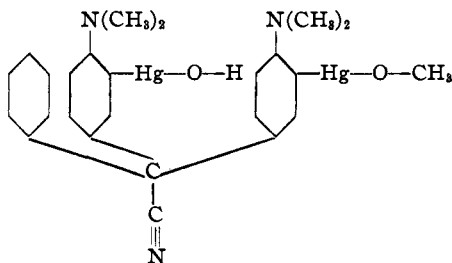
Although the mercurated dye solutions are less intensely colored than malachite green, they possess the same powerful affinity for silk and wool, and will continue to stain these fibers from a 1:5,000,000 solution, which is itself colorless. The dyeings, however, are somewhat lighter in color than those obtained from a corresponding amount of malachite green. In neutral or weakly alkaline solutions the carbinol exhausts onto silk although the fiber is only slightly colored, and the mercury compound exists in the fiber largely in the colorless form.

Dimercurated malachite green carbinol is a surface active agent. Its neutral aqueous solutions foam powerfully, and the stiff foams which are formed hold relatively high concentrations of the mercury compound.

### Experimental

**Mercuration of 4,4'-Bis-dimethylaminotriphenylacetone nitrile.**—A solution of 7.1 g. (0.02 mole) of 4,4'-bis-dimethylaminotriphenylacetone nitrile in 150 cc. of ethyl acetate was treated with 3 cc. of acetic acid and 12.8 g. (0.04 mole) of solid mercuric acetate, and the mixture was boiled gently under a reflux condenser until the mercuric acetate went into solution, which required seventy minutes. Some mercurous acetate precipitated during the boiling. The reaction mixture was cooled to room temperature, filtered from 1.56 g. of precipitate (largely mercurous acetate), evaporated *in vacuo* to 30 cc., and filtered from 0.81 g. of additional precipitate. The filtrate was diluted with 130 cc. of methyl alcohol and treated immediately with 30 cc. of 4  $N$  potassium hydroxide solution. A faintly cream colored precipitate formed quickly. After standing for four hours this precipitate was collected and dried in a desiccator, 8.55 g. of impure dihydroxymercuri-bis-dimethylaminotriphenylacetone nitrile. For purification, 4 g. of the product was dissolved in 100 cc. of methyl al-

cohol containing 1 cc. of acetic acid. The solution was filtered and the filtrate treated with 16 cc. of 2 *N* potassium hydroxide in methyl alcohol. After twenty-four hours the precipitate was collected, washed on the filter with a little methyl alcohol and water, and dried in a desiccator. The mercury content corresponds to methoxymercuri-hydroxymercuri-bis-dimethylaminotriphenylacetoneitrile



The material might, of course, be a mechanical mixture of the corresponding dimethoxymercuri and dihydroxymercuri derivatives. The position of the mercury is assumed from the products of mercuriation of other para substituted anilines to be ortho to the amino groups.

*Anal.*<sup>13</sup> The mercury analyses in this paper were made by the method of Koten with Adams. Calcd. for  $C_{25}H_{22}O_2N_2Hg_2$ : Hg, 49.98. Found: Hg, 49.80, 50.06.

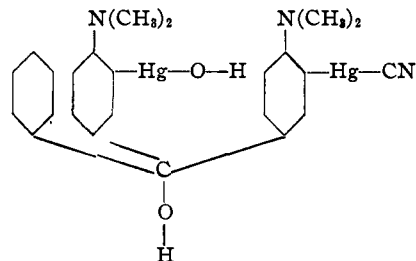
The substance is a white, clay-like material which blackens and decomposes when heated above 200°, the point of rapid decomposition varying with the rate of heating. It is little soluble in chloroform, water, ethyl acetate, benzene, toluene, acetone, and methyl alcohol. In the presence of a small amount of acetic acid the substance dissolves readily in the above organic solvents. The solution in acidulated alcohol gives only a colorless precipitate when made alkaline with ammonium hydroxide and treated with ammonium sulfide.

**Photochemical Conversion of Mercurated bis-Dimethylaminotriphenylacetoneitrile into Mercurated Malachite Green.**—Methoxymercuri-hydroxymercuri-bis-dimethylaminotriphenylacetoneitrile was dissolved in methyl alcohol containing 1% of acetic acid in the proportion of 2 g. of mercury compound per 100 cc. This solution was placed in a quartz flask which was kept below the boiling point of the alcohol by a stream of water while being exposed to the light of a double arc of ultraviolet cored ("therapeutic C") carbons. The initially colorless solution quickly assumed a blue color which deepened as the exposure to light continued. The color produced by light was permanent and was not lost on storage of the solution in the dark.

The colored photochemical reaction mixture gave a colorless precipitate when treated with ammonium hydroxide and ammonium sulfide, showing that the organic mercury had not been hydrolyzed as a result of the conversion of the nitrile into dyestuff. However, the colorless sulfide blackened more quickly than in a similar test before the exposure to light, and after standing for twenty-four hours the reaction mixture gave a gray precipitate with ammonium hydroxide and ammonium sulfide, indicating some decomposition.

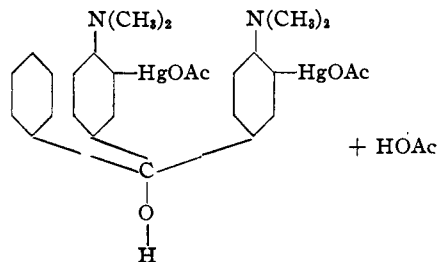
When treated with alkali the photochemical reaction

mixture gave a white precipitate which appeared to be a mixture of the unchanged nitrile and hydroxymercuri-cyanomercuri-bis-dimethylaminotriphenylcarbinol



This precipitate was partially soluble in dilute aqueous acetic acid to give a blue solution.

**Mercuriation of Malachite Green Carbinol.**—A solution of 41.6 g. (0.12 mole) of 4,4'-bis-dimethylaminotriphenylcarbinol in 1 liter of absolute ethyl acetate was treated with 76 g. (0.24 mole) of mercuric acetate, and the mixture stirred and heated to 70° until the mercuric acetate had gone into solution, which required one hour. The reaction solution was cooled to 56°, filtered from 1.45 g. of mercurous acetate, and then held for twelve hours at 8°. A voluminous precipitate formed. This was collected, washed with ethyl acetate on the filter, and dried in the air on a plate heated slightly above room temperature. The yield was 73 g., 67%, for diacetoxymercuri malachite green carbinol with one molecule of acetic acid



The substance was light green in color. It turned moist litmus paper red, and when made into a paste with water and warmed had an odor of acetic acid. Thus it appeared to contain some loosely bound acetic acid. The mercury analysis corresponds to the above formula.

*Anal.*<sup>14</sup> Calcd. for  $C_{29}H_{34}O_7N_2Hg_2$ : Hg, 43.33. Found: Hg, 43.70, 43.55.

The substance is a light green clay-like material, apparently amorphous. In drying it had lost the crystalline form of the highly solvated product which originally precipitated from the reaction solution. It is readily soluble in methyl and ethyl alcohol, benzene, chloroform and warm ethyl acetate. It easily forms a 1:1000 solution in water. It can be recrystallized from ethyl acetate.

When heated above 115° the substance decomposes, the temperature of most rapid decomposition varying with the rate of heating.

Aqueous solutions of the product have the same blue color as do solutions of malachite green, and the dyeings on

(14) In the analysis of the carbinol derivatives it is best to filter the solution after the decomposition with acid in order to remove strongly colored nitration products which interfere with observation of the titration end-point.

(13) Koten and Adams, *THIS JOURNAL*, **46**, 2769 (1924).

silk and wool are indistinguishable from those of malachite green. However, the intensity of the color of a  $M/10,000$  aqueous solution of the mercury compound which has been boiled and cooled to bring about maximum conversion to dye is only about as strong as that of a  $M/50,000$  solution of malachite green. The color of the dyeing on silk from a  $M/500,000$  solution is somewhat less intense than the color produced by a  $M/500,000$  solution of malachite green, the proportion in each case being  $1/10,000$  mole of compound per kilogram of silk. A  $1:5,000,000$  solution of the mercury compound will still produce a detectable stain on silk.

Aqueous and alcoholic solutions of the compound give colorless precipitates when made alkaline with ammonium hydroxide and treated with ammonium sulfide. In absence of large excess of ammonium sulfide these colorless precipitates will remain colorless at room temperature for at least twelve hours.

**Dihydroxymercuri Malachite Green Carbinol.**—A filtered solution of 10 g. of diacetoxymmercuri malachite green carbinol acetate in 95 cc. of methyl alcohol was treated with 20 cc. of 2 *N* potassium hydroxide solution in methyl alcohol, the resulting precipitate allowed to settle overnight and collected. The precipitate was rinsed with methyl alcohol, and washed thoroughly on the filter with water. It was then transferred to a bottle, covered with 500 cc. of water and the bottle mechanically rotated for three days. The product underwent a change during this treatment. While quite voluminous at first, it settled rapidly leaving a clear solution above it; but on mixing with water a portion of product gradually formed a milky suspension which did not settle on standing for days. After the digestion with water the dihydroxymercuri malachite green carbinol was collected and dried in a desiccator; yield 6.6 g., or 80%.

*Anal.* Calcd. for  $C_{23}H_{26}O_8N_2Hg_2$ : Hg, 51.47. Found: Hg, 51.28, 51.74, 51.71.

The product is a colorless, amorphous material which decomposes when heated above  $200^\circ$ , the point of most rapid decomposition varying with the rate of heating. It swells in chloroform to form a gel. It is little soluble in ether, benzene, toluene, ethyl acetate, acetone and methyl alcohol, but it becomes soluble on addition of acetic acid. It is soluble in something less than 3000 parts of water.

The aqueous solution foams powerfully when shaken, and the foam lasts a long time. If the solid is shaken with water, the saturated solution filtered by suction and the filtrate of solution and foam allowed to stand for some days in a closed cylinder, the foam gradually breaks. As it does so solid is precipitated at the surface of the solution, indicating a relatively high concentration in the foam.

The color of the aqueous solution varies with the hydrogen ion concentration. At about  $pH$  7 it is pale blue. At a little higher hydroxyl ion concentration it is colorless. Both the colored and colorless solutions stain silk, and the product is completely removed from solution by boiling with silk, so far as reactions with chlorides and sulfides indicate. When the slightly alkaline colorless solution is boiled with silk the silk is tinted, but not as deeply as when the more acid colored solution is used. But if the silk which had been boiled with the colorless

solution is rinsed with water and then warmed in dilute acetic acid it develops as strong a color as if it had been stained originally with the colored solution. Silk stained with a  $M/500,000$  solution of the carbinol containing 0.004% of acetic acid develops the same color as silk dyed in the same way with diacetoxymmercuri malachite green carbinol acetate.

When treated with chlorides the neutral solution of the dihydroxymercuri compound precipitates dichlorommercuri malachite green carbinol. This precipitate redissolves on raising the hydroxyl ion concentration, solution becoming apparent about  $pH$  9.

A  $M/10,000$  solution of dihydroxymercuri malachite green carbinol made up in water containing 0.2% of acetic acid was at first a very pale sea green color. On boiling for several minutes, or standing at room temperature for many days, the color deepened to a constant value corresponding approximately, at room temperature, to the color of a  $M/28,000$  solution of malachite green. This solution of malachite green was made from the oxalate, calculating 463 g. to the mole.

A similar solution of the mercury compound made up in 10% acetic acid developed a color corresponding to a  $M/20,000$  solution of malachite green.

When the solution was made up in  $N/1000$  benzene sulfonic acid the color was a little greener than before and much less intense, corresponding to only  $M/200,000$  malachite green.

The color of the mercurated dye solutions was deeper at the boiling point, and also immediately after cooling, than it was after standing for several hours at room temperature. Therefore, solutions which had been heated were allowed to stand overnight before making a color comparison.

A  $M/10,000$  solution of the mercury compound made up in 90 volume % of water and 10 volume % of concentrated hydrochloric acid was boiled to hydrolyze the organic mercury, treated with sodium acetate to the development of a blue color, cooled and examined after standing. Its color then corresponded to that of a  $M/11,000$  solution of malachite green. This result indicates that the dihydroxymercuri malachite green used in these tests was, within the limits of the experiment, in fact all derived from malachite green carbinol and was not contaminated by some compound which could not be converted into the dye by acid.

**Precipitation of Carbinol from Acid Solutions of Dihydroxymercuri Malachite Green Carbinol.**—A solution of 0.5 g. of dihydroxymercuri malachite green carbinol in 5 cc. of methyl alcohol and 0.3 g. of acetic acid was diluted with 15 cc. of water and boiled until there was no further increase in color. The solution, after cooling, was treated with 0.6 cc. of 4 *N* sodium chloride solution, and the precipitate collected and washed on the filter with water, and dried. The substance was blue, but not as intense a color as solid malachite green. The chlorine content corresponded more closely to that of the carbinol than of dichlorommercuri malachite green chloride.

*Anal.* (Microanalyses by Dr. Carl Tiedcke.) Calcd. for  $C_{23}H_{24}ON_2Cl_2Hg_2$ : Cl, 8.68; for  $C_{23}H_{23}N_2Cl_3Hg_2$ : Cl, 12.74. Found: Cl, 9.30, 9.32.

If the product were a mixture of the pure dichlorommercuri

malachite green chloride and dichloromercuri malachite green carbinol, the analysis would indicate 16% of dye and 84% of carbinol in the mixture.

### Summary

1. The difficulties in the mercuration of basic

triphenylmethane dyes have been confirmed and explained.

2. Organic mercury derivatives of malachite green have been prepared by two separate methods.

POINT PLEASANT, NEW JERSEY

RECEIVED SEPTEMBER 10, 1940

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

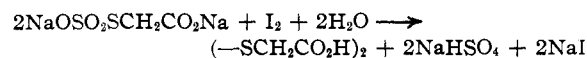
## The Use of Bunte Salts in Synthesis. II. The Preparation of Derivatives of Mercapto Aliphatic Acids

BY GEORGE G. STONER AND GREGG DOUGHERTY

Sodium thiosulfate reacts with alkyl halides to form esters of the type  $\text{RSSO}_2\text{Na}$ , called Bunte salts.<sup>1</sup> These S-alkyl thiosulfates have been used for preparing neutral mercaptans,<sup>2</sup> disulfides,<sup>3</sup> mercaptals<sup>4</sup> and mercaptols.<sup>5</sup>

This paper describes the use of Bunte salts for directly preparing dicarboxylic acids which are disulfides, mercaptals and mercaptols.

Sodium thiosulfate and sodium chloroacetate formed disodium S-carboxymethyl thiosulfate which was converted by iodine and water directly to dithiodiacetic acid.



Similarly prepared were  $\alpha, \alpha'$ - and  $\beta, \beta'$ -dithiodipropionic acids. In the latter case this method was excellent by virtue of the striking insolubility of  $\beta, \beta'$ -dithiodipropionic acid. By hydrolyzing  $\gamma, \gamma'$ -dithiodibutyronitrile,  $\gamma, \gamma'$ -dithiodibutyric acid was obtained.

Eleven dibasic acids of the thioacetal type (see Table I) were prepared directly from carbonyl compounds and halogen-substituted aliphatic acids through Bunte salts. In each case the catalyst was six equivalents of acid per mole of disodium S-carboxyalkyl thiosulfate.

### Experimental Part

**Dithiodiacetic Acid.**—Chloroacetic acid (9.5 g., 0.1 mole) was dissolved in 45 cc. of water, neutralized with anhydrous sodium carbonate and heated for one hour at 100° with a solution of 25 g. (0.1 mole) of sodium thiosulfate in 30 cc. of water. While hot, 12.7 g. (0.1 atom)

of iodine was added in small portions during a period of ten minutes while stirring. Any excess iodine was removed by passing sulfur dioxide into the cold solution momentarily. It was acidified with 3 cc. (0.05 mole) of concd. sulfuric acid and extracted with six 25-cc. portions of ether. After evaporation to dryness the residue was dissolved in 10 cc. of acetone, filtered into 100 cc. of toluene, and about 25 cc. of the solvent was distilled off. After standing at 25° for one day, 4.6 g. (50% yield) was obtained, equivalent weight calcd. 91.1, found 91.1. Recrystallization from carbon tetrachloride raised the m. p. from 102–103° to 106°.<sup>6</sup>

**$\alpha, \alpha'$ -Dithiodipropionic Acid.**—This material was prepared from 15.3 g. (0.1 mole) of racemic  $\alpha$ -bromopropionic acid in a way similar to that described above. At 5° it precipitated from the reaction solution as an oil in 57% yield (6.0 g.) in two days. After crystallization from ethanol-water and then from benzene the m. p. was 127–135°,<sup>7</sup> equivalent weight calcd. 105.1, found 106.

**$\beta, \beta'$ -Dithiodipropionic Acid.**—This compound was also similarly prepared from 10.9 g. (0.1 mole) of  $\beta$ -chloropropionic acid. It precipitated promptly when the reaction solution was cooled. After filtering, it was desiccated azeotropically by distilling considerable benzene from it to give 8.4 g. (80% yield). It was purified by dissolving it in 200 cc. of hot ethyl acetate, filtering this solution into 400 cc. of hot benzene and cooling. Within one hour 7.9 g. had crystallized, m. p. 154°,<sup>8</sup> equivalent weight calcd. 105.1, found 105.5.

**$\gamma, \gamma'$ -Dithiodibutyronitrile.**— $\gamma$ -Chlorobutyronitrile (10.4 g., 0.1 mole) was dissolved in 45 cc. of alcohol, refluxed and stirred on a steam-bath for two hours with a solution of 25 g. (0.1 mole) of sodium thiosulfate in 30 cc. of water. While hot, 12.7 g. (0.1 atom) of iodine was added and then the solution was cooled. The precipitated product was purified by refluxing in 40 cc. of alcohol with activated carbon, filtered, and reprecipitated as a colorless liquid by the addition of 200 cc. of water. After desiccation for forty hours at 1 mm. over phosphoric anhydride the yield

(1) Bunte, *Ber.*, **7**, 647 (1874).

(2) Price and Twiss, *J. Chem. Soc.*, **95**, 1727 (1909).

(3) Price and Twiss, *ibid.*, **93**, 1395, 1401, 1651 (1908); **95**, 1050, 1489, 1727 (1909); **97**, 1175 (1910); **105**, 36 (1914); *Ber.*, **41**, 4375 (1908).

(4) Westlake and Dougherty, *THIS JOURNAL*, **63**, 658 (1941).

(5) German patent 46,333, *Ber.*, **22**, 115 (1889).

(6) Biilmann, *Ann.*, **339**, 357 (1905), reported 107–108° (from ether and petroleum ether); Holmberg, *Z. anorg. Chem.*, **56**, 385 (1908), reported 108–109° (from ethyl acetate and benzene).

(7) Fredga, *Arkiv Kemi, Mineral. Geol.*, **12B**, No. 22 (1936), and **12A**, No. 13 (1937), reported 118–119° for the *meso* form and 148–149° for the racemate.

(8) Biilmann, *loc. cit.*, reported 155°.