

investigated and correlated with the oxidation of their acetyl derivatives. The phenomena observed have been found to have intimate bearing upon the benzidine and semidine rearrangements.

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[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

## THE REDUCTION OF TRIPHENYLMETHANE DYES AND RELATED SUBSTANCES WITH THE FORMATION OF FREE RADICALS

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The work of Clark and collaborators<sup>1</sup> has shown that the reduction of many different dyes by soluble reducing agents is a process analogous to the reduction of quinones in that the leuco compound and the dyestuff form a mobile oxidation-reduction system. The reduction and reoxidation occur rapidly at room temperature even in dilute solution and characteristic and significant oxidation potentials may be measured. The indigoids, many anthraquinone dyes, indophenols, indamines and methylene blue are all of this type. The reduction of azo dyes and triphenylmethane dyes is of a different sort; here, the reduction product (or products) are not rapidly reoxidized and no significant oxidation-reduction potentials can be measured by the usual methods. An examination of the behavior of the azo dyes has already been made in this Laboratory;<sup>2</sup> the present paper deals with the unraveling of the chemical reactions involved in the action of soluble reducing agents on triphenyl methane dyes; a quantitative study of certain of these reactions will be included in a later paper.

The color bases of the triphenylmethane dyes are substituted triphenylcarbinols; the dyes themselves are salts which are related to the halochromic salts of triphenylcarbinol. The exact method of formulating the structure of the colored positive ion of the triphenylmethane dyes and that of the halochromic salts has been the subject of much discussion. We shall not attempt to take sides in this controversy; the distinction between triphenylmethyl sulfate and malachite green appears to be one of degree rather than of kind as far as our work is concerned. It was shown some years ago,<sup>3</sup> that the halochromic salts of triphenylcarbinol and related substances are reduced by powerful reducing agents in appropriate solutions with the formation of the corresponding free radical (*e. g.*, triphenylmethyl). The free radical and halochromic salt form a mobile oxidation-

<sup>1</sup> W. M. Clark and co-workers, "Studies in Oxidation-Reduction," Reprints I-X Hygienic Laboratory Bulletin No. 151.

<sup>2</sup> Conant and Pratt, *THIS JOURNAL*, **48**, 2468 (1926).

<sup>3</sup> Conant, Small and Taylor, *ibid.*, **47**, 1959 (1925).

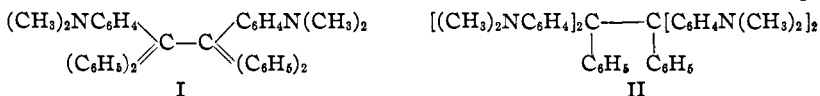
reduction system whose potential may be measured in the usual way. A similar situation would be expected in regard to the cations of the triphenylmethane dyes except that the resulting free radical would be expected to be even more unstable in acid solution than triphenylmethyl. (The sensitivity of free radicals toward acids is well known and particularly pronounced when "positive" groups like methoxyl are present in the molecule.) These expectations have been confirmed by experiment, and we may write the following general reactions in which  $R^+$  stands for the positive ion of the dye and  $M^{++}$  stands for a soluble reducing ion such as titanous, vanadous or chromous.

- (1)  $R^+ + M^{++} \rightleftharpoons R\cdot + M^{+++}$  (fast, reversible)  
           cation                                  free radical
- (2)  $2R\cdot \rightleftharpoons R-R$  (fast, reversible or irreversible depending on  
           "ethane"                                  nature of R)
- (3)  $2R\cdot + H^+ \longrightarrow RH + R^+$  (irreversible)  
           "methane"
- (4)  $2R\cdot \longrightarrow R_2$  (irreversible catalyzed by acid)  
           (Chichibabin compounds)

The factors influencing the composition of the equilibrium mixture in Reaction 1 have been outlined in a previous paper;<sup>3</sup> they include in addition to the oxidation-reduction potentials of the system  $R^+$ ,  $R$  and  $M^{++}$ ,  $M^{+++}$ , the hydrogen-ion activity and water activity of the medium, provided the reaction  $R^+ + H_2O \rightleftharpoons ROH + H^+$  is mobile. Since Reactions 3 and 4 are irreversible and since the product of Reaction 2 may be very insoluble in the medium employed, the overall reaction may go rapidly to completion even if a very small amount of product is formed in the first reaction.

We have established the validity of the foregoing account of the reduction of triphenylmethane dyes by isolating the products of Reactions 2, 3 and 4 in the case of malachite green (a typical dye) and *p*-dimethylamino-triphenylcarbinol. The latter may be regarded as a transition compound between the dyes and triphenylcarbinol. Titanous, vanadous and chromous salts were employed as reducing agents.

In order to isolate the associated free radical (the "ethane") it is necessary to take advantage of its relative insolubility in aqueous solutions of *PH* value of about 3; it is also necessary to avoid the irreversible decompositions which are brought about by strong acids (Reaction 3). *Sym.-p,p'*-tetramethyldiaminohexaphenylethane (I) and *p,p,p',p'*-octamethyltetraminohexaphenylethane (II) have been isolated as brown amorphous powders by the reduction of the corresponding chlorides in acetic acid and precipitation with water in the presence of sodium acetate. Extreme pre-

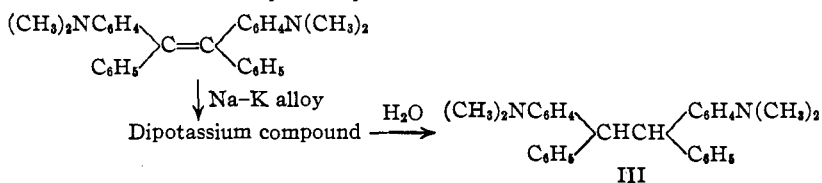




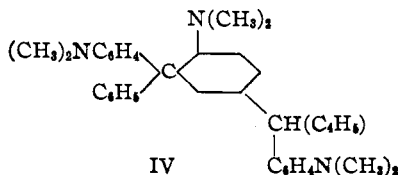
triphenylmethane, which is regarded as the leuco compound (Equations 1 and 3). The distinction between such leuco compounds and those corresponding to indigo and methylene blue is obvious; the free radical (or the corresponding ethane) should be regarded as the real leuco compound in the case of the triphenylmethane dyes. As would be expected, reducing agents such as zinc and acid reduce the ethanes to the corresponding methanes.

The action of concentrated hydrochloric acid on the free radicals appears to cause the irreversible formation of a dimer, isomeric with the dissociable ethane. Since this phenomenon is similar to the formation of *p*-benzhydryltetraphenylmethane from triphenylmethyl (a reaction first elucidated by Chichibabin), we shall designate these dimers as Chichibabin compounds. They were obtained by the use of chromous chloride in concentrated hydrochloric acid: analysis and molecular weight showed them to be isomeric with the dissociable ethanes; they are not affected by acids, oxygen or sodium-potassium alloy. Their structure has not been established, nor have they been isolated from the tarry material formed by the action of concentrated hydrochloric acid on the dissociable ethanes. Nevertheless, their mode of formation and empirical formulas show them to be dimolecular reduction products of the cations in question.

We have included in our study the mono-*p*-dimethylamino derivative of diphenylcarbinol. This substance is reduced in acetone solution containing hydrochloric acid by chromous chloride. The products are two isomeric dimers; the lower-melting and more soluble substance has been shown to be *p,p'*-tetramethyldiaminotetraphenylethane by its synthesis from the well-known ethylene by the reactions

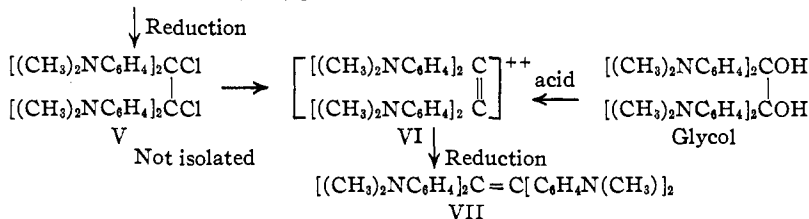


The constitution of the higher-melting isomer has not been established; presumably it is a Chichibabin compound such as represented by formula IV, though it might be a diastereoisomeride of III. The formation of both isomers probably proceeds through the formation of the same free radical.



In this case the normal association produces a tetraphenyl compound, and the reaction is therefore *irreversible* like the Chichibabin reaction.

The action of vanadous chloride or chromous chloride on the keto chloride of Michler's ketone (*p,p'*-tetramethyldiaminodiphenyl ketone) is similar to the reduction of the salts of the diphenylcarbinols. The keto chloride which is bright blue is undoubtedly a compound in which one chlorine is in the ionic condition and the cation has a structure similar to that of the triphenylmethane dyes (in regard to which there are many opinions.) On reduction one would expect to obtain the corresponding dichloroethane (V); the actual product, however, is the corresponding ethylene (VII). The steps involved in reaction appear to involve the initial formation of the dichloride V and its ionization to the corresponding salt.<sup>5</sup> This salt on reduction gives the ethylene, as we proved in a separate experiment



starting with the corresponding glycol. The mobility of the system VI-VII will be investigated by electrochemical methods.

Finally it may be noted that aryl-alkyl-carbinols may also undergo dimolecular reduction in acid solution with chromous chloride. Thus, *p*-dimethylaminophenylisopropylcarbinol is reduced to two isomeric dimers. Presumably one of these is *p,p'*-tetramethyldiaminodiisopropyl-ethane and the other a Chichibabin hydrocarbon. However, their structure has not been elucidated.

### Experimental

**Preliminary Experiments on Reductions of *p*-Dimethylaminotriphenylcarbinol.**—Six-tenths of a gram of *p*-dimethylaminotriphenylcarbinol was dissolved in the chosen solvent in a small flask directly joined to a larger one. In the larger chamber were placed 15 cc. of bromobenzene, 15 g. of crushed ice and 50 cc. of an aqueous solution containing 5.0 g. of sodium acetate and sodium hydroxide in quantity not quite equivalent to the acid in the reducing mixture. The system was swept with nitrogen, and the reducing agent was added through a stopcock in the neck of the smaller chamber. When the reduction was complete, judging from the disappearance of the halochromic color, the reduction mixture was allowed to run into the larger chamber; the apparatus was shaken vigorously until all of the bromobenzene was drawn from the bottom stopcock into a graduated test-tube filled with freshly distilled water; the organic layer displaced the water and did not come in contact with the air. It was found impossible to drain off all of the bromobenzene without including some of the aqueous layer; hence two-thirds of it was used, and the remainder allowed for in the calculation of the theoretical absorption.

<sup>5</sup> Cf. Madelung, *Ber.*, **60**, 2469 (1927); Wizinger, *ibid.*, **60**, 1377 (1927).

Experiment showed that the "blank" absorption, as well as the errors due to deviations from the standard temperature and pressure, were within the limit of experimental error. These factors were accordingly overlooked.

The results of the preliminary reductions are tabulated:

Solvent	Time, min.	Temp., °C.	Absorption, cc.	Per cent. of absorption
15 cc. acetic acid	2	20	13.2	89
15 cc. acetic acid	10	20	11.2	75
15 cc. acetic acid	30	20	12.4	83
15 cc. acetic acid	120	20	9.3	62.5
15 cc. hydrochloric acid	2	30*	0	0
10 cc. acetone, 5 cc. hydrochloric acid	3	30*	0	0
20 cc. acetic acid, 5 cc. hydrochloric acid	3	0-5	4.2	28
20 cc. acetic acid, 5 cc. hydrochloric acid	6	0-5	4.2	28

\* The heat of neutralization raised the temperature of the precipitating mixture to 30°.

*Sym.-p,p'-tetramethyldiaminohexaphenylethane*.—Three grams of *p*-di-methylaminotriphenylcarbinol was dissolved in 45 cc. of glacial acetic acid in the large chamber of the reduction apparatus. The system was evacuated and filled with nitrogen; then, against a stream of nitrogen, 20 cc. of 1 *N* chromous chloride or vanadous chloride was pipetted into the smaller chamber. The system was stoppered and swept again with nitrogen; then the two reagents were mixed by tilting the apparatus. The deep red color of the carbinol salt disappeared in about thirty seconds, the apparatus being meanwhile shaken vigorously. Nitrogen was then forced into the system, and the mixture was allowed to flow from the bottom stopcock into a freshly boiled and chilled solution of 10 g. of sodium acetate in 800 cc. of water. On dilution, a flesh-colored amorphous precipitate of *sym.-p,p'*-tetramethyldiaminohexaphenylethane appeared. The suspension was stirred for a few seconds, and was then filtered by suction as rapidly as possible. The filter cake was washed rapidly, first with water and then dilute ammonia; it was transferred as rapidly as possible to a drying pistol. More than a few moments' exposure of the precipitate to the air caused the formation of a bright red crust of oxidized product to appear on its surface. Calcium chloride was used as the drying agent; the pistol was evacuated, filled with nitrogen and re-evacuated. About thirty-six hours were necessary to dry the precipitate thoroughly.

The dried product was a fluffy flesh-colored powder, colored bright red on its surface by a crust of oxidized material. On even momentary exposure to air it decomposed instantly to a deep red tar, evolving heat and an odor of formaldehyde. The oxygen absorption of the dried amorphous powder when dissolved in bromobenzene was 70-85% of the theoretical amount. Manipulations of the solid were in carbon dioxide. The apparent molecular weight of this material was determined in *p*-chlorotoluene (freezing point) and found to be 458-507 as compared with 572.5 for the ethane.

The attempts to crystallize the free radical were unsuccessful. The crude product was found to be readily soluble in ether and benzene. When alcohol was added to an ethereal solution of the compound, the solution became deep red in color. A red solid crystallized from this mixture; it was not the pure ethane, however, since its oxygen capacity was only half of the theoretical amount. The free radical was insoluble in petroleum ether and could be precipitated in an amorphous state when this solvent was added to an ethereal solution, but no crystalline product could be obtained. The ethane could not be crystallized from a mixture of acetone and water. When an ethereal solution of the ethane was evaporated to dryness *in vacuo*, the product was a brittle froth which filled the entire system.

**Decomposition of the Ethane in Acid Solutions.**—Small weighed bulb tubes with constricted necks were swept with carbon dioxide, stoppered and weighed. The stoppers were tied to the tubes to prevent mixing. The weighed tubes were transferred in an atmosphere of carbon dioxide and charged with 0.15–0.20 g. samples of the ethane. They were stoppered and reweighed. A small separatory funnel with a side tube just below the stopcock was fastened in the mouth of a bulb tube with a rubber stopper; the tube was at once evacuated and filled with nitrogen through the side tube. Five cubic centimeters of the chosen solvent was next drawn into the tube under a slightly diminished pressure. The bulb tube was sealed off at the constriction; just before the tube was closed off, the excess pressure in the bulb was relieved through the side arm of the separatory funnel. Bulbs so prepared were kept for varying lengths of time, and were then broken in the absorption apparatus. The amount of free radical left unattacked was calculated from the volume of oxygen absorbed. This method is not sufficiently accurate to warrant the assignment of quantitative significance to the results; it merely indicates the relative rates of decomposition in acids of varying strength.

IN GLACIAL ACETIC ACID

Temperature 18°; pressure, 761 mm.

Ethane, g.	Time, minutes	Absorption, cc.	Absorption, %
0.29	0	7.6	63.5
.24	35	5.7	57
.47	120	4.3	22

DECOMPOSITION IN ONE MOLAR PYRIDINE IN GLACIAL ACETIC ACID

Temperature, 20°; pressure, 761 mm.

0.29	0	7.6	62
.23	30	5.7	59
.21	90	4.9	55
.23	360	3.6	37

*p*-Dimethylaminotriphenylmethyl Peroxide.—When an ethereal solution of *sym.-p,p'*-tetramethyldiaminohexaphenylethane was exposed to the air, its color decreased momentarily, and then gradually turned to a deep red. The fine light brown crystals which appeared on the sides of the container were filtered off and washed with acetone. They were insoluble in all the ordinary low-boiling solvents, and decomposed to a red tar when heated in high-boiling solvents. The crude crystals melted with decomposition at 145–150°, dependent on the rate of heating of the melting point bath. The peroxide dissolved in concentrated hydrochloric acid; the solution, at first light red, rapidly turned deep red, at the same time developing a strong odor of phenol.

*Anal.* Calcd. for  $C_{42}H_{46}O_2N_2$ : C, 83.4; H, 6.7. Found: C, 82.2; H, 6.6.

Sodium *p*-Dimethylaminotriphenylmethide.—Two and one-half grams of *sym.-p,p'*-tetramethyldiaminohexaphenylethane was prepared by the usual procedure. The dry product was transferred in an atmosphere of carbon dioxide to a 100-cc. flask which was then closed with a rubber stopper bearing a straight glass stopcock. The container was swept with nitrogen; then 40 cc. of anhydrous ether and 15 cc. of 1% sodium amalgam was introduced through the stopcock. The flask was shaken by hand. After about one minute the color of the solution faded momentarily; then the bright orange-red color of the sodium salt appeared, and grew rapidly in intensity. The solution was shaken on a machine for four hours, at the end of which time the concentration of the sodium salt had reached its maximum. The solution was now deep orange-red; little or none of the solid methide could be seen in the mixture. If the shaking was con-

tinued overnight, the color of the solution disappeared. The resulting colorless ethereal solution, filtered from the amalgam and evaporated, yielded two crystalline products; these were separated by crystallization from a concentrated ethereal solution. The product which remained in solution was identified by a mixed melting point as *p*-dimethylaminotriphenylmethane. The product crystallizing from ethereal solution was a white solid melting at 138°; it was not identified.

***p*-Dimethylaminotriphenylacetic Acid.**—Carbon dioxide was admitted to the flask containing the methide; decomposition took place rapidly. The ethereal layer was decanted from the amalgam, and the latter was washed several times with ether. The combined ethereal layers were extracted several times with dilute sodium hydroxide; the combined aqueous layers were extracted once with ether. The aqueous solution of the sodium salt was boiled for a few minutes to expel the ether; it was then cooled and made exactly neutral with dilute hydrochloric acid, methyl orange being used as the indicator. A thick amorphous precipitate of *p*-dimethylaminotriphenylacetic acid separated. The precipitate was filtered, washed and dried *in vacuo* over calcium chloride. The crude product weighed 0.64 g., 29% of the theoretical amount. All attempts to crystallize this acid were unsuccessful.

**Combining Weight with Sodium Hydroxide.**—0.1850 g. of the acid neutralized 4.92 cc. of 0.1013 *N* sodium hydroxide; 0.2004 g. neutralized 5.30 cc. of 0.1013 *N* sodium hydroxide. Mol. wt. calcd. for  $C_{27}H_{21}O_2N$ : 331. Found: 371, 373.

**Methyl *p*-Dimethylaminotriphenylacetate.**—A solution of about 0.18 g. of diazomethane in 25 cc. of anhydrous ether was prepared. To this was added a solution of 0.46 g. of *p*-dimethylaminotriphenylacetic acid in 15 cc. of absolute methyl alcohol. The solution was allowed to stand for forty-five minutes; then 15 cc. of weakly acidulated water was added to destroy the excess diazomethane. The layers were washed with water, dried with sodium sulfate and concentrated to a volume of 4–5 cc. on a steam-bath. The addition of petroleum ether precipitated the ester in crystalline form. The yield was 0.31 g.; the product, after a second crystallization from the same solvents, melted at 141°.

*Anal.* Calcd. for  $C_{23}H_{23}O_2N$ : C, 80.0; H, 6.7. Found: C, 79.9, 80.0; H, 6.7, 7.0.

**Molecular Weight, Micro Method.**—Sample, 0.0134; camphor, 0.1219; average depression, 13.2. Calcd. for  $C_{23}H_{23}O_2N$ : 345. Found: 330.

**“Chichibabin Product” from Dimethylaminotriphenylcarbinol.**—A solution of 4.5 g. of *p*-dimethylaminotriphenylcarbinol in 90 cc. of acetone and 45 cc. of concentrated hydrochloric acid was treated in the absence of air with 25 cc. of 1 *N* chromous chloride. The solution was allowed to stand at room temperature for twenty-four hours; it was then poured into twice its volume of water and almost neutralized with sodium hydroxide. The mixture, still warm from the neutralization, was extracted several times with benzene. The united benzene layers were washed with water, dried with sodium sulfate and diluted with *n*-butyl alcohol. The benzene was driven off on a steam-bath. Two and six-tenths grams of the crude product separated after a few days' standing. The product, after two more crystallizations from the same solvent, weighed 1.5 g. and melted at 165°. This product dissolved in hydrochloric acid without coloration.

*Anal.* Calcd. for  $C_{42}H_{40}N_2$ : C, 88.1; H, 7.0. Found: C, 88.1; H, 6.8.

**Molecular Weight, Micro Method.**—Sample, 0.0132; camphor, 0.1109; average depression, 9.1°. Calcd. for  $C_{42}H_{40}N_2$ : 572.5. Found: 525.

**The Long-Period Reduction of *p*-Dimethylaminotriphenylcarbinol with Chromous Chloride and Titanous Chloride.**—Ten cubic centimeters of 1 *N* chromous chloride was added to a solution of 1.5 g. of *p*-dimethylaminotriphenylcarbinol in 30 cc. of acetic acid. The solution was allowed to stand for ninety-six hours and was then poured into 400 cc. of 10% sodium acetate solution. A white amorphous precipitate separated. The mixture



was extracted with chloroform; the united chloroform layers were dried over sodium sulfate and concentrated. The solution was diluted with isopropyl alcohol and cooled; 0.5 g. of a white crystalline solid separated which was identified by a mixed melting point as *p*-dimethylaminotriphenylmethane.

One-half gram of *p*-dimethylaminotriphenylcarbinol and 3 g. of sodium acetate were dissolved in 18 cc. of acetic acid. To this solution 5 cc. of 20% titanous chloride was added in the absence of air. The reaction mixture was allowed to stand for forty-eight hours; it was then poured into 250 cc. of 10% sodium tartrate. The resulting suspension was filtered with suction, dried and recrystallized from benzene-isopropyl alcohol. The crystalline product weighed 0.25 g., 50% of the theoretical amount, and melted at 134°. A sample of the product did not depress the melting point of a sample of *p*-dimethylaminotriphenylmethane.

**The Reaction of *p,p'*-Tetramethyldiaminohexaphenylethane with Acetic Acid.**—One and seven-tenths grams of *sym.-p,p'*-tetramethyldiaminohexaphenylethane was dissolved in the absence of air in 50 cc. of glacial acetic acid. Solution took place rather slowly, and the solution acquired a deep red color. The solution was allowed to stand for forty-eight hours; it was then poured into 400 cc. of water. A light red precipitate came out; this precipitate was filtered out at once. Crystallization from chloroform-alcohol yielded 0.4 g. of *p*-dimethylaminotriphenylmethane; the product was identified by a mixed melting point.

**The Reaction of *Sym.-p,p'*-Tetramethyldiaminohexaphenylethane with Titanous Chloride.**—One and seven-tenths grams of *sym.-p,p'*-tetramethyldiaminohexaphenylethane and 5 g. of sodium acetate were placed in a 50-cc. Erlenmeyer flask. The flask was closed with a one-holed rubber stopper bearing a straight glass stopcock. The flask was swept with nitrogen and evacuated; then 40 cc. of 80% acetic acid and 10 cc. of titanous chloride were drawn into it through the stopcock. The flask was again swept with nitrogen, and was allowed to stand for forty-eight hours. At the end of this time the solution was poured into 300 cc. of 5% sodium tartrate; the resulting suspension was thoroughly extracted with chloroform. The washed and dried chloroform extracts were concentrated and diluted with isopropyl alcohol; on cooling, 1.2 g. of *p*-dimethylaminotriphenylmethane crystallized. The product was identified by means of a mixed melting point.

***Sym.-p,p',p'',p'''*-Octamethyltetraminohexaphenylethane.**—Two grams of commercial malachite green and 2.0 g. of fused sodium acetate were dissolved in a mixture of 20 cc. of glacial acetic acid and 20 cc. of water. The solution was filtered into the larger chamber of the reduction flask. The system was swept with pure nitrogen; then 20 cc. of 1 *N* vanadous chloride was pipetted into the smaller chamber against a counter current of nitrogen. The apparatus was again swept with nitrogen; then it was tilted and the two solutions were allowed to mix. The reduction was very rapid. As soon as the deep green color of the solution had disappeared, the lower end of the bottom stopcock was immersed in 200 cc. of freshly boiled and cooled water in which 10 g. of sodium acetate had been dissolved. Nitrogen was blown into the reduction flask, and the reduced solution was forced out of the flask into the sodium acetate solution. The reduction product came out as a light brown amorphous precipitate. The solution was stirred briskly for a few seconds; the precipitate on the surface began to turn green at once. The precipitate was filtered by suction, and washed on the filter with water and very dilute ammonium hydroxide. The moist filter cake, the surface of which was already a bright green, was transferred to a small box made of folded filter paper. The box and its contents were placed directly upon the surface of a layer of calcium chloride in a vacuum desiccator; this was at once evacuated, filled with pure nitrogen and again evacuated to the lowest pressure obtainable. The amorphous free radical was suf-

ficiently dry for ordinary use within twenty-four hours. The procedure outlined above must be followed closely if satisfactory results are to be obtained. Otherwise the product is a brittle black crust, with which very little work can be done.

If the reaction is successful, *sym.-p*-octamethyltetraminohexaphenylethane is obtained as a fluffy amorphous powder, light brown in its interior and bright green on its surface. All manipulations with the radical had to be performed in an atmosphere of carbon dioxide. Exposed to the air, the compound instantly decomposed to a black tar with the evolution of heat and a strong odor of formaldehyde.

**Oxygen Absorptions.**—In these experiments, the solid ethane was dissolved directly in the chosen solvent. The oxidation product formed a tarry coating over the undissolved ethane; the solubility and the rate of solution of this tar determined the apparent oxygen capacity of the ethane in a given solvent. The first three typical absorptions given below show the varying capacity of the same sample of ethane in different solvents.

Ethane	Solvent	Absorption, cc. (22.5°, 761 mm.)	Per cent. absorption
0.16	Bromobenzene	2.0	34
.27	Aniline	5.1	52
.30	Acetic acid	7.5	68
.10	Acetic acid	2.7	73

**Decomposition of the Ethane in Acetic Acid.**—The same procedure was followed here as in the decomposition of *sym.-p,p'*-tetramethyldiaminohexaphenylethane.

Ethane	Time, minutes	Absorption in cc. (22.5°, 761 mm.)	Per cent. absorption
0.10	3	2.2	60
.10	10	2.7	73
.30	45	2.0	18

A sample of the same ethane absorbed no oxygen whatsoever after ten minutes' solution in a mixture of equal parts of acetic acid and hydrochloric acid.

**"Chichibabin Product" from Malachite Green.**—Five grams of malachite green, dissolved in 100 cc. of concentrated hydrochloric acid, was reduced in an atmosphere of nitrogen with 25 cc. of 1 *N* chromous chloride. The reaction mixture was allowed to stand for five hours; it was then poured slowly, with constant stirring, into 1000 cc. of water in which 100 g. of sodium acetate was dissolved. The thick white amorphous precipitate which came out was filtered with suction, washed on the filter with water and dried *in vacuo*. The crude product weighed 3.7 g., 84% of the theoretical amount. It was crystallized from boiling *n*-butyl alcohol. The product weighed 2.6 g. and melted at 231–232°. Further crystallizations did not change this melting point.

The freshly prepared rearrangement product was a white crystalline solid, soluble without coloration in concentrated hydrochloric acid. On standing, the surface of the solid slowly turned green.

*Anal.* Calcd. for  $C_{48}H_{50}N_4$ : C, 83.8; H, 7.6. Found: C, 83.5; H, 7.4.

**Molecular Weight, Micro Method.**—Sample, 0.0150: camphor, 0.1353; average depression, 7.0°. Calcd. for  $C_{48}H_{50}N_4$ : 658.6. Found: 634.

**The Reaction of *Sym.-p,p',p'',p'''*-Octamethyltetraminohexaphenylethane with Sodium Amalgam.**—Two grams of *sym.-p,p',p'',p'''*-octamethyltetraminohexaphenylethane was placed in a 100-cc. round-bottomed flask corked with a rubber stopper fitted with a straight glass stopcock. The flask was swept with nitrogen and partially evacuated; 40 cc. of anhydrous ether and 15 cc. of 1% sodium amalgam were then drawn into the flask. The flask was again swept with nitrogen, and was then shaken vigorously by hand. The color of the solution, originally light red, faded at once; in two minutes

there was a momentary increase of color, which faded at once. A second similar run was made; when the transient color had reached its maximum, carbon dioxide was admitted to the flask. A small volume of gas was absorbed, but no acid could be isolated from the reaction mixture. Benzene was used as the solvent in a third similar run; the results were no more satisfactory. The ethereal solution of the decomposition products was separated from the excess amalgam, filtered and concentrated; the concentrate was diluted with ethyl alcohol. A gray-white crystalline product, melting at 93–95°, was isolated; a mixture of this product with *p,p'*-tetramethyldiaminotriphenylmethane<sup>6</sup> melted at 96–97°. The product was apparently an impure sample of the leuco base of malachite green.

**Long-Period Reduction of Malachite Green with Vanadous Chloride.**—Two grams of malachite green and 2.0 g. of sodium acetate were dissolved in 20 cc. of acetic acid and 20 cc. of water. To this solution 10 cc. of 1 *N* vanadous chloride was added in the absence of air. The solution was allowed to stand for forty-eight hours; at the end of this time it was poured into 300 cc. of 5% sodium acetate solution. A copious light green precipitate appeared. The mixture was thoroughly extracted with chloroform; the united chloroform layers were washed, dried and concentrated. On dilution with ethyl alcohol, 1.1 g. of white crystals separated; after drying, the product melted at 93–94°. A mixture of these crystals and a known sample of *p,p'*-tetramethyldiaminotriphenylmethane melted at 95–96°.

**The Reduction of Malachite Green with Titanous Chloride.**—An experiment was carried out under conditions identical with those used in the preparation of *sym.-p-p',p'',p'''*-octamethyltetraminohexaphenylethane. One-half gram of malachite green was reduced with 15 cc. of 20% titanous chloride solution buffered with sodium acetate. The deep color of the malachite green disappeared at once. The solution was allowed to stand for three minutes, and was then diluted with 300 cc. of 5% sodium acetate solution. The precipitate of the free radical was filtered with suction. The filter paper and precipitate were placed in a bottle containing an upright test-tube filled with bromobenzene; this bottle was connected with an absorption buret. When equilibrium was established, the bromobenzene was allowed to flow onto the precipitate, and the absorption of gas was noted. The free radical representing 0.5 g. of the color salt absorbed 8.0 cc. at 21° and 752 mm.; this was 51% of the calculated absorption.

One-half gram of malachite green, dissolved in 45 cc. of water, was reduced in the absence of air with 10 cc. of 20% titanous chloride buffered with sodium acetate. The reduced solution was allowed to stand for forty-eight hours; it was then poured into an excess of alkaline sodium tartrate. The resulting suspension was thoroughly extracted with chloroform. The united chloroform layers were washed, dried and concentrated; on dilution with isopropyl alcohol 0.5 g. of a white crystalline solid came out. This was identified by a mixed melting point as *p,p'*-tetramethyldiaminotriphenylmethane.

Seven-tenths gram of malachite green was dissolved in 45 cc. of boiling water. To the boiling solution 10 cc. of 20% titanous chloride was added. Decolorization took place at once, and an amorphous sandy red precipitate appeared in the solution. The mixture was thoroughly extracted with chloroform; the united chloroform layers, washed and dried, were concentrated and diluted with isopropyl alcohol. White crystals appeared in the solution; when isolated, they weighed 0.35 g., and melted at 93°. After one recrystallization their melting point was 95–96°. The product did not depress the melting point of a known sample of *p,p'*-tetramethyldiaminotriphenylmethane.

**The Reaction of *Sym.-p,-p',-p'',-p'''*-Octamethyltetraminohexaphenylethane with Titanous Chloride.**—A solution of 1.7 g. of *sym.-p,-p',-p'',-p'''*-octamethyltetraminohexaphenylethane and 5 g. of sodium acetate in 50 cc. of 80% acetic acid was treated in

<sup>6</sup> Doebner, *Ann.*, **217**, 255 (1883).

the absence of air with 10 cc. of 20% titanous chloride. The solution was allowed to stand for forty-eight hours; it was then diluted with sodium acetate solution and worked up in the usual manner. Five-tenths gram of *p,p'*-tetramethyldiaminotriphenylmethane was isolated; this represented 34% of the free radical. The remainder of the product was represented by a dark green tar from which no crystalline products could be isolated.

***p,p'*-Tetramethyldiaminotetraphenylethane.** (a) **By Reduction of Carbinol.**—One gram of *p*-dimethylaminodiphenylcarbinol was dissolved in 10 cc. of acetone; 5 cc. of concentrated hydrochloric acid was added, followed by 10 cc. of 1 *N* chromous chloride. This mixture was allowed to stand in the absence of air for three hours. The reduction commenced at once, and the originally blue solution was deep green in fifteen minutes' time. When the reaction was complete, the reaction mixture was poured into 150 cc. of water; 20% aqueous sodium hydroxide was added until a precipitate of chromic hydroxide appeared. While still warm from the heat of neutralization, the mixture was thoroughly extracted with warm benzene. The united benzene extracts were washed with warm water, dried over sodium sulfate and concentrated by distillation to a volume of 8–10 cc. This solution was cooled and allowed to stand until crystallization of the high-melting isomer (m. p. 264–267°) was complete. The filtrate was concentrated to about 5 cc. and diluted with 10 cc. of boiling ethyl alcohol. On cooling, the low-melting isomer crystallized. The crude product was suspended in benzene at room temperature for five minutes; the suspension was filtered off and added to the major portion of the high-melting isomer. The low-melting isomer was brought out of the benzene solution by concentration and dilution with hot alcohol. After several such separations the product melted at 206–207°. The yields usually obtained were from 1 g.: 0.3–0.4 g. of low-melting isomer and about 0.2 g. of the other. The ratio of the two products was independent of the time of reduction. The reduction could also be carried out in glacial acetic acid 1.5 *N* in perchloric acid. The same procedure was followed as is outlined above; the two products appeared in the same ratio.

(b) **By the Action of Sodium–Potassium Alloy upon *Sym.-p,p'*-Tetramethyldiaminotetraphenylethylene.**—Three grams of *sym.-p,p'*-tetramethyldiaminotetraphenylethylene was suspended in a mixture of 15 cc. of anhydrous ether and 15 cc. of anhydrous benzene. This mixture was shaken in the absence of air for forty-eight hours with 3 cc. of sodium–potassium alloy. A greenish-blue color formed at once, which in the course of an hour's time gave place to a bright red coloration. The bright red potassium derivative was decomposed by the introduction of moist benzene. The contents of the flask were allowed to settle, and this crystalline residue was taken up with ordinary ether and treated with small amounts of ethyl alcohol until the alloy was decomposed. The benzene solution was washed thoroughly with water, dried over sodium sulfate and concentrated by distillation. Ethyl alcohol was added to the boiling concentrated solution; on cooling, 0.5 g. of a white crystalline solid came out. This, on recrystallization from benzene–alcohol, yielded 0.3 g. of a product which melted at 205–206°; a mixed melting point of this product and that prepared by reduction of *p*-dimethylaminodiphenylcarbinol with chromous chloride melted at 206–207°.

*Anal.* Calcd. for  $C_{30}H_{32}N_2$ : C, 85.7; H, 7.7. Found: C, 85.7; H, 7.7.

**Molecular Weight, Cryoscopic, in Benzene.**—Solvent, 9.91; samples, after preliminary seeding, 0.1403, 0.0965; depressions, 0.176°, 0.110°. Calcd. for  $C_{30}H_{32}N_2$ : 420. Found: 411, 426.

**Analysis of High-Melting Isomer of *Sym.-p,p'*-Tetramethyldiaminotetraphenylethane.**—(The melting point was 264–267°, with decomposition.) *Anal.* Calcd. for  $C_{30}H_{32}N_2$ : C, 85.7; H, 7.6. Found: C, 85.5; H, 7.6.

**Molecular Weight, Cryoscopic, in Ethylene Dibromide.**—Solvent, 23.54 g. sample,

after preliminary seeding, 0.1518. A second sample did not wholly dissolve. Depression, 0.1795°. Calcd. for  $C_{30}H_{22}N_2$ : 420. Found: 424.

**Molecular Weight, Micro Method.**—Sample, 0.0139; camphor, 0.1020; depression, 13.9°. Found: 392.

**Preparation of *p,p'*-Tetramethyldiaminobenzophenone Dichloride.**—Five grams of Michler's ketone was dissolved in 150 cc. of anhydrous benzene. This solution was warmed to 30°; to the warm solution was added 3.5 g. of thionyl chloride. The solution turned an opaque blue and a dark oil separated at once. A slight evolution of sulfur dioxide was observed. The mixture was allowed to stand for a half-hour; during this time the oil crystallized on the bottom and sides of the flask. At the end of a half-hour the crystalline crust on the bottom of the flask was crushed with a stirring rod and the resultant suspension was filtered with suction. The crystalline cake was washed on the filter with benzene and then dried by a short exposure to the air. The yield was almost quantitative. The crude product was a bronze-green crystalline powder, the surface of which rapidly turned deep blue on exposure to the air. The product was used without further purification.

**Reduction of the Dichloride in Acetone-Hydrochloric Acid.**—*p,p'*-Tetramethyldiaminobenzophenone dichloride from 2.7 g. of Michler's ketone was dried for a short time, and then suspended in a mixture of 55 cc. of acetone and 5 cc. of concentrated hydrochloric acid. The deep blue solution thus formed was treated with 35 cc. of 1*N* vanadous chloride; the deep blue color of the dichloride disappeared at once. The reaction mixture was allowed to stand for two hours. At the end of this time the reaction mixture was diluted to 500 cc. with water, almost neutralized with aqueous sodium hydroxide, and thoroughly extracted with chloroform. The combined chloroform layers were washed with water, dried over sodium sulfate and concentrated. The boiling concentrated solution was diluted with boiling ethyl alcohol and again concentrated until crystals began to appear. The solution was cooled and filtered; the product weighed 1.25 g., representing 60% of the original ketone, and melted at 296°. The product did not depress the melting point of a known sample of *sym.-p*-octamethyltetramethyltetraminotetraphenylethylene prepared by the reduction of Michler's ketone with tin and hydrochloric acid.<sup>7</sup> The use of vanadous chloride and an acetic acid solution of the dichloride as well as chromous chloride in hydrochloric acid-acetone solution also yielded the ethylene.

**Reduction of Octamethyltetraminotetraphenylethylene Glycol with Chromous Chloride.**—One-half gram of the glycol was dissolved in 35 cc. of concentrated hydrochloric acid in a 50-cc. Erlenmeyer flask. Four cubic centimeters of 1 *N* chromous chloride was added against a stream of carbon dioxide; the salt color disappeared immediately leaving a light green solution which grew deeper with the passage of time. The reaction was allowed to proceed for fourteen hours; then the reaction mixture was diluted. To the resulting solution was added 5.0 g. of sodium acetate; the solution was then almost neutralized with aqueous sodium hydroxide. A yellow amorphous precipitate came out of the solution during the neutralization. The mixture was extracted with chloroform; the united chloroform layers were washed with dilute sodium hydroxide, then with water and were dried over sodium sulfate. The dry filtered solution was concentrated and diluted with boiling ethyl alcohol; on cooling, 0.2 g. of *sym.-p,p'*-tetramethyldiaminotetraphenylethylene crystallized out of the solution. The product was identified by a mixed melting point. Another reduction was carried out under similar conditions, but was worked up after four hours' standing. Although the mother liquors were yellow, no crystalline ethylene could be isolated. A reduction using vanadous chloride was carried out under conditions identical with those described above,

<sup>7</sup> Fischl, *Monatsh.*, **35**, 525 (1914).

except that 5 cc. of 1 *N* vanadous chloride was used as the reducing agent. The product weighed 0.2 g.; it melted at 218–221°.

**Reduction of *p*-Dimethylaminophenylisopropylcarbinol.**—In a 25-cc. Erlenmeyer flask, 0.8 g. of *p*-dimethylaminophenylisopropylcarbinol<sup>18</sup> was dissolved in 15 cc. of concentrated hydrochloric acid. A vigorous stream of carbon dioxide was blown through the flask to sweep out the air; then 10 cc. of 0.75 *N* chromous chloride was added. The flask was again swept with carbon dioxide; it was then allowed to stand, tightly stoppered, for ten hours. The solution, originally blue, had a distinct greenish cast at the end of a half-hour; in about two hours, needle-shaped crystals of a double salt began to come out. When the reaction was complete, the crystals of the double salt were filtered off; these, after being washed with a little cold hydrochloric acid, were dried and reserved for the preparation of the high-melting isomer. The filtrate was diluted to four times its original volume, and was neutralized with dilute sodium hydroxide until a precipitate of chromic hydroxide appeared. While still warm from the neutralization, the mixture was extracted with warm benzene. The united benzene layers were washed with warm water, dried over sodium sulfate and concentrated. On cooling, a small amount of the high-melting isomer came out which was filtered from the mother liquors. The filtrate was heated to boiling and diluted with twice its volume of boiling ethyl alcohol. On cooling, 0.3 g. of the lower-melting isomer appeared in crystalline form. This product melted at 174°; further recrystallizations did not affect the melting point.

*Anal.* (low-melting isomer). Calcd. for  $C_{24}H_{30}N_2$ : C, 81.75; H, 10.3. Found: C, 81.35; H, 10.3.

**Molecular Weight Cryoscopic, in Ethylene Dibromide.**—Solvent, 19.75 g.; samples, after preliminary seeding, 0.1192, 0.1386. Depressions, 0.213°, 0.231°. Calcd. for  $C_{24}H_{30}N_2$ : 352. Found: 338, 350.

One-gram samples of *p*-dimethylaminophenylisopropylcarbinol were reduced with chromous chloride according to the method outlined above; for various times the yields were: after one hour, 20% low-melting isomer, no high-melting isomer; after four hours, equal amounts (20%) of both isomers; after twenty-four hours, 27% low melting, 38% high melting.

**Preparation of High-Melting Isomer.**—The double salt mentioned in the preparation of the low-melting isomer was dissolved in hot water, and the solution made strongly alkaline with ammonia. A voluminous white precipitate came out. The suspension was heated for an hour on a steam-bath, cooled and filtered with suction. After drying overnight *in vacuo* the crude product from 1.67 g. of double salt weighed 1.0 g. The product after crystallization from boiling benzene weighed 0.67 g. and melted at 239–240°.

*Anal.* Calcd. for  $C_{24}H_{30}N_2$ : C, 81.75; H, 10.3. Found: C, 80.7; H, 10.1.

**Molecular Weight, Micro Method.**—Sample, 0.0172; camphor, 0.1513; depression, 13.4°. Calcd. for  $C_{24}H_{30}H_2$ : 352. Found: 335.

Both isomers were unaffected by shaking with sodium-potassium alloy and by the action of concentrated hydrochloric acid.

### Summary

1. The action of soluble reducing agents, such as vanadous chloride, on solutions of triphenylmethane dyes has been investigated using malachite green as an example, and *p*-dimethylaminotriphenylcarbinol as a transition compound between the dyes and triphenylcarbinol. The first

<sup>18</sup> Sachs and Weigert, *Ber.*, 40, 4365 (1907).

product of the reaction is a free radical which may be isolated in the associated form (derivative of hexaphenylethane); it shows the typical behavior of these compounds. Under the influence of acids the free radical may further undergo rearrangement or reduction and oxidation to the corresponding methane and carbinol.

2. Michler's ketone dichloride and octamethyltetraminotetraphenylethylene glycol are both reduced by soluble reducing agents to octamethyltetraminotetraphenylethylene.

3. Dimethylaminodiphenylcarbinol and dimethylaminophenylisopropylcarbinol are each reduced by powerful soluble reducing agents with the formation of a pair of isomeric dimers.

CAMBRIDGE, MASSACHUSETTS

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

## THE REACTION OF ORGANIC HALIDES WITH PIPERIDINE. I. ALKYL BROMIDES

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The reaction between a secondary amine and an organic halide is a common and useful method of preparation of tertiary amines. The reaction, as it is ordinarily carried out, is between two moles of the secondary amine and one mole of the halide with the formation of one mole of the tertiary amine and one mole of the secondary amine hydrohalide



In a previous communication from this Laboratory<sup>1</sup> it was pointed out that certain halogen compounds did not follow the above reaction course with 3-methylpiperidine, but that the products obtained from the reaction were one mole of the secondary amine hydrohalide and one mole of unchanged secondary amine. No tertiary amine was isolated. Presumably, hydrogen halide had split out of the halogen compound with the formation of an unsaturated compound, thus



There are scattered references<sup>2</sup> in the literature to the loss of a molecule of halogen acid from certain halides when they are treated with various organic bases, but apparently no effort has been made to study the reaction from this point of view.

It seemed desirable, therefore, to follow the rate and course of the reaction

<sup>1</sup> Thayer and McElvain, *THIS JOURNAL*, 50, 3350 (1928).

<sup>2</sup> Cf. Houben-Weyl, "Die Methoden der organischen Chemie," Vol. IV, 1924, p. 243; Menschutkin, *Z. physik. Chem.*, 5, 589 (1890); Wallach, *Ann.*, 230, 233 (1885); Nef, *ibid.*, 309, 164 (1899).