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A study of the Grignard reaction in the preparation of triphenyl methane dyes

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A Study of the Grignard Reaction in the Preparation of Triphenyl Methane Dyes

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A STUDY OF
THE GRIGNARD REACTION IN THE
PREPARATION OF
TRIPHENYL METHANE DYES

Malcolm F. Dull

Thesis submitted for
the degree of
Master of Science

MASSACHUSETTS AGRICULTURAL COLLEGE
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INTRODUCTION

The Grignard reaction is one of the most widely adaptable methods of synthesis known in the field of organic chemistry; a field which owes both its origin and its rapid growth to the study and development of synthetic methods. Observed by Barbier in 1899 (1), investigated and applied to a wider range of usage by Grignard (2), whose name it now bears, it has since been studied by a large number of investigators until at the present time its aid may be employed in the preparation of a wide variety of compounds of different types. Among these may be mentioned hydrocarbons, both saturated and unsaturated, halogen compounds, primary, secondary, and tertiary alcohols, glycols, phenols, thiophenols, selenophenols, ethers, aldehydes, ketones, acids, nitriles, nitrogen compounds such as amides, amines, anilides, hydrazine derivatives, hydroxyl amine derivatives, and diazoamino compounds. (3) Remembering something of the extremely large number of compounds of each of these classes, the importance of the reaction as a method of synthesis may readily be understood.

A brief consideration of the manner in which the reaction proceeds in a few of the above cases will be necessary to illustrate its extreme flexibility.

The preparation of the saturated hydrocarbons may be illustrated by means of methane. Metallic magnesium in the form of a powder, turnings
r o~~f~~ ribbon, reacts with an ethereal solution of methyl iodide, bromide or chloride, to form methyl magnesium halide (CH_3MgX). Upon treatment with water, this compound is hydrolyzed to methane and magnesium hydroxy halide.

This synthesis of a simple hydrocarbon may be represented by the following equations:

$$\underset{\text{Methyl halide}}{CH_3 - X} + Mg \dashrightarrow \underset{\text{Methyl magnesium halide}}{CH_3 - Mg - X}$$

$$CH_3 - (Mg - X + HO) - H \dashrightarrow \underset{\text{Methane}}{CH_4} + \underset{\text{Magnesium hydroxy halide}}{HO - Mg - X}$$

This reaction must be carried out with anhydrous reagents, as the presence of water would hydrolyze the methyl magnesium halide immediately, and thus it would no longer be available for a reaction with other substances. Too much moisture would even prevent the initial reaction from taking place.

Magnesium reacts with an ethereal solution of an aryl halide with equal ease. In this manner benzene may be prepared by a reaction exactly analogous to that by which methane was prepared.

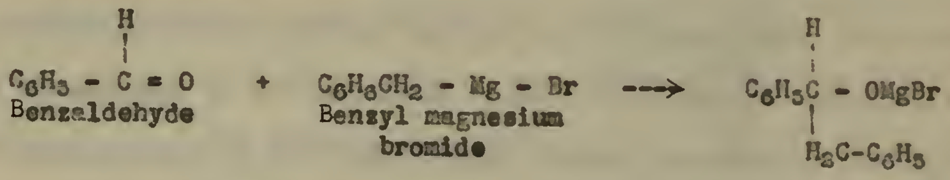
$$\underset{\text{Phenyl halide}}{C_6H_5X} + Mg \dashrightarrow \underset{\text{Phenyl magnesium halide}}{C_6H_5 - Mg - X}$$

$$C_6H_5 - (Mg - X + HO) - H \dashrightarrow \underset{\text{Benzene}}{C_6H_6} + \underset{\text{Magnesium hydroxy halide}}{HO - Mg - X}$$

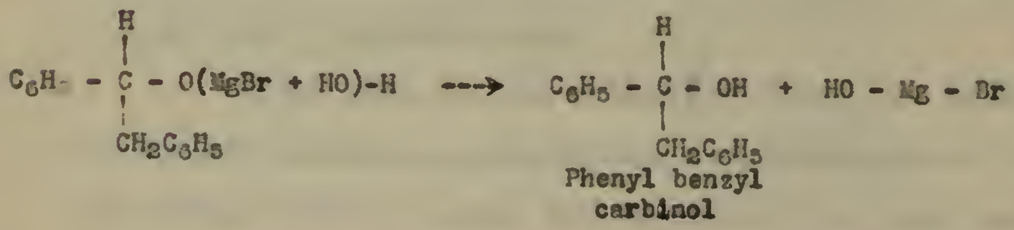
If now it is desired to prepare a slightly more complex compound, say an unsaturated hydrocarbon, one might do so by allowing the initial product of the above reaction, phenyl magnesium halide, to react with 1-bromo 2-propene ($BrCH_2CH = CH_2$) in the following manner:

$$\underset{\text{1-Bromo 2-propene}}{CH_2 = CHCH_2} - (Br + \underset{\text{Phenyl magnesium halide}}{X - Mg) - C_6H_5} \dashrightarrow \underset{\text{1-Phenyl 2-propene}}{CH_2 = CHCH_2C_6H_5} + \underset{\text{Magnesium bromo halide}}{Br - Mg - X}$$

The usual procedure, however, is to allow the magnesium addition product, termed the Grignard reagent, to react with a carbonyl oxygen. In the preparation of symmetrical diphenyl ethylene, another unsaturated hydrocarbon, the reaction is between benzyl magnesium bromide and benzaldehyde, as follows:

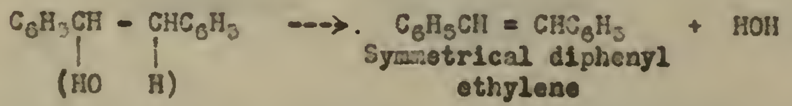


$$\underset{\text{Benzaldehyde}}{C_6H_5-\overset{H}{\overset{|}{C}}=O} + \underset{\text{Benzyl magnesium bromide}}{C_6H_5CH_2-Mg-Br} \longrightarrow C_6H_5\overset{H}{\overset{|}{C}}\underset{\underset{H_2C-C_6H_5}{|}}{}-OMgBr$$



$$C_6H_5-\underset{\underset{CH_2C_6H_5}{|}}{\overset{H}{\overset{|}{C}}}-O(MgBr + HO)-H \longrightarrow \underset{\text{Phenyl benzyl carbinol}}{C_6H_5-\underset{\underset{CH_2C_6H_5}{|}}{\overset{H}{\overset{|}{C}}}-OH} + HO-Mg-Br$$

Phenyl benzyl carbinol then loses water, and the unsaturated compound results.

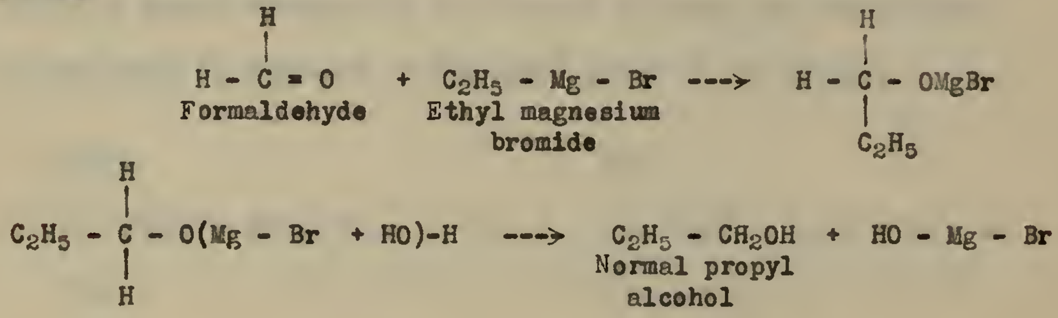


$$\underset{(HO}{\underset{|}{C_6H_5CH}}-\underset{H)}{\underset{|}{CHC_6H_5}} \longrightarrow. \underset{\text{Symmetrical diphenyl ethylene}}{C_6H_5CH=CHC_6H_5} + HOH$$

It is this peculiar behavior of the Grignard reagent toward a carbonyl oxygen which results in such a variety of products when one or more such oxygens are present in the reacting substance. This is not, however, the case in the synthesis of hydrocarbons for, as just explained, these result from the direct hydrolysis of the Grignard reagent itself, or from the reaction of the Grignard reagent with another alkyl halide.

In the reaction between the Grignard reagent and a compound containing a carbonyl group, one of the double bonds between the oxygen and the carbon of this group is broken. The bond thus liberated on the carbon atom combines with the hydrocarbon residue of the Grignard reagent, while the bond liberated on the oxygen atom is satisfied by the magnesium halide part of the reagent. The latter group is then split off by the action of water or dilute acids, the metallo-halide group being replaced by a hydrogen atom. This may be illustrated by the reactions by which alcohols are prepared, it being kept in mind that the Grignard reagent is always prepared by the reaction between metallic magnesium and an alkyl or aryl halide in a solution of anhydrous ether.

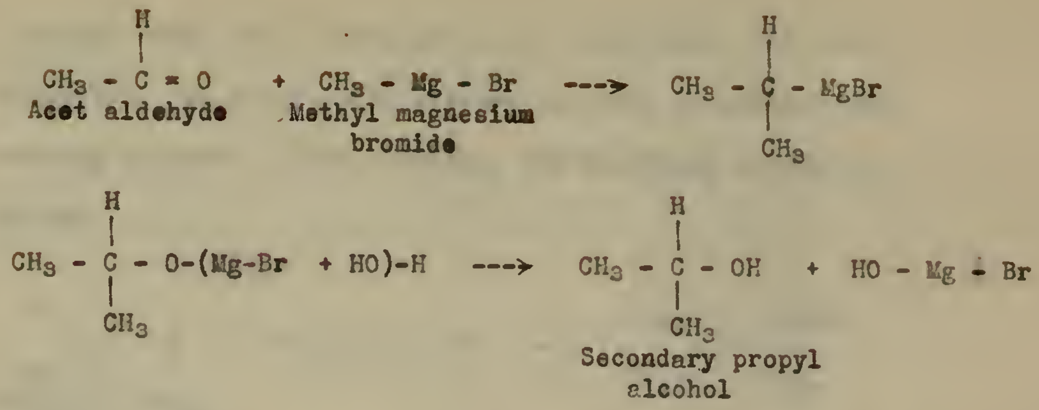
Of the three classes, primary, secondary, and tertiary, the primary alcohols are prepared only from formaldehyde as in the preparation of propyl alcohol from formaldehyde and ethyl magnesium halide.



$$\underset{\text{Formaldehyde}}{H-\overset{\overset{\displaystyle H}{|}}{C}=O} + \underset{\text{Ethyl magnesium bromide}}{C_2H_5-Mg-Br} \dashrightarrow H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle C_2H_5}{|}}{C}}-OMgBr$$

$$C_2H_5-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-O(Mg-Br + HO)-H \dashrightarrow \underset{\text{Normal propyl alcohol}}{C_2H_5-CH_2OH} + HO-Mg-Br$$

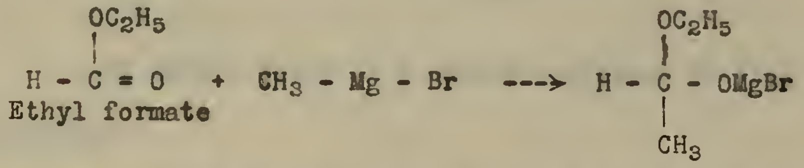
Secondary alcohols may be prepared either from aldehydes other than formaldehyde, or from esters of formic acid. In the case of the aldehydes, the reaction proceeds in a manner exactly analogous to that of formaldehyde.



$$\underset{\text{Acet aldehyde}}{CH_3-\overset{H}{\overset{|}{C}}=O} + \underset{\text{Methyl magnesium bromide}}{CH_3-Mg-Br} \longrightarrow CH_3-\underset{\underset{CH_3}{|}}{\overset{H}{\overset{|}{C}}}-MgBr$$

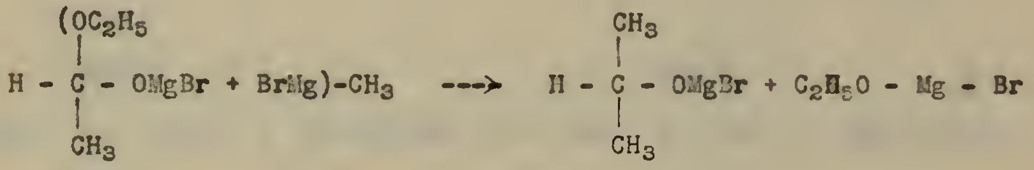
$$CH_3-\underset{\underset{CH_3}{|}}{\overset{H}{\overset{|}{C}}}-O\text{-}(Mg\text{-}Br + HO)\text{-}H \longrightarrow \underset{\text{Secondary propyl alcohol}}{CH_3-\underset{\underset{CH_3}{|}}{\overset{H}{\overset{|}{C}}}-OH} + HO-Mg-Br$$

With esters of formic acid, as also with esters of other acids, the reaction proceeds somewhat differently. With one molecule of the Grignard reagent the usual reaction takes place.



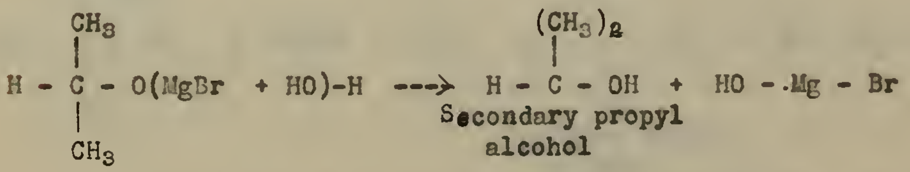
$$\underset{\text{Ethyl formate}}{H-\overset{OC_2H_5}{\overset{|}{C}}=O} + CH_3-Mg-Br \longrightarrow H-\underset{\underset{CH_3}{|}}{\overset{OC_2H_5}{\overset{|}{C}}}-OMgBr$$

But if a second molecule of the reagent be used, the alkoxy group of the ester is replaced by the alkyl group of the reagent.



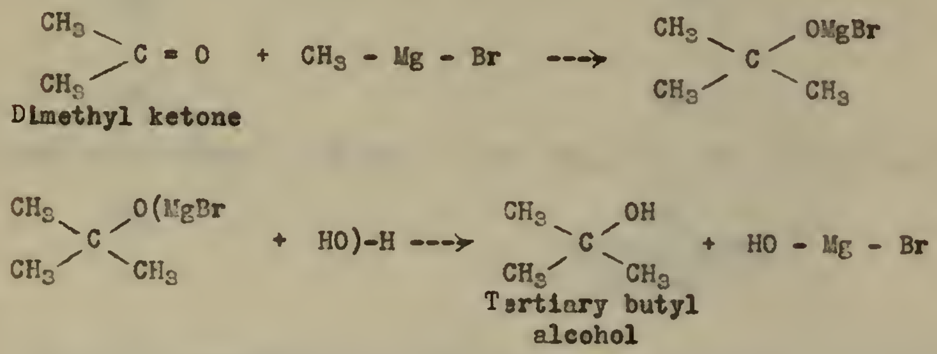
$$H-\underset{\underset{CH_3}{|}}{\overset{(OC_2H_5}{\overset{|}{C}}}-OMgBr + BrMg)\text{-}CH_3 \longrightarrow H-\underset{\underset{CH_3}{|}}{\overset{CH_3}{\overset{|}{C}}}-OMgBr + C_2H_5O-Mg-Br$$

This product then hydrolyses in the usual manner to form the alcohol.

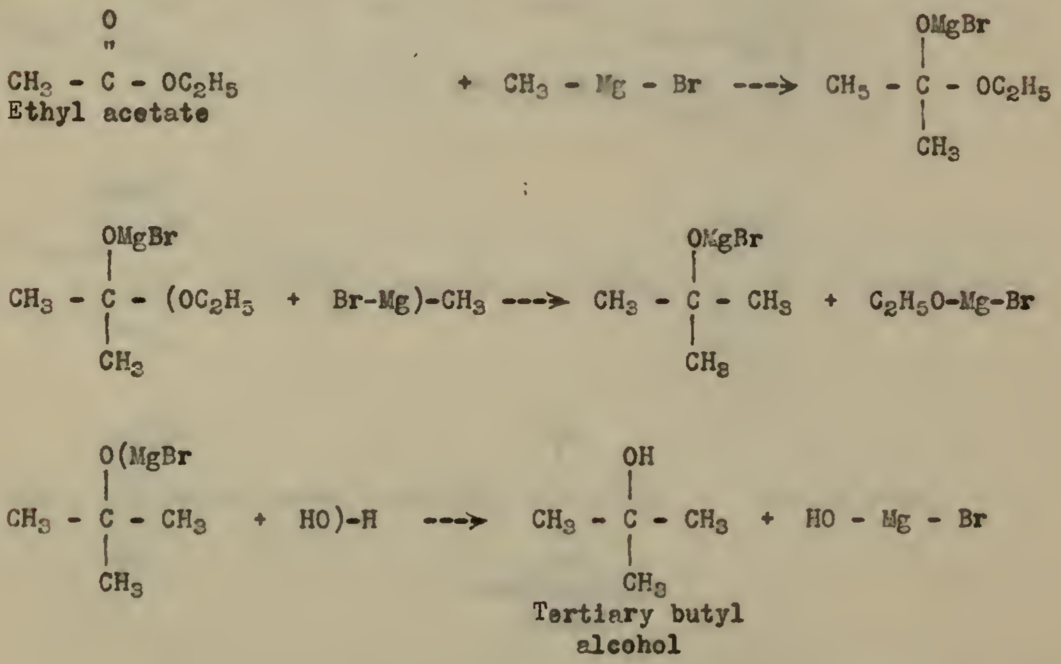


$$H-\underset{\underset{CH_3}{|}}{\overset{CH_3}{\overset{|}{C}}}-O(MgBr + HO)\text{-}H \longrightarrow \underset{\text{Secondary propyl alcohol}}{H-\overset{(CH_3)_2}{\overset{|}{C}}-OH} + HO-Mg-Br$$

There are four chief classes of substances which may be used in synthesizing the tertiary alcohols; namely, ketones, esters, of acids other than formic acid, acid chlorides, and acid anhydrides. Of these four, ketones and acid esters are most commonly employed. With a ketone, the reactions proceed as follows:



Acid esters react in a manner analogous to that of formic esters.

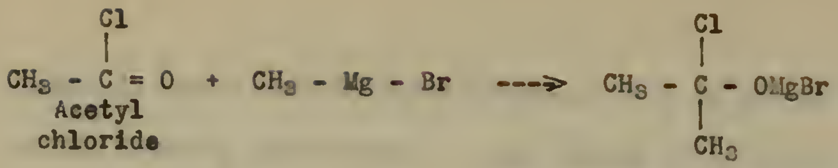


$$CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5 + CH_3-Mg-Br \longrightarrow CH_5-\underset{CH_3}{\overset{OMgBr}{C}}-OC_2H_5$$

$$CH_3-\underset{CH_3}{\overset{OMgBr}{C}}-(OC_2H_5 + Br\text{-}Mg)\text{-}CH_3 \longrightarrow CH_3-\underset{CH_3}{\overset{OMgBr}{C}}-CH_3 + C_2H_5O\text{-}Mg\text{-}Br$$

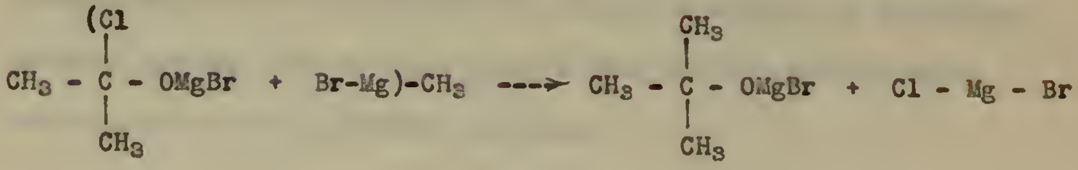
$$CH_3-\underset{CH_3}{\overset{O(MgBr}{C}}-CH_3 + HO)\text{-}H \longrightarrow CH_3-\underset{CH_3}{\overset{OH}{C}}-CH_3 + HO-Mg-Br$$

An analogous reaction occurs with acid chlorides.

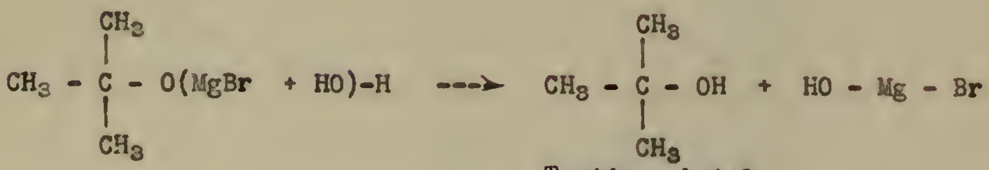


$$CH_3-\overset{\overset{Cl}{|}}{C}=O + CH_3-Mg-Br \dashrightarrow CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{Cl}{|}}{C}}-OMgBr$$

Acetyl chloride



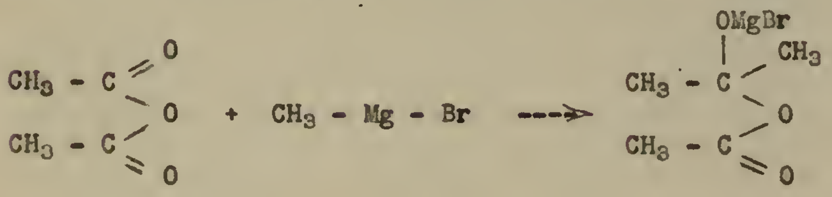
$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{(Cl}{|}}{C}}-OMgBr + Br\text{-}Mg)\text{-}CH_3 \dashrightarrow CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OMgBr + Cl-Mg-Br$$

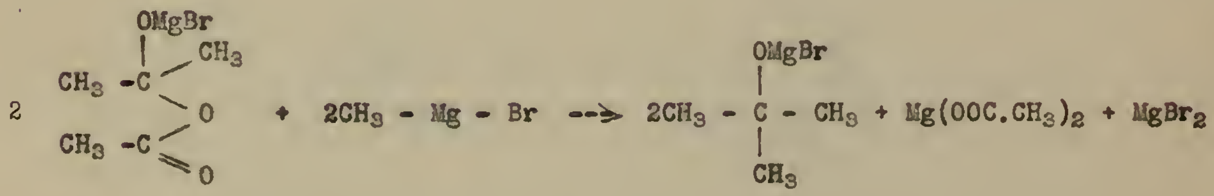


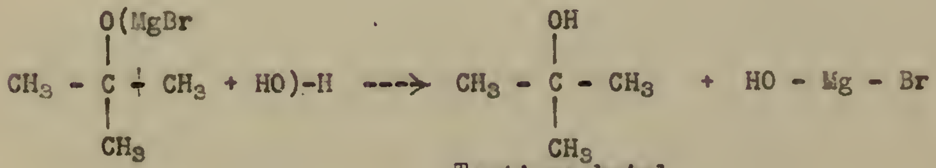
$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-O(MgBr + HO)\text{-}H \dashrightarrow CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH + HO-Mg-Br$$

Tertiary butyl alcohol

When acid anhydrides are used, there is a somewhat similar reaction.







$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{O(MgBr}{|}}{C}}\div CH_3 + HO)\text{-}H \dashrightarrow CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3 + HO-Mg-Br$$

Tertiary butyl alcohol

In all of these reactions which have been written, the alkyl group may be replaced by aryl groups without affecting in any way the manner in which the reactions proceed. Thus by proper selection of the reacting substances, a large number of compounds may be synthesized, and it is through its ability to maintain a consistent behavior through all of these changes that the Grignard reaction has assumed such an important position.

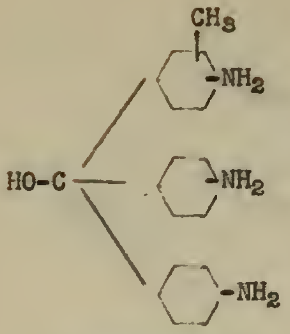
THEORETICAL DISCUSSION

Among the various classes of dyes, there is one group, the members of which are related in constitution to triphenyl methane, $H{-}C\begin{smallmatrix}\diagup C_6H_5\\ - C_6H_5\\ \diagdown C_6H_5\end{smallmatrix}$, and which are, therefore, known as triphenyl methane dyes. In the manufacture of these dyes, the actual tri-substituted methane is usually prepared by a characteristic reaction. This methane substitution product is known as the leuco base, and is a colorless material whose relation to the actual dyestuffs is that of a simple reduction product. The dye is obtained by oxidizing the remaining methane hydrogen to an hydroxyl group, thus transforming the triphenyl methane derivative, strictly speaking, into a derivative of triphenyl carbinol, $HO{-}C\begin{smallmatrix}\diagup C_6H_5\\ - C_6H_5\\ \diagdown C_6H_6\end{smallmatrix}$. This general procedure may be illustrated by the following reaction in which triphenyl methane is oxidized to triphenyl carbinol.

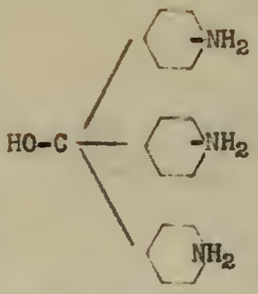
$$H - C\begin{matrix}\diagup C_6H_5\\ - C_6H_8\\ \diagdown C_3H_5\end{matrix} + O \dashrightarrow HO - C\begin{matrix}\diagup C_6H_5\\ - C_6H_5\\ \diagdown C_6H_5\end{matrix}$$

Triphenyl methane   Triphenyl carbinol

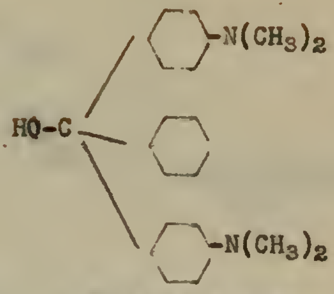
The triphenyl methane dyes may, in turn, be divided into several smaller groups known as the rosaniline, para-rosaniline, malachite green, rosolic acid, and phthalein dyes.(4) Of these five groups, the rosaniline para-rosaniline, and malachite green dyes are amino derivatives of tripheyl methane, and may be illustrated by the following examples:



Rosaniline

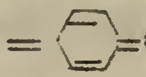


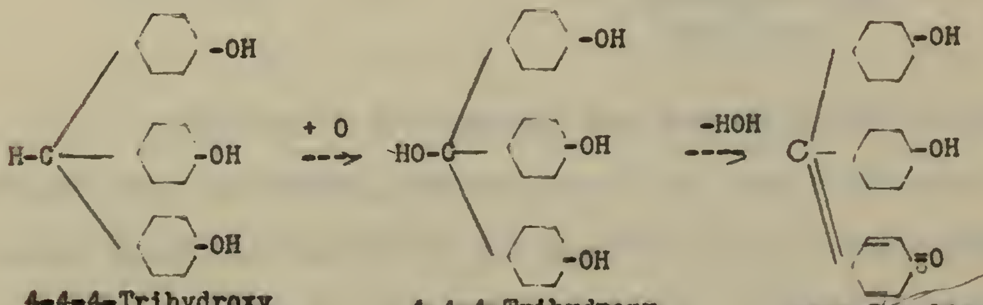
para-Rosaniline



Malachite green

These dyes exhibit the characteristic reactions of amino compounds; forming salts with acids. It is as these salts, known as dye salts, that the dyes are actually used.

The rosalic acid and phthalein dyes, on the other hand, are hydroxy derivatives of triphenyl methane, which upon oxidation of the leuco base, lose water within the molecule; the rosalic acid dyes forming a quinoid group,  and the phthalein dyes forming a lactone inner anhydride, thus

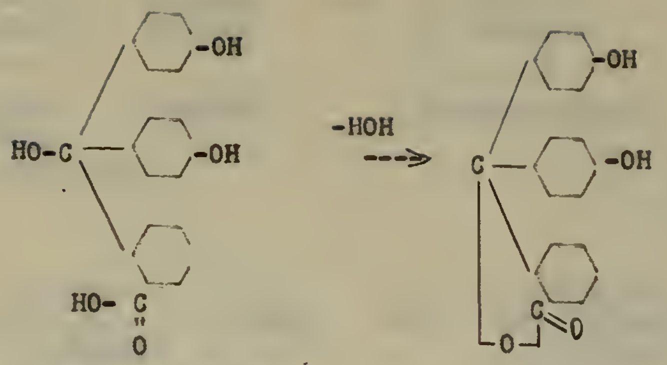


4-4-4-Trihydroxy triphenyl methane (Leuco base)

4-4-4-Trihydroxy triphenyl carbinol

para-Rosolic acid
Dye

lc



Carbinol base
2-Carboxy 4-4-dihydroxy
triphenyl carbinol

Phenolphthalein
dye

These dyes find their chief use as indicators. The rosalic acid dyes are usually prepared from the corresponding rosaniline dye by diazotization and decomposition with water.

$$H\text{-}C\left\langle\begin{matrix}C_6H_4\text{-}NH_2\\C_6H_4\text{-}NH_2\\C_6H_4\text{-}NH_2\end{matrix}\right. + 3NaNO_2 + 6HCl \dashrightarrow H\text{-}C\left\langle\begin{matrix}C_6H_4\text{-}N_2\text{-}Cl\\C_6H_4\text{-}N_2\text{-}Cl\\C_6H_4\text{-}N_2\text{-}Cl\end{matrix}\right. + 3NaCl + 6HOH$$

para-Rosaniline

Diazonium compound

$$H\text{-}C\left\langle\begin{matrix}C_6H_4\text{-}N_2\text{-}(Cl\\C_6H_4\text{-}N_2\text{-}(Cl\\C_6H_4\text{-}N_2\text{-}(Cl\end{matrix}\right. + 3H)\text{-}OH \dashrightarrow H\text{-}C\left\langle\begin{matrix}C_6H_4\text{-}OH\\C_6H_4\text{-}OH\\C_6H_4\text{-}OH\end{matrix}\right. + 3N_2 + 3HCl$$

para-Rosolic acid
Leuco base

In the case of the phthalein dyes they may be synthesized directly from the triphenyl methane derivative. This is nitrated, reduced to an amino derivative, and then treated in a manner similar to that just described for the rosolic acid dye. In this way phenolphthalein may be synthesized from phthalophenone. Phthalophenone itself, being first prepared from phthalyl chloride and benzene.

Phthalyl chloride (Unsymmetrical)

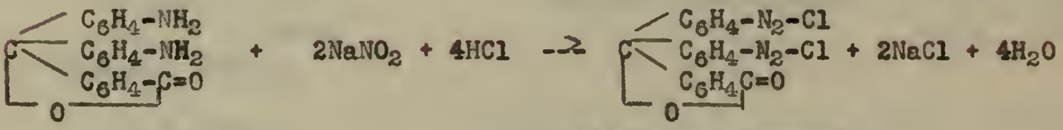
Benzene

Phthalophenone

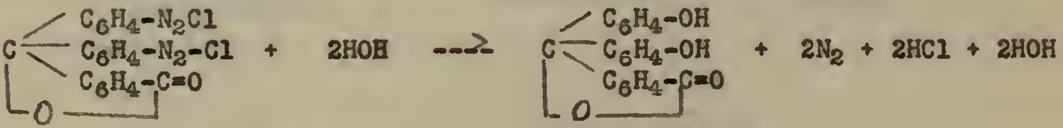
Phthalophenone

4-4-Dinitro phthalophenone

4-4-Di-amino phthalophenone

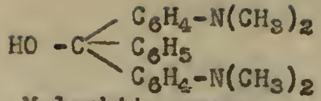


Diazonium compound



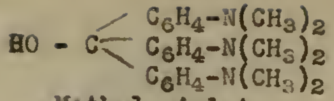
Phenolphthalein

The triphenyl methane group contains a large number of compounds, of the type previously described, which are both interesting and important as dyes and indicators. As we have shown, triphenyl carbinol is easily prepared, by the Grignard reaction, from several different substances and, therefore, it was decided to attempt to prepare a number of the dyes in this manner. Chief among those whose constitution seemed to indicate the possibility of formation by means of a Grignard reaction were the following:(5)



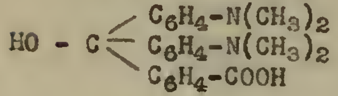
$$HO-C\begin{array}{l}\diagup C_6H_4-N(CH_3)_2\\ -C_6H_5\\ \diagdown C_6H_4-N(CH_3)_2\end{array}$$

Malachite green



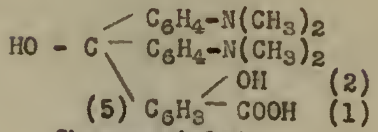
$$HO-C\begin{array}{l}\diagup C_6H_4-N(CH_3)_2\\ -C_6H_4-N(CH_3)_2\\ \diagdown C_6H_4-N(CH_3)_2\end{array}$$

Methyl violet



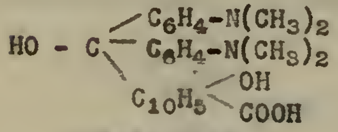
$$HO-C\begin{array}{l}\diagup C_6H_4-N(CH_3)_2\\ -C_6H_4-N(CH_3)_2\\ \diagdown C_6H_4-COOH\end{array}$$

Chrome green



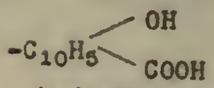
$$HO-C\begin{array}{l}\diagup C_6H_4-N(CH_3)_2\\ -C_6H_4-N(CH_3)_2\\ \diagdown (5)\ C_6H_3\begin{array}{l}\diagup OH\quad (2)\\ \diagdown COOH\quad (1)\end{array}\end{array}$$

Chrome violet



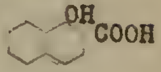
$$HO-C\begin{array}{l}\diagup C_6H_4-N(CH_3)_2\\ -C_6H_4-N(CH_3)_2\\ \diagdown C_{10}H_5\begin{array}{l}\diagup OH\\ \diagdown COOH\end{array}\end{array}$$

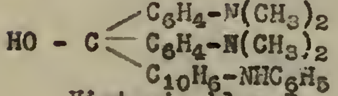
Chrome blue



$$-C_{10}H_5\begin{array}{l}\diagup OH\\ \diagdown COOH\end{array}$$

is the radical of hydroxy naphthoic acid

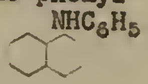


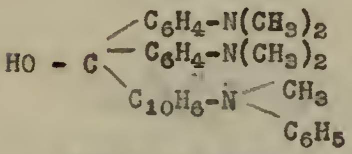


$$HO-C\begin{array}{l}\diagup C_6H_4-N(CH_3)_2\\ -C_6H_4-N(CH_3)_2\\ \diagdown C_{10}H_6-NHC_6H_5\end{array}$$

Victoria blue B

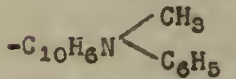
$-C_{10}H_6-NHC_6H_5$ being the phenyl naphthyl amine group.





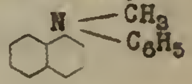
$$HO-C\begin{array}{l}\diagup C_6H_4-N(CH_3)_2\\ -C_6H_4-N(CH_3)_2\\ \diagdown C_{10}H_6-N\begin{array}{l}\diagup CH_3\\ \diagdown C_6H_5\end{array}\end{array}$$

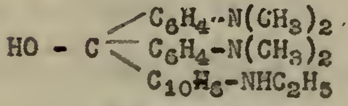
Victoria blue 4R



$$-C_{10}H_6N\begin{array}{l}\diagup CH_3\\ \diagdown C_6H_5\end{array}$$

being the methyl phenyl-naphthyl amine group.

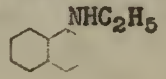


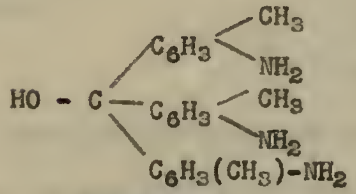


$$HO-C\begin{array}{l}\diagup C_6H_4-N(CH_3)_2\\ -C_6H_4-N(CH_3)_2\\ \diagdown C_{10}H_6-NHC_2H_5\end{array}$$

Victoria blue R

$-C_{10}H_6-NHC_2H_5$ being the ethyl naphthyl amine group.



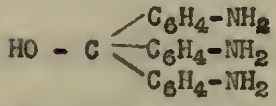


$$HO-C\begin{array}{l}\diagup C_6H_3\begin{array}{l}\diagup CH_3\\ \diagdown NH_2\end{array}\\ -C_6H_3\begin{array}{l}\diagup CH_3\\ \diagdown NH_2\end{array}\\ \diagdown C_6H_3(CH_3)-NH_2\end{array}$$

New Magenta

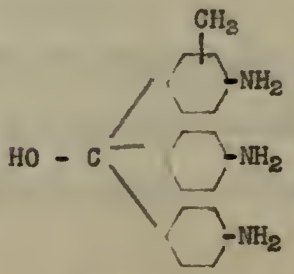
$$HO-C\begin{array}{l}\diagup C_6H_4-NHC_6H_5\\ -C_6H_4-NHC_6H_5\\ \diagdown C_6H_4-NHC_6H_5\end{array}$$

Rosaniline blue

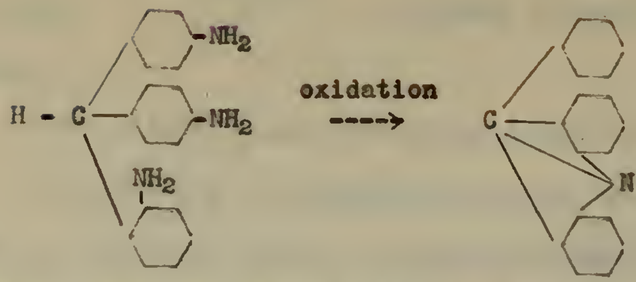


$$HO-C\begin{array}{l}\diagup C_6H_4-NH_2\\ -C_6H_4-NH_2\\ \diagdown C_6H_4-NH_2\end{array}$$

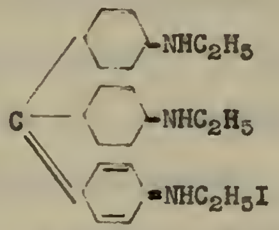
Para-rosaniline



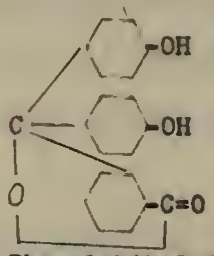
Rosaniline



4-4-2-Tri-amino tri-phenyl methane   Chrysaniline

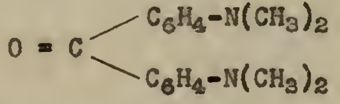


Hofmann's violet



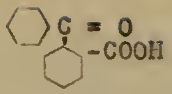
Phenolphthalein

It will be seen that the first eight of these dyes; malachite green, methyl violet, chrome green, chrome violet, chrome blue, Victoria blue B, Victoria Blue 4R, and Victoria blue R, each contain two dimethyl aniline groups. Hence it was assumed that the easiest method of preparing these substances would be to introduce the third group into Michler's ketone,



$$O = C \begin{cases} C_6H_4\text{-}N(CH_3)_2 \\ C_6H_4\text{-}N(CH_3)_2 \end{cases}$$

(4-4-tetra-methyl di-amino benzephone)

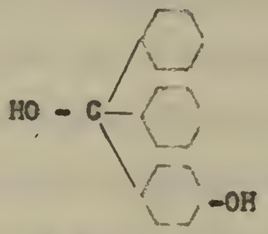
by means of the Grignard reaction. New magenta, rosaniline, para-rosaniline, rosaniline blue, the 4-4-2-tri-amino tri-phenyl methane, shown above, and Hofmann's violet would, it was assumed, be prepared by means of the Grignard reaction, by introducing one of the groups into a ketone containing the other two groups. It was thought that phenolphthalein, on the other hand might be prepared by means of the Grignard reaction, through phthalophenone which should result from the reaction of ortho-benzoyl benzoic acid  and phenyl magnesium bromide, C_6H_5-Mg-Br.

It was with these views in mind that this study was undertaken. The purpose of the investigation may, then, be stated as follows: To determine whether the Grignard reaction can be used as a method for the preparation of the important dye compounds listed on the two preceeding pages. As the time involved in carrying through one of these syntheses is considerable, it was possible to study only five of them, viz., malachite green, methyl violet, chrome green, chrome violet, and phthalophenone.

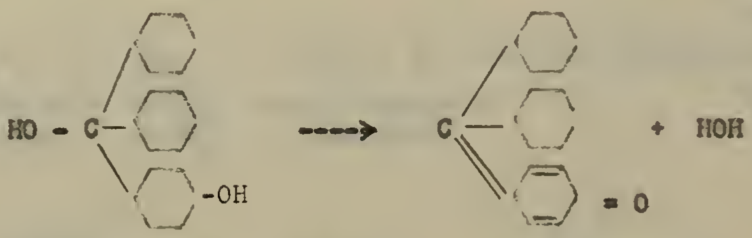
The results, as given in the Experimental Part (pages 20 - 58) satisfactorily establish the successful application of the method in three cases. In one other case the evidence is less satisfactory, and in the remaining case no supporting evidence was obtained.

REVIEW OF LITERATURE

While the literature with reference to the Grignard reaction as a method of synthesis is voluminoue, there is not a great deal which concerns its application to the preparation of dyestuffs. The first of such references appeared in 1903, and was the result of some investigations of Baeyer and Villiger in Germany (6). Hallensleben, one of their contemporaries, had found that when para-hydroxy tri-phenyl carbinol

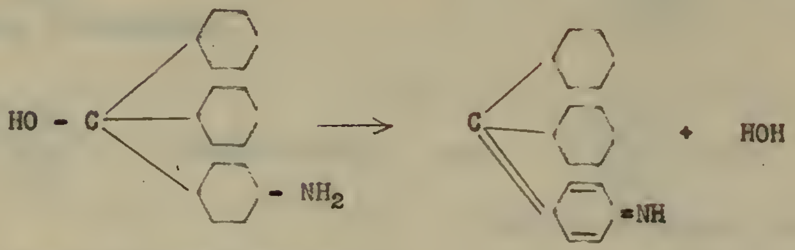


was subjected to heat, a molecule of water was split off, resulting in the formation of a quinoid structure on one of the benzene rings.



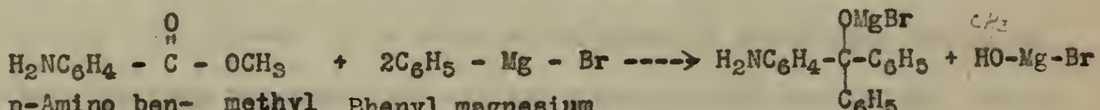
p-Hydroxy triphenyl carbinol.

Baeyer and Villiger, who had been working with o-amino triphenyl carbinol and malachite green derivatives, determined to see whether or not para-amino triphenyl carbinol would lose water in the same manner, according to the following equation :



p - Amino triphenyl carbinol

They first prepared their amino triphenyl carbinol by the method of Baeyer and Löhr (7), but in so doing, obtained a product contaminated by impurities which were not easily removed, and which they were unable to crystallize satisfactorily. In seeking a method which would give more satisfactory results, it occurred to them to use "Grignard's beautiful reaction". They knew how to prepare triphenyl methane itself in this manner, so they simply sought to vary the reacting substances sufficiently to give them the amino derivative which they desired. They succeeded in preparing it first from the methyl ester of para-amino benzoic acid.



$$H_2NC_6H_4-\overset{O}{\overset{\|}{C}}-OCH_3 + 2C_6H_5-Mg-Br \dashrightarrow H_2NC_6H_4-\underset{C_6H_5}{\overset{OMgBr}{C}}-C_6H_5 + HO-Mg-Br$$

CH_3

p-Amino benzoic acid

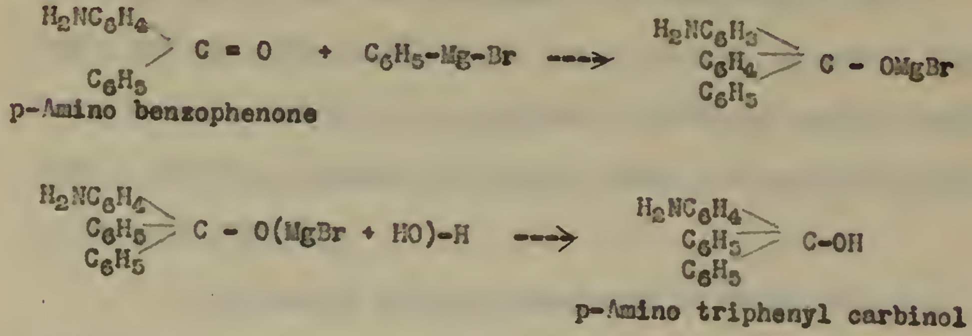
methyl ester

Phenyl magnesium bromide

$$H_2NC_6H_4-\underset{C_6H_5}{\overset{O(MgBr}{C}}-C_6H_5 + HO)-H \dashrightarrow H_2NC_6H_4-\underset{C_6H_5}{\overset{OH}{C}}-C_6H_5 + HO-Mg-Br$$

p-Amino triphenyl carbinol

Later they used para-amino benzophenone



$$\begin{matrix} H_2NC_6H_4 \\ C_6H_5 \end{matrix} > C = O + C_6H_5\text{-}Mg\text{-}Br \longrightarrow \begin{matrix} H_2NC_6H_3 \\ C_6H_4 \\ C_6H_5 \end{matrix} > C - OMgBr$$

p-Amino benzophenone

$$\begin{matrix} H_2NC_6H_4 \\ C_6H_5 \\ C_6H_5 \end{matrix} > C - O(MgBr + HO)\text{-}H \longrightarrow \begin{matrix} H_2NC_6H_4 \\ C_6H_5 \\ C_6H_5 \end{matrix} > C\text{-}OH$$

p-Amino triphenyl carbinol

Baeyer and Villiger prepared numerous derivatives of this compound, as well as many related compounds. Among these latter was malachite green, which they prepared from 4-4-tetra methyl di-amino benzophenone and phenyl magnesium bromide. This success led them to attempt to prepare methyl violet, using para-bromo dimethyl aniline to form the Grignard reagent. They found, however, that the halides of aniline and di-methyl aniline would not react with magnesium.

Sachs and Ehrlich (8) encountered the same difficulty, but they brought para-bromo-di-methyl aniline into reaction with magnesium in the following manner (9); "The magnesium was acted upon by an ethereal solution of ethyl bromide; the bulk of this latter was then poured off and replaced by an ethereal solution of para-bromo di-methyl aniline, when the magnesium was readily acted upon by the latter." Baeyer (10) raised the objection that the reaction was not quantitative and the reagent was contaminated with ethyl magnesium bromide. To avoid this, he proposed to "activate the magnesium by covering it with a thin film of magnesium iodide, which could be effected by heating magnesium in portions of about ten grams, with continuous shaking over a free flame, and adding half its weight of iodine in small portions, and in such a manner that a new portion was not added until the whole of the previous portion had been consumed. The temperature must be high, but not sufficiently so to cause the mass to melt." Baeyer found that the "activated" magnesium so obtained reacted readily with an ethereal solution of ortho-, meta-, or para-iodo aniline or di-methyl aniline.

Practically the only other work of importance with reference to the preparation of dyes by means of the Grignard reaction was done in 1913 by Votocek and Matejka (11), who prepared a number of alkoxy malachite greens, namely, ortho-, meta-, and para-methoxy malachite green, from Michler's ketone.

Some study has been made of the reaction of the Grignard reagents upon derivatives of ortho-benzoyl benzoic acid. Guyot and Catel (12), for example, found that when phenyl magnesium bromide reacted with the methyl ester of ortho-benzoyl benzoic acid, ortho-di-benzoyl benzene was obtained. No references were discovered, however, indicating how the Grignard reagent might be expected to behave towards the free acid. This particular question was studied,in a portion of the present investigation.

EXPERIMENTAL PART

The experimental work of this investigation was divided into five parts;

I. A Study of the Preparation of Malachite Green,
II. A Study of the Preparation of Methyl Violet,
III. A Study of the Preparation of Chrome Green,
IV. A Study of the Preparation of Chrome Violet, and
V. A Study of the Preparation of Phthalophenone.

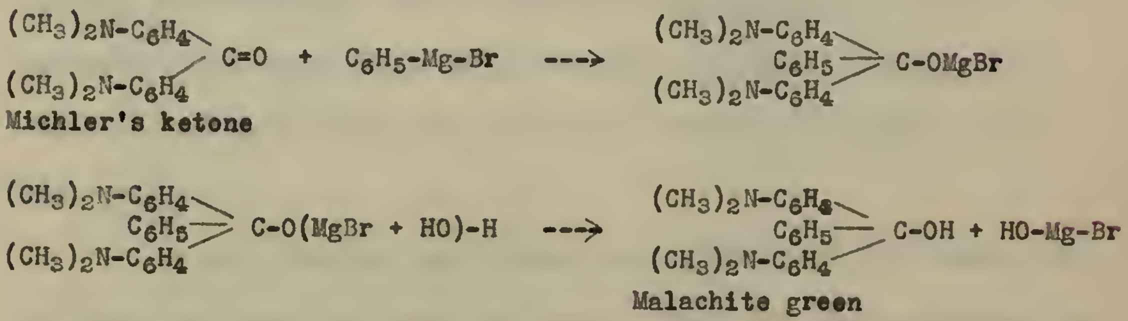
In all of these studies, the anhydrous ether used as a solvent in the Grignard reactions was prepared by drying the commercial ether over phosphorus pentoxide (13).

I. A Study of the Preparation of Malachite Green

It was assumed that the reaction would proceed in accordance with the following equations:

$$C_6H_5 - Br + Mg \dashrightarrow C_6H^5 - Mg - Br$$

Bromo benzene — Phenyl magnesium bromide



$$\begin{array}{l}(CH_3)_2N-C_6H_4\diagdown\\ \qquad\qquad\qquad C=O\\ (CH_3)_2N-C_6H_4\diagup\end{array} + C_6H_5-Mg-Br \dashrightarrow \begin{array}{r}(CH_3)_2N-C_6H_4\diagdown\\ C_6H_5 - C-OMgBr\\ (CH_3)_2N-C_6H_4\diagup\end{array}$$

Michler's ketone

$$\begin{array}{r}(CH_3)_2N-C_6H_4\diagdown\\ C_6H_5 - C-O(MgBr + HO)-H\\ (CH_3)_2N-C_6H_4\diagup\end{array} \dashrightarrow \begin{array}{r}(CH_3)_2N-C_6H_4\diagdown\\ C_6H_5 - C-OH + HO-Mg-Br\\ (CH_3)_2N-C_6H_4\diagup\end{array}$$

Malachite green

Also the following relationship would exist:

Molecular weight of Michler's ketone = 268.26

Molecular weight of malachite green = 343.34

Therefore if one gram of the ketone be used,

$$\frac{268.26}{343.34} = \frac{1}{x}$$

$$x = \frac{343.34}{268.26} = 1.28 \text{ g. of malachite green}$$

should be the theoretical yield, or from 15 grams, the amount used in this reaction, the theoretical yield of malachite green would be 19.2 grams.

The Reaction

One gram of clean magnesium turnings, a crystal of iodine, and 50 cc. of anhydrous ether were placed in a 200 cc. flask which was then connected to an upright condenser protected at the upper end by a calcium chloride tube. Eight grams of bromo-benzene were then added through the condenser, and the contents of the flask warmed gently on the steam bath in order to start the reaction. When all of the magnesium had been dissolved, the solution was cooled, and 15 grams of Michler's ketone were added in small amounts through the condenser. After all had been added, the mixture was boiled gently for an hour then cooled.

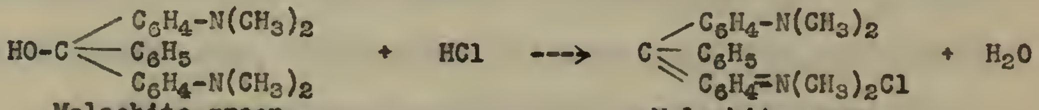
A dark resinous mass rested on the bottom of the flask, while the ether had taken on a deep red color. Above the ether solution, the sides of the flask were colored a dark green.

The apparatus was then disconnected, and the ether layer decanted and evaporated to recover any material that might have been in solution. Only a negligible amount was found. The solid material was treated with water containing a few c.c. of H_2SO_4, and washed as free as possible from the unchanged ketone. The water thus used took on a green color. Since the unchanged ketone was very slow in settling compared with the carbinol, much of it was easily decanted. After being washed, the residue was dried and further treated as described in the following paragraphs. The amount of dried material was 17.2 grams.

Identification of the Above Product

An alcohol solution of the product exhibited a bright green coloration. This indicated that the formation of the dye had been successful. Other characteristic reactions of malachite green were then tried; namely, the formation of the dye salts, the hydrochloride being first prepared.

The compound was divided into two portions, to one of which was added about 30 c.c. of water, and concentrated HCl calculated according to the reaction:



$$HO\text{-}C(C_6H_4\text{-}N(CH_3)_2)(C_6H_5)(C_6H_4\text{-}N(CH_3)_2) + HCl \dashrightarrow C(C_6H_4\text{-}N(CH_3)_2)(C_6H_5)(C_6H_4{=}N(CH_3)_2Cl) + H_2O$$

Malachite green (carbinol)

Malachite green (hydrochloride)

Molecular weight of HCl = 36.5

Molecular weight malachite green = 343.34

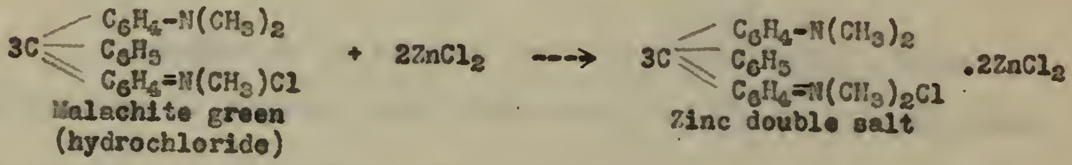
$$\text{Therefore, } \frac{343.34}{36.5} = \frac{9}{x}$$

$$343.34x = 328.5$$

x = .9 g. HCl are necessary to react

with 9 grams of the compound, assuming it to be malachite green. The product formed was quite readily soluble in water with a bright green coloration, while the untreated product was practically insoluble. The water was then evaporated and the hydrochloride dried in the air. It was considerably darker in appearance and less powdery than the untreated product.

To this hydrochloride, water was again added and an amount of zinc chloride calculated from the following equation:



$$3C\left\langle\begin{array}{l}C_6H_4-N(CH_3)_2\\ C_6H_5\\ C_6H_4=N(CH_3)Cl\end{array}\right. + 2ZnCl_2 \dashrightarrow 3C\left\langle\begin{array}{l}C_6H_4-N(CH_3)_2\\ C_6H_5\\ C_6H_4=N(CH_3)_2Cl\end{array}\right. .2ZnCl_2$$

Malachite green (hydrochloride)

Zinc double salt

Molecular weight of malachite green hydrochloride = 361.8

Molecular weight of $ZnCl_2$ = 154.3

Amount of hydrochloride = 10.5 grams.

$$\frac{1085.4}{308.6} = \frac{10.5}{x}$$

$$1085.4x = 3240.3$$

$$x = 3g. \text{ (approximately) of } ZnCl_2.$$

Immediately upon the addition of the zinc chloride, a decided reaction was observed, the zinc salt forming in a gummy mass with a beautiful turkey bronze color. Upon drying, the mass became hard and brittle.

All of these tests indicated the formation of malachite green. As a further proof, it was decided to make an analysis of the compound for carbon, hydrogen and nitrogen. In a preliminary ignition of the original carbinol base, a slight amount of ash was noticed. Two determinations of the amount of ash gave .95 per cent.

The ash was dissolved in concentrated HCl, and treated with a few drops of ammonium sulphate and ammonium oxalate. The solution was then evaporated to 5 c.c., and made alkaline with ammonium hydroxide. Disodium phosphate was then added, after which the solution was shaken and allowed to stand several minutes. A white crystalline precipitate, soluble in acetic acid, formed, which identified the metal responsible for the ash as magnesium. The reactions were:

$$MgCl_2 + Na_2HPO_4 + NH_3 \dashrightarrow NH_4MgPO_4 + 2NaCl$$

A portion of the carbinol was then treated several times with warm dilute sulphuric acid, neutralized and finally recrystallized from alcohol. It then left no ash upon ignition. The combustion, by which the carbon and hydrogen were determined then gave the following results:

Weight of substance taken = .1815 g.
" " H_2O obtained = .1260 g.
" " CO_2 " = .5317 g.

Carbon.

C. in CO_2 = 27.27%; .2727 x .5317 = .1450 g.

.1450 g. C. in .1815 g. compound = $\frac{.1450}{.1815}$ x 100 = 79.89% Carbon

Hydrogen.

H. in H_2O = 11.11%; .1111 x .1260 = .0140 g.

.0140 g. H. in .1815 g. compound = $\frac{.0140}{.1815}$ x 100 = 7.71% Hydrogen

The nitrogen content of the compound was then determined by means of the Kjeldahl method with these results.

Weight of substance taken = 1.0316 g.

Amount of .5143 N/1HCl used to absorb NH_3 = 30 c.c.

Amount of .9781 N/5 NaOH used to neutralize excess = 50.36 c.c.

Since 1 c.c. .9781 N/5 NaOH sol. contains .0078 g. of NaOH

50.36 c.c. contains 50.36 x .0078 = .3928 g. NaOH used for this neutralization.

Molecular weight of NaOH = 40

Molecular weight of HCl = 36.5

$$\frac{36.5}{40} = \frac{x}{1}$$

x = .9125 g. HCl neutralized by 1 g. NaOH

$$\frac{.3928}{x} = \frac{1}{.9125}$$

x = .3584 g. HCl neutralized.

Since 1 c.c. .5143 N/1 contains .0188 g. HCl

30 c.c. contains 30 x .0188 = .5631 g.

.5631 - .3584 = .2047 g. HCl neutralized by the NH_3 from the sample.

Molecular weight of NH_3 = 17.032

$$\frac{36.5}{17.032} = \frac{1}{x}$$

x = .4666 g. NH_3 neutralized by 1 g. HCl.

$$\frac{.2047}{x} = \frac{1}{.4666}$$

x = .0956 g. NH_3 neutralized by the HCl.

.0956 g. NH_3 contains .0786 g. <u>Nitrogen</u>

$$\frac{.0786}{1.0316} \times 100 = 7.62\% \text{ Nitrogen.}$$

100 - (79.89 + 7.71 + 7.62) = 4.78% Oxygen.

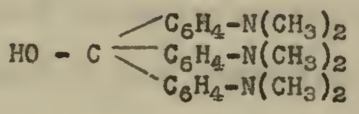
The following comparison makes clear the results of the analysis.

	Theoretical	Found
Carbon,	79.72	79.89
Hydrogen,	7.57	7.71
Nitrogen,	8.09	7.62
Oxygen,	4.62	4.78

In the face of the evidence obtained in these tests, the formation of malachite green by the Grignard reaction is clearly proven.

II. A Study of the Preparation of Methyl Violet

It was to be expected that methyl violet, having the formula



$$HO - C \begin{cases} C_6H_4\text{-}N(CH_3)_2 \\ C_6H_4\text{-}N(CH_3)_2 \\ C_6H_4\text{-}N(CH_3)_2 \end{cases}$$

might be prepared in a manner identical with that previously used to prepare malachite green, except that para-bromo di-methyl aniline instead of bromo benzene would be the halide for the Grignard reagent. Since none of this compound was available, it was necessary to prepare it from bromine and di-methyl aniline in a solution of glacial acetic acid (14). After some experimentation, the following procedure was adopted. The reaction proceeding in accordance with the equation,

$$C_6H_5\text{-}N(CH_3)_2 \quad + \quad Br_2 \quad \text{--->} \quad Br\text{-}C_6H_4\text{-}N(CH_3)_2 \quad + \quad HBr$$

Molecular weight of $C_6H_5\text{-}N(CH_3)_2$ = 122.17

Molecular weight of $Br\text{-}C_6H_4\text{-}N(CH_3)_2$ = 201.09

Atomic weight of Br = 79.92

Hence the reaction takes place in the proportion

$$\frac{122.17}{159.84} = \frac{1}{x}$$

x = 1.3 g. Br_2 for every gram of dimethyl aniline used.

Accordingly, 20 g. of dimethyl aniline were placed in a beaker, and an equal volume of glacial acetic acid added. After being thoroughly mixed, the solution was surrounded by ice, and 26 g. of bromine added slowly and with constant stirring, since the reaction was violent. After all of the bromine had been added, the product was diluted with about ten volumes of water. The resulting precipitate was dissolved in acetic acid, and then sodium hydroxide was added to neutral reaction. A bulky crystalline mass was thrown down. This was filtered by suction and thoroughly washed with water, after which it was dried at room temperature. After being purified from di-methyl aniline by repeated recrystallization from alcohol, the product was obtained as crystalline leaflets which melted at 54° and boiled at about 241°. The yield was 28 grams. The theoretical yield being calculated according to the preceding reaction from the proportion

$$\frac{122.17}{201.09} = \frac{1}{x}$$

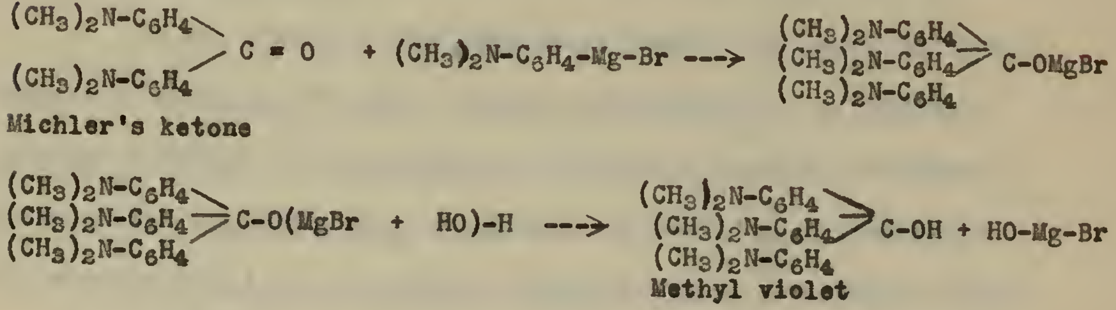
x = 1.6 g. para-bromo di-methyl aniline from one gram of di-methyl aniline, or 32 grams from 20 grams of di-methyl aniline. Thus about 87.5% of the theoretical was obtained.

Preparation of the Grignard Reagent

Assuming that the reaction would proceed in the usual manner it would be as follows:

$$(CH_3)_2N-C_6H_4-Br + Mg \dashrightarrow (CH_3)_2N-C_6H_4-Mg-Br$$

Para-bromo di-methyl aniline — Para-bromo magnesium di-methyl aniline



$$\left.\begin{matrix}(CH_3)_2N-C_6H_4\\(CH_3)_2N-C_6H_4\end{matrix}\right\rangle C=O + (CH_3)_2N-C_6H_4-Mg-Br \dashrightarrow \left.\begin{matrix}(CH_3)_2N-C_6H_4\\(CH_3)_2N-C_6H_4\\(CH_3)_2N-C_6H_4\end{matrix}\right\rangle C-OMgBr$$

Michler's ketone

$$\left.\begin{matrix}(CH_3)_2N-C_6H_4\\(CH_3)_2N-C_6H_4\\(CH_3)_2N-C_6H_4\end{matrix}\right\rangle C-O(MgBr + HO)-H \dashrightarrow \left.\begin{matrix}(CH_3)_2N-C_6H_4\\(CH_3)_2N-C_6H_4\\(CH_3)_2N-C_6H_4\end{matrix}\right\rangle C-OH + HO-Mg-Br$$

Methyl violet

From these reactions the following mathematical relatioships are calculated.

Molecular weight of Michler's ketone = 268.26

Molecular weight of $BrMgC_6H_4N(CH_3)_2$ = 224.37

Therefore if 15 g. of ketone be used,

$$\frac{268.26}{224.37} = \frac{15}{x}$$

$$268.26x = 3365.55$$

x = 12.5 g. $BrMgC_6H_4N(CH_3)_2$ are necessary to react with the ketone.

Molecular weight of magnesium = 24.32

$$\frac{224.37}{24.32} = \frac{12.5}{x}$$

$$224.37\,x = 303.9$$

x = 1.3 g. magnesium necessary to prepare 12.5 g. $BrMgC_6H_4N(CH_3)_2$.

Molecular weight of Michlers ketone = 268.26

Molecular weight of methyl violet = 389.4

$$\text{Therefore} \quad \frac{268.26}{389.4} = \frac{15}{x}$$

$$268.26x = 5841$$

$$x = 21$$ g. of methyl violet are theoretically produced.

It was stated in the literature review (see page 18) that Baeyer and Villiger (6) could obtain no reaction when an ethereal solution of bromo- or iodo-aniline or di-methyl aniline was boiled for days with magnesium with or without the addition of iodine (15). This was confirmed in the present investigation by a carefully prepared test in which an ethereal solution of 12.2 grams of para-bromo di-methyl aniline was added to 1.3 grams of magnesium in a flask connected to a return condenser, and protected at the upper end by a calcium chloride tube. The contents of the flask were boiled gently on the steam bath for three days with the addition, from time to time, of a crystal of iodine, but no reaction could be detected. Several such attempts to bring the bromo di-methyl aniline into reaction with the magnesium ended in failure in spite of the utmost care.

Baeyer (10) then succeeded in preparing a Grignard reagent with para-iodo aniline and with para-iodo di-methyl aniline by "activating" the magnesium with a thin film of magnesium iodide with which he covered it, as described in the literature review (page 18). "The activated magnesium so obtained was a dull grey powder which became brown in the course of time and was required to be carefully protected from moisture." (15)

A quantity of magnesium was treated in the above manner and used in another attempt to prepare the Grignard reagent, but without success. The process was repeated, but after prolonged refluxing of the ether solution of para-bromo di-methyl aniline with the activated magnesium, no reaction could be noted. When, however, a small quantity of Michler's ketone was added to the flask and the mixture boiled for a time, and then treated with water, a rather pronounced blue-violet color on the cork used to connect the flask to the condenser indicated that the reaction had probably taken place, but only to a slight degree.

Sachs and Ehrlich (8) brought para-bromo di-methyl aniline into reaction with magnesium by allowing the magnesium to be attacked by an ethereal solution of ethyl bromide, and then pouring off the bulk of the latter, and replacing it by an ethereal solution of para-bromo di-methyl aniline. The magnesium was then attacked by the latter.

A quantity of ethyl bromide was then prepared, carefully purified, and the following procedure adopted.

Magnesium turnings, 1.3 grams, were placed in a 150 c.c. flask and an ethereal solution of 8 grams ethyl bromide added. The flask was then connected to a return condenser and a crystal of iodine added. A vigorous reaction immediately began. After allowing this to proceed for three or four minutes, the bulk of the liquid was rapidly decanted and replaced by an ethereal solution of 12.5 grams of para-bromo di-methyl aniline. The mixture was warmed gently on the steam bath, and in a very short time a vigorous reaction was started.

When the magnesium had all dissolved, the contents of the flask were cooled and 15 grams of Michler's ketone were added through the condenser, after which the flask was warmed gently for an hour; the ether layer in the flask taking on a deep red color, and a gummy solid depositing on the bottom.

After the flask had cooled, the condenser was disconnected and the ether decanted into a beaker and evaporated. A gummy, almost black mass separated, which gave an intense violet color to water. After hydrolysis with water, the product was dried.

The solid remaining behind in the flask was treated in a similar manner. Upon drying, the product obtained was much lighter in color than the ether extract, and more powdery. It would not react upon treatment with dilute HCl and $ZnCl_2$ solution; this indicating that it was simply unchanged Michler's ketone.

Identification of the Methyl Violet

While the solid residue from the flask consisted of 7 grams of unchanged ketone, the ether extract yielded 9 grams of substance which differed in physical characteristics. Assuming it to be methyl violet, it was treated with hydrochloric acid in accordance with the equation,

$$HO\text{-}C\begin{array}{l} C_6H_4\text{-}N(CH_3)_2 \\ C_6H_4\text{-}N(CH_3)_2 \\ C_6H_4\text{-}N(CH_3)_2 \end{array} + HCl \dashrightarrow C\begin{array}{l} C_6H_4\text{-}N(CH_3)_2 \\ C_6H_4\text{-}N(CH_3)_2 \\ C_6H_4{=}N(CH_3)_2Cl \end{array} + H_2O$$

Methyl violet hydrochloride

Molecular weight of methyl violet = 389.4

Molecular weight of HCl = 36.5

$$\frac{389.4}{36.5} = \frac{7}{x}$$

x = .64 gram HCl necessary to react with 7 grams of methyl violet. About 25 cc. of water were added to the solid and then .64 grams of hydrochloric acid. The increased solubility of the compound gave evidence of a reaction. To this zinc chloride was then added in an amount determined by the reaction,

Methyl violet hydrochloride

Methyl violet. Zinc double salt

Molecular weight of hydrochloride = 407.86

Molecular weight of zinc chloride = 154.30

$$\frac{1223.58}{308.6} = \frac{7.6}{x}$$

$$1223.58x = 2345.36$$

x = 1.8 grams zinc chloride necessary to react with the 7.6 grams of hydrochloride. Upon the addition of an aqueous solution of the zinc chloride, a brilliant turkey bronze mass resembling the zinc double salt of malachite green was obtained. Its solutions, however, were violet instead of green.

As a final step in the identification of the product, a small amount of the original carbinol was purified by recrystallization from alcohol, after which an analysis was made upon it, with the following results:

Weight of sample used, .1517 g.

Weight of CO_2 obtained, .4281

Weight of H_2O obtained, .1046

Carbon

C in CO_2 = 27.27%; .2727 x .4281 = .1170 g. C

$\frac{.1170}{.1517}$ x 100 = 77.06% Carbon.

Hydrogen

H in H_2O = 11.11%; .1111 x .1046 = .0116 g. H

$\frac{.0116}{.1517}$ x 100 = 7.65% Hydrogen

Nitrogen (by the Kjeldahl method)

Weight of sample taken = .9280 g.

Amount .5143 N/HCl used to absorb NH_3 = 30 c.c.

Amount .9781 N/5 NaOH used to neutralize excess HCl = 43.47 c.c.

Since 1 c.c. .9781 N/5NaOH contains .0078 g. of NaOH.

43.47 c.c. contains 43.47 x .0078 = .3391 g. NaOH used for this neutralization.

1 g. NaOH neutralizes .9125 g. HCl

$$\frac{.3391}{x} = \frac{1}{.9125}$$

x = .3125 g. HCl neutralized by .3391 g. NaOH.

Since 1 c.c. ~~N/~~ contains .0188 g. HCl, .5143 $\frac{N}{1}$ HCl

30 c.c. contains 30 x .0188 = .5631 g. HCl

.5631 - .3125 = .2506 g. HCl neutralized by the ~~HCl~~ NH_3 from the sample.

1 g. HCl is equivalent to .4666 g. NH_3

$$\frac{.2506}{x} = \frac{1}{.4666}$$

$x = .1169$ g. NH_3 neutralized by the HCl

Since 1 g. NH_3 is equivalent to .8224 g. nitrogen

.1169 g. NH_3 is equivalent to .0960 g. nitrogen

$\frac{.0960}{.9280} \times 100 = 10.36\%$ nitrogen in sample.

$100 - (77.06 + 7.65 + 10.36) = 4.93\%$ oxygen.

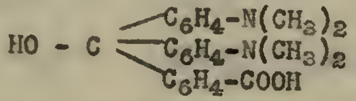
The results of the analysis may be more clearly seen in the following comparison.

	Theoretical	Found
Carbon,	77.07	77.06
Hydrogen,	8.03	7.65
Nitrogen,	10.79	10.36
Oxygen,	4.11	4.93

Thus the formation of methyl violet was proven.

III. A Study of the Preparation of Chrome Green.

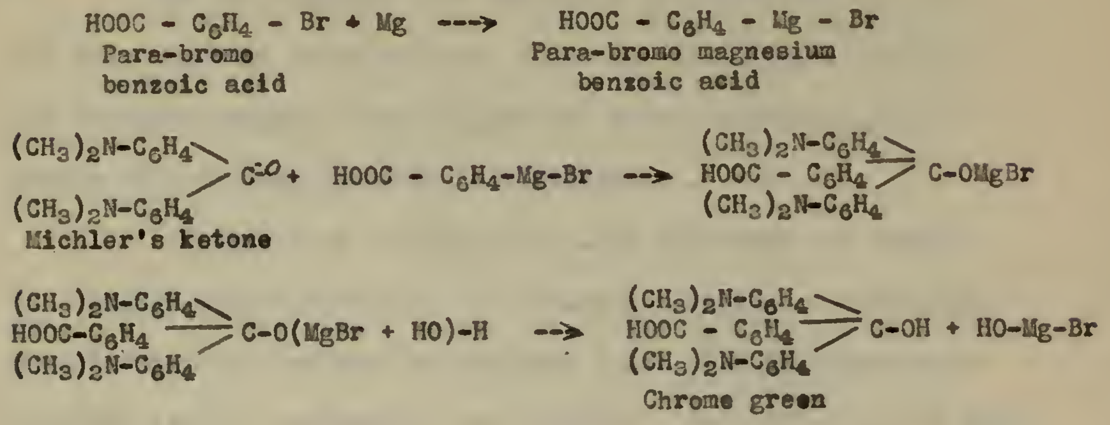
Chrome green, having the formula



$$HO-C\begin{cases}C_6H_4-N(CH_3)_2\\ C_6H_4-N(CH_3)_2\\ C_6H_4-COOH\end{cases}$$

is very similar in constitution to the two compounds already studied; the difference being that chrome green contains an acid group. Consequently, it was thought that it might be prepared from

Michler's ketone and para-bromo benzoic acid by means of the Grignard reaction, according to the following reactions:



$$HOOC - C_6H_4 - Br + Mg \longrightarrow HOOC - C_6H_4 - Mg - Br$$

Para-bromo benzoic acid → Para-bromo magnesium benzoic acid

$$\begin{matrix}(CH_3)_2N-C_6H_4 \\ (CH_3)_2N-C_6H_4\end{matrix} > C=O + HOOC - C_6H_4-Mg-Br \longrightarrow \begin{matrix}(CH_3)_2N-C_6H_4 \\ HOOC - C_6H_4 \\ (CH_3)_2N-C_6H_4\end{matrix} > C-OMgBr$$

Michler's ketone

$$\begin{matrix}(CH_3)_2N-C_6H_4 \\ HOOC-C_6H_4 \\ (CH_3)_2N-C_6H_4\end{matrix} > C-O(MgBr + HO)-H \longrightarrow \begin{matrix}(CH_3)_2N-C_6H_4 \\ HOOC - C_6H_4 \\ (CH_3)_2N-C_6H_4\end{matrix} > C-OH + HO-Mg-Br$$

Chrome green

The following mathematical relationships would then hold true.

Molecular weight of Michler's ketone = 268.26

Molecular weight of brom-benzoic acid = 201.04

Hence if 10 grams of Michler's ketone be used

$$\frac{268.26}{201.04} = \frac{10}{x}$$

$$268.26\,x = 2010.4$$

$x = 6.4$ g. bromo-benzoic acid are necessary to react with the ketone according to the equation

$$\frac{268.26}{396.34} = \frac{10}{x}$$

$$268.26x = 3963.4$$

$x = 14.4$ g. of chrome green should theoretically be prepared from 10 g. Michler's ketone.

The Grignard Reagent

It was expected that the chief difficulty in carrying out this reaction would probably arise in attempting to prepare the Grignard reagent, $Br-Mg-C_6H_4-COOH$, since no description of such a compound was found in the literature.

In the first attempt, the usual procedure was adopted in a purely qualitative way. An ethereal solution of para-bromo benzoic acid was refluxed for several hours with fine magnesium turnings with no evidence of any reaction. The refluxing was then continued for several days with no different results. At the end of this period, a small quantity of the ketone was added in order to detect any reaction so slight that it might have escaped observation. After this had been refluxed for several hours longer, the mixture was treated with water. Almost immediately a pronounced sea green color was produced. After filtering off the unchanged magnesium, the ether was evaporated, and the resulting solid was found to be light green in color. It gave a green solution in alcohol and also in hot water, although it appeared to be largely unchanged ketone colored green by the small amount of compound formed.

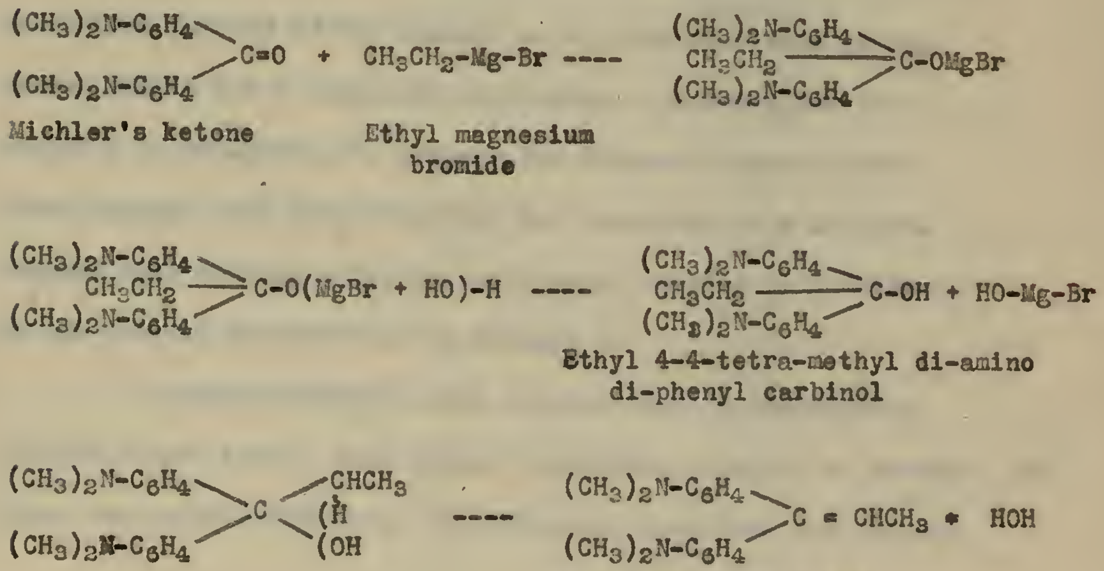
Since chrome green is a mordant dye, it was decided to attempt to apply it to a quantity of wool yarn, mordanting it with potassium dichromate and tartaric acid. (17) The result was a sea green color produced on the yarn, which would not boil out in hot water.

These facts indicated the formation of chrome green, although in amounts too small to be isolated and identified with certainty.

An attempt was then made to prepare the Grignard reagent in the manner used in preparing bromo-magnesium di-methyl aniline. A small quantity (about.7 g.) of magnesium turnings were placed in a small flask and an ethereal solution of ethyl bromide (C_2H_5-Br) was added. A crystal of iodine started the reaction off briskly. When this had proceeded a few moments, the bulk of the solution was decanted and replaced by an ethereal solution of para-bromo benzoic acid. The reaction was observed to continue for a time and then to gradually cease in spite of the fact that some of the magnesium remained unchanged.

After the reaction had entirely ceased, a quantity (about 8 g.) of ketone was added to the solution. The mixture was then refluxed for about two hours, during which time a noticeable reaction took place with the formation of a yellow substance, which upon hydrolysis with water, changed to a bright sea green. This product was soluble in hot water, forming a green solution. It was slightly soluble in ether, and somewhat more soluble in alcohol. It imparted the same color to wool yarn as the product previously obtained, and although formed in a larger amount, there was still not enough to isolate in a pure condition.

In order to ascertain whether or not any side reactions may have been responsible for the formation of the colored material, the procedure was repeated with the successive omission of bromo benzoic acid, Michler's ketone, magnesium and ethyl bromide. In no instance did any reaction occur except between magnesium, ethyl bromide and the ketone; a reaction which was expected to occur. This reaction resulted upon hydrolysis in the formation of a bright green compound which became completely colorless within a very few minutes. This loss of color was due to the fact that the carbinol formed by the reaction between ethyl magnesium bromide and Michler's ketone lost a molecule of water resulting in the formation of a colorless unsaturated hydrocarbon, as shown in the following reaction. (18)



$$((CH_3)_2N\text{-}C_6H_4)_2C{=}O + CH_3CH_2\text{-}Mg\text{-}Br \text{ ---- } ((CH_3)_2N\text{-}C_6H_4)_2(CH_3CH_2)C\text{-}OMgBr$$

Michler's ketone

Ethyl magnesium bromide

$$((CH_3)_2N\text{-}C_6H_4)_2(CH_3CH_2)C\text{-}O(MgBr + HO)\text{-}H \text{ ---- } ((CH_3)_2N\text{-}C_6H_4)_2(CH_3CH_2)C\text{-}OH + HO\text{-}Mg\text{-}Br$$

Ethyl 4-4-tetra-methyl di-amino di-phenyl carbinol

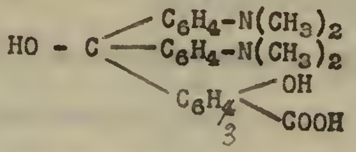
$$((CH_3)_2N\text{-}C_6H_4)_2C\langle CHCH_3 (H, (OH \text{ ---- } ((CH_3)_2N\text{-}C_6H_4)_2C = CHCH_3 + HOH$$

Colorless hydrocarbon

It is to be remembered that when ethyl bromide was used to start a reaction, it was decanted from the magnesium as soon as the reaction had begun to progress nicely, consequently the amount of ethyl magnesium bromide formed was small, and the product of a reaction between it and the ketone would appear only as an impurity in the final product. At the same time, it will be remembered that a pronounced green coloration was produced upon hydrolysis of the reaction product of bromo benzoic acid, magnesium, and Michler's ketone without the use of ethyl bromide. Consequently, it is felt that the preparation of chrome green was successful, although it was not isolated.

IV. A Study of the Preparation of Chrome Violet.

Chrome violet, having the formula

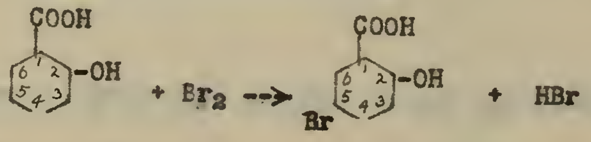


$$HO-C\begin{cases}C_6H_4-N(CH_3)_2\\C_6H_4-N(CH_3)_2\\C_6H_{\underset{3}{\cancel{4}}}\begin{cases}OH\\COOH\end{cases}\end{cases}$$

(16)

is exactly analogous to chrome green; the only difference being that instead of the benzoic acid group of chrome green, chrome violet has a salicylic acid group. Although the experience in attempting to prepare the Grignard reagent with bromo benzoic acid indicated that the formation of a Grignard reagent with 5-bromo salicylic acid might involve difficulties, it was decided nevertheless to attempt it.

5-bromo salicylic acid was prepared by introducing salicylic acid into a cold carbon disulphide solution of bromine. (19) After some experimentation, the following procedure was adopted:



Molecular weight of salicylic acid = 138.08

Molecular weight of bromo salicylic acid = 217

Molecular weight of bromine = 159.84

Hence to prepare 25 grams of bromo salicylic acid

$$\frac{138}{217} = \frac{x}{25}$$

$$217x = 3452$$

$$x = 15.9$$ g. of salicylic acid are necessary, and

$$\frac{159.84}{138.08} = \frac{x}{15.9}$$

$$138.08x = 2541.46$$

x = 18.4 g. of bromine are necessary to react with 15.9 g. of salicylic acid. Accordingly, 18.4 grams of bromine were dissolved in about 75 c.c. of carbon disulphide and salicylic acid added in portions of about one gram, with constant stirring until 15.9 grams had been added. An equal volume of water was then added and the carbon disulphide distilled off. The water was then heated to boiling and the bromo salicylic acid filtered off; the salicylic acid being soluble in hot water, white bromo salicylic acid is insoluble. It was then washed with hot water until free from salicylic acid, and finally dried in the oven. About 20 grams was obtained, the melting point of which was 165°.

The Grignard Reagent

In order to determine whether or not any reaction occurred, a qualitative test was first made. An ethereal solution of about 2 grams of 5-bromo salicylic acid was placed in a 150 c.c. flask with about .2 gram of magnesium turnings, and the mixture refluxed for about twelve hours. During this time, however, no reaction was observed. Nevertheless, about three grams of Michler's ketone were added to the flask, after which the refluxing was continued for several hours longer. The flask was then disconnected, and several cubic centimeters of water added. Immediately both the ethereal solution and the solid material in the flask assumed a bright green color. The water layer remained colorless.

The ethereal solution was separated and allowed to evaporate. A gummy, green mass was deposited, which after several days exposure to the atmosphere changed to brown, while the mass became hard and brittle.

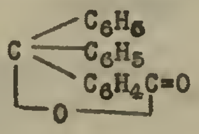
A bit of this substance was placed on a porcelain test plate and treated with a few drops of ether. It dissolved easily, with the formation of a blue color, which as the ether evaporated, was replaced by a violet, and then a green color. A green mass, which finally turned brown after being exposed to the air for several days, was deposited as before.

These same color transformations took place in an alcohol solution, although the fact that alcohol is less volatile than ether caused them to take place less rapidly.

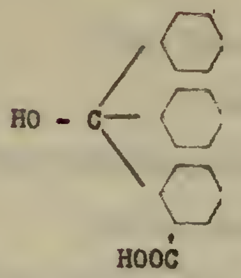
As there seemed little chance of accomplishing anything by this reaction, work on it was discontinued and a new topic was taken up.

V. A Study of the Preparation of Phthalophenone

As was said in the Theoretical Discussion, phthalophenone is the triphenyl methane derivative from which phenolphthalein may be prepared. It has the formula

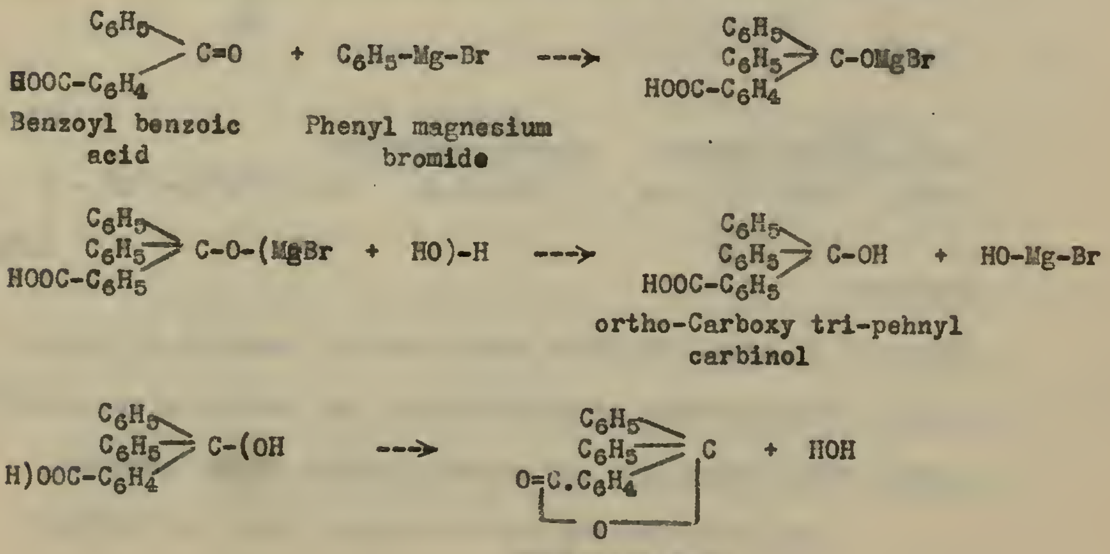


An inspection of the formula shows that it is the anhydride of ortho-carboxy triphenyl carbinol



This compound does not exist in the free state, (20) but when formed, immediately loses water to become the anhydride. This may be hydrolyzed by boiling for a time with an excess of alcoholic sodium hydroxide. Upon adidification, the acid is formed, which loses water, reforming the anhydride.

The first attempt to prepare phthalophenone by means of a Grignard reaction was made upon ortho-benzoyl benzoic acid, having the formula $C_6H_5CO.C_6H_4COOH$, or it may be written $\begin{matrix} C_6H_5 \\ HOOC.C_6H_4 \end{matrix} > C=O$. Assuming the usual reaction to take place, the preparation of the phtholophenone would be represented by the following reactions.



$$\begin{matrix} C_6H_5 \\ HOOC-C_6H_4 \end{matrix} > C=O \quad + \quad C_6H_5-Mg-Br \quad \dashrightarrow \quad \begin{matrix} C_6H_5 \\ C_6H_5 \\ HOOC-C_6H_4 \end{matrix} > C-OMgBr$$

Benzoyl benzoic acid

Phenyl magnesium bromide

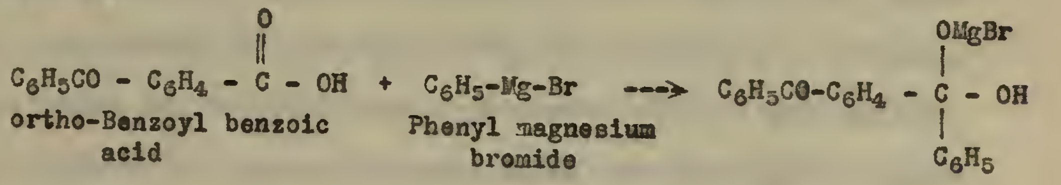
$$\begin{matrix} C_6H_5 \\ C_6H_5 \\ HOOC-C_6H_5 \end{matrix} > C-O-(MgBr \quad + \quad HO)-H \quad \dashrightarrow \quad \begin{matrix} C_6H_5 \\ C_6H_5 \\ HOOC-C_6H_5 \end{matrix} > C-OH \quad + \quad HO-Mg-Br$$

ortho-Carboxy tri-pehnyl carbinol

$$\begin{matrix} C_6H_5 \\ C_6H_5 \\ H)OOC-C_6H_4 \end{matrix} > C-(OH \quad \dashrightarrow \quad \begin{matrix} C_6H_5 \\ C_6H_5 \\ O=C.C_6H_4 \end{matrix} > C \quad + \quad HOH$$

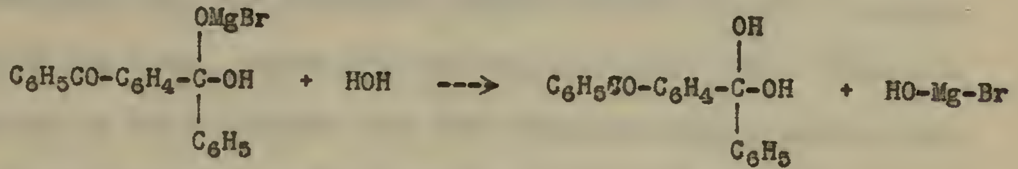
Phthalophenone

But there was now the possibility that the Grignard reagent would react with the carbonyl oxygen of the carboxyl group of ortho-benzoic acid, instead of the oxygen of the benzoyl radicle. If such a reaction took place, it would be represented as follows:



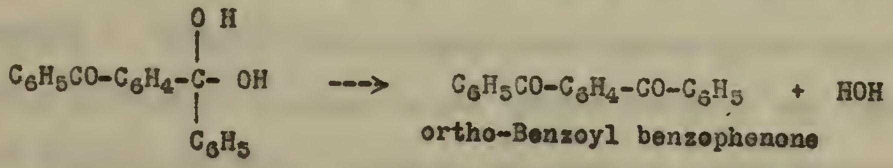
$$C_6H_5CO - C_6H_4 - \overset{\overset{O}{\|}}{C} - OH \;+\; C_6H_5\text{-}Mg\text{-}Br \dashrightarrow C_6H_5CO\text{-}C_6H_4 - \underset{\underset{C_6H_5}{|}}{\overset{\overset{OMgBr}{|}}{C}} - OH$$

ortho-Benzoyl benzoic acid — Phenyl magnesium bromide



$$C_6H_5CO\text{-}C_6H_4\text{-}\underset{\underset{C_6H_5}{|}}{\overset{\overset{OMgBr}{|}}{C}}\text{-}OH \;+\; HOH \dashrightarrow C_6H_5CO\text{-}C_6H_4\text{-}\underset{\underset{C_6H_5}{|}}{\overset{\overset{OH}{|}}{C}}\text{-}OH \;+\; HO\text{-}Mg\text{-}Br$$

This compound, since it has two hydroxyl groups attached to one carbon atom, might be expected to lose water, forming a di-ketone.



$$C_6H_5CO\text{-}C_6H_4\text{-}\underset{\underset{C_6H_5}{|}}{\overset{\overset{OH}{|}}{C}}\text{-}OH \dashrightarrow C_6H_5CO\text{-}C_6H_4\text{-}CO\text{-}C_6H_5 \;+\; HOH$$

ortho-Benzoyl benzophenone

In fact, this compound may be prepared by the reaction between phenyl magnesium bromide and the methyl ester of ortho-benzoyl benzoic acid.

Molecular weight of benzoyl benzoic acid = 212.17

Molecular weight of bromo benzene = 157.00

Molecular weight of phenyl magnesium bromide = 181.32

Atomic weight of magnesium = 24.32

Then if 5 grams of the acid were used,

$$\frac{212.17}{181.32} = \frac{5}{x}$$

$$212.17x = 906.6$$

x = 4.27 g. phenyl magnesium bromide would be required and this [illegible] require 3.69 grams of bromo benzene according to the proportion

$$\frac{181.32}{157.00} = \frac{4.27}{x}$$

$$181.32x = 670.39$$

$$x = 3.69 \text{ g. bromo benzene.}$$

Then if $\overset{3}{2}$.69 grams of bromo-benzene yield 4.27 grams of phenyl magnesium bromide, .58 gram of magnesium would be necessary.

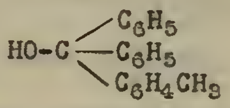
Clear magnesium turnings, .58 gram, was, therefore, placed in a 500 c.c. flask, and an ethereal solution of 3.7 grams of bromobenzene added. After being connected to a reflux condenser, it was then warmed gently to start the reaction. When the reaction had stopped, the flask was cooled, and an ethereal solution of 5 grams of ortho-benzoyl benzoic acid added in small amounts. A vigorous action resulted, which produced a bulky white solid. The mixture was refluxed for two hours, after which the ether was filtered off and the compound dried over sulphuric acid in a vacuum. When the last traces of water and ether had been removed, a bit of the compound, a powdery, white solid, was treated with water. There was no pronounced reaction, and the compound largely dissolved with the formation of a somewhat milky solution, which gradually cleared up, leaving a clear solution with a slight amount of a white solid on the bottom of the container. The solution was then acidified with dilute HCl. This threw down a bulky white precipitate, which when dried was identified through its melting point and solubility as ortho-benzoyl benzoic acid. The evaporation of the solution yielded a white, crystalline, deliquescent solid which was identified as a halogen compound of magnesium.

This evidence indicated that the compound was simply a magnesium salt of benzoyl benzoic acid formed by the replacement of the acid hydrogen by the magnesium halogen group.

$$\underset{\text{ortho-Benzoyl benzoic acid}}{C_6H_5\text{-}CO\text{-}C_6H_4\text{-}COO(H} + \underset{\text{Phenyl magnesium bromide}}{C_6H_5)\text{-}Mg\text{-}Br} \longrightarrow \underset{\text{Magnesium halogen salt}}{C_6H_5\text{-}CO\text{-}C_6H_4\text{-}COOMgBr} + \underset{\text{Benzene}}{C_6H_6}$$

$$C_6H_5CO\text{-}C_6H_4\text{-}COOMgBr + HCl \longrightarrow \underset{\text{Benzoyl benzoic acid}}{C_6H_5CO\text{-}C_6H_4\text{-}COOH} + Cl\text{-}Mg\text{-}Br$$

Some means of suppressing the carboxyl group now had to be found, consequently it was decided to attempt to prepare di-phenyl ortho tolyl carbinol,

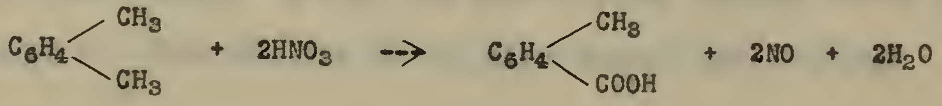


$$HO\text{-}C \begin{cases} C_6H_5 \\ C_6H_5 \\ C_6H_4CH_3 \end{cases}$$

by the Grignard reaction with the intention of later oxidizing the methyl group of the tolyl radicle to a carboxyl group, which upon loss of water would yield phthalophenone.

In attempting to prepare this compound it was necessary to start with ortho-xylene and oxidize it to ortho-toluic acid, which was then transformed into the acid chloride and treated with two molecules of the Grignard reagent, phenyl magnesium bromide, since acid chlorides behave towards Grignard reagents in a manner similar to esters. (21)

In preparing ortho-toluic acid, the method of Fittig and Bieber (22) was adopted. This method consists in the oxidation of one of the methyl groups of ortho-xylene to a carboxyl group.



$$C_6H_4 \begin{cases} CH_3 \\ CH_3 \end{cases} + 2HNO_3 \longrightarrow C_6H_4 \begin{cases} CH_3 \\ COOH \end{cases} + 2NO + 2H_2O$$

Molecular weight of xylene = 106.12

Molecular weight of nitric acid = 63

Therefore if 25 grams of xylene were used

$$\frac{106.12}{126} = \frac{25}{x}$$

$$106.12x = 3150$$

$x = 29.87$ g. of HNO_3 would be necessary.

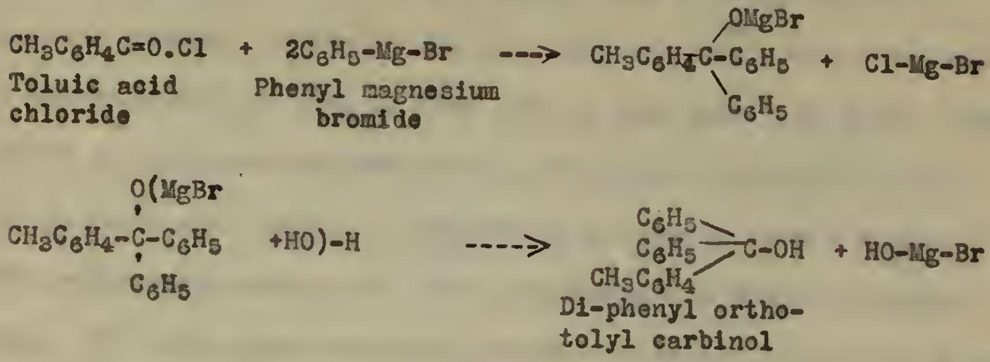
It was thought best, however, to use a slight excess.

Forty-five grams of 70 per cent nitric acid were then placed in a flask and diluted with two volumes of water. To this was added 20 grams of ortho-xylene. The mixture was refluxed gently on a hot plate for about 60 hours. Upon allowing the solution to cool, the toluic acid crystallized out and was filtered off. It was purified by repeated recrystallization from hot water, from which it crystallized in fine white needles melting at 102°. About 27.7 grams or 85 per cent of the theoretical yield, was obtained.

This acid was next transformed into the acid chloride by the method of Klages and Lickroth (23) through treatment with phosphorus pentachloride.

Twenty-five grams of ortho-toluic acid were dissolved in 65 c.c. of chloroform in a flask which was then attached to a reflux condenser. To this, 42.5 grams of phosphorus pentachloride in small amounts was now added, with constant shaking. After being boiled gently for two hours, the chloroform was distilled off and the chloride fractionated under vacuum. It distilled over at about 103°-106° at 22 m.m. of pressure. About 36 grams of the chloride were thus prepared.

It was now attempted to transform this product ihto the diphenyl ortho-tolyl carbinol by the Grignard reaction.



$$CH_3C_6H_4C{=}O.Cl + 2C_6H_5\text{-}Mg\text{-}Br \dashrightarrow CH_3C_6H_4\underset{C_6H_5}{\overset{OMgBr}{C}}\text{-}C_6H_5 + Cl\text{-}Mg\text{-}Br$$

$$CH_3C_6H_4\text{-}\underset{C_6H_5}{\overset{O(MgBr}{C}}\text{-}C_6H_5 \;+HO)\text{-}H \dashrightarrow (C_6H_5)(C_6H_5)(CH_3C_6H_4)C\text{-}OH + HO\text{-}Mg\text{-}Br$$

Molecular weight of toluic acid chloride = 154.56

Molecular weight of phenyl magnesium bromide = 181.32

Atomic weight of magnesium = 24.32

If five grams of the acid chloride were used

$$\frac{154.56}{362.64} = \frac{5}{x}$$

$$154.56x = 1813.2$$

x = 11.7 g. of C_6H_5-MgBr would be necessary. This would require

$$\frac{181.32}{157} = \frac{117}{x}$$

$$181.32x = 1836.9$$

x = 10.13 g. of C_6H_5Br, and

$$\frac{157}{24.32} = \frac{10.13}{x}$$

$$157x = 246.36$$

x = 1.6 g. of magnesium.

One and six tenths grams of magnesium turnings were placed in a flask and an ethereal solution of bromo benzene added. A crystal of iodine was added, and the whole was warmed gently until the reaction began. After it had ceased, the flask was cooled and 5 grams of the acid chloride were added drop by drop, and with constant shaking. Owing to the fact that the reaction was vigorous, it was necessary to cool it from time to time with cold water. When all of the chloride had been added, the mixture was boiled gently for an hour, after which it was cooled and poured into a beaker of cold water containing a few cubic centimeters of dilute sulphuric acid. The ether layer was then removed and shaken twice with an equal volume of water, containing a few drops of sulphuric acid. It was now evaporated, and the product, a viscous, dark brown liquid, distilled with steam and dried in a vacuum dessicator.

It was found to be readily soluble in ether, alcohol, and benzene, to which solvents it imparted a reddish-brown color. It boiled at 285° to 295°C.

According to Beilstein, (24) diphenyl ortho-tolyl carbinol is a solid, crystallizing from alcohol in rhombic crystals which melt at 98°C. The properties of this product, on the other hand coincided rather closely with those of phenyl ortho-tolyl ketone, and as it was thought that this compound may actually have been formed instead of the diphenyl ortho-tolyl carbinol, it was decided to redistill it. But in so doing it was found that only a relatively small portion came over, and that this portion came over at the boiling point of the ketone, and crystallized in the receiver. The remainder would not distill, even though the temperature was raised as high as 360°C, nor did it crystallize upon cooling. Instead, it retained the same characteristics it had previously shown. It was found, however, that the remaining substance could be distilled at reduced pressures; a viscous, yellow liquid collecting in the receiver, and a small amount of crystalline substance forming in the condenser. This latter was recrystallized from alcohol in small white cubes which did not exhibit the properties of diphenyl ortho-tolyl carbinol.

In order to determine whether or not a known sample of phenyl ortho-tolyl ketone would crystallize after being heated to a high temperature, as did the distillate in this case, a quantity was prepared after Elbs' method of preparing homologues of benzophenone.(25) Upon distilling this ketone, a large part of it crystallized in the receiver and in the condenser just as did the distillate from the Grignard reaction, and further, it had the same boiling point as well as physical appearance. Thus it was shown that a certain amount of phenyl ortho-tolyl ketone was formed in the Grignard reaction upon toluic acid chloride.

An attempt was now made to identify the other product of the reaction. It has been said that nothing further was separated by distillation at atmospheric pressure, nor could anything be made to crystallize from solutions in of the common solvents. A combustion was then run in order to gain what information this might yield. It gave the following results:

Weight of compound taken,	.3034
Weight of H_2O obtained,	.1677
Weight of CO_2 obtained,	.9301

Carbon: C in CO_2 = 27.27%

$.2727 \times .9301 = .2536$ g. carbon.

$\frac{.2536}{.3034} \times 100 = 83.58\%$ carbon.

Hydrogen: H in H_2O = 11.11%

.1111 x .1677 = .0186 g. of hydrogen.

$\frac{.0186}{.3034}$ x 100 = 6.13% hydrogen.

Oxygen = 100 - (83.58 + 6.13) = 9.29%

A second combustion gave results comparing very closely.

Weight of compound taken, . 3100

Weight of CO_2 obtained, .9492

Weight of H_2O obtained, .1686

Carbon: C in CO_2 = 27.27%

.2727 x .9492 = .2588 g. of carbon

$\frac{.2588}{.3100}$ x 100 = 83.50% carbon

Hydrogen: H in H_2O = 11.11%

.1111 x .1686 = .0187 g. of hydrogen.

$\frac{.0187}{.3100}$ x 100 = 6.03% hydrogen

Oxygen: 100 - (83.50 + 6.03) = 10.47% oxygen.

The following comparison shows the relative composition of phenyl ortho-tolyl ketone, diphenyl ortho-tolyl carbinol, and the product.

	Phenyl ortho-tolyl ketone (calculated)	Diphenyl ortho-tolyl carbinol (calculated)	Product (observed) average
Carbon,	85.67	87.54	83.54
Hydrogen,	6.16	6.65	6.08
Oxygen,	8.15	5.83	9.88

It was seen that the carbon and hydrogen found was lower than the calculated amounts in either phenyl ortho-tolyl ketone or di-phenyl ortho-tolyl carbinol. This was undoubtedly due to a small amount of ash remaining unburned after the combustion. After treatment with hot dilute sulphuric acid, the product no longer left any ash upon ignition.

Because the composition of the ketone and the carbinol compared so closely, it was felt that the results of a combustion would not be sufficiently conclusive evidence to identify the product. So in order to obtain a better means of identification, the molecular weight of the product was determined by the freezing point method. (26) It gave the following results:

Volume of solvent (benzene) = 25 c.c.
sp. gr. of solvent = .875 at 20° (Westphal balance)

Beckmann readings with pure solvent	
1 st	.804
2d	.804
3d	.806
Av.	.805

Beckmam readings with .167 g. compound in solution	
1st	.939
2d	.950
3d	.951
Av.	.947

$M = k \frac{w}{dW}$ where M is the molecular weight, k (for benzene) is 5120, w is the weight of the substance taken, W is the weight of the solvent, and d is the lowering of the freezing point.

$k = 5120$, $m = .167$, $d = (.947 - .805) = .142$, $w = (.875 \times 25) = 21.875$

$$\therefore \quad M = 5120 \; \frac{1.67}{.142 \times 21.875} = 279.78$$

This value for the molecular weight is only 2 per cent away from the true molecular weight of di-phenyl ortho-tolyl carbinol.

The fact still remained, however, that the compound did not exhibit the properties ascribed to the carbinol by other investigators.

At the same time several attempts to oxidize the compound to ortho-carboxy triphenyl carbinol ended in failure. This was not surprising since radicals in the ortho position are difficult as a rule, and often impossible to oxidize.

Further study of the reaction with ortho-benzoyl benzoic acid.

With the hope that, while one molecule of the Grignard reagent simply replaced the acid hydrogen of ortho-benzoyl benzoic acid, a second molecule might react in the desired manner, study of the reaction with the acid was resumed.

Molecular weight of ortho-benzoyl benzoic acid = 226.15

Molecular weight of bromo benzene = 157

Molecular weight of phenyl magnesium bromide = 181.32

If two molecules of the Grignard reagent, phenyl magnesium bromide were used, to one of the acid, 25 grams of the acid would require

$$\frac{226.15}{2(181.32)} = \frac{25}{x}$$

$$226.15x = 9066$$

x = 40 grams ofphenyl magnesium bromide.

And to prepare this

$$\frac{181.32}{157} = \frac{40}{x}$$

$$181.32x = 6280$$

x = 43.6 grams of bromo benzene are necessary, and 40 - 34.6 = 5.4 grams of magnesium.

Five and four tenths grams of magnesium turnings were, therefore, placed in a one liter flask, to which was then added 200 c.c. of dry ether and about 40 grams of bromo benzene, and the reaction started in the usual manner. After it had ceased and the solution had cooled, an ethereal solution of about 20 grams of ortho-benzoyl benzoic acid was added slowly and with constant shaking. After having been refluxed for about 36 hours, the flask was cooled and the ether filtered off with suction. After being washed several times with dry ether, the residue was then dried over sulphuric acid in a vacuum. When the last traces of ether had been removed, it was treated with about 200 c.c. of water containing about 20 c.c. of concentrated sulphuric acid, and at the same time cooled under running water. A rather vigorous reaction occurred, with the formation of a solid mass of yellow, gummy material. This was removed and treated four times with boiling water in order to remove any unchanged benzoyl benzoic acid. It was then treated with boiling petroleum ether to remove any unchanged bromo-benzene, and finally it was recrystallized three times from hot alcohol.

Identification

The product was difficultly soluble in cold alcohol, but easily so in hot, from which it crystallized in leaflets melting at 115°. It was soluble in ether, benzene, acetone, and hot alcoholic alkali. It was reprecipitated from a solution of the latter by dilution with water and then acidification of the mixture. It was soluble in concentrated sulphuric acid with an orange coloration, insoluble in concentrated hydrochlorid acid, petroleum ether, aqueous alkali, and hot water.

A molecular weight determination by the freezing point method gave the following results.

Beckmann readings with pure solvent		Beckmann readings with .2007 g. compound in solution	
1st	.858	1st	1.027
2d	.860	2d	1.030
3d	.861	3d	1.031
Av.	.860	Av.	1.029

Volume of solvent = 25 c.c.

Specific gravity = .875

$$M = k \frac{w}{dW}$$

$k = 5120$, $w = .2007$, $d = .169$, $W = 21.875$

$$M = 5120 \frac{.2007}{.169 \times 21.875} = 277.5$$

The compound was next analyzed for carbon and hydrogen, with the following results.

Weight of compound taken = .2081

Weight of CO_2 obtained = .6412

Weight of H_2O obtained = .0964

Carbon: C in CO_2 = 27.27%

.2727 x .6412 = .1748 g. of carbon.

$\frac{.1748}{.2081}$ x 100 = 83.99% carbon.

Hydrogen: H in H_2O = 11.11%

.1111 x .0964 = .0107 g. of hydrogen.

$\frac{.0107}{.2081}$ x 100 = 5.14% of hydrogen

Oxygen:

100 - (83.99 + 5.14) = 10.87% oxygen.

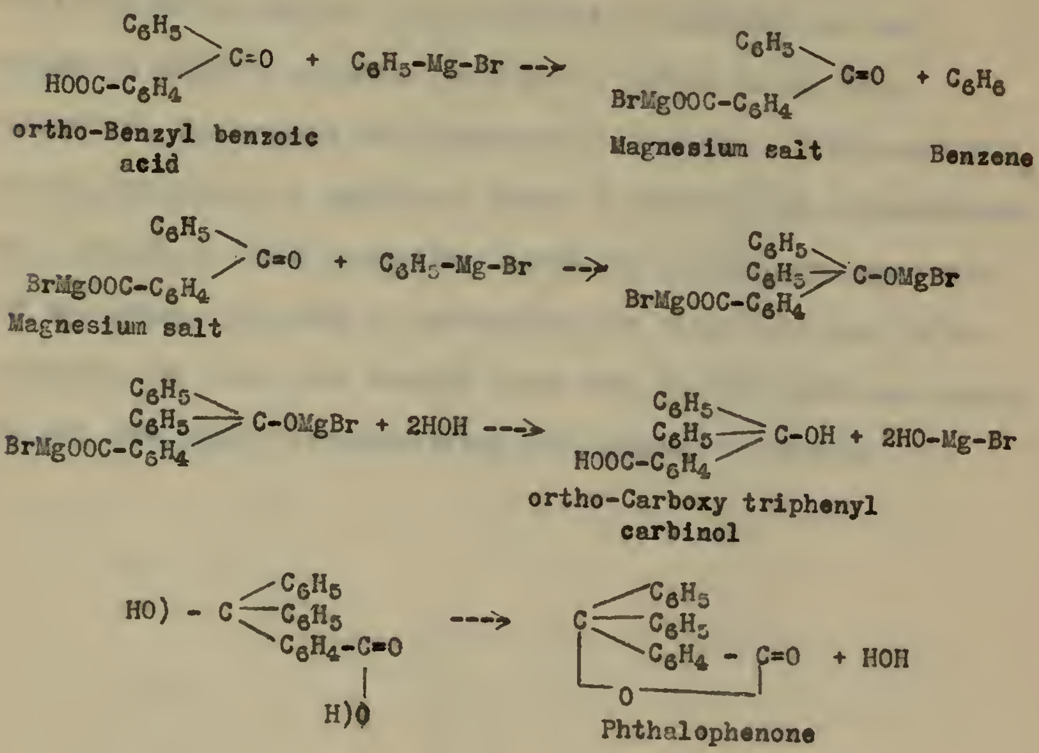
Since phthalophenone and ortho di-benzoyl benzene, either of which might have been formed by the reaction, have the same composition, the analysis does not distinguish between them. The molecular weight determination, while it indicates that there are three benzene rings in the compound, does no more towards distinguishing them since their molecular weights are identical. Hence, it now became necessary to determine to which compound its reactions corresponded. The oxime test for a ketone was first tried in the following manner.(27)

One part of the unknown compound, one part of sodium hydroxide, one part of hydroxyl amine, and five parts of alcohol were heated to boiling for 10 minutes. After being cooled the mixture was diluted with four parts of water and filtered until a clear solution was obtained. Upon neutralization with 6N. HCl, only a slight turbidity resulted.

When the solution was made slightly acid, a bulky white precipitate was thrown down. This precipitate rapidly collected into one mass which was observed to shrink in bulk until in a few moments it was no larger than a pea. Upon being recrystallized from alcohol, this substance was found to possess the same properties as did the compound which was being tested, and none of the properties of the oxime.

A blank test was then run in which the above procedure was repeated with the omission, only, of the hydroxyl amine, and results were obtained which were identical with those of the original test. This indicated that the substance was one which hydrolyzed in alcoholic alkali and was liberated again in acid solution.

The substance was thus found to exhibit none of the characteristics of ortho-dibenzoyl benzene as given by Beilstein, (28) while it did exhibit all of the properties of phthalophenone. (28) It crystallized in leaflets, melting at 115°, was insoluble in aqueous alkali solution, but was hydrolyzed upon heating in alcoholic alkali, and was soluble in alcohol, ether, benzene, and acetone. These facts, together with its composition and molecular weight, served to identify the compound as being without question, phthalophenone; its preparation being represented by the following reactions:



Molecular weight of benzoyl benzoic acid = 226.15

Molecular weight of phthalophenone = 286.2

$$\frac{226.15}{286.2} = \frac{20}{x}$$

$$226.15\,x = 5724$$

$x = 25.3$ g. of phthalophenone = theoretical yield. Ten grams was actually obtained. Therefore, $\frac{10}{25.3} \times 100 = 39.5\%$ yield was obtained. This yield could doubtless be considerably increased with a little practice.

In preparing a second lot of phthalophenone by the reaction which was developed, the mixture was cooled, as usual, after the final Grignard reaction had ceased, and the ether filtered off by suction. Then, instead of removing the last traces by means of suphuric acid over a vacuum, as has been described, the product was immediately hydrolyzed. This resulted in the liberation of sufficient ether to dissolve the phthalophenone. As a result, a thick syrup-like liquid was formed upon evaporation of the ether. In order to crystallize the phthalophenone, it was necessary to treat this several times with boiling petroleum ether. It was then easily recrystallized from alcohol as before.

CONCLUSIONS

The present investigation represents but a beginning in the study of the use of the Grignard reagent in the preparation of the tri-phenyl methane dyes as outlined in the theoretical discussion. Of the fifteen dyes which were listed therein, five were studied. Those remaining, and there are doubtless others which were not listed, still have to be investigated.

Malachite green and methyl violet were quite readily prepared through the reaction of appropriate Grignard reagents upon Michler's ketone.

There was evidence indicating the successful preparation of chrome green in a similar manner, although no positive proof was obtained.

The attempt to prepare chrome violet ended in failure.

Phthalophenone was prepared from ortho-benzoyl benzoic acid and phenyl magnesium bromide, and at the same time, the reaction between ortho-toluic acid chloride and phenyl magnesium bromide was investigated. The product of this reaction, a viscous liquid which did not exhibit the characteristics of di-phenyl ortho-tolyl carbinol which was being sought, was not identified.

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