ORGANIC OXIDATIONS WITH HYDROGEN PEROXIDE IN THE PRESENCE OF MOLYBDATES

by

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A THESIS
submitted to
OREGON STATE COLLEGE

in partial fulfillment of
the requirements for the
degree of

MASTER OF ARTS

June 1949
APPROVED:

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ACKNOWLEDGEMENT

Herewith I like to express my appreciation to Professor Bert E. Christensen for kindly allowing me to pursue and develop these studies. Sincere thanks must also be extended to Mr. C. H. Wang for his helpful assistance in the carbon and hydrogen determinations.
To my mother
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ORGANIC OXIDATIONS WITH HYDROGEN PEROXIDE IN THE PRESENCE OF MOLYBDATE

INTRODUCTION

The possibility of using molybdate catalysts in the hydrogen peroxide reactions involving organic compounds, arose from several considerations:

Molybdates, as well as oxides and salts of other so-called "peracid formers", such as tungsten, vanadium, titanium, zirconium, niobium and tantalum are very effective in catalysing certain inorganic reactions of hydrogen peroxide (1). A few illustrations may be cited:

a)- The oxidation of arsenous acid to arsenic acid (4), catalysed by salts of molybdenum.
b)- The oxidation of thiosulfates to sulfates, catalysed by salts of molybdenum (5), tungsten, vanadium, titanium, zirconium (2) niobium and tantalum (6).
c)- The oxidation of hydrobromic and hydriodic acids to bromine and iodine respectively (7).

The catalytic effect of the above mentioned elements is attributed to their ability of forming peracids with hydrogen peroxide (3). Organic acids, capable of forming peracids, as for example acetic and benzoic acids, also catalyse the above mentioned reactions, but to a much lesser degree. The decolorization of organic dyes by hydrogen peroxide has been found to be greatly accelerated by the presence of traces of "peracid formers", particularly
molybdate (8).

On the other hand, the use of peracetic and perbenzoic acids as oxidizing agents in organic chemistry, is well known. Since the inorganic peracids are so much more efficient than peracetic or perbenzoic acids in catalysing inorganic reactions, their use in connection with organic reactions should offer a fruitful field of investigation. For this reason the effect of molybdate on hydrogen peroxide oxidations of various organic compounds was studied.

Only in a few cases have molybdates been used with hydrogen peroxide in the oxidation of organic compounds. Toennies and Kolb (9) oxidized methionine to methionine sulfone with hydrogen peroxide and a mixture of perchloric acid and ammonium molybdate; Larsson (10) found that the oxidation of thioacetic acid and \( \beta,\beta' \)-thiodipropionic acids to the corresponding sulfoxides and sulfones by hydrogen peroxide proceeded rapidly in the presence of molybdic acid. In both cases, however, the amount of molybdate used seemed excessive and its universality as a catalyst in hydrogen peroxide oxidations, was by no means recognized. The only example where molybdate was used as a true catalyst, is the oxidation of acetaldehyde to acetic acid by hydrogen peroxide in the presence of molybdenum trioxide or vanadium pentoxide, described by Takigawa (11) in an analytical procedure of determining acetaldehyde by titration.
Boeseken and Lochmann von Koenigsfeldt (12) reported that a good yield of o-carboxycinnamic acid, together with a small amount of an unknown substance $C_{20}H_{14}O_4$, was obtained by the slow oxidation of $\beta$-naphthol using a dilute solution of peracetic acid. Greenspan (13) improved this procedure by using a concentrated instead of a dilute solution of peracetic acid, which resulted in an almost immediate deposition of crystals of o-carboxycinnamic acid.

There are many examples in the literature that demonstrate the decisive influence of the solvent on the course of the reaction when hydrogen peroxide or the peracids are used as reagents. In the Dakin reaction, for example, salicylaldehyde is oxidized to catechol, but only in proteolytic solvents such as glacial acetic acid, pyridine or water. In benzene or acetone, on the other hand, salicylic acid is the only product. The mode of action of peracetic and perbenzoic acids (generally used in different solvents) was also, for a long time, considered to be different, inasmuch as the former oxidizes double bonds to the glycol, whereas the latter yields the epoxide. However, it was discovered that both gave identical products when used with the same solvent (14). Therefore, in order to test the catalytic effect of molybdate on the reaction of hydrogen peroxide with $\beta$-naphthol, various experiments using different solvents were performed.
**1-Oxidation in aqueous solvents:**

\(\beta\)-Naphthol was suspended in very dilute hydrochloric acid with a trace of ammonium molybdate, and an excess 30% hydrogen peroxide added slowly. An exothermic reaction started immediately, but instead of proceeding to the colorless o-carboxycinnamic acid, the solution turned dark red and a black resin (I) precipitated. From the red solution a small amount of an orange red substance (II) separated on standing. In the absence of molybdate, the same reaction proceeded at a very slow rate; after thirty hours the solution was red and a red precipitate separated. This was found to be mostly unreacted \(\beta\)-naphthol, admixed with a small amount of a fine red precipitate.

The failure to obtain o-carboxycinnamic acid indicates that peracetic acid and molybdate catalysed peroxide (in which permolybdic acid is probably the responsible oxidizing agent) react in a completely different manner, under the prevailing conditions. This may be due to differences in the catalyst, but may also be due to differences in the solvents; the latter is probably the correct cause, as will be seen later.

The substance I was recrystallized from glacial acetic acid as shiny black crystals. However, it proved to be heterogeneous, since upon recrystallization from dilute acetone it was separated into a yellow, acetone insoluble compound III, as well as red crystals, which were identical to II.
The yellow compound III was identified as 1,1'-dinaphthalyl,3,4,3',4'-diquinone; it had a melting range of 289-295° (16) and a mixed melting point with 1,1'-dinaphthalyl-3,4,3',4'-diquinone prepared by oxidation of 3,4,3',4'-tetrahydroxy-1,1'-dinaphthyl with 3% hydrogen peroxide in the presence of molybdate (see experimental) gave no depression.

At first it appeared that compound II was an intermediate in the formation of o-carboxycinnamic acid, possibly β-naphthoquinone, with which it had many properties in common, such as melting range, color and general solubility characteristics. Furthermore, the fact that this orange compound II turned black under the influence of acids resembled the acid catalysed transformation of β-naphthoquinone to the black 1,1'-dinaphthyl diquinhydrone (IV), as described by Stenhouse and Groves (15), i.e.

\[
2 \quad \text{O} \quad \text{H}^+ \rightarrow \quad \text{IV}
\]

A comparison of the properties of β-naphthoquinone prepared according to the method of Lagodzinski and Hardine (17) with compound II, proved that these compounds were not
A systematic study of the properties of II was then undertaken; the compound was found to be soluble in all ordinary organic solvents (with the exception of carbon disulfide in which it was difficultly soluble), in sodium hydroxide, sodium carbonate and concentrated sulfuric and acetic acids. It was insoluble in sodium bicarbonate and dilute acids. The red alkaline solution turned readily dark, and compound II was not reprecipitated with dilute acids in the original form. Compound II gave a dark green color in concentrated sulfuric acid and a red color in glacial acetic. Recrystallization from dilute acetone gave shiny dark red crystals.

Molecular weight determinations gave an average value of 313, which indicates that condensation of two naphthol molecules must have taken place. The substance has an active oxygen (it liberates iodine from potassium iodide in acid solution) which is in the form of a carbonyl, since it forms a semicarbazone and a phenylhydrazone. It failed to add aniline, which indicates that no naphthoquinone group is present. Compound II gave a positive test with ferric chloride, which indicates the presence of phenolic groups. This is confirmed by the fact that II went into solution when boiled with barium carbonate and was reprecipitated by acids.

Compound II was reduced by sodium hydrosulfite or
sulfurous acid to a colorless compound V, which was slightly discolored by standing in air, characteristic of poly-phenolic materials. On reductive acetylation of II or acetylation of V identical acetyl derivatives were obtained. V was rapidly reoxidized to II by 3% hydrogen peroxide in the presence of molybdate.

Compound II has not been described in the literature, inasmuch as its properties do not correspond to any of the known compounds C$_{20}$H$_{14}$O$_4$ (13, 18, 19).

In an attempt to relate the structure of compound II to known compounds, the properties of the reduction product of II, namely V, were compared with the known tetrahydroxy-dinaphthyls derived from β-naphthol, VI, VII and VIII.

![Chemical Structures]

The melting point of V (203–204°C) was markedly different from that of VII and VIII so as to preclude the possibility of their being identical (20, 21). Since there is much controversy about the melting point of VI in the literature (174°C according to Stenhouse and Groves (15), 214°C according to Brass and Patzelt (20)), this compound
was prepared and on comparison was found to be different from V.

 Attempts to determine the parent hydrocarbon of II by zinc dust distillation and by zinc-zinc chloride fusion according to the method of Clar (22) yielded a compound, which, on the basis of melting point data and solubility characteristics, appeared to be 1,2-dinaphthyl; however there was insufficient material to confirm this result by analysis.

 On the basis of the incomplete data now available, it would appear that II may have a structure such as IX.

IX  

The formation of this kind of structure is understandable if one considers the reaction as follows: Assuming that the first step in the reaction is the formation of 1,2-dioxynaphthaline, according to
This can lose a proton, giving a radical capable of existing in the following resonance forms:

\[
\begin{align*}
X & \quad \leftrightarrow \quad \text{XI} & \quad \leftrightarrow \quad \text{XII} & \quad \leftrightarrow \quad \text{XIII} & \quad \leftrightarrow \quad \text{XIV} \\
\end{align*}
\]

The dimerization of any two of these would then give a compound \( \text{C}_{20}\text{H}_{14}\text{O}_4 \). Structure IX, for example, is obtained by combination of forms XI and XII. There is much evidence in the literature (23, 24, 25) for this type of mechanism, which would also explain the fact that a great variety of products other than II are obtained when the conditions of the reaction are changed. Evidence for side reactions is found in the isolation of the diquinone III from the reaction mixture, which indicates that intermediates such as XV, resulting from the combination of two molecules of form XIV are also produced. Whether the first step in the reaction is the loss of a proton from \( \beta \)-naphthol and dimerization of the resultant radical with consequent introduction of the missing hydroxyl group or the formation of the dihydroxy compound, is immaterial, since the result would be the same.

Due to the interesting properties of II, a series of experiments were undertaken in order to improve its yield. The reaction was tried under acid and basic conditions, in water, alcohol and acetone, with varying concentrations of
the reagent and the catalyst, with different types of molybdates and with varying temperature and reaction time. In all cases, the presence of molybdate increased the rate of the reaction very markedly, since without molybdate the reaction occurred very slowly or practically not at all. The following reactions were all performed in the presence of the catalyst.

In basic solution, a very exothermic reaction took place immediately and from the red solution an impure mixture I, composed of II and III, was precipitated upon acidi-fication.

In aqueous acetic acid solutions the reaction proceeded smoother than in either hydrochloric acid or basic solution, but nevertheless a mixture of II and III was obtained.

When the reaction was conducted in a homogeneous medium, such as aqueous alcohol or acetone, more satisfactory results were obtained. Water seemed to be necessary for the reaction, since the solution only became colored after addition of water to the reaction mixture. This might possibly be due to the solubility of the molybdate in the solvents used. The isolation of the product from the reaction mixture when alcohol or acetone were used as solvents, presented a special problem, since the precipitate obtained by pouring the solution into water was always too fine to be filtered. This difficulty was avoided by pouring the reaction mixture into a large volume of water and salting out
the orange precipitate, which was then obtained in excellent yield (see experimental).

The optimal amount of hydrogen peroxide was found to be two moles. The best temperature in the beginning of the reaction was found to be room temperature, cooling being recommended after the reaction has started. Cooling at the beginning delays the development of the reaction. Although the amount of the catalyst used is not very critical, its concentration affects the rate. A concentration of 0.01% for quantities from one to five grams, and 0.02% for smaller quantities is probably best. The type of molybdate used has a very marked influence on the rate, since with ammonium molybdate the reaction is complete in two hours, the reaction with sodium molybdate or molybdenum trioxide requires one day. These differences could be explained on the basis of differences of structure of the two types of salts.

According to Muthmann and Nagel (26), ammonium molybdate has the formula

\[
\begin{align*}
\text{(ONH}_4\text{)}_3 & \quad \text{Mo-O-Mo-O-Mo-O-Mo-O-Mo-O-Mo} \\
& \quad \text{(ONH}_4\text{)}_3
\end{align*}
\]

and gives a permolybdate of the formula:

\[
\begin{align*}
\text{(ONH}_4\text{)}_3 & \quad \text{Mo-O-Mo-O-Mo-O-Mo-O-Mo-O-Mo} \\
& \quad \text{(ONH}_4\text{)}_3
\end{align*}
\]
On the other hand, sodium molybdate is a direct derivative of molybdic acid, and gives a permolydate of the form:

\[
\begin{align*}
\text{Mo} & \quad \text{O} \quad \text{OH} \\
& \quad \text{O} \quad \text{OOH}
\end{align*}
\]

or

\[
\begin{align*}
\text{Mo} & \quad \text{O} \quad \text{OOH} \\
& \quad \text{O} \quad \text{OOH}
\end{align*}
\]

depending upon the amount of hydrogen peroxide present (27).

It is readily seen that in the ammonium permolybdate the oxygen is in a more labile form than in the relatively stable permolybdic acid, and also that the former is able to activate a larger amount of oxygen at one time.

Since all attempts in splitting the ring by employing a great excess of hydrogen peroxide failed in aqueous solution, (A great variety of high melting quinone like substances were obtained, but no acid) the reaction was then tried in glacial acetic.

2- Oxidation in glacial acetic acid

\(\beta\)-Naphthol was oxidized in glacial acetic, using the original conditions of Boeseken (12), with the exception that in one case 50 mg. of molybdate were added to the reaction mixture. Again without molybdate, the reaction occurred very slowly, a precipitate (XVI) being formed after several days, but only after an additional amount of hydrogen peroxide had been added. In the presence of molybdate, however, the precipitation of an acid (XVII) occurred immediately.
This illustrates the interesting fact that molybdate accelerates the rate of oxidation in the presence of per-acetic acid, but it also shows that the solvent is an important factor in determining the nature of the reaction product. One would expect then, that in a mixed solvent both reactions (one leading to a colored product and one to a colorless one) should compete, giving rise to a mixed reaction product. This indeed was found to be the case, inasmuch as reactions carried out in acetic acid containing 10% of water, the yield of colorless product was greatly decreased in the case without molybdate, and dropped to less than half in the presence of molybdate. Colored products were also obtained in both cases. A great difference in rate for the reactions with and without molybdate was again observed.

In order to establish definitely the similar action of peracetic acid and molybdate catalyzed peroxide when the same solvent is used, the composition of XVI and XVII had to be determined. The reported product for the uncatalyzed reaction is o-carboxycinnamic acid, for which however, there are no consistent data. Greenspan (13) gives a melting point of 204-205°, Boeseken (12) of 183-184° and finally in Beilstein the melting point is reported as being 173-174°. Heating of the acid yields a lactone, which according to Greenspan melts at 153° and according to Beilstein at 150-151°. These contradictory values may be due
to the fact that o-carboxycinnamic acid, like cinnamic acid itself, is capable of existing in several different forms of different melting point.

Upon examination, both XVI (product of the reaction without molybdate) and XVII (product of the reaction with molybdate) proved to be mixtures of at least two acids. By fractional crystallization from dilute alcohol, these products were separated into o-carboxycinnamic acid and an acid melting at 280-281° (XVIII). This acid had the properties of an acid described by Ehrlich (19), which he obtained in small yield besides o-carboxycinnamic acid in the oxidation of β-naphthol with dilute permanganate, and to which he assigned the empirical formula C₂₀H₁₂O₄. According to Ehrlich, the acid melts at 280-281°, is difficultly soluble in alcohol and practically insoluble in other solvents; from the saponification number it appears to be dibasic, but yields only monosalts and a monoethylester.

Since the acid contains twenty carbon atoms, it must be formed by combination of two naphthol molecules, both of which must therefore contain one atom of oxygen. The substance being a dicarboxylic acid, splitting of one ring must have occurred. The acid contains also one non-aromatic double bond, since on reduction with sodium amalgam it is converted to the acid C₂₀H₁₄O₄. With these
properties in mind, the acids \( \text{C}_{20}\text{H}_{12}\text{O}_4 \) and \( \text{C}_{20}\text{H}_{14}\text{O}_4 \) could
well be represented by formulas XIX and XX.

The formation of the acid should not, however, be
looked upon as an esterification of \( \text{o-carboxycinnamic acid} \)
with unreacted \( \beta \)-naphthol, since the conditions of the
reaction are not propitious for ester formation; it could
more adequately be explained by the following sequences of
reactions:

\[
\begin{align*}
\text{CH}^\text{OH} & \quad \text{H}^+ \\
\text{CH}^\text{O} & \quad \text{CH}^\text{O} \\
\text{CH}^\text{O} + \text{CH}^\text{O} & \quad \text{CH}^\text{O} \\
\end{align*}
\]
this formulation has much support from the fact that intermediate XXI has actually been isolated in the oxidation of β-naphthol with potassium ferricyanide. (25)
Oxidation of \( \alpha \)-Naphthol

When \( \alpha \)-naphthol was oxidized with hydrogen peroxide in the presence of molybdate in the manner described for \( \beta \)-naphthol, the reactions appeared to take a course similar to those of \( \beta \)-naphthol, yielding a dark red substance IIa, (see experimental).

Compound IIa was found to possess a carbonyl group (semicarbazone and phenylhydrazone formation) and hydroxyl groups. When reduced with sodium hydrosulfite it yielded a colorless compound (IIIa) melting at 179-181\(^\circ\)C, which was reoxidized to IIa with 3% hydrogen peroxide in the presence of molybdate. Reductive acetylation of IIa gave an acetyl derivative, melting at 101-102\(^\circ\)C. From analytical data, the empirical formula was found to be \( C_{20}H_{14}O_4 \), and therefore isomeric to II.

The properties of IIa are different from those of other compound of the same empirical formula derived from \( \alpha \)-naphthol (28).

Compound IIa cannot be correlated with any known compound by means of the reduction product IIIa, since it was found to be different from \( 1,4,1',4' \)-tetrahydroxy-2,2'-dinaphthyl, which is the only tetrahydroxydinaphthyl derived from \( \alpha \)-naphthol to be found in the literature.
OXIDATION OF PHENOL

In order to determine whether the formation of dimolecular condensation products in the oxidation of aromatic hydroxy compounds by molybdate catalysed peroxide is a characteristic property of this reagent, similar experiments with phenol were undertaken.

The reaction was far less rapid than with the naphthols but after half an hour the solution turned red, passing to dark purple after one day in the refrigerator; a fine dark precipitate separated on standing. This precipitate was insoluble in benzene, ether or chloroform, but soluble in acetone and alcohol. The alcoholic solution reacts with semicarbazide, yielding a dark brown, high melting semicarbazone. The reaction appears, thus, to take the same general course as with the naphthols, inasmuch as a quinone different from either one of the benzoquinones was formed.

This result also differed from the results obtained with peracetic acid, which oxidizes phenol to cis, cis-muconic acid (29).
OXIDATION OF CINNAMIC ACID

Cinnamic acid in aqueous alcoholic solution and in the presence of little sulfuric acid and fifty mg. of ammonium molybdate, was oxidized with two moles of hydrogen peroxide.

After two hours at 80°, the solution turned blue (formation of molybdenum blue) which indicated the presence of reducing substances. The solution smelled strongly of benzaldehyde and gave a precipitate with 2,4-dinitrophenylhydrazine.

Part of the reaction mixture was treated with manganous sulfate to precipitate the unreacted cinnamic acid, which was removed by filtration. The addition of water to the filtrate precipitated a crystalline product which was soluble in bicarbonate. The filtrate from this product gave a positive test with ceric nitrate; a crystalline calcium salt could be obtained by addition of calcium chloride and reducing the volume, indicating thus, the presence of a hydroxy acid, presumably phenylglyceric acid.

The experiment was repeated in the absence of molybdate and after refluxing for four days, the cinnamic acid (M.P. 133°) was quantitatively recovered.

Although no attempt was made to isolate and identify the reaction products, the fact that reaction took place, well illustrates again the catalytic effect of molybdate
in oxidations with hydrogen peroxide; organic peracids do not react with cinnamic acid, even under drastic conditions (30, 31).
EXPERIMENTAL

o-Carboxycinnamic acid: Five g. of β-naphthol and 50 mg. of ammonium molybdate were dissolved in 30 ml. of glacial acetic acid; 18.5 ml. of 30% hydrogen peroxide were then added dropwise over a period of fifteen minutes. The reaction mixture was allowed to stand for one day in order to complete the crystallization of the product; yield, 4.5 g. The product was dissolved in 8% bicarbonate and reprecipitated with dilute hydrochloric acid. The slightly colored precipitate was decolorized by treating the alcoholic solution with charcoal and then saturating the hot filtrate with water.

In order to separate the o-carboxycinnamic acid from the acid C₂₀H₁₂O₄, the mixture was extracted with 33% boiling aqueous alcohol, and the extractant cooled in the refrigerator, yielding 3 g. of a fine crystalline powder, M.P. 191-192°. The operation was repeated with 25% alcohol, yielding a product melting at 189-190°, which remained constant after many recrystallizations from aqueous alcohol. The sublimation product melted at 150-151°, which is characteristic of the lactone of o-carboxycinnamic acid.

Analysis: Calculated for C₁₀H₈O₄: 62.5% C, 4.2% H, Neut. Eq. 96.

Found: 62.3% C, 4.6% H, Neut. Eq. 96.
Acid $\text{C}_2\text{O}_{12}\text{O}_4$: The mixture of acids (0.95 g.) obtained by the procedure described above were extracted several times with hot 33% aqueous alcohol and the residue recrystallized from 95% alcohol, yielding 0.18 g. of crystals melting at 280-281°.

**Analysis:** Calculated for $\text{C}_2\text{O}_{12}\text{O}_4$: 3.83% H, 75.92% C. 
Found: 4.3% H, 75.85% C.

**Compound $\text{C}_2\text{O}_{14}\text{O}_4$ from $\beta$-naphthol:** One g. of $\beta$-naphthol and 25 mg. of ammonium molybdate were dissolved in 15 ml. of 95% alcohol containing 2 ml. of glacial acetic acid; 1.6 ml. of 30% hydrogen peroxide (2 moles) were then added dropwise and the solution saturated with water. After a maximum of 10-15 minutes the reaction mixture was placed in the refrigerator, where it was kept for two to three hours in order to complete the reaction. (It is important that the reaction time should not be prolonged, since resinous materials will then contaminate the product). After this time alcohol was added to the reaction mixture in order to dissolve the partially precipitated product and the alcoholic solution poured with stirring to 500-700 ml. of water; the orange product was then coagulated by adding salt, yield 1 g. The product, which is practically pure, was dissolved in acetone, filtered if necessary and then saturated with water in the cold. Crystallization started immediately and after two hours at room temperature, shiny dark red crystals melting at 148° were obtained.
For larger quantities this procedure is not very satisfactory, due to the large quantities of alcohol necessary to dissolve all of the precipitate and the large volumes of water necessary for the precipitation. An alternative method can be employed: Five g. of β-naphthol were suspended in 100 ml. of 0.01 N hydrochloric acid containing 50 mg. of ammonium molybdate and 9 ml. of 30% hydrogen peroxide added dropwise to the stirred solution. After forty minutes the reaction mixture was filtered and 5 g. of a black product obtained. This was purified by repeated recrystallizations from dilute acetone in the manner described above. Instead of 30% hydrogen peroxide, a corresponding amount of 3% hydrogen peroxide can also be used, and the reaction time prolonged to two and a half hours.

**Analysis**: Calculated for C_{20}H_{14}O_{4}: M.W. 318, 75.45% C, 4.43% H.

**Found**: M.W. 313, 75.1% C, 4.4% H.

**Semicarbazone of compound II**: Two tenths of a g. of compound II were dissolved in boiling 95% alcohol and a hot solution of 0.3 g. of semicarbazide hydrochloride in a minimum amount of water was added. Boiling was continued for a few minutes and the hot solution saturated with water. The bright orange semicarbazone was obtained in practically pure form. After one recrystallization from aqueous alcohol, a constant melting point of 234° was obtained. After one more recrystallization the product was
ready for analysis.

**Analysis**: Calculated for \( \text{C}_{20}\text{H}_{14}\text{O}_{3}\cdot \text{CON}_{3}\text{H}_{3} \): 67.2% C, 4.55% H, 11.3% N.

Found: 67.4% C, 4.54% H, 11.55% N.

**Reduction product V**: Five tenths of a g. of compound II were dissolved in a minimum amount of alcohol and 200 ml. of water added. In this manner a colloidal precipitate of II was obtained, which is reduced more readily. The solution was heated and solid sodium hydrosulfite added until the reaction mixture appeared white. Heating was continued until a slightly buish precipitate coagulated. The solution was then allowed to cool and the precipitate (0.49 g.) which had a silvery appearance was filtered off and recrystallized from a large volume of water containing some sulfurous acid. (When it was necessary to decolorize with charcoal, a dilute alcoholic solution was used). The product was obtained in shiny colorless crystals, M.P. 203-204°.

**Compound IIIa from \( \alpha \)-naphthol**: One gram of \( \alpha \)-naphthol and 25 mg. of ammonium molybdate were dissolved in 15 ml. of 95% alcohol containing 2 ml. of glacial acetic acid, and 1.6 ml. of 30% hydrogen peroxide (2 moles) added slowly. The reaction proceeded very rapidly and after a maximum of five minutes the reaction mixture was stored in the refrigerator for two to three hours. The alcoholic solution was then precipitated and salted out in the same manner as
described for compound II, yielding 1 g. of a dark red product melting at 138°.

**Analysis**: Calculated for $\text{C}_{20}\text{H}_{14}\text{O}_{4}$: 75.45% C, 4.43% H.

  Found: 75.5% C, 4.5% H.

1,1'-dinaphthyl-3,4,3',4'-diquinone III: 3,4,3',4'-tetrahydroxy-1,1'-dinaphthyl (0.23 g) was dissolved in acetone and 3.5 ml. of 3% hydrogen peroxide (4 moles) added at once. No color change took place, but upon addition of one drop of a 5% ammonium molybdate solution, the reaction mixture turned dark instantaneously and the yellow diquinone (M.P. range 289-295°) precipitated. Yield: 0.2 g.

2. Ibid, p. 127.


5. E. Abel, Monatshefte 34, 821 (1913); Z Elektrochem 12, 480 (1913).


31. Ernst Weitz and Alfred Scheffer, Berichte 54, 2327 (1921).