

A THESIS

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by

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Dr. E. Raymond Riegel during 1922-1924.

I wish to express my appreciation for the constant attention and guidance of my instructor, Dr.E.Raymond Riegel, in the preparation of this study.

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A STUDY OF AROMATIC OXYALDEHYDES

Florence L. "Bertz"

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I. INTRODUCTION

This work consists essentially of a study of aromatic hydroxy aldehydes, commonly referred to as oxyaldehydes, and of their oxidations to the corresponding acids. Some work has been done in this field, but opportunities for research are still available. Among the pioneers in this work we find such prominent men as Kolbe, Tiemann, Schmitt, Craft, Koch, Etard, Etard, Friedel, Gattermann, their assistants and associates. The Friedel-Craft¹ reaction is now considered a type for the preparation of aromatic aldehydes, and the Reimer-Tiemann² method is the most important in the manufacture of the hydroxy aldehydes, which are under discussion in this thesis. To Kolbe³ belongs the credit for the development of the salicylic acid method, used so extensively in the present technical industry; while Schmitt³, an associate of Kolbe, has gained prominence by certain modification processes which were developed in his work in salicylic acid. By the collaboration of Gattermann and Koch,⁴ a method was perfected for the manufacture of aldehydes from aromatic hydrocarbons (which is not applicable to the phenol ethers); and the French chemist Etard forms aromatic aldehydes by treating aromatic hydrocarbons with chromyl chloride in carbon disulfide solution.

The wide application of the foregoing research work, made in industrial processes, show that the importance of further investigation is self evident. Furthermore, the oxyaldehydes are of particular scientific interest on account of the marked effect

1. Compt. rend., 64, 1394

2. Berichte Vol. 9, 423, 824



3. J. pr (2) 10, 89: 27, 39

4. Berichte vol. 30, 1622

" 31, 1149

Annalen 347, 347

on the properties of the benzene nucleus caused by the hydroxyl group. For these reasons this field was chosen.

For the principal experimental work in this study salicyl aldehyde, the ortho hydroxy-benzaldehyde , and para oxy-benzaldehyde  were used. The reactions of benzaldehyde furnish the master type. As the substituted aldehydes do not oxidize as readily as the benzaldehyde, a close investigation renders it apparent that the substituted nucleus differs in resistance to certain reagents. An attempt has been made in this experiment to determine, if possible, more of the characteristics of these substituted aldehydes and the nature of their reactions.

For the greater part we have repeated preparations for which methods are to be found, widely scattered, in the literature; the methods are not in general use, nor are the reactions run frequently; grouped together in this way they furnish the experimenter a reliable insight into the behavior of a specific group of organic compounds. The standard methods were extended and modified wherever possible.

The extension of experimental work will be found under XIV of Table of Contents. Lithium was used to influence the entering hydroxy group and aldehyde in the phenol radicle, and proved a failure even as far as formation of any oxyaldehyde was concerned. A rapid method for the preparation of potassium phenolate was developed, which yields a good grade of product,

unlike the product made according to the standard directions. A method for bleaching salicylic acid crystals was used which was effective in producing white crystals, and pure, as shown by the melting point. An attempt was made to convert salicylic acid to the para oxy-benzoic acid by the fusion of crystalline salicylic acid with KOH. This experiment was unsuccessful.

Observations made during experimentation all tend to show that it is easy to introduce an aldehyde or acid group in the benzene nucleus, but the more numerous the substituting groups, the more difficult is the formation of these derivatives. The introduction of one aldehyde group is comparatively easy, but the introduction of a second is difficult. The first aldehyde group acts as a barrier to the entrance of the second. The same retarding action is noticed when the hydroxy group is present in the benzene nucleus. Benzoic acid easily forms from benzaldehyde when mixed with caustic, while the hydroxy-benzaldehyde has to be fused with caustic in order to oxidize the aldehyde group. Similarly in the cresols the presence of the methyl group retards the reaction. One would assume from reports in the literature¹ that the aldehyde enters the cresol molecule with ease, but we had considerable difficulty in obtaining the oxytoluyl aldehyde. The same impression² is given that a second aldehyde group is easily introduced into salicyl aldehyde and para oxy-benzaldehyde; it was found on experimentation that only oxybenzaldehyde with para structure gave the dialdehyde, a small yield, while the salicyl aldehyde gave none.

1. Gattermann "Practical Methods of Organic Chemistry" p.342
2. " " " " p.343

In his textbook¹ Cohen says that carbon tetrachloride reacts in a manner similar to chloroform in the Reimer-Tiemann reaction, producing para oxybenzoic acid directly from phenol. On refluxing we found that the reaction did not take place; on consulting the original article we found that a bomb tube was necessary, and not mere refluxing. This illustrates the unreliability of textbooks in implying, by the absence, of cautionary remarks, that a reaction which takes place readily with the type substance of a series may ~~not~~ be extended at will, with the same ease, to homologous and related substances.

1. Cohen "Organic Chemistry for Advanced Students"
Part 1, page 195

II. GENERAL REMARKS ON EXPERIMENTAL PART

Preparation of Mono Oxyaldehydes

Phenol, which furnishes the simplest hydroxyaldehyde, was the material used in this experiment. The aldehyde group had to be introduced into the phenol by special treatment, namely the Reimer-Tiemann method. Ordinary hydrocarbons take up the aldehyde group very easily when treated with formyl chloride in the presence of a catalytic agent (Friedel-Craft Reaction); but the presence of the hydroxyl in the phenol renders such action impossible. The Reimer-Tiemann reaction produces two aldehydes from the phenol, one an ortho aldehyde and the other a para aldehyde, which on oxidation give the corresponding acids.

The Reimer-Tiemann reaction is particularly adapted to the treatment of hydroxy phenols, but, during the experimentation, it was observed that the presence of other substitution besides the hydroxyl retarded the rapid reaction. When ortho, meta and para cresols were used in place of phenol, the Reimer-Tiemann reaction did not bring about initial reaction in the mixture without the aid of heat. This is very unlike the phenol, where the reaction was so violent at times that a stream of cold water was necessary to cool the flask and keep the temperature within the desired range. Another interesting result observed was the influence of the hydroxyl group on the entering aldehyde. The substitution group (methyl) in the cresol did not direct it, but the hydroxyl group determined whether the aldehyde was to go ortho, meta or para.

Preparation of Dialdehydes

The introduction of the second aldehyde group in the phenol nucleus is not as readily accomplished as the first. If it were readily introduced the Reimer-Tiemann reaction would not cease on the introduction of the first, but would continue on and form a portion of, if not all, dialdehyde. Gattermann¹ stated that it was possible to take either salicyl aldehyde or para oxybenzaldehyde at the end of the first synthesis and repeat the process using the one or the other instead of phenol. When we repeated this experiment, we obtained some dialdehyde, but only a small amount. This conclusion may be drawn, that the aldehyde already present in the ring acts as a barrier to the second, making its entrance more difficult; the action suggests steric hindrance.

1. Gattermann, page 343

Oxidation of Oxyaldehydes to Acids

A-Oxidation by Fusion

In studying the reaction of the unsubstituted benzaldehyde it was noticed that simultaneous oxidation and reduction occurred. This, known as Cannizzaro's reaction, is brought about by simply emulsifying benzaldehyde with strong caustic potash solution at room temperature. After the mixture has been allowed to stand for 12 hours, the benzaldehyde will be found changed to benzoic acid, benzyl alcohol being formed as a by-product. In fact,

benzaldehyde oxidizes so readily that a crust of benzoic acid will form around the stopper of a bottle containing benzaldehyde as it stands in the air.

Such rapid oxidation was not found to be true of the substituted aldehydes. On dissolving them in concentrated caustic soda, a sodium salt is formed from these aldehydes and this salt, which precipitates at once, precludes the reaction which is obtained in the benzaldehyde emulsion. On neutralizing the salt, it gave back the same aldehyde in an unchanged condition. Unless high heat is applied, such as when fusion is resorted to, no oxidation takes place. The more complex the structure, the slower the oxidation. Paraoxybenzaldehyde easily oxidizes by fusion, but it takes more time to oxidize the toluyl aldehydes, obtained from the cresols, into the corresponding acids. All the hydroxy acids turned purple with ferric chloride test solution, except paraoxybenzoic acid, and it was in this manner that the para oxybenzoic acid was first brought to the attention of the chemists when working with salicylic acid.

B-Other Oxidizing Agents

The action of such oxidizing agents as $KMnO_4$ solution, chromate and dichromate solutions, Fenton's Reagent (hydrogen peroxide with a trace of ferrous sulfate) were tried. The attempts to oxidize the aldehydes with varying strengths of these solutions proved unsuccessful, and no oxidation products were found in the ether extractions of the solutions. In his book¹ Cohn stated

1. Lassar-Cohn- "Arbeits Methoden", page 593

that Fenton's Reagent introduced a hydroxyl group instead of oxidizing the aldehyde, but to date that evidence has not been verified in my experimental work.


Preparation of Oxy Acids Directly from Phenol

Caustic soda and phenol are treated with carbon dioxide and heated to a temperature of 190 degrees for 9 hours; salicylic acid is produced. Potassium hydroxide and phenol, when treated with carbon dioxide, and heated to the same temperature for 9 hours also give salicylic acid; however, if potassium hydroxide and phenol are heated an additional 2 hours in a stream of carbon dioxide at a temperature of 220 degrees, the salicylic is completely changed to para oxybenzoic acid. This is a remarkable fact, which has been known for some time¹. Heating caustic soda and phenol in carbon dioxide to 220 degrees C for an additional 2 hours is of no avail; no para oxybenzoic acid is formed.

We are thus lead to believe that sodium and potassium in some way determine the place in which the hydroxyl and acid groups enter the ring. We desired to know what directing influence a third alkali metal, lithium, might exert, so lithium phenolate was prepared and treated with carbon dioxide. After three attempts at varying temperatures, we found that no oxyacid formed. Instead lithium carbonate had been formed each time, and all the phenol had distilled unchanged. We have offered an explanation under part XII.

1. Journal für praktische Chemie (2); 10,89;27,39;31,397

PRELIMINARY EXPERIMENTATION ON CRUDE PARA OXYBENZALDEHYDE

Crude para oxybenzaldehyde  was bought and proved a decidedly impure product; its melting point being 105 degrees C, which is 11 degrees too low. In the pure state it is a white crystalline powder, with a pleasing vanilla like odor. The crude product was a deep orange color.

COLD SOLVENTS

Cold solvents, such as carbon tetrachloride, carbon disulfide, petroleum ether and benzol, had no effect on the para oxybenzaldehyde. It is slightly soluble in chloroform and readily soluble in alcohol and ether, dissolving with a deep orange color.

In cold water it is soluble to a slight extent. In acids it is insoluble; but in alkalies, especially sodium, potassium and ammonium it is very soluble, dissolving with a deep red color.

Ether is the solvent used throughout my experimental work where cold solution is desired, especially in extraction processes and crystallizations.

HOT SOLVENTS

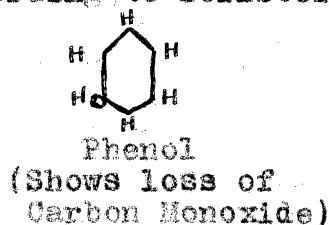
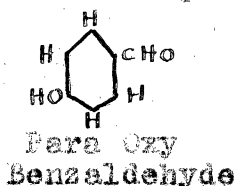
Hot solvents of the organic group, such as carbon tetrachloride, carbon disulfide and benzol, have no mere effect than the cold solvents. Hot chloroform dissolves it slightly, but not sufficient to warrant its use.

In hot water it is very soluble, so all work was carried on with hot aqueous solutions, if at all possible. The crude

aldehyde dissolves in this solvent with a deep, orange color and on the surface of the liquid an oily scum appears, later found to be the impurities.

PURIFICATION OF CRUDE SALT BY DISTILLATION
(negative)

The first step in purification was to try distillation. On heating the paraoxybenzaldehyde beyond 100 degrees C, the aldehyde decomposed, because the heat necessary to vaporize was sufficient to char the mass. Then I tried distilling in a vacuum and lowered the temperature to 53-54 degrees C. That also failed, showing the sensitivity of the aldehyde to heat. On the sides of the flask after decomposition I found a solid deposit of phenol; a decomposition product-reasonably to be expected; and in addition, a fluffy, white crystalline layer. A melting point was obtained on the white crystalline product. It was 116 degrees C, and corresponded to the pure aldehyde according to Beilstein.¹



SUBLIMATION

In my search through Beilstein for information on this aldehyde, I found that one of the properties of para oxybenzaldehyde was sublimation. So I tried to devise a method for the preparation of a considerable yield of the purified product. I used a sandbath, so that I could regulate the heat efficiently. In it I placed a watchglass containing a definite amount of aldehyde.

1. Beilstein vol. 111, page 81

Over this I suspended a funnel. On subliming the material I got a fairly good yield, but I could not get definite calculations on the crude aldehyde, because, on subliming, part of the aldehyde was converted into a resin by the high heat. If the sublimation process was concluded rapidly, I found less of this red material, than when the sublimation was interrupted too frequently. The pure sublimate is perfectly white and dissolves in its solvents with a water-white color. The red resinous material dissolved in caustic with a brilliant red color, and it is this red substance which is the main decomposition impurity.

I put a portion of the sublimed material in two bottles and placed one in the sunlight near the window and the other in a dark cupboard. In a few months I noticed a decided pink coloration in the one exposed to the light, while that in the dark cupboard was still perfectly white. Thus I have assumed that the crude material which was bought had originally a white color; but that, in the large quantity of production, there were more organic impurities hastening the process of decomposition. Methyl orange shows slight acidity with the decomposed (pink) product but not with the pure, white aldehyde, when first sublimed. This shows that there is some action going on in the material, due to light and air, which is particularly characteristic of the phenol derivatives.

PURIFICATION WITH POTASSIUM HYDROXIDE

The crude material was found to be very soluble in caustic soda solutions. One day while experimenting with a 1:1 NaOH solution I found, after dissolving the material, that crystals began to

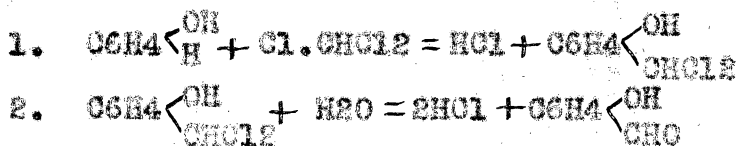
form when the liquid was allowed to stand for a few hours. This was found to be the potassium salt, which, on dissolving in water and subsequent neutralization with HCl, gave a fairly pure sample of the para oxybenzaldehyde with which I started.

Method: Dissolve the desired quantity of crude aldehyde in a 1:1 solution of NaOH or KOH, using the smallest quantity of solvent possible. Heat the mixture gently. The aldehyde dissolves with a deep, red color. The crystals which form on cooling have a faint pink or yellowish color. The impurity gives this deep-red color to the solution and the aldehyde gives only crystal formation; in this way it is possible to separate the aldehyde from the impurity. Subsequent washing of the crystals with 1:1 alkali solution gives fairly clean crystals with which one can experiment. On exposure to air these crystals form a white, amorphous powder, which turns a decided pink color.



IV. PARA OXYBENZALDEHYDE MADE BY THE
REIMER-TIEMANN REACTION ¹

The Reimer-Tiemann reaction is used extensively in the preparation of aromatic aldehydes. The action of chloroform on phenolates in the presence of caustic soda solution yields both the ortho and the para hydroxy aldehydes. The synthesis takes place in accordance with these reactions:



From 25 grams of phenol the theoretical yield of ortho aldehyde or salicyl aldehyde is 10-12 grams; and from 2-3 grams of the para form should result.

LABORATORY PROCESS

In a round bottomed flask of litre capacity I dissolved 80 grams of caustic potash in 80 cc water. Then 25 grams of phenol were added. A reflux condenser was attached to this, and, gradually adding 60 grams of chloroform, 15 cc at a time, I refluxed the solution two hours. It turned a fuchsine red and later an orange yellow color as the reaction proceeded. A constant temperature range between 65-70 degrees C was necessary throughout the synthesis. The reaction evolved heat and a stream of cold water was used to constantly cool the flask.

When the reaction was complete, the excess chloroform was distilled with steam and the solution remaining in the flask was acidified with dilute sulfuric acid. It turned from dark orange to light yellow. When this solution was again distilled with steam an oily liquid was obtained. This is the salicyl aldehyde.



ortho form

1. Berichte vol. 9, pages 423, 824

Salicyl aldehyde

This distillate containing the oil was cloudy, because of the suspension of minute globules of oily aldehyde in the water. On standing it cleared up and two distinct layers appeared. The theoretical yield of aldehyde is 10-12 grams. From the first experiment, I received 10 grams and from a second, I received 9 grams. By shaking the salicyl aldehyde with a saturated solution of sodium bisulfite, a double salt is formed. This may be filtered from the liquid impurities and, on acidifying it with sulfuric, again yields the aldehyde. This is the best method of purification. According to Beilstein¹ the boiling point is 196 degrees C. With temperature corrections, my sample boiled from 188.4-198.4 degrees C.

Para Oxybenzaldehyde

The solution remaining in the distilling flask, after the salicyl aldehyde is removed, contains the para oxybenzaldehyde. This solution is saturated with salt. Over night it will throw out the small crystals of para oxybenzaldehyde. When these are filtered, washed and recrystallized from dilute water solution of SO₂ (sulfur dioxide), white monoclinic crystals are obtained, having a melting point of 116 degrees C. as Beilstein states². The yield compared favorably with the theoretical yield of 3 grams.





The para oxybenzaldehyde, bought for experimental use, was a crude product. It had a deep red color, and a melting point 11

1. Beilstein vol. 2, page 81
2. Beilstein-vol 2, page 81

degrees too low. The experiment, showing the action of the light on the pure white aldehyde and the absence of that action when the product is placed in the dark, proves that the color changes are similar to phenol color changes.

In all stages of decomposition, however, the salt retains its pleasing odor. It smells like vanilla, and, on comparing the structural formulae of the two, it is found that the structure of vanilla is very like our aldehyde. Vanillin is a methoxy salt of para oxybenzaldehyde and it is evident that the pleasant odor is characteristic of this structure.

It may be that the success of the Reimer-Tiemann reaction with the phenols is merely that, owing to the formation of the sodium phenolate, the phenol is brought into a homogeneous system with the chloroform and caustic. As introduction of the aldehyde group is impossible in aromatic hydrocarbons, it must be the presence of the ONa in the ring reducing the resistance to reaction or attack, and balances the system. As soon as the phenolate has chloroform added to it, a red color develops. It may be that the sodium phenolate, dissolving in the chloroform, oxidizes to the quinoid. Such structure might be this  or this , and be the cause of the color change, but then other solvents ought to do the same.

PHENOL ETHERS

The phenol ethers are said to undergo the Reimer-Tiemann reaction, but anisol did not respond to us. Anisol is represented by this formula $C_6H_5.OCH_3$. It seems that polyatomic phenols when etherized must have at least one free hydroxyl left, if they are to undergo the Reimer-Tiemann reaction. If there is no free hydroxyl, the experiment will be a failure. My own experience showed that it would not react, as I reclaimed the unchanged anisol at the end of the experiment. This evidence should render the alkali phenolate structure still more important.

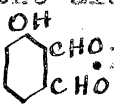
In order to introduce the aldehyde group in phenol ethers, we must use the modified Gattermann-Koch process (in which HCl and Hydrocyanic Acids are used with a catalytic agent, instead of carbon monoxide and HCl in the presence of cuprous chloride). The modification process provides for such structure as anisol, while the unmodified process will readily attack such structures as benzene and toluene.

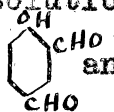
DIALDEHYDES PREPARED BY THE REIMER-TIEMANN¹ PROCESS

The introduction of one aldehyde group in phenol is a simple matter, but it is not so easy to introduce as the second group. It is perfectly obvious that if a second group went in with the same ease as the first, the ordinary Reimer-Tiemann, run the first time, would produce some dialdehyde at least. At the end of the first reaction, products of salicyl aldehyde and para oxybenzaldehyde are obtained, which are pure and show no contamination.

1. Beilstein vol.1 page 106

V. THE DIALDEHYDES

From salicyl aldehyde, the ortho aldehyde, is formed a dialdehyde, called phenoldimethylal . It is made by the action of additional caustic soda and chloroform acting on the salicyl aldehyde oil. Fine needles should separate from the solution at the end of the reaction, and should melt at 88 degrees C, form a bisulfite salt, give a red-violet color with ferric chloride test solution, readily dissolve in water and in petroleum ether.

From paraoxybenzaldehyde, by the action of caustic and chloroform, we get fine needles similar to the others; but these melt at 108 degrees C. They do not readily dissolve in alcohol or water, but are soluble in ether and chloroform. They give the same color change with ferric chloride test solution and form bisulfite salts. It forms a-oxyisophthalic acid on fusion with caustic potash. This dialdehyde may be separated from the other formed above by petroleum ether method. This dialdehyde is insoluble in petroleum ether, while the other will go into solution. The structure of this dialdehyde is represented thus  and a larger yield forms from para oxybenzaldehyde, although salicyl aldehyde may be used to prepare it, if desired.

Laboratory Process

I used both salicyl aldehyde and paraoxybenzaldehyde to prepare the dialdehydes, but could get no result from salicyl aldehyde. Para oxybenzaldehyde gave a small precipitate, melting at 106 degrees C, but the yield was very unsatisfactory.

VI. STUDY OF THE HOMOLOGUES OF OXYBENZALDEHYDE

- THE CRESOLS-

Reimer-Tiemann Reaction on Orth, Meta and Para Cresol

The experiment was made in order to study the ease with which the aldehyde groups enter the cresol compounds. Although most references required the formation of cresol ether, before the introduction of the aldehyde group, I tried it on the cresol directly. Gattermann¹ said that it could be accomplished in the same manner and as easily as aldehyde introduction in phenol, but I found the synthesis slow and difficult. However, I obtained fairly good yields and the boiling points of my products compared favorably with those listed in Beilstein.²

Laboratory Process for Preparation of 1:2 Oxytoluyl Aldehyde

To a solution of 80 grams caustic soda in 80 cc water is added 27 grams of ortho cresol; then 60 grams of chloroform are added, in three portions, while refluxing for a period of 2 hours. The temperature must be carefully controlled so that it is just a trifle higher than the boiling point of the chloroform.

On the addition of the first portion of the chloroform, the mixture assumes a deep magenta color, which turns to a blood red later as the reaction proceeds. On the addition of the second portion the color turns a deep brown and a heavy, curdy mass begins to precipitate. When the last portion of the chloroform is added the formation of two distinct precipitates becomes apparent; one is a dark brown, the other a straw color.

In this experiment no chloroform could be distilled with steam when the reaction was complete. In the phenol synthesis there

1. Gatterman, page 342. 2. Beilstein vol. 3, p. 88-89

was an excess after the reaction.

I acidified this solution with dilute sulfuric acid and it turned a light yellow, with a heavy tar-like mass floating in large globules. The mixture was filtered and distilled with steam until no more oil separated from it. The distillation was a slow process taking nearly three hours. The solution remaining in the flask was salted out, but nothing appeared; so it was discarded.

This experiment was repeated three times and with each operation an oily product, weighing between 8-9 grams, was obtained. The boiling point was 206 degrees C, as listed in Beilstein¹; with temperature corrections my product boiled at 198.7-206.7 degrees C. The boiling point of the original ortho cresol was 191 degrees C.

Preparation of 1;3 Oxytoluyl Aldehyde
(Using Meta Cresol)

Meta cresol was treated in the same manner as the ortho cresol, with similar results. In this experiment, however, I noticed more violent reaction; it frothed, bumped and very nearly foamed over into the receiver, during the steam distillation while attempting to drive off the excess chloroform.

After the reaction the mixture was acidulated with dilute sulfuric acid and, on distilling a second time with steam, an oily liquid passed into the receiver. It was similar to that in ortho cresol. The yield was 8 grams. The boiling point was 215-226 degrees C. Beilstein gives 222-223 degrees C.¹ The boiling point of the original meta cresol was 203 degrees C.

1. Beilstein Vol 3, pages 88-89

Preparation of 1:4 Oxytoluyl Aldehyde
(Using Para Cresol)

This, likewise, was treated in a manner similar to the foregoing cresols. The results were similar. The oily liquid received had a boiling point of 215-224 degrees C. Beilstein records that it should be 222-223 degrees C.¹ The original para cresol boiled at 202 degrees C.

Properties of the Oxytoluyl Aldehydes

According to Beilstein¹, the aldehydes should be solid, crystalline substances; the only one which I obtained in the solid form was para cresol derivative, and that was not stable. The oxytoluyl aldehyde made from the ortho cresol turned a deep fuchsine red on standing; and now after standing about 4 months I notice that it is forming a precipitate and that this precipitate is increasing every day. This may be due to the pure salt separating from the product obtained, and thus showing that an impurity prevented immediate formation of a solid at the time of the experiment. The oxytoluyl aldehyde obtained from the meta cresol was a liquid, likewise, and has become so dark on standing that light will not penetrate. I notice no precipitation here.

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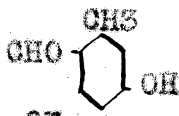
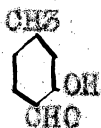
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From my experimental work, I have found that the aldehyde group enters the phenol group ortho to the hydroxyl if caustic soda is used. I may assume, therefore, that in the cresols, the aldehyde enters the molecule in like manner, ortho, to the hydroxyl, and I should have the following formulae representing my products:

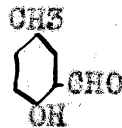
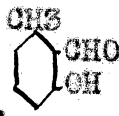
1. Beilstein vol. 3, pages 88-89



1:2 oxytoluyl aldehyde (ortho derivative)



1:3 oxytoluyl aldehydes (from meta cresol)



1:4 oxytoluyl aldehyde (para derivative)

I assume that only one form results from the meta cresol, although two other forms are possible. I assume further that no para was formed, because the boiling points of my product were within comparatively narrow limits.

My purpose, now, is to perform and study oxidation of the aldehyde groups to the corresponding cresotinic acids, as I did in the previous oxyaldehydes.

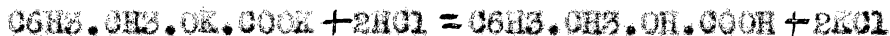
VII. OXIDATION OF THE OXYTOLUYL ALDEHYDES TO CRESOTINIC ACIDS

As the paraoxybenzaldehyde was readily oxidized by fusion with KOH, I decided to apply the same treatment to the oxytoluyl aldehydes which were obtained from the three cresols.

On fusion with caustic potash and, on subsequent neutralization of the solution obtained, a fluffy, white crystalline mass was found, which proved by its melting point to be cresotinic acid. The melting point was 151 degrees C.

Laboratory Method

To 10 grams of the oxytoluyl aldehyde, obtained from the para cresol (used because it was more nearly crystalline than any other formed), I added 8 grams of caustic potash. This was placed in a porcelain dish and fused over a fairly hot flame, while being stirred constantly. After heating for half an hour, I tested it to see if it had oxidized, but reclaimed the unchanged cresol aldehyde. Two hours of fusion were necessary to oxidize the oxytoluyl aldehyde, although it appeared to oxidize more rapidly than para oxybenzaldehyde. After the fusion, the mass was dissolved in water and filtered. HCl neutralized the alkaline solution and then the precipitate appeared:



The first reaction shows the fusion with caustic potash. The second shows acid neutralization and formation of the cresotinic acid.

The crystals are soluble in water (hot) and, after filtering from the acid solution, a clear hot concentrated solution of the acid may be obtained, which will recrystallize on standing. A

white, amorphous mass, with cresol-like odor separated. It had a melting point of 151 degrees C. Beilstein lists it at 155 C;¹ the maximum yield is 11 grams and I obtained but 6 grams.

1. Beilstein vol. 2 pages 1544, 1545, 1546

VIII. BENZOIC ACID AND BENZYL ALCOHOL¹

In a thick walled ehrlenmeyer flask I poured a solution of 36 grams of KOH in 24 grams of water. To this I added 40 gms of benzaldehyde, and, stoppering the container, shook vigorously until a thick, white, pasty emulsion formed. This was allowed to stand for 12 hours.

In the morning a curdy mass, potassium benzoate, had separated, leaving a clear liquid. I filtered the curdy mass and redissolved it in water. Then by extracting the solution with ether and later evaporation, benzyl alcohol was obtained. It weighed 17 grams, the theoretical yield being 18 grams. It is a clear, pale yellow liquid having a strong odor of benzaldehyde. According to Beilstein the boiling point is 206 degrees C; with temperature corrections my product boiled from 202 to 209 degrees C.

To the clear alkaline solution, which separated from the curdy mass on filtering, a sufficient quantity of HCl was added to neutralize the mixture. This precipitated the benzoic acid with the formation of potassium chloride. It was not as white and pure as desired, so it was reprecipitated. The following reactions show the formation of both acid and alcohol:



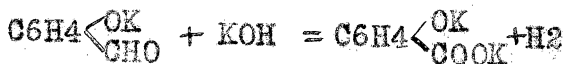
In this experiment simultaneous oxidation and reduction occur. As shown, the benzaldehyde readily oxidizes to the benzoic on mere contact with KOH solution. It is more difficult, however, to obtain this same oxidation if an OH radicle is present, as in the para-benzaldehyde. In that case it is necessary to fuse for two hours before the reaction with KOH is complete.

1. Berichte 14, page 2397

IX. PARAOXYBENZOIC ACID FROM THE ALDEHYDE BY FUSION WITH CAUSTIC

If oxidation is to be obtained by this method, it is advisable to use the purest form of para oxybenzaldehyde which can be procured. As already illustrated, the para oxybenzaldehyde undergoes a change on exposure to light and air, and turns from a white to a deep red colored material, showing the presence of decomposition products. These separate out as oily, tarlike scum when the aldehyde is dissolved in hot water. It goes through filter papers, when the solutions are hot and clings to the crystals on cooling in a hard resinous mass, making it almost impossible to separate clean crystals of the acid.

For this reason a potassium salt or a sublimed para oxybenzaldehyde is best for use. To 25 grams of the potassium salt I added 8 grams of caustic potash and fused them in a porcelain dish over a hot flame. It is necessary to allow sufficient time for the oxidation. Several times during the experiments I noticed that I obtained the original melting point 116 degrees C instead of 210 degrees C, showing an oxidized product. Thus I noticed that it was necessary to heat the mass for at least 2 hours before the action was complete. While fusing it was stirred constantly to prevent decomposition, which occurred very easily with the high heat. The reaction is as follows:



1. Beilstein Vol 2, page 1523

This mass is then dissolved in water and the solution is filtered. On neutralizing the solution with HCl acid until slightly acid, a fine, white precipitate should appear, which is para oxybenzoic acid.

$$C_6H_4OK_2COOK + 2HCl = C_6H_4OH_2COOH + 2KCl$$

This precipitate is carefully separated by filtration to rid it of the KCl in the solution and then it is redissolved in water. I have found that animal charcoal is very effective in decolorizing the solutions and the resulting crystallization is very satisfactory. Pure para oxybenzoic acid with a melting point of 210 degrees C is thus obtained.

For every 25 grams of para oxybenzaldehyde, the theoretical yield of acid is 22 grams. I received 20 grams of acid, a fairly good yield, in view of the fact that an absolute conversion to the acid is difficult to accomplish.

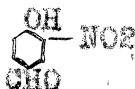
PROPERTIES OF PARA OXYBENZOIC ACID

Para oxybenzoic acid forms in clear, monoclinic crystals or in needles, if there is sufficient solvent; in concentrated solutions it is precipitated as an amorphous powder. It is insoluble in most organic solvents, with the exception of alcohol and ether. In hot water it is very soluble, also in warm ether and alcohol solutions. It does not turn purple with ferric chloride test solution. In this manner it was originally isolated from the salicylic acid with which it forms in the Kolbe Process. Another distinguishing characteristic is that it does not form an oxime like salicylic acid.

It forms the nitro body readily when a solution of the acid is boiled with concentrated nitric acid. At 150 degrees C the crystals effloresce and become opaque. They contained about 13.5 % water of crystallization, according to my determination. At very high temperatures the para oxybenzoic decomposes into CO₂ and phenol.

PREPARATION OF NITRO PARA OXYBENZOIC ACID

While experimenting with the oxidizing agents, I accidentally made nitro para oxy benzaldehyde, when boiling a concentrated nitric acid solution with some para oxybenzaldehyde. An orange-yellow precipitate formed which had a melting point of 138 degrees C. That specified in Beilstein¹ had a melting point of 139 -140.5 degrees C.



I applied the same treatment to para oxybenzoic acid in an attempt to obtain a nitro body in the same manner. It reacted violently with the nitric acid, accompanied by effervescence and liberation of nitrogen peroxide fumes. As the solution cooled a heavy, orange-yellow precipitate appeared, similar to the nitro body prepared in the previous experiment. This product has a melting point of 180 degrees C. Beilstein² gives 185 degrees C. A combustion determination will be run on this nitro body to determine the quantities of carbon, hydrogen, oxygen and nitrogen present.

1. Beilstein Vol. 11, page 83

2. Beilstein Vol. 11, page 1538

XI. THE KOLBE PROCESS¹

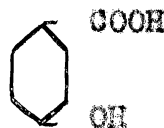
Treatment of Alkali Phenolates with Carbon Dioxide

One of the technical methods extensively used in the preparation of salicylic acid is the Kolbe process. Dried sodium phenolate is prepared and heated to a temperature of 190 degrees C with a stream of carbon dioxide for 7 or 8 hours. A sodium salt of salicylic acid is formed and some unchanged phenol remains.

A curious reaction is noticed, however, when potassium phenolate is used instead of sodium phenolate. The sodium salt reacts to give ortho form, which is called salicylic acid, while the potassium phenolate gives para oxybenzoic acid:



(ortho form)
Salicylic Acid
Made with NaOH



(para form)
Para oxybenzoic
Made with KOH

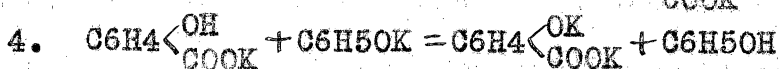
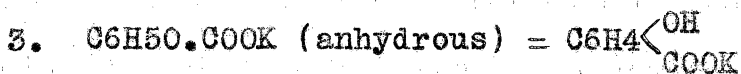
The mechanism of the reaction, for the potassium salt, is as follows: first, the potassium phenolate absorbs carbon dioxide and potassium phenyl carbonate is formed. On additional treatment with carbon dioxide above 150 degrees C, the para variety results. Below this temperature the ortho form may appear, so great care should be taken to regulate the temperature. When 220 degrees C is reached the potassium oxybenzoate salt is the only product left in the retort, the phenol having distilled.

1. Journal für praktische Chemie(2) 10,89;27,39;31,397.

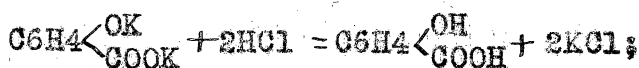
Lehrbuch der Organischen Chemie (Meyer-Jacobsen) Vol 2

#1 pages 517-518

Reactions in four steps as proposed by Gattermann: ¹



The potassium salt of the para oxybenzoic acid is then treated with concentrated hydrochloric acid:



and the para oxybenzoic acid separates in long needles, which are dark orange to brown in color. When crystallized from hot water and alcohol a second time, they appear perfectly white. The melting point is 210 degrees C. Meyer and Jacobsen claim that the foregoing changes are due to different precipitates formed from the alkaline phenolate by the intermediate steps of the phenyl-carbonate alkalies. A neutral alkaline salicylate forms first, which at higher temperatures is converted to a basic salt, and then the precipitate rearranges itself to the para compound, while the sodium remains fixed as the ortho.

LABORATORY PROCESS
(Details of Procedure)
Preparation of Potassium Phenolate

The first step in the preparation of para oxybenzoic acid is the manufacture of perfectly dry potassium phenolate. To 30 grams of crystallized phenol, add 17.5 grams of pure potassium hydroxide

1. Gattermann-Practical Methods of Organic Chemistry, p.346-347.

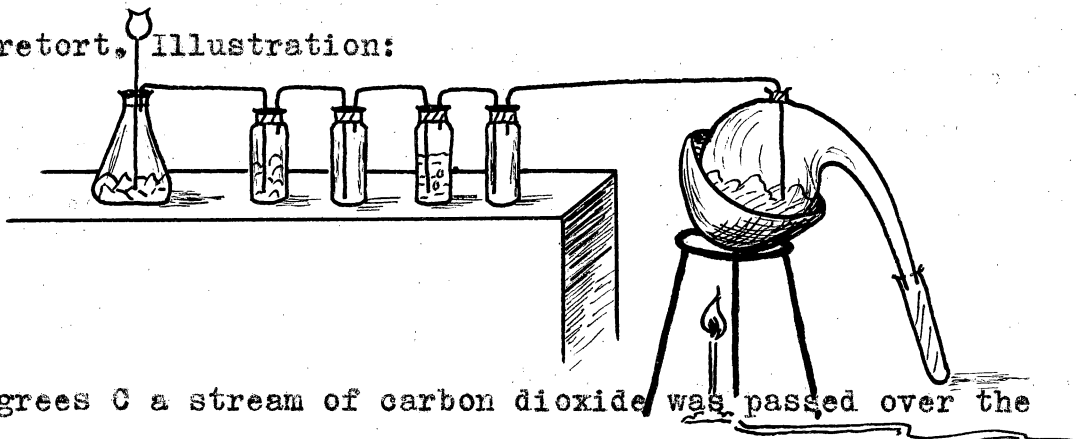
and dissolve in 20 cc of water. This is the prescribed process in Gattermann; but I found that the quantity of water was more than sufficient and its slow evaporation retarded the process, so that a large percent of decomposed phenol resulted. In order to overcome this, I took stick caustic potash and dissolved it directly in melted phenol crystals, regulating the temperature carefully by means of a constantly moving, luminous flame; and stirred during the entire process. A caked mass, of bright pink color, formed first; this grew darker as it became dry. The final product was a dry, brown, sandy granulation. This process took the greater part of one day, so the salt was placed in a dessicator over night and the carbon dioxide treatment was started the following morning. The success of the experiment depends on the use of a perfectly dry, grainy phenolate. If there is any lumping, as the treatment proceeds it is advisable to discontinue the experiment.

Treatment with Carbon Dioxide

The potassium phenolate was placed in a perfectly dry retort inclined at such an angle that moisture and phenol passed into the tube and run out of the retort. Asbestos paper was laid on the bulb of the retort to keep it warm enough to prevent condensation of moisture in the retort; this would run down the sides of the bulb into the salt and produce lumping.

The retort was paced in an oil bath, to regulate the temperature more accurately, and a carbon dioxide generator was then attached to it by means of a series of intervening drying

bottles. The tube conducting the carbon dioxide was about half an inch above the surface of the potassium phenolate, when fitted into the retort. Illustration:



At 110 degrees C a stream of carbon dioxide was passed over the salt and continued for an hour; then the temperature was gradually raised 20 degrees an hour during the course of 5 hours. When 210 degrees C was reached, the mass was heated for 2 hours up to a temperature not exceeding 220 degrees C. During the process some phenol had distilled and condensed in the test tube.

Meyer and Jacobsen say that a high temperature is needed for this reaction in order to obtain a good yield of para oxybenzoic acid, because a low temperature will produce a quantity of salicylic acid, which is converted at the higher temperature into the para oxybenzoic acid. Likewise, care should be taken to prevent a decomposition of para oxybenzoic acid into phenol and carbon dioxide at a temperature higher than 220 degrees C.

Treatment After the Oxidation

At the end of the 8 hour oxidation, the residue in the retort was dissolved in water and treated in an ice bath with concentrated HCl acid until the solution was slightly acid. A heavy precipitate resulted. This was crude para oxybenzoic acid.

The precipitate was then dissolved in hot water and refiltered with animal charcoal in order to decolorize as much as possible and purify, before setting aside to crystallize. In 24 hours light brown, monoclinic crystals formed from the aqueous solution. According to Beilstein¹ an alcoholic mixture gives larger crystals but I found that the crystals from the pure water solution were clearer and more definite in form. The melting point was 210 degrees C, and showed an absolutely pure product. This proved that there was no salicylic acid formation present. The melting point of salicylic acid is 156 degrees C, and on crystallizing it forms needle-like crystals in fluffy masses, very different from the crystals obtained here. One of the principle differences between the two acids is the reaction with ferric chloride test solution. Salicylic acid solution turns a very deep purple when a drop of ferric chloride solution is put into it, while para oxybenzoic acid solution remains unchanged in color. Aside from the melting point this is the best test for purity, when obtaining yields of the two acids, especially when potassium phenolate is used. According to Gattermann², the maximum yield for 30 grams of phenol is about 10 grams of acid. My product weighed 7.5 grams.

1. Beilstein vol. 2, page 1523

2. Gatterman, Practical Methods of Organic Chemistry, p. 345

XII. LITHIUM EXPERIMENT

In the hope that a third arrangement of hydroxyl and acid groups might be obtained, another alkali was used; namely, lithium, which has alkalinity even greater than potassium or sodium.

Six grams of lithium hydroxide were dissolved in hot water with 12 grams of phenol. A clear solution resulted, which, on cooling, showed a precipitation of pearly flakes of the salt. The physical properties of the new compound were unlike those of either the lithium hydroxide or the phenol, showing a new compound. The presence of phenol was definitely determined by para amido phenol with sodium hypochlorite; a beautiful blue color of indo-phenol being formed.

The Kolbe apparatus similar to that used with potassium phenolate was set up and the carbon dioxide gas allowed to enter the retort, which was placed in the hot oil bath. As lithium is an alkali stronger than potassium, it was suggested that a lower temperature might suffice for the reaction. So for 8 hours the temperature was allowed to range from 110 degrees C to 190 degrees C, being raised 20 degrees an hour. The phenol distilled over in a manner similar to the foregoing experiments. When the reaction was complete and the mixture was dissolved in water, a violent effervescence occurred when I tried to neutralize it with HCl. After the effervescence had ceased a clear solution remained, no oxy acid was visible; this showed the formation of lithium carbonate and the liberation of phenol during the reaction.

A second attempt was made with a very low temperature, endeavouring to determine if high temperatures decomposed the desired product as soon as formed. Although the temperature was not allowed to range above 50-60 degrees C, the lithium still formed the carbonate and gave up the unchanged phenol.

Finally, a third attempt was made in which very high temperatures were used, 190-240 degrees C, in order to obtain sufficient heat for the carbon dioxide to attack the lithium phenolate while the excess phenol was distilling; and thus test the entrance of the acid and hydroxyl into the ring; but this also was a failure.

As potassium and sodium determine the position of the entering acid and hydroxyl groups under certain temperature conditions, lithium, under similar conditions, should have given some results, in as much as it belonged to the alkali group and formed the phenolate.

From the experimental evidence here, it is assumed that the lithium was too active an alkali, its affinity for carbon dioxide too great to allow of any other formation than lithium carbonate. The phenol, liberated from lithium combination at the entrance of the carbon dioxide, was distilled in the free state, regardless of temperature conditions.

PREPARATION OF PARA OXYBENZOIC ACID BY REIMER-TIEMANN BOMB¹

METHOD

Para oxybenzoic acid may be prepared by the Reimer-Tiemann bomb method, in which carbon tetrachloride is used instead of chloroform in the reaction with caustic soda and phenol. A hard glass carius tube was used. To 28 parts of caustic soda, dissolved in the smallest quantity of water, 17 grams of carbontetrachloride were added, and 10 grams of crystallized phenol. Then enough alcohol was poured into the mixture to clear up the turbidity caused by the carbon tetrachloride. This carius tube was then put in the furnace and heated at a temperature of 100 degrees C for three days. After a few hours of heating, sodium chloride crystals begin to separate and the color of the mass becomes a bright red and remains so if the experiment is to be successful. If the color turns black, it means that there is either too strong alkali present or that the temperature rose too high. If this color change has occurred, it is useless to continue, because decomposition has already set in. If the experiment is successful, add ten volumes of water to the mass in the tube at the end of the 3 day reaction and distill off the unchanged alcohol and tetrachloride. Tars will now begin to separate, so, before proceeding further, filter the solution. Then neutralize this alkaline solution with HCl. Now distill with steam to volatilize the unchanged phenol, and allow the solution to cool. Shake it with ether. On evaporation, faint red crystals of salicylic acid should form. The para oxybenzoic crystals are also in this mass, and must be separated with chloroform by Ost's method. When the para oxybenzoic acid is completely

1. Berichte vol. 9, page 1285

separated, there will be no purple coloration with ferric chloride test solution(indicating salicylic) and transparent prisms, efflorescing at 100 degrees C, with a melting point of 210 degrees C should form.

When we preformed this experiment it was so difficult to keep a constant temperature at 100 degrees C at night, when the pressure increased or the gas was shut off, that the experiment was a failure.

XIV. ORIGINAL CONTRIBUTIONS TO THE SUBJECT

During the course of the work, numerous attempts have been made at original experimentation, either to facilitate ease and rapidity of reaction and production, or to determine results when applying type methods to homologous substances.

I. Preparation of Potassium Phenolate

In the Kolbe synthesis, it was observed that, if stick caustic were fused directly with melted phenol crystals, the fusion developed more rapidly than if the usual method is followed; namely, evaporating a solution of phenol and caustic to dryness. The reaction without the water is perfectly satisfactory, and a lighter colored product results. The evaporation of the water in the solution takes so much time, and the heat applied is so constant, that a considerable color change is caused, even charring results; and yields an unsightly product, for phenol is easily decomposed.

II. Fusion of Salicylic Acid with Potassium Hydroxide (Negative)

Sodium and potassium phenolates when treated with carbon dioxide form salicylic acid and para oxybenzoic acids respectively, depending on the temperature conditions. The sodium and potassium, curiously, determine the positions assumed by the hydroxyl and acid groups in the ring. Sodium forms only the ortho body, salicylic acid, when treated with carbon dioxide at 190 degrees C; while potassium forms first the ortho body and then is converted into the para form, if the temperature is allowed to go up to 220 degrees C. As the salicylic acid already has the hydroxyl and acid groups present in the ortho position, if fused at a higher temperature

with caustic potash, there ought to be a formation of para oxybenzoic acid. The experiment was unsuccessful and speculation deems it possible that, on additional heating, the hydroxyl and acid groups are lost and the carbon dioxide treatment is necessary to replace them; and that these take the para position in the presence of the potassium. Or too, in order to convert the ortho to the para salt, the process may have to be continuous, changing a freshly formed ortho into a para body; not an isolated attempt to convert salicylic acid formed in some previous experiment.

III. Lithium Phenolate Treated with Carbon Dioxide (negative)

If sodium and potassium have this power to influence the positions assumed by the entering hydroxyl and acid groups, lithium phenolate should also show interesting results. Lithium phenolate is similar in structure; the lithium belongs to the alkaline group just as sodium and potassium, but it is a stronger base; and it readily combines with phenol. For these reasons, lithium phenolate was treated with carbon dioxide at various temperatures, but all the experiments were unsuccessful. Neither the hydroxyl nor the carboxyl would enter the ring. The whole phenolate radicle broke away from the lithium and the carbon dioxide formed lithium carbonate.

IV. Bleaching Salicylic Acid Crystals

When salicylic acid is formed by fusion of salicyl aldehyde and either caustic soda or potash, unsightly crystals precipitate the first time. These can be purified only by repeated reprecipitation, with a loss of both time and material. If, however, a few drops of sulfur dioxide solution are put in the liquid before crystallization, perfectly white crystals will form the first time. This method not only bleaches the crystals, but it purifies them. The samples obtained in my work showed melting points of 156 degrees C, corresponding to the theoretical.

SUMMARY

Oxaldehydes of benzene have been prepared and studied; the benzene nucleus containing a hydroxyl group is more easily attacked than the unsubstituted nucleus; the aldehyde and the methyl group in the phenol interfere with further substitution.

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