Wirth

The Use of Oxalyl Chloride in a new Method for Preparing Aromatic Acid Anhydrides
THE USE OF OXALYL CHLORIDE IN A NEW METHOD FOR PREPARING AROMATIC ACID ANHYDRIDES

BY

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

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IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE DEGREE OF Bachelor of Science

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THE USE OF OXALYL CHLORIDE IN A NEW METHOD FOR PREPARING ANHYDRIDES OF AROMATIC ACIDS.

I. Work Which Lead to the Preparation of Anhydrides by this Method.

From a review of the literature on the use of oxalyl chloride it seems that it is a very valuable and convenient reagent for hydroxyl groups. Of particular interest to us is the fact that it has been found that oxalyl chloride reacts with certain phenols in pyridine solution at room or at higher temperatures to give dehydration products. We have tried its action on the hydroxyl groups of aromatic acids and have found that, by varying the conditions of the experiment we can get either the acid chloride or the dehydration product, namely, the anhydride of the acid.

We first allowed one mole of oxalyl chloride to act on one mole of benzoic acid at room temperature for about three days. Practically all of the benzoic acid was converted into benzoyl chloride. Heating would naturally hasten the reaction in this case. Therefore a mixture of benzoic acid and oxalyl chloride was refluxed for about two hours. The benzoyl chloride formed was distilled off and then the temperature of distillation vapors rapidly rose to 360°C, the boiling point of benzoic

anhydride. There was enough of the anhydride formed to justify our attempt to so regulate the conditions that we could obtain it as the main product of the reaction. The anhydride was identified by its melting point 42°, and its boiling point 360°, after it was recrystallized from a mixture of benzene and ligroin.

II. Development of the Method.

Many experiments were tried out under different conditions to find out how we could best obtain the most satisfactory yield of anhydride, varying the temperature time of refluxing, ratio of reagents, etc.

It seemed that since it requires two moles of acid to one mole of oxalyl chloride to form the anhydride, it would be advisable to drop the chloride slowly on the acid thus keeping the acid in excess. Accordingly, two moles of oxalyl chloride were dropped very slowly on one mole of molten benzoic acid. The reaction takes place rather energetically and HCl gas was seen to be evolved. The mixture was boiled under a reflux condenser for two hours, and then poured into a beaker. After it cooled, it was treated with 10% Na₂CO₃ solution. This dissolves the excess acid and leaves the anhydride behind. It was slightly dark, due to the little carbonization which had taken place during the heating. We find that where it is necessary to purify the aromatic anhydrides by crystallization, the best solvent for this purpose is a mixture of benzene or xylene and ligroin or petrol ether. Most of them are soluble in benzene or xylene and less soluble in ligroin. Accordingly, we may vary the amount
of each one to give us the desired volume. The yield in the above experiment was 75% theory.

We next attempted to obtain a pure white product by trying the reaction in some different solvent. Benzene proved to be very satisfactory. It took considerable time to find the amount of benzene necessary to give a maximum yield, but it was finally found that an 80% yield could be obtained by having the benzene in such an amount that there is still some benzoic acid left undissolved when the benzene is boiling. The product obtained is very pure and white.

Small amounts of substance were used in the preparation of the anhydrides which we made, usually 5 or 6 grams of acid. Undoubtedly the yield would figure 85% or 90% theory if much larger amounts were used.

III. Review of Other Methods Used and Comparison with this Method.

We have reviewed about ten different methods for preparing aromatic acid anhydrides. The method we use compares very well with the best methods given, from the standpoint of time of preparation, convenience, yield, quality and purity of product. We shall briefly describe some of these methods so that we may compare our method to them.

Gerhardt\(^1\), Racine\(^2\) and Pisani\(^3\) heated the sodium salt of the acid with PCC\(_3\) for one half hour on the oil bath, washed with water and Na\(_2\)CO\(_3\) solution and redistilled. Nothing was said

1. A 87, 73 & 158. 2. A 239, 74. 3. A 102, 284
about the yield. Wunder\textsuperscript{1} and Klages\textsuperscript{2} heated \( \text{PCl}_5 \) and the acid together. Klages heated them in chloroform solution for one hour on the water bath. He obtained from 40 grams of acid a mixture of 20 grams of anhydride and 12 grams of acid chloride. To separate the two he distilled the mixture. Gal\textsuperscript{3} heated \( \text{BaO} \) and the acid chloride in a tube for twenty hours at 140\textdegree - 150\textdegree and then distilled out the anhydride. Lachowitz\textsuperscript{4} obtained a 75\% yield of anhydride by heating on the water bath over an hour, a mixture of the acid chloride and lead or silver nitrate, 6 moles of lead nitrate to one of acid chloride. He extracted the anhydride from the mixture with ether and recrystallized it.

Minunni\textsuperscript{5} got the same yield by using \( \text{NaNO}_2 \) instead of \( \text{P(NO}_3)_2 \). He extracted with ether and washed with \( \text{Na}_2\text{CO}_3 \). Gerhardt\textsuperscript{6} also prepared aromatic acid anhydrides by heating the acid chlorides with the sodium salt. It is necessary here to distil off the excess benzoyl chloride and then distil off the anhydride from the sodium salt of the acid. He also heated anhydrous potassium oxalate with the acid chloride. He then poured the mixture in water and heated gently with \( \text{NH}_3 \) to get rid of the excess benzoyl chloride. This is difficult to accomplish without destroying part of the anhydride. Denham\textsuperscript{6} treated the silver salt of the acid with sulphur monochloride and decomposed the resulting product \( \left( \text{C}_6\text{H}_4\left(\begin{array}{c} \text{CH}_3 \\ \text{CO}_2\text{S} \end{array}\right) \right) \) by heating, into \( \text{S} + \text{SO}_2 \) the anhydride.

1. J. 1854
2. B. 32, 1561
3. A. 128,127
4. B. 17, 1282
5. G. 20, 655
6. Soc. 95, 1240
Here it is necessary to extract the anhydride from the sulphur with ether. Jemsen\(^1\) has a method covered by a German patent, whereby he treats one part of benzoyl trichlorate with three parts of \(\text{H}_2\text{SO}_4\) containing \(\frac{1}{2}\%\) water. The following takes place:

\[
\begin{align*}
\text{C}_6\text{H}_5\text{C}l_3 & \quad 3\text{H}_2\text{O} \quad \rightarrow \quad \text{C}_6\text{H}_5\text{CO} \\
\text{C}_6\text{H}_5\text{CO} & \quad 6\text{HCl} \\
\end{align*}
\]

This is apparently a good method, but nothing is said about the yield. Antonrieth\(^2\) obtained from 20 grams of acid, a mixture consisting of 9 grams of benzoic anhydride and 6 grams of the anhydride of benzoic and acetic acids, by refluxing for six hours a mixture of benzoic acid and acetic anhydride. This is a 50% yield.

We call attention to the fact that in most of the above methods there is some disadvantage which is not to be found in our method. For example where \(\text{POCl}_5\) or \(\text{POCl}_3\) is used we always have the disagreeable phosphoric acid residue to separate from the mixture. Where benzoyl chloride is used, we usually have to distill it from the anhydride, then distill the anhydride and recrystallize it. Some methods are inconvenient from the standpoint of the time and labor necessary to carry them out, while others involve ether extractions, recrystallization, etc.

In our method there is no discolored product obtained; no disagreeable and difficultly removable residues are obtained; no reaction products have to be distilled; no ether extractions have to be made. The only product which we get that is disagreeable and difficult to remove is the acid chloride. We find only a trace of this however, not enough to bother.

1. Ber. 12, 1495
2. B. 34, 184
IV. Directions for Preparation with Oxalyl Chloride.

In brief, our method is as follows: (The apparatus is a Liebig condenser (2ft.) set for refluxing and protected at the top by a calcium chloride tube. Since oxalyl chloride attacks cork somewhat we have found it advisable to have the round bottom distilling bulb fixed directly on the end of the condenser tube by a ground glass joint, although this is not absolutely necessary. A long stem dropping funnel is at the top of the condenser) 1.15 mole of oxalyl chloride is dropped very slowly on the boiling mixture of benzene and aromatic acid, the benzene being in such amount that the acid is not entirely dissolved in it while it is boiling. The mixture is refluxed for two or two and a half hours and then the benzene is evaporated off. The product is then washed with 10\% Na}_2\text{CO}_3 to remove any unchanged acids. The anhydride thus obtained is practically pure and for ordinary work needs no further purification. 15\% over one mole of oxalyl chloride is used to make up for volatility loss of this substance, because it is appreciably volatile.

V. The Mechanism of the Reaction and It's Advantages.

When we treat benzoic acid with oxalyl chloride the following products are formed thus:

\[2 \text{C}_6\text{H}_5\text{CO}_2\text{H} (\text{COCl})_2 \rightarrow (\text{C}_6\text{H}_5\text{CO})_2 \text{O} + \text{CO} + \text{CO}_2 + 2\text{HCl}.\]

From our later work we might suppose the mechanism of the reaction to be as follows: the mixed anhydride of oxalic and benzoic acids is formed; this breaks down with the evolution
of CO and CO₂, forming benzoic anhydride

\[ 2 \text{C}_6\text{H}_5\text{CO.OH} \cdot (\text{COCl})_2 \rightarrow \text{C}_6\text{H}_5\text{CO} \cdot \text{O} \cdot \text{CO} \cdot \text{CO} \cdot \text{C}_6\text{H}_5 \rightarrow (\text{C}_6\text{H}_5\text{CO})_2 \text{O} + \text{CO} + \text{CO}_2 \]

In either case we see that the advantage of this reaction is that the side products are all gases, (HCl, CO and CO₂). Of course when we carry it out we have left a small amount of unchanged acid and a trace of acid chloride in some cases. It is a disadvantage to have the acid chloride because it is not removed along with the acid by 10% Na₂CO₃.

Anschutz,¹ who obtained the same reaction products as we have, by heating one part of oxalic acid with four parts of acid chloride (twice the theoretical amount) has to distil off the excess acid chloride and then distil and recrystallize the anhydride.

The analogy between his reaction and ours is seen from the two equations,

1. \[ 2\text{C}_6\text{H}_5\text{CO.CI} + (\text{COOH})_2 \rightarrow (\text{C}_6\text{H}_5\text{CO})_2 \text{O} + \text{CO} + \text{CO}_2 + 2\text{HCl} \]
2. \[ 2\text{C}_6\text{H}_5\text{CO.OH} + (\text{COCl})_2 \rightarrow (\text{C}_6\text{H}_5\text{CO})_2 \text{O} + \text{CO} + \text{CO}_2 + 2\text{HCl} \]

VI. List of Anhydrides Prepared.

To show that we have a general method for the preparation of anhydrides of aromatic acids, we have prepared a series of such anhydrides which shows very well how generally applicable the method is. These compounds are as follows:

¹. A. 226, 15
<table>
<thead>
<tr>
<th></th>
<th>M.P. Found</th>
<th>M.P. Recorded</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Benzoic anhydride</td>
<td>42°</td>
<td>A. 87, 73 42°</td>
</tr>
<tr>
<td>2. Ortho-toluic anhydride</td>
<td>36-7°</td>
<td>A. 239, 74 36-7°</td>
</tr>
<tr>
<td>3. Meta-toluic anhydride</td>
<td>70°</td>
<td>Soc. 95, 1240 71°</td>
</tr>
<tr>
<td>4. Para-toluic anhydride</td>
<td>94°</td>
<td>Soc. 75, 344 95°</td>
</tr>
<tr>
<td>5. Ortho chlor benzoic</td>
<td>78-9°</td>
<td>not made before.</td>
</tr>
<tr>
<td>6. Meta chlor benzoic</td>
<td>95°</td>
<td>not made before.</td>
</tr>
<tr>
<td>7. Para chlor benzoic</td>
<td>193-4°</td>
<td>B. 43, 2229 193-4°</td>
</tr>
<tr>
<td>8. Meta-iodo benzoic</td>
<td>134°</td>
<td>not made before.</td>
</tr>
<tr>
<td>9. Ortho Nitro</td>
<td>135°</td>
<td>B. 17, 2789 135°</td>
</tr>
<tr>
<td>10. Meta</td>
<td>162°</td>
<td>not made before.</td>
</tr>
<tr>
<td>11. Para</td>
<td>189-90°</td>
<td>A. 314, 305 189-90°</td>
</tr>
<tr>
<td>12. Anhydride of anisic acid</td>
<td>95-6°</td>
<td>A. 102-284 95-6°</td>
</tr>
<tr>
<td>13. 1.3.5 di-nitro benzoic</td>
<td>209°</td>
<td>not made before.</td>
</tr>
<tr>
<td>anhydride</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14. 1.2.4 di-nitro benzoic</td>
<td>160°</td>
<td>not made before.</td>
</tr>
<tr>
<td>anhydride</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

VII. Meta-Nitro-benzoic Acid.

In working with the meta-nitro-benzoic acid, a very striking thing happened. The oxalyl chloride was dropped slowly on the boiling mixture of nitro benzoic acid and benzene. The acid not yet dissolved all went in solution when the oxalyl chloride had been added. In about twenty or thirty minutes a white crystalline product began to form in the boiling solution. The boiling was continued for about half an hour, at the end of which time the flask was almost completely filled with the prod-
uct insoluble in benzene. According to Antenrieth\textsuperscript{1}, this product could not possibly be the anhydride, because he claims to have prepared m nitro benzoic anhydride by refluxing a mixture of meta nitro benzoic acid and acetic anhydride for over six hours; his product melts at 47°. He formed nitro benzamide by treating it with ammonia and extracting with ether. The product we obtained was extremely insoluble in all the ordinary organic solvents and mixtures of these. We could only purify it by repeated washing with hot benzene. The product decomposed at about 157°, giving off gas. Further experiments showed that this gas burned with a pale blue flame and that CO\textsubscript{2} was also given off. We concluded from this, that we had formed a mixed anhydride of oxalic and nitro benzoic acids and that this substance decomposed giving off CO and CO\textsubscript{2} gas when we heated it. The mixed anhydride is

\[
\begin{align*}
\text{C}_6\text{H}_4\langle \overset{\text{NO}_2}{\text{O}} & \overset{\text{meta}}{\text{O}} - \overset{\text{0}_{2}\text{N}}{\text{O}} \rangle \text{C}_6\text{H}_4
\end{align*}
\]

and we would expect it to decompose into the benzoic anhydride if it gave off one mole of CO\textsubscript{2} and one mole of CO. Accordingly we set up simple apparatus for measuring quantitatively the amount of CO\textsubscript{2} given off and the weight of the product left after decomposition. This apparatus was simply a train consisting of a test tube with a tight fitting two holed rubber stopper. Through one hole a glass tube reached to the bottom at one end. The other end was connected to a drying tower filled with a mixture of soda lime and CaCl\textsubscript{2}. Through the other hole was a
glass tube one end of which was just flush with the bottom of the rubber stopper. The other end was connected to a Goissaler potash bulb. It was of course protected with a CaCl₂ soda lime tube. By carefully heating about 3 grams of the supposed mixed anhydride in the test tube, at first with a free flame and then with an oil bath at 170°, we were able to get the weight of CO₂ given off. When the substance which is in the molten condition at 170° was heated for about 15 minutes all the gas was freed and after flushing the train with air the KOH bulb and test tube were both weighed. In this way we could not only measure the CO₂ given off, but we could also measure the loss in weight of the substance.

VIII. Proof that Antenrieth was Wrong in His Work on the Anhydride of this Acid.

Our results show a loss of one mole of CO₂ and one mole of CO from a mixed anhydride of oxalic and meta-nitro benzoic acid. A combustion also shows the compound to be the mixed anhydride. Our results are as follows:

Calculated for $\text{C}_6\text{H}_4\left(\text{NO}_2\text{CO}_3\text{O}_2\text{N}\right)$ $\text{C}_6\text{H}_4$

$(C = 49.5) \quad \text{Found} \ (C = 49.3)$
$(H = 2.06) \quad \text{Found} \ (H = 2.26)$

Calculated percent loss if CO + CO₂ are gases given off on decomposition = 18.54% Found 18.71% Calculated CO₂ lost = 11.34 Found 11.16%. This product which we obtained by heat decomposition was recrystallized from benzene. It is a white solid
melting at $162^\circ$. Analysis showed it to have the empirical formula of m-nitro-benzoic anhydride. Going on the assumption that this was something other than the anhydride (since Antenrieth claims that he prepared the anhydride melting at $47^\circ$) we could only reasonably figure out one other way for the compound to decompose, splitting out CO and CO$_2$ as shown.

$$C_6H_4\left<\text{NO}_2\right>_{\text{CO}0\cdot\text{CO}0\cdot\text{CO}}\rightarrow C_6H_4\cdot O_2N.$$  

The resulting compound $C_6H_4\left<\text{NO}_2\right>_{\text{CO}0\cdot\text{CO}}$ should on hydrolysis give $C_6H_4\left<\text{NO}_2\right>_{\text{CO}0\cdot\text{OH}} + C_6H_4\left<\text{OH}\right>$. We find that by hydrolyzing with 10% KOH and then acidifying with HCl that we get not the above products but meta-nitro-benzoic acid, M.P. 140-1$^\circ$. According to this and our previous work we conclude that we must have meta-nitro-benzoic anhydride melting at $162^\circ$, instead of $47^\circ$ given by Antenrieth. Accordingly, we attempted to make the anhydride by the method of Antenrieth, that is, by refluxing 1 mole of m-nitro benzoic acid with 3.6 moles of acetic anhydride for more than six hours, and then distilling off the excess acetic anhydride. We refluxed our mixture for nine hours, and then distilled off the excess acetic anhydride. We did not remove the flame when the temperature of the distilling vapors went above $140^\circ$, the boiling point of acetic anhydride, but instead we allowed the temperature to go up to $170^\circ$. This, curiously enough, proved to be fortunate for us, as we shall see. We poured the molten residue on a watch glass, allowed it to
cool, pulverized it, treated it with 10% Na₂CO₃ solution, filtered and washed it. After recrystallizing from benzene we obtained a substance exactly similar in crystalline form, etc. to the product which we got by decomposing the mixed anhydride of oxalic and meta nitro-benzoic acid. Its melting point (162°) checked exactly with our former product. This lead us to believe that we have the true anhydride of m-nitro-benzoic acid and that Antenrieth had the mixed anhydride of acetic and m-nitro-benzoic acid, because in preparing the anhydride of benzoic acid with benzoic acid and acetic anhydride, he got a mixture consisting of 9 grams of benzoic anhydride and 6 grams of the mixed anhydride. We find that Greene¹ has prepared the mixed anhydride and reports a melting point of 45°. Anterieth reports 47° for his product; apparently he did not analyze it. We are inclined to think that he mistook the mixed anhydride for the real anhydride of meta-nitro-benzoic acid. The product we get hydolyzes to give two moles of m-nitro benzoic acid. We think that we have offered enough evidence to show that we have the anhydride of m-nitro benzoic acid.

As was stated before, we believe that we were fortunate in raising the temperature of our mixture of m-nitro benzoic anhydride and acetic anhydride to above 170° in distilling off the acetic anhydride, for we think the mixed anhydride may decompose to give the nitro benzoic anhydride, just as our mixed anhydride of oxalic acid and m-nitro benzoic acid decomposed.

The reaction might be as follows:

\[
2 \text{C}_6\text{H}_4<\text{NO}_2\text{CO}._0.\text{COCH}_3 \xrightarrow{\text{heat}} \text{C}_6\text{H}_4<\text{NO}_2\text{O}_2\text{N} \xrightarrow{} \text{C}_6\text{H}_4 + \text{CH}_3\text{CO}._0.\text{COCH}_3
\]

¹. 'Al.' 415
We think that Antenrieth did not heat high enough to get the result which we obtained.

IX. Pyridine m-Nitro benzoate and It's Peculiarities.

In connection with the double anhydride of oxalic acid and meta nitrobenzoic acid, we chanced upon another very interesting characteristic, which was somewhat puzzling, before we concluded that we got the anhydride when we decomposed it. If we dropped our double anhydride in cold pyridine it immediately decomposed with evolution of gas. We found this gas to be a mixture of CO and CO$_2$. After decomposing the excess pyridine with dilute HCl a white solid separated out. This was fairly soluble in water and melted at 120$^\circ$. We could only conclude that the compound lost one mole of CO and one of CO$_2$ and formed the pyridine salt of nitro benzoic acid. However, we would hardly expect this to be stable in a dilute hydrochloric acid solution. Nevertheless, to make absolutely sure that we had the pyridine salt, we dissolved some m-nitro benzoic acid in pyridine and made acid with HCl as before. Curiously enough, we obtained the same product which melted at 120$^\circ$.

In our work with ortho-nitro-benzoic acid we obtained the anhydride of the acid directly. We found no mixed anhydride. The para anhydride is being prepared and we expect it to go to the anhydride directly.

The 1.3.5 dinitro acid formed a mixture the insoluble mixed anhydride and the simple anhydride as did the 1.2.4. dinitro acid. They exhibit the same properties as the mixed anhydride of the mono-nitro benzoic acid. We are inclined to think that
it is possible to form the mixed anhydrides of aromatic acids and oxalic acid in other cases. Their formation, we believe, depends entirely on their solubility in the indifferent substance used in the reaction mixtures and their decomposition temperature. We believe that if we use some low-boiling indifferent solvent, let us say petrol ether of about 60°-70° boiling point, and reflux as before, we will get the mixed anhydride if it is insoluble in the solvent used.

X. Analysis of New Compounds.

In our work we have prepared a few anhydrides and other compounds not recorded in the literature. We have run quantitative analyses on the following compounds not hitherto recorded:

(1) Ortho-chlor benzoic anhydride m.p. 73-90°

\[
\begin{align*}
\text{C} & \quad \text{H}_8\text{O}_3\text{Cl}_2. \\
\text{Calc. Cl} & = 24.04\% \\
\text{Wt. sample} & = .2346 \\
\text{Wt. Ag Cl found} & = .2261 \\
\text{Wt. Cl} & = .0559 \\
\% \text{Cl found} & = 23.85
\end{align*}
\]

(2) Meta-chlor benzoic anhydride m.p. 95°

\[
\begin{align*}
\text{C} & \quad \text{H}_8\text{O}_3\text{Cl}_2. \\
\text{Calc. Cl} & = 24.04\% \\
\text{Wt. sample} & = .2160 \\
\text{Wt. Ag Cl found} & = .2076 \\
\text{Wt. Cl} & = .0513 \\
\% \text{Cl found} & = 23.79
\end{align*}
\]

(3) Meta Iodo Benzoic Anhydride m.p. 134°

\[
\begin{align*}
\text{C} & \quad \text{H}_8\text{O}_3\text{I}_2. \\
\text{Calc. Iodine} & = 53.12\% \\
\text{Wt. sample} & = .1923 \\
\text{Wt. Ag I found} & = .1883 \\
\text{Wt. Iodine} & = .1017 \\
\% \text{Iodine} & = 52.91
\end{align*}
\]
(4) *Meta-nitro benzoic anhydride* m.p. 162°.

C_{14}H_{8}O_{7}N_{2}.  
Calc. C = 53.16; H = 2.53; N = 8.86

Wt. sample .1840  
Wt. H_{2}O = 4.5712

Wt. H = .0051  
% H = 2.78

Wt. CO_{2} = 3.5777  
Wt. C = .0975

% C found = 53.03

Wt. sample for N_{2} determinations = .2675

cc's N_{2} found at 745.2 mm. and 22° C = 20.54

Wt. N_{2} = .0242  
% N_{2} found = 9.05

(5) *Mixed anhydride of meta nitro benzoic acid and oxalic acid*

Decomposes at 157°  
C_{16}H_{8}O_{10}N_{2}

Calc. C = 49.5; H = 2.06; N = 7.22

Wt. sample taken .1906  
Wt. H_{2}O found 3.8489

Wt. H = .0043  
% H found = 2.26

Wt. CO_{2} = 3.4453  
Wt. C = .9396

% C found = 49.30

Wt. sample taken for N_{2} determination .2419

cc's N_{2} found at 746.8 mm. and 23° C = 19.65

Wt. N_{2} found = .0181  
% N_{2} = 7.48

(6) *Mixed anhydride of 1,3,5 di-nitro nitro benzoic acid and oxalic acid.* Decomposes at 175°  
C_{16}H_{10}O_{4}N_{4}

Calc. C = 40.16%; H = 1.25%; N = 11.73%

Wt. of sample taken .1625  
Wt. H_{2}O found 2.0475

Wt. H = .0023  
% H found = 1.41

Wt. CO_{2} = 2.3769;  
Wt. C = .6482;  
% C found = 39.89

Wt. sample taken for N_{2} determination = .2400

cc's found at 740.6 mm. and 23° C = 25.57
Wt. N₂ = .0287;  % N₂ found = 11.97

(7) Anhydride of 1.3.5. dinitro benzoic acid: m.p. 209°.

\[ \text{C}_{14} \text{H}_6 \text{O}_11 \text{N}_4 \]
Calc. N = 13.79; Wt. sample taken = .2319
cc's N₂ found at 739.6 mm. and 22° C = 23.9e
Wt. N₂ = .0326; % N₂ found = 14.05

(8) Anhydride of 1.2.4 dinitro benzoic acid.

m.p. = 160°;  
\[ \text{C}_{14} \text{H}_6 \text{O}_11 \text{N}_4 \]
Calc. N = 13.79  Wt. sample taken = .2485
cc's N₂ found at 739.6 mm. and 22° C = 25.9
Wt. N₂ = .0371; % N₂ found = 14.12

(9) Mixed anhydride of 1.2.4. dinitro benzoic acid and oxalic acid. Decomposes 205° - 9° C₁₆ H₆ 14 N₄.
Not analyzed.

XI. Summary.

In summarizing our work we may say that we have found a new and general method for preparing anhydrides of aromatic acids. (See page 6). This method compares very well with the best methods given in the literature from the standpoint of convenience, time of preparation, yield, quality and purity of product. In the case of meta-nitro-benzoic acid the very insoluble mixed anhydride is formed which readily decomposes into the simple anhydride with the loss of one mole of CO and CO₂, respectively. Meta-nitro-benzoic anhydride melts at 162° instead of 47° as recorded by Antenrieth1 who undoubtedly mistook the mixed anhydride of benzoic and acetic acids for the anhydride of m-nitro-
benzoic acid. The 1.3.5 and 1.2.4 dinitro benzoic acids form the mixed anhydride together with a small amount of the simple anhydride. They also decompose readily into the anhydride. We find also that a small amount no doubt decomposes into the phenyl ester of benzoyl formic acid, losing one mole of CO and one of CO₂ as before, because on hydrolysis with NaOH, we find the characteristic red color of phenols. Phenyl benzoyl formate hydrolyzes to give the sodium salts of di-nitro phenol and benzoyl formic acid.

Owing to our limited time we cannot further investigate this fact.

We have found the very interesting and unusual fact that the pyridine salt of m-nitro benzoic acid, which is formed when we add the mixed anhydride of m-nitro benzoic acid and oxalyl chloride to pyridine, is precipitated by acidifying the mixture with dilute HCl. This is contrary to what we naturally expect of a basic salt of an organic acid. The mixed anhydride is decomposed instantaneously by cold pyridine with the evolution of one mole of CO and one of CO₂.

We recommend the above method of preparing aromatic acid anhydrides as being a clean and convenient method for preparing the pure anhydrides on a small scale for laboratory and theoretical purposes.

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Walter V. Wirth
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