

THE CONDENSATION OF BENZYL CYANIDE
WITH AROMATIC NITRO COMPOUNDS.

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WITH AROMATIC NITRO COMPOUNDS.

By

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The writer wishes to acknowledge his indebtedness to Professor H. P. Armes for the suggestion of this problem and to express an appreciation of the helpful advice and generous interest with which he has directed the investigation.

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INTRODUCTION

INTRODUCTION.

In this thesis, a study has been made of the condensation of benzyl cyanide, which contains an active methylene group, with aromatic nitro compounds, in the presence of sodium ethylate. The present investigation has been concerned with the three isomeric (o,m,p,) nitro-chlorobenzenes.

The object of the investigation was to continue the researches of Armes¹ on this new type of condensation and, if possible, to throw light on the structure of the condensation products. A substituted nitro-benzene was used in order to study the effects, if any, which the position of the substituent group might have upon the condensation. The three isomeric nitro-chlorobenzenes were chosen because of the ease of separation of the condensation products, which can be obtained in the crystalline form.

While only one set of isomers has been studied in this work, it is reasonable to assume that other mono substituted benzenes would react in a similar manner, the position of the substituent group rather than its chemical nature being the most important factor.

The experimental work to be described in the present paper may be summarized as follows :

1.) Determination of the molecular quantities of benzyl cyanide, nitro-chlorobenzene, and sodium ethylate, and the most suitable physical conditions, necessary to give a maximum yield of the condensation product.

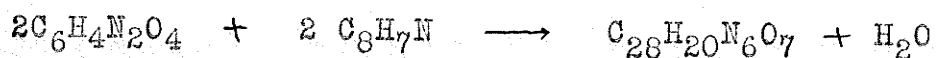
2.) A study of the structure of the reaction products, by means of conversion to known compounds, and by means of analyses.

3.) The colors produced by the condensation of benzyl cyanide with aromatic nitro compounds, and the delicacy of the color reaction.

4.) Attempt to synthesize Chloro-phenyl-Anthranil.

CHAPTER 1.

In 1904, Reissert² reported the condensation of m-Dinitro benzene with Benzyl cyanide in the presence of sodium ethylate. Reissert observed that after mixing the three substances, and on slowly raising the temperature of the mixture, a deep violet color which gradually changed to a cherry red was produced. After treating with acid, distilling off the volatile products with steam, and cooling, a brittle red brown mass was obtained. This product could not be crystallized, and possessed no constant melting point. Analysis of the product gave the formula, $C_{28}H_{20}N_6O_7$, which Reissert believed corresponded to a substance composed of two molecules of m-dinitro benzene, two molecules of benzyl cyanide, which unite with the loss of one molecule of water. Reissert wrote the reaction thus :



No attempt was made to give a structural formula for the condensation product, nor to explain the mechanism of the reaction. In concluding his paper Reissert states, "While I am not in a position to continue the work further, I give it this publicity in the hope that it perhaps may stimulate one of my colleagues to investigate further concerning the herein described reaction!"

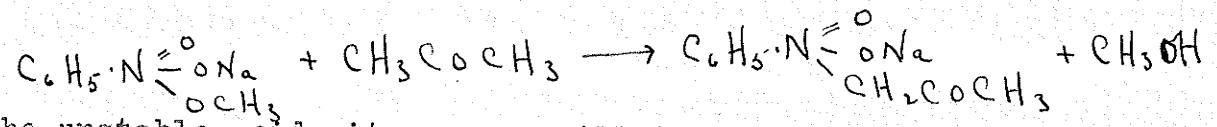
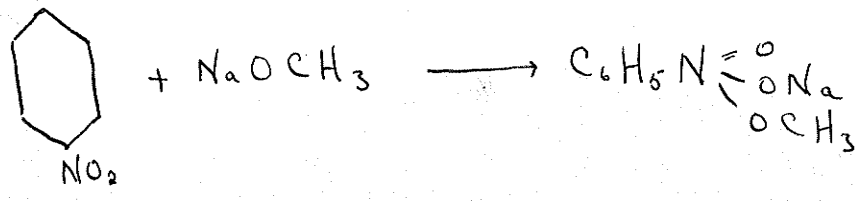
The work of Reissert appears to be the only previous attempt, described in the literature, to study the reaction of benzyl cyanide with aromatic nitro compounds.

amine, dark red; 2,4-Dinitro phenyl-o-toluidine, blue red; 2,4-Dinitro phenyl β naphthylamine, blue red solution.

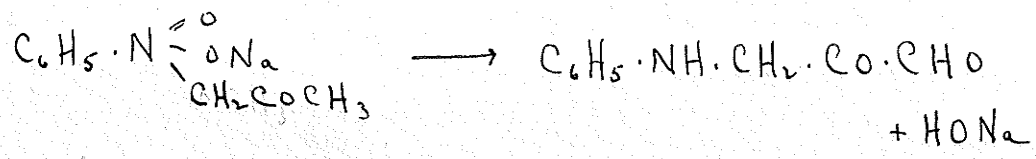
In the discussion of this reaction in the present paper, only the colors produced with a number of the most interesting type compounds have been mentioned.

A somewhat similiar color reaction of aromatic nitro compounds was observed by Belá v. Bittó⁴. He found that aromatic nitro compounds, especially m-Dinitro benzene, and also α and β Dinitronaphthalene and m-Dinitro toluene, among others, gave, with a series of aliphatic and aromatic aldehydes and ketones, by the addition of alkali, red, violet, or brownish red colors. Thus, if with m-Dinitro benzene and caustic potash, the following ~~aldehydes and~~ ketones, ^{were heated} the corresponding colors were produced : Acetone, violet black; Pulegone, and Methylheptenone, violet red; Carvon, bluish red; Thujone, brown red; Diketo hexamethylene (in nitrobenzene), brown yellow; Camphor (in nitrobenzene), brown red; Fenchone and Menthone, no color; α and β Ionone, bluish red; then reddish brown; Pseudo ionone, red; N-ethyl- α -Pyridone, reddish brown. The following aldehydes give the corresponding colors : Butylchloral, Furfural, Cinnamic aldehyde, Citral, and Citronellal, no color; Oenanthal, red; Chloracetaldehyde, dark brown; Valeraldehyde, brown.

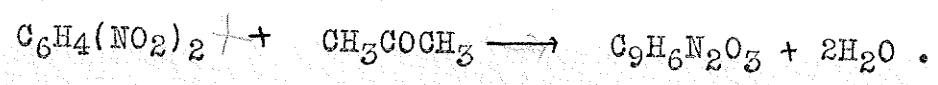
acetone in the presence of sodium methylate. He states, "It appears that in the nitro group there is probably a condensation when first Sodium ethylate is added to this group, and then an acetone residue unites with the nitrogen according to the equation :



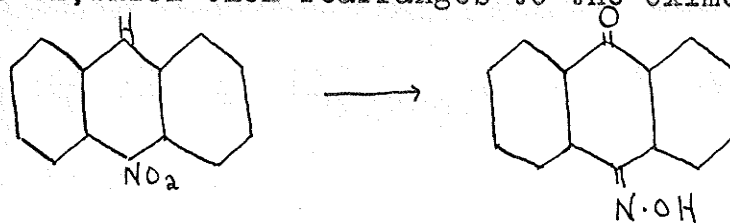
The unstable acid nitro group will then, by oxidation, alter the methyl group of the acetone residue :



In the case of the condensation of m-Dinitro benzene with acetone in the presence of Sodium methylate, quantitative experiments showed that the reaction consisted in the union of one molecule of acetone and one molecule of dinitrobenzene through the action of two molecules of sodium ethylate, accompanied by the loss of two molecules of water :



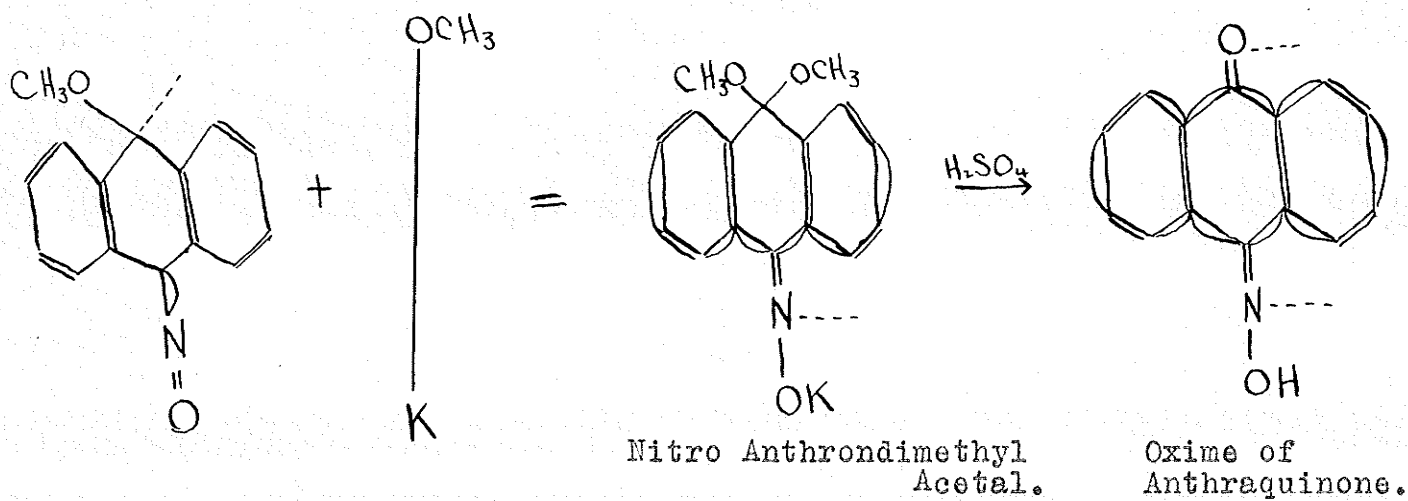
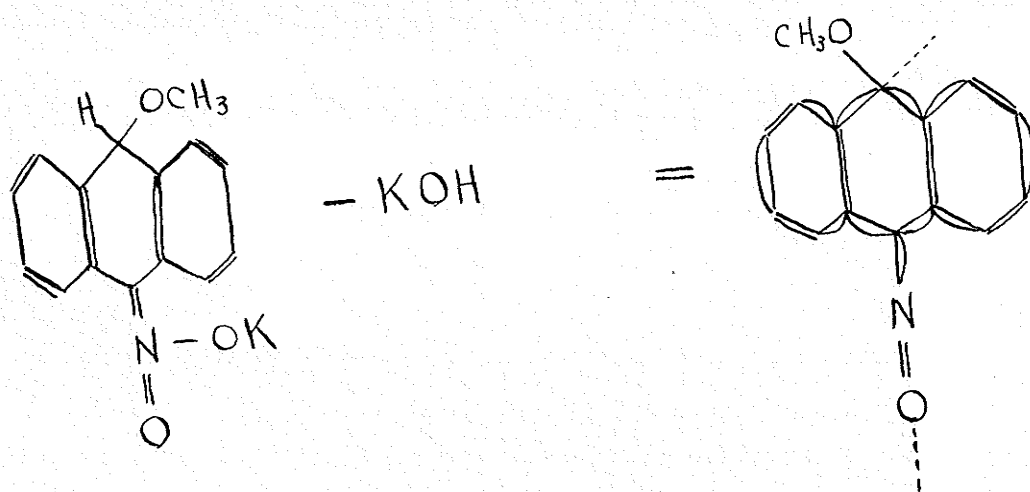
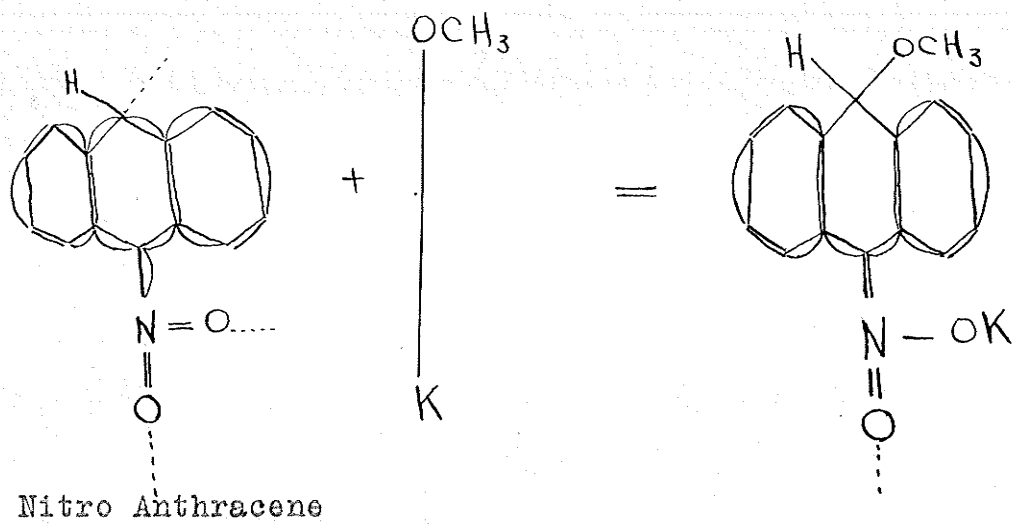
An interesting investigation which has bearing on the present work is the study of the action of potassium methylate on Nitro anthracene⁵. Meisenheimer has shown that Nitro anthracene may be transformed into the monoxime of anthraquinone by the action of potassium methylate in methyl alcohol solution. The transformation may be regarded as a change which involves intramolecular oxidation and which results in the formation of a Nitroso phenol, which then rearranges to the oxime.



It is very improbable, however, that this represents the true mechanism of the reaction, since when nitroanthracene is treated with potassium alcoholate, secondary products containing methoxy groups are formed.

It has also been shown that prolonged treatment of nitro anthracene with potassium methoxide leads to the addition of a second molecule of potassium methoxide, and results in the formation of a substance, Nitro anthrondimethyl acetal.

The formation of the Oxime of Anthraquinone and of Nitro anthrondimethyl acetal may be considered as taking place according to the following scheme, in which, use is made of Thiele's Theory of Partial Valencies :

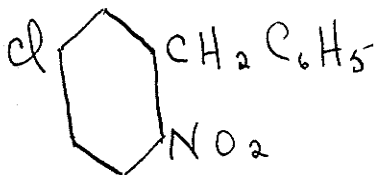


Chapter 3.

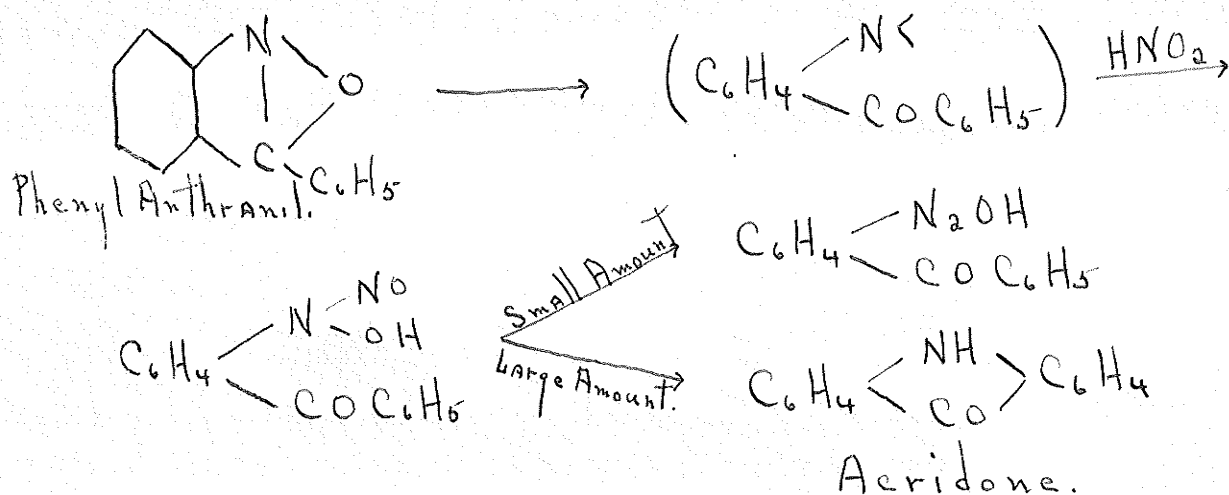
In the condensation of Benzyl Cyanide with p-Chloro nitro benzene in the presence of Sodium ethylate it has been shown experimentally in the present paper that the maximum yield of condensation product is obtained when one molecular quantity of Benzyl cyanide and p-Chloro nitro benzene, and two molecular quantities of Sodium ethylate are used.

In the hope of throwing light on the structure of the above mentioned condensation product, attempts were made to hydrolyse, oxidize, and reduce it. It was found that acid and alkaline hydrolysis had no effect upon the compound. Attempts to oxidize it by the use of Chromic acid and also Potassium permanganate were unsuccessful. Reduction of the Condensation product yielded a material melting at 97°C., but which could not be readily identified.

It was observed by Armes⁶ that the acid filtrate from the condensation product contained hydrocyanic acid. This gave the first clue as to the mechanism of the reaction, and the tentative structure shown below was assigned to the condensation product:



A short time later, however, it was also observed by Armes⁶ that the product obtained by diazotisation of the condensation product gave, in dilute alcohol, an intense blue fluorescence. It had been shown by Bamberger⁷ that diazotisation of phenyl anthranil yielded a substance, acridone, which gave an intense blue fluorescence in dilute alcohol. The mechanism of the reaction was formulated by him as follows:



It was therefore believed that the product obtained from the condensation of benzyl cyanide with p-Chloro-nitro-benzene was phenyl anthranil with a chlorine atom substituted in the benzene ring para to the position formerly occupied by the nitro group, and that this, on diazotisation, yielded Chloro-Acridone. Analysis of the condensation product indicated a compound having the empirical formula, $C_{13}H_8ONCl$, which agrees with that for Chloro phenyl anthranil. Analysis of the product obtained from diazotisation of Chloro phenyl anthranil indicated a compound having an empirical formula, $C_{13}H_8ONCl$, which agrees

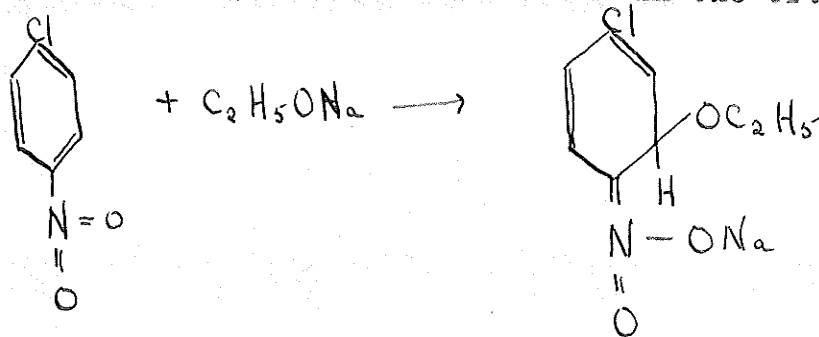
with that for Chlor-Acridone.

The melting point of Acridone is 354°C ., while the melting point of the rproduct obtained from diazotisation of the condensation product, was above 320°C ..

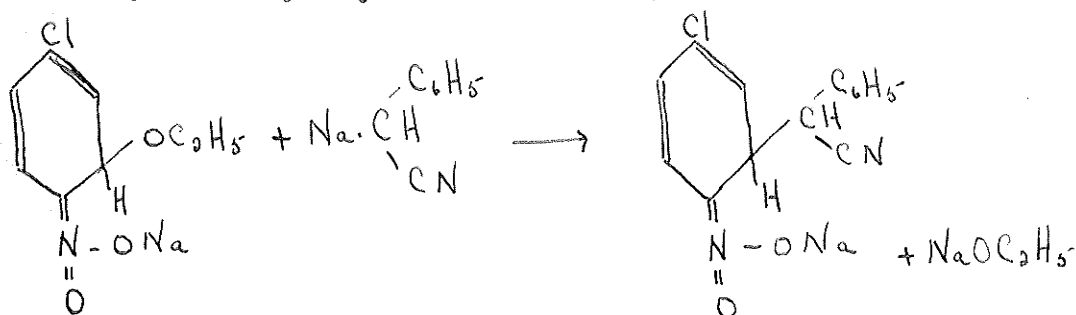
In the hope of adding further evidence to the proof of the structure of the condensation product, an attempt was made to synthesize 5-Chloro phenyl anthranil. This attempt, which is described elsewhere, was unsuccessful.

The above mentioned facts, together with the fact that both the condensation product and phenyl anthranil are relatively stable substances, appear to substantiate the belief that the condensation product is chloro phenyl anthranil.

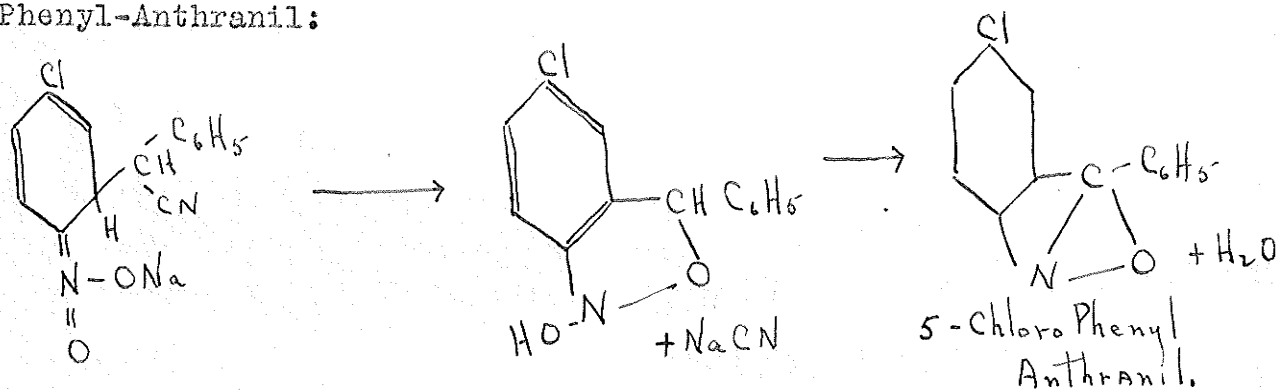
The mechanism of the reaction between benzyl cyanide and p-Chloro nitro benzene is believed to be as follows : There is a preliminary addition of sodium ethylate to the chloro nitro benzene, the Na atom adding itsrlf onto the nitro group, and the OC_2H_5 normally adding itself to the carbon atom para to the Nitro group (this point will be brought out in the study of the orkho condensation product), but when a group such as Cl is already present in that position, addition will occur in the ortho position.



The union of this compound with benzyl cyanide occurs through the displacement of the $-OC_2H_5$ radical by a benzyl cyanide residue :



On the addition of acid, sodium cyanide is split off, and there is a rearrangement of the molecule followed by the splitting off of water, to give 5-Chloro-Phenyl-Anthranil:



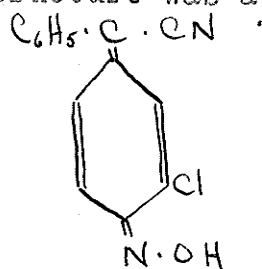
The formation of the oxime of anthraquinone from nitro anthracene⁵ through the action of potassium methylate, which was described in the previous chapter, would appear to be a reaction similar in type to the above, insofar as there is a rearrangement of the bonds of the central ring of nitro anthracene preceding the addition of potassium methylate.

In the condensation of Benzyl Cyanide with o-Chloro nitro benzene in the presence of sodium ethylate, it has been shown experimentally in the present paper that the maximum yield of condensation product is obtained when equal molecular quantities of benzyl cyanide and o-chloro nitro benzene are used. This would point to the union of one molecule of benzyl cyanide with one molecule of o-chloro nitro benzene.

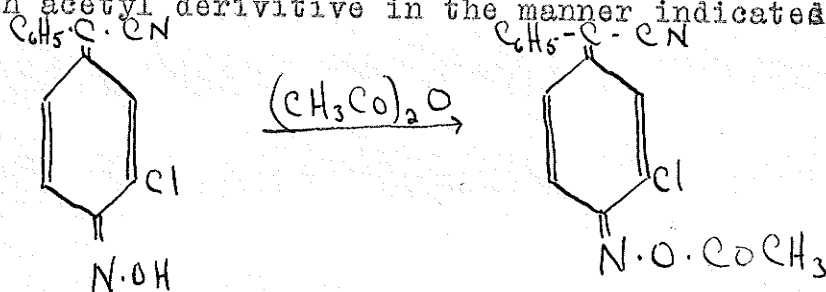
The condensation product of this reaction differed considerably in its properties from that obtained by the condensation of p-chloro nitro benzene with benzyl cyanide. For example, it was found that the o-condensation product could be dissolved in dilute sodium hydroxide imparting a deep red color to the solution, and a crystalline sodium salt was obtained on cooling the solution. By adding acid to this salt, the original condensation product could be obtained once again, and this process could be repeated indefinitely. This would indicate that the product was acid in nature. It was further found that no hydrocyanic acid could be detected in the acid filtrate from the condensation product.

Analysis of the condensation product indicated a compound having the empirical formula, $C_{14}H_9N_2OCl$. Taking into account these facts, and having a knowledge of the mechanism of the reaction between

benzyl cyanide and p-chloro nitro benzene, the following tentative structure was assigned to the condensation product :

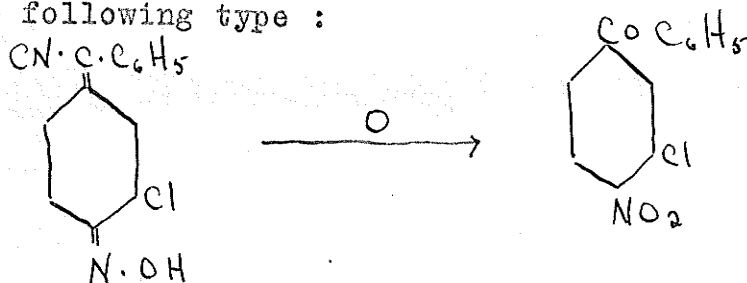


If this structure is correct the compound should form an acetyl derivative in the manner indicated below:



With acetic anhydride, a substance was obtained, melting at 178°C . having the empirical formula, $\text{C}_{16}\text{H}_{11}\text{N}_2\text{O}_2\text{Cl}$, as determined by analysis, which agrees with the empirical formula of the above mentioned acetyl derivative.

If the condensation product is a compound of the type of a quinonoid oxime, as shown above, it should, on oxidation with such mild oxidizing agents as Hydrogen Peroxide, Nitric Acid in glacial acetic acid, and possibly Potassium ferricyanide, yield a compound of the following type :

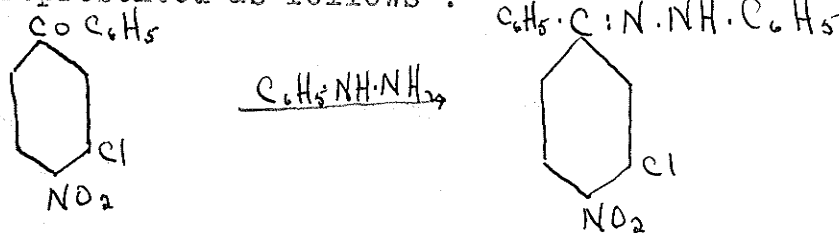


With alkaline hydrogen peroxide, the condensation product yielded a substance melting at $97^\circ\text{--}98^\circ\text{C}$., and having the

empirical formula, ~~empirical formula~~ $C_{13}H_8NO_3Cl$, which agrees with that for the above described Chloro nitro benzophenone.

With nitric acid in glacial acetic acid, the condensation product yielded a substance melting at $97^\circ C.$, and which when mixed with the product from hydrogen peroxide gave a mixed melting point of $97-98^\circ C.$. The two substances must therefore be identical. On testing the alkaline filtrate from this product of oxidation ~~for~~ hydrocyanic acid a positive test was obtained. This indicates that during the process of oxidation, $-CN$ is split off.

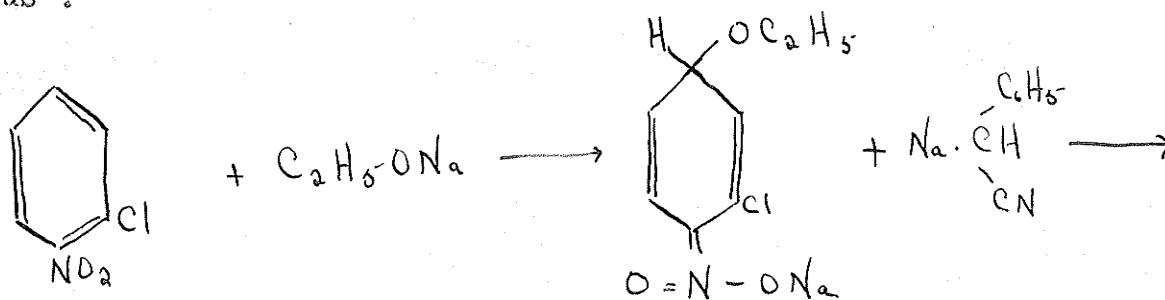
In order to add further proof to the evidence for the structure of the product of oxidation (and therefore the structure of the condensation product itself), it was converted into a hydrazone. Analysis of the compound obtained by the action of phenylhydrazine on the product of oxidation indicated a compound having the empirical formula, $C_{19}H_{14}N_3O_2Cl$. This empirical formula agrees with that for the hydrazone of Chloro nitro benzophenone. The reaction may be represented as follows :

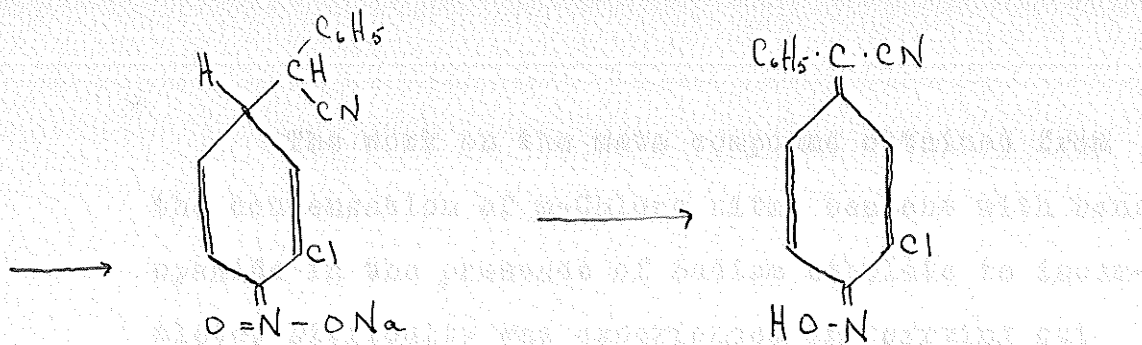


The mechanism of the reaction between Benzyl Cyanide and o-Chloro nitro benzene is believed to be as follows : There is a preliminary addition of

sodium ethylate to the o-Chloro nitro benzene, the sodium atom adding itself on to the nitro group, and the OC_2H_5 radical adding itself on to the carbon atom in the benzene ring para to the nitro group. It appears that the ring normally tends to rearrange so that addition can occur in the para position to nitro group, but that when that position is already occupied by an atom such as chlorine, addition occurs in the position ortho to the nitro group. If the ring rearranged so that addition could occur in the position in the ring ortho to the nitro group, a closed ring condensation product would be expected. It is difficult to conceive of the benzene ring rearranging so that addition can occur in the meta position. Therefore, the only alternative is that the ring rearranges so that addition occurs in the position para to the nitro group. This reasoning is borne out by the fact that two distinctly different types of compounds are obtained by the condensation of Benzyl Cyanide with ortho and para Chloro nitro benzenes.

The mechanism of the reaction between Benzyl Cyanide and o-Chloro nitro benzene may be represented thus :



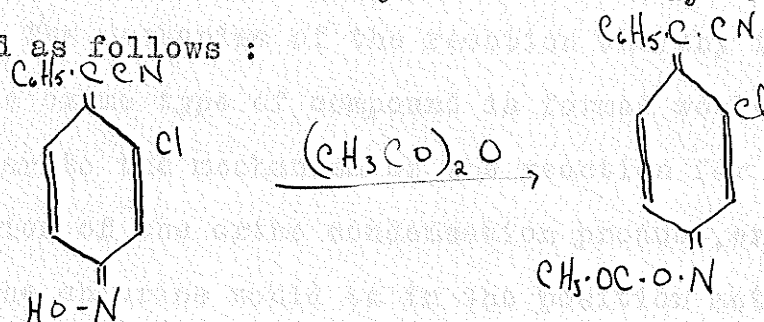


It can be seen that addition of benzyl cyanide to the benzene nucleus would probably occur in a manner analogous to that of the case of p-Chloro nitro benzene.

Addition of acid causes the splitting off of sodium hydroxide, and this is followed by rearrangement of the molecule to give as a final product, a quinone oxime.

Attempts were made in the case of both ortho and para Chloro nitro benzene to interpret the reaction with benzyl cyanide in terms of the electronic conception of valency, but the results obtained were not sufficiently successful to present them in this paper.

The condensation product was converted into an acetyl derivative, analysis of which indicated a substance having the empirical formula, $C_{16}H_{11}N_2O_2Cl$. This empirical formula is again the same as that for the acetyl derivative of the ortho condensation product. The formation of the acetyl derivative may be represented as follows :



Oxidation of the condensation product yielded a substance, upon which one analysis was carried out. This indicated a substance having the empirical formula $C_{13}H_8NO_2Cl$, which is identical with that for the product of oxidation of the ortho compound. The formation of a hydrazone, and analysis of the hydrazone was not carried out.

In the condensation of Benzyl cyanide with m-Chloro nitro benzene it might be expected that there would be produced, in addition to this quinone oxime type of compound, a quantity of an Anthranil similar to 5-Chloro phenyl Anthranil, except that the chlorine would be substituted in a different position in the benzene ring.

A qualitative test for chloro phenyl anthranil by means of the "Umlagerung" was carried out on the material which was washed out from the main part of

EXPERIMENTAL.p-Chloro Nitro Benzene.

Determination of the Molecular Quantities of Benzyl Cyanide, p-Chloro Nitro Benzene, and Sodium Ethylate, and the most suitable Physical Conditions, necessary to give a Maximum Yield of the Condensation Product.

Benzyl Cyanide	- 2 gm.	1 mol.
p-Cl NO ₂ Benzene	- 2.7 gm.	1 mol.
Sodium Ethylate	- 0.4 gm. Na.	dissolved
		in 10cc. Et. Alcohol.
		1 mol.

Four experiments were carried out using equal molecular quantities of the three substances as indicated above, in which the lengths of time of boiling the mixture on a water bath were respectively, 30 minutes, 15 minutes, 10 minutes, and 2 minutes. The method of carrying out the experiment was as follows : 2 gm. of Benzyl cyanide were added to 2.7 gm. of p-Chloro nitro benzene in a 250cc. round bottom flask. The solution of Sodium ethylate in alcohol was then added to the mixture, when a deep violet color developed almost immediately. This mixture was boiled on a boiling water bath for the periods of time mentioned above. The violet color persisted after boiling the mixture. After cooling, glacial acetic acid was added until the mixture was acid. On adding the acid, the violet color disappeared leaving a straw colored solution and a precipitate of yellow crystalline needles.

These yellow needles were filtered off, and recrystallized from alcohol.

When the molecular quantities previously indicated were used for this preparation, it was found that in addition to the yellow needles, there was also obtained, in the bottom of the flask, a solid cake of bluish black crystals which could be separated from the other crystals, and which after recrystallization from alcohol, three times, were colorless and melted sharply at $83.5^{\circ}\text{C}.$. Melting Point of p-Chloro Nitro Benzene (Mulliken) - $83.0^{\circ}\text{C}.$.

It can therefore be seen that complete condensation of the p-Chloro nitro benzene is not obtained when equal molecular quantities of the three substances are used.

It was found that when the mixture of Benzyl cyanide, p-Chloro nitro benzene, and sodium ethylate were boiled for 30 minutes, cooled, and acidified, a brown solid substance and a layer of yellow crystals were obtained in the bottom of the flask. Since it was found that after boiling the mixture from 2 to 15 minutes, none of this brown material was obtained it was concluded that boiling for this length of time was unnecessary and not conducive to the production of a maximum yield. It was further found that boiling the mixture for two minutes gave as good a yield as 10 or 15 minutes.

Yield of Condensation Product - (after recrystallizing from Alcohol four times) - 15 minutes - 1.0 gm. ;

10 minutes - 0.9 gm. ; 2 minutes - 1.2 gm. .

Melting Point of Condensation Product - in all three cases - 114.5°C..

Benzyl Cyanide	- 2.0 gm.	2 mols.
p-Cl NO ₂ Benzene	- 1.35 gm.	1 mol.
Sodium ethylate	- 0.2 gm. Na dissolved in 10cc. Et. Alcohol.	1 mol.

A condensation of Benzyl Cyanide with p-Chloro nitro benzene was tried using two molecular quantities of Benzyl Cyanide to one molecular quantity of p-Chloro nitro benzene and Sodium ethylate. The method was the same as previously described, the mixture being boiled gently for 10 minutes. As the yield was less than half those obtained in the previous condensation, and as there was a very decided odor of Benzyl cyanide about the mixture after boiling, it was concluded that the use of 2 molecular quantities of Benzyl cyanide to 1 molecular quantity of p-Chloro nitro benzene and Sodium ethylate does not produce complete condensation.

Benzyl Cyanide	- 2 gm.	1 mol.
p-Cl NO ₂ Benzene	- 2.7 gm.	1 mol.
Sodium Ethylate	- 0.8 gm. Na dissolved in 15cc. Et. Alcohol.	2 mol.

A condensation of Benzyl Cyanide with p-Chloro nitro

benzene was tried using two molecular quantities of Sodium ethylate to 1 molecular quantity of Benzyl cyanide and p-Chloro nitro benzene. The method used was that previously described, the mixture being boiled gently for 10 minutes. It was observed that after cooling, the whole mixture became a solid mass, which was deep purple in color. After acidifying, the purple color disappeared, leaving a pale orange colored solution and a precipitate of yellow needle like crystals. The crystals were filtered off, and recrystallized from alcohol four times.

Yield of pure Condensation Product - 1.6 gm.

Melting Point of Crystals - $114^{\circ}\text{C}.$

It will shortly be seen that the maximum yield of condensation product is obtained from the use of the above mentioned molecular quantities of the three substances.

Benzyl Cyanide	- 4 gm.	2 mols.
p-Cl NO ₂ Benzene	- 2.7 gm.	1 mol.
Sodium Ethylate	- 0.8 gm. Na dissolved in 15cc. Et. Alcohol.	2 mols.

A condensation of Benzyl Cyanide with P-Chloro nitro benzene using two molecular quantities of Benzyl Cyanide and Sodium ethylate and one molecular quantity of p-Chloro nitro benzene was tried. The method used was that previously described, the mixture being boiled for 15 minutes. The yield of Condensation Product obtained by using these quantities was not as great as in the

ANALYSES.Condensation Product.0.1944 gm. Substance : 0.4804 gm. CO₂.0.0627 gm. H₂O.0.2014 gm. Substance : 11.82 c.cm. N (
26 C., 747.5mm)

0.2005 gm. Substance ; 0.1264 gm. AgCl.

C ₁₃ H ₈ ONCl	Calculated :	C 67.94	H 3.51	N 6.10	Cl 15.44
	Found	67.40	3.58	6.36	15.60

0.1942 gm. Substance : 0.4787 gm. CO₂.0.0663 gm. H₂O.0.1985 gm. Substance : 11.5 c.cm. N (
23 C., 746.9mm)

0.2002 gm. Substance : 0.1269 gm. AgCl.

C ₁₃ H ₈ ONCl	Calculated :	C 67.94	H 3.51	N 6.10	Cl 15.44
	Found	67.22	H 3.70	N 6.43	Cl 15.68

Note - In the estimation of Carbon and Hydrogen in the Condensation Product it was found very difficult to oxidize the last traces of the substance, and heating had to be continued for five hours.

with 200 cc. of 10% HCl. A yellow mass was obtained which, after cooling, was filtered off.

Yield of Crude Product - 21 gm..

The crude product was recrystallized from alcohol twice, giving as a final pure product yellow (pale) needle like crystals.

Yield of Pure Product - 11 gm.. %age Yield - 56%.

Melting Point of Pure Product - 114.5 ° C..

PROPERTIES OF PRODUCT OBTAINED BY THE CONDENSATION
OF BENZYL CYANIDE WITH p-CHLORO NITRO BENZENE.

Pale yellow needle like crystals, soluble in hot alcohol, much less soluble in cold alcohol. Soluble in Glacial acetic acid, readily soluble in acetone, chloroform, ether, and benzene, at ordinary temperatures. Insoluble in hot dilute NH_4OH , NaOH , H_2SO_4 , HNO_3 , HCl . Insoluble, or practically insoluble in water. Soluble in cold concentrated H_2SO_4 , (see 'Umlagerung'). A whitish precipitate was obtained by adding water to a solution of the condensation product in conc. H_2SO_4 . This precipitate was filtered off and recrystallized from alcohol once. Very pale yellow needles were obtained, which had a melting point of 113°C.. Apparently, no chemical change is produced by the solution of the condensation product in concentrated H_2SO_4 . Soluble in hot concentrated HNO_3 , almost insoluble

in cold concentrated HNO_3 . On allowing a concentrated solution of the Condensation Product in hot concentrated nitric acid to stand, deep yellow, needle like crystals were obtained. These crystals were filtered off, washed with water, dried, and the melting point was determined. Melting Point - $250^\circ - 253^\circ\text{C}$. No further study of this product was made.

ATTEMPT TO DETERMINE THE STRUCTURE OF THE
PRODUCT OBTAINED BY THE CONDENSATION OF BENZYL
CYANIDE WITH p-CHLORO NITRO BENZENE.

Qualitative Tests for Nitrogen, Chlorine, the
Nitro group, and Hydrocyanic Acid.

The ordinary organic analytical tests were carried out for Nitrogen and Chlorine.

Test for Nitrogen - Greenish colored solution. A blue precipitate was obtained after standing for 1 day.

Test for Chlorine - A white precipitate was obtained after the addition of AgNO_3 .

These tests therefore indicated that both Chlorine and Nitrogen were present in the Condensation Product.

It was observed by Armes⁶, during the course of a preparation of this Condensation Product, that a decided odor of Prussic Acid was given off by the mixture after acidifying it. A test was therefore

carried out on a fresh sample of the filtrate from the condensation product. Dilute NaOH was added to the filtrate until it was only faintly acid. To it was added a solution of ferrous sulphate and a drop of ferric chloride. A few drops of sodium hydroxide were now added until the mixture was faintly alkaline. A bluish green precipitate was formed. Upon acidifying with HCl, the precipitate of ferrous ferric hydroxide dissolved, leaving a typical Prussian Blue.

This test was therefore positive, and indicated the presence of HCN in the filtrate.

Test for Nitro Group - (Mulliken - Identification of Pure Organic Compounds - Vol. 2, page 21.)

In carrying out this test, according to directions, it was found impossible to dissolve the condensation product in 50% alcohol without using a fairly large quantity of alcohol. The condensation product was therefore dissolved in 95% alcohol. After the addition of a pinch of zinc dust and warming, there was no chemical reaction. The solution was allowed to stand for two minutes and was filtered into ammoniacal silver nitrate. No silver mirror or metallic precipitate of silver was produced. This test was therefore negative.

Attempts to Hydrolyse, Oxidize, and Reduce the
Condensation Product.

Hydrolysis of Condensation Product. - Hydrochloric Acid.

30 cc. of concentrated hydrochloric acid were added to 1 gram of the Condensation Product. The mixture was boiled in a 150cc. round bottom flask attached to a reflux condenser for two hours. No change in color of the solution was produced during this time. After cooling, a pale yellow crystalline substance was obtained, which was filtered off, and recrystallized from alcohol twice. The crystals so obtained were pale yellow and needle like. Melting Point - $114.5^{\circ}\text{C}.$ Hydrolysis could not, then, be effected by this method.

Hydrolysis of Condensation Product. - Alcoholic Potash.

30 cc. of 20% alcoholic potash were added to 1 gram of the condensation product. The mixture was boiled in a 150cc. round bottom flask attached to a reflux condenser for two hours. It was observed that the color of the solution changed to red on first heating the mixture. After boiling for two hours, and cooling, a light brown colored substance separated out. Dilute hydrochloric acid was added until the mixture was acid, and the solid material was then filtered off, and recrystallized from alcohol three times. The crystals so obtained were needle like, and light brownish yellow in color. Melting Point - $114.5^{\circ}\text{C}.$ Melting point of a mixture of these crystals and the original condensation product - $114.5^{\circ}\text{C}.$

Hydrolysis of Condensation Product.- Sulphuric Acid.

10 cc. of concentrated sulphuric acid were mixed with 13 cc. of water, and 10 cc. of the resulting solution were added to 1 gram of the condensation product, in a 150 cc. round bottom flask. The flask was attached to a reflux condenser and the contents were boiled for two hours. The solution was then allowed to cool, and was filtered. The residue was recrystallized from alcohol twice. The crystals so obtained were needle like, and pale yellow in color. Melting Point - $114.5^{\circ}\text{C}.$

It is to be noted that hydrolysis of the condensation product could not be effected by any of the three methods described above.

Oxidation of Condensation Product.- Chromic Acid.

Glacial Acetic Acid	-	4 gm.
Chromic Oxide	-	6 gm. in 60 gm. Acetic Acid.
Condensation Product	-	2 gm..

The chromic oxide, dissolved in acetic acid was added to 2 gm. of the condensation product, in a 250 cc. round bottom flask. 4 gm. of glacial acetic acid were then added, the flask attached to a reflux condenser, and the mixture boiled for three and a half hours. It was then allowed to cool, and 100 cc. of water were added. On pouring the liquid out of the flask, a quantity of thick gummy liquid was observed

on the bottom of the flask. This gummy liquid was dissolved in boiling alcohol and the alcohol allowed to cool, when a gummy liquid again separated out. The process was repeated three times, but it was found impossible to obtain the substance in the crystalline form.

The main bulk of the solution, which was poured off from the gummy liquid, was placed in a flask and the acetic acid distilled off. Water was added and then sodium carbonate solution. The mixture was then filtered. No organic material was obtained.

The above experiment was repeated, except that the mixture was boiled for 15 minutes only. After cooling and adding water, a crystalline substance separated out together with a small amount of a gummy liquid similar to that obtained in the above experiment. The crystalline material was filtered off and recrystallized from alcohol three times. The crystals so obtained were needle like and yellow in color. Melting Point - $114.0^{\circ}\text{C}.$

Oxidation of Condensation Product.- Potassium Dichrom..

Potassium Dichromate	-	5 gm..
Glacial Acetic Acid	-	20cc.
Condensation Product	-	2 gm..

The mixture of condensation product, glacial acetic acid, and potassium dichromate were placed in a round bottom flask attached to a reflux condenser, and boiled for one and one half hours. The mixture was then

boiled for one and one half hours. The mixture was then cooled, and water was added until no further precipitate was formed. The precipitate, which was brownish yellow in color, was then filtered off, and crystallized from alcohol three times. The crystals so obtained were needle like and brownish yellow in color. Melting Point - $114.5^{\circ}\text{C}.$

It is to be noted that oxidation of the condensation product could not be effected by either of the two methods described above.

Reduction of Condensation Product.- Sodium Bisulphite.

A small quantity of the condensation product was added to a faintly alkaline solution of sodium hydrosulphite, and the mixture was gently boiled for twenty minutes. After cooling, dilute hydrochloric acid was added until the mixture was acid to litmus. From this mixture, the condensation product, which was unchanged, was obtained.

Reduction of Condensation Product.- Tin and Hydrochloric.

A small quantity of the condensation product was added to a mixture of tin and hydrochloric acid. This mixture was boiled for thirty minutes. It was found that the largest part of the condensation product remained unchanged. The mixture was allowed

to stand for one day, and then an excess of dilute sodium hydroxide was added. A whitish yellow precipitate was obtained after addition of the sodium hydroxide, but not to such an appreciable extent as in the following experiment.

The above experiment was repeated, except that sufficient alcohol to completely dissolve the condensation product was added to the boiling mixture. After boiling for thirty minutes the mixture was allowed to stand for one hour. Dilute sodium hydroxide was then added until the mixture was alkaline. A pale yellow precipitate was obtained, which was filtered off. The soluble portion of this precipitate was crystallized from alcohol three times. The crystals so obtained were needle like and greenish yellow in color. Melting Point - $97^{\circ}\text{C}.$

Reduction of Condensation Product.- Stannous Chloride.

Stannous Chloride	-	5.7 gm. ($\cdot 2\text{H}_2\text{O}$)
Hydrochloric Acid	-	7 cc. (Sp. Gr. 1.18)
Condensation Product	-	2.0 gm.
Glacial Acetic Acid		

The condensation product was dissolved in boiling glacial acetic acid. 5.7 gm. of stannous chloride and 7 cc. of concentrated hydrochloric acid were then added. The mixture was boiled gently for fifteen minutes. It was then cooled, and dilute sodium hydroxide was added

until the solution was alkaline. A very bulky yellow precipitate was formed on adding the sodium hydroxide. The mixture was filtered, and the residue was dissolved in hot alcohol. It was observed that there remained a white solid substance, which was insoluble in alcohol. The portion soluble in alcohol was crystallized from alcohol by adding dilute ammonium hydroxide to the hot solution until a cloudiness just appeared. After standing, light greenish yellow, needle like crystals were obtained. These crystals were recrystallized from alcohol in the above described manner, twice more.

Melting Point - $97^{\circ}\text{C}.$

Yield - 1.6 grams of pure product.

In a later experiment carried out in the same manner, 7 grams of Condensation Product yielded 6 grams of pure Reduced product. Percentage Yield - 86%.

It was found that this last method was the most satisfactory for carrying out reduction of the condensation product.

"UMLAGERUNG" OF CONDENSATION PRODUCT.

The method described below is that given by Bamberger⁷ for the conversion of phenyl anthranil to Acridone.

0.109 grams of finely powdered phenyl anthranil are dissolved in 3cc. of concentrated sulphuric acid, at $-15^{\circ}\text{C}.$, (Dissolved by rubbing the solid in the acid.) to a clear syrup. Add 5 drops of 1% sodium nitrite solution (~~2.5 mg., calculating 40mg. for 1 gram molecule~~). ~~The color changes, and a noticeable smell of nitrous~~

solution (2.5 mg., calculating 40 mg. for 1 gram molecule). The color changes, and a noticeable smell of nitrous acid appears. After two minutes stirring at $-15^{\circ}\text{C}.$, pour into ice water. Filter the precipitate (Acridone), wash, and dry. Almost quantitative. A solution of acridone gives an intense blue fluorescence. Melting Point $-354^{\circ}\text{C}.$

This conversion was carried out on the condensation product, and there was obtained a yellow, amorphous material which, in a solution of dilute alcohol, gave an intense blue fluorescence.

CONVERSION OF Cl PHENYL ANTHRANIL TO Cl ACRIDONE.

Certain modifications of the method described by Bamberger were made, which gave an equally good yield of Cl Acridone, and which made the experiment more easy to perform. The method finally worked out was as follows :

7 grams of Chloro Phenyl Anthranil were dissolved in 200 cc. of concentrated sulphuric acid, which had been previously cooled by running water from the tap. 0.161 gm. of sodium nitrite (powdered) were then slowly added to the mixture. The color of the solution changed, and a smell of nitrous acid appeared. The mixture was allowed to stand, immersed in cold water from the tap, for one hour. ~~It was then filtered, washed with water, and dried.~~

It was then poured into 1000 cc. of cold water, filtered, washed with water, and dried. Yield of Crude Product - 6.8 grams. Percentage Yield - 97%. The crude material appeared as a yellow amorphous substance. It was recrystallized twice from glacial acetic acid and alcohol. Melting Point - Above 320 C..

It was observed that even the solution filtered off from the solid chlor-acridone, which solution contained the 200cc. of concentrated sulphuric acid showed a distinct blue fluorescence. Chlor-acridone, dissolved in dilute alcohol shows an intense blue fluorescence.

Analysis.

0.1982 gm. of Substance ; 11.0c.cm. of Nitrogen
(21.6 742.3mm.)

$C_{13}H_8ONCl$	Calculated :	N = 6.10%.
	Found :	N = 6.12%.

In carrying out an estimation of Chlorine in the above mentioned substance by Stepanoff's Method⁸, it was observed that after adding all the sodium, and on addition of water, a light brown precipitate was formed. This precipitate, which was filtered off, and dried, was crystallized from alcohol, using a small amount of bone charcoal to remove coloring material. After recrystallizing twice, light brown, needle like crystals were obtained. Melting Point - 169°C.. The substance was soluble on hot dilute acetic acid, soluble in glacial acetic acid. It was insoluble in dilute sodium hydroxide, soluble in dilute hydrochloric, sulphuric, and nitric acid. ~~All the above solutions~~

sulphuric, and nitric acids. All the above mentioned solutions showed a green fluorescence.

A further precipitate was obtained in this estimation on acidifying the dilute solution. This was filtered off and dried. It appeared as a grey powdery substance; not readily soluble in alcohol nor acetic acid (glacial). It was insoluble in benzene.

A small amount of this substance was boiled with 20 cc. of alcohol, and the mixture was filtered. The solution was deep red in color, and gave an intense blue fluorescence.

A small amount of the substance was heated in the bottom of a test tube. It was noticed that the substance sublimed producing a yellow crystalline material on the upper part of the inside of the tube. A small quantity of this crystalline material was removed. Melting Point - Above 330°C . It was soluble in concentrated sulphuric acid, giving an intense green fluorescence. In glacial acetic acid, it gave a blue fluorescence. Qualitative tests on this crystalline material for Chlorine and Nitrogen were both positive.

On account of the presence of Chlorine in this crystalline material, Stepanoff's Method for the Estimation of Chlorine had to be abandoned in the case of Chlor-Acridone.

No further investigation of the light brown needle like material, nor of the grey powdery material was carried out.

Qualitative Test for Phenyl Anthranil.

The following qualitative test is given by Bamberger⁹ for phenyl anthranil :

Suspend a very small quantity of phenyl anthranil in 3 drops of 62% sulphuric acid at 0°C.. Rub with three or four drops of concentrated sulphuric acid until an almost clear pale yellow solution is obtained. Cool in ice and add a drop of 10% sodium nitrite solution. The color becomes deeper yellow. Add ice water, and filter the yellow precipitate of acridone. The filtrate which is fluorescent, is added to alkaline α -Naphthol. A deep red color is thus produced.

The above test was tried on a sample of the condensation product. A deep red color was obtained.

Qualitative Tests for Chlorine and Nitrogen on 'Reduced' Condensation Product and Product from 'Umlagerung'.

The ordinary organic qualitative tests for Chlorine and Nitrogen were carried out on the two substances.

Tests for Chlorine and Nitrogen in the Reduced condensation product were both Positive.

Tests for Chlorine and Nitrogen in the Product from Umlagerung were both Positive.

o-Chloro Nitro Benzene.Condensation of o-Chloro Nitro Benzene with Benzyl Cyanide in the Presence of Sodium Ethylate.

1 mol.	Benzyl Cyanide	-	2 gm.
1 mol.	o-Cl NO ₂ Benzene	-	2.69 gm.
2 mols.	Sodium Ethylate	-	0.8gm. Na dissolved in 15 cc. of Et. Alcohol.

2.7 grams of o-Chloro nitro benzene were dissolved in a minimum of ethyl alcohol at room temperature. 2 grams of Benzyl cyanide were added. To the mixture was added a solution of 0.8 grams of Sodium dissolved in 15 cc. of ethyl alcohol. A deep brown color developed almost at once. The mixture was boiled on a water bath for ten minutes. While still hot, 30 cc. of water were added, and dilute hydrochloric acid was added until the mixture reacted acid to litmus. A brownish yellow solid material separated from the solution on acidifying. It was filtered off, washed with water, dried, and crystallized from alcohol, twice.

Yield of Crude Product - 3.8 grams. Melting Point - 165° - 170°C (begins to decompose at 165°C..)

A small quantity of the crystalline product was dissolved in hot dilute sodium hydroxide. A deep red colored solution was thus obtained. A portion of this solution, while still hot, was acidified with hydrochloric acid. A yellow precipitate was obtained.

Another portion of this hot alkaline solution was

allowed to stand $\frac{3}{4}$ A crop of red crystals were obtained, on cooling of the solution.

1 mol.	Benzyl Cyanide	-	2 gm.
1 mol.	o-Cl NO ₂ Benzene	-	2.7 gm.
$\frac{3}{4}$ mol.	Sodium Ethylate	-	0.3 gm. Na dissolved in 15cc. of Et. Alcohol.

2.7 grams of o-Chloro nitro benzene were dissolved in a minimal quantity of wthyl alcohol at room temperature. 2 grams of Benzyl cyanide were added. To the mixture, was added 0.3 grams of Sodium dissolved in 15 cc. of ethyl alcohol. The mixture was boiled gently on the water bath for three minutes. It was then cooled, 50 cc. of water added, and then dilute hydrochloric acid, with stirring, until the mixture reacted acid to litmus. A thick liquid separated out, together with a quantity of solid yellow material. The mixture smelled strongly of benzyl cyanide. It was found impossible to obtain the thick liquid in solid form, even after a number of crystallizations from alcohol.

1 mol.	Benzyl Cyanide	-	2 gm.
1 mol.	o-DINO ₂ Benzene	-	2.7 gm.
$1\frac{1}{2}$ mol.	Sodium Ethylate	-	0.6 gm. dissolved in 15cc. of Et. Alcohol.

The method of carrying out this experiment was the same as in the above experiment. After acidifying with dilute hydrochloric acid, and allowing to stand overnight, the

yellow precipitate which was obtained was filtered off, washed, and dried.

Yield of Crude Product - 3.9 grams.

The condensation product was crystallized twice from a mixture of equal volumes of benzene and alcohol.

Melting Point - 165° - 170° C. (began to decompose at 165° C.).

Condensation of o-Chloro Nitro Benzene with Benzyl Cyanide in the Presence of Sodium Ethylate, on a Larger Scale.

Benzyl Cyanide	-	10 gm.
o-ClNO ₂ Benzene	-	13 gm.
Sodium Ethylate	-	3 gm. of Na dissolved in 75cc. of Et. Alcohol.

13 grams of o-Chloro nitro benzene were dissolved in a minimal quantity of ethyl alcohol at room temperature. 10 grams of benzyl cyanide were added, and then the solution of sodium ethylate. The mixture was warmed to boiling on the water bath, for three minutes. It was then cooled, 200 cc. of water added, and then dilute hydrochloric acid until the mixture reacted acid to litmus. The mixture was stirred well and allowed to stand for a number of hours. The yellow precipitate was then filtered off, washed with water, and dried.

Yield of Crude Product - 20 grams. Percentage Yield - 93%.

The crude product was then washed with 40 cc. of ether.

It was crystallized from a mixture of equal volumes of alcohol and benzene, this being repeated three times.

Yield of Pure Product - 12 grams. Melting Point - 165° - 170° C. (began to decompose at 165° C., and puffs up in the melting tube point tube).

Analyses.o-Condensation Product.

0.2041 gm. Substance : 0.4894 gm. CO₂.

0.0673 gm. H₂O.

0.1945 gm. Substance : 19.25 c.cm.N. (24.2°C.,
749.9mm.).

0.1992 gm. Substance : 0.1079 gm AgCl.

C ₁₄ H ₉ N ₂ OCl	Calculated :	C 65.50	H 3.54	N 10.92	Cl 13.84
	Found :	65.39	3.64	10.88	13.40

0.1865 gm Substance ; 19.0 c.cm.N. (26.9°C.,
736.9mm.).

0.2016 gm. Substance : 0.1092 gm. AgCl.

C ₁₄ H ₉ N ₂ OCl	Calculated :	N 10.92	Cl 13.84
	Found :	N 10.84	Cl 13.40

Acetyl Derivative.

0.2056 gm. Substance : 17.22 c.cm. N. (21.4°C.,
754.7mm.)

C ₁₆ H ₁₁ N ₂ O ₂ Cl	Calculated :	N 9.38
	Found :	N 9.40

Formation of Acetyl Derivative of o-Condensation Product.

2 grams of condensation product were dissolved in 50 cc. of acetic anhydride, and the solution was boiled gently for fifteen minutes. The solution was cooled, and allowed to evaporate until a crop of yellow crystals were obtained. These were filtered off, and recrystallized from alcohol three times.

Melting Point - $178^{\circ}\text{C}.$

Oxidation of o-Condensation Product with H_2O_2 .

200 cc. of 10% sodium hydroxide and 50 cc. of 95% ethyl alcohol were added to 2 grams of the condensation product. The mixture was warmed on the water bath until all of the sodium salt had dissolved. 100 cc. of a solution (3%) of hydrogen peroxide were then added slowly and with stirring. Warming was continued until the red color of the solution had disappeared. It was allowed to stand, when an almost white precipitate settled toward the surface of the deep yellow colored solution. The precipitate was filtered off, washed with a little water, and dried. Yield of Crude Product - 1.8 gm.. It was crystallized from dilute alcohol three times, yielding ^{almost} white crystals. Melting Point - $98.5^{\circ}\text{C}.$ Purer samples of this oxidation product prepared later had a melting point - $97^{\circ} - 98^{\circ}\text{C}.$

Analysis.

0.2000 gm. Substance ; 9.9 cc N. ($26.8^{\circ}\text{C}.$, 749.8 mm.).

$\text{C}_{13}\text{H}_8\text{NO}_2\text{Cl}$ Calculated, N - 5.35 Found, N - 5.37 .

Am About 0.4 grams of this white crystalline substance were dissolved in glacial acetic acid, and while boiling, 1 cc. of concentrated nitric acid was added. The mixture was boiled for about one minute, diluted with water until a cloudiness appeared, and allowed to cool. Needle like, white crystals separated out. They were filtered off and recrystallized from alcohol. Melting Point - $97^{\circ}\text{C}.$. Melting Point of Product from H_2O_2 - $97^{\circ} - 98^{\circ}\text{C}.$.

Oxidation of o-Condensation Product with Nitric Acid in Glacial Acetic Acid.

2 grams of condensation product were dissolved in 30 cc. of glacial acetic acid, and 10 cc. of concentrated nitric acid were added. The solution was then heated to boiling. It was observed that the solution turned green in color. Fumes of NO_2 were then given off, and the green color gradually disappeared. The solution was boiled until fumes of NO_2 were no longer given off, and the solution became yellow in color. The hot solution was then slowly poured into two liters of cold water, while stirring vigorously. A concentrated solution of sodium hydroxide was then added to the mixture, slowly and with stirring, until the solution just reacted alkaline to litmus. A yellow precipitate was obtained, which, after the solution had been allowed to stand for two hours, was filtered off. The alkaline filtrate was tested for HCN in the usual manner, and it gave a decided Prussian Blue.

The yellow precipitate was crystallized from alcohol, using a pinch of animal charcoal to remove any coloring material. It was recrystallized from alcohol twice. Yield of Pure Product - 1.4 grams. Melting Point - 97 C..

Oxidation of o-Condensation Product with Potassium Ferricyanide.

200 cc. of 10% sodium hydroxide were added to 2 grams of the condensation product, and the mixture was stirred well, any large particles of condensation product being broken up. A solution of potassium ferricyanide was then slowly added until all the red color due to the sodium salt had disappeared. The solution was allowed to stand for fifteen minutes, and the precipitate was then filtered off. An attempt was made to crystallize it from glacial acetic acid, but only a yellow amorphous material could be obtained, which turned brown in color on standing in glacial acetic acid.

Formation of Phenyl Hydrazone of Product of Oxidation.

The phenylhydrazone of the product of oxidation was obtained in the usual manner, using calculated molecular quantities of each substance, in alcohol solution.

There was obtained after crystallization from dilute alcohol three times, a crop of pale brown needle like crystals.

0.2019 gm. Substance :

Analysis. 21.76 c.cm. N (25.0°C., 742.6 mm.Hg.).

$C_{19}H_{14}N_3O_2Cl$ Calculated N - 11.95 Found N - 11.84

m-Chloro Nitro Benzene.Condensation of m-Chloro Nitro Benzene with Benzyl
Cyanide in the Presence of Sodium Ethylate.

1 mol.	Benzyl Cyanide	= 2 gm.
1 mol.	m-Cl NO ₂ Benzene	= 2.7 gm.
2 mols.	Sodium Ethylate	= 0.8gm. Na dissolved in 15cc. of Et. Alcohol.

2 grams of benzyl cyanide were added to 2.7 grams of m-chloro nitro benzene. To the mixture was added 0.8 grams of sodium dissolved in 15 cc. of ethyl alcohol. The mixture was then boiled on the water bath for three minutes, cooled, and dilute hydrochloric acid added until the mixture was acid to litmus. A thick gummy liquid separated out after acidifying the solution.

The above experiment was repeated, except that the mixture was boiled for one minute only. Again a thick gummy liquid product was obtained.

The above experiment was repeated, except that the mixture was boiled for ten minutes. A thick gummy liquid product separated out on acidifying the mixture.

The above experiment was repeated, except that the mixture was warmed on a water bath to about 65 C. for five minutes. The mixture was then allowed to stand for one hour, after which it was acidified with 60% sulphuric acid, the solution being kept cool. 100cc. of water were then added slowly. A thick gummy liquid product was obtained.

A number of other experiments were carried out in which the amount of sodium ethylate solution used was varied, and in which the period of boiling the mixture was varied. The method finally worked out as being the most satisfactory, in that the largest amount of solid condensation product could be obtained from it, is as follows :

1 mol.	Benzyl Cyanide	-	2 gm.
1 mol.	m-Cl NO ₂ Benzene	-	2.7 gm.
1 ¹ mols.	Sodium Ethylate	-	0.6 gm. Na dissolved in 15 cc. of Et. Alcohol.

2 grams of benzyl cyanide and 2.7 grams of m-chloro nitro benzene were dissolved in a minimal quantity of 95% ethyl alcohol at room temperature. The sodium ethylate solution was then added, and the mixture was heated just to boiling on the water bath for three minutes. It was observed that on first adding the sodium ethylate to the benzyl cyanide and m-chloro nitro benzene, a violet coloration was produced, which rapidly changed to a brown coloration. After boiling, the mixture was cooled, and 100 cc. of cold water were added. The mixture was then acidified using dilute hydrochloric acid, which was added slowly with stirring. On acidifying, the deep brown color of the solution disappeared, and a yellow precipitate was obtained. This was filtered off and dried. It was crystallized from a mixture of equal parts by volume of alcohol and benzene, three times. Light yellow colored needle like crystals were obtained. Melting Point - 146°-149° C., (began to decompose at 146° C..)

This experiment was repeated using larger quantities of m -benzyl cyanide, m -chloro nitro benzene, and sodium ethylate, namely, 10 grams of benzyl cyanide, 13 grams of m -chloro nitro benzene, and 3 grams of sodium dissolved in 75 cc. of ethyl alcohol. The yield of solid crude product was 12 grams.

It can be seen that the method given only produces a yield of crude product slightly over half the theoretical yield.

The crude product was purified by washing with 40 cc. of ether, and was crystallized from a mixture of equal volumes of alcohol and benzene.

Properties of m -Condensation Product.

It was observed that when a small amount of the meta condensation product was dissolved in dilute sodium hydroxide, a deep red color was produced, and when this solution was acidified, the original condensation product was again obtained.

Analysis of m -Condensation Product.

0.1963 gm. Substance : 0.4696 gm. CO_2 .

0.0668 gm. H_2O .

0.2049 gm. Substance ; 20.80 cc. N. (25.0°C.,
742.8 mm.Hg..).

0.2015 gm. Substance : 0.1090 gm. AgCl .

$\text{C}_{14}\text{H}_9\text{N}_2\text{OCl}$	Calculated :	C 65.50	H 3.54	N 10.92	Cl 13.84
	Found :	65.25	3.72	11.01	13.39

TABLE SHOWING THE COLORS PRODUCED BY
THE COMBINATION OF ARSINIC CYANIDE
WITH AROMATIC NITRO COMPOUNDS IN THE
PRESENCE OF SODIUM HYDROXIDE.

NITRO COMPOUND.	Color Produced after add. of Na.Eth.toNitroC.	Color Produced after Addition of Benzyl Cyanide	Color Produced after Warming the mixture.
p-ChloroNitroBenzene	-	Violet.(Deep)	No Change.
o-ChloroNitroBenzene	-	Deep Brown.	No Change.
m-ChloroNitroBenzene	-	Deep Brown.	No Change.
p-NitroBromoBenzene	-	Violet.(Medium)	Color Deepened.
o-NitroBromoBenzene	-	Medium Brown.	Deep Brown.
m-NitroBromoBenzene	-	Deep Brown.	No Change.
p-NitroIodoBenzene	-	Medium Violet.	Deep Violet.
O-NitroIodoBenzene	-	Medium Brown.	Deep Brown.
m-NitroIodoBenzene	-	Deep Brown.	No Change.
p-NitroAnisol	-	Light Violet.	Deep Violet.
o-NitroAnisol	-	LightRedBrown.	Deep Brown.
m-NitroAnisol	-	LightRedBrown.	Deep Brown.
p-NitroBenzaldehyde	Brown.	Medium Brown.	Deep Brown.
o-NitroBenzaldehyde	Light Brown.	Medium Brown.	Deep Brown.
m-NitroBenzaldehyde	-	Medium Brown.	Deep Brown.
p-NitroBenzoicAcid	-	No Coloration.	Brownish Yellow.
o-NitroBenzoicAcid	-	Med. RedBrown.	DeepRedBrown.
m-NitroBenzoicAcid	-	Light Brown.	Deep Brown.
p-NitroPhenol	Yellow.	No Change.	Medium Brown.
o-NitroPhenol			
m-NitroPhenol	Brown.	No Change.	DeepBrownishRed.
p-NitroToluene	-	No Change.	DeepVioletBrown.
o-NitroToluene	-	Med.BrownRed.	Deep Brown.
m-NitroToluene	Pale Yellow.	Med.RedBrown.	Deep Brown.
m-NitroBenzalChloride	-	Medium Violet	DeepVioletBrown.

NITRO COMPOUND.	Color Produced after add. of Na. Eth. to NitroComp	Color Produced after Addition of BenzylCyanide	Color Produced after Warming the mixture.
o-Nitraniline	AfterWarming - LightOrangeBrown	No Change.	Deep Cherry Red.
p-Nitraniline	AfterWarming - Medium Yellow.	Light Yellow Brown.	Medium Brown.
m-Nitraniline	AfterWarming - LightYellowBrown	No Change.	Deep Brown.
Ethyl p-Nitro Benzoate	-	Light Green.	LightYellowBrown.
Ethyl o-Nitro Benzoate	-	Light Brown.	Deep Brown.
Ethyl m-Nitro Benzoate	-	Deep Brown.	No Change.
* p-NitroDimethylAniline	Pale Yellow.	No Change.	No Change.
3-Nitro 4-Acetyl Amino Toluene (Pract.)	LightBrownYellow	No Change.	DeepCherryRed.
	AfterWarming - DeepCherryRed.	No Change.	No Change.
Nitro Benzene	VeryLightYellow	Deep Brown.	No Change.
p-Dinitro Benzene	-	Deep Violet.	No Change.
o-Dinitro Benzene	-	VioletBrown.	Deep Brown.
2,4-Dinitro Chloro Benzene.	MediumCherryRed.	Deep Brown.	No Change.
1,5-DinitroNaphthalene	-	MediumCherry Red.	Deep Brown.
6-Nitro Quinoline	-	Light Brown.	Deep Brown.
Nitro Methane	WhiteSolid separated out.	No Change.	Quantity of Solid increased.
* m-Nitro Dimethyl-Aniline.	Pale Yellow.	No Change.	DeepRedBrown.

OTHER COMPOUNDS CONTAINING NITROGEN.	Color Produced after add.of Na. Eth.to NitroComp.	Color Produced after Addition of Benzyl Cyanide	Color Produced after Warming the mixture.
Nitroso Benzene	-	-	Cherry Red.
Nitroso b-Naphthol (Practical).	Light Yellowish Green.	-	Brownish Green.
Diphenyl Nitrosamine	-	-	-
Methyl Phenyl Nitrosamine	Light Yellow	-	-
Ethyl Nitrate	-	-	BrownishYellow.
Phenylhydrazine	Light Brown	-	-
<p data-bbox="186 745 1291 1312"><u>Note.</u> - In carrying out these color tests, the method used was as follows : A small amount of nitro compound was placed in a test tube and about two c.cm. of sodium ethylate solution (5 gm. of Sodium dissolved in 100 c.cm. of alcohol) were added, noting any color produced. Three drops of benzyl cyanide were then added, the color of the solution again noted, and the mixture was boiled gently on a water bath for two minutes, and the color was once again observed.</p> <p data-bbox="178 1386 1218 1764">No general conclusions can be drawn from these results. In a certain number of cases, it appears that para nitro compounds produce a violet coloration, while ortho and meta nitro compounds produce a brown coloration. As can be seen from the results, there appear to be a number of exceptions to this rule.</p>			

DETERMINATION OF DELICACY OF COLOR TESTS.

In a test tube, 2cc. of M/10 solution of p-Chloro Nitro Benzene were added to 2cc. of M/5 solution of Sodium Ethylate. One drop of benzyl cyanide was added. No coloration was produced immediately. By warming for 1-1/2 minutes in a boiling water bath, a medium violet coloration was produced.

The above test was repeated using 2cc. of M/100 solution of p-Chloro Nitro Benzene, instead of 2cc. of M/10 solution. By warming for 1 and 1/2 minutes in a boiling water bath, a violet coloration (lighter than in the above case) was produced.

The above test was repeated using 2cc. of M/1000 solution of p-Chloro Nitro Benzene. By warming for 1 and 1/2 minutes in a boiling water bath, a violet coloration (lighter than in the above case) was produced.

The above test was repeated using 2cc. of M/10,000 solution of p-Chloro Nitro Benzene. By warming for 1 and 1/2 minutes in a boiling water bath, a violet coloration (very light, but still visible) was produced. The color became more pronounced on cooling.

A more pronounced coloration was obtained by warming the mixture for 3 minutes.

The above test was repeated using 2cc.. of M/20,000 solution of p-Chloro Nitro Benzene. After warming for 3 minutes in a boiling water bath no coloration was produced.

It appears from these results, that p-Chloro nitro benzene in a solution of as small a concentration as M/10,000 will still give a violet coloration with benzyl cyanide, in the presence of sodium ethylate, which is visible to the eye.

Note on an Attempt to Synthesize 5-Chloro Phenyl Anthranil.

In the hope of adding further evidence to the proof of the structure of the product obtained from the condensation of Benzyl Cyanide with p-Chloro nitro benzene, an attempt was made to synthesize 5-Chloro phenyl anthranil. The following method was outlined : Starting with benzoic acid, it was hoped to be able to obtain m-Chloro benzoic acid, either by the method of Otto¹⁰, or by the method given by Glud and Kempf¹¹. It would then be nitrated by the method used by Cohen and Ames¹², obtaining 2-nitro 5-chloro benzoic acid. This could then either be converted to the acid chloride and coupled with a molecule of benzene by means of the Friedel-Crafts reaction, obtaining 5-chloro 2-nitro benzophenone, or the acid could be converted directly to 5-chloro 2-nitro benzophenone by the method used and developed by Ullman and Ernst¹³. By use of the method described by Bamberger¹⁴ for the conversion of o-nitro benzophenone to phenyl anthranil, there could be obtained 5-Chloro phenyl anthranil.

The methods of Otto¹⁰ and of Glud and Kempf¹¹ for the production of m-Chloro benzoic acid were tried experimentally. It was found that in carrying out the method given by Otto, that the benzoic acid did not even go into solution, and remained unchanged at the end of the experiment. In carrying out the method described by Glud and Kempf, it was found that the

benzoic acid went into solution in the nitric and hydrochloric acids but no "oil", as described by them, was obtained, and no m-Chloro benzoic acid was obtained.

A quantity of m-Chloro benzoyl chloride was obtained, from elsewhere, which was converted into the corresponding acid by means of dilute sodium hydroxide, and this acid was nitrated by the method used by Cohen and Armes¹², obtaining 5-chloro 2-nitro benzoic acid.

When an attempt was made to convert this acid to 5-chloro 2-nitro benzophenone, by the method given by Ullman and Ernst¹³, only a charred mass was obtained.

SUMMARY.

Summary.

1. A review of the previous work on the condensation of Benzyl Cyanide with Aromatic Nitro compounds, together with a brief survey of other condensations of a similiar character, has been presented.

2. The compounds formed by the condensation of Benzyl Cyanide with o-, m-, p-, Chloro Nitro Benzenes have been prepared and studied.

3. The constitution of the Condensation Products has been established.

4. The colors produced by a number of Aromatic Nitro Compounds with Benzyl Cyanide in the presence of Sodium Ethylate, together with the delicacy of the color reaction, have been determined.

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