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" A STUDY OF METHYLENE QUINONE-OXIMES " .

- presented by H. V. Kidd.

To The

UNIVERSITY OF MANITOBA

Examination Committee on Post-graduate Studies

In the Faculty of Arts and Science

- . 1932 . -

In Candidacy for the Degree of

Master of Science.

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To Dr. H. P. Armes, Professor of Chemistry of the University of Manitoba, is expressed the sincere appreciation of the writer for the suggestion and willing direction of the problem herein presented.

The writer is also obliged to other members of the Chemistry Department who have cordially given advice and assistance; and to the staff of the Storeroom for ready and willing service.

C O N T E N T S.

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PREFATORY NOTE.

The following presentation is concerned with the generality of the activated methylene group to condense with aromatic nitro compounds in the presence of sodium ethylate. In attempting to reach a generalization, examination has been made of the behaviour of mononitro and dinitrobenzene, and the ortho and para chloro-derivatives of the former, with both aromatic and aliphatic compounds containing the activated methylene grouping.

The investigation follows directly upon the recent investigation of Armes and Coke[1] with benzyl cyanide and ortho, meta, and para chloronitrobenzene in the presence of sodium ethylate; which in turn follows up the findings of Armes[7] with benzyl cyanide and nitro compounds, and Reissert's[2] admittedly incomplete investigations of the same cyanide with m-dinitrobenzene.

Armes and Coke[1] succeeded in assigning structural formulae to their condensation products with ortho and para chloronitrobenzene, and these formulae fitted the properties possessed by the compounds obtained by them, explaining many of the reactions. The applicability of similar structures to related reactions and products afforded the starting point of the present investigation.

The major portion of the work was concerned with the results obtained by substituting nitrobenzene in place of the

chlorine derivatives used by Coke[6]; and the reaction with diphenyl methane and p-chloronitro benzene in the presence of sodium ethylate.

Related work, of which the findings were less positive in nature, was carried out on ethyl cyanacetate, malonic ester, and benzyl chloride, with nitro and di-nitrobenzene, and halogen substituted nitrobenzene.

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I N T R O D U C T I O N.

A Brief Historical Review of the Pertinent Investigations to the Work under Consideration.

Only sufficient elaboration will be indulged in to develop the main thread of the work of preceding investigators which has lead more directly into the more recent work developed under the direction of Armes. References will be made to the original papers; a more detailed tabulation of related specific color reaction has already been presented by Coke[6] in 1928.

1886.- Janovsky's Reaction of Aromatic Ninitro Compounds[3]; aromatic nitro compounds in acetone solution were shaken with caustic potash solution. In many cases yellow, orange, brown, and violet colorations were reported.

1892.- Bela von Bitto[4] observed that many aromatic nitro and dinitro compounds gave a deep coloration with certain aromatic and aliphatic aldehydes and ketones.

1902-(1907)- Meisenheimer[5] showed that nitroanthracene is converted into the monoxime of anthraquinone in the presence of alcoholic potassium methylate. Prolonged treatment of nitroanthracene with potassium methylate leads to the formation of nitroanthrondimethyl acetate.

Meisenheimer represents the formation of the monoxime of anthraquinone as resulting from the preliminary

formation of a nitroso phenol by intramolecular oxidation, and subsequent wandering of hydrogen to the nitroso group. Coke and Armes[1] explain the formation of this compound and also of the nitroanthrondimethyl acetal on the basis of the Thiele Theory of Partial Valencies. A molecule of potassium methylate adds itself to nitro anthracene by the residual valencies of carbon and oxygen respectively, the metal going to an oxygen of the nitro group and the OCH_3 attaching itself to the carbon para to the nitro group of nitroanthracene. KOH subsequently splits off, and is followed by the addition of a second molecule of potassium methylate, exactly as before; the resulting product is the potassium salt of nitroanthrondimethyl acetal. Treatment of this acetal with sulphuric acid results in the formation of the monoxime of anthraquinone.

1904.- Reissert[2] drew retrospective attention to the color changes which were to be observed when aromatic nitro compounds were mixed with certain aldehydes and ketones; he attempted investigations with the purpose of evolving an explanation of the mechanism of this type of color change.

He offered an explanation of the reaction of nitrobenzene and m-dinitro benzene with acetone in the presence of sodium methylate. Coke[6] has dealt with this in detail. Reissert[2] further observed that compounds containing an activated methylene grouping also react with

multi-nitro aromatic compounds to produce intense colorations, and frequently a colored solid.

He effected a condensation between benzyl cyanide and m-dinitrobenzene in the presence of sodium ethylate. The general treatment was to warm a mixture of these compounds on the water bath, dilute and acidify, distil volatile compounds in steam, and allow to cool. A red brittle mass was obtained. Reissert concluded his investigation with an analysis of this compound which gave the empirical formula $C_{28}H_{20}N_6O_7$; and the explanation of the formation of such a compound by the condensation of two molecules each of the benzyl cyanide and m-dinitrobenzene,-

$$2C_8H_7N + 2C_6H_4N_2O_4 \longrightarrow C_{28}H_{20}N_6O_7 + H_2O$$

He abandoned the work at this stage, intimating the incompleteness, and hinting at the possibility of its further development.

Recent Work.- Armes [7] enlarged upon this finding by discovering that a great many mono and dinitro aromatics produce an intense coloration varying from brown to violet when mixed with benzyl cyanide in the presence of sodium ethylate. On acidifying with dilute hydrochloric acid, a compound was observed to separate in the form of a solid or a liquid, and the intense coloration of the original mixture altered and became decidedly lighter. These observations were mainly of a qualitative nature.

Coke undertook[6] a very thorough quantitative and analytical examination of one set of the compounds observed by Armes - ortho, para, and meta-nitrobenzene with benzyl cyanide in the presence of sodium ethylate. The obvious reason for this choice was the blocking of alternative positions by the chlorine, which would result in a more definite course of action during condensation.

It seems advisable to survey in brief form the work of Coke to the stage from which the following presentation was continued.

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Outline of Coke's Investigations.

Coke began by preparing a condensation product between benzyl cyanide and p-chloro-nitrobenzene using sodium ethylate. The general method of preparation of a condensation product was similar to that used by Reissert[2], and that used by Armes[7]. The p-chloro-nitrobenzene was dissolved in alcohol, the benzyl cyanide was added, followed by gradual addition of the sodium ethylate. The mixture was then warmed on the water bath for a short time, cooled and diluted with a moderately large volume of water, and acidified with dilute hydrochloric acid which caused the separation of a reaction product.

Coke concluded from experimentation that one mole-

eular quantity of benzyl cyanide with one molecular quantity of p-chloro-nitrobenzene and two molecular quantities of sodium ethylate gave the maximum yield. A yellow compound in needle crystals was obtained, which had a melting point of 114.5°C.

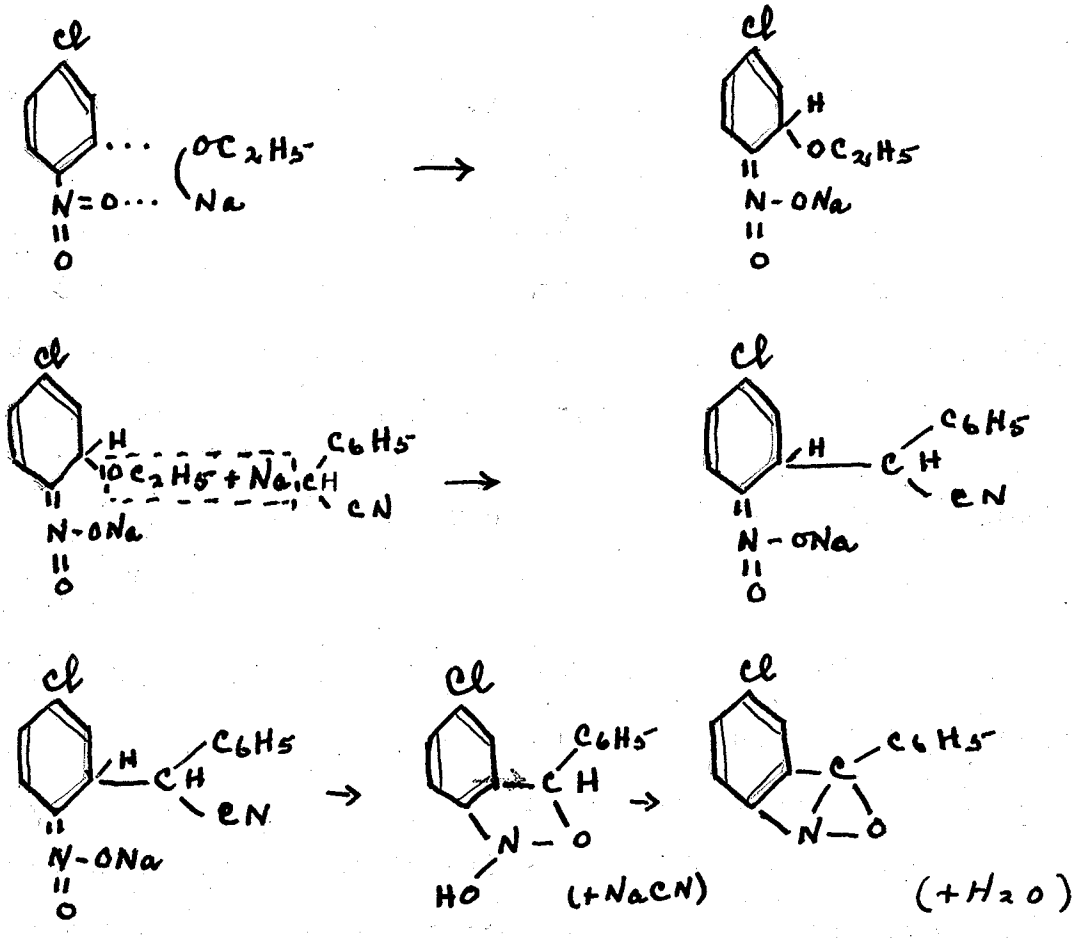
Analysis of this compound gave an empirical formulae $C_{13}H_8NOCl$.

The compound could not be hydrolised by hydrochloric acid, alcoholic potash, or sulphuric acid. Attempts to oxidize it with chromic acid and potassium dichromate were unsuccessful. The most successful method of reduction was effected with stannous chloride and hydrochloric acid.

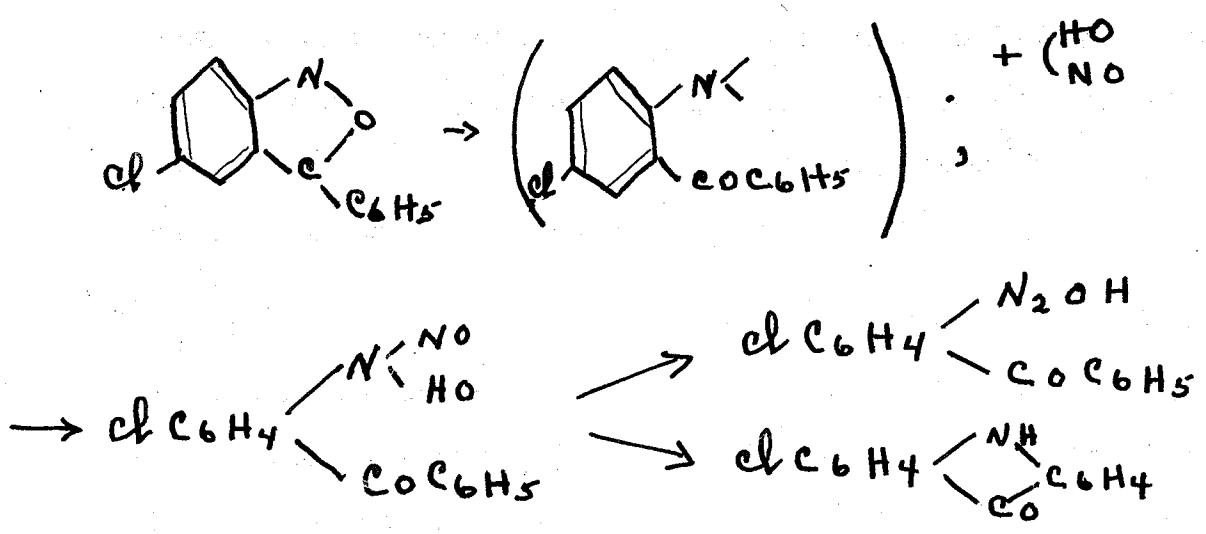
The clue to the structural formulae was obtained by diazotisation, when a substance was obtained which gave a pronounced fluorescence in alcoholic solution. This behaviour was observed to be similar to that obtained by Bamberger[4] in converting phenyl anthranil to acridone by diazotisation. This result, together with the properties observed by the other reactions, led to the identification of the condensation product as 5 chloro phenyl anthranil. The analysis agreed.

The relations are represented thus -

1. Initial condensation:



2. Conversion to chlor-acridone (after Bamberger[8]):

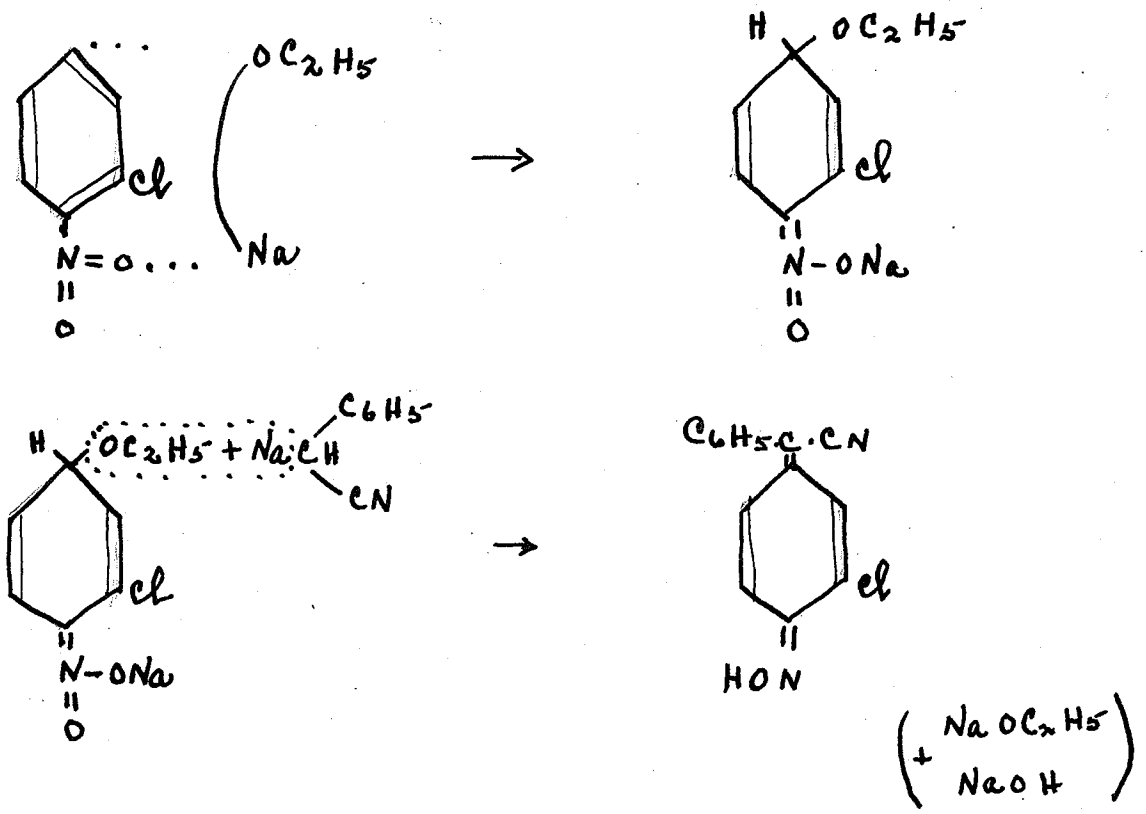


Examination of the condensation product between ortho-chloronitrobenzene was carried out by Coke in the same general manner. He found that the most suitable proportions of the compounds to use were the same as in the case of para-chloro-nitrobenzene: viz, one molecular quantity of o-chloronitro-benzene, one molecular quantity of benzyl cyanide and two molecular quantities of sodium ethylate. A yellow compound was obtained which melted ay 165°- 170°C.

Analysis of this compound gave an empirical formula $C_{14}H_9 N_2OCl$.

On treatment with hydrogen peroxide and with concentrated nitric acid, an almost white compound was obtained, which melted at 98.5°C, and gave a nitrogen percentage of 5.37. Potassium ferricyanide failed to effect an oxidation. An acetate was prepared in the form of a yellow compound melting at 178°C, and giving a nitrogen percentage of 9.40. A phenylhydrazone of the oxidation product in the form of pale brown needles was obtained, giving a nitrogen value of 11.84%. The condensation product itself was soluble in warm dilute sodium hydroxide, and yielded a salt on cooling; no hydro-cyanic acid was detected during the reaction.

These properties and analyses, in light of the inter-pretation placed on the reaction with p-chloro-nitrobenzene, led to the assigning of a quinoid oxime type of structure to this condensation product. The reactions are represented as follows:



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The condensation product of meta chloro-nitrobenzene was obtained by the same general treatment. It was found that one and a half molecular quantities of sodium ethylate to one molecular quantity each of the m-chloro-nitrobenzene and benzyl cyanide gave the best results. A compound was obtained in light yellow needles which melted at 146°- 149°C; and on analysis gave an empirical formula $C_{14}H_9N_2OCl$, as in the case of the ortho-chloronitrobenzene. A yellow acetate $C_{16}H_{11}N_2OCl$, and a white oxidation product, $C_{13}H_8NO_3Cl$, were obtained. These properties and analyses indicate a compound of the same type as that obtained with ortho-chloro-nitrobenzene, the chlorine bearing a different relative position only. The results were so interpreted.

Coke has also included tabulated results of a series of (qualitative) color tests on nitro-compounds, firstly on addition of sodium ethylate to the nitro compound; secondly, on the addition of benzyl cyanide to these; and lastly, on warming this mixture. In a very large number of cases benzyl cyanide produced an intense coloration in the cold, which deepened on warming. The usual color was brown to violet. No generalizations were drawn from the color changes observed.

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Theory Related to the Present Investigation.

It was in the light of the preceding information that the writer undertook to discover the generality of this type of reaction with activated methylene compounds, aliphatic and aromatic. The reaction carried out by Coke on the chloro-substituted nitrobenzenes was also investigated using nitro-benzene.

As was supposed, it was found with nitrobenzene that two reactions went on simultaneously and two products resulted, since the chlorine atom was not present to interfere with the addition of the benzyl cyanide group in either the ortho or para position to the nitro group. The bulk of the product was shown to be the result of a condensation in the position para to the nitro group. A small amount of the product was obtained, however, indicating that the benzyl cyanide had also added in the ortho position. This observation was strengthened by the detectable presence of hydrocyanic acid

in the filtrate from the preparation.

In order to add supporting evidence to the interpretation of the reaction, confirming the findings of Coke, analyses were carried out, and derivatives of the main condensation product were prepared and examined analytically.

The main condensation product was an orange-yellow compound melting at 167.5° - 168.5° C. It dissolved readily in warm dilute sodium hydroxide, forming a salt which yielded the original compound on acid treatment; this indicated the acid nature of the condensation product.

The second condensation product gave an intense red-blue fluorescence in dilute alcoholic solution. It was an almost white compound which melted at 56.5° - 57.5° C. Phenyl anthranil was prepared [9] for comparison, and a mixed melting point confirmed the belief that this second condensation product was phenyl anthranil.

The oxidation of the main condensation was effected with concentrated nitric acid, in glacial acetic acid, and also with hydrogen peroxide. An almost white compound was obtained in each case, which melted at 136° - 137.5° C; mixed melt same..

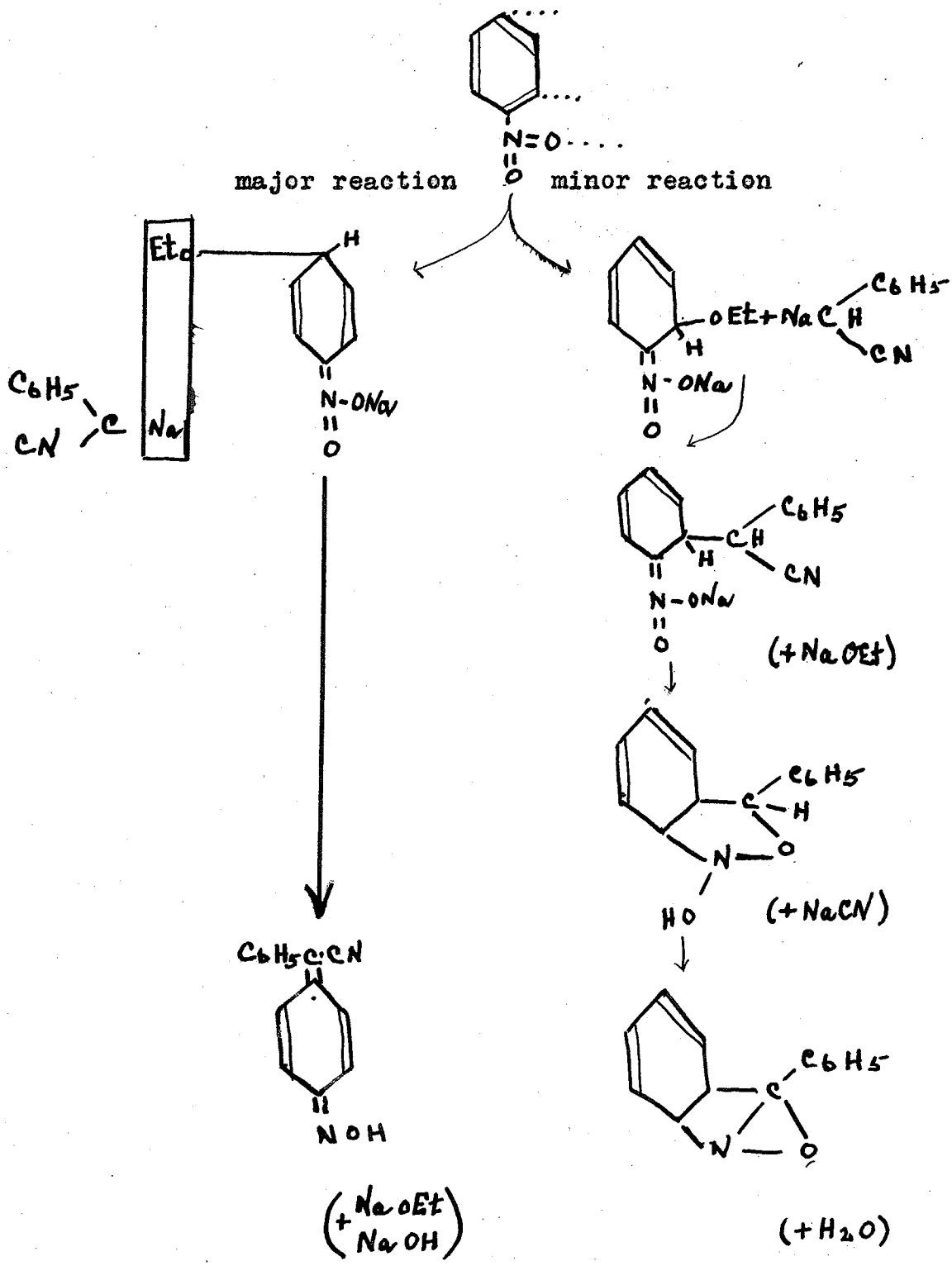
Para-nitro-benzophenone was prepared for comparison and the above oxidation was identified as p-nitro-benzophenone by a mixed melting point.

An acetate was prepared in the form of a yellow compound melting at 144°- 146°C; and a benzoate was also obtained as a light yellow compound which melted at 186°- 187.5 °C. These compounds were prepared by using acetic anhydride and benzoyl chloride respectively. They point to the presence of an OH-hydrogen (detected by salt formation with condensation product and dilute sodium hydroxide). Treatment of the condensation product with phosphorous pentachloride, gave a melting point at 180°- 183°C; which would point to the presence of an OH-group.

Analyses: Main Condensation product - C, 75.74; H, 4.98; N, 12.68; empirical formula, $C_{14}H_{10}N_2O$. Benzoate, C, 77.72; H, 4.68; N, 8.62; empirical formula $C_{21}H_{14}N_2O_2$.

These properties may be interpreted in the same manner as that used by Coke for the chloro-nitrobenzenes; and the reactions may be represented thus:-

The Condensation:



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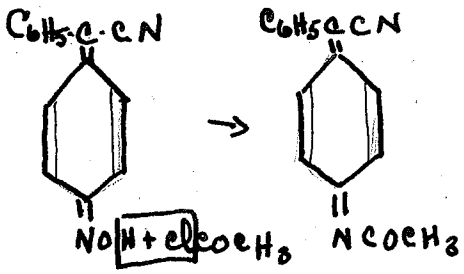
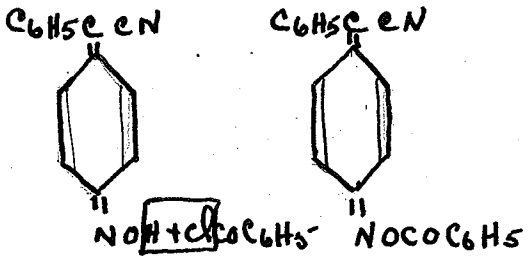
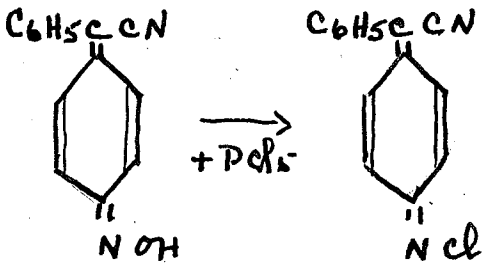
Acetylation.



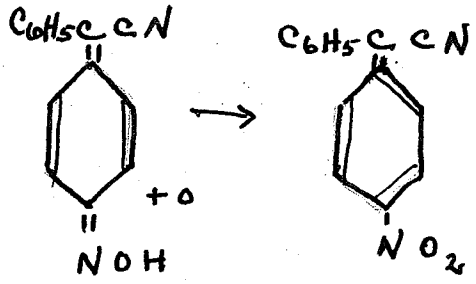
Benzoylation.



Chlorine Replacement



Oxidation



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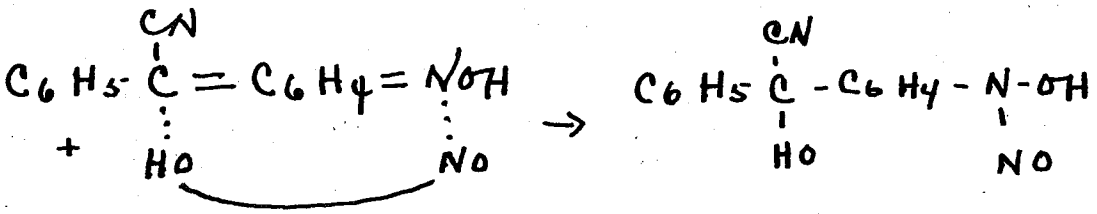
The main condensation product - phenyl cyano-methylene-quinone-oxime - was treated with nitrous acid following

indications of diazotisation occurring. Two intermediate products, which could not readily be identified, were obtained; these melted in the regions of 98°C, and 120°C.

On treating the cold solution (filtrate) which supposedly contained the diazonium compound, with alcoholic β-naphthol in basic solution, a red compound was formed. On separation and partial purification it melted at 219° - 220°C. A grass green compound was also separated from the original red, but it failed to give a definite or complete melting point. A red coloration and separation of a slight amount of red solid was obtained with α-naphthol. A tentative explanation was offered by Armes[10] involving the addition of an OH group to the quinoid nitrogen and an NO group to the quinoid carbon, the altered oxime group later giving rise to the diazonium grouping.



$$\rightarrow \quad C_6H_5COC_6H_5N_2X.$$

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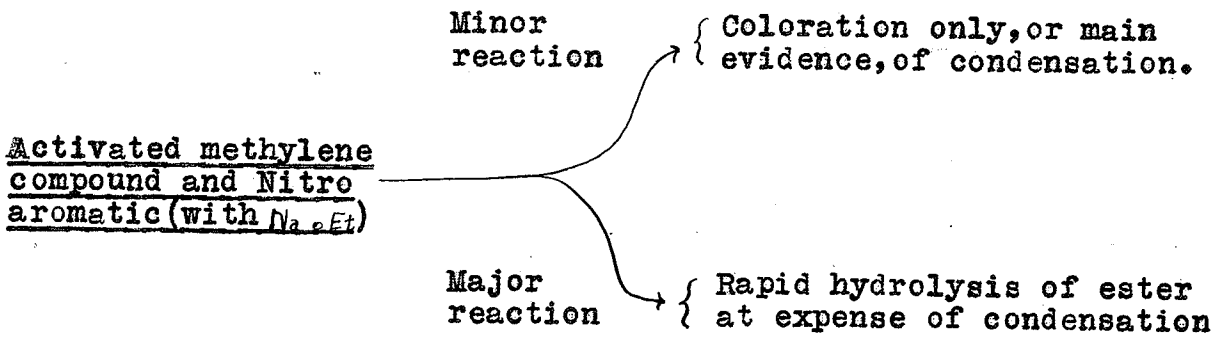
A condensation was attempted between ethyl cyanide and p-chloronitro-benzene, o-chloro-nitrobenzene, and nitro and m-dinitrobenzene in the presence of sodium ethylate. The first three compounds failed to condense beyond yielding a slight coloration (orange or yellow), for the ester hydrolysis preceeded with marked rapidity. In the case of the m-dinitrobenzene, a dark purple solid resembling potassium permanganate, and having a metallic irridescence, was separated. It melted indistinctly around 255° - 260° C; but attempts to obtain it pure enough for analysis were unsuccessful.

Ethyl malonic ester was tried with nitrobenzene, ortho-chloronitrobenzene and para-chloro-nitrobenzene. In all three cases hydrolysis proceeded at the expense of condensation, slight coloration only being observed.

Benzyl chloride failed to give any more definite results than slight coloration with ortho and para chloro-nitro-benzene. With nitrobenzene a deep red coloration was obtained, with separation of a small amount of brown semi-solid, indicating some condensation. Extractions with ether finally resulted in nothing more definite than the separation of a very small amount of a dark tarry mass having a sweet phenolic odor.

These results may be diagrammatically summarised as follows:-



In most cases the original solid compound was precipitated and identified by a mixed melt, while the salts of hydrolysis were soluble in water. From the observations made during the condensation manipulation with diphenyl methane and p-chloro nitrobenzene in the presence of sodium ethylate, it was definitely concluded that a condensation had been effected. Diphenyl methane was finally chosen after the difficulty arising in the previous cases with hydrolysis, since it is much more stable, and would therefore permit of more extended heating in an effort to effect a condensation.

No less than three products were obtained from this preparation, one a chocolate brown, of which the melting point could not be ascertained, and which appeared to be at least partially inorganic; a second, an almost black compound which melted at 115°- 125°C, and which formed in small amount; and a third, salmon-colored (impure, yellow pure) compound which melted fairly sharply at 147°- 149°C.

Attention was directed to an examination of this compound of m.p. 147°- 149°C.

An attempt to acetylate it with acetic anhydride proved unsuccessful, the compound itself remaining. Attempted benzoylation met with no more success. Reduction with stannous chloride and hydrochloric acid yielded only indefinite results. After purification to a light yellow compound of sharp melting point, analyses were made of it. It gave a nitrogen percentage of 10.776; carbon 64.66; hydrogen 4.16; chlorine 5.67. Armes found that Beilstein records a reaction between two molecules of p-chloro-nitrobenzene when warmed at length with alcoholic potash, pp-dichloro-azoxybenzene being formed. The description fitted the case under examination in several regards. The percentage composition of this compound would be: C, 53.93; H, 2.99; N, 10.49; Cl, 26.59. It will be noted that while the nitrogen shows close agreement, all the other values show wide deviation.

pp-dichloro-azoxybenzene on shaking with fuming sulphuric acid gives a deep red solution, and on dilution with water a compound is precipitated, the melting point of which is given as 183°- 184°C. This reaction was carried out on the compound under examination. A deep red solution was obtained with the fuming sulphuric acid; on dilution, a dark brown sticky compound was obtained, which purified to a deep yellow compound melting at 173°- 174°C. The rise from 149°C

of the original compound to 174°C was taken as indicative of a similar change having been effected to that of pp. dichloroazoxybenzene with fuming sulphuric.

A further factor of identification was furnished by preparing the compound obtained by digesting p-chloro-nitrobenzene with alcoholic potash. It melted in the partially pure state at 148°- 150°C. While the results in this investigation are admittedly indefinite, it was found necessary to discontinue the work at this point.

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All that can definitely be said of the condensation of compounds containing an activated methylene grouping with aromatic nitro compounds is that there appears to be a tendency towards such condensation which exhibits itself as a color change of greater or less intensity. When the compounds containing the methylene group are readily hydrolysed, the reaction proceeds in the direction of hydrolysis almost extirely. Other reactions which proceed fairly readily appear to do so at the expense of this type of condensation, possibly even inhibiting the cnndensation. Benzyl cyanide appears to hold a unique position among the methylene compounds which have fallen under the observation of the writer, in so far as it appears to condense with nitro, multi-nitro, and substituted nitro aromatic compounds, with great ease and rapidity.

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EXPERIMENTAL WORK.

E X P E R I M E N T A L.

PREPARATION OF CONDENSATION PRODUCT BETWEEN NITROBENZENE AND BENZYL CYANIDE IN THE PRESENCE OF SODIUM ETHYLATE.

10.5 gms.	nitrobenzene	1 mol.
10.0 gms.	benzyl cyanide	1 mol.
3 gms.	sodium in 75 c.c.alcohol	1½ mols.

The nitrobenzene and benzyl cyanide were introduced into a round bottom flask, and the sodium ethylate was added gradually while the flask was rotated. Immediately the ethylate entered the mixture a coloration from pink to violet was produced. The color gradually deepened on further addition of the ethylate, passing through intense red, brown, to an orange brown; by this time the mixture had become somewhat viscous. It was warmed on the water bath to boiling for six minutes. The mixture was cooled and 200 c.c's of water added. In the fume chamber , dilute hydrochloric acid was added slowly with stirring. As the basic solution approached the neutral point, a heavy dark-red liquid settled to the bottom. On further addition of acid, this was converted into an orange granular precipitate, rather waxy in appearance. The mixture was allowed to stand for 1 - 2 hours, filtered at the pump and washed well with cold water; yield approximately 16 grams of crude product.

After drying on a porous plate, the crude product melted in the region 164° - 167° C, though not very sharply. On recrystallising once from alcohol, it melted at 165° - 167° C.

A small portion of the alcoholic extract remaining in the flask was diluted with water, when it became greenish and slightly fluorescent. Addition of dilute hydrochloric acid produced no change, while adding dilute sodium hydroxide to alkalinity turned the solution a deep amber; subsequent addition of dilute hydrochloric acid again gave a green solution with slight fluorescence. The process appeared indefinitely reversible.

$$\text{Green, fluorescent} \underset{HCl.}{\overset{NAOH}{\rightleftharpoons}} \text{deep amber}$$

During the latter stages of drying the original precipitate at the pump, a few large drops of a deep-red-brown viscous liquid were drawn through; on standing these formed a red brittle mass.

This preparation was repeated a number of times, varying the time of heating from two to ten minutes. The approximate yield produced was the same in all cases; of twelve preparations using 10 grams of benzyl cyanide, 10.5 of nitrobenzene, and 3 of sodium in 75 c.c. alcohol, the average yield was 14.4 grams of crude product. In all preparations, the red oil referred to above was obtained in small quantities, suggesting the presence of a second condensation product. This product was later separated and identified. It was shown to be formed in very small quantities.

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Purification of Main Condensation Product.

The crude product was boiled with animal charcoal in alcohol twice. Subsequently it was recrystallized from hot 50% alcohol-water mixture six times successively. It finally melted within the range 166.5° -168°C. The nature of the compound prevents it from melting instantly, as it tends to smell and darken very quickly. Although repeated trials were made to further purify this condensation product, the melting point never appreciably exceeded 168°C. It was therefore assumed that the sample prepared above was in the pure state, and analyses were accordingly made to obtain its composition.

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Analysis of Main Condensation Product.

The ordinary method of combustion for the determination of carbon and hydrogen (J.B.Cohen, Prac.Org. p. 13) was attempted, but it was found that complete combustion of the compound could not be effected in this way. The compound was therefore intimately mixed with fine copper oxide, as described under nitrogen determination (Cohen , Prac. Org., p. 17). A current of air was used during the first part of the run, and was substituted for oxygen subsequently for 10-15 minites, followed again by air. Combustions using oxygen in place of air during the early stages of combustion gave increased values for carbon as much as 5% over the determinations using air. This was ascribed to the escape of oxide of nitrogen into the potash bulb. It was found

necessary to continue the early combustion in air for 2½ to 3 hours. In nine runs during which variations in method were introduced to obtain complete combustion, the following three sets of results were obtained in succession:

0.1708 grs. of compound yielded

	Found	Theoretical
0.0860 grs.water; % hydrogen	5.54	4.504
0.4702 grs.carbon dioxide;% carbon	75.08	75.675

0.3243 grs. of compound yielded

0.1582 grs.water; % hydrogen	5.42
0.9124 grs. carbon dioxide;% carbon	76.73

0.2902 grs. of compound yielded

0.1398 grs.water; % hydrogen	5.35
0.8070 grs.carbon dioxide;% carbon	75.84

While the results indicate general agreement of order with theoretical, it was decided that the compound under examination could not be of the highest order of purity. A fresh compound was therefore prepared, which was purified with animal charcoal, and recrystallized eight times from 50% alcohol-water, a relatively larger amount of solvent being used than previously, and greater care in the time of allowing the crops of crystals to precipitate, the first two crops during recrystallization being filtered before precipitation was complete. The final product melted at 167.5°- 168.5° C.

	Found	Theoretical
0.2013 grs. of compound yielded		
0.0912 grs. of water; % hydrogen	5.03	4.504
0.5591 grs. of carbon dioxide; % carbon	75.75	75.675
0.1958 grs. of compound yielded		
0.0878 grs. of water; % hydrogen	4.98	
0.5436 grs. of carbon dioxide; % carbon	75.71	
0.1985 grs. of compound yielded		
27.5 cc's. Nat.22°C and 735.59 mm; % nitrogen	12.788	12.613
0.2498 grs. of compound yielded 28.4 ccs. Nat. 20°C and 739.40 mm.; % nitrogen	12.680	

These values for carbon and nitrogen showed satisfactory agreement with theoretical; the hydrogen values (usually high) show agreement of order. The results as a whole were taken as sufficient evidence that the compound under examination had the same percentage composition as that of phenyl-cyano-methylene quinoneoxime expected from the condensation, thus establishing the identity.

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Properties of Condensation Product.

Orange-yellow, fine needle crystals; melting point, 168.5° Solubility - extremely soluble in glacial acetic, particularly on warming; soluble in alcohol, benzol, chloroform, acetone, more so on warming; almost insoluble in ether and water, hot or cold. No signs of dissolving nor other changes were observed with cold or hot dilute hydrochloric or sulphuric acid.

No change was observed with cold dilute nitric acid, but on warming the liquid became light green, and a dark brown tarry mass formed on top. With cold concentrated sulphuric acid an intense red solution resulted; on dilution a light yellow solid formed. With cold concentrated nitric acid, a dark brown tarry mass formed; it was readily soluble on heating, and on addition of water a brown semi-solid separated. Concentrated hydrochloric acid had no noticeable effect, hot or cold.

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ATTEMPTED PREPARATION OF THE ACETATE OF THE ABOVE CONDENSATION PRODUCT.

2 grams of condensation product

50 cc. acetic anhydride.

The mixture was heated on the water bath for 18 minutes. It was allowed to stand overnight, when a small crop of silky radiating crystals had formed. These were filtered at the pump. They were found to recrystallize from hot alcohol; and were recrystallized three times from 95% alcohol, and twice from absolute alcohol. A clean crop of yellow silky crystals was obtained, which melted at 145.5° - 147°C.

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An attempt was made to improve upon the yield, and obtain the acetate on a larger scale.

5.3 grs. condensation product.

199 c.c. acetic anhydrode.

The mixture was heated for 30 minutes on the water bath, and allowed to stand overnight. Only a small amount

of crystals had formed. A sample of the mixture was diluted with water, and a precipitate settled which resembled the condensation product in appearance, and also in respect to its behaviour with dilute sodium hydroxide, and dilute hydrochloric acid.

The bulk of the mixture was then heated over a low flame to boiling for 20 minutes, a dark brown solution resulting. It was cooled and poured into 200 c.c. water, with the separation of a small amount of brown precipitate. Three successive attempts were made to filter this precipitate, but it only deposited on the paper as a thin gummy film. On dilution to 2000 c.c.'s, a small amount of brown gummy precipitate settled to the bottom, and remained on decantation. It appeared as if partial decomposition, at least, had occurred during the attempted acetylation. This preparation was discarded at this point.

x x x

2.3 grs. condensation product.

5-6 c.c's, glacial acetic acid

2-3 c.c's acetic anhydride.

The mixture was boiled gently over a low flame for 20 minutes with an air condenser attached. It was then cooled and poured into 300 c.c. of cold water. A turbid yellow resulted, with the separation of a small quantity of brown sticky precipitate. After considerable stirring, a gummy lump of brown matter, resembling that obtained above, remained in the bottom of the beaker.

x x x

2 grs. condensation product.

6 c.c's glacial acetic.

2 c.c's acetic anhydride.

The mixture was heated on the water bath for 3-4 hours. On passing into cold water, a yellow turbid solution resulted, and a sticky mass separated on the bottom of the beaker. This mass did not show signs of crystallizing, even after standing some days. A very small amount of a yellow solid separated from the body of liquid.

This preparation was repeated with the same quantities of materials, but heating on the water bath was continued for only 40 minutes. The mixture, following heating, was cooled and poured into 300 c.c.'s of cold water; a turbid solution resulted, and a yellowish precipitate settled. After standing a day the turbidity cleared up fairly well.

The precipitate was composed of at least two products; one a light yellow, and the other a dark yellow; their physical states also differed. The more crystalline dark compound was less soluble in cold alcohol than the lighter-colored compound (m.p. 144° - 146°C).

These results seemed to indicate the possibility of two acetates being formed, which would suggest the existence of the condensation product in geometric isomeric forms. On the other hand, decomposition may have resulted; or a mixture of original condensation product and acetate might have resulted from the attempted acetylation. Separation of one or more pure compounds from these gummy precipitates was not very successful, so it was decided to investigate the effect

of benzoylation.

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PREPARATION OF A BENZOATE OF THE CONDENSATION PRODUCT.

A small amount of the condensation product was shaken vigorously in a large test tube with .5-1 c.c. benzoyl chloride and excess dilute sodium hydroxide. A white lardy compound formed; the supernatant liquid was decanted, and the compound washed by decantation, first with dilute sodium hydroxide and later with water. It was recrystallized three times from hot alcohol. m.p., 177° - 179°C, not very sharply.

x x x

An interesting result was obtained on substituting concentrated sodium hydroxide in the Schotten-Baumann reaction. About 2 grams of the condensation product were placed in a large test tube with 1-2 c.c.'s of benzoyl chloride. A little concentrated (50%) sodium hydroxide was added carefully. A reaction soon commenced, which proceeded quite violently and almost instantaneously, caused, partially at least, by the heat evolved between the benzoyl chloride and concentrated NaOH. The result was a mixture of two compounds, the general appearance being lardy; this preparation was lost in handling. It revived the idea of the possibility of the condensation product existing as geometric isomers, which had been suggested by acetylation. It was therefore decided to attempt a preparation of two benzoates.

x x x

2 • 7 grs. condensation product.
about 30 c.c's. dilute sodium hydroxide.
Benzoyl chloride added in small amounts from time to time.

The mixture was stirred constantly by the electrical device, in a round bottomed flask; this kept the forming compound in a fine state of division. On standing, however, it lumped together as a greasy ball. Here also - as in the case of the acetate - a darker and lighter compound were observed to be present.

The mixture was warmed with 50% benzoyl-alcohol, in which it dissolved; the darker compound appeared much more readily soluble. On cooling the yellow compound precipitated readily, and looked fairly pure. (m.p. 181° - 182°C; recrystallized from 50% benzoyl-alcohol; m.p. 185.5° - 186°C).

On concentration of the solution, a second crop of the yellow compound was obtained and filtered. (m.p. 181° - 182.5°C). After concentrating this filtrate to small volume, a brown granular precipitate formed. The precipitate was filtered at the pump; it possessed a mixed odor of phenol and ester. A sample of it was found to be moderately soluble in cold alcohol, and in chloroform; but not appreciably in petroleum ether. The bulk of the precipitate in the filter funnel was accordingly washed four times with petroleum-ether, which rendered the precipitate in a fairly pure looking state as waxy flakes of dark yellow color. They melted at 112° - 113.5°C, though not sharply; after recrystallization twice from 50% alcohol-water they melted at 116.5° - 118.5°C, still not very

sharply. Impure crystals were recovered from the petroleum-ether washings, which melted sluggishly at 114° - 118°C. This melting point range, together with the behaviour towards solvents, suggest the compound under examination to be impure benzoic acid, which may quite have resulted from carelessness in the limits of basicity in the endeavour to establish a method for preparing a second benzoate in addition to the yellow product (m.p., in neighborhood of 185°C), which forms the main product. With these results it was decided to abandon the pursuit of any second possible benzoate, and to proceed directly with the preparation, purification, and analysis of the yellow benzoate.

x x x

The method employed for preparation of the benzoate on a large scale was to dissolve the condensation product in 10% sodium hydroxide (deep red solution); this was stirred mechanically for 15 minutes, during which time benzoyl chloride was added gradually at intervals, the solution being kept basic. The red color slowly disappeared and a yellow precipitate formed, which was kept divided by the stirring device. After the 15 minutes of stirring, the mixture was diluted to about 200 c.c's, and the stirring continued for another 15 minutes, which rendered the precipitate in good form. The precipitate was filtered at the pump, washed with dilute sodium hydroxide, and then with water till neutral. The filtrate was light orange, and definitely basic.

The precipitate was recrystallized five times from hot 50% benzoyl-alcohol. This product melted sharply at 186° - 187.5°C. It was considered pure enough for combustion.

Analysis of the Benzoate of Condensation Product.

The first five nitrogen determinations showed a variation of 1%, ranging from 8.62 - 9.76. The benzoate was therefore further purified till it gave a melting point of 187° - 188°C.

Results:

	Found	Theoretical
0.1920 grs. of compound yielded		
15.7 c.c's of N at 30°C and 746.51 mm.; % nitrogen	8.62	8.59
0.1416 grs. of compound yielded		
11.7 c.c's of N at 26°C and 747.27 mm: % nitrogen	8.98	
(previously) 0.1774 grs. of compound yielded 14.8 c.c. of N at 29°C and 749.81 mm.; % nitrogen	8.62	
0.2384 grs. of compound yielded		
0.1005 grs. of water; % hydrogen .	4.68	4.29
0.6794 grs. of carbon dioxide; % carbon	77.72	77.30

These values were regarded as satisfactory evidence of the identity of the benzoate.

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OXIDATION OF THE CONDENSATION PRODUCT.

1. With Concentrated Nitric Acid.

2 grs. condensation product.

30 c.c's. glacial acetic acid.

10 c.c.'s concentrated Nitric Acid.

When the nirtic acid was added to the mixture of the condensation product and glacial acetic acid in a round-bottomed flask, the mixture turned a dark green rapidly. A short air condenser was fitted, and the mixture boiled slowly with a low flame till evolution of brown fumes had ceased. The color of the solution had cleared to a deep orange.

The warm solution was poured slowly with vigorous stirring into 1500 c.c. of cold water. Concentrated sodium hydroxide was added gradually with stirring till just basic. A flocculent solid separated and settled on the surface. This was filtered at the pump after standing for an hour. The dried compound was very light brown, melting in the impure condition in the range 125° - 135°C.

On boiling twice with animal charcoal and alcohol light yellow crystals were obtained, melting at 129° - 132 C. After four additional recrystallizations from alcohol, an almost cream-colored crop of crystals was obtained, melting at 131.5 - 133.5 C.

x x x

2. <u>With Hydrogen Peroxide</u>.

2 grs. of condensation product

250 c.c. 10% sodium hydroxide

60 c.c. ethyl alcohol.

Sodium peroxide - till reaction had ceased.

The mixture of the condensation product, sodium hydroxide, and alcohol, was heated on the water bath till the solid had completely dissolved. Hydrogen peroxide was added gradually,

the addition being accompanied by change of color. When no further reaction appeared to take place the mixture was warmed on the water bath till a white precipitate had completely settled on top of a clear orange liquid. This precipitate was filtered at the pump, washed several times, and dried. (yield 1.85 grs.) m.p. 134° - 138° C. On recrystallizing twice from 50% alcohol-water, a melting point 136° - 137.5° C was obtained; checked. A mixed melt with the product from the nitric acid oxidation gave a sluggish melting range from 131° - 135° C.

x x x

The oxidation products of phenyl-cyano-methylene quinoneoxime should be p-nitrobenzophenone. This compound was accordingly prepared for comparison.

x x x

PREPARATION OF P-NITROBENZOPHENONE.

5.05 grs. p-nitrobenzoic acid.

7.76 grs. dry phosphorous pentachloride.

8.62 grs. benzene.

6.04 grs. anhydrous aluminium chloride.

The p-nitrobenzoic acid and the benzene were mixed in a round-bottomed flask, and the phosphorous pentachloride was added gradually, immediately after weighing. A calcium chloride tube was fitted into the mouth of the flask. After a minute or two a gentle reaction set in, with the evolution of hydrogen chloride. After the reaction had ceased a viscous honey-like liquid remained. This was cooled in a mixture of

ice and water while the dry aluminium chloride was added; the calcium chloride tube was replaced, and hydrogen chloride was again evolved during a gentle reaction. The mixture was finally warmed for 25 minutes on the water bath; brownish semi-solid mass resulted. This was shaken up and poured carefully over crushed ice in a beaker, resulting in a white lard-like solid. After the ice had melted this mixture was stirred mechanically for 15 minutes, the precipitate being broken up. After allowing to stand for the evaporation of excess benzol, the mixture was filtered at the pump, washed with dilute sodium hydroxide, several times with cold water, and dried; (yield 2.9 grs.). Melting point range of the crude product 123° C - 130° C. On recrystallizing twice from absolute alcohol the melting point was raised to 133°- 135° C, though the melting was still not sharp. This product was therefore boiled twice with animal charcoal, and recrystallized from absolute alcohol. It melted at 137°- 138°C fairly sharply, but a slight shrinkage without melting was observed at 133°C. The melting point of a mixture of the para nitrobenzophenone and the oxidation product from the hydrogen peroxide treatment was fairly sharp at 135°C; this was regarded as identification.

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TREATMENT OF THE CONDENSATION PRODUCT WITH NITROUS ACID - AN INVESTIGATION OF THE POSSIBILITY OF DIAZOTISATION.

A wide variety of results was obtained during the course of a series of sixteen experiments, varying the temperature,

the time, the acid, the condition and quantity of sodium nitrite, the general method of procedure and subsequent treatment of products obtained. No satisfactory method was evolved to produce a large quantity of the diazenium compound. That diazotisation occurred was proven beyond question in many of the trials. It appeared that at least two different intermediate products were obtained which melted without much purification in the regions of 100°C and 125°C respectively; the melting was not perfectly sharp, and it may have been a mixture of compounds that was under observation. In many cases these compounds reverted to a tarry or brittle mass on standing, indicating an unstable nature. As these products were subordinate to the main purpose of the diazotisation, extensive purification and examination were carried out.

The majority of the experiments were not carried out at a temperature ranging from - 20°C to - 10°C, not raising above 0°C at any stage of the diazotisation. The cooling was effected by using a 1 : 3 mixture of salt and crushed ice, and the temperature was kept fairly constant over a period of time by a set of four beakers arranged one inside the other, with cotton batten and cork separators. Stirring was done mechanically with an electric stirrer.

x x x

1 gr. condensation product.

.5 grs. powdered sodium nitrite.

The condensation product was dissolved in the necessary quantity of glacial acetic acid. The temperatire was lowered to -20°C with a salt-ice mixture. Sufficient alcohol was

added to prevent the acid from crystallizing. As the mixture was stirred gradually the powdered sodium nitrite was slowly added. A slight perceptible evolution of gas resulted, and the mixture became a light brown in color; this changed to olive green with stirring, and on further addition of sodium nitrite reverted to brown permanently. The mixture was stirred for an hour and a half, and was then added to dilute hydrochloric acid below 0°C. A brown precipitate was thrown down. It was filtered rapidly at the pump, and washed with cold water. After drying this precipitate melted at 87 - 90 C. Yield, about .42 grs.

The cold filtrate was added to a cold basic solution of α-naphthal in alcohol. An intense red coloration resulted and a slight precipitate appeared, though not in sufficient quantity to examine.

It was decided to devote some time to the examination of the intermediate product before proceeding to the colored compound apparently forming with α-naphthal.

x x x

10 grs. condensation product.

6.2 grs. sodium nitrite (in 10 c.c's. water).

The condensation product was dissolved in sufficient glacial,acetic acid as before, and alcohol added to prevent crystallization. The temperature was held below -13° C, and stirring continued throughout. The sodium nitrite was added in 10 c.c's of water cooled in ice. After stirring for two hours a slight yellow precipitate had formed. The mixture

was added to dilute hydrochloric acid below -10°C. A yellow precipitate formed, which was filtered off, washed and dried; it melted at 98°- 100°C. (Yield, 6-7 grs.). An odor of HCN was noticeable on the addition of dilute hydrochloric acid; and this same observation was made on all such subsequent additions of the nitrite treatment to acid solution.

The filtrate was added to cold cuprous chloride (-10°C); a small amount of brown precipitate formed. After standing for an hour this precipitate was filtered; on ignition it was shown to contain a high percentage of copper. It was subsequently boiled in an attempt to complete a Sandmeyer reaction. On extraction with benzol and subsequent attempts at crystallizing, only an oil with a sweet phenolic odor was obtainable.

x x x

This reaction was again repeated, dissolving the compound in alcohol, and using concentrated sulphuric acid instead of glacial acetic; the temperature was kept below -10 C. On addition of the mixture to cold dilute hydrochloric acid a yellow precipitate was obtained which melted at 97°- 99°C, though the melting was not sharp.

x x x

On repetition with concentrated sulphuric acid, using dry powdered sodium nitrite, the same yellow compound was obtained, melting at 97°- 98°C. The filtrate from this preparation was added to a cold solution of freshly prepared sodium stannite, in the presence of sodium hydroxide till

basic. A deepening in color was observed accompanied by a slow evolution of a small amount of gas. The mixture was shaken with ether; the ether extract was dehydrated, decanted and allowed to stand after concentration. A red oil with sweet odor remained. Attempts to obtain a crystalline compound were unsuccessful.

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It was found that if the yellow precipitate referred to above(using either glacial acetic acid or concentrated sulphuric, and either dry sodium nitrite or a concentrated solution of it) changed from yellow to brown on washing with water at room temperature. This suggests a different subsequent reaction with the nitrous acid. Part of this solid was recrystallized from alcohol, and melted indistinctly at 163°-168°C, indicating the presence of some of the original condensation product. The remainder turned to a dark brown brittle mass on standing overnight. This same result was observed on repeating this experiment with washing of the precipitate with water at room temperature.

To confirm the belief of a different reaction, an experiment was carried out at room temperature (15°- 20°C). On addition to dilute hydrochloric acid at 15°, a light brown gummy mass was obtained.

x x x

Further repetition of this experiment, washing thoroughly with water at room conditions, gave similar results. Another variation was also tried. After the regular treatment in the cold for an hour and a half using concentrated sulphuric

the mixture was poured into ice-water. A yellow precipitate formed. The temperature was allowed to rise to 15° C, when a second molecular quantity of sodium nitrite was added and stirring continued for half an hour. The precipitate deepened to a brown. It was filtered, (filtrate yielded a tarry residue on standing for a week), washed with water, and subsequently with alcohol. The melting point was indistinct, the limit being 122 C.

Attempts at purification of the compound obtained by this process were not very successful. Crystallization from alcohol was adopted. Frequently the compound was found to undergo further change, exhibiting instability and conversion to a gummy mass or an oil. An unsatisfactory melting point range of 118°- 121° C was established on three separate samples of the compound.

x x x

The compound melting in the region of 98 C, was taken up with benzol, in which it was readily soluble. On adding alcohol a colloidal suspension resulted. A little water was added, and after allowing to stand overnight a gummy mass had settled. This was dried and taken up with a minimum of benzol and alcohol (or petroleum ether) added very gradually; a chrome yellow precipitate was obtained. This was repeated a second time. Precipitation was inconsistent, a reversion to a tarry compound frequently occurring. A partially pure product (insoluble in hot NaOH) obtained in this way gave a melting point range of 156°- 159°C.

An indication of the formation of both compounds during

the same preparation was obtained. Three grams of the condensation product in sufficient glacial acetic acid and alcohol were treated with three grams of sodium nitrite in 13 c.c. of water. After stirring an hour and a half an orange precipitate had settled, which was filtered immediately. On drying it melted around 120° C. The filtrate was treated with cold dilute hydrochloric acid, as usual; it yielded a yellow precipitate melting fairly sharply at 100° C-103° C.

x x x

As has been indicated, no definite result was obtainable on treating the cold filtrates from the above preparation, (supposedly containing diazonium compound) with cold sodium stannite in basic solution, nor using cuprous chloride. Treatment with precipitated copper yielded no more definite results. On addition of the copper, there appeared to be a gas evolved. The mixture was allowed to stand overnight, boiled 10-20 minutes, stirring mechanically. The ether extract on dehydrating and concentration yielded a dark green oil. Attention was consequently turned to the treatment of the filtrate with α-naphthol and β-naphthol in basic alcoholic solution. It has already been mentioned that an intense red coloration resulted on adding the cold filtrates from nitrous acid treatments to α-naphthol. It was found by testing that β-naphthol gave a deep rose coloration, and also yielded a reddish precipitate in a quantity which was capable of being handled. Since α-naphthol gave only indications of a precipitate, the β-naphthol reaction was adopted.

The nitrous acid reaction was carried out in the manner already described, keeping the temperature below -10 C. The filtrate, after removal of any solid separating, was added to a cold basic solution of β-naphthol. A deep rose coloration resulted, accompanied by the separation of a red compound. The mixture was stirred for half an hour, filtered, and washed with ice-water. The melting point was indefinitely from 76°C-86°C. Properties - slightly soluble in cold alcohol, more so on warming (dark orange solution); part readily soluble in benzol*; very slightly soluble in dilute NaOH; moderately soluble in ether .

*The bulk of the precipitate was treated with benzol; a small amount would not dissolve. The mixture was filtered leaving a grass green residue upon the filter paper, the filtrate being a deep orange. To the filtrate was carefully added petroleum ether, and a carmine red precipitate was thrown down. This compound showed signs of melting at 126°C-131°C. After recrystallizing twice from benzol ad above, and drying for three weeks, a fairly sharp melting was obtained at 219°C-222°C.

The green compound failed to melt completely, even when raised to 290°C. Ignition left a dirty white ash which did not dissolve in cold water, and in hot or cold dilute hydrochloric acid only to a limited extent. While it was clearly evident that the green product under examination was a mixture, it was never obtained in sufficient quantities to yield a precipitate on recrystallization attempts.

The only definite information obtained from these com-

pounds - which were obtained in the same colors on repetition of the experiment - was the evidence of diazotisation having been effected. The appearance of a mixture of two compounds of different color by treatment with β-napthol suggests a similarity (only) in behaviour to the mesochromes observed by Hantzsch" among the nitro phenols (and ethers); for example, the sodium salt of tribromo m-dinitro phenol, yellow O nitrophenol ether, and the red and yellow modifications of thallium picrate.

The basic filtrate from the β-napthol treatment on two occasions was made acidic with dilute hydrochloric acid, and allowed to stand . A red precipitate settled out in distinctly noticeable quantity. While this compound dissolved in dilute sodium hydroxide to give a deep rose-colored solution, it did not melt until 180°C-183°C, the first indications not appearing till 175°C.

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TREATMENT OF CONDENSATION PRODUCT WITH PHOSPHOROUS PENTACHLORIDE.

1 gr. condensation product.

1-1.5 grs. phosphorous pentachloride.

The condensation product was dissolved in dry ether, and the phosphorous pentachloride added gradually in powdered form. An evolution of hydrogen chloride resulted, with a slight rise in temperature. The ether was distilled off leaving a dark brown viscous mass. Water was added, and the

mass brought to the boil; a brown solid formed, which was filtered. The light yellow filtrate was concentrated and cooled, when a slight oil was observed floating on the surface.

The solid was insoluble in ether, benzene, toluene, and alcohol; slightly soluble in chloroform, and more so in acetone. It was moderately soluble in warm glacial acetic acid, from which it was precipitated by addition of water. A flocculent precipitate was obtained which melted at 180°C-183°C.

This reaction further points to the existence of the OH group, to be expected in the quinone-oxime type of structure assigned by Armes [7] to the condensation product.

- o O o -

EXAMINATION OF THE SECOND CONDENSATION PRODUCT OF BENZYLCYANIDE AND NITROBENZENE.

80 grams of the solid phenylcyanomethylene quinoneoxime were extracted three times by mixing with ether in a mortar and filtering at the pump. To this extract were added the extractions from the filtrate and wash waters of a 40-50 gram fresh preparation of the phenylcyanomethylene quinone-oxime. The ether extracts were shaken in a separatory funnel upwards of twelve times with dilute (10%) sodium hydroxide, until the latter was no longer colored. The ether remained a deep wine color. Cold water was added to the ether and shaken; the deep wine color lightened to deep amber, though the water became only slightly orange-colored. This process was repeated with cold water without noticeable effect. Finally the ether extract was shaken with dilute

hydrochloric; a small amount of solid formed at the inter layers. (The first acid extraction on being made basic with dilute sodium hydroxide, yielded a dark yellow precipitate moderately soluble in alcohol).

The ether extract was evaporated on the water bath, and taken up with alcohol as an orange solution. An alcoholic solution of mercuric chloride was added; after stirring 1-2 minutes a flocculent precipitate was thrown down. It was filtered at the pump, washed with small amounts of cold alcohol. The compound was colorless, though appearing dark due to the presence of impurities; yield, 1.77 grams.

This compound was boiled for upwards of half an hour in 100 c.c's of sodium cyanide solution containing 2 grams of cyanide. The mixture was cooled and extracted three times with ether; the extract was dehydrated, filtered, and evaporated on the water bath, leaving a brown syrupy residue. Petroleum-ether was added and digested for some time, a yellow solution resulting. On standing a crop of supposedly white crystals, stained with brown, was obtained. This compound was digested twice with animal charcoal in petroleum ether. On filtering and allowing to stand a crop of crystals almost white, but having a faint yellow tint, was obtained. After a week's drying, this compound melted sharply at 56.5°-57.5° C.

x x x

Bamburger's Umlagerung.

The following method was used by Bamburger[3] for the conversion of phenyl anthranil to acridone.

0.109 grams of finely powdered phenyl anthranil are

dissolved in 3 c.c's. of concentrated sulphuric acid at -15°C, by rubbing the solid in the acid. 5 drops of 1% sodium nitrite solution (2.5 mg., calculating 40 grams for 1 gr. molecule) are added. The color changes, and a noticeable smell, of nitrous acid appears. After two minutes stirring at -15°C., the mixture was poured into ice-water, filtered, washed and dried; yield almost quantitative-acridone; melting point 354°C. A solution of acridone gives an intense blue fluorescence.

x x x

This conversion was carried out on the condensation product obtained from the ether extraction above (m.p. 57°C). An intense red-blue fluorescence was obtained with the compound in dilute alcoholic solution. The filtrate obtained during the process also showed fluorescence.

x x x

The same reaction was carried out on a small scale, but the temperature was allowed to rise to 75°- 80°C. during the addition of the sodium nitrite. A similar yellow solid formed on dilution, which gave a blue fluorescence in dilute alcoholic solution.

x x x

Preparation of Phenyl Arthranil for Comparison.

The method used was that described by Kliegl (Berichte, 41, 1908, p. 1849) with modification after obtaining the ether extract.

10 grs. o-nitrobenaldehyde.

40 grs. benzol.

40 grs. concentrated sulphuric acid.

The o-nitrobenzaldehyde and benzene were well shaken together in a round-bottomed flask. The concentrated sulphuric acid was added gradually with frequent shaking, the mixture being kept cool in running water. After standing 4-5 days with occasional vigorous shaking, it was added to water and extracted with ether. A residue which had settled was also extracted with ether, and the ether extracts combined. The combined extracts were shaken several times with dilute sodium hydroxide until the latter remained clear after repeated shaking. The ether was then shaken with cold water. (On separation the water was observed to be fluorescent.)

Kleigl's[9] method was varied at this point. Instead of proceeding with the steam distillation, the ether was evaporated on the water bath, the residue taken up with alcohol, and an alcoholic solution of mercuric chloride added. After stirring and allowing to stand a short while a precipitate formed. This was filtered, decomposed by boiling with sodium cyanide solution, and extracted with ether. This extraction was shaken with cold water, the latter showing a red-blue fluorescence on separation. The ether was evaporated and the residue was digested on the water bath for 1-2 hours with animal charcoal in petroleum-ether in moderate amount. The petroleum-ether was filtered rapidly at the pump while hot. On cooling a crop of brown crystals was obtained, which appeared very impure. This solid was taken up in alcohol, and again treated with

mercuric chloride and decomposed by sodium cyanide. A crop of crystals was again obtained from petroleum-ether, as above. This appeared much purer than the original, being yellow in color. It melted at 48° - 50° C, but not sharply. It was therefore digested with animal charcoal and petroleum-ether twice, and recrystallized from petroleum-ether. An almost colorless product was obtained. It melted fairly sharply at 53° - 54.5° C, and gave an intense red-blue fluorescence in dilute alcoholic solution.

x x x

A mixed melting point was carried out with this sample of phenyl anthranil and the product of the ether extraction of the original condensation just described (m.p. 56.5° - 57.5° C) The mixture melted at 54.5° - 56° C. This, together with the intense red-blue fluorescence obtained, was then taken as sufficient evidence establishing the identity of the second product obtained from the condensation of nitrobenzene and benzyl cyanide in the presence of sodium ethylate and phenyl anthranil.

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ATTEMPTED CONDENSATION WITH OTHER COMPOUNDS CONTAINING AN ACTIVE METHYLENE GROUP.

1. <u>Ethyl Cyanacetate.</u>

31.6 grs. p-chloronitrobenzene	(1 mol.)
22.6 grs. ethylcyanacetate,	(1 mol.)
8 grs. sodium in 180 c.cs. alcohol	(1 mol.)

The p-chloronitrobenzene was dissolved in a minimum of alcohol at room temperature, and the sodium ethoxide was gradually added. The mixture turned light yellow and finally a bright orange. After all the Na O Et had been added, the mixture was boiled for three minutes on the water bath. It deepened to a red-orange, and became slightly murky. The mixture was cooled, and added to 250-300 c.cs of cold water a light yellow precipitate was immediately thrown down. It resembled p-chloronitrobenzene, and on filtering and drying melted at 82° - 83° C. A mixed melt with p-chloronitrobenzene gave the result 81.5° - 83° C, proving the identity of the precipitate as suspected from its appearance.

A further quantity of yellow precipitate was obtained when the filtrate was made acid with cold dilute hydrochloric acid. This precipitate also gave a melting point of 82° - 83° C., and the same reading for a mixture with p-chloronitrobenzene.

x x x

This experiment was repeated with the same general treatment except that the boiling was continued for thirty minutes, three separate samples being removed at different intervals.

5 grs. p-chloronitrobenzene	(1 mol.)
38 grs. ethyl cyanacetate	(1 mol.)
1.3 grs. sodium in 40 c.cs. alcohol	(1 mol.)

First sample-boiled 7-8 minutes.

On first heating the orange colored liquid became almost colorless, and slightly murky. It was cooled and on

dilution a heavy white precipitate was obtained; m.p. 82°-83°C.

The filtrate was light yellow. On treatment with dilute hydrochloric acid in the fume cupboard it became colorless, but no precipitate formed, even after standing for two days.

Second sample - boiled 10-11 minutes.

On dilution a white precipitate was obtained, as before. It melted at 81.5°- 82°C. The filtrate likewise became colorless on the addition of dilute hydrochloric acid, but no precipitate formed on standing for two days.

Third sample - boiled for thirty minutes.

A white solid had formed at the bottom of the flask. The liquid was decanted, and the solid found to be readily soluble in cold water. It was assumed to be salt resulting from hydrolysis of the ester. Hasty examination strengthened this supposition. The liquid was cooled and diluted as above, yielding a similar precipitate. It melted at 81°- 82. 5°C. The yellow precipitate on acidification changed color without precipitation after two days.

x x x

Using Orthochloronitrobenzene.

Five grams of the o-chloronitrobenzene were dissolved in alcohol and molecular quantities of ethyl cyanacetate and sodium ethoxide were added, the treatment being the same as

described in the experiments with para compound. The mixture was boiled for 3-4 minutes on the water bath. On dilution with a large volume of cold water, a light yellow precipitate was obtained which melted at 36°- 38°C. The ortho compound used melted at 36°- 39°C, without purification. A mixed melt gave 36°- 37.5°C. No apparent change resulted when the filtrate was acidified with dilute hydrochloric acid.

x x x

Using Nitrobenzene.

Three grams of nitrobenzene and molecular quantities of the ester and ethylate were used. On addition of the sodium ethylate to a mixture of ester and nitrobenzene, the color deepened to an orange-red. On allowing to stand in the cold for 5-10 minutes, the mixture formed a light orange gel-like mass. When water was added the gel disappeared, and a light orange oil floated on the bottom of the flask. Dilute hydrochloric acid was added till acidic; no observable change occurred even on standing two days. The odor of the nitrobenzene was very distinct.

This experiment was repeated with the same quantities and the same conditions, yielding like results.

x x x

The above experiment was repeated, but the gel which formed was heated on the water bath 4-5 minutes. The gel dissolved on warming, reappearing on cooling. This preparation was allowed to stand at this stage, with the addition

of a small amount of alcohol, for two days. Cold water was added and the gel disappeared. An oil remained in the bottom of the flask having the odor and appearance of nitrobenzene though slightly deeper in color.

A reaction was carried out in the usual manner, using m-dinitrobenzene with ethyl cyanacetate. On dilution with cold water a dark brown residue was obtained. Part of this residue recrystallized from hot water, giving a light brown compound which melted at 96° - 98° C. A dark granular residue remained resembling potassium permanganate, and possessing a slight metallic irridensence. It was melted around 255°-260° C. Attempts at further purification gave little success. On ignition this compound appeared to be entirely organic. A deep rose to dark red color change accompanied the condensation.

- o 0 o -

2. Ethyl Malonic Ester.

4 grs. Ethyl malonic ester.	(1 mol.)
3.9 grs. p-chloronitrobenzene	(1 mol.)
1 gr. sodium in 30 c.cs. alcohol	(1 mol.)

The ester and p-chloronitrobenzene dissolved in a minimum quantity of alcohol, were mixed and the sodium ethylate gradually added. A yellow color appeared, deepening to a light orange. On standing about one minute the color disappeared and the solution became murky white, though no precipitation occurred. Very shortly after commencing to warm on the water bath, a white crystalline compound formed on

the bottom of the flask. The mixture was heated two minutes and cooled. The liquid was decanted, and cold water added to the solid; it dissolved readily, indicating a salt which had resulted from hydrolysis.

The filtrate was diluted with cold water, a light yellow precipitate forming. After filtering, washing and drying, it melted at 81.5° - 84° C, and when mixed with p-chloronitrobenzene at 81° - 84°C. This filtrate was acidified with dilute hydrochloric acid, but no precipitate formed, even after three hours standing.

x x x

Using Ortho-chloronitrobenzene.

Molecular quantities were used, and a light orange color was produced. The mixture was heated for four minutes. The results were identical with those of the para compound. Immediately after heating was commenced a white solid began to form in the flask. This was later found to be soluble in cold water. The precipitate formed on dilution melted at the temperature for o-chloronitrobenzene, and a mixed melt confirmed this product.

x x x

Using Notrobenzene.

Molecular quantities were used. Hydrolysis was apparent by the formation of a white solid on shaking, which increased on heating. A light orange color change was observed, but

subsequent treatment showed that in the main only hydrolysis had occurred, and nitrobenzene remained as a yellow insoluble oil, on dilution with water, also when heated with dilute hydrochloric acid.

- o 0 o -

3. Benzyl Chloride - Qualitative only.

No definite indications of a condensation were obtained with either ortho or para chloronitrobenzene in the presence of sodium ethylate, with benzyl chloride. A light orange color was produced with both the ortho and para, when warming on the water bath. After heating as long as ten minutes the respective chlorinitrobenzene was precipitated on dilution with water.

x x x

With Nitrobenzene.

Benzyl chloride was mixed with nitrobenzene and sodium ethylate gradually added. A slight murkiness appeared, which readily cleared up. After heating upward of four minutes, the color deepened to an opaque dark red. This mixture seemed to contain a semi-solid residue. The liquid was decanted. To the residue in the flask cold water was added, and a dark oil appeared. This mixture was made acidic without any noticeable change.

When the liquid which was poured off was diluted with water, a red oil again separated. The intense color suggested that

condensation had proceeded to a slight degree. If so, the compound formed must have remained dissolved in the nitrobenzene, or in close admixture with it. It was decided to repeat this experiment, continuing the time of heating, and attemptimg to effect a separation from the nitrobenzene.

x x x

3.2 grs. benzyl chloride	(1 mol.)
3.1 grs. nitrobenzene	(1 mol.)
1 gr. sodium in 25 c.cs. alcohol	(1 mol.)

The preliminary treatment was as before. After heating five minutes a small amount of white solid was observed to form on the flask; after fourteen minutes the color deepened to a dark yellow and finally to a brown. Heating was continued for two hours and ten minutes. A brown liquid remained, with indications of a more viscous liquid or semi-solid in the bottom of the flask.

This mixture was steam distilled for two hours to remove any excess of nitrobenzene. A slight amount of dark residue remained adhering to the flask. Theclear liquid remaining from the distillation was decanted, and the residue dried up by carefully directing a current of air into the flask. When dry this residue was extracted with ether, and the extract set aside to crystallize. Only a small amount of a tarry mass was obtainable.

With the small satisfaction that condensation had proceeded to a very limited extent, this reaction was abandoned

at this stage to examine the result obtainable by using diphenylmethane.

- o 0 o -

4. Diphenyl Methane.

A qualitative reaction with nitrobenzene, proceeding in the same general manner, behaved in the same general manner as benzyl chloride with nitrobenzene. After heating for five minutes a red-orange color appeared, and on dilution with cold water a red oil separated. Addition of dilute hydrochloride acid only intensified the red color. The odor of an iso-cyanide was particularly noticeable in thie preparation, even before the addition of the acid.

x x x

With p-Chloronitrobenzene.

6.4 grs. p-chloronitrobenzene.

6.8 grs. diphenyl methane.

8 grs. sodium in 200 c.cs. alcohol.

The p-chloronitrobenzene was dissolved in a minimum of alcohol. The diphenyl methane was added, followed by the gradual addition of the sodium ethylate. No apparent change resulted until the mixture was heated on the water bath. After heating 5-6 minutes a red color appeared. Heating was continued for two hours and ten minutes. A dark brown solid ring had formed around the inside of the flask at the surface of the liquid; solid was also found in the bottom of the flask.

The warm liquid was decanted, leaving the brown solid in

the flask. To the flask was added cold water, which loosened the caked solid, but did not completely dissolve it. On adding dilute hydrochloric acid, the solid became almost black, and settled from the solution better. This solid (S_1) was filtered, washed several times with water, and dried. It melted at 115°- 125° C.

The original decanted liquid on cooling gave a crop of dark salmon-colored crystals (S_2); these were filtered - filtrate, F_1. The precipitate in a Hersch funnel was washed several times with cold alcohol, till the latter was only slightly colored. On attempting to further purify the precipitate by washing with ether, it was found that the bulk of the residue readily dissolved yielding an intense orange solution (F_2); a dark chocolate-brown powdery residue remained on the filter paper (S_3). This ether treatment was subsequently adopted as a means of separating these compounds during purification.

The dark chocolate powder (S_2) was briefly examined, after thorough washing with ether. It failed to melt completely when heated in a small test tube; did not dissolve in alcohol, and only partially in water, giving a red-brown solution. Addition of dilute hydrochloric acid to the water treatment gave a slight amount of almost black precipitate, but in insufficient quantity to treat in any way.

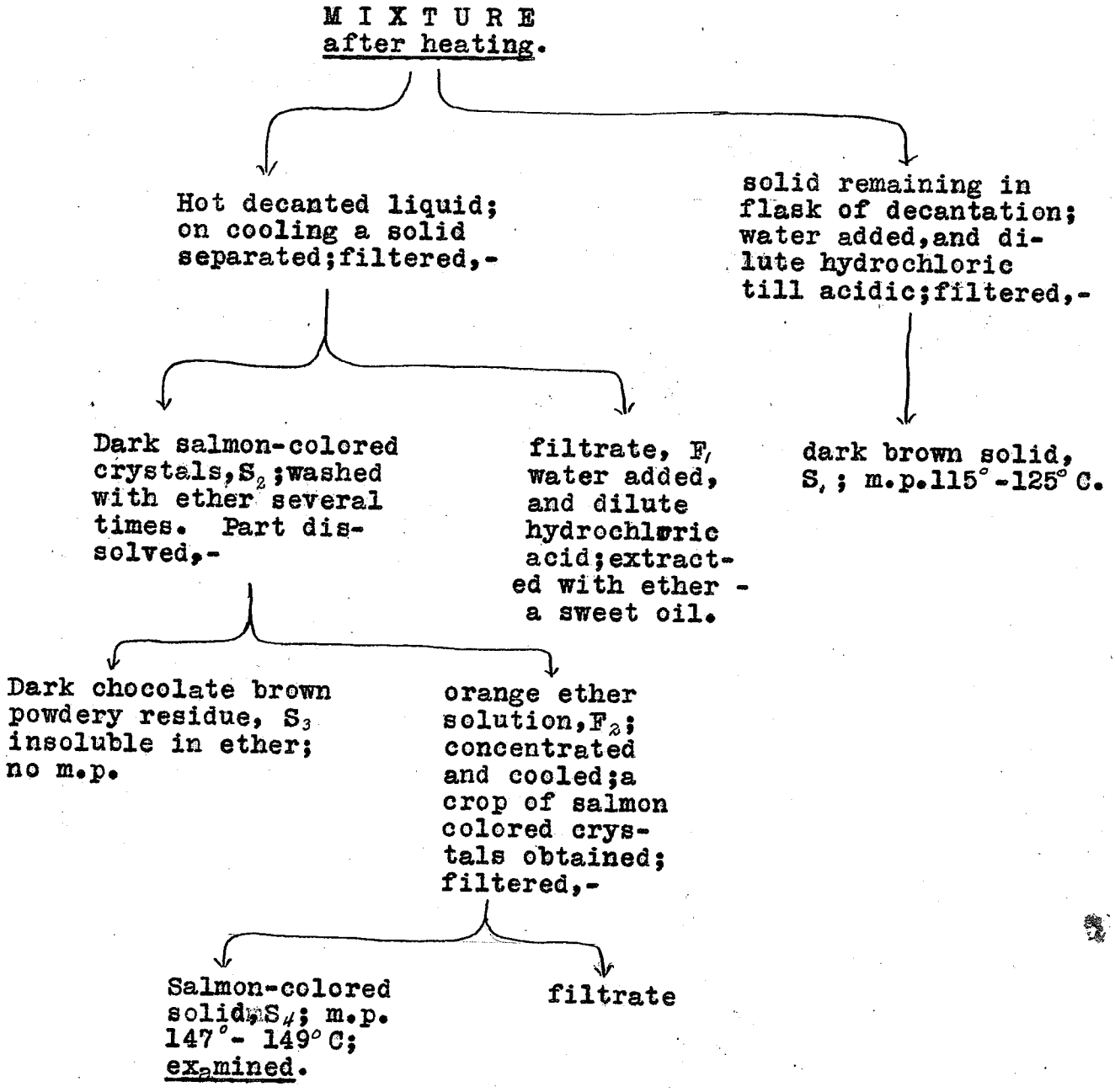
On treatment of the filtrate F_1 with cold water, a small quantity of deep orange oil separated as small globules. Dilute hydrochloric acid was added which removed the cloudiness in the liquid, and an almost black oil was observed to have

separated on the bottom. This oil was extracted with ether in the usual way, dehydrated, concentrated, and allowed to stand. Only a dark oil could be obtained, which possessed a sweet odor, not unlike diphenyl methane.

The ether filtrate F_2 was concentrated and on cooling, an appreciable crop of salmon-pink needle crystals was obtained. This compound (S_4) was filtered, washed several times with cold alcohol, and dried. It melted fairly sharply at 147°- 149° C.

A diagrammatic representation will show the relation of filtrates and solids.

x x x


M I X T U R E
after heating.
Hot decanted liquid; on cooling a solid separated;filtered,-
solid remaining in flask of decantation; water added,and dilute hydrochloric till acidic;filtered,-
Dark salmon-colored crystals,S_2;washed with ether several times. Part dissolved,-
filtrate, F_1 water added, and dilute hydrochloric acid;extracted with ether - a sweet oil.
dark brown solid, S_1; m.p.115°-125° C.
Dark chocolate brown powdery residue, S_3 insoluble in ether; no m.p.
orange ether solution,F_2; concentrated and cooled;a crop of salmon colored crystals obtained; filtered,-
Salmon-colored solid,S_4; m.p. 147°- 149° C; examined.
filtrate

The experiment was repeated on a larger scale, using 21 grams of diphenyl methane, and proportional monomolecular quantities. The heating was contimued for eight and a half hours, drawing samples off after 1.5 hours, 3 hours, 8.5 hours. Each fraction was diluted with cold water, filtered dried, washed with alcohol. In each case a dark orange ether filtrate was obtained, and a chocolate-colored powder, as in the previous experiment. On concentration and cooling the ether extracts gave good crops of salmon-colored precipitate. The yield did not appear to be appreciably increased by heating beyond three hours. The melting of the crude products ranged indefinitely from 143°- 146° C.

- o O o -

ATTEMPTED BENZOYLATION OF THE SALMON-COLORED COMPOUND, S_4.

Since only this compound (S_4) was obtained on an appreciable scale, it was decided to proceed with the investigation of it.

The compound (1 gram) dissolved readily in cold benzyl chloride giving a clear dark green solution. Dilute sodium hydroxide was added with shaking till the mixture was definitely basic; the color became very light yellow. The mixture was stirred mechanically for thirty five minutes. A cream colored waxy solid separated to the bottom in a mass. The mixture was diluted with cold water and stirred vigorously, which rendered the semi-solid in good form for filtering. It was filtered, recrystallised once from alcohol, and once from

30-70 water-alcohol solution. It melted sharply at 150°-151.5°C; the color was faint yellow. The result would indicate a purification only, but no benzoylation.

- o O o -

ATTEMPTED PREPARATION OF THE ACETATE S_4.

1 gram of the compound was dissolved in acetic anhydride, dissolving completely on warming; a green solution resulted. The mixture was boiled gently for one hour, cooled, and poured into a large volume of cold water. On vigorous stirring a cream-colored solid separated, which was filtered, and recrystallized from 20% water-alcohol solution. It melted quite sharply at 150.5°C. It is evident that acetylation did not take place, but that coloring matter as an impurity has been removed from the compound S_4.

After considerable experimentation it was found that treatment with acetic anhydride was the most effective means of purification of the compound S_4 for subsequent analysis; only by this method could all traces of the pink impurity be removed advantageously, the benzoyl chloride treatment being less easily managed.

x x x

Properties of the Compound S 4.

a. Yellow to cream-colored when pure.

b. Insoluble in hot or cold water; neutral to litmus.

c. Insoluble in, and unchanged by, dilute or cold sodium hydroxide; likewise for concentrated sodium hydroxide.

d. Concentrated hydrochloric acid had no effect.

e. It dissolved readily in concentrated sulphuric acid, giving an orange colored solution; on heating, the color deepens; when added to water a precipitate is obtained resembling the compound before dissolving.

f. It dissolves in concentrated nitric acid giving a yellow solution, from which a light colored product is precipitated on the addition of water.

g. The compound was boiled with tin and hydrochloric acid; sodium hydroxide was added till definitely basic. No indications of ammonia, nor other odors were detected.

h. On dry distillation with soda lime a sweet faint phenolic odor is noticed; tendency for fumes to sublime.

i. A drop of ferric chloride to the compound in alcoholic solution gives a yellow coloration.

j. Does not decolorize bromine water, bromine in carbon-tetrachloride, nor dilute potassium permanganate solution.

k. On heating with zinc dust, a sweet odor is noticed similar to that obtained with soda-lime.

x x x

A fresh sample was prepared on a sufficient scale for analysis. Twenty grams of p-chloronitrobenzene were used,

and proportional monomolecular quantities of diphenyl methane and sodium ethylate. Heating was continued for 2 - 2.5 hours, afterwwhich the excess alcohol first used for dissolving the p-chloronitrobenzene was distilled off (1 - 2 hours). The remainder of the procedure was that already described under previous experiments, extracting with ether. Re-crystallization from 20% water-alcohol gave a compound melting at 147°- 149°C.

Purification for Analysis.

The compound was dissolved in a little more acetic anhydride than was necessary for solution of the compound. The mixture was boiled gently for two hours, and allowed to cool. A good crop of yellow needles was obtained on cooling; a further quantity was obtained by diluting the filtered anhydride with cold water. This product, on washing and drying, melted at 149.5°- 150.5°C. It was re-crystallized four times from 14% water-alcohol solution, melting sharply at 149.5°- 150.5° C.

x x x

It occurs to the writer to suggest, from the ability to remove coloring matter as above, with the use of acetic anhydride, that s eparation of a compound from the dark colored oils obtained in some of the immediately preceding reactions, might be effected by acetylation with the anhydride and subsequent recovery by hydrolysis.

x x x

Analysis of Compound S_4.

	Found	Theoretical
0.2066 grs. of compound yielded 21.55 c.cs N at 24.5° C and 740.43 mm.: % nitrogen	10.776	10.49
0.1846 grs. of compound yielded 18.8 c.cs. N at 27.0° C and 738.89 mm.; % nitrogen	10.857	
0.1960 grs. of compound yielded 0.0869 grs. of water; % hydrogen	4.93	2.99
0.4779 grs. of carbon dioxide; % carbon	66.49	53.93
0.1650 grs. of compound yielded 0.0618 grs. of water; % hydrogen,	4.16	
0.3873 grs. of carbon dioxide; % carbon	64.02	
0.2050 grs. compound yielded 0.0470 grs. AgCl; % chlorine,	5.67	26.59
0.2039 grs. compound yielded 0.0447 grs. AgCl; % chlorine	5.42	

It is quite evident that the expected condensation with the diphenyl methane was not effected. On the basis of the nitrogen analysis Armes suggested the formation of p.pdichloro-azoxybenzene. Reference to Beilstein indicated the formation of this compound on continued heating of p-chloronitrobenzene in alcoholic potash. (Percentage composition - C, 54.13; H, 3.00; N, 10.52; O, 6.01; Cl, 26.31).

The method used for the chloride determination was Bacon's modification of the Stepanoff method[13], with metallic sodium. The results would indicate the possibility of incomplete removal of the chlorine.

x x x

Attempted reduction of S_4 with Stannous Chloride and Hydrochloric Acid.

The compound in alcohol was warmed for 1-1.5 hours, a colorless solution resulting. This was placed in an evaporating dish, the alcohol driven off, and the solution concentrated. On addition to cold water, no precipitate formed. On adding potassium hydroxide a precipitate formed, but this was completely soluble in an excess. This reduction failed to show the expected conformity.

- o 0 o -

Treatment with Fuming Sulphuric Acid.

0.5 grams of the compound were shaken with fuming sulphuric acid for 25 minutes, the solution being a very dark-orange-red. The mixture was poured carefully into cold water, and a brownish precipitate formed. This was filtered at the pump and washed several times. It was sticky and filtered with difficulty. It gave an indefinite melting point of 175° C, with darkening and shrinkage at 166° C. The increase in melting point over the original compound was taken as evidence in favour of the p.p-dichloroazoxybenzene, which yielded a compound melting at 183°- 184° C, on treatment with fuming sulphuric acid (Beilstein).

An orange-red was obtained by digesting p-chloronitrobenzene with alcoholic potash, which melted at 148°- 150° C. This lends further evidence to the identification as p.p-dichloroazoxybenzene.

Time did not permit of more exhaustive confirmation of this reaction and the work was discontinued at this point.

The foregoing exposition of the work investigated is therefore respectfully submitted to the Examining Committee in fulfilment of the requirements contingent upon the granting of the degree of Master of Science.

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SUMMARY.

1. A bried historical outline of the condensations of aromatic nitro compounds, particularly color reactions, has been given. Included is a short summary of Coke's work on benzyl cyanide with o, m, and p-chloronitrobenzene, which immediately preceded the following investigation.

2.(a) The related condensation employing nitrobenzene has been effected. The condensation product, together with typical derivatives, have been studied and identified.

(b) The possibility of a diazotisation of the condensation product has been examined with apparently positive indications; this would be an abnormal type of diazotisation process. A tentative explanation was offered by Armes.

3. It was attempted to establish a general reaction of activated methylene compounds to condense with aromatic nitro compounds, as does benzyl cyanide. The results were inconsistent.

x x x

4. The results of other unrelated investigations have been appended. The results were essentially unproductive, but they may save some unnecessary repetition.

- o 0 o -

APPENDIX.

A P P E N D I X .

The following results from a series of reactions preceding the investigations reported in the thesis are appended with the possibility of saving unnecessary repetition. As will be observed, the results are mainly either negative, or too indefinite to encourage further pursuit.

The following reactions were examined:-

(a) Anisole with aluminium chloride and sodium nitrite.

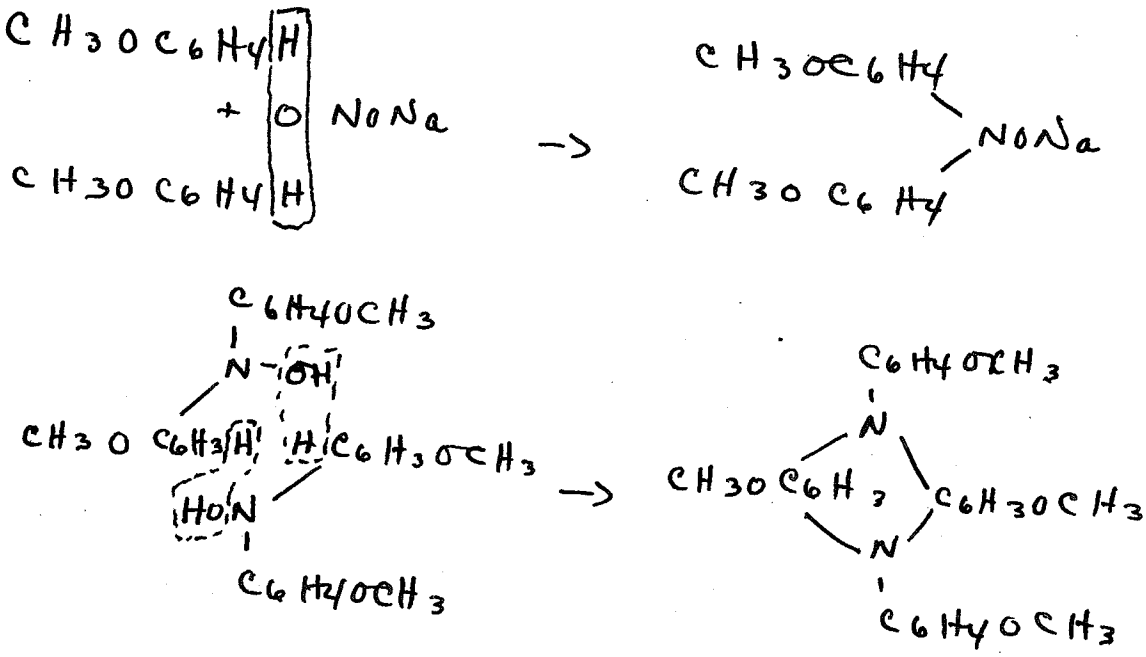
(b) Anisole and α-nitronaphthalene with aluminium chloride and sodium nitrite.

(c) α-nitronaphthalene and dimethyl aniline.

(d) Benzil and benzaldehyde with a dehydrating catalyst, as concentrated sulphuric acid.

- o 0 o -

It was hoped in the presence of aluminium chloride to effect a condensation between anisole and sodium nitrite, obtaining p.p-dimethoxy-diphenyl-hydroxylamine; two molecules of this compound might further condense to form diansyl dihydro-anisazine - a perazine. The possible course of such a reaction has been suggested by Armes as follows:



x x x

The first reaction was tried with monomolecular quantities as follows:

2.47 grs. of dry aluminium chloride were added to 2 grs. of anisole, with cooling. The cake which first formed was stirred until a pasty mass resulted. 1.28 grs. of sodium nitrite were added gradually with cooling and constant stirring. A green semi-solid resulted. The mixture was cooled and 10% sodium hydroxide added in excess with stirring. An orange-brown solid settled to the bottom, and a dark tarry mass separated to the surface. The mixture was shaken with petroleum-ether to remove excess anisole. This reaction was repeated using two molecular quantities of aluminium chloride, and one molecular quantity of sodium nitrite and anisole. Again a tar separated, and a light brown precipi-

tate settled out.

Three molecular quantities of aluminium chloride gave exactly similar results.

The tarry matter was extracted with benzol, in which it was readily soluble. The benzol was allowed to evaporate and the resulting tar taken up with boiling alcohol. Two crops of flocculent precipitate were obtained by fractional crystallization; the first had a melting point of 115°- 116°C, and the second melted indistinctly around 145°C. A portion of this latter compound dissolved in glacial acetic acid, and heated with stannous chloride and concentrated hydrochloric acid yielded a dark compound melting at 132°- 135°C. These compounds did not appear to be pure, and difficulty was experienced in obtaining them apart from tarry admixture for melting points.

The orange-brown solid, which settled to the bottom on the addition of the sodium hydroxide, was shown by ignition to be inorganic salt stained with some of the tarry matter.

x x x

Half a molecular quantity of sodium nitrite was used with equi-molecular quantities of the anisole and aluminium chloride. The method of treatment was the same, and the same results were obtained as in previous experiments.

The reaction was repeated using the same quantities, but

adding 30% hydrochloric acid instead of the sodium hydroxide. A tar resulted, which was skimmed off, dissolved in acetone filtered and allowed to evaporate. The resulting tarry mass was taken up with boiling alcohol, and on cooling a precipitate was obtained. It melted at 98°- 100° C, though not very sharply. On ignition a very small amount of light feathery ash was obtained. It was colored a deep orange-red.

- - -

10.0 grs. anisole.

12.35 grs. aluminium chloride.

16 grs. α-nitronaphthalene.

The anisole was dissolved in carbon disulphide, and the aluminium chloride added gradually with stirring, and cooling in ice. A green flocculent suspension resulted. The nitronaphthalene was added gradually with cooling and stirring. A bright red pasty mass resulted with evolution of HCl. On standing two hours in ice, the mass turned a dark green to brown. 35% hydrochloric acid was added, and a brown tarry mass formed.

The liquid was decanted from the tarry mass, and the latter was dried overnight. It was washed three times with petroleum-ether in which it appeared insoluble. This tar was slightly soluble in ether, fairly soluble in chloroform, very soluble in benzol and toluene, and extremely so in

acetone; slightly so in alcohol. In each of these solvents the tar dissolved giving a brown solution; a grey inorganic residue was left in each case.

The tar was extracted from the bulk of the material with acetone. It was filtered and the acetone distilled. The tarry residue was taken up with boiling alcohol. On cooling some light needle-like crystals formed, intimately mixed with tarry matter; melting point 46°- 48° C - which suggests impure α- nitro naphthalene.

x x x

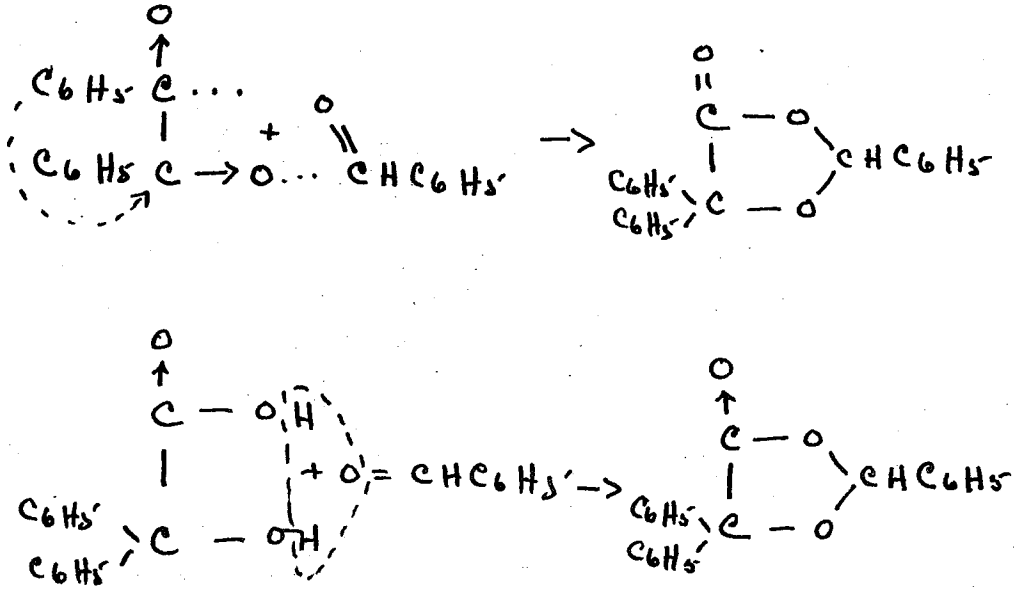
This reaction, was repeated, replacing the anisole with dimethylaniline in carbon disulphide. After the addition of the aluminium chloride, the mixture was treated with 10% sodium hydroxide, instead of hydrochloric acid. On extraction and re-crystallization of tar with boiling alcohol, orange needle crystals were obtained, melting at 59°- 60° C.,- α- nitronaphthalene.

A similar result was obtained using a relatively larger proportion of dimethylaniline. The tar which formed remained unidentified.

- - -

An intense color reaction had been observed by Armes, when benzil and benzaldehyde were mixed in glacial acetic acid, in the presence of concentrated sulphuric acid. The color soon appeared after mixing and allowing to stand.

It was hoped by this reaction to explain the benzil-benzilic acid change through the formation of an intermediate product, which it was hoped might be isolated. The relations as suggested by Armes, are illustrated below:-



x x x

1 gr. benzil.

.5 gr. benzaldehyde.

1-2 c.cs. concentrated sulphuric acid.

The benzil was dissolved in glacial acetic acid, and the benzaldehyde added. Four drops of concentrated sulphuric acid were added, and yellow crystals began to separate. 1-2 c.cs. of concentrated sulphuric were added, and after standing a short while an orange color appeared, which gradually

changed to rose. After standing 3-4 hours, the mixture was diluted with water, cooling during addition, and filtered. A orange precipitate was obtained, which when dry, melted at 94° - 96°C, indicating benzil.

The filtrate was made basic with sodium hydroxide and extracted twice with ether, to remove excess banzaldehyde. It was then acidified and allowed to stand, but no precipitate formed.

x x x

A second experiment was carried out using the same quantities of benzil and benzaldehyde, with 15 c.cs. of glacial acetic acid; 1-2 c.cs. of concentrated sulphuric were added, and the mixture allowed to stand for 24 hours. It was colored a deep rose.

Distilled water was added gradually, and three separate crops or orange crystals were obtained. Each succeeding crop was slightly more deeply colored. They all melted at 93.5 - 95 C, however, indicating colored benzil. The orange filtrate was made basic with sodium hydroxide, when it became a red-blue color. It was extracted with ether and acidified. The color changed to light golden. This indicator effect seemed almost indefinitely reversible, and the change appeared to take place fairly sharply. Quantitative measurements were not made with exactness. On allowing the acidic solution to stand, no precipitate formed.

Similar results exactly, were obtained after allowing to

stand for 36 hours.

x x x

This reaction was repeated by using monomolecular quantities in sufficient glacial acetic for solution; 1-2 c.cs of concentrated sulphuric were used, and the mixture heated on the water bath for 2 hours. After fifteen minutes the color was a dark red, which gradually deepened to almost a black with further heating. After two hours the mixture was cooled and diluted with water. A chocolate colored suspension resulted, which when filtered and dried melted at 85° C. indistinctly. On re-crystallization it melted at 93°-94° C, again indicating the presence of benzil in large amount.

The filtrate was made basic, extracted with ether twice, and acidified; no precipitate appeared on standing 24 hours.

x x x

The reaction was repeated using the same quantities of reactants, but the mixture was heated on the paraffin bath at 150° C. for 2-2.5 hours. A brown viscous mass remained, with the odor of SO_2. This mixture was cooled and poured into cold water. A brown pasty precipitate formed, which was filtered with difficulty. This residue was stirred with water and made basic with potassium carbonate. This mixture was filtered leaving a cream-colored residue; melting point 93°- 95° C. The basic filtrate was acidified with dilute hydrochloric acid, and allowed to stand without result.

The original filtrate was evaporated to a brown syrup, dooled, and extracted three times with ether. On allowing the ether to evaporate, a white waxy compound having a sweet ester odor, was obtained; it melted at 107.5°- 109°C. The acidified filtrate yielded no precipitate.

x x x

On repetition of this experiment using a molecular quantity of benzoic acid in place of benzaldehyde, a brown viscous mass was obtained. This became soluble on the addition of potassium carbonate till basic. A deep brown solution resulted, which on acidification with dilute hydrochloric acid failed to give a precipitate immediately. After a week a compound formed which melted at around 122°C.- which would suggest impure benzoic acid.

x x x

Many more experiments were repeated with benzil and benzaldehyde, varying the amount of the compounds, the time of the reaction up to three weeks, and the temperature. No more definite results were obtained. A small amount of deeply colored compound forms (orange-red) in small amount. Attempts to separate it from the benzil which always remained, were unsuccessful. It appears that this compound is orange to golden in acidic solution, and red-blue in basic solution.

x x x

In concluding the investigation an attempt was made at

separation by possible salt formation. Ammonia was used to avoid a large amount of inorganic residue forming on concentration. This addition admittedly might introduce unexpected complications; the results are briefly outlined, however.

To a monomolecular mixture which had been allowed to stand several weeks, dilute ammonium hydroxide was added till basic. The resulting deep purple solution was decanted, after shaking, leaving a purple solid. This process was repeated on the solid residue several times, combining the purple decantations. A solid residue remained which was colored violet; it will be discussed later.

The ammoniacal extracts were shaken several times with benzol, the latter becoming yellow. The benzol extractions yielded a compound melting at 95° - 97° C, obviously benzil.

On filtering the cloudy ammoniacal extracts a light brown compound was obtained which melted indistinctly around 142° C. On acidification with dilute hydrochloric no precipitate formed.

The violet colored residue referred to above was extracted several times with alcohol. At first a compound was obtained which melted at 94° - 95°. A reddish residue still remained which failed to melt when raised to 280° C. It colored alcohol slightly, and was completely soluble in acetone.

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