

THE REACTION OF AROMATIC NITRO-
COMPOUNDS WITH COMPOUNDS
CONTAINING AN ACTIVE
METHYLENE GROUP.

THE REACTION OF AROMATIC NITRO-COMPOUNDS
WITH COMPOUNDS CONTAINING AN ACTIVE
METHYLENE GROUP.

A THESIS SUBMITTED TO THE COMMITTEE ON POST-
GRADUATE STUDIES OF THE UNIVERSITY OF
MANITOBA.

BY

NANCY BERNICE MILTON, B.Sc. (H.E.)

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF MASTER OF SCIENCE.

MAY, 1936.

The writer wishes to acknowledge her indebtedness to Professor H.P.Armes for the suggestion of this problem, and to express sincere gratitude for his helpful advice and interest with which he directed the investigation.

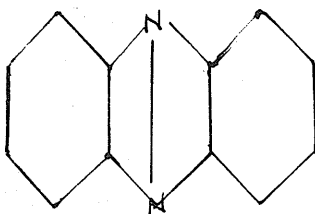
TABLE OF CONTENTS

PAGE

| | | |
|-----|---|--|
| I | Reaction of Aromatic Nitro-Compounds with Compounds Containing an Active Methylene Group..... | |
| | Introduction and Theoretical Discussion...1. | |
| | Experimental Discussion.....16. | |
| | Conclusion.....30 | |
| II | Appendix--Reaction of Aromatic Nitro-Compounds with Iso-cyanates..... | |
| | Theoretical Discussion.....1. | |
| | Experimental Discussion.....8. | |
| | Conclusion.....14. | |
| III | Bibliography.... | |

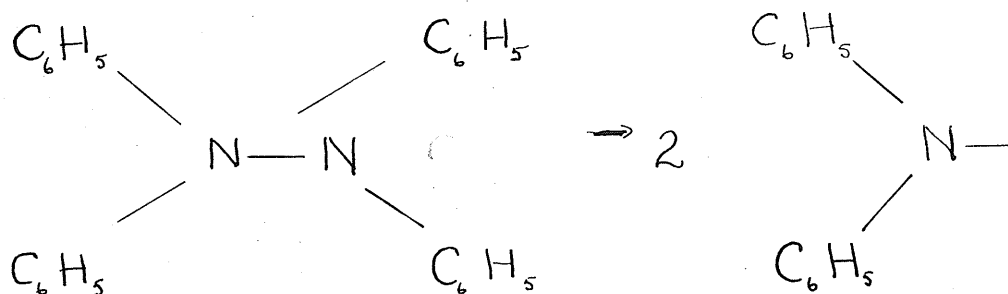
INTRODUCTION AND THEORETICAL DISCUSSION.

In the work described in this thesis an attempt was made to condense aromatic mono-nitro-compounds with active methylene groups in the presence of AlCl_3 as catalyst. A second reaction was also partially studied, that of the condensation of aromatic mono-nitro compounds with iso-cyanates in the presence of AlCl_3 . Nitro-benzene was the chief nitro-compound used; a few tests were also run with p-chloro-nitrobenzene. Condensations of a similar character have been carried out using di-nitro-compounds, but it has been thought that the mono-nitro-compounds are not reactive to such experimental conditions. In the condensation of mono-nitro-compounds with active methylene groups as conceived by Armes it was supposed that a colourless substance would be produced of a formula related to the phenazine ring structure:

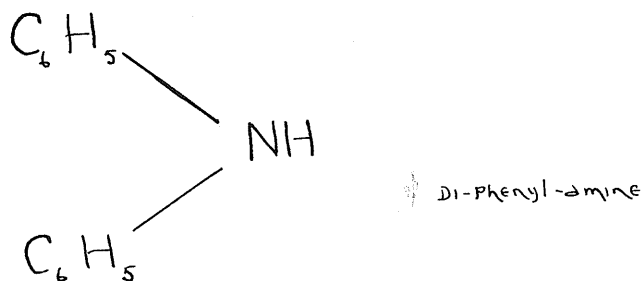


phenazine

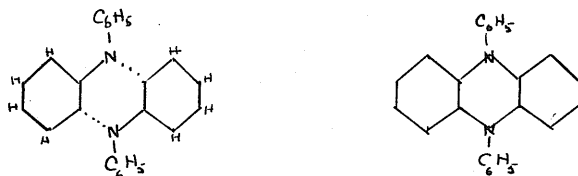
Before proceeding to an examination of the reaction under consideration, a brief resume will first be made on other reactions of an analagous character. Related to the phenazines are the perazine derivatives, which are dihydro-phenazine derivatives. Perazine derivatives have been produced by Wieland⁽²⁾ from the corresponding hydroxylamine derivatives. In 1911 Wieland⁽²⁾ obtained di-aryl-dihydro-phenazines by the dissociation of tetra-aryl-hydrazines. For example, tetra-phenylhydrazine on heating in xylol splits into two molecules of di-phenylnitride thus:



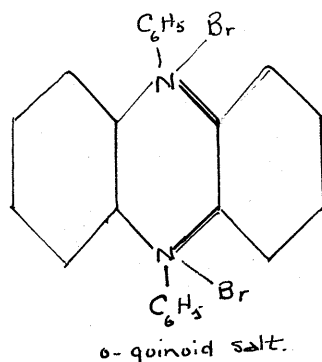
One molecule of this highly unsaturated compound forms diphenylamine:



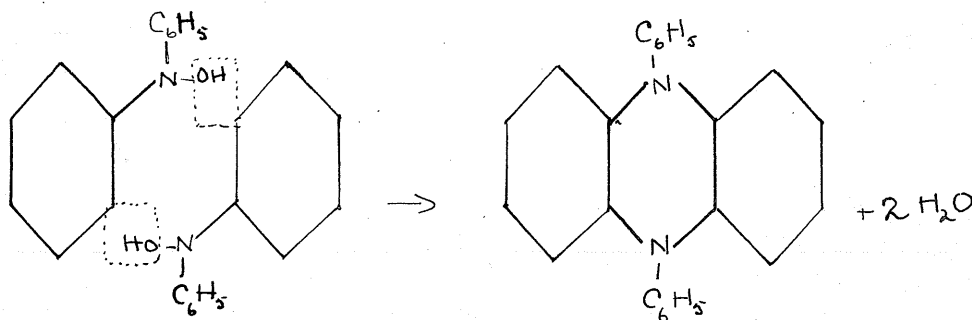
This reaction proceeds at the expense of the other molecule. Two of the latter then condense together as follows:

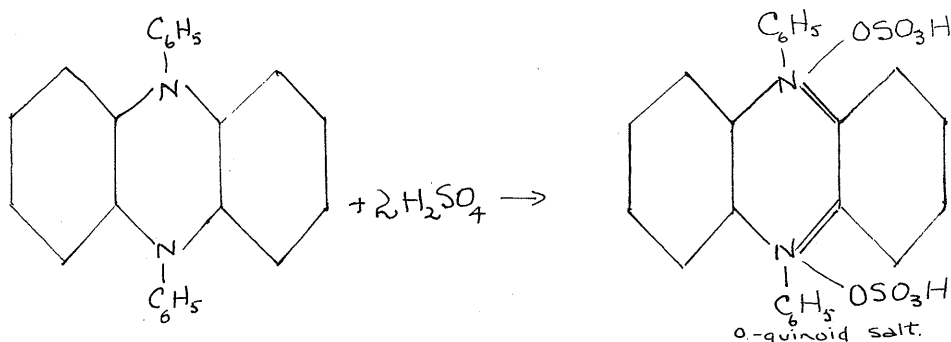


A characteristic property of perazines is their formation of highly coloured salts, for example, with bromine. Wieland⁽²⁾ also investigated this salt forming property and he regarded it to be a formation of an ortho-quinoid salt.



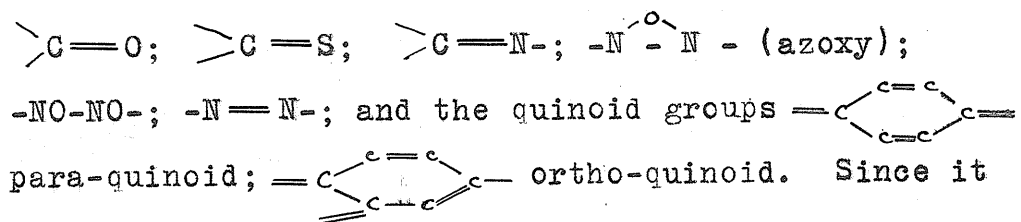
In a like manner Wieland⁽²⁾ explains the reaction of H_2SO_4 (with oxidizing agents such as HNO_3 , HNO_2 etc,) with diphenyl-amine. This compound gives a characteristic blue colour with oxidising agents. This colour is regarded as again being due to an ortho-quinoid salt formation. Di-phenyl-hydroxyl-amine first forms, and this condenses to perazine, and then forms the ortho-quinoid salt. The reaction takes place as follows:





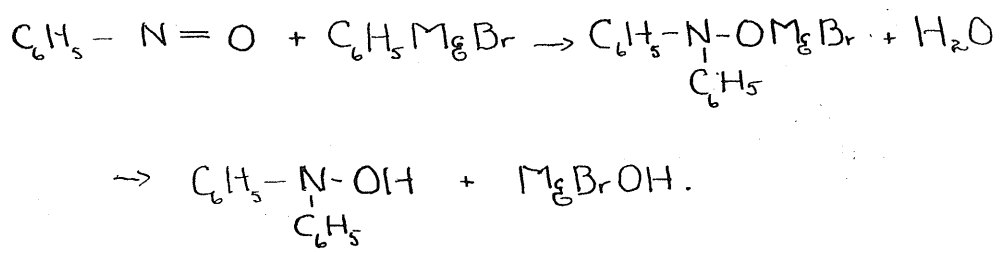
It is obvious that in both these coloured perazine derivatives the quinoid linkage is present. This brings us to a discussion of the relationship between colour and chemical composition. Witt's "chromophore theory" as outlined by Henrich⁽³⁾ attempts to establish this relationship, and to designate those groups responsible for the appearance of colour. According to this theory colour in a compound is due to the presence in the molecular structure of certain so-called "chromophore" groups. These chromophore groups give colour to the compound regardless of the nature of the rest of the compound. For example such groups as NO₂, -N=N- give colour; on reduction of these the colour disappears, but reappears again on re-oxidation. The coloured compounds containing these chromophoric groups are termed chromogens. To become a dye the molecule must contain, in addition to a chromophore group, an auxochrome group. These groups are capable of reacting with acids or bases to form salts. In addition to combining with the substance receiving the dye they intensify the chromogen colour. Witt's theory has been slightly modified and augmented,

but it is still similar in essentials to the modern conception of coloured compounds. Without going into further detail a few of the chromophoric groups will be mentioned. The most important of these are:

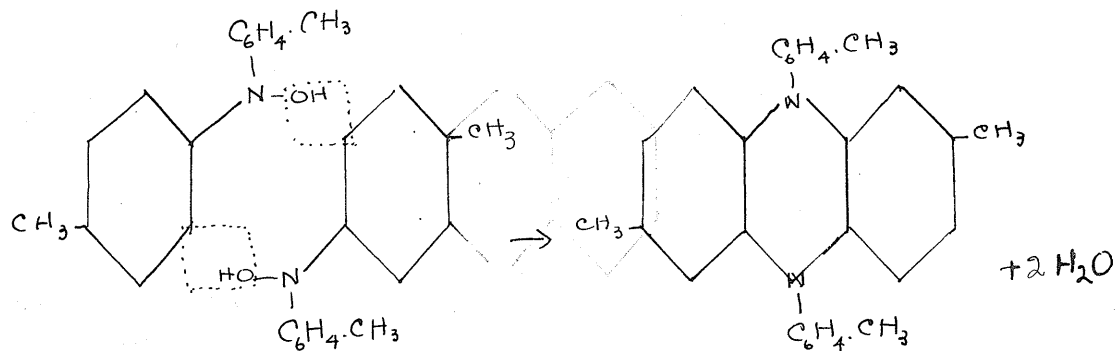


Since it was expected that salts of the quinoid type would result in the present condensation, deeply coloured compounds would be expected to occur, although they would be by no means unquestionable proof of the type of the reaction but merely supplementary evidence.

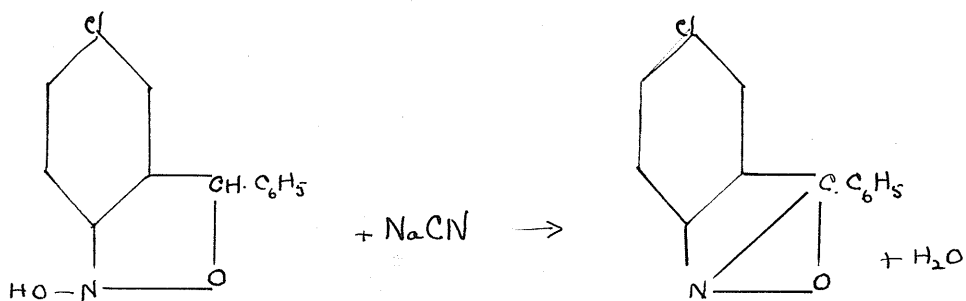
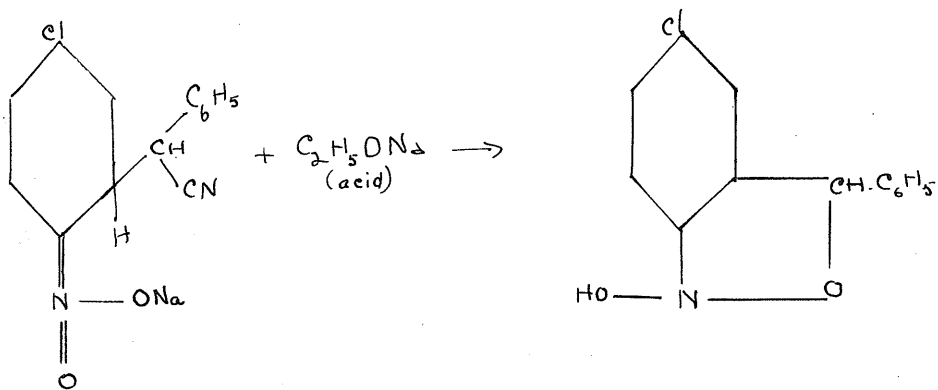
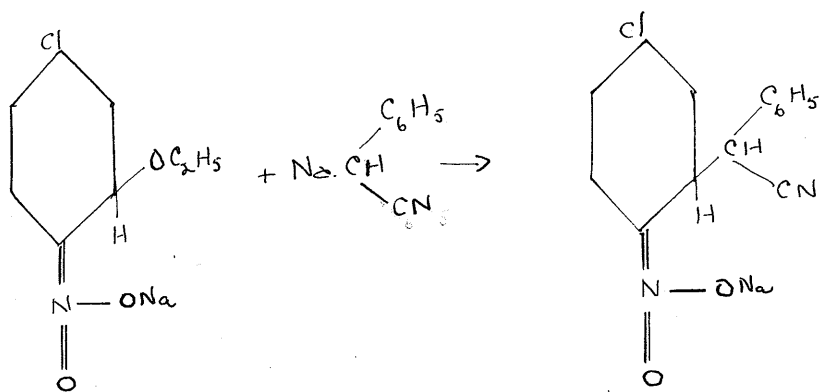
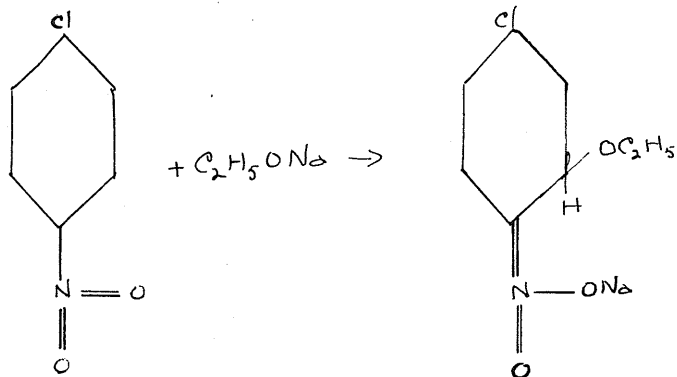
In 1912 Wieland and Roseen⁽⁴⁾ examined the preparation of di-phenyl-hydroxyl-amine prepared by the action of phenyl magnesium bromide on nitroso benzene. The reaction proceeded as follows:



The corresponding di-tolyl-hydroxyl-amine yields a perazine by the action of acids.



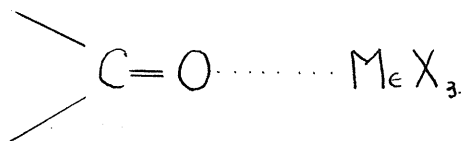
In 1928 Coke⁽⁵⁾ studied the condensation products of benzyl cyanide, (which contains the active methylene group) and aromatic nitro-compounds with NaOC_2H_5 used as catalyst. A mono-nitro-compound was used, but with a second substituted group, to observe the possible effect of this group on the condensation: chloro-nitro-benzene was used (o, m, and p). The only work on similar compounds previous to this, of which I can find record is that done by Reissert⁽⁶⁾ who condensed di-nitro-benzene with benzyl cyanide, obtaining highly-coloured solutions. Coke⁽⁵⁾ found that the condensation product obtained from benzyl cyanide and chloro-nitro-benzene was phenyl anthranil, with a chlorine atom substituted in the benzene ring para to the position formerly occupied by the nitro-group. The reaction proceeds as follows with the para-chloro-nitro-benzene:



Instead, however, of using NaOC_2H_5 as catalyst, aluminium trichloride was employed.

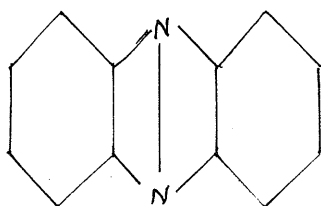
Farbenind.⁽⁷⁾ obtained condensation products by causing an aromatic compound containing a nitro- or nitroso-group, and containing hydrogen, halogen or alkoxy group, ortho or para to the nitro- or nitroso-group to react in the presence of an alkaline condensing agent with a compound containing C to which are joined at least 2 hydrogen atoms, and to which is also joined a group activating the hydrogen atoms, such as CO, CN, C=ONH₂, and ester groups. Farbenind. prepared 4-hydroxyl-amino-diphenyl-aceto-nitrile from nitro-benzene, and benzyl cyanide.

Before proceeding further with possible structure for the condensation products, let us consider for a moment the role played by the catalytic agent in the reaction, and the mechanism of its action in inducing the condensation. The use of AlCl_3 as an activating agent in bringing about condensations, both between two different molecules and within the same molecule, has long been known as the Friedel and Craft reaction. The current theory of the manner in which the catalysis takes place presumes that substances containing the carbonyl group directly add on the metallic chloride, retaining it by means of a small residual valence, thus:

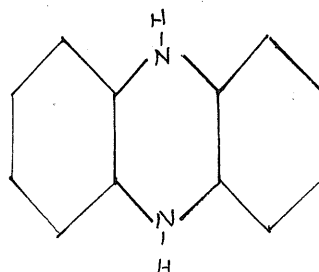


Gradually a larger proportion of the total affinity of the oxygen atom is directed towards the addendum MeX_3 , and at the same time some of the affinity of the carbon atom will be freed. This increase in the free energy of the C atom causes increased chemical activity. This activity may result in the formation of a condensation product with another molecule, or in an intermolecular rearrangement using up this excess chemical activity of the C atom. As the amount of reaction is increased with increasing amounts of catalyst, it is supposed that a stable intermediate product is formed, which tends to take out in some measure the activating agent.

The condensation product which was expected in the reaction studied was one related in structure to the phenazines.

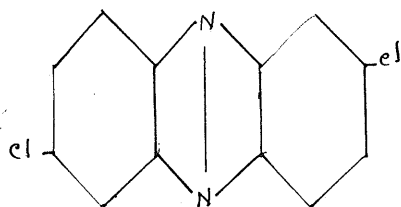


Phenazine



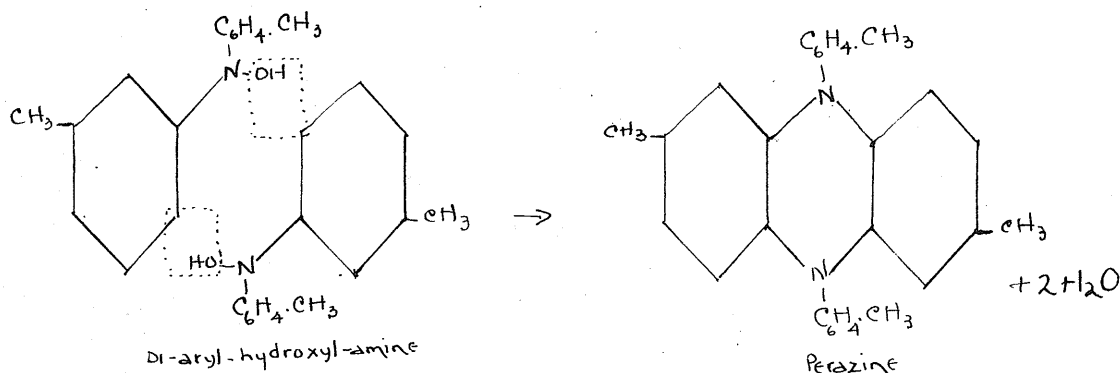
di-hydro-phenazine

In concentrated sulphuric acid a blood red solution results; in concentrated nitric a flame-coloured solution; in concentrated hydrochloric acid a yellow solution. On reduction with stannous chloride dichloro-phenazine results:



This gives lemon yellow needles from xylene. If moistened with HCl it becomes red, but its solution in the acid is yellow. Similar bromo- and iodo-derivatives may be obtained, but these have different colour reactions. Para-nitroso-toluene under similar conditions gave di-methyl-phenazine-N-oxide. A highly dilute aqueous solution of this compound exhibits a pale yellowish-green fluorescence, which is discharged by warming or on the addition of mineral acids. A peculiar phenomenon is encountered with the chloro-phenazine derivative-----
 $\text{ClC}_6\text{H}_4\text{N}(\text{OH})\text{C}_6\text{H}_4\text{NO}$, involving the loss of one Cl atom. What happens to the other Cl atom is unknown.

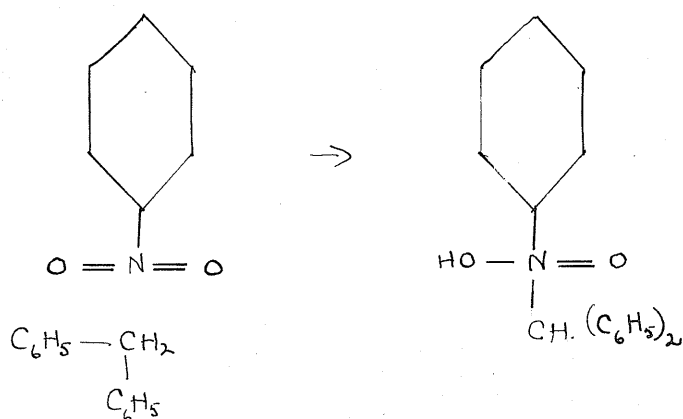
N-di-aryl-di-hydro-phenazine also may be produced by the action of acids upon di-aryl-hydroxylamines. The reaction proceeds as follows:

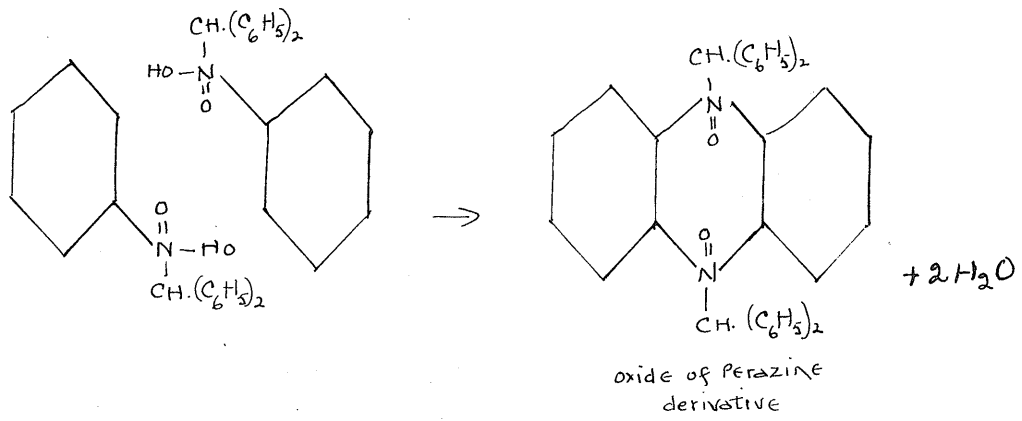


In the decomposition of tetra-aryl tetrazines and tetra-aryl hydrazines by the action of concentrated acids produces di-aryl-hydroxylamines, which are in turn converted to di-aryl-di-hydrophenazines. In the case of the tetra-aryl-hydrazines the reaction is thought to take place by first producing a quinoidal hydrazoneium chloride, which resolves itself into di-tolyl-amine and the hypothetical complex $\text{ClN}(\text{C}_6\text{H}_4\text{Me})_2$. From this the azines are thought to be produced by a process of rearrangement and combination. On boiling tetra-phenylhydrazine in toluol solution N-di-phenyl-di-hydrophenazine and di-phenylamine are produced. Di-phenyl-di-hydro-phenazine is colourless in concentrated sulphuric acid, but on addition of oxidizing agents an intense blue colour is developed, an ortho-quinoid sulphate being formed. The entrance of NH_2

and OH groups converts the phenazine into dyestuffs. (NH₂ and OH groups are both auxochromic groups, these being necessary in addition to the chromophoric group, as indicated in the discussion on colour as related to chemical constitution.)

Let us now consider the present reaction in the light of reactions already investigated. As previously mentioned Wieland⁽²⁾ prepared perazine derivatives from the corresponding hydroxyl-amine compounds. For this reason it was supposed that the perazine oxides might be produced from the corresponding hydroxylamine oxides. The complete reaction might take place in steps. A molecule of nitro-benzene^{might} first condense with an active methylene group such as is found in di-phenyl-methane. The hydroxyl-amine that might thus be formed might condense with another molecule of itself to form a perazine ring structure thus:





EXPERIMENTAL DISCUSSION

(1) Reaction of Nitrobenzene with Anthracene

2.5 gms. nitrobenzene
3.6 gms. anthracene
5.3 gms. aluminium trichloride

The first reaction investigated was that between nitrobenzene and anthracene, using $AlCl_3$ as the catalytic agent. Actually anthracene has no active methylene group but it might be supposed that the position of the CH group between two benzene rings would give it similar properties to an activated methylene grouping. As preliminary tests made by Armes seemed to indicate a reaction, probably of the nature of a condensation, further investigations along these lines were carried out.

Equimolecular quantities of anthracene and nitrobenzene were introduced into a flask carefully dried, and fitted with a stopper and air condenser. Two molecular quantities of the catalytic agent were used. This was introduced into the mixture of anthracene and nitrobenzene in small amounts, care being taken to shake the flask well after each addition. When all the $AlCl_3$ had been added there was still no visible sign of any reaction having been initiated. The flask was then placed on a water bath. For a few minutes there was still no appearance of any reaction taking place.

As the mixture became slightly warmed, however, a violent reaction occurred, which seemed to reach completion in a few seconds. Large volumes of dense fumes were given off, and a charred mass only remained in the flask. It was obvious that the reaction had taken place too rapidly probably resulting in the complete decomposition of the reacting substances. On examining the residue only carbon remained. This reaction was repeated, care being taken to raise the temperature more gradually, and with frequent shakings of the flask. A similar result was obtained. It was therefore deemed necessary that some neutral solvent must be found, preferably with a boiling point below that of water, in which the reaction could be carried on at a more moderate speed, to prevent decomposition before any condensation could occur.

(2) Reaction Between Nitrobenzene and Anthracene
with Benzene as the Solvent.

2.5 gms. nitrobenzene
3.6 gms. anthracene
5.3 gms. aluminium trichloride
Benzene.

In this reaction benzene was selected to act as a delaying influence on the reaction. Alcohol could not be used, as it undergoes a reaction itself with AlCl_3 . In addition, the benzene had a boiling point below that of water, (approximately 79.6°C), and would therefore keep the temperature of the reaction lower than had been possible by merely heating on a water bath.

The nitrobenzene and anthracene were again introduced into a dry flask and the mixture covered with C_6H_6 . Into this the AlCl_3 was carefully introduced in small additions, the flask being shaken after each addition of catalyst. Before applying heat no visible reaction occurred. The air condenser was replaced by a water condenser, and the flask heated on a water bath. The heating was carried on for from two to three hours, the reaction proceeding at a fairly slow rate of speed during the entire time of heating.

When the reaction was completed the flask was removed from the water bath and the benzene poured off into a beaker, and set aside for future examination. A dark brown gummy mass remained in the bottom of the flask. Water was added to decompose any possible addition compounds formed with the catalyst. The mixture was then treated with HCl to insure the complete separation of inorganic material and the whole subjected to steam distillation to remove any excess of nitrobenzene. After the steam distillation the contents of the flask were filtered through a suction filter, a hard lumpy brownish black precipitate being obtained. This was tested for inorganic matter by burning a small portion in a porcelain crucible, and was found to contain some small amounts even after treatment with HCl. It was necessary to repeat the heating with dilute HCl several times before the organic matter was entirely freed from the aluminium. After this partial purification the compound was dried in a vacuum dessicator over night. On examination of the benzene extract it was found to contain in solution a very small quantity of the dark-coloured condensation product, and some inorganic material.

These experimental conditions were repeated several times with similar results, and this method was then adopted as a standard in the preparation of

further amounts of the unknown.

(3) Examination of the Condensation Product.

The condensation product formed was a dark brownish black amorphous powder. It had no definite melting point but at fairly high temperatures, (i.e. above the B.P. of H_2SO_4) appeared to decompose, leaving a charred residue. With a view to finding some solvent from which it might be crystallised, or at least purified, its solubility in several reagents was tested. The actions of these various solvents on the unknown are listed below in Table I:

T A B L E I.Solubility of Unknown Product in Various Solvents.

| Solvent | Reaction to cold soln. | Reaction to hot soln. |
|-----------------|-----------------------------|--------------------------|
| Acetone | Fairly sol. | More sol. |
| Ethyl acetate | Sol. | Sol. |
| Ethyl oxalate | Sol. | Sol. |
| Benzene | Sol. | Sol. |
| Ether | Slightly Sol. | Slightly sol. |
| Chloroform | Very Sol. | Very sol. |
| Benzine | Insol. | Insol. |
| Ethyl alcohol | Insol. | Slightly sol. |
| Xylol | Very sol. | Very sol. |
| Formaldehyde | Insol. | Insol. |
| Benzaldehyde | Sol. | Sol. |
| Glacial Acetic | Insol. | Slightly sol. |
| Conc. Sulphuric | Green soln. turns black. | Turns brownish black. |
| Conc. Nitric | Insol. | Insol. |
| Conc. NaOH | Insol. | Insol. |
| Conc. HCl. | Insol. | Insol. |

In each case in which the unknown was soluble, very dark brown solutions were obtained. The terms used in the Table above are all only relative. That is where it indicates that the substance is 'very soluble', it is so by comparison with some other reagent in which it is completely insoluble. In no case was the compound extremely soluble as, for instance, we think of salt being soluble in water. But very small quantities of the material dissolving were sufficient to give a very deep colouration to the solvent. It was this peculiar degree of "insolubility", as it might be termed, that lent such great difficulties to the identification of the compound, as it was well-nigh impossible to purify the substance in large enough quantities to run the desired number of analyses. There was also great waste in the reacting materials, as huge quantities were required to produce relatively small amounts of the condensation product.

Wherever solubility was indicated in the preliminary tests, a solution was prepared, filtered, and set aside in the hope that on standing, an amorphous, if not a crystalline precipitate, would appear. But in no case was any success met with along this line. Even the strongest solutions were probably too dilute to favour any precipitation even on cooling and standing. As this method was then clearly out of the question as a means of

purification, attempts were made to at least partially purify the substance for preliminary analyses in other ways.

As may be seen from the table there were several solvents that seemed to dissolve appreciable amounts of the unknown, and still others in which it showed no disposition whatever to dissolve. It was therefore conceived as feasible that a solution of the unknown treated with some of these latter solvents in excess might induce the precipitation of the solute. With this purpose in mind several combinations were tried.

By this method it was found that a solution in xylol produced a precipitate when ethyl alcohol was added. Similarly, a solution in benzene yielded a precipitate when benzine was added. The latter combination was considered more desirable than the former because of the greater ease with which the solvents could be removed from the precipitate in drying, and also because greater amounts of the precipitate were formed. A flocculent brown product appeared, immediately on the addition of the benzine, which increased considerably on standing. It was disappointing to find, however, that although the precipitate seemed to be present in large quantities, on filtering and drying relatively small quantities were obtained. The actual weight of the yield was low,

and very large quantities of the reagents were required, also involving great losses of the product itself.

Since purification of the compound by the above method seemed to involve such waste, as well as being a very laborious procedure, it was suggested that perhaps if a salt of the unknown could be produced, it might quite conceivably have more soluble properties. As may be noted from the Table of Solubilities, the unknown was slightly soluble in hot alcohol. A solution in this reagent was therefore made, and into the hot solution, dry HCl gas was passed. A dark precipitate was formed after the gas had been passed into the solution for several minutes. The HCl was allowed to pass through the solution for about ten minutes, and the mixture left to stand. On standing more of the substance came out of solution. It is interesting to note that a similar result to leaving it stand was produced by the addition of NaOH. But this method gave no better results than that described above, and rather smaller yields were obtained. For this reason the method was abandoned in favour of the former.

As may be realized purification by the method available was a very slow one, and the results obtained rather discouraging. Repurification, as should have been done to ensure commendable results on analysis, was out of the question, as the relative

losses of the product in the solution made this prohibitive. As the first part of the term had been taken up with a study of the reaction of the same nitro-compound with iso-cyanate (as described in the Appendix), time was definitely limited, and only a few hasty preliminary analyses were possible.

It is interesting to note the reaction of the product with concentrated solutions of acids and bases. With the exception of concentrated sulphuric acid, there appears to be no reaction with either acids or bases, even on heating. The reaction with sulphuric acid does not seem to be one of just simple solution, but would appear to involve a chemical reaction. On first treating the product with the concentrated acid, a deep green colour is produced, which turns brown and then black on standing, or on the application of heat. This reaction can not be attributed to heat alone, as heating the unknown in a sulphuric acid bath (as in melting point determinations), had no effect at all. It is at temperatures above that of the boiling point of sulphuric acid that decomposition occurs. It is possible that if, as supposed, some perazine derivative has been formed in the condensation, that the reaction with sulphuric is one of the salt-formation, characteristic of perazines, as indicated earlier in this thesis in the discussion on Theory.

Attempts to reduce the compound were unsuccessful. The unknown was treated with zinc dust in glacial acetic, and the whole boiled under a reflux condenser for several hours, but no reduction took place.

Two analyses were run on the unknown: (1)..A Kjeldahl nitrogen determination; and (2)..A combustion analysis for the determination of carbon and hydrogen. The results of these analyses are discussed below.

Nitrogen Determination.

The nitrogen was estimated by the Kjeldahl method. This method consists essentially of heating the sample with concentrated sulphuric acid, with oxidising agents, the ammonia thus obtained being distilled off and determined by titration. Blanks were run on filter paper in conjunction with the sample of the unknown to detect any nitrogen that might be present in the reacting materials, and thus minimize the sources of error. The determinations were done in duplicate, using approximately .5 gms., of the unknown compound. The analysis of the unknown compound was preceded by a preliminary analysis of a known compound,

Combustion Analysis

Only sufficient quantity of the purified compound was available for two combustions. Unfortunately the first combustion was spoilt by a stoppage in the combustion tube, which caused the caustic KOH to suck back. The results of the second combustion are given below, but it is regretted that there is no confirmatory evidence. Following the usual procedure for combustion analysis, a known compound, acetanilide, was first analysed. This was followed by the analysis of the unknown itself. The results of this analysis are given below:

| | |
|---|---------------|
| Weight of sample taken ----- | .1189 gms. |
| Weight of CaCl ₂ tube before combustion----- | 43.3449 gms. |
| Weight of CaCl ₂ tube after combustion----- | 43.3975 gms. |
| Gain in weight----- | .0526 gms. |
| % H ₂ - $2 \times .0526 \times 100 \div (18 \times .1189)$ | <u>4.91%</u> |
| Weight of KOH bulb before combustion----- | 65.1448 gms. |
| Weight of KOH bulb after combustion----- | 65.5544 gms. |
| Gain in weight----- | .4096 gms. |
| % C - $12 \times .4096 \times 100 \div (44 \times .1189)$ | <u>93.94%</u> |

Reaction Between Nitrobenzene and Di-phenyl-methane.

3.2 gms. di-phenyl-methane
2.5 gms. nitrobenzene
5.3 gms. aluminium trichloride

No solvent was used in this reaction. The AlCl_3 was added very slowly. The heating on the water bath was continued for 4 to 5 hours. At the end of the heating period a brown, viscid liquid resulted. The mixture cooled; but on treating with water and HCl no solid product was produced. The liquid was extracted with ether, and the ether extract examined. The liquid would not volatilise on the water bath. Over a direct flame, a violent reaction occurred resulting in the decomposition of the compound. The substance was then heated on an oil bath to a temperature of approximately 170°C ., when the same sudden decomposition occurred. Frequent attempts to reproduce this result were met with failure. When carried out in benzene, a dark solid compound, somewhat similar in appearance to that produced with anthracene, was formed. This substance had similar properties also, being difficult of solution, and possessing no definite melting point. A more detailed examination of this compound was not carried out.

Conclusion

Owing to the great difficulties encountered in purifying the unknown, identification of the product was rendered impossible. There is little doubt, however, that a reaction occurred between the nitrobenzene and the anthracene, and it is interesting to compare the properties of the compound formed with what might be expected if the reaction had followed the theoretical possibilities presented.

(1)..A compound of fairly high molecular weight would be expected, if a condensation had occurred between the anthracene and nitrobenzene. The physical properties of the unknown substantiate this, as may be judged from the extreme insolubility, and the amorphous rather than crystalline form.

(2)..It was expected that the unknown would bear some relationship to the perazine derivatives. This class of compounds are stable substances, being impervious to the action of concentrated alkalies and acids, with the exception of sulphuric acid. With this latter they formed coloured quinoid salts. Similar results were obtained with the compound obtained, a colouration also being obtained with sulphuric acid, although it could

not be determined whether or not this colour was due to a quinoid salt.

(3)..The combustion and nitrogen analyses do not agree with the theoretical. In the results obtained it would seem to suggest a compound of greater complexity than was expected, containing little or no oxygen, and very little nitrogen. The results were: Carbon--93.94%; hydrogen--4.91% nitrogen--.65%. The percentage composition of the compound expected would be: Carbon--84.80% hydrogen --4.59%; nitrogen--4.95%; oxygen 5.65%; as derived from the molecular formula-- $C_{40}H_{26}N_2O_2$.

In conclusion, it may be stated that a reaction definitely took place between the nitro-benzene and anthracene, but the exact nature of this reaction was not discovered, nor the identity of the compound formed ascertained.

APPENDIX

REACTION OF AROMATIC NITRO-COMPOUNDS WITH ISO-CYANATES.

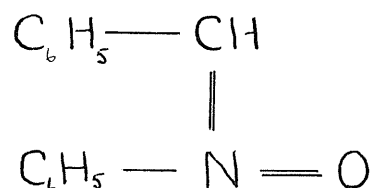
1. Theoretical Discussion.

In this reaction an attempt was made to condense aromatic nitro-compounds with the iso-cyanate group, using $AlCl_3$ to catalyse the reaction.

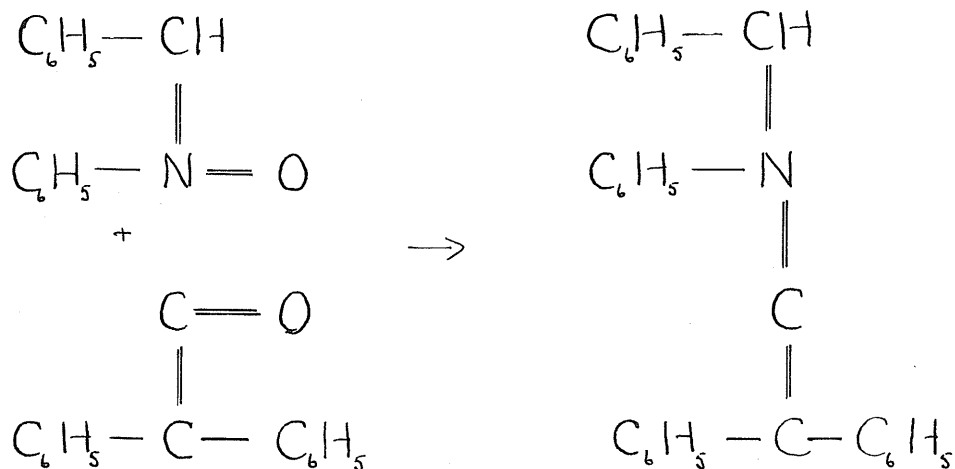
Bailey and MacPherson⁽¹¹⁾ working on double bond systems of the conjugate type, condensed 2 molecules of phenyl iso-cyanate with 1 molecule of benzalazine. This resulted in the formation of the 5,3',-di-keto-3,4,4',5',-tetra-phenyl-hexa-hydro-1,2,-triazolo-triazole. The condensation was carried on in a sealed tube at 160-170°C., a white crystalline solid resulting. This substance was not soluble in most organic substances, but was crystallised from glacial acetic acid. This compound was found to be resistant to the action of concentrated alkalies, concentrated HCl, and to nitrous acid. It did, however, reduce alkaline permanganate.

A few years later Staudinger⁽¹²⁾ prepared and studied the properties of nitrones and nitrenes.

These substances are analagous to ketenes and isocyanates; the latter may be considered to be produced by the replacement of an oxygen of CO_2 by some other divalent group such as an alkyl group; the nitrones are produced by replacing an oxygen of nitrous acid-- $\text{O}:\text{NH}:\text{O}$ in a similar manner. These give rise to compounds of constitution such as:

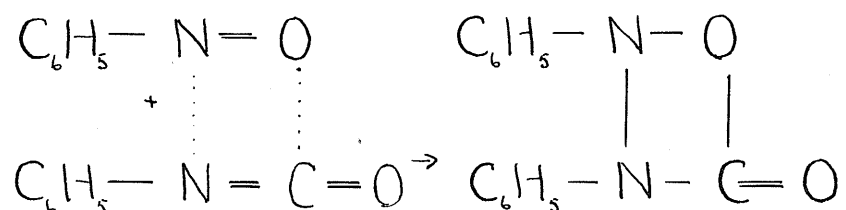


These substances are most easily produced by the alkylation of aldoximes or ketoximes⁽¹³⁾. The nitrones are well-crystallised, and coloured. They are more reactive than nitro-compounds. Nitrenes are formed by heating the addition product formed with a nitrone and a ketene, resulting in the splitting off of CO_2 :

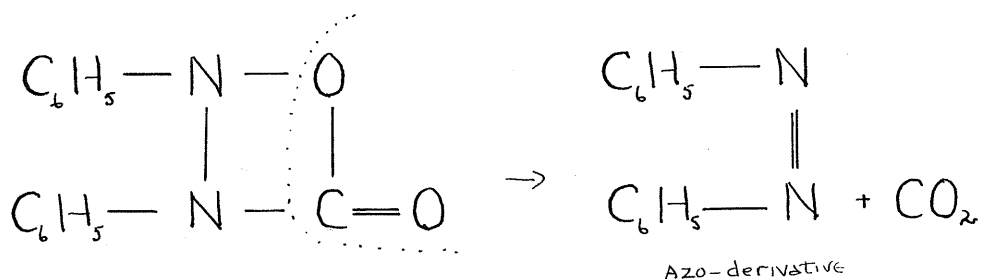


Nitrones react readily with compounds containing 2 double bonds, such as ketenes, iso-cyanates, etc., although they do not add compounds with only one double bond. For instance, di-phenyl-N-phenyl-nitrone with phenyl iso-cyanate yielded a compound of high molecular weight, having the molecular structure $C_{26}H_{20}O_2N_2$, which crystallises from ethyl acetate, giving crystals whose melting point was 164-165°C. This compound was decomposed again into its components by heating with alcohol or sodium ethylate. Nitrones also resemble ketenes in the intense colours which they develop, and in their chemical activity.

Nitroso-compounds react with iso-cyanates to produce azo-compounds. This reaction takes place in two steps, and may be indicated as follows:



The formation of the ring compound is followed by the elimination of CO_2 from the molecule resulting in the formation of the azo-compound, thus:



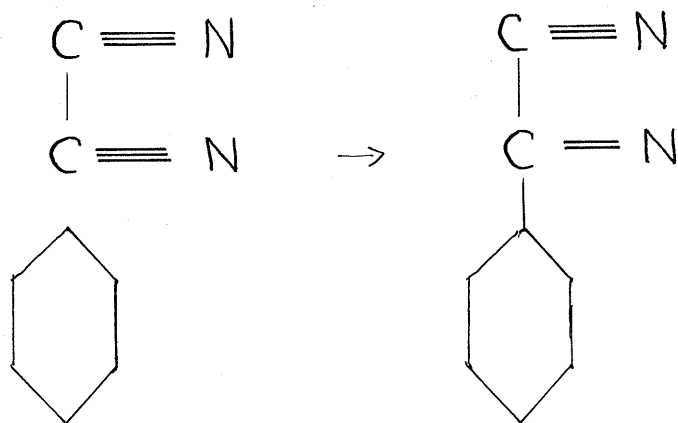
The reactivity of these compounds in showing such readiness to condense is largely due to the presence of unstable double bonds, especially in the case of the iso-cyanate, which readily forms addition compounds, or even polymerise^s very easily within itself.

As previously indicated, it is notable that although nitrones will react with such substances as iso-cyanates (which contain twin double linkages), the nitro-compounds will not. However, it was conceived by Armes,⁽¹⁴⁾ that under suitable conditions, and using an activator such as AlCl_3 , a reaction might be brought about. Before proceeding to discuss the way in which this reaction may have gone, let us consider for a moment other reactions of an analagous nature, that are catalysed by the action of AlCl_3 .

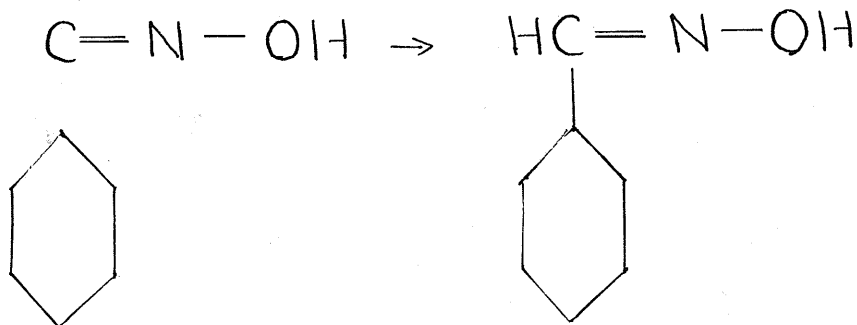
The Friedel and Craft reaction discovered in 1887, makes use of certain metallic chlorides such

cuprous or aluminium chloride, as activating agents. The mechanism of this reaction has been dealt with in this thesis in the previous discussion on theory. The application of this activating reaction in inducing condensations has a wide application in organic chemistry, and only a few examples will be dealt with here.

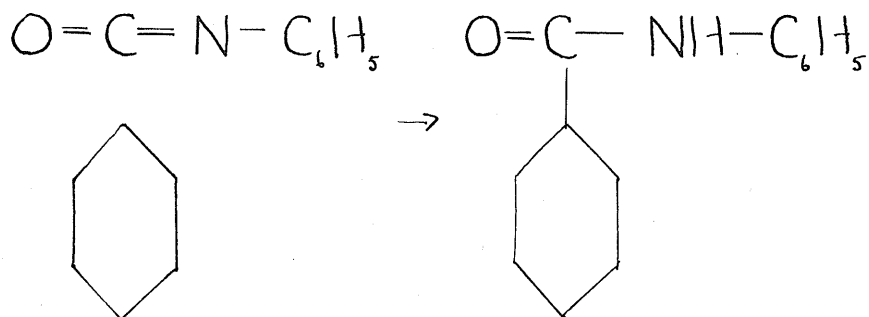
Vorlander⁽¹⁵⁾ has succeeded in condensing benzene with cyanogen using $AlCl_3$ as the catalyst:



The latter compound on hydrolysis yields benzoyl cyanide. Cyanic acid likewise condenses with benzene to yield an aldoxime.



A third reaction of an analagous nature is that of phenyl iso-cyanate with benzene to form benzyliide:



Although it is usually thought that the presence of the nitro group in the benzene nucleus inhibits similar condensation with nitrobenzene, it was thought by Armes⁽¹⁴⁾ that under suitable conditions AlCl_3 might so activate the NO_2 group as to induce condensation with the C of an active grouping such as iso-cyanate. In the latter, the presence of the twin double linkages favours condensation also.

As conceived by Armes⁽¹⁴⁾ the nitro-compound on being activated, reacts in a similar manner to the nitroso-compounds, but instead of an azo-compound an azoxy-compound might be formed. Using nitrobenzene and phenyl iso-cyanate the reaction may be represented as follows:

4.8 gms. phenyl iso-cyanate.
2.5 gms. nitrobenzene.
2.7 gms. aluminium trichloride.

This reaction was carried out in a similar manner to the previous reaction, only two molecular quantities of the iso-cyanate were used. No deep-coloured green compound was formed as in the previous reaction, however, and the mixture maintained its yellow colour throughout. After heating on the oil bath and cooling, the substance was treated with water to hydrolyse any addition compounds which might have been formed. On filtering and drying a yellow powder was formed, which crystallised readily from glacial acetic acid. The crystalline compound had a melting point of 250 °C. which is ^{approximately} that of tri-phenyl-isocyanurate a polymerisation product of phenyl iso-cyanate. A repetition of these experimental conditions produced a similar result. It was deduced from this, that an excess of the iso-cyanate favoured the formation of the polymerisation product, and prevented the formation of a condensation product with the nitro-benzene.

Examination of the Condensation Product.

An attempt was first made to reduce the unknown, as reduction should take place quite readily if, as presumed in the hypothesis, an azoxy-compound had been formed. Accordingly, the substance was treated with zinc dust in glacial acetic acid. The mixture was boiled for from 3 to 4 hours, and at the end of this time no change had occurred in the product. It was therefore concluded that the compound would not reduce.

A melting point determination was carried out in the usual manner in concentrated sulphuric acid, but the substance did not melt below the boiling point of the acid. When heated in a test tube over a direct flame, the compound decomposed before it melted.

The product was next treated with concentrated alkali. On boiling with caustic soda, the green colour disappeared and a deep blue colour was developed. This would seem to indicate that the original compound was a salt, and that the treatment with the alkali had produced the free base. The product was washed with water, and dried in a vacuum dessicator. Here, again, no melting point could be obtained.

The blue compound was found to be sparingly soluble in ether, ethyl oxalate, acetone, and chloroform, giving deep purplish-blue solutions in each case. On treatment with concentrated acid the original green product was reproduced. On treating the original green product with hot concentrated sulphuric acid, a wine-colouration was imparted to the solution, seeming to indicate some chemical reaction with the acid. Treatment with concentrated acids in the cold, however, appeared to have no effect.

Further analyses for identification of this product were impossible, as the supply of isocyanate on hand was exhausted, and it required a considerable time to obtain more. In the meantime an investigation of the reaction with active methylene groups was undertaken, and the lack of time prevented resuming the investigation of this reaction.

3.2 gms. Chloro-nitrobenzene
2.4 gms. Phenyl isocyanate
2.7 gms. Aluminium trichloride

This reaction was carried out in exactly the same way as the previous ones, but instead of using nitrobenzene, the para-substituted halogen derivative was used, to observe any effect a substituent group might exert. It was found that the action proceeded as before, resulting in the formation of a difficultly soluble substance.

When the product was heated with hot caustic soda, a change in colour was again produced, but a very noticeable increase in the intensity of the blue colour was evident. No other marked change in properties was observed. Repetition of these same experimental conditions gave a similar result.

CONCLUSION

Despite the fact that this investigation was not carried to completion, and thus prevents the making of any conclusive statements, a few salient facts may be emphasised.

(1)..According to the hypothesis upon which the reaction was based, an azoxy-compound was expected to be formed. As previously mentioned, azoxy-compounds are colourless. But, in this case, a very definitely coloured compound was obtained, both in the supposed salt and in the supposed free base. This might tend to indicate that an azoxy-compound was not formed, but some other compound with definite chromophore grouping.

(2)..Again, if the reaction had followed the proposed theoretical action, the compound formed would not be of an excessively high molecular weight. However, the amorphous nature of the compound, the great insolubility, and the lack of a definite melting point would seem to point to a very high molecular weight.

(3)..If an azoxy-compound were formed, reduction would take place with comparative ease. But although the compound was treated with zinc dust in boiling acetic acid for 3 to 4 hours, it resisted all efforts to reduce it.

These results, though not conclusive, would lead to the supposition that the reaction had not proceeded in the prescribed manner. It was regretted that no identification of the compound could be made, because, although the reaction seems to have proceeded in a manner not anticipated, there was very definitely a reaction.

BIBLIOGRAPHY

1. Armes, H.P.--Unpublished private communication.
2. Wieland, H.--Annalen, 381. Pages 200--216. (1911)
3. Henrich, F.--Theories of Organic Chemistry, translated by Johnson and Hahn from the revised fourth German edition of 1921.--Pages 403--405.
4. Wieland, H. and Roseeu, A. Ber. 45. Pages 494--499. (1912)
5. Coke, C. Eugene--Thesis presented to Faculty of the Graduate School of Manitoba University in Candidacy for M.Sc. Degree.--"Condensation of Benzyl Cyanide with Aromatic Nitro-Compounds."--(1928)
6. Reissert, Arnold. Ber. 37, Pages 831--838. (1904)
7. I. C. Farbenindustrie A.G. French patent No. 765,922. June 18 1934--Chemical Abstracts 28 (1934). Pages 6726-6727.
8. Henrich, F. Theories of Organic Chemistry, translated by Johnson and Hahn from the revised fourth German edition of 1921. Pages 168--172.
9. Bamberger, E. and Ham, W. Annalen, 382, 82.
10. Armes, H.P. Unpublished Private Communication.
11. Bailey, J.R. and McPherson, A.T. Journal of the American Chemical Society, 39, 7, Pages 1331--1333, (1917)
12. Staudinger, H. and Miescher, K. Chemical Abstracts, 13, 6. Page 561. (1919)
13. Staudinger, H. and Miescher, K. Chemical Abstracts, 14, 13. Page 1971. (1920)
14. Armes, H.P. Unpublished Private Communication
15. Cohen, Julius B. Organic Chemistry for Advanced Students, fourth edition, Pages 224--229.