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Reduction of aromatic nitro compounds to N-phenylhydroxylamines

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B O S T O N U N I V E R S I T Y
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Thesis

REDUCTION OF AROMATIC NITRO COMPOUNDS TO
N-PHENYLHYDROXYLAMINES, -

A Comparative Study of the Yields Obtained
when Aromatic Nitro Compounds are Reduced, under
Similar Conditions, to N-Phenylhydroxylamines

by

William Henry James

(Sc.B., Claflin College 1915)

Submitted in partial fulfillment of the
requirements for the degree of

Master of Arts

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Reduction of Aromatic Nitro Compounds to N-Phenylhydroxylamines.

A Comparative Study of the Yields Obtained when Aromatic Nitro Compounds are Reduced, under Similar Conditions, to N-Phenylhydroxylamines.

William H. James


May 28, 1931.

Boston, Mass.

Boston University
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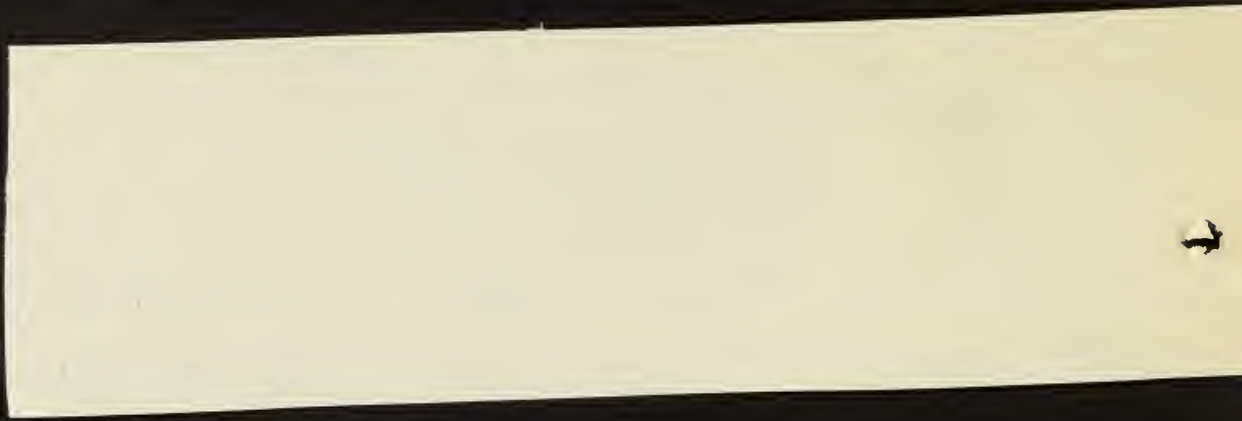
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REDUCTION OF AROMATIC NITRO COMPOUNDS TO
N-PHENYLHYDROXYLAMINES,-

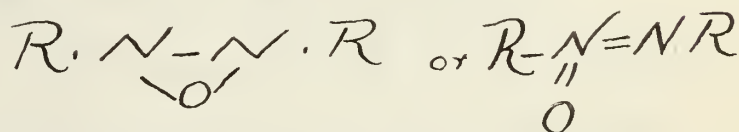
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when Aromatic Nitro Compounds are Reduced, under
Similar Conditions, to N-Phenylhydroxylamines.



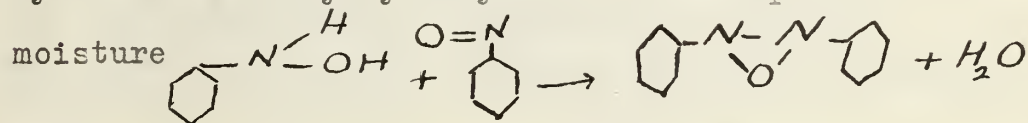
A Comparative Study of the Ease with which
Aromatic Nitro- Compounds can be reduced to
N-Phenylhydroxylamines.

A. Introduction

The reduction of aryl- nitro compounds to the corresponding amino derivatives is not a difficult matter, but the reduction of such compounds to hydroxylamino derivatives is considerably more difficult, owing to the pronounced instability of the hydroxylamino derivative and the intermediate nitroso compound. These not only show a marked tendency to react with each other to form new types of compounds of the structure



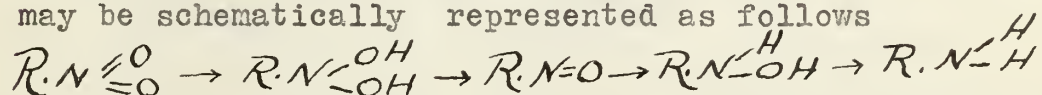
as is seen when nitrosobenzene reacts with the newly formed N-Phenylhydroxylamine in the presence of



but the hydroxylamino derivative shows great sensi-

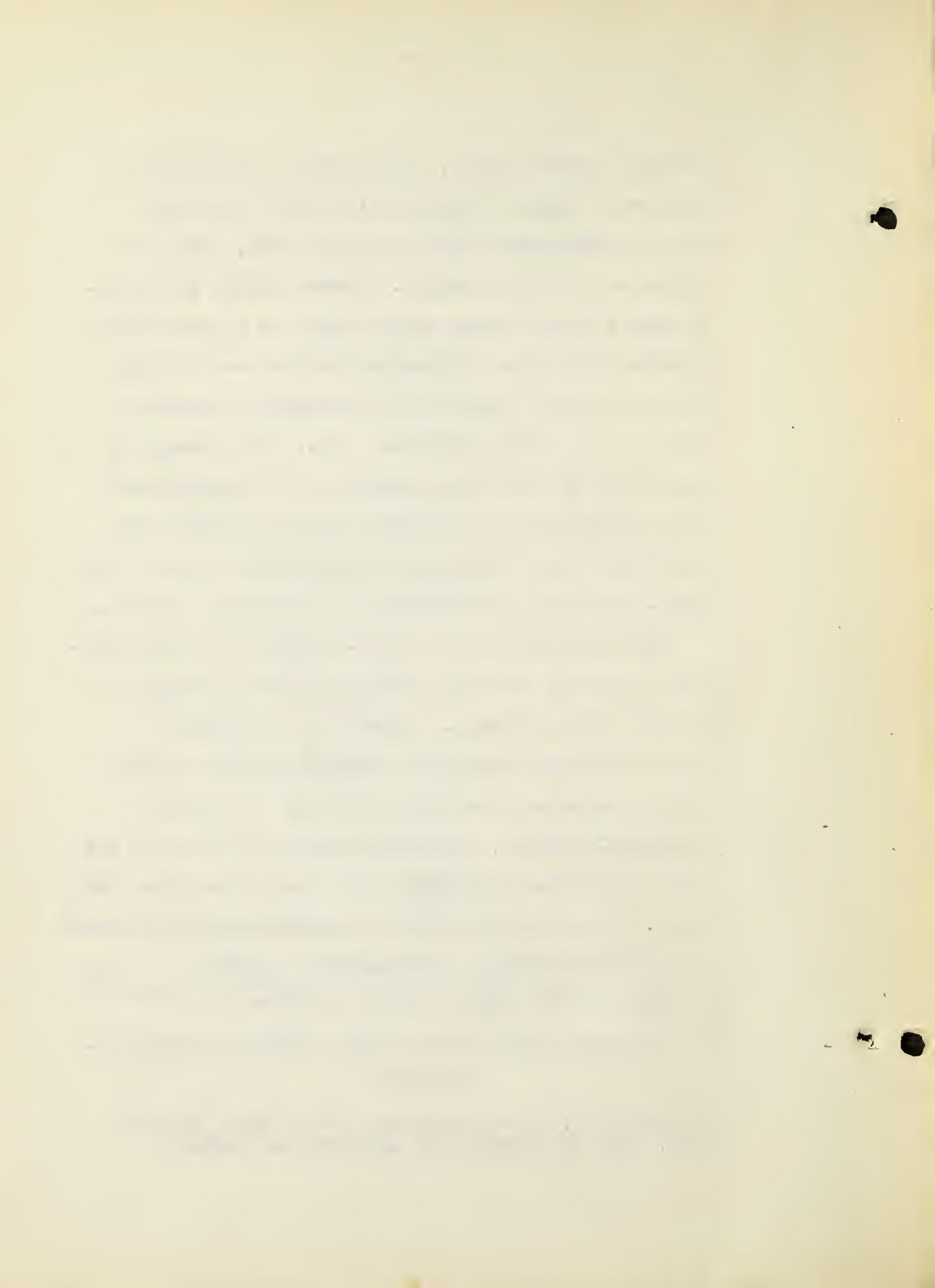
tiveness towards light, white light in particular. The latter seems to possess the power of converting the derivative into the azoxy- form. This is indicated by color changes. These changes are usually from a creamy white glossy color to a pale yellow in which the yellow coloration deepens on standing to a dark red. Even moist air converts it more or less into the above mentioned form. This change is apparently an oxidation reaction, the hydroxylamine being oxidized to the nitroso compound, which then reacts with some unchanged hydroxylamine to form the azoxy- compound, as indicated by the above equation.

The reduction of the nitro- group to the hydroxylamino type can be accomplished by either chemical or electrolytic processes. However, a distinction should be drawn between the electrolytic or primary reduction-products and the secondary or chemical reduction-products, notwithstanding the fact that the final reduction-product in each case is the same- the amine. The primary process as represented by Holleman¹ may be schematically represented as follows

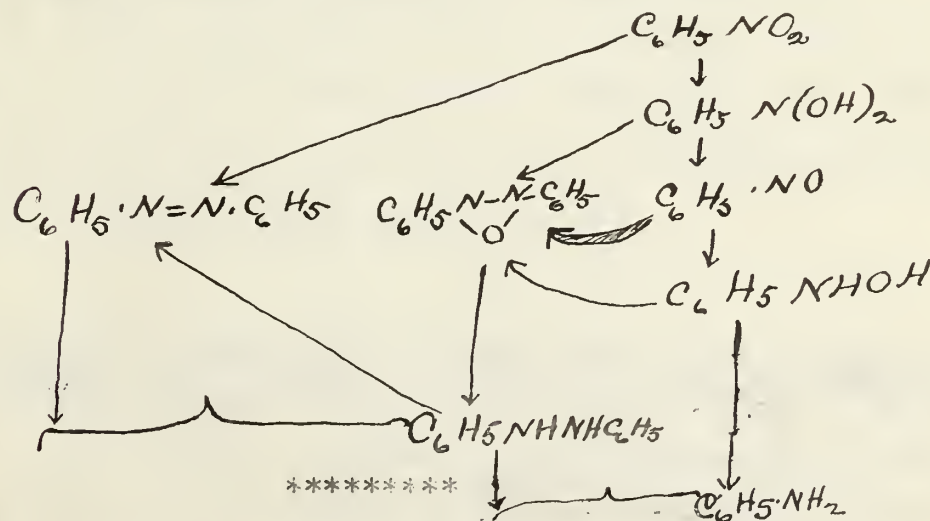


It is obvious that the so-called secondary reduction-

¹Holleman, A. F., - Text-Book of Org. Chem. 6th ed. 1925, Page 378 (Edited by Jamieson and Walker)



products are not independent as such, but are derived from the primary reduction-products. The opinion of Holleman holds that $R-NO_2$ may react during the reduction in such a way as to favor the formation of not only $R-N(OH)_2$ but also that of $R-N:N-R$. The instability of the $R-N(OH)_2$ leads directly to the formation of $R-N:O$ and a smaller amount of $R-N-N-R$. Not only is this true but both $R-N:O$ and $R-NH-OH$ yield the azoxy- form, the nitroso intermediate showing a greater tendency to revert to the azoxy- type than to continue to the ultimate amino state. Finally the azoxy- form loses oxygen and enters the hydrazo- form, the hydrazo compound can be reduced to the amine. Haber² has shown how the primary and secondary reactions are interrelated by the following scheme, in which the vertical arrows indicate primary reactions and the oblique arrows represent secondary reactions



²Holleman- A TextBook of Org. Chem.6th ed.1925, Page 380.

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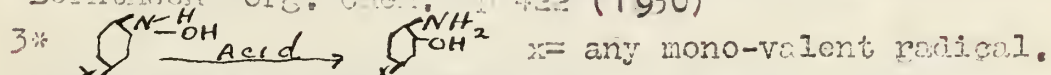
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The reduction, then, of the aryl-nitro compounds to N-Phenylhydroxylamino derivatives can be accomplished by either process. If the electrolytic process is employed, it is necessary to control the current density. The amount of current needed for a given reduction will vary with the size of the electrodes used, as well as with the composition of same. If copper electrodes are used, the amperage should not exceed 0.02 ampere nor fall short of 0.002 ampere per square centimeter of cathode surface. A difference of 0.93 volt is necessary for the reduction of the nitro group to the hydroxylamino derivative. If on the other hand a purely chemical method is used, then the behavior of the hydroxylamino derivative must determine the type of chemical reagents to be used. This choice must also consider the medium in which the reaction is to take place. If the medium is distinctively acidic, the successful formation and isolation of the hydroxylamine compound cannot be hoped for as it is further reduced to the amino state. Not only is this condition met with, but if a concentrated acid (e.g. 50 per cent H₂SO₄) medium is used, the hydroxylamino compound undergoes a molecular rearrangement³ forming a para- aminophenol^{3*}.

³Holleman, A.F., p 379 (1925) "Text Book of Org. Chem."
Henrich, (by Johnson and Hahn) "Org. Theories", 530 (1922)
Bernthsen-"Org. Chem." 422 (1930)



Also see Page 51 under "Reduction of p-Chloronitrobenzene".



In an alkaline medium the reaction proceeds rapidly to the formation of the higher reduction products of azoxy compounds, usually the greater part of the yield being a hydrazo compound with only a trace of the amino compound present. From the above facts (for the presence of all of the intermediates with the exception of $R-N(OH)_2$ can be satisfactorily established) it would seem that only in a neutral, or very slightly acidic or very slightly alkaline medium can one hope to prepare N-Phenylhydroxylamines from the corresponding aromatic nitro compounds by means of either chemical or electrolytic reduction*.

This paper, then, is concerned with a study of the comparative yields obtained by the chemical reduction of certain aromatic mono-nitro compounds, under similar conditions, to the corresponding N-Phenylhydroxylamine compounds, and the positive identification of these N-Phenylhydroxylamino compounds.

The following compounds were studied:

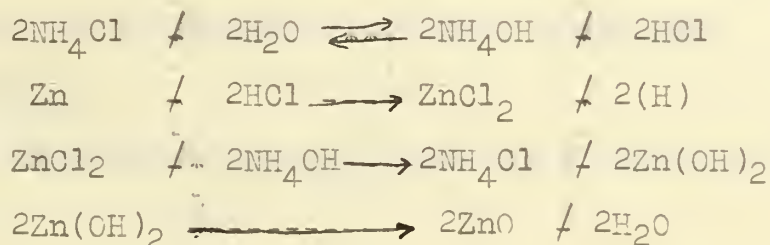
mono-Nitrobenzene⁴
ortho-Nitro-toluene
para-Nitro-toluene
para-Nitro-benzoic Acid
para-Nitro-phenol
para-Chloronitrobenzene

⁴Nitrobenzene is included in the list only because of its importance as the basis of this work and not because of a lack of information regarding its properties or any new development in the method of its reduction to N-Phenylhydroxylamine.

* For a statement of the acid concentration of the solution, please turn to "Addenda" page 64.



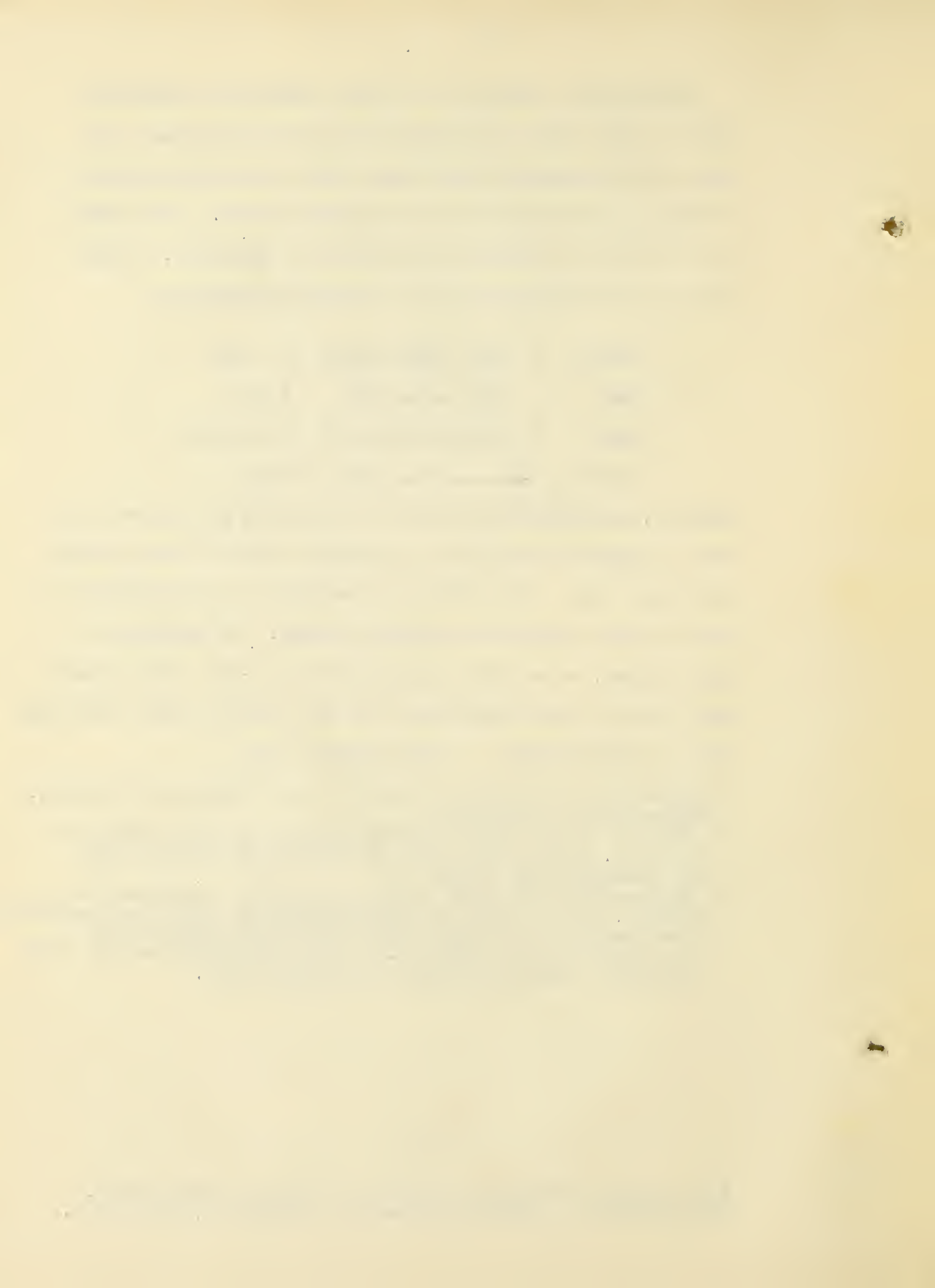
The general reduction of nitro compounds concerned with in this paper was carried out by the chemical process, which employed zinc dust, and an aqueous solution of ammonium chloride as the reducing medium. The literature refers to ammonium chloride as a catalyst. It may function as indicated in the following equations:



However, no detectable amount of hydrogen gas was evolved when an aqueous solution of ammonium chloride was treated with zinc dust. The method of reduction thus referred to was slightly modified in certain cases. In addition to this method, a few other methods were tried. The success met with in their employment did not justify their continued use or consideration. These methods were :

- 1) Reduction by hydrogen sulphide in an alcoholic solution. No reduction took place.
- 2) The use of amalgamated aluminium in dry ether was not fruitful. Only in the case of nitrobenzene was there any satisfactory yield.
- 3) Amalgamated zinc dust failed to produce satisfactory results. In the case of nitrobenzene the yield was negligible, notwithstanding the fact that Gattermann claims that the yield is quantitative⁵. Other authorities assert that the yield varies from zero to 70 per cent⁶.

⁵Gattermann- "Practical Methods of Organic Chemistry".
⁶Journal of the American Chemical Society, 41, 277 (1919).



From these observations it seems that the ammonium chloride method is the only feasible method other than the electrolytic method that can be successfully employed in the reduction of aryl- nitro compounds to N-Phenylhydroxylamino compounds.

B. Preparation and Purification of Materials.

* * *

Synthesis of p- Nitrobenzoic Acid.

*

In the literature the preparation of ortho-hydroxylaminobenzoic acid from the corresponding nitro compound is fully described by Gattermann⁷. This made it desirable for me to undertake the preparation of para- hydroxylaminobenzoic acid from para- Nitrobenzoic acid. This compound not being in stock it became necessary to prepare it. It was prepared by the oxidation of para- Nitrotoluene in the presence of of sodium dichromate in concentrated sulphuric acid solution⁸. The compound thus prepared was purified by crystallization. It melted

⁷Ber. 1909, Band II, Nr.7 (June 14) 2183, (2306-2307).
⁸Adams and Johnson- Lab. Exps. in Org. Chem. 223

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at 238 degrees C. The melting point of this compound as given in the literature is 240 degrees C. It was further checked by means of its ethyl ester derivative⁹ which melted at 56.5 degrees C. The melting point of this ester as described in the literature is 57 degrees C.¹⁰ The compound thus prepared (para - Nitrobenzoic acid) was considered pure enough for the preparation para-hydroxyl-aminobenzoic acid.

Purification

It was the plan to use only chemically pure reagents. When this could not be done, the reagents were carefully purified, the process of purification being continued until the purity test in each case was satisfactory. It was necessary to purify the following compounds: nitrobenzene, o- nitro-toluene, and p- nitro-phenol.

1. Nitrobenzene.

The nitrobenzene showed a boiling point of

⁹According to Kamm's Organic Qual. Anal. p 150.

¹⁰All melting points in this work are uncorrected. Those referred to in the literature are also uncorrected.

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204 degrees C. It was reddish-brown in color. It was purified by fractional distillation. The fraction at 210 degrees C., possessing a light yellow color, and showing a specific gravity of 1.032 at 21 degrees C. was retained for the reduction. The *boiling* point and specific gravity of nitrobenzene as recorded in the literature are 210 degrees C., and 1.033 at 21 degrees C. respectively.

2. o- Nitrotoluene.

The purification was effected through fractional distillation. The process was continued until a product was obtained which boiled at 220 degrees C. and showed a specific gravity of 1.17 at 21 degrees C. The *boiling* point checked with that found in the literature (220 degrees C.). The specific gravity as recorded in the literature is 1.168 at 21 degrees C. The compound was considered pure.

3. p-Nitrophenol.

This solid substance was very impure, being almost dark gray in color with colorless shiny needle-like crystals scattered throughout the bulk of the substance. Purification

was brought about through crystallization of the substance from hot water in which it was difficulty soluble. The carefully washed and dried crystals showed a melting point of 114 degrees C. This agreed with the melting point recorded in the literature. The purified p- Nitrophenol was reserved for use in the preparation of N-(4-oxyphenyl) hydroxylamine.

4. Determination of the purity of the zinc dust.

It was thought that the quality and quantity of the zinc dust might have something to do with the unsatisfactory yields obtained with the method. The purity of the zinc dust was determined and the amount of zinc necessary for the reaction was recalculated on the basis of the purity of the metal. The determination of the purity was made by comparing the actual amount hydrogen gas liberated from 0.10 g. of the zinc in question in the laboratory with the theoretical amount possible under the same conditions of temperature and pressure. The result of this is recorded below

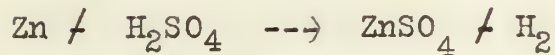
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Calculations: Purity of the Zinc Dust.

Theoretical



$$\frac{0.1}{65.37} \times 22.4 \times \frac{293}{273} \times \frac{760}{760} = 0.02856 \text{ l. or } 28.56 \text{ cc.,}$$

the amount of hydrogen gas that should be liberated from an excess of sulphuric acid 0.10 gram of zinc dust at 20 degrees C. and under one atmosphere of pressure.

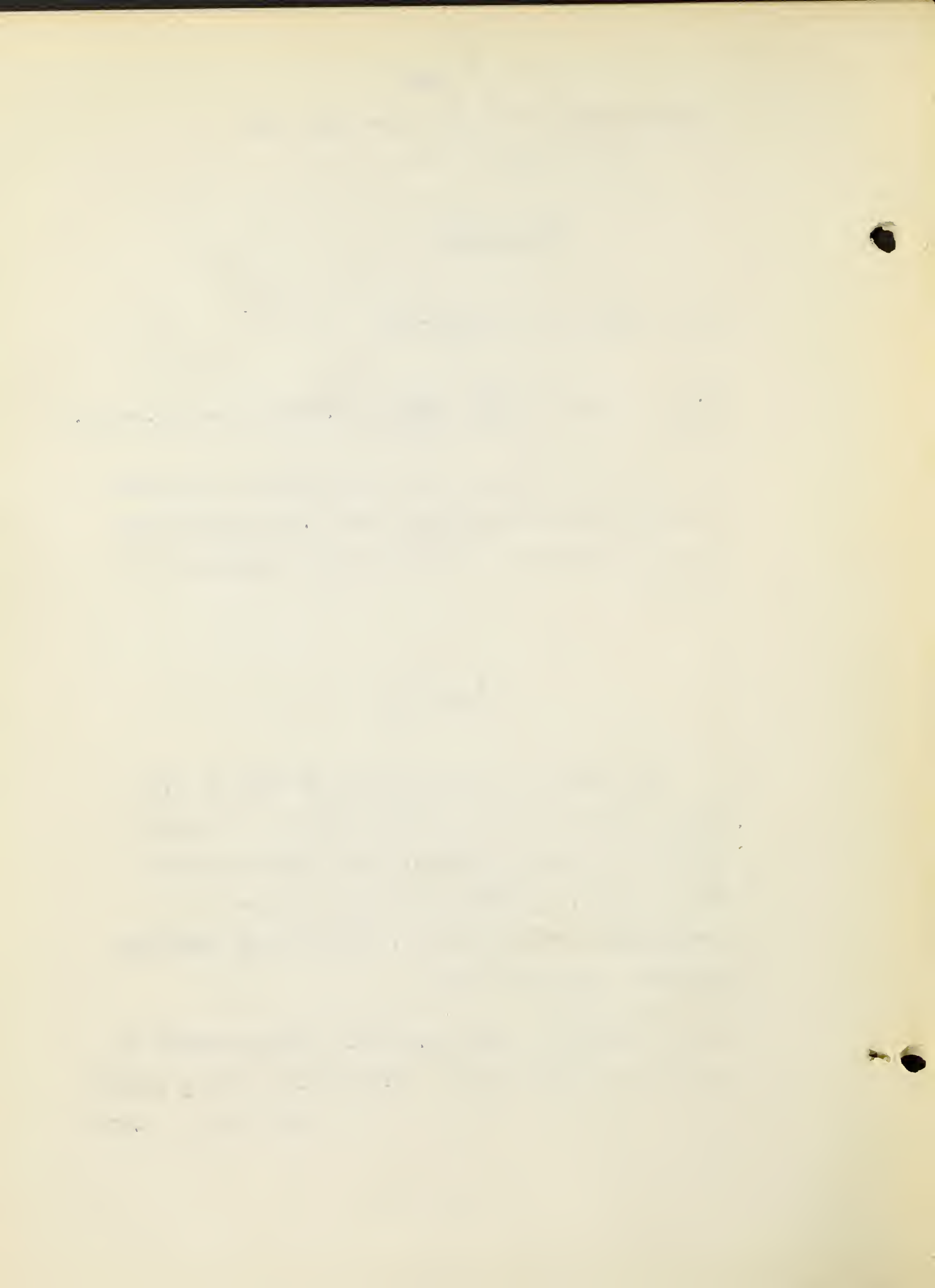
Laboratory

The amount of hydrogen gas liberated by 0.10 gram of zinc dust with a small excess of sulphuric acid in an air-free 250 cc. round bottom flask at 20 degrees C. and under a pressure of one atmosphere was 29 cc. This volume corrected for water vaopr pressure,

$$29 \times \frac{760-17.36}{760} \text{ gave } 28.37 \text{ cc. The percentage of}$$

zinc in the zinc dust is $28.37 / 28.56 \times 100 = 99.30\%$

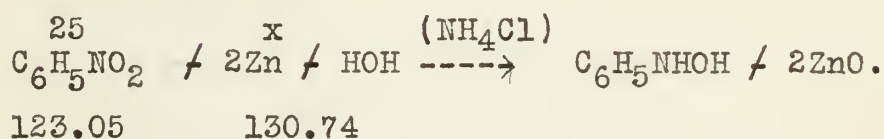
Impurities = 0.70%



Purity of the Zinc Dust.

The amount of zinc dust necessary for the reduction of 25 grams of nitrobenzene was calculated from the following relations, as expressed in the equation:

(using 25 grams of the nitro compound as a standard¹¹)

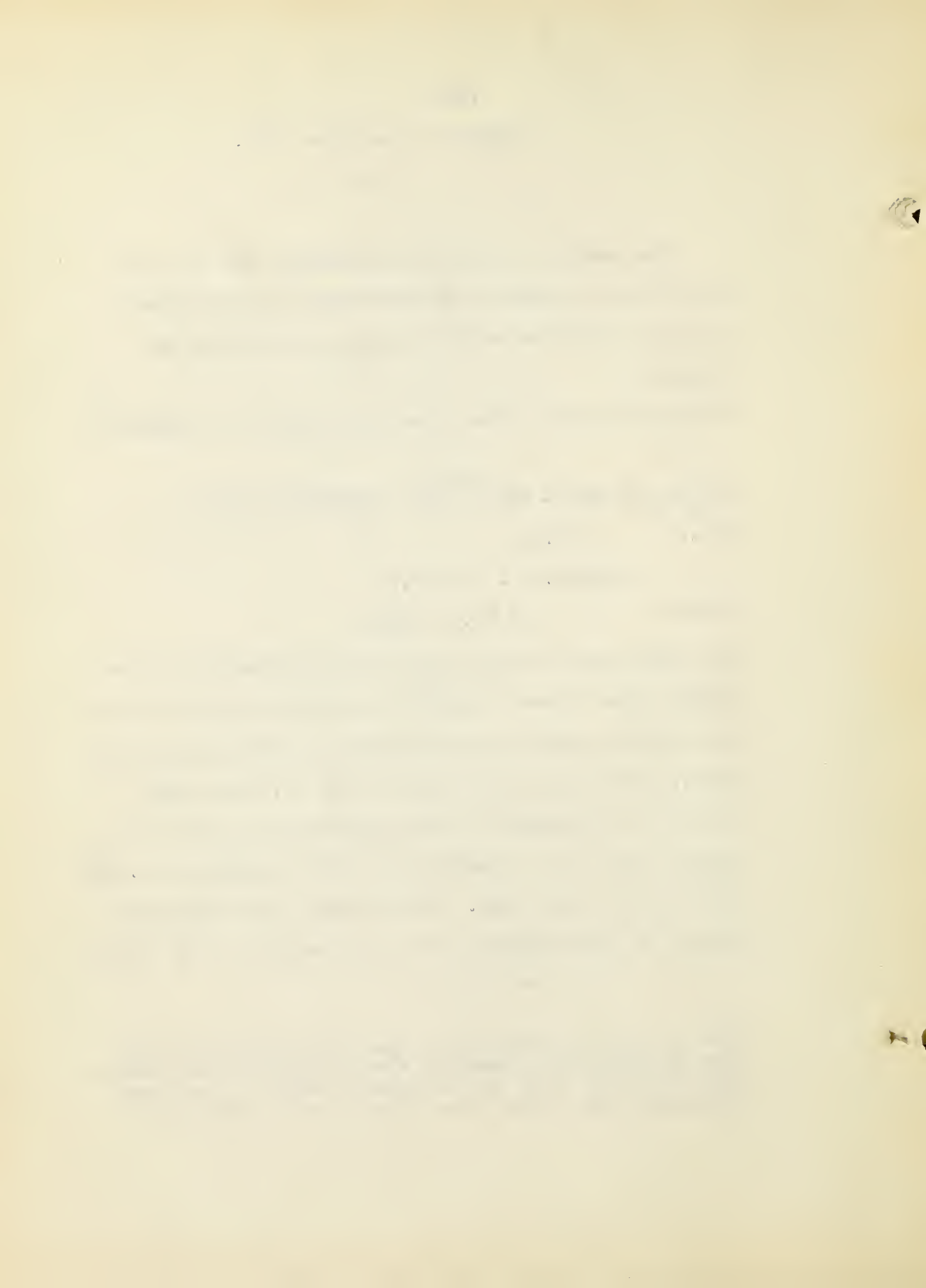


$$25/123.05 = x/130.74$$

whence $x = 26.56$ grams

This means that if the zinc dust were absolutely pure (100%), 26.56 grams would^{be} a sufficient quantity to reduce the 25 grams of nitrobenzene to N-Phenylhydroxylamine, but as the zinc dust is only 99.30 per cent pure it was necessary to use approximately 0.19 of a gram of zinc dust to make up for the impurities (0.70%) found in the zinc dust. This brought the theoretical amount of zinc necessary for the reaction, up to 26.75

¹¹ In all of the reactions (runs) of nitrobenzene the same quantity (25 grams) of the nitrobenzene was used. This was done also in the case of many of the other compounds. The object was to facilitate comparisons.



grams. After the first run, a 15 per cent excess of the zinc dust was used instead of the actual theoretical amount. This additional 3 or 4 grams brought the quantity of zinc dust up to approximately 31 grams. It was observed that the excess had no effect upon the yield of the hydroxylamine, for in every run there appeared some unused zinc dust, whether or not an excess of the theoretical amount was used.

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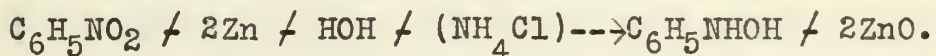
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C. Experimental Part.

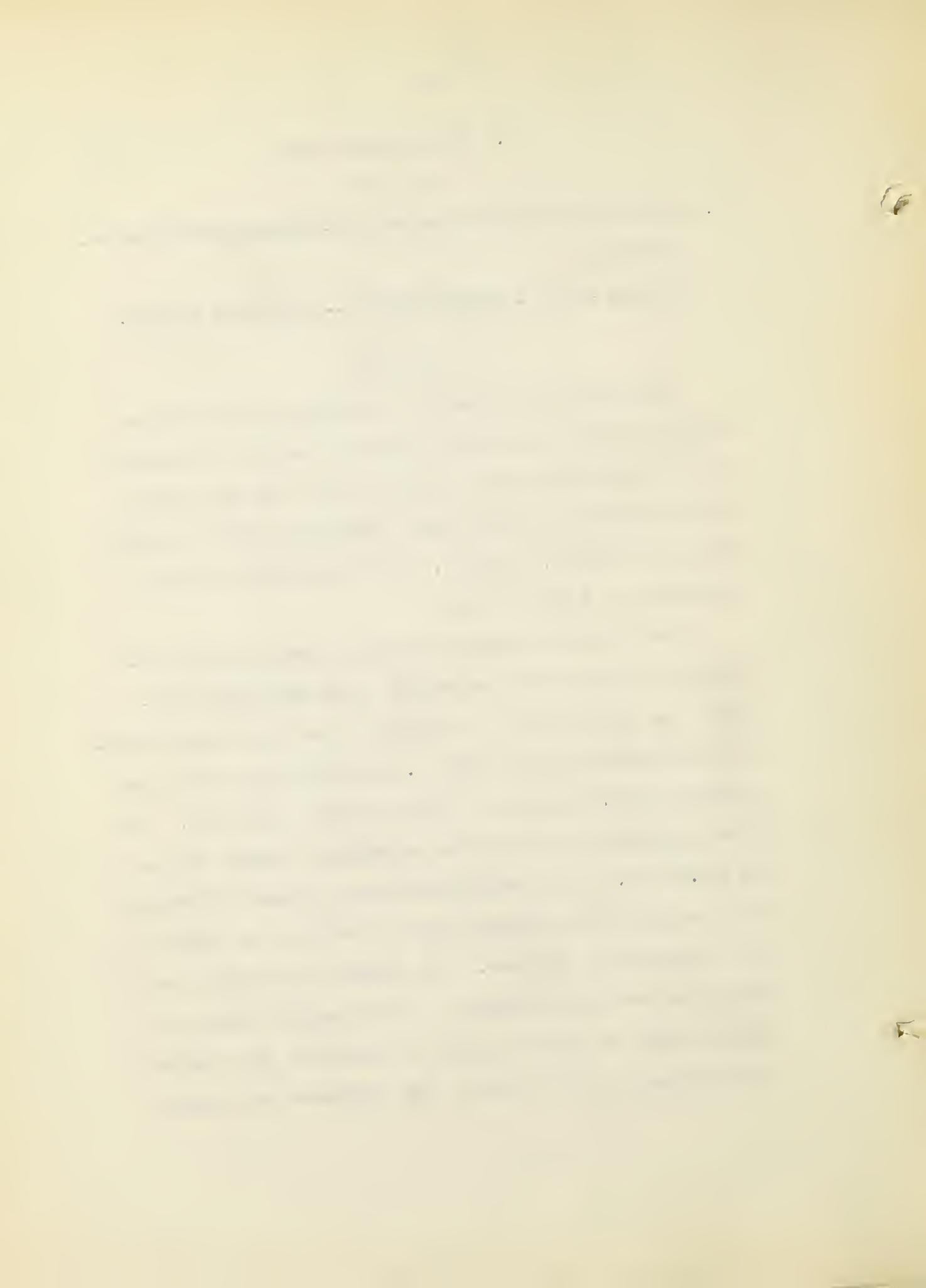
1. Reduction of Nitrobenzene to N-Phenylhydroxylamine.

Reaction:



Employing the presence of ammonium chloride as catalyst during the twelve times in which the reduction of nitrobenzene was carried out, the best yield of N-phenylhydroxylamine was obtained in the eleventh run (vide Table I, page 28). This particular run is discussed in detail below.

The reaction mentioned above, involving the reduction of mono-nitrobenzene to N-Phenylhydroxylamine was carried out as follows: In a one liter beaker containing exactly 400 cc. of distilled water, was dissolved 12.50 grams of pure ammonium chloride. To this solution was added the calculated amount (25 g. or 20.80 cc.) of recently distilled mono-nitrobenzene. This mixture was whipped into an emulsion by means of a mechanical stirrer. The beaker containing the emulsion was then placed in a one gallon crock so fitted that it could easily be heated to any desirable temperature by steam. The emulsion was again



mechanically stirred until the temperature reached a point between 65 and 70 degrees C. At this point the stirring was made much more vigorous and the addition of the zinc dust was slowly begun. The calculated amount of zinc dust which was found by analysis to be 99.30 per cent pure, was 26.56 grams. The amount actually used was 30.75 grams. This amount included 0.18592 g. (0.19 g. was used) used to off set the 0.70 per cent impurities found in the zinc dust plus 15 per cent excess (4 grams).

With the addition of each portion of zinc dust (3 or 4 grams) there was a rapid rise in temperature. By allowing a longer interval between the additions and at the same time reducing the quantity of each portion to 2 or 3 grams, the heat of the reaction was so controlled that the temperature did not rise higher than 70 degrees C. During the greater part of the reduction the reaction temperature was maintained at 68 to 69 degrees C., but along towards the end of the reduction, the heat of reaction became almost uncontrollable, making it necessary to dispense with the further use of the steam generator. However, the heat of reaction was not brought within proper control until after the application of ice water. The stirring was continued for at least 20

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minutes after the addition of the last portion of zinc dust. By this time the temperature had gradually fallen to 22-23 degrees C. At this point the reduction was thought to be complete. The stirring was discontinued. The actual time of reduction was 35 minutes. The 20 extra minutes were used for the purpose of insuring complete chemical reaction. But as the temperature after the first 35 minutes rapidly decreased until it became that of the laboratory (22-23 degrees C.) it was concluded that no further reduction took place during the 20 extra minutes mentioned.

The warm solution-mixture was filtered by suction. The residue (mostly zinc hydroxide or zinc oxide, with some unchanged zinc dust) was washed twice with 50 cc. portions of hot water on the filter. The wash water was added to the filtrate. The beaker containing the filtrate was then placed in a one gallon crock containing ice and salt. To the filtrate were added directly about 300 grams of common salt and a few pieces of ice. The mixture was stirred with a glass rod so as to dissolve as much of the salt as possible. As the filtrate began to cool, the N-Phenylhydroxylamine began to crystallize out. The filtrate acquired a temperature of

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-5 degrees C. It was allowed to stand undisturbed, except an occasional stirring, for 35 minutes. At the end of this time it was thought that all of the N-Phenylhydroxylamine had crystallized out.

The crude product of N-Phenylhydroxylamine was collected on a small filter. As it contained a small quantity of salt mixed in with it, it was necessary to free it from the salt before considering the yield. This was accomplished by extracting the N-Phenylhydroxylamine with ether in which it is extremely soluble. The ether extract was separated from the aqueous solution of salt by means of a separatory funnel. The ether extract was dried with anhydrous calcium chloride and distilled from a hot water bath. This removed the ether leaving the solid N-Phenylhydroxylamine in the beaker. This compound being very sensitive to light and moisture was colored yellow to orange on standing. It being only difficultly soluble in ligroin, was crystallized from this solvent in the hot, and later re-crystallized from hot water. During the process of purification it was necessary to protect the compound as much as possible from light. This was done by surrounding the con-

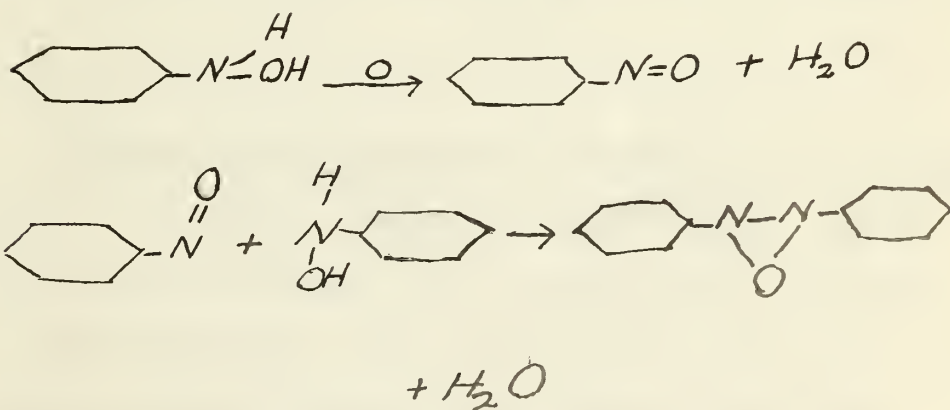
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tainer with dark paper. But even with this precaution, the compound was more or less affected.

The zinc oxide (or hydroxide) was extracted with ether in order to remove any of the hydroxylamino compound that might have escaped the hot water residue treatment. While it was observed that the ether extract was slightly colored yellow, evaporation (spontaneously) of the ether did not yield a sufficient quantity of the compound to be purified and weighed. The pure product (N-Phenylhydroxylamine) thoroughly dried weighed 17.70 grams. This was 79 per cent of the theoretical amount. The melting point was 80 degrees C. The melting point as recorded in the literature is 81 degrees C. (uncorrected). After standing for a day or so it was observed that the crystals although white and glossy at first, quickly turned yellow, then brownish and much later- red. After three days the melting point determination showed that with the increase in coloration of the compound there was also decrease in the melting point. To discover the apparent cause of this behavior a few of the pale yellow crystals were carefully removed mechanically from the uncolored N-Phenylhydroxylamine and treated with hot water.

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They did not dissolve. This indicated that the compound was different from N-Phenylhydroxylamine which is soluble in hot water. The crystals thus treated, were thoroughly dried. They melted at 36 degrees C. Qualitative analysis indicated that the compound was azoxybenzene. This was later confirmed by the literature.^{12*} The formation, isolation and positive identification of azoxybenzene led to the conclusion that the N-Phenylhydroxylamine had been oxidized by the air to nitrosobenzene, which then reacted with some of the unchanged N-Phenylhydroxylamine to form azoxybenzene. This may be expressed by the following equations-



12*

Mulliken- "Identification of Pure Organic Compounds"

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Physical Properties of N-Phenylhydroxylamine.

N-Phenylhydroxylamine crystallizes in long needles from saturated sodium chloride solution. When pure the crystals are almost colorless. The compound is only slightly soluble in hot water, but very soluble in ether, alcohol and ethyl acetate. It is difficultly soluble in ligroin and benzene. It has a very irritating effect upon the mucous membrane of the nasal passage, causing violent sneezing. It melts 81 degrees C.

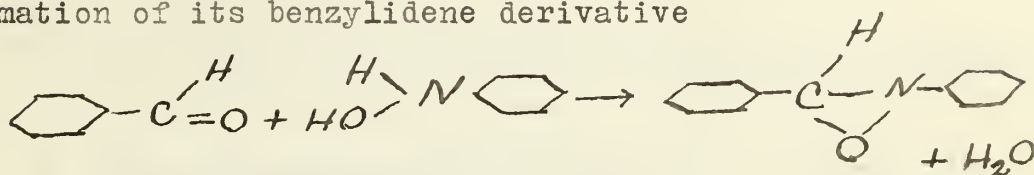
Chemical Properties of N-Phenylhydroxylamine.

N-Phenylhydroxylamine is unstable. It is readily affected by light, especially white light. It is also affected by moist air, being readily oxidized to nitrosobenzene. It has strong reducing power, reducing almost quantitatively Fehling's Reagent to cuprous oxide, and causing the formation of a silver mirror when warmed with an ammoniacal solution of silver oxide. In the presence of strong mineral acids it undergoes molecular rearrangement, forming an aminophenol. It reacts with benzaldehyde forming Benzylidene-(N-Phenylhydroxylamine). It reacts with nitrous acid forming hydroxy-nitrosobenzene.

The Benzaldehyde Derivative.

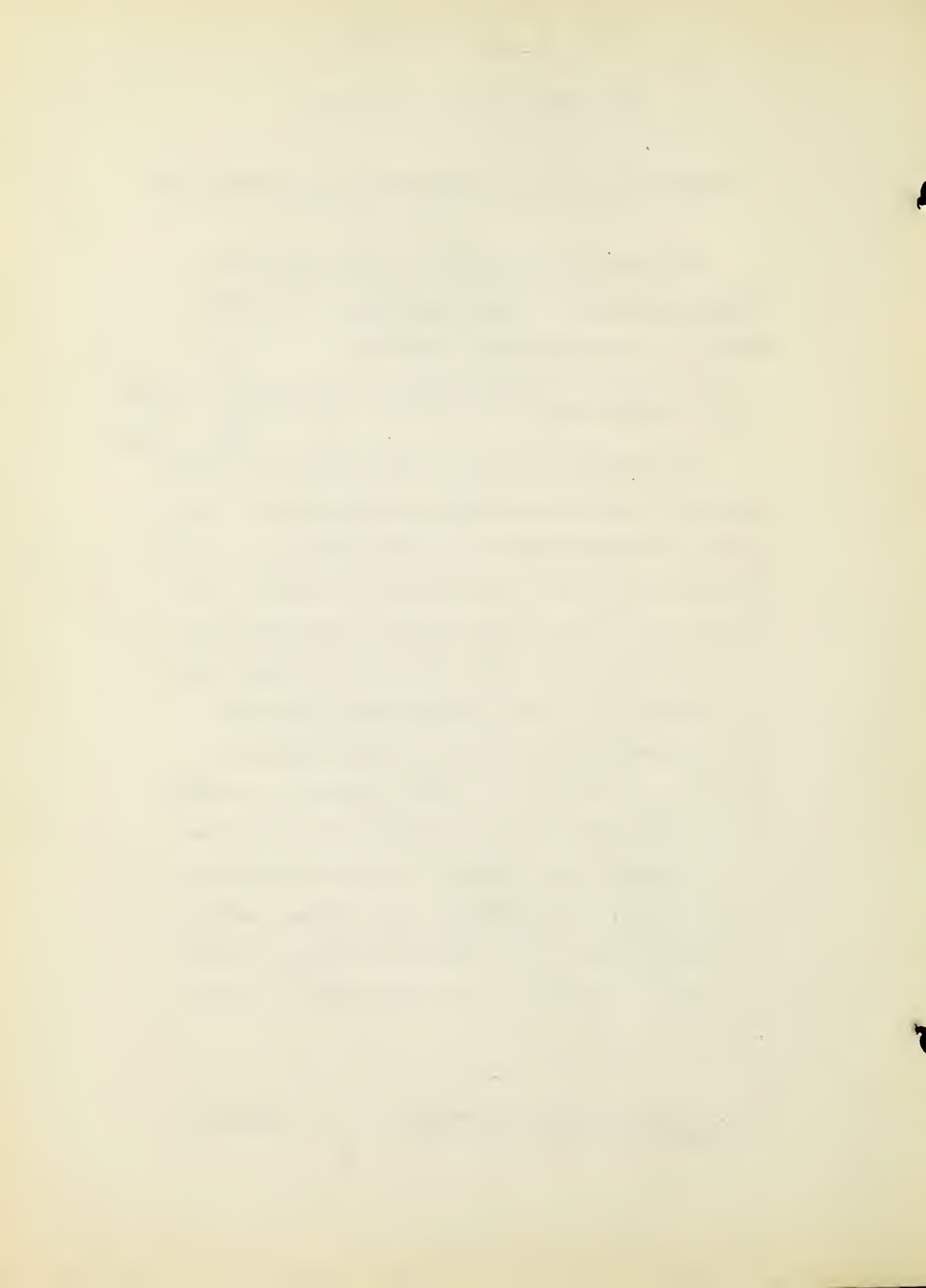
Preparation of Benzylidene-(N-Phenylhydroxylamine)

That the nitrobenzene had been reduced to N-Phenylhydroxylamine was confirmed by the formation of its benzylidene derivative



The calculated amount of the N-Phenylhydroxylamine was intimately mixed with an equi-molar proportion of chemically pure benzaldehyde and warmed on a water bath for one hour, at the end of which time it was thought that complete chemical reaction had taken place. The crude product was steam distilled until no free benzaldehyde remained. The residue was crystallized from a mixture of 95 per cent alcohol and a small quantity of water. It was dried as much as possible on a small filter by suction and allowed to stand over night in a desiccator. The perfectly dry compound melted at 107-109 degrees C. The melting point of this compound as recorded in the literature¹² is 107-108 degrees C.

¹²R. Stelzner- "Literatur-Register der Organische Chemie", Volume 2, page 784.



Thus the formation of Benzylidenephénylhydroxylamine completed the identification of N-Phénylhydroxylamine, establishing the conclusion that the nitrobenzene had undergone reduction.

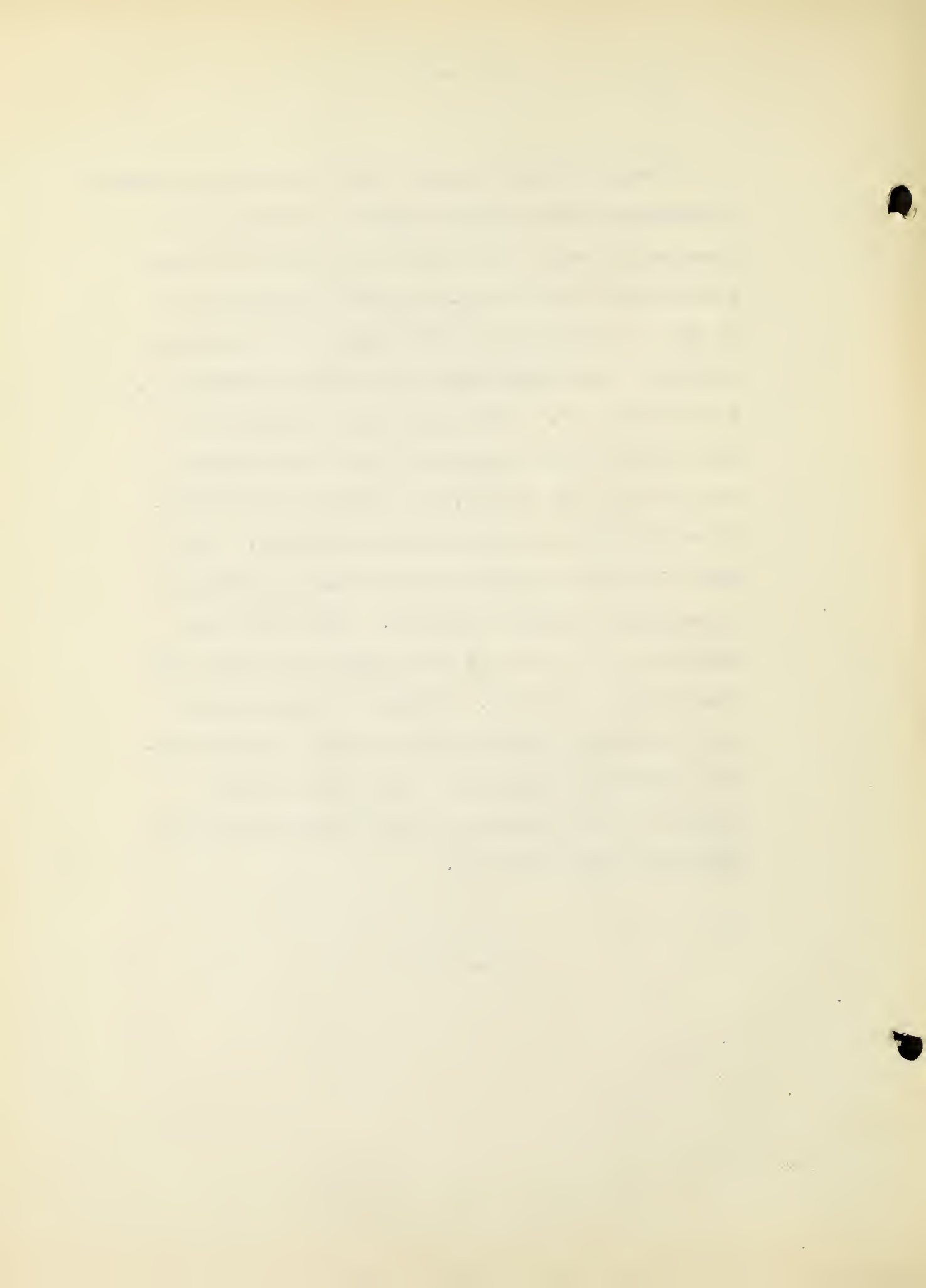
Physical Properties of Benzylidenephénylhydroxylamine.

Benzylidenephénylhydroxylamine is a light brown crystalline solid. It is insoluble in water, in dilute acids, in dilute alkalies and in ligroin. It is soluble in ether and in ethyl alcohol. It melts at 107-109 degrees C.

Chemical Properties

The compound is quite stable towards most chemical reagents, however, it is readily soluble in cold concentrated sulphuric acid. When treated with this acid there is an evolution of heat with the formation of a greenish-yellow solution.

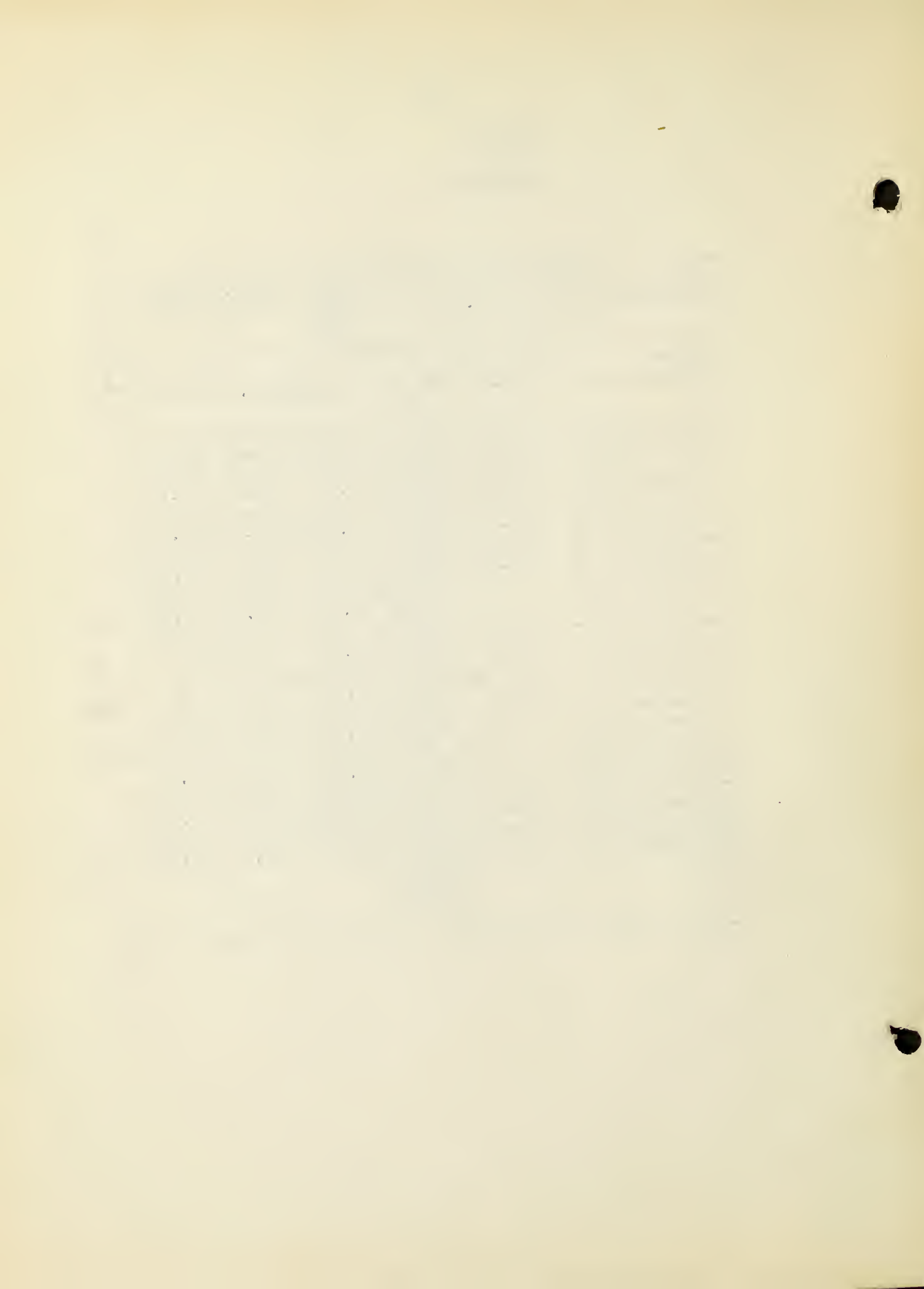
Further studies in the reduction of nitrobenzene by means of zinc dust and ammonium chloride in the presence of water were carried out under different experimental conditions. At first the quantities of the nitrobenzene and zinc dust were kept constant and the temperature varied from 0 degrees C. to 72 degrees C. The effect upon the yield was duly observed and recorded. Later the quantity of zinc dust was varied, and alcohol was partially substituted for water in the reaction. This was followed by the addition of small quantities of anhydrous calcium chloride. The effect produced upon the yield of the reduction-product was observed and recorded. Finally a minute quantity of powdered iron was added to the regular catalyst (ammonium chloride). The results accomplished by these variations are tabulated on the following page (Table I).



Summary

Table I

Run NO	Sub'nce	Am't g.	Temp. C.	Cat'st	React. Time hrs.	lab. Yield	Theo. P.C.
Nitro-1	Benzol	25	60-65	NH ₄ Cl	0.83 ¹ / ₃	10.5	47.38
2	Benzol	25	35-40	NH ₄ Cl	0.83 ¹ / ₃	11.0	50.00
3	Benzol	25	35-40	NH ₄ Cl	1.00	11.0	50.00
4	Benzol	25	22-23	NH ₄ Cl	1.16 ² / ₃	10.9	49.10
5	Benzol	25	65-70	NH ₄ Cl	1.50	12.6	56.85
6	Benzol	25	0	NH ₄ Cl	1.00	1.0	4.51
7	Benzol	25	22-23	NH ₄ Cl	1.00	0	0
8	Benzol	25	20-23	NH ₄ Cl	1.00	0	0
9	Benzol	25	20	NH ₄ Cl	1.00	7.5	33.84
10	Benzol	25	60	NH ₄ Cl	1.00	5.0	22.50
11	Benzol	25	68-69	NH ₄ Cl	0.58 ¹ / ₃	17.7	79.00
12	Benzol	25	71-72	NH ₄ Cl Fe ⁴ CaCl ₂	1.00	18.5	83.46



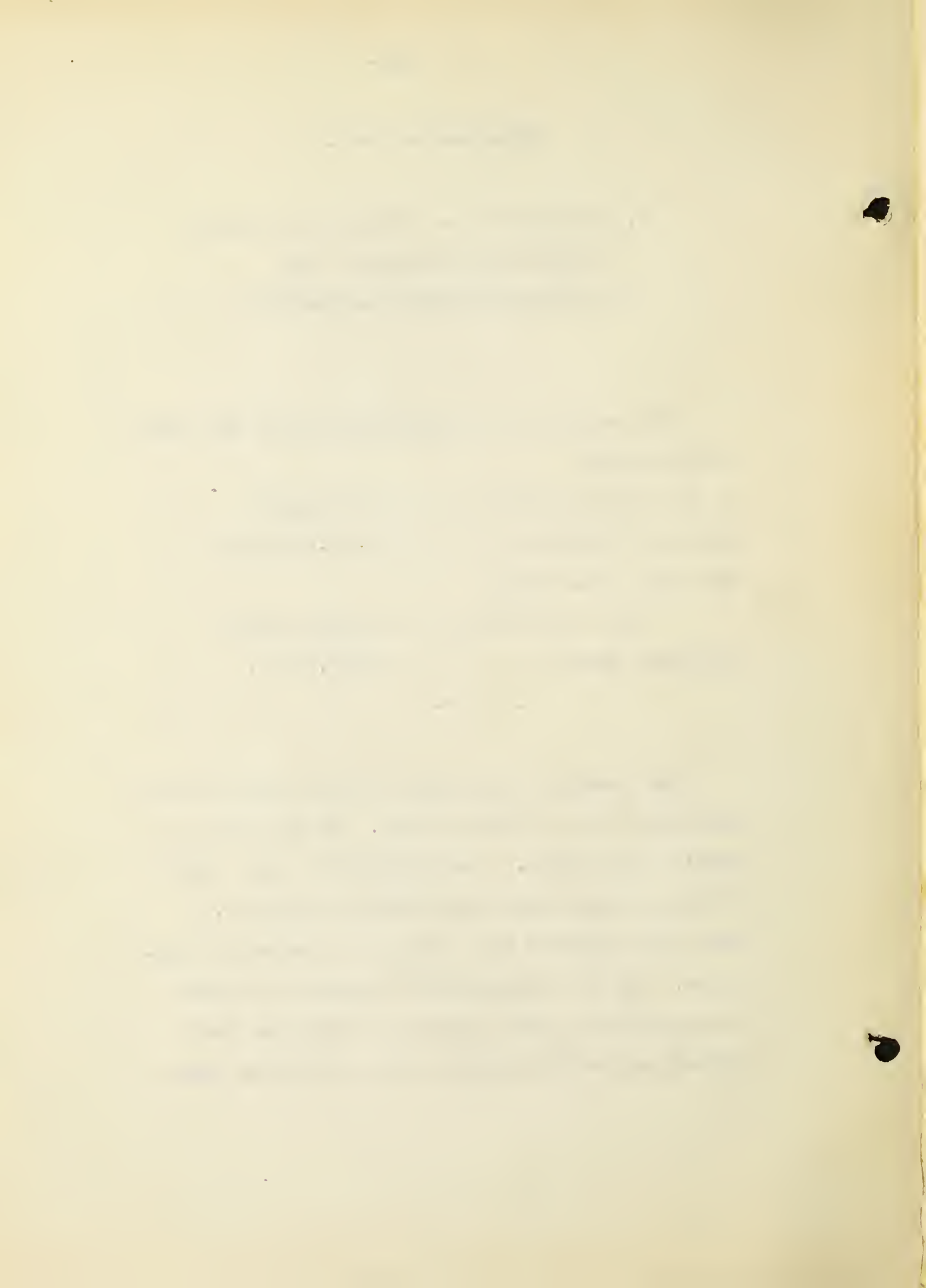
Experimental Part.

2. Reduction of p- Nitrobenzoic Acid to
p- Hydroxylaminobenzoic Acid
(p- Carboxyphenylhydroxylamine)

The quantities of materials used in the above
reaction were:

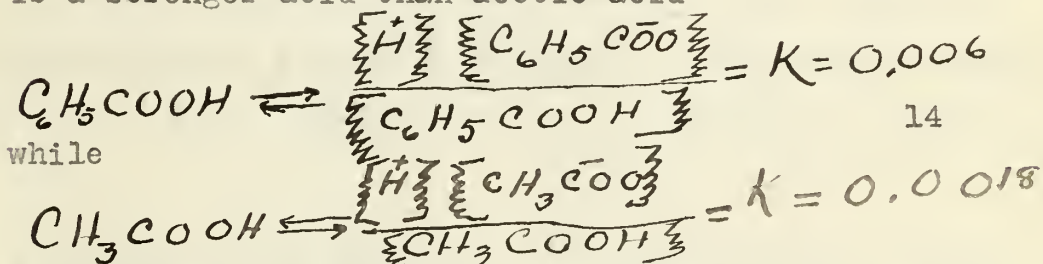
p- Nitrobenzoic Acid-----25 grams
Ammonium Chloride-----12.50 grams
Zinc dust (19.7 grams
 plus 15%^g excess-----23.00 grams
Distilled water-----400.00 cc.

The reaction temperature in the first run was
maintained at room temperature. No apparent re-
duction took place. The reaction was then tried
at the optimum temperature (65-70 degrees C.).
This also resulted in a failure to reduce the com-
pound. The two unsuccessful attempts to reduce
p- nitrobenzoic acid by means of the zinc dust
method led to the thought that perhaps the pres-



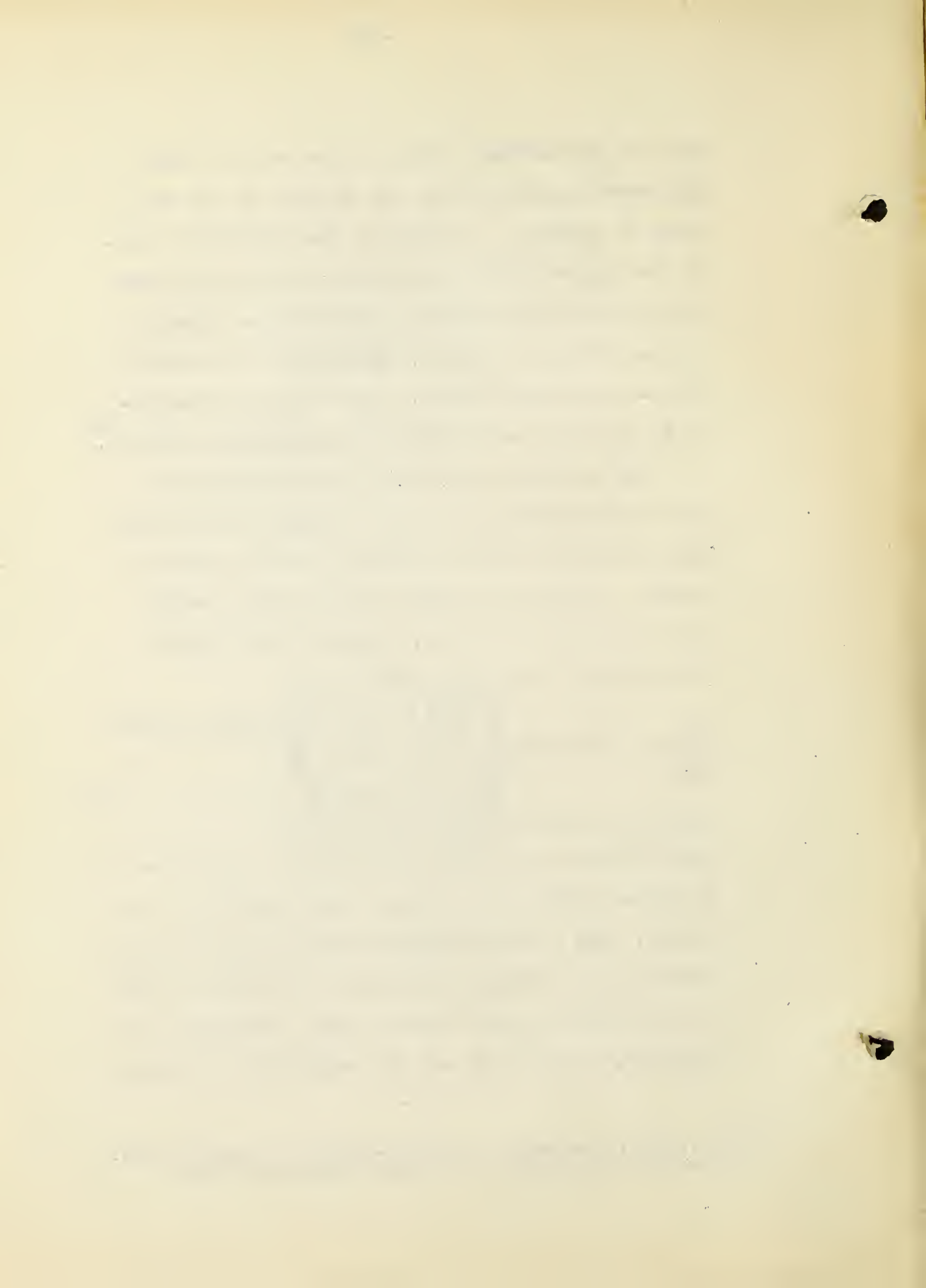
ence of the carboxyl group in some way or other had something to do with the failure of the compound to reduce. A search of the literature showed that while there is no record of this compound being reduced by zinc dust and ammonium chloride in the presence of water, Gattermann has reduced the o- nitrobenzoic acid. To do this he converted it into its barium salt and reduced the latter¹³.

The statement was made in the introduction that the reduction of nitro compounds to hydroxyl-amino compounds must be carried out in a neutral medium, neither an alkali nor an acidic medium can be successfully used. Benzoic acid itself is a stronger acid than acetic acid



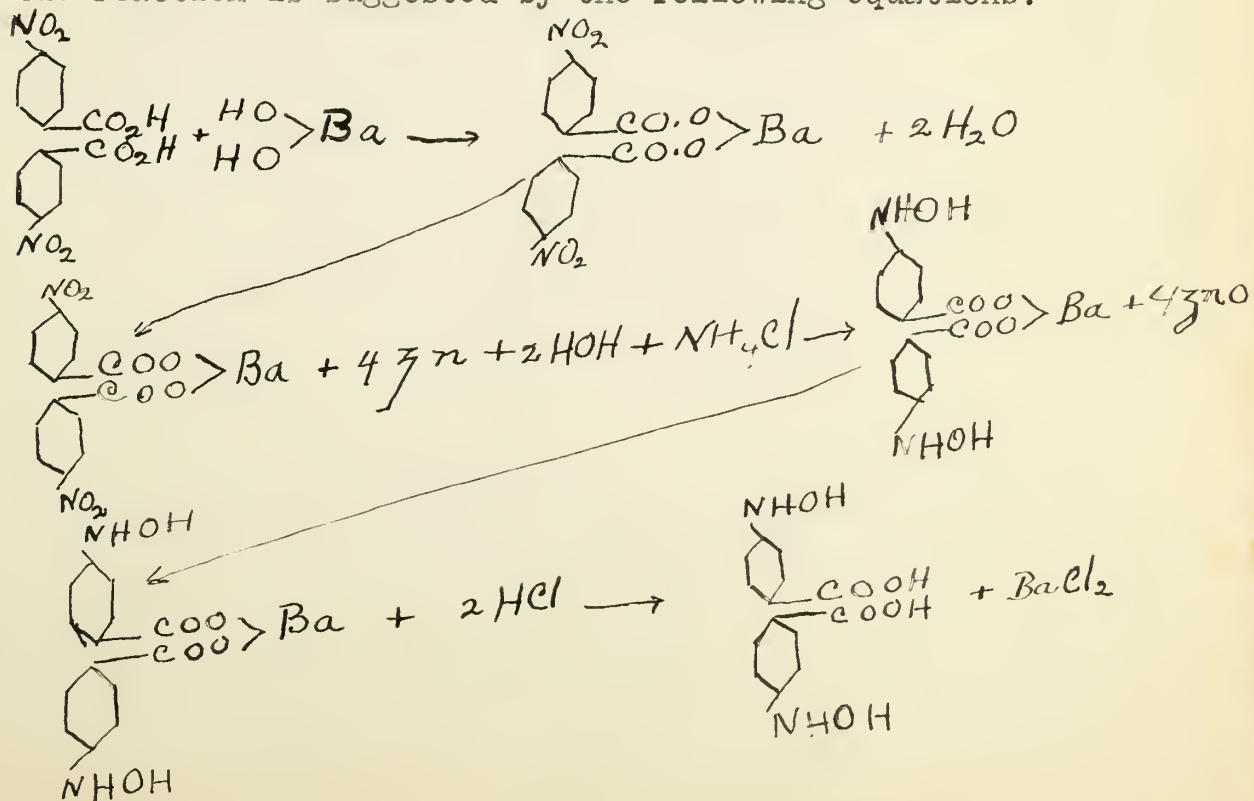
Which shows that the benzoic acid is 3 1/3 times as strong as acetic acid, from a stand point of ionization. The introduction of a nitro group into the benzoic acid molecule would have but little effect on the acidity of the benzoic acid, increasing it slightly, so it could not be reduced by the method

¹³ Ber. 1909, Protokoll der sitz.Vom.14 Jun seite 2183.
¹⁴ Norris- "Principles of Organic Chemistry" 490.



applied in the reduction of mono - nitrobenzene. This suggested the thought that the acidity caused by the carboxyl group would have to be eliminated before the reduction of the compound could take place. The acidity was eliminated by the conversion of the p-nitrobenzoic acid into its neutral barium salt containing the original nitro group which under the conditions of the experiment could readily be reduced to p-hydroxylaminobenzoic acid (some times called p-carboxyphenylhydroxylamine).

Accordingly 16.70 grams (0.10 mole) of chemically pure p-nitrobenzoic acid was dissolved in 100 cc. of boiling water and the resulting solution neutralized with 15.70 grams (0.10 mole) of chemically pure barium hydroxide. Thus the acid was converted into barium-p-nitrobenzoate, a neutral compound. The probable course of the reaction is suggested by the following equations:





The solution of the barium-p-nitrobenzoate was cooled to 10°C., and to it was added 7.50 grams of pure ammonium chloride¹⁶. The mixture was mechanically stirred for fifteen minutes. This caused uniform mixing of the barium salt and the ammonium chloride. During the following thirty minutes 15 grams of zinc dust, 99.30 per cent pure, was added to the vigorously stirred mixture in small lots of about two or three grams.

The container of the reactants was kept cool by means of an ice bath. The temperature was carefully

¹⁶Berichte, Band II, Nr. 7, Jun 14, 1909, 2306-2307.



maintained at 10-12 degrees C., and at no time during the entire reaction did the temperature rise as high as 15 degrees C. The admission of air was prevented by the use of a three-neck 500 cc. bottle. The three necks accommodated a thermometer, the shaft of the stirrer and provided a ready means of introducing the zinc dust. After the last portion of zinc dust was added the temperature rose to 12 degrees C. The stirring was continued for one hour after this. Finally the ice bath was removed and the stirring continued for 10 minutes. The temperature remained constant, indicating the completion of the reaction.

The product, barium-p-hydroxylaminobenzoate or barium-p-carboxyphenylhydroxylamine, was quickly filtered by suction and protected from direct light. Residue was washed with a little water until a sample of the wash water tested with Fehling's Reagent failed to give a positive test.¹⁷

The filtrate along with the wash water was poured into a large beaker containing 15 cc. of 25 per cent hydrochloric acid. The contents of the beaker were cooled by means of the usual ice bath and by means of small pieces of ice added directly to the contents of

¹⁷ The sample of wash water was treated with an aqueous solution of sodium bicarbonate, and filtered. The filtrate was treated with Fehling's Reagent, I and II. The Fehling's Reagent was not reduced.

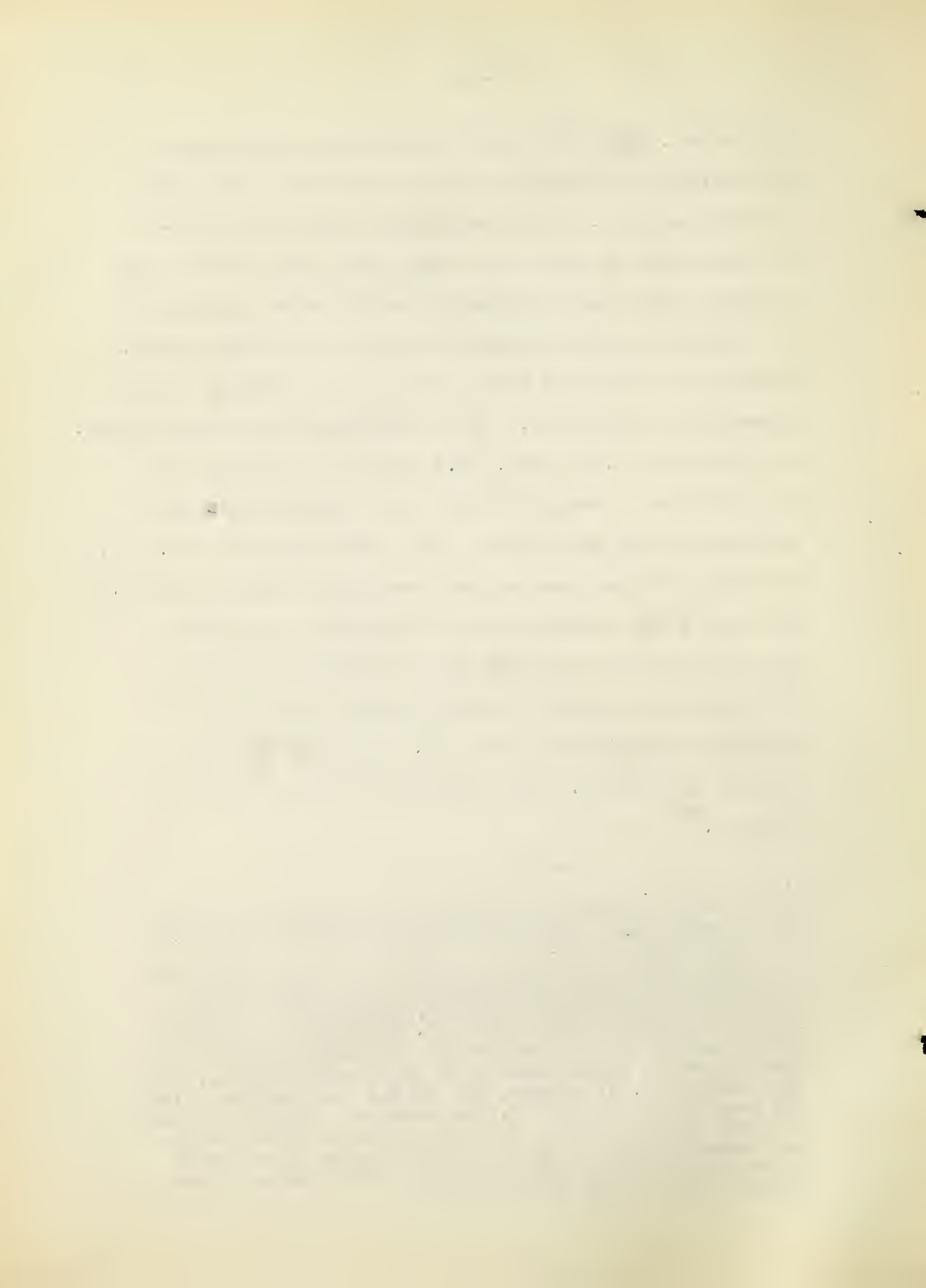
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the beaker. From the cooled solution the p-hydroxylaminobenzoic acid began to crystallize out in the form of white needles. The precipitated acid was protected from light by means of a towel and a clay plate. The crystals after being thoroughly washed were transferred to a clay plate and allowed to dry in a dark warm place. The crude product was crystallized from a mixture of hot alcohol and chloroform. It was recrystallized from benzine. The yield was 9.35 grams. 0.8 gram was extracted from the filtrate by means of ether and recrystallized from petroleum ether and ligroin. The total yield was 10.10 g. or exactly 66 per cent of the theoretical amount (15.3 g.). The zinc oxide residue was also extracted with ether and the yellowish compound when re-crystallized from the alcohol-chloroform mixture and from petroleum and benzine, increased the yield 14.1 grams or 91.61 per cent of the theory. This compound melted at 255 degrees C.¹⁸

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The p-hydroxylaminobenzoic acid as prepared and purified above demonstrated some peculiarities which seem worthy of mentioning.

The compound showed no signs of melting until the temperature reached 185 degrees C. It appeared as though it would soften a little, but as the temperature rose beyond 185 degrees C. the tendency to melt disappeared. At 250 degrees C. It acquired a sort of grayish color accompanied with signs of softening. At 255 degrees C. it melted, but as the temperature quickly rose to 257 degrees C. the compound resolidified and did not re-melt. Above 300 degrees C. it showed signs of decomposition. A portion of it placed in a closed tube (one end) and heated in the direct bunsen flame, melted into a dark brown liquid.



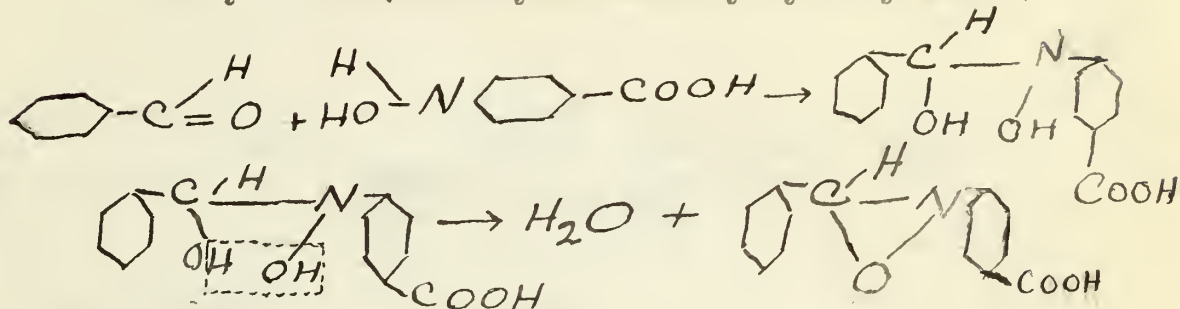
p-Carboxyphenylhydroxylamine or p-Hydroxylaminobenzoic acid like N-Phenylhydroxylamine reduces both Fehling's Reagent and an ammoniacal solution of silver oxide. The finely divided substance is very irritating to the mucous membrane of the throat and nose. When inhaled it causes violent sneezing and nose blowing. It is also irritating to the skin. It crystallizes in plates. It is more soluble in hot water than it is in ligroin, benzine, and the like. It can be crystallized from hot water by rapid cooling with ice and salt, but the presence of water and air tend to convert it into the azoxy form. This tendency is not so great when the substance is crystallized from an organic solvent.

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The Preparation of the Benzaldehyde
Derivative

Benzylidene-(N-Phenyl-4-carboxy-hydroxylamine)



The derivative crystallized from alcohol melts at 115 degrees C. When recrystallized from glacial acetic acid and thoroughly dried on a porous plate it melts at 117 degrees C.

It is a light yellow compound insoluble in water and not affected at all by dilute acids and alkalies, but is readily dissolved by cold concentrated sulphuric acid. Like Benzylidene-N-Phenylhydroxylamine it forms a greenish yellow solution when dissolved in cold concentrated sulphuric acid.

Estimation of Nitrogen¹⁹.

Nitrogen (N)

Found	Calculated from C ₁₄ H ₁₁ O ₃ N
5.768%	5.78%

¹⁹ The Kjeldahl Method was used in the determination of Nitrogen throughout the entire work of this paper.

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


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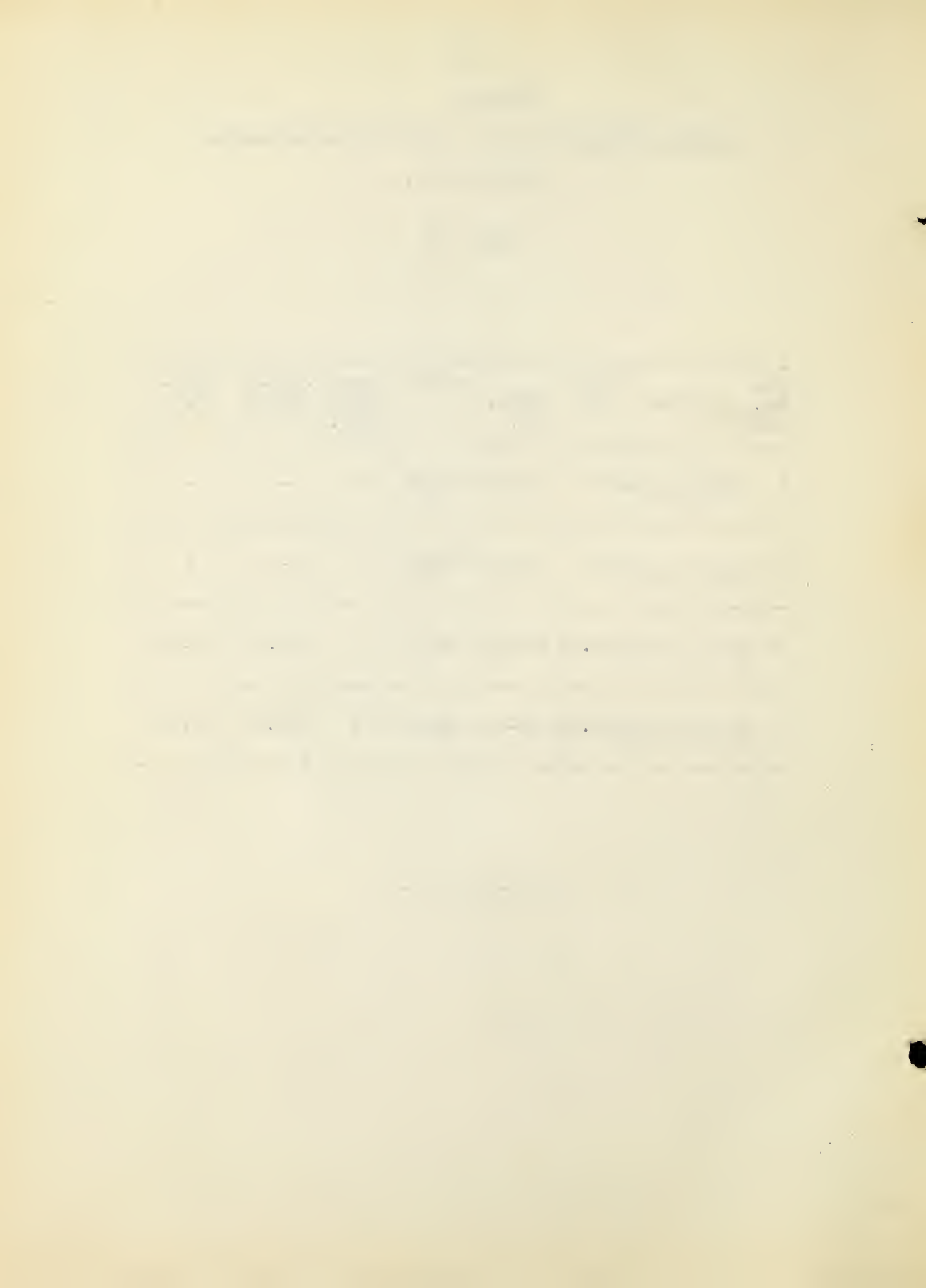
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Summary

Results obtained under different experimental
Conditions.

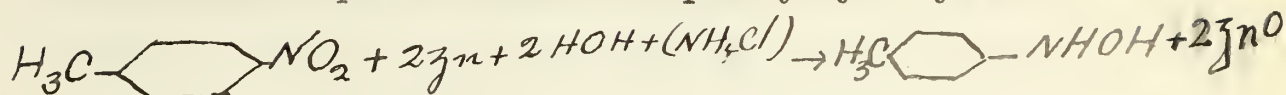
Table II

Run No.	Sub'nce	Am't g.	Temp. C.	Cat'st	React. Time hrs.	Lab. Yield	Theo. P.C.
1	O_2N  $COOH$	25	22-23	NH_4Cl	1	-	-
2	O_2N  $COOH$	25	65-70	NH_4Cl	1	-	-
3	$(O_2N$  $COO)_2Ba$	22.97	22-23	NH_4Cl	1	12.5	81.22
4	$(O_2N$  $COO)_2Ba$	22.97	22-23	NH_4Cl	1	14.1	91.61



Experimental Part

3. Reduction of p-Nitrotoluene to p-Tolylhydroxylamine.

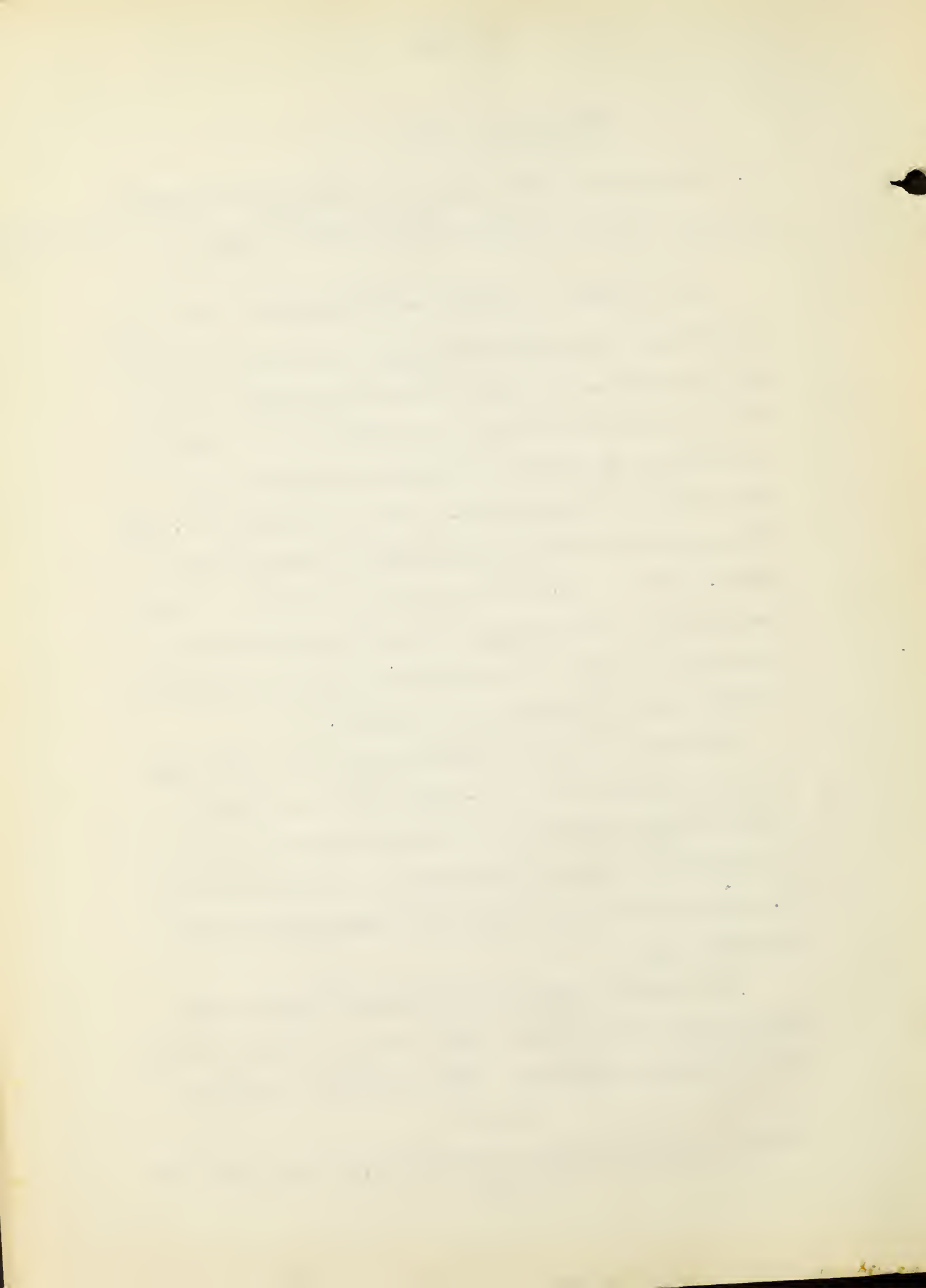


All attempts to reduce p-Nitrotoluene to the corresponding hydroxylamino compound resulted in unsatisfactory yields. 25 grams of the nitrotoluene treated with the calculated amount of zinc dust and ammonium chloride in the presence of water gave only a six gram yield at 20 degrees C., and at 45 degrees C. the same quantity of the compound gave the same yield- 6 grams. This was 22.72 per cent of the theory. Qualitative tests with Fehling's Reagent and an ammoniacal solution of silver oxide indicated that the reduction-product was an hydroxylamino compound.

The experiment was tried a third time, this time the same quantity of the p- nitrotoluene was used with the same quantities of the zinc dust and ammonium chloride, but at 71-72 degrees C. The yield was 9.5 grams or 42.6 per cent of the theoretical amount. See Table III.

The records show that Gattermann²⁰ reduced this compound by means of zinc dust and dry calcium chloride in an alcoholic solution. This method was tried for

²⁰Ber. der deut. chem. Ges. Jahrgang, 28, B.I. Feb. 1895
Page 1221



the sake of comparison as well as for the hope of obtaining a better yield of the tolylhydroxylamine. The experiment was carried out as follows:

39 grams of the p- nitrotoluene was dissolved in 105 cc. of boiling alcohol to which had been previously added 60 grams of water. To this alcoholic solution of the compound 3.75 grams of dry calcium chloride was added. The mixture was then heated to the boiling point of the alcohol and without any further outside heating 50 grams of the almost pure zinc dust (99.30%) was added. The remaining details of the experiment are the same as already described in previous experiments on this subject. The yield in this case was 14.0 grams or 40 per cent of the theory.

The compound was recrystallized from hot ligroin. The purest crystals prepared melted at 91-92 degrees C. The melting point of p-tolyhydroxylamine as recorded in the literature is 92-93 degrees C. It gave conclusive tests with both Fehling's Reagent and an ammoniacal solution of silver oxide as to its hydroxylamino character, indicating that the p-nitrotoluene had undergone reduction. The quantitative estimation of nitrogen, the record of which is tabulated below, gave results that are fairly close to that required

by the theory.

Nitrogen (N)	
Found ²¹	Calculated from formula
11.29%	11.36%
	(C ₇ H ₉ ON)

It was observed that when p-tolyhydroxylamine was purified by water crystallization, unless one is very careful to remove the last trace of moisture, it turns yellow quickly. When crystallized from hot ligroin, it does not show this tendency so quickly. In both cases the carefully purified compound melts at the same temperature. Water is much more convenient to use, but it requires more careful attention, and the product does not keep as well as it does when it is purified from ligroin. The latter process is more wasteful than the former. Whether p-tolyhydroxylamine is prepared in a water medium or in an alcoholic one, the melting point is

²¹The Kjeldahl Method was employed for the estimation of nitrogen in the p-Tolyhydroxylamine. The method was modified so as to meet the requirements of hydroxylamino compounds.

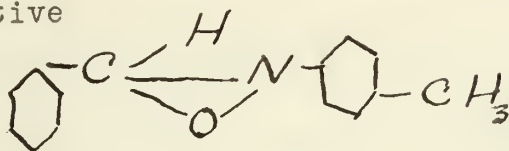


the same. The melting point depends directly upon the purity of the compound and not at all upon the process by which it was manufactured.

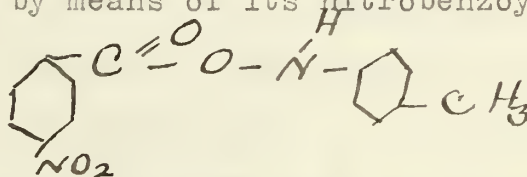
The chemical properties of p- tolylhydroxylamine are essentially the same as already seen in the cases of hydroxylamino compounds already described in these pages. Physically they differ in melting point, solubility and crystal form. The last point is relatively unimportant. When crystallized from benzene it appears colorless and leaf-like in form. When crystallized from water it appears as a mass of creamy white scales, very thin and soft. Like most, if not all, hydroxylamino compounds, it has an irritating effect upon the mucous membrane of the nasal and throat passages. It is very soluble in ether and in alcohol, while it is only difficulty soluble in gasoline, ligroin, benzene and hot water. Like N-Phenylhydroxylamine it readily reacts with benzaldehyde, forming a benzylidene compound. It is by means of the formation of this benzylidene-compound that the hydroxylamino compound is best identified.

Preparation of Derivatives.

The Benzaldehyde derivative. The identification of the newly formed compound was checked through its benzaldehyde derivative



and confirmed by means of its nitrobenzoyl derivative



The melting point of the benzaldehyde derivative-Benzylidene-p-tolylhydroxylamine, was 118 degrees C. when crystallized from alcohol, but when carefully recrystallized from glacial acetic acid and thoroughly dried, it melted at 122 degrees C.

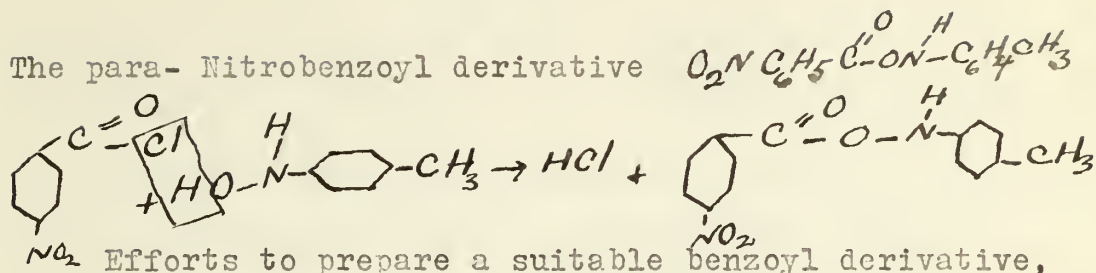
The quantitative estimation of nitrogen gave the following results:

Nitrogen (N)

Found	Calculated from formula
6.16%	6.02%
(formula, C ₁₄ H ₁₃ ON)	



Preparation of Derivatives.
(continued)



using benzoyl chloride, were unsuccessful. The product in each case was an oily substance which resisted all efforts to crystallize it. This behavior suggested the thought that the derivative thus formed was of low melting point. This thought further suggested the use of p- nitrobenzoyl chloride. The use of this particular compound being based on the assumption that since the nitro compound is a solid to begin with, with a fairly high melting point, the desired nitro derivative should be a solid with a melting point high enough to be of use in the identification of p- tolylhydroxylamine.

Preparation.

One gram of p- tolylhydroxylamine was dissolved in 10 cc. of a 1:1 mixture of crystallized sodium acetate and glacial acetic acid. To this was added 1.1 molar equivalent of p-nitrobenzoyl chloride and the mixture well shaken. The yellow crystalline substance



separated out from the mother liquid. It was filtered out and dissolved in 95 per cent alcohol and reprecipitated by means of water. It was washed with distilled water to which 1 cc. of alcohol was added. The purified crystalline product was dried on a filter by suction, and then on a water bath. Finally it was transferred to a desiccator and allowed to stand over concentrated sulphuric acid until it gave a constant melting point. It melted at 210-215 degrees C. This was in close agreement with the literature.


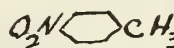



These observations led to the conclusion that the p- nitrotoluene had been reduced to p- tolylhydroxylamine.

Summary

Reduction of p-Nitrotoluene to p-Tolyhydroxylamine.

As in the case of the reduction of mono-nitrobenzene which has already been described, further studies in the reduction of p-nitrotoluene were carried out. These studies, for the most part, involved the variation of temperature and catalyst. The other factors were kept constant. The general effect of these variations upon the reduction of the nitrotoluene is recorded below

Table III

Run No.	Sub'nce	Am't g.	Temp. C.	Cat'st	React. Time Min.	Lab. Yield g.	Theo. P.C.
1		25	20	NH ₄ Cl	60	6	22.72
2		25	45	NH ₄ Cl	60	6	22.72
3		39	70	CaCl ₂	60	13.0	37.42
4		25	72	NH ₄ Cl	60	9.5	22 42.60
5		39	70	NH ₄ Cl CaCl ₂	60	14.0	23 40.00

Continued on the next page

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²³See foot note on next page.

Run No.	Sub'nce	Am't g.	Temp. C.	Cat'st	React. Time Min.	Lab. Yield	Theo. P.C.
6	<chem>O=[N+]([O-])c1ccc(C)cc1</chem>	25	0	NH ₄ Cl	60	0	0
7	<chem>O=[N+]([O-])c1ccc(C)cc1</chem>	25	23	NH ₄ Cl	60	0	0
8	<chem>O=[N+]([O-])c1ccc(C)cc1</chem>	25	65	NH ₄ Cl	60	7.5	33.20

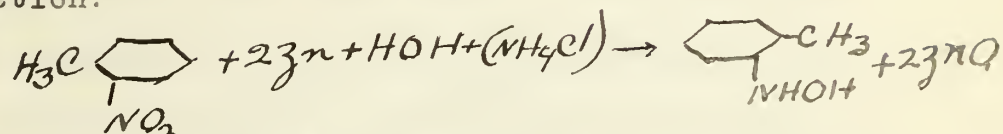
²² In this reaction the p-nitrotoluene was mixed with water and ammonium chloride used as catalyst. The amount of p-nitrotoluene used in the reaction was 25 grams instead of the 39 grams used in run number 5.

²³ In this reaction the p-nitrotoluene was dissolved in alcohol and calcium chloride employed as catalyst. A minute quantity of ammonium chloride added.

C. Experimental Part

4. Attempted Reduction of ortho- Nitrotoluene
to ortho- Tolyhydroxylamine.

Reaction:



The zinc dust-water-ammonium chloride method used in the reduction of p- nitrotoluene utterly failed to reduce o- nitrotoluene. The application of the method was the same in both cases. On one occasion the mixture of ammonium chloride solution and the o- nitrotoluene were emulsified and with the temperature at 45 degrees C., the calculated amount of zinc dust was added to the vigorously agitated mixture. The stirring lasted 6 hours. The mixture was filtered and the residue, which showed every appearance of being unchanged zinc dust, was thoroughly washed in the regular manner and the wash water combined with the filtrate. Common salt and ice were added directly to the filtrate. The beaker containing same was placed in a crock containing a freezing mixture of ice and salt. After standing an hour or so at 0 degrees C. it was observed that no crystals of o- tolyl-

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PHYSICS 439: QUANTUM MECHANICS
LECTURE 10: PERTURBATION THEORY
PROFESSOR JOHN COLLINS

DATE: [illegible]

TOPIC: [illegible]

OBJECTIVES: [illegible]

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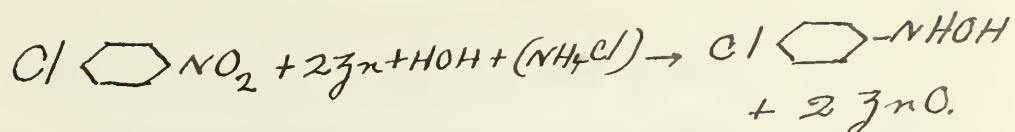
100. [illegible]

hydroxylamine separated out. Five cc. of the solution was treated with five cc. of Fehling's Reagent (I and II) and warmed. The result was negative. The effect of ammoniacal silver oxide solution was tried. The result in this case was also negative. This led to the conclusion that no reduction of the o-nitrotoluene had taken place. The reduction was then tried at room temperature and also at the optimum temperature (65-70 degrees C.). No evidence of hydroxylamine formation could be detected by either Fehling's Reagent or an ammoniacal solution of silver oxide. From these observations, it was concluded that the method of reduction used and described in these pages is not at all effectual in the reduction of o-nitrotoluene to o-tolylhydroxylamine.

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C. Experimental Part

5- Reduction of p- Chloronitrobenzene to
p- Chlorophenylhydroxylamine



Although test with silver nitrate in ammonium hydroxide solution indicated that some reduction of the nitro compound had taken place, the three or four grams of the reduction product obtained failed to give satisfactory results with Fehling's Reagent. Repeated attempts to reduce p-chloronitrobenzene by means of zinc dust and water in the presence of ammonium chloride failed to yield satisfactory results. The method was modified by dissolving the substance in 95 per cent ethyl alcohol and then slowly adding water until one drop of water caused a reprecipitation of the p- chloronitrobenzene. All attempts to reduce this compound in this condition met with failure. Finally the calculated amount of p-chloronitrobenzene (0.10 mole) 15.75 grams, was dissolved in 210 cc. of boiling ethyl alcohol. To this solution was added 3.5 grams of anhydrous calcium chloride and one gram of iron powder. To this mixture the calculated amount of zinc dust (13 g.) plus 15 per cent excess (1.95 g.) was slowly added in

portions of three or four grams. When the temperature had fallen to 50 degrees C. 5 grams of ammonium chloride and 100 cc. of hot water were added. The stirring was continued for two hours. At this time the temperature had fallen to about 20-23 degrees C. The crude product was extracted with ether and later re-crystallized from a mixture of gasoline and petroleum ether, (1:1). The crystallization was repeated three times. The product when protected from light and sucked dry on a filter, melted at 86-87 degrees C. The melting point as recorded in the literature is 87-88 degrees C. (uncorrected).

The yield realized from the 15.75 grams of the p- chloronitrobenzene was 4 grams or 22 per cent of the theoretical amount.

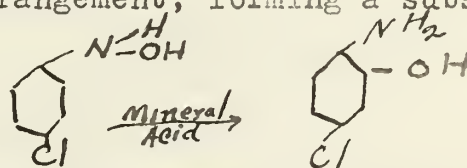
There is no record in the literature showing that this compound (p-Chlorophenylhydroxylamine) has ever been prepared by the reduction the nitro compound by means of zinc dust and water. It has been prepared many times or perhaps it is more correctly stated that it is referred to quite a few times in difference places²⁴. But each reference where the preparation of p- Chlorophenylhydroxylamine is concerned, deals with its preparation by electrolytic reduction. The purest sample that was pre-

²⁴Ber. 29(1896), 864; 32, 217; 33, 272; 38, 3078.
C. 1905(2)1243; Ber. 42, 3581,
C. 1909(2) 1850-*II 728

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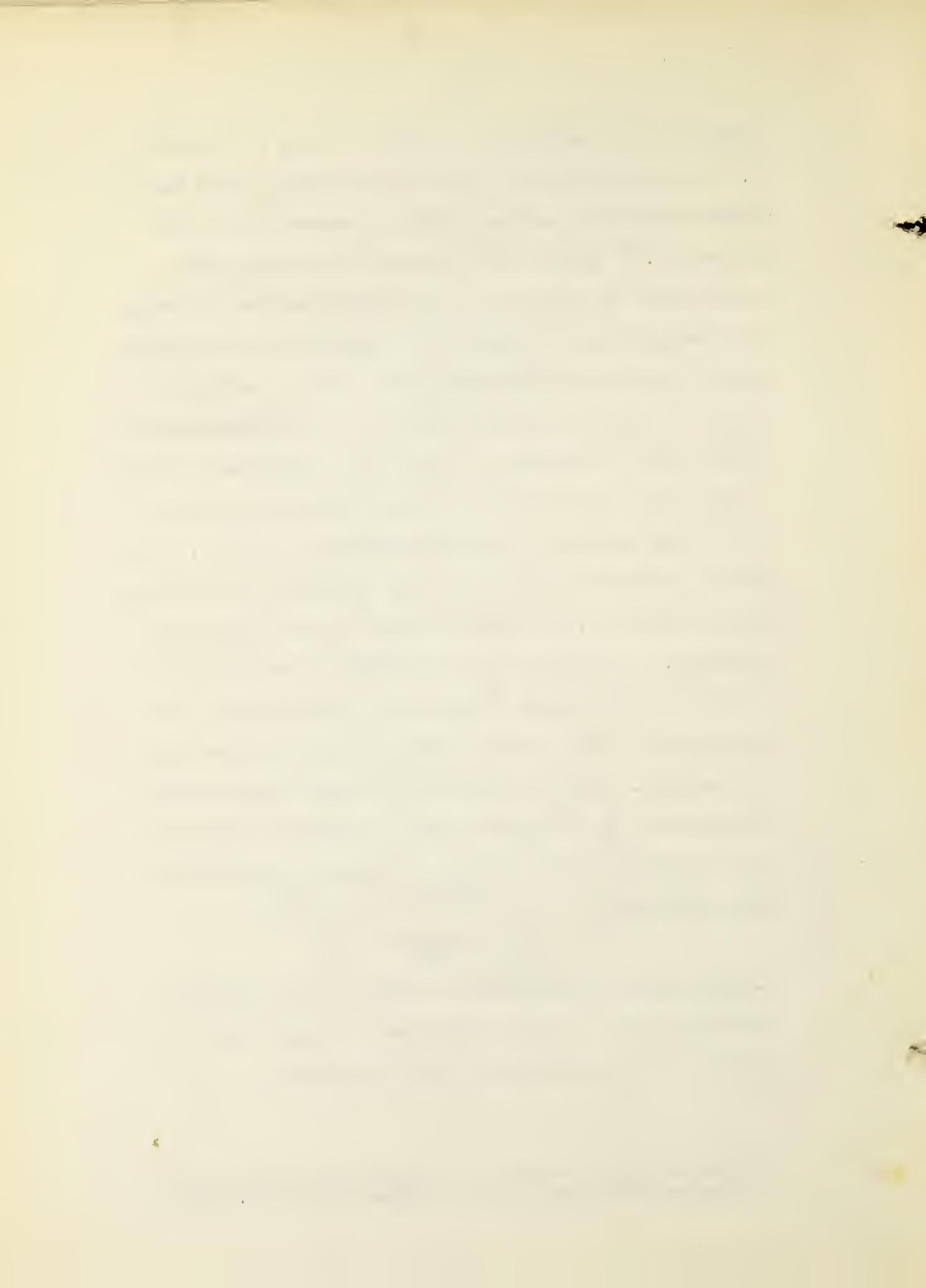
pared in this work melted between 86 and 87 degrees C. According to the literature, melting points have been reported by various authors between 86 and 88 degrees C.²⁵ Since the compound is so well known there seems to be no need for identification by means of a benzaldehyde derivative. Concerning the properties of the compound there is not much to write, it might be cited in passing that it is a lustrous glossy white solid, insoluble in cold water, somewhat soluble in hot water, from which it crystallizes when cooled. It is very soluble in both alcohol and in ether. It is quite insoluble in cold ligroin, gasoline and petroleum ether (benzine). It crystallizes in plates from hot gasoline. It readily reduces Fehling's Reagent and reduces an ammoniacal solution of silver oxide. In the case of both reagents reduction takes place even in the cold. In the presence of either concentrated hydrochloric or sulphuric acid it immediately undergoes molecular rearrangement, forming a substituted

para aminophenol



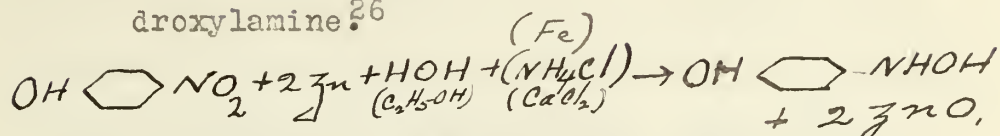
p- Chlorophenylhydroxylamine when purified by water crystallization is more sensitive to light than it is when it is crystallized from gasoline.

²⁵Richter- "Die Lexikon der Kohlenstoff Verbindungen"
4-Chlorophenylhydroxylamine, Schmelzpunkt 87.5(86).



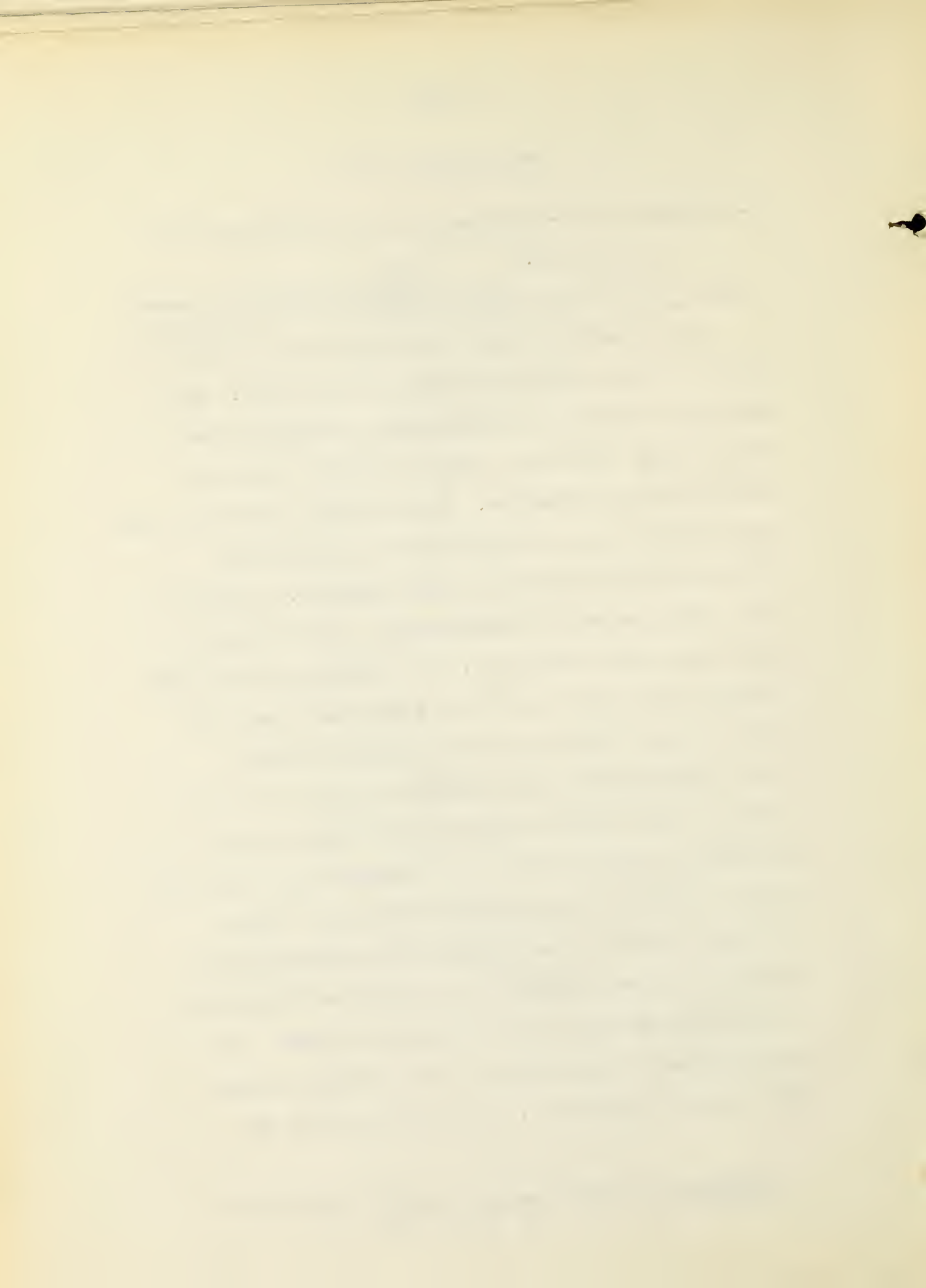
Experimental Part

6. Reduction of p-Nitrophenol to N-(4-oxyphenyl)-hydroxylamine²⁶



The reduction of p-nitrophenol marks the completion of the laboratory work of this paper. For more than a year this compound has stubbornly resisted every effort put forth to reduce it to an hydroxylamino derivative. In the early days of the experimentation the straight method of zinc dust, ammonium chloride and water was employed. The process always ended in no-reduction. Later alcohol was tried along with water. The result was the same. Knowing that phenol itself is acidic and that the presence of a NO₂ group in the phenol molecule would tend increase the acidity, it was my plan to "protect" the readily oxidizable OH group by converting the compound into a nitrophenate and then by means of zinc dust and ammonium chloride, reduce the nitro group in the phenate to an hydroxylamino group and by the removal of the metallic constituent restore the OH group in the benzene nucleus. The reaction was carried out at a temperature ranging from 50 to 65 degrees C. The reaction time was

²⁶ Stelzner- "Literatur-Register der Organische Chemie" 1916, 1917 and 1918, p 337

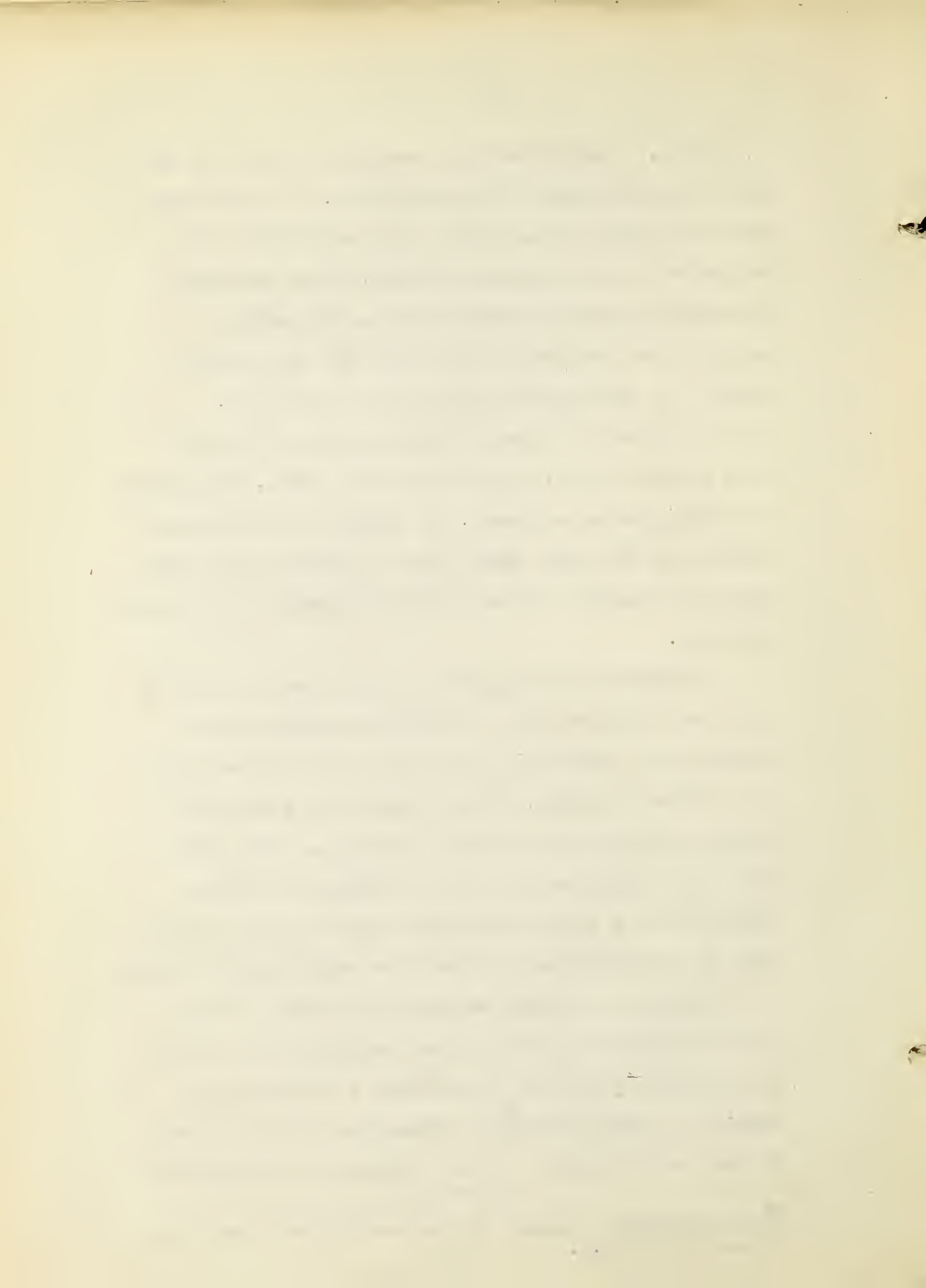


1.5 hours. The filtrate was cooled as usual and CO_2 gas was passed into it to saturation. The filtrate from the BaCO_3 was saturated with salt (NaCl) and subjected to the freezing process. No p-hydroxy-phenylhydroxylamine separated out. The saline solution was extracted with ether and the latter removed by distillation from a hot water bath. No hydroxylamino compound separated out. The zinc dust residue was also extracted with ether. It yielded no hydroxylamino compound. A sample of the solution containing the solid BaCO_3 gave a positive test with Fehling's Reagent but not with ammoniacal silver oxide solution.

A reserved portion of the dark brown filtrate which was obtained when the barium carbonate was removed, was extracted with ether in the presence of dry calcium chloride. It was allowed to stand from Friday afternoon until Monday morning. When the ether was distilled off from the lumps of calcium chloride and a little warm water added to the residue left in the bottle an intense blue solution was formed.

Finally an attempt was made to reduce the compound by means of zinc dust and calcium chloride in an alcoholic solution. Accordingly the calculated amount of p-nitrophenol²⁷ was dissolved in 300 cc. of 95 per cent alcohol. To this alcoholic solution of

²⁷ The calculated amount of the p-nitrophenol was 0.1 mole (13.90 g.).



p-nitrophenol a mixture of 3.5 grams of anhydrous calcium chloride and 2 grams of powdered iron was added. To the vigorously stirred mixture which was heated to 60 degrees C. by means of a steam generator, was added the calculated amount of zinc dust²⁸ in small portions. The addition of the zinc dust caused the formation of a dark brown mixture. With the addition of the zinc there was also a marked rise in the temperature. It rose as high as 65 degrees C. To this hot mixture which was rapidly stirred mechanically, was added 5 grams of ammonium chloride. The dark coloration was instantly bleached, the mixture taking on a whitish-yellow appearance. Evolution of ammonia was noticed. The filtrate from the zinc oxide residue turned slightly brown on cooling. This time the freezing process threw down a white feathery precipitate which crystallized in long glistening needles. These crystals were insoluble in ligroin and in gasoline but dissolved readily in hot water. The quantity obtained was too small to weigh and determine the per cent of yield. These crystals were mixed with a dark brown substance. All attempts to isolate the shiny crystals that gave positivetest with both Fehling's Reagent and an ammoniacal solution of silver oxide were futile. There

²⁸ The calculated amount of zinc dust was 13 grams, a small excess (15%) was used, making the quantity used about 15 grams.

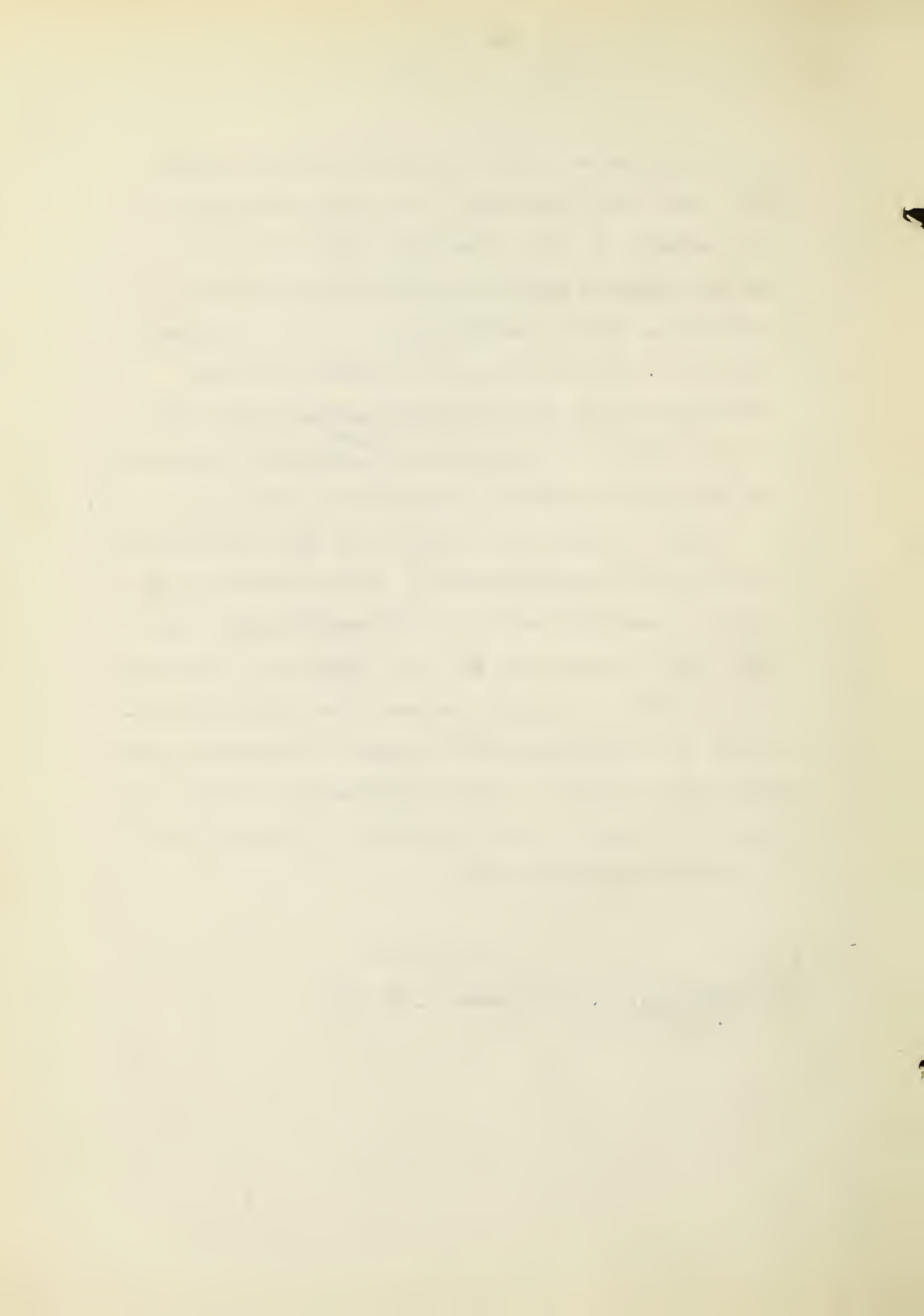


is no question as to the possibility of the reduction. The great difficulty lies in the isolation of the compound, so that a melting point can be made and the compound checked by means of a suitable derivative, such as benzaldehyde or the nitrobenzoyl derivative. The few crystals collected for the qualitative tests were separated mechanically from the brown substance in which they ^{were} scattered throughout the bulk, giving scintillating effect to the whole mass.

There is only one reference to the preparation of N-(4-Oxy-phenyl)-hydroxylamine by the reduction of the nitro compound and that reference²⁹ points out that that work was done in 1917. While I do not know it to be true, I strongly suspect that the method employed was the electrolytic process. It was not possible then (during the time the laboratory study was being made) and it is not possible now for me to get the Berichte of that year.

29

Berichte., E., Nitrosier B.50, 330
C. 1917 I 756



General Summary and Conclusion.

Basing the ease of reduction of nitro- compounds of the aromatic type upon the quantitative yield of reduction products, the laboratory observations as recorded in these pages lead to the general conclusion that in the case of zinc dust and ammonium chloride in the presence of water or alcohol, the compounds studied, with few exceptions, are more readily reduced at higher temperatures than at lower ones. This conclusion seems to be true in the case of four of the six compounds studied. One of the compounds failed to reduce at both low and high temperatures. This compound was ortho-nitrotoluene. Para- nitrobenzoic acid exhibited a similar behavior. But in considering the reduction of this compound, it is here emphasized that while the acid itself cannot be reduced by the zinc dust-water method at either high or low temperatures, its barium salt is more easily reduced than any other nitro- compound thus studied. This is shown in the accompanying chart (Table IV). Para- nitrobariumbenzoate is reduced by the method in question only at low temperatures. Vide Table IV.

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It is also observed that nitro-benzene and p-nitro-toluene are more readily reduced by the zinc dust-water method than are p-chloronitrobenzene and p-nitrophenol. Laboratory evidence, while not quantitative in scope, points definitely to the conclusion that in the case of p-nitrophenol, some reduction has been effected. This conclusion is based on the fact that a minute amount (not enough to weigh) of flat shiny crystals resembling p-tolylhydroxylamine, was found mixed in with a large quantity of dark brown material. These crystals were isolated mechanically and studied. It was observed that they readily reduced both Fehling's Reagent and an ammoniacal solution of silver oxide. This behavior strongly suggests the presence of an hydroxylamino compound. This apparent presence of such a compound, under the conditions of the experiment, points definitely to the conclusion that some reduction of the original nitro compound has been effected. It may also be pointed out that the behavior referred to above in the case of p-nitrophenol, contrasted with that of both p-nitrobenzoic acid and o-nitrotoluene, where there was not even qualitative evidence of hydroxylamino formation, leads definite-

[The text on this page is extremely faint and illegible, appearing as a series of light grey lines and shapes against the off-white background. It seems to be a multi-paragraph document.]

ly to the conclusion that the method of reduction employed is more effectual with p- nitrophenol than it is with either p- nitrobenzoic acid or o- nitrotoluene. Going a step further, interpretation of this evidence seems to lead to the conclusion that in the case of p- nitrophenol, it is not so much a question as to the actual reduction of p- nitrophenol as it is a question of the successful isolation of the hydroxylamino compound formed in solution.

Comparing the efficacy of the method itself with that employed by Gattermann, laboratory evidence points out that in the case of the reduction of p- nitrotoluene to p- tolylhydroxylamine, the zinc dust-water-ammonium chloride method is about as efficient as his zinc dust-alcohol-calcium chloride method.

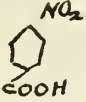
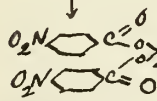
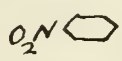
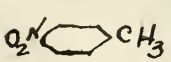
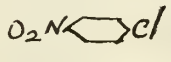
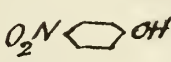
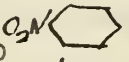
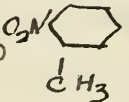
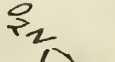
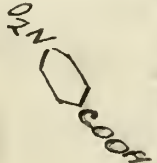
Observations lead definitely to the conclusion that a small quantity of powdered iron aids considerably in the reduction of some of the compounds. A mixture of ammonium chloride and calcium chloride appears to be more efficient than either one alone.

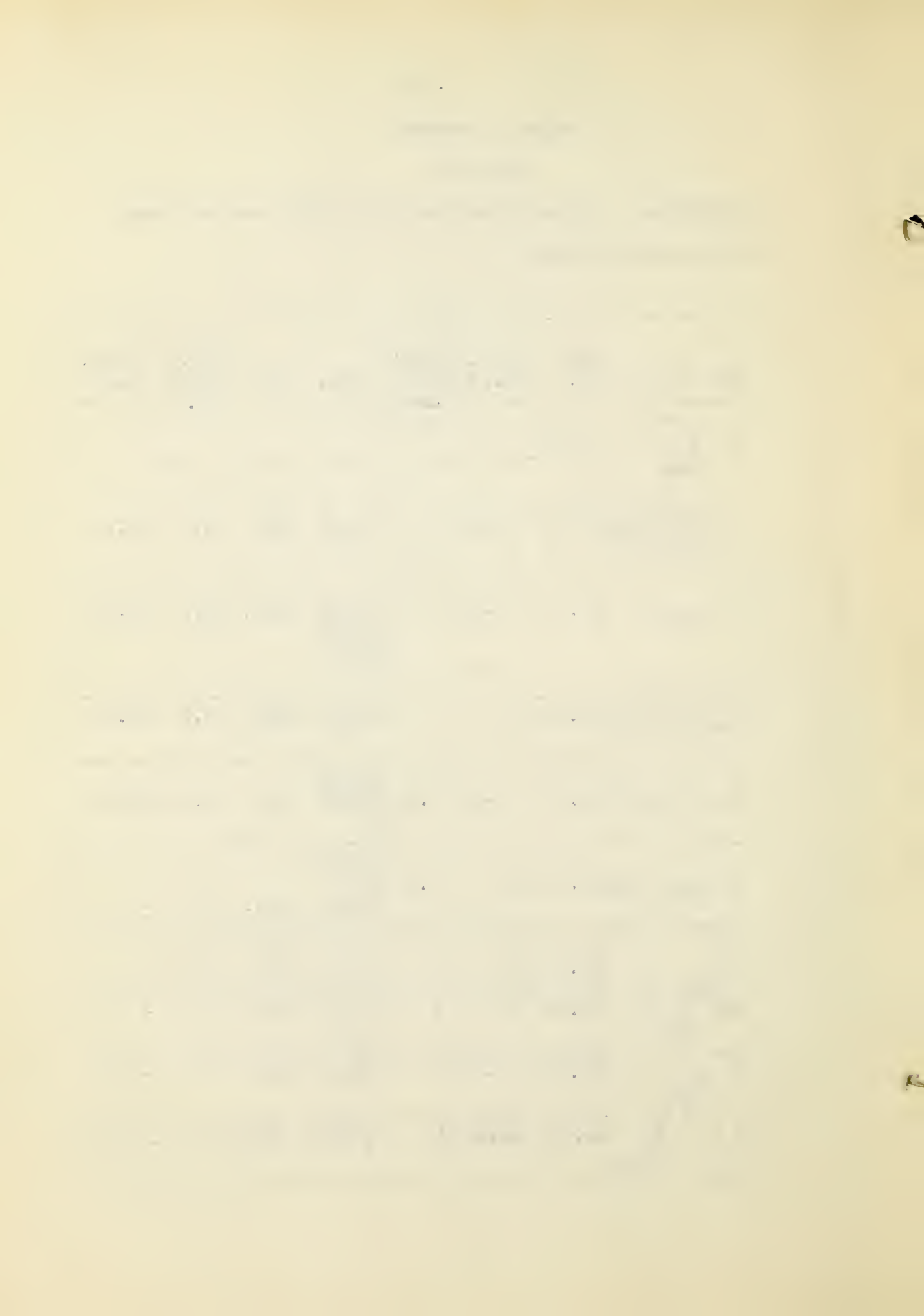


General Summary

Table IV

Conditions under which the best yield was obtained with each compound.

No	Sub'ce	Am't g.	Temp. C.	Reac'n Time hrs	Cat.	Med.	Lab. Yield g.	Theo. P.C.
1	 	16.70 22.97	10-12	1	NH ₄ Cl	HOH	14.1	91.61
2		25.00	71-72	1	CaCl ₂ NH ₄ Cl Fe	Alc.	18.5	83.46
3		25.00	72	1	NH ₄ Cl	HOH	9.5	42.60
4		15.75	78-80	2.5	CaCl ₂ NH ₄ Cl Fe	Alc.	4.0	22.00
5		13.90	65	1.5	NH ₄ Cl Fe CaCl ₂	Alc.	0	-
6a		25.00	20	6	NH ₄ Cl	HOH	0	-
6b		25.00	45	6	NH ₄ Cl	HOH	0	-
7		25.00	65-70	1	NH ₄ Cl	HOH	0	-
8		25.00	22-23	1	NH ₄ Cl	HOH	0	-



Chemical Literature

The following books and periodicals have been frequently consulted and all portions bearing upon the subject matter of this paper have been faithfully and painstakingly studied:

Books

- Schmidt- "Organic Chemistry"
Richter- "Organic Chemistry" (Volume 2)
Norris- "Principles of Organic Chemistry"
Perkin and Kipping-
 "Organic Chemistry"
Kamm- "Organic Chemistry"
Kamm- "Qualitative Organic Analysis"
Holleman- "A Text-Book of Organic Chemistry"
Reid- "Catalysis in Organic Chemistry"(Sabatier)
Reid- "Introduction to Organic Research" (Sabatier)
Mulliken- "Identification of Pure Organic Compounds"
Bernthsen- "Organic Chemistry"
Brockman- "Electro-Organic Chemistry"
Henrich- "Theories of Organic Chemistry"
Houben-Weyl-
 "Die Methoden der Organischen Chemie"
 (Zweiter Band)

Chemical Literature

Books

(Laboratory Manuals)

Gattermann- "Practical Methods of Organic Chemistry"

Lassar-Cohn- "Laboratory Methods of Organic Chemistry"

(Combustions)

Fischer- "Manual of Organic Chemistry"

Fisher- "Preparation of Organic Compounds"

Adams and Johnson-

"Laboratory Experiments in Organic
Chemistry"

Adams, Conant, Clarke, Marvel and Gilman-

"Organic Synthesis"

Periodicals

Journal of Industrial and Engineering Chemistry

119 (1920) (New York)

Journal of American Chemical Society,

41, (1919) 277 (Easton)

Berichte der deutschen chemischen,

Gesellschaft, (Berlin)

Chemical Literature

Chemisches Centralblatt, (Leipzig)

Comptes Rendus des Séances de l'Académie des Sciences
de Paris (Paris)

Zeitschrift für physikalische Chemie (Leipzig)

Richter- "Lexikon der Kohlenstoff Verbindungen"

The Critical Tables

Stelzner- "Literatur-Register der Organische Chemie"

In conclusion I wish here to express my thanks to Professor Dr. John Philip Mason, at whose suggestion and under whose careful help and guidance this work was carried out.

Boston University
Chemical Laboratory
(At the College of Liberal Arts)

May 28, 1931

William Henry James.

ADDENDA

The Hydrolysis of Ammonium Chloride.

In as much as ammonium chloride hydrolyzes in water yielding a solution which is slightly acidic, it was thought well worth the while to determine the pH value of the solution. This was done theoretically. The pH value thus determined was 4.05 which shows that while the solution is acidic, the acid content is not great enough to prevent the N-Phenylhydroxylamino formation when aryl- nitro compounds are reduced in the presence of ammonium chloride in solution.

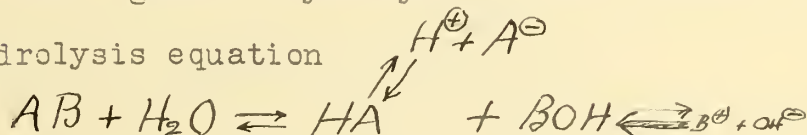
The Solution and the Zinc Dust.

An attempt was made to determine experimentally whether or not there was a sufficient quantity of acid present to react with the zinc dust. Several blank tests were made, using only the ammonium chloride solution and zinc. At first 12 grams of ammonium chloride dissolved in 400 cc. of distilled water was treated with 30 grams of zinc dust at room temperature, then at 65 degrees C. No evidence of hydrogen gas was detected. The test was then repeated, using this time only a small quantity of the zinc dust in a saturated solution of ammonium chloride in a test tube. The result was the same as in previous cases- there was no evidence of hydrogen being liberated. These experiments indicate that there is no more than a small amount of acid

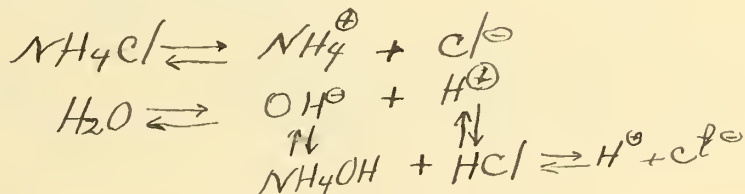
present. This result is in full agreement with the pH value of the solution. The calculation of the degree of hydrolysis of 12 grams of ammonium chloride in 400 cc. of distilled water and the determination of the hydrogen ion concentration may be seen below

-Calculation-

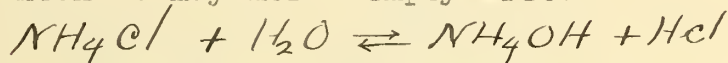
The degree of hydrolysis is calculated from the hydrolysis equation



Substituting NH_4Cl for AB, HCl for HA, and NH_4OH for BOH we get the expanded form



from which we may more simply write



The Ion Product Constant of water (K_w) at 65 degrees C.

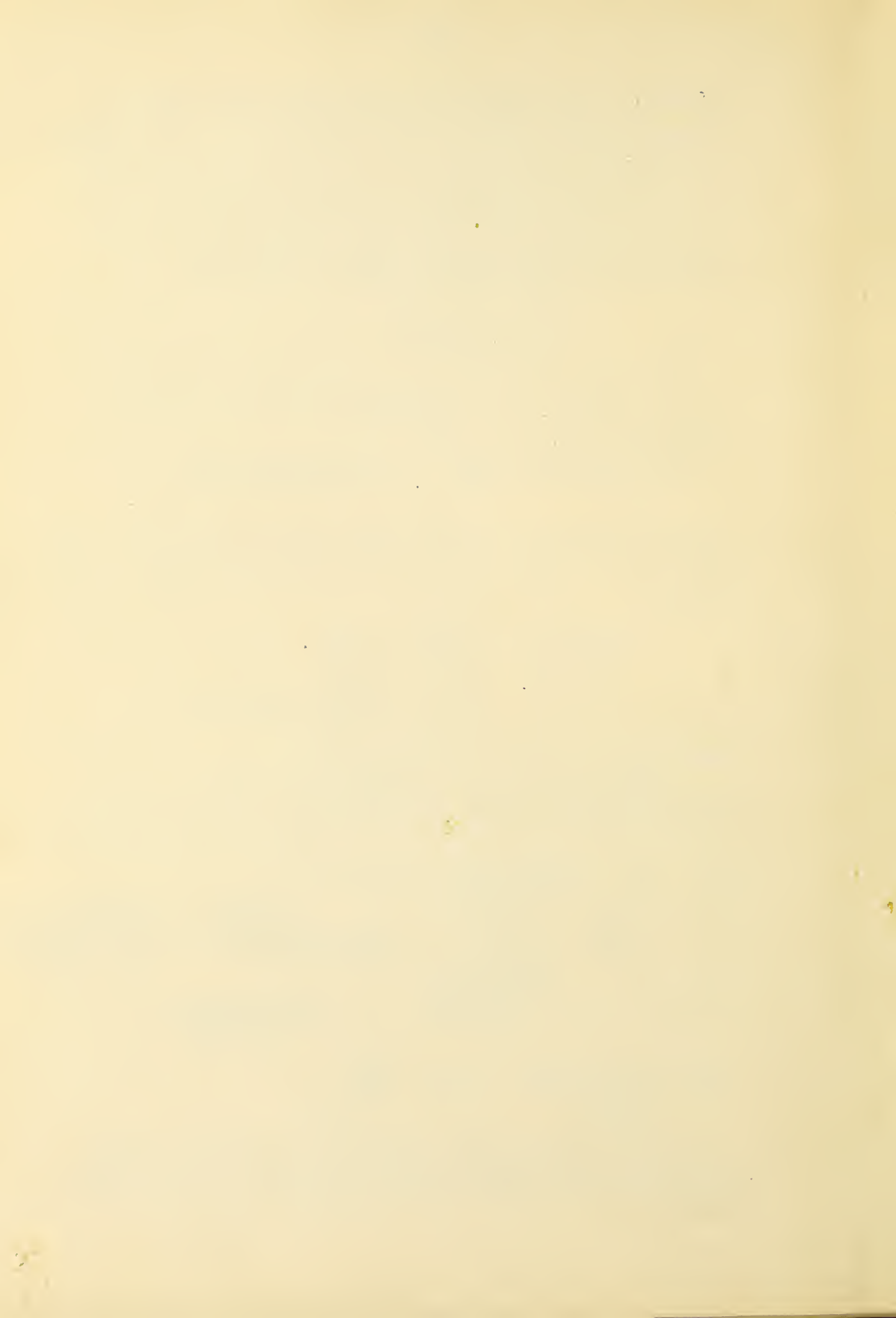
is $K_w = [H^{\oplus}][OH^{\ominus}] = 14.0 \times 10^{-14}$

$$\frac{K_w}{K_b} = \frac{(H^{\oplus})(OH^{\ominus})}{(NH_4^{\oplus})(OH^{\ominus})} = \frac{(H^{\oplus})(OH^{\ominus}) \times (NH_4OH)}{(NH_4^{\oplus})(OH^{\ominus})} = \frac{(H^{\oplus})(OH^{\ominus})(NH_4OH)}{(NH_4^{\oplus})(OH^{\ominus})}$$

$$= \frac{(H^{\oplus})(NH_4OH)}{(NH_4^{\oplus})}$$

and $\frac{(H^{\oplus})(NH_4OH)}{(NH_4^{\oplus})} = K_h = \frac{K_w}{K_b}$

If now we assume that the solution contains 1 gram-molecule of the ammonium chloride dissolved in V liters of solution, and representing portion of the salt hydro-



lyzed by h , and the fraction of the salt not hydrolyzed by $1-h$, the concentration of the hydrolyzed and not hydrolyzed portions can be represented by h/V and $1-h/V$ respectively, but in the expression

$$K_a = \frac{(H^{\oplus})(NH_4OH)}{(NH_4^{\oplus})}$$

H and NH_4OH alike are equal to h because we have assumed that the HCl is 100% dissociated and that the ammonium hydroxide is not dissociated at all. In the light of this, the expression may now be written

$$\frac{(hc)(hc)}{(1-h)} = K_a$$

$(1-h)c$ giving NH_4 from NH_4Cl only.

Dividing both sides of the equation by c , we get

$$c) \frac{(hc)(hc)}{(1-h)c} = \frac{h^2}{(1-h)} = \frac{K_a}{c}$$

however $\sqrt{1-h}$ in this connection may be considered as 1,

this gives $\sqrt{\frac{K_a}{c}} = \sqrt{\frac{K_w}{K_b c}}$ so that $h = \sqrt{\frac{K_w}{K_b c}}$

$$\text{but } \frac{K_w}{K_b NH_4OH} = \frac{(H^{\oplus})(NH_4OH)}{(NH_4^{\oplus})} \text{ and } K_a = \frac{K_w}{K_b} = \frac{14.0 \times 10^{-14}}{18.0 \times 10^{-6}}$$

$$\frac{(H^{\oplus})(NH_4OH)}{(NH_4^{\oplus})} = \frac{h^2}{(1-h)c}$$

$$\therefore \frac{h^2}{(1-h)c} = \left[\frac{K_w}{K_b} = \frac{(H^{\oplus})(NH_4OH)}{(NH_4^{\oplus})} \right] = \frac{14.0 \times 10^{-14}}{18.0 \times 10^{-6}}$$

$$\text{Whence } \frac{h^2}{(1-h)c} = \frac{14.0 \times 10^{-14}}{18.0 \times 10^{-6}}$$

But in terms of molality, c is equal to 12 g. of ammonium chloride per 400 cc. of distilled water, this is equivalent to 30 grams per liter. This expressed in moles 0.56 M. Rewriting the equation, we have

$$\frac{h^2}{(1-h) \times 0.56} = \frac{14.0 \times 10^{-14}}{18.0 \times 10^{-6}}$$

Solving for h in the expression

$$(h^2)(18.0 \times 10^{-6}) = [(1-h) \times 0.56](14.0 \times 10^{-14})$$

$$\text{where } h = 1.58 \times 10^{-4}$$



Determination of the pH value of the solution.

$$H^{\oplus} = hc$$

$$hc = (1.58 \times 10^{-4}) (0.56)$$

$$0.885 \times 10^{-4}$$

$$\text{or approximately } 0.00009, (9 \times 10^{-5})$$

$$pH = \log 1/H^{\oplus}$$

$$\text{but } 1/H^{\oplus} = 1/hc$$

$$\text{therefore } pH = \log 1/hc,$$

$$\text{as shown above } hc = 0.885 \times 10^{-4}$$

$$\text{or approximately } 9 \times 10^{-5}$$

$$\text{where } 1/hc = 1/9 \times 10^{-5}$$

$$\text{hence } pH = \log 1 - \log 9 \times 10^{-5}$$

$$\log 1 = 0.00000$$

$$= 1.00000$$

$$\log 0.00009 = \frac{.95920}{-5}$$

$$.04580$$

$$4.04580$$

$$\text{Hence the } pH = 4.05$$

This indicates that the hydrogen ion concentration of the solution is quite small, that the solution is only slightly acidic. In terms of its molality

$$H^{\oplus} = 1 \times 10^{-4.05} \text{ M.}$$

$$\text{hence } \log (H^{\oplus}) = -4.05 \text{ or } (H^{\oplus}) = 1 \times 10^{-4.05} \text{ M.}$$

The reduction of aryl-nitro compounds by means of zinc dust in an aqueous solution of ammonium chloride where the pH value is 4.05 is possible.



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