

-THESIS-

Part I. Action of Hydrogen Peroxide on Aromatic  
Compounds.

Part II. An attempt to prepare Di-para-di-amino-  
para-diphenylbenzene.

by

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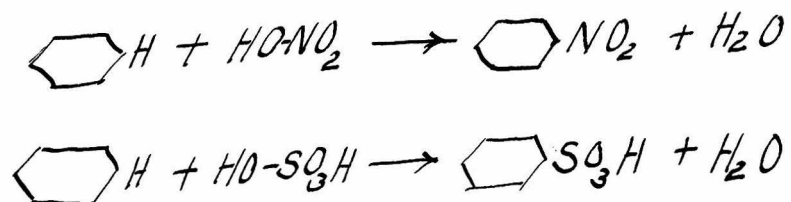
1918.

## PART I

### ACTION OF HYDROGEN PEROXIDE ON AROMATIC COMPOUNDS.

#### INTRODUCTION

The action of strong nitric acid and sulfuric acids upon aromatic hydrocarbons takes place as if the acids gave a hydroxyl group that reacted with the hydrogen of the ring to form water. In this way nitro and sulfonic groups are introduced into aromatic compounds. For example, we can write the reaction of nitric and sulfuric acids upon benzene as:



Baeyer and Villiger<sup>1</sup> in their work upon peroxides gave evidence to show that hydrogen peroxide reacts as if it contained two hydroxyl groups (i.e. HO-OH). If this is the case strong hydrogen peroxide might prove a ready means of introducing hydroxyl groups into aromatic compounds and as water is the other product the result should be rather pure products.

Leeds<sup>2</sup> has shown that when 1.2% hydrogen peroxide (2 mols) is heated with benzene in the presence of ferrous sulfate, phenol is one of the products formed. A maximum yield

1. Baeyer and Villiger, Ber. 34,738.
2. Ber. 14,975.

of 15% is recorded in this case.

Much work<sup>1</sup> has been done and many articles written on the oxidation of aliphatic compounds (especially sugars) by 2% or 3% hydrogen peroxide. The action of strong hydrogen peroxide upon the aromatic compounds is thought worthy of investigation and this paper is an attempt to prepare 100%<sup>2</sup> or nearly 100% hydrogen peroxide and to try its action upon aromatic compounds.

Much time was spent trying to concentrate the commercial 3% hydrogen peroxide without obtaining a satisfactory product. It was thought that the time which would be required to prepare 100% hydrogen peroxide would be so great that little else would be accomplished. In order to obtain more practice with a purely organic research it was decided not to attempt the preparation of the 100% hydrogen peroxide, but to take up the problem described in Part II of this thesis.

100% hydrogen peroxide is described by Wolffenstein<sup>3</sup> as anhydrous prismatic crystals (m.p. 2°C) having a b.p. of 84°C at 68mm. pressure or 69.2° at 26 mm. and

1. A recent example, J.W.E. and Milton J. Hanke.
2. The concentration of hydrogen peroxide in an aqueous solution is usually expressed in percent of hydrogen peroxide, less frequently as volume of oxygen evolved by complete decomposition.
3. Ber. 27, 3307.
4. See note 2. 100% hydrogen peroxide would be 493.5 vol.
5. Talbot and Moody, Jr. Analyt. Chem. ( ) 1892, 650.
6. Ru

a specific gravity of 1.458 at 0°. It decomposes with explosive violence at the boiling point of water.

Hanriot obtained 267 vol.<sup>1</sup> hydrogen peroxide which decomposed upon distillation in vacuo.

Talbot and Moody<sup>2</sup> obtained 294 vol. Hydrogen peroxide.

Schilow states<sup>3</sup> that he obtained 50% hydrogen peroxide by extracting with ether a 3% solution of hydrogen peroxide containing soda.

Wolfenstein<sup>4</sup> could not confirm Schilow's statement but obtained by distillation at 68 mm. pressure 99.5% hydrogen peroxide. He gives the following precautions as essential: The hydrogen peroxide must be free from:

1. All alkaline reacting compounds.
2. Every trace of heavy metal compounds.
3. Solid bodies of every kind even if of an entirely indifferent nature.

1. See note 2 page 2. 100% hydrogen peroxide would be 493.5 vol.
2. Talbot and Moody, Jr. Analyt. Chem. ( )  
1892, 650.
3. Russ. Phys. Chem. Ges., May, 1893.
4. Ber. 27, 3307.

## EXPERIMENTAL

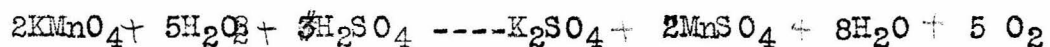
A. Preparation of hydrogen peroxide.

The hydrogen peroxide obtainable was of two brands as put up for medicinal use. The 3% 10 vol. U.S.P. "M.C.W."<sup>1</sup> and the 12 vol. "Dioxygen". Both came a little below the 3% standard required by the U.S. Pharmacopoeia. When opened, a few of the older bottles showed some pressure due to oxygen.

This 3% solution was filtered and evaporated in large flat evaporating dishes on a water bath with a large funnel inverted over it connected to the suction. The funnel caused a current of air to pass over the surface of the liquid and hastened evaporation. At about 20% concentration the remaining solution was distilled in a vacuum distilling apparatus at 68 mm. pressure following closely the method of Wolffenstein<sup>2</sup>. The vacuum was obtained by a water pump and was capable of regulation to any pressure as low as 40 mm. The receiver was a large jar with five smaller receptacles inside that could be changed without losing the vacuum.

The method of Colin<sup>3</sup> slightly modified was used to determine the hydrogen peroxide. In an acid solution the following reaction takes place:

1. "M.D.W." , made by Mallinckrodt Chemical Works.
2. Ber. 27, 3307.
3. Chem. Zeit. 9, 440 and 916.



resulting in the reduction of  $\text{KMnO}_4$  by  $\text{H}_2\text{O}_2$ . 2cc. of hydrogen peroxide solution is pipetted into a beaker, 300 cc. water added and 1 cc. 6N  $\text{H}_2\text{SO}_4$ , standard<sup>1</sup>  $\text{KMnO}_4$  pipetted in slowly until a faint pink color persists after constantly stirring for 1 minute. For concentrations above 10% a small sample is weighed out and diluted up to 100 cc. and a portion only pipetted out and assayed.

Commercial hydrogen peroxide usually contains small amounts of  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$ , and  $\text{HF}$ , alumina, lime, magnesia, potash, and soda. If carelessly made Ba and traces of Fe, Cu, Pb, and Mn may be present. A little acetanilide is frequently present as a stabilizer. The stock used gave negative tests for the heavy metals.

The yield of 20% hydrogen peroxide obtained by concentrating the 3% solution on the water bath averaged about 88%. If evaporated very rapidly the yield is lower, and if very slowly a better yield is obtained.

By fractional distillation at 68 mm. pressure this approximately 20% hydrogen peroxide gives very dilute distillates at first, the boiling point rises slowly and the impurities in the residue become so concentrated that the hydrogen peroxide decomposes and distillation has to

1. Standard  $\text{KMnO}_4$  solutions (0.2492 and 0.4144N) were made up approximately, allowed to stand a day or two, and standardized against  $\text{Na}_2\text{C}_2\text{O}_4$  by aliquot method of H. E. Eastlack, Jour. Am. Chem. Soc., 40, 620.

be stopped. Distillates obtained were all less than 14% concentration. Upon cooling, the residue in the flask is discolored and forms a sort of jelly due to impurities settling out. Since a part of this jelly when filtered off and evaporated to dryness gave a non-volatile white residue that gave negative tests for organic compounds, it could not be the acetanilide that it resembles but must be of inorganic nature at the higher concentration. Two attempts were made to extract with ether. In the first an impure solution containing 51% hydrogen peroxide was shaken up with ether and the layers separated. The aqueous layer assayed 41% hydrogen peroxide and subjected to distillation at 68 mm. pressure gave a boiling point of about 77°C and a very small amount of distillate. of 43.9% hydrogen peroxide concentration. The ether layer took out 20% of the total hydrogen peroxide and was slightly discolored. When evaporated spontaneously this ether layer left a brown residue in the dish.

In the second attempt a 3% solution was extracted with ether and then the aqueous layer evaporated and distilled at 68 mm. pressure. A boiling point of 61° was obtained as against 52° without any extraction.

The following table shows a summary of evaporation at atmospheric pressure in an open dish:

No.	Grams at start	% H <sub>2</sub> O <sub>2</sub> #	Grams at end	% H <sub>2</sub> O <sub>2</sub> at end.	yield %
1	434	2.3#	20	34.00	70
2	845	2.99	110	20.2	88
3	899	2.83	115	----	--
4	887	2.86	100	21.88	86
5	945	2.99	144	17.30	88
6	1145	2.16	135	12.50	74
7	945	2.99	145	17.20	87
8 <sup>§</sup>	981	----	232	10.5	97.5

# It is of interest to note that all came a little below the U.S.P. requirement of 3% H<sub>2</sub>O<sub>2</sub>.

§ No. 8 was extracted with ether before evaporation.

Distillation in Vacuo.

No. 1.

150 grams of 19.4% H<sub>2</sub>O<sub>2</sub>.

Pressure mm. Hg.	b.p. of H <sub>2</sub> O <sub>2</sub> sol'n.	temp. of water bath.	% H <sub>2</sub> O <sub>2</sub> in distillate	% H <sub>2</sub> O <sub>2</sub> in distilling liquid	loss of H <sub>2</sub> O <sub>2</sub> %
70	53 <sup>o</sup>	62 <sup>o</sup> C	.515		
64	52	62	.92	37.8	12.4
65	52	66	2.72	51.	

# Continued distillation of 43 grams 41% H<sub>2</sub>O<sub>2</sub>.

64	55 C	69 C			
66	61.5	80			
68	70	85	14.2		
64	77	86	43.97		

# Stopped at this point as contents of distilling flask were decomposing rapidly. The residue in flask was almost solid jelly.



## Distillation in vacuo. (cont'd)

No. 2.

282 grams of 19.4% H<sub>2</sub>O<sub>2</sub>.

Pressure mm. Hg.	b.p. of H <sub>2</sub> O <sub>2</sub> sol'n.	temp. of water bath.	H <sub>2</sub> O <sub>2</sub> in distillate. %
68	52°C	65°C	.8
70	54	68	1.2
68	60	76	3.0 (54° - 60°)
68	60	78	6.5 (60° b.p.)

No. 3.

Extracted two 1 lb. bottles of hydrogen peroxide with ether, evaporated on water bath, and distilled in vacuo the resulting 232 grams of 10.5% hydrogen peroxide.

Pressure mm. Hg.	b.p. of H <sub>2</sub> O <sub>2</sub> sol'n.	temp. of water bath.	H <sub>2</sub> O <sub>2</sub> in distillate
65	47°C	60°C	
to 65	48	66	.23
" 68	49	71	.60
" 65	49	69	.68
" 62	56	71	2.20
" 68	61	72	9.2

Stopped distillation here as solution was decomposing rapidly.

B. Action of strong hydrogen peroxide on phenol and aniline.

Since no satisfactory results were secured from the distillations and no workable amounts of concentrated hydrogen peroxide were obtained this part consists only of a few test-tube experiments the results of which are incon-  
cu

clusive.

The strongest solutions were the residues in the distilling flask and were of necessity the most impure. The mixtures obtained were not analysed as they were small in amount.

1. Action of ferrous sulfate on strong hydrogen peroxide.

Leeds<sup>1</sup> used ferrous sulfate as a catalyst in obtaining phenol from benzene. As he used only 1.2% hydrogen peroxide the purpose of this experiment is to ascertain the stability of strong hydrogen peroxide in the presence of ferrous sulfate.

The addition of 2 drops (23% ferrous sulfate solution) to 1cc. of 17.3% hydrogen peroxide caused rapid decomposition resulting in the formation of 51 cc. O<sub>2</sub>. Complete decomposition would give 57.4 cc.

Result, 51/57.4 89% decomposition.

2. Action of strong hydrogen peroxide upon phenol.

Two grams of 44% hydrogen peroxide were added to 1.2 grams molten redistilled phenol (b.p. 182.6° C). The next day the solution had turned redder. There were still two definite layers of nearly the same volume as the original, so it seems no considerable action had taken place. The addition of a little concentrated sulfuric acid turned the solution black, due to charring.

3. Action of 44% hydrogen peroxide upon aniline.

2.4 grams 44% hydrogen peroxide added to 2.7

1. Ber. 14,975.

grams aniline. The mixture turned brown but the hydrogen peroxide did not decompose noticeably. The two layers upon standing had the same relative volumes as at start so probably little if any action had taken place.

4. 5. 6. Action of 60% hydrogen peroxide upon aniline sulfate.

To one mol aniline added 1/2 mol sulfuric acid until solid white aniline sulfate was formed. 1 mol hydrogen peroxide, ~~was 2 mols,~~ and a large excess of hydrogen peroxide was added to the solid aniline sulfate in the three different experiments.

In each case the hydrogen peroxide had to be added slowly and the solution cooled to avoid heating and rapid decomposition. The solution at first turned a delicate blue, then darker as the sulfate dissolved, and finally turned black. If a long time is taken the action can be completed and no rapid decomposition noted. If allowed to heat up the mixture boils vigorously, and the action becomes almost explosive in its violence.

No analysis of these black mixtures was attempted because of the limited amounts at hand and the impurity of the hydrogen peroxide used. To obtain an analyzable amount would have necessitated preparation of fresh amounts of concentrated hydrogen peroxide, which did not seem advisable with the limited time available.

## SUMMARY AND CONCLUSIONS

It was thought that strong hydrogen peroxide, above 80% would act as a very good method of introducing hydroxyl groups into aromatic compounds.

Attempts to prepare concentrated hydrogen peroxide by distillation of commercial 3% hydrogen peroxide failed due to impurities decomposing the solutions.

Test tube experiments with these impure residues gave no conclusive results.

The conclusion is reached that:

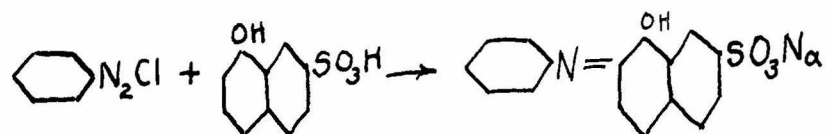
1. A concentrated solution of hydrogen peroxide if pure would be stable enough to work with.
2. This work has produced no evidence tending to show that the proposed method will not be successful.
3. To obtain this pure hydrogen peroxide some other means than evaporating the commercial product must be used.

## PART II

## AN ATTEMPT TO PREPARE DI-PARA-DI-AMINO-PARA-DIBHENYL-BENZENE.

## INTRODUCTION

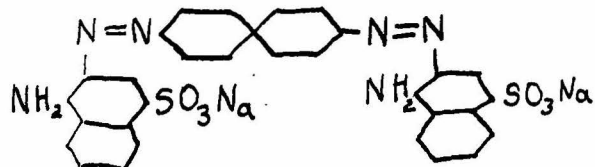
The diazo dyes are derived from diazo bodies and from phenols, amines, or their sulfonic acids. Phenyl diazonium chloride (or diazo benzene chloride) and  $\alpha$ -naphthol sulfonic acid form  $\alpha$ -naphthol-2-azo-benzene.



By diazotizing benzidine,  $\text{NH}_2\text{C}_6\text{H}_4-\text{C}_6\text{H}_4\text{NH}_2$ , tetra-azo-diphenyl-chloride is formed. G. Schultz<sup>1</sup> has shown that benzidine has the structure:



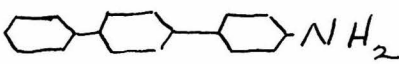
Then congo red, the condensation product of 1 mol tetra-azo-diphenyl-chloride and 2 mols sodium naphthionate<sup>2</sup> has the structure:



The next member of the series would be a diazo

1. Ann. 174, (1894), 227.

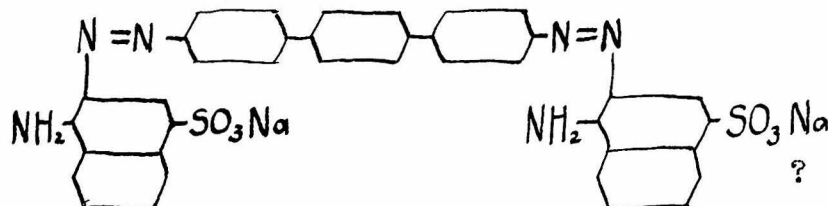
2. D.R.P. No 28753, Feb. 27, 1884.

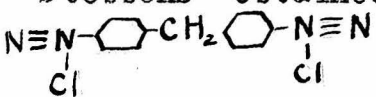
body containing three benzene residues and can be made by nitrating and then reducing the di-para di-nitro-compound of the hydrocarbon, p-diphenyl benzene. This diamine  $H_2N$    $NH_2$  is not described in the literature. This paper is a description of some preliminary work done towards obtaining this amine and the tetrazo body obtained by treating its hydrochloride with nitrous acid:

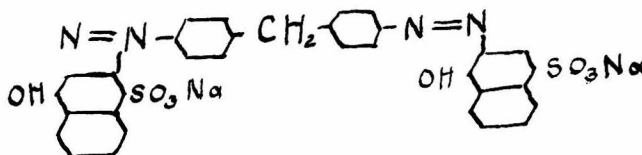


It would be of interest to find what type of dyes (if any) this heavy tetrazo-body would make by combination with complex radicals.

For example, would 1 mol combine with 2 mols sodium naphthionate to form:



Stebbens<sup>1</sup> obtained a tetrazo body of the structure  $N \equiv N$    $N \equiv N$  and found that he obtained the expected addition product with sodium  $\alpha$ -naphthol sulfonate, which differs from congo red in that it will not dye cotton without a mordant:



The effect of changing the  $-CH_2-$  radical to

1. Jr. Ind. and Eng. Chem. 10,445.

14

-C<sub>6</sub>H<sub>4</sub>- will be the main interest of this work.

The natural starting point for these experiments would be the hydrocarbon C<sub>18</sub>H<sub>14</sub>, p-diphenyl benzene. This hydrocarbon has been obtained in small amounts as one of the products formed when benzene<sup>1</sup>, and mixtures of benzene and toluene<sup>2</sup>, are passed through hot tubes. It is also formed by the action of ethyl iodide on potassium benzene<sup>3</sup>, by the action of sodium on monobrombenzene<sup>4</sup>, and on a mixture of para-dibrombenzene and monobrom benzene<sup>5</sup>, and when diazobenzene chloride reacts with diphenyl in the presence of anhydrous aluminum chloride<sup>6</sup>.

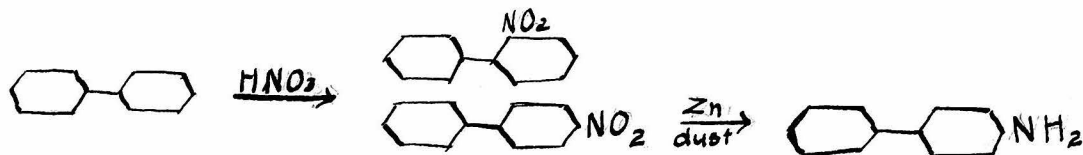
The yields obtained by means of all these syntheses are very small, however, so it was thought best to employ indirect methods for obtaining the hydrocarbon. The methods proposed necessitated the use of para-amino-diphenyl which can best be obtained by one of the following methods.

The first is the diazo reaction of R. Hirsch<sup>7</sup> in which he diazotized C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>, converted the diazo compound into diazoamino benzene, and heated the latter with a large excess of aniline. He distilled off the aniline and after neutralizing, precipitated the para-amino-diphenyl as its sulfate. The author tried this reaction three times carefully and got only a very small yield, so

1. Schultz, Ber. 6, 415.
2. Cornelley, J. Chem. Soc. 37, 712
3. Abeljanz, Ber. 29, 11.
4. Weiler, Ber. 29, 117.
5. Riese, Ann. Chem. Phar. 164, 161. (Compare Chattaway and Evans, J. Chem. Soc., 69, 981)
6. Mohlan and Berger, Ber. 26, 1998.
7. Ber. 25, 1973.

small that the method was of no value in obtaining a workable amount of para-amino-diphenyl.

The second method consists of three steps and can be graphically shown thus:



Diphenyl was made as described by Fisher<sup>1</sup> by passing benzene vapours thry a red hot iron tube. The nitration by the method of Hübner<sup>2</sup> gave a good yield and easy separation of ortho and para products. The para body is precipitated by addition of a small amount of water and is obtained pure after one crystallization from alcohol. The reduction was easily accomplished in glacial acetic acid with zinc dust. The amine distills over with steam, but at a very slow rate, and is obtained fairly pure. A long time is required and a large volume of distillate is obtained, but as the product is very slightly soluble in cold water, the method is well worth the expenditure of time involved.

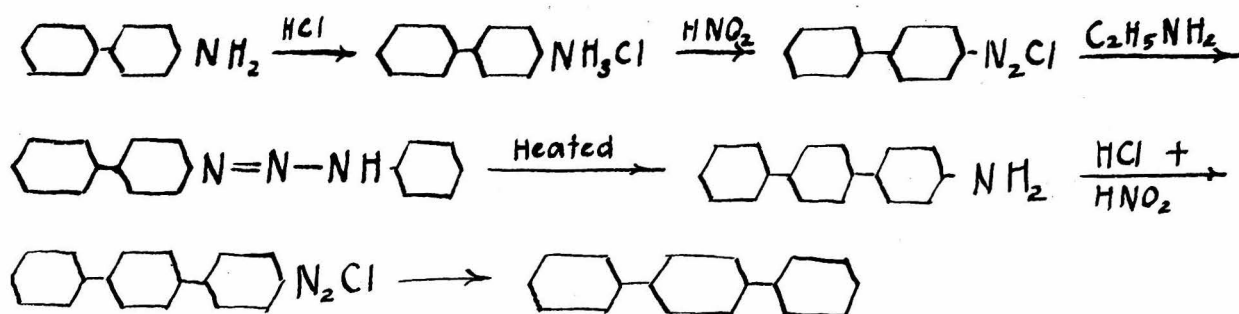
For preparing diphenylbenzene from the amino-diphenyl three methods were considered. One would have consisted in diazotizing the para-amino-diphenyl and treating with a large excess of aniline. The diazo-amino compound formed would be changed to amino diphenyl benzene

1. Anleitung sur Darstellung organischer Präparate, Braunschweig, 1908, P.64.
2. Ber. 8, 8711.



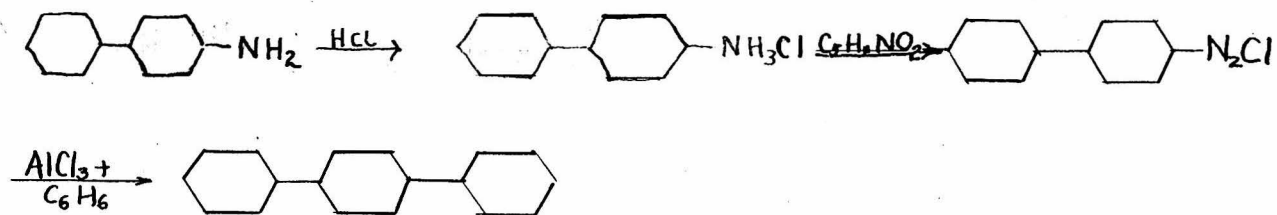
by the application of heat, as in the method of Hirsch<sup>1</sup>. This compound could be diazotized and the resulting diazobody reduced to the hydrocarbon. But as the Hirsch condensation was not a success in the preparation of para-amino-diphenyl, the method was discarded. A second method would have consisted in treating dry diazo-diphenyl chloride with benzene in presence of aluminum chloride yielding the hydrocarbon directly. The third would be to diazotize para-amino-diphenyl in aqueous solution and treat with an excess of phenol according to the method of Hirsch<sup>2</sup> for obtaining p-hydroxy-diphenyl. This should give hydroxy-para-diphenylbenzene, which when distilled with zinc dust should yield the desired hydrocarbon. The steps involved are as follows:

## Method No.1.

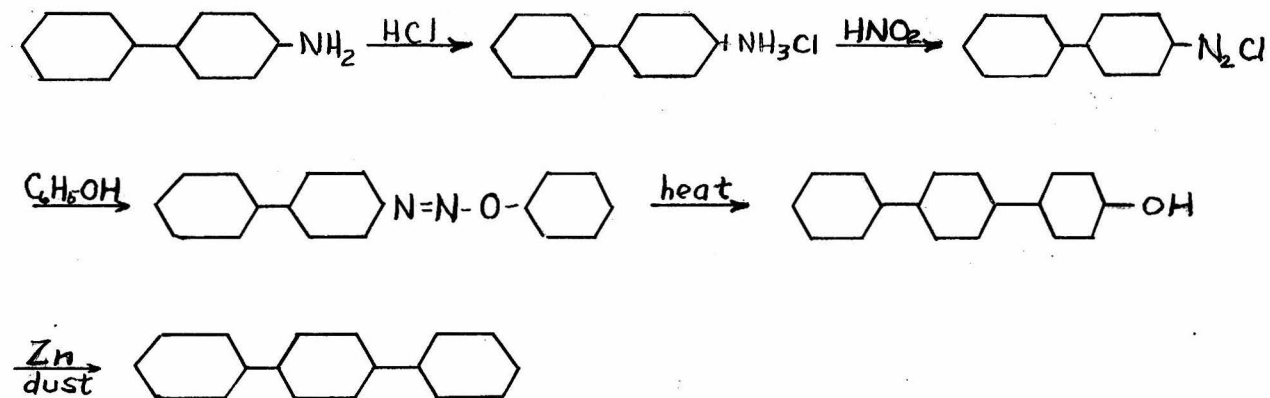


1. loc. cit.
2. Ber. 23, 3705.

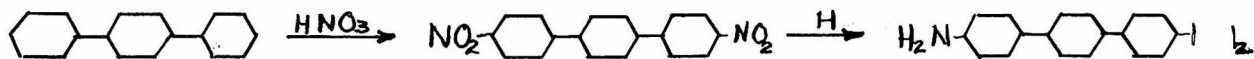
## Method No. 2.



## Method No. 3.



The hydrocarbon, para-diphenyl-benzene gives when brominated, di-para-di-brom-diphenyl-benzene<sup>1</sup>. Consequently when nitrated it would be expected to give di-para-dinitro-diphenyl-benzene, which on reduction should give the desired diamino-diphenyl-benzene.



<sup>1</sup> Olgiati, Ber. 26, 3394.

## EXPERIMENTAL

Preparation of diphenyl.

Prepared diphenyl by passing benzene vapours through a heated iron pipe filled loosely with pumice placed in a combustion furnace and heated to a high red heat as described by Emil Fisher. The apparatus was fitted with a condenser to return the  $C_6H_6$  to the boiling flask and so complete the circuit. Time was thought to be a factor in the yield of diphenyl so the process was arranged as nearly automatic as possible, requiring attention only in case of possible accident and fire. But this was reduced to a minimum by using an electric heater to boil the  $C_6H_6$  and partially surrounding the furnace with asbestos boards.

In the first experiment 350 cc.  $C_6H_6$  was put into the flask and the process kept up for 14 hours. The  $C_6H_6$  was distilled off. The boiling point went up rapidly to 240 , a fraction was collected between 240 and 270 and gave by recrystallization from alcohol 73.5 grams of pure diphenyl of m.p. 70.5 . A 47.6% yield of diphenyl was obtained calculated from the loss in weight, which was assumed to be benzene.

Smith and Lewcock<sup>1</sup> conducted some experiments on the production of diphenyl by passing benzene vapour thru tubes of different sizes using different catalytic agents. They conclude that carbon does not catalyze

1. J/ Chem. Soc. 101, 1453.

the action and that the carbon after some time causes the action to stop.

To check this the apparatus was not changed and 200 cc. benzene passed thru again for 2 hours, giving a yield of 5.5 grams. This is 2.7 grams per hour as compared with 5.2 grams per hour in the previous experiment. There is a loss in efficiency with time.

Preparation of para-amino-diphenyl by the method of Hirsch.<sup>1</sup>

50 grams (1 mol) aniline and 2.5 mols hydrochloric acid is diazotized with a solution of 39 grams sodium nitrite in 100 cc. water followed by addition of 950 grams  $C_6H_5NH_2$  and thorough shaking. The aniline layer is separated and dried with calcium chloride. The mixture is heated to 150 in an oil bath until nitrogen ceases to be evolved, the temperature gradually increased to 190 and excess  $C_6H_5NH_2$  distilled off up to 200. Distillation is stopped, the basic mixture cooled, heated with ten times its volume of water and made acid with hydrochloric acid. At this point the solution turns a deep red, due to formation of amido-azo-benzene hydrochloride. By careful neutralization the red color disappears and by careful addition of sodium hydroxide the greater part of the dissolved amido-azo benzene separates, and can be filtered off. The solution is

1. Ber. 25, 1973.

treated with sodium sulfate to bring down the amino body as the sulfate.

This experiment was tried three times and in each case the yield was very poor and only a very small yield of impure product was obtained. In the first case the calcium chloride used for drying combined with the aniline causing a loss of aniline and the dissolved product. Anhydrous sodium sulfate was used in the next two experiments.

The yield of the precipitated sulfate was very small due to inability to get the proper concentration of acid.

Preparation of para-nitro-diphenyl from diphenyl.

Dissolved 45 grams diphenyl in 180 grams of glacial acetic acid and slowly added a solution of 144 grams fuming nitric acid in 144 grams glacial acetic acid. Heated on water bath for an hour. Cooled and added 90 cc. water which brings down the para compound almost completely. If a larger amount of water is added, about equal in volume to that of acid, the impure ortho-body separates as an oil. The para-nitro-diphenyl crystallizes from alcohol in long, hard, yellow needles of m.p. 114. Yield of para body is 30%.

Preparation of para-amino-diphenyl by reduction of para-nitro-diphenyl.

Dissolved 3 grams  $C_{12}H_9NO_2$  in 30 cc. glacial

acetic acid and added slowly 6 grams of zinc dust. This is 100% excess. Heated between each addition to boiling point of acetic acid under a reflux condenser. Steam distilled after making alkaline. Upon cooling lustrous flaky crystals of the amine came down. The amino body is very slowly volatile with steam and it takes a long time and a large volume of distillate to bring over all the amine. Yield was not determined but was about 50%.

#### SUMMARY

Prepared diphenyl by passing benzene vapours thru a hot iron tube.

Attempts to prepare para-amino-diphenyl by diazo reaction of Hirsch were not successful in obtaining a workable amount of the amino body.

Nitration of diphenyl gave a fair yield of pure para-nitro-diphenyl.

Reduction of para-nitro-diphenyl with zinc in glacial acetic acid gave para-amino-diphenyl.

Completion of the work was prevented by the calling of the author to the colors.