

1926

I. The reaction of nitro compounds (including war gases and explosives) with organomagnesium halides; II. Study on anti-knock materials, the preparation of tetra-styryl lead

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I. THE REACTION OF NITRO COMPOUNDS (INCLUDING WAR  
GASPS AND EXPLOSIVES) WITH ORGANOMAGNESIUM HALIDES

II. STUDY ON ANTI-SHOCK MATERIALS. THE PREPARATION  
OF BUTA-DIENE LEAD

A Thesis Submitted  
to the Graduate Faculty in Candidacy  
for the Degree of  
DOCTOR OF PHILOSOPHY

by

Roy McCracken

Major Subject: Organic Chemistry

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## II

### ACKNOWLEDGMENT

#### PART I

The writer wishes to express his appreciation to Dr. Henry Gilman for the suggestion of these problems and for his generous advice and encouragement given during the work.

### ACKNOWLEDGMENT

#### PART II

The writer wishes to express his appreciation to Dr. C. R. Sweeney and to Dr. Henry Gilman for their suggestion of this problem and for their generous advice and encouragement given during the work.



## III

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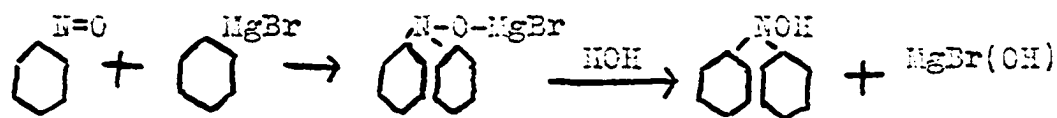
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# REACTION OF NITROSOBENZENE AND PHENYLMAGNESIUM BROMIDE

## INTRODUCTION

Wieland and Roseeu<sup>1</sup> treated nitrosobenzene,  $C_6H_5NO$ , with phenylmagnesium bromide,  $C_6H_5MgBr$ , and obtained diphenylhydroxyl amine,  $(C_6H_5)_2NOH$ . The nitrosobenzene was dropped into the phenylmagnesium bromide at a temperature of  $-15^\circ$ .

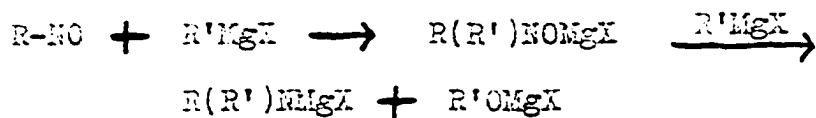
Reaction:



However in a later article<sup>2</sup> they state that the above is the expected reaction by comparison of the  $-NO$  group with the  $=C=O$  group but that as a rule the reaction does not stop at this stage; the  $R(R')N-O-MgX$  is reduced by a second mole of  $R'MgX$  and the oxygen made available converts the  $R'MgX$  into  $R'OMgX$ :



The complete reaction would then be:



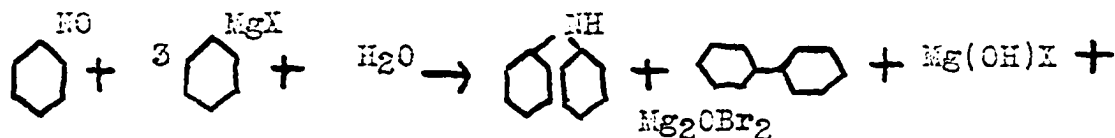
In the complete reaction one molecule of the nitroso compound would consume two molecules of  $RMgX$ .

1. Wieland and Roseeu, Ber. 45, 494-9 (1912).
2. Wieland and Roseeu, Ber. 48, 1117-21 (1915).

From our data the above interpretation of the reaction does not appear to be the correct one because:


- (1) In this scheme only two moles of  $\text{RMgX}$  react with one mole of  $\text{C}_6\text{H}_5\text{NO}$  while experimental evidence shows that three moles react.
- (2) There is always a large amount of diphenyl produced which is not accounted for by the above scheme.
- (3) There should be a molar relation between the amount of phenol and the amount of diphenylamine. An inspection of the subsequent data reveals that the amount of diphenylamine is large and the amount of phenol is very small being only that which results from the oxidation of the  $\text{RMgX}$  by the air and ether under the conditions of the experiment. Blank runs using only the  $\text{RMgX}$  gave the same amount of phenol as the reaction mixture.






From our data the reaction may be expressed as:



The first step in the reaction is no doubt, as Wieland and Roseau<sup>1</sup> suggest, the formation of the addition compound  $(\text{C}_6\text{H}_5)_2\text{N-C-MgX}$  which on treatment with water gives  $(\text{C}_6\text{H}_5)_2\text{NOH}$ . We have duplicated their experiment and obtained the diphenylhydroxylamine,  $(\text{C}_6\text{H}_5)_2\text{NOH}$ , in reasonable yield. However when the diphenylhydroxylamine was treated with phenylmag-




nesium bromide it consumed three equivalents, the first quite probably forming the same addition product as results from nitrosobenzene and phenylmagnesium bromide, namely  $(C_6H_5)_2N-O-MgBr$ . This compound then consumed two more equivalents of phenylmagnesium bromide before giving a positive test<sup>3</sup> for excess  $RMgI$ . The reaction mixture on being decomposed with dilute acid and worked up in the usual way, as described below, yielded diphenylamine (40.2%), diphenyl (70.1%) and a small amount of phenol (1.08 g.) but this amount of phenol was shown to be obtained in a blank run when diphenylhydroxylamine was absent.

The reaction of nitrosobenzene also yielded, as Wieland and Roseeu report, small amounts of azobenzene. Small quantities of p-phenyl diphenyl, () , not mentioned by Wieland and Roseeu, were also isolated.

Wieland and Kögl<sup>4</sup> treated p-nitrosodimethylaniline ( $(CH_3)_2N$ -) with phenylmagnesium bromide in the hope of obtaining phenyl-p-dimethylaminophenylhydroxylamine ( $p-(CH_3)_2N$ -) but the product was found to consist largely of a substance regenerating  $(CH_3)_2N$ - on decomposition with water, and some  $(p-(CH_3)_2N$ -)<sub>2</sub>. The crude product of the reaction gave with dil. HCl a carmine red color. This may have been due to  $p-(CH_3)_2N$ - .

3. Gilman and Schulze, J. Am. Chem. Soc. 47, 2002-5 (1925).

4. Wieland and Kögl, Ber. 55B, 1798 (1922).

Also p-tolyl- and ethylmagnesium bromide reacting with p-nitrosodimethylaniline gave p-p'-dimethylaminoazobenzene. p-Nitroso-toluene, ( $\text{CH}_3$ --NO), reacting in the cold with phenylmagnesium bromide gave the expected p-tolyl-phenylhydroxylamine ( $\text{CH}_3$ --N()-OH) a body very similar in its properties to diphenylhydroxylamine.

### EXPERIMENTAL

#### REACTION OF NITROBENZENE AND PHENYLMAGNESIUM BROMIDE

The nitrosobenzene (10.7 g., 0.1 mole) was dissolved in about 300 cc. of dry ether in a three-necked flask fitted with a reflux condenser, stirrer, dropping funnel and a tube for passing pure, dry hydrogen thru the flask. Phenylmagnesium bromide in ether solution was added dropwise with stirring and at the same time hydrogen was passed thru the flask. The heat of the reaction produced a gentle refluxing of the ether at first but which was considerably less vigorous after the addition of one-tenth mole of  $\text{C}_6\text{H}_5\text{MgBr}$ . A brown precipitate appeared at first which later darkened and disappeared.

After 0.1 mole of  $\text{C}_6\text{H}_5\text{MgBr}$  was added the reaction mixture gave no test for excess  $\text{RMgX}$ ; 0.1 mole more was added, stirred 6 hours and it then gave no test for excess  $\text{RMgX}$ ; 0.05 mole more was added and allowed to stand over night

after which it still did not show an excess; 0.05 mole more was added making a total of approximately 0.3 mole (three equivalents) after which the reaction continued to show an excess of  $\text{RMgX}$  even after 24 hours stirring.

The reaction mixture was then decomposed by the addition of small bits of ice, the ether layer separated and dried one hour over  $\text{CaCl}_2$ , filtered and the ether evaporated by water-pump suction at the same time a slow stream of hydrogen was passing over the ether. The ether was evaporated until the residue solidified, then 50 cc. of petroleum ether were added and cooled to crystallization in an effort to obtain  $(\text{C}_6\text{H}_5)_2\text{NOH}$  but only diphenyl,  $\text{C}_6\text{H}_5\text{-H}_5\text{O}_6$ , separated. The petroleum ether layer was then extracted with  $\text{NaOH}$  solution to remove the phenol which was separated as tri-bromophenol, 5.4 g. equivalent to 1.53 g. phenol being obtained. A blank run to determine the amount of phenol produced in  $\text{C}_6\text{H}_5\text{MgBr}$  when subjected to the same conditions (stirring in the flask with 300 cc. of dry ether and with a stream of hydrogen from the same tank passing over it) gave 1.53 g. of phenol.

The ether layer was then dried with  $\text{CaCl}_2$  and dry  $\text{HCl}$  passed into it to precipitate the  $(\text{C}_6\text{H}_5)_2\text{NH-HCl}$ , which was filtered out. The ether was then evaporated and the residue vacuum distilled:

$\text{F}_1$  --  $120^\circ$ - $150^\circ$  most at  $130^\circ/11$  mm. 10.3 g. (red)

F <sub>2</sub> -- 150°-200°/11 most at 165°/11 mm.	1.8 g. (very red)
F <sub>3</sub> -- 200°-250°/11	1.1 g.
F <sub>4</sub> -- Residue	1.4 g.

F<sub>1</sub> and F<sub>2</sub> being red, indicative of azobenzene, were combined and dissolved in glacial acetic acid and zinc dust added. The red color was immediately discharged, the azo compound being reduced to hydrazo compound. The acetic acid was neutralized and extracted with ether, the ether layer separated and dried with CaCl<sub>2</sub> and dry HCl passed into it to precipitate the hydrazobenzene hydrochloride which was filtered out, 1 g. being obtained. The diphenyl obtained from the ether solution amounted to 11 g. (76.4%).

The precipitate of crude diphenylamine hydrochloride was treated with NaOH solution and extracted with ether, the ether evaporated and the residue distilled:

Fraction 1	B.p. 160-170/11 mm.	5.6 g.
Fraction 2	170-260/11 mm.	.4 g.
Fraction 3	Residue	2.1 g.

Fraction 1 was diphenylamine and melted at 52°. Yield 5.6 g., 33.1%.

#### NITROSOBENZENE AND PHENYLMAGNESIUM BROMIDE

Second Run. Ten and seven-tenths grams (0.1 mole) of nitrosobenzene, C<sub>6</sub>H<sub>5</sub>NO, were treated with 0.3 mole of phenylmagnesium bromide, C<sub>6</sub>H<sub>5</sub>MgBr, in the manner described in the previous experiment. The reaction mixture was allowed to




stand over night and was then decomposed by the addition of small bits of ice in sufficient amount to have the  $\text{Mg(OH)Br}$  remain as a thick paste from which the ether layer was poured off. The ether, after drying for one hour with  $\text{CaCl}_2$ , was removed by evaporation at  $20-25^\circ$  under a vacuum. A reddish oil remained. Addition of petroleum ether at first took this into solution but the further addition (60 cc. total) threw out an oil. The addition of benzene took the oil into solution but on cooling an oil was always obtained instead of crystals of diphenylhydroxyl amine,  $(\text{C}_6\text{H}_5)_2\text{NOH}$ , as was expected. Repeated trials always produced an oil. This oil showed a qualitative test for  $(\text{C}_6\text{H}_5)_2\text{NOH}$  reducing ammoniacal  $\text{AgNO}_3$  in the cold. The oil was separated and the last traces of petroleum ether removed under vacuum. After keeping for 4 days at a temperature of  $0^\circ$  the material had not crystallized and had shown considerable darkening.

The petroleum ether layer after separation of the oil was extracted with  $\text{NaOH}$  solution to remove the phenol which was separated as the tri-bromophenol yielding the equivalent of .35 g. of phenol. The petroleum ether layer was then dried with  $\text{CaCl}_2$ , and  $\text{HCl}$  gas passed in to precipitate the diphenylamine as the hydrochloride, which was filtered out and worked up in the usual manner yielding 5.5 g. (20.7%) of diphenylamine melting at  $49-51^\circ$ . (Also a residue of 1.2 g. after distillation.)

The filtrate after removal of the  $(C_6H_5)_2NH \cdot HCl$  was vacuum distilled:

Fraction I --	125°-150°/12 mm.	7.1 g.
Fraction II --	150°-190°/12 mm.	.9 g.
Fraction III --	Residue	1.4 g.

Fraction I was diphenyl,  $C_6H_5H_5C_6$ , melting at 69-70°, yield 7.1 g., 32.7%. Fraction II on crystallization from alcohol yielded about 0.3 g. of p-phenyldiphenyl, .

Determinations of the amount of diphenyl and phenol in the original phenylmagnesium bromide solution from which the .3 mole of  $C_6H_5MgBr$  used in this experiment was taken, gave .69 g. diphenyl per 50 cc. (.1 mole) and .15 g. phenol per 50 cc. (.1 mole) or a total for the .3 mole used of 2.07 g. diphenyl and .45 g. phenol. In calculating the yields from the reaction these amounts were deducted from the amounts of products obtained.

#### REACTION OF NITROBENZENE AND PHENYLMAGNESIUM BROMIDE AT THE BOILING POINT OF ETHER

The previous experiments having failed to produce any appreciable amount of phenol and not an entirely satisfactory yield of diphenylamine, this experiment was carried out with refluxing of the reaction mixture in an effort to force the reaction to yield if possible these products. The yield of phenol was still negligible but the yield of diphenylamine

was somewhat increased under these conditions.

This run was carried out with the same equipment as the previous ones. The ether solution of 10.7 g. (0.1 mole) of nitrosobenzene,  $C_6H_5NO$ , was heated to boiling on the water-bath and phenylmagnesium bromide added slowly. After the addition of 0.2 moles of  $C_6H_5MgBr$  and at the end of 5 hours the reaction mixture showed no test for  $RMgX$ . Another 0.1 mole  $C_6H_5MgBr$  was added, making a total of three equivalents, and the refluxing continued for a total of 23 hours, after which  $C_6H_5MgBr$  was still present in excess.

The reaction mixture was then decomposed with ice, the ether layer separated and evaporated as in the previous experiments in an effort to obtain diphenylhydroxylamine,  $(C_6H_5)_2NOH$ , but none was secured. The material was then extracted with NaOH solution to remove the phenol, which after working up in the usual manner yielded .35 g. phenol.

After the NaOH extraction the ether layer was dried and HCl gas passed in to precipitate the  $(C_6H_5)_2NH \cdot HCl$  which was filtered out. The free amine was obtained from the hydrochloride by treating with NaOH solution and extracting with ether. The ether was evaporated and the residue vacuum distilled:

Fraction I -- 160-180°/14 mm. (Most 165-70°)	7.2 g.
Fraction II -- 180-250°/14 mm.	.9 g.
Fraction III -- Residue	2.8 g.

Fraction I was practically pure diphenyl amine melting at 51-52°, the percentage yield being 42.6. Fraction II was

tarry and was not worked up.

The filtrate after the removal of  $(C_6H_5)_2NH \cdot HCl$  was freed from ether and vacuum distilled yielding:

Fraction I -- 120-140°/14 mm. (Most at 130°)	10.4 g.
Fraction II -- 140-200°/14 mm.	.7 g.
Fraction III -- Residue	1.9 g.

Fraction I was practically pure diphenyl melting at 69-70° C. The yield after deducting the 2 g. present in the EtOH solution at the start was 54.5%. Both fractions I and II were tinged lightly red due no doubt to azobenzene but not in sufficient amount to separate. The quantity of phenol, .85 g., is no more than occurs in a blank run.

#### REACTION OF NITROBENZENE WITH PHENYLMAGNESIUM BROMIDE AT THE BOILING POINT OF BENZENE

Since the yield of diphenylamine was lightly improved by refluxing the reaction mixture in the previous experiment it seemed desirable to try the effect of a still higher temperature. Accordingly, this reaction was carried out in boiling benzene. Instead of obtaining a larger amount of diphenylamine than in the previous runs, the yield was much lower, accompanied by much tarry material; the amount of diphenyl was about the same as in the previous runs but was accompanied by a large amount of a very high boiling product; the amount of phenol, however, was larger than in the previous runs but this was no

doubt due to the refluxing at the higher temperature. The conclusion is that the higher temperature does not force the reaction to yield diphenylamine but that it proceeds in a different direction or else the higher temperature produces interaction of the products, side reactions, etc.

The equipment used was the same as in the previous runs. The nitrosobenzene 10.7 g. (0.1 mole) was dissolved in 200 cc. of benzene and heated to boiling on a steam bath. Phenylmagnesium bromide was added dropwise. After the addition of approximately 0.3 mole the reaction mixture gave no test for  $\text{RMgX}$  but after the addition of 0.4 mole, and at the end of four hours refluxing, showed the presence of excess  $\text{RMgX}$ .

The mixture was then decomposed with sufficient ice to give a paste of  $\text{Mg}(\text{OH})\text{Br}$  from which the benzene layer was poured off. The phenol was extracted from this benzene layer with  $\text{NaOH}$  solution, the solution acidified with  $\text{HCl}$ , and the phenol extracted from this acid solution with ether which was then separated, dried and carefully evaporated to give 3.4 g. of crystalline phenol.

The benzene layer after removal of the phenol was dried and then  $\text{HCl}$  gas passed in to precipitate the  $(\text{C}_6\text{H}_5)_2\text{NH}\cdot\text{HCl}$  which was filtered out. The free amine was obtained by treating the hydrochloride with  $\text{NaOH}$  solution and extracting with ether. The ether was evaporated and the residue vacuum distilled:

Fraction I -- 125-150°/3 mm.      2 g.

Fraction II -- Residue 4.7 g.

Fraction I was practically pure diphenylamine melting at 52°. Yield 11.8g.

The benzene layer after the removal of the hydrochloride precipitate was vacuum distilled:

Fraction I -- 125-60°/18 mm.	7.4 g.
Fraction II -- 160-250°/5 mm.	5.5 g.
Fraction III -- Residue	4.6 g.

Fraction I melted at 70° and was practically pure diphenyl.

Total yield, 7.4 g.; percentage yield, 52.5%. (Based on one mole of diphenyl being obtained from one mole of nitroso compound, but deducting 2.4 g. diphenyl which was present in the quantity of Grignard reagent used, before calculating the percentage yield.)

Fraction II was slightly yellowish brown in color and very viscous. It has not yet yielded an identified compound.

#### REACTION OF NITROSOBENZENE AND PHENYLMAGNESIUM BROMIDE

This run was made under the same conditions as the first run at room temperature with the exception that a smaller amount of nitrosobenzene was used. The nitrosobenzene, 4.6 g. (.043 mole), was dissolved in 100 cc. of dry ether and treated slowly with three equivalents of phenylmagnesium bromide. The reaction mixture was decomposed with 100 cc. of 1:5 HCl and the ether layer separated and extracted with 100 cc. of 10% NaOH solution in order to remove the phenol. The sodium phenolate

thus removed was acidified and brominated whereupon 2.1 g. of tribromophenol, equivalent to 0.6 g. phenol, were obtained. The ether solution was then dried and filtered and the diphenylamine precipitated as the hydrochloride. This was filtered out, treated with NaOH solution and the free amine extracted with ether and vacuum distilled, 2.2 g. (36.4%) being obtained.

The ether filtrate from the amine hydrochloride was vacuum distilled and yielded 6.1 g. of diphenyl. After deducting the 1 g. of diphenyl present in the phenylmagnesium bromide solution at the start this is a yield of 77%.

#### PREPARATION OF $\alpha$ - $\alpha$ -DIPHENYLHYDROXYLAMINE, $(C_6H_5)_2NOH$ , FROM NITROBENZENE AND PHENYLMAGNESIUM BROMIDE

Following the directions of Wieland and Roseau<sup>1</sup> in minute detail using the same amounts, temperature conditions, etc.,  $\alpha$ - $\alpha$ -diphenylhydroxylamine was obtained. The compound was practically white immediately after crystallization and melted at 60° (m.p. 60°). It was placed in a vacuum desiccator; after one day the compound had darkened somewhat; after two days considerable decomposition had taken place and later the material became liquid; after several days it again solidified and appeared like diphenylamine.

In a previous attempt to prepare diphenylhydroxylamine .25 mole of phenylmagnesium bromide was treated in the cold with .1 mole (10.7 g.) nitrosobenzene. The diphenylhydroxylamine was no doubt obtained but could not be made to crystal-

lize. After excessive decomposition had occurred and hope of obtaining a crystalline compound was given up, the reaction mixture was worked up as in the previous experiments and yielded:

Diphenylamine	--	6.1 g., m.p. 53-4°	36.1%
Diphenyl	--	5.5 g., m.p. 10°	27.6% <sup>a</sup>
Phenol	--	.3 g.	0.0% <sup>b</sup>
p-Phenyldiphenyl	--	.2 g., m.p. 203°	

a. After deducting the amount originally present.

b. This amount of phenol was originally present in the phenylmagnesium bromide solution.

#### REACTION OF $\alpha$ - $\alpha$ -DIPHENYLHYDROXYLAMINE AND PHENYLMAGNESIUM BROMIDE

$\alpha$ - $\alpha$ -Diphenylhydroxylamine was prepared by the method of Wieland and Roseu<sup>1</sup> by treating nitrosobenzene with phenylmagnesium bromide. The diphenylhydroxylamine (9.25 g., 0.05 mole) was dissolved in 200 cc. of dry ether in a 1-l. three-necked flask fitted with a mechanical stirrer, reflux condenser, dropping funnel and a tube for admitting dry hydrogen. Phenylmagnesium bromide was added dropwise. The first equivalent (.05 mole) of  $C_6H_5MgBr$  reacted immediately on addition, quite probably replacing the H of the hydroxyl group by  $-MgBr$  to give  $(C_6H_5)_2NOMgBr$ . This compound is the result of the first step in the reaction of nitrosobenzene with phenylmagnesium bromide. After the addition of 2.5 equivalents (0.125 mole) of  $C_6H_5MgBr$



the reaction mixture gave no test for excess  $\text{RMgX}$  at the end of 24 hours; an additional 0.025 mole, making a total of three equivalents (.15 mole) was added and stirring continued for another 24 hours at the end of which time the reaction mixture gave only a very faint test for excess  $\text{C}_6\text{H}_5\text{MgBr}$ . During the first 5 hours the reaction mixture was cooled with an ice-salt mixture; the remainder of the run was made at room temperature.

In a comparison of these experiments with those of Wieland and Roseau it should be borne in mind that these conditions do not exactly duplicate theirs thus introducing a possibility, altho we believe it slight, that their representation under their conditions may be correct.

The reaction mixture was then decomposed by the addition of 100 cc. of 1:3  $\text{HCl}$ , the ether layer separated and extracted with  $\text{NaOH}$  solution in order to remove the phenol which was separated by brominating to the insoluble tribromophenol, 3.8 g. equivalent to 1.08 g. phenol being obtained. In a blank run made under similar conditions to determine the amount of phenol formed from the trace of oxygen in the hydrogen (tank hydrogen was used) and from the oxygen of the air that came in contact with the  $\text{C}_6\text{H}_5\text{MgBr}$  during its preparation and transferal to the reaction mixture and from the ether, 1.15 g. phenol was obtained. This makes it quite improbable that any of even the small amount of phenol which was obtained came as a reaction product of the  $(\text{C}_6\text{H}_5)_2\text{NOH}$  on the  $\text{C}_6\text{H}_5\text{MgBr}$ .

The ether layer after the removal of the phenol was dried with  $\text{Na}_2\text{SO}_4$  and treated with dry  $\text{HCl}$  whereupon 5 g. of diphenylamine hydrochloride were precipitated and then filtered out. The ether layer was then evaporated and the residue distilled:

Fraction I -- 250-275° -- 5.1 g., m.p. 68-70°

Fraction II -- 275-310° -- 2.8 g.

Fraction II was treated with ether- $\text{HCl}$  and .3 g. of hydrochloride precipitated; this was filtered out and the ether evaporated leaving a residue of about 2 g. which melted at 68-70°.

This was combined with fraction I and distilled:

Fraction I -- B.p. 250-60° -- 5.4 g., m.p. 69°




This material was practically pure diphenyl melting at 69° and giving a mixed melting point with pure diphenyl of 69°. Yield 70.1%.

The combined amine hydrochlorides (5 g. and .3 g.) were treated with  $\text{NaOH}$  solution, the amine extracted with ether, the ether dried over  $\text{Na}_2\text{SO}_4$ , evaporated and the residue vacuum distilled:

Fraction I -- 160-2°/11 mm. -- 3.4 g.

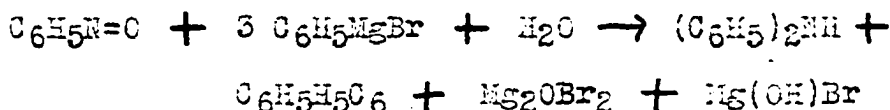
This material melted at 51° and gave a mixed melting point of 52-53° with pure diphenylamine. Yield 40.2%.

TABLE I

SUMMARY OF EXPERIMENTS WITH  N=O +  MgBr						
Experiment: and Page No.	I-4	II-6	III-8	IV-10	V-12	VI-13
Conditions:	Room Temp.	Room Temp.	Refluxing in Ether	Refluxing in Benzene	Room Temp.	-15°
Amount C <sub>6</sub> H <sub>5</sub> N=O Used	10.7 g. .1 mole	10.7 g. .1 mole	10.7 g. .1 mole	10.7 g. .1 mole	4.6 g. .045 mole	10.7 g. .1 mole
Amount C <sub>6</sub> H <sub>5</sub> MgBr Used	.3 mole	.5 mole	.5 mole	.4 mole	.15 mole	.25 mole
Obtained (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> NH	5.6 g. 33.1 %	5.5 g. 20.7 %	7.2 g. 42.6 %	2. g. 11.8 %	2.2 g. 36.4 %	6.1 g. 36.1 %
C <sub>6</sub> H <sub>5</sub> H <sub>5</sub> C <sub>6</sub>	11.0 g. <sup>a</sup> 60. %	7.1 g. 32.7 %	10.4 g. 54.5 %	7.4 g. 32.7 %	6.1 g. 77.0 %	5.5 g. 27.6 %
C <sub>6</sub> H <sub>5</sub> OH	1.53 g. .0 %	.35 g. .0 %	.85 g. .0 %	3.4 g. Note d	.6 g. .0 %	.3 g. .0 %
Remarks	:Note a : Small : amt. of: :Azoben- : zene:	: Small : amt. of: :  :Note b	: Note c	:	:	:Note e :Note f

NOTES ON TABLE I

(a). The number of grams listed in each experiment is the total quantity of compound obtained from the reaction mixture. The percentage yield, however, is not calculated on the basis of this number of grams because both diphenyl and phenol are present in the phenylmagnesium bromide solution. The quantity of diphenyl present in an ether solution of phenylmagnesium bromide prepared in the usual way was found to be approximately 0.6 g. per .1 mole  $C_6H_5MgBr$ ; using this figure as a basis for calculations the quantity of diphenyl present in the Grignard solution used was deducted from the quantity isolated before figuring the percentage yield. The percentage yields were calculated on the basis that one mole of nitroso compound produced one mole of diphenylamine and one mole of diphenyl thus:



Example: In experiment III, page 9, 10.7 g. (0.1 mole)  $C_6H_5N=O$  reacting with 0.3 mole  $C_6H_5MgBr$  produced 10.4 g.  $C_6H_5H_5C_6$ . There was present at the start in the 0.3 mole of  $C_6H_5MgBr$ , 2 g.  $C_6H_5H_5C_6$  (determined by analysis of an aliquot). Then,

$$\frac{(10.4 - 2.) 100}{15.4} = 54.5\% \text{ yield of diphenyl.}$$

Likewise, about 0.15 g. phenol per 0.1 mole  $C_6H_5MgBr$  is also present at the start. This quantity of phenol is

increased somewhat depending on the conditions under which the reaction is carried out. Blank runs under the specific conditions of the experiment were made to determine the exact quantity of phenol resulting from oxidation.

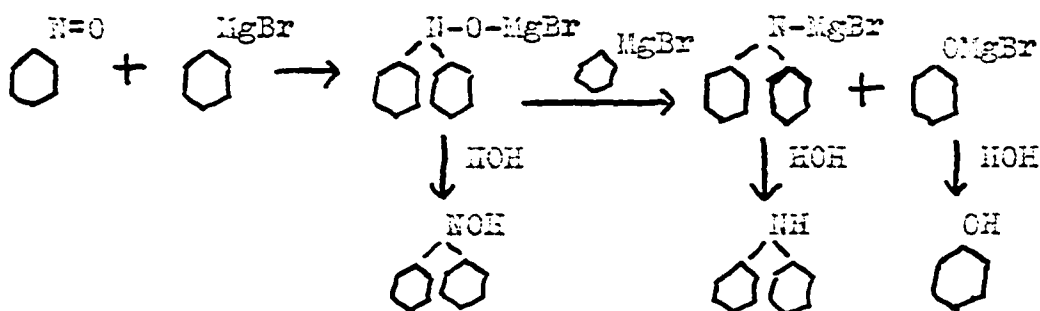
- (b). The lower yields in this experiment are no doubt due to the removal of the oil which was hoped would yield crystalline  $(C_6H_5)_2NOH$ .
- (c). The diphenyl was tinged slightly red due to azobenzene but sufficient quantity was not present to make separation advisable.
- (d). See page 5 for a discussion concerning the phenol.
- (e). A small amount of p-phenyldiphenyl was separated from the fraction which passed over immediately following the main fraction of diphenyl. There was probably a small amount present in all of the runs.
- (f). The nitrosobenzene used in all of the experiments except No. V was obtained from the Eastman Kodak Company and was purified by vacuum sublimation.

#### DISCUSSION

In all of the experiments on nitrosobenzene the end products have been diphenylamine and diphenyl, when the reaction goes to completion. If only one equivalent of phenylmagnesium bromide reacts a-a-diphenylhydroxylamine,  $(C_6H_5)_2NOH$ , is obtained. Small amounts of azobenzene as a side product are ob-

tained in each case. Small amounts of phenol have been obtained but this has been shown to result from the exposure of the RMgX to oxidation under the conditions of the experiments. It has been shown that nitrosobenzene reacts with three equivalents of phenylmagnesium bromide; furthermore that  $(C_6H_5)_2NOH$  which results from its reaction with one equivalent reacts with three equivalents of  $C_6H_5MgBr$ , the first equivalent quite probably forming  $(C_6H_5)_2NOMgBr$  which is the compound resulting also from the action of one equivalent of  $C_6H_5MgBr$  on  $C_6H_5NO$ , and the second and third equivalents going to form  $(C_6H_5)_2NH$  and  $(C_6H_5)_2$ .

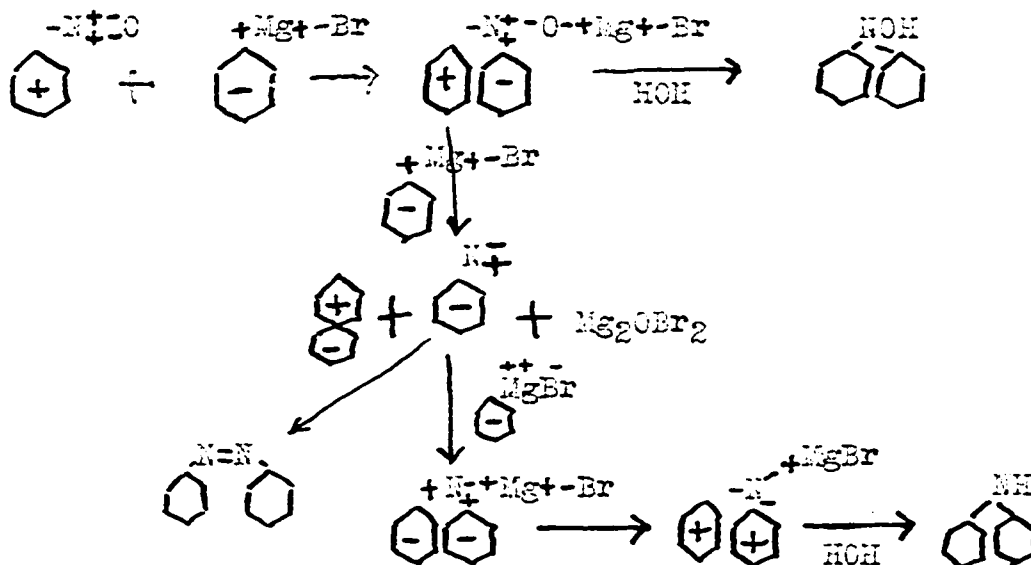
Consequently, the following course of the reaction as suggested by Wieland and Roseau<sup>1</sup> does not appear plausible:



This scheme reacts only two moles of  $C_6H_5MgBr$  with one of  $C_6H_5NO$ ; it makes no provision for the large quantity of diphenyl isolated in every case; and the quantity of phenol isolated from the reaction mixture is no more than occurs in a blank run from the phenylmagnesium bromide without using the nitrosobenzene. Furthermore, diphenylhydroxylamine which is the product of the first step in the reaction reacts with three equivalents of  $C_6H_5MgBr$  forming diphenylamine and diphenyl.

It appears that the nitroso group behaves as a negative group, orienting, on halogenation and nitration, to the ortho and para positions<sup>5</sup>. From this we might write the structure of nitrosobenzene as  $\text{C}_6\text{H}_5\text{-N}^+\text{=O}^-$  in which the nitrogen atom has a positive valence of two and a negative valence of one.

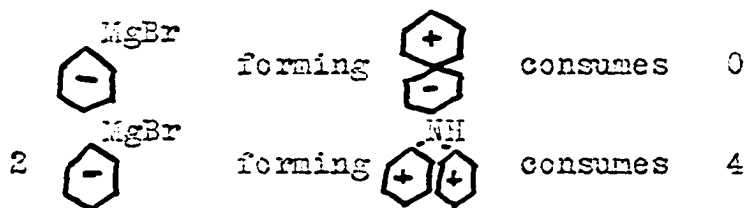
The reaction<sup>6</sup> might then be written:



In diphenylamine the nitrogen atom no doubt has a negative valence of three ( $-\text{N}^-$ ). Then in the transformation of nitrosobenzene to diphenylamine the nitrogen atom shows a drop in valence of four from ( $-\text{N}^+$ ) to ( $-\text{N}^-$ ). In bringing about this transformation with  $\text{C}_6\text{H}_5\text{MgBr}$  three moles are required which consume this change of four in valence of the nitrogen atom thus:



5. Ingold, J. Chem. Soc. 127, 515 (1925).
6. In this connection it is noted that Stieglitz and Curme, Ber. 46, 911-20 (1913) and Curme, J. Am. Chem. Soc., 35, 1145-75 (1913) have postulated the radical  $\text{PhN}$  and its condensation to  $\text{PhN=NPh}$ .



REACTION OF p-NITROSO-DIMETHYLANILINE AND  
PHENYLMAGNESIUM BROMIDE

First Run. In order to try a different and more stable nitroso compound with RMgX, p-nitroso-dimethylaniline ( $p\text{-(CH}_3\text{)}_2\text{N-C}_6\text{H}_4\text{N=O}$ ) was treated with phenylmagnesium bromide ( $\text{C}_6\text{H}_5\text{MgBr}$ ).

p-Nitroso-dimethylaniline (15 g., 0.1 mole) was treated in the usual way with phenylmagnesium bromide. The reaction mixture gave no test for excess RMgX after the addition of  $2\frac{1}{2}$  equivalents but after 3 equivalents continued to give a test even after 48 hours.

The reaction mixture was decomposed with dil. HCl, the ether layer separated, the water (acid) layer then treated with  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{OH}$  and then extracted with ether which extract was added to the first ether layer. This combined ether layer was then extracted with NaOH in order to remove the phenol. The phenolic extract was lost by accident.



The ether layer was then dried with  $\text{Na}_2\text{SO}_4$  and dry HCl passed in whereupon a large precipitate of amine hydrochloride came down. The precipitate was black and tarry. The ether was poured off from this precipitate and evaporated, leaving

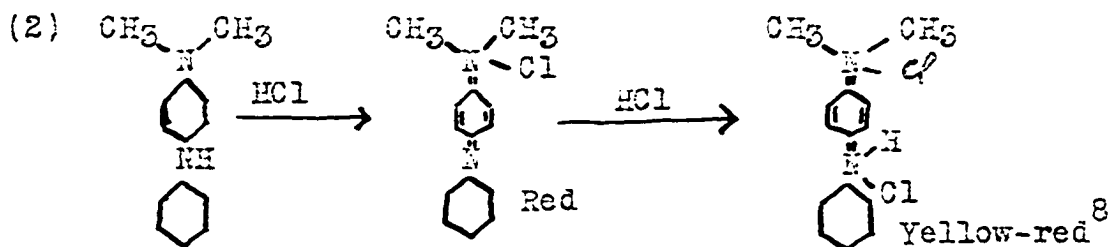


a residue which on being distilled yielded 5.6 g. (24.7%) of diphenyl, m.p. 69-70°.

The precipitate of amine hydrochloride was treated with NaOH solution, extracted with ether, which was evaporated off and the residue vacuum distilled:

F<sub>1</sub> -- 220-230°/10 mm. -- 5.6 g. (tarry)  
 F<sub>2</sub> -- 230-260°/7 mm. -- 2. g. (tarry)  
 F<sub>3</sub> -- Residue 6.3 g.

It was believed that Fraction 1 contained the amine, p-(CH<sub>3</sub>)<sub>2</sub>N  NH ; it was left in an ice box (temperature -1°) for one week but did not crystallize. It gave the following color tests for the amine:



Attempts at crystallization from various solvents have not yet yielded the material in a crystalline form.

REACTION OF p-NITROSO-DIMETHYLANILINE AND  
 PHENYLMAGNESIUM BROMIDE

Second Run. (At the Boiling Point of Ether). Due to the loss of the phenol fraction in the previous run (it was expe-

7. Fisher and Walker, Ber. 21, 2612 (1888).  
 8. Piccard, Jean, Ber. 46, 1845 (1913).

cially desired to determine whether any considerable amount of phenol was formed) a second run was made. Also, due to the low yield of the diphenyl (24.7%) and to the character of the amine fraction it was believed that the reaction had not gone to completion. Accordingly the reaction was carried out with refluxing of the ether.

Fifteen grams (0.1 mole) of the nitroso compound were treated with 3 equivalents of  $C_6H_5MgBr$  and refluxed in ether for 40 hours. The reaction mixture showed excess  $MgK$  present. The mixture was decomposed with water, the ether layer separated and extracted with  $NaOH$  to remove the phenol which was separated as tribromophenol yielding 1.01 g., equivalent to .29 g. phenol. This amount of phenol compares with the amount originally present in the  $MgK$  showing that phenol is not a reaction product.

The ether layer was dried over night with  $H_2SO_4$  and dry  $HCl$  passed in whereupon the solution was very pink at first. A black, tarry precipitate of amine hydrochloride came down. The ether layer was poured off and the diphenyl obtained from it amounted to 4.2 g. (27.3% yield, m.p.  $68-9^\circ$ , b.p.  $250-5^\circ$ ).

The amine hydrochloride was treated with  $NaOH$ , extracted with ether and sublimation attempted but this failed. Steam distillation was next tried but this also failed. The entire product was then vacuum distilled boiling at  $190-290^\circ/3$  mm. dissolved in  $C_2H_5OH$  and crystallization awaited. Up to the present time the material has produced only an intractable oil.

REACTION OF p-NITROSO-DIMETHYLANILINE AND  
PHENYLMAGNESIUM BROMIDE

Third Run. (In Boiling Toluene). The previous run having failed to give a good yield of diphenyl and of the amine this run was made in boiling toluene. Fifteen grams (0.1 mole) of the R-N=O compound were treated with two equivalents of  $C_6H_5MgBr$  in ether. The reaction mixture gave no test for excess  $RMgX$ . A third equivalent of  $C_6H_5MgBr$  was then added and the ether boiled off on a steam bath and then 200 cc. of dry toluene added and refluxed for 8 hours. The reaction mixture then gave no test for excess  $RMgX$ . It was decomposed with  $H_2O$ , the toluene layer separated and extracted with  $NaOH$  to remove the phenol which was separated as the tribromophenol giving 2.5 g. equivalent to .71 g. phenol.

The toluene layer was then extracted with 1:3  $HCl$  to remove the amine. The solution turned very red, indicative of the amine,  $p-(CH_3)_2N-C_6H_4-NHC_6H_5$ . A tarry substance separated in the bottom of the  $HCl$  extract. This was perhaps amine hydrochloride and was treated with  $NaOH$  and extracted with ether, the ether evaporated and alcohol added in the hope of obtaining crystalline amine but the material gave only a thick oil.

The red  $HCl$  layer was treated with iced  $NaOH$  solution. A compound separated and was filtered out. It gave a red color on treatment with  $HCl$ ; it was very black, tarry and leather-like. Attempts at crystallization from various solvents produced only tarry material.

The toluene layer after extraction of the basic material yielded 3.4 g. (22%) of diphenyl, melting at 69-70°.

REACTION OF p-NITRO-DIMETHYLANILINE AND PHENYL-  
MAGNESIUM BROMIDE

p-Nitro-dimethylaniline, p-(CH<sub>3</sub>)<sub>2</sub>N-C<sub>6</sub>H<sub>4</sub>-NO<sub>2</sub>, (16.6 g., 0.1 mole) was dissolved in 500 cc. of warm toluene and treated with 4 equivalents (0.4 mole) of C<sub>6</sub>H<sub>5</sub>MgBr and stirred for 6 hours. The reaction mixture was then decomposed with H<sub>2</sub>O, the toluene layer separated and extracted with 25% KOH to remove the phenol which was separated as the tribromophenol, 15.4 g. equivalent to 4.4 g. (47.9%) phenol, being obtained.

The toluene layer was then extracted with three 100 cc. portions of 1:1 HCl. A large amount of black, tarry material separated and stuck to the sides of the flask. This was separated, dissolved in and washed from the flask with acetone, the acetone evaporated, the residue treated with NaOH, extracted with ether, the ether evaporated and the residue vacuum distilled, boiling at 210-60°/3 mm. The distillate weighed 5.6 g. Attempts at crystallization have yielded only an intractable oil.

The acid extract was neutralized with NaOH whereupon a precipitate of perhaps p-(CH<sub>3</sub>)<sub>2</sub>N-C<sub>6</sub>H<sub>4</sub>-NHC<sub>6</sub>H<sub>5</sub> came down. It was filtered out and unsuccessful attempts made to crystallize it.

The toluene layer was then evaporated and 5 g. (32.5%) of diphenyl, C<sub>6</sub>H<sub>5</sub>-H<sub>5</sub>C<sub>6</sub>, b.p. 250-55°, obtained.

SUMMARY OF EXPERIMENTS ON p-NITROSO-DIMETHYLANILINE AND p-NITRO-DIMETHYLANILINE

TABLE II

No. & Pg.	Compound Used	Grams and Moles of Comp.	Moles of $C_6H_5MgBr$	Products Obtained and Yields		
				$C_6H_5OH$	Amine	$C_6H_5H_5O_6$
1 & 22	p-( $CH_3$ ) <sub>2</sub> N· $C_6H_4$ ·N=O (in ether)	15. g. : .1 mole	.3	lost : --	5.6 <sup>a</sup> : 26.4%	3.8 : 24.7%
2 & 23	p-( $CH_3$ ) <sub>2</sub> N· $C_6H_4$ ·N=O (in boiling ether)	"	"	.29 <sup>b</sup> : -- <sup>b</sup>	-- <sup>a</sup> : --	4.2 : 27.3%
3 & 25	p-( $CH_3$ ) <sub>2</sub> N· $C_6H_4$ ·N=O (in boiling toluene)	"	"	.71 <sup>c</sup> : --	-- <sup>a</sup> : --	3.4 : 22.1%
1 & 26	p-( $CH_3$ ) <sub>2</sub> N· $C_6H_4$ ·NO <sub>2</sub> (in toluene)	16.6 g. : .1 mole	4	4.4 : 47.9%	5.6 <sup>a,e</sup> : --	5. : 32.5%

NOTES ON TABLE II

- a. Believed to be p-( $CH_3$ )<sub>2</sub>N· $C_6H_4$ ·NHC<sub>6</sub>H<sub>5</sub> from color reactions but has not yet crystallized.
- b. This amount of phenol compares with that originally present so that none came from the reaction.
- c. This larger amount of  $C_6H_5OH$  is probably due to refluxing in toluene.
- d. Compound was not very soluble in ether.
- e. Does not include all fractions.

DISCUSSION

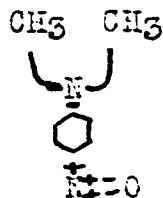
All of these runs give rather unsatisfactory results in the following sense:

- (1) The amine (if formed) is apparently formed in poor yield together with much tarry side reaction or decomposition product. The amine<sup>7</sup> is reported as yielding needles from ligroin, m.p. 130°.
- (2) The yield of diphenyl is much lower than that obtained from nitrosobenzene.

However, the results do show that phenol is not a reaction product from the nitroso group and that the nitro group gives phenol equivalent to only one of its oxygen atoms. Altho the amines from both the p-nitro- and p-nitroso-dimethylaniline have not yet crystallized they are of the same character. The amount of diphenyl is also about the same in each of these cases.

It is again noted that the only apparent difference between the nitroso and nitro group is that the nitro group yields in addition phenol equivalent to one of its oxygen atoms.

If an explanation is sought for the difference in reaction between nitrosobenzene and p-nitroso-dimethylaniline it must be remembered that (1) nitrosobenzene is rather unstable (2) is very easily oxidized to nitrobenzene (3) is not formed from nitrous acid and (4) shows peculiar orientation. The different properties of p-nitroso-dimethylaniline make it possible that its difference may be due to its different nitroso group. This difference might be expressed thus:



THE REACTION OF ORGANOMAGNESIUM HALIDES WITH AROMATIC NITRO-COMPOUNDS

Comparatively few studies have been made on the action of the Grignard reagent on nitro-compounds, and in those which have been made considerable difference in the end products and in the course of the reaction has been reported.

Moureu<sup>9</sup> obtained  $\beta$ - $\beta$ -diethylhydroxylamine by the action of ethylmagnesium iodide on amyl nitrite and nitroethane. Bewad<sup>10</sup> studied the action of alkylzinc and alkylmagnesium iodides on nitrous acid esters and on nitro-paraffins. He found that the zinc alkyl usually employed in the preparation of  $\beta$ -dialkylhydroxylamines can be advantageously replaced by zinc or magnesium alkyl iodides when nitrous acid esters are used but not when nitroparaffins are used. With the nitro-paraffins the reaction follows two courses, the RMgX adding to the enolic form of the nitro-compound in two ways, producing in each case a  $\beta$ -dialkylhydroxylamine, the one containing only one alkyl group derived from the RMgX used, the other containing two.

Iocitsch<sup>11</sup> treated phenylacetylenemagnesium bromide with nitrobenzene in ethereal solution and found that a compound was formed which, when decomposed with water, yielded a hydrocarbon of the formula  $C_{16}H_{10}$  and melting at  $87-88.5^{\circ}$ . The constitution of the hydrocarbon was not determined. We have repeated this

9. Moureu, Compt. rend. 132, 837 (1901).

10. Bewad, Ber. 40, 3065 (1907).

11. Iocitsch, J. Russ. Phys. Chem. Soc. 35, 555 (1903).

experiment and found that the hydrocarbon was, no doubt, diphenyl-di-acetylene,  $C_6H_5C\equiv C-C\equiv C\cdot C_6H_5$ , m.p.  $88^\circ$ .

Oddo<sup>12</sup> investigated the action of ethylmagnesium iodide on nitrobenzene. He found that upon the cautious addition of nitrobenzene to a well cooled ether solution of ethylmagnesium iodide, a yellow compound,  $C_6H_5N(O)(Et)OMgI$ , was precipitated, but on the further addition of nitrobenzene the precipitate suddenly became dark brown. The yellow compound gave with pyridine an additive compound  $C_8H_{10}O_2NMgI\cdot C_5H_5N$  and also, when decomposed with water, gave ethylaniline and a red uncrystallizable oil, with an odor suggestive of almonds. This oil was not investigated beyond separating it into three fractions.

Pickard and Kenyon<sup>13</sup> in a short note give the results of some preliminary experiments on the action of organomagnesium halides on aromatic nitro-compounds. They state that p-nitrotoluene reacts very vigorously with organomagnesium halides in ether solution forming an indefinite amorphous yellow compound which, when treated with acids, yields principally p-nitrosotoluene, p-tolyhydroxylamine, p-p'-azoxytoluene (probably by the interaction of the two former compounds), and p-toluidine. This note has never been followed with the details.

Nitrosyl chloride<sup>14</sup> ( $NOCl$ ) vapors on being passed into phenylmagnesium bromide and the additive product decomposed with

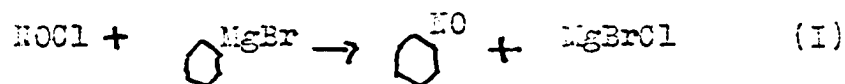
12. Oddo, Atti. R. Accad. Lincei 1904 (V) 13 ii 220. J. Chem. Soc. 1904, I, 862.

13. Pickard and Kenyon, Pro. Chem. Soc. 23, 153 (1907).

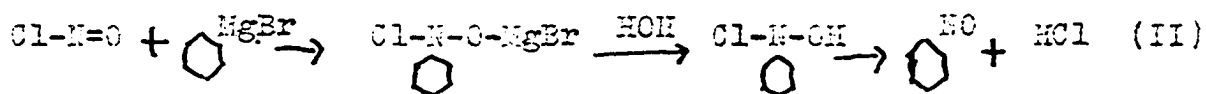
14. Oddo, Gazz. chim. ital. 39, I, 659-61. C. A. 5, 686 (1911).



water yielded nitrosobenzene. The most obvious representation,

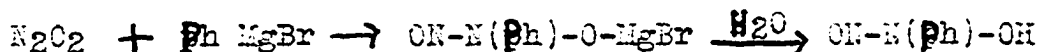


of this reaction, and as given by Odde, is probably not the correct one because the nitrosobenzene as formed would react readily with the unused phenylmagnesium bromide. Perhaps the mechanism may be expressed in this manner:



In this connection also it may be noted that nitroxyl chloride ( $\text{NO}_2\text{Cl}$ ) and nitroxyl bromide<sup>15</sup> ( $\text{NO}_2\text{Br}$ ) reacting with phenylmagnesium bromide do not yield nitrobenzene as might be expected by reasoning from analogy to  $\text{NOCl}$  thru reaction I. It yielded, however, diphenyl and chlorobenzene, or bromobenzene.

Nitric oxide<sup>16</sup> on being passed into phenylmagnesium bromide forms an additive product and appears to act as if it were dimolecular,  $\text{N}_2\text{O}_2$ , yielding after decomposition with water,  $\beta$ -phenylnitrosohydroxylamine thus:



Nitrogen dioxide<sup>17</sup> ( $\text{NO}_2$ ) yielded  $\beta$ - $\beta$ -diethylhydroxylamine ( $(\text{C}_2\text{H}_5)_2\text{NOH}$ ) with ethylmagnesium iodide but with phenylmagnesium bromide did not yield the expected diphenylhydroxylamine  $\text{Ph}_2\text{NOH}$  but yielded phenol and unidentified material.

15. Zuskiné, Bull. soc. chim. 57, 187 (1925). C. A. 19, 1245 (1925).

16. Sand and Singer, Ann. 329, 190-4 (1903).

17. Wieland, Ber. 36, 2315-19 (1903).

More recently Hepworth<sup>18</sup> has investigated the action of methylmagnesium iodide and ethylmagnesium bromide on the simple mononitro-aromatic compounds: nitrobenzene, o- and p-nitrotoluenes, and a-nitronaphthalene. In his experiments, the Grignard compound was not prepared separately, but a mixture of nitro-compound and alkyl halide, diluted with ether, was added drop by drop to well cooled ether containing magnesium powder, the rate of addition of magnesium powder being such as to keep the magnesium in excess throughout the reaction. In this way it was found that the rate of the reaction between the nitro-compounds and the Grignard reagents could be controlled fairly easily, provided that the flask in which the reaction was carried out was cooled in ice.

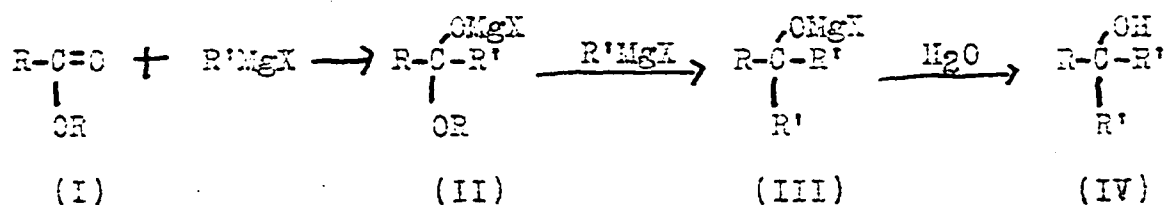
Hepworth, using nitrobenzene and methylmagnesium iodide or EtMgI, confirmed the existence of compounds corresponding with the compound,  $C_6H_5N(O)O-MgI$ , reported by Oddo (loc. cit.). It is said that these compounds are pale yellow and are best formed when the ratio of nitro-compound to alkylmagnesium halide is about two to three; on keeping for a few hours they become dark brown especially if the temperature is allowed to rise. On decomposing the yellow additive compound with water, methylaniline (or ethylaniline), and azobenzene, together with unchanged nitrobenzene were reported to be the principal products of reaction.

18. Hepworth, J. Chem. Soc. 117, 1004 (1920).

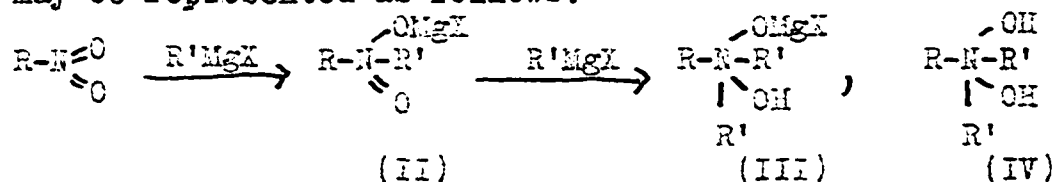


to II is known, so it is impossible to speak with any degree of certainty as to its behavior. At the same time, the loss of oxygen from such a compound is no more remarkable than the loss of carbon dioxide in the conversion of the simple monocarboxylic acid into the corresponding hydrocarbon, the more so if one accepts, what is probably the case, that compound II is very unstable and just as likely to lose oxygen as compound III is to lose water. In either case compound II must lose oxygen prior to its conversion into ethylaniline. The production of the other secondary bases may be accounted for in an analogous manner.

"It is now necessary to account for the formation of azo-compounds without postulating the formation of nitroso-compounds or hydroxylamine derivatives during the course of the reaction. In this connection it is interesting to compare the action of excess of Grignard reagent with the esters of the simpler carboxylic acids and with the aromatic nitro-compounds. In the former case the course of the reaction is as follows:



"In the case of the aromatic nitro-compounds, the reaction may be represented as follows:



"Two molecules of III may be condensed with the primary production of one molecule of an azo-compound and four molecules of  $Mg(OR)Br$ , or, on the addition of water, a compound of the type IV may be momentarily formed, two molecules of which lose four molecules of alcohol to give an azo-compound. At the same time, the intermediate formation of a compound such as the latter would be expected to give rise eventually to a dialkyl-aniline oxide."

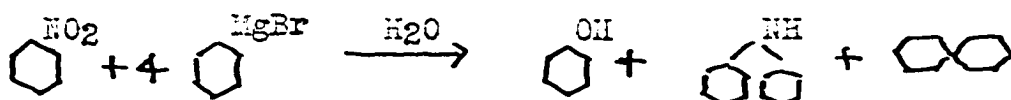
Neither of these proposed mechanisms of the reaction appears to represent the entire course of the reaction because:

- (1) The mechanism for the formation of the base represents only one molecule of  $RMgX$  reacting with one molecule of nitro-compound to form the amine; and represents only two molecules of  $RMgX$  reacting with one of nitro-compound to form azo-compound. Then under conditions in which both amine and azo-compound are formed, one mole of nitrobenzene would always consume less than two moles of  $RMgX$ . Experimental evidence shows that four moles of  $RMgX$  react with one of nitro-compound.
- (2) Neither mechanism takes into consideration the formation of R-R compound which is always obtained from the reaction in large quantity whether an aliphatic or aromatic Grignard compound is used. Nor can the presence of this R-R compound be attributed to its formation as a side product in the Grignard reaction altho a small quantity is so formed. The Grignard reagent was prepared separately and the quantity of R-R

as well as the  $\text{RMgX}$  present in it determined. The quantity obtained from the reaction mixture is many times as much as is present in the Grignard reagent solution. In those reactions in which the R-R compound is a gas large quantities are evolved during the course of the reaction with the nitro-compound.

(5) Oddo's mechanism makes no provision for the formation of ROH—alcohol or phenol as the case may be. Hepworth's mechanism links its formation with the formation of azo-compound. Large quantities of ROH are found when the quantity of azo-compound is quite small.

The reaction of phenylmagnesium bromide on nitrobenzene and subsequent treating with water may be summarized in the following way:



This, no doubt, in this case and in similar cases represents the main course of the reaction altho some side products are formed. However with different  $\text{RMgX}$  compounds considerable difference is noted. For example with benzylmagnesium chloride N-N'-di-benzyl-N-N'-di-phenyl-hydrazine,  $(\text{C}_6\text{H}_5 \cdot \text{CH}_2)(\text{C}_6\text{H}_5) \text{N}-\text{N}'-(\text{C}_6\text{H}_5)(\text{CH}_2\text{C}_6\text{H}_5)$ , is formed.

It also appears that the reaction does not proceed in well defined steps producing intermediates which are increasingly resistant to attack by  $\text{RMgX}$  but on the contrary these intermediates are more susceptible to attack than the nitro-compound. When an

insufficient amount of  $\text{RMgX}$  to complete the reaction is added to a quantity of nitro compound, small amounts of all of the end products of the reaction are isolated together with unattacked nitro compound.

It should be remembered that the conditions both as to temperature and quantity of reacting constituents used by Oddo and by Hepworth are different from those used in these experiments which fact may not entirely exclude the possibility of the correctness of the former.

#### EXPERIMENTAL

##### REACTION OF NITROBENZENE WITH PHENYLMAGNESIUM BROMIDE

The nitrobenzene (24.6 g., 0.2 mole) was dissolved in 200 cc. of dry ether in a 1-l. three-necked flask fitted with a mechanical stirrer, a reflux condenser and a dropping funnel. Phenylmagnesium bromide,  $\text{C}_6\text{H}_5\text{MgBr}$ , in ether solution was added dropwise with stirring and the reaction mixture was cooled with running water. Four-tenths (0.4) moles of  $\text{C}_6\text{H}_5\text{MgBr}$  were added within one hour after which a small portion of the reaction mixture when removed gave no test<sup>19</sup> for  $\text{RMgX}$ ; 0.2 moles more  $\text{C}_6\text{H}_5\text{MgBr}$  (making three equivalents) were added and the reaction mixture gave no test for  $\text{RMgX}$  for 5 hours; 0.1 mole more was added and the reaction mixture then showed no excess  $\text{C}_6\text{H}_5\text{MgBr}$  after 12 hours; another 0.1 mole was added and this reacted

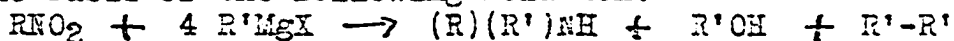
19. Gilman and Schulze, J. Am. Chem. Soc. 47, 2002 (1925).

within 24 hours. The total quantity of  $C_6H_5MgBr$  added was approximately 0.8 moles, 4 equivalents, and the total time of the reaction was 42 hours. Previous experiments had shown that the addition of more  $C_6H_5MgBr$  than this amount produced an excess which always remained.

The reaction mixture was then decomposed by the addition of 300 cc. of 1:1 HCl. The ether layer was separated and extracted with two 100 cc. portions of 10% NaOH in order to remove the phenol. The combined NaOH layer was acidified with HCl and the phenol extracted with ether and distilled, 15.5 g. (76.3)<sup>20</sup> boiling at 180-2°, being obtained.

The ether layer was then dried for 3 hours with  $Na_2SO_4$ , filtered and dry HCl passed into it in order to precipitate the diphenylamine as the hydrochloride. The crude hydrochloride was filtered out and the amine set free by treatment with NaOH solution. The amine was then extracted with ether and purified by vacuum distillation, boiling at 176-8°/20 mm. and melting at 50°. When mixed with pure diphenylamine the material melted at 52°. The yield was 19.5 g. (57.7%).

20. The number of grams listed is the total number of grams isolated from the reaction mixture. The percentage yield however is not calculated on this listed number of grams because the  $C_6H_5MgBr$  solution used contained approximately 0.6 g. diphenyl and 0.15 g. phenol per 0.1 mole  $RMgX$ . These amounts, both of diphenyl and phenol, per 0.1 mole of  $RMgX$  used were deducted from the total number of grams isolated before calculating the percentage yield. The yields were calculated on the basis of the following relation:





The ether filtrate from the hydrochloride precipitate, containing the diphenyl, etc., was then evaporated and the residue distilled:

Fraction I -- 240-75°	-- 25.5 g.	m.p. 63-7°
Fraction II -- 275°/740 mm. to 250°/30 mm.		9.2 g.
Residue		4. g.

Fraction I was redistilled and the diphenyl boiling at 252-6° collected. This fraction weighed 21 g. and melted at 69-70°. The residue was added to Fraction II both dissolved in benzene and dry HCl again passed into the solution to make sure that the amine was completely removed. No precipitate came down. The benzene was evaporated and the residue vacuum distilled:

Fraction I -- 120-60°/7 mm.	--	4.5 g.
Fraction II -- 160-200°/7 mm.	--	6.2 g.

Fraction I on crystallization from alcohol yielded 3 crops of diphenyl which together weighed 2 g. Fraction II on crystallization from alcohol yielded 1 g. of p-phenylbiphenyl, p-C<sub>6</sub>H<sub>5</sub>·C<sub>6</sub>H<sub>4</sub>·C<sub>6</sub>H<sub>5</sub>, m.p. 203. The residues from these crystallizations were combined and fractionally steam distilled whereupon 1.5 g. of diphenyl were obtained. The total quantity of diphenyl, C<sub>6</sub>H<sub>5</sub>·H<sub>5</sub>C<sub>6</sub>, obtained was 24.5 g. (64.%)<sup>20</sup>.

## THE REACTION OF o-NITROTOLUENE WITH PHENYLMAGNESIUM BROMIDE

A reaction analogous to this one has been carried out by Hepworth<sup>18</sup> who treated the ortho and para nitrotoluenes with ethylmagnesium bromide (the ethylmagnesium bromide being prepared in the presence of the nitrotoluene however) and obtained ethyl toluidine (approximately 20% yield) and azotoluene.

In the present experiment the phenylmagnesium bromide was prepared separately and its strength estimated and then a known quantity added to the nitro compound with stirring and refluxing. The following products, with their percentage yield, were obtained: o-tolyl-phenyl-anine 59.5%, diphenyl 72.7%, phenol 74.5%, p-phenyl-diphenyl .5 g., (and a residue, very tarry and not distillable under 300° at 3 mm., 5.4 g.).

The o-nitrotoluene (13.7 g., 0.1 mole) was placed in a three-necked flask fitted with a stirrer, dropping funnel, and reflux condenser, and 100 cc. of dry ether added. The ether solution of phenylmagnesium bromide was added dropwise and at the same time the air was kept swept out of the flask by a current of pure dry hydrogen. The addition of the Grignard reagent produced a vigorous reaction giving sufficient heat to boil the ether rapidly. However, after the addition of two molar equivalents the reaction was no longer vigorous nor was much heat produced. During its addition small amounts of the reaction mixture were removed at intervals and tested for the presence of excess phenylmagnesium bromide.

After the addition of approximately four molar equivalents (0.4 mole) it did not show an excess of phenylmagnesium bromide but after the addition of .6 mole and at the end of 48 hours an excess was present. The ether was then evaporated off and replaced with benzene which was then refluxed for 24 hours but at the end of this time the reaction mixture still yielded a test for excess phenylmagnesium bromide.

The reaction mixture was then decomposed with 200 cc. of 1:1 HCl and extracted with ether. The ether layer was then extracted with 200 cc. of 10% NaOH to remove the phenol. This NaOH extract was acidified and brominated whereupon 27.8 g. of tribromophenol, equivalent to 7.9 g. of phenol, were obtained. Yield<sup>20</sup>, 74.5%.

The ether layer was then dried with  $\text{Na}_2\text{SO}_4$ , the ether and benzene evaporated and the residue vacuum distilled.

Fraction I	--	125-50°/3 mm. (most at 125°)	24. g.
Fraction II	--	150-225°/3 mm.	4.3 g.
Fraction III	--	225-90°/3 mm.	2. g.
Residue			5.4 g.

Fraction I was dissolved in alcohol and about 13 g. of diphenyl crystallized out. The mother liquors were oily and would not yield more crystals even on cooling with ice. The alcohol was evaporated off and replaced with dry ether and then dry hydrogen chloride bubbled into this whereupon about 10 g.

of o-tolyl-phenyl-amine hydrochloride precipitated. This was filtered out, the ether evaporated off and the small residue distilled. It was almost entirely diphenyl.

Fraction II on crystallizing from alcohol yielded 0.5 g. of p-phenylbiphenyl melting after two crystallizations at 203° (205°). The alcohol was replaced with dry ether and dry HCl bubbled into the solution in order to precipitate the amine hydrochloride, which was filtered out, and then the filtrate added to fraction III.

Fraction III dissolved in ether, was treated with HCl as above and a small additional amount of the amine hydrochloride obtained. The mother liquor was evaporated and about 2 g. of an intractable oil remained.

The combined precipitates of amine hydrochloride were treated with NaOH solution, the free phenyl-o-tolylamine extracted with ether, dried with  $\text{MgSO}_3$  and vacuum distilled boiling at 204°/15 mm. Yield 10.8 g. (59.3%).

The total quantity of diphenyl obtained was 14.8 g. which after deducting 3.6 grams originally present in the phenylmagnesium bromide solution is a yield of 72.7%.

#### REACTION OF p-NITROTOLUENE WITH PHENYLMAGNESIUM BROMIDE

One-tenth mole (13.7 g.) of p-nitrotoluene was treated as in the previous experiment with an excess (.6 mole) of phenylmagnesium bromide in ether solution with stirring, and during the latter part of the reaction, with heating on a steam bath.

The reaction mixture was decomposed by the addition of 300 cc. of 1:1 HCl, the ether layer separated and extracted with NaOH solution to remove the phenol. This extract was acidified and the phenol brominated and separated as tribromophenol, 27.8 g. equivalent to 7.9 g. phenol, being obtained. Yield<sup>20</sup>, 74.5%.

The ether layer was then dried with Na<sub>2</sub>SO<sub>4</sub> and dry HCl passed in to precipitate the phenyl-p-toluidine hydrochloride but it came down in such a tarry condition that it seemed inadvisable to separate it. Consequently the free amine was liberated by the addition of NaOH solution and the ether layer separated, dried and, after removal of the ether, vacuum distilled.

Fraction I	up to 140°/3 mm. ....	18.5 g. m.p. about 62°
Fraction II	140-200°/3 mm. ....	10.3 g. m.p. about 80-3°
Fraction III	200-250°/3 mm. ....	1.8 g.
Fraction IV	Residue .....	5.1 g.

Fraction I was dissolved in ether and HCl passed into it. A small amount of amine hydrochloride precipitated and was filtered out. The filtrate was evaporated and yielded 16.6 g. of diphenyl. Yield, after deducting 3.6 g. originally present and adding 1 g. obtained later on was 14 g. (90.9%).

Fraction II was dissolved in ether and HCl passed in as above. A large amount of amine hydrochloride was precipitated. This was filtered out and added to that obtained from fraction I, the two weighing 11.6 g. This was treated with NaOH solution

and the free amine extracted with ether and vacuum distilled boiling at  $215^{\circ}/15$  mm. and melting at  $87^{\circ}$ . The yield was 6.7 g. (47.5%).

The ether filtrate from the hydrochloride precipitate was evaporated and left a residue of about 2 grams. This was distilled and 1 gram of diphenyl obtained. The residue was added to fraction III which was dissolved in ether and dry HCl passed in but only a very small amount (.2 g.) of amine hydrochloride was thrown down which was very black and tarry and was discarded. The ether was evaporated and replaced with alcohol, from which about 1 gram of p-phenyldiphenyl crystallized which after a second crystallization melted at  $203^{\circ}$ .

THE REACTION OF o-NITROTOLUENE WITH AN INSUFFICIENT QUANTITY OF  
PHENYLMAGNESIUM BROMIDE

In an effort to isolate, if possible, intermediate products in the reaction of the Grignard reagent upon nitro compounds, o-nitrotoluene was allowed to react with insufficient quantities of phenylmagnesium bromide to carry the reaction to normal completion. No way was found possible to stop the reaction at an intermediate stage.

It seems that once a nitro-compound molecule is attacked the reaction on this proceeds to completion before another nitro group is attacked. As the quantity of RMgI was decreased all of the reaction products continued to be produced altho in decreasing amount, and the quantity of unattacked nitro com-

pound increased. However, there was a rather sharp decrease in the quantity of diphenyl.

One-tenth mole (13.7 g.) portions of o-nitrotoluene were allowed to react in the usual way with .3 mole, with .2 mole and with .1 mole of phenylmagnesium bromide and the reaction mixture worked up in the customary manner. The quantities of the products isolated in each case are listed in the following table.

TABLE III<sup>20</sup>

REACTION OF o-NITROTOLUENE WITH VARYING AMOUNTS OF PHENYLMAGNESIUM BROMIDE

Moles of $C_6H_5MgBr$ Used	: 0.6	: 0.3	: 0.2	: 0.1
Moles of o- $CH_3 \cdot C_6H_4 \cdot NO_2$	: 0.1 13.7 g.	: 0.1 13.7 g.	: 0.1 13.7 g.	: 0.1 13.7 g.
Grams of o- $CH_3 \cdot C_6H_4 \cdot NO_2$ Recovered	: .0	: .0	: 2.7 g. 19.7%	: 7.5 g. 54.7%
Obtained Grams and % $C_6H_5OH$	: 7.9 74.5%	: 7.86 78.8%	: 4.97 49.7%	: 3.52 55.9%
o- $CH_3 \cdot C_6H_4 \cdot NH$ $C_6H_5$	: 10.8 59.5%	: 9.7 53.5%	: 4.4 24.5%	: 2.2 12.5%
$C_6H_5 \cdot C_6H_5$	: 14.8 72.7%	: 4.7 18.8%	: 3.7 16.2%	:
p- $C_6H_5 \cdot C_6H_4 \cdot C_6H_5$	: .5	: .1	:	:

THE REACTION OF NITROBENZENE, BROMOBENZENE AND MAGNESIUM IN  
ETHER SOLUTION

The experiments of Hepworth<sup>18</sup> on the reaction of ethyl bromide (and methyl iodide) and magnesium on nitrobenzene were carried out at low temperatures, the Grignard compound being formed in the presence of the nitro compound and yielding the secondary amine ( $C_6H_5NH C_2H_5$ ) and azobenzene.

Our recent experiments in which the organomagnesium halide was prepared separately and added to the nitro compound without external cooling did not yield azobenzene. Accordingly, it was undertaken to determine whether this was due to the formation of the  $RMgX$  in the presence of the nitro compound.

Three attempts were made to carry out the present reaction in the cold ( $-15^{\circ}$ ) as Hepworth did with nitrobenzene, ethyl bromide and magnesium but in all cases (even with activated magnesium) the reaction did not proceed after being cooled. This may be due to the lesser activity of bromobenzene with magnesium and to the peculiar sensitiveness of the reaction. The low temperature conditions having failed the reaction was consequently carried out without cooling under which condition it proceeded smoothly.

Eight-tenths (0.8) moles of bromobenzene and 0.8 moles of magnesium reacting on 0.2 moles of nitrobenzene produced 9.5 g. (28.1%) of diphenylamine, 8.8 g. (46.8%) of phenol, 19.7 g. (64.3%) of diphenyl, .5 g. of p-phenyldiphenyl, and .5 g. of aniline, but no azobenzene.



A three-necked flask was equipped with a stirrer, reflux condenser, dropping funnel and a tube for passing pure dry hydrogen thru the flask. There was placed in the flask 19.4 g. magnesium. Then about 25 cc. of dry ether and 5 cc. of bromobenzene were added and the Grignard reaction started. The remainder--after removing the above mentioned 5 cc.--of the 125.6 g. (0.8 mole) of bromobenzene was mixed with 24.6 g. (0.2 mole) of nitrobenzene and 400 cc. of dry ether and added dropwise. A vigorous reaction ensued causing refluxing of the ether. The mixture of bromobenzene, nitrobenzene and ether was added within three hours and the contents of the flask then refluxed for two hours and finally decomposed with 400 cc. of saturated  $\text{NH}_4\text{Cl}$  solution. The ether layer was separated and extracted with  $\text{NaOH}$  solution to remove the phenol which was brominated to tribromophenol yielding 31.1 g. equivalent to 8.8 g. phenol.

The ether layer was then dried with  $\text{Na}_2\text{SO}_4$  and  $\text{HCl}$  gas passed in whereupon an abundant precipitate of hydrochloride was thrown down. The ether solution was poured off from this and the precipitate treated with  $\text{NaOH}$  solution and the free diphenylamine extracted with ether and vacuum distilled. After removal of the ether,

Fraction I	up to $140^\circ/2$ mm. ....	.5 g. (liq.)
Fraction II	$140-80^\circ/2$ mm. ....	9. g. m.p. $50-1^\circ$
Fraction III	$180-225^\circ/2$ mm. ....	1.3 g. (tarry)
Fraction IV	Residue .....	6.2 g.

Fraction I yielded the color test for aniline with  $\text{CaOCl}_2$  but no derivative was prepared. Fraction II was practically pure diphenylamine melting at  $50-1^\circ$ .

The ether after the removal of the amine was evaporated and the residue vacuum distilled:

Fraction I	--	110-30 <sup>o</sup> /1 mm. ....	18.7 g. m.p. 67-9 <sup>o</sup>
Fraction II	--	130-200 <sup>o</sup> /1 mm. ....	3.1 g. tarry
Fraction III	--	Residue .....	13.6 g.

Fraction I was practically pure diphenyl. Fraction II on crystallization from alcohol yielded an additional 1 gram of diphenyl and about .5 g. of p-phenyl-diphenyl melting at  $203^\circ$ .

All solutions throughout were very black and tarry indicating decomposition products perhaps  $(\text{C}_6\text{H}_5)_2\text{NCH}$  and its decomposition and condensation products.

This method of carrying out the reaction possesses some inherent disadvantages which make it unsatisfactory. It is not possible to tell just how much organomagnesium halide takes part in the reaction nor how much diphenyl is formed in the Grignard reaction alone under these conditions. Also the finely divided magnesium may have some reducing action.

It should be noted here that no unchanged nitrobenzene was recovered while Hepworth reports the recovery of unchanged nitro compound. However he usually used only from  $1\frac{1}{2}$  to 2 moles of  $\text{RM}$  per mole of nitro compound.

## PREPARATION OF PHENYL- $\alpha$ -NAPHTHYLAMINE

This experiment was made as an application of the reaction to the preparation of certain secondary amines. It is believed that this method compares favorably with the other methods of preparation.

Friedländer<sup>21</sup> prepared phenyl- $\alpha$ -naphthylamine by heating for 9 hours at 280°,  $\alpha$ -naphthol (1 mole), aniline (2 moles) and CaCl<sub>2</sub> (1 mole). The reaction mass was treated with dilute HCl, extracted with NaOH, steam distilled and the distillate crystallized from petroleum ether and then from alcohol. The yield was 26.3%, m.p. 60°.

Girard and Vogt<sup>22</sup> prepared the product by heating  $\alpha$ -naphthylamine with aniline hydrochloride at 240°; Streiff<sup>23</sup> prepared it by heating  $\alpha$ -naphthylamine hydrochloride with aniline; Knoevenagel<sup>24</sup> used iodine as a catalyst in its preparation from  $\alpha$ -naphthylamine, aniline and iodine<sup>25</sup>.

Katayama<sup>26</sup>, in working over the methods of Friedländer<sup>21</sup> and of Streiff<sup>23</sup>, with a view to improving the yield, found Friedländer's the better of the two. He found that by heating the materials for 10 hours at 300° in an autoclave  $\alpha$ -naphthylphenylamine was produced in 64% yield. His improved method

21. Friedländer, Ber. 16, 2077 (1883).

22. Girard and Vogt, Jahresbericht, 1871, 718, Bull. soc. chim. 18, 68

23. Streiff, Ann. 209, 152.

24. Knoevenagel, J. fur Prakt. Chem. (2) 89, 3, 14, 17, 20, C, 1914 I, 392.

25. D. R. P. 241853. C, 1912 I, 178.

26. M. Katayama, J. Chem. Ind. Tokyo 20, 553 (1917).

is: Heat *a*-naphthol (1 mole), aniline (2 moles) and calcium chloride (1 mole) in an autoclave at 300° for 10 hours. Treat the reaction product with H<sub>2</sub>O to remove the CaCl<sub>2</sub>, with HCl to remove the aniline, with NaOH to remove the *a*-naphthol and vacuum distill the crude product in a current of H<sub>2</sub> or CO<sub>2</sub>.

By the reaction of phenylmagnesium bromide on *a*-nitronaphthalene, phenyl-*a*-naphthylamine was obtained in a 35.0% yield, melting point 60°. Altho this yield is low no doubt it could be greatly improved and the product obtained is quite good.

#### Procedure

*a*-Nitronaphthalene (17.3 g., 0.1 mole) was dissolved in 100 cc. of dry ether contained in a three-necked flask fitted with a stirrer, reflux condenser and a dropping funnel. Phenylmagnesium bromide (.7 mole) was added thru the dropping funnel within the course of 1.5 hours. The reaction mixture became very dark. It was allowed to stand overnight and then decomposed by the addition of a small amount of water. The ether layer was separated, dried with Na<sub>2</sub>SO<sub>4</sub> and dry HCl passed into the solution whereupon 14.3 g. of amine hydrochloride were precipitated. This was filtered out, treated with NaOH solution, extracted with ether, the ether evaporated and the amine vacuum distilled, boiling at 240°/25 mm. After crystallization from petroleum ether a beautiful product was obtained melting at 60°. Yield 7.8 g., 35.6%.

## DISCUSSION OF THE REACTION WITH NITROBENZENE

An inspection of the preceding data shows that the only difference in the end products obtained from nitrosobenzene and nitrobenzene is that the nitro compound yields phenol equivalent to one oxygen atom from the nitro group. The yields of amine and diphenyl are practically the same in each case. From this and from the close relationship of the nitro to the nitroso group it appeared that the nitro group when reacting with  $\text{MgH}$  might pass thru the nitroso (or potential nitroso) stage. Several attempts have been made to obtain nitroso compound from nitro but so far without success. However, the experiments have not been exhaustive. In this connection it is interesting to note that nitrosobenzene is not obtained from nitrobenzene by direct reduction. Also that  $\text{HOCl}$  with  $\text{C}_6\text{H}_5\text{MgBr}$  yields nitrosobenzene<sup>14</sup> while  $\text{NO}_2\text{Cl}$  with  $\text{C}_6\text{H}_5\text{MgBr}$  does not yield nitrobenzene<sup>15</sup> but yields diphenyl and chlorobenzene.

### ATTEMPTS TO PREPARE NITROSOBENZENE FROM NITROBENZENE AND PHENYLMAGNESIUM BROMIDE

One-half mole (61.5 g.) of nitrobenzene was treated with one mole of  $\text{C}_6\text{H}_5\text{MgBr}$ . The reaction mixture was decomposed with dilute  $\text{HCl}$  and the ether layer separated and extracted with  $\text{NaOH}$  to remove the phenol of which 17.7 g. were obtained.

The ether was then evaporated and the residue subjected to steam distillation whereupon 18 g. of unchanged nitrobenzene

were obtained. There was no indication of nitrosobenzene.

The yield of phenol on the basis of the nitrobenzene that reacted was 53.2%. From this and from the several experiments with o-nitrotoluene it appears that the formation of phenol occurs in an early stage of the reaction.

Several other attempts were made to obtain nitrosobenzene by varying both the ratio of nitrobenzene to  $\text{RMgI}$  and also the temperature. Runs were made both with and without cooling. After the slow addition of the  $\text{C}_6\text{H}_5\text{MgBr}$  the reaction mixture was decomposed with dilute  $\text{HCl}$  and the entire amount steam distilled. In no case was the green vapor of nitrosobenzene observed but in one run the nitrobenzene passing over had a faint green color.

Thinking that the failure to obtain nitroso compound may have been due, in part, to the instability of nitrosobenzene, we then attempted to prepare a more stable one, namely, p-nitrosodimethylaniline. p-Nitrosodimethylaniline (16.6 g., 0.1 mole) in benzene solution was treated with one-tenth mole of  $\text{C}_6\text{H}_5\text{MgBr}$  as above. The reaction mixture was decomposed with  $\text{H}_2\text{O}$ , turning very red, the ether-benzene layer separated and extracted with  $\text{NaOH}$  to remove the phenol. The ether-benzene layer was then cooled in an ice-salt bath whereupon 7.8 g. (47%) of unchanged p-nitro-dimethylaniline crystallized out. The mother liquor was then steam-distilled. The organic matter was extracted from the distillate with ether. This ether solution was then extracted with dilute  $\text{HCl}$  in order to separate the

nitroso compound, if present, from the diphenyl. On treating this acid extract with NaOH solution and crystallizing the precipitated product only p-nitrodimethylaniline was obtained.

THE REACTION OF PHENYLACETYLENEMAGNESIUM BROMIDE  
AND NITROBENZENE

INTRODUCTION

Iocitsch (loc. cit.) treated phenylacetylenemagnesium bromide with nitrobenzene and reported the formation of an unidentified hydrocarbon of the formula  $C_{16}H_{10}$  melting at 87-88.5°.

His experiment was repeated with only the express object of showing that this compound was, no doubt, di-phenyl-di-acetylene,  $C_6H_5C\equiv C-C\equiv C-C_6H_5$ .

Phenylacetylene,  $C_6H_5C\equiv CH$ , was prepared by heating beta-bromostyrene,  $C_6H_5CH=CH-Br$ , with solid KOH<sup>27</sup>. The phenylacetylene (10.2 g., 0.1 mole) was run slowly with warming and stirring into 0.1 mole of  $C_2H_5MgI$  in order to form the phenylacetylene iodide. The ethane was given off slowly and at the end of the reaction there were two layers. Then nitrobenzene (12.5 g., 0.1 mole) was run slowly into this with stirring for five hours. The reaction mixture was then decomposed with dilute HCl, extracted with ether and the ether layer steam-distilled. The ether passed over quickly and then 8.6 g. (weighed after subsequent fractionation) of unchanged nitrobenzene and then 1 g. of  $C_6H_5C\equiv CHI$  (m.p. 76°). (Identified by mixed melting point

27. Hessler, J. Am. Chem. Soc. 44, 425-6 (1922).

of an authentic specimen prepared according to the method of Peratoner<sup>28</sup>). This latter compound was produced from the small excess of phenylacetylene that remained and the iodine present due to decomposition. From the residue which now remained in the distilling flask there was crystallized from dilute alcohol about 2 g. of di-phenyl-di-acetylene,  $C_6H_5C\equiv C-C\equiv C-C_6H_5$ , m.p.  $88^\circ$ . This compound was identified by the picrate m.p.  $108^\circ$ .

#### REACTION OF NITROBENZENE WITH BENZYL MAGNESIUM CHLORIDE

Since the reaction of nitrobenzene with phenylmagnesium bromide had yielded phenol, diphenylamine and diphenyl it was believed that the reaction of nitrobenzene with benzylmagnesium chloride,  $C_6H_5CH_2MgCl$ , would yield benzyl alcohol,  $C_6H_5CH_2OH$ , benzylaniline,  $C_6H_5NHCH_2C_6H_5$ , and dibenzyl,  $C_6H_5CH_2CH_2C_6H_5$ . However, the reaction, at least under the conditions used, did not appear to proceed in a manner exactly analogous to the reaction of nitrobenzene and phenylmagnesium bromide. Among the products a large amount of benzaldehyde was produced for which at first no satisfactory explanation could be offered. It was conjectured that this might be due to an oxidizing action of the nitrobenzene. Accordingly, it was proposed that the use of a tertiary compound, ter-butylmagnesium bromide,  $(CH_3)_3C \cdot MgBr$ , would avoid the possibility of this oxidizing action, and that the secondary amine, ter-butylaniline, would then be obtained.

28. Peratoner, Gazz. chim. ital. 22 (2) 69. J. Chem. Soc. 64, (1) 18 (1893).



However, the results of the reaction of nitrobenzene with  $(\text{CH}_3)_3\text{C}\cdot\text{MgBr}$  threw no light at all on the formation of benzaldehyde because even in this case ter-butylaniline was not obtained nor was ter-butyl alcohol or the coupling product, di-ter-butyl,  $(\text{CH}_3)_3\text{C}\cdot\text{C}(\text{CH}_3)_3$ . This failure may have been due to the apparently unstable nature of  $(\text{CH}_3)_3\text{C}\cdot\text{MgBr}$ . It was then proposed to determine whether nitrobenzene acting on isopropylmagnesium bromide would produce the oxidation product, acetone. Acetone was not produced and it was then concluded that the explanation of the formation of benzaldehyde must be sought in some other point. Work was then resumed on the reaction of benzylmagnesium chloride with nitrobenzene. After some experiments it was determined that along with the much tarry, decomposition and condensation products the rather unstable substance, N-N'-dibenzyl-N-N'-diphenyl hydrazine,  $(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_5\text{CH}_2)$  N-N'  $(\text{CH}_2\text{C}_6\text{H}_5)(\text{C}_6\text{H}_5)$  was produced and that this under the conditions of working up the reaction mixture, reacted with water to produce the benzaldehyde, aniline and benzylaniline.

Following is a description of these experiments made and worked up in a manner in accordance with the belief that benzyl alcohol, benzylaniline and dibenzyl would be produced. Following these is an experiment in which the tetra-substituted hydrazine was obtained and in which it was shown that this hydrazine reacting with water was producing the benzaldehyde whose presence in the former experiments was unexplained.

EXPERIMENTAL

Nitrobenzene (49.2 g., 0.4 mole) was dissolved in 200 cc. of ether, cooled with an ice-salt mixture and 1.1 moles  $C_6H_5CH_2MgCl$  added slowly with stirring over 4 hours. The reaction mixture was then stirred for an additional hour. The mixture was decomposed with dilute HCl. Three layers separated. Each layer was steam-distilled and fractions collected.

Top layer (ether). Oil passed over having the odor of benzaldehyde.

Middle layer (thought to be amine·HCl). This was steam-distilled from the acid medium and a small amount of oil passed over. It was then made alkaline with NaOH and the steam distillation continued but only a small amount of oil passed over.

Water layer. Was made alkaline and steam-distilled. Only a small amount of oil passed over.

All oily fractions that appeared and smelled like benzaldehyde were combined and fractionated:

Fraction I -- up to 150

Fraction II -- 150 to 185 -- 15. g.

Fraction III -- 185 to 245

Fraction II boiled mostly at  $170-80^{\circ}$  and smelled like benzaldehyde. It gave a color with Schiff's reagent and a precipitate with phenylhydrazine which melted at  $155^{\circ}$ . Therefore it contained benzaldehyde.

Fraction III was probably a mixture of benzaldehyde, possibly benzyl alcohol, and dibenzyl.

All steam distillate fractions which appeared like dibenzyl were combined and fractionated, yielding 18 g. (gross yield 22.7%) dibenzyl,  $C_6H_5-CH_2-CH_2-C_6H_5$ , m.p.  $50-2^\circ$ .

Second Experiment. Nitrobenzene with Benzylmagnesium Chloride.

Nitrobenzene (49.2 g., 0.4 mole) was treated with 1.6 moles of  $C_6H_5CH_2MgCl$ . The reaction mixture was cooled with running water. After 6 hours the mixture was decomposed with water, the ether layer separated, dried with  $Na_2SO_4$  and dry HCl passed in to precipitate the amine. A tarry precipitate came down. The ether layer was poured off and petroleum ether (b.p.  $40-60^\circ$ ) added to it whereupon more tarry precipitate, thought to be amine hydrochloride, came down. More HCl was then passed in, and the ether-petroleum ether layer poured off.

The supposed amine hydrochlorides were treated with NaOH and extracted with ether, the ether evaporated and the residue vacuum distilled:

Fraction I	--	100-150 <sup>o</sup> /20 mm.	--	18.4 g.
Fraction II	--	150/20-200/12 mm.	--	19.7 g. (possibly $C_6H_5NHCH_2C_6H_5$ )
Fraction III	--	200/12-260/4 mm.	--	24.6 g.
Fraction IV	--	Residue	--	39.5 g.

Fraction I was redistilled and the portion boiling at  $194-214^\circ$  collected (13.8 g.). From this boiling point it was thought that this fraction might contain some benzyl alcohol carried down with the hydrochloride precipitate. A portion on oxidation with  $KMnO_4$  yielded benzoic acid; however on treatment with phe-

nylisocyanate,  $C_6H_5NCO$ , no entirely satisfactory derivative could be obtained.

Fraction II was redistilled and the portion boiling from  $270-315^\circ$  (thought to be benzylaniline,  $C_6H_5NHCH_2C_6H_5$  (b.p.  $298-300^\circ$ )) collected and put in petroleum ether to crystallize but no crystalline material could be obtained.

The ether layer containing the dibenzyl and supposedly the benzyl alcohol was then distilled at atmospheric pressure:

Fraction I	-- up to 150	-- mostly petroleum ether
Fraction II	-- 150-240	-- should contain $C_6H_5CH_2OH$ if present
Fraction III	-- 240-290	-- 35.7 g. (dibenzyl)
Fraction IV	-- 290-335	-- 4.6 g. (unknown) m.p. $75-80^\circ$
Fraction V	-- Residue	-- 4.2 g.

Fraction II was redistilled and the portion boiling near  $200^\circ$  collected. This may have contained some benzyl alcohol. The residue was added to fraction III which was distilled and the portion boiling from  $250-90^\circ$  collected. Practically all boiled at  $272-5^\circ$  (uncor.). (Known dibenzyl boiled at  $273^\circ$ ). This portion weighed 31.8 g., m.p.  $52^\circ$ . Mixed melting point with known dibenzyl  $52^\circ$ . Yield 43.7%.

Fraction IV, b.p.  $290-335^\circ$ , was combined with the residue left after distilling the dibenzyl, and dissolved in petroleum ether. Crystals separated which melted at  $110^\circ$ . Further crystallization brought the melting point to  $115^\circ$ . A mixed melting point showed the compound to be identical with the uniden-

tified compound obtained in small amount by Gilman and Beaber<sup>29</sup> from practically all of the reactions of benzylmagnesium chloride and alkyl esters of p-toluenesulfonic acid. This compound is not p-benzylidibenzyl<sup>30</sup>,  $p\text{-C}_6\text{H}_5\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\text{C}_6\text{H}_5$ , which would correspond to p-phenyldiphenyl,  $p\text{-C}_6\text{H}_5\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_5$ , obtained from the reaction of nitrobenzene and phenylmagnesium bromide. A mixed melting point also showed the compound to not be p-ditolyl,  $p\text{-p-CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{CH}_3$ .

THE REACTION OF NITROBENZENE, BENZYL CHLORIDE AND MAGNESIUM  
IN ETHER SOLUTION

The magnesium (1.6 moles) was placed in the 3-necked flask with the usual set-up and about 5 cc. of benzyl chloride (taken from 223 g., 1.6 moles) and 5 cc. of ether added and the Grignard reaction allowed to start. The remainder of the benzyl chloride and 49.2 g. (0.4 mole) of nitrobenzene were mixed with 500 cc. of ether and run in slowly, at the same time the flask being cooled with an ice-salt bath. The mixture of benzyl chloride and nitrobenzene in ether was added over a period of four hours and then allowed to stand overnight. The reaction mixture then gave a very faint test for  $\text{RMgX}$ . The small amount of unused magnesium was filtered out and the reaction mixture decomposed with dilute HCl. The whole was then steam-distilled.

29. Gilman and Beaber, J. Am. Chem. Soc. 47, 525, note f (1925).  
30. Fuson, J. Am. Chem. Soc. 48, 2941 (1926).

After removal of the ether an oil passed over at first and later a solid having the appearance of dibenzyl.

The organic layers were extracted from the water distillate with ether, the ether evaporated and the residue distilled:

Fraction I	--	160-90°	--	30. g.
Fraction II	--	190-240°	--	10. g.
Fraction III	--	Residue	--	(solid) (dibenzyl)

Fractions I and II had the odor of benzaldehyde and benzyl chloride. They were combined and treated with 40% NaHSO<sub>3</sub> solution and the addition product, C<sub>6</sub>H<sub>5</sub>CHO·NaHSO<sub>3</sub>, precipitated, 17.5 g. equivalent to 8.8 g. benzaldehyde being obtained. The benzyl chloride was distilled, yielding 19 g. free from benzaldehyde and benzyl alcohol.

The dibenzyl fractions were distilled:

Fraction I	--	260-80°	--	m.p. 45-50°
Fraction II	--	280-300°	--	m.p. 50-60°

Fraction I was redistilled and collected at 275-80°, 30.3 g. melting at 51-2° being obtained. The residue was added to fraction II and dissolved in ligroin. Large long crystals separated which melted at 95-105° and after a second crystallization brought the melting point to 115-17°. A mixed melting point showed the compound to be identical with the unidentified compound obtained in the previous experiment and by Gilman and Beaber<sup>29</sup>. Further concentration of the mother liquor gave 2 g.

dibenzyl melting at  $52^{\circ}$ . The total yield of dibenzyl was 32.3 g. (44.6%).

After the steam distillation a black, oily material remained in the flask, and was insoluble in the water. The mixture was made alkaline and steam-distilled but only a small amount of oil passed over. The steam distillation was given up as unsatisfactory and the material extracted with ether, which was evaporated and the residue vacuum distilled:

Fraction I	-- up to $100^{\circ}/5$ mm.	-- 5. g.
Fraction II	-- $100-200^{\circ}/5$ mm.	-- 14. g.
Fraction III	-- $200-80^{\circ}/5$ mm.	-- 15.1 g.
Residue	-----	30. g.

Fraction I had the odor of aniline. It boiled, however, on redistillation at  $190-215^{\circ}$ . It gave a hydrochloride from ether solution which melted at  $185^{\circ}$ ; with bromine water a precipitate melting at  $95^{\circ}$ ; with acetic anhydride a compound melting at  $175^{\circ}$ . The compound is yet unidentified.

Fraction II was redistilled:

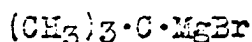
Fraction I	-- $205-340^{\circ}$ (most at $225-30^{\circ}$ )	-- 10 g.
Residue	-----	4 g.

Fraction I on being cooled gave a yet unidentified crystalline compound melting at  $110^{\circ}$ .

The reaction did not yield a fraction which appeared promising to yield benzylaniline as was expected but gave a large

amount of tarry and apparently decomposition material.

PREPARATION AND ANALYSIS OF ter-BUTYLMAGNESIUM BROMIDE



One hundred thirty-seven grams (1 mole) of ter-butyl bromide was mixed with 400 cc. of dry ether and run with stirring onto 24.5 g. Mg (one-half of which had been activated). The reaction went vigorously and was cooled with ice water. During the reaction a gas was given off which was passed into  $\text{Br}_2\cdot\text{CCl}_4$ , decolorizing it. A layer of liquid separated at the bottom of the  $\text{CCl}_4$ . On heating, the two layers went into solution. The  $\text{CCl}_4$  was fractionated and about 5 g. liquid boiling at  $145\text{-}153^\circ$  obtained, sp. g.  $1.762^{24^\circ}/20^\circ$ ,  $n_D 1.5088$ . These constants check those of  $(\text{CH}_3)_2\text{CH}\cdot\text{Br}\cdot\text{CH}_2\text{Br}$ , namely: B.p.  $148\text{-}9/735$  mm., sp. g.  $1.7981^{40^\circ}$ ,  $n_D$  (calculated)  $1.503$ .

After completion of the reaction the volume was brought up to 500 cc. with dry ether, 5 cc. samples removed and titrated for  $\text{RMgX}$ .

50 cc. HCl -- .1069N -- 26.9 cc. NaOH, 1038N)	24.6% yield
50 cc. HCl -- .1069N -- 27 cc. NaOH, 1038N)	of $(\text{CH}_3)_3\text{CMgBr}$

The unused Mg recovered was 8 g. This yield agrees reasonably well with that previously reported, 20.6%, by the authors<sup>31</sup>.

31. J. Am. Chem. Soc. 45, 2462 (1923).



REACTION OF NITROBENZENE AND ter-BUTYLMAGNESIUM BROMIDE,



Seven and four tenths grams (7.4 g.) of nitrobenzene were mixed with 200 cc. of dry ether in a 3-necked flask, and cooled with ice water. The  $(\text{CH}_3)_3\text{C}\cdot\text{MgBr}$  (0.25 mole) prepared in the previous run was run in slowly--the reaction mixture turned dark--and was allowed to stand overnight. It was then decomposed with 300 cc. 1:1 HCl, the acid layer separated, made alkaline with  $\text{NH}_4\text{OH}$  and extracted with ether to remove the oily layer. The ether was dried with  $\text{Na}_2\text{SO}_4$ , evaporated and the residue distilled:

Fraction I -- 200-225° ..... 1.5 g. (partly solid)

Fraction II -- Residue

Fraction I upon crystallization from ligroin (b.p. 60-80°) gave a small amount of an unidentified compound which melted at 148°. Since ter-butylaniline is a liquid boiling at 210° it is evident that it was not produced in this reaction.

The ether layer was then fractionated but did not yield either ter-butyl alcohol or di-ter-butyl,  $(\text{CH}_3)_3\text{C}\text{-C}(\text{CH}_3)_3$ . It gave about 10 g. of material boiling with decomposition at 40-115° and yielding a strong Beilstein test for halogen.

REACTION OF NITROBENZENE WITH iso-PROPYLMAGNESIUM BROMIDE

One mole (123 g.) of iso-propyl bromide was converted to the Grignard compound,  $(\text{CH}_3)_2\text{CHMgBr}$ . To this was added 24.6 g.

(0.2 mole) of nitrobenzene. After four hours the reaction mixture gave a faint test for excess  $\text{RMgI}$  but did not after standing overnight. The reaction mixture was then decomposed by the addition of water, the ether layer separated and treated with 200 cc. of 40%  $\text{NaHSO}_3$  solution to remove any acetone, if present; 1.7 g. of solid separated. If this were the addition product,  $(\text{CH}_3)_2\text{CO}\cdot\text{NaHSO}_3$ , it would be equivalent to only .61 g. acetone--a negligible amount. The  $\text{NaHSO}_3$  solution was then treated with  $\text{Na}_2\text{CO}_3$  and distilled. The temperature rose gradually to  $101^\circ$  when distillation was stopped. This distillate was redistilled and the temperature quickly passed  $56^\circ$  thus showing no acetone present. There was a slight pause near  $80^\circ$  showing the possibility of iso-propyl alcohol.

The ether solution containing the amine, the di-iso-propyl,  $(\text{CH}_3)_2\text{CH}\cdot\text{CH}(\text{CH}_3)_2$ , and possibly some iso-propyl alcohol was carefully fractionated:

Fraction I	-- up to $40^\circ$	-- ether
" II	-- 40-50	-- possibly ether and di-iso-propyl
" III	-- 50-75	-- " " " "
" IV	-- 75-80	-- " iso-propyl alcohol
" V	-- 80-200	-- small amount
" VI	-- 200-260	
" VII	-- 260-260/25	
" VIII	-- Residue	

It was believed that fraction VI would contain the amine,  $\text{C}_6\text{H}_5\text{NHCH}(\text{CH}_3)_2$ , b.p.  $212-3^\circ$ . It was redistilled and the frac-

tion boiling at 200-40° collected which in turn was redistilled:

Fraction I -- 200-20° ..... 5.4 g.  
" II -- 220-40° ..... 4. g.

Fraction I was soluble in HCl and yielded a negative carbamine test. It was too impure to yield a good derivative.

Fractions III and IV believed to contain the iso-propyl alcohol were combined with the alcohol fraction from the NaHSO<sub>3</sub> solution and fractionated but only ethyl alcohol (derivative, p-nitrobenzoate, m.p. 57°) was obtained. This, no doubt, came from the ether used in separating and extracting the organic layer from the water used in decomposing the reaction mixture.

Fraction II, page 64, believed to contain ether and di-isopropyl, (CH<sub>3</sub>)<sub>2</sub>CH·CH(CH<sub>3</sub>)<sub>2</sub>, was treated with concentrated H<sub>2</sub>SO<sub>4</sub> to separate the ether from it but the entire amount dissolved in the acid thus showing no di-isopropyl, b.p. 58°.

#### THE REACTION OF NITROBENZENE WITH BENZYL MAGNESIUM CHLORIDE TO YIELD *syn*-DIPHENYLDIBENZYLHYDRAZINE

One mole of benzylmagnesium chloride was prepared from 136 g. (1.08 moles) of benzylchloride and 26 g. of magnesium in ether solution in the customary way. To this, 30.8 g. (0.25 mole) of nitrobenzene were added dropwise with stirring and with cooling of the reaction flask by running water. The reaction mixture was allowed to stand overnight and was then de-

composed by the addition of 100 cc. of water. The ether layer was poured off from the solid basic magnesium bromide and the ether evaporated by blowing air over it. A dark oil remained. This had no odor of benzaldehyde nor did it give a precipitate with phenylhydrazine. The oil was vacuum distilled:

Fraction I	-- up to 100/10 mm. ....	4.0 g.	liquid
"	II -- 100-150/10 .....	40.7 g.	solid
"	III -- 150/10-200/5 .....	12.2 g.	liquid
"	IV -- 200-290/5 .....	29.7 g.	"
"	V -- Residue .....	7. g.	tar

Fraction I contained a small amount of moisture and after drying over  $\text{Na}_2\text{SO}_4$  was redistilled yielding 2.5 g. boiling at  $170-90^\circ$ . This material contained aniline as was shown by the fact that it gave a strong carbylamine test and with benzoyl chloride gave benzanilide, m.p.  $158-60^\circ$ , and with p-nitrobenzoyl chloride gave p-nitrobenzanilide, m.p.  $210^\circ$  ( $204^\circ$ ). The material did not contain benzaldehyde as was evidenced by its failure to yield a precipitate in 30% acetic acid with phenylhydrazine.

Fraction II, the greater part of which boiled at  $135-45^\circ/10$  mm., solidified on cooling and consisted mostly of dibenzyl. It was dissolved in dry ether and dry HCl passed in which precipitated a small amount (4 g.) of basic material. This was filtered out, the ether removed by evaporation and the remaining dibenzyl distilled, boiling at  $272-77^\circ$  and melting at  $50-2^\circ$ .

The yield was 31.5 g. After deducting from this amount 8.9 g. which is the amount estimated to have been formed during the Orignard reaction, the yield from the reaction was 22.6 g. (49.7%).

Fraction III was dissolved in dry ether and dry HCl passed in whereupon 4.5 g. (19% crude yield) of sym-diphenyldibenzylhydrazine hydrochloride,  $(C_6H_5)(C_6H_5CH_2)N-N(C_6H_5CH_2)(C_6H_5) \cdot 2 HCl$ , were precipitated. After crystallization from alcohol-HCl, the identity of this material was established by its melting point<sup>32</sup> 213° (215°) and by the fact that on refluxing with dilute acid it yielded<sup>32</sup> benzaldehyde (identified by the phenylhydrazone, m.p. 155°), aniline (identified by the tribromaniline, m.p. 119°) and benzylaniline (hydrochloride, m.p. 190-5°). Altho the free hydrazine boiled over a considerable range, with partial decomposition, this difficulty was also experienced by Wieland and Fressel<sup>33</sup>.

The ether-HCl filtrate from the hydrazine hydrochloride was evaporated and the residue distilled yielding 3 g. of material boiling at 250-90°. After 6 crystallizations from alcohol this yielded material melting at 115° which was identical as shown by a mixed melting point, with the corresponding material obtained from the other runs with benzylmagnesium chloride.

The material in Fraction IV was apparently such a mixture of decomposition and condensation products of the hydrazine that no compound could be separated from it.

32. Franzen and Zimmermann, Ber. 39, 2567 (1906).

33. Ann. 392, 150 (1912).

REACTION OF NITROBENZENE WITH ETHYLMAGNESIUM BROMIDE

It was believed that ethylmagnesium bromide reacting with nitrobenzene would produce sym-diethyl-diphenyl hydrazine,  $(C_6H_5)(C_2H_5)N-N(C_2H_5)(C_6H_5)$ , since benzylmagnesium chloride reacting with nitrobenzene had produced sym-dibenzyl-diphenyl hydrazine. This contention was borne out by experiment. However the isolation of sym-diethyl-diphenyl hydrazine was a rather difficult task on account of the ease with which it decomposes. It was necessary to vacuum distill the material at a pressure of 0.5 mm. or less and even then distillation was accompanied by much decomposition. Wieland<sup>34</sup> had previously experienced this difficulty and reported the material as boiling over a range and obtained only a small amount of pure material boiling at  $141^\circ/1$  mm. We find the material to boil at  $118-23^\circ/.5$  mm. or less. The product on refluxing with dilute HCl yielded acetaldehyde, aniline and ethylaniline as reported by Wieland<sup>34</sup> but would not yield the reported color reactions. This failure may perhaps be explained by the fact that Wieland prepared the hydrazine from the corresponding tetrazine which itself yields the reported color reactions.

Hepworth<sup>35</sup> treated nitrobenzene with ethyl bromide and magnesium in ether in the cold and reported the formation of ethylaniline and azobenzene under these conditions. On repeating this experiment we find that the alleged ethylaniline boils

34. Wieland and Fessel, *Ann.* 392, 133 (1912).

35. Hepworth, *J. Chem. Soc.* 117, 1004 (1920).

over a wide range, 200-70°. This may be due to the presence of the hydrazine and its decomposition products.

One-half mole (62.5 g.) of nitrobenzene was treated with 4 equivalents (2 moles) of ethylmagnesium bromide with stirring at room temperature for 4 hours. The reaction mixture was then decomposed with  $\text{NH}_4\text{Cl}$  solution, the ether layer separated, AND THEN EVAPORATED by passing a stream of air over it. The oily residue so obtained was then at once vacuum distilled at a very low pressure, 0.5 mm. or less.

Fraction I	--	80-115°	.....	14 g.
Fraction II	--	115-25° (most 118-23°)	....	9 g.
Fraction III	--	125-65°	.....	5 g.
Residue	--			

Fraction II contained the hydrazine,  $(\text{C}_6\text{H}_5)(\text{C}_2\text{H}_5)\text{N}-\text{N}(\text{C}_2\text{H}_5)(\text{C}_6\text{H}_5)$ , as was shown by the fact that on refluxing with dilute HCl, acetaldehyde (colored Schiff's reagent, also strong odor) was evolved and the acid solution yielded a strong carbonylamine test showing the presence of aniline.

ATTEMPT TO PREPARE TETRA-PHENYL HYDRAZINE FROM THE REACTION OF  
NITROBENZENE AND PHENYLMAGNESIUM BROMIDE

Since benzylmagnesium chloride and ethylmagnesium bromide had yielded hydrazines on reacting with nitrobenzene it was undertaken to determine whether under very careful procedure tetra-phenyl hydrazine,  $(C_6H_5)_2N-N(C_6H_5)_2$ , was formed and could be isolated from the reaction of nitrobenzene and phenylmagnesium bromide. On careful fractional crystallization of the products of the reaction no fraction was obtained indicative of tetra-phenyl hydrazine. Moreover the reaction mixture before any crystallization would not yield the color tests for the hydrazine<sup>36</sup>.

One-tenth mole (12.3 g.) of nitrobenzene in 100 cc. of dry ether was treated slowly with phenylmagnesium bromide (0.4 mole) with stirring at room temperature. The reaction mixture after standing overnight was decomposed with  $NH_4Cl$  solution the ether layer separated and extracted with  $NaOH$  solution in order to remove the phenol.

The ether layer was then dried over  $Na_2SO_4$  and evaporated somewhat by passing a stream of air over it. This solution did not give the color test<sup>36</sup> (green to reddish-violet on treatment with acetic acid and heat) for tetra-phenyl hydrazine. The solution was then cooled and crystals separated which were filtered out. The mother liquor was then further concentrated and

36. Wieland and Gambargan, Ber. 39, 1499 (1906).



a second crop of crystals obtained. This process was repeated until 6 different crops of crystals were obtained. Each of these crops of crystals melted lower than the melting point, 70°, of diphenyl and upon recrystallization proved to be a mixture of diphenyl and diphenylamine. After obtaining the 6 crops of crystals an oily residue remained which would not yield more crystalline material. This residue was treated in the cold with concentrated H<sub>2</sub>SO<sub>4</sub> in order to rearrange<sup>36</sup> any tetra-phenyl hydrazine, if present, to diphenyl benzidine, C<sub>6</sub>H<sub>5</sub>NHC<sub>6</sub>H<sub>4</sub>·C<sub>6</sub>H<sub>4</sub>NHC<sub>6</sub>H<sub>5</sub> which then could be separated as the hydrochloride from the diphenyl present and could be easily detected by its high melting point, 234°. After neutralizing the H<sub>2</sub>SO<sub>4</sub> with NaOH the organic material was extracted with ether, the ether dried and HCl passed into it. A hydrochloride precipitated which when filtered out and treated with NaOH yielded only diphenylamine and not diphenylbenzidine, thus showing that tetra-phenyl hydrazine was not present.

#### REACTION OF DIMETHYLANILINE OXIDE WITH PHENYLMAGNESIUM BROMIDE

Dimethylaniline oxide,  $\text{CH}_3 \overset{\text{O}}{\underset{\text{C}_6\text{H}_5}{\text{N}}}-\text{CH}_3$ , was prepared according to the method of Bamberger and Tschirner<sup>57</sup>. Two-tenths mole (27.4 g.) partially dissolved in 600 cc. of warm (40°) benzene was treated with C<sub>6</sub>H<sub>5</sub>MgBr, two equivalents (0.4 mole) reacting. The reaction mixture was decomposed with dilute HCl, the ether-

57. Ber. 32, 346 (1899).

benzene layer separated and extracted with NaOH to remove phenol which was then isolated as the insoluble tribromophenol, 12.55 g. equivalent to 3.56 g. phenol, being obtained. Yield, 19%.

The ether-benzene layer after the NaOH extraction was evaporated and the residue distilled yielding 8.6 g. diphenyl. Yield, (8.6 g. minus 2.6 g. originally present at start) 19.5%.

The water layer was purple. About 100 g. NH<sub>4</sub>Cl was added to it and then NH<sub>4</sub>OH until alkaline. The purple color was discharged and a very small amount (about 1 g.) of a solid compound separated which was easily soluble in HCl yielding a purple color. The alkaline solution was extracted with ether, the ether dried over Na<sub>2</sub>SO<sub>4</sub> and distilled yielding 2.5 g. of dimethylaniline, b.p. 192. Yield, 9.1%.

#### THE REACTION OF ETHYL NITRATE WITH PHENYLMAGNESIUM BROMIDE AT LOW TEMPERATURES

The reaction between ethyl nitrate and phenylmagnesium bromide was investigated with special reference to determining whether at very low temperatures (-60° to -100°) the first step in the reaction was as follows:



The chief concern was whether or not nitrobenzene was formed.

Kinhead<sup>38</sup> has previously studied this reaction at ice

38. Kinhead, R. W., Chem. News 122, 4-5 (1921); C. A. 15, 832.

temperatures and had reported the production of a blue solution, on extraction with  $\text{CHCl}_3$ , which had the properties of an indicator. The reaction of ethyl nitrate with other  $\text{RMgI}$  compounds had been studied by Hepworth<sup>39</sup> who found that using  $\text{CH}_3\text{MgI}$  there was produced  $(\text{CH}_3)_2\text{NOH}$  and using  $\text{C}_2\text{H}_5\text{MgBr}$ ,  $(\text{C}_2\text{H}_5)_2\text{NOH}$  was produced. The temperature was no lower than  $-15^\circ$ .

It seemed reasonable to believe that if the first step in the reaction were the formation of nitrobenzene this might be proven by using a large excess of ethyl nitrate and conducting the reaction at a very low temperature in order to prevent reaction with the nitrobenzene formed. However, the prediction was not borne out by experimental evidence since in no case was nitrobenzene obtained altho the temperature was exceedingly low ( $-100^\circ$  ?).

Phenylmagnesium bromide (0.2 mole) in ether solution was run dropwise into 0.3 mole of ethyl nitrate with stirring. The reaction flask was cooled in a slush of solid  $\text{CO}_2$  and acetone. During the first minutes of the addition the reaction mixture was dark colored and later a white precipitate appeared. At the end dilute  $\text{HCl}$  was added, the ether layer separated, dried and vacuum distilled.

The only products obtained were diphenyl and phenol which are products of the reaction with nitrobenzene.

The water layer was made alkaline and steam distilled but nothing passed over.

39. Hepworth, J. Chem. Soc. 119, 251-60.

A second run was made but with the same results.  $\text{BM}_2\text{X}$  was present at the end of one hour after addition thus introducing doubt as to whether the reaction had gone at the low temperature. A third and fourth run was made at  $-15^\circ$  and at  $0^\circ$  respectively but no nitrobenzene was formed.

## PART II

### STUDY ON ANTI-KNOCK MATERIALS.

#### THE PREPARATION OF TETRA-STYRYL LEAD, $(\text{C}_6\text{H}_5\cdot\text{CH}=\text{CH})_4\text{Pb}$ .

In connection with a series of studies being carried on by Dr. J. R. Sweeney and Dr. Henry Gilman on the effect of the structure of organo-lead compounds in suppressing the "knock" in internal combustion engines, it was deemed advisable to prepare tetra-styryl lead  $(\text{C}_6\text{H}_5\cdot\text{CH}=\text{CH})_4\text{Pb}$ . This would give a compound from which the effect of unsaturation might be determined.

Hidgley<sup>40</sup> has shown that tetra-ethyl lead has a pronounced influence even in very low concentration in suppression of gaseous detonation. He proposes the following hypothesis for the explanation of the detonation: There exists a critical pressure above which the combustion reaction proceeding through the gas must travel at the velocity of sound. When the transmission of chemical activity reaches this velocity, a condition called "detonation" is produced.

40. Hidgley, J. Eng. Chem. 14, 589, 849, 894 (1922).

Later Wendt<sup>41</sup> proposes the following explanation: "It is well known that all flames are highly ionized--that is, they are excellent carriers of an electric current. This means that the energy released in the reaction of the hydrocarbon with oxygen serves in part to liberate electrons from the reacting molecules. The advance of electrons propelled at high velocity from the flame front undoubtedly ionizes the molecules in the gaseous region just ahead of the flame. This ionization is tentatively regarded as the essential activation and the factor directly responsible for the increased acceleration of the flame. At high temperatures and high pressures, such as always obtain when detonation is excessive, the velocity of the liberated electrons is high and their energy is readily absorbed by the combustible gas. The rate of flame propagation therefore becomes extremely high. It is, then, the function of the antiknock molecules or, more particularly, the lead atoms present in the commonest example of antiknock, to attract these electrons, thus forming highly charged lead ions and preventing the former ready ionization of the unburned hydrocarbon."

Subsequently, Charch, Mack and Boord<sup>42</sup> in an extensive study of many different organolead compounds as well as other organometallic derivatives suggest that the following points are applicable:

41. Wendt and Grimm, J. Eng. Chem. 16, 890 (1924).

42. Charch, Mack and Boord, J. Eng. Chem. 18, 334 (1926).

- (1) The antiknock compound should have an appreciable vapor pressure below 400°.
- (2) Should decompose quickly on heating yielding the metal (lead) in the form of a very fine dust.
- (3) When the particles of a metal such as lead are liberated in the hot oxidizing atmosphere of the cylinder--for example, by the decomposition of lead tetraethyl--they would tend to undergo almost immediate oxidation. This immediate oxidation of the liberated metallic particles is assumed to be the third condition necessary to the functioning of the antiknock material. It is held that the nature of the oxidation of the antiknock material under the conditions of its operation and the influence of this oxidation upon that of the combustible cylinder gases are sufficient to account for its effect in causing a suppression of detonation of the fuel with which it is used.

"The very fine particles (or vapor) of the anti-knock metal are conceived as undergoing such rapid oxidation as to develop sufficient heat to raise them momentarily much above the temperature of the yet unburned gases in which they are present. There is thus created at a definite stage in the engine cycle a large number of centers, in and very close about which there is produced an abnormally high tempera-

ture. Such a condition would tend to cause a partial oxidation of the fuel rather homogeneously throughout its entire volume. The antiknock would thus function as a kind of auxiliary ignition system, tending to start oxidation of the fuel ahead of the actual flame front in a region of hot, highly compressed gases. These gases under other conditions would be chemically unchanged until the flame front had passed through them, or until their pressure and temperature had become great enough to cause their detonation."

Organolead compounds can be prepared in several ways:

- (1) Reaction of metallic lead with alkyl iodides<sup>43</sup>;
- (2) reaction of lead sodium alloys with organic halides<sup>44</sup>;
- (3) reaction of di-ethyl zinc and lead chloride<sup>45</sup>; (4) reaction of Grignard reagents with lead chloride<sup>46</sup>.

The first of these methods yields only very small quantities; the second is used on an industrial scale; the third is a bit expensive and inconvenient and the fourth finds application as an excellent laboratory method.

43. Cahours, Compt. Rend. 36, 1001 (1855); Ann. chim. 122, 67 (1862).

44. Löwig, Jour. Prakt. Chem. 60, 304 (1865).

45. Buckton, Proc. Roy. Soc. IX, 685 (1859); Ann. 109, 218 (1853).

46. Pfeiffer and Truskier, Ber. 37, 1125 (1904).

EXPERIMENTAL

One mole of styrylmagnesium bromide,  $C_6H_5CH:CH-MgBr$ , was prepared from two moles (366 g.) of beta-bromostyrene,  $C_6H_5CH:CHBr$ , and two moles (48.6 g.) of magnesium (estimated yield of  $RMgX$  about 50%). The excess magnesium was filtered from the Grignard solution and then one-half mole, (138.5 g.) of dry, finely ground  $PbCl_2$  added in small bits to it with stirring. A vigorous reaction took place and a dark precipitate separated. The reaction mixture was allowed to stand overnight after which it gave no test for  $RMgX$ . It was then decomposed by pouring into iced water and the ether layer separated. On concentration and cooling of the ether layer the coupling product of the Grignard reaction, diphenylbutadiene,  $C_6H_5-CH:CH-CH:CH-C_6H_5$ , separated in large quantities. On recrystallization 50 g. were obtained melting at  $147-8^\circ$ . The mother liquor on further concentration remained as a thick oil from which no more diphenylbutadiene would separate. Attempts were then made to vacuum distill the residue. A small quantity of diphenylbutadiene would pass over at first but the lead compound would quickly decompose with the production of a very black material even when pressures below 0.5 mm. were used. Hope of vacuum distilling the tetra-styryl lead was entirely given up and efforts<sup>were</sup>/made to separate the lead compound from the hydrocarbon by the use of various solvents. It appears that the hydrocarbon, diphenylbutadiene, is more soluble



in petroleum ether than the lead compound and when the mixture is extracted with this solvent a waxy residue is left which is quite rich in tetra-styryl lead. For the purpose of testing the antiknock property of the lead compound the presence of the hydrocarbon was not deemed objectionable.

Determination of the quantity of tetra-styryl lead present in the mixture was made by an analysis for lead. Solutions in gasoline, containing various concentrations of tetra-styryl lead were then made for testing the effect of its antiknock property.

While tetra-styryl lead has not yet been obtained in 100% pure form the impure mixture shows all the characteristics of such a lead compound. On ignition the waxy material quickly becomes very liquid then darkens somewhat and as it reaches a higher temperature quickly decomposes with a puff and with burning, yielding a smoke of finely divided lead and lead oxide and leaving a residue of lead oxide and very small globules of metallic lead. It is fairly soluble in gasoline and easily soluble in the common organic solvents. It dissolves easily in furfural also. It reacts with bromine in acetic acid solution yielding the lead as lead bromide.

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Work along the general lines suggested by the experiments in this thesis is being continued. Incomplete experiments indicated that sym-dimethyldiphenyl hydrazine is formed, as

would be expected, in the reaction of nitrobenzene with methylmagnesium iodide. It may be that hydrazines result from the reaction of nitrobenzene with all simple alkylmagnesium halides while the secondary amine is produced with arylmagnesium halides. Work on benzaldoxime indicates that there is no oxidizing action here resulting in the formation of either phenol or diphenyl.

### CONCLUSIONS

- (1) Nitrosobenzene reacts with three equivalents of phenylmagnesium bromide yielding diphenylamine and diphenyl.
- (2) Diphenylhydroxylamine,  $(C_6H_5)_2NOH$  reacts with three equivalents of phenylmagnesium bromide and yields diphenylamine and diphenyl and not phenol.
- (3) Nitro compounds such as nitrobenzene, o- and p-nitrotoluene and alpha-nitronaphthalene, react with four equivalents of phenylmagnesium bromide yielding phenol, the corresponding secondary amine as diphenylamine, o-tolylphenyl amine, alpha-naphthylphenyl amine, and diphenyl.
- (4) Benzylmagnesium chloride and ethylmagnesium bromide reacting with nitrobenzene yield the corresponding tetra substituted hydrazines, sym-dibenzyl-diphenyl hydrazine and sym-diethyl-diphenyl hydrazine.
- (4) Dimethylaniline oxide reacting with phenylmagnesium bromide yields in small amount phenol, diphenyl and dimethylaniline.

- (6) Ethyl nitrate does not yield nitrobenzene when subjected to reaction with phenylmagnesium bromide.

PART II

- (1) Lead tetra-styryl may be prepared from styrylmagnesium bromide and lead chloride. It is being used in conjunction with certain solvents in a study on anti-knock materials.