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Two investigations. An attempt to improve the yield of allyl magnesium bromide and a synthesis of o-diiodobenzene

Craver, Bradford North
Boston University

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Boston University
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GRADUATE SCHOOL

Thesis
TWO INVESTIGATIONS:
AN ATTEMPT TO IMPROVE THE YIELD OF
ALLYL MAGNESIUM BROMIDE
and
A SYNTHESIS OF O-DIODOBENZENE

by
Bradford North Craver
(A.B., Cornell University, 1932)
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Part I

AN ATTEMPT TO IMPROVE THE YIELD OF
ALLYL MAGNESIUM BROMIDE

The Problem

The present method of synthesizing the Grignard reagent from magnesium and the alkyl halide in dry ether solution has given good yields with most of the simpler alcohols; but tertiary halides and the allyl halides have been notable exceptions. This work was undertaken to improve the yield with allyl bromide.

A specific approach to the problem was undertaken, namely: it was assumed that the poor yield was attributable to a secondary reaction between the final product and unreacted allyl bromide. Experimental evidence for this viewpoint was found in the work of George O. Johnson and Homer Adkins¹ who discovered that allyl bromide alone of the alkyl halides they investigated would react with the final alkyl magnesium halide. It was thought to eliminate this undesirable contact between the halide and final product by designing a special apparatus in which the contact would be reduced to a minimum. A drawing on the next page makes the nature of this clear. A three-necked flask was fitted out as follows: in the center aperture was fitted a mechanical stirrer with the usual type of mercury

¹. J. A. C. S. 54, 1943-7 (1932)
vapor trap. In another was an open S-shaped piece of glass tubing one half inch in diameter, extending outward from the flask and upward and fused to a twenty-four inch section of glass tubing an inch in diameter. The larger tube was for the column of magnesium, glass wool being employed at the junction of the two tubes to keep the magnesium from dropping into the flask below. Two water condensers were fitted into the top of the magnesium column through a two-holed cork. They sloped upwards in opposite directions at a forty-five degree angle. Into the bottom of one was fused a separatory funnel for admitting the halide. The top of that same condenser was joined by glass tubing one half inch in diameter to the third opening of the flask below. No rubber stoppers were employed because of their retarding effect upon the Grignard reaction. The cork stoppers were, of course, so arranged that no liquid dripped over them.
Experimental

Preparation and Purification of Materials

All the ether employed was of the anhydrous grade. It was, however, allowed to stand in contact with cleaned sodium for two days before being re-distilled over sodium to remove the last traces of moisture. No attempt was made to distill the ether on days that were not dry and clear. The ether was kept in small corkstoppered bottles, the corks having been covered with tin-foil to keep out any traces of moisture. Small bottles were employed to assure a fresh supply for about every fourth experiment.

The allyl bromide employed was carefully dried over anhydrous calcium sulphate and then fractionally distilled, that only being retained which boiled at 71.3° C. This process was found necessary because early results were completely vitiated although a fresh, unopened bottle of allyl bromide had been employed, by the discovery that it was neither anhydrous nor pure.

Small magnesium turnings were employed which had been washed with ether and then dried over dessichlor. Gilman and Meyers² found that small pieces of magnesium gave a very slightly better yield as well as an appreciably more rapid reaction. While Gomberg and Bachman³ showed that the reaction rate was

2. J. A. C. S. 45, 159. (1923)
3. Ibid 42, 236, 2584. (1927)
much more rapid with magnesium powder, Gilman and Fothergill\textsuperscript{4}, in their work with benzopinacol, found that small turnings gave the same yield if given a longer time to react.

The approximately quarter normal sodium hydroxide and hydrochloric acid used for titration were of the C. P. grade and standardized against anhydrous sodium carbonate with methyl orange as indicator. The results were further checked by titration against other standard solutions.

\textsuperscript{4} J. A. C. S. 51, 3149. (1929)
Method of Analysis

Acid titration was the method of analysis employed for checking the yields. When runs were made by the usual method for the sake of comparison (employing a three-necked flask with separatory funnel, water condenser, and mercury-trap mechanical stirrer), the final product was filtered through cotton before the usual tenth aliquot was taken for analysis. With the special apparatus this filtering was unnecessary because no excess magnesium was present. In each case the total yield was measured in a graduate and the aliquot then measured in a small graduate. The aliquot was then hydrolyzed with distilled water and the excess ether boiled off on a hot-plate. The magnesium hydroxide formed was then titrated, with phenolphthalein as indicator, until the appearance of a faint pink persisting for at least one minute. The solution was continually stirred and titrated while still hot to assure more rapid reaction.
Preliminary Experiments

Early experiments were made with phenyl bromide to check the technique and method of analysis.

\[ \text{Br} + \text{Mg (in absolute ether)} = \text{MgBr} \]

These experiments, made by the ordinary method, gave yields of about 94%, which checked favorably with the yields reported by Johnson and Adkins\(^5\). A second check titration of each experiment did not vary by more than one percent from the first.

\[ 2\text{MgBr} + 2\text{H}_2\text{O} = 2\text{Br}^- + \text{MgBr}_2 + \text{Mg(OH)}_2 \]

\[ \text{Mg(OH)}_2 + 2\text{HCl} = \text{MgCl}_2 + 2\text{H}_2\text{O} \]

5. J. A. C. S. 54, 1943. (1932)
Experiments with the Magnesium Column

The following general procedure was employed for experiments in the special apparatus: 75 or 100 cc. of anhydrous ether was placed in the flask and brought to a steady boiling by means of a hot water bath heated with an electric plate. It was found that practically all of the ether thus vaporized went up the glass tube rather than the column and after being condensed in the water condenser, dripped back to the flask by way of the column. After the column, which had been previously filled with cleaned and dried magnesium, was thoroughly saturated with ether, the top layer was activated as follows: in the first experiments a small amount of iodine was mixed into the upper layer of magnesium but this failed to effect an immediate activation and it was found that a considerable quantity of the allyl bromide had already dripped through the column before the heat given off evidenced the complete activation of the upper layers of the magnesium. It might here be added that during no experiment was heat detectable in the column more than three-fifths of the distance down it. The most satisfactory method of activation was found to be the addition to the top of the column of a few small pieces of magnesium turnings which had already been partially dissolved in a test tube by the formation of ethyl magnesium bromide. These pieces had to be placed in the column quickly while ether was still dripping through it, for it was found that exposure to
air caused them to lose their activation rapidly. After this had been accomplished, the allyl bromide, diluted with ether, was allowed to drip slowly through the column, in which it underwent the following reaction with the magnesium:

\[
\text{CH}_2=\text{CHCH}_2\text{Br} + \text{Mg (abs. ether)} \rightarrow \text{CH}_2=\text{CHCH}_2\text{MgBr}
\]

After it had all dripped through the column, the ether was boiled for an additional fifteen minutes to make certain that the last traces of product had been washed out of the column into the flask below.
Tabulation of Results

It might be mentioned that separate titration of two duplicate aliquots of each experiment were an excellent check on the accuracy of the results. In addition the vigor of the hydrolysis, after experience with many experiments, gave a very rough check on the yield for the one tenth aliquots chosen were usually of comparable volume.

\[
2 \text{CH}_2=\text{CHCH}_2\text{MgBr} + 2 \text{H}_2\text{O} = 2 \text{CH}_2=\text{CHCH}_3 + \text{MgBr}_2 + \text{Mg(OH)}_2
\]
\[
\text{Mg(OH)}_2 + 2 \text{HCl} = \text{MgCl}_2 + 2 \text{H}_2\text{O}
\]

It should be further stated that any moisture and excess bromine in the allyl bromide always caused the appearance of three phases: two liquids and one solid. The fractional distillation of these liquids yielded di-allyl, whose boiling point of 58° C. checked well with Mulliken's value of 59.5° C., since no stem correction was made. The vigor with which the solid phase was hydrolyzed led to its identification as the active Grignard reagent. Since such an heterogeneous system rendered the taking of accurate aliquots impossible, the titration results of these earlier experiments are omitted. Since no accurate aliquot could be taken of the three phase system, a common solvent was sought. The results were as follows:

CS₂ and CCl₄ formed one liquid phase but would not dissolve the solid. Benzene not only would not dissolve the solid but precipitated it from the ether. Chloroform gave a homogeneous solution but a considerable quantity was required to dissolve the solid. The use of pure allyl bromide gave a homogeneous system.
save in three other separate instances: (1) when a fresh column of magnesium had been activated by one experiment and then allowed to stand for even a short interval before making a second experiment; (2) when an undiluted solution of the bromide was put through the column rapidly; (3) in the two experiments when copper amalgam was employed as a possible catalyst. No satisfactory explanation was found for the appearance of these three phases.

In the results on the next page, the average of two titrations is given unless otherwise noted. Two tenths of a mole of allyl bromide (24.2 g. or 16.85 cc.) was used in each experiment and an approximately 7% excess of magnesium, i.e. 5.2 g. in place of the 4.86 g. theoretically required. The second column gives the number of cubic centimeters of ether in the flask, the third the number used to dilute the allyl bromide, the fourth the volume of the one tenth aliquot taken, the fifth the per cent yield. The last column states any special conditions or gives a reference to a lengthier explanation of them on the next page. The use of the column is assumed unless the phrase 'ordinary method' appears under the conditions. A 22" column of magnesium was employed unless otherwise noted. A fresh column was employed for each experiment unless consecutive experiments were made.
<table>
<thead>
<tr>
<th>exper. no.</th>
<th>cc in flask</th>
<th>cc in bromide</th>
<th>cc aliquot</th>
<th>%</th>
<th>conditions</th>
</tr>
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<tr>
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<td>60</td>
<td>40</td>
<td>10</td>
<td>46.9</td>
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</tr>
<tr>
<td>2.</td>
<td>70</td>
<td>40</td>
<td>11.4</td>
<td>46.8</td>
<td>ordinary method</td>
</tr>
<tr>
<td>3.</td>
<td>100</td>
<td>100</td>
<td>20</td>
<td>33.6</td>
<td>ll&quot;column (note a-)</td>
</tr>
<tr>
<td>4.</td>
<td>100</td>
<td>50</td>
<td>16.4</td>
<td>53.9*</td>
<td>ordinary method</td>
</tr>
<tr>
<td>5.</td>
<td>75</td>
<td>50</td>
<td>15</td>
<td>54.9</td>
<td>ordinary method</td>
</tr>
<tr>
<td>6.</td>
<td>75</td>
<td>50</td>
<td>13</td>
<td>55.1</td>
<td></td>
</tr>
<tr>
<td>7.</td>
<td>75</td>
<td>50</td>
<td>10</td>
<td>42.2</td>
<td>(see note b-)</td>
</tr>
<tr>
<td>8.</td>
<td>75</td>
<td>50</td>
<td>12</td>
<td>54.8*</td>
<td></td>
</tr>
<tr>
<td>9.</td>
<td>100</td>
<td>50</td>
<td>less than 8%</td>
<td></td>
<td>ord. meth. with 10 gr. copper amalgam</td>
</tr>
<tr>
<td>10.</td>
<td>100</td>
<td>50</td>
<td>less than 8%</td>
<td></td>
<td>ord. meth. with 5 gr. copper amalgam (see note d-)</td>
</tr>
<tr>
<td>11.</td>
<td>75</td>
<td>50</td>
<td>less than 6%</td>
<td></td>
<td>(see note e-)</td>
</tr>
<tr>
<td>12.</td>
<td>75</td>
<td>50</td>
<td>16</td>
<td>47.8</td>
<td>(see note e-)</td>
</tr>
<tr>
<td>13.</td>
<td>75</td>
<td>50</td>
<td>14.3</td>
<td>52.0</td>
<td>ordinary method</td>
</tr>
</tbody>
</table>

a- This experiment and other experiments not recorded made it clear that a column of magnesium much shorter than 22" gave insufficient time for reaction.

b- The lower result of this experiment might have been due to the unusual dampness of the days preceding.

c- This experiment after an aliquot had been taken was allowed to drip through the activated magnesium column. It was then again titrated and a loss of 4.4% noted which is easily attributable to sources of experimental error. This showed that the column, even when activated, had no effect on the

*) Single titration
final product; but the color changed from dark green to light.

d- This experiment was made after the activated column had been allowed to stand overnight covered with anhydrous ether and with the whole system corked so as to be air-tight.

e- This experiment was the second removed successive experiment after the one above it. It thus took three experiments to re-activate the column sufficiently, after standing overnight, to give a yield comparable to those usually obtained.

f- This experiment was initially cooled but as that completely halted the reaction, it was completed, as usual, at the boiling point of ether.
Summary

The following conclusions were drawn from the experimental work undertaken:

1. Whereas the yields by both methods were not comparable to the maximum obtained by Johnson and Adkins\(^6\), the maxima obtained by the two separate methods used in this work, were comparable. The use of the magnesium column might have industrial application for it would permit a continuous process, the only two requirements of it being the replacement of consumed magnesium and non-interruption of the process, for the activation of the column is definitely lost after even a short interval of standing unused.

2. Copper amalgam hinders the reaction.

3. Moisture or excess bromine in the allyl bromide causes poor results.

4. Cooling the reaction mixture below the boiling point of ether greatly retards it and appreciable cooling stops it.

5. Damp weather gives poor results unless the apparatus employed is designed to negate its effect.

\(^6\) J. A. C. S. \textbf{53}, 1520. (1931)
PART II

A SYNTHESIS OF O-DIODOBENZENE

No specific synthesis of o-diiodobenzene is available in the literature although several of its physical constants may be found in the International Critical Tables and in the Central-blatt (1935). The most recent work with it was done by Thomas and Bruliat\textsuperscript{6a} in investigating the formation of the di-magnesium iodide and the latter's reaction with aldehydes, ketones, etc. They, however, do not state how the compound was prepared.

Two possible methods of synthesis presented themselves: (1) the diazotization of o-phenylene diamine in the presence of sulphuric acid and subsequent treatment with potassium iodide:

\[
\text{NH}_2\text{NH}_2 \xrightarrow{\text{H}_2\text{SO}_4} \text{NH}_2\text{H}_2\text{SO}_4 \xrightarrow{\text{HONO}} \text{N=NOSO}_2\text{OH} \xrightarrow{\text{KI}} \text{I}^\text{I}
\]

(2) the formation of o-iodonitrobenzene from o-nitroaniline by the diazotizing method, the subsequent reduction of the nitro group, and, lastly, a repetition of the diazotization me-

\text{6a. Compte Rendu, 181: 218-20 (1925) and 183: 297-9. (1926)}
The first method was attempted but no recognizable product could be isolated. Subsequently, a reference was found to the effect that the phenylene diamines, when so treated, yield complex polymerization products. The second method of synthesis given above was accordingly used.

The Synthesis of o-Iodonitrobenzene

Only two references were available in the literature for the synthesis of the above compound, if one neglects its formation by the nitration of iodobenzene. This latter method, however, was of little value because of the large preponderance of the para product. The first reference suggested its formation by diazotizing o-nitroaniline in the presence of a large excess of sulphuric acid and subsequent treatment of the diazonium compound with a solution of iodine in potassium iodide; but since both a practical and relatively inexpensive method was sought, if it could be found, the second method was chosen. By this method the o-nitroaniline was diazotized in the presence of sulphuric acid by sodium nitrite and then treated with a solution of potassium iodide alone. This method was carried out and the recommended quantities employed: 30 g. of o-nitroaniline, 45 g. of concentrated sulphuric acid, 15 g. of sodium nitrite, 60 g. of potassium iodide, and 250 g. of ice. It might be added that this same method was at first employed without the use of ice but the results were poor even with mechanical stirring and the use of an ice bath because the cooling proved inadequate. Only by an extremely slow addition of the sodium nitrite and later of the potassium iodide could the mixture be kept below five degrees Centigrade. The

o-nitroaniline was partially dissolved in the required amount of sulphuric acid for a complete solution could not be obtained and then poured slowly upon the ice which had been placed in a liter flask. The solution of sodium nitrite in 50 cc. of water was then slowly added through a separatory funnel, the mixture meanwhile being continually agitated by shaking the flask. The shaking was continued for fifteen minutes after the complete addition of the nitrite although mono-nitro and mono-halogen anilines are readily diazotized\(^\text{11}\). The solution of potassium iodide in 150 cc. of water was then added in like fashion:

\[
\begin{align*}
\text{NH}_3 \cdot \text{H}_2\text{SO}_4 + \text{H}_2\text{SO}_4 & \rightarrow \text{NH}_2\text{SO}_4 \cdot \text{H}_2\text{SO}_4 \\
\text{NH}_2\text{H}_2\text{SO}_4 + \text{HOH} & = \text{N} = \text{O}\text{SO}_2\text{OH} + 2 \text{H}_2\text{O} \\
\text{N} = \text{O}\text{SO}_2\text{OH} + \text{K} & = \text{I} + \text{H} + \text{K}_2\text{SO}_4
\end{align*}
\]

The product was then allowed to settle overnight, the supernatant liquid decanted, and the solid dried between filter papers. For purification, it was distilled as recommended. This method, however, was far from satisfactory and attempts to distill under diminished pressure brought no results. As the liquid approached the reported boiling point of 290° C. an increased darkening indicated the liberation of more and more

iodine. When the cooled distillate had crystallized, its dark brown color indicated the presence of appreciable iodine as an impurity, for only along the edges could the light yellow crystals of the pure product be noted. Furthermore, the slightest superheating causes the complete decomposition of the compound with the emission of copious iodine fumes. A solid mass of porous carbon is left in the distilling flask. Every effort at purifying the compound by distillation ended in the same manner, with a varying percent of the yield being rescued before the decomposition. The precaution of using a low flame and glass beads did not prevent the ultimate result. A more satisfactory method of obtaining the pure product was sought. After the experiment, the supernatant liquid was decanted as before. The flask was then repeatedly filled with water which was each time decanted until a final filling of the flask gave a supernatant liquid that showed no iodine color. Each time a few crystals refused to settle and were kept at the surface by surface tension. The first decantation removes the floating iodine and after that the few crystals that stay on the surface each time may be removed by decanting through a filter but their slight total weight is scarcely compensation for the trouble. The solid was then treated three times in like fashion with saturated sodium bisulphite solution, the mixture being thoroughly agitated each time and then decanted. Finally, the process was repeated four or five times more with water to remove any last traces of the water
soluble; inorganic salts which would have been formed in the treatment with sodium bisulphite. The solid was then dumped out onto a filter paper and allowed to drain. Either of two methods for drying it may then be employed. The first involves melting the solid in a beaker, then pouring it into a separatory funnel and drawing off the product from beneath the layer of water which had originally been absorbed by the crystals but which, of course, separated as a second liquid phase when they were melted. The light tan product thus obtained melts at $48.5^\circ$ without any correction, which is in good agreement with the literature value of $49.4^\circ$. The light color indicates the presence of, at most, very little free iodine. The second method involves drying the crystals between filter paper and then spreading them out in a thin layer in a desiccator. The crystals thus obtained are even slightly lighter but it has been found very difficult to dry them completely. Representative yields were between 70 and 80%, using the following quantities: 250 cc. of concentrated sulphuric acid, 300 g. of o-nitroaniline, 75 g. of sodium nitrite dissolved in 400 cc. of water, 300 g. of potassium iodide dissolved in one liter of water.
The Synthesis of o-Iodoaniline

Three references for making this by the reduction of o-iodonitrobenzene were found in the literature. The first involved reduction with zinc dust and glacial acetic\textsuperscript{12}; the second, reduction with ammonia and ferrous sulphate\textsuperscript{13}; the third reduction with stannous chloride and hydrochloric acid in alcohol solution\textsuperscript{14}. Despite repeated attempts, no product could be isolated by means of the first method. The second method likewise gave no results. In fact the original o-nitroaniline was recovered almost 100\% after the reaction with ammonia and ferrous sulphate. The original yields with the third method were less than thirty percent. A more satisfactory method was therefore sought. The reducing agents tried were as follows: (1) copper and sulphuric acid; (2) iron and sulphuric acid; (3) zinc and sulphuric acid; (4) tin and hydrochloric acid; (5) sodium sulphide; (6) ammonium polysulphide; (7) phenylhydrazine; (8) electrolytic. The first three methods may be disposed of quickly—they produced no trace of the desired product. The fourth method gave a reaction and the original product disappeared, but on making the solution alkaline and steam-distilling, only a trace of the product sought was obtained. A reference was subsequently found in

\textsuperscript{12} Journal für den praktischen Chemie, \textbf{71}, 374. (1905)
\textsuperscript{13} Gazzetta Chimica Italiana, vol. \textbf{17}, 487. (1887)
\textsuperscript{14} Berichte der Deutschen Chemischen Gesellschaft. \textbf{38}, 2760. (1905)
Houben-Weyl\textsuperscript{15} to the effect that reduction with tin and hydrochloric acid of a compound in which the para position is unoccupied leads to the introduction of a chlorine atom in that position. An attempted reduction with sodium sulphide gave no reaction and the original o-iodonitrobenzene was recovered almost 100\% by ether extraction. This result checked with a statement in Houben-Weyl\textsuperscript{15} that sodium sulphide will not reduce nitro compounds in which the ortho position is occupied. An attempted reduction with ammonium polysulphide also gave negative results and the original material was recovered. That result was not particularly surprising for ammonium polysulphide is effective only with easily reduced groups\textsuperscript{15}. More or less as a last resort recourse was had to phenylhydrazine as a reducing agent, the latter compound being decomposed in the course of a reduction to benzene and nitrogen\textsuperscript{15}. Results were negative and the starting material was recovered. One attempt at electrolytic reduction was undertaken. A procedure given in Houben-Weyl\textsuperscript{16} for the reduction of nitro compounds to amines was followed. A nickel gauze was employed as cathode with carbon as the anode. The anode compartment, inside the porous cup, contained 30\% sulphuric acid while the cathode compartment, which was cooled with an ice bath, contained 75 volumes of concentrated hydrochloric acid, 50 volumes of water, two parts of stannous chloride, and twelve parts of o-iodonitrobenzene. A 6-volt potential was used with a current

\textsuperscript{15} Houben-Weyl, vol. 2, pp.188, foll.
\textsuperscript{16} Ibid, p. 322.
density of 1000 amperes per square meter. After the electrolysis had gone on for about three hours, the carbon anode was found to be completely disintegrated. Although the solution had been vigorously stirred mechanically throughout this time, no trace whatsoever of the compound sought could be found by neutralizing the contents of the cathode compartment and steam distilling. Since it seemed undesirable to use platinum as an anode in view of the presence of hydrochloric acid, and carbon worked so poorly, electrolysis as a method of reduction was thereupon abandoned.

The only method of reduction which had provided any appreciable yield was that by stannous chloride and hydrochloric acid.

\[
\begin{align*}
3\text{NO}_2^- + 6\text{H}^+ &= 3\text{NH}_2^- + 2\text{H}_2\text{O} \\
\text{SnCl}_2 + 2\text{HCl} &= \text{SnCl}_4^- + 2\text{H}^+
\end{align*}
\]

Accordingly, the above method was again attempted with the hope of getting better results although the many first attempts with it had given nothing even approaching the more than 85% yield reported by the authors. The following quantities were employed: 900 g. of alcohol, 900 g. of concentrated hydrochloric acid, 760 g. of stannous chloride, and 180 g. of o-iodonitrobenzene. The alcohol, acid and stannous chloride were mixed and cooled to 28°. The triturated nitro com-
pound was then added slowly, at such a rate as to maintain a temperature of 30°C in the reaction mixture. The latter was continuously and rapidly stirred mechanically. An ice bath was employed for cooling only in case the temperature exceeded 31°C. This addition took approximately two hours. At the end of the reaction, small glittering crystals in a brownish green solution were obtained. These were allowed to settle overnight, the supernatant liquid then decanted, and the complex tin salt then decomposed with 30% sodium hydroxide solution. The solid was again allowed to settle and the supernatant liquid again decanted. The sodium hydroxide treatment was repeated and the remaining solid was steam-distilled. The product was extracted from the distillate with ether which was then dried with anhydrous calcium chloride before being evaporated. The solid residue in the steam-distilling flask was filtered out and partially dried before being extracted with ether. This ether solution was dried in the same fashion as the one above mentioned. The melting point of the product extracted from the distillate was 56°C, without any correction, in excellent agreement with the literature value of 56.5°C. The melting point of the product obtained by extraction of the residue, was usually a degree and a half to two degrees lower. This, of course, indicated the presence of some impurities but hardly enough to make it worthwhile removing them in view of the purpose for which the compound was to be employed. Each of these two methods of recovery accounted for about one half
the total yield. Steam-distillation is necessary for obtaining a really pure product but the ether extraction method gives a product pure enough for the purpose here required, although it undoubtedly contains some stannous chloride. The average yield of three experiments made in this manner was 70%. The highest yield was 78% and the two lower yields were each 66%.
The Synthesis of o-Diiodobenzene

Only one reference to the synthesis of this compound through the medium of diazotizing o-iodoaniline could be found in the literature. This method is so poor as not to be worth mentioning in any detail. It involved diazotization with potassium nitrite and sulphuric acid and subsequent treatment with a solution of excess iodine in potassium iodide. However, it was employed for the preparation of only small quantities, the yield was not given, a considerable excess of potassium nitrite was called for, and the amounts of iodine and potassium iodide to be used were not specified at all. In short, the reference gave only two points of value: the diazotization method would work and the product could be steam-distilled from an alkaline solution. An early experiment employed the following amounts of the materials: 75 g. of o-iodoaniline, 71 g. of concentrated sulphuric acid, 23.5 g. of sodium nitrite, 72 g. of iodine, and 95 g. of potassium iodide. The general method of diazotization was the same as that employed with o-nitroaniline and described in an earlier part of this paper. From the above experiment a rather small yield of iodobenzene resulted. Another experiment using only 0.1 mole of iodoaniline and proportionate amounts of the other materials based on above quantities, except no iodine was used, yielded nothing but the same product, iodobenzene. Several similar

17. Gazzetta Chemica Italiana, vol. 17, 391. (1887)
experiments gave the same result. It was noted in each expe-
riment, when potassium iodide was used without iodine, that
an unusually large amount of free iodine formed on the sur-
face of the reaction mixture. In the belief that the poor re-
sults might have been due to the decomposition of the potassi-
um iodide by the excess sulphuric acid, ortho-phosphoric acid
was employed instead. But this also gave negative results
whether it was employed with potassium iodide alone or in the
company of an iodine solution. It was found that in solution,
phosphoric acid would not decompose a solution of potassium
iodide. Neither would sulphuric acid decompose it unless a
relatively high concentration were present. The only other
possible agent of decomposition remaining was the nitrous acid

$$2\text{HNO}_3 + 2\text{KI} = \text{I}_2 + 2\text{KOH} + 2\text{NO}$$

Accordingly, a solution of sodium nitrite only two or three
percent in excess of the calculated amount was employed.
Throughout the diazotization the mixture was frequently tes-
ted with potassium iodide starch paper for the presence of ex-
cess nitrous acid, an immediate blue stain on the paper being
taken as a positive indication. When this test was positive
even after agitating the reaction mixture for three minutes
after the last addition of sodium nitrite, the reaction was
considered completed. Further evidence of the completion of
the reaction was always found in the complete disappearance of
the solid o-iodoaniline for it was not completely soluble in
the reaction mixture whereas the diazonium compound was solu-
ble. The excess nitrous acid was then destroyed by the addition, dropwise, of a concentrated solution of urea until the potassium iodide starch paper test was negative.

\[ \text{H}_2\text{CNO}(=\text{O})\text{NH}_2 + 2 \text{HONO} = 2\text{H}_2 + \text{H}_2\text{CO}_3 + 2 \text{H}_2\text{O} \]
\[ \text{H}_2\text{CO}_3 = \text{CO}_2 + \text{H}_2\text{O} \]

Two grams of powdered copper were then added and the mixture well shaken. A solution of potassium iodide was then added rather rapidly and the validity of the foregoing conclusions was confirmed by the complete absence of any free iodine. After the final addition of the potassium iodide, the mixture was heated on a hot water bath at 60° C. for fifteen minutes, the mixture having been first allowed to come to room temperature without the application of any heat.

\[ \text{I}^+ + \text{H}_2\text{SO}_4 = \text{I}^+ \text{H}_2\text{SO}_4 \]
\[ \text{I}^+ \text{H}_2\text{SO}_4 + \text{HONO} = \text{I} = \text{H}_2\text{O} \]
\[ \text{I} = \text{H}_2\text{O} + \text{KI} = \text{I} + \text{KH}_2\text{SO}_4 \]

The mixture was then made alkaline with 30% sodium hydroxide solution and steam-distilled. The product thus obtained was a light tan liquid with a boiling point of 285° C. which checked well with the literature value of 286.8. Distillation, however, caused a continual darkening of the liquid, indicating partial decomposition and the release of free iodine. Crystallization could be induced only by cooling in an ice
salt bath and continually scratching the sides of the containing glass vessel with a glass rod. The melting point of the crystals thus formed was 16° C. without any correction, in none too good agreement with literature value of 23.4° C.

As a check on the yield, two experiments were made in the manner above described, employing the following quantities: 55 g. (.25 moles) of o-iodoaniline, 98 g. (one mole) of sulphuric acid, 18 g. (.26 moles) of sodium nitrite, 70 g. (.42 moles) of potassium iodide. To facilitate the solution of the aniline compound, it was first dissolved in the sulphuric acid by boiling and then allowed to cool before putting into a two liter flask half full of ice. On cooling the sulphuric acid solution, the aniline compound precipitated out but these crystals were finer as well as being in the form of the acid sulphate so that their solution in the ice bath was more rapid and more nearly complete than when the o-iodoaniline was added to the sulphuric acid already diluted by pouring on the ice. The average yield of the two experiments was 64%, the first giving 63% and the second 65%.
CONCLUSION

In the earlier part of this paper a synthesis of o-iodonitrobenzene from o-nitroaniline by the diazotizing method has been described. Yields of about eighty percent were obtained. The use of crushed ice in the mixture itself for cooling was found to be more desirable and effective than an ice bath. Destroying excess nitrous acid after the diazotization with an urea solution will lessen the excess of that relatively expensive material, potassium iodide, which must be used. The method, given in the literature, of purifying the final product by distillation was found to be unsatisfactory because slight superheating will cause immediate and complete decomposition. It was found to be more satisfactory to wash the solid o-iodonitrobenzene repeatedly with water and sodium bisulphite and then remove the excess water by melting the solid and in a separatory funnel drawing off the layer of liquid o-iodonitrobenzene from beneath the water layer.

The o-iodonitrobenzene resulting from the above synthesis was reduced with stannous chloride and hydrochloric acid in alcohol solution. Several other methods of reduction were attempted but they either gave an extremely low yield or none at all. In the reduction with stannous chloride and hydrochloric acid, the temperature is a vital factor and must not be allowed to rise above thirty-five degrees Centigrade, if the substitution of a para chlorine atom is to be avoided. The average yield by this method was seventy percent.
In the formation of o-diiodobenzene from o-iodoaniline by the diazotization method, powdered copper was found to be a necessary catalyst. It was found desirable to remove any excess nitrous acid after the diazotization by adding a solution of urea dropwise until the test for excess nitrous acid with potassium iodide starch paper was negative. This prevented the decomposition of the potassium iodide by the nitrous acid to form free iodine.