

THE MONO-CHLOR, MONO-IODO DERIVATIVES
OF TOLUENE

A THESIS SUBMITTED TO THE FACULTY OF THE GRADUATE
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THE DEGREE OF MASTER OF ARTS

BY

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This page is reserved for the expression of my sincere appreciation of the valuable assistance and kindly interest of Dr. F. B. Dains under whose direction this study was made, and also to Dr. R. Q. Brewster for his cooperation and many helpful suggestions.

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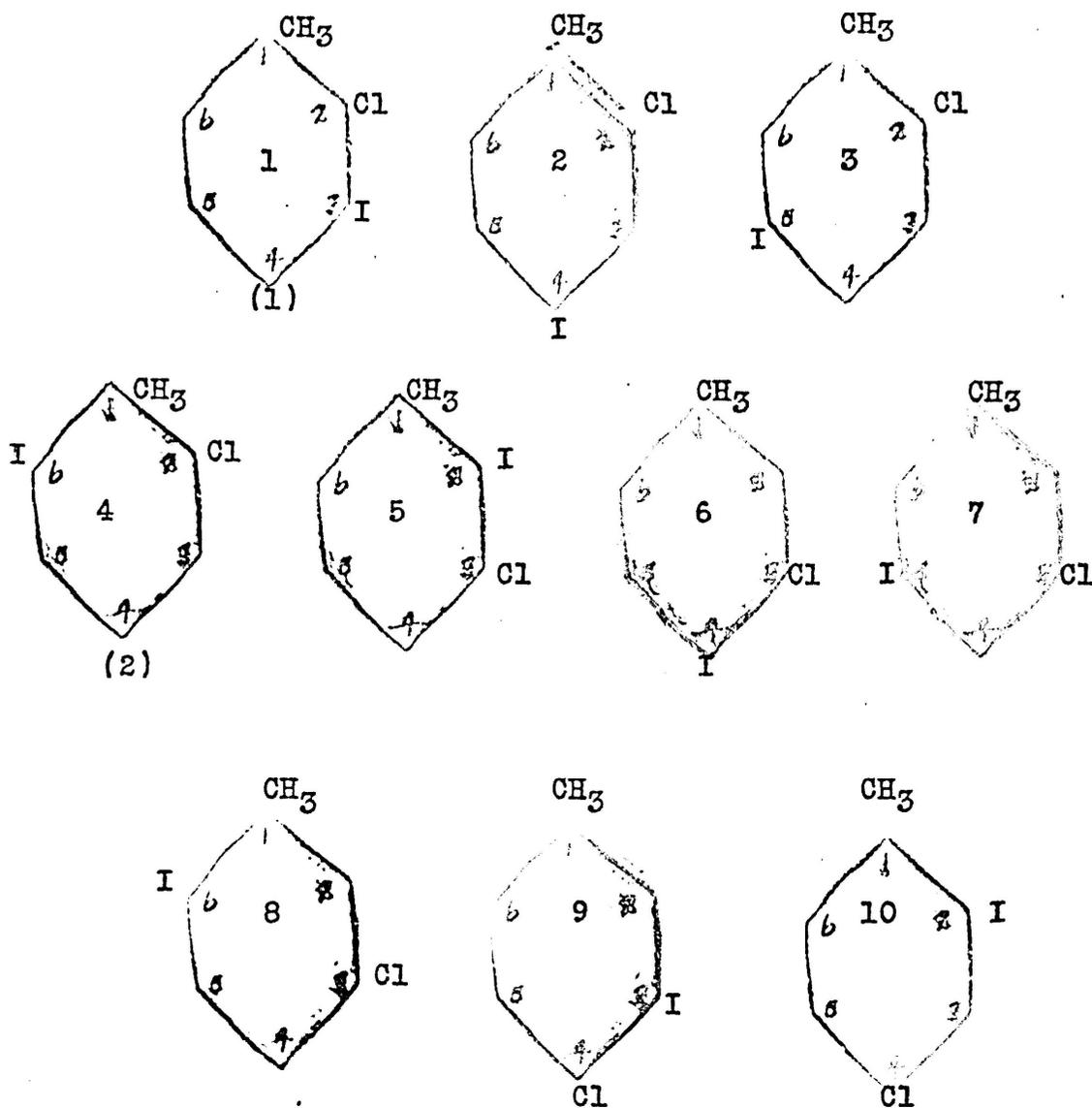
INTRODUCTION

The purpose of this work was to prepare and study some of the properties of the mono-chlor, mono-iodo derivatives of toluene. The corresponding di-iodo derivatives have been practically all made and studied by Wheeler and his assistants at Yale University.

The reason for synthesizing these compounds was to get some information regarding the structure of certain compounds prepared in different ways. Specifically, one question to be settled was the position taken by the iodine when o-chlor toluene is treated with iodine and nitric acid. There were many other similar cases to be settled.

It was thought that it would be well to prepare all of the possible isomers by synthesizing them so that any present or future work on direct iodination or chlorination could refer to it as an aid in identification.

When three different substituted groups occur in the benzene ring there may be ten different products, hence there would be ten isomeric mono-chlor, mono-iodo toluenes. The structural formulae are as follows, being numbered from one to ten so that reference can more easily be made to them in the following pages without confusion to the reader:



It will be noticed by the references that two of these, Nos. 1 and 4, have been made. According to the available literature the other eight had not yet been prepared.

(1) J. Chem. Soc. 85, 1627 (1904)

(2) Ibid

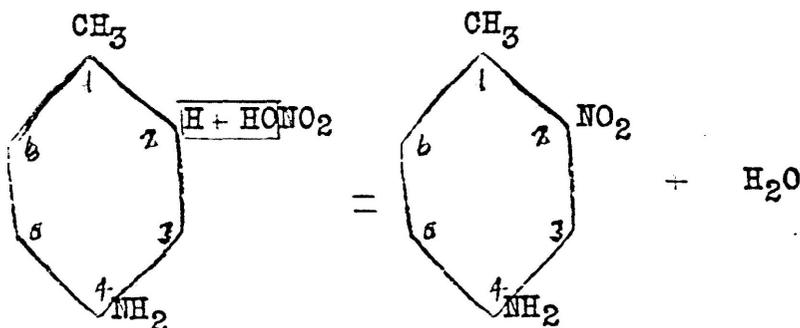
The work could perhaps be logically separated into such divisions as preparation, properties, analysis, identification, etc. but it is thought that since there are so many compounds to be kept in mind by the reader, it would be better to treat it differently. Consequently, the entire record of each compound is given consecutively.

1-METHYL, 2-CHLOR, 4-IODO BENZENE

The starting point of this compound was p-toluidine. It was nitrated according to the following method of Nolting and Collin. (3)

O-NITRO-p-TOLUIDINE

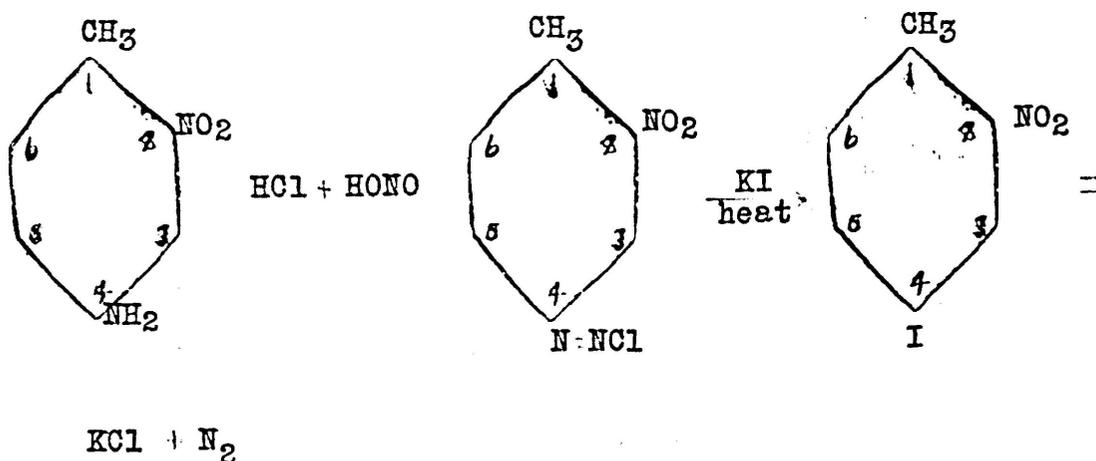
Twenty grams of p-toluidine was cooled in a beaker with four hundred grams of concentrated sulfuric acid to a temperature of 0°. This was stirred while a mixture of fifteen grams of fuming nitric acid and sixty grams of sulfuric acid was slowly added. The mixture was poured on to ice and diluted to three or four liters and the acid neutralized with sodium carbonate. This left a heavy scum of the nitro toluidine which was filtered off and recrystallized by extracting with hot dilute hydrochloric acid and precipitating with sodium carbonate or ammonia. It was in light yellow crystals whose melting point was 78-79°.



(3) Ber. 17,263 (1884)

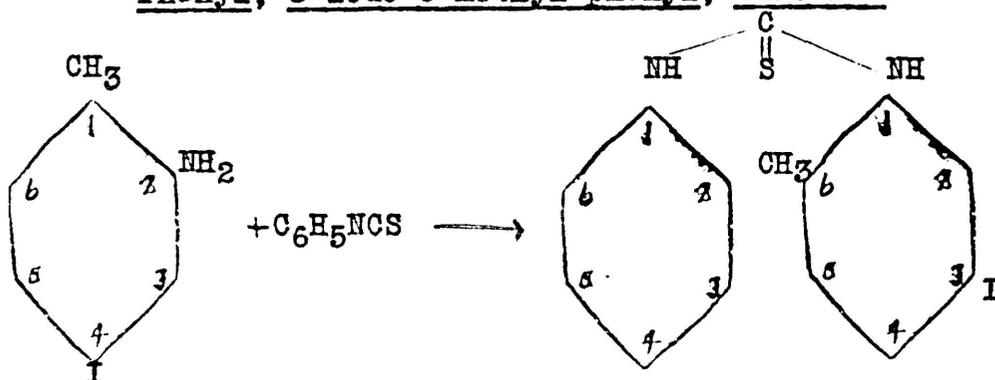
1-METHYL-2-NITRO-4-iodo BENZENE

Fourteen grams of o-nitro-p-toluidine was converted into the hydrochloride by warming with fifty grams of hydrochloric acid and dissolved in fifty c.c. It was diazotized at 0 degrees with eight and one-half grams of sodium nitrite, filtered, and treated with twenty-five grams of potassium iodide in fifty c.c. of water. After letting set for some time, it was made alkaline and steam distilled. A slightly yellowish oil soon came over solidifying in the condenser. Upon crystallization from alcohol, its melting point was about 60°. The yield was 20.5 grams or 94.9% of the theoretical.



1-METHYL-2-AMINO-4-IODO BENZENE

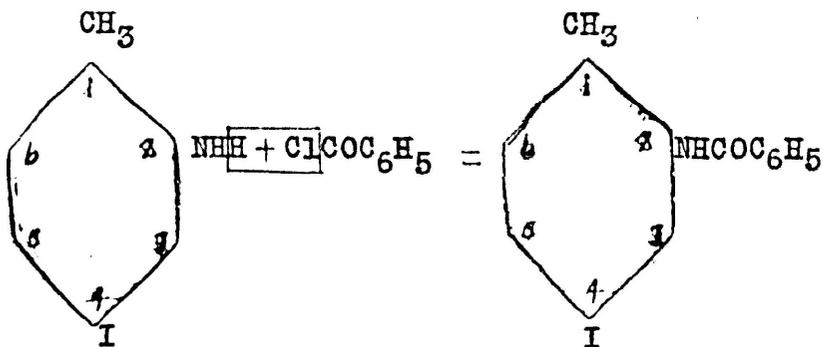
Thirty grams of 1-methyl-2-nitro-4-iodo benzene, 320 grams of ferrous sulfate, 600 c.c. concentrated ammonia and 600 c.c. hot water were placed in a large flask fitted with a Bunsen valve, and heated on a steam bath for ten or fifteen hours. After cooling, the mix was filtered and the solid extracted several times with hot alcohol. After distilling off the excess alcohol, the extracted product was steam distilled and a rather dark oil passed over. The best yield obtained by this process was about 65%. However it was found in this product that there remained a portion of unchanged nitro compound. This was discovered when it would not dissolve in an acid when it was diazotized later. For the sake of identification a number of derivatives of this base were made.

Phenyl, 3-iodo-6-methyl-phenyl, thiourea

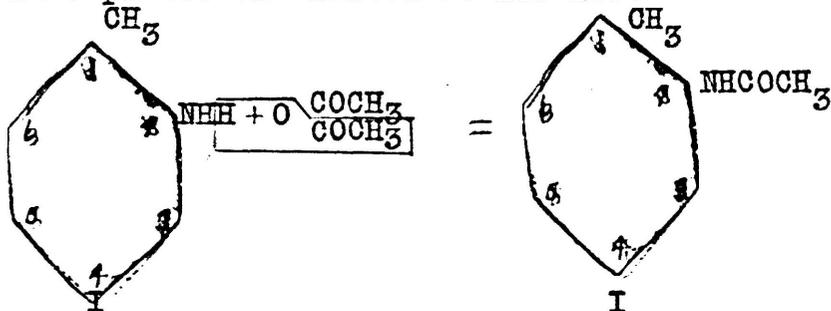
Approximately molecular portions were warmed and allowed to stand until they reacted. The product was crystallized from alcohol in white, flat, glistening plates.

1-Methyl-2-benzoyl amino-4-iodo benzene

This was made by warming with benzoyl chloride and recrystallizing from alcohol. It melted at 173-175° and was in fine white needles.

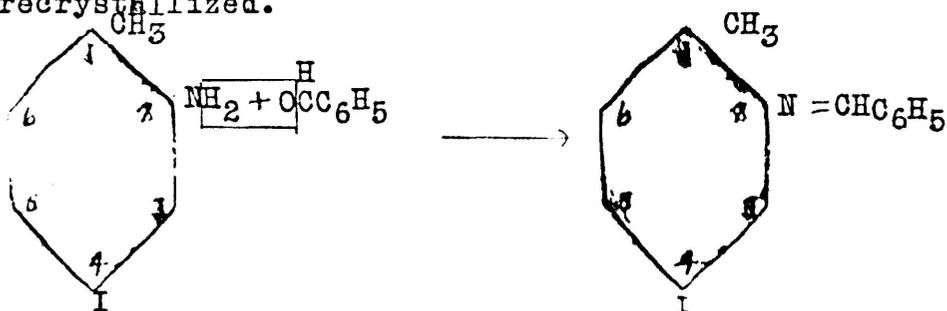
1-Methyl-2-acetyl amino-4-iodo benzene

This was made by warming with acetic anhydride and alkali. Upon recrystallizing from alcohol, it was in fine white plates and melted at 183-185°.

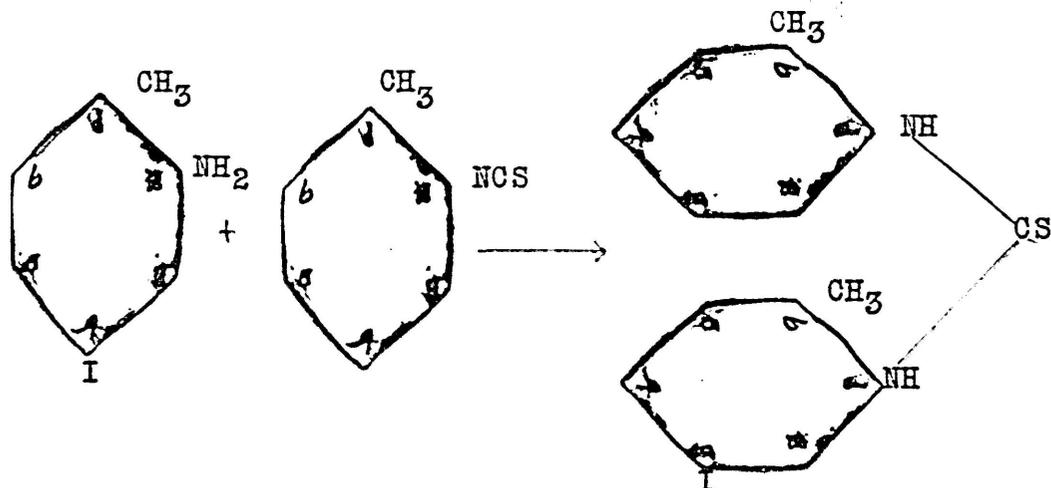


1-Methyl-2-benzal amino-4-iodo benzene

This was made by worming with benzaldehyde but a suitable solvent was not found out of which it could be recrystallized.

o-Tolyl-2-iodo-6-methyl phenyl, thio urea

This was made and recrystallized as the others and has a melting point of 162° .



1-Methyl-2-amino-4-iodo benzene hydrochloride.

The hydrochloride was made by passing HCl gas into an ether solution of the base, where upon the salt settled out as a fine white solid. It could not be recrystallized from hot water as water seemed to decompose it but could with some difficulty be recrystallized from alcohol in colorless crystals. At about 240° to 245° it seemed to dry away with a darkening of color indicating decomposition.

Analysis of the HCl salt.

Weight of sample - .5018 grams

cc of alkali (.2525N) - 7.50

HCl calculated for C_7H_9INCl

Found

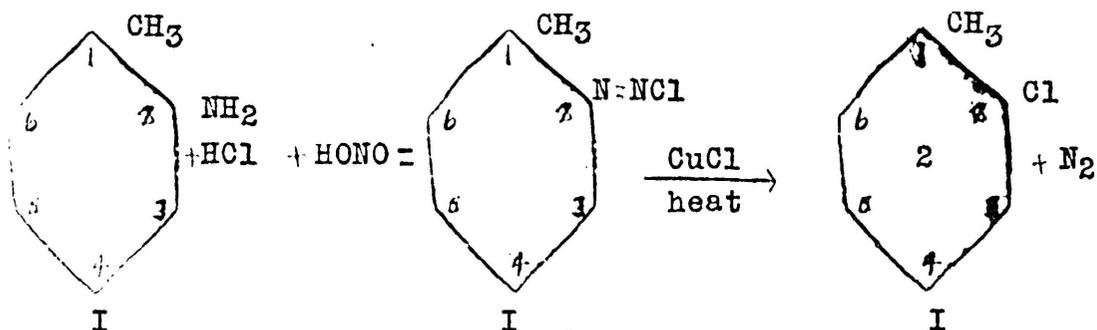
13.54%

13.74%

1-Methyl-2-chlor-4-iodo benzene.

This was made by dissolving twenty-two grams of 1-methyl-2-amino-4-iodo benzene in twenty-five c.c. hydrochloric acid and sixteen c.c. water and diazotizing cold with 8 grams sodium nitrite. The cuprous chloride solution was made by boiling six grams copper carbonate and sixty-five c.c. hydrochloric acid with excess copper turnings until clear. The clear diazo solution was filtered and treated with the cold cuprous chloride solution. It was warmed, made alkaline and steam distilled. Fifteen

grams of a reddish brown oil passed over which was sixty-four percent of the theoretical.



The oil was distilled at a pressure of twenty-three mm. at 130° to 150° C. The index of refraction was measured and found to be 1.583.

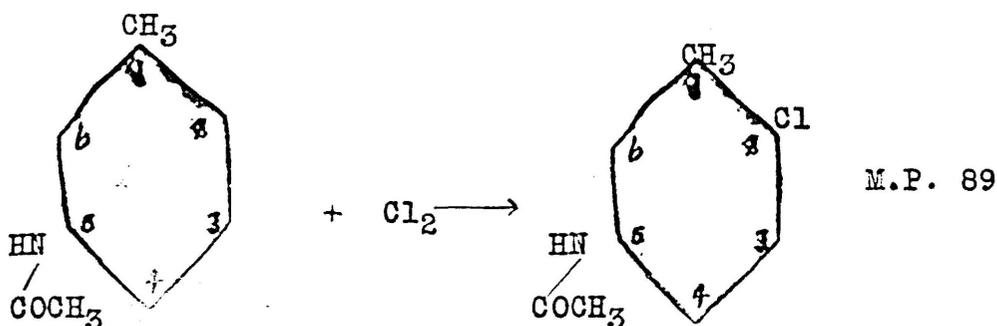
The nitro derivative of this chlor-iodo-toluene was made by treating with a mixture of a little fuming and ordinary nitric acid at room temperature. After one recrystallization from alcohol it melted fairly sharply at about 90 . It was a light yellow crystal.

1-METHYL-2-CHLOR-5-iodo BENZENE.

This compound was made in two different ways. In the one case o-toluidine is the starting point while in the other m-toluidine was.

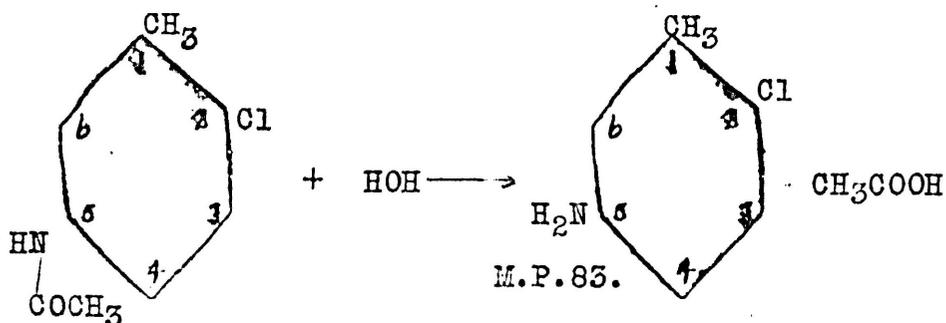
1-Methyl-2-chlor-5-acetyl amino benzene.(4)

This compound was made by dissolving twenty-two and one half grams m-acettoluid in seventy-five c.c. glacial acetic acid and thirty-five c.c. concentrated hydrochloric acid. This was cooled in an ice bath and turbinated while a solution of ten grams sodium chlorate in forty c.c. of water was slowly added. In about three hours the stirring was stopped and the mix set in a cold place (not to exceed about 15°) for about nineteen hours. Upon pouring into water a dark oil separated. This was extracted with ether and the latter distilled off.



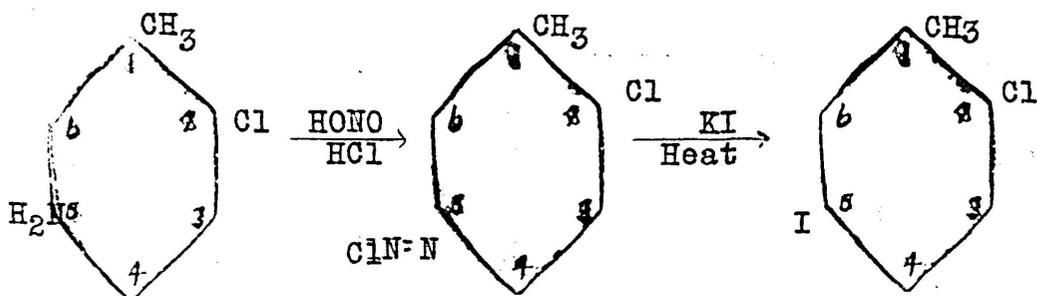
Without purifying, the 1-methyl-2-chlor-5-amino benzene was made by hydrolizing this oily residue for three or four hours with about five grams of concentrated

hydrochloric acid per gram of substance. This was made alkaline and steam distilled. The clear oil which came over soon crystallized to a white solid. This upon recrystallization melted at 83°, while its acetyl derivative at 89°.



1-Methyl-2-chlor-5-iodo benzene

This product was obtained by making the hydrochloride of the 1-methyl-2-chlor-5-amino benzene (14g.) and dissolving it in water. It was then treated with eight and one half grams of sodium nitrite in water solution and then with twenty five grams of potassium iodide in solution in water. After standing for some time it was warmed up, made alkaline and steam distilled. A brownish colored oil came over.



This 1-methyl-2-chlor-5-iodo benzene upon nitration with fuming nitric acid at 0 degrees gave a light yellow nitro compound which was readily recrystallized from alcohol in nice, slender yellow needles with a sharp melting point of 84°. The position of the nitro group was not determined but it was established that it was a mono-nitro derivative.

Analysis of nitro-derivative:

	I	II
Weight of sample	.5156	.5156
No. c.c. HCl (.1861 N)	15.0	15.0
No. c.c. NaOH (.2513 N)	4.31	4.50

N calculated on $C_7H_5INClO_2$:

4.70%

Found:

4.64%

4.51%

It was learned that an ordinary method for a Kjeldahl determination would not free all the nitrogen in these nitro compounds, so a special procedure was used.

Some effort has been made to identify this nitro compound by the following methods:

I. p-Nitro-o-toluidine was prepared. (5) This upon treatment with iodine monochloride in glacial acetic acid solution yields 5-iodo-p-nitro-o-toluidine. (6)

(5) Ber. 17, 265 (1884)

(6) Amer. Chem. Jr. 44, 500 (1910)

By replacing the amino group with chlorine in the usual way, one of the nitro derivatives of the above, 1-methyl-2-chlor-5-iodo benzene was obtained. A satisfactory crystallization and purification of this compound has not yet been made, but this will be continued.

II. 3-nitro-o-toluidine (7) was also treated with iodine monochloride in acetic acid solution. Here the 1-methyl-2-amino-3-nitro-5-iodo benzene was obtained. (8) Here again was the amino group replaced by chlorine and another nitro derivative of the above compound was obtained. This also was not satisfactorily purified as yet.

The second method for making 1-methyl-2-chlor-5-iodo benzene was as follows:

1-methyl-2-amino-5-iodo benzene

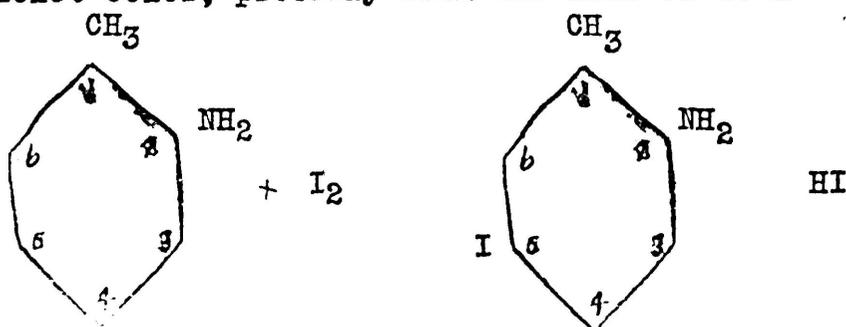
This compound was made according to Wheeler & Liddle. (9) Twenty-five grams of o-toluidine, twenty-five grams of calcium carbonate (or twenty-one grams of magnesium carbonate), 54.4 grams of iodine, 60 c.c. water, and 60 c.c. of ether were warmed on a water bath under a reflux condenser until the excess iodine vapor disappeared.

(7) Reverdin & Crepieux, Ber. 33,2498 (1900)

(8) Amer. Chem. Jr. 44,497 (1910)

(9) Amer. Chem. Jr. 42,501 (1909)

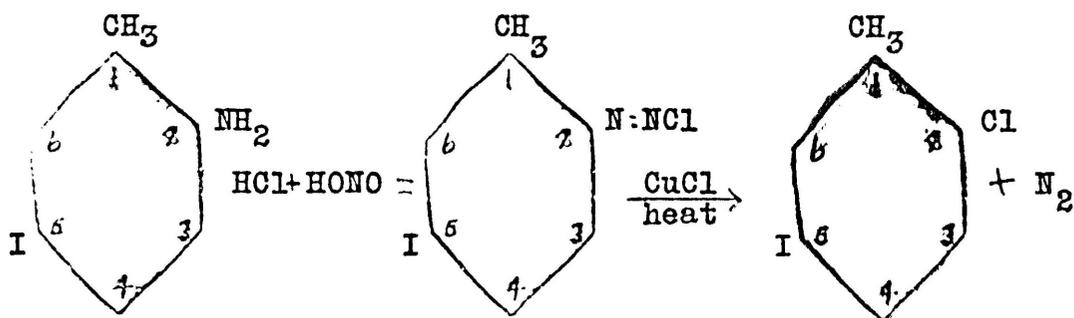
Upon steam distillation, it passed over rather slowly as a purple tinted oil which soon solidified. Upon recrystallization from gasoline, it is a white solid with a melting point of 90-91°. This substance has a decided odor of naphthalene or its derivatives, especially when impure. When allowed to stand for some time, it turns to a blue or a violet color, probably with the loss of iodine.



1-methyl-2-chlor-5-iodo benzene

Twenty-five grams of 1-methyl-2-amino-5-iodo benzene were dissolved as completely as possible by warming with 65 c.c. concentrated hydrochloric acid and 200 c.c. water. It was found to be difficultly soluble. This was diazotized at 0 degrees with about 10 grams sodium nitrite in water solution and the cold solution filtered and treated with cold cuprous chloride solution which was prepared as follows: seven grams copper carbonate, or the equivalent amount of cupric chloride, was dissolved in 100 c.c. hydrochloric acid and boiled out of contact with air with excess copper turnings until

the solution is colorless. This mixture upon warming slightly was made alkaline and steam distilled. Again, a reddish colored oil passed over.



This compound upon nitration yielded a light yellow nitro compound, the melting point of which was 84° and proved to be the same as the other which was previously prepared. This gives a check on the constitution of this chlor-iodo toluene.

The index of refraction of this oil was determined as 1.599 at 20 degrees centigrade. When distilled under reduced pressure its boiling point was 150 degrees at 26 mm. pressure.

This 1-methyl-2-chloro-5-iodo benzene was the only one of the isomers which were made here, that was found to solidify at ordinary temperatures. It crystallized in rather long reddish colored yellow crystals melting at about 20 degrees.

This compound may be the same as was obtained by treating o-chlor-toluene with iodine and nitric acid.(10) This would then show the position taken by the iodine on direct action. The compound just mentioned at least proved to be the same as was made by D. M. Hetler (11) by the same method used by Nelson. Both mono-nitro derivatives melted sharply at 84 degrees and the mixed melting point indicated that they were the same compound.

In the nitration of the various chlor-iodo-toluenes this one seemed to be acted upon most easily, or at least the resulting product was most easily crystallized.

(10). Thesis of H. A. Nelson on " Direct Iodination of Organic Compounds through the Agency of Nitric Acid", for Degree of Master of Arts at Kansas University in 1917.

(11). Work done in University of Kansas as yet unpublished.

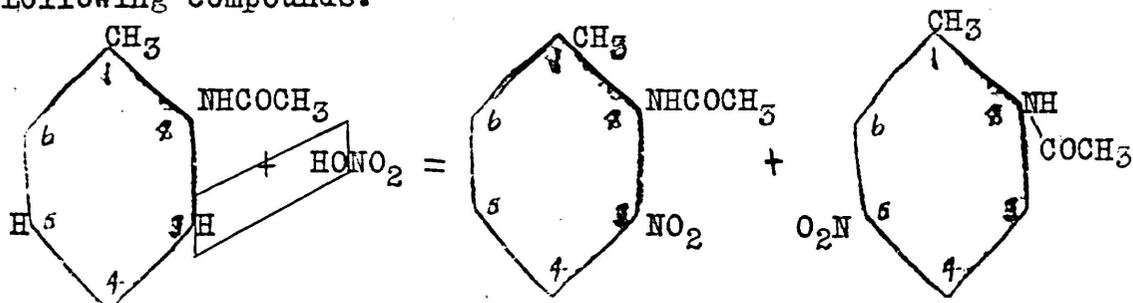
1-METHYL-2-iodo-3-CHLOR BENZENE

The starting point for this compound was o-acet-
toluide which was nitrated according to the method of
Reverdin and Crepieux. (12) Both of the following methods
were used to compare the results but much difference
could not be noticed.

I. In a bath at a temperature from 30 to 35 de-
grees, forty grams of o-acettoluide was slowly added to a
mixture of sixty-one c.c. of fuming nitric acid and
seventy-seven c.c. of ordinary concentrated nitric acid.
After the reaction was fairly quiet it was left stand-
ing for twenty-four hours. It was then poured into ice,
filtered, washed with water and dried.

II. Forty grams of o-acettoluide was slowly ad-
ded to a mixture of 170 c.c. of fuming nitric acid and
70 c.c. of glacial acetic acid at 0 temperature. After
allowing to stand for an hour or two it was poured on to
ice as in the first case.

These two methods give a mixture of the two
following compounds.

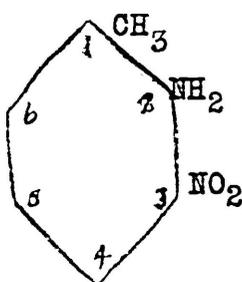


(12) Ber, 33, 2498(1900).

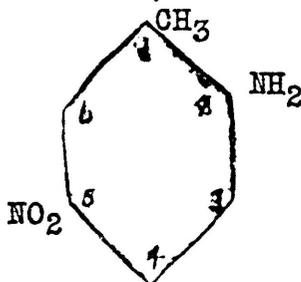
The acetyl groups are hydrolyzed off by boiling the mixed nitro compounds with about three times their own weight of 25% hydrochloric acid for three or four hours.

The free nitro ortho toluidines were separated by steam distillation. The hydrochlorides of both are decomposed by water almost completely. The 3-nitro-*o*-toluidine passes over with steam more or less readily. In one case it required about thirty-five hours to completely steam distill a sample of it while in another it was completely distilled in about four hours. It seemed to be a question in the one case of incomplete hydrolysis. Perhaps when steam distillation started the dilution decreased the rate of hydrolysis and hence the long process. In one case from forty-two grams of the mixed nitro *o*-acetotoluides was obtained eleven grams of the 3-nitro and six grams of the 5-nitro amine.

After the distillation is complete the residue in the flask is filtered and the 5-nitro-*o*-toluidine separates without making it alkaline.



M.P. 95°

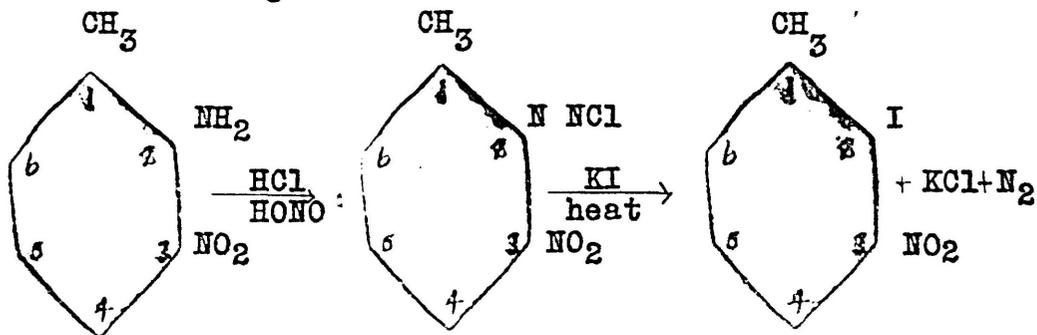


M.P. 131° (Wheeler 130)

It was learned later, however, that a more complete separation of the 5-nitro derivative could be obtained by treating the mixture with a small amount of ammonia. This difference might have been due to the difference of concentration of hydrochloric acid in the liquors.

1-Methyl-2-iodo-3-nitro benzene

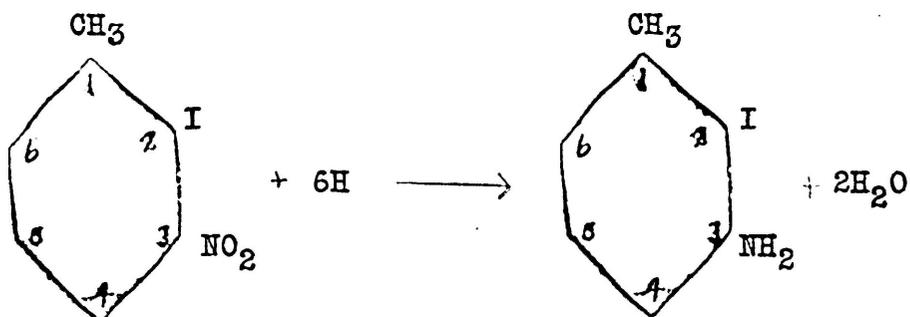
Ten grams of 1-methyl-2-amino-3-nitro benzene was dissolved in 50 c.c. of concentrated sulfuric acid and cooled in ice. Five grams of sodium nitrite was powdered and slowly added thereto. The mixture was poured into ice and allowed to stand until nearly all the solid had gone into solution. It was filtered and treated with seventeen grams of potassium iodide in water solution. After warming up and treating with a little sodium acid sulfite, the mixture was steam distilled. A brownish oil readily passed over. The yield was fifteen grams or 86% of the theoretical.



(13) Amer. Chem. Jr. 42,451 (1909)

1-Methyl-2-iodo-3-amino benzene (14)

In a flask fitted with a Bunsen valve was heated for several hours on a water bath fifteen grams of 1-methyl-2-iodo-3-nitro benzene, 160 grams of ferrous sulfate, 300 c.c. boiling water, and 300 c.c. concentrated ammonia. At the end of this time the solid was repeatedly extracted with alcohol and after the alcohol was distilled off the residue was steam distilled. A small amount of dark oil was thereby obtained.

1-Methyl-2-iodo-3-chlor benzene

About five grams of the 1-methyl-2-iodo-3-amino benzene was dissolved in 20 c.c. sulfuric acid and 75 c.c. water. (15) The mixture was cooled to 0 degrees and carefully treated with 2.2 grams of powdered sodium nitrite. It was finally treated with an excess of cuprous chloride prepared as in the former cases. After

(14) Amer. Chem. Jr. 42,452 (1909)

(15) Ibid.

allowing to stand for some time, it was made alkaline and steam distilled. About two grams of a rather dark oil passed over which was about 35% of the theoretical. There was not sufficient time to prepare more of this compound and to complete its study.

An attempt was made to nitrate this compound but it did not nitrate as readily as some of the others.

1-METHYL-3-CHLOR-4-iodo BENZENE

This was made from p-acettoluide as a starting point.

1-Methyl-3-nitro-4-amino benzene

This product was prepared by nitrating p-acet-toluide according to the method of Cosack. (16) It might be mentioned that this gives the nitro group in the 3-position, while upon nitrating free p-toluidine it takes the 2-position. The compound is hydrolized to the free amine. It is a dark red solid which has a melting point of 115 to 116°

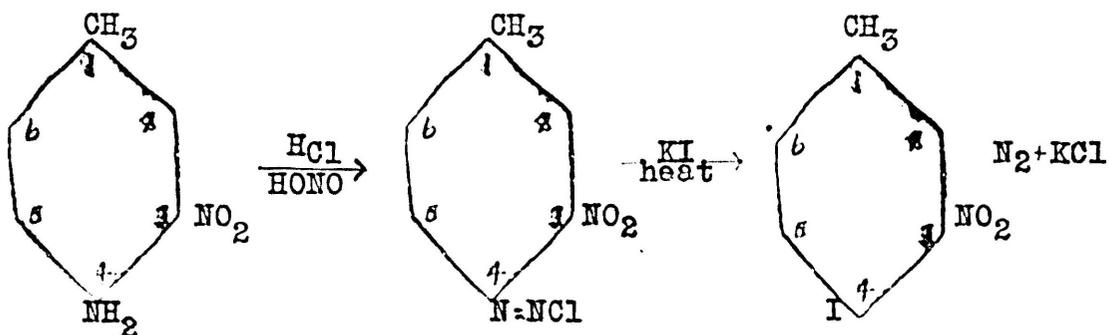
1-Methyl-3-nitro-4-iodo benzene (17)

Twenty-eight grams of 1-methyl-3-nitro-4-amino benzene was as completely as possible dissolved in 100 grams of hydrochloric acid and 300 c.c. of water. It was diazotized at 0 degrees with 17 grams of sodium nitrite in 80 c.c. of water. It was treated cold with a solution of 50 grams of potassium iodide. It was then warmed up and steam distilled.

(16) Ber. 13,1088 (1880)

(17) Amer. Chem. Jr. 44,139 (1910)

The oil which came over soon solidified and had a melting point of 54 to 56°. The yield was 34.5 grams



or about 80% of the theoretical.

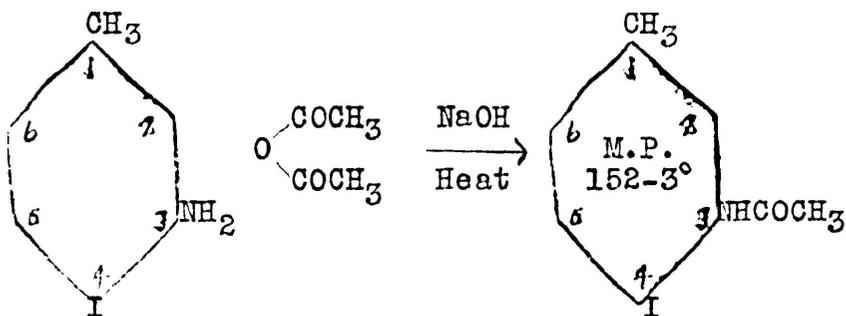
This method was varied slightly by dissolving the amine in 400 c.c. of 30% sulfuric acid and at the end instead of distilling, the dark oil was separated, washed with alkali and recrystallized from alcohol. The yield was 38 grams or nearly 88% of the theoretical.

1-Methyl-3-amino-4-iodo benzene

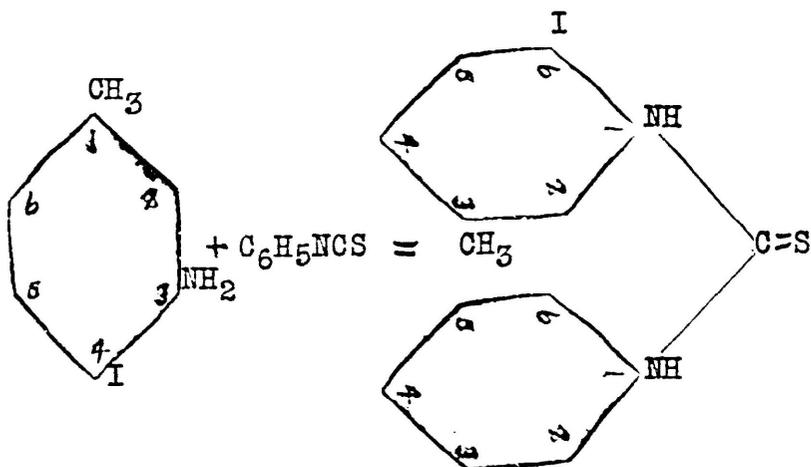
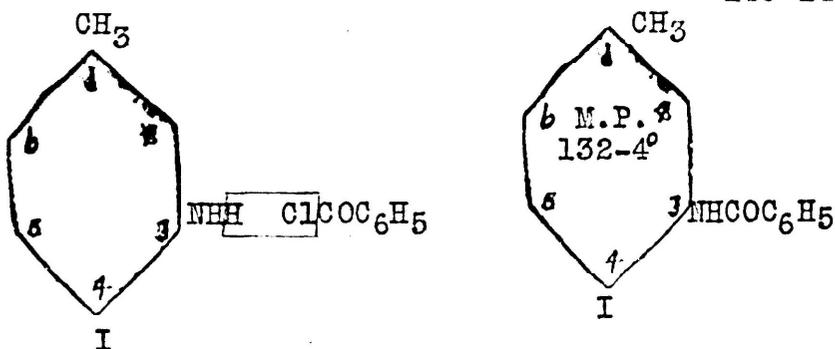
This iodo-toluidine was obtained by reducing the corresponding nitro derivative exactly as in the case of the 2-nitro compound. (18) From twenty grams of 1-methyl-3-nitro-4-iodo benzene, 213 grams of ferrous sulfate, 400 c.c. boiling water, and 400 c.c. concentrated ammonia, was obtained after steam distillation, 10 grams of a yellow oil which was 56.5% of the theoretical.

(18) Amer. Chem. Jr. 44,139 (1910)
Ber. 39,273 (1906)

For the sake of identification the following derivatives of this amine were made by the standard methods.



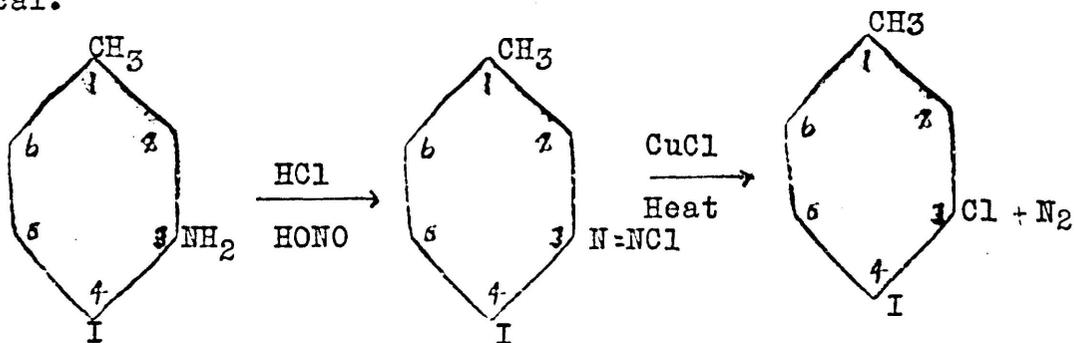
(Wheeler, 151) (Willgerot & Simonis 145-146°).



Snow white crystals, M.P. 163-4° (Wheeler, 162-3°).

1-Methyl-3-chlor-4-iodo benzene

This compound was made as usual from the 1-methyl-3-amino-4-iodo benzene by using 18.1 grams of the amine 20 grams of hydrochloric acid in 20 c.c. of water, 7 grams of sodium nitrite, cuprous chloride from 5 grams of copper carbonate in 50 c.c. of hydrochloric acid and an excess of copper turnings. The mixture was warmed, made alkaline and steam distilled. The yield was ten grams of the chlor-iodo-toluene or only about 48% of the theoretical.



When redistilled, this oil boiled at 140-150 at 23 mm. pressure.

Its index of refraction was found to be 1.615 at 20°.

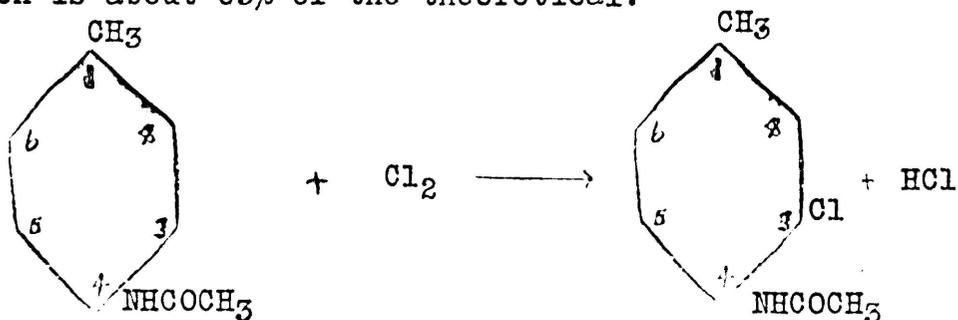
1-METHYL-3-CHLOR-4-iodo BENZENE

(Second Method)

3-Chlor-p-toluidine

p-Acettoluide was chlorinated with sodium chlorate, hydrochloric acid and glacial acetic acid as in the former cases. (19). From 22.5 grams of p-acettoluide, 75 c.c.

of glacial acetic acid, 35 c.c. of hydrochloric acid and 10 grams of sodium chlorate was obtained about 18 grams which is about 65% of the theoretical.

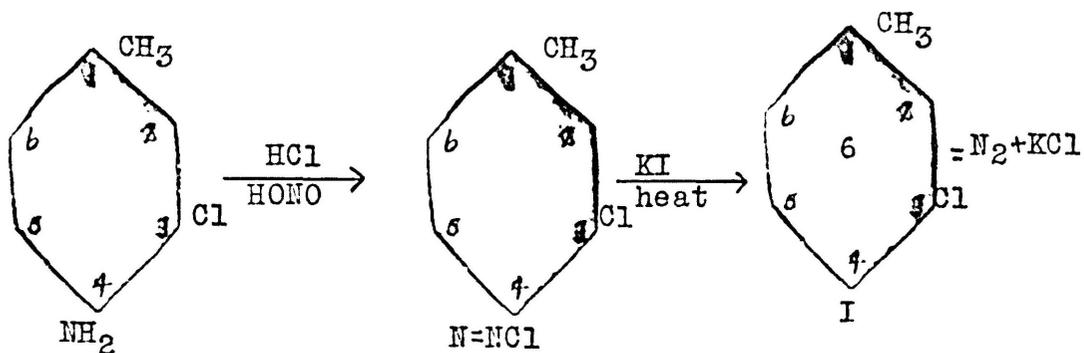


The free amine was prepared from this acetyl derivative by hydrolyzing for three or four hours. It was then made alkaline and steam distilled. It was learned that the best yields could be obtained by hydrolyzing in acid solution. It was found that the per cent of hydrolysis could be raised from such values as 30 to 40 % up to about 75 or 80 % by substituting acid for alkali. Another interesting phenomenon was noticed in this connection. In two or three instances the hydrolysis seemed to affect the amino group. The reason for assuming this was that when the mixture was made alkaline a large quantity of ammonia was liberated.

It was also observed that a better product could be obtained by hydrolyzing with about 35 % acid instead of pure acid. In one case by this method the 3-chloro-p-toluidine solidified in the condenser at ordinary temperature.

(19). Ber. 33,2500(1900).

Fourteen grams of the amine were treated as in the former cases with fifty grams of hydrochloric acid, eight and one-half grams of sodium nitrite, twenty-five grams of potassium iodide, giving a yield of nineteen grams of the chlor-iodo-toluene or 76% of the theory.



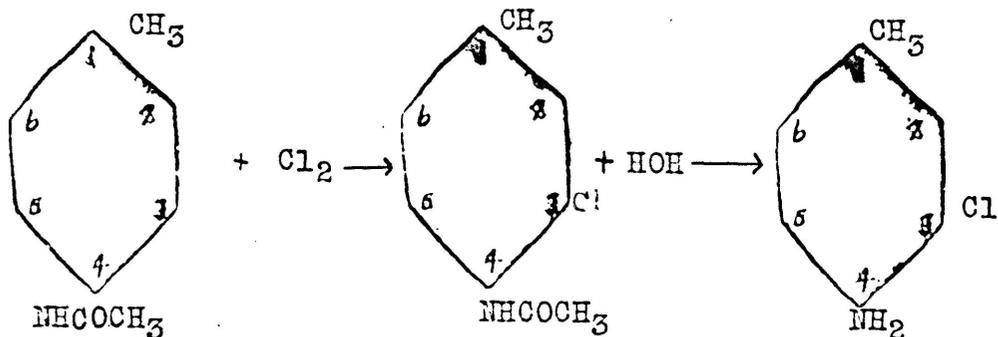
This chlor-iodo-toluene was nitrated at zero temperature with fuming nitric acid and a compound obtained which upon recrystallization twice from alcohol had a melting point of 100° to 104°.

1-METHYL-3-CHLOR-5-IODO BENZENE.

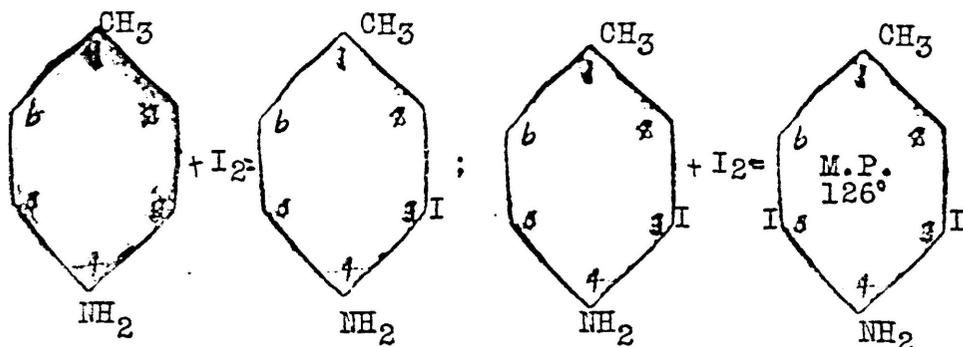
This product was prepared with para toluidine as the starting point.

3-Chlor-p-toluidine.

p-Acettoluide was chlorinated as in the previous cases by the use of sodium chlorate and hydrochloric acid in acetic acid solution.



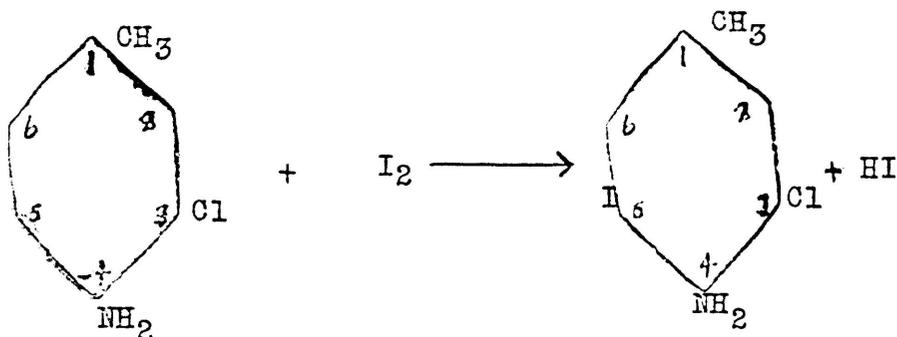
Wheeler and Liddle(20) of Yale have shown that by treating p-toluidine with iodine, calcium carbonate, water and ether with one or two molecular portions of iodine, the following succession of reactions results.



It was assumed that in the present instance an analogous reaction would result.

1-Methyl-3-chlor-4-amino-5-iodo benzene(?)

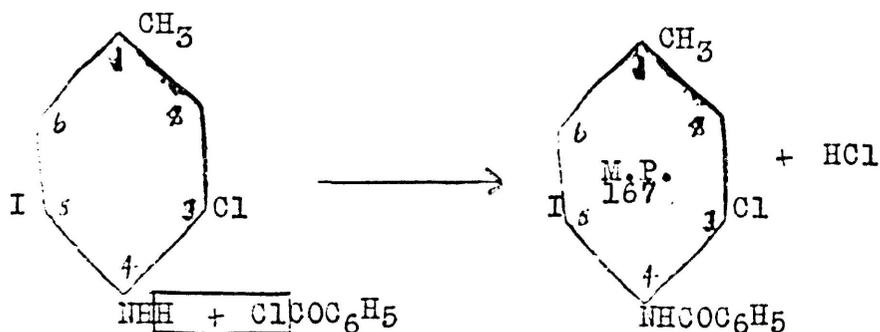
This compound was made in accordance with the previous suggestion as follows: Eleven grams of 1-methyl,-3-chlor-4-amino benzene was heated under a reflux condenser with eight and one-third grams of calcium carbonate, twenty c.c. of ether and twenty c.c. of water. When the iodine vapor seemed to nearly disappear the mixture was treated with a small amount of sodium acid sulfite. In some cases at this point the mixture was steam distilled. In others, the mass was extracted with ether by use of a Soxhlet extractor and then steam distilled. The latter seemed the best method as the calcium carbonate retarded the rate of steam distillation.



From this ether extract there passed over a fairly dark oil which as the distillation proceeded, solidified in the condenser. This was fairly easily recrystallized from alcohol, except that because of its solubility, a large part was left in the mother liquor. On two or three crystallizations from alcohol by boiling with boneblack,

a nice snow-white solid could be obtained but it was difficult to get a sharp melting point. Out of acetone, however, in which the substance was very soluble, it crystallized with a fairly sharp melting point of 87°.

For sake of identification the following derivative of this base was made.



Analysis of $C_{14}H_{11}ONCl$ for Nitrogen.

Weight of sample	.3 grams	.3 grams
HCl (.1864)	10 c.c.	10 c.c.
NaOH (.2525)	4.13 c.c.	4.17 c.c.
% Nitrogen calculated-	3.77%	
" "	3.83%	3.78%

An attempt was made to obtain the hydrochloride of this base by passing dry hydrogen chloride into a benzene solution of it for two or three hours. The melting point of the residue indicated the same material with which it was started, hence the conclusion that it is a very weak base.

Analysis of the free amine for % of Nitrogen.

Weight of sample	.3 gram
Hydrochloric acid (.1864)	10 c.c.
Sodium Hydroxide (.2525)	2.78 c.c.
Nitrogen calculated	5.52%
Nitrogen found	5.42%

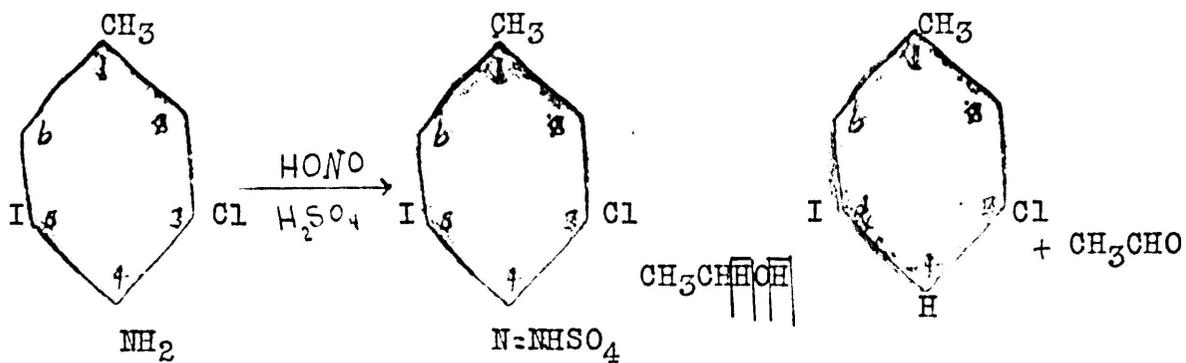
The amine upon very slow crystallization from alcohol forms in very slender needles as much as two or three inches in length.

1-Methyl-3-chlor-5-iodo benzene

This was prepared from 1-methyl-3-chlor-4-amino-5-iodo benzene simply by the removal of the amino group according to the method suggested by Wheeler. (21)

Eight grams of the base were suspended in a mixture of eight c.c. of concentrated sulfuric acid and fifty-five c.c. of absolute alcohol. The mixture was heated on a water bath while six grams of powdered sodium nitrite was slowly added. After further warming for a half-hour the mix was poured into water and a reddish brown oil separated. It was then steam distilled and about four and five-tenths grams of the oil passed over which was about 70% of the theoretical.

(21). Amer. Chem. Jr. 44, 144 (1910).



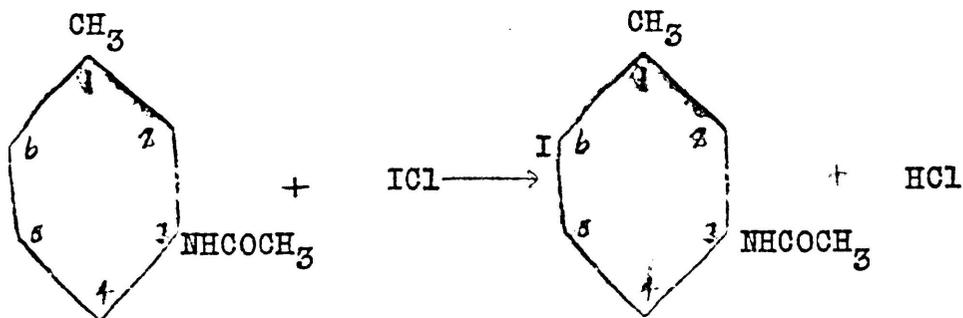
Time did not permit the preparation of a large amount of this chlor-iodo-toluene so that the physical constants could be determined. This will be continued at a later date.

1-METHYL-3-CHLOR-6-iodo BENZENE

The parent substance of this compound is m-toluidine,

6-Iodo-m-acettoluide

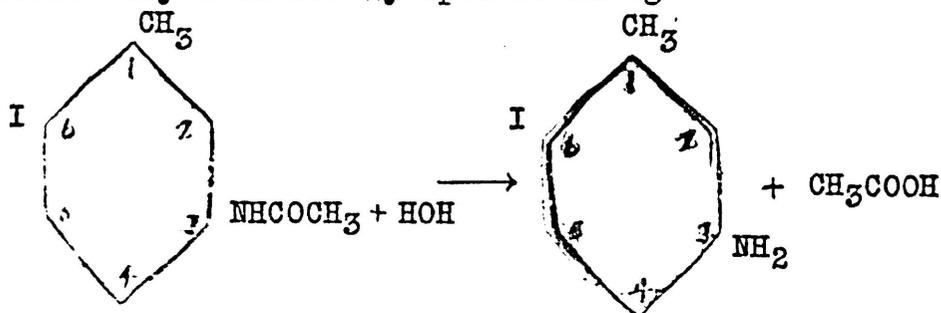
Wheeler mentions the method which is now to follow. (22) Twenty grams of m-acettoluide were dissolved in twenty c.c. of glacial acetic acid and twenty-two grams of iodine monochloride carefully added. The mass was heated to boiling under a reflux condenser for one hour. On the addition of water a dark oil separates which by treatment with sodium acid sulfite partly clears up. This compound upon recrystallization from alcohol melted at 141 degrees. Wheeler gives it as 132° to 134° while Artmann as 132°.

6-Iodo-m-toluidine

The free base was obtained from this acetyl derivative by dissolving it in alcohol and refluxing it for a couple of hours with slightly less than twice its own weight of solid sodium hydroxide.

(22) Amer. Chem. Jr. 44,130 (1910)

This product readily steam distilled as a rather dark oil. This soon solidified and upon recrystallization from petroleum ether melts at 43 degrees. (Wheeler 37° to 39°) When pure, this compound is white, but it soon becomes very dark merely upon standing.



An effort was made to hydrolyze the acetyl derivative by use of hydrochloric acid, but large amounts of iodine vapor were given off and no pure product could be obtained from the mixture after hydrolysis.

1-Methyl-3-chlor-6-iodo benzene

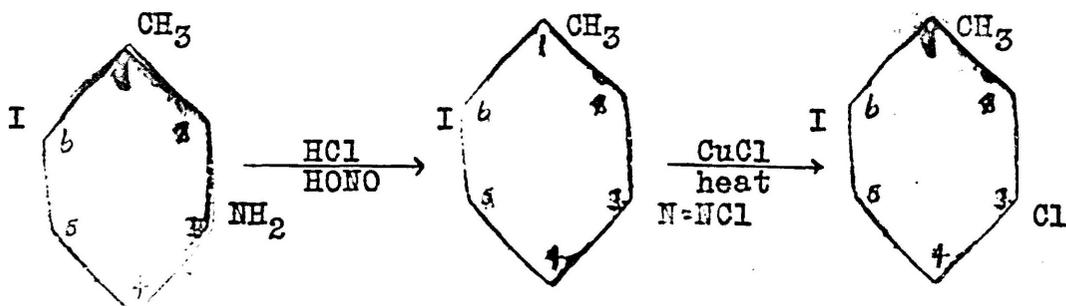
This chlor-iodo-toluene was obtained from the 1-methyl-3-amino-6-iodo benzene. Two methods were used to obtain the diazo reaction, in this case neither of which was very satisfactory.

I. Nineteen and one-third grams of the amine were dissolved with difficulty in 70 c.c. of 25% hydrochloric acid on the water bath and treated at 0° temperature with a solution of seven grams of sodium nitrite.

The diazo solution was filtered and treated with cuprous chloride, made alkaline and steam distilled.

II. In this method eighteen grams of the amine was diazotized by adding it to 120 grams of concentrated sulfuric acid at 0° temperature and this mixture after being thoroly stirred was treated with 7.2 grams of powdered sodium nitrite. This mixture was then poured on to ice. From this point the diazo solution was treated as in the previous case.

In each case after steam distillation, there was obtained but five grams of the chlor-iodo-toluene which was approximately 25% of the theoretical. In the second method, however, the oil was not so dark.



This compound was redistilled under reduced pressure at a boiling point of 130 to 140 degrees, under a pressure of 19 mm.

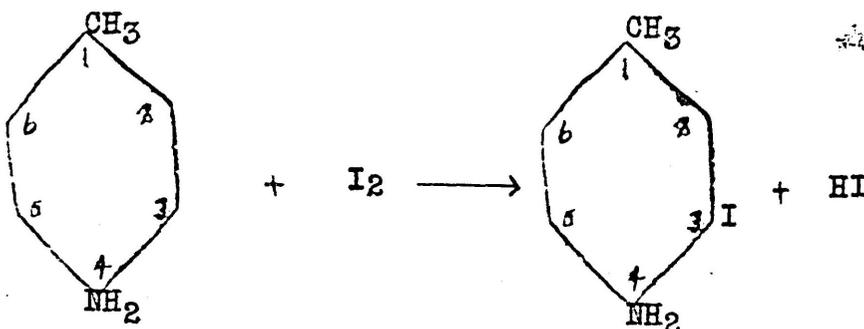
The index of refraction was 1.609 at 20 degrees.

1-METHYL-3-IODO-4-CHLOR BENZENE

The parent substance of this compound was p-toluidine.

3-Iodo-p-toluidine (23)

For the iodination of p-toluidine Wheeler & Liddle give the following method: Twenty-five grams of p-toluidine, fifty-four and four-tenths grams of iodine, twenty-five grams of calcium carbonate, sixty c.c. of ether and sixty c.c. of water were warmed in a flask on a water bath until the most of the iodine vapor had disappeared. The product was then steam distilled as a rather dark oil. the yield was thirty-seven grams which is about 69% of the theoretical. In some cases there was obtained a rather clear oil which, upon standing soon solidified.

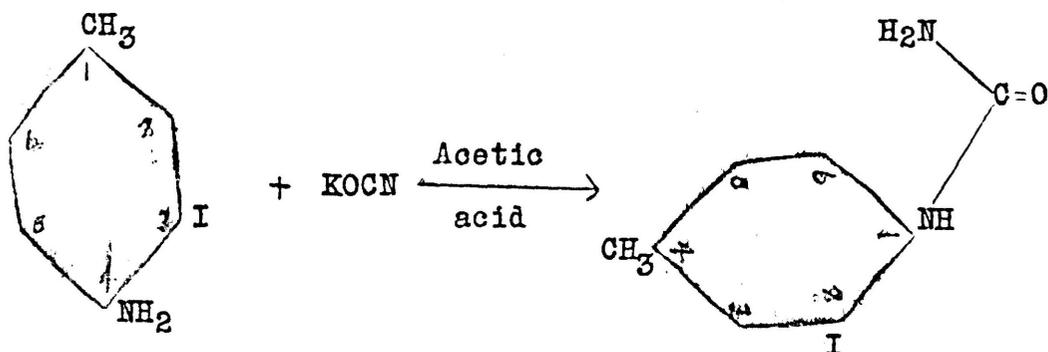


For the sake of identification of this base some derivatives of it were prepared.

(23) Amer. Chem. Jr. 42, 445 (1909).

According to Wheeler (24) the acetyl derivative of this base has a melting point of 133° but in this work it seemed difficult to get the product pure.

When this 3-iodo-4-amino-toluene was warmed with potassium cyanate in molecular proportions the urea was formed whose melting point was found to be 192 degrees.



Wheeler gives this melting point as 187 degrees (25).

The hydrochloride salt was also made and it had a melting point of 185-187 degrees.

1-METHYL-3-iodo-4-CHLOR BENZENE

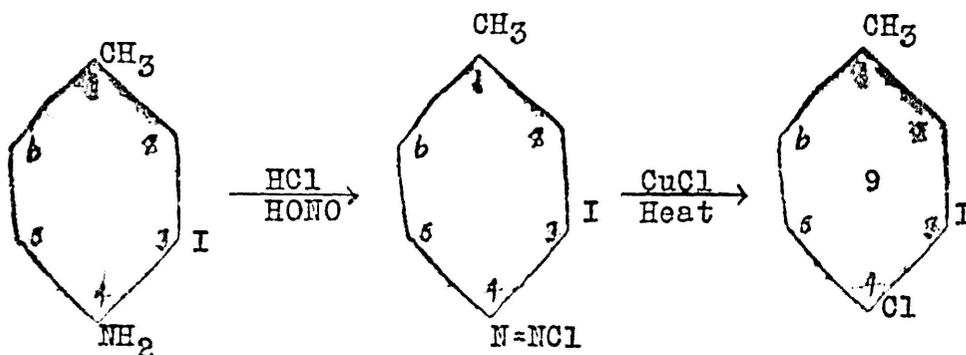
This product was made in the usual way by replacing the amino group with the halogen.

Thirty-six grams of the 3-iodo-4-amino-toluene were dissolved in forty c.c. of hydrochloric acid and an excess of water. This was diazotized with thirteen and one third grams of sodium nitrite at 0 degrees. It was then treated with cuprous chloride solution from ten grams of Copper Carbonate and one hundred c.c. of hydrochloric acid. It

(24) Amer. Chem. Jr. 42,447 (1909)

(25) Ibid.

was steam distilled after making alkaline. A very dark oil readily came over. This, however, after being redistilled was much lighter in color.



Upon redistillation at a pressure of 21 mm this oil had a boiling point of 130 to 160 degrees.

Its index of refraction was found to be 1.612 at 20 degrees temperature.

1-METHYL-2-iodo-4-CHLOR BENZENE

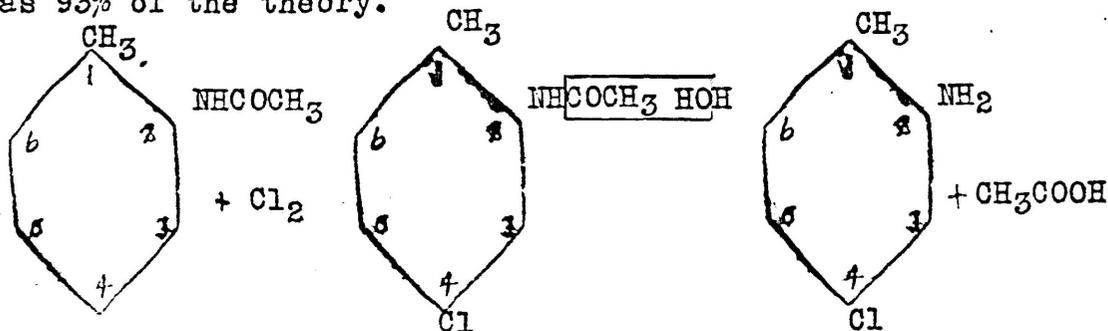
The reagent from which this compound was made was ortho toluidine.

1-Methyl-2-acetyl amino-4-chlor-benzene

(26) 45 Grams of o-acettoluide was chlorinated as in the other cases, being in solution in 150 c.c. of glacial acetic acid and 70 c.c. of hydrochloric acid while treated with 20 grams of sodium chlorate dissolved in 70 c.c. of water. The yield was 40 grams or about 73% of the theoretical.

1-Methyl-2-amino-4-chlor benzene

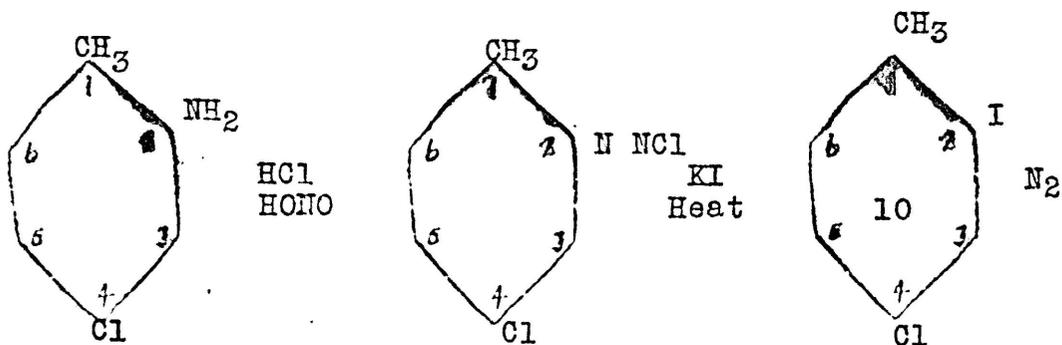
This base was made by hydrolizing the acetyl derivative in hydrochloric acid solution, 40 grams of it being refluxed with 300 c.c. of it. At the end of the hydrolysis in five hours the mixture was made alkaline and steam distilled. (27) 39 grams of the oil separated which was 93% of the theory.



(26) Ber. 7, 797 (1874); 19,2441 (1886); II, 461
 (27) BBer. 7, 797 (1874)

1-Methyl-2-iodo-4-chlor benzene

This was made from the above amine in the usual way of replacing the amino group with iodine. 28 grams of the amine were dissolved in 100 grams of hydrochloric acid and 300 grams of water, diazotized cold with 17 grams of sodium nitrite and then treated with 45 grams of potassium iodide. After allowing to stand for some time the mixture was made alkaline and steam distilled. A light brown oil readily passed over. 30 grams were obtained which was 60% of the theory.



This 2-iodo-4-chlor toluene was nitrated at 0 temperature with fuming nitric acid. It was recrystallized from petroleum ether as a white crystalline solid with a melting point of 88 degrees.

When redistilled at 28 mm pressure its boiling point was 142 degrees.

The index of refraction of this oil was found to be 1.614 at 20 degrees.

It would possibly be well to make some few statements regarding these compounds in general.

They all have a slightly yellowish color which approaches a reddish tint in some cases and a slight tendency toward the green in one or two cases. All of them have a tendency to darken in color upon standing, especially in the light. This color can be partly removed by shaking with mercury which indicates that perhaps it is iodine that is liberated.

As yet no halogen analyses of them have been made which were entirely satisfactory, as it is found that they are almost insoluble in liquid ammonia and in this condition Sodium acts very slowly upon them.

It was pointed out that only one of these oils has solidified at room temperature.

On the following page will appear a short tabulation summing up some of the more important data about these oils.

FORMULA	PHYS. STATE	INDEX OF REF. T. 20	BOILING POINT	MELTING P. OF NITRO DERIV.
I. $\text{C}_6\text{H}_3 \begin{cases} \text{CH}_3 & (1) \\ \text{Cl} & (2) \\ \text{I} & (3) \end{cases}$	Oil			
II. $\text{C}_6\text{H}_3 \begin{cases} \text{CH}_3 & (1) \\ \text{Cl} & (2) \\ \text{I} & (4) \end{cases}$	Oil	1.583	130-150° at 23 mm.	90°
III. $\text{C}_6\text{H}_3 \begin{cases} \text{CH}_3 & (1) \\ \text{Cl} & (2) \\ \text{I} & (5) \end{cases}$	Solid M. P. 20°	1.599	150° at 26 mm.	84°
IV. $\text{C}_6\text{H}_3 \begin{cases} \text{CH}_3 & (1) \\ \text{Cl} & (2) \\ \text{I} & (6) \end{cases}$	Oil			
V. $\text{C}_6\text{H}_3 \begin{cases} \text{CH}_3 & (1) \\ \text{I} & (2) \\ \text{Cl} & (3) \end{cases}$	Oil			
VI. $\text{C}_6\text{H}_3 \begin{cases} \text{CH}_3 & (1) \\ \text{Cl} & (3) \\ \text{I} & (4) \end{cases}$	Oil	1.615	140-150° at 23 mm.	100-104°
VII. $\text{C}_6\text{H}_3 \begin{cases} \text{CH}_3 & (1) \\ \text{Cl} & (3) \\ \text{I} & (5) \end{cases}$	Oil			
VIII. $\text{C}_6\text{H}_3 \begin{cases} \text{CH}_3 & (1) \\ \text{Cl} & (3) \\ \text{I} & (6) \end{cases}$	Oil	1.609	130-140° at 19 mm.	
IX. $\text{C}_6\text{H}_3 \begin{cases} \text{CH}_3 & (1) \\ \text{I} & (3) \\ \text{Cl} & (4) \end{cases}$	Oil	1.612	130-160° at 21 mm.	
X. $\text{C}_6\text{H}_3 \begin{cases} \text{CH}_3 & (1) \\ \text{I} & (2) \\ \text{Cl} & (4) \end{cases}$	Oil	1.614	142° at 28 mm.	88°