THE PREPARATION AND BEHAVIOR OF CERTAIN HALOGEN
AND NITRO DERIVATIVES OF BENZENE

by

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INTRODUCTION

The common method for the preparation of diphenyl and alkyl benzene derivatives is that of Fittig. It consists in allowing sodium to act on a mono-halogen derivative dissolved in benzene. If an alkyl benzene is to be prepared, sodium is allowed to react with a benzene solution of an alkyl halide and a halogen benzene. Alkyldiphenyl compounds can also be made from bromo alkyl benzenes by treatment with sodium. The bromides of the homologues of benzene, react in a similar manner with sodium. For example bromotoluene with methyl iodide and sodium gives xylene. However, the three isomeric bromotoluenes do not react with the same ease. While the parabromtoluene gives a good yield of paraxylene, the ortho compound does not give good results, and the meta compound generally forms no xylene. The great number of benzene derivatives which may be prepared by Fittig's reaction is apparent from the above examples. Ullmann has prepared a large number of diphenyl derivatives by heating with copper instead of sodium, but only one or two simple halogen nitro compounds. It is well known that the nitro group ortho and para or both ortho and para to halogens renders such halogens easily reactive with many of the ordinary reagents.
These reagents are sodium alkylates, sodium malonic esters, and sodium acetoacetic ester; the halogens being replaced by alkoxy groups, etc. However, in certain important instances the halogen is replaced by hydrogen only. It would, therefore, appear quite probable that such halogens would easily give Fittig's reaction.

With a view of ascertaining whether Fittig's reaction would hold if the benzene nucleus contained three or more substituents, a number of halogen and nitro derivatives in benzene solution were treated with sodium. The bodies selected for study were symmetrical tribromotrinitrobenzene, 1-iodo-2,4,6-tribromobenzene, symmetrical tribromobenzene, and 1-iodo-2,4,6-tribromo-3-nitrobenzene. A brief statement of the methods employed for the preparation of these bodies will now be given.

Symmetrical tribromotrinitrobenzene was prepared by nitrating symmetrical tribromobenzene using the method of Jackson and Wing. Symmetrical tribromobenzene is boiled with a mixture of two parts fuming nitric acid (Sp.gr.1.5) and fuming sulphuric acid (Sp.Gr.1.91) for eight hours under the reflux condenser. The body melts at 283°-285°.

Tribromoiodobenzene has been prepared according to Silberstein's method, and also according to Jackson and Calvert's method. It was found, however, that the following modi-

fication gives a smoother reaction and a better yield. Symmetrical tribromoaniline is diazotized in acetic acid solution, using twice the theoretical amount of sulphuric acid and the theoretical amount of sodium nitrite dissolved in the smallest possible amount of water. During the process of diazotisation, the solution of sodium nitrite is added very slowly, and the mixture is cooled to about 17° provided the acetic acid does not freeze. After allowing to stand for an hour, four times the theoretical amount of potassium iodide dissolved in the smallest possible amount of water is added very gradually. After standing an hour, the mixture is heated on the water bath for thirty minutes, cooled, and filtered. The filtrate is washed with a saturated potassium iodide solution to remove the free iodine formed. The solid was then purified by crystallization from a mixture of alcohol and benzene. Tribromobenzene melts at 104°-105°.

Symmetrical tribromobenzene was prepared by diazotizing tribromoaniline dissolved in a mixture of alcohol and benzene and then boiling off the nitrogen. The crude product was purified by sublimation using the Bruehl apparatus. It melts at 119.5°.

The 1-iodo-2,4,6-tribromo-3-nitrobenzene was prepared according to the method of Jackson and Jones. Tribromonitriline is diazotized in cold acetic acid solution, and after two hours a saturated water solution of potassium iodide was added.
After standing overnight the mixture was heated on the water bath, cooled, the solid filtered off and purified. Iodotribromonitrobenzene melts at 144° to 145°.

During the course of this research four new derivatives of 2,6-dibromo-4-nitroaniline were prepared. The compounds were 1-iodo-2,6-dibromo-4-nitrobenzene, 1-iodo-2,6-dibromo-4,5-dinitrobenzene, 1-chloro-2,6-dibromo-4-nitrobenzene, and 1-chloro-2,6-dibromo-4,5-dinitrobenzene. The action of sodium, sodium ethylate, and nitric acid with both the mononitro compounds was studied, as well as the action of chlorine on the iodine compounds. All attempts to prepare the dibromonitrobenzonitrile failed. In each case the compound obtained was symmetrical dibromonitrobenzene as confirmed by the halogen content and the melting point determinations.
EXPERIMENTAL PART

Action of Sodium on Symmetrical Tribromotrintrinitrobenzene. It is a well known fact that in substituted aromatic compounds, the firmness with which the halogens are attached to the benzene ring is diminished by the presence of the nitro group in the ortho and para positions. For this reason, symmetrical tribromotrintrinitrobenzene was selected for study.

Five grams of tribromotrintrinitrobenzene were dissolved in 120 cc. of dry benzene, and 0.5 gr. of sodium were added. The mixture was boiled gently, using a reflux condenser, for two hours. After standing over night, the contents of the flask were poured on a filter. The filtrate was allowed to evaporate spontaneously, and the melting point of the crystals was taken. A melting point of 284° showed that the tribromotrintritro compound was unchanged. Examination of the brown residue on the filter paper proved it to be mostly unaltered sodium, it did, however, give a slight test for sodium bromide.

Action of Sodium on 1-Iodo-2,4,6-Tribromobenzene

Jackson and Calvert have shown that the presence of three bromine atoms in tribromoiodobenzene exerts a loosening effect similar to that exhibited by nitro groups. By the ac-
tion of sodium ethylate on this body, they readily obtain symmetrical tribromobenzene. The iodine is also easily replaced by a nitro group if the tribromiodobenzene be treated with fuming nitric acid. These facts would seem to indicate that hexabromodiphenyl might easily be prepared by the interaction of sodium and the iodo group in two molecules of symmetrical tribromiodobenzene. Accordingly, equivalent amounts of this compound, dissolved in dry benzene, and sodium wire were boiled under the reflux condenser for four hours. After this time had elapsed, a small portion of the solution was removed, and the melting point of the crystals which separated out was taken. They melted at 104°-106°, proving the compound to be unaltered tribromiodobenzene. The sodium wire had taken on a dark brown color. Gattermann states that a few drops ethyl acetate sometimes starts the Fittig reaction. Consequently three drops of ethyl acetate were added to the mixture in the flask, and the boiling continued for four hours longer. After this time, the sodium wire had apparently been used up, being converted into a brown powder. This undissolved residue was filtered out, washed with benzene, and allowed to dry. It was then extracted with hot water, and tested for halides. The test was negative. The brown powder did not contain organic matter.

The filtrate was allowed to evaporate spontaneously. The tribromiodobenzol was unchanged if the melting point of
the crystals obtained be accepted as proof positive. The melting point was 104°-105°. Since benzene boils at 80° C., and, since the heating for eight hours at this temperature did not produce any appreciable change in the tribromoiiodobenzene, it was deemed advisable to try the experiment at somewhat higher temperature.

Equivalent amounts of clean sodium wire and tribromoiiodobenzene dissolved in 20 cc. dry benzene, were heated in a sealed tube for six hours at 200° C. The tube was examined when cooled and as no visible change in the substance had occurred, except a darkening of the sodium, the heating was continued for eight hours at 250°. After allowing the tube to cool, it was opened. The solution was separated from the undissolved residue, and this residue was washed with benzene to remove any of the solute. The brown residue of the filter was then allowed to dry, and then extracted with hot water. It contained some unused sodium. The washing also contained a small amount of sodium iodide with still smaller amounts of the bromide. A small portion of the residue was found, perhaps, to be organic in nature as it entirely volatilized when heated upon a platinum foil in the Meker flame. The residue had a melting point higher than 300°, and was insoluble in benzene, ligrion, ether, glacial acetic acid, chloroform, and alcohol. A portion of the benzene was evaporated but no crystals were obtained. On complete evaporation,
an uninviting brown tar resulted, except for a few white needles which sublimed out. These needles melted sharply at 119°, indicating that they were symmetrical tribromobenzene. It is interesting to note that Jackson and Calvert, as mentioned above, obtained symmetrical tribromobenzene from tribromoiiodobenzene by the action of sodium ethylate. All attempts to obtain a pure body from the tar failed.

**Action of Sodium on Symmetrical Tribromoiiodobenzene**

Since the above experiment resulted in the removal of some iodine from the tribromoiiodo derivative, it was thought advisable to attempt the introduction of an alkyl group into the benzene nucleus. The above experiment also showed that at high temperatures the greater part of the tribromoiiodobenzene was decomposed, so it was thought best to use lower temperatures in this experiment.

Five grams of tribromoiiodobenzene and 1.5 gr. of ethyl iodide were dissolved in 60 cc. of dry benzene. To the solution 0.5 gr. of clean sodium wire were added, and the mixture boiled for two hours under the reflux condenser. The solution was then filtered off from the brown residue. The residue was next washed with benzol, dried, and extracted with hot water. All of the sodium was not used. The water extract gave a strong test for sodium iodide.

The filtrate was allowed to evaporate to about 20 cc. on the steam bath, and cooled. The crystals which sep-
arated out were removed by filtration. They melted at 104°-105°.
The tribromiodobenzene was, therefore, unchanged. Fractional
crystallization of the solution obtained by filtering off the
first crystals failed to give any substance other than tribromo­
iodobenzene. The sodium iodide obtained as a result of the ex­
periment, in all probability, resulted from the interaction of
sodium and ethyl iodide to give butane and sodium iodide.

**Action of Sodium on Symmetrical Tribromobenzene**

Three and one-half grams of symmetrical tribromobenzene were dis­
solved in 50 cc. of dry benzene and 0.5 gr. of clean sodium wire
were added. The mixture was boiled ten hours, using a reflux con­
denser. The melting point of the crystals obtained from the fil­
trate after the removal of the solid material showed it to be un­
altered tribromobenzene. The solid material on the filter gave no
test for sodium bromide when extracted with water.

This experiment was repeated by the method given
above except that a few drops of ethyl acetate were added. Ac­
gording to Gattermann ethyl acetate sometimes starts the reaction.
No sodium bromide was formed. The crystals obtained from the fil­
trate melted at 119.5°, showing that the original substance re­
mained unaltered. A mixture of these crystals and those of the
original substance, also melted at 119°-120°.

**Action of Sodium on Symmetrical Tribromiododi­
trobenzene.**

The procedure was exactly the same as that
given in the preceding experiment, except that ethyl acetate was added at the beginning. Again it was found impossible to isolate any substance other than the original compound. No sodium halides were formed.

**Preparation of 1-Iodo-2,6-Dibromo-4-Nitrobenzene**

Paranitraniline was converted into 2,6-dibromoparanitraniline by the method of Körner. For this purpose, 15 gr. of paranitraniline were dissolved in 75 cc. of concentrated hydrochloric acid, and the solution diluted to two liters with water. A stream of air loaded with bromine vapor was then passed through this solution until a permanent red color was imparted to it. The precipitate, after a thorough washing with water was nearly pure dibromonitraniline, as it melted at 204°.

The amino group in the dibromonitraniline was next replaced as follows: Eighteen grams of the substance were mixed with 360 cc. of glacial acetic acid and 15 cc. of concentrated sulphuric acid diluted with an equal volume of water added. All of the dibromonitraniline did not dissolve. Disregarding this, the mixture was cooled with ice water, and 4.5 gr. of sodium nitrite dissolved in 15 cc. of water were added in small portions at a time with thorough shaking. The addition took about one-half an hour. In order to be certain that the diazo reaction was completed, the mixture was allowed to stand in the cooling bath for one hour. At the end of this time the solid present was filtered out, and 10.5 gr. of potassium iodide dissolved in the smallest
possible amount of water were added gradually, and with thorough shaking. The addition required about one-half an hour. During this time, the mixture turned from yellow to brown; a brown mass being precipitated. The diazonium iodide was apparently very unstable, as a marked evolution of nitrogen took place during the addition of potassium iodide. After the mixture had stood over night, it was heated on the steam bath for one-half hour to complete the formation of the iododibromonitrobenzene. It was then cooled in ice water to separated out as much of the compound as possible, and filtered. The solid was then washed with a saturated water solution of potassium iodide to remove the free iodine, and then it was washed with water. The light brown solid which resulted was crystallized from alcohol until it was nearly white, and showed the constant melting point of 152°-153°. The average yield of the crude product was forty-five percent of the theoretical.

0.1995 gr. of the substance gave 0.2989 gr. AgBr and AgI.
0.2057 " " " 0.3090 " " ".

Calculated for

\[ \text{Br}_2 \text{ and I) } \frac{\text{C}_8\text{H}_8\text{Br}_2\text{INO}_2}{\text{Found}} \]

\[ \begin{array}{c}
70.50 \\
70.52
\end{array} \]

Properties of 1-Iodo-2,6-Dibromo-4-Nitrobenzene.

Iododibromobenzene crystallizes from alcohol in nearly white needles which melt at 152°-153°. It is readily soluble in cold chloroform, benzene, and ether. In glacial acetic acid and ligroin
it is scarcely in the cold, but somewhat soluble in the hot; slightly soluble in cold alcohol, but insoluble in water, hot or cold. Alcohol is the best solvent for iododibromonitrobenzene.

**Action of Sodium Ethylate on 1-Iodo-2,6-Dibrom-4-Nitrobenzene**

Two grams of iododibromonitrobenzene were dissolved in 40 cc. of benzene, and mixed with a solution of sodium made from 0.5 gr. of sodium in 60 cc. of absolute alcohol. The solution was allowed to stand for three days at room temperature. At the end of this time a precipitate had deposited from the brown solution. The mixture after shaking thoroughly, was poured into a separatory funnel containing about 150 cc. of water. The contents of the separatory funnel were agitated well, and allowed to stand until the benzene had separated from the alcohol-water mixture. The benzene solution was then removed, and subjected to spontaneous fractional crystallization. The first three crops of crystals obtained consisted of iododibromonitrobenzene since they all melted at 152°-153°. The fourth crystallization yielded long, nearly white needles arranged in radiating groups, which on crystallization from alcohol melted at 58°. Such a small yield was obtained that it was impossible to study the properties of these bodies further. However, the melting point and crystalline form indicated that it was 2,6-dibrom-4-nitrophenetol. This body has been prepared by Jackson and Fisk, from 1-nitro-3,4,5-tribromobenzene by the action of sodium ethylate on it. The water-alcohol mixture obtained gave a strong test for
sodium iodide, but no test for sodium bromide.

**Preparation of 1-Iodo-2,6-Dibromo-4,5-Dinitrobenezene**

Two grams of iododibromonitrobenzene were placed in a flask with a mixture of 30 cc. of fuming nitric acid (Sp. Gr. 1.5) and 7.5 cc. of sulphuric acid (Sp.Gr. 1.83). The flask was closed with a porcelain crucible in a small funnel. The solid all dissolved in the acid mixture when the contents of the flask began to boil, but after about one-half hour solid material began to separate out. Disregarding this, the gentle boiling was continued for two hours longer. The mixture was then allowed to cool; when more crystals separated. The contents of the flask were then poured into 100 cc. of water, and this was filtered. The residue was crystallized from alcohol, and extracted with small portions of ether until it gave the constant melting point of $182^\circ$-$183^\circ$. The yield was about 70 percent of the theoretical.

0.2282 gr. gave by the Carius method 0.3072 gr AgBr and AgI

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<td>$\text{Br}_2 \text{ and I}$</td>
<td>63.51</td>
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**Properties of 1-Iodo-2,6-Dibromo-4,5-Dinitrobenezene**

It crystallizes from alcohol in well formed, light greenish-yellow prisms, melting at $182^\circ$-$183^\circ$. It is nearly insoluble in cold alcohol and water; difficultly soluble in hot alcohol. In chloroform, and benzene it is readily soluble in the cold; soluble in ether but not to such an extent as the iododibromonitrobenzene.
Several attempts were made to convert the dinitro compound into the trinitro body. With this purpose in view, 1-iodo-2,6-dibromo-4-nitrobenzene was boiled with four parts, by volume, of fuming nitric acid (Sp.Gr. 1.5) and fuming sulphuric acid (Sp.Gr. 1.92) for eight hours under the reflux condenser. The melting point of the crude product obtained was 168°-172°, and was, therefore, probably a mixture of the mono and the dinitro compound. The products obtained in this experiment were boiled for eight hours under the reflux condenser with a mixture of two parts red fuming nitric acid (Sp. Gr. 1.6) and one part of fuming sulphuric acid (Sp.Gr.1.92). The melting point of the crude product obtained was then 154°-167°. In each case the extraction of the crude product with ether and crystallization gave substances showing a mixture of iododibromonitrobenzene and iododibromodinitrobenzene. From this it would seem that continued boiling and increase of the sulphuric acid produced less nitration. Lack of time prevented a more careful investigation of the above phenomena.

**Preparation of 1-Chloro-2,6-Dibromo-4-Nitrobenzene**. In making chlorodibromonitrobenzene; dibromopara-nitraniline was prepared and diazotized in exactly the same manner as has already been given for the preparation of iodo-dibromonitrobenzene.
The diazonium solution was then filtered to remove any undissolved substance, and poured very slowly with thorough shaking into a solution made by dissolving six grams of anhydrous cuprous chloride in a mixture of 30 cc. of concentrated hydrochloric and 100 cc. of water. A dark brown solid is precipitated. After the mixture had stood over night, it was heated on the steam bath for thirty minutes in order to complete the formation of chlorodibromonitrobenzene, and allowed to cool. The mixture was then diluted with twice its volume of water, and after standing a short time was filtered. The brown solid obtained was washed thoroughly with water, dried, and extracted with ether. The ether extract was then filtered several times in order to remove any copper salts. The ether was then evaporated and the solid crystallized from alcohol until it showed the constant melting point of 92° - 93°. It was necessary to boil the crude body several times with animal charcoal in order to obtain white crystals. The yield of the crude product was fifty-five percent of the theoretical.

0.2539 gr. of substance gave by Carius' method 0.4168 gr. of AgBr and AgCl.

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<tr>
<td>( \text{C}_6\text{H}_2\text{Br}_2\text{ClNO}_2 )</td>
<td>61.94</td>
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<tr>
<td>( \text{Br}_2 ) and Cl</td>
<td>61.76</td>
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Properties of 1-Chloro-2,6-Dibromo-4-Nitrobenzene. It crystallizes from alcohol in light, white flakes melting at 92°-93°. It is much more soluble in alcohol than the corresponding iodo body; very soluble in cold benzene, ligroin, and ether; slightly soluble in cold glacial acetic acid, essentially insoluble in water, hot or cold.

Preparation of 1-Chloro-2,6-Dibromo-4,6-Dinitrobenzene. Two grams of 1-chloro-2,6-dibromo-4-nitrobenzene were placed in a flask together with a mixture of 30 cc. of fuming nitric acid (Sp.Gr. 1.5) and 7.5 cc. of sulphuric acid (Sp. Gr. 1.83). The flask was closed with a porcelain crucible in a small funnel, and boiled for two hours. The mixture was then allowed to cool, poured into 100 cc. of water and filtered. The residue was crystallized from alcohol until it gave the constant melting point of 142°-143°. The yield was nearly quantitative.

0.2019 gr. gave by Carius' method 0.2900 gr. AgBr and AgCl

Calculated for
\[ \text{Br}_2\text{Cl(NO}_2\text{)}_2 \]

\[ \begin{align*}
\text{Br}_2 & \quad 54.21 \\
\text{Cl} & \quad 54.04
\end{align*} \]

Properties of 1-Chloro-2,6-Dibromo-4,5-Dinitrobenzene. From alcohol it gives white crystals melting at 142° to 143°. It is much more soluble in alcohol than the cor-
responding iododinitro compound; easily soluble in ether, benzene, and chloroform.

**Action of Nitric Acid on 1-Iodo-2,4,6-Tribromo-benzene**. Jackson and Calvert on treatment of symmetrical tribromoiodobenzene with fuming nitric acid and allowing the mixture to stand over night, found that on dilution, that the nitration had proceeded as far as the formation of \( \text{H}^0 \text{Br}^+ \text{NO}_3^- \) with the separation of iodine in the form of scales. Jackson and Jones prepared this body by diazotizing \( \text{H}^0 \text{Br}^+ \text{NO}_3^- \) and putting in iodine.

We found that on treatment of symmetrical tribromoiodobenzene with fuming nitric acid the nitration could be stopped with the formation of \( \text{H}^0 \text{Br}^+ \text{NO}_3^- \). The experiment was carried out as follows: A small amount of tribromoiodobenzene was allowed to stand over night excess of fuming nitric acid (Sp.Gr. 1.5). The mixture was then poured into water and the solid filtered out and crystallized from alcohol. The crystals melted sharply at 145\(^0\). This is the melting point of \( \text{H}^0 \text{Br}^+ \text{NO}_3^- \), as found by Jackson and Jones. A small amount of free iodine being formed. The experiment was then repeated using 5 gr. of symmetrical tribromoiodobenzene and 100 cc. of red fuming nitric acid (Sp.Gr. 1.6). The mixture was allowed to stand for three days at room temperature, and was then poured into 500 cc. of water. The solid was filtered out, and crystallized from alcohol until it showed the constant melting point of 145\(^0\). A somewhat larger amount of iodine was formed in this experiment and the yield of \( \text{H}^0 \text{Br}^+ \text{NO}_3^- \) was about forty
percent of the theoretical amount. Further nitration of 8 was found to give a mixture of $\text{B}^{n}_n\text{O}_o$, and $\text{S}^{n}_n\text{O}_o$, but for some reason we were unable to stop smoothly with the formation of the dinitro compound alone.

No change could be detected when $\text{B}^{n}_n\text{O}_o$ and $\text{S}^{n}_n\text{O}_o$ were boiled for four hours in dry benzene solution with sodium wire in the proportion of two molecules of the aromatic substance to two atoms of sodium. Several attempts were made to prepare the iodide chlorides of $\text{B}^{n}_n\text{O}_o$, and of $\text{S}^{n}_n\text{O}_o$ by passing chlorine into the saturated chloroform solutions of these bodies. The solutions were cooled in ice water, but no solid was formed until a portion of the chloroform had evaporated. The melting point of these crystals was always the same as that of the original substance, and no evolution of chlorine was noted during the melting point determination. Iodide chlorides upon heating ordinarily decompose into the parent iodo body and chlorine. We were unable to prepare the iodoso compounds from the above crystals. This seems to show that these bodies do not form iodide chlorides.

Sodium phenate when boiled in alcoholic solutions with $\text{B}^{n}_n\text{O}_o$ and $\text{S}^{n}_n\text{O}_o$ gave small amounts of sodium halides, but as far as we were able to determine the C$_6$H$_5$O group could not be introduced into the benzene ring. However, as stated above, the ethoxy group is easily introduced into these compounds.
DISCUSSION OF RESULTS

It is evident from the above work that halogen and nitrobenzene derivatives containing three or more substituents do not react with sodium to give substituted diphenyl compounds. Therefore, Fittig's reaction which has proved so very useful in the preparation of many alkyl benzenes and diphenyls does not hold in the case of halogen and nitrobenzenes. It is interesting to note in this connection that while halogen and nitro groups exert a loosening effect on the halogen ortho and para to them; this effect is not so strongly active as would be ordinarily expected when these bodies are treated with sodium alone. The action of nitric acid on symmetrical tribromoiodobenzene is especially interesting.

It will be recalled that by allowing fuming nitric acid to interact with symmetrical tribromoiodobenzene in the cold, the was formed. On further nitration of this body using fuming nitric and sulphuric acids the iodine was completely removed. A mixture of and, being formed. For some reason the nitration could not be stopped smoothly with the formation of the dinitro compound alone. Nevertheless, it is apparent that the nitration proceeds successively according to the following scheme:
and does not give \( \text{Br}_2 \) in so far as we have been able to prove. A test for iodine in the product obtained on boiling symmetrical tribromoiodobenzene with fuming nitric acid for four hours was negative. On the other hand, if we started with a compound having the nitro group para to the iodo group as, for example, the \( \text{Br}_2 \) we obtained \( \text{Br}_2 \) with no removal of iodine even on long boiling with a mixture of two parts of fuming nitric acid and one part of fuming sulphuric acid.

It is also interesting to compare the interactions of sodium ethylate with \( \text{Br}_2 \) and \( \text{NO}_2 \). These compounds are quite similar in structure, the latter having a nitro group para to the iodo group instead of bromine. Jackson and Calvert on heating tribromoiodobenzene with sodium ethylate did not obtain a phenetol, but found that the iodine was replaced by hydrogen resulting in the formation of symmetrical tribromobenzene. On the other hand if sodium ethylate reacts with \( \text{Br}_2 \) and \( \text{NO}_2 \) results. The iodine in this case being replaced; not by hydrogen as in the case of \( \text{Br}_2 \), but by the ethyloxy group. These results are certainly peculiar. As another example of the difference in behavior of these compounds having the nitro group para to the iodo group, the following was noted: Repeating the work of McCrae, the iodide chloride of tribromoiodobenzene was easily prepared according to his method; while all attempts to prepare the iodide chloride of the body having the nitro group para to
the iodo group, that is $\text{I} + \text{NO}_2^{-}$ failed. In the light of these observations we are inclined to conclude that possibly this is a case of steric hindrance. However, Willgerodt has prepared the iodide chloride of $\text{I} + \text{NO}_2^{-}$, and this would lead to the belief that the effect is due to the more negative character of the nitro group. Of the two views we are led to believe that the phenomena is chemical rather than being due to steric hindrance.

As soon as is possible we expect to begin a more thorough and extended study of the interesting observations presented in this paper.

ACKNOWLEDGEMENT

The work described in this paper was undertaken at the suggestion of Professor Sidney Calvert, Professor of Organic Chemistry at the University of Missouri. I here take the opportunity to express my thanks for his sound counsel, and hearty encouragement throughout the course of this work.

University of Missouri
May, 1915
1. Liebig's Annalen der Chemie- 121,363
   Berichte der Deutschen Chemischen Gesellschaft-29,115
2. Richter's Organische Chemie- 2
3. Liebig's Annalen der Chemie- 332,38 (1904)
4. American Chemical Journal- 12, 167- 14, 385
5. American Chemical Journal- 10, 283 (1888)
7. American Chemical Journal- 18,300 (1896)
8. American Chemical Journal- 49,52 (1913)
10. Gazzetta chemica italiana- 4, 346 (1874)
11. American Chemical Journal- 36,64
13. Journal für praktische Chemie- (2), 33, 158
May 20, 1915.

Prof. Walter Miller,
Chairman Graduate Committee.

Dear Professor Miller:

I have carefully looked through the enclosed thesis of Mr. Harry F. Yancey and the same appears to fully represent the amount of work required for a thesis for the degree of Master of Arts. It seems logically arranged and well presented. I believe that the requirements have been met.

Very truly yours,

LDH

[Signature]
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This thesis is never to leave this room. Neither is it to be checked out overnight.