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# Iodine Monochloride Investigations

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IODINE MONOCHLORIDE INVESTIGATIONS

by

Julian Richard Mayer

A thesis presented to the Department of Chemistry of
Union College in partial fulfillment of the requirements
for the degree of Bachelor of Science in Chemistry

By _Julian Richard Mayer_

Approved by _R. W. Finholt_

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## INTRODUCTION

The purpose of the research was to investigate the reactions of iodine monochloride with non-aromatic and aromatic compounds. The role which this reagent plays in these reactions, the use of various catalysts, and the products obtained were to be studied.

It was the immediate object of these investigations to attempt a synthesis of cyclohexyl iodide directly from cyclohexane using iodine monochloride as the iodinating agent. In studying the non-aromatic compounds in this project, cyclohexane was chosen since it is readily available and yields a single product upon mono-substitution. The major portion of this thesis is concerned with the reaction which takes place when iodine monochloride is brought in contact with cyclohexane in the presence of anhydrous aluminum chloride.

It was found that although iodination did not take place, the reagent iodine monochloride took a definite part in a reaction which yielded a small amount of a high boiling liquid hydrocarbon as a product. The structure of this hydrocarbon was determined, and yields were greatly increased by an improved method.

The second part of these investigations involved the aromatic compounds naphthalene, benzene, toluene and phenol. The latter three were iodinated using iodine monochloride.

## HISTORICAL BACKGROUND

The classical methods of iodination of chemical compounds are few in number and many special cases arise in the preparation of iodo-compounds. This may be explained in part by considering the electronegativities of the atoms involved in the discussion. According to Pauling (1) carbon has been assigned an electronegativity of 2.5, iodine a value of 2.5, bromine 2.8, chlorine 3.0, and fluorine 4.0. He has explained that the strength of a bond between carbon and a halogen is greater the further separated they are in the electro-negativity scale. The close proximity of carbon and iodine in this scale shows how unstable the carbon-iodine bond may tend to be.

This instability is enhanced when disubstitution takes place, and iodine atoms which are adjacent to each other in aliphatic compounds tend to split out forming iodine. This is true when an attempt is made to iodinate ethylene with iodine for the reaction is reversible (2) and incomplete.

It is seen that the addition reactions of iodine at a double bond are of little preparative value. The preparation of alkyl iodides is best achieved through an alcohol using HI or $PI_3$.

The classical methods of direct iodination involve the use of an oxidizing agent. Datta and Chatterjee (3) iodinated toluene using iodine and nitric acid; - using the same procedure they iodinated iodobenzene and chlorobenzene (4).
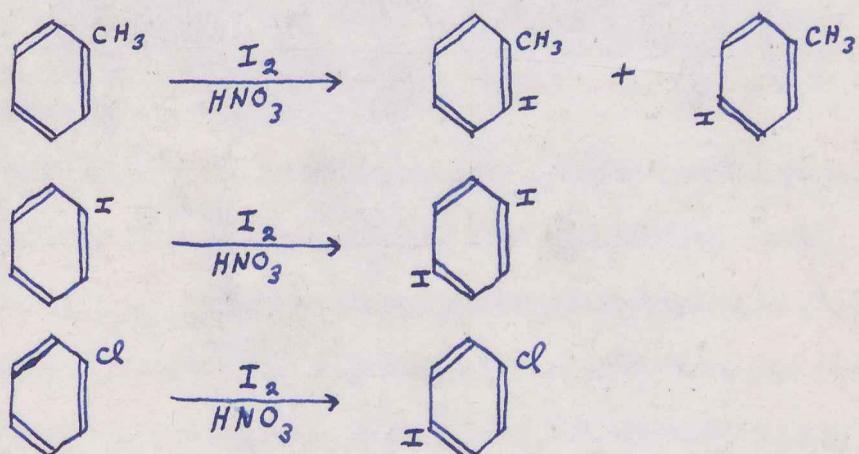






Verma, Mozumdar and Rajah (5) iodinated naphthalene using iodine in acetic acid with nitrosulfonic acid and fuming nitric acid.
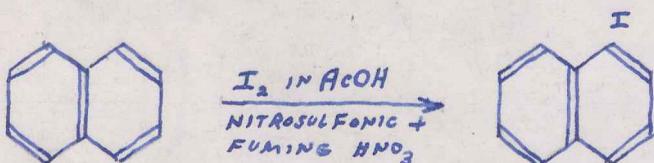


This group also iodinated B-naphthol using a solution of iodine and potassium iodide in ammonium hydroxide. Nascent HI₃ is formed, and iodination follows (5).
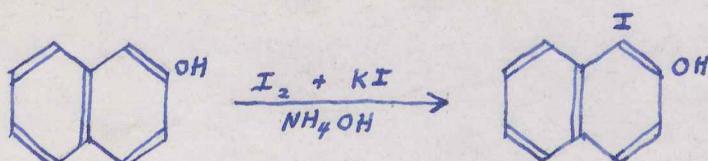
It is possible to use other oxidizing agents in these reactions. Elbs and Jaroslawzew (6) have used sodium persulfate in iodinating benzene and toluene.
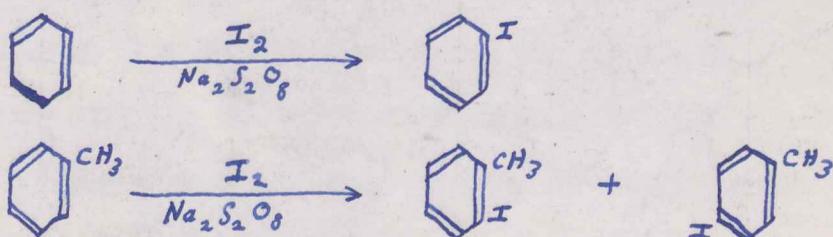


Elbs and Volk (7) have employed sodium persulfate in iodinating aniline by adding the oxidising agent to a solution of aniline in concentrated hydrochloric acid. They showed that iodination is effected by the intermediate formation of $ICl_2$. In iodination then, $ICl_2$ is a nucleophilic reagent since the $-NH_3Cl$ group is meta directing.
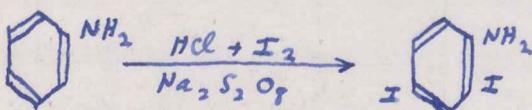


When a phenol is iodinated using iodine and nitric acid, the reactive phenol forms a nitro compound. The method may be applied to cresol ethers however (8).
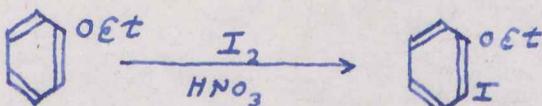


Although iodine does not tend to react at the carbon-carbon double bond to any extent, iodine monochloride will react easily. Indeed this is the basis of a quantitative determination of double bonds.

Iodine monochloride yields addition products with
olefins (9) with the iodine atom going to the carbon
atom carrying the larger number of hydrogen atoms.

The polar nature of iodine monochloride has been
clearly demonstrated by Cornog, Horrabin and Karges
(10) by reacting the reagent with silver cyanide.
The formation of only silver chloride and no silver
iodide proves that this iodine atom is positive with
respect to the chlorine atom.

$$ICl + AgCN \longrightarrow \underline{AgCl} + ICN$$

With this polar nature in mind, Ingold and Smith (11)
have shown that iodine monochloride adds to propene as
one would expect assuming a positive iodine atom.

$$CH_3CH=CH_2 + ICl \longrightarrow CH_3CHCl \cdot CH_2I \quad (60\%)$$

Iodine monochloride may be prepared from iodine and
liquid chlorine (12) or by passing dry chlorine gas
over iodine (13) until liquefaction is complete.
Iodine monochloride will decompose if it is brought in
contact with water (14).

$$ICl + HOH \longrightarrow IOH + HCl$$
$$5IOH \longrightarrow 2I_2 + HIO_3 + 2H_2O$$

Cofman believed that the first stage of this decomposition
was necessary to certain iodinations, but this was later
questioned.

Although iodine monochloride will decompose in
water, the aqueous solution can be stabilized.
Fourneau and Donard (15) showed that aqueous solutions
of hydrochloric acid or sodium chloride are stabilizing
solvents for iodine monochloride.

Beside water decomposition iodine monochloride can
decompose by heating.  Oddo and Serra (16) have shown
that when iodine monochloride is heated, iodine tri-
chloride tends to form according to the equation:

$$ICl \xrightarrow{\Delta} I_2 + ICl_3$$

The action of iodine monochloride on different organic
compounds is highly diversified and the reagent appears
to be very versatile in its reactions.  When Orton and
Blackman (17) reacted methyl amine and iodine mono-
chloride in 1900, they obtained a yellow solid
precipitate which corresponded to the formula $CH_3NI_2$.
They showed that the following reaction took place:

$$CH_3NH_2 + 2ICl \longrightarrow CH_3NI_2 + 2HCl$$

Here the hydrogen atoms on the amine group were replaced
by iodine atoms.  When an aromatic amine like aniline is
treated with iodine monochloride, iodination takes place
on the ring (18).  The amine group is a strong ortho -
para director, and 2,4,6,-tri-iodo-aniline is formed.

Iodine monochloride may act as a chlorinating agent. Bink and Shaw (19) chlorinated malonamide by using this reagent.

$$H_2N-C{=}O \diagdown CH_2 + 2ICl \longrightarrow H_2N-C{=}O \diagdown CCl_2$$
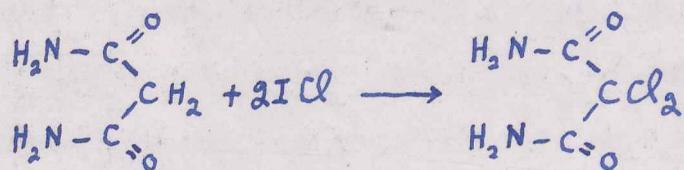
Iodine monochloride may serve to rearrange an alkyl halide. In particular, isobutyl iodide may be transformed to tertiary butyl chloride (20). The reaction may be thought of as occuring as follows:

$$CH_3 \diagdown CHCH_2I + ICl \longrightarrow \left[ CH_3 \diagdown C = CH_2 + HCl + I_2 \right] \longrightarrow CH_3{-}C{-}CH_3 \diagup Cl$$
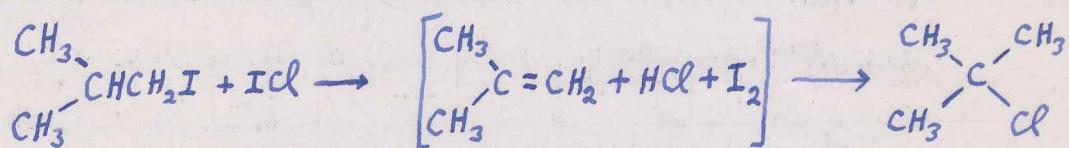
It is of interest in this investigation that in 1921 Arreguine and Garcia (21) obtained chloro-substitution of benzene with $ICl_3$ in ether in the presence of anhydrous aluminum chloride. They reported very little formation of iodo-benzene.

It would appear that in this reaction $ICl_3$ acts like an electrophilic reagent since chloro-substitution takes place. In those cases of special activation by a group like $-NH_2Cl$ (see page 4), this reagent is clearly nucleophilic and iodination results.

No evidence was found in the literature of any
attempt made to iodinate an aliphatic compound using
iodine monochloride. The inertness of the straight
chain paraffins to chemical reagents in general, is
well known. The first members of the simple alicyclic
series are the only reactive paraffin hydrocarbons.
In cyclopropane the angle of strain in accordance with
the Baeyer theory is responsible for its great
reactivity. Cyclopropane will add hydrogen in the
presence of a nickel catalyst at $120^\circ$; it will add
bromine, hydrogen bromide or sulfuric acid also (22).

As the ring of the alicyclic paraffin increases in
size, the reactivity becomes less. When cyclobutane
is studied, it is found that it will not add bromine
or hydrogen iodide (23). When cyclohexane is reached,
Sachse and Mohr showed that a non-planar, strainless
ring exists, and cyclohexane is generally as non-
reactive as a straight chain paraffin. Cyclohexane is
inert to the action of permanganate, ozone, bromine,
hydrogen bromide or hydrogen in the presence of a
nickel catalyst (24).

Cyclohexane will react with chlorine in the cold
yielding a di-substituted chloro-compound (25).
In order to brominate cyclohexane it is necessary to
use strong sunlight and bromine (26).

Clearly then, iodination using iodine is very unfavorable by nature of the above trend in the substitution of halogens in to hydrocarbons. The di-iodo derivitive formed by the action of iodine on an alkane also tends to be unstable (8).

Concentrated nitric acid or sulfuric acid has no action on cyclohexane (27) but anhydrous aluminum chloride causes it to isomerize partially to methyl cyclopentane (28). Except for this isomerization, cyclohexane is indifferent to the action of the Friedel and Crafts catalyst at 80°, the boiling point of cyclohexane (29). Under altered conditions the formation of dimethyl - dicyclopentyl in yields of .23% has been reported (30).

## EXPERIMENTAL WORK

Iodine monochloride is a reactive compound of iodine and chlorine containing a covalent bond whose electron pair is shifted toward the chlorine atom, the more electronegative of the two.

$$I \rightarrow Cl$$

The iodine atom therefore is positive with respect to the chlorine atom. With this in mind it was the first object of this investigation to observe the behavior of this reagent with non-aromatic compounds. A cyclic paraffin, cyclohexane, was chosen by nature of its availability, similarity to the open-chain paraffins, and ability to yield a single product upon mono-substitution.

The second object of this investigation was to observe the behavior of iodine monochloride with aromatic compounds. The compounds in this class which were studied are benzene, naphthalene, toluene, and phenol.

The remainder of this section is divided therefore into two parts - the first dealing with the reaction involving iodine monochloride and cyclohexane, and the second dealing with the reactions of iodine mono-chloride and benzene, naphthalene, toluene, and phenol.

EXPERIMENTAL WORK: PART I

## The Investigation of Reactions Involving
## Iodine Monochloride and Cyclohexane

Iodine monochloride is unstable under three different conditions giving rise to three different modes of decomposition. Iodine monochloride will react with water (14) and decompose as follows:

(a) $ICl + HOH \longrightarrow IOH + HCl$

(b) $5IOH \longrightarrow HI_2 + HIO_3 + 2HOH$

Upon heating, iodine monochloride will decompose forming iodine trichloride (16).

$$3ICl \xrightarrow{\Delta} I_2 + ICl_3$$

It was found that in the presence of an organic solvent acting simply as a diluent, another kind of decomposition took place. In order to investigate this kind of decomposition, solutions of iodine mono-chloride in ether, acetone, ethyl alcohol, sulfuric acid, nitric acid, and cyclohexane were studied. The original solution in each was yellow. After a few hours each of the above solutions took on a red color which became more prominent upon further standing. A simple starch test, which distinguishes between iodine monochloride and iodine, indicated that iodine had been formed in these solutions.

When iodine monochloride is dissolved in hydrochloric acid, stabilisation takes place for a number of days. This holds true for dilutions down to two molar hydrochloric acid.

When an attempt to iodinate cyclohexane was made employing a solution of iodine monochloride in cyclohexane, it became clear that there was no reaction between these two. The cyclohexane acted as a diluent, and the reagent decomposed.

In a reaction flask, 100 ml. of cyclohexane and 4.7 ml. of iodine monochloride (.082 moles) were refluxed thermally for ten hours. After this period of time the reaction mixture, having turned to a deep red, now gave a test for iodine. Upon distillation the presence of a high boiling compound became evident. This compound appeared to be a chloro-compound, and its presence substantiates the equation $2ICl = I_2 + Cl_2$ as the nature of the decomposition of the reagent in a solvent, since cyclohexane is easily chlorinated to give a disubstituted chloro-compound (23).

When a very dilute solution of iodine mono-chloride in cyclohexane was thermally refluxed, the faint orange color turned to crimson-red; When a solution of like dilution was exposed to a 200 watt incandescent lamp, the same color change took place.

These two reactions seem to show that there is essentially no tendency for iodine monochloride and cyclohexane to react together either by heat or by photochemical treatment.

An aqueous solution of iodine monochloride, stabilised by hydrochloric acid, was stirred rapidly, and cyclohexane added. After a period of time it was found that the reagent was taken into the organic phase, and then underwent the characteristic decomposition discussed above.

At this time it was desirable to study the effects which a catalyst might have in these reactions. Thus far the only reactions taking place were the decomposition of the reagent into iodine and chlorine, and the chlorination of cyclohexane.

The catalyst investigated was anhydrous aluminum chloride. A preliminary test with anhydrous $AlCl_3$ added to cyclohexane gave no other visible sign of reaction than a slight yellow coloration. When anhydrous $AlCl_3$ was added to iodine monochloride, no visible reaction occured. When these three were simultaneously brought in contact, hydrogen chloride was evolved, and a reaction involving the cyclohexane molecule appeared to take place.

A planned reaction was now run in which 13 grams of
iodine monochloride (.008 moles) were added dropwise
to 100 ml. of cyclohexane containing 13 grams of
anhydrous $AlCl_3$ (.008 moles). The mixture was
mechanically stirred at room temperature for one hour,
after which it was washed with water to decompose any
unreacted reagent and the catalyst. It was then
washed with aqueous sodium thiosulfate to decompose
the iodine formed during the reaction. The clear
solution was dried and distilled yielding 2.1 ml. of
a product boiling at $212^\circ$ and having a refractive
index of 1.472.

It was evident that a large portion of iodine mono-
chloride was simply decomposed to iodine in the course
of the reaction. In attempting to counteract this
decomposition reaction whose equilibrium lies greatly
toward the formation of iodine, the reaction mixture
at the start was saturated with respect to iodine.
This required about ten grams of iodine per 250 ml. of
cyclohexane. When this reaction was run again, a 300%
increase in yield was obtained. This product had a
refractive index of 1.475.

It seemed desirable to obtain pure cyclohexyl
iodide in order to compare its properties and constants
with the compound which was formed in the above
reaction.

Cyclohexanol was therefore reacted with red phosphorus and iodine to prepare the iodide. This was obtained as a yellow liquid having a characteristic odor. It had a refractive index of 1.555 and decomposed when heated to its boiling point. The instability of the carbon-iodine bond in this compound is clear by nature of its decomposition at moderately elevated temperatures. The reactivity of the iodine atom in this molecule is well demonstrated by its almost instantaneous reaction with alcoholic silver nitrate, either or both of which may be in fairly dilute solution. The formation of yellow silver iodide is a good test for the presence of cyclohexyl iodide.

The product from the catalyzed iodine monochloride reaction with cyclohexane did not react with alcoholic silver nitrate, was colorless, did not decompose at its boiling point, and had a refractive index much lower than that of cyclohexyl iodide. This made it evident that this catalyzed reaction yielded no cyclohexyl iodide.

By allowing a solution of cyclohexyl iodide in cyclohexane to come in contact with anhydrous $AlCl_3$, the iodide was decomposed to iodine. It was therefore of interest to modify the $AlCl_3$-$ICl$-cyclohexane reaction so that the contact time of the reaction mixture with the catalyst was very small.

A Soxhlet extractor was used in conjunction with a reaction flask, a water condenser, and a separatory funnel as shown in figure 1. The solution of iodine monochloride in cyclohexane was allowed to come in contact with the catalyst for about one minute, after which the liquid was siphoned into the flask below containing boiling cyclohexane. Any cyclohexyl iodide which formed would remain in the flask out of contact with the catalyst by nature of its higher boiling point.

The product from the reaction boiled at $215^\circ$, had a refractive index of 1.465 and a density of .85. The reaction product appeared in every way to be identical to that formed in the ordinary reaction where the catalyst was intimately mixed with the entire reaction mixture. There was no evidence of cyclohexyl iodide in the reaction mixture.

In summarizing it has been found that when iodine monochloride is added to cyclohexane stirred at room temperature in contact with anhydrous $AlCl_3$ a reaction takes place. The product from this reaction is a colorless liquid whose average boiling point is $212^\circ$-$215^\circ$ and whose average refractive index is 1.468 - 1.471.

# Figure 1

## The Soxhlet Extractor Reaction



WATER CONDENSER

SOLUTION OF
IODINE MONOCHLORIDE
IN CYCLOHEXANE

ANHYDROUS. $AlCl_3$

BOILING
REACTION MIXTURE
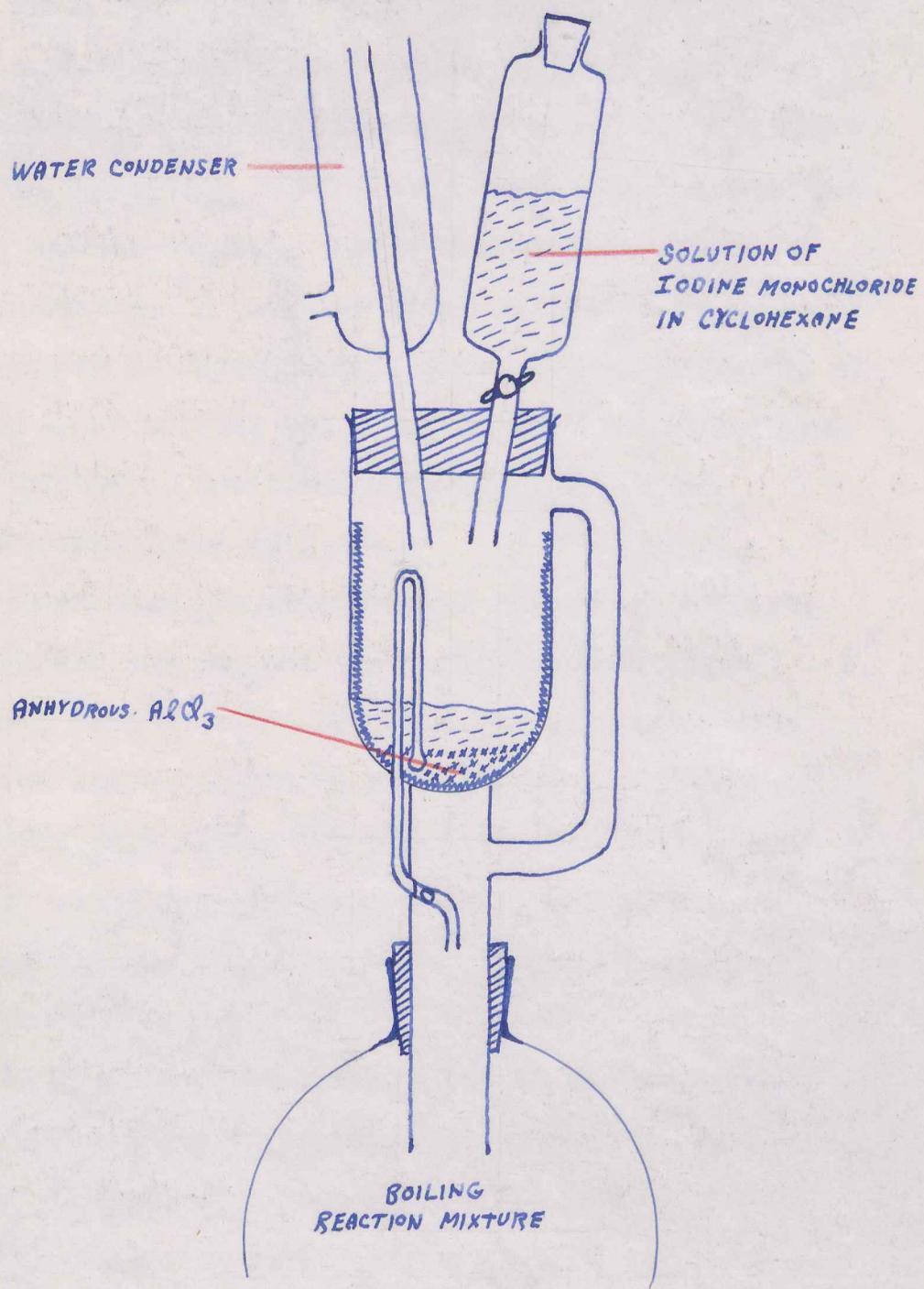
The molecular weight of this compound was determined by observing the elevation in the boiling point of carbon tetrachloride upon the addition of an accurately weighed quantity of the compound. The molecular weight calculated in this way was 167. The data and calculations may be found in appendix B.

Sodium fusion tests showed that this compound did not contain halogen, indicating that it was a hydrocarbon. A compound which satisfies these known constants is dicyclohexyl, whose molecular weight is 166, whose boiling point may be 218° depending upon the geometric configuration (31), and whose refractive index is 1.48.

There were two experimental pieces of evidence which did not support this conclusion however. First, that when the compound was subjected to a sulfur dehydrogenation, no biphenyl was detected. Second, that presumably the formation of dicyclohexyl would proceed through the compound cyclohexyl iodide, the presence of which was never detected.

It is known that cyclohexane in the presence of anhydrous $AlCl_3$ isomerizes to methyl cyclopentane (32). This suggests an isomer of dicyclohexyl, namely, dimethyldicyclopentyl. Now there are six possible isomers: 1,1; 1,2; 1,3; 2,2; 2,3; 3,3. The boiling point of the 3,3 isomer is reported as 213°-218° (32).

It was not within the scope if this investigation to study further the nature of this mixture of hydrocarbons. It was concluded that when cyclohexane is treated with iodine monochloride in the presence of anhydrous aluminum chloride, a reaction takes place in which a hydrocarbon is formed corresponding to the empirical formula $C_{12}H_{22}$ which consists largely of a mixture of dimethyldicyclopentyls.

## EXPERIMENTAL WORK:   PART II

### The Investigation of Reactions Involving
### Iodine Monochloride and Aromatic Compounds

In 1921 Arreguine and Garcia (21) investigated the
reaction which takes place between iodine trichloride
and benzene in ether solution and in the presence of
the Friedel and Crafts' catalyst.  They reported the
formation of chlorobenzene with very little iodo-
benzene formed.

This investigator was interested in the reaction
involving benzene and iodine monochloride in the
presence of the Friedel and Crafts' catalyst using
excess benzene as the reaction solvent.

A mixture of 250 ml. of benzene and eight grams
of anhydrous $AlCl_3$ was stirred at $25^\circ$ for one hour
while adding 9.7 grams of iodine monochloride in
small portions.  The procedure developed above
employing a saturated solvent with respect to iodine,
was used.  Upon working up this reaction mixture,
three to four ml. of a product were distilled at
$188^\circ$ which gave a refractive index of 1.620.  This
identifies the product as iodobenzene - formed in a
yield of about 50% to 80%.

A similar attempt was made to iodinate naphthalene
using carbon disulfide as the reaction solvent.  The
procedure was identical to that in the previous
reaction, but no product was isolated.

When toluene was used in the reaction in place of
benzene, iodination took place and a high boiling
amber liquid product was obtained which was a
mixture of iodo-toluenes. This occured to the
extent of 40% to 50%.

In the iodination of benzene and toluene a
feasible mechanism would be that of the normal
Friedel and Crafts hydrocarbon synthesis where ICl
would correspond to RCl and $I^+$, the active
carbonium ion.

In the case of phenol, a molecule containing a
functional group, a different situation was
encountered. The phenol molecule is highly reactive
toward electrophilic reagents even though, from an
electrostatic point of view, the oxygen atom tends
to withdraw electrons from the ring. From a
resonance point of view, this molecule is actually
activated - electrons being supplied to the ortho
and para positions (35).
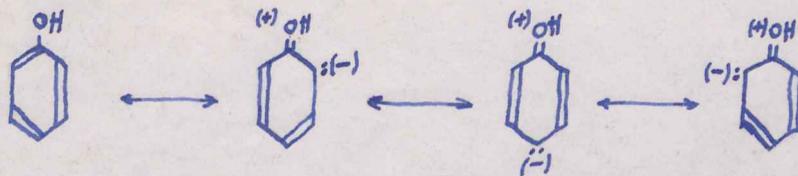


In iodine monochloride the iodine atom is the
electrophilic center being positive relative to the
chlorine atom. Hence phenol may be iodinated using
this reagent in the absence of a catalyst.

A mixture of ten grams of phenol dissolved in
carbon disulfide and 15 grams of iodine mono-
chloride was stirred for one hour at room
temperature. A product was extracted in aqueous
sodium hydroxide, treated with acid, and
extracted from the aqueous mixture in ether.
The distilled product was a mixture of ortho and
para iodophenol. The yield from this reaction
was 60% or better.

## SUMMARY AND CONCLUSIONS

With regard to the reactions which have been studied in this investigation and the literature references bearing on the reactions of iodine monochloride, several conclusions may be drawn concerning the courses of action which iodine monochloride may take.

1. When the reagent reacts with an aliphatic amine, iodination will tend to take place in which the hydrogen atoms of the amine group are replaced by iodine (17).

2. When the reagent reacts with an aromatic amine, iodination will tend to take place in which the aromatic ring will tend to be iodinated, and hydrogen chloride evolved (18).

3. When the reagent reacts with an active methylene group, chlorination will tend to take place (19).

4. When the reagent reacts with an alkyl iodide, an alkyl chloride will tend to result which is more branched than the original halide (20). See page seven of this thesis.

5. When the reagent reacts with cyclohexane in the presence of anhydrous aluminum chloride, it appears that inter-dehydrogenation takes place between molecules of the isomer methyl cyclopentane which is present, to form dimethyl-dicyclopentyls.

6. When the reagent reacts with benzene or toluene in the presence of anhydrous aluminum chloride, iodination takes place.

7. When the reagent reacts with phenol in a non-reactive solvent, iodination takes place easily in the absence of the Friedel and Crafts' catalyst.

## APPENDIX A

### Parachor Studies

It is possible to obtain a reasonable check in the conclusion reached concerning the structure of the hydrocarbon product by using Sugden's parachor, $P = M/(D-d)\gamma^{\frac{1}{4}}$, where M is the molecular weight, D and d the densities of the liquid and its vapor respectively, and $\gamma$ is the surface tension.

In calculating the parachor from the atomic parachors, the following values are used (24):

$$H = 17.1 \qquad \text{5-membered ring} = 8.5$$
$$C = 4.8 \qquad \text{6-membered ring} = 6.1$$

Using these values the calculated value of the parachor for the dimethyldicyclopentyl is 451.

Using the value 166 for the molecular weight, .86 for the density, 30.1 for the surface tension as measured, and neglecting d, then $P = 457$. The value for D is not precisely .860 and may be greater or less by .005.

The calculated value of the molecular parachor of dicyclohexyl from the atomic parachors is 446, while the calculated value from the equation is still 457.

The value for dimethyldicyclopentyl differs by only six units from the equation value, while that of dicyclohexyl differs by eleven units. These figures are in agreement with those conclusions already drawn.

## APPENDIX B

The Calculation of the Molecular Weight
of the Compound by Elevation in the
Boiling Point of Carbon Tetrachloride

The equation involving an increase in the boiling point of a solvent when a non-associating solute is added is given as follows:

$$M = 1000 \ K_B \cdot \frac{g}{G \Delta T}$$

where $M$ is the molecular weight, $K_B$ is a constant depending upon the solvent, $g$ is the number of grams of solute added to $G$ grams of solvent, and $\Delta T$ is the rise in the boiling point of the solvent.

When 1.0482 grams of the compound were added to 44.970 grams of carbon tetrachloride, the boiling point, as observed using a Beckmann thermometer, changed from 1.80 to 2.50 giving a value of .70° for $\Delta T$. Using the value 5.03 for $K_B$ (I.C.T.), the calculated value of $M$ is 167.

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