

THE PREPARATION OF SOME DERIVATIVES OF FLUOROBENZENE

by

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# THE PREPARATION OF SOME DERIVATIVES OF FLUOROBENZENE

## HISTORICAL INTRODUCTION

Very little progress had been made prior to 1927 in the preparation of compounds in which the element fluorine is linked to the benzene ring. The few compounds which had been made were made by treating a diazonium salt with hydrofluoric acid. This reaction is difficult to carry out due to the presence of hydrofluoric acid fumes and the necessity for using special apparatus of copper, silver or platinum. The meta and para amino, nitro and halogen derivatives of fluorobenzene have been prepared in this way though the yield was usually very small. The corresponding ortho compounds do not seem to be formed by this method.

Swarts<sup>(1)</sup>, using a 2 liter platinum flask, dissolved the anilines in 70% hydrofluoric acid and after cooling added a solution of sodium nitrite slowly by introducing it under the acid solution. The mixture was then refluxed and distilled. The product was purified by washing with water, sodium carbonate solution, extracted with ether, dried over calcium chloride and distilled. He was not able to prepare the ortho compounds in this manner. The presence of copper also did not influence the reaction.

Swarts prepared the fluorine compounds in order to study their heats of combustion.

Holleman<sup>(2)</sup> prepared meta and para fluor nitrobenzene by dissolving the nitroaniline in concentrated sulfuric acid and diazotizing. The diazonium solution was added slowly to 55% hydrofluoric acid heated until fumes of  $H_2F_2$  just came off. The reaction was carried out in a copper tank. The

product was steam distilled, washed with dilute potassium hydroxide and water, dried and distilled in vacuo. He obtained 30 to 33% yield.

Valentiner and Schwarz<sup>(3)</sup> prepared para fluor brom-benzene by diazotizing para bromaniline in hydrochloric acid and adding the diazonium chloride to hydrofluoric acid in a special copper vessel. After addition, the vessel was warmed until no more nitrogen came off. The reaction mixture was then neutralized, the oil separated and steam distilled and fractionated.

In 1927 Balz and Schiemann<sup>(4)</sup> succeeded in working out a method for the preparation of fluorobenzene and ortho, meta and para fluor nitrobenzene which seems to be applicable to the preparation of fluorine compounds in general. They diazotized the aniline hydrochloride in the usual way and to this cold diazonium chloride solution added a 40% solution of borofluoric acid in excess, when the diazonium borofluoride precipitated. This precipitate was filtered by suction, carefully washed with a little borofluoric acid, then with alcohol and ether and dried in a vacuum dessicator for one day. The dry salt was then placed in a dry distilling flask and heated slowly to decompose it, the following reaction, in the case of phenyl diazonium borofluoride, taking place:



The aryl fluoride distilled over during the decomposition. It was then washed with sodium hydroxide solution, dried over anhydrous sodium sulfate and distilled.

The yield for fluorebenzene was 63% of the theoretical; for para fluor nitrobenzene nearly 100%; for meta fluor nitrobenzene 80%; and for ortho fluor nitrobenzene 74%.

This method has the advantage over the other method, not only in yield, but in the fact that ordinary apparatus is used. Also ortho fluor compounds may be made by this method.

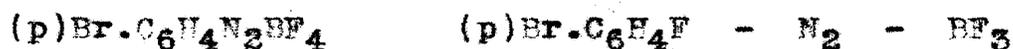
#### EXPERIMENTAL

The object of this paper is to describe the preparation of the ortho, meta and para fluor brombenzenes and also the preparation of the three fluor phenyl mercuric chlorides and some unsymmetrical mercurials in which the fluor phenyl radicals are linked opposite the phenyl and corresponding chlor phenyl radicals.

The fluor brombenzenes were made according to the method of Balz and Schiemann (with slight modifications) from the corresponding bromanilines.

The ortho, meta and para fluor phenyl mercuric chlorides were made by preparing the Grignard reagents of the fluor brom compounds and treating these reagents with mercuric chloride.

Each unsymmetrical mercurial was made in two ways; First, the fluor phenyl magnesium bromide was treated with the mercuric chloride of the other radical; second, the magnesium bromide of the other radical was treated with the fluor phenyl mercuric chloride. The following equations represent the reactions taking place in the preparation of para fluor phenyl mercuric phenyl:



For the unsymmetrical:



The mercurials were analyzed for mercury. The method used was that of Rupp modified by Koten and Adams for volumetric determination of mercury in organic compounds, with certain modifications by Drs. Kharasch, Flenner and Mr. Legault. The detailed procedure is given under "analysis of mercurials" in this paper.

## TABULATION OF EXPERIMENTS

### PREPARATION OF BOROFLUORIC ACID

The borofluoric acid used was prepared by slowly adding 1.1 moles of boric acid to 4 moles of C. P. 48 hydrofluoric acid in a copper can. The mixture was stirred vigorously and kept cool in an ice bath during the addition of the boric acid.

### PREPARATION OF ORTHO, META AND PARA FLUOR BROMBENZENE

20 g. of the bromaniline were added to 24 c.c. of concentrated HCl and cooled to 2°C, and diazotized in the usual way with 9 g. of  $NaNO_2$  dissolved in 18 c.c. of water. The clear diazonium solution was then poured into 34 c.c. of cold  $HBF_4$  solution. A heavy cream colored precipitate of brombenzene diazonium borofluoride separated at once. This was filtered by suction and washed on the filter, once with about 20 c.c. of borofluoric acid solution, twice with a

small quantity of alcohol and several times with ether. The precipitate was dried in a vacuum desiccator over  $P_2O_5$ . It was then mixed with dry sand and placed in a 200 c.c. distilling flask. The flask was fitted to a condenser which was in turn attached to a small suction flask for a receiver, a trap bottle and two wash bottles containing sodium hydroxide solution. A slight suction was applied to the system and the mixture in the distilling flask gently warmed. The diazonium borofluoride decomposed slowly and a pale yellow oil distilled over. The ortho brombenzene diazonium borofluoride decomposed at  $130^{\circ}C.$ , the meta at  $142^{\circ}C.$ , and the para at  $110^{\circ}C.$  The yellow oil was dissolved in ether and the ethereal solution washed twice with dilute NaOH, three times with water and dried over anhydrous  $Na_2SO_4$ . The ether was distilled off through a fractionating column. The oil which was nearly pure fluor brombenzene was distilled. In each case the oil distilled almost completely within two degrees. Ortho fluor brombenzene distilled between  $158^{\circ}$  and  $160^{\circ}C.$ , the meta between  $150^{\circ}$  and  $152^{\circ}C.$ , and the para between  $151^{\circ}$  and  $152^{\circ}C.$

#### PREPARATION OF META AND PARA FLUOR PHENYL MERCURIC CHLORIDE

The meta and para fluor phenyl mercuric chlorides were prepared from the corresponding fluor brom compounds as follows: 21.6 g. of the fluor brom benzene was added, drop by drop, to 3.5 g. of Mg turnings in 50 c.c. of dry ether. After about 5 g. had been added, a crystal of iodine was added and the mixture warmed slightly to start the reaction. The

reaction continued rapidly until all the fluor brombenzene had been added. The solution was refluxed for one hour to complete the reaction. The ethereal solution was decanted from the excess magnesium through glass wool (previously washed with ether and dried) into a dry Erlenmeyer flask fitted with a reflux condenser. To this solution was added 37 g. of  $\text{HgCl}_2$  (dried at  $110^\circ$  in an oven and cooled in a desiccator) in portions of about 2 g. with vigorous shaking after each addition. The reaction was vigorous. After the final addition, the solution was refluxed for about 4 hours. Only about one-third of the mercurial remained in solution in the ether. This ethereal solution was poured on cracked ice and acidulated with 1%  $\text{H}_2\text{SO}_4$  to dissolve the basic magnesium salts. The ethereal layer was separated and washed with water until the wash-water gave no test for mercury salts. The ethereal solution was then dried over anhydrous sodium sulfate, filtered and the ether evaporated off.

The solid which remained in the reaction flask was extracted with acetone (in which the mercurials are very soluble) and the mercurial precipitated from the acetone by adding several volumes of water. This precipitated mercurial was filtered out by suction and dried in a vacuum desiccator over  $\text{P}_2\text{O}_5$ . This and the mercurial obtained from the ether solution were recrystallized from hot alcohol. A portion of the recrystallized product was boiled for one-half hour with freshly precipitated  $\text{AgCl}$  to convert any fluor phenyl mercuric bromide to the fluor phenyl mercuric chloride. The acetone was evaporated off and the mercurial recrystallized from hot alcohol. The melting point of the para fluor phenyl

mercuric chloride was  $285^{\circ}$  C. and of the meta fluor phenyl mercuric chloride was  $245^{\circ}$  C.

#### PREPARATION OF ORTHO FLUOR PHENYL MERCURIC CHLORIDE

When the above procedure was used for the preparation of the ortho fluor mercurial, some difficulties were encountered. First, in the dilution of the Grignard with ether a creamy flocculent precipitate was formed. Then, in the evaporation of the ethereal solution of the mercurial (the ortho fluor phenyl mercuric chloride is much more soluble in ether than the corresponding meta and para compounds) a waxy material was formed which could not be re-crystallized from alcohol. The procedure used was as follows: 15 g. of (o)F.C<sub>6</sub>H<sub>4</sub>.Br were treated with 2 g. of Mg turnings in 30 c.c. of ether in the usual way and the ethereal solution (undiluted) was decanted from the excess Mg through glass wool. 20 g. of dry HgCl<sub>2</sub> was dissolved in dry ether, and to this solution in an Erlenmeyer flask, fitted with a reflux condenser and a dropping funnel, was added slowly and with vigorous shaking, the Grignard solution. The solution was refluxed about one hour. The ethereal solution was poured on cracked ice, acidulated with 1 % H<sub>2</sub>SO<sub>4</sub>, separated, washed with water until free from mercury salts, and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solution was then evaporated to a volume of about 20 c.c. and to this was added about 60 c.c. of petroleum ether. A white flocculent precipitate was formed. The liquid was decanted off and the precipitate washed once more with petroleum ether by decantation. This product (which was (o)F.C<sub>6</sub>H<sub>4</sub>HgCl) became

waxy when rubbed on a porous plate for a while. It melted or decomposed from  $90^{\circ}$  to  $110^{\circ}$  C.

PREPARATION OF ORTHO, META AND PARA CHLOR PHENYL MERCURIC CHLORIDES

15 g. of  $\text{Cl.C}_6\text{H}_4.\text{Br}$  were added slowly to 2 g. of Mg turnings in 50 c.c. of dry ether to which had been added a small crystal of iodine. The flask was warmed slightly to start the reaction. The reaction continued rapidly. The solution, after the addition of the chlor brombenzene, was refluxed slowly for one hour. The ethereal solution was decanted through glass wool into a dry Erlenmeyer flask fitted with a reflux condenser. To this solution was added 20 g. of dry  $\text{HgCl}_2$  in portions of about 2 g. each, with vigorous shaking after each addition. The reaction was vigorous. After the final addition, the solution was refluxed for about four hours. The ethereal solution was then poured on cracked ice to which had been added a 1% solution of  $\text{H}_2\text{SO}_4$ . The ethereal layer was separated and washed with water to free it from dissolved mercury salts. It was then dried over anhydrous sodium sulfate, filtered and evaporated. Since the chlor phenyl mercuric chlorides had been prepared and identified, it was not necessary to analyze them or boil them with  $\text{AgCl}$ , but their melting points showed them to be very pure compounds. They gave melting points as follows: (o) $\text{Cl.C}_6\text{H}_4.\text{HgCl}$ ,  $145-146^{\circ}$  C.; (m) $\text{Cl.C}_6\text{H}_4.\text{HgCl}$ ,  $210^{\circ}$  C.; (p) $\text{Cl.C}_6\text{H}_4.\text{HgCl}$ ,  $231^{\circ}$  C.

PREPARATION OF 2 FLUOR DIPHENYL MERCURY, 3 FLUOR DIPHENYL MERCURY AND 4 FLUOR DIPHENYL MERCURY

The ortho, meta and para fluor phenyl radicals were linked to mercury opposite the phenyl radical in two ways:

First. 5 g. of  $C_6H_5Br$  were treated with 1 g. of Mg turnings and the clear solution (decanted through glass wool) was diluted to about 150 c.c. with dry ether. To this solution (kept cool in an ice bath) was added a little at a time and with shaking 5 g. of the corresponding fluor phenyl mercuric chloride. After 15 minutes the solution was poured on cracked ice, acidulated with 1%  $H_2SO_4$ , the ether layer separated, washed once with water, dried over anhydrous  $Na_2SO_4$ , the ether evaporated off and the white crystalline mercurial (in the case of the meta and para compounds) washed with petroleum ether. When the ether was evaporated from the ortho compound, a brown semi-solid was left, which seemed to decompose slowly at room temperature. Due to the nature of this compound it could not be analyzed satisfactorily, nor its melting point determined.

3 Fluor diphenyl mercury melted at  $108-110^{\circ} C.$

4 Fluor diphenyl mercury melted at  $116-118^{\circ} C.$

Second. 5 g. of the fluor brombenzene was treated with 1 g. of Mg turnings. The ethereal solution was decanted through glass wool and diluted to about 150 c.c. with dry ether. To this solution (kept cool in an ice bath) was added in small portions, with shaking, 5 g. of phenyl mercuric chloride. After 15 minutes the solution was poured on cracked ice, acidulated, washed once with water and the ethereal layer separated, dried over anhydrous  $Na_2SO_4$  and the ether evaporated off. The mercurial was washed once with petroleum ether.

In the preparation of 2 fluor diphenyl mercury, the following procedure was followed: 5 g. of (o)F.C<sub>6</sub>H<sub>4</sub>.Br were treated with 2 g. of Mg turnings. The clear solution decanted through glass wool and added drop by drop (with shaking) from a dropping funnel to a solution (kept cool in an ice bath) of 5 g. of C<sub>6</sub>H<sub>5</sub>.HgCl in 150 c.c. of dry ether. After 15 minutes, the solution was poured on cracked ice, acidulated with 1% H<sub>2</sub>SO<sub>4</sub>, the ethereal layer separated, washed once with water, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and the ether evaporated off. This time also a brown semisolid remained which seemed to decompose on standing.

3 Fluor diphenyl mercury melted at 108-111° C.

4 Fluor diphenyl mercury melted at 117-118° C.

PREPARATION OF 2 FLUOR, 2' CHLOR DIPHENYL MERCURY, 3 FLUOR, 3' CHLOR DIPHENYL MERCURY AND 4 FLUOR, 4' CHLOR DIPHENYL MERCURY

These unsymmetrical mercurials were also prepared in two ways.

First. 5 g. of the chlor brombenzene was treated with 1 g. of Mg turnings and the clear solution was decanted through glass wool and diluted with dry ether to about 150 c.c. This solution was cooled in an ice bath and treated, in small portions, with shaking, with 5 g. of the fluor phenyl mercuric chloride. The solution was allowed to stand in the cold for 15 minutes, then poured on cracked ice, acidulated with 1% H<sub>2</sub>SO<sub>4</sub>. The ethereal layer was then separated, washed once with water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The ether was then evaporated. A white crystalline compound was obtained in the case of the meta and para compounds. The ortho compound gave a brown semisolid which

became oily through decomposition at room temperature.

(m m')  $F.C_6H_4.Hg.C_6H_4.Cl$  melted at  $108-110^{\circ} C.$

(p p')  $F.C_6H_4.Hg.C_6H_4.Cl$  melted at  $188-200^{\circ} C.$

Second. The meta and para compounds were prepared as follows: 5 g. of fluor brombenzene were treated with 1 g. of Mg turnings, the ethereal solution decanted through glass wool and diluted to 150 c.c. with dry ether. This solution was cooled in ice and treated as above with 5 g. of the corresponding chlor phenyl mercuric chloride. After standing 15 minutes it was poured on acidulated cracked ice, washed with water, separated and dried over anhydrous  $Na_2SO_4$  and the ether evaporated. The white residues remaining were washed once by decantation with petroleum ether.

(m m')  $F.C_6H_4.Hg.C_6H_4.Cl$  melted at  $108-112^{\circ} C.$

(p p')  $F.C_6H_4.Hg.C_6H_4.Cl$  melted at  $188-200^{\circ} C.$

(o o')  $F.C_6H_4.Hg.C_6H_4.Cl$  was prepared by the second method as follows: 5 g. of (o)  $F.C_6H_4.Br$  was treated with 2 g. of Mg turnings. The clear solution was decanted through glass wool and added drop by drop from a dropping funnel to a cooled solution of 5 g. of (o)  $Cl.C_6H_4.HgCl$  in 150 c.c. of dry ether. After 15 minutes the solution was poured on acidulated cracked ice and washed and dried in the usual manner. On evaporation of the ether a brown semisolid remained.

#### ANALYSIS OF MERCURIALS

About 0.2 g. of the mercurial was weighed into a 250 c.c. Erlenmeyer flask and 20 c.c. of glacial acetic acid added and then 5 c.c. of bromine. After standing for 15 minutes, 5 c.c.

of conc. HCl were added and then zinc dust in small amounts, care being taken to add the zinc slowly so that the temperature did not rise above 50° C. As soon as all the bromine color had disappeared, a slight excess of zinc dust was added and the mixture allowed to react for about 2 hours or longer. A small amount of finely powdered silica gel was added to retain any colloidal mercury. The supernatant liquid was then filtered through a Gooch crucible, the asbestos pad of which had been previously impregnated with silica gel. The residue in the flask was washed by decantation until free from halogens, the washings being poured through the Gooch crucible. The asbestos pad was then removed from the crucible and added to the residue in the flask, and any mercury adhering to the sides of the crucible was washed into the flask with dilute HNO<sub>3</sub>. The combined mercury residue was dissolved in 1 - 1 HNO<sub>3</sub>, about 5 c.c. of conc. H<sub>2</sub>SO<sub>4</sub> being added in case some mercury remained undissolved. When the mercury was completely dissolved, about 5 c.c. of a strong solution of KMnO<sub>4</sub> was added. Just before titration a concentrated solution of FeSO<sub>4</sub> was added to decolorize the excess KMnO<sub>4</sub>. About 2 c.c. of ferric alum indicator was then added. The mercury was immediately titrated with standard KCNS solution until a pink color persisted. Aliquots and a blank were run at the same time.

The KCNS solution was standardized against pure mercury. One c.c. of the solution was equivalent to 0.01005 g. Hg.

The analyses of the mercurials were as follows:

(p)F.C<sub>6</sub>H<sub>4</sub>.HgCl

1/2 Hg Calculated -- 60.6

(1) Wt. of sample--	0.2246 g.	c.c. KCNS--	13.3	%Hg found--	60.7
(2) Wt. of sample--	0.1631 g.	c.c. KCNS--	9.45	%Hg found--	59.4

(m)  $F.C_6H_4.HgCl$ 

% Hg Calculated -- 60.6

(1) Wt. of sample--0.2190 g. c.c. KCNS--12.9 %Hg found--60.5

(2) Wt. of sample--0.1790 g. c.c. KCNS--10.6 %Hg found--60.8

(o)  $F.C_6H_4.HgCl$ 

% Hg Calculated -- 60.6

(1) Wt. of sample--0.2122 g. c.c. KCNS--12.4 %Hg found--60.0

(2) Wt. of sample--0.2528 g. c.c. KCNS--14.7 %Hg found--59.7

(p)  $F.C_6H_4.HgC_6H_5$ 

% Hg Calculated -- 53.7

(1) Wt. of sample--0.2733 g. c.c. KCNS--14.3 %Hg found--53.7

(1) Wt. of sample--0.2359 g. c.c. KCNS--12.25 %Hg found--53.2

(m)  $F.C_6H_4.Hg.C_6H_5$ 

% Hg Calculated -- 53.7

(1) Wt. of sample--0.2278 g. c.c. KCNS--11.8 %Hg found--53.2

(1) Wt. of sample--0.2150 g. c.c. KCNS--11.2 %Hg found--53.5

(p p')  $F.C_6H_4.Hg.C_6H_4.Cl$ 

% Hg Calculated -- 49.2

(1) Wt. of sample--0.2379 g. c.c. KCNS--11.3 %Hg found--49.0

(2) Wt. of sample--0.2273 g. c.c. KCNS--10.8 %Hg found--48.8

(m m')  $F.C_6H_4.Hg.C_6H_4.Cl$ 

% Hg Calculated -- 49.2

(1) Wt. of sample--0.2349 g. c.c. KCNS--11.9 %Hg found--49.4

(2) Wt. of sample--0.2118 g. c.c. KCNS--10.1 %Hg found--48.8

## CONCLUSION

The method of Balz and Schiemann is applicable to the preparation of the fluor brombenzenes.

The corresponding Grignard reagents may be made from the

three fluor bromobenzenes, though care must be taken in the case of the ortho compound.

The fluor phenyl radicals form stable mercuric chlorides.

The meta and para fluor phenyl radicals form stable unsymmetrical mercurials with the phenyl and corresponding chlor phenyl radicals, but the ortho fluor phenyl radical does not seem to form a stable unsymmetrical mercurial with either the phenyl or the ortho chlor phenyl radical.

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