

THE USE OF CHLOROSULFONIC ACID IN THE IDENTIFICATION OF  
HALOGEN SUBSTITUTED AROMATIC COMPOUNDS

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HALOGEN SUBSTITUTED AROMATIC COMPOUNDS

By

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## INTRODUCTION

The identification of aromatic halides is generally accomplished by converting them into mono or polynitro derivatives. The reaction is not always easy to control, however, and sometimes gives mixtures hard to purify.

In view of the ready conversion of aromatic hydrocarbons into solid sulfonyl chloride derivatives by chlorosulfonic acid, it seemed profitable to extend the reaction to include aromatic halides. The method has the added advantage that, if a sulfonyl chloride is hard to purify or does not uniquely identify a compound, it may be very easily converted into the sulfonamide, which is generally a satisfactory derivative.

## HISTORICAL

A survey of the literature shows that most of the sulfonyl chloride derivatives of halogen substituted aromatic hydrocarbons have been made with the alkali salt of sulfonic acid and phosphorus pentachloride. The cases where chlorosulfonic acid is used for the same purpose are rare. This review, then, covers all known reactions of aromatic compounds and chlorosulfonic acid, to provide a background of information on the modes of reaction of this acid.

Hutchings (1) obtained p-chlorobenzene sulfonyl chloride by the action of chlorosulfonic acid on chlorobenzene.

Armstrong (2) states that chlorosulfonic acid has been used to change magnesium o-toluene sulfonate into o-toluene sulfonyl chloride.

Knapp (3) has obtained benzene sulfonic acid and benzene sulfonyl chloride by the reaction of benzene and chlorosulfonic acid.

Jacobsen and Schnapauff (4) obtained durene sulfonyl chloride, M. P.  $99^{\circ}$ \*, and durene sulfone, M. P.  $37^{\circ}$ , by adding durene slowly to cooled chlorosulfonic acid.

Lapworth (5) obtained diphenylmethane-4, 4-disulfonyl chloride, M. P.  $124^{\circ}$ , and diphenylmethane sulfone, M. P.  $169^{\circ}$ - $170^{\circ}$ , by the action of 2 mols of chlorosulfonic acid on 1 mol of diphenylmethane.

Ullmann and Lehner (6) obtained p-toluene sulfonyl chloride by the action of chlorosulfonic acid on toluene.

Ullmann and Korselt (7) added chlorobenzene to chlorosulfonic acid at a temperature of  $-15^{\circ}$ . After 2 hours at that temperature, the mixture was warmed to  $25^{\circ}$  and left for 12 hours. A 75% yield of p-

\* All temperatures cited are Centigrade.

chlorobenzenesulfonyl chloride was obtained.

Pummerer (8) found that 78 grams of benzene added to 300 cc. of chlorosulfonic acid at  $-15^{\circ}$  gave 49 grams of benzene sulfonyl chloride and 24 grams of sulfobenzid. The same amounts of reagents at  $22^{\circ}$  gave 69 grams of benzene sulfonyl chloride. Using equal number of mols of the substances and heating to  $60^{\circ}$  gave 85% benzene sulfonyl chloride.

Ullmann (9) obtained 22 grams of benzene sulfonyl chloride and 4.5 grams of sulfobenzid by the reaction of 20 grams of benzene and 80 grams of chlorosulfonic acid at  $15^{\circ}$ .

Holleman and Caland (10) succeeded in getting p-toluene sulfonyl chloride by the action of chlorosulfonic acid on toluene at  $35^{\circ}$ .

Harding (11) states that 1 mol of chlorosulfonic acid and 1 mol of toluene gave the ortho and para sulfonic acids, while an excess of chlorosulfonic acid gave toluene sulfonyl chlorides. An increase in temperature favored the formation of the para isomer. He believed that the action must take place in two steps. Using a temperature of  $-40^{\circ}$  and spraying in the toluene gave 40% yield of the ortho isomer.

Stewart (12) obtained 85% yield of 2,5-dichlorobenzene sulfonyl chloride, M. P.  $39^{\circ}$ , from p-dichlorobenzene and an excess of chlorosulfonic acid heated at a temperature of  $150^{\circ}$  for 1 hour. By the same method he obtained sulfonyl chlorides from acetanilide, salicylic acid, p-tolyl methyl ether, cinnamic acid and phenylacetic acid.

Johnson and Smiles (13) state that the action of 5 mols of chlorosulfonic acid on 1 mol of aceto-p-toluidide at  $80^{\circ}$  for 1 hour gave aceto-p-toluidide-2-sulfonyl chloride, M. P.  $124^{\circ}$ - $125^{\circ}$ . By the same method 4-acetylamino-phenetole-2-sulfonyl chloride, M. P.  $135^{\circ}$ , was obtained from



phenacetin; and aceto-p-xylylidide-6-sulfonyl chloride, M. P. 160°, was obtained from aceto-p-xylylidide.

Haworth and Lapworth (14) obtained m-cresol-4,6-disulfonic acid by the action of 2 mols of chlorosulfonic acid on 1 mol of m-cresol.

Smiles and Stewart (15) obtained p-acetaminobenzene sulfonyl chloride, M. P. 149°, by the action of 2.5 mols of chlorosulfonic acid on 0.5 mols of acetanilide at 15°, then heating the mixture to 60° for 2 hours. They state that when the action is complete, the tiny bubbles of hydrogen chloride which appear during the reaction, cease to escape.

Burkhardt and Lapworth (16) prepared sodium phenyl sulfate from phenol and chlorosulfonic acid in carbon disulfide followed by treatment with sodium hydroxide.

Pollak and Gebauer-Fulnegg (17) found that catechol, added slowly to 10 times its weight of chlorosulfonic acid, gave catechol disulfonic acid, and that if this in turn were added to chlorosulfonic acid it gave 1,2-dihydroxybenzene-3,5-sulfonyl chloride, M. P. 149°-150°. By the same method, sulfonyl chlorides were obtained from salicylic acid and hydroquinone.

Pollak, Gebauer-Fulnegg and Riesz (18) found that an excess of chlorosulfonic acid acting on o-cresol at room temperature gave o-cresol-4,6-disulfonyl chloride, M. P. 85°-86°, but that if the mixture were heated it gave o-methyl-phenylene-o-sulfonyl chloride-p-p'-disulfonyl chloride, decomposing at 280°. Allowing chlorosulfonic acid to react with phenol at room temperature gave phenol-2,4-disulfonyl chloride, M. P. 89°, and heating for 3 hours gave phenol-2,4,6-trisulfonyl chloride 193°.

Pollak and Gebauer-Fulnegg (19) used 5 mols of chlorosulfonic acid and 1 mol of resorcinol, obtaining the disulfonyl chloride. With greater excess of chlorosulfonic acid and heating, resorcinol-2,4,6-trisulfonyl chloride, M. P. 168°; was obtained.

Corbellini (20) added 1 mol of naphthalene to 2 mols of chlorosulfonic acid at 15° to 45° obtaining naphthalene-1,5-disulfonic acid and some disulfonyl chloride. When 2 to 4 mols of chlorosulfonic acid was diluted with carbon tetrachloride, naphthalene-1,5-disulfonyl chloride was always obtained.

Gebauer-Fulnegg and Figdor (21) obtained 2,5-dichlorobenzene-1,3-disulfonyl chloride, M. P. 114°, and 2,5-dichlorobenzene-1,4-disulfonyl chloride, M. P. 182°, after heating an excess of chlorosulfonic acid with p-dichlorobenzene.

Lustig and Katscher (22) found that an excess of chlorosulfonic acid reacting for 2 hours at 150° to 160° with aniline in the presence of sodium chloride gave, on pouring into water, aniline-2,4,6-trisulfonyl chloride, M. P. 175°. By the same procedure p-toluidine gives p-toluidine-3,5-disulfonyl chloride, M. P. 156°; m-phenylenediamine gives m-phenylenediamine-4,6-disulfonyl chloride, M. P. 274°-275° and p-phenylenediamine gives the tetra sulfonyl chloride derivative.

Pollak and Gebauer-Fulnegg (23) used 10 mols of chlorosulfonic acid and 1 mol of phloroglucinol, obtaining at room temperature, phloroglucinol-2,4,6-trisulfonic acid. Using 50 mols of chlorosulfonic acid at room temperature for several hours, they obtained phloroglucinol-2,6-disulfonyl chloride, M. P. 184°. By using 50 mols and heating at 150°-160° for 70 hours, they obtained  $C_6Cl_6$ .

Pollak, Gebauer-Fulnegg and Halward (24) found that 5 mols of chlorosulfonic acid reacting with 1 mol of alpha-naphthol for 2.5 hours or with .5 mol of alpha-naphthol for 1.5 hours gave alpha-naphthol-disulfonyl chloride, M. P.  $149^{\circ}$ , and with prolonged action gave the trisulfonyl chloride, M. P.  $172^{\circ}$ . At a temperature of  $160^{\circ}$  chlorination takes place and trichloronaphthalenesulfonyl chloride, M. P.  $214^{\circ}$  is formed. Using 50 mols of chlorosulfonic acid and 1 mol of alpha-naphthol, and heating for 80 hours at  $150^{\circ}$ - $160^{\circ}$  gave dichloronaphthalene. The addition of 1 mol of beta-naphthol to 1 mol of chlorosulfonic acid at  $100^{\circ}$  gave beta-naphthol-4-sulfonic acid, while heating to  $160^{\circ}$  gave trichloronaphthalene sulfonyl chloride, M. P.  $214^{\circ}$ . Excess of chlorosulfonic acid at room temperature gave two beta-naphthol-disulfonyl chlorides, M. P.  $111^{\circ}$  and  $177^{\circ}$ . If the mixture was heated to  $130^{\circ}$ - $140^{\circ}$ , beta-naphthol-3,6,8-trisulfonyl chloride, M. P.  $196^{\circ}$  was obtained.

Gebauer-Fulnegg and Meissner (25) obtained anisole-2,4-disulfonyl chloride, M. P.  $86^{\circ}$ , by the action of chlorosulfonic acid on anisole. Phenetole and chlorosulfonic acid gave the 2,4-disulfonyl chloride, M. P.  $102^{\circ}$ - $104^{\circ}$ . Chlorosulfonic acid reacted with phenyl acetate to give phenol-2,4-disulfonyl chloride. The action with acetyl thiobenzene gave 4,4'-dichlorosulfonyl diphenyl disulfide, M. P.  $131^{\circ}$ .

Gebauer-Fulnegg and Glueckman (26) found that the action of chlorosulfonic acid on alpha-naphthol-2,4,7-sulfonic acid gave the corresponding trisulfonyl chloride, M. P.  $174^{\circ}$ .

Oliver, Reisz and Landau (27) obtained hydroquinone disulfonyl chloride, M. P.  $113^{\circ}$ - $114^{\circ}$ , by the action of 400 grams of chlorosulfonic acid on 20 grams of hydroquinone for 3 hours at  $80^{\circ}$ .

Clarke, Babcock and Murray (28) found that benzene sulfonyl chloride was obtained in 75% yield by the action of 3 mols of chlorosulfonic acid on 1 mol of benzene for 3 hours at 20°. If less chlorosulfonic acid was used the amount of diphenyl sulfone was increased. Hydrolysis took place readily if the sulfonyl chloride was left in water.

Pollak, Krauss, Katscher and Lustig (29) used 1 mol of benzene and 10 mols of chlorosulfonic acid, obtaining the *m*-disulfonyl chloride; 1 mol of benzene and 2 mols of the acid gave 80% diphenyl sulfone disulfonyl chloride; and 1 mol of benzene and 40 mols of the acid gave diphenyl sulfone sulfonyl chloride. Toluene and the xylenes gave analogous reactions. 1 mol of chlorobenzene sulfonyl chloride and 3 mols of chlorosulfonic acid heated for 8 hours at 150° gave chlorobenzene-2,4-disulfonyl chloride, M. P. 90°-91°, starting with chlorobenzene gave the same result. *p*-Chloronitrobenzene, nitrobenzene, ethylphenyl sulfone, naphthalene, and biphenyl were also studied.

Katscher, Lehr, Harnish and Steinhardt (30) obtained a water soluble product by the action of chlorosulfonic acid on *o*-xylenol at -5° to 0°, while heating to 110° gave *o*-xylenol-4,6-disulfonyl chloride, M. P. 104° and 2,3,2',3'-tetramethyldiphenyl-1,6,1'6'-sulfonylide-4,4-disulfonyl chloride, decomposing at 295°. Xylenol sulfonyl chloride and sulfonylide were obtained from the action of chlorosulfonic acid on the phenol.

Steiger (31) obtained 1-methylnaphthalene-4-sulfonic acid by allowing chlorosulfonic acid to react with alphasethylnaphthalene in carbon tetrachloride at 0°.

Courtot and Lin (32), using equivalent amounts of *p*-dibromobiphenyl and chlorosulfonic acid in chloroform, obtained dibromobiphenyl sulfonic

acid and dibromobiphenylene sulfone; by increasing the amount of chlorosulfonic acid a small per cent of disulfonyl chloride was obtained, M. P. 219°.

Gebauer-Fulnegg and Haemmerle (33) state that chlorosulfonic acid may cause four distinct types of primary reactions: sulfonation, sulfochlorination, chlorination, and oxidation. In their experimental work with chlorosulfonic acid, they obtained naphthol-2,4,7-trisulfonyl chloride, M. P. 174°, from both naphthol-2,4-disulfonic acid and naphthol-4,7-disulfonic acid. Naphthol-4,8-disulfonic acid and chlorosulfonic acid gave naphthol-4,6,8-trisulfonyl chloride, M. P. 217°.

Pollak, Riesz and Wittels (34) using 5 grams of chloroacetanilide and 25 grams of chlorosulfonic acid, allowing them to react for 2 hours at 60°, obtained a sulfonyl chloride, M. P. 112°; chloroaceto-p-toluidide and chlorosulfonic acid gave a disulfonyl chloride.

Burkhardt (35) added chlorosulfonic acid slowly to phenol in carbon disulfide at -15° for 2 hours, obtaining phenyl sulfuric acid and p-phenol sulfonic acid. Long periods of reaction favored the production of the former.

Walter (36) heated 6 grams of naphthalene and 7.5 cc. of chlorosulfonic acid for 10 hours at 180°, obtaining tetrachlorophthalic anhydride, M. P. 255°. This is an example of chlorination and oxidation according to the classification of Gebauer-Fulnegg and Haemmerle (33).

Sutter, McKenzie and Maxwell (37) found that an excess of chlorosulfonic acid gave highest yields of sulfonyl chlorides and that the sulfonic acid group was directed to the para position.

## EXPERIMENTAL

The chemicals used are listed on the following pages with an indication of their source and purity.

## AROMATIC HALIDES

Fluorobenzene	- Chem. 620, student preparation. B. P. $84^{\circ}$ - $85^{\circ}$ .
Chlorobenzene	- Eastman Kodak Company product. B. P. $130^{\circ}$ - $132^{\circ}$ .
Bromobenzene	- Eastman Kodak Company product. B. P. $154^{\circ}$ - $155^{\circ}$ .
Iodobenzene	- Eastman Kodak Company product. B. P. $70^{\circ}$ - $71^{\circ}$ .
o-Dichlorobenzene	- Eastman Kodak Company product. B. P. not given. Practical grade.
m-Dichlorobenzene	- Eastman Kodak Company product. B. P. $172^{\circ}$ - $173^{\circ}$ .
p-Dichlorobenzene	- Eastman Kodak Company product. M. P. $52.5^{\circ}$ - $53^{\circ}$ .
p-Dibromobenzene	- Eastman Kodak Company product. M. P. $87^{\circ}$ - $88^{\circ}$ .
p-Diodobenzene	- Eastman Kodak Company product. M. P. $127^{\circ}$ - $128^{\circ}$ .
o-Chlorobromobenzene	- Made by the author. o-Chloroaniline was made into the diazonium compound by dissolving in sulfuric acid and cooling to $5^{\circ}$ and adding sodium nitrite. The addition of sodium bromide and copper powder produced the desired

Gattermann reaction. The product was steam distilled, dried, and redistilled.

B. P.  $200^{\circ}$ - $204^{\circ}$ .

- m-Chlorobromobenzene - Eastman Kodak Company product.  
B. P.  $81^{\circ}$ - $82^{\circ}$ /20 mm.
- p-Chlorobromobenzene - Eastman Kodak Company product.  
M. P.  $63^{\circ}$ - $65^{\circ}$ .
- o-Chloriodobenzene - Eastman Kodak Company product.  
B. P.  $119^{\circ}$ - $121^{\circ}$ .
- m-Chloriodobenzene - Eastman Kodak Company product.  
B. P.  $113^{\circ}$ - $114^{\circ}$ /14 mm.
- p-Chloriodobenzene - Eastman Kodak Company product.  
M. P.  $55^{\circ}$ - $56^{\circ}$ .
- o-Fluorochlorobenzene - Eastman Kodak Company product.  
B. P.  $135^{\circ}$ - $136^{\circ}$ .
- m-Fluorochlorobenzene - Eastman Kodak Company product.  
B. P.  $123^{\circ}$ - $125^{\circ}$ .
- p-Fluorochlorobenzene - Made by the author. p-Chloroaniline was made into the diazonium compound by dissolving in hydrochloric acid and cooling to  $5^{\circ}$  and adding sodium nitrite. Boric acid was dissolved in hydrofluoric acid and the resulting fluoboric acid added to the diazonium compound. The precipitate was washed and dried. It was decomposed by heating gently and the p-fluorochlorobenzene

	distilled, washed and dried.
p-Fluoriodobenzene	- Eastman Kodak Company product. B. P. $181^{\circ}$ - $183^{\circ}$ .
p-Fluorobromobenzene	- Eastman Kodak Company product. B. P. $152^{\circ}$ - $155^{\circ}$ .
o-Bromiodobenzene	- Eastman Kodak Company product. B. P. $124^{\circ}$ - $127^{\circ}$ /17 mm.
p-Bromiodobenzene	- Eastman Kodak Company product. M. P. $90^{\circ}$ - $91^{\circ}$ .
1,2,4-Trichlorobenzene	- Eastman Kodak Company product. M. P. $15^{\circ}$ - $16^{\circ}$ .
1,2,4,5-Tetrachloro-	
benzene	- Eastman Kodak Company product. M. P. $134^{\circ}$ - $135^{\circ}$ .
o-Chlorotoluene	- Chem. 620, student preparation. B. P. $157^{\circ}$ - $159^{\circ}$ .
p-Chlorotoluene	- Chem. 620, student preparation. B. P. $161^{\circ}$ - $165^{\circ}$ .
o-Bromotoluene	- Chem. 620, student preparation. B. P. $180^{\circ}$ - $182^{\circ}$ .
p-Bromotoluene	- Eastman Kodak Company product. M. P. $26^{\circ}$ - $27^{\circ}$ .
alpha-Chloronaphthalene	- Eastman Kodak Company product. B. P. $120^{\circ}$ - $170^{\circ}$ /20 mm.
alpha-Bromonaphthalene	- Chem. 620, student preparation. B. P. $280^{\circ}$ - $282^{\circ}$ .



## REAGENTS

Chlorosulfonic Acid	- Monsanto Chemical Company product, technical.
Ammonium Hydroxide	- C. P.

## SOLVENTS

Ethyl Alcohol	- B. P. 77°-78°. 95%.
Methyl Alcohol	-B. P. 63°-64°.
Ether	- B. P. 33°-34°.
Benzene	- B. P. 78°-79°.
Petroleum Ether	- B. P. 40°-150°.
Carbon Tetrachloride	- B. P. 75°-76°.

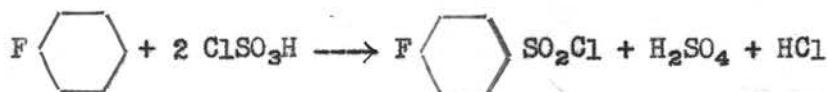
## EXPERIMENTAL PROCEDURES

In the literature survey it was found that most of the work had been done on phenols and hydrocarbons, but little research had been done on the reactions of aromatic halides and chlorosulfonic acid. The general method used here is essentially that of Clarke (38). 20 drops, unless otherwise stated, of the aromatic halide was added gradually to 5 to 10 cc. of chlorosulfonic acid with shaking. In some cases the action was moderated by diluting the acid with carbon tetrachloride. The mixture was poured slowly on 200 grams of crushed ice. The resulting insoluble material—solid, oil or mixture—was separated from the water and washed to remove the acid. The product was recrystallized from one of several solvents—ethyl alcohol, methyl alcohol, ether, benzene, or petroleum ether. If the product was an oil or if there was doubt whether it was a sulfonyl chloride, an attempt was made to change it to a sulfonamide by shaking and heating the oil or solid in concentrated ammonium hydroxide. Recrystallization was made from one of the above solvents. If a solid could not be converted into a

sulfonamide, it was presumed to be a sulfone. This supposition was verified by refluxing 1 gram of it with 40 cc. of 1 N sodium hydroxide and 10 cc. of ethyl alcohol for 30 minutes. Under these conditions a sulfonyl chloride would dissolve, whereas a sulfone would not. If the solid was insoluble its melting point was compared with that of the material before refluxing.

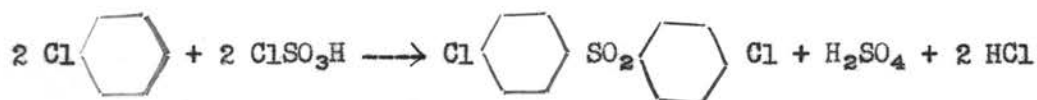
#### Fluorobenzene

20 drops of fluorobenzene was added slowly to 5 cc. of chloro-sulfonic acid and mixed by shaking for 10 minutes. The mixture was poured on crushed ice. The oil which resulted was separated from the water, and was washed and dissolved in petroleum ether. White needles crystallized from the cold ( $-10^{\circ}$ ) solution. M. P.  $30^{\circ}$ - $32^{\circ}$ .

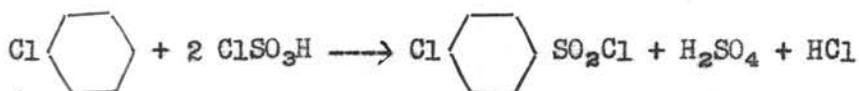


#### Chlorobenzene

20 drops of chlorobenzene was added gradually to 5 cc. of chloro-sulfonic acid and mixed by shaking for 10 minutes. The mixture was added to 200 grams of chipped ice. A white solid separated. It was washed and recrystallized 3 times from a mixture of ethyl alcohol and water. Silvery white leaflets separated, M. P.  $143^{\circ}$ - $144^{\circ}$ . The reaction was probably:



The reaction was repeated using a solution of 5 cc. of chloro-sulfonic acid in 5 cc. of carbon tetrachloride. The resulting solid was washed and recrystallized twice from ether. M. P.  $52^{\circ}$ - $53^{\circ}$ .

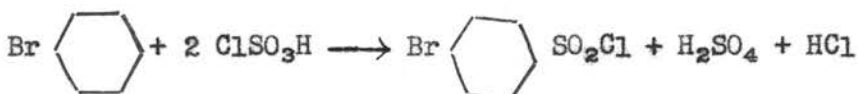


Bromobenzene

20 drops of bromobenzene was added gradually to 5 cc. of chlorosulfonic acid and mixed by shaking for 10 minutes. The mixture was added to crushed ice. A white solid separated. It was washed and recrystallized once from methyl alcohol and water, forming white needles. M. P. 155°-156°.



The procedure was repeated using a solution of 5 cc. of chlorosulfonic acid in 5 cc. of carbon tetrachloride. The solid was recrystallized once from ether. M. P. 74°-75°.



Iodobenzene

20 drops of iodobenzene was added to 5 cc. of chlorosulfonic acid and mixed by shaking for 10 minutes. The mixture was added to crushed ice. A white solid separated. It was washed and recrystallized once from ethyl alcohol. M. P. 197°-198°.

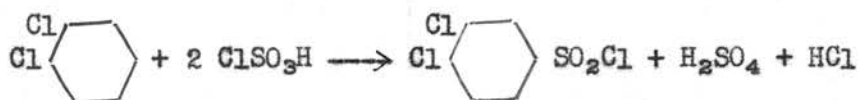


The same procedure was followed using a mixture of 5 cc. of chlorosulfonic acid in 5 cc. of carbon tetrachloride. The resulting solid, when crystallized twice from ether, formed plates. M. P. 85°-86°.

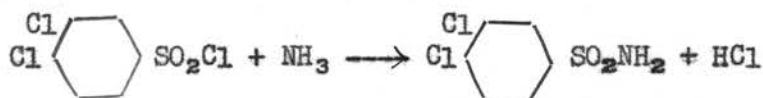


o-Dichlorobenzene

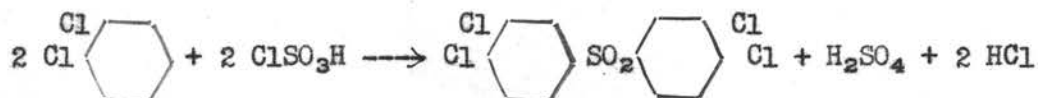
20 drops of o-dichlorobenzene was added slowly to 5 cc. of chlorosulfonic acid and mixed by shaking for 10 minutes. The mixture was added to crushed ice. A white solid separated. It was washed and solidified on a salt-ice solution. A melting point was too low to be determined accurately.



The amide was made by shaking with conc. ammonium hydroxide. The resulting white solid was recrystallized from ethyl alcohol. M. P. 139°-140°.

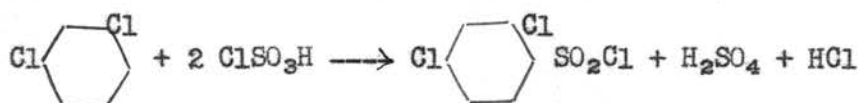


The same procedure was followed except that the mixture was heated to boiling. A white solid formed, which was recrystallized from ethyl alcohol. M. P. 172°-173°. No attempt was made to identify this substance. The reaction might be as follows:



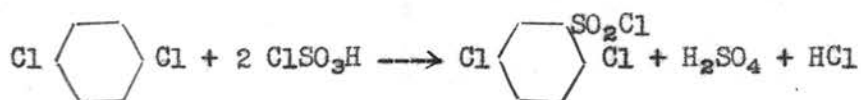
m-Dichlorobenzene

20 drops of m-dichlorobenzene was added slowly to 5 cc. of chlorosulfonic acid and mixed by shaking for 10 minutes. The mixture was added to crushed ice. A white solid was obtained. It was washed and crystals were obtained by recrystallizing twice from benzene. M. P. 53°-54°.

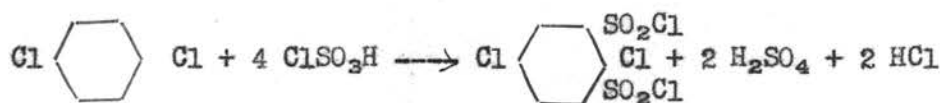


p-Dichlorobenzene

1 gram of p-dichlorobenzene was added to 5 cc. of chlorosulfonic acid and mixed by shaking for 10 minutes. The mixture was heated to boiling to dissolve the p-dichlorobenzene. It was added to crushed ice. A white solid was obtained. It was washed and crystals formed by recrystallizing from petroleum ether. M. P. 36°-38°.

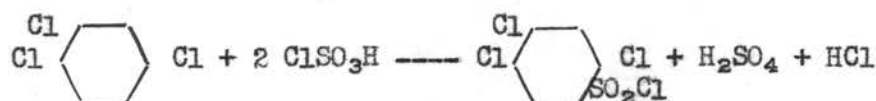


The same procedure was followed except that the mixture was heated to boiling for 10 minutes. The white solid that was formed was recrystallized from methyl alcohol. M. P. 108°-110°. No attempt was made to identify this compound, but it is probably 2,5-dichloro-1,3-disulfonyl chloride, which is known to melt at 114° (21).



1,2,4-Trichlorobenzene

20 drops of 1,2,4-trichlorobenzene was added to 10 cc. of chlorosulfonic acid and mixed by shaking for 10 minutes. The mixture was added to crushed ice, separated and washed. The solid formed crystals by recrystallizing once from methyl alcohol. M. P. 66°-67°.

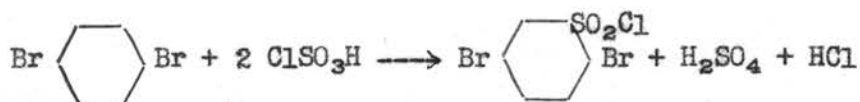


1,2,4,5-Tetrachlorobenzene

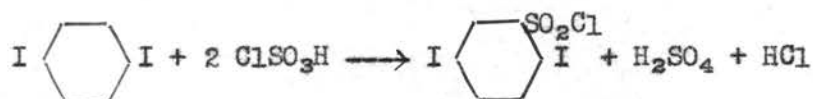
1 gram of 1,2,4,5-tetrachlorobenzene was added to 10 cc. of chlorosulfonic acid and heated to boiling to dissolve the 1,2,4,5-tetrachlorobenzene. The mixture was added to crushed ice. The original solid was recovered. The procedure was repeated several times with longer boiling without satisfactory results.

p-Dibromobenzene

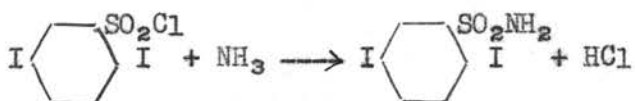
1 gram of p-dibromobenzene was added to 5 cc. of chlorosulfonic acid and mixed by shaking and heating just to boiling. The mixture was poured on chipped ice. The white solid obtained was washed and recrystallized once from ethyl alcohol and water, forming needles. M. P. 69°-71°.

p-Diodobenzene

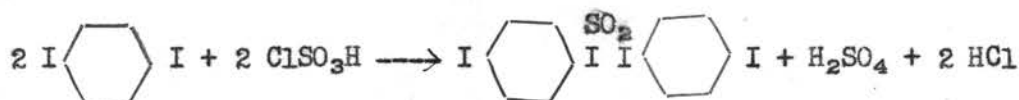
1 gram of p-diodobenzene was added to a mixture of 5 cc. of chlorosulfonic acid in 5 cc. of carbon tetrachloride and mixed by shaking for 10 minutes. Gentle heating was used to dissolve the crystals. The mixture was poured on ice. The white solid obtained was washed and recrystallized once from petroleum ether, when it formed needles. M. P. 130°-131°.



The amide was made by heating the sulfonyl chloride gently in ammonium hydroxide. The white solid was recrystallized once from ethyl alcohol. M. P. 209°-211°.



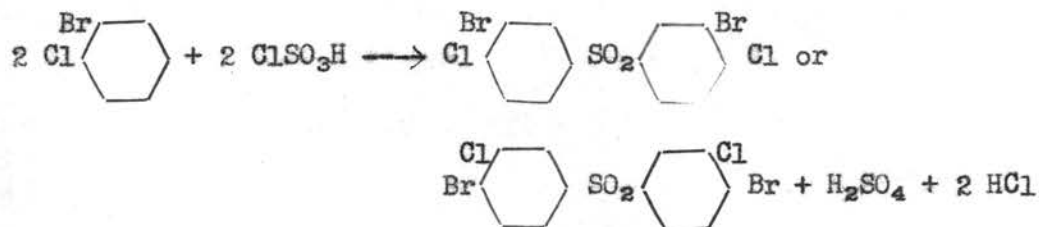
1 gram of p-diodobenzene was added to 5 cc. of chlorosulfonic acid and heated to boiling for 10 minutes. The mixture was poured on crushed ice and the solid was washed and recrystallized once from petroleum ether, when it formed crystals. M. P. 213°-214°.



This product was refluxed for 30 minutes with 40 cc. of 1 N sodium hydroxide and 10 cc. of ethyl alcohol. The original product was recovered as shown by a melting point check.

#### o-Chlorobromobenzene

20 drops of o-chlorobromobenzene was added to 10 cc. of chlorosulfonic acid and mixed with shaking for 10 minutes. The mixture was heated just to boiling and poured on crushed ice. The white solid was recrystallized once from petroleum ether as plates. M. P. 187°-190°. The sulfonamide could not be obtained. The product was refluxed for 30 minutes with 40 cc. of 1 N sodium hydroxide and 10 cc. of ethyl alcohol. The original product was recovered.

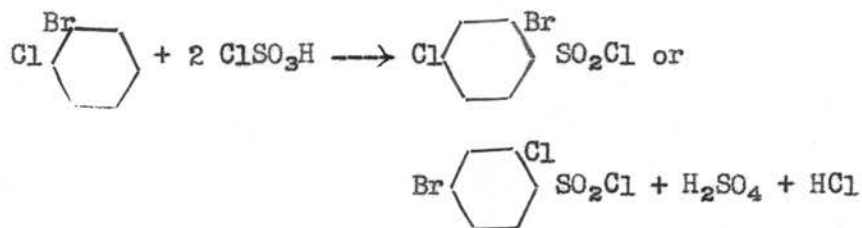


#### m-Chlorobromobenzene

20 drops of m-chlorobromobenzene was added to 10 cc. of chlorosulfonic acid and mixed by shaking for 10 minutes. The mixture was poured on

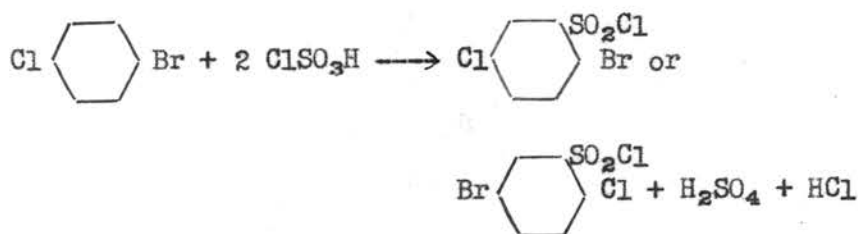
crushed ice. The solid was recrystallized twice from methyl alcohol.

M. P. 57°-58°.

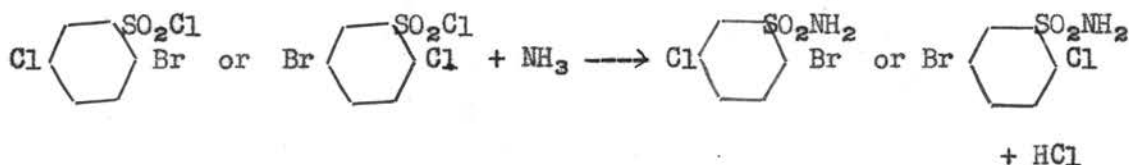


p-Chlorobromobenzene

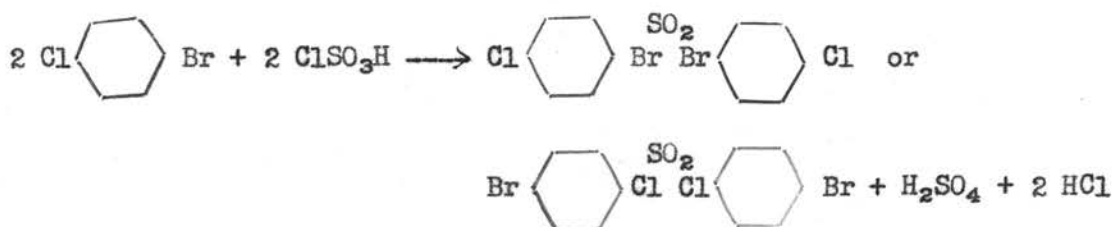
1 gram of p-chlorobromobenzene was added to 10 cc. of chlorosulfonic acid and mixed by shaking for 10 minutes. The mixture was poured on chipped ice. The white solid was recrystallized once from a mixture of petroleum ether and benzene. M. P. 45°-46°.



The sulfonamide was formed by the usual method and recrystallized once from ethyl alcohol. M. P. 190°-191°.



1 gram of p-chlorobromobenzene was added to 10 cc. of chlorosulfonic acid and heated to boiling for 10 minutes. The white solid, formed on pouring on crushed ice, was recrystallized once from ethyl alcohol. M. P. 231°-233°.

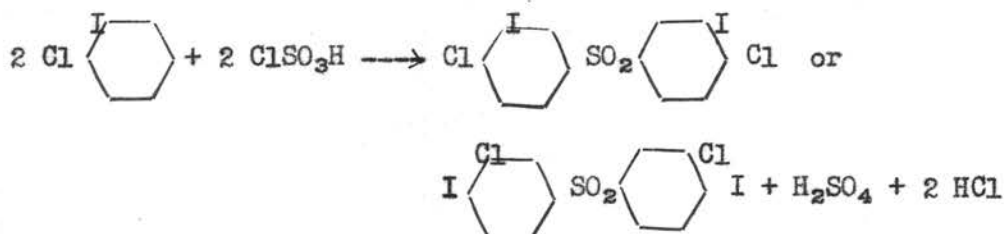




This product was refluxed for 30 minutes with 40 cc. of 1 N sodium hydroxide and 10 cc. of ethyl alcohol. The original product was recovered.

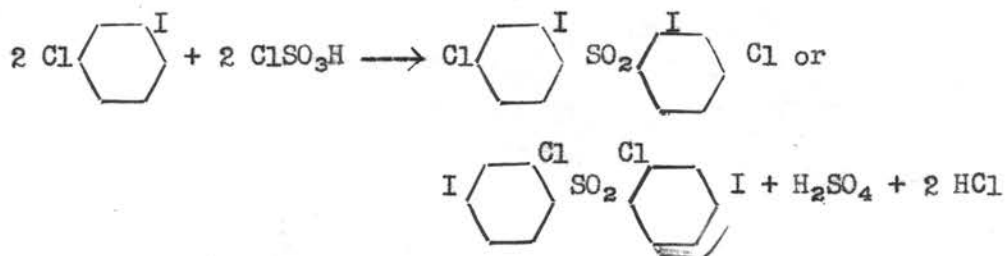
o-Chloriodobenzene

20 drops of o-chloriodobenzene was added to 10 cc. of chlorosulfonic acid and mixed with shaking for 10 minutes. The mixture was heated to boiling for 10 minutes and poured on crushed ice. The solid formed yellow crystals by recrystallizing twice from methyl alcohol. M. P. 223°-224°. The sulfonamide could not be made. The product was refluxed with 40 cc. of 1 N sodium hydroxide and 10 cc. of ethyl alcohol for 30 minutes. The original product was recovered.



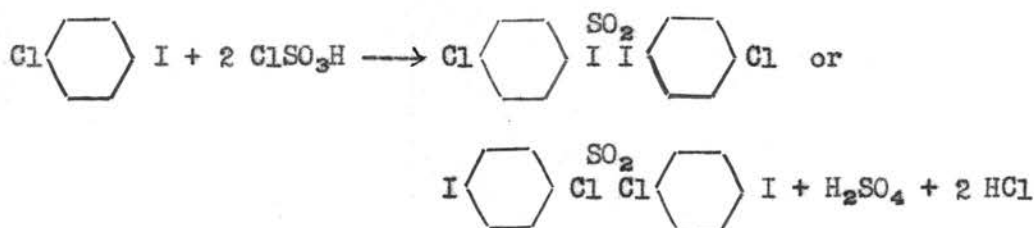
m-Chloriodobenzene

20 drops of m-chloriodobenzene was added to 10 cc. of chlorosulfonic acid and mixed by shaking for 10 minutes. The mixture was heated to boiling for 10 minutes and poured on crushed ice. The solid formed yellow needles, by recrystallizing once from methyl alcohol. M. P. 220°-221°. The sulfonamide could not be formed. The product was refluxed for 30 minutes with 40 cc. of 1 N sodium hydroxide and 10 cc. of ethyl alcohol. The original product was recovered.

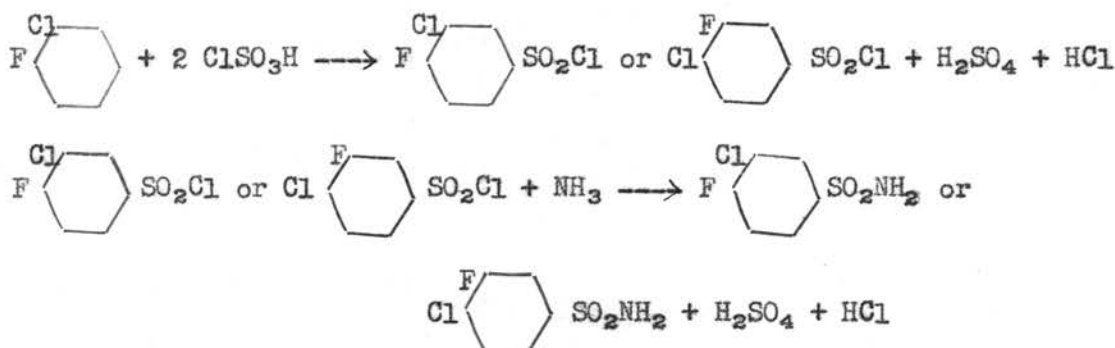


p-Chloriodobenzene

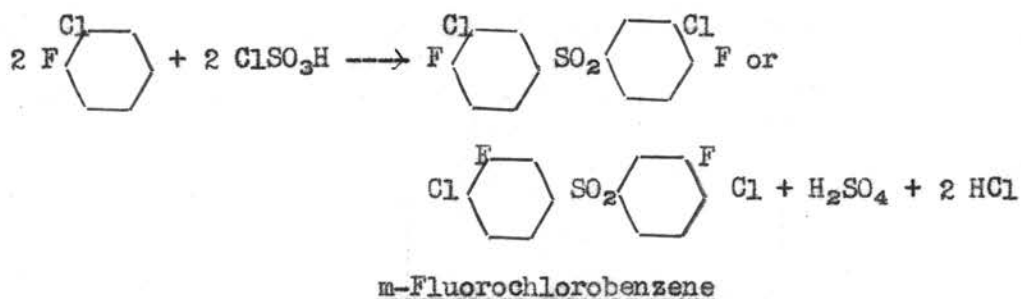
1 gram of p-chloriodobenzene was added to 10 cc. of chlorosulfonic acid and mixed with shaking for 10 minutes. The mixture was heated to boiling and poured on crushed ice. The solid was washed and recrystallized once from petroleum ether, giving needles. M. P. 225°-226°. The sulfonamide could not be obtained. The product was refluxed by the same procedure as for m-chloriodobenzene and the original product recovered.

o-Fluorochlorobenzene

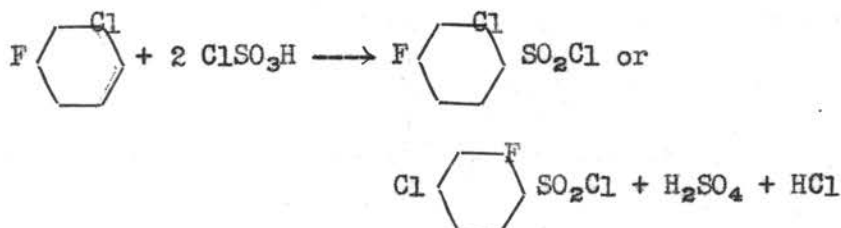
20 drops of o-fluorochlorobenzene was added slowly to 10 cc. of chlorosulfonic acid and mixed by shaking for 10 minutes. The mixture was poured on crushed ice. An oil was separated and washed. It solidified in a salt-ice solution. A satisfactory melting point was not obtained. The sulfonamide was made by shaking the sulfonyl chloride with concentrated ammonium hydroxide. It was recrystallized once from ethyl alcohol. M. P. 108°-109°.



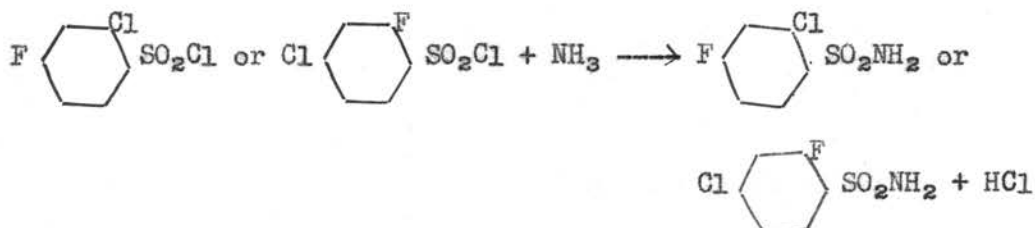
When the chlorosulfonic acid mixture was heated to boiling before pouring on the ice a solid was obtained, which formed needles after recrystallization twice from ethyl alcohol. M. P.  $146^{\circ}$ - $147^{\circ}$ . No attempt was made to identify this compound. The reaction is probably as follows:



20 drops of m-fluorochlorobenzene was added to 10 cc. of chlorosulfonic acid and mixed by shaking for 10 minutes. A solid formed after pouring the reaction mixture on chipped ice. It was washed and recrystallized twice from methyl alcohol as needles. M. P.  $98^{\circ}$ - $99^{\circ}$ . The reaction may be as follows:

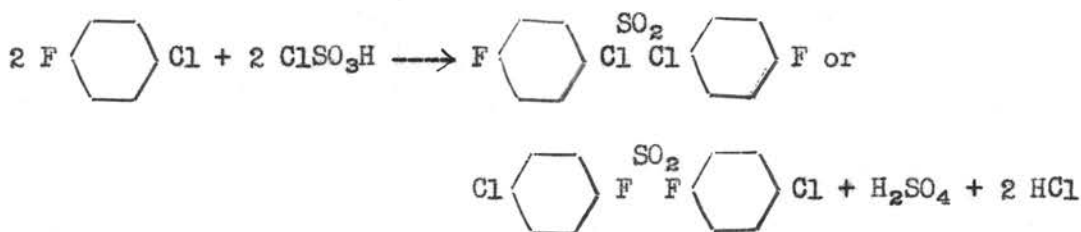


The sulfonamide was made in the usual method and the solid formed was recrystallized twice from ethyl alcohol. M. P.  $176^{\circ}$ - $180^{\circ}$ .

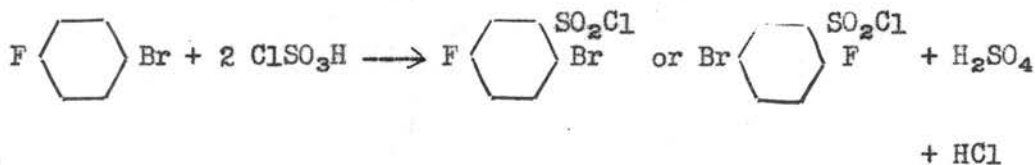


p-Fluorochlorobenzene

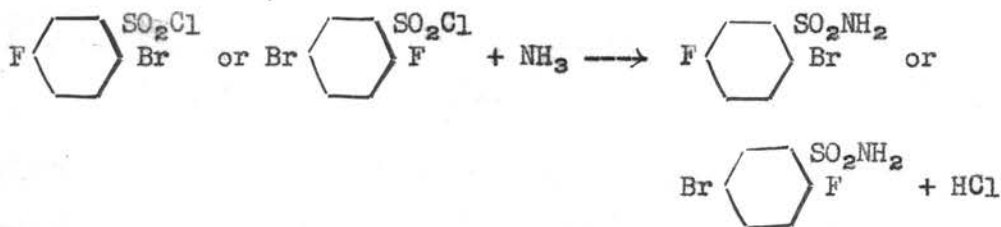
20 drops of p-fluorochlorobenzene was added to 10 cc. of chloro-sulfonic acid and mixed by shaking for 10 minutes. The mixture was heated to boiling for 10 minutes. It was poured on crushed ice and the reaction product was washed and recrystallized twice from petroleum ether. M. P. 127°-130°. The sulfonamide could not be formed. The product was refluxed for 30 minutes in 40 cc. of 1 N sodium hydroxide and 10 cc. of ethyl alcohol. The original product was recovered. The reaction may be as follows:

p-Fluorobromobenzene

20 drops of p-fluorobromobenzene was added to 10 cc. of chloro-sulfonic acid and mixed by shaking for 10 minutes. The mixture was poured on crushed ice. The solid which formed was recrystallized twice from methyl alcohol and water, forming needles. M. P. 59°-60°.

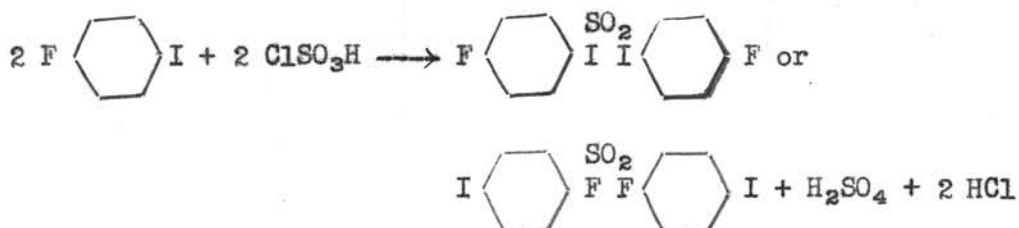


The sulfonamide was formed by the usual method. It was recrystallized once from ethyl alcohol. M. P. 142°-144°.

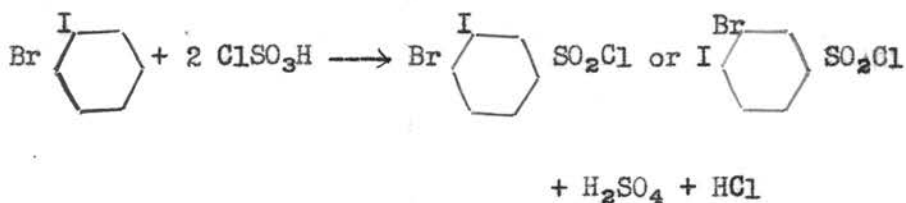


p-Fluoriodobenzene

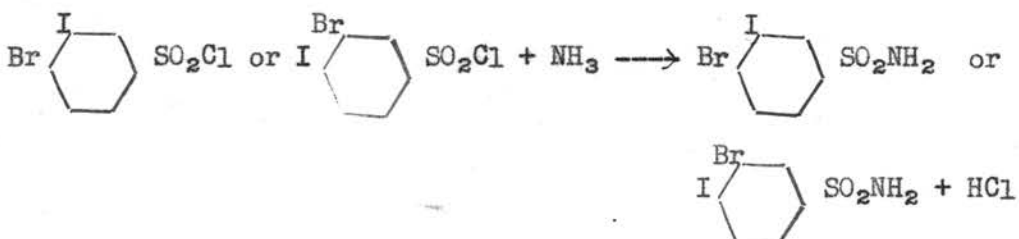
20 drops of p-fluoriodobenzene was added slowly to 10 cc. of chlorosulfonic acid and mixed by shaking for 10 minutes. The mixture was poured on crushed ice. The solid was recrystallized from methyl alcohol as needles. M. P. 144°-145°. The sulfonamide could not be made. The product was refluxed with 40 cc. of 1 N sodium hydroxide and 10 cc. of ethyl alcohol for 30 minutes. The original product was recovered.

o-Bromiodobenzene

20 drops of o-bromiodobenzene was added to 10 cc. of chlorosulfonic acid and mixed by shaking for 10 minutes. The mixture was heated just to boiling and poured on crushed ice. The solid which formed was recrystallized twice from methyl alcohol. M. P. 86°-88°.

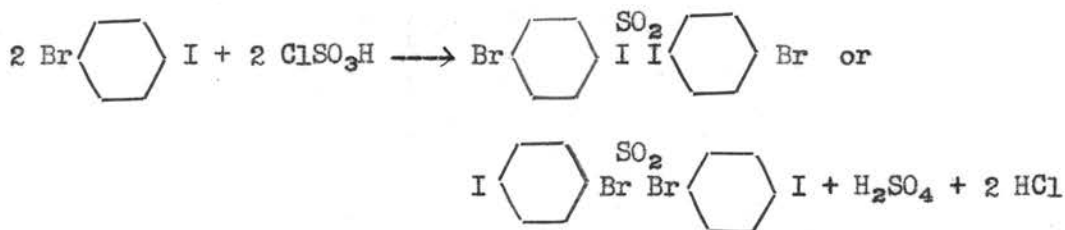


The sulfonamide was made by the usual method and the solid was recrystallized from ethyl alcohol. M. P. 157°-158°.

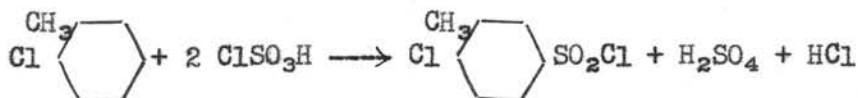


p-Bromiodobenzene

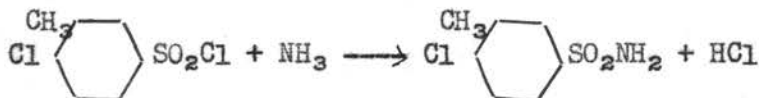
1 gram of p-bromiodobenzene was added to 10 cc. of chlorosulfonic acid and mixed by shaking. The mixture was poured on crushed ice. The solid which formed was washed and recrystallized from petroleum ether, forming needles. M. P. 225°-226°. The product was refluxed for 30 minutes with 40 cc. of 1 N sodium hydroxide and 10 cc. of ethyl alcohol. The original product was recovered.

o-Chlorotoluene

20 drops of o-chlorotoluene was added to 5 cc. of chlorosulfonic acid and mixed by shaking for 10 minutes. The mixture was heated to boiling for 10 minutes and poured on chipped ice. The white solid obtained was washed and recrystallized twice from methyl alcohol, forming crystals. M. P. 59°-60°.

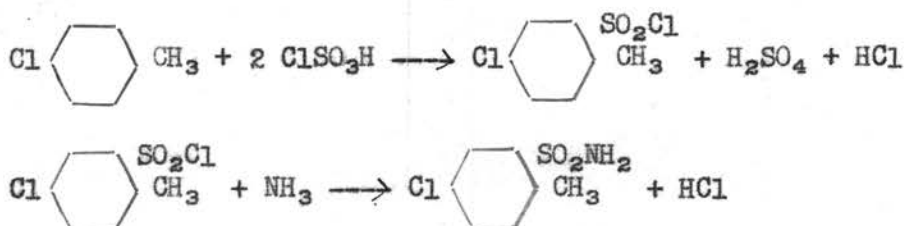


The sulfonamide was made by shaking the sulfonyl chloride with concentrated ammonium hydroxide. The product was recrystallized from ethyl alcohol. M. P. 127°-128°.

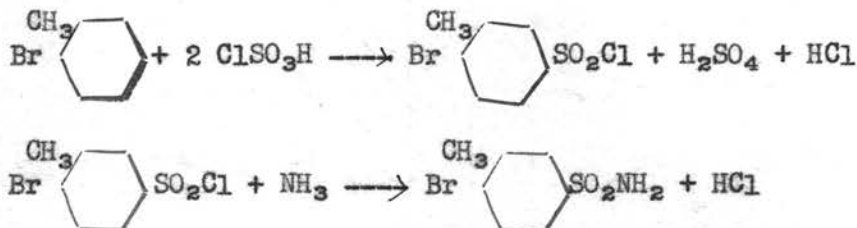


p-Chlorotoluene

20 drops of p-chlorotoluene was added to 5 cc. of chlorosulfonic acid and mixed by shaking for 10 minutes. The mixture was heated to boiling for 10 minutes and poured on chipped ice. The oil obtained could not be successfully purified nor crystallized. The sulfonamide was made in the same manner as 2-chlorotoluene-5-sulfonamide. White crystals were obtained by recrystallizing from ethyl alcohol. M. P. 140°-141°.

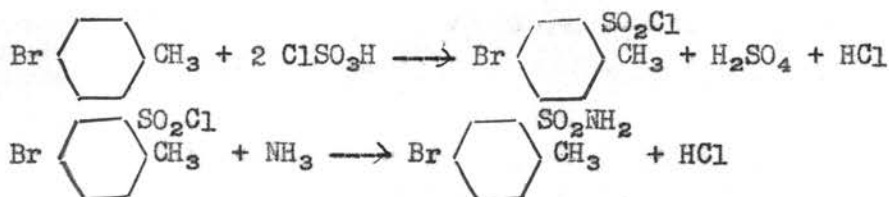
o-Bromotoluene

20 drops of o-bromotoluene was added to 5 cc. of chlorosulfonic acid and mixed with shaking for 10 minutes. The mixture was heated for 10 minutes and poured on chipped ice. The pasty mixture was washed and an unsuccessful attempt was made to purify it. The sulfonamide was made as in the procedure for o-chlorotoluene. The white solid separated out and was recrystallized twice from ethyl alcohol, forming white crystals. M. P. 95°-96°. The reaction may be as follows:

p-Bromotoluene

1 gram of p-bromotoluene was added to 5 cc. of chlorosulfonic acid and mixed with shaking for 10 minutes. The mixture was heated to

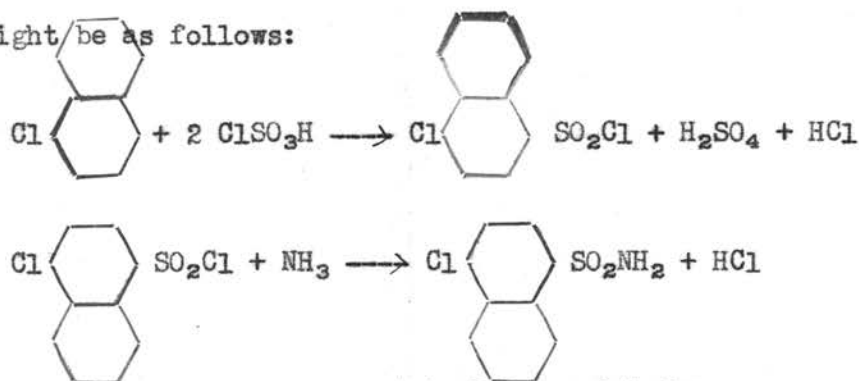
boiling for 10 minutes and poured on chipped ice. A solid could not successfully be obtained. The oil was added to concentrated ammonium hydroxide and the resulting solid was recrystallized twice from ethyl alcohol as needles. M. P.  $164^{\circ}$ - $166^{\circ}$ .



alpha-Chloronaphthalene

20 drops of alpha-chloronaphthalene was added to 10 cc. of chlorosulfonic acid and mixed by shaking for 10 minutes. The mixture was heated to boiling for 10 minutes and poured on crushed ice. The oily mixture would not solidify and was added to concentrated ammonium hydroxide. The resulting sulfonamide formed white crystals by recrystallizing twice from ethyl alcohol. M. P.  $141^{\circ}$ - $143^{\circ}$ . The reaction

might be as follows:



alpha-Bromonaphthalene

20 drops of alpha-bromonaphthalene was added to 10 cc. of chlorosulfonic acid and mixed with shaking for 10 minutes. The mixture was heated to boiling for 10 minutes and poured on crushed ice, giving an oily paste. The sulfonamide was made by shaking with ammonium hydroxide. The resulting solid was recrystallized twice from ethyl alcohol, forming



yellow crystals. M. P.  $149^{\circ}$ - $150^{\circ}$ . The reaction might be as follows:

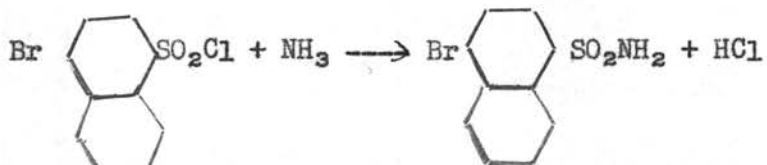
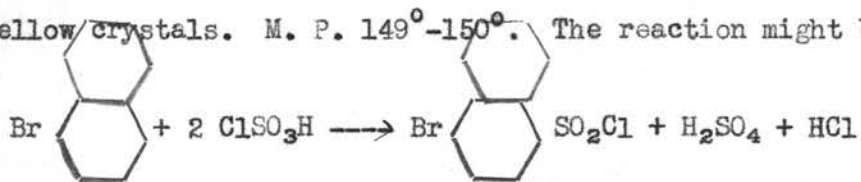


Table I gives a summary of the sulfonyl chloride derivatives, sulfonamides and sulfones found in this study as compared with the literature survey.

TABLE I

Aromatic Halide	Found in Literature		Found by Experiment		
	Sulfonyl Chloride	Sulfonamide	Sulfonyl Chloride	Sulfonamide	Sulfone
Fluorobenzene	36° (40), 36° (41)	123° (40)	30°-32°	None	None
Chlorobenzene	53° (38), 50°-3° (40) 53° (41), 55° (42), 53° (43), 53° (44), 53.3° (45), 50.5°-51.5° (46)	143 (38), 143.5 (40), 142 (42)	52°-53°	None	None
Bromobenzene	75° (38), 75°-6° (40), 75° (41), 75° (42), 75° (44), 75°-6° (47), 75°-6° (48), 75° (49)	160°-1° (38), 160°-1° (40), 161.2° (42), 160°-1° (44)	74°-75°	None	None
Iodobenzene	86°-7° (40), 81°-2° (40), 86°-7° (41), 84° (45), 81.5°-32° (46), 83°-4° (50), 84° (51)	183° (40)	85°-86°	None	None
o-Dichlorobenzene	22.4° (40)	140° (40)	None	139°-140°	None
m-Dichlorobenzene	54.5° (40)	182° (40)	53°-54°	None	None
p-Dichlorobenzene	39° (12), 36°-8° (40)	182°-6° (40)	36°-38°	None	None
1,2,4-Trichloro- benzene	None	None	66°-67°	None	None
1,2,4,5-Tetrachloro- benzene	None	None	None	None	None

TABLE I Continued

Aromatic Halide	Found in Literature		Found by Experiment		
	Sulfonyl Chloride	Sulfonamide	Sulfonyl Chloride	Sulfonamide	Sulfone
p-Dibromobenzene	71°-2° (38), 71° (40)	193° (40), 193° (44)	69°-71°	None	None
p-Diodobenzene	151°-2° (40)		130°-131°	209°-211°	213°-214°
o-Chlorobromobenzene	None	None	None	None	187°-190°
m-Chlorobromobenzene	None	None	57°-58°	None	None
p-Chlorobromobenzene	46° (40)	191° (40)	45°-46°	190°-191°	231°-233°
o-Chloriodobenzene	None	None	None	None	223°-224°
m-Chloriodobenzene	None	None	None	None	220°-221°
p-Chloriodobenzene	69° (40)	None	None	None	225°-226°
o-Fluorochlorobenzene	None	None	None	108°-109°	None
m-Fluorochlorobenzene	None	None	98°-99°	176°-180°	None
p-Fluorochlorobenzene	None	None	None	None	127°-130°
p-Fluorobromobenzene	None	None	59°-60°	142°-144°	None
p-Fluoriodobenzene	None	None	None	None	144°-145°
o-Bromiodobenzene	None	None	86°-88°	157°-158°	None

TABLE I Continued

Aromatic Halide	Found in Literature		Found by Experiment		
	Sulfonyl Chloride	Sulfonamide	Sulfonyl Chloride	Sulfonamide	Sulfone
p-Bromiodobenzene	97° (40)	None	None	None	225°-226°
o-Chlorotoluene	60°-65° (40), 60°-65° (44)	128° (40), 128° (44)	59°-60°	127°-128°	None
p-Chlorotoluene	24° (40), 24° (44)	142° (40), 142° (44)	None	140°-141°	None
o-Bromotoluene	54° (44)	151° (44)	None	95°-96°	None
p-Bromotoluene	35° (40), 35° (44)	166°-7° (40), 165°-6 (44)	None	164°-166°	None
-Chloronaphthalene	95° (40)	187° (40)	None	141°-143°	None
-Bromonaphthalene	86°-7° (40)	190°-5° (40)	None	149°-150°	None

## DISCUSSION OF RESULTS

The table of results shows that the primary object of this research-- to use chlorosulfonic acid for making derivatives of aromatic halides-- has been fairly well attained. The only total failure was with 1,2, 4,5-tetrachlorobenzene, which is so highly substituted that the sulfonyl chloride group could not replace any atom on the ring. More research, however, is necessary to find the conditions for obtaining pure sulfonyl chlorides from halogenated toluenes and naphthalenes. Of the 30 possible dihalogenated benzenes 18 have been studied in the present work; the other 12 are not obtainable commercially and therefore not likely to require identification.

It is pertinent, though not essential, to inquire as to the structure of the derivatives formed. To judge from the results of Crowell and Raiford (39) and Gebauer-Fulnegg and Haemmerle (33), the products of the action of undiluted chlorosulfonic acid on chlorobenzene, bromobenzene, iodobenzene, o-dichlorobenzene, and p-dichlorobenzene (not listed in Table I) might be sulfones. A proof of this was not attempted, since other derivatives of these compounds were obtained satisfactorily.

In the case of most of the iodo-substituted benzene compounds the sulfonyl chloride could not be obtained, but only the sulfone, which was identified by its insolubility in hot alcoholic alkali and its failure to react with concentrated ammonium hydroxide. This proof of the presence of a sulfone is not conclusive, as complete chlorination might also give inert high-melting derivatives, according to Gebauer-Fulnegg and Haemmerle (33). Quantitative analysis of these derivatives for sulfur and molecular weight determinations would probably settle the question. It will also be desirable in the future to find the conditions which will give the

sulfonyl chlorides.

In the case of 1,2,4-trichlorobenzene, the derivative, while not proved to be a sulfonyl chloride, seemed to have the characteristic odor. It will be necessary to verify this supposition.

When dihalogenated benzenes containing different halogens were sulfonated, it was impossible to determine which of the two took precedence in orientation. This will constitute a difficult problem in proof of structure. It has been assumed that only one sulfonyl chloride group is introduced, in the para position if open. It may be possible that disulfonation occasionally takes place, or ortho substitution. It is worth repeating, however, that these unanswered questions do not detract from the value of the results for their original purpose.

## SUMMARY

The action of chlorosulfonic acid on aromatic halides was used to obtain sulfonyl chlorides. Chlorobenzene, bromobenzene, p-dichlorobenzene and p-dibromobenzene were made by the literature method and agreed in melting points with earlier preparations.

The sulfonyl chlorides of fluorobenzene, iodobenzene, m-dichlorobenzene, p-diiodobenzene, p-chlorobromobenzene, and o-chlorotoluene were obtained as above. Their melting points agree with those of the same compounds made by other methods.

1,2,4-trichlorobenzene, m-chlorobromobenzene, m-fluorochlorobenzene, p-fluorobromobenzene and o-bromiodobenzene formed sulfonyl chlorides which have not hitherto been described.

Sulfones were made from p-diiodobenzene, o-chlorobromobenzene, p-chlorobromobenzene, o-chloriodobenzene, m-chloriodobenzene, p-chloroiodobenzene, p-fluorochlorobenzene, p-fluoriodobenzene and p-bromiodobenzene. The sulfones were identified by their insolubility when refluxed with sodium hydroxide and ethyl alcohol.

Sulfonamides were made from the sulfonyl chlorides of o-dichlorobenzene, p-chlorobromobenzene, p-diiodobenzene, o-fluorochlorobenzene, m-fluorochlorobenzene, p-fluorobromobenzene, o-bromiodobenzene, o-chlorotoluene, p-chlorotoluene, o-bromotoluene, p-bromotoluene, alpha-chloronaphthalene, and alpha-bromonaphthalene.

Chlorosulfonic acid is recommended as a reagent for the rapid identification of aromatic halides. The derivatives listed above make it possible to identify 29 such halides.

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