undepressed on admixture with a sample prepared by dehydrohalogenation of 2,2,2-trichloro-1,1-di-(*p*-tolyl)-ethane.[11]

Anal. Calcd. for $C_{16}H_{14}Cl_2$: C, 69.3; H, 5.1; Cl, 25.6. Found: C, 69.4; H, 5.2; Cl, 25.45.

1,2,2,2-Tetrachloro-1,1-di-(*p*-chlorophenyl)-ethane.–Gaseous chlorine was passed through a well-stirred mixture of 1,1-di-(*p*-chlorophenyl)-ethane (20.0 g.) and benzoyl peroxide (0.3 g.) at 120° during a period of 5.5 hr. by which time the take-up of chlorine ceased. Ethanol (125 cc.) was then added to the reaction mixture and on standing 1,2,2,2-tetrachloro-1,1-di-(*p*-chlorophenyl)-ethane (26.5 g., 86.5%) crystallized in colorless rhombohedric prisms, m.p. 91–92°.[19]

Anal. Calcd. for $C_{14}H_8Cl_6$: Cl, 54.76. Found: Cl, 54.05.

Although several attempts were made to stop the reaction at an earlier stage of chlorination, no 1,2,2-trichloro-1,1-di-(*p*-chlorophenyl)-ethane could be isolated.

1,1-Di-(tetrachloro-*p*-tolyl)-ethane (IV).[20]—Chlorine gas was passed through a solution of 1,1-di-(*p*-tolyl)-ethane (50.0 g.) in carbon tetrachloride (100 cc.) containing iron dust (5 g.) and kept at 25° by external cooling, for a period of 5 hr. until 81 g. of chlorine was absorbed. By this time the original thickening of the solution had stopped and the thinning just started. Making allowance for the formation of ferric chloride, about 71 g. of chlorine was absorbed by the diarylethane. The reaction mixture was filtered hot from the inorganic residue, the solvent removed under reduced pressure and the residue extracted with hot benzene leaving behind 1,1-di-(tetrachloro-*p*-tolyl)-ethane (60.3 g., 52%) as colorless prisms, m.p. 231–236°, which after recrystallization from benzene melted at 234–236° (30.9 g., 26.6%).

Anal. Calcd. for $C_{16}H_{10}Cl_8$: C, 39.55; H, 2.05; Cl, 58.4. Found: C, 39.7; H, 2.05; Cl, 58.35.

Steam distillation of the benzene extract yielded pentachlorotoluene (12.5 g.), m.p. 224°.[12]

Anal. Calcd. for $C_7H_3Cl_5$: C, 31.8; H, 1.15; Cl, 67.0. Found: C, 32.2; H, 1.4; Cl, 66.5.

1,1-Di-(trichloro-*p*-tolyl)-ethane (III).[20]—The conditions of the reaction differed from those of the above experiment in that the addition of chlorine was interrupted after 3.5 hr., when only 55 g. was absorbed. Benzene was added to the reaction mixture and the solution so obtained was filtered, washed with water and evaporated to dryness. Crystallization of the residue from petroleum ether (boiling range 65–110°) gave an isomeric mixture of 1,1-di-(trichloro-*p*-tolyl)-ethane (49.3 g., 50%) as colorless rosettes of needles, m.p. 179–189°.

Anal. Calcd. for $C_{16}H_{12}Cl_6$: C, 46.1; H, 2.9; Cl, 51.05. Found: C, 45.6; H, 2.75; Cl, 51.6.

1,2-Dichloro-1,1-di-(tetrachloro-*p*-tolyl)-ethane (V).—Chlorine gas was passed through a solution of 1,2-dichloro-2,2-di-(*p*-tolyl)-ethane (25.0 g.) in carbon tetrachloride (50 cc.) containing iron powder (1 g.) and kept at 25–35° by external cooling. After 14 hr. of addition, when 26 g. of chlorine was absorbed (*i.e.*, 24 g. absorbed by the diarylethene) the weight of the mixture remained constant. The solvent was removed under pressure and the residue redissolved in 600 cc. of hot benzene. This solution was washed 3 times with water in order to remove ferric chloride and then concentrated and cooled yielding 1,2-dichloro-1,1-di-(tetrachloro-*p*-tolyl)-ethane (32.4 g., 65%), m.p. 223–225°, which crystallized from benzene in colorless prisms, m.p. 226–227° (21.6 g., 43.3%).

Anal. Calcd. for $C_{16}H_8Cl_{10}$: C, 34.65; H, 1.45; Cl, 63.9. Found: C, 35.0; H, 1.25; Cl, 63.75.

VILLE LASALLE, QUEBEC, CANADA

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(19) O. Grummitt, A. Buck and A. Jenkins, THIS JOURNAL, **67**, 155 (1945), also give 91–92°.

(20) With the collaboration of Mr. M. A. Davis.

[CONTRIBUTION FROM THE ILLINOIS STATE GEOLOGICAL SURVEY]

Aromatic Fluorine Compounds. VI. Displacement of Aryl Fluorine in Diazonium Salts[1,2]

BY G. C. FINGER AND R. E. OESTERLING

RECEIVED DECEMBER 14, 1955

Several chlorofluorobenzenes have been isolated from the Schiemann synthesis of fluorobenzenes. These have been shown to be the products of two side reactions occurring during thermal decomposition of the dry benzenediazonium fluoborate salt containing coprecipitated sodium chloride, an unavoidable contaminant in large preparations involving the use of hydrochloric acid and sodium fluoborate. The major side reaction and its chloro product were unexpected; a unique displacement of fluorine *ortho* to the diazonium group was observed. Replacement of the diazo group with chlorine was the predicted side reaction which proved to be minor. Conditions causing the side reactions and the isolation and identification of the products are described.

Discussion

Diazotization for the Schiemann synthesis is usually effected in hydrochloric acid, and sodium fluoborate is the most convenient source of the fluoborate ion. If the precipitated diazonium fluoborate is dried as such, it contains varying amounts of coprecipitated sodium chloride, which may affect the final thermal decomposition reaction. Recrystallization of the benzenediazonium fluoborate is impractical for large-scale syntheses, and organic solvents are ineffective in removing sodium chloride. As a result, appreciable amounts of chlorobenzenes[3] may be formed in the preparation of some fluorobenzenes. The chloro mixtures from three such preparations have been isolated and identified.

A 10% yield of 2,5-difluorochlorobenzene (IV) and 1% of 2,4-difluorochlorobenzene (V) in the synthesis of 1,2,4-trifluorobenzene (II)[4] from 2,4-difluoroaniline was the first observed instance of the formation of two chloro isomers. The identical isomers were also obtained from 2,5-difluoroaniline with 2,4-difluorochlorobenzene as the major component. 2,4,6-Trifluorochlorobenzene with a trace of 2,3,5-trifluorochlorobenzene was obtained in the synthesis of 1,2,3,5-tetrafluorobenzene[5] from 2,3,5-trifluoroaniline. These compounds gave evidence

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(1) Presented in part before the XIVth International Congress of Pure and Applied Chemistry, Zurich, July 27, 1955.

(2) Published with the permission of the Chief of the Illinois State Geological Survey.

(3) G. C. Finger, F. H. Reed, D. M. Burness, D. M. Fort and R. R. Blough, THIS JOURNAL, **73**, 145 (1951). The assistance of Messrs. R. H. White and R. H. Shiley in providing residues from large scale Schiemann syntheses is kindly acknowledged.

(4) G. Schiemann, *J. prakt. Chem.*, **140**, 97 (1934).

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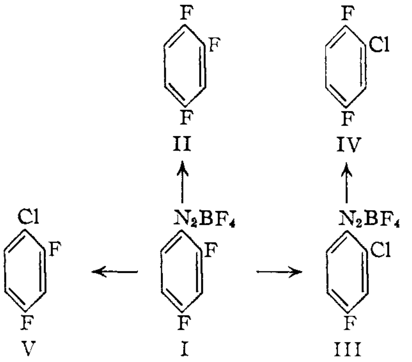

of two independent reactions forming monochloro isomers: (1) displacement of a fluorine *ortho* to the diazonium group with chlorine, and (2) replacement of the diazonium group with chlorine. The second reaction, a Griess[6] type, is more or less expected; however, the very small yield of chloro compounds produced by this reaction shifted attention to the importance of the first reaction. In other words, the predominating reaction is an aromatic nucleophilic substitution[7] of a fluorine atom strongly activated by an *ortho* diazonium[8] group.

The question arises as to whether the displacement reaction occurs in solution during the diazotization process or during thermal decomposition in the presence of sodium chloride. It was established that displacement occurs during thermal decomposition of the dry diazonium fluoborate salt and that the amount of sodium chloride present determines the yield of chloro product. A series of thermal decompositions of pure, recrystallized 2,4-difluorobenzenediazonium fluoborate (I) mixed with increasing amounts of sodium chloride gave increasing yields of difluorochlorobenzene and decreasing yields of trifluorobenzene. With a large excess of sodium chloride, the difluorochloro and trifluoro compounds were obtained in 30 and 10% yields, respectively.

The displacement reaction was found not to occur during the diazotization process in hydrochloric acid. Solutions of either the diazonium chloride or the diazonium fluoborate in hydrochloric acid heated at 60° for one hour did not result in displacement of the *o*-fluorine by chlorine.

To demonstrate that the displacement reaction is independent of the thermal decomposition reaction, recrystallized 2,4-difluorobenzenediazonium fluoborate (I) was converted to 2-chloro-4-fluorobenzenediazonium fluoborate (III) by mixing the former with dry lithium chloride and heating carefully for a short period above the melting point but below the decomposition point. In this instance, the differential between the two points is about 35°. The melt was chilled rapidly to a solid and recrystallized from water to give the pure displacement product with only slight loss due to decomposition of the diazonium group.

An experiment with 2-fluorobenzenediazonium fluoborate, where the melting and decomposition points are almost identical, gave a considerable yield of 2-chlorofluorobenzene. Here also, *o*-fluorine displacement must be of major significance rather than diazonium displacement with chlorine, which in this case also produces the same chloro compound.

Examination of residues from many large-scale Schiemann syntheses of fluorobenzene, 1,3-difluorobenzene, 1,3,5-trifluorobenzene, and 1,4-difluorobenzene usually gave a chloro by-product yield of 2% or less. From this it can be inferred that chloro compound formation does not result from *m*- or *p*-fluorine displacement. It is interesting to point out that heating a mixture of 4-fluorobenzenediazonium fluoborate with lithium chloride does not cause *p*-fluorine displacement. In regard to the formation of dichloro compounds, none were detected in any preparations.

The foregoing mechanism of isomeric chloro formation adequately explains the chloro products from 2,5-difluoroaniline and 2,3,5-trifluoroaniline; no detailed study was made of the latter except to establish the predominance of the chloro isomers from the displacement reaction. The major components were identified by comparison of derivatives with compounds of known structure; in addition, both the major and minor components were identified and estimated by infrared spectra and nuclear magnetic resonance (NMR)[9] absorption lines. Gutowsky and co-workers[10] prepared and interpreted the NMR spectra of the fluorine compounds and mixtures.

The effect of other alkali metal salts on the thermal decomposition of 2,4-difluorobenzenediazonium fluoborate was investigated. Lithium chloride appears to lower appreciably the melting point of this diazonium fluoborate, thus favoring completion of the displacement reaction before decomposition. A 2:1 mole ratio of lithium chloride to diazonium fluoborate gave a 37% yield of the chloro fraction. By NMR analysis the *chloro* mixture contained approximately 95% 2,5-difluorochlorobenzene (IV) with less than 5% 2,4-difluorochlorobenzene (V). This suggests a possible use of the displacement reaction in special preparative problems and identification studies. In contrast, heating the diazonium fluoborate with potassium chloride or sodium cyanide caused vigorous decomposition to tar and coke. From this it can be inferred that reagents providing alkaline media reduce the stability of the diazonium group and catalyze the decomposition to coupled products or tars of undetermined structure. Sodium bromide gave a low yield of 2,4-difluorobromobenzene, with no evidence of fluorine displacement by bromine. The amine hydrochloride, a possible contaminant in diazotization reactions, also causes difficulty in the thermal decomposition. Heating a mixture of one part of initial amine hydrochloride with 10 parts of recrystallized diazonium fluoborate gave very little evidence of chloro formation, and the yield of 1,2,4-trifluorobenzene was reduced to less than 10%.

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(7) J. F. Bunnett and R. E. Zahler, *Chem. Revs.*, **49**, 277 (1951).

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(10) H. S. Gutowsky, C. H. Holm and S. Fujiwara, Department of Chemistry, University of Illinois.

Experimental[11–13]

Chlorobenzenes from Schiemann Synthesis of 1,2,4-Trifluorobenzene[4] **(II).**—A mixture of 5160 g. of 2,4-difluoroaniline[4] in 16 l. of commercial hydrochloric acid (18° Be) was diazotized at 0° with 2900 g. of sodium nitrite in 4.3 l. of water. A solution of 7700 g. of sodium fluoborate in 9 l. of water was added at 0° and stirring was continued for 20 minutes. The precipitated diazonium fluoborate was removed on a vacuum filter, pressed dry, granulated, and dried overnight. The crude salt, 8900 g. of 2,4-difluorobenzenediazonium fluoborate (I), was thermally decomposed in 500-g. portions in 5-l. round-bottomed flasks connected to the usual efficient condensing system.[14] The crude steam distilled product upon fractionation gave 2900 g., or 55% yield of 1,2,4-trifluorobenzene (II), b.p. 89–91°. The distillation residue of 530 g., after the usual washing with cold concd. sulfuric acid, water and 10% sodium carbonate solution, upon further distillation gave 470 g. or 8% yield of a difluorochlorobenzene mixture, b.p. 126–127°. The chloro by-products from 2,5-difluorobenzenediazonium fluoborate[4] and 2,3,5-trifluorobenzenediazonium fluoborate[5] decompositions were isolated by similar procedures in 8–10% yields, b.p.'s 126–127° and 120–122°, respectively. No fractions could be obtained boiling in the range of 130–200° indicating the absence of dichlorofluorobenzene isomers.

2,4-Difluorochlorobenzene (V).—A mixture of 387 g. of 2,4-difluoroaniline[4] and 750 cc. of concd. hydrochloric acid was heated at 60° with stirring for two hours. Diazotization was effected at 0° with 214 g. of sodium nitrite as a 40% solution. The diazonium chloride solution was added to a stirred mixture of 400 g. of cuprous chloride in 800 cc. of concd. hydrochloric acid at 0°. After complete evolution of nitrogen and steam distillation, the crude oily product was rectified to give 308 g. or 69% yield of pure 2,4-difluorochlorobenzene as a colorless liquid, f.p. −26°, b.p. 127°, $n^{20}{}_D$ 1.4751, $d^{20}{}_4$ 1.353.

Anal. Calcd. for $C_6H_3ClF_2$: C, 48.51; H, 2.03; F, 25.58. Found: C, 48.76; H, 1.98; F, 25.72.

Highly purified samples of 2,4-difluorochlorobenzene and 2,5-difluorochlorobenzene[3] were prepared as reference standards for infrared and NMR spectra.

The infrared spectrum of the chloro product from 2,4-difluorobenzenediazonium fluoborate indicated 2,5-difluorochlorobenzene as the major component and 2,4-difluorochlorobenzene as the minor. The NMR spectrum was obtained with the apparatus[15] and technique described by Gutowsky.[16] The NMR results confirmed the interpretation of the infrared spectrum and showed a ratio of 90:10, ±5, between the two isomers.

2,5-Difluoro-4-nitroaniline.—To 116 g. of 2,5-difluoroacetanilide[17] dissolved in 500 cc. of concd. sulfuric acid and 50 cc. of glacial acetic acid, a mixture of 57.5 cc. of concd. nitric and 75 cc. of concd. sulfuric acids was added slowly at 0°. Stirring was continued for 30 minutes and the mixture poured over ice. A yield of 150 g. of crude precipitated product was obtained. Recrystallization from ethanol gave the pure nitroacetanilide as pale yellow needles, m.p. 189–190°.

Anal. Calcd. for $C_8H_6F_2N_2O_3$: N, 12.96. Found: N, 12.77.

Hydrolysis was effected by heating the nitroacetanilide in concd. sulfuric acid, and then pouring over ice. The precipitate was recrystallized from ethanol to give pure 2,5-difluoro-4-nitroaniline as yellow needles, m.p. 153–154°.

Anal. Calcd. for $C_6H_4F_2N_2O_2$: C, 41.40; H, 2.32; N, 16.10. Found: C, 41.63; H, 21.4; N, 16.31.

2,5-Difluoro-4-chloronitrobenzene.—A diazotization was performed at 0° with 108 g. of 2,5-difluoro-4-nitroaniline in 850 cc. of concd. hydrochloric acid and 65 g. of sodium nitrite as a 40% solution. After addition of the diazonium solution to 85 g. of cuprous chloride in 350 cc. of concd. hydrochloric acid in the usual manner, steam distillation gave 102 g. of pale yellow oil. Vacuum distillation gave pure 2,5-difluoro-4-chloronitrobenzene, f.p. 28°, b.p. 116° (20 mm.).

Anal. Calcd. for $C_6H_2ClF_2NO_2$: C, 37.24; H, 1.04; N, 7.24; Cl, 18.32. Found: C, 37.21; H, 1.07; N, 6.98; Cl, 18.09.

2,5-Difluoro-4-chloroaniline.—An iron reduction of 2,5-difluoro-4-chloronitrobenzene formed the amine as a white solid, volatile with steam. Vacuum sublimation gave pure 2,5-difluoro-4-chloroaniline as white needles, m.p. 79–80°.

Anal. Calcd. for $C_6H_4ClF_2N$: C, 44.05; H, 2.47; N, 8.57. Found: C, 44.27; H. 2.61; N, 8.58.

The acetyl derivative was prepared in the usual manner and recrystallized from ethanol to give white needles, m.p. 156–157°.

Anal. Calcd. for $C_8H_6ClF_2NO$: N, 6.81. Found: N, 6.59.

A nitration and reduction sequence on the major chloro by-product from the 2,4-difluorobenzenediazonium fluoborate decomposition gave the same amine and acetyl derivative as above. This gave chemical proof that 2,5-difluorochlorobenzene was formed in the decomposition.

2,4-Difluoro-5-chloronitrobenzene.—A mixed acid (nitric and sulfuric) nitration of 2,4-difluorochlorobenzene (V) at 40–50° for one hour readily gave the nitro compound as a steam volatile yellow oil. Vacuum distillation gave 86% yield of pure 2,4-difluoro-5-chloronitrobenzene, f.p. 5.5°, b.p. 105° (15 mm.), $n^{20}{}_D$ 1.5337.

Anal. Calcd. for $C_6H_2ClF_2NO_2$: C, 37.24; H, 1.04; N, 7.24. Found: C, 37.21; H, 0.98; N, 7.16.

2,4-Difluoro-5-chloroaniline.—An iron reduction of 2,4-difluoro-5-chloronitrobenzene and steam distillation gave 95% yield of the white solid amine; white plates were obtained from low boiling petroleum ether; m.p. 50–51°.

Anal. Calcd. for $C_6H_4ClF_2N$: C, 44.05; H, 2.47; N, 8.57. Found: C, 43.95; H, 2.54; N, 8.67.

The acetyl derivative, prepared in the usual manner, was recrystallized from ethanol to white needles, m.p. 141–142°.

Anal. Calcd. for $C_8H_8ClF_2NO$: N, 6.81. Found: N, 6.73.

Chemical evidence of the formation of 2,4-difluorochlorobenzene in the decomposition of 2,5-difluorobenzenediazonium fluoborate involved nitration and reduction of the chloro by-product mixture. Sufficient pure amine was isolated to prove its identity with the above authentic sample. Also the infrared spectrum indicated the 2,4-difluorochlorobenzene as the major component and 2,5-difluorochlorobenzene as the minor in the chloro mixture. The NMR spectrum analysis revealed the ratio of these isomers to be 3:1.

2,3,5-Trifluorochlorobenzene.—A mixture of 14.7 g. of 2,3,5-trifluoroaniline[5] in 100 cc. of 1:1 sulfuric acid was diazotized at 0° with 11 g. of sodium nitrite as a 40% solution. The diazonium solution was added to a mixture of 15 g. of cuprous chloride in 100 cc. of concd. hydrochloric acid at 0°. Steam distillation removed the chloro compound. Rectification gave 11 g. or 66% yield of pure 2,3,5-trifluorochlorobenzene as a colorless liquid, f.p. −45°, b.p. 123°, $n^{20}{}_D$ 1.4553.

Anal. Calcd. for $C_6H_2ClF_3$: C, 43.27; H, 1.21; Cl, 21.29; F, 34.23. Found: C, 43.13; H, 1.31; Cl, 21.15; F, 34.33.

Carefully distilled samples of 2,3,5-trifluorochlorobenzene and 2,4,6-trifluorochlorobenzene[18] were prepared as reference standards for infrared and NMR analyses.

The infrared spectrum of the chloro product from the decomposition of 2,3,5-trifluorobenzenediazonium fluoborate showed 2,4,6-trifluorochlorobenzene as the major component with a trace of 2,3,5-trifluorochlorobenzene present. The NMR analysis indicated only the first isomer: the concentration of the second was apparently below the detectable limit.

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[11] The authors are indebted to Mr. D. R. Dickerson, microanalyst of the Survey, for the analyses and infrared spectra given in this investigation.

[12] All melting points and boiling points are uncorrected; freezing points were determined with a toluene thermometer.

[13] Messrs. R. R. Blough and J. L. Finnerty prepared many of the reference compounds and intermediates.

[14] G. C. Finger and F. H. Reed, This Journal, **66**, 1972 (1944).

[15] H. S. Gutowsky, L. H. Meyer and R. E. McClure, *Rev. Sci. Instr.*, **24**, 644 (1953).

[16] "Physical Methods in Chemical Analysis," Vol. III, Chapter by H. S. Gutowsky, "Analytical Methods of Nuclear Magnetic Resonance," Academic Press, Inc., New York, in preparation.

[17] F. Swarts, *Bull. classe sci. Acad. roy. Belg.*, 241 (1913).

[18] G. C. Finger, F. H. Reed and J. L. Finnerty, This Journal, **73**, 154 (1951).

2,4,6-Trifluoro-3-chloroaniline.—A 2.5-g. sample of the nitro derivative of 2,4,6-trifluorochlorobenzene[18] was reduced to the amine with stannous chloride in concd. hydrochloric acid at 50° for one hour. Addition of excess 10% sodium hydroxide and steam distillation gave 1.7 g. or 78% yield of the white solid amine; colorless needles were obtained from low boiling petroleum ether; m.p. 41–42°.

Anal. Calcd. for $C_6H_3ClF_3N$: C, 39.69; H, 1.66; N, 7.71. Found: C, 39.90; H, 1.68; N, 7.73.

The acetyl derivative prepared in the usual manner and recrystallized from benzene gave colorless needles, m.p. 184–185°.

Anal. Calcd. for $C_8H_5ClF_3NO$: N, 6.26. Found: N. 6.50.

The same amine was obtained by nitration and reduction of the chloro by-product from 2,3,5-trifluorobenzenediazonium fluoborate decomposition. This identified 2,4,6-trifluorochlorobenzene as the major component in the Schiemann transformation.

2-Chloro-4-fluorobenzenediazonium Fluoborate (III).—Diazotization of 4 g. of 2-chloro-4-fluoroaniline[19] in 30 cc. of concd. hydrochloric acid at 0° with 2.8 g. of sodium nitrite as a 40% solution and precipitation of the diazonium salt with 6.6 g. of sodium fluoborate in 8 cc. of water gave 4.5 g. of pale yellow salt. Two recrystallizations from warm water (40°) gave pure 2-chloro-4-fluorobenzenediazonium fluoborate as near white needles, m.p. 141–143°, dec. pt. 176°. This pure salt and its β-naphthol derivative prepared by an alkaline coupling with β-naphthol served as reference compounds. The α-(2-chloro-4-fluorobenzeneazo)-β-naphthol gave red-orange plates from glacial acetic acid; m.p. 164–165°.

Anal. Calcd. for $C_{16}H_{10}ClFN_2O$: C, 63.90; H, 3.35; Cl, 11.79; N, 9.39. Found: C, 64.05; H, 3.40; Cl, 11.53; N, 9.24.

Reactions with Lithium Chloride. A. Displacement without Decomposition.—A mixture of 11.4 g. of recrystallized 2,4-difluorobenzenediazonium fluoborate (I), m.p. 149–150°, dec. pt. 185°, and 4.2 g. of lithium chloride was pulverized in a mortar, place in a large test-tube containing a thermometer and heated slowly to 120° with stirring for a few minutes. A yellow melt formed and the heating bath was removed. A mild exothermic reaction caused the temperature to rise to 130°. Slight evolution of nitrogen occurred and the reaction was arrested immediately by cooling in an ice-bath. The melt solidified and was dissolved in 40 cc. of warm water, filtered and cooled slowly to 0° to give 7 g. of pale yellow needles. Recrystallization from water gave near white needles, m.p. 140–142°. This compound gave no melting point depression when mixed with the authentic sample of 2-chloro-4-fluorobenzenediazonium fluoborate (III). Likewise, its β-naphthol derivative gave no melting point depression when mixed with the authentic α-(2-chloro-4-fluorobenzeneazo)-β-naphthol.

B. Displacement and Decomposition.—A pulverized mixture of 25 g. of recrystallized 2,4-difluorobenzenediazonium fluoborate and 9.3 g. of dry lithium chloride was heated above the decomposition point of the diazonium fluoborate. Isolated from the volatile product was 0.3 g. of 1,2,4-trifluorobenzene and 6.2 g. or 37% yield of monochlorobenzenes. The NMR analysis of the chloro fraction indicated a mixture of approximately 95% 2,5-difluorochlorobenzene and 5% 2,4-difluorochlorobenzene.

A similar reaction of a mixture of 10.5 g. of recrystallized 2-fluorobenzenediazonium fluoborate, dec. pt. 159–165° with simultaneous melting at 159–161° and 4.2 g. of lithium chloride yielded 1.2 g. (21%) of 1,2-difluorobenzene, and 1.3 g. (20%) of 2-chlorofluorobenzene.

C. No Displacement of *p*-Fluorine.—An attempted displacement reaction of a pulverized mixture of 5 g. of 4-fluorobenzenediazonium fluoborate and 5 g. of lithium chloride heated to 130° failed to give the 4-chloro product. Recrystallization from water gave only the original diazonium fluoborate.

Thermal Decomposition with Sodium Chloride.—A mixture of 100 g. of 2,4-difluorobenzenediazonium fluoborate and an equal molar ratio, 25.5 g., of sodium chloride was pulverized in a mortar, thermally decomposed, and the products collected in the usual manner. Distillation of the crude product gave 18 g. of 1,2,4-trifluorobenzene, b.p. 89–90°, and 15 g. of difluorochlorobenzene, b.p. 126–127°. With a sodium chloride–fluoborate salt mole ratio of 2:1, the yield was 14 g. of trifluorobenzene and 15 g. of the chloro compound; and with a 6:1 ratio the yield was 5.7 g. of trifluorobenzene and 9.5 g. (30% yield) of the chloro product.

Thermal Decomposition with Sodium Bromide.—Thermal decomposition of a mixture of 100 g. of 2,4-difluorobenzenediazonium fluoborate and 155 g. of dry sodium bromide gave a steam volatile oil. An ordinary distillation, gave 9.3 g. of a bromo compound as a colorless liquid, b.p. −8°, m.p. 146°, n^{20}D 1.5058. This was identified as 2,4-difluorobromobenzene, whereas 2,5-difluorobromobenzene,[3] f.p. −31.5°, n^{20}D 1.5086, was expected. In other words, *o*-fluorine displacement was not evident with sodium bromide.

2,4-Difluorobromobenzene.—Diazotization and a Sandmeyer reaction of 65 g. of 2,4-difluoroaniline[4] in dilute sulfuric acid at 0° with 36 g. of sodium nitrite as a 40% solution, added to 107 g. of cuprous bromide in 300 cc. of 48% hydrobromic acid gave 67 g. or 70% yield of distilled 2,4-difluorobromobenzene as a colorless liquid, f.p. −4°, b.p. 147°, n^{20}D 1.5059.

Anal. Calcd. for $C_6H_3BrF_2$: C, 37.34; H, 1.56; Br, 41.41; F, 19.69. Found: C. 37.41; H, 1.71; Br, 41.25; F, 19.63.

2,4-Difluoro-5-bromonitrobenzene.—Nitration of 38.4 g. of 2,4-difluorobromobenzene was effected in 80 cc. of concd. sulfuric acid at 30° with 13.9 cc. of concd. nitric acid. After steam distillation and vacuum distillation 42 g. or an 88% yield of the nitro compound was obtained as a yellow oil, f.p. 19°, b.p. 97° (5 mm.). n^{20}D 1.5590.

Anal. Calcd. for $C_6H_2BrF_2NO_2$: C, 30.28; H, 0.85; Br, 33.58; N, 5.89. Found: C, 30.33; H, 0.81; Br, 33.41; N, 6.07.

2,4-Difluoro-5-bromoaniline.—After reduction of 5 g. of 2,4-difluoro-5-bromonitrobenzene with 15.8 g. of stannous chloride dihydrate in 40 cc. of concd. hydrochloric acid at 50° and subsequent addition of excess 10% sodium hydroxide solution, steam distillation gave 3 g. or 68% yield of white, low melting solid. Recrystallization from low boiling petroleum ether gave colorless needles, m.p. 25–26°.

Anal. Calcd. for $C_6H_4BrF_2N$: C, 34.64; H, 1.94; Br, 38.42; N, 6.73. Found: C, 34.51; H, 2.02; Br, 38.32; N, 6.93.

The acetyl derivative prepared in the usual manner and recrystallized from ethanol gave colorless plates, m.p. 140–141°.

Anal. Calcd. for $C_8H_6BrF_2NO$: N, 5.60. Found: N, 5.52.

As confirmed by mixed melting point, the same amine was synthesized from the bromo compound generated in the 2,4-difluorobenzenediazonium fluoborate decomposition with sodium bromide. Therefore, 2,4-difluorobromobenzene formation takes precedence over *o*-fluorine displacement with sodium bromide.

Thermal Decompositions with Aniline Hydrochloride, Sodium Cyanide and Potassium Chloride.—Thermal decomposition of a mixture of 70 g. of 2,4-difluorobenzenediazonium fluoborate and 7 g. of 2,4-difluoroaniline hydrochloride gave essentially a tar and coke residue and only 3.3 g. or 8% yield of volatile product, 1,2,4-trifluorobenzene, with no isolable amounts of chloro products. Mixtures of 2,4-difluorobenzenediazonium fluoborate with sodium cyanide or with potassium chloride decomposed rapidly at abnormally low temperatures and gave no isolable volatile products.

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(19) G. C. Finger and R. H. Shiley, unpublished results.