remain at room temperature overnight, then opened and the volatile material removed. The remaining product was a pale yellow solid that was recrystallized from ether-petroleum ether to yield 6.3 g. of heptafluorothiobutyramide, $C_3F_7C(S)NH_2$, m.p. 49° (Table I).

Pentafluorothiopropionamide was prepared in the same manner from pentafluoropropionitrile and hydrogen sulfide at room temperature. For preparation of trifluorothioacetamide the reaction was moderated by cooling to 0° to prevent charring. This reaction could also be moderated by the use of ethyl ether as a solvent but reaction time was increased to 125 hours.

Heptafluorothiobutyramide.—B. From Heptafluorobutyramidine.—In a flask fitted with a delivery tube and protected by drying tubes was placed 15 g. (0.071 mole) of heptafluorobutyramidine dissolved in 25 ml. of ethyl ether. The solution was saturated with hydrogen sulfide and allowed to stand one hour. The ether was removed under reduced pressure and the remaining high boiling liquid fractionated under reduced pressure to yield 12 g. of a distillate that crystallized on cooling. Recrystallization from ether-petroleum ether gave heptafluorothiobutyramide, $C_3F_7C(S)NH_2$, yellow needles, m.p. 47–48°.

GAINESVILLE, FLORIDA

[CONTRIBUTION FROM THE ILLINOIS STATE GEOLOGICAL SURVEY]

Aromatic Fluorine Compounds. VII. Replacement of Aromatic –Cl and –NO_2 Groups by –F[1,2]

BY G. C. FINGER AND C. W. KRUSE

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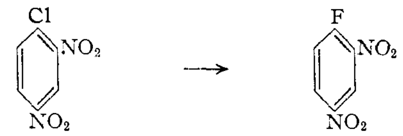
Replacement of –Cl by –F in aryl chlorides with potassium fluoride has been extended from 2,4-dinitrochlorobenzene to less activated halides by the use of non-aqueous solvents, especially dimethylformamide (DMF) and dimethyl sulfoxide (DMSO). Also replacement of –NO_2 by –F in substituted nitrobenzenes was studied in DMF. As a direct result of this study, many aromatic fluorine compounds can now be obtained by a relatively simple synthetic route.

Unactivated aryl halides do not undergo Swarts-type organic halide–inorganic fluoride exchange reactions which are common with aliphatic and acyl halides.[3,4] Activation by at least two nitro groups has generally been considered necessary for exchange between aryl halides and fluoride ion.[5a] An outstanding example of such an exchange is the replacement of chlorine by fluorine in 2,4-dinitrochlorobenzene with anhydrous potassium fluoride at 190–205° in nitrobenzene solvent.[6,7]



A preliminary experiment has shown that even without a solvent the above reaction takes place at 200–230°. However, solvent studies with other non-aqueous solvents show a significant increase in reaction rate. The preceding reaction proceeds quite smoothly at steam-bath temperature in dimethylformamide (DMF) or dimethyl sulfoxide (DMSO). The accelerating effect of various solvents upon aryl halide–fluoride ion exchanges is emphasized by Table I. The decreasing reaction rates, as reflected by the longer time and higher temperatures, parallel the decreased activation from 2,4-dinitrochlorobenzene to 4-nitrochlorobenzene. Thus, aromatic halogen exchange reactions have been extended from the highly activated dinitrohalobenzenes to the moderately activated mononitrohalobenzenes by the solvent studies.

TABLE I

REPLACEMENT OF AROMATIC –Cl BY –F

Reactant[a] (subst. $C_6H_5NO_2$)	Solvent	Time, hr.	Temp., °C.	Yield, % of fluoro analog	Expt. ref.
3-NO_2-**4**-Cl-	$C_6H_5NO_2$	4	195–210	76	I-1
	No solvent	0.5	200–230	62[b]	I-2
	C_6H_5CN	2	150–170	57[b]	I-3
	$(CH_2CN)_2$	0.5	125–140	81[b]	I-4
	DMF	0.5	140–150	77	I-5
	DMF	13	95–100	77	I-6
	DMSO	2.5	95–100	78	I-7
3-CF_3-**4**-Cl–	DMF	4	160	81	II
2-Cl-5-CF_3–	DMF	3.5	160	76	III
2-Cl-5-CH_3OCO–	DMF	4	155	67	IV
2,4,6-Cl_3–	DMSO	2	175–180	10	V
2,5-F_2-**4**-Cl–	DMSO	2	170–175	45	VI
2,3,**4**-Cl_3–	DMSO	4	180–190	23	VII
2,4-Cl_2–	DMSO	6	180	47	VIII
2-Cl–	DMF	163	170	40[c]	IX-1
	DMSO	4.5	185	38	IX-2
4-Cl–	DMSO	14	190	72	X

[a] Group replaced is set in bold type. [b] Contaminated with chloro isomer. Vacuum fractionation was ineffective for the separation of these isomers, therefore yields were estimated by index of refraction which was found to have a near linear relationship for mixtures of 2,4-dinitrochloro- and 2,4-dinitrofluorobenzenes. Values determined from known mixtures for weight-per cent. of chloro isomer *vs.* $n^{20}D$ were 80.4%-1.5952, 54.9%-1.5866 and 23.12%-1.5764. [c] Estimated.

Brown fumes and traces of lower boiling products observed in the 2,4-dinitrohalobenzene studies suggested the possibility of some –NO_2 replacement. Earlier investigators[6,7] make no mention of such observations. Such a reaction appeared reasonable as properly activated nitro groups can be replaced by other nucleophilic reagents, as, for example, the replacement of –NO_2 by –OCH_3 in 2,3,5,6-tetrachloronitrobenzene.[8] Conclusive evi-

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

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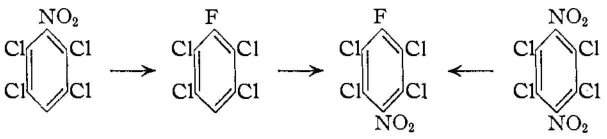

XI XV

dence of $-NO_2$ replacement by –F was first obtained when the above tetrachloronitrobenzene gave a 10% yield of 2,3,5,6-tetrachlorofluorobenzene (XI). Returning to the original reaction, 2,4-dinitrochlorobenzene was found to give 4-nitro-1,2-difluorobenzene under more vigorous conditions. Table II lists other examples of this type of $-NO_2$ replacement.

Halogen substituents are known to activate the aromatic nucleus toward nucleophilic displacement reactions.[5b] Displacements by fluoride ion are similarly effected, and this is demonstrated on a qualitative basis as follows. *Ortho* activation by fluorine makes possible the displacement of $-NO_2$ from 2,4-dinitrofluorobenzene in contrast to 1,3-dinitrobenzene which remains unchanged. The greater ease of –Cl replacement in 2,4-dichloronitrobenzene *versus* 2-chloronitrobenzene is evidence of *meta* activation by chlorine. A similar *meta* activation by bromine is probably responsible for the $-NO_2$ group displacement in 4-bromo-1,2-dinitrobenzene, since 1,2-dinitrobenzene is unreactive under the same conditions. It is interesting to note that in 2,3,5,6-tetrachloro-1,4-dinitrobenzene only one $-NO_2$ is replaced readily by –F, thus indicating that a *para* fluorine may retard the second $-NO_2$ replacement.

The reactivity of the other alkali metal fluorides was examined briefly. Sodium fluoride does not react with 2,4-dinitrochlorobenzene in nitrobenzene,[7] but 2,4,6-trinitrochlorobenzene in acetic acid forms picryl fluoride.[9] Further qualitative experiments with 2,4-dinitrochlorobenzene have been made. In DMF, lithium and sodium fluorides show no appreciable reaction under conditions for which potassium, rubidium and cesium fluorides are effective. In nitrobenzene, a NaF–KCl mixture gave no discernible reaction, whereas NaF–KF mixtures proceeded to the extent of the KF present. As contrasted to the displacement of aryl fluorine in diazonium salts[10] with lithium and sodium chlorides reported recently, these chlorides gave no reaction with 2,4-dinitrofluorobenzene in nitrobenzene.

The following observations are considered of value in future investigations. Hydroxylic compounds such as glycols cannot be used in the preparation of 2,4-dinitrofluorobenzene since potassium fluoride catalyzes the formation of aryl 2,4-dinitrophenyl ethers as does triethylamine.[11] Moisture lowers the yields by formation of potassium phenoxides which are explosive. These, however, usually undergo further reaction and are undoubtedly responsible for the formation of the substituted diphenyl ether by-products isolated. Decomposition products of the solvent may also react with the activated aryl halides; some $-SCH_3$ substituted products have been isolated from reactions in DMSO. In general, the reaction mixtures become quite viscous or gel-like either with or without a solvent. Frequently, the aryl fluorides are obtained chlorine free upon washing the crude reaction mixture with water.

Although this discussion has been confined to nitro activated aryl chlorides, further studies are underway which demonstrate that other activated aryl halides may be used.

TABLE II

REPLACEMENT OF AROMATIC $-NO_2$ BY $-F$[a]

Reactant (subst. C_6H_6)[b]	Time, hr.	Temp., °C.	Yield of fluoro analog, %	Expt. ref.
A. Mononitro				
2,3,5,6-Cl_4-**1**-NO_2–	4.5	147	37	XI
2,3,4,5,6-Cl_5-**1**-NO_2–	4	150	10	XII
B. Dinitro				
4-F-1,**3**-$(NO_2)_2$–	16	145	10	XIII-1
4-Cl-1,**3**-$(NO_2)_2$–	14	150	10	XIII-2
4-Br-1,**2**-$(NO_2)_2$–	2	100	10	XIV
2,3,5,6-Cl_4-**1**,4-$(NO_2)_2$–	0.5	140	35	XV

[a] Anhydrous KF in dimethylformamide as solvent. [b] Bold type position is replaced.

Experimental[12–14]

All reactions were carried out in glass flasks of the appropriate size equipped with a Teflon-bladed stirrer, a thermometer and an air condenser. An electric heating mantle with a temperature regulator was used.

It is essential that the potassium fluoride in the replacement reactions be anhydrous and finely divided. Commercial "anhydrous" potassium fluoride was found to contain varying amounts of moisture which were removed by two methods. For small experiments, the potassium fluoride was heated with grinding in an open dish on a hot-plate just prior to use. For larger experiments, it was convenient to grind the potassium fluoride for a short time in a ball mill and then remove the moisture by a benzene azeotrope. This operation was conveniently carried out in the reaction flask, followed by addition of the higher boiling reaction solvent and removal of the benzene by distillation. Hereafter, desiccated potassium fluoride will denote open dish drying, and azeotrope-dried will refer to the distillation operation.

The procedures for working up the reaction mixtures were as follows.

Procedure A. Reactions in Water-immiscible Solvents.—The cooled reaction mixture was filtered to remove the inorganic potassium halides and the salts were washed with hot toluene. The combined filtrate was dried and vacuum distilled.

Procedure B. Reactions in Water-miscible Solvents.—The cooled reaction mixture was diluted with water and the separated product was treated in one of the following ways: (1) solid products were separated by filtration and purified by recrystallization; (2) oils for which steam distillation was impracticable were thoroughly washed with water, dried and vacuum distilled; (3) steam volatile oils were steam distilled.[15] When necessary, further purification was accomplished by vacuum distillation.

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(12) The advice of Dr. F. H. Reed and reference compounds provided by Messrs. R. E. Oesterling, H. G. Schneider, R. H. Shiley and R. H. White are gratefully acknowledged.

(13) Analyses by D. R. Dickerson, microanalyst for Illinois Geological Survey.

(14) Yields reported herein may not be the highest attainable.

(15) When DMSO is used as solvent, malodorous sulfur by-products are formed. Permanganate oxidation of the diluted reaction mixture renders the steam distillation less offensive and also greatly reduces the quantity of sulfur-containing contaminants in the steam distillate.

2,4-Dinitrofluorobenzene (I).[16]—Seven experiments with 2,4-dinitrochlorobenzene were set up as follows (see Table I for other data).

Expt. ref.	KF, g.	Aryl chloride, g.	Solvent[b]	Procedure	Product n^{20}_{D}
1	58	50.5	$C_6H_5NO_2$	A	1.5698[c]
2	16	50.5	None	A	1.5806[d]
3	14.5	25.5	C_6H_5CN	A	1.5795[d]
4	14.5	25.5	$(CH_2CN)_2$	B-2	1.5735[d]
5	14.5[a]	25.5	DMF	B-2	1.5699[c]
6	14.5	25.5	DMF	B-2	1.5697[c]
7	14.5	25.5	DMSO	B-2	1.5695[c]

[a] Azeotrope-dried; all others desiccated. [b] Weight of solvent equal to weight of aryl chloride. [c] Pure dinitrofluorobenzene, m.p. 24–25° (supercools readily), b.p. 122–124° (1 mm.). [d] Distillation range 122–135° (1 mm.) with chloro contamination.

2-(Trifluoromethyl)-4-nitrofluorobenzene (II).—A mixture of 2-(trifluoromethyl)-4-nitrochlorobenzene[17] (45 g.), desiccated KF (23.2 g.) and DMF (55 ml.) at 160° for 4 hr. by procedure B-2 gave 34 g. or 81% yield of chlorine-free II, b.p. 105–110° (25 mm.), n^{20}_{D} 1.4658.

Anal. Calcd. for $C_7H_3F_4NO_2$: C, 40.21; H, 1.45; N, 6.70. Found: C, 40.37; H, 1.55; N, 6.91.

2-Nitro-4-(trifluoromethyl)-fluorobenzene (III).[18]—A mixture of 2-nitro-4-(trifluoromethyl)-chlorobenzene[17] (45 g.), desiccated KF (23.2 g.) and DMF (55 ml.) at 160° for 3.5 hr. by procedure B-2 gave 32 g. or 76% yield of chlorine-free III, b.p. 92° (15 mm.), n^{20}_{D} 1.4618.

Anal. Calcd. for $C_7H_3F_4NO_2$: C, 40.21; H, 1.45; N, 6.70. Found: C, 40.33; H, 1.38; N, 6.79.

2-Nitro-4-carboxymethylfluorobenzene (IV).[19]—A mixture of 4-chloro-3-nitromethylbenzoate (21.5 g.), desiccated KF (11.6 g.) and DMF (35 ml.) at 155° for 4 hr. by procedure B-2 gave 13.3 g. or 67% yield of chlorine-free IV, b.p. 116–119° (1 mm.), m.p. 55–58°.

2,4,6-Trifluoronitrobenzene (V).[20]—A mixture of 2,4,6-trichloronitrobenzene (11.3 g.), desiccated KF (17.4 g.) and DMSO (25 ml.) at 180° for 2 hr. by procedure B-3 gave 1.5 g. or 15% yield of crude V, n^{20}_{D} 1.5005. Nitration of this product yielded 1,3-dinitro-2,4,6-trifluorobenzene, m.p. 52–53°.

Anal. Calcd. for $C_6HF_3N_2O_4$: C, 32.45; H, 0.45; N, 12.61. Found: C, 32.45; H, 0.46; N, 12.70.

The melting point was not depressed when mixed with an authentic sample, prepared by dinitration of symmetrical trifluorobenzene.[20]

2,4,5-Trifluoronitrobenzene (VI).[21]—A mixture of 2,5-difluoro-4-chloronitrobenzene[10] (19.1 g.), desiccated KF (11.6 g.) and DMSO (20 ml.) at 170–175° for 2 hr. by procedure B-3 gave 8 g. or 45% yield of crude VI, n^{20}_{D} 1.4985. A small portion was reduced to the amine. The melting point of the acetyl derivative of this amine was not depressed when mixed with an authentic sample of 2,4,5-trifluoroacetanilide.[21]

2,4-Difluoro-3-chloronitrobenzene (VII).—A mixture of 2,3,4-trichloronitrobenzene (289 g.), azeotrope-dried KF (300 g.) and DMSO (400 ml.) at 180° for 4 hr. gave by procedure B-1 from methanol 56 g. or 23% yield of VII, m.p. 45.5–46.5°.

Anal. Calcd. for $C_6H_2ClF_2NO_2$: C, 37.23; H, 1.04; Cl, 18.32; N, 7.24. Found: C, 37.39; H, 0.93; Cl, 18.22; N, 7.28.

2,4-Difluoronitrobenzene (VIII).[22]—A mixture of 2,4-dichloronitrobenzene (48 g.), azeotrope-dried KF (58 g.) and DMSO (80 ml.) at 180° for 6 hr. by procedure B-3 gave 18.5 g. or 47% yield of VIII, n^{20}_{D} 1.5150. A small portion was reduced to the amine. The melting point of the acetyl derivative of this amine was not depressed when mixed with an authentic sample of 2,4-difluoroacetanilide.[22]

2-Fluoronitrobenzene (IX).[23]—1. A mixture of 2-chloronitrobenzene (47.3 g.), azeotrope-dried KF (70 g.) and DMF (50 ml.) at 170° for 163 hr. by procedure B-3 gave 35 g. of a mixture (n^{20}_{D} 1.5470) estimated to contain 17.5 g. or 40% yield of IX.

2. A mixture of 2-chloronitrobenzene (47.3 g.), desiccated KF (35 g.) and DMSO (55 ml.) 185° for 4.5 hr. by procedure B-3 gave 39 g. of a mixture, n^{20}_{D} 1.5475. Vacuum fractionation gave 16 g. or 38% yield of IX, b.p. 94–97° (13 mm.), n^{20}_{D} 1.5338. The melting point of the acetyl derivative of the reduced product was not depressed when mixed with an authentic sample of 2-fluoroacetanilide.[23] A small quantity of 2-nitrothioanisole[24] was isolated in the steam distillation tailings.

4-Fluoronitrobenzene (X).[23]—A mixture of 4-chloronitrobenzene (78.5 g.), azeotrope-dried KF (58 g.) and DMSO (80 ml.) at 185–190° for 14 hr. by procedure B-3 gave 51 g. or 72% yield of crude X, n^{20}_{D} 1.5340. The melting point of the acetyl derivative of the reduced product was not depressed when mixed with an authentic sample of 4-fluoroacetanilide.[23] A small quantity of 4-nitrothioanisole[24] was isolated from the steam distillation tailings.

2,3,5,6-Tetrachlorofluorobenzene (XI).—A mixture of 2,3,5,6-tetrachloronitrobenzene (34.9 g.), azeotrope-dried KF (62 g.) and DMF (75 ml.) at 147° for 4.5 hr. by procedure B-3 gave from ethanol 11.7 g. or 37% yield of XI, m.p. 71.5–72.5°.

Anal. Calcd. for C_6HCl_4F: C, 30.81; H, 0.43; F, 8.12; Cl, 60.64. Found: C, 30.67; H, 0.68; F, 7.89; Cl, 60.70.

The nuclear magnetic resonance spectrum[25] shows that both H^1 and F^{19} bands are doublets with an indirect spin-spin splitting of 2.2 cycles $sec.^{-1}$. This value is in agreement with other observed values for the *para* configuration. Nitration of XI with fuming nitric and fuming sulfuric acids at 45–60° gave an 85% yield of XV.

2,3,4,5,6-Pentachlorofluorobenzene (XII).—A mixture of pentachloronitrobenzene (18.5 g.), azeotrope-dried KF (35 g.) and DMF (55 ml.) at 150° for 4 hr. by procedure B-3 gave from ethanol 1.8 g. or a 10% yield of XII, m.p. 137–138°.

Anal. Calcd. for C_6Cl_5F: C, 26.85; F, 7.08; Cl, 66.07. Found: C, 26.78; F, 7.29; Cl, 65.97.

3,4-Difluoronitrobenzene (XIII).[26]—1. A mixture of I (34.5 g.), azeotrope-dried KF (30 g.) and DMF (75 ml.) at 145° for 16 hr. by procedure B-3 gave 3.9 g. or 10% of crude XIII, a portion of which was distilled, b.p. 76–80° (11 mm.), n^{20}_{D} 1.5055.

2. A mixture of 2,4-dinitrochlorobenzene (50.5 g.), azeotrope-dried KF (58 g.) and DMF (75 ml.) at 150–155° for 14 hr. by Procedure B-3 gave 4 g. or 10% yield of crude XIII. A small quantity was reduced to the amine. The melting point of the acetyl derivative of this amine was not depressed when mixed with an authentic sample of 3,4-difluoroacetanilide prepared from 3,4-difluoroaniline.[27] The 3,4-difluoroacetanilide (from ethanol) has a m.p. 123–124°.

Anal. Calcd. for $C_8H_7F_2NO$: N, 8.18. Found: N, 8.16.

2-Fluoro-4-bromonitrobenzene (XIV).—A mixture of 4-bromo-1,2-dinitrobenzene (24.7 g.), desiccated KF (29 g.) and DMF (75 ml.) at 100° for 2 hr. by procedure B-3 gave from ethanol 2 g. or 10% yield of XIV, m.p. 85–86°.

Anal. Calcd. for $C_6H_3BrFNO_2$: C, 32.75; H, 1.37; Br, 36.33; N, 6.37. Found: C, 32.63; H, 1.47; Br, 36.23; N, 6.11.

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The melting point was not depressed when mixed with an authentic sample recently prepared in this Laboratory by a Sandmeyer reaction upon 3-fluoro-4-nitroaniline.[28]

2,3,5,6-Tetrachloro-4-fluoronitrobenzene (XV).—A mixture of 2,3,5,6-tetrachloro-1,4-dinitrobenzene (3.1 g.), desiccated KF (5.8 g.) and DMF (18 ml.) at 100–140° for 30 minutes by procedure B-1 gave from ethanol 1 g. or 35% yield of XV, m.p. 80–81°.

Anal. Calcd. for $C_6Cl_4FNO_2$: C, 25.82; Cl, 50.88; N, 5.02. Found: C, 25.53; Cl, 51.10; N, 4.89.

Alkali Fluoride Comparisons.—The effectiveness of the alkali fluorides in DMF was tested qualitatively. A mixture of 0.04 mole of alkali fluoride and 2 g. (0.01 mole) of 2,4-dinitrochlorobenzene in 4 ml. of DMF was stirred at 140–150° for 15–30 minutes when a reaction was apparent and for 1 hr. when halogen interchange was questionable. After dilution of the reaction mixtures in water, the extent of exchange was judged by an aqueous chloride ion test with silver nitrate. The lithium and sodium fluoride experiments gave only traces of chloride, whereas rubidium and cesium fluorides gave heavy silver chloride precipitates. The exchange properties of the latter two are comparable to those of potassium fluoride.

A mixture of NaF (10.5 g.), KCl (9.3 g.) and 2,4-dinitrochlorobenzene (25 g.) in nitrobenzene (30 ml.) was heated at 185–205° for 18 hr. The aryl chloride was recovered, thus indicating no KCl influence upon NaF reactivity.

A mixture of KF (7.25 g.), NaF (5.25 g.) and 2,4-dinitrochlorobenzene (25 g.) in nitrobenzene (30 ml.) was heated at 200–205° for 2 hr. Estimated yield of fluoro analog was 17.9 g., or 77%. Sodium and potassium fluoride mixtures containing less than one mole of potassium fluoride per mole of aryl chloride gave conversions to the extent expected by the reaction of the potassium fluoride alone.

Inasmuch as lithium and sodium fluorides fail to give the aryl chloride–metallic fluoride exchange, the reverse exchange, aryl fluoride–metallic chloride, was examined. A mixture of 2,4-dinitrofluorobenzene (17.2 g.), LiCl (10.6 g.) in nitrobenzene (30 ml.) at 200–210° for 30 minutes showed no reaction; 97% of the aryl fluoride was recovered. Sodium chloride gave a similar result.

Miscellaneous Compounds. 2,2′-Di-(trifluoromethyl)-4,4′-dinitrodiphenyl Ether.—This ether, m.p. 115–116°, was obtained by recrystallization from ethanol of the distillation residue from II.

Anal. Calcd. for $C_{14}H_6F_6N_2O_5$: C, 42.44; H, 1.53; N, 7.07. Found: C, 42.70; H, 1.47; N, 7.16.

Stannous chloride reduction of the preceding ether gave 2,2′-di-(trifluoromethyl)-4,4′-diaminodiphenyl ether, m.p. 123–124°.

Anal. Calcd. for $C_{14}H_{10}F_6N_2O$: C, 50.00; H, 3.00; N, 8.33. Found: C, 50.03; H, 3.00; N, 8.31.

2,2′-Dinitro-4,4′-di-(trifluoromethyl)-diphenyl Ether.—This ether, m.p. 107–108°, was obtained by recrystallization from ethanol of the distillation residue from III. It melts at 114–115° when recrystallized rapidly.

Anal. Calcd. for $C_{14}H_6F_6N_2O_5$: C, 42.44; H, 1.53; N, 7.07. Found: C, 42.48; H, 1.50; N, 7.21.

Stannous chloride reduction gave the corresponding 2,2′-diamino-4,4′-di-(trifluoromethyl)-diphenyl ether, m.p. 79.5–80°.

Anal. Calcd. for $C_{14}H_{10}F_6N_2O$: C, 50.00; H, 3.00; N, 8.33. Found: C, 50.06; H, 3.26; N, 8.29.

2-Fluoro-5-trifluoromethylaniline.[18]—An iron reduction of III gave an 86% yield of the corresponding aniline, 2-fluoro-5-trifluoromethylaniline, b.p. 81° (20 mm.), n^{20}_{D} 1.4608.

Anal. Calcd. for $C_7H_5F_4N$: C, 46.94; H, 2.81; N, 7.82. Found: C, 46.86; H, 2.59; N, 7.96.

The acetyl derivative, m.p. 121.5–122°, did not depress the melting point of material prepared *via* the nitration of 4-fluorobenzotrifluoride.

Anal. Calcd. for $C_9H_7F_4NO$: N, 6.33. Found: N, 6.35.

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[28] H. H. Hodgson and D. E. Nicholson, *J. Chem. Soc.*, 766 (1941), reported erroneously the melting points of the amine and acetyl derivative as 153 and 138°, respectively. The data obtained in this Laboratory are m.p. 161° (amine) and 173–174° (acetylamino).

[CONTRIBUTION FROM SCIENTIFIC DEPARTMENT, ISRAEL MINISTRY OF DEFENCE, AND DEPARTMENT OF ORGANIC CHEMISTRY, HEBREW UNIVERSITY]

A New Method for the Preparation of Aromatic Fluorine Compounds

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Aryl fluorides have been prepared by the reaction of diazonium fluoroborates with copper powder or cuprous chloride in dry or aqueous acetone. This method avoids the difficulties of thermal decomposition of diazonium fluoroborates.

In a recent communication[1] it has been reported that certain acylamino-substituted diazonium fluoroborates are soluble in water, even in the presence of an excess of the fluoroborate ion, but can nevertheless be converted into the corresponding aryl fluorides by the addition of copper powder to their aqueous solution. This observation suggested that a radical mechanism may be operative in the synthesis of aryl fluorides from diazonium fluoroborates, of the type assumed by Waters in the Gattermann reaction.[2,3] One should, then, expect that the conditions favorable for radical decomposition of diazonium salts[4] would permit the preparation of aryl fluorides. This would mean the circumvention of the experimental difficulties attending the thermal decomposition of diazonium fluoroborates, especially in the case of the nitro-substituted compounds.[5]

It has, indeed, been found that diazonium fluoroborates decompose to give aryl fluorides when their solutions in acetone or aqueous acetone are stirred with small amounts of copper powder or—preferably—cuprous chloride at room temperature. It is possible by this method to decompose batches

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[1] E. D. Bergmann and M. Bentov, *J. Org. Chem.*, **19**, 1594 (1954).

[2] W. A. Waters, *J. Chem. Soc.*, 266 (1942).

[3] For a survey of the theories of the Schiemann reaction, see A. Roe, "Organic Reactions," Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 193; see also H. A. Hodgson, St. Birtwell and J. Walker, *J. Chem. Soc.*, 770 (1941). It is significant that the application of the Schiemann reaction to optically active 6,6′-diamino-2,2′-dimethylbiphenyl is accompanied by racemization, whilst the transformation of the amino-groups into iodine atoms gives an optically active product.

[4] *Cf.*, *e.g.*, the Meerwein reaction, in which diazonium salts react with α,β-unsaturated acids in aqueous acetone and in the presence of cupric ions. See F. Bergmann and J. Weizmann, *J. Org. Chem.*, **9**, 415 (1944); D. H. Hey and W. A. Waters, *Chem. Revs.*, **21**, 169 (1937); J. K. Kochi, THIS JOURNAL, **77**, 5090, V, 5274 (1955); **78**, 1226 (1956); S. C. Dickerman, K. Heiss and A. K. Ingberman, *J. Org. Chem.*, **21**, 380 (1956).

[5] See A. Roe, ref. 3.