remove hydrogen fluoride. The supernatant liquid was subjected to distillation in an attempt to recover $C_6H_5N(CH_3)SOF_3$, but after the ether had been removed, a vigorous reaction occurred during which the still pot was severely etched.

Phenylazide from phenylhydrazine and sulfur oxytetrafluoride. A flask fitted with a magnetic stirrer and a solid carbon dioxide-cooled condenser was chilled to −40° and charged with sulfur oxytetrafluoride (31 g., 0.25 mole) and 50 ml. of ether. A solution of phenylhydrazine (27 g., 0.25 mole) in 50 ml. of ether was added during 0.5 hr. The reaction mixture was poured onto ice and washed first with dilute alkali then with water. The odor of sulfur dioxide was quite evident, indicating reduction of sulfur oxytetrafluoride. Phenylazide (5 g.) was isolated by distillation. It was identified by its infrared and ultraviolet absorption spectra and by a color reaction[7] with aluminum chloride in benzene.

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(7) W. Borsche and H. Hahn, *Ber.*, **82**, 260 (1949).

[CONTRIBUTION FROM THE ENERGY DIVISION, OLIN MATHIESON CHEMICAL CORP.]

Aromatic Fluorine Compounds. I. Preparation of *p*-Fluoraniline by Catalytic Reduction of Nitrobenzene in Hydrogen Fluoride[1]

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A novel one-step method for the preparation of *p*-fluoroaniline by the catalytic reduction of nitrobenzene in anhydrous hydrogen fluoride is described. The suggested mechanism involves the reduction of nitrobenzene to *N*-phenylhydroxylamine followed by the *in situ* rearrangement of the latter in hydrogen fluoride to give *p*-fluoroaniline.

The primary objective of this study was to determine whether *p*-fluoroaniline (III) could be prepared by a more simplified fluorination route than the Schiemann reaction.[2,3] Thus, *p*-fluoroaniline can be prepared by the reduction of *p*-fluoronitrobenzene.[4] The latter is synthesized by the Schiemann reaction involving conversion of *p*-nitroaniline to *p*-nitrophenyldiazonium fluoborate, followed by decomposition to give *p*-fluoronitrobenzene. (Another route to *p*-fluoronitrobenzene involves nitration of fluorobenzene,[4] which in turn is obtained by the Schiemann reaction from aniline.[3]) Other known approaches to *p*-fluoroaniline such as the use of *p*-fluorobenzoic acid[5] in the Schmidt reaction or the treatment of *p*-bromofluorobenzene with potassium amide[6] also involve a prior Schiemann reaction.

Recently, two alternative routes toward the preparation of aromatic fluorine compounds have been reported. Finger and Kruse treated *p*-chloronitrobenzene with potassium fluoride to give *p*-fluoronitrobenzene.[7] Of more immediate interest to the present investigation is the observation by Titov and Baryshnikova that *p*-fluoroaniline could be obtained by the rearrangement of *N*-phenylhydroxylamine (II) in anhydrous hydrogen fluoride.[8,9] When this reaction was studied in this Laboratory, the previously reported[8] forty-eight-hour period was considerably shortened to reaction times as low as half an hour to give similar yields of *p*-fluoroaniline. In view of the reported catalytic reduction of nitrobenzene to *N*-phenylhydroxylamine,[10,11] and the rapid rearrangement of the latter in hydrogen fluoride to *p*-fluoroaniline,[8] this suggested a convenient one-step route to *p*-fluoroaniline by the catalytic reduction of nitrobenzene in anhydrous hydrogen fluoride. However, when Weinmayr catalytically hydrogenated (palladium catalyst on Nuchar) nitrobenzene in anhydrous hydrogen fluoride, only aniline and traces of *p*-aminophenol were reported.[12] Since the synthesis of *p*-chloraniline from nitrobenzene in concentrated hydrochloric acid was achieved by catalytic reduction (platinum oxide),[13] by electrolysis be-

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(1) This work was sponsored by Chemical Corps Engineering Command, U. S. Army, Contract No. DA-18-064-CML-2696.

(2) G. Schiemann and R. Pillarsky, *Ber.*, **62**, 3035 (1925).

(3) A. Roe, *Org. Reactions*, **V**, 217 (1952). A modification of the Schiemann approach involves the formation and *in situ* decomposition of the aryldiazonium fluoride, ArN_2F.

(4) H. L. Bradlow and C. A. Vander Werf, *J. Am. Chem. Soc.*, **70**, 654 (1948).

(5) K. Takatori, Y. Yamada, T. Arai, and R. Nakazawa, *Yakugaku Zasshi*, **78**, 108 (1958); *Chem. Abstr.*, **52**, 11013 (1958).

(6) J. D. Roberts, C. W. Vaughan, Jr., L. A. Carlsmith, and D. Semenov, *J. Am. Chem. Soc.*, **78**, 611 (1956).

(7) G. C. Finger and C. W. Kruse, *J. Am. Chem. Soc.*, **78**, 6037 (1956).

(8) A. I. Titov and A. N. Baryshnikova, *Zhur. Obshcheĭ Khim.*, **23**, 346 (1953). These investigators did not find *o*-fluoroaniline or *p*-aminophenol in this rearrangement.

(9) The rearrangement of *N*-phenylhydroxylamine in hydrochloric acid to give *o*- and *p*-chloraniline has also been observed. T. W. J. Taylor and W. Baker in N. V. Sidgwick's *Organic Chemistry of Nitrogen*, Clarendon Press, Oxford, 1949, p. 163.

(10) T. W. J. Taylor and W. Baker, *Organic Chemistry of Nitrogen*, Clarendon Press, Oxford, 1949, p. 162.

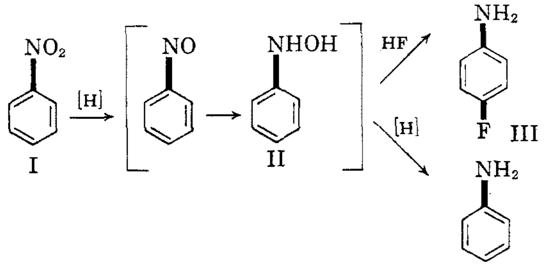
(11) K. Brand and V. Steiner, *Ber.*, **55**, 875 (1922).

(12) V. Weinmayr, *J. Am. Chem. Soc.*, **77**, 1762 (1955).

(13) C. O. Henke and J. V. Vaughen, U. S. Patent **2,198,-249** (April 23, 1940).

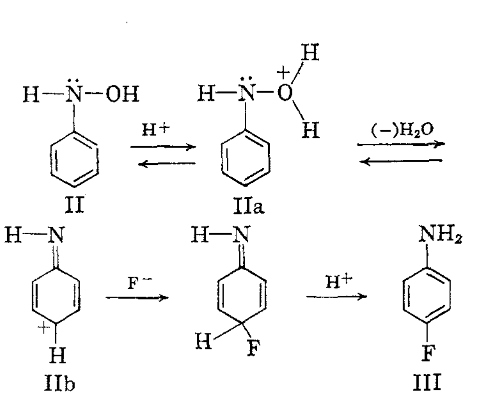
tween platinum electrodes,[14] and by reduction with tin,[15] this suggested that a further investigation of the catalytic reduction of nitrobenzene in anhydrous hydrogen fluoride to give *p*-fluoroaniline was warranted.

In the present investigation, *p*-fluoroaniline was synthesized in 61.0% yield, based on 100% conversion of nitrobenzene, when the latter was hydrogenated in anhydrous hydrogen fluoride with platinum oxide catalyst. A 12.6% yield of the principal by-product, aniline, was also obtained (Table I). The sequence suggested in Equation A is offered to account for the conversion of nitrobenzene to *p*-fluoroaniline. It has been suggested that the reaction path of nitrobenzene to *p*-chloroaniline proceeded through *N*-phenylhydroxylamine as an intermediate.[13-15] Presumably, aniline formation arises from a competitive reaction involving reduction of *N*-phenylhydroxylamine.[16]



(A)

Nitrosobenzene would also be expected to be an intermediate in the conversion of nitrobenzene to *p*-fluoroaniline, since it is the first established product in the reduction of an aromatic nitro compound under acidic or alkaline conditions.[17] However, the conversion of nitrosobenzene to *p*-fluoroaniline under the present reaction conditions was not investigated. Blanksma[15] showed that treatment of nitrosobenzene with tin and hydrochloric acid gave a 38% yield of *p*-chloroaniline and stated that the reaction sequence to this product proceeded through *N*-phenylhydroxylamine. The conversion of *N*-phenylhydroxylamine to *p*-fluoroaniline can be regarded as another example of a class of "intermolecular" aromatic nucleophilic rearrangements, of which the best known representative is the sulfuric acid-catalyzed conversion of *N*-phenylhydroxylamine to *o*- and *p*-aminophenol.[16] Equation B represents the reaction sequence suggested by Titov and Baryshnikova[8] for the acid-catalyzed conversion of *N*-phenylhydroxylamine to *p*-fluoroaniline. Presumably, the last step in Equation A, *i.e.*, the conversion of *N*-phenylhydroxylamine (II) to *p*-fluoroaniline (III), proceeds through the mechanistic sequence described in Equation B.



(B)

By this sequence, the conjugate acid (IIA) of *N*-phenylhydroxylamine (shown in the form in which it would undergo heterolysis to IIB, rather than in the more stable form with the extra proton carried by the nitrogen), loses a molecule of water to form a cation which is a resonance hybrid of several forms, of which one structure with the carbonium ionic charge in the *para*- position is depicted above (IIB). By further reaction with fluoride ion, and followed by a prototropic shift, *p*-fluoroaniline can be formed through such a sequence.

Of the catalyst systems studied, platinum oxide was found to be the most effective in the present study (Table I). While palladium-on-carbon, palladium oxide and platinum oxide-on-carbon catalyzed the formation of *p*-fluoroaniline (III) in this reaction, they were not as satisfactory as platinum oxide. It was found that chromium sesquioxide, palladium-on-carbon poisoned with lead, molybdenum sulfide on chromium sesquioxide, platinum black, copper chromite, platinum oxide on alumina gel, palladium oxide on carbon, and nickel oxide on alumina gave low yields of *p*-fluoroaniline, provided aniline as the sole product or did not reduce nitrobenzene.

A study was made to determine the identity of the by-products. Aniline was found to be the primary by-product in every experiment conducted. Qualitative ultraviolet spectral analysis of the steam distillation residues revealed the presence of hydroquinone and an aminophenol. Attempts to separate the constituents of the steam distillation residues by column chromatography were unsuccessful. However, it is conceivable that condensation products arising from *p*-fluoroaniline, *N*-phenylhydroxylamine, nitrosobenzene, or nitrobenzene should not be ruled out. It has been reported that *p*-fluoroaniline gave bimolecular con-

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[14] N. Löb, *Z. Elektrochem.*, **3**, 46 (1896); *Ber.*, **29**, 1894 (1896).

[15] J. J. Blanksma, *Rec. trav. chim.*, **25**, 365 (1906).

[16] C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, Cornell University Press, Ithaca, N. Y., 1953, p. 621. Both aniline and azoxybenzene, oxidation-reduction products of *N*-phenylhydroxylamine, have been isolated in the acid-catalyzed rearrangement of *N*-phenylhydroxylamine to *p*-aminophenol. Attempts to isolate and characterize any azoxybenzene which may have been formed by an oxidation-reduction side reaction in the present investigation were unsuccessful.

[17] Reference,[9] p. 253.

TABLE I

SYNTHESIS OF *p*-FLUOROANILINE FROM NITROBENZENE

Variable	Pressure, p.s.i.g.	Temp.	% Yield	
			p-$FC_6H_4NH_2$	$C_6H_5NH_2$
Standard expt.[a]	55	50	58.8	12.0
Decrease concentration of $C_6H_5NO_2$ (0.21 mole) and PtO_2 (0.25 g.)	55	50	61.0	12.6
Increase $C_6H_5NO_2$ concentration to 1.42 moles[b]	50	50	Trace	57.0
Removal of sulfur impurities from HF	50	50	42.5	14.4
Effect of low temperatures	30	13	26.6	46.5
Effect of high temperatures[c]	500	120	25.5	12.7
Aqueous HF (low H_2O)[d]	50	50	28.9	41.2
Aqueous HF (high H_2O)[e]	45	30–50	0	61.0
Addition of KNO_3 (10 g.)[f]	50	50	21.7	28.3
Addition of *p*-aminophenol (7.5 g.; S.S. autoclave)	200	50	21.7	18.5
Addition of azoxybenzene (4.0 g.; S.S. autoclave)	200	50	42.9	16.1
Addition of aniline (5.0 g.)	200	50	31.7	24.3
5% Pd-C (2.0 g.)	205	80	37.2	30.2
PdO (0.5 g.)	50	50	32.3	26.2
0.5% PtO_2-C (20 g.)[g]	95	50	16.9	23.9

[a] All experiments, except where noted, employed 0.41 mole of nitrobenzene, 0.50 g. of platinum oxide catalyst and 7.0 moles hydrogen fluoride. Monel autoclaves used. Conversions of nitrobenzene were 100%. [b] 25.9% conversion of nitrobenzene. [c] Stainless steel (S.S.) autoclave; 0.25 g. of platinum oxide. [d] 0.40 mole of water; 6.65 moles of hydrogen fluoride. [e] 3.75 moles of water; 4.15 moles of hydrogen fluoride; 58.8% conversion of nitrobenzene. [f] 90% conversion of nitrobenzene. [g] 79% conversion of nitrobenzene.

densation products such as *p*-fluoroazobenzene[18] or fluorinated phenazines[19] with nitrosobenzene and nitrobenzene, respectively. Since the fluorinated phenazine[19] from nitrobenzene and *p*-fluoroaniline occurred in strongly alkaline medium, it does not seem likely that this type of condensation occurred in the acidic conditions employed in the present investigation. Attempts were made toward improving the yield of *p*-fluoroaniline as well as minimizing by-product formation, by modification of reaction conditions (Table I). The use of lower (13°) or higher (200°) temperatures resulted in diminished yields of *p*-fluoroaniline. Purified hydrogen fluoride, from which sulfur contaminants had been removed, showed no improvement in product distribution. The presence of water from 5 to 50% provided aniline as the predominant or sole product. Only a trace amount of *p*-fluoroaniline was formed when a large excess of nitrobenzene was employed. Restriction of the quantity of hydrogen, so that the reaction was halted prior to completion, did not increase the yield of *p*-fluoroaniline. The addition of azoxybenzene, aniline, or *p*-aminophenol, prior to hydrogenation had no favorable effect on product distribution. The use of potassium nitrate as a hydrogen fluoride ionizing agent[20] also did not improve the yield of *p*-fluoroaniline.

Since aniline is consistently obtained as a by-product in this reaction (see Table I), and in view of the difficulty in separating mixtures of *p*-fluoroaniline and aniline because of their close boiling points,[21] a problem may arise in obtaining *p*-fluoroaniline in a highly pure state by the route outlined in Equation A. (*p*-Fluoroaniline can be obtained in a pure state by the reduction of *p*-fluoronitrobenzene[4] or by rearrangement of *N*-phenylhydroxylamine in anhydrous hydrogen fluoride.[8])

EXPERIMENTAL

Nitrobenzene was obtained from Eastman Kodak (White Label). Anhydrous hydrogen (Matheson) was usually transferred from the cylinder directly into the autoclave. In one experiment, hydrogen fluoride was further purified to remove sulfur-containing impurities.[12] Hydrogen (Air Reduction) was introduced from a 1-l. storage cylinder.

The following catalysts were obtained from Engelhardt Industries: platinum oxide; 0.5% platinum (as platinum oxide) on 4- to 8-mesh carbon or powdered carbon; and 5% palladium on powdered carbon. Palladium oxide was prepared by oxidizing palladium chloride (4.4 g., Fisher Scientific) by fusion with sodium nitrate (55 g.) at 300 to 450°, and then dried at 100°.

A monel microautoclave (total capacity, 312 ml.; American Instrument Co., Silver Spring, Md.) was employed. No pressure gauge corrections were made during this investigation. The amount of hydrogen absorbed was measured by the pressure differential on the 1-l. storage cylinder.

Rearrangement of nitrobenzene to p-fluoroaniline (Table I). A typical reduction rearrangement of nitrobenzene to *p*-fluoroaniline was conducted as follows: to a monel microautoclave cooled in Dry Ice, nitrobenzene (25 g., 0.21 mole), platinum oxide (0.25 g.), and anhydrous hydrogen fluoride (140 g., 7.0 moles) were charged. The autoclave was sealed, purged with nitrogen, agitated, and heated to 50°. Hydrogen was then introduced at a pressure of 20 p.s.i.g. over the pressure exerted by hydrogen fluoride at this temperature until there was no further hydrogen uptake. Slightly greater than the stoichiometric 2 moles of hydrogen were usually absorbed in these experiments. Cooling was necessary to maintain the temperature at 50°. The autoclave was cooled

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(18) J. Lichtenberger and R. Thermet, *Bull. Soc. Chem.*, 318 (1951).

(19) V. P. Chernetsky, L. M. Wagupolsky, and S. B. Serebryany, *Zhur. Obshcheĭ Khim.*, 25, 2161 (1955).

(20) J. H. Simons, *Fluorine Chemistry*, Vol. I, Academic Press, New York, N. Y., 1950, p. 240.

(21) J. Timmermans, *Physico-Chemical Properties of Pure Organic Compounds*, Elsevier Publishing Co., New York, 1950, pp. 551, 605.

and the contents were poured into a polyethylene beaker and hydrogen fluoride was permitted to evaporate partially by standing overnight. The reaction mixture was originally colorless upon discharge from the autoclave but became blue on exposure to the air. The product was made alkaline with 25% sodium hydroxide solution and the mixture was steam distilled until 4 l. of distillate were collected. The latter was saturated with sodium chloride and extracted three times with 200-ml. portions of diethyl ether. The ethereal extracts were combined, dried over magnesium sulfate, concentrated, and distilled. The main distillation fraction (16.0 g.) was assayed by infrared spectroscopy.

Because of the narrow difference in boiling points of aniline (184.3°/762.2 mm.) and *p*-fluoroaniline (187.4°/760.0 mm.), no attempt was made to rectify further the reaction product.[21]

Table I summarizes experiments conducted with platinum oxide and other catalysts, as well as the effect of temperature, molar ratios of reactants, presence of water, aniline *p*-aminophenol, azoxybenzene, or potassium nitrate, use of highly purified hydrogen fluoride, and the use of a stainless steel autoclave in place of the monel pressure autoclave normally employed.

One experiment was conducted to determine what effect the restriction of hydrogen absorption would have on the yield of *p*-fluoroaniline and by-product formation. In a monel microautoclave were placed 0.50 g. of platinum oxide catalyst, 0.41 mole of nitrobenzene, and 7.0 moles of anhydrous hydrogen fluoride. Hydrogen was added to the desired pressure and the contents were heated at 50°. The reaction was stopped after one half of the calculated amount of hydrogen (0.41 mole) was absorbed. After processing the reaction mixture in the manner described earlier, it was found that a 65% conversion of nitrobenzene was achieved, with 32.7 and 19.0% yields of *p*-fluoroaniline and aniline, respectively.

Analytical. The reaction product was scanned in a 0.025-mm. sodium chloride cell from 8.0 μ to 12.25 μ by use of a Perkin-Elmer Model 21 infrared spectrophotometer.

The "base line" was taken as that of carbon tetrachloride. The following analytical reference points were employed: nitrobenzene, 10.70 μ; aniline, 11.39 μ; *p*-fluoroaniline, 8.67 μ.

Attempts were made to employ ultraviolet spectroscopy in order to distinguish between aniline and *p*-fluoroaniline by diazotization and subsequent coupling with β-naphthol or α-naphthylamine. However, identically colored dyes were obtained with both anilines.

Consideration was also given to nonaqueous titration to distinguish between aniline and *p*-fluoroaniline. However, the difference in dissociation constants[22] was so small that they could not be conveniently titrated in aqueous medium or by determination in benzene with perchloric acid.

Attempts were made to isolate and characterize any by-products in the steam-distillation residues. Ultraviolet absorption spectroscopy suggested the presence of hydroquinone and an aminophenol. Separation of the constituents of the steam distillation residues by column chromatography were not successful.

Rearrangement of phenylhydroxylamine to p-fluoroaniline in hydrogen fluoride. In a typical reaction, a total of 0.34 mole of *N*-phenylhydroxylamine,[23] prepared from the reaction of nitrobenzene with zinc and ammonium chloride, was added over a 15-min. period to 8.1 moles of anhydrous hydrogen fluoride in a copper flask at 13° and permitted to stand for 48 hr. at this temperature. The reaction mixture was made alkaline with sodium hydroxide and the aqueous solution steam distilled. The steam distillate was saturated with sodium chloride, extracted with diethyl ether, the extract dried over magnesium sulfate and distilled, b.p. 186 to 187°, n_{D}^{25} 1.5349, wt. 22 g. (0.20 mole; 58% uncorrected yield of *p*-fluoroaniline). (Reported[21] for *p*-fluoroaniline, b.p. 187.4°; n_{D}^{20} 1.5395.) The *N*-acetyl derivative of *p*-fluoroaniline, was prepared, and after one recrystallization from hot water, melted at 150.0° (reported[24] for *p*-fluoroacetanilide, 150.5°).

The reaction time can be decreased to 0.5 hr. with a slightly lower yield of *p*-fluoroaniline. From 0.25 mole of *N*-phenylhydroxylamine and 5.0 moles of anhydrous hydrogen fluoride (5° to 18°), a 46% yield of *p*-fluoroaniline, b.p. 185 to 187°, n_{D}^{25} 1.5337, was obtained.

Acknowledgment. The authors wish to thank D. Robins, W. Harple, C. Guy, and H. Hyer of the Energy Division Analytical Department for the cooperation provided during this investigation.

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[22] G. M. Bennett, G. L. Brooks, and S. Glasstone, *J. Chem. Soc.*, 1821 (1935). pK_b (in 30% ethanol) aniline, 9.90; *p*-fluoroaniline, 9.92.

[23] O. Kamm, *Org. Syntheses*, **Coll. Vol. I**, 445 (1951).

[24] A. Lapworth and L. K. Pearson, *J. Chem. Soc.*, **119**, 767 (1921).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

Fluorinated C-Nitroso Compounds. III.[1] The Reaction of Nitrosyl Chloride with Some Fluoroolefins in the Presence of Ferric Chloride or Actinic Light

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Various fluorinated ethylenes, tetrafluoroethylene, trifluorochloroethylene, and 1,1-difluoro-2,2,dichloroethylene react with nitrosyl chloride in the presence of ferric chloride to give good yields of nitrosoethanes, 1,1,2,2-tetrafluoro-1-chloro-2-nitrosoethane, 1,1,2-trifluoro-1,2-dichloro-2-nitrosoethane, and 1,1-difluoro-1,2,2-trichloro-2-nitrosoethane respectively. This reaction is also accompanied by a corresponding reduction of the ferric ion to the ferrous state.

Nitroso derivatives have also been obtained from hexafluoropropene and 1,1-difluoro-2,2-dichloroethylene with nitrosyl chloride in photochemical reactions.

It has been previously shown[1] that the major products of the reaction of the fluorinated olefins tetrafluoroethylene, trifluorochloroethylene, and 1,1-difluoro-2,2-dichloroethylene, respectively, with

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[1] Paper No. II in this series, *J. Org. Chem.*, 26, 3316 (1961).

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