n_D^{20} 1.4078) and 10.2 g. (94%) of di-*n*-butylamine, b.p. 158–160°, n_D^{20} 1.4171 (lit.[15] b.p. 159°). No unchanged silylamine was observed.

B. *With liquid ammonia.* To 50 ml. of liquid ammonia was added 17.0 g. (0.084 mole) of the silylamine. The two-phase system was stirred at Dry Ice–acetone temperature for 1 hr. The excess ammonia was allowed to evaporate and the residue was fractionally distilled to yield 1.3 g. (19%) of hexamethyldisilazane, b.p. 124–126°; 2.3 g. (21%) of di-*n*-butylamine, b.p. 158–159°; and 8.7 g. (51%) of recovered silylamine, b.p. 201–203°.

Reaction of N-trimethylsilylpyrrole with ammonia. Using the same procedure as outlined above, 71.8 g. (0.52 mole) of the silylpyrrole[11] (b.p. 152–154°) and 50 ml. of liquid ammonia were sealed in a bomb and allowed to stand at room temperature for 24 hr. Distillation yielded 16.2 g. (23%) of recovered silylpyrrole, b.p. 152–154° (lit.[11] b.p. 153°). Pyrrole and hexamethyldisilazane formed an azeotrope boiling at 113°. From gas chromatographic analysis (5′ silicone column, T = 111°) of the fractions boiling in this range, an estimated 65% yield of hexamethyldisilazane and 55% of pyrrole were obtained.

Acknowledgment. The assistance of M. C. Coon and F. J. Freenor is gratefully acknowledged.

SAN JOSE, CALIF.

[CONTRIBUTION FROM THE OLIN MATHIESON CHEMICAL CORP.]

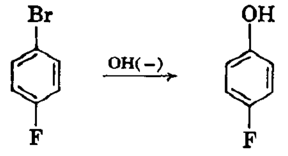
Aromatic Fluorine Compounds. II. Synthesis of *p*-Fluorophenol by the Selective Hydrolysis of *p*-Bromofluorobenzene[1]

MAX M. BOUDAKIAN, ROBERT J. EBER, W. EDWARD KUEHLEWIND, JR., AND RICHARD E. McARTHUR

Received February 1, 1961

The selective alkaline (calcium hydroxide) hydrolysis of *p*-bromofluorobenzene at pressures of 500 p.s.i.g. (250°; one to three hours) in the presence of copper salts can provide up to 79% yields of *p*-fluorophenol. The main by-product of this reaction is *p,p′*-difluorodiphenyl ether. Evidence is presented to suggest that a nonrearranging S_N2-type mechanism is occurring for this reaction. No *m*-fluorophenol was found to suggest a benzyne intermediate.

A novel method for the synthesis of *p*-fluorophenol (II) involves the alkaline hydrolysis of *p*-bromofluorobenzene (I). A survey of the literature reveals that a paucity of information is available on the selective alkaline hydrolysis of mixed *p*-dihalogenated benzenes. However, *p*-dihalogenated benzenes have been partially hydrolyzed under alkaline conditions to the *p*-halophenol, *e.g.*, *p*-chlorophenol from *p*-dichlorobenzene,[2] and *p*-fluorophenol from *p*-difluorobenzene.[3]



I II

Studies have been conducted with mixed *p*-dihalogenated benzenes and nucleophilic agents other than hydroxide ion. In most cases, the order of preferential halogen cleavage appeared to be a function of the electronegativity of the displaced halogen. Bergstrom and co-workers found the order of replacement, Br>Cl, in the reaction of *p*-bromochlorobenzene with potassium amide in ammonia.[4] Surprisingly, these investigators[4] found the order of replacement Br>I when *p*-bromoiodobenzene was treated with amide ion under similar conditions. Roberts and co-workers[5] noted a preferential cleavage of bromide ion when *p*-bromofluorobenzene was treated with potassium amide to give a mixture of *m*- and *p*-fluoroaniline.

With phenoxide ions, Leonard and Sutton[6] found that the reaction of *p*-bromofluorobenzene with potassium *p*-fluorophenate in the presence of copper bronze gave *p,p′*-difluorodiphenyl ether (III). The reaction of *p*-bromofluorobenzene with potassium phenate produced *p*-fluorodiphenyl ether as the sole product.[7,8]

III

With methoxide ion and mixed *p*-dihalogenated benzenes, the order of preferential halogen cleavage may be altered. De Crauw found that the reaction of *p*-chlorofluorobenzene with sodium methoxide

---

[1] This work was supported by the Chemical Corps, Engineering Command, U. S. Army, Contract No. DA-18-064-CML-2696.

[2] D. R. Patent 284,533 (1915); W. J. Hale and E. C. Britton, *Ind. Eng. Chem.* **20**, 114 (1928).

[3] F. Swarts, *Bull. Acad. roy. Belg., Classe des sci.*, 241 (1913); *Chem. Zent.*, **II**, 760 (1913).

[4] F. W. Bergstrom, R. E. Wright, C. Chandler, and W. A. Gilkey, *J. Org. Chem.*, **1**, 170 (1936). These investigators noted the following sequence with unsubstituted aryl halides and amide ion in ammonia; Br > I > Cl. Fluorobenzene was inert under these conditions to amide ion.

[5] J. D. Roberts, C. W. Vaughan, L. A. Carlsmith, and D. R. Semenow, *J. Am. Chem. Soc.*, **78**, 611 (1956).

[6] N. J. Leonard and L. E. Sutton, *J. Am. Chem. Soc.*, **70**, 1564 (1948).

[7] J. Lichtenberger and R. Thermet, *Bull. soc. chim. France*, 318 (1951).

[8] R. L Huang, *J. Chem. Soc.*, 3725 (1958).

TABLE I

HYDROLYSIS OF *p*-BROMOFLUOROBENZENE (I) WITH CALCIUM HYDROXIDE

FC_6H_4Br,	$Ca(OH)_2$		Catalyst,[c]	Time,[d]		Pressure,	% Conversion			% Yield
Moles	Moles	% Concn.[b]	% Concn.	Hr.	Temp.	p.s.i.g.	F^-[e]	Br^-[e]	FC_6H_4Br[g]	FC_6H_4OH
NONCATALYZED CONDITIONS										
0.6	0.3	3.1	—	4.5	225	325	0.1	[f]	26.3	39.5
1.2	0.6	6.4	—	2.25	275	910	4.1	48.7	59.4	57.8
1.2	0.6	6.4	—	2.25	300	1300	7.5	65.9	73.4	65.9[h]
1.2	0.6	6.4	—	0.75	300	1290	4.8	49.7	58.2	41.8
CATALYZED CONDITIONS										
0.6	0.6	6.4	Cu_2O:0.5	2.25	248	600	1.1	67	99	72
0.6	0.6	6.4	Cu_2O:5.0	2.25	248	600	2.5	98	99	71
0.6	0.6	6.4	Cu-N:10.0	5.0	100	Atmospheric	0	0	0	0
0.6	0.6	6.4	Cu-N:1.0	3.3	211	300	1.6	49	65	49
0.6	0.6	6.4	Cu-N:1.0	3.3	245	500	0.8	95	100	76
0.2	0.2	6.5	Cu-N:1.0	3.3	294	1000	4.5	92	99	64
0.2	0.2	6.5	Cu-N:1.0	3.3	310	1250	4.1	78	99	43[i]
0.2	0.2	6.5	Cu-N:1.0	3.3	341	2000	6.3	83	97	45[j]
0.6	0.6	6.4	Cu_2O:1.0	0	247	600	1	38	70	43
0.6	0.6	6.4	Cu_2O:1.0	1.0	250	600	2	92	100	79
0.6	0.6	6.4	Cu_2O:1.0	3.0	249	600	2	93	99	72
0.6	0.6	3.0	Cu-N:1.0	3.3	245	510	1	79	99	71
0.6	0.6	10.0	Cu-N:1.0	3.3	245	510	2	86	99	63
OTHER CATALYSTS										
0.2[a]	0.1	4.4	$CuCl_2$:1.0	2.25	275	505	0	75	77	74
0.2	0.1	4.4	CuO:1.0	2.25	275	615	1	84	99	75

[a] A total of 2.5 wt. % each (based on (I)) of Igepal CO-530 and CO-710 were employed. [b] Base concentration is with reference to water used. [c] Cu-N: copper naphthenate. Catalyst concentration is with reference to *p*-bromofluorobenzene (I) used. [d] The heating time required to reach the desired reaction conditions is 1.45 hr.; cooling the pressure vessel to room temperature requires 0.45 hr. [e] Based on assay of filter cake and aqueous filtrate. [f] Not analyzed. [g] Based on infrared analysis of distillation fractions and residue. [h] 2.7% yield of phenol. [i] 1.6% yield of phenol. [j] 10.0% yield of phenol.

in methanol resulted in 96.3% cleavage of fluorine and only 0.6% cleavage of chlorine to give *p*-chloroanisole and *p*-chlorophenol.[9] This investigator also noted that chlorine was principally cleaved in the reaction of *p*-bromochlorobenzene with sodium methoxide in methanol.

These miscellaneous studies reveal that the removal of halogen in mixed *p*-dihalogenated benzenes with nucleophilic agents does not always stand in a predicted sequence of replaceability. The order of displacement in such nucleophilic substitution reactions may be a function of several factors: nucleophilicity and basicity of the displacing agent[10]; nature of solvent employed; C—X bond strength; electronegativity of the displaced halogen; and nature of the dihalogenated benzene.

In the present study, the alkaline hydrolysis of *p*-bromofluorobenzene under superatmospheric pressure conditions (500 to 600 p.s.i.g.) and in the presence of copper-containing catalysts resulted in selective cleavage of bromine to give 70–79% yields of *p*-fluorophenol, along with 10–15% yield of *p,p'*-difluorodiphenyl ether (III) (based on 100% conversion of *p*-bromofluorobenzene by infrared spectroscopy) (Table I). The presence of *p*-bromophenol, hydroquinone, quinones, or hydroxydiphenyls in the distillation residues cannot be ruled out. Trace amounts of *p*-bromophenol could have been present due to a very weak infrared shoulder near 8.55 μ but it does not constitute unequivocal proof for its presence.[11,12]

The formation of by-product *p,p'*-difluorodiphenyl ether can be interpreted as an Ullmann reaction between calcium *p*-fluorophenate and unconverted *p*-bromofluorobenzene. *p,p'*-Difluorodiphenyl ether has been synthesized by Sutton and Leonard by the reaction of *p*-bromofluorobenzene and potassium *p*-fluorophenate in the presence of copper-bronze.[6] These investigators did not report the formation of any by-product *p,p'*-bromofluorodiphenyl ether.

The noncatalyzed hydrolysis of *p*-bromofluorobenzene also gave moderate yields of *p*-fluorophenol, but the latter generally contained phenol (as evidenced by infrared absorption at 14.55 μ). For example, with calcium hydroxide under these noncatalyzed conditions, the best data without phenol contamination were achieved at 275° (910 p.s.i.g.)

---

[9] T. De Crauw, *Rec. trav. chim.*, **50,** 573 (1931).

[10] J. O. Edwards, *J. Am. Chem. Soc.*, **76,** 1540 (1954).

(11) No evidence for hydroquinone was ever found in the distillation residues. However, these residues were usually analyzed by extraction in carbon tetrachloride and since hydroquinone is insoluble in this solvent the presence of this by-product could have been missed. R. Huisgen and J. Sauer, *Angew. Chem.*, **72,** 91 (1960) referred to unpublished results in the alkaline hydrolysis of *p*-halophenols which indicated that any hydroquinone formed was oxidized to benzoquinone in such reactions.

(12) Since H. E. Fierz-David and G. Stamm, *Helv. Chim. Acta*, **25,** 364 (1942) also found 2,4'- and 4,4'-dihydroxydiphenyl as the by-products in the reaction of *p*-chlorophenol with aqueous sodium hydroxide, it is possible that these by-products may also have been formed in the present reaction.

for 2.25 hours to give a 57.8% yield of *p*-fluorophenol (based on 59.4% conversion of *p*-bromofluorobenzene) (Table I). By-product phenol may arise from hydrogenolysis of *p*-bromofluorobenzene or sodium or calcium salts of *p*-fluorophenol. Reductive removal of halogens in aromatic nucleophilic displacement reactions involving unactivated dihalogenated benzenes at elevated temperatures was noted when benzene was found in the reaction of *p*-dibromobenzene and sodium ethoxide.[13] Support for the hydrogenolysis of *p*-fluorophenol and/or its salts is suggested by observations that treatment of *p*-chlorophenol with aqueous sodium hydroxide at 270° (320 p.s.i.g.) gave mainly phenol.[12]

By the use of copper-containing catalysts such as cuprous oxide, copper naphthenate, cupric oxide, or cupric chloride, the following improvements can be achieved as compared to the noncatalyzed hydrolysis of *p*-bromofluorobenzene: greater conversion of *p*-bromofluorobenzene; higher yield of *p*-fluorophenol; more moderate reaction conditions; and the noticeable decrease in, or absence of, by-product phenol (Table I). The effect of the catalyst on the rate of hydrolysis or on formation of by-product *p,p'*-difluorodiphenyl ether was not studied. Cupric acetate, manganese pyrophosphate, Devarda's metal (50% copper, 45% aluminum, 5% zinc), cobalt naphthenate, and copper powder also appeared to be effective catalysts. Less effective results were obtained with zinc bromide and potassium iodide. An attempt was made to develop optimum reaction conditions for the alkaline hydrolysis of *p*-bromofluorobenzene using calcium hydroxide in the presence of either copper naphthenate or cuprous oxide (Table I).

A catalyst concentration study was undertaken at concentrations of 0.5 and 5.0 weight % of cuprous oxide (based on weight of *p*-bromofluorobenzene) (Table I). Over this concentration range, there was no appreciable change in yield of *p*-fluorophenol (71 and 72%) or in conversion of *p*-bromofluorobenzene (99%).

Under atmospheric pressure reflux conditions, the alkaline hydrolysis of *p*-bromofluorobenzene occurred to a negligible extent with calcium hydroxide (in water or water-methanol), sodium hydroxide (water), or sodium formate (water). No reaction was obtained with copper naphthenate catalyst (1 wt. %) and calcium hydroxide (water) under similar atmospheric pressure conditions (Table I). With this catalyst system, the effect of higher temperatures on yield and product composition was studied. At 211° (300 p.s.i.g.), a 49% yield of *p*-fluorophenol was obtained (based on 65% conversion of *p*-bromofluorobenzene). From 245° (500 p.s.i.g.) to 294° (1000 p.s.i.g.), the conversion of *p*-bromofluorobenzene remained quantitative, with the yield of *p*-fluorophenol gradually decreasing from 76 to 64%. At the higher temperature range, the amount of fluorine cleavage began to increase. At 310° (1250 p.s.i.g.) phenol contamination occurred and was accompanied by a decrease in yield of *p*-fluorophenol.

The reaction times cited in the Tables I and II refer to the period during which the reaction mixture was maintained at a desired temperature. However, during the 1.45-hour heat-up time, some reaction would be occurring. This would also hold true for the 0.45-hour cooling period. At "zero" reaction time with cuprous oxide catalyst (1 weight %), a 43% yield of *p*-fluorophenol, based on 70% conversion of *p*-bromofluorobenzene, was obtained. Beyond this time, the conversions were quantitative, with 70 to 79% yields of *p*-fluorophenol.

The effect of higher base concentration using copper naphthenate catalyst (1 weight %), with constant base stoichiometry, did not change the conversion of *p*-bromofluorobenzene, but did lower the yield of *p*-fluorophenol.[14] (Table I).

In view of the decreasing solubility of calcium hydroxide in water with increasing temperatures,[15] the present reaction can be regarded to be heterogeneous. The use of a nonionic surfactant such as Igepal CO-630 in the cuprous oxide-catalyzed reaction of *p*-bromofluorobenzene with calcium hydroxide at 256° (600 p.s.i.g.) did not result in any significant effect on the yield or course of the reaction. However, the emulsifying agent may have become ineffective in the presence of base at the high temperature employed.

p-Fluorophenol was also obtained from *p*-bromofluorobenzene when sodium hydroxide was employed as the cleavage agent, but the reaction was accompanied more often with phenol and other by-product formation, in addition to greater fluorine cleavage. The best results without phenol contamination under noncatalyzed or copper-catalyzed conditions gave 49.5–61.6% yields of *p*-fluorophenol based on 91% conversion of *p*-bromofluorobenzene (Table II). However, the use of sodium hydroxide produced larger amounts of tars and gave erratic results either under catalyzed or noncatalyzed conditions. These problems were generally avoided when calcium hydroxide was substituted for sodium hydroxide. Some success was also achieved in the conversion of *p*-bromofluorobenzene to *p*-fluorophenol by the use of other cleavage agents. These included sodium acetate, disodium phosphate, sodium carbonate, calcium carbonate, sodium bicarbonate, and sodium formate. Because of the lower conversions of *p*-

---

[13] J. Balbiano, *Gazz. chim. Ital.*, **11**, 396 (1881); cited in J. F. Bunnett and R. E. Zahler, *Chem. Revs.*, **49**, 273 (1951).

[14] No by-product phenol was noted at the higher base concentrations.

[15] Calcium hydroxide is extremely insoluble in water: 0.185 g. at 0° and 0.077 g. at 100°. C. Hodgman, *Handbook of Chemistry and Physics*, 32nd edition, Chemical Rubber Publishing Co., Cleveland, Ohio, 1950, p. 470.

TABLE II

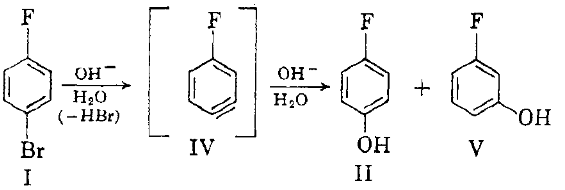
HYDROLYSIS OF *p*-BROMOFLUOROBENZENE (I) WITH SODIUM HYDROXIDE[a]

FC_6H_4Br, Moles	NaOH Moles	NaOH % Concn.	Catalyst, % Concn.	Temp.	Press., p.s.i.g.	% Conversion F^-	% Conversion Br^-	% Conversion FC_6H_4Br	% Yield FC_6H_4OH	% Yield C_6H_5OH
NONCATALYZED CONDITIONS										
0.2	0.2	4.1	—	250	550	1.6	74.8	91.3	61.6	0
1.2	1.2	6.9	—	275	925	17.5	68.3	80.6	26.5	15.8
0.6	0.6	3.3	—	300	1350	17.7	—[b]	98.7	20.1[c]	19.9
CATALYZED CONDITIONS										
0.2	0.2	4.5	CuO 1	225	300	1.2	51.0	95.4	44.0	0
0.6	0.6	3.6	$CuCl_2$ 1	225	360	6.0	86.0	91.0	49.5	0
0.2	0.2	4.7	Cu-N 1	200	120	8.0	37.0	61.0	20.0	12

[a] All reactions were conducted for 3.3 hours. [b] Not analyzed. [c] *m*-Fluorophenol was also formed in 1.95% yield.

bromofluorobenzene or due to extensive by-product formation, only a limited investigation was made with these materials.

Since the direct substitution product, *p*-fluorophenol, was consistently obtained in the present investigation, a nonrearranging S_N2-type mechanism is proposed. No evidence can be presented supporting a benzyne (elimination-addition) mechanism for the alkaline hydrolysis of *p*-bromofluorobenzene which would proceed through 4-fluorobenzyne (IV) to give a mixture of the unrearranged (*p*-fluorophenol, II) and rearranged (*m*-fluorophenol, V) products. No *m*-fluorophenol was found in any other experiments in which calcium hydroxide was employed as the base; in only one experiment with sodium hydroxide, a trace of *m*-fluorophenol, with characteristic infrared spectral bands at 8.90 and 10.50 μ, was obtained (Table II).[16]



It should be emphasized that reactions of *p*-bromofluorobenzene with nucleophilic agents other than hydroxide ion can give a product distribution which might suggest the presence of a benzyne-type intermediate (IV). Roberts and co-workers found that treatment of *p*-bromofluorobenzene with potassium amide in ammonia gave a 31% yield of fluoroanilines, consisting, respectively, of 20% *meta* and 80% *para* isomers.[5] These results have been interpreted by Roberts in terms of a benzyne mechanism and S_N2-type displacement.[5,17]

EXPERIMENTAL

p-Bromofluorobenzene (Eastman Kodak, White Label, No. 3140) was employed without further purification, n_D^{20} 1.5278, b.p. 152.0 to 152.5°.[17a]

The base concentration for sodium hydroxide (Mallinckrodt, AR, No. 7708) in Table II refers to a homogeneous solution; while in the case of calcium hydroxide (Mallinckrodt, AR, No. 4195) a slurry is obtained (Table I).[15] A sample of *m*-fluorophenol was prepared[18] in 45% yield by the diazotization-fluorination of *m*-aminophenol in anhydrous hydrogen fluoride, b.p. 65° at 9.0 mm., n_D^{25} 1.5093.

Non-ionic surface active agents, Igepal CO-160, CO-530, CO-630, and CO-710, a nonylphenoxypoly(ethyleneoxy)-ethanol (Antara Chemicals; General Aniline and Film) were employed in some experiments. The catalyst concentration is based on the weight of *p*-bromofluorobenzene employed. The following Mallinckrodt catalysts were used: cuprous oxide (AR, No. 4832); cupric chloride (AR, No. 4824). Copper naphthenate (8 wt. %, copper content) was obtained from Witco Chemical Co.

A monel microautoclave (total capacity, 312 ml.) was generally employed. For large scale studies, a monel autoclave (total capacity, 1780 ml.) was used (American Instrument Co., Silver Spring, Md.). Pressures recorded were not corrected for gauge calibration. A magne-dash autoclave (250-ml. total capacity), was also employed in some experiments (Autoclave Engineering Inc., Erie, Pa.).

Analytical. The reaction product was scanned in 0.1-mm. matched sodium chloride cells from 2.0 μ to 15.0 μ by use of a Perkin-Elmer Model 21 Infrared Recording Spectrophotometer. Samples were prepared in carbon tetrachloride (2 to 12 μ) and carbon disulfide (12 to 15 μ) solutions at a concen-

---

(16) A. T. Bottini and J. D. Roberts, *J. Am. Chem. Soc.*, **79**, 1458 (1957), studied the alkaline hydrolysis of *p*-halotoluenes to determine the balance between benzyne (elimination-addition) and the S_N2-type mechanism. They concluded that an S_N2-type mechanism was favored at decreasing temperature, in the presence of weaker bases and with the more easily ionizable halogens, I > Br > Cl.

(17) J. D. Roberts, *Chemical Society Symposia*, Special Publication No. 12, London, The Chemical Society, Burlington House, 1958, p. 115.

(17a) *p*-Bromofluorobenzene was prepared by the bromination of fluorobenzene; traces of the *ortho* isomers may be present. (Private Communication, Eastman Kodak, April 6, 1961). From other studies in this Laboratory, a maximum of 1% of *o*-bromofluorobenzene is formed from this synthesis route. Generally, Eastman Kodak *p*-bromofluorobenzene had an infrared spectrum identical to *p*-bromofluorobenzene prepared from *p*-bromoaniline by the Schiemann reaction (G. Schiemann and R. Pillarsky, *Ber.*, **64**, 1340 (1931)). Both samples of *p*-bromofluorobenzene had characteristic infrared spectral absorption at 9.39 μ (carbon tetrachloride solvent). An authentic sample of *o*-bromofluorobenzene was also prepared in a similar manner from *o*-bromoaniline (E. Bergmann, L. Engel, and S. Sandor, *Z. physik. Chem.*, **A156**, 397 (1931)), b.p. 157 to 158°C, n_D^{25} 1.5313, with characteristic infrared absorption at 13.3 μ (carbon disulfide solvent).

(18) H. L. Bradlow and C. A. VanderWerf, *J. Am. Chem. Soc.*, **70**, 654 (1948).

tration of 1 g. per 10 ml. of solvent. The following infrared spectral absorption bands were employed: *p*-bromofluorobenzene, 9.39 μ; *p*-fluorophenol, 7.55 μ (13.4 μ, for small concentrations); phenol, 14.55 μ; *m*-fluorophenol, 8.90 μ and 10.50 μ; *o*-fluorophenol, 10.82 μ; *p,p'*-difluorodiphenyl ether, 12.75 μ; and, *p*-bromophenol, 8.55 μ.

Inorganic fluoride in recovered filter cakes or aqueous layers was distilled as hydrofluosilicic acid from sulfuric acid solution. Fluoride ion was then titrated with standard thorium nitrate solution. For organic fluorine assay the sample was first oxidized in a Parr peroxide bomb using potassium nitrate as an accelerator and nitric acid to neutralize the excess peroxide.[19] An acid solution containing bromide ion was titrated potentiometrically with standard silver nitrate solution using a glass-silver electrode system.[20] *p*-Fluorophenol was also determined by use of potassium bromide-bromate reagent.[21,22]

Alkaline hydrolysis of p-bromofluorobenzene to p-fluorophenol. A typical hydrolysis reaction was conducted as follows: 1.20 moles (89.0 g.) of calcium hydroxide, 1.20 moles (210.0 g.) of *p*-bromofluorobenzene, 44.4 moles (800 g.) of water, and 2.1 g. of cuprous oxide catalyst were charged in a monel autoclave (1780-ml. capacity) and heated at 600 p.s.i.g. (250°) for 2.25 hr. Generally, the time required to reach the designated temperature was 1.45 hr.; after the specified reaction period, approximately 0.45 hr. was required to cool the reaction mixture to room temperature with air and water. The hydrolysis mixture was then poured from the pressure vessel and filtered. The pressure vessel was rinsed successively with 200 ml. each of diethyl ether and water, and the washings were also filtered. The filter cake was dried (wt. 21.3 g.) in a vacuum oven at 65° for 8 hr. prior to assay. (Found: F, 2.77; Ca, 29.5; Cu, 8.60—representing 98% recovery of copper.) The cooled (0°) filtrate containing calcium *p*-fluorophenate was acidified with concd. hydrochloric acid to *p*H 2, the organic layer was separated, and the aqueous layer was extracted successively with three 150-ml. portions of diethyl ether. (The aqueous layer was assayed for fluoride and bromide ion content to determine conversion data.) The organic layers were combined, dried over anhydrous magnesium sulfate, filtered, and distilled through a glass-helix-packed column (25 mm. × 91 cm. for this large scale experiment; 10 mm. × 25 cm. for the small scale experiments) at atmospheric pressure. The main distillation fraction, identified as *p*-fluorophenol by infrared spectroscopy, b.p. 182 to 183°, wt. 96.0 g., assayed 99.9% of *p*-fluorophenol by use of the potassium bromide-bromate reagent for total phenolics.

Anal. Calcd. for FC_6H_4OH: F, 16.95. Found, F, 16.99.

The total uncorrected yield of *p*-fluorophenol was 71.5%. Infrared spectral analysis of the distillation fractions indicated complete conversion of *p*-bromofluorobenzene, a maximum of 0.1% yield of *o*-fluorophenol and the absence of any phenol contaminant.

Tables I and II summarize the studies with calcium hydroxide and sodium hydroxide, respectively.

p-Fluorophenol was characterized as its *p*-fluorophenoxyacetic acid derivative.[23,24] From 0.10 mole of *p*-fluorophenol, 0.17 mole of sodium hydroxide, 0.13 mole of chloracetic acid, and 2.0 moles of water, a 97.0% yield of *p*-fluorophenoxyacetic acid was obtained. The product was successively recrystallized from benzene and water, m.p. 104.0 to 105.5°. (Reported for *p*-fluorophenoxyacetic acid: 105°[23]; 104.2 to 104.6°[24]).

Anal. Calcd. for $C_8H_7O_3F$: C, 56.47; H, 4.15; neut. equiv., 170.1. Found: C, 56.80; H, 4.21; neut. equiv., 170.

Effect of emulsifier. A control and emulsifier experiment were conducted concurrently. For the control experiment, cuprous oxide (2 wt. %) based on I, 0.6 mole of *p*-bromofluorobenzene, 0.6 mole of calcium hydroxide (6.4 wt. %, based on water) was heated at 256° (600 p.s.i.g.) for 2.25 hr. For the emulsifier experiment, Igepal CO-630 (5.25 g.; 5 wt. % based on *p*-bromofluorobenzene) was used. The results were identical in both experiments: 72% yield of *p*-fluorophenol based on 100% conversion. Assay of the filter cakes and aqueous layers indicated 2.5 and 93.5% of the bromine and fluorine, respectively, in *p*-bromofluorobenzene were cleaved.

Atmospheric pressure hydrolysis of p-bromofluorobenzene. Several atmospheric pressure reactions involving 0.20 mole of *p*-bromofluorobenzene and various cleavage agents were conducted in the presence of 0.0025 wt. % of Igepal CO-160 (based on water): sodium hydroxide (0.20 mole), water (150 ml.), and heated to reflux for 16 hr.; sodium formate (0.20 mole), water (150 ml.), and heated to reflux for 19 hr.; calcium hydroxide (0.10 mole), water (75 ml.), methanol (75 ml.), and heated to reflux for 9.5 hr.; calcium hydroxide (0.10 mole), water (100 ml.), and heated to reflux for 8 hr.; and, silica gel (20.0 g.), water (100 ml.), no surfactant employed, and heated to reflux for 19.0 hr. Bromide and fluoride assay of the aqueous layers indicated that halogen cleavage did not occur under the above reaction conditions.

Isolation of p,p'-difluorodiphenyl ether by-product. Following the distillation of *p*-fluorophenol, the distillation residue was further distilled to isolate the main by-product. This material (*p,p'*-difluorodiphenyl ether) had the following properties: b.p. 250.5°/760 mm.; 95 to 98°/4.0 mm.; n_D^{25} 1.5352; d_4^{20} 1.2314. (Reported[6] for *p,p'*-difluorodiphenyl ether, 240°/743 mm.) This material has characteristic infrared absorption at 12.75 μ.

Anal. Calcd. for $C_{12}H_8F_2O$: C, 69.9; H, 4.0; F, 18.5. Found: C, 70.2; H, 4.2; F, 18.2.

Acknowledgment. The authors wish to thank D. Robins, W. Harple, C. Guy, and H. Hyer of the Energy Division Analytical Department and R. A. Eber and S. Kolback of the High Pressure Laboratory for the cooperation provided during this investigation.

NEW HAVEN, CONN.

---

(19) W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis*, John Wiley & Sons, Inc., New York, N. Y., 1953.

(20) J. J. Lingane, *Electroanalytical Chemistry*, Interscience Publishers, New York, 1953, pp. 102–104.

(21) A. R. Day and W. T. Taggart, *Ind. Eng. Chem., Anal. Ed.*, **20**, 545 (1928). It is recognized that this method may be limited by the presence of phenolic impurities which could give erratic results.

(22) S. Siggia, *Quantitative Organic Analysis via Functional Groups*, John Wiley & Sons, Inc., New York, 1954.

(23) G. C. Finger, M. J. Gortatowski, R. J. Shiley, and R. H. White, *J. Am. Chem. Soc.*, **81**, 94 (1959).

(24) N. V. Hayes and G. E. K. Branch, *J. Am. Chem. Soc.*, **65**, 1555 (1943).