Aromatic Fluorine Compounds. II.[1]
A Novel Method of Introducing Fluorine into an Aromatic Ring

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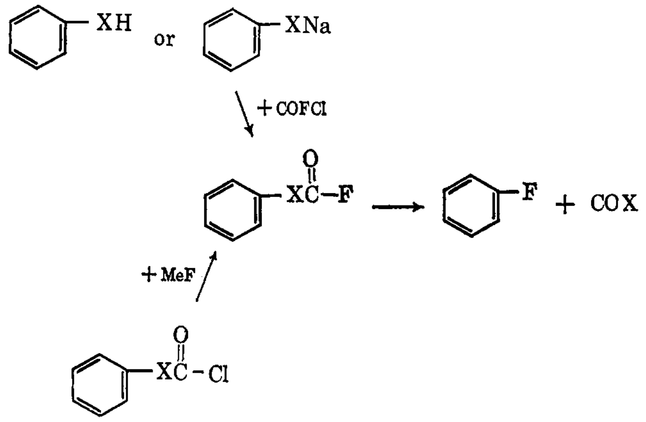
A novel and simple method for the introduction of a fluorine atom into an aromatic ring has been discovered. Fluorobenzene was prepared in high yield by the thermal decomposition of phenyl fluoroformate or thiofluoroformate. Although the reaction proceeds without catalyst, platinum surfaces give better efficiency. Attempts to prepare fluorobenzene in the liquid phase by an ionic mechanism were unsuccessful. Starting from phenol and COFCl an over-all conversion of the starting material phenol of 70% and an over-all yield of fluorobenzene of 90% was obtained. The preparation of phenyl fluoroformate and thiofluoroformate was investigated by three different methods. Attempts to decarbonylate tetrachloroterephthaloyl difluoride to *p*-difluorotetrachlorobenzene were unsuccessful.

While the introduction of a chlorine or bromine atom into an aromatic nucleus using the corresponding elementary halogen is well known in organic chemistry, the preparation of aromatic fluorine compounds has not yet been accomplished by this method. The method most frequently used for the fluorination of an aromatic ring is the Balz–Schiemann reaction[2] and its modification using a large excess of liquid HF as solvent.[3] This method, however, has its disadvantages, especially in large-scale operation. The fluorine–chlorine exchange reactions, which are commonly used in the aliphatic field, are applicable in the aromatic field only to a small number of highly activated compounds, such as chloranil[4] or nitrochlorobenzenes.[5] A third method, using halogen fluorides[6] or ClF_2^+ complexes[7] for the electrophilic fluorination of the ring, is mostly of academic interest. Simple aromatic fluorine compounds have not easily been prepared in high yield on any scale.

In the present paper we shall outline our procedure and its application to the fluorobenzene preparation. The application of this method to substituted aromatics and the introduction of more than one fluorine atom into the same nucleus will be described in parts III[8] and IV[9] of this series of publications.

The new method for the introduction of a fluorine atom into an aromatic nucleus can be described by the following scheme, where X is either an oxygen or sulfur atom.



The intermediate phenyl fluoroformate and thiofluoroformate can be prepared by different methods. Table I gives the results of these reactions. Since COFCl can be prepared relatively easily from $COCl_2$ and AsF_3,[10] SbF_3,[11] or SiF_4[12] (a waste product from fertilizer plants), its reaction with phenol appears to be the best method on a larger scale operation. It was found that the use of catalytic amounts of a tertiary amine results in nearly quantitative yield of the fluoroformate, suppressing the carbonate formation almost completely. The purity of the COFCl was not critical as long as it was in excess. Impurities of COF_2 and $COCl_2$ up to 16% in the COFCl did not decrease the yield of the fluoroformate. This is in agreement with the greater reactivity of COFCl toward cyclic ethers[10] or vicinal diols[13] compared with that of COF_2 or $COCl_2$. If no COFCl is available, a convenient laboratory method for the preparation of the fluoroformate consists of fluorinating the corresponding chloroformate with a metal fluoride or a metal hydrogen fluoride, such as NaF in acetonitrile or KHF_2, respectively.

The decomposition of chloroformates[14] or thiochloroformates[15] to the corresponding chlorides and of aliphatic fluoroformates to the fluorides[16] is known. The ionic decomposition reaction of these compounds was carried out in the liquid phase using such catalysts as tertiary amines,[14,16] dimethylformamide,[15] and BF_3–Et_2O.[16] All attempts to apply this method to aromatic fluoroformates were unsuccessful. The use of tertiary amines, such as tributylamine and pyridine, and of Lewis acids, such as BF_3 or BF_3–Et_2O, was investigated. In every case, CO_2 evolution was observed, but only high-boiling decomposition products were obtained. When completely different reaction conditions were used, such as passing gaseous phenyl fluoroformate in an nitrogen carrier stream through a hot tube, yields of fluorobenzene as high as 90% could be obtained. This behavior can be explained by a

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TABLE I

PREPARATION OF PHENYL FLUOROFORMATE AND PHENYL THIOFLUOROFORMATE

Reaction	Reactants, moles		NBu_3 catalyst, ml.	Solvent (ml.)	Reaction temp., °C.	Reaction pressure, p.s.i.	Reaction time, hr.	% conversion[a] of	% yield[a]	
	Phenol	COFCl		Toluene				Phenol	Phenyl fluoroformate	Diphenyl carbonate
1	0.106	0.24	...	75	−78 to −10	Atmospheric	3	1.5	100	...
2	0.106	0.73	...	75	40	Atmospheric	2.5	2.3	100	...
3	0.106	0.73	1	75	40	Atmospheric	2.5	6.2	100	...
4	0.106	0.73	1	75	60–80	Atmospheric	2.5	23.4	100	...
5	0.106	0.29	...	10	80	280	15	77.1	54.3	45.7
6	0.106	0.36	...	50	35	220	15	24.2	100	...
7	0.106	0.36	0.5	50	50	200	5	97.2	99.9	<0.1
	Sodium phenolate							Sodium phenolate		
8	0.086	0.36	...	50	50	200	5	13.6	100	...
	Phenyl chloroformate	KHF_2						Phenyl chloroformate		Phenol
9	0.64	1.16	...	...	100	Atmospheric	6	100	94	6
	Thiophenol	COFCl		Benzene				Thiophenol	Phenyl thiofluoroformate	
10	0.09	0.36	0.5	40	50	200	12	100	100	
	Phenyl thiochloroformate	NaF		CH_3CN				Phenyl thiochloroformate		
11	0.46	1.0	...	250	82	Atmospheric	16	95.2	100	

[a] The conversion of the starting material and the yields were determined by g.c. ratios of the crude reaction products before distillation. The yields after distillation were slightly lower owing to mechanical losses.

different reaction mechanism (in liquid phase an ionic and in gas phase an S_Ni mechanism[8]). Table II shows the influence of the tube material, filling, and reaction conditions on the conversion of the starting material and on the yield of fluorobenzene. The best results were obtained with platinum gauze as a filling material in either a platinum-lined Inconel or a quartz tube. In this case only a small amount of tar was formed in the reaction. The main by-product was phenol, one of the starting materials of step 1.

Phenyl fluoroformate is preferred over phenyl thiofluoroformate as starting material, since the amount of benzene formed in the decomposition reaction is negligible, the yield of fluorobenzene is higher, and the starting material is less expensive. In the pyrolysis reaction of phenyl thiofluoroformate larger amounts of carbon disulfide were obtained. A possible explanation is the disproportionation of the carbonyl sulfide, originally formed, to carbon dioxide and carbon disulfide. For example, at 800°, a 15.8% conversion of COS to CS_2 and CO_2 was observed.

Attempts to decarbonylate an acyl fluoride, such as tetrachloroterephthaloyl difluoride, were unsuccessful. A possible explanation is the higher thermal stability of the C–C bond compared with that of the C–O bond.

Experimental

Starting Materials.—Carbonyl chloride fluoride was prepared from $COCl_2$ and AsF_3.[10] The preparation of tetrachloroterephthaloyl difluoride from tetrachloroterephthaloyl dichloride and KF was reported earlier.[17] The AlF_3 catalyst on asbestos was prepared in our laboratory. Phenyl chloroformate can be purchased from Chemetron Chemicals and phenyl thiochloroformate from Aldrich Chemical Co. Boron trifluoride was obtained from the Matheson Co. All the other chemicals were purchased from supply houses.

Preparation of Phenyl Fluoroformate and Phenyl Thiofluoroformate. Method A.—In a typical experiment, phenol (0.106 mole), tributylamine (0.5 ml.) as a catalyst, and toluene (50 ml.) as a solvent were placed into a 150-ml. stainless steel lecture bottle, equipped with a pressure gauge and a stainless steel valve (Whitey 2RS4). Carbonyl chloride fluoride (0.36 mole) was condensed at −196° into this lecture bottle. The container was agitated for 5 hr. at 50° (external heating by one infrared lamp) with its contents at a pressure of 200 p.s.i. The volatile products, mostly HCl and excess of carbonyl halides, were bled off and the product was vacuum distilled. The results of three typical runs are listed in Table I as 5–7. Thiophenol was reacted with COFCl in the same way, except using benzene as a solvent. The result is given in Table I, reaction 10.

The following reactions were done at atmospheric pressure in standard glass equipment. Carbonyl chloride fluoride (0.24 mole) was condensed at −78° into a 300-ml. two-necked flask equipped with a magnetic stirrer, a dropping funnel, and a condenser filled with Dry Ice–acetone slush (−78°). A solution of phenol (0.106 mole) in 75 ml. of toluene was added slowly, keeping the mixture stirred and cooled (between −40 and −50°). After 1 hr. the external cooling was removed and the COFCl was kept under reflux. After another 2 hr. the Dry Ice condenser was removed and the content of the flask was allowed to warm to room temperature. The result of this reaction is given in Table I, reaction 1.

In a slight modification of this method the carbonyl chloride fluoride was passed through a solution of phenol in toluene without refluxing the COFCl. The results of these runs are given in Table I, reactions 2–4.

Method B.—Sodium phenolate (0.086 mole), toluene (50 ml.) as a solvent, and COFCl (0.36 mole) were placed into a 150-ml. stainless steel lecture bottle. The cylinder was agitated for 5 hr. at 50° with the contents at a pressure of 200 p.s.i. The volatile gases were bled off and the crude product was analyzed by gas

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Table II

Thermal Decomposition of Phenyl Fluoroformate and Phenyl Thiofluoroformate[a,b]

Starting material	Tube and filling	Temp., °C.	Contact time, sec.	% conversion of starting material	% yield			
Phenyl fluoroformate	Quartz tube				Fluorobenzene	Phenol		Tar + decompn. products
	AlF$_3$ on asbestos	650	3–4	100	2.0		98	
	Ag wool	650	4–5	100	0		100	
	Pt gauze + Ag-plated Cu wool	370–500	3–4	1.0	50		50	
	Charcoal	750	2	99.9	1.44	41.8		56.7
	Quartz granules	750	1.5	65.5	31.2	20.8		48.0
	Pt gauze	620	5	8.4	11.9	88.1		...
	Pt gauze	690	5	13.3	89.5	10.5		Trace
	Pt gauze	720	3–4	51.8	90.3	9.7		Trace
	Pt gauze	750	3	72.1	90.1	9.9		Trace
	Pt gauze	800	2–3	99.5	70.0	3.5		26.5
	Pt gauze	850	2–3	100	36.6	Trace		63.3
	Graphite tube							
	Pt gauze	750	3–4	63.2	14.6	5.5		79.1
	Monel tube							
	Hastelloy B helices	550	6	99.5	37.5		62.5	
	Hastelloy B helices	560	2.5	83.9	21.8		78.2	
	Hastelloy B helices	620	6	100	14.5		85.5	
	Pt gauze	550	2	54.2	47.0		53.0	
	Ni tube							
	Ni turnings	540	8	98.4	5.4		94.6	
	Pt-lined Inconel tube							
	Pt gauze	700	3.5	2.4	>90			...
	Pt gauze	750	3	34.5	93.0	5.8		1.2
	Pt gauze	850	2.5	61.0	86.1	9.7		4.2
Phenyl thiofluoroformate	Quartz tube				Fluorobenzene	Thiophenol	Benzene	Tar + decompn. products
	Pt gauze	600	2–3	<0.5	...	...	...	Trace
	Pt gauze	700	2–3	49.4	28.9	20.3	Trace	50.8
	Pt gauze	800	1–2	99.9	78.7	3.8	6.0	11.5

[a] All reactions were carried out at atmospheric pressure using dry nitrogen as a carrier gas. [b] The vapor pressure of the fluoroformate was kept in all cases at 100 mm.

chromatography. Table I, reaction 8, shows the results of this run.

Method C.—Phenyl chloroformate (0.64 mole) and KHF_2 (0.78 mole) were placed into a 500-ml. flask and stirred at 100°. After 5 hr., more KHF_2 (0.38 mole) was added. After one more hour of stirring the mixture at 100°, the product was extracted from the inorganic material with CH_2Cl_2 and vacuum distilled. The result of this run is given in Table I, reaction 9.

Phenyl thiochloroformate (0.46 mole) and NaF (1.0 mole) in 250 ml. of acetonitrile were heated, stirred, and refluxed. The product was filtered, the residue was washed with CH_2Cl_2, and the liquid phase was vacuum distilled. The result of this reaction is given in Table I, reaction 11.

Phenyl fluoroformate is a colorless, lachrymatory liquid, b.p. 47.1° at (7 mm.) [lit.[12] b.p. 153° (760 mm.)], $n^{26.5}\text{D}$ 1.4642, $d^{23.8}$ 1.201 g./ml., with F^{19} magnetic resonance of a singlet at 16.5 p.p.m. upfield from $CFCl_3$, characteristic of fluoroformates.[10,13] The infrared spectrum (liquid film) showed bands at 3070 (m, CH), 1830 (vs, C═O), 1595 (s, C═C), 1485 (s, C═C), 1460 (m, C═C), 1238 (vs, b), 1190 (m), 1160 (m), 1070 (m), 1022 (w), 983 (vs), 908 (m), 849 (m), 758 (vs), and 690 (s) cm.$^{-1}$.

Anal. Calcd. for $C_7H_5FO_2$: C, 60.00; H, 3.60; F, 13.56. Found: C, 60.63; H, 3.98; F, 13.66.

Phenyl thiofluoroformate is a colorless, lachrymatory liquid, b.p. 73° (9 mm.) $n^{24}\text{D}$ 1.5273, d^{24} 1.223 g./ml., with F^{19} magnetic resonance of a singlet at 43.6 p.p.m. downfield from $CFCl_3$ and proton magnetic resonance of a multiplet at 455 c.p.s. below TMS, characteristic for a phenyl group. The infrared spectrum (liquid film) showed bands at 3070 (m, CH), 1805 (vs, C═O), 1580 (m, C═C), 1482 (s, C═C), 1445 (s, C═C), 1270 (m), 1092 (s), 1032 (vs), 1020 (vs), 918 (m), 819 (m), 752 (vs), 739 (m), 702 (s), 685 (s) cm.$^{-1}$.

Anal. Calcd. for C_7H_5FOS: C, 53.85; H, 3.22; F, 12.18; S, 20.51. Found: C, 53.59; H, 3.39; F, 11.5; S, 20.42.

Preparation of Fluorobenzene by Gas Phase Pyrolysis of Phenyl Fluoroformate or Thiofluoroformate.—The same setup was used for all reactions, except for different reaction tubes and fillings of these tubes. A stream of dry nitrogen, controlled by a flowmeter, was passed through a small flask, containing the fluoroformate starting material. A fluoroformate vapor pressure of 100 mm. was controlled by external heating of the flask with an oil bath. In the case of the phenyl fluoroformate, the oil-bath temperature was kept at 100° and in the case of phenyl thiofluoroformate at 125°. The fluoroformate–nitrogen mixture was passed through an electrically heated tube and the products were quenched directly behind the exit of the tube by two cold traps, one at −78° and one at −196°. The second trap was connected to a mercury blow-off in order to prevent condensation of atmospheric moisture in the cold traps. The heating of the reaction tube was automatically controlled and the temperature of the tubular reactor was measured on its outside wall. The inlet part of the setup between the fluoroformate container and the reaction tube was heated by three infrared lamps to prevent condensation of the starting material. The conversion of the starting material and the yields were determined by weighing of the used-up starting material and of the collected products. The composition of the products was analyzed by gas chromatography. After separation, the compounds themselves were identified by infrared analyses. The difference in boiling points of benzene and fluorobenzene (80.10 and 84.85°, respectively) is large enough to distinguish between the two compounds by gas chromatography. The results of all these reactions are summarized in Table II.

Attempted Decarboxylation of Phenyl Fluoroformate in the Liquid Phase. A. Pyridine as Catalyst.—Pyridine (5 ml.) was placed into a 25-ml. flask equipped with a dropping funnel, nitrogen gas inlet, distillation head, magnetic stirrer, and an external oil bath for heating. The content of the flask was kept at 100° and stirred while phenyl fluoroformate (16 g.) was slowly added. Since no reaction was observed, the temperature was increased to 150°, whereon strong CO_2 evolution began. The volatile products were collected in a cold trap (−78°), protected through a mercury blow-off against atmospheric moisture. Analysis of the condensed product and of the residue in the flask revealed only a trace of fluorobenzene. The main product was a high-boiling solid.

B. Tributylamine as Catalyst.—The same setup was used as described under A. Decarboxylation occurred at somewhat lower temperature (100–120°), but only solid decomposition products could be isolated.

C. Pyridine as Catalyst and High-Boiling Mineral Oil as Solvent.—The same setup as described under A was used, but the size of the flask was changed from 25 to 250 ml. High-boiling mineral oil (150 ml.) was placed into the flask and heated to 150°. A mixture of 5 ml. of pyridine and 10 g. of phenyl fluoroformate was slowly added. The temperature of the oil bath was increased to 190° and all volatile products were carried over to the cold trap by passing a stream of dry nitrogen through the hot mineral oil. Analysis of the products again showed only trace amounts of fluorobenzene.

D. Boron Trifluoride as a Catalyst.—The same setup as described under A was used. Phenyl fluoroformate (4.5 g.) was placed into the flask and the temperature of the oil bath was increased to 120°. Boron trifluoride was passed through the liquid with a flow rate of 60 cc./min. The product carried over to the cold traps by the BF_3 consisted mainly of unreacted starting material and did not contain any fluorobenzene.

E. Boron Trifluoride Diethyl Etherate as a Catalyst.—The same setup as described under A was used. Freshly prepared BF_3–Et_2O (10 ml.) was placed into the flask, the oil-bath temperature was increased to 50°, and phenyl fluoroformate (5 g.) was slowly added. Then the temperature was increased to 120°. The product, collected in the cold trap, was poured into aqueous NaOH solution and extracted with ether. The ether solution was dried with $MgSO_4$ and checked for fluorobenzene by gas chromatography, but none was found.

Attempted Decarbonylation of Tetrachloroterephthaloyl Difluoride.—The decarbonylation was investigated in the liquid phase without and with catalysts such as BF_3 or AlF_3, and in the gas phase with catalysts such as BF_3, AlF_3, or TiF_4. However, in every case no decarbonylation could be obtained.

The Pyrolysis of *n*-Butyl Phosphate Esters and Salts[1]

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Separate pyrolyses of tributyl phosphate, dibutyl phosphoric acid, monobutyl phosphoric acid, and barium dibutyl phosphate each produced mixtures of butenes in high yields; barium monobutyl phosphate produced only a 40% yield of the butene mixture, but over 96% of it was butene-1. The extent of isomerization of butene-1 to *cis*- and *trans*-butene-2 varied with the acidity of the ester mixture being pyrolyzed, but the *cis*-to-*trans* ratio from ester pyrolysis remained constant at 0.74 ± 0.02. The composition of the butenes formed from any of the starting materials differed significantly from the thermodynamic equilibrium mixture.

Extensive isomerization of the olefins evolved from the pyrolysis of trialkyl phosphates was observed qualitatively by Baumgarten and Setterquist.[2] In determining the rate constants for the partial pyrolysis of tributyl phosphate (TBP) to form dibutylphosphoric acid (HDBP) and butene-1, we reported[3] that traces of the *cis–trans* isomers of butene-2 were detected after only a few per cent of the TBP had been converted to HDBP. The composition of the gases and liquids formed from the complete pyrolysis of TBP and its degradation products, HDBP and H_2MBP (monobutyl phosphoric acid), was then investigated and is reported here.

It was felt that isomerization would be inhibited if the barium salts of HDBP and H_2MBP [$Ba(DBP)_2$ and BaMBP] were pyrolyzed. Reports published[4] on the pyrolysis of dialkyl phosphates and their zinc salts[4b] and of dialkyl dithiophosphates[4b] and their zinc[4] and lead[4a] salts, however, indicate that much isomerization occurred. In the present study are included the barium salt of HDBP and the singularly acting barium monobutyl phosphate.

Results and Discussion

The composition of the gases obtained from the thermal decomposition of *n*-butyl phosphate esters and salts is shown in Table I. TBP and its acid degradation products, HDBP and H_2MBP, lost on the average over 80% of the butyl groups as butene isomers when heated at 241 to 245°. When TBP decomposed the gas initially evolved was all butene-1, but as the reaction progressed *cis*- and *trans*-butene-2 began to form.[3] More isomerization was found when HDBP decomposed, and the greatest isomerization resulted from the pyrolysis of H_2MBP.

Because the isomerization increased as the reaction mixture became more acid, and because phosphoric acid catalyzes butene isomerization,[5] the pyrolysis was also run with phosphoric acid present initially. A solution of TBP and phosphoric acid in 2:1 mole ratio (equivalent to three HDBP's) decomposed to give results the same as for HDBP. However, thermal decomposition of TBP in the presence of H_3PO_4 was not the only reaction occurring because ester interchange is known to occur more rapidly than thermal decomposition at a lower temperature[6]; the equilibrium mixture from ester interchange probably is established in minutes.

Pyrolysis of the barium salts of dibutyl and monobutyl phosphoric acids gave different results. BaMBP formed nearly pure butene-1; although the butene yield was low (40%), the composition was 98% butene-1 for the 300° product and 96% for that produced at 400–500°. The $Ba(DBP)_2$, however, pyrolyzed to yield 68% of an isomerized gas mixture that contained 60% butene-1, 18% *trans*-butene-2, and 22% *cis*-butene-2. Since *cis*-butene-2 is thermodynamically less stable than *trans*-butene-2, it is surprising to find a higher yield of it than the latter. TBP and the acid esters formed more *trans* than *cis* isomer in all cases. Haag and Pines[7] have shown that the *cis* isomer forms faster than *trans* in the isomerization of butene-1, but at equilibrium its quantity is only about half of that of the *trans* isomer. It therefore appears that the *cis*-to-*trans* conversion rate is radically altered in the case of the $Ba(DBP)_2$ pyrolysis, assuming that butene-1

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