over anhydrous sodium sulfate. After evaporation, the residue was chromatographed on silica gel (hexane–dichloromethane, 4:1) to provide the corresponding hydrazone **15** in 68%. The product **15** was identified by spectroscopic comparison with the authentic sample.[23]

Transformation of 6a into Monofluoro Carboxylic Acids. 1-Methoxy-1-(phenylthio)-2-fluoro-1-hexene (16a). To a stirred solution of 0.5 mmol of **6a** in 0.5 mL of ether was added dropwise a solution of 1 mmol of butyllithium in hexane solution (1.8 M) at −78 °C under a nitrogen atmosphere. After 3 h, the temperature was raised to room temperature, and then saturated aqueous ammonium chloride was added to the reaction mixture. The solution was extracted repeatedly with ether and washed with brine and then dried over anhydrous sodium sulfate. After evaporation, the residue was chromatographed on silica gel (hexane–AcOEt, 95:5) to provide **16a** in 70% yield: ^{1}H NMR ($CDCl_3$) δ 0.6–1.8 (m, 7 H, C_3H_7), 2.50 (dt, 2 H, CH_2CF=, J_{H-H} = 6 Hz, J_{H-F} = 22 Hz), 3.50 (s, 3 H, OCH_3), 7.1–7.5 (m, 5 H, C_6H_5); IR 1660 cm^{-1} (C=O); MS m/e 240 (M^+), 197 ($M^+ - C_3H_7$). Anal. Calcd for $C_{13}H_{17}FOS$: C, 64.97; H, 7.13. Found: C, 64.85; H, 7.18.

The other ketene hemiacetals **16b** and **16c** were prepared similarly.

1-Methoxy-1-(phenylthio)-2-fluoro-3-methyl-1-hexene (16b, isomer 1): ^{1}H NMR δ 0.93 (t, 3 H, CH_3CH_2, J_{H-H} = 7 Hz), 1.15 (d, 3 H, CH_3CH, J_{H-H} = 7 Hz), 1.47 (q, 2 H, CH_2, J_{H-H} = 7 Hz), 2.93 (sextet d, 1 H, CH, J_{H-H} = 7 Hz, J_{H-F} = 32 Hz), 3.55 (s, 3 H, OCH_3), 7.13–7.57 (m, 5 H, C_6H_5); MS m/e 240 (M^+), 255 ($M^+ - CH_3$), 211 ($<M^+ - C_2H_5$). Anal. Calcd for $C_{13}H_{17}FOS$: C, 64.97; H, 7.13. Found: C, 64.62; H, 7.12.

1-Methoxy-1-(phenylthio)-2-fluoro-3-methyl-1-hexene (16b, isomer 2): ^{1}H NMR δ 0.90 (t, 3 H, CH_3CH_2, J_{H-H} = 7 Hz), 1.13 (d, 3 H, CH_3CH, J_{H-H} = 7 Hz), 1.45 (q, 2 H, CH_2, J_{H-H} = 7 Hz), 3.03 (sex d, 1 H, CH, J_{H-H} = 7 Hz, J_{H-F} = 32 Hz), 3.63 (s, 3 H, OCH_3), 7.13–7.43 (m, 5 H, C_6H_5); MS m/e 240 (M^+), 225 ($M^+ - CH_3$), 211 ($M^+ - C_2H_5$). Anal. Calcd for $C_{13}H_{17}FOS$: C, 64.97; H, 7.21. Found: C, 64.88; H, 7.21.

1-Fluoro-1-phenyl-2-methoxy-2-(phenylthio)ethene (16c): ^{1}H NMR ($CDCl_3$) δ 3.70 (s, 3 H, OCH_3), 7.1–8.0 (m, 10 H, C_6H_5, SC_6H_5); ^{19}F NMR ($CDCl_3$) δ 28.3 (s). Anal. Calcd for $C_{15}H_{13}FOS$: C, 69.21; H, 5.03. Found: C, 69.24; H, 5.17.

2-Fluorohexanoic acid (17a): A mixture of **16a** and 5 mL of 90% H_2SO_4 was heated at 50 °C for 5 h. After cooling, the solution was extracted repeatedly with ether, washed with water, and then dried over anhydrous sodium sulfate. Evaporation of the solvent provided **17a** in 95% yield. Its spectral data were completely identical with those of the authentic sample.[24,30]

The other fluoro carboxylic acids **17b** and **17c** were similarly prepared and **17c** was identified by spectroscopic comparison with the authentic sample.[24,30]

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2-Fluoro-3-methylpentanoic acid (17b): ^{1}H NMR ($CDCl_3$) δ 0.77–1.70 (m, 9 H, s-Bu), 4.85 (dd, 1 H, CH, J_{H-H} = 4 Hz, J_{H-F} = 50 Hz), 8.73 (s, 1 H, CO_2H); ^{19}F NMR ($CDCl_3$) δ 116 (dd). Anal. Calcd for $C_6H_{11}FO_2$: C, 53.72; H, 8.26. Found: C, 53.42; H, 8.54.

Nucleophilic Substitution of 6 with Benzenes.

Phenyl 1-Phenyl-2,2,2-trifluoroethyl Sulfide (18a). To a stirred solution of 2.25 mmol of aluminum trichloride and 12 mmol of benzene in 3 mL of CH_2Cl_2 was added dropwise 1.5 mmol of **6a** at −78 °C under a nitrogen atmosphere. After 2.5 h of stirring, the solution was warmed to room temperature and 8 mL of water was added. The resulting solution was extracted repeatedly with ether and washed with aqueous sodium bicarbonate, water, and brine. The extracts were dried over anhydrous sodium sulfate and evaporated. The residue was chromatographed on silica gel (hexane–AcOEt, 20:1) to provide pure **18a** in 83% yield: ^{1}H NMR (CCl_3) δ 4.37 (q, 1 H, CH, J_{H-F} = 8 Hz), 7.0–7.5 (m, 10 H, C_6H_5); MS m/e 268 (M^+), 199 ($M^+ - CF_3$), 159 ($M^+ - C_6H_5S$); calcd for $C_{14}H_{11}F_3S$ m/e 268.0533, found 268.0522.

The other derivatives **18b** and **18c** were similarly prepared.

4-Chlorophenyl 1-Phenyl-2,2,2-trifluoroethyl Sulfide (18b). Sixty equivalents of benzene was used to react with the substrate **6b**, and the product **18b** was separated using hexane–AcOEt (9:1) as an elution solvent; ^{1}H NMR (CCl_4) δ 4.37 (q, 1 H, CH, J_{H-F} = 8 Hz), 6.8–7.9 (m, 9 H, C_6H_5 and C_6H_4); MS m/e calcd for $C_{14}H_{10}ClF_3S$ m/e 302.0143, found 302.0156.

1-(4-Isobutylphenyl)-2,2,2-trifluoroethyl phenyl sulfide (18c): ^{1}H NMR ($CDCl_3$) δ 0.91 (d, 6 H, CH_3, J_{H-H} = 6.6 Hz), 1.86 (m, 1 H, $CH(CH_3)_2$), 2.46 (d, 2 H, CH_2, J_{H-H} = 7.1 Hz), 4.45 (q, 1 H, $CHCF_3$, J_{H-F} = 8.6 Hz), 7.09–7.50 (m, 9 H, C_6H_5 and C_6H_4); ^{19}F NMR ($CDCl_3$) δ 10.6 (d); MS m/e 324 (M^+), 215 ($M^+ - C_6H_5S$); calcd for $C_{18}H_{19}F_3S$ m/e 324.1159, found 324.1161.

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Registry No. **1a**, 2262-07-9; **1b**, 129264-94-4; **1c**, 77745-03-0; **1d**, 5187-62-2; **2**, 129264-95-5; **3**, 129264-96-6; **4**, 102687-64-9; **5**, 622-38-8; **6a**, 108200-49-3; **6b**, 129285-45-6; **6c**, 129264-97-7; **6c'**, 129264-98-8; **7**, 129264-99-9; **8**, 129265-00-5; **9**, 129265-01-6; **10**, 108200-50-6; **11**, 129265-02-7; **12**, 129265-03-8; **13**, 91922-48-4; **16a**, 108200-51-7; **16b**, 129265-04-9; **16c**, 129265-05-0; **17a**, 1578-57-0; **17b**, 6087-16-7; **17c**, 1578-63-8; **18a**, 123228-00-2; **18b**, 129265-06-1; **18c**, 129265-07-2; MeOH, 67-56-1; MeONa, 124-41-4; Et_4NOTs, 35895-69-3; AcONa, 127-09-3; AcOH, 64-19-7; *n*-BuLi, 109-72-8; *s*-BuLi, 598-30-1; PhLi, 591-51-5; $SnCl_4$, 7646-78-8; $BF_3{\cdot}OEt_2$, 109-63-7; $TiCl_4$, 7550-45-0; $AlCl_3$, 7446-70-0; Pt, 7440-06-4; carbon, 7440-44-0; benzene, 71-43-2; isobutylbenzene, 538-93-2.

Lewis Acid Mediated Fluorinations of Aromatic Substrates

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Direct fluorination of aromatic substrates, PhZ (Z = Cl, CHO, $CH(OCH_2)_2$, NO_2, $CO_2CH_2CH_3$, OH, $NHCH_3$, OCH_3, CH_3), in the presence and absence of BCl_3 or $AlCl_3$, has been investigated. For PhCl and PhOH, inclusion of boron trichloride increased the percent conversion and the amount of para product. However, $AlCl_3$ caused an increase in the ortho regioselectivity in the reaction with chlorobenzene. For PhCHO, inclusion of a Lewis acid decreased the percent conversion. In the presence of BCl_3, the ethylene glycol acetal of PhCHO gave only ortho and para fluorinated derivatives with improved conversion. $PhCO_2CH_2CH_3$ was unaffected by the inclusion of Lewis acid while the percentage conversion of $PhNO_2$ increased only slightly. Fluorination of $PhNHCH_3$, $PhOCH_3$, or $PhCH_3$ gave complex reaction mixtures. *p*-Nitroanisole gave rise to only 2-fluoro-4-nitroanisole in the presence or absence of either Lewis acid.

Selective fluorination of organic molecules is of great interest to many biochemists and organic chemists because of the biological importance of these species. Within the last 10 years new reagents have been developed that

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Table I. Fluorination of Chlorobenzene in $FCCl_3$ with 5% F_2 in N_2 at -78 °C

Lewis acid	Lewis acid/PhCl, mol/mol	volume catalyst solution $FCCl_3$:CH_2Cl_2, mL	% convn	% product[f] ortho	meta	para
none	–[a]	0.0	10.5	4.7	1.2	4.6
none	–[a]	c	9.5	3.7	0.9	4.9
BCl_3	0.11[a]	1.0[d]	27.2	7.1	2.2	18.0
BCl_3	0.56[a]	5.0[d]	62.0	13.0	3.1	45.9
BCl_3	0.90[a]	8.0[d]	95.2	15.2	6.7	73.3
$AlCl_3$	0.17[b]	0.2[e]	15.2	8.2	2.4	4.6
$AlCl_3$	0.56	0.5[e]	21.2	11.2	4.0	5.9
$AlCl_3$	1.01[b]	0.9[e]	39.9	20.7	8.0	11.2

[a] 1.0 g of PhCl. [b] 0.10 g of PhCl. [c] 24.0 mL of $FCCl_3$ and 1.0 mL of CH_2Cl_2. [d] 1 M BCl_3 in CH_2Cl_2; total volume = 25.0 mL. [e] 1 M $AlCl_3$ in $PhNO_2$; total volume = 25.0 mL. [f] Determined by GC.

broaden the spectrum of available organofluorine compounds.[1] However, a general weakness remains in the methodology for the preparation of ring fluorinated aromatic compounds. Efficient means for the introduction of fluorine into aromatic substrates have been sought since Balz and Schiemann studied the thermal decomposition of aryldiazonium fluoroborates.[2] This reaction, often difficult to regulate, requires the corresponding aniline as a starting material. Ring fluorinated compounds are of particular interest for potential new drugs[3] as well as for metabolic studies.[4] One area where the use of organofluorine compounds has increased dramatically is that of photoaffinity labeling, which has recently been very well described by Soundararajan and Platz.[5] Cesium fluoroxysulfate[6] and acetyl hypofluorite[1c,7] have been used successfully to cause electrophilic fluorination of aromatic rings. Not surprisingly, different aromatic substitution patterns are observed with the different reagents.[6]

Early attempts to directly fluorinate organic compounds resulted in explosions and charring due to the low selectivity of elemental fluorine and the exothermicity of its reactions.[8] Attempts to moderate the reactivity of fluorine by dilution with inert gases such as nitrogen have been successful.[9] Reduced temperatures have also been used to help control the reaction. Rozen[10] has found that the addition of chloroform in the solvent $FCCl_3$ to polarize the fluorine molecule when fluorinating tertiary unactivated sites was essential for the selectivity observed in the reaction. It is interesting to note that the solvent/temperature used for direct fluorination of aromatic compounds affects the substitution pattern. For example, nitrobenzene gives an ortho:meta:para ratio of 1.7:6.2:1 at 5 °C in acetic acid with 29% conversion[11] while in acetonitrile at -15 °C with 38% conversion, a ratio of 1.5:9:1 is observed.[9] This difference indicates that there is probably some interaction between the solvent and the fluorine prior to reaction. Interestingly, in the nitrobenzene fluorination, addition of BF_3 increased the percent conversion and altered the ortho:meta:para ratio to 0.6:3.1:1.[11b] Two other reports note that the addition of BF_3 during direct fluorinations alters the course of the reaction.[12] In this paper, we report the results of a systematic investigation using Lewis acids to assist in electrophilic aromatic fluorinations.

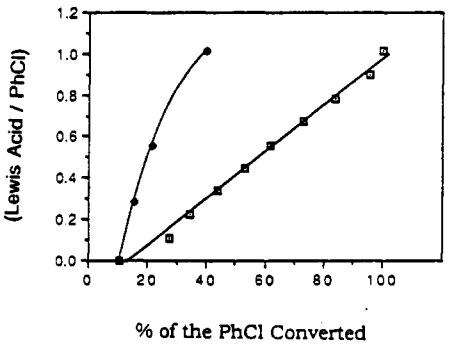
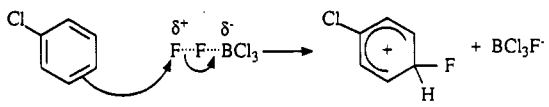


Figure 1. Millimoles of Lewis acid/PhCl vs percent PhCl consumed. (□) BCl_3, (●) $AlCl_3$.

Scheme I



Results and Discussion

Both the yield and the regioselectivity of fluorination are affected by the addition of a Lewis acid. The reaction of chlorobenzene is illustrative. As shown in Table I, only 10% of the chlorobenzene is fluorinated in $FCCl_3$, or $FCCl_3$ with added CH_2Cl_2, in the absence of Lewis acid at -78 °C using 5% F_2 in N_2. Boron trichloride (1 M) in methylene chloride was added as catalyst. In order that the chlorobenzene concentration be constant, the volume of $FCCl_3$ was decreased as the CH_2Cl_2 solution was added such that in each reaction 1.0 g chlorobenzene was dissolved in 25 mL. Several features of the Lewis acid mediated fluorination of chlorobenzene are worth noting. First, a plot of moles BCl_3/mole chlorobenzene vs percent conversion is linear with 100% conversion attained only when a 1:1 mole ratio is used (Figure 1). The time required for fluorination of chlorobenzene increased from 1.0 to 3.0 h as the amount of BCl_3 was increased. That a stoichiometric amount of BCl_3 is needed for complete conversion to product is not surprising since it is expected that the fluoride formed in the reaction will strongly co-

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Table II. Fluorination of Aromatic Substrates in $FCCl_3$ with 5% F_2 in N_2 at −78 °C

PhZ	PhZ, g	BCl_3/PhZ, mol/mol	solvent volume, mL	% convn[a]	% product[a] ortho	meta	para
PhCHO	0.3	0.0	25	2.2	–	2.2	–
PhCHO	0.3	0.5	25	2.1	–	2.1	–
PhCHO	0.3	1.1	25	0.9	–	0.9	–
$PhCH(OCH_2)_2$	0.3	0.0	150	19.7	14.6	–	5.1
$PhCH(OCH_2)_2$	0.3	0.5	150	29.2	18.1	–	11.1
$PhCH(OCH_2)_2$	0.3	1.5	150	41.7	24.2	–	17.5
$PhNO_2$	0.5	0.0	25	0.0	–	–	–
$PhNO_2$	0.5	0.5	25	2.0	–	2.0	–
$PhNO_2$	0.5	1.1	25	5.0	–	5.0	–
$PhCO_2CH_2CH_3$	0.3	0.0	25	0.0	–	–	–
$PhCO_2CH_2CH_3$	0.3	1.1	25	0.0	–	–	–

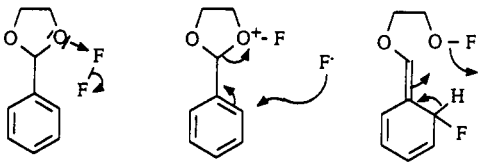
[a] Determined by GC.

ordinate with the Lewis acid. Once coordinated, the BCl_3 can no longer be effective in promoting the fluorination, as shown in Scheme I. Second, the effect of BCl_3 on the regiochemistry of fluorination of chlorobenzene is noteworthy. Under these conditions only monofluorinated products were observed. As the concentration of BCl_3 was raised, the percentage yield of all isomers increased (see Table I), but the relative amount of para product is especially enhanced. The ortho:meta:para ratio changes from 45:11:44 in the absence of BCl_3 to 17:7:76 for the case where a stoichiometric amount of BCl_3 was added. The boron trichloride complexed fluorine is larger than fluorine itself and thus the bulk of the fluorinating agent may play a role in determining the regiochemistry. As shown by the ratio of ortho:meta:para isomers, the relative yield of meta isomer is slightly decreased because of the increased electrophilicity of the fluorinating agent. The estimated error of these ratios is ±5%.

When $AlCl_3$ is used as the Lewis acid in the fluorination of chlorobenzene, the percent conversion to product is not changed as dramatically as with BCl_3 (Figure 1). A smaller quantity of chlorobenzene (0.1 g) was fluorinated in the presence of $AlCl_3$, but the ratio of moles $AlCl_3$ to chlorobenzene was the same. Aluminum chloride (1 M) in nitrobenzene was added to the solution in the same manner as the BCl_3 in CH_2Cl_2 so that the total volume was 25 mL. Again, the overall yield of each product increased with increasing $AlCl_3$ concentration (Table I). However, the ortho:meta:para ratio remains constant at 52:18:30 for all concentrations of $AlCl_3$ examined. The Lewis acid and the substrate, chlorobenzene, are mixed in the solvent prior to the addition of fluorine. Hence, one might expect coordination between the $AlCl_3$ and chlorobenzene to occur before the introduction of fluorine. The affinity of chlorobenzene for $AlCl_3$ is expected to be greater than for BCl_3. As a result the $AlCl_3$ is more likely to be near the chlorine of the aromatic substrate and therefore assist in directing the incoming fluorine to the ortho position. It is synthetically significant that one catalyst increases ortho selectivity while another increases para selectivity.

Table II provides details of the fluorination of some other substrates that were studied. In the absence of Lewis acid, benzaldehyde gives a very poor conversion to *m*-fluorobenzaldehyde. Addition of the BCl_3 gives rise to a complex which precipitates from solution and results in a decreased yield of product. Conversion of benzaldehyde to its ethylene glycol acetal, however, dramatically changes the regiochemistry of the fluorination. Due to its insolubility in $FCCl_3$, 0.1 g of the acetal was fluorinated in 150 mL of solvent. Although the conversion of benzaldehyde to its fluoro derivative is only of the order of 2%, the regioselectivity observed is exclusively meta (see Table II). By contrast, the acetal gives much higher conversions but

Scheme II



only ortho and para regioisomers are observed. It is worth noting that the para regioselectivity as well as the percent conversion increases as the ratio of Lewis acid to substrate increases. The ortho:meta:para ratio changes from 74:0:26 in the absence of BCl_3 to 58:0:42 in the presence of 1.5 molar excess. The high ortho selectivity in the absence of catalyst may be due to direct interaction of fluorine with the acetal as shown in Scheme II. This is reminiscent of the bromination of ketals studied by Garbisch.[13] Coordination of the Lewis acid with the acetal is expected to decrease the importance of this pathway.

Neither nitrobenzene nor ethyl benzoate are fluorinated in the absence of Lewis acid under the reaction conditions. With a 1:1 mole ratio of BCl_3 to $C_6H_5NO_2$ only 5% conversion to *m*-fluoronitrobenzene was realized, but the benzoate still was not fluorinated. Activated aromatic systems such as *N*-methylaniline, anisole, and toluene gave complex reaction mixtures and were not investigated further.

Misaki[12a,15] has studied the fluorination of phenols under a wide variety of conditions. His studies were conducted at −20 to 0 °C in solvents including chloroform, tetraglyme, acetonitrile, methanol, and trifluoroacetic acid. As the solvent polarity increased from $HCCl_3$ to tetraglyme to CH_3CN, Misaki[12a] noted an increase of the ortho:para ratio from 1.8 to 2.5 to 3.6 at −20 °C. Our results are consistent with his observations, at −78 °C in the less polar solvent, $FCCl_3$, a 1.1:1 ortho:para ratio was observed. In general, there is qualitative agreement between Misaki's results and those reported here; the small differences may easily be attributed to different experimental conditions.

Misaki and co-workers[16] have suggested that the ortho selectivity observed during the fluorination of phenol is due to a cyclic mechanism. Addition of a Lewis acid as described in this work would tend to decrease the availability of this pathway because of coordination and thus the para selectivity should increase. The results for BCl_3, included in Table III, show that the percentage conversion of the phenol and the para selectivity increased with BCl_3

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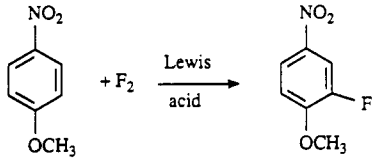
Table III. Fluorination of Phenol[a] in CH_2Cl_2 with 5% F_2 in N_2 at −78 °C

Lewis acid	Lewis acid/PhOH, mol/mol	% convn[b]	% product[b] ortho	meta	para
–	–	58	30	–	28
BCl_3	0.5	88	26	–	62
BCl_3	1.0	100	21	–	79
$AlCl_3$	0.5	100	36	–	64
$AlCl_3$	1.0	100	27	–	73

[a] In all cases 0.5 g of PhOH in 25 mL of solvent. [b] Determined by GC.

Table IV. Fluorination of *p*-Nitroanisole[a] in CH_2Cl_2



Lewis acid	Lewis acid/substrate, mol/mol	% yield[b]
none	–	54
BCl_3	1.0	33
BCl_3	2.3	52
$AlCl_3$	2.3	50
BCl_3	4.6	55

[a] In all cases, 0.1 g in 30 mL CH_2Cl_2. [b] Determined by GC.

concentration. Similarly, $AlCl_3$, when present with phenol in a stoichiometric amount, gives 100% conversion with 27% ortho and 73% para product. This was the only substrate studied where the yield of ortho product actually decreased in the presence of Lewis acid.

p-Nitroanisole which contains an activating and a deactivating group was fluorinated in CH_2Cl_2 because of its lack of solubility in $FCCl_3$. In the presence of absence or catalyst approximately 50% conversion to 2-fluoro-4-nitroanisole, a photoprobe for photoaffinity labeling studies[14] was observed. This molecule has been prepared previously using acetyl hypofluorite in 47% yield.[7a] The advantage of the procedure presented here is that, in addition to a slightly better yield, there is no need to prepare the intermediate acetyl hypofluorite. The effect of Lewis acid for this fluorination is interesting as shown in Table IV. Initially the Lewis acid may coordinate with the substrate causing a decreased yield. However, when more than a stoichiometric amount of BCl_3 or $AlCl_3$ is included, the yields are comparable to those obtained with no additive present during the fluorination. A possibility exists that the second mole of Lewis acid coordinates the fluorine.

In conclusion, we have shown that inclusion of a Lewis acid additive to an aromatic substrate in a nonpolar solvent affects not only the percent conversion to fluorinated derivatives but also the regioselectivity of the reaction. The fact that intermediate fluoroxy compounds are not necessary for the successful fluorination of aromatic compounds is also noteworthy. As noted by Grakauskas,[9] the fluorination appears to proceed by an electrophilic mechanism. The direct fluorination of aromatic substrates should be especially useful for the preparation of compounds containing ^{18}F because of its short half-life. We are continuing our investigation on the interaction of fluorine with aromatic compounds in the presence of Lewis acids.

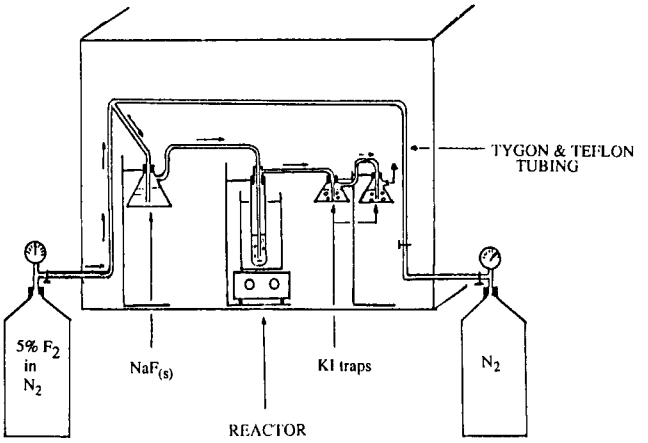


Figure 2. Fluorination system.

Experimental Section

^{19}F NMR (90 MHz) spectra were recorded with a Varian EM-390 spectrometer. Capillary GC analysis was done using a Hewlett-Packard 5880 or 5890 gas chromatograph equipped with a split/splitless injection and FID detector. A SE-30, 26-m fused silica column using a HP 3392A integrator was used with the HP 5890 and a DB-5, 15-m column using a HP 5880A terminal integrator.

General Fluorination Procedure. Caution: Fluorine is a powerful oxidant, a poisonous and corrosive gas. Needless to say, reactions using F_2 should be conducted with care. The experiments used 5% F_2 in N_2, premixed and provided by Air Products, in the set up shown in Figure 2,[17] which is constructed with glass vessels and tygon and Teflon tubing. If normal safety procedures are used, work with dilute fluorine mixtures is safe and has not resulted in any accidents over the years that we have been using them. The flow rate for all reactions was maintained as close to 1 mL/s as possible. All substrates were distilled prior to fluorination. Following fluorination, a crude ^{19}F NMR spectrum was obtained that showed only monofluoro products for all aromatic substrates other than anisole, toluene, and *N*-methylaniline. The chemical shifts obtained were in agreement with those reported in the literature.[7a,18] The crude product mixture was extracted three times with 20 mL of H_2O to remove fluoride and catalyst, dried over $MgSO_4$, filtered, and analyzed by GC without concentration. In the case of the ethylene glycol acetal of benzaldehyde, after aqueous extraction, the reaction mixture was made acidic with 10% H_2SO_4 and stirred overnight. This was neutralized with $NaHCO_3$, extracted with H_2O, dried, filtered, and analyzed. Standard monofluoro compounds were obtained from Alfa Products or Aldrich Chemical Co.

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Registry No. PhCHO, 100-52-7; $PhCH(OCH_2)_2$, 936-51-6; $PhNO_2$, 98-95-3; $PhCO_2CH_2CH_3$, 93-89-0; PhCl, 108-90-7; PhOH, 108-95-2; F_2, 7782-41-4; BCl_3, 10294-34-5; $AlCl_3$, 7446-70-0; *p*-nitroanisole, 100-17-4; 2-fluoro-4-nitroanisole, 455-93-6.

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