Photolysis of Pentafluorophenyl Azide 1 in *n*-Butane. Samples of 1 in butane were prepared in the following manner. Using a 15-in. pipet, azide 1 (4-8 mg) was transferred to the bottom of a 10-mm heavy-walled Pyrex tube. The tube was purged with N_2 and cooled to -78 °C, and ~1 mL of *n*-butane was condensed in the tube and then sealed with a torch. After the seal cooled, the mixture was slowly warmed to room temperature by first immersing the tube in an ice bath for 10 min and then removing the tube from the ice bath. The mixture was then shaken to dissolve azide 1.

The samples of 1 in *n*-butane were photolyzed at 350 nm for 4 h at 25, 0, -10, -30, -50, and -78 °C. All the samples were brought to -78 °C before the tubes were opened, and the butane was allowed to warm slowly. To the residue of each sample was added 10 mL of a solution of PhI (5.4×10^{-3} M, internal standard) in acetone and the resulting solutions were analyzed by GC.

Triplet-Sensitized Photolysis of Pentafluorophenyl Azide 1 in Butane. A sample of azide 1 (6.5 mg) and 4-methoxyacetophenone (16 mg, sensitizer) in ≈1 mL of *n*-butane was photolyzed at $\lambda > 350$ nm for 4 h at room temperature and then kept in the dark overnight. Butane was removed from the solution, and 1.0 mL of a solution of PhI (5.4×10^{-3} M, internal standard) in acetone was added to the residue and the sample analyzed by GC.

Photolysis of Pentafluorophenyl Azide 1 in 2,3-Dimethylbutane. Samples of 1 (2.26×10^{-2} M) in 2,3-dimethylbutane were photolyzed at 350 nm for 4 h at 25, 0, -25, -50, and -78 °C. The first two samples were kept in the dark at 25 and 0 °C, respectively, overnight and the last three samples at -78 °C overnight before they were brought to room temperature. To each sample was added 10 μL of a solution of 0.25 M PhI (internal standard) in acetone, and the resulting solutions were analyzed by GC.

N-(1,1,2-Trimethylpropyl)pentafluoroaniline 6 was isolated on a preparative scale experiment. Azide 1 (307 mg, 1.5 mmol) was dissolved in 50 mL of 2,3-dimethylbutane. The solution was cooled to and photolyzed at 0 °C for 4 h at 350 nm. The reaction mixture was concentrated and passed through a 15 cm × 2 cm column of neutral alumina. The first fraction passed was 200 mL of cyclohexane, which eluted unreacted azide, followed by 200 mL of cyclohexane/ethyl acetate (98:2, v/v). A yellow band eluted that gave 48 mg (13% yield) of 6 as a yellow oil: IR (neat, cm^{-1}) 3422, 3367, 2971, 2880, 2655, 2438, 1516, 1470, 1177, 1149, 1101 (CF); ^1H NMR ($CDCl_3$, δ) 1.0023 (d, J = 6.8 Hz, 6 H), 1.0950 (s, 6 H), 1.8160 (septet, J = 6.8 Hz, 1 H), 3.0087 (br, 1 H); ^{19}F NMR ($CDCl_3$, δ) -153.802 to -154.076 (m, 2 F), -168.158 to -169.637 (m, 3 F); m/e calculated for $C_{12}H_{14}F_5N$ (M^+) 267.1046, found 267.1055.

Decafluoroazobenzene (5).[20] A suspension of pentafluoroaniline (2.5 g, 14 mmol) in 90 mL of a 10.25% NaOCl solution was stirred vigorously at room temperature overnight (15 h). The mixture was extracted with three 35-mL portions of ether, and the combined extracts were washed with five 25-mL portions of demineralized water to remove chloride ions. The extracts were then dried over $MgSO_4$ and concentrated to give a red-orange solid. Recrystallization from 95% ethanol gave 526 mg (21% yield) of 5 as red-orange crystals: mp 140-141 °C (lit.[21] mp 142-143 °C); IR (CCl_4, cm^{-1}) 1258, 1150, 1039, 1006, 983 (CF); ^{19}F NMR ($CDCl_3$, δ) -151.6852 to -152.5076 (m, 3 F), -164.5177 to -165.3232 (m, 2 F); m/e calculated for $C_{12}F_{10}N_2$ (M^+) 361.9901, found 361.9884.

***N*-(2-Butyl)pentafluoroaniline (4).** This material was prepared by reaction of hexafluorobenzene and *sec*-butylamine in 15% yield as a colorless oil: bp 45-47 °C (0.35 mmHg); IR (neat, cm^{-1}) 3410 (-NH-), 2980, 2940, 2880 (aliphatic CH), 1520 (-NH-), 1150, 1125 (CF); ^1H NMR ($CDCl_3$, δ) 0.9534 (t, J = 7.4 Hz, 3 H), 1.1598 (d, J = 6.3 Hz, 3 H), 1.3711-1.6229 (m, 2 H), 3.2145-3.2429 (br, 1 H), 3.5113-3.6597 (m, 1 H); ^{19}F NMR ($CDCl_3$, δ) -163.3050 to -163.6134 (m, 2 F), -168.6573 to -169.3800 (m, 2 F), -176.3176 (t, t, J = 21.8, 6.3 Hz, 1 F); m/e calculated for $C_{10}H_{10}F_5N$ (M^+) 239.0733, found 239.0735.

***N*-Cyclopentylpentafluoroaniline.** This material was prepared from cyclopentylamine and hexafluorobenzene in 31% yield as a colorless oil: bp 60.5 °C (0.35 mmHg); IR (neat, cm^{-1}) 3430 (-NH-), 2970, 2880 (aliphatic CH), 1520, 1280 (-NH-), 1190 (CF); ^1H NMR ($CDCl_3$, δ) 1.4151-1.5081 (m, 2 H), 1.5668-1.7936 (m, 4 H), 1.9067-2.0277 (m, 2 H), 3.3927 (br, 1 H), 3.9909-4.0975 (m, 1 H); ^{19}F NMR ($CDCl_3$, δ) -163.7217 to -164.0386 (m, 2 F), -168.6592 to -169.3837 (m, 2 F), -176.5175 (t, t, J = 21.9 Hz, 6.4 Hz, 1 F); m/e calculated for $C_{11}H_{10}F_5N$ (M^+) 251.0733, found 251.0737.

Acknowledgment. One of us (M.J.T.Y.) is indebted to the Eastman Kodak Co. for a graduate fellowship, administered through the Organic Division of the ACS, and to the Amoco Corporation for a graduate fellowship. Support of this work by the NIH (GM-34823-04) is gratefully acknowledged. We are indebted to Professor Jakob Wirz for educating us about the fluorine effect on σ orbitals deduced by photoelectron spectroscopy.

Supplementary Material Available: General experimental details, gas chromatograms of **26**, and ^1H and ^{19}F NMR spectra of **44**, **45**, and **47** (13 pages). Ordering information is given on any current masthead page.

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A General Procedure for the Fluorodenitration of Aromatic Substrates[1]

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The synthesis of several fluoroaromatic compounds by a new procedure of fluorodenitration of nitroarenes is reported. The methodology is based on the principle that the nitrite ion, generated during the fluorodenitration processes and responsible for most of the undesired side reactions, can be trapped with a suitable reagent, e.g., phthaloyl difluoride or tetrafluorophthaloyl difluoride. The yields of fluoro compounds thus obtained are good to excellent, and the procedure is of general application.

The nucleophilic aromatic displacement of a nitro group plays an important role in the synthesis of substituted benzenes.[2,3] The nitro functionality can readily be introduced in an aromatic ring and easily replaced by a number of nucleophiles. In fact, the ability of the nitro group as leaving group is, in many cases, comparable with that of fluorine and much better than that of chlorine or

†Deceased February 6, 1990.

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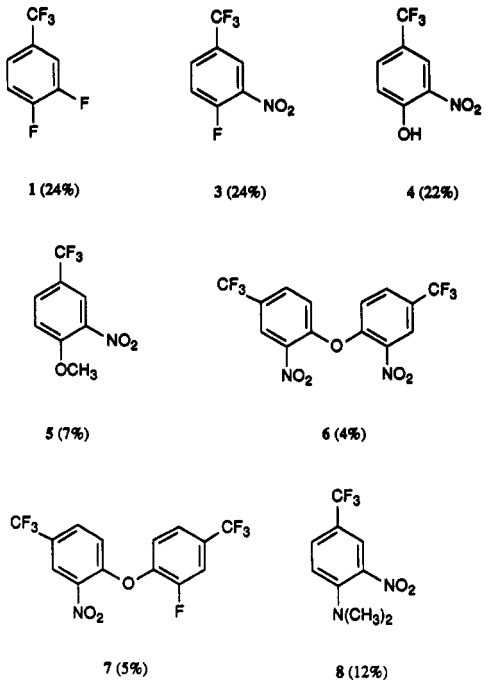
bromine.[2,3] For instance, Miller and Bolto[4] found that in the reaction with methoxide ion in methanol the mobility of the leaving group for para-substituted nitrobenzenes is $F \cong NO_2 \gg Cl$. The same results were obtained by Bartoli and Todesco[5] for the reaction of 1-substituted 2,4-dinitrobenzenes, whereas with similar substrates such as 2,6-dinitro-, 2,4-dinitro- and 2,4,6-trinitro-1-substituted benzenes and aniline as nucleophile in ethanol, the nucleofugicity of the nitro group was found to exceed that of fluorine by a factor of 15–40.[6]

This peculiarly high reactivity of the nitro group has found interesting practical applications. In their fundamental work, Beck,[7] Kornblum,[8] and Tiecco[9] have shown that the process becomes of great synthetic utility when the reactions are carried out in polar aprotic solvents. Oxygen, carbon, and especially sulfur nucleophiles were successfully used in the reaction with activated nitroaromatics.[7-9]

However, relatively little work has appeared regarding the fluorodenitration process, even though fluoroaromatic derivatives have wide application as agricultural and pharmaceutical intermediates.[10] Besides a few successful cases, where good yields of fluoroaromatics were obtained,[11,12] the occurrence of several side reactions has been reported.[13-16] It is commonly claimed that these reactions are initiated by the nitrite ion generated during the nitro displacement.[16,17] The nitrite ion is, in fact, an ambident nucleophile: it possesses two potential reaction sites, and its reactivity toward activated halobenzenes has been investigated by Rosenblatt et al.[18] and by Broxton et al.[19] The behavior of nitrite ion in terms of oxygen (O attack) or nitrogen nucleophilicity (N attack) has been studied in detail. As a general rule, it was found that O attack is favored over N attack when fluorine is displaced (as compared to Cl, Br, or I) and when a polar aprotic solvent is used (as compared to methanol).[18,19] The product of O attack of nitrite ion onto a halonitrobenzene would be a nitrite ester, too unstable under the reaction conditions, which converts to the corresponding phenoxide ion by reaction with a second nitrite ion (eq 1).

$$ArX + NO_2^- \rightarrow [ArONO] \xrightarrow{NO_2^-} ArO^- + N_2O_3 \quad (1)$$

Chart I



The phenoxide ion is still a good nucleophile and can react further (vide infra), giving rise to several byproducts. The high reactivity of the O end of nitrite ion in polar aprotic solvents and the ease of displacement of fluorine in activated aromatic rings could well be the reason for the low yields generally observed in fluorodenitrations.

In this paper, we wish to report our studies on the fluorodenitration reaction and to show, indeed, that the addition of a suitable nitrite ion trapper to the reaction mixture avoids most of the unwanted processes, thus allowing the active fluoro intermediate to survive enough to be isolated or to react further in the desired manner.

Results and Discussion

The preparation of 1,2-difluoro-4-(trifluoromethyl)-benzene (1), an interesting industrial intermediate,[20] from 1,2-dichloro-4-trifluoromethylbenzene could not be achieved by means of chlorine displacement by fluoride ion (KF, CaF_2/KF (2:1)[21]) under any reaction conditions.

On the other hand, 1-chloro-2-nitro-4-(trifluoromethyl)benzene (2) was found to be much more reactive. In sulfolane, spray-dried KF,[22] and tetramethyl ammonium chloride[23] at 130 °C, the fluorine–chlorine exchange was

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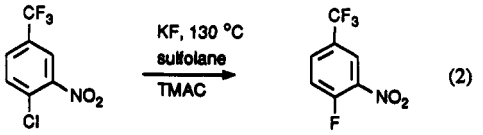
Table I. Reactions of 1-Nitro-2-chloro-4-(trifluoromethyl)benzene (2) with KF in Sulfolane. Effect of the Addition of Nitrite Ion Trap on Product Yield. Abbreviations: PhthCl, Phthaloyl Dichloride; Cl_3CN, Trichlorotriazine; TsCl, *p*-Toluenesulfonyl Chloride

trap, M	[KF],[a] M	[Me_4NCl], M	T, °C	t,[b] h	conv,[c] %	3, yield,[d] %	T, °C	t,[b] h	conv,[c] %	1, yield,[d] %
PhthCl, 1.25	6.13	0.42	160	4	100	85	160	8	60	48
PhthCl, 2.45	8.61	0.74[e]	180	2	83	95	160	2.5	53	83
PhthCl, 2.45	8.61	0.74[e]	180	1.3	95	94	160	11	71	56
PhthCl, 0.82	3.29	0.13[e]	180	1	100	87	180	7	94	51
PhthCl, 2.95	11.80	0.37	135	2	98	90	160	2	92	60
PhthCl, 2.45	11.80	0.37	135	2	100	90	180	4	44	43
PhthCl, 2.45	11.80	0.37	135	2	98	92	160	6.5	85	65[f]
Cl_3CN, 1.27	7.39	0.74[e]	180	2	93	88	160	12	66	21
Cl_3CN, 0.61	6.90	0.42	180	1.5	95	85	180	5	76	34
Cl_3CN, 1.22	7.51	2.21[e]	180	2	100	92	180	7	85	35
TsCl, 2.45	6.13	0.84[e]	180	1.5	80	96	160	5	77	6

[a] Due to the low solubility of KF in sulfolane (see text), the concentration of KF is to be intended as the total molar amount of added as a solid, most of it remaining undissolved. [b] The elapsed time at the given temperature and conversion is reported. [c] Percent of disappearance of starting material. [d] Yield in 1 is based on percent conversion. GC, unless otherwise specified. [e] The ammonium salt is added after the first step. [f] Isolated yield.

quantitative after 3 h and 1-fluoro-2-nitro-4-(trifluoromethyl)benzene (3) was isolated by distillation in 80% yield (eq 2).



(2)

2 3

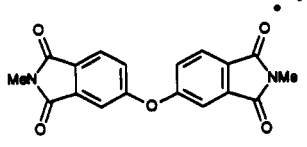
When the reaction was carried out at 180 °C as an attempt of substituting the nitro group, a range of products could be observed by means of capillary GC–MS and isolated by column chromatography (see Chart I; even with the same initial concentrations and volumes, the reaction gave no reproducible results and the reported yields refer to a random experiment).

The formation of all these products can be attributed to the nitrite ion generated during the 3 → 1 step (eq 3).

$$ArNO_2 + F^- \rightarrow ArF + NO_2^- \qquad (3)$$

Broxton et al.[19] reported that the reaction of fluoronitrobenzene 3 or chloronitrobenzene 2 with nitrite ion in DMSO affords quantitatively the phenol 4.

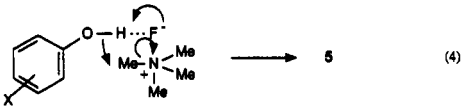
The nitrophenol 4 is probably involved as an intermediate in the formation of other products. Under the basic conditions of the reaction, it can nucleophilically attack the fluoronitrobenzene 3 affording the diaryl ether 6, which, in turn, can undergo fluorodenitration by KF giving rise to 7. Very similar results were obtained by Markezich and Zamek in the reaction of 4-nitro-*N*-methylphthalimide with potassium fluoride in DMF or DMSO.[26] The formation in high yields of 4,4′-oxybis(*N*-methylphthalimide) (9) was supposed to occur via O attack by nitrite ion on



9

either the 4-fluoro or the 4-nitro derivative to generate the phenoxide and successive attack by phenoxide on either fluoro or nitro compound. This reaction pathway was confirmed by reacting 4-nitro-*N*-methylphthalimide with potassium or sodium nitrite, where, again, good yields of bisimide 9 were obtained.[26]

Furthermore, it must be noted that in the system KF/sulfolane the reactivity of phenol is enhanced: phenol activation by fluoride ion in nucleophilic aromatic substitution has been studied by Miller and Clark.[27] The high propensity of fluoride ion to act as a powerful hydrogen-bond electron donor was found to promote the alkylation of phenols by alkyl halides providing good yields of alkyl aryl ethers.[27] Furthermore, nitrophenol 4 can displace one methyl group from the ammonium salt giving rise to methyl ether 5 (eq 4).[28]



(4)

The trimethylamine thus formed can nucleophilically attack nitrofluorobenzene 3 or nitrochlorobenzene 2 giving rise to nitroaniline 8.

If most of undesired compounds arise from O attack of nitrite ion onto activated benzene rings, an obvious solution to increase the yield of difluoro compound 1 would be to inhibit the reaction of nitrite ion by introducing a suitable nitrite trapping agent. Recently, researchers of BASF,[29] Asahi Glass Co.,[30] and Ihara Chemical Industry Co.[31] have reported that in several fluorodenitration processes the addition of phthaloyl dichloride is essential for the reaction to be successful.[29] During our work on the synthesis of 3-fluorophthalic anhydride from 3-nitro derivatives, we have observed that, in sulfolane and in the presence of KF, 3-nitrophthaloyl dichloride is readily transformed into 3-nitrophthaloyl difluoride, which can serve as an in situ trap for the nitrite ion generated during the fluorodenitration reaction. The nitrite ester can extrude nitrogen

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Scheme I

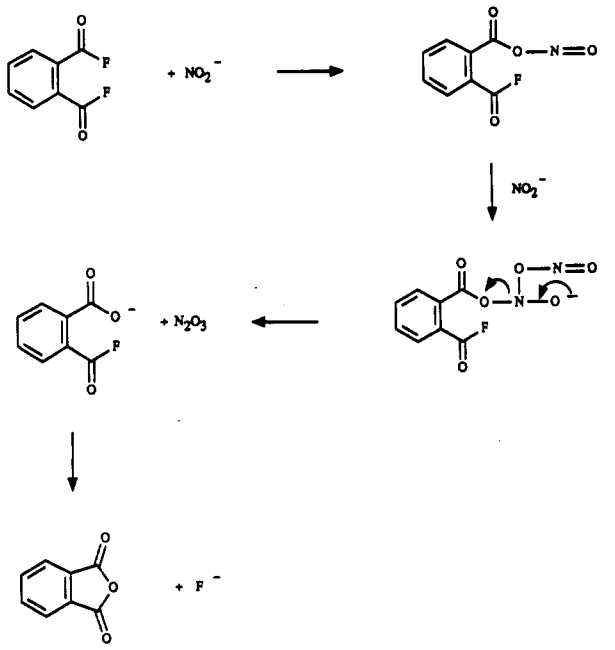

Table II. Effect of Addition of Nitrite Ion Trap on Yield of 1,2-Difluoro-4-(trifluoromethyl)benzene (1) in the Reaction of 1-Fluoro-2-nitro-4-(trifluoromethyl)benzene (3; 1.23 M) with KF (2.52 M) in Sulfolane. Abbreviations: MnO_2, Manganese Dioxide; TsCl, *p*-Toluenesulfonyl Chloride; PhthF, Phthaloyl Difluoride; PhthCN, Phthalonitrile

trap, M	NMe_4Cl, M	T, °C	t,[a] h	conv,[b] %	1, yield,[c] %	notes
MnO_2, 1.26	0.42	180	2.5	100		4 and 6 formed
TsCl, 2.52	0.42	180	3.0	47		4 and 6 formed
PhthF, 2.52	0.84	180	3.5	85	80	
PhthF, 2.52	0.84	180	3.0	90	79	
PhthF, 2.52	0.42	180	7.0	90	75	
PhthCN, 2.52	0.42	180	4.0	90	19	

[a] The elapsed time at the given temperature and conversion is reported. [b] Percent of disappearance of starting material. [c] Yields are calculated on percent conversion and are isolated.

oxides to afford the corresponding phthalic anhydride in good yields (Scheme I).[32]

The role of phthaloyl difluoride as a powerful nitrite scavenger is demonstrated by the present work: the addition of different nitrite traps in the reaction of **2** and **3** with KF in sulfolane is reported in Table I and Table II, respectively. Table I includes data for the two steps, the fluorodechlorination and the fluorodenitration.

The halogen–halogen exchange reactions are facile with good yields obtained in most cases. It must be noted that F^- shows a higher reactivity toward phthaloyl dichloride than toward chloronitrobenzene **2**; this, coupled with the low solubility of KF in sulfolane results in all the soluble fluoride ion being captured by phthaloyl dichloride initially. The fluorodechlorination reaction is not initiated until all the phthaloyl dichloride is transformed into phthaloyl difluoride (usually 2–3 h at 180 °C, GC analysis).

The second part of Table I shows that *p*-toluenesulfonyl chloride and trichlorotriazine are much less effective than phthaloyl difluoride in trapping NO_2^- (see corresponding entries in Table I). However, even in the presence of a good nitrite trap, yields were not reproducible. This can be attributed, at least in part, to the complexity of the reaction and to mass transport problems. We have found

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Scheme II

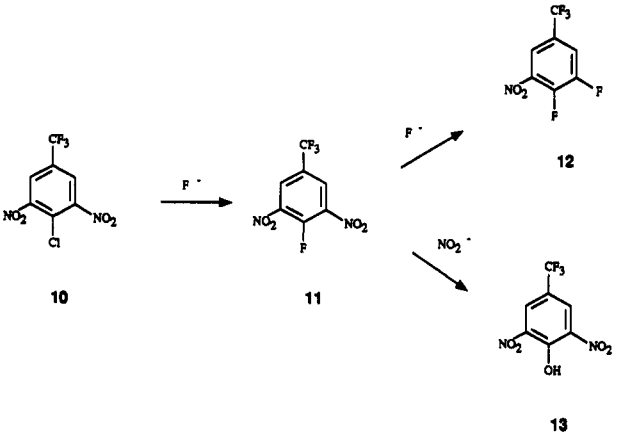
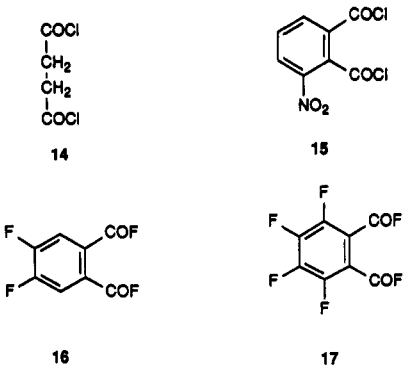


Chart II



that, for a laboratory use (up to a 100-g scale) the whole process becomes reproducible and yields are better when the two steps are carried out separately. Thus, the first step giving no problems, starting from pure **3** and using phthaloyl difluoride directly for the second step, yields of **1** were good and reproducible (see Table II).

The problem of byproduct formation derived from nitrite ions is a general one. The nitrite trap would be in competition with the substrate. It follows that the more reactive the substrate, the more efficient must be the trap. Thus, when 2-chloro-1,3-dinitro-5-(trifluoromethyl)benzene (**10**) is treated with KF, the chlorine atom is displaced readily (85% isolated yield). The 2-fluoro derivative **11** can either substitute one nitro group with fluorine or be O-attacked by nitrite ion (see Scheme II).

The fluorine atom in **11** is so reactive that under standard conditions only the phenol **13** is formed; upon addition of phthaloyl chloride yields of **12** of only 40% or less are recovered.

The need for new and more effective nitrite traps prompted us to investigate the preparation and reactivity of more electrophilic reagents: succinoyl dichloride (**14**), 3-nitrophthaloyl dichloride (**15**), 4,5-difluorophthaloyl difluoride (**16**), tetrafluorophthaloyl difluoride (**17**; Chart II).

The effect of the addition of the new nitrite traps on the reaction of **10** with KF in sulfolane to give difluoro compound **12** is reported in Table III.

The addition of succinoyl chloride is of no advantage. However, an increase of the number of fluorine atoms on the aromatic ring enhances the reactivity of the trap. The best yields are obtained with tetrafluoro derivative **17**, whereas the difluorophthaloyl **16** has an activity comparable to that of the unsubstituted difluoride.

The system spray-dried KF/sulfolane/TMAC/nitrite trap was found to be of general application in reactions

Table III. Effect of the Addition of Nitrite Traps on the Reaction of 2-Chloro-5-(trifluoromethyl)-1,3-dinitrobenzene (10, 1.3 M) with KF in Sulfolane. Abbreviations: PhthF, Phthaloyl Difluoride; F_2PhthF, 4,5-Difluorophthaloyl Difluoride; F_4PhthF, Tetrafluorophthaloyl Difluoride; SuCl, Succinoyl Dichloride; Cl_4PhthCl, Tetrachlorophthaloyl Dichloride; 3-NO_2PhthCl, 3-Nitrophthaloyl Dichloride

trap, M	KF,[a] M	T, °C	t,[b] h	conv,[c] %	12, yield,[d] %
PhthF, 1.84	5.0	130	2.5	95	40
PhthF, 1.97	5.0	130	2.0	95	43
PhthF, 2.30	10.5	150	6.0	95	44 (65)
F_2PhthF, 2.38	5.0	150	1.5	95	(33)
F_4PhthF, 2.29	4.6	150	1.5	80	79 (86)
F_4PhthF, 2.38	5.0	150	2.0	90	70
SuCl, 1.95	13.2	130	1.5	100	0
Cl_4PhthCl, 1.88	6.4	150	3.0	100	0
3-NO_2PhthCl, 1.2	6.5	130	4.0	100	(5)

[a] See footnote *a* in Table I. [b] The elapsed time at a given temperature and conversion is reported. [c] Percent of disappearance of starting material. [d] Isolated yield (GC in parentheses); calculated on percent conversion.

of differently substituted halonitrobenzenes. The results obtained in the synthesis of several interesting fluorides (Chart III) are reported in Table IV.

Conclusions

The fluorodenitration process can be an efficient method of preparation of fluoroaromatic compounds, provided that the nitrite ion initiated side reactions are suppressed: the addition of a nitrite ion trapping agent is essential for the fluorodenitration to be successful. Phthaloyl difluoride and tetrafluorophthaloyl difluoride, easy to prepare from inexpensive sources, are very reactive toward NO_2^- and act as excellent nitrite traps for even the more activated aromatic substrates. Several interesting fluoroaromatics have been synthesized in good to excellent yields.

Experimental Section

General Procedures. Distilled reagent-grade solvents were used for chromatography and extractions. All starting materials and reference samples, kindly supplied by Miteni srl, were distilled or crystallized before use. Spray-dried KF was purchased by Fluka Chemie AG and used without further purification. Tetramethylammonium chloride (TMAC) was dried under vacuum at 45 °C for 24 h before use. Sulfolane was purified by vacuum distillation. Succinoyl dichloride,[33] 3-nitrophthaloyl dichloride,[34]

Chart III

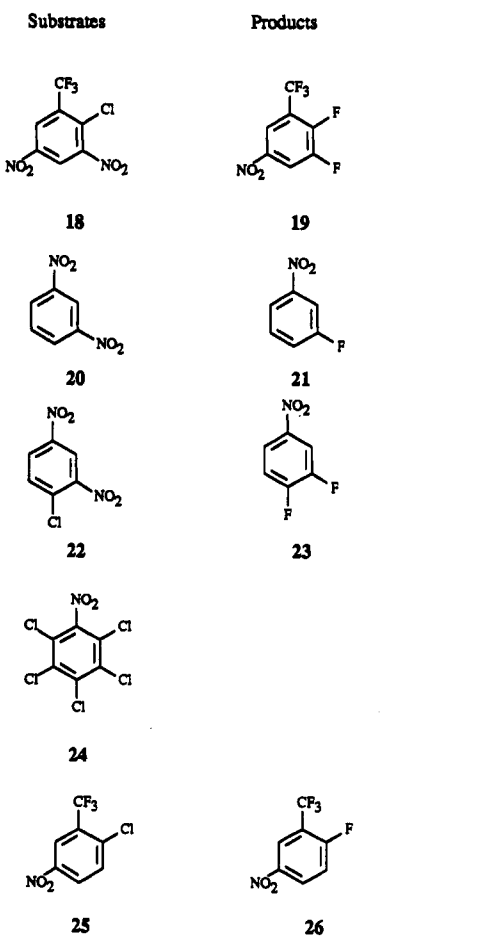


Table IV. Reactions of Substituted Nitrohalobenzenes (1.2 M) with KF in Sulfolane. Effect of the Addition of Phthaloyl Difluoride (A) and Tetrafluorophthaloyl Difloride (B) on Product Yield

substrate	KF,[a] M	trap, M	NMe_4Cl, M	T, °C	t,[b] h	product	conv,[c] %	yield,[d] %
3	2.52	A, 2.45	0.84	180	3.5	1	85	80
	2.52	A, 2.45	0.84	180	3.5		90	79
	2.52	A, 2.45	0.42	180	7.0		90	75
2	11.80	A, 2.45	0.37	135–180	2 + 7	1	85	65
18	5.0	A, 2.63		130	2.5	19	100	40
	5.0	B, 2.63		130	3.5		100	60
10	5.0	A, 2.37		130	7	12	85	43
	10.6	A, 2.33		150	6		90	44
	4.6	B, 2.29		150	1.5		80	79
	5.0	B, 2.45		150	2		90	70
20	2.63	A, 2.63	0.39	160	8	21	90	94
22	5.26			150–180	5 + 9	23	100	8[e]
	5.26	A, 2.63	0.39	160	1.5		100	51
	5.26	B, 2.63		180–200	15 + 6		100	65
	5.26	B, 2.63		200	13		85	77
24	10.5	B, 2.63		170–190	5 + 11	*f*	100	69[f]
	10.5	B, 2.63		190	10	*f*	100	74[f]
25	5.0	A, 2.37	0.37	160–180	1 + 2	26	100	96[e]

[a] See footnote *a* in Table I. [b] The elapsed time at the given temperature and conversion is reported. When two times are given, they refer to different temperatures reported in the corresponding column. [c] Percent of disappearance of starting material. [d] Isolated yields, unless otherwise noted; based on percent conversion. [e] Measured by GC. [f] Mixture of fluorodechlorination and fluorodenitration products.

and tetrafluorophthaloyl difluoride,[35] were prepared according to published procedures. GC–MS analyses were performed on a Hewlett-Packard electron impact mass spectrometer 5970 coupled with a gas chromatograph 8890 equipped with a 12 m × 0.25 mm column filled with OV-101 on Chromosorb WAW DMCS. GC analyses were obtained on a Varian 3700 gas chromatograph equipped with a 2 m × 2 mm glass column filled with SE 30 10% on Chromosorb WAW DMCS 80–100. Melting points were determined with a Büchi apparatus and are uncorrected. ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded on a Bruker WP 200 spectrometer in $CDCl_3$ with TMS or $CFCl_3$ as internal standards. The purity of all title compounds was checked to be ≥95% either by spectroscopic means (^{1}H NMR) and by GC, using biphenyl as an internal standard.

Reaction of 1-Chloro-2-nitro-4-(trifluoromethyl)benzene (2) with KF in Sulfolane at 180 °C in the Presence of Phthaloyl Dichloride. Formation of 1,2-Difluoro-4-(trifluoromethyl)benzene (1). Sulfolane (42 mL) and spray-dried KF (24.5 g) were heated at 160 °C, and ca. 4 mL of sulfolane was distilled under reduced pressure. To the cooled solution was added 20 g (0.099 mol) of phthaloyl dichloride and the mixture heated at 185 °C for 4 h. At 130 °C, 10.5 g (0.047 mol) of 1-chloro-2-nitro-4-(trifluoromethyl)benzene (2) and 1.6 g (0.015 mol) of TMAC were introduced. After 2 h (disappearance of starting material, GC), the temperature was raised to 180 °C and kept for 6 h. The mixture was then distilled, and the fraction boiling at 50–70 °C (20 mmHg) was collected. A total of 4.7 g of pure title compound[36] was obtained (65%): MS *m/e* 182 (M^+, 84), 163 (100), 132 (58), 113 (13).

Reaction of 1,3-Dinitro-2-chloro-5-(trifluoromethyl)-benzene (10) with KF in Sulfolane at 150 °C in the Presence of Tetrafluorophthaloyl Difluoride. Formation of 1,2-Difluoro-3-nitro-5-(trifluoromethyl)benzene (12). Sulfolane (45 mL) and spray-dried KF (9.4 g) were heated at 160 °C, and ca. 5 mL of sulfolane was distilled off under reduced pressure. After the solution was cooled, 1,3-dinitro-2-chloro-5-(trifluoromethyl)benzene (10.9 g, 0.04 mol) and tetrafluorophthaloyl difluoride (20 g, 0.082 mol) were added. After 1.5 h at 150 °C, the mixture was distilled under reduced pressure (25 mmHg). The fraction boiling at 70–120 °C was collected, affording 12.3 g of a liquid that contained the difluoro derivative in 47% purity (yield is 79% on 80% conversion). The major impurity was tetrafluorophthaloyl difluoride, which could be eliminated by hydrolysis. The distillate was diluted with pentane and treated with 10% aqueous sodium bicarbonate. The mixture was stirred for 3 h, and the organic layer was separated and dried over $CaCl_2$. Redistillation (53–56 °C (15 mmHg)) afforded 5.3 g of pure **12**: MS *m/e* 227 (M^+, 100), 208 (36), 181 (82), 161 (60), 119 (54); ^{1}H NMR δ 7.80 (m, 1 H), 8.19 (m, 1 H); ^{19}F NMR δ 63.35 (m, CF_3), 128.76 (m, ArF), 131.34 (m, ArF); ^{13}C NMR δ 118.68 (sextet, *J* = 3.7 Hz), 120.07 (br d, *J* = 20.35 Hz), 121.96 (qd, *J* = 272.81 and 2.77 Hz), 127.04 (qdd, *J* = 36.07, 6.47, and 5.55 Hz), 138.56 (m), 147.25 (dd, *J* = 274.66 and 15.72 Hz), 151.63 (dd, *J* = 257.09 and 12.95 Hz); EI-HRMS 226.9999 ($C_7H_2F_5NO_2$ requires 227.0006).

Preparation of Substituted Fluorobenzenes. General Procedure. Sulfolane, TMAC, and KF (in the amount reported in Table IV) were treated under the conditions used throughout this work, and then the substrate was added. After the time at the temperatures indicated in Table IV, distillation of the reaction mixture afforded the products in the yields reported in Table IV. Compounds **21** and **23** were identified by comparison with authentic specimens kindly supplied by Miteni srl. The characterization of the hitherto unreported fluoro compounds follows.

Difluoro derivative 19: slightly yellow oil, bp_{15} 57–60 °C; MS *m/e* 227 (M^+, 75), 208 (28), 181 (100), 161 (33), 119 (19); ^{1}H NMR δ 8.28–8.40 (m); ^{19}F NMR δ 58.83 (m, CF_3), 123.85 (m, ArF), 125.85 (m, ArF); ^{13}C NMR δ 117.24 (br d, *J* = 23.12 Hz), 118.13 (m), 120.92 (qd, *J* = 273.73 and 2.77 Hz), 121.29 (qd, *J* = 35.14 and 11.10 Hz), 143.41 (m), 150.61 (dd, *J* = 257.09 and 12.95 Hz), 152.31 (ddq, *J* = 270.96, 14.80, and 1.85 Hz); EI-HRMS *m/e* 226.9999 ($C_7H_2F_5NO_2$ requires 227.0006).

Monofluoro derivative 26: slightly yellow oil, bp_{35} 99–110 °C; MS *m/e* 209 (M^+, 60), 190 (18), 163 (100), 143 (24), 113 (22); ^{1}H NMR δ 7.43 (t, 1 H, *J* = 8.85 Hz), 8.53 (m, 2 H); ^{19}F NMR δ 62.50 (m, CF_3), 103.61 (m, ArF); ^{13}C NMR δ 118.35 (d, *J* = 23.12), 119.56 (qd, *J* = 35.13 and 14.80 Hz), 121.30 (q, *J* = 272.24), 123.57 (m), 129.63 (d, *J* = 10.19 Hz), 143.85 (m), 167.98 (dt, *J* = 276.26 and 1.85); EI-HRMS *m/e* 209.0092 ($C_7H_3F_4NO_2$ requires 209.0100).

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Registry No. 1, 32137-19-2; 376-86-2, 121-17-5; **3**, 367-86-2; **10**, 393-75-9; **12**, 101646-01-9; **18**, 392-95-0; **19**, 135733-71-0; **20**, 99-65-0; **21**, 402-67-5; **22**, 97-00-7; **23**, 369-34-6; **24**, 82-68-8; **25**, 777-37-7; **26**, 400-74-8; Cl_3CN, 108-77-0; PhthF, 445-69-2; PhthCN, 91-15-6; F_2PhthF, 83684-75-7; F_4PhthF, 5292-39-7; 9111-00-1, 24564-71-4; TsCl, 98-59-9; MnO_2, 1313-13-9; SuCl, 543-20-4; KF, 7789-23-3; PhthCl, 88-95-9; 4,5-dichloronaphthalic acid, 56962-08-4.

Supplementary Material Available: Synthetic procedure and analytical and spectral data of compounds that are not described in the Experimental Section (8 pages). Ordering information is given on any current masthead page.

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