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FLUORINATION OF 1,2,3,4- AND 1,2,3,5-TETRAHALOBENZENES WITH POTASSIUM FLUORIDE IN DIMETHYL SULFONE

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SUMMARY

1,2,3,4-Tetrachlorobenzene, 1,2,3,5-tetrachlorobenzene, 2,4,6-trichlorofluorobenzene, and 2,6-dichloro-1,4-difluorobenzene were fluorinated with potassium fluoride and potassium fluoride–cesium fluoride mixtures in dimethyl sulfone. By varying the concentration, temperature and reaction time, the degree of fluorination could be controlled to some extent. The optimum conditions for producing mono-, di- and tri-fluoro-substituted chlorobenzenes and trace amounts of tetrafluorobenzene from the corresponding tetrachlorobenzenes are given. 1,2,3,5-Tetrafluorobenzene was obtained in 44.8% yield from 2,6-dichloro-1,4-difluorobenzene. 1,2,3,4-Tetrafluorobenzene was obtained in only trace amounts from 1,2,3,4-tetrachlorobenzene. A total of 24 new chlorofluorobenzenes and intermediates are described. Fluorination with potassium fluoride and certain other metal fluorides was also investigated.

INTRODUCTION

Many studies have been made on the fluorination of polychlorobenzenes with potassium fluoride[1,2,3,4]. However, very little effort has been made to control preferentially the degree of fluorination, to modify isomer ratios, or to influence the composition of the by-products. Such exploratory studies were begun in our laboratory[2] some time ago in an effort to develop new sources of fluorinated benzenes for research and commercial use. Results from the use of 1,2,3,4- and 1,2,3,5-tetrachlorobenzene in this investigation are reported here.

RESULTS AND DISCUSSION

The exchange reaction was tested in two solvents, dimethyl sulfoxide (DMSO) and dimethyl sulfone ($DMSO_2$). An exploratory experiment with DMSO resulted in some monofluoro and difluoro substitution, but further experiments with this solvent were discontinued because of the excessive formation of a sulfur-containing by-product (m.p. 83–84°), which we assumed on the basis of elemental analysis was 2,3,5-trichlorophenylmethyl sulfide.

The present study involved the reactions of 1,2,3,4- and 1,2,3,5-tetrachlorobenzenes and of some chlorofluoro intermediates with potassium fluoride and/or cesium fluoride in dimethyl sulfone. The degree of fluorination was altered appreciably by varying the concentration, ratio of reactants, temperature, and reaction time.

In general, formation of monofluoro and difluoro compounds appears to be favored by less solvent, low temperature and prolonged heating. In contrast, more solvent, high temperature and short reaction time favor good yields of trifluoro compounds, and in some cases small amounts of the tetrafluorobenzenes are formed.

Poor fluorination yields were obtained when CsF alone was used as the fluorinating reagent. This can be attributed in part to its high reactivity and basic strength, which result in a higher percentage of decomposition products. However, in some exploratory KF experiments small amounts of CsF permitted shorter reaction times and lower temperatures without diminished yields.

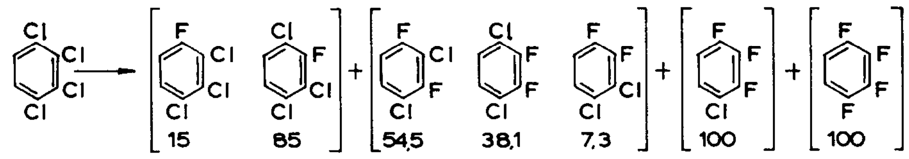
Table 1 lists 14 of the more favorable reactions. The weight percentages of each of the fluoro compounds obtained and the reaction conditions are included.

The reaction products are complex mixtures of chlorofluoro compounds and some degradation products. The reaction products from a series of fluorinations were combined, distilled through an annular Teflon spinning band column and the isomer ratios of the mono-, di- and tri-fluorinated fractions studied. These ratios are shown in Figure 1. This procedure presumes that there was very little variation in the isomer ratios between runs. The individual degradation products were not identified; however, the over-all yields of these substances were calculated on the basis of the weight obtained and their concentration as shown by integration of the GLC curve, or in some cases from ^{19}F NMR data[5]. Only the trifluorobenzene by-products are listed in the Table because the amount of chlorofluorobenzene degradation products was small. It has been shown[6] that these by-products are formed by a reductive dehalogenation in which a chlorine atom is replaced. Holbrook[7] reported the formation of reductive dehalogenation by-products but gave no indication as to whether a chlorine or a fluorine atom was involved. Yakobson[8, 9] noted rearranged products in the absence of a solvent and attributed them to the formation of a benzyne intermediate. No similar structures were found among our reaction products.

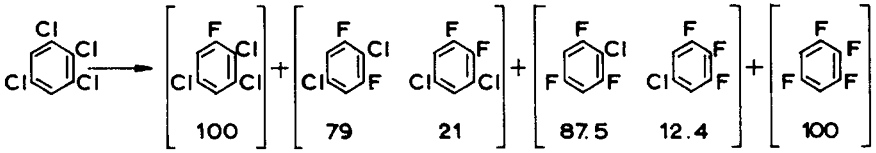
Fluorination tends to favor the replacement of a chlorine either (1) *meta* to another chlorine or fluorine, or (2) *para* to a hydrogen. This is in accord with earlier observations by various investigators[4,10], and was interpreted by Holbrook[7] and Tatlow[11] as a withdrawal of electrons, particularly from the *meta* position, and back-conjugation of electrons to the *para* position.

Pure 2,3,5-trichlorofluorobenzene[12] (32.1% yield) was obtained in the fluorination of 1,2,3,5-tetrachlorobenzene. Two intermediates are readily obtained from the fluorination of 1,2,3,4-tetrachlorobenzene; pure 2,3,4-trifluorochlorobenzene was isolated as the only trifluorochlorobenzene product, and pure 2,3,6-trichlorofluorobenzene can be obtained by fractionation of the trichlorofluorobenzene fraction by using an efficient column.

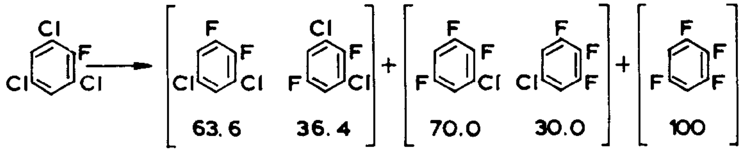
I. 1,2,3,4 - Tetrachlorobenzene



II. 1,2,3,5 - Tetrachlorobenzene



III. 2,4,6 - Trichlorofluorobenzene



IV. 2,6 - Dichloro - 1,4-difluorobenzene

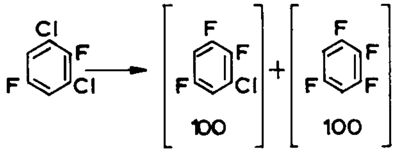


Fig. 1. Fluorination of tetrahalobenzenes. (Composition of isomer fractions given in percent throughout.)

TABLE 1

FLUORINATION OF TETRAHALOBENZENES

$C_6H_2X_4$ (Moles)	KF (Moles)	CsF (Moles)	Solvent (g)	Temp. (°C)	Time (h)	Method	Product (Mole % yield)				
							$Cl_3C_6H_2F$	$Cl_2C_6H_2F_2$	$ClC_6H_2F_3$	$C_6H_2F_4$	$C_6H_3F_3$
I. 1,2,3,4-Tetrachlorobenzene											
0.2	1.8	—	128	200	168	A	1,2,4–3(46.7)* 1,2,3–4(8.3)	1,3–2,4(10.7) 1,4–2,3(7.5) 1,2–3,4(1.4)	—	—	—
0.2	1.8	—	430	225	168	A	1,2,4–3(8.1) 1,2,3–4(1.4)	1,3–2,4(22.8) 1,4–2,3(15.6) 1,2–3,4(2.8)	1–2,3,4(11.7)	0.7	—
0.1	—	0.4	215	170	168	A	1,2,4–3(1.2) 1,2,3–4(0.3)	1,3–2,4(3.0) 1,4–2,3(2.1) 1,2–3,4(0.4)	1–2,3,4(1.5)	—	—
0.1	0.76	0.09[a]	430	200	168	A	1,2,4–3(0.1) 1,2,3–4(0.0)	1,3–2,4(14.1) 1,4–2,3(9.8) 1,2–3,4(1.9)	1–2,3,4(24.4)	0.7	—
1.0	9.0	—	645	245	240	B-1	—	1,3–2,4(8.1) 1,4–2,3(5.6) 1,2–3,4(1.1)	1–2,3,4(19.5)	—	—
1.0	8.9	0.1	645	245	96	B-1	—	1,3–2,4(15.0) 1,4–2,3(10.3) 1,2–3,4(1.7)	1–2,3,4(15.6)	0.1	—
II. 1,2,3,5-Tetrachlorobenzene											
1.05	1.6	—	300[b]	183	72	A	1,3,4–5(7.2)	1,4–3,5(0.4) 1,3–4,5(0.4)	—	—	—
0.2	2.4	—	200[b]	195	168	A	1,3,4–5(32.1)	1,4–3,5(31.8) 1,3–4,5(8.5)	—	—	—
0.25	2.25	—	500	265	6	B-1	—	1,4–3,5(2.9) 1,3–4,5(0.8)	1–2,4,6(47.0)[c] 1–3,4,5(6.6)	3.7	3.7[d]
0.25	2.0	0.25	500	265	5	B-1	—	1,4–3,5(0.8) 1,3–4,5(0.2)	1–2,4,6(8.6) 1–3,4,5(1.2)	1.4	3.5[d]

III. 2,4,6-Trichlorofluorobenzene										
0.1	1.0	—	250	240	6	B-2	—	1,3–4,5(17.4)	1–2,3,5(27.6)[e]	3.0	0.5[f]
								1,3–2,5(10.0)	1–3,4,5(11.8)		
0.1	1.0	0.5	225	250	5.5	B-2	—	1,3–4,5(5.5)	1–2,3,5(25.9)	4.7	0.75[f]
								1,3–2,5(3.2)	1–3,4,5(11.1)		
IV. 2,6-Dichloro-1,4-difluorobenzene											
0.41	1.63	—	900	265	6	B-2	—	—	1–2,3,5(28.6)	39.8	3.1[g]
0.5	2.9	0.1	1240	265	6	B-2	—	—	1–2,3,5(5.5)	44.8	3.7[g]

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* Numbers preceding hyphen refer to Cl; those after the hyphen refer to F.

[a] 0.05 mole BaF_2 added.

[b] DMSO.

[c] See Ref. 18.

[d] Mixture of 1,3,5-trifluoro- and 1,2,3-trifluorobenzene.

[e] See Ref. 15.

[f] Mixture of 1,2,4-trifluoro- and 1,2,3-trifluorobenzene.

[g] 1,2,4-Trifluorobenzene.

Only two of the possible compounds (2,3-dichloro-1,4-difluorobenzene and 2,3,6-trifluorochlorobenzene) were not obtained from 1,2,3,4-tetrachlorobenzene. In the fluorination of 1,2,3,5-tetrachlorobenzene, no 2,4,6-trichlorofluorobenzene, 3,4,5-trifluorochlorobenzene, 2,6-dichloro-1,4-difluorobenzene or 2,3,5-trifluorochlorobenzene was detected. Trace amounts of these compounds may have been formed in the reaction but may have vanished because of instability or rapid fluorination to more stable compounds.

The fact that certain chlorofluorobenzene intermediates were not detected does not rule out the possibility that one or more of them might be prime source material for more highly fluorinated derivatives. Evidence in support of this was found. Samples of 2,4,6-trichlorofluorobenzene[13] and 2,6-dichloro-1,4-difluorobenzene[14] were synthesized and studied in the halogen-exchange reaction. Only in the case of 2,6-dichloro-1,4-difluorobenzene was it possible to prepare 1,2,3,5-tetrafluorobenzene[15] in good yield (44.8%). Pure 2,3,5-trifluorochlorobenzene can be obtained in a reasonable yield (28.6%) by varying the reaction conditions.

Besides a number of KF–CsF experiments, tests were made on 33 other metal fluorides for possible synergetic effect with KF in the halogen-exchange reaction. No synergetic effects were noted.

A number of chlorofluorobenzene intermediates were synthesized by classical methods for use as reference standards for NMR and infrared spectroscopy.

EXPERIMENTAL

The potassium fluoride used in these experiments was dried at 120° for 24 h and quickly powdered in a warm mortar. The other metal fluorides were heated at 120° for 24 h prior to use; these were LiF, NH_4F, NaF, RbF, BaF_2, CaF_2, CdF_2, MgF_2, NiF_2, PbF_2, SrF_2, ZnF_2, AlF_3, BiF_3, CeF_3, CrF_3, LaF_3, MnF_3, NdF_3, ThF_4, ZrF_4, $CaSiF_6$, K_3AlF_6, KBF_4, K_3FeF_6, $KSnF_3$, K_2SnF_6, K_2TaF_7, K_2TiF_6, $KZnF_3$, K_2ZrF_6, $NaSbF_4$, and Na_2SiF_6.

Yields were determined from gas chromatographic data by using a Model 500 F & M gas chromatograph fitted with a 3% silicon rubber (SE-30) column measuring 3 m × 6 mm, and a Beckman GC-4 gas chromatograph fitted with a 3% PO-1 (Pierce Chemical Co., Rockford, Ill.) column measuring 1.8 m × 3 mm. Peak areas were determined by use of an Infotronics Integrator. The identity of all of the individual products was established by elemental analysis and by analysis of the ^{19}F NMR spectra in conjunction with gas chromatographic retention times. Infrared spectral analysis also aided in structure confirmation.

Melting and boiling points are uncorrected. Freezing points were determined with a toluene thermometer.

The halogen-exchange reactions were run in glass apparatus for mild reaction conditions and, for higher temperature experiments in a Parr 4501 stainless steel pressure reactor.

Fluorination

Method A: Glass apparatus

The polychlorobenzene was added to a mixture of the metal fluoride and dimethyl sulfoxide or melted dimethyl sulfone (m.p. 109°) in a glass reaction flask. The mixture was stirred and heated, as indicated in Table 1. After dilution with water, the fluorinated reaction products were collected by steam distillation.

Method B: Parr reactor

The polyhalobenzene was added to a heated mixture (*ca.* 200°) of dimethyl sulfone and metal fluoride in the autoclave. If solid (method B-1 in Table 1), the polyhalobenzene was added directly, and if liquid (method B-2 in Table 1), it was injected into the closed autoclave with a slight nitrogen pressure. The reaction mixtures were allowed to react under autogenous pressure and were stirred at the temperatures and time intervals indicated in the Table. The reaction products were removed from the reactor by distillation, collected in an ice-cooled trap, and finally steam distilled.

With KF and metal fluorides

1,2,3,4-Tetrachlorobenzene (0.1 mole) was added to a mixture of KF (0.81 mole), metal fluoride (0.09 mole), and $DMSO_2$ (65 g) in a glass reaction flask. The mixture was stirred for 168 h at 200°. After the mixture was diluted with water, the fluorinated reaction products were collected by steam distillation. The identity and yield of the individual monofluoro-, difluoro- and trifluoro-substituted products were established by their gas chromatographic retention times and the integration of the peak areas. No significant difference in yield was noted over that when KF was used alone.

Diazonium group replacements

Details of the modifications used for the replacement of diazonium groups by fluorine or chlorine can be found in Reference 16.

2,3,4-Trichlorofluorobenzene (nc)

A Schiemann reaction on 2,3,4-trichloroaniline gave a 75% yield of crude product. Vacuum sublimation gave 2,3,4-trichlorofluorobenzene; m.p. 41.5–42.2° (Found: C, 36.17; H, 1.07. Calcd. for $C_6H_2Cl_3F$: C, 36.13; H, 1.01%).

2,3,6-Trichlorofluorobenzene (nc)

A Sandmeyer reaction with cuprous chloride on 2,4-dichloro-3-fluoroaniline[17] gave a 41.5% yield of crude product. Vacuum distillation gave pure 2,3,6-trichlorofluorobenzene; b.p. 105° (30 mmHg), n_D^{20} 1.5509 (Found: C, 36.22; H, 0.94. Calcd. for $C_6H_2Cl_3F$: C, 36.13; H, 1.01%).

2,4-Dichloro-1,3-difluorobenzene (nc)

A Schiemann reaction on 2,4-dichloro-3-fluoroaniline[17] gave a 70% yield of crude product. Distillation gave pure 2,4-dichloro-1,3-difluorobenzene; b.p. 172° (Found: C, 39.49; H, 1.08. Calcd. for $C_6H_2Cl_2F_2$: C, 39.38; H, 1.10%).

2,3-Difluorochlorobenzene (nc)

A Schiemann reaction on 3-chloro-2-fluoroaniline[16] gave a 69.5% yield of crude product. Distillation gave pure 2,3-difluorochlorobenzene; b.p. 138.5° (Found: C, 48.73; H, 2.24; Cl, 23.81; F, 25.52. Calcd. for $C_6H_3ClF_2$: C, 48.51; H, 2.04; Cl, 23.87; F, 25.60%).

Nitration of 2,3-difluorochlorobenzene

A mixed-acid nitration of 2,3-difluorochlorobenzene at 15° to 20° gave 89% yield of steam-distilled product. Vacuum distillation gave a mixture of two difluorochloronitrobenzenes; b.p. 132° (43 mmHg) (Found: C, 37.49; H, 1.17; Cl, 18.21; N, 7.30. Calcd. for $C_6H_2ClF_2NO_2$: C, 37.23; H, 1.04; Cl, 18.32; N, 7.24%).

Reduction of the difluorochloronitrobenzene mixture

A stannous chloride and hydrochloric acid reduction of the above difluorochloronitrobenzene mixture gave 88% yield of crude product. Vacuum distillation gave 82.1% yield of a chlorodifluoroaniline mixture, b.p. 116–117° (42 mmHg). The major portion crystallized on standing. Recrystallization of a small sample of the solid from n-pentane, followed by a vacuum sublimation, gave a white solid; m.p. 42–43° (Found: C, 44.27; H, 2.54; Cl, 21.60; N, 8.49. Calcd. for $C_6H_4ClF_2N$: C, 44.07; H, 2.51; Cl, 21.69; N, 8.56%).

The structure of this product was not determined, but the major product from it in the Sandmeyer reaction was 3,4-dichloro-1,2-difluorobenzene (^{19}F NMR data) (nc); therefore, the likely structure is 2-chloro-3,4-difluoroaniline (nc). The acetyl derivative was recrystallized from a benzene, low-boiling petroleum ether mixture. Vacuum sublimation gave the pure acetyl derivative (nc); m.p. 125.5–127° (Found: C, 46.87; H, 3.01; N, 6.64. Calcd. for $C_8H_6ClF_2NO$: C, 46.73; H, 2.94; N, 6.80%).

3,4-Dichloro-1,2-difluorobenzene and 3,6-dichloro-1,2-difluorobenzene (nc)

A Sandmeyer reaction with cuprous chloride on the chlorodifluoroaniline mixture obtained above gave a 91% yield of crude product. Distillation produced a mixture of 3,4-dichloro-1,2-difluorobenzene and 3,6-dichloro-1,2-difluorobenzene; b.p. 171°.

The ^{19}F NMR spectrum corresponded to 3,4-dichloro-1,2-difluorobenzene (83%) and 3,6-dichloro-1,2-difluorobenzene (17%) (Found: C, 39.42; H, 1.18; Cl, 38.67; F, 20.60. Calcd. for $C_6H_2Cl_2F_2$: C, 39.38; H, 1.10; Cl, 38.75; F, 20.77%).

2,3-Dichlorofluorobenzene (nc)

A Schiemann reaction on 2,3-dichloroaniline gave an 81% yield of 2,3-dichlorofluorobenzene; b.p. 176° (Found: C, 43.85; H, 1.97; Cl, 42.79; F, 11.79. Calcd. for $C_6H_3Cl_2F$: C, 43.67; H, 1.83; Cl, 42.98; F, 11.52%).

2,3-Dichloro-4-fluoronitrobenzene (nc)

A mixed-acid nitration of 2,3-dichlorofluorobenzene at 15° to 20° gave a 91% yield of crude steam-distilled product. Vacuum distillation produced a mixture of 2,3-dichloro-4-fluoronitrobenzene (87%) and 3,4-dichloro-2-fluoronitrobenzene (13%); b.p. 138° (7 mmHg) (Found: C, 34.50; H, 1.08; Cl, 33.56; N, 6.78. Calcd. for $C_6H_2Cl_2FNO_2$: C, 34.32; H, 0.96; Cl, 33.77; N, 6.67%).

2,3-Dichloro-4-fluoroaniline (nc)

An iron–ammonium chloride reduction of the above dichlorofluoronitrobenzene mixture gave a 91% yield of crude product. Vacuum sublimation gave pure 2,3-dichloro-4-fluoroaniline; m.p. 63–64° (Found: C, 40.05; H, 2.34; Cl, 39.46; N, 7.84. Calcd. for $C_6H_4Cl_2FN$: C, 40.03; H, 2.24; Cl, 39.39; N, 7.79%).

The acetyl derivative (nc) was recrystallized from benzene and sublimed; m.p. 161–162.5° (Found: N, 6.19. Calcd. for $C_8H_6Cl_2FNO$: N, 6.31%).

For proof of structure, a Sandmeyer reaction was run on a small sample of the aniline and gave 2,3,4-trichlorofluorobenzene, which was identical to that obtained from the Schiemann reaction on 2,3,4-trichloroaniline.

2,3-Dichloro-1,4-difluorobenzene (nc)

A Schiemann reaction on 2,3-dichloro-4-fluoroaniline gave a 47% yield of crude product. Vacuum sublimation gave pure 2,3-dichloro-1,4-difluorobenzene; m.p. 34.5–35° (Found: C, 39.32; H, 1.15; Cl, 38.79; F, 20.81. Calcd. for $C_6H_2Cl_2F_2$: C, 39.38; H, 1.10; Cl, 38.75; F, 20.77%).

2,5-Dichloro-1,3-difluorobenzene (nc)

A Sandmeyer reaction with cuprous chloride on 4-chloro-3,5-difluoroaniline[16] gave 2,5-dichloro-1,3-difluorobenzene. Distillation of the crude product gave a 55% yield of the pure compound; b.p. 167°, n_D^{20} 1.5035 (Found: C, 39.53; H, 1.16; Cl, 38.61; F, 20.96. Calcd. for $C_6H_2Cl_2F_2$: C, 39.38; H, 1.10; Cl, 38.75; F, 20.77%).

This compound was used as a reference for studying the 1,2,3,5-isomer distribution of the $C_6H_2Cl_2F_2$ fraction.

6-Chloro-2,4-difluoronitrobenzene (nc)

A Sandmeyer reaction with cuprous chloride *via* a nitrosyl-sulfuric acid diazotization of 3,5-difluoro-2-nitroaniline[18] gave a 70.5% yield of steam-distilled nitro compound. Distillation gave pure 6-chloro-2,4-difluoronitrobenzene; b.p. 202.5°, f.p. *ca.* 19.5°, n_D^{20} 1.5068 (Found: C, 37.49; H, 0.92; N, 7.15. Calcd. for $C_6H_2ClF_2NO_2$: C, 37.23; H, 1.04; N, 7.24%).

A 52% crude yield of this compound was also obtained by a mixed acid nitration of 3,5-difluorochlorobenzene[18] at 35–40°.

6-Chloro-2,4-difluoroaniline (nc)

An iron–ammonium chloride reduction of 6-chloro-2,4-difluoronitrobenzene gave a near-quantitative yield of the aniline. Vacuum distillation gave pure 6-chloro-2,4-difluoroaniline; b.p. 100–101° (20 mmHg) or 190–191° (atm), f.p. *ca.* 19.8°, n_D^{20} 1.5327 (Found: C, 44.17; H, 2.33; N, 8.71. Calcd. for $C_6H_4ClF_2N$: C, 44.06; H, 2.47; N, 8.56%).

The acetyl derivative (nc) was recrystallized from ethanol and was vacuum sublimed; m.p. 146–147° (Found: N, 7.08. Calcd. for $C_8H_6ClF_2NO$: N, 6.81%).

4,5-Dichloro-1,3-difluorobenzene (nc)

A Sandmeyer reaction with cuprous chloride *via* a nitrosyl-sulfuric acid diazotization on 6-chloro-2,4-difluoroaniline gave a 74% yield of crude product. Distillation gave pure 4,5-dichloro-1,3-difluorobenzene; b.p. 160–161°, f.p. *ca.* 11.5°, n_D^{20} 1.5028 (Found: C, 39.51; H, 1.36; F, 20.81. Calcd. for $C_6H_2Cl_2F_2$: C, 39.38; H, 1.10; F, 20.77%).

This compound was also prepared *via* the following sequence of compounds: 2,4-difluoro-6-nitroaniline, 2-chloro-3,5-difluoronitrobenzene and 2-chloro-3,5-difluoroaniline.

2-Chloro-3,5-difluoronitrobenzene (nc)

A Sandmeyer reaction with cuprous chloride *via* a nitrosyl-sulfuric acid diazotization on 2,4-difluoro-6-nitroaniline[18] gave an 81% yield of steam-distilled crude product. Vacuum distillation gave pure 2-chloro-3,5-difluoronitrobenzene; b.p. 105.5° (20 mmHg) or 206–207° (atm), f.p. *ca.* 17.5°, n_D^{20} 1.5191 (Found: C, 37.56; H, 0.86; N, 7.54. Calcd. for $C_6H_2ClF_2NO_2$: C, 37.23; H, 1.04; N, 7.24%).

2-Chloro-3,5-difluoroaniline (nc)

An iron–ammonium chloride reduction of 2-chloro-3,5-difluoronitrobenzene gave a near-quantitative yield of the aniline. Vacuum distillation gave the pure 2-chloro-3,5-difluoroaniline; b.p. 100–101° (20 mmHg) or 201–202° (atm), f.p. *ca.* 24.5° (Found: C, 44.27; H, 2.43; N, 8.71. Calcd. for $C_6H_4ClF_2N$: C, 44.06; H, 2.47; N, 8.56%).

The acetyl derivative (nc) was recrystallized from ethanol and sublimed; m.p. 86.5–87° (Found: N, 6.99. Calcd. for $C_8H_6ClF_2NO$: N, 6.81%).

The pure aniline was converted to 4,5-dichloro-1,3-difluorobenzene by a Sandmeyer reaction with cuprous chloride for a 48% yield; b.p. 160–161°.

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