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Reactions of 1,2,4-Trichlorotrifluorobenzene with Nucleophiles

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Abstract—1,2,4-Trichlorotrifluorobenzene reacted with potassium hydrogen sulfide, potassium hydroxide, sodium isopropoxide, liquid ammonia, and ethyl cyanoacetate via nucleophilic substitution of one fluorine atom with predominant formation of the isomer in which the new substituent replaced fluorine atom in the 5-position.

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Polyfluorochlorobenzenes are important intermediate products in the synthesis of a wide range of polyfluoroaromatic compounds containing various functional groups [1]. Among polyfluorochlorobenzenes, trichlorotrifluoro derivatives remain poorly studied. The reaction of hexachlorobenzene with potassium fluoride was reported [2, 3] to give ~12% of a mixture of isomeric trichlorotrifluorobenzenes, where the major component was 1,3,5-trichlorotrifluorobenzene (~69%), and the fractions of the 1,2,3- and 1,2,4-trichloro isomers were ~18 and 13%, respectively. 1,3,5-Trichlorotrifluorobenzene was the only product isolated in the pure state [3]. 1,2,4-Trichlorotrifluorobenzene (**1**) was synthesized in 11% yield by reaction of 1,2,4,5-tetrachloro-3,3,6,6-tetrafluorocyclohexa-1,4-diene with potassium fluoride at 525°C [4]. Compound **1** was also obtained by bromination of 1,2,4-trifluorobenzene to 1,2,4-tribromotrifluorobenzene, followed by replacement of the bromine atoms by chlorine (overall yield 53%) [3].

We have recently developed a procedure for the preparation of polyhalobenzene **1** from a crude mixture of isomeric dichlorotetrafluorobenzenes formed in the reaction of hexachlorobenzene with KF [2, 3]. The procedure is based on the transformation of that mixture into isomeric dichlorotrifluorobenzenethiols by treatment with potassium hydrogen sulfide and subsequent chlorination. As a result, arene **1** was isolated in a good yield [5].

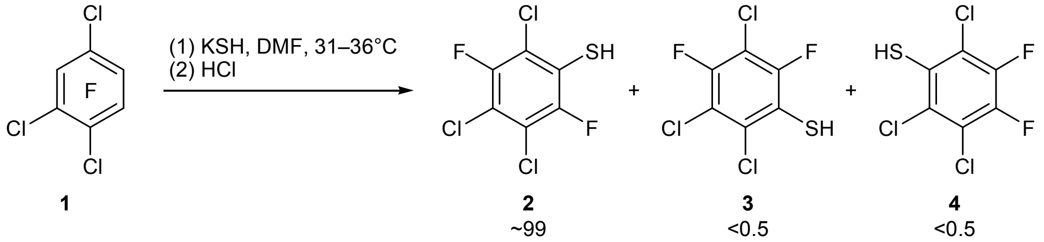
1,3,5-Trichlorotrifluorobenzene has been studied most thoroughly. In particular, the chlorine atoms in its molecule were replaced by hydrogens via reactions with copper and water [6] and with zinc in DMF in the presence or in the absence of water [7]. Fluorine atoms therein were replaced by the action of such nucleophiles as hydrazine in alcohol [8], sodium azide in DMSO [9], and potassium hydroxide in *tert*-butyl alcohol [10]. 1,3,5-Trichlorotrifluorobenzene was converted into organolithium [11], organomagnesium [12], and organozinc compounds [7]. 3,5-Dichloro-2,4,6-trifluorophenyllithium was used to introduce 3,5-dichloro-2,4,6-trifluorophenyl ligands into platinum and palladium complexes [13], and its reactions with nickel compounds were also reported [11].

Only a few data are available on the chemical transformations of 1,2,4-trichlorotrifluorobenzene (**1**). The substitution of chlorine by fluorine in isomeric trichlorotrifluorobenzenes, including compound **1**, by the action of potassium fluoride was described in [14], and chlorine atoms were replaced by hydrogen via reduction with zinc in DMF in the presence of water [7].

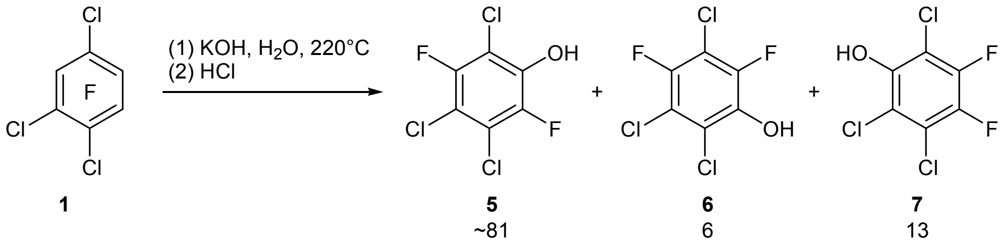
The synthesis of **1** from dichlorotetrafluorobenzenes made it possible to examine its reactions with some nucleophiles, which may be interesting from the viewpoint of synthesis of physiologically active compounds, by analogy with 1,2,4-trichlorobenzene derivatives [15, 16].

The reaction of **1** with potassium hydrogen sulfide in DMF afforded 91% of 2,4,5-trichloro-3,6-difluorobenzenethiol (**2**), while only small amounts of isomers **3** and **4** were formed (according to the ^{19}F NMR data; Scheme 1). However, our attempt to introduce a hydroxy group into molecule **1** to obtain 2,4,5-trichloro-3,6-difluorophenol (**5**) by heating with aqueous potassium hydroxide for 5 days at ~220°C resulted in a low conversion (~25%), and the reaction was accompanied

Scheme 1.



Scheme 2.

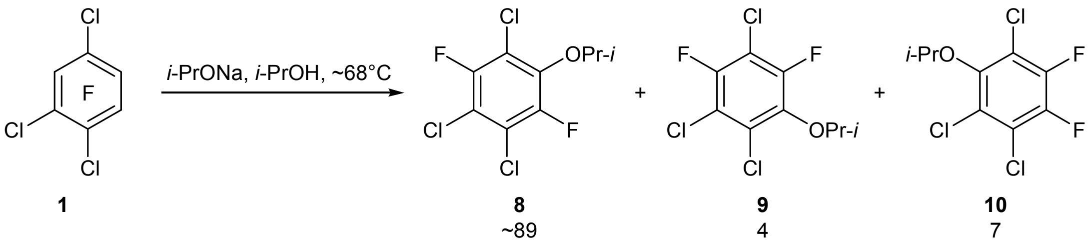


by formation of isomeric phenols **6** and **7**. The overall yield of polyfluorochlorophenols **5**–**7** was ~13% (Scheme 2).

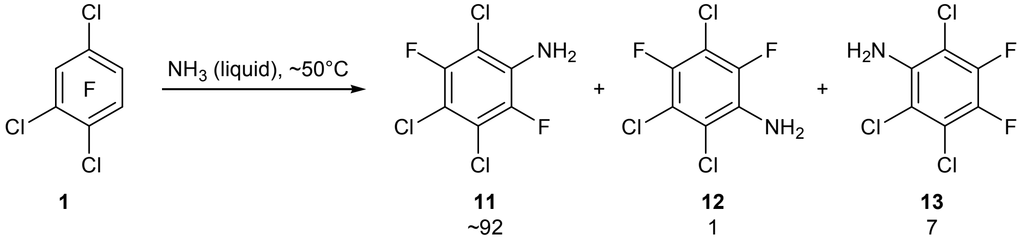
By contrast, compound **1** reacted with sodium isopropoxide in isopropyl alcohol under mild conditions, and the major product was 1,2,4-trichloro-3,6-difluoro-5-isopropoxybenzene (**8**). In addition, small amounts of 1,2,4-trichloro-3,5-difluoro-6-isopropoxybenzene (**9**) and 1,2,4-trichloro-5,6-difluoro-3-isopropoxybenzene (**10**) were obtained (Scheme 3). The overall yield of isopropoxy derivatives **8**–**10** was 91%. Treatment of mixture **8**/**9**/**10** (89 : 4 : 7) with sulfuric acid gave a mixture of polychlorofluorophenols **5**, **6**, and **7** (91 : 4 : 5) with an overall yield of 84%.

The reaction of **1** with liquid ammonia according to the procedure described in [17] afforded 2,4,5-trichloro-3,6-difluoroaniline (**11**) as the major product together with minor isomeric trichlorodifluoroanilines **12** and **13** (Scheme 4), the overall yield of **11**–**13** being 91%. By acylation of mixture **11**/**12**/**13** with acetic acid in the presence of phosphorus(III) chloride we obtained a mixture of acetyl derivatives **14**–**16** (91%; Scheme 5), and recrystallization of the product mixture gave acetanilide **14**. By alkaline hydrolysis of the latter with aqueous sodium hydroxide we isolated 90% of pure aniline **11**. Arene **1** reacted with ethyl cyanoacetate in dimethylformamide in the presence of potassium carbonate to give mainly ester **17** and

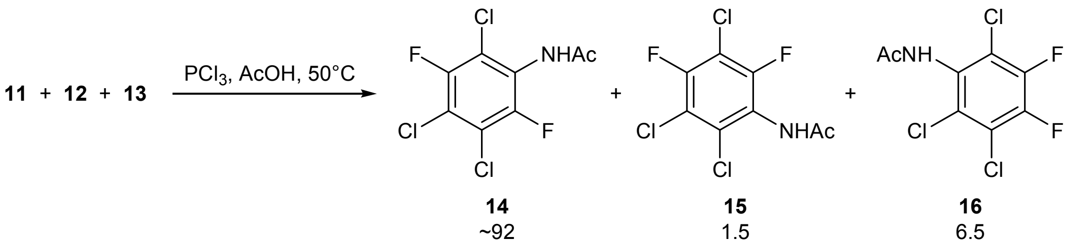
Scheme 3.



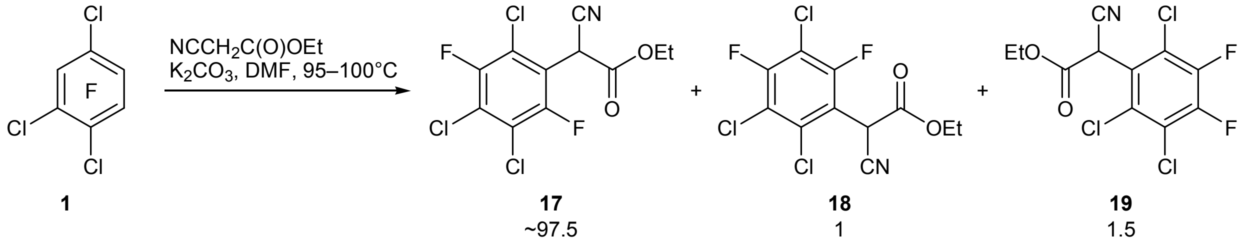
Scheme 4.



Scheme 5.



Scheme 6.



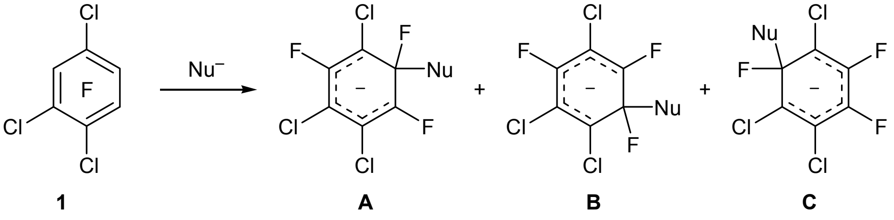
insignificant amounts of isomers **18** and **19** with an overall yield of 89% (Scheme 6).

The regioselectivity observed in the reactions of **1** with nucleophiles may be rationalized by comparing the stabilities of possible intermediate σ-complexes **A**–**C** (Scheme 7). The activating effect of chlorine atoms in different positions of benzene ring toward fluorine atoms in polyfluorochlorobenzenes (C_6F_5Cl, $C_6F_4Cl_2$) weakly depends on the nucleophile or solvent nature and can be expressed by the following relations: *ortho–meta–para* 3.2 : 0.69 : 35 (in the reactions with sodium methoxide in methanol) and 3 : 1 : 27 (in the reactions with ammonia in aqueous dioxane) [18]. Presumably, the orienting effect of chlorine atoms in molecule **1** in nucleophilic substitution reactions is also determined by their position with respect to the reaction center. Then, the stability of intermediate σ-complexes should decrease in the series **A** > **C** > **B**. The experimental isomer ratios are consistent with the above stability series of σ-complexes which are likely to represent the structures of transition states in the two-step substitution process where nucleophile addition is the rate-determining step.

EXPERIMENTAL

The analytical and spectral studies were performed at the Joint Chemical Service Center, Siberian Branch, Russian Academy of Sciences. The ^{1}H and ^{19}F NMR spectra were recorded on a Bruker AV-300 instrument at 300 and 282.4 MHz, respectively, using carbon tetrachloride with addition of $CDCl_3$ as solvent. The ^{19}F chemical shifts were measured relative to hexafluorobenzene as internal standard. Signals in the ^{19}F NMR spectra were assigned with account taken of chemical shifts calculated by the additivity scheme [19]. The IR spectra were recorded on a Bruker Vector 22 IR spectrometer. The UV spectra were registered with a Hewlett Packard 8453 spectrophotometer. The molecular weights and elemental compositions were determined from the high-resolution mass spectra which were obtained using a DFS instrument (electron impact, 70 eV). Gas chromatographic–mass spectrometric analysis was performed on HP 5890/5971 and Agilent 6890N/5973N GC/MSD systems (electron impact, 70 eV; ion source temperature 173°C; HP-5 column, 30 m × 0.25 mm × 0.25 μm; carrier gas helium, flow rate 1 mL/min; oven temperature programming

Scheme 7.



from 50 to 280°C). GLC analyses were obtained on an HP 5890 gas chromatograph equipped with a thermal conductivity detector (HP-5 column, 30 m× 0.52 mm×2.6 μm).

1,2,4-Trichlorotrifluorobenzene (**1**) with a purity of 99% (GLC) was synthesized according to [5]. A solution of potassium hydrogen sulfide in ethylene glycol (~4.1 M) was prepared by passing gaseous hydrogen sulfide through a solution of 2 mol of KOH in 330 mL of ethylene glycol until a gain in weight of 64 g was attained.

Reaction of 1,2,4-trichlorotrifluorobenzene (1) with potassium hydrogen sulfide. Compound **1**, 76.55 g (0.33 mol), was dissolved in 330 mL of DMF, and 170 mL of a solution of KSH (prepared as described above) was added under stirring over a period of 0.7 h, maintaining the temperature below 35°C. The mixture was then stirred for 2.2 h at 32–36°C and poured into 400 mL of a mixture of concentrated aqueous HCl and 700 g of ice. The precipitate was filtered off and dried in a desiccator over $CaCl_2$. The product, 75.52 g, contained 99.5% (GLC) of a mixture of thiols **2**, **3**, and **4** (yield 91%) at a ratio of ~99 : <0.5 : <0.5 (^{19}F NMR). Found (for mixture **2**/**3**/**4**), %: C 28.84; H 0.35; Cl 42.40; F 15.02; S 12.80. $C_6HCl_3F_2S$. Calculated, %: C 28.88; H 0.40; Cl 42.63; F 15.23; S 12.85.

2,4,5-Trichloro-3,6-difluorobenzenethiol (2). mp 97.5–99°C [after sublimation at 140–150°C (12 mm)]. IR spectrum (KBr), ν, cm^{-1}: 2590, 1747, 1516, 1476, 1435, 1391, 1339, 1292, 1259, 1169, 1099, 1016, 988, 951, 887, 854, 799, 777, 754, 719, 669, 629. UV spectrum (hexane), λ_{max}, nm (logε): 218 (4.35), 244 (4.14), 289 (3.34), 297 (3.36). ^1H NMR spectrum, δ, ppm: 4.08 d.d (SH, $J_{H,6\text{-}F} = 2$, $J_{H,3\text{-}F} = 1$ Hz). ^{19}F NMR spectrum, δ_F, ppm: 49.5 d.d (3-F, $J_{FF} = 12$, $J_{FH} = 1$ Hz), 54.6 d.d (6-F, $J_{FF} = 12$, $J_{FH} = 2$ Hz). Found: *m/z* 247.8831 $[M]^+$. $C_6HCl_3F_2S$. Calculated: *M* 247.8827.

2,3,5-Trichloro-4,6-difluorobenzenethiol (3). ^{19}F NMR spectrum (from the spectrum of isomer mixture), δ_F, ppm: 49.7 d (4-F, $J_{FF} = 1.5$ Hz), 56.4 m (6-F). Found: *m/z* 248 $[M]^+$. Calculated: *M* 247.88.

2,3,6-Trichloro-4,5-difluorobenzenethiol (4). ^{19}F NMR spectrum (from the spectrum of isomer mixture), δ_F, ppm: 28.2 d ($J_{FF} = 21$ Hz), 30.5 d ($J_{FF} = 21$ Hz). Found: *m/z* 248 $[M]^+$. Calculated: *M* 247.88.

Reaction of 1,2,4-trichlorotrifluorobenzene (1) with potassium hydroxide. An ampule was charged with 1.11 g (4.72 mmol) of compound **1**, 0.63 g (11.63 mmol) of potassium hydroxide, and 3.16 g of water. The ampule was sealed and heated for 5 days at 219–221°C. After cooling, the mixture was treated with 2 mL of concentrated aqueous HCl and 2 mL of water and extracted with methylene chloride (3× 3 mL). The extract was dried over $CaCl_2$, and the solvent was removed on a rotary evaporator. The residue was 0.97 g of a mixture of unreacted compound **1** and isomers **5**–**7** at a ratio of ~87 : 13 (^{19}F NMR; 85.4 : 14.6, GLC; ratio **5** : **6** : **7** ~81 : 6 : 13, ^{19}F NMR).

Reaction of 1,2,4-trichlorotrifluorobenzene (1) with sodium isopropoxide. A solution of sodium isopropoxide prepared from 1.24 g (53.93 mmol) of sodium and 100 mL of isopropyl alcohol was added under stirring to a solution of 9.81 g (41.67 mmol) of compound **1** in 30 mL of isopropyl alcohol, maintaining the temperature below 68°C. The mixture was stirred for 2 h at 65–68°C, cooled, and poured into a mixture of 50 mL of concentrated aqueous HCl and 100 mL of water. The organic layer (11.09 g) was separated and dried over $CaCl_2$. According to the GLC data, the overall concentration of isomers **8**, **9**, and **10** in the reaction mixture was 94% (yield 91%); ratio **8** : **9** : **10** ~90 : 4 : 6 (^{19}F NMR). Vacuum distillation (~33 mm) of 10.11 g of mixture **8**–**10** gave 1.64 g of a fraction boiling below 144°C, which contained 96% of **8**–**10** (GLC) at a ratio of ~89 : 4 : 7 (^{19}F NMR) and 6.26 g of a fraction with bp 144–145°C which contained 98.1% of **8**–**10** (GLC) at the same ratio (^{19}F NMR). Found (for mixture **8**–**10**), %: C 39.70; H 2.68; Cl 38.70; F 13.58. *m/z* 273.9524 $[M]^+$. $C_9H_7Cl_3F_2O$. Calculated, %: C 39.24; H 2.56; Cl 38.60; F 13.79. *M* 273.9525.

1,2,4-Trichloro-3,6-difluoro-5-isopropoxybenzene (8). ^1H NMR spectrum (from the spectrum of isomer mixture), δ, ppm: 1.36 d.d (6H, CH_3, $J_{HH} = 6$, $J_{H,6\text{-}F} \approx 1$ Hz), 4.52 sept.d (1H, CH, $J_{HH} = 6$, $J_{H,6\text{-}F} \approx 1$ Hz). ^{19}F NMR spectrum (from the spectrum of isomer mixture), δ_F, ppm: 33.5 d.m (6-F, $J_{FF} = 9.5$ Hz), 48.0 d (3-F, $J_{FF} = 9.5$ Hz).

1,2,4-Trichloro-3,5-difluoro-6-isopropoxybenzene (9). ^{19}F NMR spectrum (from the spectrum of isomer mixture), δ_F, ppm: 35.1 s (5-F), 46.8 s (3-F).

1,2,4-Trichloro-5,6-difluoro-3-isopropoxybenzene (10). ^{19}F NMR spectrum (from the spectrum of isomer mixture), δ_F, ppm: 25.8 d ($J_{FF} = 22$ Hz), 28.2 d ($J_{FF} = 22$ Hz).

Reaction of isopropoxybenzenes 8–10 with sulfuric acid. A mixture of 5.09 g (18.48 mmol) of isomer mixture **8–10** (~89:4:7, ^{19}F NMR) and 30 mL of ~83% sulfuric acid was stirred for 13 h at 95–100°C. The mixture was cooled and extracted with methylene chloride (4 × 15 mL), the extract was dried over $CaCl_2$ and evaporated on a rotary evaporator, and the residue, 4.74 g, was subjected to vacuum sublimation at 130–135°C (~10 mm). The product, 3.62 g, contained 99.5% (GLC) of a mixture of isomers **5**, **6**, and **7** at a ratio of ~91:4:5 (^{19}F NMR). Found (for isomer mixture **5–7**), %: C 30.90; H 0.45; Cl 44.92; F 16.64. *m/z* 231.9053 $[M]^+$. $C_6HCl_3F_2O$. Calculated, %: C 30.87; H 0.43; Cl 45.56; F 16.28. *M* 231.9056.

Five recrystallizations of 3.50 g of mixture **5–7** from hexane (~1 mL of the solvent per gram of substrate) gave 2.01 g of mixture **5–7** at a ratio of ~98:1.5:0.5 (^{19}F NMR).

2,4,5-Trichloro-3,6-difluorophenol (5). mp 61–63°C (from hexane). IR spectrum (KBr), ν, cm^{-1}: 3410, 1607, 1466, 1454, 1371, 1358, 1341, 1315, 1308, 1246, 1092, 881, 711, 644. UV spectrum (hexane), λ_{max}, nm (logε): 223 (4.06), 285 (3.20). ^{1}H NMR spectrum: δ 5.46 ppm, br.s (OH). ^{19}F NMR spectrum, δ_F, ppm: 25.3 d (6-F, J_{FF} = 9.5 Hz), 46.7 d (3-F, J_{FF} = 9.5 Hz). Found, %: C 30.98; H 0.75; Cl 45.50; F 16.22. *m/z* 231.9053 $[M]^+$. $C_6HCl_3F_2O$. Calculated, %: C 30.87; H 0.43; Cl 45.56; F 16.28. *M* 231.9056.

2,3,5-Trichloro-4,6-difluorophenol (6). ^{19}F NMR spectrum (from the spectrum of isomer mixture), δ_F, ppm: 27.4 d (6-F, J_{FF} = 3 Hz), 41.6 d (4-F, J_{FF} = 3 Hz). Found: *m*/*z* 232 $[M]^+$. Calculated: *M* 231.91.

2,3,6-Trichloro-4,5-difluorophenol (7). ^{19}F NMR spectrum (from the spectrum of isomer mixture), δ_F, ppm: 20.6 d (4-F, J_{FF} = 22 Hz), 27.2 d (5-F, J_{FF} = 22 Hz). Found: *m*/*z* 232 $[M]^+$. Calculated: *M* 231.91.

Reaction of 1,2,4-trichlorotrifluorobenzene (1) with liquid ammonia. A mixture of 5.21 g (22.13 mmol) of compound **1** and 11.46 g (672.91 mmol) of liquid ammonia was heated for 4 days at 45–50°C in a closed metal vessel. After cooling, unreacted ammonia was removed, the residue was extracted with methylene chloride (5 × 10 mL), the extract was dried, and the solvent was removed on a rotary evaporator. The residue, 4.81 g, contained 97.6% (GLC) of compounds **11–13** (yield 91%) at a ratio of ~92:1:7 (^{19}F NMR). Vacuum sublimation of 4.51 g of the product at 160–170°C (~10 mm) gave 4.23 g of isomer mixture **11–13** (99.1%, GLC); ratio **11**:**12**:**13** ~92:1:7 (^{19}F NMR). Found (for isomer mixture **11–13**), %: C 30.66; H 0.84; Cl 45.75; F 16.37; N 5.77. $C_6H_2Cl_3F_2N$. Calculated, %: C 31.00; H 0.87; Cl 45.76; F 16.35; N 6.03.

2,3,5-Trichloro-4,6-difluoroaniline (12). ^{19}F NMR spectrum (from the spectrum of isomer mixture), δ_F, ppm: 28.1 d (6-F, J_{FF} = 4 Hz), 36.5 d (4-F, J_{FF} = 4 Hz). Found: *m*/*z* 231 $[M]^+$. Calculated: *M* 230.92.

2,3,6-Trichloro-4,5-difluoroaniline (13). ^{19}F NMR spectrum (from the spectrum of isomer mixture), δ_F, ppm: 15.9 d (4-F, J_{FF} = 22 Hz), 26.8 d (5-F, J_{FF} = 22 Hz). Found: *m*/*z* 231 $[M]^+$. Calculated: *M* 230.92.

Acetanilides 14–16. Phosphorus(III) chloride, 0.91 g (6.63 mmol), was added to a solution of 4.01 g (17.25 mmol) of isomer mixture **11–13** (~92:1:7, ^{19}F NMR) in 7.03 g of glacial acetic acid. The mixture was stirred for 3 h at 50°C, cooled to room temperature, and poured into 30 mL of water. The precipitate was filtered off and dried in a desiccator over $CaCl_2$. The product, 4.30 g, contained 99.9% (GLC, yield 91%) of a mixture of compounds **14**, **15**, and **16** at a ratio of ~92:1.5:6.5 (^{19}F NMR). Found (for isomer mixture **14–16**), %: C 34.86; H 1.63; Cl 38.60; F 14.26; N 4.66. $C_8H_4Cl_3F_2NO$. Calculated, %: C 35.01; H 1.47; Cl 38.75; F 13.84; N 5.10.

Double recrystallization of mixture **14–16**, 4.11 g, from acetonitrile (~10 mL of the solvent per gram of substrate) gave 2.74 g of isomer **14** containing less than 0.5% of each of **15** and **16** (^{19}F NMR).

***N*-(2,4,5-Trichloro-3,6-difluorophenyl)acetamide (14).** mp 190–191.5°C. IR spectrum (KBr), ν, cm^{-1}: 3242, 3196, 3107, 3017, 2932, 2770, 1682, 1593, 1564, 1522, 1458, 1414, 1375, 1271, 1231, 1092, 1040, 1011, 986, 880, 812, 727, 708, 667, 630, 600, 584, 536. UV spectrum (hexane), λ_{max}, nm (logε): 230 sh (3.73), 288 (3.08). ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 2.17 s (3H, Me), 9.23 s (NH). ^{19}F NMR spectrum (acetone-d_6), δ_F, ppm: 47.2 d (J_{FF} = 10 Hz), 48.9 d (J_{FF} = 10 Hz). Found, %: C 34.65; H 1.59; Cl 38.73; F 13.87; N 4.79. *m/z* 272.9323 $[M]^+$. $C_8H_4Cl_3F_2NO$. Calculated, %: C 35.01; H 1.47; Cl 38.75; F 13.84; N 5.10. *M* 272.9321.

***N*-(2,3,5-Trichloro-4,6-difluorophenyl)acetamide (15).** ^{19}F NMR spectrum (acetone–$CDCl_3$) (from the spectrum of isomer mixture **14–16**), δ_F, ppm: 48.4 s, 52.6 s. Found: *m*/*z* 273 $[M]^+$. Calculated: *M* 272.93.

***N*-(2,3,6-Trichloro-4,5-difluorophenyl)acetamide (16).** ^{19}F NMR spectrum (acetone–$CDCl_3$) (from the spectrum of isomer mixture **14–16**), δ_F, ppm: 29.0 d

(J_{FF} = 22 Hz), 31.4 d (J_{FF} = 22 Hz). Found: m/z 273 $[M]^+$. Calculated: M 272.93.

Hydrolysis of *N*-(2,4,5-trichloro-3,6-difluorophenyl)acetamide (14). A mixture of 1.01 g (3.68 mmol) of compound **14** and 0.61 g (15.25 mmol) of sodium hydroxide in 3 mL of water was stirred for 4 days at 85–90°C. The mixture was cooled to room temperature, and the precipitate was filtered off and dried in a desiccator over $CaCl_2$.

2,4,5-Trichloro-3,6-difluoroaniline (11). Yield 0.78 g (90%), purity 98.9% (GLC); mp 105–107°C. IR spectrum (KBr), ν, cm^{-1}: 3499, 3400, 1620, 1589, 1474, 1447, 1364, 1350, 1288, 1232, 1113, 870, 770, 716, 637, 592, 532. UV spectrum (hexane), λ_{max}, nm (logε), 238 (4.16), 285 (3.45). ^1H NMR spectrum: δ 4.26 ppm, s (NH_2). ^{19}F NMR spectrum, δ_F, ppm: 26.7 d (6-F, J_{FF} = 10 Hz), 45.9 d (3-F, J_{FF} = 10 Hz). Found, %: C 30.90; H 1.23; Cl 45.39; F 16.59; N 6.15. m/z 230.9207 $[M]^+$. $C_6H_2Cl_3F_2N$. Calculated, %: C 31.00; H 0.87; Cl 45.76; F 16.35; N 6.03. M 230.9215.

Reaction of 1,2,4-trichlorotrifluorobenzene (1) with ethyl cyanoacetate. Compound **1**, 5.08 g (21.58 mmol), was dissolved in 50 mL of DMF, 2.94 g (25.99 mmol) of ethyl cyanoacetate and 6.04 g (43.70 mmol) of potassium carbonate were added, and the mixture was stirred for 4 h at 95–100°C. The mixture was then cooled to room temperature and poured into a mixture of 20 mL of concentrated aqueous HCl and 100 mL of water, and the off-white solid was filtered off and dried in a desiccator over $CaCl_2$. The product, 6.41 g, contained 97.9% (GLC) of a mixture of compounds **17**–**19** (yield 89%) at a ratio of ~97.5 : 1 : 1.5 (^{19}F NMR). Vacuum sublimation at 150°C (~10 mm) gave white crystals with mp 79–81°C and the same isomer ratio. Found (for isomer mixture **17**–**19**), %: C 40.14; H 1.84; Cl 31.87; F 11.55; N 4.23. $C_{11}H_6Cl_3F_2NO_2$. Calculated, %: C 40.22; H 1.84; Cl 32.37; F 11.57; N 4.26.

Ethyl 2-cyano-2-(2,4,5-trichloro-3,6-difluorophenyl)acetate (17). IR spectrum (KBr), ν, cm^{-1}: 3020, 2989, 2970, 2908, 1747, 1597, 1443, 1417, 1392, 1371, 1335, 1319, 1298, 1284, 1250, 1221, 1182, 1093, 1070, 1036, 995, 912, 881, 852, 783, 766, 729, 688, 669, 640, 559, 457, 420. UV spectrum (hexane), λ_{max}, nm (logε): 222 (4.08), 280 sh (3.41), 288 (3.48). ^1H NMR spectrum, δ, ppm: 1.38 t (3H, CH_3, J_{HH} = 7 Hz), 4.34 m (2H, CH_2), 5.20 br.s (1H, CH). ^{19}F NMR spectrum (from the spectrum of mixture **17**–**19**), δ_F, ppm: 49.2 d (J_{FF} = 12 Hz), 50.7 d (J_{FF} = 12 Hz). Found: m/z 326.9431 $[M]^+$. $C_{11}H_6Cl_3F_2NO_2$. Calculated: M 326.9427.

Ethyl 2-cyano-2-(2,3,5-trichloro-4,6-difluorophenyl)acetate (18). ^{19}F NMR spectrum (MeCN–$CDCl_3$) (from the spectrum of mixture **17**–**19**), δ_F, ppm: 51.8 d (6-F, J_{FF} = 4 Hz), 57.7 d (4-F, J_{FF} = 4 Hz). Found: m/z 327 $[M]^+$. Calculated: M 326.94.

Ethyl 2-cyano-2-(2,3,6-trichloro-4,5-difluorophenyl)acetate (19). ^{19}F NMR spectrum (MeCN–$CDCl_3$) (from the spectrum of mixture **17**–**19**), δ_F, ppm: 31.3 d (5-F, J_{FF} = 21 Hz), 38.8 d (4-F, J_{FF} = 21 Hz). Found: m/z 327 $[M]^+$. Calculated: M 326.94.

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