

# Phenols Reactions with 1,1-Difluorodichloroethene, 1,2-Di(fluorochloro)ethene, and Trifluorochloroethene

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Received May 29, 2002

**Abstract**—Phenols containing in the *para*-position of the benzene ring substituents of various electronic character add to 1,1-difluorodichloroethene in acetone in the presence of potassium hydroxide. A similar reaction with 1,2-di(fluorochloro)ethene occurs only in DMF or *N,N*-dimethylacetamide and is followed by hydrogen chloride elimination. Phenols with electron-donor substituents add to trifluorochloroethene in acetone in the presence of potassium hydroxide, the reaction of phenols with electron-acceptor substituents requires DMF as solvent.

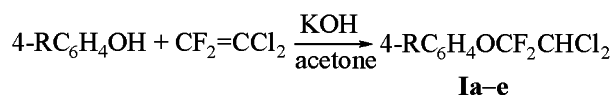
The products of substituted phenols addition to fluoroolefins attract lately a growing attention as initial compounds for preparation of substances with pesticidal and herbicidal properties. Therefore these compounds may be interesting as synthons for the synthesis of physiologically active substances.

Reactions of phenol and cresols with trifluorochloroethene were described in [1] where the phenol was shown to add to trifluorochloroethene in acetone at 40°C in the presence of potassium hydroxide affording a single product that did not eliminate hydrogen fluoride even when heated with powdered potassium hydroxide to 400°C. A similar 4-nitrophenol addition to trifluorochloroethene occurred also in the presence of potassium hydroxide in DMF medium. A substituted aniline prepared by reduction of 4-(1,1,2-trifluoro-2-chloroethoxy)nitrophenol was used in the synthesis of compounds having a pesticidal activity [2]. However the physical constants of this substituted aniline were not mentioned in [2]. The addition of phenol to 1,1-difluorodichloroethene was also described [1], and the process should be carried out at temperature below 10°C to avoid the elimination of hydrogen fluoride and the formation of phenyl fluorochloroethenyl ether.

In contrast to trifluorochloroethene, the reactions between phenol and 1,2-di(fluorochloro)ethene were not studied.

It turned out that substituted phenols both with electron-donor and electron-acceptor groups in the *para*-position of the benzene ring did not react with the 1,2-di(fluorochloro)ethene in acetone solution in the presence of potassium hydroxide even at boiling.

At the same time from the reaction mixture were isolated compounds that turned out to be addition products of substituted phenols to 1,1-difluorodichloroethene **Ia-e**. This selective reaction is apparently due to a larger positive charge on the carbon atom of CF<sub>2</sub> group in the 1,1-difluorodichloroethene than on the carbon atoms in the 1,2-di(fluorochloro)ethene.



R = H (**a**), CH<sub>3</sub> (**b**), OCH<sub>3</sub> (**c**), Br (**d**), NO<sub>2</sub> (**e**).

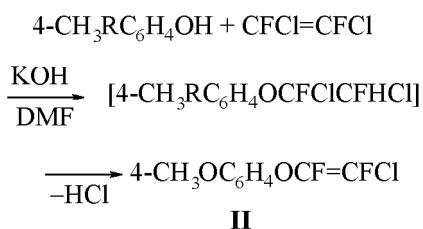
The formation of compounds **Ia-e** in reaction with 1,2-di(fluorochloro)ethene is due to the presence in the latter of about 5% of 1,1-difluorodichloroethene arising during the synthesis of the 1,2-di(fluorochloro)ethene from 1,2-difluorotetrachloroethane (Freon-112) by dechlorination with zinc. We determined the content of the impurity by means of <sup>19</sup>F NMR spectroscopy. The close values of boiling points of these olefins (21–22 and 15°C respectively [3]) prevented preparation of pure 1,2-di(fluorochloro)ethene by simple distillation. On the contrary the treating of crude 1,2-di(fluorochloro)ethene with phenol in acetone in the presence of a little potassium hydroxide removes completely the 1,1-difluorodichloroethene impurity. Thus this procedure can be used for purification of 1,2-di(fluorochloro)ethene.

We obtained compounds **Ia-e** at higher temperature than indicated in [1]; however we found no dehydrofluorinated products.

Unlike the substituted phenols the 4-methoxycarbonylaminothiophenol readily reacted with 1,2-di-

(fluorochloro)ethene in acetone in the presence of potassium hydroxide affording 4-methoxycarbonylaminothiophenyl 1,2-difluoro-2-chloroethenyl sulfide. The reaction evidently proceeds through two stages. First 4-methoxycarbonylaminothiophenol adds to 1,2-di(fluorochloro)ethene, and then dehydrochlorination takes place [4].

However the reaction of 4-methoxyphenol with 1,2-di(fluorochloro)ethene carried out in DMF or *N,N*-dimethylacetamide in the presence of potassium hydroxide at 60–80°C gave rise to 4-(1,2-difluoro-2-chloroethenyloxy)anisole (**II**) in a good yield. Like with the 4-methoxycarbonylaminothiophenol the reaction proceeds through two stages: first the 4-methoxyphenol adds to 1,2-di(fluorochloro)ethene, and then dehydrochlorination occurs.

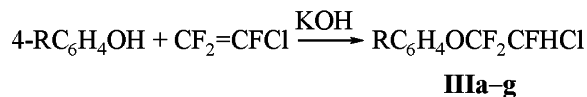


Compound **II** is a colorless fluid containing a mixture of *E*- and *Z*-isomers in 1:1 ratio as shows the <sup>19</sup>F NMR spectrum. Note that in the <sup>1</sup>H NMR spectrum of the product no difference appears in the chemical shifts of aromatic protons from *E*- and *Z*-isomers; apparently the 1,2-difluorochloroethenyloxy group weakly affects the aromatic ring. The formation of a mixture of *E*- and *Z*-isomers in this reaction is caused by the presence in the initial 1,2-di(fluorochloro)ethene of *E*- and *Z*-isomers in 1:1 ratio [3]. Thus in compound **II** the configuration of the initial compound was conserved.

We studied addition to trifluorochloroethene of *ortho*-, *meta*- and *para*-substituted *N*-acetylaminophenols. It turned out that the reaction proceeded in acetone at room temperature with a slight self-heating. Under the same conditions 4-bromo- and 4-fluorophenols also easily added to the trifluorochloroethene.

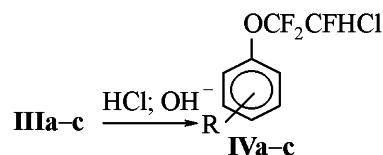
Under similar conditions the trifluorochloroethene failed to react with phenols having in the *para*-position an electron-acceptor substituent (ester or aldehyde group). Only at the use of DMF or *N,N*-dimethylacetamide we obtained the corresponding products in a good yield. Apparently in these aprotic solvents the nucleophilicity of phenolate anions is increased.

The substituted (1,1,2-trifluoro-2-chloroethoxy)-benzenes (**III**) obtained are colorless substances, either crystalline (**IIIa-c, g**) or liquid (**III d, e, h**).



R = 2-NHAc (**a**), 3-NHAc (**b**), 4-NHAc (**c**), 4-Br (**d**), 4-F (**e**), 4-COOCH<sub>3</sub> (**f**), 4-CHO (**g**).

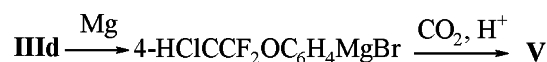
By hydrolysis of compounds **IIIa-c** in a mixture hydrochloric acid-ethanol the corresponding substituted anilines **IVa-c** were obtained as colorless fluids, and the hydrolysis of ester **III f** with a water solution of potassium hydroxide furnished acid **V** as colorless crystalline substance.



R = 2-NH<sub>2</sub> (**a**), 3-NH<sub>2</sub> (**b**), 4-NH<sub>2</sub> (**c**).



All our previous attempts to prepare organomagnesium compound from *meta*- or *para*-difluoromethoxybromobenzene both by reaction with magnesium turnings or with alkylmagnesium bromides in ethyl ether or THF resulted only in destruction of the difluoromethoxy group. In contrast to difluoromethoxy moiety the OCF<sub>2</sub>CFHCl group was stable against organomagnesium compounds, and 4-(1,1,2-trifluoro-2-chloroethoxy)bromobenzene (**III d**) cleanly afforded the Grignard reagent with magnesium turnings in ethyl ether. The carbonization of the organomagnesium compound with carbon dioxide furnished acid **V**.

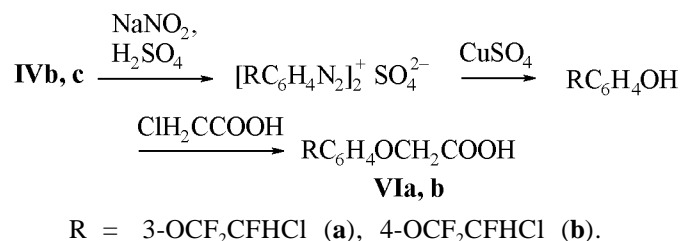


In order to extend the set of synthons for production of physiologically active compounds we prepared diazo compounds from substituted anilines **IV b** and **IV c** which were then converted into the corresponding phenols. The latter were treated with chloroacetic

<sup>1</sup>H and <sup>19</sup>F NMR spectra of compounds I–VI

Compd. no.	<sup>1</sup> H NMR spectrum (in CDCl <sub>3</sub> ), δ, ppm, <i>J</i> , Hz	<sup>19</sup> F NMR spectrum (in CDCl <sub>3</sub> ), δ, ppm, <i>J</i> , Hz
<b>Ia</b>		-79.49 d (CF <sub>2</sub> ), <i>J</i> <sub>FF</sub> 5.1
<b>Ib</b>		-79.88 d (CF <sub>2</sub> ), <i>J</i> <sub>FF</sub> 5.1
<b>Ic</b>		-79.75 d (CF <sub>2</sub> ), <i>J</i> <sub>FF</sub> 5.1
<b>Id</b>		-79.81 d (CF <sub>2</sub> ), <i>J</i> <sub>FF</sub> 5.1
<b>Ie</b>		-79.94 d (CF <sub>2</sub> ), <i>J</i> <sub>FF</sub> 5.1
<b>II</b>	3.78 s (3H, OCH <sub>3</sub> ), 6.8 d (2H, H <sub>arom</sub> , <i>J</i> <sub>HH</sub> 9) 7.0 d (2H, H <sub>arom</sub> , <i>J</i> <sub>HH</sub> 9)	Z-isomer: -143.71 d (1F, F <sup>1</sup> , <i>J</i> <sub>FF</sub> 120), -117.57 d (1F, F <sup>2</sup> , <i>J</i> <sub>FF</sub> 120) E-isomer: -128.8 d (1F, F <sup>1</sup> , <i>J</i> <sub>FF</sub> 36), -102.06 d (1F, F <sup>2</sup> , <i>J</i> <sub>FF</sub> 36)
<b>IIIa</b>	2.2 s (3H, CH <sub>3</sub> ), 6.3 d (1H, CFH, <i>J</i> <sub>FH</sub> 48), 7.2 s (1H, NH), 7.5 m (2H, H <sub>arom</sub> ), 7.6 m (1H, H <sub>arom</sub> ), 7.9 m (1H, H <sub>arom</sub> )	-83.9 d (2F, CF <sub>2</sub> , <i>J</i> <sub>FF</sub> 32), -154.5 d.t (1F, CFH, <i>J</i> <sub>FH</sub> 48, <i>J</i> <sub>FF</sub> 12)
<b>IIIb</b>	2.1 s (3H, CH <sub>3</sub> ), 6.1 d (1H, CFH, <i>J</i> <sub>FH</sub> 46), 7.2 s (1H, NH), 6.9 m (1H, H <sub>arom</sub> ), 7.3 m (1H, H <sub>arom</sub> ), 7.4 m (2H, H <sub>da_rom</sub> )	-84.5 d.d (2F, CF <sub>2</sub> , <i>J</i> <sub>FF</sub> 34), -154.6 d.t (1F, CFH, <i>J</i> <sub>FH</sub> 46, <i>J</i> <sub>FF</sub> 12)
<b>IIIc</b>	2.1 s (3H, CH <sub>3</sub> ), 6.1 d (1H, CFH, <i>J</i> <sub>FH</sub> 48), 7.1 d (1H, H <sub>arom</sub> , <i>J</i> <sub>HH</sub> 9), 7.2 s (1H, NH), 7.5 d (2H, H <sub>da_rom</sub> , <i>J</i> <sub>HH</sub> 9)	-84.0 t (2F, CF <sub>2</sub> , <i>J</i> <sub>FF</sub> 9, <i>J</i> <sub>FH</sub> 13), -154.6 d (1F, CFH, <i>J</i> <sub>FH</sub> 49)
<b>III d</b>	6.2 d (1H, CFH, <i>J</i> <sub>HF</sub> 49), 7.0 d (2H, H <sub>da_rom</sub> , <i>J</i> <sub>HH</sub> 9), 7.5 d (2H, H <sub>da_rom</sub> , <i>J</i> <sub>HH</sub> 9)	-84.7 s (2F, CF <sub>2</sub> ), -154.1 d.t. (1F, CFH, <i>J</i> <sub>FH</sub> 49, <i>J</i> <sub>FF</sub> 9)
<b>IIIe</b>	6.25 d (1H, CFH, <i>J</i> <sub>HF</sub> 48), 7.0 m (2H, H <sub>da_rom</sub> ), 7.15 m (2H, H <sub>da_rom</sub> )	-84.5 d (2F, CF <sub>2</sub> , <i>J</i> <sub>FF</sub> 15), -116.2 s (1F, F <sub>da_rom</sub> ), -154.1 d (1F, CFH, <i>J</i> <sub>FH</sub> 48, <i>J</i> <sub>FF</sub> 12)
<b>III f</b>	2.1 s (3H, CH <sub>3</sub> ), 6.5 d (1H, CFH, <i>J</i> <sub>HF</sub> 49), 7.3 d (2H, H <sub>da_rom</sub> , <i>J</i> <sub>HH</sub> 6), 7.9 d (2H, H <sub>da_rom</sub> , <i>J</i> <sub>HH</sub> 6)	-84.3 d (2F, CF <sub>2</sub> , <i>J</i> <sub>FF</sub> 13), -154.5 d (1F, CFH, <i>J</i> <sub>HF</sub> 49)
<b>III g</b>	6.3 d (1H, CFH, <i>J</i> <sub>HF</sub> 48), 7.4 d (2H, H <sub>da_rom</sub> , <i>J</i> <sub>HH</sub> 9), 7.9 d (2H, H <sub>da_rom</sub> , <i>J</i> <sub>HH</sub> 9), 10 s (1H, CHO)	-84.5 s (2F, CF <sub>2</sub> ), -154.8 d (1F, CFH, <i>J</i> <sub>HF</sub> 48)
<b>IVa</b>	3.45 br.s (2H, NH <sub>2</sub> ), 6.2 d.t (1H, CFH, <i>J</i> <sub>FH</sub> 47), 6.7 m (2H, H <sub>da_rom</sub> ), 7.0 t (1H, H <sub>da_rom</sub> ), 7.1 d (1H, H <sub>da_rom</sub> )	-84.5 d.d (2F, CF <sub>2</sub> , <i>J</i> <sub>FF</sub> 81, <i>J</i> <sub>FF</sub> 12), -154.2 d.t (1F, CFH, <i>J</i> <sub>FH</sub> 47, <i>J</i> <sub>FF</sub> 12)
<b>IVb</b>	3.7 br.s (2H, NH <sub>2</sub> ), 6.2 d.t (1H, CFH, <i>J</i> <sub>FH</sub> 48), 6.5 m (3H, H <sub>da_rom</sub> ), 7.1 t (1H, H <sub>da_rom</sub> )	-84.6 t (2F, CF <sub>2</sub> , <i>J</i> <sub>FF</sub> 17), -154.0 d.t (1F, CFH, <i>J</i> <sub>FH</sub> 48, <i>J</i> <sub>FF</sub> 12)
<b>IVc</b>	3.8 br.s (2H, NH <sub>2</sub> ), 5.9 d.t (1H, CFH, <i>J</i> <sub>FH</sub> 48), 6.9 d (2H, H <sub>da_rom</sub> , <i>J</i> <sub>HH</sub> 8), 7.1 t (1H, H <sub>da_rom</sub> , <i>J</i> <sub>HH</sub> 8)	-84.4 s (2F, CF <sub>2</sub> ), -154.1 d (1F, CFH, <i>J</i> <sub>FH</sub> 48)
<b>V</b>	7.3 d.t (1H, CFH, <i>J</i> <sub>HF</sub> 48, <i>J</i> <sub>FF</sub> 12), 7.35 d (2H, H <sub>da_rom</sub> , <i>J</i> <sub>HH</sub> 9), 8.0 d (2H, H <sub>da_rom</sub> , <i>J</i> <sub>HH</sub> 9)	-83.8 s (2F, CF <sub>2</sub> ), -155.2 d (1F, CFH, <i>J</i> <sub>FH</sub> 48)
<b>VIa</b>	4.7 s (2H, CH <sub>2</sub> ), 6.13 d (1H, CFH, <i>J</i> <sub>FH</sub> 48), 6.9 m (3H, H <sub>da_rom</sub> ), 7.15 m (1H, H <sub>da_rom</sub> )	-69.8 t (2F, CF <sub>2</sub> , <i>J</i> <sub>FF</sub> 12), -139.1 d.t (1F, CFH, <i>J</i> <sub>FH</sub> 48, <i>J</i> <sub>FF</sub> 12)
<b>VIb</b>	4.5 s (2H, CH <sub>2</sub> ), 6.1 d (1H, CFH, <i>J</i> <sub>FH</sub> 48), 6.8 d (2H, H <sub>da_rom</sub> , <i>J</i> <sub>HH</sub> 8), 7.2 d (2H, H <sub>da_rom</sub> , <i>J</i> <sub>HH</sub> 8)	-70.1 s (2F, CF <sub>2</sub> ), -139.3 d (1F, CFH, <i>J</i> <sub>FH</sub> 48)

acid to provide the corresponding phenoxyacetic acids **VIa, b**.



The data of <sup>1</sup>H and <sup>19</sup>F NMR spectra of compounds **I–VI** are given in table.

## EXPERIMENTAL

<sup>1</sup>H and <sup>19</sup>F NMR spectra were recorded on spectrometer Varian VXR-300 at operating frequencies 299.9 and 282.2 MHz respectively from solutions in CDCl<sub>3</sub> using HMDS and CCl<sub>3</sub>F as internal references.

**4-Substituted 1,1-difluoro-2,2-dichloroethoxybenzenes (Ia–e).** A mixture of 0.2 mmol of an appropriate substituted phenol, 0.1 mol of potassium hydroxide, 0.2 mol of 1,2-di(fluorochloro)ethene, and 60 ml of acetone was boiled at stirring for 48 h. The reaction mixture was then poured into water, extracted with ethyl ether, the ether extract was washed with water, and dried with  $\text{MgSO}_4$ . The solvent was distilled off, the residue was distilled in a vacuum. The yields of compounds obtained were calculated on the content of 1,1-difluorodichloroethene in 1,2-di(fluorochloro)ethene amounting to 5%.

**1,1-Difluoro-2,2-dichloroethoxybenzene (Ia),** yield 64%, bp 91–92°C (20 mm Hg),  $n_D^{22}$  1.4760. Found, %: C 42.28; H 2.84; Cl 31.11.  $\text{C}_8\text{H}_6\text{Cl}_2\text{F}_2\text{O}$ . Calculated, %: C 42.29; H 2.64; Cl 31.27.

**4-(1,1-Difluoro-2,2-dichloroethoxy)toluene (Ib),** yield 72%, bp 110–111°C (20 mm Hg),  $n_D^{22}$  1.5080. Found, %: C 45.08; H 3.28; Cl 29.39.  $\text{C}_9\text{H}_8\text{Cl}_2\text{F}_2\text{O}$ . Calculated, %: C 44.81; H 3.32; Cl 29.46.

**4-(1,1-Difluoro-2,2-dichloroethoxy)anisole (Ic),** yield 69%, bp 134–135°C (20 mm Hg),  $n_D^{22}$  1.4920. Found, %: C 42.14; H 3.11; Cl 27.58.  $\text{C}_9\text{H}_8\text{Cl}_2\text{F}_2\text{O}_2$ . Calculated, %: C 42.02; H 3.11; Cl 27.63.

**4-(1,1-Difluoro-2,2-dichloroethoxy)bromobenzene (Id),** yield 75%, bp 144–145°C (20 mm Hg),  $n_D^{22}$  1.5146. Found, %: C 31.20; H 1.85.  $\text{C}_8\text{H}_5\text{BrCl}_2\text{F}_2\text{O}$ . Calculated, %: C 31.37; H 1.63.

**4-(1,1-Difluoro-2,2-dichloroethoxy)nitrobenzene (Ie),** yield 70%, bp 164–165°C (20 mm Hg),  $n_D^{22}$  1.5168. Found, %: C 35.01; H 1.72; Cl 25.96.  $\text{C}_8\text{H}_5\text{Cl}_2\text{F}_2\text{NO}_3$ . Calculated, %: C 35.29; H 1.83; Cl 26.10.

**4-(1,2-Difluoro-2-chloroethenyloxy)anisole (II).** A mixture of 5 g (0.039 mol) of 4-methoxyphenol, 2.4 g (0.043 mol) of potassium hydroxide, 5.7 g (0.043 mol) of 1,2-di(fluorochloro)ethene, and 25 ml of DMF or *N,N*-dimethylacetamide was stirred for 8 h at 60°C. Then the reaction mixture was poured into 100 ml of water, organic reaction products were extracted with ether, the extracts were washed with 2% water solution of sodium hydroxide, with water, and dried on  $\text{MgSO}_4$ . The solvent was distilled off, the residue was distilled in a vacuum. Yield of 4-(1,2-difluoro-2-chloroethenyloxy)anisole 4.52 g (56%), bp 40–41°C (0.03 mm Hg),  $n_D^{20}$  1.4950. Found, %: C 48.80; H 3.23; Cl 16.29.  $\text{C}_9\text{H}_7\text{ClF}_2\text{O}_2$ . Calculated, %: C 48.98; H 3.20; Cl 16.09.

**Substituted (1,1,2-trifluoro-2-chloroethoxy)benzenes (IIIa–e).** Through a mixture of 0.2 mol of

an appropriate substituted phenol, 0.1 mol of potassium hydroxide, and 40 ml of acetone at stirring was bubbled at 25°C 0.5 mol of trifluorochloroethene for 5 h. The reaction mixture was poured into water, extracted with ethyl ether, the ether extract was washed with water, and dried with  $\text{MgSO}_4$ . The solvent was distilled off, the residue was recrystallized (compounds IIIa–c) or distilled in a vacuum (compounds IIId, e).

**2-(1,1,2-Trifluoro-2-chloroethoxy)acetanilide (IIIa),** yield 51%, mp 81–83°C (benzene). Found, %: C 44.64; H 3.31; Cl 13.27.  $\text{C}_{10}\text{H}_9\text{ClF}_3\text{NO}_2$ . Calculated, %: C 44.94; H 3.37; Cl 13.11.

**3-(1,1,2-Trifluoro-2-chloroethoxy)acetanilide (IIIb),** yield 63%, mp 75–77°C (benzene). Found, %: C 44.71; H 3.36; Cl 13.22.  $\text{C}_{10}\text{H}_9\text{ClF}_3\text{NO}_2$ . Calculated, %: C 44.94; H 3.37; Cl 13.11.

**4-(1,1,2-Trifluoro-2-chloroethoxy)acetanilide (IIIc),** yield 57%, mp 117–119°C (benzene). Found, %: C 44.68; H 3.29; Cl 13.18.  $\text{C}_{10}\text{H}_9\text{ClF}_3\text{NO}_2$ . Calculated, %: C 44.94; H 3.37; Cl 13.11.

**4-(1,1,2-Trifluoro-2-chloroethoxy)bromobenzene (III d),** yield 51%, bp 78–80°C (5 mm Hg)  $n_D^{22}$  1.4890. Found, %: C 32.91; H 1.69.  $\text{C}_8\text{H}_5\text{BrClF}_3\text{O}$ . Calculated, %: C 33.16; H 1.73.

**4-(1,1,2-Trifluoro-2-chloroethoxy)fluorobenzene (IIIe),** yield 54%, bp 71–73°C (5 mm Hg),  $n_D^{22}$  1.4350. Found, %: C 41.84; H 2.15; Cl 15.74.  $\text{C}_8\text{H}_5\text{ClF}_4\text{O}_2$ . Calculated, %: C 42.01; H 2.19; Cl 15.54.

**4-Substituted (1,1,2-trifluoro-2-chloroethoxy)benzenes (III f, g).** Through a mixture of 0.036 mol of methyl 4-hydroxybenzoate or 4-hydroxybenzaldehyde, 0.018 mol of potassium hydroxide, and 15 ml of DMF at stirring was bubbled at 25°C 0.04 mol of trifluorochloroethene for 3 h. The reaction mixture was poured into water, extracted with ethyl ether, the ether extract was washed with water, and dried with  $\text{MgSO}_4$ . The solvent was distilled off, the residue was distilled in a vacuum.

**Methyl 4-(1,1,2-trifluoro-2-chloroethoxy)benzoate (III f),** yield 55%, bp 85–87°C (0.02 mm Hg). Found, %: C 44.24; H 3.11; Cl 12.83.  $\text{C}_{10}\text{H}_8\text{ClF}_3\text{O}_3$ . Calculated, %: C 44.69; H 2.98; Cl 13.22.

**4-(1,1,2-Trifluoro-2-chloroethoxy)benzaldehyde (III g),** yield 53%, bp 68–70°C (0.02 mm Hg). Found, %: C 44.94; H 2.21; Cl 14.52.  $\text{C}_9\text{H}_6\text{ClF}_3\text{O}_2$ . Calculated, %: C 45.28; H 2.51; Cl 14.88.

**(1,1,2-Trifluoro-2-chloroethoxy)-substituted anilines (IVa-c).** A mixture of 26.75 g (0.1 mol) of an appropriate substituted acetanilide **IIIa-c**, 65 ml of ethanol, and 65 ml of concn. hydrochloric acid was boiled at stirring for 2 h. The reaction mixture was cooled, poured into water, filtered, and neutralized with solid sodium hydroxide till pH 8–9. The organic compounds were extracted with ethyl ether, the extract was washed with water, and dried with  $\text{MgSO}_4$ . The solvent was distilled off, the residue was distilled in a vacuum.

**2-(1,1,2-Trifluoro-2-chloroethoxy)aniline (IVa),** yield 15.3 g (68%), bp 95–97°C (5 mm Hg),  $n_D^{22}$  1.4874. Found, %: C 42.11; H 2.95; Cl 15.84.  $\text{C}_8\text{H}_7\text{ClF}_3\text{NO}$ . Calculated, %: C 42.57; H 3.10; Cl 15.74.

**3-(1,1,2-Trifluoro-2-chloroethoxy)aniline (IVb),** yield 14.9 g (66%), bp 96–98°C (5 mm Hg),  $n_D^{22}$  1.4926. Found, %: C 42.23; H 3.01; Cl 15.46.  $\text{C}_8\text{H}_7\text{ClF}_3\text{NO}$ . Calculated, %: C 42.57; H 3.10; Cl 15.74.

**4-(1,1,2-Trifluoro-2-chloroethoxy)aniline (IVc),** yield 16.0 g (71%), bp 125–127°C (15 mm Hg),  $n_D^{22}$  1.4899. Found, %: C 42.09; H 2.99; Cl 15.56.  $\text{C}_8\text{H}_7\text{ClF}_3\text{NO}$ . Calculated, %: C 42.57; H 3.10; Cl 15.74.

**4-(1,1,2-Trifluoro-2-chloroethoxy)benzoic acid (V).** (a) To 20 ml of 30% water solution of potassium hydroxide was added dropwise at stirring 2 g (7 mmol) of ester **IIIc**, the stirring was continued for 10 min. The precipitated potassium salt of acid **V** was filtered off, washed with ethyl ether, and dissolved in 10 ml of water. The water solution was acidified by concn. hydrochloric acid till pH 5–6, the precipitated crystals were filtered off, dried, and recrystallized. Yield 1.64 g (85.5%), mp 167–168°C (benzene). Found, %: C 42.21; H 2.25; Cl 13.87.  $\text{C}_9\text{H}_6\text{ClF}_3\text{O}_3$ . Calculated, %: C 42.44; H 2.36; Cl 13.95.

(b) To a mixture of 0.72 g (0.03 mol) of magnesium turnings and 20 ml of ethyl ether was added at stirring 2 ml of 1,2-dibromoethane, and then a solution of 8.69 g (0.03 mol) of bromobenzene **IIIc** in 30 ml of ethyl ether. The rate of addition was controlled so that the reaction mixture moderately boiled. After all the reagent was added the mixture was stirred for 1.5 h more and then poured on 50 g of solid carbon dioxide in 50 ml of ethyl ether. After warming to the room temperature the ether solution was washed with water ( $3 \times 15$  ml), the water washings were extracted with ethyl ether, the extract was filtered and acidified with concn. hydrochloric acid till pH 3–5. The precipitated acid was extracted with

ethyl ether. the ether extract was dried with  $\text{MgSO}_4$ , the solvent was removed in a vacuum. The residue was recrystallized from benzene. Yield 5.1 g (67%). The mixed sample with that prepared by procedure (a) did not show melting point depression.

**3- and 4-(1,1,2-trifluoro-2-chloroethoxy)phenoxyacetic acids (VIa, b).** To 125 ml of 30% aqueous sulfuric acid was added at stirring 0.1 mol of an appropriate amine **IVb** or **IVc**. The mixture was cooled to  $-5^\circ\text{C}$ , and a solution of 8 g (0.11 mol) of sodium nitrite in 25 ml of water was added thereto maintaining the temperature below  $-2^\circ\text{C}$ . To the diazo solution obtained 2 g of urea was added, and the reaction mixture was filtered. The filtrate was added dropwise at stirring to a solution of 25 g of  $\text{CuSO}_4 \cdot 9\text{H}_2\text{O}$  in 200 ml of water and then heated till the end of nitrogen liberation. The reaction mixture was cooled, the product was extracted into ethyl ether. The ether extract was washed with water and dried on  $\text{MgSO}_4$ . The solvent was distilled off, the residue was distilled in a vacuum.

A mixture of 0.043 mol of *p*- or *m*-(1,1,2-trifluoro-2-chloroethoxy)phenol, 0.064 mol of chloroacetic acid, 0.11 mol of sodium hydroxide, and 30 ml of water was stirred at  $100^\circ\text{C}$  for 4 h. On cooling the precipitated sodium salt of the phenoxyacetic acid was filtered off, the precipitate on the filter was dissolved in 100 ml of water, acidified with concn. hydrochloric acid to pH 3–5. The precipitated phenoxyacetic acid was extracted with ethyl ether ( $3 \times 30$  ml), the combined ether extracts were dried on  $\text{MgSO}_4$ , and the solvent was distilled off. The residue was recrystallized from a mixture benzene–hexane, 1:1.

**3-(1,1,2-Trifluoro-2-chloroethoxy)phenoxyacetic acid (VIa),** yield 82%, mp 82–84°C. Found, %: C 42.16; H 2.65; Cl 12.30; F 20.12.  $\text{C}_{10}\text{H}_8\text{ClF}_3\text{O}_4$ . Calculated, %: C 42.18; H 2.81; Cl 12.48; F 20.07.

**4-(1,1,2-Trifluoro-2-chloroethoxy)phenoxyacetic acid (VIb),** yield 83%, mp 103–105°C. Found, %: C 41.94; H 3.08; Cl 11.87; F 20.35.  $\text{C}_{10}\text{H}_8\text{ClF}_3\text{O}_4$ . Calculated, %: C 42.18; H 2.81; Cl 12.48; F 20.07.

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