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Reaction of pentafluoroacetanilide with zinc catalyzed by nickel complexes

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The reaction of pentafluoroacetanilide hydrodefluorination under the action of zinc in the presence of catalytic amounts of complexes, generated *in situ* from nickel chloride and 2,2´-bipyridine or 1,10-phenanthroline, was studied. The influence of the solvent, catalytic complex, and substrate : zinc molar ratio on the reaction course was investigated. On the basis of the results obtained, preparative methods for the synthesis of 3,4,5-trifluoro- and 2,3,4,5-tetrafluoroanilines were developed.

Key words: pentafluoroacetanilide, nickel complexes, 2,2´-bipyridine, 1,10-phenanthroline, catalytic hydrodefluorination, 2,3,4,5-tetrafluoroaniline, 3,4,5-trifluoroaniline.

Partially fluorinated aromatic compounds are widely used in the production of pharmaceutical preparations[1] and chemical remedies of plant protection,[2,3] as well as in nonlinear optics and molecular electronics.[4,5]

Highly reactive agents or rather drastic conditions are used in the known methods of introduction of several fluorine atoms into the aromatic ring, which results, as a rule, in the formation of perfluorinated organic derivatives.[6] One of the most promising routes for the synthesis of practically important fluorinated compounds is the selective replacement of one or several fluorine atoms in perfluorinated products by hydrogen.

Both catalytic and noncatalytic methods of hydrodefluorination of polyfluoroaromatic compounds are presently known.[7,8] When the noncatalytic methods are used, as a rule, the C—F bonds in the *para*-position to the substituent undergo activation. For instance, the reaction of perfluoroalkylpentafluorobenzenes with lithium alumohydride affords mainly products containing hydrogen in the *para*-position to the perfluoroalkyl group.[9,10] An analogous result was obtained by the reduction of polyfluoroaromatics in aqueous ammonia with zinc[11] or in a mixture of DMF and H_2O with the zinc—copper couple.[12—14] The *para*-hydrodefluorination of pentafluoropyridine, pentafluorobenzonitrile, and perfluorotoluene with $P(NEt_2)_3$ in aqueous ether, DMF, or dioxane was described.[15] Pentafluoropyridine is subjected to *para*-hydrodefluorination in the presence of zinc in aqueous bases.[16,17] The removal of fluorine from the *para*-position is observed under these conditions for polyfluoroaromatic compounds containing other functional groups (COOH, CH_2OH, $CONH_2$) and decafluorobiphenyl.[17] In the latter case, the main reaction products are 4*H*-nonafluoro- and 4,4´*H*-octafluorobiphenyls. The hydrodefluorination of pentafluoroacetanilide (**1**) with zinc in aqueous ammonia proceeds less selectively to form a mixture of *ortho*- (**2**), *para*- (**3**), and 2,5-hydrodefluorination (**4**) products.[18]

Few works describe the hydrodefluorination of polyfluoroaromatic compounds containing functional groups under the conditions of catalysis by transition metals. For example, the catalytic hydrogenolysis of pentafluoropyridine in the presence of the rhodium complexes affords the *para*-hydrodefluorination product.[19] An analogous result was obtained by the reaction of pentafluoropyridine with $Bu^i{}_2AlH$ in the presence of the zirconium cyclopentadiene complexes.[20] The catalytic hydrodefluorination of perfluoropyridine with zinc in aqueous DMF in the presence of the nickel complexes includes along with the *para*-hydrodefluorination reaction the activation of the C—F bonds in positions 2 and 4, resulting in the formation of 3,5,6-trifluoro- and 3,5-difluoropyridines.[21]

The method for the synthesis of 2,3,4,5-tetrafluorobenzoic acid by the catalytic reductive defluorination of C_6F_5COOH in the presence of the $YbCp_2$(dme) complex is known.[22] We have previously[23] described the reduction of pentafluorobenzoic acid by zinc in the presence of catalytic amounts of the nickel complexes, which occurred with the selective activation of the C—F bonds in the *ortho*-position to the carboxyl group. It was shown[24] that the reductive catalytic system $NiCl_2$—2,2´-bipyridine (bpy) or 1,10-phenanthroline (phen)—Zn in aqueous DMF can be used for the *ortho*-hydrodefluorination pentafluoroacetanilide **1**. The purpose of the present work is the systematic study of factors determining the activity of the nickel catalyst and selectivity of the reaction.

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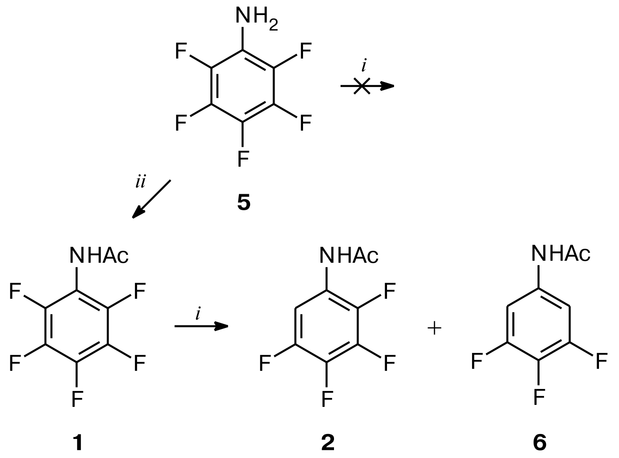
Results and Discussion

We have previously shown that pentafluoroaniline (**5**) does not react with zinc in a mixture of DMF with water at 70 °C both in the absence of a catalyst and in the presence of catalytic amounts of nickel chloride or its complexes with bpy or phen. However, the transformation of compound **5** by acylation into acetanilide **1** makes it possible to involve the latter in hydrodefluorination under the action of the catalytic system under study.[24] In this case, the highly regioselective activation of the C—F bonds in the *ortho*-position to the NHCOMe group is observed, resulting in the formation of a mixture of 2,3,4,5-tetrafluoro- (**2**) and 3,4,5-trifluoroacetanilides (**6**) (Scheme 1).

Scheme 1



i. $NiCl_2 \cdot nL$ (L = bpy or phen), Zn, DMF—H_2O, 70 °C, n = 1—3; *ii.* Ac_2O, reflux, 96% yield.

Preliminary experiments showed that the conversion of the substrate and the extent of hydrodefluorination depend on such factors as the nature of the solvent used, molar ratio nickel chloride : ligand, and the ligand nature (Table 1). When the reaction is carried out in aqueous DMF, an increase in the number of ligands bonded to nickel enhances the activity of the corresponding catalytic complex in the cases of both 2,2´-bipyridine (see Table 1, entries *1—3*, Fig. 1) and 1,10-phenanthroline (see Table 1, entries *4—6*, Fig. 1, *a*). Complex $NiCl_2 \cdot bpy$ in aqueous DMF exhibits a lower activity (TOF = 1.12 h^{-1}, see Table 1, entry *1*) compared to the analog containing 1,10-phenanthroline (TOF = 2.52 h^{-1}, see Table 1, entry *4*). In the first case, a substrate **1** conversion of 28% is achieved within 5 h (see Table 1, entry *1*), whereas the second case gave 63% conversion (see Table 1, entry *4*). The nickel complexes containing two and three ligands were more active in the case of 2,2´-bipyridine (TOF = 6.75 and 8.70 h^{-1}, see Table 1, entries *2* and *3*, respectively) than the complexes with 1,10-phenanthroline (TOF = 5.10 and 6.55 h^{-1}, see Table 1, entries *5* and *6*). As a whole,

Table 1. Results of the hydrodefluorination of pentafluoroacetanilide **1** by the zinc complexes in various solvents

Entry	Complex	Solvent	t/h	Y (%)	S (%)		TON	TOF/h^{-1}
					2-H (**2**)	2,6-H (**6**)		
1	$NiCl_2 \cdot bpy$	DMF	5	28	100	0	5.60	1.12
2	$NiCl_2 \cdot 2bpy$	DMF	4	100	65	35	27.00	6.75
3	$NiCl_2 \cdot 3bpy$	DMF	4	100	26	74	34.80	8.70
4	$NiCl_2 \cdot phen$	DMF	5	63	100	0	12.60	2.52
5	$NiCl_2 \cdot 2phen$	DMF	4	98	96	4	20.38	5.10
6	$NiCl_2 \cdot 3phen$	DMF	4	100	69	31	26.20	6.55
7	$NiCl_2 \cdot bpy$	DMA	6	19	100	0	3.80	0.63
8	$NiCl_2 \cdot 2bpy$	DMA	6	99	100	0	19.80	3.30
9	$NiCl_2 \cdot 3bpy$	DMA	6	83	100	0	16.60	2.77
10	$NiCl_2 \cdot phen$	DMA	6	49	100	0	9.80	1.63
11	$NiCl_2 \cdot 2phen$	DMA	6	100	73	27	25.40	4.23
12	$NiCl_2 \cdot 3phen$	DMF	6	85	100	0	17.00	2.83
13	$NiCl_2 \cdot bpy$	MP	6	56	100	0	11.20	1.87
14	$NiCl_2 \cdot 2bpy$	MP	6	95	100	0	19.00	3.17
15	$NiCl_2 \cdot 3bpy$	MP	6	97	11	89	36.67	6.11
16	$NiCl_2 \cdot phen$	MP	6	90	100	0	18.00	3.00
17	$NiCl_2 \cdot 2phen$	MP	4	100	23	77	35.40	8.85
18	$NiCl_2 \cdot 2phen$	MP	6	100	0	96	>40	>6.7
19	$NiCl_2 \cdot 3phen$	MP	6	100	32	68	33.60	5.60

Note. The following designations were used: t is the reaction time, Y is the conversion, S is the selectivity, TON is the number of catalytic cycles per unit of catalyst, and TOF is the turnover frequency, *i.e.*, the number of catalytic cycles per unit of catalyst per unit time.

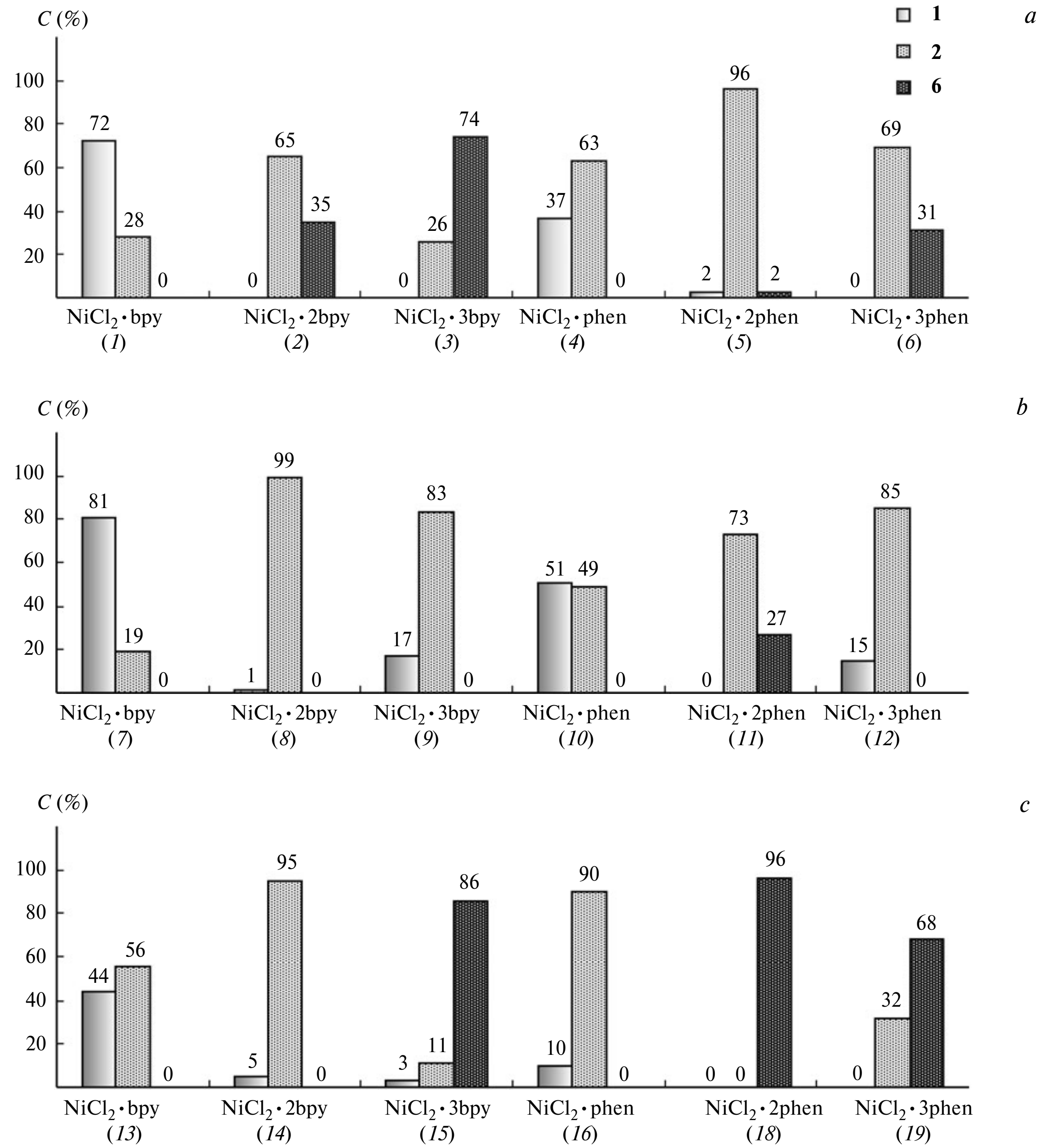


Fig. 1. Composition of the reaction mixture of the hydrodefluorination of compound **1** in aqueous DMF (*a*), DMA (*b*), and MP (*c*) obtained in various experiments (in parentheses): content of pentafluoroacetanilide (**1**), 2*H*-tetrafluoroacetanilide (**2**), and 2,6*H*-trifluoroacetanilide (**6**).

both the 2,2´-bipyridine and 1,10-phenanthroline nickel complexes demonstrate comparatively low catalytic activity in aqueous DMF. Due to this, the complete conversion of substrate **1** to product **6** was not achieved in this series of experiments.

Let us consider the influence of the solvent nature on the hydrodefluorination reaction. We carried out experiments on the hydrodefluorination of acetanilide **1** in aqueous *N*,*N*-dimethylacetamide (DMA) (see Table 1, entries *7—12*, Fig. 1, *b*) and *N*-methylpyrrolidone (MP) (see Table 1, entries *13—19*, Fig. 1, *c*), whose properties are similar to those of DMF. It was found that the replacement of DMF by DMA mainly decreases the activity of the nickel catalysts. As in the reactions in aqueous DMF, the complexes with one nitrogen-containing ligand manifest low catalytic activity (see Table 1, entries *7* and *10*), and the phenanthroline complex turned out to be more active than the bipyridine analog (TOF = 0.63 and 1.63 h^{-1}, respectively). Unlike the reactions in DMF, the highest activity in DMA is shown by the complexes containing two ligands. For the reactions in the presence of $NiCl_2 \cdot 2bpy$ and $NiCl_2 \cdot 2phen$, TOF was 3.30 and 4.23 h^{-1}, respectively (see Table 1, entries *8* and *11*), while for $NiCl_2 \cdot 3bpy$ and $NiCl_2 \cdot 3phen$ TOF = 2.77 and 2.83 h^{-1}, respectively (see Table 1, entries *9* and *12*). The complexes with 1,10-phenanthroline (TOF = 3.30 and 4.23 h^{-1} for $NiCl_2 \cdot 2bpy$ and $NiCl_2 \cdot 2phen$, respectively (see Table 1, entries *8*, *11*)) are more active than the bipyridine analogs (for $NiCl_2 \cdot 3bpy$ and $NiCl_2 \cdot 3phen$ TOF = 2.77 and 2.83 h^{-1}, respectively (see Table 1, entries *9* and *12*)). The $NiCl_2 \cdot 2phen$ complex exhibits the highest activity in DMA (see Table 1, entry *11*): the complete conversion of the initial acetanilide **1** is achieved within 6 h, and the degree of hydrodefluorination at the second *ortho*-C—F bond is 27%.

Experiments with hydrodefluorination terminated at the stage of predominant formation of product **2** are especially interesting. In aqueous DMA for a series of the nickel complexes with two and three ligands, a high conversion of the initial compound **1** is observed along with the 100% selectivity for product **2** (see Table 1, entries *8*, *9*, *10*, and *12*). In this case, the best result is achieved in the presence of the $NiCl_2 \cdot 2bpy$ complex (see Table 1, entry *8*).

Based on the data obtained, we may conclude that the use of aqueous DMA as the solvent is promising for the synthesis of 2,3,4,5-tetrafluoroacetanilide **2**.

The activity of the nickel complexes in aqueous MP (see Table 1, entries *13—18*, Fig. 1, *c*) is higher than that for the reactions in other solvents; however, in the presence of the nickel complexes with the ratio Ni : ligand = 1 : 1 (see Table 1, entries *13* and *16*), the conversion of the substrate within 6 h does not achieve 100%. As for the reaction in aqueous DMA, the $NiCl_2 \cdot phen$ complex is more active (TOF = 3.00 h^{-1}, see Table 1, entry *16*) than $NiCl_2 \cdot bpy$. When the complexes with the Ni to ligand ratio equal to 1 : 2 and 1 : 3 are used as catalysts, the conversion of substrate **1** reaches 95—100% within 6 h (see Table 1, entries *14*, *15*, *18*, and *19*). Of the nickel bipyridine complexes, $NiCl_2 \cdot 3bpy$ demonstrates the higher activity (TOF = 6.11 h^{-1}, see Table 1, entry *15*) than $NiCl_2 \cdot 2bpy$ (TOF = 3.17 h^{-1}, see Table 1, entry *14*). On the contrary, among the phenanthroline analogs, the complex with two ligands exhibits a higher activity: the use of $NiCl_2 \cdot 2phen$ results in the complete conversion of compounds **1** and **2** within 6 h (TOF > 6.7 h^{-1}, see Table 1, entry *18*; within 4 h TOF = 8.85 h^{-1}, see Table 1, entry *17*). In this case, the major product is compound **6**. Under these conditions, complex $NiCl_2 \cdot 3phen$ is less active: in the presence of the complex considered, only a 68% conversion of compound **2** is observed within 6 h (TOF = 5.60 h^{-1}, see Table 1, entry *19*). Thus, the experiments showed that complex $NiCl_2 \cdot 2phen$ in aqueous MP manifests the highest activity in hydrodefluorination.

An admixture of 3,4-difluoroacetanilide (**7**) (up to 4—8 mol.%), which is the hydrodefluorination product of acetanilide **6**, was observed along with products **2** and **6** in the reaction mixture when the reaction was carried out in the presence of $NiCl_2 \cdot 2phen$.

Thus, a relationship between the catalytic activity of the nickel complex, the nature of the complex itself, and the solvent nature was found. Most likely, the effects described above are due to the structure of the coordination sphere of the nickel complex, which depends, in turn, on the amount of bpy or phen. For instance, complexes with one, two, and three bpy molecules, depending on the amount of the added ligand, were detected[25] by the titration of a solution of nickel perchlorate with a bpy solution. If the solution contains Cl^- anions, mixed $[Nibpy_mCl_n]^{(2-n)+}$ complexes are formed.[25] In addition, the formation rate of the nickel complexes with bpy depends substantially on the reaction medium, which indirectly indicates the presence of the solvent in the coordination sphere of nickel at particular stages of the complex formation process.[26] In this case, steric structure and donor properties of solvents become significant. All the factors considered can significantly affect the catalytic activity of the nickel complexes.[27,28]

To study the influence of the amount of zinc on the conversion of the substrate and formation of by-product **7**, we carried out experiments using the catalytic systems $NiCl_2 \cdot 2phen$ (5 mol.%)—MP/H_2O in which the amount of zinc was varied (Table 2). In the presence of 1—2 equiv. of zinc (see Table 2, entries *1* and *2*) over the substrate, the reaction proceeds slowly: the substrate conversion achieved 10—20% within 7 h. An increase in the amount of zinc dust to 3—5 equiv. (see Table 2, entries *3—5*) leads to a sharp increase in the catalytic activity of the system. The substrate conversion is 70—100%, and a mixture of products **2** and **6** is formed in the presence of 4 and 5 equiv. of zinc (see Table 2, entries *4* and *5*). The further increase in the amount of zinc see Table 2, entries *6—9*) increases the reaction rate even more. The complete conversion of the initial compound **1** and intermediate product **2** is achieved within 6 h of the reaction in the presence of 10 equiv. of zinc (see Table 2, entry *8*); however, the process is accompanied by the formation of by-product **7**. An increase in the reaction time to 7 h (see Table 2, entries *7* and *9*) results in a slight increase in the content of by-product **7**. Probably, the observed effect of the sharp enhancement of the catalytic activity of the system with an increase in the amount of zinc is related to the interaction of zinc with water, which in addition to hydrodefluorination also occurs when water is in excess in the reaction. In the presence of 1—2 equiv. of zinc, the interaction with water results in the fast deactivation of the metal surface due to the formation of the hydroxide film, which, in turn, decreases the hydrodefluorination rate. An increase in the amount of zinc makes it possible to offset the effect of deactivation of the reducing agent.

Table 2. Influence of the amount of zinc on the composition of the products of hydrodefluorination of pentafluoroacetanilide **1**

Entry	Amount of Zn, equiv.	*t*/h	*Y* (%)	Selectivity (%)		
				2-H (**2**)	2,6-H (**6**)	2,5,6-H (**7**)
1	1	7	12	100	0	0
2	2	7	23	100	0	0
3	3	7	69	100	0	0
4	4	7	100	75	25	0
5	5	7	100	10	89	1
6	10	6	100	0	96	4
7	10	7	100	0	95	5
8	15	4	100	0	97	3
9	15	7	100	0	94	6

Note. For designations, see Table 1.

Based on the data obtained, the methods for the preparative synthesis of 2,3,4,5-tetrafluoro- (**8**) and 3,4,5-trifluoroanilines (**9**) from pentafluoroaniline were developed. In the both cases, the first step is the pentafluoroaniline acylation at the amino group by acetaldehyde, and the second step is the selective hydrodefluorination of pentafluoroacetanilide **1** to acetanilide **2** or **6**, the alkaline hydrolysis of which gives the corresponding aniline. Tetrafluoroacetanilide **2** can be obtained by the hydrodefluorination of **1** by zinc in the presence of 5 mol.% of the $NiCl_2 \cdot 2bpy$ complex in aqueous DMA or MP, whereas trifluoroacetanilide **6** is formed in aqueous MP in the presence of 5 mol.% of the $NiCl_2 \cdot 2phen$ complex. The both acetanilides were transformed into the corresponding fluoroanilines **8** and **9** by alkaline hydrolysis and isolated from the reaction mixture by steam distillation. Some decrease in the hydrodefluorination rate is observed upon scaling. This effect can be avoided if zinc is added as several portions during the reaction rather than as a single batch.

Thus, we developed the new approach to the current of fluoroanilines **8** and **9**, which, unlike the existing methods for synthesis of similar compounds,[29—31] serves to obtain products **8** and **9** from comparatively cheap pentafluoroaniline, *viz.*, the reaction product of hexafluorobenzene and ammonia.[32] In addition, the method developed for the synthesis allows one to selectively obtain both mono- (**8**) and bis(*ortho*-defluorinated) anilines (**9**) by the insignificant variation of the hydrodefluorination conditions.

Thus, the acylation of pentafluoroaniline makes it possible to substantially change the reactivity of the polyfluoroaromatic ring. The reaction of pentafluoroacetanilide with zinc in the presence of catalytic complexes generated *in situ* from nickel chloride and 2,2´-bipyridine or 1,10-phenanthroline results in the highly regioselective activation of the C—F bonds in the *ortho*-positions to the NHAc group. The conversion of the substrate and the extent of hydrodefluorination depend on such factors as the nature of the catalytic complex, solvent nature, and the amount of zinc used.

Experimental

The ^{19}F NMR spectra were recorded on a Bruker Avance-300 spectrometer (282.40 MHz). Chemical shifts were measured relative to CCl_3F (using C_6F_6 as the secondary internal standard, $\delta = -162.9$). The HPLC chromatograms were detected on a Milichrom A-02 instrument (column 2×75 mm, sorbent ProntoSIL 120-5C18AQ with the reverse phase, particle size 5 μm, detection at 226 nm, time 0.18 s) in the water—methanol solvent gradient.

The composition of reaction mixtures, conversion of the initial compound **1**, and yields of the products were determined by HPLC. The TON parameter was calculated as the ratio of the number of moles of the reacted substrate to the number of moles of the catalyst used, taking into account that 3,4,5-trifluoroacetanilide **6** is formed by the further hydrodefluorination of product **2**. The TOF parameter was calculated as the ratio of TON to the reaction time.

Pentafluoroacetanilide **1** was synthesized from pentafluoroaniline similarly to the procedure described[18]; DMF, DMA, and MP were used after preliminary distillation; $NiCl_2 \cdot 6H_2O$, bpy, and $phen \cdot H_2O$ were used as received.

Hydrodefluorination reactions (general procedure). *Hydrodefluorination of compound **1** in aqueous DMF, DMA, and MP.* A three-necked flask equipped with a thermometer, a magnetic stirrer, and a heating bath was filled under argon with $NiCl_2 \cdot 6H_2O$ (30 mg, 0.125 mmol), the corresponding amount of bpy or $phen \cdot H_2O$ (0.125 mmol of $NiCl_2 \cdot 1L$, or 0.250 mmol of $NiCl_2 \cdot 2L$, or 0.375 mmol of $NiCl_2 \cdot 3L$), 2.5 mL of the corresponding solvent (DMF, DMA, or MP), and 0.5 mL of water. The reaction mixture was stirred for 1 h at 70 °C, then zinc dust (1635 mg, 25 mmol) was added in one portion, the mixture was stirred for another 10 min, and compound **1** (563 mg, 2.5 mmol) was added. The reaction mixture was stirred at 70 °C. The final composition of the reaction mixtures was determined by HPLC. The experimental results are presented in Table 1. The structures of compounds **2** and **6** were confirmed by the data of ^{19}F NMR spectroscopy. 2,3,4,5-Tetrafluoroacetanilide (**2**). ^{19}F NMR (DMF), δ: −140.3 (m, 1 F, F(5), $^3J_{F,F} = 22.5$ Hz, $^3J_{H,F} = 10$ Hz); −152.0 (m, 1 F, F(2), $^3J_{F,F} = 17.7$ Hz); −158.1 (m, 1 F, F(3); $^3J_{F,F} = 20$ Hz, $^3J_{F,F} = 20$ Hz); −164.4 (m, 1 F, F(4), $^3J_{F,F} = 21$ Hz, $^3J_{F,F} = 21$ Hz) (*cf.* Ref. 18: −140.1, $J = 21$ Hz; −153.4, $J = 18.5$ Hz; −158.2, $J = 20$ Hz, $J = 18.5$ Hz; −164.8, $J = 21$ Hz, $J = 20$ Hz). 3,4,5-Trifluoroacetanilide (**6**). ^{19}F NMR (DMF), δ: −135.0 (dd, 2 F, F(3), F(5), $^3J_{F,F} = 21.3$ Hz, $^3J_{H,F} = 10.5$ Hz); −169.2 (tt, 1 F, F(4), $^3J_{F,F} = 21.5$ Hz, $^4J_{H,F} = 6.5$ Hz).

*Hydrodefluorination of compound **1** in aqueous MP by $NiCl_2 \cdot 2phen$: the influence of the amount of zinc.* The reactions were carried out similarly to the general hydrodefluorination procedure using $NiCl_2 \cdot 6H_2O$ (30 mg, 0.125 mmol), $phen \cdot H_2O$ (50 mg, 0.250 mmol), MP (2.5 mL), water (0.5 mL), compound **1** (563 mg, 2.5 mmol), and the corresponding amount of zinc dust. The final composition of the mixture was determined by HPLC. The experimental results are presented in Table 2. ^{19}F NMR for by-product **7** (MP), δ: −137.4 (m, 1 F, F(3), $^3J_{F,F} = 21.3$ Hz); −145.5 (m, 1 F, F(4), $^3J_{F,F} = 22.2$ Hz).

Preparative synthesis of partially fluorinated aromatic amines 8 and 9. 2,3,4,5-Tetrafluoroaniline (**8**). A flask equipped with a thermometer, and gas-freeing tube, a magnetic stirrer, and an oil bath with a thermoregulator was filled with $NiCl_2 \cdot 6H_2O$ (119 mg, 0.5 mmol), 2,2´-bipyridine (156 mg, 1 mmol), MP (10 mL), and water (2 mL). The reaction mixture was stirred for 1 h at 70 °C, then the first portion of zinc dust (1.87 g, 29 mmol) was added, the mixture was additionally stirred for 10 min, and pentafluoroacetanilide (2.25 g, 10 mmol) was added. The reaction mixture was stirred for 4 h at 70 °C, and the next portion of zinc (935 mg, 14 mmol) was added every hour. Totally 4.68 g (72 mmol) of zinc dust were added. The reaction mixture was diluted with water (50 mL), and the solid part was filtered off and washed with water (2×10 mL). The product was washed off from the solid phase with acetonitrile (2×20 mL). The solvent was evaporated, and water (40 mL) and sodium hydroxide (800 mg, 20 mmol) were added to the residue. The obtained mixture was stirred for 1 h at ~20 °C. 2,3,4,5-Tetrafluoroaniline was steam-distilled off from the reaction mixture and extracted with dichloromethane (3×10 mL), the extract was dried with magnesium sulfate, and the solvent was distilled off *in vacuo*. The yield was 1.16 g (61% based on pentafluoroacetanilide). ^{19}F NMR (acetone), δ: –142.2 (ddd, 1 F, F(2), $^3J_{F,F}$ = 22.2 Hz, $^5J_{F,F}$ = 12.1 Hz, $^3J_{H,F}$ = 10.4 Hz); –159.9 (dd, 1 F, F(4), $^3J_{F,F}$ = 20.4 Hz, $^3J_{F,F}$ = 20.4 Hz); –162.8 (ddd, 1 F, F(5), $^3J_{F,F}$ = 18.5 Hz, $^5J_{F,F}$ = 17.7 Hz, $^4J_{HF}$ = 8.9 Hz); –177.4 (dddd, 1 F, F(3), $^3J_{F,F}$ = 21.7 Hz, $^3J_{F,F}$ = 21.9 Hz, $^4J_{F,F}$ = 7.7 Hz, $^4J_{H,F}$ = 7.7 Hz).

3,4,5-Trifluoroaniline (**9**). A flask equipped with a thermometer, a gas-outlet tube, a magnetic stirrer, and an oil bath with a thermoregulator was filled with $NiCl_2 \cdot 6H_2O$ (119 mg, 0.5 mmol), phenanthroline (156 mg, 1 mmol), MP (10 mL), and water (2 mL). The reaction mixture was stirred for 1 h at 70 °C, then the first portion of zinc dust (1.87 g, 29 mmol) was added, the mixture was additionally stirred for 10 min, and pentafluoroacetanilide (2.25 g, 10 mmol) was added. The reaction mixture was stirred for 6 h at 70 °C, adding the next portion of zinc (935 mg, 14 mmol) every hour. In all 6.54 g (100 mmol) of zinc dust were added. The reaction mixture was diluted with water (50 mL), and the solid part was filtered off and washed with water (2×10 mL). The product was washed off from the solid phase with acetonitrile (2×20 mL). The solvent was evaporated, and water (40 mL) and sodium hydroxide (800 mg, 20 mmol) were added to the residue. The obtained mixture was stirred for 1 h at ~20 °C. The product was steam-distilled off from the reaction mixture and extracted with dichloromethane (3×10 mL), the extract was dried with magnesium sulfate, and the solvent was distilled off *in vacuo*. The yield was 1.05 g (71% based on pentafluoroacetanilide). ^{19}F NMR (acetone), δ: –136.6 (dd, 2 F, F(3), F(5), $^3J_{F,F}$ = 21.3 Hz, $^3J_{H,F}$ = 10.5 Hz); –178.9 (tt, 1 F, F(4), $^3J_{F,F}$ = 21.3 Hz, $^4J_{H,F}$ = 6.0 Hz) (*cf.* Ref. 31 (C_6F_6 as standard): –27.5, –12.6, $J_{F,F}$ = 22 Hz).

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