

Reductive Transformations of Organofluorine Compounds: III.* Hydrodefluorination of Perfluoroalkylbenzenes Effected by Zn(Cu). The Unusual Behavior of Compounds Containing Perfluorinated *tert*-Butyl Group**

B. I. Krasnov and V. E. Platonov

Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Division, Russian Academy of Sciences,
Novosibirsk, 630090 Russia

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Abstract—Perfluoroalkylbenzenes under a treatment of a system Zn(Cu)—DMF—H₂O—electrolyte give rise in high yield to products of fluorine substitution by hydrogen in position 4. In perfluoro-*tert*-butylbenzene are substituted by hydrogen the fluorine atoms in positions 2 and 4; here the DMF—water ratio affects the regioselectivity of the process. In the perfluoro-4-*tert*-butyltoluene is mainly substituted the fluorine in the ortho-position to the C(CF₃)₃ group.

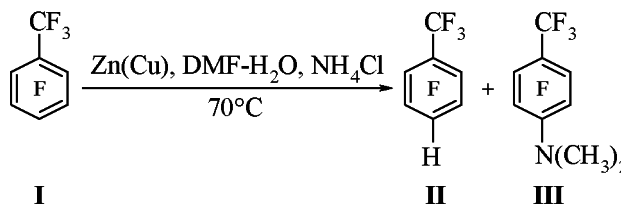
The synthetic value of hydrogen introduction into a perfluoroalkylarene consists in the possibility to replace it by functional group with the use of a Grignard reagent [2]. It is presumable that hydroperfluoroalkylarenes will turn out to be convenient precursors for preparation of perfluoroalkyllithium derivatives as has been already done e.g., with pentafluorobenzene and tetrafluorobenzenes [3, 4]. The preparation methods for hydro compounds involve nucleophilic substitution of fluorine atom in the *para*-position with respect to perfluoroalkyl group effected by LiAlH₄ or NH₂NH₂ followed in the latter case by treatment of the intermediate polyfluoroarylhydrazine with Fehling reagent [5, 6]. The yields of hydro derivatives here are moderate. Recently the hydrodefluorination of perfluorotoluene was carried out in high yield with the use of P(NEt₂)₃ in aqueous dioxane [7] and with Zn in aqueous ammonia [8]. We reported lately on substitution of fluorine in the *para*-position of perfluoroalkylbenzenes by hydrogen effected by Zn(Cu) in aqueous DMF [9].

In the present study the preparation method for hydro derivatives of perfluorinated monoalkylbenzenes was modified. The modification consists in the application of electrolytes in order to accelerate

the hydrodefluorination, and also of copper(II) chloride instead of copper powder.

The reaction of octafluorotoluene (**I**) with the system Zn(Cu)—DMF—H₂O as we stated earlier resulted in a single hydrodefluorination product, $\alpha,\alpha,\alpha,2,3,5,6$ -heptafluorotoluene (**II**). Here is important the completeness of conversion of the original compound. We found that addition of electrolytes favors the hydrodefluorination effected by Zn(Cu) [10]. The favorable effect of salts additives may be understood, e.g., as increase in the electroconductivity of the solution if the role of Zn(Cu) is that of a short-circuited voltaic couple.

Perfluorotoluene (**I**) in the presence of NH₄Cl within 20 h at 70°C is fully consumed and furnishes a mixture containing mainly toluene **II** and a little of *N,N*-dimethyl-4-trifluoromethyl-2,3,5,6-tetrafluoroaniline (**III**) (run no. 1, Table 1).



* For communication II, see [1].

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Under the same conditions but without NH₄Cl additive 21% of the initial compound remains unreacted (run no. 2, Table 1). The reaction is limited to hydrogenolysis of a single C—F bond. Hepta-

Table 1. Reactions of perfluoroalkylarenes with the systems Zn(CuCl₂)-DMF-H₂O-electrolyte and Zn(Cu)-DMF-H₂O-electrolyte

Run no.	No. of initial compound	Amount of initial compound, mmol	Metal amount, mmol ^a	Salt amount, mmol	Ratio DMF-water ^b	Temperature of process, °C (duration, h)	Reaction products, content in the reaction mixture, % (yield, %)
1	I	50	610, 155	224 ^c	31, 47	70 (20)	II , 95 (70); III , 1 (1)
2	I	50	610, 155		31, 47	70 (20)	I , 21 (14); II , 75 (55); III , 4 (2)
3	I	250	3050, 775	935 ^c	31, 42	70 (20)	II , 92 (77)
4	I	250	1525, 625	467 ^c	31, 42	70 (20)	II , 90 (77)
5	I	508	3048, 762	935 ^c	31, 41	70 (18)	II , 93 (79)
6	I	508	3048, 762	935 ^c	26, 41	70 (19)	II , 88 (77)
7	I	47.5	60.8, 80.8	467 ^c	0, 23	boil. (20)	I , 85 (72); II , 15 (14)
8	I	47.5	460.8, 80.8	428 ^d	0, 117	boil. (30)	I , 51 (39); II , 49 (40)
9	V	69.9	838.8, 209.7	210 ^d	30, 45	70 (19), Ar	V , 94 (83)
10	IV	35	420 ^e , 3.5 ^f	104 ^d	30, 45	70 (19), Ar	V , 97 (82)
11	IV	69.9	838.8 ^e , 7.0 ^f	210 ^d	30, 45	70 (19.5), Ar	V , 96 (86)
12	IV	35	105 ^e , 3.5 ^f	104 ^d	30, 45	70 (19), Ar	IV , 64 (47); V , 26 (21)
13	VI	5	60.0 ^e , 0.50 ^f	14.9 ^d	28, 45	70 (19), Ar	II , 98 (72)
14	VIII	4.2	50.4 ^e , 0.42 ^f	12.7 ^d	40, 35	70 (18), Ar	IX , 80 (71), X , 13 (12), XI , 5 (4); XII 1 (1)
15	VIII	1	30.0, 8.0		89, 17	70 (10), Ar	VIII , 19 (9), IX , 45 (22), X , 16 (8), XI , 16 (7)
16	VIII	1	30.0, 8.0		89, 167	70 (10), Ar	VIII , 28 (11), IX , 41 (17), X , 3 (1), XI , 26 (9)
17	VIII	1	31.5 ^g , 3.2		100, 20	70 (10), Ar	VIII , 2 (1), IX , 53 (40), X , 10 (7), XII , 6 (4), XI , 28 (19)
18	VIII	1	31.5 ^g , 3.2		80, 40	70 (10), Ar	VIII , 1 (<1), IX , 42 (28), X , 27 (18), XII , 9 (6), XI , 22 (15) ^h
19	VIII	1	31.5 ^g , 3.2		60, 69	70 (10), Ar	VIII , 4 (3), IX , 55 (34), X , 20 (12), XII , <1, XI , 20 (12) ^h
20	VIII	1	31.5 ^g , 3.2		20, 100	70 (10), Ar	VIII , 57 (18), IX , 34 (11), X , <1, XII , 0, XI , 9 (3) ^h
21	VIII	1	24.4, 7.8		78, 67	70 (10), Ar	VIII , 0 (0), IX , 29 (15), X , 46 (24), XII , 5 (3), XI , 18 (9)
22	II	25	305, 77.5	86 ^d	31, 42	70 (20)	II , 99 (79)
23	XIII	12.6	151.2, 37.8	43 ^d	56, 111	70 (9)	XIV , 92 (87), XV , 4 (4)

^a Zn, Cu.^b mmol mmol⁻¹ of the initial compound for DMF and H₂O respectively.^c NH₄Cl additive.^d NaCl additive.^e Zn amount given.^f CuCl₂-2H₂O additive.^g Activated zinc was prepared by washing with 1.7% hydrochloric acid, then with water followed by decantation and drying in a vacuum in an argon flow at 30–35°C.^h The composition (mol %) was estimated from ¹⁹F and ¹H NMR spectra.

fluorotoluene (**II**) treated with the system Zn(Cu)-NaCl-DMF-H₂O returned intact (run no.22, Table 1). The results of run no.1 are well reproduced at increased charge (run nos. 3–5, Table 1), and there-

with the amount of DMF and metals may be reduced (run nos. 4, 5, Table 1). Note that conversion of compound **I** into reaction product **II** occurs also on boiling with Zn(Cu) in the water solutions of NH₄Cl

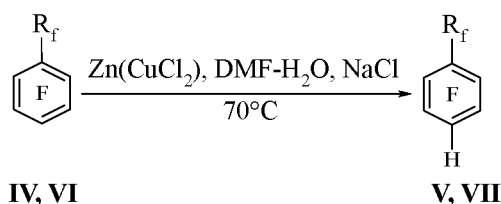
Table 2. ^1H and ^{19}F NMR spectra of compounds **IX–XII**, **XIV**

Compd. no.	^{19}F NMR spectrum, δ_{F} , ppm						^1H NMR spectrum, δ , ppm	J , Hz
	$\text{C}(\text{CF}_3)_3$	2	3	4	5	6		
IX ^a	100.7 t	34.5 m	26.9 m	–	26.9 m	34.5 m	7.36 t,t	25 ($\text{F}^\beta\text{F}^{2(6)}$), 8.5 ($\text{H}^4\text{F}^{3(5)}$), 7.0 ($\text{H}^4\text{F}^{2(6)}$)
X ^a	99.6 d	36.4 m	11.1 d d.d.d	13.6 d. d.d.d	26.0 d d.d.d	–	7.47 d.d.d.d	22 (F^βF^2), 22 (F^4F^5), 20 (F^3F^4), 18 (F^2F^3), 12.5 (H^6F^5), 11 (F^2F^5), 10.5 (F^2F^4), 7.5 (H^6F^4), 6.5 (H^6F^2), 3 (F^3F^5), 2.5 (H^6F^3)
XI ^a	100.1 t	31.6 m	11.0 m	–	11.0 m	31.6 m	3.10 t	25 ($\text{F}^\beta\text{F}^{2(6)}$), 2.5 ($\text{H}^4\text{F}^{3(5)}$)
XII ^a	99.3 d	32.0 m	18.9 m	–	37.3 m	–	7.15 m (H^6), 3.04 t (NCH_3)	21.5 (F^βF^2), 2.5 ($\text{H}^4\text{F}^{3(5)}$)
XIV	99.9 d	34.8 m	33.0 m	104.2 t (CF_3)	49.0	–	7.48 d.d.d	21.5 (F^βF^2), 20.5 (F^3F^4 and F^4F^5), 12 (H^6F^5), 5.5 (H^6F^2), 2.5 (H^6F^3)

^a The signals were assigned from analysis of ^{19}F and ^1H NMR spectra of reaction mixtures.

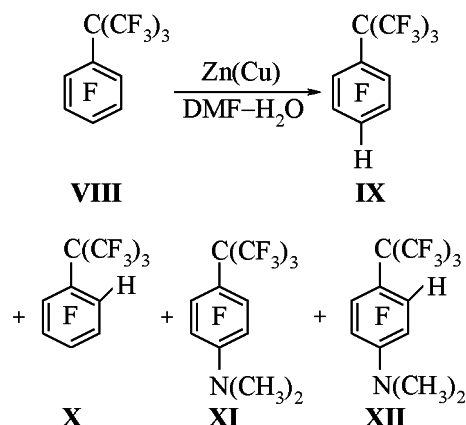
and NaCl with no DMF but the rate of the reaction is considerably slower (run nos. 7, 8, Table 1).

The treatment with the system $\text{Zn}(\text{Cu})\text{--NaCl}\text{--DMF--H}_2\text{O}$ of perfluoroethylbenzene afforded 1-pentafluoroethyl-2,3,5,6-tetrafluorobenzene (**V**) (run no. 9, Table 1). We found that in the presence of salt additive the amount of the copper used can be reduced to 0.1 mole per 1 mole of substrate when it is introduced into the system as CuCl_2 (runs nos. 10–12, Table 1). Therewith the efficiency of the dehydrofluorination remains on the same level. The complete conversion of perfluoroisopropylbenzene (**VI**) into heptafluoroisopropyl-2,3,5,6-tetrafluorobenzene (**VII**) was carried out under similar conditions (run no. 13, Table 1).



$\text{R}_\text{F} = \text{CF}_2\text{CF}_3$ (**IV**, **V**), $\text{CF}(\text{CF}_3)_2$ (**VI**, **VII**).

The treating of perfluoro-*tert*-butylbenzene (**VIII**) with $\text{Zn}(\text{Cu})$ in aqueous DMF unexpectedly provided derivatives with hydrogen atoms both in *para* and *ortho*-positions with respect to the perfluoroalkyl group unlike the behavior of perfluorobenzenes **I**, **IV**, **VI** and of perfluoropropylbenzene [9] containing less bulky substituents. In the nucleophilic reactions of arene **VIII** also was not observed substitution in the *ortho*-position [11, 12].



At complete conversion of compound **VIII** (run no. 14, Table 1) in the reaction mixture were present 1-nonafluoro-*tert*-butyl-2,3,5,6-tetrafluorobenzene (**IX**) and 1-nonafluoro-*tert*-butyl-2,3,4,5-tetrafluorobenzene (**X**) that were separated by distillation from small impurity containing *N,N*-dimethyl-4-nonafluoro-*tert*-butyl-2,3,5,6-tetrafluoroaniline (**XI**) and *N,N*-dimethyl-4-nonafluoro-*tert*-butyl-2,3,6-trifluoroaniline (**XII**) (^1H and ^{19}F NMR spectra see in Table 2). Dimethylanilines **XI** and **XII** were not isolated, and their formation in the presence of the system $\text{Zn}(\text{Cu})\text{--DMF--H}_2\text{O}$ was concluded from identity of their ^1H and ^{19}F NMR spectra to those of compounds obtained by treating perfluoroarene **VIII** or the mixture of compounds **IX** and **X** with dimethylamine solution in DMF. The distilled off mixture of compounds **IX** and **X** (run no. 14, Table 1) according to GC-MS data contained as impurity 6% of compound with molecular weight

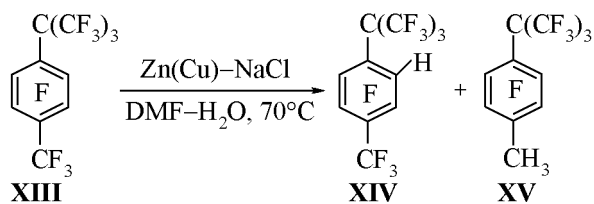
corresponding to a product with two fluorine atoms of arene **VIII** replaced by hydrogen.

The influence of the DMF-H₂O ratio on the physical characteristics of this binary system and rate constants of some reactions therein is well known [13]. We observed the change in the regioselectivity of the hydrodefluorination of arene **VIII** effected by Zn(Cu) at variation in the amounts of DMF and water (preliminary communication see [14]). For instance, ten-fold increase in water amount (the content in the binary mixture DMF-water grew from 16 to 65 mol %) at the same ratio of the other reagents and the same reaction conditions resulted in 4 times lower contribution of the *ortho*-dehydrofluorination (run nos. 15, 16, Table 1).

When the water amount reached 83% occurred prevailing *para*-dehydrofluorination (run no. 20, Table 1). The possible cause thereof are difficulty in solvation with water of the fluoride ion cleaved from the *ortho*-position with respect to perfluoroalkyl. The highest content of the *ortho*-dehydrofluorination products **IX** and **X** is observed not at the maximum content of DMF in the mixture but at intermediate amounts. At 46% of water (run no. 21, Table 1) we achieved the highest fraction of the *ortho*-isomer in the product: 1.5 times more than *para*-isomer.

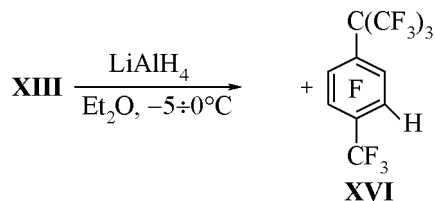
In the run no. 14 (Table 1) the ratio DMF-water was about the same, as in the run no. 19 (Table 1) but the former was carried out with NaCl additive, and the contribution from the *ortho*-dehydrofluorination was only 15%. The latter fact suggests that the presence of salts can influence the regioselectivity of the reaction. Here we wish to state that the dependence of the regioselectivity on the DMF-water ratio we treat on a qualitative level.

We observed formerly the hydrodefluorination in the *ortho*-position to the perfluorobutyl group as the prevailing path in the reaction of perfluoro-4-*tert*-butyltoluene (**XIII**) with the system Zn(Cu)-DMF-H₂O [15]. When this system was used with NaCl additive perfluoroarene **XIII** within 9 h at 70°C (run no. 23, Table 1) virtually completely was converted into 1-nonafluoro-*tert*-butyl-4-trifluoromethyl-2,3,5-trifluorobenzene (**XIV**) (87%) (NMR spectra are given in Table 2). Product **XIV** was separated by distillation from a small impurity, hydrodefluorination product at the benzyl position nanafluoro-*tert*-butyl-4-methyl-2,3,5,6-tetrafluorobenzene (**XV**) (4%). In this reaction did not occur replacement of fluorine by hydrogen in the *ortho*-position with respect to trifluoromethyl group.



At the same time in the reaction of compound **XIII** with LiAlH₄ the replacement of fluorine by hydrogen occurred to a greater degree in the *ortho* position with respect to the less bulky perfluorinated substituent. The ratio of these two routes was estimated as 1:2.3 by the integral intensities of CF₃ and C(CF₃)₃ groups of different multiplicity in the ¹⁹F NMR spectrum. The fragment CF=CR_FCF= in the ¹⁹F NMR spectrum gives a signal of the perfluoroalkyl group R_F as a triplet with the coupling constant no less than 20 Hz. In contrast the signals of the perfluoroalkyl groups in the fragment CH=CR_FCF= are doublets.

The formation of 1-nonafluoro-*tert*-butyl-4-trifluoromethyl-2,3,6-trifluorobenzene (**XVI**) is supported by the value of *m/z* measured with GC-MS method in the mass spectrum, and by analysis of ¹⁹F and ¹H NMR spectra of the reaction products mixture. In the ¹⁹F NMR spectrum after assignment of the signals belonging to compounds **XIII** and **XIV** stands out a group of intense signals (δ_F, ppm, *J*, Hz): 100.9 t (25.5), 99.3 d (12), 64.1 m, 45.4 m, 23.8 m (9:3:1:1:1). In the ¹H NMR spectrum is observed a signal of the proton in aromatic ring (δ, ppm, *J*, Hz): 7.40 d. d. d (13, 5.5, 2.5).



The revealed difference in the main products obtained by hydrodefluorination of compound **XIII** effected by LiAlH₄ and Zn(Cu) may be caused by dissimilar mechanisms of the processes. In the first case the reaction probably includes an electron transfer and goes via decomposition of the intermediate anion-radical [17] whereas in the second case apparently occurs a nucleophilic attack on the sterically the least hindered position in the aromatic ring. The effect of the size of the perfluoroalkyl substituent on the direction of the nucleophilic attack was formerly observed with perfluoro-*p*-cymene [18].

Compound **XIV** may arise both from nucleophilic substitution and electron transfer. In some studies the mechanism of halogen replacement by hydrogen effected by LiAlH_4 was regarded as electron transfer process [19, 20]. The direction of hydrodefluorination is changed with reaction mechanism also with perfluoro-*p*-xylene: The latter when treated with the system $\text{Zn}(\text{Cu})\text{-DMF-H}_2\text{O}$ yields 4-methylheptafluorotoluene [17] whereas with LiAlH_4 occurs fluorine substitution in the aromatic ring [21].

EXPERIMENTAL

NMR spectra of reaction mixtures and of solutions in CCl_4 of individual compounds ($c < 11$ mol%) were registered on spectrometer Bruker WP-200SY at operating frequencies 188.3 MHz for ^{19}F and 200 MHz for ^1H , internal references C_6F_6 and HMDS (δ 0.04 ppm). IR spectra were recorded on spectrophotometer Specord M-80. Elemental composition of molecular ions was determined from high resolution mass spectra measured on Finnigan MAT 8200 instrument. GC-MS measurements were carried out on Hewlett-Packard G1800A instrument equipped with electron-ionization detector. GLC analyses were performed on LKhM-72 device (50–270°C, column 400 × 4 mm, stationary phases 15 and 25% SKTFT-50 or 15% E-301 on Chromosorb W, carrier gas He, flow rate 60 ml min⁻¹. In reactions was used zinc powder produced in Russia according to state standard GOST 12601-76.

Reaction of perfluoroalkylbenzenes I, IV, VI, VIII and polyfluorotoluene II with the systems $\text{Zn}(\text{CuCl}_2)\text{-DMF-H}_2\text{O}$ -electrolyte and $\text{Zn}(\text{Cu})\text{-DMF-H}_2\text{O}$ -electrolyte (Table 1). A mixture of DMF, water and metals was prepared. Copper(II) chloride and the other salts were added in water solution. Copper metal was used as freshly prepared water suspension. Polyfluoroarenes were added to the reaction mixture while stirring. The reaction products were separated by steam distillation. The following individual compounds were isolated: **II** (bp 113.5°C, publ. 111–112°C [5], 110.5–111.5°C [8]), (**V**) (bp 120–122°C, publ. 124°C [6]), (**VII**) (bp 139–140°C), (**XIV**) [bp 81–82°C (65 mm Hg)].

Reaction of the mixture of polyfluoroalkylbenzenes IX, X with dimethylamine. The distillation of the reaction mixture obtained in run no. 14 afforded a mixture (bp 149–153°C) that contained according to ^{19}F NMR and GC-MS data compounds **IX** (74%), **X** (16%), and 6% of compound with molecular ion m/z 350. This mixture (0.1 g) and 0.14 g of solution containing 97.6% of DMF, 0.8%

of dimethylamine, and 1.6% of water was maintained at room temperature for 4 days. Then was added CCl_4 , and the mixture was diluted with 3.5% HCl. In the ^{19}F NMR spectrum of the reaction products were observed the signals from compounds **IX**, **X**, **XII** (Table 20 in 14:1:2 ratio).

Compounds **III**, **XV** were identified in the reaction mixtures by means of GLC, ^1H and ^{19}F NMR spectroscopy by comparison with authentic samples prepared by procedures [16] and [1] respectively.

Heptafluoroisopropyl-2,3,5,6-tetrafluorobenzene (VII). IR spectrum (3% solution in CCl_4 , ν , cm⁻¹): 3080, 1612 w, 1505 s, 1400 w, 1301 s, 1290 s, 1264 s, 1240 s, 1185, 1178, 1145 w, 1132, 1064 w, 987 s, 932 s, 960, 923, 712. ^{19}F NMR spectrum (CCl_4), δ_{F} , ppm: 27.8 (F arom), 26.7 (F arom), 25.3 (2F arom), -16.9 [$\text{CF}(\text{CF}_3)_2$], 86.2 [$\text{CF}(\text{CF}_3)_2$]. ^1H NMR spectrum (CCl_4), δ , ppm: 7.32 t.t. Found, %: C 33.71, 33.94; H 0.48, 0.39. M^+ 317.98978. C_9HF_{11} . Calculated, %: C 33.99; H 0.32. M^+ 317.99026.

1-Nonafluoro-*tert*-butyl-4-trifluoromethyl-2,3,5-trifluorobenzene (XIV). IR spectrum (3% solution in CCl_4 , ν , cm⁻¹): 3175 w, 3140 w, 1655, 1600, 1505, 1490, 1467 s, 1350, 1313 s, 1285 s, 1270 s, 1255 s, 1205, 1185, 1160 s, 1058, 1055, 975, 962, 910, 857. Found, %: C 31.14, 31.44; H 0.15, 0.19; F 67.90, 67.67. M^+ 417.98390. $\text{C}_{11}\text{HF}_{15}$. Calculated, %: C 31.60; H 0.24; F 68.16. M^+ 417.983874.

Reaction of perfluoro-4-*tert*-butyltoluene (XIII) with LiAlH_4 . To a solution of 1.03 g of compound **XIII** in 2 ml of anhydrous ethyl ether under argon atmosphere at -5...0°C within 5 min was added 0.1 g of lithium aluminum hydride in 4 ml of anhydrous ethyl ether. The mixture was stirred for 1h, then by portions was added 10 ml of 20% sulfuric acid. The ether layer was separated and dried with CaCl_2 . After the ethyl ether was distilled off we obtained 0.81 g of mixture containing according to the data of ^{19}F NMR spectrum and GC-MS method 60% of compound **XIII**, 11% of compound **XIV**, and 24% of compound with molecular ion m/z 418.

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