Acid-catalyzed polyfluoroarylation of arenes with polyfluorinated mono- and tris(phenoxy)-1-oxaspiro[2.5]octa-4,7-dienes

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4,5,6,7,8-Pentafluoro-6-pentafluorophenoxy-1-oxaspiro[2.5]octa-4,7-diene and 4,6,8-trifluoro-5,6,7-tris(pentafluorophenoxy)-1-oxaspiro[2.5]octa-4,7-diene react with electron-rich arenes in the presence of $AlCl_3$ or H_2SO_4 to give polyfluorinated phenoxybiaryls.

Key words: polyfluoroarylation, arylation, biaryls, electrophilic substitution, organofluorine compounds, oxiranes.

Polyfluorinated cyclohexa-2,5-dienones are convenient synthones for selective synthesis of various organofluorine compounds due to their high and diverse reactivity.[1] We have previously shown that they react with diazomethane at the carbonyl group giving in high yields fluorine-containing 1-oxaspiro[2.5]octa-4,7-dienes ("cyclohexadienespirooxiranes")[2] with the reactive oxirane cycle. Their interaction with aryl or alkyl isocyanates in the presence of lithium or potassium salts affords polyfluorinated dihydro-1,3-benzoxazol-2(3*H*)-ones in good yields.[2] 4,5,6,7,8-Pentafluoro-6-nitro-1-oxaspiro[2.5]octa-4,7-diene in the presence of the $AlCl_3$—α-picoline system in the reactions with electron-rich arenes acts as a pentafluorophenylating agent affording the corresponding pentafluorobiphenyls.[3] In this process, nitrocyclohexadienespirooxirane acts as a synthetic equivalent of the pentafluorophenyl cation. A close analog of this process is the formation of polyfluorinated polynuclear aromatic compounds by the reaction of stable polyfluorinated arenonium ions with aromatic compounds stable in superacidic media.[4] The methods described for the synthesis of fluorine-containing biphenyls are based on radical reactions,[5—8] reactions of nucleophilic substitution of the fluorine atom in polyfluoroaromatic compounds,[9,10] and various cross-coupling reactions.[11—13]

In this work, we present the results of studying the reactions of 4,5,6,7,8-pentafluoro-6-pentafluorophenoxy- and 4,6,8-trifluoro-5,6,7-tris(pentafluorophenoxy)-1-oxaspiro[2.5]octa-4,7-dienes with aromatic compounds in the presence of acidic catalysts.

The direction of the interaction of 4,5,6,7,8-pentafluoro-6-pentafluorophenoxy-1-oxaspiro[2.5]octa-4,7-diene (**1**) with arenes in the presence of aluminum chloride and α-picoline depends to a substantial extent on the electronic effect of substituents in the aromatic ring of the substrate.

So, the decomposition of oxirane **1** by aluminum chloride and α-picoline in a pentafluorobenzene solution affords a complex mixture in which GC/MS analysis detected products **2** (21%), **3** (3%), **4** (18%), **5** (5%), chloropentafluorobenzene (10%), and pentafluorophenol (10%), as well as a number of unidentified compounds (Scheme 1). The reaction in the absence of α-picoline gave a mixture of products with a similar composition. No formation of perfluoro-4-phenoxybiphenyl (the product of pentafluorobenzene arylation) was observed.

The reaction of compound **1** with benzene in the presence of aluminum chloride and α-picoline affords a mixture containing compounds **2** and **4**, chloropentafluorobenzene, pentafluorophenol, and diphenylmethane, as well as desired arylation product: 2,3,5,6-tetrafluoro-4-pentafluorophenoxybiphenyl (**6**) (16% yield).

In a similar reaction, more electron-rich anisole gives arylation products **7a**,**b** in an overall yield of 85%.

The main distinction in the behavior of oxirane **1** from that in the earlier studied reaction of 4,5,6,7,8-pentafluoro-6-nitro-1-oxaspiro[2.5]octa-4,7-diene[3] is the retention of the geminal OC_6F_5 group in the reaction products (biphenyls **6** and **7a**,**b** and compounds **2**—**4**). The products in which this group is absent are formed in a low yield, and only pentafluorophenol is detected in the reaction with anisole. It should be mentioned that the use of an α-picoline additive in these reactions does not play such a substantial role as in the earlier studied reactions of 4,5,6,7,8-pentafluoro-6-nitro-1-oxaspiro[2.5]octa-4,7-diene[3]: only slight changes in the ratio of products along with the total decrease in the yield are observed in the absence of α-picoline.

The formation of products **6** and **7a**,**b** can be described by Scheme 2 (*cf.* published data[3]).

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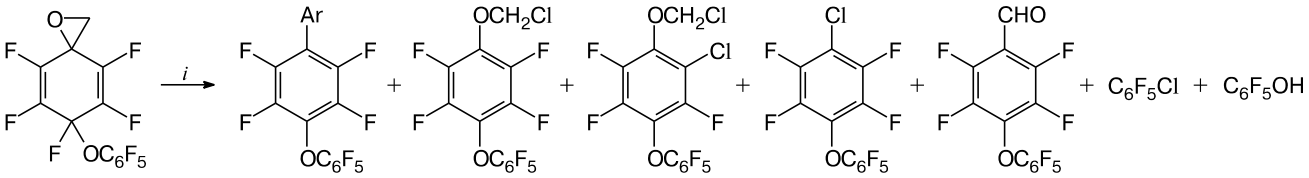
Scheme 1



i. ArH, $AlCl_3$, α-picoline.

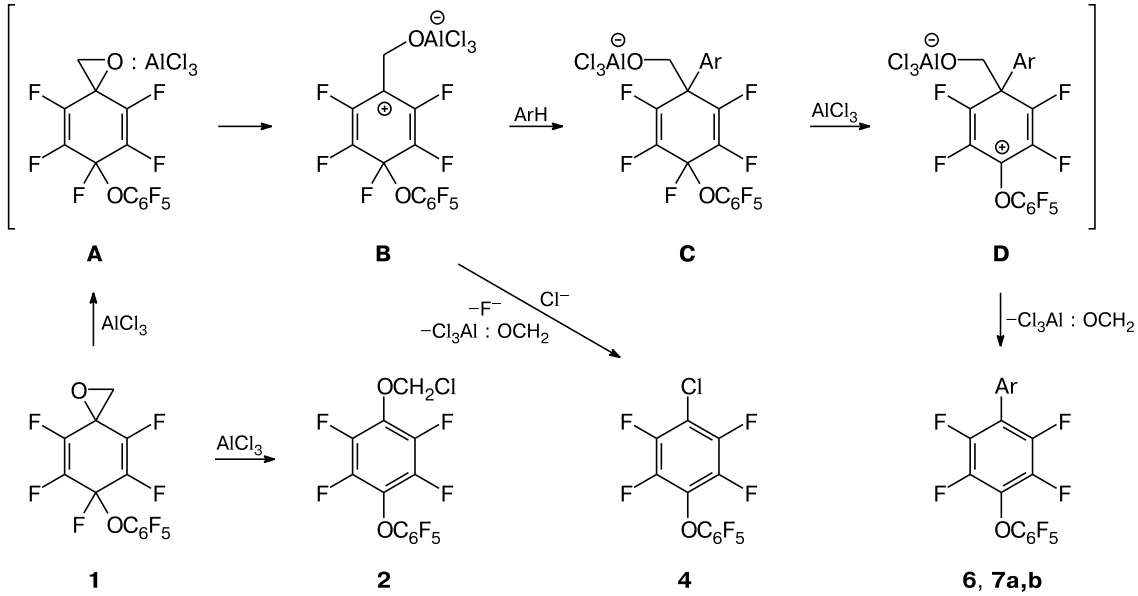
Products	Ar	Yield (%)
6	Ph	16
7a	4-$MeOC_6H_4$	54
7b	2-$MeOC_6H_4$	31

It can be assumed that the reaction proceeds in two stages. At the first stage, polarized complex **A** or arenonium ion **B** interacts with an aromatic substrate to give cyclohexadiene **C**. The formation of cyclohexadiene structures by the reactions of stable polyfluorinated arenonium ions with pentafluorobenzene is known.[4] Possibly, the aromatization of cyclohexadiene **C** resulting in biaryls **6** and **7a**,**b**, proceeds through arenonium ion **D**. The retention of the OC_6F_5 group in the reaction products can be explained by the fact that it better stabilizes the cationic centers in arenonium ion **D** compared to the fluorine atom. Analogous arguments were used earlier for the explanation of the easy aromatization of 3-difluoromethoxy-6-nitrohexafluorocyclohexa-1,4-diene by hydrogen fluoride.[14,15] It should be mentioned that the generation of stable polyfluorinated arenonium ions by the action of Lewis acid (SbF_5) on fluorine-containing cyclohexadienes is a commonly accepted method.[15]

1-Chloro-2,3,5,6-tetrafluoro-4-pentafluorophenoxybenzene (**4**) is formed in the decomposition of oxirane **1** by the action of $AlCl_3$ probably due to the interaction of arenonium ion **B** with the chloride anion, whose source is the $[AlCl_3F]^-$ anion formed in the reaction. The primary attack of $AlCl_3$ at the geminal unit $CFOC_6F_5$ of spirooxirane **1** followed by oxirane ring opening gives chloromethyl ether **2**. It is known that 1-oxaspiro[2.5]octa-4,7-dien-6-ones are compounds bearing a similar spirooxirane cycle and can give both chloroaromatic derivatives[16] and hydroquinone ethers[17] under the action of acidic reagents.

Concentrated sulfuric acid turned out to be another acidic agent catalyzing the formation of polyfluorobiarenes from spirooxirane **1** and arenes.

Scheme 2



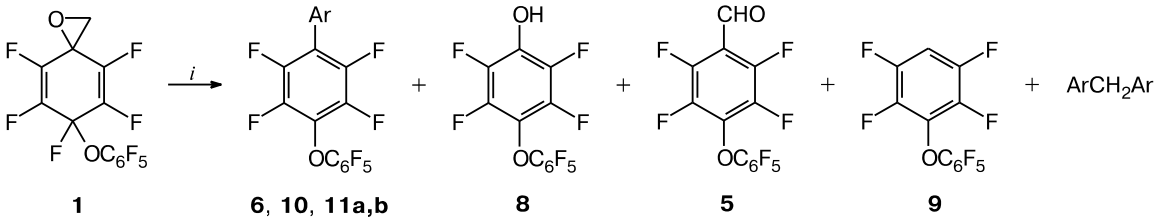
The reaction of oxirane **1** with benzene in the presence of sulfuric acid affords a mixture of products containing biaryl **6**, diphenylmethane, 2,3,5,6-tetrafluoro-4-pentafluorophenoxyphenol (**8**), 2,3,5,6-tetrafluoro-4-pentafluorophenoxybenzaldehyde (**5**), and 2,2′,3,3′,4′,5,5′,6,6′-nonafluorodiphenyl ether (**9**) (Scheme 3). The reaction of oxirane **1** with mesitylene and naphthalene in the presence of sulfuric acid affords biaryl **10** and a mixture of isomeric arylnaphthalenes **11a**,**b**, respectively, in good yields.

The formation of biaryls in the reactions of oxirane **1** with aromatic compounds in the presence of sulfuric acid proceeds, most likely, similarly to the reactions under the action of aluminum chloride (Scheme 4).

Phenoxyphenol **8** formed by the hydrolysis of arenonium ion **F**, phenoxybenzaldehyde **5**, and diphenyl ether **9** are products of the transformation of oxirane **1** under the action of sulfuric acid, which was shown by us in a special experiment. It should be mentioned that the isomerization of non-fluorinated 1-oxaspiro[2.5]octa-4,7-dien-6-ones under the action of Lewis acids to 4-hydroxybenzaldehydes is a well-known process.[18]

The OC_6F_5 group is retained in the formed reaction products, as well as in case where aluminum chloride is used as an acidic agent. It could be expected that the introduction of rather bulky substituents into the positions adjacent to the geminal unit should increase the mobility of this group. We synthesized oxirane **12** and studied its reaction with mesitylene in the presence of sulfuric acid (Scheme 5). It turned out that the major product of this reaction was also biaryl **13** retaining

Scheme 3

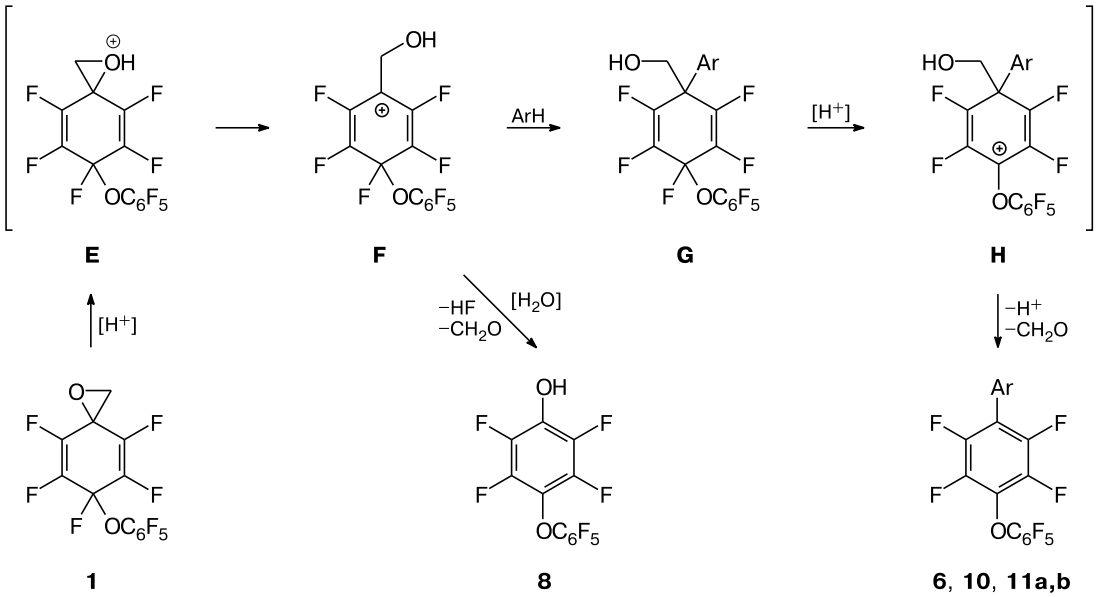


i. ArH, H_2SO_4.

Products	ArH	Yield (%)
6	Ph	18
10	2,4,6-MeC_6H_2	57
11a	1-naphthyl	45*
11b	2-naphthyl	

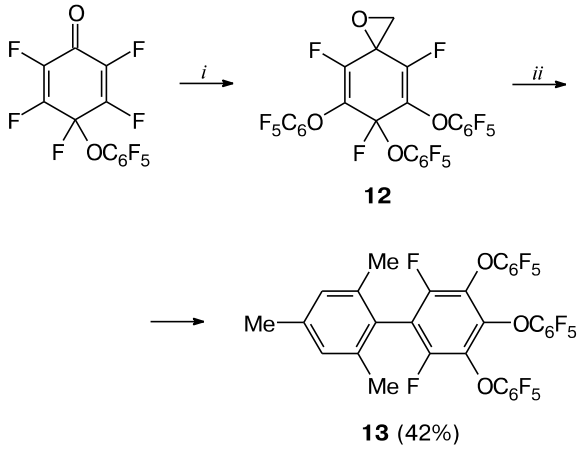
* Overall yield of **11a,b**, ratio **11a** : **11b** = 9 : 1.

Scheme 4



the OC_6F_5 group that was in the geminal unit of compound **12**.

Scheme 5



i. (1) C_6F_5ONa, acetone, 20 °C; (2) CH_2N_2, Et_2O, −15 to +20 °C.
ii. 1,3,5-$Me_3C_6H_3$, H_2SO_4.

In summary, 4,5,6,7,8-pentafluoro-6-pentafluorophenoxy- and 4,6,8-trifluoro-5,6,7-tris(pentafluorophenoxy)-1-oxaspiro[2.5]octa-4,7-dienes (compounds **1** and **12**, respectively) in the presence of $AlCl_3$ or H_2SO_4 can serve as polyfluoroarylating agents for electron-rich arenes affording polyfluorinated biaryls, and the OC_6F_5 group in the geminal unit of reactants **1** and **12** is retained in the reaction products.

Experimental

^1H and ^{19}F NMR spectra (HMDS and C_6F_6 as internal standards) were recorded on a Bruker AV III 400 spectrometer (spectra of compounds **7a**,**b**) at frequencies of 400.13 and 376.43 MHz, respectively, and on a Bruker AV 300 spectrometer (spectra of other compounds) at frequencies of 300.13 and 282.36 MHz, respectively. Signals in the ^1H and ^{19}F NMR spectra were assigned by a comparison with the spectra of pentafluorobiaryls similar in structure.[8,19,20] GC/MS analysis was carried out on a Hewlett—Packard instrument including an HP 5890 gas chromatograph (series II) and an HP 5971 mass-selective detector (EI, 70 eV). The HP5MS capillary column (diphenylsiloxane (5%)—dimethylsiloxane (95%), 30 m×0.25 mm×0.25 μm), helium as a carrier gas (1 mL min^{-1}), temperature-programmed mode: 2 min at 50 °C, from 50 to 280 °C with a rate of 10 deg min^{-1}, 5 min at 280 °C, the temperature of the injector 280 °C, the temperature of the ion source 175 °C, and the scan rate 1.2 scan s^{-1} in a mass region of 30—650 amu were used. The empirical composition of the obtained biaryls was determined by high-resolution mass spectra (HR MS) detected on a DFS Thermo Scientific GC/MS mass spectrometer (EI, 70 eV). Elemental analysis was carried out manually. The molecular weight of diastereomers of oxiranes **12** was determined on a KNAUER osmometer: found M = 707; calculated M = 708.

Compound **1** (mixture of diastereomers) was synthesized by a procedure published earlier.[2]

1-Chloromethoxy-2,3,5,6-tetrafluoro-4-pentafluorophenoxybenzene (2) and 1-chloro-2,3,5,6-tetrafluoro-4-pentafluorophenoxybenzene (4). ***A.*** Freshly sublimed $AlCl_3$ (1.51 g, 11.3 mmol) was added to a solution of α-picoline (0.65 g, 7.0 mmol) in pentafluorobenzene (4 mL). The solution was stirred for 15—20 min at room temperature and cooled down to −15 to −20 °C. Then a solution of oxirane **1** (1.12 g, 2.9 mmol) in pentafluorobenzene (3 mL) was added dropwise with stirring. The reaction mixture was slowly heated to room temperature within ~2 h and stirred for more ~20 h to the complete solidification of the viscous precipitate that formed. After 10% HCl (40 mL) was added, the reaction mixture was extracted with CH_2Cl_2 (3×50 mL). The extract was dried with $CaCl_2$. A residue (1.32 g) after distillation of the solvents was chromatographed on a SiO_2 column. Elution with CCl_4 gave 0.83 g of a mixture of products containing, according to the GC/MS data, 1-chloromethoxy-2,3,5,6-tetrafluoro-4-pentafluorophenoxybenzene (**2**) (21%), 1-chloro-2-chloromethoxy-3,4,6-trifluoro-5-pentafluorophenoxybenzene (**3**) (3%), chloropentafluorobenzene (10%), 1-chloro-2,3,5,6-tetrafluoro-4-pentafluorophenoxybenzene (**4**) (18%), pentafluorophenol (10%), 2,3,5,6-tetrafluoro-4-pentafluorophenoxybenzaldehyde (**5**) (5%), and other unidentified products.

B. Similarly, from oxirane **1** (0.76 g, 2.0 mmol) and freshly sublimed $AlCl_3$ (0.81 g, 6.0 mmol) in pentafluorobenzene (12 mL) a mixture of products was obtained (0.29 g) containing, according to the GC/MS data, compound **2** (34%), **4** (11%), pentafluorophenol (~3%), 2,3,5,6-tetrafluoro-4-pentafluorophenoxybenzaldehyde (**5**) (23%), and other unidentified products.

The mixtures of products obtained in two experiments were combined and chromatographed on a SiO_2 column (elution with petroleum ether and then with CCl_4). Compound **4** (0.10 g) and a mixture of compounds **2** and **3** (0.13 g) were isolated. A mixture of compounds **2** and **3** is viscous, partially crystallized at room temperature and contains, according to the GC/MS data, ~74% of compound **2** (*m/z* 396 $[M]^+$) and ~15% of compound **3** (*m/z* 412 $[M]^+$).

Compound **2**. ^{19}F NMR (CCl_4), δ: 0.3 (2 F, F_{meta}); 2.6 (1 F, F_{para}); 5.1 (2 F, F_{ortho}); 5.8 (2 F, F(3), F(5)); 7.4 (2 F, F(2), F(6)). ^1H NMR (CCl_4), δ: 5.82 (s, 2 H, OCH_2Cl). HR MS, *m/z*: 395.9598 $[M]^+$; calculated for $C_{13}H_2{}^{35}ClF_9O_2$: M = 395.9594.

Compound **3**. ^{19}F NMR (CCl_4), δ: 0.3 (2 F, F_{meta}); 2.5 (1 F, F_{para}); 5.8 (2 F, F_{ortho}); 9.1 (1 F, F(3)); 11.2 (1 F, F(4)); 28.8 (1 F, F(6)). The chemical shifts of the fluorine atoms of compound **3** correspond to those calculated using the additive scheme. ^1H NMR (CCl_4), δ: 5.86 (s, 2 H, OCH_2Cl).

Compound **4**. M.p. 69.5—71 °C (petroleum ether). ^{19}F NMR (CCl_4), δ: 0.4 (2 F, F_{meta}); 3.0 (1 F, F_{para}); 5.8 (2 F, F_{ortho}); 6.2 (2 F, F(3), F(5)); 22.0 (2 F, F(2), F(6)). HR MS, *m/z*: 365.9494 $[M]^+$; calculated for $C_{12}{}^{35}ClF_9O$: M = 365.9488.

2,3,5,6-Tetrafluoro-4-pentafluorophenoxybiphenyl (6) and 1-chloro-2,3,5,6-tetrafluoro-4-pentafluorophenoxybenzene (4). Similarly, from α-picoline (0.78 g, 8.4 mmol), oxirane **1** (1.27 g, 3.3 mmol), and freshly sublimed $AlCl_3$ (1.79 g, 13.4 mmol) in benzene (10 mL) at 10 °C a mixture was obtained (1.41 g) containing, according to the GC/MS data, chloropentafluorobenzene (~1%), pentafluorophenol (~4%), pentafluorobiphenyl (≤0.2%), 1-chloro-2,3,5,6-tetrafluoro-4-pentafluorophenoxybenzene (**4**) (20%), diphenylmethane (12%), 1-chloromethoxy-2,3,5,6-tetrafluoro-4-pentafluorophenoxybenzene (**2**) (6%),

2,3,5,6-tetrafluoro-4-pentafluorophenoxybiphenyl (**6**) (19%), and other unidentified products. The obtained mixture of products was chromatographed on a SiO_2 column (elution with petroleum ether) to give compound **4** (0.23 g, 19%) and biphenyl **6** (0.21 g, 16%).

Compound **6**. M.p. 95—96.5 °C (petroleum ether). ^{19}F NMR (CCl_4), δ: 0.0 (2 F, F_{meta}); 2.3 (1 F, F_{para}); 4.6 (2 F, F_{ortho}); 5.9 (2 F, F(3), F(5)); 18.8 (2 F, F(2), F(6)). ^{1}H NMR (CCl_4), δ: 7.36—7.46 (m, 5 H). HR MS, *m/z*: 408.0191 $[M]^+$; calculated for $C_{18}H_5F_9O$: M = 408.0191.

4´-Methoxy-2,3,5,6-tetrafluoro-4-pentafluorophenoxybiphenyl (7a) and 2´-methoxy-2,3,5,6-tetrafluoro-4-pentafluorophenoxybiphenyl (7b). Similarly, from oxirane **1** (1.07 g, 2.8 mmol), freshly sublimed $AlCl_3$ (1.51 g, 11.3 mmol), and α-picoline (0.65 g, 7.0 mmol) in anisole (6.5 mL) a mixture (2.43 g) was obtained containing biaryls **7a** and **7b** (**7a** : **7b** = 56 : 44 according to the GC/MS data). The obtained mixture was chromatographed on a SiO_2 column (elution with a mixture of petroleum ether and CCl_4 (gradient from 1 : 1 to 1 : 4)) to give individual compounds **7a** (0.67 g, 54%) and **7b** (0.38 g, 31%).

Compound **7a**. M.p. 135.5—137.5 °C (petroleum ether). ^{19}F NMR (CCl_4—$CDCl_3$ (4 : 1)), δ: 0.0 (2 F, F_{meta}); 2.2 (1 F, F_{para}); 4.4 (2 F, F_{ortho}); 5.9 (2 F, F(3), F(5)); 18.2 (2 F, F(2), F(6)). ^{1}H NMR (CCl_4—$CDCl_3$ (4 : 1)), δ: 3.85 (s, 3 H, OCH_3); 6.97 (d, 2 H, *J* = 8.8 Hz); 7.34 (d, 2 H, *J* = 8.8 Hz). HR MS, *m/z*: 438.0295 $[M]^+$; calculated for $C_{19}H_7F_9O_2$: M = 438.0297.

Compound **7b**. M.p. 69—71 °C (petroleum ether). ^{19}F NMR (CCl_4—$CDCl_3$ (4 : 1)), δ: –0.1 (2 F, F_{meta}); 2.0 (1 F, F_{para}); 3.7 (2 F, F_{ortho}); 6.0 (2 F, F(3), F(5)); 21.9 (2 F, F(2), F(6)). ^{1}H NMR (CCl_4—$CDCl_3$ (4 : 1)), δ: 3.82 (s, 3 H, OCH_3); 6.99 (d, 1 H, *J* = 8.3 Hz); 7.03 (t, 1 H, *J* = 7.5 Hz); 7.20 (d, 1 H, *J* = 7.5 Hz); 7.41 (dd, 1 H, *J* = 8.3 Hz, *J* = 7.5 Hz). HR MS, *m/z*: 438.0296 $[M]^+$; calculated for $C_{19}H_7F_9O_2$: M = 438.0297.

2,3,5,6-Tetrafluoro-4-pentafluorophenoxybiphenyl (6) and 2,3,5,6-tetrafluoro-4-pentafluorophenoxyphenol (8). Concentrated sulfuric acid (2.0 g) was added dropwise to a solution of oxirane **1** (0.85 g, 2.2 mmol) in benzene (10 mL) cooled to ~6 °C. The mixture was stirred at room temperature for 2 h. After water (60 mL) was added, the reaction mixture was extracted with CH_2Cl_2 (3×50 mL), and the extract was dried with $CaCl_2$. After the solvents were distilled off, the residue (1.05 g) was chromatographed on a SiO_2 column. The consecutive elution with petroleum ether, CCl_4, and $CHCl_3$ gave a mixture of products (0.27 g), which contained, according to the ^{19}F and ^{1}H NMR spectral data, ~4% of diphenyl ether **9**, ~70% of biphenyl **6**, and a crystalline product (0.45 g) containing, according to the ^{19}F NMR spectral data, ~95% of phenoxyphenol **8**. Diphenyl ether **9** was identified on the basis of the GC/MS data and a comparison with the ^{19}F NMR spectrum of the product described in the literature.[21] Biphenyl **6** (0.16 g, 18%) was isolated by crystallization from petroleum ether. Phenoxyphenol **8** (0.35 g, 45%) was isolated by sublimation.

Compound **8**. M.p. 105—107 °C (sublimation) (*cf.* Ref. 22: 106 °C). ^{19}F NMR ($CHCl_3$), δ: –0.4 (2 F, F_{meta}); –0.3 (2 F, F(2), F(6)); 1.3 (1 F, F_{para}); 2.5 (2 F, F(3), F(5)); 5.3 (2 F, F_{ortho}). MS, *m/z*: 348 $[M]^+$.

2´,4´,6´-Trimethyl-2,3,5,6-tetrafluoro-4-pentafluorophenoxybiphenyl (10). A solution of oxirane **1** (0.90 g, 2.4 mmol) in mesitylene (4 mL) was added dropwise with stirring to a mixture of concentrated sulfuric acid (2.0 g) and mesitylene (4 mL) cooled to approximately –15 °C. The mixture was stirred at room temperature for 5 h. After water (70 mL) was added, the reaction mixture was extracted with CH_2Cl_2 (3×50 mL), and the extract was dried with $CaCl_2$. After the solvents were distilled off, the residue (1.55 g) was chromatographed on a SiO_2 column (elution with petroleum ether) to give a mixture of products (0.85 g). Product **10** was isolated by triple crystallization from petroleum ether in a yield of 0.62 g (57%), m.p. 133—136 °C. ^{19}F NMR (CCl_4), δ: –0.1 (2 F, F_{meta}); 2.1 (1 F, F_{para}); 4.9 (2 F, F_{ortho}); 5.6 (2 F, F(3), F(5)); 22.1 (2 F, F(2), F(6)). ^{1}H NMR (CCl_4), δ: 2.25 (s, 6 H, 2 CH_3); 2.41 (3 H, CH_3); 6.86 (s, 2 H, H(3´), H(5´)). HR MS, *m/z*: 450.0658 $[M]^+$; calculated for $C_{21}H_{11}F_9O$: M = 450.0661.

1-(2,3,5,6-Tetrafluorophenyl-4-pentafluorophenoxy)naphthalene (11a). Concentrated sulfuric acid (2.6 g) was added dropwise with stirring to a solution of naphthalene (5.60 g, 44 mmol) and oxirane **1** (0.83 g, 2.2 mmol) in dichloromethane (10 mL) cooled to approximately –10 °C. After 30 min, cooling was removed and the reaction mixture was stirred at room temperature for 1.5 h. After water (50 mL) was added, the reaction mixture was extracted with CH_2Cl_2 (3×50 mL) and the extract was dried with $CaCl_2$. After CH_2Cl_2 was distilled off, the residue was chromatographed on a SiO_2 column (elution with petroleum ether) to give naphthalene (4.2 g) and a mixture (0.45 g, 45%). According to the ^{19}F NMR spectral data, the mixture contained ~90% of α-arylnaphthalene **11a** and ~10% of β-arylnaphthalene **11b**. ^{1}H NMR of arylnaphthalenes **11a,b** (CCl_4), δ: 7.46—7.62 (m); 7.82—8.01 (m). Found (%): C, 58.04; H, 1.53; F, 37.43. $C_{22}H_7F_9O$. Calculated (%): C, 57.66; H, 1.54; F, 37.31. HR MS, *m/z*: 458.0352 $[M]^+$; calculated for $C_{22}H_7F_9O$: M = 458.0348.

Compound **11a**. ^{19}F NMR (CCl_4), δ: 0.2 (2 F, F_{meta}); 2.4 (1 F, F_{para}); 6.0 (2 F, F_{ortho}); 5.0 (2 F, F(3), F(5)); 22.9 (2 F, F(2), F(6)).

Compound **11b**. ^{19}F NMR (CCl_4), δ: 0.2 (2 F, F_{meta}); 2.4 (1 F, F_{para}); 6.0 (2 F, F_{ortho}); 4.8 (2 F, F(3), F(5)); 19.0 (2 F, F(2), F(6)).

2,3,5,6-Tetrafluoro-4-pentafluorophenoxyphenol (8) and 2,3,5,6-tetrafluoro-4-pentafluorophenoxybenzaldehyde (5). A freshly prepared and cooled to approximately –10 °C solution of diazomethane obtained from 0.7 g of *N*-nitroso-*N*-methylurea in diethyl ether (20 mL) was added dropwise with stirring to a solution of perfluoro-4-phenoxycyclohexa-2,5-dienone (0.73 g, 2.0 mmol) in diethyl ether (10 mL) cooled to approximately –15 °C. The reaction mixture was stirred for 16 h, gradually raising the temperature to ambient one. After diethyl ether was distilled off, concentrated sulfuric acid (2.0 g) was added dropwise with stirring to a solution of the residue in CH_2Cl_2 (5 mL) cooled to ~0 °C. The mixture was stirred at room temperature for 20 h. After water (50 mL) was added, the reaction mixture was extracted with CH_2Cl_2 (3×50 mL) and the extract was dried with $CaCl_2$. After the solvent was distilled off, the residue was chromatographed on a SiO_2 column (elution successively with CCl_4 and $CHCl_3$) to give two fractions. According to the ^{19}F NMR spectral data, fraction 1 (0.14 g) contained diphenyl ether **9** (~15%), phenoxybenzaldehyde **5** (~65%), and other unidentified products. Signals of compound **5** in the ^{19}F NMR spectrum of fraction 1 ($CHCl_3$), δ: 0.8 (2 F, F_{meta}); 3.9 (1 F, F_{para}); 6.0 (2 F, F_{ortho}); 6.2 (2 F, F(3), F(5)); 17.6 (2 F, F(2), F(6)). HR MS, *m/z*: 360 $[M]^+$, 358.9750 $[M - 1]^+$; calculated for $C_{13}HF_9O_2$: M = 360, [M – 1] = 358.9749. Fraction 2 (0.51 g) contains phenoxyphenol **8**, the yield was 73%, m.p. 104—106 °C (*cf.* Ref. 22: 106 °C).

4,6,8-Trifluoro-5,6,7-tris(pentafluorophenoxy)-1-oxaspiro-[2.5]octa-4,7-diene (12). Sodium pentafluorophenoxide (0.90 g, 4.0 mmol) was added dropwise with stirring at room temperature to a solution of perfluoro-4-phenoxycyclohexa-2,5-dienone (0.73 g, 2.0 mmol) in acetone (20 mL). The solution was stirred for 30 min, and the solvent was distilled off *in vacuo* (20 Torr, $T_{bath} \leq 20$ °C). The solid residue was dissolved in diethyl ether (20 mL). A solution of diazomethane obtained from 0.7 g of *N*-nitroso-*N*-methylurea in diethyl ether (20 mL) cooled to approximately −15 °C was added dropwise with stirring. The reaction mixture was stirred for 16 h, gradually raising the temperature to ambient one. After diethyl ether was distilled off, the residue was chromatographed on a SiO_2 column (elution with CCl_4) to give a viscous oil in a yield of 1.15 g (82%). According to the ^{19}F NMR spectral data, the oil was a mixture of diastereomers **12** in a ratio of 58 : 42. Found (%): C, 42.83; H, 0.48; F, 48.31. $C_{25}H_2F_{18}O_4$. Calculated (%): C, 42.40; H, 0.28; F, 48.28.

Diastereomer *1*. ^{19}F NMR (CCl_4—$CDCl_3$ (4 : 1)), δ: −0.5 (2 F, F_{meta}); 0.1 (4 F, $F_{meta'}$); 2.4 (2 F, $F_{para'}$); 4.7 (1 F, F_{para}); 5.4 (4 F, $F_{ortho'}$); 9.8 (2 F, F_{ortho}); 12.7 (2 F, F(4), F(8)); 52.2 (1 F, F(6)).

Diastereomer *2*. ^{19}F NMR (CCl_4—$CDCl_3$ (4 : 1)), δ: −0.4 (2 F, F_{meta}); 0.1 (4 F, $F_{meta'}$); 2.4 (2 F, $F_{para'}$); 4.7 (1 F, F_{para}); 5.2 (4 F, $F_{ortho'}$); 10.3 (2 F, F_{ortho}); 13.8 (2 F, F(4), F(8)); 50.9 (1 F, F(6)).

2′,4′,6′-Trimethyl-2,6-difluoro-3,4,5-tris(pentafluorophenoxy)biphenyl (13). Concentrated sulfuric acid (2.0 g) was added dropwise with stirring to a solution of oxirane **12** (1.10 g, 1.6 mmol) in mesitylene (8 mL) cooled to −5 °C. The mixture was stirred for 1 h, gradually rising the temperature to room temperature. After water (50 mL) was added, the reaction mixture was extracted with CH_2Cl_2 (3×50 mL) and the extract was dried with $CaCl_2$. After the solvent and mesitylene excess were distilled off, the residue (1.35 g) was chromatographed on a SiO_2 column (elution with petroleum ether). According to the ^1H NMR spectral data, the viscous oil isolated (0.91 g) contained ~74% of biphenyl **13**. Biphenyl **13** was obtained by triple crystallization from petroleum ether in a yield of 0.52 g (42%), m.p. 129—132 °C. ^{19}F NMR (CCl_4), δ: 0.1 (4 F, $F_{meta'}$); 0.2 (2 F, F_{meta}); 1.3 (2 F, $F_{para'}$); 1.9 (1 F, F_{para}); 3.8 (4 F, $F_{ortho'}$); 4.8 (2 F, F_{ortho}); 30.7 (2 F, F(2), F(6)). ^1H NMR (CCl_4), δ: 2.27 (s, 6 H, 2 CH_3); 2.44 (s, 3 H, CH_3); 6.88 (s, 2 H, H(3′), H(5′)). HR MS, *m/z*: 778.0424 $[M]^+$; calculated for $C_{33}H_{11}F_{17}O_3$: M = 778.0431.

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