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Reaction of Polyfluorinated Cyclohexa-2,4-dienones with Aryl Nitrile Oxides

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Abstract—Reaction of 1,3-dipolar cycloaddition of 6-chloropentafluorocyclohexa-2,4-dienone, 6-chloro-3-(pentafluorophenoxy)tetrafluorocyclohexa-2,4-dienone, and perfluoro-6-phenoxycyclohexa-2,4-dienone with aryl nitrile oxides proceeds highly stereoselectively at the c C=O group of the dienone providing in a high yield mixtures of diastereomeric fluorine-containing 3-aryl-1,4-dioxa-2-azaspiro[4,5]deca-2,6,8-trienes. The reaction of the latter with sodium pentafluorophenolate proceeds along the type of allyl substitution affording polyfluorinated 3-aryl-8-phenoxy-1,4-dioxa-2-azaspiro[4,5]deca-2,6,9-trienes.

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Polyfluorinated cyclohexadienones possess high and versatile reactivity, therefore they are suitable for the selective synthesis of organofluorine compounds of diverse classes [1]. We showed formerly that the 1,3-dipolar cycloaddition of diazomethane and nitrile oxides with polyfluorocyclohexa-2,5-dienones proceeded exclusively at the carbonyl group providing in good yields mixtures of diastereomeric cyclohexadienespirooxiranes and cyclohexadienespirodioxazoles respectively [2, 3]. The direction of the reaction between polyfluorinated cyclohexa-2,4-dienones and diazo compounds depends both on the structure of the reagent and on the polarity of the environment [4]. For instance, the reaction of pentafluoro-6-chlorocyclohexa-2,4-dienone with diazomethane occurs at the C=O and C=C bonds of the dienone giving a mixture of two isomeric fluorine-containing derivatives of spiro[indazol-7,2’-oxirane]. The reaction of polyfluorinated cyclohexa-2,4-dienones with phenyldiazomethane in acetonitrile proceeds mainly at the C=C bond of the cyclohexa-2,4-dienone affording cyclopropanation products, polyfluorinated phenylbicyclo[4.1.0]hept-4-en-2-ones. In pentane the primary reaction of the phenyldiazomethane occurs mainly at the carbonyl group of the cyclohexa-2,4-dienone leading to the formation of a complex products mixture containing toluylenes and spiro[indazol-7,2’-oxiranes] alongside with phenylbicyclo[4.1.0]hept-4-en-2-ones [4].

Here we report on the results of the study of 1,3-dipolar cycloaddition reactions between polyfluorinated cyclohexa-2,4-dienones and aryl nitrile oxides.

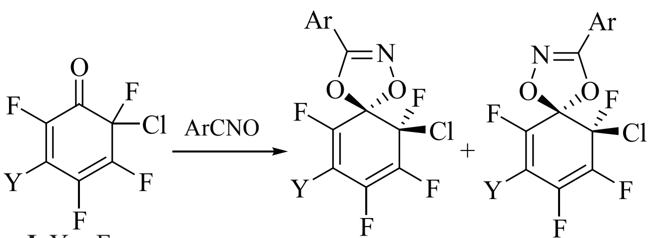
The reaction of 6-chloropentafluorocyclohexa-2,4-dienone (**I**) and 6-chloro-3-(pentafluorophenoxy) tetrafluorocyclohexa-2,4-dienone (**II**) with aryl nitrile oxides leads to the formation in a good yield of a mixture of diastereomeric fluorine-containing 3-aryl-1,4-dioxa-2-azaspiro[4,5]deca-2,6,8-trienes **IIIa, IIIb–VIIa, VIIb** (Scheme 1).

The composition and structure of compounds **III–VII** were established basing on ^{1}H and ^{19}F NMR spectra of the diastereomers mixtures and on the elemental analyses. The observed regularities in the fine structure of the signals in the ^{19}F NMR spectra of compounds **III–VII** are similar to those in the spectra of the initial polyfluorinated cyclohexa-2,4-dienones [5] and of fluorine-containing dihydro-1,3-benzoxazol-2(3*H*)-ones [2] having a fluorosubstituted cyclohexa-1,3-diene fragment.

Isomer **Va** was isolated in a pure state, and its structure was established by X-ray analysis (see the figure).

The dioxazole ring is flat, the bond lengths in it

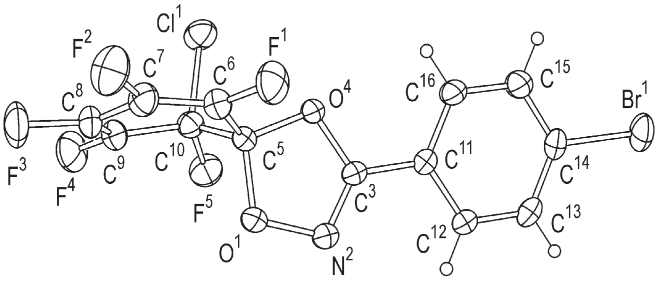
Scheme 1.



I Y = F	Ar = Ph	**IIIa**	85 : 15	**IIIb**
	Ar = 4-CH$_3$OC$_6$H$_4$	**IVa**	84 : 16	**IVb**
	Ar = 4-BrC$_6$H$_4$	**Va**	86 : 14	**VIb**
	Ar = 3-O$_2$NC$_6$H$_4$	**VIa**	86 : 14	**VIb**
II Y = OC$_6$F$_5$	Ar = Ph	**VIIa**	84 : 16	**VIIb**

are close in values to the analogous bonds in 8-pentafluorophenoxy-3-phenyl-6,7,8,9,10-pentafluoro-1,4-dioxa-2-azaspiro[4.5]deca-2,6,9-triene (**VIII**) [3] and in 7-*tert*-butyl-3,3'-bis(2,6-dichlorophenyl)spiro-{1,2-benzisoxazole-5(4*H*),5'-[1,4,2]dioxazol}-4-one [6]. The angle between the planes of dioxazole and bromophenyl equals 7.9(2)°. The hexadiene ring has the conformation of a distorted bath with deviation of atoms C^{5,6} from the plane C^{7}C^{8}C^{9}C^{10} by 0.642(5) and 0.247(5) Å respectively. In the crystal shortened intermolecular contacts Br^{1}…Br^{1} 3.5751(6) and F^{3}…F^{4} 2.755(3) Å were observed, and also a weak hydrogen bond C^{12}–H^{12}…N^{2} (H…N 2.59 Å, C–H…N 148°).

The reaction of dienone **I** with preliminary generated aryl nitrile oxide proceeds easily and in a good yield. The reaction with aryl nitrile oxides generated *in situ* [3] is accompanied with the formation of a significant amount of side products, presumably due to the high reactivity of dienone **I** with respect to nucleophilic substitution [7]. As nucleophile the pentafluorophenol may serve which is present as impurity in initial dienone **I**; this results in the formation of dienone **II**. Thus, in the reaction of dienone **I** with 4-methoxybenzonitrile oxide dioxazoles **IVa, IVb** were isolated with the admixtures of compounds whose structures were suggested basing on ^{19}F NMR spectrum to be 3-(4-methoxyphenyl)-7-pentafluorophenoxy-6,8,9,10-tetrafluoro-10-chloro-1,4-dioxa-2-azaspiro-[4.5]deca-2,6,8-trienes (**IXa, IXb**), products of the reaction of dienone **II** with methoxybenzonitrile oxide.

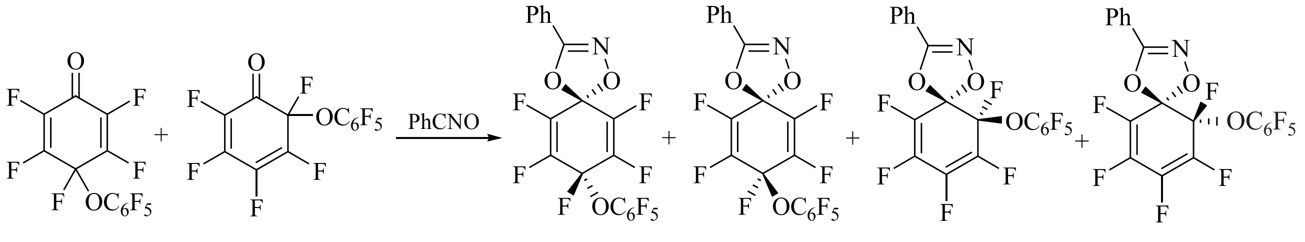


Molecular structure of 3-(4-bromophenyl)-6,7,8,9,10-pentafluoro-10-chloro-1,4-dioxa-2-azaspiro[4.5]deca-2,6,8-triene (**Va**) established by X-ray analysis.

1,2-Benzoquinones depending on the presence in the ring of bulky substituents are known to react with nitrile oxides either only at the carbonyl group, or both at the C=C and C=O bonds [6, 8]. Polyfluorinated dienone **I** reacts with aryl nitrile oxide exclusively at the carbonyl group even at long keeping with an excess of relatively stable 4-bromo- and 3-nitrobenzonitrile oxides (Scheme 1). The ratio of the formed diastereomers shows that the 1,3-dipolar cycloaddition of polyfluorinated cyclohexa-2,4-dienones with aryl nitrile oxides occurs with relatively high stereoselectivity. This stereoselectivity is apparently due to the lesser shielding of the C=O group by the fluorine atom than by the considerably large chlorine atom located at the contiguous *sp*^{3}-hybridized carbon of the polyfluorinated cyclohexa-2,4-dienone. This should result in the prevailing attack from the side of the fluorine atom leading respectively to the formation of diastereomers **IIIa–VIIa** as is proved actually by the structure of compound **Va** established by X-ray analysis. It is expectable that at the replacement of the chlorine atom for a more bulky pentafluorophenoxy group in the geminal node of the polyfluorinated cyclohexa-2,4-dienone the selectivity of the 1,3-dipolar cycloaddition with aryl nitrile oxides should grow even more. We studied the reaction with benzonitrile oxide of a mixture (33:67) of perfluoro-4-phenoxycyclohexa-2,5-dienone (**X**) and perfluoro-6-phenoxycyclohexa-2,4-dienone (**XI**). The analysis of the reaction mixture by ^{19}F NMRspectroscopy showed that the 1,3-dipolar cycloaddition of cyclohexadienone **XI** occurred with very high stereoselectivity with the formation of diastereomers **XIIa, XIIb** (~97 : 3) (Scheme 2). The formation of diastereomer **XIIb** was presumed basing on the presence in the ^{19}F NMR spectrum of the product mixture of weak signals at 5.1, 7.2, 9.7, and 23.3 ppm that we assigned to the signals of atoms F^{9}, F^{8}, F^{7}, and F^{10} respectively; the signals possessed a fine structure close to that observed in the respective signals of fluorine atoms in diastereomer **XIIa**.

At the same time the ratio of diastereomers **VIIIa, VIIIb** (54 : 46) formed in the reaction of benzonitrile

Scheme 2.



X **XI** **VIIIa** **VIIIb** **XIIa** **XIIb**

oxide with cyclohexa-2,5-dienone **X** where the pentafluorophenoxy group in the geminal node cannot effect the sterical hindrance to the reaction at the carbonyl group demonstrates the virtually total absence of the stereoselectivity [3]. Note also that the Diels–Alder reactions of polyfluorinated cyclohexa-2,4-dienones with styrenes and acetylene derivatives are also highly stereoselective due to the steric effect of the substituents in the geminal node of the dienone [9].

The perfluorocyclohexa-1,3-diene is known to react with nucleophilic reagents at the position *2* with the formation of the corresponding product of fluorine substitution at the double bond [10, 11]. The formation in a small yield of the products of allyl substitution of fluorine atom was also observed [10]. We studied the reaction of compounds **Va, Vb** (96:4), **VIa, VIb** (86 : 14), and **XIIa, XIIb** with sodium pentafluorophenolate. The reaction of compounds **Va, Vb** and **VIa, VIb** with sodium pentafluorophenolate proceeds as an allyl substitution of the chlorine atom affording in good yield the corresponding diastereomeric fluorine-containing 3-aryl-8-pentafluorophenoxy-1,4-dioxa-2-azaspiro[4,5]deca-2,6,9-trienes **XIIIa, XIIIb** and **XIVa**, **XIVb** (Scheme 3).

The reaction of compound **XII** with sodium pentafluorophenolate also occurs by the type of allyl substitution, but here the leaving group is either the pentafluorophenoxy group or the fluorine atom giving compounds **VIII, XV** (Scheme 3). We have obtained compounds **VIII, XIII, XIV** earlier by the reaction of cyclohexa-2,5-dienone **X** with the corresponding aryl nitrile oxides [3].

EXPERIMENTAL

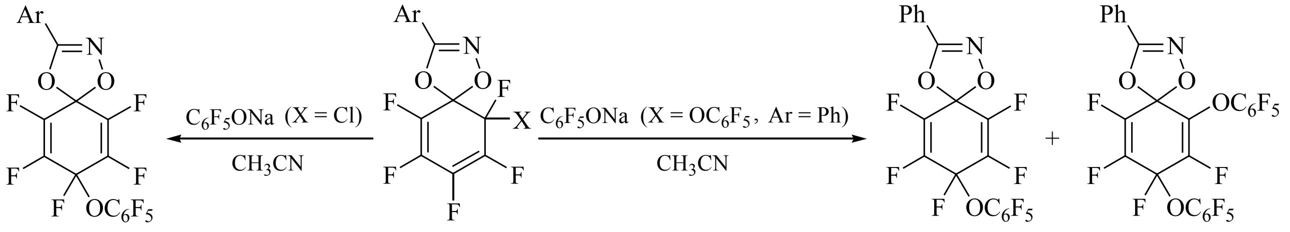
The analytic and spectral measurements were carried out in the Chemical Service Center for collective use of the Siberian Division, Russian Academy of Sciences.

^1H and ^{19}F NMR spectra were registered on a spectrometer Bruker AV300 at operating frequencies 300.13 and 282.36 MHz respectively from solutions in CCl_4 containing ~5% of DMSO-d_6. Internal references DMSO-d_6 (2.54 ppm from TMS) and C_6F_6. The reaction progress was monitored by TLC on Merck 60 F_{254} plates. The column chromatography was carried out on silica gel Merck (0.063–0.200 mm).

The composition of compounds **Va, XV** was derived from the high resolution mass spectra measured on an instrument DFS Termo Scientific (EI, 70 eV).

X-Ray experiment with compound **Va** was carried out on a diffractometer Bruker Kappa Apex (MoK$_\alpha$-radiation, graphite monochromator, CCD detector, φ,ω-

Scheme 3.



XIII, XIV **V, VI, XII** **VIII** **XV**

Ar = 4-BrC_6H_4 (**XIII**), 3-$NO_2C_6H_4$ (**XIV**).

scanning). Crystallographic parameters of compound **Va**: triclinic crystal system, *a* 5.6838(4), *b* 11.1270(9), *c* 11.4009(9) Å; α 82.780(4), β 81.209(4), γ 86.101(3)°; *V* 706.04(9) Å^3, space group *P*-1, $C_{13}H_4BrClF_5NO_2$, *Z* 2, d_{calc} 1.959 g cm^{-3}, μ 3.165 mm^{-1}, 2θ <55.2°. The intensities of 16219 reflections were measured, among them 3249 independent reflections. The results of refinement are as follows: wR_2 0.1273, *S* 1.058, *R* 0.0377 for 2596 reflections with $F > 4\sigma(F)$. The extinction was accounted for using SADABS program. The structure was solved by the direct method and refined using SHELXTL software. The refinement was carried out in the anisotropic approximation for the nonhydrogen atoms. The positions of hydrogen atoms were calculated geometrically and refined in the *rider* model. The structural data are deposited in Cambridge Crystallographic Data Center (CCDC 918661) and are available free at the address: www.ccdc.cam.ac.uk/data_request/cif.

Polyfluorinated cyclohexa-2,4-dienones **I, II**, and also the mixture of dienones **X, XI** were prepared by procedures [7, 12]. Cyclohexadienone **I** contained ~6-7% of pentafluorophenol and ~5–6% of 4-chloropentafluorocyclohexa-2,4-dienone that also reacted with aryl nitrile oxides forming fluorine-substituted 1,4-dioxa-2-azaspiro[4.5]deca-2,6,9-trienes [3] isomeric to target compounds **III–VI**.

10-Chloro-6,7,8,9,10-pentafluoro-3-phenyl-1,4-dioxa-2-azaspiro[4.5]deca-2,6,8-trienes IIIa, IIIb. To a solution of 0.40 g (3.3 mmol) of benzaldoxime in 30 ml of CH_2Cl_2 at 4°C was added dropwise under stirring 0.44 g (4 mmol) of *tert*-butyl-hypochlorite in 5 ml of CH_2Cl_2. The mixture was stirred for 1 h at 4°C, then it was shaken with 50 ml ~10% water solution of NaOH cooled to 7°C. The organic phase was separated and dried with solid NaOH at –18°C for 15–20 min. The obtained solution of benzonitrile oxide was added at stirring to a solution of 0.44 g (2 mmol) of 6-chloropentafluorocyclohexa-2,4-dienone (**I**) in 20 ml of CH_2Cl_2 cooled to –18°C, the reaction mixture was stirred for 2 h gradually warming to 20°C, and 16 h at room temperature. On evaporation the residue (0.88 g) was chromatographed on a column packed with SiO_2. By the elution with a mixture petroleum ether–CCl_4, 1 : 1, 0.53 g (79%) of fluid was isolated containing according to ^{19}F NMR data 91% of diastereomers **IIIa, IIIb**, 85 : 15. ^{1}H NMR spectrum, δ, ppm, diastereomers **IIIa**, **IIIb**: 7.33–7.46 m (3H$_{arom}$), 7.67–7.71 m (2H$_{arom}$). ^{19}F NMR spectrum, δ, ppm, diastereomer **IIIa**: 6.2 d.d.t (1F, F^{6}, *J* 17, 4, ~3 Hz), 6.6 d.d.t (1F, F^{8}, *J* 11, 6 , ~3 Hz), 6.9 d.d.t (1F, F^{9}, *J* 20, 17, ~3 Hz), 10.1 d.m (1F, F^{7}, *J* 6 Hz), 24.5 d.d.d.d (1F, F^{10}, *J* 20, 11, 4, ~2 Hz). ^{19}F NMR spectrum, δ, ppm, diastereomer **IIIb**: 7.2 d.d.t (1F, F^{6}, *J* 17, 6, ~3 Hz), 7.4 d.d.t (1F, F^{8}, *J* 12, 6, ~3 Hz), 8.5 d.d.t (1F, F^{9}, *J* 23, 17, ~3 Hz), 9.7 d.m (1F, F^{7}, *J* 6 Hz), 30.9 d.d.d.d (1F, F^{10}, *J* 23, 12, 6, ~3 Hz). Found, %: C 46.26; H 1.43; Cl 10.44; F 28.30; N 3.58. *M* 339. $C_{13}H_5ClF_5NO_2$. Calculated, %: C 46.25; H 1.49; Cl 10.50; F 28.14; N 4.15. *M* 337.63.

10-Chloro-6,7,8,9,10-pentafluoro-3-(4-methoxyphenyl)-1,4-dioxa-2-azaspiro[4.5]deca-2,6,8-trienes IVa, IVb were obtained similarly from 1.21 g (8 mmol) of 4-methoxybenzaldoxime, 1.0 g (9 mmol) of *tert*-butylhypochlorite, 100 ml of 10% NaOH solution, and 0.44 g (2 mmol) of dienone **I** in 60 ml of CH_2Cl_2. Yield 1.11 g (~76%), fluid containing according to the data of ^{19}F NMR spectrum ~80% of diastereomers **IVa, IVb**, 84 : 16, ~6% of 8-chloro-6,7,8,9,10-pentafluoro-3-(4-methoxyphenyl)-1,4-dioxa-2-azaspiro[4.5]deca-2,6,9-triene, and ~12% of 10-chloro-6,8,9,10-tetrafluoro-3-(4-methoxyphenyl)-7-(pentafluorophenoxy)-1,4-dioxa-2-azaspiro[4.5]deca-2,6,8-triene **IXa, IXb**. ^{1}H **NMR** spectrum, δ, ppm, diastereomers **IVa, IVb** and compounds **IXa, IXb**: 3.89 s (3H, OCH_3), 7.94–7.01 m (2H$_{arom}$), 7.64–7.79 m (2H$_{arom}$). ^{19}F NMR spectrum, δ, ppm, diastereomer **IVa**: 6.4 d.d.t (1F, F^{6}, *J* 17, 4, ~3 Hz), 6.5 d.d.t (1F, F^{8}, *J* 11, 6, ~3 Hz), 6.8 d.d.t (1F, F^{9}, *J* 20, 17, ~3 Hz), 9.7 d.m (1F, F^{7}, *J* 6 Hz), 24.7 d.d.d.d (1F, F^{10}, *J* 20, 11, 4, ~2 Hz). ^{19}F NMR spectrum, δ, ppm, diastereomer **IVb**: 7.2 d.d.t (1F, F^{8}, *J* 12, 6, ~2 Hz), 7.3 d.d.t (1F, F^{6}, *J* 17, 6, ~2 Hz), 8.4 d.d.t (1F, F^{9}, *J* 23, 17, ~3 Hz), 9.4 d.m (1F, F^{7}, *J* 6 Hz), 30.7 d.d.d.d (1F, F^{10}, *J* 23, 12, 6, ~3 Hz). ^{19}F NMR spectrum, δ, ppm, compound **IX**a: 0.7 m (2F, F^{m}), 3.4 t (1F, F^{p}), 6.0 m (2F, F^{o}), 6.8 m (1F, F^{9}), 8.9 d.m (1F, F^{8}, *J* 11 Hz), 11.4 d.m (1F, F^{6}, *J* 17 Hz), 23.4 d.d.d (1F, F^{10}, *J* 19, 11, 4 Hz). Found, %: C 46.09; H 1.72; Cl 9.41; F 25.76; N 3.52. *M* 366. $C_{14}H_7ClF_5NO_3$. Calculated, %: C 45.74; H 1.92; Cl 9.64; F 25.84; N 3.81. *M* 367.66.

3-(4-Bromophenyl)-10-chloro-6,7,8,9,10-pentafluoro-1,4-dioxa-2-azaspiro[4.5]deca-2,6,8-trienes Va, Vb were similarly obtained from 0.6 g (3 mmol) of 4-bromobenzaldoxime, 0.44 g (4 mmol) of *tert*-butylhypochlorite, 80 ml of 10% NaOH solution, and 0.44 g (2 mmol) of dienone **I** in 55 ml of CH_2Cl_2. Yield 0.71 g (85%), oily substance containing according to the data of ^{19}F NMR spectrum 89% of diastereomers **Va, Vb**, 86 : 14. After double crystallization from hexane we obtained 0.32 g of a crystalline mixture of diastereomers

Va, Vb, 96:4, mp 90–93°C. ^{1}H NMR spectrum, δ, ppm, diastereomer **Va**: 7.66, 7.71 (4H$_{\text{arom}}$, *AB* system, *J* ~8.5 Hz). ^{19}F NMR spectrum, δ, ppm, diastereomer **Va**: 5.9 d.d.t (1F, F^6, *J* 17, 4, ~3 Hz), 6.7 d.d.t (1F, F^8, *J* 11, 6, ~3 Hz), 7.0 d.d.t (1F, F^9, *J* 20, 17, ~3 Hz), 10.6 d.m (1F, F^7, *J* 6 Hz), 24.3 d.d.d.d (1F, F^{10}, *J* 20, 11, 4, ~2 Hz). Found $[M]^+$ 414.9026. $C_{13}H_4{}^{79}Br^{35}ClF_5NO_2$. Calculated *M* 414.9029.

The mother liquor contained 0.37 g of a mixture of diastereomers **Va, Vb** in a ratio 67:22. ^{19}F NMR spectrum, δ, ppm, diastereomer **Vb**: 7.0 m (1F, F^6), 7.5 d.d.t (1F, F^8, *J* 12, 6, ~3 Hz), 8.6 d.d.t (1F, F^9, *J* 23, 17, ~3 Hz), 10.2 d.m (1F, F^7, *J* 6 Hz), 30.7 d.d.d.d (1F, F^{10}, *J* 23, 12, 6, ~3 Hz).

10-Chloro-6,7,8,9,10-pentafluoro-3-(3-nitrophenyl)-1,4-dioxa-2-azaspiro[4.5]deca-2,6,8-trienes VIa, VIb were similarly obtained from 1.02 g (6 mmol) of 3-nitrobenzaldoxime, 0.87 g (8 mmol) of *tert*-butyl-hypochlorite, 50 ml of 10% NaOH solution, and 0.44 g (2 mmol) of dienone **I** in 65 ml of CH_2Cl_2. Yield 0.46 g (60%), fluid containing according to the data of ^{19}F NMR spectrum 87% of diastereomers **VIa, VIb**, 86:14. ^{19}F NMR spectrum, δ, ppm, diastereomer **VIa**: 5.6 d.d.t (1F, F^6, *J* 17, 4, ~3 Hz), 7.2 d.d.t (1F, F^8, *J* 11, 6, ~3 Hz), 7.3 d.d.t (1F, F^9, *J* 20, 17, ~3 Hz), 11.4 d.m (1F, F^7, *J* 6 Hz), 25.1 d.d.d.d (1F, F^{10}, *J* 20, 11, 4, ~2 Hz). ^{19}F NMR spectrum, δ, ppm, diastereomer **VIb**: 6.4 d.d.t (1F, F^6, *J* 17, ~5, ~2 Hz), 7.8 d.d.t (1F, F^8, *J* 12, 6, ~2 Hz), 8.5 d.d.t (1F, F^9, *J* 23, 17, ~2 Hz), 11.2 d.m (1F, F^7, *J* 6 Hz), 29.7 d.d.d.d (1F, F^{10}, *J* 23, 12, ~5, ~2 Hz).

10-Chloro-6,8,9,10-tetrafluoro-7-(pentafluorophenoxy)-3-phenyl-1,4-dioxa-2-azaspiro[4.5]deca-2,6,8-trienes VIIa, VIIb. To a solution of 0.22 g (1 mmol) of dienone **I** in 10 ml of CH_2Cl_2 was added by small portions 0.21 g (1 mmol) of sodium pentafluorophenolate [7]. The mixture was stirred for 2 h at 20°C, cooled to 0°C, and a cooled to –18°C solution of benzonitrile oxide obtained from 0.36 g (3 mmol) of benzaldoxime, 0.43 g (4 mmol) of *tert*-butyl-hypochlorite, and 50 ml of 10% NaOH solution in 40 ml of CH_2Cl_2 was added. The reaction was further performed analogously to the synthesis of **IIIa, IIIb**. We obtained 0.40 g (80%) of oily substance containing according to the data of ^{19}F NMR spectrum ~96% of diastereomers **VIIa**, **VIIb**, 84:16. ^{1}H NMR spectrum, δ, ppm, diastereomers **VIIa, VIIb**: 7.49–7.62 m (3H$_{\text{arom}}$), 7.81–7.89 m (2H$_{\text{arom}}$). ^{19}F NMR spectrum, δ, ppm, diastereomer **VIIa**: 0.7 m (2F, F^m), 3.5 t (1F, F^p), 6.0 m (2F, F^o), 6.9 d.d.d (1F, F^9, *J* 20, 17, ~3 Hz), 9.1 d.d.m (1F, F^8, *J* 11, ~5 Hz), 11.0 d.d.m (1F, F^6, *J* 17, 4 Hz), 23.4 d.d.d (1F, F^{10}, *J* 20, 11, 4 Hz). ^{19}F NMR spectrum, δ, ppm, diastereomer **VIIb**: 0.7 m (2F, F^m), 3.5 t (1F, F^p), 6.0 m (2F, F^o), 8.6 d.d.d (1F, F^9, *J* 23, 17, ~2 Hz), 9.9 d.m (1F, F^8, *J* 12 Hz), 11.9 d.d.m (1F, F^6, *J* 17, 5 Hz), 30.3 d.d.d (1F, F^{10}, *J* 23, 12, 5 Hz). Found, %: C 46.19; H 1.01; Cl 7.08; F 33.88; N 2.44. *M* 494. $C_{19}H_5ClF_9NO_3$. Calculated, %: C 45.49; H 1.00; Cl 7.07; F 34.08; N 2.79. *M* 501.69.

6,7,8,9,10-Pentafluoro-10-(pentafluorophenoxy)-3-phenyl-1,4-dioxa-2-azaspiro[4.5]deca-2,6,8-trienes XIIa, XIIb were obtained similarly to compounds **IIIa, IIIb** from 0.36 g (3 mmol) of benzaldoxime, 0.40 g (3.7 mmol) of *tert*-butylhypochlorite, 50 ml 10% NaOH solution, and 0.73 g (2 mmol) of the mixture of dienones **X, XI**, 33:67, in 55 ml of CH_2Cl_2. Yield 0.74 g (76%). Oily substance containing according to the data of ^{19}F NMR spectrum 29% of diastereomers **VIIIa, VIIIb**, 54:46, (cf. [3]) and 69% of diastereomers **XIIa, XIIb**, ~97 : 3. ^{19}F NMR spectrum, δ, ppm, diastereomer (**XIIa**): 1.0 m (2F, F^m), 4.9 d.d (1F, F^9, *J* 16, 15 Hz), 6.0 d.m (1F, F^8, *J* 15 Hz), 6.5 t (1F, F^p), 9.2 m (1F, F^7), 10.0 d.m (1F, F^6, *J* 16 Hz), 10.5 m (2F, F^o), 20.4 quintet (1F, F^{10}, *J* 15 Hz). Found, %: C 46.87; H 1.13; F 39.15; N 2.28. *M* 485. $C_{19}H_5F_{10}NO_3$. Calculated, %: C 47.03; H 1.04; F 39.15; N 2.89. *M* 485.24.

3-(4-Bromophenyl)-6,7,8,9,10-pentafluoro-8-(pentafluorophenoxy)-1,4-dioxa-2-azaspiro[4.5]deca-2,6,9-trienes XIIIa, XIIIb. To a solution of 0.32 g (0.8 mmol) of a mixture of compounds **Va, Vb**, 96 : 4, in 5 ml of acetonitrile was added by small portions 0.21 g (1 mmol) of sodium pentafluorophenolate, and the mixture was stirred for 16 h at room temperature. On evaporating the solvents the residue (~0.6 g) was chromatographed on a column packed with SiO_2. Eluting first with a mixture petroleum ether–CCl_4, 1 : 1, and further with CCl_4 we isolated 0.36 g (64%) of a substance containing according to the data of ^{19}F NMR spectrum 87% of diastereomers **XIIIa, XIIIb**, 81 : 19.

6,7,8,9,10-Pentafluoro-3-(3-nitrophenyl)-8-(pentafluorophenoxy)-1,4-dioxa-2-azaspiro[4.5]deca-2,6,9-trienes XIVa, XIVb were similarly obtained from 0.37 g (1 mmol) of the mixture of compounds **VIa, VIb**, 86:14, and 0.21 g (1 mmol) of sodium pentafluorophenolate in 5 ml of acetonitrile. Yield 0.47 g, oily substance containing according to the data of ^{19}F NMR spectrum ~60% of diastereomers **XIVa, XIVb**, 77 : 23, and ~23% of compounds **VIa, VIb**, 78:22. After double crystallization from ethanol we obtained 0.21 g of crystalline diastereomer **XIVa**, mp 126–129°C. ^{1}H NMR spectrum, δ, ppm, diastereomer **XIVa**: 7.81 t (1H$_{\text{arom}}$, *J* 8 Hz), 8.19 d.d.d (1H$_{\text{arom}}$, *J* 8, 2, 1 Hz), 8.48 d.d.d (1H$_{\text{arom}}$, *J* 8, 2, 1 Hz), 8.62 t (1H$_{\text{arom}}$, *J* 2 Hz). ^{19}F NMR spectrum, δ, ppm, diastereomer **XIVa** (cf. [3]): 0.6 m (2F, F^m), 6.3 t (1F, F^p), 7.5 m (2F, F^{6,10}), 9.2 m (2F, F^{7,9}), 10.4 m (2F, F^o), 41.3 m (1F, F^8). Found, %: C 43.34; H 0.89; F 36.00; N 5.28. *M* 531. $C_{19}H_4F_{10}N_2O_5$. Calculated, %: C 43.03; H 0.76; F 35.83; N 5.28. *M* 530.24.

6,7,8,9,10-Pentafluoro-8-(pentafluorophenoxy)-3-phenyl-1,4-dioxa-2-azaspiro[4.5]deca-2,6,9-trienes VIIIa, VIIIb and 6,7,8,9-tetrafluoro-8,10-bis(pentafluorophenoxy)-3-phenyl-1,4-dioxa-2-azaspiro[4.5]deca-2,6,9-trienes (XV). To a solution of 0.66 g (1.4 mmol) of the mixture containing 29% of compounds **VIIIa, VIIIb,** 54 : 46, and 69% of **XIIa, XIIb**, ~97 : 3, in 10 ml of acetonitrile was added 0.22 g (1 mmol) of sodium pentafluorophenolate, and the mixture was stirred for 18 days at room temperature. After the removal of acetonitrile the residue (~0.9 g) was chromatographed on the column packed with SiO_2. At the elution in succession with petroleum ether and a mixture petroleum ether–ethyl acetate, 200 : 1, we isolated 0.44 g of solid substance containing according to the data of ^{19}F NMR spectrum, 87% of compounds **VIIIa, VIIIb**, 70:30, and 13% of compound **XIIa**. We also isolated 0.22 g of viscous fluid containing ~74% of compound **XV**. ^{19}F NMR spectrum, δ, ppm, diastereomer **XV** (cf. [3])**:** 0.2 m (2F, F^m), 0.3 m (2F, F$^{m'}$), 3.4 t (1F, F$^{p'}$), 5.9 t (1F, F^p), 6.6 m (2F, F$^{o'}$), 7.8 d.d.t (1F, F^9, *J* 21, ~6, ~5 Hz), 8.8 d.d.d (1F, F^{10}, *J* 9, 6, ~2 Hz), 10.3 m (2F, F^o), 12.9 d.m (1F, F^7, *J* 21 Hz), 41.9 t.t.d (1F, F^8, *J* 21, 13, 9 Hz). Found *M*$^+$ 648.9973. $C_{25}H_5F_{14}NO_4$. Calculated *M* 648.9990.

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