Formation of Fluorinated 1-Oxaspiro[2.5]octa-4,7-dienes from Polyfluorinated Cyclohexa-2,5-dienones with Diazomethane and Reactions with Aryl and 2-Chloroethyl Isocyanates[‡]

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The reactions of four polyfluorinated cyclohexa-2,5-dienones **1a**–**1d**, additionally substituted with an electron withdrawing substituent at the 4-position, with diazomethane give mixtures of two diastereomeric fluorinated 1-oxaspiro[2.5]octa-4,7-dienes **2** and **3**. Compounds **2a/3a** and **2b/3b** react with aryl and 2-chloroethyl isocyanates in the presence of lithium chloride or sodium pentafluorophenoxide to form fluorinated dihydro-1,3-benzoxazol-2(3*H*)-ones **5a**–**5c** as the major products.

Introduction

Quinoid compounds are well known to be versatile building blocks for the synthesis of complex molecules.[1] Particularly, after the first synthesis of pyrazolines from *p*-benzoquinones and diazomethane by von Pechmann[2,3] and the classical investigation of Eistert[4–8] in this field, cycloadditions of diazoalkanes with quinones[4–10] and other α,β-unsaturated ketones[11–14] became one of the most common methods of pyrazoline synthesis. Thus, alkyl-substituted and 2,5-dichlorobenzoquinones[5] as well as alkylated 2,4- and 2,5-cyclohexadienones[15] gave these products of cycloaddition of diazomethane to the C=C bond exclusively. In contrast, 2,6- and 2,3-dichloro-*p*-benzoquinones under similar conditions yielded pyrazolines with an additional spiro-oxirane ring formed by reaction of diazomethane with the carbonyl group.[7,8] On the other hand, reactions of tetrahalo-*p*-benzoquinones[4] and 2,6-dimethoxy-*p*-benzoquinone[6] with diazomethane gave spiro-epoxides exclusively. It is also known that treatment of tetrafluorocyclopentadienone with diazomethane gave only the product of reaction on the carbonyl group.[16]

Fluorinated cyclohexadienones have been shown to be versatile building blocks for the preparation of complex organofluorine compounds.[17] Earlier we found that tetrafluoro-*p*-benzoquinone reacts with diazomethane mainly on one of the carbonyl groups giving an oxaspiro[2.5]octa-4,7-dienone and a small amount of a pentacycle, the product of both reaction at the C=C bonds and at the carbonyl groups.[18] We have shown also that 6-chloro-2,3,4,5,6-pentafluorocyclohexa-2,4-dienone reacted with diazomethane both on the carbonyl group and on a C=C bond, forming a fluorinated derivative of indazolo-spiro-oxirane.[19] With phenyldiazomethane polyfluorinated cyclohexa-2,4-dienones reacted mainly with formation of fluorinated 7-phenylbicyclo[4.1.0]hept-4-en-2-ones, the formal products of addition of methylene to the C=C bond.[19]

Now we present the results of the reaction of fluorinated cyclohexa-2,5-dienones **1** with diazomethane and some reactions of thus-formed diastereomeric fluorinated 1-oxaspiro[2.5]octa-4,7-dienes **2/3** with aryl and 2-chloroethyl isocyanates.

Results and Discussion

The reactions of 4-chloro-, 4-nitro-, 4-pentafluorophenoxy-2,3,4,5,6-pentafluorocyclohexa-2,5-dienones (**1a**–**1c**) and hexafluorocyclohexa-2,5-dienone (**1d**) with diazomethane in diethyl ether gave mixtures of diastereomeric pentafluoro-1-oxaspiro[2.5]octa-4,7-dienes: **2a/3a** (50:50), **2b/3b** (59:41), **2c/3c** (61:39) from **1a**–**1c**, respectively, and **2d** from **1d** (Scheme 1).

The structure of the products was attributed based on analysis of ^{1}H- and ^{19}F-NMR spectra taken from the mixture of isomers (Table 1, Experimental Section). Furthermore, all products **2**, **3** and **4** in mass spectra show the appropriate molecular ions, though with low intensities, and the same fragment ion (found 197.00028; calculated for $C_7H_2F_5O$ 197.00257) corresponding to elimination of the

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[‡] Reactions of Polyfluorinated Cyclohexadienones with Diazoalkanes, 2. Part 1: Ref.[19]

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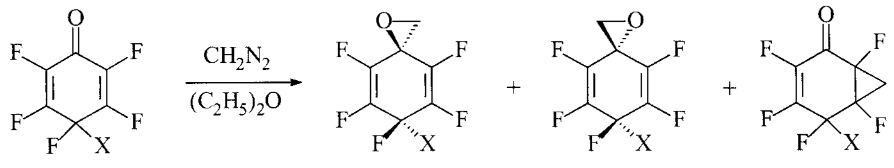
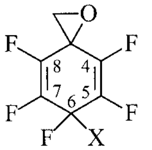


1a (X = Cl)	[73%]	**2a**	50 : 50	**3a**	**4a**
1b (X = NO_2)	[98%]	**2b**	59 : 41	**3b**	
1c (X = OC_6F_5)	[79%]	**2c**	61 : 39	**3c**	
1d (X = F)	[70%]	**2d**			

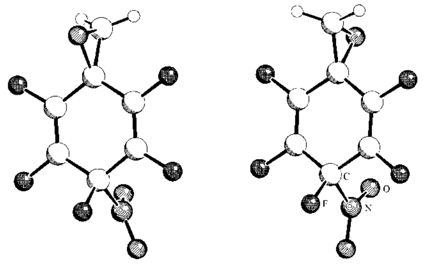
Scheme 1.

Table 1. ^{19}F- and ^{1}H-NMR chemical shifts of polyfluorinated 1-oxaspiro[2.5]octa-4,7-dienes.

		$F^{4,8}$	$F^{5,7}$	F^{6}	CH_2
X = Cl	**2a**	–155.0	–148.1	–103.0	3.5
	3a	–155.3	–149.1	–104.8	3.5
X = NO_2	**2b**	–144.7	–151.4	–126.6	3.7
	3b	–145.3	–152.1	–128.2	3.6
X = OC_6F_5[a]	**2c**	–154.1	–152.2	–112.4	3.5
	3c	–154.1	–152.2	–114.4	3.5
X = F [b]	**2d**	–152.9	–157.4	–105.5, –103.7 J_{AB} = 292 Hz	3.5

[a] OC_6F_5: *ortho* –153.2 ppm; *meta* –162.8 ppm; *para* –157.5 ppm. [b] In CH_2Cl_2.

substituent X. Isomers **2b** and **3b** were isolated in pure form in 57% and 41% yields, respectively, and their structure was determined by X-ray structural analysis (Figure 1).



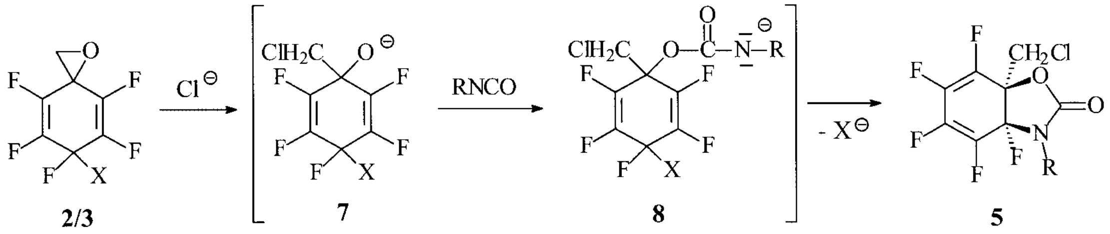
2b **3b**

Figure 1. X-ray crystal structure of the diastereomeric 4,5,6,7,8-pentafluoro-6-nitro-1-oxaspiro[2.5]octa-4,7-dienes (**2b** and **3b**).

Among the products of reaction of **1a** with diazomethane trace amount of the cyclopropane **4a** was identified by NMR spectra. The later product arises from cycloaddition of diazomethane to a C=C bond of dienone **1a**. The ^{19}F-NMR spectrum of the crude reaction product showes two signals of very low intensities at –202.6 and –209.1 ppm. Such high field signals were also found in the spectra of polyfluorinated bicyclic cyclopropane derivatives.[19] Earlier we observed a dependence from the polarity of solvent of ratio of C=C versus C=O additions of phenyldiazomethane in the reactions with polyfluorinated 2,4-cyclohexadienones.[19] However, all attempts to change the ratio of **2a** and **4a** using more polar mixtures of solvents such as diethyl ether/acetonitrile (1:2) were unsuccessful.

Thus, the polyfluorinated 2,5-cyclohexadienones **1a–d**, in contrast to alkyl-substituted 2,5-cyclohexadienones,[15] react with diazomethane mainly on the carbonyl group with formation of corresponding fluorinated 1-oxaspiro[2.5]octa-4,7-dienes. Analogous differences in reactivity were observed also with polyhalogenated and alkyl-substituted 1,4-benzoquinones both with diazomethane,[18,20] and with other 1,3-dipolar compounds.[1,20–22] The different routes, C=O versus C=C addition, of nitrile oxides to 1,4-benzoquinones have been explained based on results of frontier molecular orbital calculations.[22] The HOMO (nitrile oxide) – LUMO (quinone) interaction is the governing factor for the addition to the C=O group. In contrast, the interaction LUMO (nitrile oxide) – HOMO (quinone) is responsible for the addition to the C=C bond. The first interaction is typical for polyhalogenated benzoquinones, while the second was observed with alkyl-substituted 1,4-benzoquinones.

Since it is well known that electron withdrawing substituents strongly increase the tendency of carbonyl compounds to yield epoxides when treated with diazomethane,[23] we suppose that the electronegative fluorine atoms are chiefly responsible for the preferred reaction on C=O group. Thus, the central question seems to be whether a 1,3-dipolar cycloaddition or a two-step process via ionic intermediates is operating in the reaction of diazoalkanes with quinoid compounds. In our case the ionic reaction might be pre-

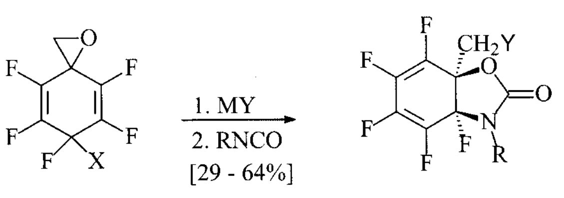


Scheme 3.

ferred but also the concerted cycloaddition of diazomethane at the carbonyl group via an oxadiazoline and subsequent N_2 extrusion is possible. The minor amount of compound **4a** may be the result of a similar attack of diazomethane on the C=C bond. For a more detailed mechanistic discussion quantum chemical calculations of the respective activation barriers as well as the reaction energies are in progress and will be communicated in due course.

One of the well-known and interesting reactions of oxiranes (also spiro-oxiranes) is the addition of alkyl or aryl isocyanates resulting in the formation of 2-oxazolidinones. Usually, this reaction proceeds in the presence of Lewis acidic catalysts, such as lithium halogenides, or quaternary ammonium salts, etc.[24–26] We studied the reactions of the fluorinated 1-oxaspiro[2.5]octa-4,7-dienes **2a/3a** and **2b/3b** with aryl and 2-chloroethyl isocyanates.

Reactions of mixtures of the oxiranes **2a/3a** prepared directly from **1a** with phenyl, 4-chlorophenyl and 2-chloroethyl isocyanates in the presence of a catalytic amount of lithium chloride resulted in the formation of fluorinated dihydro-1,3-benzoxazol-2(3*H*)-ones (**5a–c**) in 60%, 64% and 56% yields, respectively. Compound **5a** has also been formed in the reaction of fluorinated 1-oxaspiro[2.5]octa-4,7-dienes **2b/3b** with phenyl isocyanate in the presence of equimolar amount of lithium chloride. Using equimolar amount of sodium pentafluorophenoxide instead of LiCl in this reaction, we obtained 3a,4,5,6,7-pentafluoro-7a-pentafluorophenyloxymethyl-3-phenyl-3a,7a-dihydro-1,3-benzoxazol-2(3*H*)-one (**6a**) (Scheme 2).



2a/3a (X = Cl) MY = LiCl **5a** (R = C_6H_5, Y = Cl)
5b (R = C_6H_4Cl, Y = Cl)
5c (R = C_2H_4Cl, Y = Cl)
2b/3b (X = NO_2) MY = LiCl **5a** (R = C_6H_5, Y = Cl)
MY = $NaOC_6F_5$ **6a** (R = C_6H_5, Y = OC_6F_5

Scheme 2.

From both diastereomers of the fluorinated 1-oxaspiro[2.5]octa-4,7-dienes the same product was formed. X-ray structural analysis of compound **5b** shows that the rings are *cis*-connected (Figure 2).

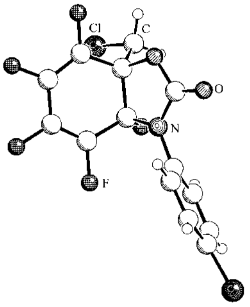


Figure 2. X-ray crystal structure of 7a-chloromethyl-3-(4-chlorophenyl)-3a,4,5,6,7-pentafluoro-3a,7a-dihydro-3*H*-benzoxazol-2-one (**5b**).

The reactivity of isomeric fluorinated 1-oxaspiro[2.5] octa-4,7-dienes **2a** and **3a** is almost equal because in the presence of 0.5 equivalents of 4-chlorophenyl isocyanate we did not observe any change in the ratio of the unreacted starting compounds **2a** and **3a**.

For the formation of fluorinated dihydro-1,3-benzoxazol-2(3*H*)-ones **5a–5c** we suggest a mechanism shown in Scheme 3. The ^1H- and ^{19}F-NMR spectra of compounds **5a–5c** and **6a** are given in Table 3 (Experimental Section).

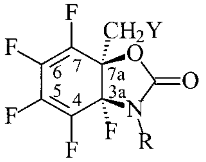
The first step is a Lewis acid catalyzed nucleophilic opening of the epoxide ring of the polyfluorinated 1-oxaspiro[2.5]octa-4,7-dienes **2/3** with chloride to give the alcoholates **7**, which react with isocyanates to produce the anions **8**. These ambident anions (oxygen- or nitrogen-centered) have also two electrophilic centers suitable for nucleophilic cyclization, the CH_2Cl-group and the neighboring fluorinated C=C bond. The nitrogen centered anion **8** in an S_N' reaction attacks the C=C bond exclusively with subsequent elimination of X^- from the geminal CFX-group to give the dihydrobenzoxazolones **5**. This is in agreement with literature data, that the 2-oxazolidinones in reactions of oxiranes with isocyanates may be produced by two subsequent S_N2 reactions, where chloride (released from LiCl) is a nucleophile in the first step and after addition of isocyanate a leaving group in the cyclization step.[27] This mechanism agrees with the fact, that the reaction proceeds only with LiCl as a catalyst, while the reaction of fluorinated 1-oxaspiro[2.5]octa-4,7-dienes **2a/3a** with 4-chlorophenyl isocyanate in the presence of $LiClO_4$ gave a multicomponent mixture. Compound **5b** has not been identified among the products in the latter case. The formation of compounds **5a** or **6a** in the reactions of fluorinated 1-oxaspiro[2.5]octa-4,7-dienes **2b/3b** with phenyl isocyanate and lithium chloride or

Table 2. Conditions of the reactions of polyfluorinated cyclohexa-2,5-dienones **1** with diazomethane and analytical data of the products

Entry	Compounds **1** g (mmol)	Diazogen g (mmol)	*T* °C	Time h	Yield g (%)	M.p. °C (from pentane)	M^+ by MS
1	**1a**, 0.87 (4)	1.43 (6.7)	–30→ room temp.	3	**2a/3a**, 0.68 (73)	viscous oil	232
2	**1b**, 094 (4)	3.21 (15)	–30→ room temp.	16	**2b** 0.55 (57), **3b** 0.40 (41)	27–29, 38–40	243, 243
3	**1c**, 0.73 (2)	1.43 (6.7)	–30→ room temp.	16	**2c/3c** 0.6 (79)	viscous oil	380
4	**1d**, 0.20 (1)	0.62[a] (6)	0→ room temp.	16	**2d** 0.24 [b]	viscous oil	216

[a] Solution of diazomethane was prepared from *N*-nitroso-*N*-methylurea. [b] Crude product containing 70% of compound **2d**.

Table 3. The ^{19}F- and ^{1}H-NMR spectroscopic data of fluorinated dihydro-1,3-benzoxazol-2(3*H*)-ones

	Chemical shift (CCl_4, δ from $CFCl_3$ or TMS)					*J*/Hz							
	F^{3a}	F^4	F^5	F^6	F^7	CH_2Y	J_{F3aF4}	J_{F3aF5}	J_{F3aF7}	J_{F4F5}	J_{F4F7}	J_{F5F6}	J_{F6F7}	J_{HF3a}
5a: R= C_6H_5, Y = Cl	–125.8	–153.1	–158.0	–155.9	–154.6	4.07; 3.92 (J_{HH} = 11.6 Hz)	26.8	12.0	4.5	≈2	18.9	6.1	4.7	4.3
5b:[a] R = C_6H_4Cl, Y = Cl	–123.3	–155.4	–157.1	–156.1	–154.4	4.04; 3.96 (J_{HH} = 11.8 Hz)	27.4	12.1	4.3	≈2	18.4	6.0	5.0	4.3
5c: R = C_2H_4Cl, Y = Cl	–129.7	–157.0	–156.8	–155.9	–154.2	[b]	≈26	12.0	≈4.5		18.5	≈5.5	≈5.0	
6a:[c] R = C_6H_5, Y = OC_6F_5	–122.6	–153.6	–158.2	–155.1	–154.9	4.63; 4.56 (J_{HH} = 10.1 Hz)	26.9	12.4	4.2	2.5	18.9	5.8	4.7	4.6

[a] In $CDCl_3$. [b] CH_2Y and NC_2H_4Cl: 3.5–4.2 ppm. [c] OC_6F_5: –157.8 ($2F_{ortho}$), –162.0 ($1F_{para}$), –163.1 ($2F_{meta}$).

Table 4. Conditions of the reactions of fluorinated 1-oxaspiro[2.5]octa-4,7-dienes **2/3** with isocyanates and analytical data of the products **5**

Entry	Compound **1** g (mmol)	*N*-nitroso-*N*-methylurea g (mmol)	Isocyanate RNCO g (mmol)	Catalyst g (mmol)	Products, yields g (%)	M.p. °C (solvent)	Molecular mass by HRMS (calculated)
1	**1a** 0.66 (3)	0.7 (6.8)	R = C_6H_5 0.7 (5.9)	LiCl 0.01	**5a** 0.63 (60)	119–122 (hexane)	351.00862 (351.00854)
2	**1a** 0.44 (2)	0.74 (3.4)[a]	R = C_6H_4Cl 0.45 (3)	LiCl 0.01	**5b** 0.49 (64)	147–150 (hexane)	384.96866 (384.96957)
3	**1a** 0.66 (3)	0.7 (6.8)	R = C_2H_4Cl 0.63 (6)	LiCl 0.01	**5c** 0.57 (56)	viscous oil	336.96962 (336.96957)
4	**1b** 0.7 (3)	1.0 (9.7)	R = C_6H_5 1.8 (15)	LiCl 0.15 (3)	**5a** 0.45 (43)	119–122 (hexane)	351.00862 (351.00854)
5	**1b** 0.7 (3)	1.0 (9.7)	R = C_6H_5 0.5 (4)	$NaOC_6F_5$ 0.6 (3)	**6a** 0.43 (29)	84–87 (hexane)	499.02686 (499.02661)

[a] Solution of diazomethane was prepared from diazogen.

sodium pentafluorophenoxide, respectively, also confirms the above mechanism. In these reactions the metal salts (LiCl or sodium pentafluorophenoxide) have to be used in equimolar amount.

Conclusions

We have shown that polyfluorinated cyclohexa-2,5-dienones **1**, in contrast to corresponding non-fluorinated cyclohexadienones, reacted with diazomethane at the carbonyl group forming mixtures of two diastereomeric 1-oxaspiro[2.5]octa-4,7-dienes **2** and **3**. Treatment of the 6-chloro-4,5,6,7,8-pentafluoro-1-oxaspiro[2.5]octa-4,7-dienes (**2a/3a**) with phenyl, 4-chlorophenyl and 2-chloroethyl isocyanates in the presence of catalytic amount of lithium chloride gave fluorinated 7a-chloromethyl-3a,7a-dihydro-1,3-benzoxazol-2(3*H*)-ones **5a**–**5c**. The reactions of 4,5,6,7,8-pentafluoro-6-nitro-1-oxaspiro[2.5]octa-4,7-diene (**2b/3b**) with phenyl isocyanate and equimolar amounts of lithium chloride or sodium pentafluorophenoxide resulted in the formation of compound **5a** or 7a-pentafluorophenoxymethyl-3a,7a-dihydro-1,3-benzoxazol-2(3*H*)-one (**6a**).

Experimental Section

General Remarks: Polyfluorinated cyclohexa-2,5-dienones **1a**–**1d** were prepared according to refs.[28–30] All other starting materials and reagents were obtained from Fluka or Acros. Solvents were dried and stored over molecular sieves 0.4 nm. Mass spectra were measured on a Finnigan MAT-8200 instrument operating at 70 eV. NMR spectra were recorded on a Bruker WP-200SY (200.00 MHz for ^{1}H and 188.28 MHz for ^{19}F) or Bruker WN-300 (300.13 MHz for ^{1}H and 282.40 MHz for ^{19}F) in $CDCl_3$ or CCl_4 solution with TMS, $CFCl_3$ or C_6F_6 (δ = –162.9 ppm from $CFCl_3$) as internal standards, respectively. Thin layer chromatography was performed with TLC plates 60 F_{254} by Merck. Column chromatography was performed using silica gel (Merck, particle size 22–63 µm). The purity of all isolated compounds was more than 95% (^{19}F-NMR spectroscopically).

General Procedure for Reactions of Polyfluorinated Cyclohexa-2,5-dienones with Diazomethane: A solution of diazomethane in diethyl ether (10–20 mL), prepared from diazogen or *N*-nitroso-*N*-methylurea according to the protocol given in ref.,[31] was added at an appropriate temperature (Table 2) to the solution of the respective cyclohexa-2,5-dienone in diethyl ether (10 mL) and stirred for 3–16 h. After evaporation of the solvent, the residue was purified by column chromatography on silica gel using pentane/diethyl ether (gradient, 20:1 to 1:1) as eluent to afford the corresponding fluorinated 1-oxaspiro[2.5]octa-4,7-dienes. The ^{1}H- and ^{19}F-NMR spectroscopic data for all products are listed in Table 1. More details on the reaction conditions and analytical data for all products are given in Table 2.

General Procedure for Reaction of Fluorinated 1-Oxaspiro[2.5]octa-4,7-dienes with Isocyanates

Reactions of 6-Chloro-4,5,6,7,8-pentafluoro-1-oxaspiro[2.5]octa-4,7-dienes (2a/3a): The crude product mixture of **2a/3a** obtained from the reaction of cyclohexa-2,5-dienone **1a** with diazomethane, and the respective isocyanate were dissolved in DMF (2–5 mL). A catalytic amount (≈0.01 g) of lithium chloride was added at room temperature and the mixture was stirred for 16 h. After treating with water (50 mL), the aqueous solution was extracted with diethyl ether (3 × 50 mL). The extract was dried over $CaCl_2$ and the solvents evaporated. The residue was purified by column chromatography on silica gel using pentane/diethyl ether (gradient, 20:1 to 1:1) as eluent to afford the corresponding fluorinated dihydro-1,3-benzoxazol-2(3*H*)-ones **5a**–**c**. The ^{19}F-NMR spectroscopic data for all products are listed in Table 3. More details on the reaction conditions and analytical data for all products are given in Table 4.

Reaction of 4,5,6,7,8-Pentafluoro-6-nitro-1-oxaspiro[2.5]octa-4,7-diene (2b/3b): An equimolar amountof lithium chloride or sodium pentafluorophenoxide was addedto a solution of the crude product mixture **2b/3b** obtained by treatment of cyclohexa-2,5-dienone **1b** with diazomethane in DMF or acetonitrile (5 mL) and stirred for 2 h at room temperature. Phenyl isocyanate was added, the solution was stirred for 16 h at room temperature and treated with water (50 mL). Work up was done as described above to obtain the corresponding fluorinated dihydro-1,3-benzoxazol-2(3*H*)-ones **5a** or **6a**. The ^{19}F-NMR spectroscopic data for all products are listed in Table 3. More details on the reaction conditions and analytical data for all products are given in Table 4.

X-ray Crystallographic Study: Data sets were collected with an Enraf Nonius CAD4 diffractometer. Programs used: data collection EXPRESS (Nonius B.V., 1994), data reduction MolEN (K. Fair, Enraf–Nonius B.V., 1990), structure solution SHELXS-97[32] structure refinement SHELXL-97[33] graphics SCHAKAL.[34]

4,5,6,7,8-Pentafluoro-6-nitro-1-oxaspiro[2.5]octa-4,7-diene (2b): $C_7H_2F_5NO_3$, M_r = 243.1, triclinic, a = 6.156(3), b = 7.658(3), c = 9.890(4) Å, α = 110.10(3), β = 91.05(3), γ = 102.97(3)°, V = 424.3(3) cm^3, 223 K, $P\bar{1}$ (No. 2), Z = 2, μ = 19.82 cm^{-1}, 1894 reflections collected, 1725 independent (R_{int} = 0.053), 1554 observed reflections [$I \geq 2\,\sigma(I)$], R = 0.052, wR^2 = 0.234.

4,5,6,7,8-Pentafluoro-6-nitro-1-oxaspiro[2.5]octa-4,7-diene (3b): $C_7H_2F_5NO_3$, M_r = 243.1, monoclinic, a = 6.103(3), b = 13.768(4), c = 10.129(2) Å, β = 90.91(1)°, V = 851.0(3) cm^3, 223 K, $P2_1/n$ (No. 14), Z = 4, μ = 19.77 cm^{-1}, 1852 reflections collected, 1737 independent (R_{int} = 0.082), 1399 observed reflections [$I \geq 2\,\sigma(I)$], R = 0.065, wR^2 = 0.209.

7a-Chloromethyl-3-(4-chlorophenyl)-3a,4,5,6,7-pentafluoro-3a,7a-dihydro-1,3-benzoxazol-2(3*H*)-one (5b): $C_{14}H_6Cl_2F_5NO_2$, M_r = 386.1, orthorhombic, a = 10.114(2), b = 19.594(3), c = 7.372(2) Å, V = 1460.9(5) cm^3, 223 K, $Pca2_1$ (No. 29), Z = 4, μ = 46.58 cm^{-1}, 1894 reflections collected and independent, 664 observed reflections [$I \geq 2\,\sigma(I)$], R = 0.068, wR^2 = 0.147, analysis is of poor quality due to very small crystal.

CCDC-232737 to -232739 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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