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Selective *ortho*-arylation of polyfluorinated hydroxyaromatic compounds with lead aryl acetates

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Abstract

Reactions of salts of pentafluorophenol and heptafluoronaphthols with lead aryl acetates have led to the formation of arylcyclohexadienones with an *ortho*-quinoid structure. The arylation of sodium pentafluorophenoxide and heptafluoro-2-naphthoxide is accompanied by nucleophilic substitution of fluorine at a double bond by pentafluorophenoxy and heptafluoro-2-naphthoxy groups, respectively. Reduction of the resulting arylcyclohexadienones gave polyfluorinated phenols and naphthols with aryl and hydroxy groups in the 1,2-position.

Introduction

Selective methods of substituent introduction into aromatic molecules occupy an important place in synthetic organic chemistry. One such method which has recently attracted the attention of researchers is arylation using organometal compounds [1]. It is known that selective *ortho*-arylation of phenols may be performed using aryl derivatives of bismuth(V) [2] and lead(IV) [3] in the presence of bases. In both cases it has been shown that the first stage involves formation of the arylphenoxy derivatives of Bi^V [1] and Pb^{IV} [3]. Their decomposition leads to C- or O-arylation products depending on the reaction conditions. The products of C-arylation are arylcyclohexadienones if the *ortho* substituent is present and *ortho*-arylphenols if it is absent. It should be noted, however, that these reactions only proceed readily for phenols containing donor substituents. When Bi^V derivatives are used as arylating agents, substitution of the donor to acceptor group only leads to O-arylation products [1]. With lead aryl triacetates, however, as reported by Bell *et al.* [3] the introduction of bromine atoms together with methyl groups into the phenol molecule decreases the reaction rate considerably. Indeed, arylation of phenols containing only accepting groups did not proceed under the reaction conditions employed ($CHCl_3$, 20 °C, equimolar ratio of reagents to pyridine).

In reactions of lead aryl acetates with different compounds, the reactivity of the latter has been reported to depend on the pK_a value of the substrate

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and the basicity of the medium [3–6]. Addition of various bases or the use of alkaline salts of the substrate have a promoting effect on the reaction. As a result it might be assumed that the C-arylation of hydroxyaromatic molecules containing accepting groups might be considerably facilitated by the use of the alkaline salts of these compounds.

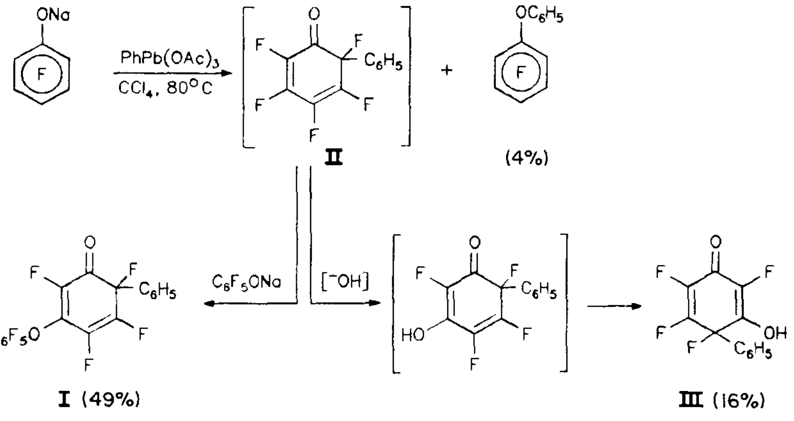
Results and discussion

We have indeed managed to perform the selective *ortho*-arylation of polyfluorinated hydroxyaromatic compounds via the reaction of their sodium or potassium salt with $ArPb(OAc)_3$ and $Ph_2Pb(OAc)_2$. Such arylation may be performed in a stepwise manner by isolating the cyclohexadienones formed at the first stage of the process. These may then be readily reduced to the corresponding phenols and naphthols. Indeed, such a transformation may be effected without isolating the intermediates formed.

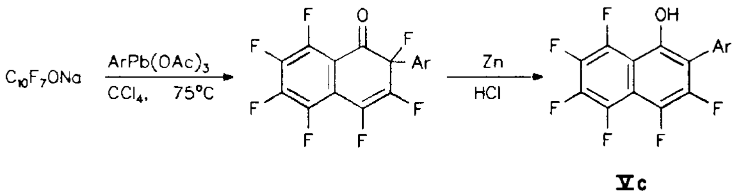
In the reaction of sodium pentafluorophenoxide with both $PhPb(OAc)_3$ and $Ph_2Pb(OAc)_2$ the main reaction product was 6-phenyl-3-pentafluorophenoxy-tetrafluoro-2,4-cyclohexadien-1-one (I) (Scheme 1).

The O-arylation product, pentafluorodiphenyl ether, was only formed in insignificant amounts in this reaction. The dienone **I** is possibly the product of the nucleophilic substitution of fluorine in the intermediate 6-phenylpentafluoro-2,4-cyclohexaden-1-one (II) by a pentafluorophenoxy group. The high reactivity of such polyfluorinated cyclohexadienones in reactions with nucleophilic reagents is well known [7]. Furthermore, in the reaction of sodium pentafluorophenoxide with $PhPb(OAc)_3$, 3-hydroxy-4-phenyltetrafluoro-2,5-cyclohexadien-1-one (III) was isolated in a low yield. The formation of this compound may result from the interaction of dienone **II** with water.

The reactions of sodium or potassium heptafluoro-1-naphthoxide with $ArPb(OAc)_3$ and $Ph_2Pb(OAc)_2$ gave the respective 2-aryl-1-oxo-heptafluoro-1,2-dihydronaphthalenes (Scheme 2).

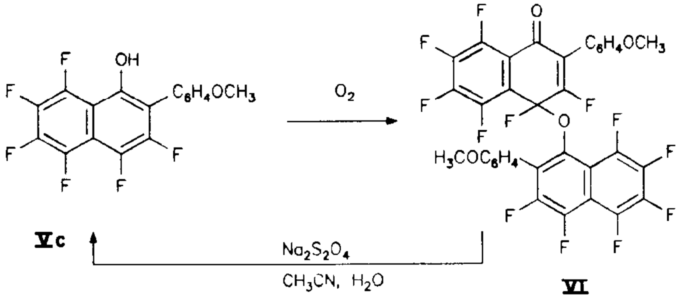


Scheme 1.



Ar = C_6H_5 (**IVa**), $C_6H_4CH_3$ (**IVb**), $C_6H_4OCH_3$ (**IVc**)

Scheme 2.



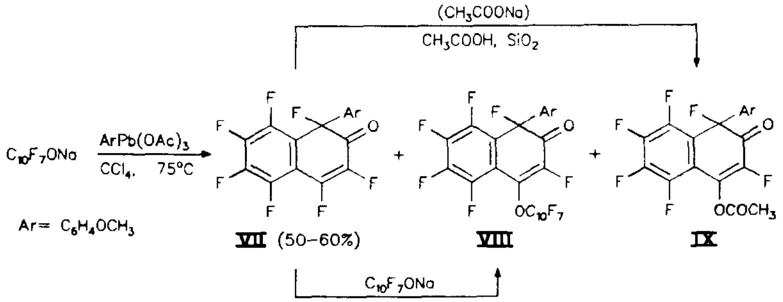
Scheme 3.

The phenyl and tolyl derivatives (**IVa, b**) have been isolated individually by us while the anisyl derivative **IVc** was reduced to the naphthol **Vc** without being isolated (*c*. 80% yield from the reaction mixture employed as shown by the corresponding ^{19}F NMR data). A characteristic feature of ^{19}F NMR spectra of the dihydronaphthalenes **IVa–c** which supports their structure is the presence of an AB system with $J = 65$ Hz for the fluorine atoms in the 4- and 5-positions.

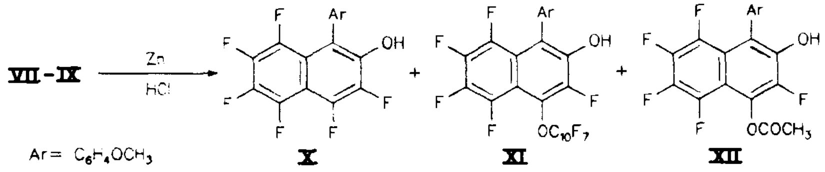
Naphthol **Vc** is unstable in air, its solutions being readily oxidized to form the dimer of the respective naphthoxyl radical (**VI**). Naphthol **Vc** may be regenerated by reducing the dimer **VI** with sodium dithionite (Scheme 3).

Reaction of sodium heptafluoro-2-naphthoxide with lead anisyl triacetate led to the formation of a mixture which was shown by ^{19}F NMR spectroscopy to contain 1-anisyl-2-oxo-heptafluoro-1,2-dihydronaphthalene (**VII**), 1-anisyl-4-(heptafluoro-2-naphthoxy)-2-oxohexafluoro-1,2-dihydronaphthalene (**VIII**) and 1-anisyl-4-acetoxy-2-oxo-hexafluoro-1,2-dihydronaphthalene (**IX**) (Scheme 4).

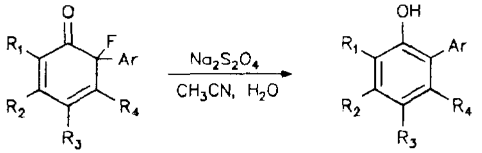
Compound **VII**, which is the main reaction product, is very reactive. According to ^{19}F NMR spectroscopy, when a mixture containing *c*. 55% of compound **VII** and 16% of compound **VIII** was separated by column chromatography on acetic acid-deactivated silica gel, compound **VII** was transformed completely to compound **IX** which was isolated in 51% yield along with 16% of compound **VIII**. Reduction of the reaction products of sodium heptafluoro-2-naphthoxide with lead *p*-anisyl triacetate (compounds **VII–IX**) in the presence of zinc in hydrochloric acid gave a mixture of compounds



Scheme 4.



Scheme 5.



I	$R_1=R_3=R_4=$ F, $R_2=$ OC_6F_5, Ar= C_6H_5	XIII
IVa	R_1–R_2= -CF=CF–CF=CF–, $R_3=R_4=$ F, Ar= C_6H_5	Va
IVb	R_1–R_2= –CF=CF–CF=CF–, $R_3=R_4=$ F, Ar= $C_6H_4CH_3$	Vb
VIII	$R_1=$ F, $R_2=$ $OC_{10}F_7$, R_3–R_4= –CF=CF–CF=CF–, Ar= $C_6H_4OCH_3$	XI
IX	$R_1=$ F, $R_2=$ $OCOCH_3$, R_3–R_4= –CF=CF–CF=CF–, Ar= $C_6H_4OCH_3$	XII

Scheme 6.

which was chromatographed on silica gel to give two naphthols (**XI** and **XII**), i.e. the products of the reduction of dienones **VIII** and **IX** respectively, in yields 6% and 10%, in addition to the main reaction product 1-anisylhexafluoro-2-naphthol (**X**) (50%) (Scheme 5).

All the polyfluorinated aryl dienones formed in the reaction of polyfluorinated hydroxyaromatic compounds with lead aryl acetates are readily reduced by sodium dithionite to afford fluorinated aryl phenols in high yields in which the aryl and hydroxy groups are in the 1,2-positions (Scheme 6).

The reactions investigated in the present work thus offer a convenient means of achieving the selective *ortho*-arylation of polyfluorinated phenols and naphthols.

Experimental

^{1}H and ^{19}F NMR spectra ($CDCl_3$, C_6F_6 as an internal standard) were measured on a Bruker AC-200 spectrometer. The ^{1}H NMR spectra of the tolyl and anisyl derivatives of the oxodihydronaphthalenes and naphthols were analyzed using the AB system approximation, the *J* constant in all cases being *c.* 8–9 Hz. UV spectra were recorded on a Specord UV–vis instrument using C_2H_5OH solutions (conc. 1×10^{-4} mol l^{-1}). Mass spectra were recorded on a high-resolution GC–MS Finnigan MAT 8200 spectrometer. Lead phenyl triacetate and diphenyl diacetate were prepared from tetraphenyllead and lead tetraacetate according to the procedure of Willemsens and Van der Kerk [8]. Lead tolyl and anisyl triacetates were obtained by the direct transformation of toluene and anisole with lead tetraacetate in the presence of trifluoroacetic acid. The transacylation reaction was performed by chromatography on silica gel treated with acetic acid, which led to the simultaneous purification of the product formed (cf. refs. 9 and 10).

6-Phenyl-3-pentafluorophenoxy-2,4,5,6-tetrafluoro-2,4-cyclohexadien-1-one (I) (nc)

Method a

To a solution consisting of 1.7 g of $PhPb(OAc)_3$ in 50 ml CCl_4 was added 1.7 g of C_6F_5ONa. After refluxing the mixture for 2 h, the precipitate was filtered off and the filtrate evaporated. The residue (1.4 g) was chromatographed on an SiO_2 column (CCl_4 as eluent) to give 1.1 g of a light yellow viscous liquid. Crystallization from petroleum ether (40–70 °C) gave 0.8 g of the crystalline dienone **I** (49%), m.p. 79–83 °C. ^{19}F NMR δ: 3.4 (F^{meta}); 3.5 (F^6); 5.5 (F^2); 7.3 (F^{para}); 8.7 (F^{ortho}); 8.8 (F^4); 25.3 (F^5) ppm. UV (heptane), $\lambda_{max.}$, nm (log ϵ): 218 (4.08); 251 sh (3.67); 263 sh (3.60); 273 sh (3.54); 332 (3.49). MS: M^+, 424.0159. $C_{18}H_5F_9O_2$ requires: M, 424.0146.

The mother liquor was evaporated. The residue (0.3 g) contained (^1H and ^{19}F NMR data) *c.* 76% of dienone **I** and *c.* 12% of the pentafluorodiphenyl ether which was identified by adding it to an authentic sample. The lead salts were treated with 30 ml conc. HCl and extracted with ether. After evaporation of the ether, the residue was chromatographed on an SiO_2 column to give 0.15 g (16%) of 3-hydroxy-4-phenyl-2,4,5,6-tetrafluorocyclohexadien-2,5-one (III) (nc). ^{19}F NMR δ: -7.9 (F^4); -4.0 (F^2); 4.8 (F^6); 26.5 (F^5) ppm. MS: M^+, 258.0309. $C_{12}H_6F_4O_2$ requires: M, 258.0304.

Method b

To a solution consisting of 1.8 g of $Ph_2Pb(OAc)_2$ in 50 ml $CHCl_3$ was added 1.6 g of C_6F_5ONa and the mixture was refluxed for 6 h. The precipitate was filtered off and the filtrate evaporated. The residue was chromatographed on an SiO_2 column (CCl_4 as eluent) to give 0.6 g of the product which was, in turn, sublimed to give 0.4 g of dienone **I**. After treatment of the lead salts in a similar manner to that described above, compound **III** could not be detected.

*1-Oxo-2-phenyl-2,3,4,5,6,7,8-heptafluoro-1,2-dihydronaphthalene (**IVa**) (nc)*

Method a

To a solution consisting of 3.7 g of $Ph_2Pb(OAc)_2$ in 75 ml $CHCl_3$ was added with stirring 2.4 g of 1-$C_{10}F_7ONa$ and the mixture was refluxed for 7 h. The resulting precipitate was filtered off and washed with $CHCl_3$, the filtrate being then evaporated. The residue was refluxed with hexane and the hexane solution filtered and evaporated. The solid crystalline product obtained was chromatographed on an SiO_2 column (CCl_4 as eluent) to afford 1.11 g of **IVa**, m.p. 120–123 °C, yield 83%. ^{19}F NMR δ: 0.0 (F^2); 12.0 (F^7); 15.2 (F^4, $J_{4,5}=65$ Hz); 20.7 (F^6); 21.3 (F^3); 22.2 (F^5); 28.6 (F^8) ppm. UV $\lambda_{max.}$, nm (log ϵ): 234 (4.53); 257 (3.64); 287 (3.58); 348 (3.40). MS: M^+, 346.0221. $C_{16}H_5F_7O$ requires: M, 346.0229.

Method b

A similar procedure using 1.6 g of $PhPb(OAc)_3$, 1.1 g of 1-$C_{10}F_7OK$ and 40 ml CCl_4 gave 1.0 g of a mixture of products from which compound **IVa** (0.6 g) was isolated by crystallization from petroleum ether (40–70 °C).

*1-Oxo-2-(p-tolyl)-2,3,4,5,6,7,8-heptafluoro-1,2-dihydronaphthalene (**IVb**) (nc)*

To *p*-$CH_3C_6H_4Pb(OAc)_3$ (2.52 g) in 60 ml CCl_4 was added with stirring 1-$C_{10}F_7ONa$ (2.54 g) and the mixture was heated for 2 h at 70 °C. The reaction mixture was filtered, the precipitate obtained washed with CCl_4, the filtrate evaporated and the resulting product mixture passed through an SiO_2 column. This gave 1.8 g of an oil which on crystallization from a 1:4 CCl_4/hexane mixture gave 0.8 g of **IVb**, m.p. 108–110 °C, yield 42%. ^{19}F NMR δ: 0.5 (F^2); 11.7 (F^7); 14.7 (F^4, $J_{4,5}=65$ Hz); 20.3 (F^6); 21.6 (F^3); 22.0 (F^5); 28.4 (F^8) ppm. ^1H NMR δ: 2.35 (CH_3); 7.22 (2CH); 7.35 (2CH) ppm. UV $\lambda_{max.}$, nm (log ϵ): 233 (4.51); 259 (3.68); 286 (3.68); 346 (3.41). MS: M^+, 360.0380. $C_{17}H_7F_7O$ requires: M, 360.0385.

Reaction of potassium heptafluoro-1-naphthoxide with lead anisyl triacetate

To a solution consisting of 2.9 g of *p*-$CH_3OC_6H_4Pb(OAc)_3$ in 50 ml CCl_4 was added with stirring 2.0 g of 1-$C_{10}F_7OK$. The mixture was refluxed for 2 h, the resulting precipitate filtered off and washed with CCl_4, and the filtrate evaporated. The residue (3.4 g) contained (^{19}F NMR) *c.* 75% of compound **IVc**. ^{19}F NMR δ: 3.29 (F^2); 11.24 (F^7); 14.5 (F^4, $J_{4,5}=64$ Hz); 19.4 (F^6); 21.5 (F^5); 21.7 (F^3); 28.0 (F^8) ppm. The reaction mixture was dissolved in 50 ml ether, 40 ml conc. HCl was added and then 5.2 g of Zn in small portions with stirring. The ether layer was separated and the aqueous layer extracted with ether. Evaporation of the ether afforded 2.3 g of a mixture of products containing (^{19}F NMR) *c.* 68% of naphthol **Vc**. This mixture was chromatographed on an SiO_2 column ($CHCl_3$ as eluent) to give 1.5 g of a product with an orange colour. Crystallization of this product from hexane gave 1.0 g of 2-anisyl-4-(2′-anisyl-3′,4′,5′,6′,7′,8′-hexafluoro-1′-naphthoxy)-1-oxo-3,4,5,6,7,8-hexafluoro-1,4-dihydronaphthalene (**VI**) (nc), m.p. 210–213 °C. ^{19}F NMR (acetone-d_6) δ: 7.1 ($F^{6'}$ or $F^{7'}$); 8.1 ($F^{7'}$ or $F^{6'}$); 12.4 (F^7); 16.1 ($F^{5'}$, $J_{4',5'}=64$ Hz); 17.3 (F^6); 18.7 ($F^{4'}$); 22.4 (F^5); 23.5 ($F^{8'}$); 26.3 (F^8); 26.7 ($F^{3'}$); 51.1 (F^3); 59.0 (F^4) ppm. ^{1}H NMR δ: 3.81 (OCH_3); 3.83 (OCH_3); 6.68, 6.99 (4CH); 6.85, 7.11 (4CH) ppm. UV $\lambda_{max.}$, nm (log ϵ): 221 (4.48); 270 (4.24); 301 sh (3.88). MS: M^+, 714.0677. $C_{34}H_{14}F_{12}O_4$ requires: M, 714.0700.

Compound **VI** (0.3 g) was dissolved in 10 ml acetonitrile and treated with a solution consisting of 1.5 g of $Na_2S_2O_4$ in 10 ml water. The product was isolated by extraction with ether. The ether was evaporated and the residue sublimed *in vacuo* (1×10^{-2} mmHg). This gave 0.2 g of naphthol **Vc** (nc). ^{19}F NMR δ: 3.1, 6.3 (F^6, F^7); 6.9 (F^4, $J_{4,5}=60$ Hz); 14.9 (F^5); 18.06 (F^8); 25.1 (F^3) ppm. ^{1}H NMR δ: 4.11 (OCH_3); 6.27 (OH, $J=5.0$ Hz); 7.26, 7.56 (4CH) ppm. UV $\lambda_{max.}$, nm (log ϵ): 217 (4.60); 267 (4.33); 304 sh (3.83); 341 (3.81). MS: M^+, 358.0420. $C_{17}H_8F_6O_2$ requires: M, 358.0428.

Reaction of sodium heptafluoro-2-naphthoxide with lead anisyl triacetate and reduction of the anisyloxodihydronaphthalene mixture

Method a

To p-$CH_3OC_6H_4Pb(OAc)_3$ (2.31 g) in 50 ml CCl_4 was added with stirring 2-$C_{10}F_7ONa$ (2.80 g). The mixture was heated at 70 °C for 3.5 h, then cooled and the precipitate filtered off and washed with CCl_4. Evaporation gave 2.21 g of a mixture of compounds which was chromatographed on an SiO_2 column (silica gel deactivated by applying *c.* 2.0 g of CH_3COOH on 100 g of SiO_2). Elution with CCl_4 and then with a 1:1 CCl_4/C_6H_6 mixture gave 0.47 g of **VIII** (16%) and 1.01 g of **IX** (51%).

1-(p-Anisyl)-4-(1′,3′,4′,5′,6′,7′,8′-heptafluoro-2′-naphthoxy)-2-oxo-1,3,5,6,7,8-hexafluoro-1,2-dihydronaphthalene (**VIII**) (nc), m.p. 157–160 °C. ^{19}F NMR δ: 8.6 ($F^{6'}$); 9.2 ($F^{7'}$); 9.5 (F^1); 10.6 (F^3); 12.3 (F^6); 12.6 ($F^{3'}$); 14.0 (F^7); 16.9 ($F^{4',5'}$); 17.4 ($F^{8'}$); 23.7 ($F^{1'}$); 25.6 (F^5); 29.4 (F^8) ppm. ^{1}H NMR δ: 3.79 (OCH_3); 6.88, 7.25 (4CH) ppm. UV $\lambda_{max.}$, nm (log ϵ): 223 (4.54); 327 (3.76). MS: M^+, 626.0160. $C_{27}H_7F_{13}O_3$ requires: M, 626.0187.

1-Anisyl-4-acetoxy-2-oxo-1,3,5,6,7,8-hexafluoro-1,2-dihydronaphthalene (**IX**) (nc), m.p. 124–126 °C. ^{19}F NMR δ: 6.5 (F^1); 11.2 (F^6); 12.6 (F^7); 18.4 (F^3); 19.7 (F^5); 28.5 (F^8) ppm. ^{1}H NMR δ: 2.38 ($OCOCH_3$); 3.74 (OCH_3); 6.85, 7.27 (4CH) ppm. UV $\lambda_{max.}$, nm (log ϵ): 203 (4.57); 239 (4.41); 326 (3.90). MS: M^+, 416.0474. $C_{19}H_{10}F_6O_4$ requires: M, 416.0483.

Method b

To p-$CH_3OC_6H_4Pb(OAc)_3$ (3.25 g) in 50 ml CCl_4 was added with stirring 2-$C_{10}F_7ONa$ (3.90 g). The mixture was heated at 70 °C for 3.5 h and then cooled. The precipitate was filtered off and washed with CCl_4. After the CCl_4 had been evaporated, the residue was dissolved in ether, 100 ml HCl (conc.) added and then 14.0 g of zinc powder in small portions. The ether layer was separated and the acid layer extracted with ether. The extract was dried with $CaCl_2$. After evaporation of the ether, the residue (3.16 g) was chromatographed on an SiO_2 column. Elution in sequence with hexane, CCl_4, 1:2, 1:1 and 2:1 $CCl_4/CHCl_3$ mixtures afforded 0.25 g of **XI** (6%), 1.2 g of **X** (50%) and 0.28 g of **XII** (10%).

1-Anisyl-4-(1′,3′,4′,5′,6′,7′,8′-heptafluoro-2′-naphthoxy)-3,5,6,7,8-pentafluoro-2-naphthol (**XI**) (nc), m.p. 178–181 °C. ^{19}F NMR (CCl_4) δ: 2.4 (F^6); 5.0 (F^7); 7.0, 7.2 ($F^{6',7'}$, AB system, $J_{6',7'}=20$ Hz); 13.1 ($F^{3'}$); 14.0 (F^3); 15.1 (F^5); 15.7, 16.2 ($F^{4',5'}$, AB system, $J_{4',5'}\sim 55$ Hz); 16.8 ($F^{8'}$, $J_{1',8'}\sim 64$ Hz); 21.5 ($F^{1'}$); 23.3 (F^8) ppm. ^1H NMR δ: 3.88 (OCH_3); 5.44 (OH); 7.06, 7.27 (4CH) ppm. UV $\lambda_{max.}$, nm (log ϵ): 225 (5.01); 286 (4.16); 294 (4.15); 328 (3.87). Analysis: Found: C, 53.54; H, 1.39; F, 37.32%, M, 593. $C_{27}H_8F_{12}O_3$ requires: C, 53.29; H, 1.32; F, 37.50%; M, 608.

1-Anisyl-3,4,5,6,7,8-hexafluoro-2-naphthol (**X**) (nc), m.p. 187–190 °C. ^{19}F NMR δ: 2.1 (F^6); 5.1 (F^7); 6.4 (F^3); 14.8 (F^5); 19.1 (F^4, $J_{4,5}=63$ Hz); 21.9 (F^8) ppm. ^1H NMR δ: 3.88 (OCH_3); 5.46 (OH); 7.05, 7.22 (4CH) ppm. UV $\lambda_{max.}$, nm (log ϵ): 230 (4.68); 284 (3.87); 294 (3.84); 332 (3.54). Analysis: Found: C, 56.97; H, 2.43; F, 32.20%. $C_{17}H_8F_6O_2$ requires: C, 56.98; H, 2.23; F, 31.84%, M, 358.

1-Anisyl-4-acetoxy-3,5,6,7,8-pentafluoro-2-naphthol (**XII**) (nc), m.p. 145–147 °C. ^{19}F NMR δ: 2.1 (F^6); 4.2 (F^7); 11.7 (F^5); 16.7 (F^3); 22.5 (F^8) ppm. ^1H NMR δ: 2.45 ($OCOCH_3$); 3.66 (OCH_3); 5.59 (OH); 7.04, 7.22 (4CH) ppm. UV $\lambda_{max.}$, nm (log ϵ): 230 (5.77); 285 (3.94); 296 (3.93); 333 (3.58). MS: M^+, 398.0564. $C_{19}H_{11}F_5O_4$ requires: M, 398.0577.

*2-(p-Tolyl)-3,4,5,6,7,8-hexafluoro-1-naphthol (**Vb**) (nc)*

To a solution consisting of 0.22 g of **IVb** in 15 ml CH_3CN, a solution consisting of 1.3 g of $Na_2S_2O_4$ in 10 ml water was added with stirring. The reaction mixture was stirred for 5–10 min, then 100 ml water was added. The product was extracted with ether. After evaporation of the extract and sublimation of the resulting mass, 0.17 g of naphthol **Vb** was obtained, m.p. 156–158 °C, yield 82%. ^{19}F NMR δ: 3.2, 6.4 (F^6, F^7); 6.6 (F^4, $J_{4,5}=60$ Hz); 14.9 (F^5); 17.5 (F^8); 24.9 (F^3) ppm. ^1H NMR δ: 2.45 (CH_3); 6.13 (OH, $J=6.0$ Hz); 7.34, 7.38 (4CH) ppm. UV $\lambda_{max.}$, nm (log ϵ): 215 (4.67); 254 (4.46); 297 (3.78); 339 (3.82). MS: M^+, 342.0454. $C_{17}H_8F_6O$ requires: M, 342.0479.

The dienones **I**, **IVa**, **VIII** and **IX** were reduced in a similar manner to yield phenol **XIII** and the naphthols **Va**, **XI** and **XII**, respectively.

5-Pentafluorophenoxy-2-phenyl-3,4,6-trifluorophenol (**XIII**) (nc), m.p. 115–118 °C, yield 83%. ^{19}F NMR δ: 0.8 (F^4); 1.7 (F^{meta}); 3.8 (F^{para}); 5.4 (F^6); 7.9 (F^{ortho}); 20.3 (F^3) ppm. UV $\lambda_{max.}$, nm (log ϵ); 205 (4.56); 222 sh (4.37); 287 (3.48); 318 (3.42). MS: M^+, 406.0249. $C_{18}H_6F_8O_2$ requires: M, 406.0240.

2-Phenyl-3,4,5,6,7,8-hexafluoro-1-naphthol (**Va**) (nc), m.p. 176–179 °C, yield 77%. ^{19}F NMR δ: 3.5, 6.7 ($F^{6,7}$); 6.8 (F^4, $J_{4,5}=60$ Hz); 15.2 (F^5); 17.1 (F^8); 24.9 (F^3) ppm. UV $\lambda_{max.}$, nm (log ϵ): 214 (4.56); 250 (4.41); 290

(3.76); 298 (3.77); 339 (3.69). MS: M$^+$, 328.0322. $C_{16}H_6F_6O$ requires: M, 328.0323.

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