

SYNTHESIS OF (POLYFLUOROALKYL)CYCLOPENTENES AS MODEL COMPOUNDS FOR FLUOROPHILIC CYCLOPENTADIENESJaroslav KVIČALA^{a1,*}, Tomáš BŘÍZA^{a2}, Oldřich PALETA^{a3} and Jan ČERMÁK^b^a Department of Organic Chemistry, Institute of Chemical Technology Prague, Technická 5, 166 28 Prague 6, Czech Republic; e-mail: ¹ kvicalaj@vscht.cz, ² ffor@seznam.cz, ³ paletao@vscht.cz^b Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, Rozvojová 135, 165 02 Prague 6, Czech Republic; e-mail: cermak@icpf.cas.cz

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Dedicated to the memory of Professor Miloš Hudlický.

Nucleophilic opening of the epoxide ring in 6-oxabicyclo[3.1.0]hexane (**1**) with ethenylmagnesium bromide was employed for the preparation of 2-ethenylcyclopentan-1-ol (**2**). Radical addition of perfluoroalkyl iodides **3** to alcohol **2** afforded (polyfluoroiodoalkyl)cyclopentanol **4**, which were deiodinated with tributylstannane to (polyfluoroalkyl)cyclopentanol **5**, followed by dehydration with Nafion-H to the target (polyfluoroalkyl)cyclopentenenes **6**, which are potential intermediates for fluororous chemistry. Attempts to synthesize (polyfluoroalkyl)cyclopentadienes or bis(polyfluoroalkyl)cyclopentadienes failed due to the exclusive formation of unexpected side product, polyfluoroiodoalkanol **7**, in the course of radical addition of perfluoroalkyl iodides **3** to ethenylcyclopentenol (**8**) or diethenylcyclopentenediol (**9**), respectively.

Keywords: Cyclopentadienes; Cyclopentenenes; Nucleophilic additions; Epoxides; Radical additions; Perfluoroalkylations; Fluorophilic ligands; Fluororous chemistry; Dehydrations.

Homogeneous catalysis plays vital and still growing role in modern industrial processes^{1,2}. The main disadvantage of these processes lies in the separation and recycling of usually toxic metal components of the catalysts employed. Attempts to reduce their environmental impact in agreement with the "green chemistry" concept has recently led to the introduction of biphasic catalytic systems with two liquid phases, one of them being aqueous or hydrophilic³. As such systems are usually not compatible with reagents or catalysts needed, search for other phase immiscible with common organic solvents resulted in the introduction of fluororous biphasic catalysis (FBC), in which the second phase is a perfluorinated solvent⁴⁻⁷. Fluoro-

philic properties required for the corresponding homogeneous catalysts are quite exclusively provided by the attached polyfluorinated ligands. Incidentally, the developed fluorophilic homogeneous catalysts are highly soluble in supercritical CO₂ and hence proved to be perspective materials for environmentally friendly processes performed in this medium^{8,9}.

Sufficient fluorophilic properties of the ligands depend on many factors, the basic one being a sufficient total fluorine content in the molecule, which should exceed 60%^{10,11}. This can be provided by attaching even a sole very long polyfluorinated chain, but ligands with multiple shorter fluorinated chains are preferable due to their better solubility in the fluorous phase¹¹. So far, phosphanes with several attached polyfluorinated chains have been predominantly used, as they could be synthesized without greater difficulties^{1,12–15}. Cyclopentadiene-derived ligands are substantial part of many homogeneous catalysts¹⁶. Nevertheless, only little attention has been paid to the preparation of fluorophilic cyclopentadienes^{17,18}. They contained only one polyfluorinated chain and had to be combined with fluorophilic phosphanes to obtain homogeneous catalysts with sufficient fluorophilic properties¹⁷. We have recently published the preparation of bis(polyfluoroalkyl)cyclopentadienes^{19,20} and their organometallic complexes^{19,21}. Their main drawbacks is that they consist of mixtures of regioisomers. We have therefore searched for an alternative pathway of the preparation of regioisomerically pure fluorophilic cyclopentadienes. In the first step of their synthesis, we concentrated on the preparation of regioisomerically pure model compounds, mono(polyfluoroalkyl)cyclopentenes and our preliminary results have recently been published¹⁹.

EXPERIMENTAL

Temperature data were uncorrected. ¹H NMR spectra were recorded with a Varian Gemini 300 HC spectrometer at 300.1 MHz using tetramethylsilane as internal standard. Other NMR spectra were recorded with a Bruker AMX3 400 spectrometer, viz. ¹³C NMR spectra at 100.6 MHz with tetramethylsilane as internal standard and ¹⁹F NMR spectra at 376.5 MHz with chlorotrifluoromethane as internal standard with upfield values designed negative. Chemical shifts are given in ppm (δ-scale), coupling constants (*J*) in Hz. FTIR spectra (wavenumbers in cm⁻¹) were recorded with a FT-IR Nicolet 740 instrument in CHCl₃.

The conversion of reactions, as well as the composition of fractions from column chromatography were followed by TLC. The spots were developed by spraying with ammonium cerium(IV) sulfate solution and heating.

All manipulations and reactions including organometallic reagents or 2,2'-azobisisobutyronitrile (AIBN) initiator were performed with exclusion of moisture and atmospheric oxygen in oven-dried apparatuses. 6-Oxabicyclo[3.1.0]hexane (1), cyclopentadiene dimer, cyclopentanone, 3-chloroperoxybenzoic acid, ethenylmagnesium bromide (1 M solution in

THF) and Nafion® beads were purchased from Aldrich. 2,2'-Azobisisobutyronitrile (AIBN) initiator was purchased from Aldrich and recrystallized prior to use from chloroform. Perfluoroalkyl iodides **3** were kindly gifted by Elf Atochem. THF and 1,2-dimethoxyethane (DME) were dried over sodium benzophenone ketyl and distilled prior to use. Concentration of ethenylmagnesium bromide solutions was estimated by titration prior to use²².

Cyclopentadiene was prepared by thermal decomposition of its dimer²³. 6-Oxabicyclo-[3.1.0]hex-2-ene (**10**) was prepared from cyclopentadiene by epoxidation with peroxoacetic acid²⁴ in a 38% yield. (1*R**,2*S**,3*S**,5*R**)-3,5-Dibromocyclopentane-1,2-diol (**11**) was obtained from cyclopenta-1,3-diene by bromination-dihydroxylation procedure²⁵ in a 16% yield. 1-Ethenylcyclopentan-1-ol (**12**) was prepared from cyclopentanone by nucleophilic addition of ethenylmagnesium bromide²⁶ in a 42% yield. 2-Ethenylcyclopentan-1-ol (**2**) was synthesized from 6-oxabicyclo[3.1.0]hexane by reaction with ethenylmagnesium bromide²⁴ in a 60% yield.

(1*R**,2*S**,4*S**,6*R**)-3,6-Dioxatricyclo[4.1.0.0^{2,4}]heptane²⁵ (**13**)

A 500 ml flask equipped with an addition funnel, reflux condenser and magnetic stirbar was charged with NaH (60% suspension in mineral oil, 4.2 g, 0.11 mol) and 1,2-dimethoxyethane (150 ml). A solution of dibromodiol **11** (9.1 g, 35 mmol) in 1,2-dimethoxyethane (100 ml) was added to the mixture while stirring. The reaction mixture was then heated to reflux for 1 h, allowed to cool to room temperature and salts were filtered off. The solvent was removed on a rotary evaporator. Vacuum distillation of the residue afforded diepoxide **13** (2.1 g, 62%, b.p. 45–50 °C/0.12 kPa; ref.²⁵ 35 °C/0.2 kPa) as a colorless oil with NMR spectra in accord with the published data²⁵.

(1*R**,2*R**)-2-Ethenylcyclopent-3-en-1-ol (**8**)

A 500 ml flask equipped with an addition funnel and magnetic stirbar, covered with aluminium foil, was charged with CuI (2.3 g, 12 mmol) and THF (40 ml). The flask was cooled to –40 °C and ethenylmagnesium bromide (180 ml, 180 mmol) was added. To the resulting mixture, a solution of epoxide **10** (10.0 g, 122 mmol) in THF (100 ml) was slowly added at –30 °C over 1 h. The reaction mixture was then allowed to warm to 0 °C and stirred for another 3 h, followed by quenching the reaction with saturated aqueous NH₄Cl solution (15 ml). Salts were filtered off and washed with diethyl ether (2 × 50 ml). Combined filtrates were extracted with saturated solution of NH₄Cl (2 × 30 ml) and dried with anhydrous MgSO₄. Solvents were removed on a rotary evaporator. Vacuum distillation of the residue afforded product **8** (8.85 g, 66%, b.p. 40–55 °C/80 Pa, colorless oil). ¹H NMR (300.1 MHz, CDCl₃): 2.12 s, 1 H; 2.28 ddq, 1 H, ²*J*_{HH} = 16.8, ³*J*_{HH} = 5.2, 3.6; 2.71 ddq, 1 H, ²*J*_{HH} = 16.8, ³*J*_{HH} = 5.2, 3.6; 3.20 m, 1 H; 4.19 ddd, 1 H, ³*J*_{HH} = 3.6, 6.9, 6.6; 5.02 ddd, 1 H, ²*J*_{HH} = 1.1, ³*J*_{HH} = 1.6, 9.1; 5.10 ddd, 1 H, ²*J*_{HH} = 1.8, ³*J*_{HH} = 1.2, 16.5; 5.62 m, 1 H; 5.76 ddd, 1 H, ³*J*_{HH} = 7.7, 10.2, 17.6, 5.68–5.78 m, 1 H. ¹³C NMR (100.6 MHz, CDCl₃): 41.0 s, 58.5 s, 77.6 s, 114.7 s, 128.9 s, 131.2 s, 138.6 s. IR (CHCl₃): 920 s, 995 m, 1 035 m, 1 205 m, 1 843 w, 2 931 m, 3 015 s, 3 062 m, 3 426 m, 3 601 m. For C₇H₁₀O (110.1) calculated: 76.31% C, 9.17% H; found: 76.40% C, 9.22% H.

(1*R**,2*S**,3*S**,4*S**)-2,4-Diethenylcyclopentane-1,2-diol (**9**)

A 100 ml flask equipped with an addition funnel, thermometer and magnetic stirbar, covered with aluminium foil, was charged with CuI (180 mg, 0.95 mmol) and THF (30 ml). The mixture was cooled to -50 °C and ethenylmagnesium bromide (15.4 ml, 15.4 mmol) was added at such a rate that the temperature did not exceed -30 °C. A solution of diepoxide **13** (280 mg, 2.85 mmol) in THF (20 ml) was then added to the mixture over 1 h. The mixture was then allowed to warm to 0 °C and stirred for 3 h, followed by quenching the reaction with saturated aqueous NH₄Cl solution (10 ml). Salts were filtered off and washed with diethyl ether (3 × 50 ml). Combined filtrates were washed with saturated NH₄Cl solution (3 × 50 ml) and dried with anhydrous MgSO₄. Solvents were removed on a rotary evaporator. Pure diethenyldiol **9** (58 mg, 14%, yellowish viscous oil) was obtained by column chromatography (silica, eluent CHCl₃/ethyl acetate 1 : 1) of the residue. ¹H NMR (300.1 MHz, CDCl₃): 1.92 ddm, 2 H, ³J_{HH} = 1.9, 14.0; 2.43 dt, 1 H, ³J_{HH} = 6.9, 7.8; 2.73 quintet, 1 H, ³J_{HH} = 8.6; 3.04 s, 2 H; 3.55 t, 1 H, ³J_{HH} = 8.5; 3.92 dt, 1 H, ³J_{HH} = 7.0, 11.0; 5.05 dd, 1 H, ²J_{HH} = 6.2, ³J_{HH} = 17.2; 5.10 dd, 1 H, ²J_{HH} = 6.2, ³J_{HH} = 11.4; 5.13 dd, 1 H, ²J_{HH} = 6.2, ³J_{HH} = 10.3; 5.16 dd, 1 H, ²J_{HH} = 6.2, ³J_{HH} = 17.2; 5.73 ddd, ³J_{HH} = 7.6, 10.2, 17.1; 5.73 ddd, ³J_{HH} = 8.1, 10.2, 17.3. ¹³C NMR (100.6 MHz, CDCl₃): 37.3, 48.9, 60.5, 74.0, 80.0, 115.3, 117.1, 137.7, 139.6. IR (CHCl₃): 923 s, 994 s, 1 066 m, 1 840 m, 2 930 m, 3 017 w, 3 083 w, 3 438 m, 3 602 m. For C₉H₁₄O₂ (154.3) calculated: 70.08% C, 9.18% H; found: 69.97% C, 9.65% H.

Radical Additions of Perfluoroalkyl Iodides **3** to Ethenylcycloalkanols **2**, **8**, **9**, **12**.

General Procedure A

A flask equipped with a reflux condenser and magnetic stirbar was charged with the corresponding ethenylcycloalkanol, perfluoroalkyl iodide **3** (1–1.5 mmol/mmol of cycloalkanol) and AIBN (0.05–0.1 mmol/mmol of cycloalkanol). The mixture was then heated to 100 °C for 1 h while stirring and then allowed to cool to room temperature. The products were obtained by column chromatography of the crude reaction mixture.

General Procedure B

A flask equipped with a magnetic stirbar was charged with the corresponding ethenylcycloalkanol, perfluoroalkyl iodide **3** (2.5 mmol/mmol of ethenyl groups), acetonitrile (20 ml/mmol of ethenylcyclopentanol), water (5 ml/mmol of ethenylcyclopentanol), sodium dithionite (10 mmol/mmol of ethenyl groups) and sodium hydrogen-carbonate (10 mmol/mmol of ethenyl groups). The mixture was then stirred vigorously for 3 h at room temperature, followed by addition of diethyl ether (50 ml). The mixture was stirred for another 15 min and filtered. The filtrate was dried with anhydrous MgSO₄, the remaining salts were removed from the filtrate on a short column and pure products were isolated by column chromatography.

Attempted addition to 1-ethenylcyclopenten-1-ol (12). Ethenylcyclopentenol **12** (500 mg, 4.46 mmol), perfluorohexyl iodide (**3b**; 2.90 g, 6.50 mmol) and AIBN (30 mg, 0.18 mmol) were treated according to General procedure A. Column chromatography (silica, dichloromethane) of the black reaction mixture afforded starting perfluoroalkyl iodide **3b** (2.5 g) as the only isolable compound.

(1*R**,2*R**)-2-(3,3,4,4,5,5,6,6-Nonafluoro-1-iodohexyl)cyclopentan-1-ol (**4a**). From 2-ethenylcyclopentan-1-ol (**2**; 250 mg, 2.23 mmol), perfluorobutyl iodide (**3a**; 1.20 g, 3.47 mmol) and

AIBN (15 mg, 0.09 mmol), polyfluoroiodocyclopentanol **4a** (700 mg, 68.6%, yellow viscous oil) was obtained according to General procedure A by column chromatography (silica, dichloromethane) as a mixture of two diastereoisomers **A**, **B** in the 42 : 58 ratio. ^1H NMR (300.1 MHz, CDCl_3): **4aA**: 1.31 m, 1 H; 1.38 m, 2 H; 1.60–1.79 m, 4 H; 2.20 s, 1 H; 2.92 m, 2 H, $J = 15.9$; 4.14 q, 1 H, $^3J_{\text{HH}} = 5.5$; 4.51 q, 1 H, $^3J_{\text{HH}} = 5.5$; **4aB**: 1.30–2.05 m, 7 H; 2.80 m, 2 H; 3.43 s, 1 H; 3.78 m, 1 H; 4.71 m, 1 H. ^{13}C NMR (100.6 MHz, CDCl_3): **4aA**: 22.1 s; 25.4 s; 31.6 s; 35.6 s; 39.7 t, $^2J_{\text{CF}} = 21$; 54.4 s; 78.4 s; 106–120 m, 4 C; **4aB**: 20.8 s; 27.4 s; 27.9 s; 34.4 s; 40.4 t, $^2J_{\text{CF}} = 21$; 53.4 s; 79.1 s; 106–120 m, 4 C. ^{19}F NMR (376.5 MHz, CDCl_3): –81.5 t, 3 F, $J_{\text{FF}} = 10$; –114.2 m, 2 F; –125.0 dm, 2 F, $^3J_{\text{FF}} = 8$; –126.5 m, 2 F. IR (CHCl_3): 879 w, 1 029 w, 1 135 m, 1 244 s, 1 354 w, 2 963 w, 3 619 w. For $\text{C}_{11}\text{H}_{12}\text{F}_9\text{IO}$ (458.0) calculated: 28.84% C, 2.65% H; found: 29.11% C, 2.63% H.

(1*R**,2*R**)-2-(3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoro-1-iodooctyl)cyclopentan-1-ol (**4b**). From 2-ethenylcyclopentan-1-ol (**2**; 500 mg, 4.46 mmol), perfluorohexyl iodide (**3b**; 2.97 g, 6.66 mmol) and AIBN (23 mg, 0.14 mmol), polyfluoroiodocyclopentanol **4b** (1.53 g, 61.5%, yellow viscous oil) was obtained according to General procedure A by column chromatography (silica, dichloromethane) as a mixture of two diastereoisomers **A**, **B** in the 69 : 31 ratio. ^1H NMR (300.1 MHz, CDCl_3): **4bA**: 1.43 m, 2 H; 1.55–2.10 m, 6 H; 3.04 m; 4.12 dt, 1 H, $^3J_{\text{HH}} = 5.5$; 4.43 q, 1 H, $^3J_{\text{HH}} = 5.5$; **4bB**: 1.42 m, 2 H; 1.59–1.90 m, 4 H; 2.02 m, 1 H; 2.08 s; 2.91 m, 2 H; 3.88 dm, 1 H, $J_{\text{HH}} = 6.1$; 4.72 q, 1 H, $^3J_{\text{HH}} = 6.6$. ^{13}C NMR (100.6 MHz, CDCl_3): **4bA**: 22.2 s; 25.5 s; 31.6 s; 35.2 s; 40.0 t, $^2J_{\text{CF}} = 21$; 54.5 s; 78.6 s; 106–122 m, 6 C; **4bB**: 20.9 s; 27.4 s; 28.1 s; 34.6 s; 40.6 t, $^2J_{\text{CF}} = 21$; 53.5 s; 79.2 s; 106–122 m, 6 C. ^{19}F NMR (376.5 MHz, CDCl_3): –81.4 t, 3 F, $J_{\text{FF}} = 10$; –114.8 dm, 2 F, $J_{\text{FF}} = 8$; –122.4 m, 2 F; –123.4 m, 2 F; –126.6 m, 2 F. IR (CHCl_3): 1 151 m, 1 244 s, 1 438 w, 2 960 w, 3 613 w. For $\text{C}_{13}\text{H}_{12}\text{F}_{13}\text{IO}$ (557.9) calculated: 27.98% C, 2.17% H; found: 28.00% C, 2.27% H.

(1*R**,2*R**)-2-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluoro-1-iododecyl)cyclopentan-1-ol (**4c**). From 2-ethenylcyclopentan-1-ol (**2**; 350 mg, 3.12 mmol), perfluorooctyl iodide (**3c**; 2.56 g, 4.60 mmol) and AIBN (77 mg, 0.47 mmol), polyfluoroiodocyclopentanol **4c** (1.31 g, 63.8%, yellow viscous oil) was obtained according to General procedure A by column chromatography (silica, dichloromethane) as a mixture of two diastereoisomers **A**, **B** in the 67 : 33 ratio. ^1H NMR (300.1 MHz, CDCl_3): **4cA**: 1.30–1.95 m, 7 H; 2.41 s, 1 H; 3.05 m; 4.10 q, 1 H, $^3J_{\text{HH}} = 6.1$; 4.45 q, 1 H, $^3J_{\text{HH}} = 5.5$; **4cB**: 1.30–1.95 m, 8 H; 2.80 m, 2 H; 3.88 q, 1 H, $^3J_{\text{HH}} = 6.6$; 4.72 q, 1 H, $^3J_{\text{HH}} = 4.3$. ^{13}C NMR (100.6 MHz, CDCl_3): **4cA**: 22.1 s; 25.7 s; 31.8 s; 35.7 s; 39.6 t, $^2J_{\text{CF}} = 21$; 54.5 s; 78.5 s; 106–122 m, 8 C; **4cB**: 20.9 s; 27.2 s; 28.2 s; 34.7 s; 40.5 t, $^2J_{\text{CF}} = 21$; 53.6 s; 79.1 s; 106–122 m, 8 C. ^{19}F NMR (376.5 MHz, CDCl_3): –81.5 t, 3 F, $J_{\text{FF}} = 10$; –115.0 m, 2 F; –122.0 m, 6 F; –123.0 m, 2 F; –124.0 m, 2 F; –127.0 m, 2 F. IR (CHCl_3): 1 151 m, 1 244 s, 1 438 w, 2 960 w, 3 613 w. For $\text{C}_{15}\text{H}_{12}\text{F}_{17}\text{IO}$ (658.1) calculated: 27.38% C, 1.84% H; found: 27.69% C, 2.07% H.

(1*R**,2*R**)-2-(3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoro-1-iodooctyl)cyclopent-3-en-1-ol (**14**). From 2-ethenylcyclopent-3-en-1-ol (**8**; 300 mg, 2.72 mmol), perfluorohexyl iodide (**3b**; 1.2 g, 2.7 mmol), AIBN (45 mg, 0.27 mmol) and CCl_4 (4 ml, solvent), polyfluoroiodocyclopentenol **14** (120 mg, 7.9%, yellow semisolid) was obtained according to General procedure A by column chromatography (silica, dichloromethane) as a mixture of two diastereoisomers **A**, **B** in the 9 : 1 ratio. ^1H NMR (300.1 MHz, CDCl_3): **14A**: 2.20 m, 1 H; 2.73–2.85 m, 5 H; 4.24 quintet, 1 H, $^3J_{\text{HH}} = 6.3$, 4.1; 4.51 dt, 1 H, $^3J_{\text{HH}} = 4.6$, 6.4. ^{13}C NMR (100.6 MHz, CDCl_3): 23.1 s; 39.2 t, $^2J_{\text{CF}} = 21$; 42.1 s; 61.9 s; 77.5 s; 129.2 s; 132.1 s; 106–122 m, 6 C. ^{19}F NMR (376.5 MHz, CDCl_3): –81.4 t, 3 F, $J_{\text{FF}} = 10$; –114.8 m, 2 F; –122.4 m, 2 F; –123.4 m, 2 F; –124.0 m, 2 F; –126.6 m, 2 F. Spectra of diastereoisomer **14B** could not be assigned due to low amount of

material available. IR (CHCl₃): 707 w, 1 072 w, 1 121 w, 1 145 m, 1 242 s, 1 362 w, 3 600 w. For C₁₃H₁₀F₁₃IO (555.9) calculated: 28.07% C, 1.82% H; found: 28.98% C, 1.94% H.

From 2-ethenylcyclopent-3-en-1-ol (**8**; 200 mg, 1.82 mmol), perfluorohexyl iodide (**3b**; 2.1 g, 4.7 mmol), sodium dithionite (2.2 g, 11 mmol), sodium hydrogencarbonate (0.9 g, 11 mmol), acetonitrile (43 ml) and water (11 ml), a mixture of products was obtained following General procedure B, which was separated by column chromatography (silica, dichloromethane) to afford polyfluoroiodoalkylcyclopentenol **14** (176 mg, 17.4%, yellow oil) as a mixture of diastereoisomers along with a side-product, 4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoro-2-iodononan-1-ol (**7**; 522 mg, 57.1%), which was identified by its ¹H, ¹³C and ¹⁹F NMR spectra²⁷.

Attempted radical addition of perfluorohexyl iodide (3b) to diethenyldiol 9. From diethenyldiol **9** (300 mg, 1.9 mmol), perfluorohexyl iodide (**3b**; 4.2 g, 9.4 mmol), sodium dithionite (3.8 g, 22 mmol), sodium hydrogencarbonate (1.8 g, 22 mmol), acetonitrile (65 ml) and water (16 ml), only the side-product, tridecafluoroiodononan-1-ol **7** (1.02 g, 52%), was obtained following General procedure B.

Reductions of (Polyfluoroiodoalkyl)cyclopentanols **4** to (Polyfluoroalkyl)cyclopentanols **5**. General Procedure A – Reduction with Tributylstannane

A flask equipped with reflux condenser and magnetic stirbar was charged with polyfluoroiodocyclopentanol **4**, toluene (10 ml/mmol of alcohol **4**) and AIBN (0.1 mmol/mmol of alcohol **4**). The mixture was heated while stirring to 60 °C and tributylstannane (2 mmol/mmol of alcohol **4**) was syringed to it over 40 min. The mixture was then stirred at 60 °C for 3 h, cooled to room temperature and quenched with methanol (10 ml/mmol of alcohol **4**). Solvents were removed on a vacuum rotary evaporator and the product was obtained by column chromatography (silica, dichloromethane) of the residue, followed by recrystallization (hexane) in the case of crystalline product.

General Procedure B – Reduction with Zinc

A flask equipped with reflux condenser was charged with polyfluoroiodocyclopentanol **4**, zinc (5 mmol/mmol of alcohol **4**) and ethanol (10 ml/mmol of alcohol **4**). Gaseous hydrogen chloride was then introduced into the reaction mixture until zinc was consumed (15 min). Ethanol was then removed on a vacuum rotary evaporator and the product was obtained by column chromatography (silica, dichloromethane) of the residue, followed by recrystallization (hexane).

General Procedure C – One-Pot Radical Addition of Perfluoroalkyl Iodide **3** and Reduction with Tributylstannane

A flask equipped with a reflux condenser and magnetic stirbar was charged with ethenylcyclopentanol, perfluoroalkyl iodide (**3**; 1.5 mmol/mmol of ethenylcyclopentanol) and AIBN (0.4 mmol/mmol of ethenylcyclopentanol). The mixture was heated to 105 °C while stirring over 1 h, cooled to room temperature and second portion of AIBN (0.6 mmol/mmol of ethenylcyclopentanol) was added to it along with toluene (1 ml/mmol of ethenylcyclopentanol). After heating the mixture to 60 °C, tributylstannane (1.2 mmol/mmol of ethenylcyclopentanol) was slowly syringed to it over 40 min. The mixture was then heated to 60 °C for another 3 h, cooled to room temperature and quenched with methanol

(3 ml/mmol of ethenylcyclopentanol). The solvents were removed on a vacuum rotary evaporator and the product was obtained by column chromatography (silica, dichloromethane) followed by recrystallization (hexane).

2-(3,3,4,4,5,5,6,6,6-Nonafluorohexyl)cyclopentan-1-ol (5a). From (polyfluoroiodoalkyl)cyclopentanol **4a** (450 mg, 0.982 mmol), tributylstannane (570 mg, 1.96 mmol) and AIBN (20 mg, 0.12 mmol), (polyfluoroalkyl)cyclopentanol **5a** (290 mg, 88.9%, colorless viscous liquid) was obtained according to General procedure A. ^1H NMR (300.1 MHz, CDCl_3): 1.51–1.83 m, 7 H; 1.81 s, 1 H; 1.93 m, 2 H; 2.10 m, 2 H; 3.78 q, 1 H, $^3J_{\text{HH}} = 6.0$. ^{13}C NMR (100.6 MHz, CDCl_3): 21.5 s; 24.0 s; 29.6 t, $^2J_{\text{CF}} = 21$; 29.7 s; 34.8 s; 47.2 s; 78.9 s; 108–122 m, 4 C. ^{19}F NMR (376.5 MHz, CDCl_3): –81.5 t, 3 F, $J_{\text{FF}} = 10$; –114.2 m, 2 F; –125.0 m, 2 F; –126.5 m, 2 F. IR (CHCl_3): 1 145 s, 1 244 s, 2 960 w, 3 610 w. For $\text{C}_{11}\text{H}_{13}\text{F}_9\text{O}$ (332.2) calculated: 39.76% C, 3.95% H; found: 40.19% C, 4.22% H.

2-(3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl)cyclopentan-1-ol (5b). From (polyfluoroiodoalkyl)cyclopentanol **4b** (300 mg, 0.538 mmol), tributylstannane (313 mg, 1.07 mmol) and AIBN (9 mg, 0.05 mmol), (polyfluoroalkyl)cyclopentanol **5b** (213 mg, 91.7%, m.p. 33–34 °C, white crystals) was obtained according to General procedure A. ^1H NMR (300.1 MHz, CDCl_3): 1.23 m, 2 H; 1.50–1.80 m, 6 H; 1.95 m, 2 H; 2.13 m, 2 H; 3.86 q, 1 H, $^3J_{\text{HH}} = 5.5$. ^{13}C NMR (100.6 MHz, CDCl_3): 21.5 s; 24.1 s; 29.7 t, $^2J_{\text{CF}} = 21$; 34.8 s; 47.3 s; 79.0 s; 106–120 m, 6 C. ^{19}F NMR (376.5 MHz, CDCl_3): –81.4 t, 3 F, $J_{\text{FF}} = 10$; –114.8 m, 2 F; –122.4 m, 2 F; –123.4 m, 2 F; –124.0 m, 2 F; –126.6 m, 2 F. IR (CHCl_3): 1 145 s, 1 244 s, 2 960 w, 3 610 w. For $\text{C}_{13}\text{H}_{13}\text{F}_{13}\text{O}$ (432.0) calculated: 36.12% C, 3.04% H; found: 35.98% C, 3.33% H.

From (polyfluoroiodoalkyl)cyclopentanol **4b** (300 mg, 0.538 mmol) and zinc (106 mg, 2.62 mmol), (polyfluoroalkyl)cyclopentanol **5b** (127 mg, 54.7%, m.p. 32–34 °C, light yellow crystals) was obtained according to General procedure B.

From 2-ethenylcyclopentan-1-ol (**2**; 500 mg, 4.46 mmol), perfluorohexyl iodide (**3b**; 2.97 g, 6.66 mmol), AIBN (70 mg, 0.43 mmol) and tributylstannane (1.56 g, 5.34 mmol), (polyfluoroalkyl)cyclopentanol **5b** (890 mg, 46.2%, m.p. 33–34 °C, white crystals) was obtained according to General procedure C.

2-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl)cyclopentan-1-ol (5c). From (polyfluoroiodoalkyl)cyclopentanol **4c** (800 mg, 1.22 mmol), tributylstannane (710 mg, 2.44 mmol) and AIBN (25 mg, 0.15 mmol), (polyfluoroalkyl)cyclopentanol **5c** (500 mg, 77.2%, m.p. 60–62 °C, white crystals) was obtained according to General procedure A. ^1H NMR (300.1 MHz, CDCl_3): 1.23 m, 2 H; 1.28–1.85 m, 6 H; 1.94 m, 2 H; 2.22 m, 2 H; 3.85 quintet, 1 H, $^3J_{\text{HH}} = 5.5$. ^{13}C NMR (100.6 MHz, CDCl_3): 21.6 s; 24.1 s; 29.8 t, $^2J_{\text{CF}} = 21$; 34.9 s; 47.4 s; 79.1 s; 106–122 m, 8 C. ^{19}F NMR (376.5 MHz, CDCl_3): –81.5 t, 3 F, $J_{\text{FF}} = 10$; –115.0 m, 2 F; –122.0 m, 6 F; –123.0 m, 2 F; –124.0 m, 2 F; –127.0 m, 2 F. IR (CHCl_3): 1 151 s, 1 243 s, 2 960 w, 3 614 w. For $\text{C}_{15}\text{H}_{13}\text{F}_{17}\text{O}$ (532.2) calculated: 33.85% C, 2.47% H; found: 34.07% C, 3.25% H.

2-(3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl)cyclopent-3-en-1-ol (15)

A flask equipped with an addition funnel, reflux condenser and a magnetic stirbar was charged with magnesium shavings (1.83 g, 75.3 mmol) and diethyl ether (5 ml). Magnesium was activated with few drops of 1,2-dibromoethane. 1,1,1,2,2,3,3,4,4,5,5,6,6-Tridecafluoro-8-iodooctane (**16**; 23.7 g, 50.0 mmol) in diethyl ether (170 ml) was then added at such a rate to maintain gentle reflux. After the addition was completed, the mixture was heated to reflux for 2 h. The mixture was cooled to room temperature, followed by addition

of cyclopentadiene oxide **10** (3.3 g, 40 mmol) over 15 min. The mixture was then refluxed for 1 h, cooled to room temperature and quenched with HCl (10%, 5 ml). Salts were filtered off and washed with diethyl ether (2 × 50 ml). Combined organic layers were washed with water (2 × 100 ml) and dried over anhydrous MgSO₄. Solvents were removed on a vacuum rotary evaporator and product **15** (700 mg, 4.0%, viscous yellow oil) was obtained by column chromatography (silica, dichloromethane) of the residue, along with huge amount of a side-product, 1,1,1,2,2,3,3,4,4,5,5,6,6,11,11,12,12,13,13,14,14,15,15,16,16,16-hexacosafuorohexadecane. ¹H NMR (300.1 MHz, CDCl₃): 2.05 m, 4 H; 2.20 dd, 1 H, ³J_{HH} = 1.9, 17.2; 2.49 m; 2.62 ddd, 1 H, ³J_{HH} = 1.9, 6.6, 16.9; 2.75 s, 1 H; 4.01 tt, 1 H, ³J_{HH} = 3.3, 6.6; 5.55 dt, 1 H, ³J_{HH} = 2.0, 6.0; 5.64 dd, 1 H, ³J_{HH} = 2.1, 6.0. ¹³C NMR (100.6 MHz, CDCl₃): 23.4 s; 28.9 t, ²J_{CF} = 21; 41.6 s; 53.7 s; 77.2 s; 106–122 m, 6 C; 129.1 s; 134.3 s. ¹⁹F NMR (376.5 MHz, CDCl₃): -81.4 t, 3 F, J_{HH} = 10; -114.8 m, 2 F; -122.4 m, 2 F; -123.4 m, 2 F; -124.0 m, 2 F; -126.6 m, 2 F. IR (CHCl₃): 707 m, 796 m, 1 056 w, 1 120 s, 1 145 s, 1 190 s, 1 248 s, 1 364 w, 1 458 w, 2 951 w, 3 014 w. For C₁₃H₁₁F₁₃O (430.2) calculated: 36.29% C, 2.58% H; found: 36.09% C, 2.85% H.

Dehydration of (Polyfluoroalkyl)cyclopentanol 5. General Procedure

A flask equipped with a reflux condenser and magnetic stirbar was charged with (polyfluoroalkyl)cyclopentanol **5**, toluene (20 ml/mmol of alcohol **5**) and Nafion® beads (0.1 mmol/mmol of alcohol **5**). The mixture was then heated to 105 °C over 24 h, cooled to room temperature and the solvent was removed on a vacuum rotary evaporator. The product was obtained by column chromatography (silica, eluent hexane) of the residue.

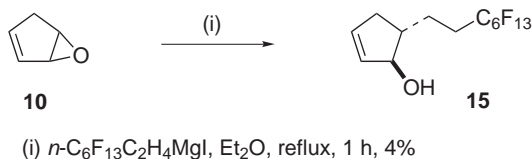
2-(3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl)cyclopent-1-ene (**6a**). From (polyfluoroalkyl)cyclopentanol **5b** (50 mg, 0.116 mmol) and Nafion® beads (12 mg, 0.01 mmol), (polyfluoroalkyl)cyclopentene **6a** (22 mg, 47%, viscous colorless oil) was obtained according to General procedure. ¹H NMR (300.1 MHz, CDCl₃): 1.38 m, 2 H; 1.77 m, 2 H; 1.99 m, 2 H; 2.12 m, 2 H; 2.38 m, 2 H; 5.47 s, 1 H. ¹⁹F NMR (376.5 MHz, CDCl₃): -81.4 t; 3 F, J_{FF} = 10; -114.8 t, 2 F, J_{FF} = 16; -122.4 m, 2 F; -123.4 m, 2 F; -124.0 m, 2 F; -126.6 t, 2 F, ³J_{HF} = 8. IR (CHCl₃): 811 w, 1 145 m, 1 243 s, 1 350 w, 1 457 w, 2 950 w, 3 010 w. ¹³C NMR spectrum was not taken and elemental analysis was not carried out due to the small amount of product obtained.

2-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl)cyclopent-1-ene (**6b**). From (polyfluoroalkyl)cyclopentanol **5c** (400 mg, 0.752 mmol) and Nafion® beads (83 mg, 0.07 mmol), (polyfluoroalkyl)cyclopentene **6b** (80 mg, 20.5%, viscous colorless oil) was obtained according to General procedure. ¹H NMR (300.1 MHz, CDCl₃): 1.22 m, 2 H; 1.74 m, 2 H; 1.93 m, 4 H; 2.30 m, 2 H; 5.43 s, 1 H. ¹³C NMR (100.6 MHz, CDCl₃): 21.7 s; 23.4 s; 29.5 t, ²J_{CF} = 21; 32.4 s; 35.0 s; 124.7 s; 141.6 s; 106–122 m, 8 C. ¹⁹F NMR (376.5 MHz, CDCl₃): -81.5 t; 3 F, J_{FF} = 10; -115.0 m, 2 F; -122.0 m, 6 F; -123.0 m, 2 F; -124.0 m, 2 F; -127.0 m, 2 F. IR (CHCl₃): 820 w, 1 151 m, 1 244 s, 1 350 w, 1 457 w, 2 949 w, 3 010 w. For C₁₅H₁₁F₁₇ (514.2) calculated: 35.03% C, 2.12% H; found: 35.29% C, 2.14% H.

RESULTS AND DISCUSSION

Our first strategy in the preparation of polyfluoroalkylated cyclopentadienes was based on the reaction of polyfluorinated organometallic reagent with an appropriate epoxide. Bearing in mind that at least a two-carbon spacer

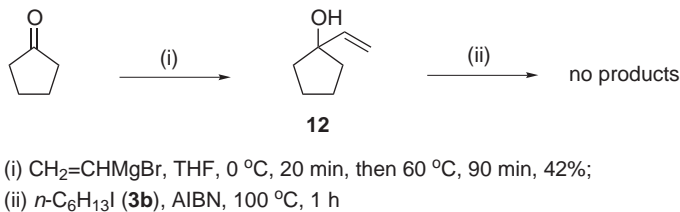
has to be inserted between the perfluorinated ponytail and the cyclopentadiene ring to preserve sufficient electron-donor properties of the ligand^{18,28}, we prepared 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-magnesium iodide from the corresponding polyfluoroalkyl iodide **16** and magnesium. Its reaction with cyclopentadiene oxide **10** afforded only poor yield of the target (polyfluoroalkyl)cyclopentenol **15** due to extensive coupling of the Grignard reagent with fluoroalkyl iodide **16** in analogy to literature data^{29,30} (Scheme 1).



SCHEME 1

We therefore decided to replace the one-step opening of the epoxide ring with the polyfluorinated organometallic reagent by a three-step reaction, *viz.* opening of the epoxide ring with ethenylmagnesium bromide followed by radical addition of perfluoroalkyl iodide **3** to the double bond and subsequent removal of iodine.

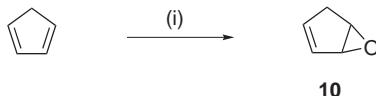
Thus, the reaction of ethenylmagnesium bromide with cyclopentanone afforded 1-ethenylcyclopentan-1-ol (**12**) according to the published procedure²⁶. Radical addition of perfluorohexyl iodide (**3b**) to alkenol **12** afforded a complex mixture of products from which no single compound could be isolated by column chromatography except for unreacted starting fluoroalkyl iodide **3b** (Scheme 2). We suspected that the allyl alcohol grouping in alkenol **12** was too labile to withstand the reaction conditions and polymerized.



SCHEME 2

Hence we turned from cyclic ketones to epoxides as the corresponding oxygen electrophiles. 6-Oxabicyclo[3.1.0]hexane (**1**) is available commer-

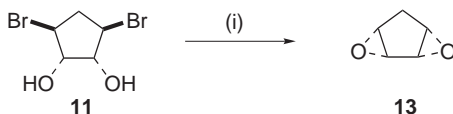
cially, 6-oxabicyclo[3.1.0]hex-2-ene (**10**) was prepared from cyclopentadiene by electrophilic epoxidation with peroxyacetic acid²⁴ (Scheme 3).



SCHEME 3

(i) $\text{CH}_3\text{CO}_3\text{H}$, CH_2Cl_2 , Na_2CO_3 , $-20\text{ }^\circ\text{C}$, 30 min, then $20\text{ }^\circ\text{C}$, 2.5 h, 38%

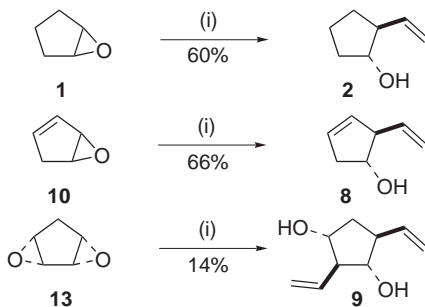
The preparation of $(1R^*,2S^*,4S^*,6R^*)$ -3,6-dioxatricyclo[4.1.0.0^{2,4}]heptane (**13**) according to ref.²⁵ had to be modified, as the published dehydrohalogenation of the intermediate $(1R^*,2S^*,3S^*,5R^*)$ -3,5-dibromocyclopentane-1,2-diol (**11**) with sodium hydroxide did not afford the target diepoxide **13**. Fortunately, substitution of sodium hydroxide for sodium hydride led to a good yield of diepoxide **13** (Scheme 4).



SCHEME 4

(i) NaH , DME, 1 h, 62%

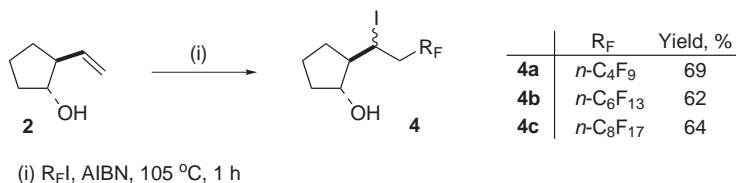
Opening of the epoxide ring in cyclic epoxides **1**, **10** and **13** with ethenylmagnesium bromide was performed in the presence of a catalytic amount of copper(I) iodide as published²⁶ for epoxide **1**. In the case of epoxides **1** and **10**, the reaction proceeded stereoselectively and only the *trans* isomers were obtained. Epoxide **13** afforded a complex mixture, from which $(1R^*,2S^*,3S^*,4S^*)$ -2,4-diethenylcyclopentane-1,2-diol (**9**) was obtained in a poor yield by column chromatography as the sole isolable product (Scheme 5).



(i) $\text{CH}_2=\text{CHMgBr}$, CuI , THF, $-30\text{ }^\circ\text{C}$, 1 h, then $0\text{ }^\circ\text{C}$, 3 h

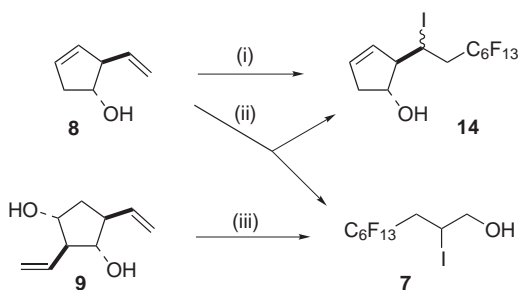
SCHEME 5

Radical addition of perfluoroalkyl iodides **3** was first carried out according to methodology described in ref.²⁷, *i.e.* using 2,2'-azobisisobutyronitrile as initiator without solvent (General procedure A). In the reaction of iodides **3** with ethenylcyclopentanol **2** the corresponding (polyfluoroiodoalkyl)cyclopentanols **4** were obtained in good yields (Scheme 6) as mixtures of two diastereoisomers **A**, **B**, which could be distinguished by ¹H and ¹³C NMR spectroscopy but neither separated nor assigned the relative configuration.



SCHEME 6

An analogous reaction with ethenylcyclopentenol **8** afforded only a complex mixture from which no individual product could be isolated. When tetrachloromethane was employed as a solvent, the target (polyfluoroiodoalkyl)cyclopentenol **14** was obtained in a poor yield. We therefore tried a different methodology, *i.e.* radical addition of perfluoroalkyl iodides **3** at aqueous conditions initiated with sodium dithionate³¹. Surprisingly, along with slightly better yield of fluoriodocyclopentenol **14**, we isolated reasonable amounts of a side-product, polyfluoroiodoalkanol **7** (Scheme 7). The same compound **7** was obtained as the exclusive product of the reaction of perfluoroalkyl iodide **3b** with diethenylcyclopentanediol **9**.

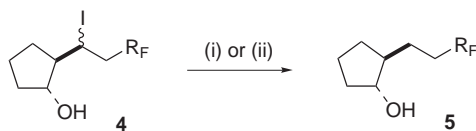


(i) *n*-C₆F₁₃I, AIBN, CCl₄, reflux, 1 h, 8%; (ii) C₆F₁₃I, Na₂S₂O₄, NaHCO₃, CH₃CN, H₂O, r.t., 3 h, 17% **5**, 57% **7**; (iii) C₆F₁₃I, Na₂S₂O₄, NaHCO₃, CH₃CN, H₂O, r.t., 3 h, 52%

SCHEME 7

Reductive removal of iodine from (polyfluoroiodoalkyl)cyclopentanols **4** was accomplished by the reaction with zinc dust³² or with tributylstannane³³. As the latter method afforded better results for fluoriodo-

cyclopentanol **4b** as the test substrate, it was used for the preparation of all (polyfluoroalkyl)cyclopentanol **5** (Scheme 8). We also successfully attempted to combine radical addition of perfluorohexyl iodide (**3b**) to ethenylcyclopentanol **2** and reduction of fluoriodocyclopentanol **4b** to fluorocyclopentanol **5b** with tributylstannane in a one-pot reaction, but the yield was lower than that in the two-step reaction (46 vs 56%).

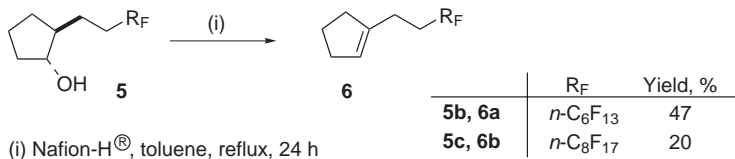


	R _F	Method	Yield, %
4a, 5a	<i>n</i> -C ₄ F ₉	(i)	89
4b, 5b	<i>n</i> -C ₆ F ₁₃	(i)	92
4b, 5b	<i>n</i> -C ₆ F ₁₃	(ii)	55
4c, 5c	<i>n</i> -C ₈ F ₁₇	(i)	77

(i) Bu₃SnH, AIBN, toluene, 60 °C, 3.5 h; Zn, HCl, EtOH, r.t., 15 min

SCHEME 8

Finally, in the last step of the preparation of polyfluoroalkylated cyclopentenes **6**, dehydration had to be carried out. We first rejected elimination of modified fluorocyclopentanol **5** using strong bases as the CF₂-CH₂ grouping could be unstable under these conditions. This has been observed recently in the course of preparation of polyfluorinated alkoxides³⁴. Under the published acidic conditions, *viz.* heating with 4-toluenesulfonic acid^{35,36}, the dehydration did not occur. However, when a stronger polymeric perfluorinated acid, Nafion H®, was employed, we obtained the target fluorocyclopentenes **6** in poor to moderate yields (Scheme 9). Lower yield of the target cyclopentenes **6** could be possibly attributed to side-reactions of both starting fluorocyclopentanol **5** and products **6** with solvent³⁷, but no explicit side-products were obtained by the analysis of the reaction mixtures.



(i) Nafion-H®, toluene, reflux, 24 h

SCHEME 9

Fluorous partition coefficients of synthesized (polyfluoroalkyl)cyclopentadienes **6** were not measured, as we knew from our previous work on fluorinated cyclopentadienes^{20,21} that cyclic compounds substituted with one polyfluorinated chain have not sufficient fluorophilic properties. On the other hand, fluorocyclopentenenes **6** could be sufficiently fluorophilic for organic-fluorous extraction³⁸ and the corresponding experiments are in progress.

Although our primary target, the preparation of bis(polyfluoroalkylated) cyclopentadienes with defined regioselectivity, failed due to an unexpected side reaction in the course of radical addition of perfluoroalkyl iodides **3** to diethenylcyclopentane-1,2-diol **9**, we succeeded in the preparation of the corresponding model compounds, polyfluoroalkylated cyclopentenenes **6**, which are potential intermediates for fluorous reagents and catalysts. An explanation of the unexpected formation of the side-product **7** is the aim of our continuing study.

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