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PERFLUOROALKYLATION OF BENZENE DERIVATIVES. AN IMPROVED SYNTHESIS OF 1,3-BIS(2-HYDROXYHEXAFLUORO-2-PROPYL)-5-(PERFLUORO-n-ALKYL)BENZENES

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SUMMARY

A three-step high yield synthesis of various 1,3-bis(2-hydroxyhexafluoro-2-propyl)-5-(perfluoro-n-alkyl)benzenes is described. Significant improvements in the iodination and perfluoro-alkylation of a perfluoro-alkylbenzene diol have been achieved. Copper coupling of straight-chain perfluoroalkyl iodides with the iodobenzene derivative in DMSO gave the desired compounds as DMSO complexes in 78-91 percent yield.

INTRODUCTION

Fluorinated carbinols obtained from benzene [1] aromatic amines [2], and phenols [3] are useful starting materials for the preparation of a variety of polymer precursors and other synthetically useful materials. These carbinols are conveniently synthesized from hexafluoroacetone and aromatic compounds in the presence of anhydrous aluminum chloride. Recently, diglycidyl ethers of highly fluorinated 1,3-bis(2-hydroxyhexafluoro-2-propyl)-5-(perfluoro-n-alkyl)benzenes have attracted increased attention as precursors for the preparation of epoxy resins and urethane coatings [4,5]. A very recent publication dealing with the chemistry of 1,3 bis(2-hydroxyhexafluoro-2-propyl)benzene derivatives further indicates the unique theoretical and synthetic challenges and opportunities which this class of compounds present [6].

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The synthetic route to 1,3-bis(2-hydroxyhexafluoro-2-propyl)-5-(perfluoro-n-alkyl)benzenes involves two key steps: the preparation of fluorinated iodobenzene 4 and the coupling of 4 with perfluoroalkyl iodides. The iodobenzene 4 has been prepared from 1,3-bis(2-hydroxyhexafluoro-2-propyl)benzene (2) by nitration, reduction of the nitro compound, diazotization of the amino group, and the exchange of the diazonium group for iodine [4,5]. Throughout these operations the hydroxy groups of 2 have been protected by methylation and the last step leading to 4 involves the difficult hydrolysis of the ether bond [4,5].

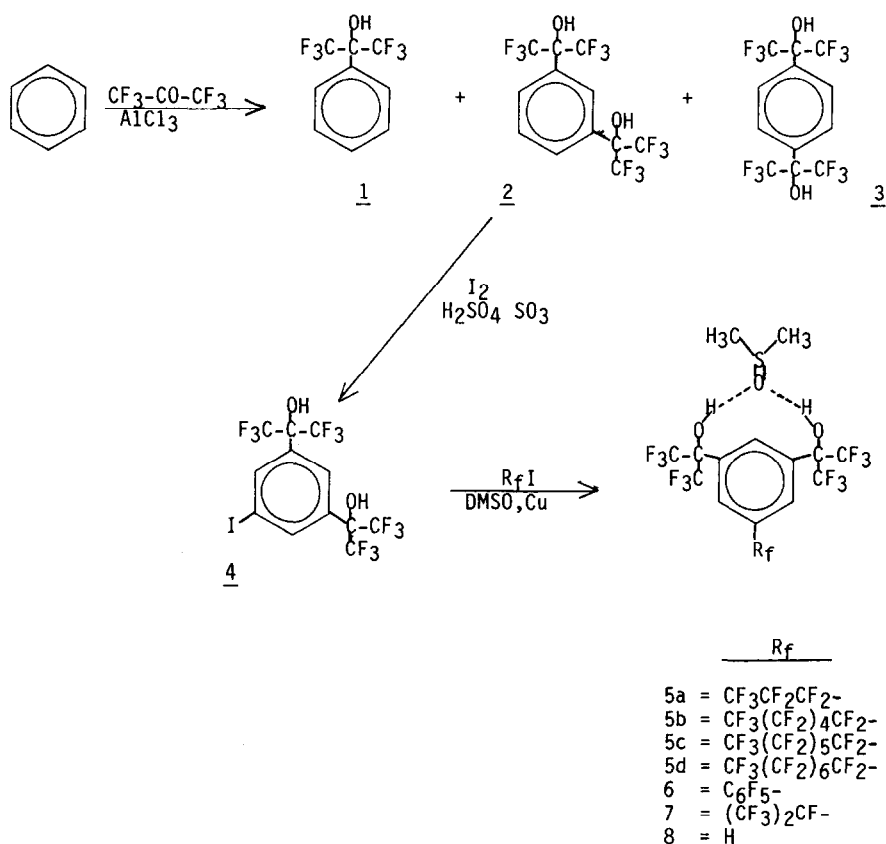
This multi-step synthesis is time consuming and requires careful purification of all intermediate products before each subsequent step is executed. An alternative route to 4 via the direct iodination of 2 with iodine in fuming sulfuric acid gives 4 in low (38%) yield with the majority of the starting diol 2 being destroyed under severe reaction conditions [4,5]. Even more frustrating have been the low yields of the coupling reaction of 4 with perfluoroalkyl iodides (51% for perfluoro-n-propyl iodide and 29% or 39% for perfluoro-n-heptyl iodide) [4,5,7]. These coupling reactions were carried out in a Parr bomb or in a sealed glass tube. Removing of traces of oxygen from the bomb and then separation of the product from unreacted iodobenzene 4 have been major additional drawbacks of this procedure [7].

RESULTS AND DISCUSSION

In this report we wish to describe a simple, high yield three-step synthesis of 1,3-bis(2-hydroxyhexafluoro-2-propyl)-5-(perfluoro-n-alkyl)benzenes as previously unreported complexes with dimethyl sulfoxide and to discuss some variations in the perfluoroalkylation of iodobenzene 4 using DMSO and copper powder (Scheme I).

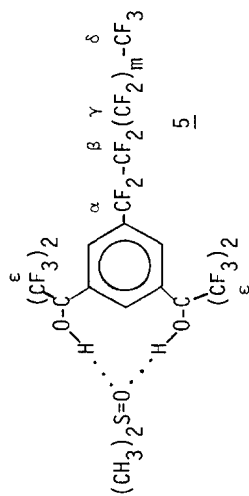
We have reinvestigated the reported synthesis of 2 from benzene and anhydrous hexafluoroacetone [1] and found that a rapid rate of absorption of HFA into the mixture of benzene and aluminum chloride appears to be essential to achieve the maximum yield of the meta diol 2. When HFA was admitted into the reaction mixture at a low (g/min.) rate and in slightly lower molecular ratio than required for the introduction of two

molecules of HFA to one molecule of benzene, the liquid product was a mixture of monosubstituted benzene 1 and meta diol 2. The water washings from the extraction of the crude mixture with chloroform deposited after several days a crystalline product easily identified as the pure para diol 3. When one mole of benzene was reacted with a slight excess of HFA (2.06 moles), a good yield of 2 as a colorless liquid was obtained. Again, the $^1\text{H-NMR}$ and $^{19}\text{F-NMR}$ analysis of this product indicated the presence of a small amount of the para diol 3. A sharp singlet at 7.74 ppm attributed to aromatic protons of 3 was superimposed on the complex multiplet of aromatic protons of 2 in the 7.48-8.02 ppm range.



Scheme I

TABLE

19F-NMR Spectra of Complexes 5a - d

Compound	m	α	β	γ	δ	ϵ
<u>5a</u>	0	-113.4 (q,2F)	-127.9 (s,2F)	-----	-81.5 (t,3F)	-76.2 (s,12F)
<u>5b</u>	3	-112.4 (t,2F)	-127.3 (m,2F)	-123.2 (m,6F)	-82.3 (t,3F)	-76.5 (s,12F)
<u>5c</u>	4	-112.4 (t,2F)	-127.5 (m,2F)	-123.2 (m,8F)	-82.2 (t,3F)	-76.6 (s,12F)
<u>5d</u>	5	-112.3 (t,2F)	-127.4 (m,2F)	-123.2 (m,10F)	-82.2 (t,3F)	-76.5 (s,12F)
<u>5a'</u> ^a	0	-113.4 (q,2F)	-127.7 (s,2F)	-----	-81.3 (t,3F)	-76.7 (s,12F)
<u>5d'</u> ^a	5	-112.4 (m,2F)	-127.3 (m,2F)	-123.0 (m,10F)	-82.2 (t,3F)	-76.7 (s,12F)

^a 19F-NMR spectra of liquid fluorinated diols after removing complexed DMSO from 5a and 5d.

Direct iodination of aromatic systems generally proceeds with difficulty due to low electrophilicity of the iodine cation and the interference of hydrogen iodide formed during the reaction. We were able to considerably increase the yield of 4 by the slow addition of 2 at room temperature to the preformed black solution of iodine in fuming sulfuric acid and then stirring and heating the mixture at 70° for several hours. The decomposition of the reaction mixture with cold water and direct extraction of 4 with ether from the acidic mixture further simplified the preparation of 4 over the previous method [4,5]. Fractionation of crude 4 under reduced pressure afforded in the first fraction a mixture of 4 and solid para diol 3. It is not clear whether the presence of 3 is the result of recovering unreacted 3 as a minor component in the starting diol 2, or the result of rearrangement of 2 to 3 under strong acidic conditions.

The perfluoroalkylation reaction of iodobenzene 4 with perfluoroalkyl iodides in the presence of copper powder and dimethyl sulfoxide was also considerably simplified over previously reported procedures [4,5,7]. The reaction mixture prepared under dry nitrogen atmosphere (glove box) was stirred and heated in an oil bath in a standard glass round-bottomed flask under a slight positive pressure of nitrogen. The progress of the reaction was indicated by the amount of precipitated yellow cuprous iodide. Filtration of cuprous iodide and then dilution of the DMSO solution with water afforded the solid products. The coupling reaction under these conditions gave good yields either on a hundred-gram scale or on a 3-5 gram scale. The volume of DMSO used seems to be of some importance for good yields and the purity of products since we found that the coupling reactions in a larger volume of DMSO proceed with a lower yield.

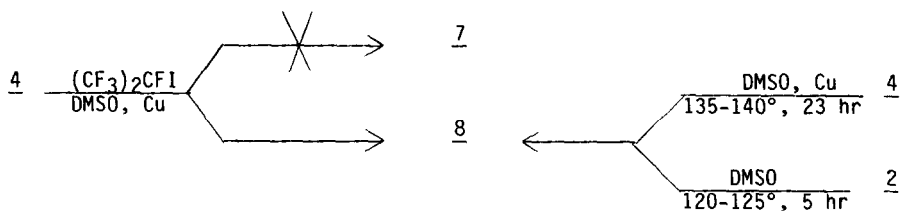
In addition to the expected pattern for signals of aromatic protons and hydroxyl protons, the ^1H -NMR spectra of the solid coupling products 5,6 revealed a sharp singlet at 2.57-2.60 ppm equivalent to six protons. This signal did not disappear on purification of the products by distillation or sublimation and crystallization. The ^{19}F -NMR spectra of these products were on the other hand totally consistent with the structure of expected 1,3-bis(2-hydroxyhexafluoro-2-propyl)-5-(perfluoro-n-alkyl)benzenes (see Table). Further data obtained from the mass and infrared spectra allowed us to conclude that the white solids were complexes of the fluorinated diols with one molecule of dimethyl sulfoxide. Complexes

5 and 6 are unexpectedly stable and can be sublimed under reduced pressure. The DMSO complex 5d was purified by vacuum distillation at 120-122° without signs of dissociation. All complexes were easily crystallized from chloroform as well formed colorless crystals. Previous reports on the reactions and physical properties of this class of meta diols have not mentioned the formation of any complexes. The ability of tertiary fluoro alcohols and especially perfluoropinacol to form 1:1 molecular complexes is well known [8]. Solids and distillable liquid complexes of fluoro alcohols with dioxane, THF, acetonitrile and pyridine have been reported. However, 5a-d, 6 appear to be the first examples of a meta aryl diol complex.

The complexes 5a-d and 6 can be freed from DMSO to give liquid fluorinated diols by heating at 80-90° with 5% solution of sodium hydroxide and then precipitation of the oily product with hydrochloric acid. However, in the case of 5d after three hours of heating at 90° substantial amount of the starting complex was recovered unchanged after acidification of the basic solution.

In contrast to the high yields of perfluoroalkylation of iodobenzene 4 with perfluoroalkyl iodides, the coupling of 4 and pentafluorophenyl iodide under similar reaction conditions gave only trace amounts of expected fluorinated biphenyl 6 as a complex with DMSO.

The reaction of iodobenzene 4 with 2-iodoheptafluoropropane in DMSO at the same mild conditions gave the complex of dimethyl sulfoxide and 2 instead of the expected benzene derivative 7. (Scheme II) The formation of the complex 8 under these conditions is the result of reductive dehalogenation of the iodobenzene 4. An analogous reaction of phenyl iodide with 2-iodoheptafluoropropane has been reported to yield 2-phenylheptafluoropropane with moderate yield [9]. In order to test the tendency of 4 to undergo the reductive dehalogenation, we heated the iodobenzene 4 alone with copper powder in DMSO for 23 hours. However, in contrast with the above described reaction only a trace amount of the complex 8 was isolated from the reaction mixture. The complex 8 was easily prepared by dissolving meta diol 2 in dimethyl sulfoxide and heating the solution at 120-125° for a few hours. The precipitated oil which solidified almost immediately after pouring the solution into water gave analytical and spectral data which were are identical with the complexes obtained by the other two routes.



Scheme II

The surprising stability and ease of formation of the DMSO complexes 5, 6, and 8 prompted us to investigate further their structure and chemistry. These studies are currently in progress and will be reported elsewhere.

EXPERIMENTAL

Melting points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 1320 spectrometer. Proton and fluorine NMR spectra were recorded on a Varian 360L instrument using TMS as an internal lock for proton NMR spectra. All ^{19}F -NMR spectra were taken as solutions in deuteriochloroform with hexafluorobenzene (-162.9 ppm) used as an internal lock. The mass spectra were obtained on a Du Pont 21-491 instrument. Chemical analyses were performed by Huffman Laboratories at Wheatridge, Colorado. The copper powder (Aldrich-20,778-0) used in all coupling reactions was stored under dry nitrogen and used as received.

Preparation of 1,3-bis(2-hydroxyhexafluoro-2-propyl)benzene (2)

a The reaction of benzene with hexafluoroacetone (HFA) (1:2.06 molar ratio)

A 1 L three-necked flask was fitted with a dry-ice condenser, thermometer, magnetic stirrer bar, and a 50 ml Erlenmeyer flask connected to one neck by a large diameter rubber tube. The condenser exit port was connected through a drying tube containing anhydrous calcium chloride and to an oil bubbler. The apparatus was purged with dry nitrogen, then anhydrous benzene (78.1 g, 1 mol) was placed into the flask and anhydrous aluminum chloride (21 g) was placed into the Erlenmeyer flask. A small amount of aluminum chloride (approx. 1 g) was added to the stirred benzene and hexafluoroacetone (HFA) was admitted under the surface of the mixture

through a flexible Teflon tube (2 mm ID, 120 cm long). The tube was directly connected to the HFA cylinder which was placed on a large double-pan balance to monitor the rate of HFA addition. The HFA was added as rapidly as possible but not to allow the excess to escape through the mineral oil bubbler. During the first hour of HFA addition, the temperature rose to 51° and was then maintained at 50-54° level. The rate of addition of HFA was approximately 10 g/8-10 min. with a total 343 g (2.06 mol) added during a 6 hr period. Only a small amount of aluminum chloride was required for the addition of the first portion of HFA (200 g). The remaining major portion of aluminum chloride was added throughout the last 2-3 hr of the reaction. Toward the end of the HFA addition the temperature dropped to 30° and refluxing HFA from dry-ice condenser was observed. The black mixture was decomposed by slow addition of cold water (500 ml) then chloroform (250 ml) was added. The organic phase was separated then washed three times with saturated solution of sodium chloride (200 ml) and dried over anhydrous magnesium sulfate. Washing of the organic phase usually caused formation of thick emulsion which was broken by gentle heating and stirring. Chloroform was distilled off and the liquid was fractionated under reduced pressure to afford 354.4 g (86 %) of 2 as colorless liquid: b.p. 107-108° /24 torr; $n_D^{25} = 1.3886$; IR (neat) 3600, 3500(br.), 1610, 1493, 1450, 1367, 1310-1095 (br. CF₃), 972, 914, 832, 800 cm⁻¹; ¹H-NMR (CDCl₃) $\delta = 8.27$ (s, 1H_{arom}); 8.02-7.48(m, 3H_{arom}); 3.50 ppm (s, 2H, -OH); ¹⁹F-NMR (CDCl₃) -77.0 ppm (s, -C(CF₃)₂OH); a weak signal of 3 at -76.9 ppm (s, -C(CF₃)₂OH) (lit., [4,5], b.p. 106°/ 20 torr; $n_D^{20} = 1.3882$).

The last fraction (14.1 g, b.p. 108-114°/24 torr) which partially solidified on storage was a mixture of 2 and 3.

b The reaction of benzene with HFA (1: 1.82 molar ratio)

The reaction of benzene (20.0 g, 0.256 mol) with hexafluoroacetone (77.5 g, 0.467 mol) and aluminum chloride (6 g) was carried out in a 100 ml three-necked flask in the same manner as described in part "a" except that HFA was admitted into the reaction mixture during a 5 hr period. Fractionation of the crude reaction mixture gave 12.5 g (20%) of 2-hydroxyhexafluoro-2-propylbenzene (1): b.p. 80-82°/25 torr; $n_D^{23} = 1.4104$; IR (neat) 3600, 3542, 1605, 1503, 1456, 1366, 1268, 1220, 1167, 1130, 1102, 1078, 1037, 972, 923 cm⁻¹;

$^1\text{H-NMR}$ (CDCl_3) δ = 7.83-7.32(m, 5H_{arom}); 3.28 ppm (s, 1H, -OH); $^{19}\text{F-NMR}$ (CDCl_3) -76.5 ppm (s, $-\text{C}(\text{CF}_3)_2\text{OH}$) (lit., [1], b.p. 55-56°/12 torr) and 56.5 g (54%) of 1,3-bis(2-hydroxyhexafluoro-2-propyl)benzene (2): b.p. 110-112°/25 torr.

The water washing which remained after extraction of crude product with chloroform deposited after several days a crystalline substance. The crystals were filtered, washed, dried and purified by repeated sublimation *in vacuo* to afford 3 (6.5 g; 6 %) of 1,4-bis(2-hydroxyhexafluoro-2-propyl)benzene (3): m.p. 86° (from CHCl_3); MS (70 eV) 410(M^+ , 3.1%), 341 (12.7), 271(14.3), 69(8.7), 18(100); IR (KBr) 3600-3180 (br.OH), 1620, 1280-1150(CF_3), 1097, 968, 937, 830 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3) δ = 7.80(s, 4H_{arom}); 3.77 ppm (s, 2H, -OH); $^{19}\text{F-NMR}$ (CDCl_3) -76.7 ppm (s, $-\text{C}(\text{CF}_3)_2\text{OH}$) (lit., [1], m.p. 85°).

1,3-Bis(2-hydroxyhexafluoro-2-propyl)-5-iodobenzene (4)

A 2 L three-necked flask was equipped with a thermometer, dropping funnel, condenser with drying tube and a mechanical stirrer with a Teflon blade. Fuming sulfuric acid containing 30-33% excess SO_3 (340 ml) then, iodine (76.0 g) was added and the black mixture was stirred for 1 hr to dissolve the iodine crystals. Diol 2 (200.0 g, 487 mmol) was slowly dropped to the stirred solution during 2.5 hr. The temperature of the mixture was slowly raised to 70-72° during a 1.5 hr period and was maintained for an additional 2 hr. The evolution of sulfur dioxide and an increase of the volume of the mixture was observed when the temperature reached 58°. The mixture was slowly poured into 4 L of cold water and the precipitated black oil was extracted with ether (3 x 200 ml). The combined ether extracts were washed with a saturated solution of sodium chloride and then with a solution of sodium bisulfite until the excess of iodine was removed and the organic phase became yellow colored. The ether solution was dried over anhydrous magnesium sulfate, filtered, and the solvent was distilled off. The crude product was fractionated under reduced pressure to afford 201.3 g (77 %) of 4 as slightly pink oil: b.p. 80-81°/0.1 torr; n_{D}^{20} = 1.4385; IR (neat) 3600, 3500, 1608, 1578, 1446, 1367, 1300-1110 (CF_3), 1010, 975, 923, 881 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3) δ = 8.19 (s, 2H_{arom}); 8.08(s, 1H_{arom}); 3.90 ppm (br.s, 2H, -OH); $^{19}\text{F-NMR}$ (CDCl_3) -76.6 ppm (s, $-\text{C}(\text{CF}_3)_2\text{OH}$), (lit., [4,5], b.p. 115°/10 torr; n_{D}^{20} = 1.4415).

Preparation of 1,3-bis(2-hydroxyhexafluoro-2-propyl)-5-(heptadecafluoro-n-octyl)benzene DMSO complex (5d) (nc)

The mixture of the fluorinated iodobenzene 4 (97.2 g, 181 mmol), perfluoro-n-octyl iodide (108.0 g, 198 mmol), copper powder (57.6 g) and DMSO (100 ml) was prepared in a 500 ml three necked flask under dry nitrogen atmosphere in a glove-box. The flask was fitted with a mechanical stirrer, a reflux condenser and a nitrogen inlet. The mixture was stirred and heated at 120-125° on an oil bath under nitrogen for 16 hr. The precipitated yellow solid and unreacted copper powder were filtered on a Buchner funnel and washed with DMSO (4 x 20 ml). The combined DMSO solutions were slowly poured with stirring into water (750 ml) giving a dark, heavy oil which soon solidified at room temperature. The solid was broken into small pieces, filtered off, washed with water, dried overnight in air, then dissolved in ether. The ether solution was dried over anhydrous magnesium sulfate, filtered, and the solvent was distilled off. The dark liquid was distilled in vacuo (b.p. 120-122°/0.5 torr) to afford 5d as yellowish liquid which solidified to an almost colorless solid. Additional amounts of 5d were sublimed from the magnesium sulfate which had been used to dry the ether solution. The total yield of 5d was 144.1 g (88 %). An analytical sample was further purified by recrystallization from chloroform to give colorless needles: m.p. 78°; MS (70 eV) 828(4.2%), 809(17.8), 791(8.1), 760(20.8), 759(96.9), 690(14.3), 689(66.4), 460(22.8), 459(100), 293(9.5), 119(8.8), 78(7.7), 69(11.5); IR (KBr) 3040, 1371, 1215(br. CF₂, CF₃), 1152, 1128, 1036, 1018, 977, 946, 895 cm⁻¹; ¹H-NMR (CDCl₃) δ = 8.36(s, 1H_{arom}); 8.06(s, 2H_{arom}); 5.40(s, 2H, -OH); 2.57 ppm (s, 6H, -CH₃). Anal. calcd for C₂₂H₁₁F₂₉O₃S: C, 29.15; H, 1.22. Found: C, 29.33; H, 0.99.

Preparation of DMSO complexes of 1,3-bis(2-hydroxyhexafluoro-2-propyl)-5-(perfluoro-n-alkyl)benzenes (5a-c) (all nc); General Procedure

Iodobenzene 4 (5.36 g, 10 mmol), perfluoro-n-alkyl iodide (11 mmol), copper powder (3.18 g, 50 mmol), and DMSO (5 ml) were placed into a 25 ml flask under nitrogen atmosphere in a dry-box. The flask was fitted with a magnetic stirrer, reflux condenser, and a nitrogen inlet. The mixture was stirred and heated under nitrogen in an oil bath at 135-140° (bath temperature) for 10 - 14 hr. Copper powder and cuprous iodide were filtered off with a Buchner funnel and washed thoroughly with DMSO.

The DMSO solution was poured into water (500 ml) to precipitate a heavy oil which solidified on standing at room temperature or on chilling in ice. The solid was filtered off, washed with water, dried in air overnight and sublimed in vacuo to afford colorless crystals. Analytical samples were purified by recrystallization from chloroform.

Using the general procedure, a mixture of 4 and perfluoro-*n*-propyl iodide gave 5.7 g (87 %) of the DMSO complex of 1,3-bis(2-hydroxyhexafluoro-2-propyl)-5-(heptafluoro-*n*-propyl)benzene (5a) (nc): m.p. 60-61°; MS (70 eV) 578(7.4%),559(13.9),541(7.8),510(15.1),509(94.5), 459(41.4),440(14.5),439(100),293(7.8),150(8.4),95(7.1),78(11.3), 69(37.6),63(13.5); IR(KBr) 3060(br.OH),1445,1353,1210(br.CF₂,CF₃), 1148, 1122,1105,1037,1006,972,947,874 cm⁻¹; ¹H-NMR (CDCl₃): δ = 8.34(s,1H_{arom}); 8.05(s,2H_{arom}); 5.92(s,2H,-OH); 2.57 ppm (s,6H,-CH₃). Anal. calcd for C₁₇H₁₁F₁₉O₃S: C, 31.11; H, 1.69. Found: C, 31.11; H, 1.65.

Using the general procedure, a mixture of 4 and perfluorohexyl iodide gave 6.3 g (78 %) of the DMSO complex of 1,3-bis(2-hydroxyhexafluoro-2-propyl)-5-(tridecafluoro-*n*-hexyl)benzene (5b)(nc): m.p. 59-60°; MS (70 eV) 728(4.1%),709(7.2),691(7.5),660(16.8),659(78.7),590(16.3),589(91.9), 460(15.2),459(100),423(8.9),293(13.6),223(6.5),97(11.4),78(6.8),69(25.7); IR (KBr) 3040,1430,1365,1310-1113(br.CF₂,CF₃),1060,1036,1006,975,948, 908,890 cm⁻¹; ¹H-NMR (CDCl₃) δ = 8.36(s,1H_{arom}); 8.06(s,2H_{arom}); 5.91 (s,2H,-OH); 2.58 ppm (s,6H,-CH₃). Anal. calcd for C₂₀H₁₁F₂₅O₃S: C, 29.79; H, 1.37. Found: C, 29.97; H,1.08.

Similarly, a mixture of 4 and perfluoroheptyl iodide gave 7.8 g (91%) of the DMSO complex of 1,3-bis(2-hydroxyhexafluoro-2-propyl)-5-(penta-decafluoro-*n*-heptyl)benzene (5c) (nc): m.p. 66-67; MS (70 eV) 778(7.0%), 760(6.9),759(32.3),741(14.3),739(9.1),710(35.9),709(100),640(29.3), 639(92.5),573(8.3),509(8.5),460(41.0),459(95.9),293(24.6),292(9.9), 223(12.4),160(7.1),131(12.7),119(15.9),97(12.9),78(20.1),69(36.6); IR(KBr) 3040,1368,1300-1177(br.CF₂,CF₃),1152,1100,1038,1009,978,948,902 cm⁻¹; ¹H-NMR(CDCl₃): δ = 8.36(s,1H_{arom}); 8.07(s,2H_{arom}); 5.80(s,2H,-OH); 2.60 ppm (s,6H,-CH₃). Anal. calcd for C₂₁H₁₁F₂₉O₃S: C, 29.45; H, 1.29. Found: C, 29.52; H, 0.97.

Preparation of the DMSO complex of 3,5-bis(2-hydroxyhexafluoro-2-propyl)-2',3',4',5',6',- pentafluorobiphenyl (6) (nc)

The mixture of iodobenzene 4 (2.68 g, 5.0 mmol), pentafluorophenyl iodide (1.61 g, 5.5 mmol), copper powder (1.59 g, 25 mmol), and DMSO (3 ml) was prepared under nitrogen in the same manner as described for 5a-c. The mixture was stirred and heated in an oil bath at 145° (bath temperature) for 16 hr and then poured into water (400 ml). The precipitated oil did not solidify and was extracted with ether (3 x 60 ml). Combined ether extracts were washed with water, dried over anhydrous magnesium sulfate and ether was distilled off. The remaining oil was distilled under reduced pressure (0.1 torr) to give small amount of solid as the last fraction. The solid was further purified by sublimation in vacuo. Recrystallization from chloroform gave 82 mg (2.5%) of 6 as colorless needles: m.p. 121-122°; MS (70 eV) 577(14.6%), 576(71.0), 539(9.2), 508(13.1), 507(69.1), 489(8.2), 438(16.9), 437(100), 393(12.0), 389(7.1), 373(8.5), 371(7.5), 341(8.0), 293(12.4), 271(16.1), 243(8.5), 242(19.3), 224(7.0), 218(20.8), 149(41.9), 121(9.3), 97(14.5), 78(21.9), 69(51.9); IR(KBr) 3120, 1473, 1440, 1330, 1300-1133(br.CF₃), 1090, 1032, 986, 953, 896 cm⁻¹; ¹H-NMR (CDCl₃) δ = 8.24(s, 1H_{arom}); 7.90(s, 2H_{arom}); 5.59(s, 2H, -OH); 2.57 ppm (s, 6H, -CH₃); ¹⁹F-NMR (CDCl₃) -76.5(s, 12F, -C(CF₃)₂OH); -144.4(d of d, 2F_{2',6'}); -155.1(t, 1F_{4'}); -162.2 ppm (d, 2F_{3',5'}). Anal. calcd for C₂₀H₁₁F₁₇O₃S: C, 36.71; H, 1.69. Found: C, 36.75; H, 1.39.

Preparation of the DMSO complex of 1,3-bis(2-hydroxyhexafluoro-2-propyl)benzene (8) (nc)

a) Iodobenzene 4 (5.36 g, 10 mmol), 2-iodoheptafluoropropane (3.25g, 11 mmol), copper powder (3.18g, 50 mmol), and DMSO (5 ml) were heated and stirred under nitrogen in an oil bath at 135-140° for 10 hr. After filtering copper powder and cuprous iodide the DMSO solution was poured into water. The precipitated oil solidified on cooling the mixture in ice. The solid was washed with water, dried and sublimed in vacuo to yield 3.8 g of the product. Recrystallization from chloroform gave 8 as colorless crystals; m.p. 87°.

b) Iodobenzene 4 (2.68 g, 5 mmol), copper powder (1.59 g, 25 mmol), and DMSO (3 ml) were heated under nitrogen at 135-140° for 23 hr. After work-up as described in part "a" the semi-solid crude product was isolated

and distilled (0.05 torr) in a micro-distillation apparatus to afford colorless oil which on standing for several days deposited crystals. The solid was separated from unreacted starting iodobenzene 4 and recrystallized from chloroform to yield 48 mg of 8; m.p. 87°.

c) 1,3-Bis(2-hydroxyhexafluoro-2-propyl)benzene (2) (410 mg, 1 mmol) was dissolved in DMSO (3 ml) and the solution was stirred and heated under nitrogen at 120-125° for 5 hr. The solution was poured into water (60 ml) to precipitate an oil which immediately solidified. The solid was isolated by suction, washed thoroughly with water, dried and sublimed in vacuo to afford 211 mg (43%) of 8: m.p. 87°; MS (70 eV) 410(39.3%), 373(19.6), 353(25.4), 342(27.1), 341(96.9), 323(14.6), 272(28.9), 271(100), 227(14.7), 223(18.8), 207(17.0), 175(14.7), 145(28.6), 127(26.6), 105(39.7), 97(15.8), 78(38.3), 77(22.9), 69(48.1), 66(20.6), 63(40.5); IR (KBr) 3080 (br.OH), 1250(br.CF₃), 1093, 998, 972, 943, 926, 912, 810 cm⁻¹; ¹H-NMR (CDCl₃) δ = 8.16(s, 1H_{arom}); 7.87-7.33(m, 3H_{arom}); 5.53(s, 2H, -OH); 2.57 ppm (s, 6H, -CH₃); ¹⁹F-NMR (CDCl₃) -76.6 ppm (s, -C(CF₃)₂OH). Anal. calcd for C₁₄H₁₂F₁₂O₃S: C, 34.44 H, 2.48. Found: C, 34.63; H, 2.11.

Decomposition of the DMSO Complex 5a

The complex 5a (1.0g, 1.5 mmol) was dissolved in 5 ml of 5% aqueous sodium hydroxide and heated to 80-90° for 20 minutes. The solution was acidified with hydrochloric acid and the organic layer removed by ether extraction. The combined ether extracts were washed with water, dried over anhydrous magnesium sulfate then concentrated to a heavy oil. Micro distillation of the crude product gave 600 mg (68%) of 1,3-bis(2-hydroxyhexafluoro-2-propyl)-5-(perfluoro-n-propyl)benzene (5a') as a colorless liquid which slowly solidified on storage to colorless crystals: m.p. 46-47° (lit., [4,5] m.p. 48°); IR (neat) 3600, 3310, 1612, 1464, 1353, 1280-1105 (br. CF₂, CF₃), 1077, 1013, 980, 893, 878 cm⁻¹; ¹H-NMR(CDCl₃) δ = 8.34 (s, 1H_{arom}); 8.09 (s, 2H_{arom}); 4.33 ppm (s, 2H, -OH). See table for ¹⁹F-NMR spectrum.

Decomposition of the DMSO Complex 5d

The complex 5d (1.0g, 1.1 mmol) was dissolved in 6 ml of 5% aqueous sodium hydroxide and heated to 90° for 3 hours. The solution was acidified and on cooling deposited the free diol as a solid. Micro-distillation of the crude product gave 500 mg (55%) of 1,3-bis(2-hydroxyhexafluoro-2-propyl)-5-(perfluoro-n-octyl)benzene (5d')(nc) as a colorless viscous liquid: b.p. 60°/0.05 torr; $n_D^{26} = 1.3538$; IR(neat) 3600,3240,1605,1465,1368,1300-1120(br. CF₂, CF₃),1010, 980,897,863 cm⁻¹; ¹H-NMR (CDCl₃) δ =8.34 (s,1H_{arom}); 8.08 (s,2H_{arom}); 4.45 ppm (s,2H-OH). See table for ¹⁹F-NMR spectrum.

The last fraction of the distillation (ca. 400 mg) solidified on the cold finger and was found to be unchanged complex 5d.

All DMSO complexes dissociated on election impact in the mass spectragraph thus showing only molecular ions of the free diols: 5a (578 M⁺); 5b (728, M⁺); 5c (778, M⁺); 5d (828, M⁺), 6 (576, M⁺); 8 (410, M⁺). The molecular ion of DMSO at mass 78 was a principal peak in all spectra.

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REFERENCES

- 1 B. S. Farah, E. E. Gilbert, J. P. Sibilis, J. Org. Chem. 30, (1965) 998.
- 2 E. E. Gilbert, E. S. Jones, J. P. Sibilis, J. Org. Chem. 30, (1965) 1001.
- 3 B. S. Farah, E. E. Gilbert, M. Litt, J. A. Otto, J. P. Sibilis, J. Org. Chem. 30, (1965) 1003.
- 4 J. G. O'Rear, J. R. Griffith, Preprint Booklet of the Organic Coatings and Plastics Division, American Chemical Society 33, No. 1, April 8-13, 1973, pps. 657-662; C. A. 82, (1975) 58626.
- 5 J. G. O'Rear, J. R. Griffith, U. S. Patent 3 879 430 (1975); C. A. 83, (1975) 58638.
- 6 Tuyen T. Nguyen, R. L. Amey, J. C. Martin, J. Org. Chem. 47, (1982) 1024.
- 7 J. R. Griffith, J. G. O'Rear, Synthesis 1974, 493.
- 8 W. J. Middleton and R. V. Lindsey, Jr., J. Am. Chem. Soc. 86 (1964) 4948.
- 9 V. C. R. McLoughlin, J. Thrower, Tetrahedron 25, (1969) 5921.