ELSEVIER

Journal of Fluorine Chemistry 84 (1997) 35–40

JOURNAL OF FLUORINE CHEMISTRY

Fluorinated diols from the mercury-photosensitized dehydrodimerization of fluorinated alcohols in the vapour phase

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Received 21 October 1996; accepted 28 February 1997

Abstract

Several fluorinated diols were synthesized from commercially available fluorinated alcohols via mercury-photosensitized dehydrodimerization in the vapour phase. In almost all cases, the corresponding *dl*- and *meso*-diols were obtained in a 50 : 50 ratio. Field-ionization (FI) and field-desorption (FD) mass spectrometry proved effective as an analytical method for these diols. The nuclear magnetic resonance (NMR) characteristics of the symmetrically substituted diols depend strongly on their stereochemical nature (*dl*- and *meso*-diastereoisomers) and substituents. The presence of the $-CF_2H$ end group, as in 1,1,4,4-tetrafluoro-2,3-butanediol and 1,1,2,2,5,5,6,6-octafluoro-3,4-hexanediol, causes an additional inequivalence in the *meso*-form due to molecular asymmetry. The ^1H and ^{19}F NMR spectra of 1,1,4,4-tetrafluoro-2,3-butanediol and the ^{19}F NMR spectrum of 1,1,2,2,5,5,6,6-octafluoro-3,4-hexanediol have been fully interpreted. © 1997 Elsevier Science S.A.

Keywords: Fluorinated alcohols; Fluorinated diols; Mercury-photosensitized dehydrodimerization; Vapour phase

1. Introduction

It is well known that highly fluorinated materials exhibit a unique set of properties, such as chemical resistance, resistance to aging, flame resistance, attractive surface properties, hydrophobicity and lubricity. Since fluorinated materials possess these unique properties, their use offers distinctive advantages, making them superior for special demands throughout the chemical industry [1]. Therefore there is a continuous interest in the synthesis of novel fluorinated compounds.

Fluorinated diols are often used as precursors for highly fluorinated polymers, namely for polyamides, polyesters and polyurethanes [2–4]. Brown and Crabtree [5,6] have previously identified a powerful method for the preparation of 1,1,1,4,4,4-hexafluoro-2,3-butanediol based on mercury-photosensitized dehydrodimerization in the vapour phase. Our laboratory previously utilized this method for the preparation of novel polyesters and polyurethanes [7]. In this study, the mercury-photosensitized dehydrodimerization method is employed for a range of fluorinated longer chain alcohols.

Most of the starting alcohols contain a $-CF_2H$ end group. The nuclear magnetic resonance (NMR) spectra of the corresponding alcohol precursors have been interpreted. Due to the formation of the diastereoisomers of the resulting diols, the interpretation of their NMR spectra is considerably more difficult. As yet, no literature data for these compounds are available. Using a home-generated computer programm (PHIP) [8], the NMR data of the products have been analysed and verified [8].

For mass spectrometry analysis, field-ionization (FI) and field-desorption (FD) techniques have been chosen, since electron impact (EI) and fast atom bombardment (FAB) produced only poor results.

2. Results and discussion

The reaction scheme is believed to follow the sequence outlined below [6]

$$\underset{(A)}{HCR_1R_2OH} \xrightarrow{Hg^*} HCR_1R_2O^{\bullet} + H^{\bullet} \quad (1)$$

$$HCR_1R_2O^{\bullet} + HCR_1R_2OH \rightarrow HCR_1R_2OH + {}^{\bullet}CR_1R_2OH \quad (2)$$

$$2{}^{\bullet}CR_1R_2OH \rightarrow \underset{(D)}{HOR_2R_1CCR_1R_2OH} \quad (3)$$

$$2HCR_1R_2O^{\bullet} \rightarrow R_2R_1CO + HCR_1R_2OH \quad (4)$$

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PII S0022-1139(97)00038-9

Table 1
Fluorinated diols obtained via mercury-photosensitized dehydrodimerization of commercially available fluorinated alcohols

Starting alcohol/boiling point (°C)	Reaction temperature (start/end) (°C)	Reaction product (diol)/yield (%)
2H-Hexafluoro-2-propanol (A1)/58	100/120	Perfluoropinacol (D1)/50
2-Fluoroethanol (A2)/102	140/160	Decomposed (D2) dark residue
2,2-Difluoroethanol (A3)/95	135/155	1,1,4,4-Tetrafluoro-2,3-butanediol (D3)/90
2,2,2-Trifluoroethanol (A4)/74	115/135	1,1,1,4,4,4-Hexafluoro-2,3-butanediol (D4)/90
2,2,3,3-Tetrafluoro-1-propanol (A5)/109	150/175	1,1,2,2,5,5,6,6-Octafluoro-3,4-hexanediol (D5)/90
2,2,3,3,4,4,5,5-Octafluoro-1-pentanol (A6)/141	180/205	1,1,2,2,3,3,4,4,7,7,8,8,9,9,10,10-Hexadecafluoro-5,6-decanediol (D6)/90
2,2,3,3,4,4,5,5,6,6,7,7-Dodecafluoro-1-heptanol (A7)/172	210/235	Decomposed (D7) dark residue

where A denotes alcohol and D denotes diol (A1, D1: $R_1 \equiv CF_3$, $R_2 \equiv CF_3$; A2, D2: $R_1 \equiv H$, $R_2 \equiv CFH_2$; A3, D3: $R_1 \equiv H$, $R_2 \equiv CF_2H$; A4, D4: $R_1 \equiv H$, $R_2 \equiv CF_3$; A5, D5: $R_1 \equiv H$, $R_2 \equiv CF_2CF_2H$; A6, D6: $R_1 \equiv H$, $R_2 \equiv (CF_2CF_2)_2H$; A7, D7: $R_1 \equiv H$, $R_2 \equiv (CF_2CF_2)_3H$).

On excitation with UV light at 254 nm, the $^3P_1$ excited state of mercury (Hg^*) is formed initially, which induces cleavage of the O–H bond (Eq. (1)). In a subsequent step (Eq. (2)), the $^{\bullet}CR_1R_2OH$ radical is formed via H abstraction from HCR_1R_2OH by $H^{\bullet}$ or $HCR_1R_2O^{\bullet}$. Two of the substrate-derived radicals of the type $^{\bullet}CR_1R_2OH$ can either recombine to give the dimer (Eq. (3)) or disproportionate to the starting alcohol and a ketone (Eq. (4)).

After several days, depending on the amount of alcohol, the reflux starts to slow down. NMR measurements indicate that only partial conversion to the diol has been achieved. To attain high yields of dimerization products, the temperature must be increased during the reaction time (i.e. continuous reflux must be maintained) (Table 1). Due to the reflux conditions, subsequent reactions of the product are prevented because of its much lower vapour pressure relative to that of the starting alcohol (''vapour pressure selectivity'') [6].

2,2-Difluoroethanol, 2,2,2-trifluoroethanol, 2,2,3,3-tetrafluoro-1-propanol and 2,2,3,3,4,4,5,5-octafluoro-1-pentanol dimerize in yields of about 90% to the corresponding *dl*- and *meso*-glycols in a 50 : 50 ratio. 2-Fluoroethanol and 2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoro-1-heptanol yield only a dark residue, which cannot be identified.

1,1,1,4,4,4-Hexafluoro-2-propanol dimerizes in a yield of about 50% to perfluoropinacol. Generally, the disproportionation reaction (Eq. (4)) competes with the transfer reaction (Eq. (2)), leading to undesirable products. Secondary alcohols exhibit a significantly higher disproportionation rate in comparison with primary alcohols [6]. For the dimerization of 1,1,1,4,4,4-hexafluoro-2-propanol, reaction (4) seems to be the major route, producing hexafluoroacetone, which reduces the yield of perfluoropinacol. Hexafluoroacetone is very volatile (b.p., −28 °C) and therefore it is readily removed from the irradiation set-up. The perfluoropinacol so obtained is a liquid, which is further purified via distillation (Table 1).

Even though perfluoropinacol has been known for a long time [9], the mercury-photosensitized dehydrodimerization provides a very convenient laboratory-scale preparation method, which reduces the risk of contact with this acutely toxic material [9]! Because of this toxicity, the analysis of perfluoropinacol has been restricted to the determination of its boiling point and ^{13}C NMR data.

The fluorinated diols obtained exhibit a similar behaviour to perfluoropinacol with various solvents, i.e. the formation of complexes with the solvent [9]. Furthermore, their solubility in conventional solvents is limited. Therefore the separation of the diastereoisomers via column chromatography is inappropriate. About 30% of the *meso*-diols of 1,1,4,4-tetrafluoro-2,3-butanediol and 1,1,1,4,4,4-hexafluoro-2,3-butanediol can be recovered via recrystallization from CH_2Cl_2. However, complete separation of the *dl*-diols from the *meso*-diols is difficult. Therefore fractionation of the *dl*-diols via distillation is necessary, even though some *meso*-diol usually remains as an impurity. Both the *meso*- and *dl*-diols of 1,1,2,2,5,5,6,6-octafluoro-3,4-hexanediol and 1,1,2,2,3,3,4,4,7,7,8,8,9,9,10,10-hexadecafluoro-5,6-decanediol are solids. Nevertheless, distillation was also chosen for their purification.

2.1. ^1H and ^{19}F NMR spectroscopy and simulation of the spectra

The NMR characteristics of the symmetrically substituted diols depend strongly on their stereochemical nature (*meso* and *dl*) and substituents (Fig. 1) [10,11]. Furthermore, as shown by Gutowsky [12], the $–CF_2H$ end group, e.g. in 1,1,4,4-tetrafluoro-2,3-butanediol and 1,1,2,2,5,5,6,6-octafluoro-3,4-hexanediol, causes an additional inequivalence in the *meso*-form due to molecular asymmetry based on differences in the conformational population [13].

2.2. meso-1,1,4,4-Tetrafluoro-2,3-butanediol $(HCF_2CHOH)_2$

In the ^1H NMR spectrum of *meso*-1,1,4,4-tetrafluoro-2,3-butanediol, we assign the triplet (5.96 ppm) to the protons

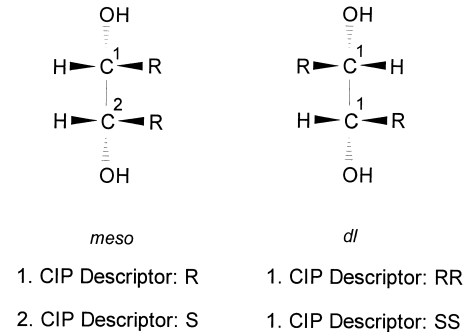

Fig. 1. CIP description of the *meso*- and *dl*-diols.

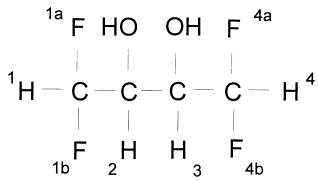

Fig. 2. *meso*-1,1,4,4-Tetrafluoro-2,3-butanediol.

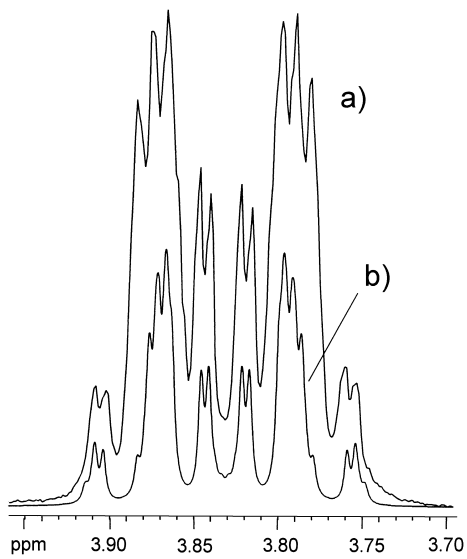

Fig. 3. Experimental ^{1}H NMR spectrum (a) and computer simulation (b) of *meso*-1,1,4,4-tetrafluoro-2,3-butanediol (multiplet 3.83 ppm, DMSO-d_6 + CF_3COOH).

H(1) and H(4) ($^{2}J_{HF}$ = 54.9 Hz) (Fig. 2). The multiplet at 3.83 ppm is assigned to the H(2) and H(3) protons. It is known that $-CX_2Y$ groups in an asymmetric environment cause ^{1}H and ^{19}F NMR splittings due to molecular asymmetry [12]. In this case, we assume that, due to the asymmetric $-CF_2H$ rotor, the fluorine atoms are chemically and magnetically inequivalent. In addition, it is necessary to consider the protons H(2) and H(3) as an A,B system, even though we might expect an AA′ spin system. Both protons show a coupling constant of 19.5 Hz to the vicinal fluorine atoms ^{19}F(a), which is within the typical range of $^{3}J_{HF}$ couplings. The multiplet only reveals a doublet splitting rather than a triplet in the ^{1}H NMR spectrum ($^{3}J_{HF}$). This observation seems to result from the fact that the coupling to the second vicinal fluorine atoms ^{19}F(b) is smaller than the resolution

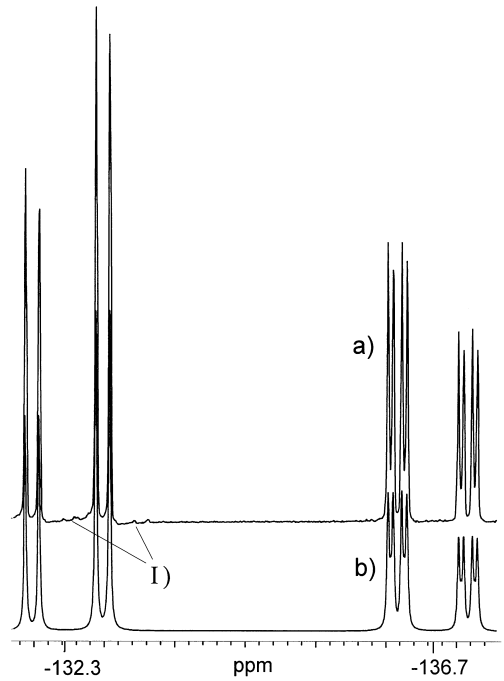

Fig. 4. Experimental ^{19}F NMR spectrum (a) and computer simulation (b) of *meso*-1,1,4,4-tetrafluoro-2,3-butanediol (DMSO-d_6); I, impurity or spinning sidebands.

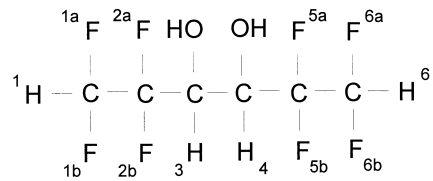

Fig. 5. *meso*-1,1,2,2,5,5,6,6-Octafluoro-3,4-hexanediol.

limit of our experiment. The ^{19}F NMR experiment confirms this conclusion, since in the ^{19}F NMR spectrum the ^{19}F(b) resonance lacks the corresponding splittings $^{3}J_{H(2)F(b)}$ and $^{3}J_{H(3)F(b)}$.

In order to analyse the multiplet at 3.83 ppm in the ^{1}H NMR spectrum, we initially omit the 19.5 Hz coupling and treat the resulting spectrum as an ABMM′XX′ system. The triplet ($^{2}J_{HF}$ = 54.9 Hz) at 5.96 ppm is assigned to the $-CF_2H$ end group. No further splitting occurs, in particular there is no evidence for a coupling between H(1), H(2) and H(3), H(4) ($^{3}J_{HH}$), according to the experimental data. The simulation of the ABMM′XX′ system reproduces the ^{1}H NMR spectrum with the correct intensities. Assuming $^{3}J_{HF}$ = 19.5 Hz, the complete ^{1}H NMR spectrum of *meso*-1,1,4,4-tetrafluoro-2,3-butanediol can be simulated (Figs. 3 and 4).

2.3. meso-1,1,2,2,5,5,6,6-Octafluoro-3,4-hexanediol ($HCF_2CF_2CHOH-)_2$

meso-1,1,2,2,5,5,6,6-Octafluoro-3,4-hexanediol (Fig. 5) exhibits the same characteristics as *meso*-1,1,4,4-tetrafluoro-2,3-butanediol, i.e. the same symmetry elements and the corresponding asymmetry of the rotors in an asymmetric environment. In order to reduce the complexity of the NMR

spectra, the letter Y is assigned to the –**CF_2H** part of the –CF_2**CF_2H** end group. This makes it obvious that we are again dealing with the corresponding, asymmetrically rotating CX_2Y end group, as in *meso*-1,1,4,4-tetrafluoro-2,3-butanediol. Therefore the splitting of the two fluorine atoms in C**F_2**CF_2H can be analysed accordingly. Furthermore, considering the CF_2H group as also rotating asymmetrically itself, it seems straightforward to interpret the splitting of the fluorine atoms in the C**F_2**H end group as above. With this approach, the ^{19}F NMR spectrum can readily be analysed.

The simulation of the ^{1}H NMR spectrum is time consuming, since it is a 14-spin system. Even when neglecting the exchanging –OH protons, there still remains a 12-spin system which, even on a fast computer, requires a long calculation time. In order to verify this approach, the ^{19}F NMR spectrum was chosen for the simulation. From the simulation of *meso*-1,1,4,4-tetrafluoro-2,3-butanediol as outlined above, it has been concluded that no $^4J_{HF}$ couplings are visible in the spectrum, and that the $^3J_{HF}$ coupling constants of H(1) and H(3) are equal. This implies that only one-half of the molecule (mirror plane) is needed for the simulation, which significantly shortens the time required for the calculation.

2.4. meso-1,1,2,2,3,3,4,4,7,7,8,8,9,9,10,10-Hexadecafluoro-5,6-decanediol ($H(CF_2CF_2)_2CHOH–)_2$

The ^{1}H NMR spectrum of *meso*-1,1,2,2,3,3,4,4,7,7,8,8,9,9,10,10-hexadecafluoro-5,6-decanediol resembles that of *meso*-1,1,2,2,5,5,6,6-octafluoro-3,4-hexanediol. Since the present case corresponds to a 22-spin system, a full simulation via computer is inappropriate. However, we can postulate the same coupling concept and analogous splittings due to asymmetric rotors as in 1,1,2,2,5,5,6,6-octafluoro-3,4-hexanediol, as discussed above.

3. Experimental details

3.1. Materials

2-Fluoroethanol, 2,2-difluoroethanol and 2,2,2-trifluoroethanol were obtained from ABCR (Karlsruhe, Germany). 1,1,1,3,3,3-Hexafluoro-2-propanol, 2,2,3,3-tetrafluoro-1-propanol, 2,2,3,3,4,4,5,5-octafluoro-1-pentanol and 2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoro-1-heptanol were gifts from Hoechst AG, Frankfurt. All alcohols were employed without further purification.

3.2. The reflux apparatus

For the dimerization of the alcohols, we used a reactor similar to that of Brown and Crabtree [5,6], consisting of a two-necked round flask (50 ml, 100 ml or 250 ml) with a magnetic stirring bar, equipped with a cylindrical quartz tube (30 cm in length, 3.5 cm in diameter) and a gas inlet. In order to work under continuous reflux conditions, we fitted the quartz tube with a conventional glass reflux condenser. As the light source for irradiation at 254 nm, six Philips TUV8W low-pressure mercury lamps were employed, surrounding only the quartz tube. This set-up provides for easy access, exchange of the quartz and glassware and cleaning, as well as for easy addition or removal of chemicals. The corresponding alcohol and a drop of mercury were placed into the flask. The apparatus was then flushed with argon for about 5 min. The alcohol was heated until a continuous reflux was visible at the reflux condenser.

The FI and FD mass spectra were obtained using a modified double focusing AEI KRATOS MS-9 mass spectrometer equipped with an FD ion source. At the applied emitter potential of 6 kV, the mass range was 1670 u. The counter electrode was kept at -6 kV, i.e. 12 kV was applied between the emitter and the counter electrode. The FD source was equipped with viewing windows and a stereomicroscope, which allowed the exact positioning of the loaded part of the emitter with respect to the counter electrode and of the ion optics of the mass analyser without the need for an ion signal.

The FD emitter was prepared by activation of a 10 μm tungsten wire with indene. The length of the needle was about 30 μm. The sample was loaded onto the emitter by dipping it into a solution of 1,1,2,2,3,3,4,4,7,7,8,8,9,9,10,10-hexadecafluoro-5,6-decanediol in acetonitrile. For recording the FI mass spectra, the gas pressure of the samples was about 10^{-4} mbar.

The mass spectra were recorded with a three-channel strip chart recorder covering a dynamic range of up to five decades. In order to obtain full mass spectra, a mass scan of 20–100 s per decade and steps of 2 mA for the emitter heating current were applied [14].

3.3. Perfluoropinacol (D1)

B.p., 128 °C (129 °C [9]). ^{13}C NMR (50 MHz, $CDCl_3$): CF_3: $\delta = 122.0$ ppm (quartet), $^1J_{CF} = 292.5$ Hz; COH: $\delta = 80.9$ ppm (septet), $^2J_{CF} = 30$ Hz.

3.4. 1,1,4,4-Tetrafluoro-2,3-butanediol (D2) ($HCF_2CHOH–)_2$ ($M = 162$ g mol^{-1})

FI-MS (m/z) of *meso*-1,1,4,4-tetrafluoro-2,3-butanediol: 163 $(M+H)^+$ 21%, 161 $(M-H)^+$ 1.4%, 111 $(M-CF_2H)^+$ 24%, 81 $(M/2)^+$ 54%, 51 $(CF_2H)^+$ 78%, 31 $(HCOH_2)^+$ 100%.

meso-1,1,4,4-Tetrafluoro-2,3-butanediol: m.p., 95 °C. ^{13}C NMR (50 MHz, D_2O, ^{1}H decoupled): CF_2H: $\delta = 114$ ppm (t), $^1J_{CF} = (241$ Hz); CH: $\delta = 67.7$ ppm (t), $^2J_{CF} = (21$ Hz). ^{1}H NMR (250 MHz, DMSO-d_6 + CF_3COOH) (Table 2): H(2): $\delta = 3.82$ ppm (m); H(3): $\delta = 3.85$ (m); CF_2H: $\delta = 5.96$ ppm (t), $^2J_{HF} = 54.9$ Hz; OH: (shifted with CF_3COOH). ^{19}F NMR (282 MHz, DMSO-d_6, internal reference $CFCl_3$) (Table 2): F(1a), F(4a): $\delta = -136.7$ ppm (ddd), $^2J_{F(a)F(b)} = 282.7$ Hz, $^2J_{HF} = 54.9$ Hz, $^3J_{HF} = 19.5$ Hz;

Table 2
Chemical shifts and coupling constants of *meso*-1,1,4,4-tetrafluoro-2,3-butanediol

H(1), H(4)	(t)	$\delta = 5.96$ ppm	$^2J_{HF} = 54.9$ Hz	$^3J_{HH} = 0$ Hz	
H(2)	(m)	$\delta = 3.82$ ppm	$^3J_{HF(a)} = 19.5$ Hz	$^3J_{HF(b)} = 1.05$ Hz	$^3J_{H(2)H(3)} = 9.5$ Hz
H(3)	(m)	$\delta = 3.85$ ppm	$^3J_{HF(a)} = 19.5$ Hz	$^3J_{HF(b)} = 1.05$ Hz	$^3J_{H(2)H(3)} = 9.5$ Hz
F(1a), F(4a)	(ddd)	$\delta = -136.7$ ppm	$^2J_{F(a)F(b)} = 282.7$ Hz	$^2J_{HF} = 54.9$ Hz	$^3J_{HF} = 19.5$ Hz
F(1b), F(4b)	(dd)	$\delta = -132.3$ ppm	$^2J_{F(a)F(b)} = 282.7$ Hz	$^2J_{HF} = 54.9$ Hz	$^3J_{HF} = 1$ Hz

Table 3
^{19}F NMR chemical shifts and coupling constants of *meso*-1,1,2,2,5,5,6,6-octafluoro-3,4-hexanediol. H(1) = H(6), δH(3) ≈ δH(4) ($J_{(3H)} = J_{(4H)}$), F(1a) = F(6a), F(1b) = F(6b), F(2a) = F(5a), F(2b) = F(5b)

	H(1), $\delta = 6.48$ ppm, tdd	F(1a), $\delta = -139.7$ ppm, ddm	F(1b), $\delta = -134.0$ ppm, ddd	F(2a), $\delta = -127.4$ ppm, dm	F(2b), $\delta = -125.1$ ppm, dm	H(3), $\delta = 3.88$ ppm, m
H(1) (Hz)	–	52.5	52.5	2.5	9.5	0
F(1a) (Hz)	–	–	299	12	7	0
F(1b) (Hz)	–	–	–	0	11.6	0
F(2a) (Hz)	–	–	–	–	286.6	19.5
F(2b) (Hz)	–	–	–	–	–	4.5

F(1b), F(4b): $\delta = -132.3$ ppm (dd), $^2J_{F(a)F(b)} = 282.7$ Hz, $^2J_{HF} = 54.9$ Hz, $^3J_{HF} = 1$ Hz.

dl-1,1,4,4-Tetrafluoro-2,3-butanediol. ^{13}C NMR (50 MHz, D_2O, ^{1}H decoupled): CF_2H: $\delta = 113.7$ ppm (t), $^1J_{CF} = 241$ Hz; CH: $\delta = 67$ ppm (t), $^1J_{CF} = 21$ Hz. ^{1}H NMR (250 MHz, DMSO-d_6 + CF_3COOH): CH: $\delta = 3.6$ ppm (td), $^3J_{HF} = 16.2$ Hz, $^3J_{HH} = 4.5$ Hz; OH: (shifted with CF_3COOH); CF_2H: $\delta = 5.9$ ppm (td), $^2J_{HF} = 55$ Hz, $^3J_{HH} = 4.5$ Hz. ^{19}F NMR (282 MHz, DMSO-d_6, internal reference $CFCl_3$): CF_2H: $\delta = 130.3$ ppm (dd), $^2J_{HF} = 55$ Hz, $^3J_{HF} = 16.5$.

3.5. 1,1,1,4,4,4-Hexafluoro-2,3-butanediol (D3) ($CF_3CHOH–)_2$ ($M = 198$ g mol^{-1})

FI-MS (m/z) of *meso*-1,1,1,4,4,4-hexafluoro-2,3-butanediol: 199 $(M+H)^+$ 8%, 197 $(M-H)^+$ 8%, 181 $(M-H_2O+H)^+$ 5%, 167 $(M-HCOH_2)^+$ 18%, 129 $(M-CF_3)^+$ 19%, 99 $(M/2)^+$ 100%, 69 $(CF_3)^+$ 11%, 31 $(HCOH_2)^+$ 80%.

meso-1,1,1,4,4,4-Hexafluoro-2,3-butanediol: m.p. 102 °C (85 °C [6]). ^{13}C NMR (50 MHz, CD_3CN, ^{1}H decoupled): CF_3: $\delta = 125.4$ ppm (quartet), $^1J_{CF} = 282.6$ Hz; COH: $\delta = 69.1$ ppm (t), $^2J_{CF} = 31$ Hz. ^{1}H NMR (250 MHz, CD_3CN): H(2), H(3): $\delta = 4.25$ ppm (m, AA′$X_3X'_3$); HO: $\delta = 4.65$ ppm (s). ^{19}F NMR (282 MHz, CD_3CN, internal reference $CFCl_3$): CF_3: $\delta = -75.0$ ppm (m).

dl-1,1,1,4,4,4-Hexafluoro-2,3-butanediol. ^{13}C NMR (50 MHz, CD_3CN, ^{1}H decoupled): CF_3: $\delta = 125.1$ ppm (quartet), $^1J_{CF} = 282.6$ Hz; COH: $\delta = 67.8$ ppm (quartet), $^2J_{CF} = 31$ Hz. ^{1}H NMR (250 MHz, CD_3CN): CH: $\delta = 4.38$ ppm (quartet), $^3J_{HF} = 7.1$ Hz; HO: $\delta = 4.65$ ppm (s). ^{19}F NMR (282 MHz, CD_3CN, internal reference $CFCl_3$): CF_3: $\delta = -76.9$ ppm (d), $^3J_{HF} = 7.1$ Hz.

3.6. 1,1,2,2,5,5,6,6-Octafluoro-3,4-hexanediol (D4) ($HCF_2CF_2CHOH–)_2$ ($M = 262$ g mol^{-1})

FI-MS (m/z)of *meso*-, *dl*-mixture (90 : 10): 263 $(M+H)^+$ 23%, 261 $(M+H)^+$ 9%, 161 $(M-HCF_2CF_2)^+$ 65%, 131 $(M/2)^+$ 100%, 101 $(HCF_2CF_2)^+$ 41%, 31 $(HCOH_2)^+$ 76%.

meso-1,1,2,2,5,5,6,6-Octafluoro-3,4-hexanediol. ^{13}C NMR (50 MHz, DMSO-d_6, ^{1}H decoupled): CF_2: $\delta = 116.3$ ppm (tt), $^1J_{CF} = 254$ Hz, $^2J_{CF} = 24$ Hz; CF_2H: $\delta = 110$ ppm (tt), $^1J_{CF} = 248$ Hz, $^2J_{CF} = 31.5$ Hz; CH: $\delta = 67.1$ ppm (t), $^2J_{CF} = 22$ Hz. ^{1}H NMR (250 MHz, DMSO-d_6 + CF_3COOH): H(1), H(6): $\delta = 6.48$ ppm (tdd), $^2J_{HF} = 52.5$ Hz, $^3J_{H(1)F(2b)} = 9.5$ Hz, $^3J_{H(1)F(2a)} = 2.5$ Hz; H(3) ≈ H(4): $\delta = 3.88$ ppm (m) ($J_{H(3)} = J_{H(4)}$). ^{19}F NMR (282 MHz, DMSO-d_6, internal reference $CFCl_3$) (Table 3): F(1a), F(6a): $\delta = -139.7$ ppm (ddm), $^2J_{FF} = 299$ Hz, $^2J_{HF} = 52.5$ Hz, $^3J_{F(1a)F(2a)} = 12$ Hz, $^3J_{F(1a)F(2b)} = 7$ Hz; F(1b), F(6b): $\delta = -134.0$ ppm (ddd), $^2J_{FF} = 299$ Hz, $^2J_{HF} = 52.5$ Hz, $^3J_{F(1b)F(2b)} = 11.6$ Hz; F(2a), F(5a): $\delta = -127.44$ ppm (dm), $^2J_{FF} = 268.5$ Hz, $^3J_{F(2a)H(3)} = 19.5$ Hz, $^3J_{F(2a)F(1a)} = 12$ Hz, $^3J_{F(2a)H(1)} = 2.5$ Hz; F(2b), F(5b): $\delta = -125.1$ ppm (dm), $^2J_{FF} = 268.5$ Hz, $^3J_{F(2b)F(1b)} = 11.6$ Hz, $^3J_{F(2b)H(1)} = 9.5$ Hz, $^3J_{F(2b)F(1a)} = 7$Hz, $^3J_{F(2b)H(3)} = 4.5$ Hz.

dl-1,1,2,2,5,5,6,6-Octafluoro-3,4-hexanediol. ^{13}C NMR (50 MHz, DMSO-d_6, ^{1}H decoupled): CF_2: $\delta = 116.8$ ppm (tt), $^1J_{CF} = 254$ Hz, $^2J_{CF} = 24$ Hz; CF_2H: $\delta = 110.5$ ppm (tt), $^1J_{CF} = 248$ Hz, $^2J_{CF} = 31.5$ Hz; CH: $\delta = 65.4$ ppm, t, $^2J_{CF} = 22$ Hz. ^{1}H NMR (250 MHz, DMSO-d_6 + CF_3COOH): CF_2H: $\delta = 6.4$ ppm (tt), $^2J_{HF} = 52.5$ Hz, $^3J_{HF} = 6$ Hz; CH: $\delta = 4$ ppm (t), $^3J_{HF} = 13$ Hz. ^{19}F NMR (282 MHz, DMSO-d_6, internal reference $CFCl_3$): HCF_2: −142.7 ppm (dm), $^2J_{HF} = 52.5$ Hz; CF_2: −133.7 ppm (m).

3.7. 1,1,2,2,3,3,4,4,7,7,8,8,9,9,10,10-Hexadecafluoro-5,6-decanediol (D5) ($H(CF_2CF_2)_2CHOH–)_2$ ($M = 462$ g mol^{-1})

FD-MS of *meso*-, *dl*-mixture (70 : 30): 463 $(M+H)^+$ 37.5%, 461 $(M-H)^+$ 40%, 261 $(M-(CF_2CF_2)_2H)^+$ 100%, 231 $(M/2)^+$ 67.5%, 201 $((CF_2CF_2)_2H)^+$ 35%, 31 $(HCOH_2)^+$ 19%.

meso-1,1,2,2,3,3,4,4,7,7,8,8,9,9,10,10-Hexadecafluoro-5,6-decanediol. ^{13}C NMR (50 MHz, CD_3CN, ^{1}H decoupled): $(CF_2CF_2)_2H$: $\delta = 105.7$–122 ppm (m); CH: $\delta = 68.6$ ppm (t), $^2J_{CF} = 23.5$ Hz. ^{1}H NMR (200 MHz, CD_3CN): H(1), H(10): $\delta = 6.44$ ppm (td), $^2J_{HF} = 52$ Hz, $^3J_{HF} = 9$ Hz; OH: $\delta = 4.65$ ppm (s); H(5) ≈ H(6): $\delta = 4.6$ ppm (m) ($J_{H(5)} = J_{H(6)}$).

dl-1,1,2,2,3,3,4,4,7,7,8,8,9,9,10,10-Hexadecafluoro-5,6-decanediol. ^{13}C NMR (50 MHz, CD_3CN, ^{1}H decoupled): $(CF_2CF_2)_2H$: $\delta = 105.4$–122 ppm (m); CH: $\delta = 66.2$ ppm (t), $^2J_{CF} = 23.5$ Hz. ^{1}H NMR (200 MHz, CD_3CN): CF_2H: $\delta = 6.4$ ppm (tt), $^2J_{HF} = 52$ Hz, $^3J_{HF} = 5.5$ Hz; CH: $\delta = 4.1$ ppm (t), $^3J_{HF} = 14$ Hz; OH: $\delta = 4.65$ ppm (s).

Acknowledgements

This work was supported by the German Ministry for Science and Technology (BMFT) and the Fonds der Chemischen Industrie. We are grateful to Hoechst AG for generously supplying the chemicals used in this research. We thank G. Klesper for the FI- and FD-MS and J. Barkemayer for the ^{19}F NMR measurements. J.V. thanks the Deutsche Forschungsgemeinschaft for a graduate fellowship within the scope of a Graduiertenkolleg.

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