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SYNTHESIS OF TEREPHTHALIC ACIDS CONTAINING POLYFLUOROALKYL GROUPS

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SUMMARY

The syntheses of new terephthalic acids (8a-d) containing various polyfluoroalkyl groups (a ; CF_3, b ; HCF_2, c ; $H(CF_2)_3$, and d ; $H(CF_2)_5$) are described in this paper. These compounds were obtained by aromatization (bromination and dehydrobromination) of Diels-Alder adducts (2a-d and 3a-d) of polyfluoro-2-alkynoic acids (1a-d) with 2-methyl-1,3-butadiene, followed by oxidation with $KMnO_4$.

INTRODUCTION

The aromatization of Diels-Alder adducts is well known as a synthetic route to aromatic compounds and is widely used for synthesis of various substituted aromatic compounds [1]. However, there are few reports on the application of the Diels-Alder reaction to the synthesis of fluoroaromatic compounds [2]. Putnam and his co-workers prepared 1,2-bis(trifluoromethyl)-4,5-dimethylbenzene by dehydrogenation of 1,2-bis(trifluoromethyl)-4,5-dimethyl-1,4-cyclohexadiene obtained in the reaction of perfluoro-2-butyne with 2,3-dimethyl-1,3-butadiene [3]. Krespan and his co-workers reported that the reaction of

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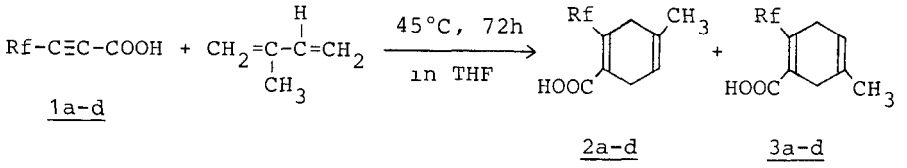
perfluoro-2-butyne with benzene at high temperature produced a mixture of trifluoromethylated benzene and naphthalene, which was probably derived from a bicyclooctatriene formed by 1,4-addition of the butyne to benzene [4]. Musgrave and his co-workers reported the formation of o-disubstituted tetrafluorobenzenes on pyrolysis of 2,3-disubstituted-1,4,5,6,7,7,8,8-octafluorobicyclo[2.2.2]octa-2,5-dienes, which were derived from the reaction of perfluorocyclohexa-1,3-diene with the appropriate alkynes [5].

We recently reported that the Diels-Alder reaction of polyfluoro-2-alkynoic acids (1a-d) with 2-methyl-1,3-butadiene (isoprene: ISP) gave the regioisomeric mixture of 1-carboxy-2-(polyfluoroalkyl)-4- (2a-d) and -5-methyl-1,4-cyclohexadienes (3a-d) [6] (Scheme 1). In this paper, we now wish to report



Rf; a) CF_3, b) HCF_2, c) $HCF_2CF_2CF_2$, d) $HCF_2CF_2CF_2CF_2CF_2$

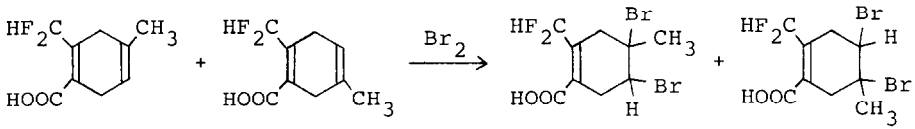
Scheme 1

the synthesis of the terephthalic acids (8) containing polyfluoroalkyl groups by the aromatization of the Diels-Alder adducts (2 and 3), followed by the oxidation of the resulting products (6 and 7).

Trifluoromethylated phthalic acids have been synthesized by various methods [7-11]. However, there have been only a few reports on the synthesis of trifluoromethylated or other polyfluoroalkylated terephthalic acids and their synthetic methods required many steps of reaction [8] or gave low yield of the product [12].

RESULTS AND DISCUSSION

The mixture of 2b and 3b was brominated in carbon tetrachloride at room temperature for 2 hours. A mixture of two products was obtained by reprecipitation of the involatile residue. The mixture proved to be inseparable by either fractional recrystallization or column chromatography and it was therefore analysed directly. The ^{1}H, ^{19}F-NMR and Mass spectra (see Experimental section) of the mixture showed that these products were a mixture of bromine adducts, 1-carboxy-2-(difluoromethyl)-4- (4b) and -5-methyl-4,5-dibromo-1-cyclohexene (5b) (Scheme 2). The product ratio (4b:5b=2.7:1),



2b 3b 4b 5b

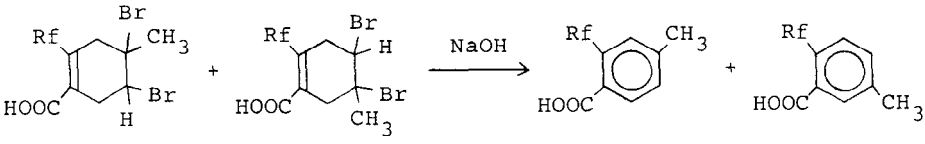
Scheme 2

which was determined by the relative intensity of two signals due to CHF_2 in ^{19}F-NMR spectrum of the reaction mixture, was equal to the isomer ratio of the starting material (2b:3b =2.7:1). This shows that bromine adds equivalently to 2b and 3b, irrespective of the position of the methyl group at the double bond and also suggests that 4b and 5b may be derived from 2b and 3b, respectively.

The other dibromides, which might be formed by bromine addition to the double bond bearing the polyfluoroalkyl and carboxyl groups, or the tetrabromides, which would be formed by bromine addition to both double bonds, were not obtained.

The bromination of the mixtures of other cyclohexadienes (2a,c,d and 3a,c,d) under the same conditions also gave the same results. The chain length of the polyfluoroalkyl group did not affect the yields (80-83%) of the bromine adducts (4a,c,d and 5a,c,d).

The dehydrobromination of the dibromides (4 and 5), with NaOH in water at room temperature for 5 hours, gave mixtures of 2-(polyfluoroalkyl)-4- (6a-d) and -5-methylbenzoic acids (7a-d) in 82-90% yields (Scheme 3). Their structures were established by IR, ^{1}H- and ^{19}F-NMR and Mass spectra. The data are listed in the Experimental section.



4a-d 5a-d 6a-d 7a-d

Scheme 3

Fortunately, the major isomers (6a-d) of the benzoic acids were isolated in high purity (ca. 95%) by recrystallization of the reaction mixtures from hexane and their structures were confirmed by the ^{1}H-NMR spectra (200 MHz, FT-NMR).

The ^{1}H-NMR spectra, in the region of δ 7.2-8.4, of the isolated major product (6b) and the mixture of 6b and 7b are shown in Fig. 1. In the study of the chemical shifts of aromatic protons in substituted benzenes, it is well known that the ortho-proton, relative to the meta-proton, is shifted to lower field by electron-withdrawing substituents [13]. Diehl [14] and Smith [15] reported that the deshielding effect of the carboxyl group on the ortho-proton was larger than that of the trifluoromethyl group. In Fig. 1b, the coupling constant (J=8.1 Hz) of the doublet at the lowest magnetic field (δ 8.09) corresponds to the value of interaction between two ortho-protons [16]. This doublet, therefore, can be assigned to Hc coupled with ortho-proton (Hb) in 6b. The signal of Hx in 7b is observed at higher field (δ 7.75) as a doublet due to the coupling with Hy. All other signals except * marked in Fig. 1a and 1b can be consistently assigned to the other aromatic protons in 6b and/or 7b.

With respect to the other benzoic acids (6a and 7a, 6c and 7c, 6d and 7d), the comparison of a similar ^{1}H-NMR spectral

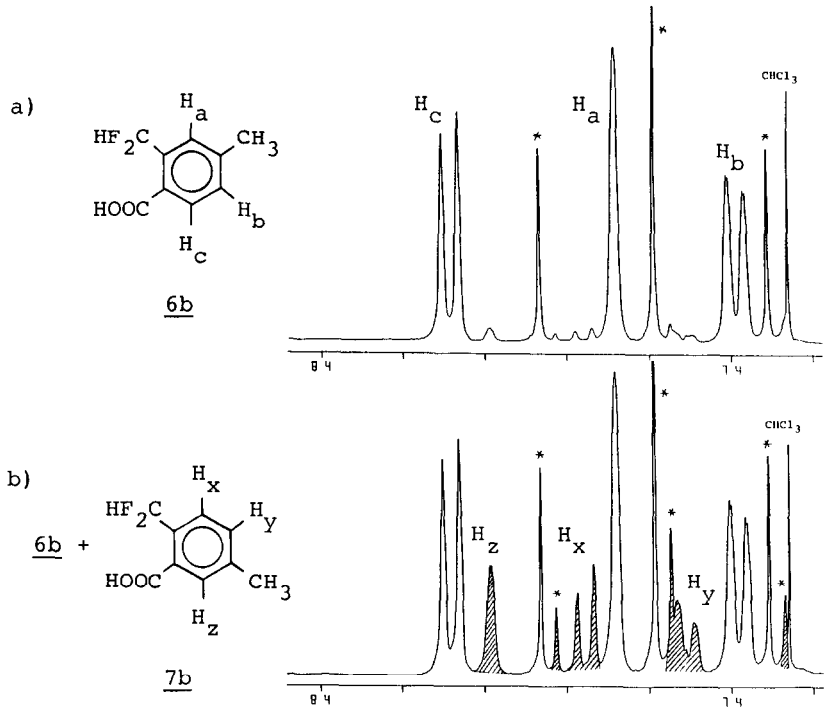


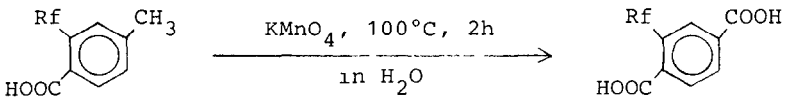
Fig. 1. ^{1}H-NMR (δ=7.2-8.4, 200 MHz, FT-NMR) of 6b and the mixture of 6b and 7b. The triplets marked with * are peaks of the proton in $-CHF_2$. a) Isolated product (6b). b) Crude mixture of 6b and 7b.

analysis for the isolated product (6a,c,d) and its original mixture (6a and 7a, 6c and 7c, 6d and 7d) gave the same conclusion that the major product was the compound 6 (6a, 6c, and 6d).

Production of the benzoic acids (6 and 7) from the cyclohexadienes (2 and 3) was also carried out in a one-pot procedure (bromination and dehydrobromination) without any isolation of intermediates. The mixtures of 6 and 7 were obtained in 72-83% yields. The regioisomer ratios of 6 to 7 (6a/7a=2.2, 6b/7b=2.6, 6c/7c=2.1, 6d/7d=1.8) were almost equal to those of the starting materials (2a/3a=2.3, 2b/3b=2.7,

2c/3c=2.1, 2d/3d=1.8) obtained in the Diels-Alder reaction of 1a-d with ISP. These results strongly suggest that the major benzoic acid (6) is derived from the major product (2) of the Diels-Alder reaction. Our previous theoretical prediction [6], based on the FMO theory, that the major product in the Diels-Alder reaction of 1 with ISP is 2, supports the present assignment of the structure of 6.

When 6a-d were treated with $KMnO_4$ in water at 100°C for 2 hours, the polyfluoroalkyl-substituted terephthalic acids (8a-d) were obtained in 89-93% yields (Scheme 4). The polyfluoroalkyl groups were stable under the oxidation conditions.



6a-d 8a-d

Scheme 4

The benzoic acids (6a-d) and the terephthalic acids (8b-d) are new compounds and their physical properties are shown in the experimental section.

A similar oxidation of the mixture of the benzoic acids (6b and 7b) gave the mixture of tere- (8b) and isophthalic acids (9b) in a 90% yield.

These phthalic acids are expected to be useful as monomers of new modified polymers [17].

EXPERIMENTAL

Melting points are uncorrected. Infrared spectra (IR) were recorded on a Shimadzu IR-400 infrared spectrometer. ^{1}H-NMR spectra were obtained with a Varian XL-200 (200 MHz) spectrometer in $CDCl_3$ or $(CD_3)_2SO$ solutions with Me_4Si as an

internal reference. A Hitachi R-24F (56.466 MHz) spectrometer was used to measure ^{19}F-NMR spectra in $CDCl_3$ or $(CD_3)_2SO$ with CF_3COOH (TFA) as an external reference. Mass spectra (MS) were taken on a Hitachi M-80B mass spectrometer operating at an ionization potential of 70 eV. All chemicals were of reagent grade. Solvents were purified in the conventional manner. Polyfluoro-2-alkynoic acids (1a-d) were prepared according to our previous literature method [18]. The mixture of two regioisomers of 1-carboxy-2-(polyfluoroalkyl)-4- (2a-d) and -5-methyl-1,4-cyclohexadiene (3a-d) was prepared by the reaction of 1a-d with isoprene [6]. 2 and 3 proved to be inseparable by either fractional recrystallization or column chromatography (silica gel/hexane).

Bromination of the cyclohexadienes (2 and 3)

To a mixture of 10 mmol of the cyclohexadienes (mixture of 2a-d and 3a-d) and 80 ml of carbon tetrachloride, a solution of 11 mmol of bromine in 20 ml of carbon tetrachloride was slowly added at 5°C with stirring. After the completion of addition, the mixture was allowed to warm to room temperature and stirred for an additional 2 hours. The solvent was evaporated from the reaction mixture under reduced pressure. The resulting residue was reprecipitated from hexane to give a mixture of 1-carboxy-2-(polyfluoroalkyl)-4-(4a-d) and -5-methyl-4,5-dibromo-1-cyclohexene (5a-d) in 80-85% yields. These regioisomers could not be separated by column chromatography (silica gel/hexane).

Mixture of 1-carboxy-2-trifluoromethyl-4-methyl-4,5-dibromo-1-cyclohexene (4a) and 1-carboxy-2-trifluoromethyl-5-methyl-4,5-dibromo-1-cyclohexene (5a)

80% Yield; Isomer ratio (4a/5a) : 2.2; IR (KBr) 1735 cm^{-1}; 1H-NMR ($CDCl_3$) δ 2.02 (s, 375 mm^2), 3.10-3.93 (m, 522 mm^2), 4.53 (m, 128 mm^2), 10.5 (bs, 136 mm^2); ^{19}F-NMR ($CDCl_3$, TFA) δ -13.6 (s, 164 mm^2, 4a), -13.8 (s, 75 mm^2, 5a); MS (m/e) 368 (M^++4), 366 (M^++2), 364 (M^+), 347 (M^+-OH), 285 (M^+-Br), 204 (M^+-2HBr).

Mixture of 1-carboxy-2-difluoromethyl-4-methyl-4,5-dibromo-1-cyclohexene (4b) and 1-carboxy-2-difluoromethyl-5-methyl-4,5-dibromo-1-cyclohexene (5b)

85% Yield; Isomer ratio (4b/5b) : 2.7; IR (KBr) 1705 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 2.02 (s, 360 mm^2), 3.12-3.95 (m, 495 mm^2), 4.52 (m, 122 mm^2), 7.16 (t, J=54.9 Hz, 118 mm^2), 10.5 (bs, 128 mm^2); ^{19}F-NMR ($CDCl_3$, TFA) δ 41.6 (d, J=54.9 Hz, 69 mm^2, 5b), 42.0 (d, J=54.9 Hz, 186 mm^2, 4b); MS (m/e) 350 (M^++4), 348 (M^++2), 346 (M^+), 329 (M^+-OH), 267 (M^+-Br), 186 (M^+-2HBr).

Mixture of 1-carboxy-2-(3H-perfluoropropyl)-4-methyl-4,5-dibromo-1-cyclohexene (4c) and 1-carboxy-2-(3H-perfluoropropyl)-5-methyl-4,5-dibromo-1-cyclohexene (5c)

83% Yield; (Isomer ratio could not be measured); IR (neat) 1710 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 2.02 (s, 368 mm^2), 2.90-3.80 (m, 497 mm^2), 4.54 (m, 123 mm^2), 6.12 (tt, J=52.6, 5.6 Hz, 120 mm^2), 10.5 (bs, 128 mm^2); ^{19}F-NMR ($CDCl_3$, TFA) δ 32.9 (m, 168 mm^2), 50.1 (m, 172 mm^2), 58.6 (dm, J=52.6 Hz, 173 mm^2); MS (m/e) 450 (M^++4), 448 (M^++2), 446 (M^+), 429 (M^+-OH), 367 (M^+-Br), 286 (M^+-2HBr).

Mixture of 1-carboxy-2-(5H-perfluoropentyl)-4-methyl-4,5-dibromo-1-cyclohexene (4d) and 1-carboxy-2-(5H-perfluoropentyl)-5-methyl-4,5-dibromo-1-cyclohexene (5d)

80% Yield; (Isomer ratio could not be measured); IR (neat) 1730 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 2.02 (s, 344 mm^2), 2.92-3.82 (m, 467 mm^2), 4.54 (m, 116 mm^2), 6.07 (tt, J=52.3, 5.5 Hz, 114 mm^2), 10.5 (bs, 121 mm^2); ^{19}F-NMR ($CDCl_3$, TFA) δ 31.3 (m, 175 mm^2), 41.2 (m, 178 mm^2), 45.0 (m, 178 mm^2), 51.3 (m, 178 mm^2), 58.5 (dm, J=52.3 Hz, 176 mm^2,; MS (m/e) 550 (M^++4), 548 (M^++2), 546 (M^+), 529 (M^+-OH), 467 (M^+-Br), 386 (M^+-2HBr).

Dehydrobromination of the dibromocyclohexenes (4 and 5)

To a stirred mixture of 10 mmol of the dibromides (mixture of 4a-d and 5a-d), 15 mmol of NaOH, and 50 ml of

water, a solution of 30 mmol of NaOH in 50 ml of water was slowly added at room temperature. After the completion of addition, the resulting mixture was stirred for an additional 5 hours, and then acidified with 20% hydrochloric acid to yield the solid in the case of a-c or the oily material in the case of d. The solid or oily material was separated, washed with cold water, and dried at ambient temperature to give an almost pure regioisomeric mixture of 6a-d and 7a-d (82-90% yields).

Mixture of 2-trifluoromethyl-4-methylbenzoic acid (6a) and 2-trifluoromethyl-5-methylbenzoic acid (7a)

85% Yield; Isomer ratio (6a/7a) : 2.2; IR (KBr) 1715 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 2.47 (s, 55 mm^2, 7a), 2.52 (s, 121 mm^2, 6a), 7.45 (d, J=8.0 Hz, 57 mm^2, 6a and 7a), 7.62 (s, 39 mm^2, 6a), 7.69 (d, J=8.0 Hz, 18 mm^2, 7a), 7.79 (s, 18 mm^2, 7a), 7.92 (d, J=8.0 Hz, 41 mm^2, 6a), 10.5 (bs, 61 mm^2, 6a and 7a); ^{19}F-NMR ($CDCl_3$, TFA) δ -18.4 (s, 135 mm^2, 6a), -18.9 (s, 61 mm^2, 7a); MS (m/e) 204 (M^+), 187 (M^+-OH), 159 (M^+-COOH).

Mixture of 2-difluoromethyl-4-methylbenzoic acid (6b) and 2-difluoromethyl-5-methylbenzoic acid (7b)

90% Yield; Isomer ratio (6b/7b) : 2.6; IR (KBr) 1690 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 2.44 (s, 109 mm^2, 7b), 2.47 (s, 281 mm^2, 6b), 7.39 (d, J=8.1 Hz, 94 mm^2, 6b), 7.50 (d, J=8.1 Hz, 36 mm^2, 7b), 7.55 (t, J=55.2 Hz, 36 mm^2, 7b), 7.60 (t, J=55.2 Hz, 94 mm^2, 6b), 7.69 (s, 94 mm^2, 6b), 7.75 (d, J=8.1 Hz, 36 mm^2, 7b), 7.98 (s, 36 mm^2, 7b), 8.09 (d, J=8.1 Hz, 94 mm^2, 6b), 11.5 (bs, 137 mm^2, 6b+7b); ^{19}F-NMR ($CDCl_3$, TFA) δ 35.0 (d, J=55.2 Hz, 57 mm^2, 7b), 35.4 (d, J=55.2 Hz, 148 mm^2, 6b); MS (m/e) 186 (M^+), 169 (M^+-OH), 141 (M^+-COOH).

Mixture of 2-(3H-perfluoropropyl)-4-methylbenzoic acid (6c) and 2-(3H-perfluoropropyl)-5-methylbenzoic acid (7c)

85% Yield; Isomer ratio (6c/7c) : 2.1; IR (KBr) 1695 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 2.44 (s, 138 mm^2, 7c), 2.47 (s, 290 mm^2, 6c), 6.21 (tt, J=52.2, 5.6 Hz, 46 mm^2, 7c), 6.24 (tt, J=52.2, 5.6 Hz, 97 mm^2, 6c), 7.40-7.55 (m, 332 mm^2, 6c+7c),

7.71 (d, J=7.9 Hz, 97 mm^2, 6c), 11.5 (bs, 148 mm^2, 6c+7c); ^{19}F-NMR ($CDCl_3$, TFA) δ 26.2 (m, 107 mm^2, 6c), 26.7 (m, 51 mm^2, 7c), 49.9 (m, 104 mm^2, 6c), 50.2 (m, 52 mm^2, 7c), 58.7 (dm, J=52.2 Hz, 159 mm^2, 6c+7c); MS (m/e) 286 (M^+), 269 (M^+-OH), 185 (M^+-CF_2CF_2H).

Mixture of 2-(5H-perfluoropentyl)-4-methylbenzoic acid (6d) and 2-(5H-perfluoropentyl)-5-methylbenzoic acid (7d)

82% Yield; Isomer ratio (6d/7d) : 1.8; IR (neat) 1695 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 2.39 (s, 117 mm^2, 7d), 2.41 (s, 207 mm^2, 6d), 6.03 (tt, J=51.8, 5.3 Hz, 108 mm^2, 6d+ 7d), 7.31-7.52 (m, 254 mm^2, 6d+7d), 7.68 (d, J=7.9 Hz, 69 mm^2, 6d), 11.5 (bs, 115 mm^2, 6d+7d); ^{19}F-NMR ($CDCl_3$, TFA) δ 25.3 (m, 105 mm^2, 6d), 25.8 (m, 58 mm^2, 7d), 40.4 (m, 106 mm^2, 6d), 40.9 (m, 59 mm^2, 7d), 45.2 (m, 165 mm^2, 6d+7d), 51.9 (m, 165 mm^2, 6d+7c), 59.0 (dm, J=51.8 Hz, 163 mm^2, 6d+7d); MS (m/e) 386 (M^+), 369 (M^+-OH), 185 (M^+-$CF_2CF_2CF_2CF_2H$).

Isolation of 2-(polyfluoroalkyl)-4-methylbenzoic acid (6a-d)

The regioisomeric mixture of 6a-d and 7a-d was dissolved in hot hexane. The hexane solution was filtered and cooled to room temperature to yield a white solid (a-c) or oily material (d). These were separated from the hexane solution and repeatedly recrystallized from hexane to afford a high purity of one regioisomer (6a-d). The hexane solution after initial removal of the solid or oily material contained ca. 1:1 mixture of 6 and 7, which could not be separated by further recrystallization.

2-Trifluoromethyl-4-methylbenzoic acid (6a)

45% Isolated yield; Mp 140-141°C; IR (KBr) 1715 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 2.52 (3H, s), 7.45 (1H, d, J=8.0 Hz), 7.62 (1H, s), 7.92 (1H, d, J=8.0 Hz), 11.5 (1H, bs); ^{19}F-NMR ($CDCl_3$, TFA) δ -18.4 (s); MS (m/e) 204 (M^+), 187 (M^+-OH), 159 (M^+-COOH).

2-Difluoromethyl-4-methylbenzoic acid (6b)

52% Isolated yield; Mp 114-116°C; IR (KBr) 1690 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 2.47 (3H, s), 7.39 (1H, d, J=8.1 Hz), 7.60 (1H, t, J=55.2 Hz), 7.69 (1H, s), 8.09 (1H, d, J=8.1 Hz), 11.5 (1H, bs); ^{19}F-NMR ($CDCl_3$, TFA) δ 35.4 (d, J=55.2 Hz); MS (m/e) 186 (M^+), 169 (M^+-OH), 141 (M^+-COOH).

2-(3H-Perfluoropropyl)-4-methylbenzoic acid (6c)

38% Isolated yield; Mp 94-96°C; IR (KBr) 1695 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 2.47 (3H, s), 6.24 (1H, tt, J=52.2, 5.6 Hz), 7.43 (1H, d, J=7.9 Hz), 7.47 (1H,s), 7.71 (1H, d, J=7.9 Hz), 11.5 (1H, bs); ^{19}F-NMR ($CDCl_3$, TFA) δ 26.2 (2F, m), 49.9 (2F, m), 58.7 (2F, dm, J=52.2 Hz); MS (m/e) 286 (M^+), 269 (M^+-OH), 185 ($M^+-CF_2CF_2H$).

2-(5H-Perfluoropentyl)-4-methylbenzoic acid (6d)

21% Isolated yield; (Oil); IR (neat) 1695 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 2.41 (3H, s), 6.03 (1H, tt, J=51.8, 5.3 Hz), 7.38 (1H, d, J=7.9 Hz), 7.48 (1H, s), 7.68 (1H, d, J=7.9 Hz), 11.5 (1H, bs); ^{19}F-NMR ($CDCl_3$, TFA) δ 25.3 (2F, m), 40.4 (2F, m), 45.2 (2F, m), 51.9 (2F, m), 59.0 (2F, dm, J=51.8 Hz); MS (m/e) 386 (M^+), 369 (M^+-OH), 185 ($M^+-CF_2CF_2CF_2CF_2H$).

One-pot synthesis of the benzoic acids (6a-d and 7a-d) from the cyclohexadienes (2a-d and 3a-d)

To a stirred mixture of 10 mmol of the cyclohexadienes (mixture of 2 and 3; 2a-d/3a-d=1.8-2.7) and 80 ml of carbon tetrachloride, a solution of 11 mmol of bromine in 20 ml of carbon tetrachloride was slowly added at 5°C. After the completion of addition, the mixture was stirred at room temperature for an additional 2 hours. The solvent was evaporated under reduced pressure, and then 50 ml of water was added to the residue. To the resulting aqueous solution, 45 mmol of NaOH in 50 ml of water was carefully added at room temperature. After stirring for an additional 5 hours, the

reaction mixture was acidified with 20% hydrochloric acid to give the almost pure products (mixture of 6 and 7; 6a-d/7a-d= 1.8-2.6) in 72-83% yields.

Oxidation of 1-carboxy-2-(polyfluoroalkyl)-4-methylbenzoic acid (6a-d)

To a mixture of 10 mmol of 6a-d, 20 mmol of NaOH, and 50 ml of water, 24 mmol of $KMnO_4$ was slowly added at 80°C with stirring. The mixture was refluxed for 2 hours, and then allowed to cool to room temperature. After filtration, the filtrate was acidified with conc. hydrochloric acid. The resulting solid was filtered off, washed with cold water, and dried to give pure polyfluoroalkylterephthalic acid (8a-d) in 89-93% yields.

Trifluoromethylterephthalic acid (8a)

92% Yield; Mp 235-236°C (219-220°C (sublime)); IR (KBr) 1710 cm^{-1}; ^{1}H-NMR ($(CD_3)_2SO$) δ 7.90 (1H, d, J=8.0 Hz), 8.22 (1H, s), 8.27 (1H, d, J=8.0 Hz), 13.8 (2H, bs); ^{19}F-NMR ($(CD_3)_2SO$, TFA) δ -19.2 (s); MS (m/e) 234 (M^+), 217 (M^+-OH), 189 (M^+-COOH).

Difluoromethylterephthalic acid (8b)

93% Yield; Mp 244-245°C; IR (KBr) 1700 cm^{-1}; ^{1}H-NMR ($(CD_3)_2SO$) δ 7.64 (1H, t, J=55.8 Hz), 8.12 (1H, d, J=7.8 Hz), 8.21 (1H, d, J=7.8 Hz), 8.28 (1H, s), 13.8 (2H, bs); ^{19}F-NMR ($(CD_3)_2SO$, TFA) δ 34.4 (d, J=55.8 Hz); MS (m/e) 216 (M^+), 199 (M^+-OH), 171 (M^+-COOH).

(3H-Perfluoropropyl)terephthalic acid (8c)

89% Yield; Mp 213-214°C; IR (KBr) 1715 cm^{-1}; ^{1}H-NMR ($(CD_3)_2SO$) δ 6.98 (1H, tt, J=50.0, 5.6 Hz), 7.83 (1H, d, J=8. Hz), 8.14 (1H, s), 8.29 (1H,d, J=8.1 Hz), 13.8 (2H, bs); ^{19}F-NMR ($(CD_3)_2SO$, TFA) δ 27.1 (2F, m), 49.4 (2F, m), 58.7 (2F, dm, J=50.0 Hz); MS (m/e) 316 (M^+), 299 (M^+-OH), 215 (M^+-CF_2CF_2H).

(5H-Perfluoropentyl)terephthalic acid (8d)

89% Yield; Mp 188-190°C; IR (KBr) 1710 cm^{-1}; ^{1}H-NMR ($(CD_3)_2SO$) δ 7.16 (1H, tt, J=50.4, 5.6 Hz), 7.84 (1H, d, J=8.4 Hz), 8.14 (1H, s), 8.30 (1H,d, J=8.4 Hz), 13.8 (2H, bs); ^{19}F-NMR ($(CD_3)_2SO$, TFA) δ 26.7 (2F, m), 41.1 (2F, m), 44.7 (2F, m), 50.8 (2F, m), 60.0 (2F, dm, J=50.4 Hz); MS (m/e) 416 (M^+), 399 (M^+-OH), 215 (M^+-$CF_2CF_2CF_2CF_2H$).

Oxidation of a mixture of 6b and 7b

The mixture of the benzoic acids (6b and 7b; 6b/7b=2.6) was oxidized as described above. The mixture of tere- and isophthalic acids (8b and 9b; 8b/9b=2.6) was obtained in a 90% yield.

Mixture of difluoromethylterephthalic acid (8b) and difluoromethylisophthalic acid (9b)

90% Yield; Isomer ratio (8b/9b) : 2.6; IR (KBr) 1700 cm^{-1}; ^{1}H-NMR ($(CD_3)_2SO$) δ 7.64 (t, J=55.8 Hz, 118 mm^2, 8b), 7.66 (t, J=55.8 Hz, 46 mm^2, 9b), 7.92 (d, J=7.8 Hz, 46 mm^2, 9b), 8.12 (d, J=7.8 Hz, 118 mm^2, 8b), 8.21 (d, J=7.8 Hz, 118 mm^2, 8b), 8.27 (d, J=7.8 Hz, 46 mm^2, 9b), 8.28 (s, 118 mm^2, 8b), 8.52 (s, 46 mm^2, 9b), 13.8 (bs, 328 mm^2, 8b+9b); ^{19}F-NMR ($(CD_3)_2SO$, TFA) δ 34.4 (d, J=55.8 Hz, 178 mm^2, 8b), 34.8 (d, J=55.8 Hz, 68 mm^2, 9b); MS (m/e) 216 (M^+), 199 (M^+-OH), 171 (M^+-COOH).

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