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New synthesis of polyfluorodiols: nine new derivatives of HOC(2-OH-C_6H_4)(CF_3)$_2$

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Abstract

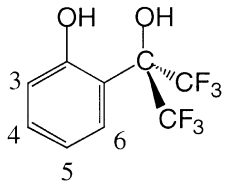
Nine new polyfluorodiols, HOC(2-OH-3-C_6H_3F)(CF_3)$_2$, HOC(2-OH-5-C_6H_3F)(CF_3)$_2$, HOC(2-OH-3,5-$C_6H_2F_2$)(CF_3)$_2$, HOC(2-OH-4,5-$C_6H_2F_2$)(CF_3)$_2$, HOC(2-OH-4,6-$C_6H_2F_2$)(CF_3)$_2$, HOC(2-OH-3,4,5-C_6HF_3)(CF_3)$_2$, HOC(2-OH-4,5,6-C_6HF_3)(CF_3)$_2$, HOC(2-OH-3-*t*-Bu-5-Me-C_6H_2)(CF_3)$_2$, HOC(2-OH-3-I-C_6H_3)(CF_3)$_2$, have been synthesized and characterized by GC, NMR spectroscopy, and high-resolution mass spectrometry.

Keywords: Gas chromatography; Mass spectrometry; Fluoroalkoxide

1. Introduction

Highly fluorinated alcohols and the metal alkoxides that can be derived from them are of interest for a number of reasons [1,2]. In general, they are chemically stable and resistant to oxidation, enabling the fluoroalkoxides to be used as ligands to stabilize metal atoms in high oxidation states. In addition, the high electronegativity of fluorinated substituents reduces the basicity of the oxygen atom, disfavoring the formation of extended alkoxy-bridged species. This leads to higher solubility in low-dielectric solvents and higher volatility of complexes with these types of ligands. Furthermore, the steric and electronic properties can be readily modified, allowing for a wide variety of possible ligands. One area where they are important is in the design of metathesis catalysts, where they are used as components of complexes based on tungsten and molybdenum [3]. As part of this research, it was found that varying the character of the fluoroalkoxide ligand had a significant effect on catalyst activity. Metal fluoroalkoxides have also found use as precursors for chemical vapor deposition of metal fluorides [4] and fluorine-doped metal oxides [5].

Among the many varieties of fluorinated alcohols, one subset is the fluorinated diols. With two oxygen atoms, these can act as chelating ligands to form complexes than are morestable, chemically and thermally, than those with monodentate fluoroalkoxide ligands. For example, the sodium salt of the $B(OC(CF_3)_2C(CF_3)_2O)_2^-$ anion is stable in aqueous solution [6], while salts of the $B(OCH(CF_3)_2)_4^-$ anion are readily hydrolyzed [7]. Also, the lithium salt of the $B(O_2C_6F_4)_2^-$ anion, which is also hydrolytically stable, has been found to be thermally stable to 270 °C [8]. This paper describes the synthesis of nine new fluorinated diols, all based on the compound HOC(2-OH-C_6H_4)(CF_3)$_2$ (see structure). This diol was first synthesized by Gilbert and coworkers [9], and numerous derivatives have been reported since that time. However, the list of halogenated derivatives is short: HOC(2-OH-4-C_6H_3Br)(CF_3)$_2$; HOC(2-OH-5-C_6H_3Br)(CF_3)$_2$; HOC(2-OH-3-C_6H_3Cl)(CF_3)$_2$; HOC(2-OH-4-C_6H_3Cl)(CF_3)$_2$; and HOC(2-OH-4-C_6H_3F)(CF_3)$_2$ [10]. Note that the last compound in this list is the only reported diol based on HOC(2-OH-C_6H_4)(CF_3)$_2$ in which a fluorine atom has been incorporated into the phenyl ring. No homologous diols in which iodine atoms have been added have been reported.



The nine new diols reported in this paper were chosen as synthetic targets as an extension of our previous work with fluoroalkoxyaluminates and borates with formulas (B,

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Al)$(OR_F)_4^-$ [11–14]. These anions were found to be excellent weakly coordinating anions [15], and most were comprised of fluoroalkoxides with the general formula $OCR(CF_3)_2^-$. As previously mentioned, hydrolysis of the B–O or Al–O bonds is a serious problem for (B, Al)$(OR_F)_4^-$ anions. Our expectation is that substituting two diolates for four alkoxides will lead to enhanced stability with respect to hydrolysis because of the chelate effect. In support of this, Barthel et al. reported that lithium borates containing two catecholate or substituted catecholate ligands possessed this property [8,16].

2. Experimental

Samples for NMR spectroscopy were solutions in 5-mm glass tubes. NMR spectra were recorded on a Varian Inova 300 spectrometer operating at the indicated frequencies: ^{1}H, 300.1 MHz; ^{19}F, 282.4 MHz. Chemical shifts (δ scale) are relative to $SiMe_4$ ($\delta = 0$ for ^{1}H NMR) and CFCl3 ($\delta = 0$ for ^{19}F NMR) external standards. High-resolution mass spectra (HRMS) were recorded on a Fisons VG AutoSpec spectrometer by liquid secondary ion mass spectrometry (LSIMS). Gas chromatography/mass spectrometry (GC/MS) was performed using an Agilent 5973 N in electron ionization (EI) mode.

Schlenk, glovebox, and high-vacuum techniques were employed, with purified argon used when an inert atmosphere was required [17]. All reagents and solvents were reagent grade or better. The compounds $AlCl_3$ (Aldrich, 99%), hexafluoroacetone (Aldrich, 97%), 2-iodophenol (Fluorochem, 98%), phenol (Aldrich, >99%), 2-*t*-butyl-4-methylphenol (Aldrich, 99%), 2-fluorophenol (Fluorochem, 98%), 4-fluorophenol (Fluorochem, 99%), 2,4-difluorophenol (Alfa Aesar, >98%), 3,4-difluorophenol (Fluorochem, 99%), 3,5-difluorophenol (Fluorochem, 99%), 2,3,4-trifluorophenol (Fluorochem, 97%), 3,4,5-trifluorophenol (Fluorochem, 97%), and $MgSO_4$ (Fisher, anhydrous) were used as received. The solvent 1,2-dichloroethane was purified by distillation under nitrogen from P_2O_5 (Fisher).

2.1. Preparation of fluorodiols

The improved synthesis of HOC(2-OH-C_6H_4)$(CF_3)_2$ and the nine new compounds were prepared using a modified version of the synthesis of HOC(2-OH-C_6H_4)$(CF_3)_2$ reported by Gilbert and co-workers [9]. In all 10 syntheses, the phenol and $AlCl_3$ were dissolved in 1,2-dichloroethane. After degassing the solution, hexafluoroacetone (HFA), which had been measured out in a calibrated bulb using a high-vacuum (10^{-5} Torr) line, was then added to the frozen mixture at −35 °C. CAUTION: HEXAFLUOROACETONE IS BOTH TOXIC AND TERATOGENIC AND MUST BE HANDLED CAREFULLY BY TRAINED PERSONNEL. The initial pressure of HFA was usually 600 ± 20 Torr. Two syntheses were carried out with a 2:1 molar ratio of HFA to phenol, but it was subsequently found that a 1:1 molar ratio did not reduce the yield of the fluorodiol. Therefore, most of the syntheses were carried out with a 1:1 molar ratio. In each case the −35 °C reaction mixture was allowed to warm to 24 ± 1 °C during 30 min and was stirred until there was no further pressure change (the pressure was monitored with an electronic manometer attached to the sealed reaction vessel). In those cases where HFA remained after the reaction was complete (i.e. no further pressure drop), it was converted to the hydrate by bubbling nitrogen through the reaction mixture into a large volume of water. The HFA-free reaction mixture was opened to the atmosphere and treated with 50 ml of distilled water, resulting in the formation of a white precipitate (hydrated $AlCl_3$). After stirring for 6 h, the organic layer was removed and the aqueous layer washed twice with 20 ml portions of fresh 1,2-dichloroethane. The three 1,2-dichloroethane fractions were combined and dried over $MgSO_4$ for 4 h. After removing $MgSO_4$ by filtration, 1,2-dichloroethane was removed using a rotary evaporator. Unless otherwise noted, the residue was recrystallized and/or sublimed to yield a white crystalline solid.

2.1.1. Preparation of HOC(2-OH-C_6H_4)$(CF_3)_2$

The reagents were $AlCl_3$ (0.0947 g, 0.692 mmol), phenol (6.50 g, 69.2 mmol), and HFA (5.74 g, 34.6 mmol) in 120 ml 1,2-dichloroethane (clear, colorless solution; stirred for 2 days; clear, tan final solution). Purification of the cloudy oil by sublimation at 60 °C yielded a white crystalline solid. Yield of HOC(2-OH-C_6H_4)$(CF_3)_2$ = 6.01 g (67% based on phenol). ^{1}H NMR (C_6D_6/C_6F_6,): δ 7.43 (s, 1H), 7.20 (d, 1H, J_{H-H} = 8.1 Hz), 6.80 (t, 1H, J_{H-H} = 7.8 Hz), 6.55 (t, 1H, J_{H-H} = 7.8 Hz), 6.13 (d, 1H, J_{H-H} = 8.1 Hz), 5.66 (s, 1H), and 5.39 (s, 1H). ^{19}F NMR (C_6D_6/C_6F_6): δ −75.98 (s). GC analysis evidenced a purity of ≥99%. HRMS: *m/z* 260.0265. $C_9H_6F_6O_2$ requires *m/z* 260.0272.

2.1.2. Preparation of HOC(2-OH-3-C_6H_3F)$(CF_3)_2$

The reagents were $AlCl_3$ (0.616 g, 4.62 mmol), 2-fluorophenol (10.3 g, 92.3 mmol), and HFA (15.3 g, 92.3 mmol) in 135 ml 1,2-dichloroethane (clear, yellow solution; stirred for 3 weeks; clear, dark yellow final solution). Purification by sublimation at 60 °C and recrystallization from hexane/$CHCl_3$ (4:1 (v:v)). Yield of HOC(2-OH-3-C_6H_3F)$(CF_3)_2$ = 9.15 g (36% based on 2-fluorophenol). ^{1}H NMR (C_6D_6/C_6F_6): δ 7.12 (m, 1H), 6.48 (m, 1H), 6.23 (m, 1H), 6.16 (s, 1H), and 5.53 (s, 1H). ^{19}F NMR (C_6D_6/C_6F_6): δ −75.35 (s, 6F) and −137.53 (m, 1F). GC analysis evidenced a purity of ≥99%. HRMS: *m/z* 278.0166. $C_9H_5F_7O_2$ requires *m/z* 278.0178.

2.1.3. Preparation of HOC(2-OH-5-C_6H_3F)$(CF_3)_2$

The reagents were $AlCl_3$ (0.616 g, 4.62 mmol), 4-fluorophenol (4.43 g, 39.6 mmol), and HFA (6.57 g, 39.6 mmol) in 100 ml 1,2-dichloroethane (clear, orange solution; stirred

for 2 days; no color change). Purification by sublimation at 55 °C and recrystallization from hexane/$CHCl_3$ (5:1 (v:v)). Yield of HOC(2-OH-5-C_6H_3F)$(CF_3)_2$ = 6.00 g (54% based on 4-fluorophenol). ^{1}H NMR (C_6D_6/C_6F_6): δ 7.31 (m, 1H), 6.46 (m, 1H), 5.93 (m, 1H), 5.57 (s, 1H), and 5.48 (s, 1H). ^{19}F NMR (C_6D_6/C_6F_6): δ −75.51 (s, 6F) and −120.74 (m, 1F). GC analysis evidenced a purity of ≥99%. HRMS: *m*/z 278.0167. $C_9H_5F_7O_2$ requires *m*/z 278.0178.

2.1.4. Preparation of HOC(2-OH-3,5-$C_6H_2F_2$)$(CF_3)_2$

The reagents were $AlCl_3$ (0.383 g, 2.87 mmol), 2,4-difluorophenol (7.47 g, 57.5 mmol), and HFA (6.39 g, 38.5 mmol) in 125 ml 1,2-dichloroethane (clear, dark amber solution; stirred for 2 days; no color change). Purification by sublimation at 70 °C. Yield of HOC(2-OH-3,5-$C_6H_2F_2$)$(CF_3)_2$ = 8.04 g (47% based on 2,4-difluorophenol). ^{1}H NMR (C_6D_6/C_6F_6): δ 7.04 (m, 1H), 6.18 (m, 1H), 5.75 (s, 1H), and 5.03 (s, 1H). ^{19}F NMR (C_6D_6/C_6F_6): δ −75.43 (s, 6F), −117.39 (m, 1F), and −132.22 (m, 1F). GC/MS analysis evidenced a purity of ≥99%. HRMS: *m*/z 296.0078. $C_9H_4F_8O_2$ requires *m*/z 296.0084.

2.1.5. Preparation of HOC(2-OH-4,5-$C_6H_2F_2$)$(CF_3)_2$

The reagents were $AlCl_3$ (0.341 g, 2.60 mmol), 3,4-difluorophenol (4.43 g, 39.6 mmol), and HFA (6.39 g, 38.5 mmol) in 40 ml 1,2-dichloroethane (clear, pink solution; stirred for 3.5 days; clear, dark pink final solution). Purification by recrystallization from hexane/$CHCl_3$ (5:1 (v:v)). Yield of HOC(2-OH-4,5-$C_6H_2F_2$)$(CF_3)_2$ = 7.07 g (62% based on 3,4-difluorophenol). ^{1}H NMR (C_6D_6/C_6F_6): δ 7.16 (m, 1H), 5.90 (s, 1H), 5.85 (m, 1H), and 4.82 (s, 1H). ^{19}F NMR (C_6D_6/C_6F_6): δ −75.76 (s, 6F), −131.33 (m, 1F), and −145.05 (m, 1F). GC analysis evidenced a purity of ≥99%. HRMS: *m*/z 296.0081. $C_9H_4F_8O_2$ requires *m*/z 296.0084.

2.1.6. Preparation of HOC(2-OH-4,6-$C_6H_2F_2$)$(CF_3)_2$

The reagents were $AlCl_3$ (0.260 g, 1.94 mmol), 3,5-difluorophenol (5.05 g, 38.9 mmol), and HFA (6.45 g, 38.9 mmol) in 40 ml 1,2-dichloroethane (clear, tan solution; stirred for 36 h; white solid suspended in tan final solution). Purification by sublimation at 55 °C and recrystallization from hexane/$CHCl_3$ (4:1 (v:v)). Yield of HOC(2-OH-4,6-$C_6H_2F_2$)$(CF_3)_2$ = 7.68 g (67% based on 3,5-difluorophenol). ^{1}H NMR (C_6D_6/C_6F_6): δ 7.71 (s, 1H), 6.09 (m, 1H), 5.92 (m, 1H), and 3.87 (s, 1H). ^{19}F NMR (C6D6/C6F6): δ −75.76 (m, 6F), −102.81 (m, 1F), and −105.60 (m, 1F). GC analysis evidenced a purity of ≥99%. HRMS: *m*/z 296.0078. $C_9H_4F_8O_2$ requires *m*/z 296.0084.

2.1.7. Preparation of HOC(2-OH-3,4,5-C_6HF_3)$(CF_3)_2$

The reagents were $AlCl_3$ (0.217 g, 1.63 mmol), 2,3,4-trifluorophenol (4.81 g, 32.5 mmol), and HFA (5.40 g, 32.5 mmol) in 100 ml 1,2-dichloroethane (clear, yellow solution; stirred for 53 h; clear, dark yellow final solution). Purification by sublimation at 65 °C. Yield of HOC(2-OH-3,4,5-C_6HF_3)$(CF_3)2$ = 7.01 g (69% based on 2,3,4-trifluorophenol). ^{1}H NMR (C_6D_6/C_6F_6): δ 6.94 (t, 1H, J_{H-F} = 9.52 Hz), 5.46 (s, 1H), and 4.85 (s, 1H). ^{19}F NMR (C_6D_6/C_6F_6): δ −75.75 (m, 6F), −142.40 (m, 1F), −153.50 (m, 1H), and −154.30 (m, 1F). GC analysis evidenced a purity of ≥99%. HRMS: *m*/z 313.9978. $C_9H_3F_9O_2$ requires *m*/z 313.9989.

2.1.8. Preparation of HOC(2-OH-4,5,6-C_6HF_3)$(CF_3)_2$

The reagents were $AlCl_3$ (0.211 g, 1.60 mmol), 3,4,5-trifluorophenol (3.25 g, 21.9 mmol), and HFA (6.45 g, 38.9 mmol) in 40 ml 1,2-dichloroethane (clear, yellow solution; stirred for 3.5 days; clear, dark yellow final solution). Purification by recrystallization from hexane/$CHCl_3$ (5:1 (v:v)). Yield of HOC(2-OH-4,5,6-C_6HF_3)$(CF_3)_2$ = 4.02 g (59% based on 3,4,5-fluorophenol). ^{1}H NMR (C_6D_6/C_6F_6): δ 7.36 (s, 1H), 5.88 (m, 1H), and 4.00 (s, 1H). ^{19}F NMR (C_6D_6/C_6F_6): δ −75.71 (m, 6F), −128.64 (m, 1F), −129.07 (m, 1H), and −169.09 (m, 1F). Based on the absence of other ^{19}F NMR resonances and the signal/noise ratio, the purity of this compound is ≥99%. HRMS: *m*/z 313.9996. $C_9H_3F_9O_2$ requires *m*/z 313.9989.

2.1.9. Preparation of HOC(2-OH-3-*t*-Bu-5-Me-C_6H_2)$(CF_3)_2$

The reagents were $AlCl_3$ (0.152 g, 1.14 mmol), 2-*t*-butyl-4-methylphenol (4.63 g, 28.3 mmol), and HFA (5.74 g, 34.6 mmol) in 120 ml 1,2-dichloroethane (clear, red solution; stirred for 50 h; clear, dark red final solution). Purification by sublimation at 60 °C. Yield of HOC(2-OH-3-*t*-Bu-5-Me-C_6H_2)$(CF_3)_2$ = 5.94 g (64% based on 2-*t*-butyl-4-methylphenol). ^{1}H NMR (C_6D_6/C_6F_6): δ 8.07 (s, 1H), 7.20 (s, 1H), 7.12 (m, 1H), 3.84 (s, 1H), 2.00 (s, 3H), and 1.42 (s, 9H). ^{19}F NMR (C_6D_6/C_6F_6): δ −75.60 (s). GC analysis evidenced a purity of ≥99%. HRMS: *m*/z 330.1054. C14H16F6O2 requires *m*/z 330.1054.

2.1.10. Preparation of HOC(2-OH-3-C_6H_3I)$(CF_3)_2$

The reagents were $AlCl_3$ (0.095 g, 0.71 mmol), 2-iodophenol (3.11 g, 14.2 mmol), and HFA (2.35 g, 14.2 mmol) in 45 ml 1,2-dichloroethane (clear, purple solution; stirred for 45 h; white precipitate in clear purple final solution). Purification by fractional vacuum distillation (10^{-3} Torr; the product distilled at 100 °C). Yield of HOC(2-OH-3-C_6H_3I)$(CF_3)_2$ = 2.71 g (50% based on 2-iodophenol). ^{1}H NMR (C_6D_6/C_6F_6): δ 7.31 (d, J_{H-H} = 9 Hz, 1H), 7.18 (d, J_{H-H} = 9 Hz, 1H), and 6.05 (t, J_{H-H} = 9 Hz, 1H). ^{19}F NMR (C_6D_6/C_6F_6): δ −75.56 (s). GC analysis evidenced a purity of 96%. HRMS: *m*/z 385.9223. $C_9H_5F_6IO_2$ requires *m*/z 385.9239.

3. Results and discussion

With the exception of HOC(2-OH-C_6H_4)$(CF_3)_2$, all of the diols described in the experimental section are new. The synthetic method is very similar to that developed by

Gilbert and co-workers, which consists of mixing a phenol with hexafluoroacetone in the presence of a catalyst (5 mol% based on phenol), using xylene as the solvent. In that work, three catalysts were studied: $AlCl_3$, BF_3, and *p*-toluenesulfonic acid. It was found that the regiochemistry of the reaction depended on the nature of the catalyst: using BF_3 yielded primarily *para*-substituted phenols, while $AlCl_3$ and *p*-toluenesulfonic acid generally produced *ortho*-substituted products. The desired ligands for this work are the *ortho* isomers, as they form a stable six-membered chelate ring with a central atom such as boron. Of the two catalysts that give rise to these forms, it was found by Gilbert et al. that $AlCl_3$ catalysis resulted in a higher yield of substituted phenol, and required less time to do so. Therefore, this catalyst was chosen to synthesize the new diols in this work. The amount used was generally 5 mol% based on phenol. The other modification on the original procedure was the solvent: 1,2-dichloroethane was used instead of xylene. Xylene has been shown to react with hexafluoroacetone in the presence of $AlCl_3$ [18], creating the possibility for an undesired side reaction to occur when it is used as the solvent.

Since the goal of this work was to synthesize new ligand precursors that could be used to make weakly coordinating anions, new diols were designed with this in mind. One important criterion for a weakly coordinating anion is a high degree of charge dispersal; that is, there are no points of high charge density located on the anion. Considering HOC(2-OH-C_6H_4)$(CF_3)_2$, the phenoxy oxygen atom is presumably the point of highest charge density on the ligand. To decrease this, one or more fluorine atoms were incorporated into the phenyl ring. Fluorine is highly electronegative, and should withdraw charge density away from the phenoxy oxygen atom, thereby enhancing the degree of charge dispersal in the overall anion. Iodine was also incorporated in one case HOC(2-OH-3-C_6H_2I)$(CF_3)_2$, to study the effect of halogen substitution. The compound HOC(2-OH-3-*t*-Bu-5-Me-C_6H_2)$(CF_3)_2$ was designed according to a different strategy: it is hoped that by sterically blocking the phenoxy oxygen atom, its nucleophilicity will decrease, thereby making the anion more weakly coordinating. The results of the work focusing on the relative weakly coordinating abilities of the anions that correspond to these diols will be reported in a subsequent paper.

The isolated yields ranged from 36 to 69%, and the modified procedure resulted in a 67% yield for HOC(2-OH-C_6H_4)$(CF_3)_2$, a modest increase from the 62% yield reported by Gilbert. Not all impurities were identified, but the major component was found to be the *para*-substituted isomer. Purification was performed by recrystallization from a mixture of hexane and chloroform or by sublimation under reduced pressure. The only exception was HOC(2-OH-3-C_6H_2I)$(CF_3)_2$, which was a liquid and was purified by distillation. Other than for the preparation of HOC(2-OH-3-C_6H_2F)$(CF_3)_2$, the reaction times ranged from 30 to 66 h. The synthesis of HOC(2-OH-3-C_6H_2F)$(CF_3)_2$ was unusual in that even after 3 weeks of stirring, the pressure of hexafluoroacetone had not decreased enough to account for the amount of phenol starting material. As a result, the isolated yield was the lowest observed. This behavior was reproducible. The reason for the slow reactivity of 2-fluorophenol under these reaction conditions is not known at this time.

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