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Preparation of α,α-difluoroalkanesulfonic acids

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Abstract

Chlorodifluoromethanesulfonic acid (**1**) was prepared using a new procedure starting from perchloromercaptan, which is readily obtained from chlorination of CS_2. Modified Swarts reaction transformed *N*,*N*-diethyl trichloromethanesulfenamide into *N*,*N*-diethyl chlorodifluoromethanesulfenamide, and the latter species was further oxidized and hydrolyzed into chlorodifluoromethanesulfonic acid. The preparations of other two new α,α-difluoroalkanesulfonic acids, phenyl difluoromethanesulfonic acid (**2**) and 2-phenyl-1,1,2,2,-tetrafluoroethanesulfonic acid (**3**), are also disclosed. The acids **2** and **3** are stable in the forms of sodium (lithium) salts or in aqueous solutions; however, the pure forms of **2** and **3** can readily undergo defluorinations. **1**–**3** and their salts have potential applications as superacid catalysts and lithium battery electrolytes.

Keywords: Chlorodifluoromethanesulfonic acid; Phenyl difluoromethanesulfonic acid; 2-Phenyl-1,1,2,2-tetrafluoroethanesulfonic acid; Fluorinations

1. Introduction

Fluorinated alkanesulfonic acids are strong Bronsted acids and they have found important applications as both acid catalysts and surfactants [1]. The strong electron-withdrawing effect of fluoroalkyl groups increase the stability of the fluoroalkanesufonate anion ($R_fSO_3^-$) and thus enhance the acidity of these acids. Fluoroalkanesulfonic acid catalysts include trifluoromethanesulfonic acid (triflic acid) [2], pentafluoroethanesulfonic acid (pentflic acid) [3], perfluorinated resinsulfonic acid (Nafion-H®) [4], Nafion/silica nanocomposites [5], etc. These perfluorinated sulfonic acids are superacids and much stronger than such acid catalysts, as sulfonated cross-linked polystyrene type resin (Dowex® and Amberlyst®) [6] and zeolites [7].

Although perfluoroalkanesufonic acids are known for decades, few selectively fluorinated α,α-difluoroalkanesufonic acids have been reported. Chlorodifluoromethanesufonic acid ($ClCF_2SO_3H$, **1**) can be considered as a superacidic analog of triflic acid. The first preparation of $ClCF_2SO_3H$ was reported by Yagupol'skii and co-workers [8] via a tedious pathway. Sweeney et al. [9] also reported the preparation of **1** by the reaction of Cl_2CHSH with HOF over $CuCl_2$–KCl in low yield. **1** was reported to have been used as an acid catalyst in the dimerization of styrenes [10] and as lithium battery electrolyte [11]. The latter study claimed its advantage over conventional $CF_3SO_3^-Li^+$ by preventing passivation of the anodes and improving the low-temperature discharge performance of the batteries. More recently, Smertenko and coworkers [12] claimed the preparation of **1** via electrochemical oxidation of sulfodifluoroactetic acid ($HOSO_2CF_2CO_2H$) in the presence of chlorine (Cl_2). But no specific synthetic procedures were made available.

Other α,α-difluoroalkanesufonic acids of potential interest such as phenyl difluoromethanesulfonic acid ($PhCF_2SO_3H$, **2**), and 2-phenyl-1,1,2,2-tetrafluoroethanesulfonic acid ($PhCF_2CF_2SO_3H$, **3**) are still unknown.

Hence, we wish to report our results on the new synthesis of α,α-difluoroalkanesufonic acids, specifically of chlorodifluoromethanesulfonic acid **1**, phenyl difluoromethanesufonic acid **2**, and 2-phenyl-1,1,2,2,-tetrafluoroethanesulfonic acid **3**. These acids are potential superacidic catalysts and lithium battery electrolytes.

2. Results and discussion

2.1. Chlorodifluoromethanesulfonic acid ($ClCF_2SO_3H$) 1

Our first approach to prepare chlorodifluoromethanesulfonic acid **1** was to synthesize the intermediate chlorodifluoromethanesulfenyl chloride ($ClCF_2SCl$) from

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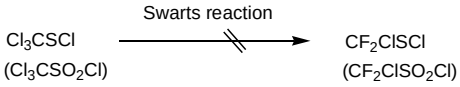


Scheme 1. Attempted Swarts reactions.

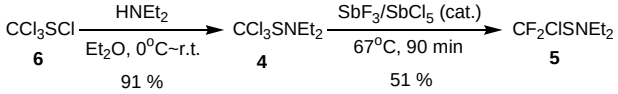
perchloromethyl mercaptan (Cl_3CSCl) by Swarts reaction. However, under reaction conditions of the Swarts (SbF_3/$SbCl_5$, 70 °C; or SbF_3/HF, RT) perchloromethyl mercaptan or trichloromethanesulfonyl chloride did not give the fluorinated product chlorodifluormethylsufenyl(sulfonyl) chloride (Scheme 1).

Yarovenko et al. [13] found that C–S bond was cleaved during the reaction between perchloromethyl mercaptan and metal fluoride. It was also observed earlier that, in the reaction of CS_2 with HF/Cl_2 or with SbF_3/$SbCl_5$, the C–S bonds were broken and fluoromethanes were formed [14].

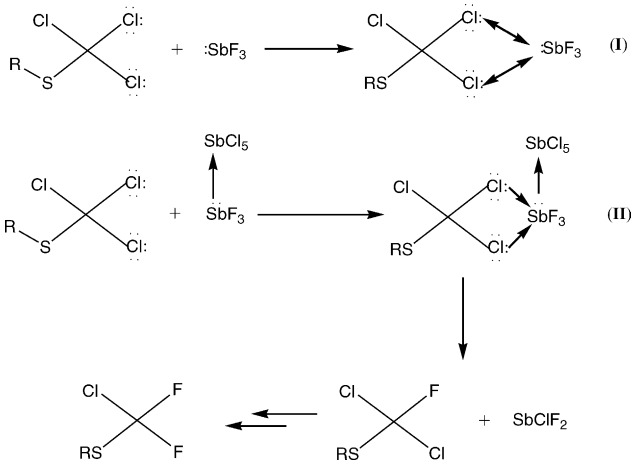
We successfully modified the approach developed by Yarovenko et al. [13] to avoid the C–S bond cleavage under Swarts reaction conditions, using the *N*,*N*-diethyl trichloromethanesulfenamide **4** as the precursor (Scheme 2). This reaction works well but is sensitive to close controls of reaction temperature and heating time.

Needed *N*,*N*-diethyl trichloromethanesulfenamide **4** was prepared from perchloromethyl mercaptan **6** and diethylamine in 91% yield. The Swarts reaction was carried out without solvent using SbF_3 as the fluorinating agent in the presence of catalytic amount of $SbCl_5$. Temperature (67–70 °C) and reaction time (1.5–2 h) were the optimized conditions for the halogen-exchange reaction. After separating from some black tar-like byproduct, product **5** was isolated via vacuum distillation in 44–51 % yields (in contrast to the results of Yarovenko et al.'s 21–24%). The reaction is also dependent on the amount of $SbCl_5$ added to the reaction mixture to initiate the exothermic reaction. It was found 5–10 mol% of $SbCl_5$ was needed to efficiently activate the halogen-exchange reaction. Without $SbCl_5$ or with trace amount of $SbCl_5$ the yields were extremely poor. The proposed role of $SbCl_5$ in the reaction is shown in Scheme 3.

Since antimony trifluoride (SbF_3) has one non-bonded electron pair, it repulses the lone-pair electrons of chlorine atoms in chlorinated compounds resulting in sluggish fluorination (Scheme 3 (I)). When the strong Lewis acid $SbCl_5$ is added, its coordination with SbF_3 diminishes interaction of the antimony's lone-pair electron with chlorine atoms, and thus increasing the fluorinating ability of SbF_3 (Scheme 3 (II)). A similar explanation was offered by Yagupol'skii and coworkers [15] for the fluorination of benzylic C–Cl bonds into the corresponding C–F bonds.



Scheme 2. Preparation of $CF_2ClSNEt_2$.



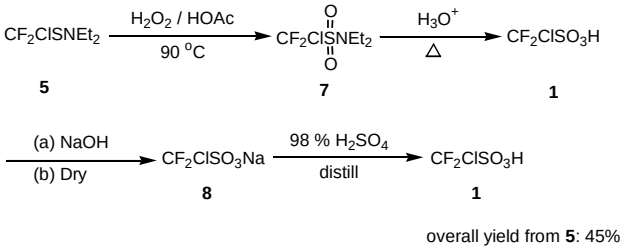
Scheme 3. Mechanistic suggestion of the role of $SbCl_5$ in halogen-exchange reaction.

N,*N*-Diethyl chlorodifluoromethanesulfenamide **5** was subsequently further oxidized by 30% aqueous hydrogen peroxide (H_2O_2) in acetic acid at 90–100 °C, which produced *N*,*N*-diethyl chlorodifluoromethanesulfonamide **7**. **7** was then hydrolyzed into chlorodifluoromethanesulfonic acid **1** (Scheme 4). Neutralization of **1** by NaOH gave sodium chlorodifluorosulfonate **8**, which was dried under vacuum at 120 °C. Dried salt **8** was mixed with 98% sulfuric acid and then distilled under vacuum to produce pure CF_2ClSO_3H as a colorless fuming liquid.

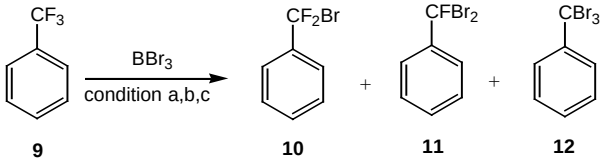
2.2. Phenyl difluoromethanesulfonic acid ($PhCF_2SO_3H$) 2

The new phenyl difluoromethanesulfonic acid **2** was prepared starting from α,α,α-trifluorotoluene **9**. In the first step, we prepared α-bromo-α,α-difluorotoluene **10** by halogen-exchange reaction between $PhCF_3$ and BBr_3 (Scheme 5). This reaction can also produce α,α,α-bromodifluoro-, dibromofluoro- and tribromotoluenes under different reaction conditions. $PhCF_2Br$ **10** was isolated in 43% yield by reacting 10 eq. of $PhCF_3$ with 1 eq. of BBr_3 under reflux for 2 h.

Sulfinatodehalogenation [16,17] of α-bromo-α,α-difluorotoluene **10** using sodium dithionite ($Na_2S_2O_4$) under basic condition gave phenyl difluoromethanesulfinic acid sodium salt ($PhCF_2SO_2^-Na^+$) **13** (Scheme 6). Oxidation of **13** by



Scheme 4. Preparation of CF_2ClSO_3H.



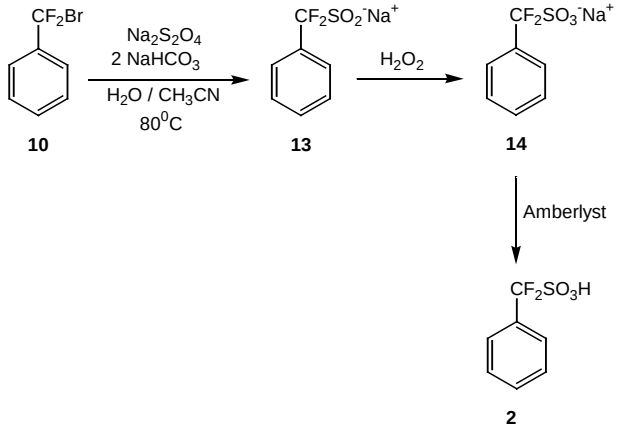
conditon	a:	43%	trace(0.3%)	24%
	b:	14%	trace	48%
	c:	-	-	92%

Condition a: neat, PhCF3 / BBr_3 = 10/1, reflux for 2 hr followed by standing overnight at r.t.
b: CH_2Cl_2 as solvent, PhCF3 / BBr_3 = 3/1, the reaction was run for 5 days at r.t.
c: CCl_4 as solvent, PhCF3 / BBr_3 = 1/1.1, at r.t. for 32 h.

Scheme 5. F/Br exchange reaction of $PhCF_3$ using BBr_3.

30% aqueous H_2O_2 yielded sodium phenyldifluoromethanesufonate ($PhCF_2SO_3^-Na^+$) **14**. The crude stable salt **14** was dried under vacuum. An aqueous solution of **14** was ion-exchanged over an acid resin Amberlyst® column, giving the acid form $PhCF_2SO_3H$ **2**. Acid **2** is stable in aqueous solution. However, attempted to remove water to obtain its pure dry form at 60–70 °C/0.1 mmHg led to decomposition. The product isolated from its decomposition residue was benzoic acid. Other attempts to isolate pure $PhCF_2SO_3H$ by vacuum distillation of the salt **14** and 98% sulfuric acid gave similar decomposition.

This decomposition is most probably an acid-catalyzed hydrolysis process. The stability of $PhCF_2SO_3H$ in water solution indicates that the hydrolysis reaction is dependent on the acidity rather than the amount of water. Due to the leveling effect of water, the acidity of $PhCF_2SO_3H$ is decreased in water solution making the hydrolysis inefficient. When the bulk of water was removed, the superacidity of $PhCF_2SO_3H$ self-catalyzes its decomposition. Another reason is the lability of benzylic C–F bonds in this acid **2**, which was confirmed by the fact that, $PhCF_3$ also readily hydrolyzes into benzoic acid in triflic acid medium.



Scheme 6. Preparation of $PhCF_2SO_3H$.

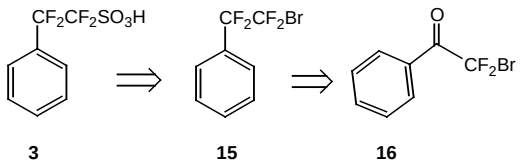
2.3. 2-Phenyl-1,1,2,2-tetrafluoroethanesulfonic acid ($PhCF_2CF_2SO_3H$) 3

Due to the unsuccessful isolation of pure $PhCF_2SO_3H$, we considered an alternative, 2-phenyl-1,1,2,2-tetrafluoroethanesulfonic acid **3** and carried out its preparation. Since there is one additional $–CF_2–$ group intervening the $–CF_2SO_3H$ moiety, it was presumed that the benzylic C–F bonds in this acid would be more stable. The retro synthetic route is shown in Scheme 7.

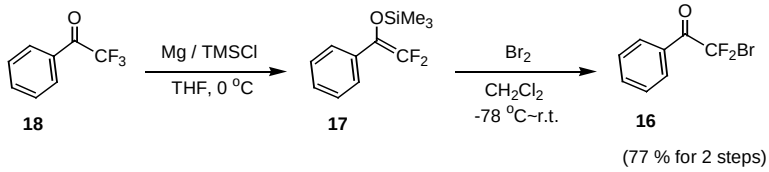
The attempted synthesis of **16** with fluoride induced bromodifluoromethylation of methyl benzoate using Me_3SiCF_2Br reagent [18], however, failed. The magnesium metal mediated defluorination [19,20] of 2,2,2,-trifluoroacetophenone provided an efficient way to prepare compound **16** from inexpensive $PhCOCF_3$ in high yield (Scheme 8). The difluorosilyl enol ether **17** was conveniently prepared, followed by bromination with bromine. The bromination reaction was facile even at −78 °C, and the reaction proceeded smoothly with high selectivity (Scheme 8).

Deoxofluorination of 2-Bromo-2,2-difluoroacetophenone **16** readily gave 2-bromo-1,1,2,2-tetrafluoroethylbenzene **19** (Scheme 9). Diethylaminosulfur trifluoride (DAST) was used as deoxofluorinating agent.

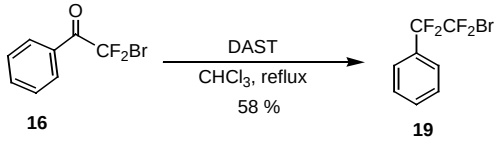
By similar approach as the preparation of $PhCF_2SO_3H$, **19** was transformed into the new acid $PhCF_2CF_2SO_3H$ **3** (Scheme 10). However, although acid **3** was stable in aqueous solution, it readily decomposed upon attempted removal of water by vacumm distillation. Similarly, when the stable salt $PhCF_2CF_2SO_3Na$ was mixed in 98% sulfuric acid followed by vacuum distillation, rapid decomposition



Scheme 7. Retro synthetic preparation of $PhCF_2CF_2SO_3H$.



Scheme 8. Preparation of $PhCOCF_2Br$.



Scheme 9. Preparation of $PhCF_2CF_2Br$ using DAST.

happened. Superacid catalyzed hydrolysis is fast and similar to that of $PhCF_2SO_3H$ (vide infra).

Both acids **2** and **3** when treated with LiOH gave the corresponding lithium salts. These lithium sulfonates can be dried. They can serve as lithium battery electrolytes.

3. Conclusions

We developed a new route for the synthesis of chlorodifluoromethanesulfonic acid **1**, a useful superacid. Syntheses of phenyl difluoromethanesulfonic acid ($PhCF_2SO_3H$) **2** and 2-phenyl-1,1,2,2-tetrafluoroethanesulfonic acid ($PhCF_2CF_2SO_3H$) **3** were also carried out. It was found that the sodium salts of latter two acids are quite stable, but the acids themselves are only stable in aqueous solution. In isolated form, both acids readily undergo self-catalyzed acid hydrolysis. The synthesized acids **1**–**3** have useful potential applications as acid catalysts and lithium battery electrolytes.

4. Experimental

4.1. General

Unless otherwise mentioned, all reagents were purchased from commercial sources. Diethyl ether and THF were all distilled under nitrogen over sodium/benzophenone ketyl prior to use. Toluene was distilled over sodium. Column chromatography was carried out using silca gel (60–200 mesh).

^1H, ^{13}C, ^{19}F NMR spectra were recorded on Bruker AMX 500 and AM 360 NMR spectrometers. $(CH_3)_4Si$ (TMS) was used as an internal standard for ^1H and ^{13}C NMR, $CFCl_3$ was used as internal standard for ^{19}F NMR. For some cases, $CDCl_3$ was used as the internal standard for ^1H NMR (7.26 ppm) and ^{13}C NMR (77 ppm). IR spectra were obtained on a Perkin-Elmer FTIR Spectrometer 2000. Mass spectra were obtained on a Hewlett-Packard 5890 Gas Chromatograph equipped with a Hewlett Packard 5971 Mass Selective Detector at 70 eV.

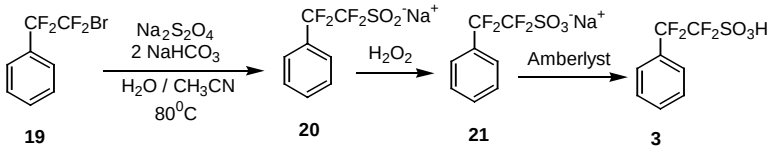
4.2. Synthesis of chlorodifluoromethanesulfonic acid (*1*)

4.2.1. Perchloromethyl mercaptan (*6*)

Into a 1 l three-neck round bottom flask equipped with a magnetic stirrer, a condenser and two septa, was added 440 ml CS_2, 280 ml of water, and 200 ml of 37% HCl. The flask was cooled to 0 °C, and chlorine gas was bubbled into the reaction mixture slowly. The chlorine bubbling rate was controlled carefully to avoid chlorine to permeate outside. The reaction was processed for 2 days, and totally 438 g (6.16 mol) chlorine gas was consumed. The organic phase was isolated, washed three times with brine and dried over $MgSO_4$. The CS_2 solvent was removed under vacuum and 144 g crude product **6** was collected, yield 63%. After fractional distillation, 131.9 g (57%) pure product **6** was obtained as a colorless liquid, bp 144–145 °C. ^{13}C NMR (62 MHz, $CDCl_3$): δ 97.49 [21].

4.2.2. N,N-Diethyl trichloromethanesulfenamide (*4*)

At 0 °C, into a mixture of 50 ml of ether and 56.5 ml (546 mmol) of diethylamine, was slowly added 50.74 g (273 mmol) of perchloromethyl mercaptan **6** in 35 ml of ether through a dropping funnel. After addition was completed, the reaction mixture was stirred for another 1 h at room temperature. Then 50 ml of 10% HCl was added, and the organic phase was separated. The aqueous phase was further extracted with 20 ml of ether. Combined ether phase was washed with 10% $NaHCO_3$ solution, and then with 30 ml of water. After drying over $CaCl_2$, the solvent was removed under vacuum. The crude product was distilled to afford 55.12 g (91% yield) of product **4** as a colorless liquid,



Scheme 10. Synthesis of $PhCF_2CF_2SO_3H$.

bp 78 °C/12.9 mmHg. ^{1}H NMR (360 MHz, $CDCl_3$): δ 1.24 (t, $^3J_{H-H} = 7$ Hz, 6H); 3.34 (m, $^3J_{H-H} = 7$ Hz, 2H); 3.59 (m, $^3J_{H-H} = 7$ Hz, 2H). ^{13}C NMR (62 MHz, $CDCl_3$): δ 14.37; 51.92; 104.46. MS (70 eV): 223 [M^+ (^{36}Cl)]; 223 [M^+ (^{35}Cl)]; 188 [$(M^{-35}Cl)^+$]; 186 [$(M^{-36}Cl)^+$]; 104 [$(SNEt_2)^+$].

*4.2.3. N,N-Diethyl chlorodifluoromethanesulfenamide (**5**)*

Under an argon atmosphere, into a 500 ml three neck round bottom flask equipped with a condenser and two septa, was added 54.5 g (245 mmol) of **4** and 32.85 g (184 mmol) of SbF_3. The reaction mixture was heated up to 67 °C with stirring, and 2 g (6.7 mmol) of $SbCl_5$ was added in via syringe. The exothermic reaction ensued immediately, and the color of reaction mixture turned brown. The reaction mixture was stirred for another 1.5 h, and then was cooled down to room temperature. The upper liquid layer was decanted out, and black tar at the bottom of flask was washed with ether (25 ml × 4). The combined organic phase was vacuum distilled to give 23.85 g (51%) of product **5** as a colorless liquid, bp 57–59 °C/50 mmHg. (*Caution*: the compound **5** must be distilled under vacuum; one attempt to distill under atmospheric pressure caused explosion!) ^{1}H NMR (360 MHz, $CDCl_3$): δ 1.16 (t, $^3J_{H-H} = 7$ Hz, 6H); 3.15 (b, 4H). ^{13}C NMR (62 MHz, $CDCl_3$): δ 13.74; 52.48; 133.76 (t, $^1J_{C-F}$= 336.7 Hz). ^{19}F NMR (338 MHz, $CDCl_3$): δ −35.57. MS (70 eV): 191 [M^+ (^{37}Cl)]; 189 [M^+ (^{35}Cl)]; 104 [$(SNEt_2)^+$]; 85 [$(CF_2{}^{35}Cl)^+$].

*4.2.4. Chlorodifluoromethanesulfonic acid (**1**)*

Into a solution of 20.79 g (110 mmol) of **5** in glacial acetic acid (100 ml) at 75–85 °C, was added dropwise 100 ml of 30% H_2O_2. Then the reaction mixture was heated at 90 °C for another 2 h. The reaction progress was monitored by ^{19}F NMR: at beginning **5** was transformed into *N,N*-diethyl chlorodifluoromethanesulfonamide **7** and then **7** was further hydrolyzed into chlorodifluoromethanesulfonic acid **1** (^{19}F NMR: −63 ppm). Subsequently, most of the water and acetic acid were distilled out from reaction mixture using a 17 cm column, and to the residue 16 ml 50% aqueous NaOH solution was added to neutralize the acids (using pH paper). After water was removed, the sodium salt **8** was dried at 120 °C/0.1 mmHg. To the dried salt **8**, 50 ml of 98% H_2SO_4 was added, and the mixture was stirred vigorously at 100 °C for 2 h, followed by careful fractional distillation to afford 8.19 g (45% yield) acid **1** as a colorless fuming liquid, bp 104–107 °C/7 mmHg. ^{13}C NMR (62 MHz, DMSO-d_6): δ 125.96 (t, $^1J_{C-F}$= 330 Hz). ^{19}F NMR (338 MHz, DMSO-d_6): δ −62.36.

*4.3. Synthesis of phenyl difluoromethanesulfonic acid ($PhCF_2SO_3H$) **2***

*4.3.1. α-Bromo-α,α-difluorotoluene (**10**)*

Under an argon atmosphere, into a 1 l three-neck round bottom flask equipped with a condenser and two septa, was added 146.1 g (1 mol) of $PhCF_3$ and then slowly was added 25.05 g (0.1 mol) of BBr_3 at room temperature. Slowly the reaction mixture became warm and gaseous BF_3 started bubbling out. The color of the mixture turned to yellow initially and amber-like. After 1 h, the effervescence ceased and the mixture started to cool down. The mixture was refluxed for another 2 h, followed by stirring at room temperature overnight. Then the reaction mixture was poured into 100 ml of ice water, and extracted with CH_2Cl_2 (50 ml × 3). The combined organic phase was washed with 30 ml of water, and then was dried over $CaCl_2$. After evaporating solvents, 48.44 g of amber color liquid was collected as the crude product, which was distilled to give 26.71 g (43% yield) of product **10** as a colorless liquid, bp 54 °C/20 Torr. ^{1}H NMR (360 MHz, $CDCl_3$): δ 7.45 (m, 3H); 7.59 (m, 2H). ^{13}C NMR (62 MHz, $CDCl_3$): δ 118.41 (t, $^1J_{C-F}$= 303.9 Hz); 124.29 (t, $^3J_{C-F}$= 5.5 Hz); 128.62; 131.24; 138.15 (t, $^2J_{C-F}$= 23.3 Hz). ^{19}F NMR (338 MHz, $CDCl_3$): δ −44.01. MS (70 eV): 189 [$(PhCFBr)^+$]; 127 [$(PhCF_2)^+$]; 108 [$(PhCF)^+$]; 77 (Ph^+).

*4.3.2. α,α-Dibromo-α-fluorotoluene (**11**)*

(0.12 g, 0.3% yield) was also obtained as a high boiling liquid. ^{1}H NMR (360 MHz, $CDCl_3$): 7.46 (m, 3H); 7.72 (m, 2H). ^{13}C NMR (62 MHz, $CDCl_3$): δ 90.65 (d, $^1J_{C-F}$ = 316.0 Hz); 124.05 (d, $^3J_{C-F}$= 7.3 Hz); 128.35; 130.37 (d, $^2J_{C-F}$= 33.5 Hz); 144.71. ^{19}F NMR (338 MHz, $CDCl_3$): −53.82.

*4.3.3. α,α,α–Tribromotoluene (**12**)*

(7.76 g, 24% yield) was obtained as a white solid. ^{1}H NMR (360 MHz, $CDCl_3$): δ 7.34 (m, 3H); 8.02 (d, 2H). ^{13}C NMR (62 MHz, $CDCl_3$): δ 36.32; 126.45; 128.03; 130.09; 146.90.

*4.3.4. Phenyl difluoromethanesulfonic acid (**2**)*

Into a mixture of 135 ml of water, 90 ml of CH_3CN, 25.66 g (305 mmol) of $NaHCO_3$ and 31.61 g (153 mmol) of $PhCF_2Br$ at room temperature, was added 53.2 g (305 mmol) of $Na_2S_2O_4$ under argon atmosphere. The reaction mixture was heated to 80 °C for 12 h. After cooling down, the reaction mixture was filtered, and the solid residue was washed with hot CH_3CN/H_2O (9:1). The combined filtrate was vacuum distilled to remove water and organic solvents to give off-white solid product, which was further washed with 10 ml of hexane and 10 ml petroleum ether. Then the solid was dried at 80 °C under high vacuum to afford 75 g of crude sodium 1-phenyl-1,1-difluoromethanesulfinate **13**. ^{19}F NMR (D_2O): δ −112.75.

Then the salt **13** was dissolved in 100 ml of water, and 30 ml of 50% H_2O_2 was added dropwise at 0 °C. After the exothermic reaction faded, the mixture was stirred at room temperature for another 2 h. After removal of water and excess H_2O_2 under vacuum, the residue salt was washed by CH_2Cl_2 and pet ether. The resulting solid was dried at 80 °C/0.1 mmHg to give 84 g of product sodium

1-phenyl-1,1-difluoromethanesufonate **14**, ^{1}H NMR (D_2O): δ 7.44 (t, $J = 7.9$ Hz, 2H); 7.51 (t, $J = 7.9$ Hz, 1H); 7.59 (d, $J = 7.9$ Hz, 2H). ^{19}F NMR (D_2O): δ −102.52.

Solid **14** was dissolved in 100 ml of H_2O, and then was passed through a Amberlyst® acid resin column (15 mm × 410 mm). The free water (∼80 ml) was evaporated from resulting solution to give a condensed aqueous solution of phenyl difluoromethanesulfonic acid **2**. ^{1}H NMR (D_2O): δ 7.58 (t, $J = 7.9$ Hz, 2H); 7.66 (t, $J = 7.9$ Hz, 1H); 7.73 (d, $J = 7.9$ Hz, 2H). ^{13}C NMR (D_2O): δ 117.05 (t, $^1J_{C-F}$= 274.7 Hz); 123.43 (t, $^3J_{C-F}$= 6.0 Hz); 125.41; 127.00 (t, $^2J_{C-F}$= 23.0 Hz); 128.50. ^{19}F NMR (D_2O): −102.55.

4.3.5. Attempted purification of acid (2)

The condensed solution of **2** prepared above (3.0 g) was vacuum distilled over a 70 °C in an oil bath under 0.1 mmHg vacuum. After all the water distilled out, the gummy solid residue immediately decomposed to give some white crystalline solid with a melting point 122–123 °C. The solid turns out to be benzoic acid. ^{1}H NMR ($CDCl_3$): δ 7.50 (t, 2H); 7.64 (t, 1H); 8.17 (d, 2H). ^{13}C NMR ($CDCl_3$): δ 128.42; 129.25; 130.15; 133.74; 172.19. MS: 122 (M^+).

4.4. Synthesis of 2-phenyl-1,1,2,2-tetrafluoromethanesulfonic acid ($PhCF_2CF_2SO_3H$) 3

4.4.1. 2-Bromo-2,2-difluoroacetophenone (16)

Into the mixture of magnesium turnings (5.31 g, 0.22 mol) and TMSCl (47.58 g, 0.44 mol) in 150 ml of THF at 0 °C, was slowly added under argon atmosphere $PhCOCF_3$ (20.00 g, 0.11 mol). The reaction mixture was stirred at 0 °C for 4 h. After removal of the solvent and excess TMSCl under vacuum, 50 ml of hexane was added. Solid species was removed via vacuum filtration, and the filtrate was concentrated to give 25.18 g crude difluoro silyl enol ether **17**. ^{1}H NMR ($CDCl_3$): δ 0.60 (s, 9H), 7.38 (t, $J = 7.5$ Hz, 1H), 7.47 (t, $J = 7.5$ Hz, 2H), 7.61 (d, $J = 8.8$ Hz, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 0.02$, 114.09 (q, $^2J_{(C,F)}$= 18.0 Hz), 125.84, 127.72, 128.25, 132.71, 154.87 (t, $^1J_{(C,F)}$= 286.8 Hz); ^{19}F NMR ($CDCl_3$): $\delta = -100.39$ (d, $^2J_{(F,F)}$= 68.0 Hz), −112.16 (d, $^2J_{(F,F)}$= 68.0 Hz). MS (70 eV) *m/z* (relative intensity): 228 (M^+, 79), 213 (2), 197 (1), 186 (5), 177 (60), 165 (1), 149 (1), 143 (1), 131 (5), 115 (9), 105 (36), 89 (45), 81 (29), 77 (75), 73 (100).

The above prepared **17** was dissolved in 100 ml of dry CH_2Cl_2, and at −78 °C bromine was added via a syringe until the brown color no longer disappeared. After stirring for another 30 min, the solvent was evaporated under vacuum, and the residue was washed and extracted with CH_2Cl_2. The organic phase was further washed with $NaHCO_3$, brine and water sequentially. After drying over $MgSO_4$, the solvent was removed to give 21.40 g crude product **16**, yield 83% calculated from $PhCOCF_3$. The crude product was further purified by fractional distillation to afford 20.03 g product **16** as a colorless liquid, bp 99–101 °C/15 mmHg, yield 77% based on $PhCOCF_3$ used. ^{1}H NMR ($CDCl_3$): δ 7.53 (t, $J = 7.8$ Hz, 2H); 7.68 (t, $J = 7.8$ Hz, 1H); 8.15 (d, $J = 8.0$ Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 113.56 (t, $^1J_{C-F}$= 319.1 Hz); 128.87; 129.05; 130.61 (t, $^3J_{C-F}$= 2.6 Hz); 135.09; 181.32 (t, $^2J_{C-F}$ = 26.0 Hz). ^{19}F NMR ($CDCl_3$): δ −58.29. MS (70 eV): 234 (M^+); 105 ($PhCO^+$); 77 (Ph^+).

4.4.2. 2-Bromo-1,1,2,2-tetrafluoroethylbenzene (19)

Under an argon atmosphere, into 9.40 g (40 mmol) **16** in 60 ml of dry chloroform was added 9.76 g (60 mmol) of DAST. The reaction mixture was then refluxed for 34 h. After cooling down to room temperature, the mixture was poured into ice water, and then the organic phase was further washed with $NaHCO_3$, brine and water successively. After drying over $MgSO_4$ and solvent removal, 8.84 g crude product **19** was obtained as a yellow liquid. Further purification by silica gel chromatography using hexane as the eluent gave 5.84 g pure compound **19** as a colorless liquid, yield 58%. ^{1}H NMR ($CDCl_3$): δ 7.47 (t, $J = 7.7$ Hz, 2H); 7.55 (t, $J = 7.5$ Hz, 1H); 7.60 (d, $J = 7.6$ Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 114.93 (tt, $^1J_{C-F}$= 255.0 Hz, $^2J_{C-F}$= 31.3 Hz); 117.66 (tt, $^1J_{C-F}$= 312.8 Hz, $^2J_{C-F}$= 44.7 Hz); 127.06 (t, $^3J_{C-F}$= 6.2 Hz); 128.51; 128.71, 131.72. ^{19}F NMR ($CDCl_3$): δ −65.34 (t, $^3J_{F-F}$= 4.8 Hz); −108.60 (t, $^3J_{F-F}$= 4.8 Hz). MS (70 eV): 256 (M^+); 177 ($PhCF_2CF_2^+$); 127 ($PhCF_2^+$); 77 (Ph^+).

4.4.3. 2-Phenyl-1,1,2,2-tetrafluoroethanesulfonic acid (3)

Under an argon atmosphere, 4.0 g (15.5 mmol) of **19** was mixed with 3.9 g (46 mmol) of $NaHCO_3$, 8.1 g (46 mmol) $Na_2S_2O_4$ in 12 ml of CH_3CN and 20 ml of H_2O, and the reaction mixture was refluxed for 20 h. After cooling down, the reaction mixture was filtered and the filtrate was condensed under vacuum to give 17.38 g of crude product sodium 2-phenyl-1,1,2,2-tetrafluoroethanesulfinate **20**. Solid compound was further washed with 5 ml CH_2Cl_2 and then dried at 80 °C/0.1 Torr to give 10.75 g dry salt **20**. ^{1}H NMR (D_2O): δ 7.43 (t, 2H); 7.49 (t, 1H); 7.52 (d, 2H). ^{19}F NMR (D_2O): δ −109.85; −129.68.

The above prepared solid **20** was dissolved in 15 ml of H_2O, cooled down to 0 °C and 5.3 ml 30% H_2O_2 was added dropwise. The reaction mixture was stirred for another 4 h. After filtration of reaction mixture, the resultant filtrate was concentrated to give 8.23 g solid, which was dried at 80 °C under high vacuum to give 8.04 g of dry crude sodium 2-phenyl-1,1,2,2-tetrafluoroethanesulfonate **21**. ^{1}H NMR (D_2O): δ 7.39 (t, $J = 7.9$ Hz, 2H); 7.46 (t, $J = 7.9$ Hz, 1H); 7.51 (d, $J = 7.9$ Hz, 2H). ^{19}F NMR (D_2O): δ −107.85; −114.05.

Above prepared solid **21** (2 g) was dissolved in 20 ml of water, and was passed through a Amberlyst® acid resin column (10 mm × 150 mm). The resulting amber colored solution was concentrated by evaporating water under high vacuum at room temperature to give 2.28 g concentrated

acid **3**. ^{1}H NMR (D_2O): δ 7.48 (t, $J = 7.9$ Hz, 2H); 7.56 (t, $J = 7.9$ Hz, 1H); 7.61 (d, $J = 7.9$ Hz, 2H). ^{13}C NMR (DMSO-d_6): δ 115.61 (tt, $^{1}J_{C-F} = 287.2$ Hz, $^{2}J_{C-F} = 37$ Hz); 117.62 (tt, $^{1}J_{C-F} = 253$ Hz, $^{2}J_{C-F} = 31$ Hz); 127.88 (t, $^{3}J_{C-F} = 6.4$ Hz); 129.63; 132.07 (t, $^{2}J_{C-F} = 25$ Hz); 132.55. ^{19}F NMR (DMSO-d_6): δ −106.54; −113.98.

*4.4.4. Attempted purification of acid (**3**)*

The condensed solution of **3** prepared above (1.0 g) was vacuum distilled over a 55–60 °C oil bath under 0.1 mmHg vacuum. After most water distilled out, the gummy solid residue was immediately decomposed to evolve gaseous compounds (possibly HF and SO_3). ^{19}F NMR of the dark liquid residue showed only one peak at −110.0 ppm.

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