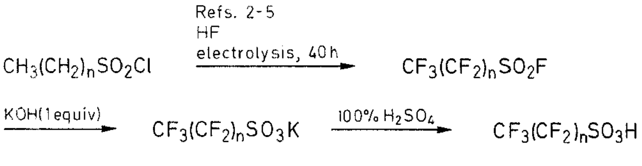
One-Pot Preparation of Pentafluoroethanesulfonic (Pentflic) Acid by the Organolithium Pathway[1]

George A. Olah,* Thomas Weber, Donald R. Bellew, Omar Farooq

Donald P. and Katherine B. Loker Hydrocarbon Research Institute and the Department of Chemistry, University of Southern California, Los Angeles, CA 90089-1661, USA

Pentafluoroethanesulfonic (pentflic) acid was prepared in high yield via the corresponding lithium pentflate obtained by lithiation of pentafluoroethyl iodide, followed by sulfonylation with sulfur dioxide, oxidation by hydrogen peroxide, and hydrolysis, in a one-pot reaction without isolation of any intermediates. The prepared pentflic acid was characterized, including by its yet unreported ^{13}C- and ^{19}F-NMR spectra.

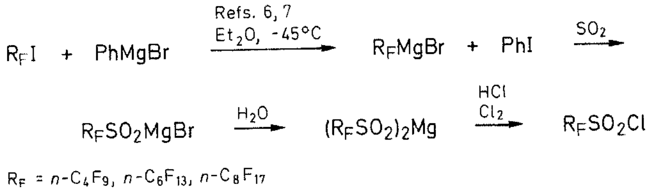
Perfluoroalkanesulfonic acids are usually prepared by electrochemical fluorination[2-5] of alkanesulfonyl chlorides, $CH_3(CH_2)_nSO_2Cl$ (n = 1-7), according to the following sequences.



$$CH_3(CH_2)_nSO_2Cl \xrightarrow{\substack{\text{Refs. 2-5} \\ \text{HF} \\ \text{electrolysis, 40 h}}} CF_3(CF_2)_nSO_2F \xrightarrow{\text{KOH(1 equiv)}} CF_3(CF_2)_nSO_3K \xrightarrow{100\%\ H_2SO_4} CF_3(CF_2)_nSO_3H$$

The procedure smoothly gives perfluoroalkanesulfonyl fluorides. In order to obtain the corresponding perfluoroalkanesulfonic acids, the sulfonyl halides have to be hydrolyzed and subsequently be treated with 100 % sulfuric acid. The yields of the perfluoroalkanesulfonyl fluorides decrease steadily with increasing chain length of the perfluoroalkyl groups. Thus, whereas both trifluoromethanesulfonic (triflic) acid and pentafluoroethanesulfonic (pentflic) acid could be obtained in 87 % and 79 % yield, respectively, C_3-C_8 perfluoroalkanesulfonic acids were obtained in moderate to very poor yields (75-25 %) only.

Preparation of perfluoroalkanesulfonyl chlorides, which are direct precursors for the preparation of perfluoroalkanesulfonic acids, has been reported for a few selected perfluorinated compounds from the corresponding bis(perfluoroalkanesulfonyl)magnesium, generated according to the following sequences,[6,7] in 30-60 % yield. In these syntheses higher yields were reported for longer chain length compounds.



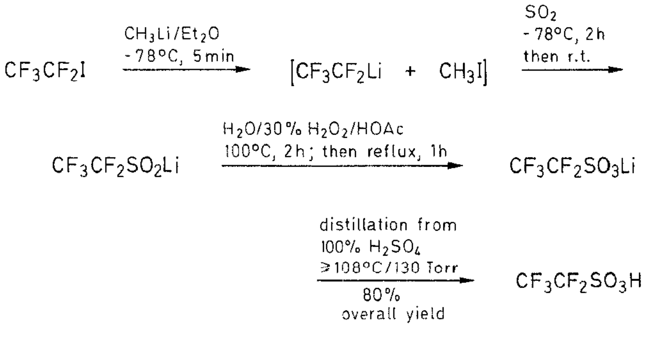
$$R_FI + PhMgBr \xrightarrow{\substack{\text{Refs. 6, 7} \\ Et_2O,\ -45^\circ C}} R_FMgBr + PhI \xrightarrow{SO_2} R_FSO_2MgBr \xrightarrow{H_2O} (R_FSO_2)_2Mg \xrightarrow{\substack{HCl \\ Cl_2}} R_FSO_2Cl$$

R_F = n-C_4F_9, n-C_6F_{13}, n-C_8F_{17}

The yields of the discussed perfluoroalkanesulfonyl chlorides could not be improved significantly by using Zn-Cu couple[8-10] with perfluoroalkyl iodide[11] and sulfur dioxide in dimethyl sulfoxide. About 40-80 % yield of the corresponding sulfonyl chlorides were obtained with increasing yields for the longer chain length compounds. In studies of the thermal decomposition[12-14] as well as the anodic oxidation,[15-17] of short-chain (e.g., C_2, C_3) perfluoroalkanesulfonic acids the above discussed organometallic Zn-Cu couple method[8] was always referred to. No mention has been given to the per cent yield of these lower homologues or the general applicability or limitation of the method. Wakselman and Tordeux more recently reported the preparation of triflic acid from trifluoromethyl bromide by reaction with zinc (aluminum, magnesium, or cadmium) metal mixed with dimethylformamide and sulfur dioxide under pressure.[18] Trifluoromethylsulfinate was isolated as the sodium salt, oxidized with hydrogen peroxide followed by hydrolysis to trifluoromethanesulfonic acid.

In continuation of our studies on perfluoroalkanesulfonic acids and their derivatives, we now wish to report an efficient one-pot procedure based on the organolithium pathway for the preparation of pentafluoroethanesulfonic (pentflic) acid under mild conditions. Pentafluoroethyllithium was found by Gassman and O'Reilly[20] to be stable at $-78^\circ C$, thus opening up the possibility for this convenient preparation.

When to a well-stirred solution of commercially available pentafluoroethyl iodide in diethyl ether cooled to $-78^\circ C$ an equimolar amount of methyllithium was added under dry nitrogen and subsequently excess of dry sulfur dioxide was passed through the resulting solution, lithium pentafluoroethanesulfinate was obtained as a white solid on warming up the reaction mixture to room temperature followed by usual workup. Lithium pentafluoroethanesulfinate is obtained in essentially quantitative yield based on pentafluoroethyl iodide used (as determined by IR spectroscopy). Oxidation of lithium pentafluoroethanesulfinate was carried out with hydrogen peroxide in aqueous acetic acid at 100 °C to give lithium pentafluoroethanesulfonate (pentflate) in quantitative yield (again determined by IR spectroscopy). Lithium pentflate on distillation from 100 % sulfuric acid at reduced pressure gave pentflic acid in near



$$CF_3CF_2I \xrightarrow{\substack{CH_3Li/Et_2O \\ -78^\circ C,\ 5\,min}} [CF_3CF_2Li + CH_3I] \xrightarrow{\substack{SO_2 \\ -78^\circ C,\ 2\,h \\ \text{then r.t.}}} CF_3CF_2SO_2Li \xrightarrow{\substack{H_2O/30\%\ H_2O_2/HOAc \\ 100^\circ C,\ 2\,h;\ \text{then reflux, 1 h}}} CF_3CF_2SO_3Li \xrightarrow[\substack{80\% \\ \text{overall yield}}]{\substack{\text{distillation from} \\ 100\%\ H_2SO_4 \\ \geq 108^\circ C/130\ Torr}} CF_3CF_2SO_3H$$

quantitative yield (based on the lithium pentflate used) (bp 108 °C/130 Torr). The pentflic acid obtained was, besides its microanalysis, also further characterized by its yet unreported ^{13}C- and ^{19}F-NMR spectra.

In further study of the preparation it was found that pentflic acid could also be prepared in an essentially one-pot reaction by efficient removal of solvents after every step to obtain the dry lithium salts. Thus, removal of ether from lithium pentafluoroethanesulfinate and the acetic acid containing aqueous mixture from the corresponding sulfonate followed by sulfuric acid treatment gave the desired pentflic acid. It is to be mentioned that extension of the present procedure to the preparation of homologue perfluoroalkanesulfonic acids as well as triflic acid itself was unsuccessful. Thus neither heptafluoropropanesulfonic, heptafluoroisopropanesulfonic, or triflic acid could be prepared from the corresponding perfluoroalkyl iodides by this procedure. Trifluoromethyllithium has been reported to decompose to give difluorocarbene and lithium iodide even at low temperature in the presence of a suitable nucleophile.[19] This is in contrast to the stability found by Gassman and O'Reilly for pentafluoroethyllithium at −78 °C,[20] as used in the present work. The presently developed preparation of pentflic acid is a simple and efficient method, which can replace the electrochemical method[2−5] or preparations from pentafluoroethyl iodide via Grignard chemistry or with use of Zn-Cu couple.[6−10]

^{13}C- and ^{19}F-NMR spectra were obtained on a Varian (VXR-200) superconducting NMR spectrometer using TMS and $CFCl_3$, respectively, as external references. Infrared spectra were recorded on a Perkin-Elmer (model 7500) FTIR spectrophotometer. Elemental analysis was carried out by Galbraith Laboratories, Inc., Knoxville, TN. Pentafluoroethyl iodide was obtained from Strem Chemicals. Methyllithium (1.4 M solution in ether) was purchased from Aldrich. Sulfur dioxide was from Matheson, hydrogen peroxide (30% aqueous solution) from Spectrum Chemical Corp., acetic acid from Baker, sulfuric acid (96%) and fuming sulfuric acid were from Fisher Scientific.

Pentafluoroethanesulfonic (Pentflic) Acid:

To ether (200 mL) placed into a 300-mL 3-necked flask cooled to −78 °C equipped with a reflux condenser, a gas inlet tube, and a septum is condensed pentafluoroethyl iodide (30 g, 122 mmol). The entire reaction sequence is carried out under a positive pressure of dry nitrogen. To the stirred solution, a 1.4 M ethereal solution of methyllithium, 122 mmol is added by means of a syringe. The resultant clear solution is allowed to stir for 5 min, then SO_2 is passed through the solution, which now becomes slightly yellow. When 10 g (150 mmol) of SO_2 has been added, the cylinder is disconnected, and the mixture is stirred at −78 °C for 2 h and then allowed to warm up to room temperature within 2 h and stirred for an additional 1 h before all solvent is carefully removed at reduced pressure: 22.8 g (120 mmol) of *lithium pentafluoroethanesulfinate* (98%) remains in the flask.

IR (KBr): ν = 960, 1010, 1030, 1060, 1135, 1165, 1210, 1350 cm^{-1}.

Oxidation is carried out in a mixture of 30% H_2O_2 (100 mL), and HOAc (10 mL). The mixture is stirred at 100 °C for 2 h, and the clear, colorless solution is subsequently refluxed for 1 h. The solvent is evaporated completely at reduced pressure, and *lithium pentafluoroethanesulfonate* remained in the flask as a colorless solid; yield: 23.8 g (115 mmol, 96%).

IR (KBr): ν = 983, 1071, 1165, 1220 cm^{-1}.

The salt is mixed with 100% sulfuric acid (50 mL) and heated at reduced pressure until product begins to distill out at 108 °C (130 Torr). As soon as the distillation ceases, the oil bath temperature is raised even higher until the distillation stopped completely, giving *pentafluoroethanesulfonic acid*; yield: 19.6 g (85%, based on lithium salt used).

$CF_3CF_2SO_3H$	calc.	C 11.7	H 0.5	F 48.2	S 16.1
(200.1)	found	12.0	0.5	47.5	16.0

^{13}C-NMR (neat, capillary acetone-d_6 reference): δ = 111.86 (t_q, ^1J = 297.5 Hz, ^3J = 42.4 Hz, CF_2); 116.53 ($_q$t, ^1J = 286 Hz, ^3J = 31 Hz, CF_3).

^{19}F-NMR (neat, capillary acetone-d_6 reference): δ = −80.9 (CF_2), −116.7 (CF_3).

Support of our work by the National Institutes of Health and a fellowship to T.W. by the Alexander von Humboldt-Foundation, Bonn, West Germany, is gratefully acknowledged.

Received: 9 September 1988; revised: 23 December 1988

(1) Synthetic Methods and Reactions. 142. Part 141, see: Prakash, G.K.S., Krishnamurti, R., Olah, G.A. *J. Am. Chem. Soc.*, submitted.
(2) Haszeldine, R.N., Kidd, J.M. *J. Chem. Soc.* **1954**, 4228.
(3) Haszeldine, R.N., Kidd, J.M. *J. Chem. Soc.* **1955**, 2901.
(4) Gramstadt, T., Haszeldine, R.N. *J. Chem. Soc.* **1957**, 2640.
(5) Brice, T.J., Trott, P.W. *US Patent* 2732398 (1956); *C.A.* **1956**, *50*, 13982.
(6) Moreau, P., Dalverny, G., Commeyras, A. *J. Fluorine Chem.* **1975**, *5*, 265.
(7) Pierce, P.R., Meiners, A.F., McBee, E.T. *J. Am. Chem. Soc.* **1953**, *75*, 2516.
(8) Blancou, H., Moreau, P., Commeyras, A. *J. Chem. Soc. Chem. Commun.* **1976**, 885.
(9) Miller, J.W.T., Bergmann, E., Fainberg, A.H. *J. Am. Chem. Soc.* **1957**, *79*, 4159.
(10) Blancou, H., Moreau, P., Commeyras, A. *Tetrahedron* **1977**, *33*, 2061.
(11) Haley, B., Haszeldine, R.N., Hewitson, B., Tipping, A.E. *J. Chem. Soc. Perkin Trans. 1* **1976**, 525.
(12) Oudrhiri-Hassani, M., Brunel, D., Germain, A. *J. Fluorine Chem.* **1986**, *32*, 163.
(13) Oudrhiri-Hassani, M., Brunel, D., Germain, A., Commeyras, A. *J. Fluorine Chem.* **1984**, *25*, 219.
(14) Oudrhiri-Hassani, M., Germain, A., Brunel, D., Commeyras, A. *Tetrahedron Lett.* **1981**, *22*, 65.
(15) Brunel, D., Oudrhiri-Hassani, M., Choukroun, H., Germain, A. *Nouv. J. Chim.* **1984**, *8*, 99.
(16) Germain, A., Commeyras, A. *Tetrahedron* **1981**, *37*, 487.
(17) Germain, A., Ortega, P., Commeyras, A. *Nouv. J. Chim.* **1979**, *3*, 415.
(18) Wakselman, C., Tordeux, M. *Bull. Soc. Chim. Fr.* **1986**, 868.
(19) Pierce, O.R., McBee, E.T., Judd, G.F. *J. Am. Chem. Soc.* **1954**, *76*, 474.
(20) Gassman, P.G., O'Reilly, N.J. *J. Org. Chem.* **1987**, *52*, 2481.