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Perfluoroalkylsulfone reactions with nucleophiles

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Abstract

Perfluorodialkylsulfones were found to react readily with metal hydroxides in water or alcohol solution and with ammonia to form fluorinated sulfonic acid derivatives.

Keywords: Perfluorodialkylsulfones; Perfluoroalkylsulfonic acid derivatives

1. Introduction

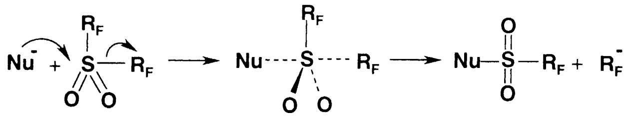
Totally fluorinated sulfones have been known since the pioneering work of Temple in 1968 [1], who prepared the sulfones via the reaction of sulfuryl fluoride or fluorinated sulfonyl fluorides with tetrafluoroethylene (TFE). Since that time, some other perfluorinated sulfones have been reported. Perfluorodimethylsulfone was prepared by direct fluorination [2] and by hydrolysis of bis(trifluoromethyl)difluorosulfoxide [3]. For synthesis of perfluoromethylethylsulfone, the addition of perfluoromethylsulfonyl fluoride (PMSF) to TFE was successfully used [4]. And finally, perfluorosulfolane was prepared by hydrolysis of corresponding cyclic sulfoxydifluoride [5] and also by electro-chemical fluorination (ECF) from 2,5-dihydrothiophen-1,1-dioxide (sulfolene) [6,7]. ECF is also a known method for preparation of perfluorinated diethylsulfone [8] and methylbutylsulfone [9].

For cyclic perfluorosulfolane and 3,4-dichloroperfluorosulfolane, the ring opening reaction with base to form fluorobutanesulfonates with difluoromethyl end group [6] or trifluorovinyl termination [10] has been reported.

Chemical reactions of acyclic perfluorodialkylsulfones are practically unknown. Thermal decomposition at 275 °C with SO_2 removal is probably the only reaction known for perfluorodialkylsulfones. The reaction makes them a good source of perfluoroethyl radicals. Perfluorodiethylsulfone is reported to be a useful initiator for preparation of amorphous TFE–HFP copolymers at high pressures [11].

2. Results and discussion

We report a new synthesis of perfluorinated sulfonic acid derivatives from the reaction of perfluorodialkylsulfones with nucleophiles shown below. The reaction mechanism is probably nucleophilic substitution of the perfluoroalkyl group at a sulfonyl sulfur atom:



The reaction was not previously reported for perfluorodialkylsulfones, nor for partially fluorinated dialkylsulfones with a perfluoroalkyl group connected to the sulfonyl groups. For instance, well-known triflones have considerable value in synthesis because the trifluoromethanesulfonyl group is one of the strongest electron-withdrawing group. When attached to carbon the group activates the adjacent methylene group to proton abstraction by bases to give the triflone α-carbanions rather than the trifluoromethyl carbanion [12]:

$$CF_3SO_2CH_2{-}R + Nu^- \rightarrow CF_3SO_2CH^-{-}R \text{ and no } CF_3^-$$

On the other hand, nucleophilic displacement of the trifluoromethyl group has been reported for trifluoromethylaryl

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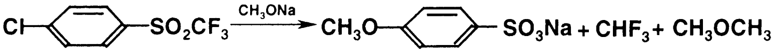
sulfones, probably by a haloform-type process [13]:



See also CF_3 substitution in the reaction of the aryltrifluoromethyl sulfone with Grignard reagents [14].

To our surprise, perfluorodiethylsulfone is easily reacted with nucleophiles to give pentafluoroethanesulfonic acid derivatives and pentafluoroethane (HFC-125), e.g.:

$$C_2F_5SO_2C_2F_5 + KOH/H_2O \rightarrow C_2F_5SO_3K + C_2HF_5$$

$$C_2F_5SO_2C_2F_5 + 2NH_3 \rightarrow C_2F_5SO_2NH^-NH_4{}^+ + C_2HF_5$$

In these cases, the pentafluoroethyl group reacts as if it is a halogen. This rare type of perfluoroalkyl group reactivity was previously reviewed by Knunyants and Cheburkov [15]. The reaction of the sulfone with sodium methoxide in methanol does not stop at methylpentafluoroethanesulfonate. The latter alkylates a second methanol molecule to give dimethylether and the sodium perfluoroethanesulfonate:

$$\begin{aligned}&C_2F_5SO_2C_2F_5 + CH_3ONa + CH_3OH\\&\quad\rightarrow C_2F_5SO_3Na + CH_3OCH_3 + C_2HF_5\end{aligned}$$

Perfluorodimethylsulfone was reacted in a similar manner with lithium hydroxide in methanol to give lithium triflate in high yield. All these reactions involve simple procedures and give high yields of the sulfonic acid derivatives. For instance, the reaction of perfluorodiethylsulfone with sodium methoxide is exothermic and takes only 10 min to complete at room temperature. The sodium pentafluoroethanesulfonate was obtained quantitatively as a white solid. The procedure in the reaction of the sulfone with liquid ammonia is more complex. The product prepared in a stainless steel pressure reactor was usually contaminated by many by-products of unknown chemical structure and sometimes deeply colored. The pentafluoroethanesulfonylamide was prepared by extended heating (65 h) of the reactants in a sealed glass tube at elevated temperature (83 °C) without any solvent. It is probably possible to shorten the reaction time by increasing the temperature, but the gaseous reaction product (HFC-125) has a very low boiling point (−48.5 °C) and does not dissolve in the primary reaction product—the amide salt. Therefore, we were reluctant to increase the temperature using a sealed glass tube. Re-crystallization of the salt from benzene or chloroform and also vacuum sublimation gives known [16] pure perfluoroethansulfonylamide, which is not moisture sensitive and is soluble in water and acetonitrile. When conducted in a glass reactor, the yield of the amide was good (isolated 70% on a 3.0 g sulfone scale) and the product was pure (97%) and did not require additional purification.

3. Experimental details

Analytical data was provided by the Specialty Materials Manufacturing Division analytical group at 3M. The 400 MHz ^1H and 376 MHz ^{19}F NMR spectra were acquired at room temperature using Varian UNITY plus 400 FT-NMR spectrometer.

p-Hexafluoroxylene was used as a cross-integration standard to facilitate the cross-correlation at the various fluorine and proton signal intensities and for quantitative evaluation of sample purity. GC–MS analysis was performed using an HP 5890 Series 2 gas chromatograph, with a 105 m × 0.32 mm Rtx-5 capillary column to introduce the sample to a Finnigan SSQ-700 mass spectrometer. The samples were ionized using chemical ionization with methane as the reagent gas. A gas chromatograph HP 5890 Series 2 with J&W Scientific fused silica capillary column DB 210 (30 m × 0.325 mm) with an FID detector was used for liquids and a Carbopack C column with thermal conductivity detector was used for gases. IR spectra were recorded on a Digilab FTS-40 FT-IR spectrometer.

3.1. *Perfluorodiethylsulfone purification*

A product mixture consisting of 49% perfluoroethanesulfonylfluoride and 49% perfluorodiethylsulfone was distilled using a concentric tube ACE Glass Inc. column with condenser at (−21 °C) to collect pefluorodiethylsulfone with bp 63–63.5 °C and purity 97.1% by GC analysis. The sulfone was contaminated with perfluoroethanesulfonylfluoride and also isomeric $C_4F_9SO_2F$ having the same boiling point range. Agitating the sulfone with concentrated ammonium hydroxide for 17 h at room temperature, followed by washing, drying and re-distillation gave the final product with purity >99% by GC (98.6% by NMR). The main impurity was identified as perfluorobutanesulfonylfluoride, which is present at nearly 1%.

3.2. *Perfluorodiethylsulfone hydrolysis—potassium perfluoroethylsulfonate and HFC-125*

Perfluorodiethylsulfone (3.0 g, 10 mmol) and 2.5 ml of 52% solution of potassium hydroxide in water (1.3 g KOH, 23 mmol) were heated with stirring at 80 °C with condenser at −10 °C and end trap at −78 °C until reflux ended and initially two-phase reaction mixture became a clear homogeneous solution. In the end trap was collected 0.9 g liquid consisting of (GC): 6% starting sulfone and 94% C_2HF_5; MS (CI): 121 [85 $(M+1)^+$], 101 [100 $(M-HF)^+$]. The yield of the pentafluoroethane (HFC-125) was 71%. The clear solution in the reaction flask became solid at room temperature. Water was added to dissolve the solid material, the solution was treated by carbon dioxide to remove the excess of KOH and dried in an oven at 95 °C. Extraction of organics in the solid residue by methanol gave 2.08 g (yield 98%) of potassium perfluoroethanesulfonate. ^{19}F NMR (−) ppm upfield of internal $CFCl_3$ (D_2O): −79.86 (CF_3, s), −118.37 (CF_2, s).

In a separate experiment, perfluorodiethylsulfone (2.02 g, 10 mmol) and potassium carbonate (2.08 g, 15 mmol) in 2.5 ml of water were heated with stirring at 80 °C for 5 h. No homogenization of the two-phase reaction mixture, nor gas evolution, was observed even after addition of a small amount of phase transfer catalyst tetrabutylammonium bromide. A total of 0.92 g of pure (99.8%) sulfone was recovered (by simple phase separation) and no C_2HF_5 was detected by GC of the gas phase. There is no sulfone hydrolysis under these conditions.

3.3. *Perfluorodiethylsulfone aminolysis—perfluoroethanesulfonylamide*

In a sealed glass tube, a mixture of 3.03 g (10 mmol) perfluorodiethylsulfone and 0.52 g (30 mmol) ammonia was heated at 83 °C for 65 h. Liquid ammonia was not completely dissolved in the sulfone at room temperature and created a small upper layer in the tube. The final mixture after heating contained three layers—1:1 clear bottom layer of pentafluoroethane and slightly colored middle layer of pentafluoroethanesulfonylamide ammonium salt and also a very small upper layer comprising excess liquid ammonia. After cooling, the tube was opened and heated to 44 °C to evaporate volatiles into a cold trap (−78 °C). A total of 1.37 g of volatiles were collected in the trap (GC): 6% NH_3, 78% C_2HF_5 and 16% of the sulfone. The yield of C_2HF_5 was 1.07 g (89%). After removal of low boilers, the liquid left in the glass tube contained 0.2 g of pure (99% purity) starting sulfone as a lower phase and 2.08 g of liquid sulfonylamide ammonium salt. Another 0.19 g of perfluorodiethylsulfone were left in the trap after reventing the trap contents. In summary, 0.39 g or 13% of the starting sulfone remained unreacted. After transferring from the glass tube, the 1.68 g of the liquid sulfonylamide salt quickly solidified in the open air to give 1.57 g of white crystalline solid with mp 67.5–70 °C. The cross-integration of the proton and fluorine NMR spectral data shows this sample appears to be a mixture of three parts $C_2F_5SO_2NH_2$ and two parts of NH_3. The IR spectrum shows broad absorptions in the 2400–3400 cm^{-1} region in addition to sulfonamide NH_2 stretching absorption (see below). Re-crystallization from chloroform gave the sulfonylamide with mp 82–83 °C and purity 98.5% (by GC) and >99% (by NMR). Perfluoroethanesulfonylamide ^{19}F NMR (−) ppm upfield of internal $CFCl_3$ (CD_3CN): −78.86 (CF_3, s), −117.50 (CF_2, s). IR (KBr) cm^{-1}: 1329.9 (m), 1359.1 (s) (SO_2); 3289.2 (m), 3383.4 (s) (NH_2). The isolated yield of the perfluoroethanesulfonylamide was 1.52 g (76%) based upon 81% consumed sulfone.

3.4. *Reaction perfluorodiethylsulfone with sodium methoxide*

The sulfone (3.0 g, 10 mmol) was added dropwise at 0 °C to 5.0 g 25% solution of sodium methoxide in methanol (1.25 g, 23 mmol CH_3ONa) in a flask with a condenser at −19 °C and end trap at −78 °C. The exothermic reaction was completed in 9 min and all gaseous products were purged by nitrogen from the trap and collected. A total of 1.66 g of liquid consisting of (GC): 60% C_2HF_5 (calculated 1.0 g, 83% yield), 36% CH_3OCH_3; MS (CI) 47 [18 $(M+1)^+$], 45 [100 $(M-H)^+$] (calculated 0.6 g, 130% yield) and 4% unconsumed perfluorodiethylsulfone was obtained. To the solid residue in the reaction flask was added 10 ml H_2O. The solution was treated with CO_2 and dried at 100 °C to give 2.87 g of white solid material. Methanol (22 ml) extraction of the material, followed by drying in the open air gave 2.23 g (101% yield) of sodium perfluoroethanesulfonate.

3.4.1. *Reaction perfluorodimethylsulfone with lithium hydroxide in methanol*

Perfluorodimethylsulfone with a bp 12.5–17 °C and purity (NMR) 89.5% (1 g, 4.43 mmol) was gradually added to solution of 0.25 g (5.95 mmol) $LiOH\cdot H_2O$ in 1.5 g methanol at 0 °C. In 30 min, the solution was treated by dry CO_2, filtered and the methanol was evaporated to give 0.667 g of white solid lithium triflate with a purity (NMR) 92.7% (3.96 mmol); yield 89%. ^{19}F NMR (−) ppm upfield of internal $CFCl_3$ (D_2O): −78.4 (CF_3, s).

3.4.2. *Reaction perfluorodimethylsulfone with lithium hydroxide in water*

Perfluorodimethylsulfone (1 g, 4.43 mmol), lithium hydroxide hydrate (0.276 g, 6.57 mmol) and 3 ml H_2O were agitated in a sealed glass tube for 4 h at 0 °C. While opening the tube, 0.36 g of gaseous products escaped. The solution was filtered to remove 0.043 g of white solid, treated with dry CO_2 to pH 8 (no solid material) and dried to give 0.65 g of solid lithium triflate with purity (NMR) 90.9% (3.78 mmol); yield 85%.

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