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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Perfluoroethanesulfonyl Fluoride: Preparation from Sultone

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Abstract—A procedure was developed for preparing perfluoroethanesulfonyl fluoride by synthesis of hexafluoropropane-2-β-sultone from sulfuric anhydride and perfluoropropene, followed by hydrolysis of the sultone to α-tetrafluoroethanesulfonyl fluoride and fluorination of the latter with elemental fluorine.

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Perfluoroalkanesulfonyl halides (PFASHs), including sulfonyl fluorides, are starting compounds for preparing perfluoroalkanesulfonic acids and their salts. They are also used as sources of perfluoroalkanesulfonyl groups in the synthesis of surfactants, dyes, antioxidants, UV stabilizers, and materials for chemical power cells [1–6]. Among PFASHs, of particular interest are lower homologs with 1–3 carbon atoms. However, application of PFASHs is limited by their high cost, caused by the lack of an efficient synthesis process. There are a number of procedures for preparing PFASHs, each having certain features and shortcomings. The best studied process is electrochemical fluorination (ECF), i.e., electrolysis of solutions of alkanesulfonyl halides in hydrogen fluoride [7, 8]:

$$RSO_2Hal \xrightarrow{HF,\ e} R_fSO_2F,$$

where Hal is F or Cl, R is alkyl, and R_f is perfluoroalkyl.

In Russia, the method is implemented at the Angarsk Electrochemical Plant for the production of trifluoromethanesulfonyl fluoride from methanesulfonyl chloride; the yield is 80–85%. Methanesulfonyl chloride, like other lower alkanesulfonyl chlorides, is not produced in Russia. Commercial electrochemical synthesis of perfluoroethanesulfonyl fluoride (PFESF) from ethanesulfonyl fluoride appeared to be unfeasible because of the low yield, which did not exceed 45%. The electrolysis is accompanied by formation of a large amount of impurities with boiling points close to that of PFESF; furthermore, a part of PFESF is mixed with hydrogen fluoride, and its significant fraction (up to 30%) remains dissolved in the electrolyte. Intermediate conversion of ethanesulfonyl chloride into ethanesulfonyl fluoride by the reaction with HF in the presence of a chromium–magnesium catalyst [9] allowed the PFESF yield to be increased to 70%, but its isolation appeared to be difficult. In electrolysis of higher alkanesulfonyl chlorides, the PFASH yields are as low as 25–30%. Another route to PFASHs is the reaction of perfluoroalkyl iodides or bromides with sodium dithionite, followed by chlorination of the resulting sodium perfluoroalkanesulfinate [10–12]:

$$R_fHal + Na_2S_2O_4 \rightarrow R_fSO_2Na,$$

$$R_fSO_2Na + Cl_2 \rightarrow R_fSO_2Cl + NaCl,$$

where R_f is perfluoroalkyl, and Hal is Br or I.

The reaction was performed in a water–acetonitrile mixture. The yield of perfluoroalkylsulfonyl chlorides reached 80%. We reproduced this procedure with perfluoroethyl iodide and obtained perfluoroethanesulfonyl chloride in 76% yield. Despite reasonable yield of PFASH, this procedure has significant drawbacks:

(1) use of expensive perfluoroalkyl iodides and bromides, which are in short supply, as starting compounds;

(2) use of sodium dithionite, which is not produced in Russia, and instability of this salt in storage, which gives rise to additional problems;

(3) strong corrosion of apparatus and pipelines, caused by chlorination of sodium perfluoroalkanesulfinates in aqueous solutions;

(4) overall complexity of the process: It involves steps of extraction, filtration, and regeneration of solvents. Implementation of the process requires a

large set of equipment, and many operations are performed manually;

(4) large amount of wastes: 1.5 t of solid and 2.5 t of liquid wastes are formed per ton of the finished product. The wastes mainly consist of toxic fluorinated compounds, and their regeneration and detoxication require additional chemicals, equipment, time, and energy.

Another procedure suggested for preparing PFASHs is based on the reaction of perfluoroolefins with sulfuryl fluoride or sulfuryl fluorochloride in the presence of cesium fluoride [13, 14]:

$$R_fCF{=}CF_2 + SO_2Hal_2 \xrightarrow{CsF} HalCF(R_f){-}CF_2SO_2Hal,$$

where Hal is Cl or F.

We checked this procedure and found that CsF, olefins, and solvents should be thoroughly dried. The water content should not exceed 0.001 wt %. However, even with such precautions the reaction mainly yielded a mixture of olefin oligomers and polymeric sulfonyl halides $Hal(R_fCF{-}CF_2)_nSO_2Hal$, $(R_fCF{-}CF_2)_n$, n = 1–50. The yield of monomeric PFASHs did not exceed 20%. It should be noted that polymeric sulfonyl halides are used as surfactants, lubricants, and components of impregnating formulations, ion-exchange membranes, and film materials.

The drawbacks of the above-considered procedures for preparing PFASHs make it necessary to search for a simple procedure for their synthesis involving chemicals commercially produced in Russia and to develop an efficient technology based on this procedure. Among possible routes to PFASHs, we chose conversion of sultones. In accordance with [15–17], polyfluorinated alkanesulfonyl fluorides are formed by hydrolysis of perfluorinated sultones which, in turn, are prepared by the reaction of sulfuric anhydride with perfluoroolefins. According to data reported by Knunyants [15, 16] and results of our experiments, the yield of hexafluoropropane-2-β-sultone is as high as 96–98%. The impurities (0.5–2%) are the linear isomer $CF_3{-}CF(SO_2F){-}COF$, six- and eight-membered sultones, and perfluoroallyl sulfate $CF_2{=}CF{-}CF_2O{\cdot}SO_2F$. Sultones are hydrolyzed to α-hydroperfluoroalkanesulfonyl fluorides (HPFSFs), which, as we expected, can be fluorinated to perfluoroalkanesulfonyl florides:

$$R_fCF{=}CF_2 + SO_3 \longrightarrow R_fCF(O_2S){-}CF_2{-}O$$

$$\xrightarrow{H_2O} R_fCFHSO_2F \xrightarrow{F_2} R_fCF_2SO_2F.$$

Experiments on optimization of the sultone synthesis showed that sulfuric anhydride should contain as low amounts of the monohydrate as possible: At 0.2% content of the monohydrate, the yield of the sultone is 98%. An increase in the monohydrate content leads to an increase in the content of impurities: monohydroperfluorocarboxylic acids $R_fCFH{-}COOH$, perfluoroalkenyl fluorosulfonates $R_fCF{=}CF{-}OSO_2F$, sulfuryl fluoride, and carbonyl fluoride. At 2% content of the monohydrate in sulfuric anhydride, the content of impurities reaches 15%.

The optimal temperature of sultone synthesis is 105°C. Above this temperature, the sultone starts to decompose, and its yield decreases. At temperatures below 100°C, the reaction becomes slower. At 50°C, the yield is 53%.

The monomer should be taken in 5–7% excess relative to the stoichiometry, to ensure complete binding of sulfuric anhydride. Free sulfuric anhydride promotes the subsequent acid hydrolysis of the sultone, with polyfluoroalkanoic and sulfonic acids becoming the major products.

Hydrolysis of hexafluoropropane-2-β-sultone involves two successive reactions: formation of (fluorosulfonyl)perfluoropropionic acid and its spontaneous decarboxylation with the formation of α-hydrotetrafluoroethanesulfonyl fluoride (TFESF):

$$CF_3{-}CF(O_2S){-}CF_2 + H_2O \longrightarrow CF_3{-}CF(SO_2F){-}COOH + HF,$$

$$CF_3{-}CF(SO_2F){-}COOH \longrightarrow CF_3CFH{-}SO_2F + CO_2.$$

The formation of hydrogen fluoride in the course of hydrolysis leads to the formation of tetrafluoropropionic acid:

$$CF_3{-}CF(SO_2F){-}COOH + H_2O \xrightarrow{HF} CF_3CFH{-}COOH + H_2SO_4 + HF.$$

The optimal hydrolysis temperature is 0–2°C. At this temperature, the yield of TFESF is 90%. TFESF contained up to 1% water. The content of other impurities did not exceed 0.03 wt %. After drying, the product was used for fluorination without additional purification.

Fluorination of polyfluorinated paraffins, ethers, tertiary amines, and their heterocyclic analogs by various procedures, including that with elemental fluorine, is a fairly well studied process, and high yields of the target products can be attained [18]. Fluorination of compounds containing an S–C bond is

much less studied. The energy of S–C bonds (about 270 kJ mol^{-1}) is appreciably lower than that of C–C (480 kJ mol^{-1}), C–O (360 kJ mol^{-1}), and even C–N (305 kJ mol^{-1}) bonds, which gives rise to certain problems in fluorination, because the cleavage of the C–S bond and formation of C–F and S–F bonds (energy 480 and 290 kJ mol^{-1}, respectively) is thermodynamically favorable. Kornilov et al. [19] studied fluorination of mercaptans with cobalt trifluoride. The major products were SF_6 and polyfluorinated paraffins. In our experiments on fluorination of TFESF with cobalt trifluoride, the yield of PFESF was 19%; the other products were SF_6, SO_2F_2, CF_4, and C_2F_6.

Fluorination of TFESF with elemental fluorine appeared to be more successful. Under static conditions, with slow supply of fluorine (0.5–0.7 ml s^{-1}) at 0–20°C into a reactor containing TFESF and packed with copper chips, the yield of PFESF was 92%. In dynamic experiments with a tubular reactor (nickel tube packed with copper chips), we sometimes observed plops when the rates of feeding the reactants changed or even without any apparent causes. In this case, SO_2F_2, SF_6, C_2F_6, CF_4, and carbon black became the major products. This result is attributable to inefficient removal of excess energy released in the course of fluorination. To remove this energy, it is recommended to use solvating solvents in combination with a heat-removing packing [20]. Among the examined compounds, the best results were obtained with HF and somewhat worse results, with TFESF and N_2. At the molar ratio F_2 : TFESF : HF = 1 : 1 : 1, 97% conversion and 95% selectivity were attained. If we consider the reactants as a donor–acceptor system [21] in which an electron is transferred from the donor (TFESF) to the acceptor (F_2)

$$CF_3CFHSO_2F + F_2 \longrightarrow CF_3\overset{\displaystyle CSO_2F}{\overset{|}{C}}\overset{+\delta}{H}\cdots F\overset{-\delta}{-}F$$

$$\longrightarrow CF_3CFSO_2F + F + HF$$

with the formation of a radical pair, a diluent is required for stabilization of this pair and absorption of excess energy. This leads to temporary stabilization of the transition state, so that the radicals have time to recombine before escape into the reaction volume:

$$CF_3CFHSO_2F + F_2\cdots HF \longrightarrow CF_3\overset{\displaystyle CFSO_2F}{\overset{|}{C}}\overset{+\delta}{H}\cdots F\overset{-\delta}{-}F\cdots HF$$

$$\longrightarrow CF_3CFSO_2F + F\cdots HF + HF,$$

$$CF_3CFSO_2F + F\cdots HF \longrightarrow HF + CF_3CF_2SO_2F.$$

Apparently, the amount of HF correlates with the amount of supplied F_2. According to the theory of one-electron transfer, the optimal HF : F_2 ratio should be 1 : 1, i.e., the molar ratio of the components should correspond to the stoichiometric ratio. Indeed, as the HF concentration is decreased to 0.71 mol per mole of F_2, the selectivity decreases by 15–20%, and when it is increased to 1.5 mol per mole of F_2, the conversion of the starting reactants decreases, apparently due to the inhibiting effect of HF and a decrease in the fluorination rate.

Another major factor affecting the reaction is temperature. We found that 120–130°C is the optimal temperature of PFESF synthesis. Based on the results obtained, a pilot plant for PFESF synthesis was constructed at the Galogen Open Joint-Stock Company. The installation consists of units for distillation of sulfuric anhydride, synthesis of sultone, hydrolysis of sultone, fluorination of TFESF, neutralization of crude PFESF with alkalis, its drying with zeolites, and fractional distillation of PFESF to obtain the 99.9% pure products. The results of studies on fluorination of polyfluorinated alkanesulfonyl fluorides were protected with RF patents [22, 23].

EXPERIMENTAL

The reaction products were analyzed by gas chromatography [LKhM-80 chromatograph, thermal conductivity detector, 2-m column packed with Silokhrom + 20% 1,1,1-tris(β-cyanoethyl)acetophenone] and gas chromatography–mass spectrometry (Aligent-5973N, DB-5ms capillary column 60 m long).

Hexafluoropropane-2-β-sultone was prepared as described in [15]. Optimal conditions: hexafluoropropene : SO_3 ratio (1.05–1.08) : 1, 105–107°C, 12–14 h. α-Tetrafluoroethanesulfonyl fluoride was prepared by the procedure described in [15] with some modifications. Namely, the sultone was fed into water, which allowed us to increase the TFESF yield to 92%.

Fluorination of tetrafluoroethanesulfonyl fluoride with cobalt trifluoride. Into a nickel tube 800 mm long and 38 mm in diameter, packed with controllable heating, TFESF was fed from a batcher at a rate of 1–3 ml min^{-1}. The best results were obtained at 260–290°C. According to the gas-chromatographic analysis, the reaction mixture (after neutralization with aqueous NaOH) contained 23% SO_2F_2, 15% SF_6, 35% C_2F_6, 8% CF_4, and 19% $C_2F_5SO_2F$.

Fluorination with elemental fluorine under static conditions. A 2.0-l 12Cr18Ni10Ti stainless steel

vessel packed with copper chips and cooled to 0°C was charged with 18.5 g of TFESF, and fluorine was fed at a rate of 0.5–0.7 ml s^{-1} for 1 h (the procedure was performed in a steel box). After 24 h, the reaction mixture was condensed in a 12Cr18Ni10Ti stainless steel trap cooled with liquid nitrogen. After warming, it was neutralized with aqueous NaOH, dried over CaA zeolite, and collected in a trap cooled to –30°C. The product (yield 20 g) contained 95% PFESF and 5% impurities (CF_3SO_2F, SO_2F_2, C_2F_6, CF_4, SF_6).

Fluorination under dynamic conditions. A solution containing 92 g of TFESF and 10 g of HF was fed at a rate of 0.8–1.0 g min^{-1} from a batcher to a vaporizer (nickel tube 38 mm in diameter and 500 mm long, heated to 80–100°C). Fluorine was also fed to this tube at a rate of 120–130 ml min^{-1}. Then the mixture of the components came into a reactor (nickel tube 38 mm in diameter and 900 mm long, packed with copper chips and heated to 130–140°C). The reaction products were collected in a 12Cr18Ni10Ti stainless steel trap cooled to –120°C. After the reaction completion, the condensate was worked up as described above. The product (yield 90 g) contained 96.5% PFESF and 3.5% impurities (CF_3SO_2F, SO_2F_2, C_2F_6, CF_4, SF_6).

CONCLUSIONS

(1) A procedure was developed for preparing perfluoroethanesulfonyl fluoride by fluorination of tetrafluoroethanesulfonyl fluoride.

(2) The steps of perfluoroethanesulfonyl fluoride synthesis were optimized, and its pilot production was set up at the Galogen Open Joint-Stock Company.

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