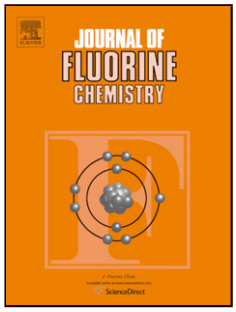


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Authors: Sheng Peng, Kenneth G. Moloy

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# Perfluoroalkyl Ethyl Alcohols via Perfluoroalkyl Acetaldehydes

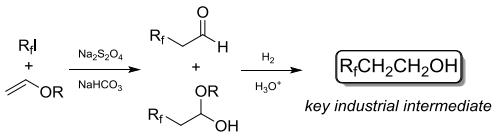
Sheng Peng[a]* and Kenneth G. Moloy[b]

[a] Chemours Company, Fluoroproducts, Experimental Station, PO Box 80262, Wilmington, DE 19880-0262 USA

[b] DuPont Central Research and Development, Experimental Station, PO Box 80328, Wilmington, DE 19880-0328 USA

* Corresponding author

Graphical Abstract for Peng & Moloy, Perfluoroethyl Alcohols *via* Perfluoroacetaldehydes, submitted to J Fluorine Chem.




Highlights

- Sulfinitodehalogenation reaction of RfI and ethyl vinyl ether gives aldehyde and hemiacetal addition products.
- Catalytic hydrogenation of this mixture gives the perfluoroalkylethanol in high overall yield.
- These alcohols are important intermediates in the commercial production of surfactants and polymers.

**Abstract**

A new route to commercially important perfluoroalkyl ethyl alcohols ($RfCH_2CH_2OH$) is described. This route involves the addition of perfluoroalkyl iodides to alkyl vinyl ethers using sulfinatodehalogenation chemistry, followed by catalytic hydrogenation of the intermediate mixture of perfluoroalkylacetaldehyde and perfluoroalkylacetal to the desired alcohol.

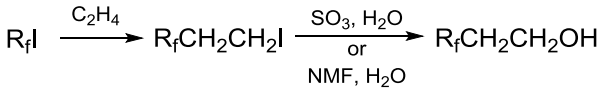
## 1. Introduction

Fluorinated alcohols are important intermediates used to manufacture many commercial products. Among them, fluorinated sulfonamido alcohols of the type $RfSO_2NHCH_2CH_2OH$ (Rf = $C_8F_{17}$) and perfluoroalkyl ethyl alcohols of the type $RfCH_2CH_2OH$ (Rf = $C_4F_9$ to $C_{14}F_{29}$) are the most important commercially available materials of this class[1-5]. For several decades they have been used to manufacture well-known commercial products such as Scotchguard® and Zonyl® surfactants, and soil,

water, and oil repellents. Because products made with perfluorinated chains of length ≥ $C_8F_{17}$ are being phased out of the commerce, shorter chain alcohols, for example $C_6F_{13}CH_2CH_2OH$, have become increasingly important.

Methods to prepare perfluoroalkyl ethyl alcohols are rather limited. Currently, all commercial methods of preparation use perfluoroalkyl ethyl iodide intermediates, as shown in Scheme 1. The most common process to convert these iodides to the alcohols uses oleum, wherein the perfluoroalkyl ethyl iodide is converted to the sulfate ester, which is then hydrolyzed with aqueous sodium sulfite to generate the alcohol[6].

**Scheme 1.** Commercial routes to perfluoroalkyl ethyl alcohols.

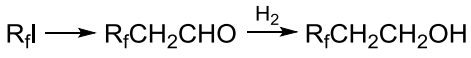



Solvolysis with formamides is an alternative process, also used commercially, where the perfluoroalkyl ethyl iodide is treated with N-methylformamide to form an intermediate formate ester that is then hydrolyzed to give the desired alcohol. Relatively mild conditions are employed for the hydrolysis process, but the reaction times are long unless forcing conditions are applied. The process also requires solvent and generates up to *ca*. 10 mol% olefin ($RfCH=CH_2$) by-product[7,8]. A recently reported route involves conversion of RfI to a Grignard reagent, followed by reaction with ethylene sulfate at -40 °C[9]. While such a route is obviously not commercially viable, it does perhaps indicate a desire for improved routes to these valuable alcohols.

Improvements in the overall process could potentially result if a more direct route to these alcohols from the perfluoroalkyl iodide (RfI) were developed. Additional improvements, such as faster reaction rates, improved selectivity, and decreased use of hazardous reagents would also be of practical utility. An alternative process that addresses many of these considerations is depicted in Scheme 2, where the alcohol is produced by simple hydrogenation of the aldehyde intermediate shown. Catalytic

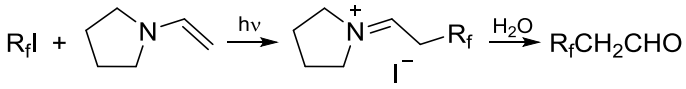
hydrogenation of the aldehyde would be expected to proceed with very high selectivity and at high rates under mild conditions, and catalysts for this transformation are readily available[10,11].

**Scheme 2.** Proposed perfluoroalkyl acetaldehyde route to perfluoroalkyl ethyl alcohols.



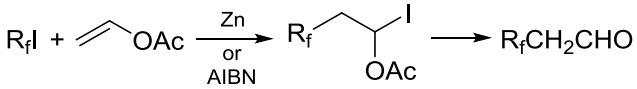

The key step in this process, then, would appear to be production of the intermediate fluoroalkyl acetaldehyde. There is literature precedent for the conversion of RfI to $RfCH_2CHO$, for example fluoroalkyl acetaldehydes of the type $C_nF_{2n+1}CH_2CHO$ (n > 1) were prepared photochemically from perfluoroalkyl iodides and enamines in 10-40% yield (Scheme 3)[12].

**Scheme 3.** Enamine route to perfluoroalkyl acetaldehydes.




These fluoroalkyl acetaldehydes have also been prepared by radical addition of RfI to vinyl acetate, mediated by zinc or AIBN, giving 1-acetoxy-1-iodo-2-perfluoroalkylethanes in moderate to good yields[13-16]. This chemistry has been further modified and improved by using either alkali halides or metal oxides to convert the intermediate 1-acetoxy-1-iodo-2-perfluoroalkylethanes ($RfCH_2CHIOAc$) to the desired aldehydes in 50-70% yield (Scheme 4)[17].

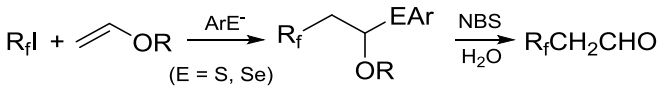
**Scheme 4.** Perfluoroalkyl acetaldehydes *via* radical addition to vinyl acetate.



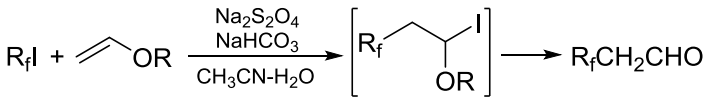

Radical addition of RfI to vinyl alkyl ethers has also been reported as a route to these fluoroalkyl acetaldehydes. For example, reaction of RfI with ethyl vinyl ether in the presence of arenesulfides or areneselenides gives the 1,1-disubstituted intermediates shown in Scheme 5; subsequent treatment with NBS then provides the desired fluoroalkyl acetaldehydes (Scheme 8)[18]. Another reported method is the

reaction of RfI with ethyl vinyl ether in the presence of sodium sulfite and sodium bicarbonate (sulfinatodehalogenation, Scheme 6)[19-24]. Indeed, quantitative yields in this reaction have been demonstrated by the *in situ* conversion to, and isolation of, the hydrazone derivatives. It is notable that these authors further report the conversion of these aldehydes to the alcohols using $NaBH_4$ reduction[24].

**Scheme 5.** Perfluoroalkyl acetaldehydes *via* addition to vinyl ethers.




**Scheme 6.** Sulfinitodehalogenation route to perfluoroalkyl acetaldehydes.



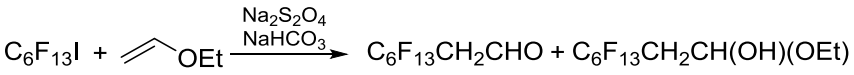

Comparing these literature methods, photochemistry is not attractive for a large scale commercial process. The routes using vinyl esters are potentially of interest, but they require two reactions steps to obtain the aldehyde. In contrast, the sulfinatodehalogenation reaction possesses some attractive features: direct and high yield aldehyde generation, mild reaction conditions, and inexpensive reagents. Coupled with the anticipated ease and simplicity of the subsequent hydrogenation step, the sulfinatodehalogenation route was therefore considered for further investigation. Herein we report our initial results on this route.

## 2. Results and Discussion

We first investigated the addition of PFHI (perfluorohexyl iodide, $C_6F_{13}I$) to EVE (ethyl vinyl ether) following the procedure described by Huang and Lü[21-23]. Thus, PFHI, ethyl vinyl ether, $Na_2S_2O_4$, and $NaHCO_3$ in 1:1 $CH_3CN/H_2O$ were combined and the reaction was monitored by GC and NMR. Consistent with the literature, GC analysis showed that complete PFHI conversion was achieved within 20 min at 5-

10 °C. The original literature report did not report the direct observation or isolation of the aldehyde products, but instead the isolation of the 2,4-dinitrophenylhydrazone derivatives. In our hands, NMR analysis of the crude product shows two products, assigned as the desired aldehyde $C_6F_{13}CH_2CHO$ and the hemiacetal $C_6F_{13}CH_2CH(OH)(OEt)$ (Scheme 7); the combined yield of these two species, based on PFHI, is nearly quantitative. Assuming that the hemiacetal reacts as an aldehyde equivalent, the NMR results are consistent with the earlier report, where the hydrazones were obtained in 85-97 % isolated yields.

**Scheme 7.** Sulfinitodehalogenation of vinyl ethers produces aldehyde and hemiacetal mixture.




Crude aldehyde/hemiacetal was isolated from this reaction mixture by solids removal (filtration) and then simple distillation (vacuum transfer) of the volatiles. This product was then hydrogenated with 5% Ru/C catalyst (3.1 MPa, 85 °C; non-optimized screening conditions). GC analysis showed conversion of the aldehyde to the desired alcohol $C_6F_{13}CH_2CH_2OH$, as expected. Surprisingly, however, GC-MS analysis also showed clear evidence of $CH_3CN$ hydrogenation, as shown by the presence of $EtNH_2$, $Et_2NH$, $Et_3N$, and $C_6F_{13}CH_2CH_2NH_2$. Alkyl redistribution and scrambling is commonly encountered in nitrile hydrogenation. However, nitrile hydrogenation typically requires much higher temperatures than those employed here[25]. In addition, supported ruthenium catalysts are preferred for the reduction of aldehydes to alcohols but are typically not preferred for nitrile hydrogenation. Palladium-, platinum-, and rhodium-based catalysts are reported to be active for nitrile hydrogenation, but the base metal catalysts nickel and cobalt are the most commonly used. Nitrile hydrogenation is reported to be effective in the temperature range 5-100 °C but most literature suggests more forcing conditions and thus a practical range of 80-150 °C[26]. Regardless, our experimental results indicate that acetonitrile is an incompatible solvent for this hydrogenation. This conclusion led us to investigate alternative solvents in which to conduct the sulfinatodehalogenation step.

Prior reports suggest that appropriate cosolvents for the sulfinatodehalogenation reaction do not necessarily need to be soluble in or miscible with water. For example, both diethyl ether and dichloromethane have been reported as solvents for this reaction[19-24]. However, these were not considered due to their volatility, flammability, and/or toxicity properties[27,28]. The addition of PFHI to EVE was investigated using methyl t-butyl ether (MTBE) as solvent but this was unsuccessful, giving recovery only of unreacted PFHI. Ethanol was found to be a good solvent for the sulfinatodehalogenation step. As observed in with acetonitrile, monitoring the reaction by GC analysis showed rapid and complete PFHI conversion. The resulting product mixture was filtered and the filtrate was subjected to simple vacuum distillation. However, in this case NMR ($^{19}F$, $^{1}H$) analysis of the crude, distilled product showed three, rather than two, fluorine-containing products. Two of these were identified as the expected aldehyde ($C_6F_{13}CH_2CHO$) and hemiacetal ($C_6F_{13}CH_2CH(OH)(OEt)$) products already discussed. The third product was identified as the diethyl acetal $C_6F_{13}CH_2CH(OEt)_2$[29]. Hydrogenation of this mixture gave the desired alcohol and complete aldehyde and hemiacetal conversion, but unreacted $C_6F_{13}CH_2CH(OEt)_2$ remained; the results of multiple experiments indicate that the acetal is inert to hydrogenation under the conditions tested. Conducting the hydrogenation in the presence of added aqueous $H_2SO_4$ in an attempt to convert the diethyl acetal *in situ* to hemiacetal and/or aldehyde, followed by subsequent hydrogenation to the alcohol, was not successful. These results necessitated the further search for a solvent.

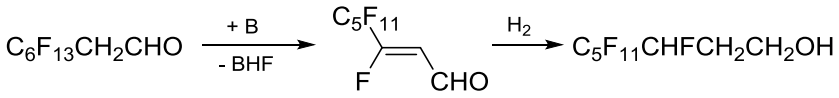
THF was next investigated and found to be a suitable co-solvent for both the sulfinatodehalogenation and hydrogenation reactions. Replacing $CH_3CN$ with THF in the sulfinatodehalogenation procedure described above gave rapid and quantitative PFHI conversion to the expected aldehyde and hemiacetal mixture, with no apparent loss of rate or yield. Similarly, hydrogenation of this crude product (filtration and simple vacuum distillation, then 5% Ru/C) gave smooth conversion to the alcohol with no by-products.

With these positive results in hand, preliminary improvements were investigated. With respect to the sulfinatodehalogenation step, it was found that low temperature is essential. As the temperature

was raised above 5-10 °C, increasing amounts of a by-product, identified as $C_6F_{13}H$ were observed. This species was not detected (< ca. 1 mol %) at 5-10 °C, but at ambient temperatures (20-30 °C) increased to represent a 3-4 % yield loss. To minimize solvent use, experiments at higher PFHI/EVE concentrations were conducted. The previous literature reports used dilute solutions, 0.125 M[23]. We find that the concentrations can be increased ten-fold (1.25 M) with no detrimental impact on yield. However, reaction times to complete PFHI conversion increased significantly with increasing concentration, from ca. 20 min to ca. 5 h for quantitative PFHI conversion at these concentration extremes. In addition, the resulting product mixture was shifted nearly entirely to the hemiacetal (> 90 mol% hemiacetal, < 10 mol% aldehyde) at higher starting reagent concentration.

The initial hydrogenation experiments were cursory in nature, and designed simply to demonstrate the desired conversion of the aldehyde/hemiacetal mixture to the target alcohol. With an improved preparation of the aldehyde/hemiacetal in hand, the hydrogenation was similarly studied in further detail. First, detailed analysis of the hydrogenation product showed two impurities, identified as $C_5F_{11}CFHCH_2CH_2OH$ and $C_6F_{13}CH_2CH_2OEt$. The partially defluorinated alcohol is likely derived by the formal elimination of HF from the aldehyde/hemiacetal to give olefin, followed by hydrogenation, as shown in Scheme 8. Elimination of HF from aldehydes $RfCH_2CHO$ has been reported with bases as weak as pyridine[18]. Our investigations did not show evidence of the formation of olefinic species during the sulfinatodehalogenation step but small amounts of olefin resonances were observed in the $^1H$ NMR of the distilled product prior to hydrogenation. Apparently, the combination of elevated temperature and base (e.g., $NaHCO_3$) are sufficient to give rise to this undesirable species. Removal of excess $NaHCO_3$ and other salts by water extraction sufficed to eliminate this problem.

**Scheme 8.** Pathway for products resulting from formal HF elimination.



The ether $C_6F_{13}CH_2CH_2OEt$ likely results from hydrogenation of the hemiacetal. Hydrogenation of hemiacetals to ethers is known and is more prone to occur with supported palladium catalysts, which is one reason why we originally chose Ru/C catalyst[30,31]. In an attempt to eliminate, or at least reduce, this undesired product, the hydrogenation was tested in the presence of acid and additional water to ensure rapid equilibration of the hemiacetal and the aldehyde. Assuming that aldehyde hydrogenation is faster than hemiacetal hydrogenation, this strategy should shift the product to the target alcohol. This effort proved successful; hydrogenation of the aldehyde/hemiacetal mixture in the presence of dilute aqueous $H_2SO_4$ (soluble acid) or water plus Amberlyst® 15 (solid acid) resulted in complete hydrogenation of the mixture to the alcohol and elimination of the ether byproduct.

With the solvent issues seemingly resolved other parameters were briefly investigated. First examined was the use of nickel catalysts. Raney nickel is commonly used for aldehyde hydrogenation. However, Raney nickel is very basic and this is borne out by the formation of products resulting from formal elimination of HF such as $C_5F_{11}CF{=}CHCH_2OH$ and $C_5F_{11}CFHCH_2CH_2OH$. Raney nickel also produced substantial amounts of the ether $C_6F_{13}CH_2CH_2OCH_2CH_3$. Because Raney nickel is incompatible with aqueous acid, which eliminated the ether formation in the case of the Ru/C catalyst, it was dropped from consideration. Raney cobalt catalysts are also used for aldehyde hydrogenation but will likely suffer from the same issues as with Raney nickel, and we have not yet examined them in this system. Finally, although the initial scouting experiments were conducted at 3 MPa, we have found that with Ru/C catalyst the hydrogenation proceeds quickly and in high yield at pressures and temperatures as low as 1 MPa and 22 °C, respectively.

In summary, we have demonstrated a new route to commercially important perfluoroalkyl ethyl alcohols. Further work is obviously required to translate these findings to a true commercial process. However, at this point the optimum conditions appear to involve the following steps: 1) sulfinatodehalogenation at 5-10 °C in THF/$H_2O$ and 1-1.5 M reagent concentration; 2) water extraction and optional distillation of the intermediate perfluoroacetaldehyde/hemiacetal mixture; 3) low

pressure/low temperature (0.9 MPa, 20-30 °C) hydrogenation in the presence of aqueous acid; 4) recovery of the product perfluoroalkyl ethyl alcohol in excellent yield by distillation. Further studies are in progress. For example, we have extended this chemistry to other perfluoroalkyl ethyl alcohols such as $C_3F_7OCF_2CF_2CH_2CH_2OH$.

## 3. Experimental

### 3.1 General Considerations.

The reagents $Na_2S_2O_4$, $NaHCO_3$, solvents, Ru/C (5%) and Amberlyst® 15 were obtained from Aldrich Chemical Company, Milwaukee, Wisconsin. Perfluorohexyliodide ($C_6F_{13}I$) was obtained from the Chemours Company, Wilmington, DE. Hydrogenation reactions were conducted in a custom reactor of Hastelloy C construction. A magnetic stir bar of length matching that of the diameter of the reactor bottom was used for mixing. This design ensured to the greatest degree possible that the heterogeneous catalyst would be fluidized during the experiment. After loading with reagents and sealing the reactor was pressure tested with nitrogen and then pressurized with hydrogen. The reactor was brought to the target reaction temperature using an external heating block with integrated magnetic stirrer. Upon reaching the target temperature additional hydrogen was added as required for the experiment. Reaction progress was monitored by pressure drop using a pressure transducer with digital readout. Products were analyzed by gas chromatography (GC) using flame ionization (FID) and mass spectral (MS) detection. Product distributions are given as area percent from the FID and are not corrected for response factors.

### 3.2 Sulfinatodehalogenation: General Procedure.

The perfluoroalkyliodide (RfI, 1 equiv.) and ethyl vinyl ether (1.3 equiv.) are added to a mixed solvent of water and THF (6:10 volume ratio of water to THF) at 5-10 °C. $NaHCO_3$ (1.4 equiv.) is added to the reaction mixture, followed by addition of $Na_2S_2O_4$ (1.4 equiv). Reaction progress is monitored by GC and/or $^{19}F$ NMR, and is generally complete in 3-5 hours as judged by the complete disappearance of RfI. The reaction mixture was filtered while cold. Water is added to

the filtrate, the lower layer is separated. This layer consists primarily of a mixture of aldehyde $C_6F_{13}CH_2CHO$ and hemiacetal $C_6F_{13}CH_2CH(OH)(OEt)$, containing THF and some water. This crude product can be directly hydrogenated or, optionally, it can be vacuum distilled and the distillate subjected to hydrogenation.

$C_6F_{13}CH_2CHO$: $^1$H NMR (400 MHz, $CDCl_3$) δ 9.81 (1H, s), 3.16 (2H, t, 18 Hz). $^{19}$FNMR (376 MHz, $CDCl_3$) δ -81.3 (3F, t-t, 10.4, 2.2 Hz), -110.5 (2F, m), -122.3 (2F, s), -123.3 (2F, s), -123.5 (2F, m), - 126.6 (2F, m).

$C_6F_{13}CH_2CH(OH)(OEt)$: $^1$H NMR (400 MHz, $CDCl_3$) δ 5.08 (1H, t, 5.2 Hz), 3.89-3.81 (1H, m), 3.59-3.52 (1H, m), 2.56-2.37 (2H, m), 1.23 (3H, t, 6.9 Hz). $^{19}$F NMR (376 MHz, $CDCl_3$) δ -81.4 (3F, t, 81.4 Hz), -113.3 (2F, m), -122.28 (2F, s), -123.3 (2F, s), -124.2 (2F, m), - 126.6 (2F, m)

**3.3 Preparation of $C_6F_{13}CH_2CH(OEt)_2$.**

A three neck flask fitted with a stir bar, condenser, and thermocouple was purged with nitrogen and then charged with $C_6F_{13}I$ (8.92 g, 20.0 mmol), ethanol (32 mL), and ethyl vinyl ether (1.8 g, 25 mmol). After cooling with ice, $Na_2CO_3$ (2.35 g, 28 mmol) and then $Na_2S_2O_4$ (7.32 g, 42 mmol) were added. The reaction was warmed to room temperature for 15 min and then heated at 60 C for 1.5 h, whereupon complete conversion of $C_6F_{13}I$ was achieved. NMR of the crude product showed ca. 80 mol % diethyl acetal $C_6F_{13}CH_2CH(OEt)_2$ and 20 mol % $C_6F_{13}H$. The mixture was filtered and solvent removed from the filtrate by vacuum. The crude product was vacuum transferred to give 3.33 g product, shown by NMR to consist of $C_6F_{13}CH_2CH(OEt)_2$ (91 mol%) and $C_6F_{13}H$ (9 mol%).

MS (EI): 435 (M+-1), 391 (M+-OEt). $^1$H NMR (400 MHz, $CDCl_3$) δ 4.84 (1H, t, 5.2 Hz), 3.64-3.45 (4H, AB), 2.36 (2H, t-d, 18.9 Hz, 5.2 Hz), 1.14 (3H, t, 7.1 Hz). $^{19}$F NMR (376 MHz, $CDCl_3$) δ -81.8 (3F, tt, 10.1 Hz, 2.5 Hz), -113.9 (2F, m), -122.5 (2F, s), -123.6 (2F, s), -124.4 (2F, s), - 126.9 (2F, m).

**3.4 Hydrogenation of $C_6F_{13}CH_2CHO$ and $C_6F_{13}CH_2CH(OH)(OEt)$ in the absence of acid.**

The hydrogenation reactor was charged with 0.5 g of Ru/C catalyst and 15.0 g of a mixture of $C_6F_{13}CH_2CHO$ and $C_6F_{13}CH_2CH(OH)(OEt)$ in THF. The reactor was brought to 80 °C and 2.1 MPa. After 3.5 h the reaction was halted and the reaction analyzed by GC and GCMS which showed quantitative conversion to a mixture of alcohol $C_6F_{13}CH_2CH2OH$ (74 %), ether $C_6F_{13}CH_2CH_2OEt$ (23 %), and acetal $C_6F_{13}CH_2CH(OEt)_2$ (3 %).

**3.5 Hydrogenation of $C_6F_{13}CH_2CHO$ and $C_6F_{13}CH_2CH(OH)(OEt)$ in the presence of Amberlyst® 15 resin.**

The reactor was charged with 0.25 g 5% Ru/C, 0.25 g of Amberlyst® 15, 5 mL of water, 5 mL of THF, and 1.0 g of a mixture of $C_6F_{13}CH_2CHO$ and $C_6F_{13}CH_2CH(OH)(OEt)$. The hydrogenation was conducted at 80 °C and 3.1 MPa for 3.5 h. GC analysis showed quantitative conversion to the desired alcohol $C_6F_{13}CH_2CH_2OH$. 1-butanol and 1,4-butanediol, resulting from hydrolysis and hydrogenation of the THF, were also observed.

**3.6 Hydrogenation of $C_6F_{13}CH_2CHO$ and $C_6F_{13}CH_2CH(OH)(OEt)$ in the presence of dilute aqueous $H_2SO_4$.**

The reactor was charged with 0.25 g of 5% Ru/C, 1.0 g of a mixture of $C_6F_{13}CH_2CHO$ and $C_6F_{13}CH_2CH(OH)(OEt)$, 5 mL of THF, and 5 mL of dilute $H_2SO_4$ (pH = 2.2). The hydrogenation was conducted at 80 °C and 3.1 MPa for 3.5 h. GC analysis showed nearly quantitative formation of the desired alcohol $C_6F_{13}CH_2CH_2OH$ and only traces of other fluorinated products or products resulting from reaction of the THF solvent.

**3.7 Hydrogenation of $C_6F_{13}CH_2CHO$ at low pressure**

The reactor was charged with 5.0 grams of $C_6F_{13}CH_2CHO$ (containing < 10 % THF and EtOH) and 0.5 g of 5% Ru/C. The sample was hydrogenated at 50 °C and 0.97 MPa for 7 hours. GC analysis showed 97 % conversion and 95 % selectivity to $C_6F_{13}CH_2CH_2OH$.

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