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DIFLUOROMETHANESULFONIC ACID. PART II. A TWO-STEP ROUTE TO THE FREE ACID FROM MONOHYDRATED SODIUM DIFLUOROMETHANESULFONATE

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SUMMARY

Anhydrous difluoromethanesulfonic acid ("diflic acid") can be obtained, in a two-step procedure, from monohydrated sodium difluoromethanesulfonate, a very stable salt not easily dehydrated. In the first step, stable hydronium difluoromethanesulfonate is distilled from a mixture of CHF_2SO_3Na,H_2O and pure sulfuric acid in a 86 % yield. In the second step, diluted oleum (10 % SO_3), containing a slight excess of sulfur trioxide, is slowly dropped into hydronium difluoromethanesulfonate and anhydrous difluoromethanesulfonic acid is distilled from the resulting mixture in a 51 % yield. The use of more concentrated oleum and excess of sulfur trioxide causes a rather violent decomposition to gaseous products for which a chain mechanism is proposed. The same process is invoked to explain the more violent degradation of hydronium difluoromethanesulfonate observed with thionyl chloride. This chain reaction seems to be governed by the great ability of the α-acidic hydrogen to form hydrogen bonds.

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INTRODUCTION

Difluoromethanesulfonic acid ('diflic' acid), a significantly more acidic compound than sulfuric acid [1] catalyses efficiently the alkylation of aromatics by olefins [1], the synthesis of ethyl acetate from acetic acid and ethylene [2] and other electrophilic reactions [3-7]. The fact that its acidity is weaker than that of triflic acid (ΔpK_A=1 in AcOH) [1] can be, in some cases, an advantage : the hydration of propene is more chemoselective with a diflic acid catalysis (yield (v.s. converted C_3H_6) = 98 % with 4.10^{-3} eq. CHF_2SO_3H) than with a triflic acid catalysis (yield = 37.7 % with 4.10^{-3} eq. CF_3SO_3H) [8].

In a previous paper [9], we described an improved route to sodium difluoromethanesulfonate (sodium "diflate") from chlorodifluoromethane, sodium sulfite and sodium hydroxide as catalyst, the carbenic nature of which has been unambiguously demonstrated. We noticed that sodium diflate was obtained as a monohydrate melting at 220°C and stable up to 300°C with only a slight loss of water. This monohydrated salt was only partially dehydrated to CHF_2SO_3Na, 0.7 H_2O by an overnight drying at 100°C under reduced pressure or to CHF_2SO_3Na, 0.3 H_2O by recrystallization in acetone.

Looking for a convenient manufacture of diflic acid which could be scaled up, it was decided to start from monohydrated sodium diflate as raw material.

RESULTS AND DISCUSSION

Synthesis of monohydrated difluoromethanesulfonic acid

It is well known that pure triflic acid is obtained by distillation from a mixture of an anhydrous metallic triflate (Ba, K or Na) and pure (100 %) sulfuric acid [10]. Hydrated triflic salts provide, under the same conditions, monohydrated triflic acid which distills unchanged from pure sulfuric acid [10-12] and can be considered as an hydronium triflate $CF_3SO_3^-$ H_3O^+ [13-16].

In our case, monohydrated difluoromethanesulfonic acid, a semi-solid deliquescent compound, was the sole product resulting from the distillation of a mixture of monohydrated sodium diflate and pure sulfuric acid :

$$\underset{1\text{ eq.}}{CHF_2SO_3Na,\ H_2O} + \underset{2\text{ eq.}}{H_2SO_4} \xrightarrow[5\text{ torrs}]{\text{distil.}} \underset{86\ \%}{CHF_2SO_3H,\ H_2O} + NaHSO_4 \quad (1)$$

This difluoromethanesulfonic acid monohydrate could be considered as a true hydronium difluoromethanesulfonate $CHF_2SO_3^-H_3O^+$ since its ^1H NMR spectrum exhibited one triplet corresponding to the CHF_2 moiety and one sharp singlet corresponding to H_3O^+, these two signals being in the ratio 1/3 (this spectrum, combined with elemental analysis, excluded the presence of $CHF_2SO_3^-H_3SO_4^+$). The potentiometric titration of presumed CHF_2SO_3H,H_2O with potassium hydroxide in isopropanol also confirmed this formula (one equivalent point different from that of anhydrous diflic acid) and was in good accord with NMR analysis.

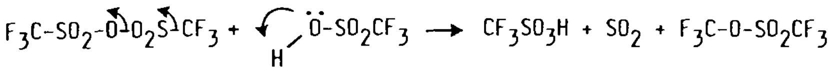
The existence of hydronium diflate is in agreement with the close acidity constants of diflic and triflic acids as determined by Brown and Bowden who measured the self-protonation of triflic acid, diflic acid and sulfuric acid in glacial acetic acid : colog K_A = 7.0, 5.7 and 4.7 for H_2SO_4, CHF_2SO_3H and CF_3SO_3H resp. [1].

It must be noted that the yield of hydronium diflate was maximum when using a two-fold amount of sulfuric acid, as in the manufacture of triflic acid from triflic salts [10].

Attempts to dehydrate hydronium difluoromethanesulfonate

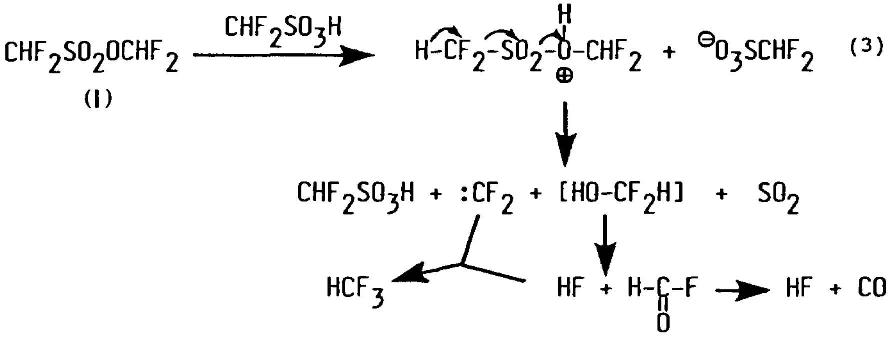
The dehydration of $HCF_2CF_2SO_3H,H_2O$ [17] or $C_6F_5SO_3H,H_2O$ [18] has been performed with thionyl chloride and that of CF_3SO_3H, H_2O with an equivalent or a slight excess of sulfur trioxide [19]. But, whether diflic acid hydrate was dropped into thionyl chloride at room temperature or thionyl chloride dropped into diflic acid hydrate at the same temperature, a violent reaction took place with evolution of large quantities of gaseous products including HF, SO_2, CO and HCl. Dropping diflic acid hydrate into a large excess of concentrated oleum (30 % SO_3) at room temperature caused a less sudden but still rather violent reaction and fluorosulfonic acid was the only liquid product isolated during further distillation.

It is known that trifluoromethyl triflate is formed when an excess of triflic acid is heated with a dehydrating agent like phosphoric oxide [20-23], oleum [21] or fluorosulfonic acid [24] but no violent phenomena have been noticed. As thionyl chloride does not react with triflic acid, the occurrence of trifluoromethyl triflate has been rationalized through the reaction of triflic acid with its anhydride [21] :



$$F_3C\text{-}SO_2\text{-}O\text{-}O_2S\text{-}CF_3 + H\text{-}\ddot{O}\text{-}SO_2CF_3 \longrightarrow CF_3SO_3H + SO_2 + F_3C\text{-}O\text{-}SO_2CF_3 \quad (2)$$

On the other hand, Chen and Zhu [25] described a sluggish reaction, between -20°C and +20°C, from equimolecular amounts of diflic acid and thionyl chloride which led to difluoromethyl difluoromethanesulfonate (I) in a poor yield. This reaction became rapid only at 120°C, distilling (I) as soon as it was formed. A slow decomposition of (I) was observed during storage at room temperature with evolution of sulfur dioxide, fluoroform and formyl fluoride. This degradation, which became rapid at 80°C, was understood as an acidic decomposition of difluoromethyl diflate, leading to difluorocarbene, which highlights the very peculiar role played by the α-acidic hydrogen :



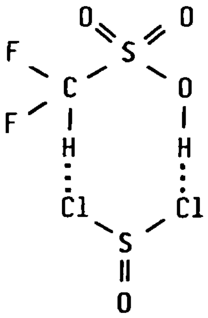
(3)

It must be noted that this proposed mechanism is not a chain process.

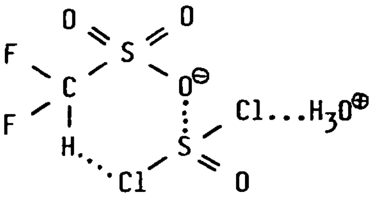
However, the very rapid reactions observed between hydronium diflate and thionyl chloride or oleum complemented Chen and Zhu's observations and modified their interpretations in the sense that :

- Hydronium difluoromethanesulfonate is more reactive towards thionyl chloride than anhydrous difluoromethanesulfonic acid : the temperature enhancement is not sufficient to explain the differences between Chen and Zhu's experiments (-20°C to +20°C) and ours (+20°C).

- As pointed out by these authors, the acidic hydrogen atom in the CHF_2 moiety undoubtedly plays an important role because it can induce hydrogen bonds which can explain that CHF_2SO_3H is more reactive than CF_3SO_3H towards $SOCl_2$, the latter being activated by hydrogen bonding. This interaction can also explain a better approach of $SOCl_2$ from hydronium diflate than from diflic acid.

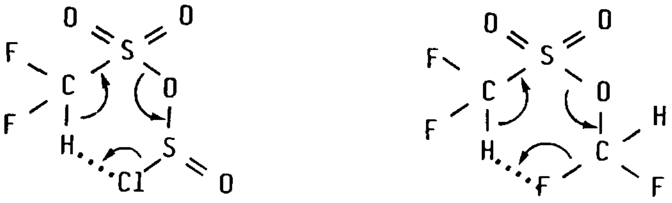


8 membered ring



6 membered ring

- A strong internal chelation can be also imagined in chlorosulfinyl diflate and difluoromethyl diflate which are suspected intermediates in the decomposition reactions. The hydrogen bonds enable electrocyclic rearrangements.



(I)

- From the violence of the reaction between hydronium difluoromethanesulfonate and thionyl chloride, a chain process may be suggested, as presented in scheme I. The first key step of this chain would be the decomposition of difluorosulfene (II) which has been already described as an unstable intermediate [26]. This instability is probably the result of a very high electronic density around the carbon atom as symbolised by the extreme resonance forms presented in scheme 1.

The second key step involves the condensation of hydronium diflate with difluorocarbene which would be easier than the condensation of anhydrous diflic acid with difluorocarbene as proposed by Chen and Zhu.

Finally, the overall reaction of hydronium diflate on thionyl chloride led to gaseous products only :

$$CHF_2SO_3^- H_3O^+ + SOCl_2 \longrightarrow 2\,SO_2 + 2\,HCl + HF + HCOF \qquad (4)$$

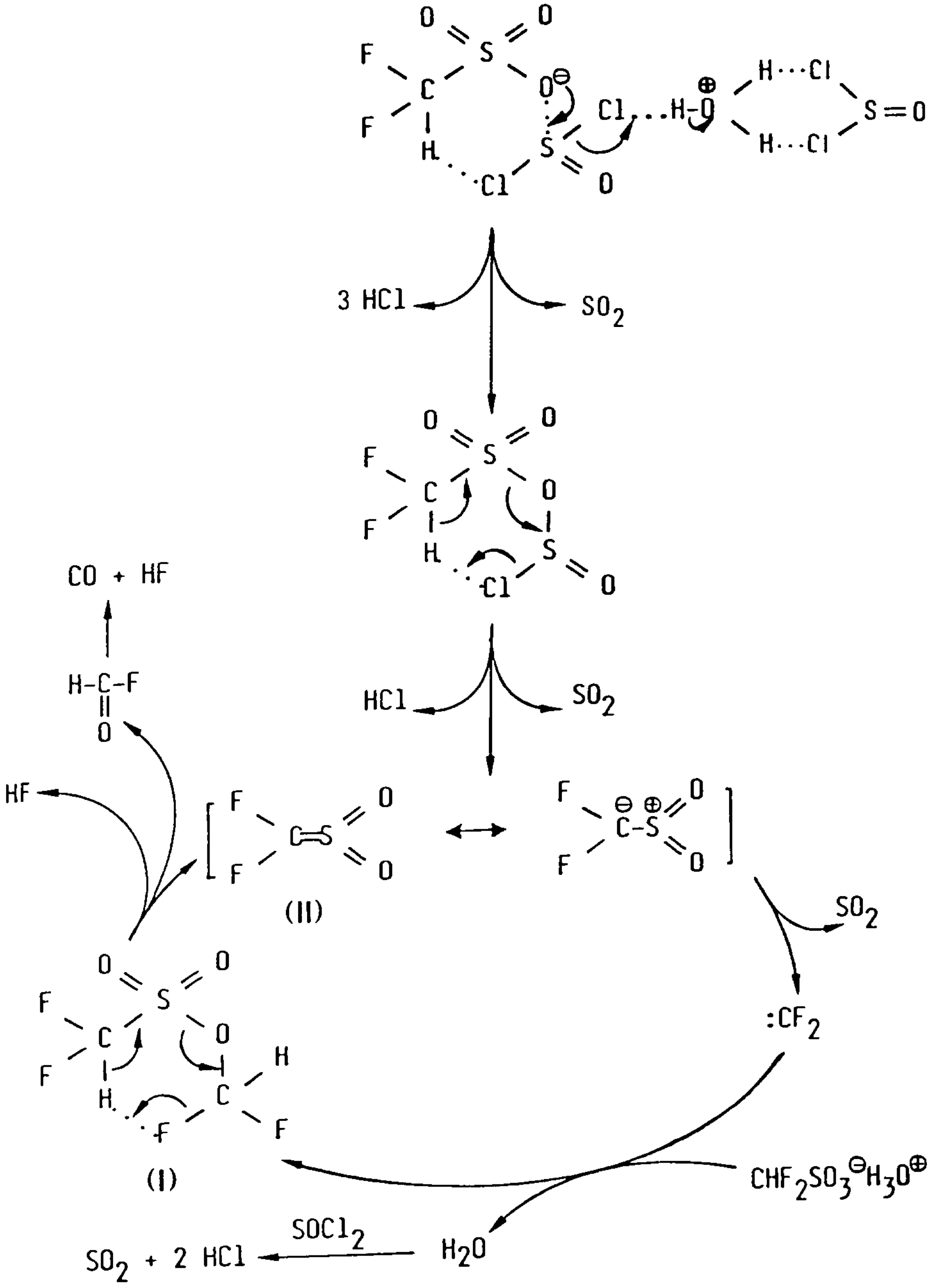
$$HCOF \rightleftharpoons HF + CO$$

By analogy, another chain mechanism can be proposed to represent the violent reaction of an excess of concentrated oleum with hydronium diflate (scheme II). The following overall reactions were observed :

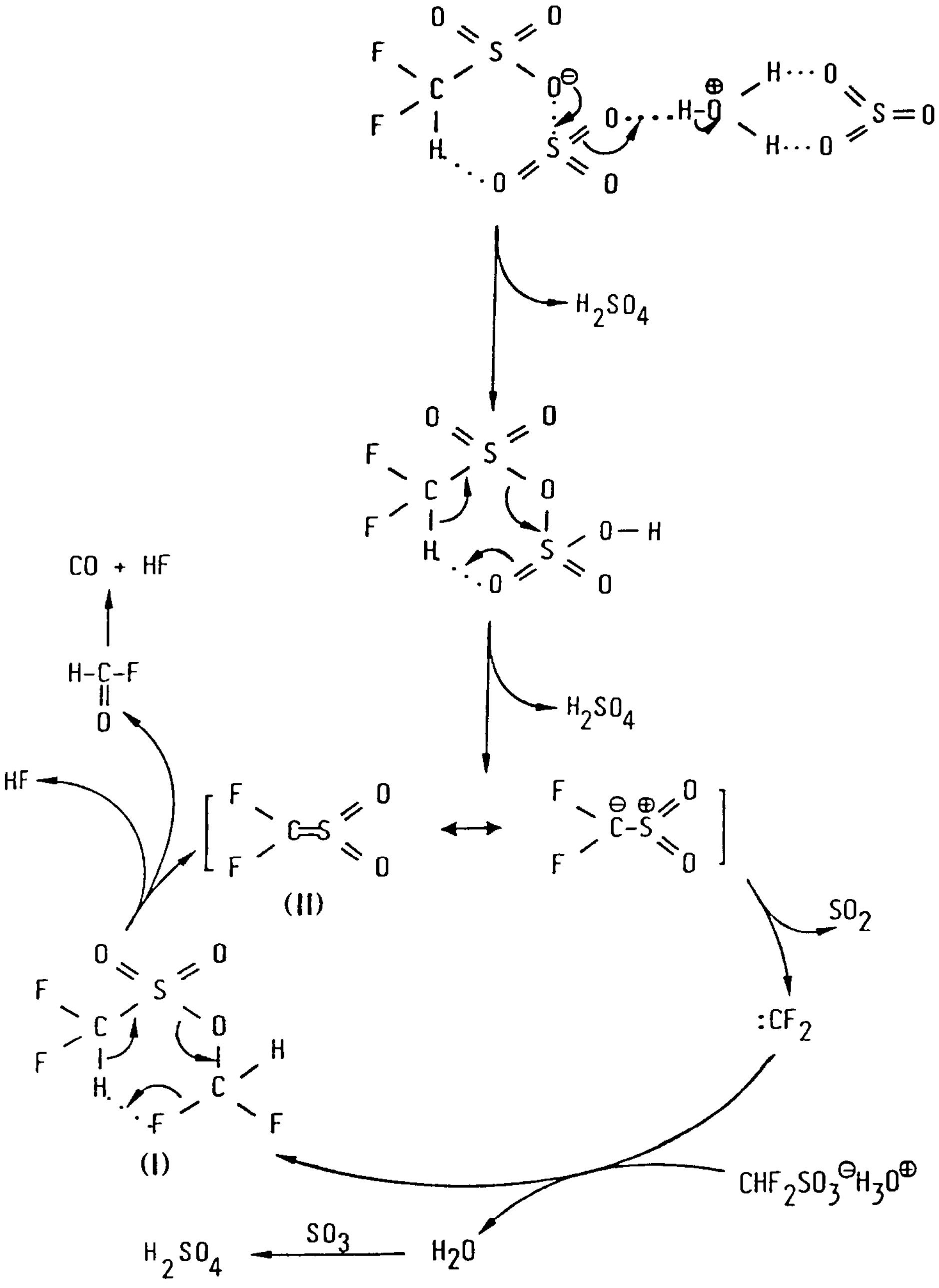
$$CHF_2SO_3^- H_3O^+ + SO_3 \longrightarrow H_2SO_4 + HCOF + HF + SO_2 \qquad (5)$$

$$HCOF \rightleftharpoons CO + HF$$

$$HF + SO_3 \rightleftharpoons FSO_3H$$


3 HCl
SO2
HCl
SO2
CO + HF
H-C-F
HF
(II)
SO2
:CF2
(I)
CHF2SO3⊖H3O⊕
SOCl2
SO2 + 2 HCl
H2O

Scheme I



Scheme II

However, the rather less violent reaction of hydronium diflate with sulfur trioxide suggests that the hydrogen bonding of the H atom in the CHF_2 moiety was weaker with sulfur trioxide than with thionyl chloride.

According to scheme II, where the first initiation step is the reaction of hydronium diflate with <u>two</u> molecules of sulfur trioxide, the decomposition reactions would be favoured by an excess of sulfur trioxide and, even if no excess is used, by high concentrations of SO_3 in sulfuric acid.

Thus, an experiment to obtain anhydrous diflic acid from hydronium diflate and the stoichiometric amount (or a slight excess) of sulfur trioxide, added as a diluted oleum (10-15 % SO_3), was attempted. After a slow addition of this oleum to CHF_2SO_3H, H_2O at room temperature, followed by distillation under reduced pressure, anhydrous difluoromethanesulfonic acid was isolated in a 51 % yield. It exhibited a correct ^1H NMR spectrum ($SO_3H/CHF_2=1/1$), a correct equivalent point by titration with potassium hydroxide in isopropanol and a good elemental analysis. It must be noted that the yield was best when dropping oleum into $CHF_2SO_3^-H_3O^+$, a procedure which avoided local overconcentrations.

CONCLUSION

Difluoromethanesulfonic acid can be obtained from monohydrated sodium difluoromethanesulfonate in a 44 % overall yield.

Though modest, this result can be considered, from an economic point of view, as an interesting one, due to the low cost of the raw materials (chlorodifluoromethane, sodium sulfite, sulfuric acid and oleum).

The most reproducible procedure is a two-step one : hydronium difluoromethanesulfonate is first isolated and treated, after checking the exact content of water by a simple ^1H NMR analysis, with the stoichiometric amount of sulfur trioxide, added as a diluted oleum.

EXPERIMENTAL

Monohydrated sodium difluoromethanesulfonate has been obtained from chlorodifluoromethane (1.8 mole), anhydrous sodium sulfite (1.2 mole), sodium hydroxide (0.5 mole) and 500 ml water heated for 20 h at 150°C under a 43 bars autogeneous pressure [9]. Pure sulfuric acid (100 % H_2SO_4) was obtained by mixing concentrated sulfuric acid (98 %) with the calculated amount of sulfur trioxide delivered as a 30 % SO_3 oleum. Its purity was verified by titration with potassium hydroxide in isopropanol. 10 % SO_3 oleum was obtained by dilution of 30 % SO_3 oleum with pure sulfuric acid. ^1H and ^{19}F NMR spectra were recorded, at 100 MHz and 93.65 MHz resp., on a Jeol FX100 spectrometer (without solvent ; tetramethylsilane and trifluoroacetic acid as external standards resp. ; positive ^{19}F chemical shifts downfield from trifluoroacetic acid). Chemical shifts from $CFCl_3$ can be deducted from chemical shifts from CF_3CO_2H following the equation :

ppm (v.s. $CFCl_3$) = ppm (v.s. CF_3CO_2H) -78.5.

Synthesis of monohydrated difluoromethanesulfonic acid from monohydrated sodium difluoromethanesulfonate

In a 100 ml four-necked glass apparatus fitted with a mechanical stirrer, a thermometer, a dropping funnel and a distillation column filled with Fenske rings, was introduced 25.8 g (0.15 mole) of monohydrated sodium difluoromethanesulfonate. 30.0 g of 100 % sulfuric acid was added over 30 min under stirring at between 22°C and 24°C. The suspension was slowly placed under a 5 torr vacuum and then heated up to 140-145°C when distillation started (column head temperature = 104°C). 19.4 g of a semi-solid product were collected (yield = 86 %), the analysis of which corresponded to $CHF_2SO_3^- \ H_3O^+$:

^1H NMR CHF_2 δ = 6.6 ppm (t) (1H) $^2J_{H-F}$ = 52.9 Hz
H_3O^+ δ = 11.6 ppm (s) (3H)
^{19}F NMR δ =-45.7 ppm (d) $^2J_{H-F}$ = 52.9 Hz
Sulfur analysis S % = 21.6 (found) 21.3 (calc.)
M.P. = 55°C [1]. Eb_5 = 104°C

Synthesis of anhydrous difluoromethanesulfonic acid from hydronium difluoromethanesulfonate

Using the same procedure as above, 35.3 g (0.235 mole) of hydronium difluoromethanesulfonate were treated with 150 g (80.5 ml) of oleum containing 13.4 % sulfur trioxide (0.25 mole SO_3). The reaction mixture was heated up to 158°C under 2 torrs. 15.7 g of anhydrous difluoromethanesulfonic acid were collected (Eb_2 = 79-80°C, yield = 51 %).

^1H NMR CHF_2 δ = 6.6 ppm (t) (1H) $^2J_{H-F}$ = 52.9 Hz
H^+ δ = 11.6 ppm (s) (1H)
^{19}F NMR δ =-45.7 ppm (d) $^2J_{H-F}$ = 52.9 Hz
d^{25} = 1.72 [1]
Eb_1 = 75-79°C [1] ; Eb_2 = 79-80°C (this work).

Difluoromethanesulfonic acid is a colourless liquid, slightly less mobile than trifluoromethanesulfonic acid, which fumes when exposed to atmosphere. Its I.R. spectrum could not be recorded because of the attack of the sodium chloride windows of the cell : the spectrum of sodium difluoromethanesulfonate was obtained. It is possible that Brown and Bowden, who described the I.R. spectrum of CHF_2SO_3H [1], used cells with coated windows.

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