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Technical Notes

Synthesis of Trifluoromethanesulfonic Acid from CHF_3

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Abstract:

Trifluoromethane is transformed to trifluoromethanesulfonic acid (TFMSA) at low temperature in a liquid-phase reaction in a strong acid such as fuming sulfuric acid as well as in a strong basic solution such as *t*-BuOK/DMF.

Introduction

Trifluoromethanesulfonic acid (TFMSA), also known as triflic acid, is a strong acid with high thermal stability and resistance to oxidation and reduction.[1] It is widely used as a catalyst in the polymer, fuel, pharmaceutical, and sugar industries. There are also recent indications that it would be a superior electroplating agent. The current commercial process for producing TFMSA, which involves the electrochemical fluorination of CH_3SO_2Cl, is expensive.[2] Alternative routes involve expensive raw materials such as $CF_3-S-S-CF_3$ which is oxidized with $K_2S_2O_8$ or H_2O_2 to TFMSA.[3] Cost intensive, low-yield processes have been reported for the synthesis of TFMSA starting from CF_3Br and CF_3I using stoichiometric amount of a reducing agent such as Zn.[4]

CHF_3 is a byproduct of the fluorochemical industry and is available in large quantities at a very low price. Prakash et al. have recently reported a novel method for synthesizing trimethyl(trifluoromethyl) silane (CF_3-TMS) from CHF_3;[5] however, there is no report of synthesizing TFMSA directly from CHF_3. Here, we will show that CHF_3 can be functionalized to TFMSA in highly acidic as well as highly basic media. Our initial approach was based on recent studies by Sen et al.[6] and by us,[7] which have shown that CH_4 can be sulfonated with SO_3 in fuming sulfuric acid to produce MSA in high yield, using $K_2S_2O_8$, CaO_2, and urea$-H_2O_2$ and $RhCl_3$ combinations as free radical initiators.[7] Since the C$-$H bond energy of CHF_3 is similar to that of CH_4, we reasoned that CHF_3 might be activated for sulfonation in a manner similar to that for CH_4.

In a typical reaction (Scheme 1), CHF_3 (650 psig) is reacted with SO_3 (21 mmol) in fuming sulfuric acid (5.67 g) for 12 h in the presence of a small amount of initiator, urea$-H_2O_2$ (0.4 mmol) and a promoter $RhCl_3$ (0.1 mmol) at 65 °C. The reaction mixture was analyzed by ^{19}F NMR to identify and quantify CF_3SO_3H (chemical shift is -15.6 with respect to trifluorotoluene). D_2O was used as the NMR solvent in a capillary. Only, 2.5% of the initial SO_3 was converted to CF_3SO_3H using the urea$-H_2O_2$ and $RhCl_3$ combination. Over 400 reactions were performed to increase the yield without success.

The problem of low yield is understood on the basis of this proposed mechanism similar to that previously proposed for methane activation (reactions 1$-$4).[7] The initiator abstracts a hydrogen atom from CHF_3 to generate $CF_3\bullet$ which then reacts with SO_3 to form $CF_3SO_3\bullet$. This species then can react with CHF_3 to form the product, TFMSA, and another $CF_3\bullet$ radical. Termination of the radical chain can occur via the reaction of two $CF_3\bullet$ radicals to generate C_2F_6, as shown in reaction 4. The observation of C_2F_6 in the headspace suggests that chain termination occurs rapidly, thereby limiting the production of TFMSA.

$$CHF_3 + I\bullet = CF_3\bullet + IH \tag{1}$$

$$CF_3\bullet + SO_3 = CF_3SO_3\bullet \tag{2}$$

$$CF_3SO_3\bullet + CHF_3 = CF_3SO_3H + CF_3\bullet \tag{3}$$

$$CF_3\bullet + CF_3\bullet = C_2F_6 \tag{4}$$

When the reaction was performed with SO_2Cl_2 (21 mmol) instead of SO_3, about 3% of SO_2Cl_2 converted to

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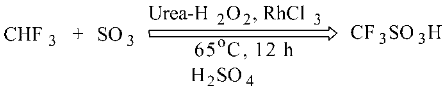
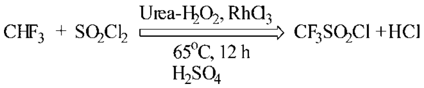
10.1021/op040007r CCC: $27.50

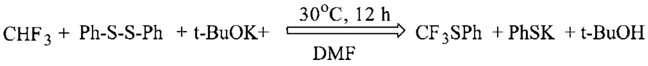
Scheme 1. Direct reaction of CHF_3 with SO_3 in fuming sulfuric acid



Scheme 2. Direct reaction of CHF_3 with SO_2Cl_2 in fuming sulfuric acid



Scheme 3. Direct reaction of CHF_3 with Ph−S−S−Ph in DMF



CF_3SO_2Cl, which could then be transformed to CF_3SO_3H by reaction with water (Scheme 2). Analysis of the reactor headspace showed the presence of C_2F_6 and CF_3Cl. These products are most likely formed via chain-termination processes involving the reaction of $CF_3\bullet$ radicals with each other radical or with a chlorine atom. The reaction, $2CHF_3 = C_2F_6 + H_2$ is not thermodynamically favourable; however, the presence of an oxygen source derived from the radical initiator makes the reaction favourable, i.e., $2CHF_3 + {}^1/_2O_2 = C_2F_6 + H_2O$.

The low yield obtained in an acidic medium motivated us to consider CHF_3 activation in a highly basic medium. This approach was stimulated by the recent work of Prakash et al. on the synthesis of CF_3-TMS. The hydrogen on CHF_3 is acidic and can be removed by reaction with a strong base such as *t*-BuOK in DMF. Thus, CHF_3 was reacted with Ph−S−S−Ph in DMF[8] in the presence of *t*-BuOK. CF_3−S−Ph ($\delta = +19.9$) was obtained in moderate yield (Scheme 3). This product was then oxidized with a mixture of HCl and H_2O_2 to CF_3SO_3H ($\delta = -15.8$). The main byproduct was CF_3SO_2Ph ($\delta = -11.9$).

Table 1 shows the effect of different process parameters on the conversion of CHF_3 to CF_3−S−Ph by the reaction of CHF_3 and Ph−S−S−Ph in the presence of *t*-BuOK as the base (Scheme 3). Since DMF is unique in its ability to stabilize CF_3^-, it was used as the solvent.[8] Increasing the CHF_3 pressure from 50 psig to 450 psig increased the conversion of CHF_3. However, the selectivity to CF_3SPh decreased with increasing CHF_3 pressure. It was observed that the temperature has a predominant role on the conversion and selectivity. The maximum conversion (53%) and selectivity to CF_3SPh (16%) were obtained at 30 °C (Table 2, entries 5−7). Another parameter affecting the progress of the reaction is the mole ratio of *t*-BuOK to Ph−S−S−Ph (Table 2, entries 8−11). The maximum conversion and selectivity were obtained using a molar ratio at 1:5.

Table 1. Effect of different parameters on the CF_3SPh synthesis[a]

entry	parameter	conv of CHF_3, %	selectivity to CF_3SPh, %
1	CHF_3, 50 psig	2	63
2	250 psig	9	54
3	350 psig	12	53
4	450 psig	14	48
5	temp, 30 °C	16	53
6	46 °C	12	50
7	55 °C	11	48
8	*t*-BuOK:PhSSPh 1:1	7	42
9	1:1.5	10	48
10	1:2	13	50
11	1:5	16	53

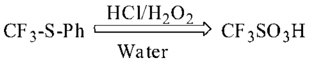
[a] Standard reaction conditions (unless otherwise stated): CHF_3, 350 psig (0.08 mol); *t*-BuOK, 1.6 g (0.0143 mol); PhSSPh, 3.42 g (0.0214 mol); temperature, 46°C; time, 16 h.

Table 2. Effect of molar ratio of HCl to H_2O_2 on the oxidation of CF_3SPh to CF_3SO_3H[a]

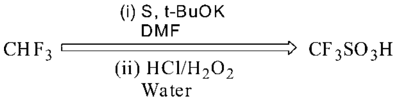
entry	molar ratio of HCl/H_2O_2	conv of CF_3SPh, %	selectivity to CF_3SO_3H, %
1	2:1	46	6
2	3:1	53	9
3	5:1	59	9
4	5:2	66	12
5	7:3	73	16

[a] Reaction conditions: CF_3SPh, 1.12 mmol; temperature, 53 °C; time, 6 h; solvent, water, 10 mL; TBAC, 0.05 g.

Scheme 4. Direct oxidation of CF_3SPh with HCl and H_2O_2



Scheme 5. Direct reaction of CHF_3 with S and subsequent oxidation



In the second step the CF_3SPh was oxidized to CF_3SO_3H using a mixture of HCl and H_2O_2 (Scheme 4). This “chlorine/water” oxidation ($2HCl + H_2O_2 \rightarrow Cl_2 + 2H_2O$) was performed at 53 °C for 6 h using 1.12 mmol of CF_3SPh in water (total 10 mL). A phase-transfer catalyst (PTC) such as tetrabutylammonium chloride (TBAC), 0.05 g was used to enhance the rate of the biphasic reaction.[9]

Table 2 shows the effect of different molar ratios of HCl to H_2O_2 on the rate of oxidation of CF_3SPh to CF_3SO_3H. It was observed that when the ratio was increased from 2 to 7 the conversion of CF_3SPh increased from 46 to 73% (Table 2, entries 1−5). The selectivity to TFMSA also increased from 6 to 16. The main byproducts were CF_3SOPh and CF_3SO_2Ph.[5]

In a simpler approach, sulfur (S) powder (0.02 mol) was reacted with CHF_3 (0.08 mol) in DMF (Scheme 5) in the presence of *t*-BuOK (0.01 mol) and ZnO (0.005 mol) at 46 °C. Presence of a small amount of ZnO or MgO was necessary, as in their absence no reaction of CHF_3 with Soccurred. A number of products were formed which are

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(8) DMF is used as a solvent as it is known in the literature that it helps to stabilize the CF_3^- anion in solution by complex formation, see Russel, J.; Roques, N. *Tetrahedron,* **1998**, *54*, 13771.

(9) Handbook of Phase transfer catalysis (Ed Sasson, Y.; Newmann, R.), Chapman & Hall, N. Y., **1997**.

difficult to identify. They are possibly of the general formula CF_3S_n. However, when the mixture was oxidized with HCl and H_2O_2, all the peaks disappeared and a new peak corresponding to CF_3SO_3H appeared, although in low yield (1.5% based on CHF_3).

In conclusion, we have developed a low-temperature reaction protocol to activate CHF_3 in acidic as well as in basic medium. The yields of triflic acid in both media are low. In acidic medium the low conversion may be due to the coupling of two $CF_3\bullet$ radicals to form C_2F_6, a process that is believed to be enhanced by the presence of an oxidant, the radical initiator. In basic medium CHF_3 can be transformed to CF_3SO_3H via a two-step process. The work presented here offers new opportunities for the conversion of CHF_3 to useful products.

CAUTION: Most of the compounds mentioned in this work are toxic and highly odorous; therefore, the entire work should be done inside a well-maintained hood.

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