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SYNTHESIS OF TRIFLUOROMETHANESULFONATE ESTERS BY REACTION OF ALKYL  
CHLORIDES WITH CHLORINE (I) AND BROMINE (I) TRIFLUOROMETHANESULFONATE

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SUMMARY

The synthesis of the first trifluoromethanesulfonate esters of the type  $CF_3SO_3(CH_2)_nO_3SCF_3$  ( $n=1,2,3$ ) are reported. The new compounds are prepared from  $Cl(CH_2)_nCl$  by substitutive electrophilic dehalogenation reactions with  $CF_3SO_2OX$  ( $x=Cl, Br$ ). The extension of this reaction to  $HCCl_3$  results in  $HC(O_3SCF_3)_3$  but the compound is unstable at  $22^\circ$ .

INTRODUCTION

The trifluoromethanesulfonate group,  $CF_3SO_3$  is an important substituent in mechanistic and synthetic organic chemistry[1,2]. The variety of methods available for the synthesis of alkyl esters include the reaction of  $CF_3SO_3H$  with alcohols, alkylsulfates and alkenes, reaction of  $(CF_3SO_2)_2O$  with alcohols and alcoholates, reactions of  $CF_3SO_3Ag$  with alkyl iodides and many others. The extension of these known synthetic methods to the preparation of diesters containing either geminal or non-geminal trifluoromethanesulfonate groups has not been reported.

Recently we have reported a variety of new trifluoromethanesulfonates from  $CF_3SO_2OX$  ( $x=Cl, Br$ ) by the electrophilic addition to alkenes[3,4], and by substitutive electrophilic dehalogenation reactions with fluorinated alkyl halides[4,5]. The extension of the latter reaction to the synthesis of the first alkyl diesters is described.

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## EXPERIMENTAL

General. Compounds were manipulated in glass and stainless-steel vacuum systems as previously described[6]. I.R. spectra were recorded on a P.E. 180 spectrometer using AgCl windows. N.M.R. spectra were recorded on a Varian XL-100-15 or T-60 spectrometers using ~15% mol. % solutions in  $\text{CFCl}_3$ .  $^{19}\text{F}$  chemical shifts are reported as  $\phi^*$  values and  $^1\text{H}$  chemical shifts as  $\delta$  values relative to external TMS. Analysis of fluorine was carried out by measuring the areas of the unknown fluorine resonance relative to  $\text{CFCl}_3$  using a sample of known concentration.

Preparation of  $\text{CF}_3\text{SO}_3\text{X}$ . The synthesis of  $\text{CF}_3\text{SO}_3\text{Cl}$  was carried out in ~15 ml Kel-F reactor fitted with a stainless-steel valve[7,8]. A weighed amount of acid (2-8 mmol) was added to the reactor, frozen at  $-195^\circ$  and a 10% excess of  $\text{ClF}$  was condensed in by vacuum transfer. The reactor was then warmed to  $-78^\circ$  for ~18-24 hr. The colorless layer of HF and unreacted  $\text{ClF}$  were then removed under dynamic vacuum at  $-78^\circ$ . The formation of  $\text{CF}_3\text{SO}_3\text{Cl}$  was assumed to be quantitative. For reaction, it was vacuum transferred via a short path into a 100 ml Pyrex bulb fitted with a glass-Teflon valve.

$\text{CF}_3\text{SO}_3\text{Br}$  was prepared from  $\text{CF}_3\text{SO}_3\text{Cl}$  in a 100 ml Pyrex bulb[8]. Bromine, corresponding to one-half the amount of  $\text{CF}_3\text{SO}_3\text{Cl}$ , was condensed into the  $\text{CF}_3\text{SO}_3\text{Cl}$  at  $-195^\circ$  by vacuum transfer. The mixture was held at  $-60^\circ$  with shaking until the liquid phase solidified. It was then warmed to  $-20^\circ$  with further shaking until a clear wine-red liquid formed (about 1 hr). The reactor was then cooled to  $-78^\circ$  and  $\text{Cl}_2$  was removed under dynamic vacuum. The  $\text{CF}_3\text{SO}_3\text{Br}$  formation was assumed to be quantitative and subsequent reactions were run directly in the reactor used for preparation. Caution! Both  $\text{CF}_3\text{SO}_3\text{Cl}$  and  $\text{CF}_3\text{SO}_3\text{Br}$  are unstable at  $22^\circ$ , and should not be allowed to warm above  $0^\circ$ . Both are powerful oxidants and will form explosive mixtures with easily oxidizable substrates. Care must be used in the preparation and handling of these compounds.

Reaction of  $\text{CF}_3\text{SO}_3\text{X}$  with Alkyl Chlorides. Onto the  $\text{CF}_3\text{SO}_3\text{X}$  at  $-195^\circ$  in the glass reactors, the appropriate alkyl halide was added by vacuum transfer. The mixture was then placed in a shielded cold bath of  $\text{CFCl}_3$  or  $\text{CF}_2\text{Cl}_2$  and allowed to warm slowly. After the appropriate reaction time, the products were separated by pumping through traps at appropriate temperatures. Details of the reactions are summarized in the Table 1.  $\text{CF}_3\text{SO}_3\text{CH}_2\text{Cl}$ : collected in  $-55^\circ$  trap after passing through  $-30^\circ$  trap; colorless liquid, mol. wt. 201.8, calcd. 198.5; I.R. ( $\sim 5.0$  torr) 2940(vw), 1438(s), 1250(m), 1227(s), 1210(m), 1152(s), 1068(w), 1005(m), 970(s), 912(w), 820(w), 783(w), 748(w), 617(m), 462(w)  $\text{cm}^{-1}$ ;  $\phi^*$  75.6, s;  $\delta$  6.13, s.

$(\text{CF}_3\text{SO}_3)_2\text{CH}_2$ : collected in  $-30^\circ$  trap; colorless oil, m.p.  $18.0$ – $19.0^\circ$ ; I.R. (gas,  $\sim 0.5$  torr), 1445(m), 1227(s), 1142(s), 1050(w), 946(s), 770(m), 716(s), 605(m), 450(w)  $\text{cm}^{-1}$ ; N.M.R.  $\phi^*$  75.5, s;  $\delta$  6.28, s.

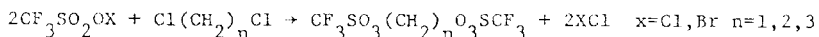
$\text{CF}_3\text{SO}_3\text{CH}_2\text{CH}_2\text{Cl}$ : collected in  $-60^\circ$ ; colorless oil, m.p.  $-50.5$  to  $50.0^\circ$ ; I.R. (gas,  $\sim 1$  torr) 2980(vw), 1438(s), 1249(s), 1228(vs), 1211(w), 1157(vs), 1100(vw), 1068(w), 1005(m), 970(s), 910(m), 820(br.-w), 878(w), 748(w), 620(m)  $\text{cm}^{-1}$ ; N.M.R.  $\phi^*$  74.4, s;  $\delta$  4.00, t,  $\text{CH}_2$ ;  $\delta$  4.93, t,  $\text{CH}_2\text{Cl}$ ;  $J_{\text{HH}} = 5.8$  Hz.

$(\text{CF}_3\text{SO}_3\text{CH}_2)_2$ : very low volatile, colorless oil; I.R. (liquid) 1422(m), 1260(sh), 1230(s), 1210(sh), 1150(s), 1035(s), 1000(w), 935(m), 795(m), 760(w), 640(m), 450(w)  $\text{cm}^{-1}$ ; N.M.R.  $\phi^*$  75.3, s;  $\delta$  4.97, s.

$(\text{CF}_3\text{SO}_3\text{CH}_2)_2\text{CH}_2$ : very low volatile, colorless oil; I.R. (liquid) 1420(s), 1253(s), 1210(s), 1143(s), 1055(m), 958(m), 930(s), 850(vw), 813(vw), 760(w), 660(m), 615(s), 580(m), 520(vw)  $\text{cm}^{-1}$ ; N.M.R.  $\phi^*$  75.5, s;  $\delta$  4.23, t,  $\text{OCH}_2$ ;  $\delta$  1.95, quintet,  $-\text{CH}_2-$ ;  $J_{\text{HH}} = 6.0$  Hz.

## RESULTS AND DISCUSSION

The low temperature reactions of alkyl chlorides with  $\text{CF}_3\text{SO}_2\text{OX}$  ( $x=\text{Cl}, \text{Br}$ ) are summarized in Table 1. The reactions proceed in excellent yield according to the equation



Substantial amounts of the monosubstituted product were observed with  $\text{ClCH}_2\text{Cl}$  and  $\text{ClCH}_2\text{CH}_2\text{Cl}$  using  $\text{CF}_3\text{SO}_2\text{OCl}$ . Other products,  $\text{CF}_3\text{Cl}$  and  $\text{SO}_3$ , from decomposition of  $\text{CF}_3\text{SO}_2\text{OCl}$  and unidentified organic compounds were also formed. The reactions are rather exothermic and can be explosive. This uncontrolled reactive

Table 1

Reactions of  $\text{CF}_3\text{SO}_3\text{X}$  with Alkyl Chlorides

$\text{X}^a$	$\text{RCl}^a$	Conditions		Products <sup>b,c</sup>
		Time (hrs)	Temp. (°C)	
Cl(5.8)	$\text{CH}_2\text{Cl}_2$ (2.5)	24	-111 to 0°	$(\text{CF}_3\text{SO}_3)_2\text{CH}_2$ (45), $\text{CF}_3\text{SO}_3\text{CH}_2\text{Cl}$ (35) $\text{Cl}_2$ (100)
Cl(8.0)	$(\text{CH}_2\text{Cl})_2$ (3.8)	6	-78 to -30°	$(\text{CF}_3\text{SO}_3\text{CH}_2)_2$ (50), $\text{CF}_3\text{SO}_3\text{CH}_2\text{CH}_2\text{Cl}$ (50), $\text{Cl}_2$ (100)
Br(3.8)	$(\text{ClCH}_2)_2\text{CH}_2$ (1.8)	16	-78 to 22°	$(\text{CF}_3\text{SO}_3\text{CH}_2)_2\text{CH}_2$ (94), $\text{BrCl}$ (100)
Cl(4.6)	$(\text{ClCH}_2)_2\text{CH}_2$ (2.3)	6	-111 to -55°	explosion at -55° <sup>e</sup>
Cl(6.0)	$\text{HCCl}_3$ (1.9)	16	-111 to -10°	$[(\text{CF}_3\text{SO}_3)_3\text{CH}]$ , $\text{Cl}_2$ (100)
		1	22°	$\text{CF}_3\text{SO}_3\text{H}$ (70), $(\text{CF}_3\text{SO}_2)_2\text{O}$ (92), $\text{CO}$

a. Amounts in (mmol).

b. (% Yield) based on starting  $\text{RCl}$ .

c. Other low boiling products such as  $\text{SO}_3$ ,  $\text{CF}_3\text{Cl}$  and others were observed small amounts. Halogens analyzed by reaction with mercury.

e. Other explosive reactions occurred with  $\text{CH}_3\text{CCl}_3$  and  $(\text{CH}_3)_3\text{CCl}$ .



All show strong IR absorptions in the  $1450-800\text{ cm}^{-1}$  region which are indicative of covalent  $\text{CF}_3\text{SO}_3$  groups [8]. Two of these bands in the  $900-1000\text{ cm}^{-1}$  region are probably due to  $\nu(\text{S-O-C})$  stretching. Bands due to the  $\text{CH}_2$  fragments should be very weak under the conditions used to record the spectra. The chemical shifts for the  $\text{CF}_3$  and  $\text{CH}_2$  groups and the multiplicity of  $\text{CH}_2$  resonances were as expected. No H-F spin-spin coupling between the  $\text{CF}_3\text{SO}_3$  and  $\text{CH}_2$  groups could be resolved. For analogous fluorinated compounds  $^5J_{\text{FF}}$  values are 4-5 Hz and the  $^5J_{\text{HF}}$  values are then expected to be considerably less than 1 Hz. [3, 5]. The  $^{19}\text{F}$  NMR were run using measured amounts of compound and  $\text{CFCl}_3$  solvent. Careful integration of the compound and solvent fluorine resonance gave the expected ratios in each case and provided a partial analysis for the compounds.

The reactions of  $\text{CF}_3\text{SO}_2\text{OX}$  ( $x=\text{Cl}, \text{Br}$ ) with organic halides provides a new and possible general method for the synthesis of organic triflates. Clearly, the strong oxidizing nature of the hypohalites makes their utilization more difficult and suitable solvents must be found to moderate these reactions. The hypohalites will, however, undergo substitutive electrophilic dehalogenation with almost any organic compound containing a carbon-chlorine or carbon-bromine bond. The few exceptions found thus far are highly fluorinated alkanes such as  $\text{CF}_3\text{Cl}$ . In this case, however,  $\text{CF}_3\text{Br}$  reacts readily. Thus by suitable choice of hypohalite and organic halide it is, in principle, possible to substitute halogen by  $\text{CF}_3\text{SO}_3$  in a wide variety of compounds. This, combined with the potential control of stereochemistry [5], renders these reactions of considerable further interest in synthesis.

#### ACKNOWLEDGMENT

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