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SOME REACTIONS OF TRIFLUOROMETHANESULFONIC ANHYDRIDE WITH VARIOUS METAL SUBSTRATES

DEBYANI G NIYOGI, SUKHJINDER SINGH, SONU GILL and R D VERMA*

Department of Chemistry, Panjab University,
Chandigarh-160 104 (India)

SUMMARY

Reactions of trifluoromethanesulfonic anhydride with various metal substrates were carried out in an attempt to prepare metal trifluoro-methanesulfonates. New trifluoromethanesulfonates, viz; $NaBi(SO_3CF_3)_4$, $Na_2Te(SO_3CF_3)_6$, $K_2SeO_2(SO_3CF_3)_4$ and $Ti(OCH_3)_2(SO_3CF_3)_2$ have been prepared by reacting $NaBi(CF_3COO)_4$, $Na_2Te(CF_3COO)_6$ or Na_2TeO_3, K_2SeO_4 and $Ti(OCH_3)_4$ respectively, with $(CF_3SO_2)_2O$. These compounds have been characterized by elemental analyses and infrared and ^{19}F NMR spectra.

INTRODUCTION

Trifluoromethanesulfonic acid and its derivatives have received increased attention lately [1]. The use of trifluoromethanesulfonates, containing the facile leaving group CF_3SO_3 in solvolytic reactions has considerably extended the range of its activities [2-4]. A number of trifluoromethanesulfonates are known to date [2,5]. A vast majority of them have been prepared by using either the acid or its silver(I) salt. Trifluoromethanesulfonic anhydride has been used to introduce the trifluoromethanesulfonate/trifluoromethanesulfonyl group into various organic moieties [2,5]. Relatively few examples are available in the literature regarding the reactions of $(CF_3SO_2)_2O$ with metal substrates [2,5]. Recently, we reported some reactions of $(FSO_2)_2O)$, fluorosulfonic anhydride, with various substrates [6] and its potential as a fluoro-sulfonating agent. In this communication, we report the reactions of $(CF_3SO_2)_2O$ with $NaBi(CF_3COO)_4$, $Na_2Te(CF_3COO)_6$, $Ti(OCH_3)_4$, Na_2TeO_3, K_2SeO_4 and Bi_2O_3 which lead to new trifluoromethanesulfonates, viz;

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$NaBi(SO_3CF_3)_4$, $Na_2Te(SO_3CF_3)_6$, $Ti(OCH_3)_2(SO_3CF_3)_2$, $Na_2Te(SO_3CF_3)_6$, $K_2SeO_2(SO_3CF_3)_4$ and the previously known $Bi(SO_3CF_3)_3$ [7], respectively, as a continuation of our earlier work on fluoro/trifluoromethane-sulfonates [8-10]. No reactions between metal alkoxides and trifluoro-methanesulfonic anhydride have been reported so far to the best of our knowledge.

EXPERIMENTAL

Materials and Methods

Trifluoromethanesulfonic acid (Aldrich) and trifluoroacetic anhydride (Aldrich) were distilled before use. Trifluoromethanesulfonic anhydride was prepared by the literature method [11] and distilled twice before use. $Na_2Te(CF_3COO)_6$ [12], $NaBi(CF_3COO)_4$ [12] and $Ti(OCH_3)_4$ [13] were prepared as described in the literature. Bismuth(III) oxide (Reidel), Na_2TeO_3 (BDH) and K_2SeO_4 (BDH) were dried overnight in an oven at 110°C. Titanium(IV) chloride (Fluka) was distilled before use. The solvents were dried and distilled before use.

Infrared spectra of the compounds were recorded either on Nujol/hexachlorobutadiene mulls or on neat solids between AgCl plates on a Perkin Elmer-1430 infrared spectrophotometer. ^{19}F NMR spectra were recorded on a JEOL FX-90Q spectrometer using $CFCl_3$ as external reference.

Sulfur and fluorine contents were determined as reported earlier [8]. Metals were analyzed by standard methods [14]. Carbon and hydrogen were determined microanalytically. All manipulations were carried out either in a vacuum line or in a dry box filled with nitrogen.

Preparation of $NaBi(SO_3CF_3)_4$

Trifluoromethanesulfonic anhydride (2.79 g, 9.9 mmol) was condensed via vacuum transfer onto 2.53 g (3.7 mmol) of $NaBi(CF_3COO)_4$ in a Pyrex reactor fitted with a Rotaflo stopcock. The contents were allowed to warm slowly to room temperature and then the reactor was heated at -60°C for 3 days. Removal of all of the volatiles gave $NaBi(SO_3CF_3)_4$ as a white solid in quantitative yield (3.07 g, 3.7 mmol). Analysis: calcd. for $C_4BiF_{12}NaO_{12}S_4$: C, 5.79; Bi, 25.24; F, 27.53; S, 15.46. Found: C, 5.65; Bi, 24.90; F, 27.21; S, 15.40%. IR: 1345ssh, 1320 mb, 1262w, 1205s, 1150s, 1030ms, 980sh, 890sh, 850vw, 805w, 770w, 735sh, 675sh, 650s, 605vw, 590ssh, 518m, 475w cm^{-1}.

Preparation of $NaBiO(SO_3CF_3)_2$

2.15 g (2.6 mmol) of $NaBi(SO_3CF_3)_4$ were loaded into a Pyrex reactor fitted with a Rotaflo stopcock and evacuated for 1/2 h. The reactor was then heated at ~160°C for 2 days and the volatiles which formed were simultaneously pumped away. This gave $NaBiO(SO_3CF_3)_2$ (1.36 g, 2.5 mmol) in > 96% yield. Analysis: calcd. for $C_2BiF_6NaO_7S_2$: C, 4.39; Bi, 38.27; F, 20.88; S, 11.72. Found: C, 4.35; Bi, 37.90; F, 21.0; S, 11.85%. IR: 1308mb, 1220sb, 1155m, 1035sb, 808w, 770m, 640vs, 570sh, 510ms, 415sh cm^{-1}.

Preparation of $Na_2Te(SO_3CF_3)_6$

Method A:

An excess of trifluoromethanesulfonic anhydride (5.65 g, 20 mmol) was transferred via vacuum onto $Na_2Te(CF_3COO)_6$ (1.53 g, 1.8 mmol) in a Pyrex reactor. The reactor was then detached from the vacuum line and fitted with a reflux condenser and drying tube. The reaction mixture was heated under reflux (80 - 85°C) for 10 h. The volatiles were pumped off carefully and the product was dried *in vacuo* at ~60°C until a constant weight of $Na_2Te(SO_3CF_3)_6$ (1.92 g, 1.8 mmol) was obtained. The yield was quantitative.

Method B:

A Pyrex reactor was loaded with Na_2TeO_3 (0.31 g, 1.4 mmol) and evacuated for 2 h. Trifluoromethanesulfonic anhydride (1.80 g, ~6.4 mmol) was then condensed into the reactor via vacuum transfer. The reaction mixture was heated at ~80°C for 14 days. Removal of volatiles *in vacuo* gave $Na_2Te(SO_3CF_3)_6$ (1.49 g, ~1.4 mmol) in nearly quantitative yield.

Analysis: calcd. for $C_6F_{18}Na_2O_{18}S_6Te$: C, 6.74; F, 32.03; S, 17.98; Te, 11.98. Found: C, 6.71; F, 32.2; S, 18.15; Te, 11.27%. IR: 1400m, 1300mw, 1245s, 1185w, 1155sb, 1065sh, 1040sb, 970w, 885vw, 805ms, 765mw, 735sh, 690sh, 640sb, 595sh, 505ms, 445sh cm^{-1}.

Preparation of $K_2SeO_2(SO_3CF_3)_4$

The reaction between K_2SeO_4 (0.332 g, 1.5 mmol) and $(CF_3SO_2)_2O$ (2.25 g, 8 mmol) was carried out for 15 days at ~60°C in a manner as described above for $Na_2Te(SO_3CF_3)_6$ by Method B. This gave $K_2SeO_2(SO_3CF_3)_4$ (1.16 g, ~1.5 mmol) as a white solid in more than 98% yield. Analysis: calcd. for $C_4F_{12}K_2O_{14}S_4Se$: C, 6.12; F, 29.04; S, 16.31; Se, 10.06. Found: C, 6.05; F, 28.42; S, 16.50; Se, 9.78%. IR: 1380w, 1300wb, 1220sb, 1195m, 1172sh, 1035ms, 995sh, 910wb, 860w, 820ms, 770m, 745sh, 640s, 595m, 515ms cm^{-1}.

Preparation of $Bi(SO_3CF_3)_3$

The reaction between Bi_2O_3 (0.70 g, 1.5 mmol) and trifluoromethanesulfonic anhydride (3.49 g, 12.4 mmol) was carried out at 120°C for 29 days as above. This gave $Bi(SO_3CF_3)_3$ (1.94 g, 2.95 mmol) as a white solid in more than 98% yield. Analysis: calcd. for $C_3BiF_9O_9S_3$: C, 5.49; Bi, 31.86; F, 26.07; S, 14.64. Found: C, 5.40; Bi, 31.27; F, 26.2; S, 14.8%. IR: 1395vw, 1300w, 1205sb, 1140sb, 1030sb, 805mw, 770w, 635vs, 592w, 505ms cm^{-1}.

Preparation of $Ti(OCH_3)_2(SO_3CF_3)_2$

Trifluoromethanesulfonic anhydride (2.80 g, ~10 mmol) was condensed onto 0.35 g (2 mmol) of $Ti(OCH_3)_4$ in a Pyrex reactor. The reaction mixture was heated at 55 - 60°C for 1 day. The volatiles were then removed under vacuum and the residual mass obtained was treated with 20 mL of dichloromethane. The fine white solid was filtered, washed with CH_2Cl_2 and finally dried *in vacuo* to constant weight. This gave 0.755 g (1.85 mmol) $Ti(OCH_3)_2(SO_3CF_3)_2$ in > 92% yield. Analysis: calcd. for $C_4H_6F_6O_8S_2Ti$: C, 11.76; H, 1.47; F, 27.94; S, 15.69; Ti, 11.76. Found: C, 11.7; H, 1.45; F, 28.1; S, 15.8; Ti, 11.21%. IR: 1450w, 1340ms, 1300w, 1240m, 1210w, 1195sh, 1168mb, 1115m, 1058ms, 1018m, 982wb, 955mw, 885sh, 845w, 798vw, 762m, 730sh, 668sh, 645m, 610ms, 540s, 510w, 478w cm^{-1}. ^{19}F NMR (CH_3NO_2): -80.3 (s, CF_3) ppm.

The completion of each reaction was determined as follows: the volatile materials were removed via vacuum and changes in weight of the reactor recorded from time to time. Each time these materials were condensed back into the reactor and the reaction was allowed to proceed under said conditions. The reaction was considered to be complete when no further change in weight of the reactor was observed.

RESULTS AND DISCUSSION

Excess trifluoromethanesulfonic anhydride reacts with Na_2TeO_3, K_2SeO_4 and Bi_2O_3 to produce the new trifluoromethanesulfonates, $Na_2Te(SO_3CF_3)_6$,

$K_2SeO_2(SO_3CF_3)_4$ and the previously known $Bi(SO_3CF_3)_3$ [7] as shown by the following equations:

$$Na_2TeO_3 + 3(CF_3SO_2)_2O \xrightarrow[80^oC]{13\ days} Na_2Te(SO_3CF_3)_6 \qquad (1)$$

$$K_2SeO_4 + 2(CF_3SO_2)_2O \xrightarrow[60^oC]{15\ days} K_2SeO_2(SO_3CF_3)_4 \qquad (2)$$

$$Bi_2O_3 + 3(CF_3SO_2)_2O \xrightarrow[110^oC]{29\ days} 2Bi(SO_3CF_3)_3 \qquad (3)$$

All salts are white hygroscopic solids which are insoluble in common organic solvents. These trifluoromethanesulfonates are stable and do not melt up to 130^oC except for $K_2SeO_2(SO_3CF_3)_4$ which starts decomposing around -85^oC. No oxygen was observed during reaction (2), indicating that selenium in this compound probably exists in +6 oxidation state.

The reactions between the metal oxides and trifluoromethanesulfonic anhydride are not unprecedented. A few examples describing the reactions of $(CF_3SO_2)_2O$ with $K_2Cr_2O_4$, $K_2Cr_2O_7$, $PbCrO_4$, Na_2MoO_4, Na_2WO_4 [15] and Ag_2O, Cu_2O or HgO in the presence of suitable complexing agents are known [16-20].

The reaction between trifluoromethanesulfonic anhydride and $NaBi(CF_3COO)_4$ or $Na_2Te(C_3COO)_6$ proceeds smoothly to give new trifluoromethanesulfonates according to the following reactions:

$$NaBi(CF_3COO)_4 + 2(CF_3SO_2)_2O \xrightarrow[60^oC]{3\ days} NaBi(SO_3CF_3)_4 + 2(CF_3CO)_2O \qquad (4)$$

$$Na_2Te(CF_3COO)_6 + 3(CF_3SO_2)_2O \xrightarrow[80 - 85^oC]{10\ h} Na_2Te(SO_3CF_3)_6 + 3(CF_3CO)_2O \qquad (5)$$

Both trifluoromethanesulfonates are white, hygroscopic solids stable up to at least 130°C and are insoluble in common organic solvents. No decomposition products were observed during the reactions. The formation of $(CF_3CO)_2O$ during each reaction was confirmed by the infrared spectrum of the volatile material. Heating of $NaBi(SO_3CF_3)_4$ at 160°C *in vacuo* for 2 days produced $NaBiO(SO_3CF_3)_2$ and $(CF_3SO_2)_2O$.

The reaction between excess $(CF_3SO_2)_2O$ and $Ti(OCH_3)_4$ yields $Ti(OCH_3)_2(SO_3CF_3)_2$ under mild conditions according to equation 6. The yields were not quantitative because some of the product always remains behind in the filtration unit. The formation of methyl trifluoro-methanesulfonate during the reaction 6 was confirmed by comparison of its infrared spectrum with the reported spectrum [21].

$$Ti(OCH_3)_4 + 2(CF_3SO_2)_2O \xrightarrow[55-60^{\circ}C]{1\ day} Ti(OCH_3)_2(SO_3CF_3)_2 + 2CH_3OSO_2CF_3 \quad (6)$$

Bis(trifluoromethanesulfonato)titanium dimethoxide $Ti(OCH_3)_2(SO_3CF_3)_2$ is a white hygroscopic solid and does not melt or decompose up to -150°C. It is insoluble in most of the common non-coordinating solvents but sparingly soluble in both CH_3NO_2 and $C_6H_5NO_2$.

The salient features of the infrared spectra of the various compounds are given in the Experimental Section. A comparison of the infrared spectra of $NaBi(SO_3CF_3)_4$, $NaBiO(SO_3CF_3)_2$, $Na_2Te(SO_3CF_3)_6$ with $NaSO_3CF_3$ [21] and that of $K_2SeO_2(SO_3CF_3)_4$ with KSO_3CF_3 [21] reveals that these compounds are definite entities and do not contain any free $NaSO_3CF_3$ or KSO_3CF_3. The analysis of infrared spectra of $CF_3SO_3^-$ is less secure than in the case of FSO_3^-. Despite the inherent problems, vibrational spectroscopy has been used on many occasions to identify bound or ionic $CF_3SO_3^-$ [22-24]. A perusal of infrared frequencies (see Experimental Section) of $NaBi(SO_3CF_3)_4$, $NaBiO(SO_3CF_3)_2$, $Na_2Te(SO_3CF_3)_6$ and $K_2SeO_2(SO_3CF_3)_4$ reveals that the CF_3SO_3 groups are covalently bound with a lowering of symmetry from C_{3v} to C_s [25]. A trifluoromethanesulfonate group with reduced symmetry can act either in unidentate or bidentate fashion. However, the situation is not so clear cut in these mixed metal trifluoromethanesulfonates regarding assignments for unidentate or bidentate CF_3SO_3 groups, because of the splitting of various vibrational modes as well as mixing of CF_3 and SO_3 vibrational modes. No attempt was made to assign unambiguously the metal-oxygen multiple bonds in $K_2SeO_2(SO_3CF_3)_4$ and $NaBiO(SO_3CF_3)_2$ because of overlap with the CF_3SO_3 vibrations.

The infrared spectrum of $Bi(SO_3CF_3)_3$ (Experimental Section) is in good agreement with the reported spectrum [7], where two types of trifluoromethane-sulfonate groups have been anticipated.

Various bands in the infrared spectrum of $Ti(OCH_3)_2(SO_3CF_3)_2$ are given in the Experimental Section. A comparison of its infrared spectrum with that of $Ti(OCH_3)_4$ (1456mw, 1434mw, 1142mb, 1088ms, 1044ms, 574mb, 460m, 398w, 260vs cm^{-1}) reveals it to be a definite entity. A careful perusal of infrared frequencies of $Ti(OCH_3)_2(SO_3CF_3)_2$ reveals splitting of E modes of CF_3SO_3 group thus lowering its symmetry from C_{3v} to C_s. The infrared bands at 1340ms, 1115m, 1018m cm^{-1} in $Ti(OCH_3)_2(SO_3CF_3)_2$ which are not present in $Ti(OCH_3)_4$ may be tentatively assigned to the bidentate CF_3SO_3 group in bis(trifluoromethane-sulfonato)titanium(IV) dimethoxide as in $TiCl_2(SO_3CF_3)_2$ [26]. The infrared bands at 1358s, 1105s, 1006ms cm^{-1} have been assigned to the bidentate CF_3SO_3 group in $TiCl_2(SO_3CF_3)_2$ [26]. The ^{19}F NMR of $Ti(OCH_3)_2(SO_3CF_3)_2$ in CH_3NO_2 shows a single peak at -80.3 ppm probably indicating the presence of only one type of CF_3SO_3 group.

In conclusion, it may be added that the reactions of mixed metal oxides, trifluoroacetates and metal alkoxides with trifluoromethane-sulfonic anhydride is a good route to prepare novel trifluoromethane-sulfonates.

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