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SILVER (FLUOROSULFONYL)DIFLUOROACETATE - A NEW ROUTE TO FLUOROSULFONYL ESTERS

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SUMMARY

New fluorinated esters of the type $FSO_2CF_2C(O)OR$ and $(FSO_2CF_2C(O)O)_2R'$, ($R = CH_3$, $CH_3CH_2CH_2$, $(CH_3)_3Si$, $BrCH_2CH_2$, $CH_3CH_2OC(O)CH_2$, $CH_2 = CHCH_2$; $R' = CH_2$, CH_2CH_2, have been prepared and characterized via the reaction of silver difluoro-(fluorosulfonyl)acetate with alkylbromides, alkyliodides, and trimethylsilyl iodide. All new compounds have been characterized by their respective IR/MS/NMR spectra.

INTRODUCTION

Sulfonyl fluoride systems and their derivatives, RSO_2F, where R represents hydrocarbon/fluorocarbon moieties continue to be of considerable interest. The incorporation of the sulfonyl fluoride group (SO_2F) into molecular systems can lead to compounds that are useful as ion-exchange resins, surface active agents,

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and strong sulfonic acids/salts [1-3] Esters containing the $FSO_2CF_2C(O)O$ moiety have been prepared from the sultone $\overline{CF_2CF_2OSO_2}$ with fluorinated or non fluorinated alcohols another route involved the reaction of $FSO_2CF_2C(O)Cl$ with alcohols [4-7]

Fluorinated silver carboxylate salts have been useful in preparing fluoroesters from alkyl iodides [8] Therefore a new silver salt silver difluoro(fluorosulfonyl)acetate $FSO_2CF_2C(O)OAg$ was prepared and characterized its reactions with $(CH_3)_3SiI$ $HOCH_2CH_2I$ and alkyl bromides/iodides were also studied

RESULTS AND DISCUSSION

We have found that difluoro(fluorosulfonyl)acetic acid $FSO_2CF_2C(O)OH$ reacts with silver oxide in diethyl ether according to the following equation

$$2FSO_2CF_2C(O)OH + Ag_2O \xrightarrow{Et_2O} 2FSO_2CF_2C(O)OAg + H_2O \qquad (1)$$

The silver difluoro(fluorosulfonyl)acetate is a white solid somewhat sensitive to light it is soluble in water at room temperature

The silver salt can be used with alkyliodides/bromides to provide a route for preparing new sulfonyl fluoride esters

$$FSO_2CF_2C(O)OAg + RBr \rightarrow FSO_2CF_2C(O)OR + AgBr \qquad (2)$$

$R - BrCH_2CH_2 \quad CH_3CH_2OC(O)CH_2 \quad CH_2{-}CHCH_2$

$$FSO_2CF_2C(O)OAg + RI \rightarrow FSO_2CF_2C(O)OR + AgI \qquad (3)$$

$R - CH_3 \quad CH_3CH_2CH_2 \quad (CH_3)_3Si$

While it was not possible to replace both bromines in $BrCH_2CH_2Br$ replacement of both iodines in CH_2I_2 was observed

$$2FSO_2CF_2C(O)OAg + CH_2I_2 \rightarrow (FSO_2CF_2C(O)O)_2CH_2 + 2AgI \qquad (4)$$

Interestingly reaction of $FSO_2CF_2CO_2Ag$ with $HOCH_2CH_2I$ gave the disubstituted ester product

$$2FSO_2CF_2C(O)OAg + HOCH_2CH_2I \rightarrow (FSO_2CF_2C(O)OCH_2)_2 + AgI/AgOH \qquad (5)$$

The esters prepared in this work are in general stable, high boiling, colorless liquids. In all cases, reaction was observed with the appearance of the yellow silver halide.

A suggested mechanism for the reaction of $HOCH_2CH_2I$ with $FSO_2CF_2CO_2Ag$ is:

$FSO_2CF_2C(O)O^- + HOCH_2CH_2\text{-}I \rightarrow HOCH_2CH_2OC(O)CF_2SO_2F + I^-$ (6)

$(Ag+)$

$FSO_2CF_2C(O)O^- + H\text{-}OCH_2CH_2OC(O)CF_2SO_2F \rightleftharpoons FSO_2CF_2C(O)OH + {}^-OCH_2CH_2OC(O)CF_2SO_2F$ (7)

$FSO_2CF_2C(O)\text{-}OH + {}^-OCH_2CH_2OC(O)CF_2SO_2F \rightarrow (FSO_2CF_2C(O)OCH_2)_2 + OH^-$ (8)

$Ag^+ + I^-/OH^- \rightarrow AgI/AgOH$ (9)

In eq. (6) the carboxylate anion displaces I^- from $HOCH_2CH_2I$ to form a monosubstituted alcohol intermediate. Then, in eq. (7) equilibrium is established between the intermediate alcohol and alkoxide anion, ${}^-OCH_2CH_2OC(O)CF_2SO_2F$, which in a subsequent reaction via nucleophilic attack on the carboxylic acid, produces the diester.

The infrared spectra of the sulfonyl fluoride esters have several common features. The stretching frequency for the carbonyl group adjacent to CF_2 is found in the 1785-1813 cm^{-1} region; for the carbonyl group next to CH_2 the corresponding frequency is located at 1757 cm^{-1}. The carbonyl bands next to the fluorinated carbon agree closely with those found for other fluorinated esters [6-10]. In the silver salt, $FSO_2CF_2C(O)OAg$, the asymmetric $-C(O)O^-$ frequency is found at 1708 cm^{-1}; in CF_3COOAg, this stretching frequency is located at 1720 cm^{-1}.

In all esters, as well as the silver salt, the asymmetric and symmetric SO_2 stretching frequencies are assigned to the 1427-1462 cm^{-1} region and the 1223-1243 cm^{-1} region, respectively. These values correspond to the SO_2 frequencies reported for other sulfonyl fluoride compounds [5-7]. The carbon-fluorine absorption bands occur at 1166 to 1321 cm^{-1}. The S-F absorptions for the sulfonyl fluoride group occur in the 794-808 cm^{-1} region as expected [5-7]. The C-H absorptions in the esters range from 2854 to 3079 cm^{-1}.

In the mass spectra a molecular ion peak was found for $FSO_2CF_2C(O)OSi(CH_3)_3$ however MH^+ ions were found for $FSO_2CF_2C(O)OCH_2C(O)OC_2H_5$ $[FSO_2CF_2C(O)O]_2CH_2$ $FSO_2CF_2C(O)OSi(CH_3)_3$ and $FSO_2CF_2C(O)OCH_3$ In all cases appropriate fragmentation peaks were found indicating cleavage at the ester linkage Bromine isotopes were detected in the compound $FSO_2CF_2C(O)OC_2H_4Br$

The ^{19}F nmr spectra for all new esters and the silver salt $FSO_2CF_2C(O)OAg$ exhibit common features The chemical shifts for the FSO_2 group (triplet) range from ϕ 37 8 to ϕ 40 4 ppm for the CF_2 group (doublet) the range is ϕ 97 2 to ϕ 109 0 ppm The chemical shifts are consistent with those of other reported esters prepared from the sultone $\overline{CF_2CF_2OS}O_2$ [5 7] For the new esters the coupling constants, $J_{CF_2\ SO_2F}$ range in value from J = 5 3 to 5 7 Hz except for $FSO_2CF_2C(O)OSi(CH_3)_3$ and the salt $FSO_2CF_2C(O)OAg$ which are J = 4 6 Hz and J = 3 5 Hz, respectively

For monosubstituted esters the ^1H nmr spectra gave splitting patterns similar to the starting alkyl bromide or iodide for diesters prepared from $HOCH_2CH_2I$ and CH_2I_2 singlets at δ 5 03 and δ 6 53 ppm respectively were found The spectrum of $FSO_2CF_2C(O)OCH_2CH_2Br$ contained triplets at δ 3 98 ppm (CH_2Br) and δ 5 13 ppm (OCH_2) the $J_{CH\ CH}$ = 6 0 Hz While the ester prepared from CH_3I has been previously synthesized [5] no spectral data has been reported

In order to determine more accurately proton couplings of the allyl group in previously reported allyl fluoroesters containing the sulfonyl fluoride grouping [6 7] the proton spectrum of $FSO_2CF_2CO_2CH_2{}^dCH^c{=}CH^aH^b$ was obtained at 300 MHz It was possible to resolve all possible couplings in the allyl group new coupling constants found were J_{bd} = 1 2 Hz and J_{ad} = 1 2 Hz The values of J_{ac} J_{bc} and J_{cd} were in good agreement with the literature [7] the J_{ab} value found was 1 2 Hz In earlier reports [6 7] the J_{ab} coupling of the allyl group for a series of allyl esters was found to be in the range of 3 5 Hz it is expected based on this study that this range should be 1 2 Hz

EXPERIMENTAL

The acid $CF_2(SO_2F)C(O)OH$ was prepared by literature method [4] The iodides and bromides $BrCH_2C(O)OC_2H_5$ $BrCH_2CH_2Br$ and $BrCH_2CH{=}CH_2$ were obtained from MCB $HOCH_2CH_2I$ $CH_3CH_2CH_2I$ and $(CH_3)_3SiI$ from Aldrich CH_2I_2 and CH_3I from Kodak Ag_2O and diethyl ether MallinKrodt In all cases the compounds were used as received The $CFCl_3$ (DuPont) was dried over silica gel prior to use

General Procedure Gases and volatile liquids were manipulated in a conventional Pyrex vacuum apparatus equipped with a Heise-Bourdon tube gauge and a Televac thermocouple gauge Infrared spectra were obtained by using a Pyrex glass cell with KBr windows or as liquids/solids between KBr disks on a Nicolet 20DX spectrometer The nmr spectra were recorded with a Varian Model EM-390 spectrometer operating at 90 0 MHz for proton and 84 67 MHz for fluorine resonances or with a General Electric QE 300 FTNMR spectrometer operating in the quadrative mode TMS and $CFCl_3$ were used as external/internal standards Gas chromatographic separation was carried out using an Aerograph Autoprep (Model A-700) instrument with a 10' x 3/8" column containing 20% carbowax on 'chromosorb W'

The mass spectra were recorded with a VG 7070 HS mass spectrometer with an ionization potential of 17 or 70 eV

Elemental analyses were determined by Beller Microanalytical Laboratory in Göttingen West Germany

General Procedure for Ester Preparation To a 90 to 150 mL Pyrex-glass reaction vessel, equipped with a Kontes Teflon valve and under a nitrogen atmosphere was added $FSO_2CF_2C(O)OAg$ The iodo- or bromo-containing compounds were either condensed via vacuum transfer or directly added in a dry box into the reaction vessel and cooled to 196°C The reaction mixtures were protected from light and allowed to warm slowly to room temperature (24 h)

$FSO_2CF_2C(O)OAg$

To a 200 mL Pyrex glass three neck reaction vessel equipped with a reflux condenser and containing a Teflon stirring bar were added 19 5 mmol of Ag_2O and 25 ml diethyl ether The 200 mL reaction vessel was covered with aluminum foil The acid $FSO_2CF_2C(O)OH$ 37 8 mmol was added slowly with stirring over a period of 0 75 h at room temperature the mixture was stirred for an additional 15 h The mixture was filtered and pumped on through a trap cooled to 196 C The salt $FSO_2CF_2CO_2Ag$ (15 4 mmol) was dried by prolonged pumping (6 d) The yield was 82%, mp 159±1°C with dec

The infrared spectrum had the following bands (cm^{-1}) 1708 (s), 1687 (s with sh 1652) 1427 (s) 1384 (m) 1230 (m) 1180 (ms sh at 1138) 998 (m sh 955) 899 (w) 843 (m) 808 (m sh 787 752) 738 (wm) 716 (wm) 649 (m) 604 (m) 562 (w) 541 (w) 484 (wm) 456 (wm)

The ^{19}F nmr spectrum contained a triplet at ϕ 38 0 ppm (SO_2F) and a doublet at ϕ-100 9 ppm (CF_2) with a coupling constant $J_{CF_2-SO_2F}$ = 3 5 Hz The relative band area for FSO_2 to CF_2 was 1 2 2 0, theor 1 0 2 0

<u>Anal</u> Calcd for $C_2F_3SO_4Ag$ C 8 43 F, 20 0 S, 11 25 Ag 37 86 Found C 8 74 F 20 5 S 11 35 Ag 37 51

$FSO_2CF_2C(O)OAg$ with CH_3I

To the reaction vessel previously described were added 2 40 mmol $FSO_2CF_2C(O)OAg$ and 3 17 mmol CH_3I The mixture was protected from light and warmed slowly to room temperature (24 h) Trap-to trap distillation gave 1 51 mmol of the ester $FSO_2CF_2C(O)OCH_3$ (40°C trap) in 63% yield

The infrared spectrum had the following bands (cm^{-1}) 2973 (mw) 1806 (s) 1462 (vs) 1321 (s) 1243 (s) 1209 (s), 1159 (s) 1061 (m) 1026 (m) 955 (w) 878 (w), 829 (ms) 801 (s) 730 (w) 646 (m) 583 (m)

The ^{19}F nmr spectrum contained a triplet at ϕ 39 1 ppm (SO_2F) and a doublet at ϕ-105 5 ppm (CF_2) with a coupling constant J = 5 7 Hz The relative band area was 1 0 1 9 (theor 1 0 2 0) The ^1H nmr spectrum contained a singlet at δ 4 17 ppm

The positive ion mass spectrum CI^+ gave peaks (m/e species %) 193 MH^+ 1 6 124 $CH_2COCF_2S^+$ 5 2 109 M SO_2F^+, 55 9 79 $CSOF^+$ 8 6 67 SOF^+ 19 1 65, SO_2H^+ 23 6 59, $CH_3CO_2^+$, 100, 51 SF^+, 4 7

<u>Anal</u> Calcd for $C_3H_3F_3SO_4$ C 18 76 H 1 57 F 29 8, S 16 69 Found C 18 80, H 1 65 F 29 5 S, 16 69

$FSO_2CF_2C(O)OAg$ with $CH_3CH_2CH_2I$

To the reaction vessel previously described were added 15 11 mmol $FSO_2CF_2C(O)OAg$ and 14 18 mmol of $CH_3CH_2CH_2I$ After reaction the volatile liquid mixture was washed with H_2O dried over $MgSO_4$ and distilled The fraction boiling at 142-143°C was further purified by gas chromatography giving 1 54 mmol of $FSO_2CF_2C(O)OCH_2CH_2CH_3$ in 11% yield

The infrared spectrum had the following bands (cm^{-1}) 2980 (m) 2945 (w) 2889 (w) 1792 (s) 1448 (s), 1398 (w), 1384 (w) 1356 (w) 1313 (s), 1237 (s) 1193 (s) 1166 (s) 1152 (s) 1103 (vw) 1082 (vw) 1054 (wm) 1012 (m) 927 (w) 899 (w) 829 (m) 801 (ms), 723 (vw) 646 (m) 604 (m), 576 (m), 484 (vw) 463 (vw)

The ^{19}F nmr spectrum of $FSO_2CF_2C(O)OCH_2CH_2CH_3$ contained a triplet at ϕ 39 7 ppm (SO_2F) and a doublet at ϕ 105 4 ppm (CF_2) with a coupling constant $J = 5\ 3$ Hz The relative band area for FSO_2 CF_2 was 1 0 1 8 (theor 1 0 2 0) The ^1H nmr spectrum contained a triplet at δ 0 68 ppm (CH_3) a sextet at δ 1 50 ppm (CH_2) and a triplet at δ 4 19 ppm (CH_2) $J_{CH_3\text{-}CH_2} = 7\ 2$ Hz and $J_{CH_3\ CH_2} = 6\ 6$ Hz The relative band area for $CO_2CH_2CH_2CH_3$ was 2 0 2 0 3 1 (theor 2 0 2 0 3 0)

The positive ion mass spectrum CI^+ gave peaks (m/e species %) 205 M CH_3^+ or MH O^+ 2 32 149 $SCF_2COC_3H_3^+$ 12 49 119 $SCFCOC_2H_4^+$ 6 18 109 SC_5HO^+ 23 63 107 $FSO_2C_2^+$ or $CF_2CO_2CH^+$ 24 87 97 SC_4HO^+ 16 55 95 FSO_2C^+ 12 36 91 $SCFCO^+$ 5 10 83 SO_2F^+ 9 92 81 $C_4O_2H^+$ 6 92 79 $FSCO^+$ 5 23 73 $CFCOCH_2^+$ 12 29 70 $COC_3H_6^+$ 6 03 69 $COC_3H_5^+$ 26 62 67 SOF^+ or $COC_3H_3^+$ 12 97 65 COC_3H^+ 100 59 $CFCO^+$ 18 53 57 CO_2CH^+ 33 55 56 $C_2O_2^+$ or SC_2^+ 7 68 55 $COC_2H_3^+$ 33 06 53 C_2OCH^+ 5 98 51 SF^+ 13 48

Anal Calcd for $C_5H_7F_3SO_4$ C 27 28 H 3 21 F 25 9 S 14 56 Found C 27 29 H 3 22 F 26 1 S 14 57

$FO_2SCF_2C(O)OAg$ with $HOCH_2CH_2I$

To the reaction vessel previously described were added 20 9 mmol of $FSO_2CF_2C(O)OAg$ and 19 55 mmol $HOCH_2CH_2I$ Distillation gave 2 38 mmol of $(FSO_2CF_2C(O)OCH_2)_2$ in 23% yield b p 96 C/70μ

The infrared spectrum had the following bands (cm ^{1}) 2987 (vw) 1792 (s) 1448 (s) 1372 (w) 1307 (ms) 1237 (s) 1208 (ms) 1159 (s) 1124 (wm) 1047 (wm) 1019 (w) 871 (wm) 808 (ms br) 723 (vw) 646 (ms) 604 (m) 569 (m) 484 (w) 463 (vw)

The ^{19}F nmr spectrum contained a triplet at ϕ 40 4 ppm (SO_2F) and a doublet at ϕ 105 0 ppm with a coupling constant J = 5 6 Hz The integration ratio was 1 0 1 9 (theor 1 0 2 0) The ^1H nmr spectrum contained a singlet at δ 5 03 ppm

The positive ion mass spectrum CI^+ gives peaks (m/e species, %) 299 $M\text{-}SO_2F^+$ 1 06 207 $C_6O_4F_2SH^+$ 17 17 206 $C_6O_4F_2S^+$, 15 33, 205 $FSO_2CF_2CO_2C_2H_4^+$ 100 155 $FSCF_2COC_2H_2^+$ 17 02 141 $FSCF_2COC^+$ 24 45 123 SCF_2COCH^+ 5 92 122 SCF_2COC^+ 7 70 119 $SFCCOC_2H_4^+$ 24 37 113 $FSCF_2C^+$ 6 74 111 $C_5O_3H_3^+$ 7 66 97 SC_4HO^+ 5 52, 91 $SCFCO^+$ 7 73 79 $FSOC^+$ 13 39 78 CF_2CO^+ 7 36 69 $C_3O_2H^+$ 8 22 67 FSO^+ 44 13 65 C_4HO^+ 50 33 51 SF^+ 13 36

Anal Calcd for $C_6H_4F_6S_2O_8$ C, 18 85 H 1 05 F 29 8 S 16 78 Found C 19 32 H 1 01 F 28 9 S 15 91

$FSO_2CF_2C(O)OAg$ with $(CH_3)_3SiI$

To the reaction vessel previously described, were added 13 46 mmol of $(CH_3)_3SiI$ and 13 30 mmol of $FSO_2CF_2C(O)OAg$ Distillation of the liquid product gave 3 84 mmol $FSO_2CF_2C(O)OSi(CH_3)_3$ in 29% yield b p 86°C/46 mm

The infrared spectrum had the following bands (cm ^{1}) 2959 sh at 2924 and 2903), 1785 (s), 1448 (s sh at 1427) 1328 (m) 1258 (m sh at 1279) 1230 (m) 1195 (m) 1152 (s) 1012 (w sh at 1047) 913 (vw) 850 (s b sh at 878) 801 (s b) 759 (w) 730 (vw) 702 (vw) 639 (m sh at 667)

The ^{19}F nmr spectrum contained a triplet at ϕ 37 8 ppm (SO_2F) and a doublet at ϕ 97 2 ppm (CF_2) with a coupling constant J = 4 6 Hz The relative band area for FSO_2 to CF_2 was 1 0 2 0 (theor 1 0 2 0) The ^1H nmr spectrum contained a singlet at δ 0 4 ppm

The positive ion mass spectrum CI$^+$ gave peaks (m/e species %) 251 MH$^+$ 153 250 M$^+$ 1 73 149 M-H$^+$ 13 81 199 $SCF_2CO_2SiC_3H_9^+$ 5 83 91 $SCFCO^+$ 4 34 88 $OSiC_2H_8^+$, 9 42 87 $OSiC_3H_7^+$, 100 74, $OSiC_2H_6^+$ 4 23 73 $SiC_3H_9^+$ 45 92, 65 SiC_3H^+ 9 29 63 SCF^+ 7 73 59, $CFCO^+$ 39 97 57 $SiC_2H_5^+$ 6 53 55 $SiC_2H_3^+$ 7 88

Anal Calcd for $C_5H_9F_3SO_4Si$ F 22 8 S 12 81 Found F, 22 3 S 11 26

$FSO_2CF_2C(O)OAg$ with $BrCH_2CH_2Br$

To the reaction vessel previously described were added 21 73 mmol of $FSO_2CF_2C(O)OAg$ and 10 0 mmol $BrCH_2CH_2Br$ The liquid $FSO_2CF_2C(O)OCH_2CH_2Br$ 3 51 mmol was transferred directly from the reaction vessel in 35% yield

The infrared spectrum gave the following bands (cm^{-1}) 2959 (vw) 2917 (w) 2854 (w), 1792 (s) 1448 (s) 1384 (w) 1314 (s), 1279 (m) 1237 (s) 1188 (s) 1152 (s) 1068 (w) 1012 (m) 976 (w) 948 (vw) 927 (vw) 843 (m) 808 (s b) 723 (vw) 646 (ms) 611 (m) 590 (ms), 484 (w) 456 (w)

The ^{19}F nmr contained a triplet at ϕ 38 3 ppm (SO_2F) and a doublet at ϕ 109 ppm (CF_2) with a coupling constant J = 5 5 Hz The relative band area for FSO_2 to CF_2 was 1 0 2 0 (theor 1 0 2 0) The ^1H nmr spectrum contained a triplet at δ 5 13 ppm ($-C(O)OCH_2-$) and a triplet at δ 3 98 ppm (CH_2Br) with a coupling constant J = 6 0 Hz The relative band area for $C(O)O\underline{CH_2}$ $\underline{CH_2}$ Br was 1 0 1 0 (theor 1 0 1 0)

The positive ion mass spectrum CI$^+$ gave peaks (m/e species %) 267 M FH$^+$ 0 40 205 M Br$^+$ 100 153 $CO_2C_2H_4Br^+$ or $FSCF_2C_3O^+$ 4 21 151 $CO_2C_2H_4Br^+$ or $CO_2C_2H_2Br^+$, 6 09 149, $CO_2C_2H_2Br^+$ or $CO_2C_2Br^+$, 8 54 141 $FSCF_2C_2O^+$, 35 16 135 $SCF_2C_3HO^+$ or $C_3H_4OBr^+$ or $C_3H_2OBr^+$ 8 89 133 $FSO_2CF_2^+$ or C_3OBr^+ or $C_3H_2Br^+$

7 82 123, $OC_2H_2Br^+$ or $OC_2H_4Br^+$ 7 16 122 $OC_2H_3Br^+$ or OC_2HBr^+ 14 63, 121 OC_2Br^+ 6 12 119 OC_2Br^+ or $SC_4FH_4O^+$ 41 63 113 $FSCF_2C^+$ 11 22 110 $SC_2F_2O^+$ 8 65 109 $C_2H_4Br^+$ 100 108 $C_2H_3Br^+$ or $CF_2C_2O_2H_2{}^+$ 39 14 107 $C_2H_4Br^+$ or $C_2H_2Br^+$ or $FSO_2C_2{}^+$ or $CF_2CO_2CH^+$, 100 106 $C_2H_3Br^+$ or C_2HBr^+ or $CF_2C_2O_2{}^+$, 32 30 103 SC_3FO^+ or C_2Br^+, 7 10, 101, $FSCF_2{}^+$ 6 57 99 $SC_2OC_2H_4{}^+$ 6 24

Anal Calcd for $C_3H_4F_3SO_2Br$ C 16 86 H 1 41 F, 20 0 S 11 25 Br 28 03 Found C, 16 68 H 1 60 F 20 3 S 11 20 Br 28 02

$FSO_2CF_2C(O)OAg$ with $BrCH_2C(O)OC_2H_5$

To the reaction vessel previously described were added 12 4 mmol of $FSO_2CF_2C(O)OAg$ and 12 6 mmol $BrCH_2C(O)OC_2H_5$ The volatile material was removed at -78°C The remaining liquid 10 9 mmol of $FSO_2CF_2C(O)OCH_2C(O)OC_2H_5$ was formed in 88% yield

The infrared spectrum had the following bands (cm ^{1}) 2988 (wm) 1792 (s) 1757 (s), 1448 (s) 1434 (m) 1398 (wm) 1384 (m) 1363 (mw) 1314 (m) 1279 (m) 1223 (s,sh at 1237), 1202 (s) 1152 (s) 1096 (w) 1068 (wm), 1047 (m) 1026 (m) 970 (w), 864 (w), 829 (m) 808 794 (ms b) 723 (w) 646 (m), 604 (wm), 569 (wm)

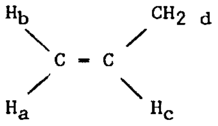
The ^{19}F nmr spectrum of $FSO_2CF_2C(O)OCH_2C(O)OCH_2CH_3$ contained a triplet at ϕ 40 4 ppm (SO_2F) a doublet at ϕ 105 5 ppm (CF_2) with a coupling constant $J_{CF_2\ SO_2F}$ = 5 4 Hz The relative band area for FSO_2 to CF_2 was 1 0 2 0 (theor 1 0 2 0) The ^1H nmr spectrum contained a singlet at δ 5 12 ppm (CH_2') a quartet at δ 4 40 ppm (CH_2) and a triplet at δ 1 40 ppm (CH_3) with a coupling constant of $J_{CH_3-CH_2}$ = 7 2 Hz The relative band area for $CH_2'CO_2CH_2CH_3$ was 2 0 2 0 3 0 (theor 2 0 2 0 3 0)

The positive ion mass spectrum, CI^+, gave peaks (m/e species %) 265, MH^+ 14 40, 239 $M-FH_6{}^+$ 5 88 237 $MH_2\ C_2H_5{}^+$ 100, 220 $FSO_2C_6O_4H^+$ 5 56 219

M-$OC_2H_5^+$ 93 92 191 $FSO_2CF_2CO_2CH_2^+$ 9 97 155 $FSCF_2C_3H_2O^+$ 7 40 153 $FSCF_2C_3O^+$ 47 08 108 $CF_2C_2H_2O_2^+$, 6 26 97 C_4SHO^+ 6 71 87 $C_4H_7O^+$ 6 89 80 C_4O^+ 13 47 78 $C_2F_2O^+$ 7 06 67 $C_4H_3O^+$ or FSO^+ 10 54 65 C_4OH^+ 20 19 59 C_2FO^+, 17 56, 57 $C_2O_2H^+$ 5 48

$FSO_2CF_2C(O)OAg$ with $BrCH_2CH{=}CH_2$

To the reaction vessel previously described were added 16 72 mmol $BrCH_2CH{=}CH_2$ and 16 49 mmol $FSO_2CF_2C(O)OAg$ Distillation of the product gave 11 2 mmol of $FSO_2CF_2C(O)OCH_2CH{=}CH_2$ in 67% yield b p 141 142 C The infrared ^{19}F nmr and ^1H nmr chemical shift spectral data agreed with that previously reported for this ester [7] The proton nmr spectrum was also obtained with a General Electric QE-300 nmr spectrometer The coupling constants for the allyl group were



J_{ab} = 1 2 Hz J_{ad} = 1 2 Hz J_{bd} = 1 2 Hz J_{cd} = 6 0 Hz

J_{ac} = 10 4 Hz J_{bc} = 17 2 Hz

$FSO_2CF_2C(O)OAg$ with CH_2I_2

To the same reaction vessel previously described 19 51 mmol $FSO_2CF_2C(O)OAg$ and 9 70 mmol CH_2I_2 were added After 7 d distillation gave 6 20 mmol of $(FSO_2CF_2CO_2)_2CH_2$ in 64% yield b p 63°/100μ

The infrared spectrum had the following bands (cm ^{1}) 3079 (vw) 3009 (vw) 1813 (s) 1455 (vs) 1321 (m) 1286 (m) 1237 (s) 1209 (ms) 1166 (s) 1117 (s) 1054 (m) 1033 (m) 998 (ms) 963 (m) 822 (ms) 808 (ms) 723 (w) 653 (m) 604 (m with sh at 562) 513 (vw) 491 (w) 423 (w)

The ^{19}F nmr spectrum contained a triplet at Ø 39 2 ppm (SO_2F) and a doublet at Ø 105 6 ppm (CF_2) with a coupling constant J = 5 5 Hz The relative band area for FSO_2 CF_2 was 1 0 2 0 (theor 1 0 2 0) The ^1H nmr spectrum contained a singlet at δ 6 53 ppm (CH_2)

The positive ion mass spectrum CI^+ gave peaks (m/e species, %) 369 MH^+ 0 16 193 $[MH_2\ OCOCF_2SO_2F]^+$ 3 73 192 $[MH\text{-}OCOCF_2SO_2F]^+$ 2 65 191 $[M\text{-}FSO_2CF_2COO]^+$, 61 74 177 $FSO_2CF_2COO^+$, 0 10 161 $FSO_2CF_2CO^+$ 5 91 133 $COOCH_2COOCF^+$ 11 36 132 $CFCOCH_2OCCF^+$ 0 13 127 $CFCOOCOCC^+$ 1 76 111 $CFCOCOCC^+$ 6 57, 109 $CCOOCHOCC^+$ 2 47, 107 CF_2COOCH^+, 1 01 105 $SCFCOCH_2{}^+$ 1 03 103 $CFCOOCO^+$ 0 17 101 $CFCOCH_2OC^+$ 0 52 100 $CFCOCHOC^+$ 1 49 99 $CFCOCOC^+$, 5 64 98 $FSOCF^+$ 2 12 97 $CCOOCHOC^+$ 87 96, 96 $CCOOCOC^+$, 0 37, 95, FSO_2C^+ 2 19 94 CF_2COO^+ 0 44 91 $SCFCO^+$ 1 01 87 $CFCOOC^+$ 1 48 85 $SCCOCH^+$ 1 59 83 SO_2F^+ 1 45 81, $CCOCHOC^+$ 3 93, 80 $CCOCOC^+$, 1 77 79 $FSOC^+$ 15 42 78 CF_2CO^+ 7 11 75 $CFCOO^+$ 0 62 71 $CFCOC^+$ 1 19 70 $CCOOCH_2{}^+$ 1 71 69 $CCOOCH^+$, 13 59 68 $CCOOC^+$ 1 67 67 SOF^+ 57 64 64 $SO_2{}^+$ 100, 63 SFC^+ 2 13 62 CF_2C^+ 1 47

Anal Calcd for $C_5H_2F_6S_2O_8$ C 16 31, H 0 55 F 31 0 S 17 41 Found C 16 42, H 0 54 F 30 8 S 17 26

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