which indicate that the $^{55}$Mn hyperfine tensor in that system is rather isotropic.

Finally, as regards the difference in oxygen affinity[4,5] between manganese porphyrin compounds and manganese globin and the corresponding heme systems, actual calculations of the electron distributions and energy levels of the oxygen-liganded systems will be needed to understand these differences in affinity from a theoretical point of view. However, the comparison between the charge and spin distributions between the five-liganded divalent manganese compound studied here and the distributions on the five-liganded heme systems[7] shows that there are small and significant differences between the two types of systems. Among these differences are the greater tendency toward neutrality of the manganese compound and about 5% larger unpaired spin population on the metal atom in the manganese compound. These small but significant differences suggest that the electronic interaction between the manganese porphyrin and oxygen molecule as compared to that between the heme group in heme systems and oxygen can be appreciably different enough to explain the differences in oxygen affinity.

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# Synthesis of Perfluoroalkyl Trifluoromethanesulfonates from Perfluoroalkyl Halides. Substitutive Electrophilic Dehalogenation with Chlorine(I) and Bromine(I) Trifluoromethanesulfonates

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**Abstract:** The reactions of chlorine(I) and bromine(I) trifluoromethanesulfonates with a variety of perfluoroalkyl halides are reported. The reactions form $Br_2$, $Cl_2$, or BrCl and the corresponding trifluoromethanesulfonate derivatives of the alkyls in good yields. Twelve new esters are reported and characterized. An $S_{E}i$-type mechanism for the reactions is proposed with complete retention of configuration by the alkyl on substitution.

## Introduction

The utility of electropositive halogen compounds in synthesis is rapidly being recognized.[3,4] In particular, the simple concept that a formal positive halogen atom in a general compound $M^{\delta-}$-$X^{\delta+}$ can react with a negatively polarized atom in $N^{\delta+}$-$Y^{\delta-}$ to give MN and XY has resulted in many interesting syntheses. In order to have a formal positive halogen, it is necessary that the halogen be bonded to an element more electronegative than itself, as in ClF, where chlorine is the formal positive halogen. In addition, if the halogen is contained in a polyatomic molecule, it must be bonded to an element of comparable or greater electronegativity and the rest of the molecule must have a group electronegativity greater than that of the halogen. This requirement is ideally met in fluorinated compounds such as $(CF_3)_2NCl$, $SF_5OCl$, $CF_3OCl$, $FSO_2OCl$, $(FSO_2)_2NCl$, etc.

One of the most interesting reactions of the above type and the first utilization of a fluorinated compound in this way was the low-temperature reaction of $BrOSO_2F$ with $CFCl_3$ as shown in the equation[5]

$$BrOSO_2F + CFCl_3 \rightarrow CFCl_2\,OSO_2F + BrCl$$

This reaction can be termed substitutive electrophilic dehalogenation. A similar transformation employing $FSO_3^-$ or $FSO_3\cdot$ is not possible under the same conditions. While the detailed mechanism of this reaction is unknown, it probably involves the initial interaction $FSO_2O$-$Br^{\delta+}$—$Cl^{\delta-}$-$CFCl_2$.

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With the discovery of the halogen(I) trifluoromethanesulfonates,[6,7] $CF_3SO_2OCl$ and $CF_3SO_2OBr$, the possibility of extending the above reaction to the preparation of a variety of trifluoromethanesulfonates was obvious. Because the $CF_3SO_3$ group is clearly one of the most electronegative groups in chemistry,[8,9] there was little doubt that $CF_3SO_3X$ ($X = Cl$, Br) could serve as very electropositive halogen compounds. This paper describes the preparation of many new perfluoroalkyl esters by substitutive electrophilic dehalogenation and some suggestions are made regarding the mechanism of this reaction. The synthetic utility of this reaction is made obvious by the fact that until now $CF_3SO_3CF_3$ was the only known perfluoro ester.[10-12]

## Experimental Section

**General.** All work was carried out in Pyrex and stainless steel vacuum systems equipped with glass–Teflon or stainless steel valves. Pressures were measured with a Wallace and Tiernan differential pressure gauge, Series 1500. Temperatures were measured using a digital readout copper–constantan thermocouple. Quantities of reactants and products were measured either by direct weighing or by *PVT* measurements assuming ideal gas behavior.

Routine IR spectra were taken on a Perkin-Elmer 337 spectrometer at 5–100 Torr. A 10-cm Pyrex glass cell fitted with AgCl windows and a small trap was employed. When the vapor pressure of the compound was less than a few Torr at 22 °C, some of the compound was pumped under vacuum into a trap on the cell cooled by liquid $N_2$. The spectrum was than taken of the gas in equilibrium with the liquid in the trap after the trap was warmed to 22 °C. IR spectra for assignment were taken on a Perkin-Elmer 180 at 0.5–5 Torr using the same techniques.

Unless otherwise noted, NMR spectra were recorded on a Varian XL-100-15 spectrometer using 20–15 mol % solutions in $CFCl_3$. Spectra were at 94.1 MHz for $^{19}F$ and 100.1 MHz for $^1H$ using $CFCl_3$ and $Me_4Si$ as internal and external references, respectively.

Molecular weights were determined by vapor-density measurements using a calibrated Pyrex bulb fitted with a glass–Teflon valve. For compounds having too low a vapor pressure at 22 °C, no values are reported. Determinations were made on successive fractions of each sample.

Complete elemental analyses of new compounds were not carried out. Approximate fluorine analysis was obtained by the integration of the fluorine resonances of the compound and the $CFCl_3$ solvent on the NMR. The NMR samples were prepared using measured amounts of $CFCl_3$ and compound. The values obtained in this way were within 5% of the calculated values in every case.

Melting points were taken in a Pyrex tube fitted with a glass–Teflon valve. The compound was pumped under vacuum onto the wall of the tube cooled by liquid $N_2$ forming a crystalline ring. The tube was placed in an ethanol bath, which was cooled to −112 °C prior to the measurement and then warmed slowly with proper agitation.

Vapor pressures and boiling points of the products were measured by a static method. Equations describing pressure as a function of temperature were obtained by a least-squares fit of the data to both linear and quadratic equations and the best fit is reported.

For further purifications, the reaction products were separated via GLC on a Victoreen Series 4000 gas chromatograph equipped for gas injection, TCD, and low-temperature collection. A 2 ft × 3/8 in. column packed with 40% Halocarbon 11-21 polymer oil on acid-washed Chromosorb P was used in most cases. For less volatile products, a 1-ft column of similar condition was used.

**Reagents.** $CF_3SO_3H$ was obtained from Aldrich Co., and $CF_3Cl$, $CF_3Br$, $CF_2Br_2$, and $CFBr_3$ were obtained from PCR Inc. They were purified by distillation. $CFCl_3$ and $CF_2Cl_2$ were obtained from Racon Inc., and were used after simple distillation at low temperature from $P_4O_{10}$ or molecular sieves. $C_2F_5Br$ and $C_3F_7Br$ were prepared from $C_2F_5COOH$ and $C_3F_7COOH$, respectively, by the standard methods. $CBrF_2CBrF_2$ was prepared by condensing equimolar amounts of $Br_2$ and $CF_2CF_2$ in a Pyrex bulb at −195 °C, followed by slow warming up to 22 °C. $CF_3SO_3CF_2CFBrCF_3$, $CF_3SO_3CF(CF_2)_3CFBr$, and *erythro*-$CF_3SO_3CHFCHFBr$ were obtained by the addition reaction of $CF_3SO_2OBr$ with the appropriate olefins.[13] *erythro*-$CF_3SO_3CHFCHFCl$ and *erythro*-$CF_3CO_2CHFCHFCl$ were obtained by the reactions of $CF_3SO_2OCl$ and $CF_3C(O)OCl$ with *cis*-CHFCHF and *threo*-$CF_3CO_2CFHCFHCl$ by addition to the trans olefin.[13] All prepared compounds were purified by trap-to-trap distillation and/or GLC separation. Chlorine monofluoride was prepared by heating equimolar amounts of $Cl_2$ and $F_2$ at 250 °C in a Monel bomb. ClF was taken out of the bomb at −112 °C to prevent contamination by $ClF_3$ and unreacted $Cl_2$. Fluorine was obtained from Air Products and was passed through a NaF scrubber before use.

**General Procedure for the Reaction of $CF_3SO_2OX$ ($X = Cl$, Br) with Fluorohalocarbons.** Each reaction was carried out on a 1–10-mmol scale in Kel-F tubes (ca. 15 mL) or 100-mL Pyrex bulbs, fitted with a stainless steel valve or a glass–Teflon valve, respectively.

$CF_3SO_3OH$ was vacuum transferred from the container at 22 °C to a Kel-F reactor at −195 °C via a short path. The amount of $CF_3SO_3H$ in the reactor was measured by weighing the $CF_3SO_3H$ container. $CF_3SO_2OCl$ was obtained by condensing a 10% excess of ClF onto the acid at −195 °C and warming slowly from −111 to −78 °C, followed by several hours at −78 °C. After reaction a colorless layer of HF appeared on a pale yellow liquid, $CF_3SO_2OCl$, and was removed by pumping at −78 °C. $CF_3SO_2OBr$ was readily obtained by the reaction of $CF_3SO_2OCl$ and $Br_2$. For each reaction, $CF_3SO_2OX$ ($X = Cl$, Br) was freshly prepared.

Onto the $CF_3SO_2OX$ ($X = Cl$, Br) in the Kel-F reactor at −195 °C, the desired amount of fluorohalocarbon was condensed. The reactor was then placed in a $CFCl_3$ bath at −111 °C and allowed to warm slowly (Table I). At the end of this period, where reaction occurred, halogen gas and a monolayer of liquid were observed at room temperature. In many cases, chlorine was easily removed from the other reaction products by trap-to-trap distillation, and its amount was measured by *PVT* measurement. When BrCl or $Br_2$ were generated, the reaction products were pumped into a Pyrex vessel containing Hg at −195 °C and shaken with the Hg at 22 °C until the color of the halogen gases disappeared (a few minutes). The reaction products were then transferred to another vessel and the amount in weight or volume of the halogens ($Br_2$, BrCl, $Cl_2$) was determined by the difference in weight or volume before and after treatment with Hg. The reaction products were then separated by pumping through traps at the appropriate temperatures as the vessel containing the reaction products warmed from −195 °C in an empty Dewar initially at 22 °C.

Some of the reactions were quite exothermic. In order to prevent too vigorous a reaction, 100-mL Pyrex bulbs having more surface and more heat conductivity were used as reactors instead of the Kel-F reactors. In these cases, $CF_3SO_2OCl$ was vacuum transferred from a Kel-F reactor at −40 °C via a short connection into a Pyrex bulb at −195 °C. For the same purpose, appropriate amounts of $CF_2Cl_2$, which was observed being practically inert to $CF_3SO_2OX$ ($X = Cl$, Br) at temperatures below −50 °C, were used as solvent.

*Caution.* $CF_3SO_2OCl$ is somewhat unstable at room temperature, especially when it is not pure, and is a strong oxidizer. Explosive mixtures are readily formed with easily oxidizable materials.

**Reactions of $CF_3SO_2OX$ ($X = Cl$, Br) with Fluorohalocarbons (1:1) (Table I). $CBrF_3$.** After removal of BrCl, the gaseous reaction products were pumped through traps at −78, −111, and −195 °C. The −78 and −111 °C traps contained pure $CF_3SO_3CF_3$. The properties of $CF_3SO_3CF_3$ were identical with those reported by Noftle and Cady.[10]

**$CClF_3$.** Under a variety of reaction conditions, only $CClF_3$ and $SO_3$ were detected after the reaction period. The reaction between $CF_3SO_2OCl$ and $CClF_3$ does not occur below the decomposition temperature of $CF_3SO_2OCl$.

**$C_2F_5Br$.** After removal of BrCl, the reaction mixture was pumped through traps at −60, −90, −111, and −195 °C. The −90 °C trap contained $CF_3SO_3C_2F_5$, the −111 °C trap contained $C_2F_5Br$, and the −195 °C trap contained $C_2F_6$, which was determined by its molecular weight and IR spectrum. A brown, polymeric material remained in the reactor.

**$CF_3SO_3C_2F_5$:** colorless liquid, bp 41.6 °C; mp −103.5 to −103.0 °C; mol wt 268.0 (calcd, 268.0); $^{19}F$ NMR $CF_3{}^ASO_3CF_2{}^BCF_3{}^C$ $\phi_A^*$ 74.38, t, $\phi_B^*$ 85.41, t–q, $\phi_C^*$ 86.76, t, $J_{AB} = 5.7$, $J_{BC} = 2.2$ Hz; IR (cm$^{-1}$) 1463 (s), 1244 (vs), 1236 (sh, s), 1211 (m), 1152 (s), 1147 (sh, s), 1080 (vs), 951 (w), 866 (s), 780 (w), 745 (w), 728 (m), 615 (m), 605 (sh, m), 500 (w); $\Delta H_{vap} = 6.74$ kcal/mol; $\Delta S_{vap} = 21.4$ eu; $\log P\ (\mathrm{Torr}) = 5.8807 - 416.02/T - 166301/T^2$.

**$C_3F_7Br$.** The reaction products were pumped through traps at −78, −111, and −195 °C. The −78 °C trap contained $CF_3SO_3C_3F_7$, the −111 °C trap contained $C_3F_7Br$, and the −195 °C trap contained a fluorinated compound $C_3F_8$, which was determined by its molecular

**Table I.** Reactions of $CF_3SO_3X$ with Halocarbons[a]

| X | halocarbon | conditions | | products[d] |
|---|---|---|---|---|
| | | h | °C | |
| Cl (4.0) | $CBrF_3$ (4.0) | 1 | −111 | $CF_3SO_3CF_3$ (3.8), BrCl (4.0) |
| Cl (1.75) | $CClF_3$ (1.8) | 24 | −111 to 22 | $CClF_3$ (3.5), $SO_3$ |
| Cl (5.0) | $C_2F_5Br$ (5.0) | 15 | −40 to −5 | $CF_3SO_3C_2F_5$ (2.9), $C_2F_6$ (0.5) BrCl (5.9) |
| Cl (6.5) | $C_3F_7Br$ (6.5) | 36 | −40 to 22 | $CF_3SO_3C_3F_7$ (4.2), $C_3F_8$ (0.6) BrCl (5.7) |
| Cl (4.6) | $CCl_2F_2$ (5.1) | 15 | −78 to 22 | $CF_3SO_3CF_2Cl$ (4.2), $Cl_2$ (4.5) |
| Cl (5.1) | $CBr_2F_2$ (5.4) | 1 | −111 | $CF_3SO_3CF_2Br$ (0.8), $COF_2$ (4.0), $(CF_3SO_2)_2O$ (2.0), BrCl |
| Cl (3.3) | $CBr_2F_2$ (4.5) | 1 | −160[b,c] | $CF_3SO_3CF_2Br$ (2.0), $COF_2$ (1.2), $(CF_3SO_2)_2O$ (0.6), BrCl |
| Cl (5.0) | $CCl_3F$ (7.0) | 15 | −78 to 22 | $CF_3SO_3CFCl_2$ (4.4), $(CF_3SO_2)_2O$ (0.2) |
| Br (3.9) | $CF_3Br$ (5.0) | 15 | −111 to −10 | $CF_3SO_3CF_3$ (2.9), $Br_2$ (3.9) |
| Br (2.0) | $CFCl_3$ (5.0) | 15 | −78 to 22 | $CF_3SO_3CFCl_2$ (1.0), BrCl |
| Cl (4.4) | $CCl_2F_2$ (2.0) | 15 | −60 to 22 | $(CF_3SO_3)_2CF_2$ (0.1), $CF_3SO_3CF_2Cl$ (1.0), $COF_2$ (0.8), $(CF_3SO_2)_2O$ (0.8), $Cl_2$ |
| Cl (1.2) | $CBr_2F_2$ (2.5) | 11 | −150 to −130[b] | $COF_2$ (1.9), $(CF_3SO_2)_2O$ (1.5), BrCl |
| Cl (6.1) | $CCl_3F$ (3.0) | 15 | −85 to −40 | $CF_3SO_3CCl_2F$ (2.2), $(CF_3SO_2)$ O (0.7), COClF, $Cl_2$ |
| Br (5.0) | $CBr_2F_2$ (2.4) | 24 | −111 to −60 | $(CF_3SO_3)_2CF_2$ (0.7), $CF_3SO_3CF_2Br$ (0.7), $(CF_3SO_2)_2O$ (0.35), $Br_2$ (4.5), $COF_2$ (0.9), $CF_3SO_3CF_3$ (0.4) |
| Br (4.1) | $CCl_2F_2$ (2.0) | 15 | −111 to −50 | $(CF_3SO_3)_2CF_2$ (0.12), $CF_3SO_3CF_2Cl$ (0.6), $(CF_3SO_2)_2O$ (0.6), $COF_2$ (1.), $CF_3SO_3CF_3$ (0.7), BrCl (2.2) |
| Cl (3.5) | $(CF_2Br)_2$ (1.6) | 15 | −88 to −30 | $(CF_3SO_3CF_2)_2$ (0.52), $CF_3SO_3CF_2CF_2Br$ (0.99), $C_2F_5Br$ (0.1), BrCl (3.6) |
| Cl (5.6) | $(CF_2Br)_2$ (2.7) | 15 | −111 to 22[b] | $CF_3SO_3CF_2CF_2Br$ (1.0), $CF_3SO_3CF_2Cl$ (2.9), $C_2F_5Br$ (1.5), BrCl-$Cl_2$ (5.4) |
| Cl (6.0) | $(CF_2Br)_2$ (3.0) | 1 | −111 to −88 | $CF_3SO_3CF_2CF_2Br$ (1.7), $CF_3SO_3CF_3$ (0.8), $C_2F_5Br$ (0.4), BrCl (3.2) |
| Cl (6.9) | $CBr_3F$ (2.3) | 15 | −111[b] | $CF_3SO_3C(O)F$ (1.6), $(CF_3SO_2)_2O$ (1.8), BrCl (1.6), COBrF |
| Cl (6.9) | $CCl_3F$ (2.3) | 24 | −78 to 22 | $(CF_3SO_2)_2O$, $Cl_2$, COClF, $CO_2$, $CF_3SO_3C(O)F$ |
| Cl (9.6) | $CCl_4$ (2.4) | 24 | −78 to 0 | $(CF_3SO_2)_2O$ (1.5), $COCl_2$, $Cl_2$, $CO_2$, $CF_3Cl$, $SO_3$ |
| Cl (3.0) | $CF_3SO_3CF_2Br$ (2.0) | 24 | −111 to 22[b,c] | $(CF_3SO_3)_2CF_2$ (0.6), $(CF_3SO_2)_2O$ (0.8), $COF_2$ (0.8), BrCl |
| Cl (3.5) | *erythro*-$CF_3CO_2CHF$ CHFCl (2.0) | 15 | −111 to 22[c] | *erythro*-$CF_3SO_3CHFCHFO_2CCF_3$ (1.6), $Cl_2$ (1.7) |
| Cl (2.0) | *threo*-$CF_3CO_2CHFCHFCl$ (1.0) | | −111 to 22[c] | *threo*-$CF_3SO_3CHFCHFO_2CCF_3$ (0.9), $Cl_2$ |
| Cl (1.0) | *erythro*-$CF_3SO_3CHFCHFBr$ (0.7) | 15 | −111 to 22[c] | $(CF_3SO_3CHF)_2$ (0.7), ClBr (0.7) |
| Cl (2.7) | $CF_3SO_3CF_2C(CF_3)FBr$ (2.1) | 15 | −111 to 22[c] | no substitution |
| Cl (3.0) | $CF_3SO_3CF(CF_2)_3CFBr$ (2.3) | 15 | −111 to 22[c] | no substitution |

[a] Amounts (mmol) are given in parentheses. [b] Approximately 10 mmol of $CF_2Cl_2$ used as a solvent. [c] 100-mL glass reactor. [d] Not all products or their amounts were identified. The main goal was to identify $CF_3SO_3$-containing products.

weight and IR spectrum. A brown, polymeric material remained in the reactor and was not characterized.

**$CF_3SO_3C_3F_7$:** colorless liquid, bp 66.2 °C; flow point below −111 °C; mol wt 319.2 (calcd, 318.0); $^{19}F$ NMR $CF_3{}^ASO_3CF_2{}^BCF_2{}^CCF_3{}^D$ $\phi_A$* 74.72, t, $\phi_B$* 81.04, q-q-t, $\phi_D$* 81.82, t, $\phi_C$* 129.8, br s, $J_{AB} = 5.5$, $J_{BD} = 8.5$, $J_{BC} = 1.2$ Hz; IR (cm$^{-1}$) 1463 (s), 1350 (w), 1327 (m), 1249 (sh, vs), 1234 (vs), 1205 (w), 1151 (s), 1137 (s), 1110 (s), 991 (vs), 809 (m), 779 (vw), 731 (m), 611 (m), 500 (w); $\Delta H_{vap} = 7.44$ kcal/mol; $\Delta S_{vap} = 21.9$ eu; log $P$ (Torr) = 6.6496 − 931.67/$T$ − 117815/$T^2$.

**$CCl_2F_2$.** The reaction products were pumped through traps at −78, −111, and −195 °C. The −111 °C trap contained $CF_3SO_3CClF_2$.

**$CF_3SO_3CClF_2$:** colorless liquid, bp 53.2 °C; flow point below −111 °C; mol wt 238.4 (calcd, 234.5); $^{19}F$ NMR $CF_3{}^ASO_3CClF_2{}^B$ $\phi_A$* 74.3, t; $\phi_B$* 25.0, q, $J = 4.2$ Hz; IR (cm$^{-1}$) 1460 (s), 1256 (vw), 1233 (vs), 1208 (m), 1177 (w), 1140 (vs), 1127 (sh, s), 1035 (s), 1017 (vs), 943 (vw), 890 (m), 860 (vw), 770 (vw), 740 (m), 611 (m), 512 (w); $\Delta H_{vap} = 6.53$ kcal/mol; $\Delta S_{vap} = 20.0$ eu; log $P$ (Torr) = 5.9991 − 608.35/$T$ − 133640/$T^2$.

**$CBr_2F_2$.** The reaction products were pumped through traps at −78, −111, and −195 °C. The −78 °C trap contained $(CF_3SO_2)_2O$ and small amount of $CF_3SO_3CBrF_2$, which were separated by a redistillation. The −111 °C trap contained $CF_3SO_3CBrF_2$. The −195 °C trap contained $COF_2$, which was identified by its molecular weight and IR spectrum.

**$CF_3SO_3CBrF_2$:** colorless liquid, bp 72.6 °C; flow point below −111 °C; mol wt 278.0 (calcd, 279.0); $^{19}F$ NMR $CF_3{}^ASO_3CBrF_2{}^B$ $\phi_A$* 74.4, t, $\phi_B$* 16.8, q, $J = 4.4$ Hz; IR (cm$^{-1}$) 1460 (s), 1255 (sh, w), 1235 (vs), 1200 (m), 1180 (w), 1141 (s), 1118 (s), 1018 (vs), 1001 (vs), 872 (m), 840 (w), 782 (w), 745 (w), 721 (w), 610 (m), 419 (br, w); $\Delta H_{vap} = 7.97$ kcal/mol; $\Delta S_{vap} = 23.0$ eu; log $P$ (Torr) = 7.4220 −1399.2/$T$ − 59180/$T^2$.

**$CCl_3F$.** The reaction products were separated by pumping through traps at −78 and −195 °C. The −78 °C trap contained $CF_3SO_3CCl_2F$.

**$CF_3SO_3CCl_2F$:** colorless liquid, bp 89.1 °C; mp −96.0 to −95.6 °C; mol wt 250.0 (calcd, 251.0); $^{19}F$ NMR $CF_3{}^ASO_3CCl_2F^B$ $\phi_A$* 74.4, d, $\phi_B$* 10.6, q, $J = 5.4$ Hz; IR (cm$^{-1}$) 1456 (s), 1253 (sh, w), 1233 (vs), 1141 (vs), 1108 (m), 985 (br, vs), 919 (m), 889 (w), 811 (m), 608 (m), 514 (w); $\Delta H_{vap} = 8.05$ kcal/mol; $\Delta S_{vap} = 22.2$ eu; log $P$ (Torr) = 6.9445 − 1185.5/$T$ − 103809/$T^2$.

**Reactions of $CF_3SO_3Cl$ with Fluorohalocarbons (2:1). $CCl_2F_2$.** The reaction products were pumped through traps at −78, −111, and −195 °C. The −78 °C trap contained $(CF_3SO_2)_2O$ and a small amount of disubstituted product $(CF_3SO_3)_2CF_2$, which were separated by GLC. The −111 °C trap contained $CF_3SO_3CClF_2$, and the

−195 °C trap contained $COF_2$ and a small amount of $CF_3Cl$, which were identified by their IR spectra.

**$(CF_3SO_3)_2CF_2$:** colorless liquid, bp 115.2 °C; flow point −105 °C; mol wt 348.7 (calcd, 348.1); $^{19}$F NMR $(CF_3{}^ASO_3)_2CF_2{}^B$ $\phi_A{}^*$ 73.75, t, $\phi_B{}^*$ 46.70, septet, $J$ = 4.0 Hz; IR (cm$^{-1}$) 1460 (s), 1265 (sh, m), 1247 (sh, s), 1230 (vs), 1167 (s), 1143 (s), 1080 (vs), 976 (w), 810 (m), 762 (vw), 750 (w), 600 (w), 500 (w); $\Delta H_{vap}$ = 8.22 kcal/mol; $\Delta S_{vap}$ = 21.2 eu; log $P$ (Torr) = 5.8731 −527.80/$T$ − 246400/$T^2$.

**$(CBrF_2)_2$.** The reaction products were pumped through traps at −30, −78, −111, and −195 °C. The −30 °C trap contained $(CF_3SO_3CF_2)_2$. The −78 °C trap contained $CF_3SO_3CF_2CBrF_2$ and the −195 °C trap contained a fluorinated product, $C_2F_5Br$. A polymeric material remained in the reaction vessel.

**$(CF_3SO_3CF_2)_2$:** colorless liquid, bp 138.0 °C; mp −38.0 to −37.0 °C; mol wt 396.8 (calcd, 398.1); $^{19}$F NMR $(CF_3{}^ASO_3CF_2{}^B)_2$ $\phi_A{}^*$ 74.18, t, $\phi_B{}^*$ 84.93, q, $J$ = 5.5 Hz; IR (cm$^{-1}$) 1462 (s), 1260 (sh, w), 1250 (sh, w), 1235 (vs), 1210 (sh, s), 1180 (w), 1160 (w), 1155 (w), 1145 (vs), 1130 (sh, s), 1100 (m), 1053 (vs), 970 (m), 940 (s), 880 (m), 838 (w), 813 (m), 800 (sh, w), 789 (w), 760 (sh, w), 755 (sh, vw), 728 (s), 707 (m), 592 (sh, w), 500 (br, w); $\Delta H_{vap}$ = 8.62 kcal/mol; $\Delta S_{vap}$ = 21.0 eu; log $P$ (Torr) = 7.4629 − 1884.3/$T$.

**$CF_3SO_3CF_2CF_2Br$:** colorless liquid, bp 91.1 °C; flow point below −111 °C; mol wt 329.0 (calcd, 329.0); $^{19}$F NMR $CF_3{}^A$-$SO_3CF_2{}^BCF_2{}^CBr$ $\phi_A{}^*$ 74.35, t, $\phi_C{}^*$ 69.51, t, $\phi_B{}^*$ 82.89, t–q, $J_{AB}$ = 5.5, $J_{BC}$ = 3.2 Hz; IR (cm$^{-1}$) 1462 (s), 1310 (m), 1259 (w), 1234 (vs), 1205 (m), 1178 (m), 1143 (vs), 1101 (vs), 970 (sh, w), 942 (vs), 845 (m), 771 (w), 730 (s), 519 (s), 570 (vs), 500 (w); $\Delta H_{vap}$ = 7.82 kcal/mol; $\Delta S_{vap}$ = 21.5 eu; log $P$ (Torr) = 6.6295 − 1021.7/$T$ − 125240/$T^2$. This material was identical with the compound obtained by the addition reaction of $CF_3SO_2OBr$ to $CF_2CF_2$.

**Reaction of $CF_3SO_2OBr$ with $CBr_2F_2$ or $CCl_2F_2$ (2:1).** The reaction products were pumped through traps at −50, −78, −111, and −195 °C. The −50, −78, −111, and −195 °C traps contained $(CF_3SO_3)$-$CF_2$, $(CF_3SO_2)_2O$, $CF_3SO_3CBrF_2$, and $COF_2$, respectively. A small amount of $CF_3SO_3CF_3$ was trapped at −111 °C.

**Reaction of $CF_3SO_2OCl$ and $CBr_3F$ or $CCl_3F$ (3:1).** In an attempt to prepare a trisubstituted product $(CF_3SO_3)_3CF$, the reaction was carried out under various conditions, but was not successful. The reaction products were pumped through traps at −65, −111, and −195 °C. The −65 and the −111 °C traps contained $(CF_3SO_2)_2O$ and $CF_3SO_3COF$, respectively. The −195 °C trap contained COClF and $CF_3Cl$ when the $CCl_3F$ was used and COBrF when $CBr_3F$ was used.

**$CF_3SO_3COF$:** colorless liquid, mp below −111 °C; mol wt 200.0 (calcd, 196.1): $^{19}$F NMR $\phi^*$ 72.6, br s ($CF_3$), 8.68, m (COF): IR (cm$^{-1}$) 1887 (s), 1464 (s), 1275 (sh, w), 1270 (sh, w), 1240 (vs), 1180 (br, vs), 1142 (vs), 975 (br, vs), 860 (w), 808 (m), 790 (m), 776 (m), 756 (s), 750 (s), 690 (wv), 600 (vs), 525 (m).

**Reaction of $CF_3SO_2OCl$ and $CCl_4$ (4:1).** The reaction mixture was pumped through traps at −50, −78, and −195 °C. The −78 °C trap contained $(CF_3SO_2)_2O$, and the −195 °C trap contained a variety of low-boiling gaseous materials including $CF_3Cl$, $Cl_2$, $COCl_2$, and $CO_2$.

**Additional Reactions of $CF_3SO_2OCl$ with Some Halocarbons. $CF_3SO_3CBrF$.** A typical procedure for this reaction will be described here. In a 100-mL Pyrex bulb 2.0 mmol of $CF_3SO_3CBrF_2$ was condensed and then 2.0 mmol of $CCl_2F_2$ was condensed onto it at −195 °C. After warming to 22 °C, this mixture was cooled to −195 °C and 3 mmol of $CF_3SO_2OCl$ was condensed onto the mixture followed by another 2.2 mmol of $CCl_2F_2$. The reactor was placed in a −111 °C bath with agitation. The color of the reaction mixture gradually turned from colorless to orange and finally deep brown as it warmed slowly to 22 °C. After removal of BrCl, the reaction products were pumped through −50, −60, −78, and −195 °C traps. The −50, −60, and −78 °C traps contained mostly $(CF_3SO_3)_2CF_2$, $(CF_3SO_2)_2O$, and $CF_3SO_3CBrF_2$, respectively. The −195 °C trap contained $CCl_2F_2$ and $COF_2$.

***erythro*-$CF_3CO_2CHFCHFCl$.** The reaction products were pumped through traps at −35, −111, and −195 °C. The −35 °C trap contained pure *erythro*-$CF_3SO_3CHFCHFOC(O)CF_3$. The −111 and −195 °C traps contained $SO_3$ and $CF_3Cl$ along with $Cl_2$, respectively.

***erythro*-$CF_3{}^ASO_3CH^BF^CCH^DF^EOC(O)CF_3{}^F$:** heavy, colorless oil, flow point −68.5 °C; $^{19}$F NMR $\phi_A{}^*$ 75.08, d–d, $\phi_F{}^*$ 75.73; s, $\phi_C{}^*$ 138.69, d–d–d–q, $\phi_E{}^*$ 147.59, d–d–d–q; $^1$H $\delta_B$ 6.42, basic d–d–d, $\delta_D$ 6.72, basic d–d–d, $J_{AC}$ = 5.3, $J_{AE}$ = 2.1, $J_{BC}$ = 51.4, $J_{BD}$ = 4.6, $J_{BE}$ = 3.6, $J_{CD}$ = 2.8, $J_{CE}$ = 10.8, $J_{DE}$ = 51.4 Hz; IR (cm$^{-1}$) 3010 (vw), 1832 (s), 1457 (s), 1335 (w), 1300 (vw), 1250 (vs), 1238 (vs), 1200 (s), 1160 (sh, w), 1145 (s), 1130 (br, s), 1098 (s), 1055 (w), 1030 (s), 943 (w), 866 (m), 835 (s), 771 (w), 742 (w), 638 (w), 618 (w), 513 (w).

***threo*-$CF_3CO_2CHFCHFCl$.** The reaction conditions were identical with those of *erythro*-$CF_3CO_2CFHCFHCl$.

***threo*-$CF_3{}^ASO_3CH^BF^CCH^DF^EOC(O)CF_3{}^F$:** heavy, colorless oil; IR spectrum essentially identical with that of the erythro isomer; NMR $\phi_A{}^*$ 74.79, d, $\phi_F{}^*$ 75.73, s, $\phi_C{}^*$ 138.6, d–d–d–q, $\phi_E{}^*$ 146.9, d–d–d; $^1$H $\delta_B$ 6.22, basic d–d–d, $\delta_D$ 6.52, basic d–d–d, $J_{AC}$ = 5.5, $J_{AE}$ < 0.5, $J_{BC}$ = 53.0, $J_{BD}$ = 4.6, $J_{BE}$ = 3.4, $J_{CD}$ = 3.8, $J_{CE}$ = 10.5, $J_{DE}$ = 50.8 Hz.

Note: In the spectra of fluorines C and E in this compound and the previous one, there is some asymmetry and the spectra are not strictly first order. The coupling constants involving these fluorines are the average of two slightly different values and the chemical shifts are the center of the observed multiplets.

***erythro*-$CF_3SO_3CHFCHFBr$.** The reaction mixture was pumped through −30 and −195 °C traps. The −30 °C trap contained $(CF_3SO_3CHF)_2$, and the −135 °C trap contained a small amount of $CF_3Cl$ and $CF_3SO_3CF_3$.

**$(CF_3{}^ASO_3CH^BF^C)_2$:** colorless, heavy oil, mp 5.3–6.3 °C; $^{19}$F NMR $\phi_A{}^*$ 74.84, m, $\phi_C{}^*$ 138.65, m (basically d–d–d–q), $J$ = 55.1, 4.1, 3.0, 7.5 Hz (CHF); $^1$H $\delta_B$ centered at 6.42, m; IR (cm$^{-1}$) 3010 (vw), 1457 (s), 1250 (sh, w), 1237 (vs), 1148 (vs), 1120 (sh, w), 1065 (vw), 1029 (s), 938 (w), 877 (w), 842 (vw), 807 (s), 762 (m), 626 (m), 515 (w).

**$CF_3SO_3CF_2CBrFCF_3$ and $CF_3SO_3CF(CF_2)_3CBrF$.** With these halocarbons $CF_3SO_2OCl$ did not react. The starting halocarbons were recovered quantitatively after the reaction period.

## Results and Discussion

The reactions of $CF_3SO_3X$ (X = Cl, Br) with halogenated alkyls are summarized in Table I. These reactions proceed readily in most instances to give high yields of the monosubstituted trifluoromethanesulfonate esters and low yields of disubstituted esters. They fail in attempts to form tri- and tetrasubstituted compounds. The conditions listed were chosen to achieve reaction at the lowest possible temperature. All reactions were carried out more than once to check reproducibility and to arrive at a reasonable set of reaction conditions.

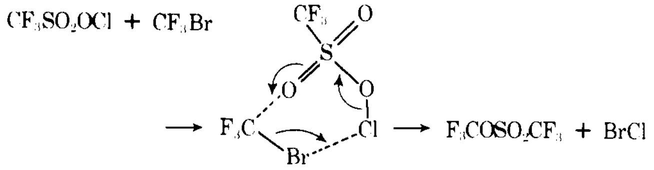
The variety of haloalkyls tried allow some ordering of reactivities. First, with a given substrate, $CF_3SO_3Cl$ is more reactive than $CF_3SO_3Br$. This difference is greatest with alkyl bromides and considerably less pronounced with alkyl chlorides. Alkyl bromides are in all cases more reactive. The reactivity of alkyl chlorides and bromides with $CF_3SO_3Cl$ decreases as the degree of fluorine substitution increases, that is, $CF_3Cl < CF_3Br < CF_2Cl_2 < CF_2Br_2$. For reactions which are difficult to control with $CF_3SO_3Cl$, $CF_3SO_3Br$ offers certain advantages because of its milder reactivity. For example, in the reaction of $CF_3SO_3Cl$ with $CF_2Br_2$, only very low yields of $(CF_3SO_3)_2CF_2$ were obtained. With $CF_3SO_3Br$, a slower reaction at higher temperatures gave respectable yields of $(CF_3SO_3)_2CF_2$.

The 12 new halogenated triflates reported in this work have all been adequately characterized by IR, NMR, and physical properties. All of the compounds are colorless liquids at 22 °C and are thermally stable at this temperature in dry glass. As an indication of thermal stability, gaseous (~1 atm) $CF_3SO_3C_2F_5$ and $(CF_3SO_3)_2CF_2$ were recovered unchanged after 1 and 4 days, respectively, at 150 °C. The IR spectra of the compounds are characteristic for each compound but the assignment of the observed frequencies on a group frequency basis is rather difficult. Only the $\nu(SO_2)$ antisymmetric stretch can be unambiguously assigned in every case and it is a strong, sharp band at ~1460 cm$^{-1}$. The $^{19}$F NMR spectra, on the other hand, provide rather convincing proof of structure in each case. The chemical shifts for the $CF_3SO_3$ groups fall in the range of 73–75 ppm relative to internal $CFCl_3$ ($\phi^*$ values) and these values are indicative of covalent trifluoromethanesulfonate groups. The fortunate observation of ${}^5J_{FF}$ values of ~5 Hz between the $CF_3SO_3$ group and $\alpha$ fluorine(s) of the alkyl groups, combined with the expected spectrum for the alkyl groups, provides sufficient information for the assignment of structures in every case but $CF_3SO_3CFHCFHOC(O)CF_3$ and $(CF_3SO_3CFH)_2$.

The NMR spectra of $CF_3SO_3CFHCFHOC(O)CF_3$ and $(CF_3SO_3CFH)_2$ require further comment. The former is discussed subsequently in the discussion relating to the proposed mechanism of the substitution reaction. For the latter, the compound is probably *meso*-$(CF_3SO_3CFH)_2$. The two CHF groups are equivalent by symmetry but magnetically nonequivalent. The spectrum, neglecting the $CF_3SO_3$ groups, would be expected to be an AA′XX′ system. It is more complex, however, and suggests the presence of different rotamers which are not rapidly averaged. The appearance of the ${}^1H$ NMR spectrum is quite similar to the ${}^{19}F$ NMR spectrum of $HCF_2CF_2H$.[14] The ${}^1H$ spectrum does not resemble the A portion of a normal AA′XX′ system. In addition, the fluorine resonances of the vicinal fluorines are appreciably broadened. No attempt was made to analyze the spectrum.

The mechanism for these reactions, which we have termed substitutive electrophilic dehalogenation, is of considerable interest. First, it is clear from the qualitative reactivity data outlined above that there is a definite steric factor in these reactions. This is clearly evident by the fact that $CF_3SO_3CF_2CFBrCF_3$ and $CF_3SO_3CF(CF_2)_3CFBr$ could not be made to react with $CF_3SO_3Cl$, and that $C_2F_5Br$, $C_3F_7Br$, and $(CF_2Br)_2$ were considerably less reactive than $CF_3Br$ with $CF_3SO_3Cl$. A second important point relates to the polarity of the C–X bond and the ease of reaction. Qualitatively, electron-withdrawing substituents on carbon decrease the reactivity and electron-donating groups increase the reactivity. The reactivity $CF_3Cl < CF_2Cl_2 < CFCl_3$ may be ascribed in part to the increasing negative charge on chlorine as the number of fluorines decreases and this favors the interaction with the electrophilic halogen of $CF_3SO_3X$. However, this rationale cannot explain the reactivity $CF_3Cl < CF_3Br$. Bromine is less negatively charged than chlorine in $CF_3X$, but clearly the greater size of bromine and the weaker carbon–bromine bond are important considerations in any mechanistic proposal.

We propose that the substitutive electrophilic dehalogenation reaction proceeds by the following $S_{Ei}$-type mechanism.[15]



A reaction involving a transition state like that shown could account for the above observations and predicts no inversion at carbon on substitution. An attempt to test the latter was made by reaction of $CF_3SO_3Cl$ with *erythro*-$CF_3CO_2CFHCFHCl$ and *threo*-$CF_3CO_2CFHCFHCl$. In each case, substitution of chlorine takes place yielding a single stereoisomer. The observation of only one isomer clearly limits the number of alternative mechanisms that can be proposed and requires either 100% retention or inversion of configuration. From the NMR data an argument can be made favoring 100% retention.

We have previously argued in a communication that the value of ${}^3J_{FF}$ could be used to assign the erythro and threo isomers.[13] Additional support for these assignments was based on the high-field chemical shift of the CFH groups in the threo isomers. A logical and consistent set of values for the two diastereomers of $CF_3SO_3CHFCHFCl$, $CF_3SO_3CHFCHFBr$, $CF_3CO_2CHFCHFCl$, and $CF_3OCHFCHFCl$ was observed. In the series, ${}^3J_{FF}$ is inversely proportional to the electronegativity of the substituents in XCHFCHFY and in each pair the ${}^3J_{FF}$ values differed by ~5 Hz. Chemical shifts for the respective CHF groups in the pairs were at higher field for one diastereomer. In each case the larger ${}^3J_{FF}$ values and higher field chemical shift are for the isomer formed by addition of the respective hypohalite to the trans olefin. On this basis, it was concluded that the additions were cis and the diastereomers erythro and threo for the cis and trans olefin, respectively.

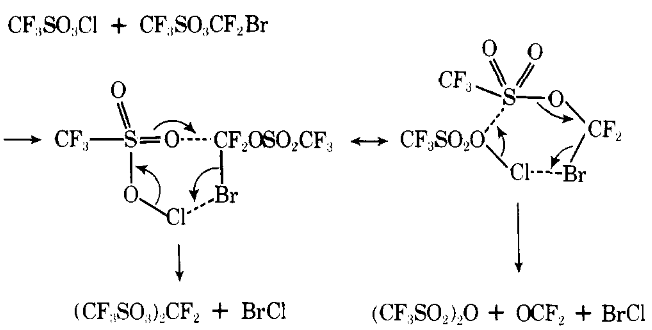
The single diastereomer $CF_3CO_2CHFCFHOSO_2CF_3$ would then be assigned as erythro by extrapolation. At the time, however, the reaction with *threo*-$CF_3CO_2CHFCFHCl$ had not been carried out. The single diastereomer, $CF_3CO_2CFHCFHOSO_2CF_3$, formed in this reaction does not have the anticipated ${}^3J_{FF}$ and chemical-shift values. The ${}^3J_{FF}$ in the two isomers are nearly identical as are the CH*F* chemical shifts, and both were anticipated to be larger for the product formed from *threo*-$CF_3CO_2CFHCFHCl$. This necessitated further analysis of the ${}^1H$ spectra.

The ${}^1H$ spectra of *erythro*- and *threo*-$CF_3CO_2CFHCFHOSO_2CF_3$ were analyzed by iterative fit of the experimental spectra to a calculated $ABNMX_3$ spin system. Within experimental error, the ${}^3J_{HH}$ values are identical for both diastereomers. The magnitude of the average ${}^3J_{HH}$ values, 4.6 Hz, indicates that there is a preference for the rotamers with the hydrogens trans.[16,17] This is only possible if the most stable rotamer is not the same in both isomers. This also appears to be true for the other four pairs of erythro and threo isomers mentioned earlier, although their spectra have not been analyzed in the same detail. It can be tentatively concluded that the most abundant rotamer for the erythro isomers in XCFHCFHY has X and Y and the vicinal fluorines trans. For *threo*-XCFHCFHY, X and Y and the vicinal fluorines are gauche. Considerable additional experimentation would be required to prove this conclusively and we are not prepared to carry out this work at this time.

The above analysis accounts for the essentially identical ${}^3J_{HH}$ values in the ten diastereomers, the normally larger ${}^3J_{FF}$ value in the threo isomers (every case except $CF_3CO_2CFHCFHOSO_2CF_3$), and the small variation of ${}^3J_{HF}$ values, which are gauche for both the erythro and threo isomers in the above rotamers. The failure to observe the anticipated relative values for ${}^3J_{FF}$ and $\phi^*(CHF)$ in *erythro*- and *threo*-$CF_3CO_2CFHCFHOSO_2CF_3$ can be attributed to the second oxy substituent.

The number of fluorinated compounds where ${}^3J_{HH}$ values have been assigned are quite limited.[18] Three compounds which provide an interesting comparison are $SF_5OCHClCHClF$,[19] $CF_3CHBrCHBrF$, and $CF_3CHICHFCF_3$.[20] In the first compound, the average ${}^3J_{HH}$ values are 4.5 and 4.8 Hz for the two isomers, with erythro and threo not specifically identified. These values are quite similar to those observed above and would imply a similar importance for trans hydrogens. In the other two compounds, the two diastereomers show characteristically small ${}^3J_{HH}$ values with erythro > threo ($CF_3CHBrCHBrF$, 5.5 and 2.8; $CF_3CHICHFCF_3$, 7.7 and 1.8 Hz). These values imply an importance for trans hydrogens in erythro and gauche hydrogens in threo, in contrast to $CF_3CO_2CFHCFHOSO_2CF_3$. Finally, a series of fluorinated alcohols provide additional values for comparison. In the compounds $PhCHFCH(OH)CO_2CH_3$,[21] $PhCHFCH(OH)CH_3$, $CH_3CHFCH(OH)Ph$, and $PhCHFCH(OH)Ph$[22] the average values of ${}^3J_{HH}$ for erythro and threo are respectively 4.0, 2.4; 7.0, 5.0; 6.1, 4.0; 7.2, 5.4 Hz. It would appear, based on these limited data, that the usual situation would be ${}^3J_{HH}(\text{erythro}) > {}^3J_{HH}(\text{threo})$. If this usual situation is not observed, then the rotamer popu-

**Scheme I**



lations in erythro and threo must be significantly different, as is apparently the case for $CF_3CO_2CFHCFHOSO_2CF_3$ and the related compounds of the type XCFHCFHY.

One additional point that can be made concerning the mechanism of these reactions relates to the low yields in the disubstitution reactions. The low yields of disubstituted products are not due to low thermal stability. $(CF_3SO_3)_2CF_2$ was recovered unchanged after heating at 150 °C in glass for 4 days. Therefore, the low yields and concurrent formation of trifluoromethanesulfonic acid anhydride and carbonyl compounds must be due to a side reaction during the displacement. Scheme I is proposed to explain this. This alternative transition state is very reasonable, and could account for the low percentage of disubstituted compounds. In addition, the failure to isolate tri- and tetrasubstituted esters can be explained in the same way; i.e., $C(OSO_2CF_3)_4$ is not necessarily kinetically unstable but is simply never formed.

In summary, the substitutive electrophilic dehalogenation reactions using $CF_3SO_3Cl$ and $CF_3SO_3Br$ offer considerable potential in synthesis. This work has greatly extended the number of perhalo esters of trifluoromethanesulfonic acid and extension to other organic and inorganic compounds should be possible. The apparent control of stereochemistry would appear to have some utility in synthesis, if wide extension of these reactions prove possible.

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# Reaction of α-Arylvinyl Halides with Antimony Pentafluoride. A $^1H$ and $^{13}C$ NMR Spectroscopic Investigation

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**Abstract:** The α-arylvinyl halides **1–7** were reacted with $SbF_5$ in $SO_2ClF$ and the solutions were investigated by $^1H$ and $^{13}C$ NMR spectroscopy. It is confirmed by the spectral data, especially by the observation of the $J_{CF}$ and $J_{CC}$ coupling constants, that vinyl cations were not generated under the described reaction conditions. $SbF_5$ reacts with the olefinic double bond of the α-arylvinyl halides **1–7** to form a σ complex to which we assign tentatively structure **11.**

Until 1969 vinyl cations in general were not considered to be very attractive intermediates, because they were thought to be highly unstable and therefore difficult to generate by bond heterolysis like a solvolysis reaction. From the extensive investigations carried out recently on the solvolysis of vinyl derivatives, especially of vinyl triflates and nonaflates,[1] it became clear that saturated and vinyl compounds show many qualitative similarities in their solvolytic reactivity. Now vinyl cations are generally accepted as reactive intermediates which are able to undergo, e.g., substitution, elimination, and rearrangement reactions.[1]

Recently we reported preliminary results on the attempts to generate vinyl cations in $SO_2ClF$ by reaction of 1-*p*-anisyl-1-fluoro-2-methylpropene-1 (**1**) with $SbF_5$.[2] Though it has been published that, e.g., the phenylvinyl chloride (**7**) could be converted with $SbF_5/SO_2ClF$ into the corresponding vinyl cation,[3] the present systematic investigation shows that arylvinyl cations are not formed under the conditions we have used.

Until now various spectroscopic investigations were carried out to demonstrate the existence of vinyl cations in solution.[1f,4] The first indication for the existence of vinyl cations was obtained using alkynyl cations, which may be regarded as vinyl cations in their mesomeric form.[4a-d,h] The alkynyl cations generated from the corresponding alkynyl alcohols by protonation under various conditions were investigated in detail

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