

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 systems⁷ 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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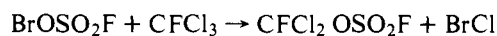
Abstract: The reactions of chlorine(I) and bromine(I) trifluoromethanesulfonates with a variety of perfluoroalkyl halides are reported. The reactions form Br_2 , Cl_2 , or BrCl and the corresponding trifluoromethanesulfonate derivatives of the alkyls in good yields. Twelve new esters are reported and characterized. An S_{Ei} -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 $\text{M}^{\delta-}-\text{X}^{\delta+}$ can react with a negatively polarized atom in $\text{N}^{\delta+}-\text{Y}^{\delta-}$ 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 $(\text{CF}_3)_2\text{NCl}$, SF_5OCl , CF_3OCl , FSO_2OCl , $(\text{FSO}_2)_2\text{NCl}$, 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 equation⁵



This reaction can be termed substitutive electrophilic dehalogenation. A similar transformation employing FSO_3^- or $\text{FSO}_3\cdot$ is not possible under the same conditions. While the detailed mechanism of this reaction is unknown, it probably involves the initial interaction $\text{FSO}_2\text{O}-\text{Br}^{\delta+}-\text{Cl}^{\delta-}-\text{CFCl}_2$.

With the discovery of the halogen(1) trifluoromethanesulfonates,^{6,7} $\text{CF}_3\text{SO}_2\text{OCl}$ and $\text{CF}_3\text{SO}_2\text{OBr}$, 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 $\text{CF}_3\text{SO}_3\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$) 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 $\text{CF}_3\text{SO}_3\text{CF}_3$ 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 then 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 \times $\frac{3}{8}$ 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. $\text{CF}_3\text{SO}_3\text{H}$ 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. $\text{C}_2\text{F}_5\text{Br}$ and $\text{C}_3\text{F}_7\text{Br}$ were prepared from $\text{C}_2\text{F}_5\text{COOH}$ and $\text{C}_3\text{F}_7\text{COOH}$, respectively, by the standard methods. $\text{CBrF}_2\text{CBrF}_2$ 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. $\text{CF}_3\text{SO}_3\text{CF}_2\text{CFBrCF}_3$, $\text{CF}_3\text{SO}_3\text{CF}(\text{CF}_2)_3\text{CFBr}$, and *erythro*- $\text{CF}_3\text{SO}_3\text{CHFCHFBr}$ were obtained by the addition reaction of $\text{CF}_3\text{SO}_2\text{OBr}$ with the appropriate olefins.¹³ *erythro*- $\text{CF}_3\text{SO}_3\text{CHFCHFCl}$ and *erythro*- $\text{CF}_3\text{CO}_2\text{CHFCHFCl}$ were obtained by the reactions of $\text{CF}_3\text{SO}_2\text{OCl}$ and $\text{CF}_3\text{C}(\text{O})\text{OCl}$ with *cis*- CHFCHF and *threo*- $\text{CF}_3\text{CO}_2\text{CHFCHFCl}$ 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 $\text{CF}_3\text{SO}_2\text{OX}$ ($\text{X} = \text{Cl}, \text{Br}$) 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.

$\text{CF}_3\text{SO}_3\text{OH}$ was vacuum transferred from the container at 22 °C to a Kel-F reactor at –195 °C via a short path. The amount of $\text{CF}_3\text{SO}_3\text{H}$ in the reactor was measured by weighing the $\text{CF}_3\text{SO}_3\text{H}$ container. $\text{CF}_3\text{SO}_2\text{OCl}$ 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, $\text{CF}_3\text{SO}_2\text{OCl}$, and was removed by pumping at –78 °C. $\text{CF}_3\text{SO}_2\text{OBr}$ was readily obtained by the reaction of $\text{CF}_3\text{SO}_2\text{OCl}$ and Br_2 . For each reaction, $\text{CF}_3\text{SO}_2\text{OX}$ ($\text{X} = \text{Cl}, \text{Br}$) was freshly prepared.

Onto the $\text{CF}_3\text{SO}_2\text{OX}$ ($\text{X} = \text{Cl}, \text{Br}$) 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, $\text{CF}_3\text{SO}_2\text{OCl}$ 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 $\text{CF}_3\text{SO}_2\text{OX}$ ($\text{X} = \text{Cl}, \text{Br}$) at temperatures below –50 °C, were used as solvent.

Caution. $\text{CF}_3\text{SO}_2\text{OCl}$ 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 $\text{CF}_3\text{SO}_2\text{OX}$ ($\text{X} = \text{Cl}, \text{Br}$) 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 $\text{CF}_3\text{SO}_3\text{CF}_3$. The properties of $\text{CF}_3\text{SO}_3\text{CF}_3$ were identical with those reported by Nofle 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 $\text{CF}_3\text{SO}_2\text{OCl}$ and CClF_3 does not occur below the decomposition temperature of $\text{CF}_3\text{SO}_2\text{OCl}$.

$\text{C}_2\text{F}_5\text{Br}$. After removal of BrCl , the reaction mixture was pumped through traps at –60, –90, –111, and –195 °C. The –90 °C trap contained $\text{CF}_3\text{SO}_3\text{C}_2\text{F}_5$, the –111 °C trap contained $\text{C}_2\text{F}_5\text{Br}$, 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.

$\text{CF}_3\text{SO}_3\text{C}_2\text{F}_5$: colorless liquid, bp 41.6 °C; mp –103.5 to –103.0 °C; mol wt 268.0 (calcd, 268.0); ^{19}F NMR $\text{CF}_3^{\text{A}}\text{SO}_3\text{CF}_2^{\text{B}}\text{CF}_3^{\text{C}}$ $\phi_{\text{A}}^* 74.38$, t, $\phi_{\text{B}}^* 85.41$, t–q, $\phi_{\text{C}}^* 86.76$, t, $J_{\text{AB}} = 5.7$, $J_{\text{BC}} = 2.2$ 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); $\Delta H_{\text{vap}} = 6.74$ kcal/mol; $\Delta S_{\text{vap}} = 21.4$ eu; log P (Torr) = $5.8807 - 416.02/T - 166301/T^2$.

$\text{C}_3\text{F}_7\text{Br}$. The reaction products were pumped through traps at –78, –111, and –195 °C. The –78 °C trap contained $\text{CF}_3\text{SO}_3\text{C}_3\text{F}_7$, the –111 °C trap contained $\text{C}_3\text{F}_7\text{Br}$, and the –195 °C trap contained a fluorinated compound C_3F_8 , which was determined by its molecular

Table I. Reactions of CF₃SO₃X with Halocarbons^a

X	halocarbon	conditions		products ^d
		h	°C	
Cl (4.0)	CBrF ₃ (4.0)	1	-111	CF ₃ SO ₃ CF 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 ₂ F ₅ Br (5.0)	15	-40 to -5	CF ₃ SO ₃ C ₂ F ₅ (2.9), C ₂ F ₆ (0.5) BrCl (5.9)
Cl (6.5)	C ₃ F ₇ Br (6.5)	36	-40 to 22	CF ₃ SO ₃ C ₃ F ₇ (4.2), C ₃ F ₈ (0.6) BrCl (5.7)
Cl (4.6)	CCl ₂ F ₂ (5.1)	15	-78 to 22	CF ₃ SO ₃ CF ₂ Cl (4.2), Cl ₂ (4.5)
Cl (5.1)	CBr ₂ F ₂ (5.4)	1	-111	CF ₃ SO ₃ CF ₂ Br (0.8), COF ₂ (4.0), (CF ₃ SO ₂) ₂ O (2.0), BrCl
Cl (3.3)	CBr ₂ F ₂ (4.5)	1	-160 ^{b,c}	CF ₃ SO ₃ CF ₂ Br (2.0), COF ₂ (1.2), (CF ₃ SO ₂) ₂ O (0.6), BrCl
Cl (5.0)	CCl ₃ F (7.0)	15	-78 to 22	CF ₃ SO ₃ CFCl ₂ (4.4), (CF ₃ SO ₂) ₂ O (0.2)
Br (3.9)	CF ₃ Br (5.0)	15	-111 to -10	CF ₃ SO ₃ CF ₃ (2.9), Br ₂ (3.9)
Br (2.0)	CFCl ₃ (5.0)	15	-78 to 22	CF ₃ SO ₃ CFCl ₂ (1.0), BrCl
Cl (4.4)	CCl ₂ F ₂ (2.0)	15	-60 to 22	(CF ₃ SO ₃) ₂ CF ₂ (0.1), CF ₃ SO ₃ CF ₂ Cl (1.0), COF ₂ (0.8), (CF ₃ SO ₂) ₂ O (0.8), Cl ₂
Cl (1.2)	CBr ₂ F ₂ (2.5)	11	-150 to -130 ^b	COF ₂ (1.9), (CF ₃ SO ₂) ₂ O (1.5), BrCl
Cl (6.1)	CCl ₃ F (3.0)	15	-85 to -40	CF ₃ SO ₃ CCl ₂ F (2.2), (CF ₃ SO ₂) ₂ O (0.7), COClF, Cl ₂
Br (5.0)	CBr ₂ F ₂ (2.4)	24	-111 to -60	(CF ₃ SO ₃) ₂ CF ₂ (0.7), CF ₃ SO ₃ CF ₂ Br (0.7), (CF ₃ SO ₂) ₂ O (0.35), Br ₂ (4.5), COF ₂ (0.9), CF ₃ SO ₃ CF ₃ (0.4)
Br (4.1)	CCl ₂ F ₂ (2.0)	15	-111 to -50	(CF ₃ SO ₃) ₂ CF ₂ (0.12), CF ₃ SO ₃ CF ₂ Cl (0.6), (CF ₃ SO ₂) ₂ O (0.6), COF ₂ (1.), CF ₃ SO ₃ CF ₃ (0.7), BrCl (2.2)
Cl (3.5)	(CF ₂ Br) ₂ (1.6)	15	-88 to -30	(CF ₃ SO ₃ CF ₂) ₂ (0.52), CF ₃ SO ₃ CF ₂ CF ₂ Br (0.99), C ₂ F ₅ Br (0.1), BrCl (3.6)
Cl (5.6)	(CF ₂ Br) ₂ (2.7)	15	-111 to 22 ^b	CF ₃ SO ₃ CF ₂ CF ₂ Br (1.0), CF ₃ SO ₃ CF ₂ Cl (2.9), C ₂ F ₅ Br (1.5), BrCl-Cl ₂ (5.4)
Cl (6.0)	(CF ₂ Br) ₂ (3.0)	1	-111 to -88	CF ₃ SO ₃ CF ₂ CF ₂ Br (1.7), CF ₃ SO ₃ CF ₃ (0.8), C ₂ F ₅ Br (0.4), BrCl (3.2)
Cl (6.9)	CBr ₃ F (2.3)	15	-111 ^b	CF ₃ SO ₃ C(O)F (1.6), (CF ₃ SO ₂) ₂ O (1.8), BrCl (1.6), COBrF
Cl (6.9)	CCl ₃ F (2.3)	24	-78 to 22	(CF ₃ SO ₂) ₂ O, Cl ₂ , COClF, CO ₂ , CF ₃ SO ₃ C(O)F
Cl (9.6)	CCl ₄ (2.4)	24	-78 to 0	(CF ₃ SO ₂) ₂ O (1.5), COCl ₂ , Cl ₂ , CO ₂ , CF ₃ Cl, SO ₃
Cl (3.0)	CF ₃ SO ₃ CF ₂ Br (2.0)	24	-111 to 22 ^{b,c}	(CF ₃ SO ₃) ₂ CF ₂ (0.6), (CF ₃ SO ₂) ₂ O (0.8), COF ₂ (0.8), BrCl
Cl (3.5)	<i>erythro</i> -CF ₃ CO ₂ CHFCHFCI (2.0)	15	-111 to 22 ^c	<i>erythro</i> -CF ₃ SO ₃ CHFCHFO ₂ CCF ₃ (1.6), Cl ₂ (1.7)
Cl (2.0)	<i>threo</i> -CF ₃ CO ₂ CHFCHFCI (1.0)		-111 to 22 ^c	<i>threo</i> -CF ₃ SO ₃ CHFCHFO ₂ CCF ₃ (0.9), Cl ₂
Cl (1.0)	<i>erythro</i> -CF ₃ SO ₃ CHFCHFCI (0.7)	15	-111 to 22 ^c	(CF ₃ SO ₃ CHF) ₂ (0.7), ClBr (0.7)
Cl (2.7)	CF ₃ SO ₃ CF ₂ C(CF ₃)FBr (2.1)	15	-111 to 22 ^c	no substitution
Cl (3.0)	CF ₃ SO ₃ CF(CF ₂) ₃ CFBr (2.3)	15	-111 to 22 ^c	no substitution

^a Amounts (mmol) are given in parentheses. ^b Approximately 10 mmol of CF₂Cl₂ used as a solvent. ^c 100-mL glass reactor. ^d Not all products or their amounts were identified. The main goal was to identify CF₃SO₃-containing products.

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

CF₃SO₃C₃F₇: colorless liquid, bp 66.2 °C; flow point below -111 °C; mol wt 319.2 (calcd, 318.0); ¹⁹F NMR CF₃ASO₃CF₂^BCF₂^CCF₃^D φ_A* 74.72, t, φ_B* 81.04, q-q-t, φ_D* 81.82, t, φ_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); Δ*H*_{vap} = 7.44 kcal/mol; Δ*S*_{vap} = 21.9 eu; log *P* (Torr) = 6.6496 - 931.67/*T* - 117815/*T*².

CCl₂F₂. The reaction products were pumped through traps at -78, -111, and -195 °C. The -111 °C trap contained CF₃SO₃CClF₂.

CF₃SO₃CClF₂: colorless liquid, bp 53.2 °C; flow point below -111 °C; mol wt 238.4 (calcd, 234.5); ¹⁹F NMR CF₃ASO₃CClF₂^B φ_A* 74.3, t, φ_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); Δ*H*_{vap} = 6.53 kcal/mol; Δ*S*_{vap} = 20.0 eu; log *P* (Torr) = 5.9991 - 608.35/*T* - 133640/*T*².

CBr₂F₂. The reaction products were pumped through traps at -78, -111, and -195 °C. The -78 °C trap contained (CF₃SO₂)₂O and small amount of CF₃SO₃CBrF₂, which were separated by a redistillation. The -111 °C trap contained CF₃SO₃CBrF₂. The -195 °C

trap contained COF₂, which was identified by its molecular weight and IR spectrum.

CF₃SO₃CBrF₂: colorless liquid, bp 72.6 °C; flow point below -111 °C; mol wt 278.0 (calcd, 279.0); ¹⁹F NMR CF₃ASO₃CBrF₂^B φ_A* 74.4, t, φ_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); Δ*H*_{vap} = 7.97 kcal/mol; Δ*S*_{vap} = 23.0 eu; log *P* (Torr) = 7.4220 - 1399.2/*T* - 59180/*T*².

CCl₃F. The reaction products were separated by pumping through traps at -78 and -195 °C. The -78 °C trap contained CF₃SO₃CCl₂F.

CF₃SO₃CCl₂F: colorless liquid, bp 89.1 °C; mp -96.0 to -95.6 °C; mol wt 250.0 (calcd, 251.0); ¹⁹F NMR CF₃ASO₃CCl₂F^B φ_A* 74.4, d, φ_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); Δ*H*_{vap} = 8.05 kcal/mol; Δ*S*_{vap} = 22.2 eu; log *P* (Torr) = 6.9445 - 1185.5/*T* - 103809/*T*².

Reactions of CF₃SO₃Cl with Fluorohalocarbons (2:1). CCl₂F₂. The reaction products were pumped through traps at -78, -111, and -195 °C. The -78 °C trap contained (CF₃SO₂)₂O and a small amount of disubstituted product (CF₃SO₃)₂CF₂, which were separated by GLC. The -111 °C trap contained CF₃SO₃CClF₂, and the

−195 °C trap contained COF₂ and a small amount of CF₃Cl, which were identified by their IR spectra.

(CF₃SO₃)₂CF₂: colorless liquid, bp 115.2 °C; flow point −105 °C; mol wt 348.7 (calcd, 348.1); ¹⁹F NMR (CF₃^ASO₃)₂CF₂^B φ_A* 73.75, t, φ_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); Δ*H*_{vap} = 8.22 kcal/mol; Δ*S*_{vap} = 21.2 eu; log *P* (Torr) = 5.8731 − 527.80/*T* − 246400/*T*².

(CBrF₂)₂. The reaction products were pumped through traps at −30, −78, −111, and −195 °C. The −30 °C trap contained (CF₃SO₃CF₂)₂. The −78 °C trap contained CF₃SO₃CF₂CBrF₂ and the −195 °C trap contained a fluorinated product, C₂F₅Br. A polymeric material remained in the reaction vessel.

(CF₃SO₃CF₂)₂: colorless liquid, bp 138.0 °C; mp −38.0 to −37.0 °C; mol wt 396.8 (calcd, 398.1); ¹⁹F NMR (CF₃^ASO₃CF₂^B)₂ φ_A* 74.18, t, φ_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); Δ*H*_{vap} = 8.62 kcal/mol; Δ*S*_{vap} = 21.0 eu; log *P* (Torr) = 7.4629 − 1884.3/*T*.

CF₃SO₃CF₂CBrF₂: colorless liquid, bp 91.1 °C; flow point below −111 °C; mol wt 329.0 (calcd, 329.0); ¹⁹F NMR CF₃^ASO₃CF₂^BCBrF₂ φ_A* 74.35, t, φ_C* 69.51, t, φ_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); Δ*H*_{vap} = 7.82 kcal/mol; Δ*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 CF₃SO₂OBr to CF₂CF₂.

Reaction of CF₃SO₂OBr with CBr₂F₂ or CCl₂F₂ (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 (CF₃SO₃)₂CF₂, (CF₃SO₂)₂O, CF₃SO₃CBrF₂, and COF₂, respectively. A small amount of CF₃SO₃CF₃ was trapped at −111 °C.

Reaction of CF₃SO₂OCl and CBr₃F or CCl₃F (3:1). In an attempt to prepare a trisubstituted product (CF₃SO₃)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 (CF₃SO₂)₂O and CF₃SO₃COF, respectively. The −195 °C trap contained COClF and CF₃Cl when the CCl₃F was used and COBrF when CBr₃F was used.

CF₃SO₃COF: colorless liquid, mp below −111 °C; mol wt 200.0 (calcd, 196.1); ¹⁹F NMR φ* 72.6, br s (CF₃), 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 (vw), 600 (vs), 525 (m).

Reaction of CF₃SO₂OCl and CCl₄ (4:1). The reaction mixture was pumped through traps at −50, −78, and −195 °C. The −78 °C trap contained (CF₃SO₂)₂O, and the −195 °C trap contained a variety of low-boiling gaseous materials including CF₃Cl, Cl₂, COCl₂, and CO₂.

Additional Reactions of CF₃SO₂OCl with Some Halocarbons, CF₃SO₃CBrF. A typical procedure for this reaction will be described here. In a 100-mL Pyrex bulb 2.0 mmol of CF₃SO₃CBrF₂ was condensed and then 2.0 mmol of CCl₂F₂ was condensed onto it at −195 °C. After warming to 22 °C, this mixture was cooled to −195 °C and 3 mmol of CF₃SO₂OCl was condensed onto the mixture followed by another 2.2 mmol of CCl₂F₂. 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 (CF₃SO₃)₂CF₂, (CF₃SO₂)₂O, and CF₃SO₃CBrF₂, respectively. The −195 °C trap contained CCl₂F₂ and COF₂.

erythro-CF₃CO₂CHFCHFCl. The reaction products were pumped through traps at −35, −111, and −195 °C. The −35 °C trap contained pure erythro-CF₃SO₃CHFCHFCl(O)CF₃. The −111 and −195 °C traps contained SO₃ and CF₃Cl along with Cl₂, respectively.

erythro-CF₃ASO₃CH^BF^CCH^DF^EOC(O)CF₃F. heavy, colorless oil, flow point −68.5 °C; ¹⁹F NMR φ_A* 75.08, d−d, φ_F* 75.73; s, φ_C* 138.69, d−d−d−q, φ_E* 147.59, d−d−d−q; ¹H δ_B 6.42, basic d−d−d, δ_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-CF₃CO₂CHFCHFCl. The reaction conditions were identical with those of erythro-CF₃CO₂CHFCHFCl.

threo-CF₃ASO₃CH^BF^CCH^DF^EOC(O)CF₃F. heavy, colorless oil; IR spectrum essentially identical with that of the erythro isomer; NMR φ_A* 74.79, d, φ_F* 75.73, s, φ_C* 138.6, d−d−d−q, φ_E* 146.9, d−d−d; ¹H δ_B 6.22, basic d−d−d, δ_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-CF₃SO₃CHFCHFBr. The reaction mixture was pumped through −30 and −195 °C traps. The −30 °C trap contained (CF₃SO₃CHF)₂, and the −135 °C trap contained a small amount of CF₃Cl and CF₃SO₃CF₃.

(CF₃ASO₃CH^BF^C)₂: colorless, heavy oil, mp 5.3–6.3 °C; ¹⁹F NMR φ_A* 74.84, m, φ_C* 138.65, m (basically d−d−d−q), *J* = 55.1, 4.1, 3.0, 7.5 Hz (CHF); ¹H δ_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).

CF₃SO₃CF₂CBrFCF₃ and CF₃SO₃CF(CF₂)₃CBrF. With these halocarbons CF₃SO₂OCl did not react. The starting halocarbons were recovered quantitatively after the reaction period.

Results and Discussion

The reactions of CF₃SO₃X (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, CF₃SO₃Cl is more reactive than CF₃SO₃Br. 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 CF₃SO₃Cl decreases as the degree of fluorine substitution increases, that is, CF₃Cl < CF₃Br < CF₂Cl₂ < CF₂Br₂. For reactions which are difficult to control with CF₃SO₃Cl, CF₃SO₃Br offers certain advantages because of its milder reactivity. For example, in the reaction of CF₃SO₃Cl with CF₂Br₂, only very low yields of (CF₃SO₃)₂CF₂ were obtained. With CF₃SO₃Br, a slower reaction at higher temperatures gave respectable yields of (CF₃SO₃)₂CF₂.

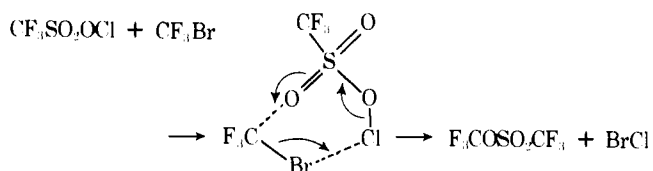
The 12 new halogenated triflates reported in this work have all been adequately characterized by IR, NMR, and physical properties. All of the compounds are colorless liquids at 22 °C and are thermally stable at this temperature in dry glass. As an indication of thermal stability, gaseous (~1 atm) CF₃SO₃C₂F₅ and (CF₃SO₃)₂CF₂ 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 ν(SO₂) antisymmetric stretch can be unambiguously assigned in every case and it is a strong, sharp band at ~1460 cm^{−1}. The ¹⁹F NMR spectra, on the other hand, provide rather convincing proof of structure in each case. The chemical shifts for the CF₃SO₃ groups fall in the range of 73–75 ppm relative to internal CFCl₃ (φ* values) and

these values are indicative of covalent trifluoromethanesulfonate groups. The fortunate observation of $^3J_{FF}$ values of ~ 5 Hz between the CF_3SO_3 group and α 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 non-equivalent. 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 $XCHFCHY$ 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.

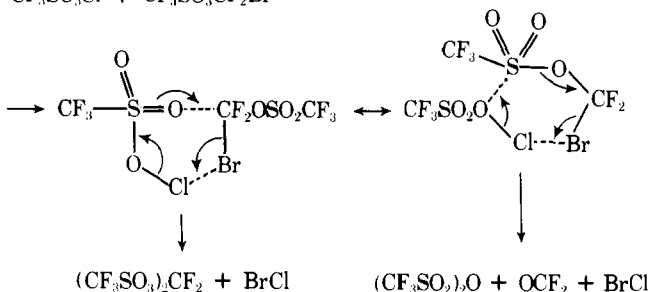
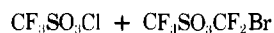
The single diastereomer $CF_3CO_2CHFCFHOSO_2CF_3$ would then be assigned as *erythro* by extrapolation. At the time, however, the reaction with *threo*- $CF_3CO_2CHFCHFCl$ had not been carried out. The single diastereomer, $CF_3CO_2CFHCFHOSO_2CF_3$, formed in this reaction does not have the anticipated $^3J_{FF}$ and chemical-shift values. The $^3J_{FF}$ in the two isomers are nearly identical as are the CHF chemical shifts, and both were anticipated to be larger for the product formed from *threo*- $CF_3CO_2CHFCHFCl$. 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 ABNMX₃ 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 $XCHFCHY$ has X and Y and the vicinal fluorines *trans*. For *threo*- $XCHFCHY$, 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 $CF_3CHClCHClF$.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; $CF_3CHClCHClF$, 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 1



lations in erythro and threo must be significantly different, as is apparently the case for $\text{CF}_3\text{CO}_2\text{CFHC}_2\text{FHOSO}_2\text{CF}_3$ and the related compounds of the type XCFHC_2FHY .

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. $(\text{CF}_3\text{SO}_2)_2\text{CF}_2$ 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., $\text{C}(\text{OSO}_2\text{CF}_3)_4$ is not necessarily kinetically unstable but is simply never formed.

In summary, the substitutive electrophilic dehalogenation reactions using $\text{CF}_3\text{SO}_2\text{Cl}$ and $\text{CF}_3\text{SO}_2\text{Br}$ 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*-ani-

syl-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 $\text{SbF}_5/\text{SO}_2\text{ClF}$ 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