Synthesis of Haloalkyl Esters of Trifluoromethanesulfonic Acid by the Regio- and Stereospecific Addition of Chlorine(I) and Bromine(I) Trifluoromethanesulfonate to Alkenes

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The synthesis of a variety of haloalkyl esters of trifluoromethanesulfonic acid was achieved by the addition of CF_3SO_2OCl and CF_3SO_2OBr to alkenes. Addition to simple alkenes such as $CH_2{=}CH_2$, $CF_2{=}CH_2$, $CF_2{=}CF_2$, $CF_2{=}CFCl$, $CF_2{=}CCl_2$, CHCl=CHCl, and CHF=CHF occur readily at low teperature to give the esters in high yield. With unsymmetrical alkenes, only one structural isomer is observed in every case. With the hypochlorite, *cis*- and *trans*-CHF=CHF form a single different diastereomer. With the hypobromite, the same result is observed, and *trans*-CHCl=CHCl also gives only one diastereomer. A regio- and stereospecific cis-addition mechanism is proposed.

The availability of chlorine(I) and bromine(I) trifluoromethanesulfonate provides new pathways for the synthesis of a variety of trifluoromethanesulfonates.[2,3] These derivatives which are often called "triflates" are important intermediates in mechanistic and synthetic organic chemistry.[4,5] We have utilized these halogen derivatives to prepare a variety of new perfluoroalkyl and alkyl esters by substitutive electrophilic dehalogenation with alkyl chlorides and bromides.[6-8] Some examples of these reactions are given in eq 1-3, where $R_f = CF_3$, C_2F_5,

$$R_fBr + CF_3SO_2OCl \rightarrow R_fOSO_2CF_3 + BrCl \quad (1)$$

$$CF_2Br_2 + 2\ CF_3SO_2OBr \rightarrow CF_2(OSO_2CF_3)_2 + 2\ Br_2 \quad (2)$$

$$Cl(CH_2)_nCl + 2\ CF_3SO_2OX \rightarrow CF_3SO_2O(CH_2)_nOSO_2CF_3 + 2\ XCl \quad (3)$$

and n-C_3F_7, X = Cl or Br, and n = 1-3. Most of these compounds are difficult or impossible to prepare by other methods, and this fact makes clear the utility of CF_3SO_2OX in synthesis.

The halogen atoms in these hypohalites are very electrophilic, and an obvious extension of their reaction chemistry would be addition reactions with unsaturated compounds. In this paper we report the high-yield synthesis of many new triflates by this method.[6] These reactions were of interest not only for their synthetic value, but also in terms of the mechanism of addition using very strong electrophiles. We were especially interested in additions to halogenated alkenes which are normally resistant to attack by electrophiles. Previous work by us and others suggested that fluorinated hypochlorites readily undergo this reaction with high regio- and stereospecificity.[9-11]

Experimental Section

General Methods. All compounds were manipulated in Pyrex and stainless-steel vacuum systems equipped with glass-Teflon or stainless-steel valves. Connections to the vacuum system were by means of compression fittings with Teflon ferrules or glass ⅌ joints lubricated by Halocarbon 25-S grease. Pressures were measured with a Wallace and Tiernan differential pressure gauge, Series 1500. Temperatures were measured by using a digital-indicating copper-constantan thermocouple. Quantities of reactants and products were measured either by direct weighing or by PVT measurements with the assumption of ideal-gas behavior.

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

Unless otherwise noted, NMR spectra were recorded on a Varian XL-100-15 spectrometer at 94.1 MHz for ^{19}F and 100.1 MHz for ^1H. Solutions were 10-15 mol % in $CFCl_3$, and ^{19}F chemical shifts are reported as ϕ^* values. ^1H chemical shifts are relative to external Me_4Si.

Molecular weights for compounds having sufficient vapor pressure at 22 °C were determined by vapor-density measurements with a calibrated Pyrex bulb fitted with a glass-Teflon valve. Determinations were made on successive fractions of each sample. Melting points were taken in a glass 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 then placed in an ethanol bath, which was cooled to -112 °C 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 data to linear and quadratic equations. The best fit is reported.

For further purification, 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 49% 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 Chemical Co. and was purified by distillation. All fluorinated alkenes were obtained from PCR Inc. They were used without further purification. ClF was prepared by heating equimolar amounts of Cl_2 and F_2 at 250 °C for 18 h in a Monel bomb. ClF for reactions

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Table I. Addition of CF_3SO_2OCl to Alkenes

reactants (amt, mmol)				
CF_3SO_2OCl	alkene	time, h	temp, °C	addition product[a] (amt, mmol/yield, %)
(3.5)	$CF_2=CF_2$ (7.0)	10	−111 to −40	$CF_3SO_3CF_2CF_2Cl$ (2.81/80)
(3.0)	$CClF=CF_2$ (3.6)	15	−111 to −5	$CF_3SO_3CClFCF_2Cl$ (2.4/80)
(6.0)	$CCl_2=CF_2$ (9.0)	15	−111 to −30	$CF_3SO_3CCl_2CF_2Cl$ (5.17/86)
(3.8)	$CF_3CF=CF_2$ (3.9)	24	−111 to 22	$CF_3SO_3CF_2CFClCF_3$ (2.95/78)
(2.0)	*cis*-CHF=CHF (2.2)	10	−111 to −40	*erythro*-$CF_3SO_3CHFCHFCl$ (1.75/88)
(4.2)	CHF=CHF (cis/trans, 62/38) (8.9)	5	−111 to −70	$CF_3SO_3CHFCHFCl$ (erythro/threo, 56/44) (3.8/90)
(2.4)	c-C_5F_8 (2.9)	24	−111 to 22	
(2.0)	$CH_2=CF_2$ (3.0)	6	−111 to −60	$CF_3SO_3CF_2CH_2Cl$ (1.3/65) $CF_3SO_3CF_2CH_3$ (0.1/5)
(3.5)	*trans*-CHCl=CHCl	6	−111 to −70[b]	$CF_3SO_3CHClCHCl_2$ (3.5/100)
(2.0)	$CH_2=CH_2$ (2.6)	6	−111 to −70	$CF_3SO_3CH_2CH_2Cl$ (1.6/80)

[a] Yields are based on the amount of CF_3SO_2OCl. [b] CF_2Cl_2 (9 mmol) solvent.

Table II. Addition of CF_3SO_2OBr to Alkenes

reactants (amt, mmol)				
CF_3SO_2OBr	alkene	time, h	temp, °C	addition product[a] (amt, mmol/yield, %)
(1.2)	$CF_2=CF_2$ (3.5)	10	−111 to −55	$CF_3SO_3CF_2CF_2Br$ (1.0/83)
(4.2)	$CClF=CF_2$ (4.6)	15	−111 to −27	$CF_3SO_3CClFCF_2Br$ (3.7/88)
(4.2)	$CCl_2=CF_2$ (6.0)	15	−111 to −5	$CF_3SO_3CCl_2CF_2Br$ (4.2/100)
(6.0)	$CF_3CF=CF_2$ (7.3)	24	−111 to −5	$CF_3SO_3CF_2CBrFCF_3$ (4.8/80)
(4.0)	*cis*-CHF=CHF (4.0)	6	−111 to −20	*erythro*-$CF_3SO_3CHFCHFBr$ (3.5/87)
(6.1)	CHF=CHF (cis/trans, 62/38) (6.3)	6	−111 to −20	$CF_3SO_3CHFCHFBr$ (erythro/threo, 58/42) (5.8/95)
(3.7)	c-C_5F_8 (4.0)	24	−111 to 22	$(CF_3S)_3CF(CF_2)_3CFBr$ (3.53/96)
(2.0)	$CH_2=CF_2$ (4.4)	6	−111 to −55	$CF_3SO_3CF_2CH_2Br$ (1.74/87)
(4.0)	*trans*-CHCl=CHCl (8.8)	1	−111 to −100[b]	*threo*-$CF_3SO_3CHClCHClBr$ (3.99/99)

[a] Yields are based on the amount of CF_3SO_2OBr. [b] CCl_2F_2 (40 mmol) solvent.

was removed after cooling the bomb to −112 °C to prevent contamination by ClF_3 and unreacted Cl_2. F_2 was obtained from Air Products and passed through a NaF scrubber before use. CF_3SO_2OCl and CF_3SO_2OBr were freshly prepared just before the reactions by the reaction between CF_3SO_3H and ClF and between CF_3SO_2OCl and Br_2, respectively.[2,3]

General Procedure for the Reaction of CF_3SO_2OX (X = Cl, Br) with Alkenes. Each reaction was carried out on a 2–7-mmol scale in a 100-mL Pyrex bulb fitted with a glass–Teflon valve. CF_3SO_2OCl, which was prepared in a Kel-F reactor fitted with a stainless-steel valve, was vacuum transferred to the glass reactors at −195 °C via a short path. CF_3SO_2OBr was prepared in the glass reactor and was utilized directly after removal of Cl_2 formed in the preparation from CF_3SO_2OCl and Br_2.

Onto the CF_3SO_2OX (X = Cl, Br) in the Pyrex reactor at −195 °C were condensed the desired amounts or excess amounts of olefins. The reactor was then placed in a −112 °C bath and slowly warmed to the indicated temperature during the time indicated (Tables I and II). At the end of this period, where reaction occurred, the pale yellow color of CF_3SO_2OCl or the wine-red color of CF_3SO_2OBr had disappeared and a colorless liquid was obtained.

The reaction mixtures were then separated by pumping through traps at appropriate temperatures as the bulb containing the reaction products warmed from −195 to 22 °C in a cooled empty Dewar flask. The product of interest was then purified by GLC if needed.

Caution. Explosions can result from contact of CF_3SO_2OX with readily oxidizable materials.

Addition Reactions of CF_3SO_2OCl to Alkenes (Table I). **CF_2=CF_2.** The reaction mixture was pumped through traps at −30, −80, −111, and −195 °C. The −80 and −111 °C traps contained an addition product, $CF_3SO_3CF_2CF_2Cl$. The −195 °C trap contained CF_2=CF_2. At the bottom of the reactor a considerable amount of white powder believed to be polytetrafluoroethylene was observed. $CF^A_3SO_3CF^B_2CF^C_2Cl$: colorless liquid; bp 76.3 °C; fp (flow point) below −111 °C; mol wt 283.9, calcd 284.5; ^{19}F NMR ϕ_A* 74.37 (t), ϕ_B* 83.87 (t, q), ϕ_C* 73.86 (t) (J_{AB} = 5.7 Hz, J_{BC} = 1.8 Hz); IR 1463 (s), 1321 (w), 1260 (sh, w), 1235 (vs), 1210 (s), 1186 (s), 1150 (vs), 1110 (vs), 1025 (w), 973 (vs), 852 (m), 775 (w), 735 (s), 613 (s), 577 (vw), 508 (w) cm^{-1}; ΔH_{vap} = 7.70 kcal/mol; ΔS_{vap} = 22.0 eu; log P (torr) = 7.7004 − 1684.2/T.

CFCl=CF_2. The reaction mixture was pumped through traps at −30, −78, and −195 °C. The −78 °C trap contained an addition product, $CF_3SO_3CClFCClF_2$. The −195 °C trap contained CClF=CF_2 (1.0 mmol). $CF^A_3SO_3CClF^BCClF^C_2$: colorless liquid; fp below −111 °C; mol wt 300.7, calcd 301.0; ^{19}F NMR ϕ_A* 74.38 (d), ϕ_B* ~74.4 (m), ϕ_C* 70.59 (m) ($J_{AB} \approx 1.0$, J_{BC} = ?, $ABXY_3$ spin system); IR 1464 (s), 1268 (sh, w), 1245 (vs), 1192 (s), 1150 (vs), 1089 (s), 1024 (vs), 935 (s), 890 (w), 858 (s), 826 (s), 800 (w), 720 (w), 710 (sh, w), 735 (w), 685 (m), 650 (br, w), 610 (s), 575 (w), 515 (br, m) cm^{-1}.

CCl_2=CF_2. The reaction mixture was pumped through traps at −30, −78, and −195 °C. The −30 and −78 °C traps contained an addition product, $CF_3SO_3CCl_2CClF_2$. The unreacted CCl_2=CF_2 was recovered in the −195 °C trap (3.63 mmol). $CF^A_3SO_3CCl_2CClF^B_2$: colorless liquid; bp 125.1 °C; fp −103.0 °C; mol wt 315.7, calcd 317.5; ^{19}F NMR ϕ_A* 74.47 (s), ϕ_B* 67.78 (s); IR 1450 (s), 1318 (s), 1254 (sh, w), 1235 (vs), 1190 (vs), 1143 (s), 1065 (s), 990 (vs), 972 (sh, m), 898 (s), 827 (s), 800 (s), 762 (m), 740 (w), 641 (m), 607 (w), 571 (s), 509 (m) cm^{-1}; ΔH_{vap} = 10.05 kcal/mol; ΔS_{vap} = 25.2 eu; log P (torr) = 9.6351 − 3183.0/T + 196 413/T^2.

CF_3CF=CF_2. The reaction mixture was pumped through traps at −80 and −195 °C. The −80 °C trap contained an addition product, $CF_3SO_3CF_2CClFCF_3$. The reacted CF_3CF=CF_2 was contained in the −195 °C trap (1.1 mmol). $CF^A_3SO_3CF^B_2CClF^CCF^D_3$: colorless liquid; bp 95.9 °C; fp −104.5 °C; mol wt. 334.3, calcd 334.5; ^{19}F NMR ϕ_A* 74.37 (t, q), ϕ_B* 77.27 (d, q, q), ϕ_C* 139.76 (t, q), ϕ_D* 74.41 (d, t, q) (J_{AB} = 5.5 Hz, $J_{AC} \leq$ 0.5 Hz, J_{AD} = 0.5 Hz, $J_{BC} \approx$ 6.0 Hz, J_{BD} = 9.0 Hz, J_{CD} = 6.0 Hz); IR 1470 (s), 1300 (w), 1281 (s), 1240 (br, vs), 1197 (w), 1146

(s), 1116 (s), 972 (vs), 840 (w), 823 (vw), 776 (vw), 743 (m), 724 (m), 618 (m), 502 (w) cm^{-1}; ΔH_{vap} = 7.25 kcal/mol; ΔS_{vap} = 19.7 eu; log P (torr) = 6.2808 − 924.80/T − 121 822/T^2.

***cis*-CHF=CHF.** This reaction was almost explosive when the reaction bulb was shaken at −80 °C and gave only 15% of the addition product. For improvement of the yield, the reactor was placed in a −111 °C CCl_3F bath and was warmed to −40 °C without any agitation. The reaction mixture was pumped through traps at −78 and −195 °C. The −78 °C trap contained an adduct, *erythro*-$CF_3SO_3CHFCHClF$. The −195 °C trap contained 0.37 mmol of unidentified gaseous materials. *erythro*-$CF^A{}_3SO_3CH^BF^CCH^DClF^E$: colorless liquid; bp 117.8 °C; fp −92.4 °C; mol wt 248.1, calcd 248.5; ^{19}F NMR ϕ_A* 74.93 (d, d), ϕ_C* 132.48 (d, d, d, q), ϕ_E* 154.18 (d, d, d, q), δ_B and δ_D, multiplet centered at 6.40 (ABMNX$_3$ spin system; $J_{AB} \approx 0$ Hz, J_{AC} = 6.0 Hz, J_{AE} = 0.8 Hz, J_{BC} = 56.1 Hz, $J_{BD} \approx 4$ Hz, J_{BE} = 5.2 Hz, J_{CD} = 3.1 Hz, J_{CE} = 15.8 Hz, J_{DE} = 48.0 Hz); IR 3000 (vw), 1450 (s), 1251 (sh, w), 1230 (vs), 1145 (s), 1130 (sh, w), 1087 (s), 1016 (m), 997 (w), 878 (m), 840 (br, m), 620 (m), 520 (vw) cm^{-1}; ΔH_{vap} = 8.91 kcal/mol; ΔS_{vap} = 22.8 eu; log P (torr) = 7.5166 − 1677.8/T − 52 731/T^2.

CHF=CHF (62/38 Cis/Trans). Reaction and separation were done by the same manner as in the case of *cis*-CHF=CHF. The NMR spectra showed there were addition products in ratio of ca. 58:42. The major isomer was the same compound obtained from *cis*-CHF=CHF, which was assigned as *erythro*-$CF_3SO_3CHFCHClF$. The minor isomer was assigned as *threo*-$CF_3SO_3CHFCHClF$ obtained from *trans*-CHF=CHF. *threo*-$CF^A{}_3SO_3CH^BF^CCH^DClF^E$ (the diastereomers could not be separated from each other; the following data were taken on the mixture): colorless liquid; mol wt 248.3, calcd 248.5; IR, not distinguishable from the erythro isomer described above; NMR (the two isomers were distinguishable from each other in the NMR spectrum of the mixture) ϕ_A* 75.01 (d,d), ϕ_C* 133.68 (d, d, d, q), ϕ_E* 154.66 (d, d, d, q), δ_B and δ_D, multiplet centered at 6.38 (ABMNX$_3$ spin system; J_{AC} = 5.4 Hz, J_{AE} = 1.8 Hz, J_{BC} = 54.5 Hz, $J_{BD} \approx 4$ Hz, J_{BE} = 6.0 Hz, J_{CD} = 3.2 Hz, J_{CE} = 20.5 Hz, J_{DE} = 48.0 Hz).

c-C_5F_8. The reaction mixture was pumped through traps at −30, −78, and −195 °C. The −30 and −78 °C traps contained $CF_3SO_3CF(CF_2)_3CClF$. The −195 °C trap contained an unknown compound(s) having a carbonyl group, along with CF_3Cl and unreacted c-C_5F_8. $CF_3SO_3CF(CF_2)_3CClF$: colorless liquid; bp 128.9 °C; mp −43.5 to −42.5 °C; mol wt 397.4, calcd 396.5; ^{19}F NMR ϕ* 73.96 (d, d) (J = 1.9 and 9.6 Hz, CF_3S; the remainder of the spectrum consisted of many multiplets between ϕ* 115.55 and 139.50); IR 1460 (s), 1335 (w), 1300 (m), 1289 (sh, w), 1235 (br, vs), 1141 (vs), 1117 (w), 1010 (m), 968 (vs), 871 (s), 790 (m), 756 (m), 610 (m), 500 (m) cm^{-1}; ΔH_{vap} = 9.49 kcal/mol; ΔS_{vap} = 23.6 eu; log P (torr) = 8.5506 − 2484.6/T − 82 412/T^2.

CH_2=CF_2. The reaction mixture was pumped through traps at −60 and −195 °C. The −60 °C trap contained $CF_3SO_3CF_2CH_2Cl$ and a small amount of $CF_3SO_3CF_2CH_3$.[12] The −195 °C trap contained unreacted CH_2=CF_2 (1.4 mmol). The mixture of the products in the −60 °C trap was separated by GLC. $CF^A{}_3SO_3CF^B{}_2CH^C{}_2Cl$: colorless liquid; fp −84.5 °C; mol wt 248.1, calcd 248.5; NMR ϕ_A* 74.87 (t), ϕ_B* 70.30 (t, q), δ_C 4.2 (t) (J_{AB} = 5.7 Hz; J_{BC} = 10.4 Hz); IR 1455 (s), 1330 (w), 1282 (w), 1240 (vs), 1152 (vs), 1063 (s), 1050 (sh, m), 1022 (w), 980 (w), 924 (vs), 840 (sh, w), 828 (w), 790 (w), 730 (m), 670 (br, w), 615 (br, w), 575 (w), 526 (w) cm^{-1}. $CF^A{}_3SO_3CF^B{}_2CH^C{}_3$: colorless liquid; mol wt 213.5, calcd 214.0; NMR ϕ_A* 75.56 (t), ϕ_B* 58.64 (q, t), δ_C 2.07 (t) (J_{AB} = 5.3 Hz, J_{BC} = 14.4 Hz); IR 1450 (s), 1410 (m), 1275 (s), 1253 (s), 1235 (br, vs), 1160 (vs), 1145 (s), 970 (m), 935 (s), 920 (s), 895 (m), 778 (w), 738 (m), 613 (m), 529 (m), 490 (br, w) cm^{-1}.

***trans*-CHCl=CHCl.** The reaction mixture was pumped through traps at −30, −111, and −195 °C. The −30 °C trap contained $CF_3SO_3CHClCHCl_2$. The −111 and −195 °C traps contained CCl_2F_2 (used as a solvent) and recovered olefin (*trans*-CHCl=CHCl, 3.5 mmol). $CF^A{}_3SO_3CH^BClCH^CCl_2$: a colorless oil; fp −69.0 °C; ^{19}F NMR ϕ_A* 74.40 (s), δ_B 6.13 (d), δ_C 6.70 (d) (J_{BC} = 4.0 Hz); IR 1440 (s), 1247 (m), 1228 (vs), 1209 (w), 1149 (s), 1067 (w), 1024 (w), 1003 (w), 968 (s), 909 (w), 858 (w), 810 (br, w), 760 (w), 742 (w), 618 (m) cm^{-1}.

CH_2=CH_2. The reaction mixture was pumped through traps at −78 and −195 °C. The −78 °C trap contained $CF_3SO_3CH_2CH_2Cl$. The −195 °C trap contained recovered CH_2=CH_2 (1.0 mmol). $CF^A{}_3SO_3CH^B{}_2CH^C{}_2Cl$: a colorless oil; mp −50.5 to −50.0 °C; NMR ϕ_A 75.41 (s), δ_B 4.00 (t), δ_C 4.93 (t) (J_{BC} = 5.8 Hz); IR 2980 (vw), 1438 (s), 1249 (s), 1228 (vs), 1211 (w), 1152 (vs), 1100 (vw), 1068 (w), 1005 (m), 970 (s), 910 (m), 820 (br, m), 782 (w), 748 (w), 620 (m) cm^{-1}.

This compound was identical with the compound obtained by the substitution reaction of CF_3SO_2OCl with CH_2ClCH_2Cl.[8]

Addition Reactions of CF_3SO_2OBr to Alkenes (Table II).

CF_2=CF_2. The reaction mixture was pumped through traps at −30, −78, and −195 °C. The −78 °C trap contained an adduct $CF_3SO_3CF_2CBrF_2$. The −195 °C trap contained $CF_3SO_3CF_2CBrF_2$, $CF_3SO_3CF_3$, $CBrF_3$, and CF_2=CF_2, which were identified by their IR and NMR spectra. $CF^A{}_3SO_3CF^B{}_2CBrF^C{}_2$: colorless liquid; bp 91.0 °C; fp below −111 °C; mol wt 328.5, calcd 329.0; ^{19}F NMR ϕ_A 74.35 (t), ϕ_B* 82.89 (t, q), ϕ_C* 69.51 (t) (J_{AB} = 5.5 Hz, J_{BC} = 3.2 Hz); IR 1462 (s), 1310 (m), 1259 (w), 1234 (vs), 1205 (m), 1177 (m), 1143 (vs), 1100 (vs), 970 (sh, w), 942 (vs), 845 (m), 771 (w), 730 (s), 610 (s), 570 (vw), 500 (w) cm^{-1}; ΔH_{vap} = 7.82 kcal/mol; ΔS_{vap} = 21.5 eu; log P (torr) = 6.6295 − 1021.7/T − 125246/T^2.

This compound was identical with the one obtained by the displacement reaction of CF_3SO_2OCl and $CBrF_2CBrF_2$.[7]

CClF=CF_2. The reaction mixture was pumped through traps at −40, −70, and −195 °C. The −40 and −70 °C traps contained $CF_3SO_3CClFCBrF_2$. The −195 °C trap contained recovered CClF=CF_2 (0.77 mmol) and other gases (0.11 mmol). $CF^A{}_3SO_3CClF^BCBrF^CF^D$: colorless liquid; fp −106.0 °C; mol wt 345.2, calcd 345.5; ^{19}F NMR ϕ_A* 74.36 (d), ϕ_B* 72.66 (m, overlapped d, d, q), ϕ_C* 65.33 (d), ϕ_D* 65.29 (d) (J_{AB} = 7.0 Hz, J_{BC} = 6.7 Hz, ABXY$_3$ spin system); IR 1463 (s), 1260 (sh, m), 1238 (vs), 1185 (s), 1145 (sh, w), 1080 (s), 1010 (s), 910 (s), 900 (sh, m), 828 (s), 809 (s), 677 (m), 644 (sh, m), 600 (m), 563 (br, w), 510 (br, m) cm^{-1}.

CCl_2=CF_2. The reaction mixture was pumped through traps at −70 and −195 °C. The −70 °C trap contained $CF_3SO_3CCl_2CBrF_2$. The −195 °C trap contained unreacted CCl_2=CF_2. A small amount of polymeric material was observed at the bottom of the reactor. $CF^A{}_3SO_3CCl_2CBrF^B{}_2$: colorless liquid; mol wt 361.4, calcd 362.0; ^{19}F NMR ϕ_A 74.38 (s), ϕ_B* 61.95 (s); IR 1465 (s), 1330 (w), 1250 (br, vs), 1180 (br, vs), 1150 (s), 1040 (s), 998 (s), 920 (br, w), 895 (m), 860 (m), 820 (m), 792 (s), 750 (w), 620 (m), 500 (br, m) cm^{-1}.

CF_3CF=CF_2. The reaction mixture was pumped through traps at −30, −100, and −195 °C. The −30 and −100 °C traps contained an addition product, $CF_3SO_3CF_2CBrFCF_3$. The −195 °C trap contained $CF_3SO_3CF_3$, $CF_3CBrFCBrF_2$, and CF_3CF=CF_2, which were identified by their IR spectra. $CF_3SO_3CF_3$ and Br_2 arise from the decomposition of CF_3SO_2OBr and $CF_3CBrFCBrF_2$ from the addition of Br_2 to CF_3CF=CF_2. $CF^A{}_3SO_3CF^B{}_2CBrF^CCF^D{}_3$: colorless liquid; bp 107.9 °C; fp below −111 °C; mol wt 380.5, calcd 379.0; ^{19}F NMR ϕ_A* 74.36 (t), ϕ_B* 75.50 (d, q, q), ϕ_C* 142.35 (t, q) (J_{AB} = 5.6 Hz, J_{AD} = 0.6 Hz, J_{BC} = 9.0 Hz, J_{BD} = 9.0 Hz, J_{CD} = 9.0 Hz); IR 1460 (s), 1285 (w), 1272 (w), 1230 (br, vs), 1189 (vw), 1170 (vw), 1140 (s), 1107 (s), 959 (s), 930 (s), 836 (w), 820 (w), 773 (vw), 740 (m), 713 (m), 610 (s), 500 (w) cm^{-1}; ΔH_{vap} = 9.32 kcal/mol; ΔS_{vap} = 24.5 eu; log P (torr) = 10.4792 − 3752.49/T + 326 666/T^2.

***cis*-CHF=CHF.** The reaction mixture was pumped through traps at −30, −111, and −195 °C. The −30 and −111 °C traps contained an adduct *erythro*-$CF_3SO_3CHFCHBrF$. The −195 °C trap contained CHF=CHF (1.1 mmol). The −30 °C trap contained a small amount of a heavier compound, which was separated from $CF_3SO_3CHFCHBrF$ by trap to trap distillation and was found to be $(CF_3SO_3CHF)_2$, obtained by a further reaction of the adduct with CF_3SO_2OBr as in eq 4.[7] *erythro*-

$$CF_3SO_2OBr + CHF{=}CHF \rightarrow CF_3SO_3CHFCHBrF \xrightarrow[-Br_2]{CF_3SO_2OBr} (CF_3SO_3CHF)_2 \quad (4)$$

$CF^A{}_3SO_3CH^BF^CCH^DBrF^E$: colorless liquid: bp 125.0 °C; fp −85.4 °C; mol wt 295.3, calcd 293.0; NMR ϕ_A* 74.84 (d, d), ϕ_C* 130.74 (d, d, d, q), ϕ_E* 159.08 (d, d, d, q), δ_B 6.50 (basic d, d, d), δ_D 6.70

(12) This product arises from the addition of CF_3SO_3H to CF_2=CH_2, which was confirmed by a known reaction between the two.

(basic d, d, d) (J_{AC} = 6.0 Hz, J_{AE} = 1.0 Hz, J_{BC} = 53.0 Hz, J_{BD} = 4.6 Hz, J_{BE} = 4.4 Hz, J_{CD} = 6.4 Hz, J_{CE} = 19.5 Hz, J_{DE} = 48.4 Hz); IR 3000 (vw), 1450 (s), 1230 (vs), 1155 (sh, w), 1143 (s), 1125 (vw), 1090 (s), 1065 (vw), 1012 (m), 978 (w), 962 (vw), 872 (m), 840 (m), 750 (m), 665 (m), 620 (m), 585 (vw), 505 (vw) cm^{-1}; ΔH_{vap} = 7.83 kcal/mol; ΔS_{vap} = 19.7 eu; log P (torr) = 5.459 31 − 341.650/T − 272 810/T^2.

CHF=CHF (62/38 Cis/Trans). Reaction and separation were done in the same way as for *cis*-CHF=CHF. The NMR studies on the addition products showed there were two stereoisomers in the ratio of 58/42. The major isomer was the same compound as that obtained from *cis*-CHF=CHF. The minor isomer was identified as *threo*-$CF_3SO_3CHFCHBrF$. *threo*-$CF^A{}_3SO_3CH^BF^CCH^DBrF^E$ (the two isomers could not be separated from each other; the following data were taken for the mixture of the isomers): colorless liquid; mol wt 294.8, calcd 293.0; the IR spectrum was indistinguishable from pure erythro isomer; the NMR spectra of the two isomers were distinguishable from each other in the NMR spectrum of the mixture, NMR ϕ_A* 74.90 (d, d), ϕ_C* 131.14 (d, d, d, q), ϕ_E* 159.34 (d, d, d, q), δ_B 6.53 (basic d, d, d), δ_D 6.77 (basic d, d, d) (J_{AC} = 5.8 Hz, J_{AE} = 1.8 Hz, J_{BC} = 52.5 Hz, J_{BE} = 4.4 Hz, J_{BD} = 4.6 Hz, J_{CD} = 6.2 Hz, J_{CE} = 6.2 Hz, J_{CE} = 25.5 Hz, J_{DE} = 49.0 Hz).

c-C_5F_8. The reaction mixture was pumped through traps at −20, −78, and −195 °C. The −20 and −78 °C traps contained $CF_3SO_3CF(CF_2)_3CBrF$. The −195 °C trap contained c-C_5F_8 (0.47 mmol), Br_2, and an unidentified compound(s) (0.08 mmol). $CF_3SO_3CF(CF_2)_3CBrF$: colorless liquid; bp ~137 °C; mp −32.5 to −31.5 °C; mol wt 440.6, calcd 441.0; ^{19}F NMR ϕ* 73.82 (d, d, CF_3S) (J = 9.65 Hz, J = 2.0), the remainder of the spectrum consisted of many multiplets between ϕ* 110.93 and 138.55 (chemical shifts were slightly different from those of $CF_3SO_3CF(CF_2)_3CClF$, but the patterns of both spectra were very similar); IR 1460 (s), 1332 (w), 1300 (m), 1285 (sh, vw), 1234 (vs), 1140 (s), 1110 (w), 1006 (w), 961 (vs), 848 (w), 827 (s), 789 (m), 751 (m), 609 (m), 495 (w) cm^{-1}.

CH_2=CF_2. The reaction mixture was pumped through traps at −35 and −195 °C. The −35 °C trap contained $CF_3SO_3CF_2CH_2Br$. The −195 °C trap contained CH_2=CF_2 (1.43 mmol) and an unidentified compound(s) (0.12 mmol). $CF^A{}_3SO_3CF^B{}_2CH^C{}_2Br$: colorless liquid; bp 128.6 °C; fp −76.0 °C; mol wt 292.8, calcd 293.0; NMR ϕ_A* 74.86 (t), ϕ_B* 67.66 (t, q), δ_C 4.10 (t) (J_{AB} = 5.7 Hz, J_{BC} = 10.1 Hz); IR 1458 (s), 1430 (sh, vw), 1298 (m), 1270 (w), 1232 (vs), 1193 (w), 1147 (s), 1128 (w), 1028 (s), 1000 (w), 911 (vs), 780 (vw), 760 (vw), 740 (vw), 715 (vw), 660 (m), 620 (br, m) cm^{-1}; ΔH_{vap} = 9.73 kcal/mol. ΔS_{vap} = 24.2 eu; log P (torr) = 7.395 94 − 1478.32/T − 129 996/T^2.

***trans*-CHCl=CHCl.** This reaction proceeded readily at −111 °C. The addition product was contaminated by the heavier byproduct(s) which was difficult to remove from the main product. Several runs of the reaction were carried out under various conditions to obtain the pure adduct. The most successful run will be described here.

Onto 4.0 mmol of CF_3SO_2OBr at −195 °C was condensed 15 mmol of CCl_2F_2. An 8.8-mmol sample of *trans*-CHC=CHCl was then condensed onto the mixture, followed by an additional 26 mmol of CF_2Cl_2. The reaction was observed to occur at −111 °C, and the color of CF_3SO_2OBr disappeared. The reaction mixture was then pumped through traps at −10, −100, and −195 °C. The −10 °C trap contained *threo*-$CF_3SO_3CHClCHBrCl$ contaminated with trace amounts of a heavier unidentified material. *threo*-$CF_3SO_3CHClCHBrCl$: colorless oil; fp −54.0 °C; IR 3000 (vw), 1448 (s), 1245 (sh, m), 1147 (s), 1060 (w), 1025 (w), 960 (br, s), 853 (br, m), 760 (w), 615 (w) cm^{-1}; NMR ϕ* 74.00 (s, CF_3); the ^{1}H spectrum was an AB spin system centered at δ 6.52 with J = 4.0 Hz and $J/\delta \simeq 0.1$.

Results and Discussion

Addition reactions of CF_3SO_2OCl and CF_3SO_2OBr to a variety of alkenes are summarized in Tables I and II. In nearly every case, the reactions proceed in high yield to give the desired product. The reactions must be carried out at low temperature to avoid degradation of the alkene and decomposition of the hypohalite. The least reactive alkene was CF_3CF=CF_2 with both compounds. The addition of the hypohalites to the alkenes takes place more readily than the substitutive electrophilic dehalogenation reaction when excess alkene is employed. As mentioned in the introduction, CF_3SO_2OCl and CF_3SO_2OBr undergo reactions with C–Cl and C–Br bonds in a variety of alkyls to form trifluoromethanesulfonates.[7,8] Thus in the addition reactions, further reaction or competing reactions were possible (eq 5 and 6).

$$CF_3SO_2OX + CH_2{=}CH_2 \rightarrow CF_3SO_2OCH_2CH_2Cl \xrightarrow{CF_3SO_2OX} (CF_3SO_2OCH_2)_2 + X_2 \quad (5)$$

$$CF_3SO_2OX + CF_2{=}CFCl \xrightarrow{-XCl} CF_3SO_2OCF{=}CF_2 \xrightarrow{CF_3SO_2OX} (CF_3SO_2O)_2CFCF_2X \text{ or } CF_3SO_2OCFXCF_2OSO_2CF_3 \quad (6)$$

These side reactions may occur to a small extent with many of the alkenes but were not observed as important reactions under the conditions used. The difficulty in controlling the reaction with *trans*-CHCl=CHCl may be due to direct reaction with the C–Cl bond and the formation of $(CF_3SO_2OCHF)_2$ in the reaction of CF_3SO_2OBr with *cis*-CHF=CHF is probably due to the subsequent substitution of the initial addition product. These types of reactions are anticipated to be more important for the partially halogenated alkenes and for bromides, on the basis of the observed reactivity of CF_3SO_2OCl and CF_3SO_2OBr with alkanes: R–Cl ≫ R_fCl and R_fBr > R_fCl.[7,8]

All of the new esters are stable in glass at 22 °C, and all probably have good thermal stability at considerably higher temperatures. Many of the compounds on which vapor pressures were determined showed no decomposition on heating up to 100 °C. The identification of the compounds by IR, NMR, and physical properties was straightforward in most cases. The IR spectra exhibit a characteristic ν(S=O) antisymmetric stretch for the CF_3SO_2O group between 1430 and 1470 cm^{-1} in each case. The remainder of the spectra contain bands in regions consistent for the compounds but not readily assignable to a specific group frequency.

The ^{1}H and ^{19}F NMR spectra provide a firm basis for structural assignment in nearly every case. The covalent CF_3SO_2O group exhibits a characteristic chemical shift very near ϕ* 75.0 in each compound and spin–spin coupling to α-fluorines of 5–6 Hz in most cases. Coupling with α-protons is of the order of 0.1–0.5 Hz and is normally not resolved. Longer range J_{FF} coupling is observed in several of the compounds, mainly to β-fluorines, and is of the order of 1–2 Hz. Rather complicated second-order spectra for the alkyl groups are observed in several instances. The addition products to c-C_5F_8 exhibit a very complicated pattern due to the eight magnetically nonequivalent fluorines in the cyclopentane ring. The addition products to CFCl=CF_2 exhibit an $ABXY_3$ spin system, with the chemical shifts of X and Y being very close. For the CF_3SO_2OBr product, the observed spectrum is much less complicated in appearance than that with the hypochlorite. This may indicate much different rotomer populations in the two derivatives. The remaining complicated spectra arise in the additions to *cis*- and *trans*-CHF=CHF. These are $ABMNX_3$ spin systems which show a nearly first-order appearance for the fluorine spectra but not for the proton spectra. All coupling constants except $^3J_{HH}$ can be closely estimated from the spectra, but $^3J_{HH}$ had to be determined

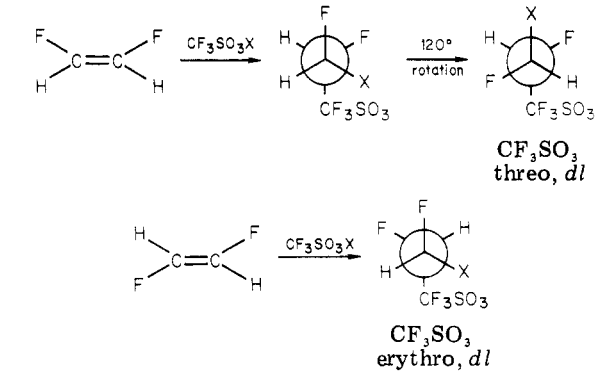
by computer simulation (LAACOON 3). An exact iterative fit was not made, but the estimated $^3J_{HH}$ values are very close to the actual values.[13]

The mechanisms of these addition reactions are of interest, and we believe we have sufficient data to make a case for a regio- and stereospecific cis addition which proceeds via a concerted pathway involving the initial interaction of the electrophilic halogen with the alkene. First, the question of nucleophilic vs. electrophilic addition must be decided. Because of the very low nucleophilicity of the $CF_3SO_3^-$ anion,[4,14] it is unreasonable to assume that the initial interaction with the alkene is nucleophilic in nature. While fluorinated olefins are readily attacked by nucleophiles,[15] weak nucleophiles need basic catalysts, and none are present here. In addition, the low reactivity of $CF_3CF{=}CF_2$ is inconsistent with a nucleophilic attack but is consistent with the expected slow reaction with a very strong electrophile.[16]

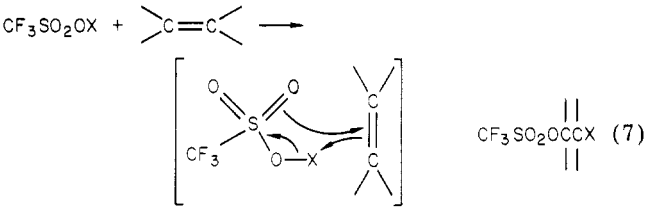
The second obvious point pertaining to these reactions is that only a single structural or geometrical isomer is observed in every case where differentiation can be made. The unsymmetrical alkenes, $CF_2{=}CFCl$, $CF_2{=}CH_2$, $CF_2{=}CCl_2$, and $CF_3CF{=}CF_2$, give only one of two possible structural isomers as determined by NMR. If the second isomer is formed it cannot be in greater than 1–2%. Otherwise, it would easily be seen in the ^{19}F NMR. With *trans*-CHCl=CHCl and CF_3SO_2OBr, a single diastereomer is formed, assuming that the chemical shifts of the CF_3SO_3 groups would be different in each diastereomer and that the ^1H spectra are not coincident. This is the case for several compounds where both diastereomers are obtained independently and for related compounds containing CF_3SO_2[7] and CF_3O[6] groups in place of CF_3SO_3. With *cis*- and *trans*-CFH=CFH, both CF_3SO_2OCl and CF_3SO_2OBr give a single different diastereomer for each. A mixture of cis and trans compounds gives the same ratio of the respective diastereomers within experimental error. Clearly, the additions of CF_3SO_2OX (X = Cl, Br) to alkenes are regio- and stereospecific. There may, of course, be examples that we have not examined where this might not be true, and one cannot say with certainty that the additions to c-C_5F_8 do not produce both cis and trans addition products.

The question that remains is whether the additions are cis (syn) or trans (anti). We propose that the additions are cis, giving rise to the erythro diastereomers with *cis*-CFH=CFH and the threo diastereomers with *trans*-CFH=CFH and CHCl=CHCl. This is based on the relative values of the $^3J_{HH}$, $^3J_{HF}$, and $^3J_{FF}$ coupling constants.[6,7] In those cases where both erythro and threo compounds are available, $^3J_{HH}$ values of ~4.0 Hz in both diastereomers imply trans hydrogens. The $^3J_{FF}$ values in *erythro*- and *threo*-$CF_3SO_3CHFCHFX$ (X = Cl, Br) are considerably larger for the addition product formed with the trans alkene, implying gauche fluorines for this case and trans fluorines for the addition product to the cis isomer. The $^3J_{HF}$ values, on the other hand, are only slightly different and are small in all cases, implying that the vicinal hydrogen and fluorine are gauche. This implies that the most stable rotomers are not the same in these

Scheme I



erythro and threo diastereomers and is logically consistent only with a cis addition (Scheme I). A more detailed discussion of this has already been presented.[6,7] The concerted cis addition can then be represented as in eq 7.



On the basis of the available data, it is not possible to say how the initial halogen–alkene interaction takes place. In some previous studies with CF_3OOCl,[9] the direction of addition to $CF_2{=}CFCl$ was opposite to that observed here. On the other hand, CF_3CO_2Cl adds in the same direction as CF_3SO_2OCl.[17] This variation in regiospecificity can be rationalized in part by the fact that the two mechanisms are not the same. One is a pseudo [2 + 2] addition and the others are pseudo [4 + 2] additions. On the other hand, all add in a Markownikoff manner to $CF_2{=}CH_2$. Clearly the real situation is complicated. What can be stated with certainty is that under the conditions specified and for the alkenes tried, the additions of CF_3SO_2OX to alkenes are regio- and stereospecific. We believe they are also cis. This control of stereochemistry along with the variety of compounds that can be synthesized should make CF_3SO_2OX (X = Cl, Br) very useful in the synthesis of triflates.

Our proposed concerted syn addition for the addition of CF_3SO_2OX to alkenes is somewhat novel. The extensive literature on the stereochemistry of electrophilic addition contains relatively few references for syn stereospecific additions involving a halogen as the electrophile.[18] The vast majority of such additions are anti additions and are believed to occur in a stepwise fashion. Direct comparison with our results is, however, difficult. Fluorinated olefins have not, in general, been used as probes for studying the stereospecificity of addition reactions, and few investigations have involved reagents as electrophilic as CF_3SO_2OX.

Acetyl hypobromite and acetyl hypochlorite are formally related compounds which could undergo reactions similar to that proposed for CF_3SO_2OX (and also CF_3CO_2Cl).[19] These hypohalites have been found to undergo electrophilic additions to olefins with a preponderance of anti over syn addition and a greater stereospecificity for the hypobromite.[20] No evidence was found to support a concerted

(13) In the compounds *erythro*- and *threo*-$CF_3SO_2OCFHCFHOC(O)CF_3$ an iterative fit of the spectra was carried out. The final $^3J_{HH}$ values differed only slightly from values estimated by simulation and visual matching of the spectra.[7]

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(19) The authors thank a reviewer for suggesting this comparison.

bimolecular addition of the type we have proposed, although the possibility of such a process was considered.[20,21] These differing results may be rationalized in part by the greater electrophilicity of CF_3SO_2OX and CF_3CO_2Cl.

Recently, an interesting discussion on the stereochemistry of electrophilic addition, based on an orbital symmetry approach, has appeared.[22] The addition of X–Y to an olefin is regarded as a $[2_\pi + 2_\sigma]$ cycloaddition, and a concerted cis addition is increasingly favored as the nucleophilicity of the olefin increases or the electrophilicity of X–Y increases. For the pseudo [4 + 2] additions of CF_3SO_2OX and CF_3CO_2Cl which we have proposed, the very pronounced electrophilicity of the hypohalites should favor the concerted syn addition.

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Registry No. CF_3SO_2OCl, 65597-24-2; $F_2C{=}CF_2$, 116-14-3; $ClFC{=}CF_2$, 79-38-9; $Cl_2C{=}CF_2$, 79-35-6; $CF_3FC{=}CF_2$, 116-15-4; *cis*-FHC=CHF, 1630-77-9; *trans*-FHC=CHF, 1630-78-0; c-C_5F_8, 559-40-0; $H_2C{=}CF_2$, 75-38-7; *trans*-ClHC=CHCl, 156-60-5; $H_2C{=}CH_2$, 74-85-1; $CF_3SO_3CF_2CF_2Cl$, 73323-71-4; $CF_3SO_3CClFCF_2Cl$, 73333-40-1; $CF_3SO_3CCl_2CF_2Cl$, 73323-72-5; $CF_3SO_3CF_2CFClCF_3$, 73323-73-6; *erythro*-$CF_3SO_3CHFCHFCl$, 73323-74-7; *threo*-$CF_3SO_3CHFCHFCl$, 73323-75-8; $CF_3SO_3CF(CF_2)_3CFCl$, 73323-76-9; $CF_3SO_3CF_2CH_2Cl$, 73323-77-0; $CF_3SO_3CF_2CH_3$, 73323-78-1; $CF_3SO_3CHClCHCl_2$, 73323-79-2; $CF_3SO_3CH_2CH_2Cl$, 73323-80-5; CF_3SO_2OBr, 70142-16-4; $CF_3SO_3CF_2CF_2Br$, 73323-42-9; $CF_3SO_3CClFCF_2Br$, 73323-43-0; $CF_3SO_3CCl_2CF_2Br$, 73323-44-1; $CF_3SO_3CF_2CBrFCF_3$, 73323-45-2; *erythro*-$CF_3SO_3CHFCHFBr$, 73323-46-3; *threo*-$CF_3SO_3CHFCHFBr$, 73323-47-4; $CF_3SO_3CF(CF_2)_3CFBr$, 73323-48-5; $CF_3SO_3CF_2CH_2Br$, 73323-49-6; *threo*-$CF_3SO_3CHClCHClBr$, 73323-50-9; $(CF_3SO_3CHF)_2$, 73323-51-0; $CF_3SO_3CF_3$, 3582-05-6; $CBrF_3$, 75-63-8.

Reactions of Acetoacetic Ester Blocked Cyclohexyl Isocyanate

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Acetoacetic ester has been widely reported to be a blocking agent for isocyanates. However, we find that only a trace of isocyanate is formed by thermolysis of acetoacetic ester blocked cyclohexyl isocyanate, **1**, at 150 °C and atmospheric pressure. The major portion is unchanged even after 8 h, with some conversion to acetylmalonic ester, **2**, and acetyl-*N*,*N*′-dicyclohexylmalonamide, **3**. Alcoholysis does not yield the "normal" urethane as blocked isocyanates do but rather esters of **1** with some diesters of **2** and smaller amounts of **3**. Significant amounts of *N*-cyclohexylacetamide, *N*-cyclohexylmalonamate ester, and some *N*,*N*′-dicyclohexylmalonamide are also obtained. Aminolysis leads to N-substituted acetamides and *N*-cyclohexylmalonamate but no substituted ureas, the "normal" products for aminolysis of blocked isocyanates. In the presence of acid catalysts, alcoholysis leads to *N*-cyclohexylmalonamates with acetate esters as the other product.

In our continuing work on blocked isocyanates,[1-3] we have investigated the reactions of acetoacetic ester blocked cyclohexyl isocyanate. Petersen reported that acetoacetic ester blocked hexamethylene diisocyanate had a low "splitting temperature" of about 140 °C based on the cross-linking of partially acetylated cellulose on heating for 0.5 h.[4] Several papers and patents also report the use of acetoacetic ester blocked isocyanates.[1] Since the cited review paper, other patents have been issued,[5] and a commercial product reported to be an acetoacetic ester blocked polyfunctional isocyanate has become available.[6] Implicit in all of these reports is the assumption that the blocked isocyanates cleave to give the isocyanate which then reacts with hydroxy groups to give polyurethanes. However, no evidence for the structure of the reaction products has been published.

In view of the "abnormal" products obtained with malonic ester blocked isocyanates,[2,3,7] we decided to investigate the reactions of an acetoacetic ester blocked isocyanate. Since two of the isocyanates in wide commercial use are bis(4-isocyanatocyclohexyl)methane and 1-(isocyanato)-3-(isocyanatomethyl)-3,5,5-trimethylcyclohexane, we selected cyclohexyl isocyanate as a monofunctional model isocyanate.

Results and Discussion

Acetoacetic ester blocked cyclohexyl isocyanates (acetyl-*N*-cyclohexylmalonamates) **1** were found to be essentially 100% enolized in $CDCl_3$ with an extreme downfield NMR shift of the enol H (δ 18.6). The products of thermolysis at 150 °C and atmospheric pressure and alcoholysis with 1-hexanol at 120–150 °C are shown in Scheme I.

In the thermolysis reaction, only a trace of isocyanate was formed, and no urethane was detected from the al-

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