Perhaloalkyl Hypochlorites and Pentafluorosulfur Hypochlorite. IV. Reactions with Olefins

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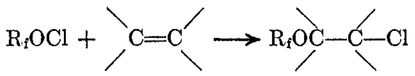
Polyfluoroalkyl hypochlorites add readily and, in most cases, nearly quantitatively to both unsubstituted and halogen-substituted terminal olefins. The direction of addition is such that when the hypochlorites are added to unsymmetrical olefins the principal product is an ether in which the chlorine atom of the hypochlorite has become bonded to the olefinic carbon bearing the greatest electron density.

We have recently described the preparation of several members of a new class of compounds, the polyfluoroalkyl hypochlorites,[1-3] and have shown that they undergo facile and nearly quantitative insertion of carbon monoxide or sulfur dioxide into the oxygen–chlorine bond to produce chloroformates and chlorosulfates, respectively.[3,4] Schack and coworkers have also prepared some of these compounds[5,6] and have briefly described the addition of trifluoromethyl hypochlorite and pentafluorosulfur hypochlorite to two fluorinated olefins, tetrafluoroethylene and chlorotrifluoroethylene.[7]

We have investigated a more extensive series of reactions between the polyfluoroalkyl hypochlorites and selected olefins and have shown that the reaction is quite general for terminal olefins and that, in most cases, the addition is nearly quantitative and predominantly unidirectional. The generalized equation below represents the reactions and products described in this work.



$R_f = CF_3$–; olefin = C_2F_4, C_2H_4, C_2F_3Cl, C_2H_3Cl, CF_2CH_2, $CF_3OCH{=}CH_2$
R_f = *i*-C_3F_7–; olefin = C_2F_4
$R_f = (CF_3)_3C$–; olefin = C_2F_4, C_2H_4
$R_f = SF_5$–; olefin = C_2F_4, C_2H_4

In appropriately substituted cases, the polyhaloethers were dehydrohalogenated to yield perfluoroalkyl vinyl ethers, $R_fOC{=}C<$, providing a simple route to the synthesis of such materials.

Experimental Section

The polyfluoroalkyl hypochlorites and pentafluorosulfur hypochlorite were prepared by methods previously described.[1-3] Ethylene was obtained from the Matheson Company and chlorotrifluoroethylene from Peninsular ChemResearch. Vinyl chloride and tetrafluoroethylene were obtained from the Allied Chemical Corporation's Plastics and Specialty Chemicals Divisions, respectively.

Infrared spectra were obtained using a Perkin-Elmer Model 137B spectrophotometer. Nuclear magnetic resonance spectra were obtained with a JEOLCO C60H or Varian 56-60 spectrometer.

All the ethers were prepared in the same general manner: A small amount (~3-15 mmol) of the desired hypochlorite (R_fOCl) was condensed into a 30-ml stainless steel cylinder using standard vacuum techniques and a nickel–Monel vacuum system. The temperature of the reaction cylinder was then brought to a temperature at which the hypochlorite was liquid but had a rather small vapor pressure. Incremental portions of the olefin were then added to the reaction cylinder through pressurization, and, when a stoichiometric amount of the olefin had been added, the temperature was allowed to warm to room temperature. Trap-to-trap fractionation followed (in some instances) by gas–liquid chromatography using a 0.25 in. × 12 ft column packed with Kel-F No. 10 oil on Teflon (20% by weight) usually produced a pure product.

The experimental conditions for preparing these compounds are given in Table I. Spectroscopic values are provided in Table II. The dehydrochlorination of $CF_3OCH_2CH_2Cl$ was performed by condensing approximately 3 mmol of $CF_3OCH_2CH_2Cl$ into a 75-ml stainless steel cylinder containing about 5 g of KOH pellets. The mixture was then heated to 100° and maintained at this temperature for about 16 hr. The resultant $CF_3OCH{=}CH_2$ was purified by trapping it at −158°. The impurities, which were more volatile, passed to a −196° trap.

Discussion

The high-yield (>90%) additions of polyfluoroalkyl hypochlorites, R_fOCl, to olefins under even the most stringent conditions (*i.e.*, direct combination of undiluted reactants in substantial amounts) is in marked contrast to the behavior of R_fOF analogs with the same olefins. Cady, for example, has shown that CF_3OF reacts violently with tetrafluoroethylene, $CF_2{=}CF_2$, over a wide range of conditions and in almost all concentrations to yield polytetrafluoroethylene and degradation products rather than the adduct $CF_3OCF_2CF_3$.[8] In the case of ethylene, addition of CF_3OF was only possible under conditions of gas-phase mixing at very high dilution with inert gas.[9] Additions of the bifunctional fluoroxy compound $CF_2(OF)_2$ to fluoro olefins were only possible when the gas-phase reactions were greatly moderated by an inert diluent, and even then explosions were common.[10]

Because of the great difficulty in moderating the additions of R_fOF compounds to olefins, the direction of addition to unsymmetrically substituted double bonds has only been established in one case. Williamson[11,12] has shown that the carefully moderated addition of

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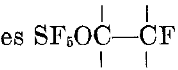
TABLE I

PREPARATION OF THE ETHERS[a]

Ether	Reactants	Reaction temp, °C	Bp, °C	Fractionation temp,[b] °C	% C		% F		% Cl	
					Calcd	Found	Calcd	Found	Calcd	Found
$CF_3OCF_2CF_2Cl$	CF_3OCl $CF_2{=}CF_2$	−80	10.6[c]	−111	16.34	16.34	60.32	60.10		
$CF_3OCH_2CH_2Cl$	CF_3OCl $CH_2{=}CH_2$	−80	63	−63					23.91	25.39
$CF_3OCHClCH_2Cl$	CF_3OCl $ClCH{=}CH_2$	−111		−45	19.7	19.04	31.15	30.50	38.8	37.71
$CF_3OCF_2CH_2Cl$	CF_3OCl $CF_2{=}CH_2$	−80	40	−80	19.51	19.47	51.49	51.00		
$(CF_3O)_2CHCH_2Cl$ + $CF_3OCHClCH_2OCF_3$	CF_3OCl $CF_3OCCl{=}CH_2$	−111		−45	17.98	17.62	42.70	41.39		
$CF_3OCF_2CFCl_2$ + $CF_3OCFClCF_2Cl$	CF_3OCl $CF_2{=}CFCl$	−80		−80					29.93	29.29
$(CF_3)_2CFOCF_2CF_2Cl$	i-C_3F_7OCl $CF_2{=}CF_2$	−20	54	−111	18.72	18.58	65.21	64.82		
$(CF_3)_2CHOCF_2CF_2Cl$	$(CF_3)_2CHOCl$ $CF_2{=}CF_2$	∼−80		−80	19.83	19.50	62.80	62.56		
$(CF_3)_3COCH_2CH_2Cl$	$(CF_3)_3COCl$ $CH_2{=}CH_2$	−45		−45	24.12	24.08	57.29	57.00	11.89	11.85
$(CF_3)_3COCF_2CF_2Cl$	$(CF_3)_3COCl$ $CF_2{=}CF_2$	−45	80	−80	19.43	19.31	66.67	66.10	9.57	9.95
$SF_5OCH_2CH_2Cl$	SF_5OCl $CH_2{=}CH_2$	−80		−63			46.00	46.93	(15.49)	(% S = 14.85)
$SF_5OCF_2CF_2Cl$	SF_5OCl $CF_2{=}CF_2$	−80		−100	8.63	8.25			12.74 (11.50)	12.67 (% S = 11.01)

[a] Several of the ethers described here have been previously prepared by others, some by alternate methods ($CF_3OCF_2CF_2Cl$,[d] $CF_3OCH_2CH_2Cl$,[e] and i-$C_3F_7OCF_2CF_2Cl$[f]) and others by essentially the same method ($CF_3OCF_2CF_2Cl$, $SF_5OCF_2CF_2Cl$, and the mixture of $CF_3OCFClCF_2Cl$ + $CF_3OCF_2CFCl_2$[7]). [b] The fractionation temperature is the higher temperature trap for a trap-to-trap fractionation. The second trap was invariably set at −196°. [c] See ref 7. [d] A. V. Tumanova, V. A. Gukanov, and I. M. Dolgopol'sk, *Zh. Obshch. Khim.*, **35**, 587 (1965). [e] P. E. Aldrich and W. A. Sheppard, *J. Org. Chem.*, **29**, 11 (1964). [f] H. R. Nychka and R. E. Eibeck, private communication.

SF_5OF to unsymmetrical olefins produces  $SF_5O\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}F$ adducts in which the fluorine atom of the OF group adds to the carbon with the *least* electron density.

For the cases investigated here, the polyfluoroalkyl hypochlorites, R_fOCl, behave toward olefins in a manner more closely resembling that of alkyl hypochlorites, $ROCl$, than of the fluoroxy compounds, R_fOF (*i.e.*, they add nearly quantitatively and predominantly unidirectionally across the double bond). The direction of addition for both R_fOCl and $ROCl$ is the same, with the result that a bond between the most electron-rich carbon of the alkene with the chlorine atom from the hypochlorite is formed. For instance, in the reaction of CF_3OCl with $CF_2{=}CH_2$, it was shown by ^{19}F and ^1H nmr studies that the $CF_3OCF_2CH_2Cl$ isomer comprised 96% of the ether product. The resonance signal of the $-CF_2-$ fluorines was observed as a 1:5:10:10:5:1 sextet, the multiplicity being attributed to near equivalence of the magnitude of J_{FH} and J_{FF}. Furthermore, the direction of addition in the reaction of CF_3OCl and vinyl chloride provided $CF_3OCHClCH_2Cl$ and not $CF_3OCH_2CHCl_2$. The configuration of the ether was indicated by the proton nmr spectrum of its dehydrochlorination product. The latter, a vinyl ether which was recovered as the sole product of the dehydrochlorination in near-quantitative yield, was found to contain a terminal $=CH_2$ group. Such a group would not result from the dehydrochlorination of $CF_3OCH_2CHCl_2$ but would be expected from $CF_3OCHClCH_2Cl$.

The predominance of the favored isomer is, expectedly, related to the degree of difference in electron density between the two carbon atoms of the olefin, and in cases where this is small ($CF_2{=}CFCl$, $CF_3CF{=}CF_2$) significant amounts of both isomers are formed.

The very highly fluorinated ethers, $R_fOCF_2CF_2Cl$, formed when tetrafluoroethylene is the substrate for hypochlorite addition, are exceptionally stable compounds. They undergo little or no change when held at temperatures in excess of 400° for over 1 week and may be held over KOH pellets at room temperature without harm (higher temperatures were not studied).

The less highly fluorinated ethers, such as $CF_3OCH_2CH_2Cl$, which have chlorine and hydrogen bonded to adjacent carbon atoms, readily undergo dehydrohalogenation as mentioned above. The resultant fluoro olefin can then be reacted again with the same or an alternate hypochlorite. In this way a number of interesting polyfluoroethers can be prepared. A simple example of this buildup is represented by the equations below.

$$CF_3OCl + CH_2CH_2 \longrightarrow CF_3OCH_2CH_2Cl$$

$$CF_3OCH_2CH_2Cl \xrightarrow{KOH} CF_3OCH{=}CH_2$$

$$CF_3OCH{=}CH_2 + CF_3OCl \longrightarrow$$
$$(CF_3O)_2CHCH_2Cl + \text{trace of } CF_3OCHClCH_2OCF_3$$

Although our studies of this area have not been sufficiently extensive to define the limits of its applicability, even the most cursory examination of the rather large number of fluorinated hypochlorites and olefins available suggests that quite large numbers of fluorine-containing polyethers may be possible by this method.

TABLE II

CHARACTERIZATION OF THE ETHERS

Compd	Registry no.	^{19}F, ppm[a]	^{1}H, ppm[b]	J, Hz	Infrared, cm^{-1}
CF$_3$OCF$_2$CF$_2$Cl a b c	1561-50-8	$\phi_a = +55.8$ (triplet) $\phi_b = +89.1$ (quartet of triplets) $\phi_c = +73.9$ (unresolved)	X X X	$J_{ab} = 9.25$ $J_{bc} = 1.8$	1369 (m), 1297 (vs), 1270 (vs), 1212 (vs), 1181 (vs), 1143 (m, shoulder), 1072 (w), 990 (m), 927 (vw), 894 (w), 862 (w), 827 (w), 695 (vw), 665 (w)
CF$_3$OCH$_2$CH$_2$Cl a b c	1645-95-0	$\phi_a = +61.6$ (singlet)	A$_2$B$_2$ $\delta_b \cong -4.18$ $\delta_c \cong -3.66$	$J_{bc} = 6.0$	3030 (w), 1470 (vw), 1408 (mw), 1280 (vs), 1258 (vs, (shoulder), 1170 (vs), 1078 (w), 1050 (w), 780 (mw), 725 (w), 694 (w)
CF$_3$OCHClCH$_2$Cl a b c	25957-32-8		$\delta_b = -5.92$ (triplet) $\delta_c = -3.78$ (dectet of triplets)	$J_{bc} = 5.5$	3000 (w), 1440 (w), 1285 (vs), 1220 (s), 1200 (s), 1110 (m), 1042 (m), 944 (w), 885 (vw), 287 (w, shoulder), 795 (m), 745 (s)
CF$_3$OCF$_2$CH$_2$Cl a b c	25957-33-9	$\phi_a = +56.2$ (triplet) $\phi_b = +77.5$ (sextet)	$\delta_c = 3.75$	$J_{ab} = 9.4$ $J_{bc} = 9.3$	3000 (vw), 1430 (m), 1333 (s), 1300 (s) 1235 (s), 1190 (s), 1118 (s), 1110 (s, shoulder), 958 (m), 925 (m), 880 (m), 837 (m), 807 (m)
(CF$_3$O)$_2$CHCH$_2$Cl + CF$_3$OCHClCH$_2$OCF$_3$		Mixture which was not separated			
CF$_3$OCF$_2$CFCl$_2$ + CF$_3$OCFClCF$_2$Cl		Mixture which was not separated			
(CF$_3$)$_2$CFOCF$_2$CF$_2$Cl a b c d	25957-34-0	$\phi_a = 80.3$ (triplet of doublets) $\phi_b = 143.1$ (complex triplet) $\phi_c = 83.8$ (complex doublet) $\phi_d = 73.2$ (complex)	X X X X	$J_{ab} = 1.8$ $J_{bc} = 21.8$ $J_{cd} = 2.1$ $J_{ac} = 6.3$	1322 (m), 1308 (m), 1250 (s), 1198 (s), 1147 (s), 1125 (s), 1111 (m), 990 (m), 970 (s), 725 (m), 710 (m), shoulder)
(CF$_3$)$_2$CHOCF$_2$CF$_2$Cl a b c d	25957-35-1	$\phi_a = 73.5$ (dectet of triplets) $\phi_c = 88.1$ (triplet) $\phi_d = 72.8$ (unresolved)	$\phi_b = -4.85$ (septet)		1356 (m), 1320 (w), 1205 (m), 1255 (s), 1220 (s), 1190 (s), 1155 (m), 1138 (m), 1120 (m), 1100 (w), 1072 (w), 972 (m), 903 (m), 805 (m), 730 (m), 690 (m)
(CF$_3$)$_3$COCH$_2$CH$_2$Cl a b c	25957-36-2	$\phi_a = +74.4$ (singlet)	$\delta_c = -4.26$ $\phi_d = -3.61$	$J_{ab} = 0.7$ $J_{bc} = 6.0$	3035 (mw), 1470 (mw), 1410 (mw), 1312 (s, shoulder), 1280 (vs), 1235 (m), 1190 (ms), 1170 (vs), 1090 (mw), 1030 (ms), 1015 (ms), 980 (s), 794 (mw), 735 (s), 693 (mw)
(CF$_3$)$_3$COCF$_2$CF$_2$Cl a b c	25957-37-3	$\phi_a = +70.3$ (triplet) $\phi_b = +84.0$ (dectet of triplets) $\phi_c = +73.3$ (unresolved)	X X X	$J_{ab} = 9.5$ $J_{bc} = 2.0$	1290 (vvs), 1232 (m), 1193 (s), 1185 (s, shoulder), 1137 (s), 1111 (m), 1098 (m), 998 (s), 981 (s), 972 (s, shoulder), 807 (mw), 796 (mw), shoulder), 769 (w), 733 (s), 671 (w)
FSF$_4$OCH$_2$CH$_2$Cl a b c d	26039-34-9	AB$_4$[c] $\phi_a = -74.9$ $\phi_b = -59.8$	A$_2$B$_2$ $\delta_c = -74.9$ $\delta_d = -3.62$	$J_{ab} = 146$ $J_{cd} = 6.2$	3005 (w), 1470 (w), 1312 (w), 1175 (ms), 1042 (s), 911 (vs), 894 (vs), 856 (ms), 785 (w), 725 (w), 695 (w)
FSF$_4$OCF$_2$CF$_2$Cl a b c d	25353-14-4	$\phi_a = -60.2^c$ $\phi_b = -71.0$ $\phi_c = +87.1$ $\phi_d = +72.5$	X X X X	$J_{ab} = 153.6^c$ $J_{ac} = 2.6$ $J_{bc} = 12.6$ $J_{cd} = 1.95$	1315 (m), 1202 (vs), 1126 (s), 995 (s, shoulder), 990 (s), 944 (s), 929 (s), 899 (ms), 820 (s), 744 (w), 675 (w)

[a] Relative to CF$_3$Cl internal standard. [b] Relative to TMS internal standard. [c] The calculations of the nmr spectra for the AB$_4$ models were accomplished by the use of a generalized seven-spin program written for the IBM 360/50 computer. An excellent fit of the theoretical and experimental plots indicated that the calculated parameters were accurate.

One surprising aspect of this study is that attempts to add trifluoromethyl hypochlorite to either perfluoro-2-butene or perfluoro-2-butyne were unsuccessful, though in each case the reaction mixture was heated to the decomposition point of the hypochlorite (~150°).

The mechanism for the reactions described here remains uncertain. The direction of addition to unsymmetrical olefins, *i.e.*, $CF_2{=}CH_2$, argues for a "Cl^+" type mechanism rather than a radical process, but the definitive experiments with radical inhibitors and with certain specialized olefins have not been performed.

Registry No.—Pentafluorosulfur hypochlorite, 22675-70-3.

Halogenated Ketenes. XV. Studies on Aldohalo- and Aldoalkylketene Cycloadditions[1]

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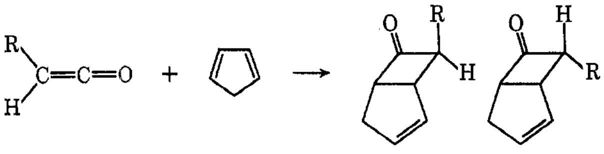
The dehydrohalogenation of haloacetyl halides in the presence of cyclopentadiene produces the corresponding 1,2 cycloadducts of fluoro-, chloro-, and bromoketenes. These unsymmetrical aldohaloketenes undergo cycloaddition stereospecifically to produce only the *endo*-halo isomer. Methyl-, ethyl-, and isopropylketenes were prepared in an analogous manner and the cycloadditions with cyclopentadiene were also stereospecific to yield only the *endo*-alkyl isomers. The results are discussed in terms of the principle of orbital symmetry conservation.

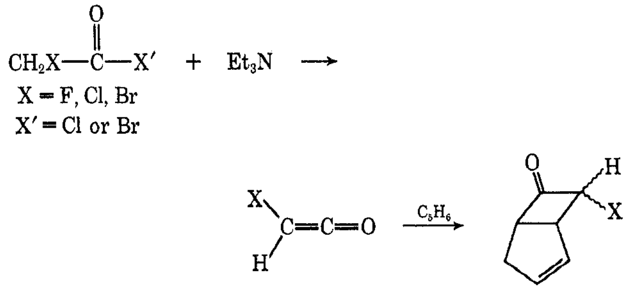
The cycloaddition of ketoketenes and olefins has received a lot of attention in the literature in the past few years. However, there have been essentially no reports on cycloadditions involving aldoketenes, presumably because of the instability of these ketenes and the necessity of performing *in situ* reactions. Since aldoketenes are unsymmetrical, the possibility exists for the formation of two stereomers in the (2 + 2) cycloaddition reaction as illustrated with cyclopentadiene. Unsymmetrical ketoketenes are, of course, also possible but the stereochemistry of these cycloadditions has apparently gone unnoticed. Hasek and Martin have reported the preparation of the cycloadduct of butylethylketene with cyclopentadiene but only mentioned that two isomers were apparently formed as evidenced by vpc.[2] Jaz and Denis have recorded in a communication the preparation of adducts of methyl-, ethyl-, *n*-propyl-, isopropyl- and *n*-butylketenes with cyclopentadiene but no mention was made about the stereochemistry.[3] We have recently reported on the stereochemistry of alkylhaloketene (unsymmetrical ketoketenes) and cyclopentadiene cycloadditions.[4-6]



Continuing our efforts in studies involving the preparation and cycloaddition of halogenated ketenes, we have investigated the aldohaloketenes. There has been only one report on this type of ketene and this was simply the mention of chloroketene by Opitz and coworkers on the cycloaddition with an enamine.[7] Consequently, the purpose of this paper is to describe the preparation of fluoro-, chloro-, and bromoketenes and relate the stereochemistry of the cycloadditions with cyclopentadiene and also the stereochemistry of some aldoalkylketene cycloadditions. Two preliminary reports of this work have appeared.[8,9]

Results

Fluoro-, chloro-, and bromoketenes were prepared by the dehydrohalogenation of the appropriately substituted acetyl halide with triethylamine at −78°. The ketenes could not be isolated but could be trapped by performing the cycloadditions in the presence of cyclopentadiene. The ketenes appeared to be quite stable in the reaction mixture at −78° but upon warming to room temperature polymerized to a black tar. The cycloaddition with cyclopentadiene does not occur at −78° as warming to room temperature is necessary to produce the bicyclo[3.2.0]hept-2-en-6-ones.



I, X = F
II, X = Cl
III, X = Br

Fluoroketene was also trapped with diisopropylcarbodiimide to form the 1,2 cycloadduct, 3-fluoro-1-isopro-

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