

The Addition of Fluorine to Halogenated Olefins¹

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The use of a mixture of lead dioxide and sulfur tetrafluoride as a reagent for the selective addition of fluorine to the double bond of halogenated olefins has been studied. This reagent generally affords higher yields under somewhat milder conditions than have been reported previously. Iodine-containing olefins have been fluorinated for the first time. Four new halocarbons, namely 1,1-dichloro-1,2-difluoroethane, *dl*-1,2-dichloro-1,2-difluoroethane, *meso*-1,2-dichloro-1,2-difluoroethane, and 1-bromo-1,2-difluoroethane, have been synthesized and characterized.

The selective addition of fluorine to the double bond of a halogen-containing olefin was first reported by Henne and Waalkes² in 1945. They employed lead tetrafluoride general *in situ* from lead dioxide and hydrogen fluoride. Seven examples were cited with yields ranging from 17–59%. Antimony pentafluoride,³ cobalt trifluoride generated *in situ* from cobaltic oxide and hydrogen fluoride,⁴ preformed cobaltic fluoride,^{5–8} mercuric fluoride generated *in situ* from mercuric oxide and hydrogen fluoride,⁹ chlorine trifluoride,¹⁰ preformed manganese trifluoride,^{6,8} preformed silver difluoride,⁸ and preformed ceric fluoride⁸ all have been used for fluorination of double bonds. In general these methods have not found widespread synthetic application even though the yields in some cases were quite good. The procedures involving the *in situ* formation of lead tetrafluoride, cobalt trifluoride, or mercuric fluoride from the oxides and hydrogen fluoride require handling of large excesses of hydrogen fluoride if satisfactory yields are to be obtained; those employing preformed metal fluorides usually involve elemental fluorine or chlorine trifluoride which require special handling techniques. The olefins studied include a variety of two-, three-, and four-carbon olefins substituted by various combinations of fluorine, chlorine, and bromine, but perfluoro olefins and those containing iodine have not been investigated. The reaction conditions usually employed would be expected to result in extensive replacement of iodine.

The recently reported preparation of metal fluorides by the reaction of the corresponding oxides with sulfur tetrafluoride¹¹ suggested the possibility of employing this reagent for the *in situ* preparation of the metal fluoride used in the fluorination of double bonds. The anticipated advantage lay in the fact that water would not be one of the products, thus eliminating the need for a large excess of the fluorinating agent to drive the formation of the metal fluoride to completion. The results obtained on treating nineteen halogenated olefins, including four perfluoro olefins and two containing

iodine, with a mixture of lead dioxide and sulfur tetrafluoride are summarized in Table I. In most cases the yields were significantly higher than those from any of the previously reported methods. The advantage of the sulfur tetrafluoride method particularly was pronounced in the case of reactive olefins and those containing iodine. Since the examples cited in Table I were all run under the same reaction conditions, the yield and conversion data provide an estimation of the relative reactivity of the various olefins.

No effort was made to maximize the yield from each olefin, but the reaction was studied in some detail with trichloroethylene. Optimum reaction temperature ranged from about 40–100° with reaction times of 2–8 hr. Increasing the reaction temperature above about 120° resulted in extensive side reactions including replacement of chlorine and carbon-carbon bond scission. The optimum ratio of lead dioxide to trichloroethylene was about 1:1.5. The particle size of the lead dioxide had a slight but measurable effect on yield, the optimum being about 40–60 mesh. Lead tetrafluoride is presumably an intermediate in the fluorination process; however, if the olefin was added to preformed lead tetrafluoride under conditions which afforded a maximum yield in the one-step process, the yields and conversions were very low. The optimum ratio of sulfur tetrafluoride to trichloroethylene was about 5:1. The function of excess sulfur tetrafluoride is most likely that of a solvent in which the olefin double bond can be easily polarized.

Fluorination of either *cis*- or *trans*-1,2-dichloroethylene yielded both *dl*- and *meso*-1,2-dichloro-1,2-difluoroethane, although in slightly different ratios. It was shown in separate experiments that the olefins were thermally stable and were not isomerized, at the reaction temperature employed, by either lead dioxide or by sulfur tetrafluoride alone. It would appear, therefore, that the two fluorines being added cannot add simultaneously, and that a cyclic intermediate cannot be involved.

The possibility that the reaction proceeds *via* addition of sulfur tetrafluoride to the double bond is not thought to be likely. The haloalkyl sulfur trifluorides that would be formed by such an addition appear to be stable at temperatures considerably above those employed here.¹² For example, heptafluoropropyl sulfur trifluoride has been prepared¹² by addition of sulfur tetrafluoride to hexafluoropropene in the presence of cesium fluoride at 150°, whereas we found that sulfur tetrafluoride and hexafluoropropene in the presence of lead dioxide at 100° gave octafluoropropane in 63%

(1) This work was performed under the auspices of the U. S. Atomic Energy Commission.

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TABLE I
 LEAD DIOXIDE-SULFUR TETRAFLUORIDE FLUORINATION OF HALOGENATED OLEFINS

Olefin	Product(s)	% yield	% conversion	Chromatography	
				Column ^a	Temp., °C.
CF ₂ =CF ₂	C ₂ F ₆	2.1	2.0	A	100
	C ₃ F ₈	5.8	5.6		
	C ₄ F ₁₀ ^b	6.7	6.4		
CF ₃ CF=CF ₂	C ₃ F ₈	63.0	42.4	A	100
CF ₃ CF=CF ₂ CF ₃	C ₄ F ₁₀		<1	A	100
cyclo-C ₄ F ₆	cyclo-C ₄ F ₈	23.0	3.2	A	100
CF ₂ =C FCl	CF ₃ CF ₂ Cl	60.0	60.1	A	100
CF ₂ =CFBr	CF ₃ CF ₂ Br	57.1	45.1	B	20
CF ₂ =CFI	CF ₃ CF ₂ I	65.2	62.7	B	20
CF ₂ =CCl ₂	CF ₃ CFCl ₂	87.8	74.1	B	20
CF ₂ CF ₂ CF ₂ CCl=CCl	CF ₂ CF ₂ CF ₂ CFCICFCI ^c	46.6	8.9	C	50
CCl ₂ =CCl ₂	CFCl ₂ CFCl ₂	77.0	77.0	C	100
CCl ₂ =CFCl	CFCl ₂ CF ₂ Cl	77.4	77.4	C	70
CF ₂ =CHF	CF ₃ CHF ₂	40.8	40.8	A	100
CCl ₂ =CHCl	CFCl ₂ CHFCI	85.1	85.1	C	50
CHF=CFCl	CHF ₂ CF ₂ Cl	95.8	89.2	A	100
CF ₂ =CHI	CF ₃ CHFI	53.4	53.4	C	70
CF ₂ =CH ₂	CF ₃ CH ₂ F	27.6	21.5	A	100
CCl ₂ =CH ₂	CFCl ₂ CH ₂ F	58.8	58.8	C	50
<i>cis</i> -CHCl=CHCl	<i>dl</i> -CHFClCHFCI	68.5	46.0	C, D, E	50
	<i>meso</i> -CHFClCHFCI	21.1	14.2		
<i>trans</i> -CHCl=CHCl	<i>dl</i> -CHFClCHFCI	54.3	43.2	C, D, E	50
	<i>meso</i> -CHFClCHFCI	26.1	20.8		
CH ₂ =CHBr	CH ₂ FCH ₂ Br	19.8	19.8	C, D, E	50

^a See under Chromatography in the Experimental section. ^b Plus large amounts of polymer. ^c Presumably a mixture of *cis* and *trans* isomers.

 TABLE II
 PHYSICAL PROPERTIES AND N.M.R. DATA

	CFCl ₂ CH ₂ F	CHFClCHFCI		CH ₂ FCH ₂ Br
		<i>dl</i>	<i>meso</i>	
A ^a	7.74437	7.83872	7.81781	7.80861
B ^a	1564.2	1649.2	1644.4	1633.6
B.p. °C. (at 760 mm.)	48.4	59.4	59.9	58.3
Δ <i>H</i> _{vap} ^b	6807	7187	7167	7167
Trouton ratio	21.2	21.6	21.5	21.6
Mol. wt.				
Obsd.	131.2 ^c	134.9 ^d	138.3 ^d	145.6 ^d
Theor.	135.0	135.0	135.0	145.0
CH ^e		-1.34 ^f	-1.34 ^f	-1.83
CH ₂	+0.21			+0.09
CF	{ -11.0 ^g +132.2 ^h	+68.4 ^f	+89.9 ^f	{ +70.2 ^g +135.9 ^h
<i>J</i> _{CH,CF} ⁱ		{ 48.8 ^j 7.0 ^k	{ 49.1 ^j 7.2 ^k	{ 51.6 ^j 11.9 ^k
<i>J</i> _{CH,CH₂}				3.5, 5.4
<i>J</i> _{CH,CH}		3.77	3.83	
<i>J</i> _{CF,CF}	22.4	26.5	20.6	22.1
<i>J</i> _{CF,CH₂}	{ 13.6 ^k 46.5 ^j			{ 20.4, 22.5 ^k 46.5 ^j

^a A and B are the constants for the vapor pressure equation $\log P_{\text{mm of Hg}} = A - B/T^{\circ}\text{K}$ in the range 300–800 mm. The vapor pressure curves and constants derived therefrom were obtained as previously described by E. R. Bissell, *J. Org. Chem.*, **26**, 5100 (1961). ^b Calories/mole at the normal boiling point. ^c Determined by means of a gas density balance [A. Liberti, L. Conti, and V. Crescenzi, *Nature*, **173**, 1067 (1956)] using nitrogen and chlorodifluoromethane as carrier gases and 1,1-dichloroethylene as an internal standard. ^d Determined by PVT measurements. ^e N.m.r. chemical shifts are reported in p.p.m. relative to water for hydrogen and to hexafluoroacetone for fluorine. See ref. 19. ^f Typical ten-line spectrum for an A₂X₂ grouping. ^g For the fluorine adjacent to the chlorine or bromine substituent. ^h For the fluorine of the CH₂F group. ⁱ Coupling constants are given in cycles per second. ^j For the hydrogen with the fluorine on the same carbon. ^k For the hydrogen with the fluorine on the adjacent carbon.

yield. It could be argued that lead dioxide or one of the various possible lead fluorides or oxyfluorides could be more efficient than cesium fluoride as a catalyst for the decomposition of heptafluoropropyl sulfur trifluoride to octafluoropropane, but there is no evidence for such a supposition.

In the course of these experiments four previously unreported halocarbons were prepared. Physical

properties and nuclear magnetic resonance data (n.m.r.) are tabulated in Table II; infrared spectral data are given in the Experimental section.

The structure of the adduct from vinyl bromide was confirmed by infrared and n.m.r. spectra, molecular weight, and dehydrobromination to *cis*-1,2-difluoroethylene. The structures of the three dichloro compounds were readily and unequivocally established from

their infrared and n.m.r. spectra, their molecular weights, and the fact that each was readily dehydrochlorinated by treatment with bases to 1-chloro-1,2-difluoroethylene. The 1,1-dichloro and *meso*-1,2-dichloro isomers yielded exclusively *cis* olefin, while *dl*-1,2-dichloro-1,2-difluoroethane gave only *trans* olefin. The assignment of *dl* and *meso* configurations was made on this basis. The assignment of *cis* and *trans* configurations to the two isomers of 1-chloro-1,2-difluoroethylene was made on the following bases: (1) the CF absorption in the infrared spectrum of the *trans* isomer appears at a higher frequency than that of the *cis* isomer^{13,14}; (2) the intensity of the C=C stretching frequency is lower for the *trans* isomer than for the *cis* isomer¹⁵; (3) the total number of absorption bands is smaller for the *trans* isomer¹⁵; and (4) we have observed that for halogenated ethylenes the vapor-liquid phase chromatography (v.p.c.) retention time for the *trans* isomer is generally less than that for the *cis* isomer.

Experimental¹⁶

Materials.—Tetrafluoroethylene was prepared by the thermal depolymerization of polytetrafluoroethylene. 1-Chloro-1,2-difluoroethylene was prepared by zinc dechlorination of 1,2-difluoro-1,1,2-trichloroethane, and 1,1-difluoro-2-iodoethylene was made by dehydrochlorination of 1-chloro-1,1-difluoro-2-iodoethane.¹⁷ The remainder of the olefins, the lead dioxide, and the sulfur tetrafluoride were commercial products used without further purification.

Fluorination Procedure.—A 25-ml. stainless steel pressure vessel¹⁸ was charged with 3.59 g. (0.015 mole) of lead dioxide, 0.010 mole of the olefin, and 0.05 mole of sulfur tetrafluoride. Lead dioxide and liquid olefins were weighed directly into the vessel before closing; sulfur tetrafluoride and olefins which were gaseous at room temperature were measured gasometrically and were condensed into the pressure vessel which previously had been cooled in liquid nitrogen and evacuated. The reaction

vessel was allowed to warm to room temperature and then rocked at 100° for 2 hr. After cooling to room temperature, the volatile portion of the contents of the reaction vessel was vaporized through a wash tower containing 300 ml. of 30% aqueous sodium hydroxide cooled to 0°. Material passing the hydroxide wash was passed through a trap cooled in 1,2-dichloroethane slush (−36°) and condensed at liquid nitrogen temperature. The total amount of material thus obtained was measured either gasometrically or by transferring to a suitable container and weighing (after further drying, if necessary). High boiling products were recovered from the −36° trap by separating from the bulk of the water and drying with anhydrous magnesium sulfate or calcium chloride. Vapor-liquid phase chromatography (v.p.c.) was employed to analyze the products and to isolate samples for identification. For those products which had been reported previously, identification was made by comparison of infrared spectra with spectra of authentic samples or with published spectra.

Chromatography.—The analytical columns were 1/4-in.-o.d. copper or stainless steel tubing packed with 20 wt. % partitioning liquid on 42–60-mesh GC-22 firebrick (except for column A, which was a silica gel adsorption column). The lengths and partitioning agents were the following: (A) 7.5 ft., none; (B) 20 ft., di-*n*-decyl phthalate; (C) 3 m., di-*n*-decyl phthalate; (D) 3 m., nonylphenoxy(polyethoxy)ethanol; and (E) 3 m., Zonyl E-91.¹⁹ The carrier gas was helium at a flow rate of 100 ml./min. The detector was a thermal conductivity cell operated at 150°. Where the amounts of materials required were too large to be handled conveniently on a 1/4-in. column, a Model A-700 Autoprep²⁰ employing a 3/8-in.-o.d. aluminum column was used for the initial separations. The samples used for measurement of the n.m.r. and physical constants reported in Table II were rechromatographed until all three columns (C, D, and E) showed less than 0.1% total impurities.

Infrared Spectra. 1,1-Dichloro-1,2-difluoroethane.—3.41 (w) (CH stretch), 6.94 (w) (CH₂ deformation), 7.30 (w), 8.00 (m), 8.60 (s) (CF), 9.14 (s) (CF), 9.40 (s) (CF), 10.25 (vw), 10.67 (vs) (CF), 11.50 (vs) (probably CF), and 13.00 (m) μ .

dl-1,2-Dichloro-1,2-difluoroethane.—3.35 (w) (CH stretch), 7.63 (w) (CH deformation), 7.90–7.96 (vw doublet), 8.23 (m), 8.70 (m), 8.98 (s) (CF), 9.03 (s) (CF), 9.45 (s) (CF), 11.00 (vw), 12.05 (s), 12.83 (m), and 13.6 (w) μ .

meso-1,2-Dichloro-1,2-difluoroethane.—3.40 (w) (CH stretch), 7.30 (w), 7.45 (w) (CH deformation), 7.80 (w), 8.30 (m), 8.63 (w), 8.82 (s) (CF), 9.10 (vs) (CF), 9.47 (s) (CF), 10.30 (m), 12.10 (s), and 12.75 (vs) μ .

1-Bromo-1,2-difluoroethane.—3.35 (m) (CH stretch), 6.90 (w) (CH₂ deformation), 7.23 (m), 7.45 (w) (CH deformation), 7.90 (w), 8.35 (w), 8.95–9.02 (vs doublet) (CF) 9.20 (s, sh) (CF), 9.60 (vs) (CF), 11.00 (m), 11.12 (m), and 13.50 (vs) μ .

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