droxide solution. It was recrystallized from acetonitryl–acetone (1:2), m.p. 223°, $[\alpha]^{24}\mathrm{D}$ $-180°$ (*c* 0.5, 1:1 pyridine–ethanol).

Anal. Calcd. for $C_{18}H_{20}O_3N_4$: C, 63.51; H, 5.92; O, 14.11; N, 16.49. Found: C, 63.55; H, 5.88; O, 14.31; N, 16.71.

Di-*O*-acetyldehydro-L-rhamnosazone was obtained by acetylation of the former compound by a mixture of pyridine–acetic anhydride at 20°. It was recrystallized from ethanol, m.p. 180–181°.

Anal. Calcd. for $C_{22}H_{24}O_5N_4$: C, 62.25; H, 5.70; N, 13.20. Found: C, 62.64; H, 5.74; N, 13.29.

Acknowledgment.—We would like to express our appreciation to Professor M.-M. Janot (Paris) and Professor R. U. Lemieux (Alberta, Canada) for their suggestions, to Mr. J. Parello for the interpretation of the n.m.r. spectra, and to Mrs. M. Mester and Mrs. L. Allais for their assistance.

Addition of Acetaldehyde to Fluoroethylenes[1]

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Free-radical addition of aliphatic aldehydes to fluorinated olefins has been shown to yield ketones derived from addition of an acyl radical to the terminal carbon of the double bond.[2,3] It also has been shown that fluoroaldehydes add to fluoroolefins to give fluorooxetanes rather than carbonyl compounds.[4] In the present work it has been shown that under certain circumstances both types of products can be produced simultaneously.

Ultraviolet irradiation in the gas phase of mixtures of acetaldehyde and a fluorinated ethylene resulted in complex mixtures from which the ketone derived from addition of an acetyl radical to the CF_2 group of the olefin and the oxetane derived from cycloaddition of the aldehyde to the olefin were isolated by vapor–liquid partition chromatography (v.l.p.c.). Four olefins, tetrafluoroethylene, chlorotrifluoroethylene, bromotrifluoroethylene, and 1,1-dichloro-2,2-difluoroethylene, were studied. The major product in each case, as expected, was the ketone. The physical properties of the three new ketones isolated in this study are listed in Table I. 1,1-Dichloro-2,2-difluorobutanone-3, which has been described previously,[3] also is listed because some of the physical properties measured have not been reported. The yield of ketone is affected by reaction conditions (see Experimental) in approximately the way that would be expected assuming a free-radical mechanism as suggested by earlier workers.[2,3,5]

It is worth noting that, although both acetaldehyde and the olefin were present in substantial amount[6] in the final reaction mixture, increasing the time of irradiation actually decreased the yield. We attribute this to decomposition of the ketone under the influence of ultraviolet light.

The orientation of the addition was established by means of the n.m.r. spectra of the addition products. The data presented in Table II clearly excludes 2-halo-1,1,2-trifluorobutanone-3 as the structure of the ketone from either chlorotrifluoroethylene or bromotrifluoroethylene. The 2-halo structure would require CH chemical shifts more like that of 1,1,2,2-tetrafluorobutanone-3. The CF_2 shifts would be closer to that of the terminal CF_2 group in the tetrafluoro compound. The splittings of the CH, CF, and CF_2 groups would all be different from those observed, and the CH–CF and CH–CF_2 coupling constants would be smaller and greater, respectively, by about a factor of ten. Similar arguments exclude 1,1-difluoro-2,2-dichlorobutanone-3 as the structure of the ketone from 1,1-dichloro-2,2-difluoroethylene. These results support the conclusion of Muramatsu and Inukai[3] that the acyl radical attacks the CF_2 group.

In addition to the ketone, from tetrafluoroethylene and 1,1-dichloro-2,2-difluoroethylene, a second 1:1 adduct was isolated; and from chlorotrifluoroethylene, two more 1:1 adducts were obtained. Oxetane structures were assigned on the basis of infrared and n.m.r. spectra. In each case the infrared spectrum showed total absence of carbonyl absorption. Bands attributable to symmetric and asymmetric deformation of the methyl group were present. The proton n.m.r. spectra showed two resonances in the ratio of 3:1.

Only one oxetane is possible from tetrafluoroethylene, namely 2H-2-methyltetrafluorooxetane. Its F^{19} n.m.r. spectrum showed two approximately equal resonances both of which exhibited a typical weak-strong-strong-weak (AB) pattern (see Table III). The high-field pattern showed doublet fine structure indicating proximity to a single spin-one-half nucleus (the single proton). The pronounced shift of the other CF_2 resonance to lower field indicates that that CF_2 group is adjacent to an oxygen.[4]

Two oxetanes are possible from 1,1-dichloro-2,2-difluoroethylene. Only one was obtained, and it was assigned the structure 2H-3,3-dichloro-4,4-difluoro-2-methyloxetane on the basis of the very low-field position of the CF_2 resonance.

From chlorotrifluoroethylene four oxetanes (two *cis–trans* pairs) are possible; only two were isolated. The striking similarity in their infrared spectra suggested that they were a *cis–trans* pair. The low-field position of the CF_2 resonance in the n.m.r. spectra of both compounds supported this assignment and indicated that they were isomers of 2H-3-chloro-2-methyltrifluorooxetane. The n.m.r. spectrum of the lower boiling isomer was too complex for complete analysis, but the large CH–CF coupling constant and the apparent lack of coupling between the CH_3 and CF groups in the higher boiling isomer indicated that the latter was the *cis* (with respect to the CH_3 and Cl groups) isomer. Harris and Coffman[4] also assigned the *cis* configuration to the higher boiling isomer of the four fluorooxetanes for which they isolated *cis* and *trans* isomers.

The mass spectra of the four oxetanes were consistent with the assigned structures. The primary cracking

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[1] This work was performed under the auspices of the U. S. Atomic Energy Commission.

[2] J. D. LaZerte and R. J. Koshar, *J. Am. Chem. Soc.*, **77**, 910 (1955).

[3] H. Muramatsu and K. Inukai, *J. Org. Chem.*, **27**, 1572 (1962).

[4] J. F. Harris and D. D. Coffman, *J. Am. Chem. Soc.*, **84**, 1553 (1962).

[5] M. S. Kharasch, W. H. Urry, and B. M. Kuderna, *J. Org. Chem.*, **14**, 248 (1949).

[6] Each was in the order of 20–30%.

TABLE I

PHYSICAL PROPERTIES OF SOME HALOGENATED 3-BUTANONES AND HALOGENATED OXETANES

Compound	Yield,[a] %	Conversion, %	Density, g./ml./°C.	A^b	B^b	N.b.p., °C.	ΔH, cal./mole	TR[c]
$CH_3COCF_2CHF_2$	7.2	4.8	1.318/19	7.88437	1700.4	66.6	7396	21.8
CH_3COCF_2CHFCl	10.0[d]	7.3	1.355/23	7.81710	1819.6	95.4	7876	21.4
CH_3COCF_2CHFBr	20.3	11.9	1.694/25	7.87013	1937.1	115.1	8385	21.6
$CH_3COCF_2CHCl_2$	5.5	4.7	1.412/22	7.79801	1967.4	126.9	8489	21.2
$CH_3\overline{CHCF_2CF_2O}$	2.8	1.8	1.279/19			44		
$CH_3\overline{CHCFClCF_2O}$[e]	1.3	0.9	1.344/22	8.00664	1741.9	66.6	7525	22.1
$CH_3\overline{CHCFClCF_2O}$[f]	1.1	0.8	1.344/26	7.77109	1716.9	77.9	7578	21.6
$CH_3\overline{CHCCl_2CF_2O}$	2.1	1.8	1.395/23	7.78871	1877.7	109.4	8107	21.2

[a] For the reaction conditions reported in the Experimental section, based on olefin consumed. [b] *A* and *B* are the constants for the vapor pressure equation $\log P_{(\text{mm. Hg})} = A - B/T$ (°*K.*) in the range 300 to 800 mm. The vapor pressure curves and constants derived therefrom were obtained as previously described: E. R. Bissell, *J. Org. Chem.*, **26**, 5100 (1961). [c] Trouton ratio. [d] 17.2% with a 2:1 ratio of acetaldehyde to olefin. [e] *trans.* [f] *cis.*

TABLE II

NUCLEAR MAGNETIC RESONANCE SPECTRA OF FLUORINATED METHYL ETHYL KETONES[a]

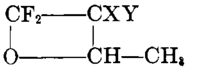
CH_3COCF_2CHXY

	X = F, Y = F	X = Cl, Y = F	X = Br, Y = F	X = Cl, Y = Cl
δ_{CH}	−0.70 T (T)	−1.45 D (Qa)	−2.00 D (Qa)	−1.23 T (S)
δ_{CH_3}	+2.95 S (T)	+2.65 T (D)	+2.43 S (T)	+2.45 S (T)
δ_{CF}		+79.63 D (T)	+82.20 D (T)	
δ_{CF_2}	+48.90 S (C)[b] +62.23 D (T)[c]	+44.13 +40.63 } AB (C)	+41.28 +37.08 } AB (Qa)	+35.73 D (Qi)
$J_{CH,CF}$		47.5	45.2	
J_{CH,CF_2}	52.3,[c] 9.8[b]	8.9, 7.3[d]	10.2, 7.6[d]	10.2
$J_{CH_3,CF}$		~0.5	~0	
J_{CH_3,CF_2}		~2	1.9	1.7
J_{CF,CF_2}		14.3	17.4	
J_{CF_2,CF_2}[e]		276	282	

[a] Chemical shifts are given in p.p.m., coupling constants in c.p.s. measured at 40 Mc. Proton shifts are with respect to external water; and F^{19} shifts are with respect to external hexafluoroacetone. The symbols following the chemical shifts give the structure of the band with fine structures given in parentheses: S, singlet; D, doublet; T, triplet; Qa, quartet; Qi, quintet; AB, weak-strong-strong-weak four-line spectrum typical of a CA_2 grouping where the two A nuclei are chemically nonequivalent; C, complex and/or not completely resolved. The authors are indebted to James A. Happe for measurement of the n.m.r. spectra. [b] For the CF_2 adjacent to the carbonyl group. [c] For the terminal CF_2 group. [d] The two fluorines of the CF_2 group are chemically nonequivalent, hence have different coupling constants. [e] J_{CF_2,CF_2} is the coupling constant between the two nonequivalent fluorine atoms of the CF_2 group.

TABLE III

NUCLEAR MAGNETIC RESONANCE SPECTRA OF FLUORINATED METHYL OXETANES[a]



	X = F, Y = F	X = Cl, Y = F[b]	X = Cl, Y = F[c]	X = Cl, Y = Cl
δ_{CH}	+0.28 Qi	0.0 Qi	0.0 Qi	−0.15 Qi (D)
δ_{CH_3}	+3.68 D	+3.50 D	+3.45 D	+3.25 D
δ_{CF}			+42.75	
δ_{CF_2}	+4.58 +0.93 } AB (C)[d] +53.05 +41.55 } AB (D)[f]	−4.28 AB[e]	+ 1.95 −8.45 } AB	−8.85 −13.28 } AB
J_{CH,CH_3}	6.8		6.2	6.3
$J_{CH,CF}$			13.5	
J_{CH,CF_2}	9.3[f]		5.4, 0.9	6.6, 0.8
J_{CH_3,CF_2}			0.9, 0.2	
J_{CF,CF_2}			9.2, 4.0	
J_{CF_2,CF_2}	104[d] 205[f]	96.0	96.1	90.5

[a] See Table II for explanation of symbols. [b] *trans.* [c] *cis.* [d] For the CF_2 group adjacent to the oxygen. [e] Average shift measured to the center of the AB spectrum. [f] For the CF_2 group adjacent to the carbon bearing the methyl group.

TABLE IV

YIELD AND CONVERSION OF HALOBUTANONE-3 AND HALOOXETANE FROM CHLOROTRIFLUOROETHYLENE UNDER VARIOUS CONDITIONS

Expt.	Ratio[a]	Pressure[b]	Temp., °C.	$t_{1/2}$[c]	% yield[d] Ketone	% yield[d] Oxetane[e]	% conversion Ketone	% conversion Oxetane[e]
1	1:1	0.79	23	295	10.0	2.4	7.3	1.7
2	1:1	0.79	21	200	5.9	2.3	5.3	2.0
3	2:1	0.79	21	210	17.2	2.6	12.6	1.9
4	1:2	0.79	20	260	6.1	2.5	4.4	1.8
5	1:1	0.53	22	265	5.5	1.3	4.6	1.1
6	1:1	0.79	55	150	11.5	1.7	8.7	1.3

[a] Mole ratio of acetaldehyde to chlorotrifluoroethylene. [b] Initial total pressure in atmospheres. [c] Time in minutes for pressure to fall to approximately one-half its initial value. The reaction was terminated at about this point except in expt. 2, which was run for 395 min. [d] Based on chlorotrifluoroethylene consumed. [e] Total of *cis* + *trans*. The ratio of *cis* to *trans* was 0.9 to 1.0 except in expt. 2 and 3 where it was about 1.6.

mode was cleavage to acetaldehyde and the olefin from which the oxetane was synthesized.

Experimental[7]

Materials.—Tetrafluoroethylene was prepared by the thermal depolymerization of polytetrafluoroethylene at 550–600° and about 10^{-6} atm. Acetaldehyde, chlorotrifluoroethylene, bromotrifluoroethylene, and 1,1-dichloro-2,2-difluoroethylene were commercial products used without further purification.

Reactions of Acetaldehyde with Fluoroolefins.—The reactor consisted of a 5-l. flask into which was inserted through a standard taper joint a water-cooled quartz well. A 100-w., high-pressure, mercury-vapor lamp[8] was suspended in the well at the center of the flask. Gaseous reactants were introduced through a vacuum manifold having a total volume of about 60 ml. and attached to a side arm on the reactor. Pressures were measured by means of a Wallace and Tiernan Type FA 145 precision dial manometer.[9] One of the reactants was introduced from a supply cylinder until the desired pressure was obtained. The second component of the reaction mixture was then introduced from a second supply cylinder until the desired total pressure was reached. The mixture was irradiated until the pressure had fallen to approximately half its initial value. This did not represent complete consumption of either component, but the yields of both ketone and oxetane actually decreased if the irradiation time was extended much further. Sizable quantities of high boiling telomeric materials accumulated in the bottom of the reactor. They were generally allowed to accumulate until a series of reactions was started with a different olefin at which time the reactor was disassembled for cleaning. The volatile portion of the reaction mixture was pumped from the reactor through an acetone–solid carbon dioxide-cooled trap and a liquid nitrogen-cooled trap in series. The contents of the two traps were measured either by weight or by PVT measurements, analyzed by v.l.p.c., and the major components isolated by preparative scale chromatography. Yields and conversions for several typical sets of reaction conditions for chlorotrifluoroethylene are given in Table IV. Yields and conversions for the other olefins under the same conditions as expt. 1 are given in Table I.

Chromatography.—Analyses employed a 0.25 in. × 3 m. stainless steel column packed with 35 g. of di-*n*-decyl phthalate (20 wt. %) on 42–60-mesh GC-22 Firebrick. Each purified component was checked for purity on this column and also on similar columns in which the partitioning liquid was Zonyl E-91[10] or nonylphenoxy(polyethoxy)ethanol. For isolation of samples for measurement of physical properties and spectra, the crude materials from the acetone–solid carbon dioxide-cooled trap were chromatographed in 0.5- to 2-ml. portions on $^3/_4$-, $^1/_2$-, or $^3/_8$-in. columns packed with the same materials as used for the analytical columns. The individually collected components were rechromatographed as often as necessary to remove all impurities. Since the larger diameter columns are much less efficient than the smaller diameter ones, they were used only for the initial separations. Purification was continued for each compound reported in Table I until all three analytical columns showed less than 0.1% total impurities.

1,1,2,2-Tetrafluorobutanone-3.—Major infrared absorption bands were at 3.32 (vw, CH stretch), 5.70 (s, C=O stretch), 7.01 (w, CH_3 asym. def.), 7.18 (m), 7.30 (m, CH_3 sym. def.), 8.00 (s, C=O), 8.80 (vs, CF), 9.47 (s, CF), 9.91 (w), 10.70 (w), and 12.10 (s) μ. The 2,4-dinitrophenylhydrazone melted at 108.2–109.2°.

Anal. Calcd. for $C_{10}H_8F_4N_4O_4$: C, 37.05; H, 2.49; N, 17.28. Found: C, 37.11; H, 2.30; N, 17.98.

1-Chloro-1,2,2-trifluorobutanone-3.—Major infrared absorption bands were located at 3.35 (vw, CH stretch), 5.70 (s, C=O stretch), 7.03 (m, CH_3 asym. def.), 7.30 (m, CH_3 sym. def.), 8.10 (s, C=O), 8.80 (s, CF), 9.04 (s, CF), 9.24 (s, CF), 9.46 (s, CF), 9.95 (w), 10.70 (w), 11.81 (s), 12.24 (s), and 12.68 (s) μ. The 2,4-dinitrophenylhydrazone melted at 102.9–103.5°.

Anal. Calcd. for $C_{10}H_8ClF_3N_4O_4$: C, 35.26; H, 2.37; N, 16.45. Found: C, 35.05; H, 2.22; N, 16.96.

1-Bromo-1,2,2-trifluorobutanone-3.—The crude reaction mixture from the addition of acetaldehyde to bromotrifluoroethylene was distilled at atmospheric pressure until the temperature at the head of a small Vigreux column reached about 30°. The residue was then chromatographed as described before to obtain the ketone. Major infrared absorption bands were at 3.40 (vw, CH stretch), 5.72 (s, C=O stretch), 7.06 (w, CH_3 asym. def.), 7.38 (m, CH_3 sym. def.), 8.14 (m, C=O), 8.85 (s, CF), 9.15 (vs, CF), 9.20 (vs, CF), 9.51 (m, CF), 9.97 (w), 10.75 (vw), 12.30 (w), 12.85 (vw), and 13.60 (m) μ. The 2,4-dinitrophenylhydrazone melted at 104.8–105.4°.

Anal. Calcd. for $C_{10}H_8BrF_3N_4O_4$: C, 31.19; H, 2.09; N, 14.65. Found: C, 30.95; H, 1.97; N, 15.10.

1,1-Dichloro-2,2-difluorobutanone-3.—Major infrared bands were at 3.37 (vw, CH stretch), 5.73 (s, C=O stretch), 7.08 (w, CH_3 asym. def.), 7.37 (m, CH_3 sym. def.), 8.03 (w, C=O), 8.21 (s, CF), 9.10 (s, CF), 9.51 (m, CF), 9.99 (m), 12.15 (s), 12.95 (m), and 13.35 (w) μ. The 2,4-dinitrophenylhydrazone melted at 126.0–126.8°.

Anal. Calcd. for $C_{10}H_8Cl_2F_2N_4O_4$: C, 33.63; H, 2.26; N, 15.69. Found: C, 33.41; H, 2.08; N, 16.01.

2H-2-Methyltetrafluorooxetane.—Major infrared absorption bands were at 3.40 (vw, CH stretch), 6.90 (w, CH_3 asym. def.), 7.13 (w, CH_3 sym. def.), 7.50 (vw), 7.75 (m), 8.10 (m), 8.47 (s, CF), 8.90 (w), 9.50 (sh), 9.60 (m), 9.68 (m), 10.38 (s), and 11.65 (w) μ.

***cis*-2H-3-Chloro-3,4,4-trifluoro-2-methyloxetane.**—Major infrared absorption bands were at 3.40 (vw, CH stretch), 6.93 (vw, CH_3 asym. def.), 7.30 (m, CH_3 sym. def.), 7.65 (m), 7.83 (s), 8.35 (sh), 8.58 (s, CF), 8.95 (m, CF), 9.40 (s), 10.35 (m), 10.70 (m), 11.53 (w), 14.00 (vw), and about 14.8 (vw) μ.

Anal. Calcd. for $C_4H_4ClF_3O$: C, 29.93; H, 2.51. Found: C, 29.93; H, 2.74.

***trans*-2H-3-Chloro-3,4,4-trifluoro-2-methyloxetane.**—Major infrared absorption bands were at 3.38 (w, CH stretch), 6.95 (w, CH_3 asym. def.), 7.30 (m, CH_3 sym. def.), 7.65 (m), 7.80 (s), 8.40 (s, CF), 8.60 (sh) (CF), 8.90 (m, CF), 9.40 (s), 9.60 (s), 10.20 (s), 10.72 (m), 11.60 (w), 13.50 (w), and about 15 (w) μ.

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(7) Melting and boiling points are corrected. Infrared absorption spectra were obtained in the vapor state on a Perkin-Elmer Model 137 Infracord spectrometer; wave lengths are in microns (μ). 2,4-Dinitrophenylhydrazones were prepared by the method of R. L. Shriner and R. C. Fuson ["The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 171] and were recrystallized to constant melting point from 95% ethanol; their analysis was performed by Robert Lim and Elinor R. Smathers. The elemental analyses of the oxetanes were performed by J. W. Frazer and R. Crawford [*Mikrochim. Acta*, **3**, 561 (1963)].

(8) Engelhard Hanovia, Inc., 100 Chestnut St., Newark 5, N. J., type SOL #608A-36 operated from a Hanovia #7654-1 reactive transformer.

(9) Wallace and Tiernan, Inc., 25 Main St., Belleville 9, N. J.

(10) E. I. du Pont de Nemours and Co., Inc., Organic Chemicals Department, Dyes and Chemicals Division, Wilmington 98, Del.

2H-3,3-Dichloro-4,4-difluoro-2-methyloxetane.—The molecular weight was determined chromatographically by means of a gas density balance,[11] using nitrogen and chlorodifluoromethane as carrier gases and 1,1-dichloro-2,2-difluorobutanone-3 as an internal reference, as 185 ± 10 (calcd. 177). Major infrared absorption bands were at 3.40 (vw, CH stretch), 6.95 (vw, CH$_3$ asym. def.), 7.35 (m, CH$_3$ sym. def.), 7.87 (vs), 8.45 (s, CF), 8.72 (s, CF), 9.15 (s, CF), 9.60 (s), 9.83 (s), 11.40 (s), and about 14 (vw) μ.

Anal. Calcd. for C$_4$H$_4$Cl$_2$F$_2$O: C, 27.15; H, 2.28. Found: C, 27.27; H, 2.46.

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[11] A. Liberti, L. Conti, and V. Crescenzi, *Nature*, **178**, 1067 (1956).

Some Isomers of Chloroiodotrifluoroethane[1]

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The synthesis of 1-chloro-2-iodo-1,1,2-trifluoroethane (I) by the addition of iodine monochloride to trifluoroethylene was first reported in 1956 by Park, Seffl, and Lacher.[2] The reaction was considered to be unidirectional, producing only I. Haszeldine and Steele[3] have offered some spectroscopic evidence that the concentration in the product of the isomer produced by reverse addition, 2-chloro-1-iodo-1,1,2-trifluoroethane (II) could not be more than 5%. However, in view of the recent discovery[4,5] that, contrary to earlier reports, both of the possible isomers from the addition of iodine monochloride to chlorotrifluoroethylene are in fact formed and, since several other addition reactions to trifluoroethylene have been shown to be bidirectional,[3,6] it was of interest to reinvestigate the trifluoroethylene–iodine monochloride system using more modern analytical techniques.

2-Chloro-1-iodo-1,1,2-trifluoroethane (II) has been prepared by addition of hydrogen iodide to chlorotrifluoroethylene.[3,7] Its ultraviolet absorption maximum was reported, but no experimental details were given for the synthesis, and the yield[3] was not stated. We were able to obtain only about 11% yields by this method. The remaining isomers of chloroiodotrifluoroethane have not been reported.

The present paper reports the results of a study of the addition of iodine monochloride to trifluoroethylene in both the presence and absence of a liquid phase and the results of a study of the effect of ultraviolet light and various metal chloride catalysts on the reaction and reaction products. One of these catalysts has lead to the synthesis of a third chloroiodotrifluoroethane isomer, 1-chloro-1-iodo-2,2,2-trifluoroethane (III).

The progress of the addition reactions was followed by observing changes in total pressure as a function of time, and the final product distribution was determined by means of vapor liquid phase chromatography (v.l.p.c.). Table I presents the results of a number of typical experiments in which a liquid phase was present. V.l.p.c. showed that along with the primary addition product (I) there was formed a small amount of a second material, which was shown by ultraviolet infrared, and n.m.r. spectra and by dehydrohalogenation to chlorotrifluoroethylene to be II. Raising the reaction temperature resulted in a decreased reaction rate but, unlike the effect of similar changes in the chlorotrifluoroethylene–iodine monochloride system,[4] did not materially effect the ratio of isomers produced. The failure of ferric chloride to catalyze the reaction or to alter the isomer ratio was also in marked contrast to its action in the chlorotrifluoroethylene system.[4] Aluminum chloride, on the other hand, did behave similarly in both systems. Stannic chloride appeared to be without effect.

The addition of iodine monochloride to trifluoroethylene was light catalyzed. Although the reaction was only slightly retarded in the dark if a liquid phase was present, it failed to occur at all in the dark if the reactants were completely in the vapor phase. Under these conditions reaction did occur in the light but at a much lower rate than when a liquid phase was present, and much larger amounts of II (26–36%) were formed.

In addition to its isolation as a by-product in the direct addition of iodine monochloride to trifluoroethylene, II was obtained from I by irradiation with ultraviolet light.[5] An equilibrium mixture containing 26–29% II was formed by irradiation of either I or II in the gas phase at room temperature.

Modification of the addition reaction by means of aluminum chloride resulted in the formation of two new compounds, III and 1-iodo-1,2,2,2-tetrafluoroethane (IV). Results for two typical small scale experiments are given in Table I (expt. 12 and 13), those for a larger scale experiment in the Experimental section. Compound III could be prepared more conveniently by treatment of I with aluminum chloride. Table II presents the results of several such experiments. The reaction was strongly exothermic, and yields decreased as the scale of the reaction was increased. However, if the temperature excursion was modified too much the reaction did not occur; for example, when I was added slowly under reflux to solid anhydrous aluminum chloride only 7–14% yields of III were obtained. The identities of III and IV were established by their ultraviolet, infrared, and n.m.r. spectra, by physical properties, and by their failure to dehydrohalogenate on treatment with bases. IV was identical with the product isolated from the addition of fluorine (from lead tetrafluoride) to 1,1-difluoro-2-iodoethylene.[8]

Reaction Mechanism.—The reaction conditions involving vapor phase and light catalysis are conditions generally associated with free-radical reactions, and the observed product distribution is in agreement with the observation of Haszeldine and Steel[3] that free-radical attack on trifluoroethylene is 60–80% on the CHF group and 20–40% on the CF$_2$ group. The fact that the isomer ratio is radically different when a liquid phase is present suggests a different mechanism under these conditions. That this mechanism is ionic, as originally proposed by Haszeldine and Steel,[3]

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