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 $C_4H_4Cl_2F_2O$: 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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[1] This work was performed under the auspices of the U. S. Atomic Energy Commission.

[2] J. D. Park, R. J. Seffl, and J. R. Lacher, *J. Am. Chem. Soc.*, **78**, 59 (1956).

[3] R. N. Haszeldine and B. R. Steele, *J. Chem. Soc.*, 2800 (1957).

[4] M. Hauptschein, M. Braid, and A. H. Fainberg, *J. Am. Chem. Soc.*, **83**, 2495 (1961).

[5] E. R. Bissell and G. C. Shaw, *J. Org. Chem.*, **27**, 1482 (1962).

[6] A. T. Coscia, *ibid.*, **26**, 2995 (1961).

[7] R. N. Haszeldine and J. E. Osborne, *J. Chem. Soc.*, 61 (1956).

[8] E. R. Bissell and D. B. Fields, unpublished results.

TABLE I

ADDITION OF IODINE MONOCHLORIDE TO TRIFLUOROETHYLENE IN THE PRESENCE OF A LIQUID PHASE

Expt.	Temp., °C.	Catalyst	Mole %	$t_{1/2}$[a]	Product distribution[b] % I	% II	% III	% IV
1	20–22			2.8	91.5	1.6	Trace	
2	38–40			4.0	95.0	1.9	Trace	
3	50–52			7.7	90.8	2.4	1.0	
4	60–65			24	88.3	3.7		
5	70–72			50	92.8	2.5		
6	21–24	Ultraviolet[c]		1.9	90.0	3.7		
7	22–26	Dark		5.5	91.6	2.6		
8	48–52	Dark		12.5	88.3	3.2		
9	20–22	$FeCl_3$	5	2.7	90.9	3.1		0.2
10	35–40	$FeCl_3$	2	3.8	87.6	3.0		3.3
11	38–42	$FeCl_3$	4	7.5	91.9	2.0	1.7	
12	18–21	$AlCl_3$	9	4.0	78.9	3.9	2.6	4.2
13	27–29	$AlCl_3$	12	8.5	71.7		3.9	9.6

[a] Time in minutes for the pressure to fall to the arithmetic average of the initial and final pressures. [b] $CF_2ClCHFCl$ (2–9%) and smaller amounts of several other unidentified by-products also were formed. [c] Ultraviolet light was supplied by a Bausch and Lomb type 33-45-65 mercury arc. Unless otherwise specified the reactions were carried out in the presence of ordinary fluorescent room lights.

TABLE II

TREATMENT OF 1-CHLORO-2-IODO-1,1,2-TRIFLUOROETHANE WITH ALUMINUM CHLORIDE

Expt.	Temp., °C.	$AlCl_3$/I, g./g.	Time, hr.	% organic recovery	Product distribution % I	% II	% III	% IV
1	21–23	0.11	23	50	12.2	1.5	55.7	2.9
2	21–23	0.12	17	50	11.4	2.7	60.5	2.5
3	21–23	0.12	8	60	28.9	6.2	44.1	1.6
4	0	0.11	24	50	46.3	1.3	30.1	2.2

seems unlikely in view of the bidirectional nature of the addition of iodine monochloride to chlorotrifluoroethylene even in the presence of a liquid phase.[4,5] The mechanism of addition to the two olefins would be expected to be the same, and ionic addition reactions have thus far been found to occur in only one direction. An alternate possible mechanism is the initial formation of a complex between the π-electrons of the olefin and iodine monochloride which subsequently is attacked by a second molecule of iodine monochloride. Such a π-complex was postulated by White and Robertson[9] to account for their observation that the rate of addition of bromine, iodine, iodine monochloride, and iodine monobromide to hydrocarbon olefins was second order with respect to the halogen. The difference in isomer ratio between trifluoroethylene and chlorotrifluoroethylene then would be attributed to differences in the electronic and/or steric nature of the olefins.

The ultraviolet equilibration of I and II probably proceeds through reversal of the iodine monochloride addition followed by readdition under free-radical conditions.

Experimental[10]

Addition of Iodine Monochloride to Trifluoroethylene. A. In the Presence of a Liquid Phase.—Iodine monochloride (0.25 ml., 0.80 g., 0.0049 mole) and the catalyst, if any, were placed in a 35-ml. Florence flask which was attached to a vacuum manifold by means of a ground glass joint. The flask was immersed in liquid nitrogen and evacuated to a pressure of 10^{-6} atm. The reactor was then isolated from the manifold and warmed to the desired reaction temperature by means of an oil bath. Agitation was provided by a magnetically driven stirring bar. The reaction was initiated by opening a stopcock connecting the reactor to a 1100-ml. reservoir containing trifluoroethylene (initially at room temperature and approximately 0.92 atm.) and was followed by periodic observation of the total pressure. After the pressure had essentially become constant the reactor was disconnected from the reservoir, and its contents were vaporized through a 10-mm. i.d. by 20-cm. column packed with 1.6-mm. 5-Å. Molecular Sieve pellets.[11] Material passing the Molecular Sieve column was trapped at liquid nitrogen temperature and analyzed by v.l.p.c. Reactions also were carried out on an 0.1-mole scale in a Parr low pressure hydrogenation apparatus. A typical experiment yielded 14–15 g. of liquid halocarbons containing 87–90% I. Preparative scale chromatography yielded pure I, n.b.p. 84.9°, log $P_{mm} = 7.56346 - 1676.7/T_{°K}$, ΔH 7282 cal./mole, Trouton ratio 20.3, $d_{22.5}$ 2.180 g./cc., ultraviolet λ_{max} 265 mμ (ϵ_{max} 295). The n.m.r. spectrum showed one CH resonance at −2.30, one CF resonance at −15.03, and one CF_2 resonance (AB_2 type) at +82.9 and +78.6 p.p.m.. The following coupling constants were determined: $J_{CH,CF}$ 43, J_{CH,CF_2} 7.7 and 5.5, J_{CF,CF_2} 23.2 and 22.2, and J_{CF_2} 159 c.p.s. Major infrared absorption bands were at 3.40 (vw), 7.52 (m), 8.22 (s), 8.77 (vs), 9.05 (s), 9.20 (s), 9.60 (s), 10.20 (vs), 12.30 (m), 13.05 (s), 13.45 (m), and 14.50 (w) μ.

B. In the Vapor Phase.—Iodine monochloride (25 μl., 81 mg., 0.0005 mole) was frozen by means of liquid nitrogen in a small side arm attached to a 5000-ml. round-bottomed flask which was then evacuated to a pressure of 10^{-6} atm. The flask was then isolated from the vacuum manifold, and the iodine monochloride was vaporized into it. An equimolar amount of trifluoroethylene was added from a reservoir of known volume. After 24 hr. at room temperature the reaction mixture was worked up as described previously.

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[9] E. P. White and P. W. Robertson, *J. Chem. Soc.*, 1509 (1939).

[10] The vapor pressure equations and constants derived therefrom were obtained as previously described [E. R. Bissell, *J. Org. Chem.*, **26**, 5100 (1961)]. Infrared absorption bands were measured in the vapor phase on a Perkin-Elmer Model 137 Infracord spectrometer and are reported in microns. Ultraviolet absorption spectra were taken in methylcyclohexane solution on a Cary recording spectrophotometer. N.m.r. spectra were measured at 40 Mc. Proton chemical shifts are quoted with respect to external water; F^{19} shifts with respect to external hexafluoroacetone. The author is indebted to James A. Happe for these measurements. Chromatographic analyses employed 6.25-mm. o.d. by 4-m. copper columns packed with 20 wt. % nonylphenoxy(polyethoxy)ethanol on 42–60-mesh GC-22 firebrick and operated at 78–80°.

[11] Linde Air Products Co., 30 East 42nd St., New York 17, N. Y.

2-Chloro-1-iodo-1,1,2-trifluoroethane (II) by Ultraviolet Light-Catalyzed Isomerization of I.—Isomerization was carried out in a 5000-ml. Pyrex reactor. The light source was a 100-w. mercury-vapor lamp[12] centrally located in a water-cooled quartz well. The reactor was surrounded by an aluminum can which was wrapped with heating tapes for the experiments above room temperatures. Samples (2.0 ml.) were introduced into the evacuated reactor as liquids by means of a hypodermic syringe through a rubber septum which could be isolated from the flask by a stopcock through which the syringe needle could be inserted. The reaction mixture was removed after irradiation by pumping it through a 25-mm. i.d. by 75-cm. column filled with 1.6-mm. 5-Å. Molecular Sieve pellets.[11] Material passing through the column was condensed in a liquid nitrogen-cooled trap. Total recovery amounted to 85–90%. After irradiation for 1 hr. at room temperature the recovered halocarbons contained 86% I and 13% II, after 3 hr. 72% I and 26% II, after 3 hr. at 65–70° 76% I and 18% II. When the sample size was reduced to 1.0 ml. the recovered material contained 66% I and 26% II. Insertion of a Pyrex sleeve between the lamp and the quartz well completely prevented isomerization. Preparative scale chromatography was employed to obtain pure II which had the following physical properties: n.b.p. 85.4°, log P_{mm} = 7.66157 − 1714.2/$T_{°K}$, ΔH 7448 cal./mole, Trouton ratio 20.8, d_{23} 2.185 g./cc., ultraviolet λ_{max} 270 mμ (ϵ_{max} 307). The n.m.r. spectrum showed one CH resonance at −1.20, one CF resonance at −21.5, and one CF_2 resonance (AB_2 type) at +63.4 and +61.3 p.p.m. The following coupling constants were measured: $J_{CH,CF}$ 48, J_{CH,CF_2} 5.8 and 4.0, J_{CF,CF_2} 21.7 and 20.9, and J_{CF_2} 191 c.p.s. Major infrared absorption bands were at 3.32 (w), 7.52 (m), 7.90 (w), 8.26 (s), 8.60 (sh), 8.80 (vs), 9.08 (s), 9.65 (vs), 10.50 (s), 11.70 (s), 12.00 (sh), 12.60 (m), and 13.55 (vs) μ.

1-Chloro-1-iodo-2,2,2-trifluoroethane (III) by Treatment of I with Aluminum Chloride.—I (1.0 ml., 2.18 g., 0.009 mole) and 0.25 g. (0.0019 mole) of anhydrous aluminum chloride were sealed in an evacuated Pyrex ampoule of about 10-ml. capacity. The ampoule was stored in the dark at the desired reaction temperature (see Table II) for 8 to 24 hr. The ampoule was then opened, and any volatile material in it was vaporized at room temperature and 10^{-6} atm. through a 10-mm. i.d. by 10-cm. bed of 5-Å. Molecular Sieve[11] and condensed in a liquid nitrogen-cooled trap. Pure III was obtained by preparative scale chromatography and had the following properties: n.b.p. 83.5°, log P_{mm} = 7.58749 − 1678.7/$T_{°K}$, ΔH 7284 cal./mole, Trouton ratio 20.4, d_{23} 2.210 g./cc., ultraviolet λ_{max} 275.5 mμ (ϵ_{max} 418). The n.m.r. spectrum showed one CH resonance at −1.30 and one CF_3 resonance at −4.50 p.p.m. The coupling constant between the CH and CF_3 groups was 6.2 c.p.s. Major infrared absorption bands were at 3.32 (w), 7.20 (s), 7.92 (vs), 8.40 (s), 8.62 (s), 9.05 (vs), 11.50/11.60 (m), 12.40 (s), and 15.00 (m) μ.

Addition of Hydrogen Iodide to Chlorotrifluoroethylene.—Chlorotrifluoroethylene (0.011 mole) and hydrogen iodide (0.016 mole) were condensed by means of liquid nitrogen into a 25-ml. stainless steel pressure vessel. After 26 days at ambient temperature the contents of the bomb were vaporized through a small Molecular Sieve[11] bed into a liquid nitrogen-cooled trap. The most volatile portion of the material held by the trap was pumped off until the remaining liquid had a vapor pressure of about 300 mm. at 23°. This liquid weighed 0.31 g. and contained 94.9% II by v.l.p.c. analysis.

1-Iodo-1,2,2,2-tetrafluoroethane (IV).—Pure IV was isolated by preparative scale chromatography from the volatile impurities produced in the preparation of III by treatment of I with anhydrous aluminum chloride, n.b.p. 39.4°, log P_{mm} = 7.55172 − 1460.1/$T_{°K}$, ΔH 6406 cal./mole, Trouton ratio 20.5, molecular weight (by PVT) 230 (theory 228), ultraviolet λ_{max} 262 mμ (ϵ_{max} 306). The n.m.r. spectrum showed one CH resonance at −5.35, one CF resonance at +90.9, and one CF_3 resonance at +0.88 p.p.m. The following coupling constants were measured: $J_{CH,CF}$ 46, J_{CH,CF_3} 5.6, and J_{CF,CF_3} 16.7 c.p.s. Major infrared absorption bands were at 3.40 (w), 7.40 (m), 7.82 (vs), 8.10 (m), 8.85 (vs), 9.20 (vs), 10.15 (w), 11.55 (s), and 14.30 (s) μ.

Rearrangement of Hydroperoxide Salts in the Oxidation of α-Trialkysilyl Organometallic Compounds[1]

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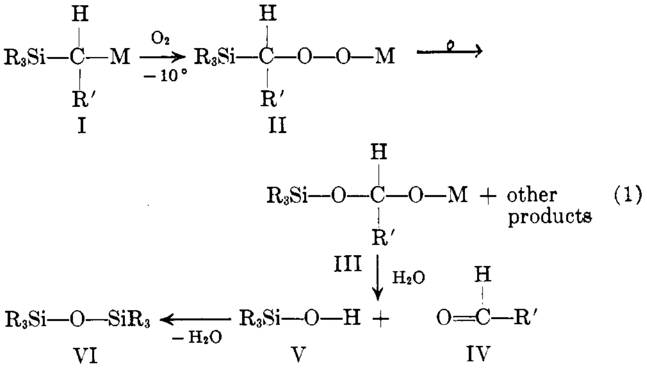
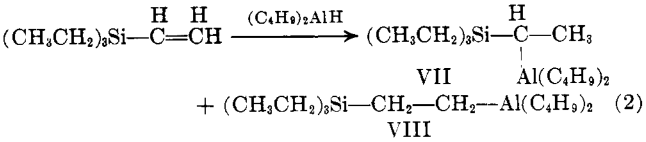
The ready oxidation of a wide variety of metal alkyls to form metal alkoxides by molecular oxygen has been shown to proceed *via* hydroperoxide salt intermediates, R–O–O–M.[2] However, despite the metalloid character of silicon, tetralkylsilanes, such as $(CH_3)_4Si$, are very resistant to the atmospheric oxidation of their carbon–silicon bonds.[3] Therefore, it was of interest to observe an extremely facile oxidation of carbon–silicon linkages when α-trialkylsilyl organometallic compounds (I) were subjected to air oxidation under very mild conditions. Thus, the air oxidation of trimethylsilylmethylmagnesium chloride (Ia) at −10° gave, upon hydrolysis, the expected alcohol, trimethylsilylmethanol, together with large amounts of trimethylsilanol (Va), hexamethyldisiloxane (VIa), formaldehyde (IVa), and higher siloxanes (Chart I). In a similar fashion, the addition products of triethylvinylsilane and diisobutylaluminum hydride (VII and VIII, eq. 2) underwent air oxidation to yield only minor amounts of the expected alcohols, 1-triethylsilylethanol and 2-triethylsilylethanol, respectively. Instead, triethylsilanol (Vb), hexaethyldisiloxane (VIb), and higher siloxanes were obtained as the principal oxidation products (Chart I). Since the relative proportion of adduct VII to adduct

CHART I



$$R_3Si\text{—}\overset{H}{\underset{R'}{C}}\text{—}M \xrightarrow[-10°]{O_2} R_3Si\text{—}\overset{H}{\underset{R'}{C}}\text{—}O\text{—}O\text{—}M \xrightarrow{\varrho}$$
$$R_3Si\text{—}O\text{—}\overset{H}{\underset{R'}{C}}\text{—}O\text{—}M + \text{other products} \quad (1)$$
$$\text{III} \downarrow H_2O$$
$$R_3Si\text{—}O\text{—}SiR_3 \xleftarrow[-H_2O]{} R_3Si\text{—}O\text{—}H + O{=}\overset{H}{C}\text{—}R'$$
$$\text{VI} \qquad \text{V} \qquad \text{IV}$$

Ia–VIa, R = CH_3; R′ = H; M = MgCl
Ib–VIb, R = C_2H_5; R′ = CH_3; M = $Al(C_4H_9)_2$



$$(CH_3CH_2)_3Si\text{—}\overset{H}{C}{=}\overset{H}{C}H \xrightarrow{(C_4H_9)_2AlH} (CH_3CH_2)_3Si\text{—}\overset{H}{\underset{Al(C_4H_9)_2}{C}}\text{—}CH_3 + (CH_3CH_2)_3Si\text{—}CH_2\text{—}CH_2\text{—}Al(C_4H_9)_2 \quad (2)$$

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[12] Engelhard Hanovia, Inc., 100 Chestnut St., Newark 5, N. J., type Sol #608A-36 operated from a Hanovia #7654-1 reactive transformer was used.

[1] Paper III in the series: Organosilicon Compounds with Functional Groups Proximate to Silicon. Previous papers: *J. Org. Chem.*, **28**, 487, 2870 (1963).

[2] *Cf.* (a) A. G. Davies, "Organic Peroxides," Butterworths Scientific Publications, London, England, 1961, pp. 120–126, 155–160; (b) H. Hock, H. Kropf, and F. Ernst, *Angew. Chem.*, **71**, 541 (1959).

[3] C. Eaborn, "Organosilicon Compounds," Academic Press Inc., New York, N. Y., 1960, pp. 123–124.