

## ORGANIC AND BIOLOGICAL CHEMISTRY

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## Reactions of Trifluoromethyl Hypofluorite with Organic Compounds

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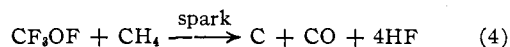
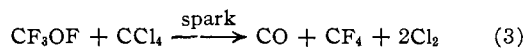
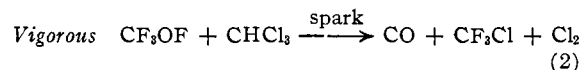
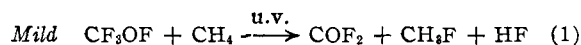
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Trifluoromethyl hypofluorite adds quantitatively across the double bond of ethylene to give trifluoromethyl 2-fluoroethyl ether. Analogous compounds appear to be formed, though not quantitatively, from cyclopropane and from benzene. Methane, chloroform and carbon tetrachloride give only fluorinated substituted derivatives upon reaction with the hypofluorite. Under more vigorous conditions all the organic compounds tested were oxidized to carbon with reduction of the hypofluorite to carbonyl fluoride or carbon monoxide.

## Discussion

Since trifluoromethyl hypofluorite was first synthesized<sup>2</sup> the only reported research performed with it has been the determination of its infrared spectrum<sup>3</sup> and a recent investigation of its decomposition and of its reactions with unsaturated fluorocarbon derivatives.<sup>4</sup> Its reactions on an equimolecular basis, at room temperature, with a few simple organic molecules now have been examined principally in the hope of introducing CF<sub>3</sub>O-groups.

The hypofluorite did not react on mixing with methane, chloroform or carbon tetrachloride (which were chosen as simple examples of saturated non-cyclic compounds). It acted as a fluorinating agent under mild reaction conditions. Under more vigorous conditions methane was dehydrogenated to carbon. The over-all reactions, which are probably of the type



illustrate the fluorinating power of the hypofluorite under various conditions. Any explosive reaction, whether spontaneous or spark induced, involved the reaction of all four fluorine atoms and the formation of carbon monoxide, whereas non-explosive reactions involved the reaction of only two fluorine atoms and the formation of carbonyl fluoride (or the product of its attack on glass, carbon dioxide).

Reactions 1, 2 and 3 all gave rise to the full spectrum of fluorinated methane derivatives, but the yield of products increased along each series to reach a maximum at the compound quoted in the particular reaction, approximately as one would expect on a statistical basis. There was no indication of any higher boiling product, suggesting that the replacement of hydrogen or chlorine by

(1) E. I. du Pont de Nemours and Co., Experimental Station, Wilmington, Del.

(2) K. B. Kellogg and G. H. Cady, *THIS JOURNAL*, **70**, 3986 (1948).

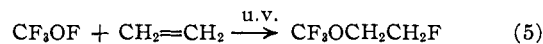
(3) R. T. Lageman, E. A. Jones and P. J. H. Woltz, *J. Chem. Phys.*, **20**, 1768 (1952).

(4) Roger S. Porter and G. H. Cady, *THIS JOURNAL*, **79**, 5625, 5628 (1957).

the trifluoromethoxyl group did not occur to any measurable extent.

With ethylene, acetylene or cyclopropane, representing unsaturated and alicyclic compounds, the hypofluorite reacted explosively upon mixing, giving carbon, carbon monoxide and hydrogen fluoride. The over-all reactions are analogous to reaction 4. When both reactants were diluted with nitrogen, and the hypofluorite was added slowly to ethylene while being irradiated with ultraviolet light, quantitative addition occurred to give trifluoromethyl 2-fluoroethyl ether. With cyclopropane, partial carbonization was noted, but there was some indication, on infrared analysis, of a small amount of product analogous to the above ether. Under these conditions of irradiation the reaction with acetylene was still explosive.

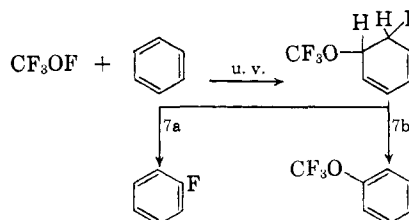
The reaction with ethylene was therefore



and with cyclopropane may have been



Benzene reacted slowly on mixing with the hypofluorite, but the only fluorine-containing aromatic product isolated was fluorobenzene. The presence of silicon tetrafluoride indicated side reactions. A mixture of the reactants exploded not only upon sparking but also upon irradiation with ultraviolet light. Upon mixing the reagents diluted with nitrogen and while irradiating, a small quantity of a product having similar infrared absorption bands in the C-F region to those of the products from ethylene and cyclopropane was detected. Since any dihydrobenzene derivative tends to return to the aromatic state, any initial hypofluorite adduct must have undergone further reaction in two ways



This scheme accounts for the two main products, but the yields were very low.

The products of reactions 5, 6 and 7b all have strong adsorption bands at 1280-1290 cm.<sup>-1</sup>. This frequency is characteristic of the CF<sub>3</sub> group

in compounds such as  $\text{CF}_4$ ,  $\text{CF}_3\text{OF}$  and  $\text{CF}_3\text{O}-\text{OCF}_3$  and lends support to the presence of the  $\text{CF}_3\text{O}$  ether grouping. In general, it appears that the hypofluorite, under moderated conditions with ultraviolet activation, will add across a reactive linkage, this adduct undergoing further reaction, if itself unstable. The reaction may be of use in the synthesis of trifluoromethyl 2-fluoroethyl ether and its homologs and, since these compounds should lose hydrogen fluoride under the influence of alkali to give unsaturated compounds, a considerable synthetic field would be opened up.

### Experimental

**Conditions and Methods of Reaction.**—All the following experimental work was carried out in a standard Pyrex glass high vacuum system, the stopcocks being lubricated with Kel F fluorocarbon grease and the exposed mercury surfaces in the manometers covered with Kel F oil no. 1. The vapor pressures of products from which reactive materials had been removed by treatment with sodium hydroxide pellets were obtained using no oil film.

Trifluoromethyl hypofluorite was prepared by the reaction of carbon monoxide with fluorine, diluted with nitrogen, over a silver difluoride catalyst at  $170^\circ$ . After standing four days over water to remove carbonyl fluoride, the gas was condensed in liquid oxygen and filtered to remove most of the carbon dioxide. The product, which still contained some carbon dioxide, a trace of carbon tetrafluoride and some bis-(trifluoromethyl) peroxide, was stored under pressure in a gas cylinder (which had previously been used for fluorine).

The chloroform, carbon tetrachloride and benzene were all reagent grade. Methane, ethylene and cyclopropane were all obtained from commercial cylinders, and acetylene was prepared as required, by the action of water on calcium carbide, followed by passage through acidified potassium dichromate solution and then concentrated sulfuric acid.

Trifluoromethyl hypofluorite and all organic materials except methane, which was used directly from the cylinder, were freed from non-condensable impurities before use by condensation under vacuum (0.1 mm.) in a trap cooled by liquid nitrogen. The non-condensable gases were pumped away.

The general procedure for following the reaction of the hypofluorite with an equimolecular amount of the organic compound was: All reactions were examined at room temperature only ( $25-28^\circ$ ). A one-liter flask equipped with two side arms for condensation (one sealed by a stopcock), a mercury manometer with Kel F oil film on the mercury in the open arm and two internal metal electrodes through which the discharge from a small spark coil could be passed was evacuated. The flask was filled to about 40 mm. pressure with trifluoromethyl hypofluorite, which then was condensed and closed off in one side arm. The flask then was filled with the same pressure of organic compound. The flask now was closed and surrounded by a protective wire basket. The trifluoromethyl hypofluorite next was allowed to evaporate into the flask. The total initial pressure was measured, when possible, and any change on standing for 12 hours, or after spontaneous explosion, was noted. The above procedure is called method 1. Mixtures non-reactive under these conditions were then activated either by sparking (method 2) which caused explosive reactions in almost all cases, or by irradiation with ultraviolet light from a Hanovia Ultra-Violet Lamp, Type 16200 (method 3) which, if there were no immediate explosion, was left in position for 12 hours. After cooling, the pressure was again determined.

The products were removed through a U-trap, cooled in liquid nitrogen or oxygen, and the non-condensable gases pumped into a 10-cm. infrared cell (barium fluoride windows) at pressures from 50 to 500 mm. using a simple mercury displacement pump and analyzed quantitatively for carbon monoxide, carbon tetrafluoride (and methane, when this was used initially) using the strong adsorption bands in the 2150, 1280 and 1300  $\text{cm}^{-1}$  regions, respectively, on a Perkin-Elmer recording infrared spectrophotometer model 21. Oxygen was assigned by difference.

The condensed material now was returned to the reaction flask and its pressure was measured. It was examined then

at suitable pressures (up to 100 mm.) by infrared analysis. Carbon dioxide and silicon tetrafluoride were determined by use of the bands in the 2300 and 1000  $\text{cm}^{-1}$  regions, respectively, and then destroyed by standing over sodium hydroxide pellets for several days. Finally the inert residue of fluorocarbon derivatives was also examined by infrared analysis. The intermediate stage of removal of silicon tetrafluoride only, by standing over sodium fluoride, was used initially but, since no loss of fluorine-containing gases of interest was observed during the subsequent sodium hydroxide treatment, the extra process was discarded.

The mixture of products was usually either distilled through a series of U-traps at different temperatures or through a 60 cm. 2.5 mm. i.d. unpacked vacuum-jacketed column. However, since both methods required rather large quantities of material and their fractionating efficiencies were not great, vapor phase chromatography was sometimes used with greater success. Helium was the carrier gas and the sample size was about 0.4 ml. of gas at S.T.P. The columns were from 2 to 6 meters long and they contained nitrobenzene or benzonitrile supported on 40 to 60 mesh powdered firebrick. They were used at room temperature. Sufficient pure product usually was obtained from one or two runs to enable a conclusive identification by infrared analysis at 1 to 5 mm. Since most fluorocarbon derivatives containing one or two carbon atoms per molecule have one or two very strong and sharp infrared adsorption bands, it was normally possible to make an analysis of a mixture of up to about four of these materials.

The initial reaction conditions were also modified by slowly mixing the diluted reactants in the presence of ultraviolet light (method 4). A sufficient amount of the gaseous organic compound was added to the 1-liter bulb to give a pressure of 20 mm. The gas was then condensed in a side arm. Enough nitrogen to give a pressure of 80 mm. was admitted to the bulb. The flask was then closed and the two gases were allowed to mix thoroughly. A second bulb (200 ml.) of known volume was then filled with a mixture of 80 mm. trifluoromethyl hypofluorite and 320 mm. of nitrogen. The reactor bulb was illuminated with ultraviolet light, and the hypofluorite was added 10 mm. at a time over a period of an hour. If no explosion or only slight carbonization occurred, irradiation was continued for 11 more hours. The pressure after cooling to room temperature was noted and the products were passed through a trap at  $-183^\circ$ . Non-condensable gases were discarded. The mixture of condensable products was analyzed as described above.

**Reactions of Trifluoromethyl Hypofluorite with Saturated Organic Compounds.**—When trifluoromethyl hypofluorite was mixed with equimolecular quantities of methane, chloroform or carbon tetrachloride (method 1), no reaction occurred over a period of 12 hours, *i.e.*, there was no pressure change, and the reactants could be recovered quantitatively. The mixtures were then sparked (method 2). An explosion resulted in each case. Methane gave carbon and the halocarbons gave chlorine. Methane and chloroform yielded silicon tetrafluoride about proportionally to their hydrogen contents. Carbon monoxide and a trace of  $\text{CF}_4$  were formed in all cases, but not carbon dioxide. The halocarbons gave the complete series of single carbon Freons, the product ratios obtained from chloroform being  $\text{CF}_4:\text{CF}_3\text{Cl}:\text{CF}_2\text{Cl}_2:\text{CFCl}_3$  as 2:15:1:trace.

The gaseous product from the reaction with methane showed no infrared adsorption bands in the  $\text{CF}_3$  region except that due to  $\text{CF}_4$ , nor was any material boiling above  $0^\circ$  detected. Apparently none of the ether  $\text{CF}_3\text{OCH}_3$  had been formed.

When a mixture of methane with trifluoromethyl hypofluorite was irradiated with ultraviolet light for 12 hours no explosion occurred (method 3). The complete series of fluorinated methanes was formed, together with carbon dioxide (no carbon monoxide) and silicon tetrafluoride. The product ratios were  $\text{CF}_4:\text{CF}_3\text{H}:\text{CF}_2\text{H}_2:\text{CFH}_3$  as "trace":2:5:10. The gas mixture was separated by vapor phase chromatography, but there was again no indication of any product boiling near  $0^\circ$  to correspond with  $\text{CF}_3\text{OCH}_3$ . The reaction was probably of the type represented by equation 1.

**Reactions of Trifluoromethyl Hypofluorite with Unsaturated and Cyclic Organic Compounds.**—When trifluoromethyl hypofluorite was mixed with cyclopropane, ethylene or acetylene, spontaneous explosions occurred after induction periods of about 5, 1 and 0.5 minutes, the main products being carbon, carbon monoxide and silicon tetrafluoride to-

gether with traces of carbon tetrafluoride (and, presumably) water. The violence of the explosion increased qualitatively in the order in which the hydrocarbons are listed above. Ethylene also gave some acetylene and a trace of hexafluoroethane, while acetylene gave carbonyl fluoride and traces of carbon dioxide and hexafluoroethane. All of the  $\text{CF}_3$  bands could be accounted for as hexafluoroethane. A mixture of  $\text{CF}_3\text{OF}$  with benzene did not explode, but the pressure started to fall and oily drops of low volatility formed in the flask. The pressure fell only to about 70% of its original value indicating that side reactions, *e.g.*, fluorination, were occurring.

A mixture of the hypofluorite with benzene then was sparked, and a second mixture was irradiated with ultraviolet light. Both exploded instantaneously to give carbon, carbon monoxide, about 5% fluorobenzene, identified by its infrared spectrum and other unidentified products of low volatility.

In other runs the hydrocarbons were diluted with nitrogen and were mixed slowly with the trifluoromethyl hypofluorite in the presence of ultraviolet light. The results given below were obtained.

Ethylene at 41 mm. pressure in a 5-liter Pyrex bulb was mixed with 159 mm. of nitrogen and was irradiated with ultraviolet light. The pressure in the bulb was raised 10 mm. at a time over a period of an hour by admitting a mixture of trifluoromethyl hypofluorite diluted with an equal volume of nitrogen until the total pressure was 282 mm. and equimolecular quantities of the reactants had been used. Irradiation was continued for 12 hours, there being no indication of explosion or carbonization. When the light source was removed and the bulb allowed to cool, the pressure fell to 244 mm. indicating quantitative addition across the double bond. When the nitrogen was pumped off, the pressure of residual gas, totally condensable at  $-195^\circ$ , was 38 mm. This fell only to 37 mm. after two days treatment with sodium hydroxide, showing the absence of side fluorination reactions which always give silicon tetrafluoride and carbon dioxide. The gas was condensed and held in a U-trap at  $-78^\circ$  while pumping was continued for several hours to remove any traces of ethylene. Its purity was confirmed by analysis of a small sample using vapor phase chromatography and its molecular weight was determined. Values of 131.5, 132.1, 127.5, 128, 130.5 and 132.5 were obtained on samples from two preparations. Trifluoromethyl 2-fluoroethyl ether,  $\text{CF}_3\text{OCH}_2\text{CH}_2\text{F}$ , has a molecular weight of 132. The vapor pressure was 84 mm. at  $0^\circ$  and 271 mm. at  $25^\circ$ .

The infrared spectrum contained a well-defined group of bands in the region of C-F adsorption:

Wave number, $\text{cm.}^{-1}$	Band strength
1287	V. strong
1240	Strong
1170	V. strong
1102	Moderate
1076	Moderate

A 0.3-ml. sample of the liquid compound was sent to Varian Associates for investigation by nuclear magnetic resonance. Their report discussed both the fluorine and the proton resonances. These were in every way in good agreement with the proposed structure,  $\text{CF}_3\text{OC}_2\text{H}_4\text{F}$ , as summarized: Fluorine resonance, lower resolution: Two peaks were present, one three times as great as the other. The magnitude of the chemical shift between the two peaks was 163 parts per million of the applied magnetic field with the larger peak at the

lower field. Fluorine resonance, higher resolution: The larger peak was split into a quintet which could be considered as the combination of a doublet (from the single F atom) further split into overlapping triplets (by the protons of the  $\text{CH}_2$  group closest to the  $\text{CF}_3\text{O}$  group). The smaller peak was split into nine lines resulting from a basic triplet (caused by the protons on the same carbon atom as the fluorine) each of whose lines was further split into a triplet (by the two protons on the adjacent carbon atom). An additional quartet splitting of each of the nine lines resulted from the fluorine atoms of the  $\text{CF}_3\text{O}$  group.

Proton resonance: Three groups of peaks resulted from the overlapping of two sets of doublets having different chemical shifts. One group had twice the area of each of the others. The large doublet splitting was due to the single fluorine atom. The magnitude of splitting and the extent of chemical shift agreed with the proposed structure. Each group of peaks had a complex fine structure largely explained by spin-spin interaction between the two groups of protons and finer coupling by the fluorine of the  $\text{CF}_3\text{O}$  group.

Cyclopropane and trifluoromethyl hypofluorite were caused to react by method 4. Some carbon was formed on the glass during the slow mixing period, but no explosion occurred. As with benzene, side reactions occurred extensively, and the condensable product, after treatment with caustic soda, consisted of 95% cyclopropane and 5% of a material showing a group of infrared bands very similar to those in the ethers described above.

Wave number, $\text{cm.}^{-1}$	Band strength
1290	Moderate
1254	Strong
1173	Strong
1155	V. strong
1106	Moderate

It appeared that some ring opening with addition of the hypofluorite had occurred.

**Acetylene.**—Even under the conditions of method 4 the mixture containing acetylene exploded after an induction period of one minute and yielded those products previously found in the absence of nitrogen.

**Benzene.**—Under the conditions of method 4, a slow reaction accompanied by a fall in pressure occurred. This may have been the "dark" reaction already observed. 5% of fluorobenzene was detected in the product by its infrared spectrum and, when allowances were made for this, 5% of a compound again showing a group of bands similar to those of trifluoromethyl 2-fluoroethyl ether was shown to be present. This may have been trifluoromethyl phenyl ether.

Wavenumber, $\text{cm.}^{-1}$	Band strength
1280	Strong
1189	Strong
1166	V. strong

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