imide was weighed exactly on a tared watch glass and washed into a 250-ml. erlenmeyer flask with 12 ml. of 95% ethanol. From a buret, 25.00 ml. of standard potassium hydroxide (about 0.2 *N*) was added and the corked flask was warmed at 50° until the solid completely dissolved. When it had cooled to room temperature, the solution was diluted to a volume of about 100 ml. and four drops of 0.05% *m*-cresol purple indicator was added. The excess base was then titrated with standard hydrochloric acid (about 0.12 *N*), taking as the end-point, the first definite yellow (no purple) tint. The saponification equivalent of the N-alkyl-4-nitrophthalimide was computed in the same manner as that of an ester.

Two compounds gave unsatisfactory results by this procedure. The N-octadecyl-4-nitrophthalimide forms a rather insoluble, soapy potassium salt and complete solution was not attained. In the case of the N-(*p*-nitrobenzyl)-4-nitrophthalimide, the basic solution containing the salt displayed a yellow-brown color rather than purple when the indicator was added.

N-Benzyl-3-nitrophthalimide.—This compound was prepared from benzylamine and 3-nitrophthalic anhydride by the procedure of Alexander and McElvain.[6] Its saponification equivalent was determined by the above procedure as 280.6 (calcd., 282.2).

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Trifluoroacetyl Hypofluorite[1]

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For some time an investigation of the reactions of elementary fluorine with volatile carbon compounds containing oxygen has been under way in these laboratories. In the early stages of the work, the compound trifluoromethyl hypofluorite[2] was obtained by the fluorination of methanol or carbon monoxide. Later it was found that numerous organic compounds containing oxygen, such as ethanol, acetic acid, cyclohexanone, ethylene glycol and acetone, would react with fluorine, even by combustion, to produce trifluoromethyl hypofluorite as well as certain fluorinated hydrocarbons.

In another series of experiments fluorine was allowed to react at room temperature with various oxygen containing substances. In one case trifluoroacetic acid was placed in a platinum boat enclosed in a Teflon tube, and undiluted fluorine was passed over it. The reaction products which condensed in a trap cooled by liquid oxygen were found to be easily exploded by an electric spark. It was at once suspected that the explosive substance might be trifluoroacetyl hypofluorite formed by replacement of the hydrogen atom by fluorine. Attempts were then made to isolate and identify the compound. These efforts were discouraging. Sometimes no explosive product was obtained. At other times the substance exploded as the preparative reaction proceeded or while in the process of distillation. Several rather elaborate systems of glass apparatus were destroyed. Metallic systems were tried but the explosive compound was not obtained. Finally, the substance was prepared in a small amount as described below, and its molecular weight and composition were established.

The present article describes only exploratory experiments. There still remains a need for additional work in order that more properties of the substance may be known with precision.

Solutions believed to contain compounds of the formulas CF_3COOBr and CF_3COOI have been prepared by Henne and Zimmer[3] by the reaction of the free halogen with silver trifluoroacetate.

Materials.—Fluorine was used directly from cylinders obtained from the Pennsylvania Salt Manufacturing Co. Anhydrous trifluoroacetic acid was obtained from the Minnesota Mining and Manufacturing Co. Usually it was used just as it came from the manufacturer; for some experiments, however, the acid was distilled. The distillation appeared to have little effect upon the reaction of the acid with fluorine.

Experimental.—Figure 1 shows the equipment finally used for the preparation and identification of the compound. Inlets for controlled and measured streams of fluorine and nitrogen were provided as shown at the left of the figure. Bubblers A and B contained water and trifluoroacetic acid held at 20 and 0°, respectively. Trifluoroacetic acid vapor and water vapor were swept by streams of nitrogen into vessels C and D, where the reaction with fluorine occurred. The part of the system between boundaries F and G was composed of polyethylene bottles and tubing, Saran tubing and rubber stoppers. A glass tube served as the inlet for fluorine into bottle C. Bottles C and D were kept at room temperature. They had a combined volume of 1060 ml. Bottle E was held at −78° and was used as a trap to condense hydrogen fluoride, water vapor and unreacted trifluoroacetic acid from the gas stream. From it the gas passed through the glass system and out through stopcock X. Among the products condensed in the trap, W, which was cooled to −183° by liquid oxygen, were: CF_3COOF, CF_4, COF_2, CO_2 and SiF_4. The remainder of the glass system was used for refining the product and for taking samples. Before use, the system was carefully cleaned and dried. Stopcocks were lubricated with a greasy wax composed of polymers of chlorotrifluoroethylene. This highly essential material was obtained from the M. W. Kellogg Co. of Jersey City, N. J., and from the Halocarbon Products Corp. of North Bergen, N. J.

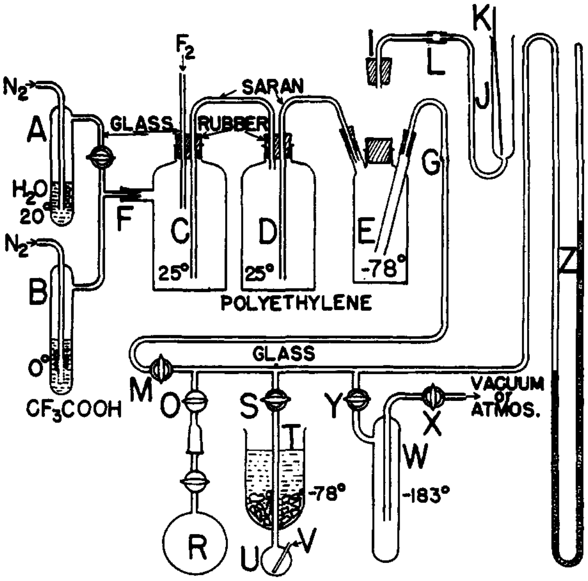

FIG. I.

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(1) This compound was mentioned in an article about the industrial production of fluorine chemicals at the Minnesota Mining and Manufacturing Co. [*Chem. Eng. News*, **29**, 4488 (1951)]. A letter to one of the authors from N. W. Taylor, Manager of the Fluorochemicals Department of that company states, "The story in Chemical and Engineering News referring to this type of product was due to a misunderstanding on the part of the editor. . . As far as 3M is concerned, you are the inventor of CF_3COOF."

(2) K. B. Kellogg and George H. Cady, This Journal, **70**, 3986 (1948).

(3) A. L. Henne and W. F. Zimmer, *ibid.*, **73**, 1362 (1951).

Before starting a run, qualitative tests were made to see that the explosive product was being formed. To do this, the cap was removed from bottle E, and stopcock M was closed. Stopper I was inserted into the neck of bottle E and the gas was passed through the glass trap J, which was cooled at the bottom to −183°. After gas had passed for a measured time of four to eight minutes, tube J was disconnected at L and it was placed in an explosion shield made of sheet iron. Copper wire K was inserted as shown. After waiting for about 100 seconds to allow the product to vaporize, a spark producing "leak tester" was touched to wire K. If this caused a sharp explosion to occur, the apparatus was known to be producing the desired substance. The flow rates given below yielded enough material in four minutes to explode with a sharp report but not with enough energy to shatter the glass tube.

The role of water vapor in the reaction is not clear. Usually the product could be obtained without adding water. However, in the case of the last cylinder of fluorine used in the study, almost none of the explosive substance was formed unless water vapor was added.

The run which finally resulted in identification of the compound involved the following flow rates: F_2 from 0.97 to 0.83 g. per hour, trifluoroacetic acid at 2.1 g. per hour, water vapor at 0.1 g. per hour and nitrogen at 9.0 liters per hour. The reaction vessels were held at 25 ± 1° and the reaction was allowed to continue for three hours while the product was condensed in trap W. At the end of this time fluorine was swept from the system by a stream of dry nitrogen; then stopcock M was closed and the glass system was pumped out for about 10 minutes with a pump connected at X. After closing stopcock X, the product was distilled from trap W to the 10-ml. bulb U. Dry nitrogen at atmospheric pressure was then admitted to the glass apparatus and the system was left open to the atmosphere. Bulb U was then allowed to warm slowly to about −60°, being kept there by the near proximity of Dry Ice held in a suitable container, leaving only a few drops of liquid in the bulb. Stopcock S was then closed and gas was pumped from all of the glass system except bulb U. Stopcocks Y, O and M were closed and bulb U was immersed in a bath of acetone and solid carbon dioxide. Stopcock S was then opened and after a few seconds was closed. The pressure of gas in the system was measured on mercury manometer Z. An unsuccessful attempt was made to explode the gas in the system using the spark producing "leak tester" held outside the manometer tube at a point about 1 cm. above the mercury meniscus. The non-reacting gas was pumped from the system through stopcocks Y and X; then another sample of gas was allowed to escape from bulb U. With stopcock S closed another attempt was made to explode the gas in the line. The fourth trial of this sort and all succeeding trials resulted in explosions. This procedure removed impurities more volatile than trifluoroacetyl hypofluorite and finally resulted in what appeared to be the nearly pure compound being the gas escaping from bulb U. Repeated sampling of this sort showed the vapor pressure of the hypofluorite at −78.5° to be about 27 mm. When the gas at this pressure was exploded, the products had a pressure of about 57 mm. A 45.4 ml. (measured at 0°, 760 mm.) sample of the explosion product was found upon a rather crude analysis to contain about 13.5 ml. of COF_2, 12.6 ml. of CO_2, 15.3 ml. of CF_4 and 4.0 ml. of a mixture of gases remaining uncondensed when bulb R was cooled to −183°. When this uncondensed mixture was examined using the mass spectrometer it was found to contain CF_4, SiF_4, CO_2, O_2 and N_2. Some carbon monoxide may also have been present.

Two low pressure samples of the unexploded gas were collected in bulbs of the type shown at R. These samples had densities corresponding to molecular weights of 137 and 136 (theoretical for CF_3COOF = 132). The total fluorine content was found to be 57.0 ± 1.0% (theoretical 57.6%).

When the gas was allowed to stand at room temperature it decomposed slowly as shown by a gradual increase in pressure. Within a few hours the decomposition was complete.

Upon contact with a solution of potassium iodide the substance was found to explode. When diluted with much nitrogen it did not explode, but it did react rapidly liberation iodine.

When the reflux condenser T was cooled by solid carbon dioxide, and trifluoroacetyl hypofluorite was then boiled in bulb U under a pressure of one atmosphere, the temperature indicated by a thermocouple in well V was −21.5 ± 1°. This is an approximate value for the normal boiling point.

As far as could be told from the small samples observed, the substance was colorless. Its odor was irritating and similar to that of fluorine and the other compounds containing an –O–F bond.

The total weight of the purified compound obtained in the above run from 2.11 g. of trifluoroacetic acid was 0.33 g. Even though a part of the material was lost during the purification process, the total yield must have been less than 25% of theoretical.

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5-Benzyloxyindole

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The recent elucidation of structure[2] and synthesis[3,4] of 5-hydroxytryptamine, a naturally occurring vasoconstrictor substance of serum and tissue fluids,[5] has prompted the investigation of a more convenient preparation of 5-benzyloxyindole, an intermediate in two of the reported syntheses.[3] Burton and Stoves[6] have described the reduction and cyclization of 2-nitro-5-benzyloxyphenylpyruvic acid in the presence of ferrous hydroxide and alkali to yield 70% 5-benzyloxyindole-2-carboxylic acid. Decarboxylation in glycerol at 210° afforded a 24% yield of benzyloxyindole.

Application of the Japp–Klingemann reaction[7] with 4-benzyloxybenzenediazonium chloride and ethyl methylacetoacetate followed by cyclization of the phenylhydrazone in absolute ethanolic hydrogen chloride yielded 46–49% ethyl 5-benzyloxyindole-2-carboxylate. Alkaline saponification of the ester (84–95%) and decarboxylation of the resulting 5-benzyloxyindole-2-carboxylic acid gave 65% crystallized 5-benzyloxyindole.

Experimental[8]

4-Benzyloxyaniline.—To a solution of 23 g. (1 mole) of sodium in 1 l. of absolute ethanol was added 151 g. (1 mole) of 4-acetylaminophenol and 127 g. (1 mole) of benzyl chloride. The mixture was refluxed with stirring for 1.5 hr., about 750 ml. of solvent removed by distillation, and the residue poured into 2 l. of cold water. The 4-benzyloxyacetanilide which precipitated as fine almost colorless needles was filtered off and washed with water. The damp filter-cake was then refluxed for 15 hr. with a solution of 280 g. (5 moles) of potassium hydroxide in 2 l. of 90% ethanol. Most of the solvent was again removed by distillation. The residue partially crystallized on cooling. The crude product was taken up in ether and the extracts were dried superficially by filtration through a layer of anhydrous magnesium sulfate. Distillation yielded 167–170 g. (84–85%) of a

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[1] Ethicon Suture Laboratories, Inc., New Brunswick, N. J.

[2] M. M. Rapport, *J. Biol. Chem.*, **180**, 961 (1949).

[3] (a) K. E. Hamlin and F. E. Fischer, This Journal, **73**, 5007 (1951); (b) M. E. Speeter, R. V. Heinzelmann and D. I. Weisblat, *ibid.*, **73**, 5514 (1951).

[4] B. Asero, *et al.*, *Ann.*, **576**, 69 (1952).

[5] Z. M. Bacq, Abstr. 2nd Int. Congr. Bioch., Paris, July 22–27, 1952, Symposium on Proteic Hormones and Protein Derivatives, page 59.

[6] H. Burton and J. L. Stoves, *J. Chem. Soc.*, 1726 (1937).

[7] C. K. Hughes, *et al.*, *J. Proc. Roy. Soc. N. S. Wales*, **71**, 475 (1938).

[8] Analyses by S. Alpert.