reaction carried out at 250° in an autoclave gave only 5% iodo compound and 37% olefin.

We wish to report a simplified method for the preparation of trifluoromethyl iodide and heptafluoroiodopropane in 70–80% yields at atmospheric pressure. These results are obtained by refluxing a suspension of the sodium or potassium salt of the corresponding fluorocarboxylic acid with a small excess of iodine in dimethylformamide. Presumably other fluoro acid salts will give similar results. When sodium heptafluorobutyrate is refluxed without iodine in dimethylformamide facile decarboxylation results in a high yield of heptafluoropropene.

Recent work on the photochemical decarboxylation of acyl hypoiodites[7] makes the following description of the mechanism for the conversions observed highly likely.

$$RCO_2^-M^+ + I_2 \longrightarrow RCO_2I + MI$$

$$RCO_2I \longrightarrow RCO_2\cdot + I\cdot$$

$$RCO_2\cdot \longrightarrow R\cdot + CO_2$$

$$R\cdot + I_2 \longrightarrow RI + I\cdot$$

A simple decarboxylation is ruled out by the reluctance of trifluoromethyl anions to be trapped by Lewis acids. An indication that the present reaction can be widely extended is given by the observation that sodium acetate treated under these conditions gives a trace (*ca.* 0.1%) of methyl iodide along with 0.4% methyl acetate.

Experimental Section

A mixture of 0.3 mole of iodine and 0.2 mole of dry sodium or potassium salt of trifluoroacetic acid or heptafluorobutyric acid was mixed with 80 ml of dry dimethylformamide (Baker Analyzed reagent grade was used) in a round-bottomed flask and heated to reflux under a condenser cooled with water maintained above the boiling point of the fluoroalkyl iodide product. The top of the condenser was connected to a trap cooled with a Dry Ice or liquid nitrogen bath in which the gaseous products were collected over a 1-hr period.

Trifluoromethyl iodide was obtained in 70% yield upon bulb-to-bulb distillation of the volatile products in a vacuum line, maintaining the "pot" at 195°K and the "receiver" at 77°K. Vapor chromatography on an 30-ft × 0.25 in. column of 60% diethyl phthalate, 20% silicone oil 710 on Anakrom at 23°, He flow rate 43 cc/min, gave a small peak for a low-boiling impurity with retention time 6.3 min (air retained 5 min under these conditions) and the major peak (93% by area) of trifluoromethyl iodide at 18 min. Gas phase infrared spectra of the product (7.2-cm path length 15 and 400 mm) were identical with those in the literature.[8]

Heptafluoroiodopropane (bp 40.5–41.5°[60]) was obtained in 70–80% yield and purified by normal distillation at atmospheric pressure.

When a mixture of 0.2 mole of anhydrous sodium acetate and 0.1 mole of iodine was refluxed in 40 ml of dimethylformamide for 8 hr the volatile material collected in liquid nitrogen was shown by vapor chromatography to consist of a mixture of methyl iodide (*ca.* 0.1% yield) and methyl acetate (*ca.* 0.4% yield).

Registry No.—Trifluoromethyl iodide, 2314-97-8; heptafluoroiodopropane, 754-34-7.

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Fluorocarbon Ortho Esters. Synthesis and Characterization of 1,4-Bis(trifluoromethyl)-2,6,7-trioxabicyclo[2.2.2]octane

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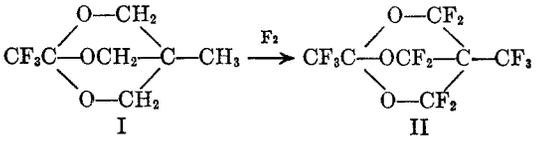
Our investigations of the chemistry of organic fluorine compounds have led to the synthesis of a completely fluorinated ortho ester of a carboxylic acid. Ortho esters of 1,1-dihydrofluorinated alcohols have been reported;[1] and perfluoromethyl thioorthoformate and thioorthocarbonate have been described;[2] but to our knowledge no ortho esters of organic carboxylic acids have been previously described, wherein the alkoxyl groups are completely fluorinated.

Fluorination of 4-methyl-1-trifluoromethyl-2,6,7-trioxabicyclo[2.2.2]octane[3] with excess fluorine has been found to result in complete substitution of fluorine for the hydrogen atoms with retention of the carbon–oxygen skeleton to give 1,4-bis(trifluoromethyl)-2,6,7-trioxaperfluorobicyclo[2.2.2]octane (II).



I II

Compound II is a thermally stable liquid and is resistant to acid hydrolysis. It is immiscible with water and may be washed repeatedly with water or aqueous sodium carbonate solution. Treatment of compound II with 95% sulfuric acid at 125° for 1 hr gave no evidence for any reaction. This behavior is in direct contrast to the characteristic sensitivity of hydrocarbon alkyl ortho esters to acidic conditions.

Experimental Section

Fluorination Apparatus.—All experiments were carried out in well-ventilated areas behind suitable barricades. Precautions appropriate for all fluorination experiments were observed, including deliberate limitation of sample size and the use of personal safety equipment such as heavy duty face shields, leather coats, and leather gloves for personnel protection. The fluorination apparatus consisted of a sealable 10-in. Monel metal tube, 1 in. in diameter, equipped with a sintered disk near the bottom, a gas inlet tube for the introduction of fluorine below the disk, a gas outlet tube near the top of the tube, and a removable brass blow-out cap on the top. The outlet tube led to an iron tube containing granular sodium fluoride at room temperature (for the removal of hydrogen fluoride) and from there to a borosilicate glass collection trap cooled by a bath of liquid oxygen at *ca.* −183°. The piping was of copper. A glass rotameter was used for nitrogen and a poly(chlorotrifluoroethylene) rotameter was used for fluorine. The fluorine was diluted with nitrogen to the desired concentration before introduction into the reactor. Commercially available fluorine (General Chemical Division, Allied Chemical Corp.) was used directly from the cylinder, and Monel fittings were used for the fluorine supply line.

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4-Methyl-1-trifluoromethyl-2,6,7-trioxabicyclo[2.2.2]octane (I).—This starting material was prepared by a modification of the procedure described previously.[3] A solution of 60 g (0.50 mole) of 2-hydroxymethyl-2-methyl-1,3-propanediol, 57 g (0.50 mole) of trifluoroacetic acid, and 200 ml of benzene in a flask equipped with a Dean–Stark trap and a reflux condenser was heated under reflux until 1 equiv of water was collected in the Dean–Stark trap (*ca.* 24 hr). To the reaction mixture was added 1.0 ml of concentrated sulfuric acid, and heating was continued for 5 days. At the end of this time nearly the theoretical amount of water was found in the Dean–Stark trap. Removal of the solvent gave a white solid, which was washed with aqueous sodium carbonate solution and recrystallized from anhydrous benzene to give 55.7 g (56% yield) of compound I as a white powder, mp 152.5–153.5° (with sublimation; lit.[3] mp 145°). The fluorine nmr spectrum[4] of this material exhibits only a single resonance peak, which is a singlet at ϕ^* +84.9 (at 95° in benzene with benzotrifluoride as internal reference). The proton nmr spectrum shows two resonance peaks, both singlets, at τ +6.04 and at +9.12 in carbon tetrachloride at 25°. The former (and stronger) absorption is assigned to the methylene hydrogens, and the latter is assigned to the hydrogens of the methyl group.

1,4-Bis(trifluoromethyl)-2,6,7-trioxabicyclo[2.2.2]octane.—A suspension of 1.0 g of compound I (5.1×10^{-3} mole) in 75 ml of perfluorotributylamine[6] was placed in the fluorination apparatus above the sintered disk. The tube was cooled to 0° and flushed for 1 hr with dry nitrogen. Fluorine was then introduced into the nitrogen stream, and the fluorine–nitrogen mixture was passed into the reaction vessel. A total of 0.43 mole of fluorine was used as the fluorine concentration was increased stepwise from 2 to 25% over a period of 6 hr. The temperature of the reaction vessel was maintained at 0°. After the fluorine flow was discontinued, the cooling bath was removed, and the reaction vessel was purged with nitrogen for 2 hr to remove fluorine and to carry over the products of the reaction into the collection trap.

The contents of the trap were then subjected to fractional distillation–condensation on a vacuum line through traps at −5°, −78°, and −196°. The middle fraction was found to contain 0.3 ml of liquid product which was purified by gas chromatography on a column 2 m in length and 0.5 in. in diameter packed with poly(chlorotrifluoroethylene) oil (33%, commercially available from Minnesota Mining and Manufacturing Co. as Kel-F polymer oil KF-8126) coated on 30–60 mesh acid-washed Celite (67%, diatomaceous earth) and maintained at 70°. Helium was used as the carrier gas at a flow rate of 150 ml/min. Compound II was obtained as a colorless liquid having a vapor pressure of 53 mm at room temperature (*ca.* 23°). The yield of pure material obtained from chromatography was about 10% of the theoretical amount (*ca.* 0.5×10^{-3} mole) based on the amount of compound I used as starting material.

The structural formula of compound II was shown by the fluorine nmr spectrum, the infrared spectrum,[7] the mass cracking pattern, and the molecular weight.[8] The fluorine nmr spectrum in trichlorofluoromethane solution contains a singlet absorption at ϕ^* +84.8 (assigned by comparison with the singlet absorption at 84.9 in the starting material to the fluorines of the CF_3 group next to the carbon atom linked to three oxygen atoms), a fourfold absorption at +70.3 (assigned to the six fluorine atoms of the CF_2 groups), and a sevenfold absorption at 62.3 (assigned to the fluorines of the remaining CF_3 group). The coupling constant is 9.3 cps. The area ratios of the fluorine absorptions are consistent with the structure assignment. The mass cracking pattern shows fragments attributable to $C_4F_7^+$ (*m/e* 181), CF_3^+ (*m/e* 69, largest peak), and $C_7F_{11}O_3^+$ (*m/e* 341, the parent structure lacking one fluorine) in addition to many other peaks consistent with the structure. All peaks attributable to fragments containing more than four carbon atoms—for example, at mass numbers 225, 275, 294, and 341—appear at mass numbers attributable to fragments containing oxygen as well as carbon and fluorine. No peaks attributable to fragments containing hydrogen were observed. The molecular weight by the gas density method was found to be 350 (calcd 360). The infrared spectrum shows no absorption in the region 2.5–7.0 μ. The positions of the absorption peaks (wavelengths in μ) are as follows: 7.49 (s), 7.71 (vs), 7.82 (shoulder), 8.01 (s), 8.25 (m), 8.38 (m), 8.60 (m), 8.76 (m), 8.94 (s), 9.77 (s), 9.95 (s), 10.20 (m), 10.78 (w), 13.07 (m), and 14.74 (w).

A sample of compound II which had been stored in the gas phase at room temperature for nearly 3 years showed no evidence for decomposition.

Other products of the reaction were low molecular weight fragmentation products (carbon tetrafluoride, carbonyl fluoride, and carbon dioxide) and partially fluorinated hydrogen-containing materials which were not further identified.

Registry No.—1,4-Bis(trifluoromethyl)-2,6,7-trioxabicyclo[2.2.2]octane, 7492-72-0; I, 878-60-4.

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(4) The nmr spectra were obtained on a Varian V-4300-2 nmr spectrometer operated at 40.00 Mcps. Positions of the fluorine absorptions are expressed in ϕ^* units[5] relative to the absorption of $CFCl_3$.

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(6) Commercially available as FC-43, Minnesota Mining and Manufacturing Co.

(7) The infrared spectra were obtained on a Perkin-Elmer Model 21 double-beam infrared spectrophotometer on gas samples. The mass cracking pattern was obtained on a Consolidated Electrodynamics Corp. mass spectrometer, Type 21-103C, with an ionization potential of 70 v and an ionization chamber temperature of 250°.

(8) Elemental analyses for carbon and fluorine were attempted by the procedure developed in these laboratories for highly fluorinated compounds[9] by combustion of the samples in moist oxygen at 1100–1200°. Repeated attempts gave erratic results even with portions of the same sample, apparently because of incomplete combustion and formation of carbon tetrafluoride in the combustion reaction. The results of three determinations with the same sample are as given. *Anal.* Calcd for $C_7F_{12}O_3$: C, 23.3; F, 63.3. Found: C, 22.8, 22.4, 22.6; F, 60.5, 61.7, 60.9.

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Dimethyl Sulfoxide Oxidations[1a]

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The use of dimethyl sulfoxide (DMSO) as a reactant in the oxidation of a variety of functional groups to carbonyl compounds has received a good deal of attention in recent years.[2-8] One of the most studied of these techniques is that involving an alcohol substrate, dicyclohexylcarbodiimide (DCC), and a proton source

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