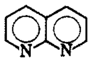
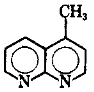
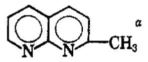
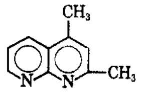
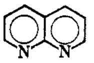
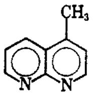
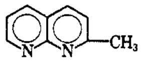
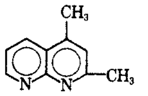
TABLE I

NUCLEAR MAGNETIC RESONANCE SPECTRAL DATA OF SOME 1,8-NAPHTHYRIDINES

Compd	Chemical shifts,							
	CH_3-2	CH_3-4	H-2	H-3	H-4	H-5	H-6	H-7
	...	...	0.87	2.52	1.78	1.78	2.52	0.87
	...	7.35	1.02	2.68	...	1.62	2.47	0.88
 [a]	7.24	...	...	2.69	1.92	1.99	2.65	0.97
	7.28	7.40	...	2.85	...	1.74	2.60	0.84

Compd	Coupling constants, cps						
	J_{H-3,CH_3}	$J_{2,3}$	$J_{3,4}$	$J_{2,4}$	$J_{5,6}$	$J_{5,7}$	$J_{6,7}$
	...	4.2	8.0	2.0	8.0	2.0	4.2
	0.90	4.2	...	...	8.2	2.0	4.2
	...	...	8.4	...	8.4	2.0	4.4
	0.90	...	...	...	8.2	2.0	4.2

[a] Because of a typographic error, the chemical shift of H-5 was not listed in a previous paper[2b] of this series.

(10%). One crystallization from cyclohexane gave straw-like needles, mp 84–85° (lit.[10] 85–86°), picrate mp 204–205° (lit.[11] 204–206°).

Registry No.—**2**, 254-60-4; **3**, 1569-16-0; **4**, 1569-17-1; **5**, 7544-64-1.

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Simplified Method for the Preparation of Fluoroalkyl Iodides

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Several methods are presently available for the synthesis of fluoroalkyl iodides. The reactions are carried out in sealed tubes and consist of treatment of fluoroolefins with iodine fluoride (IF) formed *in situ* from various halogen compounds,[2] chain lengthening of fluoroalkyl iodides with tetrafluoroethylene and an antimony halide catalyst,[3] decomposition of fluoroacyl chlorides in the presence of potassium iodide at 200°,[4] decomposition of fluoro acid anhydrides in the presence of iodine at 350–400°,[5] and decomposition of metal salts of fluoro acids in the presence of excess iodine at high temperatures.[6]

Silver salts are most commonly used in the latter method, and yields of 80 to 100% have been reported. Other metal salts such as sodium, potassium, barium, mercury and lead give lower yields of fluoroalkyl iodides.[6a,c,e] For example Haszeldine[6c] reports heating a mixture of 27.2 g of sodium trifluoroacetate and 100 g of iodine with a free flame to give 10% trifluoromethyl iodide, while a 40% yield was obtained when 13.6 g of potassium trifluoroacetate was heated with 500 g of iodine. When the reactions were carried out at 280° in a stainless steel autoclave, 61 and 55% yields of trifluoromethyl iodide were obtained from the sodium and potassium salts of trifluoroacetic acid, respectively. Heating sodium heptafluorobutyrate and a 300% excess of iodine with a free flame gave 9% heptafluoroiodopropane and 41% hexafluoropropene. The same

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[1] To whom inquiries should be addressed at the Department of Chemistry, Washington University, St. Louis, Mo. 63130

[2] (a) J. H. Simons and T. J. Brice, U. S. Patent 2,614,131 (1953); *Chem. Abstr.*, **47**, 8770c (1953); (b) R. D. Chambers, W. K. R. Musgrave, and J. Savory, *J. Chem. Soc.*, 3779 (1961); (c) W. K. R. Musgrave, J. Perret, and J. Savory, British Patent 885,007 (1962); *Chem. Abstr.*, **57**, 11018i (1962); (d) C. G. Krespan, U. S. Patent 3,052,732 (1963); *Chem. Abstr.*, **58**, 7828d (1963).

[3] R. E. Parsons, French Patent 1,385,682 (1965); *Chem. Abstr.*, **62**, 13045c (1965).

[4] C. G. Krespan, *J. Org. Chem.*, **23**, 2016 (1958).

[5] R. N. Haszeldine, British Patent 757,893 (1957); *Chem. Abstr.*, **51**, 12129h (1957).

[6] (a) R. N. Haszeldine, *Nature*, **166**, 192 (1950); (b) A. L. Henne and W. G. Finnegan, *J. Am. Chem. Soc.*, **72**, 3806 (1950); (c) R. N. Haszeldine, *J. Chem. Soc.*, 584 (1951); (d) M. Hauptschein and A. V. Grosse, *J. Am. Chem. Soc.*, **73**, 2461 (1951); (e) R. N. Haszeldine, *J. Chem. Soc.*, 4259 (1952); (f) J. H. Simons and T. J. Brice, U. S. Patent 2,554,219 (1952); *Chem. Abstr.*, **46**, 2560i (1952); (g) W. T. Miller, Jr., E. Bergman, and A. Fainberg, *J. Am. Chem. Soc.*, **79**, 4159 (1957).

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°^{6c}) 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.

Acknowledgment.—The authors wish to thank Miss Beverly Fitzhenry for her assistance with these experiments.

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(7) D. H. R. Barton, H. P. Faro, E. P. Serebryakov, and N. F. Woolsey, *J. Chem. Soc.*, 2438 (1965).

(8) M. Hauptschein, E. A. Nodiff, and A. V. Grosse, *J. Am. Chem. Soc.*, **74**, 1347 (1952).

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

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Contribution No. 396 from the Central Research Laboratories,
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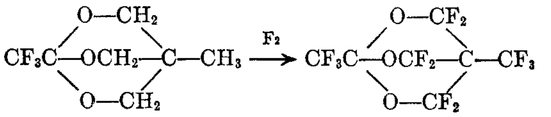
Received August 4, 1966

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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(1) M. E. Hill, D. T. Carty, D. Tegg, J. C. Butler, and A. F. Stang, *J. Org. Chem.*, **30**, 411 (1965).

(2) J. F. Harris, Jr., U. S. Patent 3,062,894 (1962).

(3) R. A. Barnes, G. Doyle, and J. A. Hoffman, *J. Org. Chem.*, **27**, 90 (1962).