Acid Hydrolysis of the Hemiketal Ester II.—A sample of 0.35 g. (0.75 millimole) of the hemiketal ester II was mixed in a separatory funnel with 70 ml. of ether and 20 ml. of 6 *N* hydrochloric acid. The reaction mixture was allowed to stand at room temperature for 15 hours with intermittent shaking. The ether layer was extracted with a sodium carbonate solution, washed once with water and dried over sodium sulfate. After concentration of the ether solution and the addition of petroleum ether, 0.05 g. (84%) of α-hydroxyketone IV, m.p. 94–95°, was obtained. When mixed with an authentic sample of IV, the melting point was 94–95°. On acidification of the sodium carbonate layer, 0.10 g. (62%) of 3,5-dinitrobenzoic acid, m.p. 195–198°, was obtained. A mixture melting point determination with an authentic sample of the acid, m.p. 204–205°, melted over the range 200–203°.

A sample of 0.35 g. of the 3,5-dinitrobenzoate IIIa was subjected to exactly the same procedure. After drying, the resulting ether solution was cooled and concentrated to give 0.27 g. (77%) of recovered starting keto 3,5-dinitrobenzoate. No acid was found upon acidification of the sodium bicarbonate layer.

Reaction of Hemiketal Ester II with Methanol.—In 25 ml. of absolute methanol 1.0 g. (0.002 mole) of II was heated on a steam-bath until solution was effected. After cooling the solution, a first crop of crystals gave 0.3 g. (33%) of the ketoester IIIa, m.p. 140–141°. A second crop, 0.17 g., corresponded to the α-hydroxyketal V, melting at 116–121°. When mixed with V the melting point was raised to 117–122°. The filtrate was evaporated to dryness and the residue was dissolved in ether and the ether solution was extracted with a 10% sodium bicarbonate solution. On acidification of the bicarbonate solution 0.14 g. of 3,5-dinitrobenzoic acid was obtained. The ether layer after evaporation left 0.15 g. of residue, m.p. 111–116°. An infrared spectrum of this solid showed absorption bands corresponding to the hydroxyketal (V) as the major constituent. Bands corresponding to the α-hydroxyketone IV and the 3,5-dinitrobenzoate ester IIIa were also present as minor constituents. The total yield of crude V was 76%.

Reaction of Epoxyether I with Absolute Methanol in the Presence of 3,5-Dinitrobenzoic Acid.—In a mortar 0.5 g. (0.002 mole) of I and 0.42 g. (0.002 mole) of 3,5-dinitrobenzoic acid were mixed thoroughly. The mixture was heated on a steam-bath with 25 ml. of absolute methanol until solution was effected. Treatment of this solution in the same manner as the solution of the hemiketal ester II gave no keto-3,5-dinitrobenzoate IIIa but only an 86% yield of crude hydroxyketal V as proved by mixture melting point determination and comparison of the infrared spectra.

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1,1-Di-H-perfluoroalkyl Halides

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A convenient, general method has been found for the preparation of 1,1-di-H-perfluoroalkyl halides from the corresponding alcohols, *via* the *p*-toluenesulfonyl (tosyl) esters. Good yields are obtained without the use of special apparatus. Physical properties are reported for the compounds prepared, and certain unusual features of the infrared spectra are discussed.

Although 1,1-di-H-perfluoroethyl chloride,[1,2,4] bromide,[2–4] and iodide[5] have previously been reported, the preparative methods are different for each halide, and are not readily extended to the synthesis of other 1,1-di-H-perfluoroalkyl halides. This article reports a convenient synthetic method of general applicability, which does not require the use of special apparatus.

The tosyl esters were readily obtained from the fluorinated alcohols, using reaction conditions satisfactory for the tosylation of phenols.[6a] The preparation of alkyl halides by reaction of alkyl tosylates with appropriate metal halides is well known.[6b,7,8] These tosyl esters, however, differ from alkyl tosylates in being quite unreactive at the usual temperatures of 50-100°. For example, it was necessary to heat 1,1-di-H-perfluorobutyl *p*-toluenesulfonate with sodium iodide in acetone in a sealed tube at 150° for 19 hours to afford a 40% yield of the corresponding iodide. No iodide was isolated after the tube was heated at 110° for 15 hours.

Much better results were obtained when higher-boiling solvents were tried. Thus, when 1,1-di-H-perfluorobutyl *p*-toluenesulfonate was heated with sodium iodide in diethylene glycol, triethylene glycol, tetraethylene glycol or tetraethylene glycol dimethyl ether, very good yields (80–95%) of 1,1-di-H-perfluorobutyl iodide were obtained.

It was necessary for both the sodium iodide and 1,1-di-H-perfluorobutyl *p*-toluenesulfonate to be dissolved in order for reaction to occur. For example, in one experiment, glycerol (in which sodium iodide is very soluble and the ester is in soluble) was used as a solvent and no reaction was noted.

In order to prepare the 1,1-di-H-perfluoroalkyl bromides and chlorides it was necessary to use lithium bromide and lithium chloride. No reaction occurred with sodium bromide or chloride, presumably due to the low solubility of these salts in the solvents used.

Now that the 1,1-di-H-perfluoroalkyl chlorides are readily accessible, they may be employed as starting materials for the preparation of the corresponding 1,1,1-trichloroperfluoroalkanes. The first member of this series, CCl_3CF_3, has been obtained by the chlorination of methylfluoroform,[9] but the higher 1,1,1-tri-H-perfluoroalkanes are not available. To illustrate the preparation, the photochlorination of 1,1-di-H-perfluorobutyl chloride was carried out by the method of Henne and Whaley.[10]

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The chlorination proceeded to completion, no dichloride being isolated upon distillation of the product. Such behavior has previously been noted in the chlorination of 1,1,1-trichloro-3,3,3-trifluoropropane.[10]

Physical properties of the compounds prepared are listed in Table I, together with analytical data.

TABLE I

PHYSICAL PROPERTIES OF SOME 1,1-DI-H-PERFLUOROALKYL HALIDES AND RELATED COMPOUNDS

Compound	B.p. (or m.p.), °C.	n^{25}_D	d^{25}_4	Analyses, %			Yield, %
					Calcd.	Found	
CF_3CH_2I	55.0	1.3981	2.142	I:	60.45	60.1	81
n-$C_3F_7CH_2Cl$	54	1.2906	1.523	C: Cl:	21.98 16.23	21.8 16.25	78
n-$C_3F_7CH_2Br$	69.1	1.3166	1.780	C: Br:	18.27 30.39	18.5 30.0	70
n-$C_3F_7CH_2I$	92	1.3603	2.019	C: I:	15.50 40.94	15.6 40.8	91
n-$C_5F_{11}CH_2Cl$	103.6	1.2993	1.651	C: Cl:	22.62 11.13	22.6 11.2	78
n-$C_5F_{11}CH_2I$	133	1.3500	2.018	F: I:	50.98 30.96	51.0 30.99	87
n-$C_3F_7CCl_3$	96.2	1.3441	1.688	C: Cl:	16.72 37.01	16.8 36.8	60
CF_3CH_2O tosyl	(41)	1.4635		F: S:	22.42 12.61	22.0 12.4	78
n-$C_3F_7CH_2O$ tosyl	(30.5)	1.4252		C: F:	37.29 37.55	37.4 37.6	85
n-$C_4F_{11}CH_2O$ tosyl	(54.5)			C: S:	34.37 7.06	34.8 7.06	71

The CH stretching band is quite weak in the infrared spectra of these compounds, appearing as a doublet at 3.3–3.4 μ. At the liquid thickness used (about 0.007 mm.) only 1,1-di-H-perfluoroethyl iodide, CF_3CH_2I, gives a well defined CH stretching band. In contrast, a fairly strong band is found at 7.0 μ in each of the 1,1-di-H halide spectra. It appears to be due to a deformation of the CH_2 group.[11a] Further evidence for this assignment is provided by the spectra of the halides CF_3CH_2Cl and CF_2BrCH_2Br.[12a] The slight shift of this band to longer wave lengths found in passing from the chlorides to the iodides is in accord with that observed in the sequence $CH_2Cl_2 \rightarrow CH_2Br_2 \rightarrow CH_2I_2$.[11a]

It has been observed[11b,12b,13] that a CF_3 group attached to a saturated, hydrogen-free carbon atom is associated with a strong infrared band in the region 7.3–7.5 μ. Consistent with this observation, a fairly strong band is found at 7.4 μ in each of the spectra except that of 1,1-di-H-perfluoroethyl iodide.

Experimental

Preparation of 1,1-Di-H-perfluoroalkyl *p*-Toluenesulfonates.—The following is an example of the procedure that was found suitable for the preparation of the tosyl esters.

In a 500-ml. flask were placed 87 g. (0.435 mole) of the alcohol n-$C_3F_7CH_2OH$, 88 g. (0.46 mole) of *p*-toluenesulfonyl chloride and 150 ml. of water. The mixture was heated to 50° and 20 g. (0.50 mole) of sodium hydroxide dissolved in 80 ml. of water was added with stirring over a period of about one-half hour. Heat was liberated during the addition of base, but the rate of addition was controlled to keep the reaction temperature below 65°. The vigorous stirring was continued until the solution became neutral. The reaction mixture was cooled, and the tosyl ester was separated from it by means of petroleum ether. To remove any unreacted tosyl chloride, the petroleum ether solution was washed repeatedly with concentrated aqueous ammonia and then with water. All traces of solvent were removed on the steam-bath.

The ester thus obtained melted at 28–30° and was adequately pure for further synthetic work; yield 131 g. (85%), n^{25}_D 1.4252 (supercooled). An analytical sample was recrystallized several times from petroleum ether, m.p. 30–30.5°.

Anal. Calcd. for $C_{11}H_9F_7O_3S$: C, 37.29; F, 37.55. Found: C, 37.4; F, 37.6.

1,1-Di-H-perfluorobutyl Iodide.—The procedure used in preparing the 1,1-di-H-perfluoroalkyl halides was similar in each case. The following is a typical experiment.

In a 1000-ml. 3-necked flask fitted with an efficient stirrer, thermometer and take-off adapter, were placed 354.2 g. (1 mole) of 1,1-di-H-perfluorobutyl *p*-toluenesulfonate, 149.9 g. (1 mole) of sodium iodide and 300 ml. of diethylene glycol. The 1,1-di-H-perfluorobutyl iodide was not evolved until the temperature of the reaction mixture reached 150°. After the reaction mixture had been heated for about two hours, and the pot temperature had risen to 220°, 280 g. of product had collected. During the reaction a thick mass of sodium *p*-toluenesulfonate was formed. The reaction mixture was stirred continuously to prevent frothing and plugging of the take-off tube. The product was washed several times with cold water and dried over Drierite. Fractionation of the material through a 35-cm. packed column gave pure 1,1-di-H-perfluorobutyl iodide, b.p. 91° (740 mm.), n^{25}_D 1.3603, yield 270 g. (84.0%).

Anal. Calcd. for $C_4H_2F_7I$: C, 15.50; I, 40.95. Found: C, 15.6; I, 40.8.

Chlorination of 1,1-Di-H-perfluorobutyl Chloride.—1,1-Di-H-perfluorobutyl chloride, 19.8 g. (0.09 mole), was chlorinated in essentially the same manner as that employed by Henne and Whaley.[10] Fractionation of the reaction mixture gave about 15 g. (60%) of pure 1,1,1-trichloroperfluorobutane, b.p. 95° (732 mm.), n^{25}_D 1.3441, plus a small amount of unidentified higher boiling material. There was no fraction which could contain dichloride in more than trace quantities, as judged by refractive indices.

Anal. Calcd. for $C_4Cl_3F_7$: C, 16.72; Cl, 37.01. Found: C, 16.8; Cl, 36.8.

Infrared spectra were taken with a Perkin–Elmer model 21 infrared spectrophotometer. Cells of approximately 0.007 mm. liquid thickness were employed.

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