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1-Iodo-Polyfluoroalkanes from Polyfluoroalkoxy Trimethylsilanes and Iodochloro Triphenylphosphorane.

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Abstract: Polyfluoroalkoxy trimethylsilanes $R_fCH_2OSi(CH_3)_3$ (from the alcohols R_fCH_2OH and HMDS), react with Ph_3PICl (from ICl and Ph_3P) eliminating $(CH_3)_3SiCl$. Pyrolysis of the residues gives Ph_3PO and pure iodides R_fCH_2I.

Primary polyfluoroalkyl iodides having the structure R_fCH_2I are possible sources of the R_fCH_2- moiety for organic synthesis. This opportunity, while attractive, has been explored infrequently[1,5]. In fact, only a few of these compounds have been reported in the past. In this communication, we describe the preparation of several representative compounds of the class by a new, general method. The reaction[1] is pictured in the following Scheme 1, products and isolated yields are shown in Table 1.

$$2\ \underset{\mathbf{1a\text{-}f}}{R_fCH_2OH} + HN(SiMe_3)_2 \xrightarrow{i} 2\ \underset{\mathbf{2a\text{-}f}}{R_fCH_2OSiMe_3} + NH_3$$

$$\underset{\mathbf{2a\text{-}f}}{R_fCH_2OSiMe_3} + \underset{\mathbf{3}}{Ph_3PICl} \xrightarrow{ii} Me_3SiCl + Ph_3P{=}O + \underset{\mathbf{4a\text{-}f}}{R_fCH_2I}$$

i: neat; ii: reflux in hexane or neat, then pyrolysis.

Scheme 1

Amongst highly fluorinated materials, *perfluoro*alkyl iodides R_fCF_2I, derived from tetrafluoroethylene[2], are a well documented class of compounds, having characteristic chemistry and manifold uses. Their radical addition to ethylene[2] gives primary iodides $R_fCH_2CH_2I$ endowed with more conventional reactivity.

The title polyfluoro alkyl iodides R_fCH_2I are much less known. Yet, the two above-mentioned classes of fluorinated iodides originate from peculiar synthetic routes, whereas, the common polyfluoroalcohols R_fCH_2OH[3] would seem obvious abundant starting materials. Unfortunately, these alcohols are most reluctant to undergo the transformations that are common for their hydrocarbon analogues. Indeed, some of the polyfluoroalkyl iodides discussed in this paper were previously obtained[4] from the alcohols, by reacting their tosylate esters with KI in glycols up to 220 °C. Such a method involves rather large quantities of reagents, and we deemed it too expensive for exploratory work.

A possibility of circumventing these difficulties was indicated by the literature: polyfluoroalkyl bromides or chlorides can be obtained directly[5] from the alcohols and dihalophosphoranes Ph_3PX_2, X = Br, Cl. This widely used conversion of alcohols (or phenols) to halides (Rydon's reaction)[6] demonstrably proceeds by rearrangement of intermediate alkoxyphosphonium salts[7]. We reasoned that a synthesis of polyfluoroalkoxy phosphonium iodide salts **5** (Scheme 2) would possibly provide polyfluoroalkyliodides.

Coupling by elimination of a volatile silicon halide[8] is a time-honoured method of forming bonds between heteroatoms, when ionic reactions may be expected to be difficult or to fail[8b,c]. In our case, the suitable precursors were the silylethers **2** [8c] and the interhalophosphorane **3** [9]. The synthesis of **3** of sufficient purity for our purpose was found easy, and the acidity[3c,d] of alcohols **1** favours greatly their reaction with HMDS.

The thermal elimination of Me_3SiCl from **2** and **3** fortunately occurs at a temperature sufficiently low to avoid decomposition[10] of either the intermediate phosphonium salts **5**[14] or of **3**. Thus, it is possible to isolate the intermediates and obtain volatile compounds, such as **4a-c**, uncontaminated, without distillation. Silylethers **2** of sufficiently large molecular weight are conveniently reacted neat.

Table 1. Synthesis of 1-Iodo Polyfluoroalkanes.

Starting Compound[a]	No	mmol used	Product[b]	No	isolated yield, %.
$CF_3CH_2OSiMe_3$	**2a**	25	CF_3CH_2I	**4a**	36
$C_2F_5CH_2OSiMe_3$	**2b**	23	$C_2F_5CH_2I$	**4b**	58
$C_3F_7CH_2OSiMe_3$	**2c**	25	$C_3F_7CH_2I$	**4c**	65
$H(CF_2)_6CH_2OSiMe_3$	**2d**	65	$H(CF_2)_6CH_2I$	**4d**	85
$H(CF_2)_{10}CH_2OSiMe_3$	**2e**	10	$H(CF_2)_{10}CH_2I$	**4e**	70[c]
$[(Me_3SiOCH_2CF_2O)_2(CF_2O)_x(C_2F_4O)_y]$	**2f**	(4)[d,c]	$[(ICH_2CF_2O)_2(CF_2O)_x(C_2F_4O)_y]$	**4f**	(50)[c]

a) Note 16; b) Note 11; c) Note 12; d) Note 13; e) calculated by NMR.

Iodochloro triphenylphosphorane (**3**): In a 500 mL flask with thermometer, reflux condenser and dropping funnel, Ph_3P (54.4 g, 0.208 mol) was suspended in 120 mL hexane. ICl (34.4 g, 0.212 mol) dissolved in 30 mL CH_2Cl_2 was added dropwise under nitrogen, with vigorous stirring, during one hour. The tea-coloured suspension was then heated at reflux for six hours. The resulting yellow product was filtered under pressure of nitrogen, washing it with hexane, and held under high vacuum for three hours. Yield 79.9 g (90%), finely divided, hygroscopic powder, decomposing above 120 °C (lit.[9] m.p. 122-124 °C).

1-Iodo-1H,1H-heptafluorobutane (**4c**): Ph_3PICl (**3**)(9.76 g, 23 mmol), then $C_3F_7CH_2OSiMe_3$ (**2c**) (6.25 g, 23 mmol) dissolved in 50 mL hexane, were loaded under nitrogen into a 100 mL flask. The suspension was refluxed with stirring for 3 hrs, taking care that the oil bath temperature did not exceed 110 °C. Filtering under pressure of nitrogen in a Schlenk funnel and eliminating the solvent in vacuum gave 11.75 g of **5c** as a yellow powder, m.p. 119-122 °C (dec., sealed tube). MS (FAB): 588 (M); 461 (M-I); 279 ($Ph_3P{=}O$); 183 ($C_3F_7CH_2$).

This powder was pyrolysed at 160-190°C in a 50 mL flask fitted with a small distillation head, collecting **4c** in an ice-cooled receiver: 4.60 g (65%).

1-Iodo-1H,1H,7H-dodecafluoroheptane (**4d**): A suspension of **3** (28.0 g, 66 mmol) in neat **2d** (26.0 g, 65 mmol) was refluxed with stirring for 2 hrs. The reflux condenser was replaced by a distillation head, and the bath temperature was increased gradually from 110 °C to 200 °C: first Me_3SiCl distilled out (58-60 °C, 6.4 mL, 75% recovery), then the head temp. subsided until **4d** distilled at 157-159 °C: 18.0 g (63 %). A further 6.5 g (22 %) were recovered by steam distillation.

$$\underset{\mathbf{2}}{R_fCH_2OSiMe_3} + \underset{\mathbf{3}}{Ph_3PICl} \longrightarrow \underset{\mathbf{5}}{[R_fCH_2OPPh_3]^+I^-} + Me_3SiCl$$

Scheme 2

We have obtained chemical and mass-spectroscopic evidence for the formation of polyfluoroalkoxy triphenylphosphonium iodides, from the dedicated method[14b] indicated in Scheme 2. The pyrolytic rearrangement of these salts affords polyfluoroalkyliodides, offering a new entry into this class of compounds.

The method described above is quite economical, especially because it permits work on comparatively small quantities. It appears to be general for the class of the title compounds **4**.

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References and notes

1. Triphenylphosphine, iodine monochloride, hexamethyldisilazane (HMDS), and starting alcohols **1** were all commercial materials and were used as received. The products **4** were at least 95% pure by NMR. The mass spectra (CI) of **4b-e** were obtained on neat samples. All had the expected molecular ions and (M-127) ions, and were also otherwise consistent with the structures. **4a** was identical with a commercial sample.
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9. Ali, M.F.; Harris, G.S. *J. Chem. Soc. Dalton Trans.* **1980**, 1545-1549 and discussion therein. The precise preparation given in that work would be inconvenient for our purposes. Our simpler preparation of a technical-grade material exploits the apparent equilibrium between different dihalophosphoranes, that favours the interhalo compound: cfr. Ref. 6a.
10. The direct reaction of alcohols **1** with Ph_3PBr_2 requires heating in a suitable solvent[5], but separation of products from solvents on a small scale may be problematic. The above reaction, without solvent in a sealed tube, is best carried out above the m.p. of the co-product $Ph_3P{=}O$ (158 °C). With Ph_3PBr_2 (dec. ca. 240 °C) it is not detrimental to heat the reaction to the required temperature, but Ph_3PICl (text, Ref. 9) decomposes already at ca. 120 °C. Also, the reaction between alcohols and interhalophosphoranes is reported to be nonselective[6a].
11. The NMR spectra ($CDCl_3$) of the products **4** have typical resonances at 3.5 δ (TMS) for the CH_2I protons and -110 δ ($CFCl_3$) with small variations in chemical shifts and H, F coupling constants (16-18 Hz). The starting silanes **2** show corresponding signals at 4 δ (TMS) and ca.-125 δ ($CFCl_3$). The downfield shift of the CF_2CH_2X signals follows the trend X = OH, $OSiMe_3$ < Cl < Br < I (cfr. Ref. 5b).
12. **2e** and **3** were heated at 110 °C 2 hrs, 115-120 °C 1 hr, 170 °C 30 min. After cooling, taking up in 100 mL of ether, filtering and evaporating, the residue was eluted with ether from a 10 cm plug of silica gel. **4e** was obtained as an off-white powder.
13. a) For a recent paper on perfluoro macrodiols, see Hung, M.H.; Farnham, W.B.; Feiring, A.E.; Rozen, S. *J. Am. Chem. Soc.* **1993**, *115*, 8954-8959. b) Formula **2f** represents the ave. composition of Fomblin Z DOL (from Aldrich, no. 37, 806-2, lot # 81570, m.w. not given). Cfr. Boutevin, B.; Robin, J.J. *Adv. Polym. Sci.* **1992**, *102*, 105 and refs. cited therein. An ave. eq.weight of 675 was approximately calculated from ^{19}F NMR (neat). **2f** has two $CF_2CH_2OSiMe_3$ signals at -83, -85 δ. **4f** shows a typical shift to -72, -74 δ. **1f**, **2f**, (**2f** + **4f**) are insoluble in all common solvents. When **2f** was heated progressively to 160 °C with **3**, initially a yellow suspension was formed, then Me_3SiCl began to reflux visibly, finally a dark residue formed which upon cooling solidified atop a clear liquid phase. This was separated and evaporated to give **4f** in 1:1 mixture with unreacted **2f**. Due to the high price of **1f** we did not optimize this experiment.
14. a) **5a**, m.p. 107-110 °C (sealed tube), 90% y. **5b**, m.p. 109-112 °C (sealed tube), 96% y., MS (FAB): 538 (M); 411; 279 . **5c**, see text. From hexafluoroisopropanol, $[(CF_3)_2CHOPPh_3]^+I^-$, MS (FAB): 557 (M); 279; was obtained as a very hygroscopic powder, dec. above 135 °C, but pyrolysis gave a very complex mixture. b) The actual degree of purity of compounds **5** cannot be assessed so far, but the satisfactory material balances, narrow m.p. ranges, and MS evidence make us confident that Scheme 2 correctly represents the reaction.
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16. To the neat alcohols **1a-d** and **1-f**, HMDS (1 eq.) was added dropwise under nitrogen, with good stirring, while cooling with an ice bath. Heat was then applied gradually during 4-5 hrs to a constant internal temperature with mild reflux (**2a-c**), or to 100°C (**2d**, **2f**). A nitrogen atmosphere was also maintained while allowing the products to cool. Solid **1e** was refluxed in hexane with excess HMDS, then the volatiles were rotary-evaporated. The silyl ethers thus obtained are usually sufficiently pure for the next step.

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