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1-(Dichloroiodo)-1*H*,1*H*-Perfluoroalkanes

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Introduction

Since the discovery of iodobenzene dichloride $PhICl_2$ in 1886, many aryl and vinyl compounds of trivalent iodine have been reported,[1] but the alkyl analogues are normally too unstable to be isolated. The only exceptions are some iodomethyl sulfones, which gave stable dichlorides,[2] and poly- or perfluoroalkyl iodides, which are oxidized to the bis-trifluoroacetates[3] by 60−80% H_2O_2 in trifluoroacetic anhydride. Herein we report that 1H,1H-perfluoroalkyl iodides **1** react with chlorine at or below room temperature producing (dichloroiodo) 1H,1H-perfluoroalkanes **2** in high yields (eq 1).

$$\underset{\textbf{1a–d}}{R_fCH_2I} + Cl_2 \longrightarrow \underset{\textbf{2a–d}}{R_fCH_2ICl_2} \qquad (1)$$

R_F	entry
CF_3	**1a**, **2a**
C_2F_5	**1b**, **2b**
C_3F_7	**1c**, **2c**
$H(CF2)_6$	**1d**, **2d**

The novel compounds **2** are remarkable for their ease of preparation and stability. They have been identified[4] by elemental analysis (I, Cl) and spectral data; this evidence is supported by chlorine-transfer (Table 1) and chlorine-exchange reactions (eq 2).

$$\underset{\textbf{2a}}{R_FCH_2ICl_2} + 2CF_3COOAg \rightarrow \underset{\textbf{5a}}{R_FCH_2I(OCOCF_3)_2} \qquad (2)$$

Results and Discussion

When a stoichiometric amount of chlorine is condensed onto **1** at −196 °C, the reactions are complete[5] upon warming to 22 °C over 30 min. Chlorination of **1** is also feasible in ordinary glassware: a few grams of **1** in a 1 L flask react completely with Cl_2 (g) in 4−12 h. The commercially available and inexpensive 1-iodo-2,2,2-trifluoroethane (**1a**) afforded iodinane **2a** on a preparative scale. The synthesis of **2a** is similar to that of iodobenzene dichloride, but it is faster and may be carried out without solvent. Surprisingly, perfluoroalkyl iodides do not form the expected dichlorides under the same conditions. The pale yellow products **2** show low sensitivity to light and atmospheric moisture. The iodinanes **2** are still pure by iodometric assay after 2−3 weeks at room temperature in the dark; for longer storage they should be refrigerated. They are poorly soluble in $CHCl_3$ or CCl_4 and very soluble in CH_2Cl_2.

Like the analogous iodobenzene dichloride,[6] **2** are effective chlorination reagents. Unhindered primary and secondary alkenes react in chloroform at room temperature and β-keto esters are also readily chlorinated (Table 1).

Additional proof of structure for iodinanes **2** is provided by the simple ligand exchange reaction by means of silver trifluoroacetate[8] (eq 2), that gave the known[3b,c] 1H,1H-perfluoroalkyliodo bis-trifluoroacetates **5** in good yields.

We have found that chlorination of 1*H*,1*H*-perfluoroalkyl iodides **1** gives a new class of remarkably stable dichloroiodinanes **2**. They are effective chlorinating agents, and the inexpensive and easily made **2a** will be a useful addition to organic chemistry in this respect. **2** are starting materials for other polyfluoroalkyl compounds of trivalent iodine. These have been shown in the past to be of great potential interest, but the necessity of using concentrated H_2O_2 for their synthesis has so far hindered this field of research. The easy preparation of **2** combined with effective ligand-exchange procedures makes the preparation of polyfluoroalkyl compounds of trivalent iodine more readily accessible.

Experimental Section

General. Commercially available starting materials **1a**, **3a−c** and **3e** (Aldrich), and **3d** (Fluorochem) were used as received. Starting iodides **1b−d** were prepared from the alcohols as reported in ref 7. HPLC grade $CHCl_3$ (Baker), CCl_4 (Carlo Erba), and FC 113 (Fluorochem) were also used as received. Melting points were measured in open capillary tubes and are uncorrected. ^1H and ^{19}F NMR spectra were measured in $CDCl_3$ or CD_2Cl_2 with TMS and $CFCl_3$ as internal standards. Microanalyses were performed by Redox Snc, Cologno M., Milano, Italy.

1-(Dichloroiodo)-2,2,3,3,3-pentafluoropropane (2b): C_2F_5-CH_2I (1.16 g, 4.5 mmol) was added to a 100 mL bulb, and then chlorine (3 mmol) was condensed into the evacuated bulb at liquid N_2 temperature. While the bulb was allowed to room temperature rapidly (10 min), a yellow-green solid formed. The bulb was then cooled to −196 °C and a second addition of Cl_2 (3 mmol) was carried out as above. Excess chlorine was vented, and after brief vacuum pumping, a pale yellow powder, 1.26 g (85%) was obtained: mp 70−71 °C (dec); ^1H NMR (CD_2Cl_2) δ 5.02 (t, J = 15 Hz); ^{19}F NMR (CD_2Cl_2) δ −83.0 (s, 3F), −110.2

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(4) The X-ray crystal structure of **2d** has been solved: DesMarteau, D. D.; Xue, L.; Pennington, W. T.; Montanari, V. Manuscript in preparation. Iodometric titrations were carried out in 50% v/v acetic acid/water with starch as indicator. The values obtained for the equivalent mol weights were 96−98% of those expected. The ^1H signal for CH_2ICl_2 at ca. 5 ppm from TMS is typical (cf. ref 3c).

(5) No other products were detected. Solutions of the iodinanes **2** in CD_2Cl_2 had partially reverted to the starting iodides **1** after 3 d at 25 °C. No signals besides those of **1** and **2** were visible.

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Table 1. Chlorine-Transfer Reactions of Iodinanes 2

substrate	product[a]	reagent (react. time, h)
$C_6H_{13}CH{=}CH_2$ **3a**	$C_6H_{13}CHClCH_2Cl$ **4a**	**2c** (1.5)
cyclohexene **3b**	*trans*-1,2-dichlorocyclohexane[b] **4b**	**2a** (1), **2b** (6), **2d** (>24)
dimedone **3c**	2-chloro-dimedone **4c**	**2d** (12)
$PhC(O)CH_2C(O)CF_3$ **3d**	$PhC(O)CHClC(O)CF_3$ **4d**	**2a** (1), **2b** (12), **2d** (>12)
$PhC(O)CH_2C(O)OEt$ **3e**	$PhC(O)CHClC(O)OEt$ **4e**	**2b** (12)

[a] All the reactions in $CHCl_3$ at room temperature. Isolated yields were nearly quantitative in all cases, as determined by 250 MHz NMR. Mass spectra were consistent with the structures. For **4d**, see the Experimental Section. [b] All *trans* isomer, identical by capillary GC and NMR with an actual sample.

(t, 2F, $J = 15$ Hz). Anal. Calcd for $C_3H_2Cl_2F_5I$: Cl, 21.43; I, 38.36. Found: Cl, 21.19; I, 38.40. The same reaction proceeded slowly in only 20% isolated yield using $CFCl_3$ as solvent.

1-(Dichloroiodo)-2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptane (2d): $H(CF_2)_6CH_2I$ (5.14 g, 11.6 mmol) was placed in a 500 mL flask fitted with an inlet for chlorine. The flask was filled with chlorine and stoppered. A precipitate formed in a few minutes. More chlorine was introduced at 30 min intervals to maintain approximately 1 atm pressure. After standing under chlorine overnight, the precipitate was washed on a glass frit with $CFCl_2CF_2Cl$ (FC 113) and evaporated in vacuum to give 4.19 g (70%) of **2d** as a crystalline powder, mp 122−123 °C (dec). Recrystallization from chloroform gave transparent needles: MS (EI) 477 (M − Cl), 442 (M − Cl_2), 127 (I); ^1H NMR (CD_2Cl_2) δ 5.1 (t, 2 H, $J = 14$ Hz), 6.15 (tt, 1 H, $J = 52, 5$ Hz); ^{19}F NMR (CD_2Cl_2) δ −106 (t, 2F, $J = 14$ Hz), −121 (m, 4F), −123 (m, 2F), −129 (m, 2F), −137 (dt, 2F, $J = 52, 5$ Hz). Anal. Calcd for $C_7H_3Cl_2F_{12}I$: Cl, 13.82; I, 24.74. Found: Cl, 13.38; I, 25.06.

1-(Dichloroiodo)-2,2,2-trifluoroethane (2a). In a 100 mL flask with reflux condenser, thermometer, and chlorine inlet was placed CF_3CH_2I (24 g, 114 mmol). Chlorine was delivered above the surface under magnetic stirring and ice−salt cooling at such a rate as to maintain the temperature at 5−10 °C and prevent evaporation of volatile **1a**. When stirring became impossible (15 min), the suspension was filtered in a Schlenk funnel, washing with 8 mL of CCl_4. Removal of the solvent in vacuum gave 6.0 g (19%) of **2a** as a shiny yellow crystalline powder. The recovered CCl_4 solution of **1a** was chlorinated in the same way for 45 min, yielding 15.1 g of **2a** for a total yield of 66%. The solvent still containing **1a** was kept for further preparations. Finely powdered **2a** had mp 108−111 °C (dec): ^1H NMR ($CDCl_3$) δ 4.95 (q, $J = 8$ Hz); ^{19}F NMR ($CDCl_3$) δ −64.1 (t, $J = 8$ Hz). Anal. Calcd for $C_2H_2Cl_2F_3I$: Cl, 25.25; I, 45.19. Found: Cl, 25.40; I, 45.03.

1,1,1-Trifluoro-3-chloro-4-phenyl-2,4-butanedione (4d). **2a** (562 mg, 2 mmol) was added portionwise to a stirred solution of **3d** (432 mg, 2 mmol) in 5 mL of $CHCl_3$ at room temperature. After 1 h the volatiles were rotary-evaporated. The resulting viscous liquid solidified on exposure to atmospheric moisture. This solid was stirred 1 h in moist acetonitrile then concentrated in vacuum: 510 mg (95%) of **4d** as the monohydrate, off-white powder, mp 67.5−69 °C; ^1H NMR ($CDCl_3$) δ 4.5−4.7 (br, 1 H), 5.35 (s, 1 H), 5.5−5.7 (br, 1 H), 7.5−8.0 (5 H); ^{19}F NMR ($CDCl_3$) δ −83.6 (s). Anal. Calcd for $C_{10}H_8ClF_3O_3$: C, 44.71; H, 3.00; Cl, 13.20. Found: C, 44.82; H, 3.29; Cl, 13.23.

1-[Bis(trifluoroacetoxy)iodo]-2,2,2-trifluoroethane (5a). **2a** (1.40 g, 5 mmol) was added in one portion to a stirred suspension of silver trifluoroacetate (2.20 g, 10 mmol) in FC 113 (30 mL) cooled in an ice bath. The reaction was allowed to return to room temperature in 3 h. The white suspension was filtered on a glass frit, and the solvent was rotary-evaporated at room temperature. The resulting amber syrup crystallized overnight in the refrigerator at +5 °C. The solid was washed with 2 mL of cold CCl_4 and dried in vacuum affording 1.80 g (83%) of **5a** as a white powder. The NMR spectrum was as reported in the literature.[3c]

Supplementary Material Available: Copies of ^1H and ^{19}F NMR spectra of **2a,b,d** and ^1H NMR only of **4d** (7 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.