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Solvent effects on the reaction of perfluoroalkyl iodides and α,ω-perfluoroalkyl diiodides with cadmium powder and dimethylcadmium

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Abstract

Reaction of R_fI ($R_f=C_6F_{13}$ or C_8F_{17}) with Cd powder in DMF at room temperature under N_2 afforded R_fCdX (X=I or R_f) in moderate (48–52%) yield. Although no reaction was observed with Cd powder and R_fI ($R_f=C_6F_{13}$ or C_8F_{17}) in CH_3CN at room temperature, reaction at reflux gave the homocoupled products C_6F_{13}–C_6F_{13} (67%) and C_8F_{17}–C_8F_{17} (61%), respectively. No *F*-alkylcadmium reagent was detected by ^{19}F NMR spectroscopy. Similarly, the reaction of $I(CF_2)_nI$ ($n=3$, 4) with Cd powder in DMF and CH_3CN was examined. In DMF at room temperature, the new dicadmium reagents $ICd(CF_2)_nCdI$ and $ICd(CF_2)_{2n}CdI$ {~3:1} (60–65% combined yield) were formed. No reaction was observed with Cd powder and $I(CF_2)_nI$ ($n=3$, 4, 6) in CH_3CN at room temperature, but at reflux a mixture of higher α,ω-diiodoperfluoroalkanes, i.e. $I(CF_2)_{2n}I$, $I(CF_2)_{3n}I$, $I(CF_2)_{4n}I$, $I(CF_2)_{5n}I$, resulted. Treatment of $I(CF_2)_nI$ ($n=3$, 4) with $CdMe_2$ (1:2) in CH_3CN afforded the new ω-iodo *F*-alkylcadmium reagents, $[I(CF_2)_n]_2Cd\cdot(CH_3CN)$, in 96% ($n=3$) and 57% ($n=4$) yields. Reaction of Me_2Cd with either ICF_2CF_2I or $BrCF_2CF_2I$ in CH_3CN or HMPA at 0 °C resulted in tetrafluoroethylene only.

Introduction

We have reported the preparation of a number of fluorinated cadmium reagents in good yields via treatment of the appropriate *F*-alkyl iodide or bromide with acid-washed cadmium powder in DMF at room temperature [1–9]. No significant amounts of homocoupled products, R_f-R_f, were observed in these reactions. However, Chen and Tamborski reported the formation of the coupled product, R_f-R_f, by refluxing a mixture of *F*-alkyl iodides and Cd powder in CH_3CN [10]. A similar dichotomy on the effect of solvent has also been observed in the fluoroalkylation of organic substrates with Cu and R_fI. The donor number (*DN*) of the solvent determined whether the reactive intermediate was an *F*-alkyl radical or an *F*-alkylcopper reagent [11, 12]. These studies prompted us to examine the reaction of R_fI ($R_f=C_6F_{13}$ and C_8F_{17}) and of $I(CF_2)_nI$ ($n=3$, 4, 6) with Cd powder in both DMF and CH_3CN. A notable omission from the list of cadmium reagents reported from this

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laboratory is a dicadmium reagent {for example $ICd(CF_2)_nCdI$ ($n=3$, 4)} or an ω-halo-*F*-alkylcadmium reagent {for example $[X(CF_2)_n]_2Cd$ ($n=2$, 3, 4 and $X=I$ or Br}. The objectives of the present study were (a) to extend the earlier work [10] and study the reactions of R_fI and of $I(CF_2)_nI$ ($n=3$, 4, 6) with Cd powder as a function of the *DN* value of the solvent employed and (b) to determine whether a dicadmium {$ICd(CF_2)_nCdI$ ($n=3$, 4)} as well as an ω-iodo *F*-alkylcadmium reagent, $[I(CF_2)_n]_2Cd$ ($n=2$, 3, 4), could be prepared.

Results and discussion

When $C_6F_{13}I$ or $C_8F_{17}I$ was treated with acid-washed Cd powder in DMF at room temperature under N_2, a 48–52% ^{19}F NMR yield of the R_fCdX ($X=I$ or R_f)* reagent was obtained. The reaction mixture also contained some insoluble material which could be extracted with $CFCl_2CF_2Cl$. One of the solid materials identified was R_f-R_f (~10%). The characterization of the R_fCdX was aided by ^{19}F NMR spectroscopy as well as by hydrolysis of the cadmium reagent to R_fH. When CH_3CN was employed as the solvent, no reaction was observed at room temperature after 4 h. However, heating the reaction mixture to 75–80 °C in CH_3CN for 30 min resulted in the homocoupled product $R_f–R_f$ (61–67% isolated yield), as observed by Chen and Tamborski [10]. In this case, we did not detect the *F*-alkylcadmium reagent in the reaction mixture by ^{19}F NMR spectroscopy. The coupled product formed in this reaction is insoluble in CH_3CN and appears as a creamy solid material. Extraction of this material with $CFCl_2CF_2Cl$ and subsequent removal of the solvent afforded crude $R_f–R_f$. Pure homocoupled products were obtained upon vacuum sublimation as waxy solids.

$$R_fI + 2Cd \xrightarrow[\text{r.t., 30 min}]{\text{DMF}} \underset{48\text{–}52\%}{R_fCdX} + \underset{\sim 10\%}{R_f-R_f}$$

$$R_fI + Cd \xrightarrow[\substack{75\text{–}80\ ^\circ\text{C}\\ 30\ \text{min}}]{CH_3CN} \underset{61\text{–}67\%}{R_f-R_f}$$

The compounds $C_6F_{13}-C_6F_{13}$ and $C_8F_{17}-C_8F_{17}$ were characterized by melting point and spectral (^{19}F NMR, GC–MS and FT-IR) analyses. Authentic samples** exhibited the same melting points and ^{19}F NMR, GC–MS and FT-IR spectra. $C_{12}F_{26}$ and $C_{16}F_{34}$ are insoluble in DMF, $CHCl_3$, CCl_4 and Me_2CO but are sparingly soluble in $CF_2ClCFCl_2$ or $CFCl_3$.

The formation of the cadmium reagent or the homocoupled product in the reaction of R_fI and Cd can be rationalized on the basis of the *DN* value [13] of the solvent employed, as proposed by Chen and Yang [11, 12]. The

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*The exact nature of the aggregation of the cadmium reagents in solvents is not known; for simplicity they are represented as R_fCdX, $ICd(CF_2)_nCdI$ and $ICd(CF_2)_{2n}CdI$.

**Authentic samples were obtained from Fluorochem. Inc., UK.

first step of the reaction most likely involves an electron transfer from Cd to R_fI to generate $R_fI^{\cdot -}$, which forms $R_f^{\cdot}$ upon loss of iodide. When the solvent employed has a low *DN* value, for example CH_3CN ($DN = 14.1$), $R_f^{\cdot}$ dimerizes to afford the coupled product R_f-R_f. The $R_f^{\cdot}$ radical formed in this reaction can be intercepted by the addition of an olefin. For example, when the reaction is carried out in the presence of 1-heptene, formation of $CH_3(CH_2)_4CHICH_2C_6F_{13}$ (64% yield, ^{19}F NMR spectroscopy) is observed with no formation of R_f-R_f. On the other hand, a solvent with a high *DN* value favors the formation of the *F*-alkyl organometallics (R_fCdX), since these solvents stabilize the resultant organometallic derivative by coordination. Thus, in DMF ($DN = 26.6$), a 48–52% yield of R_fCdX reagent along with ~10% coupled product was observed.

The reaction of $I(CF_2)_nI$ ($n = 3$, 4) and Cd (1:2) in DMF also afforded the corresponding dicadmium reagent, $ICd(CF_2)_nCdI$ and $ICd(CF_2)_{2n}CdI$ (~3:1), in 60–65% combined ^{19}F NMR yield. The signals in the ^{19}F NMR spectrum for these two cadmium reagents overlapped, but the Cd reagents were identified by hydrolysis to the reduced products $H(CF_2)_nH$ and $H(CF_2)_{2n}H$ and by quenching the Cd reagents with iodine to the diiodides, $I(CF_2)_nI$ and $I(CF_2)_{2n}I$. These products were identified by ^{19}F NMR and GC–MS analysis and by comparison with authentic samples ($I(CF_2)_3I$, $I(CF_2)_4I$ and $I(CF_2)_6I$). No formation of $I(CF_2)_nH$ was observed on hydrolysis, which rules out the possibility of an ω-iodo-*F*-alkylcadmium reagent in this reaction.

The preparations of α,ω-diiodoperfluoroalkanes in low yields, from the telomerization of tetrafluoroethylene with iodine [14a–e], hot-tube reaction of diacid chlorides with potassium iodide [14f] and photolysis of bromoiododifluoromethane with tetrafluoroethylene [14g], have been reported. Bedford and Baum have reported the isolation of $I(CF_2)_2I$ (23%), $I(CF_2)_4I$ (20.7%), $I(CF_2)_6I$ (11.2%) and $I(CF_2)_8I$ (6.4%) from the telomerization of tetrafluoroethylene with iodine [14e]. They have also isolated small amounts of the higher telomers, $I(CF_2)_{10}I$ (3.9%) and $I(CF_2)_{12}I$ (1.1%), by vapor-phase chromatography. Chen and Tamborski have identified $I(CF_2)_8I$, $I(CF_2)_{12}I$ and $I(CF_2)_{16}I$ by GC–MS methods from the reaction of Cd and $I(CF_2)_4I$ in acetonitrile [10].

The reaction of $I(CF_2)_nI$ ($n = 3$, 4 or 6) and Cd powder (1:1) in CH_3CN at 75–80 °C for 1 h gave a mixture of telomeric α,ω-diiodoperfluoroalkanes.

$$I(CF_2)_nI \xrightarrow[75\text{–}80\ ^\circ C,\ 1\ h]{Cd,\ CH_3CN} I(CF_2)_{2n}I + I(CF_2)_{3n}I + I(CF_2)_{4n}I + I(CF_2)_{5n}I + \ldots$$

($n = 3$, 4, 6)

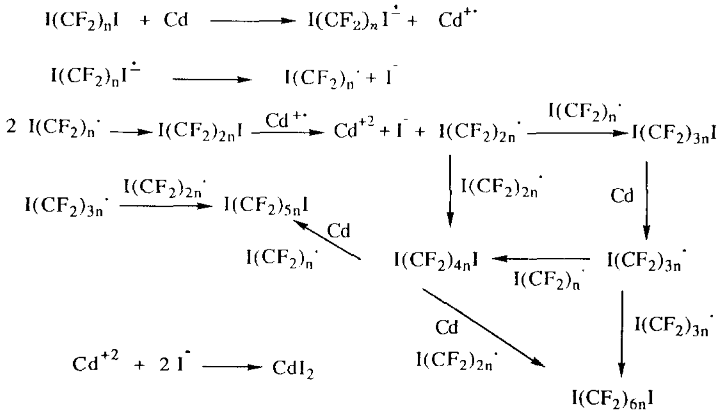
$I(CF_2)_nI$ ($n < 12$) could be removed with $CF_2ClCFCl_2$ {$I(CF_2)_{12}I$ sparingly soluble}, but diiodides with more than 12 CF_2 units were insoluble in acetone, CCl_4, $CHCl_3$, $(CF_3)_2CHOH$, $CF_2ClCFCl_2$ and $CFCl_3$. The solid material obtained after removal of the soluble materials in $CF_2ClCFCl_2$ on sublimation at 100–200 °C/0.005 mmHg separated $I(CF_2)_nI$ ($n = 12$–32) from the white solids. A major portion, presumably higher telomers {$I(CF_2)_nI$, $n > 32$}, was left in the sublimator. A possible mechanism based on Cd-mediated coupling of $I(CF_2)_nI$ to form the higher α,ω-diiodoperfluoroalkanes is depicted in Scheme 1. Mass spectral analysis of the sublimed material clearly indicated the molecular ions and other expected fragments (see Table 1). The diiodides containing 12–30 CF_2 units were found to be soluble in boiling $N(C_4F_9)_3$ (FC-43) or C_4F_4O (FC-77), but the dissolved material precipitates on cooling the solution to room temperature. Thus, the conversion of $I(CF_2)_nI$ ($n=3$, 4, 6) to higher telomers (in gram quantities) can readily be accomplished, but their separation to individual telomers proved difficult due to their insoluble nature in many solvents and relatively similar physical properties.

The reaction of Me_2Cd and 2 equiv. $I(CF_2)_nI$ ($n=3$, 4) in CH_3CN at 0–5 °C afforded the cadmium reagents $[I(CF_2)_n]_2Cd{\cdot}(CH_3CN)$. On removal of all volatiles under vacuum (~0.005 mmHg), the complexed reagents were obtained as viscous materials*.

$$2I(CF_2)_nI + Me_2Cd \xrightarrow[\text{0–5 °C, 48 h}]{CH_3CN} [I(CF_2)_n]_2Cd{\cdot}(CH_3CN)$$

$$96\%\ (n=3)$$
$$57\%\ (n=4)$$

The new ω-iodo F-alkylcadmium reagents were characterized by NMR analysis (^{19}F, ^{113}Cd and ^{1}H) and by hydrolysis to the corresponding reduced products, $I(CF_2)_nH$. The ^{113}Cd NMR (CH_3CN) spectrum of $[I(CF_2)_n]_2Cd{\cdot}(CH_3CN)$ exhibited a pentet of pentet of pentets at 261.5 ($n=3$) and a pentet of pentets at 259.7 ($n=4$) ppm. ^{1}H NMR spectra ($CDCl_3$) of the cadmium reagents displayed singlets at 2.32 ($n=3$) and 2.24 ($n=4$) ppm for coordinated CH_3CN which is shifted slightly downfield from free acetonitrile (2.07 ppm in $CDCl_3$); this is in accord with the previously reported values for coordinated acetonitrile [16]. A similar trend was also observed for the coordinated glyme in $(CF_3)_2Cd{\cdot}$glyme complex [17].



Scheme 1.

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*The exact number of CH_3CN molecules coordinated is not known. CH_3CN-complexed cadmium reagents $[(R_f)_2Cd{\cdot}2CH_3CN$ ($R_f=CF_3$, C_2F_5, C_3F_7, $(CF_3)_2CF$)] have been isolated [15].

TABLE 1

Mass spectral data for the α,ω-diiodoperfluoroalkanes[a]

Products from Cd + $I(CF_2)_nI$ in CH_3CN	M^+ m/e (% rel. intensity)	$(M-I)^+$ m/e (% rel. intensity)
n = *3*		
$I(CF_2)_6I$	554(12)	427(63)
$I(CF_2)_9I$	704(2)	577(18)
$I(CF_2)_{12}I$	854(2)	727(35)
$I(CF_2)_{15}I$	1004[b]	877(4)
$I(CF_2)_{18}I$	1154(19)	1027(8)
$I(CF_2)_{21}I$	1304(90)	1177(100)
$I(CF_2)_{24}I$	1454(89)	1327(91)
n = *4*		
$I(CF_2)_8I$	654(4)	527(47)
$I(CF_2)_{12}I$	854(2)	727(35)
$I(CF_2)_{16}I$	1054(70)	927[b]
$I(CF_2)_{18}I$	1154(19)	1027[b]
$I(CF_2)_{20}I$	1254(86)	1127(92)
$I(CF_2)_{24}I$	1454(4)	1327(4)
$I(CF_2)_{28}I$	1654(61)	1527(55)
$I(CF_2)_{32}I$	1854(38)	1727(33)
n = *6*		
$I(CF_2)_{12}I$	854(2)	727(35)
$I(CF_2)_{18}I$	1154(100)	1027(100)
$I(CF_2)_{24}I$	1454(7)	1327(8)
$I(CF_2)_{30}I$	1754(22)	1627(20)

[a] Mass spectra were obtained using a VG TRIO-1 (GC–MS) or VG ZABHF (DIP–MS) mass spectrometer at 70 eV (EI mode).

[b] Not detected.

The reaction between excess Me_2Cd and $I(CF_2)_3I$ resulted in $MeCd(CF_2)_3CdMe$, as $H(CF_2)_3H$ and CH_4 were identified by ^{19}F and ^1H NMR analysis after hydrolysis. Our attempts to prepare a β-iodotetrafluoroethylcadmium reagent from the reaction of Me_2Cd with ICF_2CF_2I or ICF_2CF_2Br in CH_3CN or HMPA at 0 °C were not successful. ^{19}F NMR analysis of the reaction mixture indicated only $F_2C{=}CF_2$. The reaction of Cd powder and ICF_2CF_2I in CH_3CN was also reported to give tetrafluoroethylene [10].

In conclusion, it is demonstrated that the *DN* value of the solvent dictates whether an *F*-alkyl organometallic derivative or the coupled product is formed in the reaction of the primary *F*-alkyl iodide or α,ω-diiodoperfluoroalkane with Cd powder. The cadmium-mediated telomerization of $I(CF_2)_nI$ ($n=3$, 4, 6) can be easily effected when acetonitrile is employed as the solvent; in contrast, dicadmium reagents are obtained with DMF as the solvent. The ω-iodo *F*-alkylcadmium reagents are readily formed in good yields on treatment of $I(CF_2)_nI$ ($n=3$, 4) with dimethylcadmium.

Experimental

General

All NMR spectra were recorded on a JEOL FX90Q or Bruker AC 300 spectrometer. ^{19}F NMR chemical shifts (83.81 MHz) are referenced to internal $CFCl_3$ standard, ^1H NMR chemical shifts (89.09 MHz or 300.17 MHz) are reported relative to internal TMS. The ^{113}Cd NMR chemical shifts (19.84 MHz) are reported relative to a saturated solution of $Cd(SO_4)_2 \cdot 8H_2O$ in D_2O (0.0 ppm). Mass spectra were acquired from a VG TRIO-1 (GC–MS) or VG ZABHF (DIP–MS) spectrometer operating at 70 eV.

Dimethylformamide and CH_3CN were distilled from CaH_2 and P_2O_5, respectively. Cadmium powder (100 mesh), $C_6F_{13}I$, $C_8F_{17}I$, $I(CF_2)_4I$, $I(CF_2)_6I$ and $CF_2ClCFCl_2$ were purchased from Aldrich Chemical Co. or PCR. Cadmium powder was activated by treatment with conc. HCl in acetone and dried under vacuum prior to use. $I(CF_2)_3I$ was prepared from $ClCO(CF_2)_3COCl$ and KI by a reported procedure [18]. Dimethylcadmium was prepared from MeLi and $CdBr_2$ in Et_2O and separated by fractionation at −78 °C. All ^{19}F NMR yield calculations were carried out with the addition of a known quantity of $C_6H_5CF_3$ to the sample solution.

Homocoupling of R_fI ($R_f = C_6F_{13}$, C_8F_{17})

C_6F_{13}–C_6F_{13} ($C_{12}F_{26}$) (cf. ref. 10)

To a stirred suspension of acid-washed Cd powder* (100 mesh) (1.12 g, 10 mmol) in CH_3CN (20 ml) in a 100 ml round-bottomed flask equipped with a septum port, nitrogen tee, magnetic stir-bar and reflux condenser, was added $C_6F_{13}I$ (4.0 g, 8.96 mmol) via a syringe. The reaction mixture was refluxed in an oil bath for 30–35 min when a white material precipitated. The reaction mixture was cooled to room temperature and added to $CFCl_2CF_2Cl$ (100 ml) and 2 M HCl (30 ml), mixed well and the solution filtered through a medium fritted funnel. The clear $CFCl_2CF_2Cl$ layer from the filtrate was separated, washed with water (2×25 ml) and concentrated on a rotary evaporator to afford a white waxy solid material which was sublimed at room temperature to 50 °C/0.005 mmHg (sublimator cold finger cooled by Dry Ice/isopropanol) to afford pure $C_{12}F_{26}$ in 67% (1.93 g) yield. M.p., 73–74 °C (lit. reported [10] 74–75 °C). ^{19}F NMR ($CFCl_2CF_2Cl$) δ: −81.5 (t, 6F, $J_{FF} = 10$ Hz); −121.9 (br s, 12F); −122.9 (br s, 4F); −126.5 (br s, 4F) ppm. GC–MS *m/e* (% relative intensity): 619 ($M^+ - F$, 0.1); 581 (0.06); 569 (0.05); 531 (0.3); 519 (0.2); 481 (0.6); 469 (0.5); 431 (1.2); 419 (1.2); 381 (2.3); 369 (2.9); 331 (5); 319 (9); 281 (9); 269 (21); 231 (19); 219 (55); 181 (29); 169 (100); 131 (71); 119 (70). FT-IR (KBr): 1418 (m); 1363(s); 1313(s); 1232(vs); 1227(vs); 1205(vs); 1151(vs); 1039(m); 847(m); 752(m); 650(m); 556(m); 556(m); 527(m). An authentic sample exhibited the same m.p. and spectral (^{19}F NMR, GC–MS and FT-IR) data.

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*Non acid-washed Cd powder also works well.

C_8F_{17}–C_8F_{17} ($C_{16}F_{34}$)

A mixture of acid-washed Cd powder (1.12 g, 10 mmol), $C_8F_{17}I$ (5.0 g, 9.2 mmol) and CH_3CN (30 ml) was refluxed for 1 h under nitrogen (apparatus as described above) and the crude $C_{16}F_{34}$ extracted in the same manner as for the $C_{12}F_{26}$ preparation. The white solid material obtained after the removal of the solvent was sublimed at 90–110 °C/0.005 mmHg to afford the title product in 61% (2.30 g) yield. M.p., 123–125 °C (lit. reported [19] 125 °C). ^{19}F NMR ($CFCl_2CF_2Cl$) δ: -81.59 (t, 6F, $J_{FF}=10$ Hz); -121.9 (br s, 20F); -123.6 (br s, 4F); -126.5 (br s, 4F) ppm. GC–MS *m/e* (% relative intensity): 731 ($M^+ - F$, 0.25); 681 (0.04); 669 (0.01); 631 (0.2); 619 (0.05); 581 (0.3); 569 (0.1); 531 (0.6); 519 (0.2); 481 (1.1); 469 (0.5); 431 (2); 419 (1); 381 (3.2); 369 (3.3); 331 (6.2); 319 (11); 281 (13); 269 (32); 231 (29); 219 (83); 181 (54); 169 (100); 131 (100); 119 (100). FT-IR (KBr) (cm^{-1}): 1371(m); 1328(m); 1208(vs); 1151(vs); 1115(vs); 1054(w); 918(w); 732(m); 646(m); 630(m); 555(m); 525(m). An authentic sample exhibited the same m.p. and spectral (^{19}F NMR, GC–MS and FT-IR) data.

Preparation of α,ω-diiodoperfluoroalkanes from $I(CF_2)_nI$ *and Cd*

$I(CF_2)_nI$ (n=6, 9, 12, *etc.*) *from* $I(CF_2)_3I$

A 50 ml round-bottomed flask equipped with a reflux condenser, nitrogen tee, magnetic stir-bar and septum port was charged with acid-washed Cd powder (1.12 g, 10 mmol), $I(CF_2)_3I$ (4.04 g, 10 mmol) and CH_3CN (12 ml). The reaction mixture was refluxed under N_2 for 1 h when a cloudy suspension resulted. The reaction mixture was cooled to room temperature and gravity-filtered. The material in the filter paper was washed with $CFCl_2CF_2Cl$ (60 ml), 10% HCl (15 ml) and water (2×20 ml). The $CFCl_2CF_2Cl$ layer was separated and concentrated on a rotary evaporator. The white solid in the filter paper was collected and dried under vacuum to afford an off-white powder (0.9 g). GC–MS analysis of the $CFCl_2CF_2Cl$ extract (0.3 g) showed the presence of $I(CF_2)_6I$, $I(CF_2)_9I$, $I(CF_2)_{12}I$, $I(CF_2)_9H$ and $I(CF_2)_{12}H$ (~1:1:0.1:0.3:0.2). Sublimation of the white powder at 110–120 °C/0.005 mmHg afforded 0.2 g of a white powder which was mainly $I(CF_2)_{12}I$; the unsublimable solid material (higher telomers) exhibited *m/e* values up to 1454 ($I(CF_2)_{24}I$) by DIP–MS (see Table 1). GC–MS *m/e* (% relative intensity): for $I(CF_2)_6I$: 554 (M^+, 12); 427 (63); 281 (15); 254 (8); 239 (9); 227 (15); 181 (18); 177 (100); 131 (67); 127 (66); 100 (34); 69 (45); for $I(CF_2)_9I$: 704 (M^+, 2); 577 (18); 431 (4); 254 (4); 239 (5); 231 (9); 181 (24); 177 (70); 131 (100); 127 (85); 100 (41); 69 (70); for $I(CF_2)_{12}I$: 854 (M^+, 2); 727 (35); 581 (10); 381 (2); 331 (3); 254 (5); 239 (10); 227 (20); 181 (32); 177 (75); 131 (100); 127 (68); 100 (20); 69 (67). [If the reaction mixture was refluxed for only 15 min under nitrogen, then the $CFCl_2CF_2Cl$ extract showed $I(CF_2)_3I$, $I(CF_2)_6I$, $I(CF_2)_9I$ and $I(CF_2)_{12}I$ (1:1:1:0.2). Trace amounts of the reduced products, $I(CF_2)_9H$ and $I(CF_2)_{12}H$, were also observed in the mass spectrum.]

$I(CF_2)_nI$ (n=8, 12, 16, etc.) from $I(CF_2)_4I$

A mixture of acid-washed Cd powder (1.12 g, 10 mmol) and $I(CF_2)_4I$ (4.54 g, 10 mmol) in dry CH_3CN (15 ml) was refluxed under nitrogen for 1 h. The $CFCl_2CF_2Cl$-soluble fraction (0.5 g) and the insoluble white solids (higher telomers, 1.20 g) were separated in the same manner as described in the previous procedure. Mass spectral analysis of the former indicated the presence of $I(CF_2)_4I$, $I(CF_2)_8I$, $I(CF_2)_{12}I$, $I(CF_2)_{16}I$ (trace), $I(CF_2)_8H$ and $I(CF_2)_{12}H$. DIP–MS analysis of the $CFCl_2CF_2Cl$-insoluble material exhibited mass units (*m/e*) up to 1854 ($I(CF_2)_{32}I$) (see Table 1). GC–MS *m/e* (% relative intensity): for $I(CF_2)_8I$: 654 (M^+, 4); 527 (47); 381 (14); 254 (6); 239 (11); 231 (8); 227 (20); 181 (28); 177 (95); 131 (100); 127 (84); 100 (36); 69 (69); for $I(CF_2)_{12}I$: same as in the previous case; for $I(CF_2)_{16}I$: 1054 (M^+, 70); 927 (1.3); 781 (1); 531 (1); 481 (1); 431 (1); 381 (2); 331 (4); 281 (14); 254 (8); 231 (35); 181 (58); 169 (72).

$I(CF_2)_nI$ (n=12, 18, 24, etc) from $I(CF_2)_6I$

The reaction was carried out in the same manner as described above except that $I(CF_2)_6I$ (15 mmol) was substituted for $I(CF_2)_4I$. GC–MS analysis of the $CFCl_2CF_2Cl$-soluble fraction (0.6 g) indicated the presence of $I(CF_2)_6I$, $I(CF_2)_{12}I$ and $I(CF_2)_{12}H$ (trace). The $CF_2Cl_2CF_2Cl$-insoluble solid material (2.5 g) was subjected to sublimation at 100–200 °C/0.005 mmHg; 0.4 g of a white material sublimed. High-resolution mass spectral analysis (EI–DIP) of this material indicated the presence of higher diiodides, containing up to 30 CF_2 units (see Table 1). High-resolution GC–MS *m/e* (% relative intensity): for $I(CF_2)_{12}I$: same as above; for $I(CF_2)_{18}I$: 1154 (M^+, 100); 1027 (100); 881 (34); for $I(CF_2)_{24}I$: 1454 (M^+, 7); 1327 (8); 1181(2); for $I(CF_2)_{30}I$: 1754 (M^+, 22); 1627 (22). (In each case, all ions corresponding to successive loss of CF_2 were observed in the mass spectrum.)

Reaction of R_fI [$R_f = C_6F_{13}$, C_8F_{17}] or $I(CF_2)_nI$ (n=3, 4) with Cd in DMF

R_fI ($R_f = C_6F_{13}$, C_8F_{17})

Acid-washed cadmium powder (2.24 g, 20 mmol) and DMF (20 ml) were placed in a 50 ml one-necked round-bottomed flask with septum port, magnetic stir-bar and a nitrogen tee. Then $C_6F_{13}I$ (4.46 g, 10 mmol) was added dropwise via a syringe to the suspension of Cd in DMF and the reaction mixture stirred for 10 min. An exotherm with the subsequent formation of a pale yellow supernatant was observed. ^{19}F NMR analysis of the supernatant indicated the formation of the corresponding cadmium reagent in 48% yield based on $C_6F_{13}I$. No $C_6F_{13}I$ was left in the reaction mixture. ^{19}F NMR δ: -82.0 (t, $J_{FF} = 10$ Hz); -118.9 to -119.5 (m); -121.0 (br s); -122.6 (br s); -123.7 (br s) -127.1 (br s) ppm. An aliquot (1 ml) of the cadmium reagent in DMF was transferred, via a syringe, to an NMR tube capped with a rubber septum and hydrolyzed with water ($\sim$0.2 ml) to afford $C_6F_{13}H$ (89% ^{19}F NMR yield based on $C_6F_{13}CdX$). ^{19}F NMR δ: -82.2 (t, 3F, $J_{FF} = 10$ Hz); -124.3 (brs, 4F); -127.3 (s, 2F); -130.3 (s, 2F); -139.7 (d, 2F,

$J_{FH}=49$ Hz) ppm. GC–MS m/e (% relative intensity): 321 ($M^+ + 1$, 0.8); 319 (0.3); 281 (3); 269 (0.8); 250 (2); 219 (2); 169 (16); 131 (32); 119 (28); 69 (100).

Isolation of $C_6F_{13}-C_6F_{13}$ — The cadmium reagent prepared as above was poured into water (50 ml) and the solid product (waxy material) was extracted with $CF_2ClCFCl_2$ (80 ml). The $CF_2ClCFCl_2$ layer was washed with 2 M HCl (5 ml) and water (2 × 10 ml) and concentrated on a rotary evaporator. The crude product was sublimed at room temperature to 50 °C/0.005 mmHg to afford 0.28 g (9%) of $C_6F_{13}-C_6F_{13}$.

In the same manner as described above, the reaction of $C_8F_{17}I$ (5.46 g, 10 mmol) and Cd powder (2.24 g, 20 mmol) in DMF (20 ml) was carried out. ^{19}F NMR yield of the cadmium reagent, 52% (based on $C_8F_{17}I$); no starting iodide was present in the reaction mixture. ^{19}F NMR δ: −82.2 (t, $J_{FF}=10$ Hz); −118.9 to −119.7 (m); −123.0 (br s); −123.8 (br s); −127.4 (br s) ppm. An aliquot (1 ml) of the cadmium reagent in DMF was transferred, via a syringe, to an NMR tube capped with a rubber septum and hydrolyzed with water (~0.2 ml) to afford $C_8F_{17}H$ (77%, ^{19}F NMR yield) based on the cadmium reagent. (Note: $C_8F_{17}H$ separates as a lower layer at the bottom of the tube on standing at room temperature for ~3 h.) ^{19}F NMR (DMF) δ: −83.1 (br s, 3F); −123.7 to −124.6 (peaks overlap, 8F); −127.8 (br s, 2F); −131.1 (s, 2F); −139.9 (d, 2F, $J_{FH}=51$ Hz) ppm for $C_8F_{17}H$.

Isolation of $C_8F_{17}-C_8F_{17}$ — Crude product was isolated from the reaction mixture in the same way as described for $C_6F_{13}-C_6F_{13}$; sublimation at 90–110 °C/0.005 mmHg afforded 0.54 g (10%) of n-perfluorohexadecane.

$I(CF_2)_nI$ (n=3, 4)

To a stirred suspension of acid-washed Cd powder (10 mmol) in dry DMF (10 ml) in a 25 ml round-bottomed flask, equipped with a nitrogen tee, septum port and a magnetic stir-bar, was added $I(CF_2)_3I$ (5 mmol) dropwise via a syringe. The reaction mixture was stirred for 15 min. A pale yellow reaction mixture resulted. ^{19}F NMR analysis indicated the complete disappearance of the starting diiodide with many resonances between −114 and −123, −131, −138 ppm (for $ICd(CF_2)_3CdI$, $ICd(CF_2)_6CdI$ and reduced products). The ^{19}F NMR yield of Cd reagents was 65%; the remaining 35% (yields based on $I(CF_2)_3I$) was comprised of reduced products [$H(CF_2)_3H$ and $H(CF_2)_6H$]. (Note: The resonances in the ^{19}F NMR spectrum could not be assigned with certainty to individual cadmium reagents since they overlapped.)

Hydrolysis of an aliquot (1 ml) of the reaction mixture with dilute HCl resulted in $H(CF_2)_3H$ and $H(CF_2)_6H$ (combined 92% ^{19}F NMR yield, based on the cadmium reagents) in a ~2:1 ratio. For GC–MS analysis, a portion of the volatile material was collected in a trap cooled by liquid N_2 via flash-distillation (r.t./0.05 mmHg). Treatment of the reaction mixture with I_2 afforded $I(CF_2)_3I$ and $I(CF_2)_6I$ (~2:1) (combined 78% ^{19}F NMR yield, based on the cadmium reagents). Both diiodides were identified by spiking with authentic samples (^{19}F NMR spectra). ^{19}F NMR ($CDCl_3$) δ: for $I(CF_2)_3I$: −58.0 (t, 4F,

$J_{FF}=5$ Hz); -105.2 (p, 2F) ppm; for $I(CF_2)_6I$: -58.8 (br s, 4F); -113.5 (s, 4F); -121.3 (s, 4F) ppm; for $H(CF_2)_3H$: -134.9 (t, 2F, ${}^3J_{FH}=5$ Hz); -138.9 (d, 4F, ${}^2J_{FH}=51$ Hz) ppm. GC–MS *m/e* (% relative intensity): 152 (M^+, 0.6); 151 (18); 131 (12); 101 (15); 100 (6); 69 (36); 51 (100). ${}^{19}F$ NMR ($CDCl_3$) δ: for $H(CF_2)_6H$: -123.1 (br s, 4F); -129.1 (br s, 4F); -137.2 (d, 4F, ${}^2J_{FH}=51$ Hz) ppm.GC–MS *m/e* (% relative intensity): 282 ((M^+-F, H), 0.2); 231 (0.2); 181 (5); 131 (7); 101 (10); 69 (21); 51 (100).

In the same manner as described above, the reaction of $I(CF_2)_4I$ (5 mmol) and Cd powder (10 mmol) in DMF (10 ml) was carried out [combined 60% ${}^{19}F$ NMR yield for cadmium reagents $ICd(CF_2)_nCdI$ ($n=4$, 8)]. ${}^{19}F$ NMR δ: -115 to -126; -131; -138 (peaks overlap) ppm. The reaction mixture was hydrolyzed with dilute HCl (~ 3 ml) and the volatile materials were collected in a trap cooled by liquid N_2 via flash-distillation (at r.t./0.01 mmHg). The mixture of $H(CF_2)_4H$ and $H(CF_2)_8H$ ($\sim$3:1) in the distilled material separated as a lower layer (combined 68% ${}^{19}F$ NMR yield, based on the cadmium reagents) ${}^{19}F$ NMR ($CDCl_3$) δ: for $H(CF_2)_4H$: -130.3 (s, 4F); -136.9 (d, 4F, $J_{HF}=51$ Hz) ppm GC–MS *m/e* (% relative intensity): 201 (M^+ $-$H, 3); 181 (5); 151 (11); 131 (21); 101 (18); 69 (36); 51 (100). ${}^{19}F$ NMR ($CDCl_3$) δ: for $H(CF_2)_8H$: -121.4 (s, 4F); -122.7 (s, 4F); -128.8 (s, 4F); -136.6 (d, 4F, $J_{HF}=50$ Hz) ppm. GC–MS *m/e* (% relative intensity): 381 ((M^+ $-$F, 2H), 0.1); 331 (0.1); 231 (2); 201 (2); 181 (7); 169 (3); 151 (10); 131 (28); 101 (21); 100 (7); 69 (46); 51 (100).

Preparation of $Cd[(CF_2)_nI]_2\cdot(CH_3CN)$ (n=3, 4)

$Cd[CF_2CF_2CF_2I]_2\cdot(CH_3CN)$

Into an NMR tube equipped with a Young valve [20] was introduced $I(CF_2)_3I$ (1.21 g, 3.0 mmol) and dry CH_3CN (1.5 ml) under nitrogen*. The tube was then attached to a standard vacuum line, degassed (at -196 °C) and Me_2Cd (0.21 g, 1.5 mmol) was condensed into the tube. The Young valve was closed and the contents in the tube mixed well and left at 0–5 °C for 48 h. After this time, all volatiles were removed (at $\sim$0.005 mmHg) from the reaction mixture to afford $Cd[CF_2CF_2CF_2I]_2\cdot(CH_3CN)$ as a viscous material (96% ${}^{19}F$ NMR yield). ${}^{19}F$ NMR (CH_3CN) δ: -57.7 (br s, 4F); -113.5 (br s, 4F); -117.2 (m, 4F) ppm; ${}^2J_{CdF}=222$ Hz, ${}^3J_{CdF}=31$ Hz. ${}^{113}Cd$ NMR (CH_3CN) δ: 261.5 (ppp) ppm; ${}^2J_{CdF}=224$ Hz, ${}^3J_{CdF}=31$ Hz, ${}^4J_{CdF}=8$ Hz. ${}^1H$ NMR ($CDCl_3$) δ: 2.32 (br s) ppm (for complexed CH_3CN). Hydrolysis of the Cd reagent produced $I(CF_2)_3H$ (90% ${}^{19}F$ NMR yield). ${}^{19}F$ NMR ($CDCl_3$) δ: -60.8 (s, 2F); -121.5 (m, 2F); -135.2 (d, 2F) ppm; ${}^2J_{FH}=51$ Hz. GC–MS *m/e* (% relative intensity): 278 (M^+, 10); 227 (1); 208 (3); 177 (30); 151 (100); 127 (47); 100 (22); 69 (77); 51 (85).

$Cd[CF_2CF_2CF_2CF_2I]_2\cdot(CH_3CN)$

This compound was prepared in the same manner as described above. ${}^{19}F$ ($CDCl_3$) δ: -57.5 (s, 4F); -112.4 (s, 4F); -117.4 (s, 4F); -119.7

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*NMR tubes with Young valves were purchased from Brunfeldt Company, Bartlesville, OK 74005, USA.

(br s, 4F) ppm (and other resonances at -58.9 (s), -111.8 (s) -118.9 and -123.5 ppm assigned tentatively to a cadmium compound containing $I(CF_2)_4Cd(CF_2)_4Cd(CF_2)_4I$ units) ^{19}F NMR yield 57% for $Cd[CF_2CF_2CF_2CF_2I]_2 \cdot (CH_3CN)$ (the remainder due to presumed $I(CF_2)_4Cd(CF_2)_4Cd(CF_2)_4I$). ^{113}Cd NMR ($CDCl_3$) δ: 259.7 (pp) ppm (other peaks overlap); $^2J_{CdF} = 228$ Hz, $^3J_{CdF} = 35$ Hz. ^{1}H NMR ($CDCl_3$) δ: 2.24 (br s) ppm (for complexed CH_3CN).

Hydrolysis of the Cd reagents gave $I(CF_2)_4H$ and $H(CF_2)_4H$ (~3:2) (combined ^{19}F NMR yield, 76%). The reduced products were flash-distilled under vacuum (0.05–0.01 mmHg) for GC–MS and NMR analysis. ^{19}F NMR ($CDCl_3$) δ: for $I(CF_2)_4H$: -59.6 (s, 2F); -114.2 (s, 2F); -127.9 (s, 2F); -137.1 (d, 2F) ppm; $^2J_{FH} = 50$ Hz. GC–MS *m/e* (% relative intensity): 289 (($M^+ - 2F$, 1H), 0.1); 277 ($M^+ - CF_2H$, 0.1); 227 (3); 201 (29); 177 (15); 131 (10); 127 (14); 84 (100); 51 (53). ^{19}F NMR ($CDCl_3$) δ: for $H(CF_2)_4H$: -130.5 (s, 4F); -137.1 (d, 4F) ppm; $^2J_{FH} = 50$ Hz. GC–MS *m/e* (% relative intensity): 202 (M^+, 0.7); 201 (0.2); 200 (3); 182 (20); 151 (13); 101 (44); 100 (9); 51 (25).

Reaction of excess Me_2Cd with $I(CF_2)_3I$

Dimethylcadmium (4.8 mmol) and $I(CF_2)_3I$ (2.04 mmol) were allowed to react in CD_3CN (1.5 ml) in the same way as described above. After the reaction, all volatile materials including excess Me_2Cd were removed under vacuum. ^{19}F NMR (CD_3CN) δ: -119.0 (m); -120.4 (br s); -131.2 (m); -132.7 (m) ppm. ^{113}Cd NMR (CD_3CN) δ: 369 (broad triplet, $^2J_{CdF} = 221$ Hz); 230 (m) ppm. ^{1}H NMR (CD_3CN) δ: -0.53 (br s) (for CH_3 attached to Cd) ppm. Hydrolysis gave $H(CF_2)_3H$ and CH_4. ^{19}F NMR δ: -134.9 (t, 2F, $^3J_{FH} = 5$ Hz); -138.9 (d, 4F, $^2J_{FH} = 51$ Hz) ppm. ^{1}H NMR ($CDCl_3$) δ; for $H(CF_2)_3H$: 5.93 (t, $^2J_{FH} = 51$ Hz) ppm; for CH_4: 0.10 (s) ppm.

Reaction of Me_2Cd with ICF_2CF_2I or $BrCF_2CF_2I$ in CH_3CN

Into an NMR tube equipped with a Young valve was introduced 1.5 ml of CH_3CN under nitrogen. The tube was then attached to a standard vacuum line, degassed (at -196 °C) and Me_2Cd (0.21 g, 1.5 mmol) and ICF_2CF_2I (1.06 g, 3.0 mmol) were sequentially condensed into it. In the same manner, CH_3CN (1.5 ml), Me_2Cd (0.21 g, 1.5 mmol) and $BrCF_2CF_2I$ (0.92 g, 3.0 mmol) were introduced into a second NMR tube equipped with a Young valve. Both tubes were sealed and warmed to 0 °C and maintained at that temperature for 10 min; evolution of a gaseous material from the reaction mixture was evident after 1 min at 0 °C. ^{19}F NMR spectra of both reaction mixtures exhibited a singlet at -132.3 ppm for C_2F_4 with complete disappearance of ICF_2CF_2I or $BrCF_2CF_2I$, respectively.

Similarly, a mixture of Me_2Cd (1.5 mmol) and ICF_2CF_2I or $BrCF_2CF_2I$ (3.0 mmol) were allowed to react in HMPA (1.5 ml) at 0 °C for 10 min under degassed conditions. ^{19}F NMR analysis of the reaction mixture indicated only the formation of C_2F_4.

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