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On the preparation of 1*H*-perfluoroalkanes and a mechanism for the reduction of perfluoroalkyl iodides

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Abstract

1*H*-Perfluoroalkanes are prepared by sodium methoxide reduction of 1-iodoperfluoroalkanes. The experimental evidence indicates that the reaction proceeds either through a radical or a thermal mechanism. We have found that a high yield of 1*H*-perfluoroalkanes at complete conversion can be accomplished at atmospheric pressure using this technology.

Keywords: 1*H*-Perfluoroalkanes; Methyl hypoiodide; Mechanism; Reduction; Mass spectrometry

1. Introduction

It is now widely accepted that chlorofluorocarbons (CFCs) deplete the stratosphere of its ozone, resulting in elevated global exposure to ultraviolet radiation [1,2]. For this reason, it is desirable to replace CFCs with 'environmentally friendly' compounds of equal or superior practical value. In addition to CFCs used for refrigerants, we have been searching for a replacement for 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113) which, in accordance with the Montreal Protocol, will be phased out on January 1, 1996. Hydrochlorofluorocarbons offer one possibility; however, because they contain chlorine, they too may be phased out in the future [3]. Perfluorocarbons offer another option, but their long atmospheric lifetimes can lead to high greenhouse warming. Hydrofluorocarbons are then leading candidates as second and third generation alternatives. Part of our research efforts have been on evaluating the 1*H*-perfluoroalkanes as CFC replacements.

1*H*-Perfluoroalkanes have been described in the literature since 1952 [4]. They are often described as nuisance by-products of different reactions involving perfluoroalkyl halides [5–10]. Few mechanistic studies have been completed, and the mechanism for reactions of perfluoroalkyl iodides is thought to be a single electron transfer [11,12]. Earlier studies have described the preparation of 1*H*-perfluoroalkanes through the reaction between perfluoroalkyl halides and various alcohols mixed with aqueous caustic [13,14]. While high yields are obtained in some cases, there was still incomplete conversion [15]. Complete conversion can only be accomplished with elevated temperatures and pressure [16]. Because of the ease of carbon–iodine bond breakage and ensuing iodine discoloration, most commercial products must be free of perfluoroalkyl iodide.

2. Results and discussion

We have found that anhydrous sodium methylate is an effective reagent for the conversion of 1-iodoperfluoroalkanes to the corresponding 1*H*-perfluoroalkanes. Further, the reactions have led to the isolation of a product containing very low levels of R_fI in reasonable reaction times.

Of importance to us was the reaction time required to completely convert all of the starting R_fI to R_fH. Our studies were conducted in two phases. The first phase, conducted in dilute solution using 10 parts of sodium methylate (25% solution) to 1 part of perfluoroalkyl iodide (R_fI), was used to study the reaction mechanism. The second phase examined a more practical stoichiometry using 2 parts of base to 1 part of iodide. **NB. During the course of our studies, a large reaction vessel ruptured violently and minor personal injury occurred**. Thus, it was important to fully understand all aspects of this reaction and mechanistic studies were conducted to explain the cause of the

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sudden over-pressure. One major observation we made is that the reaction is extremely exothermic.

2.1. Yields of various telomers

Good yields of product were obtained for each perfluoroalkyl iodide, from $R_f=C_4F_9-$, $C_6F_{13}-$, $C_8F_{17}-$ and $C_{10}F_{21}-$, when reaction was undertaken on a small laboratory scale (0.03–1 mol). The optimal stoichiometry for complete reaction in minimum time for these reactions was an R_fI/NaOMe ratio of 1:2. Because of the low boiling point of starting material and product, the best results for the preparation of C_4F_9H were obtained using a photochemical reactor. Our results contrast with those of Minert et al., who found incomplete conversion and much lower yields for $C_6F_{13}I$ (PFHI) and $C_8F_{17}I$ (PFOI) in methanol with aqueous caustic after 1 h at 70 °C [13]. They also report no reaction between sodium or potassium hydroxide and perfluorooctyl bromide. Table 1 shows the yields for each starting R_fX. In each case the conversion was quantitative. For perfluorooctyl bromide, the reaction was 99% complete in 1.3 h and no perfluorooctyl bromide was detected after 7 h. Quantitative yields were obtained in pilot operations for the conversion of $C_6F_{13}I$ to $C_6F_{13}H$ (PFHH).

2.2. Effect of stoichiometry

A determination of the effect of stoichiometry on the time required for complete conversion was made. In these experiments the 1-iodoperfluorohexane was added to refluxing sodium methylate and samples taken after 15 min, 1 h and 5 h, respectively. Table 2 shows that all the 1-iodoperfluorohexane had been converted after 5 h when the PFHI/NaOMe ratio was 1:2. In the experiment where the ratio was 1.05:1, the reaction was still incomplete after 23 h at reflux.

2.3. Effect of temperature

Fig. 1 indicates that no reaction occurred between 1-iodoperfluorohexane and sodium methylate at room temperature after 15 min. This is in contrast to the work of Meinert et al. [13] who found reactions occurring "well below 0 °C". Adding 1-iodoperfluorohexane to sodium methylate held at successively higher temperatures decreased the amount of unconverted PFHI significantly.

Table 1
Isolated yield of 1*H*-perfluoroalkanes from laboratory-scale reactions

Starting R_fI	Yield (%)
C_4F_9I	93
$C_6F_{13}I$	85
$C_8F_{17}I$	86
$C_8F_{17}Br$ [a]	81
$C_{10}F_{21}I$	87

[a] Stoichiometry: MeONa/PFOB = 4:1.

Table 2
Conversion of PFHI to PFHH at reflux

NaOMe/PFHI ratio	PFHI (%) remaining at			Yield (%)
	15 min	1 h	5 h	
1.05:1	20.7	16.6	6.1	87.0
1.5:1	8.4	3.7	0.1	86.0
2:1	0.5	0.02	0.0	73.0
4:1	0.8	0.16	0.0	81.0
10:1	0.3	NA [a]	NA	NA

[a] NA = not available.

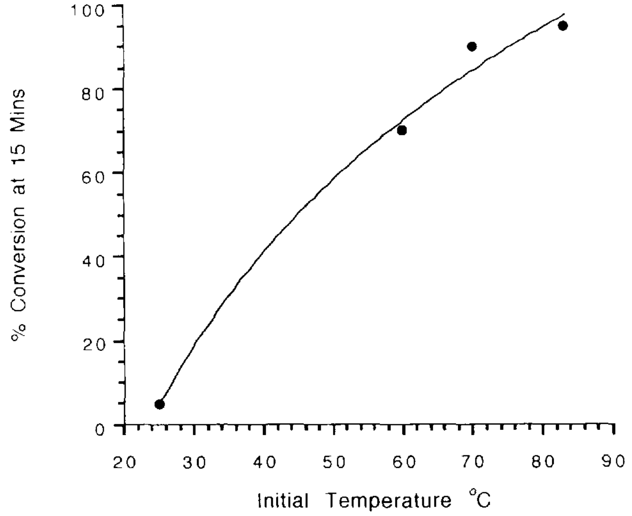


Fig. 1. The effect of starting temperature on conversion after 15 min reaction. Stoichiometry: PFHI/NaOMe = 1:10.

2.4. Effect of halogens

As our studies progressed it appeared that iodine might be enhancing the reaction rate. We noticed a more vigorous reaction occurred if the 1-iodoperfluorohexane contained small amounts of dissolved iodine. For this reason, the effects of bromine and iodine were investigated. In these experiments differing levels of X_2 in methanol containing 1-iodoperfluorohexane were added to the methylate solution held at 25 °C. Table 3 and Fig. 2 show that as the I_2 level increased the rate of reaction increased, as did the resulting exotherm. The same effect was not observed with bromine. When 7786 ppm of bromine was added to the mixture at 25 °C, there was no corresponding exotherm and no conversion of 1-iodoperfluorohexane for the first hour. Subsequently, 45 min after heating this mixture to reflux, there was complete conversion of the 1-iodoperfluorohexane to product.

Table 3
Effect of iodine on the reaction exotherm and percentage conversion [a]

I_2 concentration (ppm)	Change in temperature [b] (°C)	Conversion of R_fI after 15 min (%)
7188	27	100.0
6745	25	98.0
3594	6	14.2
1797	4	10.5
897	2	8.7

[a] Starting temperature was 25 °C, NaOMe/PFHI = 10:1.
[b] Reactions run on a 60 ml scale.

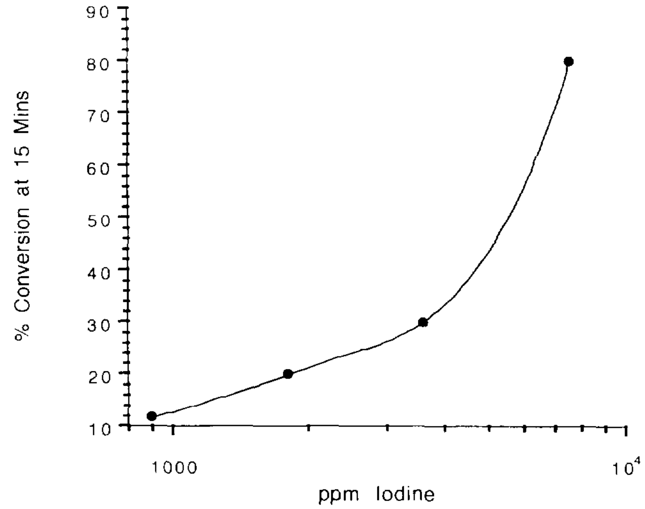


Fig. 2. The effect of I_2 concentration on the conversion of PFHI to PFHH after 15 min. Stoichiometry: R_fI/NaOMe = 1:10.

2.5. *Effect of irradiation*

Suspecting a radical-type reaction, the use of irradiation to initiate the reaction was explored. Sodium methylate and 1-iodoperfluorohexane were mixed at 25 °C and held for 15 min in the absence of light. Gas chromatographic analysis of a sample taken at that time showed no reaction. While maintaining the temperature at 25 °C, the flask was irradiated using a low-intensity sunlamp. After a further 15 min, 20% of the 1-iodoperfluorohexane remained and after 30 min only 0.06% remained.

2.6. *Effect of radical traps*

To further test the radical nature of the reaction, the effect of radical traps was studied using both *p*-dinitrobenzene (DNB) and 1-octene. In a typical reaction, sodium methylate was mixed with DNB and to this solution at 25 °C was charged 1-iodoperfluorohexane in methanol containing 7000 ppm of I_2. A stoichiometry of NaOMe/PFHI/DNB = 10:1:0.1 was employed. After 15 min, 20% of the 1-iodoperfluorohexane had been converted to 1*H*-perfluorohexane. Heating this mixture to reflux led to 90% conversion of the 1-iodoperfluorohexane at 15 min and 99% conversion at 30 min.

The reaction was repeated with 1-octene but using a stoichiometry of NaOMe/PFHI/octene = 10:1:1. The solution again contained 7000 ppm of I_2. The first sample taken after 15 min at room temperature contained 2% 1*H*-perfluorohexane. The first sample taken at 15 min after reflux showed 12% 1*H*-perfluorohexane and 32% $C_6F_{13}CH{=}CHC_6H_{13}$, as confirmed by mass spectrometry. The product observed must arise from the addition of 1-iodoperfluorohexane to the double bond in 1-octene followed by dehydrohalogenation in the basic solution.

2.7. *Reactions in deuterated methanols, CH_3OD or CD_3OH*

Additional reactions to study the source of hydrogen in the product were conducted by replacing sodium methylate with either CD_3ONa/CD_3OH or CH_3ONa/CH_3OD. A stoichiometry of PFHI/RONa = 1:2 was employed. The appropriate methylate was prepared as a 25% solution by adding sodium metal to the starting alcohol. Thermal initiation was achieved by adding R_fI to the mixture at 80–84 °C and samples taken at low conversion and after short reaction times showed that the product was R_fD almost exclusively (see Table 4). Photochemical reactions were performed while keeping the solution cold and shining a sun lamp on the mixture.

2.8. *Reactions with potassium t-butoxide in t-butyl alcohol*

Earlier reports [13,16] indicated that t-butyl alcohol or its salts do not react with perfluoroalkyl iodides. Under more forcing conditions than those reported, we have found that potassium t-butoxide in t-butyl alcohol will react with 1-iodoperfluorohexane. A mixture of PFHI/$KOC(CH_3)_3$/t-butyl alcohol at a ratio of 1:10:80 at 60 °C showed no 1-iodoperfluorohexane remaining after several hours. Gas chromatographic analysis showed the expected product, 1*H*-perfluorohexane, in low yield along with many other unidentified peaks.

Table 4
Results of deuterium experiments

Initiator	CH_3ONa/CH_3OD mixture	CD_3OH/CD_3ONa mixture
thermal	PFHD (91.5%)	NA [a]
photochemical	PFHH (100%)	PFHD (100%)

[a] NA = not available.

2.9. Control reactions

A control reaction using only methanol and 1-iodoperfluorohexane was photolyzed for several hours. Although the solution mixture turned brown indicating the presence of elemental I_2, PFHH was not detected. It is believed that the recombination of $R_f\cdot$ with $I\cdot$ was fast in a high concentration of I_2. With the addition of mercury metal to the mixture, there was complete conversion of 1-iodoperfluorohexane to 1*H*-perfluorohexane. In addition to the product, CH_3I was observed along with several per cent of $CH_3OCH_2OCH_3$, as well as traces of $Hg(CH_3)_2$. No evidence of coupling was observed.

During the deutero experiments, it appeared that the deuterium in 1*D*-perfluorohexane was being exchanged and 1*H*-perfluorohexane being formed. Complete conversion of 1*D*-perfluorohexane to 1*H*-perfluorohexane was observed in 60 min by using a large excess of methanol in sodium methylate at 60 °C.

2.10. Mechanism

We have found that perfluoroalkyl iodides react with sodium methylate through either a radical or thermal mechanism. The radical pathway can be observed in the low-temperature regime by using radical generators, either ultraviolet light or the in-situ generation of methyl hypoiodite by the addition of I_2. Standard radical traps disrupt this pathway. The thermal pathway is initiated at elevated temperatures in the absence of iodine or sunlight.

2.10.1. Thermal initiation

The mechanism for thermal initiation is shown in Eq. (1). We postulate that the methoxide ion abstracts I^+ from R_fI producing a perfluoro carbanion. The ensuing carbanion, (Eq. (2)) is quenched by a proton from the bulk solvent, forming the product and regenerating the methoxide ion. Methyl hypoiodite then thermally decomposes to formaldehyde and HI (Eq. (3)). Neither the olefin, $R_fCF{=}CF_2$, nor its expected methanolysis product, $R_fCF{=}CFOCH_3$, was observed.

$$CH_3O^- + R_fI \longrightarrow CH_3OI + R_f^- \qquad (1)$$

$$R_f^- + CH_3OH \longrightarrow R_fH + CH_3O^- \qquad (2)$$

$$CH_3OI \longrightarrow \text{`}CH_2O\text{'} + HI \qquad (3)$$

Two pieces of evidence are available for this pathway. First, in the absence of initiators, no reaction occurred at room temperature. Heating the mixture resulted in a spontaneous reaction that began between 40 °C and 60 °C and was very fast at 80 °C. The other is the high level of deuterium incorporation when R_fI was added to CH_3ONa/CH_3OD. Because the only deuterium source was CH_3OD, the only explanation for product formation is through a carbanion. The observation that less than 100% of 1*D*-perfluorohexane was obtained can be explained as follows: either HI was formed from the decomposition of CH_3OI, the HI then reacting with sodium methylate to give methanol which becomes the source of protons for R_f^-; or methyl hypoiodite underwent homolytic bond cleavage to give a partial radical pathway contribution. This contribution must be small since there was only 8.5% proton incorporation. Since deuterium exchange does occur, the exact contribution to a radical or thermal pathway could not be ascertained although there was a high contribution to the thermal pathway. The exchange of R_fCF_2D to R_fCF_2H has been reported for $R_f{=}F$, C_2F_5 and C_6F_{13} [17a–c].

2.10.2. Radical initiation by I_2

At low temperature, the addition of 7000 ppm of elemental iodine initiated the reaction. The initial product is thought to be methyl hypoiodite (Eq. (4)), although it was not fully characterized. It has, however, been reported to be thermally unstable [18]. Because the reaction was stopped by the addition of radical traps, we speculate that CH_3OI undergoes spontaneous homolytic bond cleavage into methoxy and iodide radicals, (Eq. (5)). Each of these radicals can abstract iodine from R_fI forming $R_f\cdot$ and initiating the radical pathway (Eqs. (6) and (7)). Propagation can be accomplished by abstracting a hydrogen from methanol and forming the $\cdot CH_2OH$ radical (Eq. (8)). This radical then abstracts $I\cdot$ from R_fI to give $R_f\cdot$ and ICH_2OH (Eq. (9)). The absolute incorporation of deuterium into R_fD from CD_3OH/CD_3ONa and the same for R_fH from CH_3OD/CH_3ONa demonstrates unambiguously that the hydrogen source in this radical reaction was carbon-centered.

$$I_2 + CH_3ONa \longrightarrow CH_3OI + NaI \qquad (4)$$

$$CH_3OI \longrightarrow CH_3O\cdot + I\cdot \qquad (5)$$

$$I\cdot + R_fI \longrightarrow I_2 + R_f\cdot \quad \text{(initiation)} \qquad (6)$$

$$CH_3O\cdot + R_fI \longrightarrow CH_3OI + R_f\cdot \quad \text{(initiation)} \qquad (7)$$

$$R_f\cdot + CH_3OH \longrightarrow R_fH + \cdot CH_2OH \quad \text{(propagation)} \qquad (8)$$

$$\cdot CH_2OH + R_fI \longrightarrow R_f\cdot + ICH_2OH \quad \text{(propagation)} \qquad (9)$$

$$I\cdot + \cdot CH_2OH \longrightarrow ICH_2OH \quad \text{(termination)} \qquad (10)$$

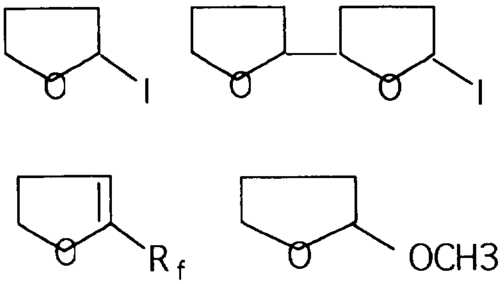
$$R_f\cdot + I\cdot \longrightarrow R_fI \quad \text{(termination)} \qquad (11)$$

$$I\cdot + I\cdot \longrightarrow I_2 \quad \text{(termination)} \qquad (12)$$

Numerous termination steps are possible; Eq. (10) shows the expected one, and the other two (Eqs. (11) and (12)) are non-productive giving starting material or iodine which would start the cycle again.

Additional evidence for both reaction pathways was found in the observation that solutions containing both iodine and radical traps, while non-reactive at room temperature, showed complete conversion to 1*H*-perfluorohexane when heated, i.e. radical initiation of the reaction was halted by radical quenchers and the thermal mechanism was operative when the solutions were heated.

If tetrahydrofuran was used as the solvent, along with solid sodium methylate and 8000 ppm of iodine as an initiator, the reaction was exothermic giving mostly R_fH and traces of the following products (identified via GC/MS).



Notably, the products are those expected from most of the various termination steps postulated above and further confirm the radical pathway.

Further proof that methyl hypoiodite can undergo homolytic bond cleavage comes from the report of the addition of MeO– and I– to the terminal double bond in selected dienes when the reaction was carried out at −10 °C with in-situ formed methyl hypoiodite [19]. Methyl hypobromite formed in situ also does not initiate this reaction, presumably due to its inability to undergo homolytic bond cleavage under the reaction conditions. At least one report on the use of methyl hypobromite indicates that it does not behave like in-situ formed methyl hypoiodite [20].

Finally, it has been shown that it is not necessary for the carbon adjacent to the alcohol moiety to possess a hydrogen atom. As shown separately, t-butoxide ion in t-butanol when reacted thermally gave the expected product. In this case the oxidized species was the stable t-butyl hypoiodite. In other reactions involving t-butyl hypoiodite, intractable masses have been observed [21]. The difference in basicity between methoxide and t-butoxide may account for the lower reactivity.

2.11. *The fate of the oxidized species*

The question as to the fate of the ICH_2OH or CH_3OI postulated as being formed in the thermal or radical-initiated reaction, respectively, is answered by the nature of the methanol solution after reaction. First, it should be noted that there are no reports of the physical characteristics of ICH_2OH or CH_3OI, so we speculate that either can lose HI spontaneously under the reaction conditions forming CH_2O and HI. In a strong base the HI is neutralized to methanol and sodium iodide (Eq. (14)) while the formaldehyde either undergoes a Cannizarro reaction forming methyl formate (Eq. (15)) or is oxidized to methyl formate by methyl hypoiodite [22] (Eq. (16)). Additionally, dimethyl carbonate was observed in the reaction mixture. We speculate that this is formed from methyl formate by a second oxidation (Eq. (17)). No precedent for this was found in the literature. Both compounds were identified from their characteristic mass spectra.

$$ICH_2OH \longrightarrow HI + CH_2O \tag{13}$$

$$HI + MeONa \longrightarrow MeOH + NaI \tag{14}$$

$$2CH_2O + MeONa/MeOH \longrightarrow CH_3OCOH + MeOH/MeONa \tag{15}$$

$$CH_2O + MeOI \longrightarrow HC(O)OCH_3 + HI \tag{16}$$

$$2HC(O)OCH_3 + MeOI \longrightarrow [CH_3O]_2CO + HI \tag{17}$$

3. Experimental details

Perfluoroalkyl iodides were obtained from the DuPont Parkersburg Plant and distilled before use. Sodium methylate was purchased from Fluka or Aldrich and used as received. Other chemical reagents were commercially available and used as received.

Gas chromatographic/mass spectrometric data were obtained using a Hewlett Packard HP 5890 Series II gas chromatograph with a Series 5972 mass selective detector. Unless otherwise reported, yields are as product isolated. The reaction was monitored with a HP 5890 GC using a 50 m HP-1 column with a 5 min hold at 40 °C and then taken to 200 °C at 15 °C min^{-1}. The flow rate was 100 cm^3 min^{-1} with a split ratio of 50:1. ^1H NMR spectra were obtained on a Varian Gemini-200 instrument at 200 MHz using $Si(Me)_4$ as internal standard. ^{19}F NMR were obtained on a Varian VXR-300 instrument at 300 MHz using $CFCl_3$ as internal standard.

3.1. *Preparation of 1H-perfluorohexane*

CAUTION: Minor personal injury occurred when this reaction was performed on a large scale (12 l flask) using fresh sodium methylate and iodine-free perfluoro-

hexyl iodide. At 59 °C, the reaction initiated and rapidly generated a pressure pulse which violently ruptured the flask.

In a typical reaction, a 250 ml three-neck Pyrex glass reactor was equipped with a magnetic agitator, a thermocouple, a reflux condenser and an addition funnel. The reactor was charged with 54 g (25 wt.%) of sodium methylate and the appropriate amount of additional reagents. While the reaction mixture was held at room temperature (15–25 °C), 13.4 g of iodine-free (83%) perfluorohexyl iodide was added slowly to the flask. The iodine was removed by washing with sodium thiosulfate solution. For the radical trap experiments, the radical trap was added to the methylate solution and the initiator added with the perfluoroalkyl iodide in methanol. A general-purpose sunlamp was used for the photolysis reactions (Sylvania 110 VAC low intensity sunlamp). To study the thermal mechanism, the methylate solution was warmed to 80–83 °C before addition of the perfluoroalkyl iodide.

The reaction mixture was held at constant temperature and sampled periodically. After 15–30 min, the mixture was heated to reflux and sampling continued for 1–4 h. At the end of the reflux period, the reaction mixture was cooled, 100 ml of water added and the 1*H*-perfluorohexane separated. Typical yields were 80%–95% and were usually free of residual perfluorohexyl iodide. Spectral data and other properties

Table 5
EI mass spectral data

m/e	Ion	C_4F_9H (220) [a]	$C_6F_{13}H$ (320)	$C_6F_{13}D$ (321)	$C_8F_{17}H$ (420)	$C_{10}F_{21}H$ (520)
31	CF	13.2	7.7	9.3	6.0	4.8
51	CF_2H	73.7	97.5		96.8	75.5
52	CF_2D			100.0		
69	CF_3	100.0	100.0	89.3	100.0	100.0
82	C_2F_3H	7.7	7.4		4.7	3.8
83	C_2F_3D			7.0		
93	C_3F_3	5.6	7.0	5.1	5.9	5.7
100	C_2F_4	20.9	22.7	16.8	21.7	20.2
101	C_2F_4H	14.7	36.4		32.7	23.5
102	C_2F_4D			31.6		
113	C_3F_4H	23.4	11.4		12.5	12.6
114	C_3F_4D			9.1		
119	C_2F_5	29.6	32.2	23.1	35.5	33.1
131	C_3F_5	27.3	4.6	33.2	54.9	57.0
132	C_3F_5H		2.0		0.4	2.3
133	C_3F_5D			0.4		
143	C_4F_5		0.4	0.2	1.0	1.6
150	C_3F_6	10.7		0.8		
151	C_3F_6H		16.2		20.3	12.8
152	C_3F_6D			10.6		
169	C_3F_7	10.2	23.7	12.3	16.6	16.7
181	C_4F_7		4.4	2.3	9.1	10.7
200	C_4F_8		0.6	0.3		
201	C_4F_8H		0.8		4.1	3.3
202	C_4F_8D			0.4		
213	C_5F_8H		3.0		0.5	0.6
214	C_5F_8D			1.6		
219	C_4F_9		1.2	0.5	4.5	4.0
231	C_5F_9		11.9	5.8	2.2	4.7
250	C_5F_{10}		5.4	2.1	0.1	
251	$C_5F_{10}H$		0.3		0.4	0.6
269	C_5F_{11}			0.0	2.2	1.7
281	C_6F_{11}				0.5	1.7
313	$C_6F_{12}H$				0.4	
319	C_6F_{13}					0.9
331	C_7F_{13}				4.1	0.5
350	C_7F_{14}				0.4	
369	C_7F_{15}					0.4
431	C_9F_{17}					2.8
450	C_9F_{18}					0.1

[a] Molecular weights listed in parentheses.

associated with the various perfluorohexane produced are listed below while electron impact (EI) mass spectral data are given in Table 5.

C_4F_9H: b.p. 16 °C [14]. ^1H NMR δ: 6.2 (t of t, $J_{H-F}=51.6$ Hz, $^1J_{H-F}=5.1$ Hz) ppm. ^{19}F NMR δ: -81.5 (t of t, 3F); -127.8 (m, 2F); -130.2 (m, 2F); -138 (d of m, 2F, $J_{H-F}=51.6$ Hz) ppm. IR (cm^{-1}): 3004 (vvw); 1338.7 (m); 1288.0 (m,sh); 1240.5 (vs); 1199.5 (s,sh); 1142.6 (s); 967.2 (m); 916.8 (m); 815.1 (m); 743.2 (m). MS (CI) *m/e*, ion, intensity: 201 (M − F) 100%.

$C_6F_{13}H$: b.p. 70 °C. ^1H NMR δ: 6.2 (t of t, $J_{H-F}=51.6$ Hz, $^1J_{H-F}=5.1$ Hz) ppm. ^{19}F NMR δ: -81.25 (t of t, 3F); -122.5 (m, 2F); -123.1 (m, 2F); -126.04 (m, 2F); -129.4 (m, 2F); -137.9 (d of m, 2F, $J_{H-F}=51.5$ Hz) ppm. IR (cm^{-1}): 3008.2 (vw); 2983.5 (vw); 1400.9 (w); 1345.6(m); 1239.3(vs); 1199.5 (s,sh); 1144.9 (s); 1081.9(m); 996.1(m); 867.2(m); 800.9(m); 743.8(m); 722.8(m sh). MS (CI) *m/e*, ion, intensity: 301 (M − F) 100%; 231 C_5F_9 95%.

$C_8F_{17}H$: b.p. 120 °C. ^1H NMR δ: 6.2 (t of t, $J_{H-F}=51.3$ Hz, $^1J_{H-F}=4.8$ Hz) ppm. ^{19}F NMR δ: -81.24 (t of t, 3F); -121.5 (m, 4F); -122.3 (m, 2F); -122.8(m, 2F); -125.95(m, 2F); -129.3 (m, 2F); -137.8 (d of m, 2F, $J_{H-F}=51.7$ Hz) ppm. IR (cm^{-1}): 3008.2 (vw); 2983.2 (vw); 1400.7 (w); 1349.7 (m); 1241.4 (vs); 1199.5 (s,sh); 1146.5 (s); 1080.1(m); 1011.6(m); 886.1(m); 795.4 (m broad); 737.9 (m). MS (CI) *m/e*, ion, intensity: 401 (M − F) 33%; 331 C_7F_{13} 100%; 269 C_5F_{11} 13%; 219 C_4F_9 13%; 151 C_3F_6H 16%; 113 C_3F_4H 19%; 69 CF_3 18%.

$C_{10}F_{21}H$: m.p. 30–31 °C (uncorrected). ^1H NMR δ: 6.4 ($J_{H-F}=51.3$ Hz, $^1J_{H-F}=5.1$ Hz) ppm. ^{19}F NMR δ: -81.25 (t of t, 3F); -121.4 (m, 4F); -121.6 (m, 2F); -122.4 (m, 2F); -123.0 (m, 2F); -126.1 (m, 2F); -129.3 (m, 2F); -138.1 (d of m, 2F, $J_{HF}=51.3$ Hz) ppm. IR (cm^{-1}): 3008.0 (vw); 2984.2 (vw); 1440.4(w); 1349.4(m); 1243.5(vs); 1199.5(s,sh); 1145.7(s); 1081.1(m); 1015.8(m); 855.2(m); 799.5(m); 776.1(m); 732.2(m); 708.4(m,sh). MS(CI) *m/e* ion, intensity: 501 (M − F) 30%; 431 C_9F_{17} 100%; 369 C_7F_{15} 14%; 319 C_7F_{13} 15%; 269 C_5F_{11} 25%; 201 C_4F_8H 45%; 151 C_3F_6H 78%; 113 C_3F_4H 55%; 69 C_7F_{13} 56%.

$C_6F_{13}CH{=}CHC_6H_{13}$: MS (EI) *m/e*, ion, intensity: 430 $C_{14}F_{13}H_{15}$ (parent) 54%; 415 $C_{13}F_{13}H_{12}$ (parent − CH_3) 2%; 402 $C_{12}F_{13}H_{11}$(parent − C_2H_4) 12%; 401 $C_{12}F_{13}H_{10}$ (parent − C_2H_5) 12%; 388 $C_9F_{13}H_9$ (parent − C_3H_6) 28%; 349 $C_9F_{11}H_8$ 10%; 169 C_3F_7 8%; 131 C_3F_5 22%; 119 C_2F_5 29%; 103 $C_4F_2H_5$ 24%; 77 $C_3F_2H_3$ 26%; 70 C_5H_{10} 96%; 69 CF_3 100%; 57 C_4H_9 50%; 56 C_4H_8 95%; 55 C_4H_7 92%; 41 C_3H_5 100%; 29 C_2H_5 47%. MS (CI) *m/e*, ion, intensity: 429 (M − H) 25%; 411 M − F 12%; 391 M − HF_2 100%; 349 M − $HF_2 \cdot C_3H_6$ 30%. ^1H NMR δ: 0.9 (singlet, 3H); 1.4–1.5 (multiplet, 8H); 2.2 (multiplet, 1H, *trans* isomer); 2.3 (multiplet, 1H, *cis* isomer); 5.4–5.6 (multiplet, 1H); 6.1 (d of t of t, 0.27H, $J_{H-H}=18$ Hz, $J_{H-CF_2}=12$ Hz, $J_{H-CH_2}=3.3$ Hz); 6.4 (d of t of t, 0.73H, $J_{H-H}=23.6$ Hz, $J_{H-CF_2}=10$ Hz, $J_{H-CH_2}=3.3$ Hz) ppm. ^{19}F NMR δ: -81.4 (t of t, 3F); -113.9 (t, 2F); -122.5 (m, 2F) −; -123.4 (m, 2F); -123.6 (m, 2F); -126.7 (m, 2F) ppm.

Illustrative mass spectral ions and intensities for products from the reaction of sodium methylate with PFHI in tetrahydrofuran are listed below.

$C_5H_{10}O_2$: MS (EI) *m/e*, ion, intensity: 102 $C_5H_{10}O$ (parent) 3%; 101 C_5H_9O 17%; 71 C_4H_7O 100%; 61 $C_2H_5O_2$ 25%; 57 C_4H_9 24%; 45 C_2H_5O 20%; 43 C_3H_7 63%; 42 C_3H_6 42%; 41 C_3H_5 83%; 39 C_3H_3 55%; 31 CH_3O 23%.

$C_{10}F_{13}H_5O$: MS (EI) *m/e*, ion, intensity: 388 $C_{10}F_{13}H_5O$ (parent) 7%; 369 $C_{10}F_{12}H_5O$ (parent − F) 5%; 319 C_6F_{13} 5%; 131 C_3F_5 8%; 119 C_2F_5 100%; 70 C_4H_6O 9%; 69 CF_3 25%; 39 C_3H_3 7%.

$C_8H_{13}O_2I$: MS (EI) *m/e*, ion, intensity: 268 $C_8H_{13}O_2I$ (parent) 100%; 254 $C_7H_{11}O_2I$ (parent − CH_2) 22%; 141 $C_8H_{13}O_2$ 56%; 127 I 73%.

C_4H_7OI: MS (EI) *m/e*, ion, intensity: 198 C_4H_7OI (parent) 38%; 128 HI 20%; 127 I 100%; 71 C_4H_7O 38%; 43 C_3H_7 33%; 42 C_3H_6 25%; 41 C_3H_5 90%; 39 C_3H_3 80%.

4. Conclusions

Perfluoroalkyl iodides and bromides can be transformed effectively into commercially pure 1*H*-perfluoroalkanes by sodium methylate, both quickly and in high yield, and using a variety of initiators. As proposed by Meinert et al. [13], we have clearly demonstrated that this reaction can proceed through either a radical or thermal pathway depending on the conditions. The source of the hydrogen on the bromine- or iodine-containing carbon in the starting material has been unambiguously demonstrated through deuterium labeling experiments. The unique ability of in-situ formed methyl hypoiodite to initiate a radical reaction has been shown. The thermal mechanism at 60–80 °C remains unexpected, while the radical reaction appears to be very usual.

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