Chinese Journal of Chemistry, **2004**, *22*, 371—376

Article

Factors Influencing Sulfinatodehalogenation Reactions of Perhalocarbons

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The study on the factors influencing sulfinatodehalogenation of perfluorohexyl chloride plus octene-1 by using $Na_2S_2O_4/NaHCO_3$ discovered that among the various solvents tested (*e.g.* Me_2SO, NMP, DMAc, CH_3CN, CH_3CN/H_2O) at different temperatures, Me_2SO was found to be the most suitable solvent and the conversion of the chloride was very dependent on the reaction temperature. When Me_2SO was used in the reaction of perfluoroalkyl iodides, the reaction temperature could be decreased by 20 ℃ as compared with that carried out in CH_3CN/H_2O to reach the comparable yields.

Keywords sulfinatodehalogenation, perfluoroalkyl chloride, perfluoroalkyl iodide, reaction temperature

Introduction

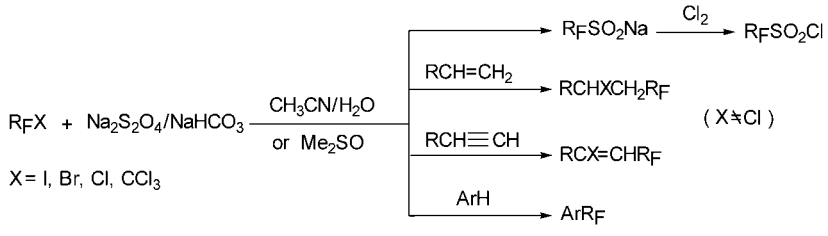
The sulfinatodehalogenation reactions of perhalocarbons, discovered and developed by Huang and his co-workers,[1-6] have been becoming one of the most important reactions in organofluorine chemistry. Using inexpensive sulfur-containing reactants (*e.g.* $Na_2S_2O_4$) under mild conditions, per- and polyfluoroalkyl halides (R_FX, X＝Br, I, CCl_3) can be smoothly transferred to the corresponding sulfinate salts. The sulfinates may be further converted to the perfluoroalkanesulfonyl halides, acids and their derivatives. More interestingly, this method has been widely applied to perfluoroalkylate alkenes, dienes, alkynes and aromatics. However, this system is confined to perhaloncarbons and cannot be applied to perfluoroalkyl chlorides, *i.e.* R_FCF_2Cl. For example, tetrachloromethane could afford the desired product, CCl_3SO_2Na with high yield, while chloroform was shown to be completely inert in sulfinatodehalogenation reaction conditions.[7] It was not until very recently that this problem has been solved: using dimethylsulfoxide (Me_2SO) as a solvent instead of CH_3CN/H_2O in $Na_2S_2O_4/NaHCO_3$ initiation system, perfluoroalkyl chlorides, ethyl chlorofluoro-, chlorodifluoroacetates, even nonfluorinated compounds such as ethyl dichloro-, chloroacetates and chloroform can either be converted to the corresponding sulfinate salts or alkylated alkenes, alkynes and aromatics.[8,9] All these reactions can be described in Scheme 1.

However, besides solvent effect, other factors such as reactant structures, reaction temperature and time might also influence the reaction. We herein present the results.

Results and discussion

In order to compare the results of sulfinatodehalogenation of perfluoroalkyl chloride in various solvents, the addition reaction of *n*-perfluorohexyl chloride (**1a**) into octene-1 (**2a**) was used as the model reaction in the presence of 1.5 equivalents of $Na_2S_2O_4$ and $NaHCO_3$ in Me_2SO, dimethyl acetamide (DMAc), *N*-methylpyrrolidinone (NMP), dimethyl formamide (DMF), CH_3CN and CH_3CN/H_2O. The results are listed in Table 1.

Scheme 1



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Received September 16, 2003; revised November 14, 2003; accepted December 16, 2003.
Project supported by the National Natural Science Foundation of China (Nos. 20272026 and D20032010).

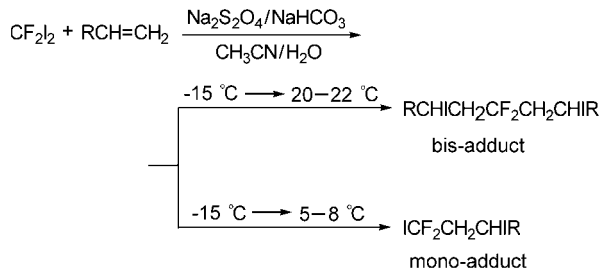
Table 1 Reactions of **1a** with **2a** [a]

Entry	Solvent	*T*/℃	*t*/h	Conversion [b]/%
1	Me_2SO	50	10	100
2	Me_2SO	40	10	＜10
3	NMP	100	5	100
4	NMP	85	6	0
5	DMAc	100	5	100
6	DMAc	85	6	0
7	DMF	120	6	＜10
8	CH_3CN	80	6	0
9	CH_3CN/H_2O [c]	80	6	0

[a] Molar ratio of **1a**∶**2a**∶$Na_2S_2O_4$∶$NaHCO_3$=1∶1.5∶1.5∶1.5. [b] Determined by ^{19}F NMR spectroscopy. [c] $V(CH_3CN)$∶$V(H_2O)$=1∶1.

It was found that the reaction did not occur in either CH_3CN or CH_3CN/H_2O (1∶1 by volume) and Me_2SO might be the most suitable solvent for the reaction although both DMAc and NMP could afford the complete conversion of **1a** at higher temperature. It is important to note that the reaction temperature has great influence on this reaction. Generally, for perfluoroalkyl iodides and bromides under standard conditions, *i.e.* $Na_2S_2O_4$/$NaHCO_3$/CH_3CN/H_2O, the reaction temperature (from room temperature to 80 ℃) does not offer significant effect on the conversion and yield except the reaction of CF_2I_2 with alkene.[10] For example, when adding CF_2I_2 to olefins at −15 ℃ and then stirring at 20 ℃ for 3—4 h, the bis-adducts were the sole product, while an addition at −15 ℃, followed by the reaction at 5—8 ℃ for 1—1.5 h, solely monoadducts formed (Scheme 2).

Scheme 2



The data in Table 1 also showed that temperature effect on the conversion of perfluoroalkyl chlorides was crucial for the reaction not only in Me_2SO but also in NMP or DMAc.

In order to examine the effect of temperature as well as structure variety on the conversion and yield, a normal alkene (**2a**, **2b**), cyclohexene (**2c**) or vinyl ethyl ether (**2d**) was allowed to react with **1a** or perfluorooctanyl chloride (**1b**) (Scheme 3).

The results, listed in Table 2, demonstrated that regardless of reactant structure difference, the most suitable temperature was 50—60 ℃, where the conversions of perfluoroalkyl chlorides were 100%. When the temperature decreased to 40 ℃, the conversion dropped dramactically to ＜10%. The yields were good except for **2d** (4%) due to the formation of large amounts of R_FSO_2Na. A low yield (28%) of adduct, $ICF_2CH_2CH(OEt)_2$, was also observed from the reaction of **2d** with CF_2I_2 and $Na_2S_2O_4/NaHCO_3$ in CH_3OH at 50 ℃, but the yield could be improved to *ca.* 60% if a mixture of solvent of CH_3CH_2OH/Me_2SO (10∶1 by volume) was employed.[11]

Scheme 3

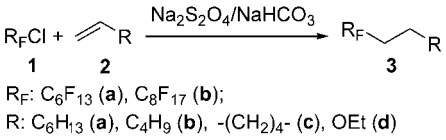


Table 2 Reaction of **1** with **2** [a]

Entry	**1**	**2**	*T*/℃	*t*/h	**3**	Conversion [b]	Yield of **3**/%
1	**1a**	**2a**	50	10	**3aa**	100	81
2	**1a**	**2a**	40	10	**3aa**	＜10	— [c]
3	**1a**	**2b**	50	9	**3ab**	100	66
4	**1a**	**2b**	40	9	**3ab**	＜10	— [c]
5	**1a**	**2c**	60	9.5	**3ac**	100	83
6	**1a**	**2c**	50	10	**3ac**	＜10	— [c]
7	**1a**	**2d**	65	7	**3ad**	100	4
8	**1b**	**2a**	50	11	**3ba**	100	68
9	**1b**	**2a**	40	10	**3ba**	＜10	— [c]
10	**1b**	**2b**	50	7	**3bb**	100	48
11	**1b**	**2b**	40	10	**3bb**	＜10	— [c]
12	**1b**	**2c**	60	7	**3bc**	100	65
13	**1b**	**2c**	50	5.5	**3bc**	＜10	— [c]

[a] Molar ratio of **1**∶**2**∶$Na_2S_2O_4$∶$NaHCO_3$=1∶1.5∶1.5∶1.5. [b] Determined by ^{19}F NMR spectroscopy. [c] Not isolate the product.

It is worthy to note that the product, **3**, in the addition reaction of perfluoroalkyl chlorides, as reported previously,[8] is chlorine-free adduct (so called hydrofluoroalkylation). The reason is that the intermediate $R_FCH_2\dot{C}HR$ formed in the chain propagation step did not abstract chlorine atom from R_FCl because of the strong carbon-chlorine bond, but easily picked a hydrogen from Me_2SO to afford the product.

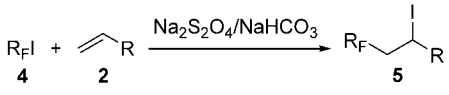
Based on aforementioned solvent and temperature effects on the sulfinatodehalogenation reaction, one might anticipate that perfluoroalkyl iodides should add more easily to alkenes to give the normal adducts in Me_2SO than that in CH_3CN/H_2O. It is indeed the case. The data listed in Table 3 show that the reaction temperature for perfluoroalkyl iodides **4** with alkene **2** may decrease by 20 ℃ in Me_2SO versus in CH_3CN/H_2O for the same period with the comparable yields (Scheme 4).

Table 3 Reaction of **2** and **4**[a]

Entry	4	2	Solvent	5	Yield/%
1	**4a**	**2a**	Me_2SO	**5aa**	83
2[b]	**4a**	**2a**	CH_3CN/H_2O[c]	**5aa**	77
3	**4a**	**2b**	Me_2SO	**5ab**	76
4[b]	**4a**	**2b**	CH_3CN/H_2O[c]	**5ab**	79
5	**4b**	**2a**	Me_2SO	**5ba**	82
6	**4b**	**2b**	Me_2SO	**5bb**	84
7[b]	**4b**	**2b**	CH_3CN/H_2O[c]	**5bb**	81

[a] Molar ratio of **4**∶**2**∶$Na_2S_2O_4$∶$NaHCO_3$=1∶1.5∶1.5∶1.5, t=1 h, T=25 ℃. [b] T=45 ℃. [c] $V(CH_3CN)$∶$V(H_2O)$=1∶1.

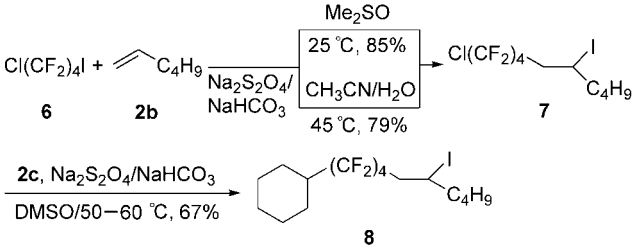
Scheme 4



R_F: C_6F_{13} (**a**), C_8F_{17} (**b**); R: C_6H_{13} (**a**), C_4H_9 (**b**)

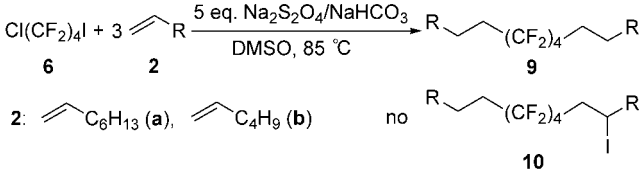
At different temperatures, ω-iodoperfluorobutyl chloride (**6**) can react with two different alkenes to produce unsymmetrical bis-substituted adduct stepwise. For example, treatment of **6** with 1.5 equivalents of hexene-1 (**2b**), $Na_2S_2O_4$ and $NaHCO_3$ either in Me_2SO at room temperature or in CH_3CN/H_2O at 45 ℃ for 1—2 h gave the same product **7** in yield of 84% and 79%, respectively. The isolated product **7** could further react with cyclohexene (**2c**) in the presence of $Na_2S_2O_4$/$NaHCO_3$ in Me_2SO at 50—60 ℃ affording bis-adduct **8** (Scheme 5).

Scheme 5



Surprisingly, when ω-iodoperfluorobutyl chloride (**6**) was treated with 3 equivalents of alkenes, *i.e.* **2a** or **2b**, and 3 equivalents of $Na_2S_2O_4$ and $NaHCO_3$ at 80 ℃ in Me_2SO for 1 h, the product was iodine-free **9a** or **9b** (61%, 63% respectively) rather than **10** (Scheme 6).

Scheme 6

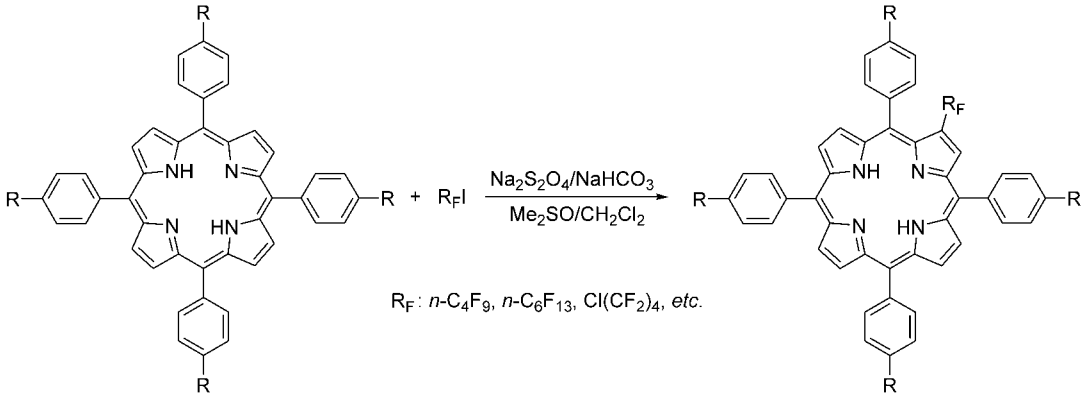


The similar, abnormal phenomenon was also met in our recent report on the fluoroalkylation of porphyrins with perfluoroalkyl iodides.[12] When a mixture of porphyrin, $Na_2S_2O_4$ and $NaHCO_3$ in Me_2SO/CH_2Cl_2 (1∶1 by volume) was treated with excess R_FI (R_FI=*n*-C_4F_9, *n*-C_4F_8Cl, *etc.*), the reaction did not take place below 10 ℃ and became very complicated above 80 ℃, but at 80 ℃, the most suitable reaction temperature, only the carbon-iodine in ω-iodoperfluorobutyl chloride (**6**) was cleaved while carbon-chlorine bond remained intact. Interestingly, the β-perfluoroalkyl tetraphenylporphyrins were obtained rather than 2,3-dihydro, and 2-hydro-3-iodoporphyrins (chlorins) (Scheme 7). The weak oxidants R_FI and Me_2SO might make the unstable chlorins dehydrogenate or eliminate HI for maintaining the aromaticity of porphyrin macrocycle.

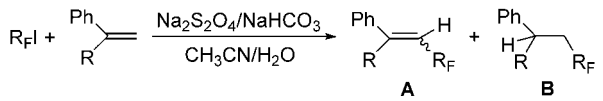
The formation of perfluoroalkyl olefin products rather than the normal adduct from perfluoroalkyl iodides in the sulfinatodehalogenation system was also not unprecedented. Thus, when styrenes with other α-substitutents, even very crowed *t*-butyl group, underwent the reaction with R_FI in the presence of $Na_2S_2O_4$ and $NaHCO_3$ in CH_3CN/H_2O at 40 ℃ for 4 h, an iodine-free mixture (**A**, **B**) with comparable ratio of fluorinated styrene and its hydrogenated product was yielded (Scheme 8).[13]

The results might be rationalized as follows: the formed intermediate $R_FCH_2\dot{C}$RPh in the chain propaga-

Scheme 7



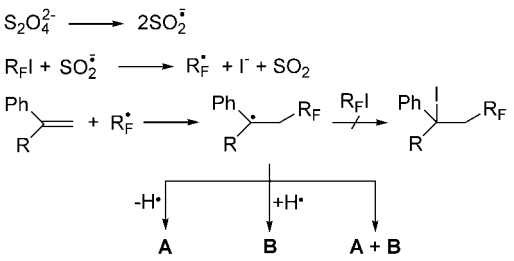
Scheme 8



$R_F = (CF_2)_nCl$ (n = 2, 4, 6), $CF_3(CF_2)_5$
R = Ph, *p*-$MeOC_6H_4$, *t*-Bu, CH_3, H

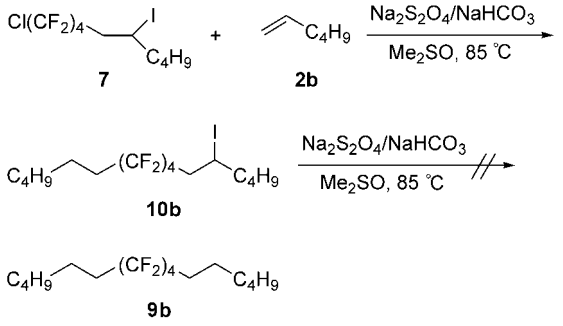
tion step could not abstract iodine from R_FI to yield thenormal adduct largely due to steric hindrance. There are three possibilities for the intermediate: i) elimination of a hydrogen giving the alkene **A**; ii) abstraction of a hydrogen from solvent affording the hydrogenated product; iii) disproportionation of the intermediate producing almost equal amount of **A** and **B** (Scheme 9).

Scheme 9

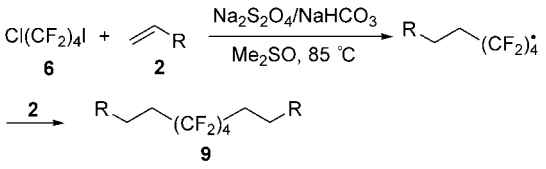


Because compound **9b** did not come from the further reduction of **10b** by $Na_2S_2O_4$ under the similar conditions (Scheme 10), a two-step dihydrofluoroalkylation of alkene **2** with iodoperfluoroalkyl chloride **6** might occur at this higher temperature in Me_2SO (Scheme 11), although we could not absolutely exclude the possibility of being through α,ω-perfluoroalkyl biradicals $\dot{C}F_2(CF_2)_2C\dot{F}$ generated in the initiation step.

Scheme 10



Scheme 11



In conclusion, we have investigated in more detail the factors influencing the sulfinatodehalogenation of perhalocarbons and found that in the reaction of perfluoroalkyl chlorides, Me_2SO was a good solvent while CH_3CN/H_2O was suitable for the corresponding iodides and bromides. Besides solvent effect, reaction temperature also plays an important role in some cases.

Experimental

Boiling points were uncorrected. ^{1}H NMR spectra were taken on a Varian Mercury-300 (300 MHz) NMR spectrometer. ^{19}F NMR spectra were obtained on a Varian Mercury-300 (282 MHz) spectrometer. Chemical shifts were reported in parts per million relative to TMS as an internal standard ($\delta_{TMS}=0$) for ^{1}H NMR spectra and $CFCl_3$ as an external standard ($\delta_{CFCl_3}=0$) for ^{19}F NMR spectra (upfield shift being designated as negative). The solvent for NMR measurement was $CDCl_3$. IR spectra were recorded on a Perkin-Elmer Jeol 983 spectrometer. MS and HRMS were recorded on a Hewlett-Packard HP-5989A spectrometer.

General procedure for the sulfinatodehalogenation reaction

Perfluorohexyl chloride (**1a**, 1.58 g, 4.46 mmol) was added to 10 mL of Me_2SO, then $Na_2S_2O_4$ (1.16 g, 6.69 mmol), $NaHCO_3$ (0.57 g, 6.69 mmol) and octene-1 (**2a**, 0.75 g, 6.69 mmol) were added to the solution. After stirring for 10 h at 50 ℃, water was added to the reaction mixture. The aqueous layer was extracted three times with ether (3×20 mL). The combined extracts were washed with brine (3×10 mL) and dried over Na_2SO_4. After removal of ether, the residue was subjected to column chromatography on silica gel to give the adduct, 1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-tetradecane (**3aa**[8]) (0.78 g, 81%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.90 (t, J=5.7 Hz, 3H), 1.30—1.42 (m, 10H), 1.56—1.64 (m, 2H), 2.03—2.09 (m, 2H); ^{19}F NMR (282 MHz, $CDCl_3$) δ: −81.13 (m, 3F), −114.75 (m, 2F), −122.28 (m, 2F), −122.22 (m, 2F), −123.91 (m, 2F), −126.48 (m, 2F); IR (KBr) ν: 2930, 2860, 1469, 1240, 1206, 706, 653 cm^{-1}; MS (CI) m/z (%): 432 (M^+, 1), 417 (2), 389 (26), 80 (92), 59 (100).

1,1,1,2,2,3,3,4,4,5,5,6,6-Tridecafluoro-dodecane (3ab[8]) Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.91 (t, J=6.9 Hz, 3H). 1.29—1.41 (m, 6H), 1.58—1.63 (m, 2H), 1.96—2.10 (m, 2H); ^{19}F NMR (282 MHz, $CDCl_3$) δ: −81.16 (m, 3F), −114.78 (m, 2F), −122.38 (m, 2F), −123.32 (m, 2F), −123.96 (m, 2F), −126.54 (m, 2F); IR (KBr) ν: 2964, 2937, 1241, 1146, 732, 708, 697 cm^{-1}; MS (EI) m/z (%): 404 (M^+, 8), 403 (65), 85 (13), 57 (50), 43 (100).

Tridecafluorohexyl-cyclohexane (3ac[8]) Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.19—1.97 (m, 10H), 2.01—2.17 (m, 1H); ^{19}F NMR (282 MHz, $CDCl_3$) δ: −80.78 (m, 3F), −118.21 (m, 2F), −120.65 (m, 2F), −122.17 (m, 2F), −122.84 (m, 2F), −126.16 (m, 2F); IR (KBr) ν: 2944, 2865, 1241, 1147, 732, 695 cm^{-1}; MS (EI) m/z (%): 402 (M^+, 3), 401 (22), 381 (23), 81 (100), 41 (38).

8-Ethoxy-1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluorooctane (3ad[8]) Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.18 (t, J=6.9 Hz, 3H), 1.99—2.12 (m, 2H), 3.46 (q, J=6.9 Hz, 2H), 3.71 (t, J=6.9 Hz, 2H); ^{19}F NMR (282 MHz, $CDCl_3$) δ: −81.08 (m, 3F), −113.71 (m, 2F), −122.19 (m, 2F), −123.22 (m, 2F), −123.89 (m, 2F), −126.52 (m, 2F); MS (EI) *m*/*z* (%): 392 (M^+, 2), 147 (11), 131 (6), 103 (23), 73 (100); HRMS calcd for $C_{10}H_9F_{13}O$ 392.0445, found 392.0457.

1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-Heptadecafluorohexadecane (3ba[8]) Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.90 (t, J=6.5 Hz, 3H), 1.22−1.41 (m, 10H), 1.57—1.61 (m, 2H), 1.97—2.05 (m, 2H); ^{19}F NMR (282 MHz, $CDCl_3$) δ: −81.09 (m, 3F), −114.75 (m, 2F), −122.25 (m, 6F), −123.06 (m, 2F), −123.87 (m, 2F), −126.46 (m, 2F); IR (KBr) ν: 2930, 1242, 1207, 704, 655 cm^{-1}; MS (EI) *m*/*z* (%): 532 (M^+, 6), 503 (6), 489 (100), 85 (25), 71 (28), 57 (98).

1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-Heptadecafluorotetradecane (3bb[8]) Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.91 (t, J=6.9 Hz, 3H), 1.30—1.44 (m, 6H), 1.55—1.63 (m, 2H), 1.99—2.09 (m, 2H); ^{19}F NMR (282 MHz, $CDCl_3$) δ: −81.03 (m, 3F), −118.44 (m, 2F), –120.84 (m, 2F), −122.21 (m, 6F), −123.0 (m, 2F), −126.41 (m, 2F); IR (KBr) ν: 2964, 2880, 1244, 1153, 705, 656 cm^{-1}; MS (EI) *m*/*z* (%): 504 (M^+, 2), 503 (10), 85 (28), 69 (31), 57 (52), 43 (100).

Heptadecafluorooctyl-cyclohexane (3bc[8]) Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.22—1.35 (m, 4H), 1.55—1.60 (m, 2H), 1.85—1.97 (m, 4H), 2.05—2.11 (m, 1H); ^{19}F NMR (282 MHz, $CDCl_3$) δ: −81.03 (m, 3F), −118.44 (m, 2F), −120.86 (m, 2F), −122.24 (m, 6F), −123.03 (m, 2F), −126.46 (m, 2F); IR (KBr) ν: 2945, 2866, 1244, 1152, 721, 655 cm^{-1}; MS (EI) *m*/*z* (%): 502 (M^+, 1), 501(4), 463 (8), 83 (100), 55 (41), 41 (23).

1,1,1,2,2,3,3,4,4,5,5,6,6-Tridecafluoro-8-iodotetradecane (5aa[14]) Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.90 (t, J=6.6 Hz, 3H), 1.29—1.43 (m, 8H), 1.75—1.85 (m, 2H), 2.76—2.95 (m, 2H), 4.29—4.38 (m, 1H); ^{19}F NMR (282 MHz, $CHCl_3$) δ: −80.77 (m, 3F), −111.17—−114.32 (m, 2F), −121.83 (m, 2F), −122.90 (m, 2F), −123.67 (m, 2F), −126.23 (m, 2F); IR (KBr) ν: 2955, 1239, 1206, 1145 cm^{-1}; MS (CI) *m*/*z* (%): 558 (M^+, 6), 557 (39), 431 (46), 389 (8), 57 (100).

1,1,1,2,2,3,3,4,4,5,5,6,6-Tridecafluoro-8-iodododecane (5ab[14]) Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.90 (t, J=6.6 Hz, 3H), 1.29—1.41 (m, 4H), 1.78—1.83 (m, 2H), 2.71—2.89 (m, 2H), 4.25—4.39 (m, 1H); ^{19}F NMR (282 MHz, $CDCl_3$) δ: −80.78 (m, 3F), −111.23—−114.28 (m, 2F), −121.82 (m, 2F), −122.90 (m, 2F), −123.62 (m, 2F), −126.22 (m, 2F); IR (KBr) ν: 2933, 2860, 1239, 1206, 698 cm^{-1}; MS (CI) *m*/*z* (%): 530 (M^+, 3), 403 (26), 361 (9), 57 (100).

1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-Heptadecafluoro-10-iodo-hexadecane (5ba[15]) Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.90 (t, J=6.9 Hz, 3H), 1.31—1.61 (m, 8H), 1.77—1.87 (m, 2H), 2.77—2.89 (m, 2H), 4.32—4.38 (m, 1H); ^{19}F NMR (282 MHz, $CDCl_3$) δ: −81.12 (m, 3F), −111.52—−115.39 (m, 2F), −121.87 (m, 2F), −122.20 (m, 4F), −123.01 (m, 2F), −123.87 (m, 2F), −126.41 (m, 2F); IR (KBr) ν: 2930, 2860, 1240, 1205, 1145, 619 cm^{-1}; MS (EI) *m*/*z* (%): 657 (M^+−1, 0.2), 531 (M^+−I, 18), 489 (24), 85 (19), 57 (100).

1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-Heptadecafluoro-10-iodo-tetradecane (5bb[14]) Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.93 (t, J=6.9 Hz, 3H), 1.27—1.57 (m, 4H), 1.78—1.86 (m, 2H), 2.84—2.89 (m, 2H), 4.32—4.38 (m, 1H); ^{19}F NMR (282 MHz, $CDCl_3$) δ: −81.03 (m, 3F), −111.52—−114.42 (m, 2F), −121.86 (m, 2F), −122.17 (m, 4F), −122.98 (m, 2F), −123.86 (m, 2F), −126.38 (m, 2F); IR (KBr) ν: 2964, 1366, 1208, 1151, 722, 655 cm^{-1}; MS (CI) *m*/*z* (%): 630 (M^+, 12), 629 (76), 503 (100), 463 (11), 55 (68).

1-Chloro-1,1,2,2,3,3,4,4-octafluoro-6-iodo-decane (7[16]) Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.91 (t, J=6.7 Hz, 3H), 1.30—1.54 (m, 4H), 1.77—1.87 (m, 2H), 2.77—2.89 (m, 2H), 4.33—4.38 (m, 1H); ^{19}F NMR (282 MHz, $CDCl_3$) δ: −68.05 (m, 2F), −111.30—−114.36 (m, 2F), −119.76 (m, 2F), −122.98 (m, 2F); IR (KBr) ν: 2933, 2861, 1434, 1191, 1136, 1091, 968, 702 cm^{-1}; MS (EI) *m*/*z* (%): 347 (M^+−I, 5), 305 (14), 71 (14), 57 (100), 43 (83).

(1,1,2,2,3,3,4,4-Octafluoro-6-iodo-decyl)-cyclohexane (8) Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.93 (t, J=6.7 Hz, 3H), 1.24—2.14 (m, 17H), 2.65—2.71 (m, 2H), 4.31 (m, 1H); ^{19}F NMR (282 MHz, $CDCl_3$) δ: −113.47 (m, 2F), −120.47 (m, 2F), −121.53 (m, 2F), −124.78 (m, 2F); IR (KBr) ν: 2942, 2864, 1455, 1303, 1171, 1035, 883 cm^{-1}; MS (EI) *m*/*z* (%): 494 (M^+, 0.1), 367 (M^+−I, 60), 347 (6), 83 (25), 43 (100); HRMS calcd for $C_{16}H_{23}F_8I$ 494.0716, found 494.06932.

9,9,10,10,11,11,12,12-Octafluoro-icosane (9a[8]) Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.89 (t, J=6.6 Hz, 6H), 1.67—1.74 (m, 20H), 1.78—1.81 (m, 4H), 1.94—2.11 (m, 4H); ^{19}F NMR (282 MHz, $CDCl_3$) δ: −114.92 (m, 4F), −124.06 (m, 4F); IR (KBr) ν: 2929, 2859, 1468, 1126, 1102 cm^{-1}; MS (EI) *m*/*z* (%): 426 (M^+, 0.68), 397 (4), 85 (13), 71 (38), 43 (100), 41 (43).

7,7,8,8,9,9,10,10-Octafluoro-hexadecane (9b[8]) Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.90 (t, J=6.6 Hz, 6H), 1.23—1.40 (m, 12H), 1.56—1.61 (m, 4H), 1.94—2.11 (m, 4H); ^{19}F NMR (282 MHz, $CDCl_3$) δ: −114.51 (m, 4F), −123.75 (m, 4F); IR (KBr) ν: 2959, 2862, 1209, 1166, 1124 cm^{-1}; MS (CI) *m*/*z* (%): 370 (M^+, 100), 330 (13), 80 (21), 55 (27).

7,7,8,8,9,9,10,10-Octafluoro-5-iodo-hexadecane (10) Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.88—0.92 (m, 6H), 1.28—1.45 (m, 12H), 1.56—1.72 (m, 2H), 1.92—2.11 (m, 4H), 4.31—4.43 (m, 1H); ^{19}F NMR (282 MHz, $CDCl_3$) δ: −114.78 (m, 2F), −120.23 (m, 2F), −123.24 (m, 2F), −124.05 (m, 2F);

IR (KBr) ν: 2962, 2864, 1469, 1193, 839, 695 cm^{-1}; MS (EI) *m*/*z* (%): 369 (M^+-I, 11), 333 (1), 135 (13), 85 (12), 433 (100); HRMS calcd for $C_{16}H_{25}F_8$ (M^+-I) 369.1828, found 369.1853.

Reaction of 10, $Na_2S_2O_4$, $NaHCO_3$ in Me_2SO solution Adduct product **10** (1.07 g, 2.17 mmol) was added to 5 mL of Me_2SO, then $Na_2S_2O_4$ (0.57 g, 3.25 mmol) and $NaHCO_3$ (0.27 g, 3.25 mmol) were added to the solution. After stirring for 10 h at 85 ℃, water was added to the reaction mixture. The aqueous layer was extracted three times with ether (3×10 mL). The combined extracts were washed with brine (3×10 mL) and dried over Na_2SO_4. After removal of ether, the residue was subjected to column chromatography on silica gel to give the unreacted product **10** (0.88 g, 82%).

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(E0309165 PAN, B. F.)