

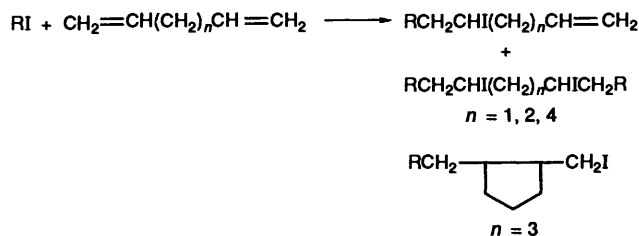
Polyfluoroalkylation of Octa-1,7-diene Promoted by Dichlorobis-(π -cyclopentadienyl)titanium and Iron Powder

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Per(poly)fluoroalkylation of octa-1,7-diene **1** with per(poly)fluoroalkyl iodides **2** or bromides **4**, in the presence of catalytic amounts of dichlorobis(π -cyclopentadienyl)titanium(IV) and iron powder, provides 1:1 linear adducts **3**, **5** and/or cyclic products **6** depending on the reactivity of the halides **2** and **4**. A radical mechanism is proposed.

It has been reported¹ that in the presence of the radical initiator azoisobutyronitrile (AIBN), perfluoroalkyl iodides add to α,ω -dienes to give 1:1 and 2:1 linear adducts except with hepta-1,6-diene when two isomeric iodomethylcyclopentanes were obtained (Scheme 1).



Scheme 1

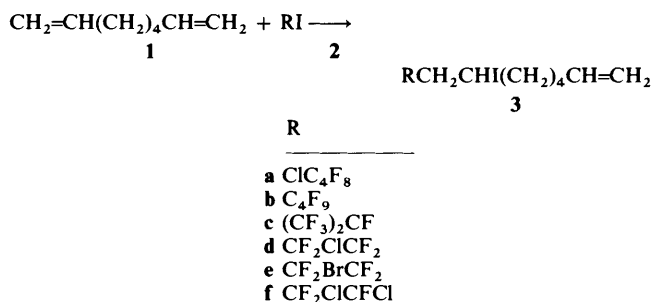
In the course of our study on per(poly)fluoroalkylation of carbon-carbon multiple bonds catalysed by transition-metal complexes,^{2,3} we found a new redox couple—dichlorobis(π -cyclopentadienyl)titanium(IV) and iron—which could initiate the addition of 1,2-dihalogenopolyfluoroalkanes with certain advantages.³ Here we report the reactivity of per(poly)fluoroalkyl iodides **2** or bromides **4** towards octa-1,7-diene **1** promoted by this system, and also a convenient method for the preparation of a per(poly)fluoroalkylcyclohexane.

Results and Discussion

Generally, a stirred mixture of the diene **1**, iodide **2** or bromide **4**, Fe powder and $\text{Ti}(\eta^5\text{-cp})_2\text{Cl}_2$ was heated at 50–65 °C in EtOH or tetrahydrofuran (THF) for 8–40 h under N_2 to give high yields of the products.

The reaction of the diene **1** with the iodides **2** afforded 1:1 linear adducts **3** (Scheme 2 and Table 1). There was no significant solvent effect on the reaction (entries 4 and 5, Table 1).

The reaction of the diene **1** with bromides **4** gave 1:1 linear



Scheme 2

Table 1 Addition of per(poly)fluoroalkyl iodides **2** to octa-1,7-diene **1** initiated by $\text{Ti}(\eta^5\text{-cp})_2\text{Cl}_2/\text{Fe}^a$

Run	RI 2	T/°C	t/h	Adduct	Yield (%) ^b
1	a	60	8	3a	87
2	b	60	13	3b	88
3	c	55	10	3c	92
4	d	60	15	3d	90
5 ^c	d	65	14	3d	85
6	e	55	15	3e	91
7	f	50	12	3f	81

^a Solvent EtOH unless indicated otherwise. ^b Isolated yield based on **2**. ^c Solvent THF.

Table 2 Addition of per(poly)fluoroalkyl bromides **4** to octa-1,7-diene **1** initiated by $\text{Ti}(\eta^5\text{-cp})_2\text{Cl}_2/\text{Fe}$

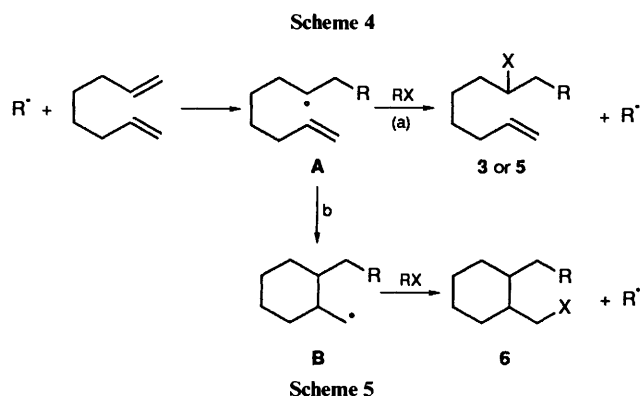
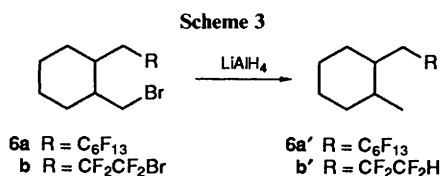
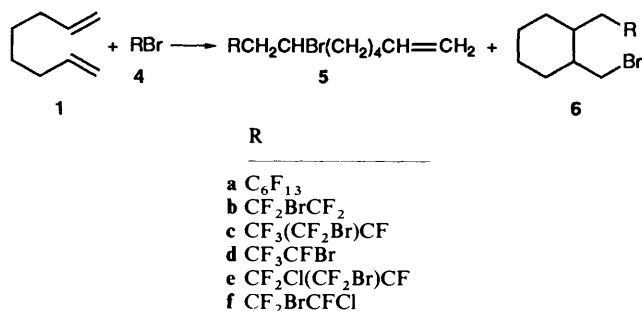
No	RBr 4	T/°C	t/h	Yield ^a (%)	5:6 ^b
1	a	65	40	75 ^c	—:97
2	b	60	20	87	—:97
3	c	60	13	88	—:97
4	d	60	10	80	5:95
5 ^d	d	60	10	81	20:80
6	e	60	15	85	30:70
7	f	50	9	78	35:65

^a Isolated yield based on **4**. ^b Ratio estimated by ¹H NMR. ^c 65% conversion (by ¹⁹F NMR), **6a** was identified as **6a'** by reduction with LiAlH_4 . ^d Solvent THF.

adducts **5** and/or cyclic products **6** (Scheme 3) depending on the reactivity of the bromide **4**. Results are summarised in Table 2.

The less reactive perfluoroalkyl or polyfluoroalkyl bromides **4a–4d**, afforded the per(poly)fluoroalkylmethyl cyclohexanes **6a–6d** as a *cis* and *trans* mixture with the latter predominating; the CH–CH₂ grouping was absent (IR, ¹H NMR). The further reduced LiAlH_4 product, e.g. **6b'** (Scheme 4), gave two isomers (4:1) with a similar GC retention time. GC–MS of compound **6b'** demonstrated that the two isomers afforded nearly the same fragmentation and intensities: both of their MS spectra produced M (212), M – Me (197), M – $\text{CH}_2\text{CF}_2\text{CF}_2\text{H}$ (97) and M – Me – $\text{CH}_2\text{CF}_2\text{CF}_2\text{H}$ + 1 (83). The 200 MHz ¹H NMR spectrum of compound **6b'** showed two doublet signals at δ 0.91 (³J_{HH} 6.6 Hz) and 0.88 (³J_{HH} 7.2 Hz) with a total integration of 3 H. Such facts confirmed the existence of an exocyclic methyl group.

The reaction of diene **1** with the more reactive polyfluoroalkyl bromides **4d–4f** gave a mixture of linear **5d–5f** and cyclic **6d–6f** products, with the latter predominating [*ca.* 65–80%, estimated



by 1H NMR; *i.e.*, $\delta_{CHX} \sim 4.6$ ($X=I$ or Br in **3** or **5**) and $\delta_{CH_2Br} \sim 3.8$ (in **6**). When THF was used instead of EtOH, the percentage of the cyclic product **6d** decreased from 95 to 80% (entries 4 and 5, Table 2).

The reaction is likely to proceed *via* a per(poly)fluoroalkyl radical R^* intermediate initiated by chlorobis(π -cyclopentadienyl)titanium(III) [$Ti(\eta^5\text{-cp})_2Cl$].^{3,4} As shown in Scheme 5, addition of R^* to diene **1** generated the intermediate **A**, which might (a) abstract a halogen atom (iodine or bromine) through an atom-transfer step⁵ to produce products **3** or **5** in the case of iodides **2** and the more reactive bromides **4d–4f**; or (b) cyclise intramolecularly to produce intermediate **B** followed by atom-transfer to give compound **6**. These results were attributed to the competition of atom-transfer and cyclisation.

Thus, the present reaction afforded for the first time a direct method for the synthesis of per(poly)fluoroalkylmethyl cyclohexanes.

Experimental

B.p.s are uncorrected. IR spectra were obtained on a Shimadzu IR-440 spectrometer using liquid films. 1H NMR spectra were measured with external TMS standard by a Varian EM-360A spectrometer at 60 MHz or Varian XL-200 spectrometer at 200 MHz. ^{19}F NMR spectra were measured with external CF_3CO_2H standard by a Varian EM-360L spectrometer at 56.4 MHz. 1H NMR (60 MHz) and ^{19}F NMR spectra were measured neat in a capillary without additional solvents. Coupling constants are reported in Hz. Mass spectra were recorded with a Finnigan GC-MS-4021 mass spectrometer. For fragments containing Cl and Br, only peaks for the ^{35}Cl and ^{79}Br isotopes are reported.

All chemicals and reagents were of analytical grade and used without further purification.

General Procedure for the Per(poly)fluoroalkylation of 1.—A mixture of iron powder (2.0 mmol), $Ti(\eta^5\text{-cp})_2Cl_2$ (0.1 mmol), diene **1** (5.0 mmol) and iodide **2** (4.0 mmol) or bromide **4** (5 mmol) was stirred in EtOH or THF (10 cm³) under N_2 . The conditions used are listed in Tables 1 and 2. After the reaction was completed, the mixture was poured into aq. HCl (2 mol dm⁻³; 10) and extracted with ether (3 \times 20 cm³). The combined ether extracts were washed successively with saturated aq. $NaHSO_3$, water, and brine (Na_2SO_4) and evaporated. Distillation of the residue *in vacuo* gave the corresponding product.

12-Chloro-9,9,10,10,11,11,12,12-octafluoro-7-iodododec-1-ene 3a.—B.p. 95 °C (3 mmHg) (Found: C, 30.2; H, 2.8; F, 32.4. $C_{12}H_{14}ClF_8I$ requires C, 30.50; H, 2.99; F, 32.10%; ν_{max}/cm^{-1} 1640 ($CH=CH_2$); δ_H 5.10–6.50 (3 H, m), 4.63 (1 H, m), 3.13 (2 H, td, $^3J_{HF}$ 20, $^3J_{HH}$ 6.0) and 1.40–2.55 (10 H, m); δ_F -9.0 (2 F, s), 36.4 (2 F, m), 43.0 (2 F, s) and 46.2 (2 F, s); m/z 471 ($M - 1$, 0.78%), 345 ($M - I$, 60.00), 303 ($M - I - CH_2CH=CH_2 - 1$, 43.05), 55 ($CH_2CH_2CH=CH_2$, 71.23) and 42 ($CH_2CH=CH_2 + 1$, 100).

9,9,10,10,11,11,12,12,12-Nonafluoro-7-iodododec-1-ene 3b.—B.p. 88 °C (4 mmHg) (Found: C, 31.4; H, 2.9; F, 37.6. $C_{12}H_{14}F_9I$ requires C, 31.60; H, 3.09; F, 37.64%; ν_{max}/cm^{-1} 1645 ($CH=CH_2$); δ_H 4.91–6.42 (3 H, m), 4.56 (1 H, quin, $^3J_{HH}$ 7.0), 3.05 (2 H, td, $^3J_{HF}$ 18.0, $^3J_{HH}$ 6.0) and 1.26–2.51 (10 H, m); δ_F 4.9 (3 F, s), 37.8 (2 F, m), 48.3 (2 F, s) and 49.6 (2 F, s); m/z 455 ($M - 1$, 0.85%), 329 ($M - I$, 95.39), 287 ($M - I - CH_2CH=CH_2 - 1$, 81.56) and 42 ($CH_2CH=CH_2 + 1$, 100).

9,10,10,10-Tetrafluoro-7-iodo-9-trifluoromethyldec-1-ene 3c.—B.p. 99 °C (18 mmHg) (Found: C, 32.5; H, 3.6; F, 33.6. $C_{11}H_{14}F_7I$ requires C, 32.53; H, 3.47; F, 32.74%; ν_{max}/cm^{-1} 1645 ($CH=CH_2$); δ_H 5.05–6.60 (3 H, m), 4.74 (1 H, m), 3.18 (2 H, dd, $^3J_{HF}$ 26.0, $^3J_{HH}$ 6.8) and 1.30–2.65 (10 H, m); δ_F -0.3 (3 F, s), 1.3 (3 F, s) and 109.3 (1 F, m); m/z 405 ($M - 1$, 10.02%), 279 ($M - I$, 33.10) and 237 ($M - I - CH_2CH=CH_2 - 1$, 100).

10-Chloro-9,9,10,10-tetrafluoro-7-iodododec-1-ene 3d.—B.p. 70 °C (1.5 mmHg) (Found: C, 31.9; H, 3.6; F, 20.7. $C_{10}H_{14}ClF_4I$ requires C, 32.24; H, 3.79; F, 20.40%; ν_{max}/cm^{-1} 1642 ($CH=CH_2$); δ_H 4.95–6.50 (3 H, m), 4.65 (1 H, quin, $^3J_{HH}$ 6.0), 3.14 (2 H, td, $^3J_{HF}$ 18.0, $^3J_{HH}$ 6.0) and 1.20–2.70 (10 H, m); δ_F -5.8 (2 F, s) and 35.8 (2 F, m); m/z 373 ($M + 1$, 4.60%), 246 ($M - I + 1$, 100) and 203 ($M - I - CH_2CH=CH_2 - 1$, 33.01).

10-Bromo-9,9,10,10-tetrafluoro-7-iodododec-1-ene 3e.—B.p. 87 °C (2 mmHg) (Found: C, 28.55; H, 3.3; F, 19.0. $C_{10}H_{14}BrF_4I$ requires C, 28.80; H, 3.38; F, 18.22%; ν_{max}/cm^{-1} 1640 ($CH=CH_2$); δ_H 5.20–6.65 (3 H, m), 4.77 (1 H, m), 3.27 (2 H, td, $^3J_{HF}$ 18.0, $^3J_{HH}$ 6.0) and 1.40–2.75 (10 H, m); δ_F -11.5 (2 F, s) and 33.3 (2 F, AB, J_{AB} 276); m/z 417 ($M + 1$, 3.42%), 289 ($M - I$, 75.83), 247 ($M - I - CH_2CH=CH_2 - 1$, 38.71) and 55 ($CH_2CH_2CH=CH_2$, 100).

9,10-Dichloro-9,10,10-trifluoro-7-iodododec-1-ene 3f.—B.p. 84 °C (1.5 mmHg) (Found: C, 29.95; H, 3.5; F, 15.5. $C_{10}H_{14}Cl_2F_3I$ requires C, 30.87; H, 3.63; F, 14.65%; ν_{max}/cm^{-1} 1645 ($CH=CH_2$); δ_H 5.20–6.65 (3 H, m), 4.85 (1 H, m), 2.85–3.80 (2 H, m) and 1.50–2.80 (10 H, m); δ_F -10.2 (2 F, s) and 41.5 (1 F, d, J 218); m/z 389 ($M + 1$, 1.58%), 261 ($M - I$, 61.11), 219 ($M - I - CH_2CH=CH_2 + 1$, 52.49) and 42 ($CH_2CH=CH_2 + 1$, 100).

(*cis/trans*)-1-Methyl-2-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)cyclohexane **6a'**.—B.p. 66 °C (3 mmHg) (Found: C, 39.4; H, 4.0; F, 57.1. $C_{14}H_{15}F_{13}$ requires C, 39.08; H, 3.51; F, 57.41%);

δ_{H} 1.16–2.55 (12 H, m), 1.04 and 0.94 (3 H, both d, $^3J_{\text{HH}}$ 7.0); δ_{F} 3.4 (3 F, s), 36.6 (2 F, m), 45.3 (2 F, s), 46.5 (2 F, s), 47.1 (2 F, s) and 50.0 (2 F, s); m/z 430 (M, 72.52%), 415 (M – Me, 17.06), 97 (M – $\text{CH}_2\text{C}_6\text{F}_{13}$, 90.37) and 83 (M – Me – $\text{CH}_2\text{C}_6\text{F}_{13}$ + 1, 22.77).

(*cis/trans*)-1-Bromomethyl-2-(3-bromo-2,2,3,3-tetrafluoropropyl)cyclohexane **6b**.—B.p. 86 °C (2 mmHg) (Found: C, 33.0; H, 3.8; F, 21.3. $\text{C}_{10}\text{H}_{14}\text{Br}_2\text{F}_4$ requires C, 32.46; H, 3.81; F, 20.54%); δ_{H} 3.55–3.88 (2 H, m) and 1.37–2.78 (12 H, m); δ_{F} –11.8 (2 F, s) and 33.2 (2 F, m); m/z 369 (M + 1, 2.85%), 289 (M – Br, 100) and 275 (M – CH_2Br).

(*cis/trans*)-1-Methyl-2-(2,2,3,3-tetrafluoropropyl)cyclohexane **6b'**.—B.p. 83 °C (42 mmHg) (Found: C, 56.5; H, 7.6; F, 35.8. $\text{C}_{10}\text{H}_{16}\text{F}_4$ requires C, 56.59; H, 7.60; F, 35.81%); δ_{H} (200 MHz, CDCl_3) 5.67 (1 H, tt, $^2J_{\text{HF}}$ 56.0, $^3J_{\text{HF}}$ 3.0), 1.00–2.40 (12 H, m), 0.91 (d, $^3J_{\text{HH}}$ 6.6) and 0.88 (3 H, d, $^3J_{\text{HH}}$ 7.2); δ_{F} 37.8 (2 F, m) and 58.6 (2 F, d, $^2J_{\text{HF}}$ 56.0); m/z 212 (M, 17.30%), 197 (M – Me, 4.85), 97 (M – $\text{CH}_2\text{CF}_2\text{CF}_2\text{H}$, 30.81) and 83 (M – Me – $\text{CH}_2\text{CF}_2\text{CF}_2\text{H}$ + 1, 13.13).

(*cis/trans*)-1-Bromomethyl-2-(3-bromo-2-trifluoromethyl-2,3,3-trifluoropropyl)cyclohexane **6c**.—B.p. 84 °C (1.5 mmHg) (Found: C, 31.4; H, 3.4; F, 28.6. $\text{C}_{11}\text{H}_{14}\text{Br}_2\text{F}_6$ requires C, 31.46; H, 3.36; F, 27.14%); δ_{H} 3.80 (2 H, m) and 1.40–2.90 (12 H, m); δ_{F} –19.5 (2 F, m), –3.3 (3 F, m) and 98.5 (1 F, m); m/z 419 (M + 1, 1.26%), 339 (M – Br, 100), 325 (M – CH_2Br , 35.24).

(*cis/trans*)-1-Bromomethyl-2-(2-bromo-2,3,3,3-tetrafluoropropyl)cyclohexane **6d**.—B.p. 78 °C (1 mmHg) (Found: C, 32.0; H, 3.9; F, 21.15. $\text{C}_{10}\text{H}_{14}\text{Br}_2\text{F}_4$ requires C, 32.46; H, 3.81; F, 20.54%); δ_{H} 3.65–3.96 (2 H, m) and 1.31–3.12 (12 H, m); δ_{F} 4.0 (3 F, s) and 46.7 (1 F, m); m/z 369 (M + 1, 1.01%), 289 (M – Br, 100) and 275 (M – CH_2Br , 18.51).

7,10-Dibromo-9-(chlorodifluoromethyl)-9,10,10-trifluorodec-1-ene **5e** and 1-Bromomethyl-2-[3-bromo-2-(chlorodifluoromethyl)-2,3,3-trifluoropropyl]cyclohexane **6e**.—B.p. 85 °C (0.5 mmHg) (Found: C, 30.3; H, 3.2; F, 22.6. $\text{C}_{11}\text{H}_{14}\text{Br}_2\text{ClF}_5$ requires C, 30.27; H, 3.23; F, 21.76%); δ_{H} 4.75 [m, CHBr (**5e**)] and 3.80 [m, CH_2Br (**6e**)]; δ_{F} –21.0 (2 F, m), –16.1 (2 F, m) and 90.5 (1 F, m); m/z 434 (M, 3.16%), 355 (M – Br, 100), 341 (M – CH_2Br , 21.83) and 313 (M – Br – $\text{CH}_2\text{CH}=\text{CH}_2$ + 1, 24.04).

7,10-Dibromo-9-chloro-9,10,10-trifluorodec-1-ene **5f** and 1-Bromomethyl-2-(3-bromo-2-chloro-2,3,3-trifluoropropyl)cyclohexane **6f**.—B.p. 93 °C (1 mmHg) (Found: C, 30.6; H, 3.6; F, 15.15. $\text{C}_{10}\text{H}_{14}\text{Br}_2\text{ClF}_3$ requires C, 31.08; H, 3.65; F, 14.75%); δ_{H} 4.76 [m, CHBr (**5f**)] and 3.73 [m, CH_2Br (**6f**)]; δ_{F} (**5f**) –16.0 (2 F, s) and 38.0 (1 F, m); (**6f**) –16.7 (2 F, s) and 39.8 (1 F, m); m/z 385 (M + 1, 1.93%), 305 (M – Br, 94.32) and 95 [$\text{CH}(\text{CH}_2)_4\text{CH}=\text{CH}_2$ – 1, 100].

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