Mechanistic Studies on Zinc-Induced Addition of CF_2Br_2 to Olefins. A Novel Radical Reductive Cyclopropanation on the Zinc Surface

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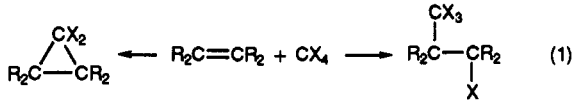
The addition reaction of dibromodifluoromethane (1) to olefins induced by zinc in ethereal solvent differs surprisingly from addition reactions hitherto reported. Both cyclopropane derivatives and 1:1 addition products were obtained from this reaction. A free-radical chain addition reaction induced by single electron transfer (SET) is proposed. This reaction is inhibited by hydroquinone and completely quenched by *p*-dinitrobenzene. The nature of the 1:1 adducts formed revealed the character of a typical radical reaction. The nature of the cyclopropane derivatives formed was also much different from the usual cyclopropane adduct derived from carbene addition. When diallyl ether (15) and norbornadiene (16) were used as substrates, only rearranged 1:1 addition products could be obtained, and no cyclopropane product could be detected. The results of addition reactions with 4-octenes (27) showed also that the cyclopropanation reaction was not stereospecific. On the basis of the above-mentioned results, a novel reductive debromocyclopropanation reaction of the γ-bromopropyl radical intermediate proceeding on the zinc metal surface is suggested.

Introduction

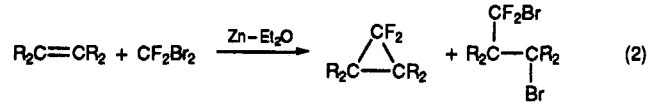
It was reported that either 1:1 adducts[1-3] or cyclopropane derivatives[4-8] could be formed from the addition reaction of polyhalomethanes to olefins (eq 1):



(1)

In general, 1:1 adducts were obtained via a radical chain addition mechanism,[1] or complexed radicals[2] which are different from the usual free radicals may also be involved in transition-metal salt catalyzed reactions.[3] Cyclopropanes were formed via addition of carbenes in most cases,[4,7,8] especially dihalocarbenes.[7] Carbenoid addition such as the Simmons-Smith cyclopropane synthesis[5] and the radical-induced methylene transfer reactions[6] were also reported. But a reaction with products derived from both the radical and the carbene intermediates had rarely been reported.

In the search for a cheaper and more effective difluorocarbene source, a reaction system (CF_2Br_2-Zn-olefin) similar to the Simmons-Smith reaction was selected and performed under nitrogen atmosphere. In addition to low yields of *gem*-diflurocyclopropane derivatives, 1:1 adducts were obtained simultaneously (eq 2):



(2)

The aforementioned results appeared unusual and intriguing and led us to a mechanistic study of this solid-liquid interface reaction.

Results and Discussion

The zinc-induced reaction of CF_2Br_2 (1) and cyclohexene (2) was conducted in several solvents with additives. A mixture of 3-5 was obtained for all of these reactions. The results are summarized in Table 1. Cyclopropane 3 is a typical carbene adduct,[7,8] and 4 is a typical 1:1 addition adduct.[1] Seemingly, both carbene and radical intermediates were involved in this reaction.

There were two experimental observations which provided us strong evidence for the reaction mechanism: (1) When the reaction was carried out in the presence of 1 mol % of *p*-dinitrobenzene which is a known radical anion inhibitor,[7b,9] total quenching of this reaction was observed. This result suggests that single electron transfer (SET) between CF_2Br_2 and zinc has taken place. (2) When 3 mol

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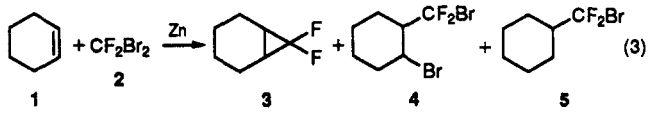
Table 1 Effects of Solvents and Additives on the Yield of 3–5[a]

condns			yield[b] (%)			
solvent	additive	time (h)	2	3	4 (a:b)	5
Et_2O		24	60	5.8	6.7 (1.1:1)	3.0
DME		24		6.8	6.5 (1.1:1)	5.7
dioxane		24		1.0	11 (1.5:1)	2.3
Et_2O	*c*	24	5	2.6	22 (2.2:1)	40
Et_2O	*d*	24	20	3.2	16 (1.2:1)	20
Et_2O	*e*	24	>95	<0.1	<0.1	<0.1
Et_2O	*f*	24	90	2.6	0.37	1.2

[a] 1 mmol of 2 (2:1:Zn = 1:2:4) and 20 mL of solvent was used. [b] Analyzed by gas chromatography and calibrated with internal standard. [c] 25 mol % CuCl. [d] Zinc powder was activated by hydrochloric acid containing 0.3 mol % $HgCl_2$. [e] 1 mol % *p*-dinitrobenzene. [f] 3 mol % hydroquinone.

Scheme 1



(3)

% of hydroquinone, a known radical inhibitor,[10] was added, the yield of **3–5** was decreased by 2.2, 18, and 2.5 times, respectively. This result suggests that formation of **3** and **5** proceeds via radical processes and formation of **4** via a radical chain process. It has been suggested by Burton[7b] that in DMF SET between zinc and CF_2Br_2 will lead to the formation of a radical anion **6** (eq 4). A second electron transfer will produce the difluorobromomethyl anion (**7**) (eq 5) which subsequently dissociates to give difluorocarbene (**8**) (eq 6):

$$CF_2Br_2 + Zn \rightarrow [Zn^+CF_2Br_2^{\bullet -}] \quad (4)$$
6

$$6 \rightarrow Zn^{2+} + Br^- + CF_2Br^- \quad (5)$$
7

$$7 \rightarrow :CF_2 + Br^- \quad (6)$$
8

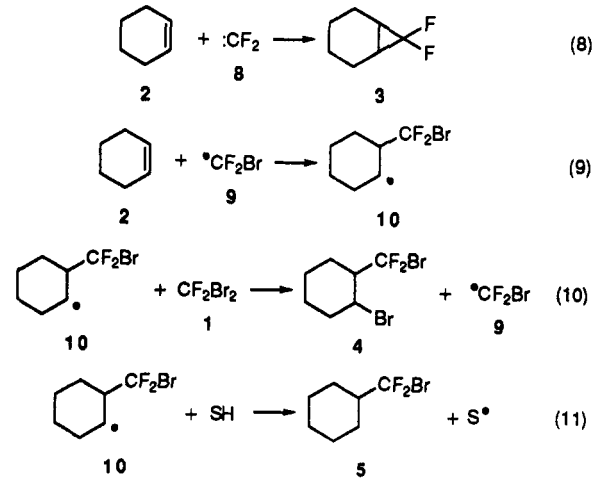
Presumably, the above reactions might also proceed in our reaction. However, radical anion **6** might also dissociate to form the difluorobromomethyl radical (**9**), as radical anions often do (eq 7).[11]

$$6 \rightarrow Br^- + {}^{\bullet}CF_2Br \quad (7)$$
9

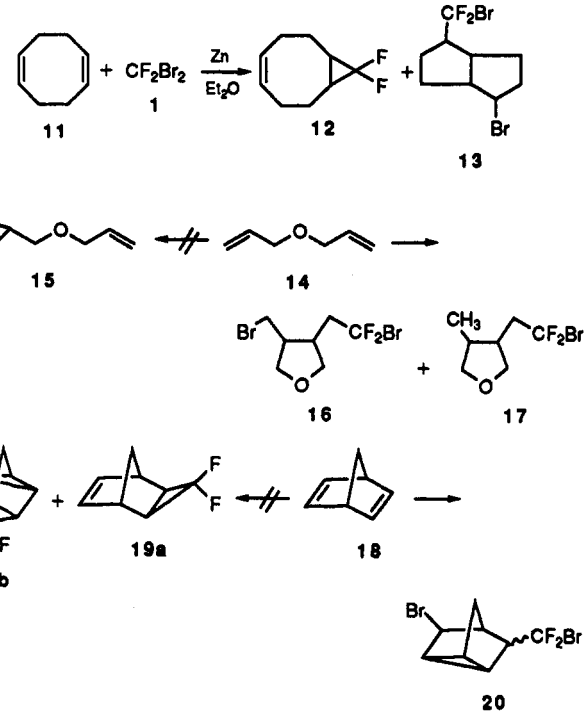
We suggest, therefore, the following mechanism (Scheme 2) to rationalize the formation of the addition products. Capture of the difluorocarbene (**8**) by cyclohexene (**2**), will lead to the formation of the cyclopropane product **3** (eq 8). Capture of radical **9** by cyclohexene (**2**) will yield the radical intermediate **10** (eq 9). Bromine atom abstraction from CF_2Br_2 by the radical **10** will yield the 1:1 adduct as well as radical **9** (eq 10). The intermediate **10** can also abstract a hydrogen from the solvent (SH) to form **5** (eq 11).

The above-mentioned reaction scheme was tested by the use of other olefins as substrates. Again, both carbene and radical-type products were obtained.

Scheme 2



Scheme 3



When 1,5-cyclooctadiene (**11**) was used as the substrate, the expected cyclopropane **12** and cyclized 1:1 adduct **13** were obtained. However, when diallyl ether (**14**) or bicyclo[2.2.1]hepta-2,5-diene (**18**) were used as substrates, only cyclized products **16**, **17**, and **20** were obtained, but the expected cyclopropane products **15**, **19**[12] were not found. Notably, cyclopropane products **15** and **19** cannot be found from the reaction of CF_2Br_2 and olefins on zinc surface, but both **15** and **19** can be easily obtained from the classical difluorocarbene[8c] route. Therefore, difluorocarbene does not seem to be the intermediate in this kind of reaction, rather, in its stead, radicals appear to be the true intermediates. For instance, the radical intermediate **21** (or **22**) can be formed by the addition reaction of the difluorobromomethyl radical ($^{\bullet}CF_2Br$) to diallyl ether (**14**) (or norbornadiene (**18**)). These adduct radicals, **21** or **22**, may cyclize faster to form radical intermediate **23** or **24** than they can form the cyclopropane products, **15** or **19**.

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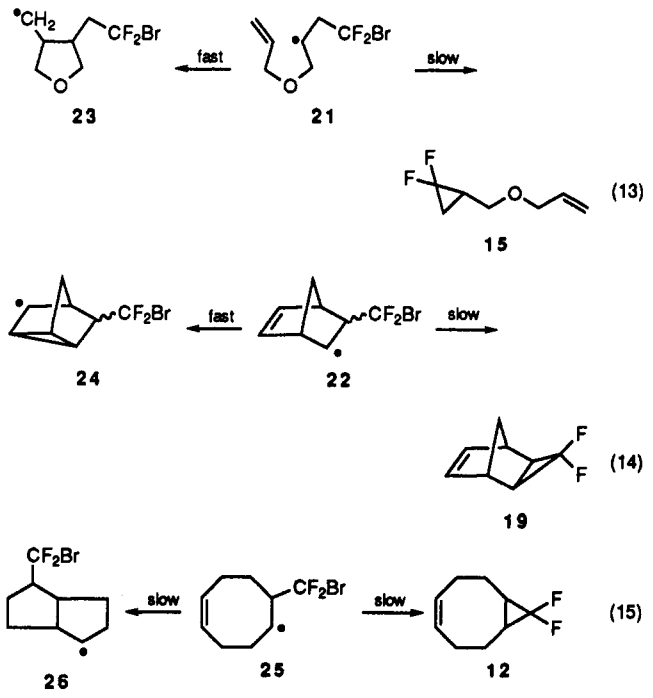
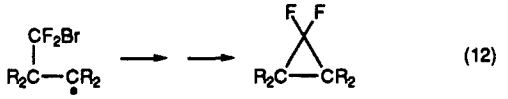
Scheme 4



At this juncture, an interesting mechanistic question appears. Could it be that all our reactions were treading radical paths? In other words, could it be that even our cyclopropane products **3** and **12** were formed from radical intermediates? To answer this question, we propose the radical debromocyclopropanation reaction (eq 12) for the rationalization of our experimental results, as summarized in Scheme 4.



As Scheme 4 suggests, if the proposed radical debromocyclopropanation reaction (eq 12) proceeds much slower than the intramolecular radical addition reactions, i.e., **21** to **23** and **22** to **24**, then only **16**, **17** and **20** will be formed. If, however, the intramolecular ring closure step (eq 15), i.e., from **25** to **26**,[13] is also slow, then both **12** and **13** may become the main products.

The radical nature of the cyclopropanation reaction could be examined by observation of the stereospecificity of cyclopropane formation, since the addition reaction of difluorocarbene (:CF_2) to olefins is highly stereospecific,[8] on the contrary, the radical addition reaction of olefins often proceeds nonstereospecificly.[14] In fact, when *trans*-4-octene (**27a**) was used as the substrate, the *trans*-cyclopropane product (**28a**) was always accompanied by 10% of the cis isomer (**28b**), independently of the conversion of octene. This result indicates the existence of a cyclopropanation reaction other than the carbene or related concerted mechanism. In other words, a radical debromocyclopropanation process appears very likely.

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Scheme 5

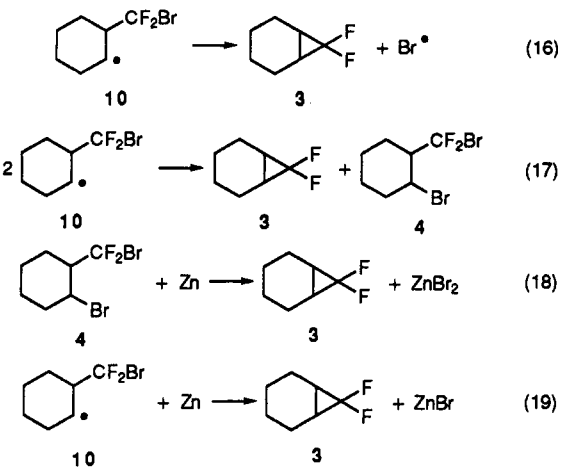

Table 2. Reaction of 1 and Alkene Initiated by Benzoperoxide[a]

	yield[b] (%)			
alkene	alkene	cyclopropane	1:1 adduct	others
2	39	3:<0.1	4:11 (a:b = 63:37)	5:7.5
11	40	12:<0.1	13:15	
18	1	19:<0.1	20:75	

[a] 1 mmol of alkene, 3 mmol of 1, 0.1 mmol of benzoperoxide, 1.0 mL of Et_2O, 80 °C, 72 h. [b] Determined by gas chromatography and calibrated by standard solutions.

For the formation of cyclopropane product **3**, four radical paths appear as possibilities, namely, (1) direct dissociation of **10** (eq 16), (2) disproportionation of **10** (eq 17), (3) reduction of **4** by zinc (eq 18), and (4) direct reduction of **10** by zinc (eq 19). Processes similar to eqs 16 and 17 were previously suggested by Kaplan to explain the cyclopropanation addition reaction of CH_2I_2 and alkene induced by benzoperoxide.[6a] Equations 18 and 19 could be compared to the Grignard reaction of 1,3-dibromopropane which gives a high yield of cyclopropane.[15]

In order to pick the right answer among the above-mentioned four possible paths, we first ran the reaction under typical radical reaction conditions; i.e., a mixture of CF_2Br_2, alkene, ether, and benzoyl peroxide was reacted in a sealed tube at 80 °C for 72 h. Gas chromatographic analysis indicated that 1:1 adducts were similarly obtained, but the cyclopropane product was not detected as summarized in Table 2. This result eliminates the two possible paths described by eqs 16 and 17.

Finally, the reduction of **4** under the same reaction conditions, i.e., Zn–Et_2O at room temperature, was also performed. Gas chromatography and GC–MS analysis indicated that the crude product contained about 19% of **3**, and 81% was byproducts which had never been detected before. This result indicates that the path depicted by eq 18 is not the main reaction path, even though it might be involved in the reaction. We conclude, therefore, that the *gem*-diflurocyclopropanes formed under our reaction conditions are mainly products derived from a zinc-participated reductive debromocyclopropanation, as depicted by eq 19 for **10**.

Experimental Section

^1H NMR spectra were taken on an EM360A(60MHz) spectrometer with TMS as an internal reference. ^{19}F NMR spectra were taken on an EM 360L (60 MHz) spectrometer with CF_3-

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CO_2H as external reference, chemical shifts are reported relative to $CFCl_3$ equal zero. GC–MS were obtained with a Finnigan MAT-4510 GC–MS spectrometer. Infrared spectra were recorded on a Shimadzu IR 440 spectrophotometer. Analytical gas chromatography was performed on a Model 103 (Shanghai) gas chromatograph equipped with a HP 3390A integrator. A SE-30 supported capillary column (length = 40 m, i.d. = 0.2 mm) was used with a flame ionization detector and nitrogen as carrier gas. Preparative vapor-phase chromatography were performed on a Model 102G (Shanghai) gas chromatography with a thermal conductivity detector and hydrogen as carrier gas. An aluminum column (5 m × 7 mm) packed with 15% SE30 on 60/80 mesh supporter was used.

Diethyl ether was dried by reflux and distillation with $LiAlH_4$. Zinc powder (100 mesh) was activated by washing with 10% hydrochloride acid, ethanol, and absolute ether in that order. Commercial CF_2Br_2 was carefully fractionated (bp 24–25 °C). Sodium iodide was dried at 300 °C (1 mmHg) for 2 h. **11**, **14**, **18**, and **27a** were obtained from Aldrich.

$PhHgCF_3$ (mp 139–140 °C (lit.[8c] mp 138–140 °C)) was prepared by a previously reported method.

All experiments were conducted in pure and dry nitrogen atmosphere.

Preparation of Authentic *gem*-Difluorocyclopropane Derivatives. 15. A mixture of 10 mmol of diallyl ether (**14**), 6 mmol of $PhHgCF_3$, 18 mmol of NaI and 10 mL of benzene was stirred and refluxed for 48 h. After cooling, the resulted white solid was filtered off, the solution was concentrated to about 2 mL, and **15** was separated and purified by preparative GC in 20% yield; ^1H NMR (CCl_4) 0.8–2.0 (3H, m), 3.3 (2H, d, J = 6.4 Hz), 3.8 (2H, d, J = 4.6 Hz), 5.0–5.3 (2H, m), 5.3–6.0 (1H, m); ^{19}F NMR (CCl_4) 128.6 (dm, $^2J_{FF}$ = 162 Hz, $^3J_{HF}$ = 13 Hz, F_{trans}), 143.3 (dm, $^3J_{HF}$ = 11.6 Hz, F_{cis}); IR (film) 3090 (w), 3025 (w), 1646 (m), 1295 (s), 1260 (m), 1212 (s) cm^{-1}; MS (EI) m/z (M^+, 148 (0.1)), 41 (100). Anal. Calcd for $C_7H_{10}F_2O$: C, 56.75; H, 6.80. Found: C, 56.81; H, 6.77.

28. A mixture of 2.5 mmol of 4-octene (**27**) (**a:b** = 22:78), 6 mmol of $PhHgCF_3$, 18 mmol of NaI, and 10 mL of benzene was stirred and refluxed for 24 h, the resulted solution was worked up as usual, and **28** was separated and purified by GC in 50% yield. Anal. Calcd for $C_9H_{16}F_2$: C, 66.64; H, 9.94. Found: C, 66.61; H, 10.30. **28a**: ^1H NMR (CCl_4) 0.8–1.1 (8H, m), 1.1–1.5 (8H, m); ^{19}F NMR (CCl_4) 139.3 (t, $^3J_{HF}$ = 3.5 Hz); IR (film): 3010 (m), 1257 (s), 1239 (s), 1189 (s) cm^{-1}; MS (EI) m/z ($(M - HF)^+$, 142 (0.7)), 77 (100). **28b**: ^1H NMR (CCl_4) 0.7–1.1 (6H, m), 1.1–1.7 (10H, m); ^{19}F NMR (CCl_4) 125 (d, $^2J_{FF}$ = 156 Hz, F_{trans}), 154.6 (d, F_{cis}); IR (film) 3020 (m),1265 (s), 1245 (s), 1190 (s) cm^{-1}; MS (EI)m/z ($(M - HF)^+$, 142 (0.4)), 77 (100).

General Procedure for the Reaction of Alkene with CF_2Br_2 (1) in the Presence of Zinc. A 5.2-g (80 mmol) portion of Zn, 20 mmol of alkene, and 20 mL of Et_2O were stirred and cooled with an ice–water bath, and then 8.4 g (40 mmol) of difluorodibromomethane (**1**) was added dropwise during 2 h. The reaction took place smoothly. The unreacted Zn was filtered off 24 h later, and the organic layer was washed with a saturated aqueous solution of NH_4Cl. The solvent was fractionally distilled off, and the products were separated from the resulted crude oily product by preparative GC. The spectroscopic data of **3**[8c] and **28** were identical with the data reported in the literature or that of authentic sample. The spectra data of the other products were as follows:

4a: ^1H NMR ($CDCl_3$) 1.0–2.5 (9H, m), 4.1 (1H, td, $^4J_{HF}$ = 7.8Hz, $^3J_{HH}$ = 4.0 Hz); ^{19}F NMR ($CDCl_3$) 41.2 (tm); IR (film) 1200 (s) cm^{-1}; MS (EI)m/z (M^+, 292 (0.6)), 131 (100). Anal. Calcd for $C_7H_{10}Br_2F_2$: C, 28.80; H, 3.45. Found: C, 29.20; H, 3.47.

4b: ^1H NMR ($CDCl_3$) 1.0–2.5 (9H, m), 4.6 (1H, s); ^{19}F NMR ($CDCl_3$) 46.1 (1F, dd, $^2J_{FF}$ = 155 Hz,$^3J_{HF}$ = 12 Hz), 50.9 (1F, dd, $^3J_{HF}$ = 12 Hz); IR (film): 1200 (s, CF) cm^{-1}; MS (EI) m/e (M^+, 294, 292, 290 (0.1, 0.2, 0.1)), 131 (100). Anal. Calcd for $C_7H_{10}Br_2F_2$: C, 28.80; H, 3.45. Found: C, 29.20; H, 3.41.

5: ^1H NMR ($CDCl_3$) 1.0–2.0 (10H, m), 2.2 (1H, m); ^{19}F NMR ($CDCl_3$) 49.0 (d, $^3J_{HF}$ = 9.8 Hz); IR (film) 1200 (s, CF) cm^{-1}; MS (EI) m/z ($(M - Br)^+$, 133 (30)), 113 (100). Anal. Calcd for $C_7H_{11}BrF_2$: C, 39.46; H, 5.2. Found: C, 39.18; H, 4.86.

12: ^1H NMR (CCl_4) 1.0–2.4 (10H, m), 5.4–5.6 (2H, m); ^{19}F NMR (CCl_4) 150.1 (d, $^2J_{FF}$ = 156 Hz, F_{endo}), 124.4 (dt, $^3J_{HF}$ = 12 Hz, F_{exo}); IR (film) 3030 (m), 1655 (w), 1295 (s), 1224 (s) cm^{-1}; MS (EI) m/z (M^+, 158 (0.32)), 67 (100). Anal. Calcd for $C_9H_{12}F_2$: C, 68.33; H, 7.65. Found: C, 68.45; H, 7.56.

13: ^1H NMR (CCl_4) 1.0–2.4 (8H, m), 2.4–3.0 (3H, m), 4.0 (1H, m); ^{19}F NMR (CCl_4) 47.2(dd, $^2J_{FF}$ = 152 Hz, $^3J_{HF}$ = 11 Hz); IR (film) 1293 (s), 1215 (s), 1170 (s) cm^{-1}; MS (EI) m/z ($(M - Br)^+$, 239, 237 (6.0, 6.2)), 157 (100). Anal. Calcd for $C_9H_{12}Br_2F_2$: C, 39.99; H, 3.80. Found: C, 39.98; H, 3.70.

16. Anal. Calcd for $C_7H_{10}Br_2F_2O$: C, 27.30; H, 3.27. Found: C, 27.15; H, 3.22. **16a**: ^1H NMR (CCl_4) 2.2–2.9 (4H, m), 3.3–3.5 (2H, m), 3.5–4.1 (4H, m); ^{19}F NMR (CCl_4) 44.6 (t, $^3J_{HF}$ = 12Hz); IR (film): 1200 (s) cm^{-1}; MS (EI) m/z ($(M - Br)^+$, 229, 227 (30, 32), 117 (100). **16b**: ^1H NMR (CCl_4) 2.2–2.9 (4H, m), 3.2–3.5 (2H, m)), 3.5–4.0 (4H, m); ^{19}F NMR (CCl_4) 43.3 (t, $^3J_{HF}$ = 13Hz); IR (film) 1190 (s) cm^{-1}; MS (EI) m/z (M^+, 308 (0.5)), 117 (100).

17: ^1H NMR (CCl_4) 0.95 (3H, d, $^3J_{HF}$ = 14 Hz, CH_3), 2.0–2.8 (4H, m), 3.0–4.1 (4H, m); ^{19}F NMR(CCl_4) 42.4 (t, $^3J_{HF}$ = 14Hz); IR (film) 1200 (s), 1175 (s)cm^{-1}; MS (EI) m/z (M^+, 230, 228 (6.4, 7.8)), 55 (100). Anal. Calcd for $C_9H_{12}F_2$: C, 36.70; H, 4.84. Found: C, 36.31; H, 4.82.

20: IR (film) 3100 (m), 3025 (m), 1290 (s), 1220 (s) cm^{-1}. Anal. Calcd for $C_8H_8Br_2F_2$: C, 31.82; H, 2.67. Found: C, 31.88; H, 2.46. **20a**: ^1H NMR (CCl_4) 1.2–1.8 (4H, m), 2.0 (1H, s), 2.4 (1H, s), 2.5 (1H, t, $^3J_{HF}$ = 12 Hz), 4.2 (1H, s); ^{19}F NMR (CCl_4) 44.6 (t); MS (EI) m/z ($(M - Br)^+$, 229, 227 (30, 32)), 117 (100). **20b**: ^1H NMR (CCl_4) 1.26–1.81 (4H, m), 1.86–2.04 (1H, m), 2.38 (1H, s), 3.22 (1H, t, $^3J_{HF}$ = 15Hz), 3.85 (1H, s); ^{19}F NMR (CCl_4) 47.6 (1F, dd, $^2J_{FF}$ = 157 Hz, $^3J_{HF}$ = 15.4 Hz), 42.1 (dd, 1F); MS (EI) m/z (M^+, 304, 302, 300 (0.03, 0.06, 0.03)), 141 (100); **20c**: ^1H NMR (CCl_4) 1.2–1.8 (4H, m), 1.83–2.00 (2H, m), 2.37 (1H, s), 2.45 (1H, t, $^3J_{HF}$ = 15 Hz), 3.80 (1H, s); ^{19}F NMR (CCl_4) 47.7 (1F, dd, $^2J_{FF}$ = 156 Hz, $^3J_{HF}$ = 15 Hz), 44.5 (1F, dd); MS (EI) m/z (M^+, 304, 302, 300 (0.25, 0.58, 0.20)), 141 (100).

Addition of CF_2Br_2 to Olefins under Typical Radical Conditions. The reaction conditions and the results are summarized in Table 2.

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