**Acknowledgments.**—The author is indebted to Dr. Derick Ovenall, Mr. Donald Nickerson, Mr. Lou Rizzardi, and Mr. Lou Walther for invaluable aid in obtaining the nmr spectra. Useful and stimulating discussion with Dr. Frank J. Weigert is also acknowledged. The reluctant ionic bromination of certain γ-fluorine substituted olefins was originally brought to my attention by Dr. James E. Nottke.

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# Fluorinated Bicyclics. II. Steric Control in the Free-Radical Addition of Polyhalomethanes to 5,5,6,6-Tetrafluoro-2-norbornene

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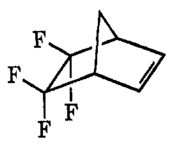
The free-radical addition of carbon tetrachloride, bromotrichloromethane, and *n*-heptafluoropropyl iodide to 5,5,6,6-tetrafluoro-2-norbornene (1) gave cis and trans adducts in the ratios of 2.7:1, 2.1:1, and 1:3.8, respectively. These results contrast with norbornene itself, where 95–100% trans addition is observed, and suggest that the endo fluorine substituents play a dominant role in directing the stereochemistry of these additions.

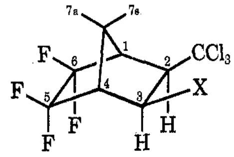
In a previous paper, the importance of endo fluorine coulombic effects in the stereospecific cis-exo-bromination of 5,5,6,6-tetrafluoro-2-norbornene (1) and related compounds was demonstrated.[1] The free-radical additions of carbon tetrachloride,[2] bromotrichloromethane,[2b] and *n*-heptafluoropropyl iodide[3] to norbornene itself are known to afford >95% trans adduct in each case. In order to investigate the influence of fluorine substitution, a detailed comparative study of the free-radical addition of these polyhalomethanes to 5,5,6,6-tetrafluoro-2-norbornene (1) was undertaken.

## Results

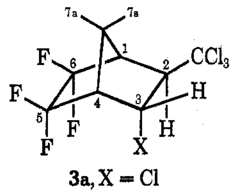
The benzoyl peroxide initiated addition of carbon tetrachloride to **1** at 80° afforded a mixture of 73% cis **2a** and 27% trans **3a** adducts in 72% yield as well as a substantial amount of telomeric residue. A similarly initiated reaction between **1** and bromotrichloromethane at 104° gave a mixture of 68% **2b** and 32% **3b** in 84% yield. Control experiments indicated that there was no product interconversion under either the reaction or vpc analytical conditions.



**1**



**2a**, X = Cl
**b**, X = Br



**3a**, X = Cl
**b**, X = Br

The 100-MHz nmr spectra of adducts **2a** and **3a** are shown in Figures 1a and 1b, and chemical shifts and coupling constants are tabulated in Tables I and II. Appropriate double-resonance experiments allowed for the assignment of long-range couplings. The spectra of **2b** and **3b** were quite similar to those of **2a** and **3a**, respectively, and the same analysis was applicable.

TABLE I

CHEMICAL SHIFTS[a] FOR POLYHALOMETHANE ADDUCTS IN CARBON TETRACHLORIDE

| Nucleus | **2a** | **2b** | **4** | **3a** | **3b** | **5** |
|---|---|---|---|---|---|---|
| $H_1H_4$ | 3.09, 2.91 | (3.06)[b] | 3.18, 2.94 | (2.99) | (3.03) | (2.90) |
| $H_{2n}$ | 3.52 | 3.48 | ~3.0[c] | 3.42 | 3.40 | 3.05 |
| $H_3$ | 4.58 | 4.56 | 4.36 | 4.28 | 4.26 | 4.21 |
| $H_{7a}$ | 2.04 | 2.09 | 2.15 | 1.98 | 1.96 | 1.86 |
| $H_{7s}$ | 2.73 | 2.76 | 2.45 | 2.36 | 2.40 | 1.91 |
| $F_{5x}$ | 120.5 | 120.4 | *c* | 110.9 | 110.6 | *c* |
| $F_{5n}$ | 126.5 | 126.7 | *c* | 118.0 | 117.7 | *c* |
| $F_{6x}$ | 119.0 | 118.5 | *c* | 119.9 | 119.8 | *c* |
| $F_{6n}$ | 119.3 | 119.0 | *c* | 126.0 | 125.6 | *c* |

[a] All proton chemical shifts are reported in parts per million (δ) relative to internal tetramethylsilane. All fluorine chemical shifts are in parts per million (φ) relative to fluorotrichloromethane (F-11) internal standard. All values refer to the high-field side of F-11. [b] Values in parentheses indicate that the $H_1$, $H_4$ protons were not resolved. [c] Could not be determined accurately owing to interferences.

TABLE II

COUPLING CONSTANTS (HERTZ) FOR POLYHALOMETHANE ADDUCTS IN CARBON TETRACHLORIDE

| Nuclei | **2a** | **2b** | **4** | **3a** | **3b** | **5** |
|---|---|---|---|---|---|---|
| $H_2H_3$ | 6.9 | 7.1 | 7.8 | 6.9 | 6.7 | 7.8 |
| $H_{7s}H_{7a}$ | 12.5 | 12.5 | 12–13 | 12.5 | 12 | 13 |
| $H_{3x}H_4$ |  |  |  | 3.7 | ~4 |  |
| $H_{3x}F_{5x}$ |  |  |  | 3.7 | ~4 |  |
| $H_{7s}F_{5n}$ |  |  |  | 5.7 | 5.7 |  |
| $H_{7s}F_{6n}$ | 5.7 | 5.8 |  | 5.7 | 5.7 |  |
| $F_{5x}F_{5n}$ | 228 | 228 |  | 241 | 240 |  |
| $F_{6x}F_{6n}$ |  |  |  | 226 | 230 |  |

The vicinal $H_2$, $H_3$ protons in **3a** appeared as an AB quartet of multiplets at δ 3.42 and 4.28. The downfield resonance was assigned to the proton geminal to chlorine, $H_3$, which was further split into an apparent triplet ($J$ = 3.7 Hz). The next higher field resonance was assigned to the proton adjacent to the trichloromethyl group. Double-irradiation experiments indicated that proton $H_3$ was coupled to both bridgehead proton $H_4$ and fluorine $F_{5x}$ by 3.7 Hz. The presence and magnitude of these couplings indicate that $H_3$

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(1) B. E. Smart, *J. Org. Chem.*, **38**, 2027 (1973).

(2) (a) C. L. Osborne, T. V. Van Auken, and D. J. Trecker, *J. Amer. Chem. Soc.*, **90**, 5806 (1968). (b) E. Tobler and D. J. Foster, *J. Org. Chem.*, **29**, 2839 (1964).

(3) N. O. Brace, *J. Org. Chem.*, **27**, 3027 (1962).

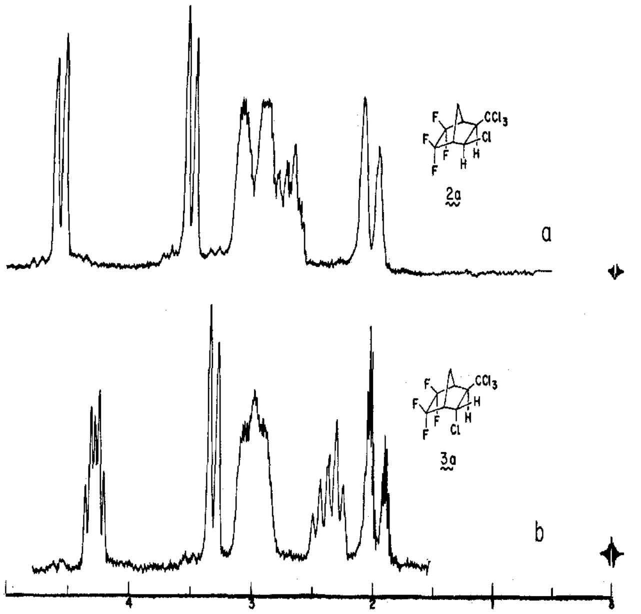
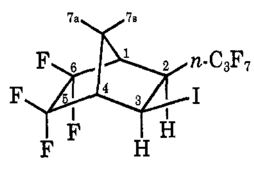


Figure 1.—Nmr (100 MHz) spectrum: a, *exo*-2-trichloromethyl-*exo*-3-chloro-5,5,6,6-tetrafluoronorbornane (**2a**); b, *exo*-2-trichloromethyl-*endo*-3-chloro-5,5,6,6-tetrafluoronorbornane (**3a**).

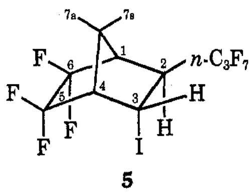
is exo. Proton $H_2$ gave a sharp resonance, suggestive of an endo proton. Simultaneous irradiation of $H_4$ and $F_{5x}$ revealed an AB quartet for $H_2$, $H_3$ (Figure 2) with a coupling constant $J_{H_2,H_3} = 6.9$ Hz. This vicinal trans coupling constant is anomalously large and is normally observed for cis vicinal proton couplings in these systems.[2a,4-8]

The nmr spectrum of compound **2a** (Figure 1a) was analyzed similarly. The vicinal $H_2$, $H_3$ protons again appear as an AB quartet with $J_{H_2,H_3} = 6.9$ Hz. The magnitude of this coupling is consistent with a cis orientation for the vicinal protons. Neither the downfield proton $H_3$ adjacent to chlorine at $\delta$ 4.58 nor proton $H_2$ adjacent to trichloromethyl at $\delta$ 3.52 was coupled to $H_1$ or $H_4$ by the expected value of *ca.* 4 Hz, and the lack of appreciable coupling for these protons suggests that both $H_2$ and $H_3$ are endo.[9]

The benzoyl peroxide initiated addition of *n*-heptafluoropropyl iodide to **1** gave a mixture of 21% cis adduct **4** and 79% trans adduct **5** in 95% yield.



**4**



**5**

The 220-MHz nmr spectra of **4** and **5** are shown in Figures 3 and 4. These nmr spectra were much more difficult to interpret owing to extensive H–F couplings between proton $H_2$ and the adjacent perfluoroalkyl group. Unfortunate overlap of $H_2$ and the bridgehead protons $H_1$ and $H_4$ further complicated analysis. However, a general comparison of the downfield $H_3$ proton patterns of 2, **3** and **4**, **5** suggested the appropirate stereochemistry for **4** and **5**.

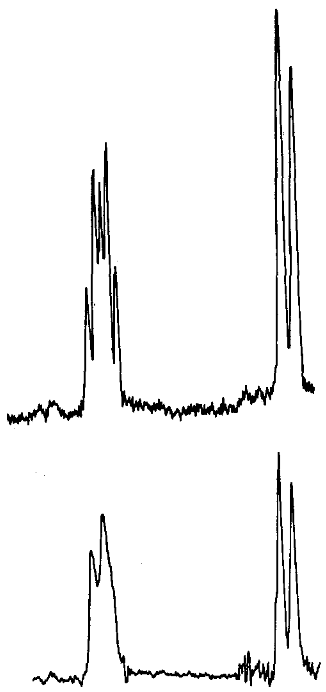


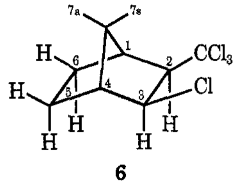
Figure 2.—Vicinal $H_2$, $H_3$ protons in **3a** (top); $H_2$, $H_3$ upon irradiation of $H_4$ and $F_{5x}$ (bottom).

The proton adjacent to iodine, $H_3$ in **4**, appeared as approximately a doublet (half of an AB quartet) at $\delta$ 4.36 with $J_{H_2,H_3} = 7.8$ Hz. The lack of appreciable further coupling and the similarity with the downfield proton resonance shapes in **2a** and **2b** indicate that this proton is endo. The $H_3$ proton in **5** was a broad multiplet at $\delta$ 4.21, suggestive of an exo proton.

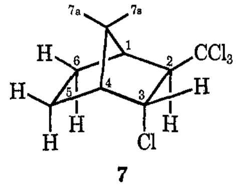
The proton adjacent to heptafluoropropyl in **5** appeared as an apparent doublet of triplets at $\delta$ 3.05. This pattern can be interpreted as a doublet ($J$ = 7.8 Hz) of doublets ($J$ = 23 Hz) of doublets ($J$ = 7.8 Hz) with a vicinal coupling of 7.8 Hz and vicinal couplings of the nonequivalent methylene fluorines of the *n*-heptafluoroalkyl group with $H_{2n}$ of 7.8 and 23 Hz. The anomalous equivalence of cis and trans vicinal proton couplings, which was observed for **2a,b** and **3a,b**, is apparent in the *n*-heptafluoropropyl iodide adducts as well.

A comparison of the chemical shifts of the protons adjacent to halogen indicates that the endo proton is downfield from the exo proton by 0.15–0.30 ppm. The opposite has been observed for 2,3-dihalogenated norbornanes.[5]

The proton chemical shifts for **2a**, **3a**, and the carbon tetrachloride adducts of norbornene **6** and **7** are compared in Table III. The $H_{2n}$, $H_{3n}$ protons in the fluorinated derivatives **2a**, **3a** are markedly deshielded



**6**



**7**

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[4] P. Lazslo and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **84**, 2112 (1962).

[5] P. Subramanian, M. T. Emerson, and N. A. LeBel, *J. Org. Chem.*, **30**, 2624 (1965), and references cited therein.

[6] F. L. Anet, H. H. Lee, and J. L. Submeier, *J. Amer. Chem. Soc.*, **89**, 4431 (1967).

[7] S. J. Cristol and B. B. Jarvis, *ibid.*, **89**, 5885 (1967).

[8] A. G. Ludwick and J. C. Martin, *J. Org. Chem.*, **34**, 4108 (1969).

[9] The similarity of the vicinal $H_2$, $H_3$ nmr resonances in **2a** and *exo*-2-trichloromethyl-*exo*-3-chloronorbornane (**6**) (ref 2a) should be noted.

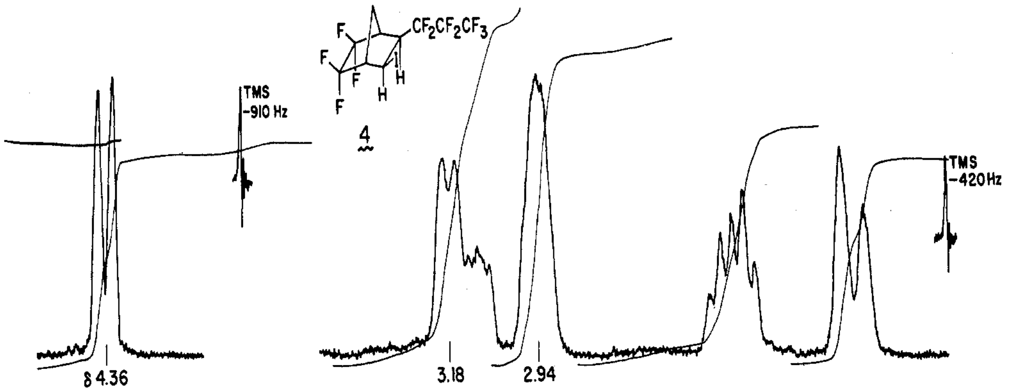


Figure 3.—Nmr (220 MHz) spectrum of *exo*-2-(*n*-heptafluoropropyl)-*exo*-3-iodo-5,5,6,6-tetrafluoronorbornane (4).

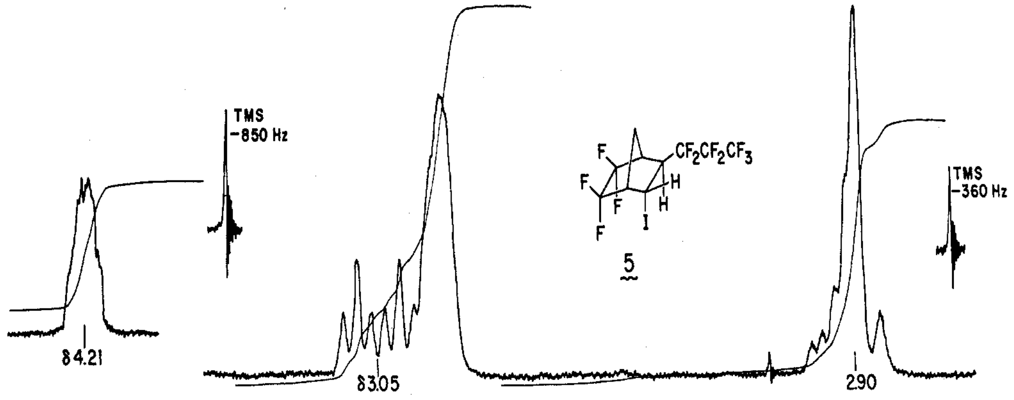


Figure 4.—Nmr (220 MHz) spectrum of *exo*-2-(*n*-heptafluoropropyl)-*endo*-3-iodo-5,5,6,6-tetrafluoronorbornane (5).

TABLE III

CHEMICAL SHIFTS[a] FOR CARBON TETRACHLORIDE ADDUCTS OF 5,5,6,6-TETRAFLUORO-2-NORBORNENE (1) AND NORBORNENE IN CARBON TETRACHLORIDE

| Chemical shift | 2a | 6[b] | 3a | 7[b] |
|---|---|---|---|---|
| $H_1$ | 3.09 | 2.74 | 2.99[c] | 2.6[d] |
| $H_4$ | 2.91 | 2.54 | | |
| $H_{2n}$ | 3.52 | 2.94 | 3.42 | 2.6[d] |
| $H_{3n}$ | 4.58 | 4.18 | | |
| $H_{3x}$ | | | 4.28 | 4.23 |
| $H_{7a}$ | 2.04 | | 1.98 | 1.38 |
| $H_{7s}$ | 2.73 | 2.38 | 2.36 | 2.10 |

[a] See Table I, footnote *a*. [b] Values taken from ref 2a. [c] $H_1$, $H_4$ not resolved. [d] Not determined accurately owing to interferences.

(0.4–0.8 ppm) relative to the nonfluorinated adducts **6**, **7**. Note, however, that $H_{3x}$ is not appreciably deshielded (0.05 ppm) from **2a** and **7**. Comparison of the methylene bridge protons indicates that $H_{7a}$ is deshielded (0.6 ppm) from **3a** and **7**, whereas $H_{7s}$ is deshielded less (0.26 ppm). These data suggest a *positive* magnetic anisotropy for the carbon–fluorine bond. Endo 5,6 fluorines deshield $H_2$, $H_3$ and exo 5,6 fluorines deshield $H_{7a}$. Fluorine substitution, however, does not affect $H_{3x}$, in agreement with a "through space" proximity effect. Introduction of endo 5,6 fluorines and the resultant deshielding of endo 2,3 protons, while not affecting the exo protons, thus has reversed the normal relative exo,endo proton shifts relationship for 2,3-halogenated norbornenes.[10]

## Discussion

Table IV summarizes the comparative additions of polyhalomethanes to norbornene and 5,5,6,6-tetrafluoro-2-norbornene (**1**). The predominance of trans addition with norbornene clearly is not the case for **1**. Cis addition is in fact preferred for carbon tetrachloride and bromotrichloromethane.

TABLE IV

FREE-RADICAL ADDITION OF POLYHALOMETHANES TO 5,5,6,6-TETRAFLUORO-2-NORBORNENE (1) AND NORBORNENE

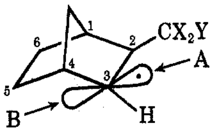
| | Norbornene | | Tetrafluoronorbornene (1) | |
|---|---|---|---|---|
| Adduct | % trans | % cis | % trans | % cis |
| $CCl_3$ | 95 | 5[a] | 27 | 73 |
| $CCl_3Br$ | 100 | 0[b] | 32 | 68 |
| *n*-$C_3F_7I$ | 100 | 0[c] | 79 | 21 |

[a] Reference 2a. [b] Reference 2b. [c] Reference 3.

The overwhelming predominance of exo attack by trichloromethyl and *n*-heptafluoropropyl radicals has been noted previously by Osborne[2a] and Brace.[3] Subsequent transfer of halogen occurred primarily by path B, owing to major nonbonded interaction with the exo polyhalomethyl substituents, with resultant trans product formation. The initial addition of $\cdot CX_2Y$ should be independent of fluorine substitution at $C_5$ and $C_6$ and this was the case for **1**. The relative nonbonded repulsions between endo 5-fluorine and the 2-exo polyhalomethyl group with the approaching polyhalomethane molecule will then determine the preference for cis or trans product formation. The endo fluorine substituents are known to direct the stereo-

[10] The $^{19}F$ spectra of the polyhalomethane adducts and related systems will be discussed in a future publication.

chemistry of free-radical attack by bromine.[1] The preference for cis addition of carbon tetrachloride and bromotrichloromethane to **1** also illustrates the importance of fluorine nonbonded interactions. Coulombic repulsion from the 5-endo fluorine toward the incoming polyhalomethane molecule is greater than the nonbonded interaction of the exo trichloromethyl group with polyhalomethane, and attack from side A in **8** is preferred with the result that predominantly cis adducts **2a** and **2b** are formed.[11] The slightly greater amount of trans addition observed with bromotrichloromethane reflects the increased importance of steric interaction of trichloromethyl with the larger polyhalomethane molecule.



$X = Y = Cl$

$X = F; Y = CF_2CF_3$

**8**

The *n*-heptafluoropropyl group in **8** ($X = F$; $Y = CF_2CF_3$) is sterically large and rich in electron density. Attack from side A is subject to electronic repulsion from a number of fluorines of the large *n*-heptafluoropropyl group, while attack from B is repulsed by a single endo 5-fluorine substituent. The overall preference for trans addition reflects these factors. The fact that 21% cis addition is observed when none is observed for norbornene itself indicates that the endo fluorine substituents still play an important role in directing the stereochemistry of attack by *n*-heptafluoropropyl iodide.

## Experimental Section

All melting and boiling points are uncorrected. The gas chromatography work was performed on a Varian Aerograph Series 200 gas chromatograph fitted with a Brown Potentiometer recorder. The following columns were employed: column A, 6 ft × 0.375 in. 20% QF-1 fluorosilicone on 60/80 Chromosorb P; column B, 6 ft × 0.375 in. 20% silicone 200 on 60/80 Chromosorb W; column C, 6 ft × 0.375 in. 20% Zonel E7 on 60/80 Chromosorb P. The $^1H$ and $^{19}F$ nmr spectra and decoupling experiments were run as before.[1]

***exo*-2-Trichloromethyl-*exo*-3-chloro-5,5,6,6-tetrafluoronorbornane (2a) and *exo*-2-Trichloromethyl-*endo*-3-chloro-5,5,6,6-tetrafluoronorbornane (3a).**—A mixture of 11.6 g (0.07 mol) of 5,5,6,6-tetrafluoro-2-norbornene (**1**), 77 g (0.5 mol) of carbon tetrachloride, and 1.2 g (5 mmol) of benzoyl peroxide was refluxed for 20 hr in a nitrogen atmosphere. A mixture of 84% **2a** and **3a** and 16% unreacted **1** was present by nmr. Vpc analysis (columns A and B, 165°) indicated a mixture of 73% **2a** and 27% **3a**. Removal of the solvent and fractionation afforded two major cuts, 9.9 g (97% **2a**, 3% **3a**), bp 64-54° (0.5 mm), and 3.7 g (10% **2a**, 90% **3a**), bp 68-69° (0.5 mm). A dark, viscous residue (5.7 g) remained. Preparative vpc (column A, 165°) gave pure **3a** as an oil, and pure **2a**, mp 36-38°.

*Anal.* Calcd for $C_8H_6Cl_4F_4$: C, 30.03; H, 1.89; Cl, 44.32. Found (**2a**): C, 30.30; H, 1.81; Cl, 44.42. Found (**3a**): C, 30.17; H, 1.96; Cl, 44.05.

A mixture of 0.5 g of 90% **3a** and 10% **2a**, 4 g of carbon tetrachloride, and 50 mg of benzoyl peroxide was refluxed for 4 hr under nitrogen. Vpc analysis indicated no change in the **3a**:**2a** ratio.

***exo*-2-Trichloromethyl-*exo*-3-bromo-5,5,6,6-tetrafluoronorbornane (2b) and *exo*-2-Trichloromethyl-*endo*-3-bromo-5,5,6,6-tetrafluoronorbornane (3b).**—A mixture of 11.6 g (0.07 mol) of **1**, 99 g (0.5 mol) of bromotrichloromethane, and 1.2 g of benzoyl peroxide was refluxed for 24 hr in a nitrogen atmosphere to afford a mixture of 68% **2b** and 32% **3b** (vpc, column B, 175°). No unreacted **1** was present. Fractional distillation afforded the following cuts, bp 69-72° (0.3 mm): 3.5 g (99% **2b**, 1% **3b**), bp 72-73° (0.3 mm); 1.8 g (93% **2b**, 7% **3b**), bp 73-74° (0.3 mm); 13.2 g (74%, **2b**, 26% **3b**), bp 74-75° (0.3 mm); 2.9 g (15% **2b**, 85% **3b**). Treatment of the first cut with a small amount of pentane and chilling afforded pure **2b**, mp 42-44°. Pure **3b** was obtained as an oil by preparative vpc (column B, 175°).

*Anal.* Calcd for $C_8H_6BrCl_3F_4$: C, 26.37; H, 1.66; Br, 21.93; Cl, 29.19. Found (**2b**): C, 26.47; H, 1.69; Br, 22.14; Cl, 29.66. Found (**3b**): C, 26.45; H, 1.58; Br, 22.14; Cl, 29.67.

***exo*-2-(*n*-Heptafluoropropyl)-*exo*-3-iodo-5,5,6,6-tetrafluoronorbornane (4) and *exo*-2-(*n*-Heptafluoropropyl)-*endo*-3-iodo-5,5,6,6-tetrafluoronorbornane (5).**—A 100-ml Carius tube charged with 8.3 g (0.05 mol) of **1**, 15 g (0.0507 mol) of freshly distilled *n*-heptafluoropropyl iodide, and 0.2 g of benzoyl peroxide was degassed and heated on a steam bath for 4.5 hr. Vpc (column C, 155°) and nmr analysis indicated 18% unreacted **1** and a mixture of 21% **4** and 79% **5**. Fractional distillation afforded 1.4 g of **1**, bp 48.5° (17 mm) (solidified), 2.2 g of 24% **4** and 76% **5**, bp 86-90° (17 mm): and 16.0 g of 19% **4** and 81% **5**, bp 90-100° (17 mm). Refractionation afforded the following mixtures, bp 86-93° (17 mm): 64% **4**, 36% **5**, bp 93-99° (17 mm); 41% **4**, 59% **5**, bp 99-100° (17 mm); 14% **4**, 86% **5**. Pure **5** was collected as a viscous, colorless oil by vpc (column C, 155°) and pure **4** was a white solid, mp 31-32°.

*Anal.* Calcd for $C_{10}H_6F_{11}I$: C, 26.00; H, 1.31; F, 45.23. Found (41% **4**, 59% **5**): C, 25.69; H, 1.28; F, 45.33.

**Registry No.**—**1**, 2822-56-2; **2a**, 39037-43-9; **2b**, 39037-44-0; **3a**, 39037-45-1; **3b**, 39037-46-2; **4**, 39037-47-3; **5**, 39037-48-4; $CCl_4$, 56-23-5; $CBrCl_3$, 75-62-7; *n*-heptafluoropropyl iodide, 754-34-7.

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[11] The formation of telomeric residues from the addition of polyhalomethanes to **1** reflects the importance of hindrance to chain transfer in **8**. For a discussion of this point, see ref 2a.