condenser and a magnetic stirrer was placed 50 ml of IAE and 2.0 g (19 mmol) of anhydrous sodium carbonate, and the mixture was heated to 173°. At this point 2.0 g (4.3 mmol) of dienol **1** was added as a solid all at once and the resulting mixture was heated at 173° for 7 hr. After this time a small sample was removed, worked up as previously described, and then chromatographed on Woelm acid alumina using carbon tetrachloride as eluent. The first band which was eluted afforded 1.7 g (3.7 mmol, 86%) of ketone **4**, while the second band gave 0.2 g (0.43 mmol, 10%) of recovered unreacted dienol **1**. Glpc analysis of the sample removed showed 10.4% of dienol **1**, 86.2% of ketone **4**, and 3.4% of ketone **3** to be present.

Repeating the above experiment but using sodium bicarbonate as the base afforded after work-up 1.6 g (3.4 mmol, 80%) of ketone **4** and 0.2 g (0.52 mmol, 12%) of dienol **1**. Glpc analysis of the sample removed showed 12.7% of dienol **1**, 80.5% of ketone **4**, and 6.8% of ketone **3**.

V. Using Sodium Amide.—Into a 100-ml, three-necked, round-bottomed flask equipped with a reflux condenser, a magnetic stirrer, a nitrogen inlet tube, and a serum cap was placed 40 ml of IAE which was heated to 173°. At this point a mixture of 0.008 g (0.2 mmol) of sodium amide and 1.0 g (2.2 mmol) of dienol **1** was added all at once. (Caution! This experiment should only be performed on a small scale and the stirring should be stopped until after the addition. Ammonia is liberated very vigorously at this temperature.) Samples of 1 ml each were taken at various times by inserting a hypodermic syringe through the serum cap. These samples were analyzed exactly the same as described in IA. Comparison of the glpc results obtained for these samples with the results obtained in IA showed them to be identical.

Rearrangement of 2,2,3,4,5-Pentaphenyl-3-cyclopenten-1-one (3) to 2,3,4,5,5-Pentaphenyl-2-cyclopenten-1-one (4) in Isoamyl Ether with Sodium Hydroxide.—Into a 100-ml, one-neck, round-bottomed flask equipped with a reflux condenser and a magnetic stirrer was placed 50 ml of IAE and 1.0 g (25 mmol) of sodium hydroxide and the mixture was heated to the boiling point of IAE (173°). At this temperature, 1.0 g (2.1 mmol) of ketone **3**[1a,b] was added as a solid all at once. The heterogeneous mixture was heated for 6 hr, cooled to room temperature, and poured into 100 ml of cold water, and the organic layer was separated, washed several times with 100-ml portions of water, and dried over anhydrous magnesium sulfate. Concentration of this dried solution under vacuum gave a viscous yellow oil which was crystallized from 50 ml of a mixture of benzene–petroleum ether to give a quantitative yield (1.0 g, 2.1 mmol) of pale yellow crystals of ketone **4**, mp 169–170° (lit.[1a,b] mp 169–170°).

Registry No.—**1**, 2137-74-8; **3**, 34759-47-2; **4**, 34759-48-3.

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Fluorinated Bicyclics. I. Exo-Cis-Bromination of Fluorinated Norbornenes[1]

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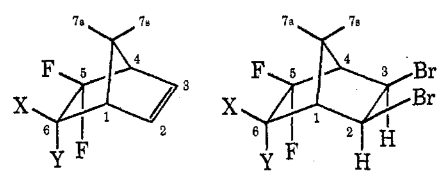
A number of fluorinated norbornenes **1a–h** brominate stereospecifically by a purely radical pathway in methylene dichloride or carbon tetrachloride at 25° to afford exclusively exo-cis dibromides **2a–h**. The radical bromination of 5,5-difluoro-6-*exo*-fluoro-2-norbornene (**1i**) affords a 2.1:1.9 mixture of exo-cis dibromide **2i** and trans dibromide **9**. These results suggest that the stereochemistry of the reaction is directed by endo fluorine substituents. Bromination of 5,5,6,6-tetracyano-2-norbornene (**13**) and *endo-cis*-5,6-dichloro-2-norbornene (**14**) is similarly stereospecific. The nmr spectra of the trifluoronorbornenes **1h** and **1i** and the dibromides **2**, along with dehydrobromination results, are discussed.

The reaction of bicyclo[2.2.1]-2-heptene (norbornene) with molecular bromine in CH_2Cl_2 at 25° readily affords a plethora of rearrangement products characteristic of reactions involving norbornyl cation intermediates.[2] It was therefore surprising to find 5,5,6,6-tetrafluoro-2-norbornene (**1a**) inert under these conditions, although bromination readily takes place under radical conditions (illumination) to afford exclusively *exo-cis*-2,3-dibromo-5,5,6,6-tetrafluoronorbornane (**2a**). A number of fluorinated norbornenes have been prepared and brominated to further investigate the scope of this reaction.



1a–i **2a–i**

a, X = Y = F
b, X = Y = CF_3
c, X = Y = Cl
d, X = CF_3; Y = F
e, X = F; Y = CF_3
f, X = CF_2Cl; Y = Cl
g, X = Cl; Y = CF_2Cl
h, X = H; Y = F
i, X = F; Y = H

Results

Norbornene Syntheses.—The norbornenes **1a–i** are readily prepared from the cycloaddition of the appropriate fluoro olefin and cyclopentadiene. The cycloaddition of cyclopentadiene and hexafluoropropene has been reported, although no description of the isomeric product mixture was presented.[3] At 155° for 72 hr a 53:47 mixture of **1d,e** (by nmr) was obtained. The structure of the respective isomers could not be unambiguously assigned by nmr. These derivatives

(1) Presented in part at the 164th National Meeting of the American Chemical Society, New York, N. Y., Aug 1972.

(2) (a) D. R. Marshall, J. R. Robinson, *et al.*, *Can. J. Chem.*, **49**, 885 (1971); (b) H. Kwart and L. A. Kaplan, *J. Amer. Chem. Soc.*, **76**, 4072 (1954).

(3) H. P. Braendlin, *et al.*, *J. Amer. Chem. Soc.*, **84**, 2112 (1962).

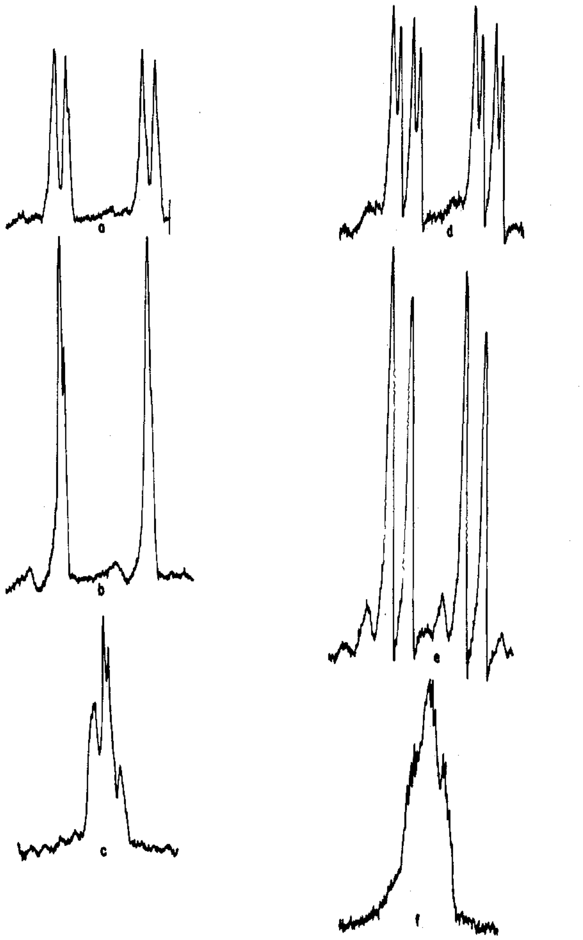
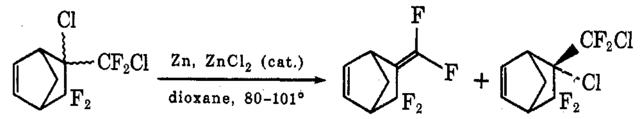


Figure 1.—^{19}F nmr spectra: a, F_{6n} in **1h**; b, F_{6n} upon H_{7s} irradiation; c, F_{6n} upon H_{6x} irradiation; d, F_{6x} in **1i**; e, F_{6x} upon H_1 irradiation; f, F_{6x} upon H_{6n} irradiation.

resisted separation by vpc and the bromination studies were performed on the **1d,e** mixture.

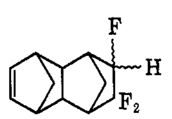
The cycloaddition of 2,3-dichlorotetrafluoropropene and cyclopentadiene at 155° for 48 hr gave a 3:2 mixture (76% yield) of norbornenes **1f,g**. These



1f,g **3** **1f**

isomers also resisted efficient separation by vpc. Partial dehalogenation of the 3:2 mixture (20 mequiv) with Zn in dioxane at 80° for 4 hr afforded a 1:1 mixture of olefin **3** and unreacted starting material which was a single isomer. Structure **1f** was tentatively assigned to the recovered isomer, which assumes a lower reactivity for the endo 5-chlorine in **1f** *vis-à-vis* the exo 5-chlorine in **1g**. Isomer **1f** was also the major Diels–Alder adduct.

Trifluoroethylene and cyclopentadiene at 155° for 72 hr afforded a 67:33 mixture of monoadducts **1h,i** in 72.5% yield based on consumed cyclopentadiene and diadduct **4** formation. The isomers were readily



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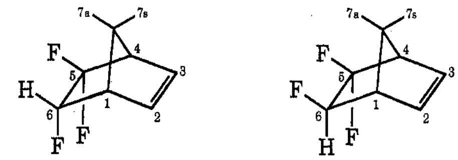
separable by vpc and the major isomer was assigned structure **1h** based on the following nmr data (see Table I).

TABLE I
CHEMICAL SHIFTS AND COUPLING CONSTANTS FOR 5,5-DIFLUORO-*endo*-6-FLUORO-2-NORBORNENE (**1h**) AND 5,5-DIFLUORO-*exo*-6-FLUORO-2-NORBORNENE (**1i**) IN CARBON TETRACHLORIDE



1h **1i**

Chemical Shifts[a]

Nuclei	1h	Isomer 1i
H_2, H_3	6.28	6.24
H_1, H_4	3.06	2.93
H_{6x}	4.88	
H_{6n}		4.37
H_{7s}	1.80	2.00
H_{7a}	1.68	2.27
F_{6x}		191.4
F_{6n}	191.9	
F_{5x}	100.2	112.8
F_{5n}	113.6	102.8

Coupling Constants, Hz

Nuclei	1h	Isomer 1i
$H_{7a}H_{7s}$	10.5	11
H_1F_6		5.7
$H_{6x}F_{5x}$	17	
H_6F_6	55.0	55.1
$H_{6n}F_{5n}$		~9.5
$H_{7s}F_{6n}$	6.5	
$F_{6x}F_{5x}$		12.5
$F_{5x}F_{5n}$	234	234

[a] All proton chemical shifts are reported in parts per million (δ) relative to internal tetramethylsilane. All fluorine chemical shifts in parts per million (φ) relative to fluorotrichloromethane (F-11) internal standard. All values refer to the high-field side of F-11.

The ^{19}F nmr spectrum of **1i** displayed a doublet (J = 55.1 Hz) of doublets (J = 12.5 Hz) of doublets (J = 5.7 Hz) at ϕ 191.4 for F_6 (Figure 1c) and an AB quartet of multiplets for F_{5x} and F_{5n} (J_{AB} = 234 Hz). Nucleus A (ϕ 102.8) was further split into a doublet of multiplets ($J \cong 9.5$ Hz) as was nucleus B (J = 12.5 Hz). Double-resonance experiments assigned the 55.1-Hz splitting to the geminal F_6H_6 coupling and the 5.7-Hz splitting resulted from coupling of the H_1 bridgehead proton to F_6 (Figure 1e,f). The exo stereochemistry of F_6 was therefore established. The 12.5-Hz splitting, which was undisturbed by proton–fluorine decoupling, was assigned to the $F_{5x}F_{6x}$ coupling.

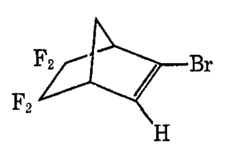
For **1h**, F_6 appeared as a doublet (J = 55.0 Hz) of doublets (J = 6.5 Hz) at ϕ 191.9 (see Figure 1a) and F_{5x} and F_{5n} gave an AB quartet of multiplets (J_{AB} = 234 Hz) with nucleus A (ϕ 100.2) further split into a doublet (J = 17 Hz) of multiplets and B (ϕ 113.6) split into a triplet ($J \cong 4$ Hz) of multiplets. Selective decoupling experiments established that H_6 and F_6 were coupled (55.0 Hz) and a long-range coupling (6.5 Hz) of F_6 and H_{7s} was present (Figure 1b,c). The 17-Hz splitting was assigned to $H_{6x}F_{5x}$ coupling.

The H_{6n} proton in **1i** appeared as a doublet (J_{HF} = 55.1 Hz) of doublets (J_{HF} = 9.6 Hz) of doublets (J = 2.4 Hz) at δ 4.37 in the pmr spectrum (Figure 2). In **1h**, H_{6x} was at a lower field (δ 4.88) as a doublet (J_{HF} = 55.0 Hz) of doublets (J_{HF} = 17 Hz) of doublets (J = 4 Hz). These observations are consistent with the usual upfield shift of endo 5,6 protons relative to exo 5,6 protons in 5,6-halogenated 2-norbornenes.[4–7]

The unreliability of structure assignment based on fluorine chemical shifts of exo and endo fluorines in this system should be emphasized. Roberts and coworkers found a consistent pattern of upfield chemical shift of the endo relative to the exo fluorine in a number of saturated *gem*-difluoronorbornanes.[8] However, recent work by Homer and Callaghan on fluorinated norbornenes demonstrated that the shielding effects were reversed relative to the saturated systems.[9] In the trifluoronorbornenes **1h** and **1i** F_{6n} is slightly upfield (0.5 ppm) relative to F_{6x}, and in **1h** F_{5n} is upfield (13.4 ppm) from F_{5x}, which is in accord with Robert's observations. In contrast, F_{5x} appears upfield (10 ppm) to F_{5n} for **1i** in agreement with Homer and Callaghan. These relative shift deviations suggest substantial sensitivity toward the vicinal neighboring group.

Bromination Studies.—The olefins **1a–i** were inert to molecular bromine in CCl_4 or CH_2Cl_2 at 25° in the dark under oxygen. Bromination was instantaneous at 25° in a nitrogen atmosphere when the reaction mixture was illuminated with a 275-W sun lamp. Small-scale runs in CCl_4 were examined by nmr and vpc. Quantitative conversion to a single dibromide product (>98%) was indicated for **1a–h**. Preparative scale runs were performed in CH_2Cl_2 solvent at 25° in a nitrogen atmosphere. Vpc and nmr analysis again indicated the formation of a single product and the crude product was isolated in >90% yield in all cases.

The dibromide isolated from **1a** was assigned structure **2a** based on chemical and spectroscopic evidence. Dehydrobromination of the dibromide product with potassium *tert*-butoxide in ether afforded a single elimination product, assigned structure **5**. The nmr



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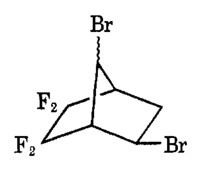

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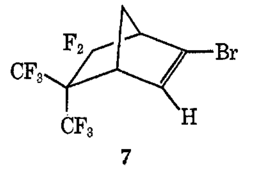

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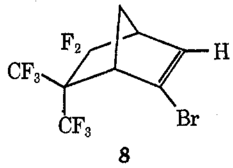

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spectrum of **5** exhibited a single vinyl proton resonance at δ 6.35. Hence, structure **6** is eliminated as a possible dibromide product. The vicinal protons H_2, H_3 in **2a** appeared as a sharp doublet (J = 1.8 Hz) at δ 4.58. A double-resonance experiment established the methylene bridge proton H_{7a} (δ 2.05) as the source of this splitting. The cis-exo stereochemistry of the vicinal bromides in **2a** therefore was established.

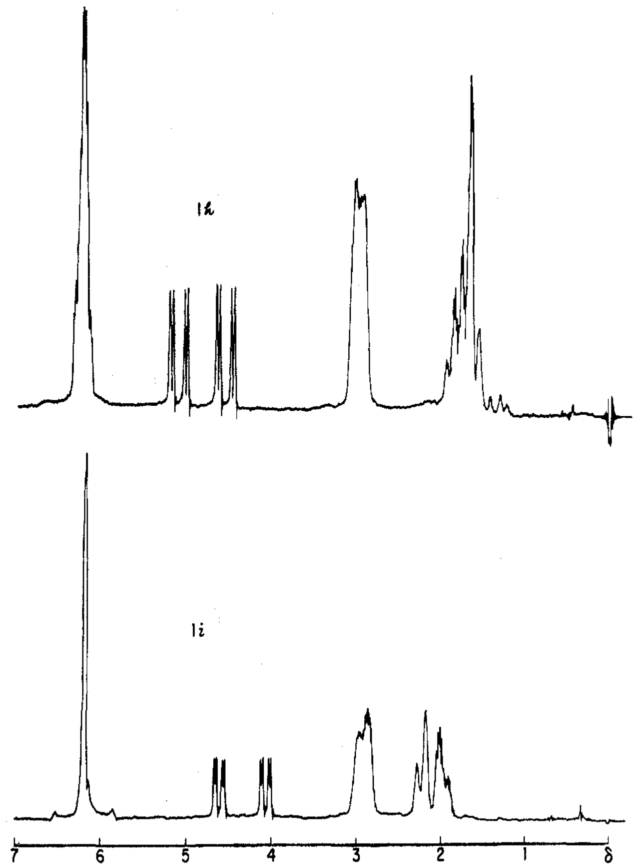


Figure 2.—Nmr spectrum (100 MHz) of 5,5-difluoro-5-*endo*-fluoro-2-norbornene (**1h**) and 5,5-difluoro-6-*exo*-fluoro-2-norbornene (**1i**).

The dibromide structures **2b–h** were confirmed by nmr. The vicinal H_2, H_3 protons appeared as an AB quartet of multiplets in each case with J_{H_2,H_3} = 6.9–7.0 Hz (Table III). The magnitude of this coupling is consistent with a cis orientation of the vicinal protons.[4,5,10–13] The AB quartets were further split by 1.7–1.9 Hz from the methylene bridge proton H_{7a}. Figures 3a–d display typical AB multiplets for dibromides **2b**, **2c**, **2h**, and **2f** + **2g**.

Dehydrobromination of **2b** with potassium *tert*-butoxide in ether at 25° afforded an 11.5:1 mixture of products **7** and **8**. A sharp resonance at δ 6.53 (1 vinyl hydrogen) was present in the nmr of the product mixture.

The bulky *endo*-trifluoromethyl group at C_5 is anticipated to provide substantial steric hindrance toward approach of the large *tert*-butoxide base at H_{2n}. Base therefore attacks the more sterically accessible proton H_{3n} in **2b** to give predominantly **7**.

The norbornenes **1h** and **1i** displayed a similar reluctance to brominate in CH_2Cl_2 or CCl_4 in the dark.

(4) P. Laszlo and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **86**, 1171 (1963).
(5) P. Subramanian, M. T. Emerson, and N. A. Le Bel, *J. Org. Chem.*, **30**, 2624 (1965).
(6) R. R. Fraser, *Can. J. Chem.*, **40**, 78 (1962).
(7) J. Paasivirta, *Suom. Kemistilehti B*, **36**, 76 (1963).
(8) J. B. Grutzner, J. D. Roberts, *et al.*, *J. Amer. Chem. Soc.*, **93**, 7107 (1970).
(9) J. Homer and D. Callaghan, *J. Chem. Soc. B*, 2430 (1971).
(10) F. L. Anet, H. H. Lee, and J. L. Submeier, *J. Amer. Chem. Soc.*, **89**, 4431 (1967).
(11) S. J. Cristol and B. B. Jarvis, *J. Amer. Chem. Soc.*, **89**, 5885 (1967).
(12) C. L. Osborne, T. V. Van Auken, and D. J. Trecker, *J. Amer. Chem. Soc.*, **90**, 5806 (1968).
(13) A. G. Ludwick and J. C. Martin, *J. Org. Chem.*, **34**, 4108 (1969).

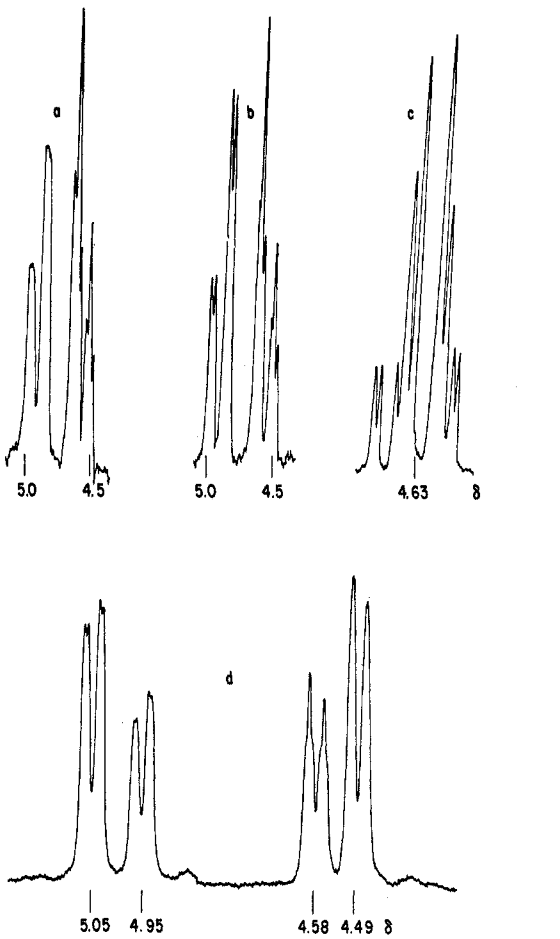
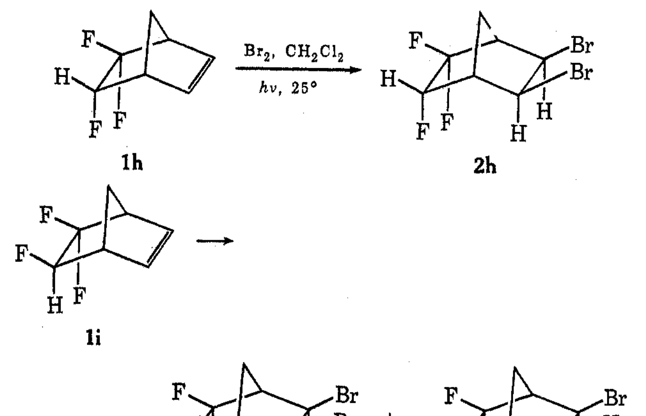


Figure 3.—Nmr spectrum of vicinal H_2, H_3 protons: a, compound **2b** (60 MHz); b, compound **2c** (60 MHz); c, compound **2h** (220 Mz); d, 3:2 mixture of **2f** and **2g** (220 mHz).



1h **2h** **1i** **2i** 52.5% **9** 47.5%

Irradiation during bromination in a nitrogen atmosphere induced immediate and quantitative conversion of **1h** to **2h**, whereas **1i** afforded a 1.1:1 mixture of dibromides **2i** and **9**, respectively.[14] Structures **2h** and **2i** were readily confirmed by their characteristic AB quartets with $J_{AB} = 6.9\text{–}7.0$ for protons H_2, H_3

(14) Dibromides **2i** and **9** were both stable under the reaction and vpc conditions. This mixture therefore represents the kinetically controlled product distribution.

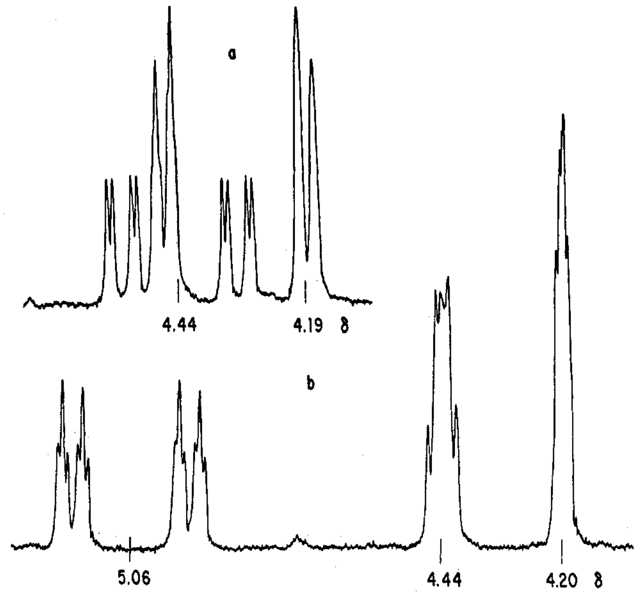
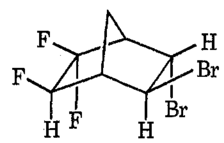


Figure 4.—Nmr spectra (220 MHz) of vicinal H_2, H_3, and H_6 protons: a, compound **2i**; b, compound **9**.

(Figures 3c, 4a; Tables II and III). The dibromide **9**, separated from **2i** by preparative vpc, gave a markedly different nmr pattern for the vicinal protons H_2, H_3 (Figure 4b). Two different multiplets appear at δ 4.20 and 4.44 with the downfield proton split into approximately a doublet ($J \cong 3.8$ Hz) of triplets ($J \cong 3.2$ Hz), whereas the upfield proton gave a much narrower resonance. Long-range H_2F_{6x} coupling gave rise to the 3.8-Hz splitting. A doublet of doublets with $J_{H_2H_1} \cong J_{H_2H_3} \cong 3.2$ Hz gave the fortuitous triplet pattern. These splitting patterns suggest exo stereochemistry for one downfield proton (δ 4.44). The 3.2-Hz vicinal H_2H_3 coupling is indicative of trans stereochemistry;[4,5,12,13] hence, the upfield proton (δ 4.20) is endo.

A comparison of the relative chemical shifts of the proton H_{6n} geminal to fluorine in **2i** and **9** illustrates an interesting deshielding effect. Proton H_{6n} in **9** (δ 5.06) was shifted appreciably downfield (0.62 ppm) relative to H_{6n} in **2i**. This suggests that the bromine substituent at C_2 is endo and a deshielding proximity effect is operable.[15,16] The alternative trans isomer **10** cannot account for this shielding.



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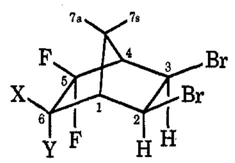
Dehydrobromination of **9** with *tert*-butoxide in ether afforded a single product containing one vinyl proton (δ 6.16), whereas **2i** gave a 4:1 mixture of elimination products. The major product proved to be identical with that obtained from **9**. The minor product also exhibited a single vinyl proton resonance (δ 6.18).

(15) Laszlo and Schleyer (ref 4) have observed a similar proximity effect in 5-halogenated 2-norbornenes. Introduction of an exo 5-chlorine substituent causes a downfield shift (*ca.* 0.4 ppm) of the anti 7-proton relative to norbornene itself. A slight upfield shift (0.05–0.1 ppm) is produced by endo 5-chlorine substitution.

(16) (a) G. S. Reddy and J. H. Goldstein, *J. Chem. Phys.*, **38**, 2736 (1963); (b) R. F. Zürcher, *J. Chem. Phys.*, **37**, 2421 (1962).

TABLE II

CHEMICAL SHIFTS[a] FOR DIBROMONORBORNANES IN CARBON TETRACHLORIDE



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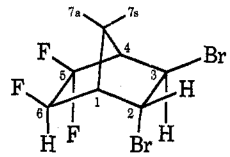

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Dibromide	H_2 H_3	H_1 H_4	H_{7a}[b]	H_{7s}[b]	X	Y	F_{5x}[b]		F_{5n}[b]
2a, X = Y = F	4.58	2.96	2.05	2.47	118.6	122.4	118.6		122.4
	d	t of m	m	t of m	br t	br d			
2b, X = Y = CF_3	(4.57, 4.92)[c]	2.94	2.8–3.3[d]		64.4	60.8	99.1		114.2
	AB q of m	m	m		d of q	d of q of d	q of m		br q of m
2c, X = Y = Cl	(4.34, 4.62)	(3.01, 3.22)	2.32	2.57			94.7		106.5
	AB q of m	d of m, m	m	d of m			m		d of m
2d,e,[e] X, Y = CF_3, F	(4.51, 4.74)	2.59	(2.08, 2.28)		75.6 d of d of d	179.8 m		(109.9, 117.6)	
	AB q of m	2.93–3.16[d]			171.2 m	72.9 d of d of d		(111.5, 118.0)	
2f, X = CF_2Cl; Y = Cl	(4.49, 5.05)	(2.98, 3.18)	2.38	2.64	54.4, 57.2			(104.8, 105.6)	
	AB q of m	m	m	d of m	AB q of m				
2g, X = F; Y = CF_2Cl	(4.58, 4.95)[f]								
	AB q of m								
2h, X = H; Y = F	(4.58, 4.66)	(2.89, 2.99)	1.69	2.39	4.63	203.5	98.2		121.8
	AB q of m	d of m, m	m	t of m	d of d of d	d of d	d of d		d of m
2i, X = F; Y = H	(4.19, 4.47)	2.85	2.21	2.41	194.4	4.44	111.3		116.5
	AB q of m	m	m	m	d of br t	d of d of d	d of m		m
9	4.44, 4.20	2.77	2.22	2.30	204.5	5.06		114.2[d]	
	d of d of d[g] m	m	m	m	br d	d of d of t		m	

[a] See Table I, footnote *a*. [b] AB q of m for $H_{7a}H_{7s}$ and $F_{5x}F_{5n}$ in each case. [c] Values in parentheses indicate that the respective chemical shifts are unassigned. [d] Individual resonances not resolved. [e] Determined in a mixture of **2d** and **2e** (respective isomers unknown). [f] Determined in a 3:2 mixture of **2f** and **2g**, other assignments not possible owing to overlapping resonances. [g] Appears as a d of t.

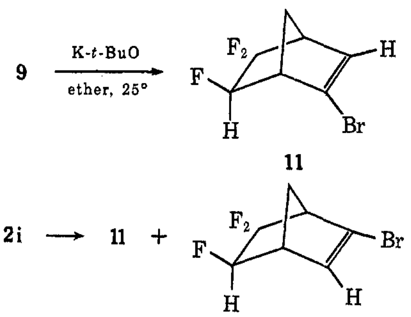
TABLE III

COUPLING CONSTANTS (HERTZ) FOR DIBROMONORBORNANES IN CARBON TETRACHLORIDE

Dibromide	H_2H_3	$H_{7s}H_{7a}$	H_2H_{7a}[a]	$F_{5x}F_{5n}$	$H_{7s}F_{5n}$	Miscellaneous
2a		12.5	1.8	241	5.3	$H_1H_{6x} \sim 5$
2b	7.0		1.7	255		$CF_{3x}CF_{3n} = 13.5$, $F_{5n}CF_{3n} = 23$, $F_{5x}CF_{3x} = 19.5$
2c	7.0	13	1.8	224	4.9	
2d,e[b]	6.9		1.7–1.9	252	6–7	$(CF_3)_xF_{6n} = 14$, $(CF_3)_xF_{5x} = 8$
	6.9			254		$(CF_3)_nF_{6x} = 14–15$, $(CF_3)_xF_{5n} = 8$
2f	6.9	14	1.9			$(CF_AF_BCl)_x = 172$
2g[c]	6.9					
2h	7.0	12		248	7	$H_6F_6 = 53$, $H_6F_{5x} = 19.5$, $H_4F_{5x} \sim 6.5$, $F_6H_{7a} \sim 8$
2i	6.9	12		251		$H_6F_6 = 51$, $H_6F_{5n} = 10.6$, $F_6F_{5x} \sim 9.5$
9	~3.2	12				$H_6F_6 = 51.3$, $H_6F_{5n} = 8.3$, $H_{2x}F_{6x} \sim 3.8$, $H_{2x}H_1 \sim 3.2$

[a] $H_2H_{7a} = H_3H_{7a}$ (± 0.1 Hz) for **2a–i**. [b] Respective isomer assignments not made; see Table II, footnote *e*. [c] See Table II, footnote *f*.

Dibromide **9** allows for facile exo-cis coplanar elimination[17] of $H_{2x}Br_{3x}$ and the exclusive product is assigned structure **11**. Only trans elimination is possible



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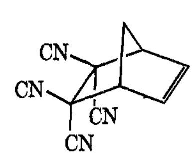
4 : 1

for **2i**, and the product distribution reflects the ease of *tert*-butoxide approach at C_2 *vs.* C_3. The endo fluorine substituent at C_5 provides sufficient interference (*vide infra*) toward approach of base at H_{3n} that elimination of H_{2n} is preferred. The minor dehydrobromination product therefore is assigned structure **12**.

The tetracyanoethylene adduct **13** brominated only under radical conditions to afford exclusively **15**. The



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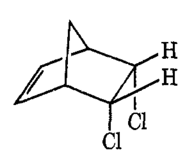

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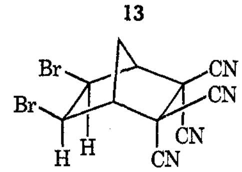

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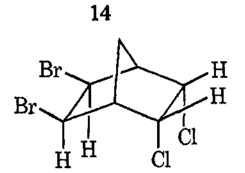

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reaction of the endo-cis dichloride **14** with bromine in CH_2Cl_2 at 25° was very sluggish under ionic conditions, although bromination was instantaneous under radical conditions. The cis-exo dibromide was the only product formed. Structures **15** and **16** were readily established by nmr. Both **15** and **16** displayed sharp

(17) J. Sicher, *Angew. Chem., Int. Ed. Engl.*, **11**, 200 (1972), and references cited therein.

doublets with $J_{H_{2,3}H_{7a}} = 2.2$ and 2.0 Hz, respectively, for the vicinal endo-cis protons.

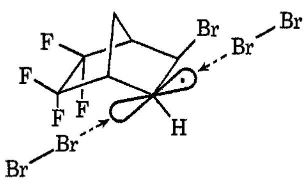
Discussion

The electron-withdrawing γ substituents clearly exert an appreciable deactivating influence on the norbornene double bond. Ionic bromination of norbornene proceeds smoothly at even $-78°$, whereas **1a–i** failed to brominate under similar ionic conditions at 25°. A very facile free-radical bromination pathway, however, has been demonstrated at 25°.

This deactivation of the norbornene double bond is not unique to γ-fluorine substitution; the γ-cyano- and γ-chloro-substituted norbornenes **13** and **14** are similarly unreactive.[18]

The stereospecificity of the free-radical brominations of **1a–h** is striking. Free-radical additions of large addenda to norbornene itself generally proceed to give predominantly trans adducts. For example, CCl_4,[12] CCl_3Br,[19] n-C_3F_7I,[20] and CBr_2F[13] give >95% trans addition. Free-radical chlorination of norbornene gives 38% trans and 34% cis addition.[21] Although the stereospecificity of free-radical bromination of norbornene itself has not been studied in detail, it has been suggested that addition is preferentially trans.[2a,22] The highly stereospecific cis-bromination of **1a–h** is unanticipated and demands further examination.

The free-radical bromination of olefin **1a** first involves addition from the less hindered exo side, which is unexceptional for bulky attacking groups,[12,23] to afford **20**. The direction of subsequent attack on **20**



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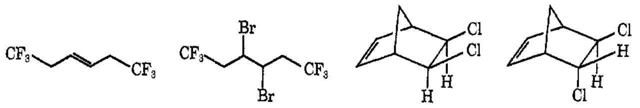
by the propagating bromine molecule is determined by the relative nonbonded interactions with the 2-exo-bromo substituent and the 5,6-endo substituents.[24]

(18) The primary mode of transmission of the γ-substituent inductive effect is a moot point. A "through bond" or "through space" (field effect) mechanism may be operative. 1,4-Bis(trifluoromethyl)-2-butene (**17**) displays unreactivity similar to that of **1a** toward ionic bromination. Free radical bromination at 25° affords a 1.16:1 mixture of *erythro*-**18**–*threo*-**18**.



17 **18** **19** **20**

Whereas **14** is very sluggish toward ionic bromination, both **19** and **20** brominate, albeit very slowly relative to norbornene itself, under ionic conditions. The latter observations suggest the importance of a field effect (B. E. Smart, unpublished results).

(19) E. Tobler and D. J. Foster, *J. Org. Chem.*, **29**, 2839 (1964).

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

(21) M. L. Poutsma, *J. Amer. Chem. Soc.*, **87**, 4293 (1965).

(22) The exo-cis dichloride **19** (footnote 18) gives *ca.* 90% trans dibromide under radical conditions in CH_2Cl_2 at 25° in contrast to exclusive cis-exo addition to **14** (B. E. Smart, unpublished results).

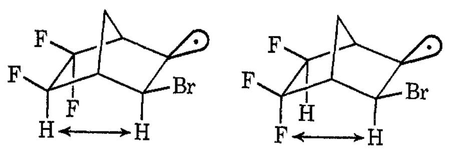
(23) For a recent review of the subject, see D. I. Davies and S. J. Cristol in "Advances in Free Radical Chemistry," Vol. I, G. H. Williams, Ed., Logos Press, London, 1965, Chapter 5.

(24) This discussion uses compound **1a** as an example throughout, although similar arguments follow for **1b–h**.

For norbornene itself, the less hindered path is from the endo direction with trans product formation.

The observed exo-cis product from **1a** suggests that the endo 5,6-fluorine substituents effectively shield **20** from endo approach. The introduction of bulky 5,6-endo substituents is known to direct attack to the exo side in the free addition of polyhalomethanes to norbornene.[12,13] Although the difference in steric size of fluorine and hydrogen is small, nonbonded repulsion between fluorine with its tight sphere of outer core electrons and an electron-rich species in close approach is more severe than for hydrogen which lacks nonbonding electrons.[25] Approach of bromine from the endo side in **20** is unfavorable owing to coulombic repulsion from the endo fluorine substituents, so that the normally hindered exo attack becomes more facile. Similar effects are exhibited by endo chlorine and nitrile substituents in the brominations of **13** and **14**.

The trifluoronorbornene **1i** demonstrates a case in which only one endo fluorine substituent is present. Attack of bromine on **1i** can afford either **21** or **22**.



21 **22**

Based on the nearly equivalent amounts of cis (**2i**) and trans (**9**) products formed (1.1:1), the endo fluorine substituent exerts little influence on the initial attack by bromine. Attack at C_2 or C_3 is differentiated sterically only by the endo,endo repulsions of H_{2n},H_{6n} *vs.* H_{2n},F_{5n}, which result from movement of the olefin hydrogen to an endo position as sp^3 development at the carbon attacked proceeds. The carbon atom which accommodates the odd electron retains its sp^2 configuration and little change in geometry is anticipated. The small difference in 1,3-H,F *vs.* 1,3-H,H repulsion may account for the slight preference of attack at C_2 leading to **21**.[26] The influence of the endo fluorine on the stereochemistry of chain transfer, however, is significant. Attack on the carbon p orbital in **21** proceeds from the exo direction as in **20**. However, in **22** attack along the p-orbital axis from the endo direction is hindered by only an endo proton and predominantly trans product **9** results.

Dehydrobromination of **2i** with *tert*-butoxide also illustrates this endo-fluorine shielding effect. Approach of base at H_{3n} is repulsed by the 5-endo fluorine substituent, whereas approach at H_{2n} involves interaction with only an endo proton H_{6n}. The preference for **11** formation reflects these factors.

The fluorine substituent, although relatively small in size, can nonetheless significantly control the stereospecificity of chemical reactions. The recognition of potential coulombic interactions provides a reasonable explanation for these observations.

(25) See B. E. Smart, *J. Org. Chem.*, **38**, 2035 (1973), for further discussion of this point.

(26) Similar arguments were presented by Osborne and coworkers (ref 12) to explain the effect of *endo*-5-methyl substitution on the stereochemistry of free-radical addition of carbon tetrachloride to norbornene.

Experimental Section

Proton nmr spectra were recorded on Varian Associates A-60, HA-100, or HR-220 MHz spectrometers. ^{19}F nmr spectra were determined on a Varian Associates A56-60 or a HA-100 spectrometer operating at either 56.4 or 100 MHz. The proton–fluorine decoupling experiments were performed on the HA-100 spectrometer with fluorotrichloromethane (F-11) as a lock (9.3 kHz upper side band signal) by selective irradiation of the proton spectra with the basic radiofrequency provided by a Schomandl Synthesizer. All compounds were run as 20–30% solutions in CCl_4 or $CDCl_3$ with either tetramethylsilane (TMS) or F-11 as an internal reference. All chemical shifts are reported in parts per million downfield from TMS and upfield from F-11.

All melting and boiling points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 237 spectrometer and the gas chromatography work was performed on a Varian Aerograph Series 200 gas chromatograph fitted with a Brown Potentiometer recorder. The following columns were used: 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. 25% diglyceride on Gas-Chrom R; column D, 6 ft × 0.375 in. 25% Triton X305 on Chromosorb W; column E, 5 ft × 0.25 in. 3% SE-30 on 100/120 Aeropak 30.

Commercially available samples of tetrafluoroethylene, trifluoroethylene, perfluoroisobutylene (PFIB), perfluoropropene (PFP), and 1,1-dichlorodifluoroethylene were used directly without further purification. 2,3-Dichlorotetrafluoropropene was prepared following the reported literature procedures from commercially available 1,3-dichlorotetrafluoroacetone.[27] Freshly cracked cyclopentadiene was used in all cases for the cycloadditions. The olefins **1a**,[28] **1c**,[29] and **14**[30] were prepared by literature procedures. Freshly sublimed **1a** and preparative vpc samples of **1c** (column D, 125°) were employed. Olefin **14** was recrystallized from *n*-hexane prior to use. All olefins employed in the bromination studies were >99% pure by vpc.

5,5-Difluoro-6,6-bis(trifluoromethyl)-2-norbornene (1b).—Two 250-ml thick-walled Carius tubes, each charged with 25 g (0.125 mol) of PFIB, 6.6 g (0.1 mol) of cyclopentadiene, and 0.5 g of hydroquinone, were heated at 155° for 48 hr. The unreacted PFIB was distilled off, and the semisolid residues were combined and sublimed (80 mm, 25°) to afford 30.3 g of material composed of 87% **1b** and 13% dicyclopentadiene by nmr and vpc (column B, 100°). Fractional distillation afforded material of bp 88° (100 mm) which still contained *ca.* 10% dicyclopentadiene. This material was dissolved in CH_2Cl_2 and "titrated" with bromine in the dark. Removal of the solvent and resublimation (80 mm, 25°) afforded pure **1b** as a waxy, colorless solid: mp 82–84°; ir (CCl_4) 1550 cm^{-1} (very weak, C=C); nmr (CCl_4) ^1H δ 1.86, 2.61 (AB m of m, 2, J_{AB} = 11 Hz, A, d of m, $J \cong 5$ Hz), 3.12 (broad s, 1), 3.30 (broad s, 1), 6.38 (narrow m, 2); ^{19}F ϕ 59.7 (p of m, 3, J = 16, ~5 Hz), 64.1 (p of m, 3, $J \cong 16$ Hz), 97.3, 100.4 (AB m of m, 2, J_{AB} = 246 Hz, B, q of m, J = 16 Hz).

Anal. Calcd for $C_9H_6F_8$: C, 40.62; H, 2.27. Found: C, 40.68; H, 2.21.

5,5,6-Trifluoro-6-(trifluoromethyl)-2-norbornenes (1d and 1e).—A mixture of 78 g (0.52 mol) of PFP, 35 g (0.53 mol) of cyclopentadiene, and 1.8 g of hydroquinone was heated at 155° for 72 hr in a 500-ml bomb. Nmr of the reaction mixture indicated a 52.7:47.3 mixture of products. Fractionation *in vacuo* afforded 78.4 g (70%) of a 53:47 mixture of **1d** and **1e**: bp 63° (50 mm) (lit.[3] bp 140–140.5°); nmr (CCl_4 mixture) ^1H δ 1.7–2.5 (unresolved AB m of m, 2), 4.82 (m, 2), 6.27 (minor), 6.33 (major) (narrow m, 2); ^{19}F (major isomer) ϕ 77.9 (complex m, 3), 107.8, 108.8 (AB m of m, 2), 170.8 (broad m, 1); ^{19}F (minor isomer) 74.7 (q, 3, J = 7.2 Hz), 107.8 109.0 (AB m of m, 2), 170.2 (broad m, 1). Isomers **1d** and **1e** could not be separated by vpc (columns A–C).

5,5-Difluoro-6-(chlorodifluoromethyl)-6-chloro-2-norbornenes (1f and 1g).—A 500-ml bomb charged with 100 g (0.547 mol) of 2,3-dichlorotetrafluoropropene, 33 g (0.5 mol) of cyclopentadiene, and 0.5 g of hydroquinone was heated at 155° for 48 hr. Fractional distillation afforded 94.6 g (76%) of a 3:2 mixture of **1f** and **1g**: bp 87–88° (20 mm); nmr (CCl_4) ^1H (major isomer) δ 1.97, 2.37 (AB m of m, 2, J_{AB} = 10.5 Hz), 3.18 (broad m, 1), 3.45 (broad m, 1), 6.44 (sharp m, 2); ^{19}F (major isomer) ϕ 53.7, 56.7 (AB m of m, 2, J_{AB} = 172 Hz, A, d of m, J = 18.5 Hz, B, d of m, J = 22.5 Hz); 93.1, 105.6 (AB m of m, 2, J_{AB} = 230 Hz, B, broad t of m, $J \cong 21$ Hz); ^{19}F (minor isomer) 52.4 (broad t, 2, $J \cong 20$ Hz), 87.0, 103.7 (AB m of m, 2, J_{AB} = 228 Hz, B, broad t of m, $J \cong 20$ Hz).

Anal. Calcd for $C_8H_6Cl_2F_4$: C, 38.59; H, 2.43; Cl, 28.49. Found: C, 38.75; H, 2.45; Cl, 28.89.

Attempted vpc separation of **1f** and **1g** on column C, 115°, gave a 43:7 mixture. The major product was that of the original 3:2 mixture.

5-(Difluoromethylene)-6,6-difluoro-2-norbornene (3).—A solution of 24.9 g (0.1 mol) of **2f** and **2g** (3:2 mixture) in 25 ml of dry dioxane was added dropwise to a well-stirred slurry of 50 g of Zn dust in 175 ml of refluxing dioxane containing 0.5 g of anhydrous $ZnCl_2$. After complete addition, the mixture was allowed to reflux for an additional 16 hr in an N_2 atmosphere. After cooling to room temperature the mixture was filtered; the filtrate was quenched in 300 ml of cold H_2O and extracted with CH_2Cl_2. The organic extract was washed with H_2O and saturated aqueous NaCl, and finally dried ($MgSO_4$). Fractionation afforded 11.8 g (94% conversion, 71% yield) of **3**: bp 54–55° (50 mm); ir (CCl_4) 1777 cm^{-1} ($C{=}CF_2$); nmr (CCl_4) ^1H δ 1.95 (s, 2), 3.09 (broad m, 1), 3.48 (broad m, 1), 6.20, 6.46 (AB m of m, 2, $J_{AB} \cong 6$ Hz); ^{19}F ϕ 87.6, 88.7 (AB m of m, 2, J_{AB} = 48 Hz, B, q of m, $J \cong 5$ Hz), 99.3, 104.9 (AB m of m, 2, J_{AB} = 232 Hz).

Anal. Calcd for $C_8H_6F_4$: C, 53.94; H, 3.40. Found: C, 53.61; H, 3.34.

Further distillation gave 1.4 g (6%) of **1f**, bp 67° (7 mm). A similar reaction with 5.0 g (20 mmol) of **1f** and **1g** (3:2), 10 g of Zn dust, and 50 mg of anhydrous $ZnCl_2$ catalyst in 50 ml of dry dioxane at 80° for 4 hr afforded a 1:1 mixture of **3**:**1f** by nmr. No **1g** (>2%) was present.

5,5,6-Trifluoro-2-norbornenes (1h and 1i).—A mixture of 164 g (2.0 mol) of trifluoroethylene, 66 g (1.0 mol) of cyclopentadiene, and 1 g of hydroquinone was heated at 155° for 72 hr in a 1-l. bomb. Fractionation afforded a mixture (57.4 g) of 67% **1h** and 33% **1i**, bp 86–90° (170 mm), and 32.8 g of **4**, bp 88–90° (4 mm). The high-boiling pot residue, 11.8 g, contained mostly tricyclopentadienes. An analytical sample of **4** (mixture of isomers) was collected by preparative vpc (column B, 175°): nmr (CCl_4) δ 0.82 broad doublet (half of AB m, 1, J = 12 Hz), 1.15–1.60 (AB m of m, 2), 1.9–2.25 (complex m, 7), 4.42 (d of d of d, 1, J = 54, 19.5, ~4.5 Hz), 6.05 (m, 2); ^{19}F (major isomer) ϕ 98.2, 124.3 (AB m of m, 2, J_{AB} = 234 Hz, A, d of d of m, J = 19.5, 8.2 Hz), 205.0 (d of d of d, 1, J = 54, 9.5, ~4.5 Hz); ^{19}F (minor isomer) 116.0 (m, 2), 193.8 (d of m, 1, J = 54 Hz).

Anal. Calcd for $C_{12}H_{13}F_3$: C, 67.28; H, 6.12. Found: C, 67.25; H, 6.11.

Preparative vpc (column C, 115°) afforded pure **1h**, mp 76–77.5°, ir (CCl_4) 1583 (very weak C=C), 1660 cm^{-1} (weak), and **1i**, mp 71–73°, ir (CCl_4) 1579 (very weak C=C), 1647 cm^{-1} (weak).

Anal. Calcd for $C_7H_7F_3$: C, 56.76; H, 4.76. Found (**1h**): C, 57.01; H, 4.58. Found (**1i**): C, 56.53; H, 4.86.

Brominations. General Procedures.—Small-scale runs were performed in an nmr tube by the dropwise addition of molecular bromine to *ca.* 20% solutions of the appropriate norbornene in CCl_4 under illumination with a 275-W sun lamp. Bromine uptake was instantaneous in all cases. No bromine uptake was evident when the reactions were run in the dark. The reactions were run to *ca.* 75% completion and examined by nmr and vpc.

Preparative-scale runs were performed at 25° with degassed CH_2Cl_2 solvent under a nitrogen atmosphere. A 275-W sun lamp *ca.* 6 in. from the reaction vessel was employed. After the complete addition of bromine (1–1.1 equiv), illumination was continued for an additional 5 min. The reaction mixture was then washed with 5% aqueous sodium thiosulfate and saturated NaCl, and finally dried ($MgSO_4$). Vpc analysis showed complete conversion of starting olefin in each case. The CH_2Cl_2 solvent was removed on a rotary evaporator (25–40°) to afford the crude dibromide product.

***exo-cis*-2,3-Dibromo-5,5,6,6-tetrafluoronorbornane (2a).**—Treatment of 8.3 g (50 mmol) of **1a** in 45 ml of CH_2Cl_2 with 8.2 g (51.3 mmol) of bromine in 5 ml of CH_2Cl_2 afforded a quantitative yield of crude **2a** (>99%), mp 57–59°. Recrystallization from hexane afforded pure **2a**, mp 58.0–58.5°.

(27) J. E. Bissey, H. Goldwhite, and D. G. Rousell, *J. Org. Chem.*, **32**, 1542 (1967).

(28) J. J. Drysdale, *et al.*, *J. Amer. Chem. Soc.*, **80**, 245, 3672 (1959).

(29) P. D. Bartlett, L. K. Montgomery, and B. Seidel, *J. Amer. Chem. Soc.*, **86**, 616 (1964).

(30) D. D. Tanner and G. C. Gidley, *J. Org. Chem.*, **33**, 38 (1968).

Anal. Calcd for $C_7H_6Br_2F_4$: C, 25.80; H, 1.86; Br, 49.02. Found: C, 25.73; H, 1.80; Br, 48.81.

exo-cis-**2,3-Dibromo-5,5-difluoro-6,6-bis(trifluoromethyl)norbornane (2b)**.—Addition of 12.8 g (0.08 mol) of bromine in 10 ml of CH_2Cl_2 to 20 g (0.075 mol) of **1b** in 90 ml of CH_2Cl_2 afforded 33 g (99%) of crude **2b** (>98%). Sublimation (20 mm, 65°) gave 26.2 g (78.5%) of pure **2b**, mp 59.5–61.5°.

Anal. Calcd for $C_9H_6Br_2F_8$: C, 25.38; H, 1.42; Br, 37.52. Found: C, 25.63; H, 1.46; Br, 37.07.

exo-cis-**2,3-Dibromo-5,5-difluoro-6,6-dichloronorbornane (2c)**.—The reaction of 1.99 g (10 mmol) of **1c** in 10 ml of CH_2Cl_2 with 1.7 g (10.6 mmol) of bromine in 2 ml of CH_2Cl_2 afforded 3.41 g (95%) of **2c** (>98%). Recrystallization from petroleum ether (bp 40–60°) afforded pure **2c**, mp 48.5–50°.

Anal. Calcd for $C_7H_6Br_2F_2Cl_2$: C, 23.43; H, 1.69; Cl, 19.76. Found: C, 23.67; H, 1.65; Cl, 20.09.

exo-cis-**2,3-Dibromo-5,5,6-trifluoro-6-(trifluoromethyl)norbornane (2d and 2e)**.—Treatment of 21.6 (0.1 mol) of **1d** and **1e** (53:47) in 100 ml of CH_2Cl_2 with 17.6 g (0.11 mol) of bromine in 15 ml of CH_2Cl_2 afforded 35.5 g (97%) of crude **2d** and **2e** (>98%). Distillation afforded 32.4 g (86%) of pure product, bp 77–78° (5 mm) [lit.[31] bp 92–93°, (10 mm)]. The isomeric dibromides **2d,e** could not be separated by vpc. The chemical shifts of H_{2n}, H_{3n} in the isomers were indistinguishable at 220 MHz in CCl_4.

exo-cis-**2,3-Dibromo-5,5-difluoro-6-(chlorodifluoromethyl)-6-chloronorbornane (2f and 2g)**.—Bromination of 20 g (0.08 mol) of **1f** and **1g** (3:2) in 90 ml of CH_2Cl_2 with 13 g (0.081 mol) of bromine in 10 ml of CH_2Cl_2 afforded 31.7 g (97%) of crude **2f** and **2g** (>98%, 3:2 by 220-MHz nmr). Distillation gave 28.7 g (88%) of pure product, bp 84–86° (0.7 mm).

Anal. Calcd for $C_8H_6Br_2Cl_2F_4$: C, 23.50; H, 1.48; Cl, 17.34. Found: C, 23.68; H, 1.45; Cl, 17.71.

exo-cis-**2,3-Dibromo-5,5-difluoro-*endo*-6-fluoronorbornane (2h)**.—Bromination of 3.00 g (20.3 mmol) of **1h** in 30 ml of CH_2Cl_2 with 3.25 g (20.6 mmol) of bromine in 10 ml of CH_2Cl_2 afforded 5.80 g (92%) of crude **2h** (>95%). A pure sample of **2h** was obtained by preparative vpc (column A, 170°), mp 29.5°.

Anal. Calcd for $C_7H_7Br_2F_3$: C, 27.30; H, 2.29. Found: C, 27.56; H, 2.45.

exo-cis-**2,3-Dibromo-5,5-difluoro-*exo*-6-fluoronorbornane (2i)** and ***endo*-2-Bromo-*exo*-3-bromo-5,5-difluoro-*exo*-6-fluoronorbornane (9)**.—Bromination of 6.00 g (40.6 mmol) of **1i** with 6.57 g (41.2 mmol) of bromine as for **2h** afforded 11.87 g (95%) of 52.5% **2i** and 47.5% **9** (vpc, column A, 175°). Pure **2i**, mp 48–50°, and **9** (an oil) were collected by preparative vpc (column A, 165°).

Anal. Calcd for $C_7H_7Br_2F_3$: C, 27.30; H, 2.29. Found (**2i**): C, 27.18; H, 2.48; (**9**) C, 27.47; H, 2.25.

Irradiation (275-W sun lamp) of small samples of pure **2i** and **9** in CH_2Cl_2 containing bromine had no effect. The isomers were stable to the vpc conditions (165–175°).

exo-cis-**2,3-Dibromo-5,5,6,6-tetracyanonorbornene (15)**.—A solution of 5.82 g (30.0 mmol) of **13** in 175 ml of CH_2Cl_2 was treated dropwise with a solution of 5.60 g (31.1 mmol) of bromine in 10 ml of CH_2Cl_2. After *ca.* 75% bromine addition, a white solid precipitated from the reaction mixture. The reaction mixture was filtered after complete addition and the filter cake was washed with cold CH_2Cl_2 to afford 6.96 g (62%) of **15**, mp 270–271° dec. Work-up of the filtrate gave an additional 3.26 g (29%) of **15**. Recrystallization from benzene afforded pure **15**: mp 270° dec; ir (Nujol mull) 2330 cm^{-1} (very weak, CN); nmr (acetone-d_6) δ 2.45, 2.90 (AB m of m, 2, J_{AB} = 13.4 Hz, B, t of m, J = 1.5 Hz), 3.94 [t (1.5 Hz), 2], 4.96 (d, 2, J = 2.2 Hz).

Anal. Calcd for $C_{11}H_6Br_2N_4$: C, 37.32; H, 1.71; N, 15.83. Found: C, 37.21; H, 1.43; N, 15.67.

exo-cis-**2,3-Dibromo-*endo-cis*-5,6-dichloronorbornane (16)**.—Bromination of 8.2 g (0.05 mol) of **14** in 65 ml of CH_2Cl_2 with 8.5 g (0.053 mol) of bromine in 10 ml of CH_2Cl_2 gave >98% **16** by vpc (column E, 180°). Work-up afforded 14.5 g (89.5%) of white solid, mp 158–159°. Recrystallization from hexane-benzene (6:1) afforded pure **16**: mp 158–159°; nmr ($CDCl_3$) δ 1.62, 2.53 (AB m of m, 2, J_{AB} = 11.8 Hz, B, t of m, J = 1.9 Hz), 2.90 (m, 2), 4.41 [t (2.1 Hz), 2], 4.88 (d, 2, J = 2.0 Hz).

Anal. Calcd for $C_7H_8Br_2Cl_2$: C, 26.04; H, 2.50; Br, 49.50; Cl, 21.96. Found: C, 26.40; H, 2.31; Br, 49.86; Cl, 21.99.

Dehydrobrominations. General Procedures.—The appropriate dibromide was dissolved in ether and a slight excess of dry potassium *tert*-butoxide was added in portions. All operations were performed in an N_2 atmosphere. The heterogeneous reaction mixture was allowed to stir for 16 hr, quenched in cold water, dried ($MgSO_4$), and analyzed by vpc. Removal of the ether solvent on a rotary evaporator (25°) gave the crude product, which was examined by nmr. Small amounts (⩽5%) of *tert*-butoxide substitution products were evident in each case but were not further examined.

2-Bromo-5,5,6,6-tetrafluoro-2-norbornene (5).—A mixture of 34.6 g (0.10 mol) of **2a** and 11.5 g (0.103 mol) of potassium *tert*-butoxide in 500 ml of ether gave a single dehydrobromination product (vpc, column A, 110°) after 16 hr. Examination of the crude product by nmr indicated *ca.* 16% of unreacted **2a**. Fractionation of the crude product afforded 17.2 g of **5**: bp 160° (10 mm); ir (neat) 1588 cm^{-1} (C=C); nmr (CCl_4) ^{1}H δ 2.12, 2.54 (AB m of m, 2, J_{AB} = 10.5 Hz), 3.11 (m, 2), 6.35 (m, 1); ^{19}F φ 113.7, 115.3 (AB m of m, 2, J_{AB} = 228 Hz). Starting material **2a**, 5.6 g, bp 64–65° (2 mm), was also recovered.

Anal. Calcd for $C_7H_5BrF_4$: C, 34.32; H, 2.06; Br, 32.67. Found: C, 34.42; H, 2.05; Br, 32.18.

2-Bromo-6,6-difluoro-5,5-bis(trifluoromethyl)-2-norbornene (7).—The reaction of 22.3 g (0.05 mol) of **2b** with 6.00 g (0.0535 mol) of potassium *tert*-butoxide in 250 ml of ether afforded 17.2 g (94.5%) of crude product. Vpc analysis (column B, 100°) indicated a mixture of 92% **7** and 8% **8**. Distillation afforded 13.7 g of the same mixture of **7** and **8**: bp 48–51° (4 mm); ir (neat) 1590 cm^{-1} (C=C); nmr (CCl_4) ^{1}H δ 2.19, 2.46 (AB m of m, 2, J_{AB} ≅ 11.5 Hz), 3.22 (m, 1), 3.38 (m, 1), 6.53 (sharp m, 1); ^{19}F φ 57.3 (m, 3), 95.3 ,106.8 (AB m of m, 2, J_{AB} = 251 Hz, B, q of m, J ≅ 20.5 Hz).

Anal. Calcd for $C_9H_5BrF_8$: C, 31.33; H, 1.46; Br, 23.16. Found: C, 31.52; H, 1.53; Br, 22.56.

2-Bromo-5,5-difluoro-*exo*-6-fluoro-2-norbornene (11).—A mixture of 726 mg (2.36 mmol) of **9** and 290 mg (2.6 mmole) of potassium *tert*-butoxide in 12 ml of ether afforded pure **11** by vpc (column A, 125°). No ureacted **9** was present. An analytical sample of **11** was collected (vpc, column A, 125°) as an oil from the crude product (4.42 mg, 82.6%): ir (neat) 1588 cm^{-1} (C=C); nmr (CCl_4) ^{1}H δ 2.18 (m, 2), 2.93 (m, 2), 4.45 (d of d of m, 1, J = 53, 9 Hz), 6.16 (d of d, J = 3.5, ∼0.6 Hz); ^{19}F φ 102.9, 111.2 (AB m of m, 2, J_{AB} = 234 Hz, A, d of m, J = 9 Hz, B, d of m, J ≅ 10 Hz), 193.5 (d of d of m, 1, J = 53, 10 Hz).

Anal. Calcd for $C_7H_7BrF_3$: C, 37.03; H, 2.66. Found: C, 36.90; H, 2.46.

3-Bromo-5,5-difluoro-*exo*-6-fluoro-2-norbornene (12) and 11.—The procedure for **11** with 975 mg (3.16 mmol) of **2i** and 37 mg (3.3 mmol) of base in 15 ml of ether afforded 614 mg (85.7%) of crude product. Vpc analysis (column A, 125°) indicated that two products were present in a 4:1 ratio with respective retention times of 6.6 and 9.5 min. The individual products were collected by preparative vpc. The major product (6.6 min) was identical with **11** (vpc retention times, nmr, ir). The minor product (9.5 min) was identified as **12**: ir (neat) 1590 cm^{-1}; nmr (CCl_4) ^{1}H δ 2.23 (m, 2), 2.93 (m, 2), 4.45 (d of d of m, 1, J = 53, 9 Hz), 6.18 (d of d, J = 3.2, 1.3 Hz); ^{19}F φ 102.9, 111.3 (AB m of m, 2, J_{AB} = 236 Hz, A, d of m, J = 9 Hz, B, d of m, J ≅ 10.5 Hz), 193.6 (d of d of m, 1, J = 53, ∼10.5 Hz).

Anal. Calcd for $C_7H_6BrF_3$: C, 37.03; H, 2.66. Found: C, 36.99: H, 2.51.

Registry No.—**1a**, 2822-56-2; **1b**, 39037-71-3; **1c**, 1643-76-1; **1d**, 39037-24-6; **1e**, 39004-83-6; **1f**, 39037-25-7; **1g**, 39037-26-8; **1h**, 37580-00-0; **1i**, 37579-98-9; **2a**, 39037-29-1; **2b**, 39037-30-4; **2c**, 39037-31-5; **2d**, 39004-84-7; **2e**, 39037-32-6; **2f**, 39037-33-7; **2g**, 39037-34-8; **2h**, 39037-35-9; **2i**, 39037-36-0; **3**, 39037-72-4; **4**, 39037-73-5; **5**, 39037-74-6; **7**, 39037-75-7; **9**, 39037-37-1; **11**, 39037-38-2; **12**, 39037-39-3; **13**, 6343-21-1; **14**, 2843-35-8; **15**, 39037-41-7; **16**, 39037-42-8; PFIB, 382-21-8; cyclopentadiene, 542-92-7; PFB, 116-15-4; 2,3-dichlorotetrafluoropropene, 684-04-8; trifluoroethylene, 359-11-5.

(31) E. McBee, *et al.*, *J. Amer. Chem. Soc.*, **77**, 915 (1955). This reference includes a number of brominated norbornenes, although no stereochemistry is reported.

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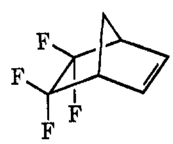
The free-radical addition of carbon tetrachloride, bromotrichloromethane, and *n*-heptafluoropropyl iodide to 5,5,6,6-tetrafluoro-2-norbornene (1) gave cis and trans adducts in the ratios of 2.7:1, 2.1:1, and 1:3.8, respectively. These results contrast with norbornene itself, where 95–100% trans addition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

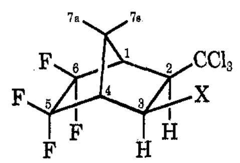
In a previous paper, the importance of endo fluorine coulombic effects in the stereospecific cis-exo-bromination of 5,5,6,6-tetrafluoro-2-norbornene (1) and related compounds was demonstrated.[1] The free-radical additions of carbon tetrachloride,[2] bromotrichloromethane,[2b] and *n*-heptafluoropropyl 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

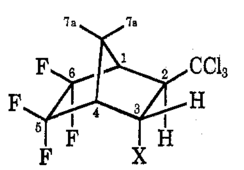
The benzoyl peroxide initiated addition of carbon tetrachloride to **1** at 80° afforded a mixture of 73% cis **2a** and 27% trans **3a** adducts in 72% yield as well as



1



2a, X = Cl
b, X = Br



3a, X = Cl
b, X = Br

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.

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

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 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.

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

(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).