attack with retention. On the other hand, 9 or its epimer could be the first intermediate, leading on the one hand to 2 and on the other to 4.
(13) E. Ciganek, *J. Amer. Chem. Soc.*, **88**, 2883 (1966).
(14) R. G. Curtis, I. Heilbron, E. R. H. Jones, and G. F. Woods, *J. Chem. Soc.*, 457 (1953).
(15) G. C. Schloemer, Ph.D. Thesis, University of Colorado, 1972.
(16) A. L. Noreen, Ph.D. Thesis, University of Colorado, 1970.
(17) "Handbook of Chemistry and Physics," 40th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1958, p 811.

# Fluorinated Bicyclics. IV.[1] Ionic and Free-Radical Bromination of 5-(Difluoromethylene)-6,6-difluoro-2-norbornene

B. E. Smart

*Contribution No. 2073 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898*

*Received October 31, 1973*

Ionic bromination of 5-(difluoromethylene)-6,6-difluoro-2-norbornene (1) in methylene dichloride at 25° gave 1-(bromodifluoromethyl)-3-bromo-7,7-difluorotricyclo[2.2.1.$0^{2,6}$]heptane (2) and 2,7-dibromo-5,5-difluoro-6-(difluoromethylene)norbornane in the ratio of 4:1. In contrast, free-radical bromination gave 29% 2, 22% *exo*-2-bromo-*endo*-3-bromo-5-(difluoromethylene)-6,6-difluoronorbornane, and 49% *exo-cis*-2,3-dibromo-5-(difluoromethylene)-6,6-difluoronorbornane. The nature of the ionic and free-radical intermediates is discussed. Dominant homoallylic participation from the exocyclic difluoromethylene moiety is further support for the stability of $\alpha$-fluorinated electron-deficient carbon.

Previous investigations from this laboratory have demonstrated the importance of $\gamma$-fluorine polar and steric effects on additions to the norbornene double bond.[1-3] In particular, fluorine substituents at the 5,6 positions deactivate the norbornene double bond toward electrophilic addition and only free-radical addition is observed. Furthermore, 5,6-endo fluorine substituents shield the endo side of the system from attack in comparison with norbornene itself.

These studies are extended here to a more complex molecule, 5-(difluoromethylene)-6,6-difluoro-2-norbornene (1).[2] Unlike other fluorinated norbornenes, *e.g.*, 5,5,6,6-tetrafluoro- or 5,5,6-trifluoro-2-norbornene, 1 readily undergoes ionic bromination. The importance of homoallylic participation from the difluoromethylene moiety will be discussed.

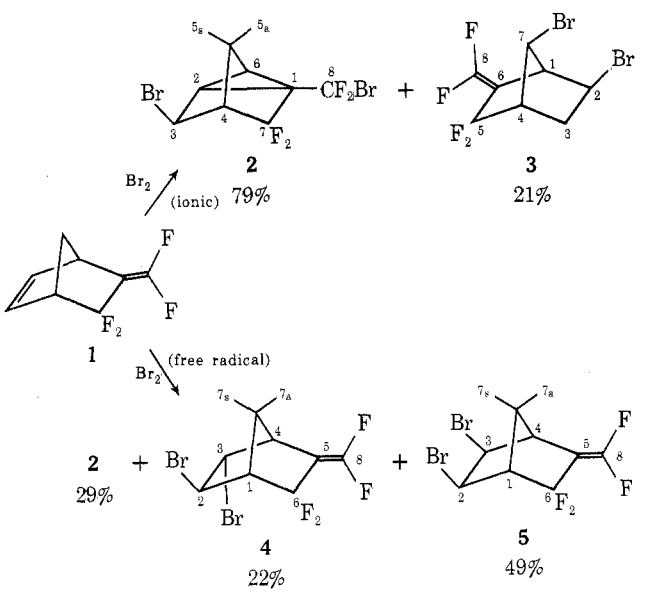
Free-radical bromination of 1 was also investigated. Studies with other methylenenorbornenes have shown that products can arise from initial radical attack at either the exocyclic[4-6] or endocyclic double bond,[7] and homoconjugate addition is often observed.[6] In this regard, the free bromination product distribution was examined and also compared with the ionic addition results.

## Results

Olefin 1 rapidly consumed bromine in methylene dichloride solvent in the dark and under oxygen at 25° (ionic conditions) to afford a mixture of 79% 2 and 21% 3 by glpc.

Bromination of 1 under free-radical conditions[2] gave a mixture of 38% 2, 3.5% 3, 18% 4, and 40.5% 5 by glpc and nmr analysis (see Experimental Section). With the assumption that 3 arose only *via* an ionic pathway (*vide infra*), 17% superimposed ionic reaction was present. Correction of the observed results gave a free-radical product distribution of 29% 2, 22% 4, and 49% 5.

The reported dibromides accounted for >98% of the observed products. *No 1,2-dibromides resulting from addition across the difluoromethylene functionality were detected in either the ionic or free-radical reaction.* All dibromides were stable to the reaction and analytical conditions, and the respective product distributions are those of the kinetically controlled addition reactions.




**Structural Assignments.** The respective dibromide structures were established by $^1H$ and $^{19}F$ nmr and ir analyses. Appropriate double-resonance experiments at 100 and 220 MHz allowed for the assignment of long-range couplings. The chemical shift data are presented in Table I.

The dibromide 2 gave a narrow downfield resonance at $\delta$ 4.41 for a *single* proton geminal to bromine (Figure 1). The bridgehead proton $H_4$ appeared at $\delta$ 2.46 and the cyclopropane ring protons $H_2$ and $H_6$ gave an unresolved singlet at $\delta$ 2.21. Irradiation of $H_3$ revealed a 1.3-Hz coupling with proton $H_{5a}$. The characteristic $^{19}F$ AB multiplet of the geminal vinyl fluorines was absent and a narrow triplet ($J_{FF} \cong 4$ Hz) was observed at $\phi$ 42.0 for the fluorines adjacent to bromine. The absence of a C=$CF_2$ double bond stretching frequency at 1760–1777 $cm^{-1}$, which was observed for 1 and 3–5, and the characteristic[8] ir bands observed at 828, 833, and 867 $cm^{-1}$ further confirmed the nortricyclene structure.

The 100-MHz spectrum of dibromide 3 is shown in Figure 2. Irradiation of the upfield protons $H_{3x}$, $H_{3n}$ at $\delta$ 2.63 and 2.70 collapsed the $H_2$ triplet ($J$ = 6.5 Hz) at $\delta$ 4.04 to a broad singlet. Irradiation of the allylic proton $H_1$ at $\delta$

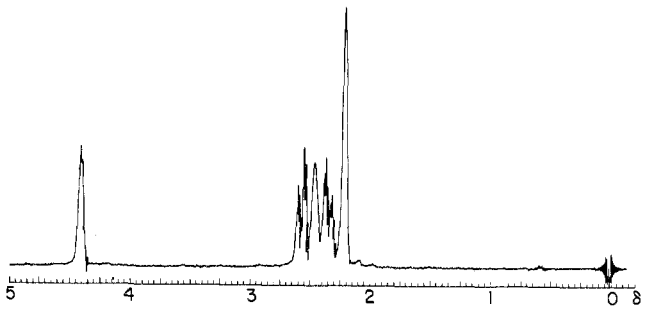



**Figure 1.** Nmr spectrum (100 MHz) of 1-(bromodifluoromethyl)-3-bromo-7,7-difluorotricyclo[2.2.1.$0^{2,6}$]heptane (2).

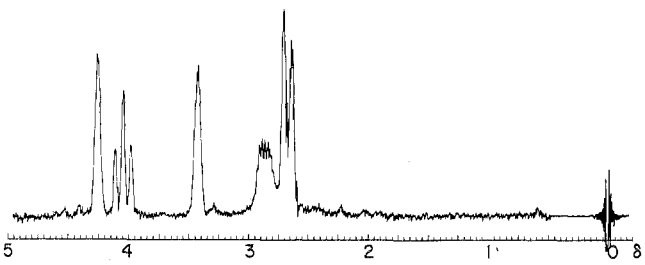



**Figure 2.** Nmr Spectrum (100 MHz) of 2,7-dibromo-5,5-difluoro-6-(difluoromethylene)norbornane (3).

3.43 did not perturb the $H_2$ or $H_{3x}$, $H_{3n}$ resonances. The proton adjacent to bromine at $\delta$ 4.04 therefore is endo and vicinal to $H_1$ and not $H_4$. The higher field methine proton $H_4$ exhibited a complex multiplet resulting from 4–5 Hz proton and fluorine couplings. Proton $H_7$ exhibited no appreciable coupling and appeared as an unresolved singlet at $\delta$ 4.26. A strong ir band at 1767 $cm^{-1}$ confirmed the retained difluoromethylene functionality.

The assignment of structure 4 was more complicated, since isomers 2 and 4 could not be efficiently separated by glpc (see Experimental Section). The 2:1 mixture of **2:4** was examined (Figure 3). Careful integration of the downfield $\delta$ 4.4 multiplet indicated that one proton adjacent to bromine in 4 overlaps with $H_3$ in **2**. A second proton geminal to bromine appeared at $\delta$ 4.14, while the bridgehead protons appeared at $\delta$ 2.88 and 3.21. At 220 MHz the downfield $\delta$ 4.4 proton could not be resolved. Double irradiation of the $\delta$ 4.4 and 4.14 multiplets sharpened the $\delta$ 3.21 multiplet while the $\delta$ 2.88 multiplet was unaffected. This establishes coupling between the allylic proton $H_4$ and an exo proton. Proton $H_2$ at $\delta$ 4.14 is an apparent doublet of triplets which resulted from 3.4 Hz $H_2H_3$, ~2 Hz $H_2H_7$, and ~2 Hz $H_2F_6$ couplings. Proton $H_2$ is therefore endo and the magnitude of $H_2H_3$ coupling is consistent with a trans orientation of the vicinal protons.[2,9-12] These results agree with structure 4 and not with the trans isomer having an exo proton vicinal to $H_1$. The difluoromethylene moiety was confirmed by $^{19}F$ nmr and ir (1775 $cm^{-1}$, C=$CF_2$).

Dibromide **5** gave a characteristic[2] AB multiplet with $J$ = 6.9 Hz for cis-oriented protons $H_2$,$H_3$ (Figure 4). A long-range $H_{2,3}H_{7a}$ coupling of 2 Hz established the cis-endo stereochemistry of $H_2$,$H_3$. The retained exocyclic double bond was established by $^{19}F$ nmr and ir (1760 $cm^{-1}$, C=$CF_2$)

## Discussion

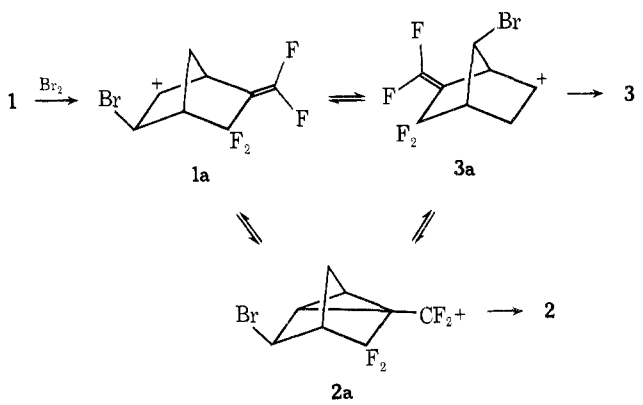
The reactivity of 1 toward ionic bromination when compared with other fluorinated norbornenes[2] and the dominant homoallylic participation of the exocyclic fluorinated double bond are support for the stability of $\alpha$-fluorinated electron-deficient carbon. The proposed reaction intermediates are shown in Scheme I.[13]

**Table I**
**Chemical Shifts[a] for Dibromides in Carbon Tetrachloride**

| Nucleus | 2 | 3 | 4 | 5 |
|---|---|---|---|---|
| $H_1$ | | 3.43 | 2.88 | 2.96 |
| $H_2$ | 2.21[b] | 4.04 | 4.14 | |
| $H_{3n}$ | 4.41 | 2.70 | | (4.35, 4.56)[c] |
| $H_{3x}$ | | 2.63 | ~4.4[d] | |
| $H_4$ | 2.46 | 2.85 | 3.21 | 3.29 |
| $H_{5a}$, $H_{5s}$ | 2.35, 2.57 | | | |
| $H_6$ | 2.21[b] | | | |
| $H_{7a}$, $H_{7s}$ | | 4.26 | 2.0–2.2[d] | 1.96, 1.37 |
| $F_{5x}$, $F_{5n}$ | | (98.1, 106.7) | | |
| $F_{6x}$, $F_{6n}$ | | | (95.5, 114.2) | (98.2, 113.8) |
| $F_{7x}$, $F_{7n}$ | (115.8, 120.8) | | | |
| $F_6$ | 42.0 | (78.8, 79.8) | (79.5, 81.7) | (79.5, 80.8) |

[a] All proton chemical shifts are reported in parts per million ($\delta$) relative to internal tetramethylsilane. All fluorine chemical shifts are in parts per million ($\phi$) relative to fluorotrichloromethane (F-11) internal standard. All values refer to the high-field side of F-11. [b] $H_2$, $H_6$ not resolved. [c] Values in parentheses indicate respective resonances unassigned. [d] Not determined accurately owing to interferences.

Scheme I




Preferential attack of electrophile occurs on the endocyclic double bond at the 2 position followed by charge delocalization through homoallylic (**2a**) or $\sigma$ participation (**3a**). Initial attack at the 3 position would generate positive charge $\gamma$ to the geminal fluorines, which is known to be unfavorable.[2] Furthermore, initial attack on the exocyclic double bond is unlikely owing to the known unreactivity of related fluoro olefins to electrophilic addition.[14,15] Such attack followed by synchronous homoallylic participation would again unfavorably position positive charge $\gamma$ to the geminal fluorines. Therefore, major product **2** arises from preferred intermediate **2a**.

The effects of fluorine substitution on carbonium ion stabilities is a recent topic of interest.[16-21] Stabilization is possible through p-$\pi$ overlap of the fluorine 2p lone-pair electrons into the vacant carbon p orbital, whereas the electronegativity of fluorine relative to hydrogen serves to destabilize positive charge on carbon. The stabilizing influence of fluorine substitution has been demonstrated theoretically[16,17] and experimentally.[18-22] Postulation of **2a** as the preferred intermediate is therefore reasonable. The regiospecific addition to 1 is also noteworthy. Several

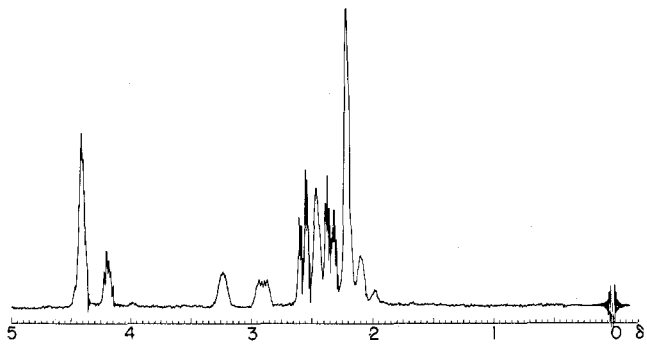



**Figure 3.** Nmr spectrum (100 Mz) of **2** and *exo*-2-bromo-*endo*-3-bromo-5-(difluoromethylene)-6,6-difluoronorbornane (**4**) (2:1 mixture).

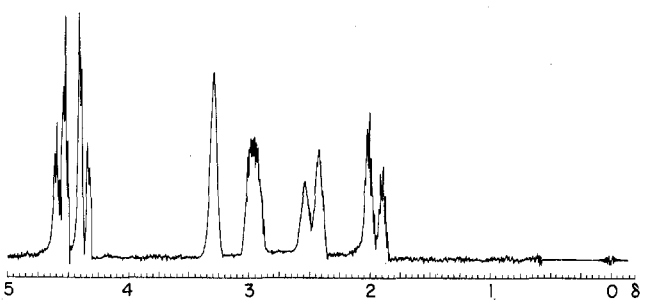
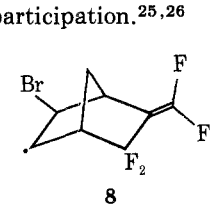


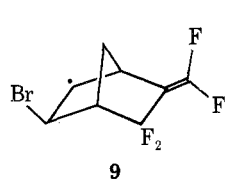

**Figure 4.** Nmr spectrum (100 MHz) of *exo-cis*-2,3-dibromo-5-(difluoromethylene)-6,6-difluoronorbornane (**5**).

examples of electrophilic additions to fluoro olefins that proceed in accordance with the double-bond polarity are known.[14,15] However, strongly polarized olefins *e.g.*, 1,1-difluoroethylene,[23] are required for unequivocal electrophilic addition, and regiospecific addition is guaranteed in these instances, which, *a priori*, is not the case for **1**.[24]

These results contrast with the free-radical addition. Free-radical attack occurs initially on the internal double bond of **1** from the exo direction to give **8** or **9**. Subsequent attack by a chain-propagating bromine molecule on **8** occurs from the exo side to give **5**. Such stereochemical control by endo fluorine substituents has been demonstrated.[1-3] Attack on **9** gives **4**, and rearrangement prior to bromine attack leads to **2**. The nearly equivalent amounts of (**2** + **4**) and **5** formed suggests that there is no preference for the formation of radical **9** or subsequent homoallylic participation.[25,26]




**8**




**9**

## Experimental Section

All melting and boiling points are uncorrected. The gas chromatography work was performed as before[2] with a 6 ft × 0.375 in. 20% QF-1 fluorosilicone on 60/80 Chromosorb P column. The $^1H$ and $^{19}F$ nmr spectra and decoupling experiments followed previous procedures.[2,27] Olefin **1** was available from a previous study.[2] The free-radical and ionic reaction experimental procedures have been described in detail.[2,27]

**Ionic Bromination.** A solution of 1.78 g (10 mmol) of **1** in 9 ml of methylene dichloride was brominated under ionic conditions with 1.60 g (10 mmol) of bromine in 1 ml of methylene dichloride. Work-up afforded a quantitative yield of a mixture of 79% 1-(bromodifluoromethyl)-3-bromo-7,7-difluorotricyclo[2.2.1.$0^{2,6}$]heptane (**2**) and 21% 2,7-dibromo-5,5-difluoro-6-(difluoromethylene)norbornane (**3**) by glpc (150°). Collection of the 9.4- (**2**) and 11.7-min (**3**) peaks *via* preparative glpc gave pure **2**, an oil, and **3**, mp 55–57°. A cold pentane wash gave an analytical sample of **3**, mp 58.5–60°.

*Anal.* Calcd for $C_8H_6Br_2F_4$: C, 28.43; H, 1.79; Br, 47.29. Found (**2**): C, 28.69; H, 1.87; Br, 47.20; (**3**): C, 28.41; H, 1.70.

The reaction was scaled up fivefold and distillation of the product mixture afforded 14.3 g of product, by 73–76° (4 mm). The cut with bp 73° (4 mm) was pure **2**; the 75–76° cut contained ~46% **3**.

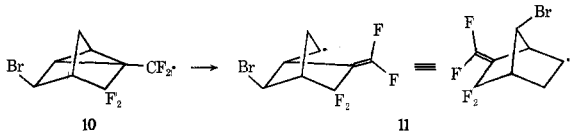
**Free-Radical Bromination.** Bromination of 10 mmol of **1** with 10 mmol of bromine under free-radical conditions gave a quantitative yield of crude dibromides. Glpc (150°) revealed three peaks with respective retention times of 9.4, ~9.8, and 11.8 min. The 9.4- and 9.8-min peak products (56%) were collected together, and the 11.8-min peak product (44%) was collected separately. Examination of the first collection by $^1H$ and $^{19}F$ nmr and ir indicated a mixture of 68% **2** and 32% **4**. The 11.8-min retention time material, mp 46–49°, was a mixture of 92% **5** and 8% **3** by $^{19}F$ and $^1H$ nmr. Several washings with cold pentane gave pure **5**, mp 51–53°.

*Anal.* Found (**2** + **4**): C; 28.71; H, 1.80; (**5**): C; 28.64; H, 1.78.

**Registry No.**—**1**, 39037-72-4; **2**, 50357-81-8; **3**, 50357-82-9; **4**, 50357-83-0; **5**, 50357-84-1.

## References and Notes

(1) Previous paper in this series: B. E. Smart, *J. Org. Chem.*, **38**, 2039 (1973).
(2) B. E. Smart, *J. Org. Chem.*, **38**, 2027 (1973).
(3) B. E. Smart, *J. Org. Chem.*, **38**, 2035 (1973).
(4) E. S. Huyser and G. Echegaray, *J. Org. Chem.*, **27**, 429 (1962).
(5) C. K. Alden and D. I. Davies, *J. Chem. Soc. C*, **1017** (1967).
(6) See J. W. Wilt in "Free Radicals," Vol. I, J. K. Kochi, Ed., Wiley, New York, N. Y., 1973, pp 466–480, for a discussion of homoallylic radical rearrangements.
(7) S. J. Cristol, T. W. Russell, and D. I. Davies, *J. Org. Chem.*, **30**, 207 (1965).
(8) G. E. Pollard, *Spectrochim. Acta*, **18**, 837 (1962).
(9) P. Laszlo and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **86**, 1171 (1964).
(10) . Subramanian, M. T. Emerson, and N. A. LeBel, *J. Org. Chem.*, **30**, 2624 (1965).
(11) C. L. Osborne, T. V. Van Auken, and D. J. Trecker, *J. Amer. Chem. Soc.*, **90**, 5806 (1968).
(12) A. G. Ludwick and J. C. Martin, *J. Org. Chem.*, **34**, 4108 (1969).
(13) The intermediates are shown as equilibrating classical species for convenience only. Representation by nonclassical entities, especially for the fluorinated system, is a moot point.
(14) W. A. Sheppard and C. M. Sharts, "Organic Fluorine Chemistry," W. A. Benjamin, New York, N. Y., 1969.
(15) B. L. Dyatkin, E. P. Mochalina, and I. L. Knunyants in "Fluorine Chemistry Reviews," Vol. 3, P. Tarrant, Ed., Marcel Dekker, New York, N. Y., 1969.
(16) N. C. Baird and R. K. Dalta, *Can. J. Chem.*, **49**, 3708 (1971).
(17) L. D. Kispert, *et al.*, *J. Amer. Chem. Soc.*, **94**, 5979 (1972).
(18) G. A. Olah, M. B. Comisarow, and C. A. Cupas, *J. Amer. Chem. Soc.*, **88**, 362 (1966).
(19) G. A. Olah, R. D. Chambers, and M. B. Comisarow, *J. Amer. Chem. Soc.*, **89**, 1268 (1967).
(20) G. A. Olah, Y. K. Mo, and Y. Halpern, *J. Amer. Chem. Soc.*, **94**, 3551 (1972).
(21) T. B. McMahon, *et al.*, *J. Amer. Chem. Soc.*, **94**, 8934 (1972).
(22) P. E. Peterson, R. J. Bopp, and M. M. Ajo, *J. Amer. Chem. Soc.*, **92**, 2834 (1970).
(23) R. N. Hazeldine and J. E. Osborne, *J. Chem. Soc.*, *61* (1956).
(24) These results do not necessarily support the contention[16-21] that fluorine stabilizes a carbonium ion relative to hydrogen. Ionic bromination of 5-methylene-2-norbornene also gave *ca.* 80% homoconjugate addition: B. E. Smart, unpublished results. A kinetic study on unfluorinated, monofluorinated, and difluorinated compounds is required to demonstrate whether fluorine stabilization is operative in the rate-determining step. However, the ionic bromination results do indicate the preference for the α-fluorinated electron-deficient structure **2a** over **1a**, **3a**, and other possible intermediates.
(25) In contrast, *ca.* 80% of the products (including 36–50% homoconjugate addition) from the free-radical addition of thiophenol to 5-methylene-2-norbornene results from initial attack at the 2 position; see ref 7.
(26) The assumption that **3** is not a free-radical reaction product but a result of the superimposed ionic reaction demands further comment. Rearrangement of radical **9** to **10** followed by ring opening to **11** is a possibility. Subsequent attack on **11** is anticipated to afford a mixture of exo (**3**) and predominantly endo products. However, no endo 2,7-dibromide was observed. For a discussion of steric control from syn 7 substituents see ref 6 and D. I. Davies in "Essays on Free-Radical Chemistry," Special Publication No. 24, The Chemical Society, Burlington House, London, 1970.




**10** **11**

(27) B. E. Smart, *J. Org. Chem.*, **38**, 2366 (1973).