25 °C. After 20 min the reaction mixture was diluted with methylene chloride, washed with 10 ml of 5% $NaHCO_3$, and dried over anhydrous $MgSO_4$. The solvent was evaporated at room temperature. The reaction mixture was analyzed by NMR and showed 70% of trans and 30% of cis adduct. The reaction was repeated several times, and the reproducibility was better than 99%. The product were separated by preparative GLC (SE-30, Chromosorb A/AW 45/60, 10% at 160 °C). Trans difluoride (56%) and cis difluoride (16%), both colorless, liquid compounds, were isolated. The cis difluoride was found to be very unstable. Mass spectrum: calcd for $C_9H_8F_2$ *m/e* 154.0603, found *m/e* 154.0595, *m/e* 154 (M^+, 100), 153 (61), 134 (34), 133 (59), 127 (11), 115 (11), 107 (11). NMR data are stated in Scheme IV.

Acknowledgments. We thank Professor J. Slivnik for xenon difluoride, Professor J. Marsel for providing facilities, and Professors N. Bartlett, P. H. Westheimer, and G. M. Whitesides for helpful discussion. The financial assistance of the Boris Kidrič Foundadion is acknowledged.

Registry No.—3 (R = CH_3), 61047-36-7; 3 (R = $C(CH_3)_3$), 61047-39-0; 4 (R = CH_3), 61076-20-8; 4 (R = $C(CH_3)_3$), 61047-40-3.

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Fluorination with Xenon Difluoride. Fluorination of Bicyclic Olefins

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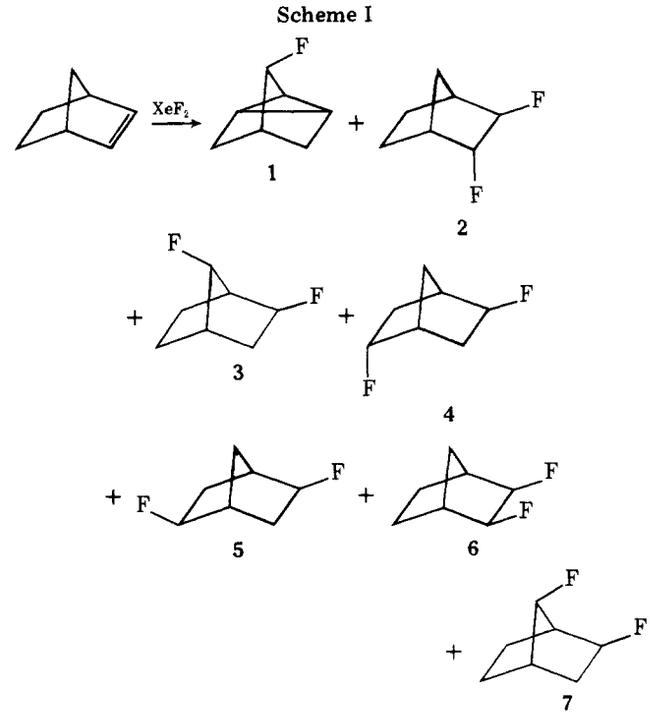
Received June 7, 1976

The reaction of norbornene has been used as a mechanistic probe to elucidate the reaction mechanism and the stereochemistry of the acid-catalyzed, liquid-phase fluorination with xenon difluoride, which resulted in the formation of seven products: fluoronortricyclane (**1**), 2-*endo*,3-*exo*-difluoronorbornane (**2**), 2-*exo*,7-*anti*-difluoronorbornane (**3**), 2-*endo*,5-*exo*-difluoronorbornane (**4**), 2-*exo*,5-*exo*-difluoronorbornane (**5**), 2-*exo*,3-*exo*-difluoronorbornane (**6**), and 2-*exo*,7-*syn*-difluoronorbornane (**7**). The fluorination of benzonorbornadiene resulted in the formation of 2-*exo*,7-*syn*-difluorobenzonorbornane (**8**), while the fluorination of norbornadiene resulted in the formation of 3-*endo*,5-*exo*-difluoronortricyclane (**9**), 3-*exo*,5-*exo*-difluoronortricyclane (**10**), and 2-*exo*,7-*syn*-difluoronorbornene-5 (**11**). A heterolytic Xe–F bond cleavage is suggested, resulting in an open β-fluorocarbonium ion intermediate or in a nonclassical ion, which undergoes the Wagner–Meerwein rearrangements and hydride shifts, thus forming fluorinated products. For the formation of the products **2** and **6** a free-radical intermediate is suggested.

With our continuing interest in acid-catalyzed liquid-phase fluorination of olefinic compounds[1] with xenon difluoride, we found it instructive to fluorinate some bicyclic alkenes, i.e., norbornene, benzonorbornadiene, and norbornadiene, in order to establish the reaction mechanism. The reactions of the bicyclic olefins norbornene and benzonorbornadiene have been used as a mechanistic probe to elucidate the mechanism of various reactions.[2] On the other hand, halogenations of norbornadiene have been studied much less intensively. Winstein[3] has studied bromination of norbornadiene and has pointed out the possibly dangerous properties of the products. We now report evidence for the formation of ionic intermediates in acid-catalyzed liquid-phase fluorination with xenon difluoride.

Scheme I



Results and Discussion

Fluorination of Norbornene. A 1-h reaction of norbornene with xenon difluoride in methylene chloride at room temperature and in the presence of a catalytic amount of hydrogen fluoride resulted in the formation of seven products. Analysis of the reaction mixture by GLC gave the relative yields which are listed in Table I. The products of the reaction were collected by preparative GLC. The structures of the compounds were determined on the basis of their mass, ^{19}F, and ^1H NMR spectra. The products formed in the reaction were fluoronortricyclane (**1**), 2-*endo*,3-*exo*-difluoronorbor-

Table I. Variation in Composition of Products from Addition of Xenon Difluoride to Norbornene at 25 °C[a]

Concn of norbornene, mg/ml	Solvent	Reaction times, min	1	2	3	4	5	6	7
200	CCl_4[b]	120	38	2.5	16	17.5	12	1.5	8
200	$CHCl_3$[b]	60	46	14	13	10.5	5	6.5	4
200	CH_2Cl_2	60	41.5	10.5	16.5	13.5	6	5.5	5
75	CH_2Cl_2	60	37.5	6	18	19	10	4	5.5
75	CH_2Cl_2	3	44	6	17	15.5	9	4	4.5
75	CH_2Cl_2/O_2	60	37.5	3.5	20	20	10	2	6
37.5	CH_2Cl_2	60	38	3.5	19.5	20	11	2	6
25	CH_2Cl_2	60	37	1.5	20	23	12	0.5	6

[a] Each experiment was repeated several times, average data being presented, and relative yields determined by GLC; maximum error is ±1.5% (Chromosorb Regular 100, 10% DDP with temperature program 45–120 °C). [b] Difference between 100% is one unidentified trifluoro product.

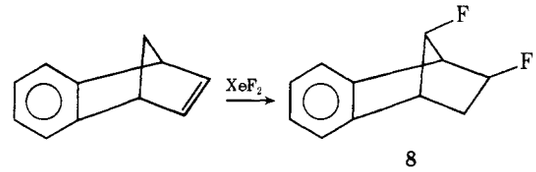
nane (**2**), 2-*exo*,7-*anti*-difluoronorbornane (**3**), 2-*endo*,5-*exo*-difluoronorbornane (**4**), 2-*exo*,5-*exo*-difluoronorbornane (**5**), 2-*exo*,3-*exo*-difluoronorbornane (**6**), and 2-*exo*,7-*syn*-difluoronorbornane (**7**) (the numbering of the products is in the order of increasing retention times). One can see that the retention times of the products **1**, **2**, **3**, **4**, **5**, and **7** are in the same order as those observed for dibromides by bromination of norbornene.[4] Products **1**, **3**, and **7** are known,[5] while products **4** and **5** have very similar mass spectra [*m/e* 132 (M^+), 86 ($M^+ - C_2H_3F$), 85 ($M^+ - C_2H_4F$)], which is also the case with **2** and **6** [*m/e* 132 (M^+), 68 ($M^+ - C_2H_2F_2$), 67 ($M^+ - C_2H_3F_2$)], with very little differences in the intensities of peaks. The similarity in fragmentation led us to the conclusion that **4** and **5** and **2** and **6** are isomeric compounds. Product **2** shows two signals in its ^{19}F NMR spectra, the first at δ −189.6 ppm (ddm) and the second at δ −219.0 ppm (ddt), and in its ^1H spectrum two signals at a lower field: δ 5.21 (ddd) and 4.72 ppm (ddd). Since endo-bonded hydrogen and fluorine atoms appear in the NMR spectrum at a higher field[6] than the exo-bonded ones, we have established the structure of the product **2** as 2-*exo*,3-*endo*-difluoronorbornane. Product **6** shows in its ^{19}F NMR spectrum one signal at δ −218 ppm (dm), and in its ^1H spectrum one signal at a lower field at δ 4.86 ppm (dm) corresponding to the two protons. The chemical shift of the two protons is characteristic of endo-bonded protons. On the other hand, the chemical shift for the fluorine atom is too high for an exo-bonded fluorine. However, a similar upfield effect on the chemical shift of two fluorine atoms in the nearly eclipsed position was also observed in the case of cis adducts formed in the fluorination of indene.[7] On the basis of mass spectral and NMR data, we have established the structure of the product **6** as 2-*exo*,3-*exo*-difluoronorbornane.

Compound **5** shows in its ^{19}F NMR spectrum a multiplet at δ −181.5 ppm and in its ^1H spectrum a doublet of multiplet signal at a lower field at δ 4.88 ppm, corresponding to two protons. The chemical shift for the fluorine atom corresponds to exo-bonded fluorine, and the chemical shift for lower field protons to the two endo-bonded protons. On the other hand, in the ^{19}F NMR spectrum of compound **4** we observed two signals, the first at δ −175.1 ppm (dm) and the second at δ −207.8 ppm (dddt), and in ^1H spectrum we observed two signals at a lower field, the first at δ 5.16 ppm (dd) and the second at δ 4.89 ppm (d). The fluorine atom at the lower field is exo and the one at higher field is endo bonded. The proton at the lower field corresponds to an exo- and that at a higher field to an endo-bonded proton. On the basis of the NMR and mass spectral data we have assigned the structure of the product **5** as 2-*exo*,5-*exo*-difluoronorbornane and the structure of the product **4** as 2-*endo*,5-*exo*-difluoronorbornane.

Product distribution as a function of solvent polarity, concentration of norbornene, and the presence of oxygen as an inhibitor of carbon radicals is given in Table I. The formation of the products **2** and **6**, depending significantly upon the conditions mentioned above, decreases in the presence of oxygen to one-half. Studying product stability under the reaction conditions, we observed no appreciable changes (3.5% decrease of product **4** and 6.5% increase of product **1**) in the distribution of the products **2**–**7** by shortening the reaction time to 3 min. However, significant isomerization took place when higher amounts of hydrogen fluoride in methylene chloride (at 25 °C) were used. Product **1** reacted with hydrogen fluoride, thus forming **2**, **3**, **4**, **5**, and **7**, product **3** isomerized into **2**, **4**, **5**, and **7**, while **7** isomerized into compounds **3**, **4**, **5**, and **6**, and product **4** was converted into **5** and **5** into **4**. On the other hand, under the above-mentioned conditions only **2** and **6** remained unchanged. The observed transformations of the products could be explained by the fact that hydrolysis of fluorinated compounds is acid catalyzed.[8]

Fluorination of Benzonorbornadiene. A 1-h reaction resulted in the formation of one major product and two trace products (we were unable to determine the structures of these latter two). The structure of compound **8** was determined on

Scheme II



8

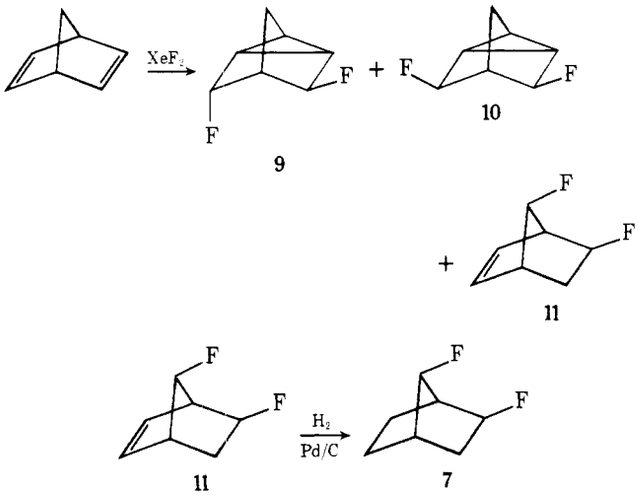
+ 2 unidentified minor products

the basis of its mass, ^1H, and ^{19}F NMR spectra. The major product shows in its ^{19}F NMR spectrum two signals, the first one as a multiplet at δ −182.25 ppm and the second one as a doublet of doublet at δ −183 ppm, and in its ^1H NMR spectrum two protons at lower field, the first at δ 4.75 ppm as a doublet of a multiplet and the second at δ 4.7 ppm as a doublet signal. Product **8** shows a fragmentation in its mass spectrum similar to those of 2-*exo*,7-*syn*- (**7**), 2-*exo*,7-*anti*-difluoronorbornane (**3**), and 2-*exo*,7-*syn*-difluoronorbornene-5 (**11**). The major peaks are *m/e* 147 ($M^+ - CH_2F$), 134 ($M^+ - C_2H_3F$), 133 ($M^+ - C_2H_4F$), and 129 ($M^+ - CHF_2$). The likeness in fragmentation led us to the conclusion that the structure of product **8** is very similar to those of **3**, **7**, and **11**. The signal in the ^{19}F NMR spectra, corresponding to a fluorine atom bonded at C-7, is shifted by about 50 ppm toward lower field than that of product **3** or **7**. However, if we compare the NMR data to those of product **11** formed in the fluorination of norbornadiene, whose structure was determined by hydrogenation, we observe very similar values for chemical shifts for fluorine atoms and signals for hydrogen atoms at a lower field. On the basis of its ^1H and ^{19}F NMR spectra, we have

established the structure of product 8 as 2-*exo*,7-*syn*-difluorobenzonorbornane.

Fluorination of Norbornadiene. Acid-catalyzed liquid-phase fluorination with xenon difluoride resulted in the formation of three products in relative yields of 50% of **9**, 40% of **10**, and 10% of 11 (determined by GLC or NMR spectroscopy),

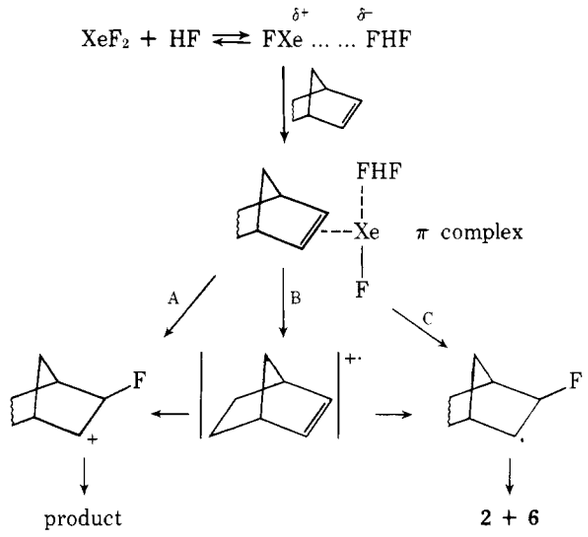
Scheme III



which could be separated by preparative GLC and whose structures were determined on the basis of their mass, ^{19}F, and ^{1}H NMR spectra and chemical transformations. product **9** shows in its ^{19}F NMR spectra two doublets, the first one at δ −201.8 ppm, corresponding to an exo-bonded fluorine atom, and the second one at δ −213 ppm, corresponding to an endo-bonded fluorine atom, with coupling constants of 60 Hz, and in its ^{1}H NMR two doublets at lower field, the first one at δ 5.22 ppm and the second one at δ 4.74 ppm, corresponding to exo- and endo-bonded protons, respectively. The molecular peak for product **9** was *m/e* 130. On the basis of the above-mentioned data we have established the structure of product **9** as 3-*endo*,5-*exo*-difluoronortricyclane. Product **10** shows in its ^{19}F NMR spectrum one doublet signal at δ −201.4 ppm with a coupling constant of 60 Hz, corresponding to the exo-bonded fluorine atom, and in its ^{1}H NMR a doublet signal at lower field at δ 4.53 ppm, corresponding to the two endo-bonded protons. The molecular peak was also *m/e* 130. By means of the above-mentioned data, the structure was found to be 3-*exo*,5-*exo*-difluoronortricyclane. The minor product formed (**11**) shows in its ^{19}F NMR spectrum one doublet of doublet signal at δ −180 ppm and one multiplet signal at δ −187.5 ppm, and in its ^{1}H NMR three signals at lower field. These were a multiplet signal at δ 6 ppm corresponding to two vinyl protons, a doublet of triplet signal at δ 4.74 ppm with coupling constants of 57 and 3 Hz, and a doublet signal at δ 4.6 ppm with a coupling constant of 60 Hz. The molecular peak was *m/e* 130. From the data mentioned above, we propose the structure as 2-*exo*-7-difluoronorbornene-5. However, from the data just described, we were unable to make a decision about the stereochemistry at C-7. In order to establish the stereochemistry we converted product 11 to previously synthesized 2-*exo*,7-*syn*-difluoronorbornane (**7**) by catalytic hydrogenation.

Mechanism of the Fluorination with Xenon Difluoride. On the basis of the experimental results, we suggest the mechanism presented in Scheme IV. The mechanism of fluorination must involve catalysis by hydrogen fluoride since the reaction proved to be very slow without it. It might be expected that in the presence of hydrogen fluoride, xenon difluoride behaves as an electrophile. Previously this has been suggested by Filler et al.[9] for the fluorination of aromatic

Scheme IV



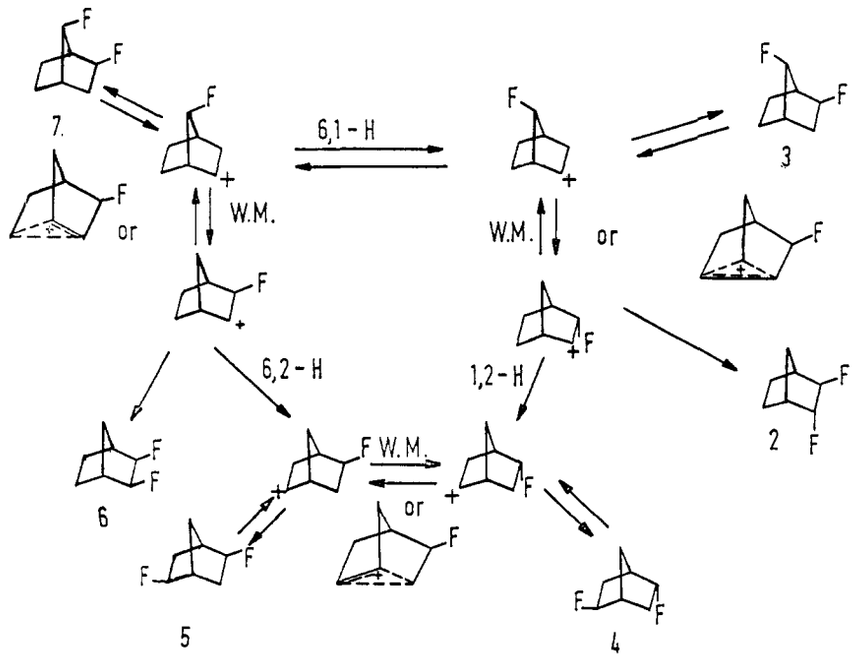
compounds. In the next step a π complex is probably formed between this electrophilic species and the bicyclic olefin, which could be transformed by the heterolytic Xe–F bond cleavage into an open β-fluorocarbonium ion intermediate (or into a nonclassical ion) (path A), which undergoes Wagner–Meerwein and hydride rearrangements, thus forming difluorides. Furthermore, another possible explanation for the formation of carbonium ion intermediates could be the formation of an ion radical (path B), which has already been observed in the fluorination of benzene and its derivates,[9] transforming in the next step by $XeF\cdot$ or XeF_2 to a carbonium ion or to a radical species. The lower oxidation potentials of olefins (in comparison to those of benzo derivates) make the above suggested path (B) quite reasonable.[16] For an explanation of the formation of the products **2** and **6**, whose differences in amount depend upon the concentration of norbornene and the presence of oxygen, we suggest another possible reaction path C, involving a free-radical species, formed by homolytic Xe–F bond cleavage or from an ion radical. We feel that the main intermediate formed in the acid-catalyzed liquid-phase fluorination with xenon difluoride is of carbonium ion nature, but also a free-radical intermediate is present.

An explanation of the formation of seven products in the reaction with norbornene is presented in Scheme V. The primarily formed β-fluorocarbonium ion intermediate (or nonclassical ion) undergoes hydride shifts and Wagner–Meerwein rearrangements,[10] thus forming difluorides **2**, **3**, **4**, **5**, **6**, and **7**.

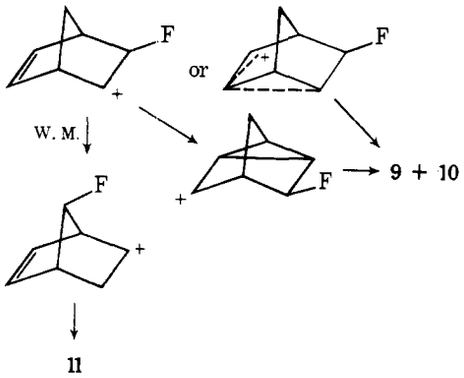
However, we suggest in the mechanism the irreversible hydride shifts 6,2-H and 1,2-H, based on the observation of the isomerization of the products in methylene chloride in the presence of hydrogen fluoride, where similar carbonium ions are formed. Explanation of the formation of three products in the reaction with norbornadiene is presented in Scheme VI. The primarily formed β-fluorocarbonium intermediate or delocalized ion undergoes Wagner–Meerwein rearrangement, thus forming difluoride **11**, while the formation of the products **9** and **10** could be explained by the attack of the fluorine anion on the fluoronortricyclyl cation or delocalized ion. The formation of 2-*exo*,7-*syn*-difluorobenzonorbornane (**8**) could be explained by Wagner–Meerwein rearrangement of the primarily formed β-fluorocarbonium ion.

Experimental Section

IR spectra were recorded using a Perkin-Elmer 257 spectrometer, and ^{1}H and ^{19}F NMR spectra by a JEOL JNM-PS-100 from CCl_4 solution with Me_4Si or CCl_3F as internal reference. Mass spectra and high-resolution measurements were taken on a CEC-21-110 spec-



Scheme VI



trometer. Gas–liquid partition chromatography was carried out on a Varian Aerograph Model 1800.

Materials. Benzonorbornadiene was prepared;[12] other olefins were commercially available and purified before use. Hydrogen fluoride of Fluka Purum quality was used without further purification. Methylene chloride, chloroform, and carbon tetrachloride were purified and stored over molecular sieves.[13] Xenon difluoride was prepared by a photosynthetic method[14] and its purity was better than 99.5%.

Addition and Isolation Procedures. To a solution of 1 mmol of olefin in methylene chloride (6 ml) in a Kel-F vessel, 1 mmol of xenon difluoride was added at 25 °C and under stirring anhydrous hydrogen fluoride (0.5–1 mmol) was introduced into the reaction mixture. After a few seconds the colorless solution turned dark blue and xenon gas was slowly evolved. After 60 min gas evolution had ceased and the reaction appeared to be complete. The reaction mixture was diluted with methylene chloride (15 ml), washed with 10 ml of 5% $NaHCO_3$ and water, and dried over anhydrous sodium sulfate. The solvent was evaporated in vacuo. The crude reaction mixtures were separated by preparative GLC.

Fluorination of Norbornene. Products were separated by preparative GLC (DDP-10%, Chromosorb Regular 100, 45–120 °C).

Fluoronortricyclane (1): yield 30%; mp 44–45 °C (lit.[15] 48–50 °C) (sealed capillary); NMR δF −218 ppm (dt), δCHF 5.05 ppm (dt) (J_{FH} = 69 Hz); the NMR spectrum is similar to that of the product synthesized from norbornadiene and HF.

2-*endo*,3-*exo*-Difluoronorbornane (2): yield 1.5% of volatile, waxy solid product; mp (sealed capillary) 96–97 °C; NMR (CCl_4) δF_{exo} −189.6 (ddm), δF_{endo} −219.0 (ddt), δCF**H**$_{endo}$ 4.72 (ddd), δCF**H**$_{exo}$ 5.21 ppm (ddd), $J_{FH\text{-}gem}$ = 60, $J_{F\text{-}exo\text{-}H\text{-}exo}$ = 31, $J_{P\text{-}endo\text{-}H\text{-}endo}$ = 18 Hz; mass spectrum calcd for $C_7H_{10}F_2$ *m/e* 132.0750, found 132.0759, *m/e* 132 (M^+, 8), 99 (24), 72 (38), 68 (96), 67 (100). Anal. Calcd for $C_7H_{10}F_2$: C, 63.60; H, 7.63. Found: C, 63.74; H, 7.30.

2-*exo*,7-*anti*-Difluoronorbornane (3): yield 13% of volatile, waxy solid product; mp (sealed capillary) 101–102 °C (lit.[5] 107–110 °C); NMR (CCl_4) δF2 −176.2 (dm), δF_7 −232.3 (dt), δH_2 4.28 (dm), δH_7 5.48 ppm (d), $J_{F_2H_2}$ = 60, J_{F_2H} = 30, 7.5 $J_{F_7H_7}$ = 65, J_{F_7H} = 3 Hz; mass spectrum calcd for $C_7H_{10}F_2$ *m/e* 132.0750, found *m/e* 132.0753, *m/e* 132 (M^+, 10), 99 (30), 86 (44), 85 (60), 81 (100), 72 (50). Anal. Calcd for $C_7H_{10}F_2$: C, 63.60; H, 7.63. Found: C, 63.44; H, 7.70.

2-*endo*,5-*exo*-Difluoronorbornane (4): yield 14% of volatile, waxy solid product; mp (sealed capillary) 82–84 °C; NMR (CCl_4) δF_2 −207.8 (dddt), δF_5 −175.1 (dm), δH_2 5.16 (dd), δH_5 4.89 ppm (d), $J_{F_2H_2}$ = 60, J_{F_2H} = 31.5, 15, 1.5, $J_{F_5H_5}$ = 60, J_{F_5H} = 40, 20, 7.5 Hz; mass spectrum calcd for $C_7H_{10}F_2$ *m/e* 132.0750, found *m/e* 132.0759, *m/e* 132 (M^+, 14), 99 (10), 86 (100), 85 (82). Anal. Calcd for $C_7H_{10}F_2$: C, 63.60; H, 7.63. Found: C, 63.44; H 7.70.

2-*exo*,5-*exo*-Difluoronorbornane (5): yield 8% of waxy solid product; mp (sealed capillary) 96–98 °C; NMR (CCl_4) δF −181.5 (m), δH_2H_5 4.88 ppm (dm), $J_{F_2H_2}$ = 60 Hz; mass spectrum calcd for $C_7H_{10}F_2$ *m/e* 132.0750, found *m/e* 132.0750, *m/e* 132 (M^+, 10), 99 (10), 86 (100), 85 (78). Anal. Calcd for $C_7H_{10}F_2$: C, 63.60; H, 7.63. Found: C, 63.63; H, 7.70.

2-*exo*,3-*exo*-Difluoronorbornane (6): yield 2.5% of waxy solid product; mp (sealed capillary) 121–122 °C; NMR (CCl_4) δF −218 (dm), δH_2H_3 4.86 ppm (dm), mass spectrum calcd for $C_7H_{10}F_2$ *m/e* 132.0750, found *m/e* 132.0750, *m/e* 132 (M^+, 6), 99 (30), 72 (46), 68 (100), 67 (76). Anal. Calcd for $C_7H_{10}F_2$: C, 63.60; H, 7.63. Found: C, 63.20; H, 7.66.

2-*exo*,7-*syn*-Difluoronorbornane (7): yield 4% of volatile, waxy solid product; mp (sealed capillary) 116–119 °C (lit.[5] 95–97 °C); NMR (CCl_4) δF_2 −179.5 (dm), δF_7 −223.5 (dm), δH_2 5.1 (dd), δH_7 5.2 ppm (d), $J_{F_2H_2}$ = 60, J_{F_2H} = 40, $J_{F_7H_7}$ = 63, J_{F_7H} = 12.6 Hz; mass spectrum calcd for $C_7H_{10}F_2$ *m/e* 132.0750, found *m/e* 132.0752. Anal. Calcd for $C_7H_{10}F_2$: C, 63.60; H, 7.63. Found: C, 63.32; H, 7.40.

Fluorination of Benzonorbornadiene. 2-*exo*,7-*syn*-Difluorobenzonorbornane (8) was purified by preparative GLC (SE-30, Chromosorb A/AW 45/60 10%, at 150 °C); yield 68% of waxy solid product; mp (sealed capillary) 40–43 °C; NMR (CCl_4) δF_2 −182.25 (m), δF_7 −183 (dd), δCF$\mathbf{H}_2$ 4.75 (dm), δCF$\mathbf{H}_7$ 4.7 (d), δH_1 3.7 (d), δH_4 3.45 ppm (s); mass spectrum calcd for $C_{11}H_{10}F_2$ *m/e* 180.0750, found *m/e* 180.0755, *m/e* 180 (M^+, 88), 159 (47), 147 (76), 146 (62), 134 (100), 133 (89), 129 (87), 116 (50), 115 (55).

Fluorination of Norbornadiene. Products were separated by preparative GLC (Carbowax 20M–25% Varaport 30 70/80, 160 °C).

3-*endo*,5-*exo*-Difluoronortricyclane (9): yield 35% of waxy solid product; mp (sealed capillary) 75–76 °C; NMR (CCl_4) δF_{exo} −201.8 ppm (d) J_{FH} = 60 Hz, δF_{endo} −213 ppm (d), J_{FH} = 60 Hz, δCF$\mathbf{H}_{exo}$ 5.22 (d), δCF$\mathbf{H}_{endo}$ 4.74 ppm (d); mass spectrum calcd for $C_7H_8F_2$ *m/e* 130.0594, found *m/e* 130.0597, *m/e* 130 (M^+, 58), 115 (53), 109 (30), 97 (100), 84 (35), 79 (65).

3-*exo*,5-*exo*-Difluoronortricyclane (10): yield 30% of waxy solid product; mp (sealed capillary) 76–77 °C; NMR (CCl_4) δF −201.4 (d),

δCF**H** 4.53 ppm (d), J_{FH} = 60 Hz; mass spectra calcd for $C_7H_8F_2$ *m/e* 130.0594, found *m/e* 130.0597, *m/e* 130 (M^+, 35), 115 (45), 109 (25), 97 (100), 84 (38), 79 (57).

2-*exo*,7-*syn*-Difluoronorbornene-5 (11): yield 6% of waxy solid product; mp (sealed capillary) 82–83 °C; NMR (CCl_4) δF_2 −187.5 (m), δF_7 −180 (dd), δCF**H**$_2$ 4.74 (dt), δCF**H**$_7$ 4.6 (d), δFC**H** 6.0 ppm (m, 2 H), $J_{F_7H_7}$ = 60, J_{F_7H} = 12, $J_{F_2H_2}$ = 57 Hz; mass spectrum calcd for $C_7H_8F_2$ *m/e* 130.0594, found *m/e* 130.0589, *m/e* 130 (M^+, 25), 109 (10), 97 (18), 84 (100), 79 (65).

Hydrogenation of 2-*exo*,7-*syn*-Difluoronorbornene-5 (11). **11** (0.5 mmol) was dissolved in 3 ml of methanol, and 0.3 g of 10% Pd on carbon was added, stirred at room temperature in a hydrogen atmosphere. After 0.3 mmol of hydrogen had reacted, the catalyst was filtered off and the reaction mixture was analyzed by GLC. The retention time of the product formed above was identical with that of 2-*exo*,7-*syn*-difluoronorbornane (**7**). The NMR spectra of the two compounds were the same.

Fluorination of Norbornene in the Presence of Oxygen. Norbornene (1 mmol) was dissolved in 2 ml of methylene chloride, 1 mmol of xenon difluoride was added at 25 °C, and under stirring a mixture of anhydrous hydrogen fluoride and oxygen was introduced into the reaction mixture for 60 min. The reaction mixture was diluted with methylene chloride, washed with 10 ml of 5% $NaHCO_3$ and water, dried ($MgSO_4$), and filtered, the solvent was evaporated in vacuo at room temperature, and the residue was analyzed by GLC. The product distribution is stated in Table I. It can be seen that the relative yields of products **2** and **6** are diminished to one-half.

The effects of solvent polarity and the concentration of norbornene on the product distribution are stated in Table I. The workup procedure was carried out in the usual way.

Isomerization of Norbornene Difluorides 2–7 and the Reaction of Fluoronortricyclane with Hydrogen Fluoride in Methylene Chloride. Pure difluorides or nortricyclane (0.3 mmol) was dissolved in methylene chloride (1 ml) at room temperature and under stirring 2 mmol of hydrogen fluoride was introduced into the reaction mixture. After 1 h the reaction mixture was washed with 1 ml of 5% $NaHCO_3$ and water and dried (Na_2SO_4). The composition of the mixture was determined by glc.

Fluoronortricyclane (**1**) gave a mixture of **2** (1%), **4** (37%), **5** (26%), **3** (26%), and **7** (10%).

2-*exo*,7-*anti*-Difluoronorbornane (**3**) gave a mixture of **2** (1%), **4** (34%), **5** (32%), **3** (29%), and **7** (4%).

2-*exo*,7-*syn*-Difluoronorbornane (**7**) gave a mixture of **6** (1%), **4** (20%), **5** (22%), **3** (9%), and **7** (48%).

2-*endo*,5-*exo*-Difluoronorbornane (**4**) gave a mixture of **4** (62%) and **5** (38%).

3-*exo*,5-*exo*-Difluoronorbornane (**5**) gave a mixture of **4** (24%) and **5** (76%).

Under the above-mentioned conditions only difluorides **2** and **6** remained unchanged.

Acknowledgments. We thank Professor J. Slivnik for xenon difluoride, Professor J. Marsel for providing facilities, and Professors N. Bartlett, F. H. Westheimer, and G. M. Whitesides for helpful discussion. The financial assistance of the Boris Kidrič Foundation is acknowledged.

Registry No.—**1**, 695-03-4; **2**, 61026-28-6; **3**, 36914-49-5; **4**, 61026-29-7; **5**, 61091-30-3; **6**, 61091-31-4; **7**, 36914-50-8; **8**, 61026-30-0; **9**, 61026-31-1; **10**, 61091-32-5; **11**, 61026-32-2; norbornene, 498-66-8; benzonorbornadiene, 4453-90-1; norbornadiene, 121-46-0; xenon difluoride, 13709-36-9; hydrogen fluoride, 7664-39-3.

References and Notes

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