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HALOFLUORINATION OF NORBORNADIENE. EVIDENCE FOR *ENDO* AND *EXO* ATTACK BY ELECTROPHILES

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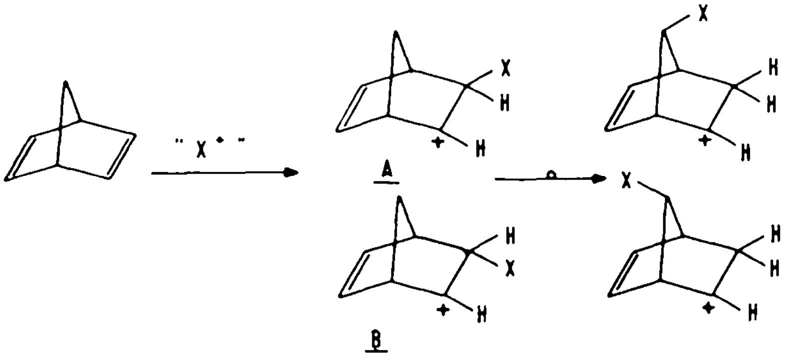
Abstract—Halofluorination of norbornadiene with N-bromosuccinimide, N-chlorosuccinimide or xenon difluoride in the presence of polyhydrogen fluoride-pyridine resulted in the formation of three products: 3-*endo*-halo-5-*exo*-fluoro (2) and 3-*exo*-halo-5-*exo*-fluoronortricyclane (3), and 2-*exo*-fluoro-7-*syn*-halo-norbornene-5 (4). The *exo*-attack of the electrophile on norbornadiene is slightly predominant (65% X = Br, 64% X = Cl, 73% X = F) over the *endo*-attack. The Meerwein-Wagner rearrangement occurred only in the case of chlorine or fluorine halo-substituents of β-carbonium ions formed by *exo*-attack of the electrophile.

The reactions of the bicyclic olefin norbornene have been used as a mechanistic probe to elucidate the mechanism of various reactions.[1] On the other hand, halogenation of norbornadiene has been studied much less intensively. Winstein[2] has studied bromination of norbornadiene and has pointed out the possibly dangerous properties of the products. In norbornene there is preferentially (or exclusively) *exo*-attack by the electrophile, while in norbornadiene there is the possibility of both *exo* and *endo*-attack. This problem could not be solved with attack by X_2 species, because the stereo-evidence is lost and for this reason we need and electrophilic reagent of XY type. There is also the question as to whether the *exo*-**A** or *endo*-**B** β-halosubstituted carbocation (Scheme 1) undergoes a Meerwein-Wagner rearrangement preferentially. We now report evidence for both *exo* and *endo*-attack by an electrophilic species of "XF" type (X = Br, Cl, F) which was generated in a solution of polyhydrogen fluoride-pyridine[3] in conjunction with N-bromosuccinimide (NBS), N-chlorosuccinimide (NCS) or xenon difluoride. Further, we have found that only *exo*-β-halocarbocation (**A**) undergoes the Meerwein-Wagner rearrangement.

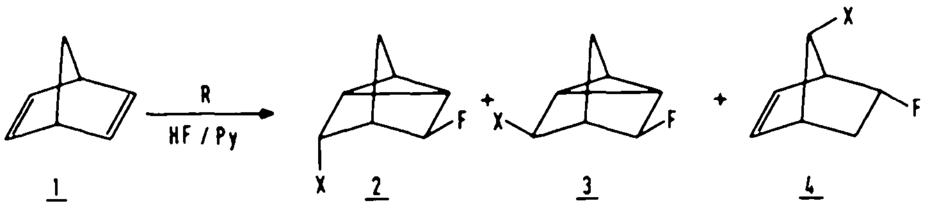
RESULTS AND DISCUSSION

A 1-hr reaction of norbornadiene (**1**) at room temperature in a mixture of polyhydrogen fluoride-pyridine, ether and NBS resulted in the formation of two products (**2a** and **3a**, Scheme 2). Analysis of the mixture by glc gave the relative yields listed in Scheme 2. The structure of the compounds was determined on the basis of their mass and ^1H and ^{19}F NMR spectra. Both products have very similar mass spectra with the following major fragments: *m/e*: 192, 190 ($M^+ + 2$, M^+), 111, 109, 91, with very little difference in peak intensities. High resolution measurements on the molecular peaks indicated, the formula to be C_7H_8BrF. Both products show in their ^{19}F spectrum one doublet signal: δ −200.25 ppm (**2a**), δ −194.25 ppm (**3a**) and in their ^1H spectrum two signals at lower field: δ 4.75 ppm (d, J = 60 Hz), δ 4.55 ppm (s) for **2a**, and 4.54 ppm (d, J = 60 Hz) and δ 3.87 (s) for **3a**. A comparison of NMR data of **2a** and **3a** with those of the other halogen substituted products (**2b**, **2c**, **3b**, **3c**) is presented in Table 1. Chemical shifts for the F atom are typical for those of *exo*-bonded fluorine, while in the proton NMR spectra the singlet signals at lower field indicate an *exo* **2a** or an *endo*-**3a** bonded proton. On the basis of the above NMR data and mass spectra, we have established the structure of **2a** as 3-*endo*-bromo-5-*exo*-fluoronortricyclane and **3a** as 3-*exo*-bromo-5-*exo*-fluoronortricyclane.

Chlorofluorination of norbornadiene with NCS under the same conditions as those for bromofluorination resulted in the formation of three products (**2b**, **3b**, **4b**). Analysis of the mixture by glc gave the relative yields listed in Scheme 2. Products **2b** and **3b** have very similar mass spectra (*m/e*: 148 ($M^+ + 2$), 146 (M^+), 111, 109, 91, 84, 79) with very little difference in peak intensities. The chemical shifts for signals in their ^{19}F and ^1H NMR spectra are very similar to those of the bromofluorides



Scheme 1.



RELATIVE YIELDS[a)]

R	X	2	3	4
XeF_2	F	27	68	5
NCS	Cl	36	59	5
NBS	Br	35	65	—

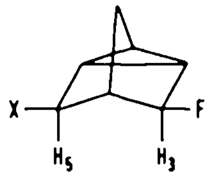
a) DETERMINED by g.l.c.

Scheme 2.

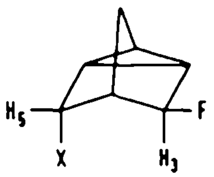
(Table 1). On the basis of the above data, we have established the structure of **2b** as 3-*endo*-chloro-5-*exo*-fluoronortricyclane, and of **3b** as 3-*exo*-chloro-5-*exo*-fluoronortricyclane. The minor product formed (**4b**) has different mass fragments to those of **2b** and **3b**. In its ^{19}F NMR spectrum it shows a signal at δ −184.5 ppm (dm), in its proton NMR three signals at lower field: δ 6.09 ppm (two olefinic protons), δ 4.6 ppm (dt, corresponding to a proton bonded at the same carbon as the F atom) and δ 4.0 ppm (s, corresponding to a proton bonded at the same C atom as the Cl atom). From the data, we propose the structure of **4b** as 2-*exo*-fluoro-7-chloronorbornene-5. However, from the data just described we were unable to make a decision about the stereochemistry at C7. In order to establish this, we converted product **4b** to previously synthesised 2-*exo*-fluoro-7-*syn*-chloronorbornane (**5a**) by catalytic hydrogenation.[1]

The fluorination of norbornadiene with xenon difluoride in the presence of polyhydrogen fluoride-pyridine also resulted in three products (**2c**, **3c**, **4c**) with relative yields as stated in Scheme 2. Products **2c** and **3c** have very similar mass spectra, while **4c** has the same molecular peak *m*/*e* 130 but different mass fragments. Product **2c** shows in its ^{19}F NMR spectrum two doublets (δ = 201.8 ppm and δ = 213 ppm, corresponding to *exo*- and *endo*-bonded fluorine) and in its ^1H NMR spectrum two

Table 1.



X	δF	δH_3	δH_5
F	−201.4	4.53	4.53
Cl	−195	4.51	3.81
Br	−194.25	4.54	3.87



X	δF	δH_3	δH_5
F	−201.8	4.74	5.22
Cl	−200.25	4.72	4.42
Br	−200.25	4.75	4.55

doublets at lower field ($\delta = 5.22$ ppm and $\delta = 4.74$ ppm, corresponding to *exo*- and *endo*-bonded protons). Product **3c** shows in its ^{19}F NMR spectrum one doublet signal at $\delta = -201.4$ ppm, corresponding to *exo*-bonded F atoms, and in its ^1H NMR a doublet signal at lower field at $\delta = 4.53$ ppm corresponding to the two *endo*-bonded protons. On the basis of the data, we have established the structure of **2c** as 3-*endo*-5-*exo*-difluoronortricyclane and of **3c** as 3-*exo*-5-*exo*-difluoronortricyclane. The minor product formed (**4c**) shows in its ^{19}F NMR spectrum one doublet of doublet signal at δ − 180 ppm and one multiplet signal at $\delta = -187.5$ ppm, and in its ^1H NMR three signals at lower field: a multiplet signal at $\delta = 6$ ppm (two vinyl protons), a doublet of triplet signal at $\delta = 4.6$ ppm ($J = 60$ Hz). We propose the structure of **4c** as 2-*exo*-7-difluoronorbornene-5. However, from the data we were unable to make a decision about the stereochemistry at C7. In order to establish this, we converted product **4c** into previously synthesised 2-*exo*-7-*syn*-difluoronorbornane (**5b**) by catalytic hydrogenation.[4]

The reaction pathways leading to the products formed by halofluorination are presented in Scheme 3. In all cases *endo*- and *exo*-β-halo substituted carbonium ions are formed. Both cations are transformed to halonortricyclyl cations which are attacked by a fluorine anion, thus forming halofluorides **2** and **3**. In a polyhydrogen fluoride-pyridine-ether solution, fluorine anion attack on the halonortricyclyl cation is exclusively *exo*. The formation of the products **4b** and **4c** could be explained by Meerwein–Wagner rearrangement of halocarbonium ions formed by *exo*-attack of the electrophile.

It is very interesting that Meerwein–Wagner rearrangement occurs only in the case of chlorine or fluorine halo-substituents and β-substituted carbonium ions, formed by an *exo*-attack of the electrophile. From the data stated in Scheme 2 it can be seen that *exo*-attack by the electrophile on norbornadiene is slightly predominant (65% X = Br, 73% X = F) over *endo*-attack.

EXPERIMENTAL

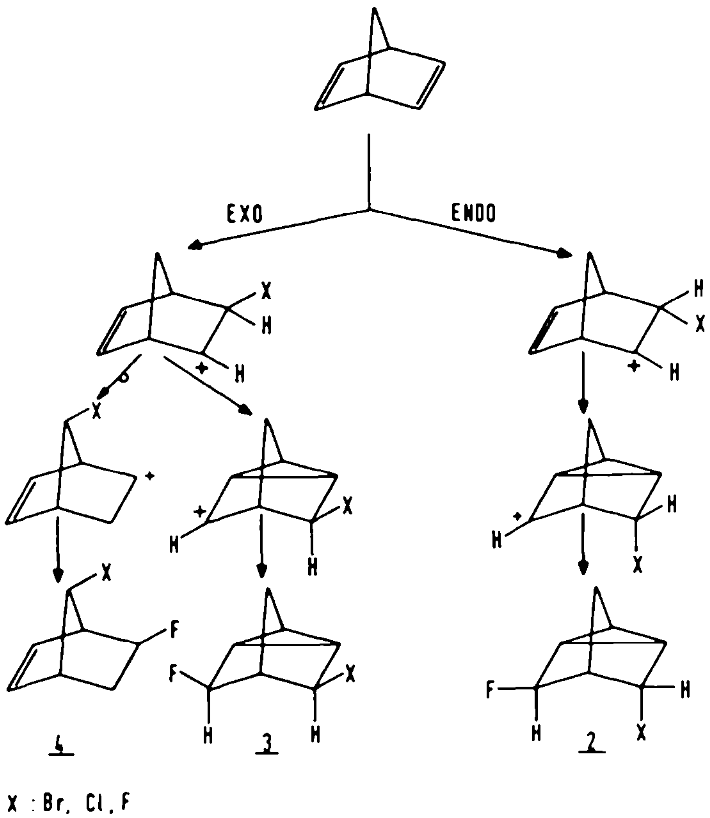
I.R. spectra were recorded with a Perkin–Elmer 257 spectrometer, and ^1H and ^{19}F NMR spectra with a JEOL JMN-PS-100 (CCl_4 as solvent and Me_4Si or CCl_3F as internal reference). Mass spectra and high resolution measurements were obtained with a CEC- 21-110 spectrometer. Glc was carried out with a Varian Aerograph 1800 instrument.

Materials. Commercially available norbornadiene and norbornene were purified before use. Polyhydrogen fluoride-pyridine soln was prepared according to Olah *et al.*,[3] xenon difluoride was prepared by a photosynthetic method[4] and its purity was better than 99.5%.

Addition and isolation procedures

Bromo- and chlorfluorination of norbornadiene. In a mixture of 70% HF-pyridine (2 ml) and ether (2 ml), NBS or NCS (1.4 mmol) was dissolved with stirring at m = 0° and then norbornadiene (1 mmol) was added. The mixture was stirred for 1 hr at 15°, then poured into ice water and extracted with ether. The ether layer was washed with water, $NaHCO_3$ aq and water again, dried (Na_2SO_4) and evaporated. The NMR data were taken on the crude mixture. This was analyzed by glc (Carbowax, 20M–25%, Varaport 30 70/80, T − 160°). The products were separated by preparative glc, and NMR, mass and IR spectra were taken.

3 - endo - *Bromo* - 5 - exo - *fluoronortricyclane* (**2a**), yield 20% of liquid product, NMR (CCl_4): δ $CBr\underline{H}_{exo}$ 4.55 ppm(s), δ $CF\underline{H}_{endo}$ 4.75 ppm(d), δ $CH\underline{F}_{exo}$ −200.25 ppm(d), $J_{FH} = 60$ Hz, mass spectra calcd. for C_7H_8BrF 189.9794. Found: 189.9792, *m/e*



Scheme 3.

192(M^+ + 2, 4%), 190(M^+, 4), 111(100), 109(27), 91(58), 65(12). Calc. for C_7H_8BrF: C, 44.01; H, 4.22%). Found: C, 44.42; H, 4.53.

3 - exo - *Bromo* - 5 - exo - *fluoronortricyclane* (**3a**), yield 50% of liquid product, NMR (CCl_4): δ CBr$\underline{H}_{endo}$ 3.87 ppm(s), δ CF$\underline{H}_{endo}$ 4.54 ppm(d), δ CH$\underline{F}_{exo}$ −194.25 ppm(d), J_{FH} = 60 Hz, mass spectra calc. for C_7H_8BrF 189.9794. Found: 189.9793, *m/e* 192(M^+ + 2, 4%), 190(M^+, 3), 111(100), 109(22), 91(35), 65(10). (Found: C, 44.13; H, 4.32. Calc. for C_7H_8BrF: C, 44.01; H, 4.22%).

3 - endo - *Chloro* - 5 - exo - *fluoronortricyclane* (**2b**), yield 20% of liquid product, NMR (CCl_4): δ CCl$\underline{H}_{exo}$ 4.42 ppm(s), δ CF$\underline{H}_{endo}$ 4.75 ppm(d), δ CH$\underline{F}_{exo}$ −200.25 ppm(d), J_{FH} = 60 Hz, mass spectra calc. for C_7H_8ClF 146.0296. Found: 146.0296, *m/e* 148(M^+ + 2, 13%), 146 (M^+, 40), 111(100), 109(57), 91(84), 84(24), 83(20), 79(45), 66(32), 51(22). Found: C, 57.01; H, 5.70. Calc. for C_7H_8ClF: C, 57.36; H, 5.50%).

3 - exo - *Chloro* - 5 - exo - *fluoronortricyclane* (**3b**), yield 40% of liquid product, NMR (CCl_4): δ CCl$\underline{H}_{endo}$ 3.81 ppm(s), δ CF$\underline{H}_{endo}$ 4.51 ppm(d), δCH$\underline{F}_{exo}$ −195 ppm(d), J_{FH} = 60 Hz, mass spectra calc. for C_7H_8ClF 146.0296, found 146.0299, *m/e* 148 (M^+ + 2, 12%), 146(M^+, 38), 111(100), 109(67), 97(35), 91(88), 84(54), 79(98), 66(47), 51(30). Found: C, 56.93; H, 5.41. Calc. for C_7H_8ClF: C, 57.36; H, 5.50%).

2 - exo - *Fluoro* - 7 - syn - *chloronorbornene* - 5 (**4b**), yield 3% of liquid product, NMR (CCl_4): δ CH$\underline{F}_{exo}$ −184.5 ppm(dm), δ CF$\underline{H}_{endo}$ 4.6 ppm(dt), δ CCl$\underline{H}$ 4.0 ppm(s), δH_5, H_6 6.09 ppm(m), δ H_1 3.1 ppm(m), δH_4 2.9 ppm(m), δ H_3 2.1 ppm (dm), 1.9(m), mass spectra (Found: 146.0307, *m/e* 148(M^+ + 2, 8%), 146(M^+, 25), 111(26), 109(32), 102(27), 100(81), 97(26), 91(34), 79(100), 65(49), 51(19). Calc. for C_7H_8ClF: 146.0296,.

Halofluorination was repeated three times and the average product distributions are stated in Scheme 2. To test the stability of the halofluorination products in the reaction mixture, a sample (0.1 g) containing 2, 3 or 4 was added to 70% HF-pyridine (2 ml), ether (2 ml) and NBS or NCS (0.2 mmol) and the mixture was stirred at 20° for 1 hr. After work-up, the NMR spectra showed no significant differences.

Fluorination of norbornadiene

In a mixture of 70% HF–pyridine (2 ml) and ether (2 ml), 1 mmol of norbornadiene was dissolved at 25° and under stirring 1 mmol of xenon difluoride was added. After 30 min gas evolution had ceased and the reaction appeared to be complete; the mixture was poured into ice water and extracted with ether. The ether was washed with water, $NaHCO_3$ aq, then water again, dried (Na_2SO_4) and evaporated. The crude mixture was analyzed by NMR and glc (the relative yields of the products are stated in Scheme 2). The mixture was purified by preparative glc (Carbowax, 20M-25%, Varaport 30 70/80, 160°). The products were separated by preparative glc and mass, NMR and ir spectra were taken.

3 - endo - 5 - exo - *Difluoronortricyclane* (**2c**), yield 35% of waxy solid product, mp(sealed capillary) 75–76°, NMR (CCl_4): δ F_{exo} −201.8 ppm(d), J_{FH} = 60 Hz, δ F_{endo} − 213 ppm(d), J_{FH} = 60 Hz, δ CF$\underline{H}_{exo}$ 5.22 ppm(d), δ CF$\underline{H}_{endo}$ 4.74 ppm(d), mass spectrum. Calc. for $C_7H_8F_2$: *m/e* 130.0594. Found: 130.0597, *m/e* 130(M^+, 58%), 115(53), 109(30), 97(100), 84(35), 79(65). (Found: C, 64.65; H, 6.08. Calc. for $C_7H_8F_2$: C, 64.61; H, 6.18%).

3,5-*Di*-exo-*difluoronortricyclane* (**3c**), yield 30% of waxy solid product, mp(sealed capillary) 76–77°, NMR (CCl_4): δ F−201.4 ppm(d), δ CF$\underline{H}$ 4.53 ppm(d), J_{FH} = 60 Hz, mass spectra Calcd. for $C_7H_8F_2$: 130.0594. Found: 130.0597, *m/e* 130(M^+, 35%), 115(45), 109(25), 97(100), 84(38), 79(57). (Found: C, 64.33; H, 5.95. Calc. for $C_7H_8F_2$: C, 64.61; H, 6.19%).

2 - exo - 7 - syn - *Difluoronorbornene* - 5(**4c**), yield 6% of waxy solid product, m.p. (sealed capillary) 82–83°, NMR (CCl_4): δ F_2 − 187.5 ppm(m), δ F_7 − 180 ppm(dd), δ CF$\underline{H}_2$ 4.74 ppm(dt), δ CF$\underline{H}_7$ − 4.6 ppm(d), δ C$\underline{H}$ 6.0 ppm(m, 2H), J_{F7H7} = 60 Hz, J_{F-H} = 12 Hz, J_{F2H2} = 57 Hz, mass spectrum calc. for $C_7H_8F_2$ *m/e* 130.0594, found 130.0589, *m/e* 130(M^+ 25%), 109(10), 97(18), 84(100), 79(65).

Hydrogenation of 2-exo-*fluoro*-7-syn-*halonorbornene*-5 (**4b**, **4c**)

[Compound **4b** or **4c** (0.5 mmol) was dissolved in 3 ml MeOH, 0.3 g of 10% Pd–C was added and stirred at room temp. under H_2. After 0.5 mmol of H_2 had reacted, the catalyst was filtered off and the mixture was analyzed by glc. The retention time of the product formed above was identical to that of **5a**[3] in the case of **4b**, and to that of **5b**[4] in the case of **4c**. The NMR spectra of **5a** and **5b** were identical to those of indepenently prepared compounds.[3,4]

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