HALOFLUORINATION OF NORBORNENE AND BENZONORBORNENE*

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Halofluorination of norbornene (*I*) with xenon difluoride or N-chlorosuccinimide or N-bromosuccinimide in the presence of polyhydrogen fluoride–pyridine results in the formation of five products: halonortricyclane (*II*), 2-*exo*-fluoro-7-*anti*-halonorbornane (*III*), 2-*exo*-fluoro-5-*endo*-halonorbornane (*IV*), 2-*exo*-fluoro-5-*exo*-halonorbornane (*V*) and 2-*exo*-fluoro-7-*syn*-halonorbornane (*VI*). Relative yields of the products depend on the reagent. Halofluorinations of benzonorbornene (*VII*) results in the formation of 2-*exo*-fluoro-7-*syn*-halobenzonorbornane (*VIII*).

Available data on the stereochemistry of addition of "BrF" species are sparse. In the steroids[1], stereospecific *anti*-addition with anti-Markovnikov type regioselectivity is observed. On the other hand, bromofluorination of carbohydrates[2] is stereospecifically *syn*. Using polyhydrogen fluoride–pyridine in conjunction with N-bromosuccinimide or N-chlorosuccinimide for fluorination of aliphatic olefins, Olah and his coworkers[3] observed a typical Markovnikov type regioselectivity. Bromofluorination of phenyl-substituted olefins, *e.g.* 1,1-diphenyletens, β-alkylstyrenes, proceeds with Markovnikov type regioselectivity. The reaction is stereospecific *anti* for *trans* and nonstereospecific for *cis* olefins[4].

The reaction of the bicyclic olefin norbornene (*I*) has been used as a mechanistic probe to elucidate the mechanism and stereochemistry of various reactions[5]. From the identification of the products it is possible to differentiate between the possible mechanistic pathways leading to those products, *i.e.*: i) a concerted *cis* molecular addition, ii) a free radical reaction, or iii) a reaction path proceeding *via* cationic intermediates. In this publication we would like to report our work on the mechanism of halofluorination of two unsaturated systems with xenon difluoride, N-bromo- or N-chlorosuccinimide in the presence of polyhydrogen fluoride–pyridine.

The preparation of fluoro alkanes presents a different problem from other halogeno alkanes and necessitates a specific method of fluorination[6]. Halofluorination with polyhydrogen fluoride–pyridine avoids some experimental difficulties[3], *e.g.*: low temperature, high pressure techniques, and polymerisation of olefins. Olah with coworkers[3] has observed in the reactions of chlorofluorination or bromofluorination

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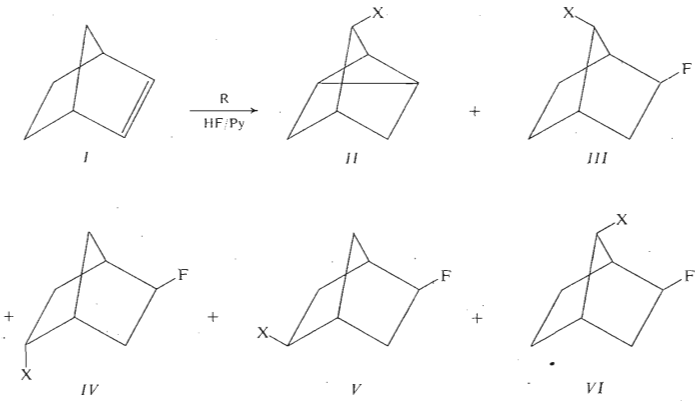
of norbornene the formation of only two products: 2-*exo*-fluoro-7-*anti*-halonorbornane and 2-*exo*-fluoro-7-*syn*-halonorbornane. On the other hand, in low temperature bromofluorination the formation of three products was observed[7]. By the fluorination of norbornene with xenon difluoride and a catalytic amount of hydrogen fluoride in dichloromethane at room temperature, we have isolated seven products[8]; fluoronortricyclane (*II*), 2-*exo*-7-*anti*-difluoronorbornane (*III*), 2-*exo*-5-*endo*-difluoronorbornane (*IV*), 2-*exo*-5-*exo*-difluoronorbornane (*V*), 2-*exo*-7-*syn*-difluoronorbornane (*VI*) and 2-*exo*-3-*exo*-difluoronorbornane and 2-*exo*-3-*endo*-difluoronorbornane. Similar dihalides were also observed by the bromination of norbornene under ionic conditions[9].



Relative Yields by GLC

R[a]	X	*II*	*III*	*IV*	*V*	*VI*
XeF_2	F	14	35	19	10	22
NCS	Cl	26	31	3	2	38
NBS	Br	20	37	5	3	35

[a] NBS N-Bromosuccinimide, NCS N-chlorosuccinimide.

SCHEME 1

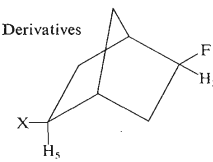
A 1-h reaction of norbornene with xenon difluoride in the presence of polyhydrogen fluoride–pyridine in ether solution at room temperature resulted in the formation of five products. Analysis of the reaction mixture by GLC gave the relative yields listed in Scheme 1. The products of the reaction were collected by preparative GLC. The structures of the compounds were determined on the basis of their mass, ^{19}F- and ^{1}H-NMR spectra. The products formed in the reaction were fluoronortricyclane (*II*), 2-*exo*-7-*anti*-difluoronorbornane (*III*), 2-*exo*-5-*endo*-difluoronorbornane (*IV*), 2-*exo*-5-*exo*-difluoronorbornane (*V*), and 2-*exo*-7-*syn*-difluoronorbornane (*VI*). (The numbering of the products is in the order of increasing retention times). One can see that the retention times of the products are in the same order as those observed for dibromides by the bromination of norbornene[9]. Products *II*, *III* and *VI* are known[10], while products *IV* and *V* have very similar mass spectra with very small differences in the peak intensities. The similarity in fragmentations led us to the conclusion that *IV* and *V* are isomeric compounds. Compound *V* shows in its ^{19}F-NMR spectrum a multiplet at $\delta = -181{\cdot}5$ ppm and in its ^{1}H-NMR spectrum a doublet of multiplet signal at lower field at $\delta = 4{\cdot}88$ ppm, corresponding to two protons. The chemical shift for the two fluorine atoms corresponds to *exo*-bonded fluorine, while the chemical shifts for lower field protons correspond to the two *endo*-bonded protons. On the other hand, in the ^{19}F-NMR spectrum of compound *IV* we observed two signals; the first at $\delta = -175{\cdot}1$ ppm (dm) and the second at $\delta = -207{\cdot}8$ ppm (dddt), and in its ^{1}H-NMR spectrum we observed two signals at lower field; the first at $\delta = 5{\cdot}16$ ppm (dd) and the second at $\delta = 4{\cdot}89$ ppm (d). The fluorine atom at the lower field is *exo* and the one at higher field is *endo* bonded The proton at lower field corresponds to an *exo* and that at higher field to an *endo*-bonded proton. On the basis of the NMR and mass spectral data, we have assigned the structure of products *V* as 2-*exo*-5-*exo*-difluoronorbornane and the structure of products *IV* as 2-*exo*-5-*endo*-difluoronorbornane. It is interesting that under these reaction conditions only five products were formed, while fluorination in the presence of only catalytic amounts of hydrogen fluoride resulted in seven products[8].

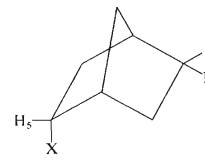
Chlorofluorination of norbornene with N-chlorosuccinimide in the presence of polyhydrogen fluoride–pyridine resulted in the formation of five products. Analysis of the reaction mixture by GLC gave the relative yields listed in Scheme I. The products of the reaction were collected by preparative GLC and their structures were determined on the basis of their mass, ^{19}F and ^{1}H-NMR spectra. The products formed in the reaction were chloronortricyclane (*II*), 2-*exo*-fluoro-7-*anti*-chloronorbornane (*III*), 2-*exo*-fluoro-5-*endo*-chloronorbornane (*IV*), 2-*exo*-fluoro-5-*exo*-chloronorbornane (*V*) and 2-*exo*-fluoro-7-*syn*-chloronorbornane (*VI*). (The numbering of the products is in the order of increasing retention times). Products *II*, *III* and *VI* are known[11,3], while products *IV* and *V*, formed in very low yield, have very similar mass spectra: m/e 148 (M^+), 113, 86, 85, 67, with very little differences in the intensities of peaks. The similarity in fragmentation led us to the conclusion

that *IV* and *V* are isomeric compounds. Product *IV* shows in its ^{19}F-NMR spectrum one signal at $\delta = -162{\cdot}75$ ppm (m) and in its proton spectrum two signals at lower field, the first at $\delta = 4{\cdot}57$ ppm (dd) and the second at $\delta = 4{\cdot}06$ ppm (m). Comparison of the NMR data with other 2,5-disubstituted norbornane derivates is shown in Table I. Product *V* shows in its ^{19}F-NMR spectrum a signal at $\delta = 167{\cdot}25$ ppm (m) and in its ^{1}H-NMR spectrum two signals at lower field at $\delta = 4{\cdot}39$ ppm (dm) and at $\delta = 3{\cdot}66$ ppm (m). On the basis of the mass spectra and comparison of the NMR data (Table I), we have assigned the structure of the product *IV* as 2-*exo*-fluoro-5--*endo*-chlorononorbornane and of the product *V* as 2-*exo*-fluoro-5-*exo*-chlorononorbornane.

Bromofluorination of norbornene with N-bromosuccinimide in polyhydrogen fluoride–pyridine also resulted in the formation of five products. Analysis of the reaction mixture gave the relative yields listed in Scheme 1. The products of the reaction were collected by preparative GLC and their structures were determined on the basis of their mass, ^{19}F and ^{1}H-NMR spectra. The products formed in the reaction were: bromonortricyclane (*II*), 2-*exo*-fluoro-7-*anti*-bromonorbornane (*III*), 2-*exo*-fluoro--5-*endo*-bromonorbornane (*IV*), 2-*exo*-fluoro-5-*exo*-bromonorbornane (*V*) and 2-*exo*--fluoro-7-*syn* bromonorbornane (*VI*). (The numbering of the products is in the order of increasing retention times). Products *II*, *III* and *VI* are known[7,3], while products *IV* and *V*, formed in very low yield, have very similar mass spectra: *m/e* 192 (M^+), 113, 67, 57, 44, 43, with very little differences in the intensities of peaks. The similarity in fragmentation led us to the conclusion that *IV* and *V* are isomeric compounds. Products *IV* and *V* show very similar NMR spectra to those obtained by chlorofluorination (Table I). Product *IV* shows in its ^{19}F-NMR spectrum one signal at $\delta =$

TABLE I
NMR-Data of the 2,5-Dihalo Derivatives





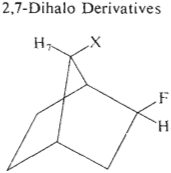
X	δF	δH$_2$	δH$_5$	X	δF	δH$_2$	δH$_5$
F	−181·5	4·88	4·88	F	−175·1	4·89	5·16
Cl	−167·25	4·39	3·66	Cl	−162·75	4·57	4·06
Br	−167·25	4·5	3·75	Br	−163·5	4·57	4·1

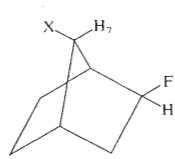
= −163·5 ppm (m) and its proton spectrum two signals at lower field; the first at $\delta = 4{\cdot}57$ ppm (dd) and the second at $\delta = 4{\cdot}1$ ppm as a broad singlet. Product *V* shows in its ^{19}F-NMR spectrum a signal at $\delta = -167{\cdot}25$ ppm (m) and in its proton spectrum two signals at lower field; the first at $\delta = 4{\cdot}5$ ppm (dd) and the second at $\delta = 3{\cdot}75$ ppm (d). On the basis of the mass spectra and comparison of the NMR data (Table I), we have assigned the structure of the product *IV* as 2-*exo*-fluoro-5-*endo*--bromonorbornane and of the product *V* as 2-*exo*-fluoro-5-*exo*-bromonorbornane. From the data listed in Table I we can see that the values of ^{19}F chemical shifts of products *IV* and *V* are very similar and characteristic for an *exo* bonded fluorine. The values of the ^{1}H chemical shift of the proton bonded at the same carbon atom as the fluorine atom are also nearly the same in both isomers and are characteristic for an *endo* bonded proton. On the other hand the signal in the ^{1}H-NMR spectrum corresponding to the other proton at lower field occurs in the case of isomer *IV* at lower field than that of isomer *V*. Differences are characteristic for an *exo* and *endo*--bonded proton. It is also known from the literature[12] that *exo*-bonded protons appear at lower field in ^{1}H-NMR spectrum than *endo*-bonded protons.

In Table II we have summarized characteristic NMR data for 2-*exo*-fluoro-7-*syn*--halonorbornane and 2-*exo*-fluoro-7-*anti*-halonorbornane. We can see great differences in chemical shifts for the *endo* bonded proton at $C_{(2)}$ depending on the stereochemistry at $C_{(7)}$ in the case of difluoronorbornane; the signal for the proton in the *syn* isomer appears at lower field than that in the *anti* isomer. However, in the case of a bromo or chloro substituent at $C_{(7)}$ there are no differences. More significant are differences in the chemical shifts of $H_{(7)}$, appearing in the *anti* isomer at lower

TABLE II

NMR Data of the 2,7-Dihalo Derivatives

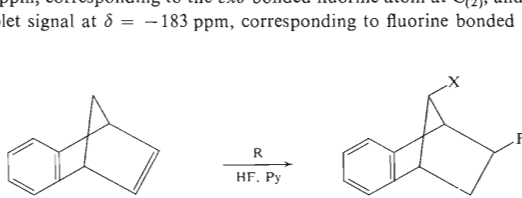




X	δF	δH$_2$	δH$_7$	X	δF	δH$_2$	δH$_7$
F	−179·5	5·1	5·2	F	−176·2	4·28	5·48
Cl	−163·5	4·51	3·8	Cl	−162·75	4·51	4·18
Br	−162	4·5	3·78	Br	−162·75	4·5	4·18

field than in the *syn* isomer, which could be explained by the through-space interaction of *exo* bonded $F_{(2)}$ on $H_{(7)}$ in the *anti* isomer *III*.

Fluorination of benzonorbornene (*VII*) with xenon difluoride in the presence of polyhydrogen fluoride–pyridine, and also chlorofluorination and bromofluorination, results in the formation of only one product *VIII* (Scheme 2). Mass spectra of the products indicate that halo fluorides are formed. Difluoride *VIII* formed in the fluorination shows two signal in its ^{19}F-NMR spectrum: a multiplet signal at $\delta = -182{\cdot}25$ ppm, corresponding to the *exo*-bonded fluorine atom at $C_{(2)}$, and a doublet of doublet signal at $\delta = -183$ ppm, corresponding to fluorine bonded at $C_{(7)}$.



VIII

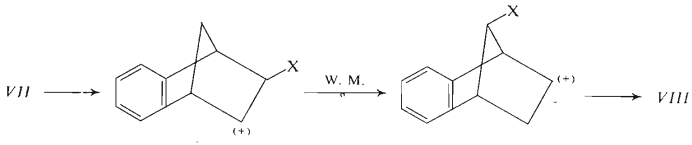
R[a]	X	δF	δH_2	δH_7
XeF_2	F	−182.25	4.75	4.70
NCS	Cl	−179.25	4.68	3.99
NBS	Br	−177.75	4.74	4.11

[a] NBS N-Bromosuccinimide, NCS N-chlorosuccinimide.

SCHEME 2

However, from the data just described we were unable to make a decision about the stereochemistry at the position $C_{(7)}$. A comparison of characteristic NMR data of 2-*exo*-7-*syn* and 2-*exo*-7-*anti*-difluoronorbornane and 2-*exo*-7-*syn*-difluoronorborn-4-ene is given in Table III. We can see very similar values for the chemical shifts of $F_{(7)}$, $H_{(2)}$ and $H_{(7)}$ in the case of 2-*exo*-7-*syn*-difluoronorborn-4-ene (the stereochemistry at $C_{(7)}$ was determined on the basis of catalytic hydrogenation[8] compared to its effects on *VIII*). On the basis of similarity in the NMR spectra, we have established the structure of *VIII* as 2-*exo*-7-*syn*-difluorobenzonorbornane. The products formed by chlorofluorination and bromofluorination have very similar NMR data (Scheme 2) and a comparison of the chemical shifts of 2-*exo*-fluoro-7-chlorobenzonorbornane (*VIII*) to those of 2-*exo*-fluoro-7-*syn* (*VI*) and 2-*exo*-fluoro-7-*anti* chloro norbornane and 2 *exo*-fluoro-7-*syn*-chloronorborn-4-ene is presented in Table III.

The agreement between δH_2, δH_7 and δF_2 is also observed in the case of 2-*exo*-fluoro-7-*syn*-chlorononborn-4-ene and the product *VIII*. On the basis of the above mentioned data, we have established the structure of *VIII* as 2-*exo*-fluoro-7-*syn*-halobenzonorbornane. An explanation of the formation of 2-*exo*-fluoro-7-*syn*-halobenzonorbornane is presented in Scheme 3. The primarily formed β-halocarbonium ions undergo Meerwein–Wagner rearrangement, resulting, after the exo nucleophilic atack of fluoride anion, in corresponding products.



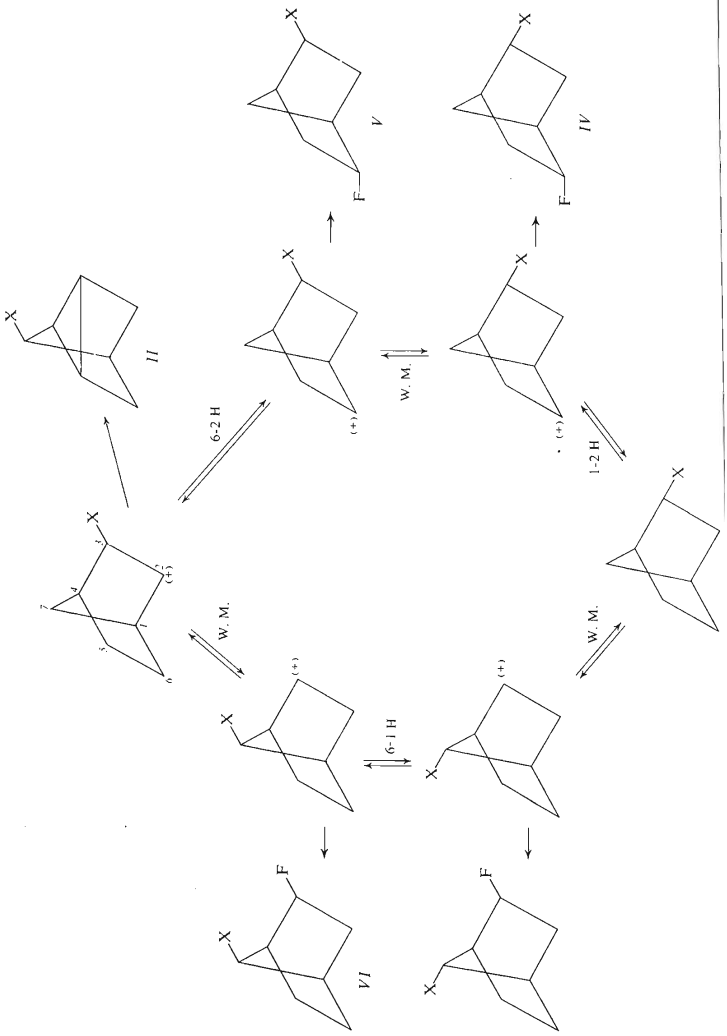
SCHEME 3

If we now compare the product distribution of the halofluorination of norbornene (Scheme 1), we can see that products *III* and *VI* are major products. On the other hand, the formation of low amounts of products *IV* and *V* in the case of chloro- and bromofluorination is observed. The formation of halonortricyclane (*II*) also depends on the nature of the electrophile. However, we have observed that fluorononortricyclane is very unstable under the reaction conditions and is easily transformed to the products *III* – *VI*. Transformations of chloro- and bromonortricyclane into the products

TABLE III

NMR Data Comparison of 2-*exo*-Fluoro-7-*syn*-halobenzonorbornane (*VIII*), 2-*exo*-Fluoro-7-*syn*-halonorborn-4-ene (*A*), 2-*exo*-Fluoro-7-*syn*-halonorbornane (*VI*) and 2-*exo*-Fluoro-7-anti-halonorbornane (*B*)

X	Shift	*VIII*	*A*	*VI*	*B*
F	F_2	−182·25	−187·5	179·5	−176·2
	F_7	−183	−180	−223·5	−232·3
	H_2	4·75	4·74	5·1	4·28
	H_7	4·70	4·6	5·21	5·48
Cl	F_2	−179	−184·5	−163·5	−162·75
	H_2	4·68	4·6	4·51	4·51
	H_7	3·99	4·0	3·8	4·18


X
II
6-2 H
W. M.
1-2 H
W. M.
6-1 H
W. M.
(+)
F
V
IV
VI

III – *VI* were also observed, yet they occured to a lower degree in this case. These facts must be taken into account when interpreting the products distribution in Scheme 1. The mechanism of formation of five products formed by halofluorination of norbornene is presented in Scheme 4. Primarily formed β-halocarbonium ions undergo either a Meerwein–Wagner rearrangement or 6,2-hydride shift, resulting, after an *exo* attack by the fluorine anion, in products *V* and *VI* respectively; *via* further hydride shifts (1,2; 1,6; 6,1; 2,1) and Meerwein–Wagner rearrangements, the formation of products *III* and *IV* is explained. However, when interpreting the formation of difluorides in the reaction of xenon difluoride with norbornene, the irreversible hydride shifts 6,2 and 1,2, based on the observation of isomerization of the products in dichlormethylene and in the presence of hydrogen fluoride, where similar carbonium ions are formed[8], must be taken into account.

EXPERIMENTAL

IR spectra were recorded with a Perkin–Elmer 257 spectrometer, and 1H- and ^{19}F-NMR spectra with a JEOL JNM-PS-100 (CCl_4 as solvent and $(CH_3)_4Si$ 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.

A solution of polyhydrogen fluoride–pyridine was prepared according to[3]. N-Bromo- and N-chlorosuccinimide (Fluka) were crystallised and dried (P_2O_5) before use. Xenon difluoride was prepared by a photosynthetic method[13] and its purity was better than 99·5%. Benzonorbornene was prepared according to[14], and norbornene (Fluka) was purified before use.

Fluorination with Xenon Difluoride

In a mixture of 70% hydrogen fluoride (2 ml) and ether (2 ml), 1 mmol of olefin was dissolved with stirring at 0°C and 1 mmol of XeF_2 was added. The mixture was stirred for 1 h at 15°C, then poured into ice-water and extracted with ether. The ether layer was washed with water, aqueous sodium hydrogen carbonate, and water, dried (Na_2SO_4) and evaporated. The crude reaction mixture was analysed by GLC and NMR and the products were separated by preparative GLC.

Fluorination of Norbornene

The products were separated by preparative GLC (DDP-10%, Cromosorb Regular 100, Temperature 45–120°C):

Fluoronortricyclane (I): yield 8%, mp. 44–45°C sealed capillary; (lit.[10] 48–50°C, NMR $\delta F = -218$ ppm (dt), δCHF 5·05 ppm (dt), $J_{FH} = 69$ Hz); the NMR spectrum is similar to the product synthezed from norbornadiene and HF.

2-exo-7-anti-*Difluoronorbornane* (III): yield 22% of volatile, waxy product, m.p. 101–102°C (sealed capillary), lit.[10] 107–110°C, mass spectrum: calculated 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). For $C_7H_{10}F_2$ (132·1) calculated: 63·60% C, 7·63% H; found: 63·44% C, 7·70% H.

2-endo-5-exo-*Difluoronorbornane* (IV): yield 13% of volatile, waxy product; m.p. 82—84°C (sealed capillary); 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* (V): yield 7% of waxy solid, m.p. 96—98°C (sealed capillary); mass spectrum calculated for $C_7H_{10}F_2$ *m/e* 132·0750, found 132·0750, *m/e* 132 (M^+ 10%), 99 (10), 86 (100), 85 (78). For $C_7H_{10}F_2$ (132·1) calculated: 63·60% C, 7·63% H; found: 63·63% C, 7·70% H.

2-exo-7-syn-*Difluoronorbornane* (VII): yield 15% of volatile, waxy solid, m.p. 116—119°C (sealed capillary), lit.[10] 95—97°C; mass spectrum: calculated for $C_7H_{10}F_2$ *m/e* 132·0750, found *m/e* 132·0752. For $C_7H_{10}F_2$ (132·1) calculated: 63·60% C, 7·63% H; found: 63·32% C, 7·40% H.

Fluorination of Benzonorbornene

2-exo-7-syn-*Difluorobenzonorbornane* (VIII) was purified by preparative GLC (Se-30, Chrom A/AW 45/60 10%, at 150°C, yield of waxy solid, m.p. 40—43°C (sealed capillary) mass spectrum calcd. for $C_{11}H_{10}F_2$ *m/e* 180·0750, found: 180·0755, *m/e* 180 (M^+ 88%), 159 (47), 147 (76), 146 (62), 134 (100), 133 (89), 129 (87), 116 (50), 115 (55).

Halofluorination with N-Chlorosuccinimide or N-Bromosuccinimide

In a mixture of 70% hydrogen fluoride (2 ml) and ether (2 ml), N-bromo or N-chlorosuccinimide (1·4 mmol) was dissolved with stirring at 0°C, and the olefin (1 mmol) was added. The mixture was stirred for 1 h at 15°C, poured into ice-water and extracted with ether. The ether layer was washed with water, aqueous sodium hydrogen carbonate, and water, dried (Na_2SO_4), and evaporated. After separation by preparative GLC, NMR, mass and IR spectra were taken.

Chlorofluorination of Norbornene

Products were separated by preparative GLC (DDP-10%, Chromosorb Regular 100, temperature 130—150°C).

Chloronortricyclane (II): yield 18% of a liquid, the spectroscopic data are similar to the product synthesized from norbornene and chlorine[11].

2-exo-*Fluoro*-7-anti-*chloronorbornane* (III): yield 23% of a liquid; mass spectrum calculated for $C_7H_{10}ClF$ *m/e* 148·0454; found: 148·0455, *m/e* 148 (M^+, 27%), 133 (100), 106 (22), 99 (62), 86 (43), 79 (55), 72 (26), 67 (88); NMR data are stated in Table II.

2-exo-*Fluoro*-5-endo-*chloronorbornane* (IV): yield 1·5% of a liquid; mass spectrum calculated for $C_7H_{10}ClF$ *m/e* 148·0454; found: 148·0456, *m/e* 148 (M^+, 13%), 113 (10), 86 (100), 85 (60), 67 (38); NMR data are stated in Table I.

2-exo-*Fluoro*-5-exo-*chloronorbornane* (V): yield 1% of liquid product, mass spectrum calcd. for $C_7H_{10}ClF$ *m/e* 148·0454; found: 148·0456 *m/e* 148 (M^+, 10%), 113 (10), 86 (54), 85 (40), 67 (42), 58 (100); NMR data are stated in Table I.

2-exo-*Fluoro*-7-syn-*chloronorbornane* (VI): yield 29% of a liquid; mass spectrum calculated for $C_7H_{10}ClF$ *m/e* 148·0454; found: 148·0454, *m/e* 148 (M^+, 38%), 113 (100), 106 (24), 99 (68), 86 (42), 81 (73), 79 (62), 72 (31), 67 (87); NMR data are stated in Table II.

Bromofluorination of Norbornene

Products were separated by preparative GLC (DDP-10% Chromosorb Regular 100, temperature 135—150°C).

Bromonortricyclane (II) 15% of a liquid, the spectroscopic data are similar to the product synthesized from norbornene and bromine[9].

2-exo-*Fluoro*-7-anti-*bromonorbornane* (III), yield 22% of a liquid; mass spectrum calculated for $C_7H_{10}BrF$ *m/e* 191·9951; found: 191·9952, *m/e* 194 ($M^+ + 2$, 11%), 192 (M^+, 11), 113 (20), 93 (9), 67 (100), 44 (20); NMR data are stated in Table II, an are in agreement with the literature[7].

2-exo-*Fluoro*-5-endo-*bromonorbornane* (IV), yield 3% of a liquid; mass spectrum calcd. for $C_7H_{10}BrF$ *m/e* 191·9951; found: 191·9943, m/3192 (M^+, 2%; 113 (20), 96 (8), 67 (10), 57 (15), 55 (13), 44 (100), 43 (67); NMR data are stated in Table I.

2-exo-*Fluoro*-5-exo-*bromonorbornane* (V), yield 1·5% of a liquid; mass spectrum calcd. for $C_7H_{10}BrF$ *m/e* 191·9951; found: 191·9946, *m/e*; 192 (M^+, 2%), 113 (23), 96 (7), 67 (15), 57 (13), 55 (12), 44 (10), 44 (10), 43 (58); NMR data are stated in Table I.

2-exo-*Fluoro*-7-syn-*bromonorbornane* (VI), yield 28% of a liquid; mass spectrum calculated for $C_7H_{10}BrF$ *m/e* 191·9951; found: 191·9948, *m/e* 194 ($M^+ + 2$; 18%), 192 (M^+, 18), 113 (33), 93 (11), 85 (24), 67 (100), 44 (13); NMR data are stated in Table II and are in agreement with the literature[7].

Chlorofluorination of Benzonorbornene (*VII*)

Product was separated by preparative GLC (SE-30, Chrom A/AW 45/60 at 170°C).

2-exo-*Fluoro*-7-syn-*chlorobenzonorbornane* (VIII), yield 72% of a liquid; mass spectrum calculated for $C_{11}H1_0ClF$ 196·0454, found: 196·0460, *m/e*; 196 (M^+, 39), 150 (45), 147 (42), 129 (80), 115 (100); NMR data are stated in Scheme 2 and Table III.

Bromofluorination of Benzonorbornene (*VII*)

Product was separated by preparative GLC (SE-30, Crom A/AW 45/60 10%, at 200°C).

2-exo-*Fluoro*-7-syn-*bromobenzonorbornan* (VIII), yield 76% of a liquid; mass spectrum calculated for $C_{11}H_{10}BrF$ 239·9966, found: 239·9952, *m/e*; 242 ($M^+ + 2$, 7%) 240 (M^+, 7), 129 (48), 115 (83), 110 (100), 64 (59), 63 (47); NMR data are stated in Scheme 2 and Table III.

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