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NEW PROCESSES FOR THE HALOFLUORINATION OF NORBORNADIENE. STRUCTURAL REEXAMINATION OF THE PRODUCTS. EVIDENCE FOR EXCLUSIVE EXO ATTACK BY ELECTROPHILES.

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Summary : The bromofluorination of norbornadiene using NBS in the presence of the new fluorinating agent $Et_3N/3HF$ leads to a 3:2 mixture of 3-exo-bromo-5-exo-fluoronortricyclane 1 and 3-exo-bromo-5-endo-fluoronortricyclane 2. The structures of these compounds were proven by independent syntheses and extensive NMR spectroscopic studies. The structure (3-endo-bromo-5-exo-fluoronortricyclane) given for the minor compound in the literature[10] was revised especially in terms of the comparison of $^3J_{CF}$ coupling constants in the ^{13}C NMR spectra of both compounds. No evidence for an endo attack of the bromonium species on norbornadiene as stated in the literature[10] was observed.

Introduction

The reagents most widely used in the past for the introduction of fluorine atoms into unsaturated molecules were somewhat difficult to handle because of their corrosive nature and toxicity. Usually, special polyethylene or polypropylene equipment and working at low temperatures are necessary when using anhydrous hydrogen fluoride by itself or dissolved in various solvents. These precautions should also be observed with pyridinium poly(hydrogen fluoride) (Olah's reagent) or other combinations with amines[1]. In former papers, we have shown that triethylamine tris-hydrofluoride ($Et_3N/3HF$)[2] is a highly versatile and easy-to handle source of fluoride ions for the introduction of the fluoro substituent by ring opening of various aziridines[3], aziridinium ions[4], epoxides[5,6] as well as for the nucleophilic substitution of sulphonates by fluoride ion[7]. Very recently, we have used this reagent in halofluorination reactions of unsaturated hydrocarbons using respectively N-chloro-, N-bromo- and N-iodo-succinimide, as sources for the halonium ions[8].

We have recently observed that selectivity and/or reaction pathway in ring opening of epoxides[5] or bromofluorination of cycloalka-1,5-dienes[9] depend on the fluorinating agent used. In particular, we have shown that the difference in selectivity between Olah's reagent and the Et_3N, 3HF complex is due to the acidity of the former, while the latter exhibits a nucleophilic character[4,5,9]. It was therefore interesting to compare the Et_3N, 3HF complex with Olah's reagent (or polymer-supported hydrogen fluoride) used by Gregorcic and Zupan[10] as regards the selectivity of the norbornadiene bromofluorination.

Results and discussion

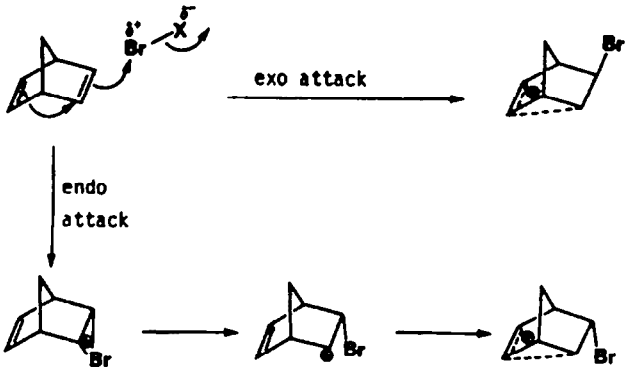
The reaction of norbornadiene with NBS and Et_3N/3HF leads to a mixture of three compounds 1, 2 and 3 (Scheme 1) in a ratio of 53:38:5 and in nearly quantitative yield.

Scheme 1

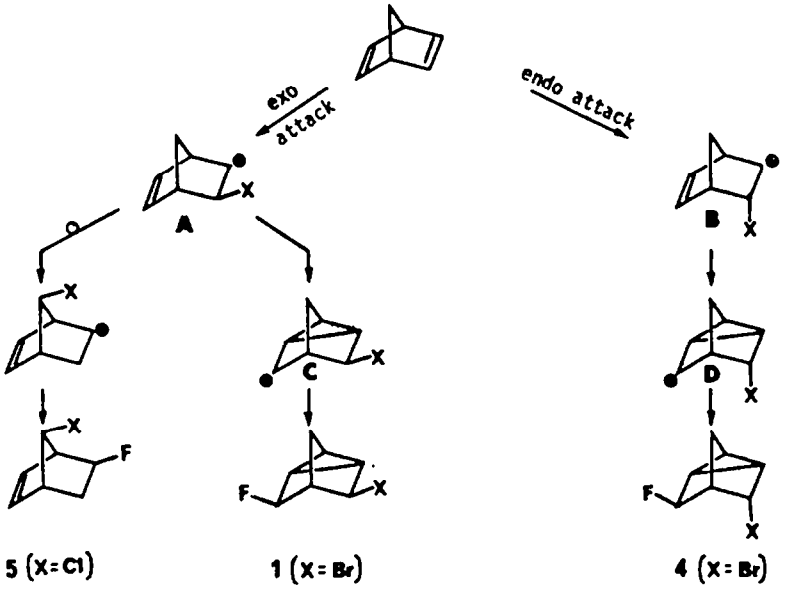
The minor product 3 is a dibromo nortricyclane which was previously known[12] and the main products are bromo fluoro derivatives. The ^1H NMR and especially the ^{13}C NMR spectra are in good agreement with structures 1 and 2. However, Gregorcic and Zupan[10] gave structures 1 and 4 for the products they obtained in the reaction of norbornadiene with NBS/Olah's reagent. We repeated this reaction and found that the two isolated isomeric bromofluoro compounds formed in that way were identical with our compounds 1 and 2, although the product distributions were different. Taking into account our disagreement concerning the structure of the minor bromofluoro compound 2 or 4, it seemed necessary to determine the correct structure by an independant synthesis together with an extensive NMR study because the formation of compound 4 would establish the possibility of an unusual endo-attack of electrophiles on norbornadiene. An endo-attack was only observed in a 5 % yield during the radical addition of bromotrichloromethane to norbornadiene[13]. Actually, in the literature, such electrophiles as bromine[12,14,15], nitrosylchloride[16], phosphorous tribromide[17], peracids[18], chlorosulphonylisocyanate[19,20], sulphur[21], arylsulphenylchlorides[22], chlorosulphamates[23] or arylsulphenylsulphamates[24] gave an exclusive exo-attack. Only the exo-attack allows the participation of the second double bond leading to a homoallylic carbocation without the necessity of the formation of an intermediary α-bromo carbocation (Scheme 2).

The determination of the exact structure 2 or 4 would allows us to answer some questions arising from the mechanism proposed by Zupan (Scheme 3) : why the Wagner-Meerwein like transposition of the cation A leading to compound 5 (X=F or X=Cl) is not observed starting from the cation B and why the bromonium species attacks norbornadiene from exo and endo face while the F^- attacks the

cation D and especially C exclusively from the exo side, since, especially for the latter, no steric hindrance could be claimed to explain such unusual behavior ?



Scheme 2



Scheme 3

We therefore made an extensive structural study of the reaction products especially because no ^{13}C NMR data has been reported for this class of fluorinated compounds.

The ^{13}C NMR spectra (table 1) and in particular the $^{3}J_{CF}$ coupling constants are in good agreement with structures 1 and 2. It is a well-known effect[25] that the coupling constants are maximum for the anti-arrangement of the CCCF

Table 1

^{13}C-magnetic resonance spectral assignments for compounds 1, 2, 3, 6, 8, 9 and 12.

(δ and J_{C-F} values)

Products	C-1	C-2	C-3	C-4	C-5	C-6	C-7
1	13.6 -	23.2 ^3J=6.0	50.2 ^3J=3.1	41.6 ^2J=16.5	93.4 ^1J=196.2	19.4 ^2J=24.9	28.4 -
2	15.9 ^3J=6.7	19.9 -	53.2 -	41.7 ^2J=16.0	97.2 ^1J=190.4	18.3 ^2J=22.9	27.8 ^3J=3.3
3	13.4	22.2	51.0	41.0	51.0	22.2	29.1
6	11.4 -	14.1 ^2J=22.8	98.2 ^1J=188.4	33.9 ^2J=16.2	29.3 ^3J=4.4	13.9 ^3J=7.3	30.0 -
7	44.2 ^3J=17.3	133.1 ^3J=8.5		44.2 ^2J=17.3	21.6 -		97.7 ^1J=204.7
8	12.7	20.5*	52.6	43.0	72.8	22.2*	27.5
9	15.2	19.1*	54.8	43.2	76.2	19.9*	28.9
12	21.0	25*	50.7	45.3	205.1	28.1*	30.0

*J_{C-F} constants values may be interchanged within each line

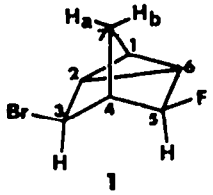
system and are minimum for skew conformations ; $^3J_{CF}$ coupling constants between 3.1 and 6.7 Hz are experimentally observed in the spectra of 1 for C-2 and C-3 and in that of 2 for C-1 and C-7. Consequently, the fluoro substituent is in exo configuration in compound 1 and in the endo position in compound 2. For a structure such as 4 instead of 2, the values of $^3J_{CF}$ coupling constants for C-2 and C-3 should be the same than those observed for 1. Very similar $^3J_{CF}$ coupling constants were also observed in the ^{13}C NMR spectrum of 3-fluoro-nortricyclane 6[26], for which we found a simple synthesis with a nearly quantitative yield (see experimental part).

The chemical shifts observed in the ^{1}H NMR spectra are in good agreement with structures 1 and 2, especially the observed downfield shift effects (cf. table 2) initiated by the halogens to the syn-1,3-diaxial protons (well-known in the cyclohexane series[27]) support these structures. Nevertheless, in this case the dihedral angles are different from those usually observed in a classical cyclohexane chair conformation. In compound 2, the endo fluoro substituent actually causes a downfield shift of $\Delta\delta = \delta_{H-3}$ (2)- δ_{H-3}(1) = 0.49 ppm and the exo bromo substituent shifts the proton H-7a in 2 by 0.49 ppm downfield

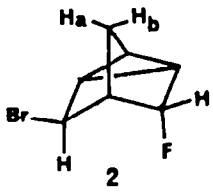
as compared to H-7b in 2. Furthermore, in compound 1, the chemical shifts caused by the bromo and the fluoro substituents which are both in exo configuration are in the same range for H-7a and H-7b. It should also be noted that the H-5 protons have similar chemicals shifts in 1 and 2, while for the pair 1 and 4 one should expect a significant shift difference $\Delta\delta$ as a consequence of the syn diaxial Br and H-5 interaction in compound 4.

Table 2

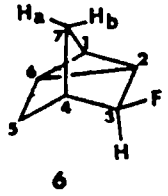
^{1}H magnetic resonance for compounds 1 and 2 (200 MHz) and, for comparison 6 (350 MHz), protons assignements for 1 and 2 using 2D NMR. (^{13}C-^{1}H correlations)



1



2



6

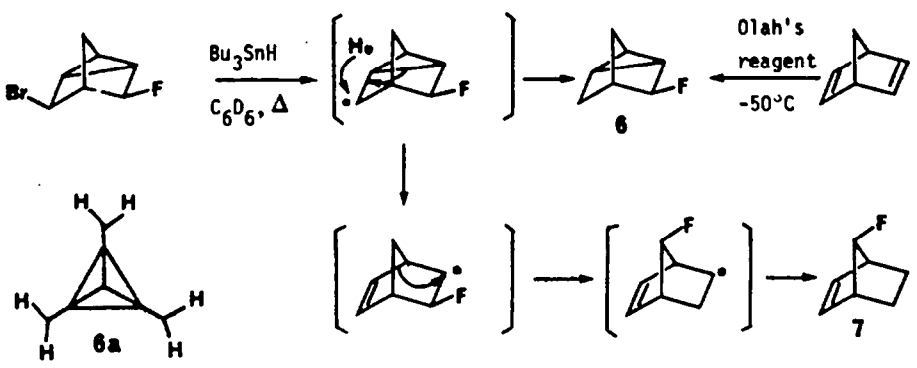
	δ	coupling (Hz)	δ	coupling (Hz)	δ	coupling (Hz)
H-1	1.72	t	1.59	t	-	-
H-2	1.82	t	1.79	t	-	-
H-3	3.96 (3.87)[10]	d $^3J_{HH}$=1.36	4.45 (4.55)[10]	s broad	4.68 (4.58)[26]	dt $^2J_{HF}$=59.5 $^3J_{H2H3}$=$^3J_{H3H4}$=1.9
H-4	2.37	s broad	2.22	s broad	2.02	s
H-5	4.65 (4.54)[10]	dt $^2J_{HF}$=58.3 $^3J_{H4H5}$=$^3J_{H5H6}$=1.8	4.73 (4.75)[10]	dt $^2J_{HF}$=58.6 $^3J_{H4H5}$=$^3J_{H5H6}$=1.8	-	-
H-6	1.54	t	1.41	t	-	-
H-7a	2.13*	part A of a AB system $^2J_{HaHb}$=11.2	1.99	part A of a AB system $^2J_{HaHb}$=11.3	1.32	part A of a AB system $^2J_{HaHb}$=10
H-7b	2.03*	part B of a AB system	1.50	part B of a AB system	1.90	part B of a AB system

Between brackets, values given in the literature[10,26] (CCl_4).

* Values may be interchanged within column.

In comparison, it should be mentioned that the proton on carbon C-3 of the fluoronortricyclane 6 (which is neither endo nor exo because of the C_{3v} symmetry of the nortricyclane skeleton 6a) has a chemical shift (4.68 ppm) very close to those observed for H-5 in 1 and 2 (4.65 and 4.73 ppm, respectively) since for 6, there is no syn-1,3-diaxial halogen effect on the H-5 proton. In contrast, such an effect is actually observed for the proton H-7b ($\Delta\delta$ = 0.58 ppm) of 6 as well as for H-7a of 2 (vide supra). Furthermore, in the ^{19}F NMR spectra, the irradiation of H-3 causes a NOE effect of 9 % on the F substituent in position 5 of compound 2 and only a negligible effect in compound 1.

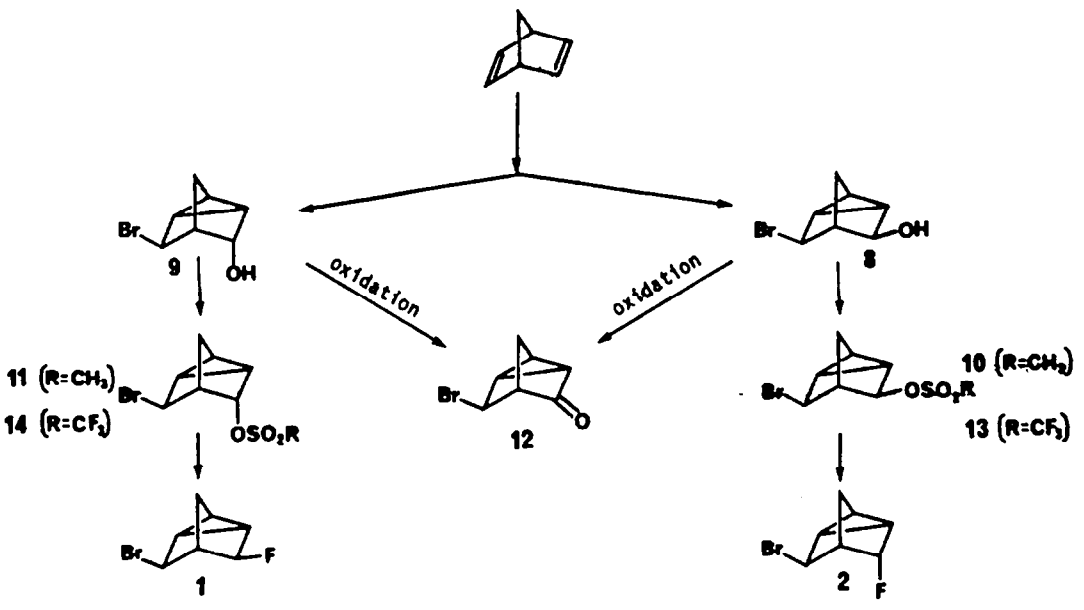
In addition to these spectroscopic proofs, we tried to make some chemical transformations to confirm our structural assignments. The reduction of 3-exo-bromo-5-exo-fluoronortricyclane 1 using Bu_3SnH in benzene yielded a mixture of two compounds in nearly 1:1 ratio. One of them was identical to the authentic sample of 6 and the other one was identified to be 7-anti-fluoronorbornene 7 (Scheme 4). Unfortunately the reduction of compound 2 under the same conditions gave nonfluorinated compounds.



Scheme 4

On the other hand, we synthesized compounds 1 and 2 using another independant pathway.

The formation of the bromohydrins 8 and 9 should give some additional structural evidence. Their oxidation into bromoketone should indicated whether the bromine orientation in the two isomers is the same or not. The study of these bromohydrins and of their derivatives should complete the observation obtained by ^1H NMR concerning the syn-1,3-diaxial effect in these series. Furthermore, the substitution of the hydroxyl groups by fluorine atom via a S_N2 mechanism should be a second route to these bromofluoro compounds (Scheme 5).



Scheme 5

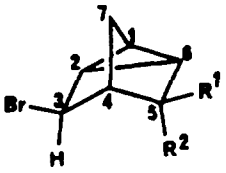
The hydroxybromination of norbornadiene has previously been reported in a patent[28]. However, no informations concerning the yield, the number of isomers and the products structure are mentioned. Therefore, we submitted norbornadiene to bromohydroxylation reaction using NBS in a mixture of water and DMSO and obtained two products 8 and 9 in very close proportions with a yield of 90 %. These crystalline products were separated by column chromatography. The ^1H NMR spectra of 8 and 9 (table 3) are in good agreement with these structures, especially the deshielding $\Delta\delta$ (0.66 or 0.54 ppm) confirms the respective endo and exo orientations of the hydroxyl group of 9 and 8. The mesylation of 8 and 9 leads respectively to the mesylate compounds 10 and 11 and causes a deshielding of the proton attached to C-5 which allows the unambiguous attribution of H-3 and H-5 for 9 (only the proton at δ = 3.86 ppm in the spectrum of 9 is deshielded after mesylation). In addition, the syn-1,3-diaxial effect is of related importance for the mesylate 11 ($\Delta\delta$ = 0.50 ppm) compared to 10.

The oxidation of the bromohydrins by pyridinium chlorochromate leads in 80 % yield to a single bromoketone 12 (^1H and ^{13}C NMR) which clearly proves the same orientation of the C-Br bond in the two bromohydrins 8 and 9. This fact excludes the possibility of a simultaneous exo and endo attack on the norbornadiene during the reaction with NBS and H_2O/DMSO. The same observation was made in the reactions of N-halosuccinimides with norbornadiene in the presence of alcohols or acetic acid.

In order to manage a nucleophilic substitution by the fluoride ion, we prepared the corresponding trifluoromethanesulfonates of the bromohydrins in $CDCl_3$ using trifluoromethane sulphonic anhydride in the presence of pyridine. After going up to room temperature and usual work up the ^1H NMR spectra indicate the presence of two trifluoromethanesulfonates 13 and 14 in a 3:2 ratio no matter what starting bromohydrin is used.

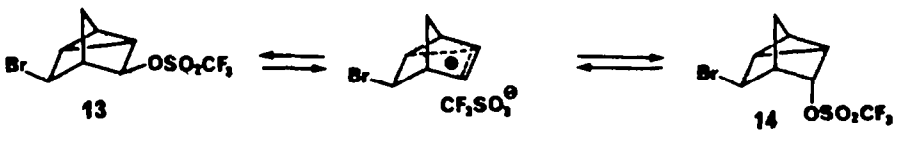
Table 3

Chemical shifts of H-3 and H-5 protons of 3,5-disusbtituted nortricyclanes
*Values may be interchanged within the line



	Products	H-3	H-5
1	R^1 = F, R^2 = H	3.96	4.65
2	R^1 = H, R^2 = F	4.45	4.73
3	R^1 = H, R^2 = Br	4.60	3.95
8	R^1 = OH, R^2 = H	3.77*	3.89*
9	R^1 = H, R^2 = OH	4.43	3.86
10	R^1 = OMs, R^2 = H	3.93	4.56
11	R^1 = H, R^2 = OMs	4.43	4.67
13	R^1 = OTfl, R^2 = H	3.89	4.78
14	R^1 = H, R^2 = OTfl	4.41	4.91

These results clearly establish that a thermodynamic equilibrium exists between the two trifluoromethanesulfonates. However, such an equilibrium is quite uncommon[29] and rather than a simple equilibration by ion pair one can consider a homoallylic carbocation-like transition state (Scheme 6) in good agreement with the very easy solvolysis of chloromethylcyclopropane[30] and with the studies concerning the solvolysis of bromobenzene sulphonyloxy-nortricyclane[31]. The extent of this epimerization may be minimized by carrying out the sulphonylation at -30°C then adding the $Et_3N/3HF$ complex to the reaction mixture at the same temperature. Therefore, we obtained a solution containing the bromofluoro derivatives 1 and 2 in a 3:1 ratio respectively starting from 9 and in a 1:3 ratio starting from 8. Thus, S_N2 displacement mainly occurs and the structures of the bromohydrins confirm those of the bromofluoro compounds.



Scheme 6

Conclusion

Our study actually demonstrates that the minor 3-bromo-5-fluoro compound obtained by the action of NBS together with $Et_3N/3HF$ as well as with Olah's reagent on norbornadiene has structure 2 and not structure 4. The wrong attribution of the structure reported in the literature[10] for this compound obviously comes from the fact that the effect of an halogen on the chemical shift of an 1,3-syn-diaxial proton was neglected, according too much importance to endo or exo orientations of the H-5 hydrogens in the compound 1 and the proposed compound 4. However, it is quite evident that a substituent in 3, 5 or 7 position of a mono-substituted nortricyclane system is neither endo nor exo because of the system's symmetry (cf. 3-fluorononortricyclane 6). The observed chemical shift effects on the H-3 or H-7 protons are in fact caused predominantly by the trough-space influence of neighbouring groups.

Therefore, we can assume that there is no electrophilic endo attack of a bromonium species on norbornadiene, which means that the right side of Scheme 3 does not exist. In the case of the action of NBS on norbornadiene, only the two possibilities of exo or endo attacks on cation C by the nucleophile occur, leading to compounds 1 or 2 respectively.

After completion of this work, Evans and Schauble[32] published a new synthesis of fluoroiodonortricyclanes starting from norbornadiene using a source of I^+ and subsequent addition of BF_4^-. With reference to Gregorcic and Zupan[10,11], they probably attributed an erroneous structure for the 3-endo-fluoro-5-exo-iodonortricyclane. More recently, after our manuscript had been submitted for publication, Chizhov and al.[33] published an exhaustive ^1H and ^{13}C NMR study of 3,5-disubstitued nortricyclanes ; their data are in good agreement with ours ; in particular, they proposed that the 3-endo-bromo-5-exo-fluorononortricyclane structure given by Gregorcic and Zupan[10,11] should be replaced by a 3-exo-bromo-5-endo-fluoro structure.

EXPERIMENTAL

Caution : Although triethylamine tris-hydrofluoride (Fluka) is less corrosive than Olah's reagent or anhydrous hydrogen fluoride itself, any contact with the skin should be avoided. The reagents have been tested for laboratory use only. The experiments should be done under a very efficient hood, wearing personnal safety protection equipment.

GENERAL - Melting points were determined in capillary tubes on a BÜchi apparatus and are uncorrected.

^1H NMR spectra were recorded either on a Varian EM 360 (60 MHz), Varian XL 100 (100 MHz), Bruker AC 200 (200, 13 MHz) or Cameca 350 (350 MHz) spectrometer as indicated. Unless otherwise stated NMR spectra were taken in $CDCl_3$ and chemical shifts are given in ppm downfield from TMS for ^1H and ^{13}C and upfield from $CFCl_3$ for ^{19}F.

Column chromatographies were carried out on SiO_2 (silica gel 60, Merck, 230-400 mesh) using light petroleum ether (Eb_{760} = 45 to 65°C) as eluant unless otherwise stated. Microanalyses were performed by "Service Central de Microanalyses du CNRS", 69 SOLAIZE (France). All new compounds were fully characterized by spectroscopic and satisfactory elemental analyses ($\pm$ 0,4 % of theory). Unstability of trifluoromethanesulfonates and mesylates did not allowed us to get satisfactory analyses.

BROMOFLUORINATION OF NORBORNADIENE

A/ With NBS and Olah's reagent (Zupan's method[10]). At 0°C under stirring NBS (11 mmol) is added to a mixture of 20 ml of Olah's reagent in 20 ml of anhydrous ether (or CH_2Cl_2). After 15 min NBS is almost completely dissolved. Norbornadiene (10 mmol) is added dropwise and the reaction mixture is stirred for one additional hour at room temperature, then poured into icy water, extracted with ether. The organic phase is washed with water, aqueous $NaHCO_3$, water, dried over $MgSO_4$ and concentrated on rotavapor under vacuum. The ^{19}F NMR of the crude shows the presence of two fluoro compounds in the ratio 66:34. The reaction mixture was purified by column chromatography to give the compounds 1 and 2 in an almost quantitative yield. For ^1H and ^{13}C spectroscopic data see tables 1 - 3 ; ^{19}F NMR : ϕ (1) = -191.7, ϕ (2) = -197.1 (lit.[10], solvent CCl_4 : ϕ (1) = -194.3, ϕ (2) = -200.3).

- 3-exo-bromo-5-exo-fluoronortricyclane : Anal. Calc. for C_7H_8BrF : C, 44.01 ; H 4.22 ; F, 9.94. Found : C, 43.90 ; H 4.32 ; F 9.74.
- 3-exo-bromo-5-endo-fluoronortricyclane : Anal. Calc. for C_7H_8BrF : C, 44.01 ; H, 4.22 ; F, 9.94. Found : C, 44.14 ; H 4.20 ; F, 10.01.

B/ With NBS and triethylamine tris-hydrofluoride. In an usual glass round-bottomed flask a mixture of norbornadiene (20 mmol), triethylamine tris-hydrofluoride (10 ml, 50 mmol) and dichloromethane (or ether) (20 ml) is treated with NBS (22 mmol). After 15 min at 0°C, stirring is continued at 15-20°C for 5 h. Then the mixture is poured into icy water (500 ml), neutralized with aqueous 28 % ammonia and extracted with dichloromethane (or ether) (3 x 100 ml). The combined extracts are washed with $\sim$ 0.1 normal HCl (2 x 100 ml) and with 5 % $NaHCO_3$ (2 x 100 ml) and dried over $MgSO_4$. Evaporation of the solvent under vacuum and chromatographic separation of the crude gave the products 1, 2 and 3 in the ratios 57:38:5 respectively. For spectroscopic comparison authentic sample of 3-exo-5-endo-dibromonortricyclane 3 was prepared by addition of bromine on norbornadiene according to the method of Winstein[12] (see tables 1 and 3).

3-FLUORONORTRICYCLANE 6

The action of Olah's reagent in ether at -50°C on norbornadiene during 5 h followed by extraction, washing with water, 28 % ammonia, water, drying over $MgSO_4$ leads, after removal of solvent, almost quantitatively to 3-fluoronortricyclane 6 identical to Tanner's one[26]. Mp = 54-55°C, lit. 52-54°C. For spectroscopic data see tables 1 and 2.

ACTION OF TRIBUTYLTIN HYDRIDE ON 3-EXO-BROMO-5-EXO-FLUORONORTRICYCLANE 1

The action of tributyltin hydride on compound 1 in benzene in the usual manner[34] lead after 40 h of reaction to a mixture of 3-fluoronortricyclane 6 and 7-anti-fluoro-2 norbornene 7 which were identified by comparison of their spectroscopic data with those of the literature[26] (see tables 1 and 2).

SYNTHESIS OF BROMOHYDRINS 8 AND 9

Norbornadiene was treated in DMSO at 0°C under vigourous stirring with 1.1 equivalent of NBS for 15 min. A large excess of water was then added and the reaction mixture kept at room temperature for 24 h. After washing with water and extraction with ether, the organic layer was dried ($MgSO_4$) and concentrated under vacuum. Compounds 8 and 9 were separated by column chromatography (light pet. ether/ether, 1/2, v/v). Spectroscopic data : see tables 2 and 3.

- 8 Anal. Calc. for C_7H_9BrO ; M = 189.04 ; C, 44.47 ; H, 4.36 ; Br, 42.26 ; O 8.46. Found : C, 44.61 ; H, 4.86 ; Br, 41.99.

- 9 Found : C, 44.42 ; H, 4.84 ; Br, 42.39.

- Mesylate 10 of the bromhydrin 8 (OH-"exo")

In a three-necked round-bottomed flask fitted with septum, thermometer, calcium chloride guard, under vigourous stirring, bromhydrin (0.189 g, 1 mmol) dissolved in ether (10 ml) was introduced. 0.6 ml of (4 mmol) Et_3N are added at -60°C. Then 0.170 ml (2.2 mmol) of methanesulfonyl chloride were added dropwise under stirring. Temperature is allowed to rise slowly to room temperature. The stirring is kept at r.t. during 3 h. The reaction mixture is dissolved in ether (50 ml), washed with water, dried over $MgSO_4$. After evaporation under vacuum of the solvent the thick yellow oil is purified by column chromatography (light pet. ether/ether, 1/2, v/v) to give 0.245 g of a thick oil (yield 88 %). Spectroscopic data : see table 3.

- Mesylate 11 of the bromhydrin 9 (OH-"endo")

Same procedure as above. Reaction was finished after 15 h to give 0.235 g of a thick oil (yield 92 %). Spectroscopic data : see table 3.

OXIDATION OF BROMHYDRINS 8 AND 9

To 0.380 g (2 mmol) of bromhydrin 8 or 9 in 20 ml of dry dichloromethane were added 2.15 g (10 mmol) of pyridinium chlorochromate. The flask was safely stoppered and vigorously stirred at room temperature for 1.5 h. The reaction was followed by TLC (light pet. ether/ether, 1/2, v/v). When all bromhydrin was consumed 20 ml of ether were added ; the resulting suspension was then filtered over a silica-gel column. After evaporation of solvant under vacuum a pale yellow oil (0.300 g, 80 %) is obtained. Both bromhydrins 8 and 9 gave the same compound 12 as shown by spectroscopic data (see table 1).

Anal. Calc. for C_7H_7BrO ; M = 187.04 ; C, 44.95 ; H, 3.77 ; Br, 42.72 ; O, 8.55. Found : C, 44.55 ; H, 3.81 ; Br, 43.00 ; O, 9.00.

TRIFLUOROMETHANESULFONATES 13 AND 14

0.095 g (0.5 mmol) of bromhydrins 8 or 9 are dissolved in $CDCl_3$ (1 ml) containing 0.2 ml of pyridin (2.5 mmol). The reaction vessel is then safely stoppered with a septum. After cooling at -20°C was added with a syringe 0.170 ml (1 mmol) of trifluoromethanesulfonic anhydride. The mixture is allowed to rise to room temperature. The reaction mixture is then washed at 0°C with 3N HCl, water, $NaHCO_3$ and water again. After drying over $MgSO_4$ and concentration under vacuum ^1H NMR shows the presence of a mixture of trifluoromethanesulfonates 13 and 14 (55:45) whatever was the starting bromohydrin.

CONVERSION OF THE TRIFLUOROMETHANESULFONATES 13 AND 14 INTO THE BROMOFLUORONORTRICYCLANES 1 AND 2

0.4 g (25 mmol) of Et_3N, 3HF are added to the preceding mixture of trifluoromethanesulfonates 13 and 14 (55:45) in solution in $CDCl_3$. The reaction flask is stoppered and kept a r.t. for 15 h. After washing of the solution ($NaHCO_3$, H_2O, HCl, H_2O) and drying, the ^1H NMR spectrum shows the presence of the bromofluoronortricyclanes 1 and 2 in the ratio 55:45.

ONE-POT CONVERSION OF THE BROMOHYDRINS 8 AND 9 INTO THE BROMOFLUORONORTRICYCLANES 2 AND 1

To a solution of 0.095 g of bromohydrin (0.5 mmol) in 1 ml of dichloromethane were added one or two crystals of 4-dimethylaminopyridine and 0.105 ml (1.3 mmol) of pyridine. After cooling at -35°C 0.1 ml (0.6 mmol) of trifluoromethanesulfonic anhydride was added dropwise with a microsyringe. The reaction mixture was stirred for 45 mn at -30°C. Et_3N, 3HF (0.4 g ; 25 mmol) was then added under stirring. After 36 h at room temperature the mixture is washed ($NaHCO_3$, H_2O, HCl, H_2O) and dried. ^1H NMR spectra indicate the presence of the bromofluoronortricyclanes 1 and 2 in the ratio 7:3 starting from bromhydrin 9 and the ratio 3:7 starting from bromhydrin 8.

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