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Fluorination with Xenon Difluoride. XXII. The Role of Catalyst and Temperature on the Fluorination of Norbornene and Norbornadiene

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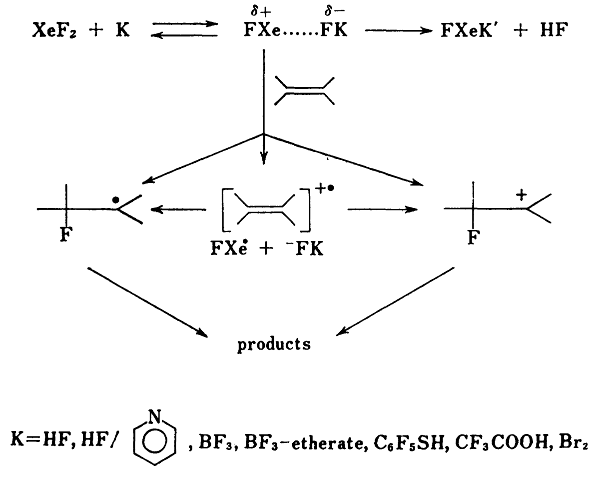
The reaction of norbornene was used as a mechanistic probe to elucidate the effect of catalyst (HF, HF–pyridine, BF_3, BF_3–etherate, and pentafluorothiophenol) and temperature (from −61 °C to 25 °C) on liquid phase fluorination with xenon difluoride, resulting in the formation of seven products, depending on the reaction conditions: fluoronortricyclane, 2-*endo*-3-*exo*-difluoronorbornane, 2-*exo*-7-*anti*-difluoronorbornane, 2-*endo*-5-*exo*-difluoronorbornane, 2-*exo*-5-*exo*-difluoronorbornane, 2-*exo*-3-*exo*-difluoronorbornane, and 2-*exo*-7-*syn*-difluoronorbornane. The catalyst has a significant effect on the reaction pathways, boron trifluoride etherate favouring the formation of 2-*endo*-5-*exo*- and 2-*exo*-5-*exo*-difluoronorbornane, while pentafluorothiophenol favoured the formation of fluoronortricyclane. The catalyst and temperature has much less effect on the reaction pathways in the case of norbornadiene, four products being formed: fluoronortricyclane, 3-*endo*-5-*exo*-difluoronortricyclane, 3-*exo*-5-*exo*-difluoronortricyclane, and 2-*exo*-7-*syn*-difluoro-5-norbornene. Pentafluorothiophenol as a catalyst, when used in a greater amount, favours the formation of fluoronortricyclane.

Xenon difluoride is a mild fluorinating agent for the fluorination of alkenes, acetylenes, aromatic and heteroaromatic compounds.[1] The mechanism of fluorine addition to olefins with xenon difluoride depends on structure of the olefin, the catalyst used, solvent polarity, and temperature. The formation of *β*-fluorocarbonium ions, free radical intermediates or ion radicals has been suggested (Scheme 1). The following substrates are convenient catalysts for the fluorination of olefins: hydrogen fluoride,[2] HF–pyridine,[3] trifluoroacetic acid,[4] bromine,[5] and boron trifluoride etherate.[6]

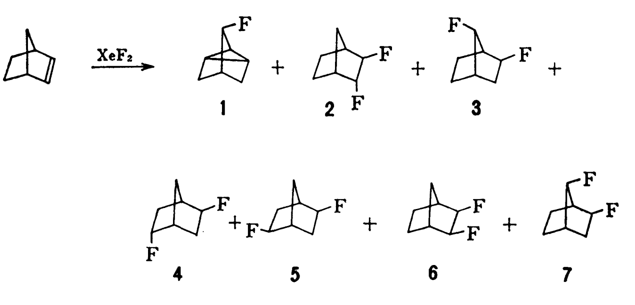


Scheme 1.

Recently it was found that boron trifluoride[7] is a convenient catalyst for the fluorination of less reactive organic compounds, while in the case of more sensitive organic compounds pentafluorothiophenol proved to be preferable to hydrogen fluoride, which causes acid catalyzed decomposition. The fluorination of norbornene with xenon difluoride in the presence of HF resulted in the formation of seven products. Besides the formation of carbonium ions free radical intermediates have also been observed.[8] Shackelford found that low temperature fluorination of norbornene, catalyzed by boron trifluoride etherate, gives only three products.[9] The reaction of norbornene has been used several times as a mechanistic device to elucidate the mechanism and stereochemistry of diverse reactions.[10] We have utilized the sensitivity of the reactions of norbornene to the reaction conditions for studying the effect of catalyst and temperature on the fluorination with xenon difluoride. The effect of catalyst and temperature on the fluorination of norbornadiene has also been studied.

Results and Discussion

The reaction of norbornene with xenon difluoride in dichloromethane at various temperatures and in the presence of various catalysts resulted in the formation of seven products (Scheme 2). Analysis of the reaction mixture by GLC gave the relative yields given in Table 1. The products of 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 and are in agreement with those reported.[8] The effect of catalysts, *i.e.* hydrogen fluoride, hydrogen fluoride–pyridine, boron trifluoride etherate, boron trifluoride, and pentafluorothiophenol, is most evident from the formation of fluoronortricyclane (**1**), 2-*endo*-3-*exo*-difluoronorbornane (**2**), 2-*exo*-3-*exo*-difluoronorbornane (**6**), and 2-*exo*-7-*syn*-difluoronorbornane (**7**).



Scheme 2.

We have established that the formation of products **2** and **6** can partly be ascribed to free radical intermediates. The great selectivity in the formation of

TABLE 1. EFFECTS OF CATALYST AND TEMPERATURE ON THE ADDITION OF XeF_2 TO NORBORNENE

Catalyst	Temp/°C	Time/min	1	2	3	4	5	6	7	
HF	25	3	44	6	17	15.5	9	4	4.5	Ref. 8
	25	60	37.5	6	18	19	10	4	5.5	Ref. 8
HF–Pyridine	15	60	14	—	35	19	10	—	22	Ref. 3
BF_3/OEt_2	−61	10	4	—	38	33	18	—	7	
	−61→25	1275	2	—	3	33	61	—	1	
		1275	—	—	4.3	29.7	66	—	—	Ref. 9
	−46→−39	105	—	—	42.2	25.5	32.2	—	—	Ref. 9
	0	1	4	—	34	33	22	1	6	
	25	1	5	—	28	26	33	1	7	
	25	60	6	1	4	31	57	trace	1	
BF_3	25	60	11	3	29	27	20	3	7	
C_6H_5SH	25	10	64	—	13	12	7	—	4	
	25	60	63	—	14	12	7	—	4	

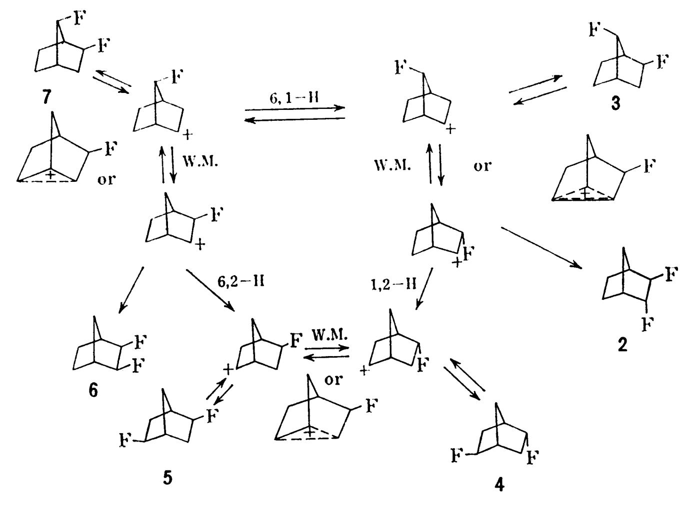
TABLE 2. EFFECT OF THE AMOUNT OF PENTAFLUOROTHIOPHENOL ON PRODUCT IN THE FLUORINATION OF NORBORNENE

C_6F_5SH/C_7H_{10} (mmol/mmol)	1	2	3	4	5	6	7
0.125	44	1	19	19	10	—	6
0.25	45	1	18	18	11	—	7
0.50	76	—	8	8	5	—	3
1.00	99	—	trace amount			—	—

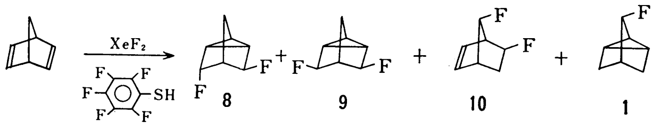
2-*endo*-5-*exo*-difluoronorbornane (**4**), and 2-*exo*-5-*exo*-difluoronorbornane (**5**), pointed out by Shackelford,[9] arises from secondary isomerisation of 2-*exo*-7-*anti*-difluoronorbornane (**3**). In order to clarify the primary formed products in the BF_3–etherate catalyzed reaction, we made a 10 min experiment at −61 °C and confirmed that five products are formed. Besides difluoronorbornanes **3**, **4**, and **5**, fluoronortricyclane (**1**) and 2-*exo*-7-*syn*-difluoronorbornane (**7**) were formed as well. The experiment performed under the same conditions as reported[9] (temperature from −61 °C to +25 °C) resulted in a similar product distribution, while small amounts of fluoronortricyclane (**1**) and 2-*exo*-7-*syn*-difluoronorbornane (**7**) were also detected. The effect of temperature on the reaction pathways in BF_3–etherate catalyzed fluoronations is given in Table 1.

BF_3-catalyzed fluorination of norbornene at room temperature resulted in the formation of seven products. The formation of fluoronortricyclane as the major prodyct in pentafluorothiophenol catalyzed reactions (Table 1) stimulated us to study the effect of the amount of catalyst on product distribution (Table 2). The increase in the amount of pentafluorothiophenol is reflected in the increased formation of fluoronortricyclane (**1**), while the experiment with equimolar amounts of catalyst and norbornene resulted in only trace amounts of difluoronorbornanes **3**, **4**, and **5**.

The formation of seven products resulting from the fluorination of norbornene under various conditions (catalyst, temperature) can be mainly ascribed to the intermediately formed *β*-fluorocarbonium ion, which further undergoes Wagner-Meerwein rearrangements and hydride shifts (Scheme **3**). The mechanism involves the irreversibile hydride shifts 6,2-H and 1,2-H, based on the observation of isomerization of the products in dichloromethane in the presence of hydrogen fluoride, where similar carbonium ions are formed.[8] The formation of 2-*exo*-3-*endo*-difluoronorbornane (**2**) and 2-*exo*-3-*exo*-difluoronorbornane (**6**) formed in room temperature fluorination catalyzed by BF_3–etherate and BF_3, can be partly ascribed to the formation of free



Scheme 3.



Scheme 4.

Table 3. Effects of catalyst and temperature on the addition of XeF_2 to norbornadiene

Catalyst	Temp °C	Time min	**8**	**9**	**10**	
HF	25	60	50	40	10	Ref. 8
HF–Pyridine	25	30	27	68	5	Ref. 11
BF_3	0	60	45	50	5	
	25	60	47.5	49	3.5	
BF_3/OEt_2	−61	10	36.5	58.5	5	
	0	1	38.5	55	6.5	
	25	1	39.5	53.5	7	
	25	60	41.5	50	8.5	

radical intermediates (Scheme 1). The effect of catalyst (HF, HF–pyridine, BF_3–etherate, BF_3, pentafluorothiophenol) on the reaction pathways is reflected most significantly in the amount of fluoronortricyclane formed.

The fluorination of norbornadiene resulted in the formation of four products, depending on the catalyst used (Scheme 4). It is evident that variation of catalyst, *i.e.* HF, HF–pyridine, BF_3–etherate, and temperature from −61 °C to 25 °C, has much less effect on the reaction pathways than in the case of norbornene (Table 3). However, in the pentafluorothiophenol catalyzed reaction, fluoronortricyclane (**1**) was formed besides[8] 3-*endo*-5-*exo*-difluoronortricyclane (**8**), 3-*exo*-5-*exo*-difluoronortricyclane (**9**), and 2-*exo*-7-*syn*-difluoronorbornene-5 (**10**). The effect of the amount of catalyst is shown diagramatically in Fig. 1. As in the case of norbornene, fluoronortricyclane became the main product when greater amounts of catalyst were used. An explanation for the formation of four products in the pentafluorothiophenol catalyzed reaction is given in Scheme 5. In the first step, polarization of XeF_2 by pentafluorothiophenol is suggested, which is then followed by the formation of two β-fluorocarbonium ions, giving two fluoronortricyclyl cations. The preferential *exo* attack[11] of the fluorine anion leads to the formation of difluoronortricyclane products (**8**, **9**), while reaction with pentafluorothiophenol results in the formation of fluoronortricyclane (**1**). In halofluorinations[11] of norbornadiene only the primary formed β-*exo*-fluorocarbonium ion undergoes Wagner-Meerwein rearrangement, leading to the formation of 2-*exo*-7-*syn*-5-norbornene (**10**).

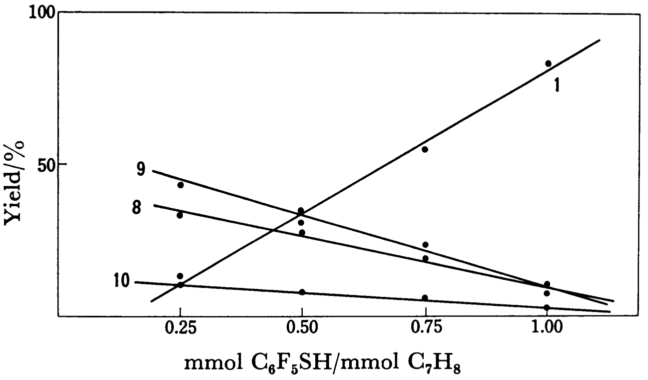
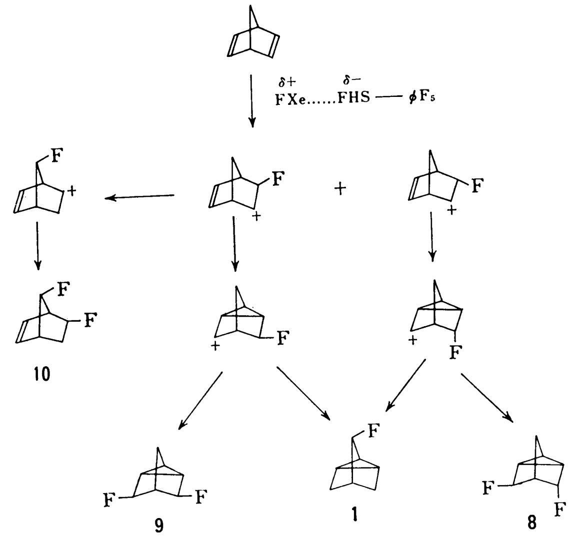


Fig. 1. Effect of the amount of pentafluorothiophenol on product distribution in fluorination of norbornadiene.



Scheme 5.

Experimental

IR spectra were recorded with a Perkin Elmer 257 spectrometer and ^1H and ^{19}F NMR spectra with a JEOL JNM PS-100 from CCl_4 solution with Me_4Si and CCl_3F as internal references. Mass spectra were taken on a CEC 21-110 spectrometer. Gas-liquid partition chromatography was carried out on a Varian Aerograph Model 1800.

Materials. Norbornene, norbornadiene and pentafluorothiophenol were purified before use. Hydrogen fluoride and boron trifluoride of Fluka Purum quality were used without further purification. Dichloromethane and diethyl ether were purified and stored over molecular sieves.[12] Xenon difluoride was prepared by a photosynthetic method,[13] the purity being higher than 99.5%.

Addition and Isolation Procedures. To a solution of 1 mmol of olefin in dichloromethane (2 ml) in a Kel-F vessel was added 1 mmol of xenon difluoride at an appropriate temperature, the corresponding catalyst (HF, BF_3, BF_3–etherate, or pentafluorothiophenol) being introduced into the reaction mixture with stirring. The reactions were stopped by addition of dichloromethane (15 ml) and 10 ml of 5% $NaHCO_3$. The reaction mixture was washed with water, and dried over anhydrous sodium sulfate. The solvent was evaporated *in vacuo*. The crude reaction mixtures were analyzed by GLC, the products being isolated by preparative GLC. The structures of the products were established by a comparison of their spectroscopic data with those published.[8)] Each experiment was repeated several times, the average data being given in the tables; relative yields were determined by GLC (DDP-10%, Chromosorb Regular 100, 45—120 °C in the case of norbornene reaction, and Carbowax 20 M 25%, Varaport 30 70/80, 130 °C for norbornadiene). The maximum error between parallel experiments was ±1.5%.

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