Fluorination with Xenon Difluoride. Stereochemistry of Fluorine Addition to Phenyl-Substituted Olefins

Marko Zupan* and Alfred Pollak

Department of Chemistry and "Jožef Stefan" Institute, University of Ljubljana, 61000 Ljubljana, Yugoslavia

Received June 7, 1976

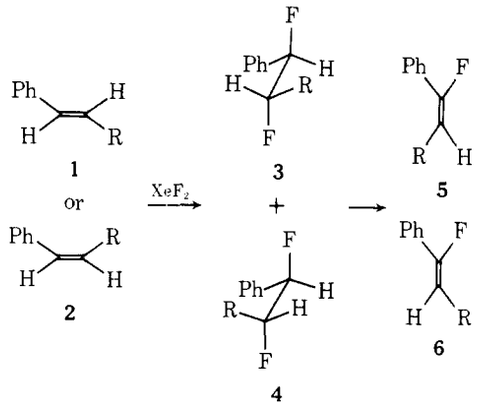
Acid-catalyzed liquid-phase fluorine addition with xenon difluoride to phenyl-substituted olefins, e.g., *cis*- and *trans*-1-phenylpropene, *cis*- and *trans*-stilbene, and *cis*- and *trans*-1-phenyl-2-*tert*-butylethene, results in the formation of vicinal difluorides in high yield. The reaction is nonstereospecific. Reaction with indene results in the formation of 70% trans and 30% cis adduct. The formation of β-fluorocarbonium ions is suggested.

The preparation of fluoroalkanes presents a different problem from that of the other haloalkanes, and necessitates a specific method of fluorination.[1] Recently, we observed that xenon difluoride readily adds fluorine to phenyl-substituted olefins[2,3] and acetylenes[4] in the presence of hydrogen fluoride as catalyst, to give the corresponding 1,2-difluoro- or 1,1-2,2-tetrafluorophenylethanes in high yields and under mild conditions. When the same reactions were catalyzed by trifluoroacetic acid, the competitive fluoro trifluoroacetates also accompanied the difluorides.[3] In the course of our efforts to elucidate the stereochemistry and the reaction mechanism of fluorine addition to olefinic double bonds with xenon difluoride, and to compare it to molecular fluorine addition, or in general to other halogen additions, we found it instructive to fluorinate some trans (**1**) and cis (**2**) isomers of phenyl-substituted olefins. We chose these olefins because the stereochemistry of their halogenations is well known,[5] and so there was a possibility of drawing conclusions from the stereochemical results about the reaction pathway.

Results and Discussion

First we shall consider the identification of the products formed in the HF-catalyzed reactions of isomeric olefins (**1**, **2**) with XeF_2 in various less polar solvents (methylene chloride, chloroform, carbon tetrachloride). Under these conditions *dl*-erythro (**3**) and *dl*-threo (**4**) difluorides were formed. They were separated by preparative GLC or TLC and their mass and ^{19}F and ^1H NMR spectra were recorded. The structures of the products were assigned from the products formed when the difluorides (**3** or **4**) were treated with base under conditions suitable for trans elimination. The products (*cis*-fluoro **5** and *trans*-fluoro **6** alkenes) were identified on the basis of differences in their NMR spectra: $J_{FH\text{-}trans} > J_{FH\text{-}cis}$ (Scheme I). The product distribution in the HF-cat-

Scheme I



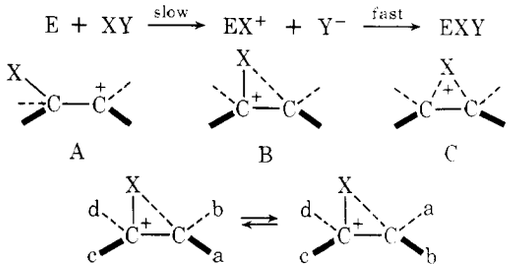
R = CH_3, Ph, $C(CH_3)_3$

alyzed addition of fluorine with xenon difluoride to each of the six olefins is presented in Table I. The results from all olefins show that fluorine addition is clearly a nonstereospecific process. The nonstereospecific addition could be the result of an open or partly bridged cation as the product-determining intermediate, or the result of radical processes, and finally the result of the isomerization of the olefins or difluorides under the reaction conditions. We found that the lack of stereospecificity cannot be ascribed to the prior isomerization of the olefins (in the cis series we observed isomerization of the order of 10% for stilbene) or to secondary isomerization of the difluorides, since all have been shown to be stable under the reaction and isolation conditions. The absence of a free-radical inhibition effect (molecular oxygen) on the product distributions ruled out free-radical processes. It is clear that the stereochemical results must be explained within the framework of an electrophilic mechanism. The fact that these reactions are very strongly catalyzed by hydrogen fluoride and the nature of the products obtained in the fluorination of norbornene[6] confirm this view.

The mechanisms of electrophilic addition of halogens to alkenes has been extensively investigated, from both kinetic and stereochemical points of view.[5,7] The most important mechanism for a electrophilic addition in the liquid phase is a stepwise addition via a carbonium ion intermediate (AdE2). It is now known that the nature of the intermediates (Scheme II) depends on the halogen X, on the structure of the sub-

Scheme II

Ad_E2 mechanism



strate, and on the reaction medium, ranging from a strongly bridged ion of type C to a weakly bridged species of type B, or an open-chain ion like A. If the cation has an open (A) or partly bridged (B) structure, a mixture of syn and anti adducts is generally expected.

Turning to the results obtained with cis and trans olefins, we see that the ratios of *dl*-erythro (**3**) and *dl*-threo (**4**) difluorides (Table I) are nearly independent of the starting olefin, and that in the trans series of olefins, anti addition of fluorine predominates (3/4—1.50–1.70). On the basis of our experimental results obtained in HF-catalyzed fluorine addition to phenyl-substituted olefins with xenon difluoride, the following mechanism could be suggested. The mechanism of the 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

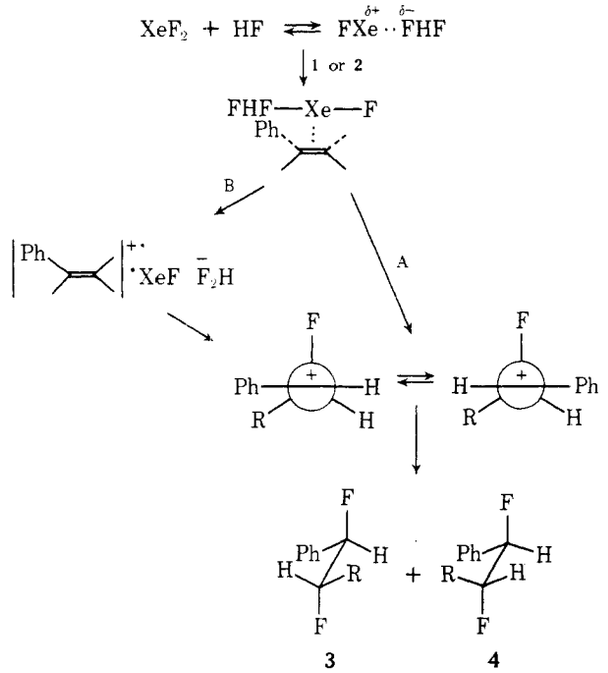
Table I. Product Distribution in Fluorination of Substituted 1-Phenylethylenes (1 and 2) with Xenon Difluoride in Methylene Chloride at 25 °C

Registry no.	Olefin	R	Rel yields, %[a] *dl*-erythro (3)	Ratio 3/4
873-66-5		CH_3	60	1.50
103-30-0	Trans (1)	Ph	62	1.67
3846-66-0		$C(CH_3)_3$	63	1.70
766-90-5		CH_3	64	1.78
645-49-8	Cis (2)	Ph	53	1.13
3740-05-4		$C(CH_3)_3$	64	1.78

[a] Determined by ^{19}F NMR spectroscopy.

suggested by Filler et al.[8] for the fluorination of aromatic compounds. In the next step, a π complex is probably formed between this electrophilic species and olefin 1 or **2**, which could be transformed by a heterolytic Xe–F bond cleavage (Scheme III, path A) into an open β-fluorocarbonium ion intermediate.

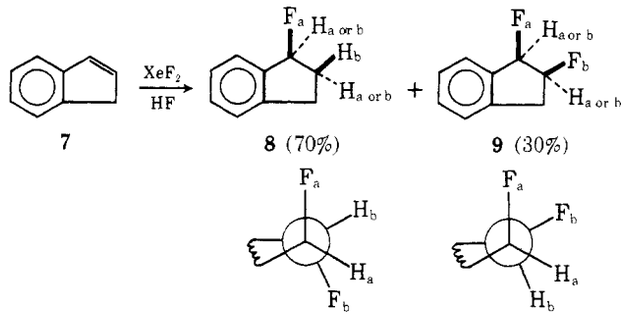
Scheme III



The intermediate from a trans olefin collapses preferentially to an anti adduct; on the other hand, the cis olefin intermediate can freely rotate about the newly formed single bond, thus assuming a sterically more favorable conformation, identical with that of the trans olefin intermediate. It is therefore clear why the product ratios are independent of the starting olefin. The proposed mechanism is also supported by the well-known fact that fluorine is a very poor neighboring group, preventing any bridging phenomena in the above mentioned β-fluorocarbonium ion intermediate. Furthermore, another possibility (path B) is the formation of an ion radical, which has already been observed in the fluorination of benzene and its derivates,[8] in the next step transforming by XeF· or XeF_2 into an open carbonium ion. The lower oxidation potentials of olefins (in comparsion to those of benzo derivates) make the suggested path (B) quite reasonable.[9]

We extended our studies on fluorine addition to cycloolefin so as to eliminate a complexity which exists in acyclic systems, in which there is the possibility of rotation about the carbon–carbon single bond in the β-fluorocarbonium ion, depending on its lifetime and on the energy barrier resisting free rotation about the newly formed single bond. Indene (**7**), which we might assume to be a "cyclic analogue" of *cis*-1-phenylpropene, adds fluorine preferentially anti (70%) but not syn, as was observed in fluorination of *cis*-1-phenylpropene. This fact also supports the idea of an open β-fluorocarbonium ion intermediate which cannot rotate in the case of a cyclic olefin such as indene (Scheme IV).

Scheme IV



NMR data	Trans adduct	Cis adduct
δ_{Fa}, ppm	−195.5	−211.5
δ_{Fb}, ppm	−207.5	−223.0
δ_{Ha}, ppm	5.8	5.5
δ_{Hb}, ppm	5.2	5.0
$J_{F_aF_b}$, Hz	9	4.5
$J_{F_aH_b}$ Hz	17	15
$J_{F_bH_a}$, Hz	16	5
$J_{H_aH_b}$, Hz	3	5

It is of interest to mention that in the fluorination of indene with molecular fluorine studied by Merrit,[10] a fluorine adduct was obtained which was interpreted as a trans product on the basis of its NMR spectra. By comparing our data for both cis (**9**) and trans (**8**) products to those of Merritt we deduced the cis structure for Merrit's product. We can see that there is little difference in H_aH_b coupling constants (Scheme IV), but there are differences in coupling constants F_bH_a between the two isomers. Following the Karplus rule,[11] the higher constant in the trans adduct is in full agreement with this assignment.

One of the reasons for undertaking the present study was to obtain data on the stereochemistry of fluorine addition to phenyl-substituted olefins with xenon difluoride which could be compared with the results of other halogen additions to this type of olefin. Stereochemical results for addition of various halogens to *cis*- and *trans*-1-phenylpropene are summarized in Table II. One can see that the stereochemistry of addition depends on the nature of the reagent. The reasons for these changes are known. Since fluorine and chlorine are poor neighboring atoms, electrophilic additions proceed via open carbonium ions and are nonstereospecific. The tendency toward syn addition observed with these reagents is the logical consequence of ion-pairing phenomena in nonpolar solvents. Bromine, which is a better bridging atom than chlorine, but poorer than iodine, represents an intermediate case. The addition of bromine is preferentially anti, and might be interpreted by an initially formed carbonium ion intermediate with a partly bridged structure. On the other hand, data on the electrophilic addition of iodine are not available. If we now compare the stereochemical results of fluorine addition with xenon difluoride to other halogen additions, we see that our results are very similar to the results of chlorine addition in methylene chloride, but differ from molecular fluorine addition, where ion-pairing phenomena are more dominant than in xenon difluoride fluorination.

The final conclusion of this study would be that xenon difluoride appears to be a mild, selective, electrophilic reagent for fluorine addition to olefins with some advantages in comparison to known fluorinating agents such as molecular

Table II. Stereochemistry of Halogen Addition to 1-Phenylpropene-1

Registry no.	Halogen	Solvent	Trans olefin		Cis olefin		Ref
			dl-erythro	*dl*-threo	*dl*-erythro	*dl*-threo	
7782-41-4	F_2	CCl_3F	31	69	78	22	12
7782-50-5	Cl_2	CCl_4	38	46	62	29	13
		CH_2Cl_2	55	28	62	22	13
7726-95-6	Br_2	CCl_4	88	12	17	83	14
13709-36-9	XeF_2	CH_2Cl_2	60	40	64	36	

fluorine, metal fluorides, etc. Some of them might be mentioned: (1) the good solubility of XeF_2 in organic solvents and no hazards in handling it; (2) no necessity for low temperature experiments, since reactions proceed smoothly at room temperature; (3) the only side product is xenon gas, which could be nearly quantitatively recycled to xenon difluoride.

Experimental Section

IR spectra were recorded using a Perkin-Elmer 257 spectrometer, ^1H 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 spectrometer. Gas–liquid partition chromatography was carried out on a Varian Aerograph Model 1800 and TLC on Merck PSC-Fertigplatten silica gel F-254 (activated for 3 h at 120 °C before use).

Materials. Pure samples of olefins were prepared by known methods: *cis*-1-phenylpropene,[15] *trans*-1-phenylpropene,[16] *cis*-1-phenyl-2-*tert*-butylethylene,[17] *trans*-1-phenyl-2-*tert*-butylethylene.[17] 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.[18] Xenon difluoride was prepared by a photosynthetic method[19] 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 30 min gas evolution ceased and the reaction appeared to be complete. The reaction mixture was diluted with methylene chloride (15 m), washed with 10 ml of 5% $NaHCO_3$ and water, and dried over anhydrous sodium sulfate. The solvent was evaporated in vacuo. The crude reactions mixtures were separated by preparative GLC or TLC.

***dl*-erythro- and *dl*-threo-1,2-Difluoro-1-phenylpropane (3 and 4).** Products were separated by preparative GLC (DDP, Chromosorb Regular 80/100, 170 °C). *dl*-erythro (45%) and *dl*-threo (30%) isomers were isolated, both as colorless, liquid compounds. NMR for *dl*-erythro (3): δF_1 −202, δF_2 −216, δH_1 5.35, δH_2 4.67, δCH_3 1.28 ppm, $J_{F_1F_2}$ = 16.5, $J_{F_1H_1}$ = 48, $J_{F_2H_2}$ = 46.5, $J_{F_1H_2}$ = 16.5, $J_{F_2H_1}$ = 18, $J_{H_1H_2}$ = 3.75, $J_{F_2CH_3}$ = 22.5, $J_{H_2CH_3}$ = 6, $J_{F_1CH_3}$ = 1.5 Hz. *dl*-threo (4): δF_1 −204, δF_2 −208.5 ppm, δH_1 5.25, δH_2 4.71, δCH_3 1.17, $J_{F_1F_2}$ = 16.5, $J_{F_1H_1}$ = 48, $J_{F_2H_2}$ = 46.5, $J_{F_1H_2}$ = 16.5, $J_{F_2H_1}$ = 17, $J_{H_1H_2}$ = 5.25, $J_{F_2CH_3}$ = 22.5, $J_{H_2CH_3}$ = 6, $J_{F_1CH_3}$ = 0.5 Hz.

NMR data are in agreement with those in the literature.[12] The structures of the products were also established by elimination of hydrogen fluoride under basic conditions, thus converting them to *cis*-1-fluoro-1-phenylpropene (NMR J_{FH} = 22, J_{FCH_3} = 3, J_{HCH_3} = 7.2 Hz, δF −113.2 ppm) and *trans*-1-fluoro-1-phenylpropene (NMR J_{FH} = 36, J_{FCH_3} = 2, J_{HCH_3} = 6.75 Hz, δF −133.7 ppm).

***dl*-erythro- and *dl*-threo-1,2-Difluoro-1-phenyl-2-*tert*-butylethane (3 and 4).** Products were separated by preparative GLC (DDP-Chromosorb Regular 80/100, 170 °C). *dl*-erythro (40%) and *dl*-threo (32%) isomers were isolated, both as colorless, liquid compounds. NMR for *dl*-erythro (3): δF_1 −198, δF_2 −212 ppm, δH_1 5.33, δH_2 4.18, $\delta C(CH_3)_3$ 1.00, $J_{F_1F_2}$ = 18, $J_{F_1H_1}$ = 45, $J_{F_2H_2}$ = 43, $J_{F_1H_2}$ = 7.5, $J_{F_2H_1}$ = 7.5, $J_{H_1H_2}$ = 7.5 Hz. *dl*-threo (4): δF_1 −211, δF_2 −224 ppm, δH_1 5.51, δH_2 4.07, $\delta C(CH_3)$ 1.05, $J_{F_1F_2}$ = 7.5, $J_{F_1H_1}$ = 46.5, $J_{F_2H_2}$ = 43.5, $J_{F_1H_2}$ = 24, $J_{F_2H_1}$ = 27, $J_{H_1H_2}$ = 2.5 Hz. Mass spectrum: calcd for $C_{12}H_{16}F_2$ *m/e* 198.1220, found 198.1217, *m/e* 198 (M^+, 40), 109 (100), 91 (30), 89 (26).

***meso*- and *dl*-1,2-Difluoro-1,2-diphenylethane (3 and 4).** The crude reaction mixture was purified by preparative TLC and isolated in 78% yield. (The products were not separated.) The structures of the products were determined by elimination under basic conditions. One millimole of the reaction mixture of the difluorides (meso:*dl* products 2.5) was dissolved in 3 ml of *tert*-butyl alcohol and 1.5 mmol of potassium-*tert*-butoxide was added. The reaction mixture was stirred at room temperature for 20 h and 5 h at 50 °C, then cooled, mixed with water, and extracted with methylene chloride. The extract was washed with dilute acid and water, dried ($MgSO_4$), filtered, and evaporated and the residue was analyzed by GLC and NMR spectroscopy. The product was a 2.2:1 mixture of *cis*- and *trans*-fluorostilbene. The two compounds were separated by preparative GLC (Carbowax 20M, Varaport 30 70/80 at 180 °C). The spectroscopic data of fluorostilbenes are in agreement with the literature ones.[12]

To test the stability of the difluorides in the reaction mixture, a sample (0.2 g), containing pure difluorides 3 or 4 or the mixture of 3 and 4, was dissolved in 2 ml of methylene chloride, 20 mg of xenon difluoride, and a catalytic amount of hydrogen fluoride, and the mixture was stirred at 25 °C for 30 min. After workup, the NMR spectra showed no significant differences. By using a mixture of 3 and 4 of known composition, it was demonstrated that no significant product fractionation occurred during the isolation.

Fluorination in the Presence of Oxygen. Trans olefin 1 (1 mmol) was dissolved in 6 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 30 min. The reaction mixture was diluted with methylene chloride, washed with 10 ml of 5% $NaHCO_3$ and water, dried ($MgSO_4$), filtered, and evaporated and the residue was analyzed by NMR spectroscopy. The product distribution was 61% of meso and 39% of *dl* difluorides in the case of *trans*-stilbene, and 60% of *dl*-erythro and 40% of *dl*-threo difluorides in the case of *trans*-phenylpropene. It can be seen that the free-radical inhibitor had no effect on the product distribution (Table I).

Isomerization of the Olefins under the Reaction Conditions. A. The olefin 1 or 2 (1 mmol), dissolved in methylene chloride, was stirred at room temperature in the presence of anhydrous hydrogen fluoride for 1 h. After adding water, washing with aqueous $NaHCO_3$ and water, drying over $MgSO_4$, and evaporation, the reaction mixture was analyzed by GLC. No significant isomerization of the olefin was observed.

B. In experiments made under the same reaction conditions as those for fluorination, in which a smaller amount (0.4, 0.5, or 0.6 mmol) of xenon difluoride and 1 mmol of olefin were used, the unchanged olefins were analyzed by GLC. No significant isomerization of trans olefins was observed, while the isomerization of cis olefins took place in the range of 5–7%.

Effect of Solvent Polarity on the Fluorination of *cis*- and *trans*-Stilbene. *trans*- or *cis*-stilbene (1 mmol) was dissolved in 6 ml of solvent (CCl_4, $CHCl_3$, or CH_2Cl_2), 1 mmol of xenon difluoride was added at 25 °C, and under stirring anhydrous hydrogen fluoride was introduced into the reaction mixture. After isolation in the usual manner, the NMR spectra were taken on the crude reaction mixture. The product distribution was as follows.

	Trans olefin		Cis olefin	
	Meso (3)	*dl* (4)	Meso (3)	*dl* (4)
CCl_4	56	44	53	47
$CHCl_3$	60	40	53	47
CH_2Cl_2	62	38	53	47

Studies of the effect of solvent polarity are limited to the above-mentioned solvents, because the reaction did not take place under similar conditions in other solvents (aliphatic alcohols, acetonitrile). The reaction is faster in methylene chloride than in chloroform or carbon tetrachloride.

Fluorination of Indene. To a solution of 1 mmol of indene in methylene chloride (6 ml), 1 mmol of xenon difluoride was added at

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.

References and Notes

(1) For a review, see W. A. Sheppard and C. M. Sharts, "Organic Fluorine Chemistry", W. A. Benjamin, New York, N.Y., 1969.
(2) M. Zupan and A. Pollak, *J. Chem. Soc., Chem. Commun.*, 845 (1973).
(3) M. Zupan and A. Pollak, *Tetrahedron Lett.*, 1015 (1974).
(4) M. Zupan and A. Pollak, *J. Org. Chem.*, **39**, 2646 (1974).
(5) R. C. Fahey, *Top. Stereochem.*, **3**, 280 (1968).
(6) M. Zupan, A. Gregorčič, and A. Pollak, *J. Org. Chem.*, following paper in this issue.
(7) P. B. D. de la Mare and R. Bolton, "Electrophilic Additions to Unsaturated Systems", American Elsevier, New York, N.Y., 1966.
(8) M. J. Shaw, J. A. Weil, H. H. Hyman, and R. Filler, *J. Am. Chem. Soc.*, **92**, 5096 (1970); M. J. Shaw, H. H. Hyman, and R. Filler, *ibid.*, **92**, 6498 (1970); *J. Org. Chem.*, **36**, 2917 (1971); S. P. Anand, L. A. Quarterman, H. H. Hyman, K. G. Migliorese, and R. Filler, *ibid.*, **40**, 807 (1975); S. P. Anand, L. A. Quarterman, P. A. Christian, H. H. Hyman, and R. Filler, *ibid.*, **40**, 3796 (1975).
(9) N. L. Weinberg and H. R. Weinberg, *Chem. Rev.*, **68**, 449 (1968).
(10) R. F. Merritt and F. A. Johnson, *J. Org. Chem.*, **31**, 1859 (1966).
(11) A. M. Ihring and S. L. Smith, *J. Am. Chem. Soc.*, **92**, 759 (1970).
(12) R. F. Merritt, *J. Am. Chem. Soc.*, **89**, 609 (1967).
(13) R. C. Fahey and C. Schubert, *J. Am. Chem. Soc.*, **87**, 5172 (1965).
(14) R. C. Fahey and H. J. Schneider, *J. Am. Chem. Soc.*, **90**, 4429 (1968).
(15) M. J. Dewar and R. C. Fahey, *J. Am. Chem. Soc.*, **85**, 3645 (1963).
(16) V. J. Traynelis, W. L. Hergenrother, J. R. Livingston, and J. A. Valicenti, *J. Org. Chem.*, **27**, 2377 (1961).
(17) K. Yates and R. S. McDonald, *J. Org. Chem.*, **38**, 2465 (1973).
(18) A. Weissberger, Ed., "Technique of Organic Chemistry", Vol. VII, "Organic Solvents", Interscience, New York, N.Y., 1955.
(19) S. M. Williamson, *Inorg. Synth.*, **11**, 147 (1968).

Fluorination with Xenon Difluoride. Fluorination of Bicyclic Olefins

Marko Zupan,* Ana Gregorčič, and Alfred Pollak

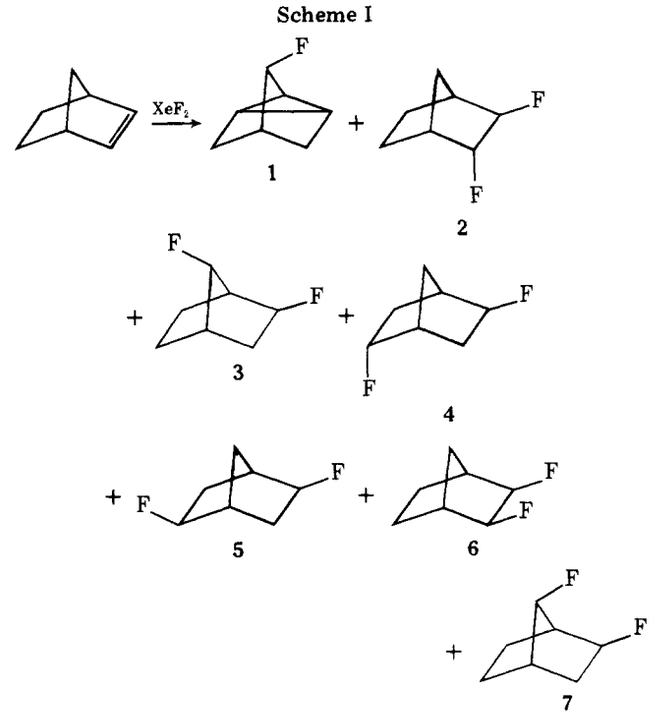
Department of Chemistry and "Jožef Stefan" Institute, University of Ljubljana, 61000 Ljubljana, Yugoslavia

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-