Use of hydrogen fluoride and its complexes with bases for introduction of fluorine atoms into organic molecules

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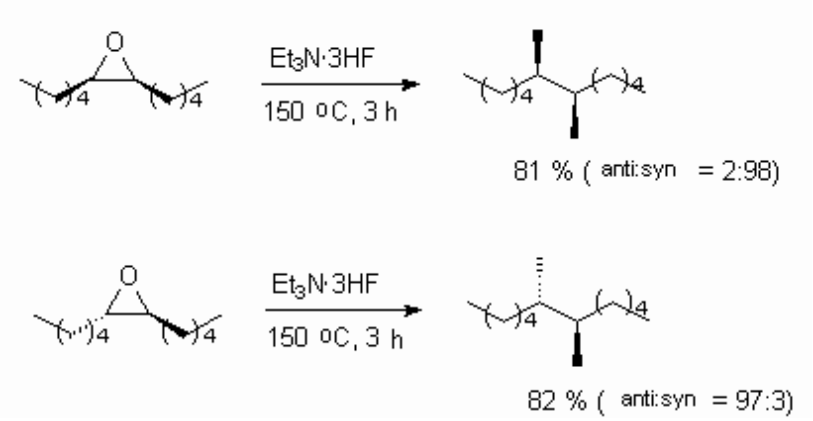
Annotation

The review summarizes and systematizes up-to-date data on fluorinating ability of anhydrous hydrogen fluoride and its complexes with bases of unsaturated organic compounds, alcohols, diazoketones, hydrazones and oximes of ketones, 3,3-dialkyl-1-aryltriazenes, aryldiazosulfides etc.. It contains an analysis of main achievements in use of anhydrous hydrogen fluoride as a fluorinating agent to produce ozone-friendly freons in gas and liquid phases both without catalysts and in the presence of latter. There has been examined factors influencing opening three-membered cycles containing oxygen and nitrogen atoms. The review contains examples of practical application of different groups of fluoroorganic compounds, rational methods of their production and their role in development of modern industry .

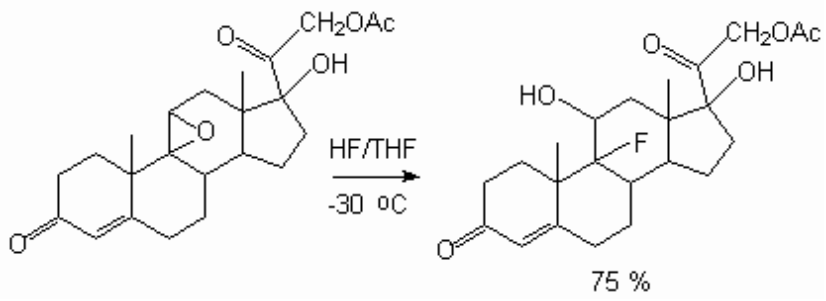
Contents

3.1.Opening an epoxy ring by anhydrous hydrogen fluoride and its complexes with bases.

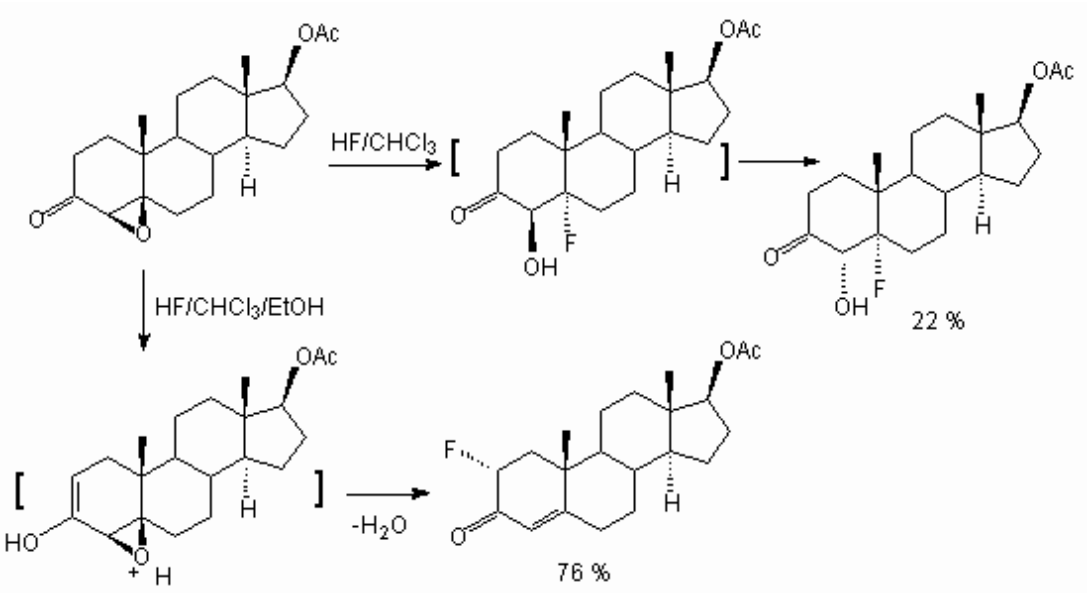
Symmetrically substituted oxiranes under the influence of $Et_3N/3HF$ open the epoxy cycle with high*anti-syn* selectivity to form*syn*- and*anti*-fluoro-derivatives [358].



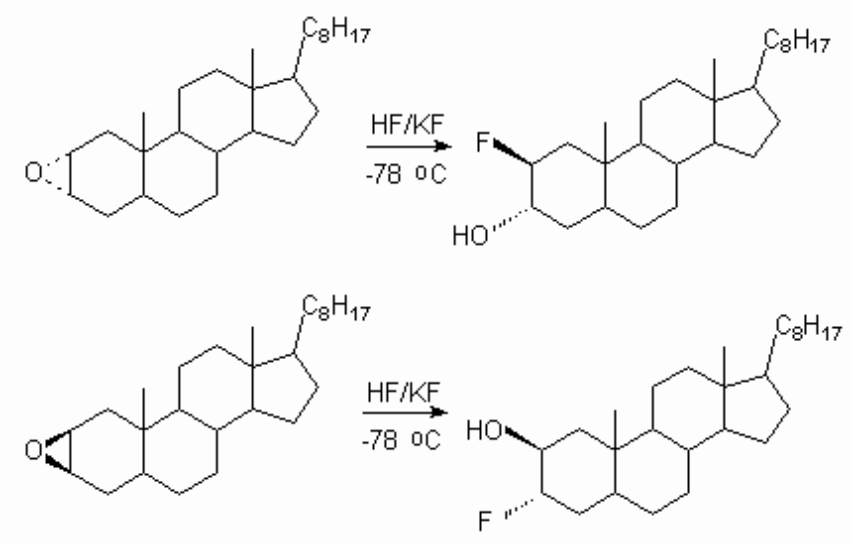
The reaction of opening the epoxy ring under the effect of hydrogen fluoride to forмβ-fluoro-alcohols is of great importance for steroids particularly [341,359,360]. The influence of solvents and additives of urea type has been studied.



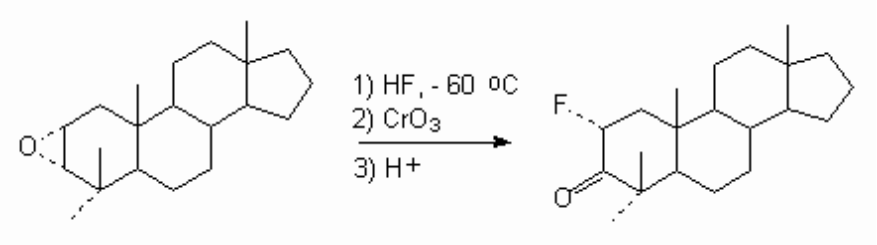
The position of the epoxy cycle in a molecule is not of great importance for the opening process, in all cases formation of fluoro-alcohol takes place and the solvent plays a considerable role [361-363].



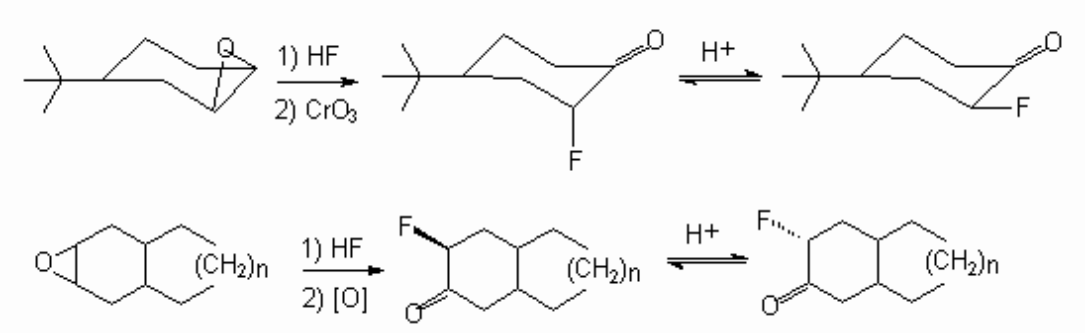
2,3-a- and b-epoxides of cholestane react with hydrogen fluoride in the presence of KF to form trans-*dioxial* derivatives [364].



Simultaneous effect of oxidizers results β-fluoro-ketone as a reaction product [365].

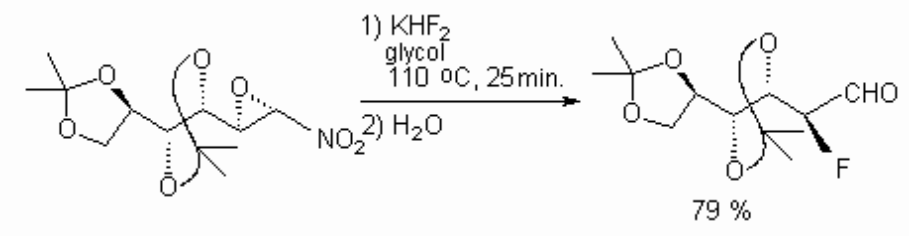


Different non-steroid epoxides under the effect of hydrogen fluoride in the presence of oxidizers give β-fluoro-ketones also.



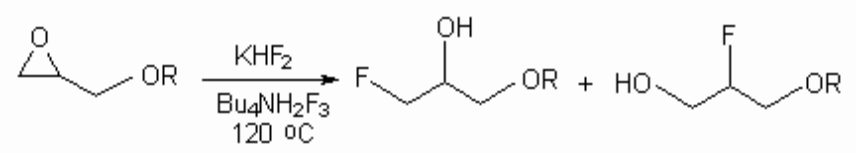
Good results are obtained when the reaction is carried out in ethylene glycol with using KHF_2[319,324-326, 366]. The epoxy ring is opened under the influence of KHF_2 for different classes also, such as sugars [367], prostaglandins (table 26)[323]. In these cases boiling in high-boiling solvents(such as ethylene glycol, dimethylformamide) is necessary that follows with formation of products in high yields.

As a rule when KHF_2 affects epoxides containing one substituent at the epoxy ring there are formed both isomeric fluoro-alcohols which ratio depends on the substituent nature (table 27)[345]. If there is a nitro-group at the epoxy ring the α-fluoroaldehyde is formed.



The use of $KH[^{18}F]F_2$ for opening the epoxy cycle makes possible introduction of ^{18}F isotope [380].

Tetrabutylammonium fluoride/2HF reacts only with very reactive epoxides and has found a rather limited application in hydrofluorination process [381-383]. But addition of KHF_2 to this system makes possible to carry out the process which runs regioselectively and the reaction product yield is high enough [384-387].

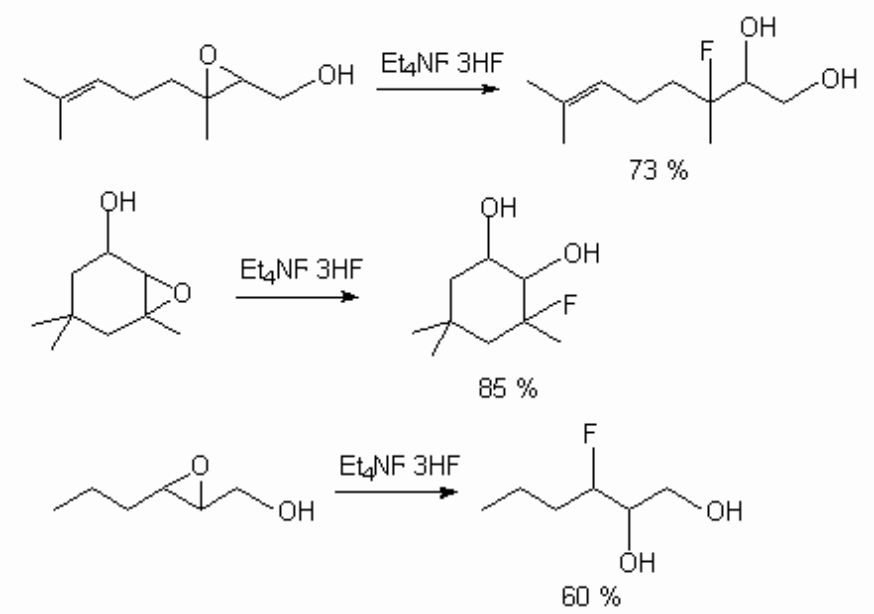


R	Time, h	Ratio	Yield, %
H	30 [a]	100:0	47
Me	3	100:0	74
Ph	8	100:0	90
Bn	6	96:4	74

[a] temperature of 80^{o}C

Such a system is found very effective in hydrofluorination of epoxylactones which runs regioselectively to form fluorodesoxylactones (table 28)[388].Thus, treatment of 2,3-anhydro-L-erythrono-1,4-lactone with a mixture of collidine-3HF (70^{o}C, 3 days) a mixture of 2-desoxy-2-fluoro-D-erythrono- and 3-desoxy-3-fluoro-threono-1,4-lactones is obtained [389]. Similarly , 6-bromo-2,6-didesoxy-2-fluoro-D-glucono-1,4-lactone is synthesized in 68% yield from 6-bromo-6-desoxy-D-monnono-1,4-lactone and Et_3N* 3HF whereas the effect of collidine-3HF gives a mixture (2:1) of this lactone and 6-bromo-3,6-didesoxy-3-fluoro-D-altrono-1,4-lactone [389].

Either HF/Py system or KHF_2 is used to open the epoxy cycle of cyclic compounds [390]. Epoxy-alcohols containing two or three substituents at the epoxy cycle can be opened by the effect of Et_4NF*3HF in the presence of $Ti(OPr^i)_2F_2$ catalyst [391]. Here fluorodiols are formed and the process runs regioselectively [392].



An increase in hydrogen fluoride quantity does not result in an increase in the fluorination product yield. Thus, when Et_4NF* 3HF system is used the yield of fluoro-alcohol is 73% whereas in Et_4NF*4HF it is only 67%, At the same time without catalyst the yield is only 22%.

Table 26. *Opening the epoxy cycle under the effect of KHF_2 complex*

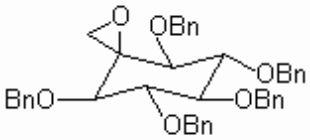
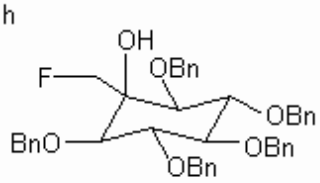
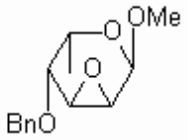
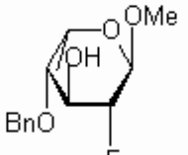
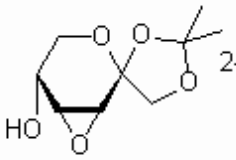
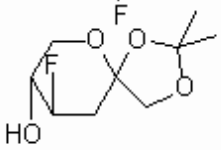
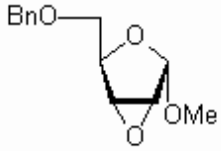
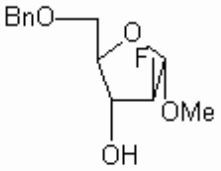
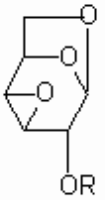
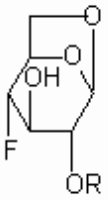
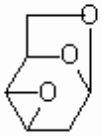
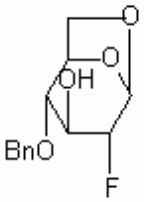
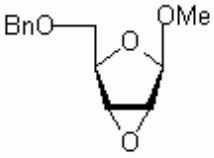
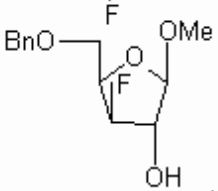
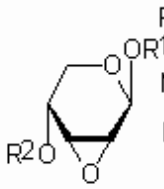
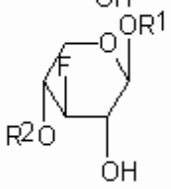
Substrate	Conditions	Product	Yield,%	Ref.
	Solvent T,°C Time. h			
	DMF 158-160 5		68	**367**
	$(CH_2OH)_2$ 180 3		44	**368**
	2-метокси-этанол 125 16		80	**369**
	$(CH_2OH)_2$ RT 1.5		40	**370**
	R = Bz $(CH_2OH)_2$ RT 4		55	**371**
	R = H $(CH_2OH)_2$ RT 1		65	**372,373**
	$(CH_2OH)_2$ RT 1.5		40	**374-376**
	$(CH_2OH)_2$ RT 1.5		35	**377**
	Me Bn $(CH_2OH)_2$ RT 40 Bn H		70 -	**378** **379**

Table 27. *Use of KHF_2 for opening the epoxy cycle of different sustrates*

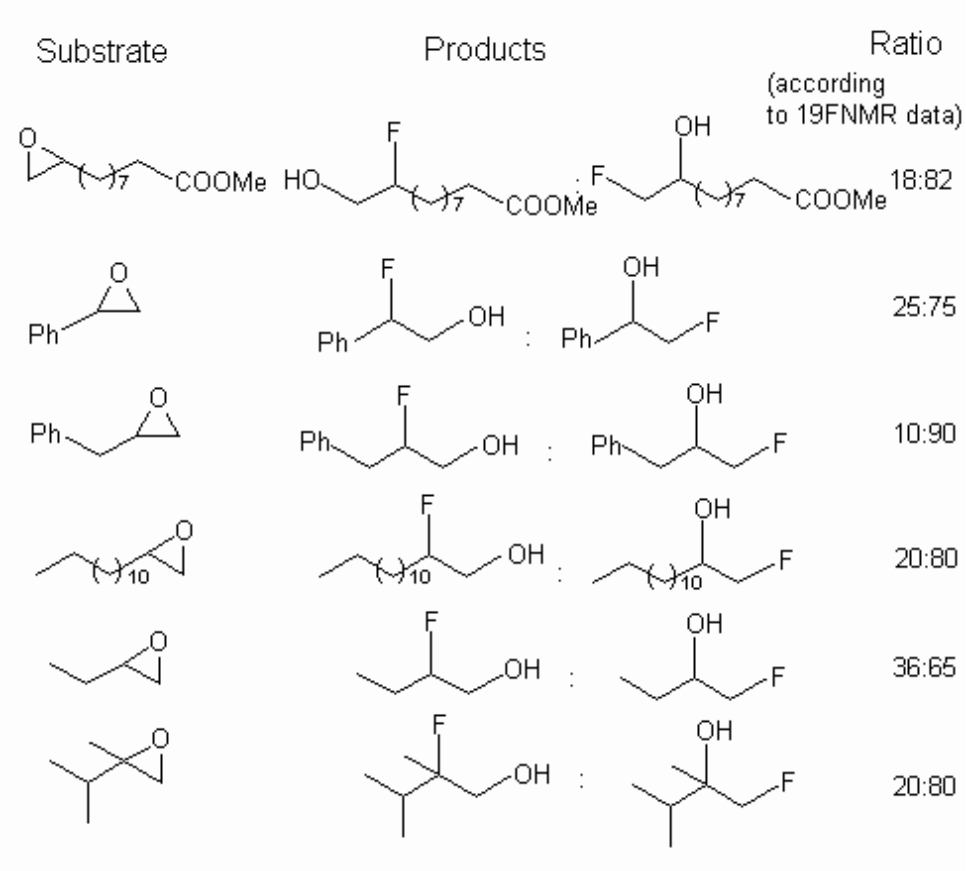
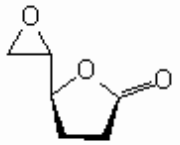
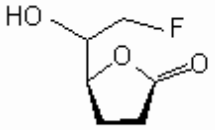
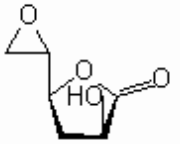
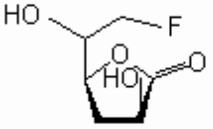
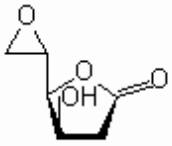
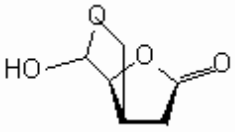
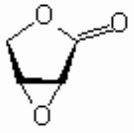
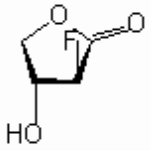
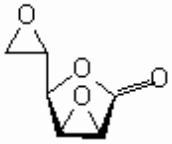
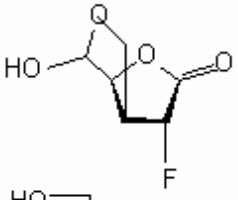
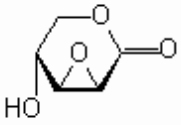
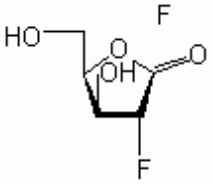
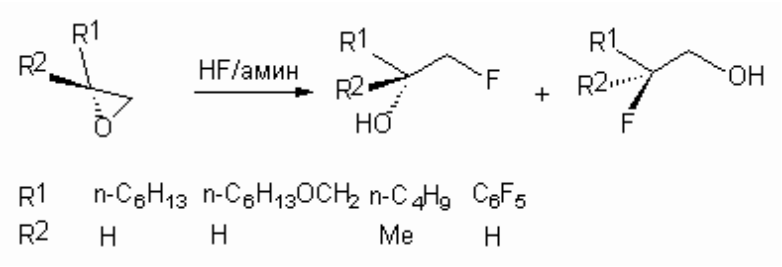
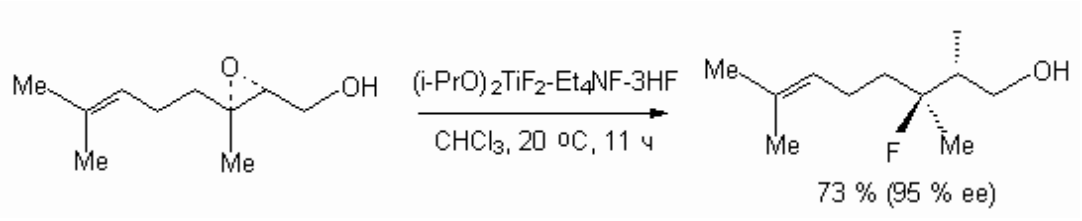


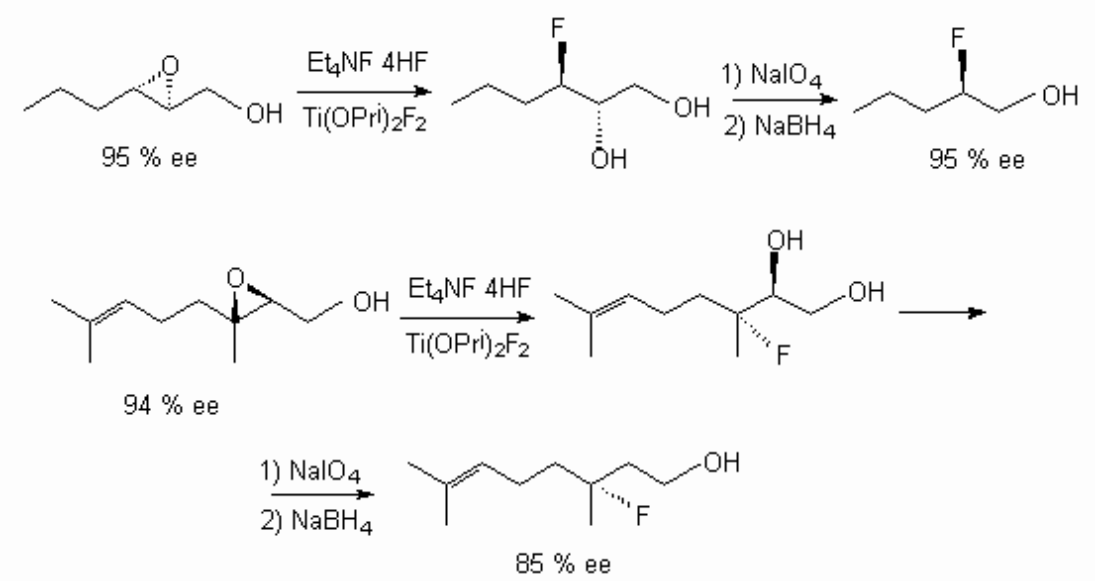
Table 28. *Hydrofluorination of epoxylactones [388]*

Substrate	Conditions			Product	Yield,%
	T,°C	Time,h	Catalyst		
	75	39	$Bu_4N^+ \cdot H_2F_3^-$ KHF_2		70
	75		KHF_2		65
			$Bu_4N^+ \cdot H_2F_3^-$ KHF_2		10
	75	6	KHF_2		35
	75	8	KHF_2		10
	75	63	KHF_2		25

In case of using optically active epoxyalcohols there are formed optically active fluoroalcohols [393,394]. Complexes of hydrogen fluoride with trialkylamines are used also [395-400]. But it should be noted that a great excess of HF/amines complex increases the percentage of oligomerization products.

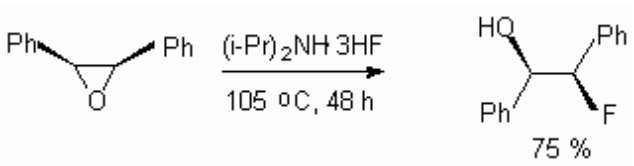




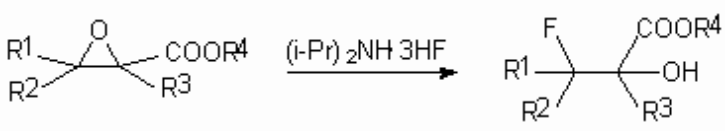


The use of $(i\text{-PrO})_2TiF_2$-Et_4NF-nHF system for opening the epoxy cycle results in regio- and stereoselective fluorination of the cycle with formation of appropriate fluoroalcohols [410]. That was used for synthesis of optically active 3-fluoro-1,2-diols.

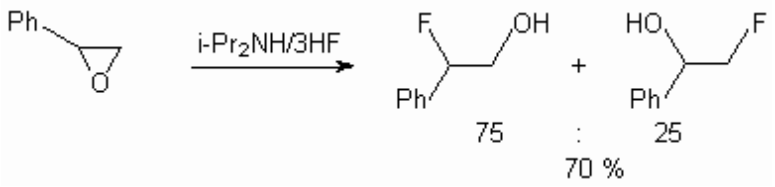
Complexes of $(i\text{-Pr})_2NH$*3HF are of great importance among hydrogen fluoride complexes and they were successfully used for opening the epoxy cycle. But relatively elevated reaction temperatures (from 78°C to 140°C) [41] made necessary to look for new complexes which would be able to use under more mild fluorination conditions. Therefore in future this task will find a solution because the result of this method gained a special attention. Nevertheless let us treat a question of using a system of hydrogen fluoride-alkylamines for opening the epoxy ring. In 1960 Jullien proposed for these purposes a system of $(i\text{-Pr})_2NH$*3HF which was found effective and opened the epoxy cycle with high regio- and stereoselectivity at high yield of the reaction products. (table 29)[341]. Thus, cis-2,3-diphenyloxirane gives syn-2-fluoro-1,2-diphenylethanol [328].

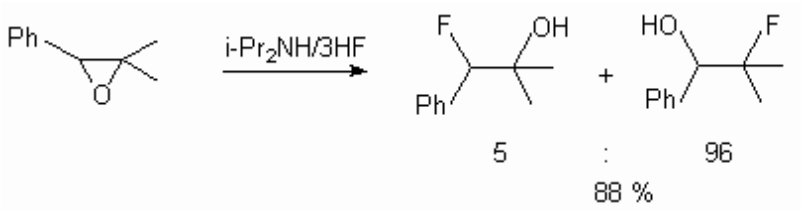


Substituted epoxides of olefins are opened by the influence of $(i\text{-Pr})_2NH$*3HF system to fornβ-fluorα-hydroxy derivatives [402].



Steric factors of the substituents at the epoxy cycle influence considerably on the direction of regioselective opening the cycle (table 30), as a rule mixtures of two isomeric fluoroalcohols **32**and **33** are formed [403]. A system of Me_3N* 2HF opens the epoxy cycle in a similar way (table 30)[341]. If phenyl as a substituent is present at the epoxy cycle or in case of non-simmetrically substituted epoxides there are always formed two isomeric fluoroalcohols. In case of phenyl mainly fluoroalcohol is formed which fluorine atom is at the carbon connected with this substitutuent. A fluoroalcohol, which fluorine atom is at the carbon linked with a donor substituent, prevails for non-simmetrically substituted epoxides .





Hydrofluorination of indene and tetraline epoxides with $(i\text{-}Pr)_2NH$*3HF complex results in formation of isomeric fluoroalcohols for indene and in formation of only one isomeric fluoroalcohol for tetraline [341].

Table 29. *Opening the epoxy cycle under the influence of $Pr^i{}_2NH$* 3HF [341]*

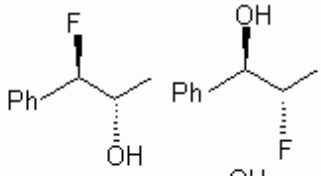
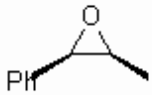
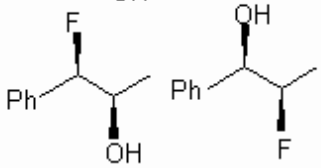
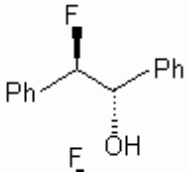
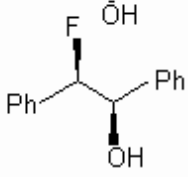
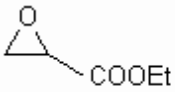
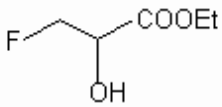
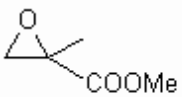
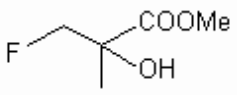
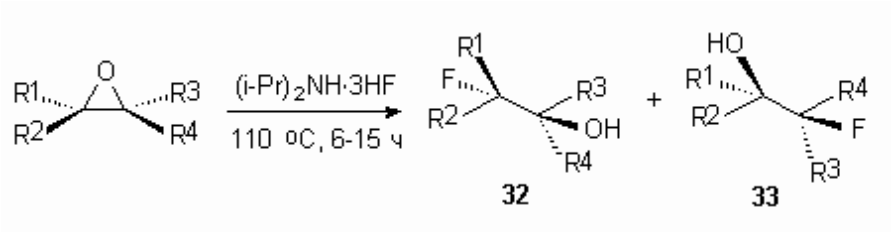
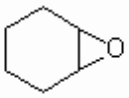
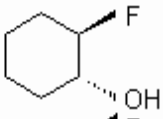
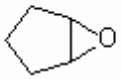
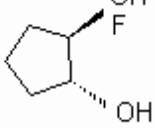
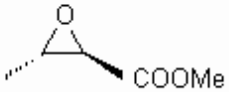
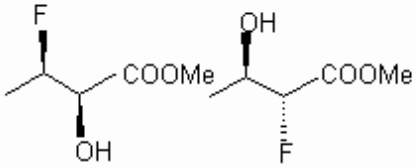
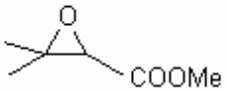
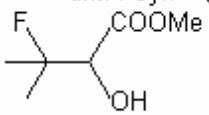
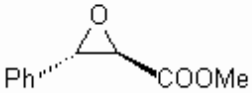
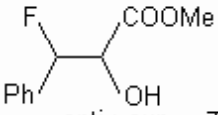
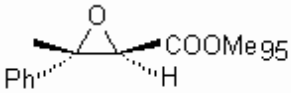
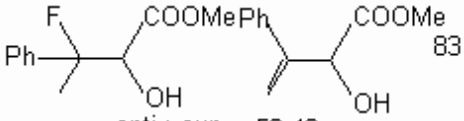
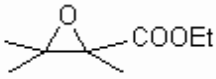
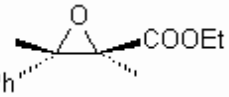
Epoxide	Conditions T,°C	Time,h	Product	Ratio	Yield,%
	132	23		83:10	83
	134	23		10:90	88
	115	24			64
	105	48			75
	125	17			15
	150	21			80

Table 30. *Hydrofluorination of substituted epoxides under the effect of $(i\text{-}Pr)_2NH$*3HF [402]*

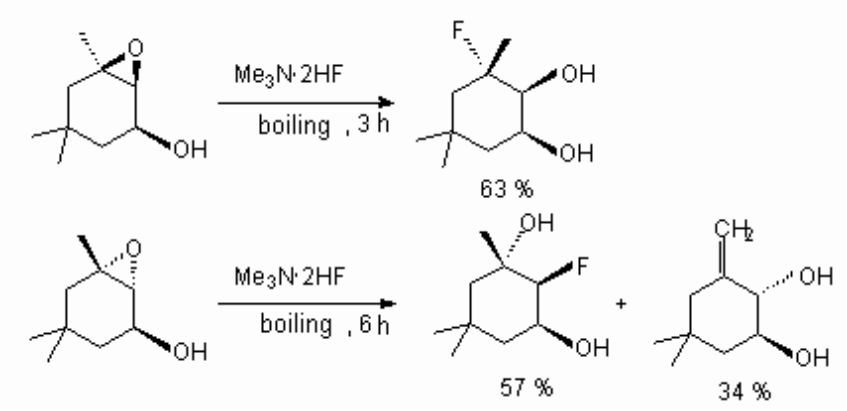


R^1	R^2	R^3	R^4	Yield, %		Ratio **32** : **33**
				32	**33**	
H	H	H	CH_2OBn	70	5	94:6
Me	H	H	CH_2OBn	66	13	83:17
Me	Me	H	CH_2OBn	66	10	89:11
H	H	H	$C(Me_2)OBn$	62	2	96:4
H	H	H	$(CH_2)_2OBn$	69	12	86:14
H	H	Me	$(CH_2)_2OBn$	47	31	60:40
H	H	H	$(CH_2)_3OBn$	63	6	92:8

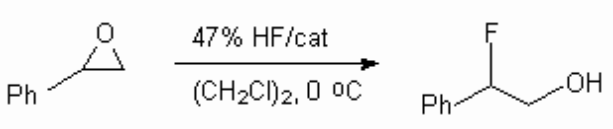
Table 31. *Opening the epoxy cycle under the effect of Me_3N*2HF [341]*

Epoxide	Conditions		Product	Yield,%
	T,°C	Time, h		
	120	18		75
	110	18		65
	120	20	 anti : syn = 62:38	65
	140	18		72
	95	6.5	 anti : syn = 74:26	65
	95	7	 anti : syn = 52:48	83
	110	20	Does not react	
	110	20	Does not react	

Regioselective opening the epoxy ring under the effect of Me_3N*2HF is observed for many epoxides, in particular for cis- and trans-epoxide of *isophorol* (table 31). Thus, cis-epoxide of isophorol gives 3-fluoro-1,2-diol whereas trans-epoxide of isophorol gives 2-fluoro-1,3-diol [404,405]. That may be explained by the influence of the substituent in thα-position on conformation of transient state.

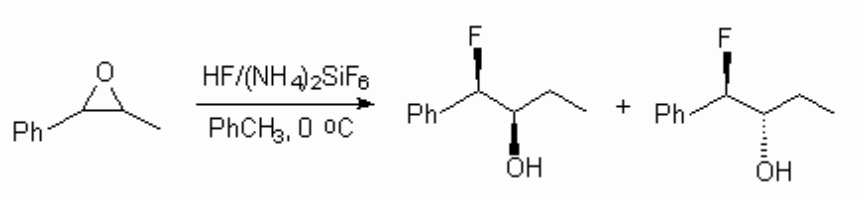


It should be noted that in many cases addition of a metal fluoride gives a desirable result. Apart different salts can be used as catalyst also, silicon derivatives in particular. Nucleophilicity of fluoride-ion is sufficient for realization of hydrofluorination in this case even in aqueous solutions of hydrogen fluoride. So phenyl-substituted epoxide under the influence of 47% hydrogen fluoride in the presence of silicon salts gives fluoroalcohol in a rather good yield [406].



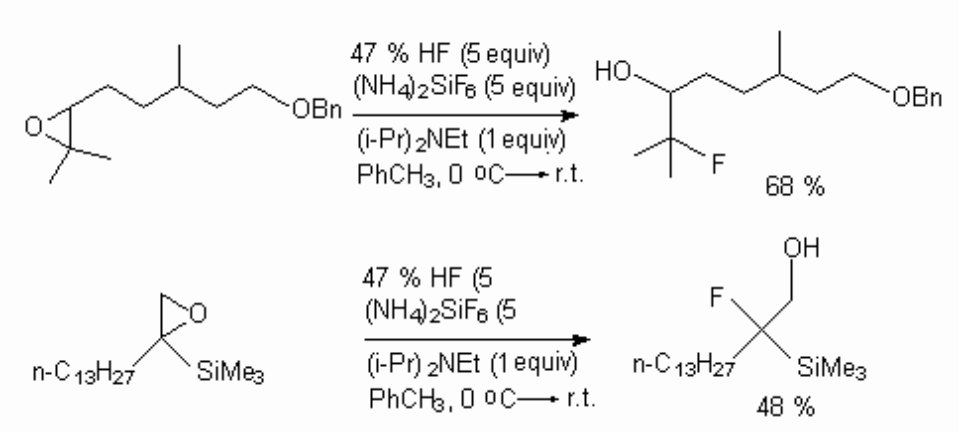
Catalyst	Yield, %
$(NH_4)_2SiF_6$	46
$(NH_4)_2SiF_6$, CsF	67
$(NH_4)_2SiF_6$, SnF_2	47
Cs_2SiF_6	59
$BaSiF_6$	46
$(BnMe_3N)_2SiF_6$	21

Anhydrous hydrogen fluoride in diethyl ether does not react with di-substituted epoxides, whereas in aqueous 47% hydrogen fluoride in catalysis of $(NH_4)_2SiF_6$ in toluene they give a mixture of fluoroalcohols in a yield up to 62%. The ratio of *syn:anti* isomeric fluoroalcohols depends on the catalyst used. Thus at the same yield of the reaction products (41-45%) the ratio of *syn:anti* is different [406].

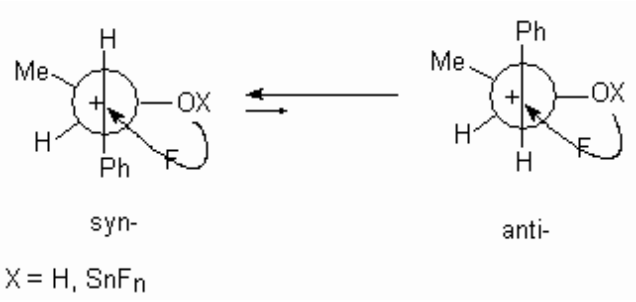


HF	Catalyst (equiv)	Yield,%	Syn/anti ratio
47%	$(NH_4)_2SiF_6$ (5.0)	45	7:1
47%	i-Pr_2NEt (1.0)	41	5:1
47%	$(NH_4)_2SiF_6$ (5.0) CsF (1.2)	45	20:1
Anhydrous HF	$PhSiF_3$ (5.0)	25	11:1

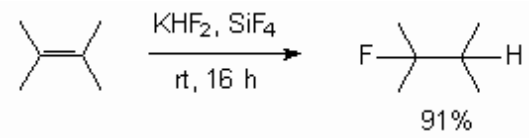
Hydrofluorination of 2,2,3-tri-substituted epoxides and enoxysilane under the effect of aqueous 47% hydrogen fluoride in the presence of $(NH_4)_2SiF_6$ gives solely one isomeric fluoroalcohol [406].



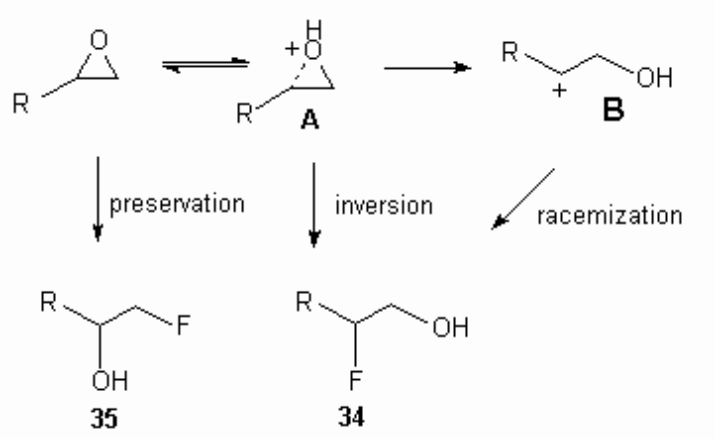
The authors suppose that the formation of prevailing quantity of syn-isomer is due to rearrangement of intermediate carbcation.



Silicon tetrafluoride was used as a catalyst also that is shown on the example of formation of 2-fluoro-2,3-dimethylbutane in hydrofluorination of 2,3-dimethylbutene-2[407].



The mechanism of opening epoxides under the effect of hydrogen fluoride and its complexes with bases has gained considerable attention of researchers. Several ways of the reaction course were proposed, they explain high regioselectivity of the process and the influence of the nature of the substituent at the epoxy cycle, the role of solvent and process conditions. They can be illustrated by the following scheme:

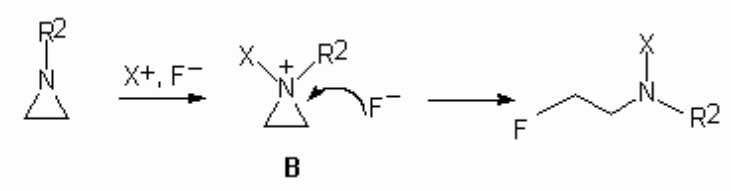


Electronic properties of the substituent influence regio- and stereoselectivity in hydrofluorination under the effect of HF/Py, i.e. 2-fluoro-2-phenylethanol **34**was obtained from styrene oxide via secondary b-hydroxycarbenium ion (Sn1 process) at the account of high-stable benzyl cation, whereas 1,1,1-trichloro-3-fluoropropanol-2 **35** (SN2 process) is obtained from 3,3,3-trichloro-2-epoxypropane. These two mechanisms may be realized in the hydrofluorination process. Steric factors are of great importance in determination of regioselectivity in opening the epoxy ring.

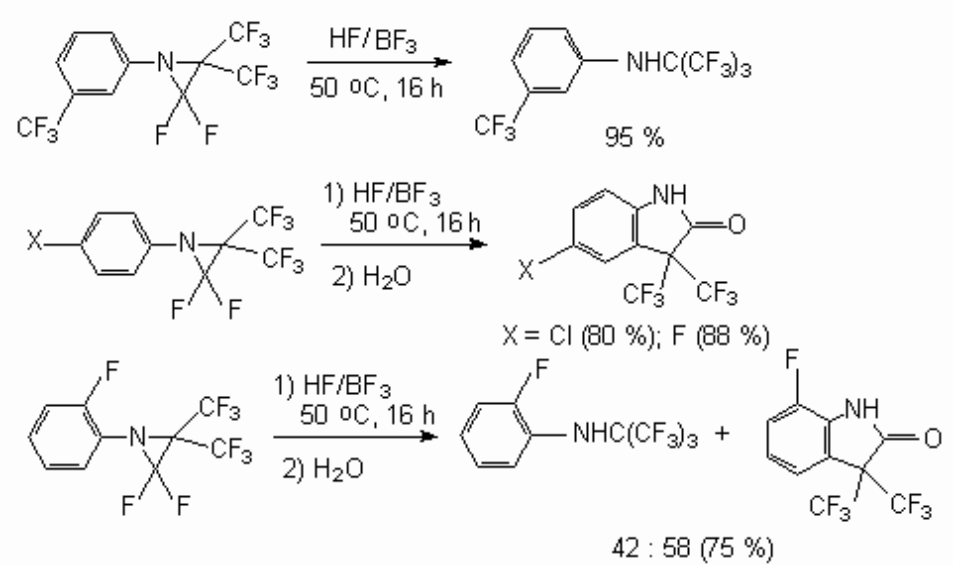
3.2.Opening nitrogen-containing three-membered heterocycles

As it is seen from the data review [408] the opening of the aziridine cycle under the influence of different nucleophilic reagents has drawn great attention. The effect of anhydrous hydrogen fluoride on aziridines became an important method to produce interesting 1-amino-2-fluorocompounds i.β-fluoroamineα,-amino- arβ-fluoro-acids arβ-b-

fluoroazaalkanes [38, 407-418]. The process runs through an intermediate formation of quaternary ammonium salt B in which fluoride-ion attacks carbα-atom of the three-membered cycle.



N-Aryl-2,2-difluoro-3,3-bis(trifluoromethyl)aziridines were obtained in a reaction of imines with difluorocarbenes by the effect of anhydrous hydrogen fluoride in the presence of BF_3 as a catalyst, the three-membered cycle was open to form secondary amines [419]. But there was observed formation of cyclic compounds also in dependence on the nature of the substituent in the benzene ring. Opening the aziridine cycle runs at the account of initial protonation of the nitrogen atom, whereas opening cyclic compound takes place at the account of the attack of carbcation generated in the opening of the protonated cycle. The presence of BF_3 in the system increases the Hammett acidity constant sharply and makes the cyclization process easier (anhydrous HF(99.5%) has Ho = -11 and Ho of a 7% HF solution has a value of -16.6) [419].

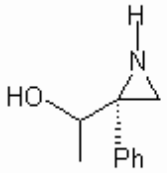
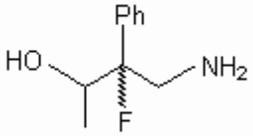
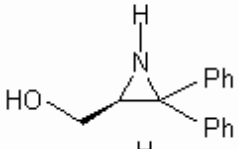
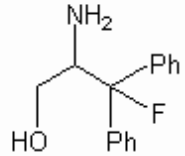
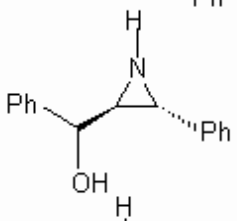
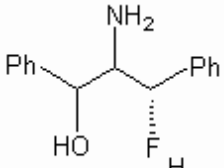
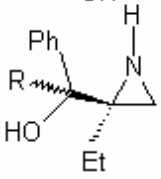
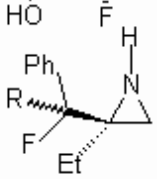
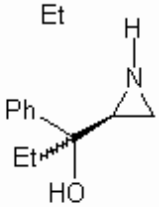
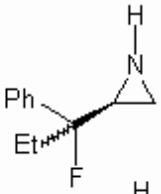
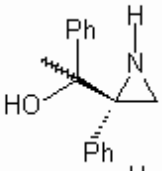
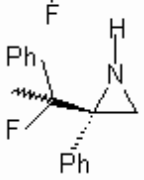
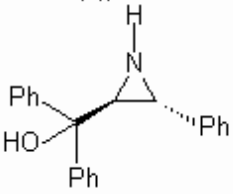
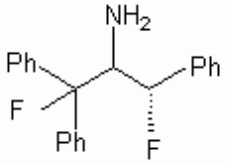


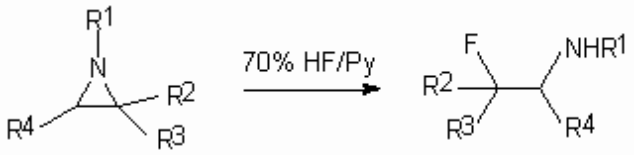
Opening the cycle of 1-phenyl-1-allylaziridine under the effect of Et3N 3HF runs regioselectively to forrα-fluoroamines. Regioselectivity in this case also is determined by the nature of the substituent at the aziridine cycle.

αa-Hydroxyaziridines by the effect of HF/Py complex depending on the reaction conditions are converted into appropriate fluoroalcohols and in very many cases the OH group is replaced with fluorine while the structure of the aziridine ring is not changed (table 32)[234].

Aziridines containing alkyl groups under the effect of hydrogen fluoride and its complexes with amines open the cycle to form 2- fluoroalkylamines [395, 413,416,420-424]. The effect of the mole ratio of HF/pyridine on regio- and stereo-selectivity can be explained as the effect of solvation of intermediate carbene ions.

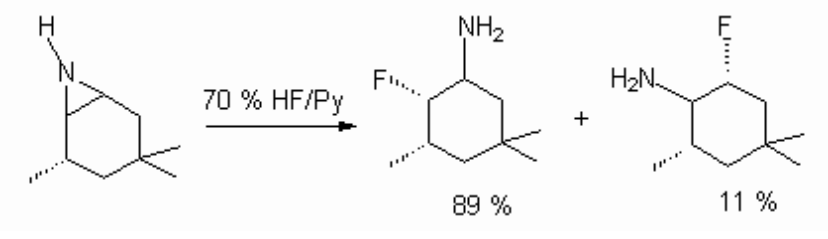
Table 32. Effect of HF/Py α-hydroxyaziridines

Substrate	Conditions		Product	Yield,%
	T,°C	Time,h		
	55	90		100
	20	6		87
	20	6		80
	R = Me R = Et	20 90 20 72		28 82
	20	120		65
	20	256		5
	20	9		65

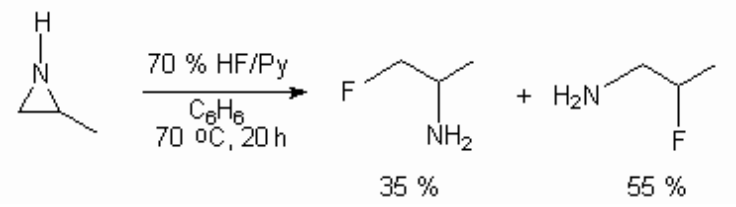


R^1	R^2	R^3	R^4	T, °C	Time, h	Yield, %
H	Ph	H	H	20	1	78
H	Me	Me	Et	70	24	90
Et	Ph	H	H	70	1	47
cis-H	Ph	H	Me	20	6 days	69
trans-H	Ph	H	Me	20	5	71

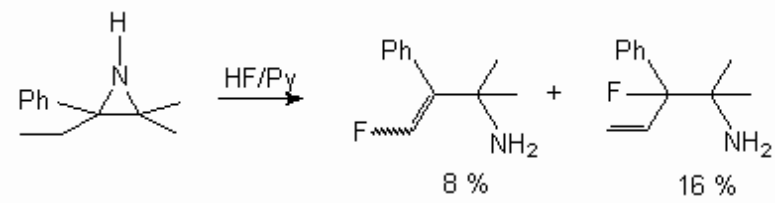
Opening the aziridine cycle with a 70% HF/Py system makes possible to obtain iso-butyl-3-fluoroalanine, methyl-3-fluorophenylalanine [407]. Stereochemistry of the reaction depends both on the fluorinations agent and on the aziridine structure. As a rule there is formed a mixture of diastereomeres [407, 411, 420] For example, two regioisomers of 2-fluorocyclohexylamine are formed in hydrofluorination of cis- and trans-***eriminocyclohexane***with 70% HF/Py [412].



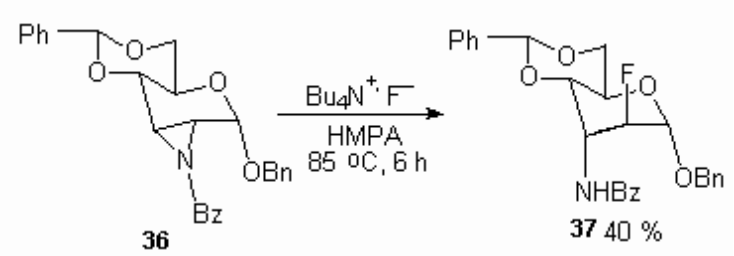
Great attention of researchers has been drawn to regioselectivity and stereochemistry of the cycle opening [413, 421]. In case of non-symmetrically substituted aziridines the both isomeric fluoroalkylamines are formed.



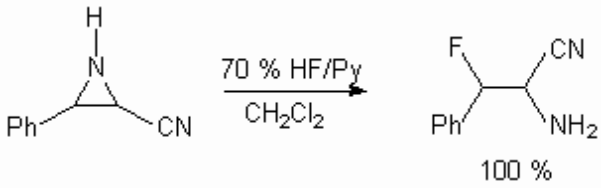
Phenylvinylaziridine reacts with HF/Py to form β-fluoroallylamine along with β-fluoroamine, but in this case the total yield of the reaction products is very small [421].



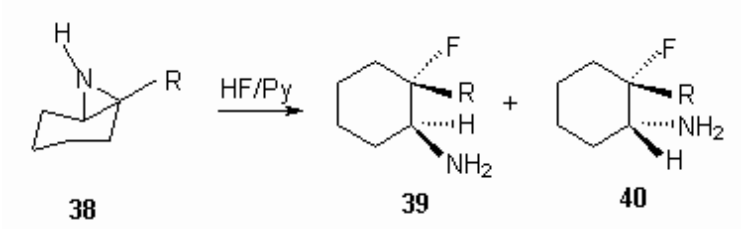
Bicyclic aziridines such as derivatives of *pyranosidines* and *furanosidines* are hydrofluorinated to form fluoroamine derivatives. So, aziridine derivative 36 under the effect of tetrabutylammonium fluoride gives (benzoyloamino) fluoropyranoside 37 [425,426].



The availability of such substituents at the aziridine cycle as phenyl and nitrile brings to formation of only one isomeric product under the effect of 70%HF/Py system [420].

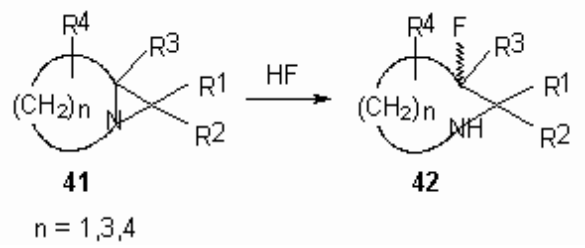


The HF/Py complex hydrofluorinates aziridines containing cyclic fragments **38** to form a mixture of fluorocycloamines **39**and **40** with cis-isomers **40** prevalence. Probably , isomerization of trans-isomer **39** into cis-isomer **40** takes place in this process due to thermodynamic control [38].

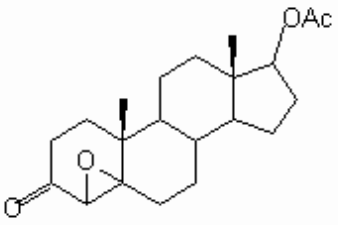
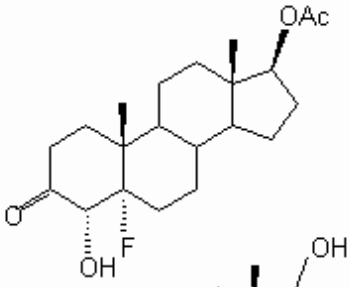
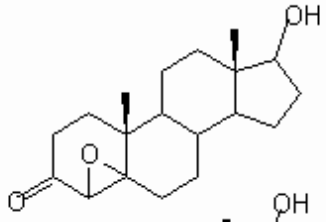
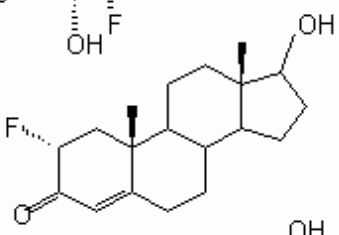
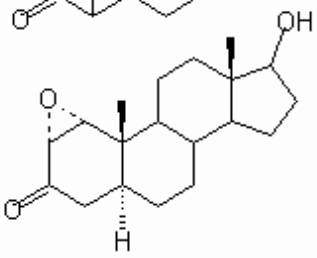
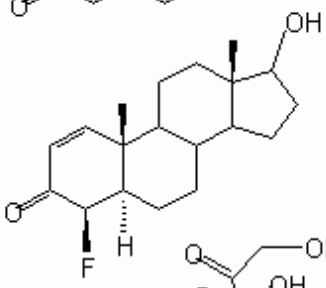
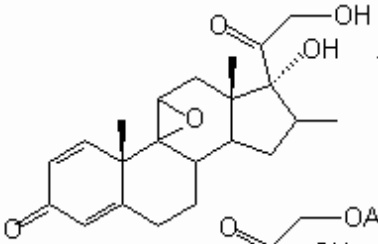
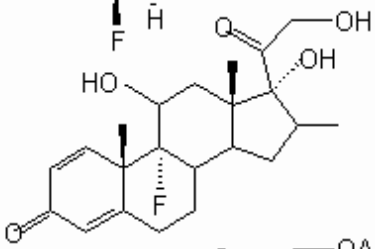
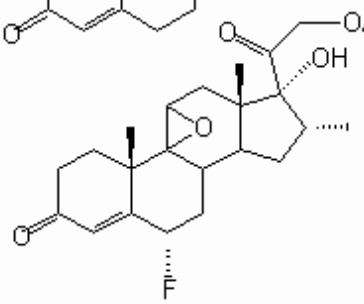
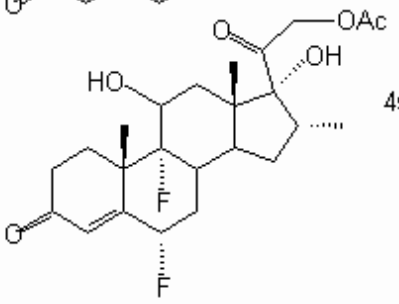


R= Ph	0 100
Et	22 78
H	33 66

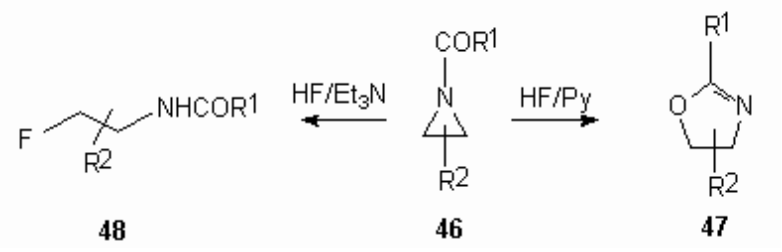
Bicyclic aziridines **41** react with 1-azabicyclo[n.1.0.]alkane under the effect of hydrogen fluoride in diethylether or with HF/Py to give 3-fluoro-1-azacycloalkanes **42** [416,417].



Stereochemistry in case of bicyclic aziridines also depends on the fluorinating agent used and on the reaction conditions. For example, interaction of bicyclic aziridine **43** with HF/Py results in formation of cis-3-fluoro-2,3-diphenylazetidine **44** at a short reaction time whereas an increase in the reaction time or using anhydrous hydrogen fluoride results in formation of trans-isomer **45** more thermodynamically stable [417].

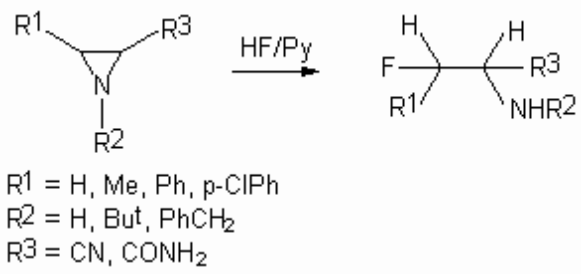
Epoxide	Solvent	Conditions T, °C	Time, h	Product	Yield,%	Ref.
	HF $CHCl_3$	25	2		22	**315**
	HF DMF	23	3		65	**315**
	HF DMF	23	3		83	**315**
	70% HF	-20	4		83	**316**
	HF THF CH_2Cl_2	-10	6		45	**317**

Aziridines containing alkyl group at the nitrogen are less reactive in comparison with the same containing carbonyl group. Heating N-activated aziridines (COR^1 as the substituent at nitrogen) **46** with HF/Py gives oxazoline derivative **47** mainly and a small amount of fluoroamine **48**, whereas the effect of Et_3N*3HF complex results in the opposite picture [38, 411, 413]. That points to the importance of steric effects at the nitrogen atom and to the influence of effectiveness of the nucleophilic agent.

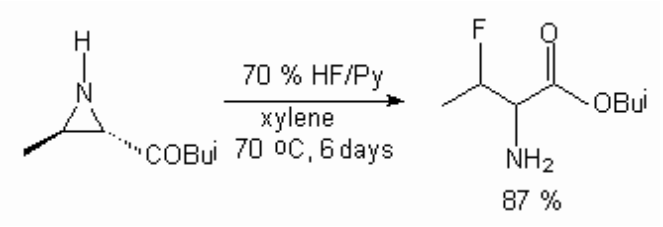


48 **46** **47**

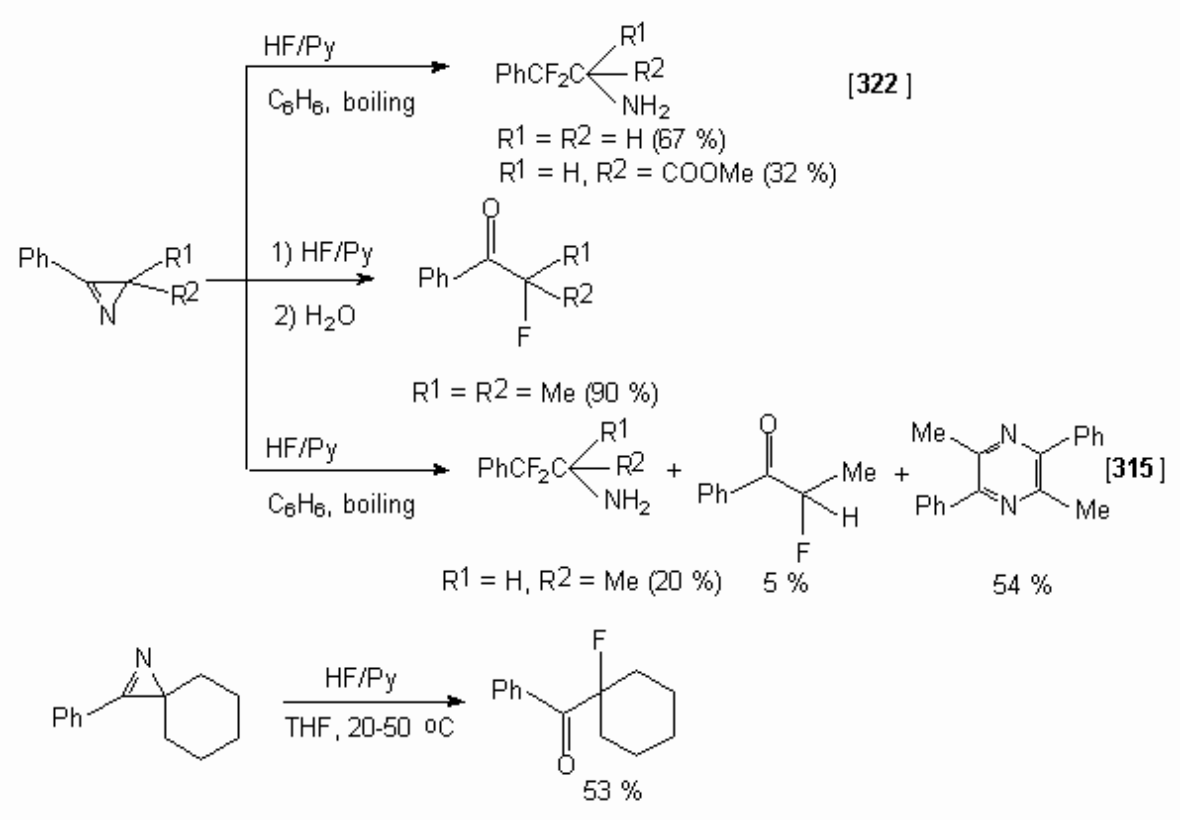
Interaction of cis-cyano-2- and cis-amido-2-aziridines with HF/Py complex results in formation β-fluoro-α-amino acid and esters in good yield. Cis-2-cyanoaziridine gives a mixture of threo- and erythro-2-amino-3-fluoronitrile (ratio of 57:43)[410,414,415].



R^1 = H, Me, Ph, p-ClPh
R^2 = H, Bu^t, $PhCH_2$
R^3 = CN, $CONH_2$

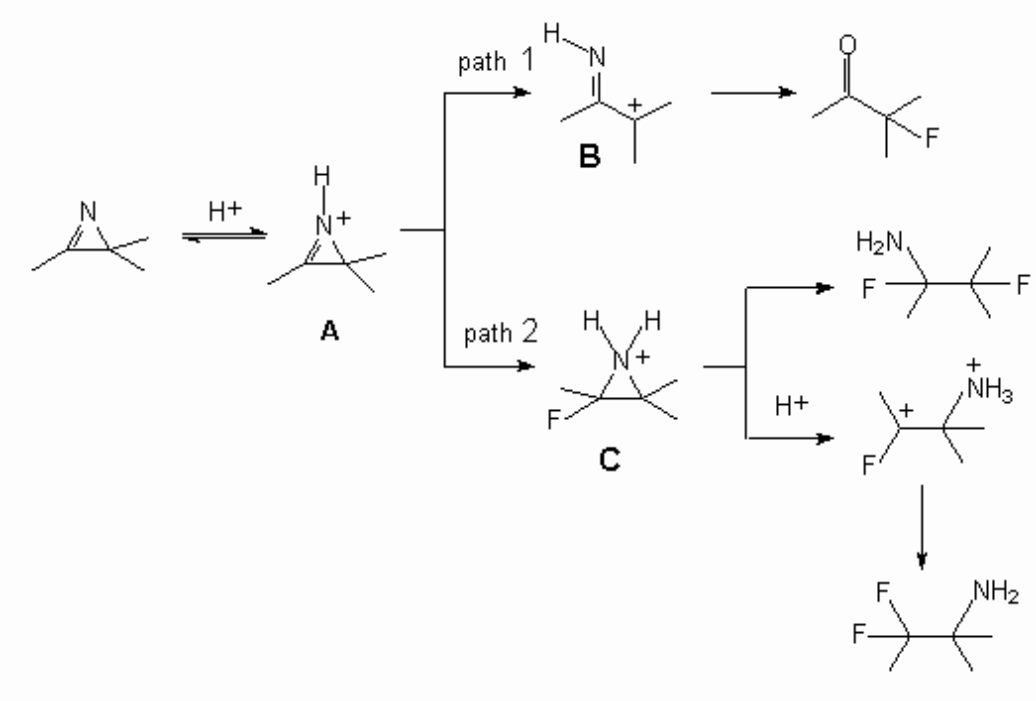


Phenyl-substituted azirine under the effect of HF/Py complex converts either in α-fluoroketone or in β-difluoroamine [2,38,410,415,420,422,423,427].



In a number of cases there was observed formation of pyrazine derivatives (table 33)[220, 221a, b, 416, 422].

It is supposed that interaction of azirine with hydrogen fluoride runs via initial protonation of the nitrogen atom of the azirine derivative with generation of cation **A**.

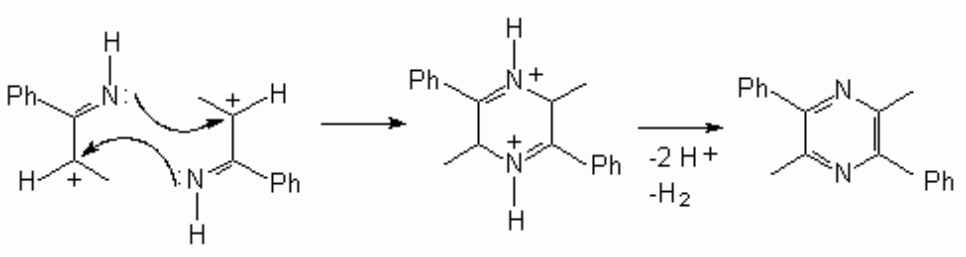


Further there are several ways to realize conversions of the cation:

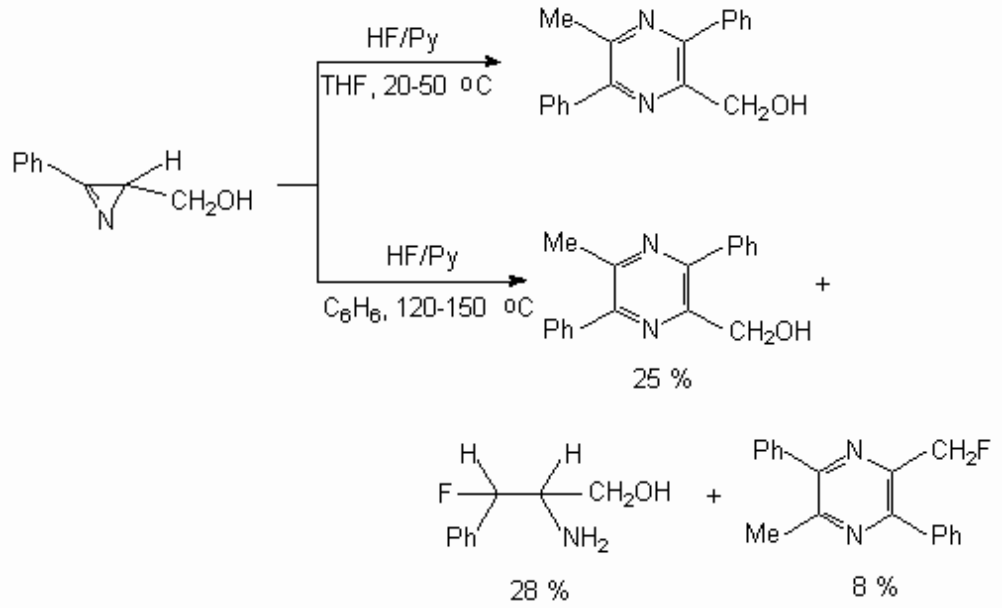
1.conversion into intermediate **B** from which eithα-fluoroketones are formed or pyrazine at the expense of condensation of two molecules of intermediate **B**.

2. Conversion into intermediate **B** from whiβ-difluoroamines are formed via further conversions under the effect of the system proton .

Formation of compound 51 can be explained by the following scheme:



The substituents at the aziridine cycle plays the key role in realization of either direction. So, azirines ,containing alkyl substituents only, foiβ-difluoroamines (way 2 is realized) whereas those containing electron-acceptor groups form pyrazine derivatives ancα-fluoroketones (way 1 is realized) [427]. For example, interaction of 1-phenyl-3-hydroxyaziridine with HF/Py results in formation of the appropriate pyrazine derivative anα-fluoropropiophenone [427] . A temperature increase to 20-50 ^{o}C gives the pyrazine derivative only.



In this case cationoid intermediate **B** is not stabilized by one alkyl substituent and electron-acceptor groups and the reaction runs via intermediate B. When two alkyl substituents or one phenylgroup in position 2 are present,

intemediate B is stabilized by these groups that results in formation α-fluoroketone as the main product.

Steroids containing the azirine cycle under the effect of HF/Py in tetrahydrofurane give fluoroketones, not amines [38].

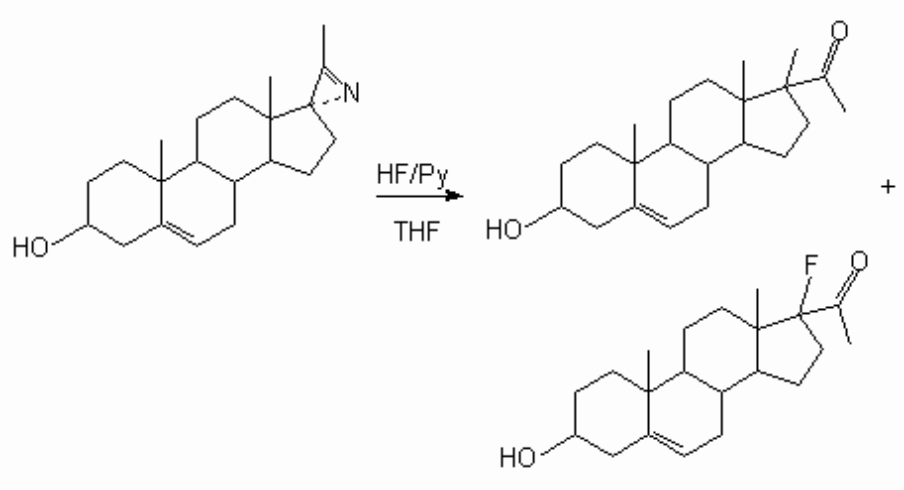
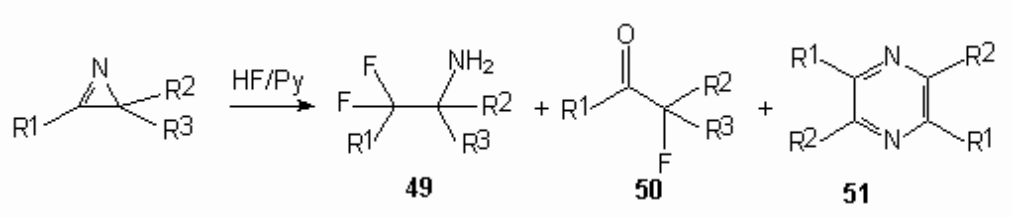
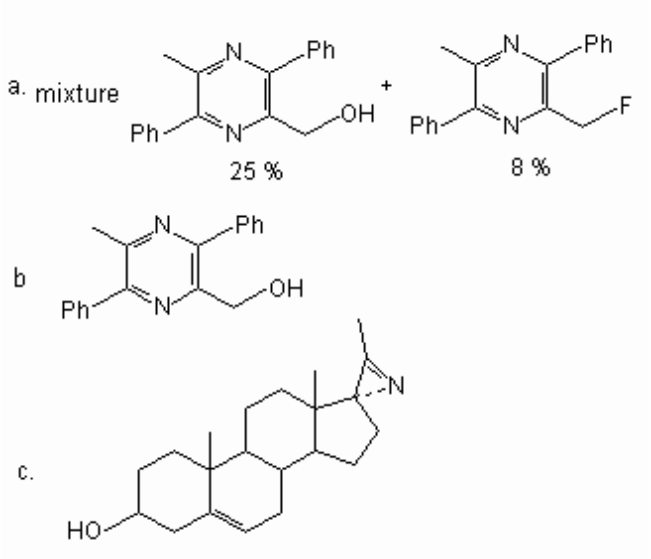


Table 33. Fluorination of 2H-azirine derivatives under the effect of HF/Py



R^1	R^2	R^3	Conditions			Yield, %			Ref.
			Solvent	T, °C	Time,h	**49**	**50**	**51**	
C_8H_{17}	H	H	C_6H_6	r.t.	3	58	-	-	**423**
Pr	Pr	H	C_6H_6	r.t.	10	43	-	-	**423**
Ph	H	H	C_6H_6	r.t.	1	67	-	-	**416,423**
Ph	Me	H	C_6H_6	r.t.	1	20	5	54	**423**
Ph	Me	H	C_6H_6	r.t.	1	74	traces	16	**427**
Ph	Me	H	THF	-20	2	-	-	81	**421**
Ph	Me	Me	THF	-20	2	-	90	-	**421**
Ph	-$(CH_2)_5$-		THF	-20	7	-	53	-	**421**
Ph	Ph	H	C_6H_6	r.t.	1	-	93	-	**427**
Ph	Ph	H	THF	-20	16	-	25	-	**421,427**
Ph	CH_2OH	H	C_6H_6	-20	1	28	-	a	**427**
Ph	CH_2OH	H	THF	-20	2	-	-	6	**427**
Ph	COOMe	H	C_6H_6	r.t.	1	32	-	-	**423**
Me	COOMe	H	C_6H_6	r.t.	3	43	-	-	**423**
	-$(CH_2)_6$-	H	C_6H_6	r.t.	10	35	-	-	**423**
c.			CH_2Cl_2	-78	5	-	10	-	**427**



Conclusion

The examples of using hydrogen fluoride in organic synthesis given in the review have shown that the old time-proved fluorinating agent has been used actively. The new process conditions and new view on the potential of anhydrous hydrogen fluoride and its complexes allow to hope for their wide practical application not in laboratory practice only but in technology of industry of little-fluorinated organic compounds. Anhydrous hydrogen fluoride is an important Lewis acid used not only as fluorinating agent but as a component of catalytic systems also, which wide application predetermines progress in general organic synthesis of little-fluorinated compounds. The author does hope that the review will help investigators to enter this interesting and perspective part of organic chemistry as well as will stimulate and provide development and improvement of methods of direct fluorination that will clear horizons of wide practical application of very many perspective substances.

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