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Isomerization of Hydrofluorocyclopentenes Promoted by Fluoride Anion

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Abstract

The isomerization of hydrofluorocyclopentenes promoted by fluoride anion was investigated. It was found that two processes were responsible for interconversion of the isomers: an allylic syn-addition/elimination of fluoride anion that does not change the mutual positions of hydrogen atoms but is responsible for transfers of fluorine atoms, and a fluoride anion-assisted deprotonation/protonation which does not change the mutual positions of fluorine atoms but is responsible for transfers of hydrogen atoms. In the deprotonation, HF can easily capture excess fluoride anion to form HF_2^- anion which can probably inhibit the protonation.

Keywords

Hydrofluorocyclopentene, Allylic Syn-Addition/Elimination, Deprotonation/Protonation

1. Introduction

In order to fulfill the Montreal Protocol and the Kyoto Protocol, which mandate to phase out the applications of both ozone depleting substances (ODS) and high greenhouse substances in the field of chlorofluorocarbons (CFCs), many countries have looked for alternatives of CFCs. Hydrofluoroolefins (HFOs) have short atmospheric lifetimes, leading to distinct environmental benefits. Thus, HFOs have been considered as alternatives to HCFCs and HFCs. Heptafluorocyclopentenes, including 1H-heptafluorocyclopentene (F7E-1H), 3H-heptafluorocyclopentene (F7E-3H) and 4H-heptafluorocyclopentene (F7E-4H), are one kind of alternatives that have zero ODP and low GWP. It is used as dry etching gas, fluorine-containing medicine intermediate, and hydrofluorocarbon-based solvent [1].

Today, HFOs can be synthesized by fluorine-chlorine exchange of hydrochlorofluoroolefins (HCFOs) [2], dehydrohalogenation of HFCs or HCFCs [3], hydrogenation of HCFOs or HFOs [4], addition of hydrofluoroalkyne with HF [5], or isomerization of HFOs [6]-[11]. In the above methods, the isomerization of HFOs plays an important key role in the synthesis of HFOs. 1,3,3,3-tetrafluoropropene (HFO-1234ze) has some momentous isomers, such as Z-1,3,3,3-tetrafluoropropene (Z-HFO-1234ze), E-HFO-1234ze, 1,1,3,3-tetrafluoropropene (HFO-1234zc) and 2,3,3,3-tetrafluoropropene (HFO-1234yf), and they can be realized into the mutual transformation in the presence of various catalysts. Z-HFO-1234ze was changed into E-HFO-1234ze catalyzed by fluorinated Cr_2O_3, FeF_3, AlF_3 or 0.5%Co/C at 20˚C - 100˚C [7]. And E-HFO-1234ze was turned into Z-HFO-1234ze and a small amount of HFO-1234zc at 200˚C - 550˚C [8]. HFO-1234zc was isomerized into E-HFO-1234ze and Z-HFO-1234ze when promoted by Cr_2O_3 in the presence of HF at 250˚C - 280˚C [11]. HFO-1234yf was converted to E-HFO-1234ze and Z-HFO-1234ze promoted by Cr_2O_3 catalyst at 350˚C [10]. In addition, Z-1,1,3,3,3-pentafluoropropene (Z-HFO-1225ye) was generated in the isomerization of E-HFO-1225ye promoted by AlF_3 catalyst at 30˚C [9]. And Z-1,1,1,4,4,4-hexafluoro-2-butene (Z-HFO-1336mzz) was produced by the isomerization of E-HFO-1336mzz in the presence of fluorinated chromuium-based catalyst at 250˚C [6].

The above isomerization technologies focused mainly on the isomerization between geometric isomers of HFOs [6] [7] [8] [9], while the isomerization between positional isomers of HFOs was rarely reported. The latter type of isomerization of HFOs always occurred at high temperature in the presence of special catalysts [10] [11], such as Cr_2O_3, which are always considered as business secrets, and for competitive reasons, details of these catalysts are probably not public. Until now, few literatures reported that the isomerization between positional isomers of HFOs promoted by simple catalysts occurred under mild conditions.

Here, we reported the isomerization of hydrofluorocyclopentenes (c5-HFOs) promoted by fluoride anion under mild conditions. The structures of c5-HFOs were confirmed by GC-MS, ^{1}H NMR and ^{19}F NMR. Based on the results of our experiments, the mechanisms of the isomerizations of c5-HFOs in liquid-phase were proposed.

2. Experimental

2.1. Chemicals

CCl_3F (CFC-11) 99.0+% was purchased from Synquest Labs, Lnc. Chloroform-d ($CDCl_3$) at 99.8 atom %D, H_2 99.9% were obtained from Kanto Denka Co. (Japan). $(NH_4)_2CO_3$ 99.9%, tetra-n-butylammonium bromide 99.8+%, LiF 99.8+%, NaF 99.8+%, KF 99.8+%, RbF 99.8+%, CsF 99.8+%, N,N-dimethyl-formamide (DMF) 99.8+%, molecular sieve 4A 1/8 were purchased from J & K Scientific Ltd. (China). Cis-1H,2H-octafluorocyclopentane (cis-F8A) 98.0+%, 1H,1H,2H-

heptafluorocyclopentane (F7A) 98.0+%, 1,2,3-trichloropentafluorocyclopentene (F5-123) 98.0+%, CCl_3F (CFC-11) 99.0+% were purchased from Synquest Labs, Lnc. (USA). A mixture of 1,4-dichlorohexafluorocyclopentene (F6-14) and 1,3-dichlorohexafluorocyclopentene (F6-13) (total purity: +98%) was synthesized by the fluorine-chlorine exchange of F5-123 with KF in DMF [12], and 2.0% Pd + 0.1% Bi/PAF (surface area 72.3 m^2/g) was used in the synthesis [13].

2.2. Instrument

The mass spectrometer was a GC-MS-QP2010 Ultra (Shimadzu). The column temperature program of GC-MS was as follows: 40˚C for 4 min; 15˚C/min to 230˚C; hold for 8 min. Both the injection port and the thermal conductivity detector were maintained at 200˚C, and the carrier gas was He introduced at a rate of 10 ml/min.

^{19}F NMR spectra of the intermediates and products during the synthesis were recorded on a Bruker AVANCE 400 (400 MHz) NMR with CFC-11 as internal standards in $CDCl_3$ at 25˚C. ^1H NMR spectra of the intermediates and products during the synthesis were recorded on a Bruker AVANCE 400 (400 MHz) NMR in $CDCl_3$ at 25˚C. A distillation tower with 3 meters long was used to rectify various products.

2.3. Experiment Procedure

Preparation of raw materials F7E-1H and F7E-4H: $(NH_4)_2CO_3$ (0.50 mol), tetra-n-butylammonium bromide (0.05 mol) and 500.0 ml of H_2O were placed into a 1000 mL, three-necked, round-bottomed flask equipped with a thermometer and an agitating device. Then cis-F8A (0.50 mol) was added by drops into the above solution. Under magnetic stirring for 6 h at 50˚C, the organic phase of the products from the above system was dried with 4A molecular sieve. Then, the organic phase was detected by ^{19}F-NMR. The conversion of F8A was 89.3%, and the yield of F7E-1H, F7E-4H and F7E-3H was 74.3%, 14.7% and 0.3%, respectively. The above organic phase was directly rectified by a distillation tower with 3 meters long, and F6E-4H and F6E-1H were obtained. And F7E-4H was obtained by the following liquid-phase isomerization of F7E-3H promoted by fluoride anion.

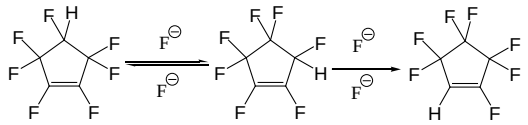
Preparation of raw materials F6E-33H, F6E-14H and F6E-13H: A mixture of F6-14, F6-13 (molar ratio: n(F6-14)/n(F6-13) = 33/67), and H_2 was supplied to the reactor made of Inconel through a vaporizer kept at 200˚C under the conditions as follows: hydrogenation catalyst 2%Pd + 0.1%Bi/AlF_3 10 mL, molar ratio n(H_2)/n(F6-13 + F6-14) = 2 (mol/mol), P = 0.1 MPa and contact time = 13 s. The products were washed by water, which separated the liquid-phase organic product from HCl. Next, the liquid organic products were dried by a molecular sieve and then detected by ^{19}F-NMR. The result was shown as follows: the total conversion of F6-13 and F6-14 was 87.3%, and the yield of F6E-33H, F6E-13H, F6E-14H and F6E-44 was 16.8%, 45.1%, 10.6% and 2.5%, respectively. The above

organic phase was directly rectified by a distillation tower with 3 meters long, F6E-33H, F6E-14H and F6E-13H were obtained, respectively.

Preparation of raw materials F6E-12H and F6E-15H: $(NH_4)_2CO_3$ (0.50 mol), tetra-n-butylammonium bromide (0.05 mol) and 500.0 ml of H_2O were placed into a 1000 mL, three-necked, round-bottomed flask equipped with a thermometer and an agitating device. Then F7A (0.50 mol) was added by drops into the above solution. Under magnetic stirring for 6 h at 50˚C, the organic phase of the products from the above system was dried with 4A molecular sieve. Then, the organic phase was detected by ^{19}F-NMR. The conversion of F7A was 70.5%, and the yield of F6E-12H, and F6E-15H was 64.0%, and 6.5%, respectively. The above organic phase was directly rectified by a distillation tower with 3 meters long, F6E-12H and F6E-15H were obtained, respectively.

Liquid-phase isomerization of isomers of heptafluorocyclopentene: metal fluoride (0.015 mol) and 20.0 ml of N.N-dimethylformamide were placed into a 50 mL, three-necked, round-bottomed flask equipped with a thermometer, and an agitating device. Then F7E-3H, F7E-1H or F7E-4H (0.03 mol) was added by drops into the above solution. Under magnetic stirring for a certain time at room temperature (25˚C), the products from the above system were scrubbed with 100 mL H_2O to remove metal fluoride and N.N-dimethylformamide. Later, the products were dried with 4A molecular sieve to obtain the organic phase of the product, which was detected by ^{19}F-NMR. The results were shown in **Table 1**.

Table 1. Impact of catalyst on the isomerization of heptafluorocyclopentene[a].



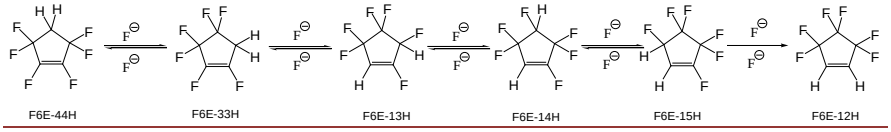
F7E-4H F7E-3H F7E-1H

Material	Catalyst	Amount of F7E-4H[b]/%	Amount of F7E-1H[b]/%	Amount of F7E-3H[b]/%
F7E-3H	LiF	2.1	0.7	97.2
F7E-3H	NaF	4.0	0.8	95.2
F7E-3H	KF	39.7	6.3	54.0
F7E-3H	RbF	48.2	2.5	49.3
F7E-3H	CsF	0.0	99.9	0.1
F7E-4H	LiF	1.5	1.2	97.3
F7E-4H	NaF	3.7	1.4	94.9
F7E-4H	KF	37.8	8.9	53.3
F7E-4H	RbF	49.0	4.3	46.7
F7E-4H	CsF	11.5	84.8	3.7
F7E-1H	LiF	0.1	94.7	5.2
F7E-1H	NaF	0.1	99.8	0.1

[a]Reaction conditions: F7E-1H, F7E-3H or F7E-4H: 0.03 mol, catalyst: 0.015 mol, Temperature = 25˚C, DMF 20 mL, Time = 6 h. [b]Amount was determined by ^{19}F NMR versus a calibrated internal standard.

Liquid-phase isomerization of isomers of hexafluorocyclopentene: metal fluoride (0.015 mol) and 20.0 ml of N.N-dimethylformamide were placed into a 50 mL, three-necked, round-bottomed flask equipped with a thermometer and an agitating device. Then F6E-33H, F6E-13H, F6E-14H, F6E-15H or F6E-12H (0.03 mol) was added by drops into the above solution. Under magnetic stirring for a certain time at room temperature (25˚C), the products from the above system were scrubbed with 100mL H_2O to remove metal fluoride and N.N-dimethylformamide and were dried with 4A molecular sieve to obtain the organic phase of the product. The organic phase of the product was detected by ^{19}F-NMR. The results were shown in Table 2.

Table 2. Impact of catalyst on the isomerization of hexafluorocyclopentene[a].



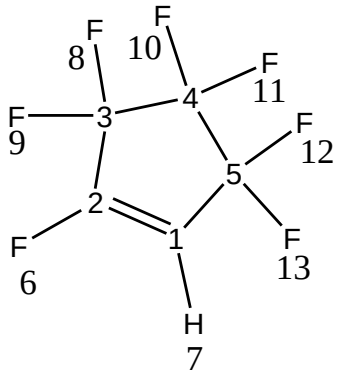
Material	Catalyst	Amount of F6E-44H[b]/%	F6E-33H[b]/%	F6E-14H[b]/%	F6E-13H[b]/%	F6E-12H[b]/%	F6E-15[b]/%
F6E-33H	LiF	1.2	25.2	7.9	43.4	21.2	1.1
F6E-33H	NaF	0	24.8	7.4	44.7	20.1	3.0
F6E-33H	KF	0	21.4	8.1	46.8	22.4	1.3
F6E-33H	RbF	0	19.4	9.8	47.2	22.0	1.8
F6E-33H	CsF	0	17.4	8.2	48.7	21.6	4.2
F6E-14H	LiF	0.0	0.0	29.1	67.3	3.6	0.0
F6E-14H	NaF	0.0	0.0	25.5	66.5	8.1	0.0
F6E-14H	KF	0.0	0.0	24.2	66.0	9.9	0.0
F6E-14H	RbF	0.0	0.0	22.6	65.4	12.0	0.0
F6E-14H	CsF	0.0	0.0	24.2	63.6	12.3	0.0
F6E-13H	LiF	0.0	0.0	26.6	67.6	5.9	0.0
F6E-13H	NaF	0.0	0.0	24.4	67.0	8.7	0.0
F6E-13H	KF	0.0	0.0	24.0	67.2	8.8	0.0
F6E-13H	RbF	0.0	0.0	20.0	67.2	9.9	0
F6E-13H	CsF	0.0	0.0	19.2	67.4	13.4	0.0
F6E-15H	LiF	0.0	0.0	0.0	0.0	0.9	99.1
F6E-15H	NaF	0.0	0.0	0.0	0.0	1.6	98.4
F6E-15H	KF	0.0	0.0	0.0	0.0	8.4	91.6
F6E-15H	RbF	0.0	0.0	0.0	0.0	52.1	47.9
F6E-15H	CsF	0.0	0.0	0.0	0.0	82.4	17.6
F6E-12H	LiF	0.0	0.0	0.0	0.0	99.9	0.1
F6E-12H	NaF	0.0	0.0	0.0	0.0	100.0	0.0
F6E-12H	KF	0.0	0.0	0.0	0.0	99.9	0.1
F6E-12H	RbF	0.0	0.0	0.0	0.0	100.0	0.0
F6E-12H	CsF	0.0	0.0	0.0	0.0	100.0	0.0

[a]Reaction conditions: F6E-33H, F6E-14H, F6E-13H, F6E-15H or F6E-12H: 0.03 mol, catalyst: 0.015 mol, Temperature = 25˚C, DMF 20 mL, Time = 6 h. [b]Amount was determined by ^{19}F NMR versus a calibrated internal standard.

2.4. Analytic Results of and by-Products

2.4.1. F7E-1H

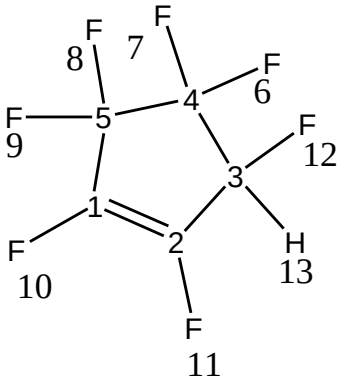
Molecular structure:



MS m/e: 194 (M^+); 175 (M^+-F); 144 (M^+-CF_2); 125 (M^+-CF_3); 113 (M^+-C_2F_3); 106 (M^+-CF_4); 87 (M^+-CF_5); 75 (M^+-C_2F_5); 69 (M^+-C_4HF_4); 56 (M^+-C_2F_6); 44 (M^+-C_3F_6); 37 (M^+-C_2F_7); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.05 (s, ***H*7**, 1H); ^{19}F NMR (377 MHz, Chloroform-d) δ − 107.29 (s, ***F*12** and ***F*13**, 2F), −120.72 (s, ***F*8** and ***F*9**, 2F), −124.83 (s, ***F*7**, 1F), −130.84 (s, ***F*10** and ***F*11**, 2F).

2.4.2. F7E-3H

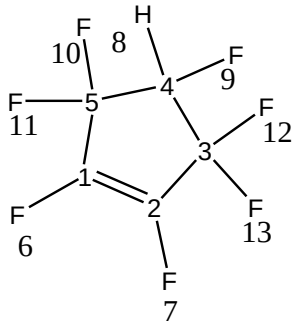
Molecular structure:



MS m/e: 194 (M^+); 175 (M^+-F); 144 (M^+-CF_2); 125 (M^+-CF_3); 113 (M^+-C_2F_3); 106 (M^+-CF_4); 93 (M^+-C_2HF_4); 87 (M^+-CF_5); 75 (M^+-C_2F_5); 69 (M^+-C_4HF_4); 56 (M^+-C_2F_6); 51 (M^+-C_4F_5); 37 (M^+-C_2F_7); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.43 (d, J = 28.4 Hz, ***H*13,** 1H); ^{19}F NMR (377 MHz, Chloroform-d) δ − 110.26 (dm, J= 127.80, ***F*6**, 1F), −118.81 (dm, J = 126.48 Hz, ***F*7**, 1F), −122.06 (dm, J = 124.60 Hz, ***F*8**, 1F), −128.38 (dm, J = 127.61 Hz, ***F*9**, 1F), −137.72 (m, ***F*10**, 1F), −194.240 (m, ***F*10**, 1F).

2.4.3. F7E-4H

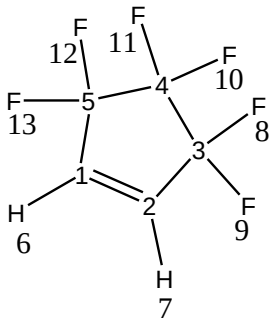
Molecular structure:



MS m/e: 194 (M^+); 175 (M^+-F); 144 (M^+-CF_2); 125 (M^+-CF_3); 113 (M^+-C_2F_3); 106 (M^+-CF_4); 93 (M^+-C_2HF_4); 87 (M^+-CF_5); 75 (M^+-C_2F_5); 69 (M^+-C_4HF_4); 56 (M^+-C_2F_6); 51 (M^+-C_4F_5); 37 (M^+-C_2F_7); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.05 (d, J = 24.8 Hz, ***H*8,** 1H); ^{19}F NMR (377 MHz, Chloroform-d) δ − 109.98 (dm, J = 124.79, ***F*11** and ***F*13**, 2F), −115.09 (dm, J = 128.75, ***F*10** and ***F*12,** 2F), −152.27 (m, ***F*6** and ***F*7**, 2F), −214.47 (dm, J = 24.32, ***F*7**, 1F).

2.4.4. F6E-12H

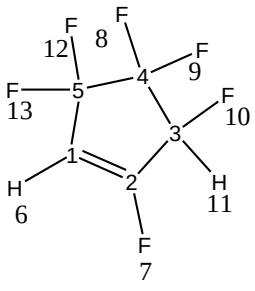
Molecular structure:



MS m/e: 176 (M^+); 157 (M^+-F); 137 (M^+-HF_2); 126 (M^+-CF_2); 113(M^+-CHF_2); 107 (M^+-CF_3); 100 (M^+-$C_2H_2F_2$); 88 (M^+-CF_4); 75 (M^+-C_2HF_4); 69 (M^+-CF_5); 57 (M^+-C_2F_5); 51 (M^+-C_4HF_4); 38 (M^+-C_2F_6); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.56 (m, ***H*6** and ***H*7,** 2H); ^{19}F NMR (377 MHz, Chloroform-d) δ − 109.92 (m, ***F*8, *F*9, *F*12** *and* ***F*13**, 4F), −132.46 (m, ***F*10** and ***F*11**, 2F).

2.4.5. F6E-13H

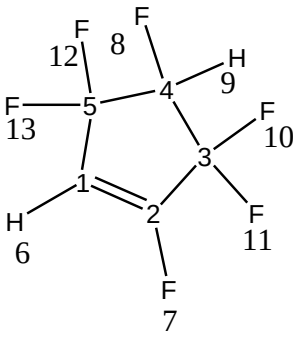
Molecular structure:



MS m/e: 176 (M^+); 157 (M^+-F); 137 (M^+-HF_2); 126 (M^+-CF_2); 113 (M^+-C_2F_2H); 107 (M^+-CF_3); 94 (M^+-C_2HF_3); 88 (M^+-CF_4); 75 (M^+-C_2HF_4); 69 (M^+-CF_5); 57 (M^+-C_2F_5); 51 (M^+-C_4HF_4); 44 (M^+-C_3HF_5); 38 (M^+-C_2F_6); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.81 (s, ***H*6,** 1H), 5.31 (ddd, J = 26.60 Hz, 8.80 Hz, 5.20 Hz, ***H*11,** 1H); ^{19}F NMR (377 MHz, Chloroform-d) δ -100.99 (dm, J = 127.80 Hz, ***F*12**, 1F), -110.68 (dd, J = 134.86 Hz, 7.16 Hz, ***F*13**, 1F), −111.78 (m, ***F*7**, 1F), −120.81 (dm, J = 125.35 Hz, ***F*8**, 1F), −128.55 (dm, J = 125.16 Hz, ***F*9**, 1F), -196.84 (dd, J = 53.16 Hz, 26.01 Hz, ***F*10**, 1F).

2.4.6. F6E-14H

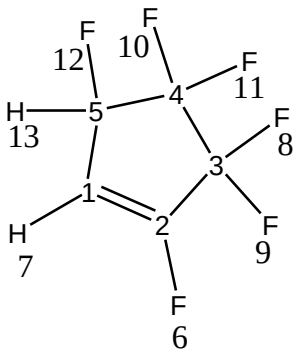
Molecular structure:



MS m/e: 176 (M^+); 157 (M^+-F); 137 (M^+-HF_2); 126 (M^+-CF_2); 107 (M^+-CF_3); 93 (M^+-$C_2H_2F_3$); 88 (M^+-CF_4); 75 (M^+-C_2HF_4); 69 (M^+-CF_5); 57 (M^+-C_2F_5); 51 (M^+-C_4HF_4); 44 (M^+-C_3HF_5); 37 (M^+-C_2HF_6); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.91 (s, ***H*6,** 1H), 5.02 (dt-quartet, J = 24.00 Hz, 10.00 Hz, 2.00 Hz, ***H*9,** 1H); ^{19}F NMR (377 MHz, Chloroform-d) δ − 94.81 (dm, J = 262.02 Hz, ***F*12**, 1F), −104.73 (dd, J = 261.64 Hz, 11.31 Hz, ***F*13**, 1F), −110.95 (ddm, J = 268.05 Hz, 4.52 Hz, ***F*10**, 1F), −118.11 (dd, J = 255.61 Hz, 15.08 Hz, ***F*11**, 1F), -151.16 (s, ***F*7**, 1F), −210.05 (dm, J= 49.76 Hz, ***F*8**, 1F).

2.4.7. F6E-15H

Molecular structure:

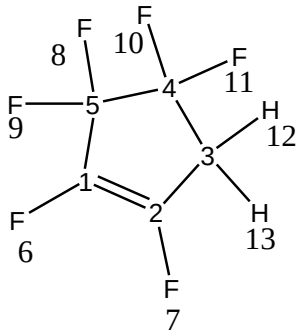


MS m/e: 176 (M^+); 157 (M^+-F); 137 (M^+-HF_2); 126 (M^+-CF_2); 113(M^+-CHF_2);

107 (M^+-CF_3); 93 (M^+-CH_2F_3); 88 (M^+-CF_4); 75 (M^+-C_2HF_4); 69 (M^+-CF_5); 57 (M^+-C_2F_5); 51 (M^+-C_4HF_4); 38 (M^+-C_2F_6); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.00 (m, ***H*7,** 2H); 5.45 (ddd, J = 9.60 Hz, 5.60 Hz, 1.60 Hz, ***H*13,** 2H); ^{19}F NMR (377 MHz, Chloroform-d) δ -113.48 (dm, J = 130.01 Hz, ***F*8**, 1F), −120.40 (dm, J = 67.48 Hz, ***F*9**, 1F), −125.70 (dm, J = 68.41 Hz, ***F*10**, 1F), −129.11 (m, ***F*6,** 1F), −186.14 (dm, J = 56.93 Hz ***F*12**, 1F).

2.4.8. F6E-33H

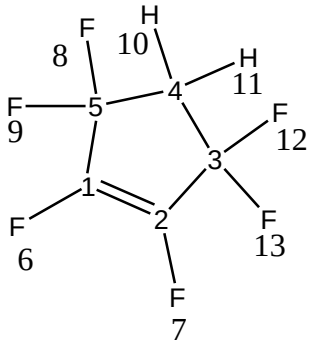
Molecular structure:



MS m/e: 176 (M^+); 157 (M^+-F); 137 (M^+-HF_2); 126 (M^+-CF_2); 113 (M^+-C_2F_2H); 107 (M^+-CF_3); 94 (M^+-C_2HF_3); 88 (M^+-CF_4); 75 (M^+-C_2HF_4); 69 (M^+-CF_5); 57 (M^+-C_2F_5); 51 (M^+-C_4HF_4); 44 (M^+-C_3HF_5); 38 (M^+-C_2F_6); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.08 (m, ***H*12** *and* ***H*13,** 2H); ^{19}F NMR (377 MHz, Chloroform-d) δ − 113.65 (tdd, J = 10.93 Hz, 5.66 Hz, 1.89Hz, ***F*12** *and* ***F*13**, 2F), −117.21 (tt, J = 12.44 Hz, 3.77 Hz, ***F*8** and ***F*9**, 2F), −128.16 (m, ***F*7**, 1F), -163.36 (m, ***F*6**, 1F).

2.4.9. F6E-44H

Molecular structure:



MS m/e: 176 (M^+); 157 (M^+-F); 137 (M^+-HF_2); 126 (M^+-CF_2); 113 (M^+-C_2F_2H); 107 (M^+-CF_3); 94 (M^+-C_2HF_3); 88 (M^+-CF_4); 75 (M^+-C_2HF_4); 69 (M^+-CF_5); 57 (M^+-C_2F_5); 51 (M^+-C_4HF_4); 44 (M^+-C_3HF_5); 38 (M^+-C_2F_6); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.94 (quintet-t, J = 9.60 Hz, 1.60 Hz, ***H*10** *and* ***H*11**, 2H); ^{19}F NMR (377 MHz, Chloroform-d) δ − 62.18 (m, ***F*8**, ***F*9**, ***F*12** ***and*** ***F*13**, 4F), −136.39 (m, ***F*6**

and ***Fn***, 2F).

Note: The number (***n***) of ***Fn*** or ***Hn*** in NMR data is in agreement with the number in the molecular structure.

3. Results and Discussion

In DMF, promoted by various alkali metal fluoride such as LiF, NaF, KF, RbF or CsF at 25˚C for 6 hours, F7E-3H was isomerized into F7E-1H and F7E-4H (See Table 1). The conversion of F7E-3H increased with the increasing atomic number of alkali metal. The larger the atomic number of alkali metal, the stronger the reactivity of alkali metal fluoride in halogen exchange [14]. And the efficacy of the alkali fluorides with respect to replacement reactions ranked in the sequence: CsF > RbF > KF > NaF > LiF [15] [16] [17]. Therefore, CsF owned the highest activity in the isomerization of F7E-3H. In addition, the solubility of the alkali metal fluoride in DMF affect the reactivity at a certain, but not only reason. In DMF, RbF (1.05 mM) has a higher solubility than CsF (0.60 mM) in DMF [18], but its reactivity is weaker than CsF in the isomerization of F7E-3H. The isomerizations of c5-HFOs belong to a kind of special halogen exchange (fluorine-fluorine exchange), which are probably not simply solution reactions but probably occurring on the surface. The system usually involve an excess of the solid metal fluoride present and, indeed, in some reactions it has been observed that the amount of solid metal fluoride is important [14]. Therefore, alkali metal fluoride was always excess in the isomerizations of c5-HFOs.

As shown in Table 1, F7E-4H was isomerized into F7E-1H and F7E-3H, while F7E-1H was isomerized into F7E-3H and F7E-4H in a small amount. This indicated that there existed difficultiesin the isomerization of F7E-1H into F7E-3H and F7E-4H probably due to the high energy barrier between F7E-1H and F7E-3H (or F7E-4H). Thus, F7E-1H was the absolutely preferred isomer.

As listed in Table 2, isomers of hexafluorocyclopentene can be interconverted in DMF in the presence of alkali metal fluoride, including 3H,3H-hexafluorocyclopentene (F6E-33H), 4H,4H-hexafluorocyclopentene (F6E-44H), 3H,3H-hexafluorocyclopentene (F6E-33H), 1H,5H-hexafluoro-cyclopentene (F6E-15H), 1H,4H-hexafluorocyclopentene (F6E-14H), 1H,3H-hexafluorocyclopentene (F6E-13H) and 1H,2H-hexafluorocyclopentene (F6E-12H). F6E-33H was isomerized into F6E-44H, F6E-15H, F6E-14H, F6E-13H and F6E-12H, and the conversion of F6E-33H was 82.6%, the yield of F6E-13H was 48.7% in the presence of CsF. F6E-14H was converted to F6E-13H and F6E-12H, while F6E-13H was turned into F6E-14H and F6E-12H. In the isomerization of F6E-14H or F6E-13H, neither F6E-44H nor F6E-33H was produced. It will be explained in the discussion part of this paper. F6E-15H was isomerized into F6E-12H, and the conversion of F6E-15H was 82.4%, the yield of F6E-12H was 82.4% when promoted by CsF. F6E-12H was difficult to be isomerized into F6E-15H. Thus, F6E-12H is the absolutely preferred isomer among the various isomers of hexafluorocyclopentene. In addition, the selectivity of various c5-HFOs can be

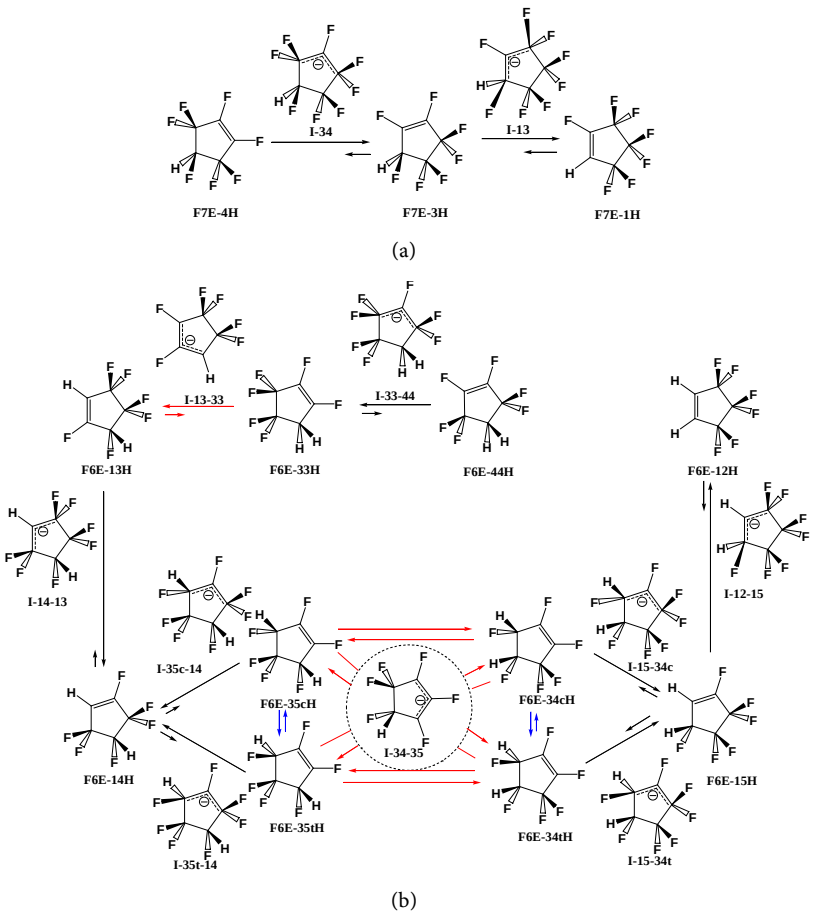
controlled when the different alkali metal fluoride is chosen as a catalyst.

Based on the results of our experiments, the possible reaction path of liquid-phase isomerizations of c5-HFOs was proposed as follows (**Scheme 1**):

1) Alkali metal fluoride was partially soluble in DMF [18]. This provided the naked fluoride anions to catalyze the isomerizations of c5-HFOs.

2) In DMF, the C=C of F7E-4H underwent nucleophilic attack by the incoming fluoride anion to give a tetrahedral intermediate I-34, which proceeded to the product F7E-3H by elimination of fluoride anion. The whole process belonged to an allylic syn-1-addition/3-elimination of fluoride anion [12] [19] [20], which was reversible. This is because the syn-elimination reaction of the five membered ring is easier to form a co-planar transition state, which reduces the energy barrier and makes the reaction easy to occur [21].

3) In DMF, the C=C of F7E-3H underwent nucleophilic attack by the incoming fluoride anion to give a tetrahedral intermediate I-13, which proceeded to the product F7E-1H by elimination of fluoride anion. The above



Scheme 1. The possible reaction path of Isomerization reactions of c5-HFOs promoted by fluoride anion (Black arrows: allylic syn-addition/elimination of fluoride anion; Red arrows: fluoride anion-assisted deprotonation/protonation; Blue arrows: geometric isomerization). (a) *Isomerization of hydrofluorocyclopentene*; (b) *Isomerization of hexafdfluorocyclopentene.*

process belonged to an allylic syn-1-addition/3-elimination of fluoride anion [12] [19] [20], which was not a chemical equilibrium.

4) In DMF, the C=C of F6E-44H underwent nucleophilic attack by the incoming fluoride anion to give a tetrahedral intermediate I-33-44, which proceeded to the product F6E-33H by elimination of fluoride anion. It belonged to an allylic syn-1-addition/3-elimination of fluoride anion [12] [19] [20], which was a chemical equilibrium.

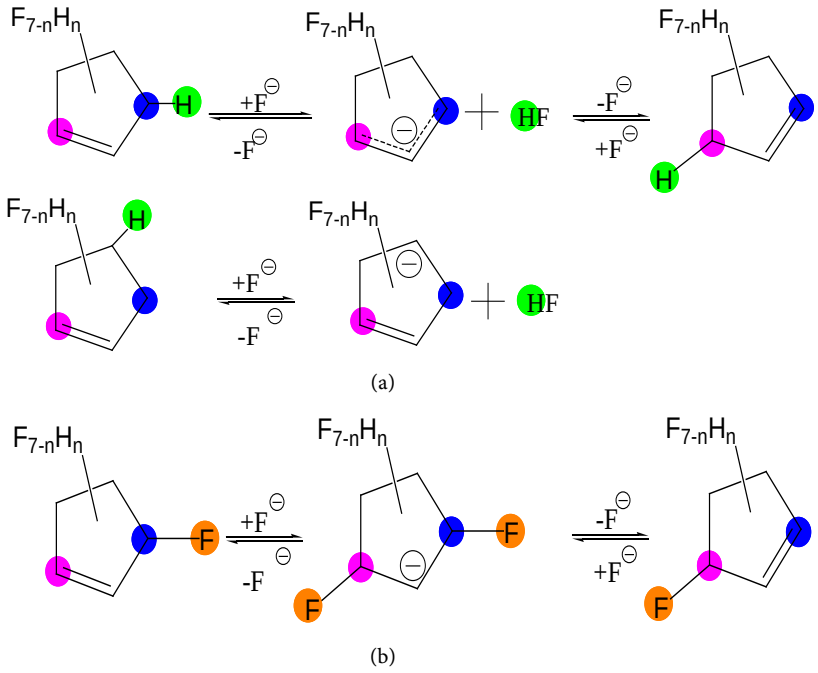
5) In DMF, F6E-33H underwent deprotonation with fluoride anion in 3-position on the C(sp^3) atom to give an intermediate I-13-33 with the release of HF, which proceeded to the product F6E-13H by protonation of I-13-33 with HF in 1-position on the carbon atom with the release of fluoride anion [22]. This was a chemical equilibrium. Here, fluoride anion acted as a catalyst.

6) In DMF, the C=C of F6E-13H underwent nucleophilic attack by the incoming fluoride anion to give a tetrahedral intermediate I-14-13, which proceeded to the product F6E-14H by elimination of fluoride anion. The process belonged to a syn-1-addtion/3-elimination of fluoride anion [12] [19] [20], which was a chemical equilibrium.

7) In DMF, the C=C of F6E-14H underwent nucleophilic attack by the incoming fluoride anion to give tetrahedral intermediates I-35c-14 (cis-isomer) and I-35t-14 (trans-isomer), which proceeded to the products F6E-35cH and F6E-35tH by elimination of fluoride anion. The whole process belonged to an allylic syn-1-addition/3-elimination of fluoride anion [12] [19] [20], which was a chemical equilibrium; Then, F6E-35cH or F6E-35tH underwent deprotonation with fluoride anion in 3-position on the C(sp^3) atom to give an intermediate I-34-35 with the release of HF, which proceeded to the product F6E-34cH or F6E-34tH by protonation of I-34-35 with HF in 1-position on the carbon atom with the release of fluoride anion [21], and the C=C of F6E-34cH or F6E-34tH underwent nucleophilic attack by the incoming fluoride anion to give tetrahedral intermediates I-15-34c (cis-isomer) and I-15-34t (trans-isomer), which proceeded to the products F6E-15H by elimination of fluoride anion. The whole process belonged to an allylic syn-1-addition/3-elimination of fluoride anion [12] [19] [20], which was not a chemical equilibrium.

8) In DMF, the C=C of F6E-15H underwent nucleophilic attack by the incoming fluoride anion to give a tetrahedral intermediate I-12-15, which proceeded to the product F6E-12H by elimination of fluoride anion. The whole process belonged to a syn-1-addtion/3-elimination of fluoride anion [12] [19] [20], which was not a chemical equilibrium.

In the above mechanisms of the isomerizations of c5-HFOs, the fluoride anion-assisted deprotonation/protonation is one important process. Its occurrence is closely related to the position of the hydrogen atom on the five-element ring (See **Scheme 2(a)**). When hydrogen atom is in 3-position, 4-position or 5-position on C(sp^3) atom in c5-HFOs, c5-HFOs easily react with fluoride anion via deprotonation/protonation, and the hydrogen atom can



Scheme 2. Two processes of isomerization of c5-HFOs promoted by fluoride anion. (a) Deprotonation/protonation (0 = 0 or 1); (b) Addition/elimination (n = 1 or 2).

transfer on the five-membered ring due to the rearrangement of the pentacyclic anions, but the hydrogen atom in 4-position maintains its position because that the pentacyclic anions cannot rearrange. When hydrogen atom is only in 1-position or/and 2-position on C(sp^2) atom in c5-HFOs, c5-HFOs difficultly react with fluoride anion via deprotonation/protonation due to the strong attraction of C=C double bond towards fluorine atom. The allylic syn-addition/elimination of fluoride anion is another important process in the isomerizations of c5-HFOs (See **Scheme 2(b)**). The fluorine atom can transfer on the five-membered ring via the allylic syn-addition/elimination of fluoride anion due to the rearrangement of the pentacyclic anions.

Now, we explain why neither F6E-44H nor F6E-33H was found in the isomerization of F6E-14H or F6E-13H. In DMF, the c5-HFO that contained C(sp^3)-H, such as F6E-13H, F6E-14H orF6E-35cH, underwent deprotonation with fluoride anion in 3 (4, or 5)-position on the C(sp^3) atom to give an intermediate with the release of HF (See **Scheme 2(a)**). According to the Gibbs free energies of the formation HF_2^- anion and the ionization of HF_2^- from the quantum chemical calculations using Gaussian09 (See **Table 3**), once HF captured excess fluoride anion, with the formation of a very stable anion HF_2^-, the protonation of the intermediate was terminated because the anion HF_2^- was incapable of neither catalyzing isomerizations nor returning the proton back. Thus, the reaction was "frozen". When quenched with H_2O in the experiments, the intermediate returned to its raw material. Therefore, neither F6E-33H nor F6E-44H was found in the isomerization of F6E-14H or F6E-13H.

Table 3. Gibbs free energies calculations for the formation of HF_2^- and the ionization of HF_2^- using Gaussian 09 (in DMF, 25˚C).

Reaction	Gibbs free energy (kcal·mol^{-1})
1) $HF + F^- = HF_2^-$	−28.1783
2) $HF = H^+ + F^-$	+190.5848
3) $HF_2^- = H^+ + 2F^-$	+218.7631

4. Conclusion

In the isomerization of c5-HFOs promoted by fluoride anion, two main processes are responsible for the interconversion of the isomers. An allylic syn-addition/elimination of fluoride anion that does not change the mutual positions of hydrogen atoms but is responsible for transfers of fluorine atoms, and a fluoride anion-assisted deprotonation/protonation which does not change the mutual positions of fluorine atoms but is responsible for transfers of hydrogen atoms. It was also revealed that HF_2^- anion in the deprotonation can inhibit the protonation. This is probably the reason that neither F6E-33h nor F6E-44H was found in the isomerization of F6E-13H or F6E-14H.

Acknowledgements

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