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Synthesis of 1,1,2,2,3,3,4-heptafluorocyclopentane as a new generation of green solvent

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ABSTRACT

1,1,2,2,3,3,4-Heptafluorocyclopentane is a new generation of green solvent. It was synthesized by the liquid-phase fluorination reactions from hexachlorocyclopentadiene to 1-chloroheptafluoro-cyclopentene in the presence of KF in DMF and by the vapor-phase hydrogenation reaction from 1-chloroheptafluorocyclopentene to 1,1,2,2,3,3,4-heptafluorocyclopentane in the presence of Pd-based hydrogenation catalyst. Quantum chemical calculations for the isomers energies using Gaussian09 were conducted to verify the chemical equilibriums between isomers of trichloropentafluorocyclopentene or dichlorohexafluorocyclopentene in the fluorination reactions. Possible mechanisms for 1,1,2,2,3,3,4-heptafluorocyclopentane synthesis were proposed.

1. Introduction

In order to fulfill the Montreal Protocol and the Kyoto Protocol, which try to eliminate the usage of ozone depleting substances (ODS), 1,1,2-trifluoro-1,2,2-trichloroethane (CFC-113), 1,1,1-trichloroethane and 1,1-dichloro-1-fluoroethane (HCFC-141b) in the field of cleaning agent, many countries have promoted upgrades of substitutes of the solvents. Acceptable alternatives with zero ozone depletion potential (ODP) value, such as 1,1,1,3,3-pentafluorobutane (HFC-365mfc), 1,1,1,2,2,3,4,5,5,5-decafluoropentane (HFC-4310mee) and 1,1,1,2,2,3,3,4,4-nonafluoro-4-methoxybutane (HFE-449s1) have been found for many applications (Table 1). However, these alternatives have resulted in greenhouse effect due to large global warming potential (GWP) and due to long atmospheric life time [1]. Therefore, search for other suitable alternatives continues.

Ideal substitutes for ODS solvents should have beneficial safety and excellent properties such as non-flammability, acceptable toxicity, adequate solvency and high stability. Furthermore, they should have minimal environmental impact [3]. 1,1,2,2,3,3,4-heptafluorocyclopentane (F7A) is an alternative that is zero ozone depleting and possesses many of these desirable attributes as follows: short atmospheric lifetime and minimal GWP; non-flammability, chemical and thermal stability; higher cleaning capacity than HFC-4310mee and HFE-449s1; easy-to-use boiling point (82.5 °C) and higher recyclability; low toxicity [1]. Therefore, F7A is an ideal substitute for ODS solvents. It has been accepted as a substitute for HCFC-141b and 1,3-dichloro-1,1,2,2,3-pentafluoroethane (HCFC-225cb) in metals, precision and electronics cleaning [4]. F7A is an environmentally friendly new generation of green solvent [1].

F7A was synthesized by liquid-phase fluorination reaction and gas-phase hydrogenation reaction from the starting material like hexachlorocylopentadiene (HCCPD) or octachlorocyclopentene as follows: Firstly, HCCPD or octachlorocyclopentene reacted with the fluorination reagents to generate the intermediate 1,2-dichlorohexaflurocyclopentene (F6-12). The fluorination reagents were SbF_5 [5,6], SbF_3Cl_2 [7], SbF_xCl_{5-x} ($0 < x < 5$) [8], a mixture of SbF_3 and SbF_3Cl_2 [9] or anhydrous hydrogen fluoride in the presence of chlorine and fluorination catalysts like $SbCl_5$ [10–12], or catalysts containing bismuth and iron [13]. Secondly, F6-12 was fluorinated with KF to produce the intermediate 1-chloro-heptafluorocylopentene (F7-1) [14]. Thirdly, F7-1 was hydrogenated to synthesize F7A in the presence of Pd-based hydrogenation catalyst via gaseous phase [15–18].

The above studies concentrated on how the technical process could be developed and optimized but neglected the intermediates such as 1,4,4-trichloropentafluorocyclopentene

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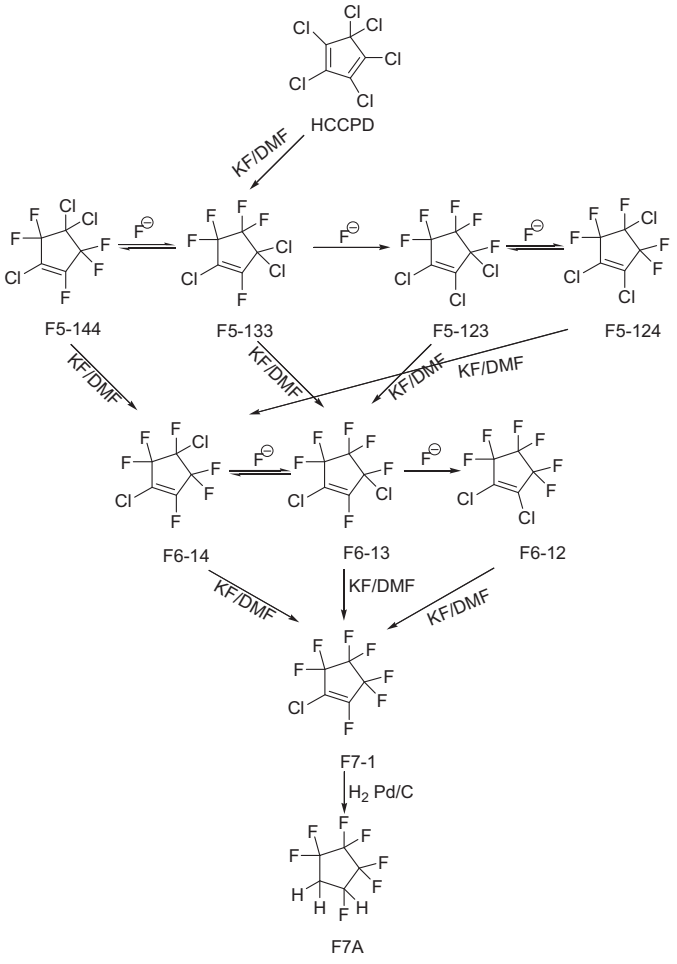
Table 1
Environmental impact of various acceptable alternatives.

Compound	HFC-365mfc	HFC-4310mee	HFE-449s1	HCFC-225cb	F7A
ODP	0	0	0	0.03	0
Lifetime/year	8.7[b]	16.1[b]	4.7[b]	5.9[b]	3.4[a]
GWP (100 year)	804[b]	1650[b]	421[b]	525[b]	195[a]

[a] The data is derived from [1].
[b] The data is derived from [2].

(F5-144), 1,3,3-trichloropentafluorocyclopentene (F5-133), 1,2,3-trichloropenta-fluorocyclopentene (F5-123), 1,2,4-trichloropenta-fluorocyclopentene (F5-124), 1,4-dichlorohexafluorocyclopentene (F6-14) and 1,3-dichlorohexafluorocyclopentene (F6-13). Until 2008, Yamada reported that a mixture of tetrachlorotetrafluorocyclopentene, F5-124 and F6-12 was fluorinated to give by-products F6-14 and F6-13, which were treated as wastes to be removed from crude products [13]. Especially, these literatures could not provide distinctly the structures of the intermediates. More importantly, no literature has reported extensively the synthesis of F7A from HCCPD via multi-step reactions.

Here, we reported comprehensively for the first time the synthesis of F7A from starting material HCCPD by multi-step reactions, which were comprised of the liquid-phase fluorination from HCCPD to F7-1 in the presence of KF in N,N-dimethylmethanamide (DMF) and the vapor-phase hydrogenation from F7-1 to F7A in the presence of Pd-based hydrogenation catalyst (Scheme 1). We confirmed that the structures of intermediates by GC, GC–MS, ^{19}F NMR, ^{13}C NMR, etc. The reactivity of various



Scheme 1. Synthesis of 1,1,2,2,3,3,4-heptafluorocyclopentane.

chlorine was arranged in order from stronger to weaker in the liquid-phase fluorination of perhalogenated cyclopentene as follows: –CCl=CCl– > –CClF– > –CCl_2– > –CCl=CF–. Quantum chemical calculations for the isomers energies using Gaussian09 were conducted to verify the chemical equilibriums between the isomers of intermediates in the fluorination reactions. Based on the results of our experiments, the mechanisms of the fluorination reactions from HCCPD to F7-1 in liquid-phase and the hydrogenation reaction from F7-1 to F7A in vapor phase were proposed.

2. Results and discussion

HCCPD reacted with KF in DMF to produce F5-144, F5-133, F5-123 and F5-124 at various temperatures. The results are listed in Table 2.

In the fluorination of HCCPD, the yield of F5-144 decreased with increasing temperature in the range of 100–150 °C, while the yield of F5-133 increased with increasing temperature. In addition, the yield of F5-123 and F5-124 first increased and then decreased with increasing temperature in the range of 100–150 °C, which was attributed to that F5-123 and F5-124 transferred into F6-14 and F6-13 in the advanced fluorination. In addition, the total yield of F5-144 and F5-133 was far larger than the one of F5-123 and F5-124, which indicated that the chlorine from –CClF– owned stronger reactivity than the one from –CCl_2– in the fluorination of HCCPD.

F5-144, F5-133, or mixture of F5-123 and F5-124 reacted with KF in DMF solution to produce F6-14, F6-13 and F6-12, respectively, the results are listed in Table 3.

F5-144 reacted with KF in DMF to generate main products such as F5-133, F6-14 and F6-13. The yield of F5-133 decreased with increasing temperature ranged 90–130 °C. In the fluorination process, the existence of F6-14 other than 4,4-dicholrohexafluorocyclopentene showed that the reactivity of sp^3-Cl from –CCl_2– was stronger than the one of sp^2-Cl from –CCl=CF–. In addition, F5-133 was formed in the fluorination of F5-144 with KF in the solvent DMF (seen Table 2), which displayed the isomerization from F5-144 to F5-133 occurred in the fluorination of HCCPD. And in a sense, the yield of F5-144 decreased with increasing temperature in the fluorination of HCCPD due to the isomerization from F5-144 to F5-133 at a higher reaction rate. The mixture of F5-123 and F5-124 was further fluorinated to produce F6-14, F6-13 and F6-12, the yield of F6-13 was around two times of that of F6-14.

F5-133 reacted with KF in DMF to generate main products such as F5-144, F6-14 and F6-13. The yield of F5-144 decreased with increasing temperature ranged 90–130 °C. The existence of F6-14 other than 4,4-dicholrohexafluorocyclopentene unfolded that the reactivity of the chlorine from –CCl_2– was stronger than the one from –CCl=CF–. The formation of F5-133 and F5-124 at the temperature of 90 °C reflected the isomerization from F5-133 to F5-144, F5-123 and F5-124 in the fluorination process of F5-133. However, the products F5-123 and F5-124 reacted easily with KF to be exhausted with increasing temperature. The yield of F6-12

Table 2
Temperature impact in the fluorination of hexachlorocyclopentadiene.

Temperature [°C]	Yield of F5-144 [%][a]	Yield of F5-133 [%][a]	Yield of F5-123 and F5-124 [%][a]
100	49.2	8.1	0.3
110	16.3	18.1	2.8
120	0.4	32.0	9.6
130	0.0	50.1	2.3
140	0.0	67.8	2.2
150	0.0	80.8	0.6

[a] Yield was determined by GC and ^{19}F NMR versus a calibrated internal standard.

Table 3
Temperature impact in the fluorination of different isomers of trichloropentafluorocyclopentene.

Material	Temperature [°C]	Amount of F5-144 [%][a]	Amount of F5-133 [%][a]	Amount of F5-123 + F5-124 [%][a]	Yield of F6-14 [%][a]	Yield of F6-13 [%][a]	Yield of F6-12 [%][a]
F5-144	90	12.5	84.1	3.4	0.0	0.0	0.0
F5-144	110	10.6	67.2	0.0	4.3	9.6	0.0
F5-144	130	9.1	58.9	0.0	5.9	12.7	0.0
F5-133	90	13.0	80.6	1.9	0.8	1.7	0.0
F5-133	110	9.7	7.9	0.0	2.1	4.5	0.1
F5-133	130	0.0	0.0	80.0	2.3	5.2	71.2
F5-123 + F5-124[b]	90	0.0	0.0	46.1	4.2	9.0	0.6
F5-123 + F5-124[b]	110	0.0	0.0	12.8	10.7	22.8	2.5
F5-123 + F5-124[b]	130	0.0	0.0	0.0	16.9	36.5	2.0

[a] Amount and yield were determined by ^{19}F NMR versus a calibrated internal standard, respectively.
[b] F5-123 + F5-124 was comprised of F5-123 (70%) and F5-124 (30%) by ^{19}F NMR.

Table 4
Temperature impact in the fluorination of various isomers of dichlorohexafluorocyclopentene.

Material	Temperature [°C]	Amount of F6-14 [%][a]	Amount of F6-13 [%][a]	Amount of F6-12 [%][a]	Yield of F7-1 [%][a]	Yield of F8E[b] [%][a]
F6-14	50	29.1	66.1	3.8	0.9	0.1
F6-14	80	30.8	67.4	0.0	1.1	0.7
F6-14	110	28.6	34.4	0.0	4.5	32.5
F6-13	50	29.1	70.5	0.0	0.3	0.1
F6-13	80	30.6	68.6	0.0	0.4	0.4
F6-13	110	22.3	51.4	0.0	4.7	21.6
F6-12	50	0.0	0.0	98.7	1.3	0.0
F6-12	110	0.0	0.0	19.7	78.8	1.7

[a] Amount and yield were determined by ^{19}F NMR versus a calibrated internal standard, respectively.
[b] F8E represented octafluorocyclopentene.

increased sharply to 71.2% with the increasing temperature in the range 90–130 °C.

The mixture of F5-123 and F5-124 reacted with KF in DMF to generate main products such as F6-14, F6-13 and F7-1. The yield of F6-13 increased with increasing temperature ranged 90–130 °C, which was greater than F6-12 possibly due to the stronger activity of the chlorine from –CCl=CCl– group compared with the one from –CClF– group.

F6-14, F6-13 or F6-12 reacted with KF in DMF solution to produce F7-1 and octafluorocyclopentene (F8E). The results are listed in Table 4.

In the fluorination of F6-14, the yield of F7-1 increased gently from 0.9% to 4.5% with increasing temperature in the range of 50–110 °C, while the yield of F8E increased sharply from 0.1% to 32.5% with increasing temperature in the range of 50–110 °C. The formation of F6-13 and F6-12 at 50 °C indicated the isomerization from F6-14 to F6-13 and F6-12 in the fluorination process of F6-14 with KF in the solvent DMF. However, the product F6-12 can react easily with KF and can be exhausted with increasing temperature. In the fluorination, the existence of F7-1 other than 4-chloroheptafluorocyclopentene revealed that the reactivity of sp^3-Cl from –CClF– was stronger than the one of sp^2-Cl from –CCl=CF–.

In the fluorination of F6-13, the yield of F7-1 increased gently from 0.3% to 4.7% with increasing temperature in the range of 50–110 °C, while the yield of F8E increased sharply from 0.1% to 21.6% with increasing temperature in the same range. The yield of F6-12 maintained zero at temperatures between 50 and 110 °C, which is properly resulted from that F6-12 reacted easily with KF and can be exhausted with increasing temperature. In the fluorination, the existence of F7-1 other than 3-chloroheptafluorocyclopentene illustrated that the reactivity of sp^3-Cl from –CClF– was stronger than the one of sp^2-Cl from –CCl=CF–.

In the fluorination of F6-12, the yield of F7-1 increased sharply from 1.3% to 78.6% with increasing temperature in the range of 50–110 °C, while the yield of F8E increased gently from zero to 1.7% in the same range of temperature.

In addition, compared with F6-14 and F6-13, F6-12 can be easily fluorinated to produce more F7-1 other than F8E, which is more favorable in the preparation of F7-1. In order to increase the availability of the starting material HCCPD, fluorination conditions should be hold in such a way as to produce more F5-133 and F6-12 and to decrease the productions of by-products F8E. According to the results from our experiment, the fluorination of HCCPD, F5-133 and F6-12 can be controlled at the temperature of, 150 °C, 130 °C and 110 °C, respectively, which could achieve our purpose effectively.

F7-1 reacted with hydrogen in the presence of Pd-based catalyst at different temperatures to produce our target compound F7A as well as by-products such as 1-chloro-2,2,3,3,4,4,5-heptafluorocyclopentane (F7A-1), 1,3,3,4,4,5,5-heptafluorocyclopentene (F7E) and 1,1,2,2,3,3-hexafluorocyclopentane (F6A) [15].

The quantum chemical calculations for the compounds F5-144, F5-133, F5-123, F5-124, F6-14, F6-13 and F6-12 using Gaussian09 were conducted. Geometry optimizations were performed at the RB_3LYP/6-311+G(2d, p) level, and the optimized structures were used for the subsequent calculations of molecular properties. GIAO nuclear magnetic shielding values were calculated at all atomic positions at the closed-shell restricted RB_3LYP levels of theory using the 6-311+G(2d, p) basis set. The energies of the compounds F5-144, F5-133, F5-123, F5-124, F6-14, F6-13 and F6-12 were obtained under the reaction conditions (KF/DMF, 110 °C), respectively (Table 5).

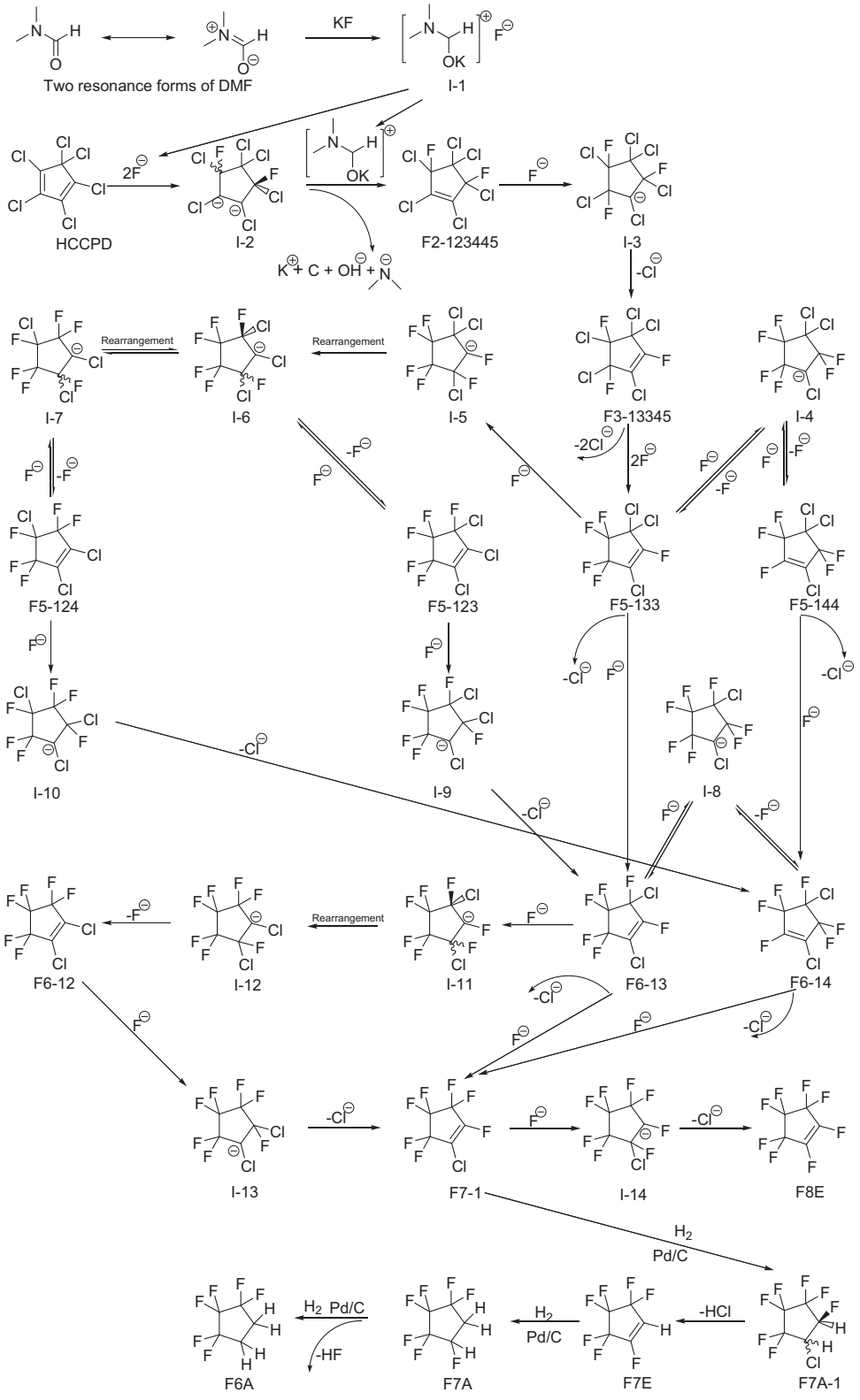
F5-133 has higher energy than F5-123, and the difference is larger than 5.5 kcal/mol. This leads to the conclusion that the

Table 5
Compound energy calculations using Gaussian09.

Compounds	E_{SCF}/Hartree[a]
F5-144	−2070.59077091
F5-133	−2070.59352292
F5-123	−2070.60232192
F5-124	−2070.60259146
F6-14	−1710.24504538
F6-13	−1710.24419985
F6-12	−1710.25740780

[a] 1 Hartree = 627.5095 kcal/mol.

isomerization from F5-133 to F5-123 was not a chemical equilibrium due to the huge difference between F5-133 and F5-123 in compound energy. In addition, the energy of F5-133 is lower than that of F5-144 by 1.73 kcal/mol, which shows that F5-133 and F5-144 are in a chemical equilibrium due to the small difference between F5-144 and F5-133 in compound energy. The theoretical value for equilibrium constant (K_1) from F5-144 to F5-133 is approximately 9.7, which was calculated as follows: $K_1 = \exp[-\Delta G/(RT)] \approx \exp[-\Delta E_{SCF}/(RT)] = \exp[1.727^*4184/(8.314^*383)] = \exp(2.269) = 9.7$. On the other hand, the experimental value for the equilibrium constant was calculated from the results of F5-144 at the temperature of



Scheme 2. The mechanisms of multi-step reactions for preparation of 1,1,2,2,3,3,4-heptafluorocyclopentene.

110 °C in Table 2 as follows: $K_1' = [\text{F5-133}]/[\text{F5-144}] = 67.2\%/10.6\% = 6.4$. Therefore, the experimental value K_1' for equilibrium constant was not in agreement with the theoretical value K_1, which was probably attributed to shorter reaction time compared with long enough equilibrium time. Besides, the energy of F5-123 is larger than that of F5-124 by 0.17 kcal/mol, which shows that F5-123 and F5-124 are in a chemical equilibrium due to the small difference between F5-123 and F5-124 in compound energy.

F6-12 has lower energy than F6-13, and the difference is larger than 7 kcal/mol. This leads to the conclusion that the isomerization from F6-13 to F6-12 was not a chemical equilibrium due to the huge difference between F6-13 and F6-12 in compound energy. In addition, the energy of F6-13 is lower than that of F6-14 by 0.53 kcal/mol, which shows that F6-13 and F6-14 are in a chemical equilibrium due to the small difference between F6-14 and F6-13 in compound energy. The theoretical value for equilibrium constant (K_2) from F6-14 to F6-13 is approximately 2, which was calculated as follows: $K_2 = \exp[-\Delta G/(RT)] \approx \exp[-\Delta E_{SCF}/(RT)] = \exp[0.53*4184/(8.314*383)] = \exp(0.6977) = 2$. On the other hand, the experimental value for the equilibrium constant was calculated from the results of mixture of F5-123 and F5-124 at the temperature of 110 °C in Table 2 as follows: $K_2' = [\text{F6-13}]/[\text{F6-14}] = 22.8\%/10.7\% = 2.1$. Therefore, the experimental value K_2' for equilibrium constant was in agreement with the theoretical value K_2, which reflected the rationality of our speculation on the isomerization equilibrium between F6-14 and F6-13.

Based on the results of our experiments, the possible mechanisms of multi-step reactions for preparation of F7A were proposed as follows (Scheme 2): (1) in DMF, the carbonyl carbon was bonded to a nitrogen, the nitrogen was less electronegative than the oxygen and was very able to transfer electron density through resonance to the carbonyl oxygen [19]; (2) KF could be dissolved in DMF [20] to produce the intermediate I-1, which could provide F anion and $[(DMF)K]^+$ complex cation; (3) in the presence of KF in DMF, the C=C of HCCPD underwent nucleophilic attack by the incoming F anion to give a tetrahedral intermediate I-2 with two negative charges, which proceeded to the product F2-123445 by elimination of two negative charges followed via formation of C=C bond during the oxidation-reduction reaction. It comprised 1,4-addition of F anions to a strongly deficient C=C bond followed by 2,3-elimination of negative charges; (4) the C=C of F2-123445 underwent nucleophilic attack by the incoming F anion to give a tetrahedral intermediate I-3, which proceeded to the product F3-13345 by elimination of Cl anion. It comprised 1-addition of F anion to a strongly deficient C=C bond followed by 3-elimination of Cl anion; (5) in the presence of KF in DMF, the attack of F anion on F3-13345 resulted in F5-133, with Cl anion ejected as the leaving group; (6) the C=C of F5-133 underwent nucleophilic attack by the incoming F anion to give a tetrahedral intermediate I-4, which proceeded to the product F5-144 by elimination of F anion. It comprised 2-addition of F anion to a strongly deficient C=C bond followed by 5-elimination of F anion. It was a chemical equilibrium; (7) the C=C of F5-133 underwent nucleophilic attack by the incoming F anion to give a tetrahedral intermediate I-5, which proceeded to the intermediate I-6 and the product F5-123 via arrangement of I-5 followed by elimination of Cl anion. It comprised 1-addition of F anion to a strongly deficient C=C bond followed by arrangement of 3-Cl and 1-elimination of F anion; (8) the C=C of F5-123 underwent nucleophilic attack by the incoming F anion to give a tetrahedral intermediate I-6, which proceeded to the intermediate I-7 and the product F5-124 via arrangement of I-6 followed by elimination of F anion. It comprised 1-addition of F anion to a strongly deficient C=C bond and arrangement of 3-Cl followed by 1-elimination of F anion; (9) in the presence of KF in DMF, the attack of F anion on F5-144 resulted in F6-14, with Cl anion ejected as the leaving group; (10) the C=C of F6-14 underwent nucleophilic attack by the incoming F anion to give a tetrahedral intermediate I-8, which proceeded to the product F6-13 by elimination of F anion. It comprised 2-addition of F anion to a strongly deficient C=C bond followed by 5-elimination of F anion, which was a chemical equilibrium; (11) the C=C of F6-13 underwent nucleophilic attack by the incoming F anion to give a tetrahedral intermediate I-11, which proceeded to the intermediate I-12 and the product F6-12 via arrangement of I-11 followed by elimination of F anion. It comprised 1-addition of F anion to a strongly deficient C=C bond and transfer from 3-Cl into 2-Cl and followed by 1-elimination of F anion, which was not a chemical equilibrium; (12) in the presence of KF in DMF, the attack of F anion on F5-133 resulted in F6-13, with Cl anion ejected as the leaving group; (13) the C=C of F5-123 underwent nucleophilic attack by the incoming F anion to give a tetrahedral intermediate I-9, which proceeded to the product F6-13 by elimination of Cl anion. It comprised 2-addition of F anion to a strongly deficient C=C bond followed by 2-elimination of Cl anion; (14) the C=C of F5-124 underwent nucleophilic attack by the incoming F anion to give a tetrahedral intermediate I-10, which proceeded to the product F6-14 by elimination of Cl anion. It comprised 2-addition of F anion to a strongly deficient C=C bond followed by 2-elimination of Cl anion; (15) in the presence of KF in DMF, the attack of F anion on F6-14 resulted in F7-1, with Cl anion ejected as the leaving group; (16) in the presence of KF in DMF, the attack of F anion on F6-13 resulted in F7-1, with Cl anion ejected as the leaving group; (17) the C=C of F6-12 underwent nucleophilic attack by the incoming F anion to give a tetrahedral intermediate I-13, which proceeded to the product F7-1 by elimination of Cl anion. It comprised 1-addition of F anion to a strongly deficient C=C bond followed by 1-elimination of Cl anion; (18) the C=C of F7-1 underwent nucleophilic attack by the incoming F anion to give a tetrahedral intermediate I-14, which proceeded to the product F8E by elimination of Cl anion. It 1-addition of F anion to a strongly deficient C=C bond followed by 1-elimination of Cl anion; (19) F7-1 reacted with hydrogen to generate F7A-1 in the presence of Pd-based catalyst via 1,2-addition; (20) F7A-1 was dehydrochlorinated to form F7E; (21) F7E reacted with hydrogen to generate F7A in the presence of Pd-based catalyst via 1,2-addition; (22) F7A was hydrodefluorinated to form F6A in the presence of Pd-based catalyst via hydrodefluorination of –CHF– group [21].

3. Conclusions

In conclusion, the synthesis of F7A was studied by liquid-phase fluorinations followed via gas-phase hydrogenation. The results from the fluorination experiments showed that various chlorine were arranged in order from stronger to weaker reactivity in perhalogenated cyclopentene as follows: –CCl=CCl– > –CClF– > –CCl_2– > –CCl=CF–. Quantum chemical calculations for the isomers energies using Gaussian09 were conducted to verify the chemical equilibrium between isomers in the fluorination reactions. Possible mechanisms for 1,1,2,2,3,3,4-heptafluorocyclopentane synthesis were proposed.

4. Experimental

4.1. Chemicals

Hexachlorocyclopentadiene (HCCPD) 99.5+% was purchased from Leap Labchem Co., Ltd. (China). Chloroform-d ($CDCl_3$) at 99.8 atom%D, potassium fluoride 99.0+%, N,N-dimethylformamide (DMF) 99.8+%, molecular sieve 4A 1/8, 5%Pd/C (unreduced) were

purchased from J&K Scientific Ltd. (China). CCl_3F (CFC-11) 99.0+% was purchased from Synquest Labs, Inc. (USA).

4.2. Instruments and apparatus

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; 10 °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.

The gas chromatograph was a GC-2010 (Shimadzu) with a Poraplot Q capillary column (i.d. 0.32 mm; length 25 m; J&W Scientific Inc.). The column temperature program was as follows: 40 °C for 4 min; 10 °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.

^{13}C NMR spectra and ^{1}H NMR spectra of the intermediates and products during the synthesis were recorded on a Bruker AVANCE 400 (400 MHz) NMR $CDCl_3$ at 25 °C.

4.3. Synthesis processes

Synthesis of F5-144, F5-133, F5-123 and F5-124: KF 29.05 g (0.50 mol) and 100 mL of DMF were placed into a 250 mL, three-necked, round-bottomed flask equipped with a thermometer and an agitating device. The flask was dipped in the oil bath and heated to a different temperature. Then HCCPD of 27.28 g (0.10 mol) was added by drops into the above solution. Under magnetic stirring for 18 h, the products from the above system experienced a temperature decrease to room temperature and were scrubbed with 300 mL H_2O to remove KF, KCl and DMF and dried with 4A molecular sieve to obtain the organic phase of the product. The organic phase of the product was detected by GC and then converted into mole percent by the factor from GC area percent to ^{19}F NMR area percent. The results were shown in Table 2.

Synthesis of F6-14, F6-13 and F6-12: KF 3.49 g (0.06 mol) and 20.0 mL of DMF were placed into a 50 mL, three-necked, round-bottomed flask equipped with a thermometer and an agitating device. The flask was dipped in the oil bath and heated to a different temperature. Then F5-144, F5-133 or the mixture of F5-123 (70%) and F5-124 (30%) of 7.80 g (0.03 mol) was added by drops into the above solution. Under magnetic stirring for 7 h, the products from the above system experienced a temperature decrease to room temperature and were scrubbed with 100 mL H_2O to remove KF, KCl and DMF and 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 3.

Synthesis of F7-1: KF 3.49 g (0.06 mol) and 20.0 mL of DMF were placed into a 50 mL, three-necked, round-bottomed flask equipped with a thermometer and an agitating device. The flask was dipped in the oil bath and heated to a different temperature. Then F6-14, F6-13 or F6-12 of 7.32 g (0.03 mol) was added by drops into the above solution. Under magnetic stirring for 6 h, the products' temperature dropped to room temperature, and they were scrubbed with 100 mL H_2O to remove KF, KCl and DMF and 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 4.

Synthesis of F7A: F7-1 reacted with hydrogen in the presence of Pd-based catalyst at different temperatures to produce our target compound F7A [15].

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jfluchem.2015.10.012.

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