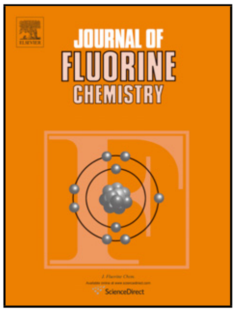

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Synthesis of 1H-polychlorofluorocycloolefins

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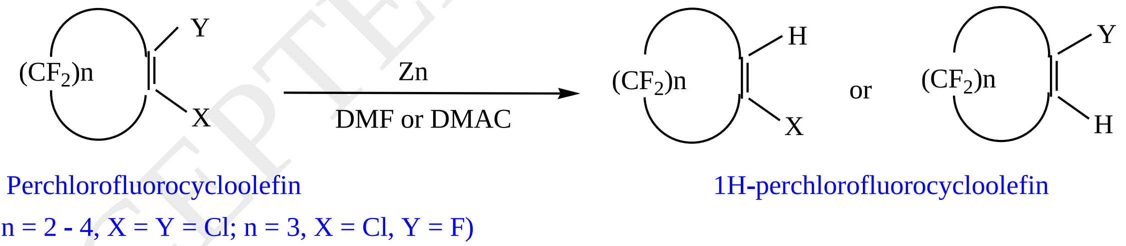
Graphical Abstract – Synopsis

The synthesis of 1H-polychlorofluorocycloolefin by the hydrodehalogenation of perchlorofluorocycloolefin containing –CCl=CCl– or –CCl=CF– group in dimethylformaide (DMF) or dimethylacetamide (DMAC) over Zn was investigated. It was found that the hydrodehalogenation of perchlorofluorocycloolefin occurred only on the C (sp^2) position with high conversion rate and selectivity, where the active hydrogen resource was supplied by DMF or DMAC.

Graphical Abstract – Pictogram



Highlights

- DMF or DMAC provides active hydrogen anion in the hydrodehalogenation of perchlorofluorocycloolefin over Zn.
- The hydrodehalogenation of perchlorofluorocycloolefin occurred only on the C(sp^2) position but not the C(sp^3).

- The hydrodehalogenation of perchlorofluorocycloolefin occurred only on the first C(sp^2) position but not second.
- A series of 1H-polychlorofluorocycloolefins were prepared with high yield.

Abstract: The synthesis of 1H-polychlorofluorocycloolefin by the hydrodehalogenation of perchlorofluorocycloolefin containing –CCl=CCl– or –CCl=CF– group in dimethylformaide (DMF) or dimethylacetamide (DMAC) over Zn was investigated. It was found that the hydrodehalogenation of perchlorofluorocycloolefin occurred only on the C (sp^2) position but not on C (sp^3) position. In addition, the mechanisms of the hydrodehalogenation of perchlorofluorocycloolefin were proposed.

Keywords: Hydrodehalogenation, 1H-perchlorofluorocycloolefins, DMF, DMAC, Cl-H exchange.

1. Introduction

Dehalogenation reactions are widely used for industrial purposes [1], handling organic liquids [2], and remedying soil and groundwater [3-5]. Methods of dehalogenation include direct incineration, catalytic incineration, pyrolysis, reaction with alkali metals or their compounds and catalytic hydrogenolysis [6-8].

The vapour-phase catalytic hydrodehalogenation with H_2 is an important method for dehalogenation of halogenated organic compounds [9-12]. When this method is used to hydrodehalogenation of organic compounds containing C (sp^2)-Cl groups, not only H-Cl substitution but also simple H addition (without substitution) occurs. In fact, the addition occurs more easily than the substitution due to the former's lower activation energy [13, 14]. As a result, the product from the hydrodehalogenation of compounds containing C (sp^2)-Cl always contains a significant portion of the original compounds that only underwent hydrogen addition, which cannot be easily separated from those compounds that did undergo the H-Cl substitution. This difficulty is attributed to the azeotrope formed by these products and the raw materials. For example, in the hydrodehalogenation of 1,2- dichlorotetrafluorocyclobutene (c-CFO-1314xxcc) with H_2 promoted by nickel-chromium catalyst, the products were composed of 3,3,4,4-tetrafluorocyclobutene (c-HFO-1334zzcc, boiling point of 54 °C), 1-chloro-3,3,4,4-tetrafluorocyclobutene (c-HCFO-1324xzcc, boiling point of 59 °C) and 3,3,4,4-tetrafluorocyclobutane (c-HFC-1354ccff, boiling point of 50 °C) and difficult to purify because of the azeotropic behaviour among the above three products [15]; And in the hydrodehalogenation of 1,2- dichlorocyclohexafluoropentene (c-CFO-1416xxccc, boiling point of 90 °C) with H_2 promoted by nickel-chromium catalyst, the products were composed of 3,3,4,4,5,5-hexafluorocyclopentene (c-HFO-1436zzccc, boiling point of 70.5 °C), 1-chloro-3,3,4,4,5,5-dichlorohexacyclofluoropentene (c-HCFO-1426xzccc, boiling point of 73.5 °C) and 3,3,4,4,5,5-hexafluorocyclopentane (c-HFC-1456cccff, boiling point of 84.5 °C) and difficult to isolate from each other due to the fact that the products and the raw material had similar boiling points [15, 16]. Therefore, it is a great challenge to synthesize the target product with higher selectivity with C(sp^2)-H group by hydrodehalogenation of C(sp^2)-Cl group. Liquid-phase Zn catalytic reductive dehalogenation is another important method. In the reductive dehalogenation of straight chain aliphatic or aromatic compounds, double bond or alkyne bond is always formed by the removal of one molecular halogen, and H-Cl substitution almost does not happen. Some examples of the method are the following: Pentachloroethane (PCA) reacted with Zn in a batch reactor to produce reductive β-elimination (93%) and hydrolysis (7%) [17]; the azo and azoxy compound can be obtained by the reduction of nitroarenes with zinc powder and ammonium chloride in dimethylformaide (DMF) [18]; (E/Z)-2,3-dichlorohexafluoro-2-butene (E/Z-CFO-1316mxx) reacted with Zn in DMF to obtain 1,1,1,4,4,4-hexafluoro-2-butyne [19]; the dehalogenation of octachlorodibenzo-p-dioxin with zero-valent zinc, aluminum, iron, or nickle occurred in aqueous solution [20]; polyfluoroarenes can be prepared by reductive dehalogenation with aqueous ammonia [21]. The polyfluorcycloolefin with -CCl=CH- group was synthesized by the reaction of polyfluorcycloolefin~~s~~ containing -CCl=CCl- group and either of $LiAlH_4$ or n-C_4H_9Li [22]. It is limited in the industrial application due to the usage of expensive reagents contained Li.

Here, a facile preparation of 1H-polychlorofluorocycloolefin by the hydrodehalogenation of perchlorofluorocycloolefin with dimethylformaide (DMF) or dimethyl acetamide (DMAC) over Zn was reported, where perchlorofluorocycloolefins included c-CFO-1314xxcc, c-CFO-1416xxccc, 1,2-dichlorooctafluorocyclohexene (c-CFO-1518xxcccc) and 1-chloroheptafluorocyclopentene (c-CFO-1417xyccc). It was found that the hydrodehalogenation of perchlorofluorocycloolefin occurred not on the C(sp^3) position but only on the C(sp^2) position with high conversion rate and selectivity, where the hydrogen was supplied by either DMF or DMAC. And the mechanisms of hydrodehalogenation of perchlorofluorocycloolefin were proposed.

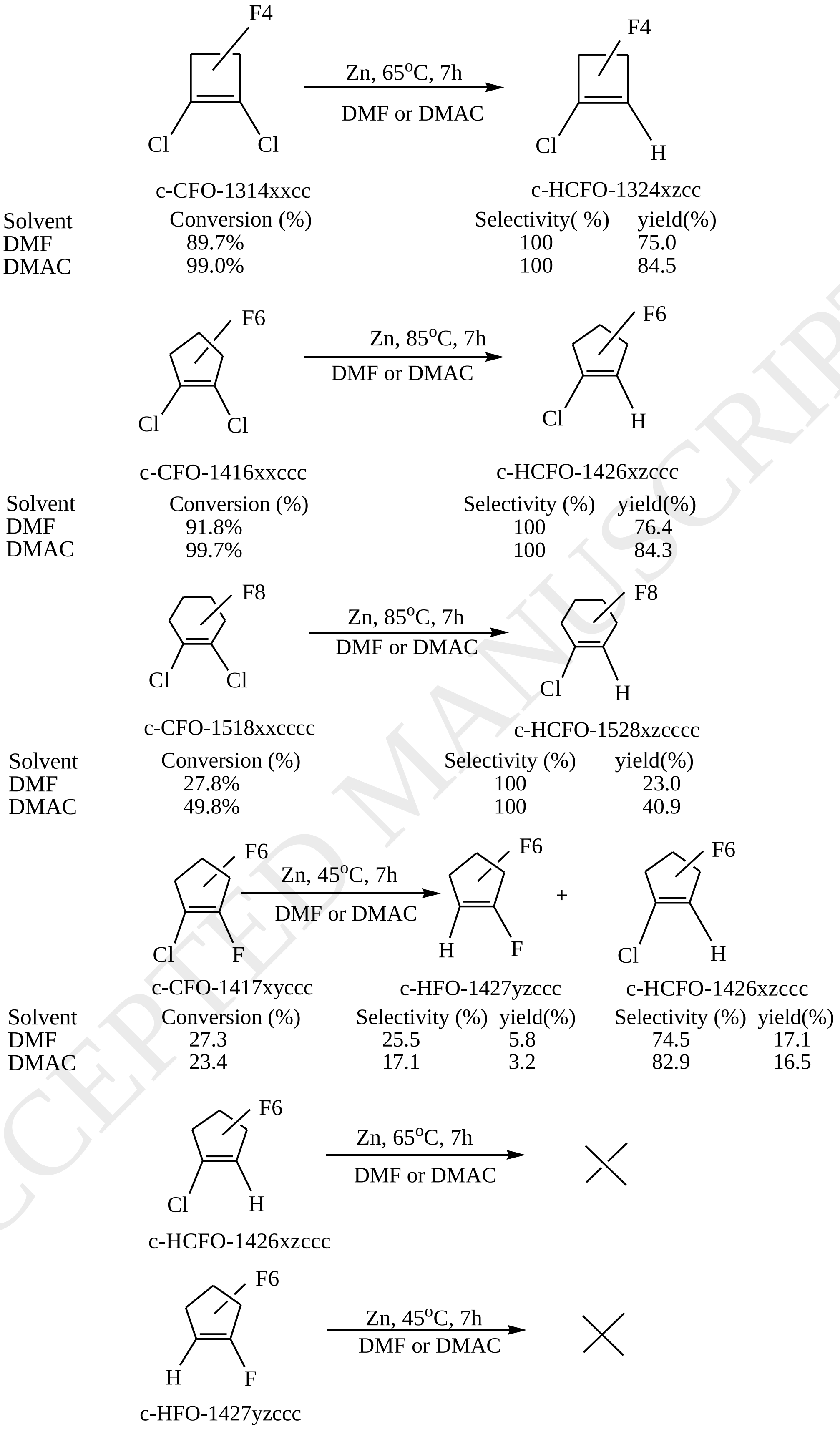
2. Results and Discussion

2.1 Hydrodehalogenation reactions of perchlorofluorocycloolefin

As shown in Scheme 1, while the hydrodehalgenation of c-CFO-1314xxcc, c-CFO-1416xxccc or c-CFO-1518xxcccc over Zn reached a conversion rate of 89.7%, 91.8% or 27.8% in DMF, the rate was higher in DMAC, namely, 99.0%, 99.7% or 49.8%. The selectivity was 100% in all cases. The results indicated that the hydrodehalogenation of c-CFO-1314xxcc, c-CFO-1416xxccc or c-CFO-1518xxcccc occurred only on the C(sp^2) position and not on the C(sp^3) position. They also indicated that the reactivity of c-CFO-1314xxcc, c-CFO-1416xxccc or c-CFO-1518xxcccc in DMAC was stronger than that in DMF. This was attributed to the fact that DMAC has stronger acidity than DMF due to the activity of hydrogenation at the α-position, so that the hydrogen resource is more easily obtained in DMAC than in DMF (See Scheme 2) [23, 24].

In addition, the yield of c-CFO-1324xzcc is nearly equal to that of c-CFO-1426xzccc at lower reaction temperature, and the yield of c-CFO-1528xzcccc was lower than c-CFO-1426xzccc at the same reaction conditions. Thus, the reactivty of perchlorofluorocycloolefins at the same conditions was arrenged in order of c-CFO-1314xxcc > c-CFO-1416xxccc > c-CFO-1518xxcccc. This is probably attributed to that the increasing ring tension in order of C4 > C5 > C6 can decrease the dissociation energy of C-Cl bond [25].

As also shown in Scheme 1, while the hydrodehalgenation of c-CFO-1417xyccc over Zn reached a conversion rate of 27.3% in DMF, the rate was lower in DMAC, namely, 23.4%. In addition, the selectivity of c-HCFO-1426xzccc was higher than that of c-HFO-1427yzccc in DMF or DMAC, the total selectivity of c-HCFO-1426xzccc and c-HFO-1427yzccc is 100%. The results indicated that the hydrodehalogenation of c-HFO-1427yzccc only occurred on the C (sp^2) position other than C (sp^3) position. Hydrodehalogenation of c-HCFO-1426xzccc or c-HFO-1427yzccc over Zn did not occur in DMF or DMAC (as in Scheme 2), which explained well that the hydrodehalogenation of c-CFO-1314xxcc, c-CFO-1416xxccc and c-CFO-1518xxcccc occurred only on the first C(sp^2) position but not on the second one. This ensured a high selectivity of 1H-polychlorofluorocycloolefins.



c-CFO-1314xxcc → c-HCFO-1324xzcc

Solvent	Conversion (%)	Selectivity(%)	yield(%)
DMF	89.7%	100	75.0
DMAC	99.0%	100	84.5

c-CFO-1416xxccc → c-HCFO-1426xzccc

Solvent	Conversion (%)	Selectivity (%)	yield(%)
DMF	91.8%	100	76.4
DMAC	99.7%	100	84.3

c-CFO-1518xxcccc → c-HCFO-1528xzcccc

Solvent	Conversion (%)	Selectivity (%)	yield(%)
DMF	27.8%	100	23.0
DMAC	49.8%	100	40.9

c-CFO-1417xyccc → c-HFO-1427yzccc + c-HCFO-1426xzccc

	c-CFO-1417xyccc	c-HFO-1427yzccc		c-HCFO-1426xzccc	
Solvent	Conversion (%)	Selectivity (%)	yield(%)	Selectivity (%)	yield(%)
DMF	27.3	25.5	5.8	74.5	17.1
DMAC	23.4	17.1	3.2	82.9	16.5

Scheme 1. Synthesis of 1H-polychlorofluorocycloolefins

2.2 Mechanisms of hydrodehalogenation

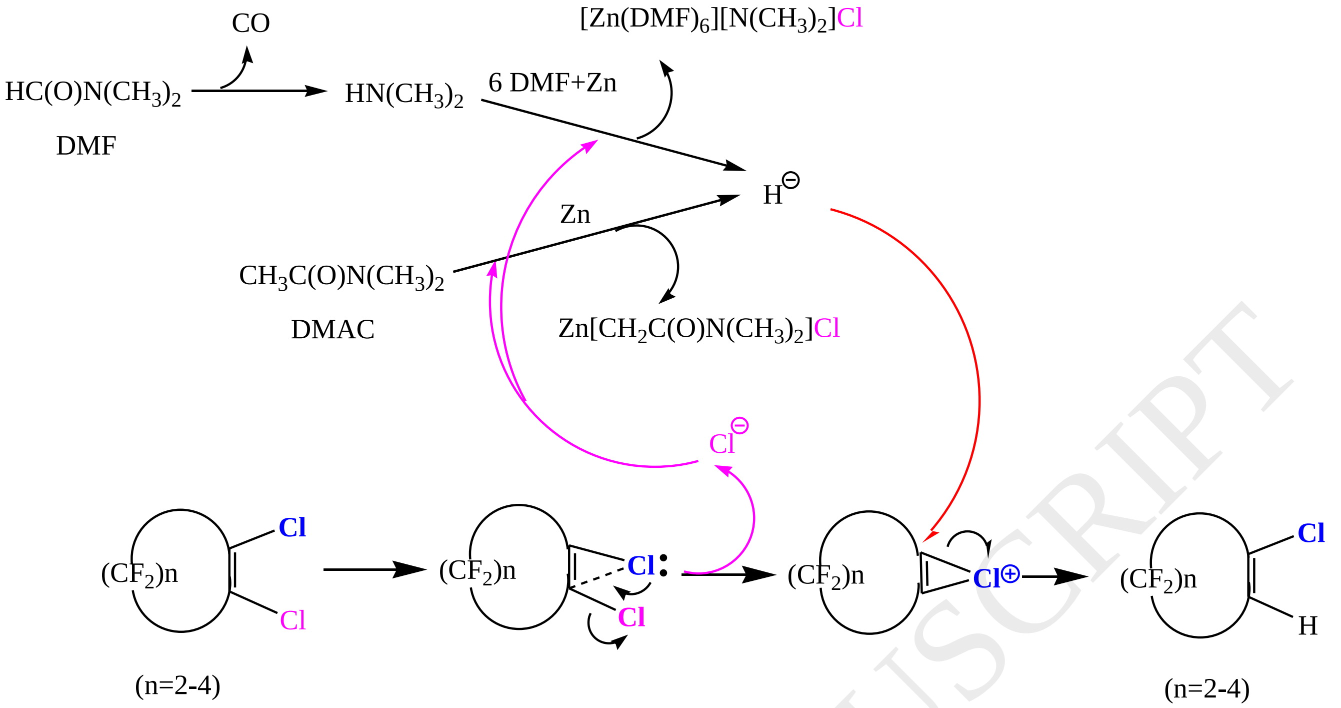
Based on the above experimental results, the mechanisms of the hydrodehalogenation of perchlorofluorocycloolefin with –CCl=CCl– group over Zn were proposed as follows (Scheme2):

(1) In DMF, $HN(CH_3)_2$ (dimethylamine) was firstly obtained by the decomposition of DMF [26,27], then Zn reacted with $HN(CH_3)_2$ to produce active hydrogen anion with the formation of $[Zn(DMF)_6][N(CH_3)_2]Cl$ [23, 24]; In DMAC, α-H of DMAC owns obvious acidity, which can reacted with Zn to produce active hydrogen anion with the formation of $Zn[CH_2C(O)N(CH_3)_2]Cl$ [24].

(2) CF_2 group of perchlorofluorocycloolefin decreased the density of the charge on a double bond, which led to easily form an intermediate unsaturated cyclic chloronium ion because of the effect of Zn-Cl complex compound in polar solution [28-31].

(3)The active hydrogen anion can react with the intermediate unsaturated cyclic chloronium ion [35,36]. This led to the fracture of cyclic chloronium ion bond and the regeneration of a double bond. At last, the 1H-polychlorofluorocycloolefin was obtained.

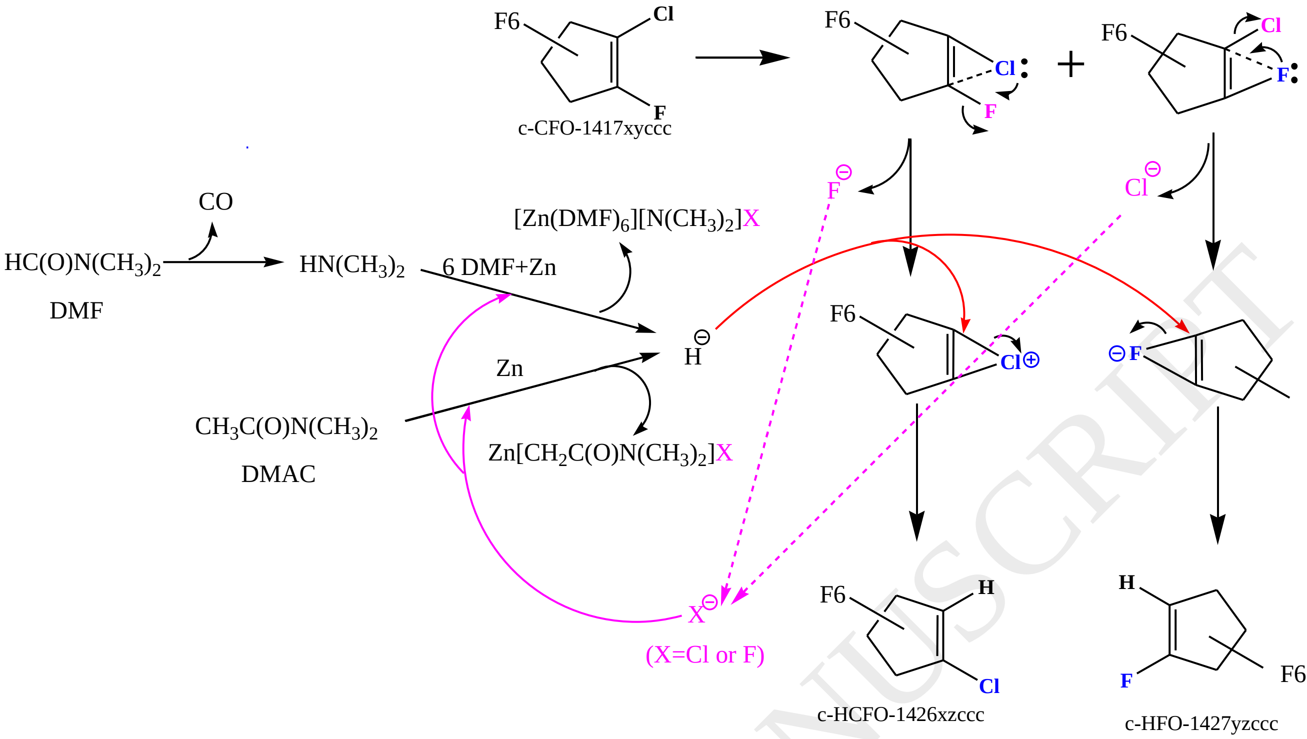
In the above process, Zn was a reduction reagent. In addition, DMAC has stronger acidity than DMF due to the activity of hydrogenation at the α-position [24]. Comparing with DMAC, DMF belongs to weak alkalescence [23]. This leads to that DMAC owns higher reactivity than DMF. It is well agreement with the results from the hydrodehalogenation of c-CFO-1314xxcc, c-CFO-1416xxccc or c-CFO-1518xxcccc in DMAC or DMF.



Scheme 2. The mechanism of dechlorination of perchlorofluorocycloolefin with –CCl=CCl– group

The mechanism of the dehalogenation of c-CFO-1417xyccc with –CCl=CF– group is similar with perchlorofluorocycloolefin with –CCl=CCl– group, which was shown as follows (Scheme 3): (1) When fluorine and chlorine are at the double bond, the unsaturated cyclic fluoronium ion $[\text{-C-F-C}]^+$ or $[\text{-C-Cl-C-}]^+$ was obtained under the induction of CF_2 group in DMF or DMAC solution [37-39]; (2) Then, active hydrogen anion joins the carbon atom carrying fluorine atom or chlorine atom of the double bond; (3) At last, the double bond is regenerated by the disconnection of fluoronium ion or chloronium ion, and the two kinds of 1H-polychlorofluorocycloolefins were formed. In the reaction, fluoronium ion is more unstable than chloronium ion. Thus, the selectivity of c-HCFO-1426xzccc was higher than c-HFO-1427xyccc [37, 38].

The H-Cl exchange of c-HCFO-1426xzccc or c-HCFO-1427yzccc cannot occur in the same conditions, which are probably explained as follows: the C-H bond is nonpolar covalent bond, which has no lone pair electrons. Therefore, the onium ion $[\text{C-H-C}]^+$ does not exist, which results that the H-Cl exchange of c-HCFO-1426xzccc or c-HCFO-1427yzccc cannot occur [40].



Scheme 3. The mechanism of dehalogenation of c-CFO-1417xyccc with –CCl=CF– group

According to our previous results, E/Z-CFO-1316mxx reacted with Zn in DMF to produce only 1,1,1,4,4,4-hexafluorobutyne, but not 2-chloro-1,1,1,4,4,4-hexafluoro-2-butene (E/Z-HCFO-1326mxz) or 2H,3H-1,1,1,4,4,4-hexafluoro-2-butene (E/Z-HFO-1336mzz) [19]. This indicated that the dechlorination of the straight chain olefin with -CCl=CCl- group with Zn occurred, and the hydrodechlorination with DMF over Zn cannot be carried out. It is just contrary to the experimental results from the reaction of 1,2-dichloroperfluorocycloolefin in the presence of Zn and DMF, which is probably attributed to the restriction of ring tension [41]. According to the traditional views, the dehalogenation reaction belongs to the E2-elimination, and trans-elimination is always favored over cis-elimination to a greater degree [42]. In the dehalogenation of E/Z-CFO-1316mxx, Z-CFO-1316 can be easily converted into E-CFO-1316mxx and can be dehalogenated by trans-elimination. While the confirmation of 1, 2-dichloroperfluorocycloolefin is only cis-type but no trans-type due the existence of ring and double bond. Thus, the dehalogenation of 1,2-dichloroperfluorocycloolefin will occur only by cis-elimination. However, the cis-elimination of 1,2-dichloroperfluorocycloolefin is hard to occur, and the H-Cl exchange of 1,2-dichloroperfluorocycloolefin with DMF or DMAC occurs easily.

3. Conclusions

The hydrodehalogenation of perchlorofluorocycloolefin with DMF or DMAC over Zn was investigated. It was found that hydrodehalogenation of perchlorofluorocycloolefin occurred not on the C (sp^3) position but only on the C (sp^2) position, and the hydrogen resource came from DMF or DMAC. DMAC has stronger acidity than DMF due to the activity of hydrogen at the α-position, which led to its higher reactivity in the hydrodehalogenation of c-CFO-1314xxcc, c-CFO-1416xxccc or c-CFO-1518xxcccc. In DMF or DMAC, the hydrodehalogenation of c-CFO-1314xxcc, c-CFO-1416xxccc, c-CFO-1518xxcccc or c-CFO-1417xyccc always occurred only on the first C (sp^2) position but not on the second C (sp^2) position, which led to the high selectivity of 1H-perchlorofluorocycloolefin. As a result, the method of the hydrodehalogenation investigated in our experiments is a promising way of preparing 1H-polychlorofluorocycloolefin with high selectivity.

4. Experimental Section

4.1 Chemicals:

1,2-dichlorotetrafluorocyclobutene (c-CFO-1314xxcc, 99.0+%) and 1,2-dichlorooctafluoro cyclohexene (c-CFO-1518xxcccc, 99.0+%) were purchased from Ockwood Chemical Co., Ltd. 1,2-dichlorohexafluorocyclopentene (c-CFO-1416xxccc, 97.0+%), 1-chloroheptafluorocyclopentene (c-CFO-1417xyccc, 97.0+%) and 1,3,3,4,4,5,5-heptafluorocyclopentene (c-HFO-1427yzccc, 97.0+%) were from Shaanxi Shenguang Chemical Industry Co., Ltd. Zn powder was from Tokyo Chemical Industry Co., Ltd. DMF and DMAC were purchased from Wako Pure Chemical Industries, Ltd. Chloroform-d ($CDCl_3$, 99.8 atom%D) at was obtained from Aldrich Chem .Co. (Japan). CCl_3F (CFC-11, 99.0+%) was purchased from Synquest Labs, Lnc.

4.2 Instrument

The reactor used for all experiments was a 50 ml round bottom flask with magnetic stirring using a Magmix stirrer tough mixer (MRK Co., LTD.).

^{1}HNMR and ^{19}FNMR of c-CFO-1314xxcc, c-CFO-1416xxccc, c-CFO-1518xxcccc, c-HCFO-1324xzcc, c-CFO-1417xyccc, c-HCFO-1426xzccc, c-HCFO-1528xzcccc and c-HFO-1427yzccc were recorded on a Bruker AVANCE 400 (400 MHZ) at 25 °C with $CFCl_3$ as internal references in $CDCl_3$ solvent. The patterns were compared with those of authentic samples.

The GC–MS consisted of a Shimadzu GC-MS-QP2010 and a Shimadzu GC-2014plus. The capillary column was DB-VRX with 30 m length and 0.32 mm diameter (film: 0.10 mm) from Agilent Technologies Inc. The operating conditions of the GC were as follows: the column temperature was initially 40 °C; then, it was increased to 230 °C at a rate of 10 ^{o}C/min; after that, it was held at 230 °C for 8 minutes. Both the injection port and the thermal conductivity detector were maintained at 200 °C, and the carrier gas He was introduced at a rate of 10 ml/min.

The gas chromatograph was a Shimadzu GC-2014S with DB-VRX column with 30 m length and 0.32 mm i.e. (film: 0.10 mm) from Agilent Technologies Inc. The operating conditions of the GC were as follows: 33 °C for 10 min; 10 °C/min to 230 °C; hold for 15 min. Both the injection port and the thermal conductively were maintained at 150 °C, and the carrier gas was a mixture of H_2, He and air introduced at a rate of 3 ml/min.

4.3 Experiment procedure

Hydrodehalogenation of c-CFO-1314xxcc: Zn powder 1.00 g, DMF or DMAC 4.62 ml and c-CFO-1314xxcc 1.50 g were placed into a 20 ml three-necked round-bottomed flask equipped with a thermometer, a reflux device and an agitating device. The flask was dipped into the oil bath and heated to a temperature of 65 °C. Under magnetic stirring for 7h, the products from the above system were detected by GC-MS and ^{19}F NMR. The products were as follows: DMF solvent: (c-CFO-1314xxcc) 0.15 g, (C-HCFO-1324xzcc) 0.93 g;   DMAC solvent: (c-CFO-1314xxcc) 0.02 g, (C-HCFO-1324xzcc) 1.05 g.

Hydrodehalogenation of c-CFO-1416xxccc: Zn powder 130.00 g, DMF or DMAC 600ml and c-CFO-1416xxccc 244.00 g were placed into a 1000 ml three-necked round-bottomed flask equipped with a thermometer, a reflux device and an agitating device. The flask was dipped into the oil bath and heated to a temperature of 85 °C. Under magnetic stirring for 7 h, the products from the above system were obtained by vacuum distillation at 110 °C, then were washed by 2×1000 ml water and were dried by 50ml 4A molecular sieves, at last were detected by GC-MS and ^{19}F NMR. The products were as follows: DMF solvent: (c-CFO-1416xxccc) 21.00 g, (C-HCFO-1426xzccc) 160.40 g; DMAC solvent: (c-CFO-1416xxccc) 4.70 g, (C-HCFO-1426xzccc) 177.00 g.

Hydrodehalogenation of c-CFO-1518xxcccc: Zn powder 0.64 g, DMF or DMAC 2.94 ml and c-CFO-1518xxcccc 1.47 g were placed into a 30 ml three-necked round-bottomed flask equipped with a thermometer, a reflux device and an agitating device. The flask was dipped into the oil bath and heated to a temperature of 85 °C. Under magnetic stirring for 7 h, the products from the above system were detected by GC-MS and ^{19}F NMR. The products were as follows: DMF solvent: (c-CFO-1518xxcccc) 1.06 g, (C-HCFO-1528xzcccc) 0.30 g;   DMAC solvent: (c-CFO-1518xxcccc) 0.74 g, (C-HCFO-1528xzcccc) 0.53 g.

Hydrodehalogenation of c-CFO-1417xyccc: Zn powder 0.85 g, DMF or DMAC 4.00ml and c-CFO-1417xyccc 1.57 g were placed into a 30ml three-necked round-bottomed flask equipped with a thermometer, a reflux device and an agitating device. The flask was dipped into the oil bath and heated to a temperature of 45 °C. Under magnetic stirring for 7h, the products from the above system were detected by GC-MS and ^{19}F NMR. The products were as follows: DMF solvent: (c-CFO-1417xyccc) 1.14

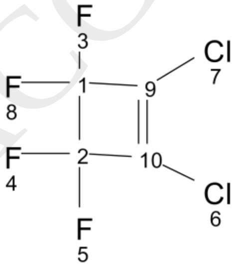
g, (C-HCFO-1426xzccc) 0.25 g, (c-HFO-1427yzccc) 0.08 g; DMAC solvent: (c-CFO-1417xyccc)1.20g, (C-HCFO-1426xzccc) 0.24 g, (c-HFO-1427yzccc) 0.05 g.

Hydrodehalogenation of C-HCFO-1426xzccc: Zn powder 0.85 g, DMF or DMAC 4.00 ml and C-HCFO-1426xzccc 1.50 g were placed into a 30 ml three-necked round-bottomed flask equipped with a thermometer, a reflux device and an agitating device. The flask was dipped into the oil bath and heated to a temperature of 65 °C. Under magnetic stirring for 7 h, the products from the above system were detected by GC-MS and ^{19}F NMR. The products were as follows: DMF solvent: (C-HCFO-1426xzccc) 1.47 g; DMAC solvent: (C-HCFO-1426xzccc) 1.48 g.

Hydrodehalogenation of c-HFO-1427yzccc: Zn powder 0.85 g, DMF or DMAC 4.00 ml and c-HFO-1427yzccc 1.47 g were placed into a 30 ml three-necked round-bottomed flask equipped with a thermometer, a reflux device and an agitating device. The flask was dipped into the oil bath and heated to a temperature of 45 °C. Under magnetic stirring for 7 h, the products from the above system were detected by GC-MS and ^{19}F NMR. The products were as follows: DMF solvent: (c-HFO-1427yzccc) 1.45 g; DMAC solvent: (c-HFO-1427yzccc) 1.45 g.

4.4 Analytic results

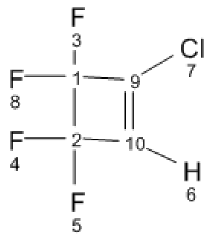
4.4.1 c-CFO-1314xxcc



MS m/e: 194 (M$^+$); 175 (M$^+$-F); 159 (M$^+$-Cl); 128 (M$^+$-CFCl); 109(M$^+$-CF$_2$Cl); 74(M$^+$-CF$_2$Cl).

^{19}F NMR (377 MHz, Chloroform-d) δ -117.53 (s, F3, F4, F5 and F8, 4F).

4.4.2 c-HCFO-1324xzcc

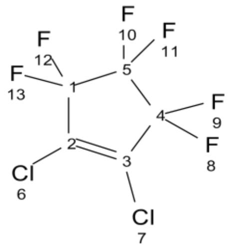


MS m/e: 160 (M^+); 141 (M^+-F); 125 (M^+-Cl); 100 (M^+-C_2ClH); 109(M^+-CF_2Cl); 74(M^+-CF_2Cl).

^{19}F NMR (377 MHz, Chloroform-d) δ-106.80 (s, F3, 1F), -112.57(m, F5, 1F), -113.40(m, F8, 1F), -116.63(m, F4, 1F).

^{1}H NMR (400MHz, Chloroform-d) δ 6.48(tt, J = 10.0, 1.6 Hz， H6, 1H).

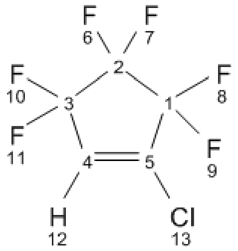
4.4.3 c-CFO-1416xxccc



MS m/e: 244 (M^+); 225 (M^+-F); 209 (M^+-Cl); 194 (M^+-CF_2); 175 (M^+-CF_3); 159 (M^+-CF_2Cl); 155 (M^+-FCl_2); 140 (M^+-CF_3Cl); 125 (M^+-CF_2Cl_2); 109 (M^+-C_2F_4Cl); 90 (M^+-C_2F_5Cl); 85 (M^+-C_4F_4Cl); 69 (M^+-$C_4F_3Cl_2$).

^{19}F NMR (377 MHz, Chloroform-d) δ -113.75 (dt, J = 10.1, 4.0 Hz, F8, F9, F12 and F13, 4F), -129.73 (ddt, J = 10.8, 6.4, 3.4 Hz, F10 and F11, 2F).

4.4.4 c-HCFO-1426xzccc

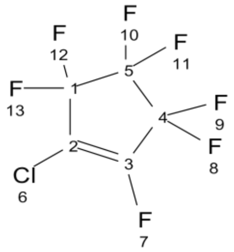


MS m/e: 210 (M^+); 191 (M^+-F); 160 (M^+-CF); 125 (M^+-CClF); 106 (M^+- $CClF_2$); 100 (M^+-C_3HClF); 93 (M^+- C_2HClF); 91 (M^+-C_2F_4);; 75 (M^+-$CClF_3$); 69 (M^+- C_4HClF_2).

^{19}F NMR (377 MHz, Chloroform-d) δ.-108.48 (m, F8 and F9, 2F), -115.34 (m, F10 and F11, 2F), -130.51 (m, F6 and F7, 2F),

^{1}HNMR (400MHz, Chloroform-d) δ6.55 (t, J= 1.2 Hz, H12, 1H).

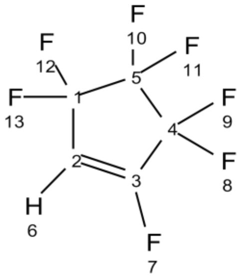
4.4.5 c-CFO-1417xyccc



MS m/e: 228 (M^+); 209 (M^+-F); 193 (M^+-Cl); 178 (M^+-CF_2); 159 (M^+-CF_3); 143 (M^+-CF_2Cl); 124 (M^+-CF_3Cl); 109 (M^+-C_2F_5); 100 (M^+-C_3F_3Cl); 93 (M^+-C_2F_4Cl); 69(M^+-C_4F_4Cl).

^{19}F NMR (377 MHz, $CDCl_3$) δ -113.52 (dm, J=10.20 Hz, F12 and F13, 2F), -118.41 (dm, J= 14.7 Hz, F8 and F9, 2F), -129.19 (m, F7, 1F), -129.50 (m, F10 and F11, 2F).

4.4.6 c-HFO-1427yzccc

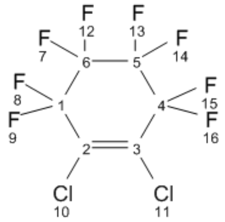


MS m/e: 194 (M^+); 175 (M^+-F); 156 (M^+-F_2); 144 (M^+-CF_2); 125(M^+-CF_3); 113 (M^+-C_2F_3); 106 (M^+-CF_4); 94 (M^+-C_2F_4); 87 (M^+-CF_5); 75 (M^+-C_2F_5).

^{19}F NMR (377 MHz, Chloroform-d) δ -107.29 (d, J=12.1Hz, F12 and F13, 2F), -120.72 (m, F8 and F9, 2F), -124.83 (m, F7, 1F), -130.84 (m, F10 and F11, 2F).

^{1}H NMR (400MHz, Chloroform-d) δ 6.07 (m, H6, 1H).

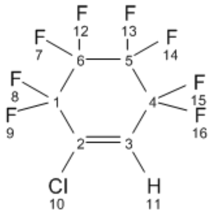
4.4.7 c-CFO-1518xxcccc



MS m/e: 294 (M^+); 275 (M^+-F); 259 (M^+-Cl); 240 (M^+-ClF); 225(M^+-CF_3); 194 (M^+-C_2F_4); 131 (M^+-$C_3F_3Cl_2$); 109 (M^+-C_3F_6Cl); 100 (M^+-$C_4F_4Cl_2$); 85 (M^+-C_5F_6Cl).

^{19}F NMR (377 MHz, Chloroform-d) δ -109.84 (s, F8, F9, F15 and F16, 4F), -133.50 (s, F7, F12, F13 and F14, 4F),

4.4.8 c-HCFO-1528xzcccc



MS m/e: 260 (M^+); 241 (M^+-F); 212 (M^+-CHCl); 191 (M^+-CF_3); 160(M^+-C_2F_4); 125 (M^+-C_2F_4Cl); 109 (M^+-C_3F_6Cl); 100 (M^+-C_4F_4ClH); 75 (M^+-C_3F_6Cl).

^{19}F NMR (377 MHz, Chloroform-d) δ-107.70 (s, F8 and F9, 2F), -113.28 (d, J= 7.54 Hz, F15 and F16, 2F), -133.61 (m, F7 and F12, 2F), -135.17 (m, F13 and F14, 2F).

^{1}H NMR (400MHz, Chloroform-d) δ 6.63(m, H6, 1H).

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