PAPER

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From hexafluoropropylene to perfluoroisobutyronitrile *via* high-yield and scalable three-step synthesis

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To replace sulfur hexafluoride (SF_6), a potent greenhouse gas with high global warming potential (GWP) and long lifetime, perfluoroisobutyronitrile (C_4F_7N) has emerged as the next-generation insulating gas to advance the development of the power industry, especially gas-insulated equipment. However, most reported synthesis routes for perfluoroisobutyronitrile require expensive reagents or complex procedures and harsh reaction conditions, which are impractical for scalable production and cost reduction for real applications. Herein, we report a three-step synthetic process from perfluoropropylene to perfluoroisobutyronitrile, involving addition with carbonyl fluoride, nucleophilic substitution with ammonia and dehydration. It achieved a 77% total yield of high-purity perfluoroisobutyronitrile (99.9%), which is significantly higher than that of other synthetic routes. This new synthesis process also offers compelling cost benefits and scalable production, which may promote the broader application of C_4F_7N.

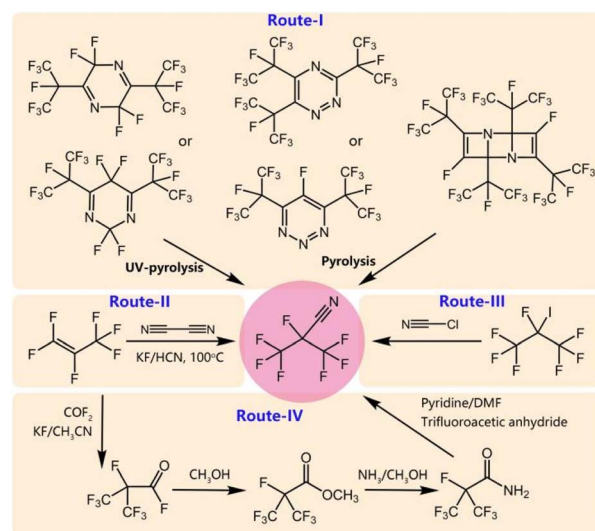## Introduction

Sulfur hexafluoride (SF_6) is widely used in smelting, semiconductor etching, and high-voltage electrical equipment due to its excellent chemical stability, thermodynamic stability, and high arc extinguishing capability.[1–3] However, due to its high global warming potential (GWP) value (23 900) and a long atmospheric lifetime (3200 years), SF_6 was declared to be one of the six limited greenhouse gases in the 1997 Kyoto Protocol.[4,5] Perfluoroisobutyronitrile (C_4F_7N), a promising SF_6 alternative, was first reported in 2014 by Alstom and 3M company. It exhibits high dielectric strength, good thermal stability, and non-toxicity with a low GWP.[6,7] According to recent studies, the atmospheric lifetime of C_4F_7N is 54 years, with a 100-year GWP of 1705. The values are significantly lower than SF_6.[8,9]

To promote the adoption of C_4F_7N for industry applications, researchers are committed to developing and optimizing different synthesis protocols. To date, four main synthetic routes to perfluoroisobutyronitrile have been reported (Scheme 1). The first method is based on the pyrolysis of nitrogen-containing aromatic rings, including diazine, triazine, and nitrogen-containing polycyclic compounds, at high temperatures or under ultraviolet light. Certain fluorinated diaza-

cyclohexadiene generate C_4F_7N under prolonged UV irradiation (254 nm, 240–340 h).[10] However, due to incomplete diazine fragmentation *via* photopyrolysis, the yield remains low (11–35%).[11] In contrast, triazine compounds undergo more efficient N–N bond cleavage during pyrolysis, enabling higher selectivity and yield in C_4F_7N formation.[12] It was reported that pyrolysis of perfluorotri(isopropyl)-1,2,4-triazine to 560 °C could yield C_4F_7N with 99.3% efficiency.[13,14] While alternative triazine and nitrogen-containing precursors can produce C_4F_7N through thermal or photolytic decomposition,[15,16] their practical utility

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Scheme 1 The four main synthesis route for perfluoroisobutyronitrile.

remains limited by stringent reaction conditions, costly catalysts, and complex precursor synthesis.

The second route involves the addition reaction of hexafluoropropene and cyanides. Using potassium fluoride (KF) as the catalyst, Oxenrider et al. obtained C_4F_7N in 31% yield via a one-step reaction of hexafluoropropylene with acetonitrile.[17] Li et al. reported the addition reaction of hexafluoropropylene with cyanogen or cyanide chloride to generate C_4F_7N with a yield of 64%.[18] Although the direct introduction of the –CN group makes this route simple, short, and efficient, it largely relies on highly toxic cyanogen or cyanide chloride. Other potential cyanides and cyanating reagents may still pose significant toxicity risks or face challenges in achieving high yields.[19,20] Therefore, this route fails to meet the requirements for green preparation and is unsuitable for large-scale production.

The third route involves the substitution reaction of iodoperfluoropropane. Vöhringer et al. found that the reaction of 2-iodo-perfluoropropane and chloroacetonitrile may form C_4F_7N as a minor by-product, with primary production of 2-chloro-perfluoropropane.[21] It thus can only have low synthetic efficiency for C_4F_7N.

The fourth way comprises a four-step transformation of hexafluoropropene. The process included (1) the reaction of hexafluoropropylene in acetonitrile with KF as catalyst, (2) heptafluoroisobutyryl fluoride reacts with methanol at 0 °C and yield heptafluoroisobutyric acid methyl ester, (3) the reaction of heptafluoroisobutyric acid methyl ester with ammonia in methanol to produce heptafluoroisobutyramide, (4) dehydration of heptafluoroisobutyramide in dimethyl fumarate (DMF) with pyridine and trifluoroacetic anhydride, to obtain C_4F_7N.[22–24] The total yield was about 48.6%. Recently, Gao et al. reported the three-step formation of C_4F_7N based on the amidation of bis-(perfluoroisopropyl) ketone and dehydration of heptafluoroisobutyramide by using oxalyl dichloride as the starting agent. The total yield of C_4F_7N was 42% under the optimal conditions.[25]

It can be seen that these synthetic protocols remain limited by the use of expensive or scarce starting materials, toxic volatile reagents, complex procedures, and low yields, making them unsuitable for scalable C_4F_7N production. Herein, we developed a novel route for the synthesis of perfluoroisobutyronitrile from starting material hexafluoropropene via a three-step process (Scheme 2). Firstly, the addition of hexafluoropropene with carbonyl fluoride in the presence of KF/18-crown-6 complex; then, the nucleophilic substitution of perfluoroisobutyryl fluoride with ammonia. Finally, the dehydrating reaction of heptafluoroisobutyramide in the presence of phosphorus pentoxide. The structural characterization of intermediates and final product was performed by GC-MS, ^{19}F-NMR, ^{13}C-NMR, and IR spectroscopy. This optimized protocol afforded C_4F_7N in high yield via a relatively short synthetic route.
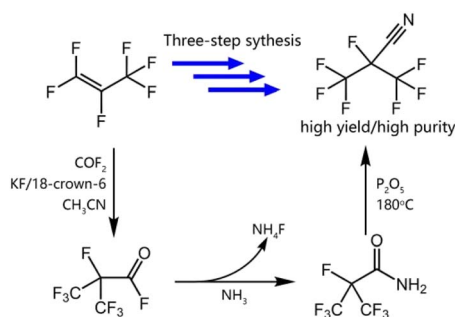
Experimental section

Materials

CCl_3F (CFC-11) (purity >99%), COF_2 (purity >95%), and hexafluoropropylene (purity >98.5%) were purchased from Synquest Labs, Lnc. Chloroform-d (CDCl₃) at 99.8 atom% D, acetonitrile-d_3 at 99.8 atom% D, acetone-d_6 at 99.8 atom% D, KF (purity >99.8%), 18-crown-6 (purity >99.0%), anhydrous acetonitrile (purity >99.5%), dichloromethane (purity 99.0%), phosphorus pentoxide (P_2O_5) (purity >98.0%) were purchased from Kanto Denka Co. (Japan). Pure NH_3 was purchased from Sumitomo Seika Chemicals Co., Ltd (Japan).

Characterization

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⁻¹ 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 He was introduced at a rate of 10 mL min⁻¹ ^{19}F NMR spectra of the intermediates and products during the synthesis were recorded on a Bruker AVANCE 400 (377 MHz) NMR with trichlorofluoromethane (CFC-11) as internal standards at 25 °C. ^{13}C NMR spectra of the intermediates and products during the synthesis were recorded on a Bruker AVANCE 400 (101 MHz) NMR at 25 °C.

Three-step synthesis of perfluoroisobutyronitrile

Synthesis of perfluoroisobutyryl fluoride. 0.5 mol potassium fluoride (KF) and 0.1 mol 18-crown-6 were added into an autoclave made of 316 material with a volume of 1 L. After evacuating the system to a vacuum state, 400 mL of anhydrous acetonitrile was transferred into the autoclave. At −100 °C, 1 mol of hexafluoropropylene and 1 mol of carbonyl fluoride were then rapidly introduced into the autoclave. The reaction system was then maintained at 80 °C under constant stirring for 24 h. A 200 mL 316 stainless steel cylinder was evacuated and cooled with liquid nitrogen to condense and collect the gas from the reaction system. The product of perfluoroisobutyryl fluoride was confirmed by ^{19}F-NMR, ^{13}C-NMR, and IR. The perfluoroisobutyryl fluoride weighed 207.8 g, with a purity of 99.7% and a yield of 95.9%. ^{19}F NMR(377 MHz, acetonitrile-d_3): δ 34.26 (d-heptet, J = 22.24 Hz, 6.03 Hz, –COF, 1F), −73.66 (t, J = 6.41 Hz, –CF₃, 6F), −180.38 (d-heptet, J = 21.87 Hz, 7.54 Hz, –CF–COF, 1F) (Fig. S1). ^{13}C NMR (101 MHz, acetonitrile-d_3): δ 148.94 (ddd, J = 374.00 Hz, 53.53 Hz, 27.98 Hz, –COF, 1C),

Scheme 2 The three-step synthesis scheme for perfluoroisobutyronitrile from hexafluoropropylene in this work.

118.90 (quartet-dd, $J = 289.57$ Hz, 25.25 Hz, 16.06 Hz, $-CF_3$, 2C), 88.86 (d-heptet, $J = 192.71$ Hz, 30.01 Hz, $-CF-COF$, 1C) (Fig. S2). IR (gas, cm^{-1}): 1890, 1878, 1318, 1279, 1195, 1156, 998, 753, 705, 645.

Synthesis of heptaflurorooisobutyramide. The autoclave made of 316 material with a volume of 1 L was pumped into a vacuum state. Then under the condition of -100 °C provided by liquid nitrogen, 1 mol perfluoroisobutyryl fluoride and 3.5 mol ammonia were quickly passed into the autoclave one by one. After the addition of raw materials, the reaction system was kept at 15 °C under normal stirring conditions for 20 h. After releasing the gases in the reaction system, the remaining solid was extracted with dichloromethane 200 mL × 3 times to obtain the organic liquid, with the removal of NH_4F. The organic liquid was distilled to remove dichloromethane, and heptaflurorooisobutyramide was then obtained. The hepta-flurorooisobutyramide weighed 207.8 g, with a purity of 99.7% and a yield of 89.3%. ^{19}F NMR (377 MHz, chloroform-d): δ 75.02 (d, $J = 7.54$ Hz, $-CF_3$, 6F), 180.54 (heptet, $J = 6.78$ Hz, $-CF-CONH_2$, 1F) (Fig. S3). ^{13}C NMR (101 MHz, chloroform-d): δ 159.74 (d, $J = 20.40$ Hz, $-CONH_2$, 1C), 118.82 (quartet-dd, $J = 287.85$ Hz, 26.66 Hz, 1.62 Hz, $-CF_3$, 2C), 88.38 (d-heptet, $J = 219.47$ Hz, 32.93 Hz, $-CF-CONH_2$, 1C) (Fig. S4). IR (KBr, cm^{-1}): 3432, 3198, 1711, 1608, 1401, 1305, 1280, 1234, 1179, 1144, 1034, 991, 746, 655, 539, 511.

Synthesis of perfluoroisobutyronitrile. 0.1 mol hepta-flurorooisobutyramide and 0.5 mol P_2O_5 were added into an autoclave made of 316 material with a volume of 1 L and pumped into a vacuum state. To prevent direct contact with water, which could trigger a violent exothermic reaction forming phosphoric acid, P_2O_5 was gradually added to the reaction vessel under a nitrogen atmosphere within a glovebox. After the addition of raw materials, the reaction system was kept at 180 °C under stirring for 16 h. After the reaction system was cooled to room temperature, a cylinder (200 mL 316 material) was firstly vacuumed by pump, then frozen by liquid nitrogen, and collected the gas from the reaction system. It was proved to be perfluorobutyronitrile by ^{19}F-NMR, ^{13}C-NMR, IR, and GC-MS. The perfluorobutyronitrile weighed 17.6 g, with a purity of 99.9% and a yield is 90.0%. ^{19}F NMR(377 MHz, acetone-d_6): δ 75.91 (d, $J = 10.56$ Hz, $-CF_3$, 6F), 176.99 (heptet, $J = 9.98$ Hz, $-CF-CN$, 1F) (Fig. S5). ^{13}C NMR (101 MHz, acetone-d_6): δ 117.66 (quartet-d, $J = 289.97$ Hz, 27.27 Hz, $-CF_3$, 2C), 106.56 (d, $J = 30.10$ Hz, $-CN$, 1C), 82.67 (d-heptet, $J = 220.08$ Hz, 38.38 Hz, $-CF-CN$, 1C) (Fig. S6). IR (gas, cm^{-1}): 2277, 1314, 1263, 1239, 1166, 1075, 989, 730, 668. MS m/z: 195 (M$^+$); 176 (M$^+$–F); 150 (M$^+$–CFN); 131 (M$^+$–CF$_2$N); 126 (M$^+$–CF$_4$); 119 (M$^+$–CF$_3$); 107 (M$^+$–C$_2$F$_2$N); 100 (M$^+$–C$_2$F$_3$N or F$_5$); 88 (M$^+$–C$_2$F$_5$); 76 (M$^+$–C$_3$F$_3$N); 69 (M$^+$–CF$_3$); 57 (M$^+$–C$_2$F$_6$); 50 (M$^+$–C$_3$F$_5$N or CF$_2$); 38 (M$^+$–C$_4$F$_5$N or C$_2$F$_7$) (Fig. S7 and S8).

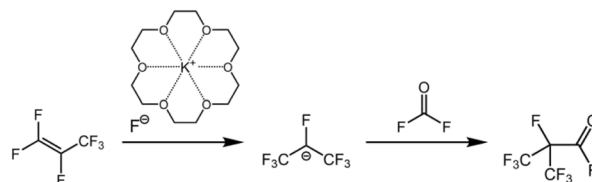## Results and discussion

To address the limitations of existing C_4F_7N synthesis methods, we selected hexafluoropropylene as a safer and more readily available starting material. The initial step is the reaction of hexafluoropropene with carbonyl fluoride to produce

perfluoroisobutyryl fluoride in acetonitrile. Since the key precursor carbonyl fluoride has a boiling point of 190 K (-83 °C), a cryogenic environment must be maintained to ensure sufficient liquefaction and precise dosing. The ethanol-liquid nitrogen cooling system can achieve temperatures as low as -116 °C, which should meet the experimental requirements. Hexafluoropropylene and carbonyl fluoride were mixed at -100 °C and then heated to 80 °C with stirring for 24 h. The KF/18-crown-6 complex was used as a catalyst to enhance the substitution. 18-crown-6 has a higher selectivity for potassium ion (K$^+$) over other alkali metal cations.[26] The stable complex of 18-crown-6 with K$^+$ could increase the solubility of KF in organic solvents.[27,28] Experimental measurements revealed that upon the addition of 18-crown-6, the solubility of KF in acetonitrile increased more than 30 times at 25 °C.[29] In this reaction, the fluoride anion (F$^-$) of KF reacts with hexafluoropropylene to form a fluorocarbon anion intermediate, which subsequently reacts with carbonyl fluoride to yield perfluoroisobutyryl fluoride (Scheme 3). The complexation could reduce electrostatic K$^+$–F$^-$ interactions, thereby enhancing fluoride's nucleophilicity and accelerating the reaction rate.[30] Under reacting at 80 °C for 24 h, the production of perfluoroisobutyryl fluoride from the reaction of hexafluoropropylene and carbonyl fluoride was shown a high yield of 95.9% with a purity of 99.7% according to the analysis by IR, ^{19}F-NMR and ^{13}C-NMR. While for the process without the addition of 18-crown-6, the yield of per-fluoroisobutyl fluoride was only 80%.[22] These results confirmed the critical role of 18-crown-6 in enhancing the reaction yield of the first step.

The second step is the formation of hepta-flurorooisobutyramide from perfluoroisobutyl fluoride. The reaction was conducted under both solvent-free and catalyst-free conditions. Perfluoroisobutyl fluoride (b. p. 7–9 °C) and ammonia were first mixed at -100 °C. The reaction was conducted using pure liquid ammonia. Since the product is hydrolytically unstable and decomposes upon exposure to water, this process must strictly exclude all water. Although ammonia is an irritant reagent, it is far less toxic and does not inhibit cellular respiration. As a widely employed reagent in industrial processes, ammonia may offer practical advantages for this application.

The mixture gradually warmed to 15 °C and stirred for 20 h. Under these conditions, the reaction proceeds efficiently in the gas phase due to the volatility of perfluoroisobutyl fluoride, ensuring homogeneous mixing of reactants. The reaction product, heptafluoroisobutyramide, was isolated by

Scheme 3 The synthesis step for the formation of perfluoroisobutyryl fluoride by using KF/18-crown-6 as the catalyst.

dichloromethane extraction. Unlike conventional methanol-mediated reactions that generate HF as a byproduct, this process can eliminate this hazardous byproduct. Any HF byproduct will immediately react with excess ammonia to form solid NH_4F, enabling facile separation from the reaction mixture. Based on the analysis, it can achieve the production of heptafluoroacetamide with high yield (89.7%) and purity (99.7%).
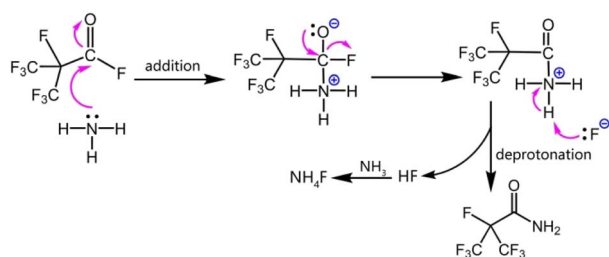
The reaction presumably proceeds *via* a mechanism analogous to ammonia's nucleophilic attack on acyl chlorides, involving sequential addition–elimination steps (Scheme 4).[31,32] It was proposed that carbon–halogen bond heterolysis may generate a carbocation and a halogen anion with a high activation energy barrier.[33] Ammonia may act as both nitrogen nucleophile and catalyst for the reaction. In the process, the lone pair on the nitrogen atom of ammonia attacks the carbonyl with the fairly positive carbon in perfluoroisobutyl fluoride (the addition stage). In perfluoroisobutyryl fluoride, C-1 is the standard nucleophilic site, bearing a significant positive charge and thus highly susceptible to nucleophilic attack as the primary reactive center. C-2 carries a partial positive charge due to the strong electron-withdrawing effect of the trifluoromethyl group, enabling deprotonation by strong bases—though this occurs only under specific conditions. C-3 exhibits a relatively balanced charge distribution with minimal charge polarization, rendering it virtually unreactive toward nucleophilic substitution. Notably, this experiment observed no NH_3 attack at C-2, likely attributable to the insufficiently strong basicity of ammonia. Subsequently, the carbonyl double bond will reform and eliminate a fluoride ion, which is followed by deprotonation of the N–H bond (the elimination stage). In polar solvents, coordination and induction effects may disperse the positive charge of the carbocation and diminish its electrophilic reactivity.[34] The solvent's cage effect could also increase the activation energy of the reaction to some extent.[35] Therefore, this neat reaction for heptafluroroisobutyramide demonstrates enhanced reaction efficiency and also minimizes safety concerns from HF release.

The final step comprises the dehydration of hepta-fluroroisobutyramide. Dehydration is one of the fundamental routes to convert primary amides to nitriles.[36,37] The combination of low-cost dehydrates and mild reaction conditions render this direct synthesis particularly appealing for sustainable scale-up, and green chemistry principles. Various dehydration
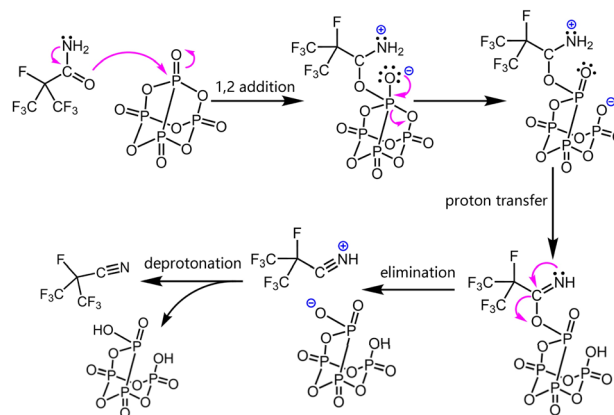
systems have been developed, including $NaBH_4$, lithium hydride, $PdCl_2$, phosphorous pentoxide (P_2O_5), $TiCl_4$, $AlCl_3$/NaI, $(COCl)_2$/Et_3N/Ph_3PO, and silanes/transition metal catalysts, *etc*.[38] In this process, we choose P_2O_5 as the dehydrating agent. In certain transformations, P_2O_5 exhibits insufficient dehydrating activity, necessitating either modified P_2O_5 composites or metal-catalyzed systems to achieve satisfactory reaction rates and yields.[39–41] However, as we carry out the dehydration of heptafluoroisobutyramide in a non-solvent condition, we think that P_2O_5 alone should be sufficient to ensure the formation of C_4F_7N. The strong hygroscopic nature of P_2O_5 may also help remove water from the reaction, potentially preventing the formation of side products. In this step, hepta-fluoroisobutyramide and P_2O_5 were directly mixed and heated to 180 °C with stirring for 16 h. The gas product of C_4F_7N was collected after freezing the reaction mixture.

To determine the optimal amount of P_2O_5 for this reaction, we evaluated the catalytic efficiency across a range of P_2O_5 loadings (1–5 equivalents). The results demonstrated that increasing the P_2O_5 loading significantly improves the yield of C_4F_7N, with product purity exceeding 99% under all conditions (Table S1). At 5 equivalents of P_2O_5, a maximum yield of 90% with 99.9% purity could be achieved. It should be mentioned that since the reaction system is strictly anhydrous (all products are hydrolytically unstable and decompose upon exposure to water), P_2O_5 as a catalyst can be reused or maintained effectively for extended periods. As a result, its use may not significantly increase costs or contribute to high waste accumulation.

According to the dehydration mechanism by P_2O_5, the reaction initiates with the oxygen attack on hepta-fluoroisobutyramide in the presence of P_2O_5 (Scheme 5).[42] The nitrogen lone pair delocalized into the N–C bond, breaking the π-bond. It leads to nitrogen with a positive formal charge and oxygen with a negative charge. The oxygen, acting as a nucleophile, abstracts the hydrogen bound to nitrogen, returning the electrons to the nitrogen atom. Then, the lone pair of nitrogen will form a triple bond and expel a leaving group. The negatively charged oxygen of the byproduct abstracts the remaining

Scheme 4 The synthesis step for the formation of hepta-fluroroisobutyramide in the solvent-free and catalyst-free condition.

Scheme 5 The synthesis step for the formation of per-fluoroisobutyronitrile using P_2O_5 as dehydrating agent and in the solvent-free condition.

proton, yielding the final nitrile product. Since only phosphonic acid is generated as a byproduct, this method likely produces fewer side products compared to other catalytic or solvent-based synthetic routes. Moreover, C_4F_7N was readily separated from the solidified system with minimal loss, enabling high-yield production of high-purity C_4F_7N. In comparison, the preparation of C_4F_7N *via* the reaction of trifluoroacetic anhydride with pyridine in DMF solvent provides a yield of only 74.9%, which is suggested owing to the non-negligible solubility of C_4F_7N in DMF.[24]

In this three-step route, the total yield of C_4F_7N was calculated to be 77.1%. Compared to other reported methods, our route offers significant advantages: (1) inexpensive and readily available raw materials, (2) shorter synthetic sequence, (3) easy reaction control, and (4) high product quality (yield and purity). This may also greatly reduce the production costs. It may enable scalable production of C_4F_7N for industry applications.

Conclusions

In conclusion, we have developed an efficient three-step synthetic route to C_4F_7N from readily available hexafluoropropylene. KF/18-crown-6 complex promotes the formation of perfluoroisobutyryl fluoride in the first step. The solvent-free neat reaction with ammonia in the second step enables rapid and quantitative conversion of heptafluoroisobutyramide while preventing the formation of hazardous HF by-products. In the final step, P_2O_5 effectively minimized by-product formation while facilitating straightforward isolation of the target product. This synthetic route offers multiple advantages, including high yield, operational simplicity, and cost efficiency. It demonstrates great potential for scalable production of C_4F_7N, which may also enable wider adoption of C_4F_7N in the sustainable energy industry.

Author contributions

Synthesis, L. D. and Q. G.; investigation and data analysis, L. D., Q. G. and X. J.; draft writing, L. D., Q. J. and H. Q.; and project supervision, H. Q. All authors approved this version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the SI.

Supplementary information including NMR spectra of all products, gas chromatography-mass spectra of perfluoroisobutyronitrile and reaction efficiencies of heptafluoroisobutyramide dehydration at varying P_2O_5 feed ratio is available. See DOI: **https://doi.org/10.1039/d5ra03945b**.

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