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# Environmentally Benign Processes for Making Useful Fluorocarbons: Nickel- or Copper(I) Iodide-Catalyzed Reaction of Highly Fluorinated Epoxides with Halogens in the Absence of Solvent and Thermal Addition of $CF_2I_2$ to Olefins[§]

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Highly fluorinated epoxides react with halogens in the presence of nickel powder or CuI at elevated temperatures to provide a useful and general synthesis of dihalodifluoromethanes ($CF_2X_2$) and fluoroacyl fluorides ($R_FCOF$) in the absence of solvent. At 185 °C, hexafluoropropylene oxide and halogens produce $CF_2X_2$ ($X = I$, Br) in 68−90% isolated yields, along with small amounts of $X(CF_2)_nX$, ($n = 2, 3$). With interhalogens I−X (X = Cl, Br), a mixture of $CF_2I_2$, $CF_2XI$, and $CF_2X_2$ was obtained. The fluorinated epoxides substituted with perfluorophenyl, fluorosulfonyl, and chlorofluoroalkyl groups also react cleanly with iodine to give $CF_2I_2$ and the corresponding fluorinated acyl fluorides in good yields. The reaction probably involves an oxidative addition of fluorinated epoxides into metal surfaces to form an oxametallacycle, followed by rapid decomposition to difluorocarbene−metal surfaces, which alters the reactivity of the difluorocarbene carbon from electrophilic to nucleophilic. The increase of nucleophilicity of difluorocarbene facilitates the reaction with electrophilic halogens. $CF_2I_2$ reacted with olefins thermally to give 1,3-diiodofluoropropane derivatives. Both fluorinated and nonfluorinated alkenes gave good yields of the adducts. Reaction with ethylene, propylene, perfluoroalkylethylene, vinylidene fluoride, and trifluoroethylene provided the corresponding adducts in 58−86% yields. With tetrafluoroethylene, a 1:1 adduct was predominantly formed along with small amounts of higher homologues. In contrast to perfluoroalkyl iodides, $CF_2I_2$ also readily adds to perfluorovinyl ethers to give 1,3-diiodoperfluoro ethers.

## Introduction

Catalytic reactions are one of the most benign processes for sustainable production of chemicals and related materials.[1] Transition-metal-catalyzed reactions have been widely used in hydrocarbon transformations, but most of these catalytic reactions still produce unwanted wastes along with the target products. Moreover, solvent recovery is usually inefficient and complicated by environmental problems. Catalytic conversions in perfluorocarbons are largely unexplored, and current production of fluorocarbons usually requires corrosive or harmful starting materials and generates a fair amount of toxic and unwanted byproducts.[2] Although huge numbers of transition-metal complexes containing fluorinated ligands have been reported, these complexes usually lack the catalytic activity necessary for useful transformations of fluorocarbons. This is due to the fact that they exhibit dramatically different structural and bonding characteristics with enhanced thermal stability in comparison with their hydrocarbon counterparts.[3] While fluorinated organometallic reagents have recently received much attention, catalytic reactions are much more attractive for the synthesis of fluorocarbons.[4] Catalytic hydrogenations and halogen exchange reactions of fluorochlorocarbons have been widely used in the production of hydrofluorocarbons, and catalytic defluorinations of perfluorocarbons have been disclosed recently.[5] Other useful metal-

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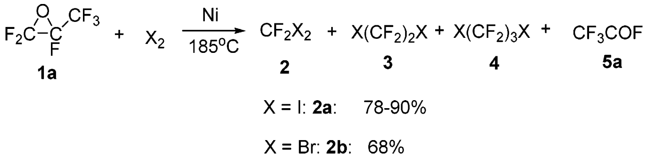
catalyzed reactions, even under conventional conditions, remain unknown to the best of my knowledge. It is therefore highly desirable to invent new reactions with a high atom economy to produce waste-free products in the absence of solvent. In this paper, I report Ni- and CuI-catalyzed reactions of highly fluorinated epoxides with halogens to produce fluorinated dihalides and acyl fluorides. Also reported is the thermal addition of $CF_2I_2$ to various fluorinated or nonfluorinated olefins to give useful 1,3-diiodofluoropropane derivatives. These reactions seem to be environmentally benign, since they proceed in the absence of solvent and the solid catalysts used can be readily recovered or removed by either filtration or distillation. In addition, the reactions are atom economical and no meaningful amounts of unwanted waste products are produced. Small amounts of the higher homologues, $X(CF_2)_nX$, are also useful materials for industrial applications and the other major coproducts, fluoroacyl fluorides, can be utilized to make high-value fluorocarboxylic acids or fluorinated monomers such as perfluorovinyl ethers.[2]

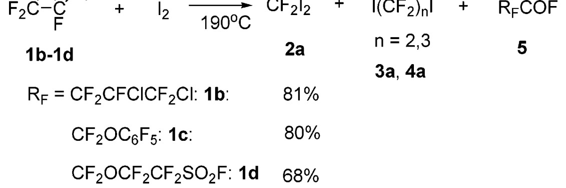
Although $CF_2Br_2$ and $CF_2Cl_2$ have been manufactured industrially and used as synthetic intermediates and fire extinguishers, $CF_2I_2$ has been difficult to make until recently. Fluorination of $CI_4$ with $HgF_2$ produced $CF_2I_2$ in only 26% yield.[6] Difluorocarbene precursors such as $(CF_3)_2PF_3$, $ClCF_2CO_2Na/Ph_3P$, and hexfluoropropylene oxide (HFPO) reacted with $I_2$ to give $CF_2I_2$ in poor yields.[7] Chen and co-workers developed a better process for making $CF_2I_2$ by reaction of halodifluoroacetate with iodine and potassium iodide in the presence of CuI in DMF.[8] In this reaction, a full equivalent of CuI is necessary to obtain $CF_2I_2$ in good yields (50−60%). I previously discovered a novel and efficient method for preparation of $CF_2I_2$ in high yield by a nickel-catalyzed reaction of fluorinated epoxides with halogens.[9]

## Results and Discussion

**I. Nickel-Powder-Catalyzed Reaction of Fluorinated Epoxides with Halogens.** Similar to a report in the literature, reaction of hexafluoropropylene oxide (HFPO, **1a**), a well-known difluorocarbene precursor,[10] with $I_2$ in a stainless steel (containing 10−14% Ni) or glass tube afforded less than 15% yield of $CF_2I_2$ with most of the iodine being recovered.[7e] The reaction of HFPO with $I_2$ in the presence of 3−20 mol % of Ni powder in the absence of solvent in a stainless steel or glass tube resulted in high yields of $CF_2I_2$, **2a**, with the major coproduct $CF_3COF$, **5a**, along with small amounts of $I(CF_2)_nI$ ($n = 2, 3$), **3**, and **4**. The reaction can be run on gram scale in a glass tube and on kilogram scale in an autoclave.



The nickel-catalyzed reaction is a general method and works well with other fluorinated epoxides. Chlorofluorocarbon, perfluorophenyl, and perfluorosulfonyl fluoride groups in the epoxides **1b**−**1d** did not interfere with the reaction. The reaction of these fluorinated epoxides with $I_2$ in the presence of Ni powder in a sealed glass tube at 190 °C afforded **2a** in 68−81% yields and the corresponding fluorinated acyl fluorides **5b**, **5c**, and **5d**, respectively.



In the absence of nickel powder, all these reactions gave low yields of $CF_2I_2$. Since it was a metal-surface-catalyzed reaction, vigorous shaking or agitating was critical to achieve high yields of the desired products. The reaction could also be carried out in inert solvents such as fluorochlorocarbons or perfluorocarbons, but the absence of solvent greatly simplified the workup process and minimized waste with similar yields and selectivity.

**II. Nickel-Alloy- or CuI-Catalyzed Reaction of Fluorinated Epoxides with Halogens.** Although HFPO failed to react with halogens to give $CF_2X_2$ in high yields in the absence of nickel powder in glass or stainless steel reactors, high yields of $CF_2X_2$ were formed when the reaction was conducted in a Hastelloy C vessel. This was found to occur even in the absence of nickel powder under similar conditions. Hastelloy C alloy contains a high percentage of nickel (56.4% Ni, 15.5% Cr, 16% Mo and small amounts of other elements)[11] and is known to be inert to iodine up to 260 °C.[12] Upon reaction of HFPO with $I_2$ in a Hastelloy C autoclave at 180−200 °C for 6 h, $CF_2I_2$ in greater than 87% yield was obtained along with small of amounts of $I(CF_2)_2I$ and $I(CF_2)_3I$. The Hastelloy C vessel worked particularly well for the reaction of HFPO with bromine. For example, reaction of HFPO with bromine in a Hastalloy C vessel at 185 °C for 12 h gave a 56.3:1:3.3 (mole ratio) mixture of $CF_2Br_2$, $Br(CF_2)_2Br$, and $Br(CF_2)_3Br$ in 80% total yield in addition to $CF_3COF$.

The reaction can be extended to interhalogens such as I−X (X = Br, Cl). With I−Br and HFPO at 190 °C in a Hastelloy C shaker tube, a 1:1:0.29 (mole) mixture of $CF_2I_2$, $CF_2Br_2$, and CF2IBr was isolated in 74% total

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yield. Similarly, the major product with I−Cl was $CF_2I_2$ (58% yield base on I−Cl) along with $CF_2ICl$ (9% yield based on I−Cl) and $CF_2Cl_2$, although the latter was not isolated due to its volatility. In both cases, trace higher homologues, $X(CF_2)_nY$ (X, Y = halogen and $n = 2, 3$), were also detected by GC−MS and $^{19}F$ NMR analysis.

Other nickel alloys can also catalyze the reaction, but the distribution of halide products may change slightly. Ni/Zn (Urushibara catalyst), prepared by reduction of $NiCl_2$ with Zn, followed by treatment with 10% HCl,[13] can catalyze the reaction of HFPO with $I_2$. Under the same conditions, a 14:1:1.1 (GC area) mixture of $CF_2I_2$, $I(CF_2)_2I$, and $I(CF_2)_3I$ was isolated in 60% total yield, whereas nickel powder gave a ratio of 64.3:1:4.7. Ni/Cu/Zn, prepared by reduction of a mixture of $NiCl_2$ and $CuSO_4$ (1:1 mole ratio) in water with 2 equiv of Zn, followed by washing with 10% HCl and water, was also effective and gave a 39:1:3 mixture of $CF_2I_2$, $I(CF_2)_2I$, and $I(CF_2)_3I$ in 50% total yield. Interestingly, the CuI-catalyzed reaction of HFPO with $I_2$ afforded products in a ratio of 52:1:2.5 in 68% total yield, but 10% Pd/C was ineffective.

**III. Mechanism of Metal-Catalyzed Reaction of Fluorinated-Epoxides with Halogens.** Fluorinated transition-metal complexes exhibit dramatically different structural and bonding characteristics in comparison with their hydrocarbon counterparts.[3] Metal−carbon bond distances in fluorinated organometallic reagents are significantly shorter than those of their hydrocarbon analogues, resulting in stronger metal−carbon bonds.[14] On the other hand, the acceptor capacity of the perfluoroalkyl group results in a drift of the $d_\pi$ electrons from the metal into the C−F antibonding orbitals, weakening the C−F bonds.[15] Clark and Tsai proposed a "non-bond" resonance structure ($CF_2{=}MF$) based on IR analysis.[16] Hughes reported the hydrogenolysis of perfluoroalkyl iridium complexes to give dihydrofluorocarbons through fluorocarbene metal complexes in solution.[17] A great number of difluorocarbene−transition-metal complexes have been prepared and characterized, but only a limited number of these difluorocarbene−transition-metal complexes have been reported to have synthetic utility.[18] Surface-bound difluorocarbene−metal has also been studied, but no catalytic reaction has been reported with these metal−difluorocarbenes in surface and solution systems.[19]

**a. Mechanism of the Nickel-Catalyzed Reaction of Fluorinated-Epoxides with Halogens.** Free difluorocarbene is the most electrophilic carbene known and is a ground-state singlet.[20] Nucleophiles add readily to $:CF_2$ to form difluorocarbanions because of the electronic match-up. This has been demonstrated by reaction of $CF_2$ with KF and iodine to make $CF_3I$.[21] Other examples include the trapping of $:CF_2$ with carbanions, sulfoxides, phenoxide, and so on to give the insertion products.[22] In the reaction of neutral substrates such as olefins with $:CF_2$, charge is transferred from the olefin to the $:CF_2$ in its transition state, leading to the formation of cyclopropane products.[23] However, electrophiles such as halogens are reluctant to react with electrophilic species such as $:CF_2$, failing to give $CF_2X_2$ in high yields. In the presence of nickel powder, HFPO reacted with halogens smoothly to produce $CF_2X_2$ in high yields, indicating that nickel changes the reactivity of free difluorocarbene. Initially, $NiI_2$ generated from the reaction of iodine with nickel powder was suspected as a catalytic species. However, authentic $NiI_2$ (Aldrich, 99.99%) failed to catalyze the reaction under identical conditions. Upon reaction of HFPO, $I_2$, and $NiI_2$ in a sealed glass tube at 185 °C for 8 h, only a low yield (<15%) of $CF_2I_2$ was observed, similar to the reaction in the absence of nickel catalyst. In fact, nickel powder is not completely converted to $NiI_2$ upon reaction with neat iodine. When an excess of $I_2$ (78.7 mmol) and nickel powder (53.6 mmol) were heated in an evacuated sealed glass tube at 180−185 °C for 10 h, the dark powder obtained after removing excess $I_2$ was a mixture of Ni and $NiI_2$, as determined by powder X-ray diffraction. Two distinct peaks at $2\theta$ 44.49° and 51.82° were observed with nickel powder obtained from Aldrich. The solvent-washed solid ($I_2$ free) from the reaction of nickel and $I_2$ still showed the two peaks at $2\theta$ 44.49° and 51.52° along with other peaks, which corresponded to the X-ray diffraction patterns of $NiI_2$. These results indicate that at least some solid nickel remains, even after heating with iodine for 10 h. In addition, the dark powders recovered after reaction of HFPO and iodine with nickel powders was found to be a mixture of Ni(0) and Ni(II)$I_2$, as determined by X-ray diffraction. Subhalide Ni(I)I has also been considered as a potential catalytic species under these reaction conditions, because Ni(I) complexes, either in homogeneous solutions or supported on silica, were formed by reaction of Ni(0) and Ni(II) complexes or by reduction of Ni(II).[24] Catalysis by Ni(I)I is probably not the case in this reaction, because when a mixture of powdered nickel and Ni(II)$I_2$ was heated at above 185 °C for 1−3 h, its X-ray diffraction patterns remained unchanged. Even in the molten state of 9% $NiCl_2$ in nickel, no evidence for the formation of subhalide Ni(I) was observed by X-ray diffraction and

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neutron diffraction spectra.[25] Thus, Ni(I)I seems unlikely to be the catalytic species in the nickel-powder-catalyzed reaction and the active catalyst is nickel metal.

The catalytic reaction is believed to take place on the surface of the powdered nickel metal, where a fluorinated epoxide first adsorbs. The adsorption of ethylene oxide (EO) on the surfaces of transition metals such as Ni, Cu, Ag, and Pd has been investigated.[26] These studies suggest that EO adsorbs on transition-metal surfaces through the overlap of the molecular oxygen lone pair orbitals with the surface orbitals of nickel. Unlike EO, the oxygen of fluorinated epoxides has poor coordination ability, due to the electron-withdrawing effect of the fluorinated group. However, small ring compounds, such as fluorinated cyclopropanes and fluorinated epoxides, have extraordinarily high strain energies. The high strain energies are due to donation of the fluorine lone pair electrons into the $\sigma^*$ antibonding orbitals of the ring, resulting in $\pi$-like electronic properties and lowering LUMO energies.[27] In the adsorption of fluorinated epoxides on nickel surfaces **A**, the electron orbitals of the metal surface overlap with the LUMO of the fluorinated epoxides, and partial electrons are transferred from nickel to the lowest antibonding orbitals of the epoxide, resulting in activation of both C−C or C−O bonds. The fluorinated epoxide undergoes a ring-opening reaction to give fluorinated oxanickellacycles on the nickel surfaces. In homogeneous media, a single nickellaoxetane intermediate generated by insertion of a nickel atom into the C−O of epoxides was observed in an argon matrix.[28] Insertion of nickel into C−O bonds in Ni ion beams in the gas phase and on metal surfaces has also been proposed.[29] Although, the C−O bond is stronger than the C−C bond in perfluoro ethers, recent density-functional calculation revealed that fluorine substitutions on oxiranes significantly weaken the C−O bonds of oxiranes.[30] As a result, nickel inserted in to the C−O bond of fluorinated epoxides exclusively. In metal surface reactions, both oxametallacycles and metallaoxetane were proposed, but the two intermediates have distinctly different properties.[31] The metallaoxetane tends to undergo ring closure to an epoxide, whereas oxametallacycle decomposes to various fragments through breakage of C−C, C−O, and C−H bonds. In a previous communication, I proposed that a metallaoxetane intermediate was involved in the nickel-catalyzed reaction of fluorinated epoxides with halogens.[9] It now appears that surface oxanickellacycle intermediates **B** are more reasonable. The surface oxametallacycle is extremely reactive and has been generally difficult to observe. Recently, a relatively stable oxametallacycle on a silver surface, prepared by reaction of EO with silver, has been synthesized and directly observed through vibrational spectra.[31] These oxametallacycles decomposed rapidly, and fluorinated versions are expected to be even more reactive, since surface oxametallacycles are destabilized by any ligands or solvents present. Previous reports demonstrated that the thermal stability of transition-metal complexes containing fluorocarbon groups are strongly dependent on the ligands bound to the metal. Coordinatively unsaturated complexes are much less stable than coordinatively saturated ones. For example, $(PPh_3P)_2NiICF_3$ is a very thermally stable complex and melts above 200 °C without decomposition, whereas $CF_3NiBr$ is much less stable, only 1% $CF_3NiBr$ being trapped with $Et_3P$ at −78 °C.[32] In this work, the intermediate oxametallacycles, **B**, rapidly decompose to $CF_3COF$ and surface nickel difluorocarbenoid, **C**.

Nickel carbenoids has been well-studied in homogeneous gas phase and on metal surfaces. Metal complexes with singlet carbenes have relative weak donor/acceptor bonds rather than strong covalent bonds.[18] Ion beam studies have demonstrated that the Ni−C bond strength in $NiCF_2^+$ is 40 kcal/mol less than that in $NiCH_2^+$,[29a] due to its donor/acceptor bonding. For low-valent later-transition-metal complexes, the donor/acceptor bonds result in significantly reduced electrophilicity of the $CF_2$ carbon center.[33] Therefore, the formation of $Ni{=}CF_2$ **C** alters the reactivity of the carbene carbon from electrophilic to nucleophilic and thus reacts readily with halogens to give intermediate **E**. Finally, reductive elimination gives $CF_2X_2$ and regenerated nickel metal, as shown in Scheme 1.

The byproducts $I(CF_2)_2I$ and $I(CF_2)_3I$ were formed via the intermediate, tetrafluoroethylene (TFE). TFE can be formed by dimerization of free difluorocarbene or difluorocarbenoid on metals such as Ni surfaces **C**. It is well-documented that TFE forms when HFPO is heated at about 160 °C.[10] In the Ni-catalyzed reaction of HFPO and halogen, a trace of TFE was produced, which reacted with $I_2$ to form $I(CF_2)_2I$. The $CF_2I_2$ formed could also add to

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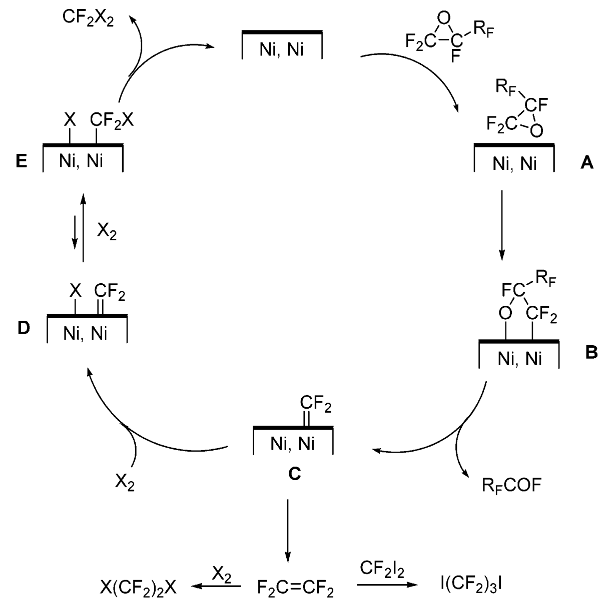
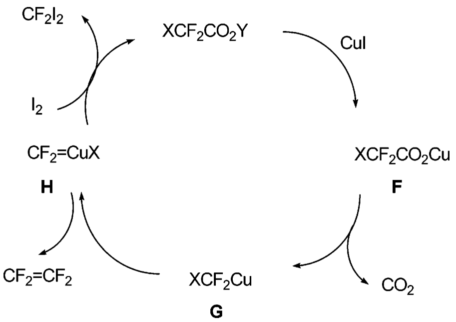
**SCHEME 1**



**SCHEME 2**



TFE to form $I(CF_2)_3I$. Amounts of $I(CF_2)_2I$ and $I(CF_2)_3I$ depended on the stoichiometry of HFPO to halogen. In reactions with a large excess of HFPO, the major product was $I(CF_2)_3I$. For example, when a 3 mol excess of HFPO was used to react with $I_2$ in a Hastaloy C reactor, $I(CF_2)_3I$ was obtained in 78% yield, along with $CF_2I_2$ and $ICF_2CF_2I$. Interestingly, $I(CF_2)_2I$ was only ever found as a minor product, even in the presence of excess HFPO, indicating that the formation of $CF_2I_2$ was faster than the generation of TFE. Once all of the iodine is consumed, $CF_2I_2$ can add to the TFE produced through decomposition of excess HFPO giving $I(CF_2)_3I$. This case can be further supported by the reaction with $Br_2$. When an excess of HFPO was reacted with bromine in a Hastaloy C vessel at 190 °C, $CF_2Br_2$ was still the major product, because $CF_2Br_2$ does not readily add to TFE under these conditions. There was no bromine left when the TFE or/and hexafluorocyclopropane were produced from the excess HFPO,[10] resulting in lack of the formation of $Br(CF_2)_2Br$ and $Br(CF_2)_3Br$.[34] The results also ruled out the formation $I(CF_2)_3I$ from a ring-opening reaction of hexafluorocyclopropane with $I_2$, since the reaction of hexafluorocyclopropane with $Br_2$ also readily produced $Br(CF_2)_3Br$ at 185 °C.[34]

**b. Mechanism of CuI-Catalyzed Reaction of Fluorinated Epoxides with Halogens.** Copper(I) salts have been widely used as catalysts for cyclopropanation of olefins with diazo compounds.[35] A carbenoid with copper(I) was proposed but never observed directly until Arduengo's isolation of the homoleptic copper–carbene complex.[36] X-ray structure analysis indicated that the carbon–copper bond in the carbene–copper complex is shorter than a carbon–copper single bond.[37] A $CH_2$ on a copper surface has a covalent $\sigma$ bond between the carbon and copper atoms, while a $\pi$ electron is mainly located on the $CH_2$, and the density function calculation predicts the transfer of 0.2 electron from copper to carbene.[28] Copper difluorocarbenoid was also proposed when it was observed that trifluoromethylcopper inserted into the carbon–copper bond of fluorinated aryl and vinylcopper agents.[39] Chiang and co-workers directly observed $CF_2$ insertion into the carbon–metal bond and C–F bond activation of trifluoromethyl groups on a Cu(111) surface through a $Cu{=}CF_2$ intermediate.[40] Chen and co-workers reported that the presence of CuI is necessary to give $CF_2I_2$ in good yields when bromodifluoroacetates reacted with iodine and potassium iodide, although a copper difluorocarbenoid was not proposed as an intermediate.[8] In the reaction of HFPO with halogen and CuI as a catalyst, copper difluorocarbenoid $CF_2{=}CuX$ probably was formed as an active species. The copper difluorocarbenoid may be generated by decomposition of the insertion intermediate of the F-epoxide, metallaoxetane, followed by elimination of $CF_3COF$, similar to the mechanism of the nickel-catalyzed reaction. An alternative is the absorption of $CF_2$ generated from thermal decomposition of HFPO on the CuI surface. In the reaction of halodifluoroacetate with $I_2$/KI and CuI in DMF, the mechanism may be slightly different, but $CF_2{=}CuX$ is likely an intermediate as illustrated in Scheme 2. The proposed mechanism involves a CuI-facilitated decarboxylation of copper halodifluoroacetate (**F**) to generate $XCF_2Cu$, **G**. Since the electron-rich copper(I) donates electrons to the C–X antibonding orbitals, strengthening the C–Cu bond and weakening the C–X bond, the $XCF_2Cu$ decomposes to form $CF_2{=}CuX$, **H**. This type of reaction is known and $CF_3Cu$ has been used as a $CF_2{=}Cu$ synthon for $CF_2$ insertion reactions.[39b] The copper difluorocarbenoid, $XCF_2Cu$ ($X \neq F$), is more reactive toward decomposition than $CF_3Cu$, due to the weakness of the C–X bond as compared to the C–F bond.

It is expected that copper difluorocarbenoid should have different reactivity than free difluorocarbene generated via thermal decomposition of HFPO or halodifluoroacetates. As with the Ni system, copper difluorocarbenoid may alter the reactivity of the carbene carbon from electrophilic to nucleophilic,[21] although, to the best of my knowledge, no calculation has been reported. In

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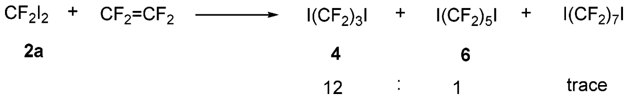
addition, attempts to trap the difluorocarbene generated with tetramethylethylene resulted in formation of $CF_3$-Cu.[39b]

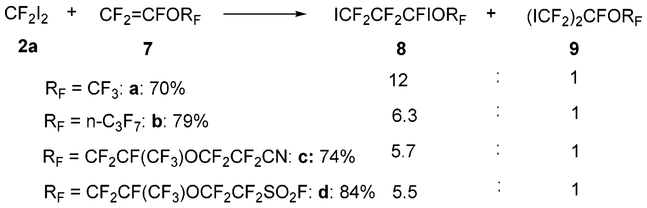
It was reported that $CF_2$=Cu reacted with a carbene such as $:CH_2$ to give vinylidene fluoride along with dimerization to give TFE.[19b] In the CuI-catalyzed reaction of HFPO, a small amount of TFE was always formed as a byproduct that reacted with $CF_2I_2$ or $I_2$ to form $I(CF_2)_3I$ and $I(CF_2)_2I$, respectively.

**IV. Addition of Diiododifluoromethane to Olefins.** $\alpha,\omega$-Diiodoperfluoroalkanes are one of the most important building blocks for the preparation of other fluorinated compounds and polymers.[41] The most common perfluoroalkylene diiodides are those with an even number of $CF_2$ units, which can be prepared from tetrafluoroethylene and iodine in moderate yields.[42] Fluorinated diiodides with an odd number of $CF_2$ units have been difficult and costly to prepare, although our recent discovery of the ring-opening reaction of fluorinated cyclopropanes with iodine makes 1,3-diiodofluorocompounds more accessible.[34] A more economical alternative approach to fluorinated 1,3-diiodides would be telomerization of $CF_2I_2$ with olefins. $CF_2I_2$ should be an excellent telogen, since it not only readily forms a radical but also undergoes a chain transfer reaction rapidly, which is particularly important to give 1,3-diiodides selectively when it reacts with a polymerizable olefin such as TFE. In contrast, the addition of perfluoroalkyl iodides or $CF_2Br_2$ to TFE usually lacks selectivity, and a broad distribution of telomers with significant amounts of higher homologues is obtained.[43] With vinylidene fluoride, $R_FI$ gives 27% of the 1:2 adduct and 60% of 1:1 adduct, while dibromodifluoromethane gave a mixture with almost equal amounts of the 1:1 and 1:2 adducts, even when a 4-fold excess of $CF_2Br_2$ was used.[44] The reaction of $CF_2I_2$ with hydrocarbon olefins, initiated by peroxide or UV, was previously reported. A mixture of adduct, addition−elimination product, and other byproducts was obtained in most cases.[45] Chen and co-workers recently reported the addition of $CF_2I_2$ to fluorinated or nonfluorinated alkenes and alkynes initiated by sodium dithionite or other metals.[46] I have found an effectively thermal addition of $CF_2I_2$ to olefins, particularly fluoroolefins, to make fluorinated diiodides with an odd number of $CF_2$ units in the absence of solvent. $CF_2I_2$ was found to have good thermal stability in the absence of a substrate.[47] When a mixture of $CF_2I_2$ (94.5%) containing 1.7% $ICF_2CF_2I$ and 1.8% % $I(CF_2)_3I$ was heated in a Hastelloy C tube at 185 °C for 30 h, the ratio of $CF_2I_2$, $ICF_2CF_2I$, and $I(CF_2)_3I$ was found to be relatively the same (89.3:5.1:4 as determined by GC analysis). Either the C−I bonds in $CF_2I_2$ are stable under these conditions or, more likely, a reversible breaking and forming of the C−I bonds take place. In fact, $CF_2I_2$ readily adds to a variety of olefins at 180 °C to give the corresponding adducts.

Perhaps most interesting is that $CF_2I_2$ reacts with tetrafluoroethylene to give high yields of the lower telomers with relatively high selectivity. When 1 mol of $CF_2I_2$ was reacted with 1 mol of TFE at 185 °C, a 12:1 mixture of the 1:1 and 1:2 adducts was obtained in 84% isolated yield. Only a trace of the 1:3 adduct was observed, in striking contrast to the reaction of perfluoroalkyl iodides or $CF_2Br_2$ with TFE.[43]



The unique behavior of $CF_2I_2$ as a telogen prompted us to study its reaction with perfluorovinyl ethers, **7**, which are important monomers for making fluoropolymers but fail to react cleanly with other telogens such as perfluoroalkyl iodides. Indeed, $CF_2I_2$ cleanly added to perfluoroalkyl vinyl ethers to give adducts **8** along with small amounts of their regioisomers, **9**. When perfluoromethyl vinyl ether (PMVE) and $CF_2I_2$ were heated at 185 °C for 3.5 h, a 12:1 mixture of **8a** and **9a** was obtained in 70% yield with 77% conversion of $CF_2I_2$. With perfluoropropyl vinyl ether (PPVE), the isomeric ratio of **8b**:**9b** decreased to 6.3:1. A careful analysis of the reaction mixture by GC and $^{19}F$ NMR revealed that $ICF_2CF_2COF$, **11**, and $C_3F_7I$, **12b**, were also formed, indicating that the major isomer **8b** decomposed into $ICF_2CF_2COF$ and $C_3F_7I$, which resulted in the decrease of the ratio of **8b**:**9b**. Perfluorovinyl ethers containing functional groups such as nitrile and sulfonyl fluoride also give similar isomeric mixture of adducts in addition to small amounts of **11** and **12**.



Our previous work has demonstrated that the major adducts $R_FOCFICF_2CF_2I$, **8**, are thermally labile and decompose to form $ICF_2CF_2COF$ and $R_FI$ in quantitative yields at temperatures above 220 °C,[34] whereas their isomeric adducts $(ICF_2)_2CFOR_F$ are expected to remain intact. When a mixture of $CF_2I_2$ and **7d** was heated at 185 °C for 4 h followed by further heating to 240 °C for several hours, a mixture of $R_FI$, $ICF_2CF_2COF$, and $(ICF_2)_2CFOR_F$ was obtained in good yield, which indicated that $R_FOCFICF_2CF_2I$ decomposed completely. The mechanism of this transformation is through a radical intermediate. The iodine−carbon bond is readily cleaved to produce a radical intermediate **10** at high temperature due to the stabilization of the radical by the adjacent

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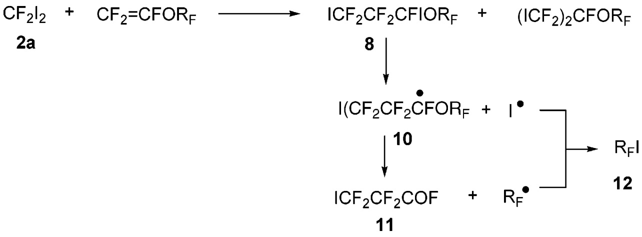
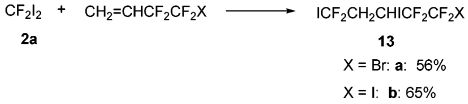
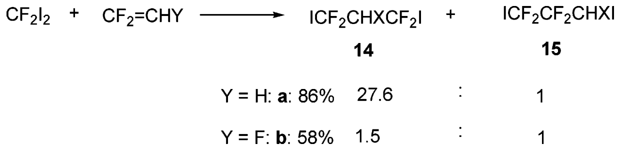
oxygen. The intermediate **10** undergoes bond scission, giving a perfluoroalkyl radical to form **11** and recombination of the perfluoroalkyl radical with iodine produces **12**. The bond scission is dependent on the nature of the perfluoroalkyl group. Trifluoromethyl is the most resistant toward bond scission, whereas secondary and tertiary radicals are more easily cleaved. This bond scission is well-known in copolymerizations of perfluorovinyl ethers. In the $CF_2I_2$ addition reaction reported here, much less decomposition of **8a** (from PMVE) was observed compared to the adducts **8b**−**8d** from PPVE and other vinyl ethers.



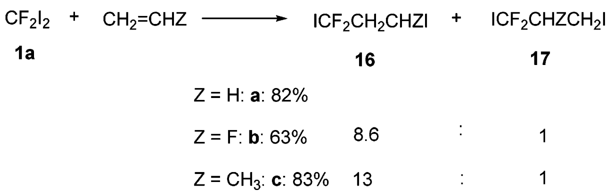
Interestingly, only one regioisomer, $ICF_2CH_2CHICF_2CF_2X$, **13**, was obtained from reaction of $CF_2I_2$ with $CH_2$═$CHCF_2CF_2X$. Steric effects in this case must control the regioselectivity, since the electrophilic radical $ICF_2^•$ is electronically favored to add to the internal carbon of the fluoroalkylethylene.



With an excess of $CF_2$═$CH_2$ or $CF_2$═$CFH$, $CF_2I_2$ gave the 1:1 adducts, indicating that $CF_2I_2$ is a much better chain transfer agent than perfluoroalkyl iodides or $CF_2Br_2$, which gave a mixture of telomers.[44] The $ICF_2$ radical mainly adds to less fluorine substituted carbons. A 27.6:1 isomeric mixture of **14a** and **15a** was formed with $CF_2$═$CH_2$, whereas a 1.5:1 mixture of regioisomers **14b** and **15b** was obtained with $CF_2$═$CFH$.



Addition of $CF_2I_2$ to ethylene proceeded smoothly in an autoclave and the reaction pressure rapidly dropped to a steady state after 3.5 h at 180 °C. The reaction was very clean with the crude product formed in 98.7% purity; the pure adduct **16** was isolated in 82% yield. With substituted ethylene, $CF_2I$ adds to the terminal $CH_2$ carbon predominately. A 13:1 mixture of regioisomers **16c** and **17c** was formed with propylene in 83% yield. Similarly, vinyl fluoride also gave a 8.6:1 ratio of **16b**:**17b**.



In conclusion, I have discovered an unprecedented nickel- or CuI-catalyzed reaction of highly fluorinated epoxides with halogens at elevated temperatures. Since HFPO is a readily available material, the reaction provides a useful synthesis of $CF_2I_2$, which is an important building block for the preparation of other fluorinated compounds. In addition, the high value of the fluoroacyl fluoride byproduct, as well as the absence of solvent and high yields, make this reaction very attractive for the synthesis of functional fluorocarbons on a large scale. The reaction is believed to involve oxidative addition of fluorinated epoxides onto metal surfaces to form oxametallacycles, which rapidly decompose to difluorocarbene−metal surfaces. The difluorocarbene metal complexes react with halogens to give $CF_2X_2$. $CF_2I_2$ reacted with olefins thermally to give 1,3-diiodofluoropropane derivatives. Both fluorinated and nonfluorinated alkenes gave good yields of adducts. Reaction with ethylene, propylene, perfluoroalkylethylene, vinylidene fluoride, and trifluoroethylene provided the corresponding adducts in 58−86% yields. With tetrafluoroethylene, a 1:1 adduct was predominantly formed along with small amounts of higher homologues. In contrast to perfluoroalkyl iodides, $CF_2I_2$ also readily added to perfluorovinyl ethers to give 1,3-diiodoperfluoro ethers.

## Experimental Section

HFPO is DuPont's product and is used without purification. $CFCl_3$ is used as an internal reference in $^{19}F$ NMR.

**Reaction of Hexafluoropropylene Oxide (HFPO) with Iodine in the Presence of Ni in a Stainless Steel Shaker Tube.** A 0.4-L stainless steel shaker tube was charged with 127 g of iodine and 5.0 g of nickel powder (99.99%, 100 mesh from Aldrich) and then evacuated at low temperature. After 90 g of HFPO was added, the resulting mixture was heated at 185 °C for 8 h. Then, 146.8 g of dark liquid was obtained which was distilled to give 116.8 g (74%) of a mixture of $CF_2I_2$, $ICF_2CF_2I$, and $ICF_2CF_2CF_2I$ in a ratio of 64.3:1:4.7 (GC area). $^{19}F$ NMR: for $CF_2I_2$, +18.6 (s); for $ICF_2CF_2I$, −53.3 (s); for $I(CF_2)_3I$, −58.2 (t, $J$ = 5 Hz, 4F), −105.3 (m, 2F). HRMS: calcd for $CF_2I_2$, 303.8058; for $C_2F_4I_2$, 353.8026; for $C_3F_6I_2$, 403.7994. Found: for $CF_2I_2$, 303.8002; for $C_2F_4I_2$, 353.7975; for $C_3F_6I_2$, 403.7992.

**Reaction of Hexafluoropropylene Oxide (HFPO) with Iodine in a Stainless Steel Shaker Tube.** A 0.4-L stainless steel shaker tube was charged with 127 g of iodine and then evacuated at low temperature. After 90 g of HFPO was added, the resulting mixture was heated at 185 °C for 8 h. Iodine (71.1 g) was recovered and 23.1 g of liquid was obtained, which was washed with aqueous $Na_2SO_3$ solution and brine and distilled to give 16.9 g (10.8%) of a mixture of $CF_2I_2$, $ICF_2CF_2I$, and $ICF_2CF_2CF_2I$ in a ratio of 95:1:3.3 (mole).

**Reaction of Hexafluoropropylene Oxide (HFPO) with Iodine in a Hastelloy C Autoclave.** A 1-L Hastelloy C autoclave was charged with 381 g of iodine and then evacuated at low temperature. After 266 g of HFPO was added, the resulting mixture was heated at 185 °C for 10 h. Gas (184 g) was obtained, which was mainly $CF_3COF$ as determined by $^{19}F$ NMR. Then, 458 g of liquid was washed with aqueous $Na_2SO_3$ solution and brine and distilled to give a 395 g (86.7%) of a mixture of $CF_2I_2$, $ICF_2CF_2I$, and $ICF_2CF_2CF_2I$ in a ratio of 240:1:4.8. Bp: 104−106 °C. $^{19}F$ NMR for $CF_2I_2$, +18.6 (s); for $ICF_2CF_2I$, −53.3 (s); for $I(CF_2)_3I$, −58.2 (t, $J$ = 5 Hz, 4F), −105.3 (m, 2F). HRMS: calcd for $CF_2I_2$, 303.8058; for $C_2F_4I_2$, 353.8026; for $C_3F_6I_2$, 403.7994. Found: for $CF_2I_2$, 303.8002; for $C_2F_4I_2$, 353.7975; for $C_3F_6I_2$, 403.7992.

**Reaction of Excess Hexafluoropropylene Oxide (HFPO) with Iodine in a Hastelloy C Autoclave.** A 1-L Hastelloy C autoclave was charged with 254 g of iodine and then evacuated at low temperature. After 340 g of HFPO was added, the resulting mixture was heated at 185 °C for 12 h. GC analysis of 239 g of liquid products indicated the formation of $CF_2I_2$, $ICF_2CF_2I$, and $ICF_2CF_2CF_2I$ in a ratio of 90.7:2:6.7 (area).

**Reaction of Hexafluoropropylene Oxide (HFPO) with Iodine in the Presence of CuI in a Stainless Steel Shaker Tube.** A 0.4-L stainless steel shaker tube was charged with 127 g of iodine and 10 g of CuI (from Aldrich) and then evacuated at low temperature. After 90 g of HFPO was added, the resulting mixture was heated at 185 °C for 8 h to give 126.9 g of a mixture that was distilled to give 103.6 g total of $CF_2I_2$, $ICF_2CF_2I$, and $ICF_2CF_2CF_2I$ in a ratio of 51.9:1.0:2.5 (GC area).

**Reaction of Hexafluoropropylene Oxide (HFPO) with Bromine in a Hastelloy C Shaker Tube.** A 0.4-L Hastelloy C shaker tube was charged with 80 g of bromine and then evacuated at low temperature. After 90 g of HFPO was added, the resulting mixture was heated at 200 °C for 6 h. Then, 91.3 g of liquid was obtained, which was washed with aqueous $Na_2SO_3$ solution and brine and distilled to give 71.3 g of $CF_2Br_2$. Bp: 23−25 °C. $^{19}F$ NMR: +6.5 (s).

**Reaction of Excess Hexafluoropropylene Oxide (HFPO) with Bromine in a Hastelloy C Shaker Tube.** A 0.4-L Hastelloy C shaker tube was charged with 80 g of bromine and then evacuated at low temperature. After 170 g of HFPO was added, the resulting mixture was heated at 185 °C for 12 h. $^{19}F$ NMR analysis of 84 g of liquid indicated a mixture of $CF_2Br_2$, $BrCF_2CF_2Br$, and $BrCF_2CF_2CF_2Br$ in a ratio of 56.3:1:3.3 (mole). Distillation gave 68.5 g of 95% pure $CF_2Br_2$. Bp: 23−27 °C. $^{19}F$ NMR: +6.5 (s).

**Reaction of Hexafluoropropylene Oxide (HFPO) with Iodine Monochloride in a Hastelloy Shaker Tube.** A 0.4-L Hastelloy shaker tube was charged with 114 g of iodine monochloride and then evacuated at low temperature. After 120 g of HFPO was added, the resulting mixture was heated at 185 °C for 8 h. Then, 112.3 g of crude liquid products was obtained, which were distilled to give 14.7 g of $CF_2ICl$ (bp: 31−34 °C) and 61.7 g of $CF_2I_2$ [Bp: 103−104 °C. $^{19}F$ NMR: for $CF_2ICl$, +8.2 (s)]. HRMS: calcd for $CF_2ICl$, 311.8637. Found: 311.8678. A trace of $ClCF_2CF_2CF_2I$ was also observed by GC−MS.

**Reaction of Hexafluoropropylene Oxide (HFPO) with Iodine Monobromide in a Hastelloy Shaker Tube.** A 0.4-L Hastaloy shaker tube was charged with 62 g of iodine monobromide and then evacuated at low temperature. After 58 g of HFPO was added, the resulting mixture was heated at 185 °C for 6 h. Liquid products were washed with aqueous $Na_2SO_3$ solution and water to give 42.3 g of a mixture of $CF_2I_2$, $CF_2BrI$, and $CF_2Br_2$ in a ratio of 1.7:1:2.5 and small amounts of $Br(CF_2)_3Br$, $ICF_2CF_2I$, and $ICF_2CF_2CF_2I$, as detected by GC−MS. $^{19}F$ NMR: for $CF_2BrI$, +13.6. HRMS: calcd for $CF_2BrI$, 255.8196. Found: 255.8103.

**Reaction of Perfluoro-3-phenoxylpropylene Oxide with Iodine and Nickel in a Glass Tube.** A 10-mL glass tube was charged with 2.5 g of iodine, 0.1 g of Ni powder, and 2.5 g of perfluorophenoxylpropylene oxide. After being evacuated at −78 °C, the tube was sealed, placed in a shaker tube, and then heated at 190 °C for 10 h. Liquid was transferred to a −78 °C trap in a vacuum to give 3.5 g (80%) of a 64.5:55.5:3.4:1 (mole) mixture of $CF_2I_2$, $C_6F_5OCF_2COF$, $I(CF_2)_3I$, and $ICF_2CF_2I$. $^{19}F$ NMR: for $C_6F_5OCF_2COF$, +16.7 (t, $J = 2.4$ Hz, 1F), −77.3 (m, 2F), −151.2 (m, 2F), −154.2 (t, $J = 22$ Hz, 1F), −160.8 (m, 2F). HRMS: calcd for $C_8F_8O_2$, 279.9771. Found: 279.9719.

**Reaction of 4,5-Dichlorooctafluoropentene 1-Oxide with Iodine and Ni in a Glass Tube.** A 10-mL glass tube was charged with 2.5 g of iodine, 0.1 g of Ni powder, and 2.4 g of 4,5-dichlorooctafluoropentene 1-oxide. After being evacuated at −78 °C, the tube was sealed, placed in a shaker tube, and then heated at 190°C for 10 h. Liquid was transferred to a −78 °C trap in a vacuum and yielded 3.6 g (81%) of a 18:17:1:0.08 (mol) mixture of $CF_2I_2$, $CF_2ClCFClCF_2COF$, $I(CF_2)_3I$, and $ICF_2CF_2I$. $^{19}F$ NMR: for $CF_2ClCFClCF_2COF$, +26.2 (t, $J = 2.4$ Hz, 1F), −63.5 (dm, $J = 175$ Hz, F), −64.7 (dm, $J = 175$ Hz, 1F), −110.4 (dm, $J = 270.3$ Hz, 1F), −113.2 (dm, $J = 270.2$ Hz, 1F), −131.4 (m, 1F). HRMS: calcd for $C_4F_6Cl_2O{-}COF$, 200.9297. Found: 200.9257.

**Reaction of $FO_2SCF_2CF_2OCFCF(CF_3)OCF{=}CF_2$ with Iodine in Glass Tube.** A 25-mL glass tube was charged with 3.5 g of iodine and 4.1 g of $FO_2SCF_2CF_2OCFCF(CF_3)OCF{=}CF_2$ and then evacuated at low temperature. After the tube was sealed, the resulting mixture was heated at 200 °C for 8 h. Then, 2.8 g of liquid products with small amounts of iodine was transferred into a −78 °C trap. $^{19}F$ NMR analysis indicated that the liquid was 34% (mol) $CF_2I_2$, 62.5% $FO_2SCF_2CF_2OCF_2COF$, 3.4% $I(CF_2)_3I$, and 0.8% $ICF_2CF_2I$. $^{19}F$ NMR: for $FO_2SCF_2CF_2OCF_2COF$, +45.6 (m, 1F), +14.9 (s, 1F), −76.7 (t, $J = 11.7$ Hz, 2F), −82.1 (m, 2F), −112.5 (m, 2F). HRMS: calcd for $C_4F_8SO_4COF$, 248.9456. Found: 248.9468.

**Reaction of $CF_2I_2$ with Tetrafluoroethylene.** A 400-mL shaker tube was charged with 152 g of $CF_2I_2$ and cooled to −78 °C. After the tube was evacuated and then heated to 185 °C, 20 g of TFE was added and the tube kept at 185 °C for 2 h. An additional 20 g of TFE was added and the tube was kept at 185 °C for 2 h. Finally, 10 g of TFE was added and the tube kept at 185 °C for 6 h. Finally, 192.3 g of crude products was obtained and GC indicated a mixture of 82% $I(CF_2)_3I$ and 7% $I(CF_2)_5I$. Distillation gave 169.6 g of $I(CF_2)_3I$ with 2.5% of $I(CF_2)_5I$ (bp: 76−80 °C/150 mmHg) and 13.1 g of high-boiling residue containing 20% $I(CF_2)_3I$, 70% $I(CF_2)_5I$, and 5% $I(CF_2)_7I$. $^{19}F$ NMR: for $I(CF_2)_3I$, −58.2 (t, $J = 4.7$ Hz, 4F), −105.2 (t, $J = 4.7$ Hz, 2F); for $I(CF_2)_5I$, −59.4 (t, $J = 4.6$ Hz, 4F), −113.6 (s, 4F), −120.6 (m, 2F).

**Reaction of $CF_2I_2$ with Perfluoromethyl Vinyl Ether.** A 75-mL shaker tube was charged with 30.5 g of $CF_2I_2$ and cooled to −78 °C. The tube was evacuated and then 22.0 g of perfluoromethyl vinyl ether was added. After the tube was heated at 185 °C for 3.5 h, GC indicated 76% conversion, and 37.2 g of crude products was distilled to give 13.8 g of byproducts (47.6% $CF_2I_2$ and 46.7% adduct; bp: 50−79 °C/100 mmHg) and 18.4 g of 99% pure adduct. Yield: 70%. Bp: 87−89 °C/50 mmHg. $^{19}F$ NMR and GC indicated a mixture $ICF_2CF_2CFIOCF_3$ and $(ICF_2)_2CFOCF_3$ in a ratio of 12:1. $^{19}F$ NMR: for $ICF_2CF_2CFIOCF_3$, −55.0 (dm, $J = 204.1$ Hz, 1F), −55.3 (d, $J = 11.3$ Hz, 3F), −58.4 (ddm, $J = 205$ Hz, $J = 26.4$ Hz, 1F), −68.0 (m, 1F), −102.6 (dt, $J = 276.2$ Hz, $J = 7.7$ Hz, 1F), −104.2 (dt, $J = 276.4$ Hz, $J = 7.2$ Hz, 1F); for $(ICF_2)_2OCF_3$, −51.7 (m, 3F), −53.9 (m, 4F), −124.2 (m, 1F); HRMS: calcd for $C_4F_8I_2O$, 469.7911. Found: 469.7930 for $ICF_2CF_2CFIOCF_3$; 469.7967 for $(ICF_2)_2CFOCF_3$.

**Reaction of $CF_2I_2$ with Perfluoropropyl Vinyl Ether.** A 75-mL shaker tube was charged with 30.5 g of $CF_2I_2$ and cooled to −78 °C. The tube was evacuated and then 60.0 g of perfluoropropyl vinyl ether was added. After the tube was heated at 185 °C for 3.5 h, 78.5 g of crude products was distilled to give 29.0 g of perfluoropropyl vinyl ether, 6.2 g of 72% pure adduct (bp: 30−80 °C/40 mmHg), 27.6 g of pure adduct (bp: 83−84 °C/40 mmHg), and 4.4 g of 68% pure adduct (bp 85 °C/40 mmHg to 74 °C/15 mmHg), yield 79%. $^{19}F$ NMR and GC indicated a mixture $ICF_2CF_2CFIOCF_2CF_2CF_3$ and $(ICF_2)_2CFOCF_2CF_2CF_3$ in a ratio of 85.4:13.6. $^{19}F$ NMR: for $ICF_2CF_2CFIOCF_2CF_2CF_3$, −55.3 (d, $J = 204.6$ Hz, 1F), −58.8 (ddd, $J = 204.6$ Hz, $J = 27$ Hz, $J = 6.3$ Hz, 1F), −68.7 (m, 1F), −81.3 to −81.9 (m, 4F), −90.7 (d, $J = 147.6$ Hz, 1F), −102.4 (dt, $J = 276.7$ Hz, $J = 8$ Hz, 1F), −104.4 (dt, $J = 276.6$ Hz, $J = 7.5$ Hz, 1F), −130.4 (s, 2F); for $(ICF_2)_2OCF_2CF_2CF_3$, −53.8 (m, 4F), −79.4 (m, 2F), −81.3 (M, 3F), −122.3 (m, 1F), −129.3 (M, 2F). HRMS: calcd for $C_6F_{12}I_2O$, 569.7847. Found: 442.8824 for $ICF_2CF_2CFIOCF_2CF_2CF_3I$; 569.7796 for $(ICF_2)_2CFOCF_2CF_2CF_3$. Anal. Calcd for $C_6F_{12}I_2O$: C, 12.65; I, 44.55. Found: C, 12.72; I, 44.23.

**Reaction of $CF_2I_2$ with $CF_2=CFOCF_2CF(CF_3)OCF_2CF_2CN$.** A 240-mL shaker tube was charged with 30.5 g of $CF_2I_2$ and 45.0 g of $CF_2=CFOCF_2CF(CF_3)OCF_2CF_2CN$ and cooled to −78 °C. After being evacuated at −78 °C, the tube was heated at 185 °C for 4 h to give 67.8 g of crude products. Distillation gave 15 g of mainly $CF_2=CFOCF_2CF(CF_3)OCF_2CF_2CN$ (bp: 85−100 °C) and 37.6 g of adduct (bp: 115−116 °C/30 mmHg). The adduct was a mixture of $ICF_2CF_2CFIOCF_2CF(CF_3)OCF_2CF_2CN$ and $(ICF_2)_2CFOCF_2CF(CF_3)OCF_2CF_2CN$ in a ratio of 5.7:1. $^{19}F$ NMR: for $ICF_2CF_2CFIOCF_2CF(CF_3)OCF_2CF_2CN$, −55.5 (d, $J$ = 205.2 Hz, 1F), −58.9 (ddd, $J$ = 205.5 Hz, $J$ = 27.3 Hz, $J$ = 6.0 Hz, 1F), −69.4 (m, 1F), −79.1 to −80.4 (m, 4F), −84.1 to −85.2 (m, 2F), −90.0 (dm, $J$ = 152.5 Hz, 1F), −102.0 (dm, $J$ = 277.7 Hz, 1F), −104.5 (dm, $J$ = 277.7 Hz, 1F), −108.6 (m, 2F), −145.1 (t, $J$ = 21.2 Hz, 0.5F), −145.6 (t, $J$ = 21.3, Hz, 0.5F); for $(ICF_2)_2CFOCF_2CF(CF_3)OCF_2CF_2CN$, −53.1 (m, 2F), −54.5 (m, 2F), −78.2 (m, 2F), −80.1 (m, 3F), −84.1 (m, 2F), −108.4 (m, 2F), −121.2 (m, 1F), −144.6 (m, 1F). HRMS: calcd for $C_9F_{15}I_2NO_2I$, 565.8734. Found: 565.8716 ($M^+ - I$). Anal. Calcd for $C_9F_{15}I_2NO_2$: C, 15.60; N, 2.02; I, 36.63. Found: C, 16.26; N, 2.02; I, 35.74.

**Reaction of $CF_2I_2$ with $CF_2=CFOCF_2CF(CF_3)OCF_2CF_2SO_2F$.** A 240-mL shaker tube was charged with 30.5 g of $CF_2I_2$ and 50.0 g of $CF_2=CFOCF_2CF(CF_3)OCF_2CF_2SO_2F$ and cooled to −78 °C. After being evacuated at −78 °C, the tube was heated at 185 °C for 4 h to give 71.3 g of crude products. Distillation gave 10.3 g of $CF_2I_2$ (66.3% conversion), 42 g (84.5%) of adduct, (bp: 95−97 °C/5.4 mmHg). The adduct was a mixture of $ICF_2CF_2CFIOCF_2CF(CF_3)OCF_2CF_2SO_2F$ and $(ICF_2)_2CFOCF_2CF(CF_3)OCF_2CF_2SO_2F$ in a ratio of 5.2:1.$^{19}F$ NMR: for $ICF_2CF_2CFIOCF_2CF(CF_3)OCF_2CF_2SO_2F$, +45.3 (m, 1F), −55.6 (d, $J$ = 204.7 Hz, 1F), −58.9 (ddd, $J$ = 204.7 Hz, $J$ = 27.2 Hz, $J$ = 6.3 Hz, 1F), −69.3 (m, 1F), −79.3 to −80.2 (m, 4F), −89.8 (dm, $J$ = 144.3 Hz, 1F), −101.9 (dm, $J$ = 277.9 Hz, 1F), −104.6 (dt, $J$ = 277.8 Hz, $J$ = 7.7 Hz, 1F), −112.2 (m, 2F), −145.4 (m, 1F); for $(ICF_2)_2CFOCF_2CF(CF_3)OCF_2CF_2SO_2F$, −53.2 (m, 2F), −54.5 (m, 2F), −78.2 (m, 2F), −80.1 (m, 5F), −112.4 (m, 2F), −121.2 (m, 1F), −144.6 (m, 1F). Anal. Calcd for $C_8F_{16}I_2O_4S$: C, 12.81; I, 33.84. Found: C, 13.05. F, 32.80.

**Reaction of $CF_2I_2$ with $CF_2=CFOCF_2CF(CF_3)OCF_2CF_2SO_2F$ at High Temperature.** A 240-mL shaker tube was charged with 30.6 g of $CF_2I_2$ and 50.0 g of $CF_2=CFOCF_2CF(CF_3)OCF_2CF_2SO_2F$ and cooled to −78 °C. After being evacuated at −78 °C, the tube was heated at 185 °C for 4 h and 240 °C for 8 h to give 71.5 g of crude products. GC indicated a mixture of $ICF_2CF_2COF$, $ICF_2CF(CF_3)OCF_2CF_2SO_2F$, and $(ICF_2)_2CFOCF_2CF(CF_3)OCF_2CF_2SO_2F$ in a ratio of 4.1:6.6:1 (area ratio). Distillation gave 12.6 of 93% pure $ICF_2CF_2COF$ (bp: 58−63 °C), 6.0 g of a mixture of $ICF_2CF_2COF$ and $ICF_2CF(CF_3)OCF_2CF_2SO_2F$ (bp: 26−100 °C/200 mmHg), 17.9 g of $ICF_2CF(CF_3)OCF_2CF_2SO_2F$ (bp: 100−102 °C/200 mmHg), 16.7 g of a mixture of 75% $ICF_2CF(CF_3)OCF_2CF_2SO_2F$ and 16% $(ICF_2)_2CFOCF_2CF(CF_3)OCF_2CF_2SO_2F$, and 4.3 g of $(ICF_2)_2CFOCF_2CF(CF_3)OCF_2CF_2SO_2F$. $^{19}F$ NMR: for $ICF_2CF(CF_3)OCF_2CF_2SO_2F$, +45.5 (m, 1F), −58.7 (dm, $J$ = 213.7 Hz, 2F), −60.0 (dm, $J$ = 214 Hz, 2F), −76.9 (m, 3F), −77.9 (dd, $J$ = 139.2 Hz, $J$ = 22.7 Hz, 1F), −79.7 (dm, $J$ = 139.2 Hz, 1F), −122.2 (s, 2F), −133.6 (m, 1F).

**Reaction of $CF_2I_2$ with 4-Bromo-3,3,4,4-tetrafluorobutene-1.** A 75-mL shaker tube was charged with 30.5 g of $CF_2I_2$ and 21.0 g of $BrCF_2CF_2CH=CH_2$ and cooled to −78 °C. The tube was evacuated and then heated at 180 °C for 2.5 h to give 31.6 g of crude product, which was washed with aqueous $Na_2SO_3$ solution and distilled to yield 28.7 g (56%) of $ICF_2CH_2CHICF_2CF_2Br$ (bp: 53 °C/19 mmHg). $^{19}F$ NMR: −36.7 (ddd, $J$ = 176.1 Hz, $J$ = 16.2 Hz, $J$ = 7.1 Hz, 1F), −39.7 (dt, $J$ = 176 Hz, $J$ = 15.8 Hz, 1F). −59.9 (dd, $J$ = 178.6 Hz, $J$ = 7.6 Hz, 1F), −61.0 (dd, $J$ = 178.6 Hz, $J$ = 5.6 Hz, 1F), −94.6 (dt, $J$ = 260.6 Hz, $J$ = 7.2 Hz, 1F), −109.8 (ddd, $J$ = 261.0 Hz, $J$ = 18 Hz, $J$ = 7.4 Hz, 1F). $^1H$ NMR: 4.56 (m, 1H), 3.54 (m, 1H), 3.09 (m, 1H). Anal. Calcd for $C_5H_3F_6BrI_2$: C, 11.76; H, 0.59; F, 22.32. Found: C, 12.05; H, 0.75; F, 22.27.

**Reaction of $CF_2I_2$ with 4-Iodo-3,3,4,4-tetrafluorobutene-1.** A 75-mL shaker tube was charged with 42.3 g of 1:1 mixture of $CF_2I_2$ and $ICF2CF_2CH=CH_2$ and cooled to −78 °C. The tube was evacuated and then heated at 180 °C for 2.5 h to yield 36 g of crude product, which was washed with aqueous $Na_2SO_3$ solution and distilled to give 23.5 g (56%) of $ICF_2CH_2CHICF_2CF_2I$ (bp: 118−120 °C/10 mmHg). $^{19}F$ NMR: −36.7 (ddd, $J$ = 175.5 Hz, $J$ = 16.0 Hz, $J$ = 7.7 Hz, 1F), −39.6 (dt, $J$ = 175.5 Hz, $J$ = 16.0 Hz, 1F). −54.8 (ddt, $J$ = 202.2 Hz, $J$ = 7.3 Hz, $J$ = 2.3 Hz, 1F), −56.0 (dd, $J$ = 203.0 Hz, $J$ = 7.0 Hz, 1F), −88.3 (dt, $J$ = 261.0 Hz, $J$ = 7.0 Hz, 1F), −106.2 (ddd, $J$ = 261.0 Hz, $J$ = 19 Hz, $J$ = 8.4 Hz, 1F). $^1H$ NMR: 4.60 (m, 1H), 3.56 (m, 1H), 3.10 (m, 1H). Anal. Calcd for $C_5H_3F_6I_3$: C, 10.77; H, 0.54; F, 20.44; I, 68.35. Found: C, 11.32; H, 0.71; F, 20.47; I, 68.59.

**Reaction of $CF_2I_2$ with Vinylidene Fluoride.** A 75-mL shaker tube was charged with 30.5 g of $CF_2I_2$ and cooled to −78 °C. The tube was evacuated and then 10.0 g of $CF_2=CH_2$ was added. After the tube was heated at 185 °C for 8 h, GC indicated 10% $CF_2I_2$ and 79.5% adduct (area ratio).Finally, 35.1 g of crude products was obtained which was distilled to give 4.1 g of 50% pure adduct and 26.4 g (86%) of pure adduct (bp: 80−81 °C/60 mmHg). $^{19}F$ NMR and GC indicated a mixture of $ICF_2CH_2CCF_2I$ and $ICF_2CF_2CH_2I$ in a ratio of 27.6: 1. $^{19}F$ NMR: for $ICF_2CH_2CF_2I$, −39.6 (m); for $ICF_2CF_2CH_2I$, −59.6 (t, $J$ = 4 Hz, 2F), −101.5 (t, $J$ = 16.4 Hz, 2F). HRMS: calcd for $C_3H_2F_4I_2$, 367.8182. Found: 367.8168 for $ICF_2CH_2CF_2I$; 367.8150 for $ICF_2CF_2CH_2I$. Anal. Calcd for $C_3H_2F_4I_{2:}$ C, 9.80; H, 0.55; I, 69.00. Found: C, 9.76; H, 0.62; I, 68.48.

**Reaction of $CF_2I_2$ with Trifluoroethylene.** A 75-mL shaker tube was charged with 30.5 g of $CF_2I_2$ and cooled to −78 °C. The tube was evacuated and then 16.0 g of trifluoroethylene was added. After the tube was heated at 185 °C for 10 h, GC indicated 70% conversion, and 26.3 g of crude product was obtained which was washed with aqueous $Na_2SO_3$ solution and distilled to give 1.5 g of 55% pure adduct, 2.5 g of 84% pure adduct, and 12.8 g of pure product (bp: 83 °C/80 mmHg), total yield 58% (70% conversion). $^{19}F$ NMR and GC indicated a mixture $ICF_2CHFCF_2I$ and $ICF_2CF_2CHFI$ in a ratio of 1.5:1. $^{19}F$ NMR: for $ICF_2CHFCF_2I$, −52.6 (dm, $J$ = 207.8 Hz, 2F), −54.8 (dm, $J$ = 207.8 Hz, 2F), −176.2 (m, 1F); $ICF_2CF_2CHFI$: −57.9 (dm, $J$ = 207.8 Hz, 1F), −59.8 (dt, $J$ = 207.8 Hz, $J$ = 6.5 Hz, 1F), −101.0 (ddt, $J$ = 273.1 Hz, $J$ = 32.3 Hz, $J$ = 6.3 Hz, 1F), −116.3 (dm, $J$ = 273.1 Hz, 1F), −165.7 (m, 1F). HRMS: calcd for $C_3HF_5I_2$, 385.8088. Found: 385.8023. Anal. Calcd for $C_3HF_5I_2$: C, 9.34; H, 0.26; F, 24.62; I, 65.78. Found: C, 9.25; H, 0.27; F, 24.39; I, 65, 81.

**Reaction of $CF_2I_2$ with Ethylene.** A 75-mL shaker tube was charged with 30.5 g of $CF_2I_2$ and cooled to −78 °C. The tube was evacuated and then 4.0 g of ethylene was added. After the tube was heated at 185 °C for 5 h, 30.3 g of crude product was obtained which was distilled to give 27.3 g (82%) of adduct with 100% GC purity (bp: 94−95 °C/50 mmHg). $^{19}F$ NMR: −39.1 (t, $J$ = 14.3 Hz). $^1H$ NMR: 3.21 (t, $J$ = 7.3 Hz, 2H), 2.95 (m, 2H). HRMS: calcd for $C_3H_4F_2I_2$, 331.8371. Found: 331.8336. Anal. Calcd for $C_3H_4F_2I_2$: C, 10.86; H, 1.21; F, 11.45; I, 76, 48. Found: C, 10.84; H, 1.25; F, 11.59; I, 75.96.

**Reaction of $CF_2I_2$ with Propylene.** A 75-mL shaker tube was charged with 30.5 g of $CF_2I_2$ and cooled to −78 °C. The tube was evacuated and then 5.0 g of propylene was added. After the tube was heated at 185 °C for 5 h, 31.6 g of crude product was obtained which was distilled to give 28.7 g (83%) of adducts (bp: 106−107 °C/4.8 mmHg). GC and NMR indicated a mixture of $ICF_2CH_2CHICH_3$ and $ICH_2CH(CF_2I)CF_3$ in a ratio of 13:1. $^{19}F$ NMR: for major product, −35.4 (ddd, $J$ = 173 Hz, $J$ = 18.4 Hz, J − 8.7 Hz, 1F), −38.3 (dt, $J$ = 173 Hz, $J$ = 16.4 Hz, 1F). $^1H$ NMR: 4.35 (m, 1H), 3.28 (m, 1H), 2.90 (m, 1H), 2.00 (d, $J$ = 7.0 Hz, 3H). HRMS: calcd for $C_4H_7F_2I_2$, 345.8527. Found: 345.8565 for $ICF_2CH_2CHICH_3$ and

345.8510 for $ICH_2CH(CF_2I)CH_3$. Anal. Calcd for $C_4H_7F_2I_2$: C, 13.89; H, 1.75; F, 10.98; I, 73.38. Found: C, 13.99; H, 1.98; F, 10.80; I, 73.34.

**Reaction of $CF_2I_2$ with Vinyl Fluoride.** A 75-mL shaker tube was charged with 30.5 g of $CF_2I_2$ and cooled to −78 °C. The tube was evacuated and then 6.0 g of vinyl fluoride was added. After the tube was heated at 185 °C for 5 h, GC indicated 90% conversion and 27.8 g of crude product was obtained which was distilled to give 4.9 g of 55% pure adduct and 17.1 g (63%) of pure product (bp: 87−89 °C/50 mmHg). $^{19}F$ NMR and GC indicated a mixture of $ICF_2CH_2CCFHI$ and $ICF_2CFHCH_2I$ in a ratio of 8.6:1. $^{19}F$ NMR: for $ICF_2CH_2CHFI$, −37.6 (dm, $J = 178.5$ Hz, 1F), −40.33 (dm, $J = 178.5$ Hz, 1F), −144.7 (m, 1F); for $ICF_2CFHCH_2I$, −51.8 (ddd, $J = 195.5$ Hz, $J = 21.0$ Hz, $J = 7.4$ Hz, 1F), −56.3 (ddd, $J = 196$ Hz, $J = 21.7$ Hz, $J = 7.3$ Hz, 1F), −176.8 (m, 1F). HRMS: calcd for $C_3H_3F_3I_2$, 349.8280. Found: 349.8391 for $ICF_2CH_2CFHI$; 349.8307 for $ICF_2CFHCH_2I$. Anal. Calcd for $C_3H_3F_3I_2$: C, 10.30; H, 0.86. Found: C, 10.26; H, 1.00.

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