8140 J. Am. Chem. Soc. **1996,** *118,* 8140−8141

Nickel-Catalyzed Reaction of Highly Fluorinated Epoxides with Halogens[⊥]

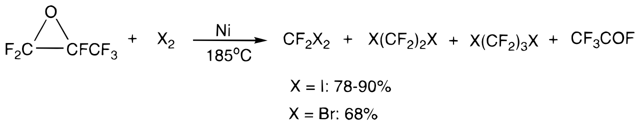
Zhen-Yu Yang

DuPont Central Research & Development
Experimental Station, Wilmington, Delaware 19880-0328

Received April 29, 1996

Transition metal catalyzed reactions have been widely used in hydrocarbon transformations, but the analogous chemistry in perfluorocarbons is largely unexplored. 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. That is due to the fact that they exhibit dramatically different structural and bonding characteristics with enhanced thermal stability in comparison with their hydrocarbon counterparts.[1] Fluorinated organometallic reagents have recently received much attention, but catalytic reactions are much more attractive for the synthesis of fluorocarbons.[2] Although transition metal complex catalyzed defluorinations of perfluorocarbons have been reported very recently, other useful metal catalyzed reactions under conventional conditions remain unknown to the best of our knowledge.[3] We report here the first example of a transition metal catalyzed reaction of highly fluorinated epoxides with halogens, which may involve the metal CF_2 complex, to give dihalodifluoromethanes and fluorinated acyl fluorides in good yields.

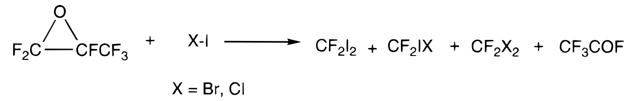
Difluorocarbene and its precursors react with iodine to give very poor yields of CF_2I_2.[4] Reaction of hexafluoropropylene oxide (HFPO), a well-known difluorocarbene precursor, with I_2 in a stainless steel tube or in a glass tube affords only less than 15% yield of CF_2I_2.[5,6] We discovered that the reaction of HFPO with I_2 in the presence of 3−10 mol % of Ni powder in a stainless steel shaker tube or a glass tube resulted in high yields of CF_2I_2 and CF_3COF, along with small amounts of $I(CF_2)_nI$ ($n = 2, 3$).



A 400-mL stainless steel shaker tube was charged with 3 g of Ni powder (Aldrich, 99.99%, 100 mesh) and 127 g of I_2 and cooled to −78 °C. After evacuating, 90 g of HFPO was added and the tube was vigorously shaken at 185 °C for 8 h. Gas (CF_3COF) was transferred into a −78 °C trap and 146.3 g of crude liquid product was distilled to give 116.8 g (78%) of a 64.3:1:4.7 (GC area) mixture of CF_2I_2, $I(CF_2)_2I$, and $I(CF_2)_3I$. Other catalysts containing nickel such as Ni/Zn (Urushibara catalyst) and Ni/Cu/Zn also catalyze the reaction.[7,8] The success in the reaction with Ni alloys prompted us to use a vessel with high nickel content as a reactor. Indeed, the reaction proceeded well in a Hastelloy C reactor to give greater than 85% of CF_2I_2 in the absence of added nickel catalyst.[9]

Reaction of HFPO with bromine under similar conditions gave CF_2Br_2 and CF_3COF with traces of $Br(CF_2)_nBr$ ($n = 2$, 3). The reaction proceeded in a Hastelloy C vessel or in a stainless steel vessel with Ni powder, but only a very low yield (<5%) of CF_2Br_2 was observed in the absence of nickel powder in a stainless steel tube. Since this is a heterogeneously catalyzed reaction, vigorous shaking or agitating is 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 selectivites compared to the reaction in solvents.

The nickel catalyzed reaction also can be carried out with 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 (mol) mixture of CF_2I_2, CF_2Br_2, and CF_2IBr was isolated in 74% total yields. 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.[10] In both cases, traces of higher homologues $X(CF_2)_nY$ (X, Y = halogen and $n = 2$, 3) were also detected by GC-MS and ^{19}F NMR analysis.



The nickel catalyzed reaction is general and works well with other fluorinated epoxides. The perfluorophenyl, perfluorosulfonyl fluoride, and chlorofluorocarbon groups in the epoxides did not interfere with the reaction. The reaction of these fluorinated functionalized epoxides with I_2 in the presence of Ni powder in a sealed glass tube with vigorous shaking at 190 °C afforded good yields (68−81%) of CF_2I_2 and the corresponding fluorinated acyl fluorides.

[⊥] Publication No. 7414.

(1) (a) Kiplinger, J. L.; Richmond, T. G.; Osterberg, C. E. *Chem. Rev.* **1994**, *94*, 373. (b) Hughes, R. *Adv. Organomet. Chem.* **1990**, *31*, 183. (c) Stone, F. G. A. *Pure Appl. Chem.* **1972**, *30*, 5451. (d) Bruce, M. I.; Stone, F. G. A. *Prep. Inorg. React.* **1968**, *4*, 177. (e) Treichel, P. M.; Stone, F. G. A. *Adv. Organomet. Chem.* **1964**, *1*, 143.

(2) (a) Burton, D. J.; Yang, Z. Y.; Morken, P. A. *Tetrahedron* **1994**, *50*, 2993. (b) Burton, D. J.; Yang, Z. Y. *Tetrahedron* **1992**, *48*, 189. (c) *Chemistry of Organic Fluorine Compounds II. A Critical Review*; Hudlicky, M., Pavlath, A. E., Eds.; ACS Monograph 187; American Chemical Society: Washington, DC, 1995.

(3) (a) Aizenberg, M.; Milstein, D. *Science* **1994**, *265*, 359. (b) Kiplinger, J. L.; Richmond, T. G. *J. Am. Chem. Soc.* **1996**, *118*, 1805. (c) Burdeniuc, J.; Crabtree, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 2525.

(4) (a) Mahler, W. *Inorg. Chem.* **1963**, *2*, 230. (b) Mitsh, R. A. *J. Heterocycl. Chem.* **1964**, *1*, 233; (c) Kesling, H. S.; Burton, D. J. *Tetrahedron Lett.* **1975**, 3358; (d) Wheaton, G. A.; Burton, D. J. *J. Org. Chem.* **1978**, *43*, 3643.

(5) HFPO as a CF_2 precursor: (a) Sargeant, P. B.; Krespan, C. G. *J. Am Chem. Soc.* **1969**, *91*, 415. (b) Sargeant, P. B. *J. Org. Chem.* **1970**, *35*, 678. (c) Chepik, S. D.; Petrov, V. A.; Galakhov, M. V.; Belen'kii, G. G.; Mysov, E. I.; German, L. S. *Izv. Akad. Nauk SSSR, Seri. Khim.* **1990**, *8*, 1844. (d) Millauer, H.; Schwertfeger, W.; Siegemund, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 161.

(6) (a) John, E. O.; Kirchmeier, R. L.; Shreeve, J. M. *Inorg. Chem.* **1992**, *31*. 329. (b) We repeated the reaction of HFPO with I_2 in a stainless steel 316 tube to give less than 15% yield of CF_2I_2. In a glass tube, no yield was improved.

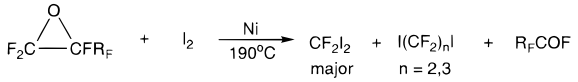
(7) *New Hydrogenation Catalysts: Urushibara Catalysts*; Hata, K.; John Wiley & Son, Inc.: New York, 1972; pp 29−60.

(8) (a) Ni/Cu/Zn catalyst was prepared by reaction of $NiCl_2/CuSO_4$ with Zn in water. To a stirred solution of 13.0 g of $NiCl_2$ and 16.0 g of $CuSO_4$ in 100 mL of water was slowly added 13.0 g of Zn at room temperature. Solids were filtered and poured into 10% HCl, and the resulting mixture was stirred for 30 min. After filtration, the solids were washed with water and acetone and dried under vacuum at 60 °C to give 11.3 g of Ni/Cu/Zn catalyst. (b) A 0.4-L stainless steel Shaker tube was charged with 127 g of iodine and 5.0 g of Ni/Cu catalyst and then evacuated at low temperature. After 90 g of HFPO was added, the resulting mixture was heated at 185 °C for 8 h. 112.0 g of dark liquid was obtained which was distilled to give 79.3 g of a mixture of CF_2I_2, ICF_2CF_2I, and $ICF_2CF_2CF_2I$ in a ratio of 39.3:1:3 (GC area).

(9) (a) Hastelloy C alloy contains 56.43% Ni, 15.5% Cr,16% Mo, and small amounts of other elements while stainless steel 316 alloy contains only 12% Ni. (b) A 1-L Hastelloy autoclave was charged with 381 g (1.5 mol) of I_2 and cooled to −78 °C. After evacuating, 266 g (1.6 mol) of HFPO was added and the autoclave was heated at 185 °C for 10 h. After cooling to 0 °C, gas (CF_3COF) was vented and 458 g of liquid was washed with aqueous Na_2SO_3 solution and distilled to give 395 g of a 240:1:4.8 (mol) mixture of CF_2I_2, $I(CF_2)_2I$, and $I(CF_2)_3I$, bp 106−107 °C. ^{19}F NMR for CF_2I_2: +18.6 ppm (s). HRMS: calcd for CF_2I_2 303.8057; found 303.8065.

(10) CF_2ICl, bp 31−34 °C, ^{19}F NMR: +8.2 ppm (s) and CF_2Cl_2 is too volatile to be isolated.

S0002-7863(96)01408-4 CCC: $12.00



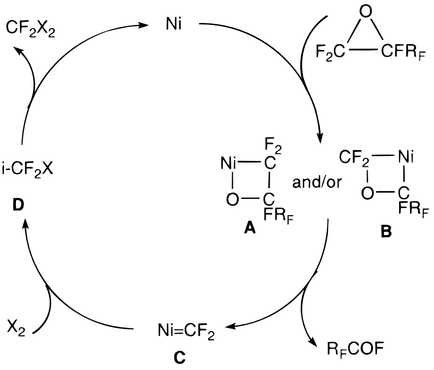
$R_F = CF_2CFClCF_2Cl$: 81%

$CF_2OC_6F_5$: 80%

$CF_2OCF_2CF_2SO_2F$: 68%

The precise mechanism for this nickel catalyzed reaction is unclear. Initially, $Ni^{II}I_2$ generated from the reaction of iodine with nickel powder was suspected as a catalytic species. However, the recovered dark powder after reaction was a mixture of Ni(0) and $Ni^{II}I_2$ as determined by X-ray diffraction.[11] As a control experiment, we carried out the reaction with $Ni^{II}I_2$ (Aldrich, 99.99%) as a catalyst under identical conditions; no desired CF_2I_2 was obtained. Subhalide $Ni^{I}I$ has also been considered as a catalytic species, since Ni(I) complexes in either homogeneous solution or on silica support were formed by reaction of Ni(0) and Ni(II) complexes or by reduction of Ni(II).[12] Such a possibility may not be the case in this reaction because when a mixture of powdered nickel and $Ni^{II}I_2$ was heated at above 180 °C, even in the molten state, no evidence for the formation subhalide NiI was observed; thus, $Ni^{I}I$ seems unlikely to be the catalytic species.[13] We propose that nickel atoms are the catalytic center where the fluorinated epoxide first adsorbs and then undergoes oxidative addition to give fluorinated oxanickel cyclobutane **A** and/or **B**, which rapidly decompose to CF_3COF and nickel difluorocarbene **C**.[14−16] The formation of Ni═CF$_2$ **C** may alter the reactivity of the carbene carbon from electrophilic to nucleophilic, resulting in facile reaction with halogens to give intermediate **D**.[17] Finally, reductive elimination could give CF_2X_2 and regenerated nickel (Scheme 1). The formation of small amounts of higher homologues $X(CF_2)_nX$ ($n = 2, 3$) is consistent with reaction of halogens with the dimer or trimer of CF_2.[18]

Scheme 1



In conclusion, we have discovered an unprecedented nickel catalyzed reaction of highly fluorinated epoxides with halogens at elevated temperatures. Since HFPO is a readily available material, the reaction provides the first useful synthesis of CF_2I_2 which is an important building block for the preparation of other fluorinated compounds, but heretofore has been extremely difficult to obtain.[4,5,16,19] In addition, the high value of by-product, fluoroacyl fluoride, the absence of solvent, and high yields make this reaction more attractive for the synthesis of functional fluorocarbons on a large scale. Mechanistic studies and further applications of the novel chemistry are currently in progress.

Acknowledgment. We wish to thank Drs. R. R. Burch, C. G. Krespan, P. A. Morken, and B. E. Smart for valuable discussion and R. E. Smith for technical assistance.

Supporting Information Available: Experimental details and characterization of all products (5 pages). See any current masthead page for ordering and Internet access instructions.

JA961408S

---

(11) Nickel powder is not completely converted into NiI_2 upon reaction with iodine in the solid phase. When a large excess of I_2 (20 g) and nickel powder (3.0 g) was heated in an evacuated sealed glass tube at 180 °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. The X-ray diffraction pattern of this mixture is almost identical to that of recovered catalyst.

(12) Ni(I) complexes: (a) Heimbach, P. *Angew. Chem., Int. Edi. Engl.* **1964**, *3*, 648. (b) Nilges, M. J.; Barefield, E. K.; Belford, R. L.; Davis, P. H. *J. Am. Chem. Soc.* **1977**, *99*, 755. (c) Tsou, T. T.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 6319. (d) Ratliff, K. S.; Broeker, G. K.; Fanwick, P. E.; Kubiak, C. P. *Angew. Chem.* **1990**, *102*, 405. (e) Morgenstern, D. A.; Wittrig, R. E.; Fanwick, P. E.; Kubiak, C. P. *J. Am. Chem. Soc.* **1993**, *115*, 6470. (f) Cai, F. X.; Lepetit, C.; Kermarec, M.; Olivier, D. *J. Mol. Catal.* **1987**, *43*, 93. (g) Sibille, S.; Coulombeix, J.; Perichon, J.; Fuchs, J. Mortreux, A.; Petit, F. *J. Mol. Catal.* **1985**, *32*, 239. (h) Bonneviot, L.; Olivier, D.; Che. M. *J. Mol. Catal.* **1983**, *21*, 415.

(13) Upon heating Ni/NiI_2 powder at 185 °C in He for 1, 2, and 3 h, no changes of X-ray diffraction patterns were observed. A neutron diffraction investigation also indicated no evidence for the formation of subhalide NiI in 9% Ni in molten nickel(II) iodide, see: Allen, A. D.; Howe, R. A. *J. Phys.: Condens. Matter* **1991**, *3*, 97. Little reaction of Ni−Cr alloys (Hastelloy) with I_2 was observed at or below 250 °C, see: Ginzburg, V. I.; Kabakova, O. I. *Zashch. Met.* **1969**, *5*, 672.

(14) The oxidative additions of hydrocarbon epoxides to nickel complexes in homogeneous solution and to Ni ion beams in the gas phase were proposed. The oxidative addition product in gas phase decomposes to give Ni carbene complex, see: (a) De Pasquale, R. J. *J. Chem. Soc., Chem. Commun.* **1973**, 157. (b) Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L. *Organometallics*, **1983**, *2*, 1829. For carbon−oxygen bond activation of epoxides by other transition metal complexes, see: (c) Walter, D. *Cood. Chem. Rev.* **1987**, *79*, 135. (d) Backvall, J. E.; Karlsson, O.; Ljunggren, S. O. *Tetrahedron Lett.* **1980**, *21*, 4985. (e) Trost, B. M.; Angle, S. R. *J. Am. Chem. Soc.* **1985**, *107*, 6123. (f) Aye, K.-T.; Gelmini, L.; Payne, N. C.; Vittal, J. J.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 2464. Intermediate **B** may also be possible in this reaction since the C−O bond is stronger than the C−C bond in perfluoroethers, see: *Molecular Structure and Energetics*; Liebman, J. F., Green berg, A., Eds.; VCH Publishers: Deerfield Beach, FL, 1986; Vol. 3, Chapter 4.

(15) The thermal stability of transition metal complexes containing fluorocarbon groups strongly depends on the ligands. The coordinatively unsaturated complexes are much less stable than coordinatively saturated ones. For example, $(PPh_3P)_2NiICF_3$ is a highly thermally stable complex and melts above 200 °C without decomposition, see: Ashley-Smith, J.; Green, M.; Stone, F. G. A. *J. Chem. Soc. A* **1969**, 3019. However, CF_3NiBr is much less stable and only 1% CF_3NiBr could be trapped with Et_3P at −78 °C. See: Klabunde, K. J. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 287. We believe that the intermediates **A** and/or **B** are highly reactive.

(16) An alternative mechanism for the formation of complex **C** is the reaction of $:CF_2$ with Ni atoms rather than through intermediates **A** and **B**. However, reaction of other $:CF_2$ precursors such as $ClCF_2CO_2K$ with I_2 and catalytic nickel powder at 180 °C gave no CF_2I_2 in the absence of solvent and low yield of CF_2I_2 in DMF as reported, although I_2 reacted with the salt in the presence of equimolar amounts of KI and CuI to give good yields of CF_2I_2. See: Su, D. B.; Duan, J. X.; Chen. Q. C. *J. Chem. Soc., Chem. Commun.* **1992**, 807.

(17) Difluorocarbene is the most electrophilic carbene known and is a ground state singlet, see: (a) Carter, E. A.; Goddard, W. A., III *J. Chem. Phys.* **1988**, *88*, 1752. (b) Dixon, D. A. *J. Phys. Chem.* **1986**, *90*, 54. (c) Bauschlicher, C. W., Jr.; Schaefer, H. F., III; Bagus, P. S. *J. Am. Chem. Soc.* **1977**, *99*, 7106. The metal complexes with singlet carbene give relative weak donor/acceptor bonds rather than strong covalent bonds, see: Brothers, P. J.; Roper, W. R. *Chem. Rev.* **1988**, *88.*, 1293. Ion beam studies on Ni−C bond strength have demonstrated that the bond strength is 40 kcal/mol less for $NiCF_2^+$ than $NiCH_2^+$.[14b] The donor/acceptor bonds have significantly reduced electrophilicity of carbon center of CF_2 in low valent later transition metal and CF_2 complexes, see: (d) Clark, G. R.; Hoskins, S. V.; Jones, T. C.; Roper, W. R. *J. Chem. Soc., Chem. Commun.* **1983**, 719. (e) Gallop, M. A.; Roper, W. R. *Adv. Organomet. Chem.* **1986**, *25*, 121.

(18) Yang, Z. Y.; Krusic, P. J.; Smart, B. E. *J. Am. Chem. Soc.* **1995**, *117*, 5397.

(19) Elsheimer, S.; Dolbier, W. R.; Murla, M. *J. Org. Chem.* **1984**, *49*, 205