

Examples of interesting non-metal compounds derived from elemental fluorine

Darryl D. DesMarteau*

Chemistry Department, Clemson University, 218 AMRL, 91 Technology Drive, Anderson, SC 29625, USA

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Abstract

Elemental fluorine is essential for the preparation of many fluorine-containing compounds. A few examples from the author's past research are presented to illustrate this in tribute to the Centenary of the awarding of the Nobel Prize to Henri Moissan.

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1. Introduction

Moissan's isolation of elemental fluorine in 1886 paved the way to many novel fluorine compounds. While the large majority of all known fluorine-containing compounds have been obtained from other sources, elemental fluorine is essential in the preparation of many compounds. The year 2006 marks the 100th anniversary of the awarding of the Nobel Prize to Henri Moissan for his pioneering research [1]. In commemoration of this centenary, it is appropriate to present some selected examples of interesting compounds from past research by the 2006 Moissan Laureate wherein elemental fluorine was required for their preparation.

2. Background

I was first introduced to elemental fluorine in 1963 at the University of Washington during my early Ph.D. studies under Professor G.H. Cady [2]. Fluorine was used routinely in Cady's laboratories and as a beginning graduate student I was awed by its reactivity and perfume-like odor (in low concentrations!). As I gained familiarity with handling fluorine, I tried numerous unsuccessful reactions to prepare new fluoroxy derivatives of

sulfur and the first example of a phosphorous derivative. Ultimately, I used fluorine to prepare the known peroxide $S_2O_6F_2$, and its reaction chemistry was the major part of my Ph.D. thesis [3].

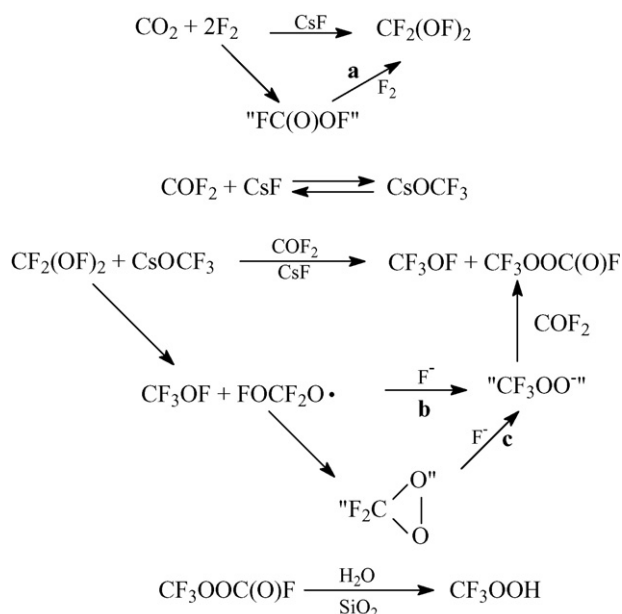
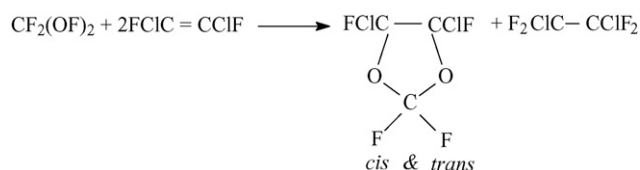
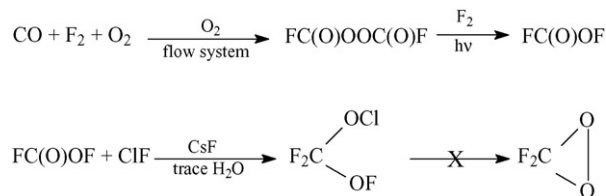
Since those early days of working with fluorine, my coworkers and I have used fluorine to prepare many examples of new non-metal fluorine compounds [4]. Fluorine was utilized in two ways: preparation of key starting materials, or in a direct reaction to a new compound. The following compounds illustrate both approaches. These four examples have been chosen to show some of the rich chemistry made possible by reactions of fluorine. An exhaustive review of all known compounds requiring fluorine in their syntheses would be both interesting and substantial.

3. An interesting hydroperoxide

The reactive peroxide CF_3OOH was first observed by 3 M chemists from hydrolysis of the peroxyformate $CF_3OOC(O)F$ [5]. The latter was obtained as one of many minor products from the fluorination of sodium trifluoroacetate. We discovered a preparative route to the peroxyformate using the fluoroxy compound $CF_2(O)F$ [6]. The latter is prepared by the cesium fluoride catalyzed fluorination of CO_2 . This quantitative reaction is a remarkable example of fluoride catalysis and the use of fluorine to generate a highly reactive molecule. When $CF_2(O)F$ is combined with excess carbonyl fluoride and cesium fluoride under the right conditions, excellent yields of

* Tel.: +1 864 656 1251; fax: +1 864 656 0627.

E-mail address: fluorin@clemson.edu.

Scheme 1. Synthesis of CF₃OOH.Scheme 3. Cycloaddition of CF₂(OF)₂ to alkenes.

Scheme 4. Attempted synthesis of difluorodioxirane.

the peroxyformate can be obtained for conversion to CF₃OOH. These transformations are shown in Scheme 1.

The intermediates in Scheme 1 have never been isolated in these reactions, but the transformations *a*, *b* and *c* have been independently verified, lending strong support to the suggested intermediates [7–9]. With a preparative route to the peroxyformate CF₃OOC(O)F, controlled hydrolysis provided CF₃OOH for investigation of its chemistry. A variety of interesting new molecules were found from reactions of this hydroperoxide and some examples are shown in Scheme 2 [10–17].

4. A fascinating cyclic peroxide

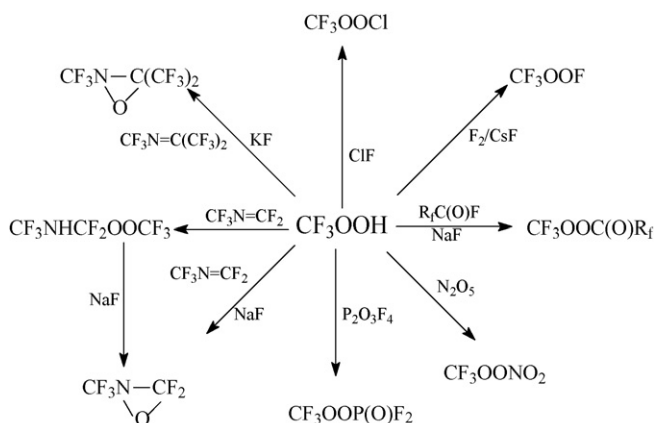
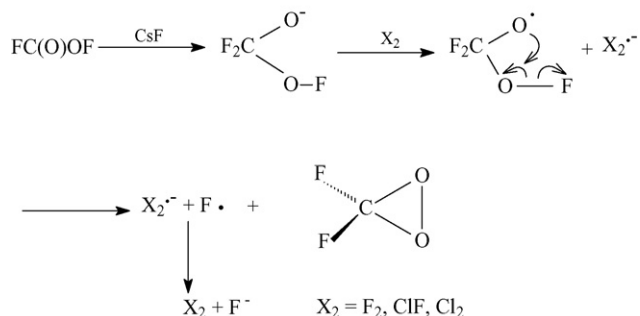
The idea of preparing a perfluorinated dioxirane was mentioned in research proposals by the author in the late 1970s, but no effort was made to do this until 1993. Chemists at

Ausimont (now Solvay Solexis) in Italy had discovered a very interesting cycloaddition reaction of CF₂(OF)₂ to fluorinated olefins as illustrated in Scheme 3 [18,19].

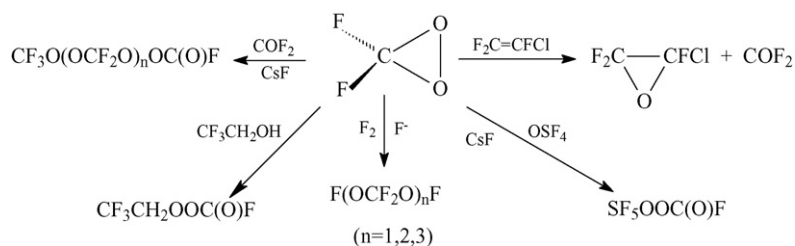
Subsequent dechlorination of this and other related 1,3-dioxolanes gave reactive dioxoles useful for the preparation of amorphous fluoropolymers. It was proposed that the cycloaddition reaction proceeded via the difluorodioxirane and in collaboration we set out to prepare this dioxirane. My proposed route was based on the elimination of ClF from the unknown F₂C(OCl)OF which might be prepared from the known FC(O)OF. The reaction sequence used is shown in Scheme 4.

The successful preparation of F₂C(OCl)OF was achieved but the latter did not readily form the desired dioxirane [20]. Fortunately in the course of this work a flow system was tried to improve the yields of the chloroxyfluoroxy derivative. This serendipitous experiment using a gaseous mixture of FC(O)OF/ClF through CsF gave the first evidence of the dioxirane. Scheme 5 shows the synthesis and proposed mechanism [21].

Difluorodioxirane is a remarkable molecule with the longest O–O bond observed to date [22]. It is a powerful oxygenating agent and undergoes a remarkable ring opening by nucleophiles at the O–O bond. However, it is not the intermediate in

Scheme 2. Some reactions of CF₃OOH.

Scheme 5. Synthesis of difluorodioxirane.

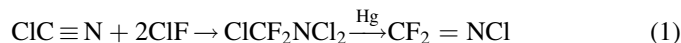


Scheme 6. Some reactions of difluorodioxirane.

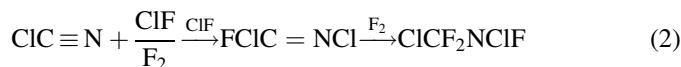
preparation of dioxoranes from $\text{CF}_2(\text{OF})_2$. Some reactions of the dioxirane are shown in Scheme 6 [7,9,21].

5. A novel *N*-fluoroimine

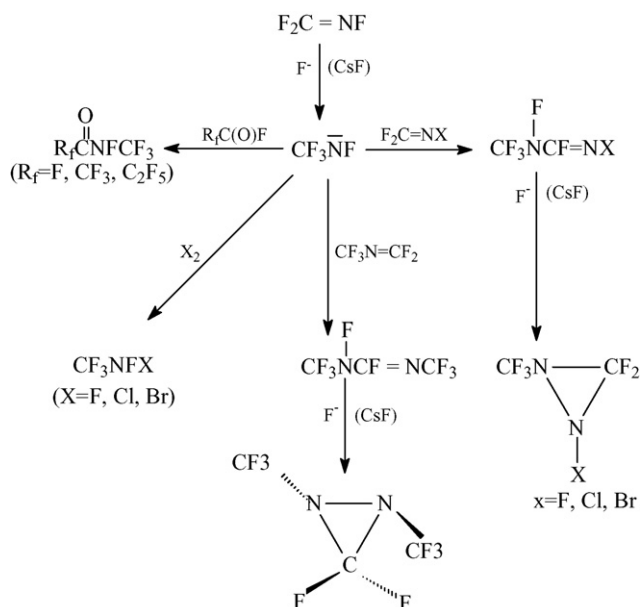
The interesting *N*-chloroimine $\text{F}_2\text{C} = \text{NCl}$ was isolated by Fox and coworkers by reaction of cyanogen chloride with chlorine monofluoride, followed by dechlorination with mercury [23]:



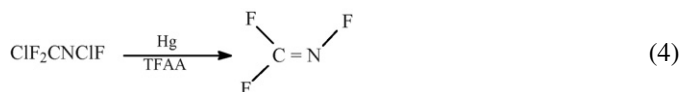
For a variety of reasons, we wanted to prepare the analog $\text{F}_2\text{C} = \text{NF}$. We reasoned that the synthesis of $\text{ClCF}_2\text{NCl}_2$ must involve a stepwise addition of ClF and perhaps we could trap the intermediate with fluorine:



This reaction worked well but we found that the reaction proceeded via a novel displacement reaction [24]:

Scheme 7. Some reactions of $\text{F}_2\text{C} = \text{NF}$.

The neat mercury dechlorination of ClF_2CNCIF did not work well but ultimately a high yield route was found using trifluoroacetic anhydride (TFAA) as a solvent [25]:



This imine was very reactive with fluoride ion to make the trifluoromethanamide anion and several facile reactions are shown in Scheme 7 [26–30].

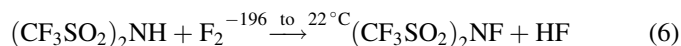
Difluoromethanimine could also be polymerized by SbF_5 . This energetic material was never fully characterized but MS showed oligomers up to $n = 10$ upon vacuum pyrolysis of the white solid [31]:



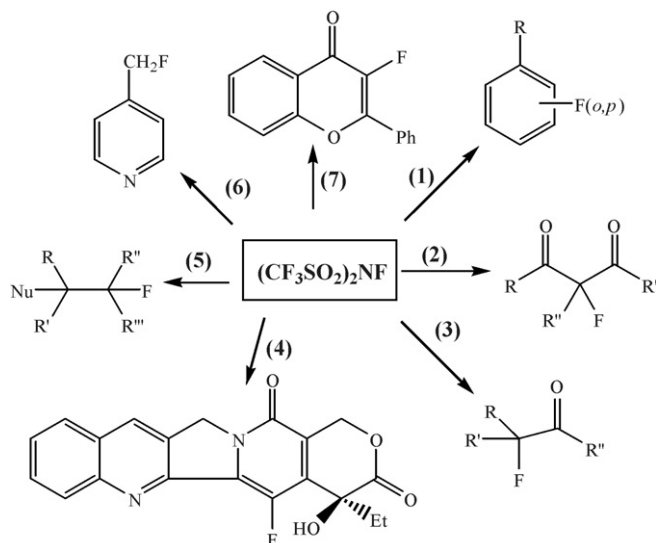
6. A powerful electrophilic fluorination reagent

The remarkable Bronsted acid $(\text{CF}_3\text{SO}_2)\text{NH}$ was originally synthesized by us to prepare a xenon–nitrogen bond analogous to our first example with $(\text{FSO}_2)_2\text{NH}$ to form $\text{FXeN}(\text{SO}_2\text{F})_2$. The interesting history of this work is summarized in Ref. [4]. This acid and its many possible analogues have led to much interesting research and potential applications in fuel cells and lithium batteries. However, a very interesting application depends on fluorine.

Selective fluorination of organic molecules is of long-standing interest in the search for new bioactive compounds. Perchloryl fluoride and fluoroxytrifluoromethane are examples of good electrophilic-like fluorination reagents, but these compounds have many safety issues associated with their use. Efforts to develop safer reagents of this type have focused on *N*-fluoro derivatives. An early report on the use of *N*-fluoro-*N*-alkylsulfonimides to fluorinate carbanions led us to explore the newly discovered *N*-fluorobis((trifluoromethyl)sulfonyl)imide $\text{FN}(\text{SO}_2\text{CF}_3)_2$ as a fluorination reagent. The latter was easily prepared in high yield [32]:



The first reaction to fluorinate a carbanion using toluene as a solvent, resulted in the ring fluorination of the toluene. This indicated that the compound was indeed a powerful electrophilic fluorination reagent. Subsequently many N–F fluorination reagents have been developed but to date $(\text{CF}_3\text{SO}_2)_2\text{NF}$ is



Scheme 8. Examples of selective fluorinations with $(\text{CF}_3\text{SO}_2)_2\text{NF}$. (1) Aromatics (2) 1,3-dicarbonyls; (3) monocarbonyls; (4) camptothecin; (5) olefins; (6) methylpyridines; (7) flavones.

probably the most powerful one [33]. Some of the many interesting examples of selective fluorinations with $(\text{CF}_3\text{SO}_2)_2\text{NF}$ are shown in Scheme 8 [34,35].

7. Conclusion

These examples of molecules enabled by reactions of elemental fluorine give only a glimpse of the fascinating chemistry made possible by Moissan's discovery 120 years ago. Using elemental fluorine requires some special consideration but the opportunities for discovery are worth the effort.

Acknowledgments

I pay tribute to the late G.H. Cady for introducing me to the exciting field of fluorine chemistry and I thank my many coworkers and collaborators for all their contributions. Lastly I thank all the organizations that provided financial support for our research during the past 40 years and the Prix Moissan jury for selecting me as the 2006 Moissan Laureate.

References

- [1] R.E. Banks, *J. Fluorine Chem.* 33 (1986) 3–26; J. Flahaut, C. Viel, *J. Fluorine Chem.* 33 (1986) 27–42.
- [2] A.W. Jache, *J. Fluorine Chem.* 71 (1995) XIII–XIV.
- [3] D.D. DeMarteau, Ph.D. Thesis, University of Washington, 1966.
- [4] D.D. DesMarteau, in: R.E. Banks (Ed.), *Fluorine Chemistry at the Millennium; Fascinated by Fluorine*, Elsevier, New York, USA, 2000, pp. 179–198.
- [5] R.L. Talbott, *J. Org. Chem.* 33 (1968) 2095–2099.
- [6] D.D. DesMarteau, *Inorg. Chem.* 9 (1970) 2179–2181.
- [7] Q. Huang, D.D. DesMarteau, *Inorg. Chem.* 39 (2000) 4670–4672.
- [8] Q. Huang, D.D. DesMarteau, *Chem. Commun.* (1999) 1671–1672.
- [9] Q. Huang, Ph.D. Thesis, Clemson University, 2000.
- [10] P.A. Bernstein, F.A. Hohorst, D.D. DesMarteau, *J. Am. Chem. Soc.* 93 (1971) 3882–3886.
- [11] D.D. DesMarteau, *Inorg. Chem.* 11 (1972) 193–195.
- [12] P.A. Bernstein, D.D. DesMarteau, *J. Fluorine Chem.* 2 (1972/1973) 315–320.
- [13] F.A. Hohorst, D.D. DesMarteau, *Inorg. Chem.* 13 (1974) 715–719.
- [14] F.A. Hohorst, D.D. DesMarteau, *J. Inorg. Nucl. Chem., Suppl.* (1976) 63–66.
- [15] N. Walker, D.D. DesMarteau, *J. Am. Chem. Soc.* 97 (1975) 13–17.
- [16] E.R. Falardeau, D.D. DesMarteau, *J. Am. Chem. Soc.* 98 (1976) 3529–3532.
- [17] L. Brigante, D.D. DesMarteau, *J. Fluorine Chem.* 53 (1991) 181–197.
- [18] W. Navarrini, L. Brigante, S. Fontana, V. Tortelli, A. Zedda, *J. Fluorine Chem.* 71 (1995) 111–117.
- [19] W. Navarrini, V. Tortelli, A. Russo, S. Corti, *J. Fluorine Chem.* 95 (1999) 27–39.
- [20] A. Russo, D.D. DesMarteau, *Inorg. Chem.* 34 (1995) 6221–6222.
- [21] A. Russo, D.D. DesMarteau, *Angew. Chem. Int. Ed. Engl.* 32 (1993) 905–907.
- [22] H. Burger, P. Weinrath, G.A. Arguello, B. Julicher, H. Willner, D.D. DesMarteau, A. Russo, *J. Mol. Spectrosc.* 168 (1994) 607–620.
- [23] D.E. Young, L.B. Anderson, W.B. Fox, *J. Chem. Soc. D* (1970) 395.
- [24] A. Sekiya, D.D. DesMarteau, *Inorg. Chem.* 20 (1981) 1–3.
- [25] A. Sekiya, D.D. DesMarteau, *J. Org. Chem.* 46 (1981) 1277–1280.
- [26] S.-C. Chang, D.D. DesMarteau, *Polyhedron* 1 (1982) 129–130.
- [27] S.-C. Chang, D.D. DesMarteau, *J. Org. Chem.* 48 (1983) 771–774.
- [28] S.-C. Chang, D.D. DesMarteau, *Inorg. Chem.* 22 (1983) 805–809.
- [29] Y.Y. Zheng, C.W. Bauknight, D.D. DesMarteau, *J. Org. Chem.* 49 (1984) 3590–3595.
- [30] C.W. Bauknight, D.D. DesMarteau, *J. Org. Chem.* 53 (1988) 4443–4447.
- [31] D.D. DesMarteau, unpublished results.
- [32] S. Singh, D.D. DesMarteau, S.S. Zuberi, M. Witz, H.-N. Hwang, *J. Am. Chem. Soc.* 109 (1987) 7194–7196.
- [33] G.S. Lal, G.P. Pez, R.G. Syvret, *Chem. Rev.* 96 (1996) 1737–1755.
- [34] W. Ying, D.D. DesMarteau, Y. Gotoh, *Tetrahedron* 52 (1996) 15–22.
- [35] W. Ying, D.D. DesMarteau, G.B. Jones, in: *Proceedings of the 215th National ACS Meeting*, Dallas, TX, USA, March 29–April 12, 1998, ORGN 11.