Efficient Preparations of Fluorine Compounds

Edited by
HERBERT W. ROESKY

With a Foreword by Nobel Laureate, Karl Barry Sharpless

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A JOHN WILEY & SONS, INC., PUBLICATION

Published by John Wiley & Sons, Inc., Hoboken, New Jersey
Published simultaneously in Canada.

Library of Congress Cataloging-in-Publication Data:

Efficient preparations of fluorine compounds / edited by Herbert W. Roesky.
pages cm
Includes index.
ISBN 978-1-118-07856-3 (hardback)
1. Fluorine compounds. I. Roesky, H. W., editor of compilation.
QD181.F1E34 2012
546′.7312–dc23

2012025732

Printed in the United States of America

ISBN: 9781118078563

10 9 8 7 6 5 4 3 2 1

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FOREWORD

When Herbert W. Roesky asked if I might write a foreword for his book, I accepted instantly, without even glancing at the list of authors or topics! The reason is very simple and it goes back many years.

Herbert W. Roesky and I have only met in person on a few occasions, yet I feel I know him well, mainly because I read his early papers in the Chemistry Library at Stanford where I was a graduate student in the 1960s. In hindsight, I realize we both like the idea of mixing up simple, readily available chemicals from all around the periodic table and seeing what happens. There are vast *terrae incognitae* of descriptive chemistry throughout "the table" still waiting to be entered that could provide access to materials and functions not yet imagined.

Berzelius was the first to make the distinction between organic and inorganic compounds, and to strictly entail their origins as animate and inanimate, respectively. The first shock for believers in the *vis vitalis* origin was delivered by Berzelius's own student, Friedrich Wöhler, who, in an 1828 issue of *Annalen der Physik und Chemie* disclosed the synthesis of "organic" urea by simple union of two "inorganics": water and isocyanate. Organic chemists since Wöhler rationally know that natural products contain no 'magic' force or aura. Nevertheless, the synthesis of natural products has long been and remains a central research endeavor in organic chemistry. In retrospect, this bias was very likely ordained by the field's "birth" under vitalism.

Every chemist needs to know physical chemistry, just as every natural scientist needs to know the basic laws of physics, above all thermodynamics. But, beyond that, I prefer to just be a chemist. The idea of there being organic and inorganic chemists is bad enough, but today there are now so many qualifiers before *chemist* I suggest we need to start over. The only subtype of chemist I am not ashamed of being is a "reactivity" chemist or a 'process' chemist, which are nearly the same thing and which I will define as a *real* chemist for the moment. A *real* chemist should have a quick, hence intuitive sense, of the most likely chemical reactions occurring when any element, or simple compound thereof, is combined with others from around *The Table*.

In my view, process/reactivity chemists are a breed apart, and, in fact, are the only real chemists. Fluorine chemists, for example, are by definition good process chemists or they could not survive, literally! Many years of experience, together with deep and catholic knowledge of chemical reactivity principles, is the important coin in this realm. The specific backgrounds of process chemists matter little, but they are united by an intense focus on issues affecting chemical reactivity and have a sixth sense for the critical points in the overall sequence. The best of this breed take great

pride in anticipating serious obstacles and avoiding them altogether. Of course, even the most carefully considered routes hit unknowable barriers in the real world. For a gifted process chemist, such unexpected encounters elicit excitement, not anxiety. I personally like the cases where the fix involves the realization that one or more of the fundamental reaction parameters is the culprit.

For example, it is not uncommon for the pH to take a damaging excursion when a process aims for production scales. On a small lab scale, with everything being added quickly the pH problem is barely noticeable. However at scale, where one of the crucial reactants must be added slowly for safety reasons, there will be predictable circumstances in which the pH will transit a wide range over the course of the addition stage. This problem is easily solved by having the right buffer system present. This may sound like trivial "reaction doctoring" but, when it works perfectly as planned, it makes my day. Reactions that proceed smoothly—as if gliding along the desired path—can leave the chemist in charge with the whimsical sense of wielding power over the molecules, which of course is just plain absurd!

The contributors to this volume are all "reactivity hounds," hence real chemists by definition. The level of experimental detail here is extraordinary and thus fully enabling for those less experienced in dealing with highly reactive species. Nearly all the famous names in fluorine chemistry were included by the editor. I imagine he is hard to turn down in any case, but his plan was also compelling: reach out to all chemists with favorite recipes and transformations from the best in the field.

When I am with fellow process chemists or following their recipes, I love to glean the "hints" for success that inevitably pop up. These "hints" are precious gems that need years in the trenches to reach crystalline perfection. I can see this book serving researchers and students for years to come in the many fields dependent on new compounds possessed of new or better properties. Fluorine is already famous as a giver of unique, even unimagined, properties. The practical value of fluorine substitution in molecules can only continue to grow. Fluorine is abundant in the Earth's crust as gem quality crystalline forms of CaF_2, so its uses in the future are limited only by existing reactivity constraints on crucial reaction paths.

Chemists' power/value to society derives almost entirely from our ability to manipulate reactivity. Some reactions are easily manipulated; at the other extreme are reactions that we may never succeed in manipulating. Fluorine chemistry is an area rich in reactivity constraints but also in compounds with valuable properties, and is thus a fertile hunting ground for chemists. As chemists, it falls to us to either lower the constraining barrier for the desired reaction, or discover workaround routes skirting the high passes.

In short, I see a very bright future for new fluorine-containing products. If you are the monovalent element at the end of the electronegativity universe, your presence in a molecule could prove absolutely crucial for function. A stand-in (e.g., C-Cl) for a C-F group might suffice in some applications but, wishful thinking aside, an **honest** surrogate for a C-F unit does not exist—nothing even comes close.

KARL BARRY SHARPLESS

PREFACE

The idea to publish a book with the title *Efficient Preparations of Fluorine Compounds* resulted on behalf of two observations. Firstly, about 20% of pharmaceutical products as well as 30% of agrochemical compounds contain fluorine, and the proportion is increasing. This indicates the importance of organofluorine compounds worldwide. Secondly, the interest in fluorine chemistry at the university level is steadily decreasing during the last two decades. Therefore authors working in the fluorine field were asked to write about their discoveries in a way that young scientists may reproduce their results, and use the fluorine-containing compounds to add new facets to their research.

This book brings together contributions written by leading researchers and covering a wide scope of fluorine chemistry. Karl O. Christe describes an easy laboratory method for the preparation of elemental fluorine as the first experiment. This method guarantees an easy access to fluorine when compared with that of Henri Moissan. He discovered fluorine in 1886 by electrolysis of potassium fluoride in anhydrous hydrogen fluoride. Moissan was awarded the Nobel Prize in Chemistry in 1906 for the discovery of "le fluor."

Fluorine is a poisonous diatomic gas at room temperature. It is a very versatile reagent and can form compounds with almost every element. A milestone in fluorine chemistry was achieved in 1962, when Neil Bartlett obtained the noble gas compound Xenon fluoride. The general accepted view that noble gases were inert ended with this experiment. It led to the preparation of a great number of noble gas fluoride and their derivatives.

Fluorine continues to fascinate chemists who overcome the fear of handling fluorine for the preparation of new compounds and materials. Fluorine compounds play a key role in electric cars, electronic devices, space technology, pharmaceuticals, and agrochemicals. However, especially in fluorine chemistry, the words of Winston Churchill are true: "Success is the ability to go from one failure to another with no less of enthusiasm."

Finally and most importantly, I am very thankful to the authors for their excellent contributions, and I hope that this book will inspire a young generation to do research in fluorine chemistry.

HERBERT W. ROESKY

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CHAPTER 1

Preparation of Elemental Fluorine

KARL O. CHRISTE

Although the syntheses of fluorinated compounds usually do not involve the use of elemental fluorine (F_2), F_2 can be considered to be the mother of all fluorine compounds. Because fluorine is the most electronegative element, its synthesis presented an enormous challenge and had been pursued unsuccessfully for almost a century, until finally in 1886 Moissan succeeded to prepare it electrochemically [1]. For the next 100 years, every major chemistry textbook stated that for the above reasons F_2 cannot be prepared by purely chemical means. This dogma was shattered in 1986 by Christe who prepared and isolated in a 3-day tour de force [2] F_2 in high yield from potassium hexafluoromanganate (K_2MnF_6) and antimony pentafluoride (SbF_5), two compounds that had already been known in the days of Moissan. He used a combination of two very simple and well-known principles for his synthesis: (1) that stronger acids can displace weaker acids from their salts and (2) that high oxidation states are stabilized by formal negative charges. Thus, a high oxidation state complex fluoro anion can be prepared with relative ease and when converted by the acid displacement reaction to its neutral parent molecule, the latter, if thermodynamically unstable, might spontaneously decompose to a lower oxidation state and thereby liberate F_2.

$$K_2MnF_6 + 2\,SbF_5 \rightarrow 2\,KSbF_6 + [MnF_4]$$

$$2\,[MnF_4] \rightarrow 2\,MnF_3 + F_2$$

In view of the relative ease, simplicity, and historical significance of this synthesis, it has been included in this book. It might be attractive for demonstration purposes or when only smaller amounts of fluorine are desired and the costs of either setting up an electrochemical cell or a compressed F_2 gas-handling system are prohibitive. Since SbF_5 is commercially readily available from at least 38 global and 14 U.S.

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suppliers, its synthesis is not described in this chapter. However, if desired, it can be prepared in high yield by purely chemical means from $SbCl_5$ and HF [3]. The other starting material, K_2MnF_6, is more difficult to buy commercially and, therefore, its one-step, one-pot synthesis [2,4,5] from $KMnO_4$, KF, H_2O_2, and aqueous HF is described here.

$$2\,KMnO_4 + KF + 10\,HF + 3\,H_2O_2 \rightarrow 2\,K_2MnF_6 \downarrow + 8\,H_2O + 3\,O_2$$

1.1 PREPARATION OF K_2MNF_6

Apparatus Two 4-L polyethylene beakers, Teflon-coated magnetic stirrer, polyethylene Buchner funnel with Teflon filter paper, safety glasses, laboratory coat, and protective gloves.

Chemicals $KMnO_4$, KF, 48–50% reagent grade aqueous HF (caution: technical grade HF should be avoided because it contains a significant amount of H_2SiF_6, resulting in a product containing significant amounts of K_2SiF_6 as impurity), and 30% aqueous H_2O_2.

Attention! Safety glasses and protective gloves must be used at all times because HF and H_2O_2 can cause skin burns.

Experimental Procedure A 4-L polyethylene beaker, equipped with a Teflon-coated magnetic stirring bar, is charged with 50% aqueous HF (1 L) and cooled with an ice bath. Then KF (240 g, 4.13 mol) and finely powdered $KMnO_4$ (15 g, 94.9 mmol) are added and the mixture is vigorously stirred for 15 min. The stirring is stopped and any undissolved material is allowed to settle. The supernatant solution is decanted into a second beaker to assure the absence of any undissolved $KMnO_4$, which could make the endpoint recognition in the subsequent titration step difficult. To the cold dark purple solution, 30% aqueous H_2O_2 is slowly added with an eyedropper. After the addition of each 5–10 drops, further additions are halted until O_2 evolution has ceased. After the addition of about 20 mL of H_2O_2, the endpoint is being approached. A brownish golden precipitate is formed and the endpoint can be judged by stopping the stirring and observing the color of the supernatant solution. The reaction is complete when the color of the solution has changed from purple to medium reddish brown. The golden yellow K_2MnF_6 precipitate is collected using a plastic Buchner funnel with Teflon filter paper. The precipitate is washed twice with cold acetone (10 mL each) and pumped to dryness to yield 18.44 g (78.6% based on $KMnO_4$) of yellow K_2MnF_6.

Characterization Data Yellow, non-hygroscopic, crystalline solid. IR (AgCl, cm^{-1}): $\bar{\nu}$ 620 vs, 340 s. RA (glass melting point (mp) capillary): $\bar{\nu}$ 601 vs, 512 m, 307 ms. Crystal data: hexagonal, $P6_3mc$, $a = 5.719(1)$ Å, $c = 9.330(3)$ Å [6].

Application In addition to serving as convenient starting materials for the chemical synthesis of F_2, alkali metal hexafluoromanganates can be used in acidified HF solutions as fluorinating agents or as starting materials for the synthesis of $(NF_4)_2MnF_6$ for solid propellant NF_3/F_2 gas generators for chemical HF/DF lasers [7,8].

1.2 PREPARATION OF F_2

Apparatus The apparatus used in Christe's original synthesis of F_2 is shown in Figure 1.1, which shows a typical set up for the transfer of a compound of relatively low volatility, such as SbF_5, in a dynamic vacuum from a storage vessel into a reaction U-tube. The reactor can be a $^1/_2$-in. or $^3/_4$-in. o.d. Teflon-FEP (perfluoroethylene/perfluoropropylene copolymer) or metal (Monel, nickel, copper, or stainless steel) U-tube reactor, closed at both ends with Hoke stainless steel valves. Since Teflon-FEP starts softening and being attacked by the nascent fluorine at about 200 °C, the use of a Monel U-tube is preferred, unless the visual observation of the reaction is desired. The connections can be made with either Teflon or preferentially metal tubing. The T-piece connector between the SbF_5 vessel and the reactor allows evacuation and passivation of the connection. The

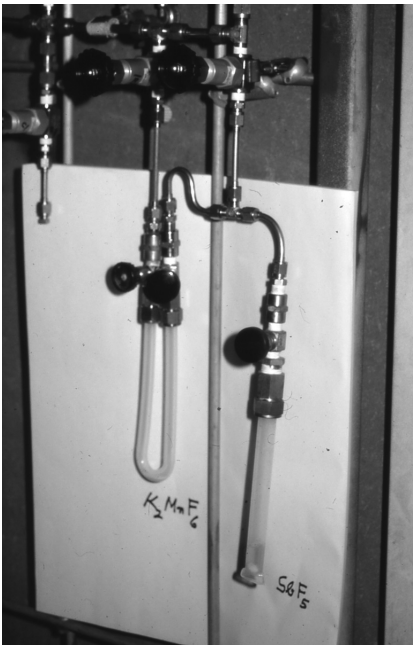

FIGURE 1.1 The original apparatus used by Christe in 1986 for the first chemical synthesis of F_2. (For a color version of the figure, please see color plates.)

exit side of the U-tube reactor is also connected to the vacuum manifold. The Teflon U-tube can be prepared by tightly packing a desired length of straight Teflon tubing with crystalline NaCl, closing both ends with rubber stoppers, heating the central part of the tube with a heat gun to the softening point of the Teflon, wrapping it 180° around an approximately 2-in. o.d. metal cylinder, allowing it to cool and removing the NaCl by pouring it out, and washing out any imbedded salt with water. The metal U-tubes are easily prepared with a tube bender. Safety requirements include face shield, safety glasses, laboratory coat, and protective gloves.

Chemicals Silicon-free $K_2[MnF_6]$, distilled SbF_5.

Attention! F_2 is a highly reactive gas with a very intense halogen odor and is easily detected already at very low concentrations (0.02 ppb) by its characteristic smell. Inhalation or contact with the skin must be strictly avoided. Laboratory coat, face shield, safety glasses, and protective gloves must be used at all times.

Experimental Procedure A passivated (with F_2 or preferentially ClF_3) $^3/_4$-in. o.d. Teflon-FEP ampoule, equipped with a valve, and a passivated $^1/_2$-in. o.d. Monel U-tube, closed at each end by a valve, are loaded in the dry box with distilled SbF_5 (~7 g or 32 mmol) and silicon-free K_2MnF_6 (1.912 g, 7.744 mmol), respectively, and are then connected to the vacuum manifold as shown in Figure 1.1. The connections are leak-checked and passivated. The Monel U-tube is cooled to −196 °C, and the SbF_5 is transferred in a dynamic vacuum from the Teflon ampoule to the Monel U-tube. After closing the valves, the Monel reactor is heated with an oil bath to 180 °C for 1 h and then cooled to −78 °C. The only product volatile at this temperature is the desired F_2 (56 mg, 1.47 mmol) in 38% yield, based on the limiting reagent K_2MnF_6.

Assay of the F_2 The formation, purity, and exact amount of fluorine formed in the above experiment can be verified easily by reacting the gas with mercury (Hg) and measuring the change in the volume of the gas by standard pressure–volume–temperature (PVT) techniques and monitoring the weight uptake of Hg. A typical experimental setup for this step is shown in Figure 1.2. Care must be taken to pump on Hg only at low temperatures (–78 °C or −196 °C), because Hg has some volatility at ambient temperature and even small losses will severely impact this analysis due to the high atomic weight of Hg.

Characterization Data Faint yellow-green, highly toxic, corrosive gas, mp −219.62 °C, boiling point (bp) −188.12 °C, standard atomic weight, 18.9984032 g/mol, first ionization energy, 1681.0 kJ/mol [9].

Waste Disposal The aqueous HF solution from the K_2MnF_6 preparation can be disposed of as NaF after neutralization with sodium bicarbonate. The $KSbF_6 \cdot nSbF_5$ and Mn-containing by-products from the chemical synthesis of F_2 have to be collected and properly deposited in a labeled container for toxic metal waste.

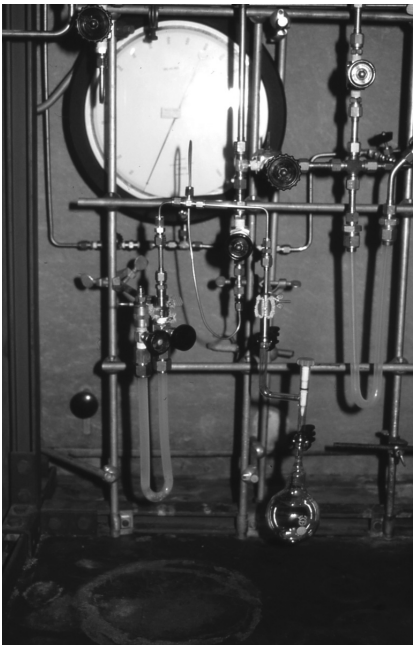

FIGURE 1.2 The original apparatus used by Christe in 1986 for the assay of F_2. On the left is the Teflon-FEP U-tube reactor containing the F_2 gas. It is connected to a glass bulb containing the mercury, and the whole system is connected to the Heise gauge for the pressure measurements. (For a color version of the figure, please see color plates.)

Application Due to its high reactivity and toxicity, F_2 is rarely used as a fluorinating agent in industrial processes. The major applications are the preparations of UF_6 for uranium isotope separation and SF_6 as a dielectric medium in transformers, and its use in the electronics industry for plasma etching and chamber cleaning.

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CHAPTER 2

Preparation of Highly Active Cesium Fluoride

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Cesium fluoride (CsF) acts as a fluoride ion source in organic and inorganic chemistry. For example, it is used for C–Si cleavage reactions, halogen exchange reactions, or the isolation of highly coordinated anions AF_n^- or AF_n^{2-}. There are many sources for fluoride ions. But obviously the closest relatives to CsF, namely, NaF, KF, and RbF, are not so effective, although they are cheaper and easier to obtain in pure state. Alternatively, there is a good number of organic ammonium fluoride, the most prominent example is $(CH_3)_4NF$. Many of these are not easily prepared, and usually are thermally unstable, even $(CH_3)_4N^+F^-$ decomposes above 150 °C.

From a structural viewpoint, CsF is a very simple compound, having the NaCl structure. This is insofar surprising because the ionic radii of Cs^+ and F^- are such that a CsCl structure should be more stable, if only the ionic radii are considered. Therefore, CsF may be described as having an inverted NaCl structure, where the large Cs^+ ions form a cubic closest packing and the smaller F^- ions fill octahedral holes.

The unfortunate cation–anion size relation may explain the reactivity of CsF: It is extremely hygroscopic, similar to P_4O_{10}. Hydration would take place at the anionic sites to increase their sizes. Therefore, any CsF varies in reactivity, depending on the water content.

For many purposes, extreme dryness of CsF may not be necessary; in some cases, it may be too reactive, since it may catalyze side reactions. The reason why certain reactions of CsF are "source dependent" is certainly explained by its water content and surface area.

Efficient Preparations of Fluorine Compounds, First Edition. Edited by Herbert W. Roesky.

2.1 PREPARATION OF PURE CsF

Apparatus Platinum cup, heating furnace up to 800 °C, dry box, ball mill, and stainless steel plate.

Chemicals CsF, HF/H_2O.

Attention Safety glasses and gloves must be used at all times.

Caution All reactions should be carried out in a well-ventilated hood, if not done in closed systems (dry box, ball mill).

Experimental Procedure A small amount of CsF is dissolved in water and tested for neutrality. If it is basic, a few milliliters of HF/H_2O is given to the bulk amount. This is placed into the platinum cup and slowly heated up to 650 °C, until all solid has melted. As soon as this state is reached, the molten CsF is poured on the stainless steel plate, where it solidifies.

CsF is volatile at its melting point, so prolonged heating will make some or all CsF disappear! Mp 682 °C, bp 1251 °C. The molten CsF must be poured out of the platinum cup, because solid CsF, if it remains in there, will be difficult or impossible to get out without destroying the platinum vessel.

The solidified CsF chunks with the stainless steel plate are immediately, when they are still very hot, brought into the evacuation chamber of the dry box. The dry box should have a moisture content of 1 ppm or less. CsF is given into the ball mill capsule that needs to be kept free from moisture. The CsF is powdered in the ball mill. It is transferred back into the dry box, but even there it needs to be stored in airtight vessels.

The first traces of water will change the appearance of this CsF: it will start to become sticky, less powdery, very much like physical change of the uptake of water by P_4O_{10}.

Recycling of used CsF If larger amounts of used CsF have been accumulated, recycling may be considered. If it is without cationic impurities, the Cs salt mixture is dissolved in concentrated sulfuric acid in a platinum bowl. It is heated to red heat, until all volatiles have disappeared to about 800 °C. The solid, pure Cs_2SO_4 (mp 1019 °C) is weighted and reacted in water with the exact equivalent of $Ba(OH)_2$. Filtration of $BaSO_4$ and neutralization with HF/H_2O gives an aqueous solution of CsF, which then is dehydrated to CsF as described above. This recycled CsF will inevitably contain a small amount of a barium impurity.