

ELECTROCHEMICAL FLUORINATION OF ORGANIC COMPOUNDS

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This review covers the recent remarkable advances in electrochemical partial fluorination of organic compounds such as olefins, aromatic compounds, carbonyl compounds, heteroatom compounds and heterocycles.

INTRODUCTION

New applications for fluorinated compounds are continuously being found. In areas such as agrochemicals, pharmaceuticals and fine chemicals, the enhanced activity of compounds in which one or more hydrogen atoms have been replaced by fluorine is the subject of a large body of research in universities and companies around the world.¹⁻⁹ It is estimated that between 40 and 45% of all new agrochemicals being developed contain fluorine. The physical, chemical and biological properties of chemical compounds, including boiling points, surface energies, polarity, acidity and reactivity can be greatly altered by substitution with one or more fluorine atoms. These effects are in general result of the following facts:

The size of fluorine is similar to that of hydrogen. Fluorine can, therefore, imitate hydrogen in enzymatic processes.

The strength of the C-F bond leads to increased thermal stability.

Fluorine is highly electronegative.

The high lipophilicity of the C-F bond.

The high reactivity can be attributed to a combination of the very weak F-F bond and the very strong bonds of fluorine to most other elements. The strength of C-H, C-C and C-F bonds in highly fluorinated compounds gives rise to the extraordinary thermal and oxidative stability that generally characterized fluorine-containing organic compounds. Of all types of bonds in organic

chemistry, the carbon-fluorine bond is the most inert and the most resistant to oxidative degradation. In addition, fluorine can participate in hydrogen bonding interactions as an electron donor.¹⁰

The introduction of fluorine substituents into an organic molecule can radically change the physico-chemical properties of that molecule. In the course of the last decades, several investigations leading to the developing of new fluorination methods for organic compounds were made.

Partially fluorinated organic compounds are prepared by two different approaches: (i) by insertion of a group already containing C-F bonds into an existing molecule (the building-block approach), or (ii) by creating new C-F bonds by fluorination. The building-block approach makes use of the traditional methods of organic synthesis, and small molecules such as fluoroalkyl iodides and bromides and hexafluoroacetone are used mainly in the synthesis of fluoroaliphatic compounds. For the synthesis of fluoroaromatic compounds important commercial building blocks include monofluorobenzene and benzotrifluoride.

In many cases, the use of these reagents can be highly hazardous and selectivities are low. In addition to these drawbacks, both inorganic and organic by products can be produced in large quantities.

On the contrary, electrochemical fluorination methodology proved to be highly attractive and more promising than the above-mentioned methods and it serves as a new tool in fluorination of organic compounds.¹¹⁻¹³

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ELECTROCHEMICAL FLUORINATIONS

Electrochemistry has for almost 50 years made a significant contribution in the area of fluorination of organic compounds with the development and commercialization of the Simons process.¹⁴ By this route, it is possible to produce perfluorinated compounds (compounds in which all the hydrogen atoms are replaced by fluorine) and at the same time some functional groups are unaffected (Electrochemical Perfluorination, **ECPF**). Although in many ways analogous to complete fluorination with fluorine, in which C-C bond cleavage and rearrangements also take place to a great extent, usually with poor selectivities and yields, the electrochemical approach offers the considerable advantages of not having to handle fluorine gas and being able in many cases to conserve molecule functionality.¹⁵

In the last years, the Electrochemical Partial Fluorination (**ECF**) is used to achieve highly selective fluorinations by introduction of either single fluorine atoms or small fluorinated groups into organic molecules of interest. Much effort has been spent in the past three to four decades to increase the selectivity and yield of this type of reactions, and many synthetically useful results have been reported.

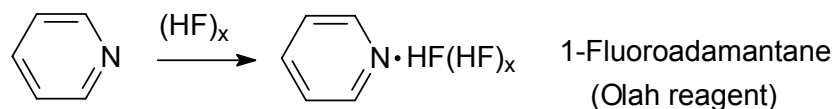
In contrast with chemical methods using fluorinated reagents, which are hazardous, difficult

to handle, or very costly, electrochemical partial fluorination is an ideal method for direct fluorination since fluorine atoms can be introduced into organic molecules in one step under safe conditions.

To overcome the need to carry out fluorinations with anhydrous hydrogen fluoride at superatmospheric pressure, the possibility of using less volatile complexes of HF with various n-donor bases was studied.

However, electrochemical partial fluorination has not been developed owing to low selectivity for the fluorination, low nucleophilicity of fluoride ions, and passivation of electrodes.

In 1970, the first major breakthrough in electrochemical partial fluorination occurred when triethylamine-3HF ($\text{Et}_3\text{N}\cdot 3\text{HF}$) dissolved in acetonitrile was employed as electrolyte in an anodic fluorination of naphthalene. Nuclear monofluorination of aromatic compounds could be achieved in this medium. Since then, electrochemical partial fluorinations of many organic compounds have been reported. In 1973, George Olah reported the use of a remarkably stable pyridinium poly(hydrogen fluoride), (30% pyridine - HF 70%) as convenient and inexpensive fluorinating agent for hydrofluorination of alkenes and alkynes, in tetrahydrofuran solution (Olah's reagent) (Scheme 1).¹⁶



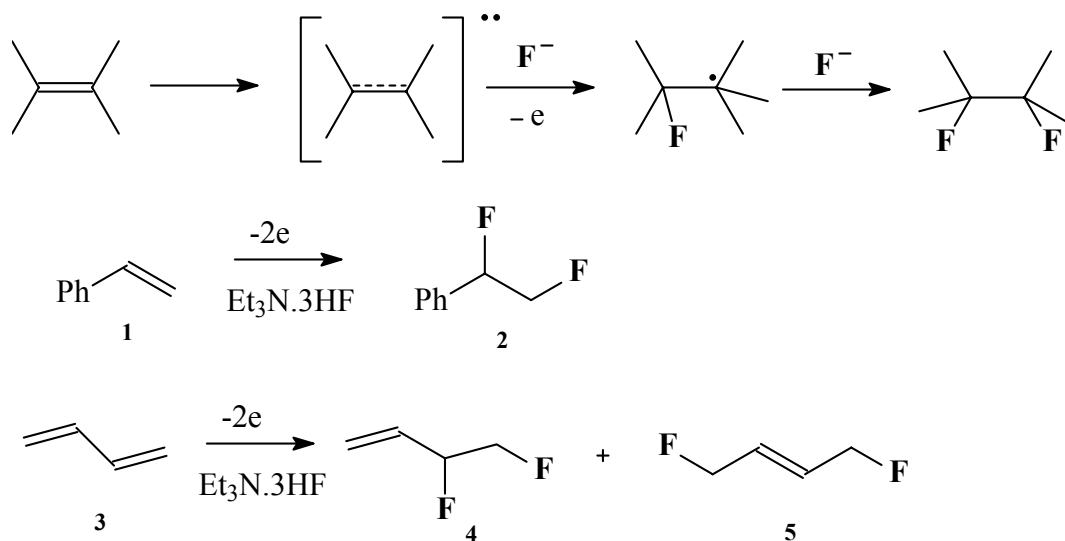
Scheme 1

The hydrogen fluoride-pyridine reagent can be used for the hydrofluorination of alkenes,¹⁷ alkynes,¹⁷ cyclopropanes,¹⁷ and diazo compounds,¹⁸ the halofluorination of alkenes,¹⁹ the preparation of fluoroformates from carbamates,²⁰ the preparation of α -fluorocarboxylic acids from α -amino acids,²¹ and as a deprotecting reagent in peptide chemistry.²²

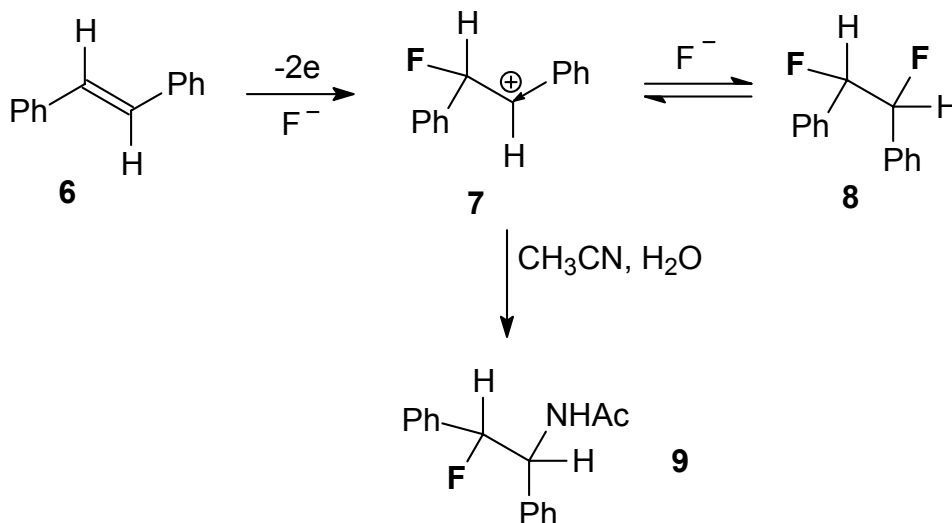
Olefins and Derivatives. The anodic fluorination of double bonds using different fluorine sources and electrolytic solvents proceeds through *cis* addition to give the corresponding *vicinal* difluorocompounds.²³ Electrofluorination of styrene (**1**) using $\text{Et}_3\text{N}\cdot 3\text{HF}$ as fluorine source and acetonitrile as electrolytic solvent gave the corresponding *vic*-difluorocompound **2** in good yields. If a conjugated diene is used as substrate for

fluorination, for example butadiene (**3**), a 1:2 mixture of 1,2- and 1,4-adducts, **4** and **5** respectively, was obtained (Scheme 2).

The substrates having cation-stabilizing groups on double bond, for example stilbene **6**, underwent fluoroacetamidation in $\text{Et}_4\text{NF}\cdot 3\text{HF}/\text{MeCN}$.²⁴ The monofluorinated cation intermediate **7** is stabilized by phenyl group (Scheme 3). Two competitive reactions occur owing to competition of the two nucleophiles H_3F_4^- and MeCN, one of them by the attack of fluoride ion yielding difluoro-product **8**, the other one by the attack of MeCN at carbocation **7**. A mixture of **8** and **9** is obtained. To avoid the formation of acetamides, the choice of a solvent with a lower nucleophilicity such as CH_2Cl_2 may be effective.



Scheme 2



Scheme 3

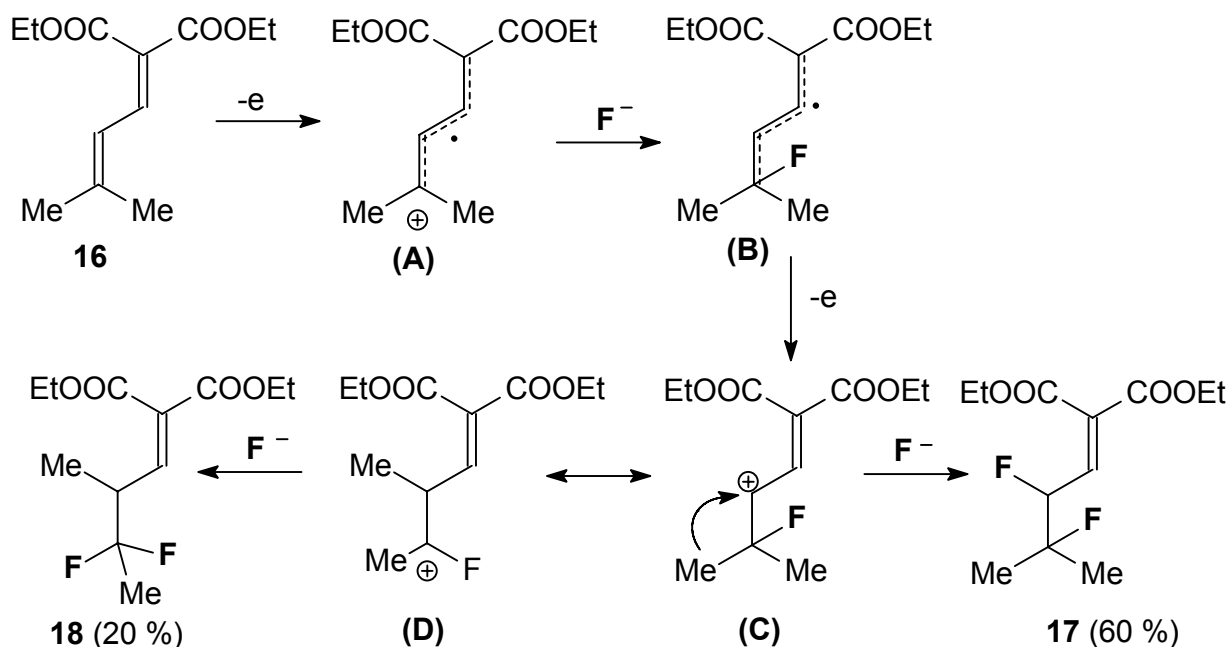
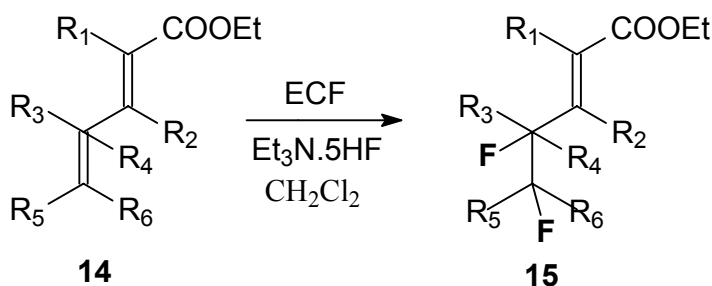
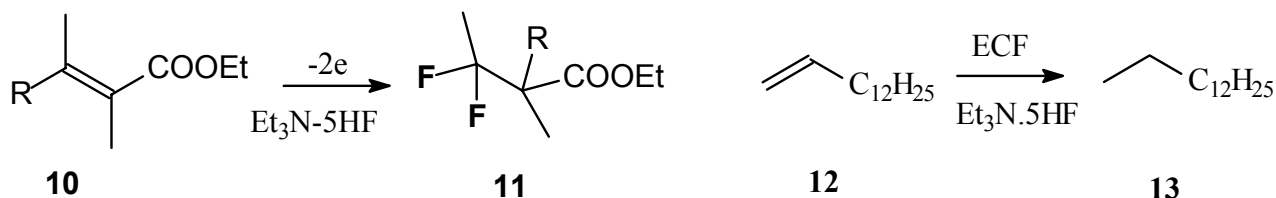
One of the big problems of electrochemical partial fluorination is the anodic passivation. For solving these problems, other electrolytes, such as $\text{Et}_4\text{NF}\cdot 4\text{HF}$, $\text{Et}_3\text{N}\cdot 4\text{HF}$ and $\text{Et}_3\text{N}\cdot 5\text{HF}$ have been developed.^{25,26} $\text{Et}_3\text{N}\cdot 5\text{HF}$ has been found to be an electrochemically highly stable and an excellent electrolyte for the electrochemical fluorination of aldehydes and ketones to produce the corresponding acylfluorides and alkylfluorides in good yields²⁷. In the case of compounds with high oxidation potential, the fluorination is possible using $\text{Et}_3\text{N}\cdot 5\text{HF}$ which is a hard-oxidation electrolyte. But compounds with low oxidation potential are not applied to $\text{Et}_3\text{N}\cdot 5\text{HF}$ as electrolyte, in this case, $\text{Et}_3\text{N}\cdot 3\text{HF}$ was found to afford better results⁴.

Activated Olefins. The electrochemical partial fluorination of α,β -unsaturated esters **10** takes place by the rearrangement of the β -substituted alkyl groups to the α -position to afford *gem*- β,β -difluoroesters **11** in good yields under the pulse electrolysis conditions using $\text{Et}_3\text{N}\cdot 5\text{HF}$ ²⁸ (Scheme 4): Under similar conditions, ECF of an alkene without EWG group (ester), such as dodecene-1, **12**, did not take place and a reductive product, dodecane, **13**, was obtained (Scheme 4).

Dinoiu et al.²⁹ reported the anodic fluorination of conjugated diene esters (**14**) in the presence of $\text{Et}_3\text{N}\cdot 5\text{HF}$ as fluorine source and supporting electrolyte and CH_2Cl_2 as electrolytic solvent. Fluorination occurs at the distal olefin yielding the corresponding *vic*-difluoro compounds **15**. It is

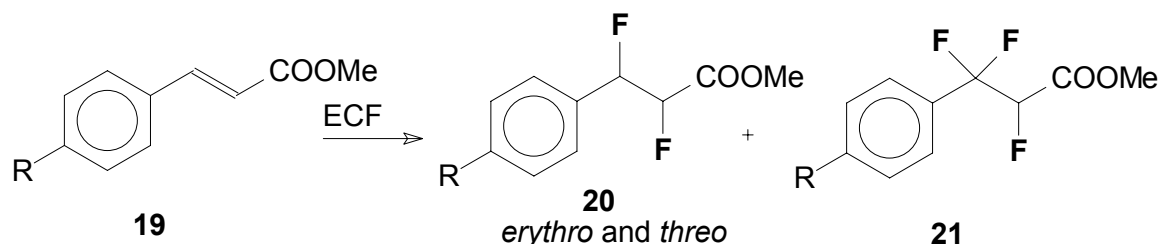
interesting to note that the electrolytic behaviour of conjugated diene ester **14** (having one ester group) is quite different from that of the conjugated diene ester **16** that has two ester (attracting) groups yielding a mixture of *vic*- and *gem*-difluorinated alkene esters, **17** and **18** respectively. It is believed that the presence of another withdrawing group changed the reaction mechanism as is shown in Scheme 5. Two competitive reactions take place at

allylic carbocation (**C**); the two carboxy groups, destabilize carbocation center and methyl group migrates at allylic carbon, a new rearranged carbocation (**D**) is formed, and the second nucleophilic attack of fluoride ion yielded *gem*-difluoro product **18**. In the second reaction mechanism, fluoride ion attacks carbocation (**C**) that is more stable than cation (**D**) and *vic*-difluoro product **17** is formed, as major product.



The anodic fluorination of methyl esters of cinnamic acids **19** was studied by W. Dmowski and T. Kozłowski.³⁰ The expected *vic*-

difluorocompounds **20**, as a mixture of *erythro* and *threo* isomers were obtained along, in some cases, with trifluoroderivatives **21** (Scheme 6).

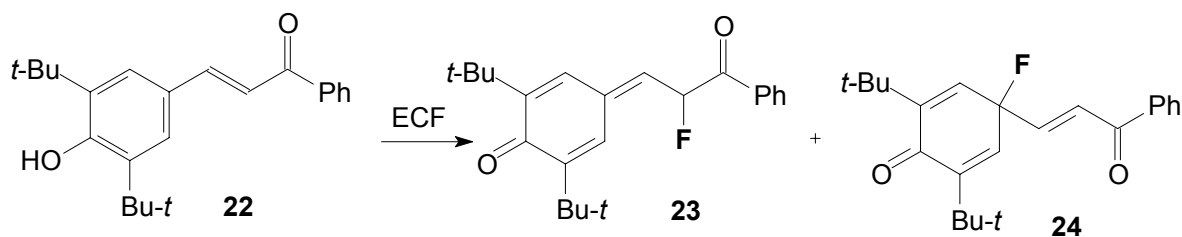


Scheme 6

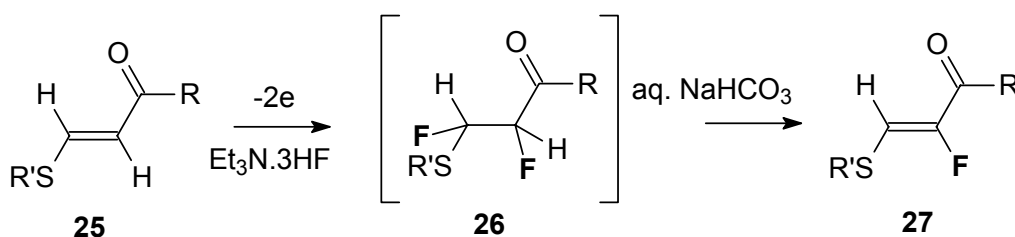
V. Dinoiu and Japanese co-workers³¹ reported the anodic fluorination of some electrophilic alkenes, (alkenes conjugated with electron-withdrawing groups), such as α,β -unsaturated esters (ethyl cinnamates), cinnamitrile, and α,β -unsaturated ketones (phenyl styryl ketone, *t*-butyl styryl ketone and phenyl 3,5-di-*t*-butyl-4-hydroxystyryl ketone) using $\text{Et}_3\text{N}\cdot n\text{HF}$ ($n = 3,5$) and $\text{Et}_4\text{NF}\cdot n\text{HF}$ ($n = 2,4$) as supporting electrolytes and fluorine sources in CH_2Cl_2 as electrolytic solvent.³¹ An interesting fluorination occurs when phenyl 3,5-di-*t*-butyl-4-hydroxystyryl ketone **22** (a

chalcone), was anodically fluorinated in the presence of $\text{Et}_4\text{NF}\cdot 2\text{HF}$ as fluorine source and supporting electrolyte in CH_2Cl_2 as electrolytic solvent (Scheme 7) yielding a mixture of two monofluoro-semiquinone derivatives **23** and **24** in ratio 1:1 (yields are 20% for each of them).

Vinyl sulfides **25** bearing carbonyl functions were electrochemically fluorinated using $\text{Et}_3\text{N}\cdot 3\text{HF}$ in acetonitrile to give the monofluorinated vinyl sulfides **27** stereoselectively.³² The latter compounds were obtained through dehydrofluorination of the adduct intermediate **26** (Scheme 8).



Scheme 7

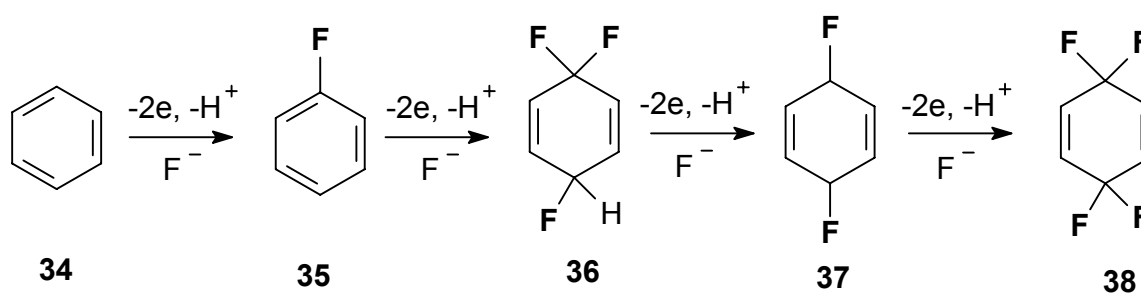
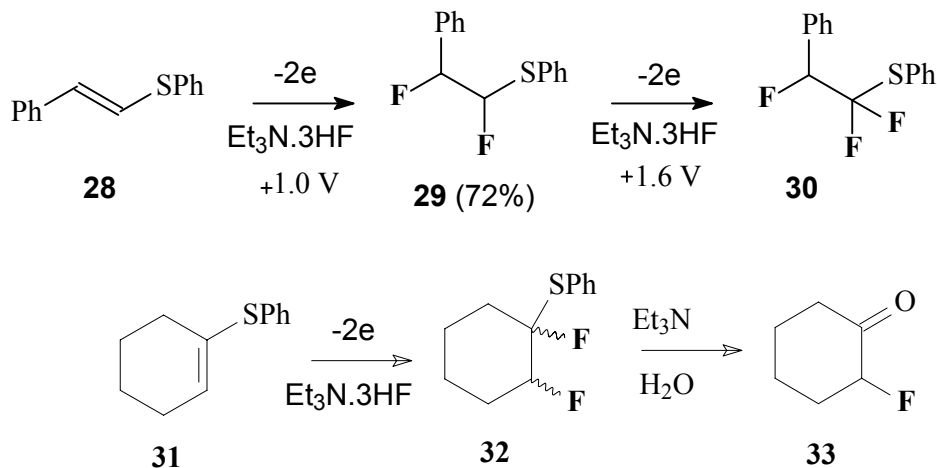


Scheme 8

Anodic fluorination of 2-(phenylthio)styrene (**28**) in $\text{Et}_3\text{N}\cdot 3\text{HF}$ under constant potential gave the *vic*-difluorinated product **29** that upon further fluorination at higher potential yielded the trifluorinated compound **30**.³³ Electrofluorination of 1-(phenylthio)cyclohexene (**31**) resulted in the formation of the 1,2-difluoro-1-phenylthiocyclohexane (**32**) that could be converted into α -monofluorocyclohexanone (**33**) in the presence of traces of Et_3N ,³³ as shown in Scheme 9.

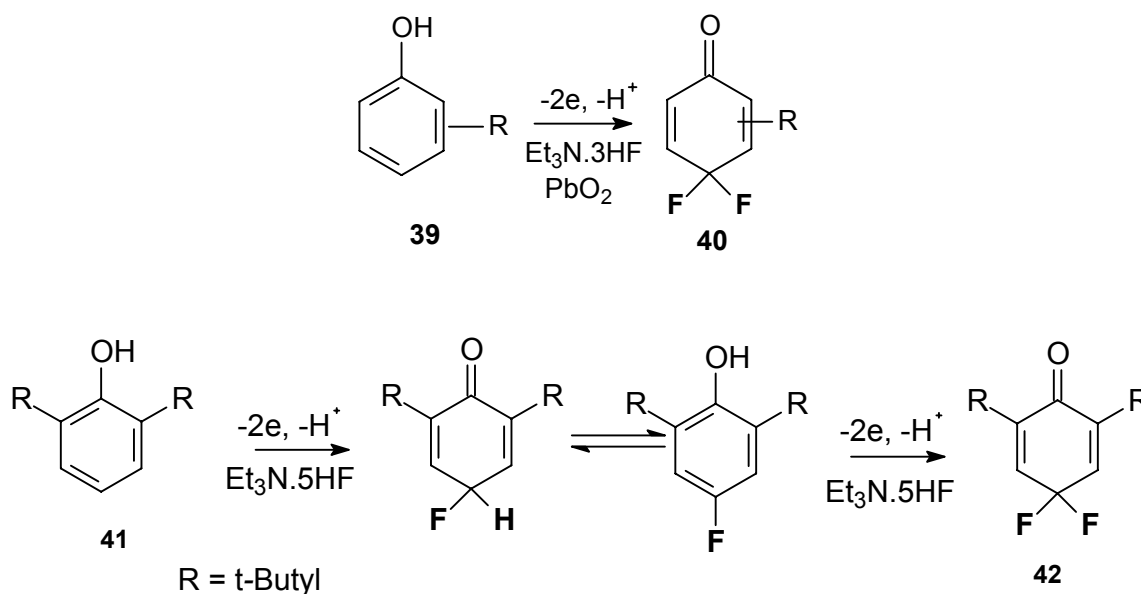
Arenes. G. Olah³⁴ and I.N. Rozhkov³⁵ used hydrogen fluoride base complexes as sources of

fluorine in oxidative fluorination of benzene but owing to the high oxidation potential of benzene, low yields were obtained and passivation occurred at electrode by the formation of polymers. K. Momota et al.³⁶ reported the electrochemical fluorination of benzene, in $\text{Et}_4\text{NF}\cdot 4\text{HF}/\text{MeCN}$, with the formation of 1,4-difluorobenzene (**37**) as main product. Further oxidation of fluorobenzene (**35**) afforded 3,3,6-trifluorocyclohexadiene (**36**), which undergoes dehydrofluorination to give 1,4-difluorobenzene (**37**). A subsequent anodic fluorination of **37** yielded 3,3,6,6-tetrafluorocyclohexadiene (**38**) (Scheme 10).^{37,38}



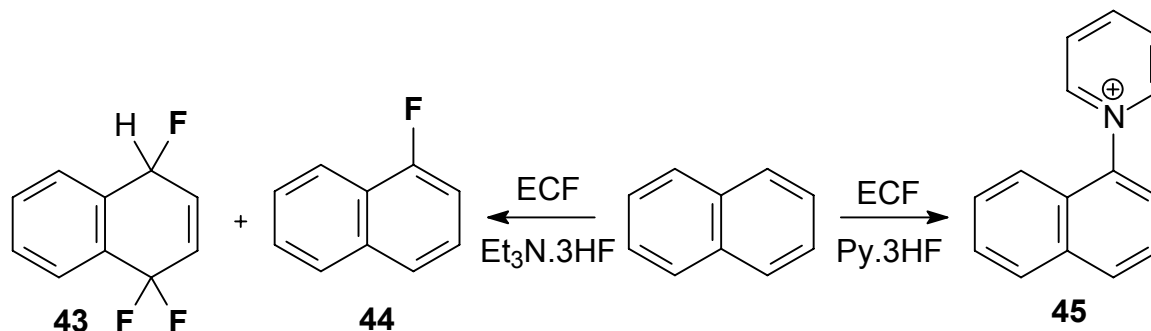
Jan Meurs and Wolf Eilenberg reported a system that overcomes electrode passivation and solvent participation by oxidizing the substrate in neat amine-HF mixtures³⁹. In this way phenols **39** are converted in dienones **40** in an HF/base mixture in the presence of PbO_2 or $\text{Pb}(\text{OAc})_4$ (Scheme 11).³⁹ Without addition of bases no

dienones are formed, but only polymers.⁴⁰ Anodic fluorination of hindered phenol **41** successfully occurred in the presence of $\text{Et}_3\text{N}\cdot 5\text{HF}$ as fluorine source and supporting electrolyte yielding 4,4-difluorocyclohexadien-1-one (**42**)^{41,42} according with the reaction mechanism shown in Scheme 11.



A pronounced amine effect was observed in the electrolysis of naphthalene.⁴³ Using $\text{Et}_3\text{N}\cdot 3\text{HF}$ the electrolysis afforded **43** (18%) together with 1-fluoronaphthalene (**44**, 6%). Using $\text{Py}\cdot 3\text{HF}$ as

fluorine source, not even traces of fluoronaphthalene were formed and the reaction afforded a pyridinium salt **45**, which was isolated in 50% yield (Scheme 12).

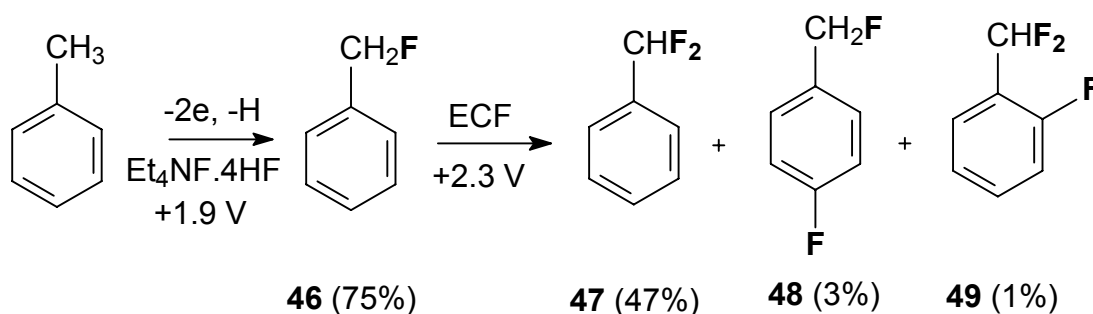


Scheme 12

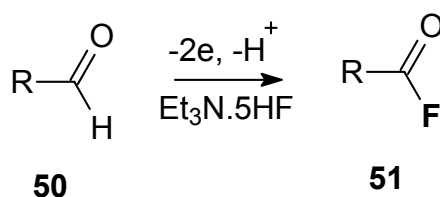
Electrolytic fluorination of toluene in the presence of neat liquid $\text{Et}_4\text{NF}\cdot 4\text{HF}$ gave exclusively benzylfluoride (**46**). Further oxidation of **46** afforded mainly difluoromethylbenzene (**47**), along with small amounts of ring-fluorinated by products **48** and **49** (Scheme 13).⁴⁴

successfully use of $\text{Et}_3\text{N}\cdot 5\text{HF}$ as a more stable and convenient fluorine source and electrolyte in anodic fluorination of aldehydes and ketones. Acyl fluorides **51** were obtained by a selective displacement of formyl hydrogen by fluorine atom in aliphatic aldehyde **50** (Scheme 14).

Carbonyl compounds. Beginning with 1994, N. Yoneda and co-workers⁴⁵⁻⁴⁷ reported the



Scheme 13



R = n-heptyl, 3-heptyl, n-pentyl, t-Bu

Scheme 14

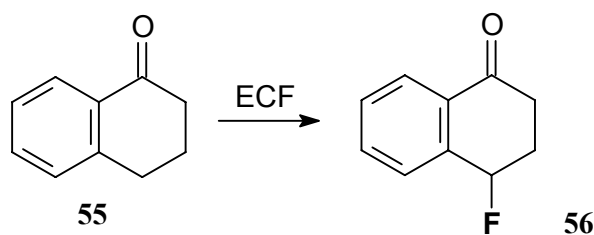
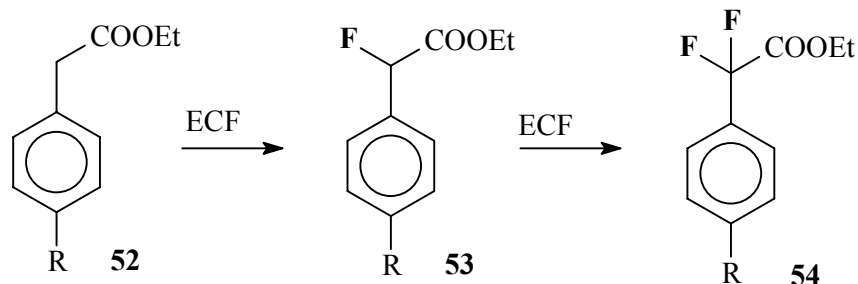
Benzyl derivatives. Dinouï et al.⁴⁸ reported the anodic oxidation of some benzyl derivatives (phenylacetic acids esters) **52**, and 1-tetralone **55** using ammonium fluorides or ammonium tetrafluoroborate as fluorine sources and supporting

electrolytes and CH_2Cl_2 as solvent, which allowed to introduce a fluorine atom in α position of electron withdrawing group. A subsequent oxidation of fluorinated derivative **53**, using $\text{Et}_4\text{NF}\cdot 2\text{HF}$ as fluorine source and CH_2Cl_2 as

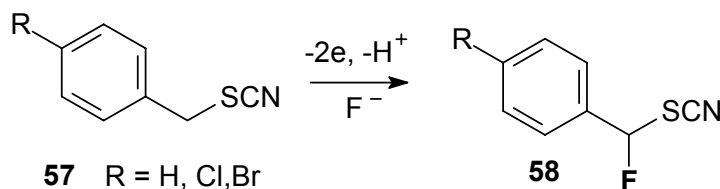
solvent, yields *geminal* difluoro compound **54**, (Scheme 15). It was found that good yields are obtained when the substrates in anodic fluorination contained two or three methoxy groups in aromatic ring. An EC_BEC_N (electrochemical-chemical-electrochemical-chemical) mechanism is widely accepted for that type of fluorinations. The anodic fluorination of benzylphosphonate derivatives $ArCH_2P(O)(OEt)_2$ was carried out under various

conditions to provide the corresponding α -mono- and/or α,α -difluoro-products, $(ArCHFP(O)(OEt)_2)$ and/or $ArCF_2P(O)(OEt)_2$ respectively, in moderate to good yields.⁴⁹

Benzyl thiocyanates **57** were also fluorinated using $Et_4NF \cdot 4HF$ as fluorine source, at the benzylic carbon to give the corresponding α -fluorothiocyanates **58** in moderate yields, 47-77.5%, (Scheme 16)⁵⁰.



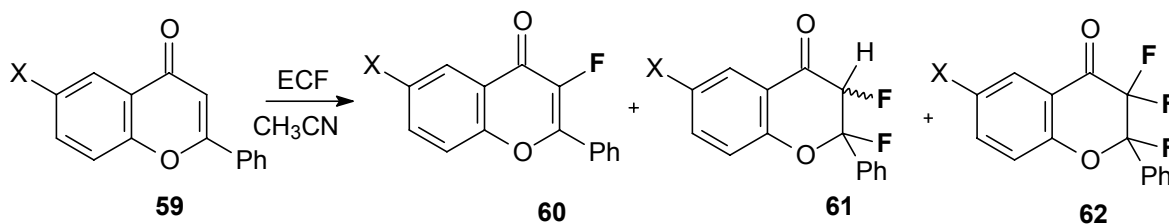
Scheme 15



Scheme 16

Heterocycles. The selective fluorination of flavone and 6-chloroflavone **59** was carried out using $Et_3N \cdot 3HF$ and $Et_4NF \cdot 4HF$ as supporting electrolytes. The former supporting electrolyte provided 3-monofluorinated flavones **60** preferentially, while the latter one gave mainly 2,3-difluorinated flavones **61** as a stereoisomeric mixture and only small amount of

monofluoro derivative **60** was formed.⁵¹ It was confirmed that **60** was formed by dehydrofluorination of **61** with free Et_3N in $Et_3N \cdot 3HF$ (Scheme 17). Further oxidation of **60** (more easily oxidized than starting flavone, at only 0.08 V) gave the trifluoro product **62**.

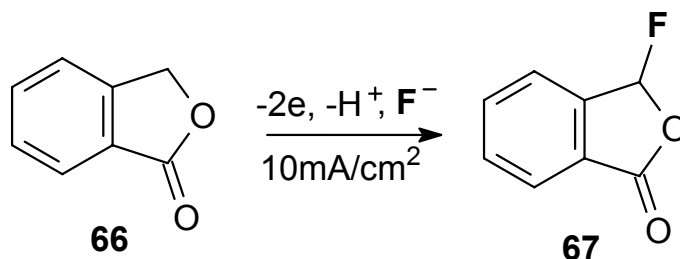
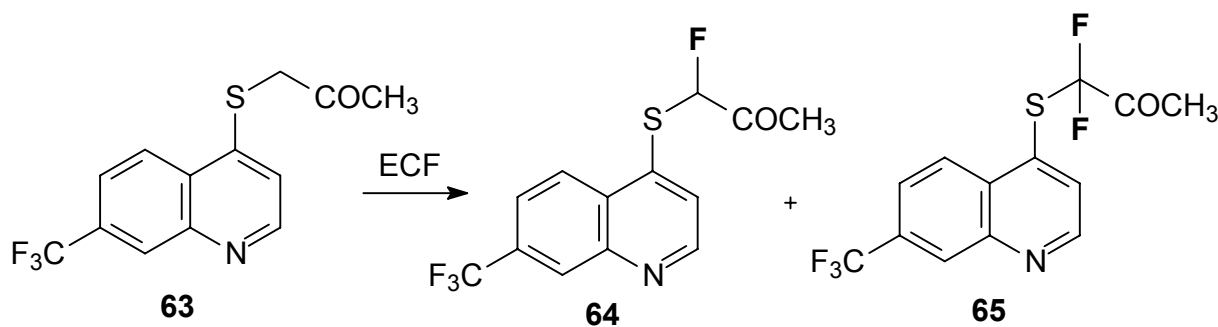


Scheme 17

The anodic oxidation of quinolyl sulfide **63** took place regioselectively at the position α to the sulfur atom. The yield was extremely high when an $\text{Et}_4\text{NF}\cdot 3\text{HF}$ supporting electrolyte in dimethoxyethane (DME) as electrolytic solvent was used under constant current electrolysis (5 mA cm^{-2}). The α -monofluorinated product **64** was obtained in a high yield and a small amount of α,α -difluorinated

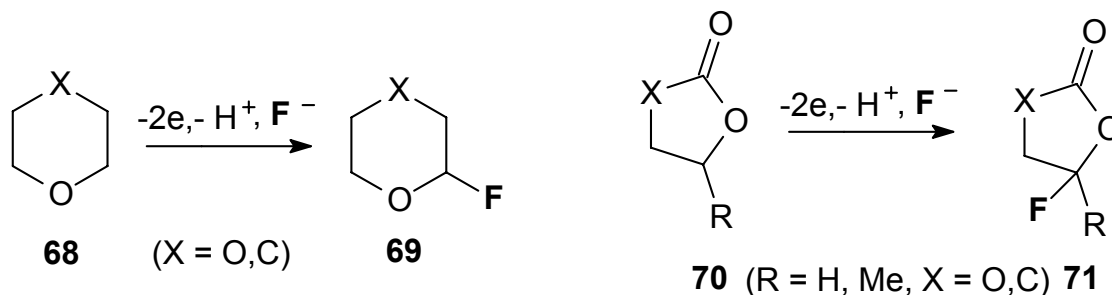
by product **65** was generated with a ratio of 15:1 (Scheme 18).⁵²

Anodic fluorination of phthalimide **66** and its derivatives (Scheme 19) was carried out using $\text{Et}_4\text{NF}\cdot 4\text{HF}$, $\text{Et}_3\text{N}\cdot 5\text{HF}$ and imidazolium ionic liquids like 1-ethyl-3-methyl-imidazolium triflate $[\text{emin}][\text{OTf}]$.⁵³



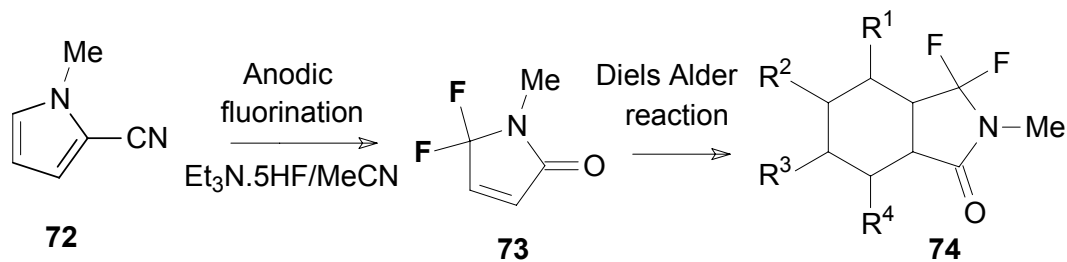
The first regioselective anodic fluorination without solvent of cyclic ethers **68**, lactones and a cyclic carbonate **70** using $\text{Et}_4\text{NF}\cdot n\text{HF}$ ($n = 4,5$) as fluorine sources and supporting electrolytes was

successfully carried out to give the corresponding monofluorinated products **69** and **71** respectively, in moderate yields (Scheme 20).⁵⁴

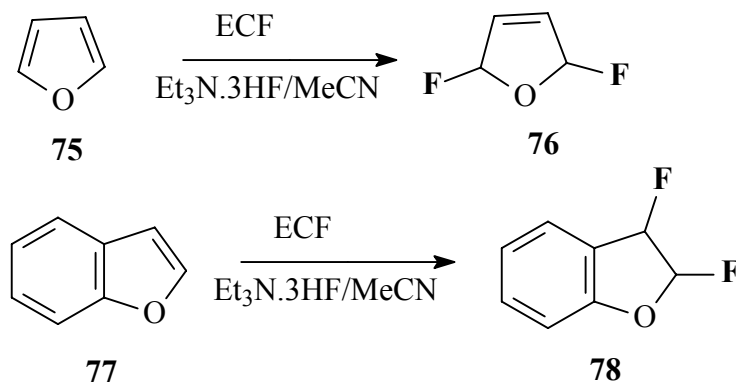


Anodic fluorination of 2-cyano-1-methylpyrrole **72** using $\text{Et}_3\text{N}\cdot 5\text{HF}$ provided 5,5-difluoro-1-methyl-3-pyrrolin-2-one **73**. The Diels Alder reaction with various dienes was successfully carried out yielding *gem*-difluorinated heterocyclic compounds **74** in excellent yields (Scheme 21).⁵⁵

The electrolytic fluorination of furan (**75**) and benzofuran (**77**) using $\text{Et}_3\text{N}\cdot 3\text{HF}$ afforded difluoro products.²³ In the case of furan, a 1,4-addition of fluorine took place to give difluoro product **76**, while 1,2-addition was observed in the fluorination of benzofuran to give **78** (Scheme 22).



Scheme 21

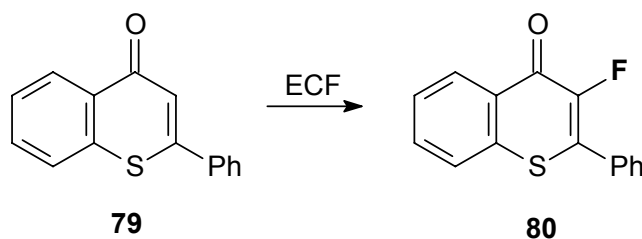


Scheme 22

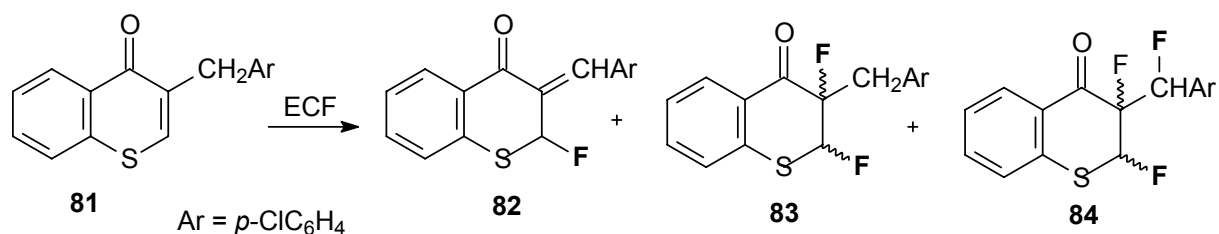
$\text{Et}_3\text{N}\cdot 3\text{HF}$ was found to be a convenient fluorine source for the electrolytic fluorination of thioflavone (79) under controlled potential to give 3-fluorothioflavone (80), as is shown in Scheme 23.³²

Recently, Dawood et al.⁵⁶ reported that anodic fluorination of the homoisothioflavone derivative

81 proceed in a different manner to that of thioflavone (79), using $\text{Et}_4\text{NF}\cdot 4\text{HF}/\text{DME}$ affording mainly the 2-fluoro-3-benzylidene-thiocromanone derivative 82 in addition to its di- and trifluorinated derivatives 83 and 84, respectively (Scheme 24).



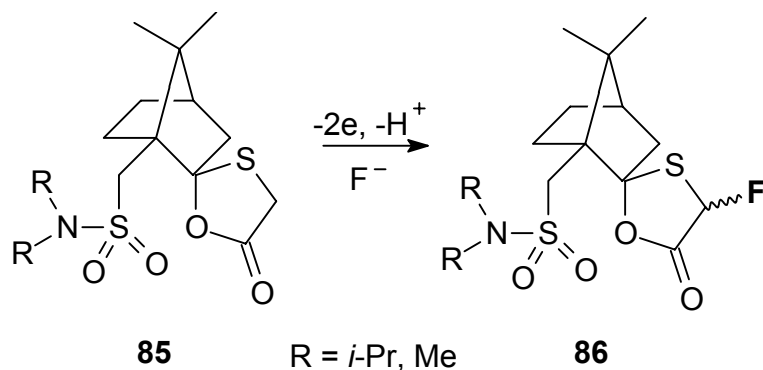
Scheme 23



Scheme 24

Anodic fluorination of chiral 1,3-oxathiolan-5-ones 85, derived from camphorsulfonamide and thioglycol acid, was carried out under various conditions. When dimethoxyethane (DME) containing $\text{Et}_4\text{NF}\cdot 4\text{HF}$ was used, the corresponding

monofluorinated products 86 were obtained in good yield as a single diastereomer (Scheme 25).⁵⁷ It is interesting that chemical fluorination using *N*-fluoropyridinium salts, however did not proceed at all.

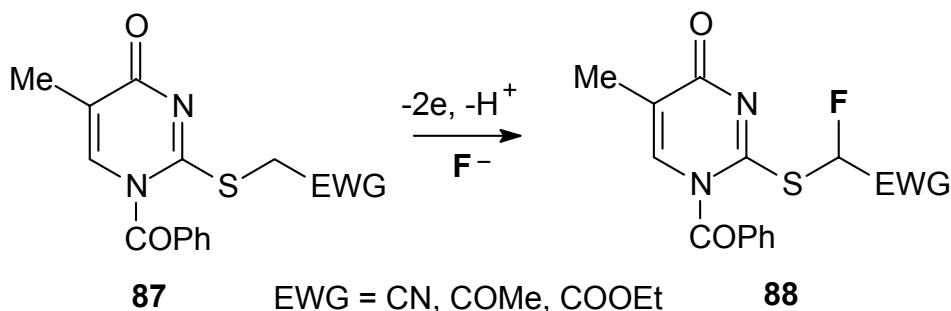


Scheme 25

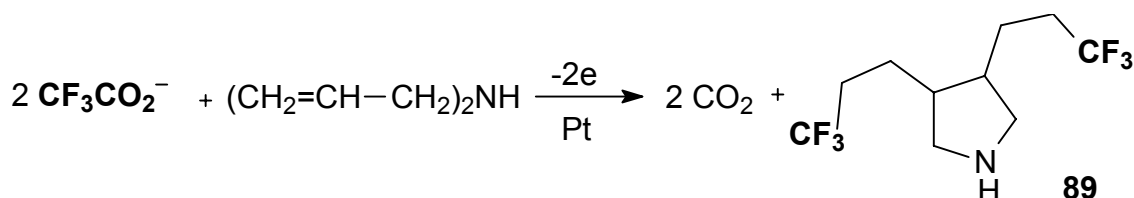
Electrolytic fluorination of the side chain of various heterocycles was studied by Fuchigami's group (Tokyo Institute of Technology). For example, regioselective anodic monofluorination of 4-oxo-2-pyrimidyl sulfides (**87**) was investigated under various electrolytic conditions. Anodic fluorination was successfully carried out using $\text{Et}_4\text{NF}\cdot 4\text{HF}$ in dimethoxyethane (DME) to provide the corresponding α -fluorinated products **88** in good yields (Scheme 26).⁵⁸ In contrast, acetonitrile (MeCN) was not suitable for the anodic fluorination due to the severe anode passivation during the electrolysis. A mixed solvent of DME and MeCN was found to be also effective for the fluorination, and the product yield increased with an increase of the ratio of DME to MeCN. The nucleophilicity of fluoride ion in the

presence of dimethoxyethane (DME) is much higher than in MeCN or CH_2Cl_2 . This is attributed to the ability of DME to solvate the cationic part of the fluoride salt, leaving fluoride anion to easily attack the cationic intermediate of the substrate.

Not only heterocycles are electrolytically fluorinated but also through electrochemical fluorination new heterocycles can be synthesized. Norbert Muller⁵⁹ reported the electrochemical synthesis of *cis*-3,4-bis(2,2,2-trifluoroethyl)pyrrolidine (**89**) by anodic oxidation of trifluoroacetate in the presence of diallylamine. The reaction product was isolated as crystalline hydrochloride in 8% yield, and converted to the *N*-butyl derivative, whose NMR spectra showed the trifluoroethyl groups to be on the same side of the ring (*cis* configuration), as is shown in Scheme 27.



Scheme 26



Scheme 27

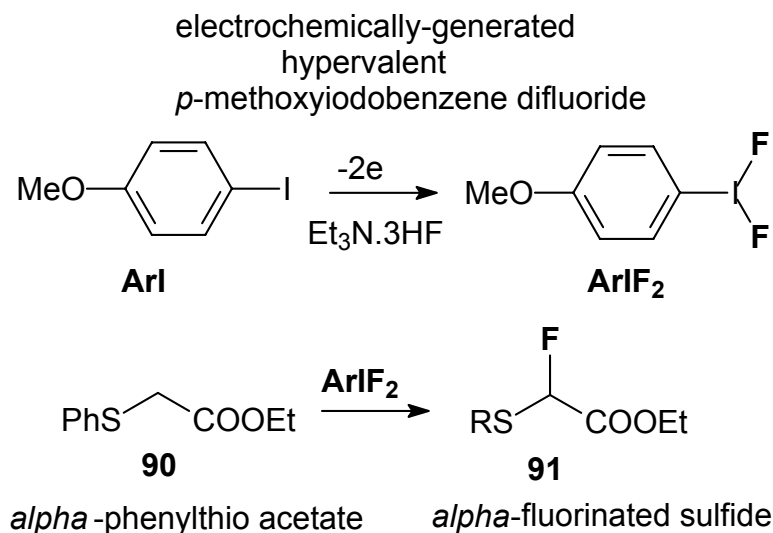
It is important to note that, occasionally, direct electrolytic fluorination does not work well, due to the passivation of anode by formation of a polymer

layer. This problem can be solved by using organic mediators instead of substrate for anodic oxidation. The organic mediators are electrochemically

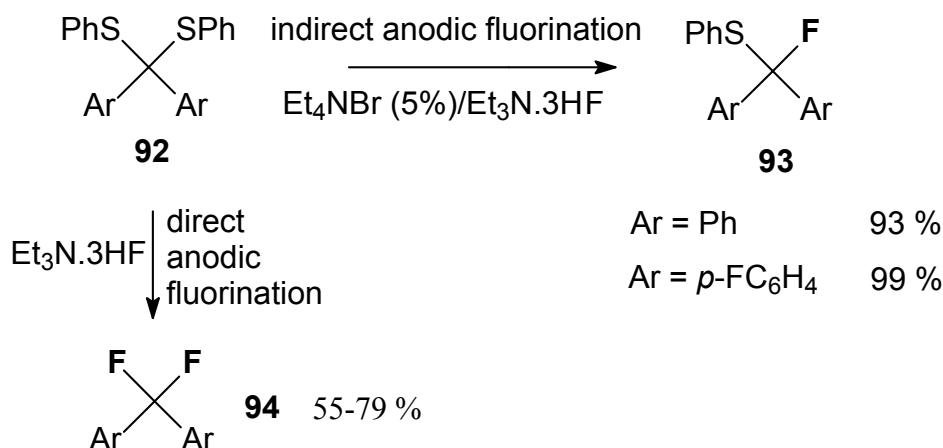
synthesized and they release fluoride to attack the substrate, that is not oxidized at the anode and passivation no occurs. This is the indirect electrolytic fluorination. Such organic mediators are *p*-methoxyiodobenzene (that generate by anodic oxidation the hypervalent iodobenzene difluoride (Scheme 28)⁶⁰, *p*-methoxyiodobenzene chlorofluoride or Et₄NBr.

Direct and indirect electrolytic fluorination can be used for a selective introduction of fluorine(s) in

organic structures. Fuchigami et al. reported that by indirect electrochemical fluorination of dithioacetals **92** using catalytic amount of Et₄NBr as mediator in Et₃N·3HF, the corresponding monofluorothioethers **93** are obtained in very good yields and no difluoro compounds were obtained. (Scheme 29).⁶¹ Same author reported the direct anodic fluorination of same substrate **92** using Et₃N·3HF as supporting electrolyte affording *gem*-difluorinated derivatives **94**.⁶²



Scheme 28



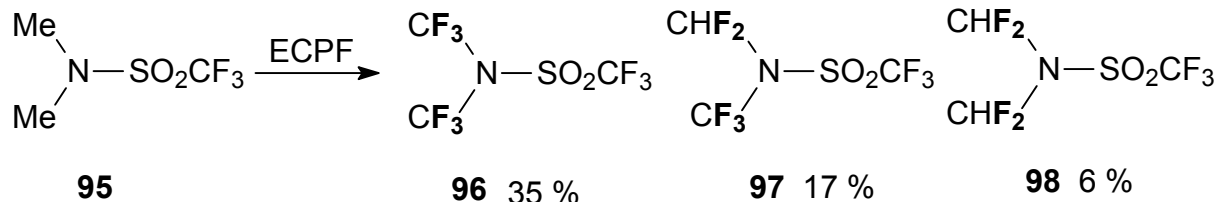
Scheme 29

ELECTROCHEMICAL PERFLUORINATION (ECPF) OF ORGANIC COMPOUNDS

It is known that perfluorinated compounds (compounds in which all the hydrogen atoms are replaced by fluorine and at the same time some

functional groups are unaffected) are useful as artificial blood and oxygen carriers⁶³ or polymers (Teflon).⁶⁴ For conversion of all C-H to C-F bonds, anhydrous HF (AHF) is the most common reagent used in electrochemical perfluorination. AHF is, however, an extremely hazardous substance due to its low boiling point and high toxicity, in addition

to giving poor yields of products. Generally, the yields of perfluorinated compounds are low and they are accompanied by lower fluorinated by products. For example, the electrochemical perfluorination of *N,N*-dimethyltrifluoromethane



Scheme 30

CONCLUSIONS

The electrochemical fluorination of organic compounds is a convenient method for a selective introduction of fluorine atom(s) into organic molecules in one step under safe conditions. The aim of this review paper was to prove that electrochemical fluorination is a widely applicable method for the synthesis of various organofluorine compounds in good to excellent yields, with high selectivity that are difficult to obtain by the chemical methods. On the other hand, ECF methods are easy to perform and do not require hazardous reagents. ECF is a type of green chemistry, where the secondary pollution can be avoided because electricity is used as an oxidizing reagent.

The article presents the use of new fluorine sources based on HF combined with organic bases (amines) like $\text{Et}_3\text{N}\cdot n\text{HF}$ ($n = 2-5$), $\text{Et}_4\text{NF}\cdot 4\text{HF}$ or $\text{Bu}_4\text{N}\cdot \text{BF}_4$; the role of HF combined to organic bases was found to be superior to HF itself, the latter leading to a complete conversion of all C-H to C-F bonds without any selectivity and with low yields. The choice of suitable electrolytic solvent, substrate or fluorine source and supporting electrolyte is very important for an optimal electrochemical fluorination of organic compounds. New results are expected for higher selectivity in partial fluorination of organic compounds and the recent report by Huffman et al.⁶⁴ (Merck Research Laboratories, USA) of a new fluorinating agent, $n\text{BuSO}_2\text{F}\cdot \text{NR}_3(\text{HF})_3\cdot \text{NR}_3$, for the high-yielding conversion of primary, secondary and tertiary alcohols to the corresponding fluorides is an example of the efforts made by chemists in this field of organic chemistry.

sulphonamide (**95**) gave the corresponding perfluorinated *N,N*-bis(trifluoromethyl) perfluoroalkanesulphonamide (**96**) along with by products **97** and **98** (Scheme 30).⁶³

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