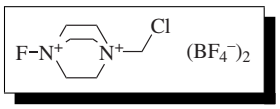
1-(Chloromethyl)-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane Bis(tetrafluoroborate)



[140681-55-6] $C_7H_{14}B_2ClF_9N_2$ (MW 354.26)

InChI = 1/C7H14ClFN2.2BF4/c8-7-10-1-4-11(9,5-2-10)6-3-10;2*2-1(3,4)5/h1-7H2;;/q+2;2*-1

InChIKey = TXRPHPUGYLSHCX-UHFFFAOYAI

(easily handled, cost-effective, site-selective electrophilic fluorinating agent applicable to a wide variety of organic substrates possessing overt or masked carbanionic character[1–4])

Alternate Names: F-TEDA-BF_4; Selectfluor™.

Physical Data: apparent mp 190 °C (thermal behavior is complicated; exothermic decomposition can occur at temperatures >80 °C); *d* 1.731 g cm^{-3}.

Solubility: v sol cold H_2O (176 g L^{-1} at 20 °C), dil HCl (decomposed by dil NaOH); sol MeCN; sl sol MeOH, EtOH, Me_2CO; sol DMF (reacts slowly on heating), pyridine (reacts), and DMSO (reacts rapidly and exothermically).

Form Supplied in: free-flowing, virtually nonhygroscopic, white solid. Available commercially.

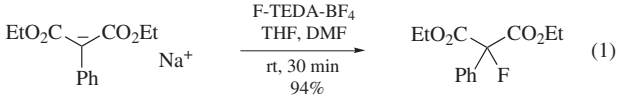
Analysis of Reagent Purity: NMR (^{1}H, ^{19}F; soln. in D_2O);[1] iodimetric titration [acidified (HCl) soln. in H_2O–Me_2CO (1:1) + excess KI; I_2 determined with thiosulfate/starch (1 $I_2 \equiv 1\ ^+$NF)]. Note that the reagent (known as F-TEDA-BF_4;[3] TEDA = triethylenediamine) oxidizes aqueous bromide ion to bromine at rt but not chloride to chlorine.[5]

Handling, Storage, and Precautions: store below 38 °C (lower temperatures are advisable for bulk storage); use in solution or suspension; do not heat the solid reagent above 80 °C. Take standard precautions to avoid breathing dust or vapors (evolved during reaction), contact with eyes or skin (dust or its solutions), and contamination of clothing. F-TEDA-BF_4 is moderately toxic (male rat oral LD_{50} 640 mg kg^{-1}; female rat 350–500 mg kg^{-1}), and is an irritant to the eye and respiratory system. Always use approved dust mask (or respirator), gloves, and safety glasses when handling the solid. Carry out solubility tests on a sensible scale when seeking alternative solvents (note the problem with DMSO referred to above). An MSDS (Material Safety Data Sheet) and further information is available from Air Products and Chemicals, Inc., Speciality Gases Dept., 7201 Hamilton Boulevard, Allentown, PA 18195-1501, USA.

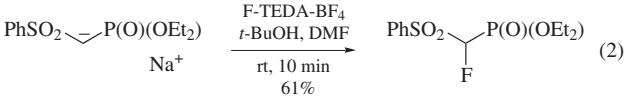
Original Commentary

R. Eric Banks & Vincent Murtagh
University of Manchester Institute of Science and Technology, Manchester, UK

Fluorination of Stabilized Carbanions. Highly stabilized carbanions [e.g. alkali metal salts of substituted malonates (eq 1), phosphonates (eq 2)] react rapidly and efficiently with this reagent.[2–4] Only low yields (<20%) of α-fluoro ketones can be obtained from highly reactive ketone-derived metal enolates; this drawback can be overcome by using enol acetate or silyl enol ether derivatives of ketones as substrates (see below).[3]

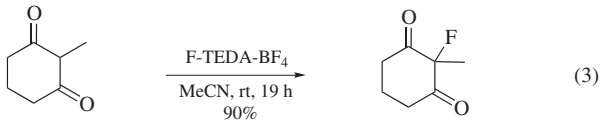


(1)

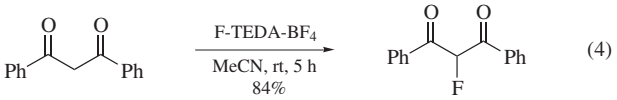


(2)

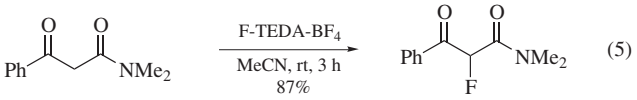
Fluorination of Enols, Enol Acetates, Silyl Enol Ethers, and Enamines. Numerous enolizable substrates of the 1,3-dicarbonyl class ($RCOCH_2COR'$) have been monofluorinated efficiently under mild conditions with an equimolar proportion of F-TEDA-BF_4 (e.g. eqs 3–6); difluorination can be achieved (e.g. eq 6; yields here estimated by NMR), but efficient introduction of the second fluorine may require a two-step procedure (depending on the equilibrium enol content of the monofluoride) (eq 7).[4]



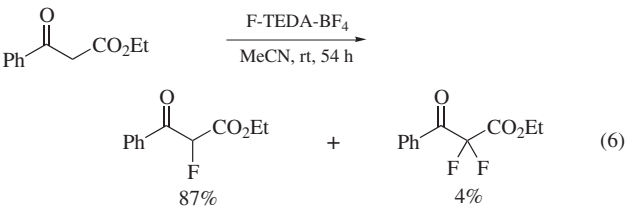
(3)



(4)

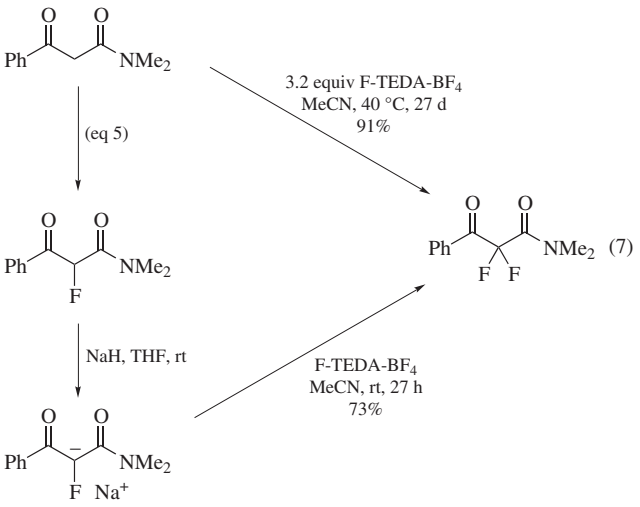


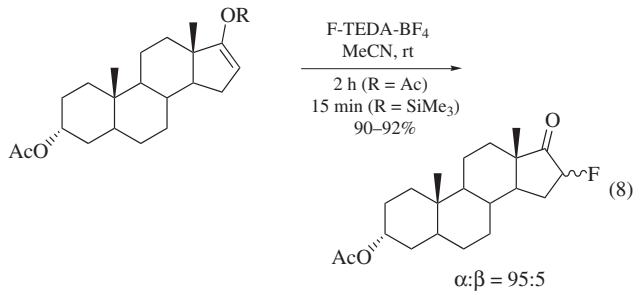
(5)

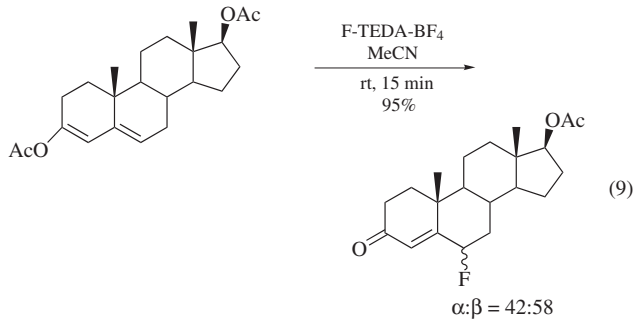


(6)

F-TEDA-BF_4 is highly effective for introducing fluorine selectively at positions 6 or 16 in steroids via attack on enol acetate or silyl enol ether derivatives.[2,3] High yields of 16-fluoro targets can be achieved with excellent stereoselectivity (e.g. eq 8). Fluorination at position 6 (e.g. eq 9) proceeds cleanly and more rapidly (typically, reactions are complete within 15 min at rt in MeCN).

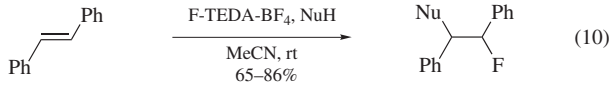






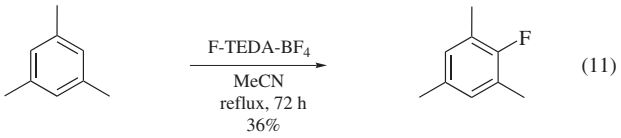
Fluorination of the prototypical enamine 1-morpholinocyclohex-1-ene with a suspension of the 1,1,1-trifluoroethyl analog of F-TEDA-BF_4, $CF_3CH_2\overset{+}{N}(CH_2CH_2)_3\ \overset{+}{N}F\ (CF_3SO_3^-)_2$,[1] in CH_2Cl_2 at 20 °C gives 2-fluorocyclohexanone in 81% yield.[2] [Note that within the *Selectfluor* range of 1-alkyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane salts, ease of 'F^+' transfer increases as the electronegativity of the 1-alkyl group increases ($CF_3CH_2 > CH_2Cl > CH_3$).[1]] Fluorination of enamines of Δ^4- or $\Delta^{1,4}$-3-keto steroids with F-TEDA-BF_4 is said to produce a mixture of 4-fluoro and 6-fluoro products.[3]

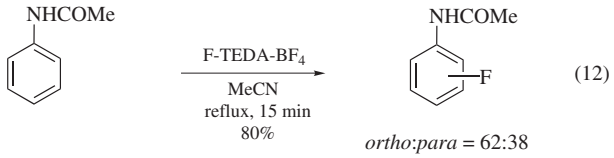
Fluorination of Alkenes. Alkenes capable of producing highly stabilized carbocations through notional addition of 'F^+' (e.g. styrene, α-methylstyrene, *trans*-stilbene, 1-phenylcyclohexene) react smoothly with F-TEDA-BF_4 at room temperature in the presence of weak nucleophiles (e.g. H_2O, MeOH, AcOH, HF– pyridine) (e.g. eq 10).[3]

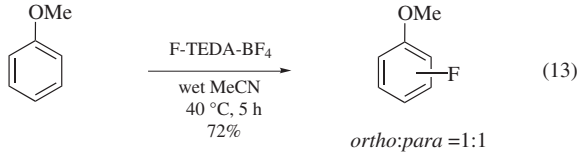


Nu = F, OMe, OAc, OH *erythro*:*threo* = 60–72:40–28

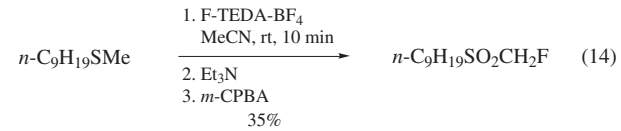
Fluorination of Aromatic Compounds. Benzene resists attack by F-TEDA-BF_4 under normal conditions. The introduction of electron-releasing (*+I*, *+M*) ring substituents facilitates fluorination (e.g. eqs 11–13).[1,2,3,6]

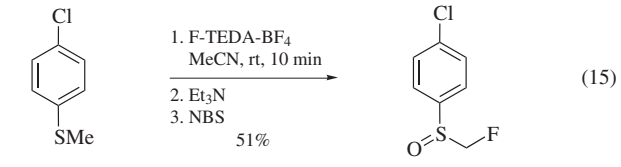


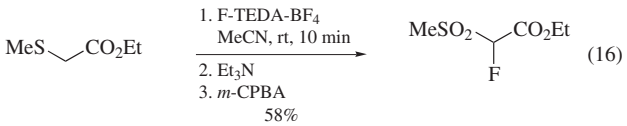




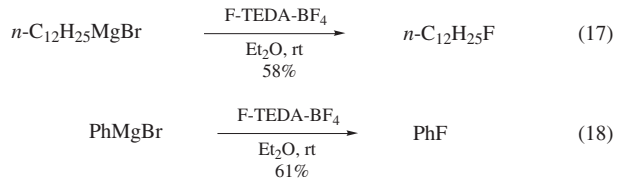
Organosulfur Compounds. The first step in the sequence $RSCH_2R^1 \rightarrow R\overset{+}{S}(F)CH_2R^1 \rightarrow RSCHFR^1 \rightarrow RS(O)_xCHFR'$ (x = 1, 2) can be effected smoothly with F-TEDA-BF_4, the Pummerer-like rearrangement of the fluorosulfonium salt (not isolated) being effected with a nitrogenous base (***Triethylamine*** or ***1,8-Diazabicyclo[5.4.0]undec-7-ene***) (e.g. eqs 14–16).[3]



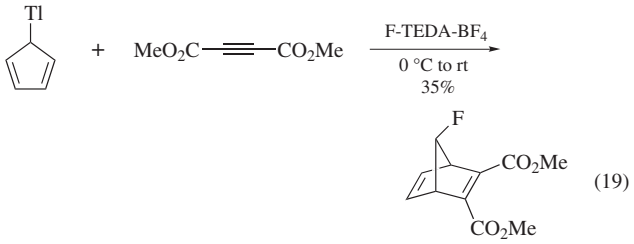




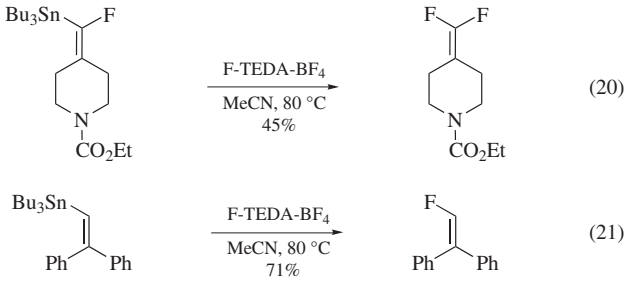
Fluorination of Carbon–Metal Bonds. Grignard reagents react slowly with suspensions of F-TEDA-BF_4 in dry diethyl ether or THF at rt to provide the corresponding monofluorides (eqs 17 and 18).[3]



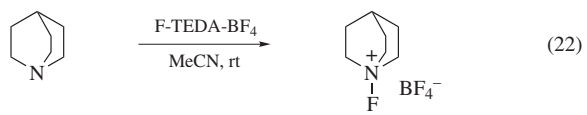
The availability of F-TEDA-BF_4 has at last made possible the synthesis of 5-fluorocyclopentadiene, the fugitive nature of which requires it to be trapped in situ (eq 19).[7] Treatment of ***Thallium(I) Cyclopentadienide*** with positive halogen sources such as NBS and NCS is a known route to other 5-halogenocyclopentadienes.



Electrophilic fluorination of vinylstannanes with F-TEDA-BF_4 provides easy access to fluoroalkenes carrying a variety of functional groups (e.g. eqs 20 and 21).[8]



Fluorination of Quinuclidine. Quantitative transfer of 'F^+' occurs from F-TEDA-BF_4 to quinuclidine at rt in acetonitrile (eq 22).[9] This method provides easy access to *N*-fluoroquinuclidinium tetrafluoroborate (NFQNBF_4), one of a family of *N*-fluoroammonium salts (fluoride,[10] triflate,[11] tetrafluoroborate,[11] perfluoroalkanecarboxylate[11]) originally developed in response to worldwide demand for more generally acceptable (less aggressive, nonexplosive, less toxic, inexpensive) site-selective electrophilic fluorinating agents than ***Perchloryl Fluoride***, O–F reagents (e.g. ***Trifluoromethyl Hypofluorite***, ***Cesium Fluoroxysulfate***), ***Xenon(II) Fluoride***, and ***Fluorine*** itself.[12]



F-TEDA salts arose out of research aimed at the development of a similar yet more powerful family of *N*-fluoroammonium salts than NFQN salts; 'tunable' fluorinating ability and considerably greater commercial prospects were also targets. [Fluorinating power can be adjusted via the electronegativity of the quaternizing alkyl group (see earlier).[2]] In-house synthesis of both NFQN and F-TEDA salts is an unwelcome prospect in many laboratories since fluorine is required;[1,10,11] the commercial availability of F-TEDA-BF_4 has resolved this major problem, making possible renewed interest in NFQN salts.

At present, not enough information is available to provide a proper appraisal of advantages to be gained by using an NFQN salt rather than its F-TEDA analog; given the current relative costs and availability of quinuclidine and TEDA, F-TEDA-BF_4 will normally be preferred. Limited data indicate that highly basic carbanions give better yields of C–F products with NFQN salts than with F-TEDA salts.

Some Comparisons. Electrochemical measurements (reduction potentials),[5] supported by practical experience, indicate the following order of fluorinating power for *N*-fluoro reagents: $(CF_3SO_2)_2NF$, $ClCH_2\overset{+}{N}(CH_2CH_2)_3\overset{+}{N}F$ $(BF_4^-)_2$ (*F-TEDA BF*$_4$; A), $MeN(CH_2CH_2)_3\overset{+}{N}F$ $(TfO^-)_2$, $HC(CH_2CH_2)_3\overset{+}{N}F$ TfO^-, pyF^+ TfO^- (A), $(PhSO_2)_2NF$ (A), *p*-$MeC_6H_4SO_2NFMe$ (A) (TfO^- = $CF_3SO_3^-$; A = available commercially). The electrophilic fluorination power of F-TEDA-BF_4 falls not far short of that of the powerful so-called DesMarteau N-F reagent,[13] *N*-fluoro[bis(trifluoromethyl)sulfonyl]imide, $(CF_3SO_2)_2NF$, the only liquid in this group (bp 90–91 °C). This reagent is not available commercially, and its preparation entails a costly multistep synthesis terminating in a direct fluorination procedure [$(CF_3SO_2)_2$ $NH + F_2 \rightarrow (CF_3SO_2)_2NF + HF$] requiring considerable expertise and special equipment.[14] Not all power-variable Meinert–Umemoto[15] *N*-fluoropyridinium salts (e.g. ***N-Fluoropyridinium Triflate***) are available commercially, and sensitivity to attack by moisture or bases can be a drawback.[16] *N*-Fluorobenzene- sulfonimide, $(PhSO_2)_2NF$ (Differding's reagent),[17] and *N*-fluoro-*N*-alkylarenesulfonamides (Barnette reagents),[18] developed for the fluorination of carbanions, seem too unreactive to be viewed as general-purpose reagents.

Overall, F-TEDA-BF_4 is probably the best general-purpose electrophilic fluorinating agent available at the time of writing: it fluorinates a wide variety of electron-rich carbon centers rapidly under mild conditions with high efficiency and selectivity, and no special apparatus or handling techniques are required. Soluble in a number of useful reaction solvents (including aqueous systems), F-TEDA-BF_4 is compatible with common reactor materials and offers the additional advantage of being degradable into manageable waste products.[19] A most welcome alternative to the use of highly toxic and potentially explosive electrophilic fluorinating agents such as F_2, $FClO_3$, and CF_3OF, F-TEDA-BF_4 was already in commercial use just four years after its design and synthesis by Banks and Sharif.[2,19]

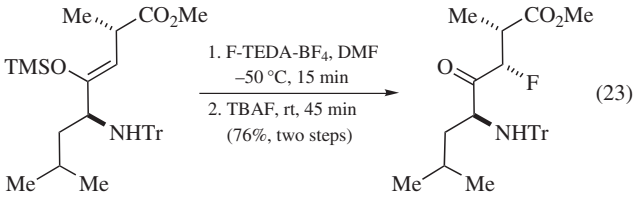
First Update

Ilhwan An & Robert E. Maleczka, Jr
Michigan State University, East Lansing, MI, USA

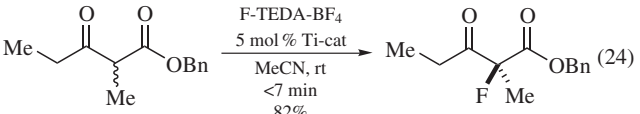
Since the first article on F-TEDA-BF_4 (a.k.a. Selectfluor™ or 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis (tetrafluoroborate)), numerous new applications of this reagent have been reported. In addition to this update, readers will likely find the recent F-TEDA-BF_4 reviews by Stavber,[20] Wong,[21] and

Shreeve[22] helpful.[23] Even among the traditional F-TEDA-BF_4 mediated fluorinations, new advances have been made such as the ability to carry out fluorinations in water,[24] room temperature ionic liquids,[25] or under microwave irradiation.[26]

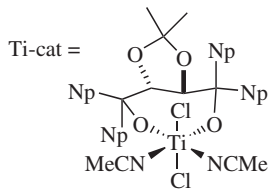
Other Fluorinations of Enols, Silyl Enol Ethers, Enamines, and Imines. Another important area of recent development has been in the use of F-TEDA-BF_4 for stereoselective fluorinations. (*Z*)-Trimethylsilyl enol ethers can be fluorinated to yield monofluoro ketomethylene dipeptide isosteres in generally good yields (65–76%).[27] In the reaction shown in eq 23, the *N*-tritylamino group on the substrate played a stereodetermining role during fluorination. Reagent controlled enantioselective fluorinations are also possible. For example, monosubstituted β-ketoesters were efficiently fluorinated in a highly enantioselective manner using F-TEDA-BF_4 in combination with a Lewis acidic titanium catalyst (eq 24).[28] Alternatively, up to 91% ee's have been observed during the fluorination of silyl enol ethers with F-TEDA-BF_4, when catalyzed by chincona alkaloid derivatives (eq 25).[29]

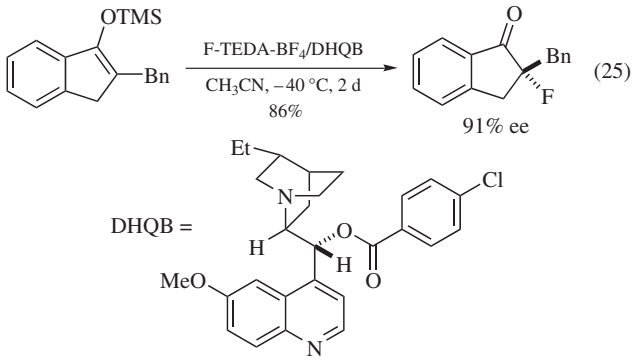


(23)



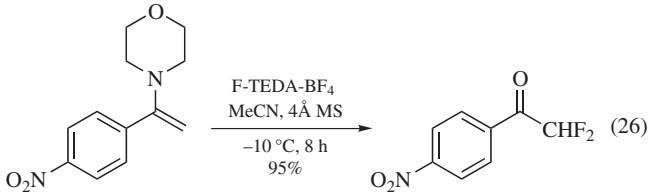
(24)



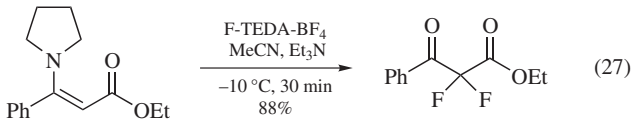


(25)

F-TEDA-BF_4 has proven to be an efficient reagent for the difluorination of enamines to provide α,α-difluoroketones (eqs 26 and 27).[30] Electron-poor enamines (eq 26) tend to afford higher yields than those bearing electron-donating substituents. For some enamines, the addition of 1 equiv of Et_3N was required to obtain the difluorinated ketones without the presence of monofluorinated by-products (eq 27).

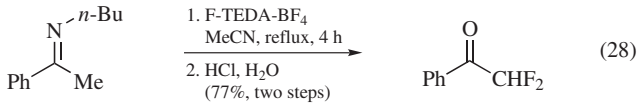


(26)



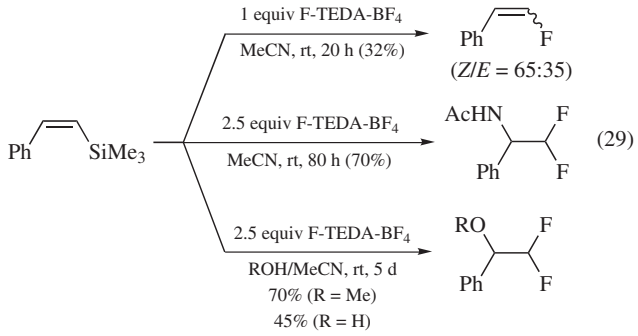
(27)

Imines have also been fluorinated, albeit under more forcing conditions.[31] Here, imines derived from aryl alkyl and alkyl *tert*-alkyl ketones work best (eq 28). In contrast, imines derived from dialkyl ketones fluorinate with very poor levels of selectivity. Finally, several new and instructive findings on previously described reactions have emerged. For example, for the preparation of α-fluorinated phosphonoacetate derivatives (eq 2), the F-TEDA-BF_4 method was more selective, more convenient, and considered safer than the same fluorinations with perchloryl fluoride ($FClO_3$).[32] Additionally, the reactions of silyl enol ethers have been extended to acyl silanes, which once fluorinated can undergo Sakurai reactions to form either α-silylated ketones by way of Brook- and retro-Brook isomerization or, in the absence of the Brook process, homoallylic alcohols.[33]

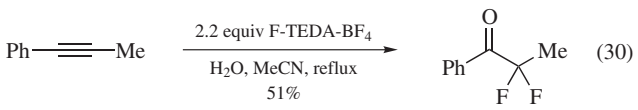


(28)

Other Fluorinations of Alkenes and Alkynes. Alkenyltrimethylsilanes are suitable substrates for F-TEDA-BF_4 mediated fluorodesilylations to form fluoroalkenes.[34] In the presence of excess F-TEDA-BF_4 and acetonitrile, or MeCN/alcohol or MeCN/water, the products are difluoromethyl substituted amides, ethers, or alcohols, respectively (eq 29). The fluorine addition to alkynes follows Markovnikov regioselectivity (eq 30).[35]



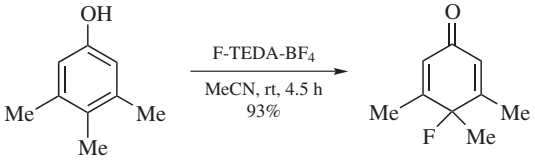
(29)



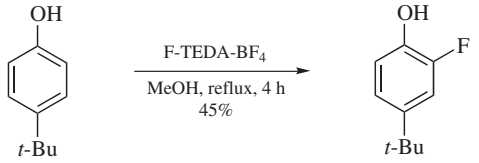
(30)

Fluorination of Phenols. Reactions of phenols with F-TEDA-BF_4 in MeCN give 4-fluorocyclohexa-2,5-dienone derivatives in good yields (eq 31).[36] Electron-donating substituents increase the

rate of formation and yield of the fluorinated products.[37] In the presence of external nucleophiles (e.g., ROH/MeCN (1:9)) phenols can also be converted to the corresponding oxygen addition products[22,37] or when the reactions are run in straight MeOH they can afford the ortho fluorinated phenols (eq 32).[38]

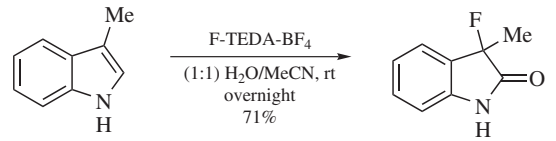


(31)

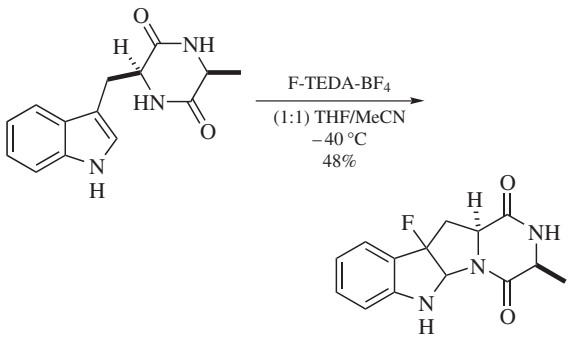


(32)

Fluorination of Indoles and Isoxazoles. A limited number of heteroarenes have been fluorinated with F-TEDA-BF_4. For example, fluorination of 3-substituted indole derivatives with F-TEDA-BF_4 can provide the 3-fluorooxindoles in good to excellent yields (eq 33).[39] Mixtures of acetonitrile with water, methanol, or trifluoroethanol may be used as solvent; however, use of straight acetonitrile causes product decomposition. Ionic liquids as a reaction media afford high yields and superior chemoselectivity.[25a] Cyclized products can be obtained by electrophilic attack of fluorine at the 3-position of the indole followed by nucleophilic addition at the 2-position (eq 34).[40]

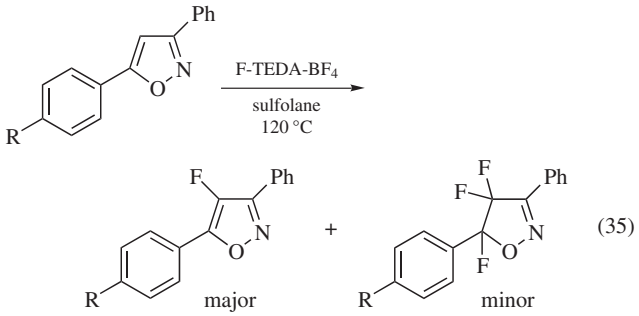


(33)



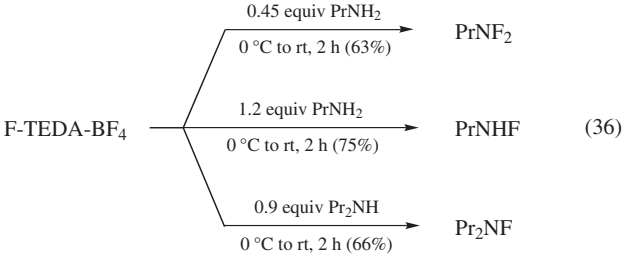
(34)

3,5-Diarylisoxazoles fluorinate at the C-4 position using F-TEDA-BF_4.[41] Activated substrates react efficiently at room temperature or refluxing MeCN, whereas deactivated systems require the higher temperatures (~120 °C) available with the use of sulfolane as solvent. At 120 °C, a unique trifluorination of the isoxazole nucleus occurred as a side reaction (eq 35).



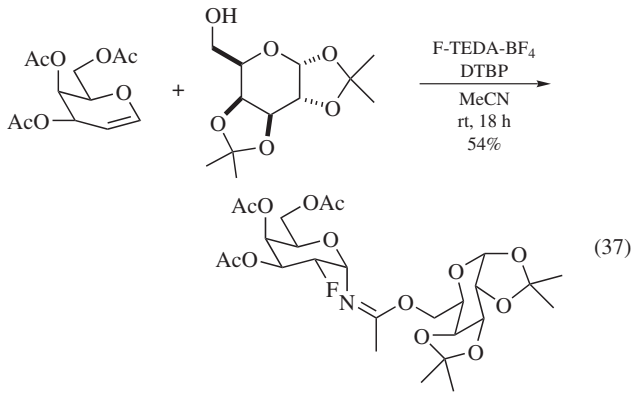
(35)

Fluorination of Aliphatic Amines. Primary and secondary amines react with F-TEDA-BF_4 to form mono or difluorinated products depending on reaction stoichiometry (eq 36).[42] In addition to MeCN, DMA or DMF are also suitable solvents for these reactions.

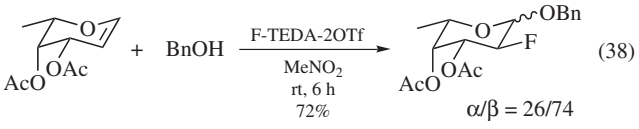


(36)

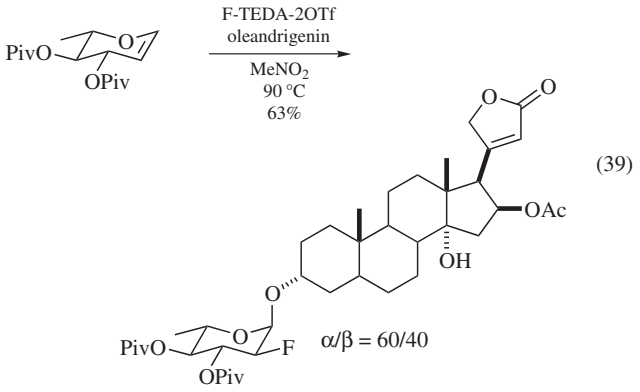
Fluorination of Glycals. Electrophilic fluorination of glycals with F-TEDA-BF_4 in the presence of nucleophilies provides a useful avenue for accessing 2-deoxy-2-fluoro sugars and their glycosides.[43] Use of nitromethane can help to avoid unwanted participation of acetonitrile as a nucleophile (eqs 37 and 38). It should be noted that F-TEDA-2OTf has been reported to give fewer side products and higher yields than F-TEDA-BF_4 (eq 39). Additions across the glycal olefin tend to occur in a *syn*-fashion. However, if enough time is allowed for epimerization to the thermodynamically more stable intermediate, production of the α-anomers is increased. Also, sterically bulky nucleophiles lead to a greater α-selectivity.



(37)

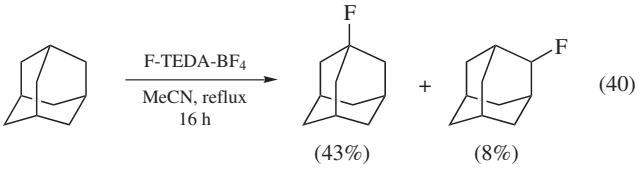


(38)



(39)

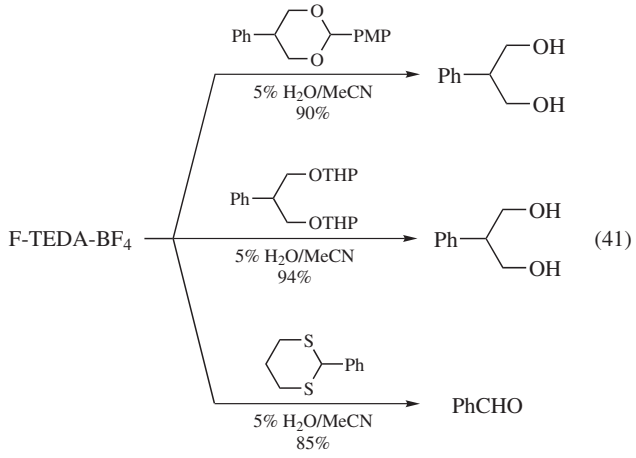
Fluorination of Aliphatics. Upon reaction with F-TEDA-BF_4, saturated secondary and tertiary carbon–hydrogen bonds have be transformed to carbon–fluorine bonds (eq 40).[44] Such C–H activations require relatively long reaction times and reflux conditions.



(40)

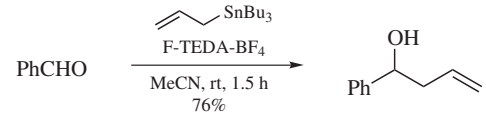
Other F-TEDA-BF_4 Mediated Organic Reactions.

Removal of p-Methoxybenzylidene (PMP), Tetrahydropyranyl (THP), and 1,3-Dithiane Protecting Groups. PMP and THP protective groups can be mildly cleaved by F-TEDA-BF_4 with 5% H_2O in acetonitrile as the solvent. The addition of stoichiometric amounts of F-TEDA-BF_4 has smoothly and efficiently cleaved 1,3-dithianes in less than 5 min at room temperature (eq 41).[45]

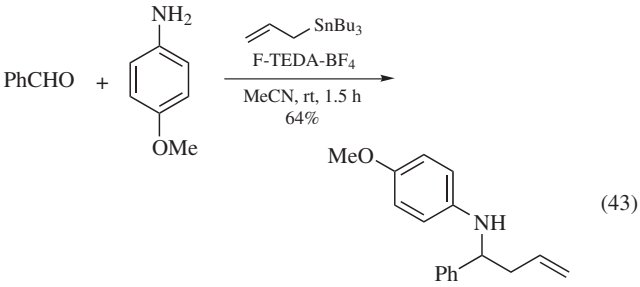


(41)

Allylation of Aldehydes and Imines. F-TEDA-BF_4 can work as an efficient promoter for the allylation of aldehydes and imines to form homoallylic alcohols and amines (eqs 42 and 43).[46] Allylation of aryl and alkyl aldehydes and imines with allyltributyltin in acetonitrile can be performed in the presence of a stoichiometric amount of F-TEDA-BF_4. The reaction conditions are tolerant of moisture and air. Use of a catalytic amount of F-TEDA-BF_4 can also afford the same products. However, under catalytic conditions longer reaction times and decreased yields are the norm.

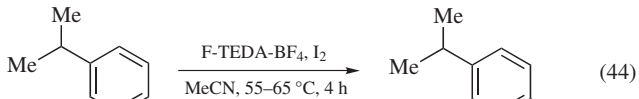


(42)

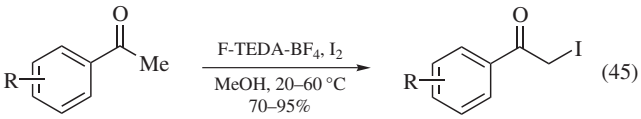


(43)

F-TEDA-BF_4 Mediated Iodinations and Related Reactions. An iodine atom can be introduced at the most electron-rich and the least sterically hindered position on a benzene ring when such arenes are reacted in the presence of F-TEDA-BF_4 (eq 44).[47] Like the fluorination of indoles, these reactions also respond well to being run in room temperature ionic liquids.[25b] Aryl alkyl ketones, including indanones,[48] can also be converted into the corresponding α-iodoketones in excellent yields (eq 45) via solvent directed reactions with elemental iodine and F-TEDA-BF_4.[49] F-TEDA-BF_4 can also mediate the electrophilic addition of other common anions. For example, the reaction between F-TEDA-BF_4 and the sodium or potassium salts of Br^-, Cl^-, SCN^-, and NO_2^- results in bromo, chloro, thiocyano, or nitro-substitued benzenes.[50] In general, the reactivity decreases in the order $Br^- > Cl^- > SCN^- > NO_2^-$. Reactions of hexamethylbenzene with F-TEDA-BF_4 in the presence of alcohols, carboxylic acids, nitriles, form alkoxy, amido, azido, or halogeno functional groups at one of the benzylic positions (eq 46).[51]

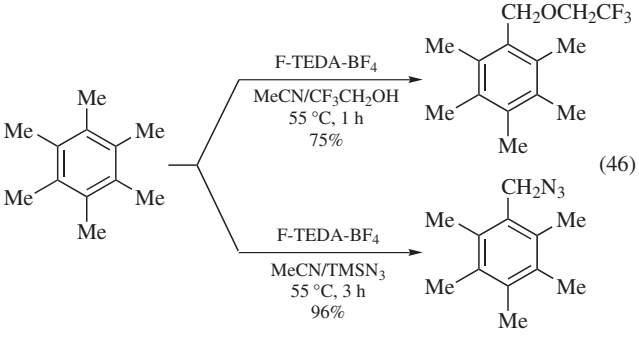


(44)



(45)

R = H, *p*-OMe, *p*-Me, *p*-F, *m*-CF_3, *m*-NO_2



(46)

Related Reagents. 1-Chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane Bis(trifluoromethanesulfonate) (a.k.a. F-TEDA-CH_2Cl 2OTf or Selecfluor Triflate);[43] 1-Fluoro-4-hydroxy-1,4-diazoniabicyclo[2,2,2]octane Bis(tetrafluoroborate) (a.k.a. Accufluor^{TM}).[52]

1. Banks, R. E.; U. S. Patent 5 086 178, 1992.
2. Banks, R. E.; Mohialdin-Khaffaf, S. N.; Lal, G. S.; Sharif, I.; Syvret, R. G., *J. Chem. Soc., Chem. Commun.* **1992**, 595.
3. Lal, G. S., *J. Org. Chem.* **1993**, *58*, 2791.
4. Banks, R. E.; Lawrence, N. J.; Popplewell, A. L., *J. Chem. Soc., Chem. Commun.* **1994**, 343.
5. Gilicinski, A. G.; Pez, G. P.; Syvret, R. G.; Lal, G. S., *J. Fluorine Chem.* **1992**, *59*, 157.
6. Banks, R. E.; Sharif, I. in preparation.
7. McClinton, M. A.; Sik, V., *J. Chem. Soc., Perkin Trans. 1* **1992**, 1891.
8. Matthews, D. P.; Miller, S. C.; Jarvi, E. T.; Sabol, J. S.; McCarthy, J. R., *Tetrahedron Lett.* **1993**, *34*, 3057.
9. Abdul-Ghani, M; Banks, R. E.; Besheesh, M. K.; Sharif, I; Syvret, R. G., *J. Fluorine Chem.* **1995**, *73*, 255.
10. Banks, R. E.; Du Boisson, R. A.; Morton, W. D.; Tsiliopoulos, E., *J. Chem. Soc., Perkin Trans. 1* **1988**, 2805.
11. Banks, R. E.; Sharif, I., *J. Fluorine Chem.* **1991**, *55*, 207.
12. For recent reviews of electrophilic fluorination, see *New Fluorinating Agents in Organic Synthesis*; German, L.; Zemskov, S. Eds.; Springer: Berlin, 1989; and Purrington, S. T.; Kagen, B. S.; Patrick, T. B., *Chem. Rev.* **1986**, *86*, 997.
13. See, for example, Xu, Z.-Q.; DesMarteau, D. D.; Gotoh, Y., *J., Fluorine Chem.* **1992**, *58*, 71 and references cited therein.
14. DesMarteau, D. D.; Witz, M., *J. Fluorine Chem.* **1991**, *52*, 7.
15. (a) Meinert, H.; Cech, D., *Z. Chem.* **1972**, *12*, 292. (b) Umemoto, T.; Fukami, S.; Tomizawa, G.; Harasawa, K.; Kawada, K.; Tomita, K., *J. Am. Chem. Soc.* **1990**, *112*, 8563.
16. Umemoto, T.; Harasawa, K.; Tomizawa, G.; Kawada, K.; Tomita, K., *Bull. Chem. Soc. Jpn.* **1991**, *64*, 1081.
17. (a) Differding, E.; Ofner, H., *Synlett* **1991**, 187. (b) Differding, E.; Duthaler, R. O.; Krieger, A.; Rüegg, G. M.; Schmit, C., *Synlett* **1991**, 395.
18. (a) Barnette, W. E., *J. Am. Chem. Soc.* **1984**, *106*, 452. (b) Lee, S. H.; Schwartz, J., *J. Am. Chem. Soc.* **1986**, *108*, 2445.
19. *Chem. Eng. News* **1993**, *71*(*36*), 29.
20. Stavber, S.; Zupan, M., *Acta Chim. Slov.* **2005**, *52*, 13.
21. Nyffeler, P. T.; Durón, S. G.; Burkart, M. D.; Vincent, S. P.; Wong, C.-H., *Angew. Chem., Int. Ed.* **2005**, *44*, 192.
22. Singh, R. P.; Shreeve, J. M., *Acc. Chem. Res.* **2004**, *37*, 31.
23. Also see: (a) Manral, L., *Synlett* **2006**, 807. (b) Banks, R. E., *J. Fluorine Chem.* **1998**, *87*, 1.
24. Stavber, G.; Zupan, M.; Jereb, M.; Stavber, S., *Org. Lett.* **2004**, *6*, 4973.
25. (a) Baudoux, J.; Salit, A.-F.; Cahard, D.; Plaquevent, J.-C., *Tetrahedron Lett.* **2002**, *43*, 6573. (b) Chiappe, C.; Pieraccini, D., *ARKIVOC* **2002**, *11*, 249.
26. (a) Xiao, J. C.; Shreeve, J. M., *J. Fluorine Chem.* **2005**, *126*, 473. (b) Bluck, G. W.; Carter, N. B.; Smith, S. C.; Turnbull, M. D., *J. Fluorine Chem.* **2004**, *125*, 1873.
27. Hoffman, R. V.; Tao, J., *J. Org. Chem.* **1999**, *64*, 126.
28. (a) Hintermann, L.; Togni, A., *Angew. Chem., Int. Ed.* **2000**, *39*, 4359. (b) Piana, S.; Devillers, I.; Togni, A.; Rothlisberger, U., *Angew. Chem., Int. Ed.* **2002**, *41*, 979.
29. (a) Shibata, N.; Suzuki, E.; Asahi, T.; Shiro, M., *J. Am. Chem. Soc.* **2001**, *123*, 7001. (b) Baudequin, C.; Loubassou, J.-F.; Plaquevent, J. C.; Cahard, D., *J. Fluorine Chem.* **2003**, *122*, 189. (c) Fukuzumi, T.; Shibata, N.; Sugiura, M.; Nakamura, S.; Toru, T., *J. Fluorine Chem.* **2006**, *127*, 548.
30. Peng, W.; Shreeve, J. M., *J. Org. Chem.* **2005**, *70*, 5760.
31. Pravst, I.; Zupan, M.; Stavber, S., *Synthesis* **2005**, 3140.
32. (a) Marma, M. S.; Khawli, L. A.; Harutunian, V.; Kashemirov, B. A.; McKenna, C. E., *J. Fluorine Chem.* **2005**, *126*, 1467. (b) Hamilton, C. J.; Roberts, S. M., *J. Chem. Soc., Perkin Trans. 1* **1999**, 1051.
33. Chung, W. J.; Welch, J. T., *J. Fluorine Chem.* **2004**, *125*, 543.
34. Greedy, B.; Gouverneur, V., *J. Chem. Soc., Chem. Commun.* **2001**, 233.
35. (a) Zupan, M.; Iskra, J.; Stavber, S., *J. Org. Chem.* **1995**, *60*, 259. (b) Stavber, S.; Sotler, T.; Zupan, M., *Tetrahedron Lett.* **1994**, *35*, 1105.
36. Stavber, S.; Jereb, M.; Zupan, M., *Synlett* **1999**, 1375.
37. Stavber, S.; Jereb, M.; Zupan, M., *ARKIVOC* **2001**, *5*, 98.
38. Pravst, I.; Iskra, M. P.; Jereb, M.; Zupan, M.; Stavber, S., *Tetrahedron* **2006**, *62*, 4474.
39. Takeuchi, Y.; Tarui, T.; Shibata, N., *Org. Lett.* **2000**, *2*, 639.
40. Shibata, N.; Tarui, T.; Doi, Y.; Kirk, K. L., *Angew. Chem., Int. Ed.* **2001**, *40*, 4461.
41. Stephens, C. E.; Blake, J. A., *J. Fluorine Chem.* **2004**, *125*, 1939.
42. Singh, R. P.; Shreeve, J. M., *J. Chem. Soc., Chem. Commun.* **2001**, 1196.
43. Vincent, S. P.; Burkart, M. D.; Tsai, C.-Y.; Zhang, Z.; Wong, C.-H., *J. Org. Chem.* **1999**, *64*, 5264.
44. (a) Chambers, R. D.; Kenwright, A. M.; Parsons, M.; Sandford, G.; Moilliet, J. S., *J. Chem. Soc., Perkin Trans. 1* **2002**, 2190. (b) Chambers, R. D.; Parsons, M.; Sandford, G.; Bowden, R., *J. Chem. Soc., Chem. Commun.* **2000**, 959.
45. Liu, J.; Wong, C.-H., *Tetrahedron Lett.* **2002**, *43*, 4037.
46. Liu, J.; Wong, C.-H., *Tetrahedron Lett.* **2002**, *43*, 3915.
47. (a) Stavber, S.; Kralj, P.; Zupan, M., *Synthesis* **2002**, 1513. (b) Stavber, S.; Jereb, M.; Zupan, M., *J. Phys. Org. Chem.* **2002**, *15*, 56. (c) Stavber, S.; Kralj, P.; Zupan, M., *Synlett* **2002**, 598.
48. Jereb, M.; Stavber, S.; Zupan, M., *Tetrahedron* **2003**, 5935.
49. Stavber, S.; Jereb, M.; Zupan, M., *J. Chem. Soc., Chem. Commun.* **2002**, 488.
50. Syvret, R. G.; Butt, K. M.; Nguyen, T. P.; Bulleck, V. L.; Rieth, R. D., *J. Org. Chem.* **2002**, *67*, 4487.
51. Stavber, S.; Kralj, P.; Zupan, M., *Synlett* **2001**, 1152.
52. Stavber, S.; Zupan, M., *Tetrahedron Lett.* **1996**, *37*, 3591.