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Synthesis of organofluorine compounds using α-fluorine-substituted silicon reagents

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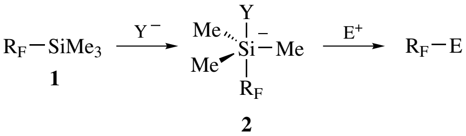
α-Fluorinated organosilanes Me_3SiCF_2X serve as versatile reagents for the synthesis of organofluorine compounds. Most reactions start from Lewis base activation of carbon–silicon bond through the intermediacy of five-coordinate siliconate species. Interaction of these silanes with suitable electrophiles leads to products of nucleophilic fluoroalkylation; an alternative pathway involves generation of difluorocarbene. These reagents can also be considered as equivalents of difluoromethylene radical anion and bis(carbanion) when carbon–heteroatom bond C–X is activated.

Introduction

The field of organofluorine chemistry started its development in the middle of 20th century, when the utility of fluorinated compounds was recognized.[1] Since then and for a long time, fluorine chemistry had been considered as a specialized area, with the major focus being placed on polyfluorinated compounds and materials. However, during the last twenty years, molecules bearing a single fluorinated fragment or a fluorine atom have come to the forefront of practical applications (*e.g.*, in medicinal chemistry), and nowadays the demand in partially fluorinated products is increasing steadily. For example, about 20% of approved drugs contain at least one fluorine, while for agrochemicals this percentage is even higher.[2] Consequently, this area has attracted general organic chemists, and, as a result, the methodology for the synthesis of organofluorine compounds has tremendously been advanced during last decade.[3]

Among wide variety of approaches to fluorine-containing molecules, the use of silicon reagents **1** for the introduction of fluorinated carbanions has become particularly widespread.[4] Trifluoromethyl lithium or magnesium reagents are unstable even at low temperatures owing to Lewis acidic nature of the metal, while silicon reagents are air stable and easy-to-handle compounds. Reagents **1** should be activated by a Lewis base to generate five-coordinate intermediate **2**, which serves as a source of fluorinated carbanion with respect to electrophiles (Scheme 1).



Scheme 1

This process was first disclosed by Prakash in 1989 for trifluoromethylation of carbonyl compounds using trifluoromethyl(trimethyl)silane (Me_3SiCF_3, **3a**) and tetrabutylammonium fluoride (TBAF) as basic activator.[5] The successful application of Me_3SiCF_3, which had previously been obtained by Ruppert,[6] as a source of CF_3^- carbanion was further developed into a powerful methodology for the introduction of CF_3 group into various carbon- and heteroatom-centered electrophiles, as well as in transition metal catalyzed cross-coupling reactions.[4] Correspondingly, this silane is frequently named as the Ruppert–Prakash reagent. Afterwards, reagents bearing other fluorinated fragments were investigated, and besides nucleophilic reactivity, some novel transformations were found.

For the period over last fifteen years a great number of papers describing applications on fluorinated silicon reagents, and several reviews covering this topic have been published.[4] Herein we describe results obtained mainly in our group, whereas when necessary for completeness of the discussion, other relevant data are provided.

Synthesis of silicon organofluorine reagents

A number of fluorinated silicon reagents were described in the literature, and some of them are shown in Scheme 2. Parent silane Me_3SiCF_3 **3a** is now commercially available on multi-kilogram scale from numerous suppliers at affordable prices. Its

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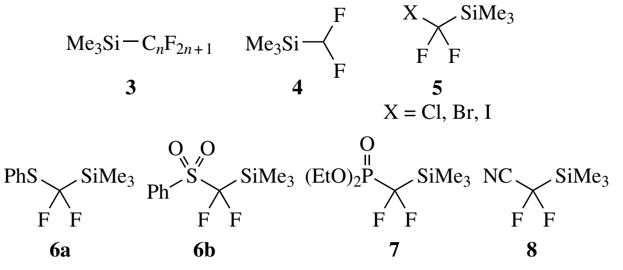
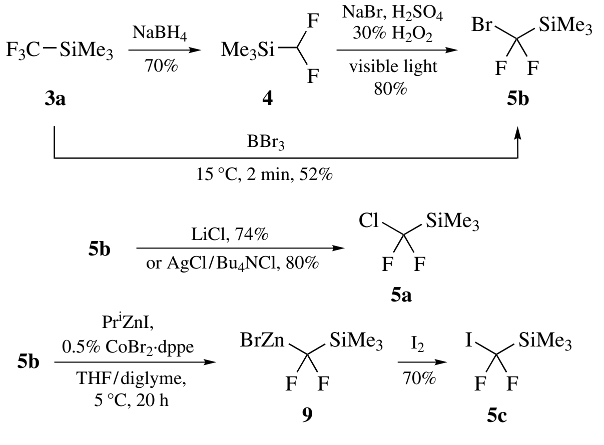


Scheme 2

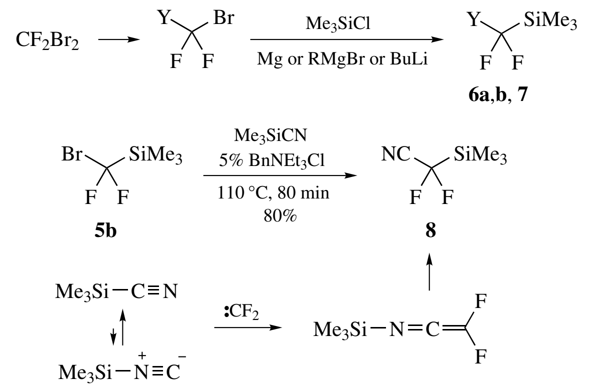
higher homologues (**3**, $n > 1$) were also prepared and typically exhibited reactivity similar to that of **3a**.

Reduction of silane **3a** with sodium borohydride affording difluoro-substituted reagent **4** was reported[7] (Scheme 3). Despite uncertainty of reduction mechanism, and the fact that experimental procedure is hazardous (likely due to formation of borane), silane **4** has already found numerous applications for the direct introduction of difluoromethyl group.[8] Importantly, this reagent is now commercially available. Bromination of C–H bond of silane **4** can be performed with NaBr/H_2O_2 system under acidic conditions furnishing silane **5b**. The bromination proceeds by a radical mechanism, and is promoted by irradiation with conventional household light bulb.[9] Alternatively, direct transformation of **3a** to **5b** can be carried out using boron tribromide.[10] Silane **5b** can also be obtained from CF_2Br_2 and Me_3SiBr under reductive conditions.[11] Iodo-substituted reagent **5c** was synthesized from bromide **5b** by cobalt-catalyzed bromine/zinc exchange to generate organozinc species **9** followed by treatment with iodine.[12]



Scheme 3

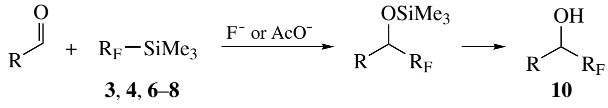
Reagents **6a**,**b**, **7**, and **8** also received significant attention, since the presence of a functional group opens up opportunities for additional transformations. Compounds **6a**,[13] **6b**[13(*a*),14] and **7**[15] can be obtained starting from the corresponding brominated derivatives, which in turn are prepared from dibromodifluoromethane (Scheme 4). However, this approach cannot be applied to the preparation of silane **8**, since transformation of bromodifluoroacetonitrile into **8** was unsuccessful. Reagent **8** was produced from silane **5b** by heating with trimethylsilyl cyanide in the presence of 5 mol% of benzyltriethylammonium chloride. Presumably, in these reactions silane **5b** serves as a source of difluorocarbene (*vide infra*) which interacts with isonitrile tautomer of silyl cyanide followed by N,C-silyl migration affording compound **8**.



Scheme 4

Applications of silicon organofluorine reagents

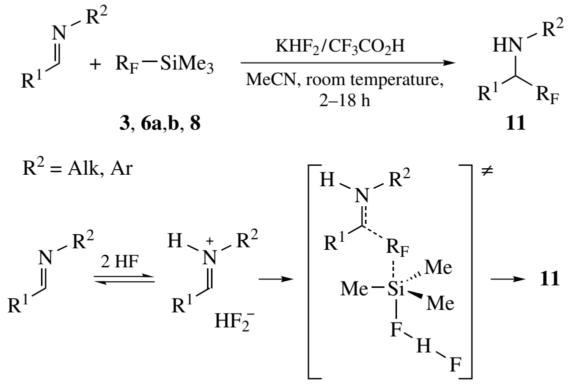
Reagents **3**, **4** and **6**–**8** can be coupled with aldehydes under activation with Lewis bases furnishing, after desilylative work-up, fluorinated alcohols **10** (Scheme 5). Fluoride ion (in Bu_4NF, $Bu_4NPh_3SiF_2$, CsF) or simply acetate or even carbonate anion usually taken in catalytic amounts can serve as activators.[4] Importantly, this reaction can be performed enantioselectively, as examplified by trifluoromethylation of aryl ketones with silane **3a** using chiral quaternary ammonium salts as catalysts.[16]



Scheme 5

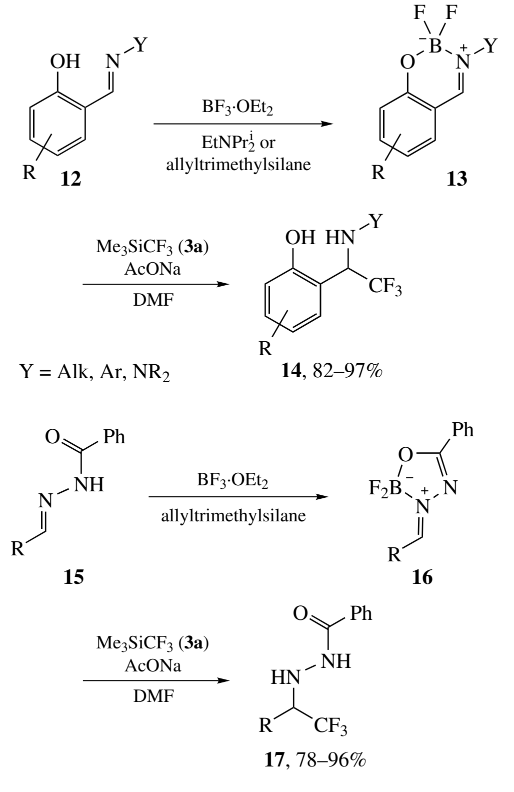
N-Tosyl and *N*-sulfinylimines behave similarly though stoichiometric quantities of a basic activator may be required owing to ineffective silylation of intermediate formed after step of nucleophilic addition to C=N bond.[4(*c*)] However, imines bearing alkyl group at nitrogen are completely unreactive under standard conditions, since alkyl group does not stabilize incipient negative charge on nitrogen. For these substrates, different protocols were elaborated.[17,18] The reactions are performed in the presence of potassium hydrodifluoride and strong acid (trifluoroacetic or triflic) in acetonitrile or dimethylformamide[17(*a*)] (Scheme 6). Under these conditions, hydrofluoric acid is formed which serves as activator of both components – it protonates imines to generate iminium ions, while hydrodifluoride activates the silicon reagent. The key C–C bond forming event, presumably, proceeds as a concerted transfer of the fluorinated group from five-coordinate silicon species to iminium electrophile. In support of this mechanism is the fact that the slight excess of strong acid is employed, which would be expected to protonate intermediate free carbanionic species, if the latter were produced. It should be pointed out, that these reactions can be performed in a regular glassware, and no glass etching was noted.

Direct trifluoromethylation of substrates **12** and **15** is problematic due to their decreased reactivity (Scheme 7). However, they can be transformed into difluoroboryl complexes **13** and



Scheme 6

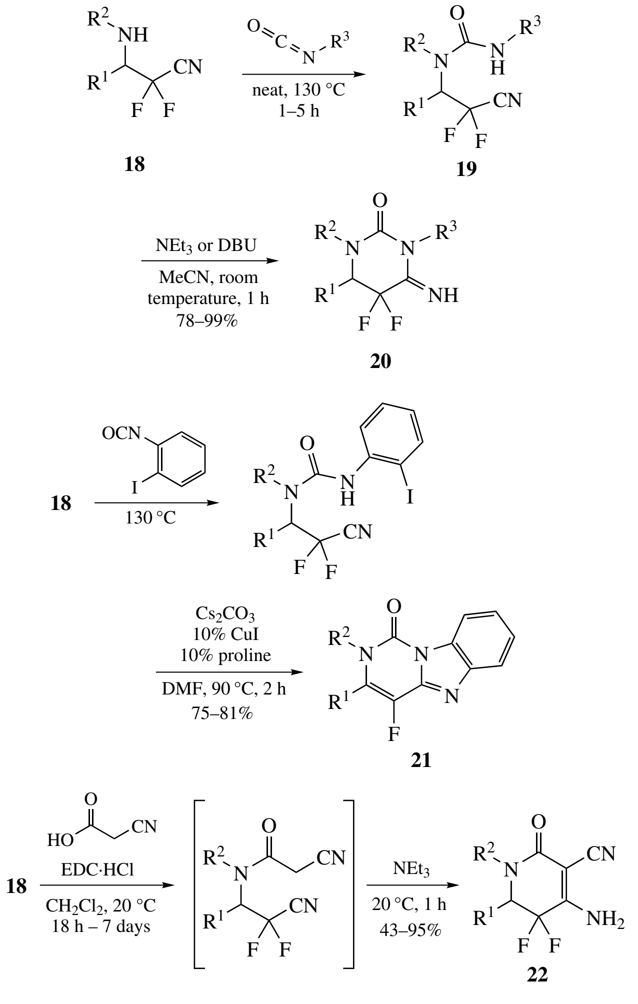
16 by treatment with boron trifluoride etherate and a suitable scavenger of hydrofluoric acid such as Hunig's base or allyltrimethylsilane. Complexes **13** and **16** undergo smooth trifluoromethylation using the Ruppert–Prakash reagents to afford after hydrolytic work-up compounds **14** and **17**.[18]



Scheme 7

Secondary amines **11** are valuable building blocks for drug design, since this functionality is isosteric to amide fragment.[19] Furthermore, when R_F is not merely fluoroalkyl group, but contains a functional group, subsequent transformations involving this group are possible.

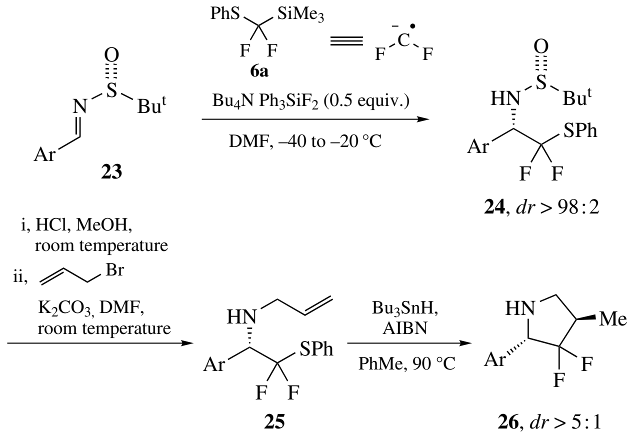
For example, aminonitriles **18** (obtained from imines and silane **8**) can serve as precursors to various heterocycles (Scheme 8). Reaction of amines **18** with isocyanates proceeds at elevated temperatures leading to the corresponding ureas **19** (heating is required due to decreased nucleophilicity of amine nitrogen in compounds **18**). Ureas **19** undergo facile cyclization into difluorinated pyrimidine-1,3-diones **20**, which can be readily transformed into pharmacophoric 5-fluorouracyl derivatives.[20] If isocyanate contains *o*-iodophenyl substituent, the use of base along with a copper(I) catalyst allows one to directly obtain fluorinated fused heterocycles **21**.[20] Finally, acylation of amines **18** with cyanoacetic acid promoted by ethyl 3-ethyl-1-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC·HCl) with subsequent addition of triethylamine afforded 4-amino-5,6-dihydropyridine-2(1*H*)-ones **22** *via* Thorpe–Ziegler cyclization.[21] The reaction efficiency is determined by acylation step, which is sensitive to steric effect of the substituent at nitrogen.



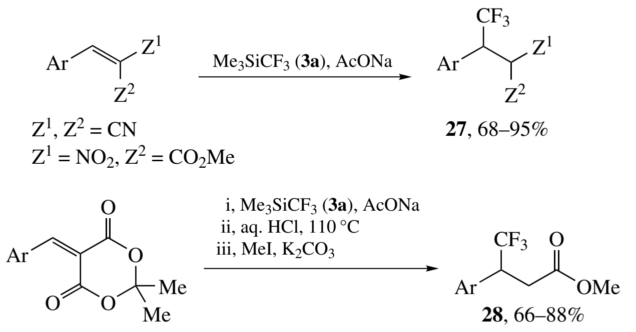
Scheme 8

Reaction of chiral *N*-sulfinyl imines **23** with reagent **6a** gives rise to adducts **24** with high diastereoselectivity (Scheme 9). Removal of *tert*-butylsulfinyl group under acidic conditions and allylation at nitrogen leads to amines **25**, which are good substrates for radical cyclization. Treatment of **25** with tributyltin hydride in the presence of AIBN results in abstraction of thiophenyl group followed by intramolecular radical addition. In this process, *gem*-difluorinated pyrrolidines **26** are produced with good *trans* selectivity.[22] Overall transformation of **23** to **26** suggests that silicon reagent **6a** serves as an equivalent of difluoromethylene radical carbanion.

Nucleophilic trifluoromethylation of Michael acceptors has been a longstanding problem. Indeed, when α,β-unsaturated carbonyl compounds are reacted with Me_3SiCF_3, only products of carbonyl addition are formed.[23] First examples of nucleophilic trifluoromethylation of conjugate double bond were reported for quite specific substrates.[24] Later alkenes obtained by condensation of aromatic aldehydes with malononitrile or methyl nitroacetate were found to serve as excellent Michael acceptors, leading to products **27** in high yields[25] (Scheme 10). Arylidene derivatives of Meldrum's acid also smoothly reacted with silane **3a**; subsequent hydrolysis, decarboxylation, and esterification



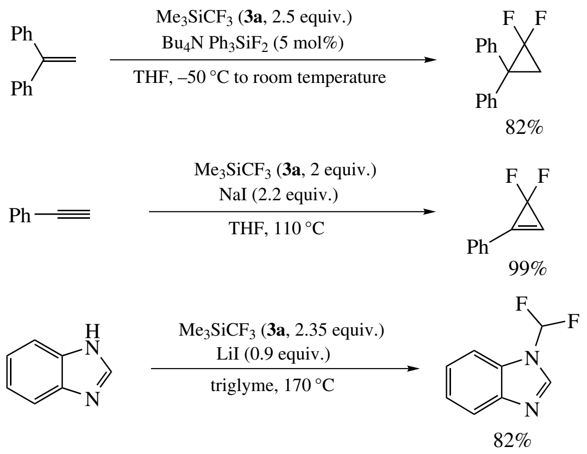
Scheme 9



Scheme 10

afford β-trifluoromethyl-substituted esters **28**.[26] Reactions shown in Scheme 10 are inefficient when applied to alkylidene substrates bearing acidic hydrogen, presumably, because of high basic nature of the system arising from the combination of the Ruppert–Prakash and a Lewis basic activator.

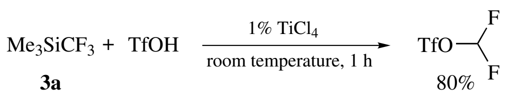
Difluorocarbene is an important reactive intermediate, which can be used for the synthesis of various organofluorine compounds.[27,28] The groups of Prakash and Hu reported that reagent **3a** can also serve as a source of difluorocarbene (Scheme 11). Difluorocyclopropanation of alkenes and alkynes can be performed either using tetrabutylammonium fluoride starting from –50 °C or sodium iodide at 110 °C.[29] Later, iodide ion-mediated generation of difluorocarbene from **3a** was employed for the difluoromethylation of imidazoles and benzimidazoles, athough in this case temperatures around 170 °C were required.[30] Despite drastic conditions, these methods for difluorocarbene generation are very useful, primarily, due to ready availability of reagent **3a**.



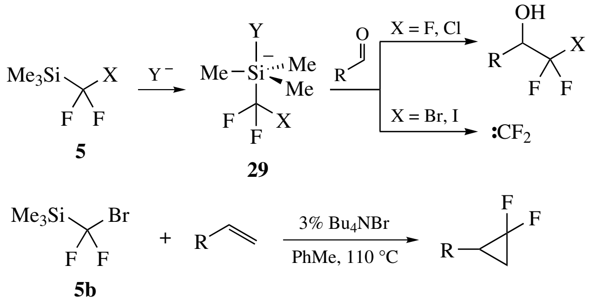
Scheme 11

A process that stands apart from conventional chemistry of fluorinated silanes is the reaction of the Ruppert–Prakash reagent with perfluorosulfonic acids (Scheme 12). The reaction is accelerated by catalytic amounts of titanium tetrachloride, and affords difluoromethyl triflate in good yield.[31] The mechanism of this transformation was not studied, but the intermediacy of difluorocarbene which is trapped by strong acid seems likely.

Silicon reagents **5b** (X = Br) and **5c** (X = I) cannot be involved in reactions with electrophiles under typical conditions, in contrast to the Ruppert–Prakash reagent or chlorine-substituted analogue **5a** (X = Cl).[11] Indeed, when reagents **5b,c** are combined with Lewis basic activators, the five-coordinate intermediate **29** decomposes rapidly to generate difluorocarbene, and no adduct at aldehyde is formed (Scheme 13). Moreover, it was demonstrated[10] that compound **5b** can serve as a source of difluorocarbene under the action of bromide anion at elevated temperatures, and this can be exploited for the synthesis of difluorinated cyclopropanes and cyclopropenes.

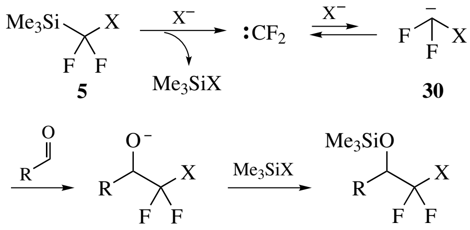


Scheme 12



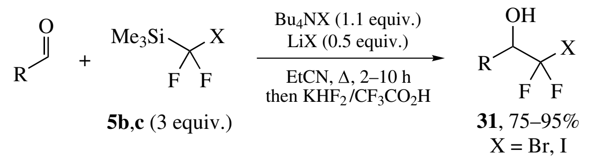
Scheme 13

It was proposed that difluorocarbene generated in this way may reversibly interact with halide anion to give a carbanionic species **30** (Scheme 14). If this is true, the halide anion used in excess can provide carbanion **30** in concentration sufficient to be trapped by aldehyde.[12(a)]



Scheme 14

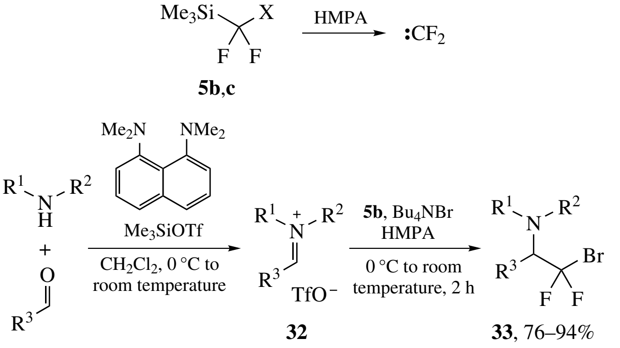
In fact, aromatic aldehydes react with reagents **5b,c** in the presence of combination of tetrabutylammonium and lithium halides in refluxing propionitrile (Scheme 15). Alcohols **31** were obtained in high yields after desilylative work-up.[12(a)] The role of lithium salt is to accelerate the reaction by coordination to the carbonyl group. However, this methodology cannot be extended to enolizable aliphatic aldehydes.



Scheme 15

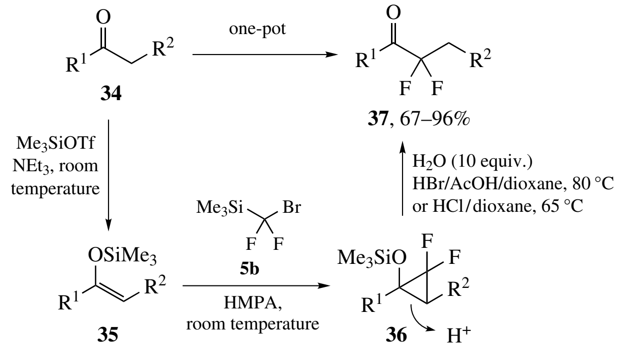
Iminium ions **32** constitute another type of important electrophiles,[32] which are more labile compared to carbonyl compounds. To effect halodifluoromethylation of iminium ions, a different protocol was developed. It was found that hexamethylphosphoramide (HMPA) triggers decomposition of reagents **5b,c** to generate difluorocarbene at room or even lower temperatures[33] (Scheme 16). Iminium ions **32** were generated *in situ* from aldehydes and secondary amines using 1,8-bis(dimethylamino)naphthalene and trimethylsilyltriflate. Subsequent addition of the silicon reagent **5b**, bromide ion and HMPA effected smooth bromodifluoromethylation furnishing amines **33**.

Combination of silicon reagent **5b** with HMPA is one of the mildest methods to generate difluorocarbene.[27] Indeed, room



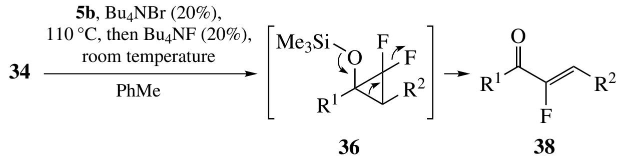
Scheme 16

temperature and virtually non-basic medium make this conditions preferable when products forming after the reaction of a substrate with difluorocarbene are labile. This is exactly the case for difluorocyclopropanation of silyl enol ethers. In particular, cyclopropanes **36** are highly sensitive to basic conditions and high temperatures, and readily decompose.[34] It was found that difluorocyclopropanation of silyl enol ethers **35** can be performed using reagent **5b** and HMPA, and cyclopropanes **36** upon treatment with strong acid (HBr or HCl) undergo cyclopropane ring opening (Scheme 17). It should be pointed out that transformation of **36** to **37** proceeds readily only in the presence of water which presumably hydrolyzes silyl ether into free cyclopropanol with the the latter undergoing protonation. The whole sequence of reactions (**34** to **37**) can be performed in a one-pot manner, and corresponds to difluorohomologation of starting ketones **34**. This homologation method was applied to wide variety of ketones (aliphatic, aromatic, cyclic), and allows one to obtain valuable α,α-difluoro ketones **37** in one synthetic step from readily available ketones **34**.[35,36]



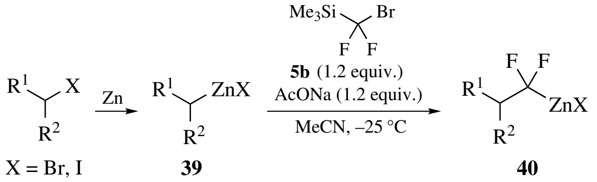
Scheme 17

Most recently, the group of Chinese chemists developed transformation of ketones **34** into α-fluoro-α,β-enones **38** with the use of reagent **5b**[37] (Scheme 18). In this case, the instability of intermediate cyclopropanes **36** was exploited, and transformation of ketones **34** into enones **38** was carried out as a one-pot procedure.



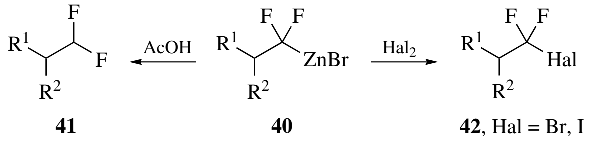
Scheme 18

Mild conditions for the generation of difluorocarbene based on reagent **5b** were exploited to develop insertion of difluoromethylene unit into carbon–zinc bond[38] (Scheme 19). Thus, organozinc reagents **39** prepared in a conventional manner from benzyl or alkyl bromides (or iodides) were reacted with silane **5b**. The silicon reagent was activated with sodium acetate in acetonitrile at low temperatures (–25 °C). A new organozinc species **40** was identified by NMR spectroscopy in solution. Reagents **40** possess limited stability, and decompose within hours at room temperature. Nevertheless, addition of at least two equivalents of DMF provides notable stabilization, while further increases of the stability of **40** may be achieved if DMF is used as the solvent instead of acetonitrile.



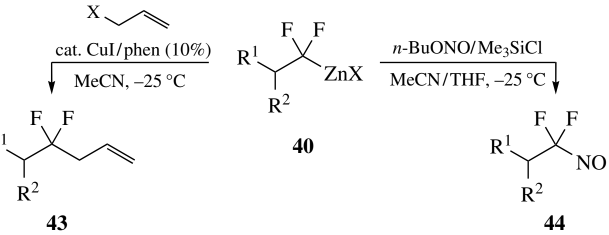
Scheme 19

Reagents **40** can serve as nucleophiles in reactions with various electrophiles, though their nucleophilic reactivity is diminished compared to non-fluorinated organozincs. Protonation of carbon–zinc bond of **40** with acetic acid leads to compounds **41**. Halogenation can also be easily performed using elemental bromine or iodine[38,39] (Scheme 20). However, reaction of organozincs **40** with chlorinating reagents affords only brominated products **42** (Hal = Br) because of facile oxidation of bromide ion. To effect chlorination, *gem*-difluorinated reagents should be obtained from organozinc chlorides RZnCl using chloro-substituted silane Me$_3$SiCF$_2$Cl (**5a**).[40]



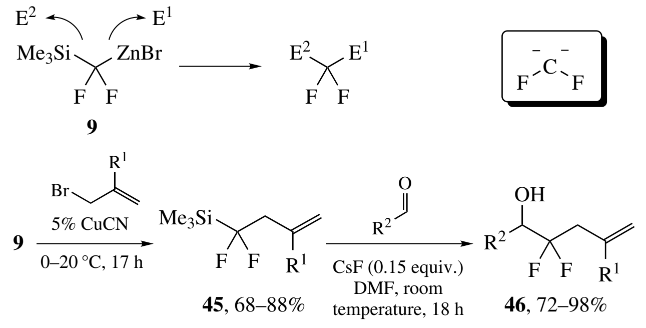
Scheme 20

Reagents **40** can be involved into cross-coupling with allyl halides (Scheme 21). The allylation is catalyzed by copper iodide and 1,10-phenanthroline, and is performed at low temperature, giving products **43** in high yields.[41] Nucleophilic properties of organozincs **40** can be exploited in reactions with nitrosating system – *n*-butylnitrite/chlorotrimethylsialne.[42] It should be pointed out that resulting *gem*-difluorosubstituted compounds **44** are themselves good electrophiles, and interaction of organozincs **40** with **44** can decrease the yield of nitroso products.



Scheme 21

Reagent **9**, which is prepared from silane **5b** (see Scheme 3) can sequentially react with two different electrophiles, thereby acting as equivalent of difluoromethylene bis(carbanion) (Scheme 22). First, more reactive C–Zn bond of organozinc species **9** is involved into copper catalyzed allylation leading to new silicon reagents **45**. The latter reagents may be coupled with aldehydes in the presence of catalytic amounts of cesium fluoride, finally affording *gem*-difluorinated alcohols **46**.[12(b)]



Scheme 22

Conclusion

Silicon organofluorine reagents have emerged as a powerful tool for the synthesis of fluorine containing compounds. Typically, these silanes serve as efficient reagents for nucleophilic fluoroalkylation reactions. The addition of fully or partially fluorinated fragment to C=O or C=N bonds has been very well developed, and these processes have wide scope, and can be considered as reliable synthetic methods. Most recently, silicon reagents have been used as precursors of difluorocarbene, and this direction would likely be intensively exploited in the near future.

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References

1 (*a*) W. R. Dolbier Jr., *J. Fluorine Chem.*, 2005, **126**, 157; (*b*) P. Kirsch, *Modern Fluoroorganic Chemistry*, Wiley-VCH, Weinheim, 2004.

2 (*a*) K. Müller, C. Faeh and F. Diederich, *Science*, 2007, **317**, 1881; (*b*) J. Wang, M. Sanchez-Roselló, J. L. Aceña, C. del Pozo, A. E. Sorochinsky, S. Fustero, V. A. Soloshonok and H. Liu, *Chem. Rev.*, 2014, **114**, 2432; (*c*) D. O'Hagan, *J. Fluorine Chem.*, 2010, **131**, 1071; (*d*) W. K. Hagmann, *J. Med. Chem.*, 2008, **51**, 4359; (*e*) *Fluorine in Medicinal Chemistry and Chemical Biology*, ed. I. Ojima, John Wiley & Sons, Chichester, 2009; (*f*) J.-P. Begue and D. Bonnet-Delpon, *Bioorganic and Medicinal Chemistry of Fluorine*, Wiley-VCH, Weinheim, 2008.

3 T. Liang, C. N. Neumann and T. Ritter, *Angew. Chem. Int. Ed.*, 2013, **52**, 8214.

4 (*a*) G. K. S. Prakash and A. K. Yudin, *Chem. Rev.*, 1997, **97**, 757; (*b*) X. Liu, C. Xu, M. Wang and Q. Liu, *Chem. Rev.*, 2015, **115**, 683; (*c*) A. D. Dilman and V. V. Levin, *Eur. J. Org. Chem.*, 2011, 831; (*d*) R. P. Singh and J. M. Shreeve, *Tetrahedron*, 2000, **56**, 7613; (*e*) K. Uneyama, *J. Fluorine Chem.*, 2008, **129**, 550.

5 G. K. S. Prakash, R. Krishnamurti and G. A. Olah, *J. Am. Chem. Soc.*, 1989, **111**, 393.

6 I. Ruppert, K. Schlich and W. Volbach, *Tetrahedron Lett.*, 1984, **25**, 2195.

7 A. A. Tyutyunov, V. E. Boyko and S. M. Igoumnov, *Fluorine Notes*, 2011, **74**, 1.

8 (*a*) Y. Zhao, W. Huang, J. Zheng and J. Hu, *Org. Lett.*, 2011, **13**, 5342; (*b*) A. A. Tyutyunov, V. E. Boyko and S. M. Igoumnov, *Fluorine Notes*, 2011, **78**, 1; (*c*) P. S. Fier and J. F. Hartwig, *J. Am. Chem. Soc.*, 2012, **134**, 5524; (*d*) C. Matheis, K. v. Jouvin and L. J. Goossen, *Org. Lett.*, 2014, **16**, 5984; (*e*) X.-L. Jiang, Z.-H. Chen, X.-H. Xu and F.-L. Qing, *Org. Chem. Front.*, 2014, **1**, 774; (*f*) Y. Gu, X. Leng and Q. Shen, *Nat. Commun.*, 2014, 5.

9 M. D. Kosobokov, A. D. Dilman, V. V. Levin and M. I. Struchkova, *J. Org. Chem.*, 2012, **77**, 5850.

10 L. Li, F. Wang, C. Ni and J. Hu, *Angew. Chem. Int. Ed.*, 2013, **52**, 12390.

11 A. K. Yudin, G. K. S. Prakash, D. Deffieux, M. Bradley, R. Bau and G. A. Olah, *J. Am. Chem. Soc.*, 1997, **119**, 1572.

12 (*a*) M. D. Kosobokov, V. V. Levin, M. I. Struchkova and A. D. Dilman, *Org. Lett.*, 2014, **16**, 3784; (*b*) M. D. Kosobokov, V. V. Levin, A. A. Zemtsov, M. I. Struchkova, A. A. Korlyukov, D. E. Arkhipov and A. D. Dilman, *Org. Lett.*, 2014, **16**, 1438.

13 (*a*) G. K. S. Prakash, J. Hu and G. A. Olah, *J. Org. Chem.*, 2003, **68**, 4457; (*b*) D. Soorukram, C. Kuhakarn, V. Reutrakul and M. Pohmakotr, *Synlett*, 2014, **25**, 2558.

14 C. Ni and J. Hu, *Tetrahedron Lett.*, 2005, **46**, 8273.

15 A. V. Alexandrova and P. Beier, *J. Fluorine Chem.*, 2009, **130**, 493.

16 S. Mizuta, N. Shibata, S. Akiti, H. Fujimoto, S. Nakamura and T. Toru, *Org. Lett.*, 2007, **9**, 3707.

17 (*a*) V. V. Levin, A. D. Dilman, P. A. Belyakov, M. I. Struchkova and V. A. Tartakovsky, *Eur. J. Org. Chem.*, 2008, 5226; (*b*) M. D. Kosobokov, A. D. Dilman, M. I. Struchkova, P. A. Belyakov and J. Hu, *J. Org. Chem.*, 2012, **77**, 2080.

18 (*a*) A. D. Dilman, D. E. Arkhipov, V. V. Levin, P. A. Belyakov, A. A. Korlyukov, M. I. Struchkova and V. A. Tartakovsky, *J. Org. Chem.*, 2007, **72**, 8604; (*b*) A. D. Dilman, V. V. Levin, P. A. Belyakov, A. A. Korlyukov, M. I. Struchkova and V. A. Tartakovsky, *Mendeleev Commun.*, 2009, **19**, 141; (*c*) A. D. Dilman, D. E. Arkhipov, V. V. Levin, P. A. Belyakov, A. A. Korlyukov, M. I. Struchkova and V. A. Tartakovsky, *J. Org. Chem.*, 2008, **73**, 5643.

19 (*a*) M. Sani, A. Volonterio and M. Zanda, *ChemMedChem*, 2007, **2**, 1693; (*b*) J. Y. Gauthier, N. Chauret, W. Cromlish, S. Desmarais, L. T. Duong, J.-P. Falgueyret, D. B. Kimmel, S. Lamontagne, S. Leger, T. LeRiche, C. S. Li, F. Masse, D. J. McKay, D. A. Nicoll-Griffith, R. M. Oballa, J. T. Palmer, M. D. Percival, D. Riendeau, J. Robichaud, G. A. Rodan, S. B. Rodan, C. Seto, M. Therien, V.-L. Truong, M. C. Venuti, G. Wesolowski, R. N. Young, R. Zamboni and W. C. Black, *Bioorg. Med. Chem. Lett.*, 2008, **18**, 923.

20 M. D. Kosobokov, M. I. Struchkova, D. E. Arkhipov, A. A. Korlyukov and A. D. Dilman, *J. Fluorine Chem.*, 2013, **154**, 73.

21 M. D. Kosobokov, M. I. Struchkova and A. D. Dilman, *Russ. Chem. Bull., Int. Ed.*, 2014, **63**, 549 (*Izv. Akad. Nauk, Ser. Khim.*, 2014, 549).

22 Y. Li and J. Hu, *Angew. Chem. Int. Ed.*, 2007, **46**, 2489.

23 R. P. Singh, R. L. Kirchmeier and J. M. Shreeve, *Org. Lett.*, 1999, **1**, 1047.

24 (*a*) V. Y. Sosnovskikh, D. V. Sevenard, B. I. Usachev and G.-V. Röschenthaler, *Tetrahedron Lett.*, 2003, **44**, 2097; (*b*) V. Y. Sosnovskikh, B. I. Usachev, D. V. Sevenard and G. V. Röschenthaler, *J. Org. Chem.*, 2003, **68**, 7747; (*c*) V. Y. Sosnovskikh, B. I. Usachev, D. V. Sevenard and G.-V. Röschenthaler, *J. Fluorine Chem.*, 2005, **126**, 779; (*d*) V. Ya. Sosnovskikh, B. I. Usachev, M. N. Permyakov, D. V. Sevenard and G.-V. Röschenthaler, *Russ. Chem. Bull., Int. Ed.*, 2006, **55**, 1687 (*Izv. Akad. Nauk, Ser. Khim.*, 2006, 1628).

25 (*a*) A. D. Dilman, V. V. Levin, P. A. Belyakov, M. I. Struchkova and V. A. Tartakovsky, *Tetrahedron Lett.*, 2008, **49**, 4352; (*b*) A. A. Zemtsov, V. V. Levin, A. D. Dilman, M. I. Struchkova and V. A. Tartakovsky, *J. Fluorine Chem.*, 2011, **132**, 378.

26 A. A. Zemtsov, V. V. Levin, A. D. Dilman, M. I. Struchkova, P. A. Belyakov and V. A. Tartakovsky, *Tetrahedron Lett.*, 2009, **50**, 2998.

27 C. Ni and J. Hu, *Synthesis*, 2014, **46**, 842.

28 O. M. Nefedov and N. V. Volchkov, *Mendeleev Commun.*, 2006, 121.

29 F. Wang, T. Luo, J. Hu, Y. Wang, H. S. Krishnan, P. V. Jog, S. K. Ganesh, G. K. S. Prakash and G. A. Olah, *Angew. Chem. Int. Ed.*, 2011, **50**, 7153.

30 G. K. S. Prakash, S. Krishnamoorthy, S. K. Ganesh, A. Kulkarni, R. Haiges and G. A. Olah, *Org. Lett.*, 2014, **16**, 54.

31 V. V. Levin, A. D. Dilman, P. A. Belyakov, M. I. Struchkova and V. A. Tartakovsky, *J. Fluorine Chem.*, 2009, **130**, 667.

32 V. V. Levin, M. A. Kozlov, Y.-H. Song, A. D. Dilman, P. A. Belyakov, M. I. Struchkova and V. A. Tartakovsky, *Tetrahedron Lett.*, 2008, **49**, 3108.

33 A. V. Tsymbal, M. D. Kosobokov, V. V. Levin, M. I. Struchkova and A. D. Dilman, *J. Org. Chem.*, 2014, **79**, 7831.

34 S.-H. Wu and Q. Yu, *Acta Chim. Sinica*, 1989, **7**, 253.

35 (*a*) M. D. Kosobokov, V. V. Levin, M. I. Struchkova and A. D. Dilman, *Org. Lett.*, 2015, **17**, 760; (*b*) O. V. Fedorov, M. D. Kosobokov, V. V. Levin, M. I. Struchkova and A. D. Dilman, *J. Org. Chem.*, 2015, **80**, 5870.

36 Y. Kageshima, C. Suzuki, K. Oshiro and H. Amii, *Synlett*, 2015, **26**, 63.

37 X. Song, J. Chang, D. Zhu, J. Li, C. Xu, Q. Liu and M. Wang, *Org. Lett.*, 2015, **17**, 1712.

38 V. V. Levin, A. A. Zemtsov, M. I. Struchkova and A. D. Dilman, *Org. Lett.*, 2013, **15**, 917.

39 V. V. Levin, A. A. Zemtsov, M. I. Struchkova and A. D. Dilman, *J. Fluorine Chem.*, 2015, **171**, 97.

40 V. O. Smirnov, A. S. Maslov, V. V. Levin, M. I. Struchkova and A. D. Dilman, *Russ. Chem. Bull., Int. Ed.*, 2014, **63**, 2564 (*Izv. Akad. Nauk, Ser. Khim.*, 2014, 2564).

41 A. A. Zemtsov, N. S. Kondratyev, V. V. Levin, M. I. Struchkova and A. D. Dilman, *J. Org. Chem.*, 2014, **79**, 818.

42 V. O. Smirnov, M. I. Struchkova, D. E. Arkhipov, A. A. Korlyukov and A. D. Dilman, *J. Org. Chem.*, 2014, **79**, 11819.

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