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RECENT ADVANCES IN THE SYNTHESIS AND TRANSFORMATIONS OF HETEROCYCLES MEDIATED BY FLUORIDE ION ACTIVATED SILANES

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Modern methodologies that use silanes in the presence of fluoride ion for the preparation and transformation of three-, four-, five-, six-, and seven-membered heterocycles have been reviewed, covering literature from January 2010 to December 2012. Characteristic reactions in side chains of heterocyclic compounds are presented.

Keywords: *silanes, fluoride ion, heterocycles, arynes, carbonyl compounds, alkenes*

INTRODUCTION

Reactions of organosilicon compounds catalyzed by nucleophiles have been under intense study more than twenty five years. In this field two excellent classical reviews have been published [1, 2]. Recently a monograph [3] and reviews [4, 5] dedicated to hypervalent organosilicon compounds have also been published. There are also two reviews on fluoride mediated reactions of fluorinated silanes [6, 7], as well as on the Tamao-Kumada-Fleming oxidation of silanes [8] and the role of Lewis bases (such as ammonium fluorides) for activation and stereoselectivity in the additions of trimethylsilyl nucleophiles [9]. Fluoride ion as an activator of silicon bonds is widely described in these works. Recently we published three reviews dedicated to activation of silicon bonds by fluoride ion [10–12]. Our aim was to describe the modern methodologies in heterocyclic compound synthesis and transformations mediated by silanes with fluoride ion activation. The influence of different sources of fluoride ion (Bu_4NF [13], KF, CsF, tris(dimethylamino)sulphur (tri-methylsilyl) difluoride (TASF), tetrabutylammonium triphenyldifluorosilicate (TBAT) [14], diethylaminosulphur trifluoride (DAST), bis(2-methoxyethyl)aminosulphur trifluoride (Deoxo-Fluor) [15], AgF, CuF_2) on the chemical processes is discussed in this review. In addition, the synthesis and catalytic properties of novel fluoride ion sources, such as anhydrous phosphazenium fluorides [16], and solid-supported ammonium fluorides [17] are presented here. Beside this, a series of reviews concerning the transformation of benzynes generated from 2- (trimethylsilyl) phenyl triflates and related compounds in the presence of fluoride ion can be found in the literature [18–27].

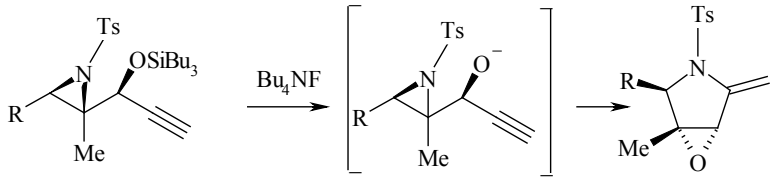
The present work was carried out in continuation of our reviews on synthesis and transformations of heterocycles mediated by fluoride-activated silanes

published in 2002, 2006, and 2009 [28–30]. However, we did not include syntheses of heterocyclic compounds in the presence of both transition metal complexes and fluoride ion.

1.THREE-MEMBERED RINGS

Aza-Payne reaction of aziridines **1** with Bu_4NF afforded derivatives of 3,4-dihydroxypyrrolidines **2** (Scheme 1) [31]. Reaction of 2-silylsubstituted phosphirenes **3** with benzaldehyde in the presence of Bu_4NF led to the addition products **4**. However, reaction of silane **3** with 1 equivalent of Bu_4NF in THF gave the phosphirene ring opening products **5** (Scheme 2) [32].

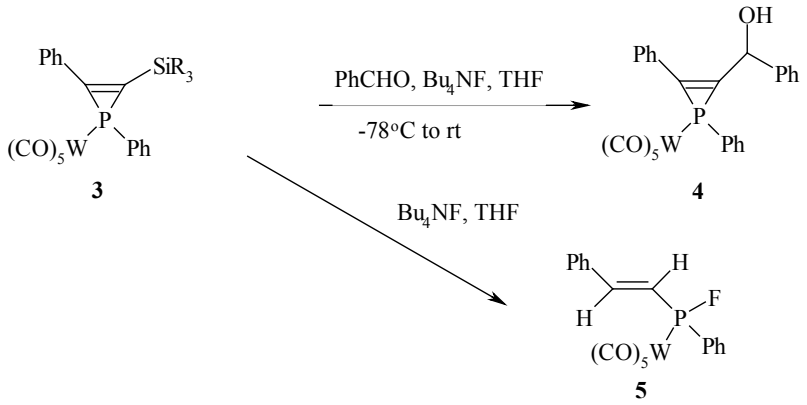
Scheme 1



1 **2**

Ts = p-$MeC_6H_4SO_2$

Scheme 2

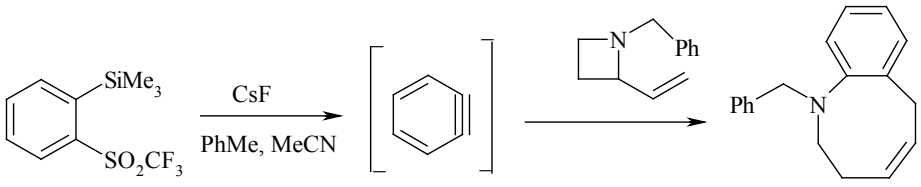


3 **4** **5**

2. FOUR-MEMBERED RINGS

Cycloaddition of benzyne, generated from 2-trimethysilylphenyl-trifluoromethanesulfonate and CsF in a mixture of toluene and CH_3CN, to 1-benzyl- 2-vinylazetidine afforded the benzazocine derivative **6** (Scheme 3) [33].

Scheme 3



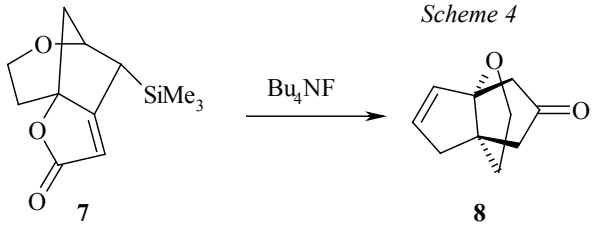
6

3. FIVE-MEMBERED HETEROCYCLES

3.1. Furans and thiophenes

Synthesis of polycyclic ring systems including tetrahydrofuran ring from silane derivatives was described in an article [34]. Thus, desilylation-rearrangement of compound **7** with Bu_4NF afforded the tricyclic derivative **8** (Scheme 4) [34].

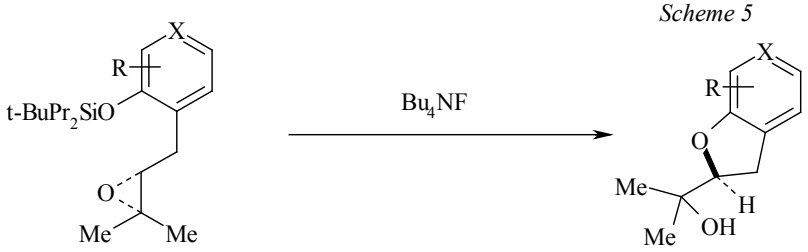
Scheme 4



7 **8**

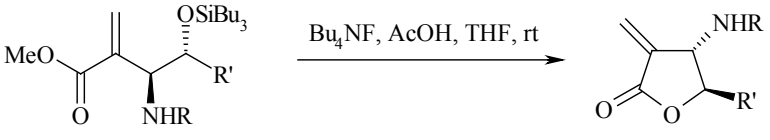
Rearrangement of O-silylated epoxy derivatives of *o*-allylphenols **9** in the presence of Bu_4NF afforded the dihydrobenzofurans **10** with *ee* up to 97% (Scheme 5) [35]. *Trans*-γ-butyrolactone derivatives **12** were obtained in good yields (64-86%) from *erythro*-silanes **11** in the system *Bu_4NF / AcOH / THF* at room temperature (Scheme 6) [36]. Beside this, fluoride induced desilylation-cyclization of silane **13** in 1,2-dimethoxyethane (DME) at 70°C in the presence of TBAT led to cyclopenta[*d*]furo[2,3-*b*]pyridine (**14**) in 71% yield (Scheme 7) [37].

Scheme 5



9 **10**

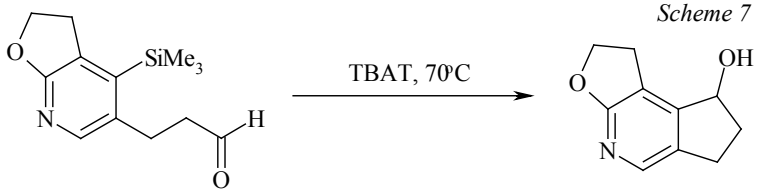
Scheme 6



11 **12**

R, R' = alkyl, aryl

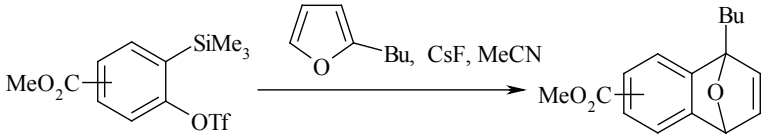
Scheme 7



13 **14**

Reactions of benzynes, generated from 2-trimethysilylphenyl-trifluoromethanesulfonate **5** and fluoride ion, with furans were described in several articles [38-41]. Thus, treatment of silane **15** with 2-*tert*-butylfuran in the system CsF / MeCN afforded the addition product **16** in 83% yield (Scheme 8). A novel three-component coupling reaction of arynes, isocyanides and cyanoformate provided a new route to iminoisobenzofurans [42].

Scheme 8



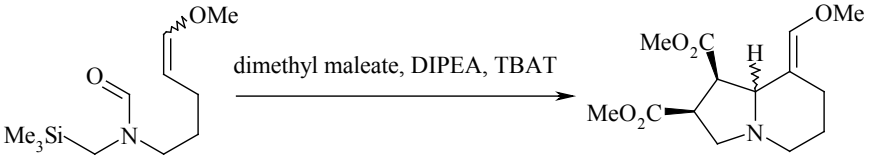
15 **16**

Fluoride ion mediated desilylation reactions of furans [43], furanosides [44] and thiophenes [45] were well presented in some recent articles.

3.2. Pyrrolidine, pyrrole, indole

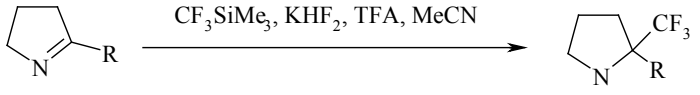
Treatment of silane **17** with triflic anhydride (Tf_2O) / DIPEA and diethyl maleate, followed by TBAT in CH_2Cl_2 afforded dimethyl (*E*)-8- (methoxymethylene) octahydroindolizine-1,2-dicarboxylate (**18**) in 47% yield. (Scheme 9) [46]. Reaction of pyrrolines **19** with Ruppert-Prakash reagent (CF_3SiMe_3) in the presence of KHF_2 / TFA (trifluoroacetic acid) / MeCN led to 2-trifuoromethylpyrrolidines **20** (Scheme 10) [47].

Scheme 9



17 **18**

Scheme 10



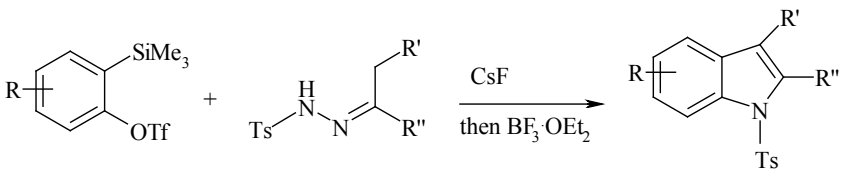
49-79%

19 **20**

R = alkyl, aryl, hetaryl

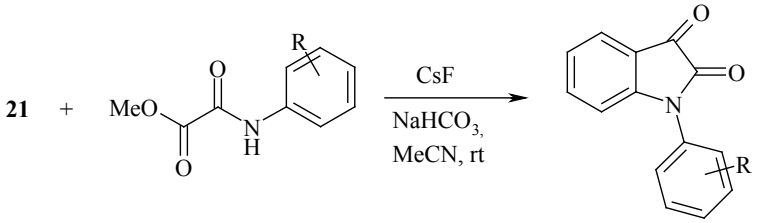
Synthesis of indoles [48-54] and isatins [55] by the reaction of benzynes, generated from 2-trimethysilylphenyl trifluoromethanesulfonate **5** and fluoride ion, with various amino-substituted compounds were described in some articles. Thus, interaction of silane **21** with *N*-tosylhydrazones in the presence of CsF (then $BF_3 \cdot OEt_2$) led to polysubstituted indoles **22** (Scheme 11) [52]. Isatins **23** were successfully prepared from 2-oxo-2-(arylamino)acetates and arynes, generated from silanes **21** and CsF / $NaHCO_3$ in MeCN (Scheme 12) [55].

Scheme 11



21 **22**

Scheme 12

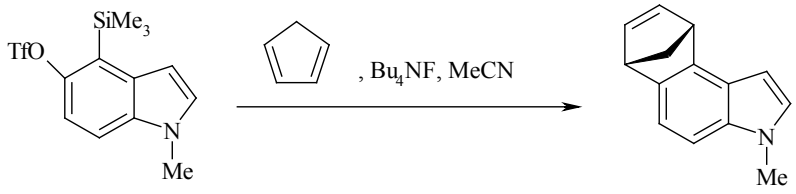


51-92%

23

In some articles there were data on the generation and regioselective reactivity of indolynes obtained by fluoride ion catalysis from the corresponding *o*-trimethylsilyl derivatives of indole triflates [56-59]. For example, treatment of indole **24** with cyclopentadiene in the presence of CsF in MeCN gave the addition product **25** in 85% yield (Scheme 13) [59].

Scheme 13



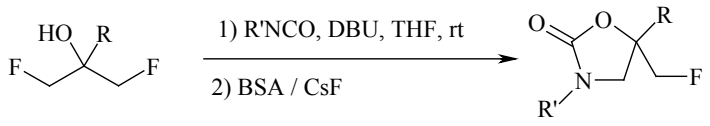
24 **25**

3.3. Oxazole, isoxazole, and thiazole

Construction of novel oxazole ring **27** by transformation of 2-aryl-1,3-difluoropropanols **26** in the system alkyl cyanate / DBU (followed by bis(trimethylsilylacetamide) (BSA) / CsF) has been described (Scheme 14) [60]. Transformation of oxazoline ring under fluoride mediated hydrosilylation conditions was also presented [61]. Nucleophilic ring-opening of benzoxazinones to α-amino 2,2,2-trifluoroacetophenones in Me_3SiCF_3 / TBAT / DMF system was described in article [62]. A number of recent publications were dedicated to the synthesis of isoxazole ring containing heterocyclic compounds from benzyne, generated from 2-(trimethylsilyl)phenyl triflates and related compounds in the presence of fluoride ion source, and nitrile oxides [63-65], nitrones [66, 67], or oxaziridines [68]. Thus, triflate **28** and an oxime derivative in the presence of CsF in MeCN at room temperature afforded the isoxazoles **29** in 36-93% yields (Scheme 15) [63].

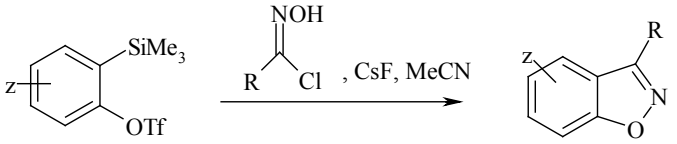
Beside this, desilylation of thiazole derived silyl ethers readily proceeded in the Bu_4NF / DMSO system [69].

Scheme 14



26 **27**

Scheme 15



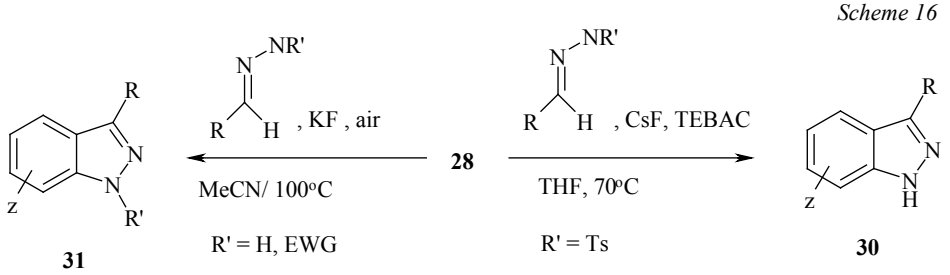
28 **29**

R = alky, aryl, hetaryl

3.4. Indazoles and imidazoles

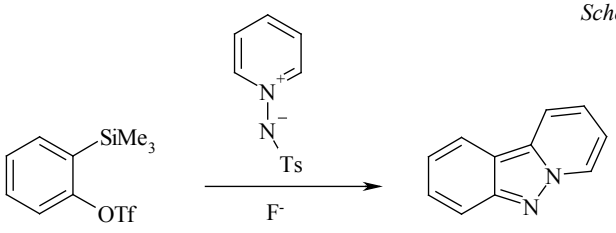
Synthesis of indazoles from benzynes, generated *in situ* from 2-trimethysilylphenyl trifluoromethanesulfonates or related compounds by action of fluoride ion, and hydrazones [70-73], sydnones [74, 75], or diazocarbonyl compounds [76] were recently described in literature. Thus, treatment of silane **28** with *N*-tosylhydrazones in the CsF/ TEBAC ($BnEt_3NCl$) / THF system afforded indazoles **30** (Scheme 16). A similar reaction under aerobic conditions led to *N*-substituted indazoles **31** [73]. Besides this, treatment of silane **32** with *N*-tosylpyridinium imide gave a [3+2] cycloaddition product - pyrido[1,2-b]indazole **33** (Scheme 17) [77].

Scheme 16



31 **30**

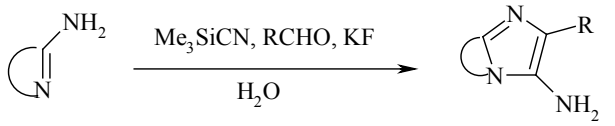
Scheme 17



32 **33**

Two recent articles were dedicated to the synthesis of imidazole containing compounds mediated by fluoride ion activated silanes [78, 79]. Thus, interaction of 2-aminoheterocycles **34** with aldehydes and Me_3SiCN in the presence of KF solution in H_2O afforded the fused imidazoles **35** (Scheme 18) [79]. 1-Imidazolylmethyloxy-2-trimethylsilylbenzene can serve as novel benzyne precursor in the fluoride mediated reactions [80].

Scheme 18



34 **35**

3.5. Triazoles

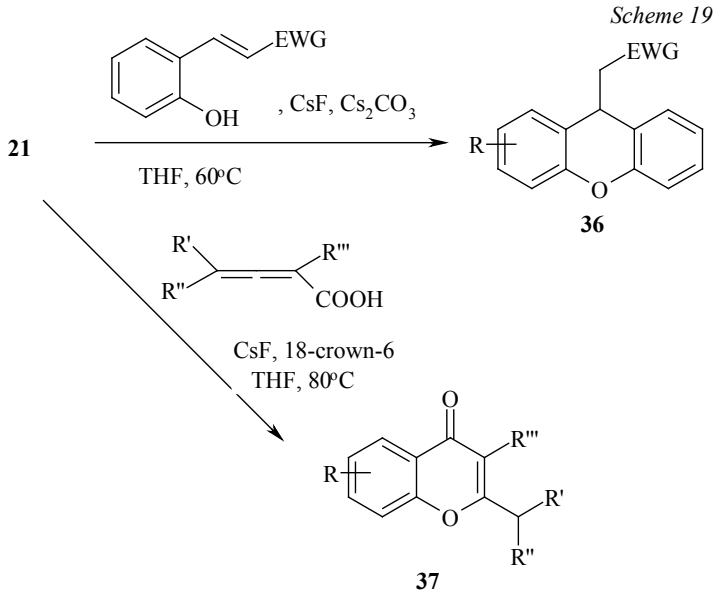
Triazolylpyranosides were prepared by click chemistry reaction of the correspondding silylated pyranoside alkynes and alkyl azides in the presence of a fluoride ion source [81]. Besides this, desilylation of 4-trialkylsilylimidazoles in the Bu_4NF / THF system was also presented in literature [82].

4. SIX-MEMBERED HETERCYCLES

4.1. Pyrans, chromenes and coumarins

Fluoride mediated synthesis of xanthenes [83, 84], coumarins [85] and chromenes [86] from benzyne precursors were described in some articles. Thus, treatment of silane **21** with *o*-hydroxychalcones in the CsF / Cs_2CO_3 / THF system at 60°C led to xanthones **36** in 46-84% yields [83]. Reaction of compounds **21** with 2,3-allenoic acid in the two-phase system of KF / 18-crown-6 / THF at 80°C afforded chromenes **37** (Scheme 19) [86].

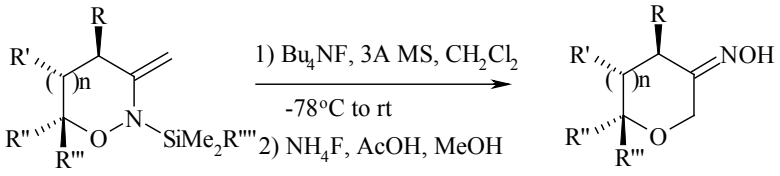
Scheme 19



Synthesis of six-membered oxygen heterocycles by fluoride ion mediated rearrangement of cyclic ene nitroso acetals [87], Diels-Alder reaction [88], epoxide-opening cascades [89] or intramolecular cyclization reactions of silicon derived substrates [90] were described in some articles. Thus, silyl ethers **38** in the system of Bu_4NF / 3Å molecular sieves / CH_2Cl_2 (followed by NH_4F / AcOH / MeOH) afforded furanone and pyranone oximes **39** in 53-97% yields

(Scheme 20) [87]. Epoxide **40** opening by a cascade reaction in the system of CsF/ Cs_2CO_3 / MeOH afforded the polycyclic compound **41** (Scheme 21) [89].

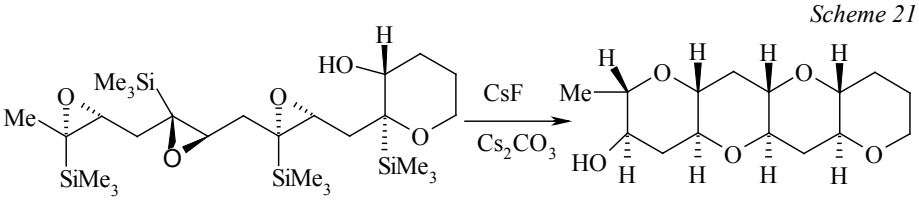
Scheme 20



38 **39**

R = H, alkyl, aryl; R' = H, alkyl; R'' = H, alkyl, Ph; R''' = H, alkyl

Scheme 21



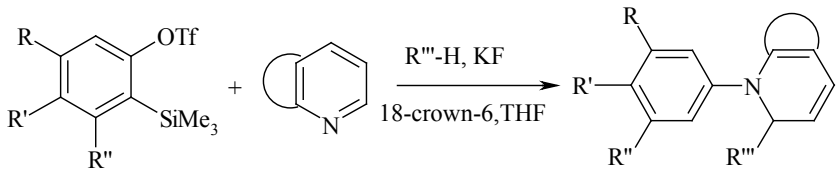
40 **41**

Highly sensitive fluorescence „turn-on“ indicator for fluoride anions with remarkable selectivity in organic and aqueous media was derived from silyl ethers of six-membered fluorinated oxygen heterocycles, which was recently presented [91].

4.2. Pyridines, quinolines and acridines

Synthesis of novel pyridine and quinoline derivatives from benzynes, generated *in situ* from 2-trimethysilylphenyl trifluoromethanesulfonates or related compounds by action of fluoride ion, and pyridines [92] or pyridinium salts [93, 94] were recently described in literature. Thus, treatment of benzyne precursor **42** with pyridines, alkynes or ketones led to the *N*-arylated dihydropyridine **43** (Scheme 22) [92].

Scheme 22

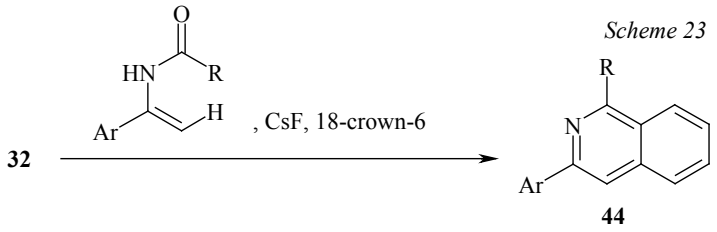


42 **43**

R''' = R'''', CH_2COR''''

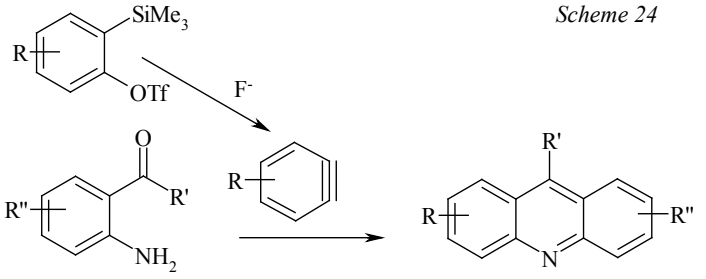
Addition of benzynes to enamines and related compounds was described in two articles [95, 96]. Typically, treatment of silanes **32** with enamine in CsF / 18-crown-6 system afforded disubstituted isoquinolines **44** (Scheme 23) [95]. Isoquinolines were also successfully prepared by cycloaddition of alkynes and 3,4 -pyridynes in the presence of fluoride ion source and a Ni catalyst [97].

Scheme 23

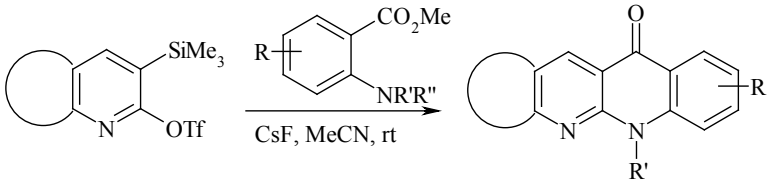


Synthesis of acridones [98–100] or benzonaphthyridones [101] by reaction of benzynes or pyridynes, generated from 2-trimethylsilylphenyl trifluoromethanesulfonates or the respective pyridine analogues and fluoride ion, with amides, β-lactams or amines have been reported by several sources. Thus, the [4+2] annulation of arynes and 2-aminoarylketones **45** afforded acridones **46** (Scheme 24) [98]. Synthesis of the benzonaphthyridone derivatives **48** (48-72% yields) was achieved in 2-aminobenzoate/silane **47**/CsF/MeCN system at room temperature (Scheme 25) [101]. Reaction of 2-alkynylbenzaldoxime [102] or *N'*-(2-alkynylbenzylidene)hydrazide [103] with 2-trimethylsilylphenyl trifluoromethanesulfonates in the presence of fluoride ion led to fused polycyclic isoquinoline derivatives.

Scheme 24



Scheme 25



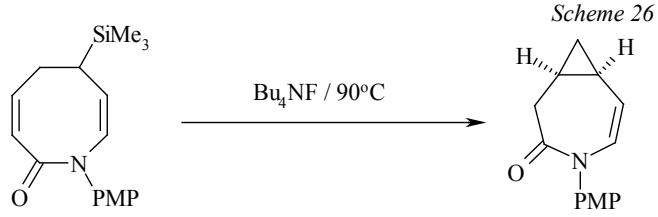
R = H, Cl, Br, I, CO_2Me; R' = alkyl; R" = H, alkyl

Finally, some articles were dedicated to fluoride-mediated addition of silane reagents to the C=O bond in pyridones [104], to the C=N bond in 3,3 -dihydroisoquinolines [105], or copper/KF mediated trifluoromethylation of isoquinolines with CF_3SiMe_3 [106]. Intramolecular hydride addition to silicon substituted pyridinium salts in the presence of Bu_4NF was also described [107].

5. SEVEN-MEMBERED RINGS

An unusual silicon-mediated transannular cyclopropanation of silane **49** in the presence of Bu_4NF afforded azepinone **50** (Scheme 26) [108]. $[Me_2SSMe]^+ BF_4^-$ mediated medium-sized ring formation leading to derivatives of Asteri-scunolidine D was also described [109].

Scheme 26



49 **50**

PMP= p-methoxyphenyl

R E F E R E N C E S

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SILĪCIJA SAIŠU AKTIVĀCIJAS AR FLUORĪDA JONU LIETOJUMS HETROCIKLU SINTĒZĒ UN TO REAKCIJĀS. NESENIE SASNIEGUMI

E. Ābele

K O P S A V I L K U M S

Trīs-, četr-, piec- un sešlocekļu heterociklisko savienojumu sintēze un reakcijas fluorīda aktivētu silānu klātbūtnē ir iekļautas apskatā. Aplūkota arī makrociklisko heterociklisko savienojumu sintēze fluorīda jona klātbūtnē. Apskatā ir iekļauti literatūras dati, kas publicēti no 2010. līdz 2012. gadam.

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