Synthesis of multi-substituted furan rings: the role of silicon

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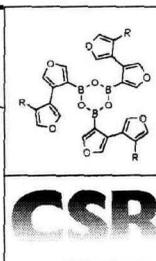
Silanes have proven extremely useful for the synthesis of multi-substituted furan rings. Their judicious placement on a furan ring can be used to control either the placement of new groups around the furan ring or the silane can be directly replaced *via* an *ipso*-substitution. This paper will briefly review the role silicon has played in the preparation of furan rings having a variety of substituent patterns.

1 Introduction

Compounds that have a multi-substituted furan ring as their main component or have a furan ring fused with other rings have exhibited a vast array of activity.[1] Thus, the design of synthetic routes towards furan rings having specific substitution patterns has interested chemists for decades.[2] Of the many strategies developed for the preparation of a multi-substituted furan ring, one of the simplest involves starting with either furan itself or a mono-substituted furan followed by the introduction of functional groups at various positions around the furan ring. This approach, however, has some drawbacks. First, the introduction of functional groups into the 3- and 4-positions is difficult as furan rings lithiate and add electrophiles preferentially at the 2 and 5 positions. Second, placement of a group at C-3 results in the 2 and 5 positions becoming regioisomeric so that either regioselective methods or blocking groups must be used to introduce new moieties.[2] The use of an organosilyl group as a blocking group has been the most useful in furan chemistry. Not only are they easy to introduce and remove, but they can be

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replaced by electrophiles *via* an *ipso*-substitution. In addition, their size has had a pronounced influence on the regioselectivity for introduction of other groups on the furan ring and on some rearrangements. This paper will briefly review the role organosilyl groups have played in the synthesis of multi-substituted furan rings. This will not be an exhaustive review, but will concentrate on how silyl groups have been used to prepare specific substitution patterns with furan rings.

2 The role of silyl groups on furan rings

In 1948 Benkeser and Currie reported[3] not only the introduction of a trimethylsilyl group at the C-2 position of furan, but that the silyl group could later be replaced by a bromine atom *via* an *ipso*-substitution (Scheme 1). Treatment of furan (**1**) with BuLi

Scheme 1

followed by the addition of trimethylsilyl chloride provided 2-(trimethylsilyl)furan (**2**), which when treated again with BuLi followed by the addition of CO_2 gave 5-(trimethylsilyl)-2-furoic acid (**3**). Subsequent treatment of **3** with Br_2 in CCl_4 gave 5-bromo-2-furoic acid (**4**, no yield given). This work also confirmed that furan (**1**) lithiated at the C-2 position when treated with BuLi. To my knowledge this was the first report of the introduction of an organosilyl group onto a furan ring and the first example of an *ipso*-substitution on a furan ring.

In order to introduce functional groups regioselectively around the furan ring, it is sometimes prudent to use a group to block a particular position. Organosilyl moieties have been used as blocking groups as they are easily introduced and removed. Carpenter and Chadwick[4] required the synthesis of 2,3-disubstituted furan rings, but as mentioned above, the introduction of groups into the 3 position of a furan ring is difficult. They achieved the introduction of a group at the C-3 position of 2-furoic acid (**5**) by first blocking the C-5 position with a trimethylsilyl group, which afforded acid **3**, according to the protocol developed by Knight[5] (Scheme 2). Treatment of **3** with BuLi (THF, −78 °C, 0.5 h) resulted in a regiospecific lithiation at C-3. Quenching the anion with CO_2 followed by an acidic workup gave **6**. The trimethylsilyl group was then removed to give furan-2,3-dicarboxylic acid (**7**). The yield for the overall sequence was 78%. A similar sequence (but using different reagents) was also reported by Chadwick[6] using 2-(4,4-dimethyl-4,5-dihydro-1,3-oxazol-2-yl)furan **8** instead of 2-furoic

Scheme 2

close to the C-4 hydrogen atom so that when BuLi was added, the C-4 hydrogen atom was preferentially abstracted instead of the C-5 hydrogen atom. This chemistry also provided a route to directly access 3,4-disubstituted furan rings, which of all the possible furan patterns, are the most difficult to prepare.[2] Treatment of **11** with TBAF in THF resulted in the direct removal of the C-2 silyl group to provide 3,4-substituted furans **12**. Interestingly, the silyl group could be reused to protect the hydroxy group at C-3 by treating **11** with NaH in DMF. This resulted in an intramolecular [1,4] C→O silyl migration to form **13**.[9] The complete sequence in Scheme 3 illustrates the importance and usefulness of a silyl group. This approach was used recently by Scott and co-workers to prepare furan **12a**.[11]

It is interesting to note that if the hydroxymethyl group of **10** is protected as a triethylsilyl[12] or *tert*-butyldimethylsilyl group,[13] to give **14**, and **14** is then treated with 1.3 equiv. of BuLi, lithiation occurs exclusively at C-5 (Scheme 4). Trapping

acid (**5**) and has been expanded upon by Gilchrist[7] and Queguiner.[8]

Keay and co-workers[9,10] have developed a strategy for the synthesis of a variety of polysubstituted furan rings by taking advantage of the silyl groups: 1) ability to be a blocking group; 2) tendency to undergo silyl migrations; and 3) size. In this manner they have been able to develop routes towards the synthesis of 2,3-, 2,3,4-, 2,4-, and the more difficult 3,4-substituted furan systems starting from a common 3-substituted furan ring.

First it was shown that a variety of silyl protected 3-hydroxymethylfurans **9** undergo an intramolecular [1,4] O→C silyl migration to produce 2,3-disubstituted furans **10** in good to excellent yield by treating **9** with a mixture of BuLi and HMPA in THF (Scheme 3).[9] Treatment of **10** with 2.2 equiv. of BuLi in
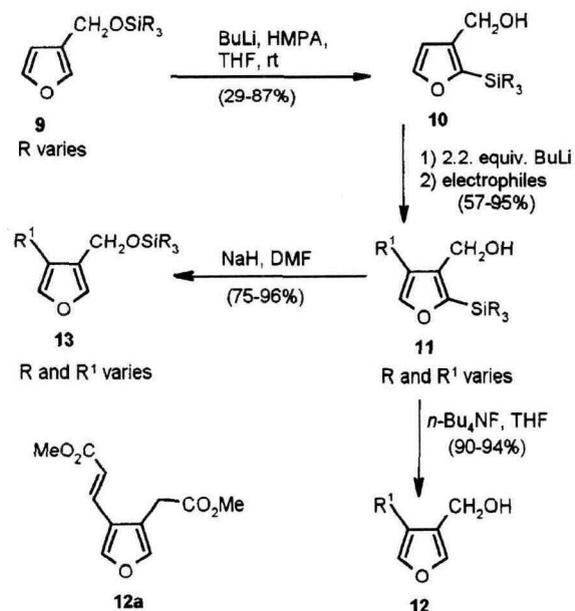
Scheme 3

DME resulted in a regiospecific C-4 lithiation. Quenching the anion with a variety of electrophiles provided 2,3,4-trisubstituted furans **11** in good to excellent yields.[10] To our knowledge, this was the first example of a direct C-4 lithiation in the presence of an unprotected C-5 position on a furan ring. This regiospecific lithiation was a result of the presence of the silyl blocking group at C-2 and also was a result of the size of the silyl group forcing the hydroxymethyl group to reside very

Scheme 4

the C-5 anion with electrophiles provided 2,3,5-trisubstituted furans **15**. When the triethylsilyl group was used, it could be selectively removed (AcOH–THF–H₂O; 8:8:1) to provide alcohol **16**. The hydroxy group in **16** could be re-protected by the silyl group at C-2 *via* a [1,4] C→O silyl migration thereby providing access to 2,4-disubstituted furan rings **17**. In addition, both silyl groups could be removed by treatment with TBAF in THF to provide furans like **18**. Recently Katsumura used this chemistry to prepare tetrasubstituted furan rings as precursors towards butenolides.[14]

One of the more difficult transformations with 2- or 3-furaldehyde is their direct oxidation to 2- or 3-furoic acid, since the furan ring is very sensitive to acidic reagents and normally most oxidations of aldehydes to acids involve using acidic reagents. Thus attempts to oxidize **12** to the corresponding furoic acid failed. To overcome this difficulty, Keay and co-workers showed that silyl esters of 3-furoic acid **19** also undergo a [1,4] O→C silyl migration to provide 2-silylated-3-furoic acids **20** in moderate yield (Scheme 5).[9] Acids **20** when treated with BuLi resulted in a regiospecific C-4 lithiation. Trapping the anion with a variety of electrophiles provided 2,4-disubstituted-3-furoic acids **21** in good to excellent yield.[10] The silyl group was easily removed with TBAF and the acid converted to the methyl ester (for ease of workup) by treatment with diazomethane to provide 4-substituted-3-furoic esters **22**. Quayle and co-workers have used the silyl migration of silylesters **19** to prepare 2-silylated tetrahydrofurans **23**.[15]
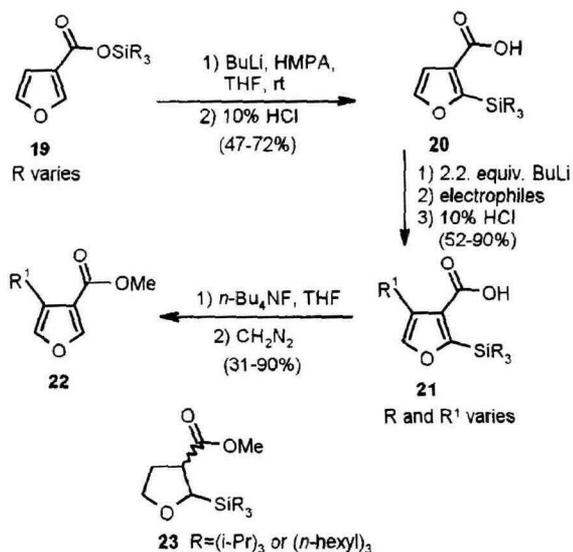
Scheme 5

Scheme 7

In order to illustrate the usefulness of our silyl strategy, we investigated the introduction of other groups into the C-4 position of furan **10** (Scheme 6).[16] The C-4 anion of furan **10**

Scheme 6

Finally, a tetrasubstituted furan ring can be generated very easily by the metalation of furan **29** (Scheme 8), which was prepared using the strategy illustrated in Scheme 7. For
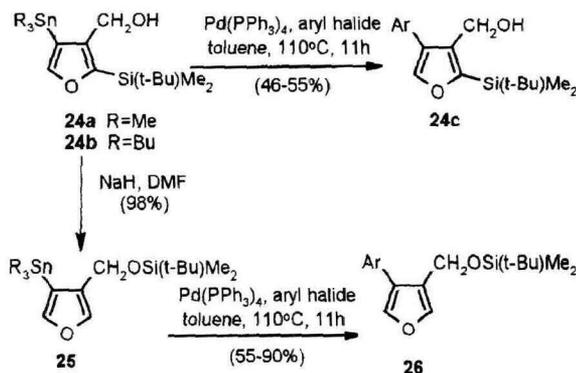
Scheme 8

could be trapped with tributyl- or trimethylstannyl chloride providing furans **24a** and **24b**. The direct Stille coupling with **24a** or **b** provided disappointing yields of furans **24c**; however, when the silyl group at C-2 was migrated to the hydroxy group at C-3 (to give **25**), the Stille coupling proceeded in yields ranging from 55–90% to provide **26**. This gave access to a variety of 3,4-disubstituted furans in which one of the substituents was an aromatic ring.

Since the Stille coupling with **24a** and **24b** was sluggish, we investigated trying a Suzuki coupling. This required the preparation of boronic acid **27** (Scheme 7). Unfortunately, the isolation of boronic acid **27** after quenching the C-4 anion of **10** with trimethylborate was extremely difficult. Thus, we developed an *in situ* variant of the Suzuki reaction in which the boronic acid component does not have to be isolated.[17,18] The reaction is easy to perform. Trimethylborate is added to the anion and the reaction is stirred for 1 h. Then instead of working up the mixture, an aryl or vinyl halide or triflate is added, along with Pd(PPh₃)₄, water, and Na₂CO₃ and the mixture is refluxed for 1–20 h. A variety of products **28** were isolated in yields ranging from 20–93%. The *in situ* variant of the Suzuki reaction is a general reaction and is not limited to just furan systems; a variety of vinyl and aryl carbanions can be treated in a similar manner.[18]

example, furan **29**, when treated with BuLi, provided the C-5 anion **30**, which when quenched with acid chloride **31** provided tetrasubstituted furan **32**. Both silyl groups in **32** were easily removed to provide a 2,3,4-tribsubstituted furan **33**, which is structurally different than the 2,3,4-trisubstituted furan that can be prepared *via* Schemes 3, 6 and 7.

Furan **33** was required as an intermediate towards the synthesis of (+)-xestoquinone (**34**, Scheme 8).[19] Conversion of the hydroxy group in **33** into a triflate (quantitative) followed by an asymmetric palladium-catalyzed polyene cyclization formed rings C and D (82% yield, 68% ee). Two additional steps afforded (+)-**34**.

Tanaka and co-workers[20] have been investigating how silylated furan rings behave towards conditions that favor *ipso*-substitution. Treatment of **35a** or **35b** (prepared *via* Diels–Alder chemistry), with sulfuryl chloride, bromine or iodine mono-chloride afforded **36a–e** in yields ranging from 64–76% (Scheme 9). In related work, they also reported an interesting [1,2] C→C silyl migration.[21] When furan **37** was treated with sulfuryl chloride in acetonitrile, the expected *ipso*-substituted product **38** was obtained.[22] However, when the solvent was changed to CH₂Cl₂ a 24:76 mixture of **38**:**39** was obtained in which the major compound **39** had the silyl group at C-4 and a

Scheme 9

35a R=H
35b R=Me

SO₂Cl₂, Br₂ or ICl
(64-76%)

36a R=H; X=Br
36b R=H; X=I
36c R=Me; X=Cl
36d R=Me; X=Br
36e R=Me; X=I

37

SO₂Cl₂, CH₃CN
(91% of **45**)
or
SO₂Cl₂, CH₂Cl₂
(65% of **46**)

38

39

Scheme 9

Scheme 11

42

1) BCl₃, -78°C
2) 5% HCl
(98%)

44

R¹X, Pd(PPh₃)₄,
PhMe-MeOH
120°C, 14-18h
(45-97%)

1) BCl₃, -78°C
2) 5% HCl (41-61%)
3) R²X, Pd(PPh₃)₄,
PhMe-MeOH
120°C, 2.5-5.5h
(61-92%)

46

45
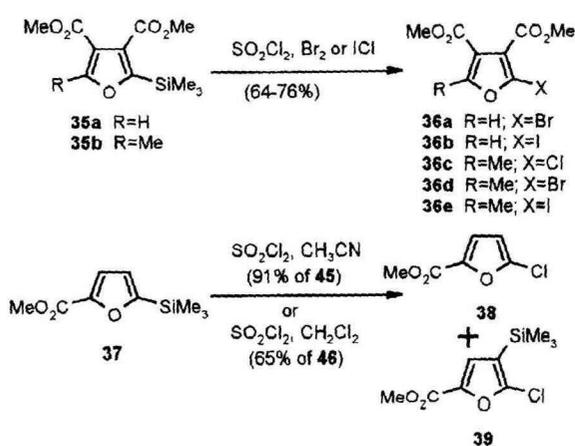
Scheme 11

chlorine atom at C-5. This is the first example of a [1,2] C→C silyl migration with a furan ring.

Wong and co-workers have reported some very interesting furan chemistry starting from 3,4-bis(trimethylsilyl)furan (**42**, Scheme 10). A Diels–Alder reaction between oxazole **40** and

Scheme 10

40 + 41

300°C
(80%)

42

CO₂Me

CO₂Me

75°C
(54%)

43
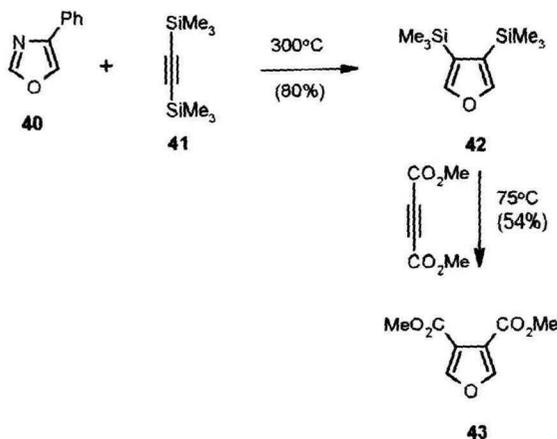
Scheme 10

bis(trimethylsilyl)acetylene (**41**) followed by a retro-Diels–Alder reaction of the initial adduct liberates benzenenitrile and furan **42**.[23] From this relatively simple furan, they have designed routes to 3,4-, 2,4-, and 2,3,5-substituted furan rings. For example, heating **42** with acetylenic dienophiles, like dimethyl acetylenedicarboxylate, provided 3,4-disubstituted furans like **43** (54% yield).

Wong has extended this chemistry by developing a route to the preparation of 3,4-disubstituted furans starting with **42** by performing two successive sequences.[24,25] The first reaction of each sequence was an *ipso*-substitution with one equivalent of BCl₃ to provide boroxine **44** in 98% yield (Scheme 11). The second reaction in the sequence was a Suzuki coupling between **44** and a variety of aryl and heteroaryl halides to provide **45**. Repeating this sequence on **45** provided 3,4-disubstituted furans **46** in which two aryl or heteroaryl groups are present (they could be the same group or could be different).

A year later, Wong[26] expanded upon this sequence by showing that when **44** or **47** was treated with *o*-bis(bromomethyl)arenes in the presence of a palladium catalyst, **48** and/or **49** were formed in various ratios depending on the arene that was used. For example, when the reaction between **44** and 2,3-bis(bromomethyl)quinoxaline (**50**) was performed, only **49**
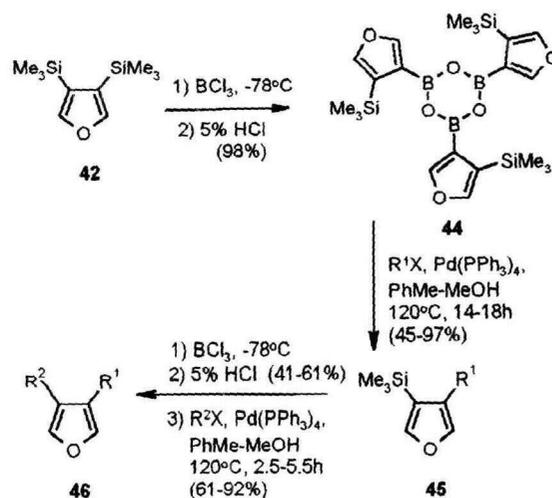
was obtained in 90% yield. He used this unique result with quinoxaline **50** to his advantage by homo-coupling a variety of boroxines **47** (R = CH₂C₆H₄-*p*-CO₂Me, n-Bu, C₆H₄-*o*-Me, C₆H₄-*p*-Me, and C₆H₅) in yields ranging from 52–80%. One interesting application of the chemistry shown in Scheme 12

Scheme 12

44 R=SiMe₃
47 R=aryl

+

Pd(PPh₃)₄,
PhMe-MeOH
2M Na₂CO₃
120°C, 2.5-5.5h
(28-90%)

48

+

49

50
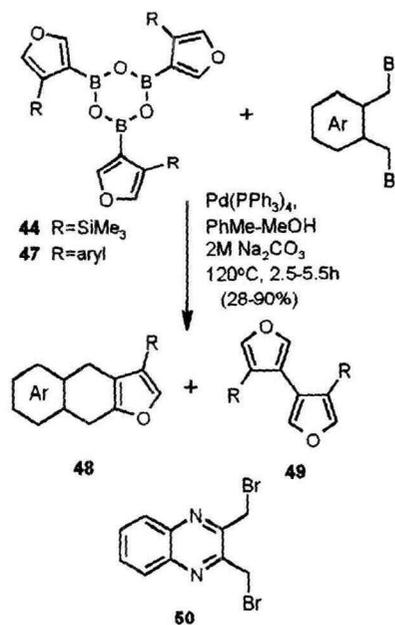
Scheme 12

was to take compound **49** (R = SiMe₃) and treat it with one equivalent of BCl₃ to form the boroxine **51** (Scheme 13). When **51** was homo-coupled in the presence of **50** and a palladium catalyst, quaterfuran **52** was formed. A repeat of the sequence provided octifuran **53**.

In addition to the above interesting chemistry, Wong and co-workers[27] have reported a mono-*ipso*-iodination of **42** and its use in the preparation of 3,4-disubstituted furan rings (Scheme 14). Treatment of **42** with iodine in the presence of silver trifluoroacetate provided furan **54** in 80% yield. With **54** in hand, the authors performed Heck, Stille and Suzuki reactions that provided a large number of 3-substituted-4-(trimethylsilyl)furans **55**. The second trimethylsilyl group was then replaced using Wong's boroxine protocol (see Scheme 11) to

51 R=SiMe₃

Pd(PPh₃)₄,
PhMe-MeOH
1M Na₂CO₃
120°C, 2.5-5.5h
(79%)

52 R=SiMe₃

1) BCl₃, -78°C, 50h
2) Homo-coupling as above
(20%)

53 R=SiMe₃

Scheme 13

Scheme 14

give **56**. Furan **56** could be treated with I₂ in the presence of AgBF₄ to provide iodide **57**, which was used to prepare acetylenic furans like **58**. Or, **56** could be used directly in a Suzuki coupling to give 3,4-disubstituted furans **59**. The mono-replacement of the trimethylsilyl groups in **42** clearly expands the scope of the use of furan **42** in synthesis.

Most recently, Wong and colleagues[28] have reported new strategies towards the synthesis of 2,3-, 2,4-, 2,3,4-, and 2,3,5-substituted furan rings. The approach towards the preparation of 2,3-disubstituted furan rings was developed by observing that when furan **42** is heated in a sealed tube at 160 °C in the presence of trifluoroacetic anhydride containing a catalytic amount of trifluoroacetic acid, one of the silyl groups undergoes a [1,2] C→C silyl migration to provide 2,4-bis(trimethylsilyl)furan (**60**) in 80% yield (Scheme 15). Direct lithiation of **60**

Scheme 15

with BuLi and trapping of the anion with electrophiles, provided furan **61**. The TMS group at C-5 could be selectively *ipso*-iodinated to give **62**. The iodine was easily removed by treatment of **62** with LAH providing 2,3-disubstituted furan **63**. Finally, 2,3-disubstituted furans **64** were prepared by using Wong's boroxine protocol followed by a Suzuki coupling.

An alternative strategy was developed towards compounds like **64** as the overall yield of **64** was low starting with **42**.[28] Furan **65**[23,29] was lithiated exclusively at the less hindered C-2 position with *t*-BuLi (Scheme 16). Trapping of the anion with

Scheme 16

electrophiles yielded **66**, which could be proto-desilylated with trifluoroacetic acid to give **67** in high overall yield.

Scheme 13

Scheme 14

give 56. Furan 56 could be treated with I_2 in the presence of $AgBF_4$ to provide iodide 57, which was used to prepare acetylenic furans like 58. Or, 56 could be used directly in a Suzuki coupling to give 3,4-disubstituted furans 59. The mono-replacement of the trimethylsilyl groups in 42 clearly expands the scope of the use of furan 42 in synthesis.

Most recently, Wong and colleagues[28] have reported new strategies towards the synthesis of 2,3-, 2,4-, 2,3,4-, and 2,3,5-substituted furan rings. The approach towards the preparation of 2,3-disubstituted furan rings was developed by observing that when furan 42 is heated in a sealed tube at 160 °C in the presence of trifluoroacetic anhydride containing a catalytic amount of trifluoroacetic acid, one of the silyl groups undergoes a [1,2] C→C silyl migration to provide 2,4-bis(trimethylsilyl)furan (60) in 80% yield (Scheme 15). Direct lithiation of 60

Scheme 15

with BuLi and trapping of the anion with electrophiles, provided furan 61. The TMS group at C-5 could be selectively ipso-iodinated to give 62. The iodine was easily removed by treatment of 62 with LAH providing 2,3-disubstituted furan 63. Finally, 2,3-disubstituted furans 64 were prepared by using Wong's boroxine protocol followed by a Suzuki coupling.

An alternative strategy was developed towards compounds like 64 as the overall yield of 64 was low starting with 42.[28] Furan 65[23,29] was lithiated exclusively at the less hindered C-2 position with t-BuLi (Scheme 16). Trapping of the anion with

Scheme 16

electrophiles yielded 66, which could be proto-desilylated with trifluoroacetic acid to give 67 in high overall yield.

Starting from furan **68**, Wong was able to prepare 2,4-disubstituted furans (Scheme 16).[28] Treatment of **68** with *t*-BuLi in THF at 0 °C and trapping of the anion with benzyl bromide provided only furan **69** in which a regiospecific lithiation at the C-5 position of **68** had occurred. Using his boroxine chemistry followed by a Suzuki coupling resulted in the preparation of 2,4-disubstituted furans **70**. As might be expected, the boroxine generated and isolated by the treatment of **69** with BCl₃ can either be homo-coupled to provide **71** or iodo-deboronated to provide **72**, which can be used further to prepare other 2,4-disubstituted furan rings.

Compound **54** has been used to prepare 2,3,4-trisubstituted furan rings (Scheme 17).[28] A nickel catalyzed cross-coupling
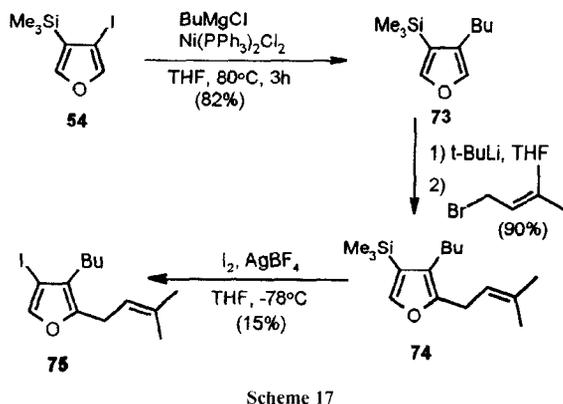
Scheme 17

reaction with butylmagnesium chloride and **54** gave **73**. Regiospecific lithiation of **73** at C-2 with *t*-BuLi and trapping the anion with an electrophile provided **74** in which the silyl group could be replaced by an iodine atom, albeit in low yield, thereby providing a route to 2,3,4-trisubstituted furans **75**.

Finally, Wong[28] has developed a route to 2,3,5-trisubstituted furans **77** (Scheme 18). Furan **62**, prepared according to Scheme
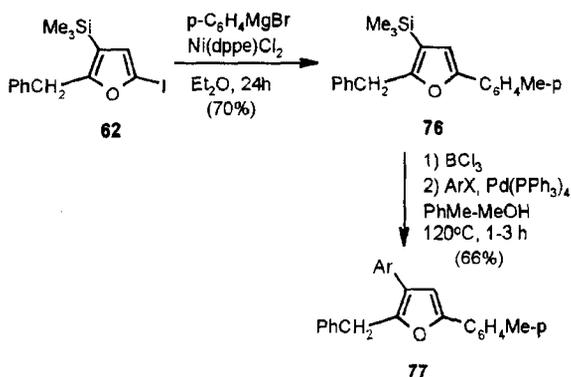
Scheme 18

15, was treated with *p*-tolylmagnesium bromide in the presence of a nickel catalyst to provide **76**. The trimethylsilyl group in **76** was then replaced with aromatic rings *via* Wong's boroxine chemistry, followed by a Suzuki reaction giving **77**. The last few schemes clearly show the important role that a trimethylsilyl group plays in the preparation of a variety of furan substitution patterns. Not only can the silyl group be *ipso*-substituted by boron and iodine, but the steric size of the group can help direct lithiation to a site remote (*i.e.* less hindered) from the silane.

So far the silyl groups have been used for *ipso*-substitution, directing metalation reactions and removed completely by

treatment with TBAF, through a silyl migration, or through a proto-desilylation reaction with acid. An additional use of the trimethylsilyl group is to treat 2-substituted silylated furans with either a peracid or singlet oxygen. This results in a regiospecific conversion of the silylated furan to a butenolide in which the carbonyl group is attached to the carbon atom that the silyl group was initially attached. For example, Kuwajima[30] reported that furan **78** when treated with peracetic acid formed but-3-enolide **79** in yields ranging from 36–84% (Scheme 19).
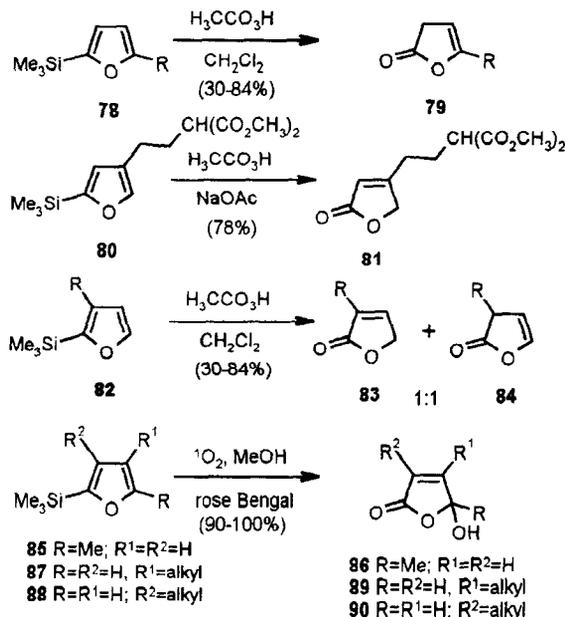
Scheme 19

Goldsmith and Liotta[31] later showed that 2-silylated-4-substituted furan ring **80** also underwent an oxidation reaction with peracetic acid, but provided but-2-enolide **81** in 78% yield. Tannis[32] has also shown that 2-silylated-3-substituted furan rings **82** undergo a similar regiospecific oxidation to give a 1 : 1 mixture of but-2- and -3-enolides **83** and **84** in 78% yield. Adam and Rodriguez[33] have reported that 5-substituted-2-(trimethylsilyl)furan **85** can be oxidized to 4-hydroxy-4-substituted-but-2-enolide **86** in quantitative yield. Similarly, 3- or 4-substituted-2-(trimethylsilyl)furans **87** and **88** can be oxidized regiospecifically to 2- or 3-substituted-4-hydroxy-but-2-enolides **89** and **90** respectively in yields ranging from 89–94%.[34]

Conclusions

This brief review clearly shows the important role that silicon has played in the development of new strategies for the preparation of multi-substituted furan rings. The size, migratory aptitude, tendency to undergo *ipso*-substitutions and their ease of attachment to and removal from furan systems of silyl groups has been used to the fullest. Some future endeavors might include using fluorinated silanes so that they can be directly replaced by other functionalities using palladium-coupling reactions.[35] This would eliminate the need for an *ipso*-replacement of the silane with an iodine or boron atom. Very little work has been done with the more robust *tert*-butyldimethylsilyl group. Methods for its replacement with other functionalities, rather than just removing it, would offer additional alternatives to those involving the trimethylsilyl group.

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Review 8/09439J