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Citation:

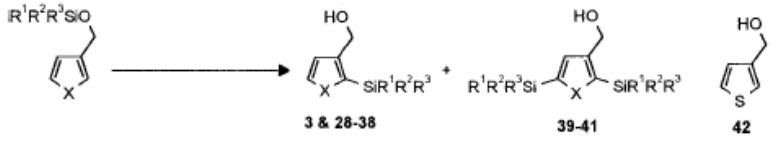
Regioselective Preparation of 2,4-, 3,4-, and 2,3,4-Substituted Furan Rings. 1. [1,4] O →C and [1,4] C →O Silyl Migrations of Silyl Ethers and Esters Attached to Furan and Thiophene Rings
Edward Bures, Patrick G. Spinazzé, Giovanna Beese, Ian R. Hunt, Christine Rogers, and Brian A. Keay
pp 8741 – 8749.

Abstract:

[1,4] O →C and [1,4] C →O rearrangements are described for a variety of furans and thiophenes. Treatment of 3-((silyloxy)methyl)furans and -thiophenes with *n*-BuLi in HMPA provided 2-silylated-3-(hydroxymethyl)furans and -thiophenes in good to excellent yields. The reaction was shown by crossover studies to proceed via an intramolecular [1,4] O →C silyl migration. Silyl esters of 3-furoic acids also underwent an intramolecular [1,4] O →C silyl migration to provide 2-silylated-3-furoic acids in moderate to good yield when treated with a mixture of LDA and HMPA. Finally, the above silyl migrations were shown to be reversible. Treatment of 2-silylated-3-(hydroxymethyl)furans and -thiophenes with NaH in DMF provided 3-((silyloxy)methyl)furans and -thiophenes in excellent yields via a [1,4] C →O silyl migration. The [1,4] C →O silyl migration was also shown to be an intramolecular process by a crossover study.

Tables:

Table 1. Results of the [1,4] O → C Silyl Migration of Silyl Ethers

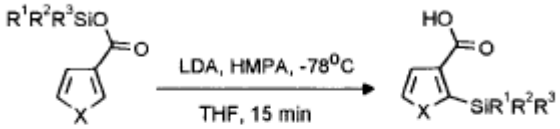


3 & 28-38 39-41 42

entry	starting material		product(s) (% yield)[a]
1	1	X = O; $R^1 = R^2$ = Me; R^3 = *t*-Bu	3 (87)
2	15	X = S; $R^1 = R^2$ = Me; R^3 = *t*-Bu	28 (87)
3	16	X = O; $R^1 = R^2 = R^3$ = i-Pr	29 (86)
4	17	X = S; $R^1 = R^2 = R^3$ = i-Pr	30 (89)
5	18	X = O; $R^1 = R^2$ = Ph; R^3 = *t*-Bu	31 (87)
6	19	X = S; $R^1 = R^2$ = Ph; R^3 = *t*-Bu	32 (63)
7	20	X = O; $R^1 = R^2 = R^3$ = *n*-Bu	33 (85)
8	21	X = O; $R^1 = R^2 = R^3$ = Et	34 (79)
9	22	X = S; $R^1 = R^2$ = Ph; R^3 = Me	35 (75)
10	23	X = S; $R^1 = R^2$ = Me; R^3 = i-Pr	36 (29)[a] + 23 (11)[b] + 42 (40)[b] + 39 (15)[a]
11	24	X = O; $R^1 = R^2$ = Me; R^3 = i-Pr	37 (24)[a] + 24 (15)[b] + 10 (43)[b] + 40 (12)[a]
12	25	X = S; $R^1 = R^2$ = Me; R^3 = Ph	38 (38)[a] + 25 (15)[b] + 42 (25)[b] + 41 (10)[b]
13	26	X = O; $R^1 = R^2 = R^3$ = Me	
14	27	X = S; $R^1 = R^2 = R^3$ = Me	

[a] Isolated yields. [b] GC yields.

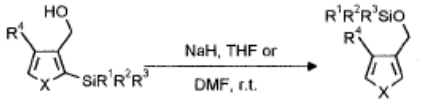
Table 2. Results of the [1,4] O → C Silyl Migration of Silyl Esters



entry	starting material		product(s) (% yield)[a]
1	2	X = O; $R^1 = R^2$ = Me; R^3 = *t*-Bu	4 (72)[b]
2	54	X = S; $R^1 = R^2$ = Me; R^3 = *t*-Bu	61 (47)[c]
3	55	X = O; $R^1 = R^2 = R^3$ = i-Pr	62 (56)[b]
4	56	X = S; $R^1 = R^2 = R^3$ = i-Pr	63 (57)[c]
5	57	X = O; $R^1 = R^2$ = Ph; R^3 = *t*-Bu	64 (43)[b]
6	58	X = S; $R^1 = R^2$ = Ph; R^3 = *t*-Bu	65 (64)[c]
7	59	X = O; $R^1 = R^2 = R^3$ = *n*-Bu	66 (51)[b]
8	60	X = O; $R^1 = R^2 = R^3$ = Et	67 (57)[b]

[a] Isolated yields. [b] 3-Furoic acid was also isolated. [c] 3-Thiophene carboxylic acid was also isolated.

Table 3. Results of the [1,4] C → O Silyl Migration of Silyl Ethers



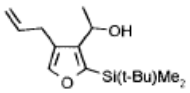
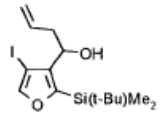
Entry	Starting Material		Product, Time (% Isolated Yield)	
			DMF	THF
1	**3**	X=O; R^1=R^2=Me; R^3=*t*-Bu; R^4=H	**1**, 1h (88)	**1**, 16h (86)
2			1, 5 min (93)	
3	**28**	X=S; R^1=R^2=Me; R^3=*t*-Bu; R^4=H	**15**, 1h (76)	**15**, 16h (89)
4			**15**, 5 min (85)	
5	**29**	X=O; R^1=R^2=R^3=i-Pr; R^4=H	**16**, 1h (89)	**16**, 16h (86)
6	**30**	X=S; R^1=R^2=R^3=i-Pr; R^4=H	**17**, 1h (86)	**17**, 16h (90)
7	**31**	X=O; R^1=R^2=Ph; R^3=*t*-Bu; R^4=H	**18**, 1h (89)	**18**, 16h (91)
8	**32**	X=S; R^1=R^2=Ph; R^3=*t*-Bu; R^4=H	**19**, 1h (88)	**19** 16h (93)
9	**33**	X=O; R^1=R^2=R^3=*n*-Bu; R^4=H	**20**, 1h (75)	**20**, 16h (81)
10	**34**	X=O; R^1=R^2=R^3=Et; R^4=H	**21**, 1h (81)	--
11	**35**	X=S; R^1=R^2=Ph; R^3=Me; R^4=H	**22**, 5 min (91)	**10**, 16h (95)
12			**10**, 1h (92)	
13	**37**	X=O; R^1=R^2=Me; R^3=i-Pr; R^4=H	**24**, 5 min (88)	**10**, 16h (92)
14			**10**, 1h (89)	
15	**68**	X=O; R^1=R^2= R^3=Me; R^4=H	**10**, 1h (96)	**10**, 16h (91)
16	**69**	X=O; R^1=R^2=Me; R^3=*t*-Bu; R^4=CHO	**74**, 5 min (88)	--
17	**70**	X=O; R^1=R^2=Me; R^3=*t*-Bu; R^4=CH_2CHCH_2	--	**75**, 16h (83)
18	**71**	X=O; R^1=R^2=Me; R^3=*t*-Bu; R^4=Sn(*n*-Bu)$_3$	**76**, 5 min (98)	--
19	**72**		**77**, 5 min (95)	--
20	**73**		**78**, 5 min (88)	--

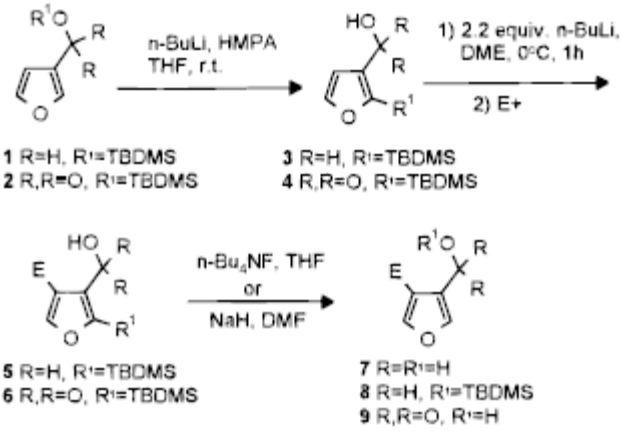
Table 4. Effect of Various Solvents and Bases on the [1,4] C → O Silyl Migration of Furan 3

entry	base	solvent	time	product (% yield)
1	5 equiv of NaH	DMF	seconds	**1** (88)
2	5 equiv of NaH	DME	0.5 h	**1** (96)
3	5 equiv of NaH	THF	16 h	**1** (80)
4	5 equiv of NaH	Et_2O	7 d [DMF][a]	S.M. [**1** (88)][b]
5	1 mol % of NaH	DMF	15 min	**1** (92)
6	5 equiv of KH	THF	2 d	**1** (61)
7	5 equiv of NaOH	DMF	1 h	**1** (64) + **10** (23)
8	1 equiv of vinyl-MgBr	THF	1 d [DMF][a]	S.M. [**1** (85)][b]
9	1 equiv of MeLi	THF	1 d [DMF][a]	S.M. [**1** (89)][b]
10	1 equiv of *n*-BuLi	THF	1 d [DMF][a]	S.M. [**1** (88)][b]

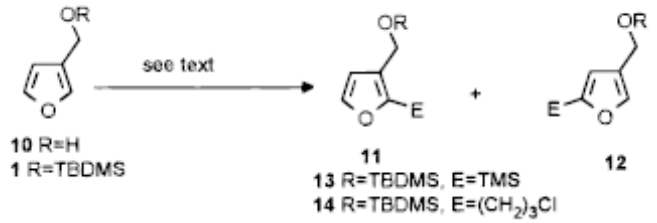
[a] After stirring at rt for the time shown excess DMF was added. [b] Product and yield after excess DMF was added to the solution. S.M. = starting material.

Schemes:

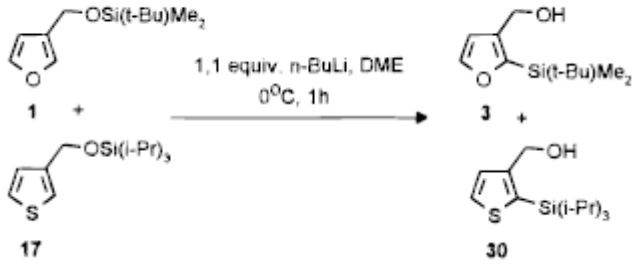
Scheme 1



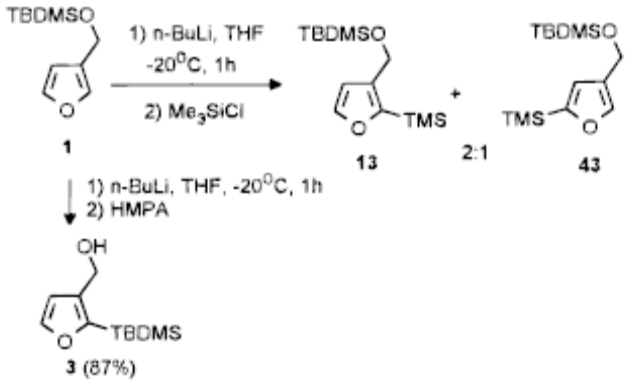
Scheme 2



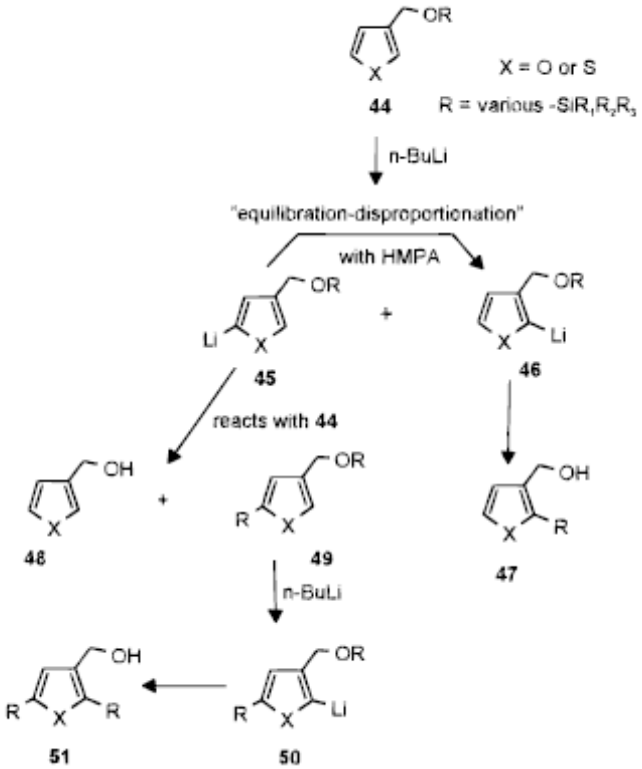
Scheme 3



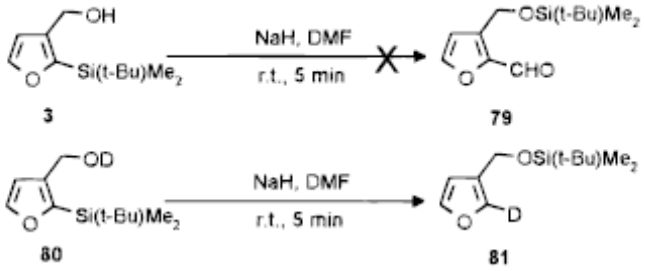
Scheme 4



Scheme 5



Scheme 6



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