## THE 1,4 $0 \rightarrow c$ SILVL MIGRATIONS OF VARIOUS 3-[(TRIALKYLSILVL)-OXYMETHYL]-FURANS AND -THIOPHENES

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<u>Summary</u>: Numerous  $3-[(trialkylsilyl) \circ xymethyl]-furans and -thiophenes undergo$  $a 1,4 0<math>\rightarrow$ C silyl migration when treated with n-BuLi/HMPA in THF or DME to produce 2-(trialkylsilyl)-3-(hydroxymethyl)-furans and -thiophenes in good yields.

That 3-[(t-butyldimethylsilyl) oxymethyl]furan <u>1</u> can be lithiated at C-2(n-BuLi/ether/r.t./6h) and the resulting anion quenched with electrophiles iswell known<sup>1</sup>. Treatment of the above anion with 1-bromo-3-chloropropane resulted in a poor yield of <u>2</u>; however, changing the reaction conditions (n-BuLi/THF/0°C/6h) and then adding HMPA with the electrophile resulted in the isolation of<u>1</u> (40% by <sup>1</sup>H NMR) and 2-(t-butyldimethylsilyl)-3-(hydroxymethyl)furan <u>3</u> (60%by <sup>1</sup>H NMR) (Scheme 1). That the silyl group was indeed at C-2 was confirmed bytreating <u>4</u> with 2.2 equivalents of n-butyllithium<sup>2</sup> and quenching the resultinganion with 1.0 equivalent of t-butyldimethylsilyl chloride; the spectral dataof <u>3</u> prepared from both <u>1</u> and <u>4</u> were identical<sup>3</sup>. As 1,4 0→C silyl migrationsare rare<sup>4</sup> we decided to investigate this unexpected result.

Optimized results were obtained by treating <u>1</u> with 1.1 equivalents of n-BuLi in the presence of HMPA in either THF or DME at  $-20^{\circ}$ C for 1 hour to produce <u>3</u> in 87% yield. This silyl migration turned out to be a general <u>SCHEME 1</u>



## TABLE 1: 1,4 O->C SILYL MIGRATIONS



	COMPOUND		PRODUCT (YIELD)
1)	<u>1</u>	Y=0; R1=R2=Me; R3=t-Bu	<u>3</u> (87)
2)	5	Y=S; $R1=R2=Me$ ; $R3=t-Bu$	<u>17</u> (87)
3)	<u>6</u>	Y=0; R1=R2=R3=i-propyl	<u>18</u> (86)
4)	7	Y=S; R1=R2=R3=i-propyl	<u>19</u> (89)
5)	8	Y=0; R1=R2=Ph; R3=t-Bu	20 (87)
6)	<u>9</u>	Y=S; R1=R2=Ph; R3=t-Bu	<u>21</u> (63)
7)	10	Y=S; R1=R2=Ph; R3=Me	<u>22</u> (75)
8)	<u>11</u>	Y=O; R1=R2=Me; R3=i-propyl	<u>23</u> (24) <sup>b</sup>
9)	12	Y=S; R1=R2=Me; R3=i-propyl	<u>24</u> (29) <sup>b</sup>
10)	<u>13</u>	Y=0; R1=R2=Me; R3=Ph	<u>25</u> (27) <sup>b</sup>
11)	<u>14</u>	Y=S; R1=R2=Me; R3=Ph	<u>26</u> (38) <sup>b</sup>
12)	<u>15</u>	Y = 0; $R1 = R2 = R3 = Me$	()
13)	<u>16</u>	Y = S; $R1 = R2 = R3 = Me$	()
a) all yields refer to isolated, purified products			
b) also isolated were the following:			



reaction and was not limited to either the t-butyldimethylsilyl group or furans. Table 1 summarizes our results to date. The reaction is high yielding for both furans and thiophenes when the substituents on the silane are bulky (entries 1-7). As the silane substituents were reduced in size the expected products were obtained with concomitant formation of desilylated starting material ( $\underline{27}$ ), starting material ( $\underline{11}$ - $\underline{14}$ ) and 2,5-disilylated compounds ( $\underline{28}$ ) in varying ratios (entries 8-11)<sup>5</sup>. Treatment of  $\underline{15}$  and  $\underline{16}$  with n-BuLi resulted in cleavage of the silane to form  $\underline{4}$  and  $\underline{27}$ (Y=S) respectively (entries 12 and 13).

A general experimental procedure follows. A solution of  $\underline{1}$  (0.69 g, 3.3 mmol) and HMPA (0.62 mL, 3.6 mmol) in THF (10 mL) were cooled to  $-78^{\circ}$ C under argon and treated with n-butyllithium (1.43 mL of 2.5 M in hexane, 3.6 mmol). The solution was stirred at  $-20^{\circ}$ C for 1 hour and then treated with saturated

aqueous ammonium chloride. An ethyl acetate extraction , silica gel column (to remove the HMPA) followed by a distillation afforded 3 (87%).

Crossover experiments showed that the silyl migration probably occurs by an <u>intramolecular</u> nucleophilic substitution at silicon (Scheme 2). Thus an equimolar mixture of <u>1</u> and <u>7</u> yielded <u>3</u> and <u>19</u> only. Analogous <u>intramolecular</u> mechanisms have been proposed recently for 1,4  $0 \rightarrow C^{4\alpha}$ , 1,4  $0 \rightarrow 0^{6\alpha}$ , 1,5  $0 \rightarrow 0^{6b}$ and 1,4  $C \rightarrow C^{6c}$  silyl migrations.

SCHEME 2



Treatment of <u>1</u> (n-BuLi/THF/-20<sup>o</sup>C/1h) and quenching an aliquot with trimethylsilyl chloride provided a 1:2 ratio of <u>29</u> and <u>30</u> (Scheme 3)<sup>7</sup>; no 2,5disilylated furan product was observed (by MS and <sup>1</sup>H NMR) indicating that a C-2/C-5 dianion of <u>1</u> was not occurring. Subsequent addition of HMPA to the above mixture of C-2 and C-5 anions resulted in the isolation of only <u>3</u> (87%, Scheme 3). Therefore an "equilibration-disproportionation"<sup>8</sup> of the C-5 anion must be occurring in the cases where substituents on the silane are large (Table 1, entries 1-7). SCHEME <u>3</u>



With the examples involving less bulky substituents on the silane, such as <u>11</u>. (Table 1, entries 8-11) we envision the formation of a mixture of anions <u>31</u> and <u>32</u>. Compound <u>32</u> then rearranges to produce, after workup, <u>23</u> (Scheme 4). Compound <u>31</u>, on the other hand, presumably attacks <u>11 inter-</u>molecularly at silicon to form <u>33</u> and <u>4</u>. If this latter reaction is faster than the anion forming reaction to produce <u>31</u> and <u>32</u>, then <u>33</u> can react with

some remaining n-BuLi to form the C-5 anion of <u>33</u> which can then rearrange to give, after workup, <u>28</u>. The utilization of some of the n-BuLi to form this latter C-5 anion of <u>33</u> explains the presence of starting material <u>11</u> in the product mixture.

Synthetic applications of these rearrangements are now under investigation. SCHEME 4



## Acknowledgements

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## References and Notes

- 1) Goldsmith, D.; Liotta, D.; Saindane, M.; Waykole, L.; Bowen, P. <u>Tetrahedron</u> Lett., 1983, <u>24</u>, 5835.
- Katsumura, S.; Hori, K.; Fujiwara, S.; Isoe, S. <u>Tetrahedron Lett.</u>, 1985, <u>26</u>, 4625; Tannis, S.P.; Head, D.B. <u>ibid</u>, 1984, <u>25</u>, 4451.
- 3) Compound <u>3</u>: colourless oil; bp 95-100°C/20 torr; <sup>1</sup>H NMR(300 MHz, CDCl<sub>3</sub>) δ 0.01(s, 6H), 0.89(s, 9H), 1.5(s, 1H, 0H), 4.57(s, 2H), 6.46(d, 1H, J=1.8 Hz) 7.57(d, 1H, J=1.8 Hz); <sup>13</sup>C NMR(75 MHz, CDCl<sub>3</sub>) δ -5.7, 18.1, 25.7, 57.1, 110.5, 135.9, 146.7, 155.0; MS(EI) 212(M<sup>-+</sup>).
- 4) To date only three 1,4 0→C silyl migrations have been reported: a) Rucker.
  C. <u>Tetrahedron Lett.</u>, 1984, <u>25</u>, 4349; b) Mora, J.; Costa A. <u>ibid</u>, 1984, <u>25</u>, 3493; c) Evans, D.A.; Takacs, J.M.; Hurst, K.M. <u>J. Am. Chem. Soc.</u>, 1979, <u>101</u>, 371.
- 5) All new compounds provided analytical and/or spectroscopic data consistent with their structures.
- 6) a) van Boeckel, C.A.A.; van Aelst, S.F.; Beetz, T. <u>Rec Trav. Chim. Pays-Bas.</u> 1983, <u>102</u>, 415; b) Torisawa, Y.; Shibasaki, M.; Ikegami, S. <u>Chem. Pharm.</u> <u>Bull.</u>, 1983, <u>31</u>, 2607; c) Daney, M.; Lapouyade, R.; Bouas-Laurent, H. <u>J.</u> <u>Org. Chem.</u>, 1983, <u>48</u>, 5055.
- 7) The spectral data of  $\underline{29}$  and  $\underline{30}$  were identical to those reported by D. Goldsmith (see reference 1).
- 8) Ziegler, F.E.; Fowler, K.W. <u>J. Org. Chem.</u>, 1976, <u>41</u>, 1564; Leonard, N.J.; Bryant, J.D. <u>ibid</u>, 1979, <u>44</u>, 4612. (Received in USA 1 July 1987)