



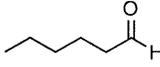
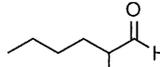
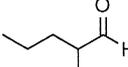
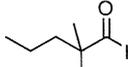
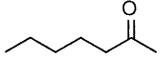
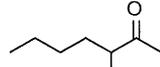
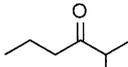
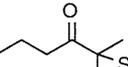
Table 1  
 $\alpha$ -Sulfonylation of acylsilanes with *N*-phenylthiosuccinimide **3**<sup>a</sup>

entry	substrate $\Sigma = \text{SiPh}_2\text{Me}$	imide <b>3</b> (equiv)	acid (equiv)	solvent	time (h)	product (% yield) $\Sigma = \text{SiPh}_2\text{Me}$
1	<b>1</b>	1	TsOH (0.1)	CH <sub>2</sub> Cl <sub>2</sub>	15	<b>2</b> (92)
2	 <b>4</b>	1	TsOH (0.1)	CH <sub>2</sub> Cl <sub>2</sub>	15	 <b>5</b> (10)
3	<b>4</b>	1	TsOH (0.1)	CH <sub>3</sub> CN	8	<b>5</b> (80)
4	 <b>6</b>	1	TsOH (0.1)	CH <sub>3</sub> CN	6	 <b>7</b> (92)
5	 <b>8</b>	1	TsOH (0.1)	CH <sub>3</sub> CN	6	 <b>9</b> (88)
6	 <b>10</b>	2.2	TsOH (0.1)	CH <sub>3</sub> CN	6	no reaction
7	<b>10</b>	1	TsOH (1)	CH <sub>3</sub> CN	5	 <b>11</b> (90)
8	 <b>12</b>	1	BF <sub>3</sub> •OEt <sub>2</sub> (0.5)	CH <sub>3</sub> CN	6	 <b>13</b>
						 <b>14</b>
						<b>13</b> : <b>14</b> : <b>12</b> = 1 : 0.6 : 1 <sup>b</sup>
9	 <b>15</b>	2.2	TsOH (0.1)	CH <sub>3</sub> CN	6	 <b>16</b> (83)
10	 <b>17</b>	1.2	TsOH (0.1)	CH <sub>3</sub> CN	6	 <b>18</b> (86)

<sup>a</sup>All reactions were performed at room temperature.

<sup>b</sup>Products were not isolated, and the ratio was determined by <sup>1</sup>H NMR analysis.

Table 2  
 $\alpha$ -Sulfenylation of aldehydes and ketones with *N*-phenylthiosuccinimide **3**<sup>a</sup>

entry	substrate	imide <b>3</b> (equiv)	acid (equiv)	time (h)	product (%yield)
1	 <b>19</b>	1.0	BF <sub>3</sub> •OEt <sub>2</sub> (1.0)	21	 <b>20</b> (19)
2	 <b>21</b>	1.0	BF <sub>3</sub> •OEt <sub>2</sub> (1.0)	3	 <b>22</b> (68)
3	 <b>23</b>	2.0	TsOH (1.0)	7	 <b>24</b> (24)
4	 <b>25</b>	1.0	BF <sub>3</sub> •OEt <sub>2</sub> (1.0)	14	 <b>26</b> (22)

<sup>a</sup>These reactions were performed in acetonitrile at room temperature.

**3** turned out to be quite useful for analogous acylsilanes **6** and **8** (entries 4 and 5). However, for shorter acylsilanes such as **10** (entry 6), no reaction occurred when using 0.1 equivalent of *p*-toluenesulfonic acid. In the presence of 1 equivalent of *p*-toluenesulfonic acid, propanoysilane **10** reacted with imide **3** in acetonitrile for 5 h to afford a 90% yield of sulfide **11**.

Ethanoysilane **12** (entry 8) was the least reactive one that we have studied. Under the conditions described above for the preparation of sulfide **11** (entry 7), we observed no reaction for ethanoysilane **12**. Reaction occurred when we used borontrifluoride etherate; however, bis-sulfenylation became competitive. As shown in entry 8, the reaction of ethanoysilane **12** with imide **3** in the presence of borontrifluoride etherate (0.5 equiv.) in acetonitrile for 6 h proceeded in about a 60% conversion. The monosulfide **13** and bis-sulfide **14** were present in a 3:2 ratio, respectively.

The  $\alpha$ -sulfenylation reactions are not limited to acylmethyldiphenylsilanes. As shown in entry 9 (Table 1), bromoacylsilane **15**<sup>2</sup> with a bulky *t*-butyldimethylsilyl group (TBDMS) underwent  $\alpha$ -sulfenylation with imide **3** (2.2 equiv.) in the presence of *p*-toluenesulfonic acid (0.1 equiv.) in acetonitrile (6 h) to give sulfide **16** in an 83% yield. Under similar reaction conditions, acyltrimethylsilane **17**<sup>8</sup> (entry 10) afforded sulfide **18**<sup>4a</sup> in good yield (86%).

When we applied this method to aldehydes and ketones, only  $\alpha$ -substituted aldehydes were sulfenylated in mild yields. As shown in Table 2, a dismal 19% yield of sulfide **20**<sup>9</sup> (entry 1) was obtained by the reaction of straight chain hexanal **19** with imide **3** in the presence of borontrifluoride etherate (1 equiv.)

at room temperature in acetonitrile for 21 h. With the presence of an  $\alpha$ -methyl substituent, aldehyde **21** (entry 2) led to 68% of sulfide **22** in 3 h under similar conditions. All the ketones that we have studied reacted poorly as shown in entries 3 and 4. Sulfenylation occurred preferentially at the more substituted side of the unsymmetric ketones with low yields.

The reactivity pattern observed in these sulfenylation reactions correlates well with the enol content of the carbonyl compounds.<sup>10</sup> It was reported recently that the enol content of acylsilanes is higher than aldehydes and ketones.<sup>11</sup> In this study, the acylsilanes show the highest reactivity towards imide **3** under acidic conditions. Among the acylsilanes, ethanoylsilane **12** is the least reactive. Presumably, acylsilane **12** is the least enolizable acylsilane that we have studied. Ketones are known to have lower enol content than aldehyde.<sup>10</sup> Here, we found that the ketones are poor substrates in this reaction.

## Acknowledgements

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