

AN IMPROVED RADICAL CHAIN PROCEDURE FOR THE DEOXYGENATION OF SECONDARY  
AND PRIMARY ALCOHOLS USING DIPHENYLSILANE AS HYDROGEN ATOM DONOR AND  
TRIETHYLBORANE-AIR AS INITIATOR

Derek H. R. Barton\*, Doo Ok Jang and Joseph Cs. Jaszberenyi

Department of Chemistry, Texas A&M University, College Station, TX  
77843

**Abstract.** Thiocarbonyl derivatives of secondary alcohols are readily reduced by diphenylsilane in a radical chain process at room temperature using triethylborane-air as an initiator. Primary alcohols react similarly at 80°. Comparison is made with the similar reactivity of *tris*(trimethylsilyl)silane.

Radical deoxygenation of alcohols is important in synthesis.<sup>1</sup> Barton and McCombie<sup>2</sup> demonstrated that secondary alcohols can be deoxygenated in high yield by reduction of suitable thiocarbonyl derivatives at 80-110° with  $(n\text{-Bu})_3\text{SnH}$  using azobisisobutyronitrile as initiator. Later, this method was extended to primary alcohols<sup>3</sup> using temperatures of 130-150°.

Although tin hydrides are useful in small scale work, they are toxic, high molecular weight reagents, of variable Sn-H content when purchased commercially. It seemed to us some years ago that an alternative based on the Si-H bond would be more suitable. Prior work by Jackson and his colleagues<sup>4</sup> involved the reduction of primary and secondary chlorocarbonates at 140° in a sealed tube using  $(n\text{-Pr})_3\text{SiH}-(t\text{-BuO})_2$ . Clearly milder conditions would be preferable.

It has recently been shown that thiocarbonyl derivatives of secondary alcohols can, in fact, be reduced<sup>5</sup> at room temperature, or lower, by  $(n\text{-Bu})_3\text{SnH}$ , if the reaction is initiated with triethylborane and a controlled amount of air.<sup>6</sup> The initiating species is the ethyl radical<sup>6,7</sup> which reacts mostly with the tin hydride to make a tin radical, which then attacks the thiocarbonyl derivative at the thione function and initiates the desired chain reaction.

A systematic examination of the following silane derivatives: triethylsilane, triethoxysilane, phenylsilane, diphenylsilane and triphenylsilane was made in a triethylborane-air initiated reduction of cyclododecyl xanthate at room temperature. The first three silanes were unreactive. Triphenylsilane gave somewhat lower yields. However, diphenylsilane was an excellent reducing agent.

Table 1<sup>a</sup>

Entry	R	R'	Time (min.)	Temp. °C	Et <sub>3</sub> B equiv.	O <sub>2</sub> equiv.	RH (%)
1	c-C <sub>12</sub> H <sub>23</sub>	4-FC <sub>6</sub> H <sub>4</sub>	10	25	0.2	0.2	96
2	c-C <sub>12</sub> H <sub>23</sub>	Ph	10	25	0.2	0.2	91
3 <sup>b</sup>	c-C <sub>12</sub> H <sub>23</sub>	Me	10	25	1.1	1.1	81
4	<u>14</u>	4-FC <sub>6</sub> H <sub>4</sub>	30	25	0.25	0.25	82
5	<u>14</u>	4-FC <sub>6</sub> H <sub>4</sub>	30	80	0.25	0.25	93
6	<u>15</u>	4-FC <sub>6</sub> H <sub>4</sub>	40	25	1.1	1.1	94
7	<u>16</u>	4-FC <sub>6</sub> H <sub>4</sub>	30	25	0.25	0.25	83
8	Ph(CH <sub>2</sub> ) <sub>2</sub>	4-FC <sub>6</sub> H <sub>4</sub>	30	25	0.25	0.25	19 (79) <sup>c</sup>
9	Ph(CH <sub>2</sub> ) <sub>2</sub>	4-FC <sub>6</sub> H <sub>4</sub>	30	80	0.25	0.25	80 (12) <sup>c</sup>
10	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>16</sub> CH <sub>2</sub>	4-FC <sub>6</sub> H <sub>4</sub>	30	25	0.25	0.25	38 (39) <sup>c</sup>
11	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>16</sub> CH <sub>2</sub>	4-FC <sub>6</sub> H <sub>4</sub>	30	80	0.25	0.25	87

<sup>a</sup> A typical experiment (Entries 1-2) was as follows. To the substrate (0.4 mmol) in dry benzene (5 ml) under argon was added diphenylsilane (0.44 mmol) and triethylborane (0.08 mmol) in hexane (1M). Dry air (8.3 ml) was injected into the solution through a septum during one minute and then the solution was stirred for 9 min. For longer times the air was introduced by a syringe pump (20 min. for Entries 4, 5, 7-11; 30 min. for Entry 6.)

<sup>b</sup> This experiment used the xanthate. The dry air was injected into the solution at a rate of 10 ml /min.

<sup>c</sup> Thioformate derivatives.

Typical results are summarized in Table 1. Introduced for the first time is a new thiocarbonyl derivative based on the relatively inexpensive 4-fluorophenol. Like its analogues<sup>2c</sup> this permits smooth and fast reduction when used either with tin hydride or, as here, with diphenylsilane. All the yields for the deoxygenation of secondary positions at room temperature are very satisfactory. An increase of temperature to 80° (entry 5) does not change the yield greatly.

The two primary alcohols (entries 8 and 10) gave, on reduction at room temperature, a mixture of deoxygenated alcohol and the alcohol thioformate. The thioformate probably comes from an elimination reaction on the reduced radical 3 when the fragmentation process to 4 and 5 is slow. Simply raising the temperature to 80° (entries 9 and 11) gave good yields of hydrocarbon.

The reactions involved are summarized in the Scheme. The silyl radical

2, generated from the ethyl radical, reacts with 1 to give the radical 3, which fragments to 4 and radical 5 which is reduced by  $\text{Ph}_2\text{SiH}_2$  to give 6 and radical 2 again. Intermediate 4 readily loses  $\text{COS}$  and affords 7. In most cases 7 was derived from 4-fluorophenol. An authentic specimen was synthesized for comparison. Hydrolysis with water afforded 4-fluorophenol and  $\text{Ph}_2\text{SiHOH}$  9. This sequence was the major pathway. A minor pathway (10%) involved radical 10, derived from 7, and the sequence 11, 12 and 13. An authentic specimen of 13 ( $\text{R}'=4\text{-fluorophenyl}$ ) was also prepared.

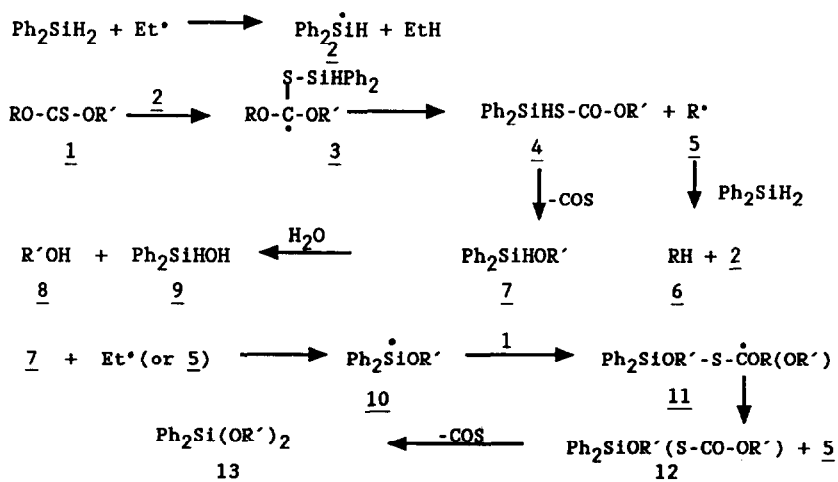
During the course of this work we were encouraged by the excellent publications of Chatgililoglu<sup>8</sup> and others, and of Giese<sup>9</sup>, on the use of *tris*(trimethylsilyl)silane as a radical reducing reagent. Table 2 shows

Table 2<sup>a</sup>

Entry	R	Time (Min.)	$\text{Et}_3\text{B}$ equiv.	$\text{O}_2$ equiv.	RH (%)
1 <sup>b</sup>	$\text{c-C}_{12}\text{H}_{23}$	10	0.2	0.2	80
2	$\text{c-C}_{12}\text{H}_{23}$	10	0.2	0.2	98
3	14	30	0.25	0.25	95
4	15	40	1.1	1.1	94

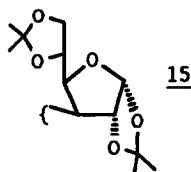
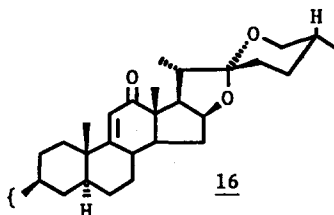
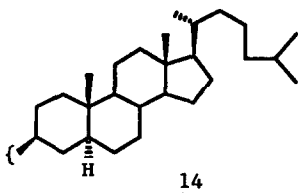
a. All experiments with the 4-fluorophenyl derivatives at 25°. Typical experiment as under (a) Table I except that *tris*(trimethylsilyl)silane replaced  $\text{Ph}_2\text{SiH}_2$ .

b. Entries 1, 3 and 4 used 1.1 equivs. of the silane. Entry 2 used 2.2 equivs.



Scheme 1

that this reagent also works at room temperature using triethylborane-air as initiator. The yields obtained with either silane (Tables 1 and 2) are comparable. However, at present, diphenylsilane is 30 times cheaper (mole for mole) than *tris*(trimethylsilyl)silane.



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