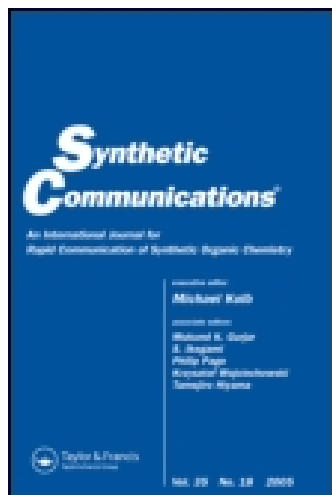


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# PHENYLSILANE: A CONVENIENT REAGENT FOR THE RADICAL DEHALOGENATION OF ORGANIC HALIDES

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**Abstract:** Phenylsilane has been used for the reduction of alkyl and aryl halides. The method offers mild, neutral reaction conditions, easy work-up process, and high yields of the dehalogenated products.

Since the first observation, the reductive removal of a halogen atom by a tin hydride has become a standard radical chain reaction.<sup>1</sup> At present, the process is the most general method for the replacement of halogen atom by a hydrogen atom. Tributyltin hydride has played an almost exclusive role as a hydrogen atom source in the radical dehalogenation.<sup>2</sup> The tin-hydrogen bond is weak and tributyltin radical is a good radical chain carrier. However, tributyltin hydride is toxic and expensive, and is difficult to remove the tin residue from the desired products. Especially non-functional organic compounds need the special treatment to remove the tin residue.<sup>3</sup> It has been reported that silanes are useful alternatives of tributyltin hydride.<sup>4</sup>

**Table 1.** Reduction of 1-Bromoadamantane (**1b**) in Boiling PhSiH<sub>3</sub> with Various Radical Initiators

Entry	Initiator	Amount of Initiator (eq)	Time (min)	Adamantane (%) <sup>b</sup>
1 <sup>a</sup>	Benzoyl peroxide	1.0	150	50 (45) <sup>c</sup>
2	Benzoyl peroxide	1.0	150	88
3	<i>t</i> -Butyl peroxide	1.0	150	85
4	Et <sub>3</sub> B-O <sub>2</sub>	1.0	150	87
5	AIBN	0.3	70	93
6	1,1'-Azobis (cyclohexanecarbonitrile)	0.7	110	89
7	4,4'-Azobis (4-cyanovaleric acid)	0.4	80	95

<sup>a</sup> The reaction was carried out with 5 eq of PhSiH<sub>3</sub> in boiling dioxane.

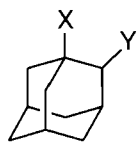
<sup>b</sup> Measured by GLC. <sup>c</sup> The recovered yield of the starting material is shown in parentheses.

It was thought that among silanes, phenylsilane<sup>5</sup> would be a convenient reagent for the radical dehalogenation of halides. This paper reports a convenient method for the dehalogenation of various halides using phenylsilane.

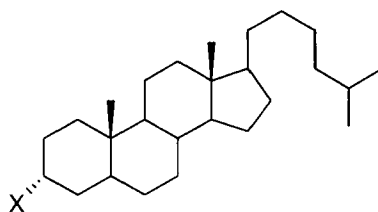
When 1-bromoadamantane (**1b**) was treated with 5 eq of phenylsilane and benzoyl peroxide in boiling dioxane, the reaction was not so efficient (Table 1, entry 1). However, when phenylsilane was used as a solvent, the reaction is very effective giving adamantane (**1e**) in 88 % yield. The optimal reaction condition was investigated by varying the radical initiator. Compared to oxygen centered radical, carbon centered radicals are more effective to initiate the reaction. Azobisisobutyronitrile (AIBN) is the most suitable radical initiator for the reaction (entry 5).

Various substrates have been used to examine their reactivity under the reaction conditions. Alkyl iodides and bromides are good substrates for the process (Table 2, entry 1-3 and 5-6). However, phenylsilane is not reactive enough to reduce the alkyl chlorides. The large amount of the starting material

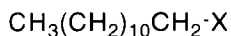
(**1d**) was recovered after adding 1.0 equivalent of AIBN (entry 4). It was noteworthy that non-functionalized compound **2b** and **3c** were isolated without interference of silicon residue (entry 5 and 6). Aryl bromides and iodides are also good substrates under the reaction conditions (entry 8 and 9). The method was also applicable to carbohydrates offering high isolated yields (entry 10 and 11).



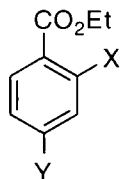
- 1a** X = I, Y = H  
**1b** X = Br, Y = H  
**1c** X = H, Y = Br  
**1d** X = Cl, Y = H  
**1e** X = Y = H



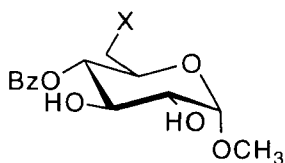
- 2a** X = I  
**2b** X = H



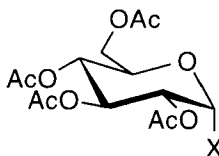
- 3a** X = I  
**3b** X = Br  
**3c** X = H



- 4a** X = I, Y = H  
**4b** X = Br, Y = H  
**4c** X = Y = H



- 5a** X = Br  
**5b** X = H



- 6a** X = Br  
**6b** X = H

From the practical point of view, its low boiling point make it easy to work-up the reaction and isolate the dehalogenated products. It is possible to recover and recycle the excess of phenylsilane by distillation. Compared to tributyltin hydride, mole per mole, phenylsilane is inexpensive. It is less toxic than tributyltin hydride

**Table 2.** Reduction of Various Halides in Boiling PhSiH<sub>3</sub> with AIBN as an Initiator

Entry	Substrate	Product	AIBN (eq)	Time (min)	Yield (%) <sup>a</sup>
1	<b>1a</b>	<b>1e</b>	0.3	70	89
2	<b>1c</b>	<b>1e</b>	1.0 <sup>b</sup>	150	90
3	<b>1c</b>	<b>1e</b>	0.3	70	86
4	<b>1d</b>	<b>1e</b>	1.0	150	36 (63) <sup>c</sup>
5	<b>2a</b>	<b>2b</b>	0.3	70	90 <sup>d</sup>
6	<b>3a</b>	<b>3c</b>	0.3	70	95 (85) <sup>d</sup>
7	<b>3b</b>	<b>3c</b>	0.3	70	92
8	<b>4a</b>	<b>4c</b>	0.3	70	93
9	<b>4b</b>	<b>4c</b>	0.3	70	95
10	<b>5a</b>	<b>5b</b>	0.3	70	85 <sup>d</sup>
11	<b>6a</b>	<b>6b</b>	0.3	70	90 <sup>d</sup>

<sup>a</sup> Measured by GLC. <sup>b</sup> Benzoyl peroxide was used. <sup>c</sup> The recovered yield of the starting material is shown in parentheses. <sup>d</sup> Isolated yield.

and it is much easier to isolate the products after the radical reaction. Therefore, the use of phenylsilane results in improvements in radical dehalogenation reaction methodology.

**Typical procedure:** To a solution of the starting halide **2a** (0.3 g, 0.6 mmol) in phenylsilane (1mL) under argon was added 0.3 mL of a solution of AIBN in dioxane (0.1 g AIBN was dissolved in 1.0 mL dioxane) with syringe pump for 40 min during reflux. The solution was heated for 30 min further. The reaction was monitored by TLC. When the reaction was completed, phenylsilane was distilled and the residue was purified by column chromatography on silica gel (eluent: hexanes) giving 0.2 g (90 %) of cholestane **2b**.

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