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2-Functionalized Allyl Tris(trimethylsilyl)silanes as Radical-Based Allylating Agents

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Abstract: Radical allylations with 2-functionalized allyl tris(trimethylsilyl)silanes occur under mild conditions in good to excellent yield provided that the radical precursor and the silane have the appropriate electronic pairing. These reactions offer tin-free alternatives for transformations that are currently conducted with allyl stannanes. Copyright © 1996 Elsevier Science Ltd

Radical-based allylation reactions have been carried out mainly by using allyl stannanes as reagents (eq 1)[2-4] and much attention has recently been focused on their application in natural product chemistry, including synthesis of nucleosides,[5] α-amino acids,[6] prostaglandins,[7] β-lactams.[8] However, like organotin hydrides, these tin reagents have significant limitations.[9] The major one is that the final products are frequently contaminated by traces of highly toxic organotin compounds.[9] Therefore, more environmentally benign radical allylating reagents are desirable.

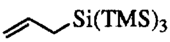
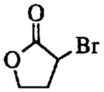
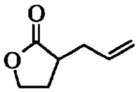
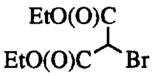
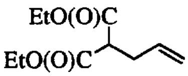
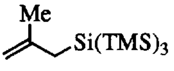
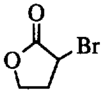
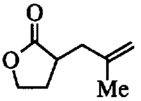
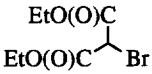
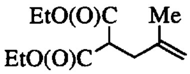
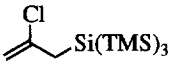
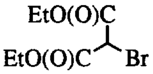
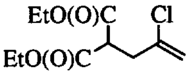
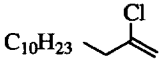
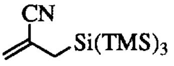
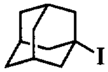
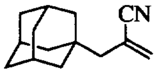
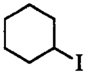
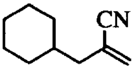
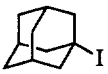
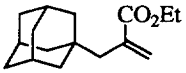
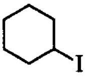
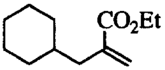
(1)

In the preceding paper, we reported the synthesis of allyl and 2-functionalized allyl tris(trimethylsilyl)-silanes. Here we describe the use of these silanes as radical-based allylating agents.[10] The basic transformation of these reagents is summarized in equation 2. The reactions were conducted via standard radical procedures with α,α'-azoisobutyronitrile (AIBN) and di-*tert*-butyl peroxide (BOOB) as initiators at 80 and 140 °C, respectively. Table 1 records the precursors, conditions, products and yields.[11] In general, good yields are obtained when the more electron rich allyl-, methallyl, and 2-chloro allyl tris(trimethylsilyl)silanes were allowed to react with moderately or strongly electrophilic radicals (entries 1-3), as well as when the electron poor 2-cyano and 2-carboethoxy allyl tris(trimethylsilyl)silanes were allowed to react with nucleophilic radicals (entries 4 and 5).

(2)

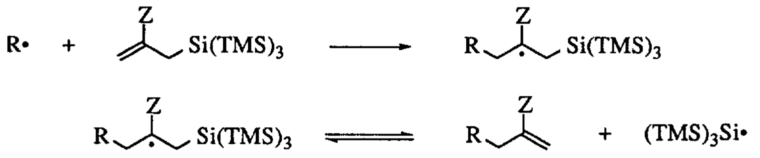
$Z = H, Me, Cl, CN, CO_2Et$

Table 1. Reactions of allyl and 2-functionalized allyl tris(trimethylsilyl)silane with alkyl halides

Entry	Reagent^a	Halide	Conditions^b	Products	Yield,^{f} %
1			AIBN/80 °C^c		87
			AIBN/80 °C^c BOOB/140 °C^d		89^g 91^g
2			AIBN/80 °C^c		84
			AIBN/80 °C^c BOOB/140 °C^d		93^h 92^h
3			AIBN/80 °C^c BOOB/140 °C^c		91^h 88^h
		$C_{10}H_{23}$—I	AIBN/80 °C^c		70^h
4			BOOB/140 °C^e		66,91^g
			BOOB/140 °C^e		81^h
5			BOOB/140 °C^e		80,89^g
			BOOB/140 °C^e		75

[a] 0.2 M in benzene or *tert*-butylbenzene. [b] AIBN = α,α'-azoisobutyronitrile (10 mol %); BOOB = di-*tert*-butyl peroxide (10 mol %). [c] [Reagent]:[Halide] = 3:1. [d] [Reagent]:[Halide] = 1.2:1. [e] [Reagent]:[Halide] = 4:1. [f] Isolated yields or as indicated otherwise. [g] GC yields. [h] NMR yields.

The mechanism that we conceived for these reactions is outlined in eqs 3-5 and it is analogous to tin allylations. Thus, alkyl radicals add to the double bond (eq 3) giving rise to a radical intermediate that undergoes β-scission (eq 4) to form tris(trimethylsilyl)silyl radicals. Halogen abstraction (eq 5) from the alkyl halide completes the cycle of these chain reactions. The elimination of the tris(trimethylsilyl)silyl radical (eq 4) may be reversible, depending on the rate of the competing halogen abstraction (eq 5).



(3)

(4)

$$(TMS)_3Si\bullet \quad + \quad RX \quad \longrightarrow \quad (TMS)_3SiX \quad + \quad R\bullet \tag{5}$$

An important feature of allylations with allyl stannanes (eq 1) is that they are relatively tolerant of reactions in which the "polar effects" of the radical precursor (RX) and the allyl stannane are not well matched.[12,13] For example, it is possible to add alkyl radicals to the parent allyltributylstannane in good yield under mild conditions, even though this reaction does not have a favorable "polar effect" (both the radical and the radical acceptor are considered "nucleophilic"). In contrast, the reactions of allyl tris(trimethylsilyl)silanes are more sensitive to polar effects. For example, attempts to add adamantyl iodide to allyl- or methallyl tris(trimethylsilyl)silane were unsuccessful under a variety of conditions, presumably due to a mismatch in polar effects. However, as expected, additions of adamantyl iodide to the electron poor 2-cyano- and 2-carboethoxy-tris(trimethylsilyl)silanes worked well. Likewise, attempts to add electrophilic radicals to these two electron poor acceptors failed, but electrophilic radicals added smoothly to the electron rich allyl tris(trimethylsilyl)silanes.

In summary, the present results suggest that allyl- and 2-substituted-allyl tris(trimethylsilyl)silanes can be practical and safe alternatives to allyl stannanes provided that attention is paid to matching the reactivity of the allylating agent with the radical.

Typical experiment: Allyl tris(trimethylsilyl)silane (1.05 g; 3.63 mmol) and AIBN (0.020g; 0.12 mmol) were added consecutively to a magnetically stirred, degassed solution of α-bromo-γ-butyrolactone (0.2 g; 1.21 mmol) in benzene (6 mL) under argon. The mixture was mantained at reflux, and additional AIBN (0.020g; 0.12 mmol) was added every hour. The reaction was monitored by TLC or GC until the starting material was consumed (6 h), and it was then worked up by passage through a short silica gel column (eluent: ether/pentane 2:1). The silyl material eluted in the first fraction;[14] α-(prop-2-enyl)-γ-butyrolactone was then collected as pure product (0.132 g; 1.05 mmol; 87% yield).

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14. It is also possible to recover any unreacted allyl tris(trimethylsilyl)silane in the same eluent.

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