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TRIS(TRIMETHYLSILYL)SILANE AS MEDIATOR IN ORGANIC SYNTHESIS VIA RADICALS

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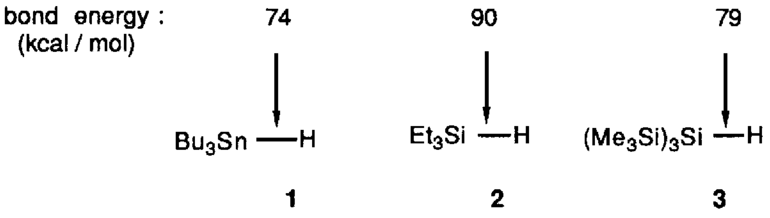
Summary: Silane **3** is an effective mediator in organic synthesis via radicals. Reactions with this silane give smaller amounts of unwanted reduction products than reactions with toxic stann*anes.*

Radical chemistry has gained considerable importance in organic synthesis the last years.[1) Although several mediators are known that generate and trap radicals,[1,2) most frequently tributyltin hydride **1** has been used in synthetic radical chemistry.[3) This is because (a) organotin radicals generate from many functional groups carbon centered radicals, and (b) tributyltin hydride traps radicals with sufficient rate and regenerates the tin radicals.

$$RX + Bu_3Sn^\bullet \longrightarrow R^\bullet + Bu_3SnX$$

$$R^\bullet + Bu_3SnH \longrightarrow RH + Bu_3Sn^\bullet$$

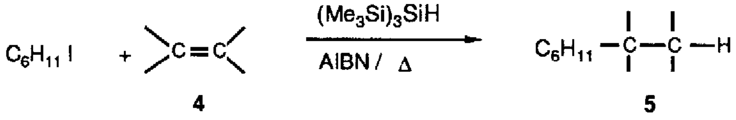
The disadvantage of organotin compounds is their toxicity as well as the difficulty for their complete elimination from the reaction products. Attemps to substitute stannane **1** by triethylsilane **2** have failed, because of the high Si-H bond energy. Only recently, one of us has shown, that tris(trimethylsilyl)silane **3** can be used for reduction reactions[4) because its Si-H bond energy is low enough.[5) This is probably due to the bonding interaction between β-silicon d orbitals and the semioccupied p orbital on the central silicon atom in the corresponding silyl radical.[6)

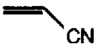
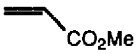
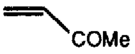
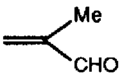
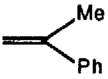


We have now found, that silane **3** can also be used as mediator for radical chain reactions where the first formed alkyl radical undergoes inter- or intramolecular reactions before the hydrogen abstraction step occurs.

$$R^1\text{—}X \xrightarrow{(Me_3Si)_3Si\,\bullet} R^1\bullet \longrightarrow R^2\bullet \xrightarrow{(Me_3Si)_3SiH} R^2\text{—}X$$

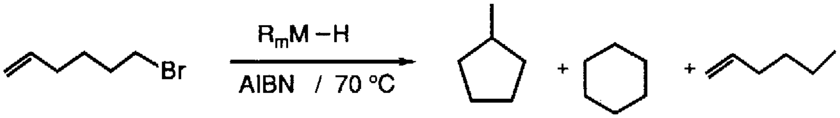
Thus, the reaction of cyclohexyl iodide, 1.2 equivalents of silane **3**, 1-10 equivalents of alkene **4**, and catalytic amounts of AIBN in toluene gives after 4-5 h at 70-90° products **5** in yields that are comparable or higher than using tributyltin hydride as reagent.



Alkene **4**	Equivalents of **4**	Yield of isolated products **5** (%)
	1	90
	1	85
	1	65 (90)[a)]
	1	70
	10	40 (55)[a)]
	10	45 (55)[a)]

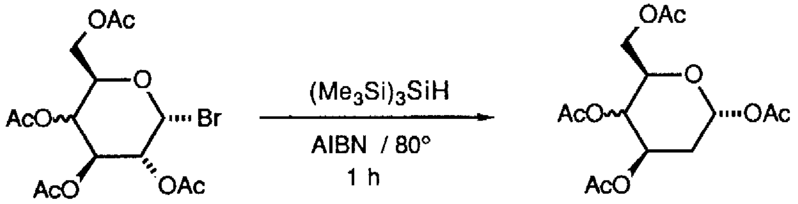
[a)] GC yield

It is noteworthy that in syntheses with silane **3** low concentrations of alkenes can be used. This is because silane **3** has a higher M-H bond energy than stannane **1**.[5] For the same reason silane **3** also gives higher yields in cyclization reactions than stannane **1**. Thus, 50 mmolar solutions of hexenyl bromide **6** and silane **3** lead to a 24:1 ratio of cyclized versus uncyclized products whereas with stannane **1** the product ratio is only 6:1.



6		**7**	**8**	**9**
$(Me_3Si)_3SiH$	:	93 %	2.0 %	4.1 %
Bu_3SnH	:	83 %	1.2 %	15.0 %

This observation could be important for slow cyclization reactions.[7] The replacement of stannane **1** by silane **3** improves also the synthesis of 2-deoxysugars **11** from glycosyl halides **10**.[8] Because of the slow rearrangement[9] of glycosyl radicals the reactive tin hydride **1** has to be added in low concentrations over several hours to the glycosyl bromide solution.[8] With silane **3** glycosyl halides **10** and hydride **3** can be mixed directly, thus using 50 mmol solutions the time reduces from 8 h with stannane **1** to 1 h with silane **3**.



10 **11**

gluco	:	71%
galacto	:	70%

Therefore, application of tris(trimethylsilyl)silane not only avoids the use of toxic stannanes it also lowers the formation of unwanted reduction products.

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