Intramolecular Cyclizations of α-Stannyl Radicals to Acylsilanes: Regiospecific Syntheses of Five-membered Cyclic Silyl Enol Ethers

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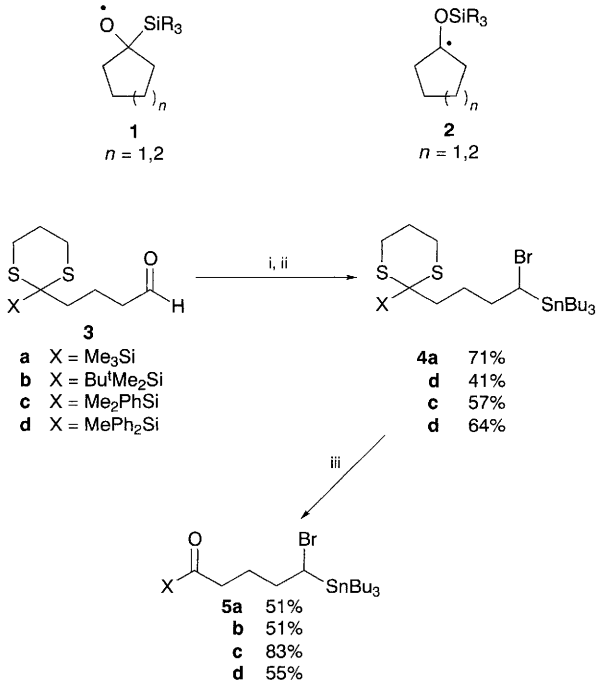
α-Stannyl radicals generated from acylsilanes **5**, **13** and **14** cyclize to give good yields of cyclic silyl enol ethers after sequential cyclizations, radical Brook rearrangements and β-scissions.

Acylsilanes have gained more and more attention in recent years.[1] Radical cyclization reactions of acylsilanes involve the formation of β-silyl alkoxy radicals **1** which quickly rearrange to give α-silyloxy radicals **2**.[2] This special feature creates opportunities for further elaboration.[3] Here we report the use of α-stannyl radicals to cyclize with acylsilanes and give cyclic silyl enol ethers in a regiospecific way.

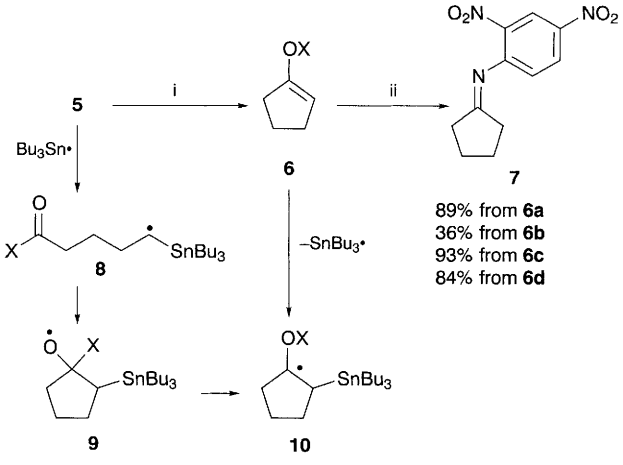
Aldehydes **3**[3a] were treated with tributyltin anions and the resulting α-stannyl alcohols were converted to α-stannyl bromides **4** using triphenylphosphine and tetrabromomethane (Scheme 1). Hydrolysis of **4** with ceric ammonium nitrate (CAN)[4] gave acylsilanes **5** in moderate yields over the three steps.

Cyclizations of **5** in refluxing benzene with slow addition of a catalytic amount of tributyltin hydride (0.15 equiv.) and AIBN (0.05 equiv.) gave silyl enol ethers **6** (Scheme 2).† The presence of **6** was confirmed by comparing their crude ^{1}H NMR spectra with those of the authentic samples prepared from cyclopentanone. However, the crude products of **6** were converted to the 2,4-dinitrophenylhydrazone of cyclopentanone to estimate the yields of the cyclizations. In the cases of **6a**, **c** and **d**, the overall conversion yields were very good. The low yield in the case with a bulky *tert*-butyldimethylsilyl group **6b** indicated that the cyclization was not efficient. This may attributable to the steric interactions between the silyl group and the tributylstannyl group. The whole process invovles the generation of α-stannyl radicals **8** which cyclize to give radicals **9**. These radicals undergo radical Brook rearrangements[5] to give radicals **10** which are set up to perform facile β-scissions and give silyl enol ethers **6** with concomitant formation of a tributyltin radical. The tin radical then abstracts the bromine atom from **5** to regenerate radicals **8**, thus completes the cycle.

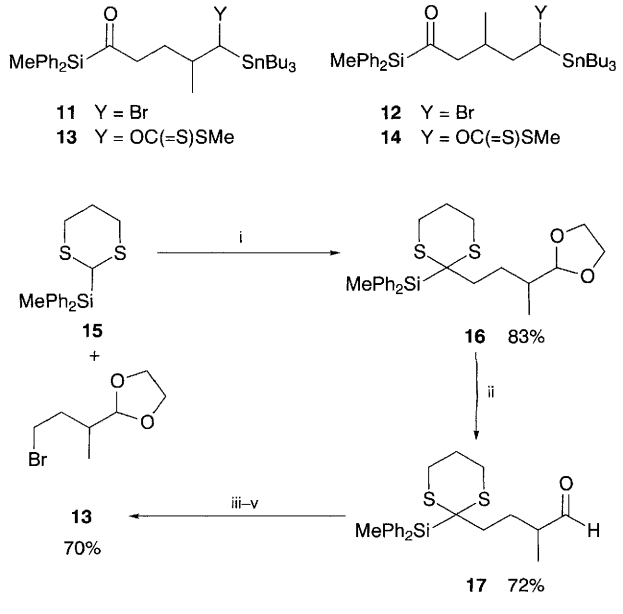


Scheme 1 *Reagents*: i, Bu_3SnLi; ii, Ph_3P, CBr_4; iii, CAN, MeCN, H_2O

To demonstrate the regiospecific nature of this approach for the preparation of cyclic silyl enol ethers, we intended to synthesize bromides **11** and **12**. However, the same route used for the synthesis of **5** gave low yields in these cases. This was probably due to the instability of the structures of type **4** in which a nucleophile and an electrophile coexist.[6] Therefore, a different route was developed. Alkylation of the 2-silyl-1,3-dithiane **15** with 2-(3-bromo-1-methylpropyl)-1,3-dioxolane[7] gave **16** in 83% yield (Scheme 3). The aldehyde **17** obtained from hydrolysis of **16** was treated with tributyltin lithium, and the resulting alkoxide was trapped sequentially with carbon disulfide and methyl iodide to construct the xanthate moiety. The dithiane was then hydrolysed with



Scheme 2 *Reagents and Conditions*: i, Bu_3SnH (0.15 equiv.), AIBN (0.05 equiv.), C_6H_6, 80 °C; ii, 2,4-dinitrophenylhydrazine, H^+, EtOH



Scheme 3 *Reagents*: i, BuLi; ii, *p*-Me-$C_6H_4SO_3H$ (cat.), H_2O, THF; iii, Bu_3SnLi; iv, CS_2, MeI; v, $(CF_3CO_2)_2IC_6H_5$, H_2O, MeCN, THF, $NaHCO_3$

iodobenzene bis(trifluoroacetate) to give **13** in 70% yield from the aldehyde.[8] The xanthate **14** was synthesized accordingly in similar yields.

Radical cyclizations of **13** and **14** under the same conditions as stated above gave the two regioisomeric silyl ethers **18** and **19**, respectively. To confirm the structures, the crude products were treated with phenylselenyl bromide in dichloromethane at −78 °C. The selenide **20** was obtained in 68% yield from **13** as a mixture of *cis*/*trans* (1:2) isomers.[9] The selenide **21** was obtained in 77% yield from **14** as an 8.8:1 mixture of two stereoisomers.‡

Attempted radical cyclization of **22** initiated with tributyltin hydride (0.15 equiv.) and AIBN (0.05 equiv.) was not successful. Only the reduction product **23** was observed along with mostly unreacted **22**. With a full equivalent of tributyltin hydride, the acylsilane **23** was isolated in 80% yield. It has been reported for radical cyclizations of acylsilanes that 1,5-hydrogen atom transfer was a competing process with 1,6-cyclization.[3a] In the case of **22**, the unfavourable interactions between the silyl and stannyl groups probably blocked the cyclization completely.

In summary, the radical cyclizations described herein represent a novel regiospecific approach to the syntheses of five-membered cyclic silyl enol ethers. This report also demonstrates that α-stannyl radicals can be very useful if properly designed. The potential of α-stannyl radicals is currently under investigations.

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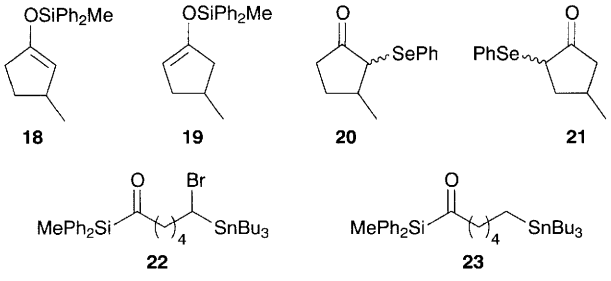

Footnotes

† *Typical procedure*: Tributyltin hydride (21 μl, 0.078 mmol) and AIBN (5 mg, 0.03 mmol) in benzene (5 ml) were added over 1 h to a solution of **5c** (295 mg, 0.503 mmol) in benzene (5 ml) heated at 80 °C. The resulting solution was heated for a further hour and then concentrated *in vacuo* to obtain the crude product which was used directly in the subsequent reaction.

‡ The major isomer was presumably the *trans* isomer; however, the stereochemistry was not determined. The characteristic ^{1}H NMR (400 MHz, $CDCl_3$) signal for the major isomer appears at δ 3.82 (br d, *J* 6.6 Hz), and that of the minor one appears at 3.72 (br dd, *J* 11, 8.4 Hz).

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