

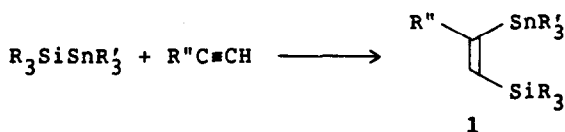
REACTIONS OF CIS-SILYL TIN OLEFINS: (ANTI-DENMARK) NAZAROV
CYCLIZATION OF β -SILYL DIVINYL KETONES

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Summary: Readily available silyl tin olefins efficiently couple with acid chlorides (Stille Reaction) to give β -silyl divinyl ketones. These ketones with large silyl groups (Et_3Si , $t\text{-BuMe}_2\text{Si}$) undergo Nazarov cyclizations wherein the silicon group is retained in the product.

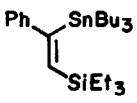

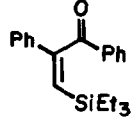
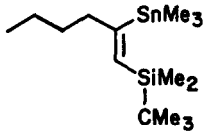
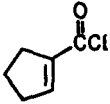
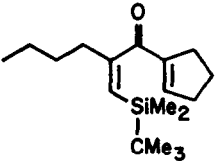
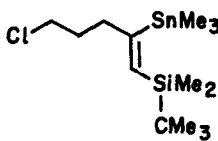
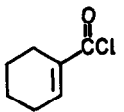
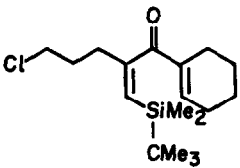
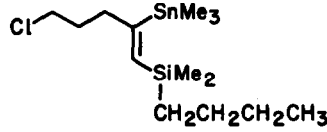
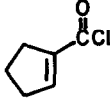
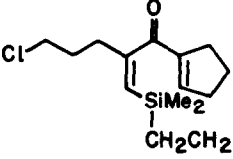
Recently, we have been exploring the organic chemistry of silyl stannanes. These little used but easily accessible reagents³ were found to react with terminal acetylenes under palladium catalysis to give differentially bis functionalized adducts 1 in a highly regio- and stereoselective fashion.⁴ In principal, adducts 1 should be versatile



intermediates since both the vinyl silane and vinyl stannane moieties might be independently manipulated for the construction of complex molecules. We report here the direct conversion of 1 to β -silyl divinyl ketones 2 and the subsequent Nazarov cyclization of these adducts; a reaction which is very sensitive to the size of the silicon group.

Initial attempts to couple 1 ($\text{R}=\text{Me}$, $\text{R}'=\text{Bu}$, $\text{R}''=\text{Ph}$) with benzoyl chloride in a Stille type reaction⁵ was complicated by considerable desilylation.⁶ With larger silyl groups (Et_3Si , $t\text{-BuMe}_2\text{Si}$, $n\text{-BuMe}_2\text{Si}$) however, the coupling with acid chlorides was clean affording 60-85% yields of adducts (Table I).

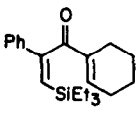
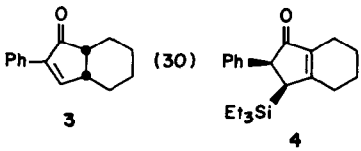
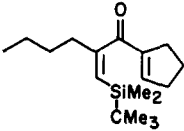
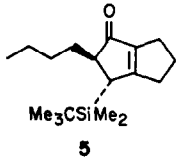
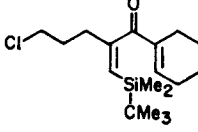
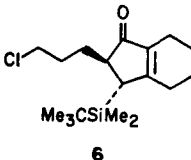
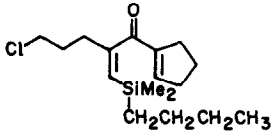
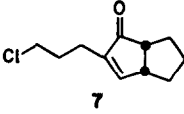
Table I: Stille Coupling of cis Silyl Tin Olefins^a

OLEFIN	ACID CHLORIDE	PRODUCT (% ISOLATED YIELD)
 <p style="text-align: center;">1b</p>		 <p style="text-align: center;">2a (65-69)</p>
 <p style="text-align: center;">1c</p>		 <p style="text-align: center;">2c (87)</p>
 <p style="text-align: center;">1d</p>		 <p style="text-align: center;">2d (58)</p>
 <p style="text-align: center;">1e</p>		 <p style="text-align: center;">2e (77)</p>

^aAll reactions run in CHCl₃ at 60°C for 18-24h with (ACN)₂PdCl₂ catalyst.

Based on Denmark's work with β -silyl divinyl ketones, the Nazarov reaction should give cyclopentenones wherein the silyl group has been eliminated while directing double bond formation.⁷ Surprisingly, when 2b was treated with FeCl₃ a 1:1 mixture of cyclized products was obtained. The expected known product 3⁸ was identified by its melting point 64-65°C and spectroscopic data. The side product 4, which had retained the silyl group, was characterized by HRMS m/e 326.2063 (m/e calcd for C₂₁H₃₀OSi: 326.2066) and NMR evidence. Olefinic protons were absent from the spectrum. Furthermore, the proton α to the carbonyl was a doublet (J=6Hz) which we used

Table II: Nazarov Cyclization of β -Silyl Divinyl Ketones

KETONE	LEWIS ACID ^a	PRODUCTS
 2b	$\text{BF}_3 \cdot \text{Et}_2\text{O}^b$ SnCl_4 (-78°C , 2h) FeCl_3 (0°C , 4h)	 3 (30) 4 (37) (18) (18) (18) (24)
 2c	$\text{BF}_3 \cdot \text{Et}_2\text{O}$	 5 (69)
 2d	$\text{BF}_3 \cdot \text{Et}_2\text{O}$	 6 (80)
 2e	SnCl_4 (-78°C , 1h)	 7 (100)

^aOther Lewis acids (TMS triflate, TiCl_4 , Et_3OPF_6) gave inferior results.
^b $\text{BF}_3 \cdot \text{Et}_2\text{O}$ conditions: Combine at -78°C ; 4h at -20°C ; then 0°C for 24h.

to assign the *cis* configuration to **4**.⁹ Also the IR spectrum contained a carbonyl stretch at 1692 cm^{-1} indicative of the olefin conjugation. A number of other Lewis acids were examined including boron trifluoride etherate, tin tetrachloride, and trimethylsilyl triflate with BF_3 etherate giving the highest yield of cyclized products **3** and **4** (67% combined yield).

Based on subsequent reactions, we believe the loss of the triethylsilyl group was substantial for **2b** cyclization only because of the pendant phenyl group which served to further stabilize the cation center a beta to the silicon.¹⁰

As can be seen in Table II, with other large silicon groups, the cyclization is directed to introduce the olefin exclusively at the ring fusion. The products are obtained in good yield after simple chromatography

and short path distillation. Only with 2e containing the smaller n-butyldimethylsilyl group were we able to observe the Denmark directed cyclization and in this case SnCl_4 was the Lewis acid of choice. Other acids produced a multitude of products with this system.

In summary, the cis-silyl tin olefins are useful precursors to β -silyl divinyl ketones with large silicon groups. These compounds undergo Nazarov cyclizations to give cyclopentenones which generally retain the silyl group. This results in generation of an allyl silane unit which may be useful for further chemical reactions. Finally based on our work in this area, we find that no blanket statement can be made concerning the best Lewis acid for the Nazarov cyclization.¹¹ In our work BF_3 etherate has been most useful; however, each system must be tested experimentally to ensure the highest yield of product.

References and Notes

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1. Summer Du Pont Resident Research Participant, 1985.
 2. Contribution #4010 from the department.
 3. Schumann, H.; Ronecker, S. Z. Naturforsch. B., 1967, 22B, 452-453. Tamborski, C.; Ford, F.E.; Soloski, E.J. J. Org. Chem., 1963, 28, 237-239.
 4. Chenard, B.L.; Laganis, E.D.; Davidson, F.; RajanBabu, T.V. J. Org. Chem., 1985, 50, 3666-3667. Also see Mitchell, T.N.; Killing, H.; Dicke, R.; Wickenkamp, R.J. J. Chem. Soc., Chem. Commun., 1985, 354-355.
 5. Labadie, J.W.; Tueting, D.; Stille, J.K. J. Org. Chem., 1983, 48, 4634-4642.
 6. This was somewhat surprising as Stille had coupled a trans-silyl tin olefin with no apparent problems. See Crisp, G.T.; Scott, W.J.; Stille, J.K. J. Amer. Chem. Soc., 1984, 106, 7500-7506.
 7. James, T.K.; Denmark, S.E. Helv. Chim. Acta, 1983, 66, 2377-2396.
 8. Khand, I.U.; Pauson, P.L. J. Chem. Res.(S), 1977, 9.
 9. All new compounds gave acceptable elemental analysis ($\text{C} \pm 0.33$, $\text{H} \pm 0.3$) and/or high resolution mass spectral data.
 10. Denmark has reported one example of a silicon directed Nazarov reaction which used a large triisopropylsilyl group apparently without the complication we observe. See Jones, T.K.; Denmark, S.E. Helv. Chim. Acta, 1983, 66, 2397-2411.
 11. Denmark uses FeCl_3 (see ref. 10) and Stille uses BF_3 etherate (see ref. 6) for Nazarov reactions. Other Lewis acids (e.g. SnCl_4 , TiCl_4) have also been used.

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