Å [O1–C1] and 1.48 (1) Å [C13–O1], and the C–C distances are 1.55 (1) Å [C1–C14] and 1.57 (2) Å [C13–C14].

The dictyoxetane carbon skeleton has not been reported previously. Since dictyoxetane (1) cooccurs with dolabellanes in *Dictyota dichotoma*, it is most likely formed by 3,9-cyclization of a "dolabellane" precursor. The structures of the dolabellanes from this collection of *D. dichotoma* will be reported in the near future.[11]

Acknowledgment. We thank Prof. M. Umamheswara Rao, Department of Botany, Andhra University, for identifying the algae and scientists from the Central Marine Fisheries Research Institute of Mandapam Camp for assistance with collections. This research was generously funded by the Council of Scientific and Industrial Research, New Delhi, and the California Sea Grant College Program (NA80AA-D-00120). K.F.A. thanks the National Institutes of Health for a postdoctoral fellowship (F32 CA07458-01). H.C.-h. and J. C. thank the New York State Sea Grant (NSF INT14133 and NIH CA24487) for financial support.

Registry No. 1, 97732-59-7.

Supplementary Material Available: Tables of fractional coordinates, thermal parameters, interatomic distances, and interatomic angles for dictyoxetane (1) (5 pages). Ordering information is given on any current masthead page.

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[11] Pullaiah, K. C. Ph.D. Thesis, Andhra University, 1984.

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Received May 7, 1985

Silylstannanes: Useful Reagents for Bis Functionalization of α,β-Unsaturated Ketones and Acetylenes[†]

Summary: A series of silylstannanes have been prepared for use in the difunctionalization of organic molecules.

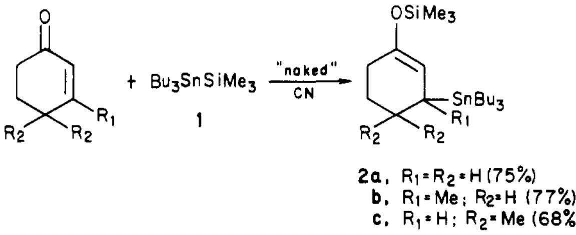
Sir: Synthetic methodology based on the use of silylated and stannylated reagents has grown explosively in the last few years. Both the Si–C and Sn–C bonds are capable of undergoing a variety of useful transformations,[1] yet unprovoked these moieties possess good stability. We have begun a program to examine the chemistry of silylstannanes as reagents which could allow the introduction of both silicon and tin directly into organic substrates. Subsequent individual manipulation of the silicon and tin groups could provide powerful new synthetic methods. This report describes our initial results in the silylstannylation of α,β-unsaturated ketones and acetylenes.

Silylstannanes 1 with methyl, butyl, and phenyl substituents have been known for some time;[2] however, the literature concerning their organic chemistry is sparse.[3] We have prepared a series of silylstannanes using several of the standard procedures.[2] For large-scale synthesis the Still preparation of R_3SnLi[1b] from the corresponding hydride and LDA followed by quenching with a silyl chloride is the method of choice (eq 1).[4]

$$R_3SnH \xrightarrow[(2)\ R^1{}_3SiCl]{(1)\ LDA} R_3SnSiR^1{}_3 \qquad (1)$$

$$R_3 = Me_3,\ Bu_3,\ Ph_3;\ R^1{}_3 = Me_3,\ Et_3,\ t\text{-}BuMe_2$$

The first attempts to add 1 ($R_3 = Bu_3$; $R^1{}_3 = Me_3$) to cyclohexenone in the presence of Lewis acids[5] ($BF_3{\cdot}Et_2O$, $Ti(O\text{-}i\text{-}Pr)_4$, $Me_3SiOSO_2CF_3$) were unsuccessful; however, the use of "naked" cyanide ion catalysis (KCN/18-crown-6,[6] Bu_4NCN, TASCN[7]) efficiently catalyzed an exothermic Michael addition to produce **2a** in high yield (eq 2).[8] The moisture-sensitive product was isolated by distillation directly from the reaction vessel.[9,10] We later found that potassium *tert*-butoxide also catalyzed the addition reaction albeit in lower yield (~45% conversion after 72 h). Somewhat surprising was the observation that this reaction was not catalyzed by fluoride ion.[11]



(2)

We have briefly examined the scope of this reaction and find it to be sensitive to steric bulk on the silicon atom. Thus while Me_3Si, $PhMe_2Si$, and n-$BuMe_2Si$ groups all participate in the Michael addition, the Et_3Si and t-$BuMe_2Si$ groups prevent the reaction. In contrast, steric bulk on tin is apparently of little consequence as both

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[1] (a) For a general review of the functional group transformations of silanes, see: Colvin, E. "Silicon in Organic Synthesis"; Butterworths: New York, 1981. (b) For leading references to the transformations of organotin compounds, see: Still, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 1481–1487; **1977**, *99*, 4836–4838.

[2] Tamborski, C.; Ford, F. E.; Soloski, E. J. *J. Org. Chem.* **1963**, *28*, 237–239. Schumann, H.; Ronecker, S. *Z. Naturforsch. B: Anorg. Chem., Org. Chem. Biochem., Biophys., Biol.* **1967**, *22*, 452–453.

[3] Azizian, H.; Eaborn, C.; Pidcock, A. *J. Organomet. Chem.* **1981**, *215*, 49–58. Kosugi, M.; Ohya, T.; Migita, T. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 3539–3540.

[4] We thank Dr. M. H. Fisch and Argus Chemical Co. for a generous sample of trimethyltin hydride.

[5] Suzuki, M.; Kawagishi, T.; Noyori, R. *Tetrahedron Lett.* **1981**, *19*, 1809–1812.

[6] Evans, D. A.; Truesdale, L. K.; Grimm, K. G.; Nesbitt, S. L. *J. Am. Chem. Soc.* **1977**, *99*, 5009–5017.

[7] Middleton, W. J. U.S. Patent 3940402.

[8] Still has prepared compounds analogous to 2 by conjugate addition of Bu_3SnLi to enones and trapping the intermediate with trimethylsilyl chloride. See ref 1b and: Still, W. C. *J. Am. Chem. Soc.* **1979**, *101*, 2493–2495.

[9] All new compounds gave acceptable elemental analyses (C ± 0.27, H ± 0.33) and/or high-resolution mass spectral analyses.

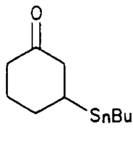
[10] General procedure: The enone (30 mmol) and (trimethylsilyl)tributylstannane (30 mmol) were combined in a dry flask with magnetic stirrer under a nitrogen atmosphere. Tetrabutylammonium cyanide (50 mg, 0.06 mmol) was added, and a mildly exothermic reaction began immediately. When the exotherm subsided, the mixture was warmed to 40 °C until the reaction was complete by GLC analysis (4–15 h). The product was distilled directly from the reaction vessel as a clear colorless oil.

[11] Gerlach, H.; Kunzler, P. *Helv. Chim. Acta* **1978**, *61*, 2503–2509. RajanBabu, T. V. *J. Org. Chem.* **1984**, *49*, 2083–2089.

Me_3Sn and Bu_3Sn are tolerated.

Interestingly, steric crowding in the enone was not a problem as illustrated by additions to 3-methylcyclohexenone and 4,4-dimethylcyclohexenone. In these reactions **2b** and **2c** were formed in high yield, but longer reaction times were required. The efficient preparation of **2b** was especially noteworthy as a quaternary carbon was generated.

The reactions of **2** have not yet been fully explored; however, simple desilylation with tetrabutylammonium fluoride gives **3**, which has previously been prepared by conjugate addition of Bu_3,SnLi to cyclohexenone.[1b] We also find that fluoride-catalyzed aldol condensation with benzaldehyde under conditions similar to those of Noyori[12] is efficient providing **4** in 60% yield as a 1:1 mixture of *threo* and *erythro* isomers.



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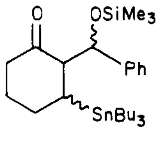

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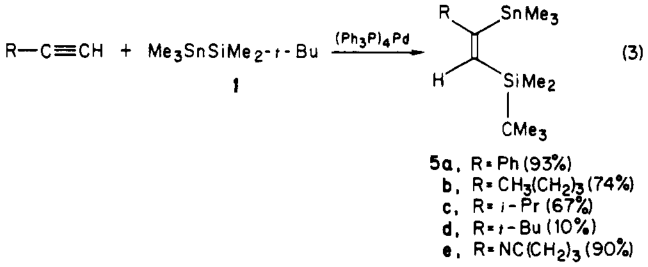
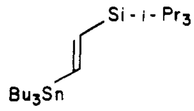
The silylstannylation of acetylenes was also examined. We reacted 1 (R_3 = Me_3; $R^1{}_3$ = *t*-$BuMe_2$) with phenylacetylene in the presence of catalytic tetrakis(triphenylphosphine)palladium in THF solution.[13] Within 4–8 h at 65 °C the starting materials were consumed, and the adduct **5a** was obtained in 90% yield upon Kugelrohr distillation (eq 3).[14] This addition was regio- and stereoselective with the ^{119}Sn and ^{117}Sn couplings to the vinyl proton (182 and 174 Hz, respectively) being diagnostic.[13b]



(3)

Silylstannylation of terminal acetylenes appears to be quite general, though we have not examined many functionalized molecules. Note that a cyanoalkyl side chain (**5e**) was tolerated. A *tert*-butyl substituent appears to retard the addition as indicated by the low yield of adduct **5d**.

In conclusion, we have demonstrated that the readily available silylstannanes are useful reagents for the bis functionalization of α,β-unsaturated ketones and terminal acetylenes. The adducts obtained may serve as intermediates for a variety of useful transformations. For example, a trans silyl tin olefin (**6**)[15] has found great utility as an intermediate in Denmark's silicon-directed Nazarov cyclization reaction.[15,16] We envision a similar application for **5**.



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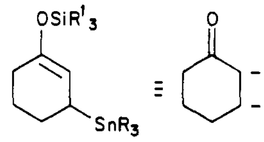
We are presently developing a protocol to use **2** as a synthon for an α,β-dianion of a ketone (eq 4) where the nucleophilicity of the α and β sites in the ketone may be expressed by means not presently available. This new methodology should nicely compliment the tandem Michael addition–alkylation (aldol) sequence afforded by conventional organometallic chemistry.[17,18]



(4)

Acknowledgment. The fine technical assistance of D. R. Sanderson is gratefully acknowledged.

† Contribution #3791 from the Department.

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[12] Noyori, R.; Nishida, I.; Sakata, J. *J. Am. Chem. Soc.* **1983**, *105*, 1598–1608; **1981**, *103*, 2106–2108. Nakamura, E.; Shimizu, M.; Kuwajima, I.; Sakata, J.; Yokoyama, K.; Noyori, R. *J. Org. Chem.* **1983**, *48*, 932–945.

[13] (a) For related disilane addition to acetylenes, see: Watanabe, H.; Kobayashi, M.; Saito, M.; Nagai, Y. *J. Organomet. Chem.* **1981**, *216*, 149–157. (b) For related distannane addition to acetylenes, see: Mitchell, T. N.; Amamria, A.; Killing, H.; Rutschow, D. *J. Organomet. Chem.* **1983**, *241*, C45–C47. Killing, H.; Mitchell, T. N. *Organometallics* **1984**, *3*, 1318–1320.

[14] The synthesis of **5a** was typical. Phenyl acetylene (3.25 g, 29.7 mmol) and (*tert*-butyldimethylsilyl)trimethylstannane (8.27 g, 29.7 mmol) were dissolved in dry THF (30 mL) in a dry flask with magnetic stirrer under a nitrogen atmosphere. Tetrakis(triphenylphosphine)palladium (100 mg) was added, and the mixture was refluxed gently for 6 h. The solvent was removed at reduced pressure, and the crude product was Kugelrohr distilled [100 °C (0.1 mm) pot temperature] to give 10.6 g, 93%, of **5a** as a white solid, mp 47–78 °C.

[15] Jones, T. K.; Denmark, S. E. *Helv. Chim. Acta* **1983**, *66*, 2397–2411.

[16] Jones, T. K.; Denmark, S. E. *Helv. Chim. Acta* **1983**, *66*, 2377–2396.

[17] For leading references, see: Noyori, R.; Suzuki, M. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 847–876.

[18] As this stage of our work was completed the reaction of silyl stannanes with acetylenes was independently discovered by Mitchell and co-workers. Mitchell, T. N.; Killing, H.; Dicke, R.; Wickenkamp, R. *J. Chem. Soc., Chem. Commun.* **1985**, 345–355.

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Received July 9, 1985

Synthetic Application of Photochemical Electron Transfer to Direct Amination of Arenes by Ammonia and Primary Amines[1]

Summary: Direct photoamination of arenes efficiently occurs with ammonia and various primary amines in the presence of *m*-dicyanobenzene to give aminated dihydroarenes in fairly good yields.

Sir: The preparation of aromatic amines is usually carried out by means of indirect methods involving reductions of nitro, azo, and azide arenes or substitution of the halogen, hydroxy, and alkoxy groups.[2,3] On the other hand, direct amination of arenes is limited to Fridel–Crafts reaction with activated amination reagents or nucleophilic addition of amide anion to highly activated substrates.[2] From

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[1] Photochemical Reactions of Aromatic Compounds. Part 40. Part 39: Pac, C.; Fukunaga, T.; Ohtsuki, T.; Sakurai, H. *Chem. Lett.* **1984**, 1847–1850.

[2] Gibson, M. S. In "The Chemistry of the Amino Group"; Patai, S., Ed.; Interscience: New York, 1968; pp 37–77.

[3] Cornelisse, J.; Havinga, E. *Chem. Rev.* **1975**, *75*, 353–388.