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Transmetalation as a Route to Novel Styryllithium Reagents

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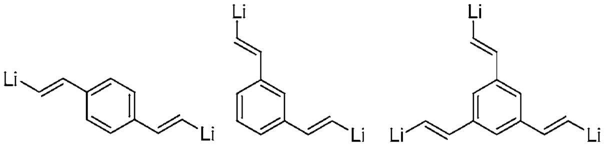
ABSTRACT

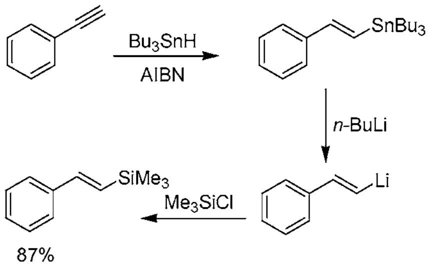


Transmetalation of *β*-tributyl(styryl)stannanes with *n*-BuLi gives the functional equivalents of the corresponding styryllithium intermediates. Reaction of the intermediates with chlorotrimethylsilane, iodomethane, or dimethyl sulfate gives the substituted styryl products in moderate to good yields. In all cases, the configuration about the double bond was retained in the products.

In recent years, considerable effort has focused on the synthesis of conjugated oligomers and polymers for application as novel optoelectronic materials.[1] As part of our own research program, we have focused on the synthesis of oligomers and polymers with alternating π-conjugated and silylene units.[2] Polymers such as these are known to possess what is commonly called "$\sigma-\pi$ conjugation" along the polymer backbone.[3] As part of our continuing efforts in this area, we sought to develop new reagents for the construction of these materials. To this end, we describe herein the synthesis of new lithiated styrene reagents prepared by transmetalation of the corresponding tributyl(styryl)stannanes. In addition to their expected value in the synthesis of new $\sigma-\pi$ conjugated organosilicon systems, we believe these reagents will also be useful in the construction of new organic conjugated polymers via conventional metal-catalyzed coupling methods.

Early on, we decided to synthesize these reagents by tin−lithium exchange (transmetalation) reactions of styrylstannanes, which could be prepared by the hydrostannation of the corresponding ethynylbenzene compounds with readily available tributyltin hydride. We chose this route because of the reported successful preparation of (*E*)-β-styryllithium by transmetalation of (*E*)-β-trimethyl(styryl)stannane or (*E*)-β-triphenyl(styryl)stannane with methyllithium or phenyllithium.[4] We initially attempted the synthesis of (*E*)-β-styryllithium by the transmetalation of (*E*)-β-tri*butyl*(styryl)stannane (itself prepared in high yield by the AIBN-catalyzed hydrostannation of phenylacetylene with tributyltin hydride) with *n*-BuLi. As expected, the lithium reagent was formed as evidenced by the isolation of the trimethylsilyl-substituted product in 87% yield when the dark purple intermediate was treated with chlorotrimethylsilane (Scheme 1). As in the earlier report,[4] the (*E*)-β-isomer was formed exclusively with tetrabutyltin as the only byproduct.

Scheme 1



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[1] (a) Yamamoto, T. *Macromol. Rapid Commun.* **2002**, *23*, 583. (b) Tour, J. M. *Acc. Chem. Res.* **2000**, *33*, 791.

[2] (a) Yao, J.; Son, D. Y. *Organometallics* **1999**, *18*, 1736. (b) Xiao, Y.; Wong, R. A.; Son, D. Y. *Macromolecules* **2000**, *33*, 7232.

[3] Ohshita, J.; Kunai, A. *Acta Polym.* **1998**, *49*, 379.

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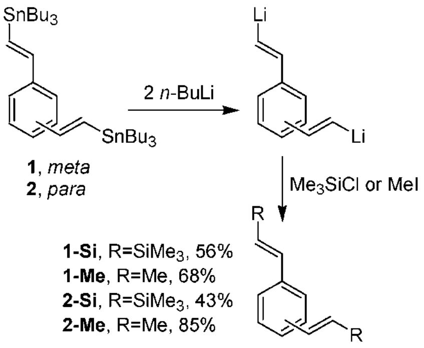
We then turned our attention to the synthesis of the previously unknown dilithiated reagents. Free-radical hydrostannation of *m*-diethynylbenzene with tributyltin hydride gave exclusively 1,3-bis((*E*)-2-(tributylstannyl)vinyl)benzene, **1**, in 90% yield. The structure of **1** was confirmed by ^{1}H NMR spectroscopy. Addition of *n*-BuLi to a THF solution of **1** at −15 °C gave a dark purple intermediate, which when quenched with either chlorotrimethylsilane or iodomethane gave the corresponding substituted styryl compounds **1-Si** and **1-Me** in 56 and 68% yields, respectively (Scheme 2).

Scheme 2

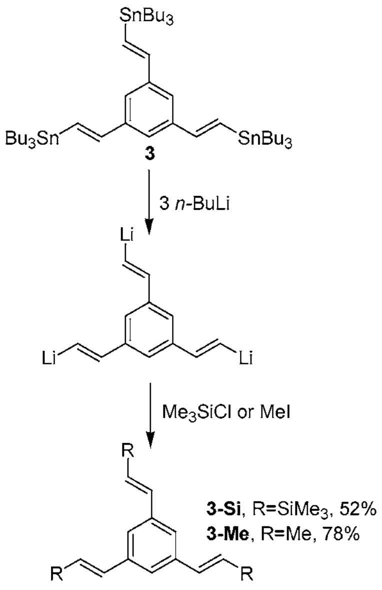


The pure products could be separated from tetrabutyltin by flash chromatography. The (*E*)-*β* configuration in the products was retained, as determined by ^{1}H NMR spectroscopy.

Application of this method to *p*-diethynylbenzene was not completely successful. Hydrostannation of *p*-diethynylbenzene by free-radical methods was unsuccessful and gave rise to an unidentified mixture of products. We eventually utilized a cyanomethyltributylstannyl cuprate reagent[5] and obtained 1,4-bis((*E*)-2-(tributylstannyl)vinyl)benzene, **2**, in 40% NMR yield. This product could not be purified (chromatography resulted in decomposition) but was used as is for the transmetalation step. Addition of *n*-BuLi to a THF solution of **2** followed by addition of chlorotrimethylsilane or iodomethane resulted in the formation of the corresponding disubstituted compounds **2-Si** and **2-Me** in 43 and 85% yields, respectively (Scheme 2). As in the case of **1**, the products retained the (*E*)-*β* configuration.

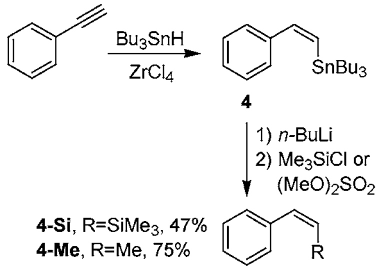
We then attempted to synthesize the 1,3,5-trilithium reagent using the methods described above. AIBN-catalyzed hydrostannation of 1,3,5-triethynylbenzene with tributyltin hydride was successful and gave exclusively 1,3,5-tris((*E*)-2-(tributylstannyl)vinyl)benzene, **3**, in 82% yield. Treatment of **3** with *n*-BuLi in THF at −15 °C followed by quenching with chlorotrimethylsilane or iodomethane gave the corresponding trisubstituted compounds **3-Si** and **3-Me** in 52 and 78% yields, respectively, evidence of the formation of the novel trilithium reagent, or at least its functional equivalent (Scheme 3).

Scheme 3



In all of the cases described above, the (*E*)-*β* compounds were formed exclusively. In view of recent successes in regioselective hydrostannation of acetylenes to form (*Z*)-*β*-vinylstannanes,[6] we examined the possibility of extending this transmetalation chemistry to the synthesis of (*Z*)-*β*-styryllithiums. Accordingly, reaction of phenylacetylene with tributyltin hydride in the presence of $ZrCl_4$ gave the known (*Z*)-*β*-tributyl(styryl)stannane, **4**, in 92% yield. Treatment of **4** with *n*-BuLi in the usual manner followed by addition of chlorotrimethylsilane or dimethyl sulfate gave the corresponding substituted styryl compounds **4-Si** and **4-Me** in 47 and 75% yields, respectively (Scheme 4). In both cases, the (*Z*)-*β* configuration was retained, as determined by ^{1}H NMR spectroscopy. These results are in marked contrast to the earlier referenced report in which transmetalation of (*Z*)-*β*-

Scheme 4



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(4) Seyferth, D.; Vaughan, L. G.; Suzuki, R. *J. Organomet. Chem.* **1964**, *1*, 437.

(5) (a) Barero, A.; Cuadrado, P.; Fleming, I.; Gonzalez, A. M.; Pulido, F. J.; Rubio, R. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1657. (b) Barero, A.; Cuadrado, P.; Fleming, I.; Gonzalez, A. M.; Pulido, F. J.; Rubio, R. *Chem. Commun.* **1992**, 351. (c) Lipshutz, B. H.; Kozlowski, J. A.; Wilhem, R. S. *J. Org. Chem.* **1984**, *49*, 3943.

(6) (a) Asao, N.; Liu, J.-X.; Sudoh, T.; Yamamoto, Y. *Chem. Commun.* **1995**, 2405. (b) Asao, N.; Liu, J.-X.; Sudoh, T.; Yamamoto, Y. *J. Org. Chem.* **1996**, *61*, 4568.

trimethyl(styryl)stannane with methyllithium gave only polymeric products when the transmetalated intermediate was treated with chlorotrimethylsilane.[4] Thus far, extension of this chemistry to synthesize (*Z*)-β-di- and trilithium reagents has been hampered by our inability to obtain exclusively (*Z*)-β-tributyl(styryl)stannanes consistently using the $ZrCl_4$-catalyzed hydrostannation method.

In conclusion, we have successfully demonstrated that lithiated styrenes can be synthesized by transmetalation reactions.[7] The tributyl(styryl)stannane reagents can be easily prepared by hydrostannation of ethynylbenzenes. We are currently examining the application of these reagents in the synthesis of new linear and branched organosilicon polymeric systems. Furthermore, we believe these reagents should be of utility in the synthesis of extended organic conjugated networks via Stille[8] and Negishi[9] coupling protocols. These results will be reported in due course.

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Supporting Information Available: Complete experimental details and analytical data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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[7] It should be noted that the existence of the discrete di- and trilithium reagents in solution was not proven (the reactions could in theory proceed in a stepwise fashion, for example), but at the very least these reagents are functional equivalents of the corresponding lithium compounds. We thank a reviewer for pointing this out.

[8] Farina, V.; Krishnamurthy, V.; Scott, W. J. *The Stille Reaction*; Wiley: New York, 1998.

[9] Negishi, E. I.; Liu, F. In *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F., Stang, P., Eds.; Wiley: New York, 1998; p 1.