

A Novel Palladium-Catalyzed Homocoupling of Alkynylstannanes: A New Synthetic Approach to Extended Linear-Carbon Polymers

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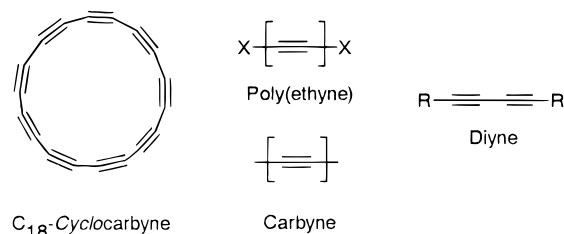
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A catalytic and highly efficient synthesis of sp–sp carbon–carbon bonds will play a key role in the synthesis of not only linear-carbyne but also many other molecules such as poly(ynes) and other materials that approach an all-carbon composition (Chart 1).¹ Alkynylstannanes are readily available and stable synthetic intermediates and have been effectively employed in palladium-catalyzed cross-coupling reactions.² The Stille cross-coupling reaction using alkynylstannanes currently provides a very efficient and mild method for the construction of sp–sp² carbon–carbon bonds.³ However, the construction of an sp–sp carbon–carbon bond has received relatively little attention. The Hay modification⁴ of the Glaser reaction is the most commonly used synthetic methodology for the synthesis of diynes. The methodology has been used to prepare low molecular weight polymeric poly(ethynyl) materials.⁵ More recently, the synthesis of diynes has been accomplished using a copper-mediated cross-coupling of iodonium alkynyl salts with copper(I) acetylides.⁶

In this paper, we present methodology for the creation of sp–sp carbon–carbon bonds based on a palladium-catalyzed homocoupling of alkynylstannanes. The new synthetic methodology can be used to prepare diynes, poly(yne) materials, and, through the addition of carbon monoxide, a unique functional group of yne-(E)-ene-one-yne.

Treatment of (trimethylstannyl)ethynyl derivatives with (E)-diiodoethene⁷ in acetonitrile/chloroform (3:1, v/v, respectively) and in the presence of our palladium catalyst, [(Me₂Si(2-pyridyl)₂)]PdCl₂,⁸ hereafter referred to as (SiPy)PdCl₂, affords rapid and complete homocoupling of the organostannane reagent at ambient temperature (Scheme 1, Table 1).⁹ In cases where the diyne is sterically encumbered (Table 1, entry 2), the palladium species (SiPy)PdI₂ crystallizes from the reaction mixture.¹⁰ The latter species can be isolated and reused as catalyst. The (E)-diiodoethene shows a remarkable selectivity for oxidation of the palladium(0) species, leaving the easily

Chart 1



Scheme 1

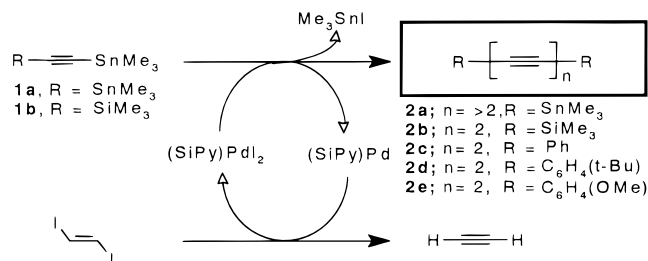


Table 1. Homocoupling of (Trimethylstannyl)alkynes^a

entry	organostannane	product	yield (%) ^b
1	Me ₃ Sn-C≡C-SnMe ₃	2a , n > 2	
2	Me ₃ SiC≡C-SnMe ₃	2b	95
3	Ph-C≡C-SnMe ₃	2c	93
4	(4-t-BuC ₆ H ₄)-C≡C-SnMe ₃	2d	85
5	(4-MeOC ₆ H ₄)-C≡C-SnMe ₃	2e	90

^a Reactions were carried out in CD₃CN/CDCl₃ (3/1, v/v) at ambient temperature, 2 mol % of (SiPy)PdCl₂, and 1.0 mol equiv of (E)-1,2-diiodoethene. *Caution:* Toxic organotin are used and produced in this reaction. Precautions should be taken to avoid any contact with these chemicals and to dispose of the waste properly. ^b NMR yields based on an internal standard, 1,1,1-trichloroethane.

oxidized alkynylstannane bond intact. Use of (Ph₃P)₂PdCl₂ as the precatalyst using conditions in Table 1 showed no significant catalytic homocoupling of the alkynylstannane.¹¹

Treatment of bis(trimethylstannyl)ethyne under the homocoupling conditions produces oligomeric and polymeric poly(ethyne). The formation of high molecular weight material (Table 1, entry 1) is best evidenced by the change in UV–vis absorption maxima to a λ_{max} of 460 nm. Furthermore, we observe a series of well-defined λ_{max} peaks (262, 282, 298, 326, 354, and 374 nm) for oligomeric materials. These bands correspond well with previously synthesized SiMe₃-capped oligomeric materials.¹² Gel permeation chromatography analysis of the polymerization mixture produces a peak corresponding to a polymeric material with a M_n of 2100 (polydispersity of 2.8) relative to polystyrene standards.¹³ Raman spectral analysis (514 nm excitation, calibrated to p-Si(111) at 521 cm⁻¹) of films for polymer **2a** cast from the polymerization reaction mixture show a strong absorption band at 2150 cm⁻¹, consistent with the proposed structure.

(11) We have also noted that (2,2'-bipyridine)PdCl₂ will also catalyze the dimerization of alkynylstannanes. A more complete study probing ligand effects is underway.

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(13) GPC data was collected using a variable wavelength UV–vis detector which enabled us to distinguish the polymeric material from coproducts of the polymerization (in particular Me₃SnI). By making incremental changes, starting at 500 nm, and going to shorter wavelength, we could observe a concomitant decrease in the average MW of the polymer. This is consistent with the λ_{max} decreasing with MW (i.e., chain length). Spectral data: ¹H NMR (CDCl₃) δ 6.85 (d, J = 16 Hz, 1 H, HC≡), 6.45 (d, J = 16 Hz, 1 H, HC≡), 0.19 (s, 18 H, SiCH₃); ¹³C NMR (CDCl₃) δ 177.1 (CO), 140.0 (≡CHCO), 128.7 (≡CH), 110.1 (C≡CCO), 101.1 (C≡CCH≡), 99.7, 99.6 (C≡CSiMe₃), -0.78 (SiCH₃). Anal. Calcd for C₁₃H₂₀O₂Si₂: C, 62.83; H, 8.11. Found: 62.51; H, 7.88.

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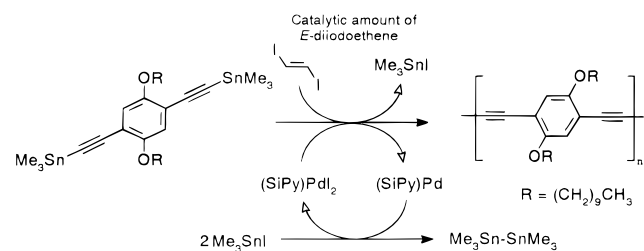
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(9) The acetonitrile cosolvent is found to greatly accelerate the reaction rate and leads to improved chemical conversion of the alkynylstannane reagent.

(10) The single-crystal molecular structure was determined by X-ray diffraction. General cell parameters were the following: monoclinic C2/c, a = 8.278(2), b = 8.278(2), and c = 17.179(3) Å, β = 111.45(1)°, V = 3251.6 Å³, Z = 8, R₁ = 5.45%, R₂ = 6.10%. Details of the structure determination are available upon request.

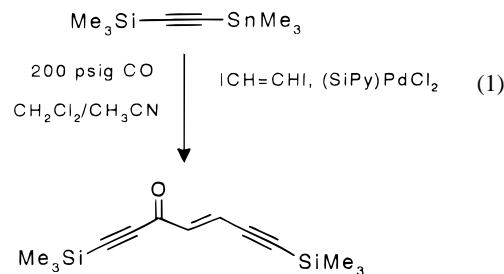
Scheme 2



The palladium-catalyzed polycondensation produces polymeric materials $\{M_n = 4000\text{--}10000$; polydispersity = 2.5 $\}$ in only 30 min, at ambient temperature, and in reasonable chemical yield (85%, Scheme 2). The polycondensation can be run in acetonitrile or other polar solvents such as dimethylformamide. The polar solvent facilitates iodine atom transfer from the vinyl diiodide partner. If we limit the diiodoethene, we find that $\text{Me}_3\text{-SnI}$ is capable of oxidizing palladium(0) [producing $\text{Me}_3\text{-SnSnMe}_3$]; hence, complete consumption of the alkyne monomer is observed (Scheme 2).

The carbonylative homocoupling of $\text{Me}_3\text{Si-C}\equiv\text{C-SnMe}_3$ produces 1,7-bis(trimethylsilyl)hept-1,6-diyn-4(*E*)-en-3-one in moderate isolated yield (eq 1).¹⁴ We find that only a single molecule of carbon monoxide is used per cross-coupling

(14) The product was purified by bulb-to-bulb distillation (0.1 mmHg) to afford 1,7-bis(trimethylsilyl)hept-4(*E*)-en-1,6-diyn-3-one (45%, bp 120–125 °C at 0.1 mmHg).



reaction. To our knowledge, this is the first catalytic route to this interesting compilation of functional groups.¹⁵

We are continuing to explore the full synthetic potential for the both the homocoupling and carbonylative cross-coupling reactions. We have also initiated a mechanistic study to better understand how polymer chain growth is occurring and then to use this knowledge to prepare well-defined poly(ethyne)-based materials.

Acknowledgment. Support of this work by the Office of Naval Research is greatly appreciated. M.J.P. wishes to thank the Alexander von Humboldt Foundation for financial support through a Feodor Lynen Fellowship.

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