C, 65.85; H, 4.41; N, 12.80. Found: C, 65.70; H, 4.57; N, 12.69.

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Registry No. **1a**, 75314-80-6; **1b**, 98263-41-3; **2a**, 83478-57-3; **2b**, 98263-44-6; **2b**·2HCl, 109864-52-0; **6**, 67902-64-1; **7**, 98263-36-6; **7**·HCl, 109864-47-3; **8**, 98263-37-7; **11**, 15128-52-6; **12**, 95955-94-5; **13**, 6116-76-3; **14**, 98263-35-5; **15**, 13414-95-4; **16**, 98263-33-3; **17**, 98263-34-4; **18a**, 98263-45-7; **18b**, 106252-03-3; **18d**, 106252-04-4; **19**, 98263-40-2; **20a**, 109864-48-4; **20b**, 109864-49-5; **20c**, 109864-50-8; **20d**, 109864-51-9; **20d**·HCl, 109864-53-1; phenylhydrazine, 100-63-0; (*p*-chlorophenyl)hydrazine, 1073-69-4; (*p*-nitrophenyl)hydrazine, 100-16-3; (*p*-methoxyphenyl)hydrazine, 3471-32-7.

Formation of 1,3-Diynes, 1,3-Dienes, and Biphenyls via the Copper(II) Nitrate Mediated Coupling of Organotin Compounds

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A method for the preparation of symmetrically substituted 1,3-diynes, 1,3-dienes, and biphenyls based on the copper(II) nitrate mediated coupling of organotin compounds **1** (R = alkynyl, alkenyl, aryl) is described. The addition of alkynylstannane **1a**, **1b**, or **1c** (**a**, R = THPOCH$_2$C≡C; **b**, R = *n*-C$_4$H$_9$C≡C: **c**, R = C$_6$H$_5$C≡C) to 1 equiv of Cu(NO$_3$)$_2$·3H$_2$O in THF at 23 °C afforded 1,3-diynes **2a-c** in 85%, 60%, and 50% yield, respectively. Similar treatment of alkenylstannanes **1d**, **1e**, **1f**, or **1g** (**d**, R = O(CH$_2$)$_3$CH=C; **e**, (*E*)-PhCH$_2$OCH$_2$CH=CH; **f**, (*Z*)-PhCH$_2$OCH$_2$CH=CH; **g**, 3,4-(CH$_3$O)$_2$C$_6$H$_3$C(=CH$_2$)) afford the 1,3-dienes **2d-g** in 80%, 72%, 75%, and 71% yield, respectively. In the case of (*E*)- or (*Z*)-vinylstannanes, the dimerization process is found to be highly stereospecific. For example, copper(II) nitrate induced coupling of **1f** (R = (*Z*)-PhCH$_2$OCH$_2$CH=CH) afforded a 23:1 ratio of (*Z,Z*)/(*E,Z*)-diene stereochemistry for **2f** (R = PhCH$_2$OCH$_2$CH=CH). Also prepared by this method were the substituted biphenyls **2h-k** (**h**, R = 4-CH$_3$C$_6$H$_4$; **i**, R = 4-CH$_3$OC$_6$H$_4$; **j**, R = 2-CH$_3$OC$_6$H$_4$; **k**, R = 4-(CH$_3$)-2,6-(CH$_3$O)$_2$C$_6$H$_3$) in 14-66% yield. Aspects about the possible mechanism of dimerization are discussed.

The oxidative dimerization of terminal alkynes to symmetrical diynes (the Glaser[1] and Eglinton[2] reactions) is a classical synthetic reaction which has recently emerged as a cornerstone transformation in the synthesis of several macrocyclic cage compounds that are capable of accomodating organic guest molecules with a high degree of selectivity binding.[3] The fundamental process for the coupling of terminal alkynes is mediated by copper(II) salts ($CuCl_2$ or $Cu(OAc)_2$), in basic media (pyridine or TMEDA), although, this general strategy has undergone numerous alterations in specific experimental conditions. The yields of diynes vary considerably as a function of substrate structure, choice of copper(II) complexes, reaction solvent and temperature.[4] An exception to the copper-mediated method is the recent Pd(II)-catalyzed coupling of alkynes,[5] but this method is limited to the dimerization of *aryl*acetylenes.

We report a new and versatile variation on this transformation leading to good yields of symmetrically coupled products under mild conditions in short reaction times using copper(II) nitrate with the corresponding alkynylstannanes according to eq 1. An especially interesting discovery is the applicability of this procedure to the dimerization of *vinyl*- and *aryl*stannanes.

$$\underset{\mathbf{1}}{\mathrm{RSn}(n\text{-}\mathrm{C_4H_9})_3} \xrightarrow{\mathrm{Cu(NO_3)_2{\cdot}3H_2O}} \underset{\mathbf{2}}{\mathrm{R{-}R}} \qquad (1)$$

R = alkynyl, alkenyl, aryl

Results and Discussion

Coupling of Alkynylstannanes: Preparation of 1,3-Diynes. The addition of neat alkynylstannane **1a** (cf. Table I) to a solution of 1 equiv of Cu(NO$_3$)$_2$·3H$_2$O in tetrahydrofuran at 23 °C gave, after 10 min, the symmetrical diyne **2a** in 85% isolated yield (see eq 2). By con-

$$\underset{\mathbf{1a-c}}{\mathrm{RC{\equiv}CSnBu_3}} \xrightarrow{\mathrm{Cu(NO_3)_2{\cdot}3H_2O}} \underset{\mathbf{2a-c}}{\mathrm{RC{\equiv}CC{\equiv}CR}} \qquad (2)$$

trast, the Glaser-type coupling of the corresponding alkyne, 3-(tetrahydro-2*H*-pyran-2-yloxy)-1-propyne,[6] with either $CuCl/O_2$ or $Cu(OAc)_2$ in TMEDA at 40 °C for 5 h afforded, at best, a 34% yield of diyne **2a**. Surprisingly, alkynylstannane **1a** was inert toward $Cu(OAc)_2$, $CuCl_2$, $CuBr_2$, and $CuSO_4$ under similar conditions. However, dimerization using $AgNO_3$[7] gave results identical with those from the Cu(NO$_3$)$_2$-mediated coupling. Brief studies using Cu(NO$_3$)$_2$ and alkynylstannane **1a** showed that a variety of nonaqueous solvents (DME, DMF, dioxane, acetone, methanol) were suitable for the coupling reaction, but no reaction was

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Table I. Yields of Dimer 2 from the $Cu(NO_3)_2$-Mediated Coupling of Organotin Compounds 1[a]

entry	substr 1, R	product 2	reacn time, min	isol yield, %
a	$THPOCH_2C{\equiv}C$	$(THPOCH_2C{\equiv}C)_2$	10	85
b	n-$C_4H_9C{\equiv}C$	$(n$-$C_4H_9C{\equiv}C)_2$	10	60
c	$C_6H_5C{\equiv}C$	$(C_6H_5C{\equiv}C)_2$	30	50
d	2,3-dihydro-4H-pyran-6-yl	2,2′,3,3′-tetrahydro-6,6′-bi-4H-pyran	10	80
e	(E)-$C_6H_5CH_2OCH_2CH{=}CH$	$(C_6H_5CH_2OCH_2CH{=}CH)_2$	10	72[b]
f	(Z)-$C_6H_5CH_2OCH_2CH{=}CH$	$(C_6H_5CH_2OCH_2CH{=}CH)_2$	10	75[c]
g	3,4-$(MeO)_2C_6H_3C(=CH_2)$	$[3,4\text{-}(MeO)_2C_6H_3C(=CH_2)]_2$	25	71
h	4-MeC_6H_4	$(4\text{-}MeC_6H_4)_2$	10	67
i	4-$MeOC_6H_4$	$(4\text{-}MeOC_6H_4)_2$	10	66
j	2-$MeOC_6H_4$	$(2\text{-}MeOC_6H_4)_2$	120[d]	45
k	2,6-$(MeO)_2$-4-MeC_6H_2	$[2,6\text{-}(MeO)_2\text{-}4\text{-}MeC_6H_2]_2$	100	14

[a] All reactions were performed with 1 mmol of 1 and 1.0 mmol of $Cu(NO_3)_2{\cdot}3H_2O$ in tetrahydrofuran at 23 °C. [b] $E,E/E,Z$ ratio was 19:1. [c] $Z,Z/E,Z$ ratio was 23:1. [d] Reaction was approximately 80% complete.

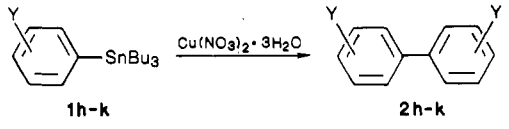
observed in 5% aqueous THF; the starting material was recovered unchanged. The reason that the additional water nullifies the dimerization process is not apparent since the copper nitrate used for the coupling reaction is the trihydrate.[8]

Coupling of Alkenylstannanes: Preparation of 1,3-Dienes. Especially interesting was the extension of the copper nitrate mediated method to alkenylstannanes **1d–g** (eq 3), to afford the symmetrical dienes **2d–g** in

$$\underset{\textbf{1d–g}}{R^1CH{=}C(R^2)SnBu_3} \xrightarrow{Cu(NO_3)_2{\cdot}3H_2O} \underset{\textbf{2d–g}}{R^1CH{=}C(R^2)C(R^2){=}CHR^1} \quad (3)$$

70–80% isolated yields. Additionally, for the (E)-vinylstannane **1e**, the dimerization proceeded largely with retention of the original alkene stereochemistry to give the (E,E)-diene **2e** as determined by ^1H and ^{13}C NMR. Careful scrutiny of the crude product by gas chromatography showed an $E,E/E,Z$ ratio of 19:1 with less than 5% contamination by the isomeric (Z,Z)-diene. Similarly high stereospecificity was observed for the dimerization of the (Z)-vinylstannane **1f**, where the $Z,Z/E,Z$ ratio was 23:1. Of particular note, the dimerization of vinylstannane **1g** afforded a 71% yield of 2,3-bis(3,4-dimethoxyphenyl)-1,3-butadiene (**2g**), a key intermediate in the synthesis of the alkaloid septicine.[9]

Coupling of Arylstannanes: Preparation of Biphenyls. The $Cu(NO_3)_2$-mediated procedure was found to be equally effective for the coupling of arylstannanes **1h–k** to give the corresponding substituted biphenyls in 14–67% yield (eq 4). For example, the addition of (2-



1h-k 2h-k (4)

methoxyphenyl)tributylstannane (**1j**) to $Cu(NO_3)_2$/THF afforded a 43% yield of 2,2′-dimethoxybiphenyl and a 40% yield of the destannylated product, anisole. Unfortunately, the formation of anisole could not be suppressed by variation of the substrate concentration or by changes in solvent and/or temperature. This suggested the yield of dimerized product is largely controlled by steric factors. Consistent with this view, the para-substituted arylstannanes **1h** and **1i** gave better yields of the biphenyls **2h** and **2i** (67% and 66% yields, respectively) than did the ortho-substituted stannane **1j**. Attempts to couple the more sterically encumbered stannane (2,6-dimethoxy-4-methylphenyl)tributylstannane afforded only a dismal 14% yield of biphenyl **2k**;[10] 3,5-dimethoxytoluene was the predominant product.

Attempts to couple benzylic tri-n-butylstannanes with $Cu(NO_3)_2$ in THF proved unsuccessful. For example, treatment of (phenylmethyl)tributylstannane[11] with $Cu(NO_3)_2{\cdot}3H_2O$ led to slow consumption of the organotin compound to afford numerous products but none of the expected 1,2-diphenylethane was detected chromatographically. Similar results were obtained when dimethylformamide or acetonitrile were used as the solvent.

Mechanistic Considerations. Some aspects of the possible mechanism deserve comment. On the basis of related transmetalation of organotin compounds by mercury(II) salts,[12] we anticipated that the first step of the reaction involves transmetalation of the unsaturated stannane to afford an organocopper(II) species and tributyltin nitrate as depicted in eq 5. Indeed, tributyltin

$$RSnBu_3 \xrightarrow{Cu(NO_3)_2} [RCu^+] \xrightarrow{?} R^{\bullet} \begin{matrix} \nearrow R{-}R \\ \searrow R{-}H \end{matrix} \quad (5)$$

$$+ \; Bu_3SnONO_2$$

nitrate[13,14] could be isolated in high yield for each of the cases shown in Table I. The fate of the presumed organocopper(II) species which leads to both dimerized and destannylated products presently remains uncertain and may involve decomposition to free radicals. To the tenuous extent that the stereospecific nature of the dimerization may infer mechanism, the stereospecificity observed for alkenylstannanes **1e** and **1f** does not support the notion that long-lived free radicals are intermediates in the reaction.[7a] We are currently probing these aspects of the reaction.

Summary

The method described herein offers a versatile and useful procedure for the preparation of symmetrically substituted diynes, dienes, and biphenyls. Also, the reaction is shown to be highly stereospecific for the coupling of (E)- or (Z)-vinylstannanes. The ease in preparing the different classes of organotin compounds employed in this

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(14) During the coupling of the hexynylstannane (**1b**), we noted the formation of a small amount of an isolable yellow precipitate whose melting point, IR, and ^1H NMR spectra were consistent with those of the known organocopper(I) reagent $C_4H_9C{\equiv}CCu$.

study, coupled with the simplicity of the method, contributes to the synthetic merit of this procedure for the dimerization of organometallic compounds. We are currently examining the possibility of a catalytic variation of this reaction.

Experimental Section

Infrared spectra were determined on a Perkin-Elmer 1420 spectrometer. The abbreviation TF denotes thin film. NMR spectra were determined on either a Perkin-Elmer FT R-600 or a Varian FT-80A spectrometer. GC analyses were performed on a Varian Aerograph 2400 with an SGE 50QC2/BP5 0.1 capillary column. Elemental analyses were performed by Atlantic Microlabs, Atlanta, GA.

The following organotin compounds were prepared according to the literature procedures: 1-hexyn-1-yltributylstannane (**1b**);[15] (2-phenylethynyl)tributylstannane (**1c**);[16] [(1*E*)-3-(benzyloxy)-1-propen-1-yl]tributylstannane (**1e**);[17] (4-methylphenyl)tributylstannane (**1h**);[18] (4-methoxyphenyl)tributylstannane (**1i**);[18] (2-methoxyphenyl)tributylstannane (**1j**).[19]

Preparation of 3-(Tetrahydro-2*H*-pyran-2-yloxy)-1-propyn-1-yltributylstannane (1a). To a solution of 1-lithio-3-(tetrahydro-2*H*-pyran-2-yloxy)-1-propyne[20] (30 mmol) in 50 mL of THF at −20 °C under a nitrogen atmosphere was added 8.95 mL (33 mmol) of tri-*n*-butyltin chloride. After being stirred for 30 min at −20 °C, the mixture was diluted with 500 mL of ether and washed successively with 100 mL of water, 2 × 100 mL of 5% aqueous ammonia, and 100 mL of brine and dried over anhydrous magnesium sulfate. Evaporation of solvent followed by distillation, in vacuo, afforded 11.7 g (91%) of **1a**: bp 130–135 °C (0.35 Torr); IR (TF) 2160, 1030 cm^{-1}, ^1H NMR ($CDCl_3$) δ 0.92–1.58 (m, 33 H), 3.70 (m, 2 H), 4.28 (s, 2 H), 4.85 (m, 1 H). Anal. Calcd for $C_{20}H_{38}O_2Sn$: C, 55.96; H, 8.92. Found: C, 55.98; H, 8.93.

Preparation of 2,3-Dihydro-4*H*-pyran-6-yltributylstannane (1d). The procedure described for the preparation of **1a** was repeated using lithiated dihydropyran[21] (30 mmol) to afford after distillation 10.3 g (92%) of **1d**: bp 105–110 °C (0.1 Torr); IR (TF) 1610, 1065 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.92–1.50 (m, 27 H), 1.94 (m, 4 H), 3.88 (t, J = 6 Hz, 2 H), 4.72 (t, J = 4 Hz, 1 H). Anal. Calcd for $C_{17}H_{34}OSn$: C, 54.72; H, 9.18. Found: C, 54.80; H, 9.17.

Preparation of [(*Z*)-3-(Benzyloxy)-1-propen-1-yl]tributylstannane (1f). The procedure of Czernecki et al.[22] was repeated using 1.74 g (5 mmol) of (*Z*)-*n*-$Bu_3SnCH{=}CHCH_2OH$[23] to afford after distillation 1.84 g (84%) of **1f**: bp 140–150 °C (0.1 Torr); IR (TF) 1600, 1500, 1460 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.92–1.58 (m, 27 H), 3.98 (d, J = 6 Hz, 2 H), 4.52 (s, 2 H), 6.5 (m, 2 H), 7.34 (s, 5 H). Anal. Calcd for $C_{22}H_{38}OSn$: C, 60.43; H, 8.76. Found: C, 60.51; H, 8.80.

Preparation of [1-(3,4-Dimethoxyphenyl)ethen-1-yl]tributylstannane (1g). The procedure of Matsubara et al.[24] was repeated using 810 mg (5 mmol) of 3,4-$(CH_3O)_2C_6H_3C{\equiv}CH$[25] to afford, after flash silica gel chromatography in 1:10 ethyl acetate–hexane, 1.62 g (40%) of **1g**: IR (TF) 1600, 1570, 1510, 1250, 860, 820 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.92–1.58 (m, 27 H), 3.78 (s, 3 H), 3.80 (s, 3 H), 5.39 (d, J = 3 Hz, 1 H), 6.06 (d, J = 3 Hz, 1 H), 6.82 (m, 3 H). Anal. Calcd for $C_{22}H_{38}O_2Sn$: C, 58.30; H, 8.45. Found: C, 58.22; H, 8.45.

General Procedure for the Copper Nitrate Coupling of Organotin Compounds 1. Preparation of 1,6-Bis(tetrahydro-2*H*-pyran-2-yloxy)-2,4-hexadiyne (2a). To a solution of 242 mg (1.0 mmol) of $Cu(NO_3)_2{\cdot}3H_2O$ in 1 mL of THF at 23 °C was added in one portion 429 mg (1 mmol) of stannane **1a**. After being stirred for 10 min at 23 °C, the mixture was diluted with 75 mL of ethyl acetate, washed successively with 50 mL of 5% aqueous ammonia, 50 mL of water, and 50 mL of brine, and dried over anhydrous magnesium sulfate. Evaporation followed by chromatography on a 2.5 × 20 cm silica gel column in 1:20 ethyl acetate–hexane afforded 118 mg (85%) of **2a**: IR (TF) 2260, 1200 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.60 (br s, 12 H), 3.67 (m, 2 H), 4.29 (s, 4 H), 4.75 (m, 2 H). Anal. Calcd for $C_{16}H_{22}O_4$: C, 69.04; H, 7.97. Found: C, 69.10; H, 7.99.

Summary of Spectral Data for Coupled Products 2. The following compounds gave physical properties and spectra data consistent with those reported previously: **2b**,[26] **2c**,[26] **2d**,[27] **2g**,[9] **2h**,[28] **2i**,[28] **2j**,[28] **2k**.[10]

2e: IR (TF) 1600, 1500, 1100 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.11 (d, J = 7 Hz, 4 H), 4.56 (s, 4 H), 5.54–6.34 (m, 4 H), 7.38 (m, 10 H). Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. Found: C, 81.70; H, 7.56. Capillary GC analysis of this material on a SGE 50QC2/BP5 0.1 column at 240 °C showed two diene components, **2e** and the corresponding *E,Z* isomer in a ratio 19:1 which had retention times of 14.53 and 13.04 min, respectively. Compound **2e** had spectral characteristics and a capillary GC chromatographic retention time identical with that of an authentic sample synthesized independently by the benzylation (2 equiv of NaH, 6 equiv of $PhCH_2Br$, THF, 23 °C) of the known (*E,E*)-2,4-hexadiene-1,6-diol.[29]

2f: IR (TF) 1600, 1500, 1100 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.24 (d, J = 7 Hz, 4 H), 4.56 (s, 4 H), 5.54–6.34 (m, 4 H), 7.38 (m, 10 H). Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. Found: C, 81.71; H, 7.56. Capillary GC analysis of this material on a SGE 50QC2/BP5 0.1 column at 240 °C showed two diene components, **2f** and the corresponding *E,Z* isomer in a ratio 23:1, which had retention times of 12.33 and 13.04 min, respectively.

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Registry No. **1a**, 109669-44-5; **1b**, 35864-20-1; **1c**, 3757-88-8; **1d**, 109669-45-6; (*E*)-**1e**, 84666-31-9; (*Z*)-**1f**, 109669-46-7; **1g**, 109669-47-8; **1h**, 31614-66-1; **1i**, 70744-47-7; **1j**, 86487-17-4; **1k**, 109669-48-9; **2a**, 105448-76-8; **2b**, 1120-29-2; **2c**, 886-66-8; **2d**, 109669-49-0; (*E,E*)-**2e**, 109669-50-3; (*E,Z*)-**2e**, 109669-52-5; (*Z,Z*)-**2f**, 109669-51-4; **2g**, 73786-25-1; **2h**, 613-33-2; **2i**, 2132-80-1; **2j**, 4877-93-4; **2k**, 27921-29-5; $THPOCH_2C{\equiv}CLi$, 37566-51-1; $SnBu_3Cl$, 1461-22-9; (*Z*)-$Bu_3SnCH{=}CHCH_2OH$, 74141-13-2; lithiated dihydropyran, 72081-15-3; 3,4-$(MeO)_2C_6H_3C{\equiv}CH$, 4302-52-7.

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