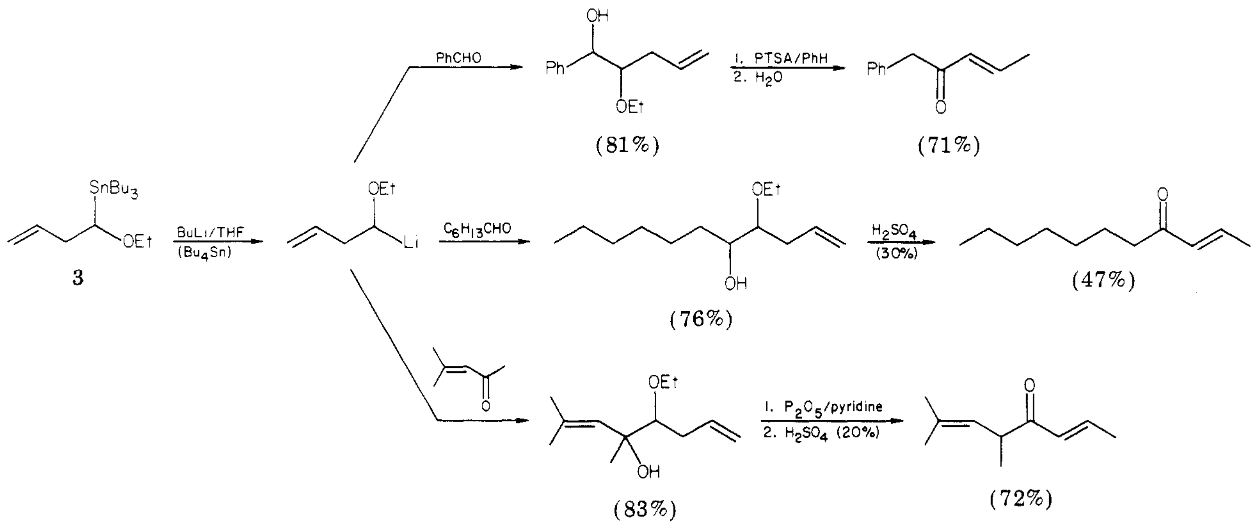
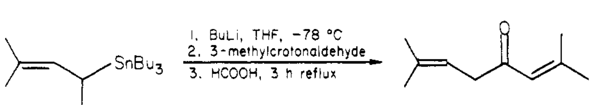
Scheme I[13]

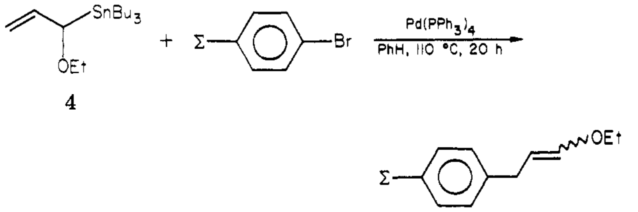


crotonaldehyde via transmetalation with undetectable rearrangement:



65% (isolated)

However direct reactions typical of allyltin compounds may be of much more interest. **4** reacts with aryl bromides in the presence of a palladium catalyst[18] to form the substitution product accompanied by complete allylic shift.

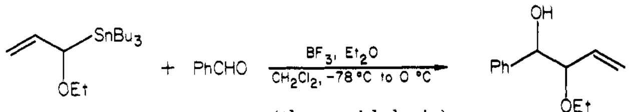


4

Σ = H (91%, Z/E = 5:95)
Cl (88%, Z/E = 35:65)
F (89%, Z/E = 40:60)

This reaction provides a way for bonding a three-carbon aldehyde (d_3 propionaldehyde synthon[2]) to an aromatic ring.

Another typical reaction is the boron trifluoride catalyzed addition to aldehydes,[19–21] which occurs, probably, with a double allylic shift in the case of **4** (one at the reagent level and the second in the addition reaction):



4

(then acidolysis)

70%
(93% SS + RR)

Such highly functionalized products may be used for various further transformations, especially for the synthesis of carbonyl derivatives.

This set of preliminary results shows the high potential of (ethoxyalkenyl)tributyltins in organic synthesis. Current work is concerned with extending the number of new organotin precursors as well as examining their synthetic applications.

Acknowledgment. Generous gifts of organotin starting materials from Schering-France are warmly acknowledged.

Supplementary Material Available: Preparative procedures and full NMR data for compounds **1–7** (3 pages). Ordering information is given on any current masthead page.

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Received August 6, 1982

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[22] Isomers **4**, **5**, and **6** have been identified by using their ^{1}H NMR spectra (see supplementary material), and the isomerization process has been most easily followed and quantified by ^{119}Sn NMR spectra (**4**, δ = −34.8; **5**, δ = −16.4; **6**, δ = −19.6).

Palladium-Catalyzed Cross-Coupling Reaction of α-Heterosubstituted Alkenylmetals. A Stereoselective Route to Heterosubstituted Dienes Suitable for the Diels–Alder Reaction[1]

Summary: Alkenylmetals of Zn or Al containing α-alkoxy, α-alkylthio, or α-trialkylsilyl substituents react readily with aryl or alkenyl halides in the presence of a Pd catalyst to produce arylated alkenes or conjugated dienes, respectively, the stereospecificity of the reactions for the synthesis of **1**, **3**, **4**, and **5** being ≥98%.

Sir: Despite the recent development of a plethora of proximally heterosubstituted organometals containing alkali metals and magnesium as novel reagents,[2] their inability to react readily with alkenyl, aryl, or alkynyl halides and other related electrophiles has severely limited their

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[1] Selective Carbon–Carbon Bond Formation via Transition-Metal Catalysis. 33. Part 32: Negishi, E.; Luo, F. T.; Pecora, A. J.; Silveira, A., *J. Org. Chem.*, in press.

[2] For reviews see: (a) Negishi, E. "Organometallics in Organic Synthesis"; Wiley-Interscience: New York, 1980; Vol. I, Chapter 4. (b) Gröbel, B. T.; Seebach, D. *Synthesis* **1977**, 357.

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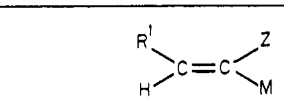
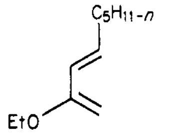
Table I. Palladium-Catalyzed Reaction of α-Heterosubstituted Alkenylmetals with Organic Halides[a]



R^1	Z	M	R^{2}X		reaction time, h	product[b]	yield, %	
			R^2	X			isolated	GLC
H	OEt	ZnCl	(*E*)-1-heptenyl	I	1	1	74	80
H	SEt	ZnCl	vinyl	Br	3	2	69	76
H	SEt	ZnCl	(*E*)-1-heptenyl	I	3	3	81	93
n-hexyl	$SiMe_3$	AlR_2[c]	vinyl	Br	3	4	74	77
n-hexyl	$SiMe_3$	BR_3Li[d]	vinyl	Br	3	4		61
n-hexyl	$SiMe_3$	AlR_2[c]	(*E*)-1-heptenyl	I	3	5	68	73
n-hexyl	$SiMe_3$	BR_3Li[d]	(*E*)-1-heptenyl	I	3	5		43
H	OEt	ZnCl	C_6H_5	I	1	6	80	91
H	OEt	ZnCl	*p*-ClC_6H_4	I	1	7	65	91
H	SEt	ZnCl	C_6H_5	I	3	8	70	80

[a] The Pd-catalyzed cross-coupling reaction was carried out in THF at room temperature (ca. 22 °C). [b] All products have been identified by IR, ^{1}H NMR, and mass spectrometry. All stereodefined products were further identified by ^{13}C NMR. All stereodefined products are isomerically $\geq$98% pure. [c] AlR_2 = $Al(Bu\text{-}i)_2$. The reaction of alkenylalanes was carried out in the presence of 1 equiv of dry $ZnCl_2$. [d] BR_3Li = $B(C_6H_{11})_2(Bu\text{-}n)Li$. The reaction was carried out in the presence of 1 equiv of dry $ZnCl_2$.

usefulness. While the Pd- or Ni-catalyzed cross-coupling[3] could help solve this problem, its application in the past has largely been limited to cases where α- or β-heterosubstituted reagents are heteroaromatic.[4] In fact, many attempts by us to promote cross-coupling of alkylmetals containing donor-type α-hetero substituents with unsaturated organic halides using Pd and Ni catalysts have been uniformly unsuccessful, with the organic halides remaining largely unreacted. Such organometallic reagents include those obtained by converting Me_2S, MeSPh, Me_2SO, Me_2SO_2, $MeSO_2Ph$, dithiane, α-(phenylthio)tetrahydropyran,[5] and $MeNO_2$ into α-metalated derivatives of Li, Na, and Mg as well as the corresponding Zn derivatives. We were therefore pleased to find that alkenylmetals containing α-alkoxy,[6] α-alkylthio, or α-trialkylsilyl substituents react readily and stereospecifically with aryl or alkenyl halides in the presence of a Pd catalyst, e.g., $Pd(PPh_3)_4$, to produce the corresponding arylated alkenes or conjugated dienes, respectively. The experimental results are summarized in Table I, and the structures of the products are shown in 1–8. Although the number of examples provided in this work is still small, the method described here promises to provide a convenient and selective entry into stereodefined and heterofunctional conjugated dienes that are potentially attractive as reagents for selective synthesis of cyclohexenes via the Diels–Alder reaction.[7]



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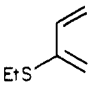

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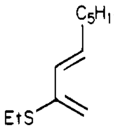

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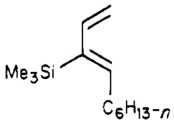

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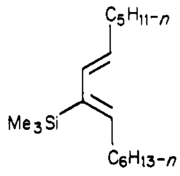

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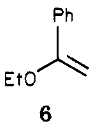

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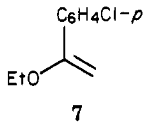

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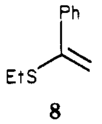

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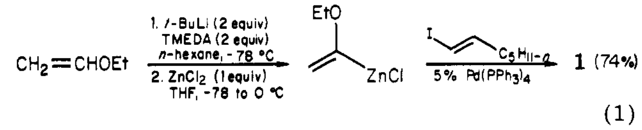
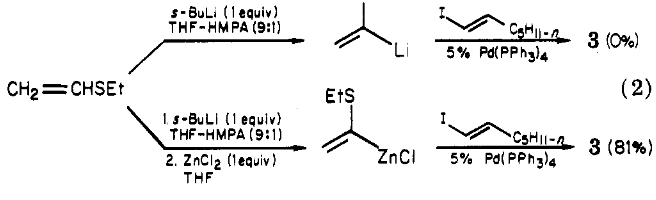
The following observations are worth noting. First, no cross-coupling occurs in the absence of the Pd catalyst, i.e., $Pd(PPh_3)_4$, indicating that the reaction is indeed catalyzed by the Pd complex. Second, all four stereodefined dienes, i.e., 1, 3, 4, and 5, were obtained as isomerically ≥98% pure species, as judged by ^{1}H and ^{13}C NMR spectroscopy as well as by GLC. In no case were any special attempts such as chromatography to separate isomers required. In light of our previous observation that nickel–phosphine catalysts tend to induce stereoisomerization of dienes,[8] they were not used in this study. However, nickel–phosphine complexes may still be satisfactory in cases where no such difficulty arises. Third, the EtO- or EtS-containing products were prepared by the Pd-catalyzed reaction of the corresponding alkenylzinc reagents (eq 1 and 2), which in turn were obtained by treating α-ethoxyvinyllithium[9] or α-(ethylthio)vinyllithium[10] with 1 equiv of dry $ZnCl_2$. When the alkenyllithiums themselves were used under otherwise comparable conditions, little or no desired products were obtained (e.g., eq 2), again pointing to a major advantage of using Zn derivatives in the Pd- or Ni-catalyzed cross-coupling.[3] A Pd-catalyzed reaction α-(phenylthio)alkenyl phosphate (9) with organoalanes containing alkyl, alkenyl, and alkynyl groups reported recently[11] represents a charge-affinity inverted version of



(1)



(2)

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(3) For a review, see: Negishi, E. *Acc. Chem. Res.* **1982**, *15*, 340.

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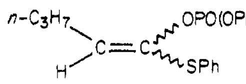

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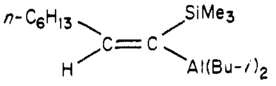

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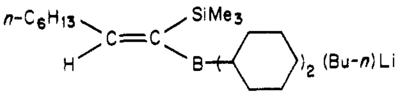

11

the α-(thioalkenyl) metal reaction such as that shown in eq 2. However, the reported reaction as such does not provide a stereoselective route to alkenyl sulfides. Fourth, the dienes 4 and 5 were prepared by the Pd-catalyzed reaction of 10, that was obtained by hydroalumination of 1-octynylsilane with i-Bu$_2$AlH in ether[12] for 2 h under reflux, with vinyl bromide and (E)-1-iodo-1-heptene, respectively, in the presence of 1 equiv of dry $ZnCl_2$.[13] In its absence, no desired product was produced. These dienes were also obtained by the corresponding reactions of the alkenylborate 11. Interestingly, unlike a recently reported related organoborane reaction requiring the temperature of refluxing benzene,[14] the above reactions were complete within 1–3 h at 22 °C. The major difference in rate between the two related reactions could be due to (a) different bases used in these two related reactions, i.e., n-BuLi in one and alkali metal alkoxides, or hydroxides, in the other,[14] (b) the presence of α-Me_3Si group in one and its absence in the other, and/or (c) the presence of $ZnCl_2$ in one and its absence in the other. The yield of 4 obtained by the Pd-catalyzed reaction of 11 with vinyl bromide increased from 37% to 61% by the addition of 1 equiv of $ZnCl_2$. The fact that this reaction did proceed, albeit unsatisfactorily, at room temperature in the absence of $ZnCl_2$ suggests that this factor alone cannot account for the major difference mentioned above. It should also be noted that the product yields realized in the organoalane reactions are considerably higher than the corresponding organoborate reactions. A few minor unidentified byproducts having GLC retention times similar to those of 4 or 5 were formed in the reaction of 11, while no more than traces ($\leq$1%) of such byproducts were detectable in the organoalane reactions.

The following procedure for preparing (6E,8Z)-8-(trimethylsilyl)-6,8-pentadecadiene is representative. To 1-(trimethylsilyl)-1-octyne (1.82 g, 10 mmol) in 20 mL of ether was added, under nitrogen atmosphere, diisobutylaluminum hydride (1.82 mL, 10 mmol). The reaction mixture was refluxed for 2 h. To this was added a mixture of (E)-1-iodo-1-heptene[15] (2.24 g, 10 mmol), $Pd(PPh_3)_4$[16] (0.57 g, 0.5 mmol), and $ZnCl_2$ (1.36 g, 10 mmol), freshly dried at 50 °C and $\leq$ 1 mm, in 20 mL of THF. The resultant mixture was stirred for 3 h at room temperature, quenched with 3 N HCl (30 mL), and extracted with pentane. The organic extracts were washed with brine, dried over $MgSO_4$, and distilled to give 1.90 g (68%) of 5: bp 92–95 °C (0.05 mm); n^{24}_{D} 1.4650; IR (neat) 1595 (m), 1250 (s), 960 (s), 840 (s), 755 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.15 (s, 9 H), 0.88 (t, J = 7 Hz, 6 H), 1.1–1.7 (m, 14 H), 1.8–2.4 (m, 4 H), 5.47 (dt, J = 15, 7 Hz, 1 H), 6.01 (d, J = 15 Hz, 1 H), 6.11 (t, J = 7 Hz, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 0.34, 13.79, 22.36, 22.44, 28.94, 29.24, 29.97, 31.26, 31.70, 32.82, 128.55, 135.00, 138.26, 143.06. High-resolution MS calcd for $C_{18}H_{36}Si$: 280.2586. Found: 280.2600.

Acknowledgment is made to the National Science Foundation and the National Institutes of Health for support of this work. We thank Vahid Bagheri of our laboratories for sharing the preparation of 7. We also thank Professor L. S. Hegedus of Colorado State University for informing us of their unpublished results and Professor R. K. Boeckman, Jr., of University of Rochester for helpful discussions.

Registry No. 1, 85318-56-5; 2, 7326-63-8; 3, 85318-57-6; 4, 85318-58-7; 5, 85318-59-8; 6, 6230-62-2; 7, 6230-80-4; 8, 22914-07-4; 11, 60366-85-0; $CH_2{=}CHOEt$, 109-92-2; $CH_2{=}CHSEt$, 627-50-9; $Pd(PPh_3)_4$, 14221-01-3; $ZnCl_2$, 7646-85-7; C_6H_5I, 591-50-4; p-ClC_6H_4I, 637-87-6; vinyl bromide, 593-60-2; 1-(trimethylsilyl)-1-octyne, 15719-55-8; (E)-1-iodo-1-heptene, 60595-37-1.

Supplementary Material Available: ^{1}H and ^{13}C NMR and IR spectral data as well as boiling points and n_D data for compounds 1–8 and the experimental procedures for preparing 3 (Zn) and 4 (B) (2 pages). Ordering information is given on any current masthead page.

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Facile and Regioselective Epoxidations of Olefins with a Peroxysulfur Intermediate Generated from Superoxide Anion ($O_2^-\bullet$) and Nitrobenzenesulfonyl Chlorides

Summary: A peroxysulfur intermediate generated from the reaction of o- or p-nitrobenzenesulfonyl chloride with superoxide anion ($O_2^-\cdot$) is found to be an excellent oxidizing reagent for the facile and regioselective epoxidation of olefins at −35 °C.

Sir: Recently intensive research interests[1] in physical properties and chemical reactivities of superoxide ion have stimulated the development of organic synthesis using superoxide anion. Only a few works on the oxidation of sulfur compounds such as thiols,[2] thiouracils,[3] disulfides,[4] and sulfur halides[5] have been reported. Earlier, peroxysulfonate intermediate was postulated by Berger[6] to be the key in alkaline autoxidation of thiols to the sulfonate.

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[9] When the reactions of superoxide anion with **1a**, **1b**, and **1c** were stopped after 45 min, starting materials of **1a** (41%), **1b**(46%), and **1c** (71%), respectively, were recovered: this results suggest that the formation rate **2a** and **2b** is not so different but the **2a** is more stable than **2b** because the epoxidation using **2a** afforded better yield of epoxide (**8**′, X = H, 84% 1.5 h) than that using **2b** (**8**′, = H, 75%, 3.0 h).

[10] ^{1}H NMR (60 MHz, $CDCl_3$) δ 2.97 (1 H, epoxide), 1.3 (3 H, Me, epoxide), 1.92 (3 H), 1.10–1.60 (4 H), 1.60 (3 H, Me, =C—), 4.75 (2 H, =C—).

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