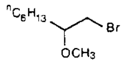
Thus, we have found a new method of allylation of cyclic β-bromo ethers with allylsilanes. However, the following acyclic and bicyclic bromo ethers **5**, **6**, and **7** failed to react in the same manner with allylsilane in the presence of $AgBF_4$ and instead gave many products. Assistance by an ether-oxygen lone pair is thought to be required in order to achieve specific allylation in a flexible furan or pyran ring system as shown in IV. Despite these limitations on substrates, it is noteworthy that the special utilization of allylsilanes in the presence of silver ion will allow a new type of allylation of β-bromo ethers in a cationic process.



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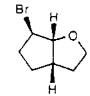

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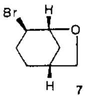
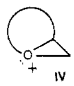


7



IV

Acknowledgment. We are indebted to the Ministry of Education, Science, and Culture for the Grant-in-Aid for Developmental Scientific Research (No. 57850273) and to Gen-ichi Uematsu for experimental assistance.

Registry No. **1a**, 85267-97-6; **1b**, 85267-98-7; **1c**, 85267-99-8; **1d**, 85268-00-4; **1e**, 85268-01-5; **1f**, 85268-02-6; **1g**, 85268-03-7; **1h**, 85268-04-8; **2a**, 85268-05-9; **2b**, 85268-06-0; **2c**, 85268-07-1; **2d**, 85268-08-2; **2e**, 85268-09-3; **3a**, 85268-10-6; **3b**, 85268-11-7; **3c**, 85268-12-8; **3d**, 85268-13-9; **3e**, 85268-14-0; **3f**, 85268-15-1; **3g**, 85268-16-2; **3h**, 85268-17-3; **3i**, 85268-18-4; **3j**, 85268-19-5; $(CH_3)_3SiCH_2CH{=}CH_2$, 762-72-1; $(CH_3)_3SiCH_2CH{=}CHCH_3$, 18292-28-9; $AgBF_4$, 14104-20-2.

Supplementary Material Available: Details of the preparation and spectral data on compounds **1**, **2**, and **3** (11 pages). Ordering information is given on any current masthead page.

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Received December 23, 1982

(α-Ethoxyalkenyl)tins: New Reagents for the Synthesis of Carbonyl Compounds

Summary: (α-Ethoxybutenyl)tributyltin and (α-ethoxyallyl)tributyltins, obtained from the appropriate Grignard reagents and (chloroethoxymethyl)tributyltin, have been used for the synthesis of carbonyl compounds via enol ethers or monoprotected 1,2-diols.

Sir: As a consequence of the central role played by carbonyl groups in organic synthesis, new routes to carbonyl compounds starting from α-heterosubstituted organometallics have been developed in recent years.[1–3] We have contributed to this field by the synthesis and the use of [bis(ethoxy)methyl]tributyltin (**1**) whose transmetalation with butyllithium leads to a masked aldehyde group.[4]

1 reacts with acetyl chloride, at room temperature, to give (chloroethoxymethyl)tributyltin (**2**), a highly functionalized reagent that can react further, for instance with cyclohexene or benzaldehyde, leading respectively to ethoxynorcaranes[4] or benzyl ethyl ether.[5] It also reacts readily with Grignard reagents, giving various ethoxymethyl-substituted organotins:

$$\underset{\mathbf{1}}{Bu_3SnCH(OEt)_2} \xrightarrow[20\ ^\circ C]{CH_3COCl} \underset{\mathbf{2}}{Bu_3SnCH(Cl)OEt} \xrightarrow{RMgX} Bu_3SnCH(R)OEt$$

This communication is concerned with the formation of the related butenyl and allyl organotin compounds[6] (see paragraph at the end of paper about supplementary material) and their use in the synthesis of several types of carbonyl compounds.

(α-Ethoxybutenyl)tributyltin (3): Reagent **3** is obtained from **1** via **2** by the addition of allylmagnesium bromide (1 h, 0 °C in ether) in over 80% yield. It can be purified by fast liquid chromatography on silica gel. Upon transmetalation with butyllithium (−78 °C, 5 min in THF[9]), **3** gives, in 95% yield, a new unsaturated lithium reagent that, by reaction with a variety of aldehydes or ketones (−78 °C, 15 min in THF), is converted into β-ethoxy alcohols. Acid hydrolysis of the latter leads to α-enones[11,12] as described in Scheme I.

Several other β-ethoxy alcohols, which might be considered as monoprotected diols,[14] have been similarly obtained from aliphatic and aromatic ketones, aliphatic and aromatic aldehydes, and α,β-unsaturated aldehydes and ketones.

(α-Ethoxyallyl)tributyltin (4): Reagent **4** is obtained in 72% yield (evaluated from **1**) by adding vinylmagnesium bromide to **2** in THF (1 h, −30 °C). Some vinyltributyltin is also formed due to the relative instability of the starting chloride **2**, which partly decomposes to tributyltin chloride. Compound **4**, on standing for a few days or on gentle warming or on attempted purification by liquid chromatography, gives the corresponding rearranged organotin vinylic ethers **5** (*Z* isomer, 88%) and **6** (*E* isomer, 12%).[22] By contrast (α-ethoxy-γ,γ-dimethylallyl)tributyltin (**7**), a potential reagent for the synthesis of terpene derivatives, was obtained in 69% yield and does not isomerize under similar conditions ($\delta(^{119}Sn)$ for **7** = −34.2).

Allyltin derivatives like **3** are less useful in transmetalation reactions because the lithium reagents can also be obtained directly from allyl ethers; furthermore their reactions with carbonyl derivatives lead generally to regioisomers[15–17] except **7**, which reacts with 3-methyl-

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(1) D. J. Peterson, *Organomet. Chem. Rev., Sect. A*, **7**, 295 (1972).

(2) D. Seebach, *Angew. Chem., Int. Ed. Engl.*, **18**, 239 (1979).

(3) A. Krief, *Tetrahedron*, **36**, 2531 (1980).

(4) J. P. Quintard, B. Elissondo, and M. Pereyre, *J. Organomet. Chem.*, **212**, C31, (1981).

(5) (a) J. P. Quintard, B. Elissondo, and D. Mouko Mpegna, *J. Organomet. Chem.*, in press (ref JOM 04100). (b) D. Mouko Mpegna, Ph.D Thesis, Bordeaux, 1981.

(6) It must be noticed that RMgX also reacts with **2** when R is alkyl, aryl, alkynyl, or tributylstannyl, giving in the last case bis(tributylstannyl)ethoxymethane ($\delta(^{119}Sn) = -18.8$; $^2J(^{117}Sn-^{119}Sn) = 116$ Hz). The synthesis of similar compounds with R = alkyl or aryl maybe achieved using stannylanionoids with α-chloroalkyl ethers or aldehydes[7–9] but until now these methods have given unsatisfactory results with unsaturated aldehydes.[10]

(7) J. P. Quintard and M. Pereyre, *Rev. Silicon, Germanium, Tin Lead Compd.*, **4**, 151 (1980).

(8) (a) J. C. Lahournère and J. Valade, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **270**, 2080 (1970). (b) J. C. Lahournère, Ph.D Thesis, Bordeaux, 1973.

(9) (a) W. C. Still, *J. Am. Chem. Soc.*, **100**, 1481 (1978). (b) W. C. Still and C. Sreekumar, *ibid.*, **102**, 1201 (1980).

(10) J. P. Quintard, unpublished results.

(11) H. Normant and C. Crisan, *Bull. Soc. Chim. Fr.*, 459 (1959).

(12) (a) D. Bardan, *Bull. Soc. Chim. Fr.*, **49**, 1875 (1931). (b) D. Bardan, *ibid.*, **1**, 370 (1934).

(13) Yields are reported for isolated products. In the last example (mesityl oxide) the intermediate vinyl ether is isolated in 86% yield before transformation into the α-enone.

(14) P. G. M. Wuts and S. S. Bigelow, *J. Org. Chem.*, **47**, 2498 (1982).

(15) D. A. Evans, G. C. Andrews, and B. Buckwalter, *J. Am. Chem. Soc.*, **96**, 5560 (1974).

(16) W. C. Still and T. L. MacDonald, *J. Am. Chem. Soc.*, **96**, 5561 (1974).

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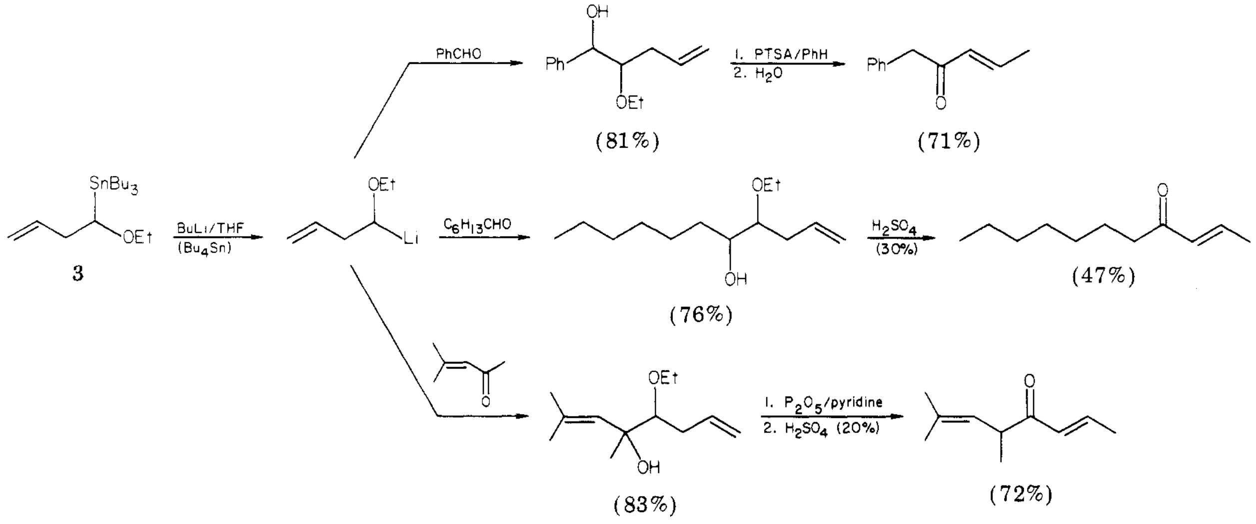
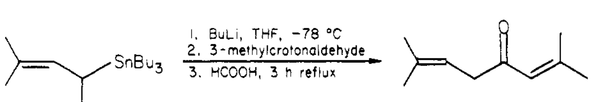
Scheme I[13]

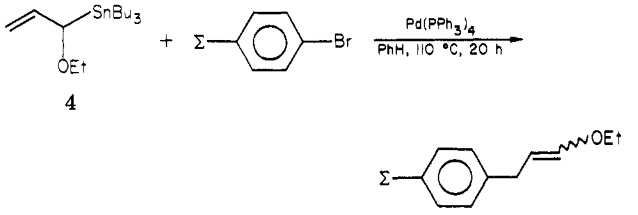


crotonaldehyde via transmetalation with undetectable rearrangement:



65% (isolated)

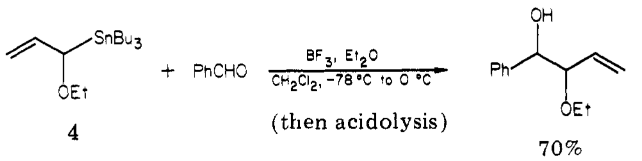
However direct reactions typical of allyltin compounds may be of much more interest. **4** reacts with aryl bromides in the presence of a palladium catalyst[18] to form the substitution product accompanied by complete allylic shift.



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):



(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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[17] Y. Yamamoto, H. Yatagai, and K. Maruyama, *J. Org. Chem.*, **45**, 195 (1980).

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[19] Y. Naruta, S. Ushida, and K. Maruyama, *Chem. Lett.*, 919 (1979).

[20] H. Yatagai, Y. Yamamoto, and K. Maruyama, *J. Am. Chem. Soc.*, **102**, 4548 (1980).

[21] Y. Yamamoto, H. Yatagai, Y. Naruta, and K. Maruyama, *J. Am. Chem. Soc.*, **102**, 7107 (1980).

[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**, $\delta = -34.8$; **5**, $\delta = -16.4$; **6**, $\delta = -19.6$).

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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