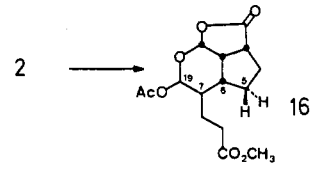
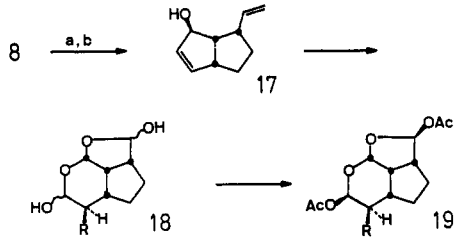
regioselective manner to produce **13**.[15] Hydrolysis of the acetals followed by acetylation afforded a major diacetate, which was not identical by ^1H and ^{13}C NMR with that derived from the natural product.[16]

In light of our unambiguous synthesis of **2**, it appeared that the original structure assignment for this derivative of udoteatrial, and hence the natural product, was incorrect. The assignment of the hydrocarbon skeleton's stereochemistry was based on analysis of the γ-lactone **16**



(derived from **2** by ozonolysis, Jones oxidation, and methylation). The assignment of stereochemistry of C-7 was based on the observation of a nuclear Overhauser enhancement[17] of H-5 endo (δ 1.41) upon irradiation of the acetate signal at δ 2.12. However, such an NOE is unlikely with a conformationally mobile substituent such as an acetate group, and the observed enhancement was more likely the result of simultaneous irradiation of H-5 exo at δ 2.16. Indeed, the 9-Hz coupling observed in **16** between protons H-7 and H-6 is in better agreement with a revised structure in which these hydrogens have a trans relationship, with the side chain at C-7 exo.

Synthesis of the C-7 epimer **18** required introduction of the side chain from the exo face. This was accomplished by inversion of the alcohol **8** using diethylazodicarboxylate,



(a) Ph_3P (2 equiv), THF, DEAD (2 equiv), 25 °C, 1 h. (b) (i) $LiAlH_4$ (8 equiv), Et_2O, 0 °C, 1 h, (ii) minimal saturated aqueous NH_4Cl (35% from **8**).

triphenylphosphine, and benzoic acid,[18] followed by LAH reduction, cleanly affording the exo alcohol **17**.

The sequence of reactions described above was now repeated on the isomeric alcohol **17**, affording ultimately the diacetate **19**, identical by proton and carbon NMR with that derived from udoteatrial. These completely stereoselective syntheses demonstrate once again the utility of bicyclo[3.3.0]octanes in terpene synthesis.

Acknowledgment is gratefully made to the National Institutes of Health (No. GM-29195) for financial support of this research.

(15) Okukado, N.; Negishi, E. I. *Tetrahedron Lett.* **1978**, 2357-2360.
(16) We are grateful to Professer Faulkner for providing copies of the proton NMR spectra of the diacetates of udoteatrial and the triacetate of the LAH reduction product.
(17) Hall, L. D.; Saunders, J. K. M. *J. Am. Chem. Soc.* **1980**, *102*, 5703-5711.
(18) (a) Grynkiewicz, G.; Burzynska, H. *Tetrahedron* **1976**, *32*, 2109-2111. (b) Mitsunobu, O. *Synthesis* **1981**, 1-28.

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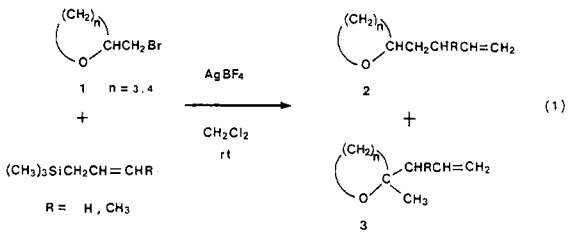
Silver-Induced Allylation of β-Bromo Ethers with Allylsilanes

Summary: Cyclic β-bromo ethers can be allylated with allyltrimethylsilanes in the presence of silver tetrafluoroborate via the corresponding carbocations. Direct substitution of the bromine atom in the cyclic ethers by an allyl group was observed, but in the case of tetrahydropyranyl derivatives the allylation occurred exclusively via the carboxonium ions which were generated by debromination and subsequent hydrogen shift.

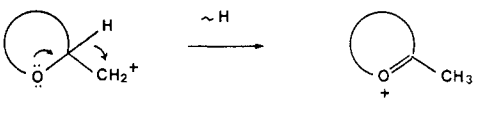
Sir: Effective alkylation of β-halo ethers has not been generally achieved yet, since substitution of the halogen atom with nucleophilic reagents is inherently in difficulty due to competition in facile undesirable elimination. Keck and Yates recently succeeded in allylation of several organic halides, including β-bromo ethers by the use of allyltrialkylstannanes in a free radical process.[1] During the course of our studies on the synthetic utility of allylsilanes,[2] we have attempted the regiospecific allylation of β-bromo ethers with allylsilanes in a cationic process. We describe here a new allylation reaction of β-bromo ethers, including cyclic ethers, with allylsilanes in the presence of silver tetrafluoroborate.

To a solution of **1**[3] and allylsilane (2.5 equiv/equiv of **1**) in anhydrous dichloromethane (5 mL/mmol of **1**) was added well-dried silver tetrafluoroborate (2.0 equiv/equiv of **1**)[4] under an argon atmosphere (eq 1). The mixture was



stirred at ambient temperature in the dark, and the reaction was monitored by TLC. The reaction mixture was diluted with ether (ca. 20 mL), filtered, and treated with aqueous sodium bicarbonate. The extract was concentrated, and the residual oil was purified by silica gel column chromatography to give a mixture of the corresponding isomeric ethers **2** and **3** in good yield (Table I).

2-(Bromomethyl)tetrahydrofurans **1a** and **1b** gave predominantly the ethers **2a**, **2b**, **2c**, and **2d**, respectively, by way of electrophilic attack of the silver-induced primary carbonium ions I on the allylsilanes. On the other hand,



(1) Keck, G. E.; Yates, J. B. *J. Am. Chem. Soc.* **1982**, *104*, 5829.
(2) (a) Nishiyama, H.; Itagaki, K.; Sakuta, K.; Itoh, K. *Tetrahedron Lett.* **1981**, 5285. (b) Nishiyama, H.; Narimatsu, S.; Itoh, K. *Ibid.* **1981**, 5289. (c) Nishiyama, H.; Yokoyama, H.; Narimatsu, S.; Itoh, K. *Ibid.* **1982**, 1267. (d) Nishiyama, H.; Narimatsu, S.; Sakuta, K.; Itoh, K. *J. Chem. Soc., Chem. Commun.* **1982**, 459. (e) Nishiyama, H.; Itoh, K. *J. Org. Chem.* **1982**, *47*, 2496.
(3) Starting cyclic β-bromo ethers **1** were prepared by treatment of the corresponding ω-hydroxyolefins with *N*-bromosuccinimide in CH_2Cl_2; see supplementary material for preparation and structural characterization.
(4) A 0.25 molar equiv of $AgBF_4$ did not cause a reaction even after 6 days. Equimolar amount of $AgBF_4$ gave ca. 50% conversion of **1a** for 1 day.

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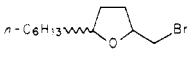
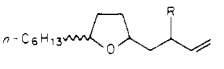
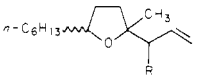
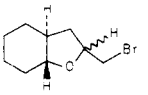
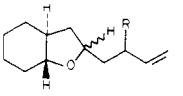
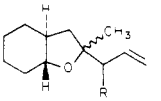
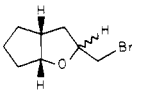
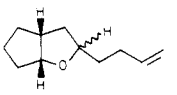
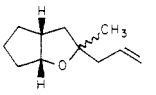
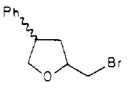
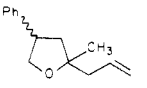
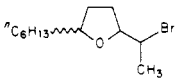
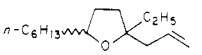
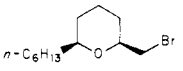
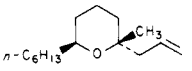
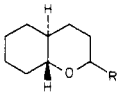
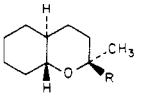
Table I. Reaction of Cyclic β-Bromo Ethers with Allylsilanes in the Presence of Silver Tetrafluoroborate[a]

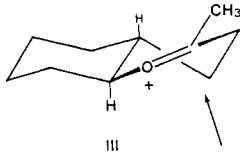
substrate,[b] 1	allyl-silane[c]	time, h	products 2	products 3	yield,[d] ratio[e] (%), [2:3]
					
1a	A	21	R = H 2a	3a	(66) [62:38]
	B	44	R = CH_3 2b	3b	(76) [79:21]
					
1b	A	22	R = H 2c	3c	(82) [84:16]
	B	45	R = CH_3 2d	3d	(78) [74:26]
					
1c	A	19	2e	3e	(54) [8:92]
					
1d	A	24		3f	(71) [0:100]
					
1e	A	48		3g	(15) [0:100]
					
1f	A	42		3h	(88) [0:100]
					
R =  1g	A	90		R = $CH_2CH{=}CH_2$ 3i	(73) [0:100]
	B	70		R = $CH(CH_3)CH{=}CH_2$ 3j	(97) [0:100]
R =  1h	A	44		3i	(41) [0:100]

[a] 1 (ca. 0.5–1.2-mmol scale), allylsilane (2.5 equiv), $AgBF_4$ (2.0 equiv), CH_2Cl_2 (ca. 2.5–5 mL), room temperature, unless otherwise noted; for 1b, B (5.0 equiv), $AgBF_4$ (4.0 equiv); for 1g, B (3.0 equiv), $AgBF_4$ (2.6 equiv). [b] See ref 3. [c] (A) $(CH_3)_3SiCH_2CH{=}CH_2$; (B) $(CH_3)_3SiCH_2CH{=}CHCH_3$. [d] Isolated yield of the mixture of 2 and 3. Structure was determined by ^1H NMR (90 MHz), ^{13}C NMR, IR, and mass spectroscopy after purification by GPLC (stainless steel column, 3 m, PEG, 120–180 °C, He). [e] Determined by GPLC mentioned above.

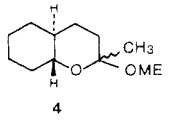
the concurrent formation of the ethers **3** can be accounted for the formation of products derived from the more stable carboxonium ions II, generated from I by [1,2]-hydrogen shift in the course of the reaction.

In contrast, 2-(bromomethyl)tetrahydropyrans **1f**, **1g**, and **1h** afforded only the ethers **3**. In the allylation of **1g**, the high degree of stereoselection is accounted for the excusive axial attack on the half-chair conformation for the six-membered ring as shown in III.[5,6] The ether **3i** was also confirmed to be identical with the product obtained by the reaction of 2-methoxyethyl ketal **4** with allyltrimethylsilane in the presence of $TiCl_4$.[7]

It should be also noted that no reaction of **1a** with allylsilane was observed in the presence of $BF_3{\cdot}Et_2O$ or $TiCl_4$ at room temperature for 1 day.[8]



III

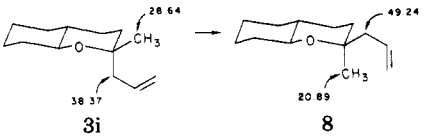


4

ME = $CH_2CH_2OCH_3$

(5) For recent findings in the alkylation of furan and pyran ring in terms of stereochemistry, see: (a) Murata, S.; Noyori, R. *Tetrahedron Lett.* **1982**, 2601. (b) Kozikowski, A. P.; Sorgi, K. L. *Ibid.* **1982**, 2281. (c) Lewis, M. D.; Cha, J. K.; Kishi, Y. *J. Am. Chem. Soc.* **1982**, *104*, 4976.

(6) The stereochemical assignment was confirmed on the basis of ^{13}C NMR spectra. The stereoisomer **8** was synthesized from **3i** in three steps: O_3, EtOAc, −78 °C/Me_2S, 52%; MeONa, MeOH, room temperature, 13 h, conversion 47%; $Ph_3P{=}CH_2$, THF, 83%.



3i 8

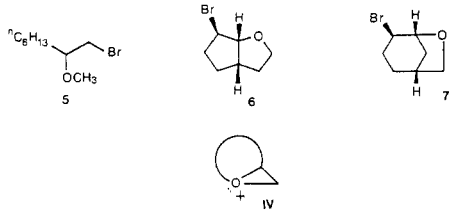
(7) See ref 1d and Hosomi et al. (Hosomi, A.; Endo, M.; Sakurai, H. *Chem. Lett.* **1976**, 941).

(8) The net equation of the reaction is considered as follows:

$$1 + (CH_3)_3SiCH_2CH{=}CH_2 \rightarrow 2 + 3 + AgBr + (CH_3)_3SiBF_4$$

However, $(CH_3)_3SiBF_4$ component will probably exist as $(CH_3)_3SiF + BF_3$ or make a complex with AgBr or excess $AgBF_4$.

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.

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:

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

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-

(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]
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