Acknowledgment. The financial support from the National Institutes of Health is gratefully acknowledged (Grant No. GM 10937-21). We thank Glidden Organics, SCM Corporation, P.O. Box 389, Jacksonville, FL 32201, for a gift sample of (+)-3-carene of high optical purity.

Registry No. 1, 5989-27-5; 2, 18172-67-3; 3, 475-20-7; 4, 7785-70-8; 5, 38359-49-8; 6, 498-15-7; acetaldehyde, 75-07-0; *B*-allyldiisocaranylborane, 92055-65-7; *B*-allylimonylborane, 92055-66-8; *B*-allyldi-10-pinanylborane, 92055-67-9; *B*-allyldilongifolylborane, 92055-68-0; *B*-allyldiisopinocamphenylborane, 85116-38-7; *B*-allylbis(10-methylisopinocamphenyl)borane, 92055-69-1; (*R*)-4-penten-2-ol, 64584-92-5; (*S*)-4-penten-2-ol, 55563-79-6.

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(8) For recent success with (3,3-dimethylallyl)diisopinocampheylborane, see: Brown, H. C.; Jadhav, P. K. *Tetrahedron Lett.* **1984**, *25*, 1215.

(9) Dale, J. A.; Mosher, H. S. *J. Am. Chem. Soc.* **1973**, *95*, 512.

(10) Additional proofs for % ee and absolute configurations were obtained by catalytic (5% Pt on C) hydrogenation of (−)-4-penten-2-ol and (+)-5-hexen-3-ol to (*R*)-(−)-2-pentanol in 100% ee and (*R*)-(−)-3-hexanol in 93% ee, respectively.

(11) Research associate on Grant 2 R01 GM 10937-21 from the National Institutes of Health.

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Stereospecific Synthesis of Metalated Alkoxymethyl Vinyl Ethers

Summary: The thermolysis of substituted bicyclo[2.2.1]hept-5-enes provides expedient access to stannylated vinyl ethers of defined stereochemistry. Alkoxymethyl substitution on the vinyl oxygen is found to significantly improve the hydrolytic stability of several substituted vinyl ethers.

Sir: As part of a program addressing the synthesis of natural products bearing 1,2- and/or 1,3-oxygenation patterns, we sought to establish the utility of the strategy represented in Figure 1 (boxed). Recognizing the problems inherent in stereoselectively generating species I and II without competing β-elimination,[1] we considered equivalent methods of effecting the desired transformations. Following this reasoning, a sequence involving the condensation of the starting aldehyde with a vinyl ether anion (e.g., 1)[2] to give an adduct (e.g., 2) which might be transformed into the desired product(s) was explored. An appealing feature of this approach is the possibility of preparing polyols of complimentary stereochemistries from a single intermediate through control over the hydration of the vinyl ether adduct (2). Successful implementation of this scheme requires the general availability of metalated vinyl ethers of defined stereochemistry which afford condensation products sufficiently stable to allow subsequent elaboration. This requirement is addressed in the efficient, stereospecific synthesis of metalated vinyl ethers described below.

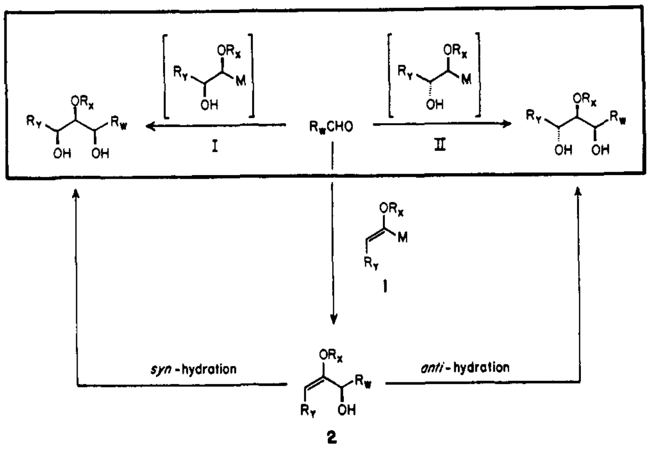

Figure 1.

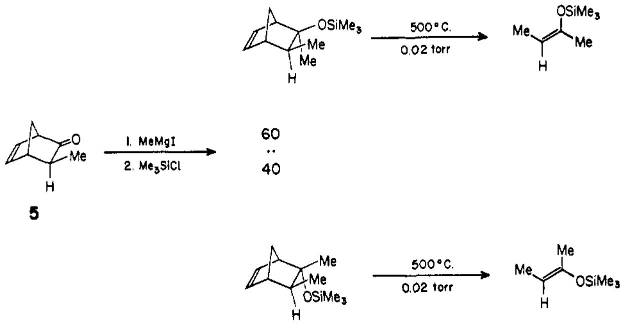

Figure 2.

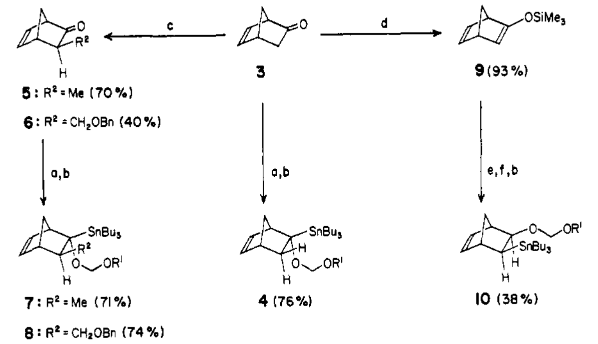

Figure 3. (a) n-Bu_3SnLi, THF, −78 °C.[7] (b) R^1OCH_2Cl, Hünig's base, CH_2Cl_2. (c) LDA, THF, −78 °C; MeI or $BnOCH_2I$. (d) LDA, THF, −78 °C; Me_3SiCl. (e) n-Bu_3SnH, AIBN, PhMe, Δ. (f) n-Bu_4NF, THF.

Our synthetic approach to vinyl ethers was suggested by several observations. First, Rouessac and co-workers reported that the retro-Diels–Alder reaction of silylated bicyclo[2.2.1]hept-5-en-2-ols proceeded to stereospecifically generate silyl enol ethers (Figure 2).[3] Second, related studies in our laboratories indicated that alkoxymethyl substitution on oxygen conferred enhanced stability upon vinyl ethers.[4] Third, tin–lithium exchange has been demonstrated to be an efficient means of preparing lithiated vinyl ethers.[2b,5] It was our hope that analogous tri-*n*-butylstannylated derivatives of alkoxymethyl-protected bicyclic heptenols could be prepared in a highly

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(1) Examples which suppress β-elimination: (a) Nájera, C.; Yus, M.; Seebach, D. *Helv. Chim. Acta* **1984**, *67*, 289. (b) Barluenga, J.; Florez, J.; Yus, M. *J. Chem. Soc., Chem. Commun.* **1982**, 1153. (c) Barluenga, J.; Fañañas, F. J.; Villamaña, J.; Yus, M. *J. Org. Chem.* **1982**, *47*, 1560.

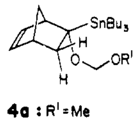
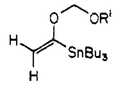
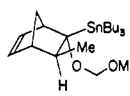
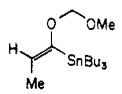
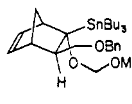
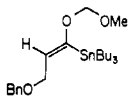
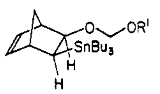
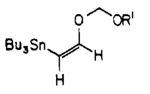
(2) Examples of vinyl ether anions: (a) Baldwin, J. E.; Höfle, G. A.; Lever, O. W., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 7125. (b) Wollenberg, R. H.; Albizati, K. R.; Peries, R. *J. Am. Chem. Soc.* **1977**, *99*, 7365. (c) Gould, S. J.; Remillard, B. D. *Tetrahedron Lett.* **1978**, 4353. (d) Boeckman, R. K., Jr.; Bruza, K. J. *J. Org. Chem.* **1979**, *44*, 4781. (e) Boeckman, R. K., Jr.; Bruza, K. J. *Tetrahedron* **1981**, *37*, 3997. (f) Miyata, O.; Schmidt, R. R. *Tetrahedron Lett.* **1982**, *23*, 1793. (g) Smithers, R. H. *J. Org. Chem.* **1983**, *48*, 2095. (h) Russell, C. E.; Hegedus, L. L. *J. Am. Chem. Soc.* **1983**, *105*, 943.

(3) Gringore, O.; Haslouin, J.; Rouessac, F. *Bull. Soc. Chim. Fr.* **1976**, 1523.

(4) McGarvey, G. J.; Kimura, M., unpublished results.

(5) Sonderguist, J. A.; Hsu, G. J.-H. *Organometallics* **1982**, *1*, 830.

Table I. Pyrolytic Generation of Stannylated Vinyl Ethers

entry	bicyclic precursor	vinyl ether	yield
			
1	**4a**: $R' = Me$	**11a**: $R' = Me$	98%
2	**4b**: $R' = Bn$	**11b**: $R' = Bn$	95%
3	**4c**: $R' = (CH_2)_2OMe$	**11c**: $R' = (CH_2)_2OMe$	95%
			
4	**7**	**12**	85%
			
5	**8**	**13**	98%
			
6	**10a**: $R' = Me$	**14a**: $R' = Me$	75%
7	**10b**: $R' = (CH_2)_2OMe$	**14b**: $R' = (CH_2)_2OMe$	70%

stereocontrolled fashion to serve as precursors to stannylated vinyl ethers.

As shown in Figure 3, this expectation was realized through straightforward elaboration of a simple common intermediate, bicyclo[2.2.1]hept-5-en-2-one (**3**).[6] α-Alkoxy stannanes were prepared as single isomers[8] through addition of tri-n-butylstannyllithium[7,9] to ketones **3**, **5**, and **6**, while the β-alkoxy species **10** could be realized through hydrostannation of silyl enol ether **9**.[8] The stereoselection in products **4** and **10** reflects the attachment of the stannyl group to the least hindered face of the π-system, whereas the formation of the tin bond in the most congested position in **7** and **8** may reflect the previously observed reversibility of such anionic additions.[9]

With suitable bicyclic alkoxymethyl-protected stannanes available in quantity, the critical thermolytic fragmentation was examined. The bicyclic stannanes (neat) were introduced dropwise to an evacuated, heated (0.25 torr, 400 °C) vertical quartz column packed with crushed quartz (34 cm × 2.6 cm).[12] The pyrolyzates, collected in a cooled round-bottomed receiver (CO_2(s)/acetone), were found to consist of nearly pure stannylated vinyl ethers in the yields given in Table I. The stereochemistries of products **12**, **13**, and **14** are supportive of the stereospecificity of the retro-Diels–Alder process.[3] Also of mechanistic note are the results of entries 6 and 7 wherein no norbornadiene formation via elimination of the β-alkoxy stannanes was observed to compete with the desired fragmentation reaction.[13]

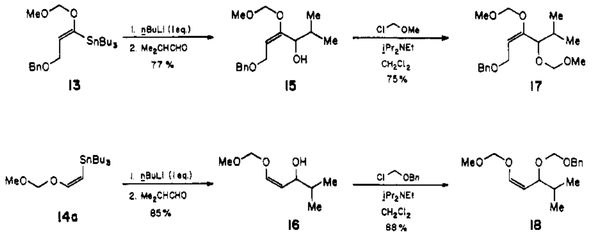


Figure 4.

As anticipated, compounds **11–14** participated in smooth tin–lithium exchange without loss of geometry by the action of n-BuLi (1 equiv in THF at −78 °C: 20 min for **11–13**, 90 min for **14**). The resulting vinyllithium species cleanly condensed with aldehydes to afford adducts of gratifying stability. To illustrate, isobutyraldehyde adducts **15** and **16** were isolated in the indicated yields following purification by flash chromatography (Figure 4).[14] Routine protections of the allylic alcohols affords derivatives **17** and **18** which exhibit still greater resistance to eliminative hydrolysis to the corresponding α,β-unsaturated aldehydes. Furthermore, the conversion of **18** → **16** may be effected by warming the protected compound in acetone with pyridinium tosylate.[14]

Having secured stereospecific access to metalated vinyl ethers and demonstrated the relative stability of alkoxymethyl substitution on the vinyl oxygen, completion of the strategy outlined in Figure 1 may be pursued. The stereoselective elaboration of compounds of the types **15–18** will be reported in due course.

Acknowledgment is gratefully given to the National Institutes of Health for their generous support. We also thank Professor Timothy L. Macdonald for helpful discussions.

Registry No. **3**, 694-98-4; **4a**, 92012-59-4; **4b**, 92012-60-7; **4c**, 92012-61-8; **5**, 51100-02-8; **6**, 92012-62-9; **7**, 92012-63-0; **8**, 92012-64-1; **9**, 68364-22-7; **10a**, 92012-65-2; **10b**, 92012-66-3; **11a**, 92012-67-4; **11b**, 92012-68-5; **11c**, 92012-69-6; **12**, 92012-70-9; **13**, 92012-71-0; **14a**, 92012-72-1; **14b**, 92012-73-2; **15**, 92012-74-3; **16**, 92012-75-4; **17**, 92012-76-5; **18**, 92012-77-6; Me_2CHCHO, 78-84-2; n-Bu_3SnLi, 4226-01-1; chloromethoxymethane, 107-30-2; ((chloromethoxy)methyl)benzene, 3587-60-8.

Supplementary Material Available: Spectral data for compounds **11–14** (3 pages). Ordering information is given on any current masthead page.

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[8] The stereochemistry of product **4** was determined through stereospecific tin–proton exchange[9] and comparison of the result with both protected norbornenol isomers. Alkylation products **5** and **6** are obtained through expected exo selectivity.[10] Stannanes **7**, **8**, and **10** were analyzed by NMR comparisons with related bicycloheptenes.[11]

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[11] Marchand, A. P. "Stereochemical Applications of NMR Studies in Rigid Bicyclic Systems"; Verlag Chemie: Deerfield Beach, FL, 1982.

[12] This method is based upon the description given in Stork, G.; Guthikonda, R. N. *Tetrahedron Lett.* **1972**, 2755.

[13] (a) Kauffmann, T.; Kriegesmann, R.; Altepeter, B.; Steinseifer, F. *Chem. Ber.* **1982**, *115*, 1810. (b) Kauffmann, T.; Kriegesmann, R.; Hamsen, A. *Chem. Ber.* **1982**, *115*, 1818.

[14] For example, compare the acid stability of **16** with similar compounds in ref 2b.

Palladium-Catalyzed Conversion of Esters of 4-(Trimethylsilyl)-2-buten-1-ol to Trimethylsilyl Esters. A New Carboxyl Protecting Group

Summary: Carboxylic acids protected as esters of 4-(trimethylsilyl)-2-buten-1-ol are catalytically converted by $Pd(PPh_3)_4$ to trimethylsilyl esters which are readily hydrolyzed by treatment with an alcohol.