aldol reactions of silyl enolates with carbonyl compounds proceed via the acyclic (nonchelated) transition states.[10] In the present case, the use of tin(II) triflate as a promoter is essential for the cyclic transition states,[11] and one of the most characteristic points in these transition states is that the divalent tin predominantly coordinates to the sulfur atom rather than the oxygen atom of the enolates,[12] forming the six-membered transition state consisting of three carbon, oxygen, sulfur, and tin atoms. Consequently, syn aldols are obtained from (*Z*)-enolates while anti aldols from (*E*)-enolates, *which are opposite selectivities to those observed in the conventional cyclic transition states in the aldol reaction.*[13-15]

Finally, enantioselective synthesis of α-methyl-β-hydroxy-β-methyl units was surveyed by using a chiral tin(II) promoter.[16] When 1*Z* was treated with methyl phenylglyoxylate in the presence of tin(II) triflate, (*S*)-1-pentyl-2-[(piperidin-1-yl)methyl]pyrrolidine, and tributyltin fluoride, the reaction smoothly proceeded to give the syn isomer in high yield with high diastereo- and enantioselectivities. Similarly, 1*Z* smoothly reacted with methyl pyruvate to give the corresponding syn adduct in high ee (Scheme II). On the other hand, 1*E* reacted with methyl phenylglyoxylate or methyl pyruvate very slowly under the same reaction conditions.[17]

In summary, a novel general method for the preparation of the α-methyl-β-hydroxy-β-alkyl(aryl) units including their optically active forms has been developed by use of the tin(II) triflate-mediated aldol reaction of 1-(ethylthio)-1-(trimethylsiloxy)propene with α-keto esters. In the course of this study, a unique character of tin(II) triflate as a Lewis acid to realize high selectivities has also been found.

Further progress to apply the present methodology to the synthesis of pyrrolizidine alkaloids as well as to utilize the unique character of tin(II) triflate as a Lewis acid are now under investigation.

Acknowledgment. The authors are grateful to Professor Teruaki Mukaiyama, Science University of Tokyo, for his helpful discussion.

Supplementary Material Available: Experimental procedures (2 pages). Ordering information is given on any current masthead page.

(10) Heathcock, C. H.; Davidsen, S. K.; Hug, K. T.; Flippin, L. A. *J. Org. Chem.* **1986**, *51*, 3027. Murata, S.; Suzuki, M.; Noyori, R. *Tetrahedron* **1988**, *44*, 4259 and references cited therein. The cyclic transition states in the reaction of ketene silyl acetals with aldehydes were reported: Chan, T. H.; Aida, T.; Lau, P. W. K.; Gorys, V.; Harpp, D. N. *Tetrahedron Lett.* **1979**, *20*, 4029. Gong, L.; Streitwieser, A. *J. Org. Chem.* **1990**, *55*, 6235.

(11) Other Lewis acid ($TiCl_4$, $SnCl_4$, BF_3OEt_2, $EtAlCl_2$) mediated reactions would proceed via the acyclic transition states: Gennari, C.; Beretta, M. G.; Bernardi, A.; Moro, G.; Scolastico, C.; Todeschini, R.; *Tetrahedron* **1986**, *42*, 893.

(12) Yura, T.; Iwasawa, N.; Narasaka, K.; Mukaiyama, T. *Chem. Lett.* **1988**, 1025.

(13) Heathcock, C. H. *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1984; Vol. 3, Part B, Chapter 2. Zimmerman, H. E.; Traxler, M. D. *J. Am. Chem. Soc.* **1957**, *79*, 1920.

(14) In the recent report on the diastereoselective aldol reactions using β-keto imide derived tin(II) enolates, four-coordinated tin(II) is postulated: Evans, D. A.; Clark, J. S.; Metternich, R.; Novack, V. J.; Sheppard, G. S. *J. Am. Chem. Soc.* **1990**, *112*, 866. See also ref 15.

(15) For five-coordinated tin(II): Shields, K. G.; Seccombe, R. C.; Kennard, C. H. L. *J. Chem. Soc., Dalton Trans.* **1973**, 741. See also: Mukaiyama, T.; Kobayashi, S.; Uchiro, H.; Shiina, I. *Chem. Lett.* **1990**, 129.

(16) The aldol reactions of the acetic acid enolates with α-keto esters for the synthesis of 2-substituted malates including their optically active forms were reported. Kobayashi, S.; Fujishita, Y.; Mukaiyama, T. *Chem. Lett.* **1989**, 2069.

(17) Similar results had also been observed in the reactions of 1*Z* and 1*E* with achiral aldehydes. These enantioselective reactions may not proceed via the six-membered cyclic transition state shown in Scheme I, probably due to the strong coordination of the chiral diamine to tin(II) metal.[18]

(18) Kobayashi, S.; Uchiro, H.; Fujishita, Y.; Shiina, I.; Mukaiyama, T. *J. Am. Chem. Soc.* **1991**, *113*, 4247.

Stereocontrolled Formation of Cis and Trans Ring Junctions in Hydrindane and Decalin Systems by Palladium-Catalyzed Regioselective and Stereospecific Hydrogenolysis of Allylic Formates

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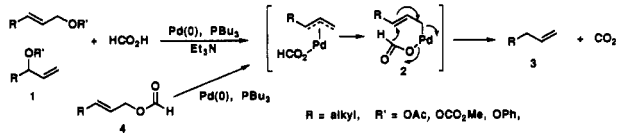
Summary: Both cis and trans ring junctions can be generated selectively in hydrindane, decalin, and steroid systems by the palladium-catalyzed regioselective and stereospecific hydrogenolysis of allylic formates.

Stereocontrolled generation of cis or trans ring junctions in hydrindane or decalin derivatives is a desirable but elusive synthetic goal. An elegant method for stereospecific generation of cis and trans ring junctions via free-radical cyclization using stereo-defined allylic alcohols in decalin and hydrindane systems has been reported.[1] In this case, however, a carbon unit is introduced. We now wish to report a solution to this general problem based on π-allylpalladium chemistry. We have reported that the palladium-catalyzed hydrogenolysis of terminal allylic compounds **1** with ammonium formate proceeds regioselectively to afford 1-olefins **3**.[2] This regioselective hydrogenolysis can be explained by the attack of the hydride generated from σ-allylpalladium formate **2** on the more substituted end of the allylic system to afford terminal olefins **3**. We also found that allylic formates **4** can be used for the same transformation without use of ammonium formate.



We hoped to apply this regioselective hydrogenolysis reaction to hydrindane and decalin systems, expecting high regio- and stereoselectivities, if the hydride attacks the

(1) (a) Stork, G.; Kahn, M. *J. Am. Chem. Soc.* **1985**, *107*, 500. (b) Stork, G.; Sofia, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 6826.

(2) (a) Tsuji, J.; Yamakawa, T. *Tetrahedron Lett.* **1979**, 613. (b) Tsuji, J.; Shimizu, I.; Minami, I. *Chem. Lett.* **1984**, 1017.

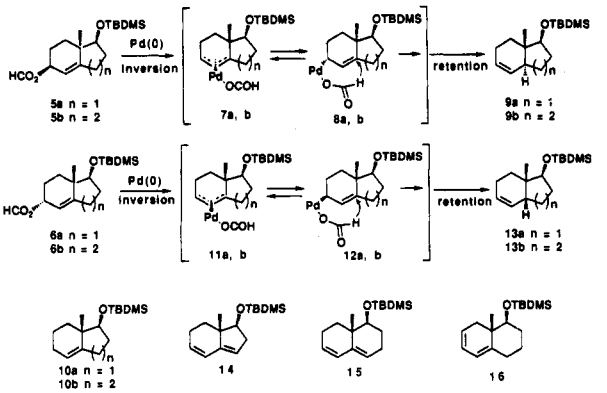
0022-3263/92/1957-1326$03.00/0

more substituted carbon of the allylic system in the bicylic systems (see **8a,b** or **12a,b**), giving the disubstituted olefins **9a,b** or **13a,b**, rather than the trisubstituted olefins **10a,b**. In addition to the regioselectivity, stereospecificity was expected based on mechanistic considerations. In palladium-catalyzed allylation reactions of nucleophiles via π-allylpalladium complexes, it is well-established that the initial step in π-allylpalladium complex formation involves inversion of stereochemistry. The subsequent addition of a soft carbon nucleophile to the π-allyl system takes place from the opposite side of palladium resulting in net retention.[3] On the other hand, the addition of a hard nucleophile to a π-allylpalladium complex proceeds from the same side as palladium, and hence overall inversion takes place. Based on the above stereochemical considerations, we expected that the attack of Pd(0) on **5a,b** or **6a,b** to form π-allylpalladium formate **7a,b** or **11a,b** would take place with inversion of stereochemistry. The subsequent migration of the hydride from the Pd formate to the angular carbon should occur with retention (**8a,b** → **9a,b**, and **12a,b** → **13a,b**). Therefore, overall inversion was expected. Thus the stereospecific formation of trans hydrindene **9a** and octahydronaphthalene **9b** is expected from the β-allylic formate **5a,b**, and the cis compounds **13a,b** would be formed from the α-allylic formate **6a,b**. We were pleased to find that these reactions in fact proceeded as expected.

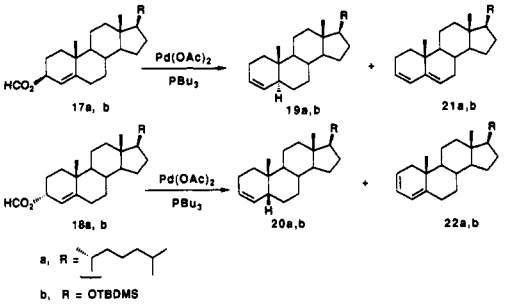
Both the α- and β-formates **6a** and **5a** were treated with the catalyst prepared from $Pd(acac)_2$ and n-Bu_3P (1:1) in THF.[4] The reactions proceeded in 30 min at room temperature to give only the 4-hydrindenes **9a** (82%) from **5a** and **13a** (57%) from **6a** with no regioisomeric 3a-hydrindene **10a** being formed. In addition, formation of the trans product **9a** (NMR, angular CH_3, $\delta = 0.73$) and *cis*-**13a** (NMR, CH_3, $\delta = 0.89$) shows that the hydrogenolysis reactions are stereospecific. As a byproduct, the heteroannular conjugated 3,4-diene **14** was formed (13% from **5a** and 38% from **6a**).[5]

In the decalin systems **5b** and **6b**, only the 3-olefins **9b** and **13b**, respectively, were formed regioselectively and stereospecifically after 1 h. As byproducts, the heteroannular-conjugated 3,5-diene **15** (3%) was produced from **5b** and the homoannular 2,4-diene **16** (6%) from **6b**.[5]

One application of this methodology is the stereoselective generation of both cis and trans AB ring junctions in steroids. The β-formates **17a,b** and the α-formates **18a,b** were prepared and subjected to the palladium catalysis



[$Pd(OAc)_2$ and n-Bu_3P (1:1)] at room temperature for 1.5–2 h. The β-formates **17a,b** were converted to the AB *trans*-cholestene (**19a**)[6] (80%) and *trans*-androstene derivative **19b** (94%) with high regioselectivity and stereospecificity. Also the heteroannular conjugated 3,5-dienes **21a,b** (15% and 5%) were byproducts. The AB *cis*-cholestene **20a**[7] (89%) and *cis*-androstene derivative **20b** (87%) were obtained cleanly from the α-formates **18a,b**. The homoannular 2,4-dienes **22a,b** (7% and 8%) were byproducts in these reactions. The steroids **19a**, **20a**, and **19b**, **20b** (after desilylation) are known and were identified by comparison of their optical rotations and mps with reported data. Also unequivocal stereochemical assignments were made by ^1H NMR analysis at 400 MHz.



Supplementary Material Available: Experimental procedures for main steps and physical data including NMR spectra for important compounds (13 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(3) (a) Trost, B. M.; Verhoeven, T. R. *J. Org. Chem.* **1976**, *41*, 3215. (b) Trost, B. M.; Verhoeven, T. R. *J. Am. Chem. Soc.* **1980**, *102*, 4730.

(4) The use of pure n-Bu_3P was critical for consistent results. n-Bu_3P in a Sure-Seal bottle, purchased from Aldrich, was used.

(5) Studies on the palladium-catalyzed regioselective formation of the homo- and heteroannular conjugated dienes from the corresponding α- and β-allylic carbonates will be reported.

(6) Preparation of 5α-cholestene (**19a**) by the hydroboration of cholest-4-en-3-one has been reported: Caglioti, L.; Cainelli, G.; Maina, G.; Selva, A. *Tetrahedron* **1964**, *20*, 957.

(7) Preparation of *cis*-cholestene (**20a**) from cholest-4-en-3-one has been reported: Kabalka, G. W.; Hutchins, R.; Natale, N. R.; Yang, D. T. C.; Broach, V. *Organic Syntheses*; Wiley: New York, 1988; Collect. Vol. VI, p 293.

Titanium-Mediated Carbonyl Olefinations. 2. Benzylidenations of Carbonyl Compounds with Dibenzyltitanocene

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Summary: Mild thermolysis of carbonyl compounds with dibenzyltitanocene affords phenyl-substituted olefins, enol ethers, and enamines.

Several complexes of Ti,[1-3] Ta,[4] Zr,[5] Mo,[6] or W[7] were shown to perform Wittig-like olefinations of carbonyl compounds. While some of these[1-3] have found applica-

(1) Reetz, M. T. *Organotitanium Reagents in Organic Synthesis*; Springer-Verlag: Berlin, 1986.

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