Asymmetric γ-Selective Pentadienylation of Aldehydes Catalyzed by BINAP·Ag(I) Complex

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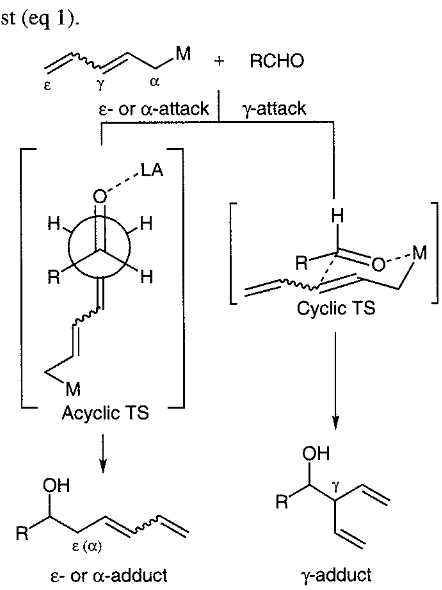
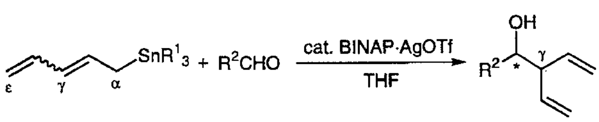
Abstract: Reaction of aldehydes with (*E*)-2,4-pentadienyltributyltin or trimethyltin in the presence of a catalytic amount of BINAP·silver(I) complex affords the corresponding γ-pentadienylated optically active alcohols with high enantioselectivities.

Condensation of 2,4-pentadienylmetal compounds with aldehydes affords two regioisomeric dienols, ε (or α)-adduct and γ-adduct, which are both useful synthetic intermediates of various natural products, and numerous regioselective methods to introduce pentadienyl group into organic molecules have been developed using a variety of metal reagents (Scheme 1).[1] The ε- or α-attacked conjugated dienols can be selectively obtained by the reaction of pentadienylsilanes or stannanes with aldehydes in the presence of strong Lewis acid, such as $BF_3·OEt_2$ and $TiCl_4$, via an acyclic transition-state structure.[2] In contrast, employment of more reactive pentadienylmetal compounds (M = Mg, Zn, B, etc.) results in predominant formation of the unconjugated γ-adducts via a cyclic transition-state structure.[3] However, as far as we know, the asymmetric version of these reactions has not been yet achieved since the γ-pentadienylated products are not obtained by the Lewis acid-promoted reactions using silane and stannane reagents which are effective for asymmetric synthesis.[4] In this paper, we describe a catalytic enantioselective γ-pentadienylation reaction of aldehydes with pentadienylstannanes[5] using BINAP·silver(I) complex[6] as a catalyst (eq 1).

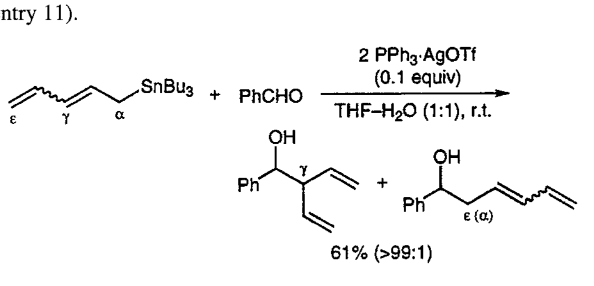


Scheme 1. Reactions of Pentadienylmetal Reagents with Aldehydes



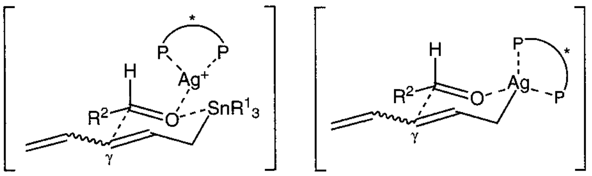
(1)

Recently crotyltributyltin has been proven to react selectively at the γ-position with an aldehyde in the presence of a catalytic amount of BINAP·silver(I) complex.[7] We initially investigated the addition of pentadienyltins to aldehydes using achiral phosphine–silver(I) catalysts with the anticipation that such γ-substituted allyltin compounds should also exhibit similar high γ-selectivity. When benzaldehyde was reacted with 1 equiv of pentadienyltributyltin and 0.1 equiv of bis(triphenylphosphine)–silver(I) triflate in a 1:1 mixture of THF and H_2O at 20 °C for 3 h,[8] the γ-adduct was produced nearly exclusively in 61% yield (eq 2). This γ-allylation preference led us to employ BINAP·silver(I) complex as a catalyst for the pentadienylation under anhydrous reaction conditions. Treatment of benzaldehyde with pentadienyltributyltin in dry THF under the influence of 10 mol% of (*S*)-BINAP·AgOTf at -20 °C for 8 h gave the optically active γ-pentadienylated alcohol in 61% yield with 90% ee (Table 1, entry 1). Other results gained for the reaction of various aldehydes and pentadienyltin reagents catalyzed by (*R*)-BINAP·AgOTf are summarized in Table 1 and several key findings are as follows: (1) no remarkable differences in chemical yield or enantioselectivity were observed between pentadienyltributyltin and pentadienyltrimethyltin (compare entries 1, 2, 6, and 7); (2) substituted aromatic aldehydes and furfural offered comparable enantioselectivity to that of benzaldehyde (entries 3–5); (3) a 1,2-addition took place exclusively in the reaction of α,β-unsaturated aldehydes (entries 6–9); (4) an alkyl substituent at the α-position of α,β-unsaturated aldehyde raised the enantiomeric excess of the pentadienylated product, though the chemical yield was low (entry 9); (5) ketone was inert under the standard reaction conditions (entry 11).



(2)

These results unambiguously indicate that the BINAP·silver(I) catalyzed pentadienylation proceeds via a cyclic transition-state structure since a γ-adduct is obtained as the sole product without exception. Two plausible models are shown in Figure 1. If the BINAP·Ag(I) complex acts as Lewis acid, the reaction should go through a six-membered cyclic model A. In contrast, a similar cyclic transition-state model B containing a BINAP-coordinated silver atom instead of trialkylstannyl group is a probable alternative when the transmetallation to pentadienylsilver occurs rapidly.

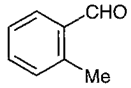
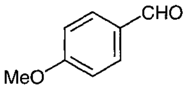
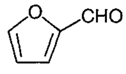
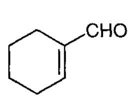


A (Lewis acid mechanism) **B** (transmetallation mechanism)

Figure 1. Plausible Cyclic Transition-state Structures

A representative experimental procedure is given by (*R*)-BINAP·AgOTf catalyzed reaction of benzaldehyde with (*E*)-2,4-pentadienyltrimethyltin (entry 2 in Table 1): A mixture of AgOTf (26 mg, 0.10 mmol) and (*R*)-BINAP (62 mg, 0.10 mmol) was dissolved in dry THF (4 mL) under

Table 1. Enantioselective addition of pentadienylstannane to aldehydes catalyzed by BINAP·AgOTf complex[a]

Entry	SnR^1_3	Aldehyde	Yield (%)[b]	% ee[c]
1[d]	$SnBu_3$	PhCHO	61	90
2	$SnMe_3$		68	89
3	$SnMe_3$		57	90
4	$SnMe_3$		41	87
5	$SnMe_3$		62	89
6	$SnBu_3$	(*E*)-PhCH=CHCHO	73	58
7	$SnMe_3$		68	58
8	$SnMe_3$	(*E*)-CH_3CH=CHCHO	65	62[e]
9	$SnBu_3$		13	90[e]
10	$SnBu_3$	$PhCH_2CH_2CHO$	52	71
11	$SnBu_3$	$PhCOCH_3$	<1	—

[a] Unless otherwise specified, the reaction was carried out using (*R*)-BINAP·AgOTf (0.1 equiv), pentadienyltributyltin (R^1 = *n*-Bu, *E*:*Z* = 97:3, 1 equiv) or pentadienyltrimethyltin (R^1 = Me, *E*:*Z* = 90:10, 1 equiv), and aldehyde (1 equiv) in THF at -20 °C for 8 h. [b] Isolated yield. [c] Determined by HPLC analysis (Chiralcel OD-H or AD, Daicel Chemical Industries, Ltd.). [d] (*S*)-BINAP·AgOTf was used. [e] Determined by HPLC analysis (Chiralcel AD) of the benzoate ester of the product.

argon atmosphere and with exclusion of direct light, and stirred at 20 °C for 10 min. To the resulting solution was added benzaldehyde (100 μL, 0.98 mmol) and then pentadienyltrimethyltin (*E*/*Z* = 90/10, 229 mg, 0.99 mmol) was added over a period of 4 h with a syringe pump at -20 °C. After being stirred for 4 h at this temperature, the mixture was treated with a mixture of 1 N HCl (3 mL) and solid KF (ca. 1 g) at ambient temperature for 30 min. After the resulting precipitate was filtered off by glass filter funnel filled with Celite® and silica gel, the filtrate was dried over anhydrous $MgSO_4$ and concentrated *in vacuo* after filtration. The residual crude product was purified by column chromatography on silica gel to afford the γ-pentadienylated alcohol (116.5 mg, 68% yield) as a colorless oil: TLC R_f0.33 (1:5 ethyl acetate/hexane); IR (neat) 3625-3130, 3081, 3031, 2980, 2880, 1636, 1605, 1495, 1455, 1416, 1194, 1040, 999, 918 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.19 (d, 1 H, J = 3.2 Hz, OH), 3.11 (dt, 1 H, J = 7.1, 7.9 Hz, CH), 4.59 (dd, 1 H, J = 3.1, 7.0 Hz, CH), 5.01 (d, 1 H, J = 17.9 Hz, vinyl), 5.05 (d, 1 H, J = 10.4 Hz, vinyl), 5.19 (d, 1 H, J = 17.1 Hz, vinyl), 5.25 (d, 1 H, J = 10.4 Hz, vinyl), 5.68 (ddd, 1 H, J = 7.1, 10.4, 17.2 Hz, vinyl), 5.83 (ddd, 1 H, J = 8.2, 10.4, 18.2 Hz, vinyl), 7.25-7.38 (m, 5 H, aromatic); $[\alpha]^{29}_D$ +60.8 (*c* 1.1, $CHCl_3$). The IR and ^1H NMR spectral data indicated good agreement with reported data.[3i] The γ/ε (or α) ratio was determined to be >99/1 by ^1H NMR analysis. The enantioselectivity of the γ-product was determined to be 89% ee by HPLC analysis using chiral column (Chiralcel OD-H, Daicel Chemical Industries, Ltd., hexane/*i*-PrOH = 20/1, flow rate = 0.5 mL/min): t_{minor} = 18.7 min, t_{major} = 22.5 min.

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References and Notes

(1) Reviews: (a) Courtois, G.; Miginiac, L. *J. Organomet. Chem.* **1974**, *69*, 1. (b) Yasuda, H.; Nakamura, A. *J. Organomet. Chem.* **1985**, *285*, 15.

(2) Pentadienyltrimethylsilane/$TiCl_4$: (a) Seyferth, D.; Pornet, J. *J. Org. Chem.* **1980**, *45*, 1721. (b) Seyferth, D.; Pornet, J.; Weinstein, R. M. *Organometallics* **1982**, *1*, 1651. Pentadienyltrimethylsilane/BF_3·OEt_2: (c) Hosomi, A.; Saito, M.; Sakurai, H. *Tetrahedron Lett.* **1980**, *21*, 3783. Pentadienyltrimethylstannane/BF_3·OEt_2: (d) Naruta, Y.; Nagai, N.; Arita, Y.; Maruyama, K. *Chem. Lett.* **1983**, 1683. Pentadienylstannanes/$TiCl_4$: (e) Boeckman, R. K., Jr.; Demko, D. M. *J. Org. Chem.* **1982**, *47*, 1789. (f) Nishigaichi, Y.; Fujimoto, M.; Takuwa, A. *J. Chem. Soc. Perkin Trans. 1* **1992**, 2581. Molybdenum-η^3-pentadienyl complex/BF_3·OEt_2: (g) Lin, S.-H.; Yang, Y.-J.; Liu, R.-S. *J. Chem. Soc., Chem. Commun.* **1991**, 1004. (h) Lin, S.-H.; Lee, G.-H.; Peng, S.-M.; Liu, R.-S. *Organometallics* **1993**, *12*, 2591.

(3) Pentadienylzincs: (a) Gérard, F.; Miginiac, P. *Bull. Soc. Chim. Fr.* **1974**, 1924. (b) Yasuda, H.; Ohnuma, Y.; Nakamura, A.; Kai, Y.; Yasuoka, N.; Kasai, N. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1101. (c) Kang, S.-K.; Kim, D.-Y.; Hong, R.-K.; Ho, P.-S. *Synth. Commun.* **1996**, *26*, 1493. (d) Jung, M. E.; Nichols, C. J. *Tetrahedron Lett.* **1996**, *37*, 7667. Pentadienylmagnesiums: (e) Yasuda, H.; Yamauchi, M.; Nakamura, A.; Sei, T.; Kai, Y.; Yasuoka, N.; Kasai, N. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1089. Pentadienylberylliums: ref. 3b. Pentadienylboranes: (f) Hutchings, M. G.; Paget, W. E.; Smith, K. *J. Chem. Res. (S)* **1983**, 31. See also: (g) Fujita, K.; Schlosser, M. *Helv. Chim. Acta* **1982**, *65*, 1258. Pentadienyltrichlorosilane: (h) Kobayashi, S.; Nishio, K. *Chem. Lett.* **1994**, 1773. (i) Kobayashi, S.; Nishio, K. *J. Org. Chem.* **1994**, *59*, 6620.

(4) Review: Santelli, M.; Pons, J.-M. *Lewis Acids and Selectivity in Organic Synthesis*; CRC Press: New York, 1996; p 91. Unusual γ-selectivity was observed for addition of pentadienyltrimethylstannane to aldehydes promoted by $ZnCl_2$: Nishigaichi, Y.; Fujimoto, M.; Takuwa, A. *Synlett* **1994**, 731.

(5) Pentadienylstannanes were efficiently prepared by reaction of a pentadienyl Grignard reagent, generated from 1-chloro-2,4-pentadiene and magnesium turnings, with R_3SnCl in ether, for R = *n*-Bu, *E*:*Z* = 97:3; for R = Me, *E*:*Z* = 90:10. Preparation and spectral data of these pentadienylstannanes: (a) Seyferth, D.; Goldman, E. W.; Pornet, J. *J. Organomet. Chem.* **1981**, *208*, 189. (b) Paz-Sandoval, M. d. l. A.; Powell, P. *J. Organomet. Chem.* **1981**, *219*, 81. (c) Naruta, Y.; Nishigaichi, Y.; Maruyama, K. *Chem. Lett.* **1986**, 1857. (d) Naruta, Y.; Nishigaichi, Y.; Maruyama, K. *Org. Synth.* **1993**, *71*, 118.

(6) Yanagisawa, A.; Nakashima, H.; Ishiba, A.; Yamamoto, H. *J. Am. Chem. Soc.* **1996**, *118*, 4723.

(7) Yanagisawa, A.; Ishiba, A.; Nakashima, H.; Yamamoto, H. *Synlett* **1997**, 88.

(8) In general, reactions of allylic tin compounds with aldehydes catalyzed by bis(triphenylphosphine)-silver(I) complex give higher yields in aqueous solvent than in anhydrous solvent, see ref. 6.