4: a) Aminophosphane **1** (5 g) is dissolved in a mixture of pentane (150 mL) and diethyl ether (50 mL), and the resulting solution is stirred for 2 d at ambient temperature. After all volatile components have been removed in vacuo, the obtained crude product mixture is subjected to chromatography on silica gel that has been pretreated with chlorotrimethylsilane. Elution with pentane furnishes **4** ($R_f = 0.9$) as a colorless solid; yield: 0.2 g (10.5 %). M.p. 80 °C. b) Alternatively, the zirconium complex **2b** (4 g, 6 mmol) is dissolved in diethyl ether (150 mL) and treated at ambient temperature under stirring with triethylammonium chloride (0.83 g, 6 mmol). After the mixture has been stirred for 4 h, all volatile components are removed in vacuo, and the remaining solid residue is extracted with pentane. The combined extracts are evaporated to dryness, and **4** is obtained after chromatographic workup as described above; yield: 0.29 g (23 %). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): $\delta = 4.7$ (t, $^2J(P,P) = 17.6$ Hz, P_X), -0.5 (d, $^2J(P,P) = 17.6$ Hz, P_K); $^1H\{^{31}P\}$ NMR (300 MHz, $CDCl_3$): $\delta = 7.23$ (d, $^4J(H,H) = 2.7$ Hz, 2H, H_A), 7.05 (t, $^4J(H,H) = 2.7$ Hz, 1H, H_N); ^1H NMR (500 and 300 MHz, $CDCl_3$): $\delta = 7.23$ (m, 2H, H_A), 7.05 (m, 1H, H_N), (iteration with WINDAISY gave the following coupling constants (the signs given are based on a positive sign for $^1J(P,H)$): $^1J(P_K,H_A) = +580.0$, $^3J(P_X,H_A) = +6.4$, $^3J(P_K,H_A) = +8.8$, $^4J(H_A,H_A) = -5.2$, $^4J(H_A,H_N) = +2.8$, $(^2J(P_K,P_K) = +10.6$, $^2J(P_K,P_X) = +16.9$, $^1J(P_X,H_N) = +589.4$, $^3J(P_K,H_N) = +7.8)$, 3.1 (m, $|^3J(P,H) + ^5J(P,H)| = 6$, $^3J(H,H) = 11.7$, 3.6 Hz, NC*H*, 4H), 3.0 (dtt, $^3J(P,H) = 8$, $^3J(H,H) = 11.7$, 3.5 Hz, NC*H*, 2H), 1.9 – 0.9 (m, CH_2, 60H); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): $\delta = 54.9$ (d, $^2J(P,C) = 5.4$ Hz, N*C*), 54.2 (pseudo t, $|^2J(P,C) + ^4J(P,C)| = 5.4$ Hz, N*C*), 34.4 (pseudo t, $|^3J(P,C) + ^5J(P,C)| = 1.5$ Hz, NCCH_2), 34.3 (d, $^3J(P,C) = 3.2$ Hz, NCCH_2), 34.1 (pseudo t, $|^3J(P,C) + ^5J(P,C)| = 1.5$ Hz, NC*C*H_2), 27.25, 27.20, 27.15 (s, NCCCH_2), 26.3, 26.2 (s, NCCCCH_2); MS (EI, 70 eV): *m/z* (%): 678 (1) [M^+], 595 (2) [$M^+ - c$-Hex], 498 (7) [$M^+ - N(c\text{-Hex})_2$], 180 (100) [$N(c\text{-Hex})_2^+$]; HR-MS (EI, 70 eV): calcd for $C_{36}H_{69}N_6P_3$: 678.4797, found: 678.4797.

Received: April 7, 1997 [Z 11695 IE]
German version: *Angew. Chem.* **1998**, *110*, 2486 – 2488

Keywords: phosphazenes · phosphorus heterocycles · zirconium

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Catalytic Asymmetric Allenylation: Regulation of the Equilibrium between Propargyl- and Allenylstannanes during the Catalytic Process**

Chan-Mo Yu,* Sook-Kyung Yoon, Kwangwoo Baek, and Jae-Young Lee

Dedicated to Professor Elias J. Corey on the occasion of his 70th birthday

The availability of efficient synthetic methods for achieving absolute stereoselectivity by catalytic processes in the production of enantiomerically pure compounds is of considerable current interest because such products can be used as chiral building blocks for the synthesis of valuable chiral substances.[1] In this regard, allyl-transfer reactions provide excellent stereoselective routes for converting aldehydes into the corresponding alcohols.[2] Subsequent to early studies by Hoffmann et al.[3] on the use of chirally modified allyl boranes to accomplish asymmetric induction, many research groups have made important contributions to the extension of this

[*] Prof. Dr. C.-M. Yu, S.-K. Yoon, K. Baek, J.-Y. Lee
Department of Chemistry and Institute of Basic Science
Sungkyunkwan University, Suwon 440 – 746 (Korea)
Fax: (+82) 331-290-7075
E-mail: cmyu@chem.skku.ac.kr

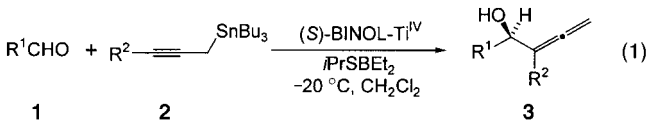
[**] This research was supported by grants from the Ministry of Education (BSRI 97-3420) and the Korea Science and Engineering Foundation (KOSEF 97-0501-02-01-3).

protocol to achieve high levels of stereoselectivity.[4] The exceptional power of the allyl transfer reactions in forming enantioenriched alcohols from aldehydes has been enhanced by newly developed catalytic variations, especially the chiral Lewis acid catalyzed addition of allyl-transfer reagents to carbonyl functionalities.[5] Although there have been several elegant reports regarding the enhancement of the catalytic ability for practical use,[6] the scope of the catalytic allyl-transfer reactions is still limited to allyl systems.

Recently, we demonstrated that the utilization of molecular synergetic reagents, designed on the basis of mechanistic speculation, for catalytic asymmetric allylation and propargylation resulted in not only a significant increase in the reaction rate but also a reduced dosage of the chiral catalyst.[7] This strategy should prove to be effective for the catalytic allenylation of achiral aldehydes—an efficient method should enable the many useful functional group transformations of allenyl alcohols to be realized.[8]

Practical methods for the synthesis of allenyl alcohols are often limited by the tendency of propargylic reagents to couple with carbonyl groups to produce allenyl alcohols, which is mainly a consequence of their lack of regiochemical selectivity.[9] An efficient method for the enantioselective synthesis of allenyl alcohols through the self-immolative transfer of chirality by the use of stoichiometric amounts of nonracemic propargylstannanes with aldehydes has been reported.[10] While the reaction of some propargylboranes with stoichiometric chiral auxiliaries has been developed to achieve a highly enantio- and regioselective synthesis of allenyl alcohols,[11] a catalytic version of the allenylation of aldehydes has not yet been realized. Described herein is an extension of the molecular accelerating strategy aimed at finding new reagents and realizing useful and practical ways to advance to new levels of asymmetric synthesis. In the present research, two major observations have been made in the enantioselective synthesis of allenyl alcohols: 1) bifunctional synergetic reagents expedite the catalytic process of asymmetric allenylation of achiral aldehydes in high enantioselectivity, and 2) the reaction procedes with dramatic regiochemical selectivities as a result of the equilibrium between the tin reagents.

The starting point of this investigation was the availability of the tin reagent **2** in a regiochemically pure form. This compound was prepared by the following reaction in large quantites and purified by distillation: The treatment of 1-bromo-2-butyne (1.2 equiv) with magnesium (2.0 equiv) and Bu_3SnCl (1 equiv) in the presence of $PbBr_2$ (5 mol%) in THF afforded 2-butynyltributylstannane (**2**, $R^2 = Me$) in 81% yield after purification by distillation with a regioselectivity of over 98%.[12] The first study focused on the feasibility of **2** for the catalytic asymmetric allenylation of achiral aldehydes that were promoted by a chiral Lewis acid catalyst. Our initial studies were carried out with **1** ($R^1 = PhCH_2CH_2$) and **2** ($R^2 =$ Me) in the presence of a (*S*)-BINOL–Ti^{IV} complex together with various bifunctional synergetic reagents R_nMSR^1 (M = B, Al, Si) [Eq. (1); BINOL = 2,2′-dihydroxy-1,1′-binaphthyl]. Several key findings emerged from the study: 1) the control experiment revealed that the reaction proceeded only marginally in the absence of a synergetic reagent (10 mol% of



1 2 3 (1)

catalyst, −20°C, 20 h, <10% yield); 2) *i*PrSBEt$_2$ exhibited quite high efficiency for the catalytic process; 3) a 2:1 mixture of the BINOL–Ti(O*i*Pr)$_4$ complex in the presence of 4-Å molecular sieves provided the most efficient catalyst;[13] and 4) the best chemical yields and enantioselectivities were obtained at −20°C in CH_2Cl_2.

Under optimal conditions, the catalytic allenyl-transfer reaction was conducted by the dropwise addition of *i*PrSBEt$_2$ (1.2 equiv) in CH_2Cl_2 at −20°C to a mixture of **1** (R = CH_2CH_2Ph, 1 equiv) and **2** (R = Me, 1.2 equiv) in the presence of the (*S*)-BINOL–Ti^{IV} complex (10 mol%) in CH_2Cl_2. After 9 h at −20°C, the reaction mixture was quenched by the addition of a saturated aqueous solution of $NaHCO_3$. Workup and chromatography on silica gel afforded alcohol **3a** in 85% yield and with 93% *ee*. This discovery prompted us to carry out more experiments with other aldehydes and tin reagents (Table 1).

Table 1. Catalytic asymmetric allenylation of achiral aldehydes [Eq. (1)].[a]

Entry	R^1	R^2	**3**	yield [%][b]	*ee* [%][c]
1	$PhCH_2CH_2$	Me	**a**	85	93
2	$PhCH_2CH_2$	Et	**b**	77	96
3	$PhCH_2CH_2$	Pr	**c**	71	93
4	*n*-C_6H_{13}	Me	**d**	97	92
5	*n*-C_6H_{13}	Et	**e**	82	95
6	*n*-C_6H_{13}	Pr	**f**	72	90
7	Me_2CHCH_2	Me	**g**	62[d]	81
8	Me_2CHCH_2	Et	**h**	49[d]	81
9	Me_2CHCH_2	Pr	**i**	41[d]	85
10	Ph	Me	**j**	74	90
11	Ph	Et	**k**	78	97
12	Ph	Pr	**l**	73	91

[a] All reactions were carried out at −20°C; (*S*)-BINOL:Ti(O*i*Pr)$_4$ = 2:1 (10 mol%); reaction times t = 9 h, unless otherwise stated. [b] Yields refer to isolated and purified products. [c] Enantiomeric excesses were determined by preparation of (+)-MTPA ester derivatives, analysis by ^{1}H NMR (all entries) and/or ^{19}F NMR spectroscopy (entries 3, 6), and by HPLC analysis on a chiral stationary phase (Chiracel OD-H, *i*PrOH/hexane 10/90, entries 11, 12). [d] t = 11 h.

The absolute configuration of the predominating enantiomer of the adducts was unambiguously established by comparison of their specific rotations with that of known alcohols.[11b] The absolute sense of the asymmetric induction parallels previous observations on catalytic asymmetric allylations that employed the (*S*)-BINOL–Ti^{IV} complex.[7] Table 1 shows that the catalytic process is effective for a variety of aldehydes and tin reagents in terms of chemical yield and enantioselectivity. However, a reduced dosage of chiral catalyst (5 mol%) resulted in diminished chemical yields and longer reaction times (**3a**, −20°C, 24 h, 41% yield). The reaction also produced none or only trace amounts of isomeric propargylic carbinols (<3%) as judged by ^{1}H (500 MHz) NMR analysis of the crude products.

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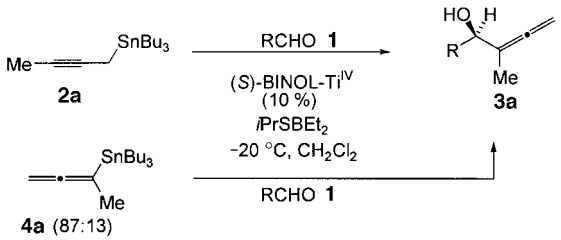
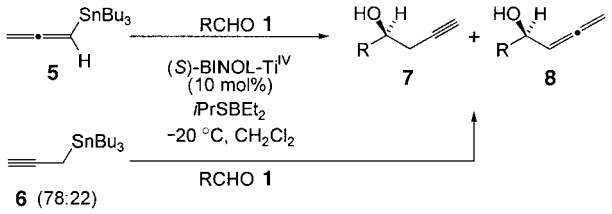
We turned our attention next to the application of this approach with other allenic or propargylic tin reagents to enlarge the scope of allylic transfer reactions. During our investigations, we observed the remarkable regulation of the equilibrium between allenyl- and propargylstannane reagents under the reaction conditions used. We were surprised to find that the reaction of **4a** (87:13 mixture) with **1** (R = $PhCH_2CH_2$, 1 equiv) under the same conditions afforded the alcohol **3a** (R = $PhCH_2CH_2$) in 81% yield and with 91% *ee*.[14] This high regio- and enantioselectivity in the formation of allenyl alcohol **3a** from allenyltin **4a** at $-20\,^{\circ}C$ mediated by the BINOL–Ti^{TV} complex is virtually identical to that seen with propargyltin **2a** (Scheme 1). This is not the common case; allenyltin reagents usually convert aldehydes



Scheme 1. Catalytic asymmetric allenylation of aldehydes; **3a** is precipitated in over a 97% purity together with the isomers of propargyl alcohol. For yields and *ee* values with **2a**, see Table 1. With **4a**: R = $PhCh_2CH_2$: 81%, 91% *ee*; R = *n*-C_6H_{13}: 78%, 92% *ee*.

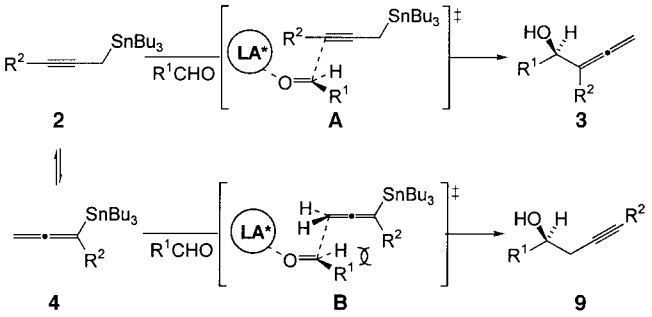
into propargyl alcohols in a reaction mediated by a Lewis acid catalyst in the absence of equilibrating reagents such as $BuSnCl_3$.[15] On the other hand, both allenyltin **5** and propargyltin **6**, under identical conditions, produced the same propargyl carbinol **7** as a major component (Scheme 2). In general, allenyl reagents lead mainly to propargylic adducts,



	R =	7:8	%	*ee* (%)
5:	$PhCH_2CH_2$	>98:2	86	94
	nC_6H_{13}	>98:2	75	92
6:	$PhCH_2CH_2$	89:11	71	91
	nC_6H_{13}	87:13	70	92

Scheme 2. Catalytic asymmetric propargylation with **5**[7c] and **6**.

and propargylic reagents to allenyl adducts by S_E2' addition to the aldehyde. These apparent contradictions could be explained by products being formed in the reaction that originated from the equilibrium between allenyl- and propargyltin reagents under the reaction conditions. Since antiperiplanar attack would lead to the particular product **3** or **9** via transition state **A** or **B**, the major reaction pathway could be dependent on the stability of the transition state under kinetic control or on orientations and steric factors, without a necessary link to the product stability (Scheme 3). Thus, the origin of regiochemical selectivity for these transformations might be a result of the thermodynamic stability of the tin



Scheme 3. Formation of **3** and **9** from the equilibrium between **2** and **4**. LA* = chiral Lewis acid catalyst.

reagents as well as subtle geometrical preferences for orientation in the transition states offered by the complex catalytic system rather than the original concentration of the reaction.

Experimental Section

Typical procedure for the catalytic allenylation (entry 12 of Table 1): A flame-dried flask containing (*S*)-BINOL (57.3 mg, 0.2 mmol) and activated powdered 4-Å molecular sieves (0.7 g) was evacuated and carefully purged with nitrogen three times, and then charged with dry CH_2Cl_2 (2 mL) followed by freshly distilled $Ti(OiPr)_4$ (freshly prepared, 0.5 M in CH_2Cl_2, 0.2 mL, 0.1 mmol). The mixture was stirred at 25 °C for 3 h. The red-brown mixture was cooled to $-20\,^{\circ}C$ in a dry ice–CCl_4 bath, and a solution of benzaldehyde (**1**, R^1 = Ph, 0.11 g, 1.0 mmol) in CH_2Cl_2 (0.5 mL) was added. A solution of tributyl-2-hexynylstannane (**2**, R^2 = Pr, 0.45 g, 1.2 mmol) in CH_2Cl_2 (1 mL) was added dropwise to this mixture, followed by the addition of *i*PrSBEt$_2$ (0.18 g, 1.25 mmol) in CH_2Cl_2 (1 mL; by gas-tight syringe with a syringe pump) over 1 h along the wall of the flask while keeping the temperature below $-20\,^{\circ}C$. After the reaction mixture was stirred for 8 h at $-20\,^{\circ}C$, aqueous $NaHCO_3$ (5 mL) was added and then CH_2Cl_2 (5 mL). The molecular sieves were removed by filtration, and the aqueous layer was extracted with CH_2Cl_2 (ca. 20 mL). The combined organic solution was dried over anhydrous Na_2SO_4, and the solvents were then removed under reduced pressure. Purification of the residue by column chromatography (EtOAc/hexanes 15/85) afforded **3** (R^1 = Ph, R^2 = Pr; 0.137 g, 0.73 mmol, 73%) as a colorless liquid: TLC: R_f = 0.33 (hexane/EtOAc 85/15); $[\alpha]_D^{20} = -120$ (c = 1.75, $CHCl_3$); FT-IR (neat): $\tilde{\nu}$ = 3389, 1956 cm^{-1}; EI-MS: *m*/*z* (%): 188 (M^+, 30.6), 173 (24.2), 106 (37.8), 79 (100); ^1H NMR (500 MHz, $CDCl_3$): δ = 0.86 (t, J = 7.5 Hz, 3H), 1.36–1.46 (m, 2H), 1.70–1.86 (m, 2H), 2.24 (d, J = 4.5 Hz, 1H), 4.96–5.04 (m, 2H), 5.09 (ddd, J = 4.5, 2.5, 2.5 Hz, 1H), 7.20–7.50 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.74, 20.70, 30.01. 74.11, 79.57, 108.05, 126.67, 127.70, 128.26, 142.15, 204.21.

Received: March 31, 1998 [Z11670IE]
German version: *Angew. Chem.* **1998**, *110*, 2504–2506

Keywords: aldehydes · asymmetric catalysis · Lewis acids · synthetic methods · titanium

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Monocyclic $(CH)_9^+$—A Heilbronner Möbius Aromatic System Revealed**

Michael Mauksch, Valentin Gogonea, Haijun Jiao, Paul von Ragué Schleyer*

Dedicated to Professor Edgar Heilbronner

In 1964 Heilbronner predicted that singlet [4*n*]annulenes would be aromatic systems in twisted conformations where the p orbitals lie on the surface of a Möbius strip (Figure 1).[1]

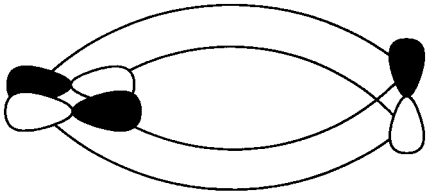

Figure 1. Schematic representation of the Möbius type overlapping p orbitals in $(CH)_9^+$. The C_2 axis lies horizontally; the carbon atom on it (right) is across from the phase inversion (left).

Although the Möbius concept has been employed extensively to interpret reactions and bonding,[2,3] Möbius annulenes conforming to Heilbronner's original idea have still not been reported. Heilbronner pointed out that rings with twenty atoms or more might adopt Möbius geometries "without any apparent angle or steric repulsion strain".[1] However, we have discovered computationally that Möbius aromaticity is possible in a much smaller ring system, namely, the cyclononatetraenyl cation. Moreover, judging from early experimental evidence,[4,5] this species may actually have been encountered more than once almost three decades ago!

A monocyclic $(CH)_9^+$ cation of unspecified nature, but which allowed isotope label scrambling, was first postulated in 1971 as a short-lived intermediate in the solvolysis of *exo*-9-chlorobicyclo[6.1.0]nona-2,4,6-triene in aqueous acetone at $75\,^{\circ}C$.[4] The reactant containing deuterium at C9 (**1**, Scheme 1) gave a bicyclic product, *cis*-8,9-dihydroindene-1-ol (**3**, X = OH), with uniformly distributed deuterium label.[4] Shortly afterwards Anastassiou and Yakali succeeded in preparing 9-chlorocyclononatetraene (**2**, stereochemistry undetermined).[6] Under ionizing conditions (liquid SO_2 at $-66\,^{\circ}C$), D-labeled **2** gave **3** (X = Cl) by ion-pair return, again with complete statistical distribution of the label (1/9 D per C atom).[5]

[*] Prof. Dr. P. von R. Schleyer, Dipl.-Chem. M. Mauksch, Dr. V. Gogonea, Dr. H. Jiao
Computer-Chemie-Centrum
Institut für Organische Chemie der Universität Erlangen-Nürnberg
Henkestrasse 42, D-91054 Erlangen (Germany)
Fax: (+49) 9131-85-9132
E-mail: pvrs@organik.uni-erlangen.de

[**] We thank Prof. Emel Yakali (Raymond Walters College, Cincinnati, OH) for helpful discussions and Holger Bettinger (CCQC, Athens, GA) for the CCSD(T) computations. We are grateful to the Deutsche Forschungsgemeinschaft, the Humboldt Foundation (fellowship for V.G.), and the Fonds der Chemischen Industrie for their financial support.

  1433-7851/98/3717-2395 $ 17.50+.50/0