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STUDIES ON THE REACTION OF α-IMINO ESTERS WITH ORGANOMETALLIC COMPOUNDS

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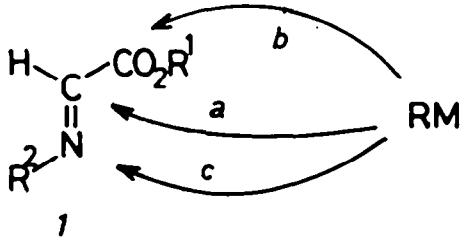
Abstract-Benzylzinc reagent reacted with α-imino ester (**2**) at the α-carbon exclusively, though other organometallic reagents such as Mg, Al, Cu, Ti, and B derivatives reacted at the nitrogen atom. Use of the (S)-amine as a chiral auxiliary of **2** created the R chirality at the imino carbon. Very high chiral induction was realized in the reaction of prenylzinc reagent with α-imino 8-(-)phenylmenthyl ester (**10**). The reaction of **2** with heteroatom substituted allylic organometallic compounds (**15**) gave the corresponding α-heteroatom substituted amino acid derivatives (**16**). Here again, the allylic zinc reagent gave the adduct in higher yield than the corresponding Ti, Al, and B reagents.

The reaction of the α-imino-esters (**1**) with organometallic compounds (RM) should be a highly promising reaction for the synthesis of amino acids and related compound, if the carbon-carbon bond formation takes place regioselectively at the imino carbon. The nucleophile may attack three possible electrophilic centers via paths a, b, or c.[2] For example, simple Grignard reagents such as ethyl-, propyl-, benzyl- and iso-butyl-magnesium halides react predominantly through path c, while t-butyl- and allyl-magnesium halides exclusively attack the imino carbon via path a.[2] We previously reported that very high enantio- and



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diastereo-selective synthesis of certain amino acids may be realized through the reaction of α-imino-esters with 9-allyl-, 9-(2-methyl)prop-2-enyl-, and 9-but-2-enyl-9-borabicyclo[3.3.1]nonane.[3] It is now clear that less basic but more reactive allylic boron compounds react regio- and stereo-selectively at the imino carbon center. We report further extension of the previous study; (i) organozinc reagents regioselectively react through path a, (ii) very high enantioselective synthesis of amino acid derivatives is realized via the reaction of α-imino esters having a chiral auxiliary at the R^1 group of 1, (iii) the reaction of heteroatom substituted allylic organometallic compounds produces β-heteroatom substituted amino acid derivatives.

RESULTS AND DISCUSSION

Reaction of benzyl organometallic reagents. Since the pioneering work of Kagan reveals that benzyl Grignard reagent attacks the nitrogen atom of 1 exclusively[2], we first investigated the regioselectivity on the reaction of 2 with various benzyl organometallic reagents. The results are summarized in Table 1. Benzylzinc bromide produced 3 exclusively, while other benzyl

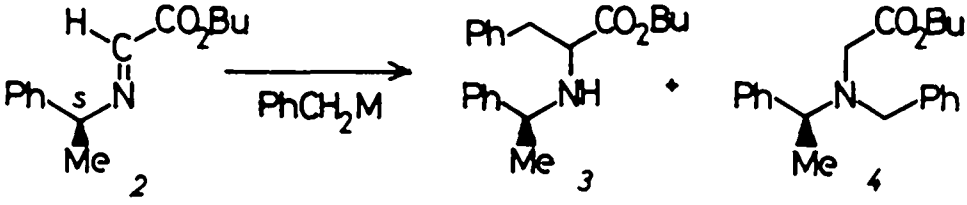
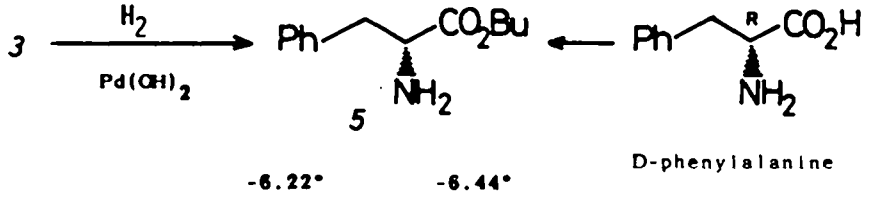


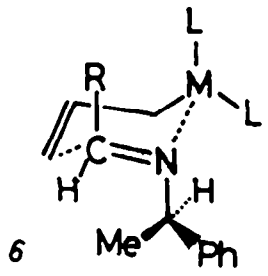
Table 1. Reaction of 2 with benzyl organometallic compounds[a]

% M	ZnBr	MgCl	$AlEt_3$ MgCl	Cu	Cu BF_3[b]	$Ti(OiPr)_3$	$B(OMe)_2$
3	50(74:26)[c]	-	-	-	-	-	-
4	-	95	78	22	50	55	42

[a] Benzyl organometalls were prepared from $PhCH_2MgCl$ by addition of $ZnBr_2$, $AlEt_3$, CuI, $Ti(OiPr)_3Cl$, or $B(OMe)_3$. [b] One equivalent of BF_3 OEt_2 was added to benzylcopper at -78°C. For RCu BF_3, see ref. 4. [c] Diastereomer ratio.

organometals gave 4 in either very high yields (MgCl) or low yield (Cu). The diastereomer ratio of 3 was determined by 400 MHz ^1H NMR analysis. To determine the stereochemistry at the α-carbon, 3 (a major isomer) was converted to phenylalanine butyl ester (5) upon treatment with $H_2/Pd(OH)_2$; $[\alpha]_D^{24}$ -6.22°





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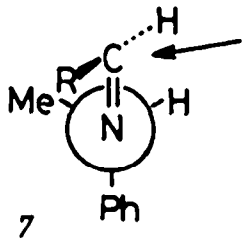

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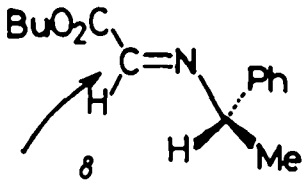
amine	chirality
R ⟶	R
S ⟶	S



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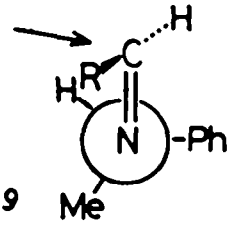

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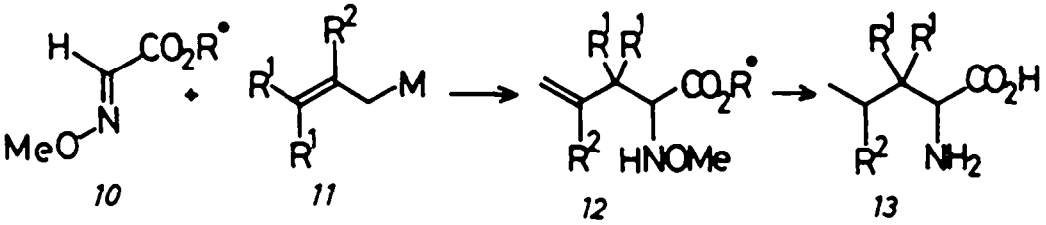
amine	chirality
R ⟶	S
S ⟶	R

(c 6.69, $CHCl_3$). Authentic D-phenylalanine (R form) was also transformed into **5**, with a comparable $[\alpha]_D^{24}$ of -6.44°(c 21.4, $CHCl_3$). Consequently, the (S)-amine auxiliary of **2** created the R chirality at the α-carbon. The sense of chiral induction via benzylzinc bromide is reverse in comparison with the induction via allyl- and but-2-enyl-9-borabicyclo[3.3.1]nonane, in which the (S)-amine produces the S chirality.[2] The reaction of allyl-9-BBN proceeds through the six-membered cyclic transition state (**6**). This ring system forces the chiral center to take the conformation **7**, in which the hydrogen is in the inside of the six membered ring to minimize the steric interaction. On the other hand, ordinary nucleophiles which can not form a cyclic transition state attack the imine as shown in **8**; the present chiral induction can be rationalized by the comformation **9**.

Chiral induction via α-imino 8-(-)-phenylmenthyl ester (**10**). We next examined the chiral induction based upon a chiral auxiliary at the ester group. We chose 8-(-)-phenylmenthyl group, since this chiral auxiliary frequently exhibited very high enantioface selectivity.[5] The reaction of **10** with allylic



10 11 12 13

R*= 8-(-)-phenylmenthyl

12a; $R^1 = R^2 = H$

12b; $R^1 = R^2 = Me$

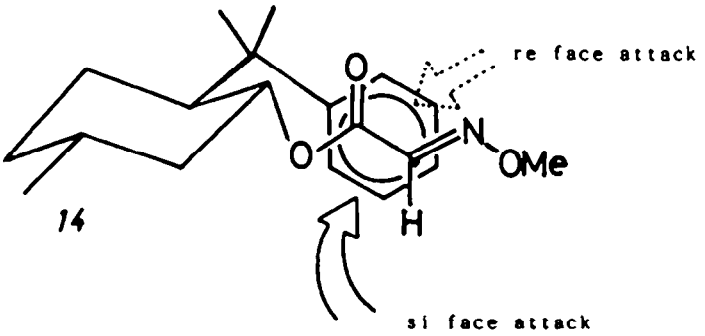
boron or zinc reagents (**11**) produced **12** in reasonable yields, which was further converted to amino acids **13** via the usual hydrogenation and hydrolysis. The results are summarized in Table 2. The allylic zinc reagent gave the adduct

Table 2. Reaction of **10** with allylic boron and zinc reagents.

Entry	**11** R^1	R^2	M	Product **12**	Isolated yield, %	d.e.	Amino acid, **13**
1	H	H	B	**12a**	39	20	norvaline
2	H	H	ZnBr	**12a**	52	74	norvaline
3	H	H	$B(OMe)_2$	**12a**	29	6	norvaline
4	Me	Me	ZnBr	**12b**	55	> 98	

in higher yield than the allylic boron reagent. Poor electrophilicity of the oxime nitrogen in comparison with the imine nitrogen[3] may diminish coordination of boron atom of allylic boron compounds, resulting in low yield. On the other hand, the allylic zinc reagent does not necessarily require coordination to the nitrogen atom to induce the allylation reaction. The sense of chiral induction in entry 2 was determined by transforming the adduct into norvaline (**13**, $R^1 = R^2 = H$). The major isomer of **12a** was converted into norvaline with $[\alpha]_D^{23.5}$ of + 12.0° (c 1.2, 6N HCl). An authentic L-norvaline (S-form) indicated $[\alpha]_D^{20}$ of +24° (c 10, 6N HCl). Therefore, the 8-(-)-phenylmenthyl group induces S-chirality at the α-carbon center.

Allylzinc reagent presumably attacks the imine carbon of **14** from the si-face, since the phenyl group blocks the attack from the re-face.[5] Induction of S-chirality indicates that the metal chelation from syn-form is more favorable than the anti-chelation. The same tendency is also observed in the reaction of 8-phenylmenthyl glyoxylate with allylic tin-BF_3[5d, 6] and with alkene-$SnCl_4$ (ene reaction)[5c]. Zinc may coordinate more strongly to both oxygen and nitrogen atoms than boron, resulting in higher diastereoselectivity (entries 2 and 4). In entry 4, the absolute stereochemistry was not determined.



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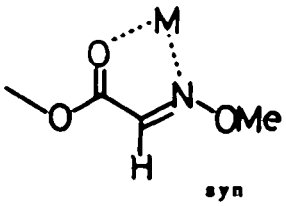
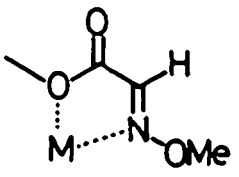


syn



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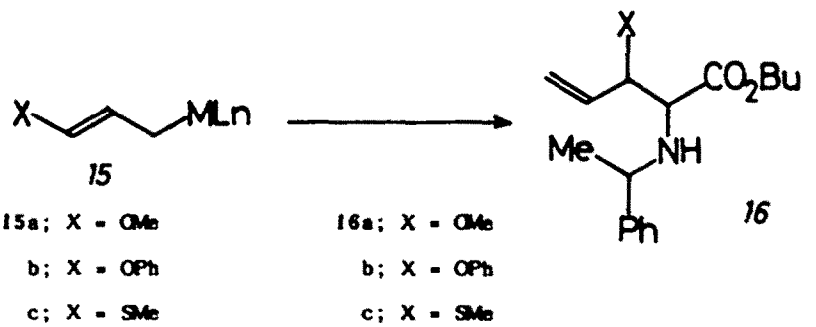
Allylic 9-BBN exhibits very high enantioselectivity when a chiral auxiliary is introduced to the R^2 group of 1(1,3-asymmetric induction).[3] However, the present result indicates that the chiral auxiliary at the R^1 group of 1 does not exert a strong influence on the chiral induction via allylic boron reagents.

Reaction of hetero-substituted allylic organometallic compounds (15). The reaction of **2** with **15** are summarized in Table 3. Here again, the allylic zinc derivatives gave the adduct **16** in reasonable yields (entries 1, 4, and 6). Other metals such as Al, Ti, and B were not effective for the condensation at the α-carbon, since attack at the nitrogen atom was accompanied in the reaction with these allylic metals. Although the allylic boronate gave **16c** in 42% yield (entry 7), the corresponding allylic 9-BBN did not produce the desired adduct from **15a** and **15b**. The stereochemistry of **16a** was determined by transforming the adduct to the cyclic compounds as described previously.[3,7] The absolute

Table 3. Reaction of **2** with hetero-substituted allylic organometallic compounds

					Isomer ratio, %[a]					
entry	X	MLn	Product	%	C-E	aC-E	C-T	aC-T	T/E	C/aC
1	OMe	ZnBr	**16a**	67	13	2	73	12	5/1	6/1
2	OMe	$Ti(OiPr)_3$	**16a**	20	32	20	30	18	1/1	2/1
3	OMe	$AlEt_3Li$	**16a**	14	19	19	39	23	2/2	2/1
4	OPh	ZnBr	**16b**	54	5	4	50	41	10/1	1/1
5	OPh	$AlEt_3Li$	**16b**	21	11	5	59	25	5/1	2/1
6	SMe	ZnBr	**16c**	50	15	12	42	31	3/1	1/1
7	SMe	$B(OMe)_2$	**16c**	42	16	17	38	29	2/1	1/1

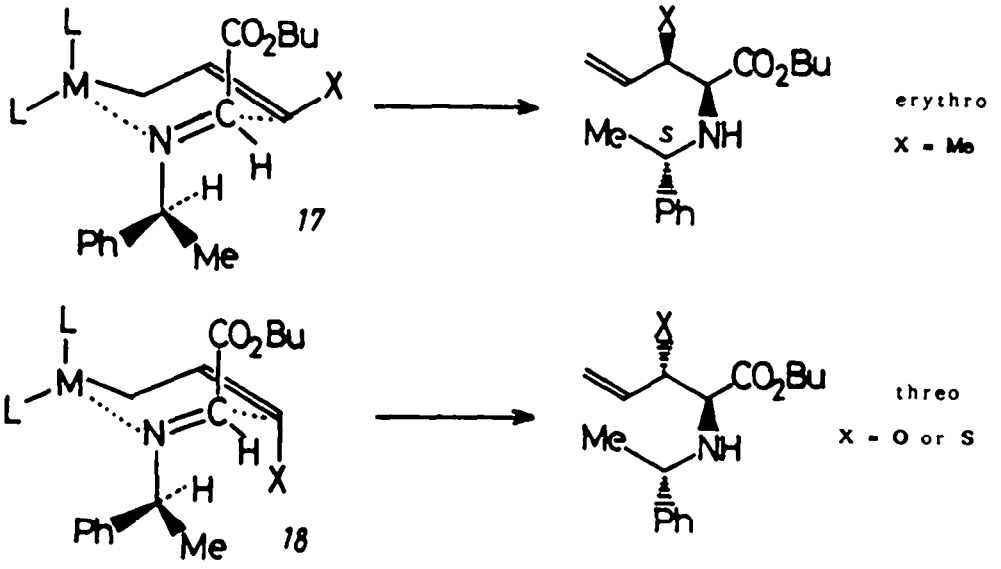
[a] C; Cram. aC; anti-Cram. T; threo. E; erythro. For these nomenclatures, see ref. 3.



stereochemistry was not determined, since an authentic heteroatom-substituted amino acid was not available. The stereochemistries of **16b** and **16c** were tentatively assigned by analogy with the stereochemistry of **16a**. Quite interestingly, the threo isomer predominated over the erythro isomer regardless of the metal used. As previously reported[3], the reaction of crotyl 9-BBN (X = CH_3) gives the erythro adduct predominantly via the cyclic transition state **17**. The heteroatom substituted allylic organometals take the Z-geometry owing to the coordination ability of the heteroatoms toward Zn, Ti, Al, and B[8]. Therefore, the reaction presumably proceeds through **18** to give the threo isomer

predominantly.

In conclusion, organozinc reagents give the best result among the organometallic reagents examined. This is presumably due to their soft characteristics which enable to attack selectively the imino carbon of 1. Organoboron compounds are also soft, but only allylic boron derivatives can react with 1; alkyl-boron compounds produce the coordination compound rather than the alkylation product.



EXPERIMENTAL

General information concerning instrumentation and materials is described previously.[3,7]

Reactions of 2 with benzyl organometals. The reaction of benzylzinc reagent is representative. To a solution of 0.5 mmol of benzyl Grignard reagent in 10 ml of dry THF was added 1.1 eq of $ZnBr_2$ dissolved in dry THF (0.5M) at -78°C under N_2. After stirring for 10 min, 0.5 mmol of 2[3] was added to the solution. The mixture was allowed to warm up to room temperature. The stirring continued overnight, and the reaction was quenched with water. Crude product was purified by silica gel column chromatography with hexane-ether (10 : 1) as an eluant.

Butyl 2-(N-(1-phenylethyl)amino)-3-phenylpropanoate (3). ^{1}H NMR(CCl_4), δ of major isomer, 0.83 (3H, t, J = 6Hz), 1.22 (3H, d, J = 6Hz), 1.0-1.5 (4H, m), 1.83(1H, br), 2.81(2H, d, J=7Hz), 3.38(1H, t, J = 6Hz), 3.57(1H, q, J = 6Hz), 3.78(2H, t, J = 6Hz), 7.05(5H, S), 7.11(5H, S); δ of minor isomer, 0.83(3H, t, J = 6Hz), 1.22(3H, d, J = 6Hz), 1.0-1.5(4H, m), 1.83(1H, br), 2.74(2H, d, J = 7Hz), 3.10(1H, t, J = 7Hz), 3.57 (1H, q, J = 6Hz), 3.93 (2H, t, J = 6Hz), 7.05(5H, s), 7.11(5H, s); IR(CCl_4) 700, 770, 790, 1040, 1180, 1460, 1500, 1740, 2980, 3320 cm^{-1}; MS calcd for $C_{21}H_{27}NO_2$ m/z 325.2040, found m/z 325.2048.

Butyl 2-(N-benzyl-N-(1-phenylethyl)aminoacetate (4). ^{1}H NMR (CCl_4) δ 0.94 (3H, t, J = 6Hz), 1.37(3H, d, J = 6.5 Hz), 1.2-1.6(7H, m), 3.12(1H, d, J = 9Hz), 3.40(1H, d, J = 9Hz), 3.75(2H, s), 4.05(2H, t, J=6Hz), 4.14(1H, q, J = 6.5Hz), 7.27(5H, s), 7.32(5H, s); IR(CCl_4) 700, 740, 1030, 1160, 1190, 1460, 1500,

1740, 2960 cm^{-1}; MS calcd for $C_{21}H_{27}NO_2$ m/z 325.2040, found m/z 325.2050.

Phenylalanine butyl ester (5). Hydrogenation of **3** and esterification of D-phenylalanine were carried out as described previously.[3] ^1H NMR(CCl_4) δ 0.90 (3H, t, J = 6Hz), 1.1-1.7(4H, m), 1.50(2H, s), 2.81(1H, dd, J = 12,5, 7.5Hz), 3.05(1H, dd, J = 12.5, 5Hz), 3.65 (1H, dd, J = 7.5, 5Hz), 4.03(2H, t, J = 6Hz), 7.16(5H, s); IR(CCl_4) 730, 780, 900, 1180, 1720, 2760 cm^{-1}; MS calcd for $C_{13}H_{19}NO_2$ m/z 221.1415, found m/z 221.1402.

Preparation of 8-(-)-phenylmenthyl N-methoxy-iminoacetate (**10**). 8-(-)-Phenylmenthol was prepared in 79% yield from pulegone according to the literature[5a]; $[\alpha]_D^{23}$ -26° (c 2.0, EtOH). 8-(-)-Phenylmenthyl glyoxylate was prepared in 56% yield from bromoacetic acid according to the method of Kornblum.[9] To a solution of 1.83g(6.35 mmol) of 8-(-)-phenylmenthyl glyoxylate dissolved in 50 ml of ethanol was added 0.3g(1eq) of methoxyamine dissolved in 5 ml of pyridine, and the mixture was stirred overnight under reflux. The reaction mixture was concentrated, and the residue was taken up with ether, washed with water, dried over $MgSO_4$ and the solvent was evaporated. The desired imine was obtained in 96% yield. ^1H NMR(CCl_4) δ 0.89(3H, d, J = 5.5Hz), 1.20(3H, s), 1.31 (3H, s), 1.4-2.0(8H, m), 3.94(3H, s), 4.85(1H, dt, J =11, 4Hz), 6.76 (1H, s), 7.21(5H, s); IR(CCl_4) 670, 760, 780, 1050, 1200, 1270, 1600, 1700, 1730 ; MS calcd for $C_{19}H_{27}NO_3$ m/z 317.1989, found m/z 317.1986; $[\alpha]_D^{24.5}$ -4.83(c26.4, $CHCl_3$).

Reactions of **10** with allylic organometals. The allylic organometallic reagents were prepared as described previously. The reaction was carried out according to the reported procedure.[3] The product **12a** was isolated by a column chromatography on silica gel (hexane:ether = 10 : 1). The two diastereomers exhibited very similar ^1H NMR spectra, so the diastereomer ratio was determined by the ^{13}C NMR spectra. ^1H NMR(CCl_4) δ 0.88(3H, d, J = 6Hz), 1.1-1.7 (9H, m), 1.21 (3H, s), 1.31 (3H, s), 2.04 (2H, dd, J = 6, 6Hz), 3.07 (1H, t, J = 6Hz), 3.42 (3H, s), 4.74 (1H, dt, J = 11, 4Hz), 4.92-5.08 (2H, m), 5.44-5.77 (1H, m), 7. 2 (5H, S); ^{13}C NMR ($CDCl_3$) δ of major isomer, 172.16, 151.24, 133.02, 127.67, 125.27, 124.95, 117.62, 75.28, 62.02, 61.47, 50.10, 41.31, 39.51, 34.33, 33.31, 31.02, 27.09, 26.42, 25.35, 21.55; δ of minor isomer, 172.06, 151.04, 133.02, 128.15, 125.10, 124.95, 117.62, 75.06, 62.06, 61.47, 50.27, 41.31, 39.46, 34.66, 33.31, 31.28, 28.34, 26.27, 25.88, 21.78; IR (CCl_4) 700, 790, 920, 1000, 1040, 1100, 1200, 1380, 1400, 1450, 1500, 1600, 1740, 2940, 2980, 3500 cm^{-1}; MS calcd for $C_{22}H_{33}NO_3$ m/z 359.2459, found m/z 359.2466.

Absolute stereochemistry of **12a**. Hydrogenation of **12a** over $Pd(OH)_2$ catalyst was carried out as described previously.[3] The hydrolysis of the resulting saturated ester was perfermed by refluxing the ester in 6N HCl for 6 hr. After neutralization with a saturated aqueous Na_2CO_3 solution, the organic layer was separated. The aqueous layer was extracted with $CHCl_3$. The combined organic layers were concentrated and 8-phenylmenthol was recovered. The aqueous layer was acidified and extracted with THF. The combined organic layers were dried and concentrated. The norvaline thus obtained exhibited $[\alpha]_D^{23.5}$ of +12.0° (c 1.2, 6N HCl).

Preparation of **12b** via prenylzinc reagent. The reaction of **10** with prenylzinc reagent was carried out in the same procedure described above. Preparation of prenylzinc reagent was described previously.[3] ^1H NMR ($CDCl_3$, 400MHz) δ 0.857 (3H, d, J = 6.40Hz), 0.960 (3H, s), 1.004 (3H, s), 1.237 (3H, s), 1.329 (3H, s), 2.387 (1H, s), 2.962 (1H, s), 3.447 (3H, s), 4.752 (1H, dt, J = 3.97, 6.71 Hz), 4.87-4.97 (2H, m), 5.68-5.76 (1H, m). The isomer could

not be detected by 400 MHz ^{1}H NMR analysis. We also examined ^{13}C NMR analysis to make clarify whether the adduct was obtained as a single isomer. ^{13}C-NMR ($CDCl_3$) δ 172.48, 151.18, 143.53, 134.01, 127.67, 125.44, 124.75, 112.60, 95.93, 75.90, 60.87, 50.49, 41.37, 39.82, 38.12, 34.51, 31.14, 26.60, 26.01, 24.66, 23.84, 23.65, 21.64. So, we concluded that a single isomer was produced in entry 4. IR (CCl_4) 700, 790, 1000, 1040, 1100, 1380, 1400, 1600, 1740, 2940, 2980, 3500 cm^{-1}; MS calcd for $C_{24}H_{37}NO_3$ m/z 387.2771, found m/z 387.2760.

Reactions of hetero-substituted allylic organometals (15). The allylic metals were generated as described previously.[6] The reaction of **15a** with **2** is representative. To a solution of 1 mmol of allyl methyl ether dissolved in 10 ml of dry THF was added 1.2 eq of n-BuLi dissolved in hexane under N_2 at -30°C. After stirring for 30 min at this temperature, 1.1 eq of $ZnBr_2$ dissolved in THF was added to the solution and then 1 mmole of **2** was added. The reaction mixture was allowed to warm up to room temperature over a period of 12hr. The reaction was quenched by H_2O and the product was isolated via the usual work-up procedure. The major isomer (C-T) in entry 1 was isolated in a pure form, but other isomers could not be isolated. Only the chemical shifts of OCH_3 of minor isomers are shown. The isomer ratio was determined by the signals of OCH_3. Although the stereochemistry of the major isomer was determined unambiguously as mentioned later, the stereochemistries of minor isomers were tentatively assigned by the analogy of the previous results[3, 7, 8] on the reagent, substrate, and reaction types. The same procedure was used for **16b** and **16c**.

Butyl 3-methoxy-2-(1-phenylethylamino)-4-pentenoate (**16a**). ^{1}H NMR ($CDCl_3$, 400MHz) δ of C-T, 0.908 (3H, t, J = 7.32Hz), 1.320 (3H, d, J = 6.41Hz), 1.32-1.39 (2H, m), 1.51-1.56 (2H, m), 1.964 (1H, br), 3.222 (3H, s), 3.372 (1H, d, J = 6.10Hz), 3.751 (1H, m), 3.796 (1H, q, J = 6.41Hz), 3.95-4.03 (2H, m), 5.26-5.33 (2H, m), 5.73-5.83 (1H, m), 7.294 (5H, s); δ of C-E 3.261 (3H, s); δ of aC-E, 3.253 (3H, s); δ of aC-T, 3.216 (3H, s); IR (CCl_4) 700, 760, 1100, 1180, 1450, 1490, 1730, 2960, 3320(br)cm^{-1}; MS calcd for $C_{18}H_{27}NO_3$ m/z 305.1989, found m/z 305.1982.

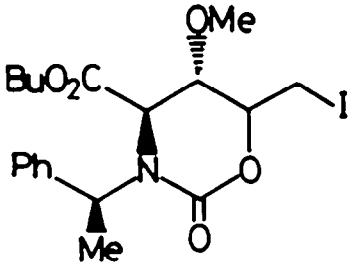
Butyl 3-phenoxy-2-(1-phenylethylamino)-4-pentenoate (**16b**). ^{1}H NMR($CDCl_3$, 400MHz) δ of C-T, 0.875 (3H, t, J = 7.33Hz), 1.348 (3H, d, J = 6.71Hz), 1.26-1.41 (2H, m), 1.49-1.54 (2H, m), 2.077 (1H, br), 3.577 (1H, d, J = 6.11Hz), 3.859 (1H, q, J = 6.71Hz), 4.823 (1H, dd, J = 6.11, 5.80Hz), 5.24-5.36 (2H, m), 5.96-6.05 (1H, m), 6.85-6.92 (3H, m), 7.19-7.25 (2H, m), 7.275 (5H, s); δ of C-E, 3.590 (1H, d, J = 6.11Hz); δ of aC-E, 3.277 (1H, d, J = 3.66Hz); δ of aC-T, 3.371 (1H, d, J = 6.10Hz), these signals were due to the proton at the α-amino carbon; IR (CCl_4) 700, 760, 790, 1490, 1600, 1730, 2960, 3320 cm^{-1}; MS calcd for $C_{23}H_{29}NO_3$ m/z 367.2146, found m/z 367.2155.

Butyl 3-methylthio-2-(1-phenylethylamino)-4-pentenoate (**16c**). ^{1}H NMR ($CDCl_3$, 400MHz) δ of C-T, 0.92 (3H, t, J = 6.5Hz), 1.32 (3H, d, J = 6.5Hz), 1.2-1.7 (4H, m), 1.97 (3H. s), 3.09 (1H, br), 3.19 (1H, m), 3.35 (1H, d, J = 6.5Hz), 3.69 (1H, q, J = 6.5Hz), 3.93 (2H, t, J = 7Hz), 4.8-5.1 (2H, m), 5.5-5.9 (1H, m), 7.21 (5H, s); δ of C-E, 1.89 (3H, s); δ of aC-E, 1.95 (3H, s); δ of aC-T, 1.88 (3H, s), these signals were due to SCH_3; IR (CCl_4) 700, 760, 790, 920, 1200, 1460, 1740, 2980cm^{-1}; MS calcd for $C_{18}H_{27}NO_2S$ m/z 321.1761, found m/z 321.1772.

Stereochemistry of **16a**. The iodocyclization of **16a** was carried out as described previously.[3,7]

4-Butoxycarbonyl-5-methoxy-7-(iodomethyl)-3-(1-phenylethyl)perhydro-1,3-oxazin-2-one (**19**). ^{1}H NMR ($CDCl_3$, 400MHz) 0.841 (3H, t, J = 7.63Hz), 1.284 (2H, sex,

J = 7.63Hz), 1.354 (3H, d, J = 7.32Hz), 1.547 (2H, quintet, J = 7.63Hz), 2.632 (3H, s), 3.132 (1H, dd, J = 4.58, 2.14Hz), 3.275 (1H, d, J = 9.77Hz), 3.745 (1H, dd, J = 6.09, 2.14Hz), 4.121 (1H, t, J = 7.63Hz), 4.092 (1H, t, J = 7.63Hz), 4.256 (1H, dd, J = 9.77, 8.54Hz), 5.803 (1H, q, J = 7.32Hz), 7.250 (5H, s); δ of the proton at C-4, 3.328 (1H, d, J = 4.28Hz). The relative stereochemistry was determined by the coupling constant[3]; J = 9.77Hz for threo isomer and J = 4.28Hz for the erythro isomer. IR (CCl_4) 690, 720, 900, 1020, 1050, 1090, 1130, 1180, 1290, 1370, 1420, 1450, 1690, 1740, 2920, 2960; MS calcd for $C_{19}H_{26}NO_5I$ m/z 475.0853, found m/z 475.0838. Stereochemistries of **16b** and c were assigned by deducing from the result of **16a**, and thus the assignment was not unambiguous.



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REFERENCES

(1) Department of Chemistry, Faculty of Science, Kyoto University.
(2) J. -C. Fiaud and H. B. Kagan, Tetrahedron Lett., 1970, 1813; 1971, 1019.
(3) Y. Yamamoto, W. Ito, and K. Maruyama, J. Chem. Soc. Chem. Commun., 1985, 1131. Y. Yamamoto, S. Nishii, K. Maruyama, T. Komatsu, and W. Ito, J. Am. Chem. Soc., 1986, **108**, 7778.
(4) Y. Yamamoto, Angew. Chem. Int. Ed. Engl., 1986, **25**, 947.
(5) (a) E. J. Corey and H. E. Ensley, J. Am. Chem. Soc., 1975, **97**, 6908. (b) W. Oppolzer and H. J. Loher, Helv. Chim. Acta, 1981, **64**, 2808. (c) J. K. Whitesell, A. Bhattacharya, and K. Henhe, J. Chem. Soc. Chem. Commun., 1982, 988; 989. J. K. Whitesell, Acc. Chem. Res., 1985, **18**, 280. (d) Y. Yamamoto, N. Maeda, and K. Maruyama, J. Chem. Soc. Chem. Commun., 1983, 774. (e) P. Grossen, P. Herold, P. Mohr, and C. Tamn, Helv. Chim. Acta, 1984, **67**, 1625.
(6) Y. Yamamoto, H. Yatagai, Y. Ishihara, N. Maeda, and K. Maruyama, Tetrahedron Symp., 1984, **40**, 2239.
(7) Y. Yamamoto, T. Komatsu, amd K. Maruyama, J. Org. Chem., 1985, **50**, 3115.
(8) Y. Yamamoto, Y. Saito, and K. Maruyama, J. Organomet. Chem., 1985, **292**, 311.
(9) N. Kornblum, H. W. Frazier, J. Am. Chem. Soc., 1966, **88**, 865.