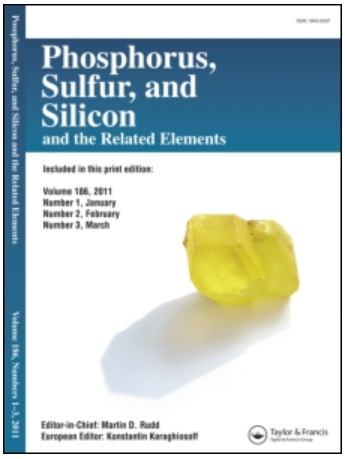

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Asymmetric *Trans*-Addition Reactions Using Chiral Selenobinaphthyls

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ASYMMETRIC *TRANS*-ADDITION REACTIONS USING CHIRAL SELENOBINAPHTHYLS

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Abstract Asymmetric *trans*-addition reactions of (*E*)-phenylpropene, a mechanistically novel reactions, have been achieved by using chiral selenium-containing binaphthyl derivatives. Introduction of an amide group at 2'-position in the binaphthyl skeleton enhances considerably the diastereomeric excess (d.e.) of the asymmetric reaction presumably due to attractive interaction between the nitrogen lone pair and the seleniranium intermediate. Introduction of another chiral center in the amide group further enhances the d.e. as high as 79 %, which is the highest asymmetric induction ever achieved in the asymmetric *trans*-addition reaction.

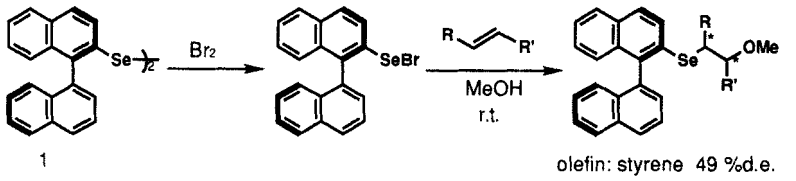
INTRODUCTION

In spite of the importance of organoselenium reagents in selective organic synthesis[1], little attention has been paid to their application to asymmetric synthesis. Examples thus far reported are quite few; asymmetric selenenylation of 4-substituted 2-cyclohexen-1-ones with selenols in the presence of (-)-cinchonidine[2], oxidation of methyl phenyl selenide with chiral 2-sulfonyloxaziridines[3], and α-selenenylation of ketone or aldehyde with chiral selenenamides[4,5].

Recently we have reported asymmetric ring-opening of cyclohexene oxide using optically active selenobinaphthyls which have shown relatively high degree of asymmetric recognition[6]. In this paper we wish to report their application to asymmetric *trans*-addition reaction across carbon-carbon double bond, which has been little investigated to date[7] because of significant difficulty in controlling the enantiomeric reaction transition state[8]. We also present some discussion on the mechanistic aspects of asymmetric induction.

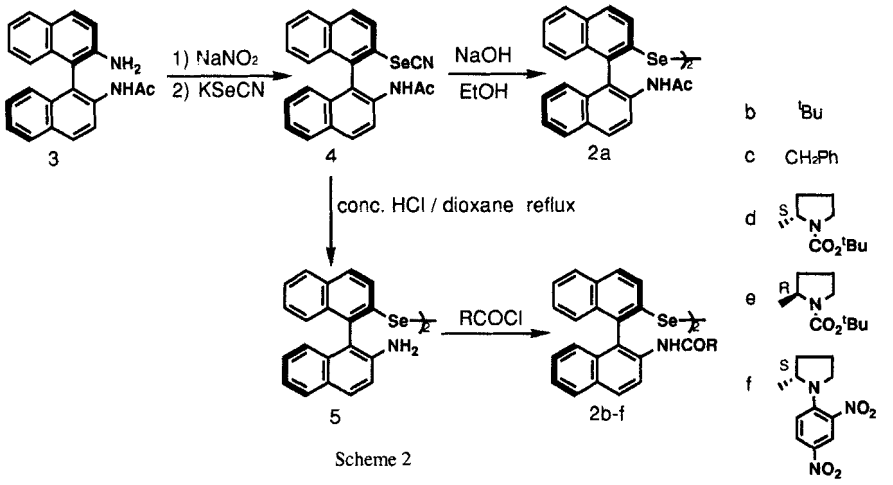
RESULTS AND DISCUSSION

In our previous paper on the first *trans*-addition reaction using optically active selenobinaphthyl compound 1[9], diastereomeric excess(d.e.) of the methoxyselenenylation adducts with various olefins was as high as 49 %d.e. (Scheme 1). With the hope that confinement of the transition state by a coordinating

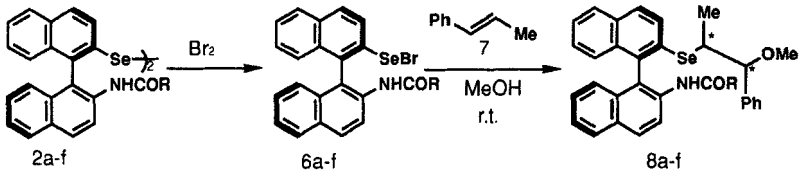


Scheme 1

amide group would be an effective approach to improve the d.e., we synthesized optically active selenobinaphthyls (2a-2f) according to Scheme 2. We carried out the asymmetric *trans*-addition reaction, methoxyselenenylation, according to Scheme 3. Diastereomeric excess of the methoxyselenenylation product (8) was determined by integration of ^{1}H-NMR absorptions due to the methoxy group at 500MHz. The results are listed in Table 1.



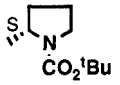
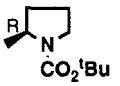
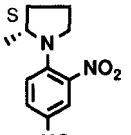
Scheme 2



Scheme 3

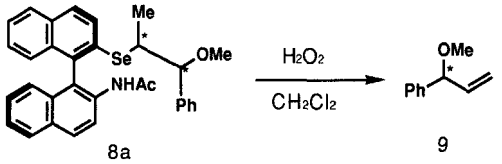
The NMR signals due to the methoxy group of the major diastereoisomer of 8 were, in all case, shifted to the lower field relative to the minor diastereoisomers. We therefore thought that the stereochemistry of the major isomer remained unchanged for all the substituents on the 2'-position of the selenobinaphthyl skeleton examined here. To determine the absolute stereochemistry of the asymmetric methoxyselenenylation, we oxidized 8a with hydrogen peroxide in methylene chloride (Scheme 4), and quantitatively obtained 9, the optically active form of

Table 1. Asymmetric methoxyselenenylation of (R)-selenobinaphthyl compounds(2) with 7 according to Scheme 3.

Entry	Diselenide	R	Yield (%)[a]	d.e.(%)[b]	^{1}H-NMR/ δ [c] Major	Minor
1	1[d]		49	24	3.15	3.01
2	2a[e]	CH_3	63	54	3.17	3.05
3	2b	^{t}Bu	73	19	3.15	3.07
4	2c	CH_2Ph	73	53	3.13	3.06
5	2d[e]		90	59	3.16	3.02
6	2e[e]		77	36	3.12	3.00
7	2f[e]		100	79	3.23	3.07

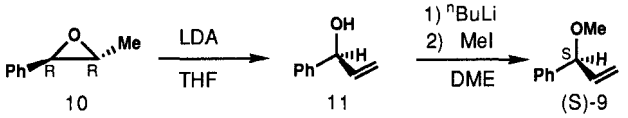
a) Isolated yield. b) Determined by integration of ^{1}H-NMR absorptions due to methoxy group. c) Mesured in chloroform-d_1 at 500MHz with TMS as internal standard. d) Ref. 9 e) Ref. 10

which (S)-9 was independently prepared from 10 according to Scheme 5[11]: The absolute configuration of the major enantiomer of 9, obtained by the asymmetric reaction, was determined to be (R)-9 as revealed by ^{1}H-NMR with Eu(hfc)$_3$.



8a 9

Scheme 4



10 11 (S)-9

Scheme 5

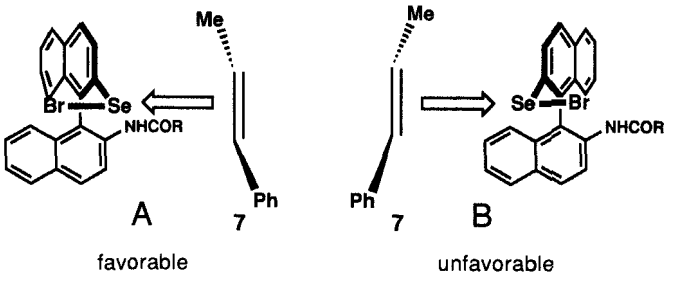


Figure 1

In the initial stage of the reaction between **6a** and 7, two approaches seem possible (Figure 1). In approach A, 7 approaches the electrophilic selenium from the direction near the amide group located at the 2'-position of the binaphthyl skeleton. The methoxyselenenylation adduct produced via approach A should be the one having absolute stereochemistry of the major diastereoisomer, which could be converted to (R)-9 by oxidation. In the other approach (approach B), 7 approaches the selenium from the opposite side of approach A. The adduct via approach B should be the minor diastereoisomer. The reason why approach A is more favorable than approach B might be due to the attractive interaction between the amide nitrogen and the cationic intermediate, seleniranium cation. This mechanistic consideration is in agreement with the fact that the d.e. of the asymmetric methoxyselenenylation was indeed increased by introduction of the acetylamide group on the 2'-position of the binaphthyl skeleton (see Table 1, Entry 1 and 2). When the bulky amide group was introduced at the 2'-position (Entry 3), the d.e. was decreased significantly because 7 may be sterically prevented from the preferential approach (approach A). However the bulky group located somewhat distant from the selenium atom did not reduce the d.e. (Entry 4).

In order to improve the d.e. of asymmetric methoxyselenenylation, another chiral center was introduced in the amide group at the 2'-position of the binaphthyl skeleton (Entry 5,6,7). The chiral reagent **2d**, which possesses another chiral center as (S)-proline skeleton, gave much better d.e. than **2e** probably due to the double stereodifferentiation between the (S)-proline skeleton and the (R)-binaphthyl skeleton. We then examined the effects of N-substituents in the proline ring having the (S)-configuration. Among these, **2f** which has a 2,4-dinitrophenyl group on the proline nitrogen, gave 79 %d.e. This is the highest optical yield ever achieved in the asymmetric *trans*-addition to olefins. We are now trying to further enhance the d.e. of the asymmetric *trans*-addition, by some other approaches, which will be disclosed in due course.

EXPERIMENTAL

90MHz ^{1}H-NMR and 500MHz ^{1}H-NMR were measured on a Varian EM390 instrument and a Bruker AM-500 instrument, respectively, in chloroform-d_1 containing tetramethylsilane (TMS) as internal standard. ^{13}C-NMR and ^{77}Se-NMR were measured on a Jeol FX90Q instrument in chloroform-d_1. Chemical shifts represent the lower field shift from TMS as internal standard and from dimethylselenide as external standard for ^{13}C-NMR and ^{77}Se-NMR, respectively. Rotatory powers were measured in the general method indicated in parentheses in each case.

(R)-2'-acetylamino-2-selenocyanato-1,1'-binaphthyl (4). 4 was synthesized from 3[12,13] in a way of similar to the reported literature[14].The yellow precipitates were extracted with dichloromethane and the organic layer was washed with saturated aq.Na_2CO_3 and dried over Na_2SO_4. The solvent was evaporated at reduced pressure, and after purification by column chromatography (benzene-acetone as eluent) , pure 4 (54 %yield) was obtained as pale yellow powder. ^{1}H-NMR: δ 8.41(d,J=8.5Hz,1H), 8.21-6.38(m,12H), 1.83(s,3H), ^{77}Se-NMR: δ 321.2ppm. ^{13}C-NMR: δ 168.6, 101.7, 24.1ppm. MS(m/z): 416(M^+), 268(base). Anal Calc'd for $C_{23}H_{16}N_2OSe$: C, 66.51; H,3.88; N, 6.74 % Found: C, 66.42; H, 4.14; N, 6.58 %

Bis[(R)-(2'-acetylamino-1,1'-binaphthalene)-2-yl] diselenide (2a). 4 (271mg, 0.65mmol) was dissolved in ethanol (20ml) and excess amount of sodium hydroxide was added to the solution. The mixture was stirred at room temperature until the spot of 4 completely disappeared on TLC. Aq.NH_4Cl was then added and the mixture was extracted with dichloromethane. After the organic layer was dried over Na_2SO_4, the solvent was evaporated at reduced pressure. Purification of the crude product thus obtained by column chromatography (benzene-acetone as eluent) afforded optically pure 2a (236mg, 92%) as yellow crystals (from ethanol-benzene). m.p.194.4-196.0 °C. ^{1}H-NMR: δ 8.42(d,J=8.1Hz,2H), 8.02-6.50(m,24H), 1.55(s,6H). ^{77}Se-NMR: δ 415.3ppm. ^{13}C-NMR: δ 168.4, 24.2ppm. MS(m/z): 780(M^+), 267(base). $[\alpha]_D^{25}$: +30.0 (c 3.01×10^{-1} , CH_2Cl_2). Anal Calc'd for $C_{44}H_{32}N_2O_2Se_2$: C,67.87; H,4.14; N,3.60% Found: C,67.76; H,4.29; N,3.55%.

Bis[(R)-(2'-amino-1,1'-binaphthalene)-2-yl] diselenide (5). 5 was synthesized from 4 in similar to deacetylation procedure reported by literature[13] . ^{1}H-NMR: δ 8.00-6.71(m,24H), 3.32(s,4H). ^{77}Se-NMR: δ 409.9ppm. MS(m/z): 696(M^+), 348(base). Anal Calc'd for $C_{40}H_{28}N_2Se_2$: C,69.17; H,4.06; N,4.03% Found: C,69.12; H,4.16; N;4.07%.

2b-2f were synthesized in good yields from the reaction of 5 with appropriate acid chlorides in the presence of triethylamine as base. In the case of 2d, 2e and 2f, acid chlorides were synthesized in situ from corresponding N-substituted proline by the reaction with oxalyl chloride[15].

Compound2b m.p.: 294.3-296.0 ℃. ^{1}H-NMR: δ 8.62(d,J=8.7Hz, 2H), 8.06-6.86(m,24H), 0.69(s,18H). ^{77}Se-NMR: δ 405.5ppm. ^{13}C-NMR: δ 176.4, 39.4 ppm. MS(m/z): 864(M^+), 332(base). $[\alpha]_D^{25}$:+60.5 (c 5.62×10^{-2}, CH_2Cl_2). Anal Cal'd for $C_{50}H_{44}N_2O_2Se_2$: C,69.60; H,5.14; N,3.24 % Found: C,69.54; H,5.11; N,3.25 %.

Compound2c ^{1}H-NMR: δ 9.00(d,J=8.7Hz, 2H), 8.45-6.60(m,34H), 3.64(s,4H). ^{77}Se-NMR: δ 407.7ppm.^{13}C-NMR: δ 169.2, 44.8ppm. MS(m/z):932(M^+), 332(base). $[\alpha]_D^{25}$: -60.7 (c 4.12×10^{-2}, CH_2Cl_2). Anal Cal'd for $C_{56}H_{40}N_2O_2Se_2$: C,72.26; H,4.33; N,3.01 % Found: C,72.17; H,4.50; N,3.07 %

Compound2d ^{1}H-NMR: δ 8.68(d,J=9Hz,2H), 8.11-6.93(m,24H), 4.12-3.79(m,2H), 3.02-2.57(m,4H), 2.07-1.65(m,8H), 1.03(s,18H). ^{13}C-NMR: δ 171.0, 80.1, 61.9, 46.6, 27.9, 22.6, 14.1 ppm.

Compound2e. ^{1}H-NMR: δ 8.63(d,J=9Hz,2H), 8.20-6.77(m,24H), 4.15-3.87(m,2H), 3.01-2.77(m,4H), 2.25-1.72(m,8H), 1.12(s,18H). ^{77}Se-NMR: δ

398.3ppm. ^{13}C-NMR: δ 170.9, 80.4, 61.6, 46.4, 28.2, 23.2, 17.4 ppm.
Compound2f ^{1}H-NMR: δ 8.37(d,J=9Hz,2H), 8.20-6.55(m,28H), 6.08 (d,J=10Hz,2H), 4.06(t,J=7.0Hz,2H), 3.20-2.77(m,4H), 2.66-2.27(m,4H), 2.27-1.43(m,4H). ^{77}Se-NMR: δ 411.6ppm. ^{13}C-NMR: δ 169.0, 65.5, 53.1, 25.2, 22.7 ppm.

Asymmetric methoxyselenenylation: general procedure

To a dichloromethane solution (2ml) of 2a (33.4mg, 0.0428mmol) 0.1M-tetrachloromethane solution of bromine(1.5ml) was added dropwise at room temperature under nitrogen atmosphere. After removal of the solvent and the excess amount of bromine, remained selenenyl bromide was dissolved in MeOH and the solution was added with (*E*)-phenylpropene(60.8mg, 0.514mmol) under nitrogen atmosphere. After stirred for several hours, the mixture was added with triethylamine(8.6mg, 0.086mmol) and extracted with dichloromethane. The organic layer was dried over sodium sulfate and evaporated at reduced pressure. After purification by column chromatography (benzene-acetone as eluent), methoxyselenenylation product(29.2mg, 63%) was obtained as colorless oil. ^{1}H-NMR: δ 8.57(d,J=9.9Hz,1H), 8.06-6.79(m,17H), 4.31(d,J=4.6Hz,0.77x1H), 4.16(d,J=4.4Hz,0.23x1H), 3.65-3.56(m,1H), 3.17(s,0.77x3H), 3.05(s,0.23x3H), 1.82(s,0.23x3H), 1.78(s,0.77x3H), 1.31(d,J=7.3Hz,0.23x3H), 1.21 (d,J=7.3Hz,0.77x3H). MS(m/z): 539(M^{+}), 280(base).

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REFERENCES

1. (a) C.Paulmier, "*Selenium Reagents and Intermediates in Organic Synthesis*", Pergamon Press, 1986, Oxford. (b) D.Liotta, "Recent Aspects of Organoselenium Chemistry", *Tetrahedron, 41*, 4727 (1985).
2. H.Pluim and H.Wynberg, *Tetrahedron Lett.*, 1251 (1979).
3. F.A.Davis, O.D.Stringer and J.P.McCanley,Jr., *Tetrahedron, 41*, 4747(1985).
4. K. Hiroi and S. Sato, *Synthesis*, 635 (1985).
5. C. Paulmier, F. Outurquin, and J-C. Plaquevent, *Tetrahedron Lett.*, 5889 (1988).
6. S. Tomoda and M. Iwaoka, *J. Chem. Soc., Chem. Commun.*, 1283 (1988).
7. J. Oda, T. Nakagawa, and Y. Inoue, *Bull. Chem. Soc. Jpn., 40*, 373 (1967). M. Kawana and S. Emoto, *Bull. Chem. Soc. Jpn., 40*, 618 (1967).
8. Control of the enantiomeric transition state is now becoming rather easy in asymmetric *cis*-addition across the carbon-carbon double bond. T. Katsuki and K. B. Sharpless, *J. Am. Chem. Soc., 102*, 5974 (1980). R. Noyori, M. Ohta, Yi Hsiao, and M. Kitamura, *J. Am. Chem. Soc., 108*, 7117 (1986). H. C. Brown, M. Srebnik, R.K.Bakshi, and T. E. Cole, *J. Am. Chem. Soc., 109*, 5420 (1987). J. H. Brewster, *Aldrichimica Acta, 20*, 3 (1987) and references cited therein. E. N. Jacobsen, I. Markó, W. S. Mungall, G. Schröder, and K. B. Sharpless, *J. Am. Chem. Soc., 110*, 1968 (1988).
9. S. Tomoda and M. Iwaoka, *Chem. Lett.*, 1895 (1988).
10. S. Tomoda, K. Fujita and M. Iwaoka, *J. Chem. Soc., Chem. Commun.*, 129 (1990).
11. J. K. Crandall and Luan-Ho Chang, *J. Org. Chem., 32*, 435 (1967). D. R. Dimmel and S. B. Gharpure, *J. Am. Chem. Soc., 93*, 3991 (1971).
12. K. T. Brown and M.S. Berry, *J. Org. Chem., 50*, 4345 (1985).
13. H. Akimoto and S. Yamada, *Tetrahedron, 27*, 5999 (1971).
14. K. B. Sharpless and M. W. Young, *J. Org. Chem., 40*, 947 (1975).
15. T. J. Curphey, *J. Org. Chem., 44*, 2805 (1979).