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Asymmetric Oxyselenenylation of Olefins Using Optically Active Selenobinaphthyls and *d*-Menthol as a Nucleophile

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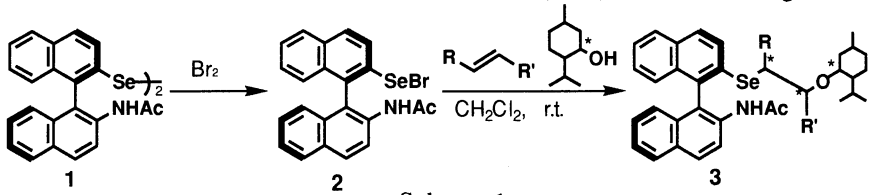
In order to improve the diastereomeric excess (d.e.) in asymmetric oxyselenenylation of symmetrical *cis*-olefins using bis [(*R*)-2'-acetylamino-1,1'-binaphthalene)-2-yl] diselenide, the use of *d*- and *l*-menthol was examined as nucleophiles. The d.e. was further enhanced for symmetrical *cis*-olefins as well as *trans*-β-methylstyrene by using *d*-menthol due to double stereodifferentiation between the (*R*)-binaphthyl and *d*-menthol.

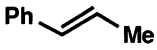
A number of highly efficient asymmetric addition reactions of prochiral olefins have been extensively investigated to date.[1] Most of them are mechanistically classified as the asymmetric *cis*-addition reactions across carbon-carbon double bond: Little attention has been paid to the other mechanistic alternative, the asymmetric *trans*-addition reactions.[2] As the first successful instance of such reactions, we recently reported the asymmetric methoxyselenenylation using optically active selenobinaphthyls, which showed decent asymmetric induction for various olefins.[3] When they were modified with (*S*)-proline at the 2'-position in the binaphthyl skeleton, diastereomeric excess (d.e.) of the products for *trans*-β-methylstyrene significantly increased due to double stereodifferentiation between (*R*)-binaphthyl skeleton and the (*S*)-proline ring.[4,5] In the case of symmetrical *cis* olefins, however, significant d.e. of methoxyselenenylation products was not observed even though optically modified selenobinaphthyls were employed. This is because the d.e. determining step for *trans*-olefins as well as unsymmetrical *cis*-olefins is the addition of optically active selenenyl cation to olefins producing diastereomeric seleniranium cation while that for symmetrical *cis*-olefins is the step involving capture of the nucleophile by the seleniranium cation.[3] Thus in order to improve the d.e. for symmetrical *cis*-olefins, we have examined the use of an optically active nucleophile. We wish to report here that the d.e. indeed increased up to 69% by the use of *d*-menthol due to double stereodifferentiation between the selenobinaphthyl skeleton and *d*-menthol and that the enhancement of d.e. was achieved also for *trans*-β-methylstyrene.

Asymmetric reaction was carried out as follows (Scheme 1). Diselenide 1 was synthesized according to the previous procedure.[5] To a dichloromethane solution (2 ml) of 1 (27 mg, 0.035 mmol) 0.1 M



Scheme 1.

Table 1. Asymmetric oxyselenenylation of olefins using bis [(*R*)-(2'-acetylamino-1,1'-binaphthalene)-2-yl] diselenide 1

Entry	Olefins	Nucleophiles	Yield / %[a]	d.e. / %
1		*d*-menthol	15	59 [b]
2		*l*-menthol	14	22 [b]
3		MeOH	77	17 [d]
4		*d*-menthol	38	69 [b]
5		*l*-menthol	43	18 [c]
6		MeOH	100	15 [d]
7		*d*-menthol	26	80 [b,e]
8		*l*-menthol	17	12 [c,e]
9		MeOH	63	54 [d,f]

a) Isolated yield. b) Determined by integration of ^{1}H-NMR absorption due to OC*H* of the menthyl group. c) Determined by integration of the absorptions due to -CH_3 of the menthyl group. d) Carried out in methanol according to Ref. 3. Determined by integration of the absorptions due to the methoxy protons. e) It is assumed that the configuration of the major isomer is similar to that of Entry 9. f) The absolute configuration of the major isomer is referred to Ref. 5.

tetrachloromethane solution of bromine (1.5 ml) was added dropwise at room temperature under nitrogen atmosphere. After removal of the solvent and the excess amount of bromine, the residual selenenyl bromide 2 was dissolved in dichloromethane and to the solution was added an excess amount of *d*- or *l*-menthol (1.40 mmol) and olefin (0.70 mmol) and pyridine (0.14 mmol) successively under nitrogen atmosphere. The mixture was stirred for two days at room temperature. Oxyselenenylation products 3 were isolated by the usual aqueous workup in the yields indicated in Table 1. Although the yields of 3 were not high presumably due to low nucleophilicity of bulky menthol, it should be mentioned that 3 was obtained as a major product and that 1 was recovered in all cases as the reduction product of 2.

In the case of cyclooctene and cyclohexene, the d.e.'s were significantly enhanced by using *d*-menthol as a nucleophile (59 and 69% d.e. respectively, Entries 1 and 4), while by using *l*-menthol they were as low as the case using methanol as a nucleophile. This may be caused by the double stereodifferentiation between the binaphthyl skeleton and menthol. The enhancement of d.e. by using *d*-menthol indicates that the use of chiral nucleophiles is an effective strategy in the asymmetric *trans*-addition reaction of symmetrical *cis*-olefins. When similar reaction conditions were applied to the case of *trans* - β -methylstyrene, the enhancement of d.e. was also observed by using *d*-menthol (80% d.e., Entry 7; the highest d.e. by using optically active selenobinaphthyls). This is because the double stereodifferentiation between the (R)-binaphthyl skeleton and *d*-menthol also affects the d.e. of the product 3. It was shown in the present experiment that the d.e. could be improved by using a chiral nucleophile for various olefins.

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