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Asymmetric Trans-addition Reactions of a Chiral Selenobinaphthyl with Prochiral Olefins.1) The Case of Methoxyselenenylation

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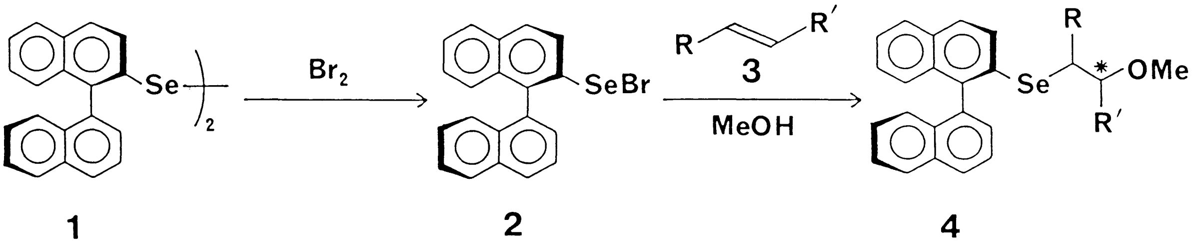
The first asymmetric methoxyselenenylation reaction between bis[R-(1,1'-binaphthalene)-2-yl] diselenide and olefins has been achieved with optical yields of up to 49%.

Among a number of highly efficient asymmetric syntheses, many of them involve addition reactions across the carbon-carbon double bond, such as asymmetric epoxidation,2) hydrogenation,3) hydroboration,4) or bis-1,2-hydroxylation.5) These useful asymmetric reactions however are mechanistically classified as cis-addition without exception: the other mechanistic alternative, the asymmetric trans-addition, has been little investigated to date.6) We now report some preliminary results on the first asymmetric methoxyselenenylation of simple alkenes, which give the highest optical yield (49 d.e.%) ever achieved in asymmetric trans-addition reactions thus far reported.

The design of asymmetric organoselenium reagents required some consideration not only because the carbon-selenium bond is relatively weak but also because removal of the selenium moiety by oxidative syn-elimination of the selenoxide is not generally regioselective when the organic residue on the selenium atom is not an aromatic ring. As the optimum compromise between dissymmetry and the problem associated with selenoxide elimination, we came up to the conclusion that the best choice would be the binaphthyl skeleton3,7) as the organic residue.

The compound we have chosen to induce chirality in methoxyselenenylation is bis[R-(1,1'-binaphthalene)-2-yl] diselenide (**1**),8) which can be prepared in optically active form in two steps from 2-amino-1,1'-binaphthyl. A typical procedure of methoxyselenenylation is as follows (Scheme 1). Treatment of **1** with excess amount of bromine in dichloromethane at room temperature followed by



Scheme 1.

Table 1. Asymmetric methoxyselenenylation of alkenes using bis[R-(1,1'-binaphthalene)-2-yl] diselenide (**1**)[a)]

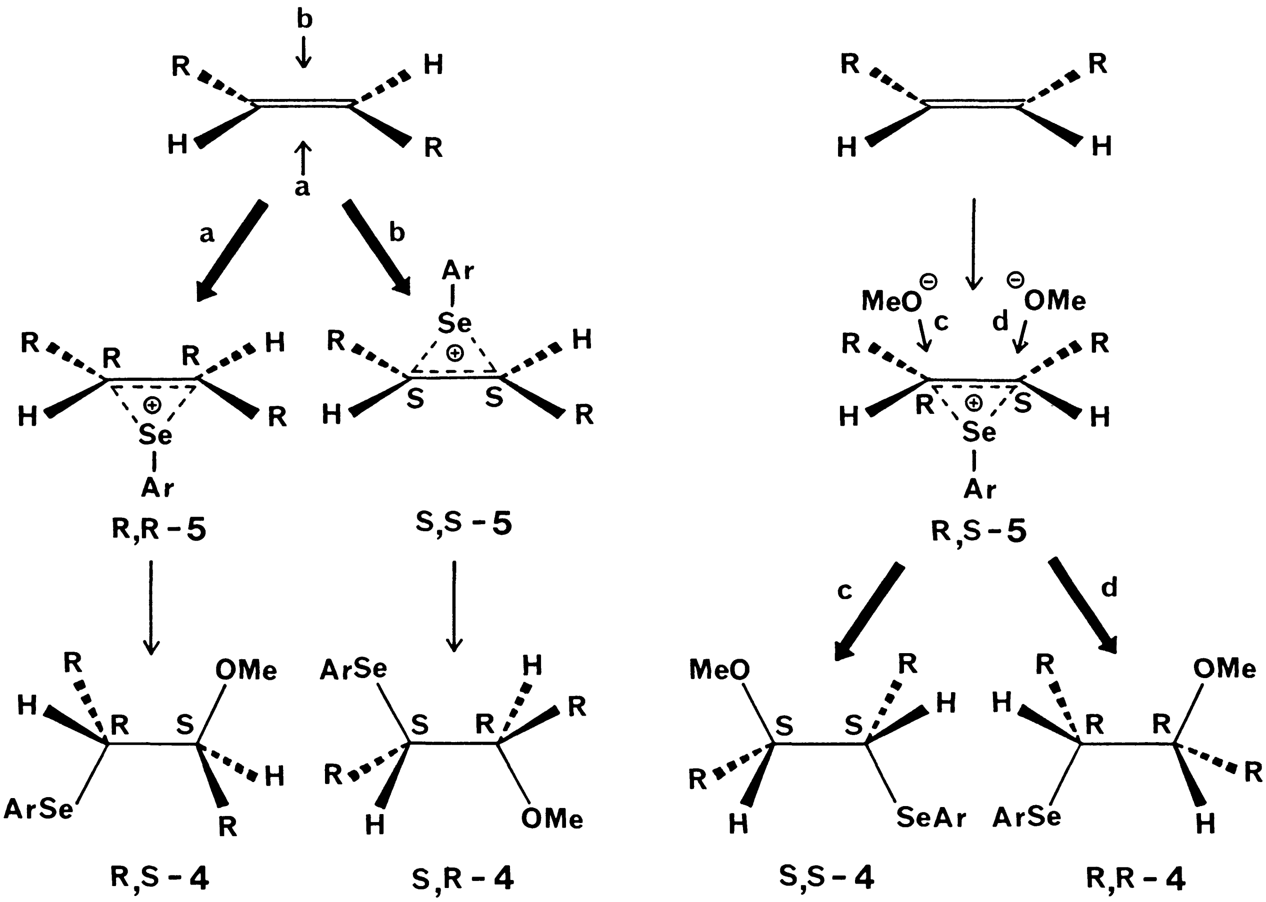
Entry	Alkenes	Temp / °C	Yield of **4**[b)] / %	d.e.[c)] / %	^{1}H-NMR[d)] major	^{1}H-NMR[d)] minor
1	trans-2-butene	rt -78	48 95	20 4	3.23	3.10
2	cis-2-butene	rt	59	13	3.18	3.25
3	trans-4-octene	rt	68	4	3.28	3.08
4	cyclopentene	rt	59	12	3.17	3.23
5	cyclohexene	rt	80	3	3.16	3.24
6	cyclooctene	rt	61	17	3.11	3.20
7	α-methylstyrene	rt -78	52 58	0 17	2.95	2.97
8	trans-β-methylstyrene	rt	49	24	3.15	3.01
9	styrene	rt	49	49	3.11	3.04

a) Reaction conditions are described in the text. b) Isolated yield of methoxyselenenylation product after purification by silica gel column chromatography. c) Diastereomeric excess determined by integration of ^{1}H-NMR[d)] absorptions due to methoxy group at ten times expanded sweep width. d) Measured in $CDCl_3$ at 90 MHz using tetramethylsilane as internal standard.

removal of the solvent under vacuum provided dark red crystalline material, which we assume to be 1,1'-binaphthalene-2-selenenyl bromide (**2**). The solid compound **2** was dissolved in methanol and an excess alkene (**3**) was introduced. The reaction mixture turned colorless immediately. The solvent and excess **3** were then removed *in vacuo*. The residue was purified by column chromatography to give methoxyselenenylation products (**4**) in the chemical and optical yields shown in Table 1. These products (**4**) were identified by spectroscopic data (^{1}H-NMR, MS, and IR). Since the enantiomeric excess (e.e.%) is directly correlated with diastereomeric excess (d.e.%) in this case, only d.e.%'s are listed in the Table 1.

Although the isolated yields of **4** are not good in many cases because of loss in the workup procedure due to micro-scale reactions, each reaction was clean and provided single regio- and stereo-chemically pure methoxyselenenylation product at room temperature or at -78 °C as revealed by TLC analysis. The optical yields for symmetric simple alkenes (entry 1 through 6), whether they are cis or trans, were uniformly low (3 - 20 d.e.%). It should be mentioned here that the d.e.-determining step for cis- and trans-alkenes is not the same (Scheme 2). If one assumes the mechanism of methoxyselenenylation to involve the generally accepted three-membered seleniranium cation **5**,9) three diastereomeric intermediates **5** could exist: two of which would be derived from enantiofacial stereoselection from trans-alkenes, the last possibility (R,S-**5**) being produced from cis-alkenes. The methoxyselenenylation products would then be generated by attack of methanol at one of the alkene carbons. One may notice here that whereas the d.e.-determining step for trans-alkenes is the first step, that for cis-alkenes is the step involving capture of the nucleophile. The low d.e. for entries 1 through 6 indicates that both steps give nearly the same degree of enantioselection when **1** is used as the chiral inducer under various temperature conditions.

In contrast to these cases (entry 1 through 6), phenyl-substituted alkenes provided comparatively high optical yields (entries 7, 8, and 9) of up to 49%. In these cases, the reactions are regioselective to give only Markovnikov products and the d.e. is determined by stereofacial selection of the selenium reagent like the case for trans-alkene. Particularly noted is the reaction with styrene, in



Scheme 2.

which 49 d.e.% is obtained. Although the d.e.'s achieved in the present work by no means attain to a useful level, it is interesting that such a simple chiral selenium reagent gave decent optical yields in some cases under the conditions which were not particularly optimized.

The result implies that further elaboration in the design of chiral selenium reagents as well as subtle control of reaction conditions may offer unique opportunity to efficient asymmetric trans-addition reactions. Research along this line is now in progress and will be reported in due course.

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